

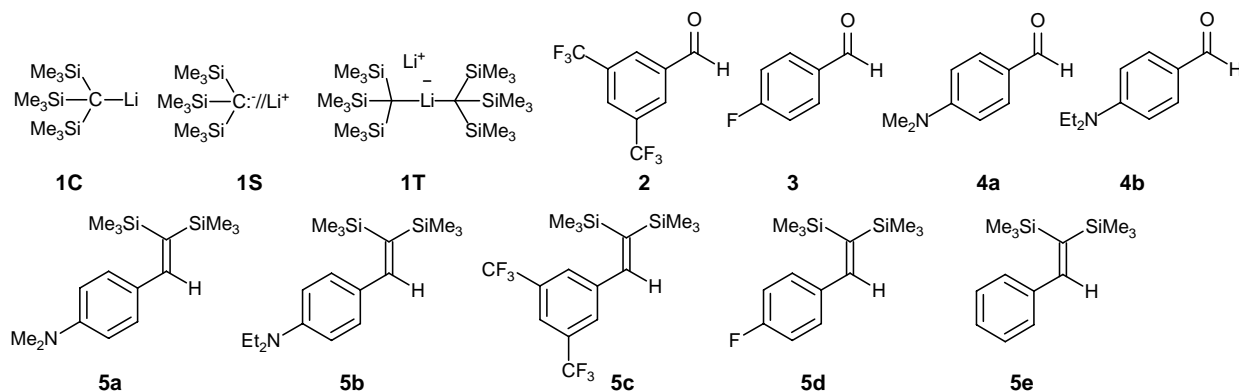
Reactivity of the Triple Ion and Separated ion pair of Tris(trimethylsilyl)methylithium with Aldehydes – a RINMR Study

Amanda C. Jones, Aaron W. Sanders, William H. Sikorski, Kristin L. Jansen, Hans J. Reich*
Department of Chemistry, University of Wisconsin Madison, WI 53706

Supporting Information

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S1. General Experimental

Tetrahydrofuran (THF) and diethyl ether (ether) were freshly distilled from sodium benzophenone ketyl before use. Glassware was placed overnight in a 110 °C oven or flame-dried before purging with N₂ to remove moisture. Common lithium reagents 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 and -20 °C with a chemical freezer. NMR tubes, injection needles and syringes were kept dry by storing them in an evacuated glove box antechamber. Probe temperatures were measured internally with 5-10 μL of the ¹³C chemical shift thermometer (Me₃Si)₃CH (10% ¹³C enriched).^[S2] This material contributes to the varying fractions of **1-H** in each sample, the relative amount dependant upon the concentration of **1**. This material was prepared by diluting ¹³CHCl₃ with 9 volumes of natural abundant CHCl₃ and converting to (Me₃Si)₃CH using the procedure of Yus and Guijarro, or by diluting (Me₃Si)₃¹³CH with 9 volumes of natural abundant material.^[S3]

Commercially available starting materials and reagents were obtained from Aldrich Chemical Company and included: iodomethane, 3,5-*bis*(trifluoromethyl)benzaldehyde (**2**), *p*-fluorobenzaldehyde (**3**), *p*-dimethylaminobenzaldehyde (**4a**), *p*-diethylaminobenzaldehyde (**4b**), diethyl disulfide. *Tris*(trimethylsilyl)methane was purchased, or prepared by reductive silylation of CHCl₃.^[S3]

S2. RINMR Experiments

The apparatus and techniques for performing RINMR experiments have been described previously.^[S4] 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 (δ 0.27).

The temperature of the RINMR sample is 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 has been determined in a number of control cases^[S4] and depends on the injection volume. There is approximately a 1° temperature jump for a 0.05 mL injection. Single scan ¹H RINMR spectra were typically collected with a 1 s acquisition time and a 14 ppm sweep width. For fast reactions, initial spectra were collected with a 0 s delay between spectra. A longer delay (15-60 s) was selected for the remainder of an experiment if/when the reaction rates were slower.

Individual spectra were processed using NUTS data processing software (Acorn NMR, Inc.). Peak areas were determined using the NUTS line fitting routine. The concentrations of **1** were determined relative to PhSiMe₃ using spectra prior to the injection but included the added volume from the injection. Substrate concentrations are reported as the external concentration of the solution to be injected, as well as the initial internal concentration after the solution has been injected into the sample (i.e., the in situ concentration). The solvent composition is reported uniformly as 3:1 THF/Me₂O, however, each sample contains ≤3% hexanes (from the *n*-BuLi used to prepare **1**) and in some cases ≤3% Et₂O from the solution injected. While these deviations are not reported, the solvent composition was measured using quantitative ¹³C NMR and taken into account for both concentration and temperature calculations.

Preparation of Solutions of *Tris*(trimethylsilyl)methylithium (1**) for RINMR Experiments.** A 10 mm NMR tube sawed to a length of 18 cm was sealed with a greased septum and parafilm and purged with argon. The ¹³C chemical shift thermometer (10% ¹³C labeled *tris*(trimethylsilyl)methane (**1-H**), 4 μL),^[S2] an internal standard for concentrations (PhSiMe₃, 28 mg, 0.186 mmol) and *tris*(trimethylsilyl)phenylselenomethane (**1-SePh**) (0.02 g-0.1 g, 0.05 mmol - 0.26 mmol) were weighed in using Hamilton syringes, followed by addition of 1 mL of freshly distilled THF. The NMR tube was cooled in a dry ice/acetone bath. Me₂O (3 mL) was distilled via cannula into the NMR tube from a graduated conical cylinder containing *n*-BuLi (for drying). *n*-BuLi in hexanes (2.5 M, 0.02-0.1 mL) was added by syringe to

form **1**. Reactions to monitor the reactivity of **1T** were typically done at higher concentrations (≥ 0.05 M **1**) where the triple ion comprised ca 40% of the total concentration of **1**. Reactions to monitor the reactivity of **1C** and **1S** were done at low concentration (≤ 0.02 M **1**) where the triple ion comprised ca 20 % of the total concentration of **1**.

¹H RINMR Spectroscopy of the Reaction 1S and 1C with MeI. MeI (0.1 mL, 3.5 M in 1:1 THF/Et₂O or NEAT) was injected into a solution of **1** (0.017 M) in 4 mL of 1:3 THF/Me₂O at -133 °C (Fig. S-1). The spectrometer was not warmed during the injection, so the experimental temperature is expected to be ca -132 °C. The separated ion **1S** has reacted when the first spectrum was acquired after the injection (1 s), so to estimate a lower limit for the rate we assume $\leq 5\%$ of the initial concentration of **1S** is present without being detectable. The triple ion **1T** does not react on this time scale. ¹H NMR spectra and a time vs concentration plot for a similar experiment with injection of 0.1 mL of MeI (20 equiv) are shown in the body of the communication (Fig. 1).

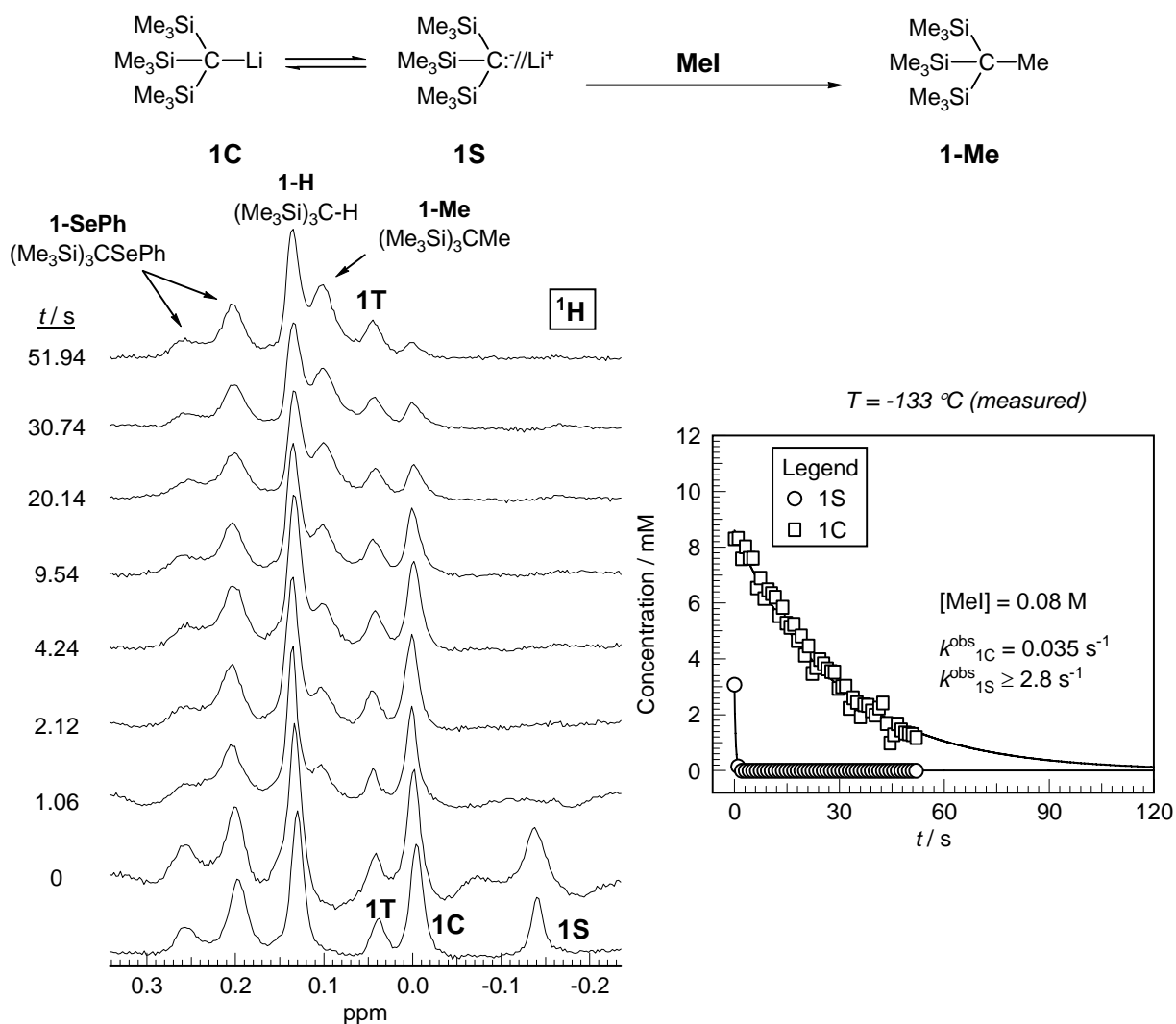


Figure S-1. ¹H NMR spectra and time vs concentration plot for the injection of MeI as a 3.5 M solution in 1:1 THF/Et₂O (0.08 M *in situ*) into a solution of **1** (0.016 M) in 4 mL of 1:3 THF/Me₂O at -133 °C (initial temperature).

^1H RINMR Spectroscopy for the Reaction of **1T with MeI at Various Temperatures.** MeI (0.1 mL, 5.6 M THF) was injected into a solution of **1** (0.07 M) in 4 mL of 1:3 THF/Me₂O at -78 °C, -86 °C and -96 °C. Representative ^1H NMR spectra and first order plots are shown in Fig. S-2. A series of experiments at several temperatures showed that the reaction rate was independent of [MeI].

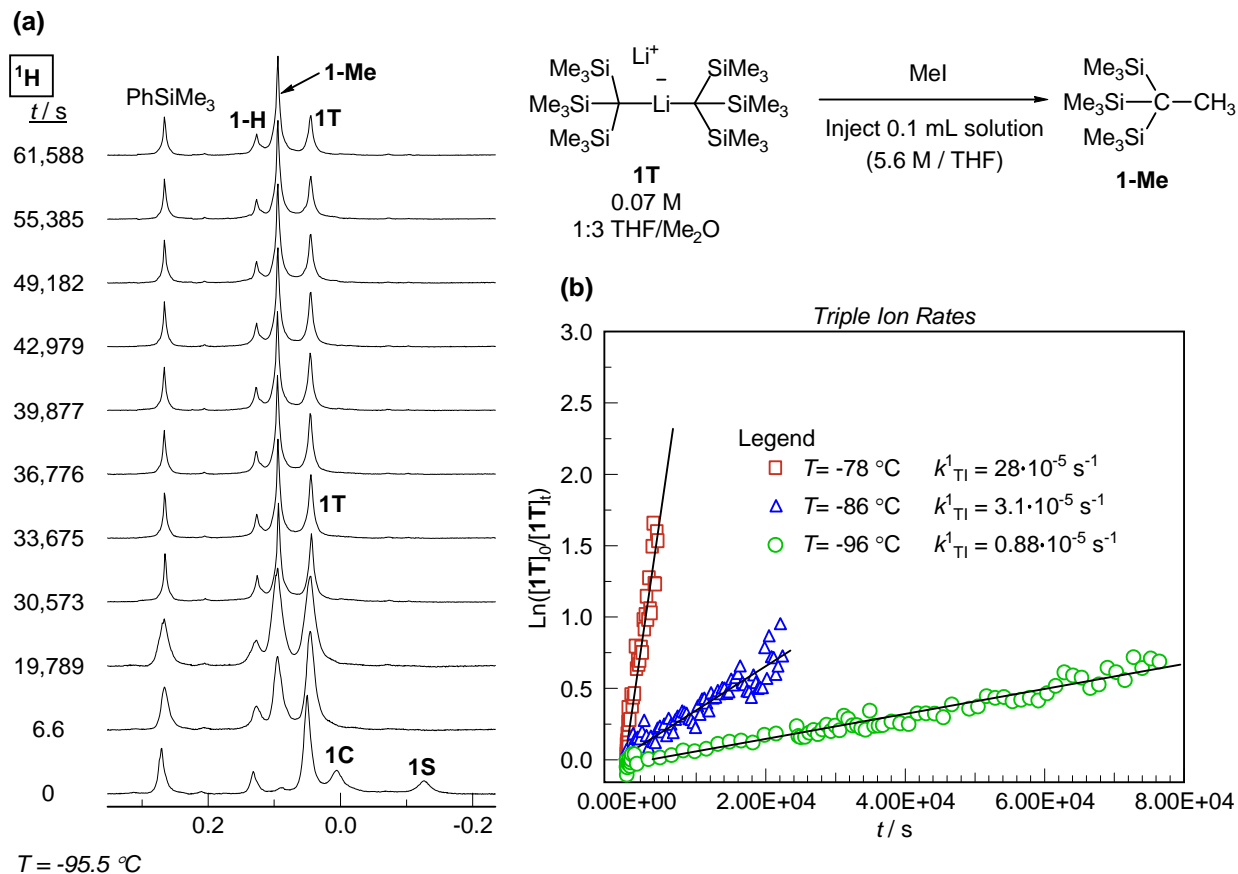


Figure S-2. (a) ^1H NMR spectra for injection of 0.1 mL a 5.6 M THF solution of MeI (0.13 M *in situ*) into a solution of **1** (0.06 M) in 4 mL of 1:3 THF/Me₂O at -96 °C. (b) First order plots for the 0.1 mL injections of a 5.6 M THF solution of MeI (0.13 M *in situ*) into solutions of **1** (0.06-0.07 M) in 1:3 THF/Me₂O at -77 °C, -86 °C and -96 °C.

Activation Parameters for the Dissociation of **1T as Measured by the Reaction with MeI.** Activation parameters were determined by converting first order rate constants (Fig. S-2b) to ΔG^\ddagger using the equation: $\Delta G^\ddagger = 1.987 \cdot T \cdot [23.76 + \ln(T/k)]$. The plot of T vs. ΔG^\ddagger is shown in Fig. S-3. At -132 °C, k_{1T} is calculated from the equation $k_{1T} = e^{(23.76 + \ln(T) - \Delta G/(1.987 \cdot 1.987))} = 4 \cdot 10^{-10} \text{ s}^{-1}$. Because the triple ion does not react with MeI faster than it dissociates to the monomers, this rate can be used as an upper limit on the possible rate of reaction of **1T** with MeI. Comparison to the mixing-limited rate of **1S** ($k_{1S-\text{MeI}} \geq 2 \text{ s}^{-1}$) indicates that **1S** is at least $5 \cdot 10^{10}$ times as reactive as **1T** with MeI.

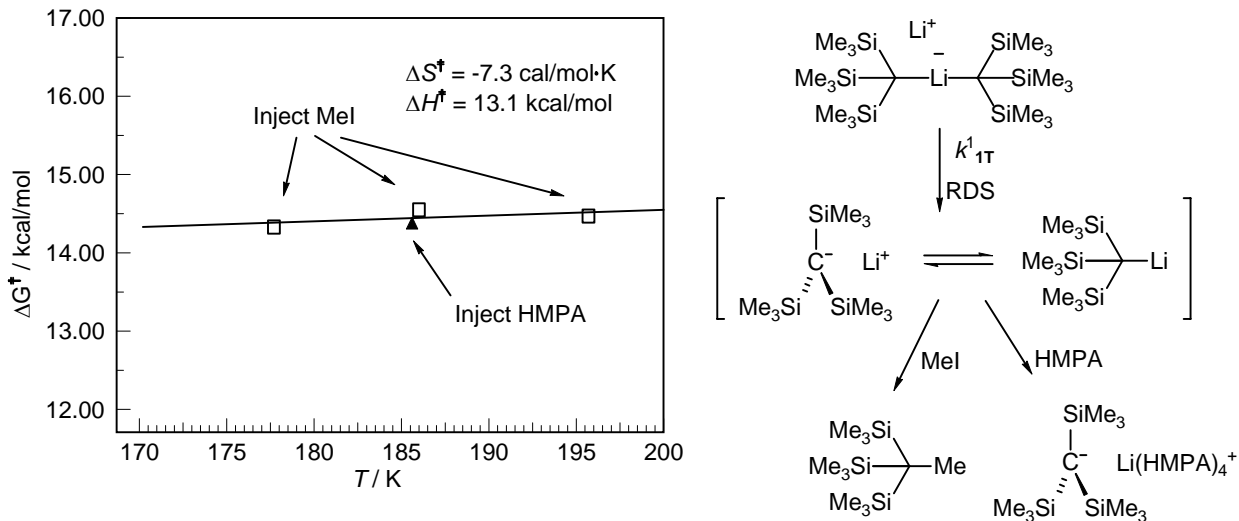


Figure S-3. Eyring plot for the first order reaction of **1T** with MeI and HMPA in 3:1 Me₂O/THF.

^1H RINMR Spectroscopy of the Reaction of **1 with 3,5-Bis(trifluoromethyl)benzaldehyde at ca -132 °C.** 3,5-Bis(trifluoromethyl)benzaldehyde (**2**) (0.1 mL, 1.1 M in 1:1 THF/Et₂O) was injected into a solution of **1C** and **1S** (0.017 M) in 4 mL of 1:3 THF/Me₂O at -134 °C (Fig. S-4). The spectrometer was not warmed during the injection so the actual temperature is expected to be ca -132 °C. To determine $k_{1\text{S}}^{\text{obs}}$ we estimate an undetectable 5% of the initial concentration of **1S** present at the second spectrum ($t = 1$ s). The triple ion was monitored for 4 h and showed negligible change in concentration. In the following aldehyde experiments, the signals labeled “LiOSiMe₃” were not securely identified as such, and sometimes changed from early to later parts of the experiment.

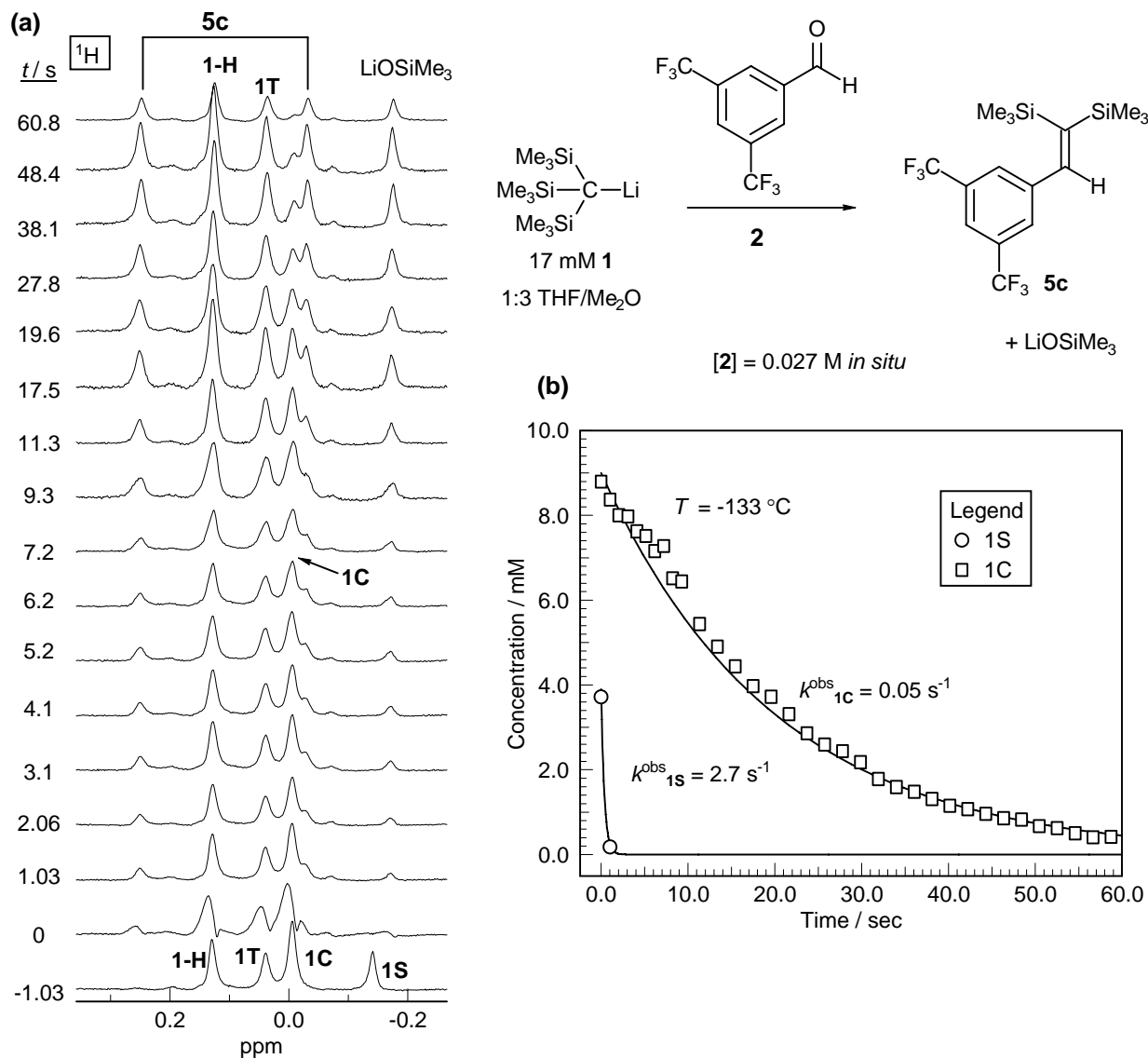


Figure S-4. (a) ^1H NMR spectra and (b) plot of **1S** and **1C** disappearance for the 0.1 mL injection of a 1.1 M THF solution of **2** (0.027 M *in situ*) into a solution of **1** (0.017 M) in 4 mL of 1:3 THF/Me₂O at ca -132 °C.

^1H RINMR Spectroscopy of the Reaction of **1 with Benzaldehyde and *p*-Fluorobenzaldehyde (**3**).**
 Benzaldehyde (0.1 mL, 1.2 M in 1:1 THF/Et₂O) was injected into a solution of **1** (0.018 M) in 4 mL of 1:3 THF/Me₂O at -134 °C (Fig. S-5). The spectrometer was not warmed during the injection so the actual temperature is expected to be ca -132 °C.

A solution of **3** (0.1 mL, 7.5 M in Et₂O) was injected into a solution of **1** (0.018 M) in 1:3 THF/Me₂O at -135 °C. The spectrometer was not warmed during the injection. The two-phase behavior in the disappearance of **1C** is attributed to the effect of the initial sample warming due to injection, followed by efficient cooling.

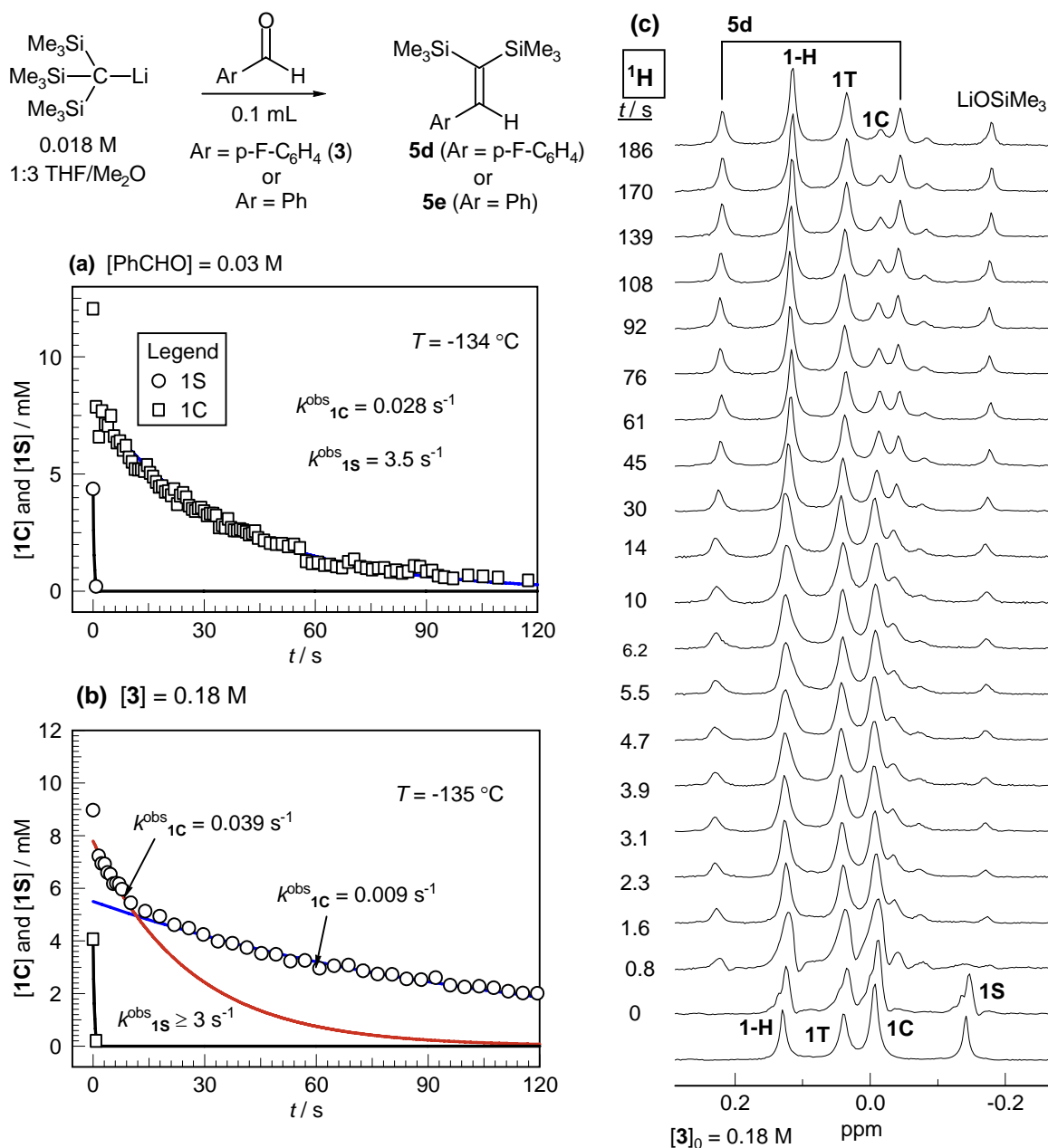
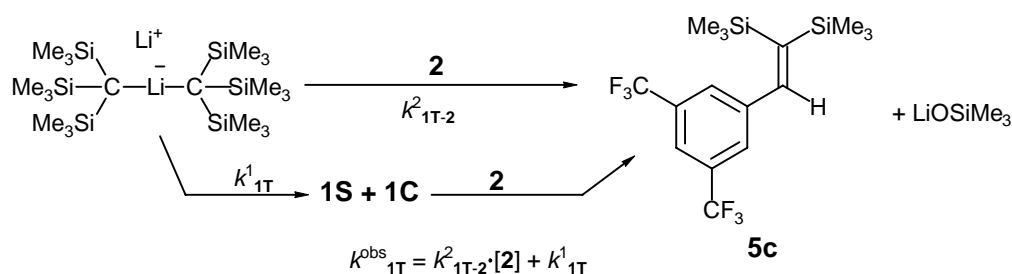


Figure S-5. Time vs concentration plots for the injection of (a) benzaldehyde (0.1 mL, 1.2 M in 1:1 THF/Ether) and (b) *p*-fluorobenzaldehyde (**3**) (0.1mL, 7.45 M in 1:1 THF/ether) into a solution of **1** (0.018 M) in 4 mL of 1:3 THF/Me₂O. (c) Selected ^1H NMR spectra for the experiment with (**3**)



¹H RINMR Spectroscopy of the Reaction of 1T with 3,5-Bis(trifluoromethyl)benzaldehyde (2) at Various Temperatures. Six trials of RINMR experiments were run with **1** and **2** in 4 mL of 1:3 THF/Me₂O, at three different temperatures: -95 °C, -87 °C, -73 °C. The reactions of **1S** and **1C** are too fast to measure. An average order in **2** of $n = 0.7$ was determined from plots of $\ln[2]$ vs $\ln[k^{obs}_{1T}]$. The order less than 1 indicates the pathway of zero order (in aldehyde) dissociation of **1T** to **1S** and **1C** significantly competes with the second order process. The first and second order rate constants (k^2_{1T-2} and k^1_{1T}) were determined for each temperature from plots of $[2]$ vs. k^{obs}_{1T} . The aldehyde was injected as a solution in 1:1 THF/Et₂O. Representative ¹H NMR spectra are shown in Fig. S-6. The rate data are shown in Table S-1.

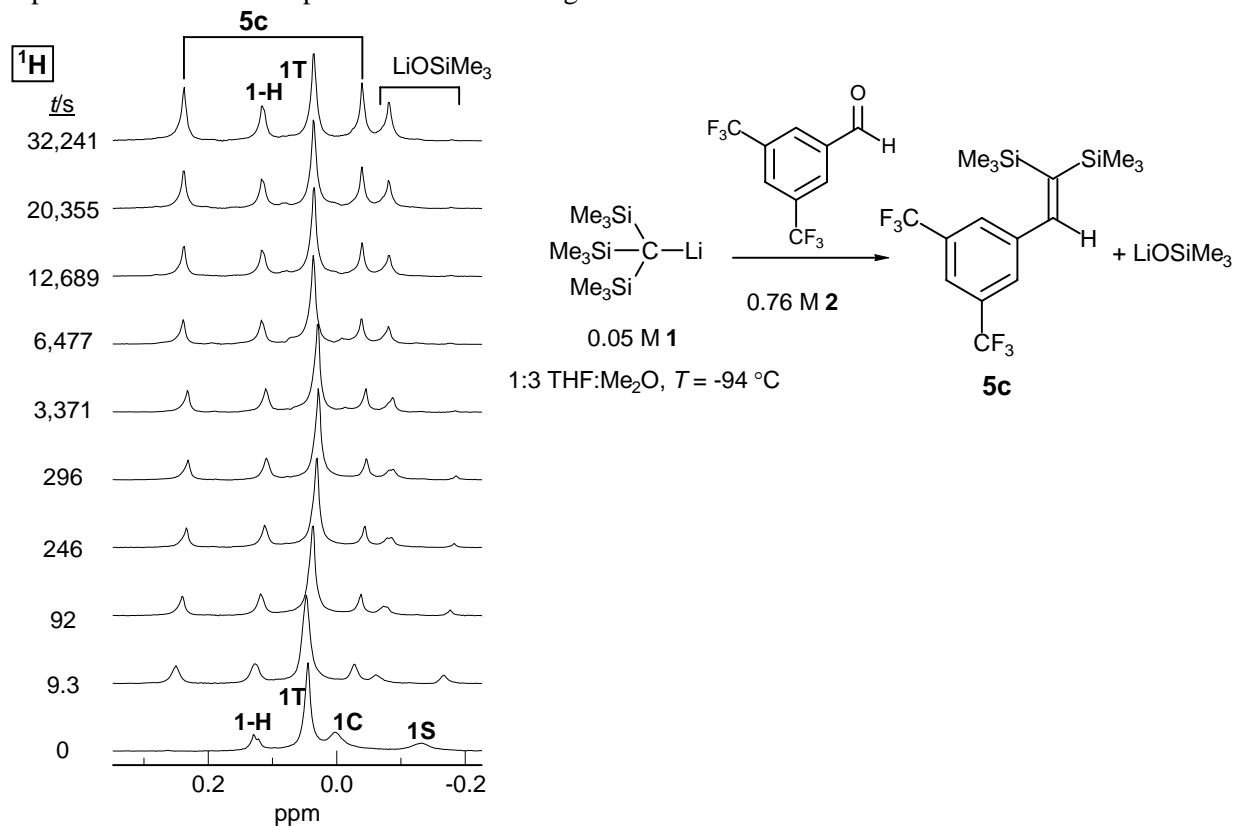


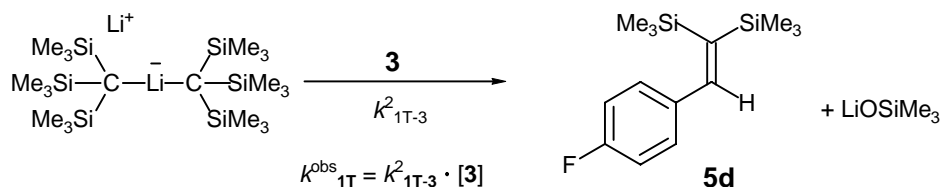
Figure S-6. ¹H NMR spectra for the 0.1 mL injection of a 3.8 M THF/Et₂O solution of **2** (0.76 M *in situ*) into a 0.05 M solution of **1** in 4 mL of 1:3 THF/Me₂O at -95 °C.

Table S-1. Rate constants for the injections of **2** into solutions of **1** (0.05-0.06 M) in 4 mL of 1:3 THF/Me₂O.

T / °C	k_{1T}^{obs} / s^{-1}	[2] / mM ^a	k_{1T}^1 / s^{-1}	$k_{1T-2}^2 / M^{-1} s^{-1}$	n
-95	$1.5 \cdot 10^{-5}$	50			
-94	$4.8 \cdot 10^{-5}$	270	$7.7 \cdot 10^{-6}$	$1.5 \cdot 10^{-4}$	0.8
-87	$5.5 \cdot 10^{-5}$	60			
-87	$11.8 \cdot 10^{-5}$	300	$3.9 \cdot 10^{-5}$	$2.6 \cdot 10^{-4}$	0.5
-78				$1.6 \cdot 10^{-4}$ ^b	
-73	$34 \cdot 10^{-5}$	50			
-73	$150 \cdot 10^{-5}$	360	$1.4 \cdot 10^{-4}$	$3.7 \cdot 10^{-3}$	0.8

^a The reported concentration of **2** is calculated following the reaction of **1S** and **1C**.

^b Extrapolated rate constant used for the relative rates reported in Fig. 2 in the main body of the communication.



¹H RINMR Spectroscopy of the Reaction of 1T with *p*-Fluorobenzaldehyde (3**) at Various Temperatures.** Seven trials of RINMR experiments were run with **1** and **3** in 4 mL of 1:3 THF/Me₂O, at four different temperatures: -105 °C, -95 °C, -82 °C, -87 °C. The reactions of **1S** and **1C** are too fast to measure. An average order in **3** of n=1.1 was determined from plots of ln[**3**] vs ln[k_{1T}^{obs}]. The first order behavior indicates that the dissociation of **1T** to **1S** and **1C** does not compete significantly with the second order process. Second order rate constants (k_{1T-3}^2) were determined from plots of [**3**] vs. k_{1T}^{obs} . The aldehyde **3** was injected either as a solution in 1:1 THF/Et₂O or pure THF. Representative ¹H NMR spectra and conditions are shown in Fig. S-7. The rate data are shown in Table S-2.

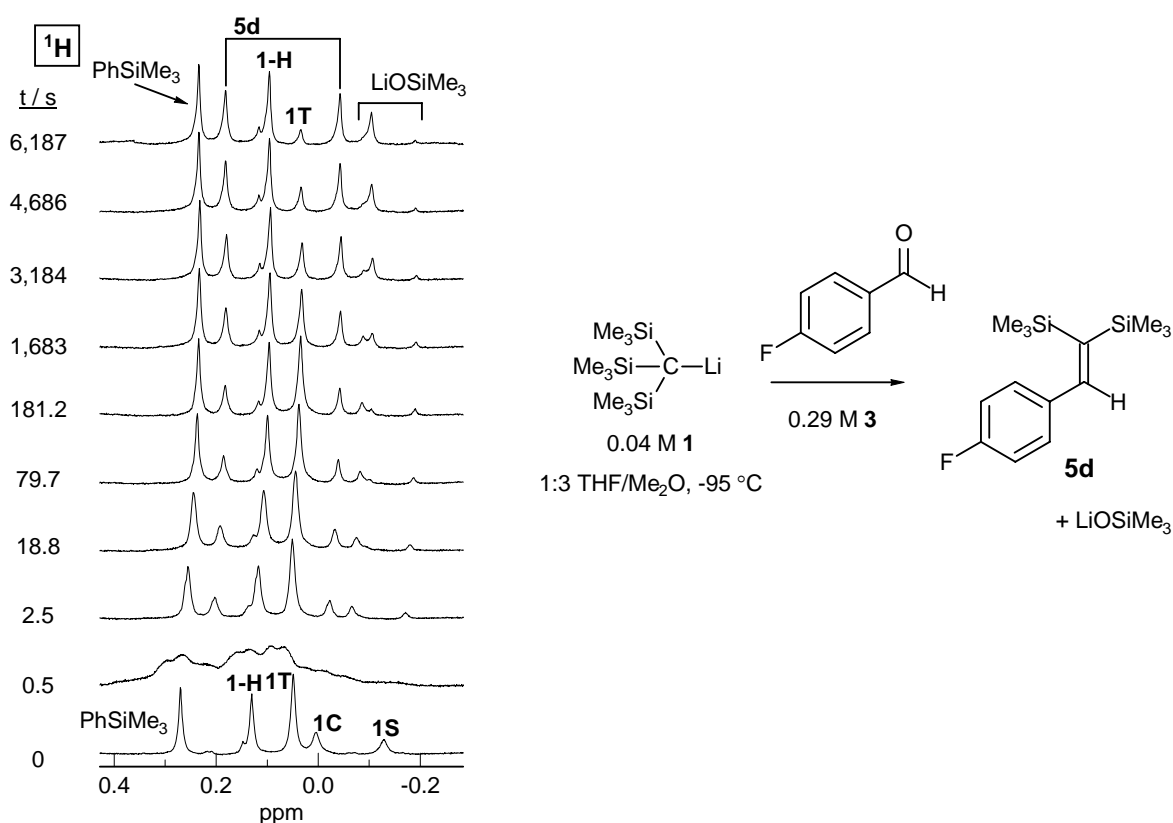


Figure S-7. ^1H NMR spectra for the 0.2 mL injection of a 7.2 M THF solution of **3** (0.3 M *in situ*) into a 0.04 M solution of **1** in 4 mL of 1:3 THF/Me₂O at -95 °C.

Table S-2. Rate constants for the injections of **3** into solutions of **1** (0.04-0.06 M) in 4 mL of 1:3 THF/Me₂O.

T / °C	$k_{\text{IT}}^{\text{obs}} / \text{s}^{-1}$	[3] / mM ^a	$k_{\text{IT-3}}^2 / \text{M}^{-1} \text{s}^{-1}$	n
-105	$1.6 \cdot 10^{-5}$	40		
-104	$9.7 \cdot 10^{-5}$	210	$4.9 \cdot 10^{-4}$	1.2
-94	$8.2 \cdot 10^{-5}$	40		
-95	$57 \cdot 10^{-5}$	270	$2.1 \cdot 10^{-3}$	1.1
-87	$2.4 \cdot 10^{-3}$	230	0.011 ^b	N/A
-83	$0.8 \cdot 10^{-3}$	30		
-83	$7.4 \cdot 10^{-3}$	360	0.02	0.9
-78			0.039 ^c	

^a The reported concentration of **3** is calculated following the reaction of **1S** and **1C**.

^b A second order rate constant was estimated using the equation $k_{\text{IT}}^{\text{obs}}/[\mathbf{3}]$.

^c Extrapolated rate constant used for the relative rates reported in Figure 2 in the main body of the communication.

^1H NMR Spectroscopy for the Reaction of 1T with *p*-Dimethylaminobenzaldehyde (4a) at $-80\text{ }^\circ\text{C}$ in THF/Me₂O. *p*-Dimethylaminobenzaldehyde (0.25 mL, 0.6 M or 1.5 M THF) was injected into a solution of **1** (0.022-0.024 M) in 4 mL of 1:3 THF/Me₂O at ca $-80\text{ }^\circ\text{C}$. An order of 1.1 in **4a** was determined from a plot of $\ln[\mathbf{4a}]$ vs $\ln[k_{1\text{T}}^{\text{obs}}]$. A second order rate constant ($k_{1\text{T-4a}}^2$) was determined from a plot of $[\mathbf{4a}]$ vs. $k_{1\text{T}}^{\text{obs}}$. Representative spectra and plots of triple ion disappearance are shown in Fig. S-8. The rate data are listed in Table S-3.

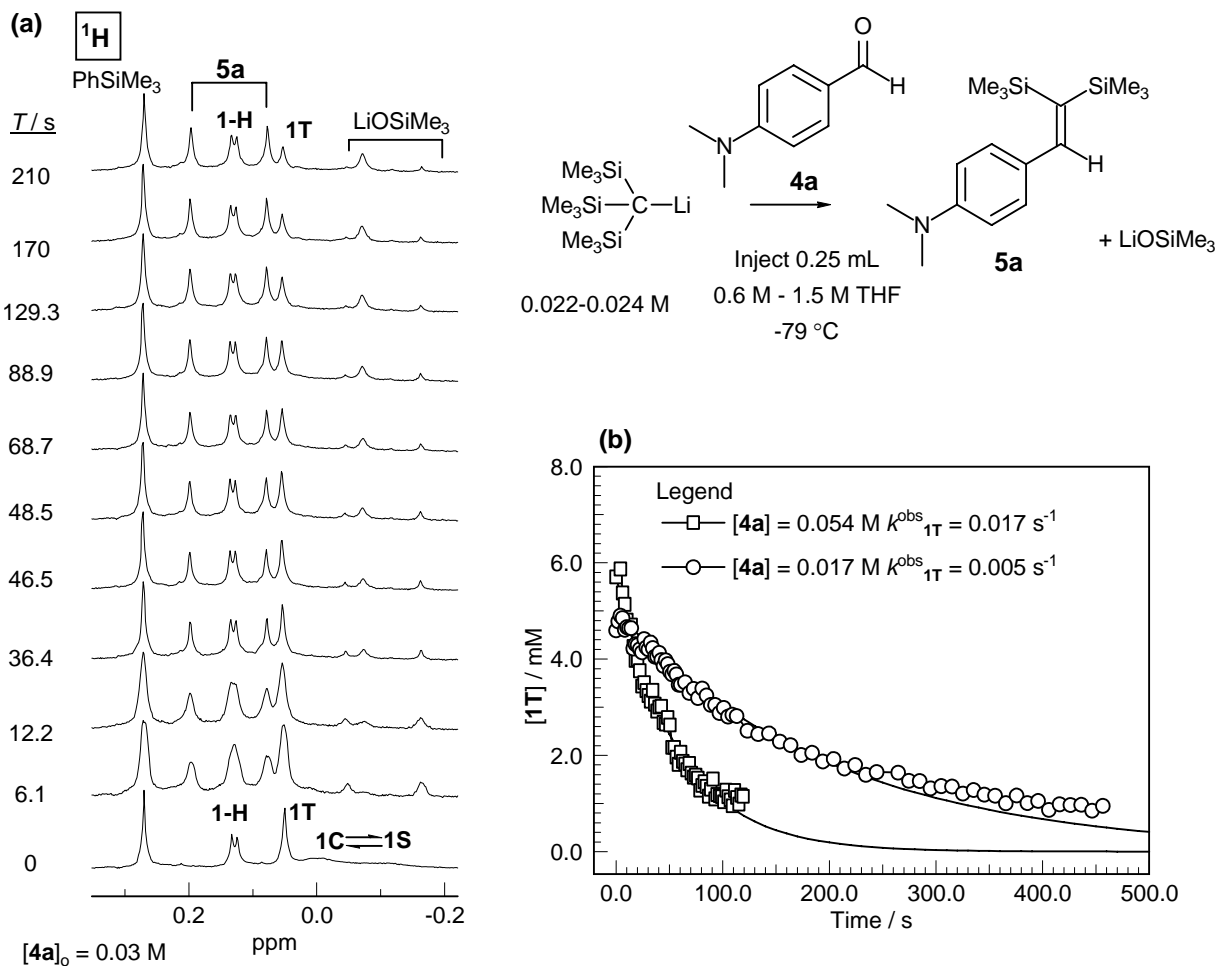
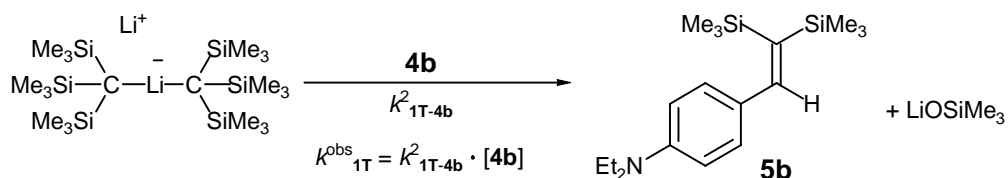


Figure S-8. (a) ^1H NMR spectra for the 0.25 mL injection of a 0.6 M THF solution of **4a** (0.03 M *in situ*) into a 0.022 M solution of **1** in 4 mL of 1:3 THF/Me₂O at $-79\text{ }^\circ\text{C}$ and (b) raw plots for the decay of triple ion after two injections of **4a** into a solution of **1** in 4 mL of 1:3 THF/Me₂O.

Table S-3. Rate data for the injections of **4a** into solutions of **1** (0.022-0.024 M) in 4 mL of 1:3 THF/Me₂O.

$T / ^\circ\text{C}$	$k_{1\text{T}}^{\text{obs}} / \text{s}^{-1}$	$[\mathbf{4a}] / \text{mM}$	$k_{1\text{S-4a}}^2 / \text{M}^{-1} \text{s}^{-1}$	n
-79	0.005	17	0.32 ^a	1.1
-80	0.017	86		

^a Used for the relative rates reported in Figure 2 of the main body of the paper.



¹H RINMR Spectroscopy of the Reaction of **1 with *p*-Diethylaminobenzaldehyde (**4b**) at Various Temperatures.** Aldehyde **4b** (0.2-0.3 mL, 1.2-7.1 M THF) was injected into a solution of **1** (0.04-0.07 M) in 4 mL of 1:3 THF/Me₂O at -131 °C, -93 °C, -87 °C and -81 °C. At $T \geq -93$ °C, the reaction of **1S** and **1C** are too fast to measure. The experiment at -131 °C is described in further detail below.

For the reaction of **1T** at the various temperatures, an average order in **4b** of $n=1$ was determined from plots of $\ln[4b]$ vs $\ln[k_{1T}^{obs}]$. The first order behavior indicates that dissociation of **1T** to **1S** and **1C** does not compete significantly with the second order process. Second order rate constants (k_{1T-4b}^2) were determined from plots of $[4b]$ vs. k_{1T}^{obs} . Representative ¹H NMR spectra and conditions are shown in **Fig. S-9**. The rate data are shown in **Table S-4**.

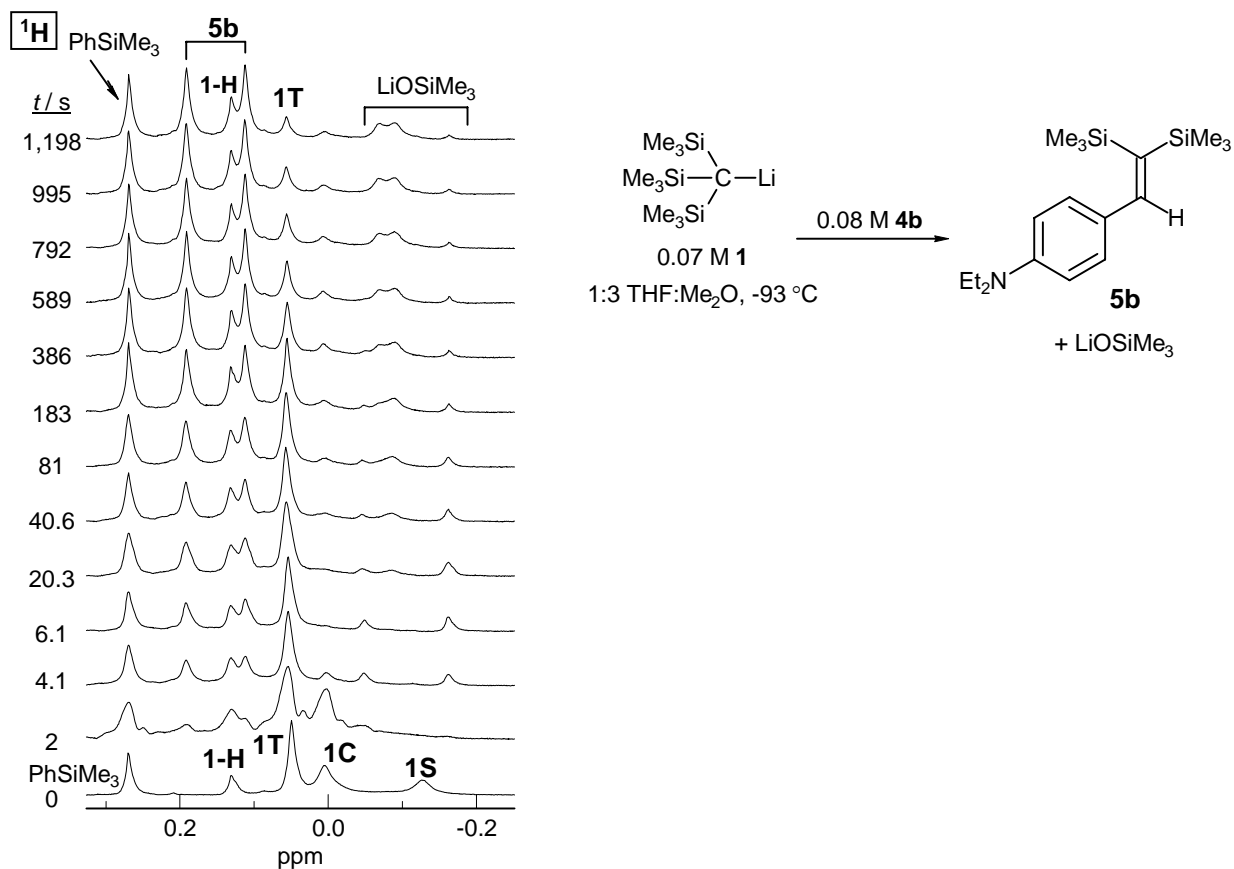


Figure S-9. ¹H NMR spectra for the 0.25 mL injection of a 1.8 M THF solution of **4b** (0.08 M *in situ*) into a 0.07 M solution of **1** in 4 mL of 1:3 THF/Me₂O at -93 °C.

Table S-4. Rate constants for injections of **4b** into solutions of **1** (0.04-0.06 M) in 4 mL of 1:3 THF/Me₂O.

T / °C	k_{IT}^{obs} / s^{-1}	[4b] / mM ^a	$k_{IT-4b}^2 / M^{-1} s^{-1}$	n
-131	$1.3 \cdot 10^{-5}$	45		
-130	$2.8 \cdot 10^{-5}$	110	$23 \cdot 10^{-5}$	0.9
-93	0.0032	30		
-93	0.016	110	0.16	1.3
-87	0.04	150	0.3 ^b	N/A
-81	0.02	44		
-81	0.07	140	0.5	1
-78			0.82 ^c	

^a The reported concentration of **4b** is calculated following the reaction of **1S** and **1C**.

^b A second order rate constant was calculated using the equation $k_{IT-4b}^{obs}/[4b]$.

^c Extrapolated rate constant used for the relative rates reported in Fig. 2 in the main body of the communication.

At -131 °C, **4b** was injected (0.25 - 0.4 mL, 1.2 - 2.5 M) as a solution in 3:1 and 3:2 THF/Et₂O (Fig. S-10). A higher concentration injection was not possible due to precipitation of **4b** and sample freezing. For the same reasons, experiments with *p*-dimethylaminobenzaldehyde (**4a**) could not be performed at this temperature. Whereas in the case of MeI, benzaldehyde, **2**, and **4**, the rate of disappearance of **1C** was constant and determined by rate-limiting dissociation to **1S**, the disappearance of **1C** upon reaction with **4b** was inhibited by a factor of ca 100. Although the observed inverse first order dependance on **2b** is inconclusive based upon the small change in [**4b**] for the two trials, the fact of the inhibition is striking and outside of the range of normal error. When sample freezing becomes problematic a similar “apparent” inhibition can be observed, but in such cases **1S** is affected as well and the plots of decay of **1S** and **1C** are highly irregular. The immediate reaction of **1S**, and the fairly regular first order decay of **1C** leads us to believe freezing was not the issue in these experiments. Since we have observed a strong interaction between **4b** and **1T**, it might also be expected that **4b** interacts strongly with **1C**, however a mechanistic investigation of this interaction was not pursued further.

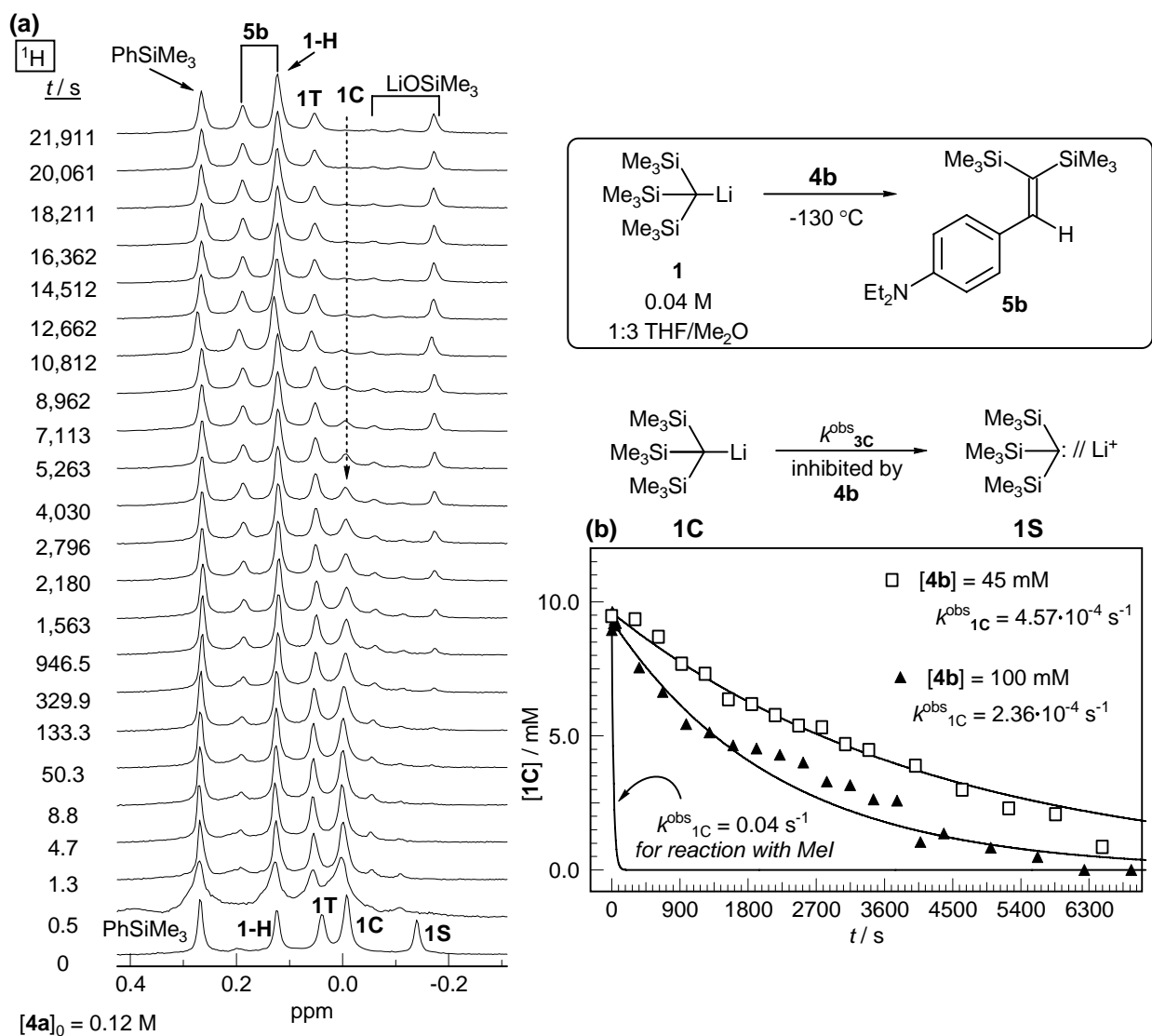


Figure S-10. (a) ^1H NMR spectra for the injection of *p*-diethylaminobenzaldehyde (0.25 mL, 2.5 M in THF, 0.12 M in situ) into a solution of **1** (0.04 M) in 4 mL of 1:3 THF/Me₂O at -131 °C and (b) raw plots of disappearance of **1C** for two concentrations of **4b**.

Activation Parameters for the reaction of Aldehydes (2, 3, 4b) with 1T. Activation parameters were determined by converting second order rate constants (Tables S-1, S-2, S-4) to ΔG^\ddagger using the equation: $\Delta G^\ddagger = 1.987 \cdot T \cdot [23.76 + \ln(T/k)]$. If the temperature of the variable concentration experiments differed slightly, an average temperature was used for the plot below (Fig. S-11).

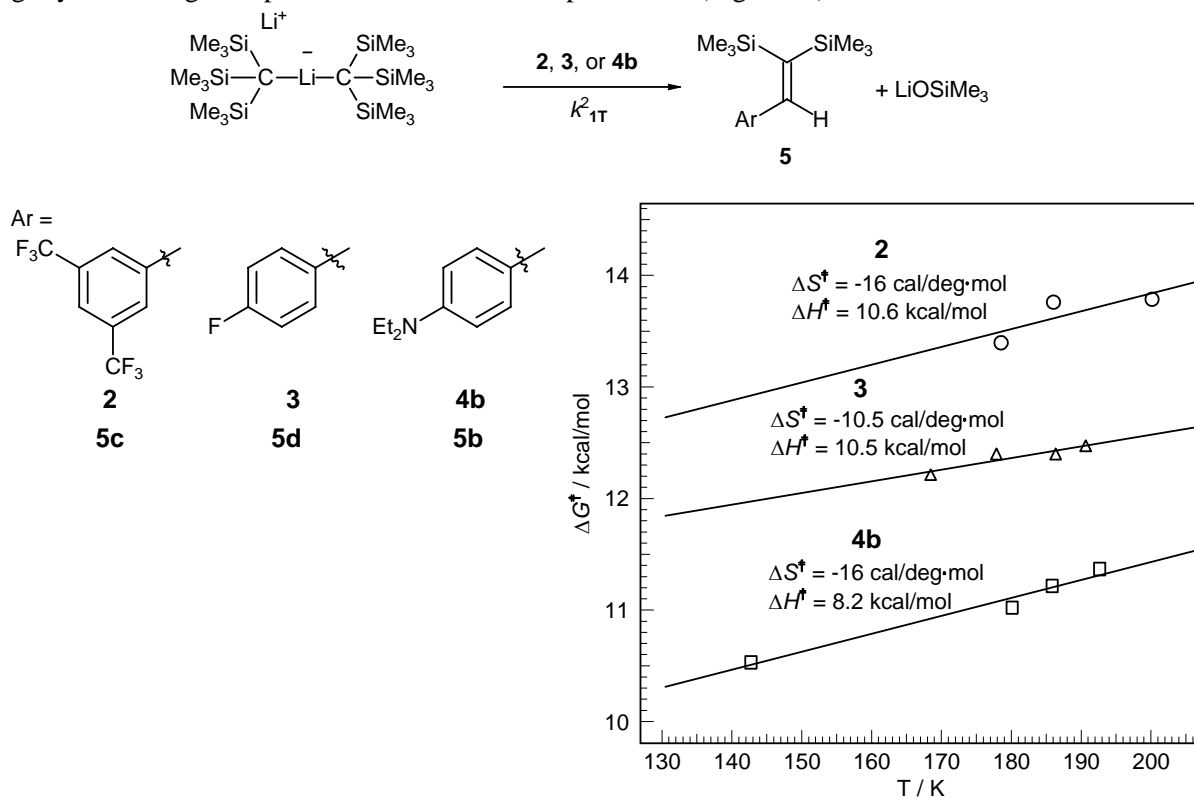


Figure S-11. Eyring plot for the second order reactions of 1T with aldehydes 2, 3, 4b in 1:3 THF/Me₂O.

^1H RINMR Spectroscopy of the reaction of 1T with HMPA at $-86\text{ }^\circ\text{C}$. HMPA (0.2 mL, 4.3 M in THF) was injected into a solution of **1** (0.04 M) in 4 mL of 1:3 THF/Me₂O (Fig. S-12). The rate determined for dissociation of **1T** is shown on the Eyring plot of Fig. S-3. It is within error of that measured by the injection of MeI..

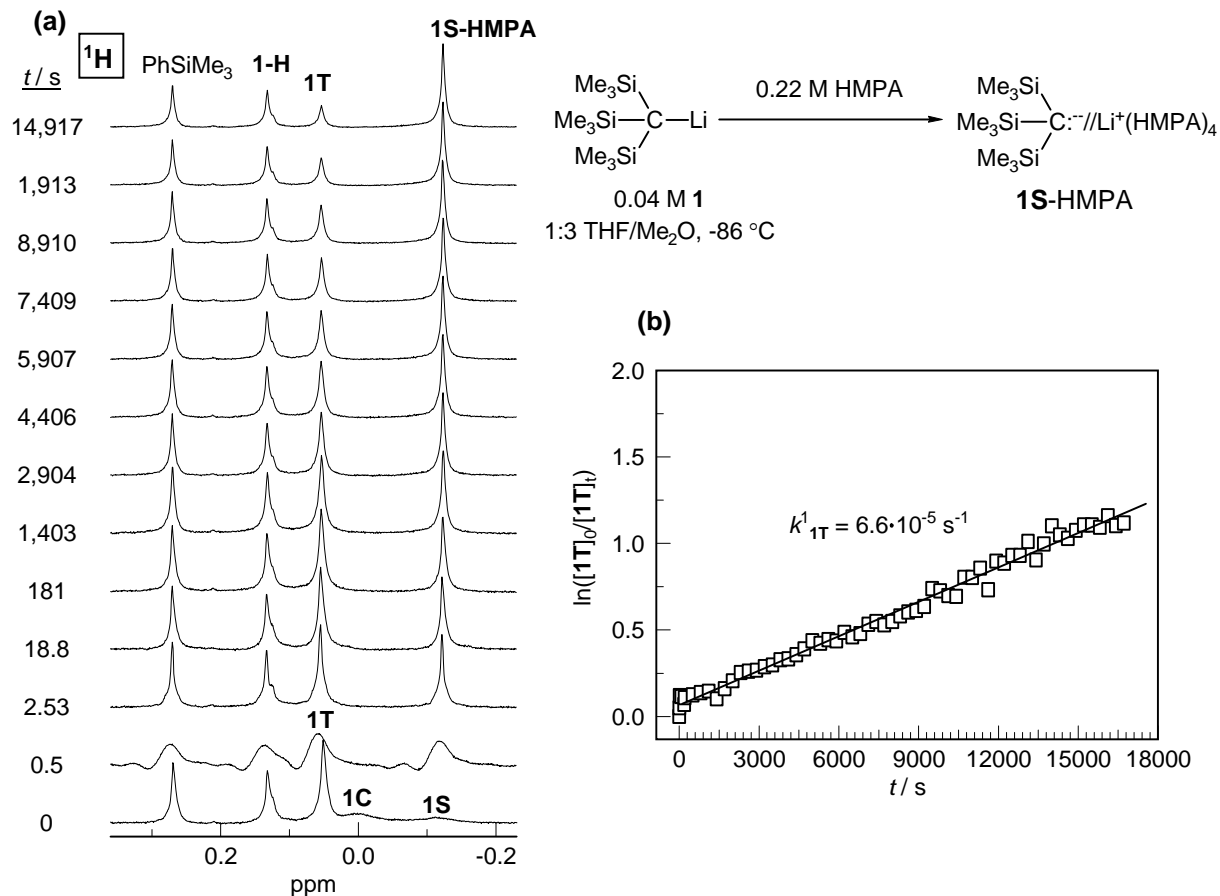


Figure S-12. (a) ^1H NMR spectra and (b) first order plot for the 0.2 mL injection of a 4.4 M THF solution of HMPA (0.22 M in situ) into a 0.04 solution of **1** in 4 mL of 1:3 THF/Me₂O at $-86\text{ }^\circ\text{C}$.

^1H NMR Spectroscopy for the Reaction of **1T with *p*-Dimethylaminobenzaldehyde (**4a**) in THF/Me₂O/HMPA.** The rate of **1T** with **4a** was determined by injecting 0.25 mL of a solution of **4a** (0.22 or 1.5 M) in HMPA (0.77 mL, 4.4 mmol) and THF (0.25 mL) into a solution of **1** (0.06 M) in 4 mL of 1:3 THF/Me₂O at -80 °C (in situ [HMPA] = 0.25 M and [**4a**] = 0.01 or 0.06 M). An order of 0.85 in **4a** was determined from a plot of $\ln[\mathbf{4a}]$ vs $\ln[k_{\text{1T}}^{\text{obs}}]$ for two concentrations of aldehyde. A second order rate constant ($k_{\text{1T-4a}}^2$) was determined from a plot of [**4a**] vs. $k_{\text{1T}}^{\text{obs}}$, and is within error of the rate of **1T** in the absence of HMPA (compare to data in Table S-3). Representative spectra are shown in Fig. 3 of the communication and plots of triple ion disappearance are shown in Fig. S-13.

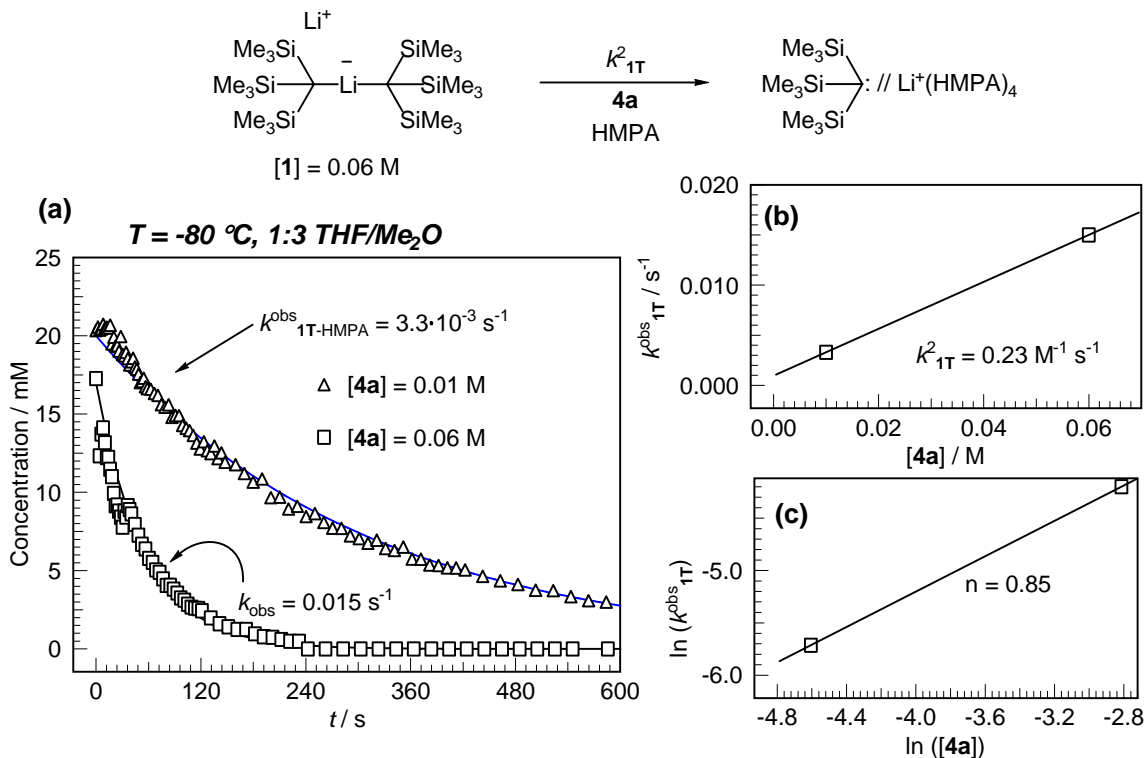


Figure S-13. (a) Raw plots for the decay of triple ion after the injection of *p*-dimethylaminobenzaldehyde and HMPA (0.25 M in situ) into a solution of **1** in 4 mL of 1:3 THF/Me₂O. Plots of (b) $k_{\text{1T}}^{\text{obs}}$ vs. [**4a**] to determine a second order rate constant and of (c) $\ln[\mathbf{4a}]$ vs $\ln(k_{\text{1T}}^{\text{obs}})$ to determine order in aldehyde.

^1H NMR Spectroscopy for the Reaction of 1S-HMPA with 3,5-Bis(trifluoromethyl)benzaldehyde (2). HMPA (0.13 mL, 0.075 mol) was added to an NMR sample of **1** (0.027 M) in 4 mL of 1:3 THF/Me₂O at -78 °C. A solution of **2** (0.1 mL, 2.5 M in 1:1 THF/Et₂O) was injected by RINMR at -131 °C (Fig. S-14). The rate is too fast to measure.

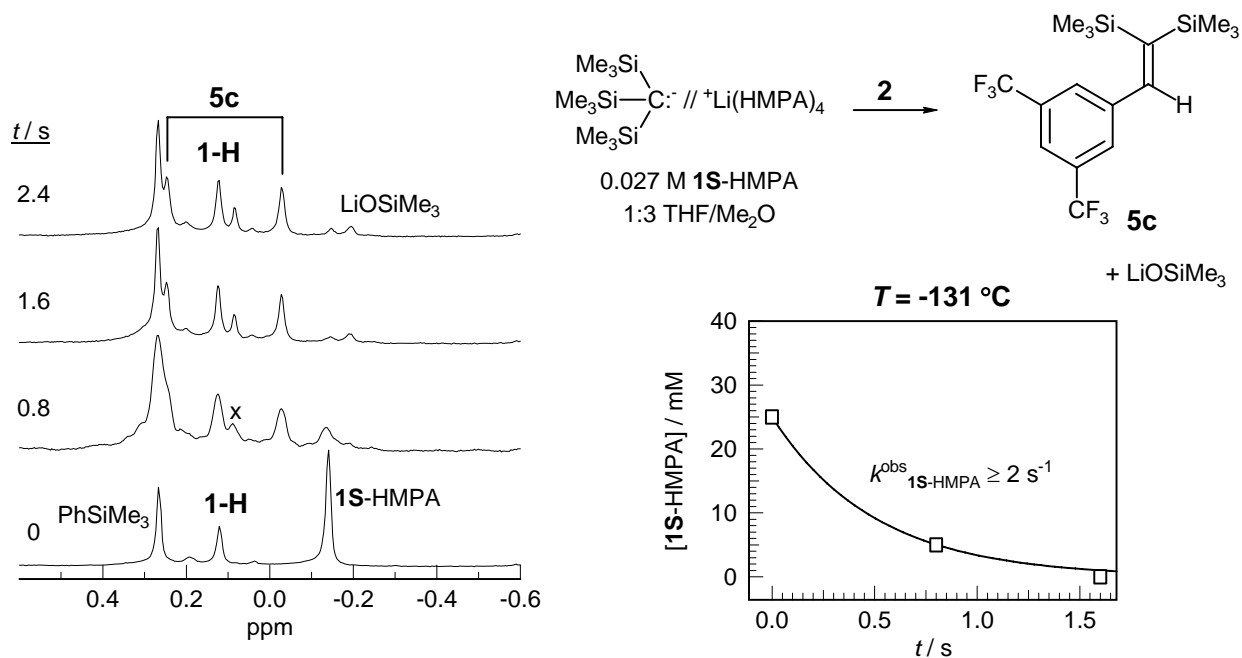


Figure S-14. ^1H NMR and plot of 1S-HMPA disappearance for the 0.1 mL injection of **2** (0.03 M *in situ*) into a solution of **1** (0.027 M) in 4 mL of 1:3 THF/Me₂O with 6.3 equivalents of HMPA at -131 °C.

^1H NMR Spectroscopy for the Reaction of 1S-HMPA with *p*-Fluorobenzaldehyde (3**).** HMPA (0.12 mL, 0.072 mol) was added to an NMR sample of **1** (0.02 M) in 4 mL of 1:3 THF/Me₂O at -78 °C. A solution of **3** (0.1 mL, 1.87 M in 1:1 THF/Et₂O) was injected by RINMR at -133 °C (Fig. S-15). The spectrometer was not warmed during the injection so the experimental temperature is expected to be ca -132 °C.

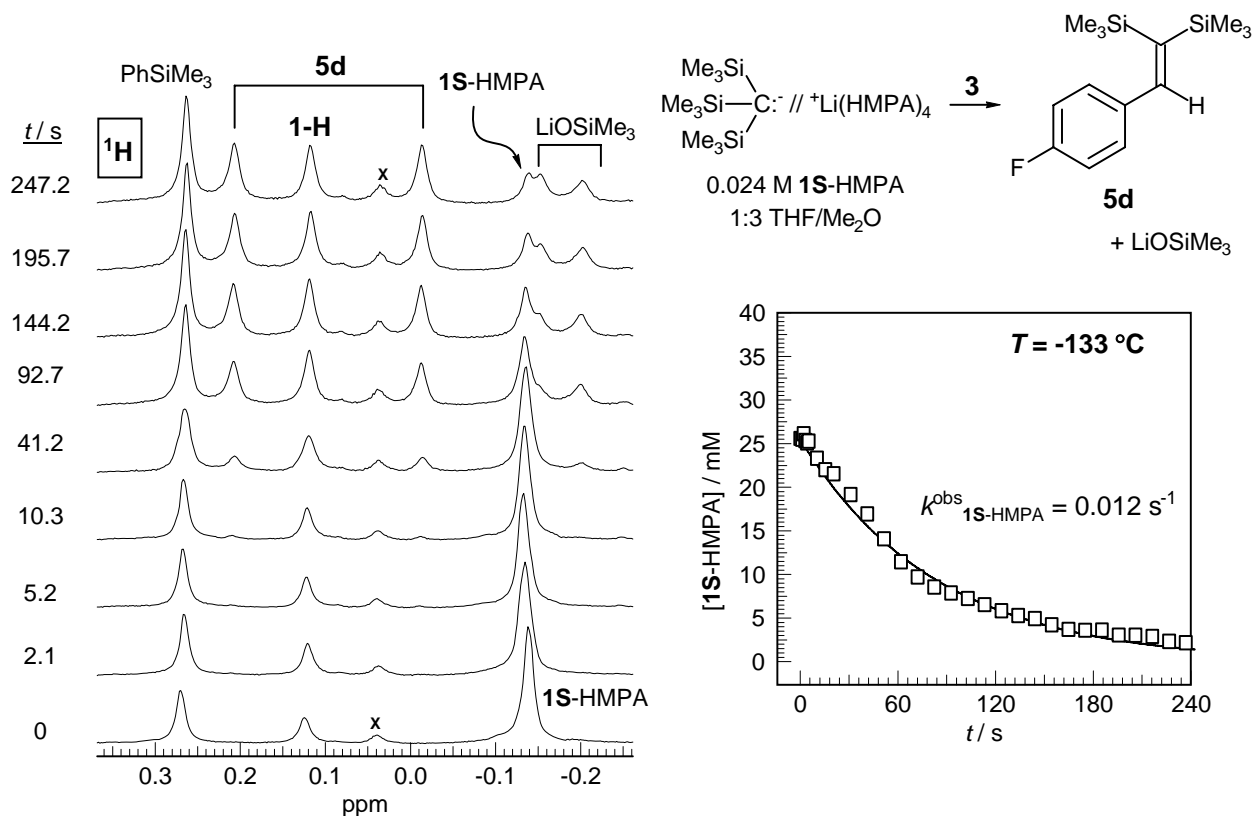


Figure S-15. ^1H NMR and plot of 1S-HMPA disappearance from the 0.1 mL injection of **3** (0.044 M *in situ*) into a solution of **1** (0.024 M) in 4 mL of 1:3 THF/Me₂O with 6.6 equivalents of HMPA at ca -132 °C.

^1H RINMR Spectroscopy of the Reaction of 1S-HMPA with *p*-Diethylaminobenzaldehyde (4b**) at Various Temperatures.** The rates of **1S**-HMPA with **4b** were determined either by injecting **4b** into a pre-formed solution of **1S**-HMPA, or by injecting a mixture of **4b** and HMPA as a THF solution ($[\mathbf{1}] = 0.02 - 0.04 \text{ M}$). Representative spectra for the latter method are shown in Fig. S-16. In such experiments, the triple ion is converted rapidly to **1S**-HMPA at a rate ($k_{\text{IT}}^{\text{obs}} = 0.011 \text{ s}^{-1}$ at $-84 \text{ }^\circ\text{C}$ and $k_{\text{IT}}^{\text{obs}} = 0.08 \text{ s}^{-1}$ at $-69 \text{ }^\circ\text{C}$) within error of that extrapolated for solutions in the absence of HMPA (compare to rates in Table S-4 and activation parameters in Figure S-11). An order in **4b** of $n = 0.8$ was determined from a plot of $\ln[\mathbf{4b}]$ vs $\ln[k_{\text{IS-HMPA}}^{\text{obs}}]$ at $-58 \text{ }^\circ\text{C}$, for two concentrations of **4b**. We assume that is within error of being first order in aldehyde; deviation from 1 could result from the 1 degree temperature difference for the two trials). Second order rate constants are calculated from the equation $k_{\text{IS}}^{\text{obs}} / [\mathbf{4b}]$ (Table S-5) and converted to ΔG^\ddagger using the equation: $\Delta G^\ddagger = 1.987 * T * [23.76 + \ln(T/k)]$ (Fig. S-17).

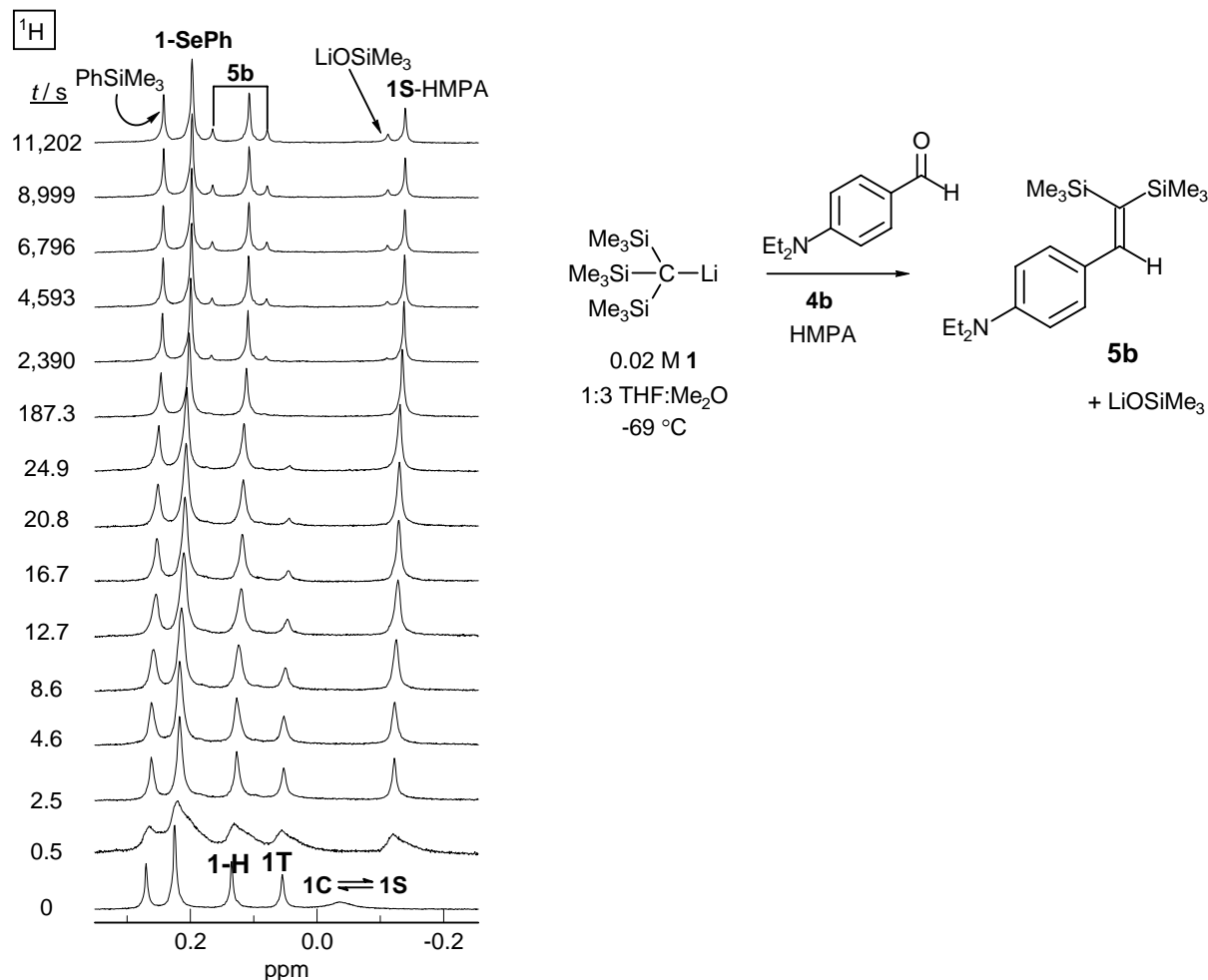
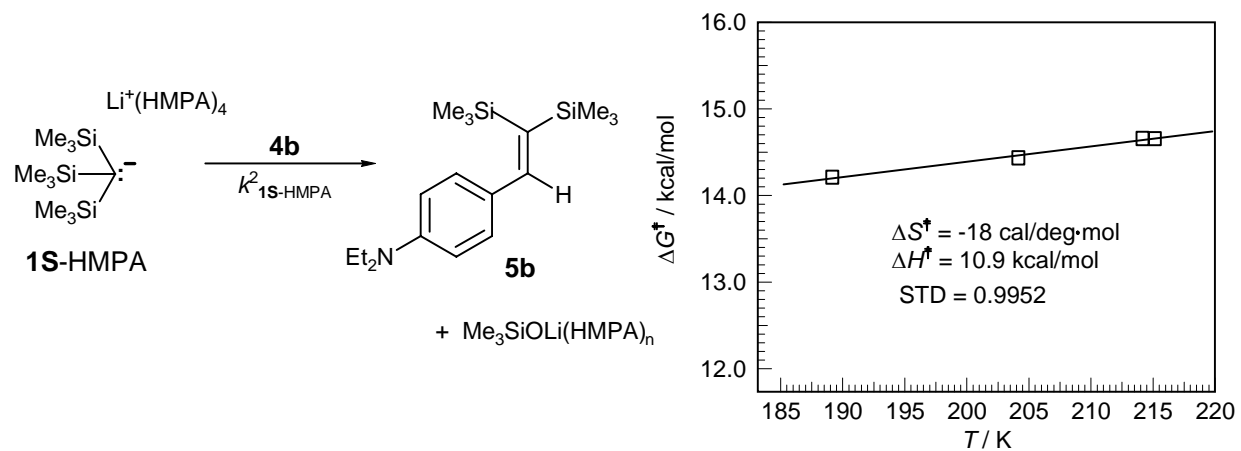


Figure S-16. ^1H NMR spectra for the 0.25 mL injection of a 1.6 M HMPA solution of **4b** (0.044 M **4** and 0.24 M HMPA *in situ*) into a 0.02 M solution of **1** in 4 mL of 1:3 THF/ Me_2O at $-69 \text{ }^\circ\text{C}$.

Table S-5. Rate data for the reaction of **1S-HMPA** and **4b**.

T / °C	k_{1S}^{obs} / s^{-1}	[4b] / mM	$k_{1S-4b}^2 / M^{-1} s^{-1}$	n	[HMPA] / mM
-84	$7.3 \cdot 10^{-6}$	50	$0.15 \cdot 10^{-3}$	n.d.	240
-69	$70 \cdot 10^{-6}$	44	$1.5 \cdot 10^{-3}$	n.d.	240
-58	$3.5 \cdot 10^{-4}$	60	$5.8 \cdot 10^{-3}$		230
-59	$7.3 \cdot 10^{-4}$	150	$4.9 \cdot 10^{-3}$	0.8	170

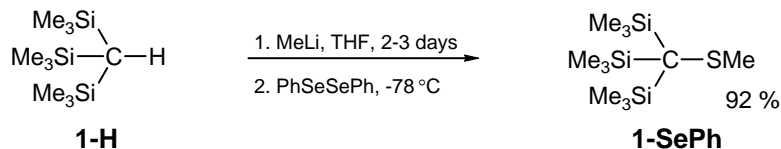
**Figure S-17.** Eyring plot for the second order reaction of **1S-HMPA** and **4b**.

S3. Competition Experiments

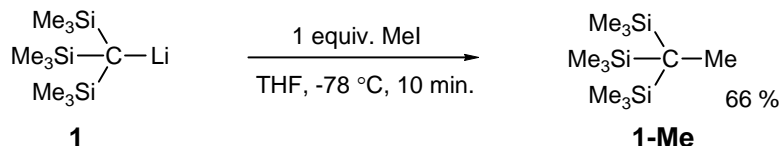
For two reactants (A and B) competing for a deficiency of the same reagent (C) (where both reactions have the same order) the relative rates can be calculated using the formula $k_A/k_B = \ln(X_A \text{ left})/\ln(X_B \text{ left})$. “X_A left” and “X_B left” are defined as the mole fractions of the two starting materials remaining at the end of the reaction relative to the amount of starting materials at the beginning of the reaction. For these competitions, we sought to determine the specific relative reactivity of **1T** with aldehydes. Since there is no way to thermodynamically prepare a solution of **1** that is 100% triple ion, we pre-treated the solution of **1** with MeI to selectively quench the monomers (**1S** and **1C**). Triple ion dissociation is slow enough ($t_{1/2}$ = 36 min) that the aldehyde solution can be added before a significant amount of the monomers have been regenerated.

To a dry 5 mL long-neck round bottom flask equipped with stir bar and purged with N₂ was added (Me₃Si)₃CSePh (0.12 g, 0.39 mmol) and 1 mL of THF. The reaction was cooled to -78 °C and 3 mL of Me₂O was added. *n*-BuLi (0.15 mL, 2.5 M in hexanes) was added to generate the lithium reagent **1**. These conditions closely match those used in the NMR experiments so we can assume that roughly half of the reagent is in the monomeric form. In a separate flask a solution of two aldehydes is prepared (0.39 mmol each in 0.3 mL THF). Half an equivalent of MeI (12 μL, 0.2 mmol) was added to the lithium solution at -78 °C, and immediately after (< 60 s) the solution of the mixture of aldehydes was added. The reaction was stirred for 20 mins and then warmed to room temperature, allowing the Me₂O to evaporate. Water was added (2 mL) and the solution extracted with 5 mL Et₂O. The organic layer was separated, dried with MgSO₄ and concentrated under low pressure. Product and remaining starting material ratios were determined by integrating the aldehyde and vinyl protons. Relative rates of $k_3/k_{4a} = 7$ and 15 and $k_2/k_3 = 3$ were determined.

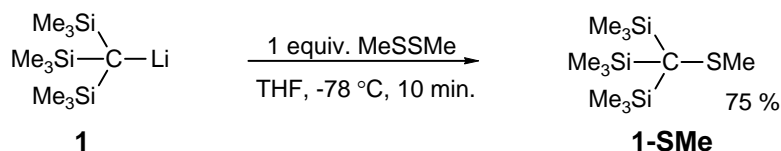
S4. Syntheses



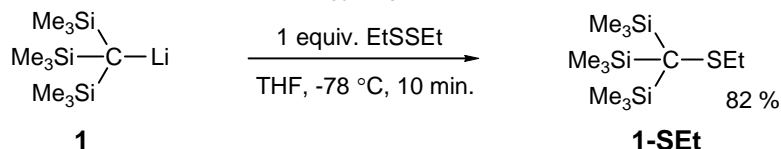
Tris(trimethylsilyl)phenylselenomethane (1-SePh). This compound was synthesized using a slight modification of the procedure described by Sikorski.^[S2] To an oven dried, 50 mL rb flask with stir bar was added 3.0 g (10.7 mmol) of *tris*(trimethylsilyl)methane (**1-H**). The flask was fitted with a septum, purged with N₂, and 20 mL of THF and 10.0 mL (11.1 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 metallation was complete the flask containing a pale yellow clear solution was cooled to -78 °C, and 3.5 g (11.1 mmol) of diphenyl diselenide in 5 mL of THF was added via cannula. The solution was stirred for 20 min, and 1.0 mL (14.1 mmol) of acetyl chloride was added and the solution warmed to r.t. The reaction was diluted with 100 mL of 1:1 ether/hexanes, washed with NaHCO₃ (2 x 120 mL) and brine (1 x 80 mL), dried over Na₂SO₄. Removal of the solvent by rotary evaporation yielded a clear pale yellow liquid. Purification of the crude product by preparatory TLC using hexanes as eluent (R_f = 0.5) yielded 3.80 g (9.82 mmol, 92 %) of a clear yellow liquid which solidifies at refrigerator temperature (the literature reports a melting point of 4 °C^[S5]). ¹H NMR (300 MHz, CDCl₃): δ 0.20 (Si(CH₃)₃, s), 7.18-7.33 (3-Ph, m), 7.81-7.85 (2-Ph, m). ¹³C NMR (75.4 MHz, CDCl₃): δ 3.57 (Si(CH₃)₃), 16.54 (CSi₃Se), 128.22 (o-PhSe), 128.61 (p-PhSe), 129.31 (i-PhSe), 138.45 (m-PhSe).



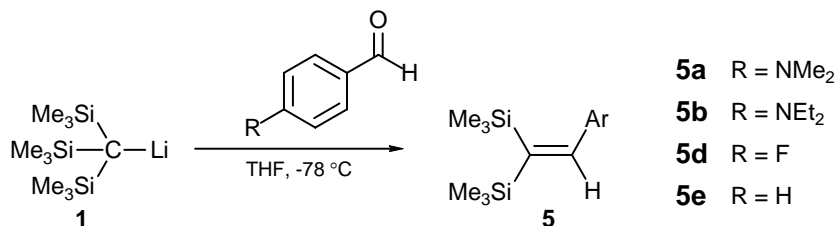
1,1,1-Tris(trimethylsilyl)ethane (1-Me). To an oven dried, N₂ purged, 25 mL rb flask with stir bar, fitted with a septum was added 12 mL of THF and 5.0 mL (1.0 mmol) of 0.2 M **1** in THF. The solution was cooled to -78 °C and 63 μL (1.0 mmol) of iodomethane was added. The reaction was stirred for 10 minutes at -78 °C, and warmed to r.t. over 1 h. The reaction was diluted with 30 mL of 1:1 ether/hexanes, washed with water (2 x 50 mL) and brine (1 x 30 mL), dried over Na₂SO₄. Removal of the solvent by rotary evaporation yielded a clear colorless liquid. Preparatory TLC of the crude product using hexanes as eluent (R_f = 0.44) yielded 180 mg (0.66 mmol, 66 %) of a clear colorless liquid. Note: There is no chromophore for this compound, so small bands were removed until the product was recovered. ¹H NMR (300 MHz, CDCl₃): δ 0.07 (Si(CH₃)₃, s), 1.07 (CH₃, s). ¹³C NMR (75.4 MHz, CDCl₃): δ 0.99 (Si(CH₃)₃), 3.26 (CSi₃), 13.81 (CH₃). Mass Spec: M⁺ = 274.1649 (calc. for C₁₁H₃₀Si₃ = 246.1655).



Tris(trimethylsilyl)(methylthio)methane (1-SMe). To an oven dried, N₂ purged, 25 mL rb flask with stir bar, fitted with a septum was added 12 mL of THF and 5.0 mL (1.0 mmol) of 0.2 M **1** in THF. The solution was cooled to -78 °C and 90 μL (1.0 mmol) of MeSSMe was added. The reaction was stirred for 10 minutes at -78 °C, and warmed to r.t. over 1 h. The reaction was diluted with 30 mL of 1:1 ether/hexanes, washed with water (2 x 50 mL) and brine (1 x 30 mL), dried over Na₂SO₄. Removal of the solvent by rotary evaporation yielded a clear colorless liquid. Preparatory TLC of the crude product using hexanes as eluent (R_f = 0.58) yielded 210 mg (0.75 mmol, 75 %) of a clear colorless liquid. ¹H NMR (300 MHz, CDCl₃): δ 0.20 (Si(CH₃)₃, s), 2.18 (CH₃S, s). ¹³C NMR (75.4 MHz, CDCl₃): δ 0.99 (CSi₃), 2.54 (Si(CH₃)₃), 17.97 (SCH₃). Mass Spec: M⁺ = 278.1371 (calc. for C₁₁H₃₀SSi₃ = 278.1376).



Tris(trimethylsilyl)(ethylthio)methane (1-SEt). To an oven dried, N₂ purged, 25 mL rb flask with stir bar, fitted with a septum was added 12 mL of THF and 5.0 mL (1.0 mmol) of 0.2 M **1** in THF. The solution was cooled to -78 °C and 123 μL (1.0 mmol) of EtSSEt was added. The reaction was stirred for 10 minutes at -78 °C, and warmed to r.t. over 1 h. The reaction was diluted with 30 mL of 1:1 ether/hexanes, washed with water (2 x 50 mL) and brine (1 x 30 mL), dried over Na₂SO₄. Removal of the solvent by rotary evaporation yielded a clear colorless liquid. Preparatory TLC of the crude product using hexanes as eluent (R_f = 0.58) yielded 204 mg (0.82 mmol, 82 %) of a clear colorless liquid. ¹H NMR (300 MHz, CDCl₃): δ 0.21 (Si(CH₃)₃, s), 1.16, (CH₃, t), 2.67 (CH₂S, q). ¹³C NMR (75.4 MHz, CDCl₃): δ 0.99 (CSi₃), 2.57 (Si(CH₃)₃), 14.00 (CH₃), 27.63 (SCH₂). Mass Spec: M⁺ = 292.1539 (calc. for C₁₂H₃₂SSi₃ = 292.1532).

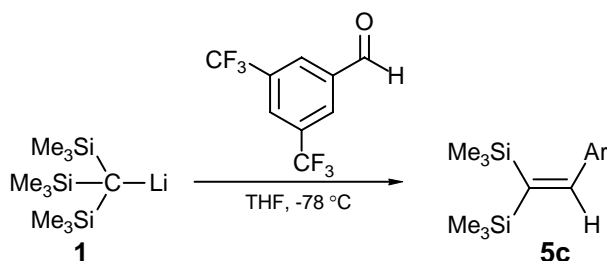


1,1-Bis(trimethylsilyl)-2-phenylethene (5e). To an oven dried, N₂ purged, 25 mL rb flask with stir bar, fitted with a septum was added 12 mL of THF and 5.0 mL (1.0 mmol) of 0.2 M **1** in THF. The solution was cooled to -78 °C and 101.6 μL (0.98 mmol) of benzaldehyde was added. The reaction was stirred for 10 min at -78 °C, and warmed to r.t. over 1 h. The reaction was diluted with 30 mL of 1:1 ether/hexanes, washed with water (2 x 50 mL) and brine (1 x 30 mL), dried over Na₂SO₄. Removal of the solvent by rotary evaporation yielded a clear colorless liquid. Preparatory TLC of the crude product using hexanes as eluent (R_f = 0.78) yielded 175 mg (0.70 mmol, 70 %) of a clear colorless liquid. ¹H NMR (300 MHz, CDCl₃): δ -0.05, 0.20 (Si(CH₃)₃, 2-s), 7.15-7.32 (Ph, m), 7.77 (CHPh, s). ¹³C NMR (75.4 MHz, CDCl₃): δ 0.56, 2.00 (Si(CH₃)₃), 126.97, 127.73, 127.82 (o, m, p-Ph), 142.81 (i-Ph), 146.39 (CMe₃Si₂), 154.93 (PhHC=C). Mass Spec: M⁺ = 248.1419 (calc. for C₁₄H₂₄Si₂ = 248.1416).

1,1-Bis(trimethylsilyl)-2-(4-dimethylaminophenyl)ethene (5a). ¹H NMR (300 MHz, CDCl₃): δ 0.04 (s, 9H), 0.17 (s, 9H), 2.96 (s, 6H), 6.66 (d, J = 8.6 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H), 7.66 (s, 1H). ¹³C NMR (90.556 MHz, CDCl₃): δ 1.12 (CH₃), 2.58 (CH₃), 40.87 (CH₃), 111.90 (CH), 127.73 (C), 129.65 (CH), 142.35 (C), 150.11 (C), 155.71 (CH). Mass Spec: [M+H]⁺ = 292.1916 (calc. for C₁₆H₃₀NSi₂ = 292.1912).

1,1-Bis(trimethylsilyl)-2-(4-diethylaminophenyl)ethene (5b). $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 0.05 (s, 9H), 0.16 (s, 9H), 1.15 (t, $J = 7.1$ Hz, 6H), 3.35 (q, $J = 7.0$ Hz, 4H), 6.59 (d, $J = 8.8$ Hz, 2H), 7.09 (d, $J = 8.6$ Hz, 2H), 7.62 (s, 1H). $^{13}\text{C NMR}$ (75.4 MHz, CDCl_3): δ 1.15 (CH_3), 2.61 (CH_3), 12.91 (CH_3), 44.74 (CH_2), 111.31 (CH), 127.75 (C), 130.01 (CH), 141.23 (C), 147.48 (C), 155.81 (CH). Mass Spec: $[\text{M}+\text{H}]^+ = 320.2226$ (calc. for $\text{C}_{18}\text{H}_{34}\text{NSi}_2 = 320.2225$).

1,1-Bis(trimethylsilyl)-2-(4-fluorophenyl)ethene (5d). $^1\text{H NMR}$ (300 MHz, CDCl_3): δ -0.050 (s, 9H), 0.181 (s, 9H), 6.978 (t, $J = 8.8$ Hz, 2H), 7.13 (dd, $J = 8.6, 5.4$, 2H), 7.67 (s, 1H). $^{13}\text{C NMR}$ (75.4 MHz, CDCl_3): δ -0.125 (CH_3), 1.36 (CH_3), 113.97 (CH, d, $^2J_{\text{CF}} = 21.2$ Hz), 128.82 (CH, d, $^3J_{\text{CF}} = 8.0$ Hz), 138.10 (C), 138.15 (C), 146.44 (CH), 152.98 (C), 161.39 (CF, d, $^1J_{\text{CF}} = 245.5$ Hz). Mass Spec: $\text{M}^+ = 266.1329$ (calc. for $\text{C}_{14}\text{H}_{23}\text{FSi}_2 = 266.1317$).



1,1-Bis(trimethylsilyl)-2-(3,5-bis(trifluoromethyl)phenyl)ethene (5c). $^1\text{H NMR}$ (300 MHz, CDCl_3): δ -0.05 (s, 9H), 0.21 (s, 9H), 7.6 (bs, 2H), 7.68 (s, 1H), 7.76 (bs, 1H). $^{13}\text{C NMR}$ (75.4 MHz, CDCl_3): δ 0.70 (CH_3), 2.13 (CH_3), 121.00 (CH, sept, $^3J_{\text{CF}} = 3.2$ Hz), 123.72 (CF_3 , q, $^1J_{\text{CF}} = 272$ Hz), 128.48 (CH, q, $^3J_{\text{CF}} = 1.8$ Hz), 131.48 (C, q, $^2J_{\text{CF}} = 32.6$ Hz), 144.79 (C), 150.938 (CH), 152.45 (C). Mass Spec: $\text{M}^+ = 384.1152$ (calc. for $\text{C}_{16}\text{H}_{22}\text{F}_6\text{Si}_2 = 384.1159$).

S5. References

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