

Supporting Information

A Multinuclear NMR Study of the Solution Structure and Reactivity of

Tris(trimethylsilyl)methylithium and its Iodine Ate Complex

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Table of Contents

S1. General Experimental

General	S-3
NMR Spectroscopy	S-3
Temperature Measurement	S-4

S2. Syntheses

¹³ C-Labeled <i>Tris</i> (trimethylsilyl)methane (1 { ¹³ C}- H)	S-5
¹³ C-Labeled Phenylseleno(<i>tris</i> (trimethylsilyl))methane (1 { ¹³ C}- SePh)	S-5
<i>Tris</i> (phenylseleno)(trimethylsilyl)methane	S-5
<i>Bis</i> (phenylseleno) <i>bis</i> (trimethylsilyl)methane	S-6
Phenylseleno(phenyldimethylsilyl) <i>bis</i> (trimethylsilyl)methane (2-<i>SePh</i>)	S-6
Phenylseleno(isopropyldimethylsilyl) <i>bis</i> (trimethylsilyl)methane (3-<i>SePh</i>)	S-7
<i>Tris</i> (trimethylsilyl)iodomethane (1-I)	S-7
<i>Tris</i> (trimethylsilyl)iodomethane-[¹³ C] (1 { ¹³ C}- I)	S-7

S3. Spectroscopy

¹³ C NMR Variable Temperature Study of 1-<i>SePh</i>	S-8
¹³ C NMR Variable Temperature Study of 1-I	S-8
<i>Tris</i> (trimethylsilyl)methylithium (1-Li) - Typical Metalation Procedure	S-8
Variable Concentration Studies of 1-Li	S-10
<i>Tris</i> (trimethylsilyl)methylithium (1-⁶Li) - Typical procedure for Preparation from 1-<i>SePh</i>	S-12
¹³ C-Labeled <i>Tris</i> (trimethylsilyl)methylithium (1 { ¹³ C}- ⁷Li) Variable Temperature Study	S-15
¹³ C-Labeled <i>Tris</i> (trimethylsilyl)methylithium (1 { ¹³ C}- ⁶Li) Variable Temperature Study	S-16
HMPA titration of 1-Li in THF/ether	S-18
Variable Temperature ¹ H NMR Study of 1-Li	S-19
⁶ Li, ³¹ P, and ¹³ C NMR Spectroscopy of 0.08 M 1-⁶Li in Ether Titrated with HMPA	S-20
⁶ Li, ¹³ C NMR Spectroscopy 1-⁶Li in 3:2:1 Me ₂ O/THF/ether Titrated with PMDTA	S-21
⁶ Li, ³¹ P, and ¹³ C NMR Spectroscopy of 2-⁶Li in 3:2 THF/ether Titrated with HMPA	S-22
⁶ Li, ³¹ P, and ¹³ C NMR spectroscopy of 2-⁶Li in Ether Titrated with HMPA	S-23
⁷ Li, ³¹ P, and ¹³ C NMR Spectroscopy of 3-Li in 3:2 THF/ether Titrated with HMPA	S-24
⁶ Li, ³¹ P, and ¹³ C NMR Spectroscopy of 3-⁶Li in Ether Titrated with HMPA	S-25

S4. Kinetics Experiments with 1-Li

RINMR Experiments.	S-27
Reaction of 1-Li with MeI - Concentration Dependence	S-27
¹³ C RINMR spectroscopy of the reaction of 1T with EtSSEt in 3:2:1 Me ₂ O/THF/Et ₂ O	S-29
Activation Parameters for the Dissociation of 1T as Measured by the Reaction with MeI	S-29

S5. Experiments Related to the Iodine Ate Complex **4**

¹³ C RINMR spectroscopy of the reaction of 1 { ¹³ C}- I with <i>n</i> -BuLi	S-30
⁶ Li and ¹³ C NMR spectroscopy of 1-⁶Li with 1 Equivalent of 1-I in 3:2THF/ether	S-30
¹³ C RINMR Spectroscopy of the Reaction of 1-Li with MeI (2 & 8 equiv) in 3:2 THF/Et ₂ O ...	S-30
⁶ Li and ¹³ C NMR Variable Temperature Experiment of a Mixture of 4 with excess 1-Li	S-32
¹ H, ¹³ C and ²⁹ Si NMR Variable Temperature Experiment of 4 with excess 1-I	S-33
¹ H RINMR and ⁷ Li RINMR Spectroscopy of the Reaction of <i>n</i> -BuLi with 1-I in 3:1 Me ₂ O/THF	S-34
¹ H RINMR Spectroscopy of the Reaction of 1-Li with 1-I in 3:1 Me ₂ O/THF	S-35
⁷ Li and ³¹ P NMR Spectroscopy of an HMPA Titration of Lithium Diphenyliodanide in THF	S-35
⁷ Li and ³¹ P NMR Spectroscopy of an HMPA Titration of Lithium Triphenylmercury in THF ..	S-36
Reproductions of ¹ H and ¹³ C NMR spectra	3-37

S6. Supporting Information References

S1. General Experimental

General: All reactions requiring a dry atmosphere were performed in glassware flame-dried or dried overnight in a 110 °C oven to remove moisture, sealed with septa and flushed with dry N₂.

Tetrahydrofuran (THF) and diethyl ether (ether) were freshly distilled from sodium benzophenone ketyl before use. Dimethyl ether (Me₂O) was distilled via cannula into the NMR tube from a graduated conical cylinder at -78 °C containing *n*-BuLi (for drying). Common lithium reagents were handled with septum and syringe-based techniques and were titrated using *n*-propanol in THF with 1,10-phenanthroline as an indicator.^{S1} Temperatures of -78 °C were achieved with a dry ice/acetone bath. NMR tubes, injection needles and syringes were kept dry by storing them in an evacuated glove box antechamber.

Tris(trimethylsilyl)methane was purchased, or prepared by reductive silylation of CHCl₃.^{S2} The preparations of 1,1,1-*tris*(trimethylsilyl)ethane (**1-Me**), *tris*(trimethylsilyl)(ethylthio)methane (**1-SEt**) and *tris*(trimethylsilyl)(phenylseleno)methane (**1-SePh**) have been reported previously.^{S3}

NMR Spectroscopy. Routine ¹H and ¹³C NMR spectra were acquired on a 300 MHz spectrometer with CDCl₃ as the solvent and tetramethylsilane as the internal standard (or Ph₃P = -6.0 ppm for ³¹P).

All multinuclear NMR experiments were performed in 10 mm NMR tubes using a wide-bore AM-360 spectrometer at 360.15 MHz (¹H), 52.00 MHz (⁶Li), 139.96 MHz (⁷Li), 90.56 MHz (¹³C), 71.54 MHz (²⁹Si), or 145.78 MHz (³¹P). The digital resolution was 0.15 Hz for ¹H, 0.10 Hz for ⁶Li, 0.51 Hz for ⁷Li, 0.64 Hz for ¹³C, 0.87 Hz for ²⁹Si, and 0.61 Hz for ³¹P. For a typical 0.15 M solution, excellent signal to noise ratios were obtained after 32 transients for ¹H, 96 for ⁶Li (enriched), 32 for ⁷Li, 200 for ¹³C, 128 for ²⁹Si (INEPT), and 80 for ³¹P. All spectra were run with the spectrometer unlocked. ¹³C NMR spectra were referenced internally to the C-O carbon of THF (* 67.96), Et₂O (* 66.57) or Me₂O (* 60.25), and Lorentzian multiplication (LB) of 2-3 Hz was applied. ⁶Li and ⁷Li spectra were referenced externally to 0.3 M LiCl in MeOH (* 0.00) or internally to Li⁺(HMPA)₄ (* -0.40). ³¹P NMR spectra were referenced externally to 1.0 M PPh₃ in THF (* -6.00) or internally to free HMPA (* 26.40). ⁷Li and ³¹P spectra were generally transformed with Gaussian multiplication, with the GB parameter set to the fractional duration of the FID and the LB parameter set to -(digital resolution)/GB.

The lithium reagent samples were prepared in 10 mm thin-walled NMR tubes which were oven-dried, fitted with a septum (9 mm i.d.), and N₂-flushed. The outside top portion of the tube was lightly greased to make a better seal for the septum, which was held securely in place with parafilm. Silicon grease was placed on the septum top to seal punctures, and the tubes were stored at -78 °C until the experiment was performed. Since non-deuterated solvents were used, the spectrometer was run unlocked, and shimming was performed on the ¹³C FID of C-3 of THF or other solvent peak. When a substance had to be added (HMPA, for example), the sample was ejected and placed in a -78 °C bath. In order to get HMPA to dissolve, the tube had to be repeatedly shaken, but each time was returned quickly to the cold bath. Temperatures were measured using either a thermocouple submerged in a second NMR tube containing the same solvent mixture or the internal ¹³C chemical shift thermometer (Me₃Si)₃CH as described below.

Temperature Measurement. The internal NMR sample temperature was routinely measured using the ^{13}C chemical shift difference between the C-H and CH_3 carbon signals of $(\text{Me}_3\text{Si})_3\text{CH}$ (**1-H**) as a shift thermometer.^{S4} Approximately 2-5 μL of 10% ^{13}C enriched reagent in a 3 mL sample (10 mm NMR tube) is adequate to get the temperature in a few scans. With 20 μL the temperature can be measured in one scan, allowing real time measurements of sample temperature, for example, during a RINMR experiment.^{S5} This material was prepared by diluting $^{13}\text{CHCl}_3$ with 9 volumes of natural abundant CHCl_3 and converting to $(\text{Me}_3\text{Si})_3\text{CH}$ using the procedure of Yus and Guijarro (procedure given below),^{S2} or by diluting $(\text{Me}_3\text{Si})_3^{13}\text{CH}$ with 9 volumes of natural abundant material. The calibrations in the original paper (Figure S-1a), as well as some additional new ones (Figure S-1b) are reported below. The equations relating chemical shifts and temperatures are reported in Table 1.

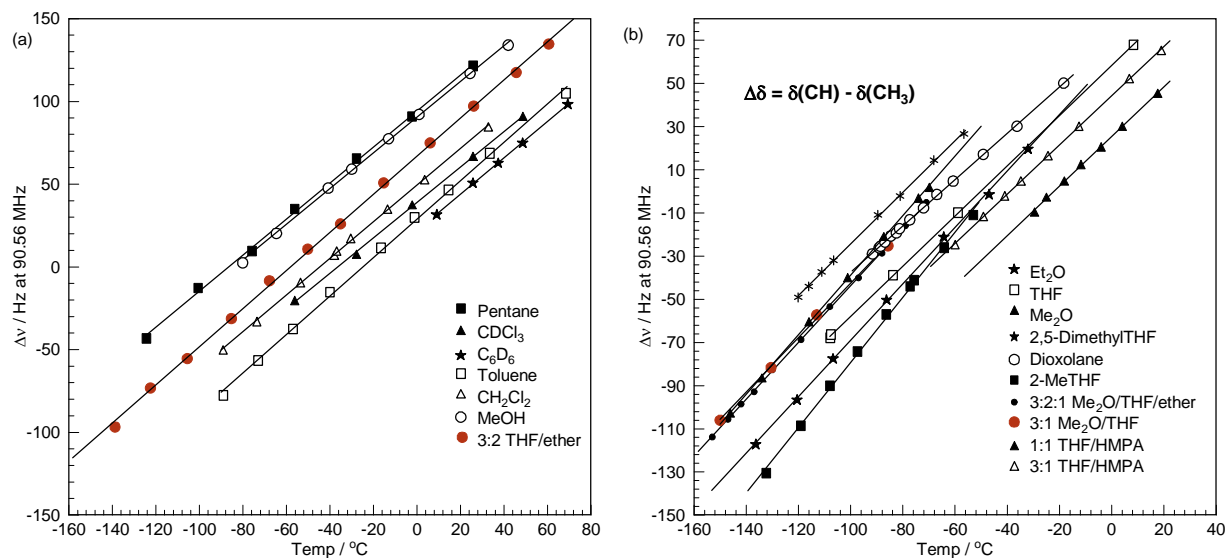
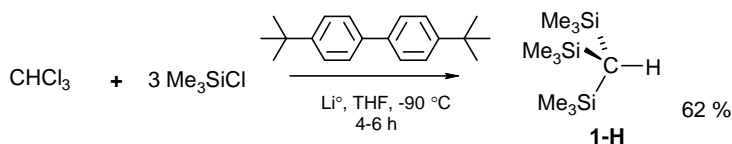
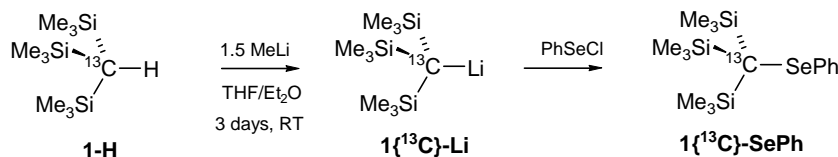


Figure S-1. Calibrations for the use of **1-H** as a chemical shift thermometer. (a) Original data as reported previously.^{S4} (b) New calibrations reported herein.

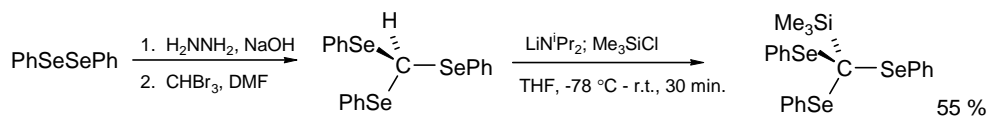
S2. Syntheses



^{13}C -Labeled *Tris*(trimethylsilyl)methane ($1\{^{13}\text{C}\}\text{-H}$) was prepared as previously reported,^{S4} or by a more efficient method involving reductive silylation of $^{13}\text{C}\text{HCl}_3$.^{S2} To a 250 mL rb flask containing a stir bar, in a glove bag under Ar, was weighed 1.4 g of Li^o powder (or chopped lithium wire). The flask was sealed with a septum, removed and 90 mL of THF was added. The flask was cooled to -90°C and 10 mL of THF containing 118 mg (0.44 mmol) of 4,4'-di-*t*-butylbiphenyl was added. The septum was replaced with a dropping funnel containing 1.0 g (8.31 mmol) of $\text{CHCl}_3\text{-}[^{13}\text{C}]$ and 3.16 mL (24.9 mmol) of Me_3SiCl in 50 mL of THF. The mixture was added dropwise over 6 h at -90°C (the reaction is very exothermic and careful addition is recommended), after which the solution was stirred an additional 10 min. The solution was carefully poured over 800 mL of ice in a 1.5 L crystallization dish. The mixture was neutralized with 2 N HCl, extracted with ether (3 x 50 mL), washed with brine (50 mL), and dried over Na_2SO_4 . Removal of the solvent by rotary evaporation yielded a clear pale yellow liquid. Purification of the crude product by kugelrohr distillation (5 mm Hg, $80\text{-}100^\circ\text{C}$) yielded 1.20 g (5.14 mmol, 62 %) of a clear colorless liquid. ^1H NMR (300 MHz, CDCl_3): * -0.78, ($^{13}\text{C}\text{H}$, $^1J_{^{13}\text{C}\text{-}^1\text{H}} = 100$ Hz, d), 0.10 ($\text{Si}(\text{CH}_3)_3$, $^3J_{^{13}\text{C}\text{-}^1\text{H}} = 1.5$ Hz, d). ^{13}C NMR (75.4 MHz, CDCl_3): * 3.98 ($^{13}\text{C}\text{Si}_3$), 3.11 ($\text{Si}(\text{CH}_3)_3$, $^2J_{^{13}\text{C}\text{-}^{13}\text{C}} = 3$ Hz). Mass Spec: $(\text{M}-\text{CH}_3)^+ = 218.1254$ (calc. for $^{13}\text{CC}_9\text{H}_{28}\text{Si}_3 - \text{CH}_3 = 218.1298$).

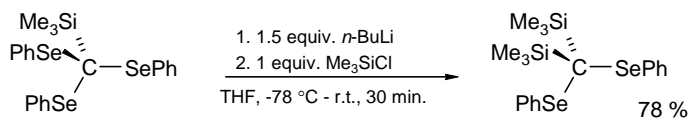


^{13}C labeled Phenylseleno(*tris*(trimethylsilyl)methane ($1\{^{13}\text{C}\}\text{-SePh}$) To a dried, N_2 -purged 10 mm NMR tube (the course of the metalation was studied spectroscopically) were added 0.271 g (1.16 mmol) of ^{13}C -labeled $1\{^{13}\text{C}\}\text{-H}$, 2.1 mL of THF, and 1.4 mL (1.75 mmol) of 1.25 M MeLi in Et_2O . The NMR tube was maintained under positive N_2 pressure (CH_4 is evolved) at room temperature for 3 days. After a VT study (see below), the solution was cooled to -78°C and 0.35 g (1.83 mmol) of PhSeCl was added. The solution was shaken until homogenous and allowed to warm to room temperature. The reaction mixture was taken up in 30 mL of 1:1 Et_2O / hexane, washed with 20 mL of 10% HCl, 20 mL of H_2O , and 20 mL of brine. The solvents were removed by rotary evaporation, and the compound was purified by preparative TLC (with hexane as eluent, $R_f = 0.6$), resulting in 0.16 g (0.41 mmol, 35.3 %) of a pale yellow liquid. The solution contained about 10% of $1\{^{13}\text{C}\}\text{-H}$, which is useful as an internal temperature reference, so further purification was not attempted. ^1H NMR (300 MHz, CDCl_3): * 0.20 (CH_3 , d, $^3J_{\text{H-C}} = 1.29$ Hz, 27 H), * 7.17-7.33 (Ph, m, 3H), * 7.81-7.85 (Ph, m, 2H). ^{13}C NMR (75.4 MHz, CDCl_3): * 3.61 (CH_3 , d, $^2J_{\text{C-C}} = 3.18$ Hz), * 16.54 (C, $^1J_{\text{C-Se}} = 73.1$ Hz, $^1J_{\text{C-Si}} = 35.6$ Hz), * 128.22 (CH), * 128.61 (CH), * 129.37 (C), * 138.46 (CH).

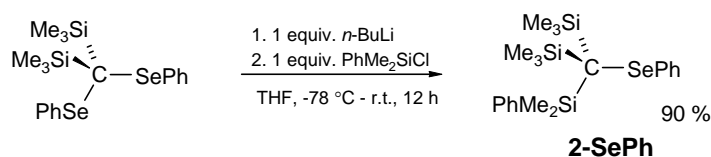


***Tris*(phenylseleno)(trimethylsilyl)methane.** To an oven dried, 25 mL round bottom flask, equipped with a stir bar was added 1.514 g (3.15 mmol) of *tris*(phenylseleno)methane (prepared from bromoform and sodium phenylselenolate^{S6}). The flask was fitted with a septum, purged with N_2 , and 10 mL of THF

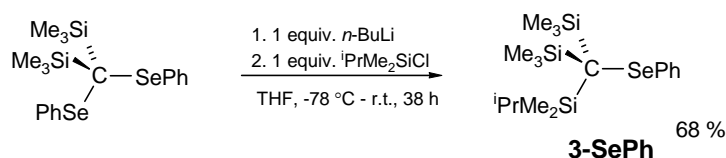
was added. The solution was cooled to -78°C and 2.63 mL (3.16 mmol) of 1.2 M LDA in hexanes was added followed by 405 μL (3.19 mmol) of Me_3SiCl . The reaction was stirred for an additional 15 min at -78°C , and then allowed to warm to r.t. The reaction was diluted with 50 mL of 1:1 ether/hexanes, washed with water (2 x 80 mL) and brine (1 x 50 mL), dried over Na_2SO_4 . Removal of the solvent by rotary evaporation yielded a clear red liquid. Recrystallization of the crude product from hexanes yielded 0.86 g (1.55 mmol, 55 %) of off-white prisms (mp $114 - 117^{\circ}\text{C}$). $^1\text{H NMR}$ (300 MHz, CDCl_3): * -0.24 ($\text{Si}(\text{CH}_3)_3$, s), 7.27-7.42 (9-PhSe, m), 7.83-7.87 (6-PhSe, m). $^{13}\text{C NMR}$ (75.4 MHz, CDCl_3): * 0.04 ($\text{Si}(\text{CH}_3)_3$), 128.51 (o-Ph), 129.25 (p-Ph), 130.12 (i-Ph), 137.69 (m-Ph). Mass Spec: $[\text{M}-\text{SePh}]^+ = 398.9573$ (calc. for $\text{C}_{16}\text{H}_{19}\text{SiSe}_2 = 398.9581$).



Bis(phenylseleno)bis(trimethylsilyl)methane. To an oven dried, 50 mL round bottom flask, equipped with stir bar, was added 4.43 g (8.0 mmol) of *tris*(phenylseleno)(trimethylsilyl)methane. The flask was fitted with a septum, purged with N_2 , and 25 mL of THF was added. The solution was cooled to -78°C and 2.55 mL (8.0 mmol) of 3.15 M *n*-BuLi in hexanes was added followed, after 5 min., with 1.5 mL (11.8 mmol) of Me_3SiCl . The reaction was stirred for an additional 5 min at -78°C , and then allowed to warm to r.t. The reaction was diluted with 50 mL of 1:1 ether/hexanes, washed with water (2 x 80 mL) and brine (1 x 50 mL), dried over Na_2SO_4 . Removal of the solvent by rotary evaporation yielded a clear red liquid. Removal of PhSeBu (by product of Li-Se exchange) was accomplished by kugelrohr distillation (80°C at 0.01 mmHg). Recrystallization of the remaining crude product from hexanes yielded 2.92 g (6.2 mmol, 78 %) of white needles (mp $78 - 79^{\circ}\text{C}$). $^1\text{H NMR}$ (300 MHz, CDCl_3): * -0.06 ($\text{Si}(\text{CH}_3)_3$, s), 7.18-7.35 (6-PhSe, m), 7.86-7.91 (4-PhSe, m). $^{13}\text{C NMR}$ (75.4 MHz, CDCl_3): * 1.10 ($\text{Si}(\text{CH}_3)_3$), 128.47 (o-Ph), 128.95 (p-Ph), 129.49 (i-Ph), 137.51 (m-Ph). Mass Spec: $\text{M}^+ = 472.0071$ (calc. for $\text{C}_{19}\text{H}_{28}\text{Se}_2\text{Si}_2 = 472.0063$).

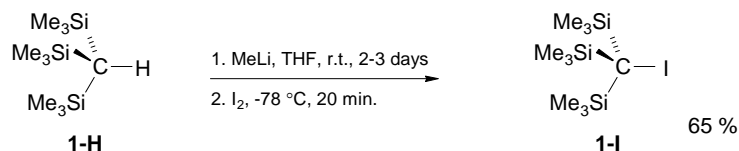


Phenylseleno(phenyldimethylsilyl)bis(trimethylsilyl)methane (2-SePh). To an oven dried, 50 mL rb flask with stir bar was added 3.17 g (6.74 mmol) of *bis*(phenylseleno)*bis*(trimethylsilyl)methane. The flask was fitted with a septum, purged with N_2 , and 20 mL of THF was added. The solution was cooled to -78°C and 2.30 mL (6.74 mmol) of 2.9 M *n*-BuLi in hexanes followed by 1.13 mL (6.74 mmol) of PhMe_2SiCl were added. The reaction was stirred for an additional 1 h at -78°C , and then allowed to warm to r.t. overnight. The reaction was diluted with 50 mL of 1:1 ether/hexanes, washed with water (2 x 80 mL) and brine (1 x 50 mL), dried over Na_2SO_4 . Removal of the solvent by rotary evaporation yielded a clear orange liquid. Removal of the byproducts (mainly PhSeBu) by kugelrohr distillation (0.05 mm Hg, $120-130^{\circ}\text{C}$) yielded 2.72 g (6.0 mmol, 90 %) of a clear yellow liquid. $^1\text{H NMR}$ (300 MHz, CDCl_3): * 0.04 ($\text{Si}(\text{CH}_3)_3$, s), 0.58 ($\text{Si}(\text{CH}_3)_2$, s), 7.14-7.39 (6-Ph, m), 7.66-7.72, 7.87-7.91 (4-Ph, m). $^{13}\text{C NMR}$ (75.4 MHz, CDCl_3): * 1.10 (CSi_3Se), 2.38 ($\text{Si}(\text{CH}_3)_2$), 3.61 ($\text{Si}(\text{CH}_3)_3$), 127.32 (o-PhSi), 128.18 (o-PhSe), 128.63 (p-PhSe), 129.04 (i-PhSe), 135.70 (m-PhSi), 138.33 (m-PhSe), 137.47 (p-PhSi), 140.19 (i-PhSi).



Phenylseleno(isopropyl-dimethylsilyl)bis(trimethylsilyl)methane (3-SePh). To an oven dried, 25 mL round bottom flask with stir bar was added 1.91 g (4.06 mmol) of bis(trimethylsilyl)phenylselenane. The flask was fitted with a septum, purged with N₂, and 20 mL of THF was added. The solution was cooled to -78 °C and 1.10 mL (4.17 mmol) of 3.8 M *n*-BuLi in hexanes was added, followed after 20 min with 0.654 mL (4.16 mmol) of *i*PrMe₂SiCl. The reaction was warmed to r.t. and stirred for 38 h. The reaction was diluted with 50 mL of 1:1 ether/hexanes, washed with water (2 x 80 mL) and brine (1 x 50 mL), dried over Na₂SO₄. Removal of the solvent by rotary evaporation yielded a clear orange liquid. The byproducts (mainly PhSeBu) was removed by kugelrohr distillation (0.01 mm Hg, 90 °C). Preparatory TLC using hexanes as eluent (R_f = 0.5) yielded 1.15 g (2.75 mmol, 68 %) of a clear pale yellow liquid. ¹H NMR (300 MHz, CDCl₃): * 0.18 (Si(CH₃)₃, s), 0.20 (Si(CH₃)₂, s), 1.10 ((CH₃)₂, d), 1.24 (Si(CH), m), 7.17-7.33 (3-Ph, m), 7.80-7.85 (2-Ph, m). ¹³C NMR (75.4 MHz, CDCl₃): * -0.42 (Si(CH₃)₂), 3.98 (Si(CH₃)₃), 14.50 (Si(CH)), 20.31 ((CH₃)₂), 128.24 (o-PhSe), 128.60 (p-PhSe), 129.52 (i-PhSe), 138.33 (m-PhSe). Mass Spec: {M-*i*Pr}⁺ = 373.0760 (calc. for C₁₅H₂₉SeSi₃ = 373.0742).

A variable temperature ¹³C NMR experiment on **1-SePh** is shown in Figure 1a, demonstrating dynamic properties of the trimethylsilyl groups.



Tris(trimethylsilyl)iodomethane (1-I). This compound was prepared using a literature procedure.^{S7} To an oven dried, 25 mL round bottom flask with stir bar was added 1.0 mL (3.56 mmol) of tris(trimethylsilyl)methane (**1-H**). The flask was fitted with a septum, purged with N₂, and 15 mL of THF and 4.0 mL (4.44 mmol) of 1.11 M MeLi in ether. The septum was greased and the solution stored at r.t. for 3 days during which the methane was allowed to escape periodically by inserting a needle. After metalation was complete the flask containing a pale yellow clear solution was cooled to -78 °C, and 1.13 g (4.45 mmol) of iodine in 3 mL of THF was added via cannula. The solution was stirred for 20 min and warmed to r.t. The solution was diluted with water (40 mL) and extracted with 30 mL of 1:1 ether/hexanes, washed with Na₂S₂O₃ (2 x 80 mL) and brine (1 x 50 mL), dried over Na₂SO₄. Removal of the solvent by rotary evaporation yielded a yellow paste. Recrystallization of the crude product from methanol yielded after 3 crops 826 mg (0.65 mmol, 65 %) of very small white needles. ¹H NMR (300 MHz, CDCl₃): * 0.27 (Si(CH₃)₃, s). ¹³C NMR (75.4 MHz, CDCl₃): * 3.26 (CSi₃I), 3.42 (Si(CH₃)₃).

Tris(trimethylsilyl)iodomethane-[¹³C] (1-¹³C-I). The ¹³C-labeled analog of **1-I** was prepared using the procedure described for the unlabeled compound. ¹H NMR (300 MHz, CDCl₃): * 0.27 (Si(CH₃)₃, d, ³J_{C-H} = 2.2 Hz). ¹³C NMR (75.4 MHz, CDCl₃): * 3.95 (C-I), 3.71 (Si(CH₃)₃, d, ²J_{C-C} = 39 Hz). Mass Spec: M⁺ = 359.0495 (calc. for ¹³CC₉H₂₇Si₃I = 359.0499).

S3. Spectroscopy

^{13}C Variable Temperature Study of 1-SePh. To a dried, N_2 -purged, 10 mm NMR tube fitted with a septum and maintained under positive N_2 pressure were added 0.195 g (0.503 mmol) of *tris*(trimethylsilyl)methyl phenyl selenide (**1-SePh**), 1.8 mL of THF, and 1.2 mL of Et_2O . A ^{13}C VT study was performed on the selenide. Spectra are shown in Figure 1a.

^{13}C Variable Temperature Study of 1-I. To a dried, N_2 -purged, 5 mm NMR tube fitted with a septum and maintained under positive N_2 pressure were added 0.07 g (0.195 mmol) of *tris*(trimethylsilyl)methyl iodide (**1-I**), 0.6 mL of THF, and 0.4 mL of Et_2O . A ^{13}C and ^1H VT study was performed on the iodide. Spectra are shown in Figure 1b. To avoid interference, the experiment was performed without the ^{13}C chemical shift thermometer,^{S4} then 2 : L was added and the experiment repeated to get accurate temperatures.

***Tris*(trimethylsilyl)methyl lithium (**1-Li**) - Typical Metalation Procedure.** To a dried, N_2 -purged, 10 mm NMR tube fitted with a septum and maintained under positive N_2 pressure were added 116 mg (0.500 mmol) of *tris*(trimethylsilyl)methane (**1-H**), 1.8 mL of THF, 1.6 mL of Et_2O , and 0.54 mL (0.70 mmol) of 1.29 M MeLi in Et_2O . The tube was maintained at room temperature for 4 days. When not being studied spectroscopically, the NMR tube was maintained under positive N_2 pressure, or was vented regularly to release the CH_4 formed. A series of ^{13}C NMR spectra were taken over the course of 4 days to monitor the room temperature metalation. Figure S-2 shows room-temperature ^{13}C NMR spectra of the sample, and a log-log plot of the concentration of the two species formed, showed a 2:1 relationship (dimer **1T** and monomers).

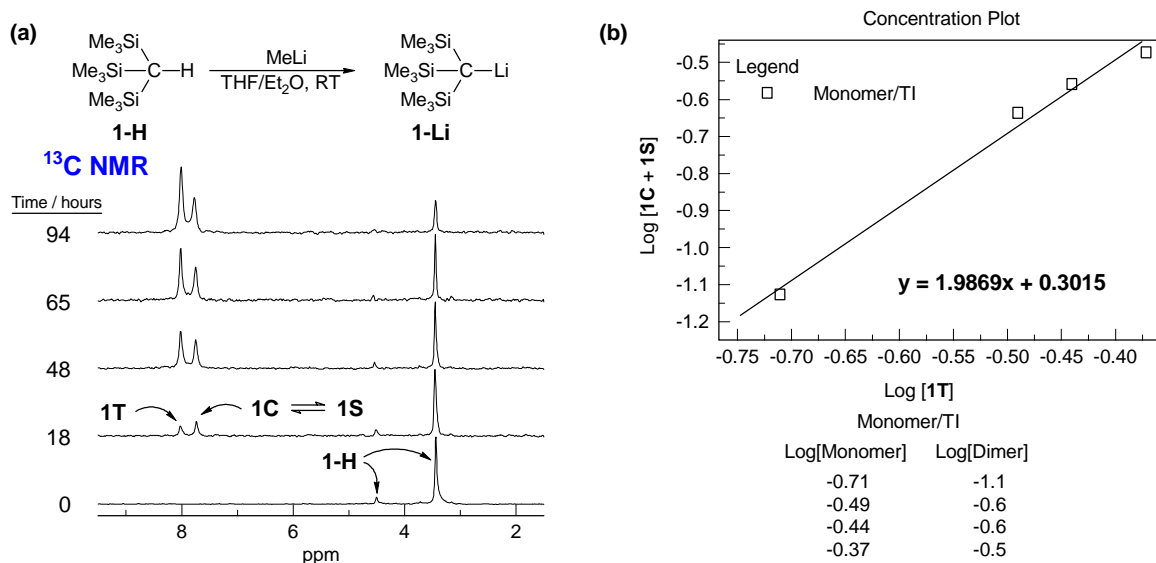


Figure S-2: ^{13}C NMR spectra showing the progress of the metalation of 0.16 M *tris*(trimethylsilyl)methane (**1-H**) by MeLi in 1:1 THF/ Et_2O at room temperature over 4 days. Spectra were acquired at 25 $^\circ\text{C}$.

Results from a variable temperature ^{13}C NMR study on this sample are reported in Figure S-3.

A similar sample was used for a ^{29}Si VT Study using the INEPT pulse sequence. Spectra in Figure S-4.

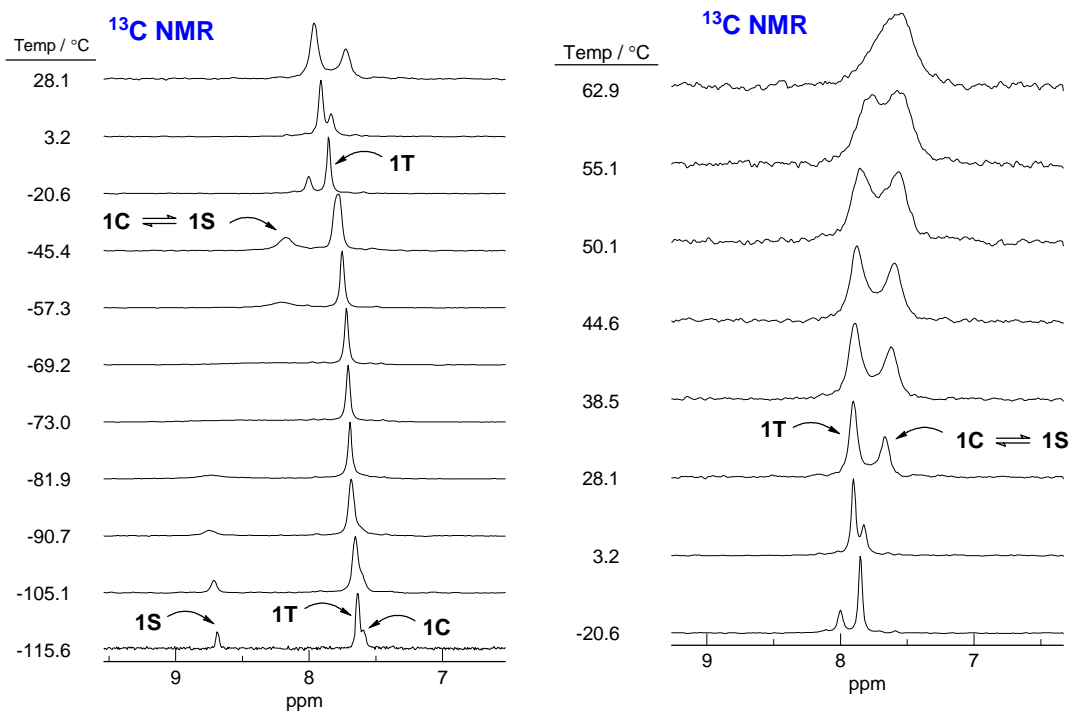


Figure S-3. ^{13}C NMR spectra from a variable temperature study of 0.16 M **1-Li** in 1:1 THF/Et₂O.

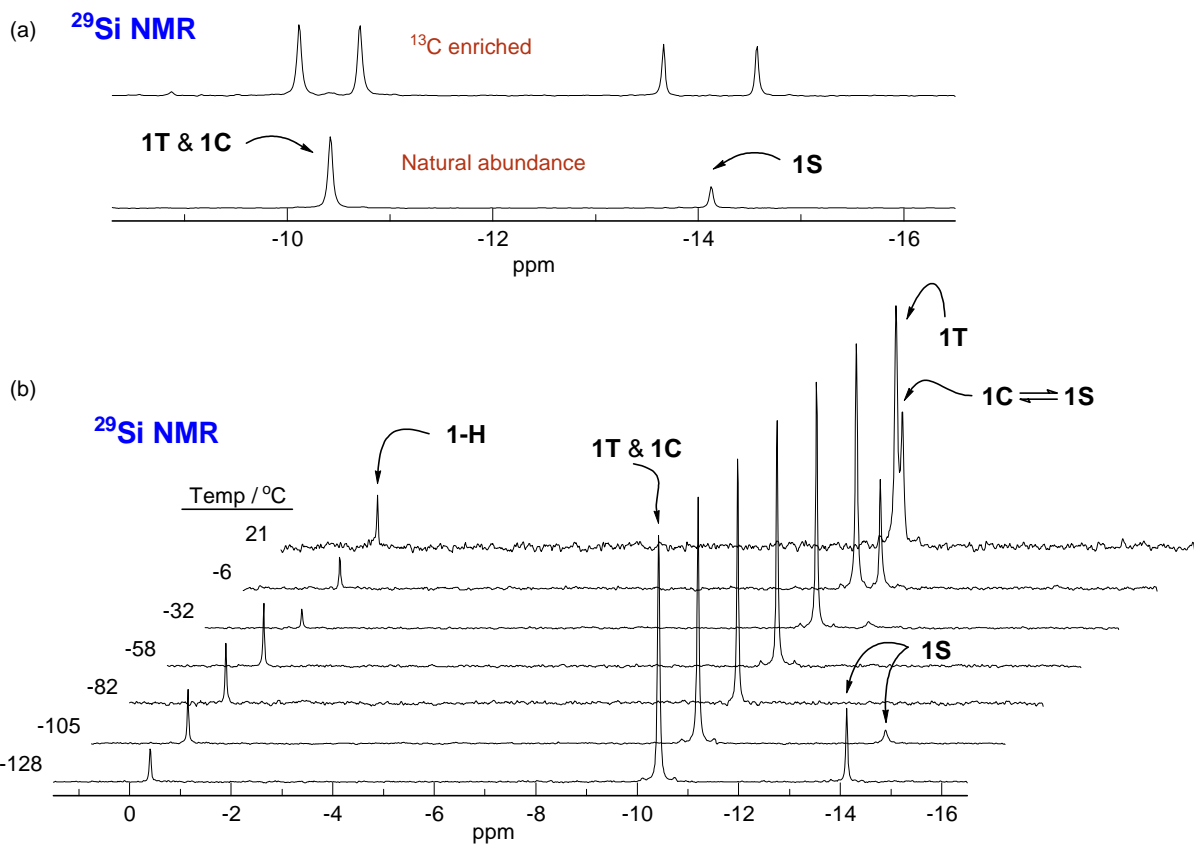


Figure S-4. (a) ^{29}Si NMR spectra of unlabeled (1:1 THF/Et₂O) and ^{13}C -labeled **1-Li** (3:2 THF/Et₂O) at -128 °C. (b) ^{29}Si NMR spectra from a variable temperature study of 0.16 M **1-Li** in 1:1 THF/Et₂O.

Variable Concentration Studies. To a flame-dried, N₂ purged flask was added 4.9 mL of THF and 3.3 mL of Et₂O. In a separate flame-dried, N₂ purged flask was weighed **1-SePh** (0.267 g, 0.69 mmol). To that flask was added 1.53 mL of the previously prepared 3:2 THF/Et₂O solvent mixture. The flask was then cooled in a dry ice/acetone bath and *n*-BuLi (2.52 M in hexanes, 0.26 mL, 0.66 mmol) was added to form a 0.4 M solution of **1-Li** in 3:2:0.87 THF/Et₂O/Hexanes. After warming to room temperature, four aliquots of the lithium reagent solution (0.1 mL, 0.2 mL, 0.4 mL and 0.8 mL) were transferred to separate 5 mm NMR tubes. In order to maintain the same solvent composition in each of the four samples, 1.26 mL of hexanes was added to the remaining 6.7 ml of 3:2 THF/Et₂O solution for a 3:2:0.95 THF/Et₂O/Hexanes stock solution. Aliquots of this mixture were then added to each sample in order to bring the total volume to 0.8 mL. The samples were transferred to the NMR spectrometer. ¹H NMR spectra were collected on each sample at ambient temperature and at -118 °C. Each sample contained small amounts of protonation product **1-H**. The total concentration of (Me₃Si)₃C-X (X= H, Li) for each sample was calculated from the concentration of the original lithium reagent solution, and the concentrations of the individual species were calculated as the fraction of the total concentration. The relative amounts of each species were determined by peak areas measured using WINDNMR simulation.^{S8} Results are shown in Tables S-1 and S-2, Figure 3, and Figure S-5.

Table S-1. Concentrations of separated ion, contact ion and triple ion for four concentrations of *tris*(trimethylsilyl)methyl lithium in 3:2:0.9 THF/Et₂O/Hexanes at ambient temperature, where the CIP and SIP are coalesced into a single peak.

Experiment:	A	B	C	D
[(Me ₃ Si) ₃ C-Li]	0.049 M	0.098 M	0.2 M	0.39 M
[1T]	0.015 M	0.045 M	0.12 M	0.25 M
[1C+1S]	0.027 M	0.045 M	0.065 M	0.12 M

Table S-2. Concentrations of separated ion, contact ion and triple ion for four concentrations of *tris*(trimethylsilyl)methyl lithium in 3:2:0.9 THF/Et₂O/Hexanes at -118 °C.

Experiment:	A	B	C	D
[(Me ₃ Si) ₃ C-Li]	0.049 M	0.098 M	0.2 M	0.39 M
[1T]	0.015 M	0.051 M	0.12 M	0.28 M
[1C]	0.018 M	0.025 M	0.038 M	0.057 M
[1S]	0.005 M	0.009 M	0.016 M	0.027 M

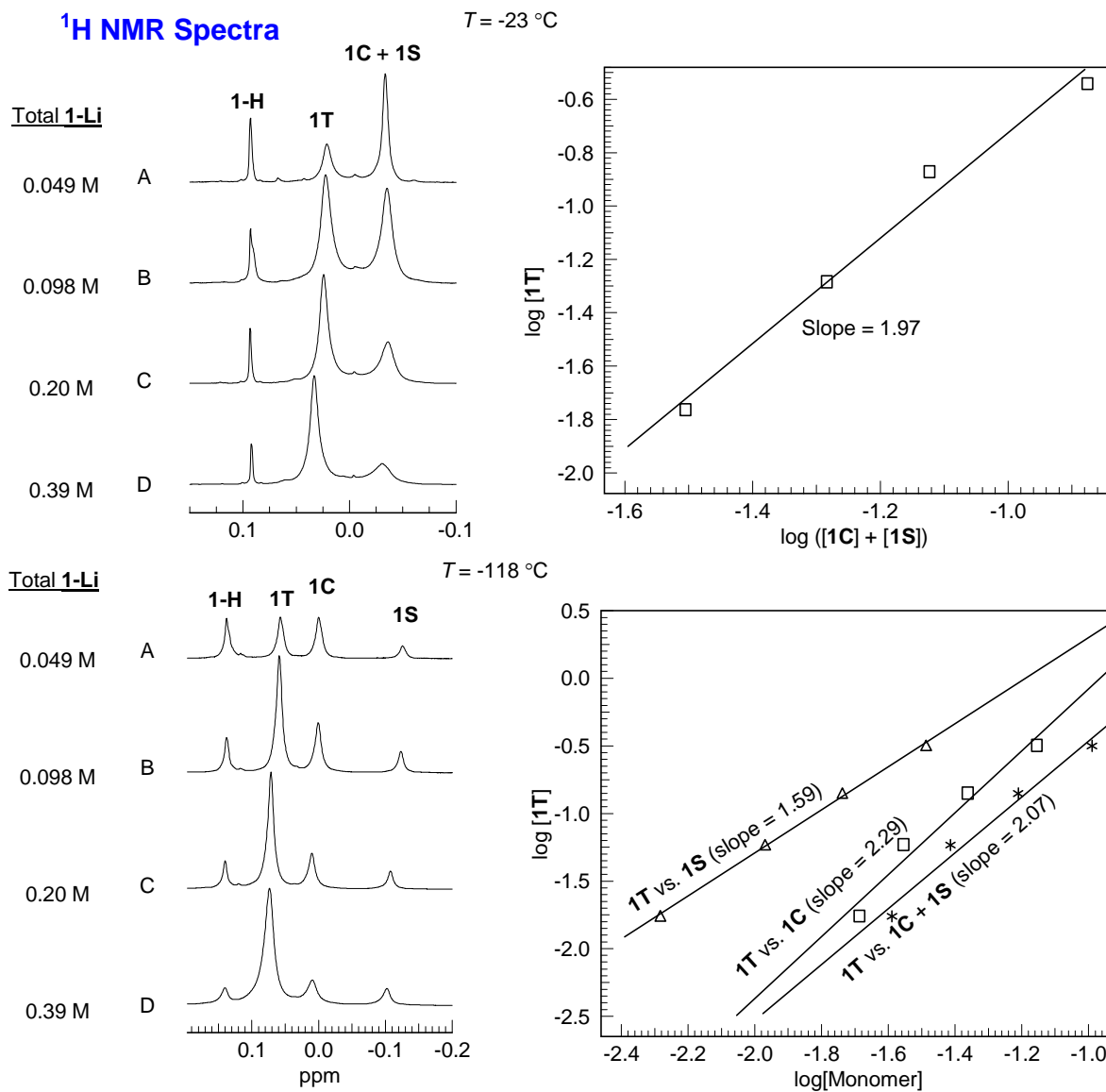


Figure S-5. ^1H NMR spectra of variable concentration solutions of **1-Li** in 3:2:0.9 THF/Et₂O/Hexanes at ambient temperature and at $-118\text{ }^\circ\text{C}$. Plots of $\log[1\text{T}]$ vs. $\log[\text{Monomer}]$ at ambient temperature and of $\log[1\text{T}]$ vs. $\log[1\text{C}]$ and $\log[1\text{T}]$ vs. $\log[1\text{S}]$ at $-118\text{ }^\circ\text{C}$. Least squares lines are shown.

Tris(trimethylsilyl)methylithium (1-⁶Li) - Typical procedure for Preparation of 1-⁶Li from 1-SePh. To a dried, N₂-purged, 10 mm NMR tube fitted with a septum and maintained under positive N₂ pressure were added 0.204 g (0.526 mmol) of **1-SePh**, 7 : L of the ¹³C chemical shift thermometer^{S4} (1:10 ratio of ¹³C-labeled and unlabeled **1-H**), 1.8 mL of THF, and 1.2 mL of Et₂O. The solution was cooled to -78 °C and 0.34 mL (0.524 mmol) of 1.54 M *n*-Bu⁶Li in pentane were added.

Variable Temperature ¹H and ⁶Li NMR Study. A variable-temperature NMR study using proton and lithium nuclei are shown in Figure S-6.

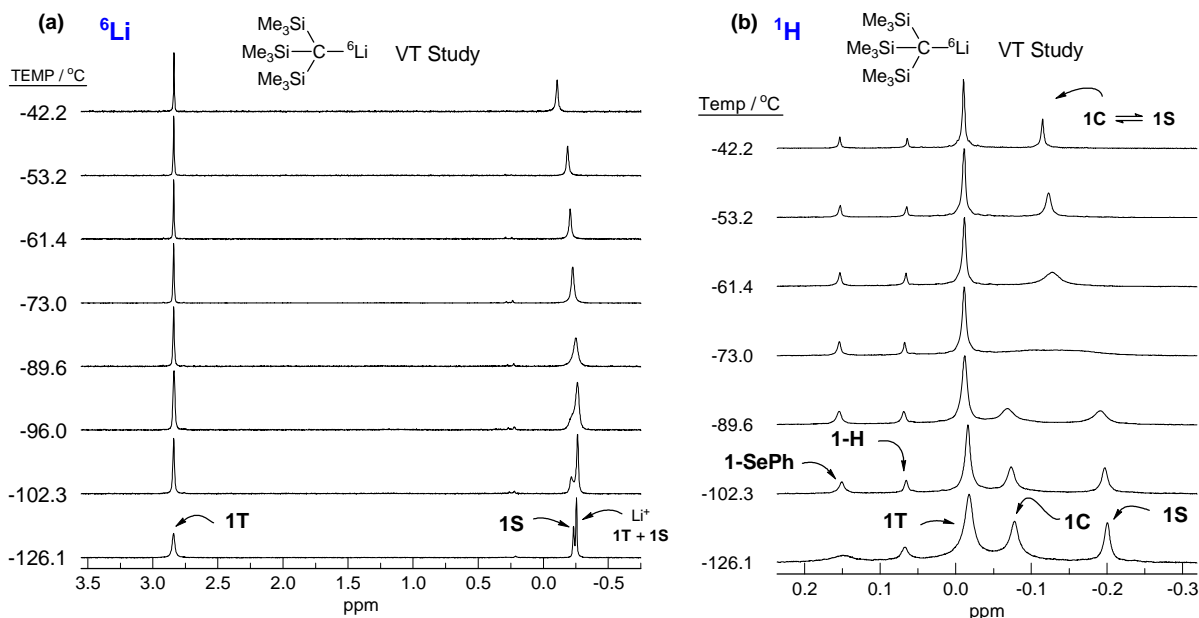


Figure S-6. ⁶Li (a) and ¹H (b) NMR spectra from a variable temperature study of 0.16 M ⁶Li-enriched *tris*(trimethylsilyl)methylithium (**1-⁶Li**) in 3:2 THF/Et₂O.

Variable Temperature ¹³C NMR Study. A ¹³C NMR VT study was performed on the sample prepared above from -135 to +50 °C in 5 to 10 degree increments. The temperature was allowed to stabilize for 20 min at each new temperature before acquiring data. Internal sample temperatures were measured using the ¹³C shift thermometer.^{S4} The Me₃Si signals for the low-temperature region (Figures S-7 and S-8a) were simulated using WINDNMR as a 3-spin system, but with the rate constants for formation and decomposition of **1T** set to zero, since the rates are insignificant in this region. The high temperature region (Figure S-7b and S-8b) was simulated as a two-site exchange, since the signals for **1S** and **1C** are fully coalesced in this region. The principal peaks in the difference spectra (spectrum-simulation) were the ²⁹Si satellites, which were not included in the simulation. The activation parameters reported in Figure S-8 and Figure 8 were determined in this experiment.

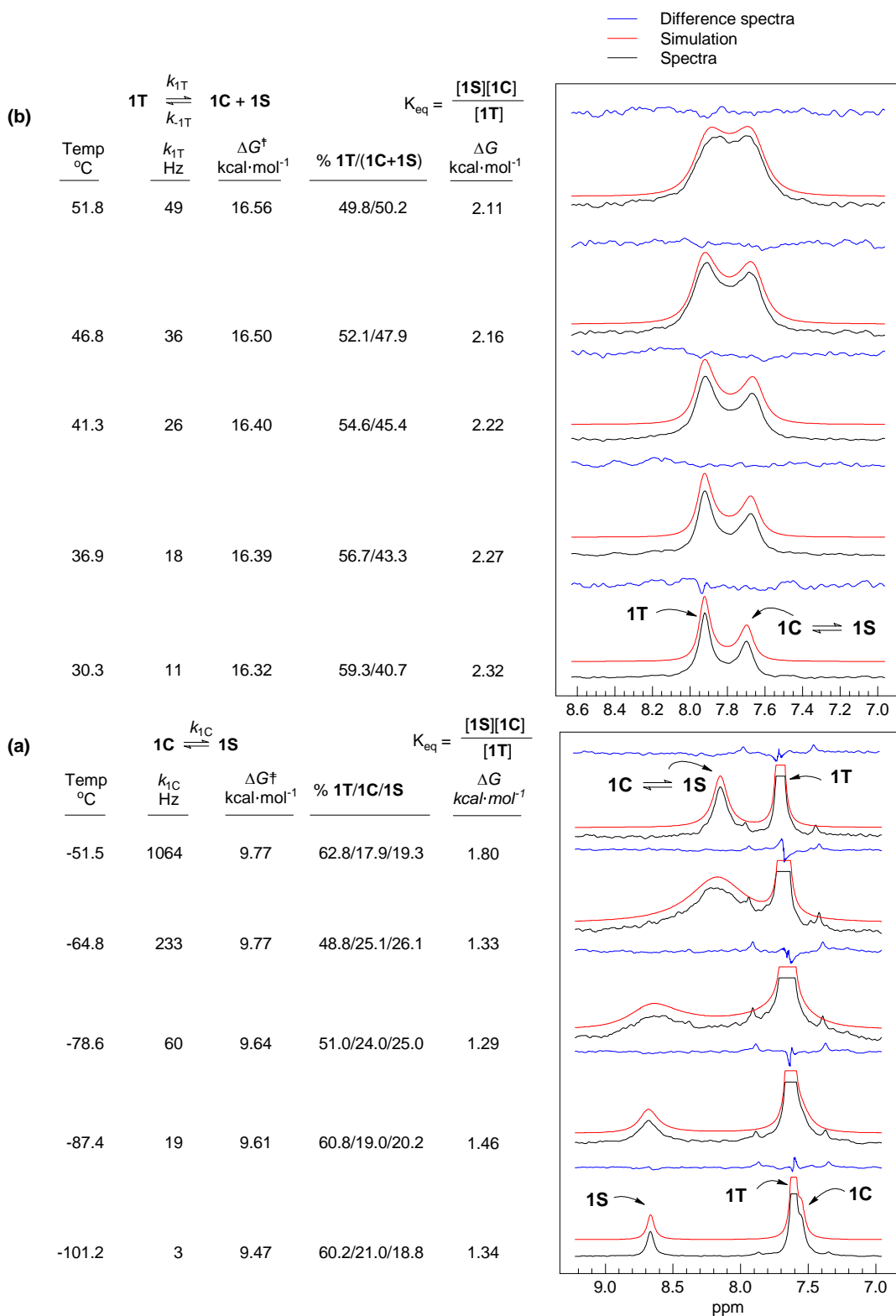


Figure S-7. NMR spectra, simulations and difference spectra of ¹³C NMR spectra (Me₃Si signals) from a variable-temperature NMR study of 0.15 M **1-⁶Li** in 3:2 THF/Et₂O. (a) Coalescence of **1C** and **1S**. (b) Coalescence of **1T** with the averaged signal of **1C** and **1S**. The concentrations of **1C** and **1S** could not be individually measured in the high temperature region, and were assumed to be equal in the calculation of ΔG .

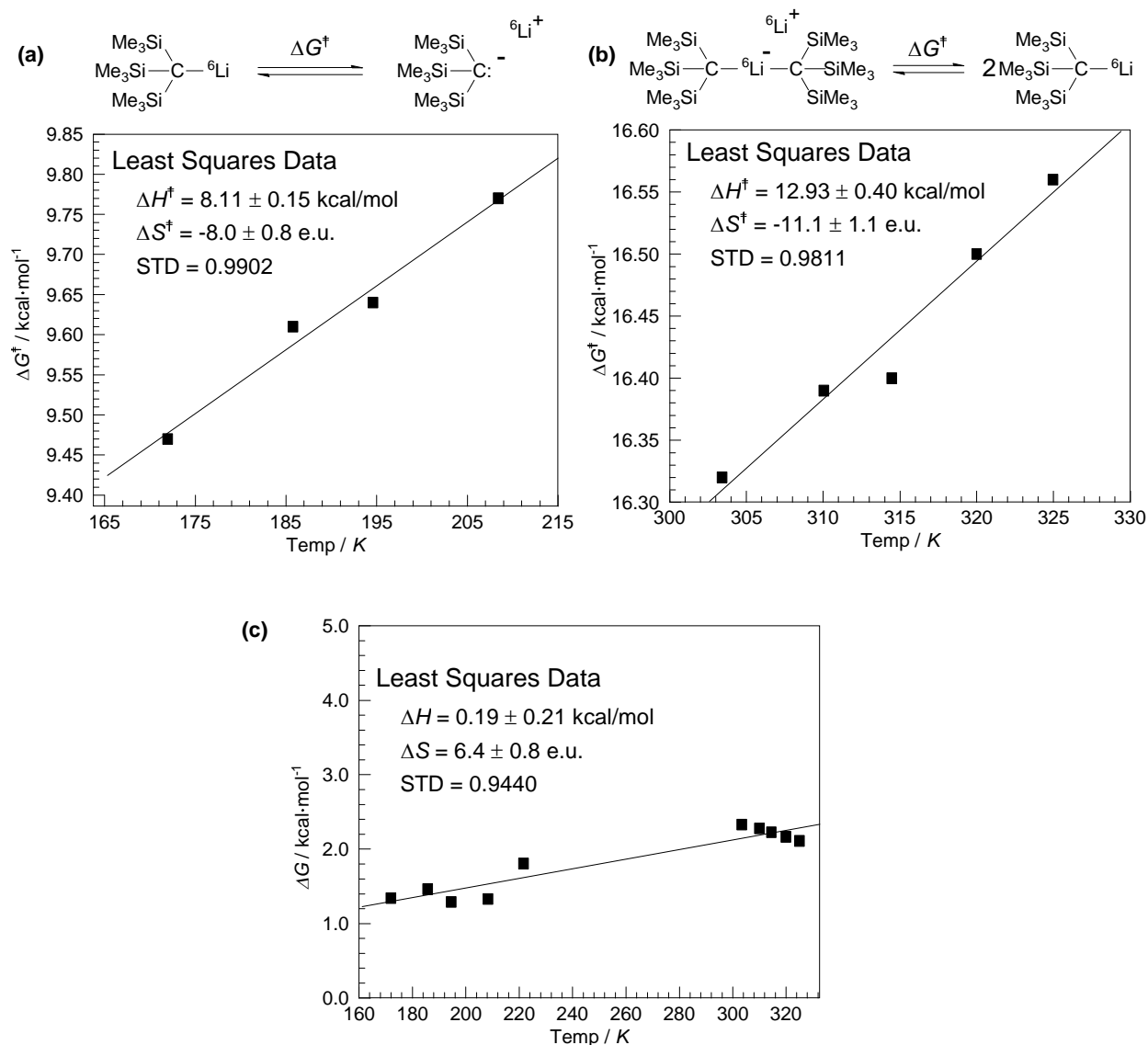


Figure S-8. Determination of thermodynamic and activation parameters for interconversion of **1T**, **1C** and **1S**. (a) Plot of ΔG^\ddagger vs temperature for the conversion of **1C** to **1S**. (b) Plot of ΔG^\ddagger vs temperature for the conversion of **1T** to **1C/1S** in 3:2 THF/Et₂O for 0.15 M **1-⁶Li** in 3:2 THF/Et₂O. A second measurement of the high-temperature coalescence taken on a different sample under slightly different conditions gave $\Delta H^\ddagger = 13.43 \pm 0.48 \text{ kcal/mol}$, $\Delta S^\ddagger = -11.1 \pm 1.1 \text{ e.u.}$ (c) Temperature dependence of the equilibrium between **1T** and **1C/1S**.

^{13}C -Labeled *Tris(trimethylsilyl)methyl*lithium ($1\{^{13}\text{C}\}\text{-}^7\text{Li}$) Variable Temperature Study. To a dried, N_2 -purged, 10 mm NMR tube fitted with a septum and maintained under positive N_2 pressure were added 0.271 g (1.16 mmol) of ^{13}C -labeled *tris(trimethylsilyl)methane* ($1\{^{13}\text{C}\}\text{-H}$), 2.1 mL of THF, and 1.4 mL (1.75 mmol) of 1.25 M MeLi in Et_2O (in theory producing a 0.33 M solution of $1\{^{13}\text{C}\}\text{-Li}$). The course of the room temperature metalation was followed over three days with ^{13}C NMR spectra acquired at $-135\text{ }^\circ\text{C}$. After 72 h, the metalation was 97% complete. A ^{29}Si NMR spectrum was taken at this temperature, followed by a ^{13}C VT study. Results are shown in Figures 7 and S-9. The anion was quenched with PhSeCl, generating $1\{^{13}\text{C}\}\text{-SePh}$ for reuse in other experiments.

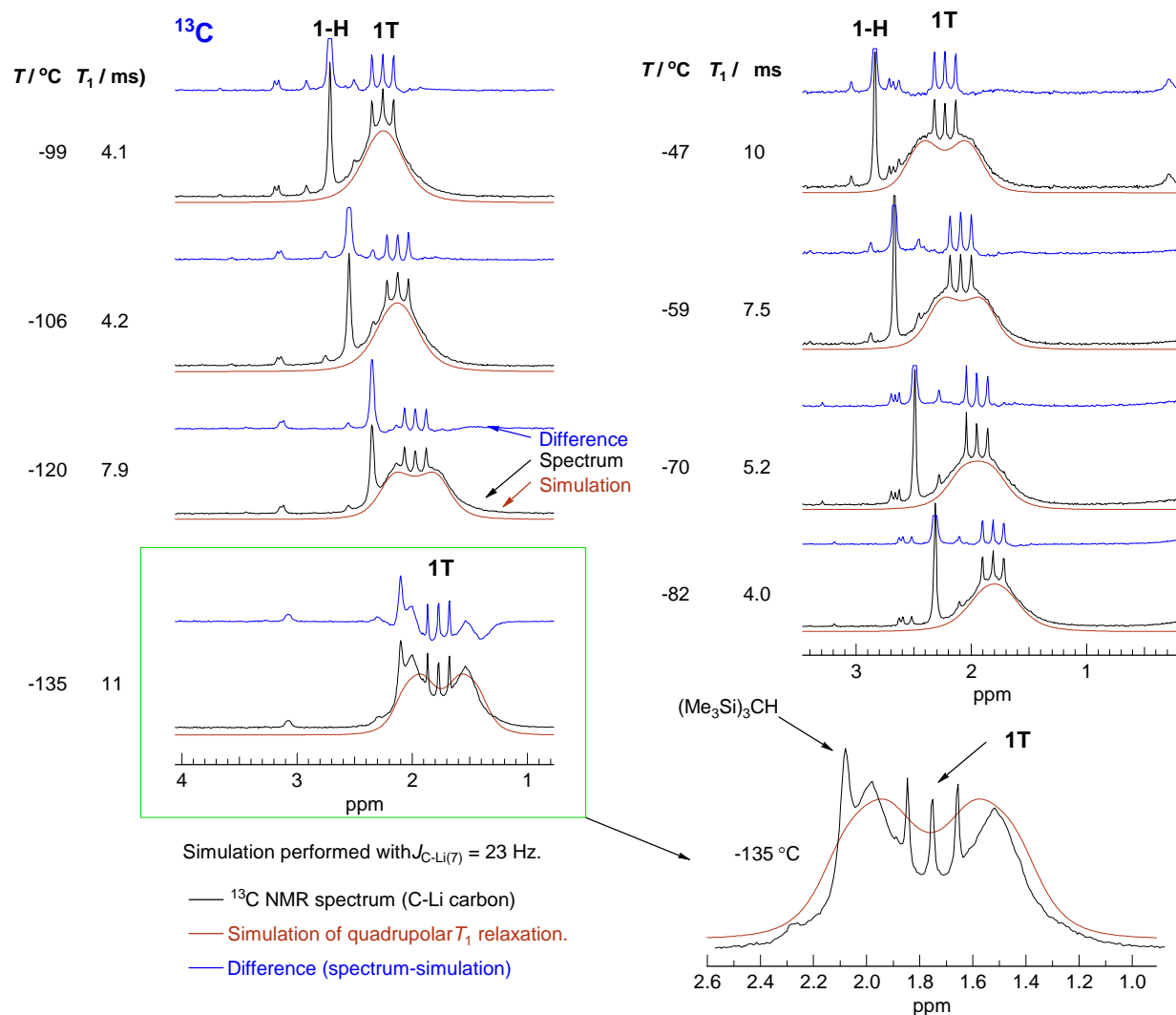


Figure S-9. Variable temperature ^{13}C NMR study of $[^{13}\text{C}]\mathbf{1}\text{-Li}$ in 3:2 THF/ Et_2O (these are the same spectra reported in Figure 7). The black curves are the ^{13}C NMR spectra of the C-Li carbon, the red lines are simulation of the $\text{C-}^7\text{Li}$ portion of the signal, and the blue curves are difference spectra (spectrum-simulation). The simulation were carried out^{S8} using the exchange matrix for quadrupolar relaxation of the spin $3/2\ ^7\text{Li}$ signal reported,^{S9,S10} with $J_{\text{C-Li}} = 23\text{ Hz}$ and the indicated T_1 relaxation times. Note that a good fit could not be obtained for the $-135\text{ }^\circ\text{C}$ spectrum, the experimental spectrum shows a much deeper dip between the signals of the “doublet” than could be achieved with the simulation at any setting of $J_{\text{C-Li}}$ and T_1 (quadrupolar). A similar line shape has been observed for a $^{31}\text{P}\text{-}^7\text{Li}$ coupled signal.^{S11} Perhaps there are additional contributions to the relaxation rate which lead to the altered line shape.

^{13}C -Labeled *Tris*(Trimethylsilyl)methyl lithium ($1\{^{13}\text{C}\}\text{-}^6\text{Li}$) Variable Temperature Study. To a dried, N_2 -purged, 10 mm NMR tube fitted with a septum and maintained under positive N_2 pressure were added 0.159 g (0.409 mmol) of $1\{^{13}\text{C}\}\text{-SePh}$, 1.8 mL of THF, and 1.2 mL of Et_2O . The NMR tube was frozen in $\text{N}_2(l)$ before submerging the length of the tube in a $-130\text{ }^\circ\text{C}$ bath of $\text{N}_2(l)$ / pentane. To the tube were added 0.23 mL of *n*-Bu ^6Li (0.354 mmol — the starting material contained 10% $1\{^{13}\text{C}\}\text{-H}$), slowly along the inside of the NMR tube, cooling it in the process. The NMR tube was alternately shaken and re-submerged until the solution had completely melted. The solution was frozen again in $\text{N}_2(l)$ and transferred to the NMR probe, which had been cooled to $-130\text{ }^\circ\text{C}$. The probe was warmed to $-120\text{ }^\circ\text{C}$ to allow the sample to melt (the progress of which could be followed by monitoring the increase in the FID area). A ^{13}C and ^6Li VT study was performed. Some spectra from this study are shown in Figures 6, 9, S-4a, S-10, S-11 and S-12.

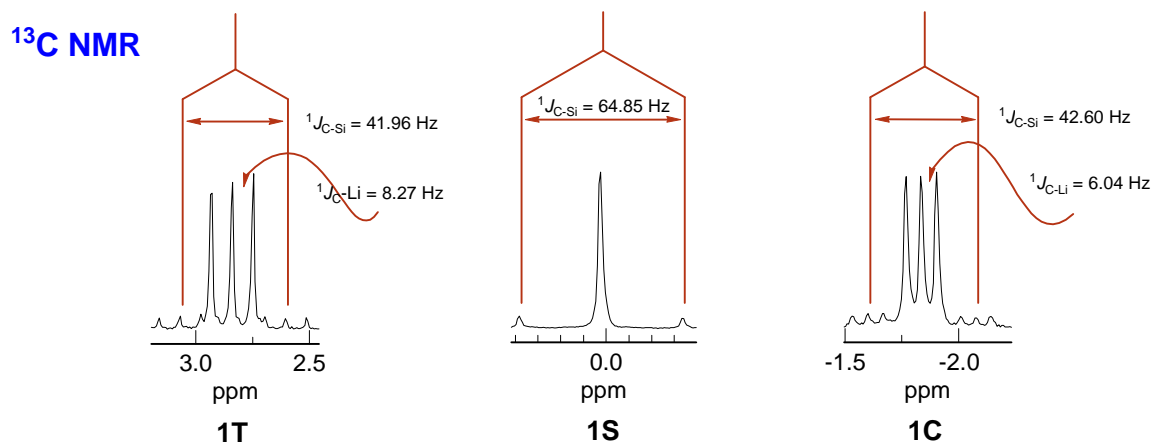


Figure S-10. Expansions of the carbanion carbons of **1T** (at $-45\text{ }^\circ\text{C}$), **1S** ($-111\text{ }^\circ\text{C}$), and **1C** ($-111\text{ }^\circ\text{C}$) for ^{13}C - and ^6Li -labeled 0.12 M *tris*(trimethylsilyl)methyl-lithium ($1\{^{13}\text{C}\}\{^6\text{Li}\}\text{-Li}$) in 3:2 THF/ Et_2O .

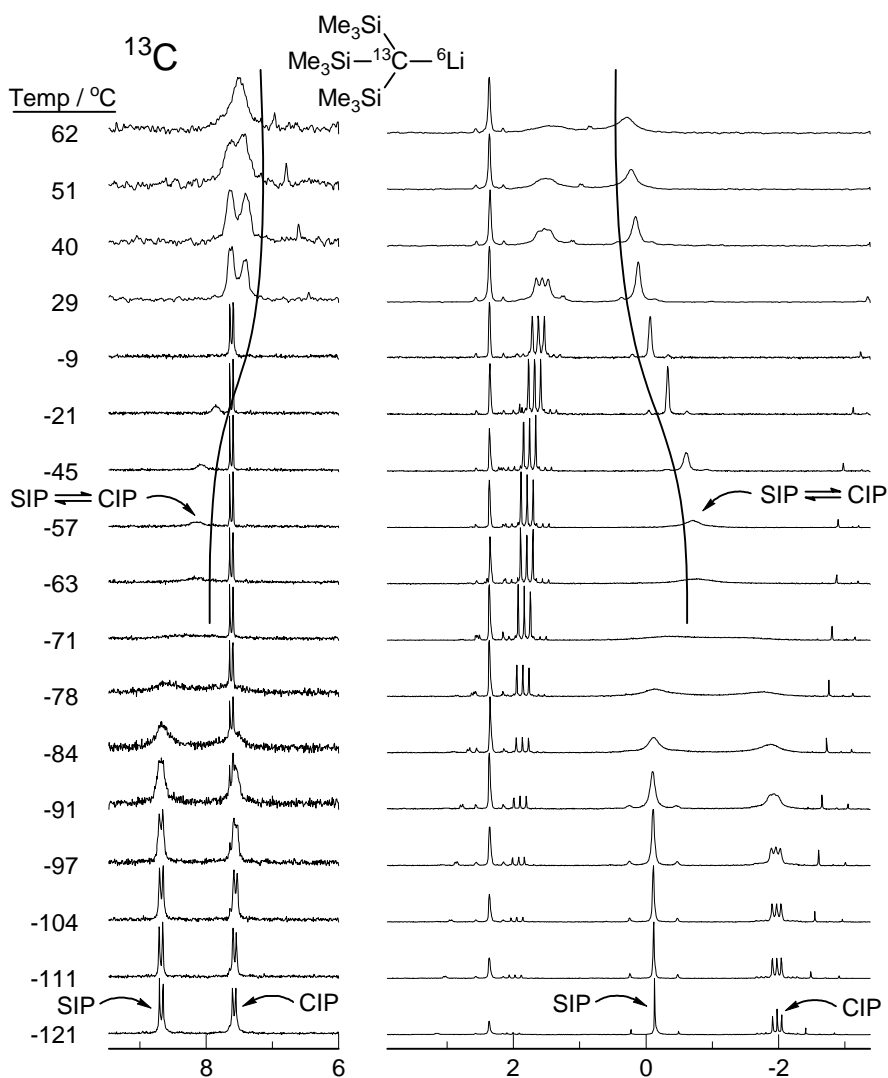


Figure S-11. ^{13}C NMR spectra from a variable temperature study of ^{13}C - and ^6Li -enriched 0.12 M tris(trimethylsilyl)methyl lithium ($1\{^{13}\text{C}\}\text{-}^6\text{Li}$) in 3:2 THF/Et₂O generated at low temperature under conditions where the triple ion does not form. The spectra have been artificially aligned as follows to highlight a sudden chemical shift change for the monomer signal between -60 and +30 °C (indicated by the curved lines): the stack plot on the left has been aligned about the Me_3Si doublet of the triple ion **1T**, while the stack plot on the right has been aligned about the ^{13}C -labeled carbon of $1\{^{13}\text{C}\}\text{-H}$. These references were chosen because they showed approximately linear chemical shift changes with temperature and at low temperature their movements nicely paralleled those of the signals of interest (the Me_3Si carbons of the **1S** and **1C** in the former case and the carbanion carbons of **1S** and **1C** in the latter). Note that, due to the artificial alignment of the spectra, the referencing is only valid for the bottom spectrum.

HMPA titration of 1-Li in THF/ether. After taking the above sample as high as 62 °C, it was cooled again to -120 °C, and an HMPA titration was performed (1 equiv. of HMPA = 61.6 : L). Spectra are shown in Figure 4.

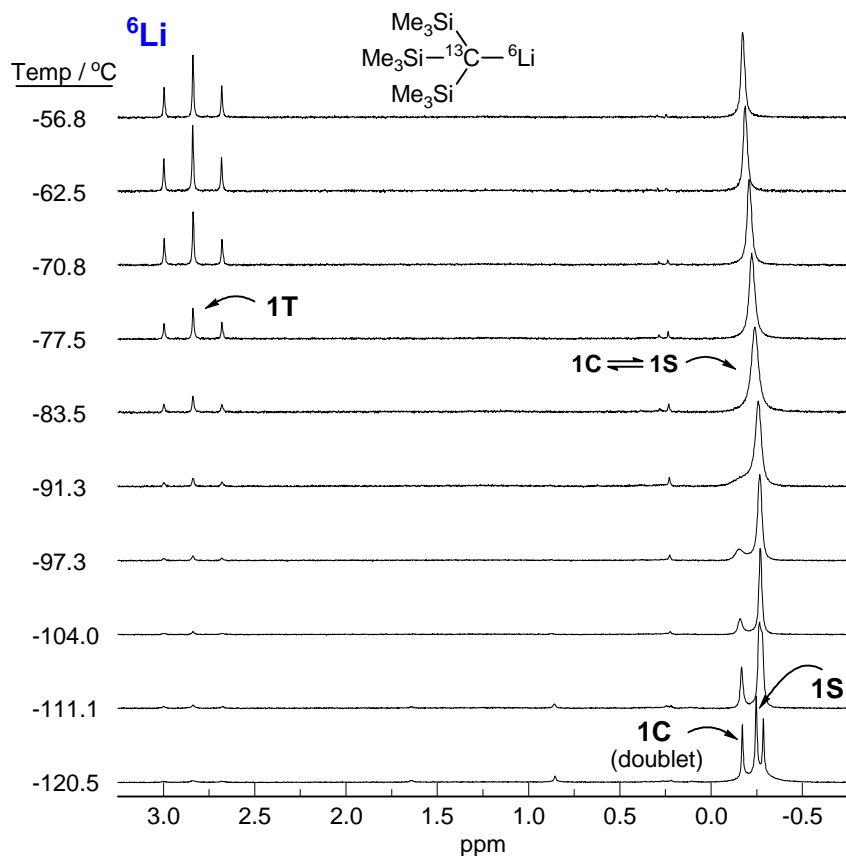


Figure S-12. ^6Li NMR spectra from a variable temperature study of ^{13}C - and ^6Li -enriched 0.12 M *tris*(trimethylsilyl)methyl lithium (^6Li -1) in 3:2 THF/ Et_2O generated at low temperature under conditions where the triple ion does not form. This is a subset of the spectra shown in Figure 6.

Variable Temperature ^1H NMR Study of **1-Li.** An NMR sample of **1-Li** was prepared in a 10 mm NMR tube from **1-SePh** (0.03 g, 0.08 mmol) and *n*-BuLi (0.07 mL, 2.4 M) in 4 mL of 1:3 THF/Me₂O with 4 μL of **1-H**. Variable temperature ^7Li , ^{13}C , and ^1H spectra were collected near coalescence. A separate flask of LiSMe was prepared by first dissolving MeSSMe (66 μL , 0.72 mmol) in 6 mL of THF. The flask was cooled to -78 $^\circ\text{C}$ and *n*-BuLi (0.27 mL, 2.4 M) added to it. An aliquot of 0.2 ml was removed via syringe and added to the NMR sample. Another set of variable temperature ^7Li , ^{13}C , and ^1H spectra were collected near coalescence. Spectra are shown in Figure S-13. These spectra show that the barriers to interconversion of **1C** and **1S** are nearly identical in 1:3 THF/Me₂O and 3:2 THF/ether (compare Figure 7). They also show that LiSMe catalyzes the interconversion of **1S** and **1C**.

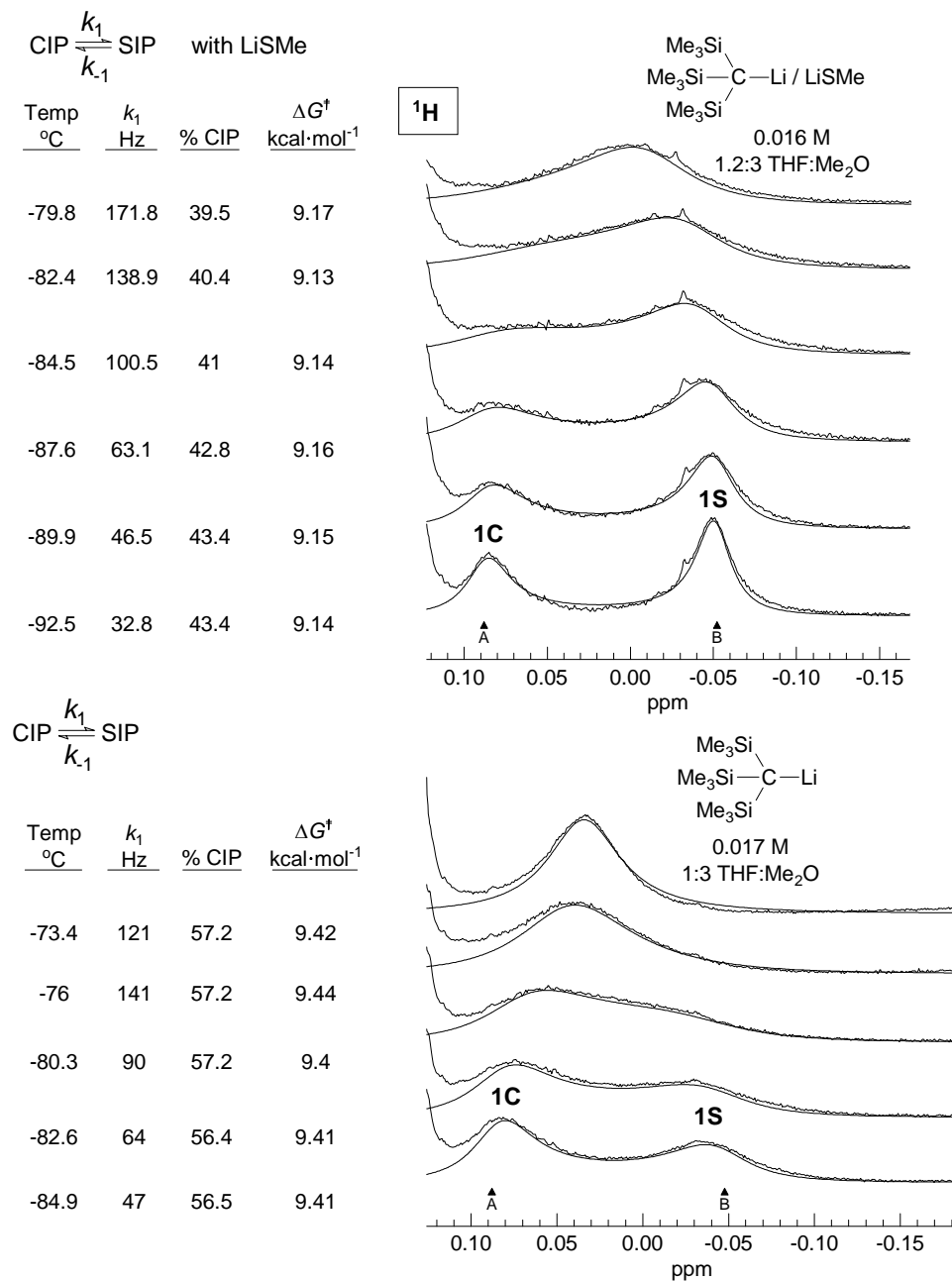


Figure S-13. Spectra and simulation data from a VT experiment of **1-Li** with (bottom) and without (top) LiSMe.

^6Li , ^{31}P , and ^{13}C NMR spectroscopy of 0.08 M $1\text{-}^6\text{Li}$ in Ether Titrated with HMPA. To a dried, N_2 purged 10 mm thin walled NMR tube was added 100 : L (0.28 mmol) 1-SePh , and 3.0 mL of ether. The tube was cooled to $-78\text{ }^\circ\text{C}$ and 0.40 mL (0.28 mmol) of 0.73 M $n\text{-Bu}^6\text{Li}$ in hexanes was added to give a 0.08 M solution of the lithium reagent. ^6Li , ^{31}P and ^{13}C NMR spectra were acquired at 0, 0.10, 0.20, 0.50, 1.0, 2.0, and 4.0 equiv of HMPA. The temperature of the sample during the experiment was $-122\text{ }^\circ\text{C}$. Spectra are shown in Figures 5 and S-14.

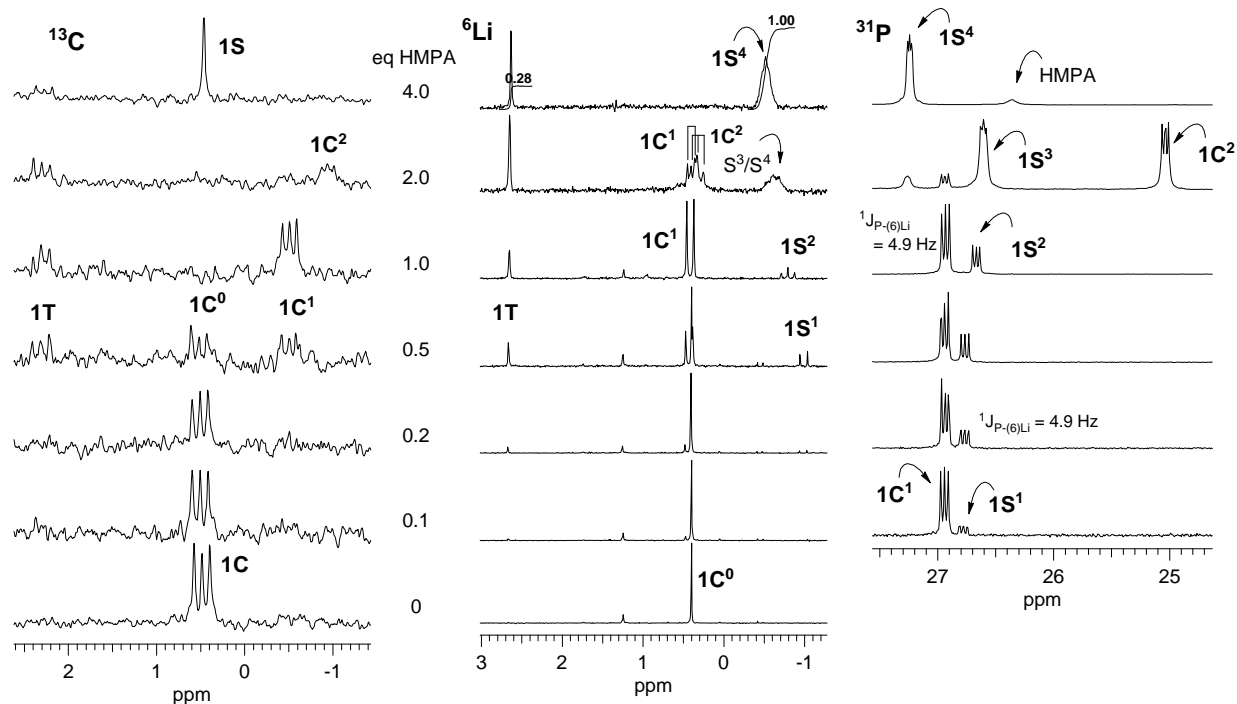


Figure S-14. ^{31}P , ^{13}C and ^6Li NMR spectra of an HMPA titration of a 0.09 M solution of $1\text{-}^6\text{Li}$ in ether at $-122\text{ }^\circ\text{C}$. Superscripts indicate the number of coordinated HMPA molecules ($1\text{S}^2 = (\text{Me}_3\text{Si})_3\text{C}^- // \text{Li}^+(\text{HMPA})_2$)

^6Li , ^{13}C NMR Spectroscopy 1- ^6Li in 3:2:1 $\text{Me}_2\text{O}/\text{THF}/\text{ether}$ Titrated with PMDTA. To a dried, N_2 purged 10 mm thin walled NMR tube was added 100 : L (0.28 mmol) of **1-SePh**, 0.5 mL of ether, and 1.0 mL of THF. The tube was cooled to $-78\text{ }^\circ\text{C}$ and 1.5 mL of Me_2O was condensed in, followed by 0.34 mL (0.27 mmol) of 0.79 M *n*-Bu ^6Li in hexanes to give a 0.08 M solution of the lithium reagent. ^6Li and ^{13}C NMR spectra were acquired at 0, 0.07, 0.14, 0.28, 0.56, 1.0, 2.0, and 4.0 equiv of PMDTA. The temperature of the sample during the experiment was $-126\text{ }^\circ\text{C}$. Spectra are shown in Figure S-15.

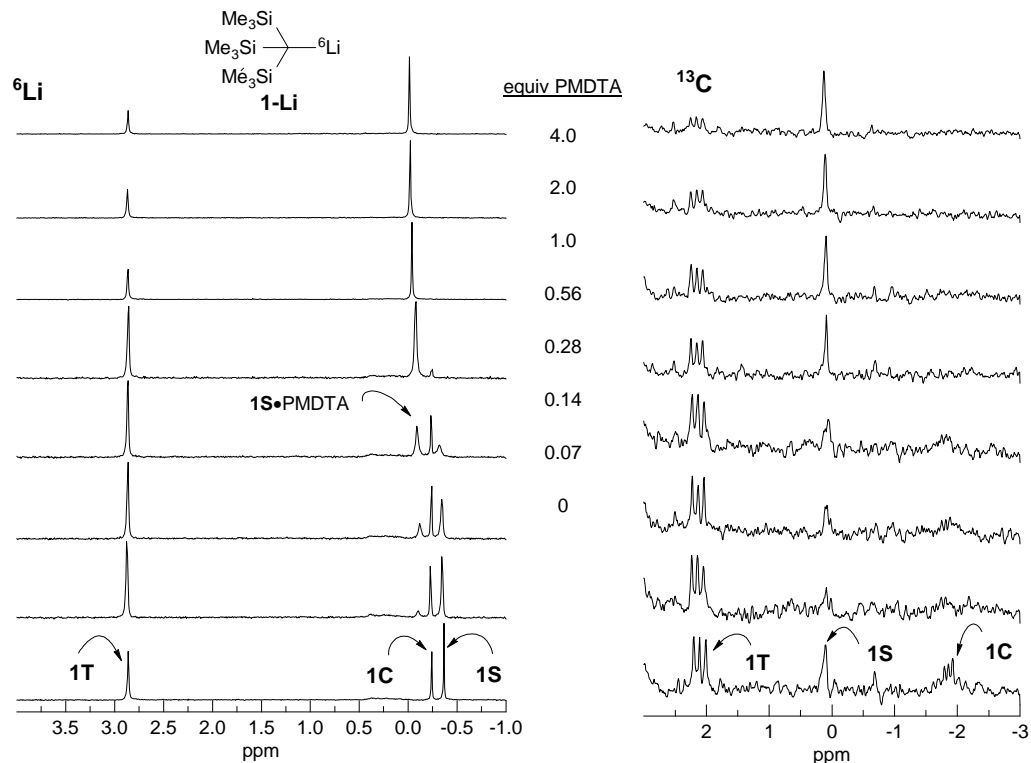


Figure S-15. ^6Li and ^{13}C NMR spectra of a PMDTA titration of a 0.09 M solution of **1- ^6Li** in 3:2:1 $\text{Me}_2\text{O}/\text{THF}/\text{ether}$ at $-126\text{ }^\circ\text{C}$.

^6Li , ^{31}P , and ^{13}C NMR Spectroscopy of 2- ^6Li in 3:2 THF/ether Titrated with HMPA. To a dried, N_2 purged 10 mm thin walled NMR tube was added 220 mg (0.49 mmol) of 2-**SePh**, 1.2 mL of ether, and 1.8 mL of THF. The tube was cooled to $-78\text{ }^\circ\text{C}$ and 0.62 mL (0.49 mmol) of 0.79 M *n*-Bu ^6Li in hexanes was added to give a 0.14 M solution of the lithium reagent. ^6Li , ^{31}P and ^{13}C NMR spectra were acquired at 0, 0.06, 0.12, 0.24, 0.35, 0.60, 1.2, and 1.9 equiv of HMPA. The temperature of the sample during the experiment was $-118\text{ }^\circ\text{C}$. Spectra are shown in Figure S-16.

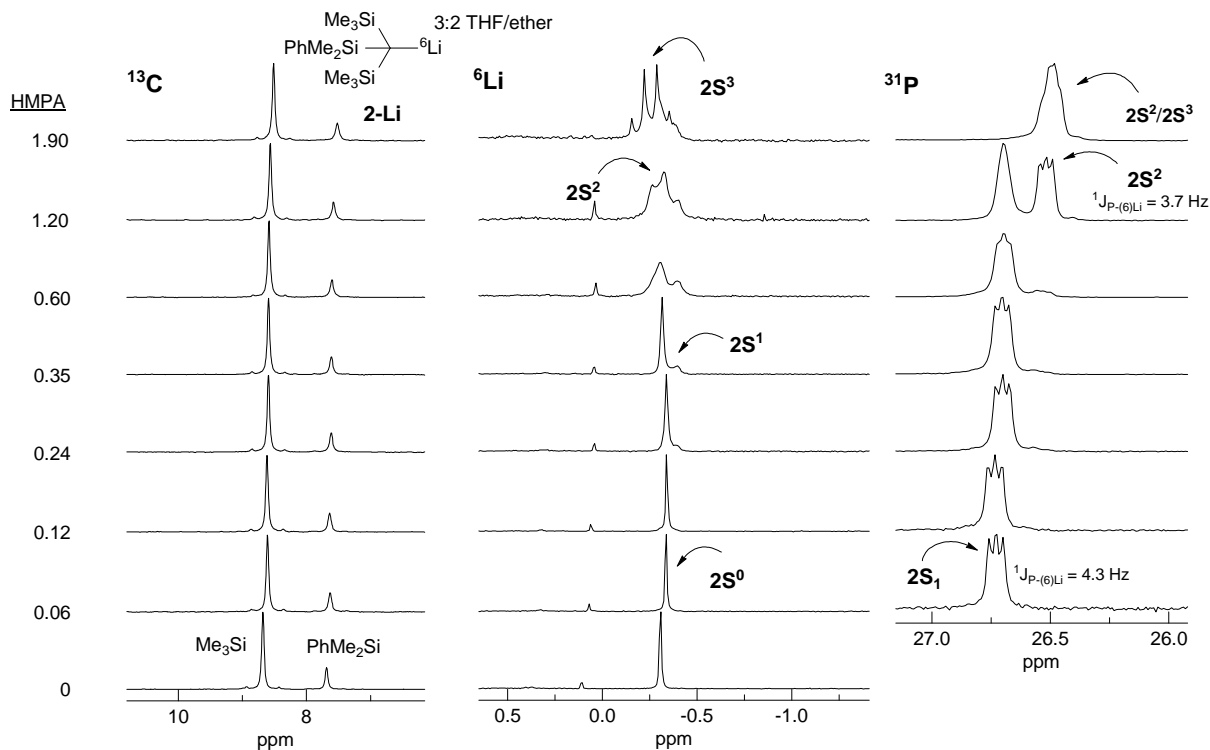


Figure S-16. ^6Li , ^{31}P and ^{13}C NMR spectra of a HMPA titration of a 0.09 M solution of 2- ^6Li in 3:2 THF/ether at $-118\text{ }^\circ\text{C}$. The amount of HMPA is too low, since S^3 cannot be the predominant species with only 1.9 equiv of HMPA. Superscripts indicate the number of coordinated HMPA molecules ($2\text{S}^2 = (\text{Me}_3\text{Si})_2(\text{PhMe}_2\text{Si})\text{C}^- // \text{Li}^+(\text{HMPA})_2$).

^6Li , ^{31}P , and ^{13}C NMR spectroscopy of 2- ^6Li in Ether Titrated with HMPA. To a dried, N_2 purged 10 mm thin walled NMR tube was added 121 mg (0.27 mmol) 2-**SePh**, and 3.0 mL of ether. The tube was cooled to $-78\text{ }^\circ\text{C}$ and 0.33 mL (0.24 mmol) of 0.73 M *n*-Bu ^6Li in hexanes was added to give a 0.07 M solution of the lithium reagent. ^6Li , ^{31}P and ^{13}C NMR spectra were acquired at 0, 0.10, 0.20, 0.50, 1.0, 2.0, and 4.0 equiv of HMPA. The temperature of the sample during the experiment was $-110\text{ }^\circ\text{C}$. Spectra are shown in Figure S-17.

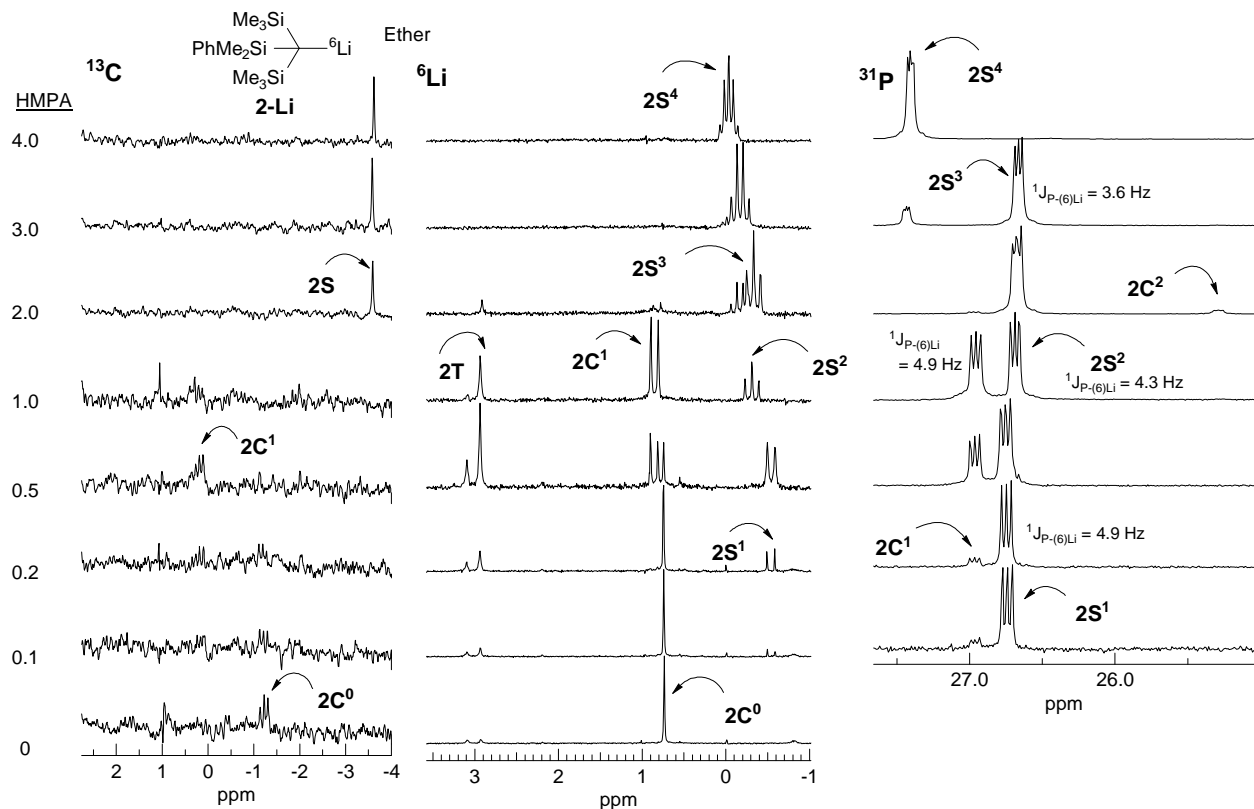


Figure S-17. ^{13}C , ^6Li and ^{31}P NMR spectra of a HMPA titration of a 0.09 M solution of 2- ^6Li in ether at $-110\text{ }^\circ\text{C}$. Superscripts indicate the number of coordinated HMPA molecules ($2\text{S}^2 = (\text{Me}_3\text{Si})_2(\text{PhMe}_2\text{Si})\text{C}^- // \text{Li}^+(\text{HMPA})_2$).

^7Li , ^{31}P , and ^{13}C NMR Spectroscopy of **3-Li in 3:2 THF/ether Titrated with HMPA.** To a dried, N_2 purged 10 mm thin walled NMR tube was added 108 mg (0.26 mmol) **3-SePh**, 1.2 mL of ether, and 1.8 mL of THF. The tube was cooled to $-78\text{ }^\circ\text{C}$ and 0.13 mL (0.25 mmol) of 1.91 M *n*-BuLi in hexanes was added to give a 0.08 M solution of the lithium reagent. ^7Li , ^{31}P and ^{13}C NMR spectra were acquired at 0, 0.10, 0.20, 0.50, 1.0, 2.0, and 4.0 equiv of HMPA. The temperature of the sample during the experiment was $-123\text{ }^\circ\text{C}$. Spectra are shown in Figure S-18.

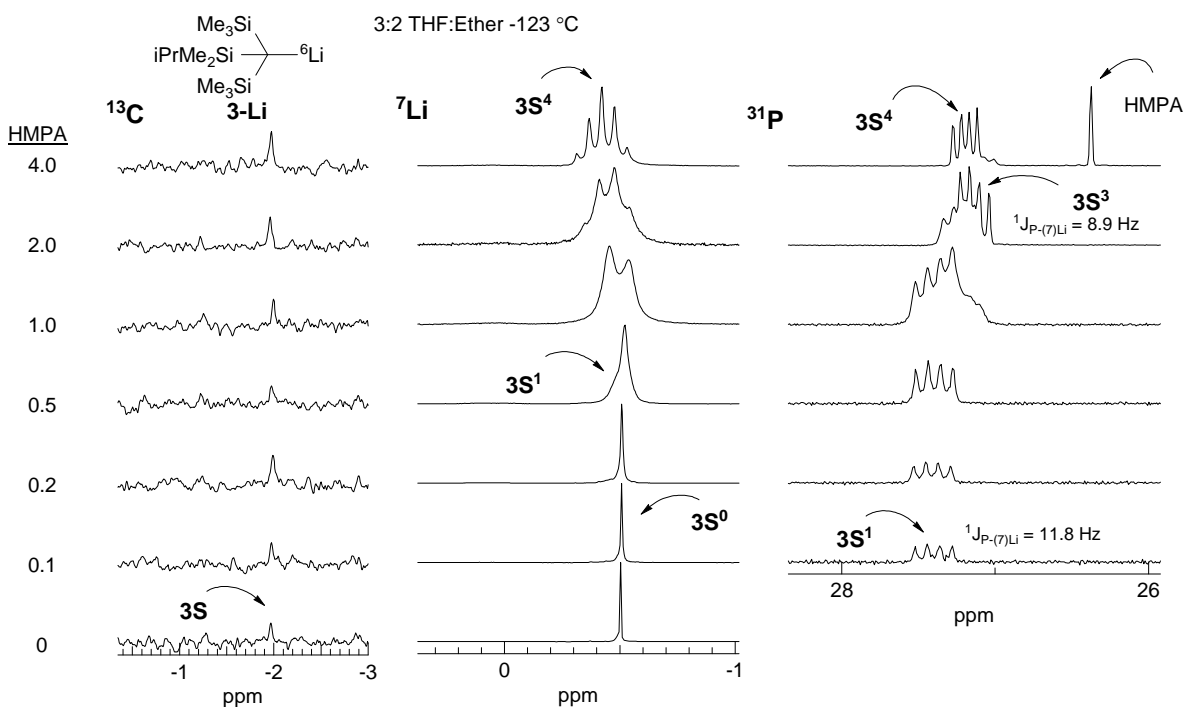


Figure S-18. ^{13}C , ^6Li and ^{31}P NMR spectra of a HMPA titration of a 0.08 M solution of **3-Li** in 3:2 THF/ether at $-123\text{ }^\circ\text{C}$. Superscripts indicate the number of coordinated HMPA molecules ($3\text{S}^3 = (\text{Me}_3\text{Si})_2(\text{iPrMe}_2\text{Si})\text{C}^- // \text{Li}^+(\text{HMPA})_3$).

^6Li , ^{31}P , and ^{13}C NMR Spectroscopy of $3\text{-}^6\text{Li}$ in Ether Titrated with HMPA. To a dried, N_2 purged 10 mm thin walled NMR tube was added 108 mg (0.26 mmol) 3-SePh , and 3.0 mL of ether. The tube was cooled to -78°C and 0.37 mL (0.26 mmol) of 0.73 M $n\text{-Bu}^6\text{Li}$ in hexanes was added to give a 0.08 M solution of the lithium reagent. ^6Li , ^{31}P and ^{13}C NMR spectra were acquired at 0, 0.10, 0.20, 0.50, 1.0, 2.0, and 4.0 equiv of HMPA. The temperature of the sample during the experiment was -120°C . Spectra are shown in Figure S-19.

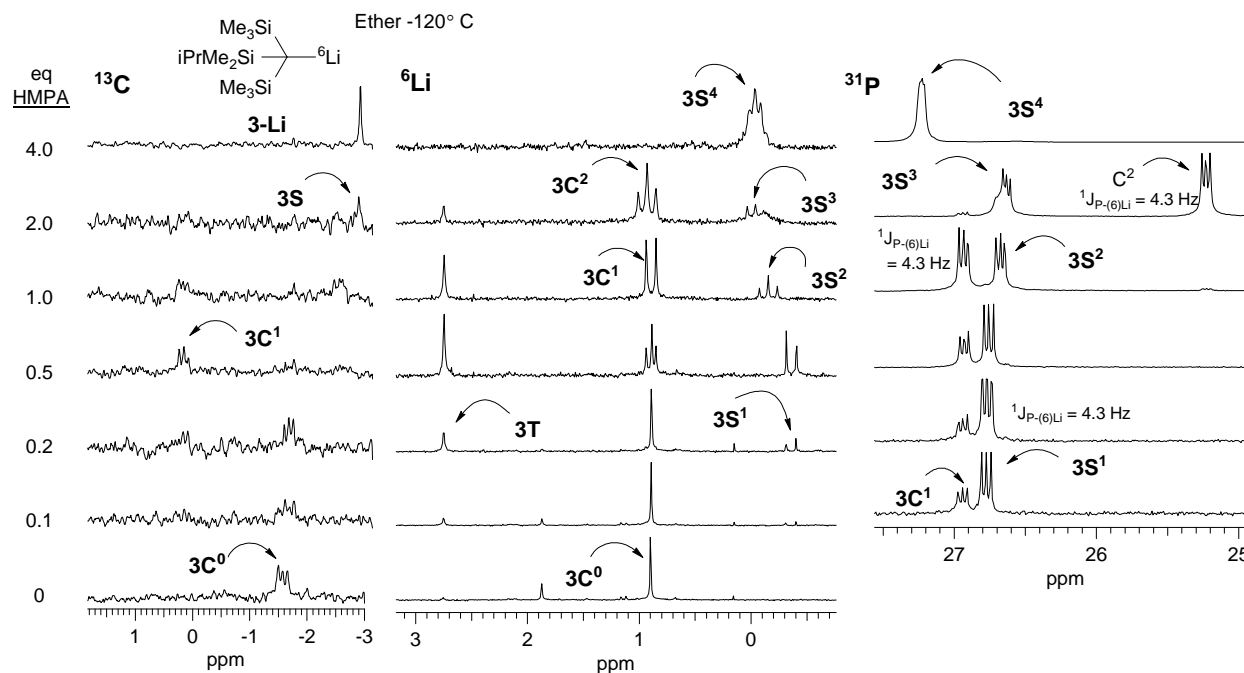


Figure S-19. ^6Li and ^{31}P NMR spectra of a HMPA titration of a 0.08 M solution of 3-Li in ether at -120°C . Superscripts indicate the number of coordinated HMPA molecules ($3\text{S}^3 = (\text{Me}_3\text{Si})_2(\text{iPrMe}_2\text{Si})\text{C}^- // \text{Li}^+(\text{HMPA})_3$).

Table S-3. Compilation of Selected NMR Parameters, see Footnotes for Specific Conditions

	[*] Li	¹ J _{C-(6)Li}	[*] C-X	[*] CH ₃	[*] Si	[*] H	¹ J _{C-Si}	³ J _{CSiCH}	² J _{CSiC}
1C	-0.23 ^{a, g}	6.0 ^{a, g}	-1.83 ^{a, g}	7.34 ^{e, l}	-10.4 ^{d, l}	0.55 ^{e, l}	42.6		4.3
1S	-0.25 ^{a, g}	--	0.08 ^{a, g}	8.14 ^{e, l}	-14.1 ^{d, l}	0.42 ^{e, l}	64.9		5.4
1T	2.84, -0.2 ^{a, h}	8.3 ^{a, h}	2.85 ^{a, h}	7.65 ^{e, l}	-10.4 ^{d, l}	0.59 ^{e, l}	42.0		4.3
1-H^f	--	--	4.51 ^{d, j}	3.16 ^{e, l}	-0.40 ^{e, l}	0.68 ^{e, l}	50.6	1.5	3.2
1-I	--	--	7.32 ^{a, k}	3.16 ^{e, l}	-4.22 ^{e, k}	0.83 ^{e, l}	50.9	2.2	3.4
1-SePh	--	--	16.5 ^m	3.61		0.2	35.6	1.3	3.2
2C	0.73 ^{b, g}	7.6 ^{b, g}	-1.22 ^{b, g}						
2S	-0.3 ^{a, i}	--	-3.6 ^{a, i}	8.68, 7.68 ^{a, i}					
2T	3.1 ^{c, i}								
3C	0.90 ^{b, i}	8.3 ^{b, i}	-1.57 ^{b, i}						
3S	0.50 ^{a, i}	--	-2.0 ^{a, i}						
3T	2.76 ^{c, i}								
4	-0.25 ^{a, l}	--	5.93 ^{e, l}	-5.93 ^{e, l}	-7.0 ^{e, k}	0.64 ^{e, l}	49.6		

All ^{*} are in ppm, *J*-couplings are in Hz.

^a 3:2 THF:Et₂O, ^b Et₂O, ^c Et₂O +HMPA, ^d 1:1 THF:Et₂O, ^e 3:1 Me₂O:THF, ^f ¹J_{C-H} = 100 Hz, ^g -111 °C, ^h -45 °C, ⁱ -120 °C, ^j 25 °C, ^k -105 °C, ^l -130 °C, ^m ¹J_{C-Se} = 73.1 Hz

S4. Kinetics Experiments on 1-Li

RINMR Experiments. The apparatus and techniques for performing RINMR experiments have been described previously.^{S3} Low-temperature RINMR experiments were performed on a 360 MHz spectrometer with a 10 mm broadband probe. ¹H RINMR spectra were observed through the decoupler channel tuned to 360.132 MHz. Spectra were obtained in non-deuterated ether solvents with the spectrometer unlocked and were referenced internally to the trimethylsilyl peak of Me₃SiPh (* 0.27) or that of Me₂SiPh₂ (* 1.13). The temperature of the RINMR sample was checked at the beginning and the end of an RINMR experiment. For many experiments, the probe temperature was raised a few degrees ca 10 s prior to the injection. This offsets the warming that results from the injection itself. The size of the offset depends on the injection volume and has been determined in a number of control cases by real-time monitoring of the internal sample temperature using the **1-H** chemical shift thermometer described above.^{S3} There is approximately a 1° temperature jump for a 0.05 mL injection. Single scan ¹H RINMR spectra were typically collected with a 0.8 s acquisition time and a 3 ppm sweep width. For fast reactions, initial spectra were collected with a 0 s delay between spectra. A longer delay (10 s) was selected for the remainder of an experiment if/when the reaction rates were slower.

Reaction of 1-Li with MeI - Concentration Dependence. Solutions of 0.18 M **1-Li** in 3:2 THF/ether (3 mL, containing 4 μL of 10% ¹³C enriched **1-H**^{S4}) were prepared at -78 °C by reaction of **1-SePh** (0.232 g, 0.60 mmol) with *n*-BuLi (0.28 ml of 2.05 M, 0.57 mmol). In separate experiments, 1, 2, 4, and 8 equiv of MeI were injected (as 0.3 to 0.4 mL of 2 to 11 M solutions in THF), and the reaction was followed by ¹³C NMR spectroscopy at -81 to -86 °C, with sampling every 5-40 min. Sample spectra and a plot of the percent reaction as a function of time are shown in Figure S-20. In all cases the monomers **1S** and **1C** were completely consumed before the first acquisition. The product, 1,1,1-*tris*(trimethylsilyl)ethane (**1-Me**), was consequently observed in ~ 50 % yield in the first spectrum after injection. The triple ion signal, however, was unchanged, and was observed to decrease slowly over 2 h. The first-order rate constant derived from decay of the triple ion signals varied little with changes in MeI concentration, ranging from 0.9 to 1.3x10⁻⁴ s⁻¹. The differences in rate changes are likely due to the unavoidable differences in temperature between experiments since they were in the same order as the measured temperatures. Thus reaction is zero order in MeI. Data is reported in Figure S-20 and S-21.

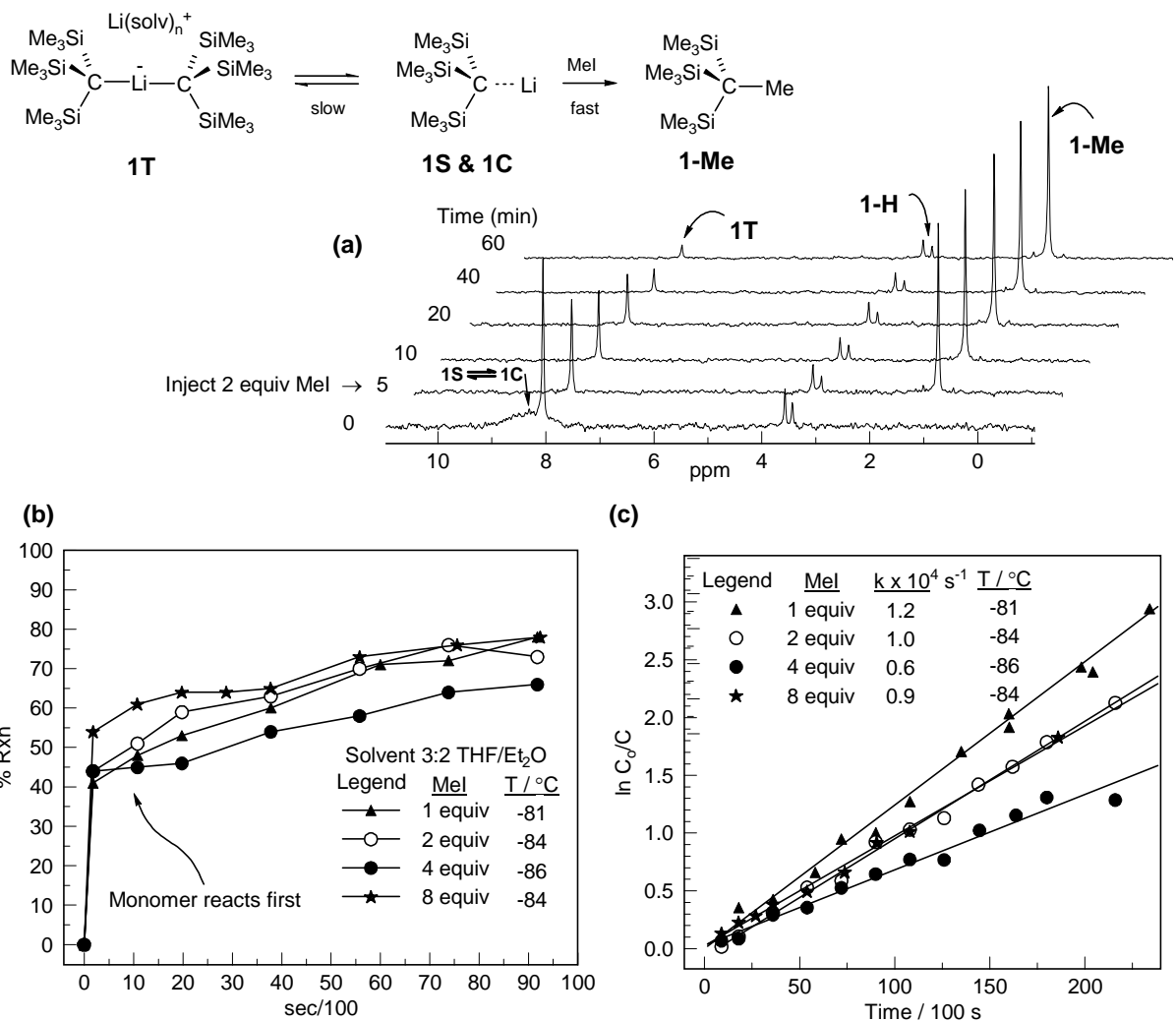


Figure S-20. (a) ^{13}C NMR spectra of a RINMR experiment the reaction of 0.18 M **1-⁶Li** in 3:2 THF/ether with 2 eq of MeI at -81 to -86 °C. (b) A plot of % reaction as a function of time for experiments with 1, 2, 4, and 8 equiv of MeI. (c) Least squares first order plots.

^{13}C RINMR spectroscopy of the reaction of $1\text{-}^6\text{Li}$ (1T) with EtSSEt (1 & 4 equiv) in 3:2:1 $\text{Me}_2\text{O}/\text{THF}/\text{Et}_2\text{O}$ at various temperatures. For all experiments identical samples were prepared. To a dried, N_2 purged 10 mm thin walled NMR tube was added 100 : L (0.28 mmol) of **1-SePh**, 0.5 mL of ether, and 1.0 mL of THF. The tube was cooled to -78°C and 1.5 mL of Me_2O was condensed in followed by 0.40 mL (0.29 mmol) of 0.73 M $n\text{-Bu}^6\text{Li}$ in hexanes to give a 0.08 M solution of the lithium reagent. During the experiment 100 : L (0.29 mmol, 1 equiv) of 2.9 M EtSSEt in THF or 200 : L (0.58 mmol, 4 equiv) of 5.8 M EtSSEt in THF was injected using the manual apparatus. For the experiments a ^{13}C spectrum was obtained within 15 s of the injection (only the monomers react by this time) and using an automation routine transient spectra were obtained every 5 min after that. The products of the reactions were not isolated. Kinetic plots and sample spectra are shown in Figure S-21, these data points are also shown in Figure 8. The rates were essentially independent of disulfide concentration, and within experimental error of the rates for reaction with MeI.

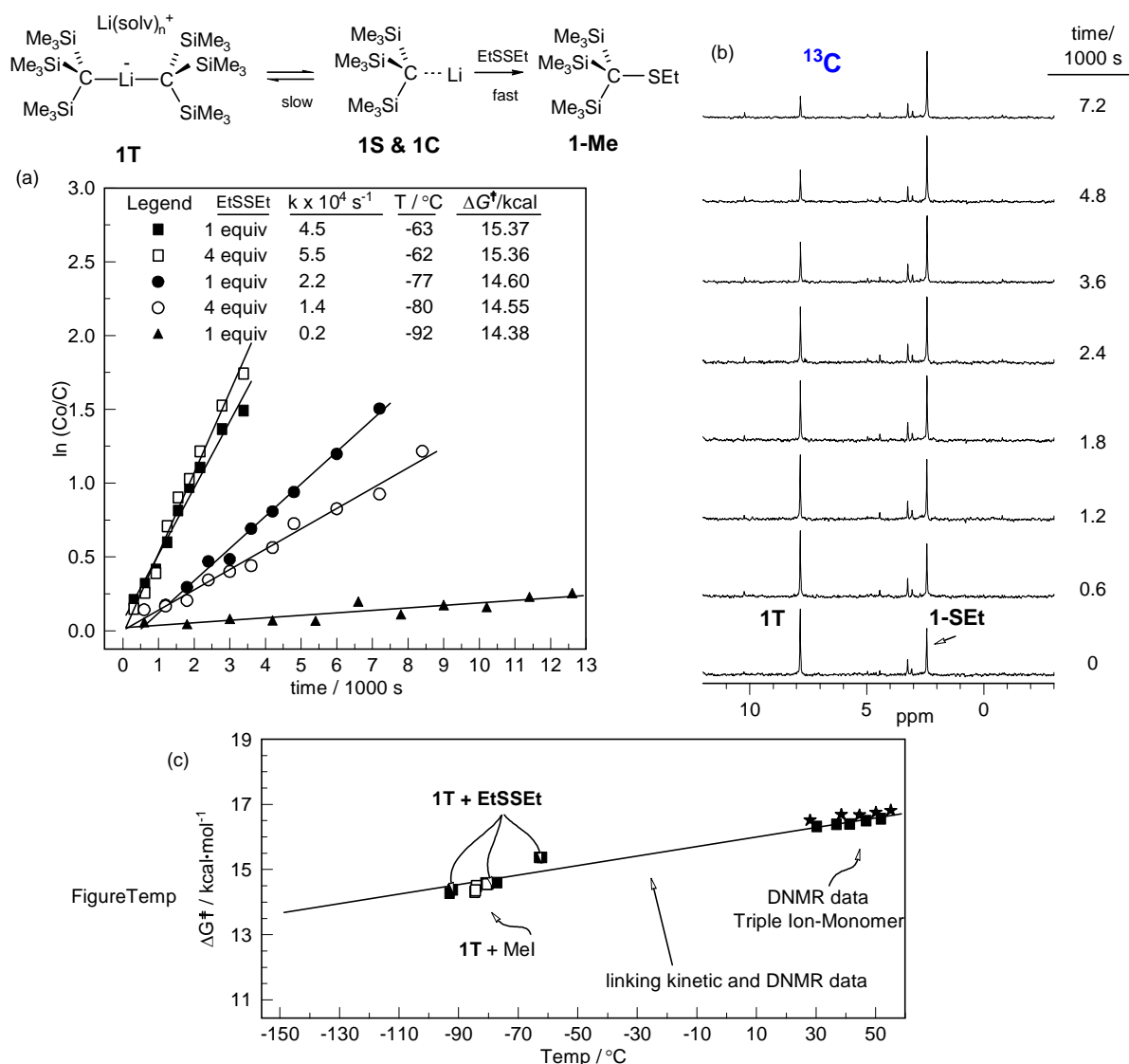


Figure S-21. (a) Least squares first order plot for the reaction of 0.16 M $1\text{-}^6\text{Li}$ with 1 and 4 equiv of EtSSEt in 3:2 THF/ether at -62 to -92°C . (b) ^{13}C NMR spectra of the reaction with 1 equiv of EtSSEt at -92°C . (c) Free energy of activation of the dissociation of **1-Li** (1T) in 3:2 THF/ether plotted as a function of temperature for rates of reaction with MeI and EtSSEt, and the DNMR experiments for coalescence of ^{13}C signals for **1T** and **1C/1S**.

Activation Parameters for the Dissociation of 1T as Measured by the Reaction with MeI. ^{S12}

S5. Experiments Related to the Iodine Ate Complex 4

^{13}C RINMR spectroscopy of the reaction of $1\{^{13}\text{C}\}\text{-I}$ with $n\text{-BuLi}$. To a dried, N_2 purged 10 mm thin walled NMR tube was added 0.5 mL of ether and 1.0 mL of THF. The flask was cooled to $-78\text{ }^\circ\text{C}$ and 1.5 mL of Me_2O was condensed in followed by 0.50 mL (0.8 mmol) of 1.6 M $n\text{-Bu}^6\text{Li}$ in hexanes to give a 0.22 M solution of the $n\text{-Bu}^6\text{Li}$. During the experiment 200 : L (0.25 mmol, 0.3 equiv) of 1.26 M $1\{^{13}\text{C}\}\text{-I}$ in THF using the automated RINMR apparatus. ^{13}Li spectra were obtained within 10 s of injection and using the automation routine MULTIZG every 10 s after that. The temperature of the sample during all of the experiments was $-136\text{ }^\circ\text{C}$. The products of the reactions were not isolated. Results are shown in Figure 12.

^6Li and ^{13}C NMR spectroscopy of $1\text{-}^6\text{Li}$ with 1 Equivalent of 1-I in 3:2THF/ether. To a dried, N_2 purged 10 mm thin walled NMR tube was added 100 : L (0.28 mmol) 1-SePh , 1.8 mL of THF, and 1.2 mL of ether. The tube was cooled to $-78\text{ }^\circ\text{C}$ and 0.40 mL (0.29 mmol) of 0.73 M $n\text{-Bu}^6\text{Li}$ in hexanes was added to give a 0.08 M solution of 1-Li . During the experiment 104 mg (0.29 mmol) of 1-I in 0.6 mL of THF was added by syringe to give a solution of 4 . ^6Li and ^{13}C NMR spectra were acquired before and after the injection at $-123\text{ }^\circ\text{C}$. Spectra are shown in Figure 13.

^{13}C RINMR Spectroscopy of the Reaction of 4 with MeI (2 & 8 equiv) in 3:2 THF/ Et_2O . For both experiments identical samples were prepared. To a dried, N_2 purged 10 mm thin walled NMR tube was added 100 : L (0.28 mmol) 1-SePh , 1.2 mL of ether, and 1.8 mL of THF. The flask was cooled to $-78\text{ }^\circ\text{C}$ and 0.26 mL (0.28 mmol) of 1.11 M $n\text{-Bu}^6\text{Li}$ in hexanes was added followed by 100 mg (0.28 mmol, 1 equiv) 1-I in 0.1 mL of THF to give a 0.08 M solution of 4 . During the experiments, the sample was cooled to $-125\text{ }^\circ\text{C}$ and 100 : L (0.6 mmol, 2.1 equiv) of 6.0 M MeI in THF or 200 : L (2.4 mmol, 8.4 equiv) of 12 M MeI in THF was injected using the manual apparatus. A ^{13}C spectrum was obtained 60 s after the injection (only the monomers react by this time) and using the automation routine ASKINET.AU, 40 transient spectra were obtained at 10, 15, 25, 45, and 66 min or 6, 10, 15, and 25 minutes. The products of the reactions were not isolated. Spectra of the 2 equiv reaction are shown in Figure 13, both experiments are shown in Figure S-22, and the derived rate plots in Figure S-23. The reaction is essentially first order in MeI (2.9 fold rate increase for 4 fold increase in concentration of MeI).

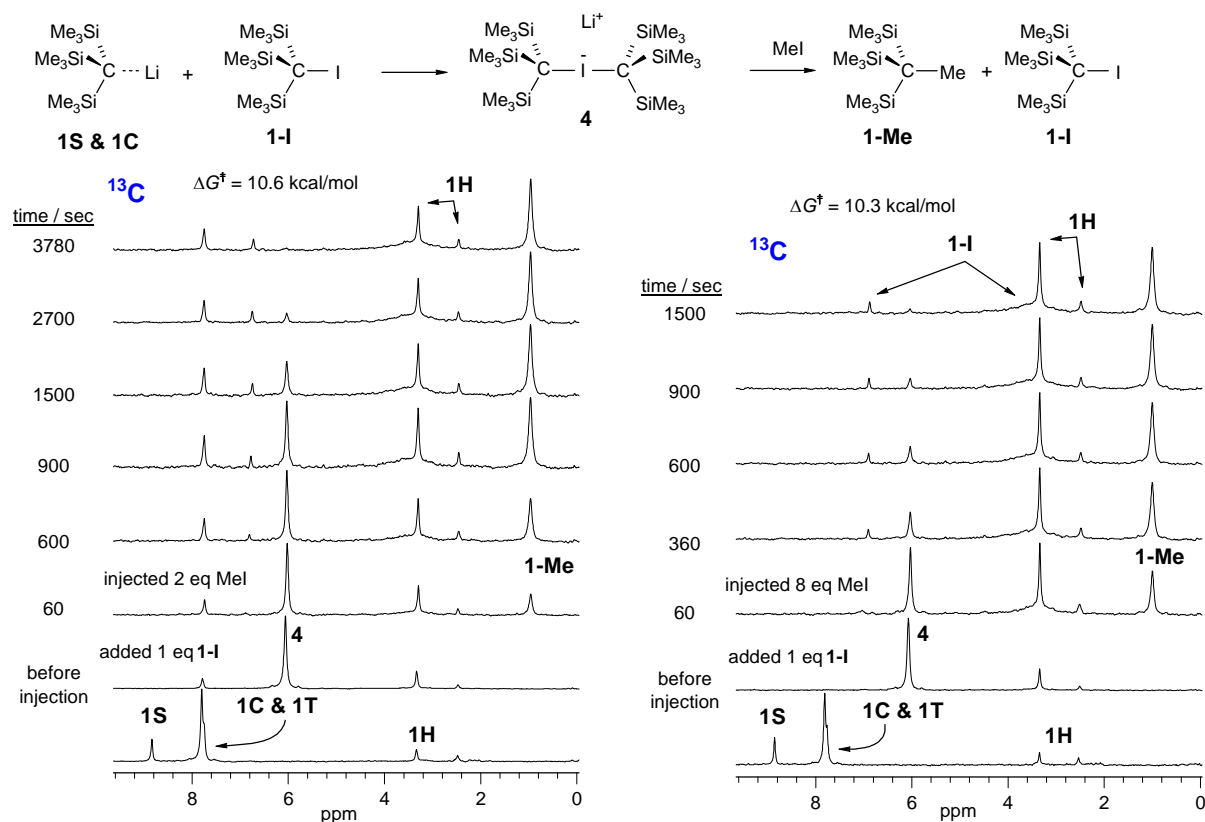


Figure S-22. ^{13}C NMR spectra of the addition of the formation of a 0.1 M solution of **4** by addition of **1-I** to **1-Li**, followed by injection of MeI (2 equiv, left pane, and 8 equiv, right panel) in 3:2 THF/ether at -125 °C. The rate of disappearance of **4** for the two experiments is plotted in Figure S-23.

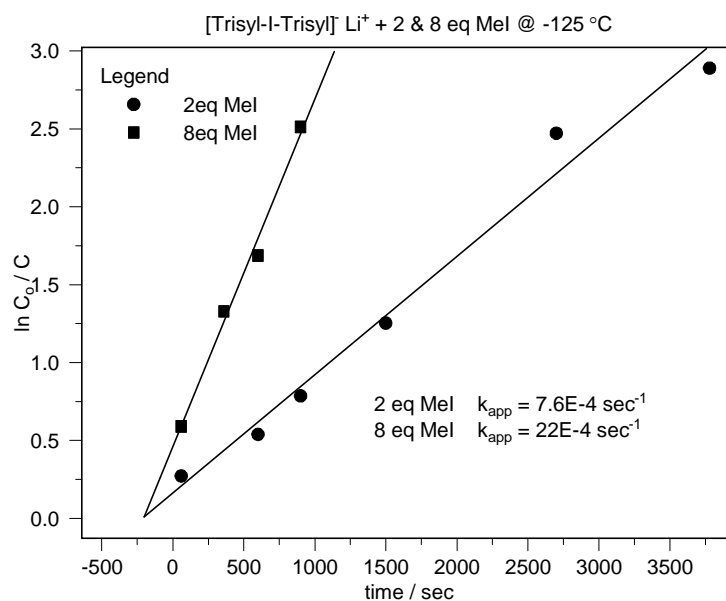


Figure S-23. Rate plots for the reaction of **4** with MeI in 3:2 THF/ether at -125 °C.

^6Li and ^{13}C NMR Variable Temperature Experiment of a Mixture of **4 with excess **1-Li**.** To a dried, N_2 purged 10 mm thin walled NMR tube was added 100 : L (0.28 mmol) of **1-SePh**, 1.8 mL of THF, and 1.2 mL of ether. The tube was cooled to $-78\text{ }^\circ\text{C}$ and 0.38 mL (0.28 mmol) of 0.73 M $n\text{-Bu}^6\text{Li}$ in hexanes was added to give a 0.08 M solution of the lithium reagent. During the experiment 52 mg (0.14 mmol) of **1-I** in 0.3 mL of THF was added via syringe. This produced a solution of **4** with excess **1-Li** present. ^6Li and ^{13}C NMR spectra were acquired at $-31, -44, -51, -58, -62, -69, -82, -93, -105, -116,$ and $-129\text{ }^\circ\text{C}$. Selected spectra are shown in Figure S-24. Line shape simulation of the signal for **4** at $-69\text{ }^\circ\text{C}$ gave $k = 39\text{ s}^{-1}$, $G^\ddagger = 10.3\text{ kcal/mol}$. The coalescence between **1C** and **1S** occurs at a few degrees lower temperature than that between **4** and **1C/1S**. Thus, coincidentally, the rate of dissociation of **1C** to **1S** is just a little faster than the rate of dissociation of **4** to **1-I** and **1C/1S**.

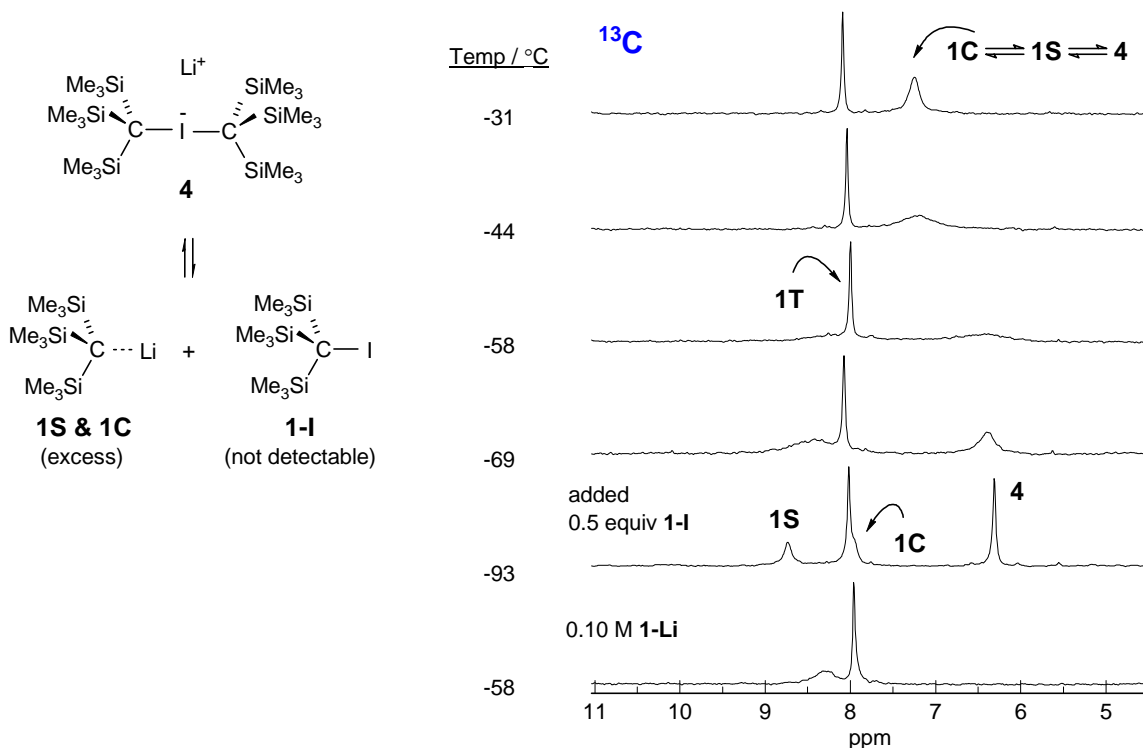


Figure S-24. Variable temperature ^{13}C NMR spectra of a mixture of 0.10 M **1-Li** and 0.05 M **1-I** in 3:2 THF/ether (coalescence of **1S**, **1C**, and **4**).

^1H , ^{13}C and ^{29}Si NMR Variable Temperature Experiment of **4 with excess **1-I**.** To a dried, N_2 purged 10 mm thin walled NMR tube was added 0.066 g (0.22 mmol) of **1-SePh**, 1.8 mL of THF, and 1.2 mL of ether. The tube was cooled to $-78\text{ }^\circ\text{C}$ and 0.09 mL (0.22 mmol) of 2.48 M *n*-BuLi in hexanes was added to give a 0.07 M solution of the lithium reagent. During the experiment 63 mg (0.44 mmol) of **1-I** in 0.10 mL of THF was added via syringe in two aliquots. This produced a solution of **4** and excess **1-I**. ^{13}C NMR spectra were acquired at -50 , -59 , -69 , -88 , -91 , and $-105\text{ }^\circ\text{C}$, selected spectra are shown in Figure S-25. Line shape simulation of the signal for **4** at $-69\text{ }^\circ\text{C}$ gave $k = 80\text{ s}^{-1}$ ($\Delta G^\ddagger = 10.0\text{ kcal/mol}$) for the rate of dissociation of **1T**.

The small amount of **1T** in the -105 , -88 and $-69\text{ }^\circ\text{C}$ spectra is left over from the sample preparation at $-78\text{ }^\circ\text{C}$. Apparently the sample was cooled to $-105\text{ }^\circ\text{C}$ before all of **1T** had dissociated to form **1C/1S**, and then **4**. When the sample was cooled back down to $-90\text{ }^\circ\text{C}$ after the $-50\text{ }^\circ\text{C}$ spectra were taken, there was no detectable amount of **1T** left.

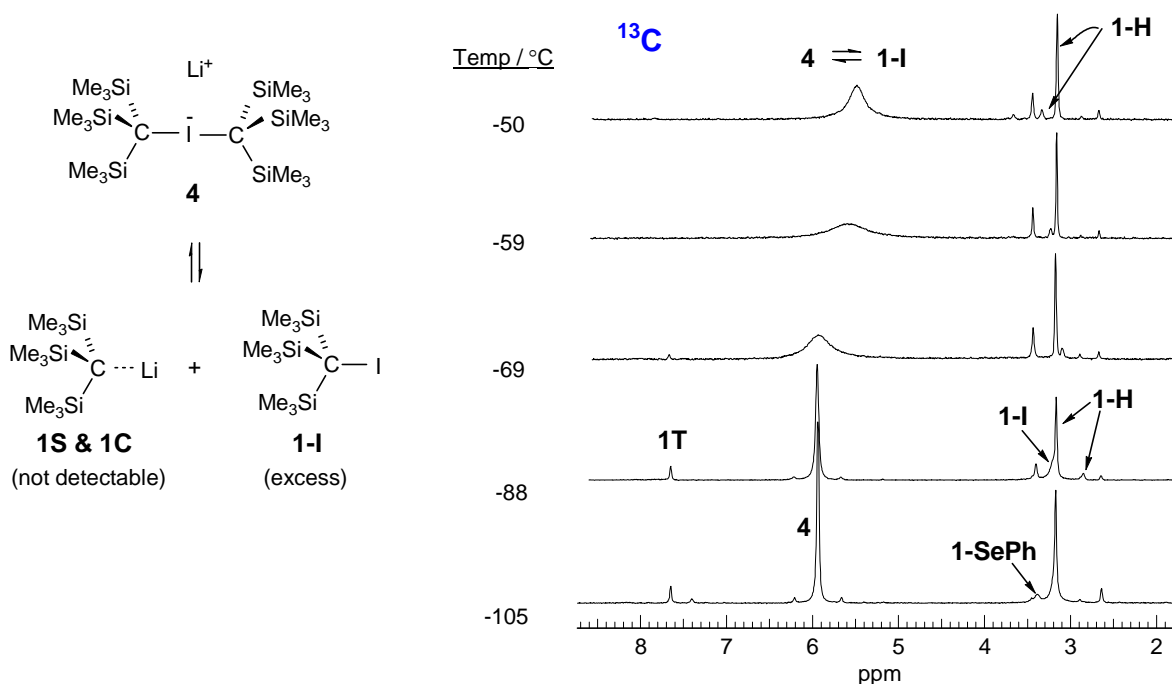


Figure S-25. ^{13}C NMR spectra of a variable temperature study of a mixture of 0.07 M **1-Li** and 0.14 M **1-I** in 3:2 THF/ether (coalescence of **1-I** and **4**).

^1H RINMR and ^7Li RINMR Spectroscopy of the Reaction of $n\text{-BuLi}$ with **1-I in 3:1 $\text{Me}_2\text{O}/\text{THF}$.** Two identical experiments were run, one followed by ^7Li NMR spectroscopy, the other by ^1H NMR. To a dried, N_2 purged 10 mm thin walled NMR tube was added 10 mL of dimethyldiphenylsilane (0.046 mmol, integration standard) and 1.0 mL of THF. The flask was cooled to $-78\text{ }^\circ\text{C}$ and 3 mL of Me_2O and 0.20 mL (0.50 mmol) of 2.53 M $n\text{-BuLi}$ in hexanes was added. During the experiments 0.15 mL (0.1 mmol) of 0.64 M **1-I** in THF was injected using the automated apparatus (the amount of iodide injected was 1.35 times the amount of $n\text{-BuLi}$ dimer in the sample). For the experiments a ^1H or ^7Li spectrum was obtained every 0.8 s after the injection for 200 cycles followed by 90 cycles with an additional 10 s delay. The products of the reactions were not isolated. ^1H and ^7Li spectra of the reaction are shown in Figure S-26.

These spectra provide some indication that a second transient intermediate (similar Me_3Si proton chemical shift to **4**) was present at 10 s, but the signal was poorly resolved from that of **4** ($\delta = 0.01\text{ ppm}$), and it was no longer detectable after 16 s. We did not attempt to characterize this species further, but a possible structure is the mixed ate complex $(\text{Me}_3\text{Si})_3\text{C-I-Bu-Li}^+$.^{S13}

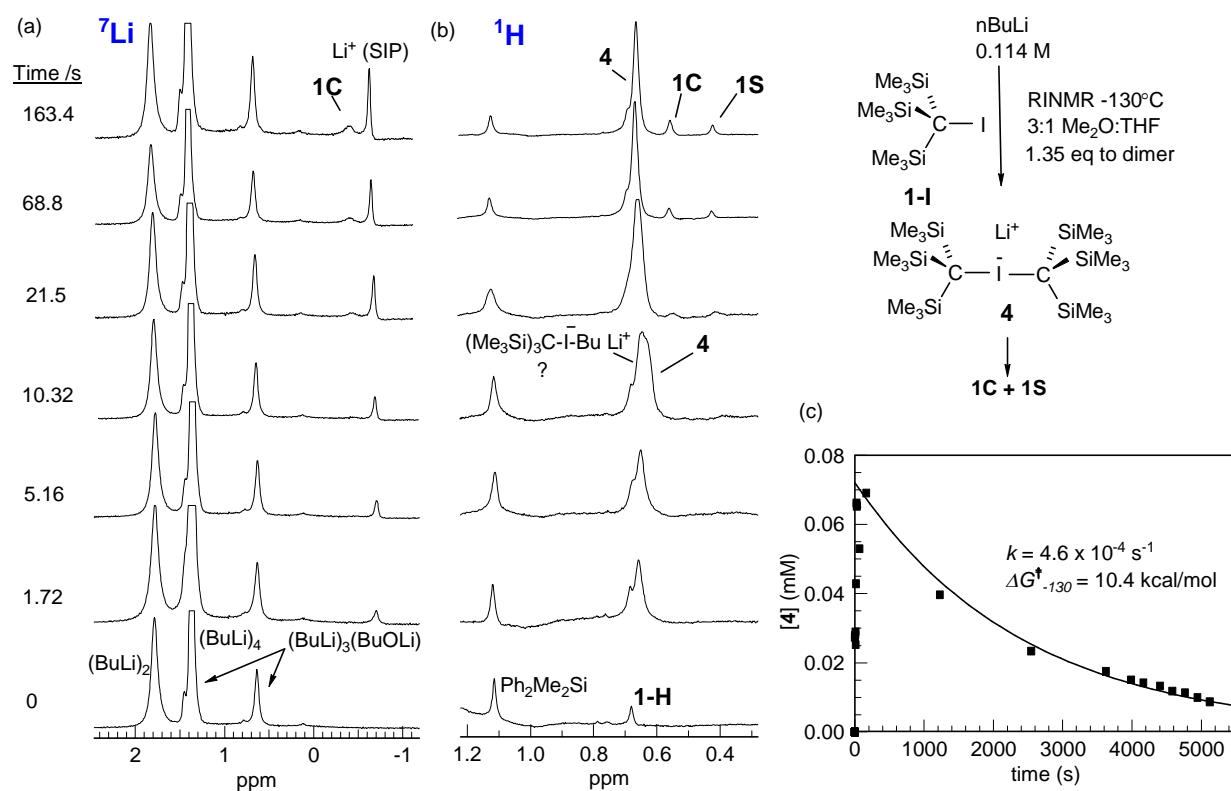


Figure S-26. RINMR experiments in which 1.35 eq (to dimer) of **1-I** at $-130\text{ }^\circ\text{C}$ were injected into a 0.115 M $n\text{-BuLi}$ solution in 3:1 $\text{Me}_2\text{O}/\text{THF}$. (a) Experiment in which the ^7Li NMR signals were observed. (b) A separate identical experiment in which ^1H signals were observed. (c) Rate plot for the appearance and disappearance of **4** during this experiment determined from integration of the ^1H NMR spectra.

^1H RINMR Spectroscopy of the Reaction of **1-Li with **1-I** in 3:1 $\text{Me}_2\text{O}/\text{THF}$.** To a dried, N_2 purged 10 mm thin walled NMR tube was added 10 : L of dimethyldiphenylsilane as an internal standard (0.046 mmol), 0.040 g (0.131 mmol) of **1-SePh** and 1.0 mL of THF. The flask was cooled to $-78\text{ }^\circ\text{C}$ and 3 mL of Me_2O and 0.05 mL (0.125 mmol) of 2.5 M *n*-BuLi in hexanes was added. During the experiments the sample was cooled to at $-130\text{ }^\circ\text{C}$ and 0.15 mL (0.25 mmol, 2 eq) of 1.67 M **1-I** in THF was injected using the automated apparatus. A ^1H NMR spectrum was obtained every 0.8 s after the injection for 200 cycles followed by 90 cycles with an additional 10 s delay. The products of the reactions were not isolated. Spectra of the reaction are shown in Figure S-27.

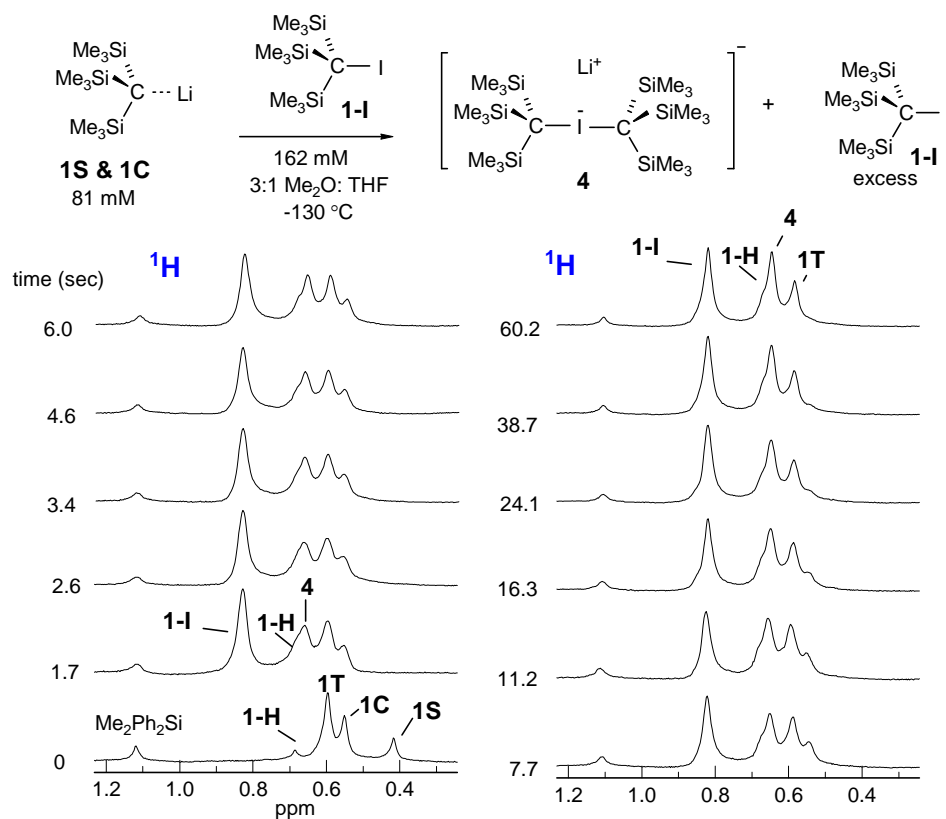


Figure S-27. ^1H NMR spectra of a RINMR experiment in which 2 eq of **1-I** were injected into a 0.081 M solution of **1-Li** in 3:1 $\text{Me}_2\text{O}/\text{THF}$ at $-130\text{ }^\circ\text{C}$.

^7Li and ^{31}P NMR Spectroscopy of an HMPA Titration of Lithium Diphenyliodide in THF. The standard procedure reported^{S14} was followed. PhI (53.5 : L, 98 mg, 0.478 mmol) and THF (2.3 mL) were added to the reference and sample NMR tubes. The tubes were cooled to $-78\text{ }^\circ\text{C}$, and salt free recrystallized PhLi (0.70 mL, 0.476 mmol, 0.68 M in THF)^{S14} was added to each tube. The samples were stored overnight. Reference spectra were taken at 0.0, 0.25, and 4.0 equiv of HMPA. The temperature of the probe before the experiment was $-122.3\text{ }^\circ\text{C}$; after the experiment it was $-125.6\text{ }^\circ\text{C}$. The NMR sample was quenched with 2 equiv of Me_2S_2 (90.0 : L, 1.00 mmol, 94.2 mg). G.C. analysis of PhSMe and PhI gave a 75% recovery of PhLi (PhSMe) and an 82% recovery of PhI. Spectra are shown in Figure S-28.

The HMPA titrations of $\text{Ph}_2\text{I}^- \text{Li}^+$ and of $\text{Ph}_3\text{Hg}^- \text{Li}^+$ are nearly identical, and show all of the characteristics shown by authentic SIPs like trityllithium and fluorenyllithium. Thus ate complexes of this type are separated ion pairs in THF.

^7Li and ^{31}P NMR Spectroscopy of an HMPA Titration of Lithium Triphenylmercury in THF. The standard procedure reported^{S14} was followed. $\text{Ph}_3\text{Hg}^- \text{Li}^+$ (tube with references: 217 mg, 0.612 mmol; sample tube: 217 mg, 0.613 mmol) and THF (2.9 mL) were added to the tubes. The tubes were cooled to -78°C , and PhLi (0.90 mL, 0.613 mmol, 0.68 M in THF)^{S14} was added to each tube. The samples were stored overnight. Reference spectra were taken at 0.0, 0.25, and 4.0 equiv of HMPA. The temperature of the probe before the experiment was -122.6°C ; after the experiment it was -117.0°C . The NMR sample was quenched with 2 equiv of Me_2S_2 (110.0 : L, 1.22 mmol, 114.9 mg). G.C. analysis of PhSMe gave an 85% recovery. Spectra are shown in Figure S-28.

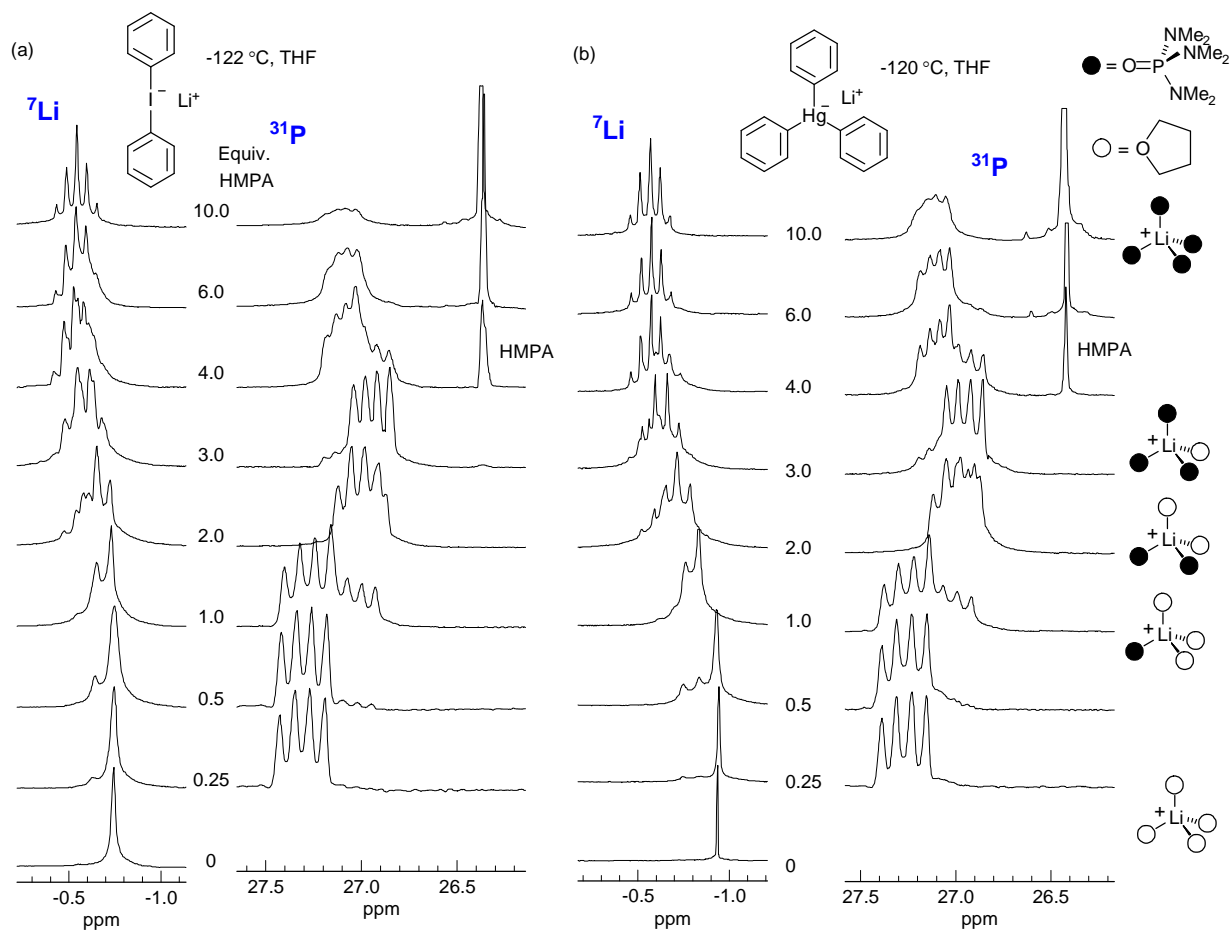
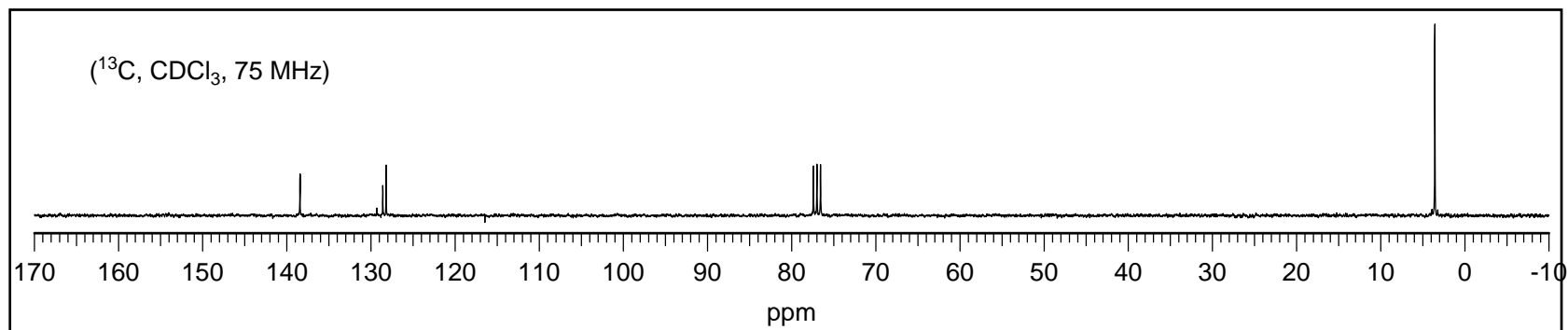
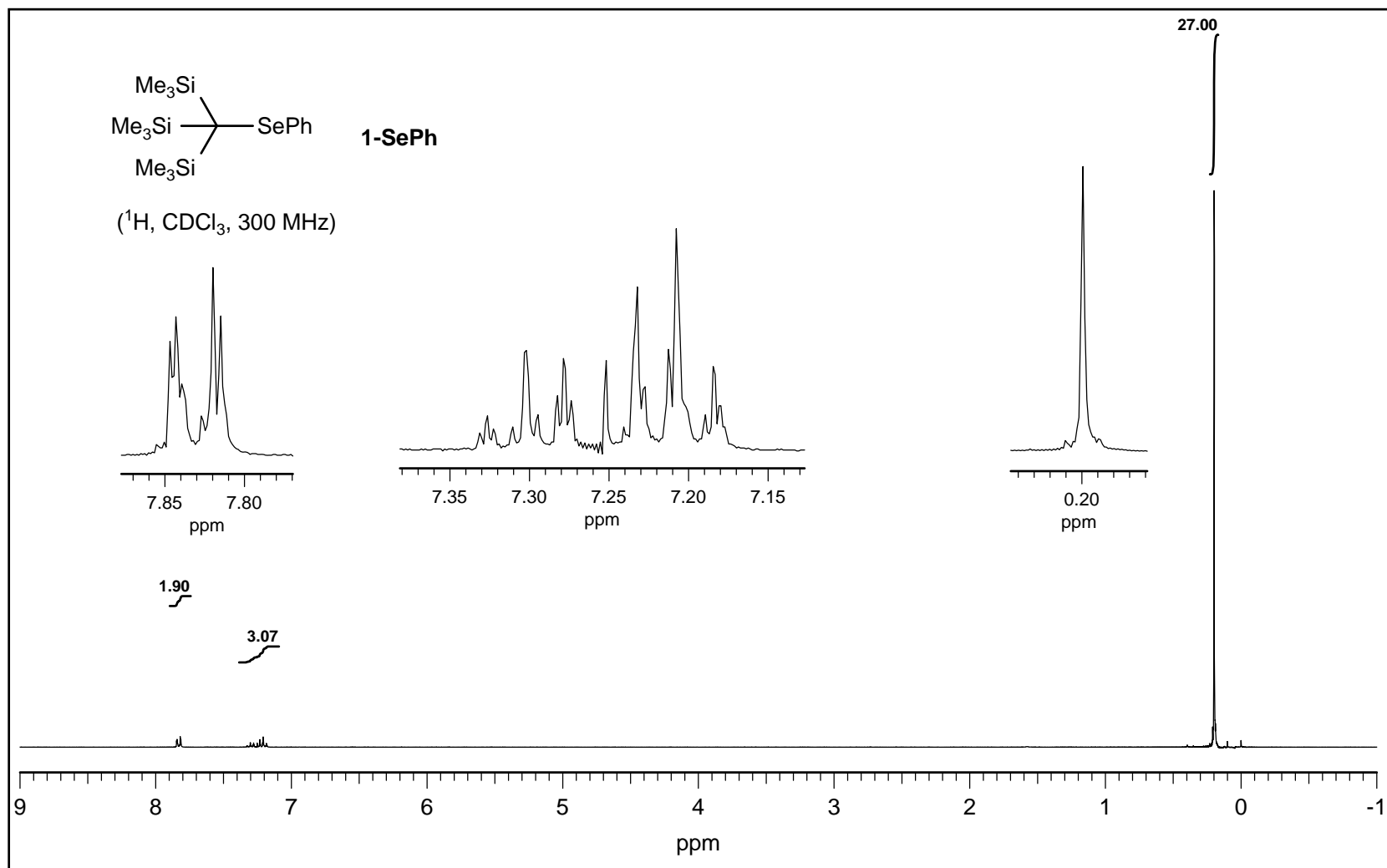
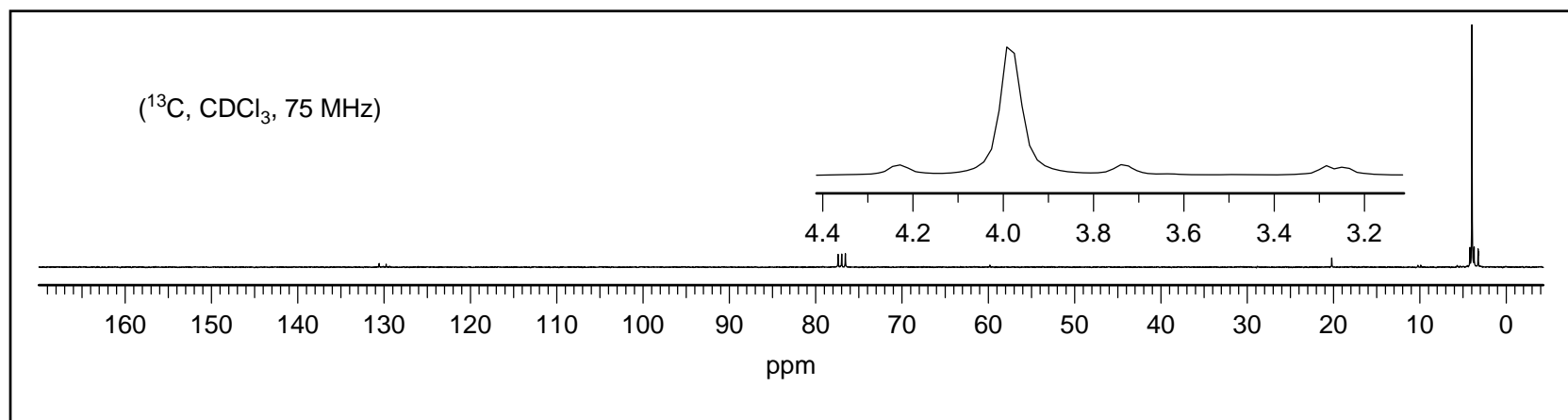
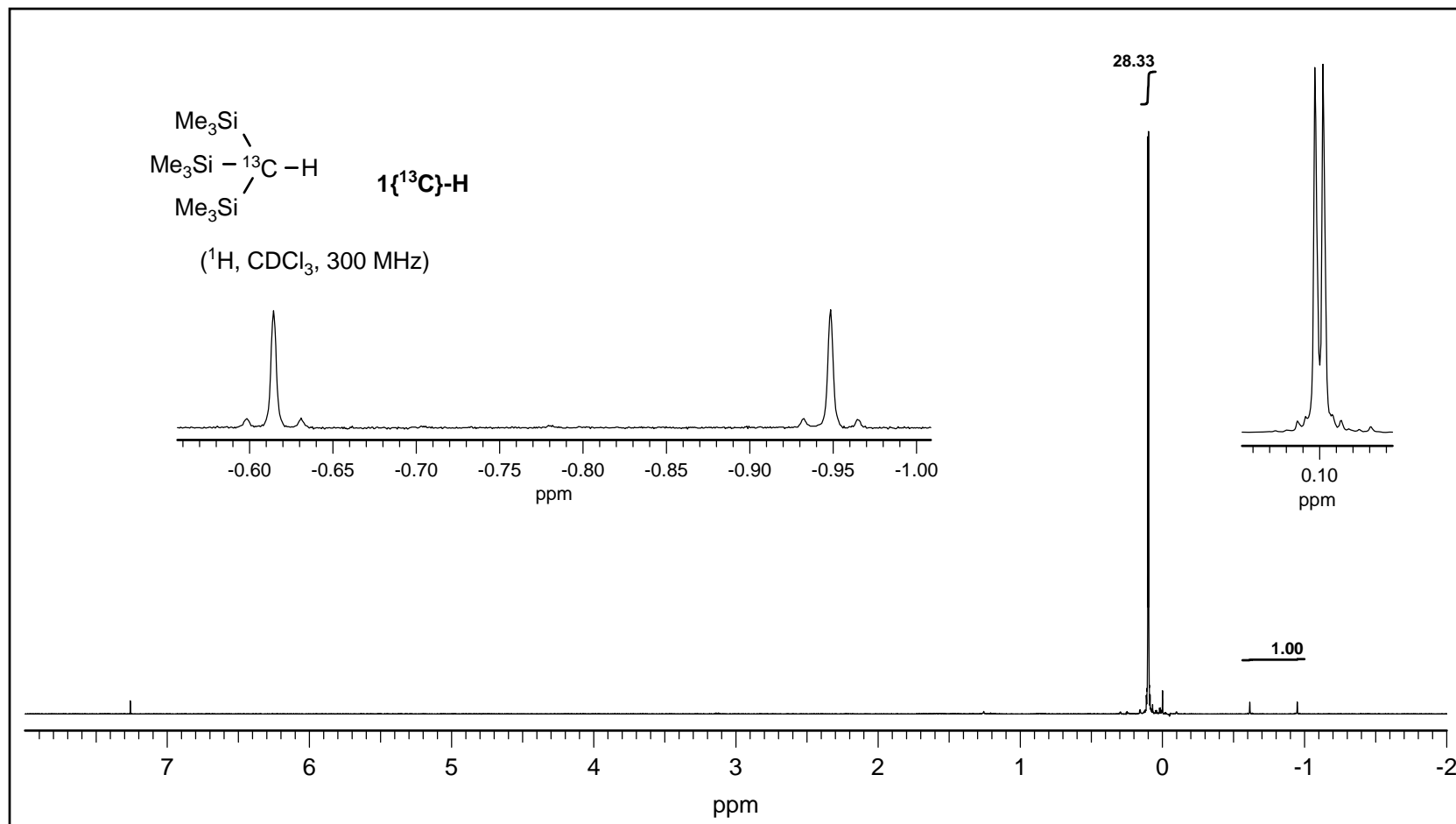
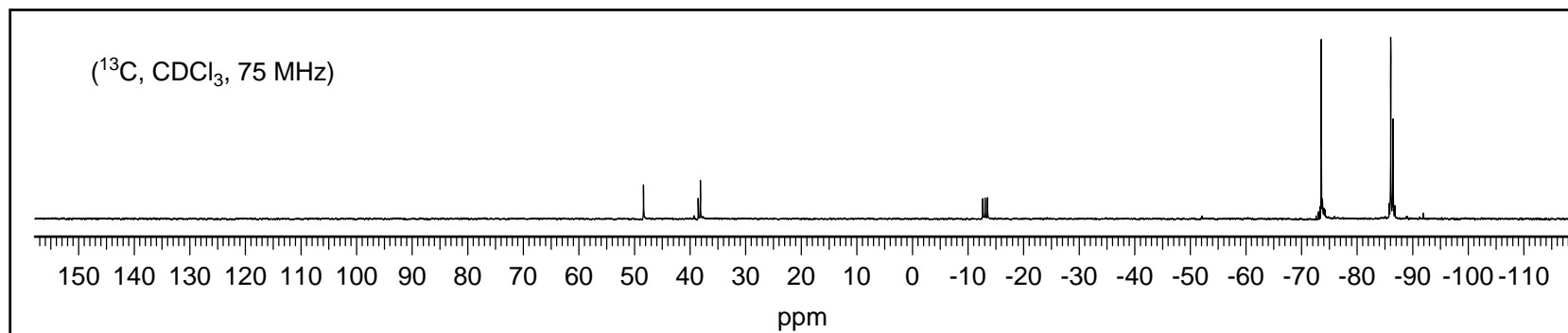
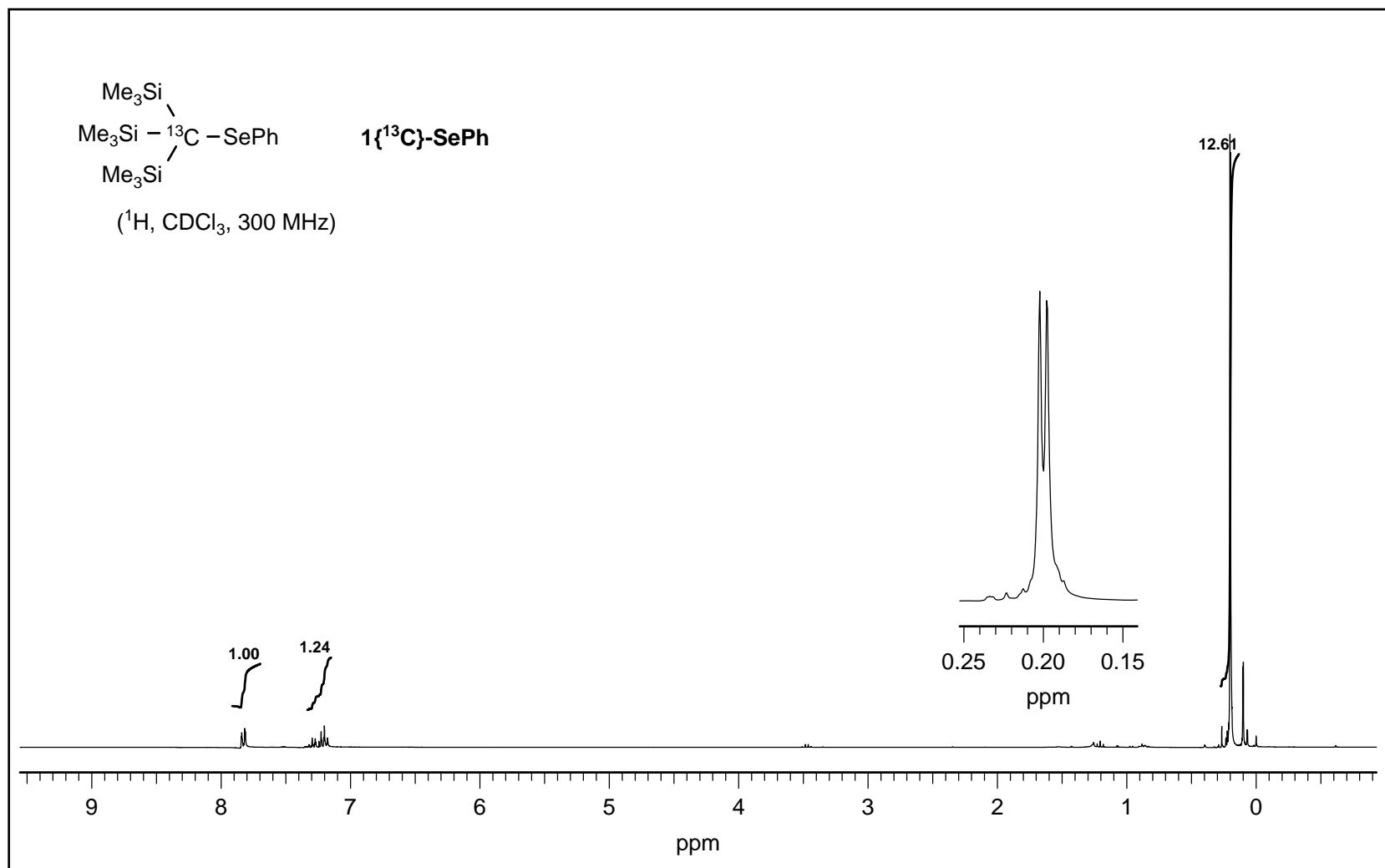


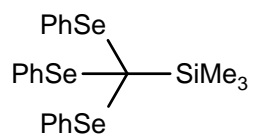
Figure S-28. HMPA titrations of two ate complexes in THF at 120°C . (a) $\text{Ph}_2\text{I}^- \text{Li}^+$. (b) $\text{Ph}_3\text{Hg}^- \text{Li}^+$.



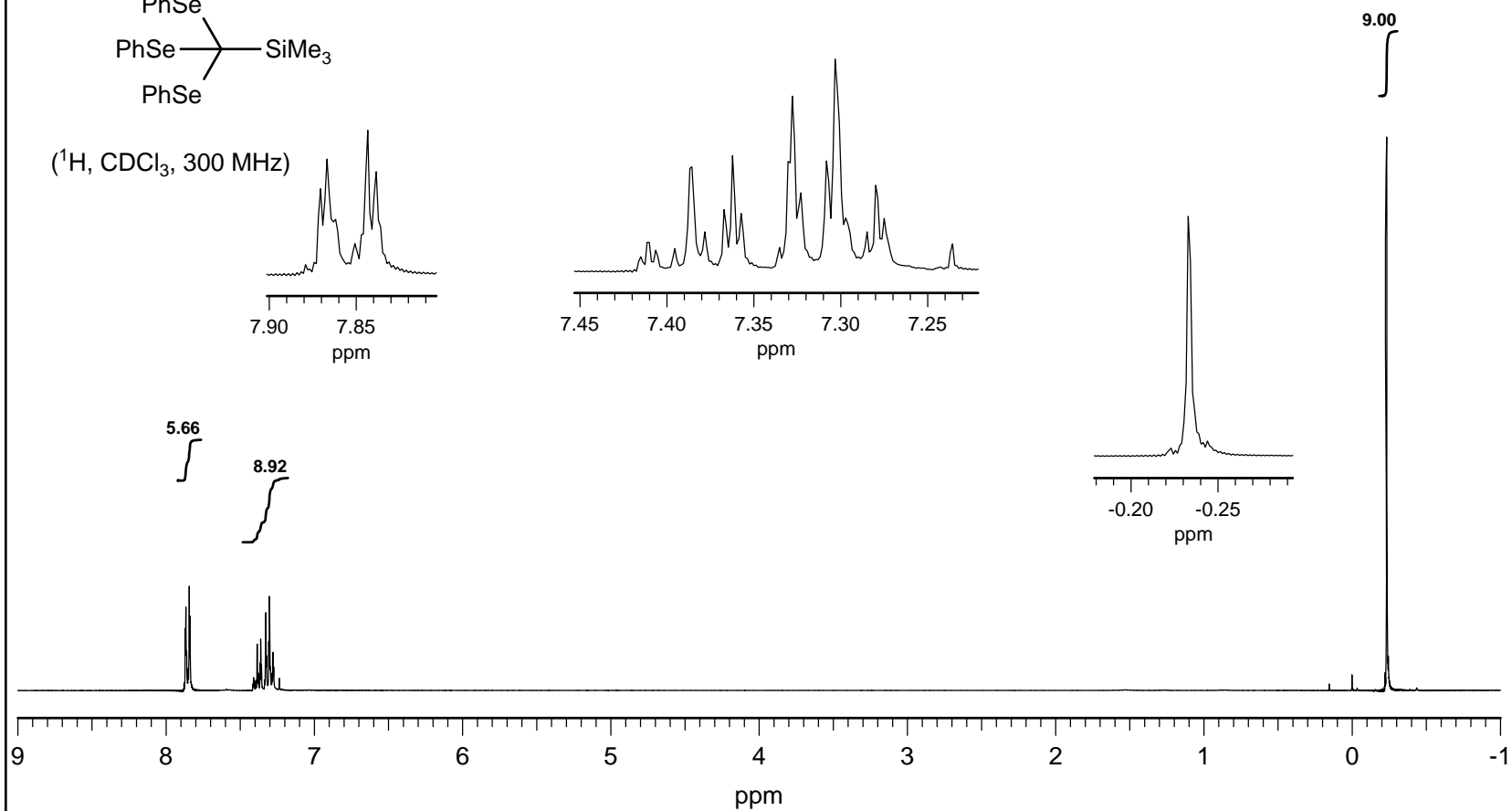
S-38



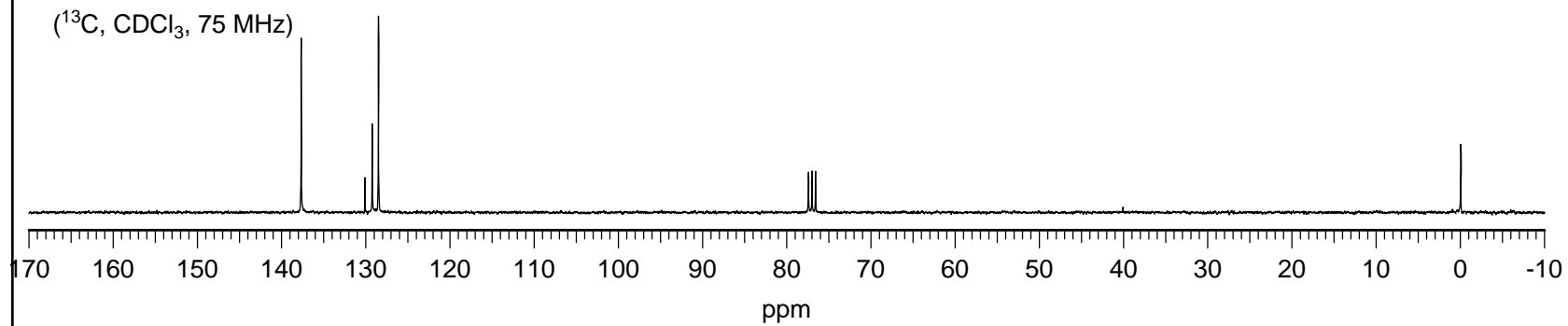


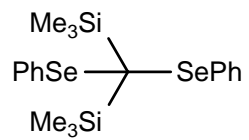


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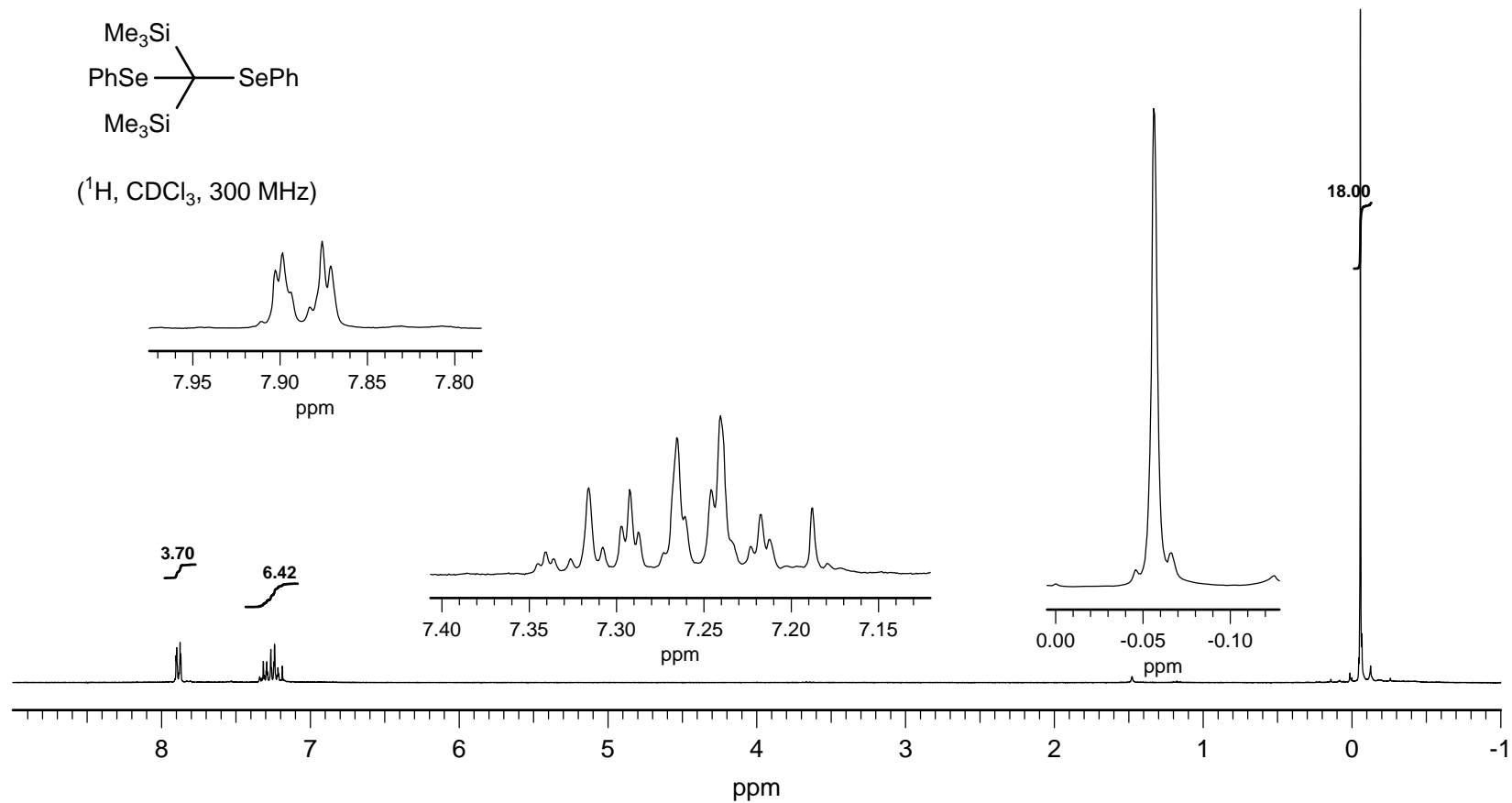


(¹³C, CDCl₃, 75 MHz)

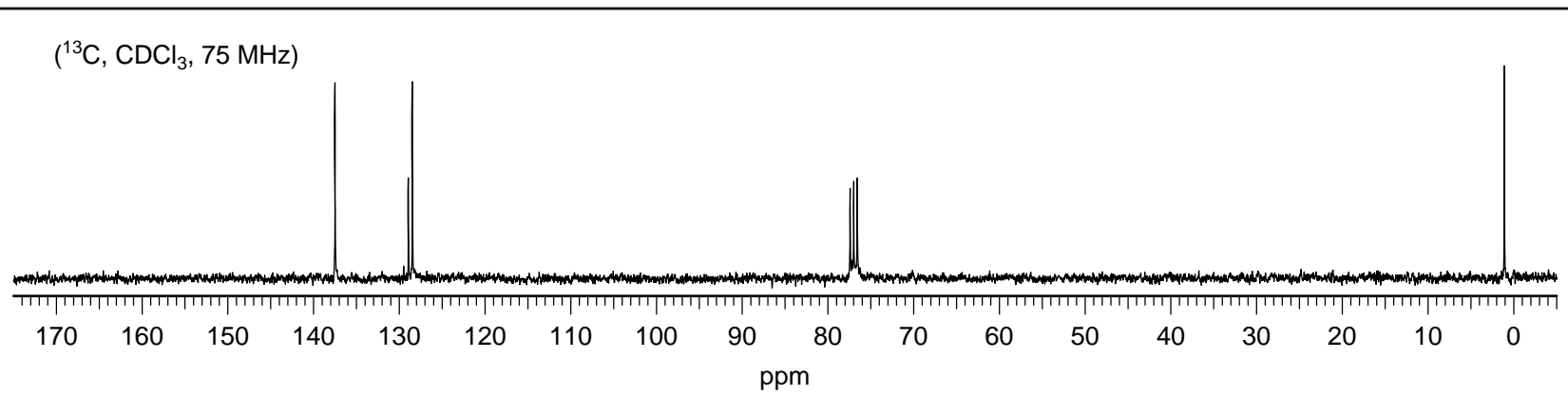


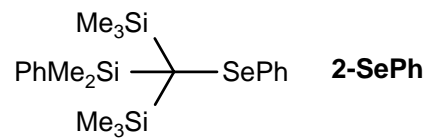


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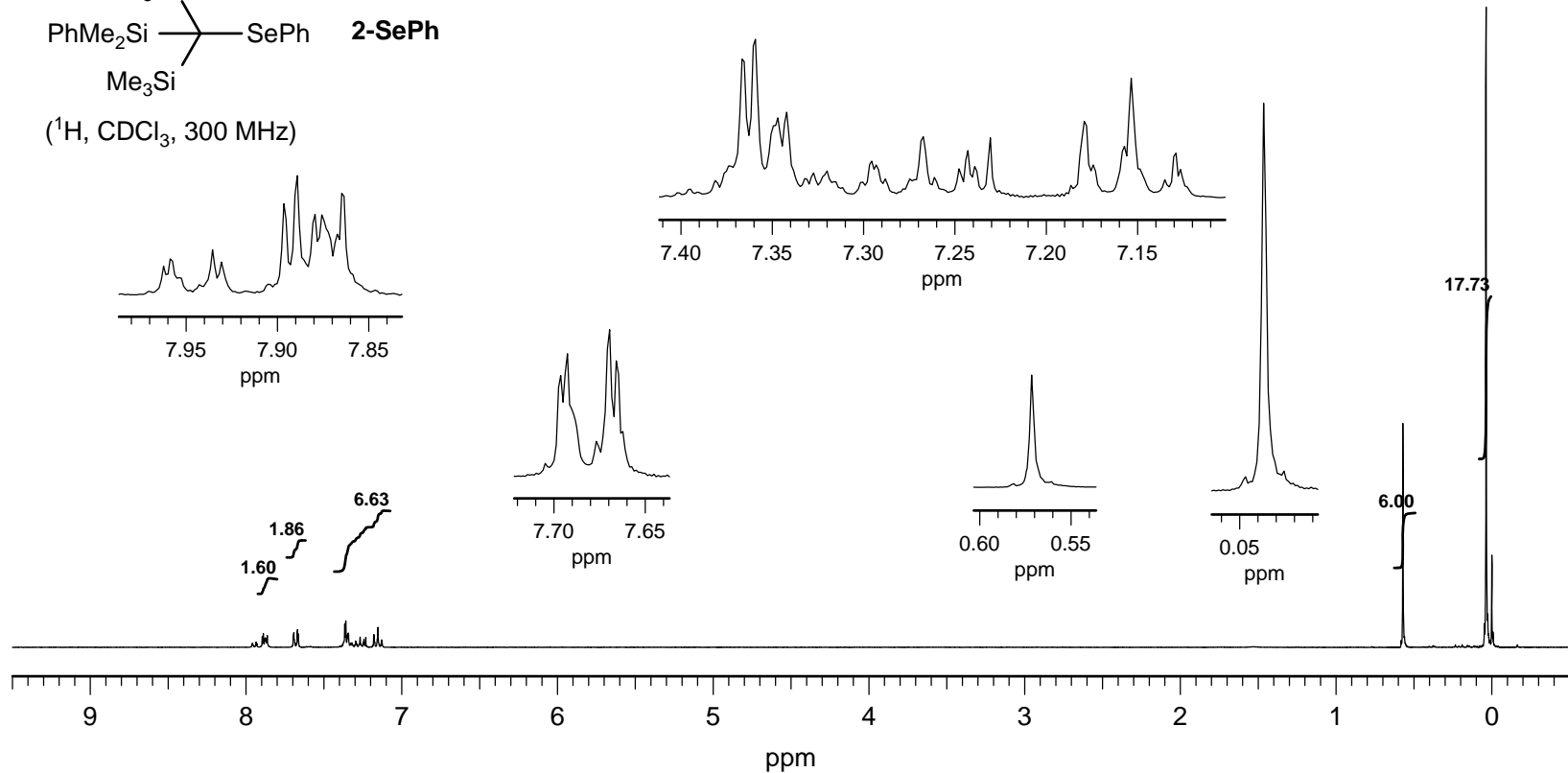


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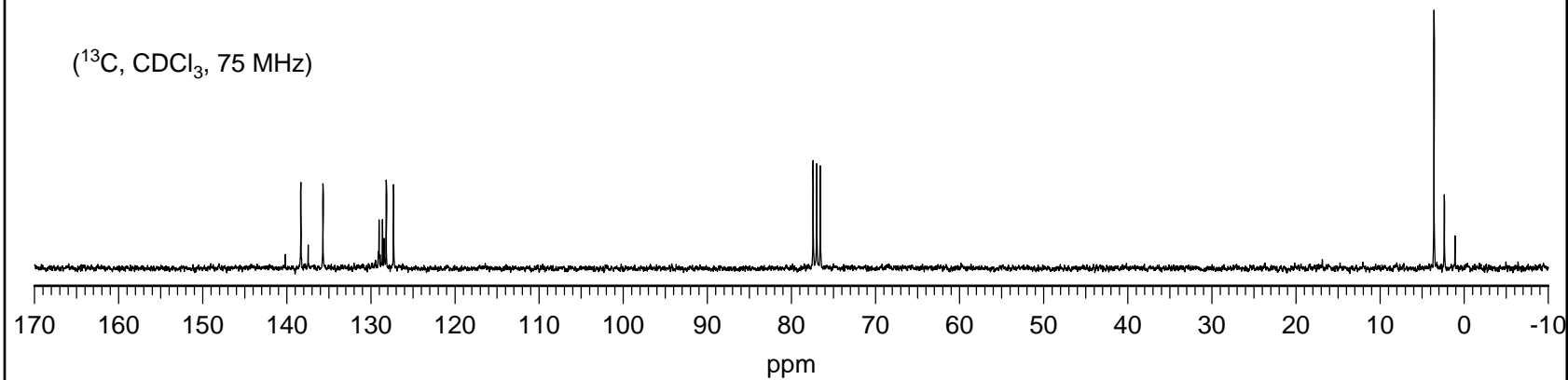


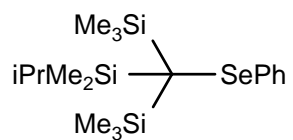


(^1H , CDCl_3 , 300 MHz)



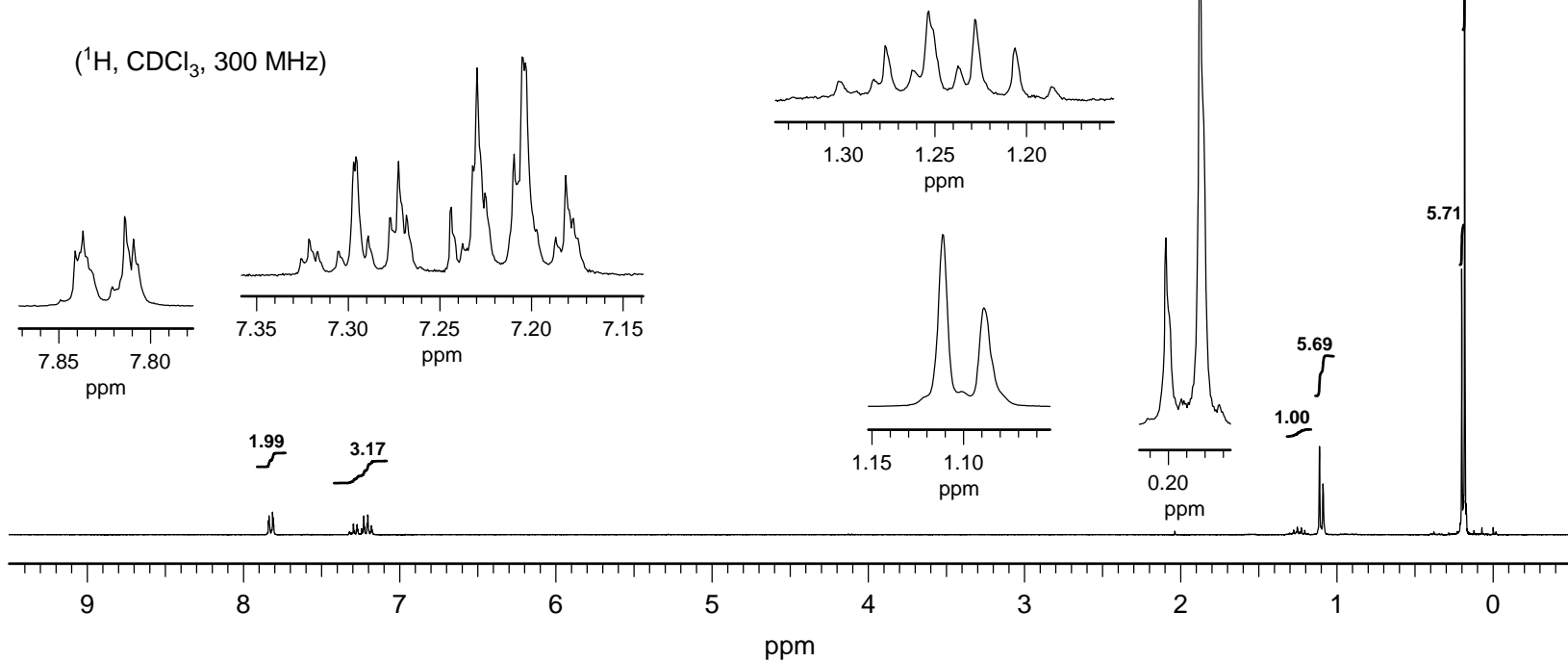
(^{13}C , CDCl_3 , 75 MHz)



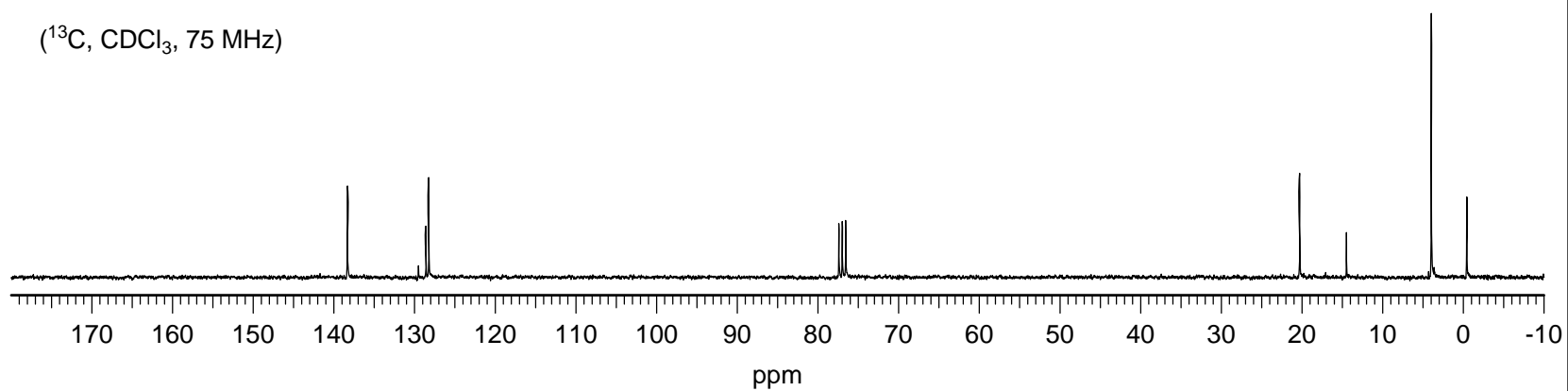


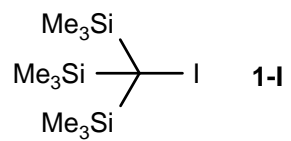
3-SePh

(¹H, CDCl₃, 300 MHz)

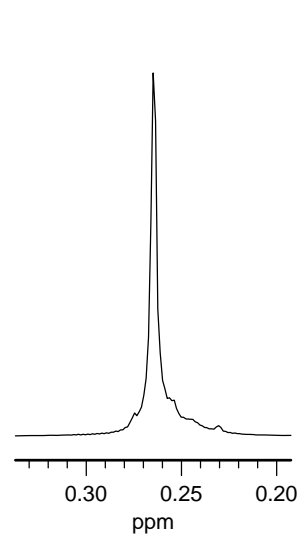


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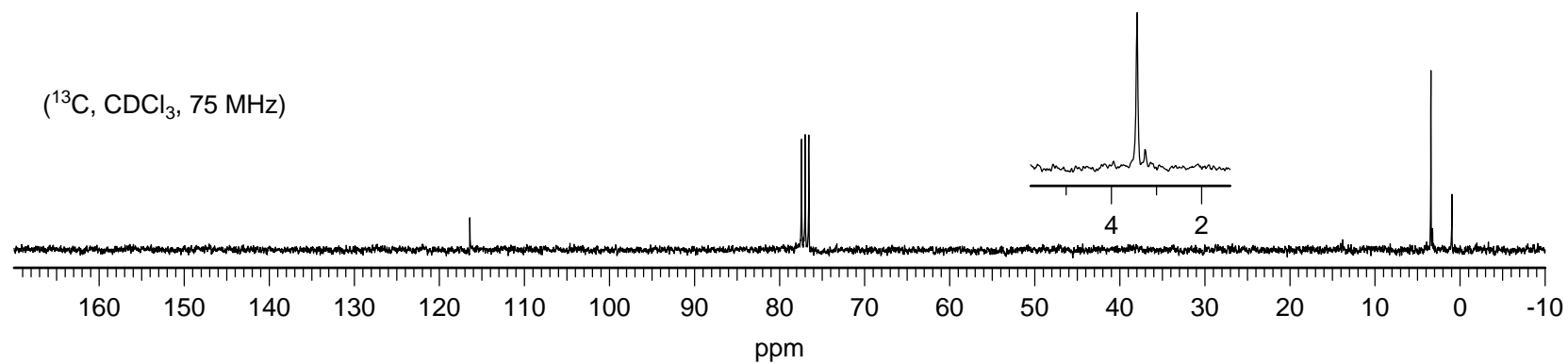


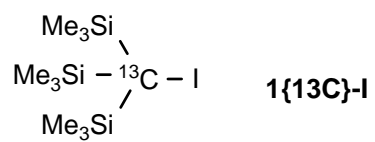
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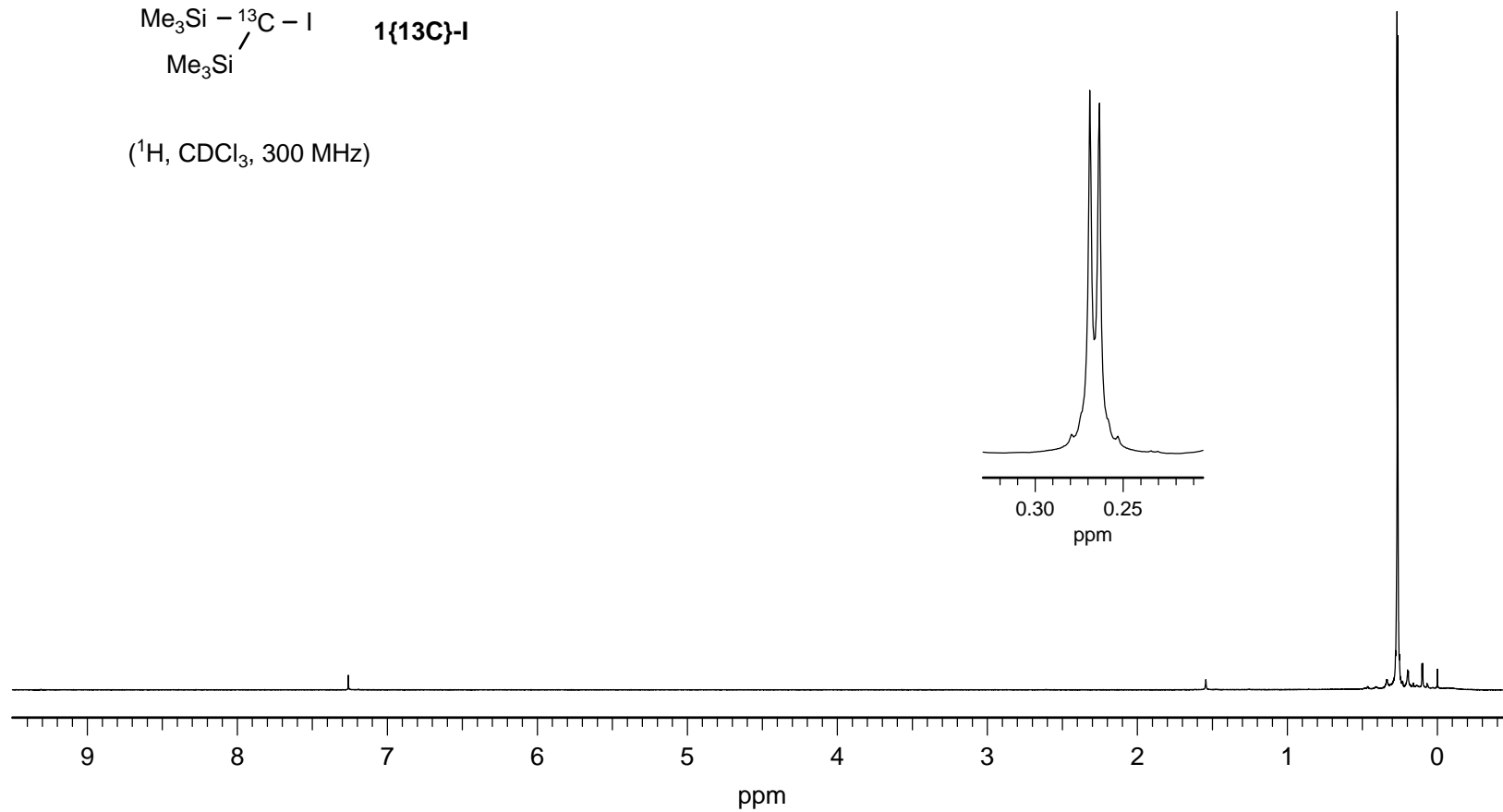
S-45

(¹³C, CDCl₃, 75 MHz)

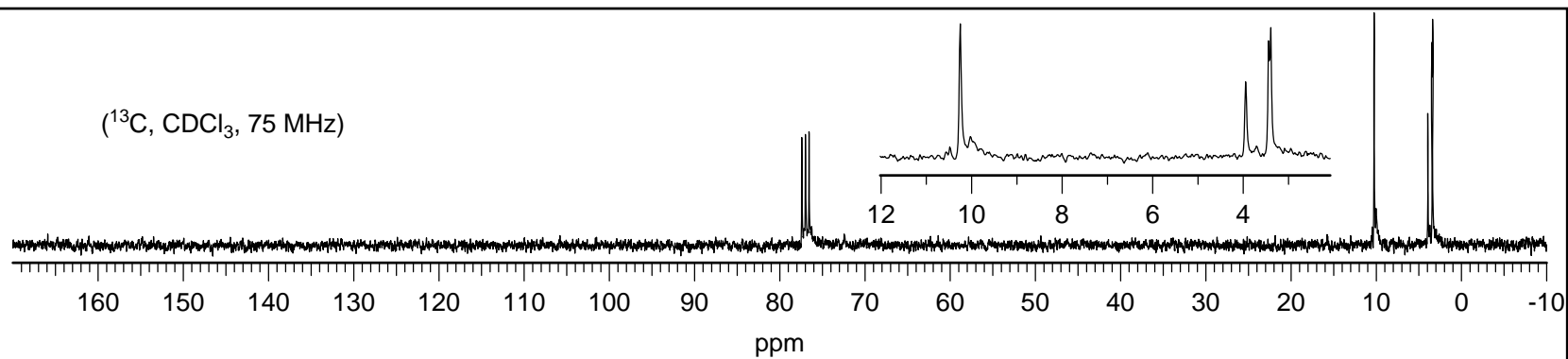




(^1H , CDCl_3 , 300 MHz)



(^{13}C , CDCl_3 , 75 MHz)



S6. Supporting Information References

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