Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Metallocene Influence on Poly(Cyclosilane) Structure and Properties

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1. General Information

General Experimental Procedures: All experiments were performed under an atmosphere of dry nitrogen or argon with the rigid exclusion of air and moisture using standard Schlenk techniques or in a nitrogen glove box. All glassware was oven-dried overnight in a 175 °C oven.

Instrumentation: ^{1}H NMR, ^{13}C {^{1}H} NMR and ^{29}Si {^{1}H} NMR were recorded on either a Bruker Avance 300, 400 or III HD 400 MHz Spectrometer and chemical shifts are reported in parts per million (ppm). Spectra were recorded in benzene-d_6 or toluene-d_8 with tetramethylsilane or the residual solvent peak as the internal standard (^{1}H NMR: C_6H_6 $\delta = 7.16$, toluene-d_8 = 2.08). Multiplicities are as indicated: s (singlet), d (doublet), t (triplet), dd (doublet of doublets), tt (triplet of triplets), m (multiplet), and br (broad). Coupling constants, J, are reported in Hertz and integration is provided as indicated. The UNIlab Plus Glove Box by MBRAUN was maintained under nitrogen atmosphere. Polymer molecular weights were measured by gel permeation chromatography (GPC) on a Tosoh Bioscience EcoSEC GPC workstation with UV detection at 254 nm using butylated hydroxytoluene stabilized tetrahydrofuran (THF) as the eluent (0.35 mL min^{-1}, 40 °C) through TSKgel SuperMultipore HZ-M guard column (4.6 mm ID x 2.0 cm, 4 μm, Tosoh Bioscience) and a TSKgel SuperMultipore HZ-M column (4.6 mm ID x 15 cm, 4 μm, Tosoh Bioscience). Polystyrene standards (EasiVial PS-M, Agilent) were used to build a calibration curve. Processing was performed using EcoSEC Data Analysis software (Version 1.14, Tosoh Bioscience). Polymers were dissolved in THF (1 mg mL^{-1}), filtered (Millex-FG Syringe Filter Unit, 0.20 µm, PTFE, EMD Millipore), and injected using an auto-sampler (10µL). UV-Vis spectroscopy was performed on a Shimadzu UV-1800 UV-Vis spectrophotometer. The spectra were measured at room temperature in non-stabilized THF in a quartz cuvette (10 mm).

Materials: Unless otherwise specified, all chemicals were used as purchased without further purification. Reaction solvents THF (Fisher, HPLC grade), diethyl ether (Fisher, anhydrous, butylated hydroxytoluene stabilized, certified ACS), dichloromethane (Fisher, cyclohexane stabilized, HPLC grade), pentane (Fisher, certified ACS), and toluene (Fisher, certified ACS) were dried on a J. C. Meyer Solvent Dispensing System (SDS) using stainless steel columns packed with neutral alumina (except for toluene which is dried with neutral alumina and Q5 reactant, a copper(II) oxide oxygen scavenger), following the manufacturer's recommendations for solvent preparation and dispensation unless otherwise noted.

Bis(cyclopentadienyl)hafnium dichloride (Cp_2HfCl_2), bis(cyclopentadienyl) zirconium(IV) dichloride (Cp_2ZrCl_2), *n*-butyllithium (2.5 M in hexanes), diphenylmethane, and anhydrous ethyl acetate were purchased from Sigma Aldrich. Alkyllithium reagents were diluted in toluene, then titrated with diphenylacetic acid before use. Concentrations were determined as an average of two titrations.

Bis(cyclopentadienyl)titanium(IV) dichloride (Cp_2TiCl_2) and trifluoromethanesulfonic acid (triflic acid) were purchased from Acros Organics.

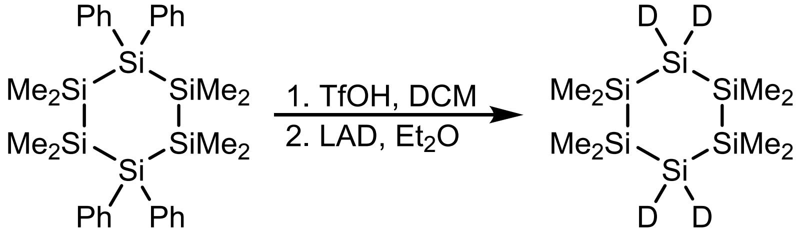
Bis(cyclopentadienyl)dimethylzirconium(IV) (Cp_2ZrMe_2), lithium aluminum deuteride (LAD), pentamethylcyclopentadienylzirconium trichloride (Cp^*ZrCl_3), and sodium cyclopentadienylide (2-3 M THF) were purchased from Strem Chemicals.

Bis(pentamethylcyclopentadienyl)zirconium dichloride ($Cp^*_2ZrCl_2$) was purchased from Alfa Aesar.

Standard polymerization conditions, and the synthesis of **1**, **1,4Si$_6$** and $CpCp^*ZrCl_2$ were conducted as previously reported.[1,2]

2. Experimental Procedures and Tabulated Characterization Data

2.1 Deuterated Monomer Synthesis



1 **1,4Si₆**-*d₄*

A 100 mL Schlenk flask equipped with a stir bar was charged with **1** (1.0 equiv., 2.54 mmol, 1.50 g) and cycled under argon three times. Dichloromethane (36 mL) was added to the Schlenk flask. In a glove box, triflic acid (5.0 equiv., 12.7 mmol, 1.12 mL) was placed in an addition funnel. The addition funnel was sealed and removed from the glove box. Under a heavy flow of argon, the addition funnel was equipped to the Schlenk flask. The reaction mixture was cooled to 0 °C with an ice water bath and the triflic acid was added dropwise and stirred for 30 minutes at 0 °C followed by 2 hours at room temperature. After two hours, volatile materials were removed under vacuum to yield a yellow solid. The resulting compound was dissolved in diethyl ether (18 mL) and cooled to 0 °C in an ice water bath. A suspension of LAD (2.4 equiv., 6.10 mmol, 0.254 g in 18 mL of diethyl ether) was added dropwise via syringe and stirred at 0 °C for 30 minutes followed by 1.5 hours at room temperature.

1,4Si₆-*d₄* was isolated by cooling the reaction mixture to 0 °C and 2.75 mL of anhydrous ethyl acetate was added and allowed to stir for 30 min. The mixture was brought into a glove box where it was filtered through Celite and washed with diethyl ether. The resulting filtrate was concentrated under vacuum to yield a white solid. The product was isolated by sublimation at 65 °C under vacuum to yield **1,4Si₆**-*d₄* as a white, crystalline solid (0.574 g, 77%).

Tabulated Characterization Data for 1,4Si₆-*d₄*.

δ_H (400 MHz, C_6D_6) 0.30 (24 H, s).

δ_{Si} (79 MHz, C_6D_6) -39.62, -102.02 (q, *J* 26.1).

δ_C (101 MHz, C_6D_6) -3.83.

2.2 Kinetic Isotope Effect NMR Experiments

Inside a glove box, a stock solution of diphenylmethane standard (0.446 mmol, 0.075 g) and either **1,4Si$_6$** or **1,4Si$_6$**-*d$_4$* (0.222 mmol, 0.0650 g (**1,4Si$_6$**), 0.0659 g (**1,4Si$_6$**-*d$_4$*)) in toluene-*d$_8$* (1.10 mL) was prepared in a 2 dram vial. In a separate 2 dram vial, a stock solution of Cp_2ZrCl_2 (0.103 mmol, 0.030 g) in toluene-d$_8$ (2.00 mL) was prepared. 0.6 mL of the Cp_2ZrCl_2 stock solution was added to a separate vial with stir bar and 0.11 mL of *n*-BuLi (0.575 M) was added and allowed to stir for 30 min. 0.25 mL of the monomer stock solution was added to an NMR tube and sealed with an NMR septum. 0.12 mL of activated Cp_2ZrCl_2/*n*-BuLi was added via syringe to the NMR tube and immediately placed inside an NMR instrument preheated to 50 °C for analysis. A ^{1}H NMR spectrum was collected at 50 °C every 2 minutes for up to 52 minutes. Multiple trials were conducted for both **1,4Si$_6$** and **1,4Si$_6$**-*d$_4$*.

2.3 Catalyst Refresh Experiment

After subjecting **$1{,}4Si_6$** to standard polymerization conditions for 24 hours,[1] the solution of poly(**$1{,}4Si_6$**) was divided into three separate 1 dram vials, each with a stir bar (0.46 mL of poly(**$1{,}4Si_6$**) solution per vial). To each vial either Cp_2ZrCl_2 (0.0068 mmol, 0.0020g), *n*-BuLi (0.0139 mmol, 0.03 mL) or a solution of Cp_2ZrCl_2/*n*BuLi in toluene (0.0020g Cp_2ZrCl_2, 0.03 mL *n*BuLi, 0.15 mL toluene) was added. Each vial was allowed to stir for an additional 24 hours before toluene was removed under vacuum.

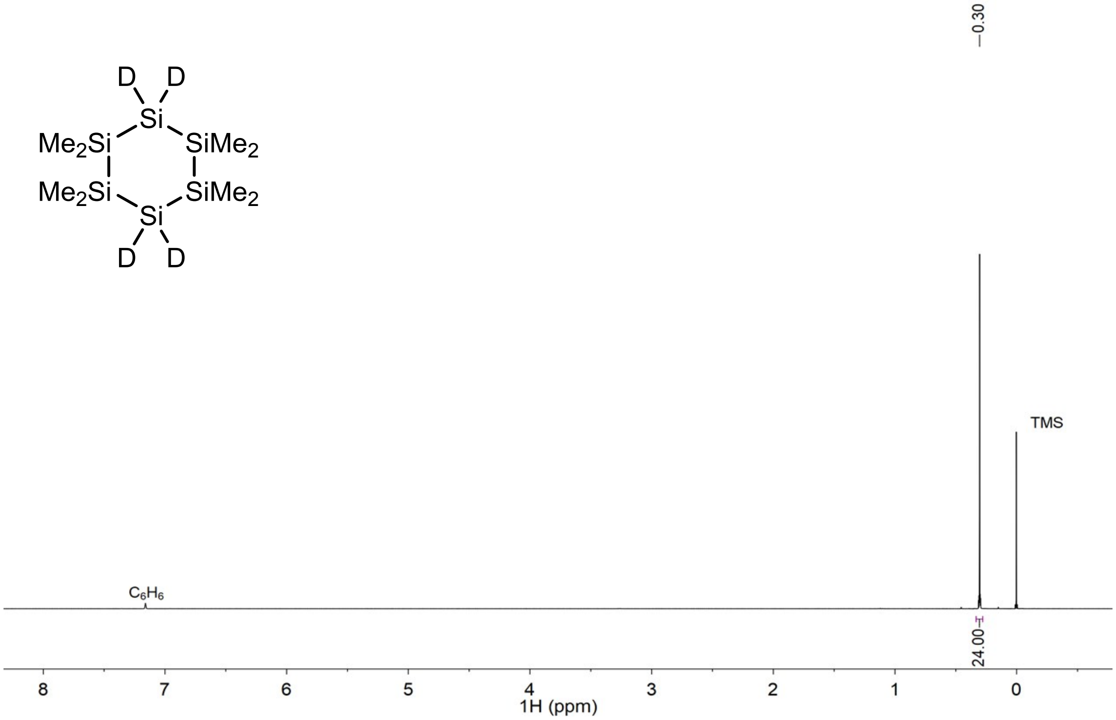
Table S1. Molecular weight characteristics from adding additional promoter added to poly(**$1{,}4Si_6$**) after initial polymerization conditions.

Entry	Additional Promoter Added	M_n (Da)[a]	M_w (Da)[a]	Đ
1	Cp_2ZrCl_2	2370	3270	1.38
2	*n*BuLi	1450	2100	1.45
3	Cp_2ZrCl_2/*n*BuLi	2250	3150	1.40

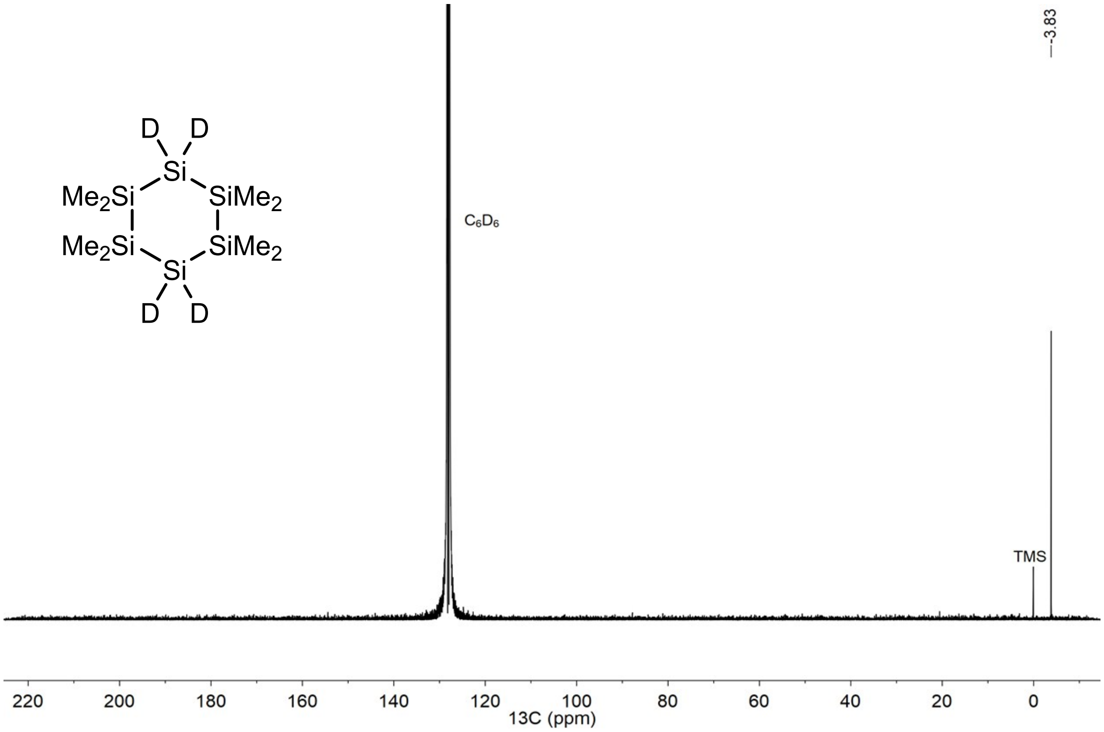
3. NMR Spectra

3.1 NMR Spectra of 1,4Si$_6$-*d$_4$*

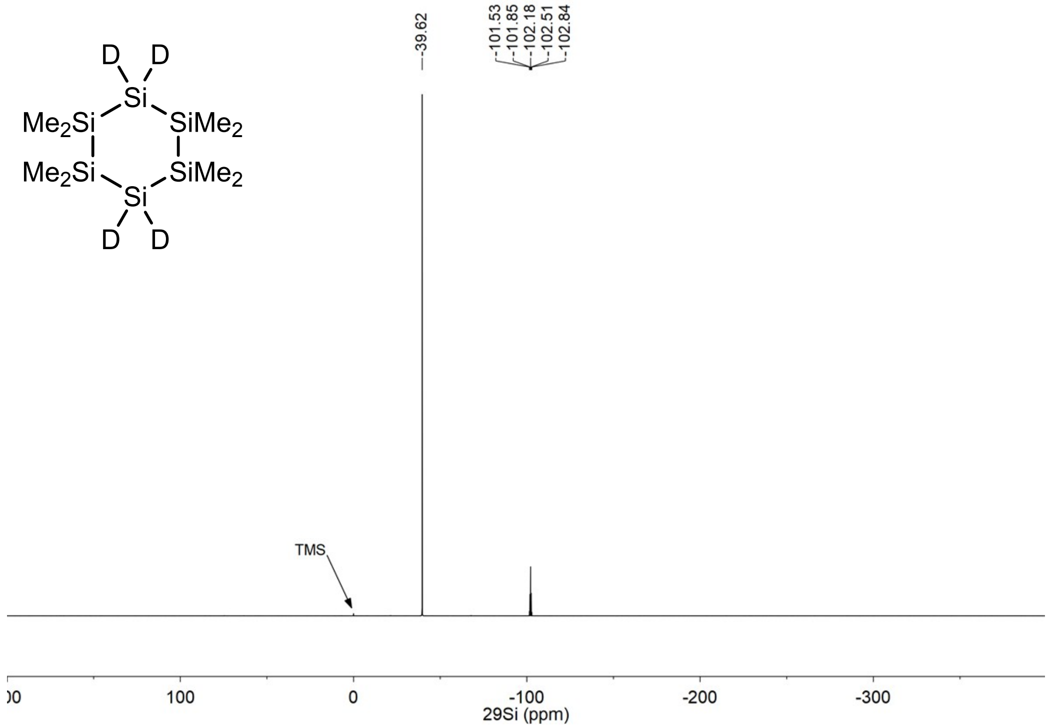
3.1.1 ^{1}H NMR Spectrum (400 MHz, C_6D_6)



3.1.2 ^{13}C {^{1}H} NMR Spectrum (101 MHz, C_6D_6)

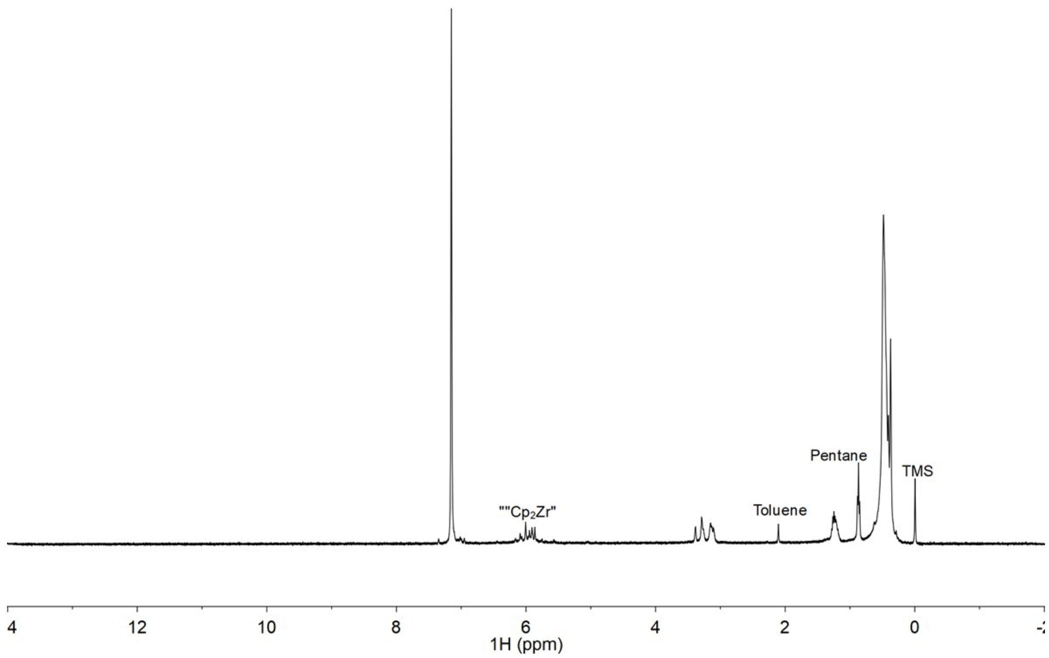


3.1.3 ^{29}Si {^{1}H} DEPT NMR Spectrum (79 MHz, C_6D_6))

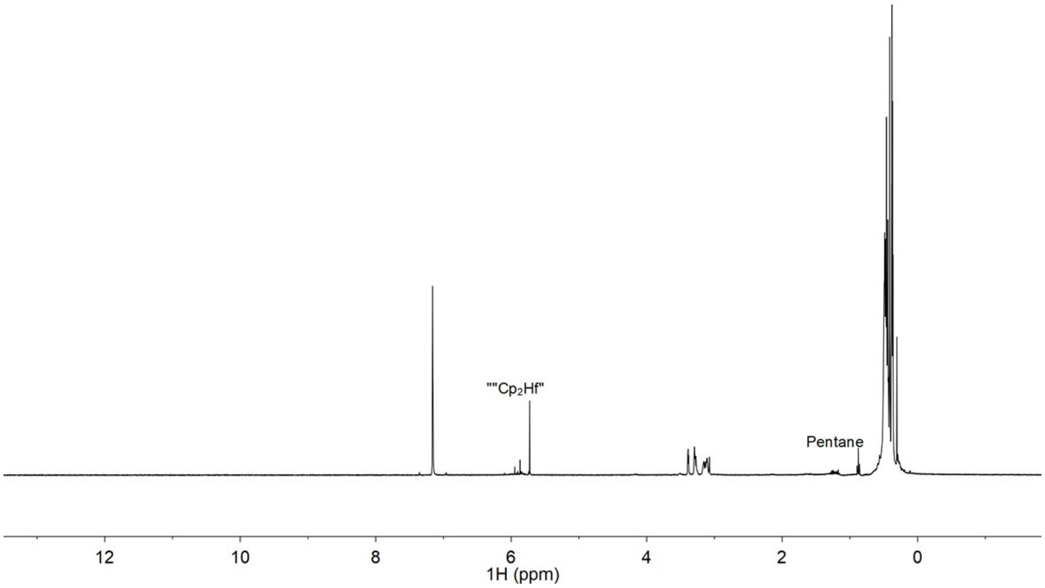


3.2 ^{1}H NMR Spectra of poly(1,4Si$_6$)

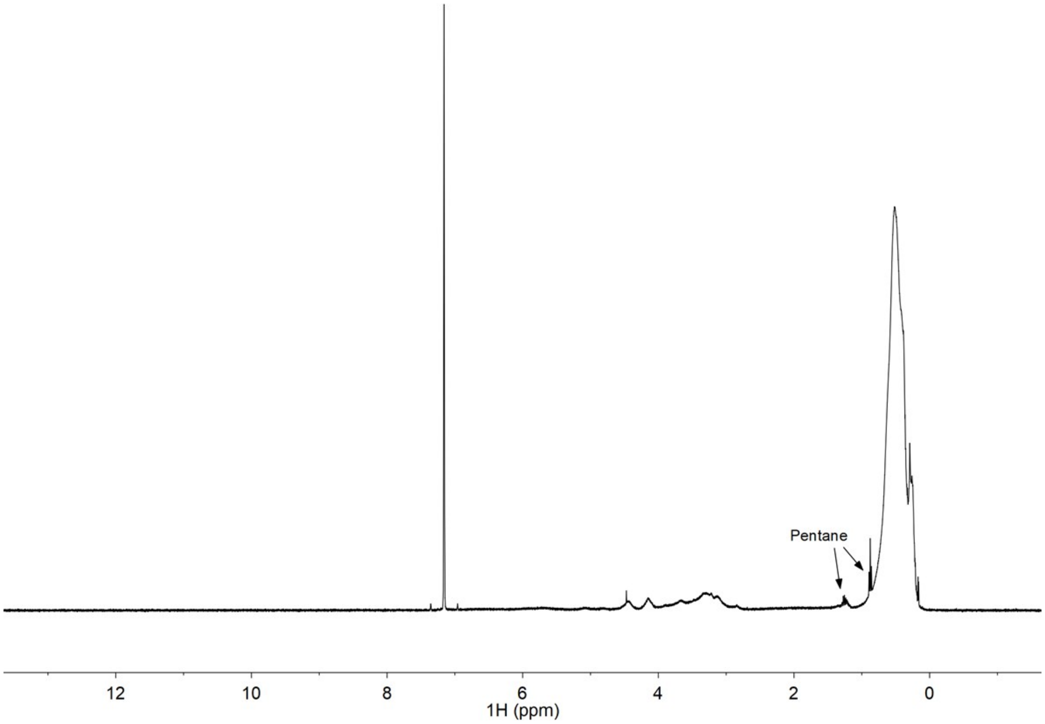
3.2.1 Zr-derived.^{1}H NMR spectrum (400 MHz, C_6D_6)



3.2.2.Hf-derived. ^{1}H NMR Spectrum (400 MHz, C_6D_6)

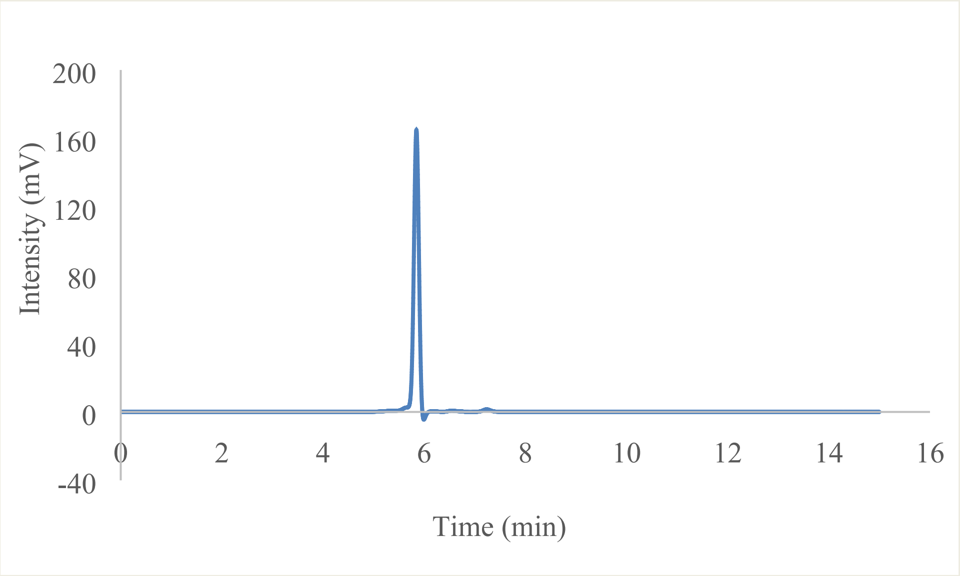


3.2.3. Ti-derived. ^{1}H NMR Spectrum (400 MHz, C_6D_6)



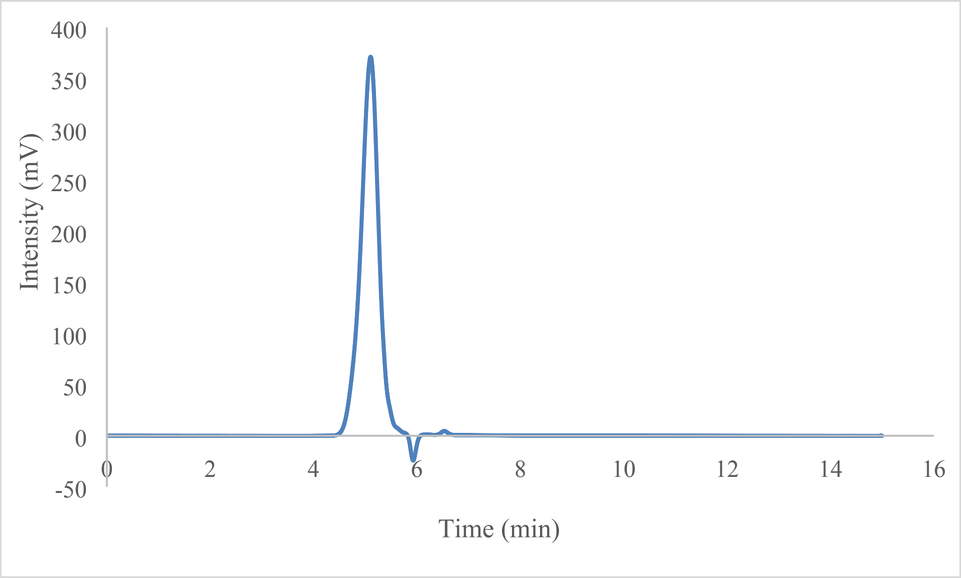
4. GPC Spectra

4.1 1,4Si_6 monomer



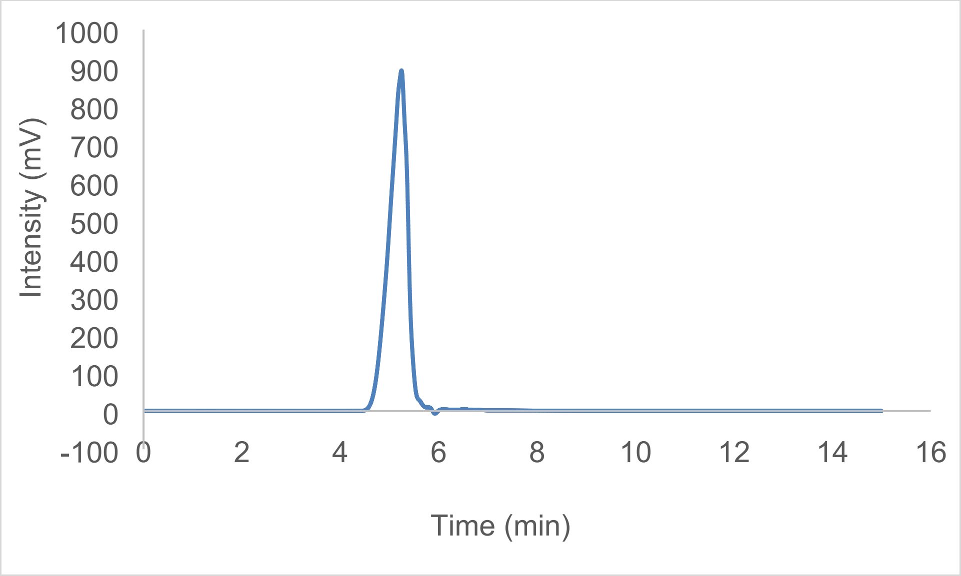
Peak No	M_n	M_w	Đ
1	321	327	1.02

4.2 Cp_2ZrCl_2/*n*-BuLi



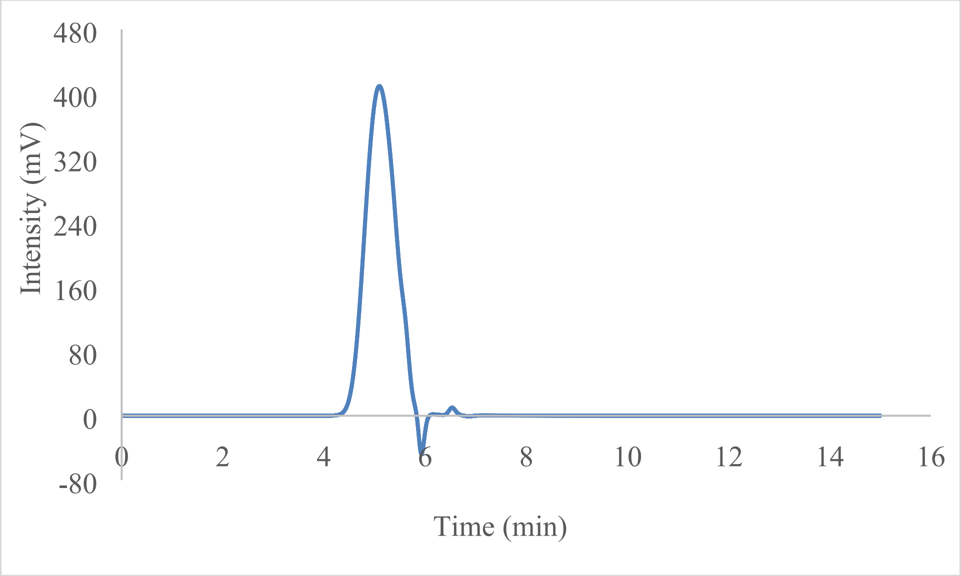
Peak No	M_n	M_w	Đ
1	2670	3580	1.34

4.3 Cp_2HfCl_2/*n*-BuLi



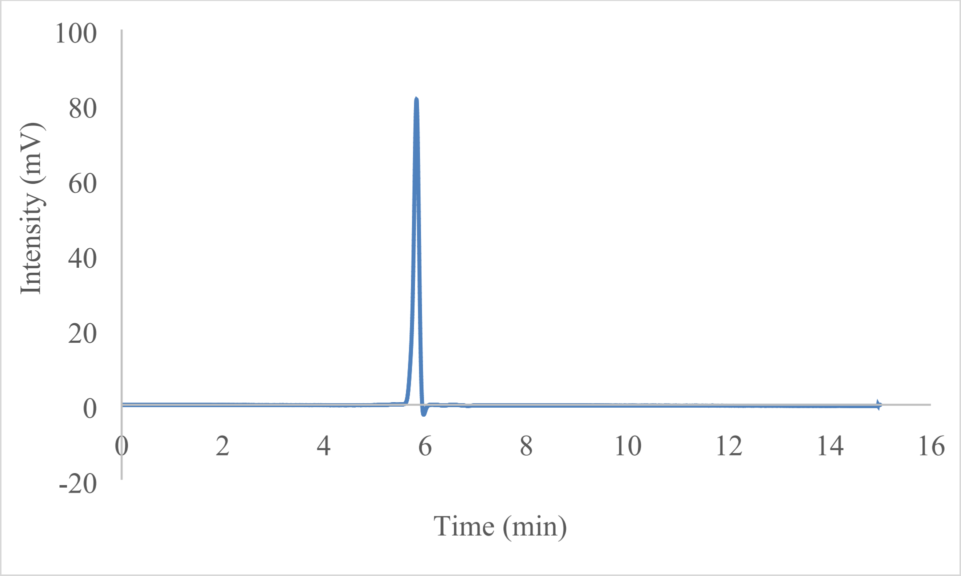
Peak No	M_n	M_w	Đ
1	2150	2920	1.36

4.4 Cp_2TiCl_2/*n*-BuLi



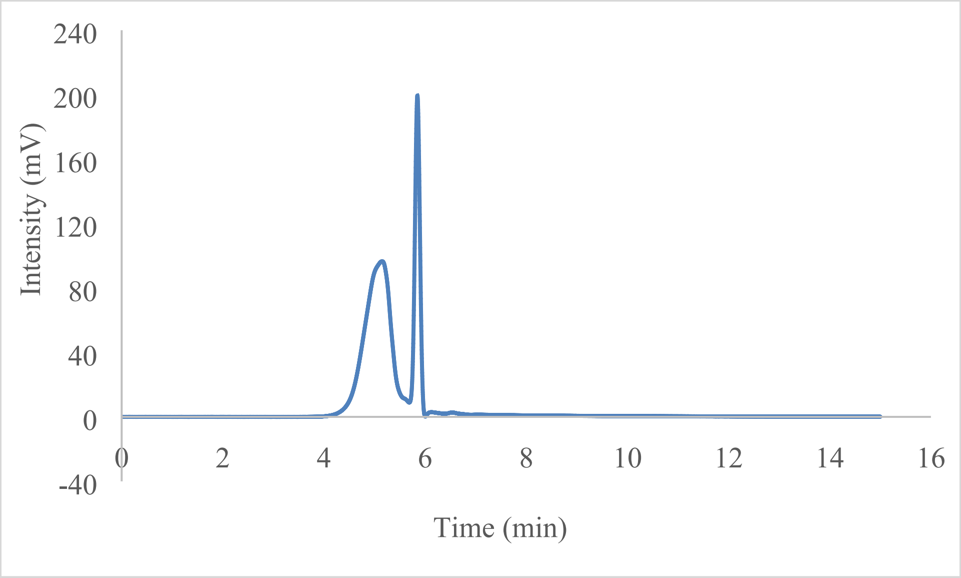
Peak No	M_n	M_w	Đ
1	1980	3650	1.85

4.5 Cp_2ZrCl_2 (no *n*-BuLi)



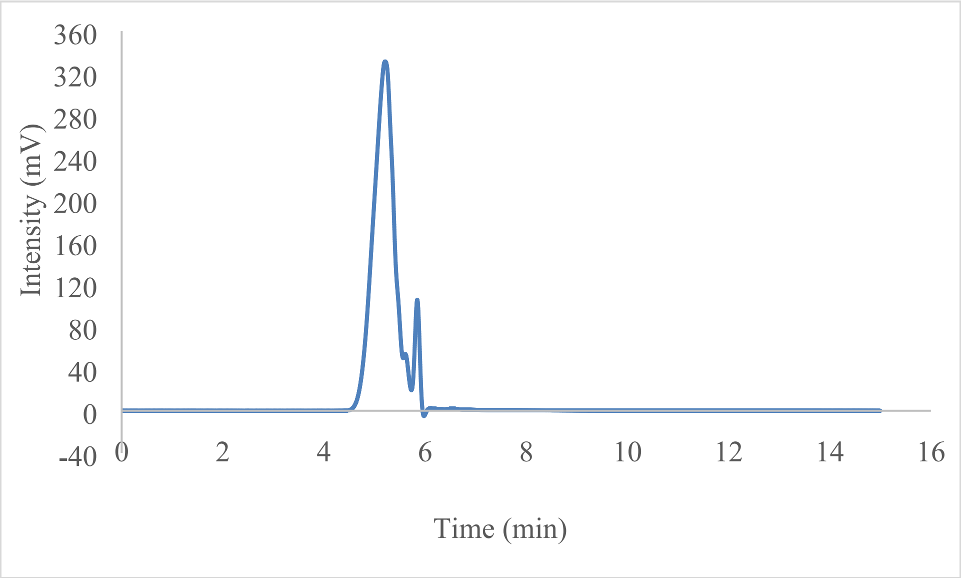
Peak No	M_n	M_w	Đ
1	346	355	1.03

4.6 Cp_2ZrMe_2



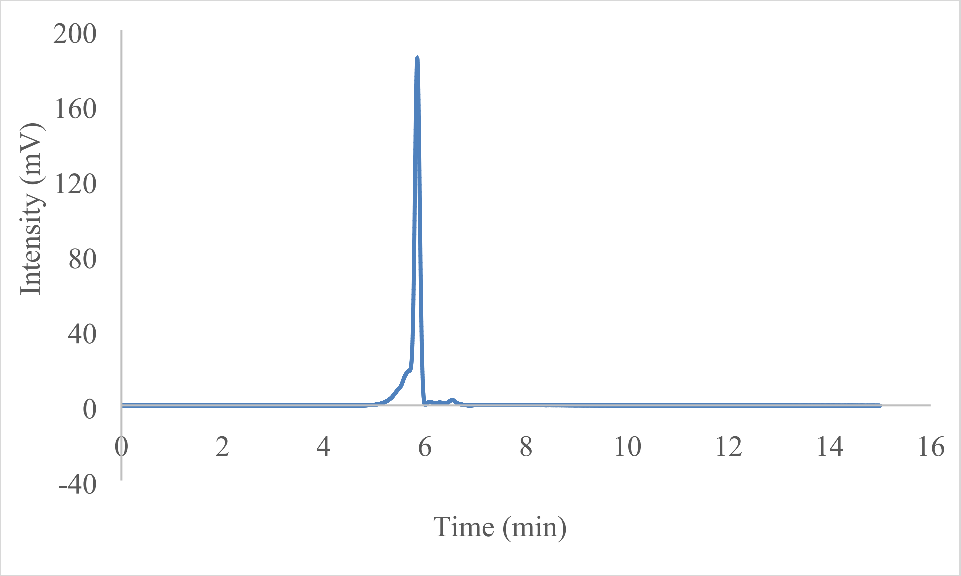
Peak No	M_n	M_w	Đ
1	2650	4720	1.78
2	319	327	1.02

4.7 CpCp*ZrCl$_2$/*n*-BuLi



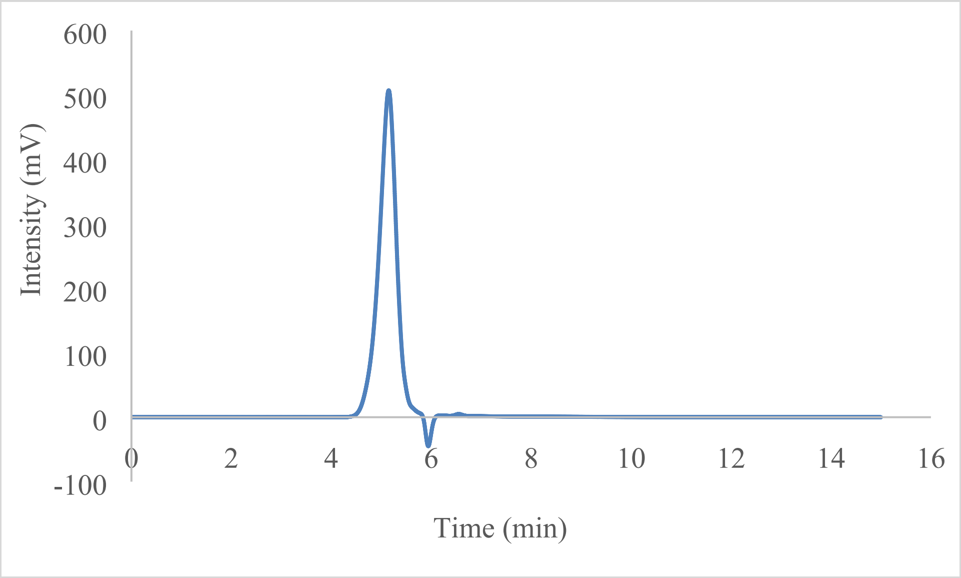
Peak No	M$_n$	M$_w$	Đ
1	2100	2840	1.36
2	595	605	1.02
3	326	332	1.02

4.8 Cp*$_2$ZrCl$_2$/*n*-BuLi



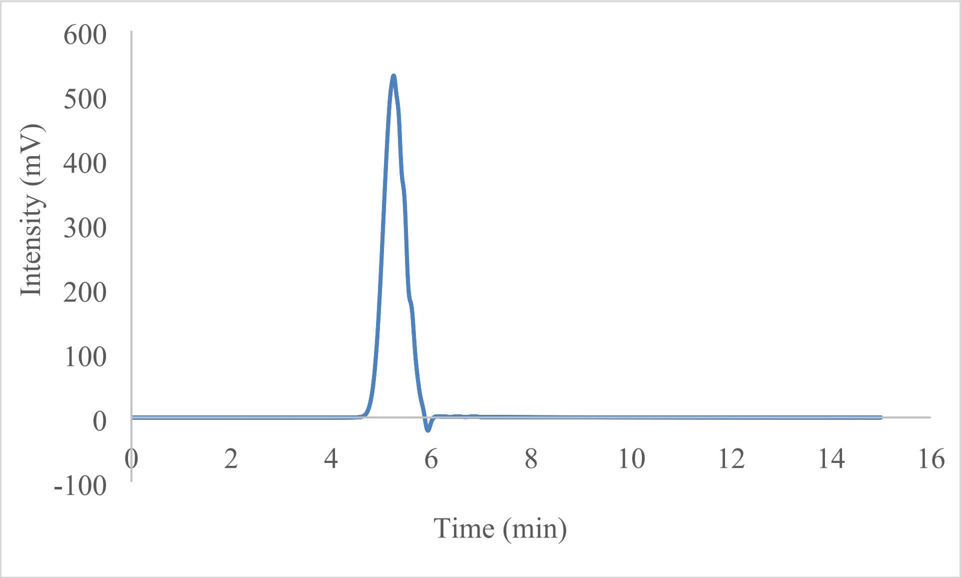
Peak No.	M$_n$	M$_w$	Đ
1	354	430	1.22

4.9 Resubjected with Cp_2ZrCl_2



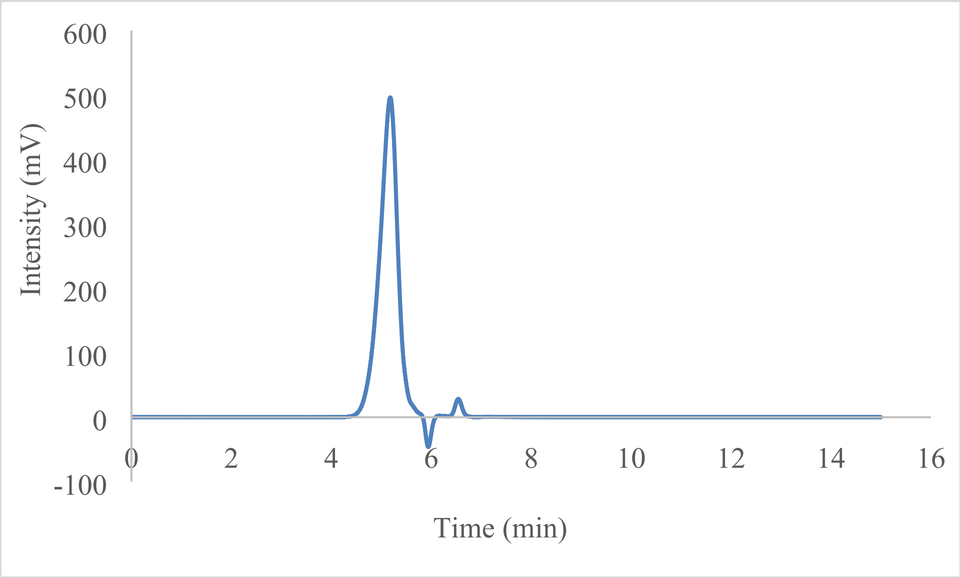
Peak No.	M_n	M_w	Đ
1	2370	3270	1.38

4.10 Resubjected with *n*-BuLi



Peak No.	M_n	M_w	Đ
1	1450	2100	1.45

4.11 Resubjected with Cp_2ZrCl_2/*n*BuLi



Peak No.	M_n	M_w	*Đ*
1	2250	3150	1.40

5. Supplemental Figures

Figure S1. Stacked ^1H NMR spectra (C_6D_6, 400 MHz) Si*H* signals (2.4-4.6 ppm) of Cp_2MCl_2/*n*BuLi (M = Ti, Zr, Hf) promoted polymers.

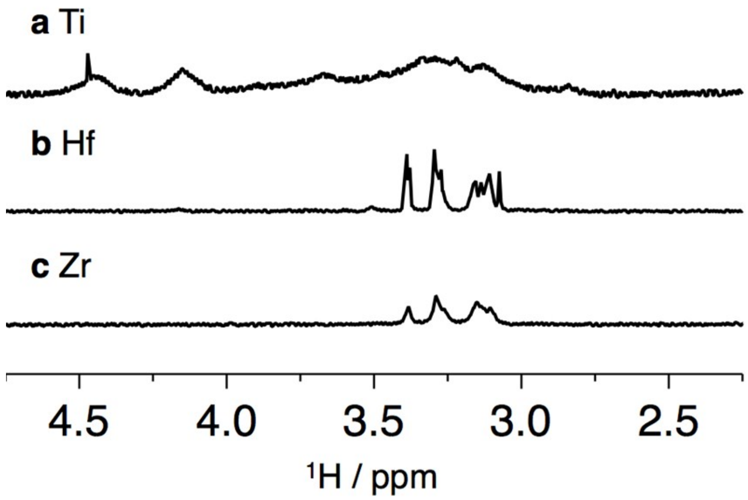


Figure S2. Potential Ti-catalyzed alkyl scrambling of **1,4Si$_6$** to yield various substituted silanes.

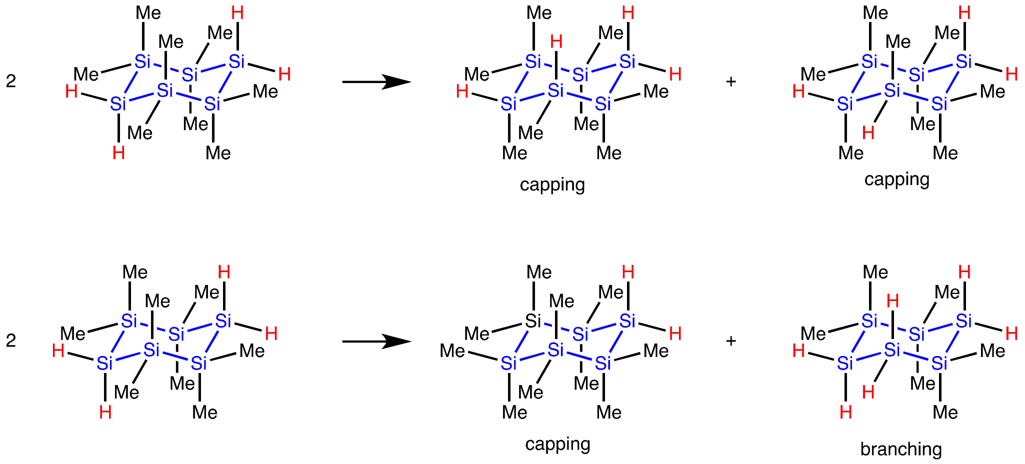
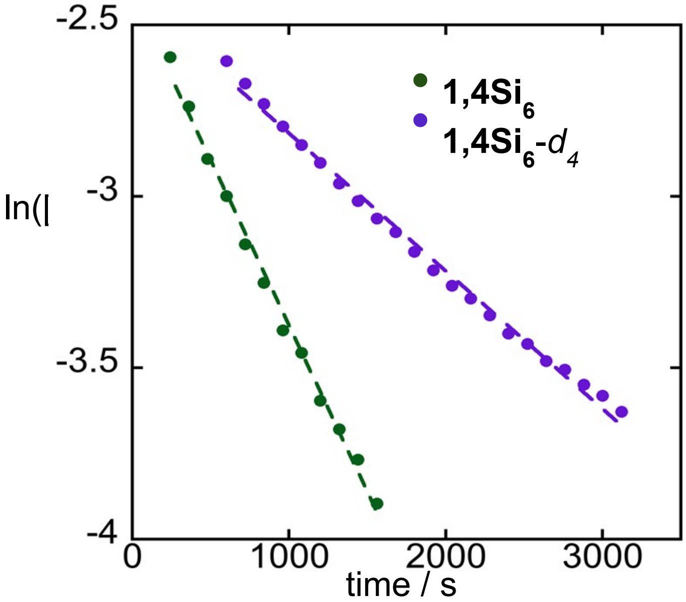


Figure S3. First order integrated rate plots of **1,4Si$_6$** (green) and **1,4Si$_6$**-*d$_4$* (purple). Plot of ln([monomer]) versus time. Each point is an average of 2-3 experiments. Dashed lines are linear fits ($R^2 = 0.995$ (green), $R^2 = 0.994$ (purple)).



6. References

(1) Press, E. M.; Marro, E. A.; Surampudi, S. K.; Siegler, M. A.; Tang, J. A.; Klausen, R. S. *Angew. Chemie Int. Ed.* **2017**, *56*, 568–572.

(2) Wolczanski, P. T.; Bercaw, J. E. *Organometallics* **1982**, *1*, 793–799.