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(54) Title: TIN CONTAINING ORGANOMETALLIC COMPOUNDS

(57) **Abstract:** Disclosed are Tin containing organometallic compounds of Formula I: $R_xSn(A)_{4-x}$, wherein R is selected from unsaturated hydrocarbons having 2 to 10 carbon atoms and optionally substituted Cp, A is selected from amine groups, alkoxy groups, and halides, and x is an integer from 1 to 3, as well as highly purified forms of the organometallic compounds for use in the deposition of high purity tin oxide and compositions that result in improved reactivity and better stability.

TIN CONTAINING ORGANOMETALLIC COMPOUNDS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. provisional application number 63,334,430 filed April 25, 2022, which is incorporated herein in its entirety.

TECHNICAL FIELD

[0002] The present disclosure relates to organometallic compounds useful for the deposition of high purity tin oxide and highly purified forms of the organometallic compounds. More specifically, the present disclosure describes specific compounds useful in deposition of high purity tin oxide as well as compositions that result in improved reactivity and better stability.

BACKGROUND

[0003] Extreme ultraviolet (EUV) lithography enables a superb resolution of patterns that have been transferred onto a wafer substrate to form microchips. Unfortunately, traditional chemical amplified resists are highly transparent at an EUV wavelength of 13.5nm (92 eV). Thus, there is a need in the industry to develop a new generation of photosensitive materials to enable production of smaller microchips for an array of technical applications.

[0004] One strategy to increase the sensitivity of photosensitive materials is an incorporation of atoms with enhanced absorptivity in the EUV regime, such as Sn, into the resist composition. Thus, there is a desire for Sn organometallics having high reactivity and stability for use as photo-sensitive materials in EUV processes and deposition processes.

SUMMARY

[0005] Applicant determined that decreasing the bond energy of the Sn-C bond could improve performance of the Sn photosensitive materials in certain uses (photolytic cleavage of Sn-C bonds during exposure to EUV would promote cross-linking hence making these materials superior negative photoresist). Ligands containing unsaturated hydrocarbons, such as allyl, may provide decreased bond energy of the Sn-C bond.

[0006] Despite the foregoing advantages of decreasing the bond energy of the Sn-C bond in photosensitive materials, it is also contemplated that strengthening the Sn-C bond in photosensitive materials may also be advantageous in photosensitive materials in other uses. Ligands containing unsaturated hydrocarbons, such as vinyl, may provide increased bond energy of the Sn-C bond. By strengthening the Sn-C bond, some ligands bonded to Sn may be retained in the deposited film for further EUV treatment, which may be advantageous in particular uses.

[0007] In addition, amino, alkoxy, or halide ligands enable reactivity with OH groups of wafers/substrate layers for effective ALD deposition. Thus, Applicant discovered that organometallics of tin having a combination of ligands containing unsaturated hydrocarbons and ligands containing amino, alkoxy, or halide ligands have improved properties for deposition, especially atomic layer deposition, and for use as a photosensitive material in patterning applications.

[0008] In one aspect, disclosed are organometallic compounds of Formula I, below:

$$(R)_xSn(A)_{4-x} \qquad \text{Formula I}$$

wherein:

R is substituted Cp, unsubstituted Cp, or a non-cyclic unsaturated hydrocarbon having 2 to 10 carbon atoms, or 2 to 8 carbon atoms, or 2 to 4 carbon atoms;

A is NR^1R^2, OR^3, pyrrolidinyl, pyrrolyl, or halide;

R^1 and R^2 are each an alkyl group having from 1 to 10 carbon atoms;

R^1 and R^2 can be the same or different;

R^3 is an alkyl group having 2 to 8 carbon atoms;

x is an integer from 1 to 3; and

when A is NR^1R^2, pyrrolidinyl, pyrrolyl, or halide, R is substituted Cp or a non-cyclic unsaturated hydrocarbon having 2 to 10 carbon atoms, or 2 to 8 carbon atoms, or 2 to 4 carbon atoms.

[0009] In embodiments, R is an allyl or vinyl group. In some embodiments, the allyl or vinyl group can be straight chain. Alternatively, the allyl group can be a substituted allyl group having the general formula: $CR^4R^5CR^6{=}CR^7R^8$, wherein R^4, R^5, R^6, R^7, and R^8 are each independently selected from the group consisting of H and alkyl groups having from 1 to 4 carbon atoms. Similarly, the vinyl group can be a substituted vinyl group having the general formula: $CR^9{=}CR^{10}R^{11}$, wherein R^9, R^{10}, and R^{11} are each independently selected from the group consisting of H and alkyl groups having from 1 to 4 carbon atoms.

[0010] In other embodiments, R is Cp, which is a cyclopentadienyl group having R^{12}, R^{13}, R^{14}, R^{15}, and R^{16} constituents. Depending on A, Cp can be substituted or unsubstituted. R^{12}, R^{13}, R^{14}, R^{15}, and R^{16} each independently selected from H and an alkyl group having from 1 to 10 carbon atoms, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, or decyl. R^{12}, R^{13}, R^{14}, R^{15}, and R^{16} can be the same or different. However, when A is NR^1R^2, pyrrolidinyl, pyrrolyl, or halide, at least one of R^{12}, R^{13}, R^{14}, R^{15}, and R^{16} is an alkyl group having from 1 to 10 carbon atoms.

[0011] In any of the above-mentioned embodiments, A is NR^1R^2. In such embodiments, R^1 and R^2 are independently selected from an alkyl group having from 1 to 4 carbon atoms. In embodiments R^1 and R^2 are methyl or ethyl. In embodiments R^1 and R^2 are different.

[0012] Alternatively, A can be OR^3. In such embodiments R^3 is an alkyl group having from 1 to 4 carbon atoms. In embodiments R^3 is methyl, ethyl, or tert-butyl. In other embodiments, A is one of pyrrolyl, pyrrolidinyl, or halide.

[0013] In embodiments, the organometallic compound is selected from the group consisting of $(CH_2{=}CHCH_2)Sn(NMe_2)_3$, $(CH_2{=}CHCH_2)Sn(NEt_2)_3$, $(CH_2{=}CHCH_2)Sn(NEtMe)_3$, $(CH_2{=}CHCH_2)Sn(Pyrrolidinyl)_3$, $(CH_2{=}CH)Sn(NMe_2)_3$, $(CH_2{=}CH)Sn(NEt_2)_3$, $(CH_2{=}CH)Sn(NEtMe)_3$, $(CH_2{=}CH)Sn(Pyrrolidinyl)_3$, $(Cp)Sn(NMe_2)_3$, $(Cp)Sn(NEt_2)_3$, $(Cp)Sn(NEtMe)_3$, $(Cp)Sn(Pyrrolidine)_3$, $(CH_2{=}CHCH_2)_2Sn(NMe_2)_2$, $(CH_2{=}CHCH_2)_2Sn(NEt_2)_2$, $(CH_2{=}CHCH_2)_2Sn(NEtMe)_2$, $(CH_2{=}CHCH_2)_2Sn(Pyrrolidine)_2$, $(CH_2{=}CH)_2Sn(NMe_2)_2$, $(CH_2{=}CH)_2Sn(NEt_2)_2$, $(CH_2{=}CH)_2Sn(NEtMe)_2$, $(CH_2{=}CH)_2Sn(Pyrrolidine)_2$, $(Cp)_2Sn(NMe_2)_2$, $(Cp)_2Sn(NEt_2)_2$, $(Cp)_2Sn(NEtMe)_2$, $(Cp)_2Sn(Pyrrolidine)_2$, $(CH_2{=}CHCH_2)_3Sn(NMe_2)$, $(CH_2{=}CHCH_2)_3Sn(NEt_2)$, $(CH_2{=}CHCH_2)_3Sn(NEtMe)$, $(CH_2{=}CHCH_2)_3Sn(Pyrrolidine)$, $(CH_2{=}CH)_3Sn(NMe_2)$, $(CH_2{=}CH)_3Sn(NEt_2)$, $(CH_2{=}CH)_3Sn(NEtMe)$, $(CH_2{=}CH)_3Sn(Pyrrolidine)$, $(Cp)_3Sn(NMe_2)$, $(Cp)_3Sn(NEt_2)$, $(Cp)_3Sn(NEtMe)$, $(Cp)_3Sn(Pyrrolidine)$.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] Embodiments of the invention will now be described by way of example with reference to the accompanying drawings, of which:

[0015] FIG. 1 shows a ^1H NMR spectrum of a reaction mixture comprising $(CH_2{=}CHCH_2)Sn(Cl)_3$ in toluene (300 MHz, C_6D_6).

[0016] FIG. 2 shows a ^{119}Sn NMR spectrum of a reaction mixture comprising $(CH_2{=}CHCH_2)Sn(Cl)_3$ in toluene (186.55 MHz, C_6D_6).

[0017] FIG. 3 shows a ^1H NMR spectrum of a reaction mixture comprising $(CH_2{=}CHCH_2)_2Sn(Cl)_2$ in toluene (300 MHz, C_6D_6).

[0018] FIG. 4 shows a ^1H NMR spectrum of an isolated product mixture comprising $(CH_2{=}CHCH_2)Sn(NMe_2)_3$, $(CH_2{=}CHCH_2)_2Sn(NMe_2)_2$, and $(CH_2{=}CHCH_2)_3Sn(NMe_2)$ after 12 hours at 22°C (300 MHz, C_6D_6).

[0019] FIG. 5 shows a ^{119}Sn NMR spectrum of an isolated product mixture comprising $(CH_2{=}CHCH_2)Sn(NMe_2)_3$, $(CH_2{=}CHCH_2)_2Sn(NMe_2)_2$, and $(CH_2{=}CHCH_2)_3Sn(NMe_2)$ after 12 hours at 22°C (187 MHz, C_6D_6).

[0020] FIG. 6 shows a ^1H NMR spectrum of a product mixture comprising $(CH_2{=}CHCH_2)_2Sn(NiPr_2)_2$ and $HNiPr_2$ (300 MHz, C_6D_6).

[0021] FIG. 7 shows a ^1H NMR spectrum of $(CH_2{=}CH)_3Sn(NEt_2)$ (500 MHz C_6D_6).

[0022] FIG. 8 shows a ^1H NMR spectrum of $(CH_2{=}CH)_3Sn(NEt_2)$ (186 MHz C_6D_6).

[0023] FIG. 9 shows a vapor pressure curve of $(CH_2{=}CH)_3Sn(NEt_2)$.

[0024] FIG. 10 shows a ^{119}Sn NMR spectrum of $Cp^{iPr}Sn(NMe_2)_3$ (186 MHz, C_6D_6).

[0025] FIG. 11A shows a cross section of a deposited intermediate product.

[0026] FIG. 11B shows a cross section of a developed intermediate product.

[0027] FIG. 11C shows a cross section of an etched intermediate product.

[0028] FIG. 11D shows a cross section of a final product.

[0029] FIG. 12 shows a schematic of a multistage vacuum distillation apparatus.

DETAILED DESCRIPTION

[0030] Before describing several exemplary embodiments, it is to be understood that the invention is not limited to the details of construction or process steps set forth in the following description. The invention is capable of other embodiments and of being practiced or being carried out in various ways.

[0031] Reference throughout this specification to “one embodiment,” “certain embodiments,” “one or more embodiments” or "an embodiment" means that a particular feature, structure, material, or characteristic described in connection with the embodiment is included in at least one embodiment. Thus, the appearances of the phrases such as “in one or more embodiments,” “in certain embodiments,” “in one embodiment” or “in an embodiment” in various places throughout this specification are not necessarily referring to the same embodiment. Furthermore, the particular features, structures, materials, or characteristics may be combined in any suitable manner in one or more embodiments.

[0032] Although reference herein is to particular embodiments, it is to be understood that these embodiments are merely illustrative of the principles and applications of the present invention. It will be apparent to those skilled in the art that various modifications and variations can be made to the method and apparatus of the present invention without departing from the spirit and scope of the invention. Thus, it is intended that the present invention include modifications and variations that are within the scope of the appended claims and their equivalents.

[0033] Reference throughout this specification to “a” or “an” represents one or more and is not limited to singular form, unless explicitly stated.

[0034] The following detailed description can be read in connection with the accompanying drawings in which like numerals designate like elements.

[0035] Disclosed are organometallic compounds of Formula I, below:

$(R)_xSn(A)_{4-x}$ Formula I

wherein:

R is substituted Cp, unsubstituted Cp, or a non-cyclic unsaturated hydrocarbon having 2 to 10 carbon atoms, or 2 to 8 carbon atoms, or 2 to 4 carbon atoms;

A is NR^1R^2, OR^3, pyrrolidinyl, pyrrolyl, or halide;

R^1 and R^2 are each an alkyl group having from 1 to 10 carbon atoms;

R^1 and R^2 can be the same or different;

R^3 is an alkyl group having 2 to 8 carbon atoms;

x is an integer from 1 to 3; and

when A is NR^1R^2, pyrrolidinyl, pyrrolyl, or halide, R is substituted Cp or a non-cyclic unsaturated hydrocarbon having 2 to 10 carbon atoms, or 2 to 8 carbon atoms, or 2 to 4 carbon atoms.

[0036] Also disclosed are high-purity organometallic compounds and methods of purifying the organometallic compounds.

[0037] Applicant discovered that during synthesis of compounds of Formula I, dissociation occurred. For example, molecules of $(CH_2{=}CHCH_2)_2Sn(NMe_2)_2$, a product, underwent significant ligand exchange, resulting in the formation of side products, such as $(CH_2{=}CHCH_2)Sn(NMe_2)_3$ and $(CH_2{=}CHCH_2)_3Sn(NMe_2)$. It is contemplated that bulkier ligands, such as substituted allyl, substituted vinyl, substituted or unsubstituted Cp, which is cyclopentadienyl, heavier amines, or heavier alkoxies in the compound of Formula I may be able to prevent side product creation and improve stability by reducing ligand exchange.

[0038] In embodiments, R is an allyl group having the general formula: $CR^4R^5CR^6{=}CR^7R^8$, wherein R^4, R^5, R^6, R^7, and R^8 are each independently selected from the group consisting of H and alkyl groups having from 1 to 4 carbon atoms, such as methyl, ethyl, propyl, iso-propyl, tert-butyl, iso-butyl, or n-butyl. R^4, R^5, R^6, R^7, and R^8 can be the same or different. In embodiments, at least one of R^4 and R^5 is not H, such as 1,1-dimethylallyl, wherein R^4 and R^5 are both methyl. In embodiments R^6 is not H, such as 2-methylallyl. In embodiments at least one of R^7 and R^8 is not H, such as 3,3-dimethylallyl. In some embodiments, x is 2 and compounds of Formula I are represented by the following formula: $(CR^4R^5\ CR^6{=}CR^7R^8)_2Sn(A)_2$, wherein A is NR^1R^2, OR^3, pyrrolidinyl, pyrrolyl, or halide.

[0039] In other embodiments, R is a vinyl group having the general formula: $CR^9{=}CR^{10}R^{11}$, wherein R^9, R^{10}, and R^{11} are each independently selected from the group consisting of H and alkyl groups having from 1 to 4 carbon atoms, such as methyl, ethyl, propyl, iso-propyl, tert-butyl, iso-butyl, or n-butyl. R^9, R^{10}, and R^{11} can be the same or different. In embodiments, R^9 is not H, such as 1-ethylvinyl. In embodiments at least one of R^{10} and R^{11} is not H, such as 2,2-dimethylvinyl. In some embodiments, x is 2 and compounds of Formula I are represented by the following formula: $(CR^9{=}CR^{10}R^{11})_2Sn(A)_2$, wherein A is NR^1R^2, OR^3, pyrrolidinyl, pyrrolyl, or halide.

[0040] Any of the above-mentioned compounds of Formula I include those in which x is 1. In such embodiments, Compounds of Formula I are represented by the following formula: $(R)Sn(A)_3$, wherein R is a non-cyclic unsaturated hydrocarbon having 2 to 10 carbon atoms.

Compounds of Formula I also include those in which x is 3. In such alternative embodiments, compounds of Formula I are represented by the following formula: $(R)_3Sn(A)$, wherein R is a non-cyclic unsaturated hydrocarbon having 2 to 10 carbon atoms.

[0041] Any of the above-mentioned compounds of Formula I represented by the formula: $(R)_xSn(A)_{4-x}$ include those in which R is a non-cyclic unsaturated hydrocarbon having 2 to 8 carbon atoms. Further, Compounds of Formula I include those in which R is a non-cyclic unsaturated hydrocarbon having 2 to 4 carbon atoms.

[0042] Any of the above-mentioned compounds of Formula I include those in which A is NR^1R^2. R^1 and R^2 are independently selected from H, alkyl groups having from 1 to 10 carbon atoms, aryl groups, or acyl groups. R^1 and R^2 can be the same or different. In a particular embodiment, R^1 and R^2 are each alkyl groups having 1 to 10 carbons atoms. In a more particular embodiment, R^1 and R^2 are each alkyl groups having from 2 to 4 carbon atoms. More particularly, R^1 and R^2 can each be selected from the group consisting of methyl, ethyl, propyl, iso-propyl, tert-butyl, iso-butyl, and n-butyl.

[0043] For any of the above-mentioned compounds, it is contemplated that R can be either a straight-chain unsaturated hydrocarbon or a branched unsaturated hydrocarbon.

[0044] Any of the above-mentioned compounds of Formula I also include those in which A is OR^3. In such embodiments, compounds of Formula I are represented by the formula: $(R)_xSn(OR^3)_{4-x}$, wherein R^3 is an alkyl group having 2 to 8 carbon atoms. In other embodiments, R^3 is selected from the group consisting of an alkyl group having from 1 to 4 carbon atoms. More particularly, R^3 can be selected from the group consisting of methyl, ethyl, propyl, iso-propyl, tert-butyl, iso-butyl, and n-butyl.

[0045] When A is an alkoxy group, such as OR^3, R can be Cp. In such embodiments, compounds of Formula I are represented by the formula: $(Cp)_xSn(OR^3)_{4-x}$, wherein Cp is a cyclopentadienyl group having R^{12}, R^{13}, R^{14}, R^{15}, and R^{16} constituents. Cp can be unsubstituted, wherein R^{12}, R^{13}, R^{14}, R^{15}, and R^{16} are H, or substituted, wherein at least one of R^{12}, R^{13}, R^{14}, R^{15}, and R^{16} is independently selected from an alkyl group having from 1 to 10 carbon atoms, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, or decyl. R^{12}, R^{13}, R^{14}, R^{15}, and R^{16} can be the same or different.

[0046] When A is an amine group, such as NR^1R^2, or pyrrolidinyl, pyrrolyl, or halide, R can be substituted Cp, wherein at least one of R^{12}, R^{13}, R^{14}, R^{15}, and R^{16} is independently selected from an alkyl group having from 1 to 10 carbon atoms, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, or decyl. R^{12}, R^{13}, R^{14}, R^{15}, and R^{16} can be the same or different.

[0047] Compounds of Formula I include those in which A is pyrrolidinyl or pyrrolyl. Such embodiments are respectively represented by the general formula: $(R)_xSn(Pyrrolidinyl)_{4-x}$ or $(R)_xSn(Pyrrolyl)_{4-x}$. It is contemplated that A could also be a halide, such as chloro, bromo, or iodo.

[0048] When R is Cp, compounds of Formula I, $(Cp)_xSn(A)_{4-x}$ may be synthesized as follows. In a glovebox, load a 1L round bottom flask with $SnCl_4$ and anhydrous hexanes. Add 1 equiv. of NaCp* (NaC_5Me_5) drop-wise while cooling. Leave the reaction mixture stirring at room temperature for 1 hour. Return the reaction flask into a cooling bath and add 3 equiv. of NaOMe in anhydrous THF to the flask. Remove solvents via reduced pressure distillation. Isolate the product via sublimation.

[0049] Particular organometallic compounds of Formula I include the following: $(CH_2{=}CHCH_2)Sn(NMe_2)_3$, $(CH_2{=}CHCH_2)Sn(NEt_2)_3$, $(CH_2{=}CHCH_2)Sn(NEtMe)_3$,

$(CH_2{=}CHCH_2)Sn(Pyrrolidinyl)_3$, $(CH_2{=}CH)Sn(NMe_2)_3$, $(CH_2{=}CH)Sn(NEt_2)_3$, $(CH_2{=}CH)Sn(NEtMe)_3$, $(CH_2{=}CH)Sn(Pyrrolidinyl)_3$, $(Cp)Sn(NMe_2)_3$, $(Cp)Sn(NEt_2)_3$, $(Cp)Sn(NEtMe)_3$, $(Cp)Sn(Pyrrolidine)_3$, $(CH_2{=}CHCH_2)_2Sn(NMe_2)_2$, $(CH_2{=}CHCH_2)_2Sn(NEt_2)_2$, $(CH_2{=}CHCH_2)_2Sn(NEtMe)_2$, $(CH_2{=}CHCH_2)_2Sn(Pyrrolidine)_2$, $(CH_2{=}CH)_2Sn(NMe_2)_2$, $(CH_2{=}CH)_2Sn(NEt_2)_2$, $(CH_2{=}CH)_2Sn(NEtMe)_2$, $(CH_2{=}CH)_2Sn(Pyrrolidine)_2$, $(Cp)_2Sn(NMe_2)_2$, $(Cp)_2Sn(NEt_2)_2$, $(Cp)_2Sn(NEtMe)_2$, $(Cp)_2Sn(Pyrrolidine)_2$, $(CH_2{=}CHCH_2)_3Sn(NMe_2)$, $(CH_2{=}CHCH_2)_3Sn(NEt_2)$, $(CH_2{=}CHCH_2)_3Sn(NEtMe)$, $(CH_2{=}CHCH_2)_3Sn(Pyrrolidine)$, $(CH_2{=}CH)_3Sn(NMe_2)$, $(CH_2{=}CH)_3Sn(NEt_2)$, $(CH_2{=}CH)_3Sn(NEtMe)$, $(CH_2{=}CH)_3Sn(Pyrrolidine)$, $(Cp)_3Sn(NMe_2)$, $(Cp)_3Sn(NEt_2)$, $(Cp)_3Sn(NEtMe)$, $(Cp)_3Sn(Pyrrolidine)$.

[0050] Decreasing the bond strength of the Sn-C bond could improve performance of the Sn photosensitive materials during photolytic cleavage of Sn-C bonds upon exposure to EUV. It would promote cross-linking hence making these materials superior negative photoresist. Unsaturated hydrocarbons, such as allyl ligands, are great compounds for this application. Additionally, the presence of a Sn-allyl bond would improve the reactivity of this molecule during SnO_2 film formation.

[0051] Increasing the bond strength of the Sn-C bond may also be advantageous in photosensitive materials. Ligands containing unsaturated hydrocarbons, such as vinyl, may provide increased bond energy of the Sn-C bond. By strengthening the Sn-C bond, some ligands bonded to Sn may be retained in the deposited film for further EUV treatment, which may be advantageous.

[0052] Compounds of Formula I may be prepared by processes known in the art. The examples below are illustrative of such processes but are not intended to be limiting.

Example 1: Synthesis of $(CH_2{=}CHCH_2)Sn(Cl)_3$

[0053] On a double manifold, a small Schlenk flask was loaded with 6.0 mL of $SnCl_4$ (51mmol), ca. 60mL of anhydrous toluene, and a magnetic stir bar. While stirring at room temperature, 4.1mL of Sn(allyl)$_4$ (17mmol) was added drop-wise. The reaction mixture was stirred at 22°C for 90 minutes. A small aliquot was collected for ^{1}H NMR and ^{119}Sn NMR analysis and confirmed the formation of $(CH_2{=}CHCH_2)Sn(Cl)_3$ as shown in Figures 1 and 2. Removal of the solvent may affect stability. Characterization: ^{1}H NMR (300MHz, C_6D_6) (FIG. 1): 1.72ppm (m, $^2J_{H119Sn}$ = 120Hz, $^2J_{H117Sn}$ = 124Hz, 1H, allyl C*H*$_2$), 1.75ppm (m, $^2J_{H119Sn}$ = 118Hz, $^2J_{H117Sn}$ = 124Hz, 1H, allyl C*H*$_2$), 4.69ppm (m, $^3J_{HH}$ = 16.6Hz, 1H, allyl C*H*$_2$), 4.74ppm (m, $^3J_{HH}$ = 9.7Hz, 1H, allyl C*H*$_2$), 5.15ppm (m, 1H, allyl C*H*). ^{119}Sn NMR (186.55MHz, C_6D_6) (FIG.2): -26.8ppm.

Example 2: Synthesis of $(CH_2{=}CHCH_2)_2Sn(Cl)_2$

[0054] On a double manifold, a small Schlenk flask was loaded with 2.0 mL of $SnCl_4$ (17mmol), ca. 30mL of anhydrous toluene, and a magnetic stir bar. While stirring at room temperature, 4.1 mL of Sn(allyl)$_4$ (17mmol) was added drop-wise. The reaction mixture was stirred at 22°C for 90 minutes. A small aliquot was collected for ^{1}H NMR and ^{119}Sn NMR analysis and confirmed the formation of $(CH_2{=}CHCH_2)_2Sn(Cl)_2$ as shown in Figure 3. Removal of the solvent may affect stability. Characterization: ^{1}H NMR (300MHz, C_6D_6) (FIG. 3): 1.96ppm (m, 1H, allyl C*H*$_2$), 1.99ppm (m, 1H, allyl C*H*$_2$), 4.80-4.88ppm (m, 2H, allyl C*H*$_2$), 5.57ppm (m, 1H, allyl C*H*). ^{119}Sn NMR (186.55MHz, C_6D_6): 48.3ppm.

Example 3: Synthesis of $(CH_2{=}CHCH_2)_2Sn(NMe_2)_2$

[0055] On a double manifold, a 1L round bottom flask was loaded with 82mL of BuLi (2.5M in hexanes, 0.205mol), ca. 500mL of anhydrous toluene and a magnetic stir bar. The flask was placed in an ice-water bath and $HNMe_2$ was bubbled through the reaction mixture for 20 minutes at a rate of 284mL per minute (0.251mol). The reaction flask was removed from the cooling bath and left to stir at 22°C for 90 minutes.

[0056] Meanwhile, $(CH_2{=}CHCH_2)_2Sn(Cl)_2$ was prepared by reacting 6.0mL of $SnCl_4$ (0.051mol) in ca. 100mL of anhydrous toluene and 12.3mL of $Sn(allyl)_4$ (0.051mol). This reaction was stirred at 22°C for 60 minutes. The flask containing $(CH_2{=}CHCH_2)_2Sn(Cl)_2$ was returned to an ice-water bath where an $LiNMe_2$ mixture was slowly added drop-wise via cannulation to the flask. The final reaction mixture was removed from the cooling bath and stirred at 22°C for 50 minutes.

[0057] Stirring was stopped to allow the LiCl salts to settle down overnight. The next day, the liquid layer was transferred into a new round bottom flask. The solvent was removed via reduced pressure distillation. The final product was isolated via reduced pressure distillation (40°C at $2.0\text{–}4.5\times10^{-2}$ Torr). A significant ligand exchange of $(CH_2{=}CHCH_2)_2Sn(NMe_2)_2$ has been detected resulting in the formation of $(CH_2{=}CHCH_2)SN(NMe_2)_3$ and $(CH_2{=}CHCH_2)_3Sn(NMe_2)$ Eventually, the product distribution reaches 50:25:25 mol%.

[0058] Characterization:

[0059] $(CH_2{=}CHCH_2)_3Sn\ (NMe_2)$: ^1H NMR (300MHz, C_6D_6) (FIG. 4): 1.87ppm (dd, $^2J_{HH}$ = 1.2Hz; $^3J_{HH}$ = 0.7Hz, 3H, allyl CH_2), 1.90 ppm (dd, $^2J_{HH}$ = 1.2Hz; $^3J_{HH}$ = 0.7Hz, 3H, allyl CH_2), 2.73ppm (s, $^3J_{H119Sn}$ = 42.6Hz, $^3J_{H117Sn}$ = 41.1Hz, 6H, NMe_2), 4.82ppm (m, 3H, allyl CH_2), 4.93ppm (ddd, $^3J_{HH}$ = 16.8Hz, $^4J_{HH}$ = 3.2Hz, $^2J_{HH}$ = 1.2Hz; 3H, allyl CH_2), 5.9ppm (m, 3H, allyl CH). ^{119}Sn NMR (186.55MHz, C_6D_6) (FIG. 5): -6.9ppm.

[0060] $(CH_2{=}CHCH_2)_2Sn(NMe_2)_2$: ^{1}H NMR (300MHz, C_6D_6) (FIG. 4): 1.92ppm (dd, $^2J_{HH}$ = 1.2Hz; $^3J_{HH}$ = 0.7Hz, 2H, allyl CH_2), 1.94 ppm (dd, $^2J_{HH}$ = 1.2Hz; $^3J_{HH}$ = 0.7Hz, 2H, allyl CH_2), 2.78ppm (s, $^3J_{H119Sn}$ = 43.6Hz, $^3J_{H117Sn}$ = 41.6Hz, 12H, NMe_2), 4.83ppm (m, 2H, allyl CH_2), 4.97ppm (ddd, $^3J_{HH}$ = 16.8Hz, $^4J_{HH}$ = 3.0Hz, $^2J_{HH}$ = 1.2Hz; 2H, allyl CH_2), 5.9ppm (m, 2H, allyl CH). ^{119}Sn NMR (186.55MHz, C_6D_6) (FIG. 5): -21.6ppm.

[0061] $(CH_2{=}CHCH_2)Sn(NMe_2)_3$: ^{1}H NMR (300MHz, C_6D_6) (FIG. 4): 1.93ppm (dd, $^2J_{HH}$ = 1.5Hz; $^3J_{HH}$ = 1.0Hz, 1H, allyl CH_2), 1.95 ppm (dd, $^2J_{HH}$ = 1.5Hz; $^3J_{HH}$ = 1.0Hz, 1H, allyl CH_2), 2.81ppm (s, $^3J_{H119Sn}$ = 46.1Hz, $^3J_{H117Sn}$ = 44.1Hz, 18H, NMe_2), 4.83ppm (m, $^3J_{HH}$ = 9.9Hz, 1H, allyl CH_2), 4.97ppm (ddd, $^3J_{HH}$ = 16.8Hz, $^4J_{HH}$ = 3.0Hz, $^2J_{HH}$ = 1.2Hz; 1H, allyl CH_2), 5.9ppm (m, 1H, allyl CH). ^{119}Sn NMR (186.55MHz, C_6D_6) (FIG. 5): -64.9ppm.

Example 4: Synthesis of $(CH_2{=}CHCH_2)_2Sn(NEt_2)_2$

[0062] On a double manifold, a Schlenk flask was loaded with 27.5mL of nBuLi (2.5M in hexanes, 0.069mol), ca. 125mL of anhydrous toluene and a magnetic stir bar. The flask was placed in an ice-water bath and $HNEt_2$ (7.4mL, 0.072mol) in ca. 20mL of anhydrous toluene was added to the reaction flask drop-wise. The reaction flask was removed from the cooling bath and left to stir at 22°C for 40 minutes.

[0063] Meanwhile, $(CH_2{=}CHCH_2)_2Sn(Cl)_2$ was prepared by reacting 2.0mL of $SnCl_4$ (0.017mol) in ca. 80mL of anhydrous toluene and 4.1mL of $Sn(allyl)_4$ (0.017mol). This reaction was stirred at 22°C for 60 minutes. The flask containing $(CH_2{=}CHCH_2)_2Sn(Cl)_2$ was returned to an ice-water bath and the $LiNMe_2$ mixture was slowly added drop-wise via cannulation to the flask. The final reaction mixture was removed from the cooling bath and stirred at 22°C for 30 minutes before proceeding with distillation under reduced pressure to removed solvent and collect the product (80 °C at 0.05Torr).

[0064] Characterization: ^{1}H NMR (300MHz, C_6D_6): 1.08ppm (t, $^{3}J_{HH}$=6.9Hz, 12H, $N(CH_2CH_3)$), 1.95ppm (dd, $^{2}J_{HH}$ = 1.5Hz; $^{3}J_{HH}$ = 1.0Hz, 2H, allyl CH_2), 1.98 ppm (dd, $^{2}J_{HH}$ = 1.5Hz; $^{3}J_{HH}$ = 1.0Hz, 2H, allyl CH_2), 3.04ppm (q, $^{3}J_{HH}$=6.9Hz, 8H, $N(CH_2CH_3)$), 4.86ppm (m, 2H, allyl CH_2), 4.98ppm (m, 2H, allyl CH_2), 5.9ppm (m, 2H, allyl CH). ^{119}Sn NMR (134.35MHz, C_6D_6): -24.8ppm.

Example 5: Synthesis of $(CH_2{=}CHCH_2)_2Sn(NiPr_2)_2$

[0065] On a double manifold, a 1L round bottom flask was loaded with 29.9mL of nBuLi (2.5M in hexanes, 0.075mol), ca. 500mL of anhydrous toluene and a magnetic stir bar. The flask was placed in an ice-water bath and $HNiPr_2$ (11mL, 0.079mol) in ca. 20mL of anhydrous toluene was added to the reaction flask drop-wise. The reaction flask was removed from the cooling bath and left to stir at 22°C overnight. The reaction flask was then transferred into the ice-water bath.

[0066] Meanwhile, $(CH_2{=}CHCH_2)_2Sn(Cl)_2$ was prepared by reacting 2.19mL of $SnCl_4$ (0.019mol) in ca. 100mL of anhydrous toluene and 4.49mL of $Sn(allyl)_4$ (0.019mol). This reaction was stirred at 22°C for 3h. The $(CH_2{=}CHCH_2)_2Sn(Cl)_2$ mixture was slowly added drop-wise to the round bottom flask via cannulation. The final reaction mixture was removed from the cooling bath and stirred at 22°C overnight. After removing solvents from the final product mixture, the product and some free amine in the residue have been characterized. This product is a solid and shows no signs of ligand exchange.

[0067] Characterization: ^{1}H NMR (300MHz, C_6D_6) (FIG. 6): 0.89ppm (d, $^{3}J_{HH}$=6.7Hz, 24H, iPr-CH_3), 1.89ppm (dd, $^{2}J_{HH}$ = 1.0Hz; $^{3}J_{HH}$ = 1.2Hz, 2H, allyl CH_2), 1.92 ppm (dd, $^{2}J_{HH}$ = 1.0Hz;

$^3J_{HH}$ = 1.2Hz, 2H, allyl CH_2), 3.17ppm (sept, $^3J_{HH}$=6.7Hz, 4H, iPr-CH), 4.68ppm (m, 2H, allyl CH_2), 4.78ppm (m, 2H, allyl CH_2), 5.80ppm (m, 2H, allyl CH).

Example 6: Synthesis of $(CH_2{=}CH)_3SnCl$

[0068] Synthesis of this complex was based on Sanders D. Rosenberg & Ambrose J. Gibbons Jr., *The Disproportionation of Tetravinyltin with Tin Tetrachloride and the Cleavage of Some Vinyltin Compounds with Bromine*, 79 J. AM. CHEM. SOC'Y. 2138 (1957), https://doi.org/10.1021/ja01566a029 [hereinafter Rosenberg & Gibbons]. This complex was not isolated and was used in the following salt metathesis reaction steps. Characterization: ^{1}H (300MHz, C_6D_6): dd 5.77ppm ($^3J_{HH}$ = 2.7Hz, $^3J_{HH}$ = 19.9Hz, 3H, vinyl-CH), dd 5.98ppm ($^3J_{HH}$ = 2.7Hz, $^3J_{HH}$ = 13.4Hz, 3H, vinyl-CH), dd 6.14ppm ($^3J_{HH}$ = 13.4Hz, $^3J_{HH}$ = 19.9Hz, 3H, vinyl-CH). ^{119}Sn (186MHz, C_6D_6): s -53.8ppm.

Example 7: Synthesis of $(CH_2{=}CH)_3Sn(NEt_2)$

[0069] On a double manifold, a 500mL round bottom flask was loaded with 10.5mL of nBuLi (2.5M in hexanes, 0.0263mol), ca. 250mL of anhydrous hexane and a magnetic stir bar. $HNEt_2$ (2.8mL, 0.027mol) was added to the reaction flask drop-wise. The reaction mixture was left to stir at 22°C for 60 minutes.

[0070] Meanwhile, $(CH_2{=}CH)_3SnCl$ was prepared by reacting 3.5mL of Sn(vinyl)$_4$ (0.019mol) and 0.8mL of $SnCl_4$ (0.0068mol). This reaction was stirred at 40°C for 90 minutes. *See* Rosenberg & Gibbons.

[0071] Proceed with a slow addition of $(CH_2{=}CH)_3SnCl$ mixture into $LiNEt_2$ mixture via cannulation. The final reaction mixture was stirred at 22°C overnight. Next day proceed with solvent removal via reduced pressure distillation followed by product collection in a separate receiving flask (0.08Torr at 35°C) to collect 5.2g of the product (75% yield).

[0072] Characterization: ^{1}H (500MHz, C_6D_6) (FIG. 7): t 1.10ppm ($^3J_{HH}$ = 6.9Hz, 6H, NEt-CH_3), q 3.08ppm ($^3J_{HH}$ = 6.9Hz, 4H, NEt-CH_2), dd 5.82ppm ($^3J_{HH}$ = 3.2Hz, $^3J_{HH}$ = 20.5Hz, 3H, vinyl-C*H*), dd 6.16ppm ($^3J_{HH}$ = 3.2Hz, $^3J_{HH}$ = 13.7Hz, 3H, vinyl-C*H*), dd 6.40ppm ($^3J_{HH}$ = 13.7Hz, $^3J_{HH}$ = 20.5Hz, 3H, vinyl-C*H*). ^{119}Sn (186MHz, C_6D_6) (FIG. 8): s -104.1ppm.

[0073] FIG. 9 shows a vapor pressure curve for $(CH_2{=}CH)_3Sn(NEt_2)$. Vapor pressure measurements: $\log_{10}P = -2691.6 / T + 8.6502$. The vapor pressure measurements were obtained as follows: A small amount of liquid is evaporated in a closed system with controllable temperature and pressure. At a set temperature, the pressure slowly drops until the liquid sample evaporates at a certain rate which is determined by measuring the drop rate of the liquid from a condenser directly above the liquid. This is repeated for 8-10 temperatures and run in duplicate. The results are compared with a side-by-side run of a calibration standard which helps adjust the pressure at the measured drop rate and temperature vs the known vapor pressure at that temperature.

Example 8: Synthesis of $Cp^{iPr}Sn(NMe_2)_3$

[0074] In the glovebox, a small Schlenk flask was loaded with 1.2mL of $Sn(NMe_2)_4$ (4.7mmol) and ca. 13mL of anhydrous THF. Add 0.679g of $NaCp^{iPr}$ (5.2mmol). Transfer this Schlenk flask onto the double manifold and proceed with reflux at 76°C for 4 hours. NMR analysis of the reaction mixture confirms formation of $Cp^{iPr}Sn(NMe_2)_3$. When isolated, this product is a solid.

[0075] Characterization: ^1H (500MHz, C_6D_6): d 1.36ppm ($^3J_{HH}$ = 6.7Hz, 6H, iPr-CH_3), s 3.06ppm ($^3J_{H119Sn}$ = 42.1Hz, $^3J_{H117Sn}$ = 40.4Hz, 18H, NMe_2), sept 3.18 ($^3J_{HH}$=6.7Hz, 1H, iPr-C*H*), m 6.21 (2H, Cp-*H*), m 6.32 (2H, Cp-*H*).^{119}Sn (186MHz, C_6D_6) (FIG. 10): s 63.9ppm.

[0076] Compounds of Formula I could have improved thermal stability and surface reactivity compared to those known in the art, which may result in improved ALD films. Poor thermal stability can hinder reactivity of the precursor with the substrate surface during ALD deposition, that is, the precursor should not decompose prior to ALD deposition. In contrast to ALD, in CVD processes, high energy and temperature are used to react the precursors at process temperature. Then, the already-reacted precursors react on the substrate. Because the CVD process uses substantially larger energy and breaks apart the precursors prior to the reaction, the reactivity of the precursors is not as important in CVD processes as in ALD processes.

Negative Resist Deposition

[0077] Figures 11A–11D show an exemplary process of negative resist deposition using a compound of Formula I. A multi-layer substrate 10 is provided. In the illustrated example, layer 10A is the only layer of the substrate that is to be patterned. A layer of photosensitive material 30 including the compound of Formula I is subsequently deposited onto the layer 10A. Then, mask(s) 40 is selectively applied over portions of the layer of photosensitive material 30 such that unexposed portions 30A of the layer of photosensitive material 30 are covered by the mask 40 and exposed portions 30B of the layer of photosensitive material 30 are not covered by the mask 40. Lastly, in the illustrated example, a mask glass layer 50 is applied over the mask(s) 40 and layer of photosensitive material 30. Thus, forming a deposited intermediate part 1a as shown in Figure 11A.

[0078] The deposited intermediate part 1a is then illuminated with extreme ultraviolet (EUV) light through the mask(s) 40 resulting in a photolytic cleavage of Sn—C bonds that promotes cross-linking. After illumination, the deposited intermediate part 1a is baked to densify the SnO_2 layers. Then, the glass mask 50 is removed.

[0079] A development step is illustrated in Figure 11B. During the development step, the unexposed portion 30A of the layer of photosensitive material 30 that was not exposed to EUV light during illumination is removed such that only the exposed portion 30B of the layer of photosensitive material 30 remains. The unexposed portion 30B is positioned over the layer 10A of the multi-layer substrate 10, as shown in Figure 11B. Thus, forming a developed intermediate product 1b as shown in Figure 11B.

[0080] During the etching step, shown in Figure 11C, the layer 10A of the multi-layer substrate 10 is etched to produce a desired pattern. The etching results in layer 10B, which is covered by the exposed portion 30B of the layer of photosensitive material 30. Thus, forming an etched intermediate product 1c as shown in Figure 11C.

[0081] Lastly, the exposed portion 30B of the layer of photosensitive material 30 is removed, leaving behind the desired pattern. Figure 11D illustrates that resulting pattern. Thus, forming the product 1 as shown in Figure 11D.

[0082] Compounds of Formula I are particularly advantageous for negative resist deposition methods because tuning the bond energy of Sn—C by using allyl or vinyl ligands improves performance of the Sn photosensitive materials. It is contemplated that photolytic cleavage of Sn—C bonds during exposure to EUV light will promote cross-linking, thus making these materials superior over those known in the art.

Multistage Distillation

[0083] From theoretical modeling of the activation energy required to strip off ligands from molecules via hydrolysis reaction, a wide range in activation energies between molecules is observed. Hence differences in reactivity are observed. This shows the likelihood that the molecule would be a highly reactive molecule for the formation of SnO_2 when the activation energy is low, but this value also shows that the molecule might be more prone to decomposition and reaction during the synthesis and purification processes. Accordingly, obtaining purity of compounds within the scope of Formula I will be difficult to obtain, especially assay purity of greater than 95% or even greater than 99%.

[0084] However, using multistage vacuum distillation can obtain greater than 95% or even greater than 99% assay purity for compounds in the scope of Formula I. Various forms of multistage distillation are known in the chemical manufacturing industry, but have not been employed for the purification of organometallic materials that include compounds of Formula I.

[0085] As illustrated by the schematic shown in Figure 12, multiple-effect or multistage distillation (MED) is a distillation process often used for sea water desalination. It consists of multiple stages or "effects". (In schematic in Figure 14 the first stage is at the top. Top areas of each stage are vapor, bottom areas of each stage are liquid feed material. The material running through the pipe along the left side of the figure and in the bottom of the VC is condensate. It is not shown how feed material enters other stages than the first, however those should be readily understood. F - feed in. S - heating steam in. C - heating steam out. W – purified material (condensate) out. R – waste material out. O - coolant in. P - coolant out. VC is the last-stage cooler.) In each stage the feed material is heated by steam in tubes. Some of the feed material evaporates, and this steam flows into the tubes of the next stage, heating and evaporating more of the distillate. Each stage essentially reuses the energy from the previous stage.

[0086] The apparatus can be seen as a sequence of closed spaces separated by tube walls, with a heat source at one end and a heat sink at the other. Each space is at pressure below atmospheric conditions via vacuum. Each space consists of two communicating subspaces, the exterior of the tubes of stage n and the interior of the tubes in stage n+1. Each space has a lower temperature and pressure than the previous space, and the tube walls have intermediate temperatures between the temperatures of the fluids on each side. The pressure in a space cannot be in equilibrium with the temperatures of the walls of both subspaces; it has an intermediate pressure. As a result, the pressure is too low or the temperature too high in the first subspace, and the feed material evaporates. In the second subspace, the pressure is too high or the temperature too low, and the vapor condenses. This carries evaporation energy from the warmer first subspace to the colder second subspace. At the second subspace the energy flows by conduction through the tube walls to the colder next space.

What is claimed is:

1. An organometallic compound of Formula I:

$(R)_xSn(A)_{4-x}$ Formula I

wherein:

R is substituted Cp, unsubstituted Cp, or a non-cyclic unsaturated hydrocarbon having 2 to 10 carbon atoms, or 2 to 8 carbon atoms, or 2 to 4 carbon atoms;

A is NR^1R^2, OR^3, pyrrolidinyl, pyrrolyl, or halide;

R^1 and R^2 are each independently selected from the group consisting of an alkyl group having from 1 to 10 carbon atoms, an aryl group, and an acyl group;

R^3 is selected from the group consisting of an alkyl group having 1 to 10 carbon atoms, an aryl group, or an acyl group;

x is an integer from 1 to 3; and

when A is NR^1R^2, pyrrolidinyl, pyrrolyl, or halide, R is substituted Cp or a non-cyclic unsaturated hydrocarbon having 2 to 10 carbon atoms, or 2 to 8 carbon atoms, or 2 to 4 carbon atoms.

2. The organometallic compound according to claim 1, wherein x is 1 or 2.

3. The organometallic compound according to any one of claims 1–2, wherein R is an allyl or vinyl group.

4. The organometallic compound according to any one of claims 1–3, wherein R is a straight-chain unsaturated hydrocarbon.

5. The organometallic compound according to any one of claims 1–3, wherein R is an allyl group having the general formula: $CR^4R^5CR^6=CR^7R^8$, wherein R^4, R^5, R^6, R^7, and R^8 are each independently selected from the group consisting of H and alkyl groups having from 1 to 4 carbon atoms

6. The organometallic compound according to any one of claims 1–3, wherein R is a vinyl group having the general formula: $CR^9=CR^{10}R^{11}$, wherein R^9, R^{10}, and R^{11} are each independently selected from the group consisting of H and alkyl groups having from 1 to 4 carbon atoms.

7. The organometallic compound according to any one of claims 1–2, wherein R is Cp.

8. The organometallic compound according to any one of claims 1–7, wherein x is 2.

9. The organometallic compound according to any one of claims 1–8, wherein A is NR^1R^2.

10. The organometallic compound according to claim 9, wherein R^1 and R^2 are independently selected from an alkyl group having from 1 to 4 carbon atoms.

11. The organometallic compound according to claim 10, wherein R^1 is Me or Et.

12. The organometallic compound according to claim 10, wherein R^2 is Me or Et.

13. The organometallic compound according to any one of claims 1–12, wherein R^1 and R^2 are different.

14. The organometallic compound according to any one of claims 1–8, wherein A is OR^3.

15. The organometallic compound according to claim 14, wherein R^3 is an alkyl group having from 1 to 4 carbon atoms.

16. The organometallic compound according to claim 15, wherein R^3 is Me, Et, or ^{t}Bu.

17. The organometallic compound according to any one of claims 1–8, wherein A is pyrrolyl.

18. The organometallic compound according to any one of claims 1–8, wherein A is pyrrolidinyl.

19. The organometallic compound according to any one of claims 1–8, wherein A is halide.

20. The organometallic compound according to claim 1, wherein the organometallic compound is selected from the group consisting of $(CH_2{=}CHCH_2)Sn(NMe_2)_3$, $(CH_2{=}CH)Sn(Pyrrolidinyl)_3$, $(CH_2{=}CHCH_2)Sn(OEt)_3$, $(Cp)Sn(O^iPr)_3$, $(CH_2{=}CHCH_2)_2Sn(NMe_2)_2$, $(CH_2{=}CHCH_2)_2Sn(NEt_2)_2$, $(CH_2{=}CHCH_2)_2Sn(NEtMe)_2$, $(CH_2{=}CHCH_2)_2Sn(Pyrrolidinyl)_2$, $(CH_2{=}CHCH_2)_2Sn(OMe)_2$, $(CH_2{=}CHCH_2)_2Sn(OEt)_2$, $(CH_2{=}CHCH_2)_2Sn(O^tBu)_2$, $(CH_2{=}CH)_2Sn(NMe_2)_2$, $(CH_2{=}CH)_2Sn(NEt_2)_2$,

$(CH_2{=}CH)_2Sn(NEtMe)_2$, $(CH_2{=}CH)_2Sn(Pyrrolidinyl)_2$, $(CH_2{=}CH)_2Sn(OMe)_2$, $(CH_2{=}CH)_2Sn(OEt)_2$, $(CH_2{=}CH)_2Sn(O^tBu)_2$, $(Cp)_2Sn(OMe)_2$, $(Cp)_2Sn(OEt)_2$, $(Cp)_2Sn(O^iPr)_2$, $(CH_2{=}CHCH_2)_3Sn(NMe_2)$, $(CH_2{=}CH)_3Sn(Pyrrolidinyl)$, $(CH_2{=}CHCH_2)_3Sn(OEt)$, and $(Cp)_3Sn(O^iPr)$.

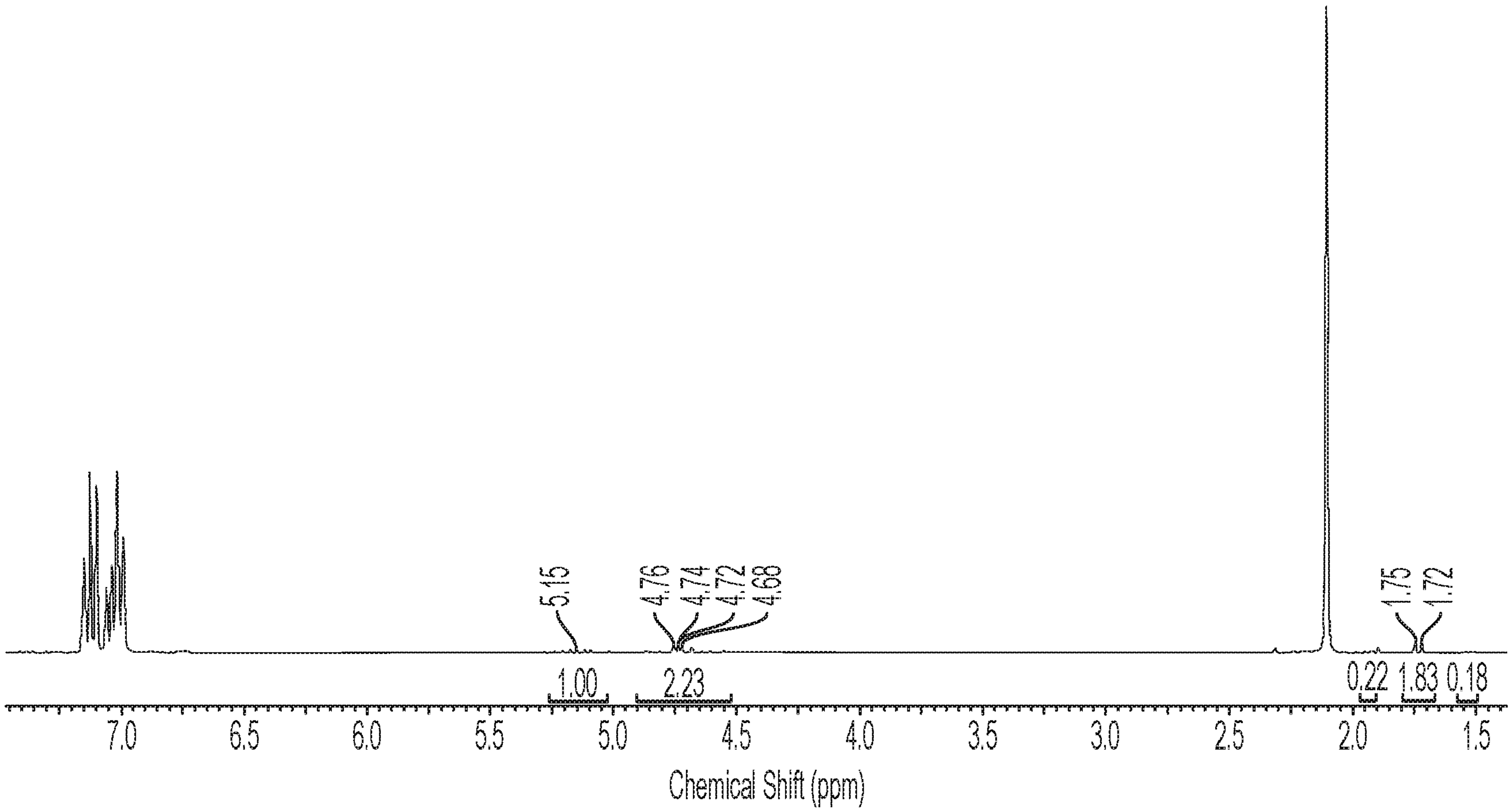

FIG. 1. ^{1}H NMR spectrum of a reaction mixture comprising $(CH_2{=}CHCH_2)Sn(Cl)_3$ in toluene (300 MHz, C_6D_6).

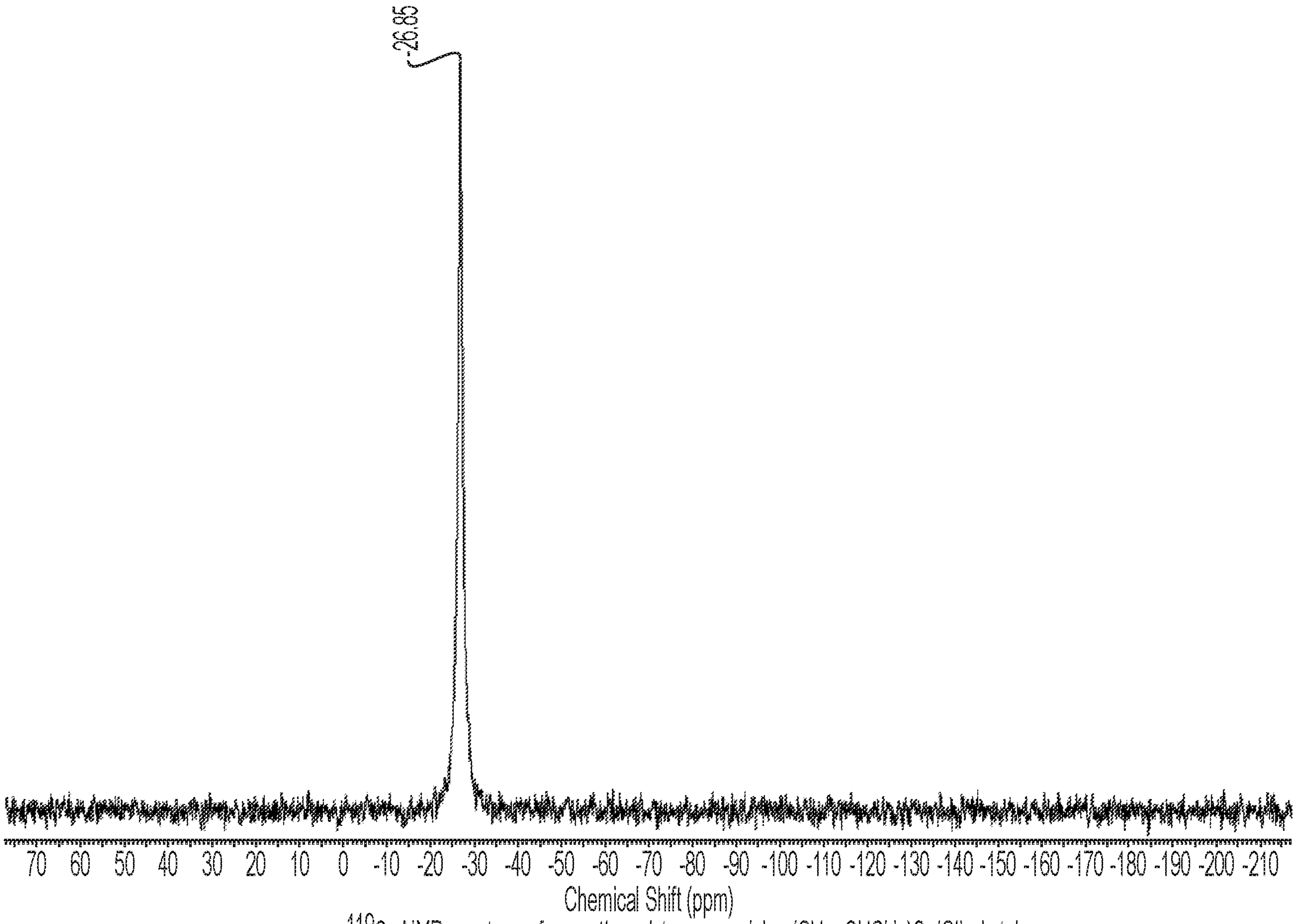

FIG. 2. ^{119}Sn NMR spectrum of a reaction mixture comprising $(CH_2{=}CHCH_2)Sn(Cl)_3$ in toluene (186.55 MHz, C_6D_6).

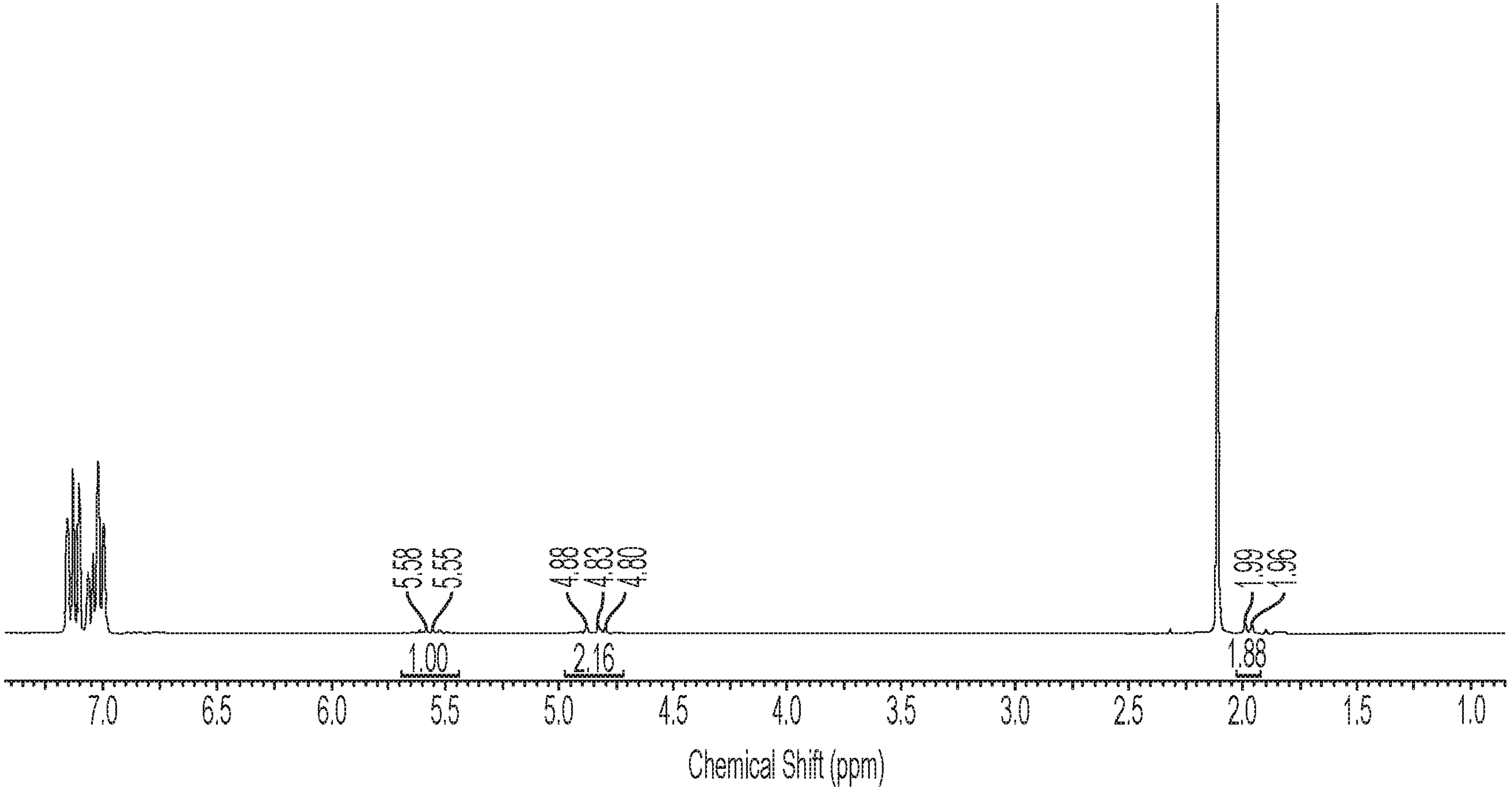

FIG. 3. ^{1}H NMR spectrum of a reaction mixture comprising $(CH_2{=}CHCH_2)_2Sn(Cl)_2$ in toluene (300 MHz, C_6D_6).

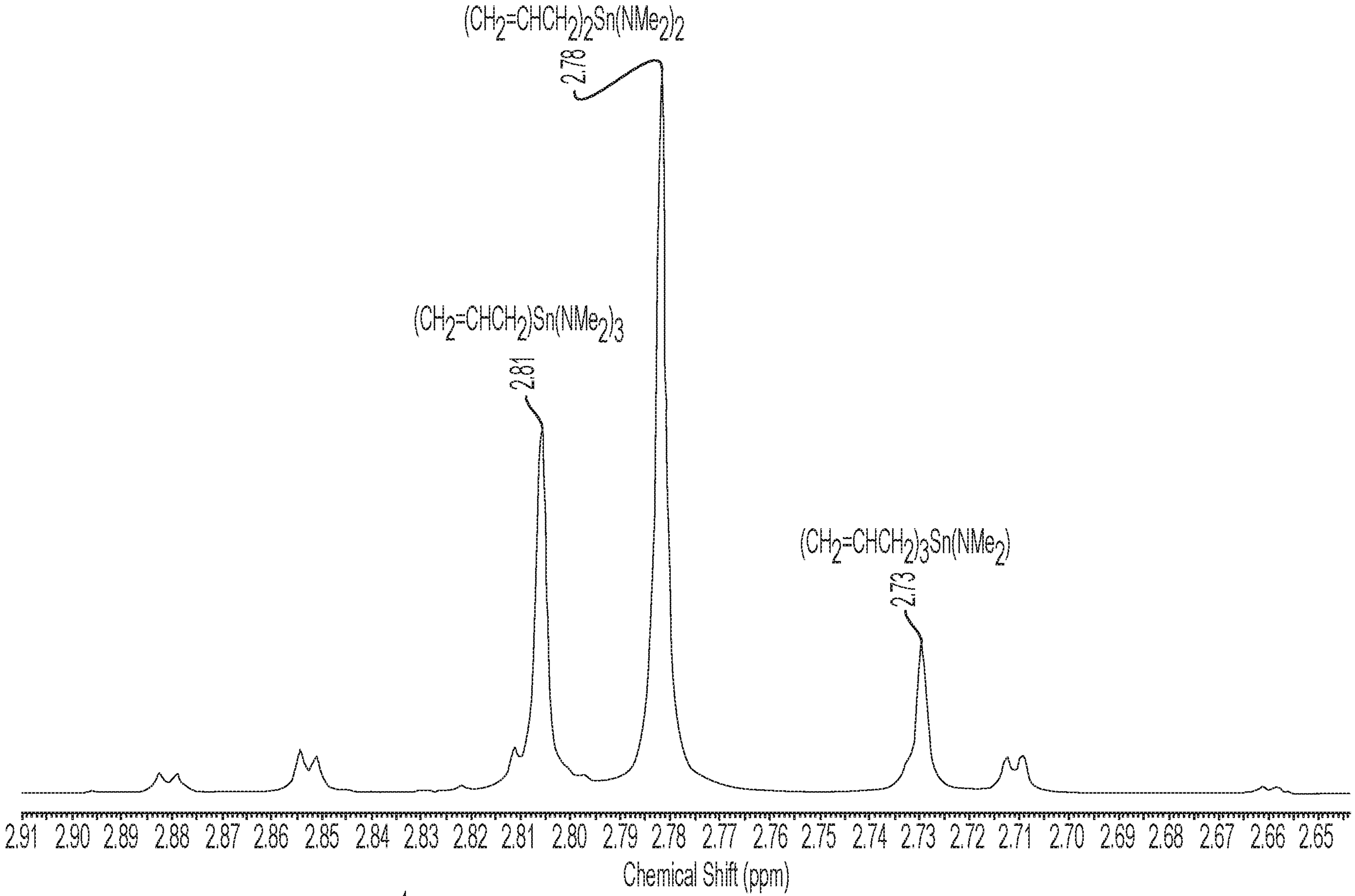

FIG. 4. ^1H NMR spectrum of an isolated product mixture comprising $(CH_2{=}CHCH_2)Sn(NMe_2)_3$, $(CH_2{=}CHCH_2)_2Sn(NMe_2)_2$, and $(CH_2{=}CHCH_2)_3Sn(NMe_2)$ after 12 hours at 22°C (300 MHz, C_6D_6).

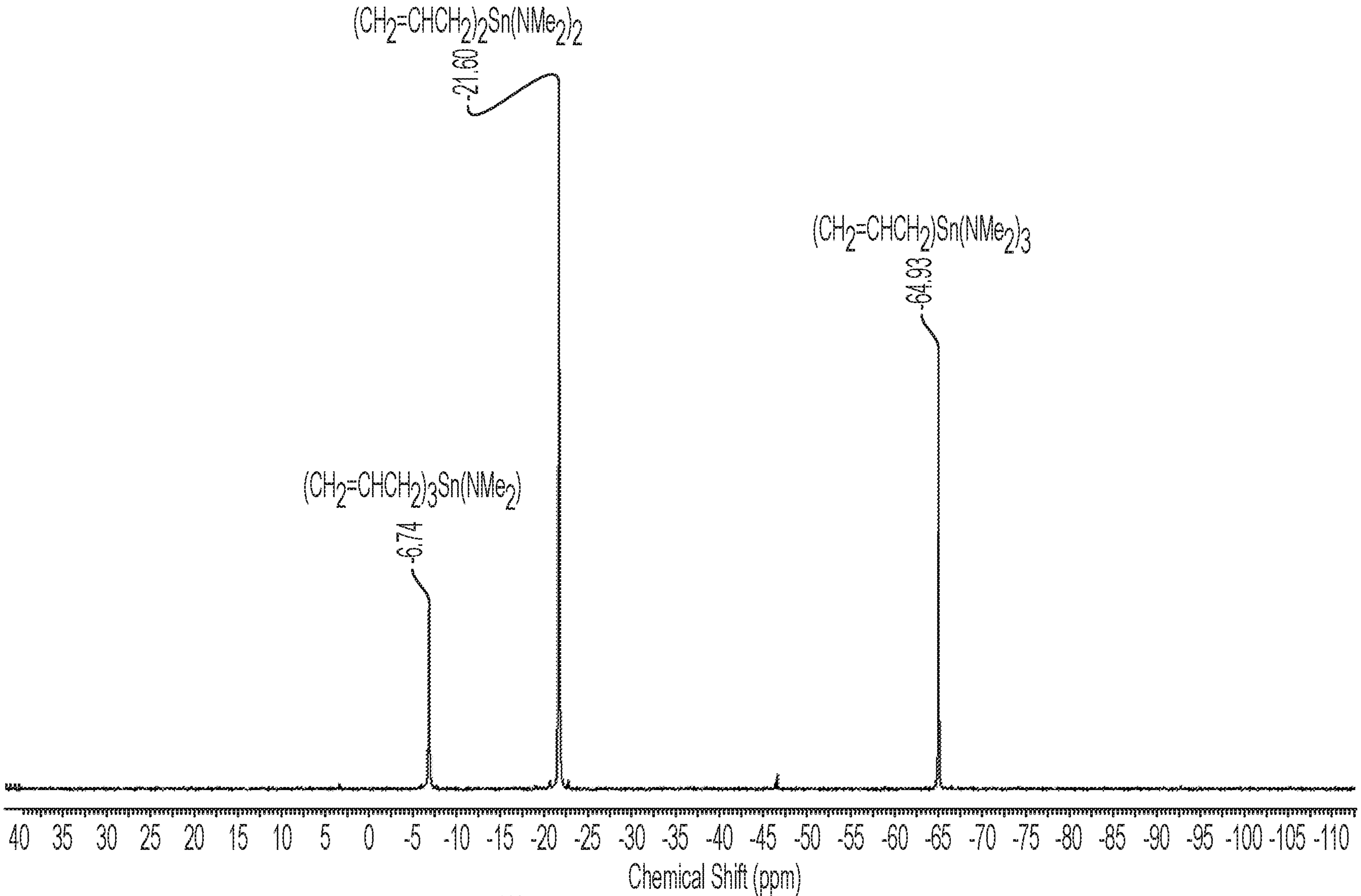

FIG. 5. ^{119}Sn NMR spectrum of an isolated product mixture comprising $(CH_2{=}CHCH_2)Sn(NMe_2)_3$, $(CH_2{=}CHCH_2)_2Sn(NMe_2)_2$, and $(CH_2{=}CHCH_2)_3Sn(NMe_2)$ after 12 hours at 22°C (187 MHz, C_6D_6).

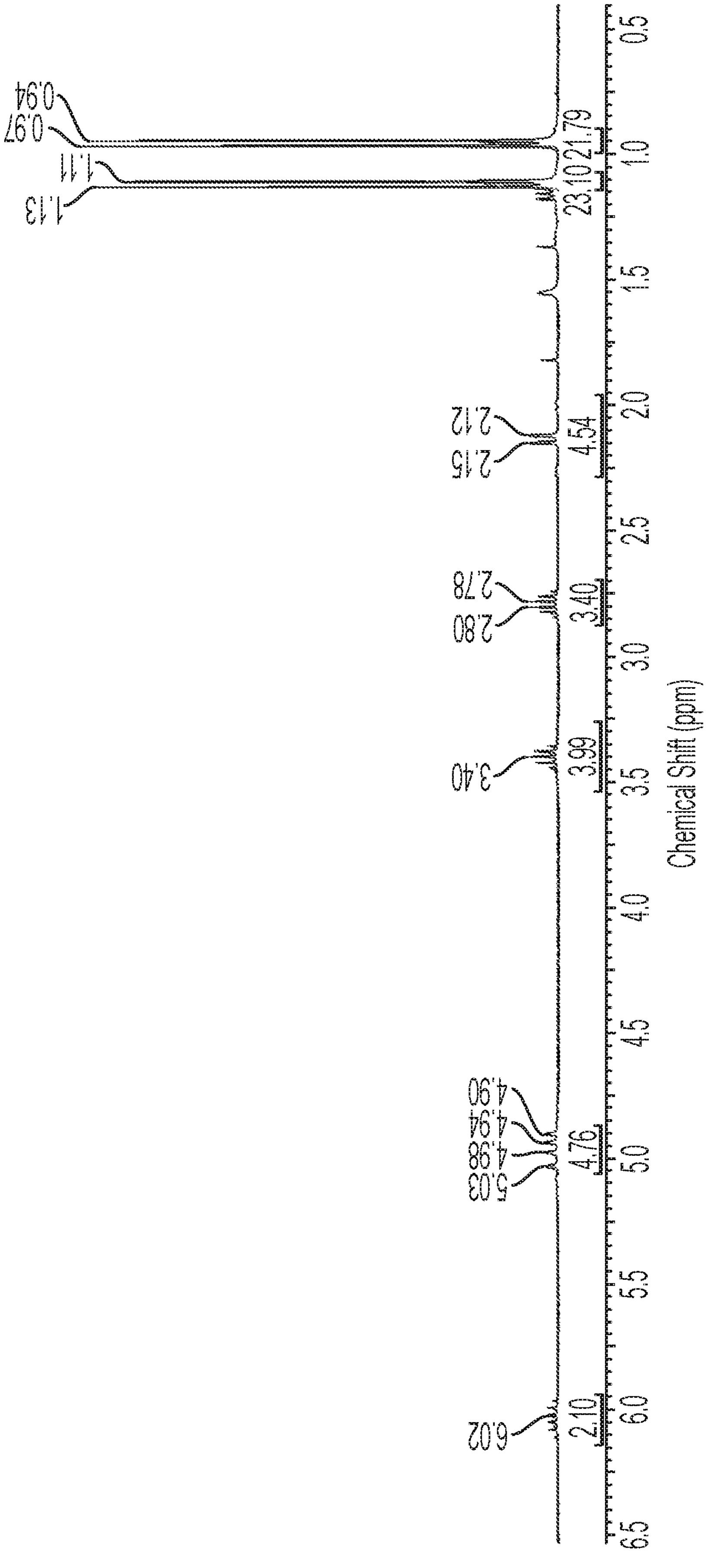

FIG. 6. ^{1}H NMR spectrum of a product mixture comprising $(CH_2{=}CHCH_2)_2Sn(NiPr_2)_2$ and $HNiPr_2$ (300 MHz, C_6D_6).

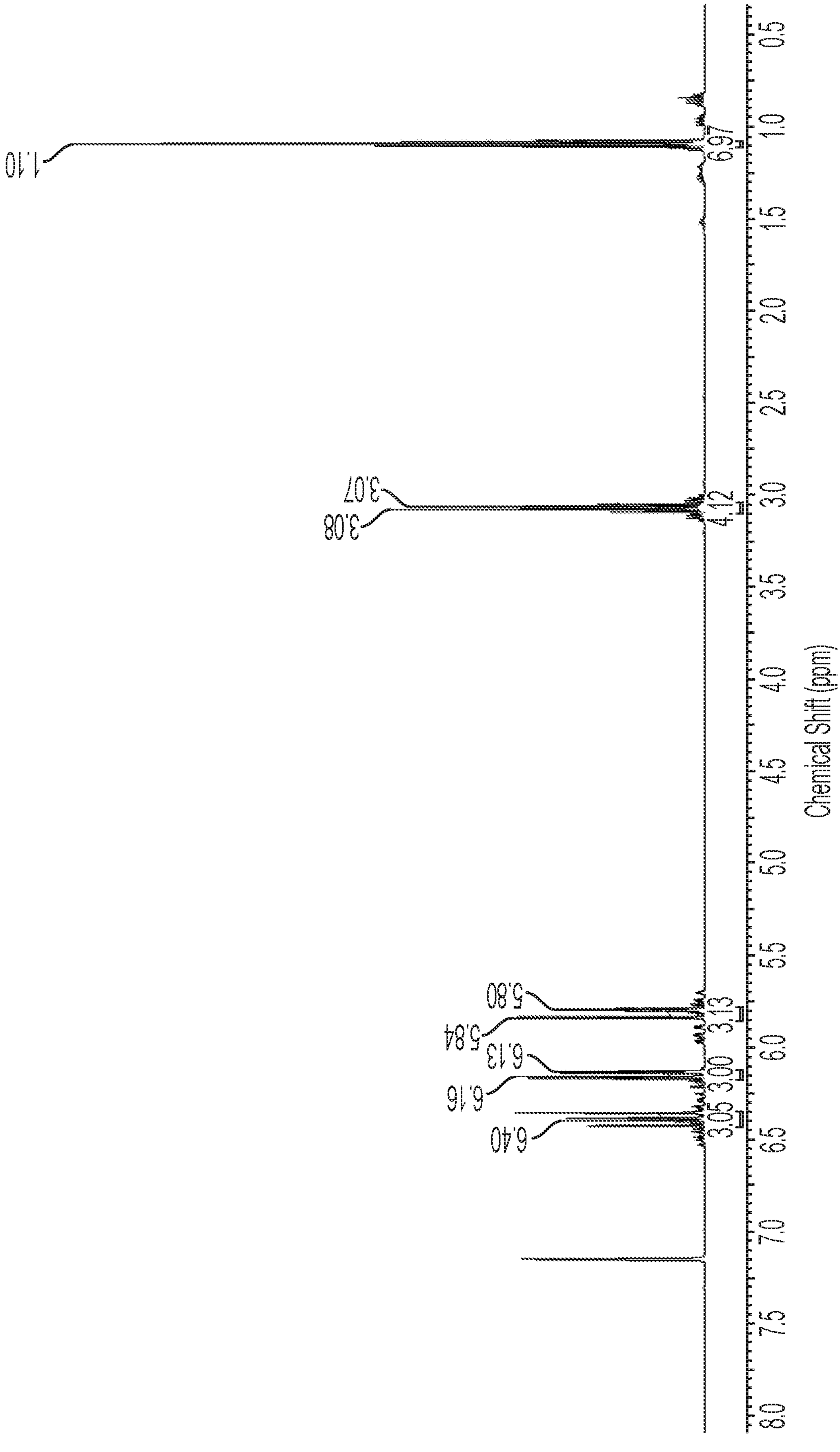

FIG. 7. ^{1}H NMR spectrum of $(CH_2{=}CH)_3Sn(NEt_2)$ (500 MHz C_6D_6).

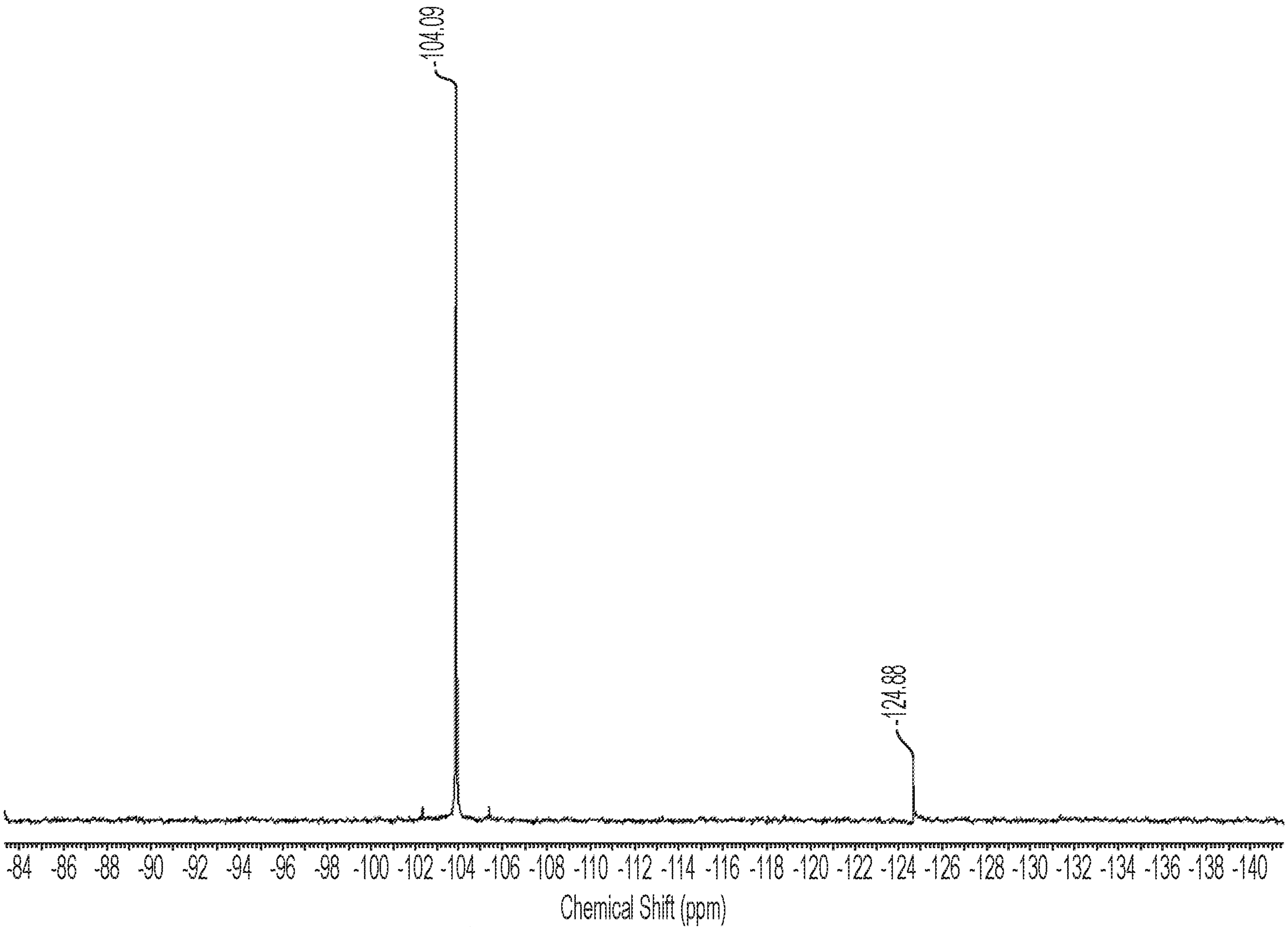

FIG. 8. ^1H NMR spectrum of $(CH_2{=}CH)_3Sn(NEt_2)$ (186 MHz C_6D_6).

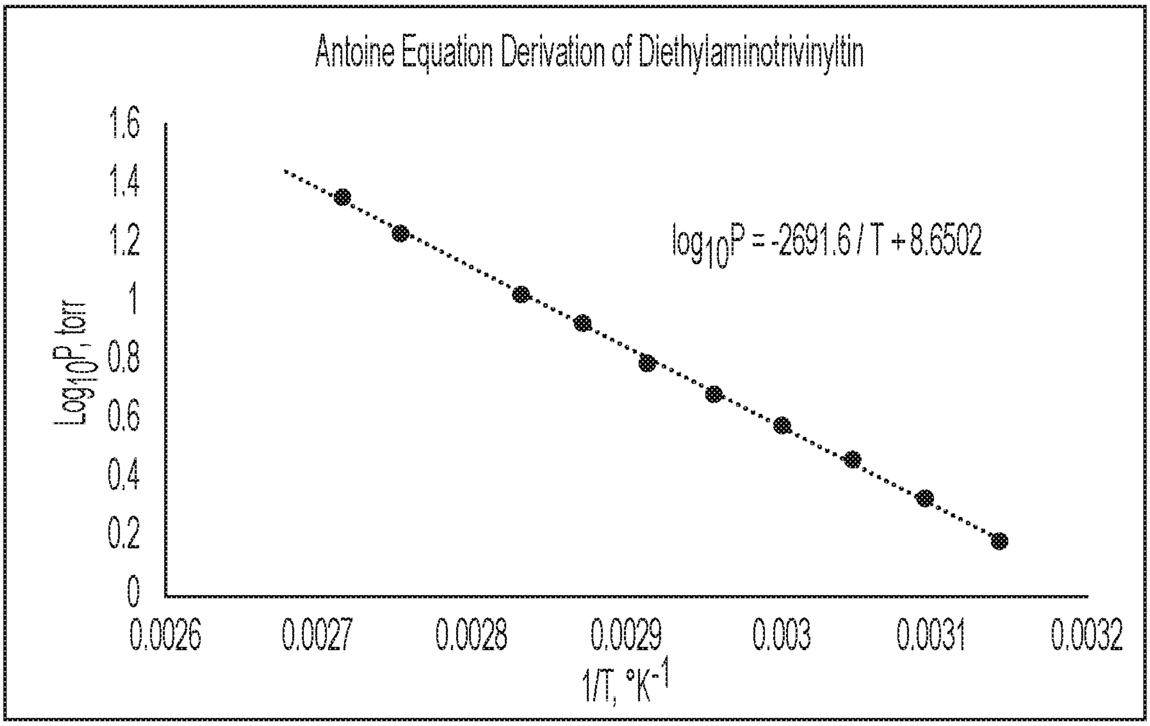

FIG. 9. Vapor pressure curve of $(CH_2{=}CH)_3Sn(NEt_2)$.

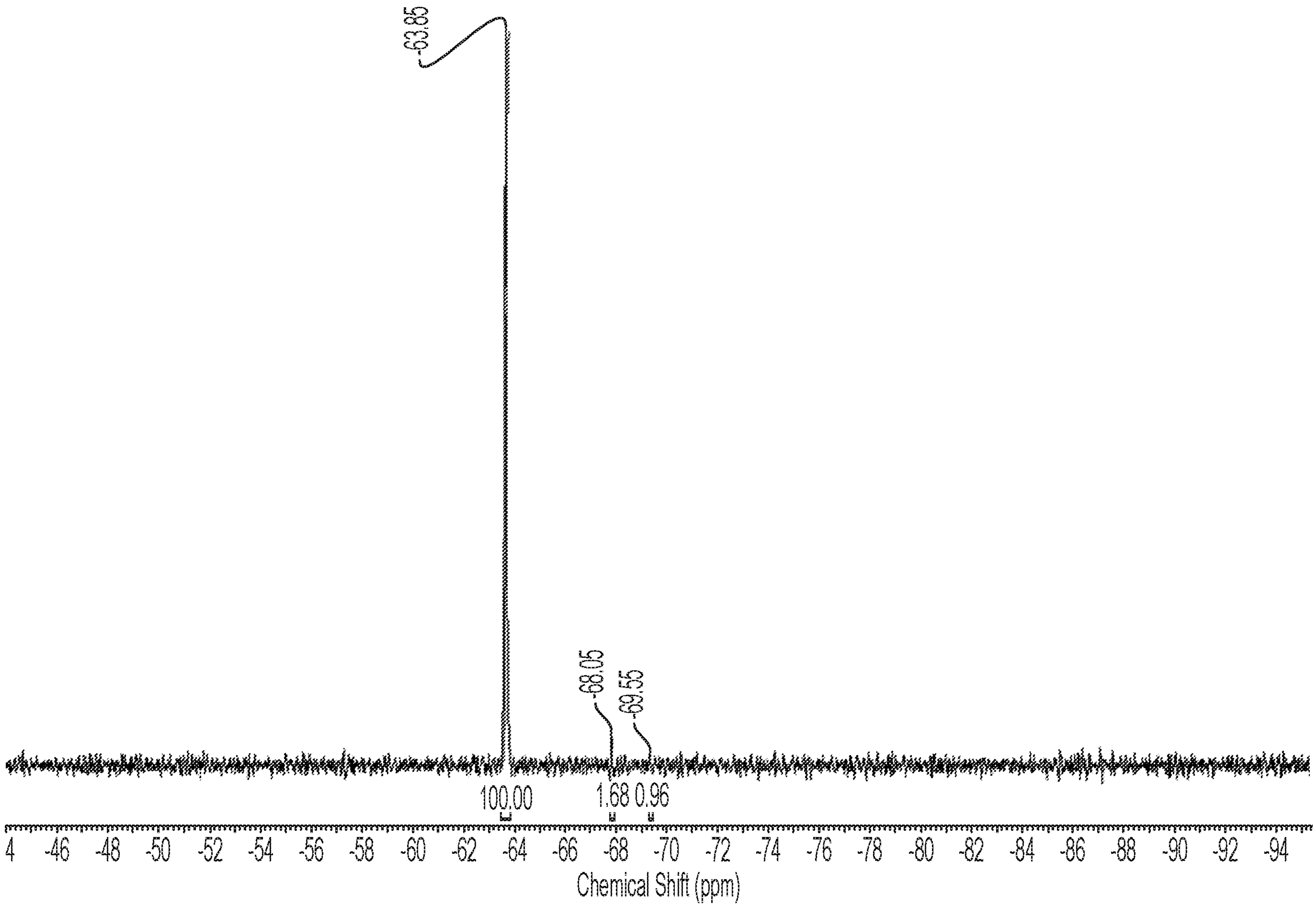

FIG. 10. ^{119}Sn NMR spectrum of Cp^{iPr}Sn (NMe$_2$)$_3$ (186 MHz, C$_6$D$_6$).

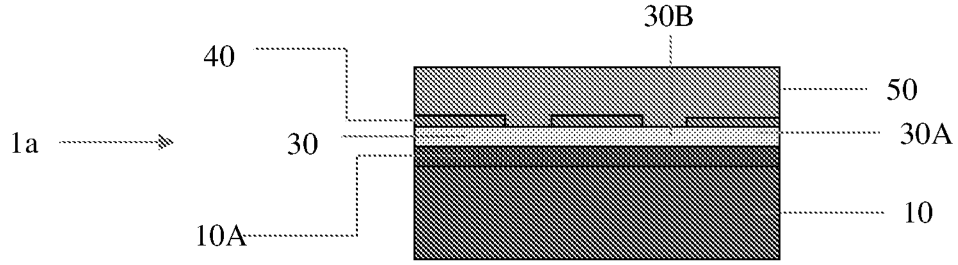

FIG. 11A

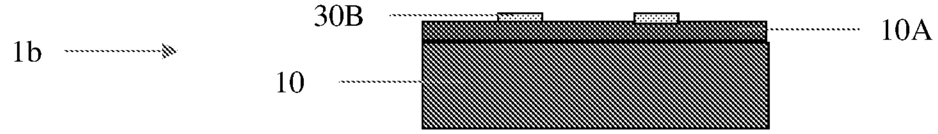

FIG. 11B

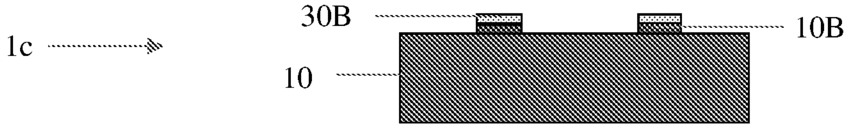

FIG. 11C

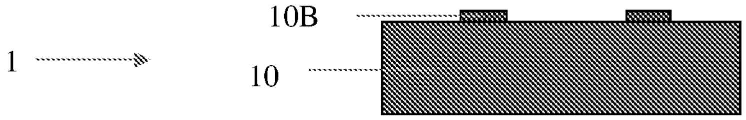

FIG. 11D

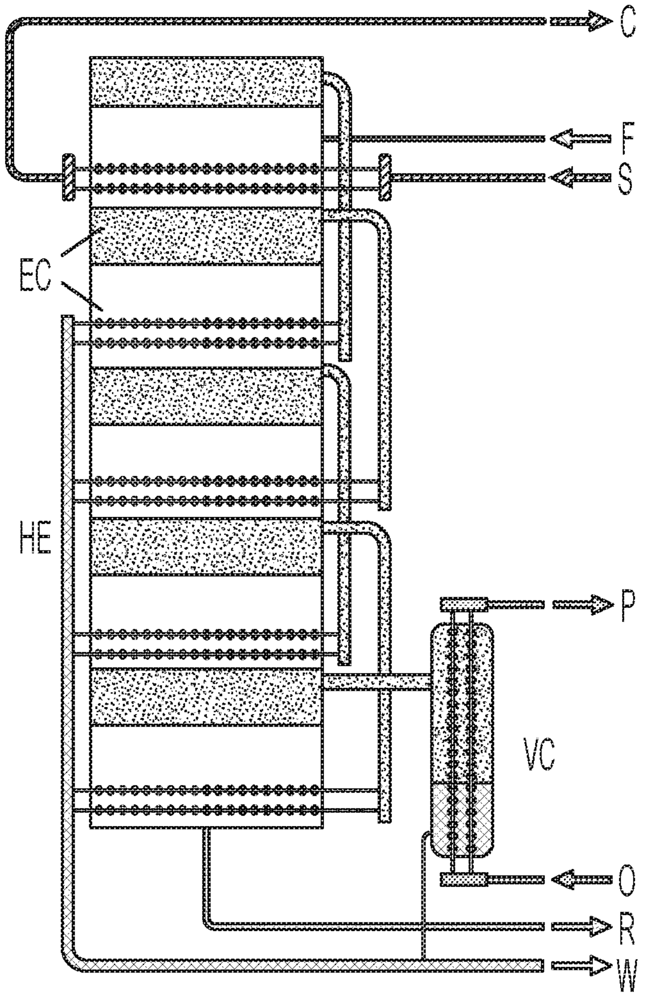

FIG. 12. Schematic of multistage vacuum distillation apparatus.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2023/054018

A. CLASSIFICATION OF SUBJECT MATTER

IPC: ***C07F 7/22*** (2006.01)

CPC: ***C07F 7/2224*** (2020.01) , ***C07F 7/2284*** (2020.01)

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)

IPC: ***C07F*** (2006.01)

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

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)

QUESTEL (FAMPAT: Inventor and Applicant search) and STN (Registry: compound search; CAPlus)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP 2008091215 A (OKADA et al.) 17 April 2008 (17-04-2008) See Examples 6-10, 17-22 and 25-25 in Table 28 and Examples 32-36, 43-48 and 51-52 in Table 32.	1-5, 8, 14, 19 1-2, 9-13, 17-18, 20
Y	WO 2021/038523 A1 (FABULYAK et al.) 04 March 2021 (04-03-2021) See Examples, especially 11 and 12.	1-2, 9-13, 17-18, 20
X	US 2018/0030174 A1 (KANG et al.) 01 February 2018 (01-02-2018) See compound 2m.	1-5, 14-16, 20
X	JP 60067488 A (OODERA et al.) 17 April 1985 (17-04-1985) See the whole document.	1-5, 8, 14-16, 20

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 27 July 2023 (27-07-2023)	Date of mailing of the international search report 01 August 2023 (01-08-2023)
Name and mailing address of the ISA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 819-953-2476	Authorized officer Lu Jiang (819) 639-4540

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	JUTZI P. et al.: “Synthesis and Reactions of Pentamethylcyclopentadienyltin Compounds”; *J. Organometal. Chem.* **1979**, *164(2),* 141-152. See the whole document.	1-2, 19
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