Electronic Supplementary Material (ESI) for Chemical Science.

Electronic Supplementary Information

Fast and Scalable Solvent-Free Access to Lappert's Heavier Tetrylenes $E\{N(SiMe_3)_2\}_2$ (E = Ge, Sn, Pb) and $ECl\{N(SiMe_3)_2\}$ (E = Ge, Sn)

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Abstract: Iconic Lappert´s heavier tetrylenes $E\{N(SiMe_3)_2\}_2$ (E = Ge (**1**), Sn (**2**), Pb (**3**)) have been efficiently prepared from $GeCl_2$·(1,4-dioxane), $SnCl_2$ or $PbCl_2$ and $Li\{N(SiMe_3)_2\}$ *via* a completely solvent-free one-pot mechanochemical route followed by sublimation. This fast, high-yielding and scalable approach (**2** has been prepared in a 100 mmol scale), which involves a small environmental footprint, represents a remarkable improvement over any synthetic route reported over the last five decades, being a so far rare example of the use of mechanochemistry in the realm of main group chemistry. This solventless route has been succesfully extended to the preparation of other heavier tetrylenes, such as $ECl\{N(SiMe_3)_2\}$ (E = Ge(**4**) and Sn(**5**)).

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General experimental data

All reactions were performed with Retsch MM400, MM500 Vario and PM100 ball mills using stainless steel (440B type) grinding jars with stainless steel (440B type) ball bearings. All reagent and product manipulations were carried out under argon in an MBraun UNIlab Pro glovebox, sealing the grinding jars with Teflon tape. $SnCl_2$, $GeCl_2$·(dioxane) and Li{$N(SiMe_3)_2$} were purchased from commercial suppliers and stored in the glove box. NMR spectra were run on Bruker NAV-400, AV-400 and DPX-300 instruments, using as standards the residual protic solvent resonance for ^1H [$\delta(C_6HD_5)$ 7.16 ppm], the solvent resonance for ^{13}C [$\delta(C_6D_6)$ 128.1 ppm], external $SnMe_4$ in $CDCl_3$ for ^{119}Sn (δ 0.0 ppm) and calculated on a 9.4 T instrument for ^{207}Pb [$\delta(PbMe_4)$ 0 ppm, Ξ 20.920599%]. The liquid-assisted grinding (LAG) parameter (η) is defined as the ratio of liquid (in µL) to the combined weights of solid reactants (in mg).

Synthetic procedures and characterization data

Ge{N(SiMe$_3$)$_2$}$_2$ (1): A mixture of $GeCl_2$·(1,4-dioxane) (1.16 g, 5 mmol, η = 0.21) and Li{$N(SiMe_3)_2$} (1.67 g, 10 mmol) was ball-milled for 15 min at 30 Hz in a 25 mL jar having one ball bearing (9/16 in (i.e.,15 mm), 13.62 g). A pale orange slurry was formed inside the jar. An aliquot of the crude reaction outcome was analysed by ^1H NMR (Figure S1), showing the almost quantitative formation of compound **1**. After cooling at –20 °C to facilitate manipulation, the reaction crude was transferred to a cold finger sublimation apparatus, allowing the isolation of **1** as yellow crystals (1.80 g, 92% yield). The sublimation was performed at 75 ºC *in vacuo* (7.1×10^{-2} mbar). ^1H NMR (C_6D_6, 300.1 MHz, 298 K; Figure S2): δ 0.33 (s) ppm. $^{13}C\{^1H\}$ (C_6D_6, 75.5 MHz, 298 K; Figure S3): δ 5.3 (s) ppm.

Test to prepare Sn{N(SiMe$_3$)$_2$}$_2$ (2) using no 1,4-dioxane: A mixture of $SnCl_2$ (0.95 g, 5 mmol) and Li{$N(SiMe_3)_2$} (1.67 g, 10 mmol) was ball-milled for 16 h at 30 Hz rpm in a 25 mL jar having one ball bearing (9/16 in (i.e.,15 mm), 13.62 g). A bright orange slurry was formed inside the jar. An aliquot of the crude reaction outcome was analysed by ^1H NMR at different reaction times (see Figures S4 and S6).

Test to prepare Sn{N(SiMe$_3$)$_2$}$_2$ (2) using 1 µL of 1,4-dioxane: A mixture of $SnCl_2$ (0.95 g, 5 mmol), Li{$N(SiMe_3)_2$} (1.67 g, 10 mmol) and 1,4-dioxane (1 µL, $\eta = 4\times10^{-4}$) was ball-milled for 5 h at 30 Hz in a 25 mL jar having one ball bearing (9/16 in (i.e.,15 mm), 13.62 g). A bright orange slurry was formed inside the jar. An aliquot of the crude reaction outcome was analysed by ^1H NMR at different reaction times (see Figures S7 and S8).

Sn{N(SiMe$_3$)$_2$}$_2$ (2): A mixture of $SnCl_2$ (0.95 g, 5 mmol), Li{$N(SiMe_3)_2$} (1.67 g, 10 mmol) and 1,4-dioxane (500 µL, η^{solv} = 1, which corresponds to η = 0.19) was ball-milled for 15 min at 30 Hz in 25 mL jar having one ball bearing (9/16 in (i.e.,15 mm), 13.62 g). A bright orange slurry was formed inside the jar. An aliquot of the crude reaction outcome was analysed by ^1H NMR (Figure S9), showing the almost quantitative formation of compound **2**. After cooling at –20 °C to facilitate manipulation, the reaction crude was transferred to a cold finger sublimation apparatus, allowing the isolation of **2** as orange crystals (1.84 g, 84% yield). The sublimation was performed at 75 ºC *in vacuo* (3.1×10^{-2} mbar). ^1H NMR (C_6D_6, 300.1 MHz, 298 K; Figure S10): δ 0.29 (s) ppm. $^{13}C\{^1H\}$ (C_6D_6, 100.6 MHz, 298 K; Figure S11): δ 5.8 (s) ppm. $^{119}Sn\{^1H\}$ (C_6D_6, 149.5 MHz, 298 K; Figure S12): δ 768.5 (br) ppm.

Pb{N(SiMe$_3$)$_2$}$_2$ (3): A mixture of $PbCl_2$ (1.39 g, 5 mmol), Li{$N(SiMe_3)_2$} (1.67 g, 10 mmol) and 1,4-dioxane (500 µL, η^{solv} = 1, which corresponds to η = 0.16) was ball-milled for 2 h at 30 Hz in a 25 mL jar (the reaction progress was monitored by ^1H NMR at 15 min and 45 min; see Figures 13 and 14) having one ball bearing (9/16 in (i.e.,15 mm), 13.62 g). A bright yellow slurry was formed inside the jar. An aliquot of the crude reaction outcome was analysed by ^1H NMR (Figure S15), showing the formation of compound **3** as major species. After cooling at –20 °C to facilitate manipulation, the reaction crude was transferred to a cold finger sublimation apparatus, allowing the isolation of **3** as orange crystals (1.74 g, 67% yield). The sublimation was performed in the dark at 75 ºC *in vacuo* (3.5×10^{-2} mbar). ^1H NMR (C_6D_6, 400.1 MHz, 298 K; Figure S16): δ 0.24 (s) ppm. $^{13}C\{^1H\}$ (C_6D_6, 100.6 MHz, 298 K; Figure S17): δ 5.6 (s) ppm. $^{207}Pb\{^1H\}$ (C_6D_6, 84.1 MHz, 298 K; Figure S18): δ 4900 (br) ppm.

Preparation of Sn{N(SiMe$_3$)$_2$}$_2$ (2) at larger scale: A 250 mL jar was charged with 450 g of ball bearings (8/16 in (i.e.,12 mm) and 9/16 in (i.e.,15 mm)), $SnCl_2$ (18.96 g, 100 mmol), Li{$N(SiMe_3)_2$} (33.46 g, 200 mmol) and 1,4-dioxane (8 mL, η^{solv} = 1, which corresponds to η = 0.19). The jar was sealed with a safety closure device and put in a planetary mill for 30 min at 600 RPM (10 Hz). A bright orange-brown slurry was formed inside the jar. An aliquot of the crude reaction outcome was analysed by ^1H NMR (Figure S19), showing the almost quantitative formation of compound **2**. After cooling at –20 °C to facilitate manipulation, the reaction crude was transferred to a round-bottom flask equipped with a PTFE-coated magnetic bar and connected to a Schlenk flask using an angled tube adapter. Vacuum distillation (110–120 ºC at 3×10^{-2} mbar) allowed the isolation of **2** as a red-orange liquid which slowly solidified at room temperature (38.60 g, 88% yield). ^1H NMR (C_6D_6, 400.1 MHz, 298 K; Figure S20): δ 0.30 (s) ppm. $^{13}C\{^1H\}$ (C_6D_6, 100.6 MHz, 298 K; Figure S21): δ 5.8 (s) ppm. $^{119}Sn\{^1H\}$ (C_6D_6, 149.3 MHz, 298 K; Figure S22): δ 768.0 (br) ppm.

GeCl{N(SiMe$_3$)$_2$} (4): A mixture of $GeCl_2$·dioxane (0.46 g, 2 mmol, η = 0.16) and **1** (0.79 g, 2 mmol) was ball-milled for 2.5 h at at 30 Hz in a 5 mL jar having one ball bearing (6/16 in (i.e.,10 mm), 6.99 g). A pale yellow dusty slurry was formed inside the jar. An aliquot of the reaction crude was analysed by ^1H NMR (Figure S23), showing the almost quantitative formation of compound **5**. The reaction crude was vacuum-dried to give **4** as a pale orange (1.01 g, 94% yield). ^1H NMR (C_6D_6, 300.1 MHz, 298 K; Figure S24): δ 0.25 (s) ppm. $^{13}C\{^1H\}$ (C_6D_6, 75.5 MHz, 298 K; Figure S25): δ 4.9 (s) ppm.

SnCl{N(SiMe$_3$)$_2$} (5): A mixture of $SnCl_2$ (0.38 g, 2 mmol), **2** (0.88 g, 2 mmol) and 1,4-dioxane (0.17 mL, 2 mmol, η = 0.14) was ball-milled for 2.5 h at 30 Hz in a 5 mL jar having one ball bearing (6/16 in (i.e.,10 mm), 6.99 g). A white dusty material was formed inside the jar. An aliquot of the reaction crude was analysed by ^{1}H NMR (Figure S26), showing the almost quantitative formation of compound **5**. The reaction crude was vacuum-dried to give **5** as an off-white solid (1.18 g, 94% yield). ^{1}H NMR (C_6D_6, 300.1 MHz, 298 K; Figure S27): δ 0.35 (s) ppm. ^{13}C{^{1}H} (C_6D_6, 75.5 MHz, 298 K; Figure S28): δ 5.6 (s) ppm. ^{119}Sn{^{1}H} (C_6D_6, 149.2 MHz, 298 K; Figure S29): δ 123.9 (br s) ppm.

Attempts to prepare PbCl{N(SiMe$_3$)$_2$} (6): *Method (a)*: A mixture of $PbCl_2$ (0.56g, 2 mmol), **3** (1.06 g, 2 mmol) and 1,4-dioxane (0.17 mL, 2 mmol, η = 0.12) was ball-milled for 2.5 h at 30 Hz in a 5 mL jar having one ball bearing (6/16 in (i.e.,10 mm), 6.99 g). A bright yellow dusty material was observed inside the jar. An aliquot of the reaction crude was analysed by ^{1}H NMR (Figure S30-top), showing **3** and free 1,4-dioxane as the only two products (a large amount of a white precipitate was observed inside the NMR tube). *Method (b)*: A mixture of $PbCl_2$ (0.28 g, 1 mmol), Li{N(SiMe$_3$)$_2$} (0.17 g, 1 mmol) and 1,4-dioxane (0.09 mL, 1 mmol, η = 0.19) was ball-milled for 15 min at 30 Hz in a 5 mL jar having one ball bearing (6/16 in (i.e.,10 mm), 6.99 g). A bright yellow slurry material was observed inside the jar. An aliquot of the reaction crude was analysed by ^{1}H NMR (Figure S30-bottom), showing **3** and free 1,4-dioxane as the only two products (a large amount of a white precipitate was observed inside the NMR tube). The outcome of the jar was extracted with toluene (6 mL) and filtered through a glass-fibre filter. The filtrate was evaporated *in vacuo* to give a bright yellow solid corresponding to **3** according to its ^{1}H, ^{13}C{^{1}H} and ^{273}Pb NMR spectra.

Reaction of 5 with ^{i}PrNCN^{i}Pr: A mixture of **5** (31 mg, 0.1 mmol) and ^{i}PrNCN^{i}Pr (16 μL, 0.1 mmol) was ball-milled for 20 min at 30 Hz in a 5 mL jar having one ball bearing (6/16 in (i.e.,10 mm), 6.99 g). A white dusty material was formed inside the jar. An aliquot of the reaction crude was analysed by ^{1}H NMR (Figure S31), showing the almost quantitative formation of SnCl[^{i}PrNC{N(SiMe$_3$)$_2$}N^{i}Pr] (**7**), which results from the addition of N(SiMe$_3$) to ^{i}PrNCN^{i}Pr.[8] The reaction crude was extracted with toluene (2 mL) and the resultant solution was vacuum-dried to give **7** as an off-white solid (32 mg, 72% yield). ^{1}H NMR (C_6D_6, 400.1 MHz, 298 K; Figure S32): δ 3.88 (sp, *J* = 6.4 Hz, 2 H, C*H*Me$_2$), 1.07 (br s, 12 H, CH$_3$ of CHMe$_2$), 0.16 (s, 18 H, SiMe$_3$) ppm. ^{13}C{^{1}H} (C_6D_6, 100.6 MHz, 298 K; Figure S33): δ 167.6 (s, NCN), 45.2 (s, *C*HMe$_2$), 26.0 (s, CH$_3$ of CHMe$_2$), 2.1 (s, SiMe$_3$) ppm. ^{119}Sn{^{1}H} (C_6D_6, 149.2 MHz, 298 K; Figure S34): δ –26.5 (br s) ppm.

NMR spectra

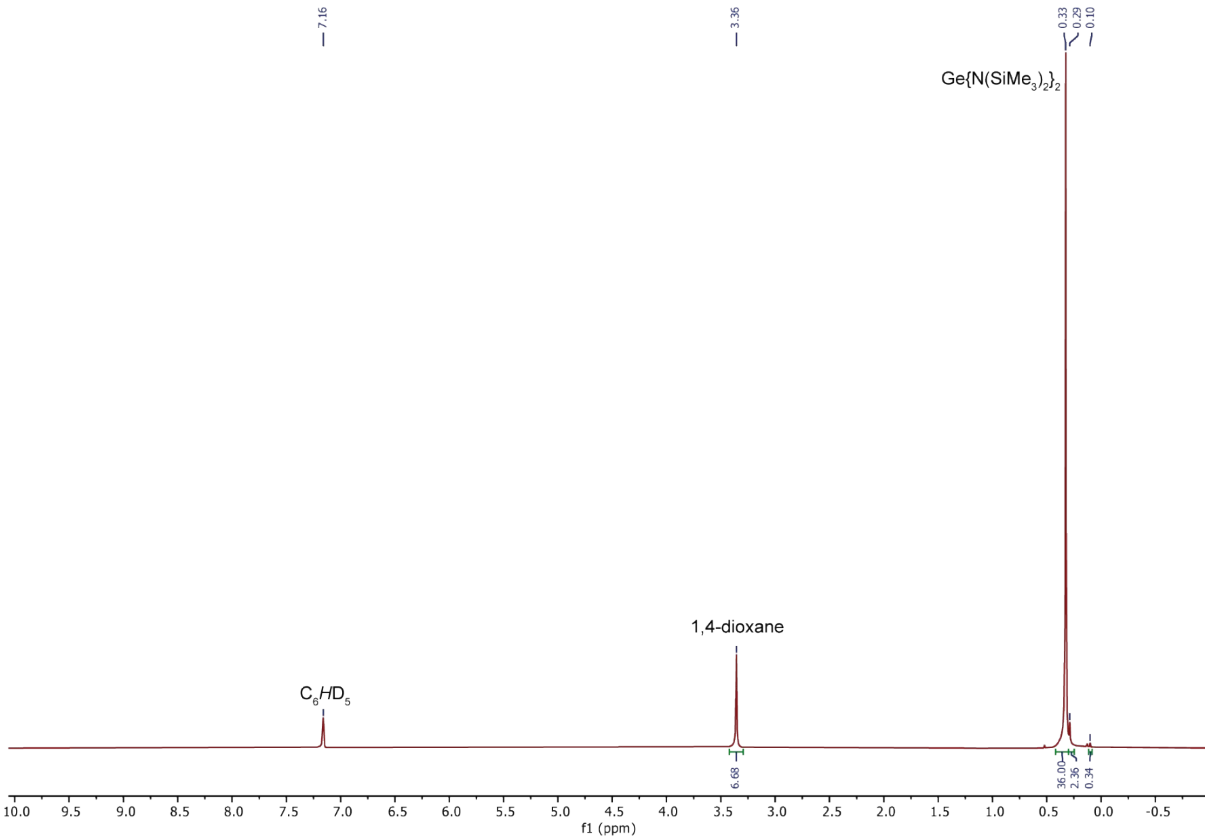

Figure S1. ^{1}H NMR spectrum (C_6D_6, 300.1 MHz, 298 K) of the crude outcome of the reaction of $GeCl_2$·(1,4-dioxane) with two equivalents of Li{N(SiMe$_3$)$_2$} after 15 min of reaction.

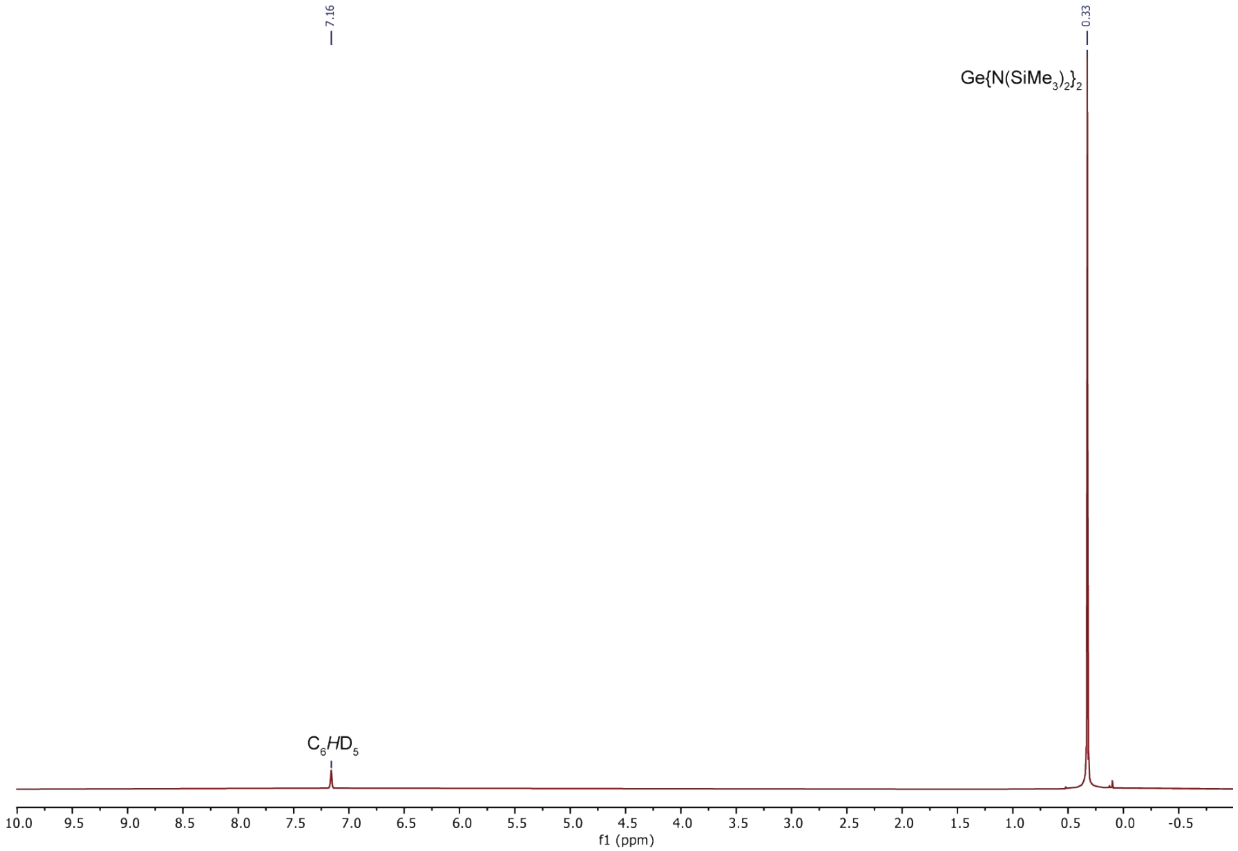

Figure S2. ^{1}H NMR spectrum (C_6D_6, 300.1 MHz, 298 K) of Ge{N(SiMe$_3$)$_2$}$_2$ (**1**).

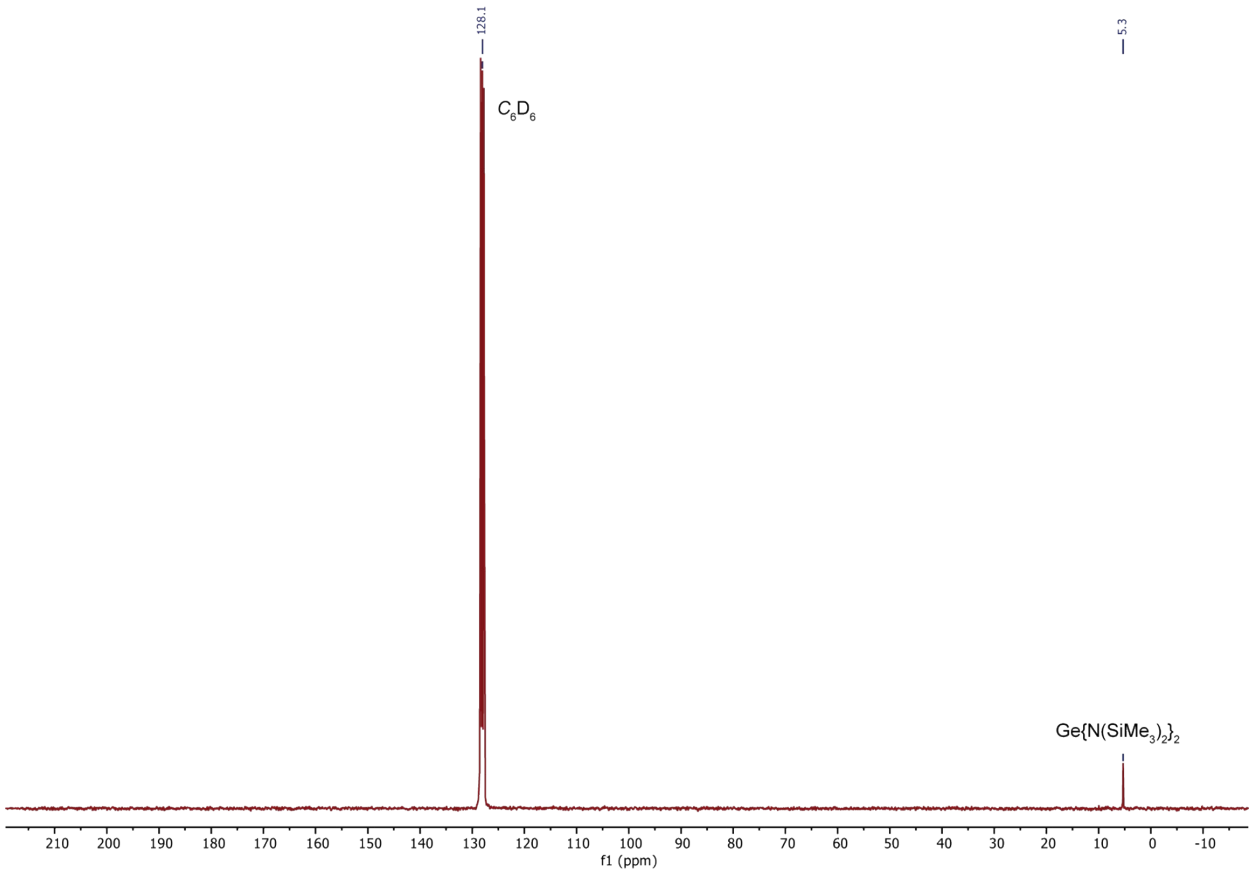

Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 75.5 MHz, 298 K) of $Ge\{N(SiMe_3)_2\}_2$ (**1**).

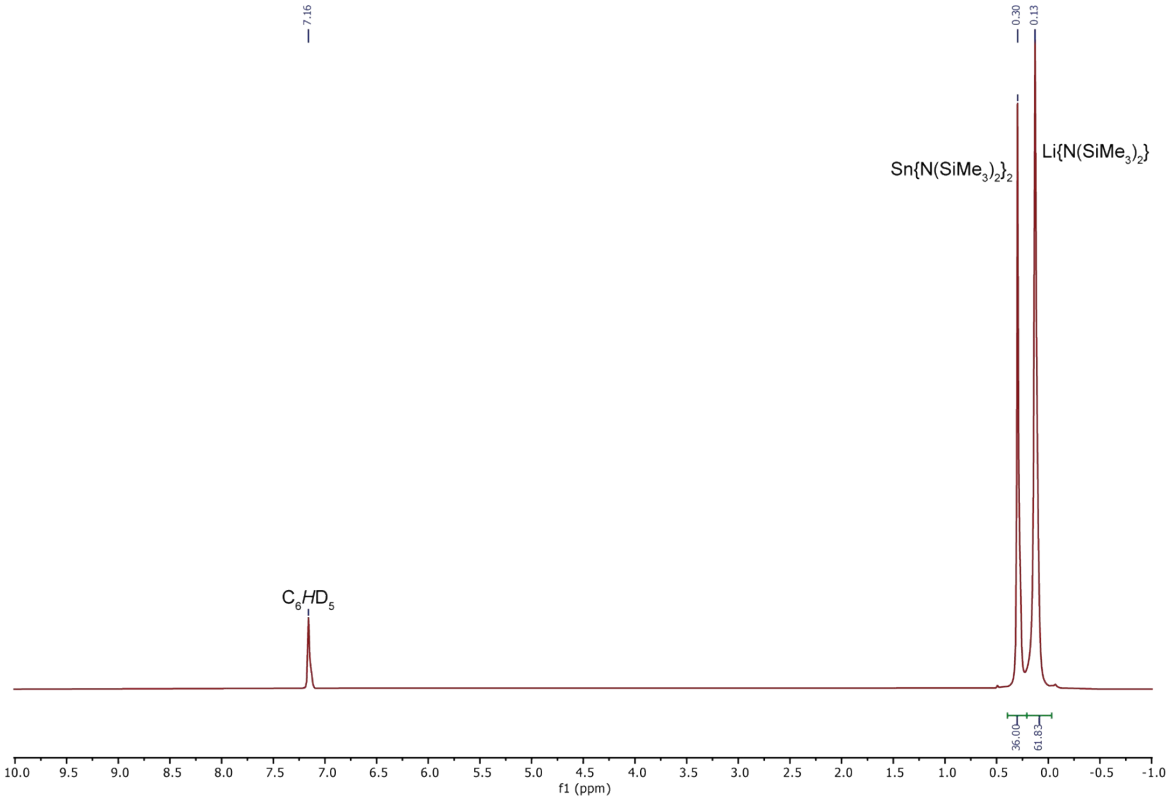

Figure S4. ^{1}H NMR spectrum (C_6D_6, 300.1 MHz, 298 K) of the crude outcome of the reaction of $SnCl_2$·with two equivalents of $Li\{N(SiMe_3)_2\}$ after 15 min of reaction.

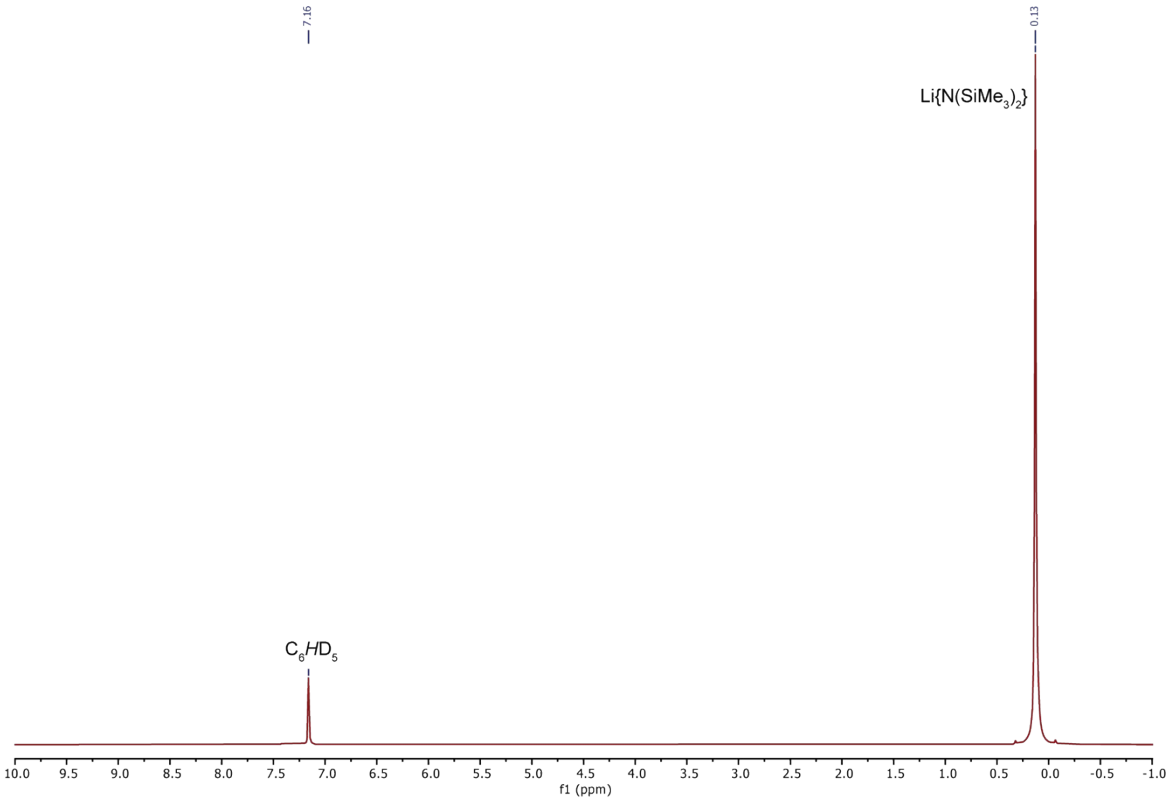

Figure S5. ^{1}H NMR spectrum (C_6D_6, 300.1 MHz, 298 K) of Li{N(SiMe$_3$)$_2$}.

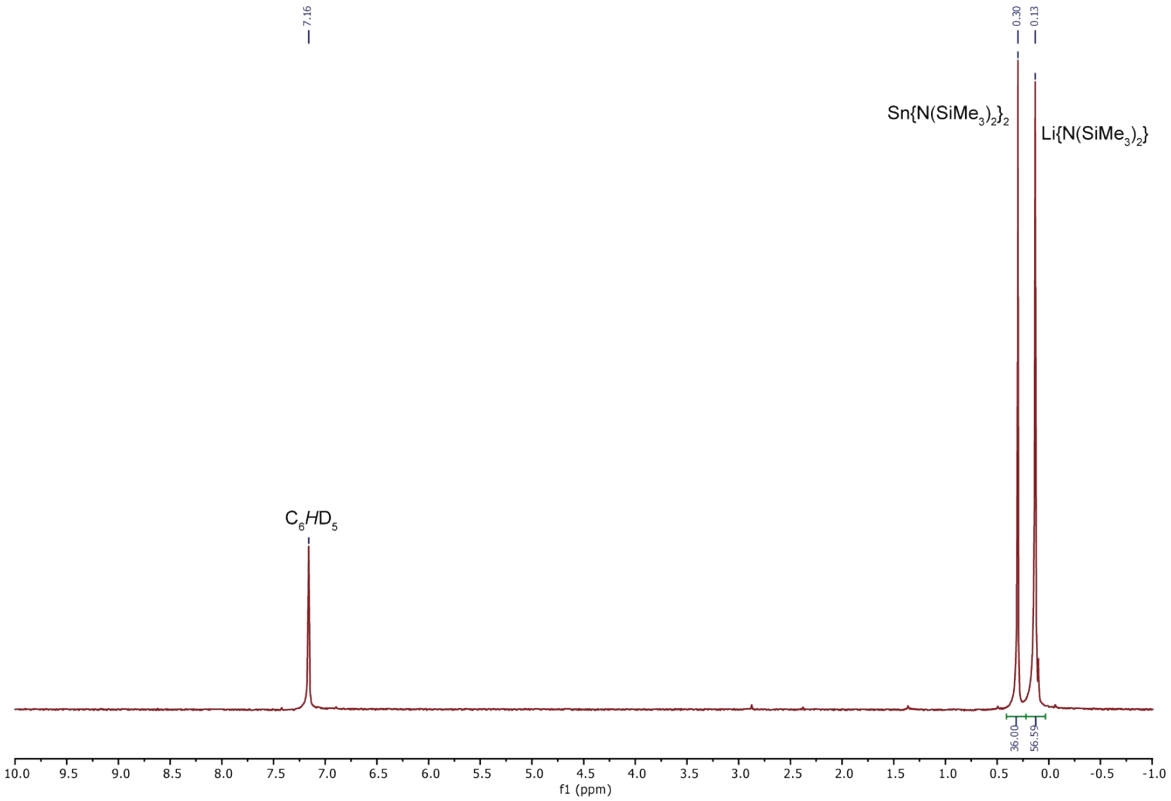

Figure S6. ^{1}H NMR spectrum (C_6D_6, 300.1 MHz, 298 K) of the crude outcome of the reaction of $SnCl_2$·with two equivalents of Li{N(SiMe$_3$)$_2$} after 16 h of reaction.

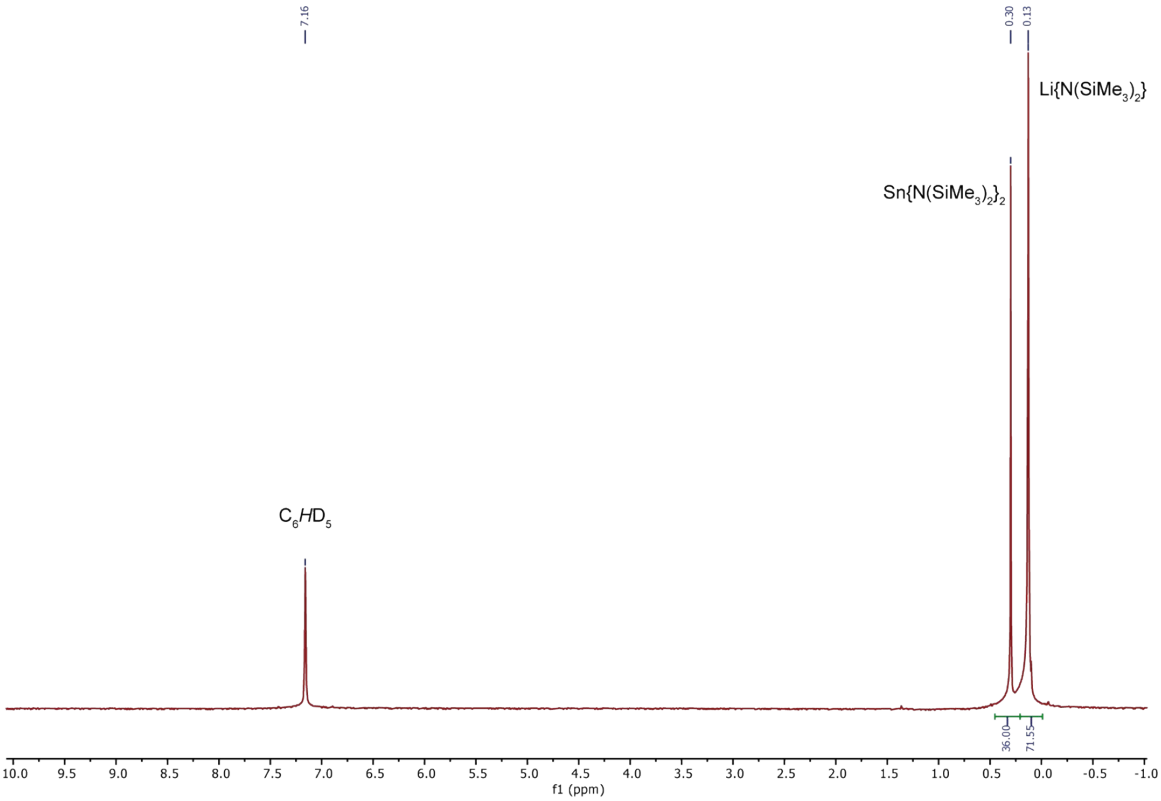

Figure S7. ^{1}H NMR spectrum (C_6D_6, 300.1 MHz, 298 K) of the crude outcome of the reaction of $SnCl_2$·with two equivalents of Li{N(SiMe$_3$)$_2$} and 1μL of 1,4-dioxane after 15 min of reaction.

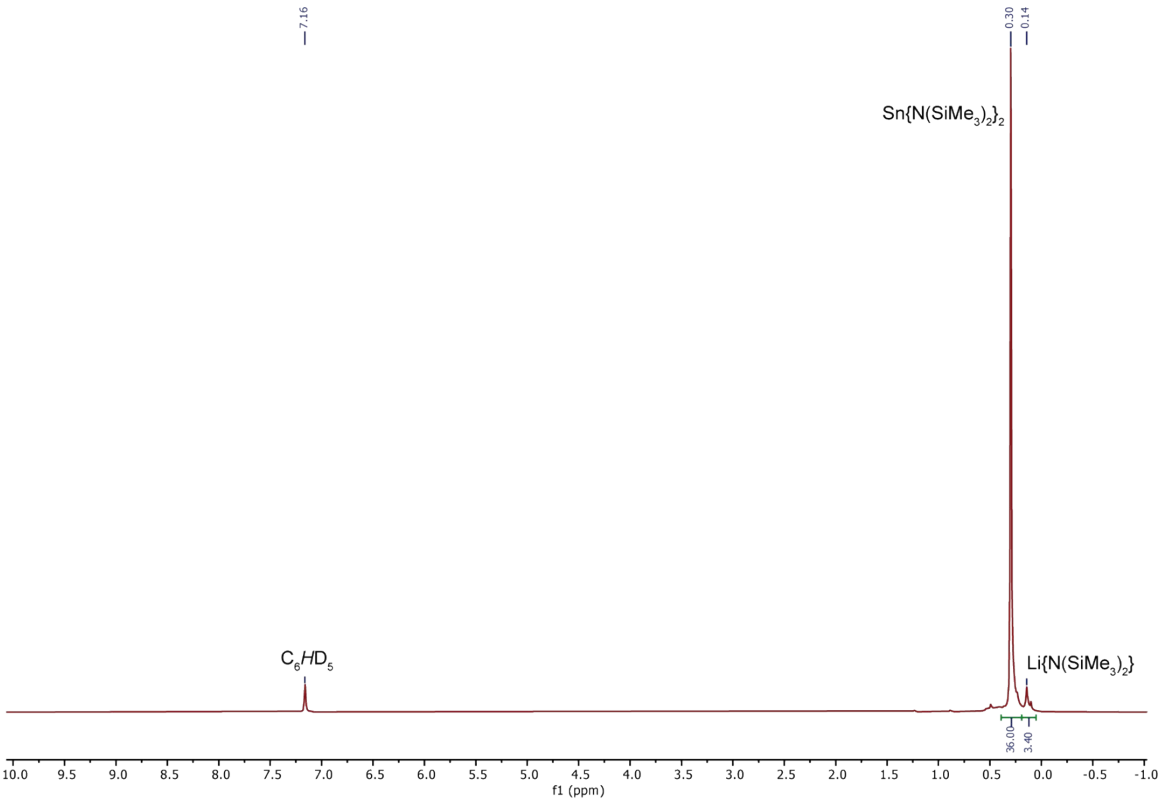

Figure S8. ^{1}H NMR spectrum (C_6D_6, 300.1 MHz, 298 K) of the crude outcome of the reaction of $SnCl_2$·with two equivalents of Li{N(SiMe$_3$)$_2$} and 1μL of 1,4-dioxane after 5 h of reaction.

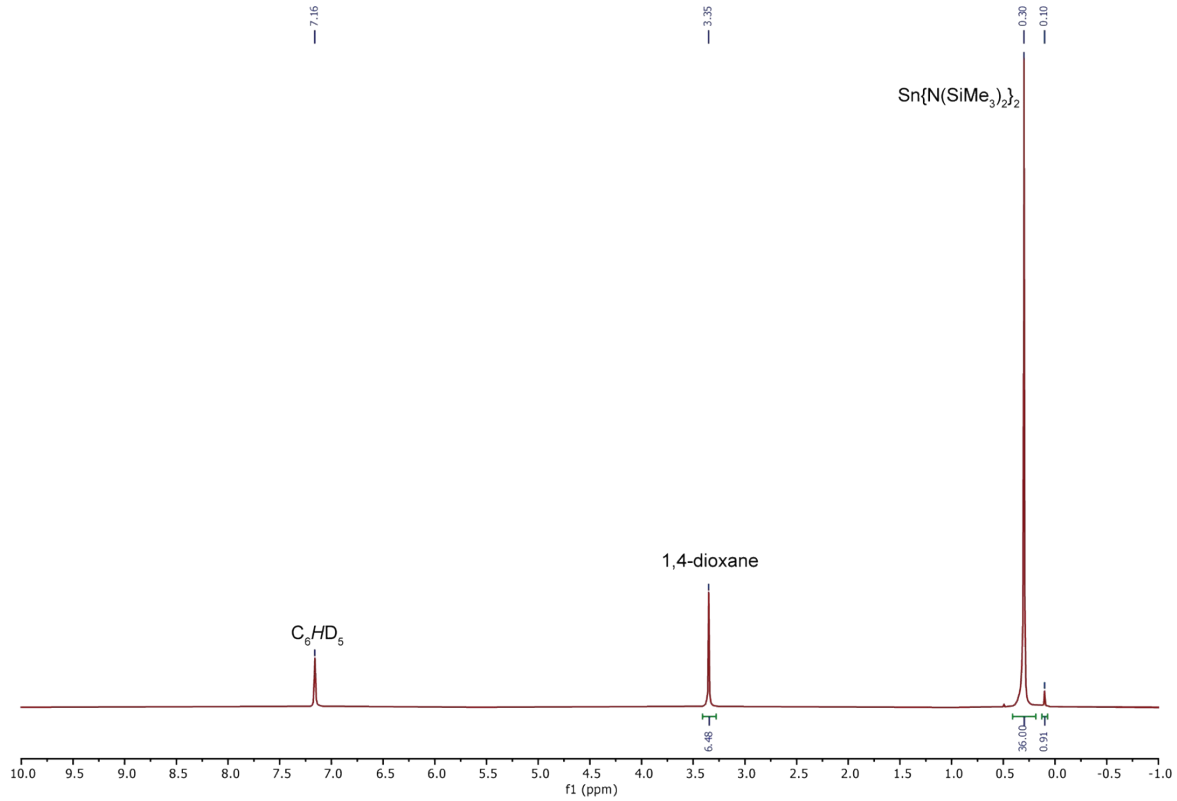

Figure S9. ^{1}H NMR spectrum (C_6D_6, 300.1 MHz, 298 K) of the crude outcome of the reaction of $SnCl_2$·with two equivalents of Li{$N(SiMe_3)_2$} and one equivalent of 1,4-dioxane after 15 min of reaction.

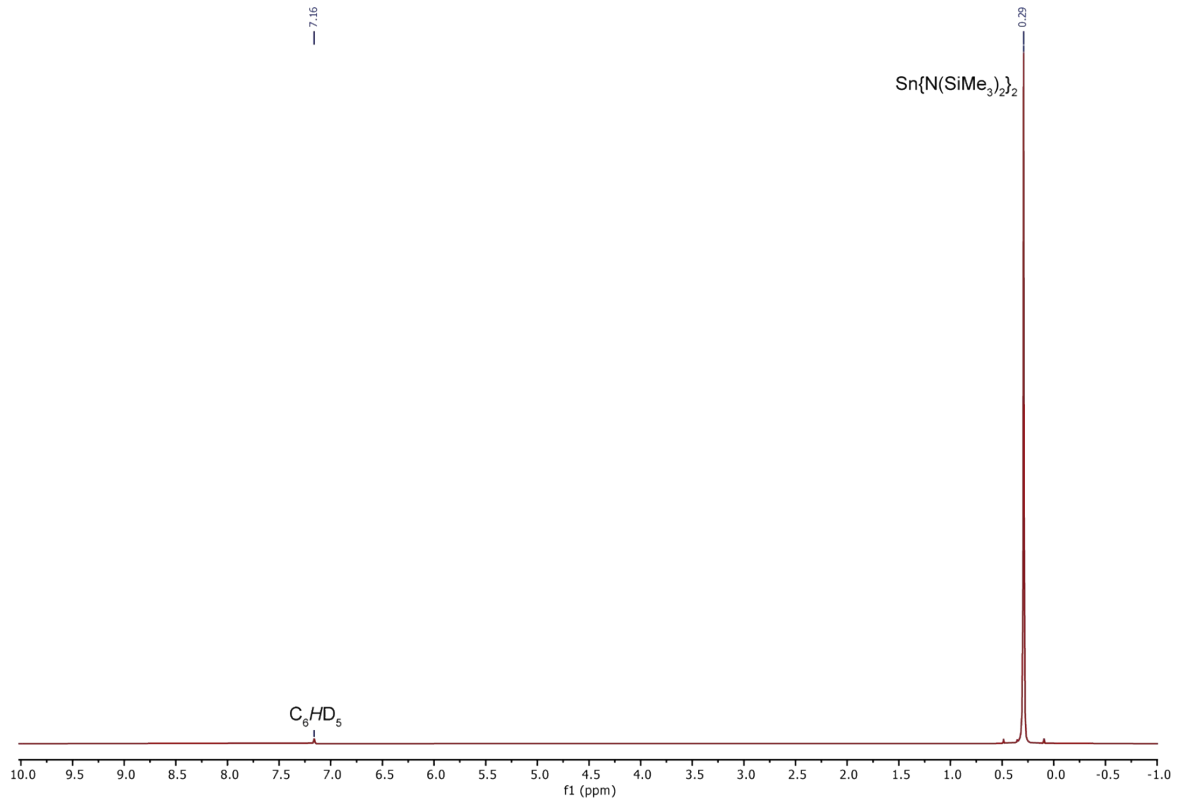

Figure S10. ^{1}H NMR spectrum (C_6D_6, 300.1 MHz, 298 K) of Sn{$N(SiMe_3)_2$}$_2$ (**2**).

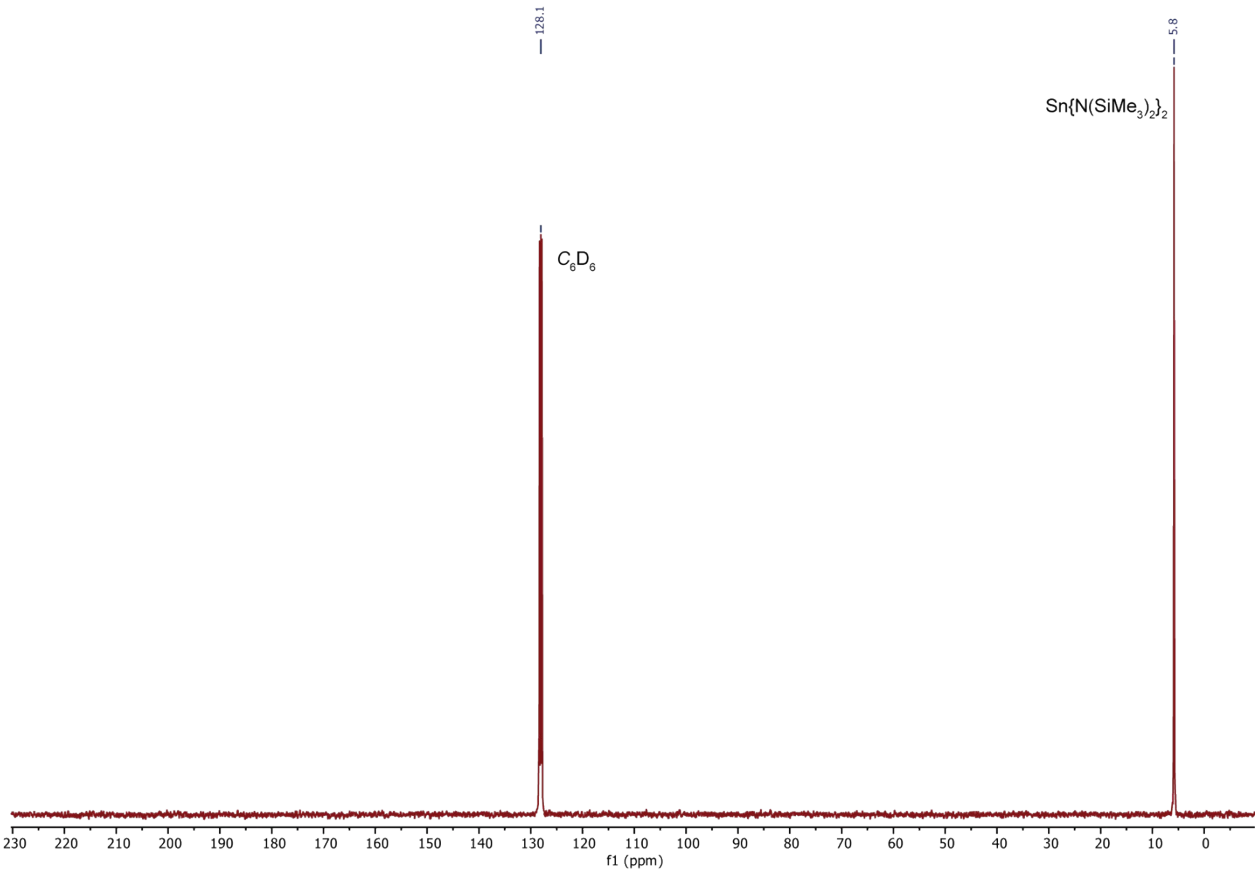

Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 100.6 MHz, 298 K) of $Sn\{N(SiMe_3)_2\}_2$ (**2**).

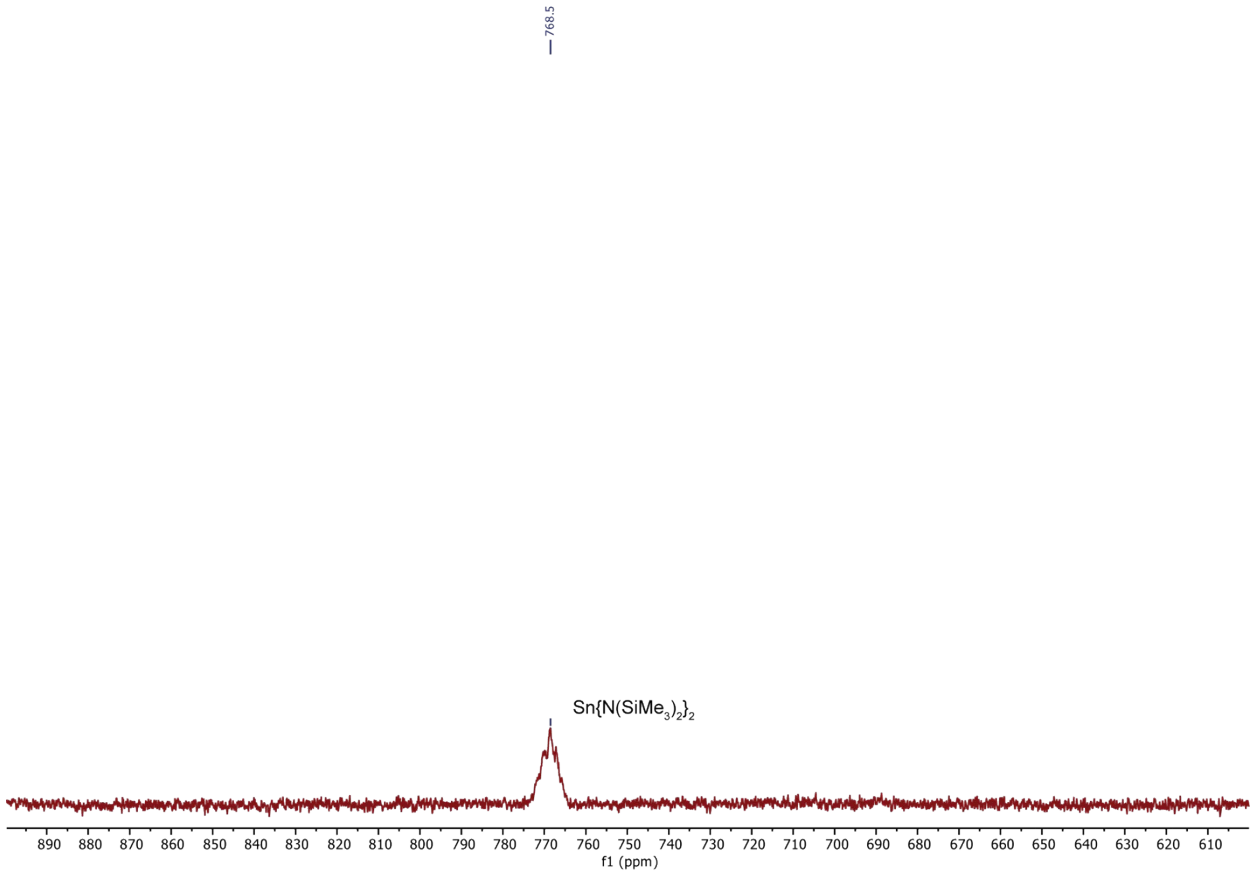

Figure S12. $^{119}Sn\{^{1}H\}$ NMR spectrum (C_6D_6, 149.5 MHz, 298 K) of $Sn\{N(SiMe_3)_2\}_2$ (**2**).

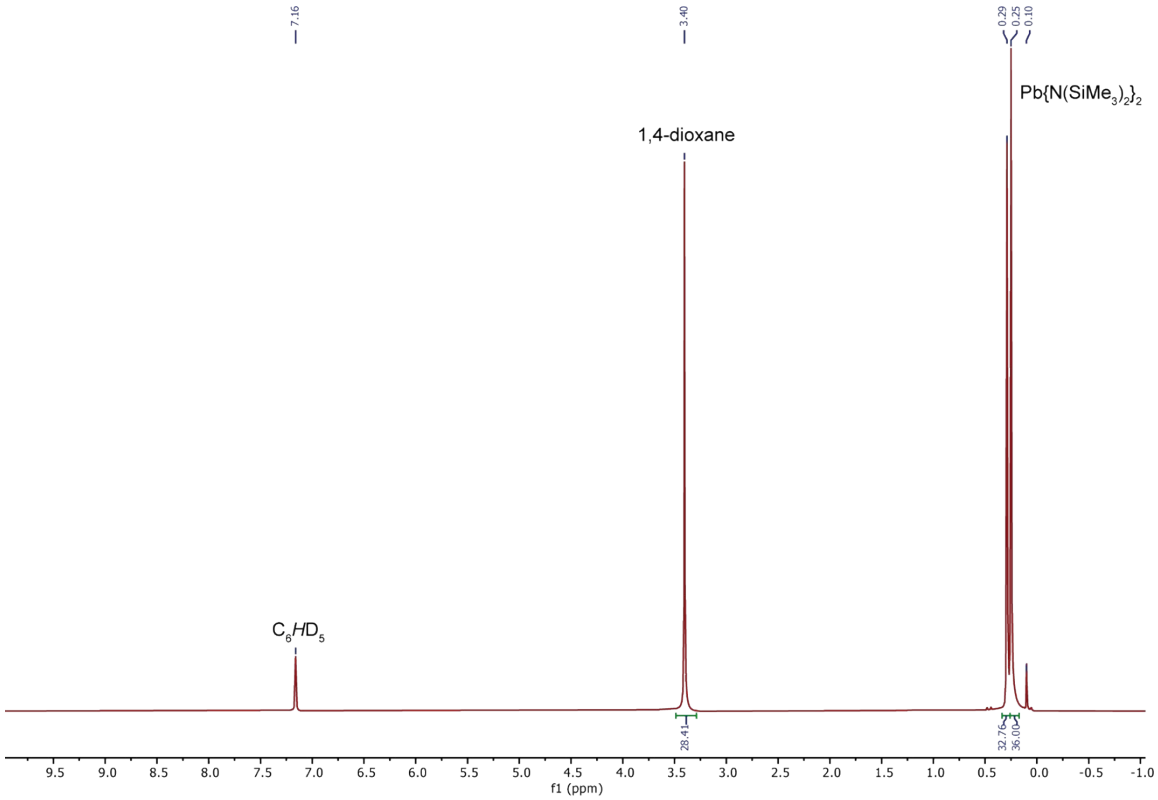

Figure S13. ^{1}H NMR spectrum (C_6D_6, 300.1 MHz, 298 K) of the crude outcome of the reaction of $PbCl_2$·with two equivalents of Li{N(SiMe$_3$)$_2$} and one equivalent of 1,4-dioxane after 15 min of reaction.

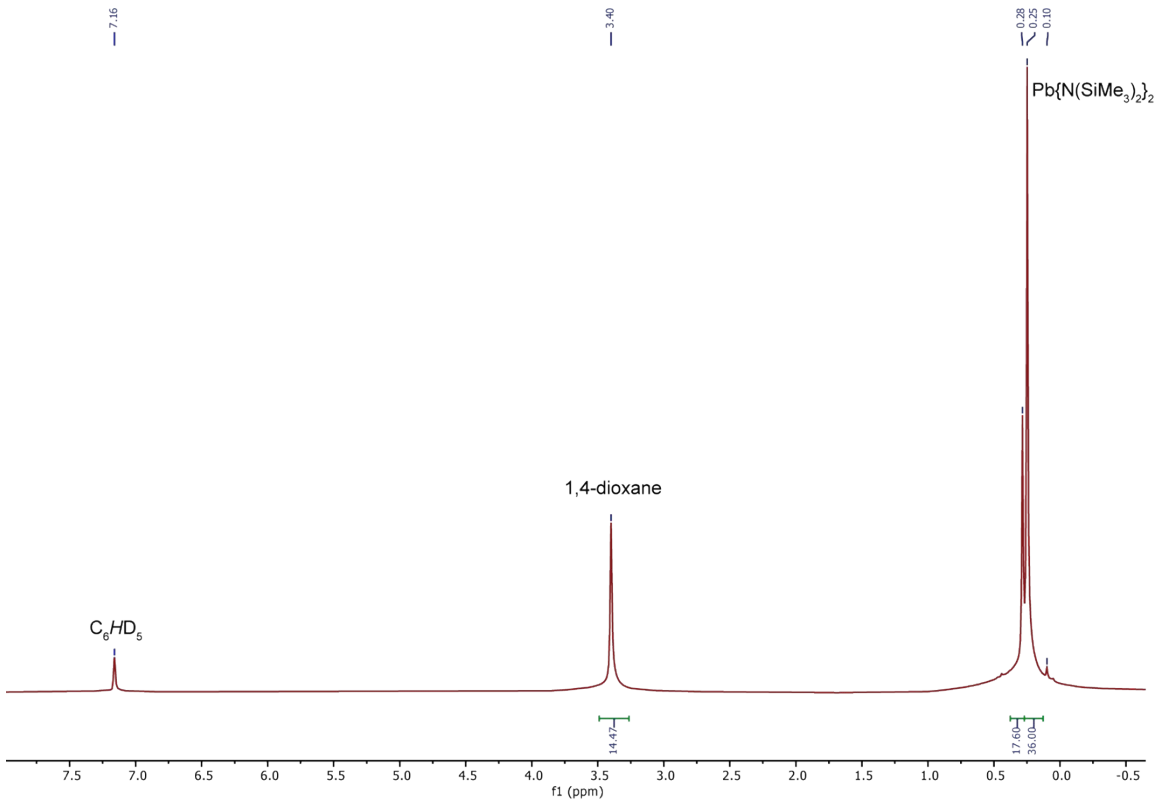

Figure S14. ^{1}H NMR spectrum (C_6D_6, 300.1 MHz, 298 K) of the crude outcome of the reaction of $PbCl_2$·with two equivalents of Li{N(SiMe$_3$)$_2$} and one equivalent of 1,4-dioxane after 45 min of reaction.

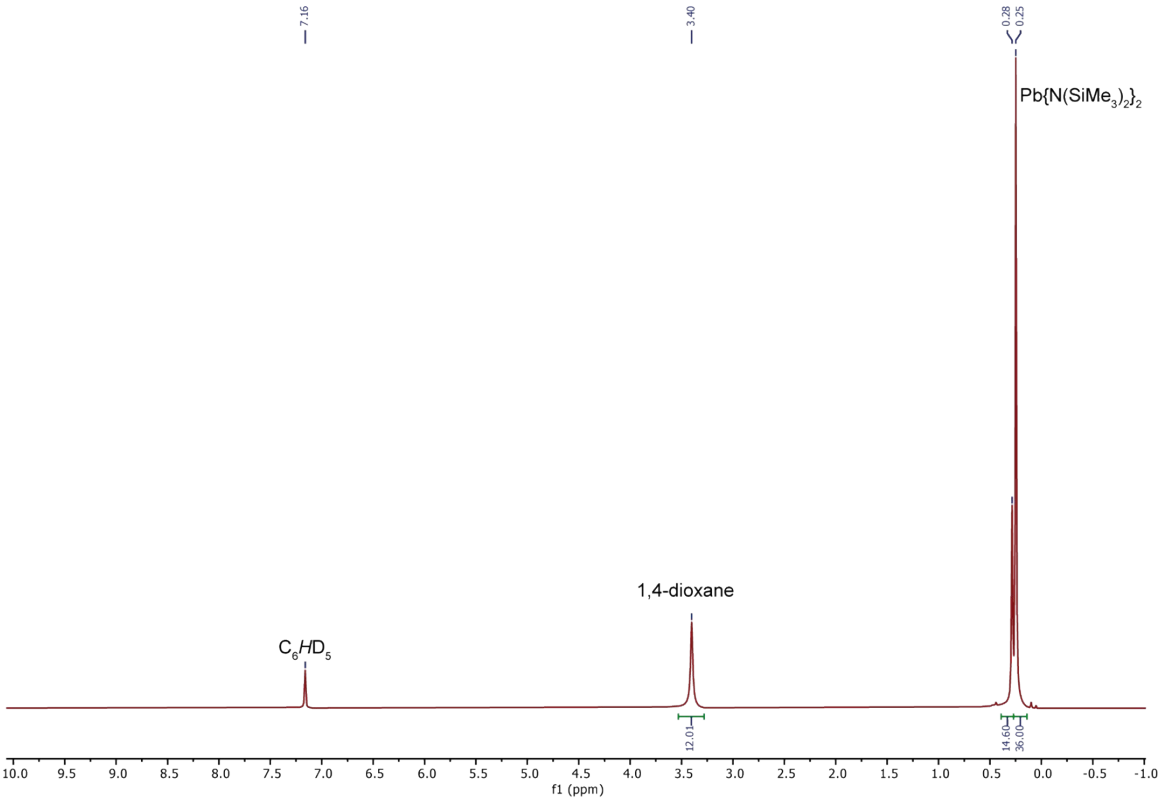

Figure S15. ^{1}H NMR spectrum (C_6D_6, 300.1 MHz, 298 K) of the crude outcome of the reaction of $PbCl_2$·with two equivalents of Li{N(SiMe$_3$)$_2$} and one equivalent of 1,4-dioxane after 2 h of reaction.

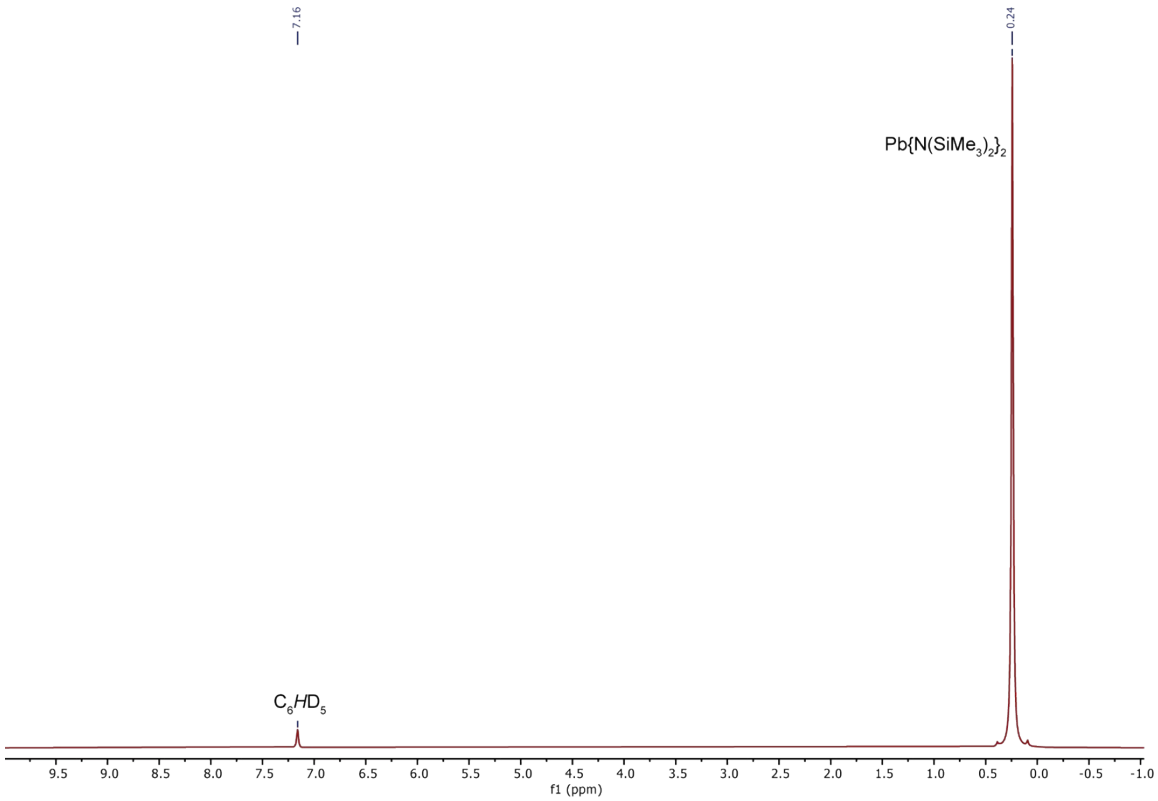

Figure S16. ^{1}H NMR spectrum (C_6D_6, 400.1 MHz, 298 K) of Pb{N(SiMe$_3$)$_2$}$_2$ (**3**).

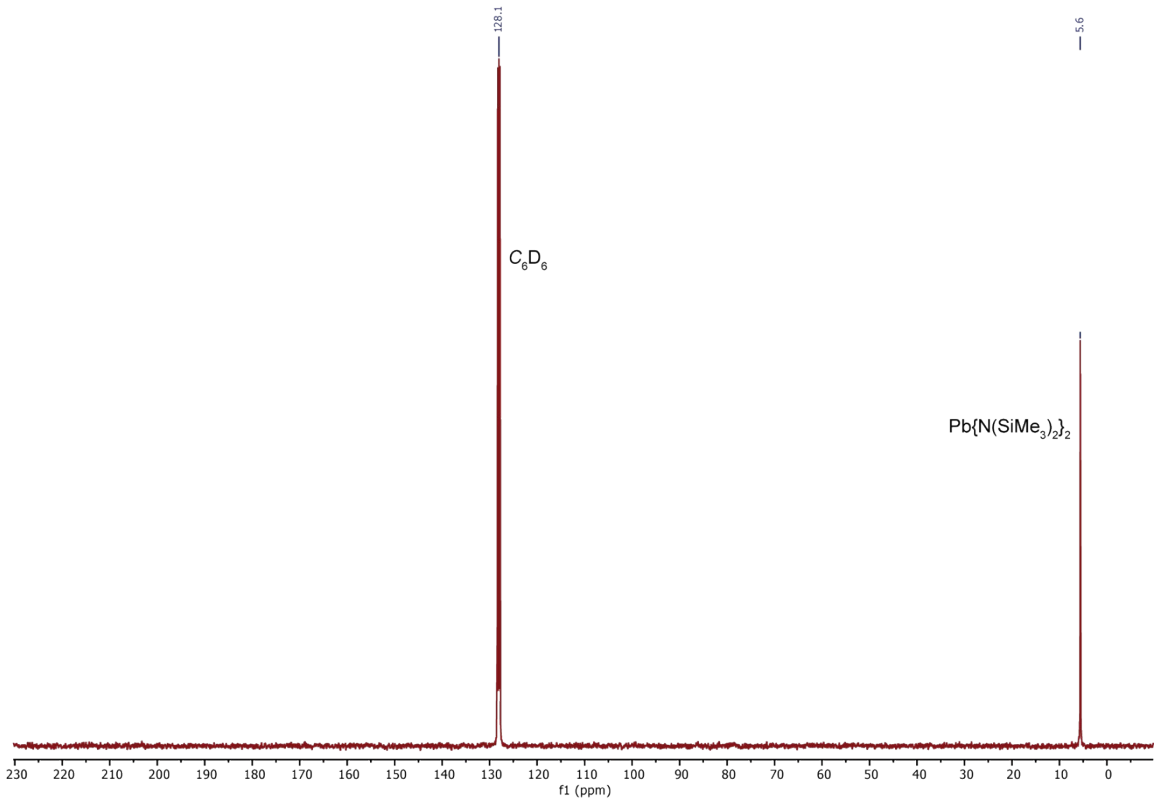

Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 75.5 MHz, 298 K) of $Pb\{N(SiMe_3)_2\}_2$ (**3**).

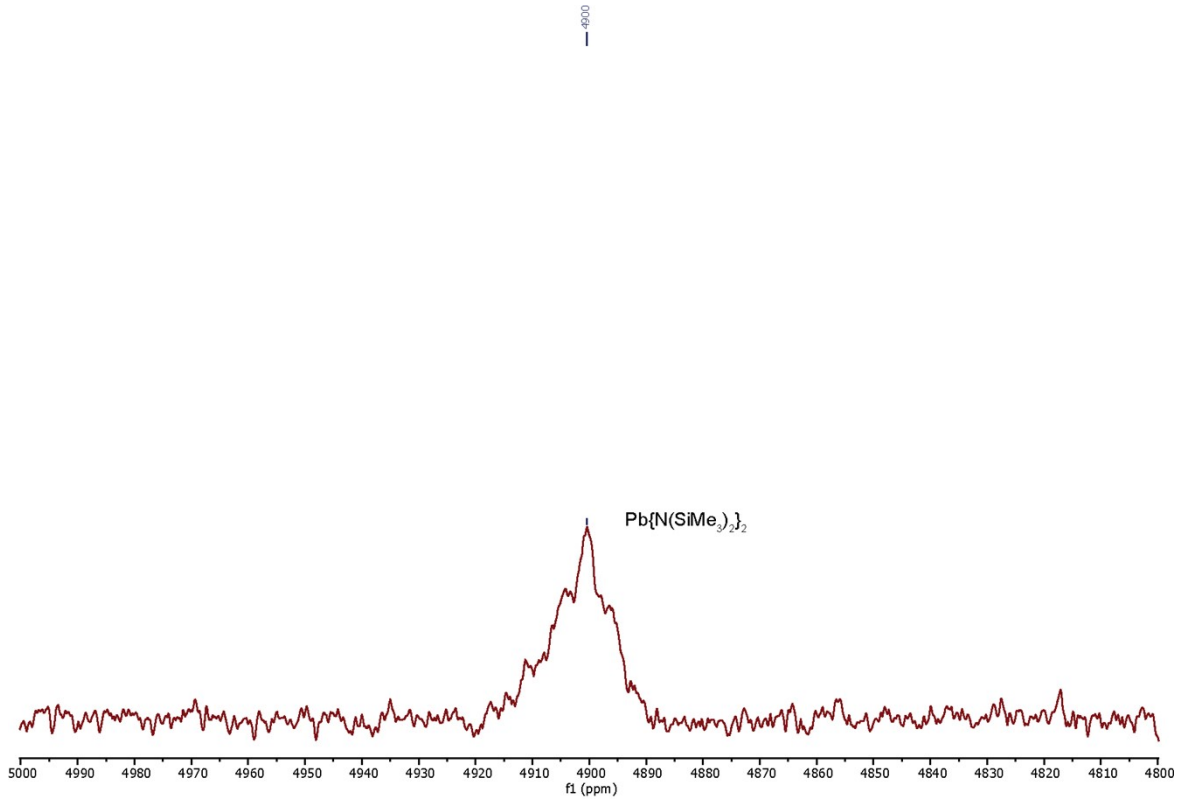

Figure S18. $^{207}Pb\{^{1}H\}$ NMR spectrum (C_6D_6, 84.1 MHz, 298 K) of $Pb\{N(SiMe_3)_2\}_2$ (**3**).

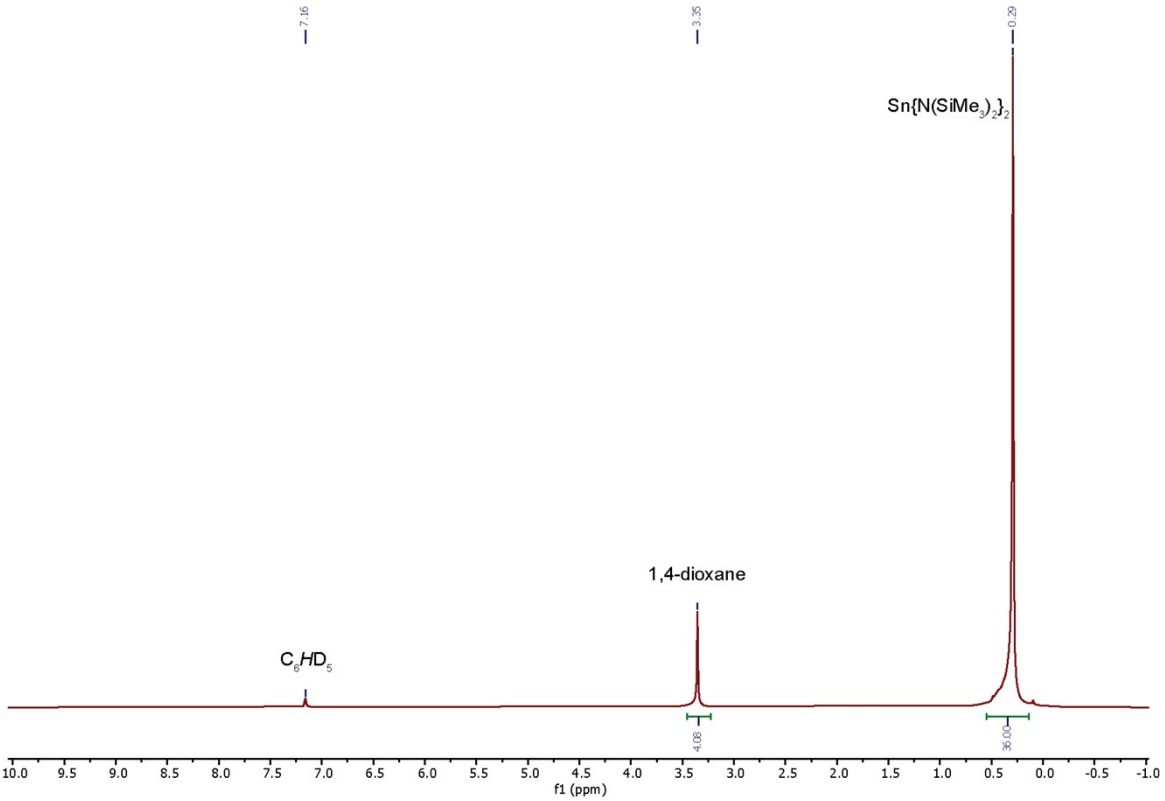

Figure S19. ^{1}H NMR spectrum (C_6D_6, 300.1 MHz, 298 K) of the crude outcome of the reaction of $SnCl_2$·with two equivalents of Li{N(SiMe$_3$)$_2$} and one equivalent of 1,4-dioxane after 30 min of reaction (larger scale preparation).

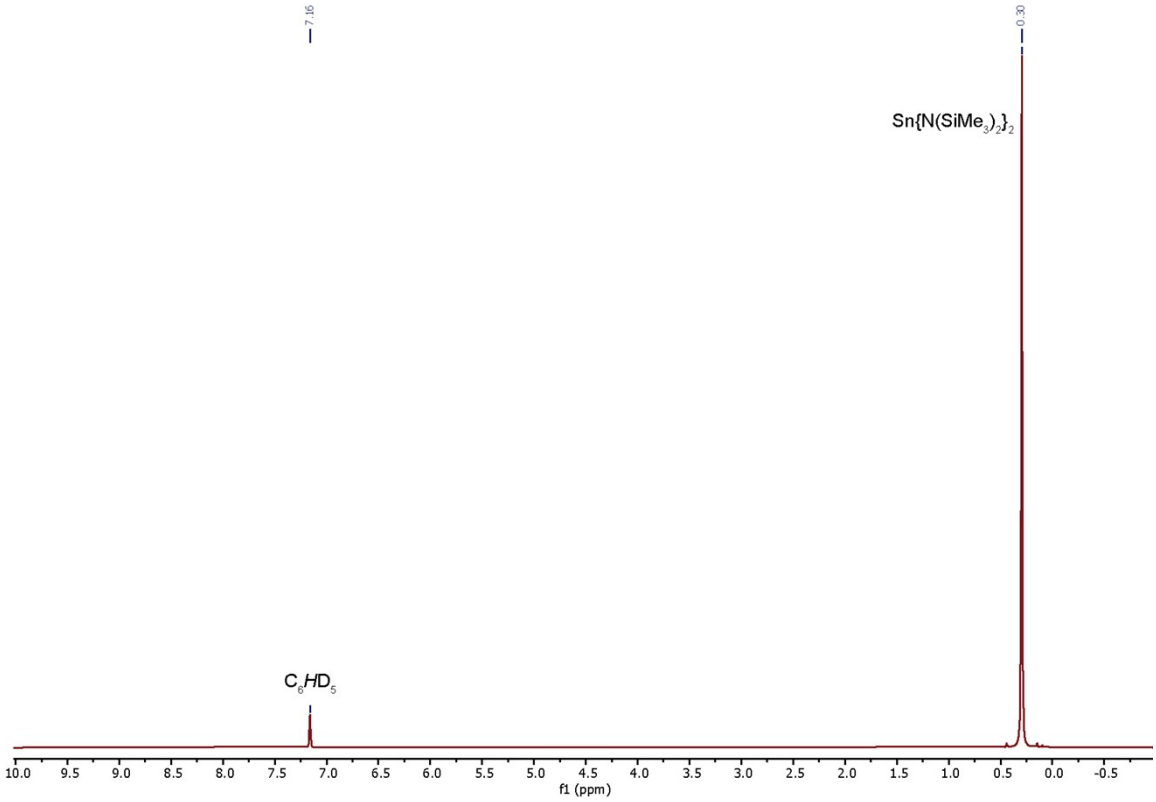

Figure S20. ^{1}H NMR spectrum (C_6D_6, 400.5 MHz, 298 K) of Sn{N(SiMe$_3$)$_2$}$_2$ (**2**) obtained in the larger scale preparation.

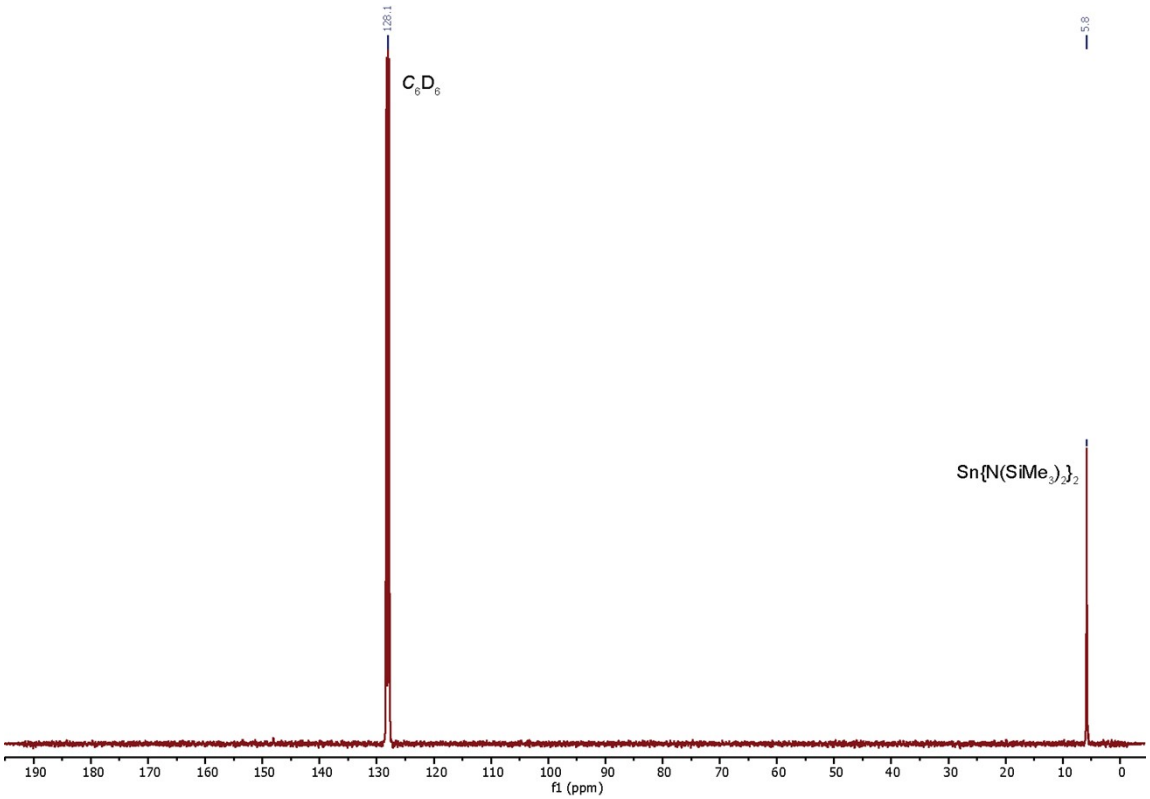

Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 100.6 MHz, 298 K) of $Sn\{N(SiMe_3)_2\}_2$ (**2**) obtained in the larger scale preparation.

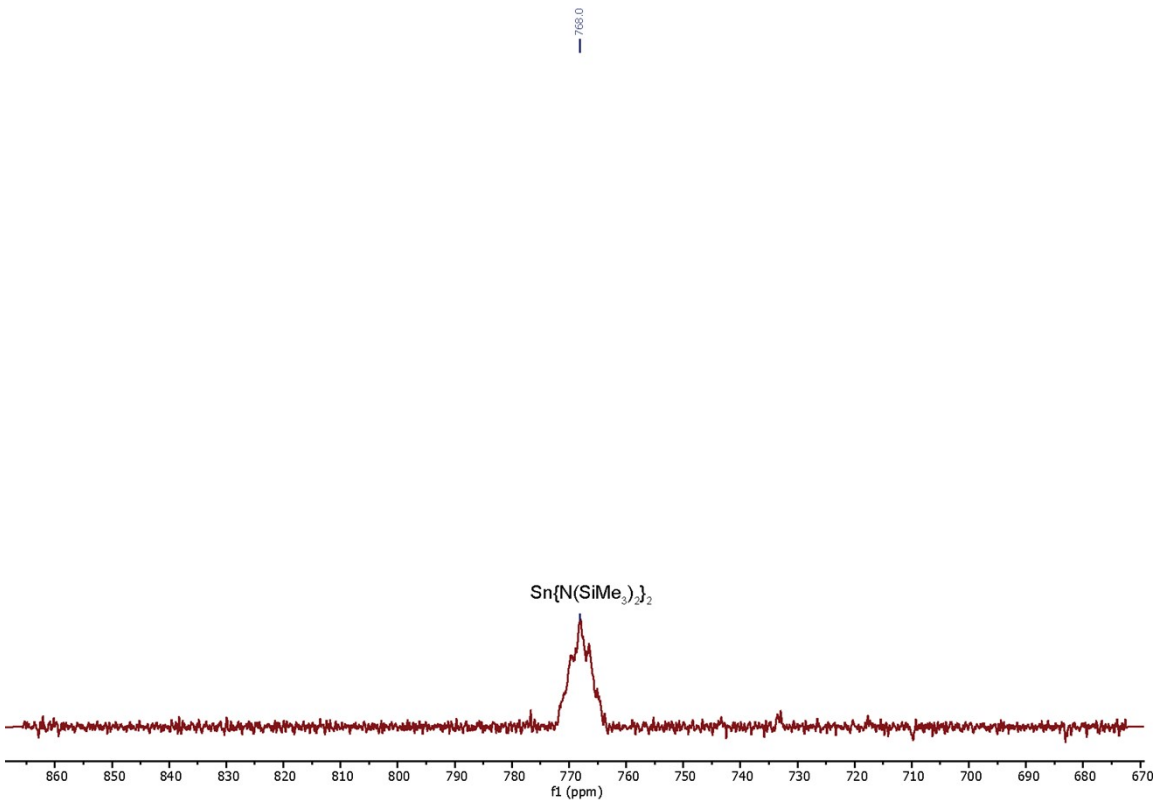

Figure S22. $^{119}Sn\{^{1}H\}$ NMR spectrum (C_6D_6, 149.5 MHz, 298 K) of $Sn\{N(SiMe_3)_2\}_2$ (**2**) obtained in the larger scale preparation.

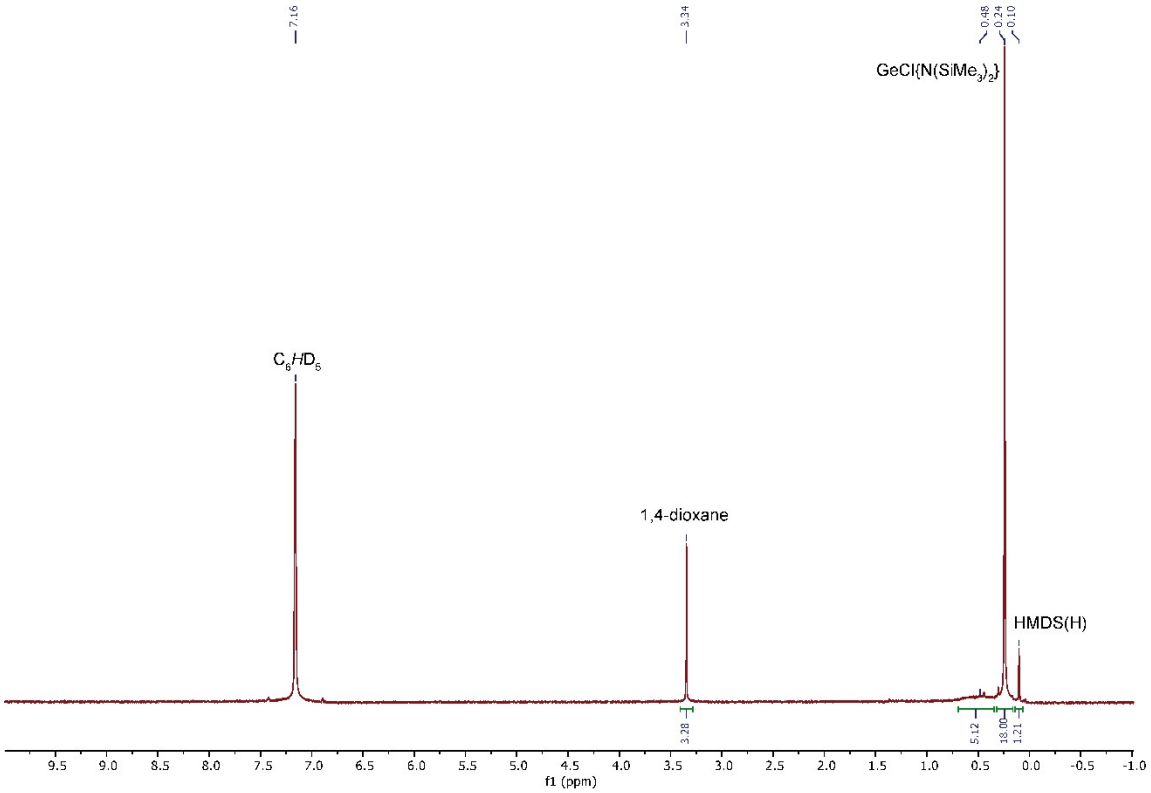

Figure S23. ^{1}H NMR spectrum (C_6D_6, 300.1 MHz, 298 K) of the crude outcome of the reaction of $GeCl_2$ 1,4-dioxane with one equivalent of **1** after 2.5 h of reaction.

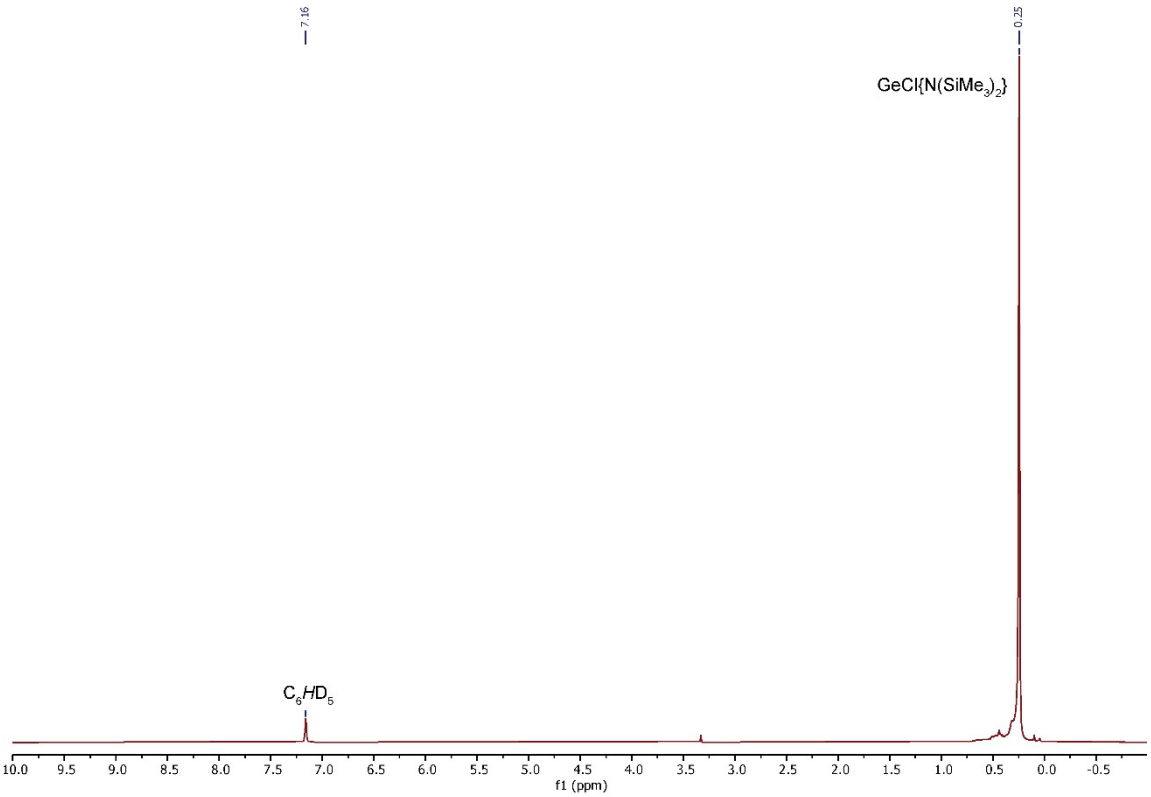

Figure S24. ^{1}H NMR spectrum (C_6D_6, 300.1 MHz, 298 K) of $GeCl\{N(SiMe_3)_2\}$ (**4**).

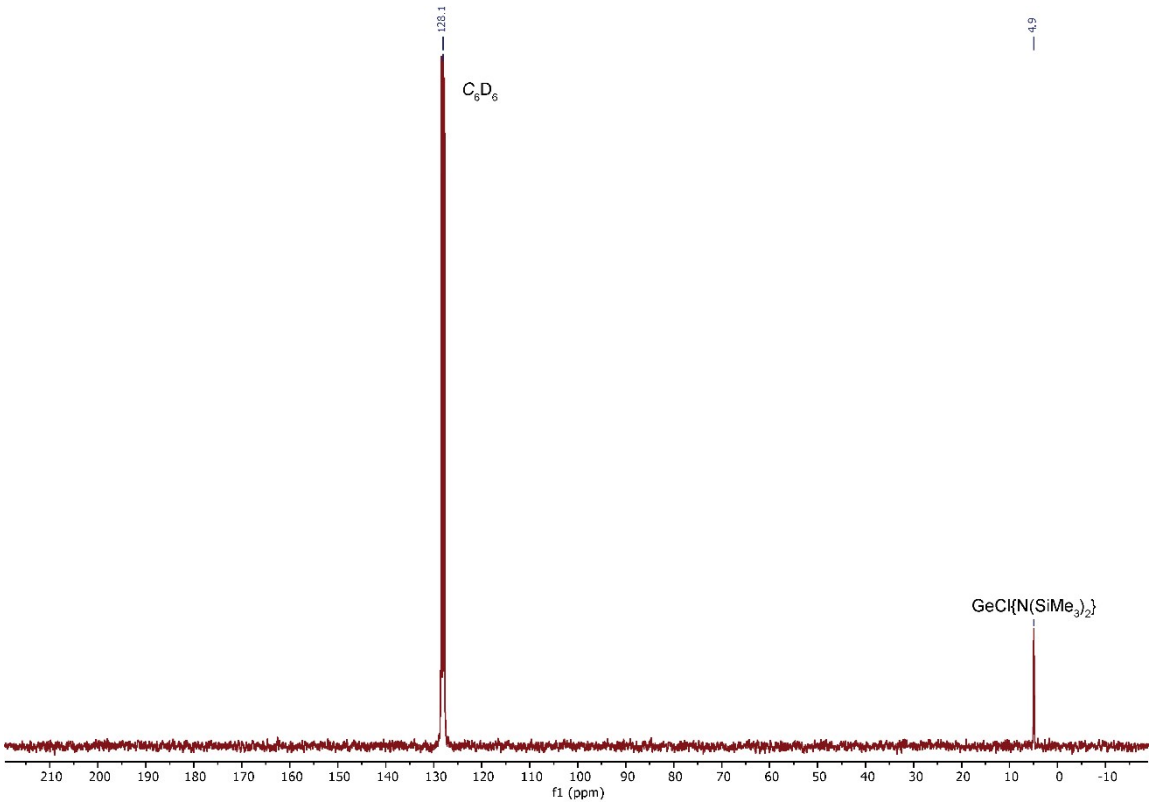

Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 75.5 MHz, 298 K) of $GeCl\{N(SiMe_3)_2\}$ (**4**).

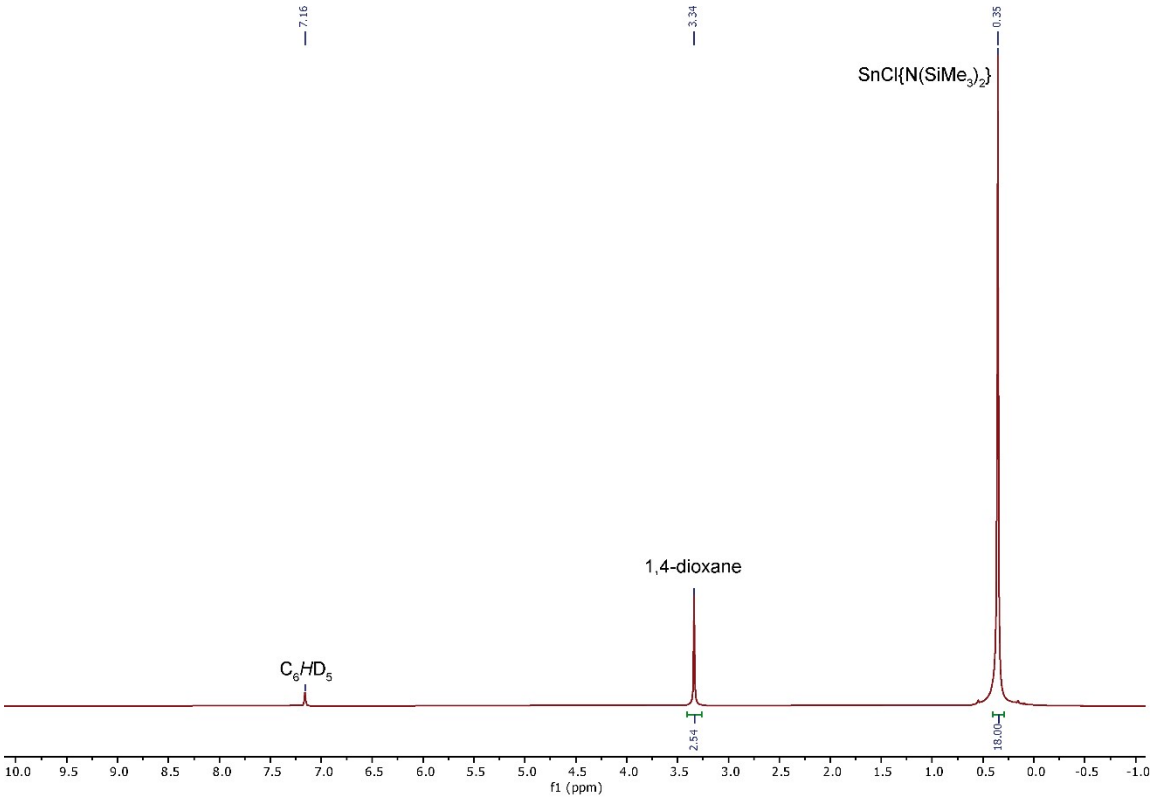

Figure S26. ^{1}H NMR spectrum (C_6D_6, 300.1 MHz, 298 K) of the crude outcome of the reaction of $SnCl_2$ with one equivalent of **2** and one equivalent of 1,4-dioxane after 2.5 h of reaction.

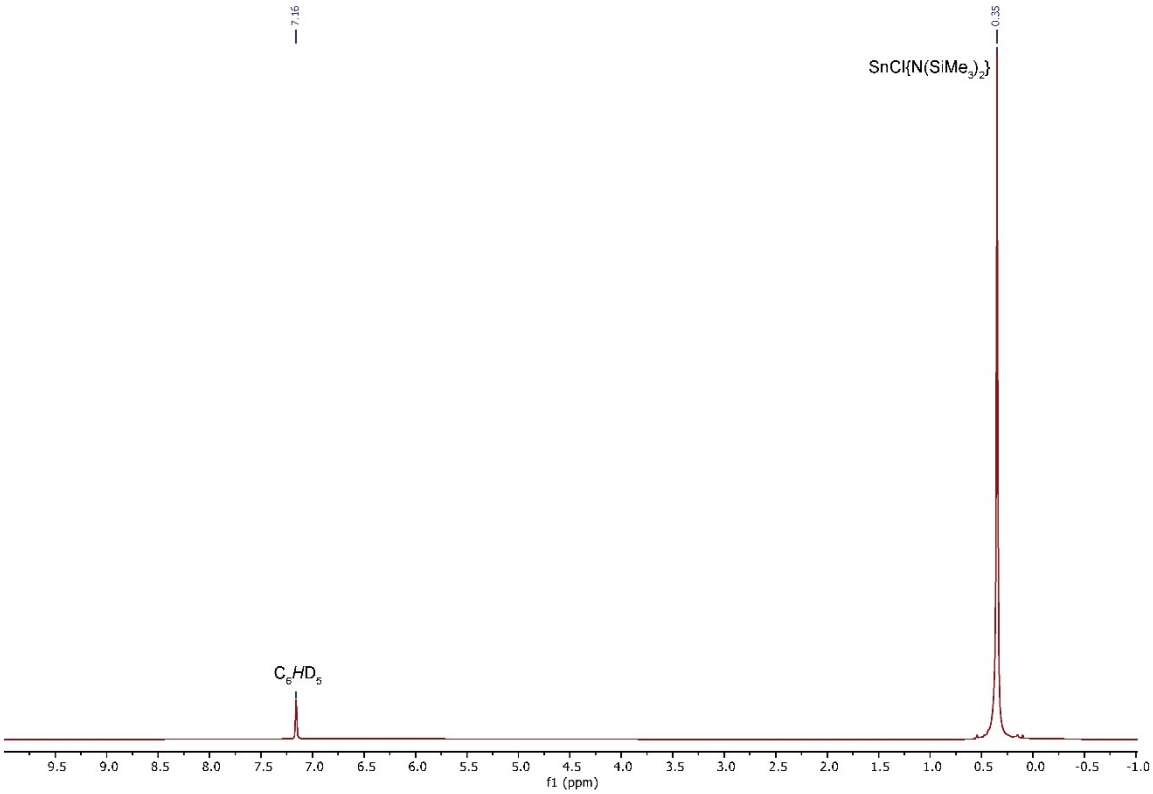

Figure S27. ^{1}H NMR spectrum (C_6D_6, 300.1 MHz, 298 K) of SnCl{N(SiMe$_3$)$_2$} (**5**).

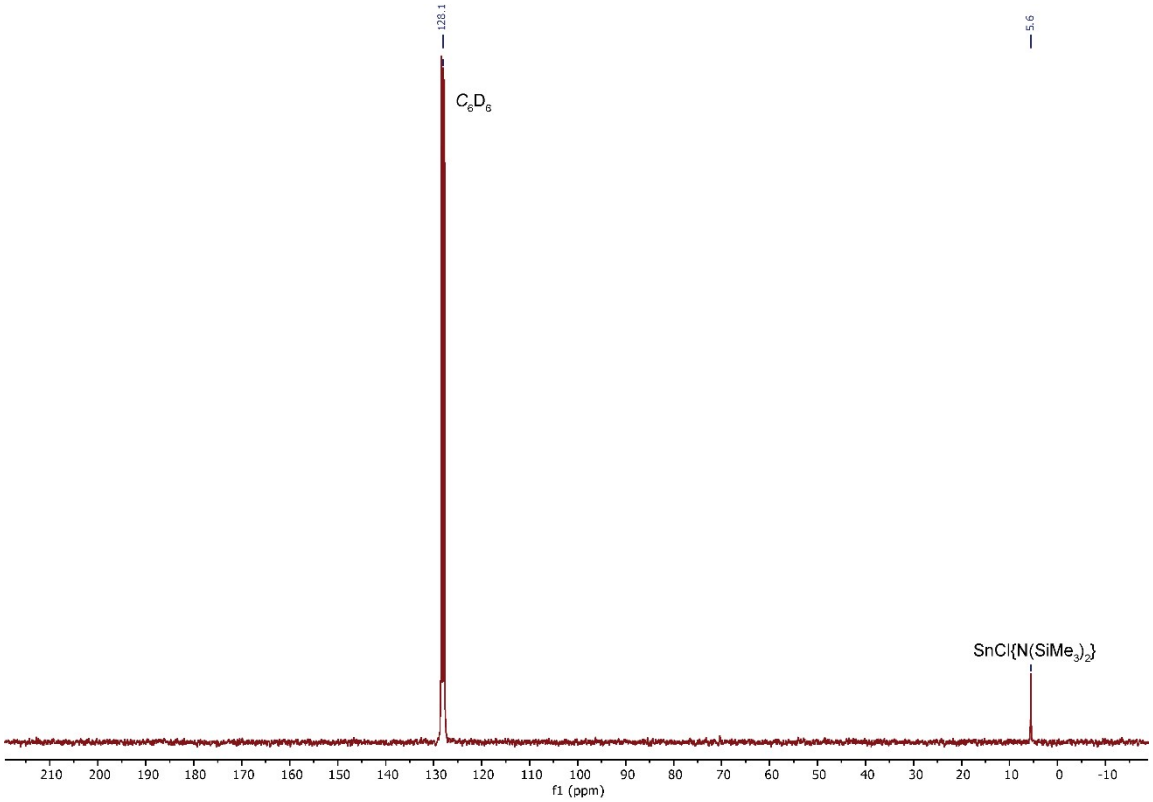

Figure S28. ^{13}C{^{1}H} NMR spectrum (C_6D_6, 75.5 MHz, 298 K) of SnCl{N(SiMe$_3$)$_2$} (**5**).

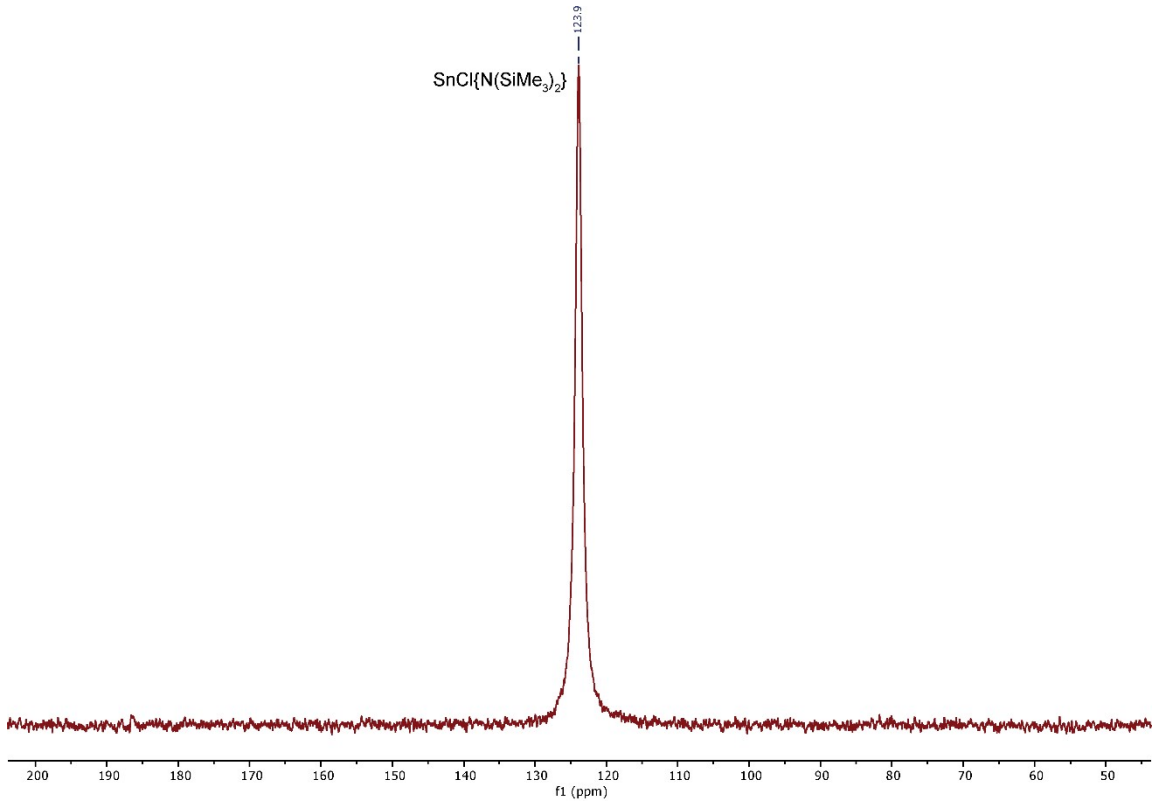

Figure S29. $^{119}Sn\{^{1}H\}$ NMR spectrum (C_6D_6, 149.2 MHz, 298 K) of $SnCl\{N(SiMe_3)_2\}$ (**5**).

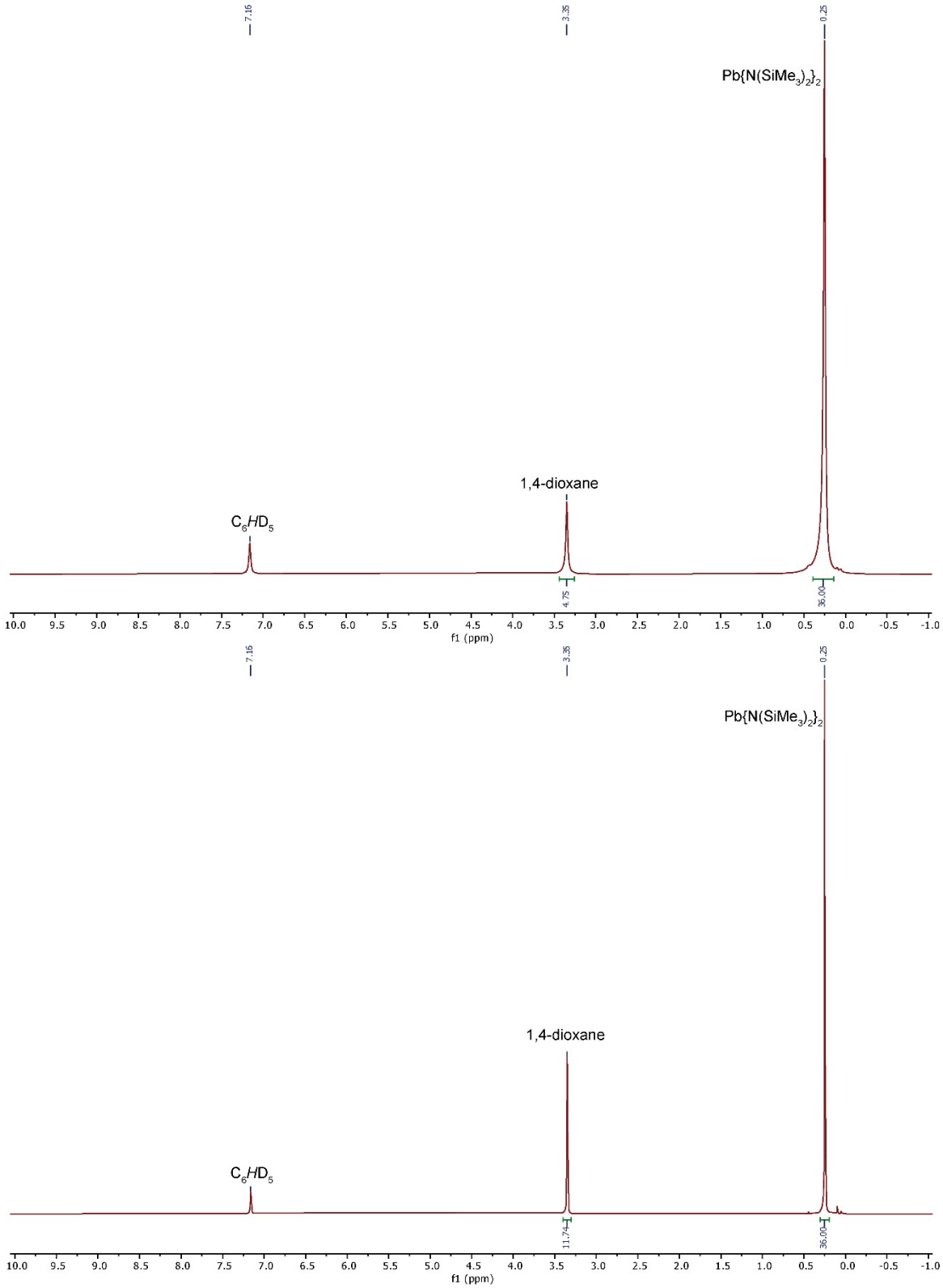

Figure S30. ^{1}H NMR spectra (C_6D_6, 300.1 MHz, 298 K) of the crude outcome of the reaction of $PbCl_2$ with one equivalent of **3** and one equivalent of 1,4-dioxane after 2.5 h of reaction (top) and the reaction of $PbCl_2$ with one equivalent of $Li\{N(SiMe_3)_2\}$ and one equivalent of 1,4-dioxane after 15 min of reaction (bottom).

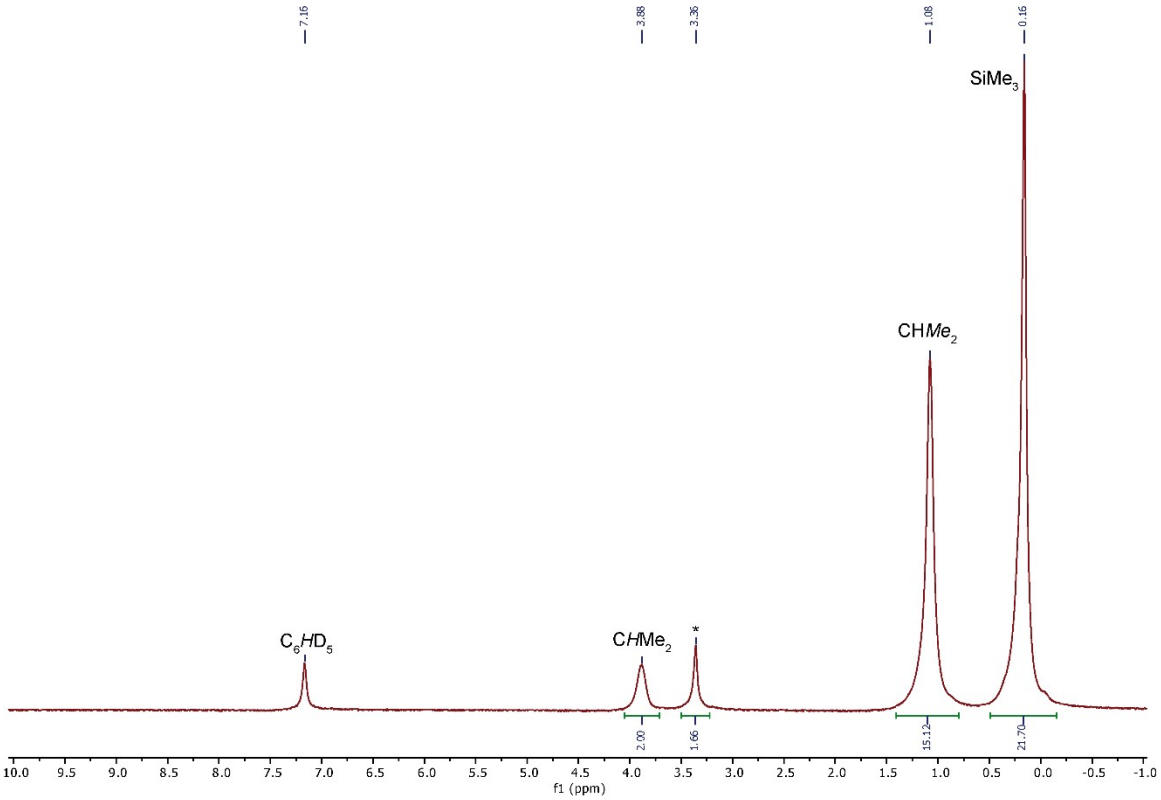

Figure S31. ^{1}H NMR spectrum (C_6D_6, 300.1 MHz, 298 K) of the crude outcome of the reaction of **5** with one equivalent of ^{i}PrNCN^{i}Pr after 20 min of reaction. *1,4-dioxane.

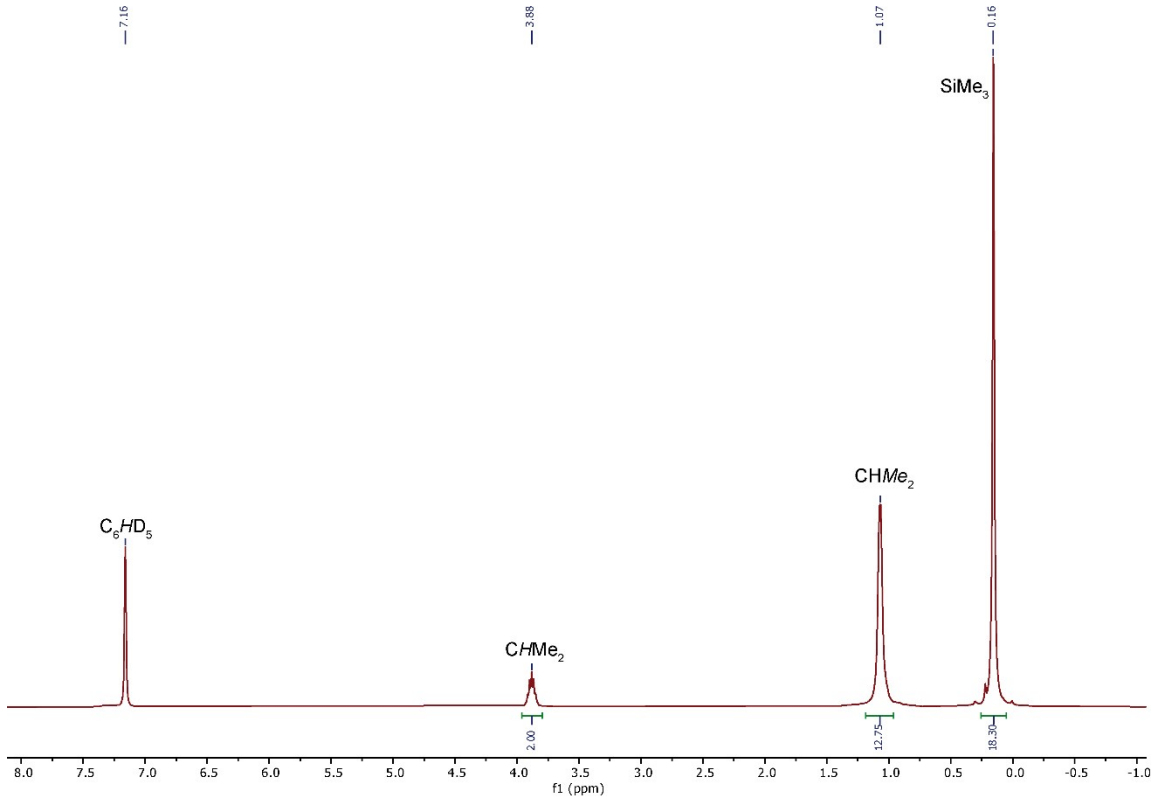

Figure S32. ^{1}H NMR spectrum (C_6D_6, 400.1 MHz, 298 K) of SnCl[^{i}PrNC{N(SiMe$_3$)$_2$}N^{i}Pr] (**7**).

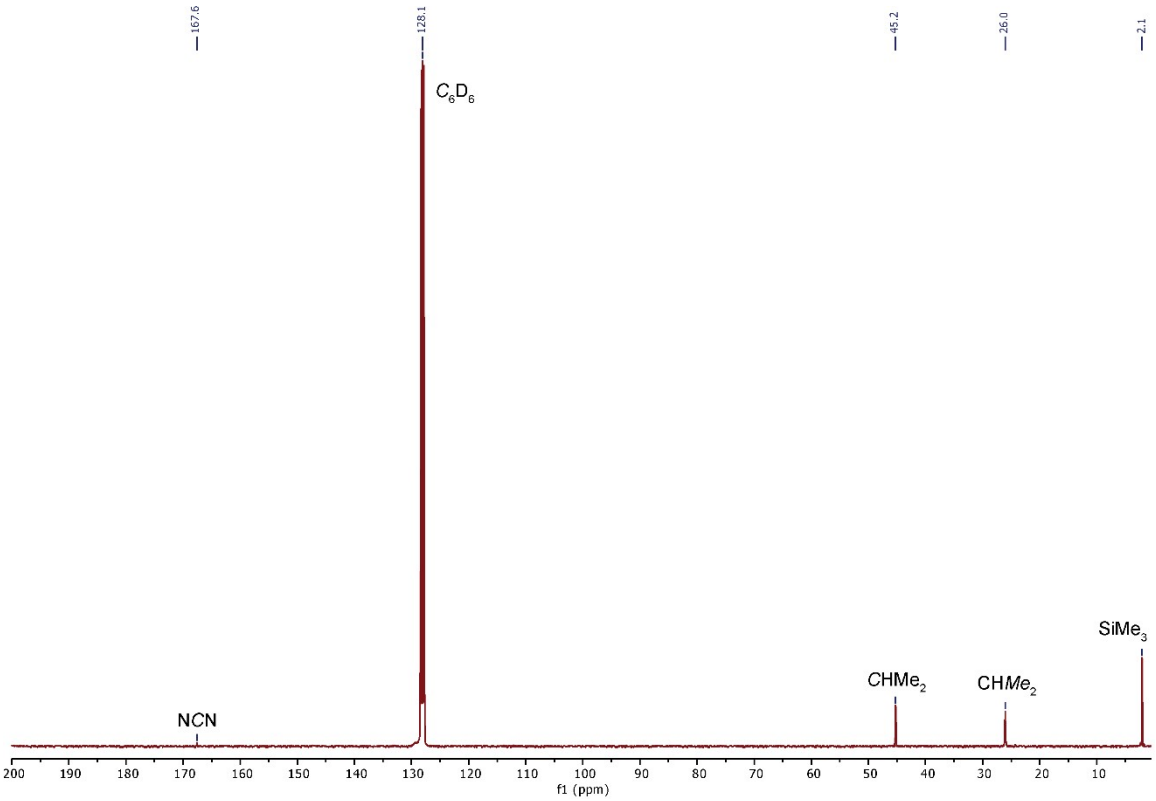

Figure S33. $^{13}C\{^1H\}$ NMR spectrum (C_6D_6, 100.6 MHz, 298 K) of SnCl[^{i}PrNC{N(SiMe$_3$)$_2$}N^{i}Pr] (**7**).

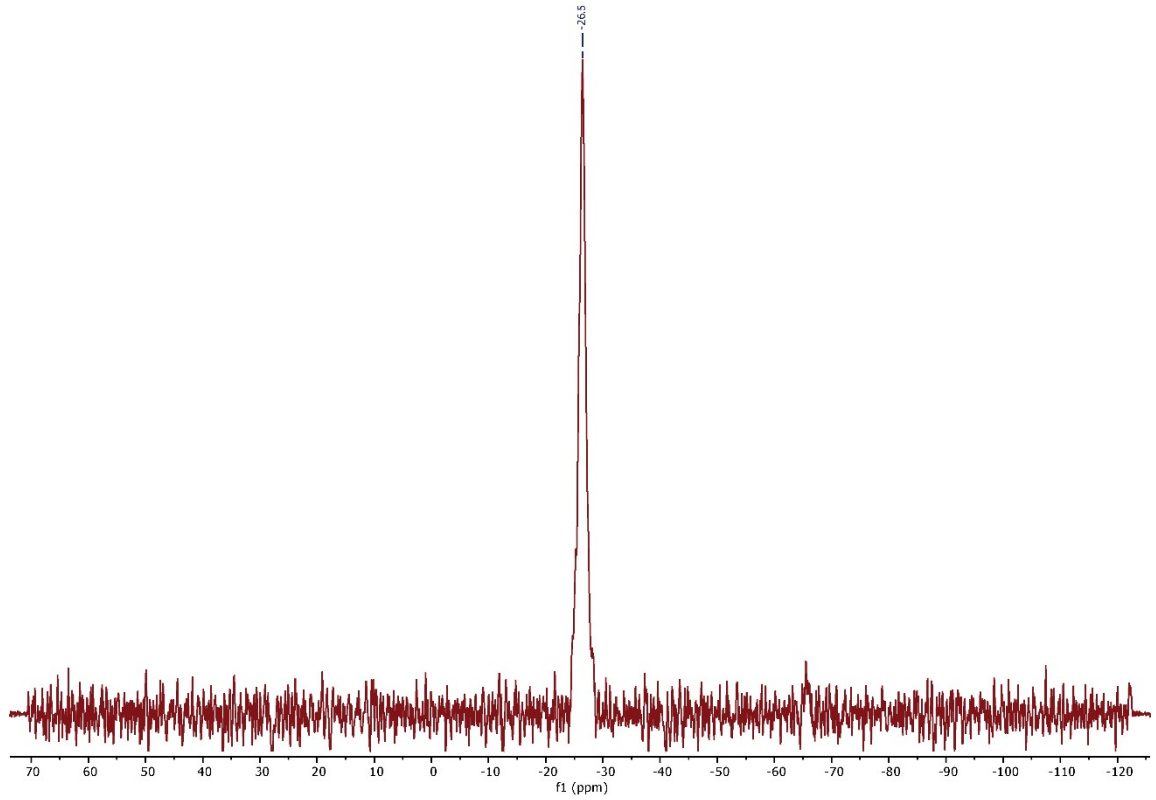

Figure S34. $^{119}Sn\{^1H\}$ NMR spectrum (C_6D_6, 149.2 MHz, 298 K) of SnCl[^{i}PrNC{N(SiMe$_3$)$_2$}N^{i}Pr] (**7**).

Table S1. Relevant methodological information for representative synthetic routes found for the preparation of **1**-**3**

Year	Ref.	Compound	Yield (%)	$Li\{N(SiMe_3)_2\}$ synthesis	Transmetalation with ECl_2 (E = Ge, Sn, Pb)[a]		Solvent removal	Compound extraction	LiCl filtration	Solvent removal	Additional purification step
1974	1	**1**	67	not detailed	In Et_2O at 0 ºC		not detailed	not detailed	not detailed	not detailed	not detailed
		2	79								
		3	69								
1974	2	**2**	50	not detailed	not detailed		not detailed	not detailed	not detailed	not detailed	not detailed
1990	4	**2**	75	$HN(SiMe_3)_2\}$ + ^{n}BuLi (solution in hexanes) at 0 ºC	$SnCl_2$ in THF transferred slowly to $Li\{N(SiMe_3)_2\}$ in THF at 0 ºC and stirred for 3-4.5 h at room temperature.		NO	NO	YES	YES	Distillation
1977	3	**1**	67	$HN(SiMe_3)_2\}$ + ^{n}BuLi in Et_2O	$Li\{N(SiMe_3)_2\}$ in Et_2O transferred slowly to a suspension of ECl_2 in Et_2O and stirred for 2 h		YES	In hexane or bencene	YES	YES	Distillation
		2	79								
		3	69								
2014	5	**1**	57	$HN(SiMe_3)\}$+ ^{n}BuLi (solution in heptane) at -196 ºC stirred 30 min while thawing	Solution of ECl_2 in Et_2O (E = Ge) or THF (E = Sn) added slowly to $Li\{N(SiMe_3)\}$ solution and stirred for 2h		YES	NO	NO	*NA*	Distillation
		2	81								
2018	6	**1**	75	Solid $Li\{N(SiMe_3)_2\}$ commercially obtained	$Li\{N(SiMe_3)_2\}$ in Et_2O transferred slowly (40-45 min) to ECl_2 in Et_2O (E = Ge, Pb) or Et_2O/THF (E = Sn) and stirred for 3-4.5 h. LiCl allowed to settle for 30 min		NO	NO	YES	YES	Distillation
		2	73								
		3	69								
2022	7	**2**	84	Solid $Li\{N(SiMe_3)_2\}$ commercially obtained	$Li\{N(SiMe_3)_2\}$ and $SnCl_2$ cooled to −78 ºC followed by addition of THF. Slow warming to RT.		YES	In toluene	YES	YES	NO

[a]*For E = Ge, ECl_2 is ECl_2·1,4-dioxane*

Green metrics calculations

Green chemistry metrics (GCM)

Metric	Abbreviation	Formula	Optimal value
Atom Economy	AE	$\frac{Formula\ weight\ product\ (g/mol)}{Formula\ weight\ of\ all\ reactants\ used\ in\ reaction\ (g/mol)} \times 100$ FW: Formula weight in g.mol^{-1}	100%
Reaction Mass Efficiency	RME	$\frac{Formula\ weight\ product\ (g/mol)}{Formula\ weight\ of\ all\ reactants\ used\ in\ reaction\ (g/mol)} \times Yield$	100%
Environmental Factor	E-factor	$\frac{Mass\ of\ wastes\ (g)}{Mass\ of\ the\ product\ of\ interest\ (g)}$	0
Process Mass Intensity	PMI	$\frac{Total\ mass\ used\ in\ the\ process\ (g)}{Mass\ of\ product\ (g)}$	1

E-factor calculations

Ge{N(SiMe$_3$)$_2$}$_2$

- *General formula used for mechanochemical synthesis*:*

$$E-factor=\frac{GeCl2\cdot dioxane\ +Li\{N(SiMe3)2\}\ -Ge\{N(SiMe3)2\}2}{Ge\{N(SiMe3)2\}2}$$

** All quantities are expressed in grams*

$$E-factor=\frac{1.16\ +1.67\ -1.80}{1.80}$$

E = 0.57

- *General formula used for Inorganic Syntheses 2018*:*

$$E-factor=\frac{GeCl2\cdot dioxane\ +Li\{N(SiMe3)2\}+\ Et2O(10\%)-Ge\{N(SiMe3)2\}2}{Ge\{N(SiMe3)2\}2}$$

** All quantities are expressed in grams*

$$E-factor=\frac{5.002\ +7.224+\ 10.344-6.402}{6.402}$$

$E-factor$ *= 2.53*

Density of ether: 0.7134 g/cm^3 145 mL = 103.443g => 10% = 10.344 g

Sn{N(SiMe3)2}2

- *General formula used for mechanochemical synthesis*:*

$$E=\frac{SnCl2\ +Li\{N(SiMe3)2\}+dioxane\ -Sn\{N(SiMe3)2\}2}{Sn\{N(SiMe3)2\}2}$$

** All quantities are expressed in grams*

$$E=\frac{0.95\ +1.67+\ 0.51685\ -1.84}{1.84}$$

E = 0.70

Density of dioxane: 1.0337 g/cm^3 500µL = 0.51685 g

- *Considering dioxane as "solvent"**

$$E=\frac{SnCl2\ +Li\{N(SiMe3)2\}+dioxane\ (10\%)\ -Sn\{N(SiMe3)2\}2}{Sn\{N(SiMe3)2\}2}$$

** All quantities are expressed in grams*

$$E=\frac{0.95+1.67+0.051685-1.84}{1.84}$$

E = 0.45

Density of dioxane: 1.0337 g/cm^3 500µL = 0.51685 g => 10% = 0.051685 g

- *General formula used for Inorganic Syntheses 2018*:*

$$E=\frac{SnCl2\ +Li\{N(SiMe3)2\}+\ Et2O(10\%)+THF(10\%)-Sn\{N(SiMe3)2\}2}{Sn\{N(SiMe3)2\}2}$$

** All quantities are expressed in grams*

$$E=\frac{10.00\ +17.65+\ 20.886+1.7752-20.31}{20.31}$$

E= 1.48

Density of ether: 0.7134 g/cm^3 290 mL = 206.886 => 10% = 20.886
Density of THF: 0.8876 g/cm^3 20 mL = 17.752 => 10% = 1.7752

Pb{N(SiMe3)2}2

- *General formula used for mechanochemical synthesis*:*

$$E = \frac{PbCl2 + Li\{N(SiMe3)2\} + dioxane - Pb\{N(SiMe3)2\}2}{Pb\{N(SiMe3)2\}2}$$

** All quantities are expressed in grams*

$$E = \frac{1.39 + 1.67 + 0.51685 - 1.74}{1.74}$$

E = 1.06

Density of dioxane: 1.0337 g/cm³ 500µL = 0.51685 g

- *Considering dioxane as "solvent"**

$$E = \frac{PbCl2 + Li\{N(SiMe3)2\} + dioxane\ (10\%) - Pb\{N(SiMe3)2\}2}{Pb\{N(SiMe3)2\}2}$$

** All quantities are expressed in grams*

$$E = \frac{1.39 + 1.67 + 0.051685 - 1.74}{1.74}$$

E = 0.79

Density of dioxane: 1.0337 g/cm³ 500µL = 0.51685 g => 10% = 0.051685 g

- *General formula used for Inorganic Syntheses 2018*:*

$$E = \frac{PbCl2 + Li\{N(SiMe3)2\} + Et2O(10\%) - Pb\{N(SiMe3)2\}2}{Pb\{N(SiMe3)2\}2}$$

** All quantities are expressed in grams*

$$E = \frac{10.00 + 12.03 + 17.216 - 15.31}{15.31}$$

E = 1.56

Density of ether: 0.7134 g/cm³ 240 mL = 171.216 => 10% = 17.216

Process mass intensity (PMI) calculations

Ge{N(SiMe3)2}2

General Formula used for mechanochemical synthesis:*

$$PMI = \frac{(\ GeCl2{\cdot}dioxane\ + Li\{N(SiMe3)2\}\ )}{Ge\{N(SiMe3)2\}2}$$

** All quantities are expressed in grams*

$$PMI = \frac{1.16\ +\ 1.67}{1.80}$$

PMI = 1.57

General formula used for Inorganic Syntheses 2018:*

$$PMI = \frac{(\ GeCl2{\cdot}dioxane\ + Li\{N(SiMe3)2\} + Et2O\ )}{Ge\{N(SiMe3)2\}2}$$

** All quantities are expressed in grams*

$$PMI = \frac{5.002 +\ 7.224 +\ 103.443}{6.402}$$

PMI = 18.07

Density ether: 0.7134 g/cm^3 145 mL = 103.443g

Sn{N(SiMe3)2}2

- *General Formula used for mechanochemical synthesis*:*

$$MI = \frac{(\ SnCl2 +\ dioxane\ + Li\{N(SiMe3)2\}\ )}{Ge\{N(SiMe3)2\}2}$$

** All quantities are expressed in grams*

$$PMI = \frac{0.95 + 0.51685 +\ 1.67}{1.84}$$

PMI = 1.70

Density dioxane: 1.0337 g/cm^3 500µL = 0.51685 g

- *General formula used for Inorganic Syntheses 2018*:*

$$PMI = \frac{SnCl2\ + Li\{N(SiMe3)2\} +\ Et2O + THF}{Sn\{N(SiMe3)2\}2}$$

** All quantities are expressed in grams*

$$PMI = \frac{10.00g\ + 17.65 +\ 206.886 + 17.752}{20.31}$$

PMI= 12.42

Density of ether: 0.7134 g/cm^3 290 mL = 206.886

Density of THF: 0.8876 g/cm^3 20 mL = 17.752

Pb{N(SiMe3)2}2

- *General Formula used for mechanochemical synthesis*:*

$$MI = \frac{(\ PbCl2 +\ dioxane\ + Li\{N(SiMe3)2\}\ )}{Pb\{N(SiMe3)2\}2}$$

** All quantities are expressed in grams*

$$PMI = \frac{1.39 + 0.51685 +\ 1.67}{1.74}$$

PMI = 2.06

Density of dioxane: 1.0337 g/cm^3 500µL = 0.51685 g

- *General formula used for Inorganic Syntheses 2018*:*

$$PMI = \frac{PbCl2\ + Li\{N(SiMe3)2\} +\ Et2O}{Pb\{N(SiMe3)2\}2}$$

** All quantities are expressed in grams*

$$PMI = \frac{10.00g\ + 12.03 +\ 171.216}{15.31}$$

PMI= 12.62

Density of ether: 0.7134 g/cm^3 240 mL = 171.216

Generalized Reaction Mass Efficiency (RME)

Ge{N(SiMe3)2}2

*General Formula used for mechanochemical synthesis and for Inorganic Synthesis 2018**

$$RME = \frac{Mw\ Ge\{N(SiMe3)2\}2}{(Mw\ GeCl2{\cdot}dioxane\ + 2\ x\ Mw\ Li\{N(SiMe3)2\}\ )} x\ Yield$$

** All quantities are expressed in grams/mol*

$$RME = \frac{393.38}{231.65 + 2x167.33}\ x\ 92$$

RME = 63.91 (mechanochemical)

$$RME = \frac{393.38}{231.65 + 2x167.33}\ x\ 75$$

RME = 52.10 (*Inorganic Syntheses* 2018)

Mw GeCl2·dioxane = 231.65
Mw $Ge\{N(SiMe3)2\}2 =$ 393.38
Mw $Li\{N(SiMe3)2\}$= 167.33

Sn{N(SiMe3)2}2

*General Formula used for mechanochemical synthesis and for inorganic synthesis 2018**

$$RME = \frac{Fw\ Sn\{N(SiMe3)2\}2}{(\ Fw\ SnCl2\ + 2\ x\ Li\{N(SiMe3)2\})} x\ Yield$$

** All quantities are expressed in grams*

$$RME = \frac{439.48}{189.62 + 2\ x\ 167.33}\ X\ 84$$

RME = 70.41 (mechanochemical)

$$RME = \frac{439.48}{189.62\ + 2\ x\ 167.33}\ x\ 73$$

RME = 61.19 (*Inorganic Syntheses* 2018)

Mw **SnCl2** = 189.62
Mw $Sn\{N(SiMe3)2\}2 =$ 439.48
Mw $Li\{N(SiMe3)2\}$**=** 167.33

Pb{N(SiMe3)2}2

General Formula used for mechanochemical synthesis

$$RME = \frac{Fw\ Pb\{N(SiMe3)2\}2}{(\ Fw\ PbCl2\ + 2\ x\ Li\{N(SiMe3)2\})} x\ Yield$$

** All quantities are expressed in grams*

$$RME = \frac{527.97}{278.11 + 2\ x\ 167.33}\ X\ 67$$

RME = 57.72

General formula used for Inorganic Syntheses 2018:*

$$RME = \frac{Sn\{N(SiMe3)2\}2}{SnCl2\ + Li\{N(SiMe3)2\}x2}\ x\ Yield$$

** All quantities are expressed in grams*

$$RME = \frac{527.97}{278.11\ + 2\ x\ 167.33}\ x\ 69$$

RME = 59.45

Mw PbCl2 = 278.11
Mw $Pb\{N(SiMe3)2\}2 =$ 527.97
Mw $Li\{N(SiMe3)2\}$= 167.33

Generalized Atom Economy (AE)

Ge{N(SiMe3)2}2

*General Formula used for mechanochemical synthesis and for Inorganic Syntheses 2018**

$$RME = \frac{Mw\ Ge\{N(SiMe3)2\}2}{(Mw\ GeCl2{\cdot}dioxane\ + 2\ x\ Mw\ Li\{N(SiMe3)2\}\ )} X100$$

** All quantities are expressed in grams*

$$RME = \frac{393.38}{231.65 + \ 2x167.33} x100$$

RME = 69.46

Mw GeCl2·dioxane = 231.65
Mw $Ge\{N(SiMe3)2\}2 =$ 393.38
Mw $Li\{N(SiMe3)2\}$= 167.33

Sn{N(SiMe3)2}2

*General Formula used for mechanochemical synthesis and for Inorganic Syntheses 2018**

$$RME = \frac{Fw\ Sn\{N(SiMe3)2\}2}{(\ Fw\ SnCl2\ + 2\ x\ Li\{N(SiMe3)2\})} X100$$

** All quantities are expressed in grams*

$$RME = \frac{439.48}{189.62 + 2x167.33} x100$$

RME = 83.83

Mw SnCl2 = 189.62
Mw $Sn\{N(SiMe3)2\}2 =$ 439.48
Mw $Li\{N(SiMe3)2\}$= 167.33

Pb{N(SiMe3)2}2

*General Formula used for mechanochemical synthesis and for Inorganic Syntheses 2018**

$$RME = \frac{Fw\ Pb\{N(SiMe3)2\}2}{(\ Fw\ PbCl2\ + 2\ x\ Li\{N(SiMe3)2\})} X100$$

** All quantities are expressed in grams*

$$RME = \frac{527.97}{278.11 + 2x167.33} x100$$

RME = 86.16

Mw PbCl2 = 278.11
Mw $Pb\{N(SiMe3)2\}2 =$ 527.97
Mw $Li\{N(SiMe3)2\}$= 167.33

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