

PHOTOACID GENERATOR, METHOD FOR MANUFACTURING THE SAME, AND RESIST COMPOSITION COMPRISING THE SAME

Technical Field

5 The present invention relates to a photoacid generator, a method for manufacturing the same, and a resist composition containing the same. More particularly, the present invention relates to a photoacid generator capable of producing, at the time of exposure, an acid which has a low diffusion rate, has a short diffusion distance, and exhibits an appropriate degree of acidity so that the line width roughness (LWR) characteristics can
10 be improved, and elution of which in a solvent such as pure water that is used in the process can be controlled, and to a method for manufacturing the photoacid generator, and a resist composition containing the photoacid generator.

Background Art

15 As the generations of microprocessing methods using photolithography change, there have been demands for photoresists of higher resolution, and in response to these demands, chemically amplified type resists have been developed. Such chemically amplified resist compositions contain photoacid generators.

 The photoacid generator in a chemically amplified resist composition is an
20 important element which imparts excellent properties to the chemically amplified resist in terms of resolution, LWR, sensitivity and the like, together with the resist composition. Therefore, studies on various types of photoacid generators are underway, so as to prepare chemically amplified resist compositions having appropriate properties.

 Particularly, those compounds that are used as photoacid generators in order to
25 improve the diffusion rate of acid, transparency or the like, which are some of the

properties that exhibit characteristics such as excellent resolution, LWR and sensitivity, have been subjected to a large extent of modifications and experiments on the cation moiety. However, the study for improving the properties of chemically amplified resists by modifying the anion moiety of the photoacid generators is still insufficient at the
5 current level.

Based on experimental data reporting that the anion moiety can exert greater influence than the cation moiety on the physical and chemical properties which substantially improve the fluidity of acid and the properties of the resist composition, new inventions related to the anion moiety of photoacid generators have recently been achieved.
10 Furthermore, there is an increasing demand for a photoacid generator which can regulate penetrability while decreasing the diffusion rate of acid.

In addition, recently the light source for chemically amplified resists requires even shorter wavelengths than the conventionally used region of g-line or i-line, and thus investigations are being conducted on lithography using far-ultraviolet radiation, KrF
15 excimer laser light, ArF excimer laser light, extreme ultraviolet (EUV) radiation, X-rays and electron beams. Particularly, since the exposure process is carried out using pure water in an immersion ArF process, the photoresist composition used in such an immersion ArF process is required to have a feature that the photoacid generator contained in the photoresist composition or the acid generated from this photoacid generator is not
20 eluted out into pure water.

Disclosure of the Invention

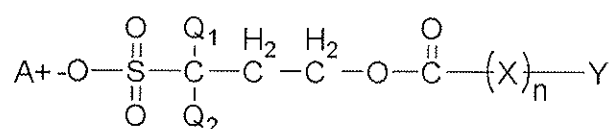
An object of the present invention is to provide a photoacid generator capable of producing, at the time of exposure, an acid which has a low diffusion rate, has a short
25 diffusion distance, and exhibits an appropriate degree of acidity so that the line width

roughness (LWR) characteristics can be improved, and elution of which in a solvent such as pure water that is used in the process can be controlled.

In order to achieve the above-described object, according to an embodiment of the present invention, there is provided a photoacid generator represented by the following

5 formula 1:

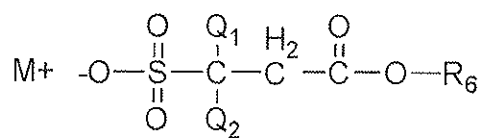
[Formula 1]



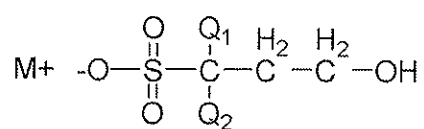
In the formula 1, Y represents any one selected from the group consisting of an alkyl group substituted with an aryl group, and an aromatic hydrocarbon group; Q₁ and Q₂ each independently represent a halogen atom; X represents any one selected from the group consisting of an alkanediyl, an alkenediyl, NR', S, O, CO and combinations thereof; R' represents any one selected from the group consisting of a hydrogen atom and an alkyl group; n represents an integer from 0 to 5; and A⁺ represents an organic counterion.

According to another embodiment of the present invention, there is provided a method for manufacturing a photoacid generator, which includes a first step of dissolving a compound represented by the following formula 8 in a solvent, and reacting the solution with a reducing agent to obtain a compound represented by the following formula 6; a second step of reacting a compound represented by the following formula 7 with the compound represented by the following formula 6 in the presence of a basic catalyst to obtain a compound represented by the following formula 4; and a third step of subjecting the compound represented by the following formula 4 and a compound represented by the following formula 5 to a substitution reaction, and thereby obtaining a compound represented by the following formula 1.

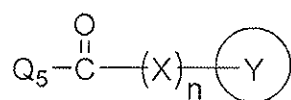
[Formula 8]



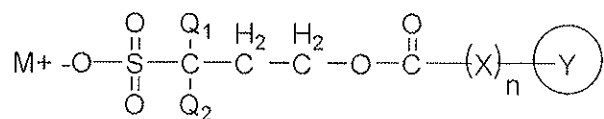
[Formula 6]



[Formula 7]



[Formula 4]

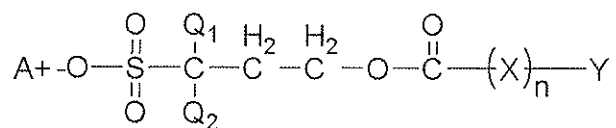


5

[Formula 5]

A+Z-

[Formula 1]



In the formula 1, formula 4, formula 5, formula 6, formula 7 and formula 8, R₆ represents an alkyl group, Q₁, Q₂ and Q₅ each independently represent a halogen atom; Y

represents any one selected from the group consisting of an alkyl group substituted with an aryl group, and an aromatic hydrocarbon group; X represents any one selected from the group consisting of an alkanediyl, an alkenediyl, NR', S, O, CO and combinations thereof; R' represents a hydrogen atom and an alkyl group; n represents an integer from 0 to 5; and
5 A+ represents an organic counterion. M+ represents any one selected from the group consisting of Li+, Na+ and K+; and Z- represents any one selected from the group consisting of (OSO₂CF₃)-, (OSO₂C₄F₉)-, (OSO₂C₈F₁₇)-, (N(CF₃)₂)-, (N(C₂F₅)₂)-, (N(C₄F₉)₂), (C(CF₃)₃)-, (C(C₂F₅)₃)-, (C(C₄F₉)₃)-, F-, Cl-, Br-, I-, BF₄-, AsF₆- and PF₆-.

According to another embodiment of the present invention, there is provided a
10 chemically amplified resist composition containing the photoacid generator described above.

Hereinafter, the present invention will be described in more detail.

The definitions of the terms used in the present specification are as follows.

Unless particularly stated otherwise herein, the halogen atom means any one
15 selected from the group consisting of fluorine, chlorine, bromine and iodine.

Unless particularly stated otherwise herein, the alkyl group includes a primary alkyl group, a secondary alkyl group, and a tertiary alkyl group.

Unless particularly stated otherwise herein, the alkanediyl is a divalent atomic group obtained by detaching two hydrogen atoms from an alkane, and can be represented
20 by general formula: -C_nH_{2n}-. Furthermore, the alkenediyl is a divalent atomic group obtained by detaching two hydrogen atoms from an alkene, and can be represented by general formula: -C_nH_n-.

Unless particularly stated otherwise herein, the perfluoroalkyl group means an alkyl group in which a part of the hydrogen atoms or all of the hydrogen atoms are
25 substituted with fluorine, and the perfluoroalkoxy group means an alkoxy group in which

a part of the hydrogen atoms or all of the hydrogen atoms are substituted with fluorine.

Unless particularly stated otherwise herein, all of the compounds and substituents may be substituted or unsubstituted. Here, being substituted means that a hydrogen atom has been replaced with any one selected from the group consisting of a halogen atom, a hydroxyl group, a carboxyl group, a cyano group, a nitro group, an amino group, a thio group, a methylthio group, an alkoxy group, a nitrile group, an aldehyde group, an epoxy group, an ether group, an ester group, a carbonyl group, an acetal group, a ketone group, an alkyl group, a perfluoroalkyl group, a cycloalkyl group, a heterocycloalkyl group, an allyl group, a benzyl group, an aryl group, a heteroaryl group, derivatives thereof, and combinations thereof.

Unless particularly stated otherwise herein, the prefix "hetero" means that a carbon atom is substituted with one to three heteroatoms selected from the group consisting of N, O, S and P.

Unless particularly stated otherwise herein, the alkyl group means a linear or branched alkyl group having 1 to 10 carbon atoms; the alkanediyl means an alkanediyl having 1 to 10 carbon atoms; the alkenediyl means an alkenediyl having 2 to 10 carbon atoms; the allyl group means an allyl group having 2 to 10 carbon atoms; the alkoxy group means an alkoxy group having 1 to 10 carbon atoms; the perfluoroalkyl group means a perfluoroalkyl group having 1 to 10 carbon atoms; the perfluoroalkoxy group means a perfluoroalkoxy group having 1 to 10 carbon atoms; the cycloalkyl group means a cycloalkyl group having 3 to 32 carbon atoms; the heterocycloalkyl group means a heterocycloalkyl group having 2 to 32 carbon atoms; the aryl group having an aryl group having 6 to 30 carbon atoms; and the heteroaryl group means a heteroaryl group having 2 to 30 carbon atoms.

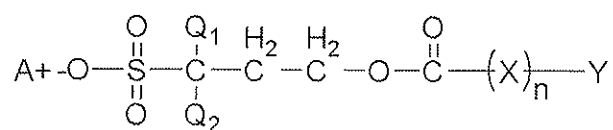
Unless particularly stated otherwise herein, the aromatic hydrocarbon means a

monocyclic or polycyclic compound having 6 to 30 carbon atoms and including one or more benzene rings, or a derivative thereof. Examples of the aromatic hydrocarbon include a benzene ring; toluene, xylene or the like, in which an alkyl side chain is attached to a benzene ring; biphenyl or the like, in which two or more benzene rings are bonded by a single bond; fluorene, xanthene, anthraquinone or the like, in which a benzene ring is condensed with a cycloalkyl group or a heterocycloalkyl group; and naphthalene, anthracene or the like, in which two or more benzene rings are condensed.

As used herein, Me is an abbreviation of a methyl group.

The photoacid generator according to an embodiment of the present invention is represented by the following formula 1:

[Formula 1]



In the above formula 1, Q₁ and Q₂ each independently represent a halogen atom, and preferably a fluorine atom.

n is an integer from 0 to 5, and preferably an integer from 0 to 2.

X represents any one selected from the group consisting of an alkanediyl, an alkenediyl, NR', S, O, CO and combinations thereof, and R' represents any one selected from the group consisting of a hydrogen atom and an alkyl group.

X may represent any one selected from the group consisting of -O-, -OCH₂-, -OCH(Cl)-, -CO-, -COCH₂-, -COCH₂CH₂-, -CH₂-, -CH₂CH₂-, -CH₂O-, -CH₂O-CH₂-, -CH₂CH₂O-, -CH₂O-CH₂CH₂CH₂-, -CH₂CH₂O-CH₂CH₂-, -CH₂CH₂CH₂O-CH₂-, -CH(CH₃)-, -C(CH₃)₂CH₂-, -CH(CH₃)CH₂-, -CH(CH₂CH₃)-, -CH(OCH₃)-, -C(CF₃)(OCH₃)-, -CH₂S-, -CH₂S-CH₂-, -

CH₂CH₂-S-, -CH₂-S-CH₂CH₂-, -CH₂CH₂-S-CH₂-, -CH₂CH₂CH₂-S-, -CH₂-S-CH₂CH₂CH₂-,
-CH₂CH₂-S-CH₂CH₂-, -CH₂CH₂CH₂-S-CH₂-, -CH(CH₂)CH-, -C(CH₂CH₂)-, -CH₂CO-, -
CH₂CH₂CO-, -CH(CH₃)CH₂CO-, -CH(OH)-, -C(OH)(CH₃)-, -CH(F)-, -CH(Br)-, -
CH(Br)CH(Br)-, -CH=CH-, -CH₂CH=CH-, -CH=CHCH₂-, -CH=CH-O-, -CH=CH-S- and
5 -CH=CHCO-.

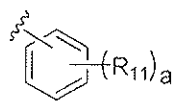
In the above formula 1, Y represents any one selected from the group consisting of
an alkyl group substituted with an aryl group, and an aromatic hydrocarbon.

Y may represent any one selected from the group consisting of a phenyl group, a
naphthyl group, a biphenyl group, an anthryl group, a phenanthrene group, a fluorenyl
10 group, a pyrene group, a phenalene group, an indene group, a biphenylene group, a
diphenylmethyl group, a tetrahydronaphthyl group, a dihydroanthryl group, a
tetraphenylmethyl group, and a triphenylmethyl group.

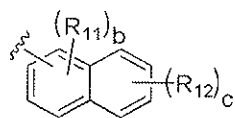
Among the carbon atoms of Y, one to three carbon atoms may be substituted with
any one selected from the group consisting of -O-, -CO-, -S- and combinations thereof,
15 and one to five hydrogen atoms among the hydrogen atoms of Y may be substituted with
any one selected from the group consisting of an alkyl group having 1 to 6 carbon atoms,
an alkoxy group having 1 to 6 carbon atoms, a perfluoroalkyl group having 1 to 4 carbon
atoms, a perfluoroalkoxy group having 1 to 4 carbon atoms, a hydroxyalkyl group having
1 to 6 carbon atoms, a halogen atom, a hydroxyl group, a cyano group, a nitro group, an
20 amino group, a thio group, a methylthio group, a methoxy group, OR', COR' and COOR'.
R' represents any one selected from the group consisting of an alkyl group and an aryl
group.

Preferably, Y may represent any one selected from the group consisting of the
following formulas 1-a to 1-l.

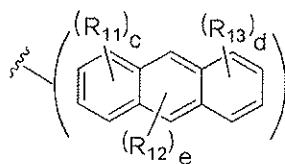
25 [Formula 1-a]



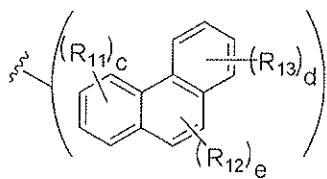
[Formula 1-b]



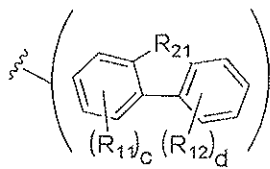
[Formula 1-c]



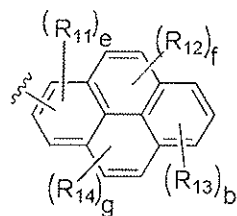
[Formula 1-d]



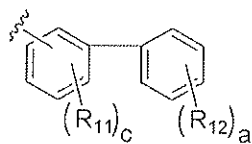
[Formula 1-e]



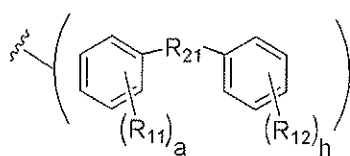
[Formula 1-f]



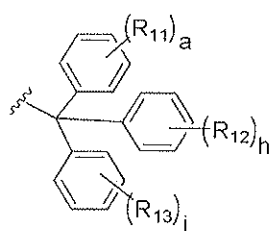
[Formula 1-g]



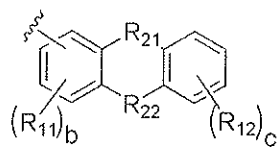
[Formula 1-h]



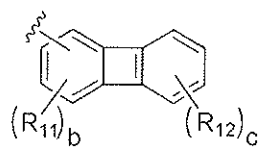
[Formula 1-i]



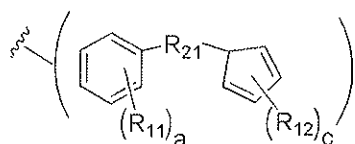
[Formula 1-j]



5 [Formula 1-k]



[Formula 1-l]



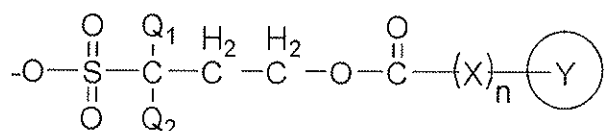
In the formulas 1-a to 1-l, R_{11} , R_{12} , R_{13} and R_{14} may each independently represent an alkyl group, an alkoxy group, a perfluoroalkyl group, a perfluoroalkoxy group, a halogen atom, a hydroxyl group, a cyano group, a nitro group, an amino group, a thio group, a methylthio group, a methoxy group, OR' , COR' , and $COOR'$. R' represents any one selected from the group consisting of an alkyl group and an aryl group.

R_{21} and R_{22} each independently represent any one selected from the group consisting of $CR_{24}R_{25}$, O, CO, S and NR_{23} , and R_{23} to R_{25} each independently represent any one selected from the group consisting of a hydrogen atom, an alkyl group and an aryl group.

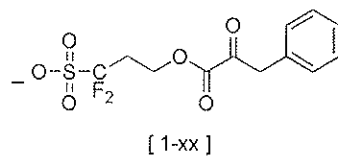
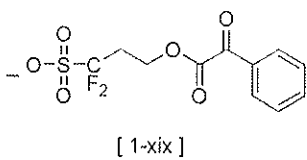
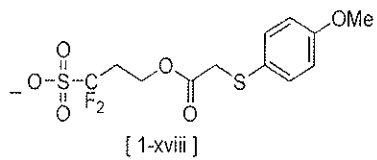
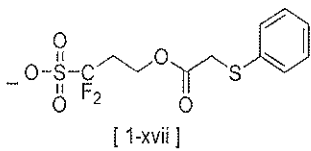
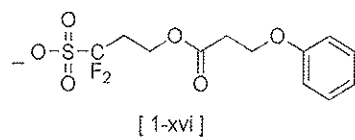
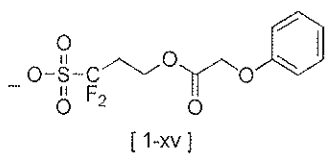
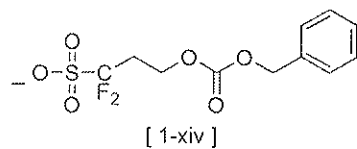
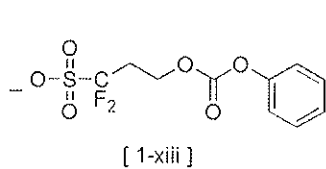
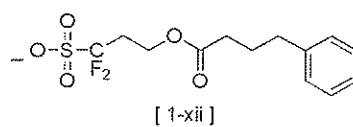
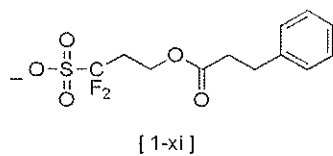
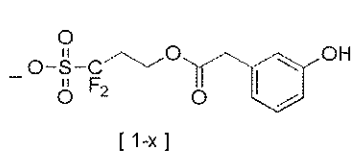
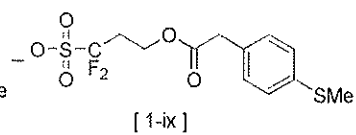
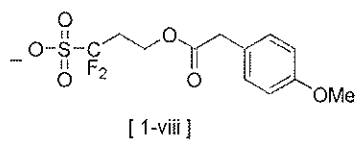
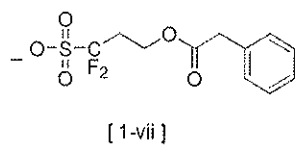
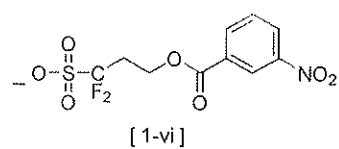
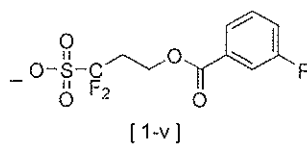
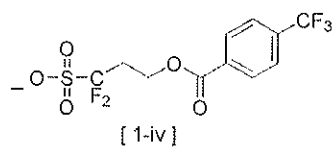
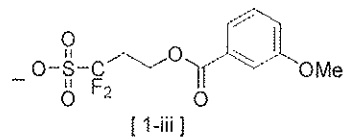
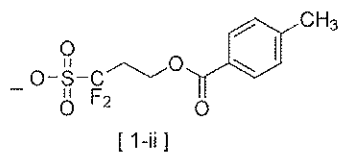
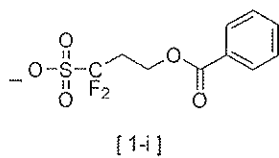
a, h and i each independently represent an integer from 0 to 5; b represents an integer from 0 to 3; c and d each independently represent an integer from 0 to 4; e, f and g each independently represent an integer from 0 to 2; and $0 \leq c+d+e \leq 9$.

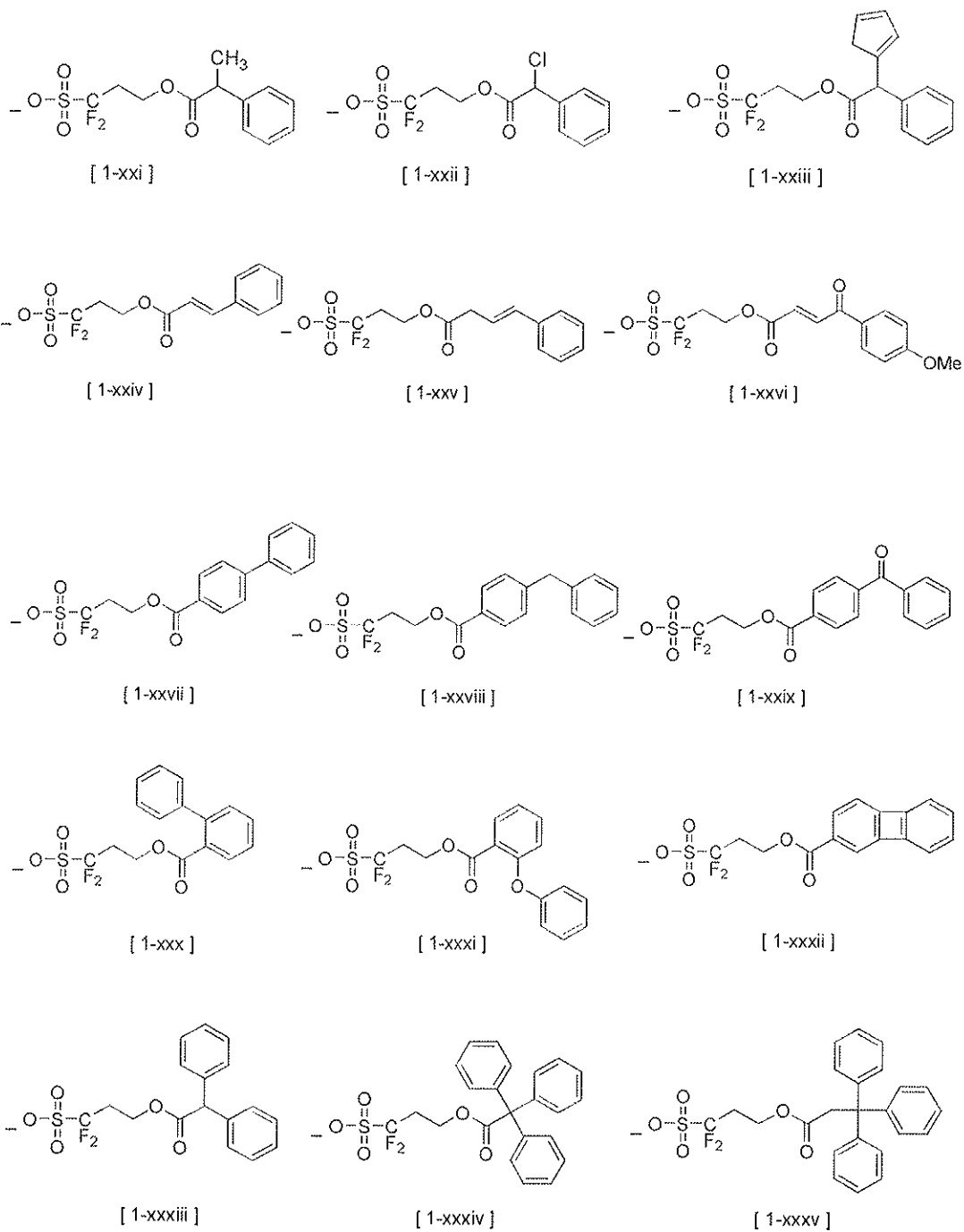
The moiety represented by the following formula 3, which is an anion moiety of the compound represented by the formula 1 shown above, may represent any one selected from the group consisting of the following formulas 1-i to 1-xxxxxi.

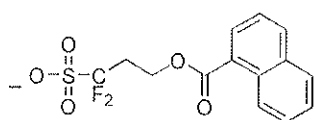
[Formula 3]



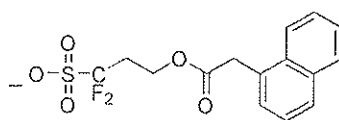
[Formulas 1-i to 1-xxxxxi]



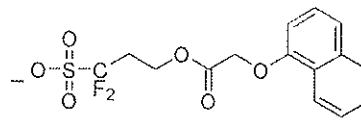




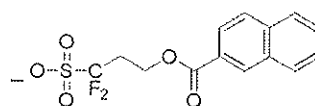
[1-xxxvi]



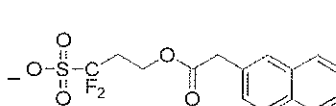
[1-xxxvii]



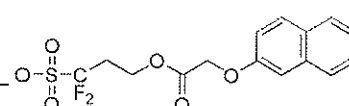
[1-xxxviii]



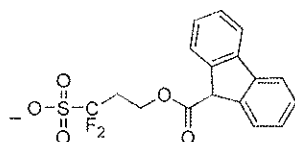
[1-xxxix]



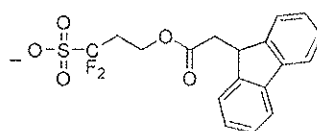
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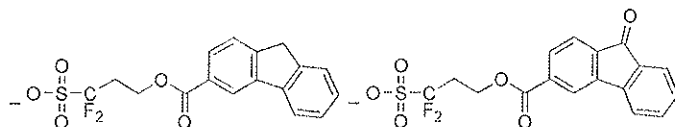
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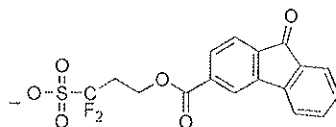
[1-xxxixii]



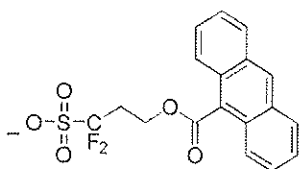
[1-xxxixiii]



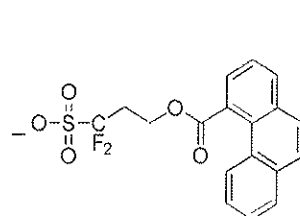
[1-xxxixiv]



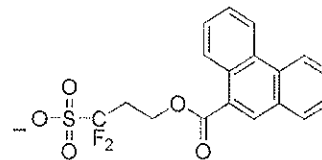
[1-xxxixv]



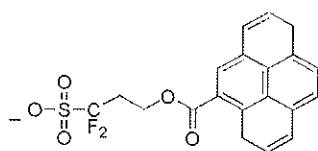
[1-xxxixvi]



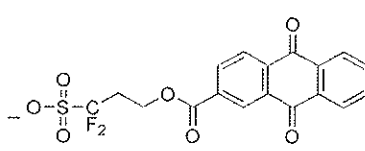
[1-xxxixvii]



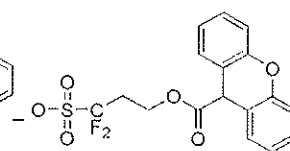
[1-xxxixviii]



[1-xxxixix]



[1-xxxxx]



[1-xxxxxi]

The photoacid generator described above is obtained by introducing an aromatic ring into a compound represented by the above formula 3, which is an anion moiety of the compound represented by the formula 1, and the photoacid generator can give variation in the characteristics such as the diffusion rate of acid, the acid diffusion distance and the degree of acidity, depending on the form or size of the anion, can exhibit a lower acid diffusion rate as compared with existing simple anions in the form of triflate or nonaflate, can shorten the diffusion distance so that the line width roughness can be improved, and also has strong organic characteristics so that elution into pure water can be reduced or controlled.

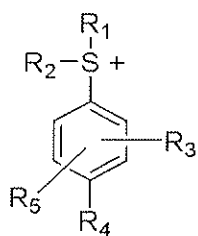
In the formula 1, A⁺ represents an organic counterion.

Specifically, the moiety represented by the following formula 2, which is a cation moiety of the compound represented by the formula 1, may represent any one selected from the group consisting of the following formulas 2a and 2b.

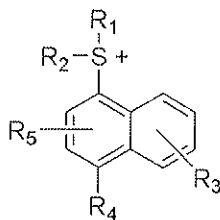
[Formula 2]

A⁺

[Formula 2a]



[Formula 2b]



In the above formulas 2a and 2b, R₁ and R₂ each independently represent any one selected from the group consisting of a hydrogen atom, an alkyl group, an allyl group, a perfluoroalkyl group, an aryl group and combinations thereof, and R₁ and R₂ may be bonded to each other to form a saturated or unsaturated hydrocarbon ring having 3 to 30 carbon atoms.

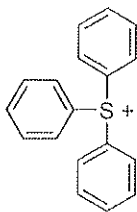
R₄ represents any one selected from the group consisting of a halogen atom, an alkyl group, an alkoxy group, an aryl group, a thioalkoxy group, an alkoxycarbonylmethoxy group, a thiophenoxy group, and combinations thereof.

R₃ and R₅ each independently represent any one selected from the group consisting of a hydrogen atom, an alkyl group, an allyl group, a perfluoroalkyl group, an aryl group, and combinations thereof.

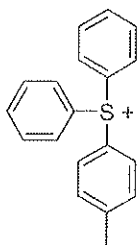
In the formulas 2a and 2b, examples of the alkyl group include a methyl group, an ethyl group, a propyl group, an isopropyl group, an n-butyl group, a phenyl group, a hexyl group, and an octyl group, and examples of the alkoxy group include a methoxy group, an ethoxy group, a propoxy group, a butoxy group, a hexyloxy group, and an octyloxy group.

Furthermore, the moiety represented by the formula 2, which is the cation moiety of the compound represented by the formula 1, may represent any one selected from the group consisting of the following formulas 2-i to 2-xx.

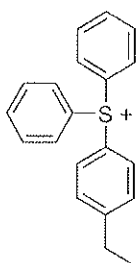
[Formulas 2-i to 2-xx]



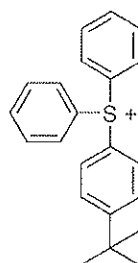
[2-i]



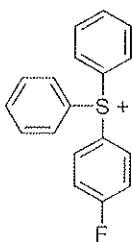
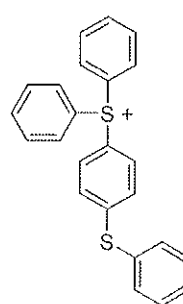
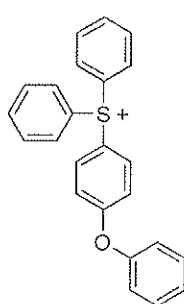
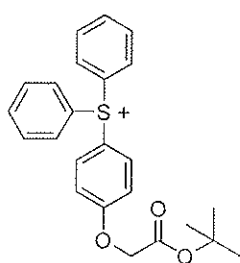
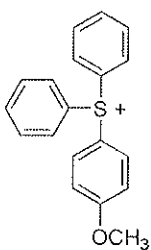
[2-ii]



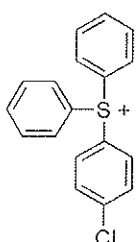
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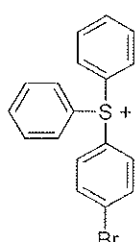
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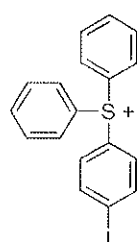
[2-ix]



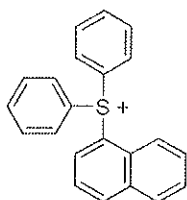
[2-x]



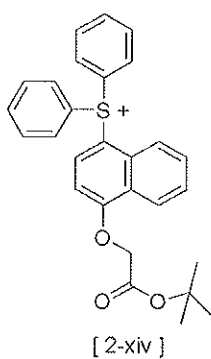
[2-xi]



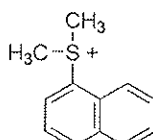
[2-xii]



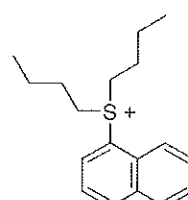
[2-xiii]



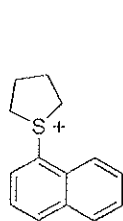
[2-xiv]



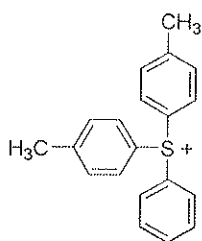
[2-xv]



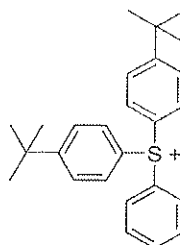
[2-xvi]



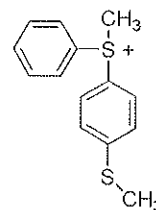
[2-xvii]



[2-xviii]



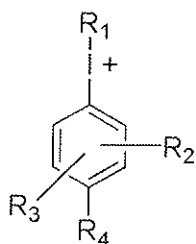
[2-xix]



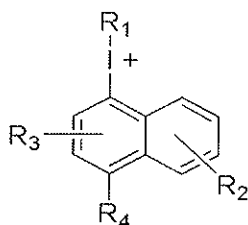
[2-xx]

The moiety represented by the formula 2, which is the cation moiety of the compound represented by the formula 1, may represent any one selected from the group consisting of the following formulas 3a and 3b.

5 [Formula 3a]



[Formula 3b]



In the formulas 3a and 3b, R₁ represents any one selected from the group consisting of a hydrogen atom, an alkyl group, an allyl group, a perfluoroalkyl group, an aryl group and combinations thereof.

10 R₂ and R₃ each independently represent any one selected from the group consisting

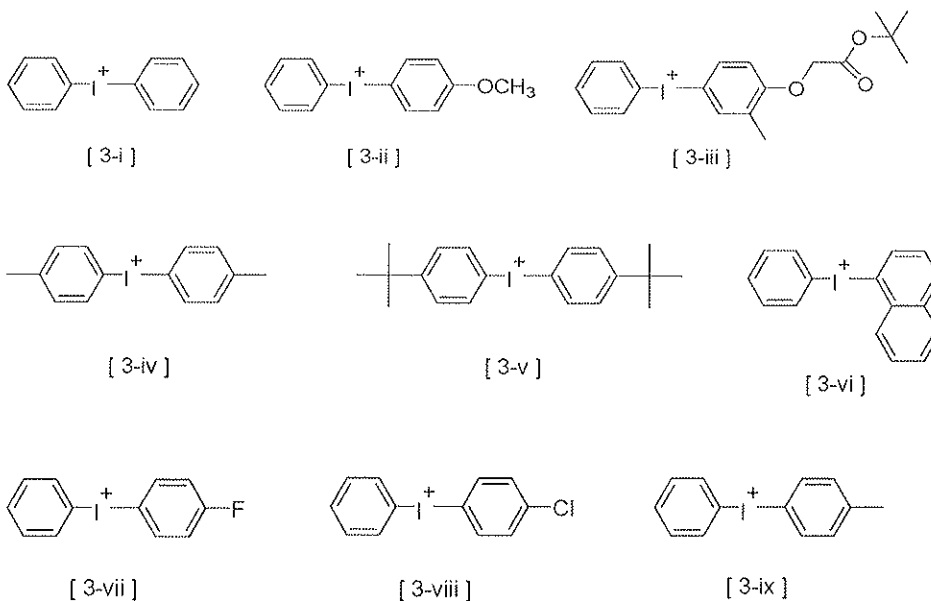
of a hydrogen atom, an alkyl group, an allyl group, a perfluoroalkyl group, an aryl group, and combinations thereof.

R₄ represents any one selected from the group consisting of a halogen atom, an alkyl group, an alkoxy group, an aryl group, a thioalkoxy group, an alkoxycarbonylmethoxy group, a thiophenoxy group, and combinations thereof.

In the formulas 3a and 3b, examples of the alkyl group include a methyl group, an ethyl group, a propyl group, an isopropyl group, an n-butyl group, a phenyl group, a hexyl group, and an octyl group, and examples of the alkoxy group include a methoxy group, an ethoxy group, a propoxy group, a butoxy group, a hexyloxy group, and an octyloxy group.

Furthermore, the moiety represented by the formula 2, which is the cation moiety of the compound represented by the formula 1, may represent any one selected from the group consisting of the following formulas 3-i to 3-ix.

[Formulas 3-i to 3-ix]

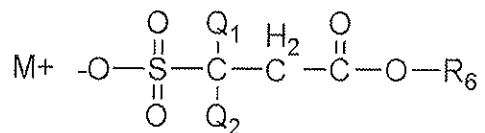


The method for manufacturing the photoacid generator represented by the formula 1 according to another embodiment of the present invention, includes a first step of

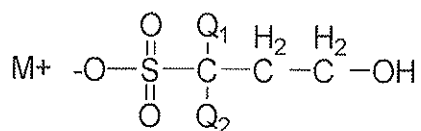
dissolving a compound represented by the following formula 8 in a solvent, and reacting the solution with a reducing agent to obtain a compound represented by the following formula 6; a second step of reacting a compound represented by the following formula 7 with a compound represented by the following formula 6 in the presence of a basic catalyst, to obtain a compound represented by the following formula 4; and a third step of
 5 subjecting a compound represented by the following formula 4 and a compound represented by the following formula to a substitution reaction, and thereby obtaining a compound represented by the formula 1.

The first step includes a process of dissolving a compound represented by the
 10 following formula 8 in a solvent, adding a reducing agent, and thereby obtaining a compound represented by the following formula 6.

[Formula 8]



[Formula 6]



In the formula 6 and formula 8, R₆ represents an alkyl group, and may specifically
 15 represent any one selected from the group consisting of a methyl group, a trifluoromethyl group, a trichloromethyl group, a tribromomethyl group, a triiodomethyl group, an ethyl group, a propyl group, and a butyl group. Q₁ and Q₂ each independently represent a halogen atom, and preferably a fluorine atom. M⁺ represents any one selected from the group consisting of Li⁺, Na⁺ and K⁺.

In regard to the solvent used to dissolve the compound represented by the formula 8 in the first step reaction, any solvent can be used without any limitations as long as the solvent is capable of dissolving the ester compound represented by the formula 8 and bringing on a reduction reaction.

5 For the solvent, any one selected from the group consisting of esters, ethers, lactones, ketones, amides, alcohols and combinations thereof can be used, and preferably, an alcohol-based solvent can be used together with any one selected from the group consisting of dichloromethane, chloroform, dichloroethane, acetonitrile, toluene, dimethylformamide, tetrahydrofuran, dimethylformamide, dimethyl sulfoxide, and
10 combinations thereof, but the present invention is not intended to be limited to these.

The alcohol-based solvent may be any one selected from the group consisting of methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, t-butyl alcohol, oxobutyl alcohol, undecyl alcohol, hydroxydecyl alcohol, heptyl alcohol, 2-methyl-1-pentyl alcohol, allyl alcohol, ethoxycarbonylmethyl alcohol, methoxyethyl alcohol, 1-methoxy-2-propyl alcohol, benzyl alcohol, phenethyl alcohol,
15 cyclohexyl alcohol, menthyl alcohol, tetrahydrofurfuryl alcohol, tetrahydropyranyl alcohol, cyanobutyl alcohol, 4-hydroxy-2-butanone, and combinations thereof, but the present invention is not intended to be limited to these.

As the reducing agent, any one selected from the group consisting of NaBH_4 ,
20 LiAlH_4 , $\text{BH}_3\text{-THF}$, $\text{NaBH}_4\text{-AlCl}_3$, $\text{NaBH}_4\text{-LiCl}$, LiAl(OMe)_3 , and combinations thereof can be used.

The compound represented by the formula 8 and the reducing agent can be used at a molar ratio of 1:1 to 1:5, and preferably used at a molar ratio of 1:2 to 1:3.5. When the compound represented by the formula 8 and the reducing agent are used at the molar ratios
25 described above, the yield of the product relative to the amount of the reducing agent used

can be increased.

The first reaction can include, specifically, a step of dissolving the compound represented by the formula 8 in the solvent mentioned above in an ice bath, adding a reducing agent dropwise to the solution to prepare a reaction mixture liquid, removing the
5 reaction mixture liquid from the ice bath, and heating and stirring the reaction mixture liquid.

The process of stirring can be carried out preferably at 20°C to 120°C for 2 to 6 hours, and more preferably at 45°C to 80°C for 3 to 5 hours. When the process of stirring is achieved in the temperature and time ranges described above, the yield of the product
10 can be increased, and the formation of side products can be minimized.

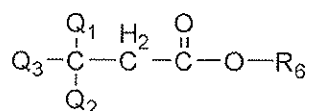
The reaction of the reaction mixture liquid is terminated by quenching, the solvent is removed, and then the reaction product is crystallized.

In regard to the method for crystallization, any method can be used without limitations as long as the method is a usual method of removing the solvent from the
15 reaction mixture liquid and crystallizing the reaction product, but preferably, a method of removing the solvent from the reaction mixture liquid, dissolving the residue in distilled water, subsequently acidifying the solution to pH 5 to 6, concentrating the reaction mixture liquid, adding an alcohol again to the concentrate to remove inorganic salts in a slurry form, filtering the residue, and crystallizing the filtrate using diethyl ether or the
20 like, can be used.

The compound represented by the formula 8 can be produced through an intermediate production step of reacting an alkoxide with a halide to produce a dialkoxyhalide compound having two alkoxy groups, subsequently oxidizing one of the two alkoxy groups of the dialkoxyhalide compound to produce a compound represented
25 by the following formula 9; and a sulfonation step of reacting the compound represented

by the formula 9 with an inorganic sulfite to produce the compound represented by the formula 8.

[Formula 9]



In the formula 9, R₆ represents an alkyl group, and may specifically represent any one selected from the group consisting of a methyl group, a trifluoromethyl group, a trichloromethyl group, a tribromomethyl group, a triiodomethyl group, an ethyl group, a propyl group, and a butyl group; and Q₁ to Q₃ each independently represent a halogen atom, and preferably a fluorine atom.

Specifically, the alkoxide used in the intermediate production step may be an alkoxyalkene having 3 to 10 carbon atoms, which contains a carbon-carbon double bond, and specifically, the alkoxide may be methoxyethene, ethoxyethene, or the like. The halide may be an alkyl halide, and may be specifically perfluoromethane, dibromodifluoromethane, perbromomethane, or perchloromethane.

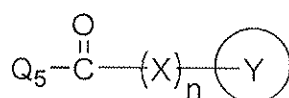
In the intermediate production step, the alkoxide and the halide are allowed to react in an alcohol-based solvent, and the compounds can also be reacted with sodium hydrosulfite (Na₂S₂O₄) and sodium hydrogen carbonate (NaHCO₃). Furthermore, the reaction of oxidizing one of the two alkoxy groups of the dialkoxyhalide compound produced as described above can be carried out in the presence of an oxidizing agent, and a specific example of the oxidizing agent that can be used is KHSO₅.

As the inorganic sulfite used in the sulfonation step, specifically sodium hydrosulfite can be used, and the reaction can also be carried out after adding sodium hydrogen carbonate (NaHCO₃). When the sulfonation reaction is carried out using sodium

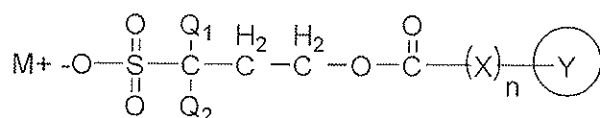
hydrosulfite, the compound represented by the formula 8 can be produced by oxidizing the organic sulfonate thus produced. In this case, hydrogen peroxide (H₂O₂), sodium tungstate (Na₂WO₄) or the like can be used as the oxidizing agent.

The second step includes a process of reacting a compound represented by the following formula 7 with the compound represented by the formula 6 in the presence of a basic catalyst, and thereby obtaining a compound represented by the following formula 4.

[Formula 7]



[Formula 4]



In the formula 4 and formula 7, Q₁, Q₂ and Q₅ each independently represent a halogen atom, and preferably a fluorine atom; and n represents an integer from 0 to 5, and preferably an integer from 0 to 2.

M⁺ represents any one selected from the group consisting of Li⁺, Na⁺ and K⁺.

X and Y have the same definitions as described above for the compound represented by the formula 1, and the definitions will be not repeated.

As the basic catalyst, any one selected from the group consisting of triethylamine, diethylamine, pyridine, diethylisopropylamine, and combinations thereof can be used. When a basic catalyst is used in the second step reaction, the desired product can be obtained within a minimal reaction time.

The reaction of the second step can be carried out in the presence of a solvent, and any one selected from the group consisting of esters, ethers, lactones, ketones, amides, alcohols, and combinations thereof can be used as the solvent. Preferably, the solvent may be any one selected from the group consisting of dichloromethane, chloroform, dichloroethane, acetonitrile, toluene, and combinations thereof.

The compound represented by the formula 6 and the compound represented by the formula 7 can be used in the reaction at a molar ratio of 2:1 to 1:3, and preferably can be used at a molar ratio of 1.5:1 to 1:1.5. When the compound represented by the formula 6 and the compound represented by the formula 7 are allowed to react at the molar ratio described above, the two compounds can be completely consumed, and thereby the efficiency of the reaction can be increased.

Furthermore, the compound represented by the formula 6 and the basic catalyst can be used in the reaction at a molar ratio of 1:1 to 1:4, and preferably used at a molar ratio of 1:1.1 to 1:1.8. When the compound of formula 6 and the basic catalyst are used in the reaction at the molar ratio described above, the reaction time can be accelerated, and removal of any residual basic catalyst can be made easier.

The second step reaction can specifically include a process of dissolving the compound represented by the formula 6 and the compound represented by the formula 7 in the solvent mentioned above to prepare a reaction mixture, stirring the reaction mixture at 15°C to 30°C, adding the above-mentioned basic catalyst dropwise to the reaction mixture, and then stirring the resulting mixture.

The process of stirring can be carried out preferably at a temperature of 10°C to 40°C for 0.5 to 6 hours, and more preferably at a temperature of 18°C to 30°C for 1 to 3 hours. When the process of stirring is carried out in the temperature and time ranges described above, the yield of the product can be increased, and the formation of side

products can be minimized.

The reaction of the reaction mixture liquid is terminated by quenching, the solvent is removed, and then the reaction product is crystallized. Thus, the compound represented by the formula 4 can be obtained.

5 In regard to the method for crystallization, any method can be used without limitations as long as the method is a usual method of removing the solvent from the reaction mixture liquid and crystallizing the reaction product, but preferably, a method of removing the solvent from the reaction mixture liquid, adding an alcohol again to the residue, filtering a slurry thus obtained, washing the solids obtained by filtration using
10 distilled water, ethyl ether and the like, and drying and crystallizing the solids, can be used.

The third step includes a process of subjecting the compound represented the formula 4 shown above and the compound represented by the following formula 5 to a substitution reaction, and thereby obtaining a compound represented by the following formula 1.

15 [Formula 5]



In the formula 5, Z- represents any one selected from the group consisting of (OSO₂CF₃)-, (OSO₂C₄F₉)-, (OSO₂C₈F₁₇)-, (N(CF₃)₂)-, (N(C₂F₅)₂)-, (N(C₄F₉)₂), (C(CF₃)₃)-, (C(C₂F₅)₃)-, (C(C₄F₉)₃)-, F-, Cl-, Br-, I-, BF₄-, AsF₆- and PF₆-; A+ represents an organic counterion. Since the specific definition of this organic counterion is the same as the
20 definition provided for the compound represented by the formula 1, the description will not be repeated.

The compound represented by the formula 4 and the compound represented by the formula 5 can be used at a molar ratio of 1:1 to 5:1, preferably at a molar ratio of 1:1 to

3:1, and even more preferably at a molar ratio of 1:1 to 2:1. When the compounds are used at the molar ratio described above, the reaction treatment time can be minimized, and any side reaction caused by the use of an excessive amount of the reaction product can be suppressed.

5 The substitution reaction can be carried out by using a recrystallization method or a method of solidifying and recovering the salt obtained from the reaction using a mixture of a solvent that satisfactorily dissolves the salt (good solvent) and a solvent that poorly dissolves the salt (poor solvent), and a method of extracting with a solvent, or a method of concentrating and recovering the salt obtained can also be used.

10 Preferably, the compounds are dissolved in dichloromethane and water to form two layers, and then the layers can be stirred to allow a substitution reaction to occur. In the case of using such a two-layer reaction method, it is advantageous in that no additional methods are needed for the separation of the product. The stirring can be carried out for 2 to 6 hours, and may also be carried out for 2 to 4 hours. When the reaction is carried out
15 in the time range described above, the yield of the product can be maximally increased.

 When the compound represented by the formula 1 is produced through the processes described above, the compound represented by the formula 1 can be produced by an efficient and simple method.

20 The resist composition according to another embodiment of the present invention contains the photoacid generator represented by the formula 1 shown above. The resist composition is based on the constitution of conventional resist compositions, and therefore, the description on the resist composition will not be repeated herein.

 The photoacid generator according to the present invention can produce, at the time of exposure, an acid which has a low diffusion rate, has a short diffusion distance, and
25 exhibits an appropriate degree of acidity so that the line width roughness (LWR)

characteristics can be improved, and elution of which in a solvent such as pure water that is used in the process can be controlled. Furthermore, the method for manufacturing a photoacid generator according to the present invention can produce the photoacid generator described above, through an efficient and simple method.

5

Best Mode for Carrying Out the Invention

Hereinafter, the present invention will be described in detail by way of Examples so that a person having ordinary skill in the art pertained to the present invention can easily carry out the invention. However, the present invention can be carried out in various alterations and modifications, the scope of which is not limited to the Examples that are described herein.

10

Synthesis of photoacid generator

[Synthesis Example 1 for photoacid generator]

Synthesis of Benzoic acid-2,2-difluoro-2-sulfo-propyl ester diphenyl methylphenyl

15 sulfonium salt

(Step 1) As shown in the following Reaction Scheme 1, 83 g (0.376 mol) of sodium 1,1-difluoro-3-methoxy-3-oxopropane-1-sulfonate was dissolved in 160 ml of methanol (MeOH) and 1.2 L of tetrahydrofuran (THF) as solvents, in an ice bath. 44 g (1.16 mol) of sodium borohydride (NaBH_4) was slowly added dropwise to the solution, and thus a reaction mixture liquid was prepared. After completion of the dropwise addition, the reaction mixture liquid was removed from the ice bath and was heated to 60°C. While maintained at the temperature, the reaction mixture liquid was stirred for about 4 hours.

20

The reaction mixture liquid was quenched with distilled water, and then the solvent was removed. The crude reaction mixture was dissolved in distilled water, and the

25

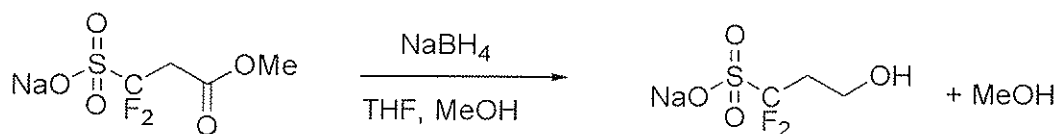
solution was acidified with concentrated hydrochloric acid to pH 5 to 6.

The acidified reaction mixture was concentrated, and then methanol was added thereto again. The slurry thus obtained was filtered to remove inorganic salts. The filtrate obtained by removing the slurry was washed two times with hexane, and the methanol layer was concentrated again and then was crystallized using diethyl ether.

The white solids obtained by crystallization were dried in a vacuum, and thus 68.5 g (0.346 mol) of sodium 1,1-difluoro-3-hydroxypropane-1-sulfonate (yield 95%) was obtained.

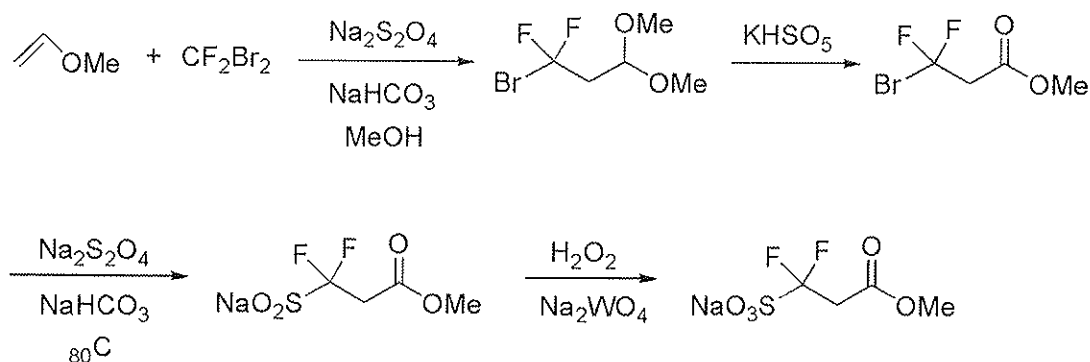
$^1\text{H-NMR}(\text{D}_2\text{O})$: (ppm) 2.38(t, 2H), 4.18(t, 2H)

[Reaction Scheme 1]



For reference, sodium 1,1-difluoro-3-methoxy-3-oxopropane-1-sulfonate shown above can be produced by a reaction such as the following Reaction Scheme 2.

[Reaction Scheme 2]



(Step 2) As shown in the following Reaction Scheme 3, 20 g (0.101 mol) of the

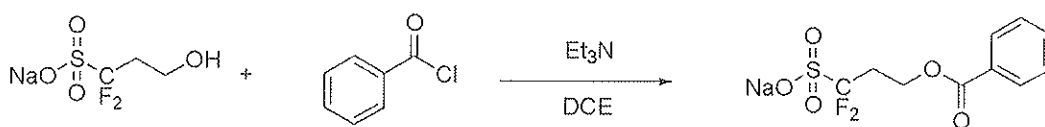
sodium 1,1-difluoro-3-hydroxypropane-1-sulfonate produced in Step 1, and 11.5 g (0.0818 mol) of benzoyl chloride were dissolved in 150 ml of dichloroethane to prepare a reaction mixture, and the reaction mixture was stirred at ambient temperature. 11 g (0.1087 mol) of triethylamine (Et₃N) was slowly added dropwise to the reaction mixture at 20°C to 25°C, and then the mixture was stirred for 2 hours.

After completion of the reaction of the reaction mixture, the reaction solvent was removed from the reaction mixture, and the residue was made into slurry using ethyl ether, which was then filtered. The solid obtained by filtering the slurry were washed using distilled water and ethyl ether, and then were dried in a vacuum.

The vacuum-dried solids were subjected to ¹H-NMR, and the structure was confirmed. Thus, 11.5 g (yield 73.5%) of sodium 3-(benzoyloxy)-1,1-difluoropropane-1-sulfonate having the following structural formula was obtained.

¹H-NMR (Dimethyl sulfoxide-*d*₆, tetramethylsilane): (ppm) 2.38(t, 2H), 4.18(t, 2H), 7.37(t, 2H), 7.47(t, 1H), 7.97(d, 2H)

[Reaction Scheme 3]



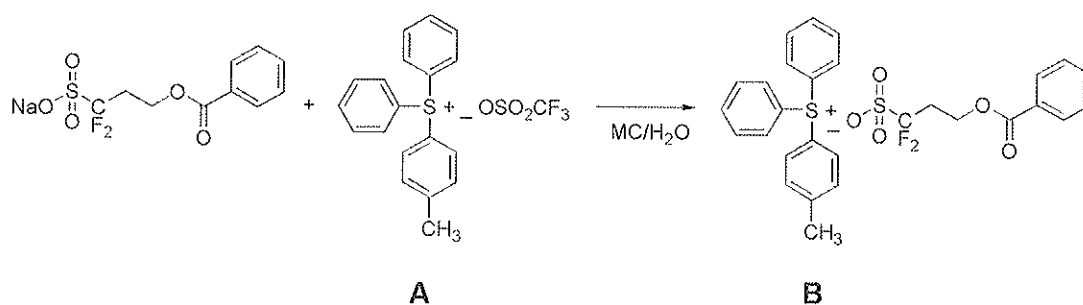
(Step 3) As shown in the following Reaction Scheme 4, 4 g (0.013 mol) of the sodium 3-(benzoyloxy)-1,1-difluoropropane-1-sulfonate produced in Step 2, and 4.22 g (0.0099 mol) of diphenyl methylphenyl sulfonium trifluoromethanesulfonate were dissolved in 40 ml of dichloromethane (or methylene chloride, MC) and 40 ml of water to form a reaction mixture with two layers. The reaction mixture was vigorously stirred for 3 hours so as to allow a reaction (two-layer reaction) to occur.

When the stirring of the reaction mixture was completed, an aliquot of the organic

layer was taken to check the progress of the reaction by ^{19}F -NMR. When the reaction was completed, the organic layer was collected, and the solvent was removed. The slurry thus obtained was washed using dichloromethane as a good solvent and hexane as a poor solvent, and thus solids were obtained. The solids were dried under reduced pressure, and thus a compound represented by formula B in the following Reaction Scheme 4 was obtained. Thus, 3.2 g (0.0078 mol) of benzoic acid-2,2-difluoro-2-sulfo-propyl ester diphenyl methylphenyl sulfonium salt (yield 59.5%) was obtained, and the structure was confirmed by ^1H -NMR.

^1H -NMR (Chloroform- d_3 , tetramethylsilane): (ppm) 2.45(s, 3H), 2.81(m, 2H), 4.64(t, 2H), 7.38-7.76(m, 17H), 8.01(d, 2H)

[Reaction Scheme 4]



[Synthesis Example 2 for photoacid generator]

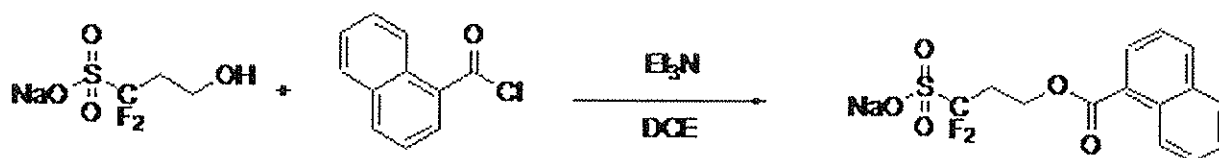
Synthesis of benzoic acid-2,2-difluoro-2-sulfo-propyl ester diphenyl methylphenyl sulfonium salt

(Step 1) The process was carried out in the same manner as in Step 1 of the Synthesis Example 1, and thus sodium 1,1-difluoro-3-hydroxypropane-1-sulfonate was obtained.

(Step 2) The process was carried out in the same manner as in Step 2 of the

Synthesis Example 1, except that 1-naphthalenecarbonyl chloride was used instead of benzoyl chloride. Thus, sodium naphthalene-1-carboxylic acid-3,3-difluoropropane-1-sulfonate as shown in the following Reaction Scheme 5 was obtained.

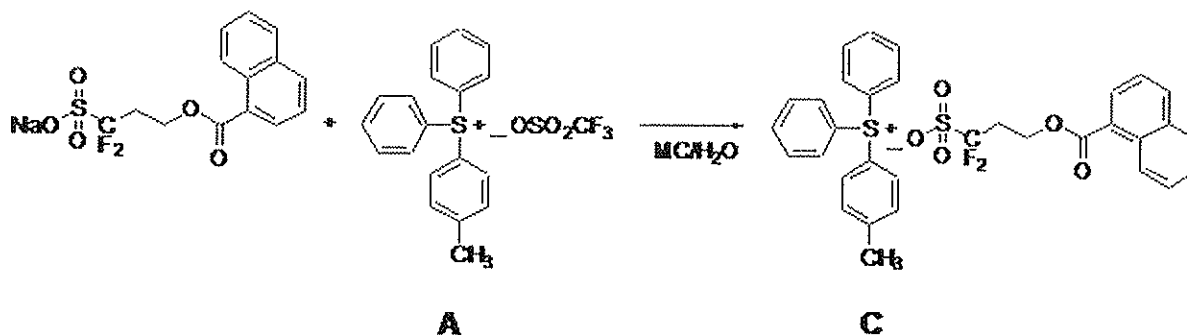
[Reaction Scheme 5]



(Step 3) The sodium naphthalene-1-carboxylic acid-3,3-difluoropropane-1-sulfonate produced in Step 2 and diphenyl methylphenyl sulfonium trifluoromethanesulfonate represented by formula A in the following Reaction Scheme 6 were allowed to react, and thus naphthalene-1-carboxylic acid-3,3-difluoropropane-1-sulfonate diphenyl methylphenyl sulfonium salt represented by formula C in the following Reaction Scheme 6 was obtained.

¹H-NMR(Chloroform-*d*₃, tetramethylsilane): (ppm) 2.42(s, 3H), 2.88(m, 2H), 4.75(t, 2H), 7.42-7.87(m, 17H), 7.94(d, 1H), 8.11(d, 1H), 8.19(d, 1H), 9.12(d, 1H)

[Reaction Scheme 6]



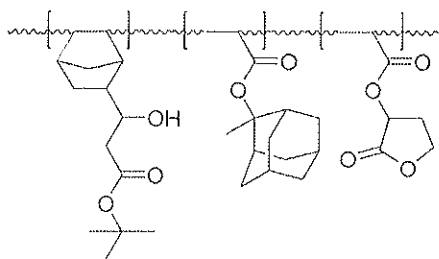
Synthesis of resin

[Synthesis Example 1 for resin]

3-Bicyclo[2.2.1]hept-5-en-2-yl-3-hydroxypropionic acid t-butyl ester, 1-methyladamantane acrylate (2-methyl-2-adamantyl acrylate), and γ -butyrolactone methyl acrylate (2-oxotetrahydrofuran-3-yl acrylate) were added at a molar ratio of 1:1:1 (33 parts:33 parts:33 parts), and 1,4-dioxane was used as a polymerization solvent, in an amount equivalent to 3 times the total mass of the reaction monomer. As an initiator, azobisisobutyronitrile was used at a proportion of 4 mol% based on the total molar amount of the monomer, and the system was allowed to react for 16 hours at 65°C.

After the reaction, the reaction solution was precipitated using n-hexane, and the precipitate was dried in a vacuum. Thus, a resin represented by the following formula 10 was obtained. The copolymer obtained as the precipitate had a weight average molecular weight of 8,500.

[Formula 10]



Preparation of resist

[Comparative Example 1]

100 parts by weight of the resin represented by the formula 10, which was obtained in Synthesis Example 1 for resin, 5 parts by weight of adamantane-1-carboxylic acid-2,2-difluoro-2-sulfo-propyl ester diphenyl methylphenyl sulfonium salt as a photoacid generator (PAG), and 0.5 parts by weight of tetramethylammonium hydroxide as a basic additive (BASE) were dissolved in 1,000 parts by weight of propylene glycol methyl ether

acetate, and then the solution was filtered through a 0.2- μ m membrane filter. Thus, a resist solution was prepared.

The resist solution was applied on a substrate using a spinner, and the resist solution was dried at 110°C for 90 seconds to form a film having a thickness of 0.20 μ m.

5 The film thus formed was exposed using an ArF excimer laser stepper (lens aperture number: 0.78) , and was heat treated at 110°C for 90 seconds. The film thus formed was developed for 40 seconds using a 2.38 wt% aqueous solution of tetramethylammonium hydroxide, and then the film was washed and dried. Thus, a resist pattern was formed.

[Example 1]

10 A resist solution was prepared in the same manner as in Comparative Example 1, except that 3 parts by weight of benzoic acid-2,2-difluoro-2-sulfo-propyl ester diphenyl methylphenyl sulfonium salt represented by formula B in the Reaction Scheme 4, which was produced in Synthesis Example 1, was used as a photoacid generator. The properties of the resist solution were evaluated.

15 [Example 2]

A resist solution was prepared in the same manner as in Comparative Example 1, except that 5 parts by weight of benzoic acid-2,2-difluoro-2-sulfopropyl ester diphenyl methylphenyl sulfonium salt represented by formula B in the Reaction Scheme 4, which was produced in Synthesis Example 1, was used as a photoacid generator. The properties
20 of the resist solution were evaluated.

[Example 3]

A resist solution was prepared in the same manner as in Comparative Example 1, except that 7 parts by weight of benzoic acid-2,2-difluoro-2-sulfopropyl ester diphenyl methylphenyl sulfonium salt represented by formula B in the Reaction Scheme 4, which
25 was produced in Synthesis Example 1, was used as a photoacid generator. The properties

of the resist solution were evaluated.

The properties of Comparative Example 1 and Examples 1 to 3, such as sensitivity, resolution, and LWR were evaluated, and the results are presented in the following Table 1.

In the case of LWR, the pattern roughness of a 0.10- μ m line-and-space (L/S) pattern formed after the development was observed, and the degree of improvement in the LWR was ranked from number 1 to number 5 while the pattern obtained in Comparative Example 1 was ranked as 1. A larger number indicates better LWR characteristics.

In the case of sensitivity, an amount of exposure that forms a 0.10- μ m line-and-space (L/S) pattern at a line width of 1:1 was designated as the optimum amount of exposure, and the minimum pattern dimension obtained by imaging when the sensitivity was set equal to the optimum amount of exposure, was designated as the resolution.

[Table 1]

	Resin (100 parts by weight)	PAG ⁽¹⁾ (parts by weight)	BASE ⁽²⁾ (parts by weight)	Sensitivity (mJ/cm ²)	Resolution (nm)	LWR
Example 1	Synthesis Example 1 for resin	3	0.5	18	70	5
Example 2	Synthesis Example 1 for resin	5	0.5	15	80	3
Example 3	Synthesis Example 1 for resin	7	0.5	13	70	3
Comparative Example 1	Synthesis Example 1 for resin	5	0.5	14	90	1

(1) Photoacid generator (PAG)

Examples 1 to 3: Benzoic acid-2,2-difluoro-2-sulfo-propyl ester diphenyl methylphenyl sulfonium salt represented by formula B in the Reaction Scheme 4, which was produced in the Synthesis Example 1

Comparative Example 1: Adamantane-1-carboxylic acid-2,2-difluoro-2-sulfo-
propyl ester diphenyl methylphenyl sulfonium salt

(2) Basic accitive (BASE): Tetramethylammonium hydroxide

The photoacid generator (PAG) used in Examples 1 to 3 was produced by
5 introducing an aromatic ring into the anion of a photoacid generator. This photoacid
generator maintained a degree of acidity similar to that of triflate as compared with
existing triflate or nonaflate photoacid generators, had a low diffusion rate of acid and a
short diffusion distance. Thus, this photoacid generator had characteristics suitable for the
realization of finer L/S patterns.

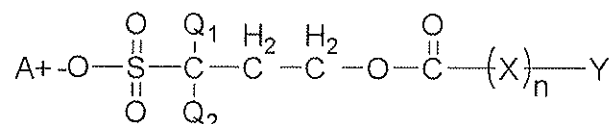
10 When the properties analysis results of Table 1 are examined, the photoacid
generator shows superior performance as compared with existing triflate type photoacid
generators, in terms of the LWR and resolution. Introduction of an aromatic ring into the
anion of a photoacid generator exhibited excellent results even in terms of transparency
when irradiated with light. Once an acid is generated from the photoacid generator and
15 moves in the form of an anion, the aromatic ring does not affect transparency at all, and
there is obtained an advantageous effect of being capable of controlling the diffusion rate
and diffusion distance of the acid depending on the size of the aromatic ring. Thus, the
photoacid generator shows features that are distinguished from existing photoacid
generators.

20 As such, preferred embodiments of the present invention have been described in
detail, but the scope of the present invention is not intended to be limited thereto, and
various modifications and improvements that can be made by an ordinarily skilled person
using the fundamental concept of the present invention as defined in the following claims
are also included in the scope of the present invention.

CLAIMS

1. A photoacid generator represented by the following formula 1:

[Formula 1]



wherein in the formula 1,

5 Y represents any one selected from the group consisting of an alkyl group substituted with an aryl group, and a monocyclic or polycyclic aromatic hydrocarbon group;

Q₁ and Q₂ each independently represent a halogen atom;

10 X represents any one selected from the group consisting of an alkanediyl, an alkenediyl, NR', S, O, CO and combinations thereof, wherein R' represents any one selected from the group consisting of a hydrogen atom and an alkyl group;

n represents an integer from 0 to 5; and

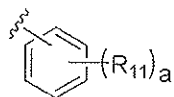
A⁺ represents an organic counterion.

15 2. The photoacid generator according to claim 1, wherein Y represents any one selected from the group consisting of a phenyl group, a naphthyl group, a biphenyl group, an anthryl group, a phenanthrene group, a fluorenyl group, a pyrene group, a phenalene group, an indene group, a biphenylene group, a diphenylmethyl group, a tetrahydronaphthyl group, a dihydroanthryl group, a tetraphenylmethyl group, and a
20 triphenylmethyl group.

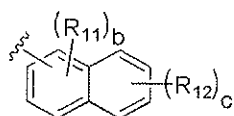
3. The photoacid generator according to claim 1, wherein Y represents any one

selected from the group consisting of the following formulas 1-a to 1-l:

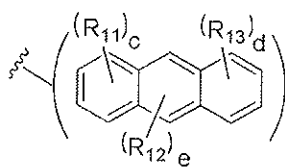
[Formula 1-a]



[Formula 1-b]

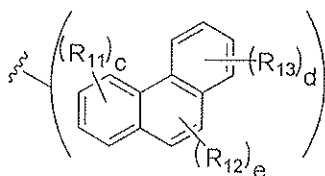


[Formula 1-c]

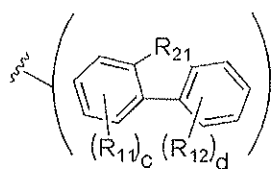


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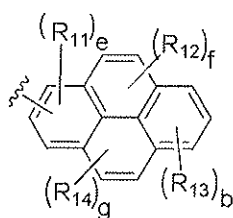
[Formula 1-d]



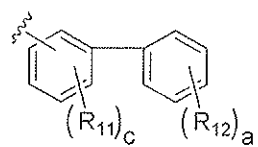
[Formula 1-e]



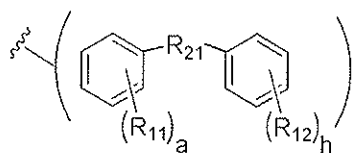
[Formula 1-f]



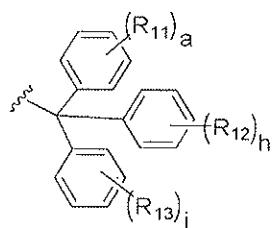
[Formula 1-g]



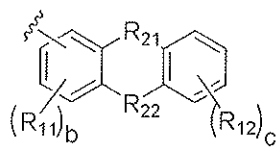
[Formula 1-h]



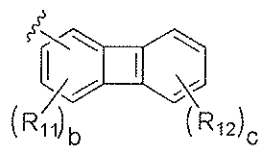
[Formula 1-i]



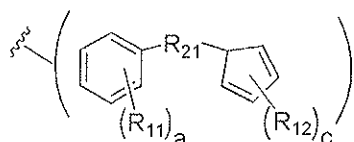
[Formula 1-j]



5 [Formula 1-k]



[Formula 1-l]



wherein in the formulas 1-a to 1-l,

R₁₁, R₁₂, R₁₃ and R₁₄ may each independently be substituted with any one selected from the group consisting of an alkyl group, an alkoxy group, a perfluoroalkyl group, a perfluoroalkoxy group, a halogen atom, a hydroxyl group, a cyano group, a nitro group, an amino group, a thio group, a methylthio group, a methoxy group, OR', COR' and COOR, wherein R' represents any one selected from the group consisting of an alkyl group and an aryl group;

R₂₁ and R₂₂ each independently represent any one selected from CR₂₄R₂₅, O, CO, S and NR₂₃, wherein R₂₃ to R₂₅ each independently represent any one selected from the group consisting of a hydrogen atom, an alkyl group and an aryl group;

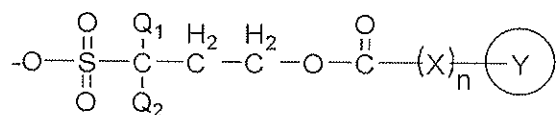
a, h and i each independently represent an integer from 0 to 5; b represents an integer from 0 to 3; c and d each independently represent an integer from 0 to 4; e, f and g each independently represent an integer from 0 to 2; and $0 \leq c+d+e \leq 9$.

4. The photoacid generator according to claim 1, wherein X in the formula 1 represents any one selected from the group consisting of -O-, -OCH₂-, -OCH(Cl)-, -CO-, -COCH₂-, -COCH₂CH₂-, -CH₂-, -CH₂CH₂-, -CH₂-O-, -CH₂-O-CH₂-, -CH₂CH₂-O-, -CH₂-O-CH₂CH₂-, -CH₂CH₂-O-CH₂-, -CH₂CH₂CH₂-O-, -CH₂-O-CH₂CH₂CH₂-, -CH₂CH₂-O-CH₂CH₂CH₂-, -CH₂CH₂CH₂-O-CH₂-, -CH(CH₃)-, -C(CH₃)₂CH₂-, -CH(CH₃)CH₂-, -CH(CH₂CH₃)-, -CH(OCH₃)-, -C(CF₃)(OCH₃)-, -CH₂-S-, -CH₂-S-CH₂-, -CH₂CH₂-S-, -CH₂-S-CH₂CH₂-, -CH₂CH₂-S-CH₂-, -CH₂CH₂CH₂-S-, -CH₂-S-CH₂CH₂CH₂-, -CH₂CH₂-S-

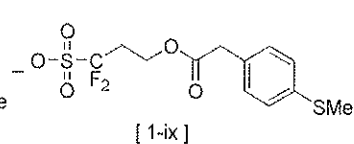
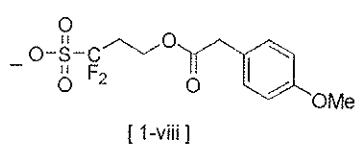
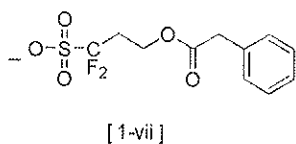
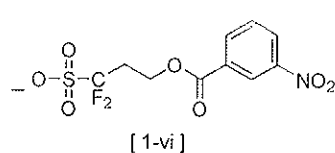
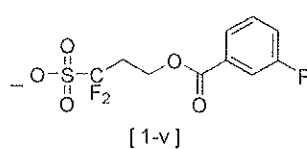
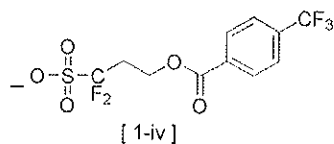
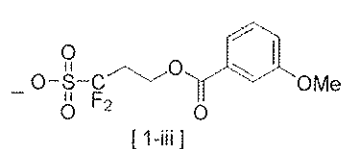
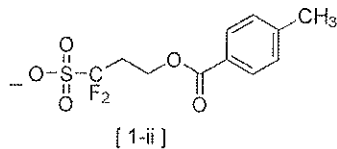
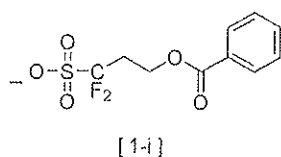
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 -CH(CH₃)CH₂CO-, -CH(OH)-, -C(OH)(CH₃)-, -CH(F)-, -CH(Br)-, -CH(Br)CH(Br)-, -
 CH=CH-, -CH₂CH=CH-, -CH=CHCH₂-, -CH=CH-O-, -CH=CH-S- and -CH=CHCO-.

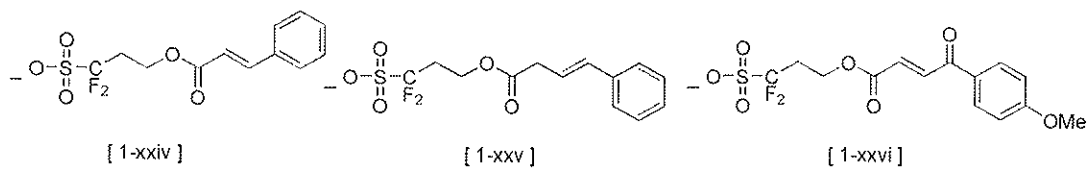
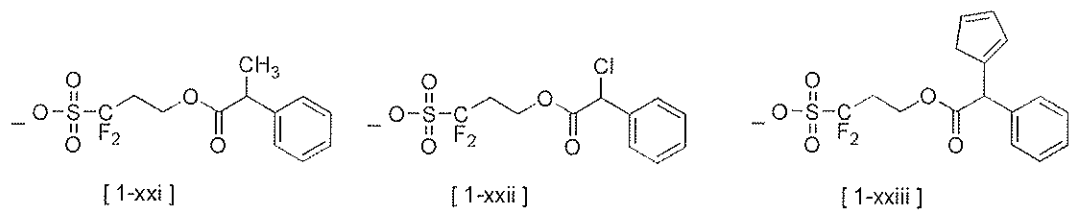
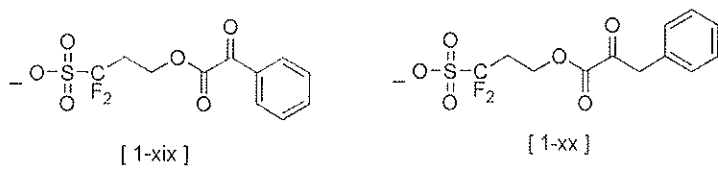
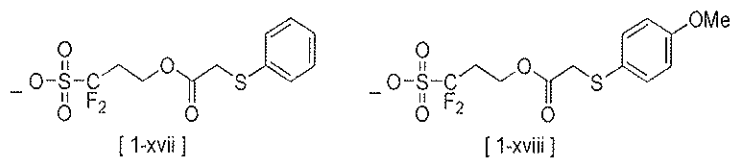
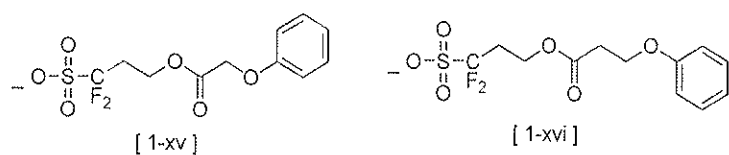
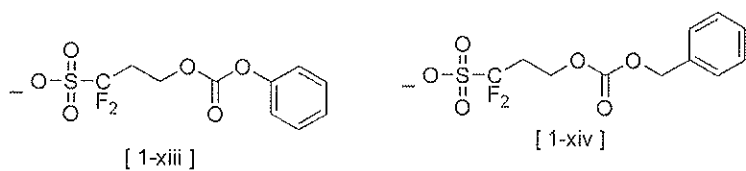
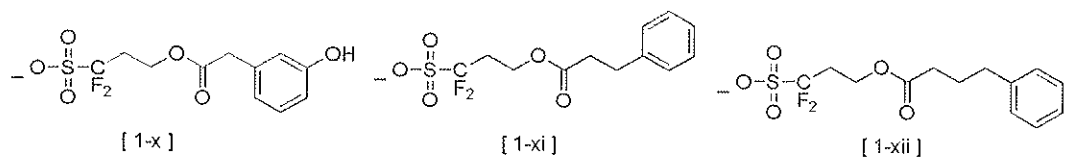
5 5. The photoacid generator according to claim 1, wherein a moiety represented by
 the following formula 3, which is an anion moiety of the compound represented by the
 formula 1, represents any one selected from the group consisting of the following
 formulas 1-i to 1-xxxxxi:

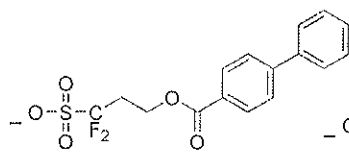
[Formula 3]



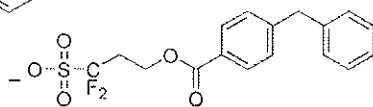
10 [Formulas 1-i to 1-xxxxxi]



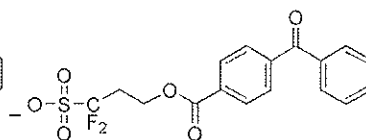




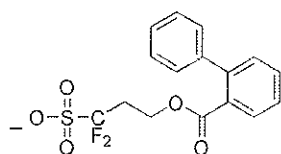
[1-xxvii]



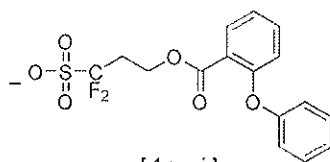
[1-xxviii]



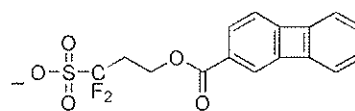
[1-xxix]



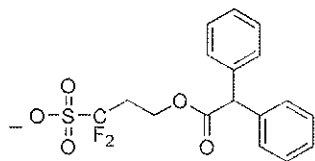
[1-xxx]



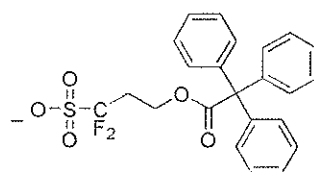
[1-xxxi]



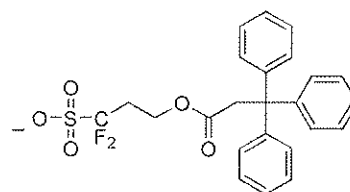
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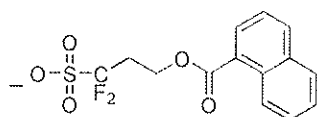
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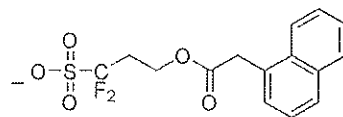
[1-xxxiv]



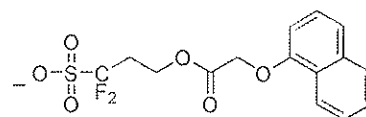
[1-xxxv]



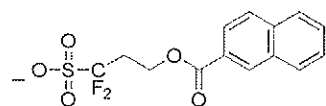
[1-xxxvi]



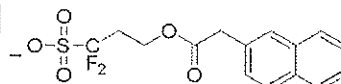
[1-xxxvii]



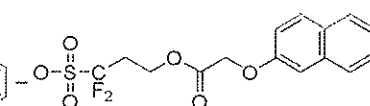
[1-xxxviii]



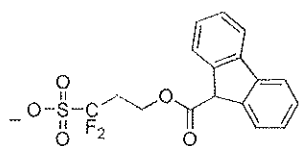
[1-xxxix]



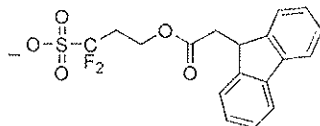
[1-xxxx]



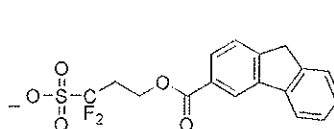
[1-xxxxi]



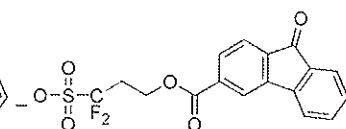
[1-xxxxii]



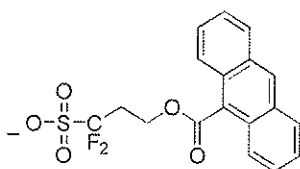
[1-xxxxiii]



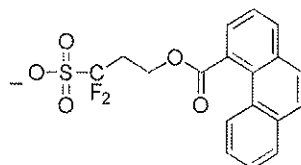
[1-xxxxiv]



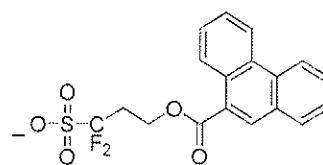
[1-xxxxv]



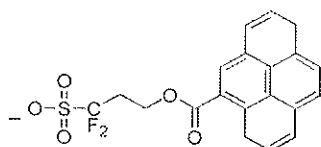
[1-xxxxvi]



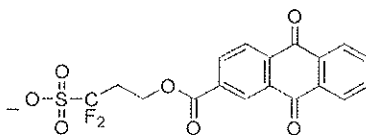
[1-xxxxvii]



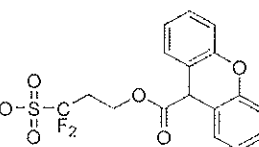
[1-xxxxviii]



[1-xxxxix]



[1-xxxxx]



[1-xxxxxi]

5

6. A method for manufacturing a photoacid generator represented by the following formula 1, the method comprising:

a first step of dissolving a compound represented by the following formula 8 in a solvent, and reacting the solution with a reducing agent to obtain a compound represented by the following formula 6;

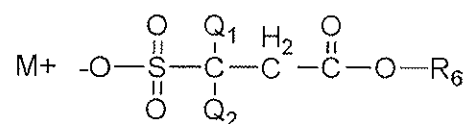
10

a second step of reacting a compound represented by the following formula 7 with the compound represented by the following formula 6 in the presence of a basic catalyst,

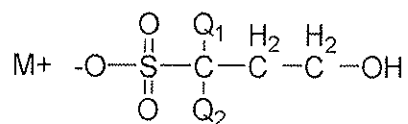
and thereby obtaining a compound represented by the following formula 4; and

a third step of subjecting the compound represented by the following formula 4 and a compound represented by the following formula 5 to a substitution reaction, and thereby obtaining the compound represented by the following formula 1:

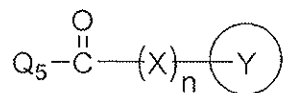
5 [Formula 8]



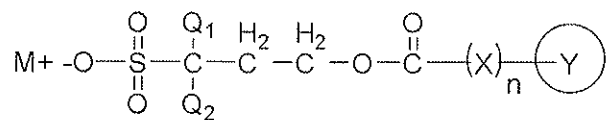
[Formula 6]



[Formula 7]



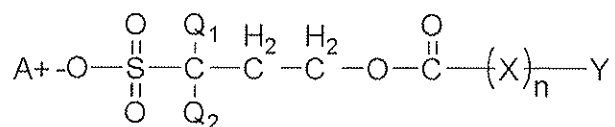
[Formula 4]



[Formula 5]

A+Z-

10 [Formula 1]



wherein in the formula 1, formula 4, formula 5, formula 6, formula 7 and formula 8,

R_6 represents an alkyl group;

Q_1 , Q_2 and Q_5 each independently represent a halogen atom;

Y represents any one selected from the group consisting of an alkyl group
5 substituted with an aryl group, and an aromatic hydrocarbon group;

X represents any one selected from the group consisting of an alkanediyl, an
alkenediyl, NR' , S , O , CO and combinations thereof, wherein R' represents any one
selected from the group consisting of a hydrogen atom and an alkyl group;

n represents an integer from 0 to 5;

10 A^+ represents an organic counterion;

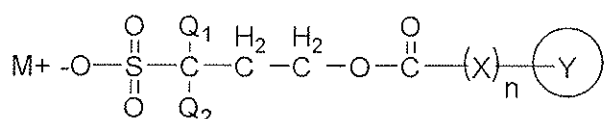
M^+ represents any one selected from the group consisting of Li^+ , Na^+ and K^+ ; and

Z^- represents any one selected from the group consisting of $(OSO_2CF_3)^-$,
 $(OSO_2C_4F_9)^-$, $(OSO_2C_8F_{17})^-$, $(N(CF_3)_2)^-$, $(N(C_2F_5)_2)^-$, $(N(C_4F_9)_2)^-$, $(C(CF_3)_3)^-$, $(C(C_2F_5)_3)^-$,
 $(C(C_4F_9)_3)^-$, F^- , Cl^- , Br^- , I^- , BF_4^- , AsF_6^- and PF_6^- .

15

7. A compound represented by the following formula 4:

[Formula 4]



wherein in the formula 4,

Y represents any one selected from the group consisting of an alkyl group substituted with an aryl group, and an aromatic hydrocarbon group;

X represents any one selected from the group consisting of an alkanediyl, an alkenediyl, NR', S, O, CO and combinations thereof, wherein R' represents any one

5 selected from the group consisting of a hydrogen atom and an alkyl group;

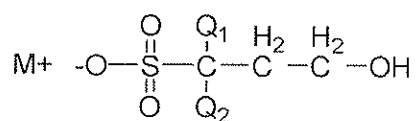
Q₁ and Q₂ each independently represent a halogen atom;

n represents an integer from 0 to 5; and

M⁺ represents any one selected from the group consisting of Li⁺, Na⁺ and K⁺.

10 8. A compound represented by the following formula 6:

[Formula 6]



wherein in the formula 6,

M⁺ represents any one selected from the group consisting of Li⁺, Na⁺ and K⁺; and

Q₁ and Q₂ each independently represent a halogen atom.

15

9. A chemically amplified resist composition comprising the photoacid generator according to any one of claims 1 to 5.

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