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(54) **Title**: METHOD OF PRODUCING A HYDROLYZABLE SILICON-CONTAINING COMPOUND

(57) **Abstract**: The present invention provides a safe, inexpensive, and high yield means of producing a hydrolyzable silicon-containing compound, e.g., an organooxysilane and the like. A compound (A) represented by the general formula R^1-O-R^2 wherein R^1 represents a C_{4-30}, substituted or unsubstituted, tertiary alkyl group or aralkyl group and R^2 represents a C_{1-30}, substituted or unsubstituted, monovalent hydrocarbyl group or acyl group, is reacted in the presence of a Lewis acid catalyst with a halosilane (B) represented by the general formula $R^3{}_mSiX_{4-m}$ wherein R^3 represents the hydrogen atom or a C_{1-30} substituted or unsubstituted monovalent hydrocarbyl group, X is independently bromine or chlorine, and m represents an integer from 0 to 3.

DESCRIPTION

METHOD OF PRODUCING A HYDROLYZABLE SILICON-CONTAINING COMPOUND

Technical Field

[0001] The present invention relates to a method of producing a hydrolyzable silicon-containing compound. The present invention also relates to a hydrolyzable silicon-containing compound that is produced by this method and that substantially does not contain a hydrogen halide or an acyl halide. Priority is claimed on Japanese Patent Application No. 2010-292639, filed on December 28, 2010, the content of which is incorporated herein by reference.

Background Art

[0002] It is known that an organooxysilane can be produced by reacting an alcohol or acetic acid or acetic anhydride with a chlorosilane. For example, the production of an alkoxysilane by the reaction ≡Si–Cl + ROH = SiOR + HCl, wherein R is a monovalent hydrocarbyl group, is described in JP 08-041077 A. The production of an acetoxysilane by the reaction of acetic acid and acetic anhydride with a chlorosilane is described in JP 2000-063390 A. The production of a diacetoxydialkoxysilane by the reaction of an alcohol and acetic anhydride with a chlorosilane is described in JP 10-168083 A. The preparation of trimethoxysilane by the direct reaction of trichlorosilane and methanol in xylene solvent is described in a German patent (DE 19670906). It has been reported, in J. Org. Chem., Vol. 42, No. 23 (1977), that the reaction of iodotrimethylsilane with an alkyl ether at room temperature in the absence of a catalyst yields the trimethylsilylated alcohol corresponding to the alkyl ether. It has also been reported, in J. C. S. Chem. Commun., pp. 874-875 (1978), that trimethylchlorosilane, sodium iodide, and, for example, an ester may be used to obtain a trimethylsilylated reaction product corresponding to the ester etc.

[0003]

[Patent Reference 1] JP 08-041077 A

[Patent Reference 2] JP 2000-063390 A

[Patent Reference 3] JP 10-168083 A

[Patent Reference 4] German patent application DE 19670906 (DE 1298972 B)

[0004]

[Nonpatent Reference 1] J. Org. Chem., Vol. 42, No. 23 (1977)

[Nonpatent Reference 2] J. C. S. Chem. Commun., pp. 874-875 (1978)

Disclosure of Invention

Technical Problems to be Solved

[0005] However, in the case of the reaction of an alcohol and a chlorosilane to produce an organooxysilane, the hydrogen chloride released during the reaction reacts with the starting materials and product to produce unwanted by-products, which then creates the problem of a reduction in product yield. For example, the released hydrogen chloride reacts with the alcohol to produce the chloride and water. A substantial amount of the alcohol is lost to this reaction. In addition, the water produced in this secondary reaction hydrolyzes the chlorosilane or the organooxysilane, resulting in the production of unwanted polysiloxane and the production of much more hydrogen chloride. Moreover, the hydrogen chloride reacts, either by itself or in combination with the alcohol, with other functional groups that may be present in the chlorosilane. In particular, in the case of the production of a diorganodialkoxysilane or a triorganoalkoxysilane using the reaction of an alcohol and a chlorosilane to produce the organooxysilane, the result is that either the yield is drastically reduced or production does not occur at all.

[0006] These same problems also appear in the production of an organooxysilane by the reaction of acetic anhydride and a chlorosilane, and the acetyl chloride is flammable and irritating. In addition, since hydrogen chloride is again produced by the reaction of water and acetyl chloride, removal by a special treatment must be performed in order to ensure safety; also, this reaction is an exothermic

reaction with water and is very hazardous. The execution of this treatment makes the production of an organooxysilane by the above-described production reaction quite problematic and is also disadvantageous from the standpoint of production costs. In the case of the production method that uses iodotrimethylsilane as a starting material, iodotrimethylsilane is very reactive with light and moisture and is readily decomposed by atmospheric humidity with the production of toxic and irritating hydrogen iodide, and thus its handling is highly problematic and the utilization of this method as a large-scale industrial production method is a problematic proposition. Similarly, in the case of the reactions using sodium iodide, large amounts of sodium iodide are consumed by the reaction when the chlorosilane is converted by the sodium iodide and an iodinated hydrocarbon is also produced. As a result, large amounts of waste materials are produced and the environment burden is therefore substantial.

[0007] The present invention was accomplished in view of the state of the prior art as described above. An object of the present invention is therefore to provide a safe, inexpensive, and high yield means of producing a hydrolyzable silicon-containing compound, e.g., an organooxysilane and so forth.

Solution to Problems

[0008] The inventors accomplished the present invention as a result of intensive investigations directed to achieving the previously described object. Thus, the object of the present invention is achieved by a method of producing a hydrolyzable silicon-containing compound by reacting

(A) a compound represented by the general formula

$$R^1\text{–}O\text{–}R^2$$

wherein R^1 represents a $C_{4\text{-}30}$, substituted or unsubstituted, tertiary alkyl group or aralkyl group and R^2 represents a $C_{1\text{-}30}$, substituted or unsubstituted, monovalent hydrocarbyl group or acyl group, with

(B) a halosilane represented by the general formula

$$R^3{}_mSiX_{4-m}$$

wherein R^3 independently represents the hydrogen atom or a C_{1-30} substituted or unsubstituted monovalent hydrocarbyl group, X is independently bromine or chlorine, and m represents an integer from 0 to 3,

in the presence of a Lewis acid catalyst.

[0009] The Lewis acid catalyst can be a metal-containing Lewis acid. There are no particular limitations on the type of metal-containing Lewis acid as long as it can promote the above-described reaction, but it is preferably at least one Lewis acid selected from the group consisting of metal halides, metal oxides, and metal sulfate salts. Specific examples are at least one Lewis acid selected from the group consisting of gallium(III) chloride, gallium(III) bromide, indium(III) chloride, indium(III) bromide, bismuth(III) chloride, aluminum(III) chloride, iron(II) chloride, iron(III) chloride, iron(II) bromide, iron(III) bromide, nickel(II) chloride, cadmium(II) oxide, chromium(III) oxide, molybdenum(VI) oxide, iron(III) oxide, iron(II) sulfate, and iron(III) sulfate. At least one Lewis acid selected from bismuth(III) chloride, aluminum(III) chloride, and iron(III) chloride is particularly preferred.

[0010] Compound (A) can be an ether. This ether is preferably at least one ether selected from methyl tert-butyl ether, ethyl tert-butyl ether, methyl diphenylmethyl ether, and methyl triphenylmethyl ether.

[0011] Compound (A) can also be an ester. This ester is preferably tert-butyl acetate or diphenylmethyl acetate.

[0012] The halosilane (B) is a chlorosilane or a bromosilane wherein a chlorosilane is particularly preferred. It can specifically be a monochlorosilane, dichlorosilane, trichlorosilane, or tetrachlorosilane and may be either an organochlorosilane, which has an organic group bonded to the silicon atom, or a hydrochlorosilane, which has a hydrogen atom bonded to the silicon atom.

[0013] The aforementioned hydrolyzable silicon-containing compound is preferably an alkoxysilane, a phenoxysilane, or an acetoxysilane.

[0014] The hydrolyzable silicon-containing compound produced by the above-described production method substantially does not contain a hydrogen halide or an acyl halide.

Advantageous Effects of Invention

[0015] The production method of the present invention uses a relatively easy-to-handle chlorosilane or bromosilane as a starting material and can efficiently produce a hydrolyzable silicon-containing compound in excellent yields. In addition, the production method of the present invention can be carried out safely and at low cost because it exhibits a high reaction selectivity and because a tertiary alkyl halide or an aralkyl halide is substantially the only by-product. In addition, the amount of neutralizing agent — which has been used in conventional production methods for the purpose of bringing the reaction to completion — can be reduced. Accordingly, the production method of the present invention is useful as an industrial production method for the large-scale synthesis of hydrolyzable silicon-containing compounds.

[0016] With regard to the use of an ether and particularly methyl tert-butyl ether, ethyl tert-butyl ether, methyl diphenylmethyl ether, or methyl triphenylmethyl ether as compound (A), these compounds exhibit a high stability and a high safety and are also inexpensive and for these reasons make it possible to carry out alkoxysilane production safely and at low cost.

[0017] When an ester and particularly tert-butyl acetate or diphenylmethyl acetate is used as compound (A), almost no secondary production of acetyl chloride occurs and its treatment is rendered unnecessary as a result. The acetoxysilane can thus be stably produced at low cost and this method is therefore particularly useful as an industrial production method.

[0018] The use of a Lewis acid catalyst — and particularly bismuth(III) chloride, aluminum(III) chloride, or iron(III) chloride — as the catalyst provides a low catalyst toxicity and a small environmental burden and for these reasons makes possible a favorable execution of the reaction.

[0019] The hydrolyzable silicon-containing compound yielded by the production method of the present invention substantially does not contain a reactive hydrogen halide or acyl halide, and a

deactivation treatment for this hydrogen halide or acyl halide is therefore unnecessary. Accordingly, this hydrolyzable silicon-containing compound is advantageous, for example, as a starting material for silicones for solar cell applications and semiconductor applications, and as a starting material for various products used, for example, as construction and building materials, such as sealants and so forth.

Brief Description of the Drawings

[0020]

Figure 1 is a ^{13}C-NMR chart of the reaction product in Practical Example 1;

Figure 2 is a ^{13}C-NMR chart of the reaction product in Practical Example 9;

Figure 3 is a ^{13}C-NMR chart of the reaction product in Comparative Example 1;

Figure 4 is a ^{29}Si-NMR chart that compares the reaction product from Practical Example 9 with the reaction product from Comparative Example 1;

Figure 5 is a ^{13}C-NMR chart of the reaction product in Practical Example 11;

Figure 6 is a ^{13}C-NMR chart of the reaction product in Practical Example 14;

Figure 7 is a ^{13}C-NMR chart of the reaction product in Practical Example 15;

Figure 8 is a ^{13}C-NMR chart of the reaction product in Practical Example 16; and

Figure 9 is a ^{13}C-NMR chart of the reaction product in Practical Example 17.

Description of the Invention

[0021] The production method of the present invention produces a hydrolyzable silicon-containing compound by reacting

(A) a compound represented by the general formula

$$R^1\text{–}O\text{–}R^2$$

wherein R^1 represents a $C_{4\text{-}30}$, substituted or unsubstituted, tertiary alkyl group or aralkyl group and R^2 represents a $C_{1\text{-}30}$, substituted or unsubstituted, monovalent hydrocarbyl group or acyl group, and

(B) a halosilane represented by the general formula

$$R^3{}_mSiX_{4-m}$$

wherein R^3 independently represents the hydrogen atom or a C_{1-30} substituted or unsubstituted monovalent hydrocarbyl group, X is independently bromine or chlorine, and m represents an integer from 0 to 3,

in the presence of a Lewis acid catalyst.

[0022] R^1 in the general formula given above for compound (A) is a tertiary alkyl group or an aralkyl group. Since cleavage of the R^1–O bond produces a very stable cation when this tertiary alkyl group or aralkyl group is present, the hydrolyzable silicon-containing compound can be obtained in high yields in the reaction according to the present invention. This tertiary alkyl group encompassed by R^1 has a total of 4 to 30 carbons and contains at least one tertiary carbon atom, but is not otherwise particularly limited, and branched-chain alkyl groups and cyclic alkyl groups are preferred examples. More specific examples are tertiary alkyl groups such as the tert-butyl group, tert-pentyl group, tert-hexyl group, and tert-octyl group and cycloalkyl groups such as the 1-methylcyclopentyl group and 1-methylcyclohexyl group. The carbon atom bonded to the oxygen atom in the general formula given above is preferably a tertiary carbon atom, and the tert-butyl group is particularly preferred. Similarly, the aralkyl group is preferably a secondary or tertiary aralkyl group from the standpoint of the reactivity and particularly preferably has a secondary carbon atom with at least one phenyl group bonded to the carbon atom. In a more favorable embodiment, the aralkyl group preferably has a secondary or tertiary carbon atom with at least two phenyl groups bonded to the carbon atom. Such a secondary or tertiary aralkyl group is preferably the diphenylmethyl group ($H(C_6H_5)_2C$–) or triphenylmethyl group ($(C_6H_5)_3C$–). The hydrogen in the alkyl group or aralkyl group may be at least partially replaced by halogen, e.g., fluorine, and particularly by chlorine.

[0023] R^2 in the general formula given above for compound (A) is a monovalent hydrocarbyl group or acyl group that has a total of 1 to 30 carbons, but is not otherwise particularly limited.

[0024] The monovalent hydrocarbyl group having a total of 1 to 30 carbon atoms can be exemplified by C_{1-30} straight-chain and branched-chain alkyl groups such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, decyl, dodecyl, myristyl, palmityl, stearyl, isostearyl, and behenyl; C_{3-20} cycloalkyl groups such as cyclopentyl and cyclohexyl; C_{2-30} alkenyl groups such as vinyl, allyl, and butenyl; C_{6-30} aryl groups such as phenyl, tolyl, xylyl, naphthyl, and styryl; and C_{7-30} aralkyl groups such as benzyl. Straight-chain C_{1-6} alkyl groups and the phenyl group are preferred, while methyl, ethyl, and phenyl are more preferred.

[0025] The acyl group having a total of 1 to 30 carbons can be exemplified by aliphatic monocarboxylic acid-type acyl groups such as formyl, acetyl, propionyl, butyryl, valeryl, pivaloyl, lauroyl, myristoyl, palmitoyl, and stearoyl, and by aromatic ring-containing acyl groups such as benzoyl and cinnamoyl. Aliphatic monocarboxylic acid-type acyl groups are preferred, and the acetyl group is more preferred.

[0026] The carbon-bonded hydrogen in these groups may be at least partially replaced by, for example, halogen, e.g., fluorine, but the absence of substitution is preferred.

[0027] R^2 is particularly preferably a primary alkyl group, secondary alkyl group, aryl group, or acyl group.

[0028] An ether or ester can thus be favorably used as compound (A). The ether can be exemplified by methyl tert-butyl ether, ethyl tert-butyl ether, propyl tert-butyl ether, methyl tert-pentyl ether, ethyl tert-pentyl ether, propyl tert-pentyl ether, methyl tert-hexyl ether, ethyl tert-hexyl ether, propyl tert-hexyl ether, methyl tert-octyl ether, ethyl tert-octyl ether, propyl tert-octyl ether, methyl diphenylmethyl ether ($H(C_6H_5)_2C–O–CH_3$), methyl triphenylmethyl ether ($(C_6H_5)_3C–O–CH_3$), benzyl methyl ether, and benzyl phenyl ether. Methyl tert-butyl ether, ethyl tert-butyl ether, methyl diphenylmethyl ether, and methyl triphenylmethyl ether are particularly preferred. The ester can be exemplified by tert-butyl formate, tert-butyl acetate, tert-butyl propionate, tert-pentyl formate, tert-pentyl acetate, tert-pentyl propionate, tert-hexyl formate, tert-hexyl acetate, tert-hexyl propionate, tert-octyl formate, tert-octyl acetate, tert-octyl propionate, tert-butyl laurate, and diphenylmethyl

acetate. tert-Butyl acetate and diphenylmethyl acetate are particularly preferred. Two or more different selections from these ethers may be used in combination or two or more different selections from these esters may be used in combination.

[0029] Component (B) is a halosilane represented by the general formula

$$R^3{}_mSiX_{4-m}$$

wherein R^3 independently represents the hydrogen atom or a C_{1-30} substituted or unsubstituted monovalent hydrocarbyl group, X is independently bromine or chlorine, and m represents an integer from 0 to 3. The monovalent hydrocarbyl group here is as already described, and the hydrogen bonded to the carbon in the monovalent hydrocarbyl present in the halosilane may be at least partially replaced by halogen, e.g., fluorine, or by an organic group containing, e.g., an acyl group, carboxyl group, amino group, methacryloxy group, acryloxy group, ureido group, polysulfide group, mercapto group, isocyanate group, and so forth.

[0030] The halosilane (B) is preferably a chlorosilane wherein X is chlorine, and may be either an organochlorosilane, which has an organic group bonded to the silicon atom, or a hydrochlorosilane, which has a hydrogen atom bonded to the silicon atom. The halosilane (B) can be exemplified by dichlorosilane (H_2SiCl_2), trichlorosilane ($HSiCl_3$), tetrachlorosilane, methyldichlorosilane, dimethylmonochlorosilane ($(CH_3)_2HSiCl$), dimethyldichlorosilane, trimethylchlorosilane, ethyldichlorosilane, vinyltrichlorosilane, methylvinyldichlorosilane, phenyldichlorosilane, phenyltrichlorosilane, diphenyldichlorosilane, cyclohexylmethyldichlorosilane, (chloropropyl)trichlorosilane, bis(3,3,3-trifluoropropyl)dichlorosilane, tris(3,3,3-trifluoropropyl)chlorosilane, 3-methacryloxypropylmethyldichlorosilane, 3-methacryloxypropyltrichlorosilane, 3-acryloxypropyltrichlorosilane, 3-aminopropyltrichlorosilane, 3-mercaptopropylmethyldichlorosilane, and 3-mercaptopropyltrichlorosilane. The halosilane (B) may also be a bromosilane wherein X is bromine. Species provided by the partial or complete replacement of the chlorine atom in the chlorosilanes listed above with the bromine atom may be used as the component (B) bromosilane without particular limitation.

[0031] The amount of use of compound (A) and the amount of use of the halosilane (B) are not limited as long as a hydrolyzable silicon-containing compound is obtained; however, the compound (A)/halosilane (B) molar ratio can be, for example, in the range from 50 to 300% of stoichiometric equivalence. This molar ratio is preferably in the range from 0.75 to 2; is more preferably in the range from 0.95 to 1.3; and even more preferably is in the range from 1.1 to 1.3. Stoichiometric equivalence is defined as 1 mol of compound (A) per 1 mol of silicon-bonded halogen atom in the halosilane (B) added to the reaction system.

[0032] The reaction between the compound (A) and the halosilane (B) is run in the presence of a Lewis acid catalyst. The type of Lewis acid catalyst is not limited as long as this reaction is promoted, but metal-containing Lewis acid catalysts are preferred.

[0033] Metal-containing Lewis acid catalysts for the production method of the present invention can be exemplified by metal halides, metal oxides, and metal sulfate salts. The metal halides can be exemplified by lithium chloride, bismuth(III) chloride, aluminum(III) chloride, iron(II) chloride, iron(III) chloride, iron(II) bromide, iron(III) bromide, zinc(II) chloride, beryllium(II) chloride, antimony(III) chloride, antimony(V) chloride, boron chloride, cesium chloride, cobalt(II) chloride, cobalt(III) chloride, nickel(II) chloride, titanium(III) chloride, titanium(IV) chloride, tin(II) chloride, tin(IV) chloride, rhodium(III) chloride, cadmium(II) chloride, germanium(IV) chloride, gallium(III) chloride, gallium(III) bromide, indium(III) chloride, indium(III) bromide, lead(II) chloride, manganese(II) chloride, and palladium(II) chloride. The metal oxides can be exemplified by beryllium(II) oxide, vanadium(V) oxide, chromium(III) oxide, iron(II) oxide, iron(III) oxide, cobalt(III) oxide, cadmium(II) oxide, and molybdenum(VI) oxide. The metal sulfate salt can be exemplified by iron(II) sulfate and iron(III) sulfate.

[0034] Among the preceding, gallium(III) chloride, gallium(III) bromide, indium(III) chloride, indium(III) bromide, bismuth(III) chloride, aluminum(III) chloride, iron(II) chloride, iron(III) chloride, iron(II) bromide, iron(III) bromide, nickel(II) chloride, cadmium(II) oxide, chromium(III) oxide, molybdenum(VI) oxide, iron(III) oxide, iron(II) sulfate, and iron(III) sulfate are favorable

Lewis acid catalysts for the present invention, while the use of bismuth(III) chloride, aluminum(III) chloride, and iron(III) chloride is particularly preferred. The metal halide may be used in anhydrous form or as the hydrate; however, when water is present in the system, it can cause a hydrolysis reaction with the starting chlorosilane or bromosilane and the thereby produced silanol group can cause a polymerization reaction to occur, and for this reason the anhydrous form is preferred. At the same time, depending on the scale of the reaction, the water of crystallization may also have an almost negligible effect.

[0035] Expressed per 1 mole of the halosilane (B), the quantity of use for the Lewis acid catalyst is, for example, 0.0001 to 1.0 mol, preferably 0.05 to 0. 5 mol, more preferably 0.03 to 0.1 mol, and even more preferably 0.01 to 0.05 mol. When too little Lewis acid catalyst is used, the reaction may be slow and/or the reaction may come to a halt while still incomplete. When too much Lewis acid catalyst is used, there is a risk that the halosilane (B) may undergo undesirable reactions, such as cleavage of the Si–C bond.

[0036] The reaction between compound (A) and the halosilane (B) can be carried out in a homogeneous system or a heterogeneous system depending on whether the Lewis acid catalyst dissolves in component (B). When a Lewis acid catalyst is used that has a low solubility in component (B), such as bismuth chloride, the reaction can be run by adding the Lewis acid catalyst to component (B) and then adding compound (A) and stirring. In this case, a residue originating from the catalyst in the system (this residue is a black tarry substance in the case of bismuth chloride) will precipitate to the bottom of the reaction mixture when the reaction is complete and as necessary can be separated from the reaction product by a known means, e.g., centrifugal separation. When, on the other hand, a Lewis acid catalyst is used that exhibits a high solubility in component (B), such as iron(III) chloride, the reaction can be run by dissolving the catalyst in the halosilane (B) and then adding compound (A) and stirring. In this case, the reaction solution as a whole is transparent and homogeneous and the separation and precipitation of a catalyst-based residue upon the completion of the reaction does not occur; this offers the advantage making it possible to avoid

problems such as the accumulation of this residue in the pipework of the facility and clogging of the pipework by this residue. When the Lewis acid catalyst is readily soluble in compound (A), the catalyst may be dissolved in component (A) and the halosilane (B) may then be added.

[0037] The temperature of this reaction is preferably from 0 to 150°C and, considered at one atmosphere, is more preferably 0 to 90°C and particularly preferably 20 to 40°C, while running the reaction at so-called room temperature (25°C) is particularly favorable. On the other hand, depending on the catalyst and starting material selection, the reaction can also be accelerated by selecting elevated temperature conditions from 50 to 90°C. Even higher temperatures may of course be selected under pressurized conditions. When the reaction temperature is too low, the reaction rate ends up being slow and long reaction times may then be required. When, on the other hand, the reaction temperature is too high, there is a risk that the hydrolyzable silicon-containing compound product may participate in undesirable reactions. The reaction time will vary with the reaction scale and reaction temperature, but is, for example, 10 minutes to 1 week and can preferably be from 1 to 40 hours. When in particular bismuth chloride or iron(III) chloride is used as the Lewis acid catalyst, from 4 to 36 hours at one atmosphere and room temperature (25°C) is preferred.

[0038] This reaction is preferably run under an inert gas atmosphere, and the inert gas can be exemplified by nitrogen and argon. This reaction may be run under reduced pressure, at ambient pressure, or under an overpressure, but is preferably run at ambient pressure from the standpoint of the processability.

[0039] The reaction between compound (A) and the halosilane (B) may be run in a solvent. The solvent used is preferably a solvent that does not react with compound (A) and/or the halosilane (B) and is preferably an inert solvent that is a liquid at ambient temperature and atmospheric pressure and has a boiling point no greater than 150°C. Such solvents can be exemplified by hydrocarbon solvents such as toluene, xylene, hexane, nonane, pentane, and octane; chlorinated hydrocarbon solvents such as carbon tetrachloride, methylene chloride, dichloroethane, dichloroethylene, 1,1,1-trichloroethane, trichloroethylene, perchloroethylene, and tetrachloroethane; and acetonitrile.

[0040] The reaction between compound (A) and the halosilane (B) can be run using a batch or continuous regime. When the reaction is run using a continuous regime, compound (A) and the halosilane (B) may be reacted and, after the reaction has reached equilibrium, it may be advanced while removing the hydrolyzable silicon-containing compound product from the reaction system by reducing the pressure within the system; the reaction may also be advanced still further while removing from the reaction system the halogenated hydrocarbon by-product originating with the tertiary alkyl group or the aralkyl group. The reaction selectivity is very high in this reaction since there is almost no production in this reaction of by-products other than the halogenated hydrocarbon. Moreover, this reaction is safe since there is almost no secondary production in this reaction of a hydrogen halide such as hydrogen chloride, and the reaction can be run at lost costs because there is almost no requirement for the addition of a base, such as an amine, as a neutralizing agent for the hydrogen halide. Furthermore, since this reaction is almost entirely free of the production of a flammable · irritating acyl halide such as acetyl chloride, this reaction can be run safely and with a low environmental burden.

[0041] When a Lewis acid catalyst is used that has a low solubility in component (B), such as bismuth chloride, the catalyst resists transfer into the system and due to this is particularly useful as a supported-type catalyst in a batch process, which presupposes filtration, or in a continuous process. A Lewis acid catalyst that dissolves uniformly in component (B), such as iron(III) chloride, is useful in a batch process. After the reaction, a Lewis acid catalyst such as iron(III) chloride can as necessary be deactivated and easily isolated from the product by distillation.

[0042] After the reaction, the solution is approximately neutral and as a consequence the obtained hydrolyzable silicon-containing compound can be directly recovered from the reaction solution by, for example, distillation. In addition, as necessary the hydrolyzable silicon-containing compound can also be recovered from the reaction system by adding a small amount of a compound that acts as a Lewis base in order to deactivate the Lewis acid catalyst remaining after the reaction between compound (A) and the halosilane (B), followed by, for example, distillation. The obtained

hydrolyzable silicon-containing compound may also be used directly, without isolation, in an ensuing reaction.

[0043] The hydrolyzable silicon-containing compound yielded by the production method of the present invention has at least one silicon-bonded hydrolyzable group, e.g., an alkoxy group, acetoxy group, phenoxy group, and so forth. The hydrolyzable silicon-containing compound is preferably an alkoxysilane, acetoxysilane, or phenoxysilane. The alkoxysilane can be exemplified by methoxysilane, methoxytrimethylsilane, ethoxysilane, butoxysilane, dimethyldimethoxysilane, dimethylmethoxychlorosilane, trimethoxychlorosilane, trimethoxysilane, tetramethoxysilane, tert-butyltrimethoxysilane, isobutyltrimethoxysilane, isobutylmethoxysilane, octadecyltrimethoxysilane, dodecyltrimethoxysilane, cyclohexylmethyldimethoxysilane, triethoxysilane, vinyltrimethoxysilane, methylvinyldimethoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, diphenyldimethoxysilane, phenylmethoxychlorosilane, triphenylmethoxysilane, 2-phenylpropylmethyldimethoxysilane, methylhexanedienyldimethoxysilane, (chloropropyl)trimethoxysilane, (3,3,3-trifluoropropyl)trimethoxysilane, bis(3,3,3-trifluoropropyl)dimethoxysilane, tris(3,3,3-trifluoropropyl)methoxysilane, 3-methacryloxypropylmethyldimethoxysilane, 3-methacryloxypropyltrimethoxysilane, 3-acryloxypropyltrimethoxysilane, 3-aminopropyltrimethoxysilane, 3-mercaptopropylmethyldimethoxysilane, 3-mercaptopropyltrimethoxysilane, and so forth. The acetoxysilane can be exemplified by vinyltriacetoxysilane, trimethylacetoxysilane, and so forth. The phenoxysilane can be exemplified by methyltriphenoxysilane, ethyltriphenoxysilane, vinyltriphenoxysilane, phenyltriphenoxysilane, dimethyldiphenoxysilane, methylvinyldiphenoxysilane, divinyldiphenoxysilane, methylphenyldiphenoxysilane, diphenyldiphenoxysilane, and so forth. Hydrolyzable silicon-containing compounds such as the preceding can be obtained in high yields using the production method of the present invention.

[0044] Because the reaction between compound (A) and the halosilane (B) results in almost no production or in the complete absence of production of reactive hydrogen halide or acyl halide, the

hydrolyzable silicon-containing compound yielded by the production method of the present invention substantially does not contain hydrogen halide or acyl halide. Here, "substantially" means not more than 5% of the total mass (weight) of the hydrolyzable silicon-containing compound and preferably not more than 1%, more preferably not more than 0.1%, and even more preferably not more than 0.01% of the total mass (weight) of the hydrolyzable silicon-containing compound. Accordingly, the hydrolyzable silicon-containing compound yielded by the production method of the present invention may be used in an ensuing or follow-on process without having to carry out a deactivation treatment for hydrogen halide or acyl halide.

[0045] The hydrolyzable silicon-containing compound yielded by the production method of the present invention contains no or almost no hydrogen halide or acyl halide and therefore inherently contains little impurity, but as necessary may be subjected to purification by a known method, e.g., distillation, chromatography, and so forth, in order to provide an even higher purity hydrolyzable silicon-containing compound.

[0046] The hydrolyzable silicon-containing compound yielded by the production method of the present invention can be used in known applications. For example, the alkoxysilane is useful as a silane coupling agent and as a starting material for the synthesis of a variety of organopolysiloxanes. In particular, alkoxysilane obtained using the production method of the present invention is useful as a starting material for silicones for solar cell and semiconductor applications, which are applications where high purity is required. The acetoxysilane, on the other hand, is useful as a silane coupling agent, silylating agent, crosslinking agent, and so forth; in particular, acetoxysilane obtained using the production method of the present invention is useful as a starting material for, e.g., sealants used for, e.g., construction and building materials. Similarly, since the previously described reaction produces almost no flammable · irritating acyl halide, e.g., acetyl chloride, the advantage accrues of obtaining a silane starting material that is favorable for application as a high-purity material and for application as an electronic material.

Examples

[0047] The description continues below with practical examples of the present invention, but the present invention is not limited by these. The products in the practical examples and comparative examples were identified using NMR for the ^{29}Si, ^{13}C, and ^{1}H nuclides. Specifically, a JEOL JNM-ECX-500 NMR measurement instrument from JEOL, Ltd., was used. The measurements were performed using deuterated chloroform ($CDCl_3$) as the solvent; a small amount of chromium acetylacetate was added as a relaxation accelerator; and tetramethylsilane ($\delta = 0$, ^{1}H-NMR, ^{13}C-NMR, ^{29}Si-NMR) was used as an internal standard. The reaction product yield was determined based on the ratio of the integrated value of signals assigned to the reactants and product.

[0048] [Practical Example 1]

A magnetic stir bar was introduced into a 30-mL roundbottom flask (Schlenk tube) provided with a two-way cock; 0.16 g (0.5 mmol) of bismuth chloride ($BiCl_3$) was introduced; and the flask was sealed with a septum and nitrogen substitution was carried out. 2.91 g (33 mmol) of methyl tert-butyl ether was then introduced into the flask using a syringe and the flask was placed in an ice bath (0°C). While on the ice bath (0°C), 2.11 g (10 mmol) of phenyltrichlorosilane was introduced into the flask by gradual dropwise addition from a syringe; the system was returned to room temperature (25°C) after the completion of dropwise addition; and a reaction was carried out overnight (15 hours) while stirring the solution using a magnetic stirrer. After the completion of the reaction, the solution was measured by ^{29}Si-NMR, ^{13}C-NMR, and ^{1}H-NMR and the product was identified and the product yield was determined from the measurement results. The results are given in Table 1. A small amount of a black, catalyst-derived precipitate was precipitated in the solution after the reaction.

[0049] [Practical Example 2]

A reaction was run as in Practical Example 1, but using the same molar amount (= 1.70 g) of tetrachlorosilane in place of the phenyltrichlorosilane. The results are given in Table 1.

[0050] [Practical Example 3]

A reaction was run as in Practical Example 1, but using the same molar amount (= 1.35 g) of hydrotrichlorosilane in place of the phenyltrichlorosilane. The results are given in Table 1.

[0051] [Practical Example 4]

A reaction was run as in Practical Example 1, but using the same molar amount (= 3.04 g) of dodecyltrichlorosilane in place of the phenyltrichlorosilane. The results are given in Table 1.

[0052] [Practical Example 5]

A reaction was run as in Practical Example 1, but using the same molar amount (= 1.62 g) of vinyltrichlorosilane in place of the phenyltrichlorosilane. The results are given in Table 1.

[0053] [Practical Example 6]

A reaction was run as in Practical Example 1, but using the same molar amount (= 3.37 g) of ethyl tert-butyl ether in place of the methyl tert-butyl ether. The results are given in Table 1.

[0054] [Practical Example 7]

A reaction was run as in Practical Example 2, but using the tetrachlorosilane and methyl tert-butyl ether in a proportion of 3 moles methyl tert-butyl ether per 1 mole of tetrachlorosilane. Thus, a reaction was run as in Practical Example 2, but using 2.64 g (30 mmol) for the amount of methyl tert-butyl ether used. The results are given in Table 1.

[0055] [Practical Example 8]

A reaction was run as in Practical Example 1, but using dimethyldichlorosilane in place of the phenyltrichlorosilane and using a dimethyldichlorosilane : methyl tert-butyl ether molar ratio of 1 : 2.6. Thus, a reaction was run as in Practical Example 1, but using 2.29 g (26 mmol) for the amount of methyl tert-butyl ether used and using 1.29 g (10 mmol) of dimethyldichlorosilane in place of the phenyltrichlorosilane. The results are given in Table 1.

[0056] [Practical Example 9]

A reaction was run as in Practical Example 1, but using cyclohexylmethyldichlorosilane in place of the phenyltrichlorosilane; using a cyclohexylmethyldichlorosilane : methyl tert-butyl ether in molar ratio of 1 : 2.6; and using a cyclohexylmethyldichlorosilane : bismuth chloride in molar ratio of 1 :

0.01. Thus, a magnetic stir bar was introduced into the 30-mL roundbottom flask provided with a two-way cock; 0.03 g (0.1 mmol) of bismuth chloride ($BiCl_3$) was introduced; and the flask was sealed with a septum and nitrogen substitution was carried out. 2.29 g (26 mmol) of methyl tert-butyl ether and 1.97 g (10 mmol) of cyclohexylmethyldichlorosilane were then introduced into the flask as in Practical Example 1, after which the reaction was run as in Practical Example 1. The results are given in Table 1.

[0057] [Practical Example 10]

A reaction was run as in Practical Example 1, but using trimethylchlorosilane in place of the phenyltrichlorosilane; using a trimethylchlorosilane : methyl tert-butyl ether in molar ratio of 1 : 1.3; and using a trimethylchlorosilane : bismuth chloride in molar ratio of 1 : 0.01. Thus, a magnetic stir bar was introduced into the 30-mL roundbottom flask provided with a two-way cock; 0.03 g (0.1 mmol) of bismuth chloride ($BiCl_3$) was introduced; and the flask was sealed with a septum and nitrogen substitution was carried out. 1.15 g (13 mmol) of methyl tert-butyl ether and 1.09 g (10 mmol) of trimethylchlorosilane were then introduced into the flask as in Practical Example 1, after which the reaction was run as in Practical Example 1. The results are given in Table 1.

[0058] [Practical Example 11]

A reaction was run as in Practical Example 5, but using the same molar amount (= 3.83 g) of tert-butyl acetate in place of the methyl tert-butyl ether. The results are given in Table 1. The secondary production of acetyl chloride could not be identified from the NMR chart, and the obtained vinyltriacetoxysilane thus had a high purity.

[0059] [Practical Example 12]

A reaction was run as in Practical Example 10, but using the same molar amount (= 1.51 g) of tert-butyl acetate in place of the methyl tert-butyl ether. The results are given in Table 1. The secondary production of acetyl chloride could not be identified from the NMR chart, and the obtained trimethylacetoxysilane thus had a high purity.

[0060] [Practical Example 13]

A reaction was run as in Practical Example 1, but using the same molar amount (= 2.12 g) of chloropropyltrichlorosilane in place of the phenyltrichlorosilane. The results are given in Table 1.

[0061] [Comparative Example 1]

A magnetic stir bar was introduced into a 30-mL roundbottom flask provided with a two-way cock and the flask was sealed with a septum and nitrogen substitution was then carried out. 0.70 g (22 mmol) of methanol and 1.97 g (10 mmol) of cyclohexylmethyldichlorosilane were then introduced into the flask as in Practical Example 1, after which a reaction was run as in Practical Example 1. The reaction solution in Comparative Example 1 was a more viscous liquid than in the other, practical examples. The results are shown in Table 1.

[0062] [Comparative Example 2]

A reaction was run as in Practical Example 2, but omitting the use of bismuth chloride ($BiCl_3$) and extending the reaction time from 15 hours to 3 days. The results are shown in Table 1. Under conditions in which the Lewis acid catalyst was not present, a hydrolyzable silicon-containing compound was not produced by the reaction of tetrachlorosilane and methyl tert-butyl ether, even when the reaction time was extended to 3 days, and no change was seen in the NMR chart of the solution pre-versus-post-reaction.

[0063] As shown in Table 1, the reactions in Practical Examples 1 to 13 could provide the products indicated in Table 1 in high yields.

[0064] On the other hand, a complex mixture of a large number of species was produced by the reaction in Comparative Example 1 and it was not possible to identify the product at all. It is thought that the hydrogen chloride that is a reaction by-product in Comparative Example 1 reacts with unreacted methanol to produce water by the reaction $MeOH + HCl \rightarrow MeCl + H_2O$; that this water further reacts with the chlorosilane to provide a silanol; and that this silanol undergoes an increase in molecular weight by polymerization. The reaction system in Comparative Example 1 became a highly viscous liquid and was unable to produce a hydrolyzable silane in the high yields shown in the practical examples. For purposes of comparison, the post-reaction ^{29}Si-NMR charts are shown in

Figure 4 for Comparative Example 1 and Practical Example 9, which used the same cyclohexylmethyldichlorosilane starting material.

[0065] In the case of the reaction in Comparative Example 2, the reaction between tetrachlorosilane and methyl tert-butyl ether did not proceed and a comparison with Practical Example 2 showed that this reaction required a Lewis acid catalyst.

[0066] [Table 1.]

Table 1.

	catalyst	halosilane	ether/ester	product	yield (%)
Practical Ex. 1	$BiCl_3$	$PhSiCl_3$	tert-BuOMe	$PhSi(OMe)_3$	94
Practical Ex. 2		$SiCl_4$	tert-BuOMe	$Si(OMe)_4$	88
Practical Ex. 3		$HSiCl_3$	tert-BuOMe	$HSi(OMe)_3$	74
Practical Ex. 4		$CH_3(CH_2)_{11}SiCl_3$	tert-BuOMe	$CH_3(CH_2)_{11}Si(OMe)_3$	90
Practical Ex. 5		CH_2=$CHSiCl_3$	tert-BuOMe	CH_2=$CHSi(OMe)_3$	96
Practical Ex. 6		$PhSiCl_3$	tert-BuOEt	$PhSi(OEt)_3$	99
Practical Ex. 7		$SiCl_4$	tert-BuOMe	$ClSi(OMe)_3$	80
Practical Ex. 8		Me_2SiCl_2	tert-BuOMe	$Me_2Si(OMe)_2$	83
Practical Ex. 9		cyc-$HexMeSiCl_2$	tert-BuOMe	cyc-$HexMeSi(OMe)_2$	90
Practical Ex. 10		Me_3SiCl	tert-BuOMe	Me_3SiOMe	88
Practical Ex. 11		CH_2=$CHSiCl_3$	tert-BuOAc	CH_2=$CHSi(OAc)_3$	93
Practical Ex. 12		Me_3SiCl	tert-BuOAc	Me_3SiOAc	77
Practical Ex. 13		$Cl(CH_2)_3SiCl_3$	tert-BuOMe	$Cl(CH_2)_3Si(OMe)_3$	90
		halosilane	alcohol	product	yield (%)
Comp. Ex. 1	—	cyc-$HexMeSiCl_2$	MeOH	not detected	—
		halosilane	ether/ester		
Comp. Ex. 2	—	$SiCl_4$	tert-BuOMe	no reaction (**)	0**

*) The functional group abbreviations used in the table are as follows.

Me : methyl group

Ph : phenyl group

cyc-Hex: cyclohexyl group

tert-Bu: tert-butyl group

Ac: acetyl group

**) No progress by the reaction could be seen by NMR even at a reaction time of 3 days.

[0067] [Practical Example 14]

A magnetic stir bar was introduced into a 50-mL roundbottom flask (Schlenk tube) provided with a two-way cock; 16 mg (0.1 mmol) of iron(III) chloride ($FeCl_3$) was introduced; and the flask was sealed with a septum and nitrogen substitution was carried out. 2.90 g (33 mmol) of methyl tert-butyl ether and 2.11 g (10 mmol) of phenyltrichlorosilane were then introduced into the flask as in Practical Example 1; the system was returned to room temperature (25°C); and a reaction was carried out overnight (15 hours) while stirring the solution using a magnetic stirrer.

[0068] After the reaction, the iron(III) chloride-containing solution was uniform throughout and was a transparent, light yellow solution. Unlike the case of Practical Example 1, a residue or precipitate was not produced. A portion of the post-reaction solution was removed and measured by ^{29}Si-NMR, ^{13}C-NMR, and ^{1}H-NMR and the product was identified from the measurement results, which confirmed that, as in Practical Example 1, $PhSi(OMe)_3$ had been produced. The results are given in Table 2.

[0069] [Practical Example 15]

A reaction was run as in Practical Example 14, but using in place of the iron(III) chloride the same molar amount (= 13 mg) of aluminum chloride ($AlCl_3$). The results are given in Table 2.

[0070] After the reaction had been run overnight (15 hours), the aluminum chloride-containing post-reaction solution was uniform throughout and was a transparent, milky white solution. Unlike the case of Practical Example 1, a residue or precipitate was not produced. A portion of the post-reaction solution was removed and measured by ^{29}Si-NMR, ^{13}C-NMR, and ^{1}H-NMR and the product was identified from the measurement results, which confirmed that $PhSi(OMe)_3$ had been produced. However, unlike Practical Example 1 and Practical Example 14, a majority of the phenyltrichlorosilane was unreacted after the reaction time of 15 hours.

[0071] On the other hand, when the reaction time was extended and the reaction was continued for 3 days (72 hours) with stirring, the aluminum chloride-containing post-reaction solution was uniform

throughout and had become a transparent, pale pink solution. A portion of the post-reaction solution was removed and measured by ^{29}Si-NMR, ^{13}C-NMR, and ^{1}H-NMR and the product was identified from the measurement results, which confirmed that, as in Practical Example 1, $PhSi(OMe)_3$ had been produced.

[0072] Based on the preceding results, it was confirmed that the hydrolyzable silicon-containing compound of the present invention could also be obtained when a metal salt acting as a Lewis acid catalyst other than bismuth chloride was used. In particular, the reaction was found to progress rapidly in a uniform reaction system when iron(III) chloride was used.

[0073] [Practical Example 16]

A magnetic stir bar was introduced into a 100-mL roundbottom flask (Schlenk tube) provided with a two-way cock; 0.24 g (0.75 mmol) of bismuth(III) chloride ($BiCl_3$) was introduced; and the flask was sealed with a septum and nitrogen substitution was carried out. 21.9 g (248 mmol) of methyl tert-butyl ether and 19.62 g (75 mmol) of 3-methacryloxypropyltrichlorosilane were then introduced into the flask as in Practical Example 1; the system was returned to room temperature (25°C); and a reaction was carried out for 3 days (72 hours) while stirring the solution using a magnetic stirrer and shielding the entire flask from light using aluminum foil. Due to the precipitation of the bismuth chloride in the post-reaction solution, the bismuth chloride was removed by a Celite filtration and the yield of the product was then determined. The results are given in Table 2.

[0074] A portion of this post-reaction solution was removed and measured by ^{29}Si-NMR, ^{13}C-NMR, and ^{1}H-NMR and the product was identified from the measurement results, which confirmed that 3-methacryloxypropyltrimethoxysilane $CH_2=C(CH_3)COOC_3H_6–Si(OMe)_3$ had been produced.

[0075] [Practical Example 17]

A magnetic stir bar was introduced into a 30-mL roundbottom flask (Schlenk tube) provided with a two-way cock; 32 mg (0.10 mmol) of bismuth(III) chloride ($BiCl_3$) was introduced; and the flask was sealed with a septum and nitrogen substitution was carried out. 4.03 g (33 mmol) of methyl benzyl ether and 2.11 g (10 mmol) of phenyltrichlorosilane were then introduced into the flask as in

Practical Example 1; the system was heated to 80°C; a reaction was carried out overnight (15 hours) while stirring the solution using a magnetic stirrer; and the product yield was determined. The results are given in Table 2. The post-reaction solution had undergone a color change to black and the bismuth chloride had precipitated.

[0076] A portion of this post-reaction solution was removed and measured by ^{29}Si-NMR, ^{13}C-NMR, and ^{1}H-NMR and the product was identified from the measurement results, which confirmed that, as in Practical Example 1, $PhSi(OMe)_3$ had been produced.

[0077] [Practical Example 18]

32 mg (0.10 mmol) of bismuth(III) chloride ($BiCl_3$) was introduced into a stirrer-equipped 30-mL roundbottom flask (Schlenk tube) provided with a two-way cock and the flask was sealed with a septum and nitrogen substitution was carried out. 6.08 g (33 mmol) of phenyl benzyl ether and 1.50 g (10 mmol) of methyltrichlorosilane were then introduced into the flask as in Practical Example 1; the system was heated to 60°C; a reaction was carried out overnight (15 hours); and the product yield was determined. The results are given in Table 2. The bismuth chloride had precipitated in the post-reaction solution.

[0078] A portion of this post-reaction solution was removed and measured by ^{29}Si-NMR, ^{13}C-NMR, and ^{1}H-NMR and the product was identified from the measurement results, which confirmed that the phenoxysilane represented by $MeSi(OPh)_3$ had been produced.

[0079] [Practical Example 19]

32 mg (0.10 mmol) of bismuth(III) chloride ($BiCl_3$) was introduced into a stirrer-equipped 30-mL roundbottom flask (Schlenk tube) provided with a two-way cock and the flask was sealed with a septum after nitrogen substitution. 6.54 g (33 mmol) of methyl diphenylmethyl ether with the chemical formula CH_3–O–$CH(C_6H_5)_2$ and 1.50 g (10 mmol) of methyltrichlorosilane were then introduced into the flask as in Practical Example 1; the system was returned to room temperature (25°C); a reaction was carried out overnight (15 hours); and the product yield was determined. The results are given in Table 2. The bismuth chloride had precipitated in the post-reaction solution.

[0080] A portion of this post-reaction solution was removed and measured by ^{29}Si-NMR, ^{13}C-NMR, and ^{1}H-NMR and the product was identified from the measurement results, which confirmed that $MeSi(OMe)_3$ had been produced.

[0081] [Table 2.]

Table 2.

	catalyst	silicon compound	ether/ester	product	yield
Practical Ex. 14	$FeCl_3$	$PhSiCl_3$	tert-BuOMe	$PhSi(OMe)_3$	93
Practical Ex. 15	$AlCl_3$	$PhSiCl_3$	tert-BuOMe	$PhSi(OMe)_3$	52**
Practical Ex. 16	$BiCl_3$	methacryloxypropyl $SiCl_3$	tert-BuOMe	methacryloxypropyl $Si(OMe)_3$	92
Practical Ex. 17		$PhSiCl_3$	$C_6H_5CH_2OMe$	$PhSi(OMe)_3$	47
Practical Ex. 18		$MeSiCl_3$	$C_6H_5CH_2OPh$	$MeSi(OPh)_3$	58
Practical Ex. 19		$MeSiCl_3$	$(C_6H_5)_2CHOMe$	$MeSi(OMe)_3$	59

*) The functional group abbreviations used in the table are as follows.

Me : methyl group

Ph : phenyl group

tert-Bu: tert-butyl group

methacryloxypropyl: 3-methacryloxypropyl group $CH_2=C(CH_3)COOC_3H_6-$

**) The reaction time was 3 days.

[0082] The ^{13}C assignments for the individual hydrolyzable silanes are as shown in the figures. The sharp signal in the vicinity of σ = 34.5 ppm is assigned to the tert-BuCl that is produced, while the sharp signal in the vicinity of δ = 27.0 ppm is assigned to the excess tert-BuOMe. According to the comparison of Comparative Example 1 and Practical Example 9 shown in Figure 4, there was almost no production of the corresponding hydrolyzable silane in the direct reaction with methanol. In addition, as shown in Figure 5, the production of acetyl chloride could not be confirmed at all by NMR.

[0083] < Description of the NMR charts >

The functional group abbreviations are as follows.

Me: methyl group

Ph: phenyl group

cyc-Hex: cyclohexyl group

Ac: acetyl group

methacryloxypropyl: 3-methacryloxypropyl group $CH_2=C(CH_3)COOC_3H_6-$

Figure 1: A signal in the vicinity of δ = 128.0-135.0 ppm assigned to the phenyl group in $PhSi(OMe)_3$ and a signal in the vicinity of δ = 50.5 ppm assigned to the methoxy group in $PhSi(OMe)_3$ are present.

Figure 2: A signal in the vicinity of δ = 50.3 ppm assigned to the methoxy group in cyc-$HexMeSi(OMe)_2$ and a signal in the vicinity of δ = 24-27.96 ppm assigned to the cyclohexyl group in cyc-$HexMeSi(OMe)_2$ are present.

Figure 3: The signal shapes are completely different from Figure 2 and the individual signals cannot be assigned.

Figure 4: A signal in the vicinity of δ = –3.57 ppm assigned to the ^{29}Si in cyc-$HexMeSi(OMe)_2$ is present in the upper section, which concerns Practical Example 9, and a signal in the vicinity of δ = 32.6 ppm assigned to the ^{29}Si in the cyc-$HexMeSiCl_2$ starting material is present in the lower section, which concerns Comparative Example 1.

Figure 5: Signals in the vicinity of δ = 140.5, 125.5, and 22.5 ppm assigned to $CH_2=CHSi(OAc)_3$ were present, while the signal in the vicinity of 33.68 ppm assigned to acetyl chloride was not observed.

Figure 6: The signal shapes are about the same as in Figure 1 and the product is therefore the same. A signal in the vicinity of δ = 128.0-134.9 ppm assigned to the phenyl group in $PhSi(OMe)_3$ and a signal in the vicinity of δ = 50.8 ppm assigned to the methoxy group in $PhSi(OMe)_3$ are present.

Figure 7: Signals for the unreacted starting materials are observed, but the signals agree with Figure 1 and Figure 6 and the same product can therefore be confirmed. A signal in the vicinity of δ =

128.0-134.9 ppm assigned to the phenyl group in $PhSi(OMe)_3$ and a signal in the vicinity of δ = 50.8 ppm assigned to the methoxy group in $PhSi(OMe)_3$ are present.

Figure 8: Signals assigned to methacryloxypropyl$Si(OMe)_3$ in the vicinity of δ = 167.4, 136.6, 125.2, 66.6, 50.5, 22.2, 18.3, and 5.8 ppm are present.

Figure 9: Considering the signals other than those for the starting materials, the signal shapes are about the same as in Figure 1 and the product is therefore the same. A signal in the vicinity of δ = 127.6-134.8 ppm assigned to the phenyl group in $PhSi(OMe)_3$ and a signal in the vicinity of δ = 50.7 ppm assigned to the methoxy group in $PhSi(OMe)_3$ are present.

CLAIMS

1. A method of producing a hydrolyzable silicon-containing compound by reacting

(A) a compound represented by the general formula

$$R^1\text{–}O\text{–}R^2$$

wherein R^1 represents a $C_{4\text{-}30}$, substituted or unsubstituted, tertiary alkyl group or aralkyl group and R^2 represents a $C_{1\text{-}30}$, substituted or unsubstituted, monovalent hydrocarbyl group or acyl group, and

(B) a halosilane represented by the general formula

$$R^3{}_mSiX_{4-m}$$

wherein R^3 independently represents the hydrogen atom or a $C_{1\text{-}30}$ substituted or unsubstituted monovalent hydrocarbyl group, X is independently bromine or chlorine, and m represents an integer from 0 to 3,

in the presence of a Lewis acid catalyst.

2. The production method according to claim 1, wherein the Lewis acid catalyst is a metal-containing Lewis acid.

3. The production method according to claim 1 or 2, wherein the Lewis acid catalyst is at least one Lewis acid selected from the group consisting of metal halides, metal oxides, and metal sulfate salts.

4. The production method according to any of claims 1 to 3, wherein the Lewis acid catalyst is at least one Lewis acid selected from the group consisting of gallium(III) chloride, gallium(III) bromide, indium chloride, indium bromide, bismuth chloride, aluminum chloride, iron(II)

chloride, iron(III) chloride, iron(II) bromide, iron(III) bromide, nickel chloride, cadmium oxide, chromium oxide, molybdenum(VI) oxide, iron(III) oxide, iron(II) sulfate, and iron(III) sulfate.

5. The production method according to any of claims 1 to 4, wherein the halosilane (B) is a chlorosilane.

6. The production method according to any of claims 1 to 5, wherein the compound (A) is an ether.

7. The production method according to claim 6, wherein the ether is at least one ether selected from methyl tert-butyl ether, ethyl tert-butyl ether, methyl diphenylmethyl ether, and methyl triphenylmethyl ether.

8. The production method according to any of claims 1 to 5, wherein compound (A) is an ester.

9. The production method according to claim 8, wherein the ester is tert-butyl acetate or diphenylmethyl acetate.

10. The production method according to any of claims 1 to 9, wherein the hydrolyzable silicon-containing compound is an alkoxysilane, a phenoxysilane, or an acetoxysilane.

11. A hydrolyzable silicon-containing compound that is produced by the production method according to any of claims 1 to 10 and that substantially does not contain a hydrogen halide or an acyl halide.

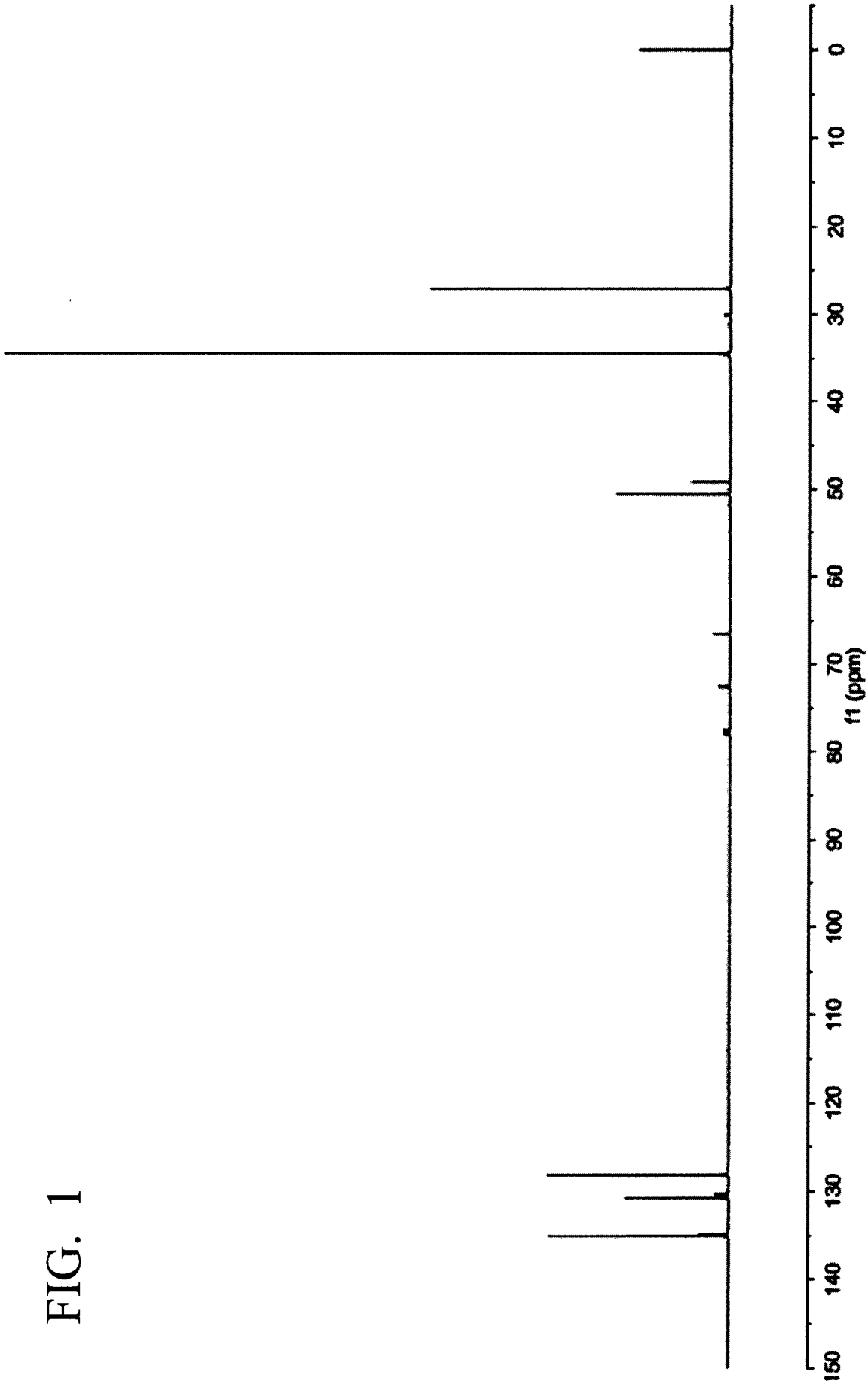


FIG. 1

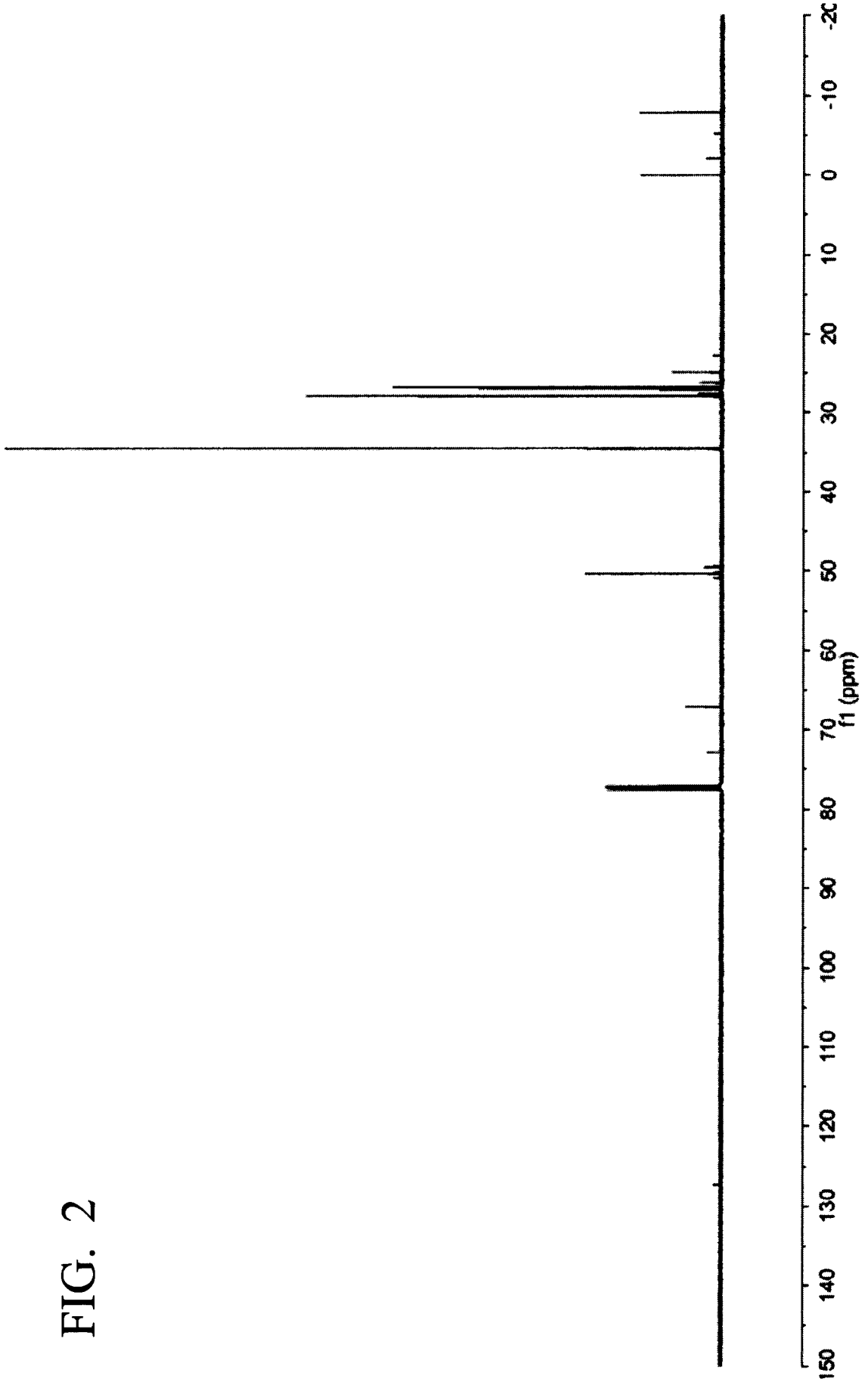


FIG. 2

FIG. 3

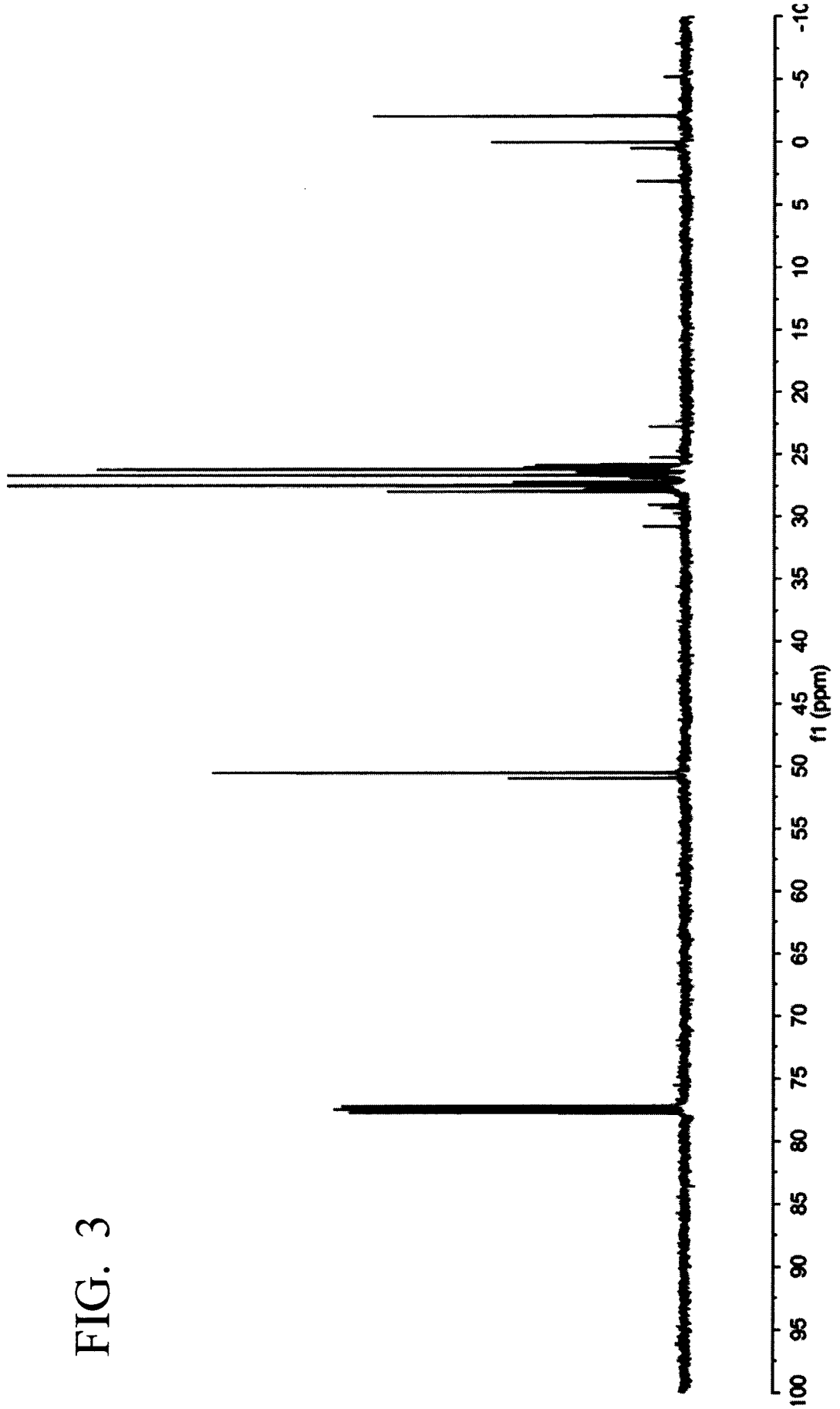


FIG. 4

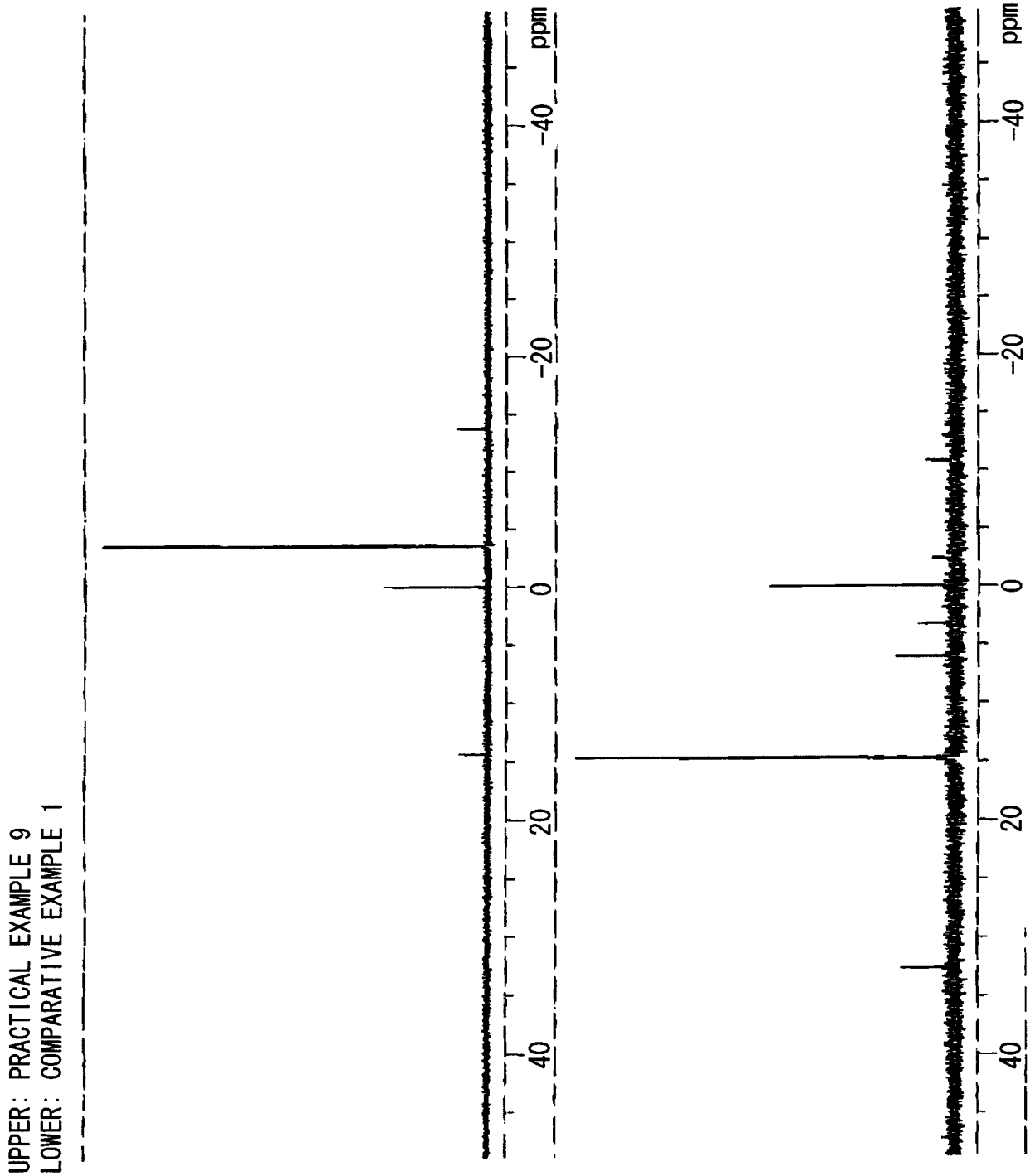

UPPER: PRACTICAL EXAMPLE 9
LOWER: COMPARATIVE EXAMPLE 1
40
20
0
-20
-40
ppm
40
20
0
-20
-40
ppm

FIG. 5

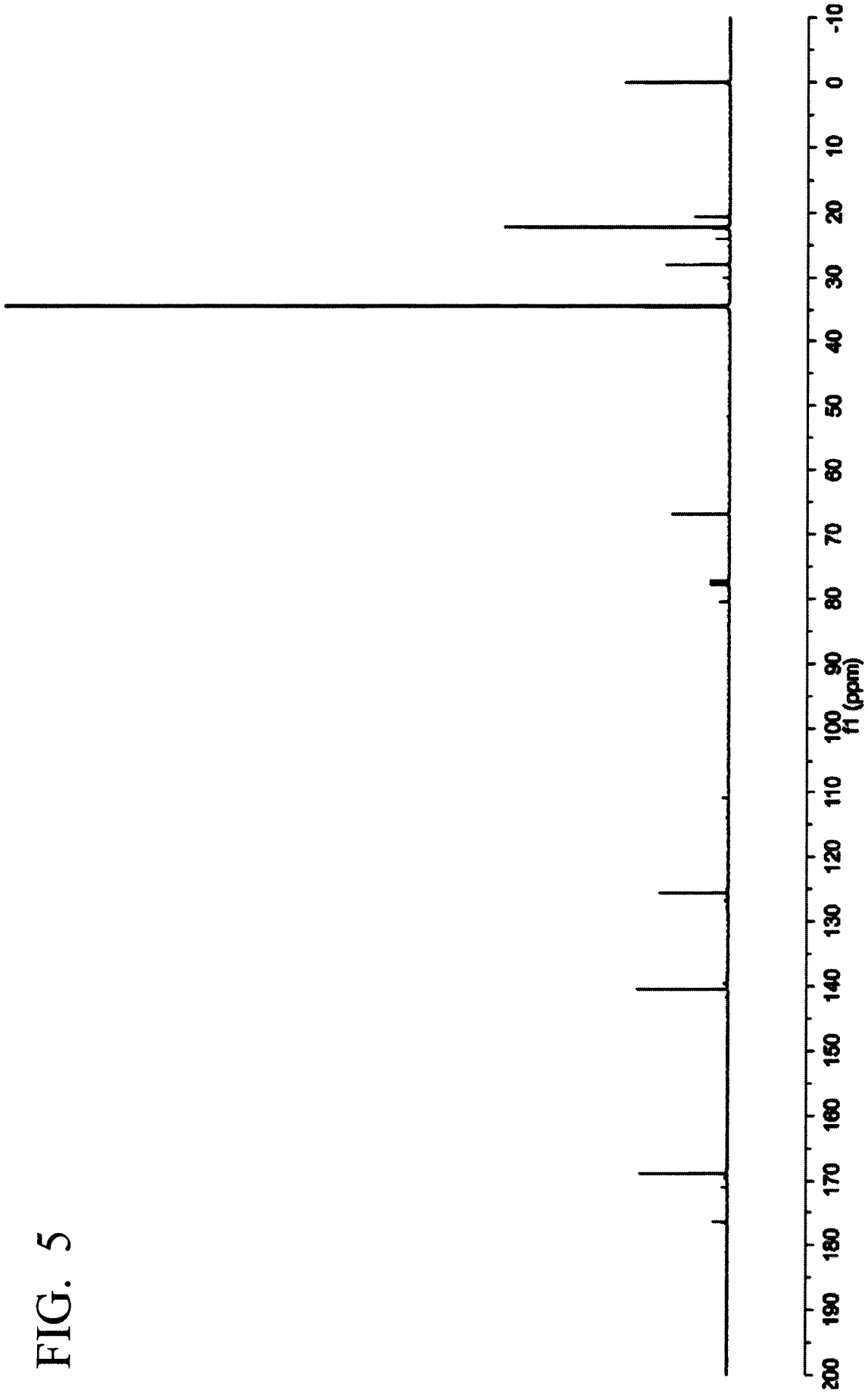

-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
f1 (ppm)

FIG. 6

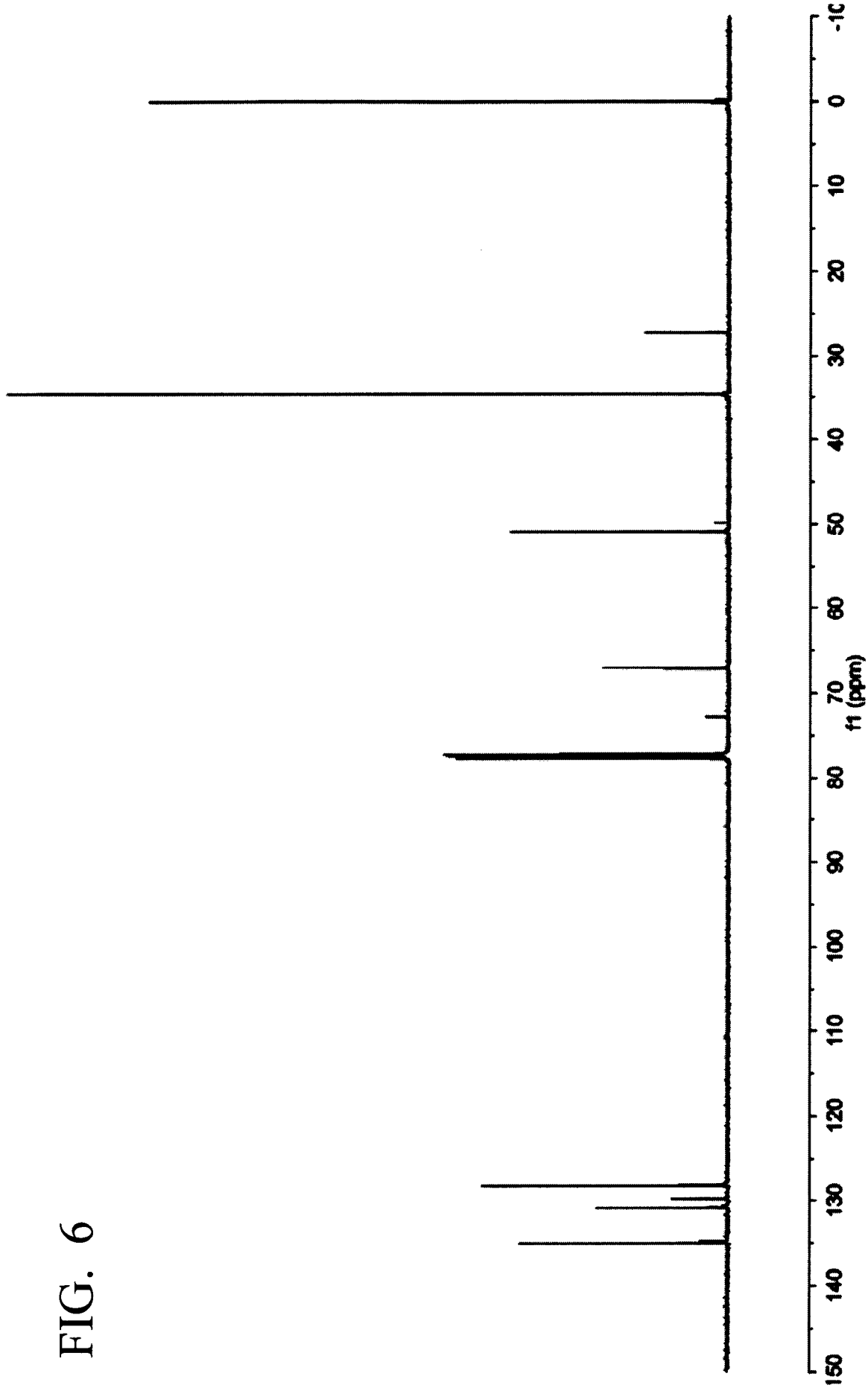


FIG. 7

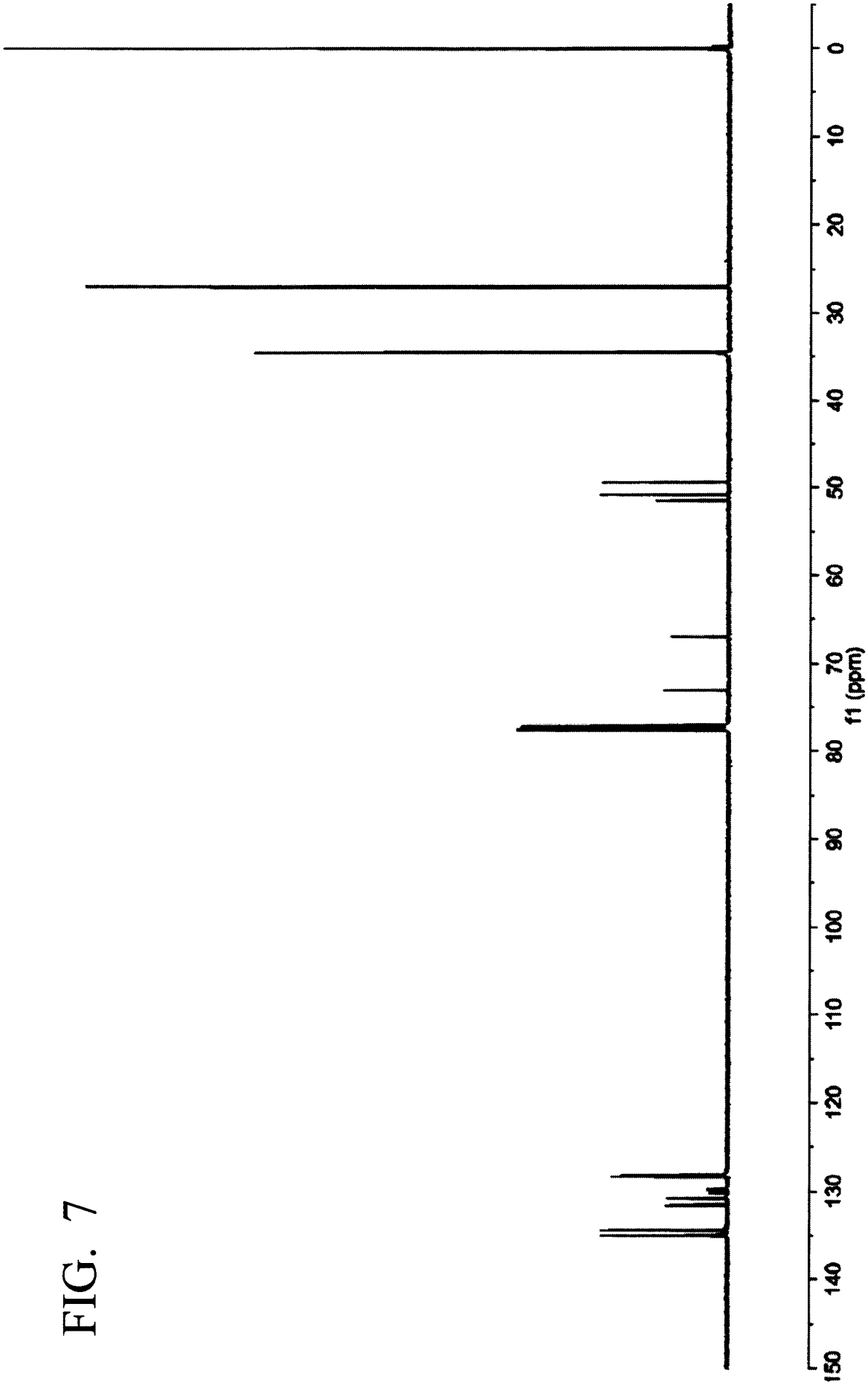


FIG. 8

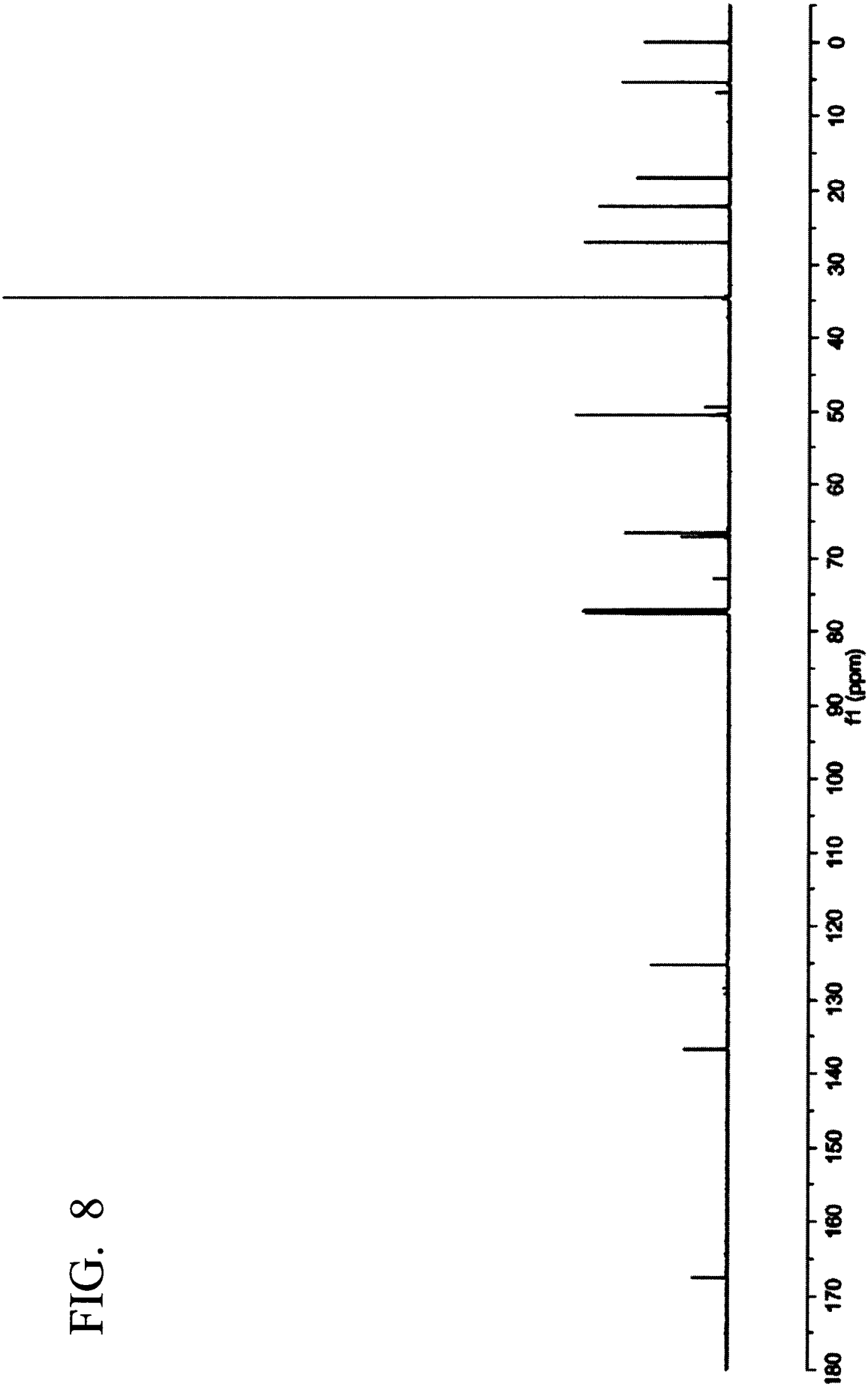
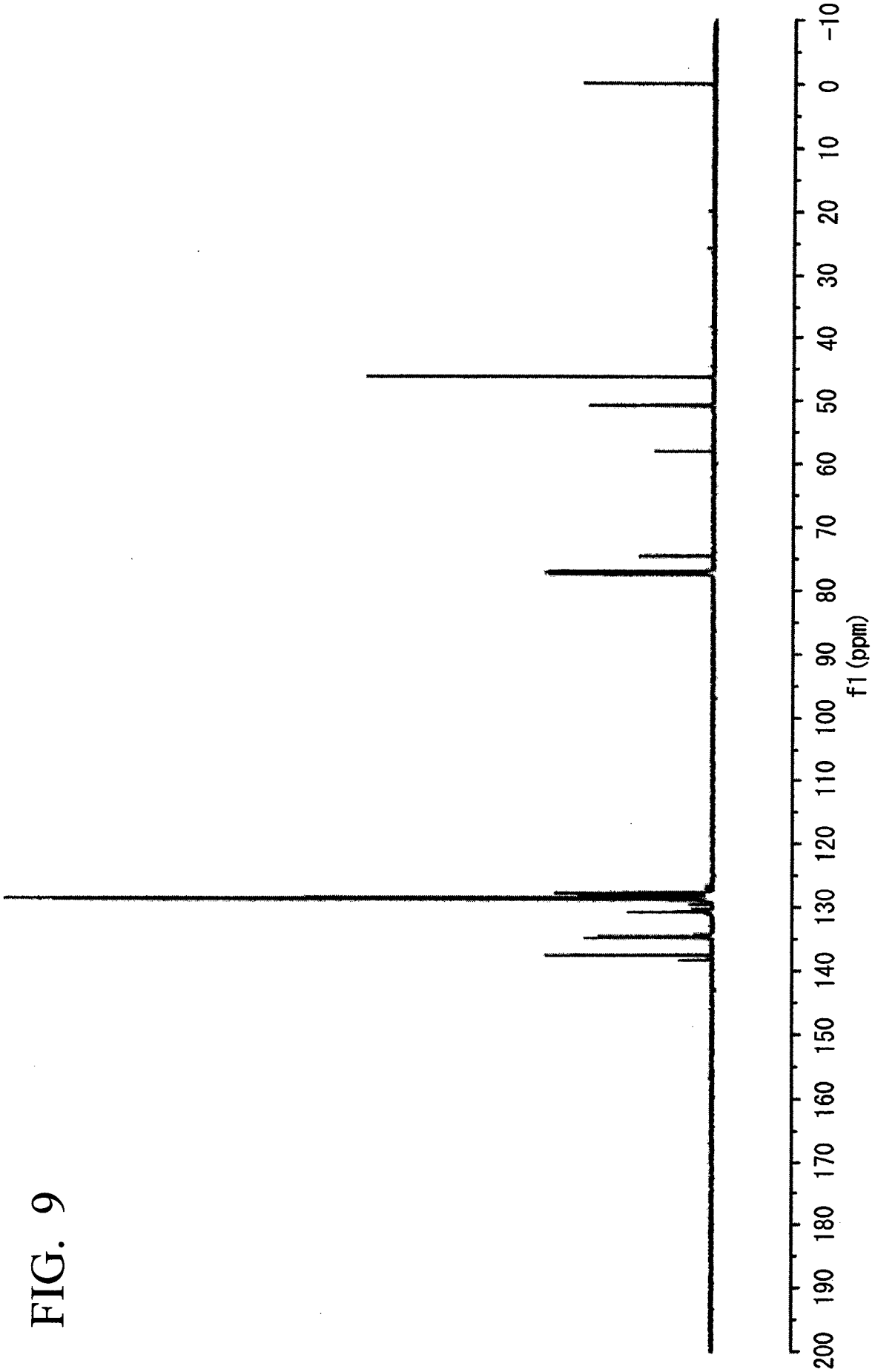

0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
f1 (ppm)

FIG. 9


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2011/080569

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07F7/08
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	RYUTARO WAKABAYASHI ET AL: "Practical Conversion of Chlorosilanes into Alkoxysilanes without Generating HCl", ANGEWANDTE CHEMIE INTERNATIONAL EDITION, vol. 50, no. 45, 4 November 2011 (2011-11-04), pages 10708-10711, XP55019223, ISSN: 1433-7851, DOI: 10.1002/anie.201104948 the whole document ----- -/--	1-11

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 February 2012	23/02/2012

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Richter, Herbert

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INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2011/080569

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JUNG M E ET AL: "Quantitative dealkylation of alkyl ethers via treatment with trimethylsilyl iodide. A new method for ether hydrolysis", JOURNAL OF ORGANIC CHEMISTRY, AMERICAN CHEMICAL SOCIETY, EASTON.; US, vol. 42, no. 23, 11 November 1977 (1977-11-11), pages 3761-3764, XP002139433, ISSN: 0022-3263, DOI: 10.1021/JO00443A033 cited in the application table 1; compounds d,e	1,6,11
X	MORITA T ET AL: "NOVEL METHOD FOR DEALKYLATION OF ESTERS, ETHERS, AND ACETALS BY CHLOROTRIMETHYLSILANE-SODIUM IODIDE", JOURNAL OF THE CHEMICAL SOCIETY, CHEMICAL COMMUNICATIONS, CHEMICAL SOCIETY. LETCHWORTH, GB, no. 20, 1 January 1978 (1978-01-01), page 874/875, XP009053312, ISSN: 0022-4936, DOI: 10.1039/C39780000874 cited in the application reaction scheme underneath table 1; page 875; table 1	1,5,8-11
X	US 2 534 149 A (SAUER ROBERT O) 12 December 1950 (1950-12-12) example 13	1-3,5,6, 11

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/JP2011/080569

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2534149 A	12-12-1950	NONE	