# Supplementary Materials: [Bis(Trimethylsilyl)Methyl]Lithium and -Sodium: Solubility in Alkanes and Complexes with O- and N- Donor ligands

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**General Procedures**

*n*-Hexane, THF, and deuterated solvents were dried with potassium and distilled. TMEDA was dried with $CaH_2$ and distilled. All synthetic work was carried out under an inert argon or nitrogen atmosphere using standard Schlenk and glove-box techniques. Bis(trimethylsilyl)methyllithium was prepared from bis(trimethylsilyl)bromomethane [1] and lithium in diethyl ether [2] followed by sublimation. Bis(trimethylsilyl)methylsodium was synthesized following literature procedure [3].

$^1$H, DOSY, COSY, HSQC, HMBC, $^{13}$C NMR, $^7$Li and $^{29}$Si spectra were recorded on a Bruker AV 400 spectrometer. All spectra were referenced to the resonances of the deuterated solvent ($C_6D_6$, D8-THF, and $C_6D_{12}$) used. The diffusion ordered spectroscopy (DOSY) experiments were performed at 294 K on a Bruker Avance DRX 400 NMR spectrometer operating at a frequency of 400.31 MHz and equipped with a z-gradient dual channel inverse probe head with a gradient strength of 55 G·cm$^{-1}$. Stimulated echo sequence with bipolar gradient pulses and a longitudinal eddy current delay was used. The gradient strength was incremented in 16 steps from 2% to 95 % of the maximum gradient strength. The diffusion time and the gradient pulse length for all measured samples were respectively 200 ms and 2.8 ms. After Fourier transformation and baseline correction the diffusion dimension of the 2D DOSY spectra was processed using the Bruker Topspin software package. The diffusion analysis was performed using the T1/T2 relaxation Topspin package. Melting points were measured on a Stuart Scientific SMP10 melting point apparatus, and Elemental analyses on an Elementar Vario EL Cube. Microanalyses were carried out, but due to instability, oxidation/hydrolysis, desolvation and possibly silicon-carbide formation [4] satisfactory elemental analysis could be obtained only for compound **1b**.

Single crystals were mounted in inert oil under protective atmosphere by applying the X-Temp2 device [5]. Data for X-ray crystal structure determination were obtained with a Bruker SMART Apex II diffractometer using Mo $K_\alpha$ radiation ($\lambda$ = 0.71073 Å). All structures were refined to convergence against $F^2$ using programs from the SHELX family [6].The THF or TMEDA groups showed significant positional disorder in compounds **1a** (0.53/0.47), **1b** (0.68/0.32 and 0.75/0.25), and **2b** (0.78/0.22) [16]. In compound **1b** one trimethylsilyl group showed rotational disorder (0.50/0.50). Disorder was treated using SADI cards (**1a**, **1b**) or SAME cards (**1b**, **2b**). The atoms of the minor components of disordered groups were modelled as isotropic

The cryoscopic measurements were prepared in the glove-box by placing a defined amount of **1** or **2** into a sample vial, which was placed into a Schlenk flask. After connecting the Schlenk flask to the Schlenk line, a defined amount of cyclohexane was added under argon atmosphere. A calibrated Beckmann thermometer was placed into the Schlenk flask using a Quick-Fit joint. An ice-bath was used to reach the necessary temperature.

**Syntheses**

Experimental Procedure for [LiCH(SiMe$_3$)$_2$-THF] (**1a**)

Bis(trimethylsilyl)methyllithium **1** (0.17 g, 1.0 mmol) was dissolved in *n*-hexane (20 ml), THF (0.16 ml, 2.0 mmol, 2 eq) was added under stirring. A portion of solvent was removed under vacuum and the solution was stored at RT to yield a crop of colourless blocks (0.14 g, 52 % yield). $^1$H NMR (400 MHz, 300 K, $C_6D_{12}$): $\delta$ = -2.39 (s, 1 H, C*H*), -0.02 (s, 18 H, Si*Me*$_3$), 1.89 (m, 4 H,  -THF), 3.88 (m, 4 H,  -THF) ppm. $^{13}$C NMR (100 MHz, 300 K, $C_6D_{12}$): $\delta$ = 2.0 (*C*H),

5.7 (Si*Me*$_3$), 26.1 (β-THF), 69.2 ( -THF) ppm. $^7$Li NMR (155 MHz, 300 K, $C_6D_{12}$): 2.9 ppm. $^{29}$Si NMR (80 MHz, 300 K, $C_6D_{12}$): -6.0 (*Si*Me$_3$) ppm. Melting point: 72°C.

Experimental Procedure for [LiCH(SiMe$_3$)$_2$-TMEDA] (**1b**)

Bis(trimethylsilyl)methyllithium **1** (0.17 g, 1.0 mmol) was dissolved in *n*-hexane (20 ml), TMEDA (0.16 ml, 1.05 mmol, 1.05 eq) was added under stirring. A portion of solvent was removed under vacuum and the solution was stored at 6°C to yield a crop of colourless platelets (0.10 g, 34 % yield). $^1$H NMR (400 MHz, 300 K, $C_6D_{12}$): $\delta$ = -2.05 (s, 1 H, C*H*), -0.10 (s, 18 H, Si*Me*$_3$), 2.30 (s, 12 H, Me-TMEDA), 2.37 (s, 4 H, CH$_2$-TMEDA) ppm. $^{13}$C NMR (100 MHz, 300 K, $C_6D_{12}$): $\delta$ = 2.3 (*C*H), 6.4 (Si*Me*$_3$), 45.1 (s, 12 H, Me-TMEDA), 57.3 (s, 4 H, CH$_2$-TMEDA) ppm. $^7$Li NMR (155 MHz, 300 K, $C_6D_{12}$): 3.1 ppm. $^{29}$Si NMR (80 MHz, 300 K, $C_6D_{12}$): -7.9 (*Si*Me$_3$) ppm. Melting point: 58°C. Elemental analysis (%) calcd. for $C_{13}H_{35}LiN_2Si_2$ (M =282.54 g/mol): C, 55.26; H, 12.49; N, 9.92; found: C, 54.69; H, 13.54; N, 10.08.

Experimental Procedure for [NaCH(SiMe$_3$)$_2$-THF] (**2a**)

Bis(trimethylsilyl)methyllithium **2** (0.07 g, 0.4 mmol) was dissolved in *n*-hexane (5 ml), THF (0.07 ml, 0.9 mmol, 2.2 eq) was added under stirring. A portion of solvent was removed under vacuum and the solution was stored at -20°C to yield a crop of yellowish needles (0.017 g, 17 % yield). The compound slowly decomposes at room temperature. $^1$H NMR (400 MHz, 300 K, $C_6D_{12}$): $\delta$ = -2.28 (s, 1 H, C*H*), 0.0 (s, 18 H, Si*Me*$_3$), 1.83 (m, 4 H, -THF), 3.76 (m, 4 H, -THF) ppm. $^{13}$C NMR (100 MHz, 300 K, $C_6D_{12}$): $\delta$ = 1.1 (*C*H), 6.7 (Si*Me*$_3$), 27.0 (β-THF), 68.7 ( -THF) ppm. $^{29}$Si NMR (80 MHz, 300 K, $C_6D_{12}$): -10.1 (*Si*Me$_3$) ppm.

Experimental Procedure for [NaCH(SiMe$_3$)$_2$-TMEDA] (**2b**)

Bis(trimethylsilyl)methyllithium **2** (0.18 g, 1.0 mmol) was dissolved in *n*-hexane (5 ml), TMEDA (0.30 ml, 2.0 mmol, 2 eq) was added under stirring. A portion of solvent was removed under vacuum and the solution was stored -20°C to yield a crop of large colourless blocks. $^1$H NMR (400 MHz, 300 K, $C_6D_{12}$): $\delta$ = -2.04 (s, 1 H, C*H*), -0.08 (s, 18 H, Si*Me*$_3$), 2.25 (s, 12 H, Me-TMEDA), 2.34 (s, 4 H, CH$_2$-TMEDA) ppm. $^{13}$C NMR (100 MHz, 300 K, $C_6D_{12}$): $\delta$ = 1.0 (*C*H), 6.7 (Si*Me*$_3$), 46.2 (s, 12 H, Me-TMEDA), 58.0 (s, 4 H, CH$_2$-TMEDA) ppm. $^{29}$Si NMR (80 MHz, 300 K, $C_6D_{12}$): -8.5 (*Si*Me$_3$) ppm. Melting point: <0°C.

Table S1: Preparation of cryoscopic measurements in cyclohexane and results.

| **Amount of 1 or 2** | **Amount of cyclohexane** | **Concentration [mol/l]** | **T [K]** | **M(exp) [g/mol]** | **M(oligomer) [g/mol]** | **M** |
|---|---|---|---|---|---|---|
| **1**: 0.080 g | 11.90 ml | 0.040 | -0.50 | 345 | 332.68(**1**-dimer) | +3.7% |
| **2**: 0.045 g | 11.97 ml | 0.021 | -0.12 | 804 | 729.52 (**2**-tetramer) | +10.2% |
| **2**: 0.091 g | 12.05 ml | 0.041 | -0.29 | 663 | 729.52 (**2**-tetramer) | -9.1% |
| **2**: 0.182 g | 11.50 ml | 0.087 | -0.35 | 1175 | 1094.28 (**2**-hexamer) | +7.4% |
| **2**: 0.182 g | 11.52 ml | 0.087 | -0.37 | 1098 | 1094.28 (**2**-hexamer) | +0.3% |

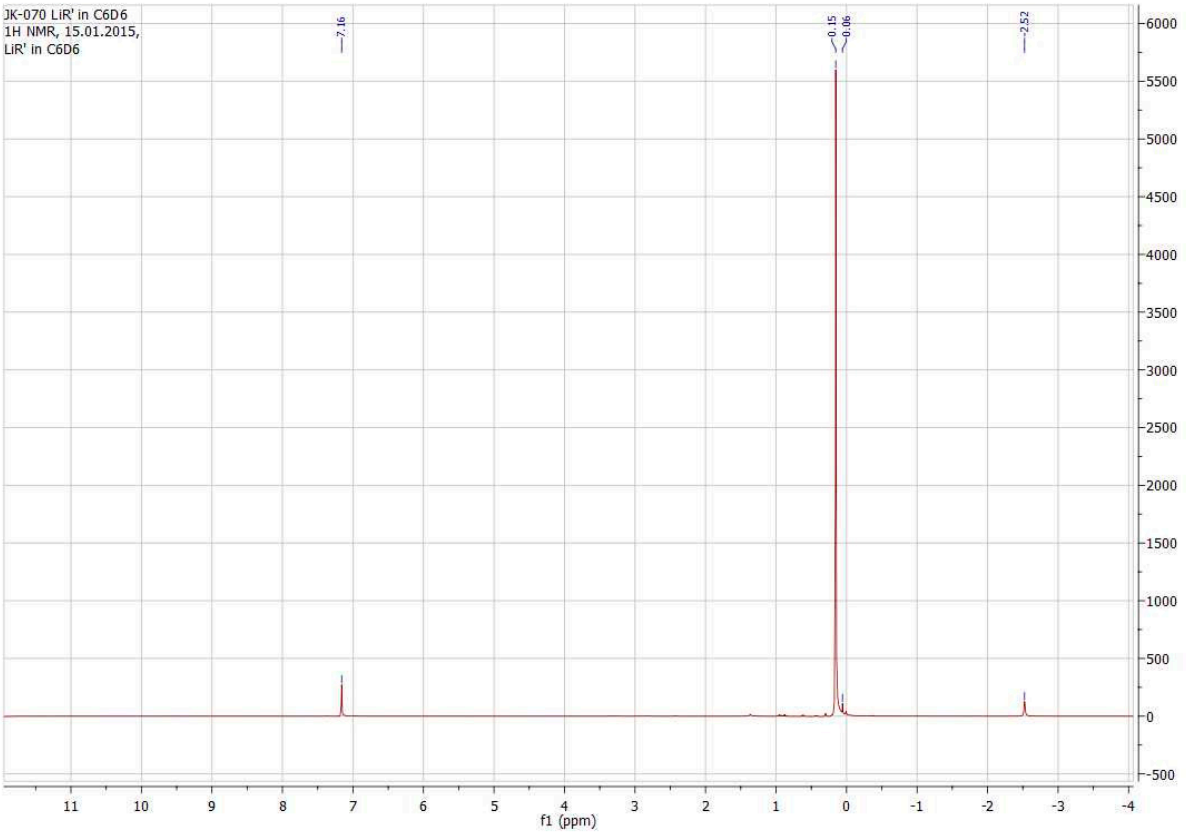


Figure S1: $^{1}H$ NMR of $LiCH(SiMe_3)_2$, **1**,in $C_6D_6$

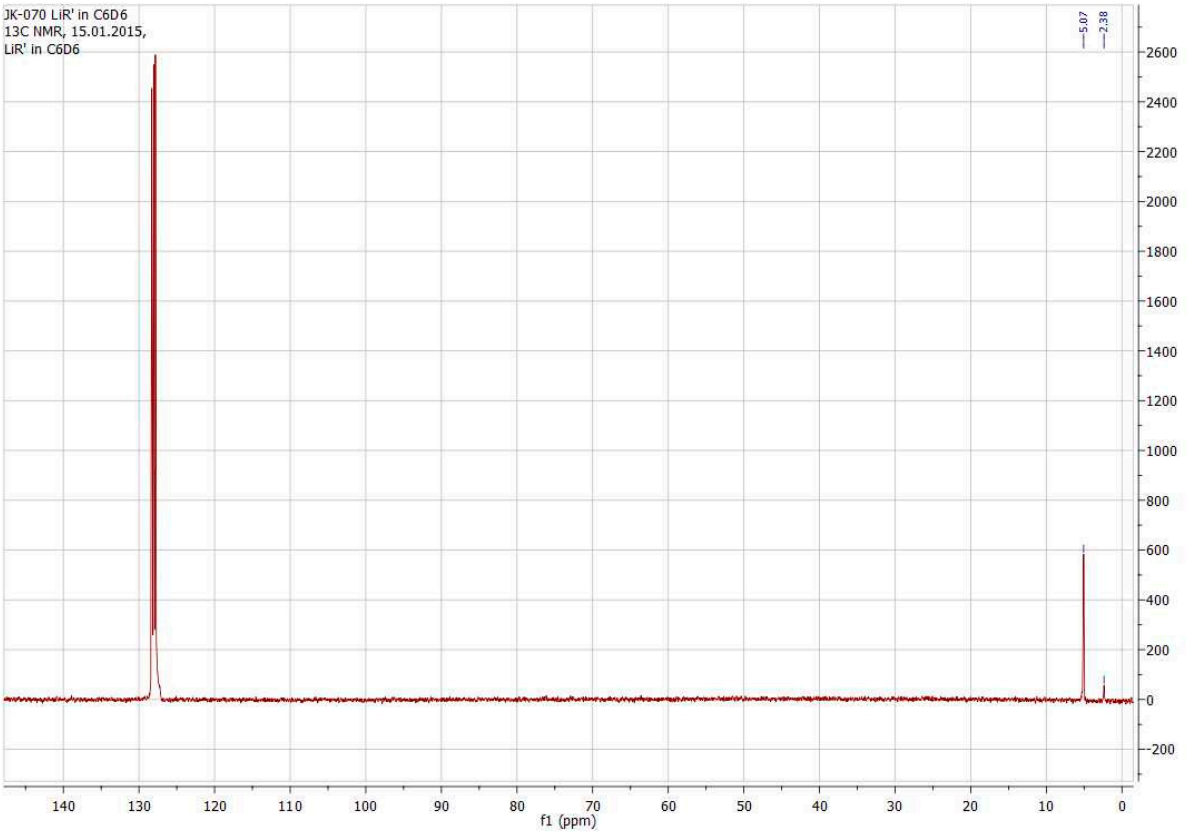


Figure S2: $^{13}C$ NMR of $LiCH(SiMe_3)_2$, **1**,in $C_6D_6$

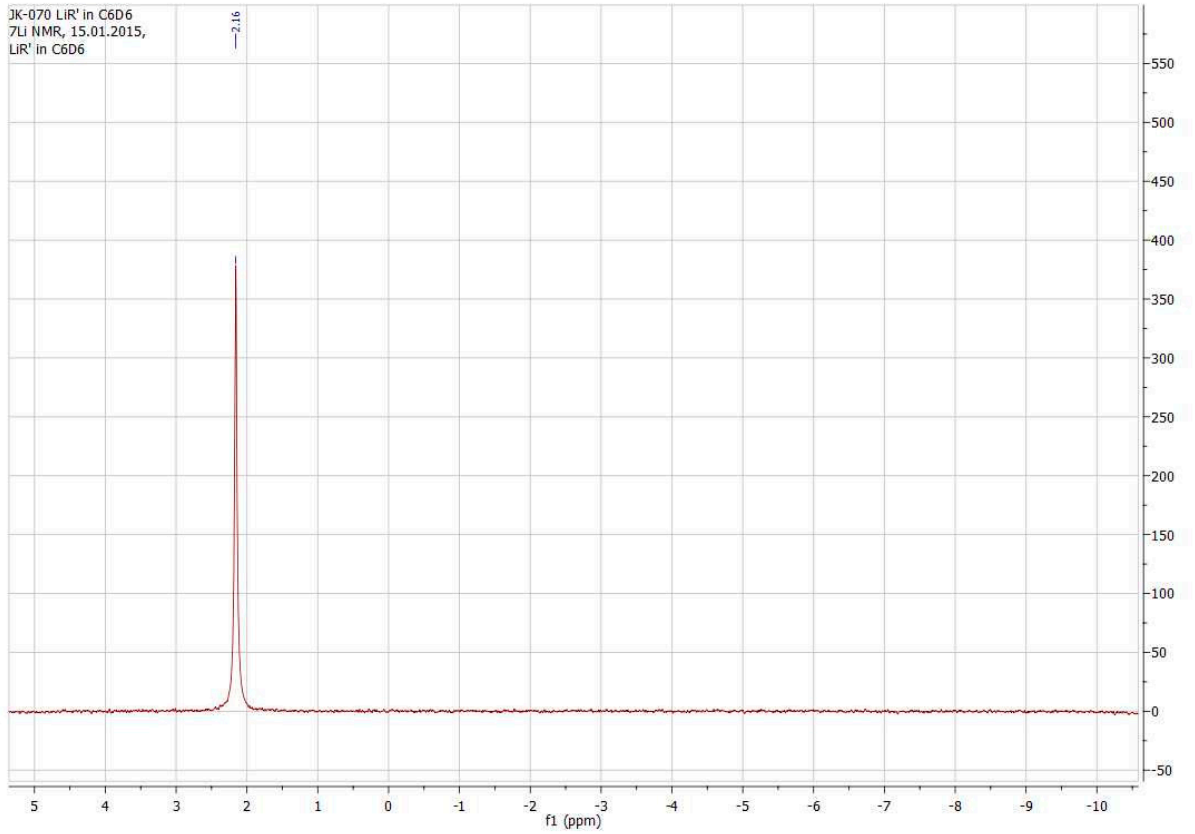


Figure S3: $^{7}$Li NMR of LiCH(SiMe$_3$)$_2$, **1**, in $C_6D_6$

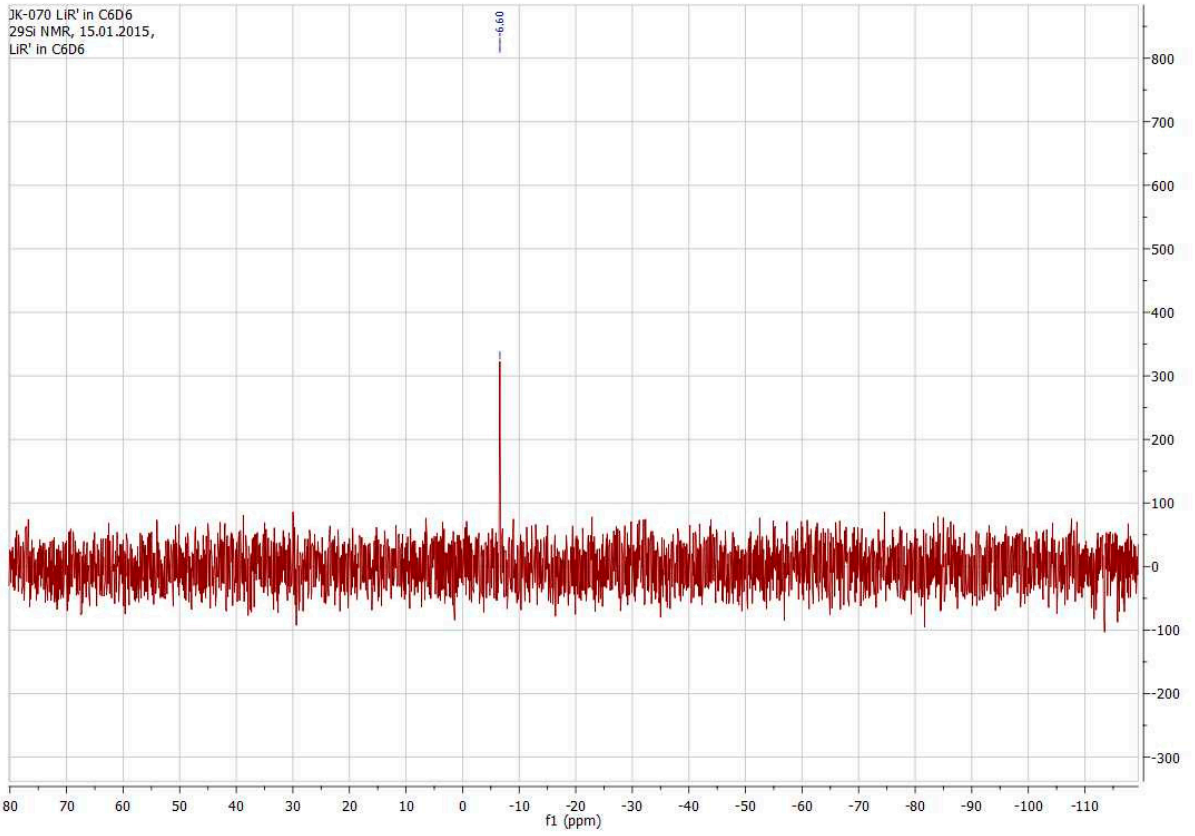


Figure S4: $^{29}$Si NMR of LiCH(SiMe$_3$)$_2$, **1**, in $C_6D_6$

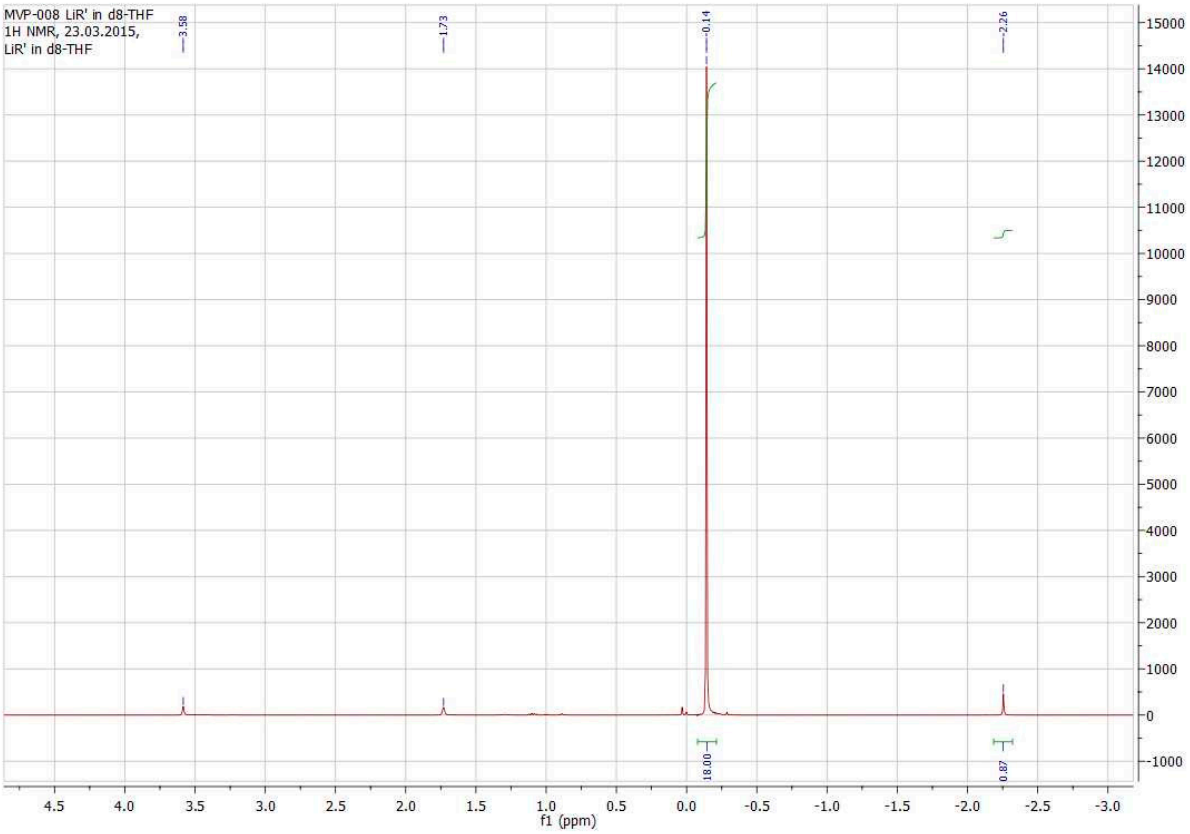


Figure S5: $^{1}H$ NMR of $LiCH(SiMe_3)_2$, **1**, in d8-THF

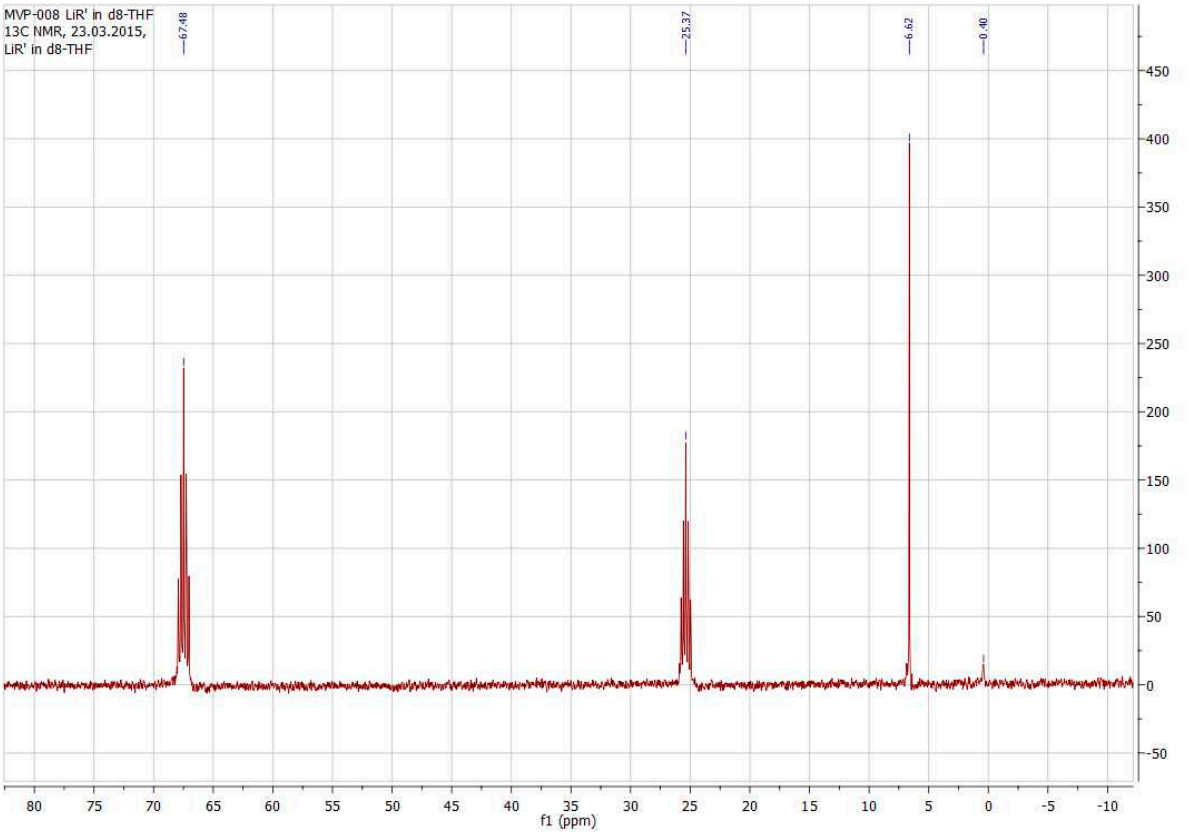


Figure S6: $^{13}C$ NMR of $LiCH(SiMe_3)_2$, **1**, in d8-THF

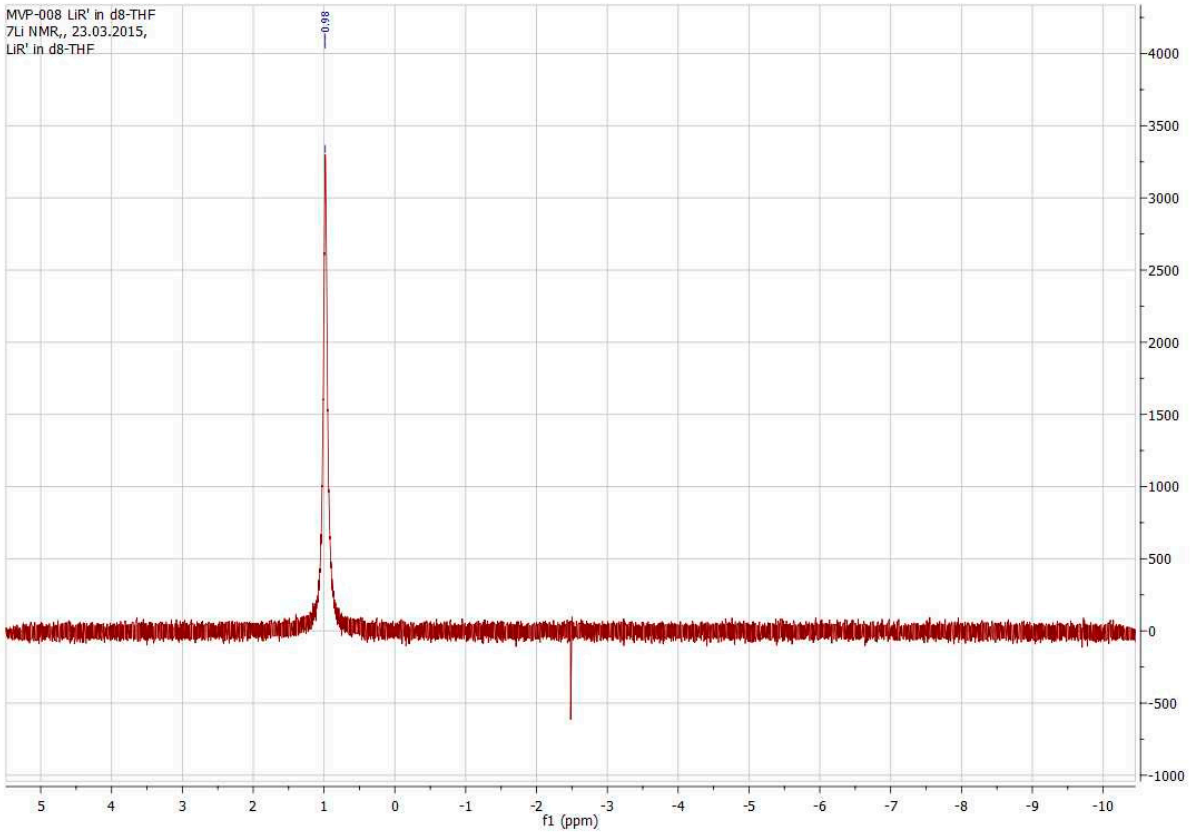


Figure S7: $^{7}$Li NMR of LiCH(SiMe$_3$)$_2$, **1**, in d8-THF

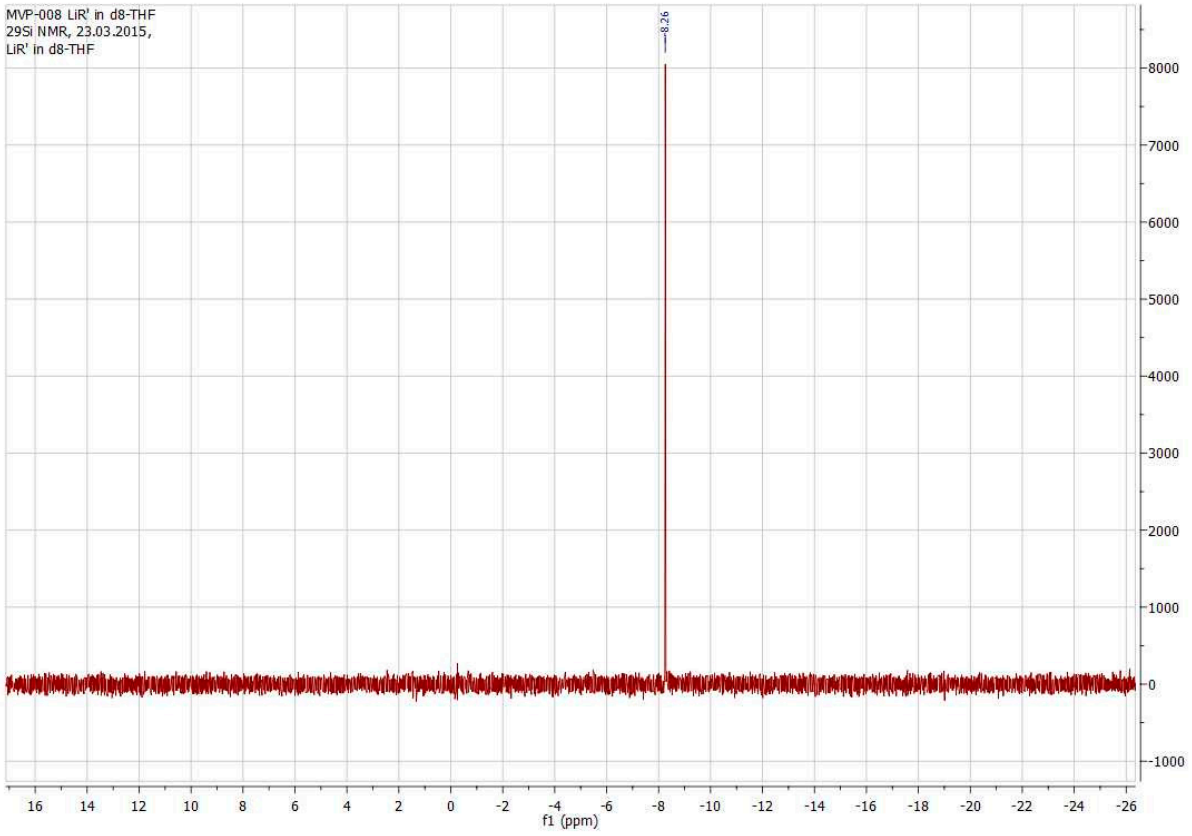


Figure S8: $^{29}$Si NMR of LiCH(SiMe$_3$)$_2$, **1**, in d8-THF

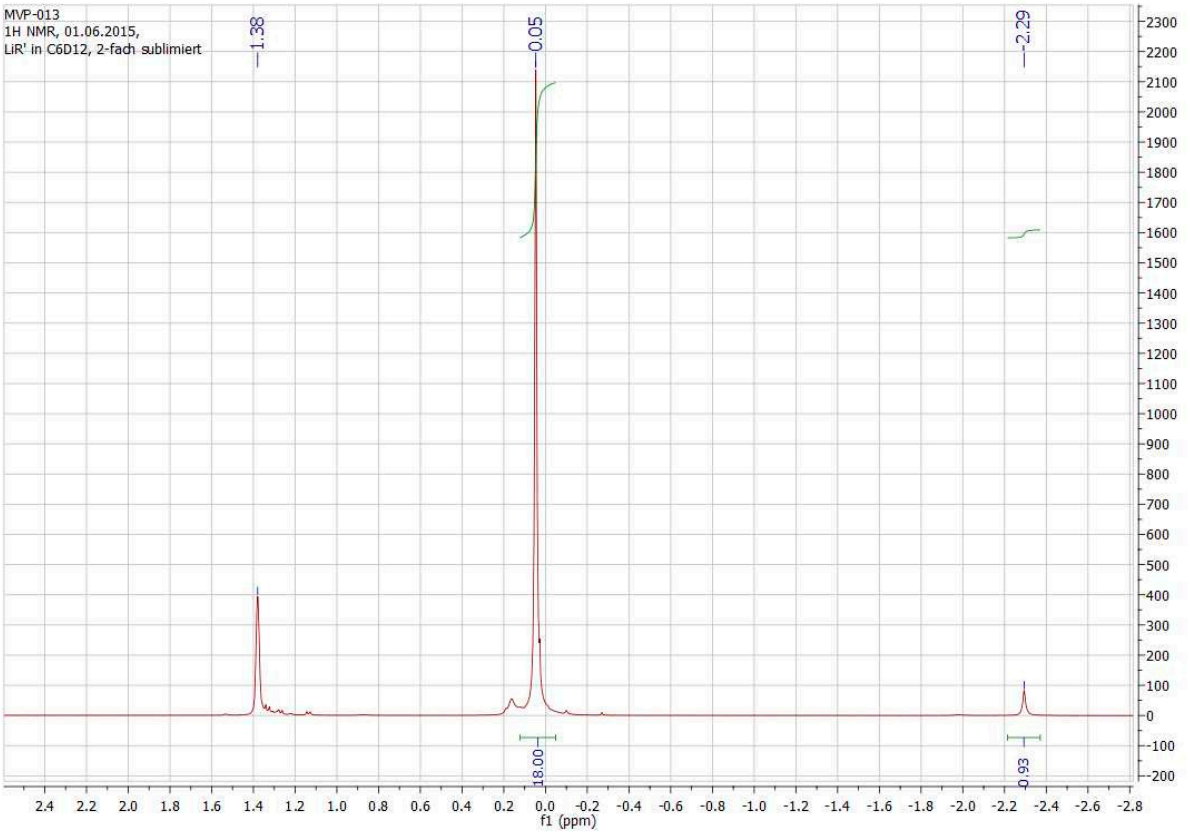


Figure S9: $^{1}H$ NMR of $LiCH(SiMe_3)_2$, **1**, in $C_6D_{12}$

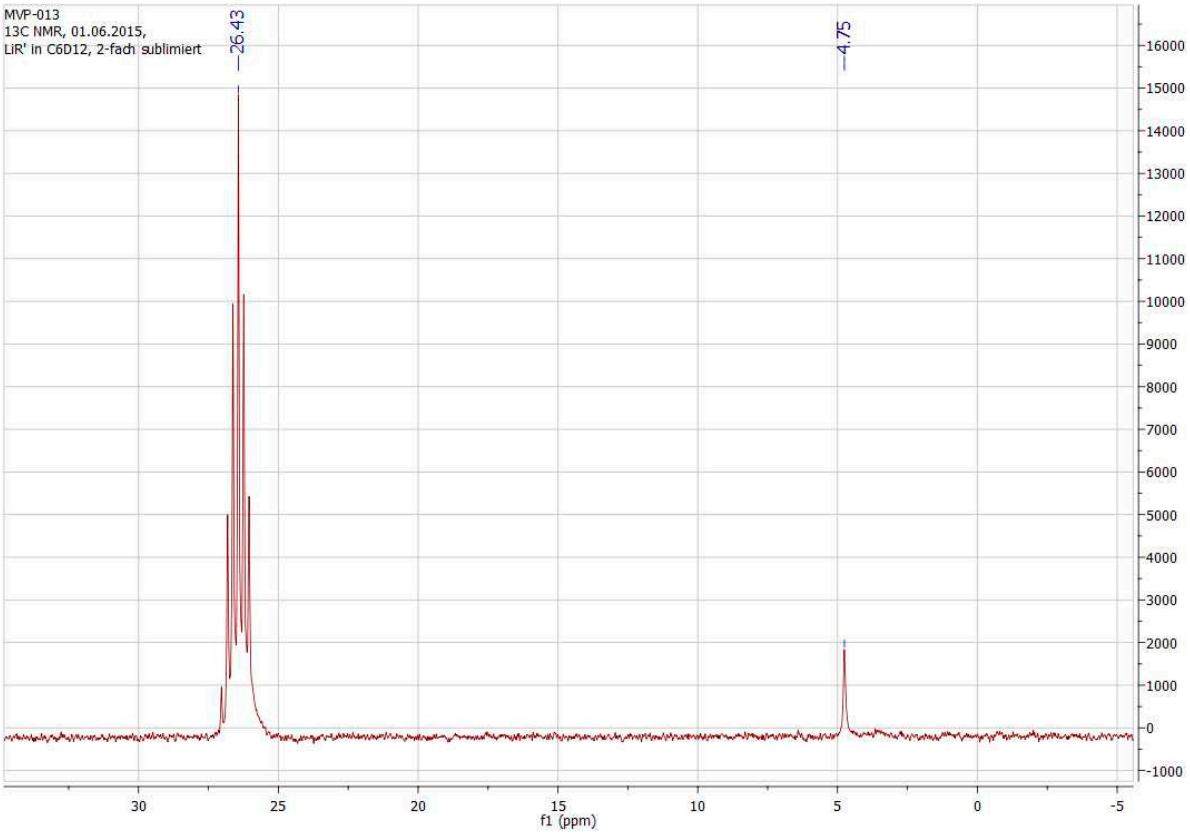


Figure S10: $^{13}C$ NMR of $LiCH(SiMe_3)_2$, **1**, in $C_6D_{12}$

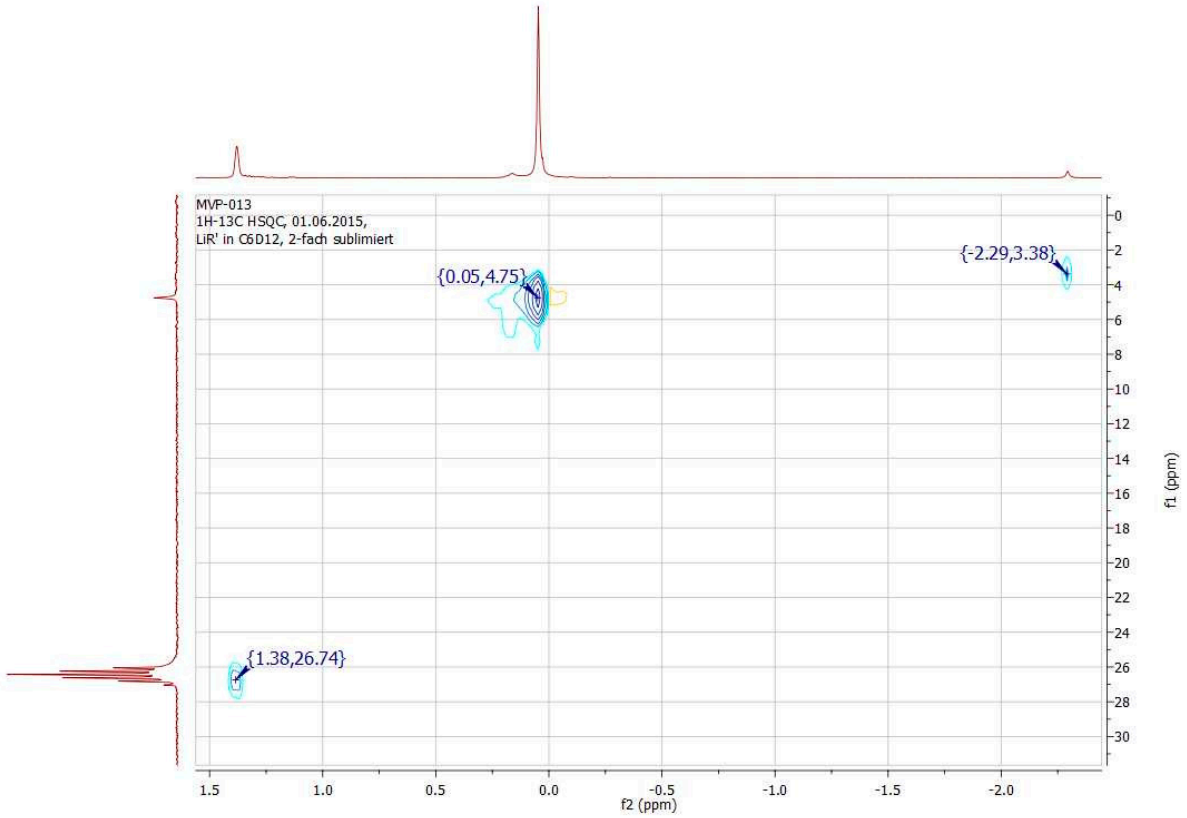


Figure S11: $^{1}H$-$^{13}C$ HSQC NMR of $LiCH(SiMe_3)_2$, **1**, in $C_6D_{12}$

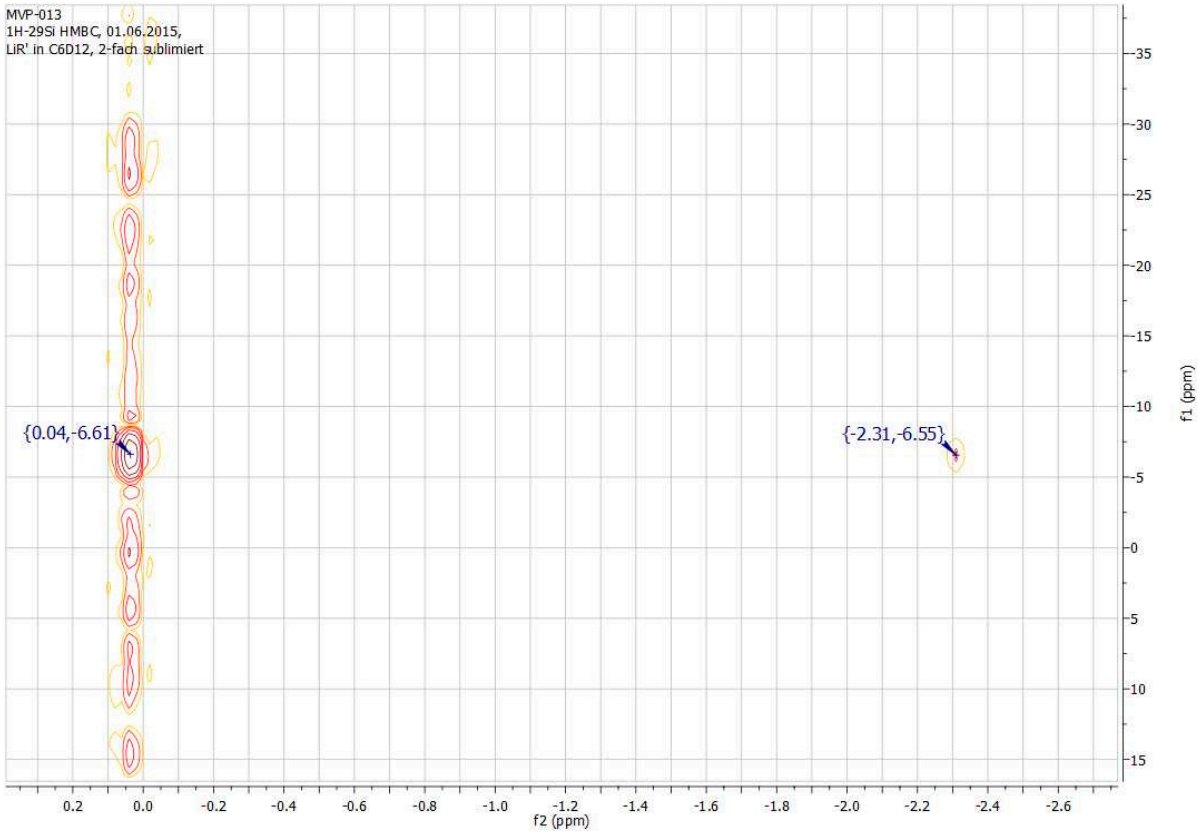


Figure S12: $^{1}H$-$^{29}Si$ HMBC NMR of $LiCH(SiMe_3)_2$, **1**, in $C_6D_{12}$

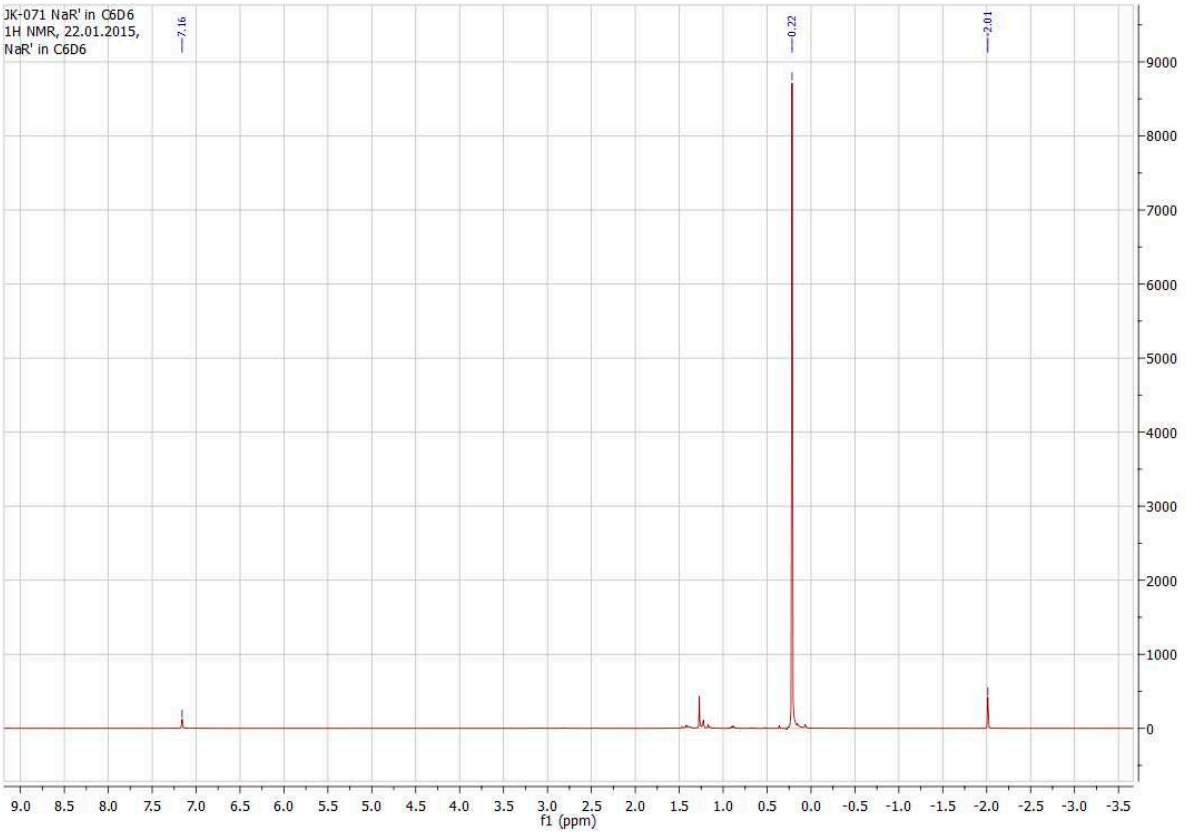


Figure S13: $^{1}H$ NMR of $NaCH(SiMe_3)_2$, **2**, in $C_6D_6$

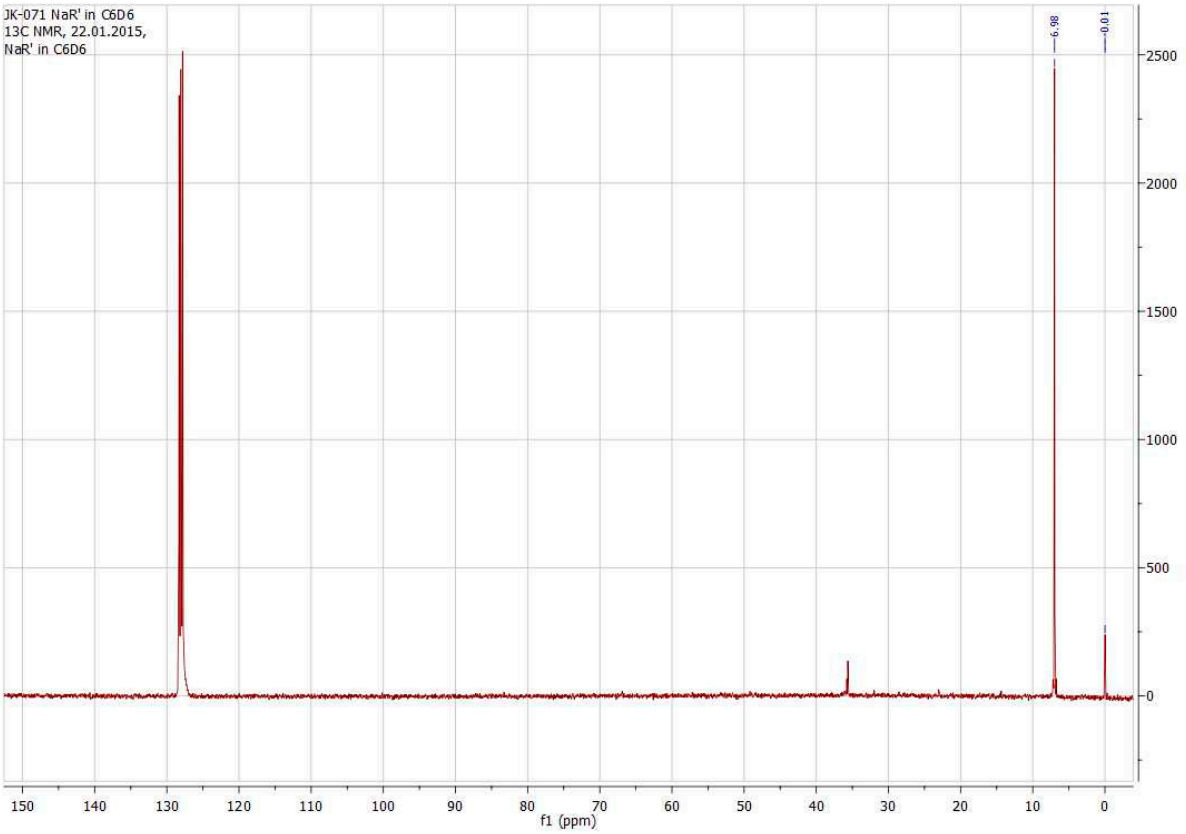


Figure S14: $^{13}C$ NMR of $NaCH(SiMe_3)_2$, **2**, in $C_6D_6$

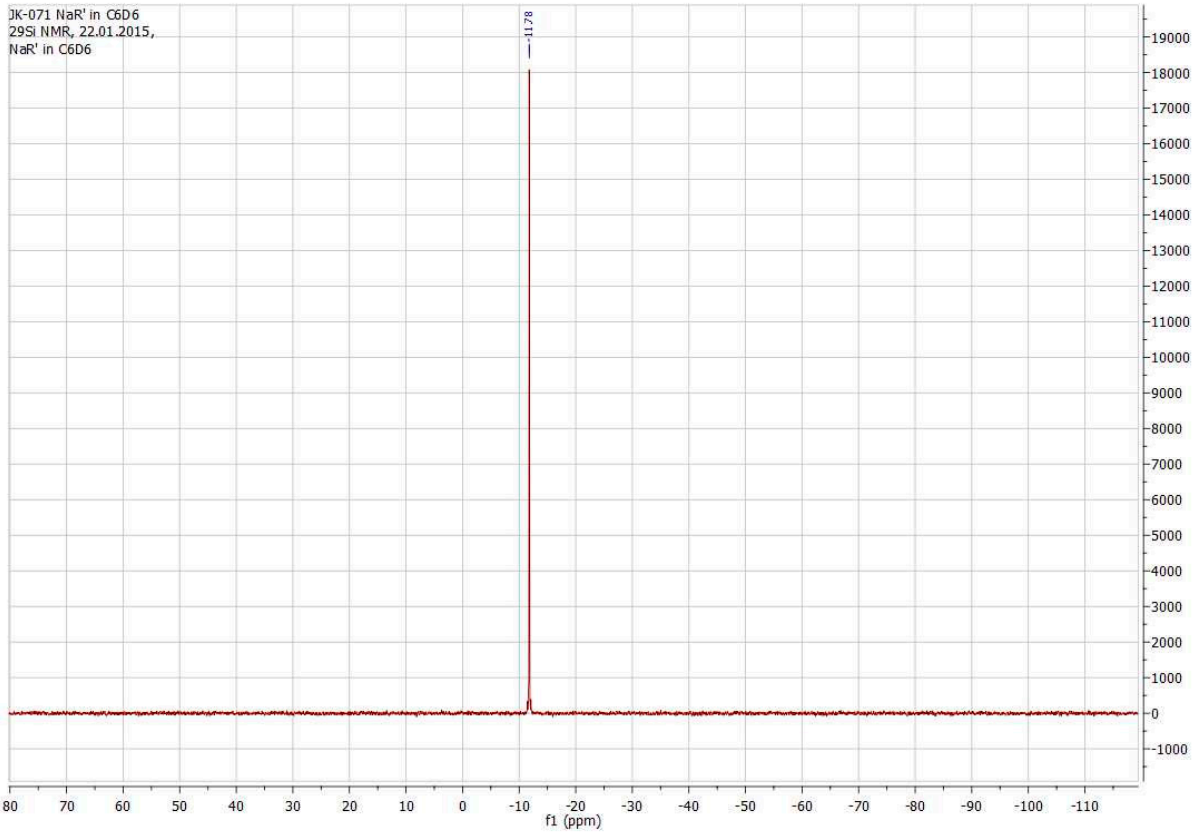


Figure S15: $^{29}Si$ NMR of $NaCH(SiMe_3)_2$, **2**, in $C_6D_6$

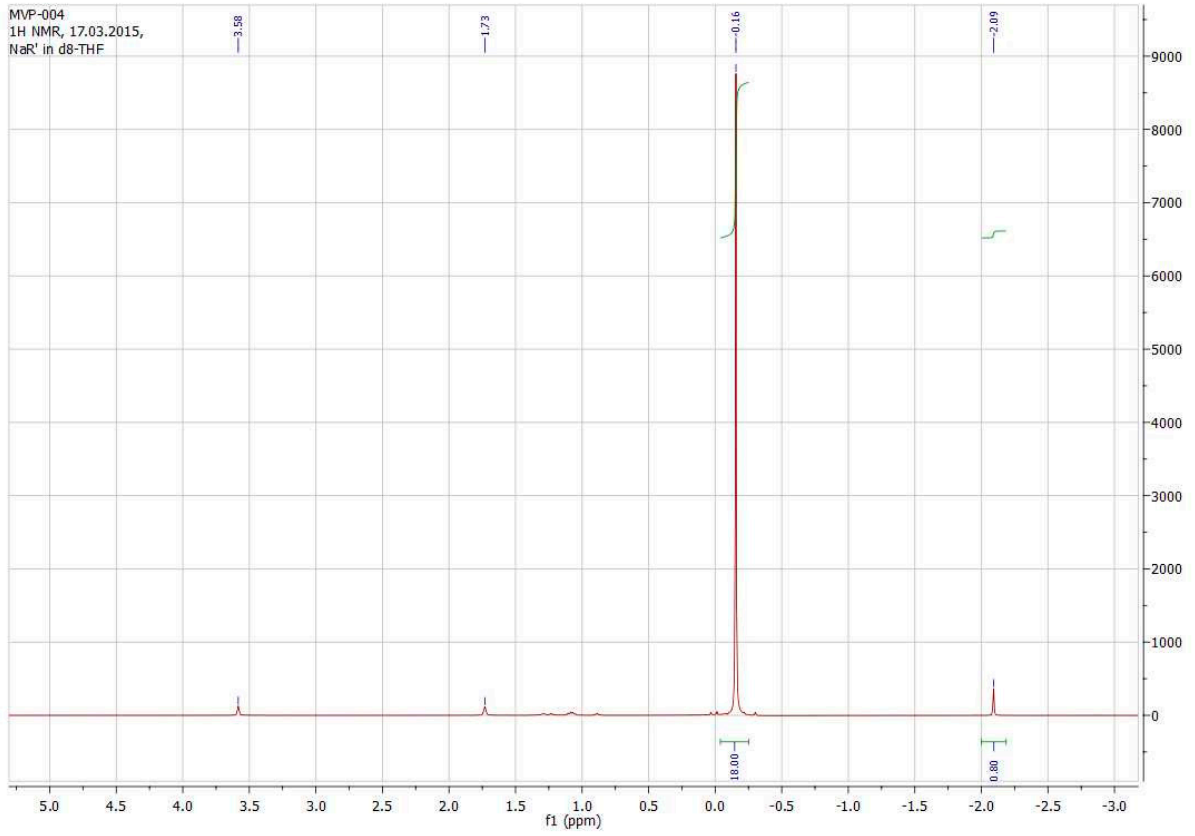


Figure S16: $^{1}H$ NMR of $NaCH(SiMe_3)_2$, **2**, in d8-THF

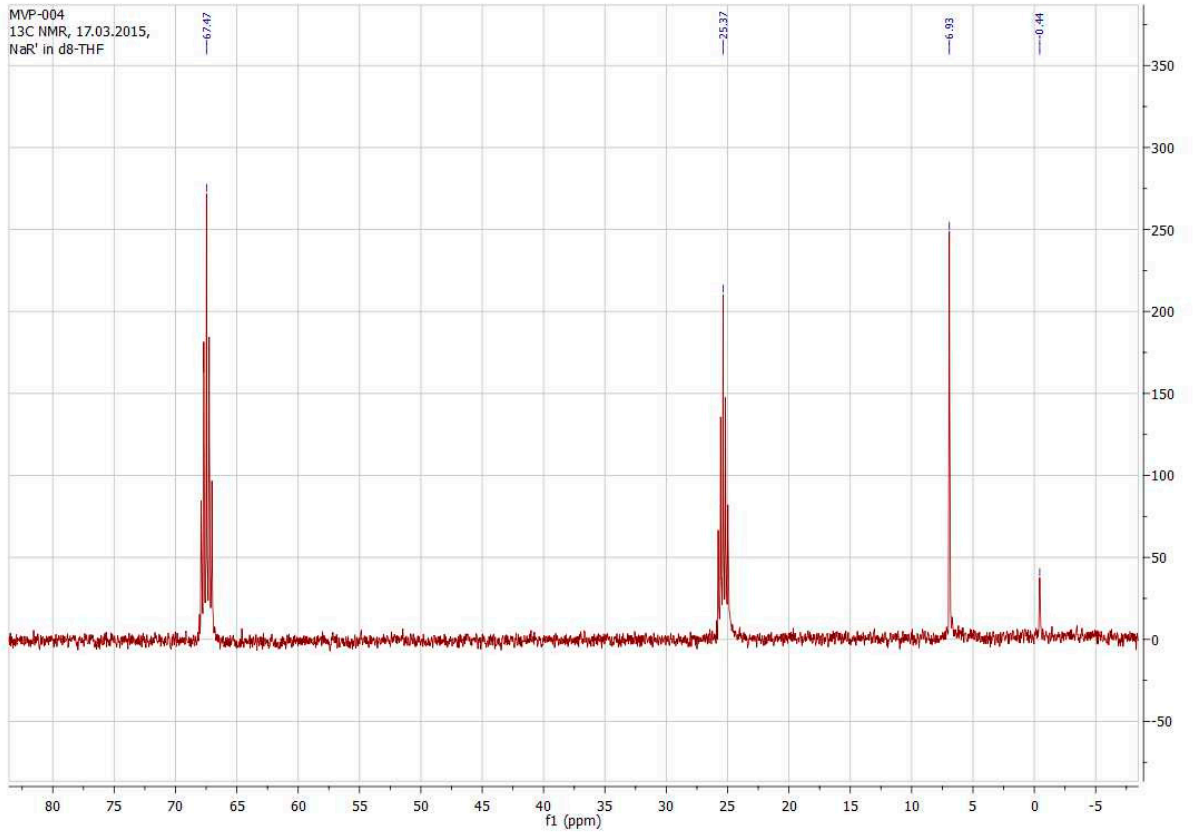


Figure S17: $^{13}C$ NMR of $NaCH(SiMe_3)_2$, **2**, in d8-THF

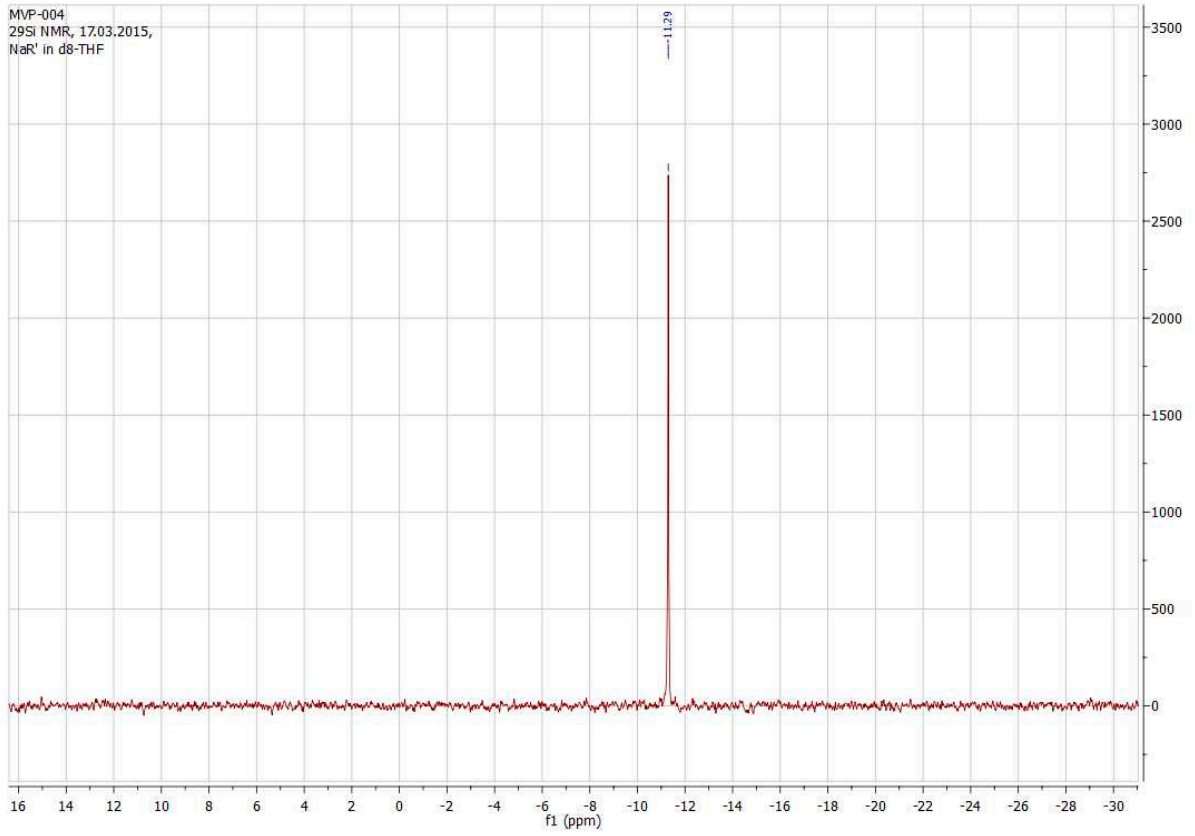


Figure S18: $^{29}Si$ NMR of $NaCH(SiMe_3)_2$, **2**, in d8-THF

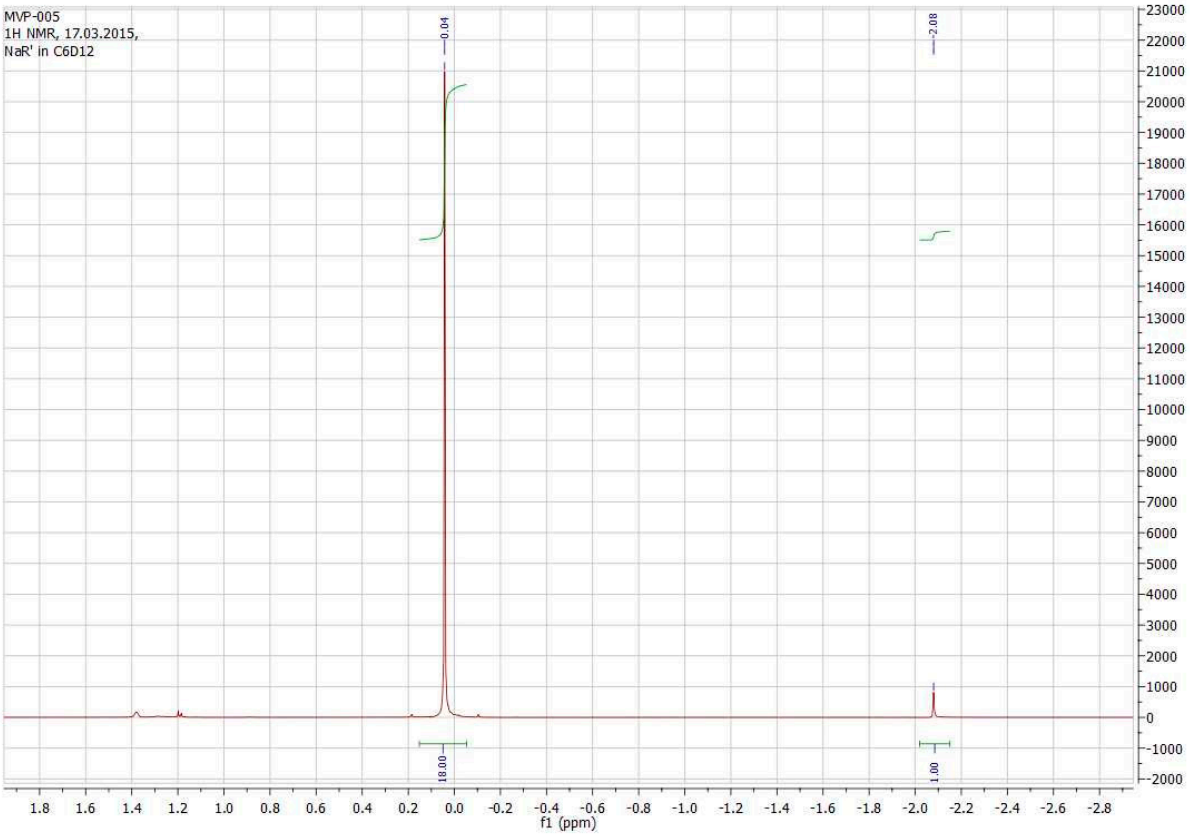


Figure S19: $^{1}H$ NMR of $NaCH(SiMe_3)_2$, **2**, in $C_6D_{12}$

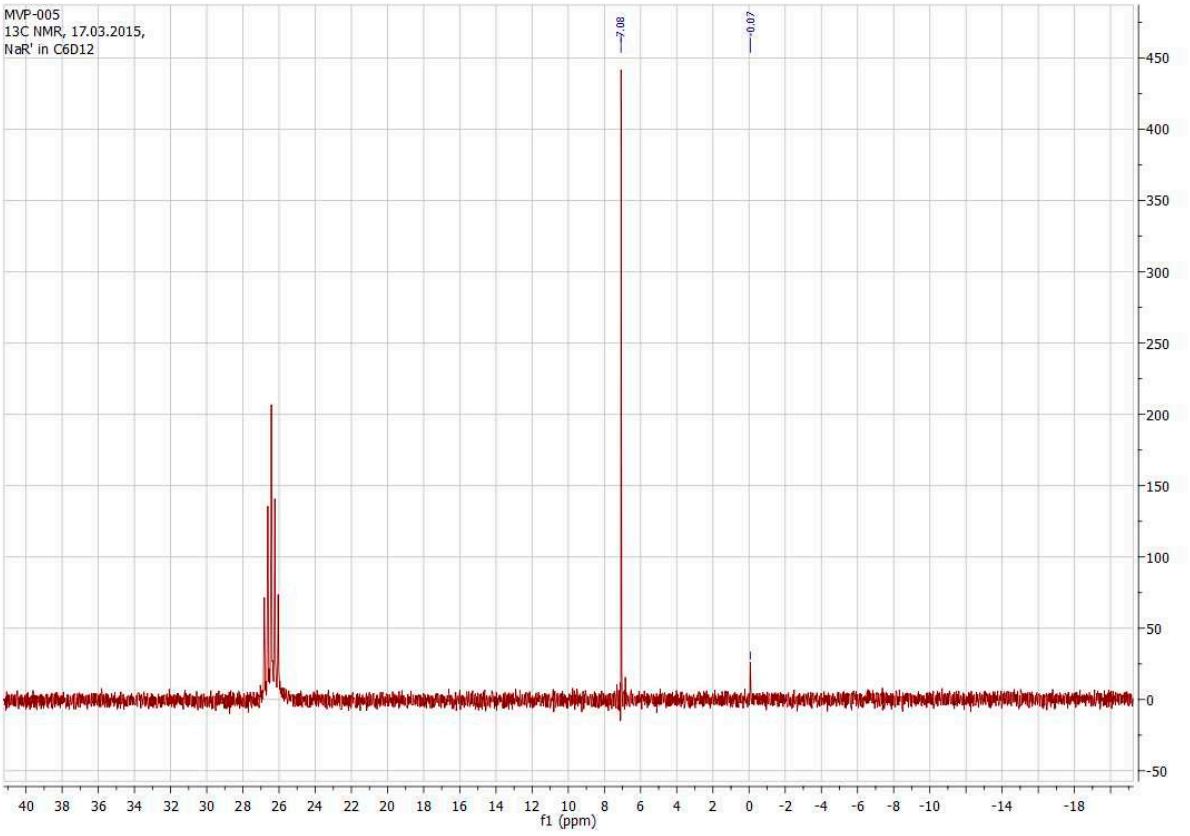


Figure S20: $^{13}C$ NMR of $NaCH(SiMe_3)_2$, **2**, in $C_6D_{12}$

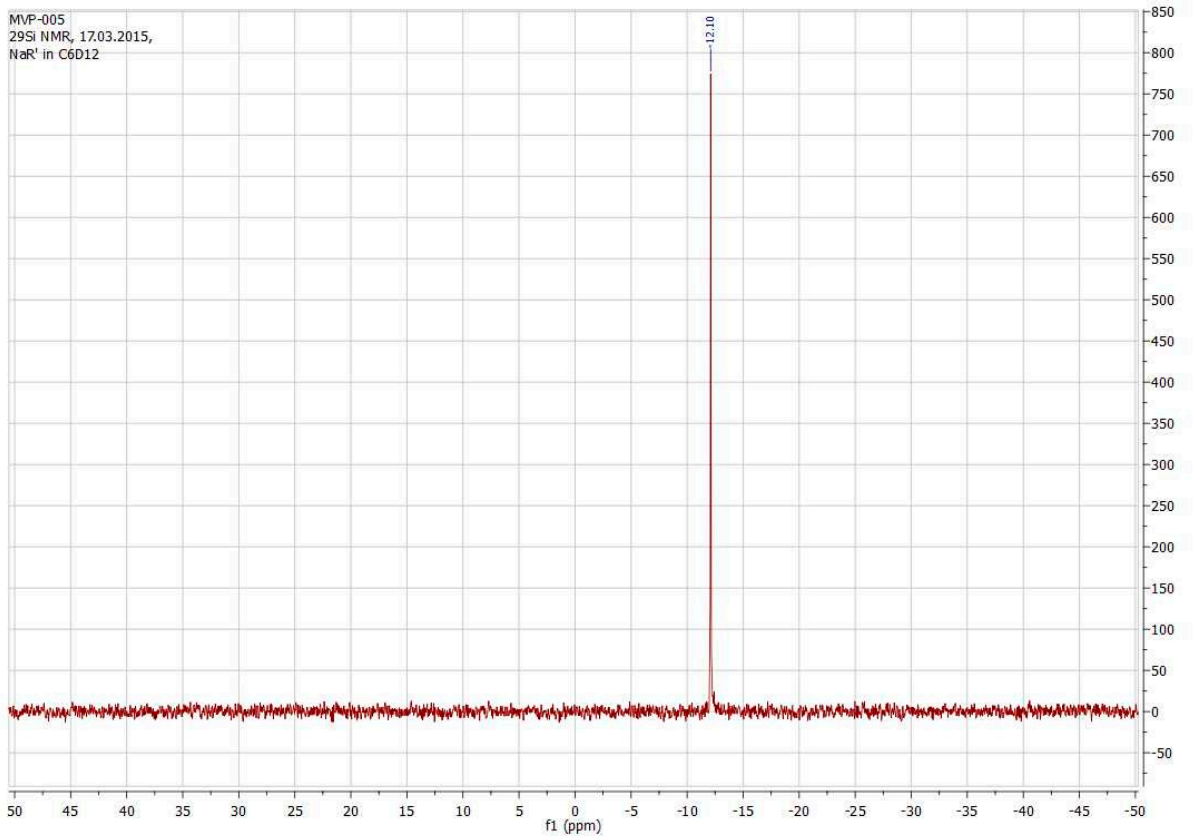


Figure S21: $^{29}Si$ NMR of $NaCH(SiMe_3)_2$, **2**, in $C_6D_{12}$

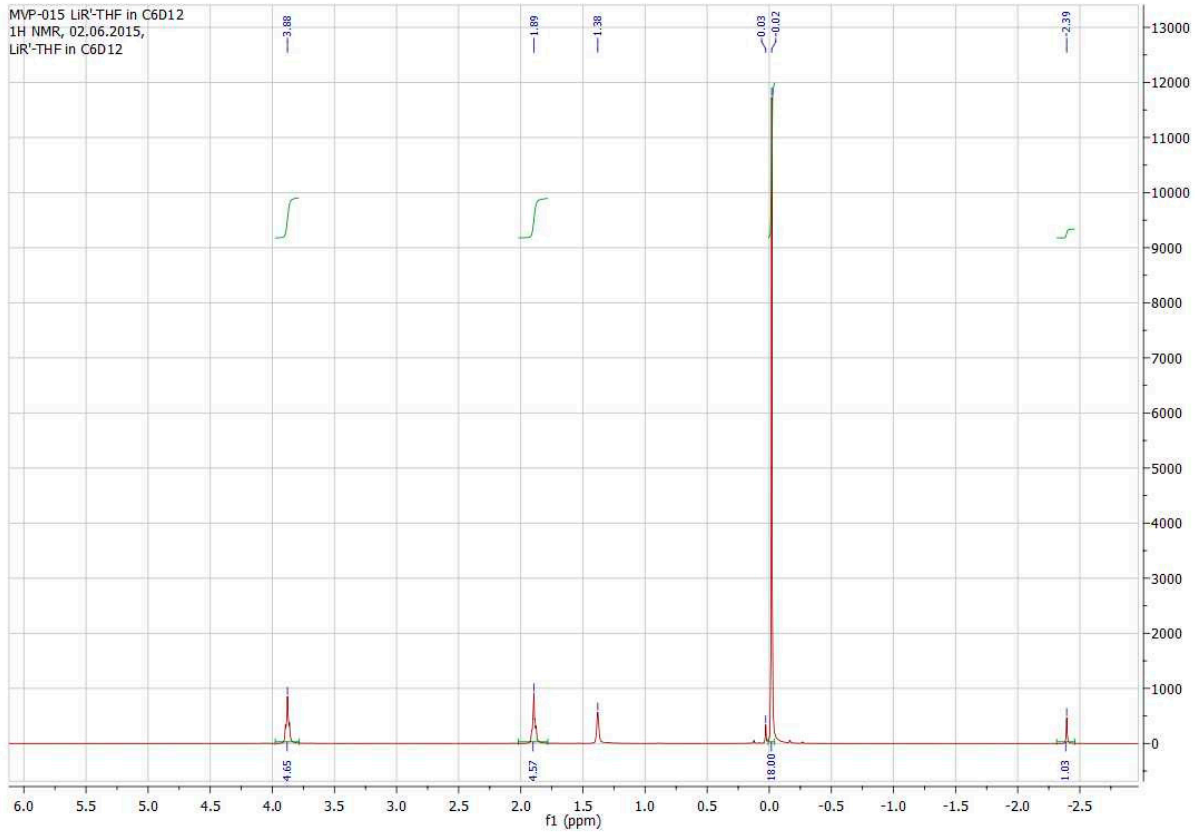


Figure S22: $^{1}H$ NMR of $LiCH(SiMe_3)_2$-THF, **1a**, in $C_6D_{12}$

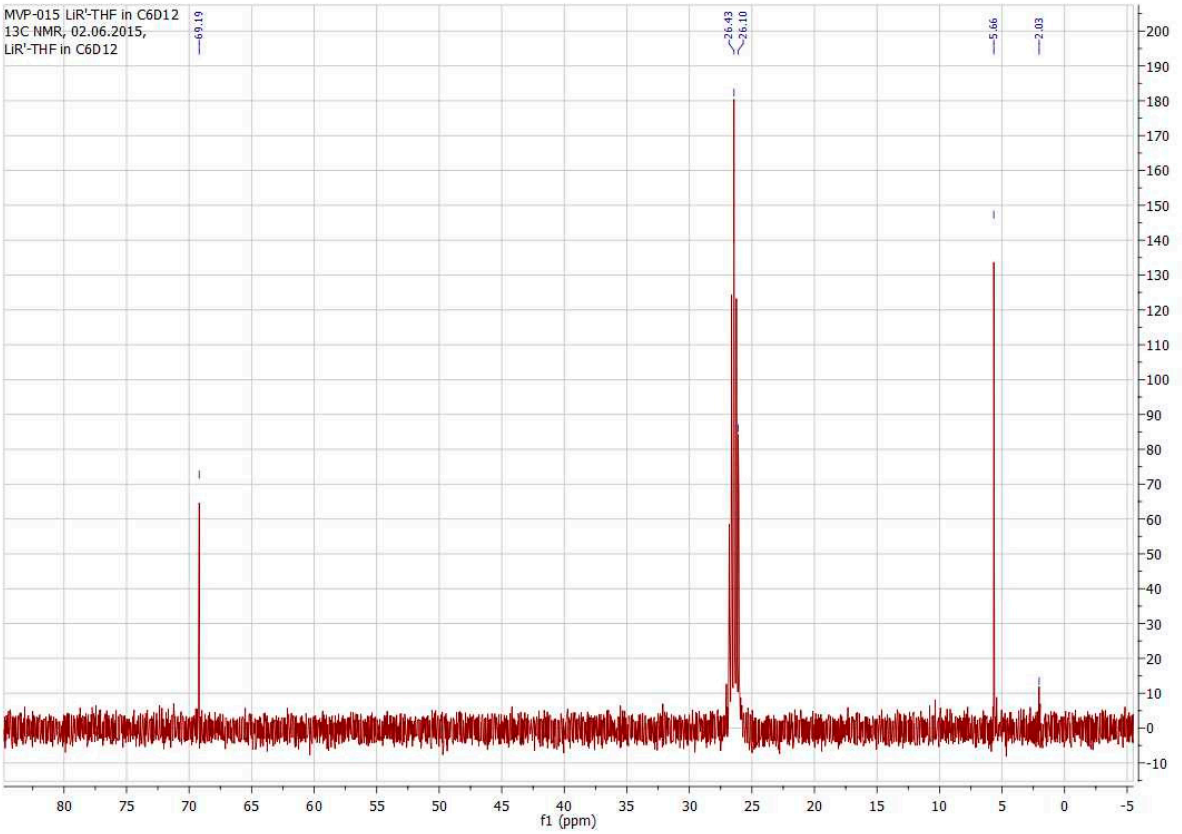


Figure S23: $^{13}C$ NMR of $LiCH(SiMe_3)_2$-THF, **1a**, in $C_6D_{12}$

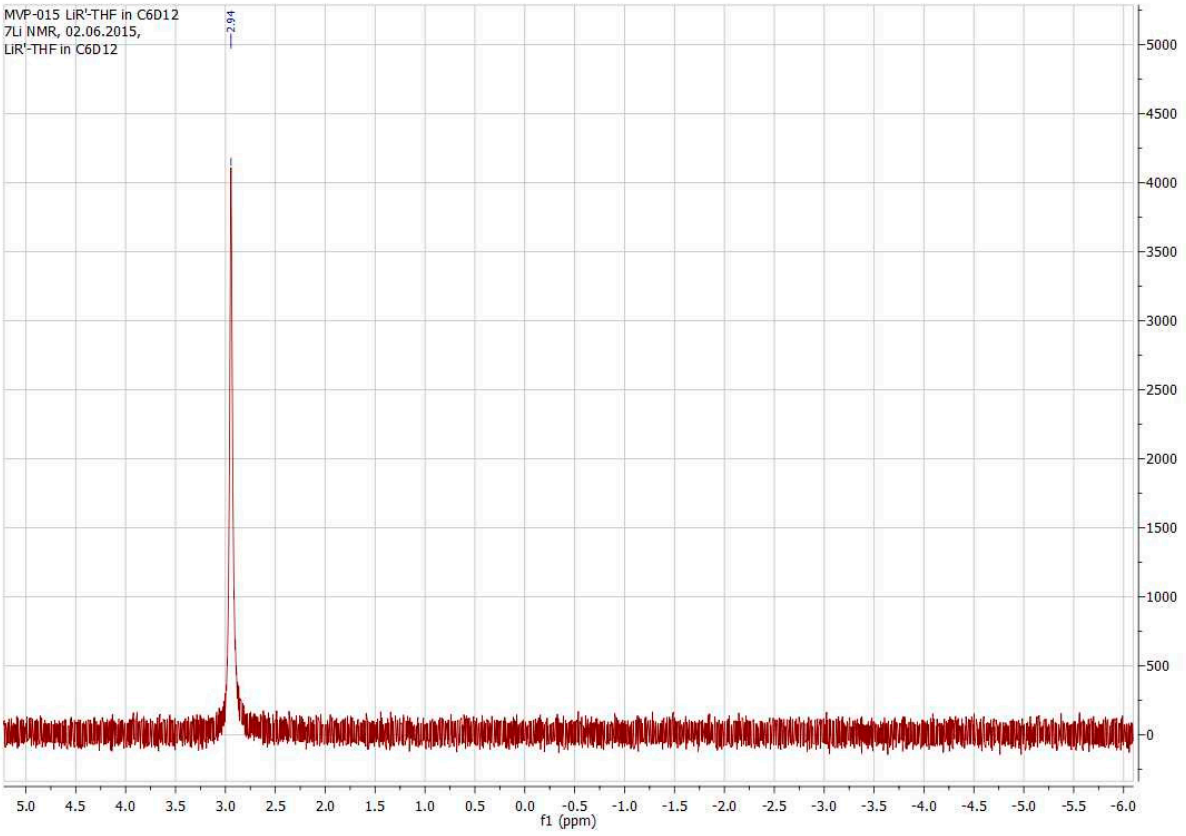


Figure S24: $^{7}Li$ NMR of $LiCH(SiMe_3)_2$-THF, **1a**, in $C_6D_{12}$

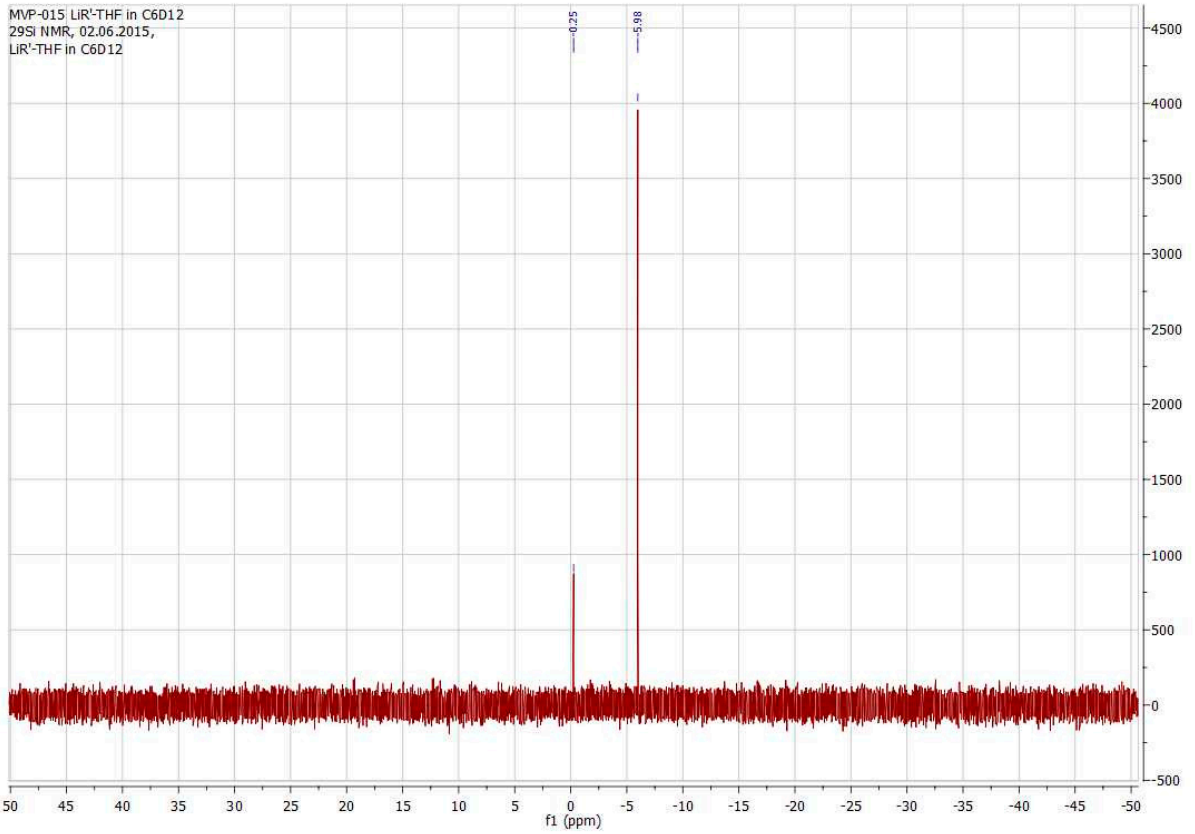


Figure S25: $^{29}Si$ NMR of $LiCH(SiMe_3)_2$-THF, **1a**, in $C_6D_{12}$

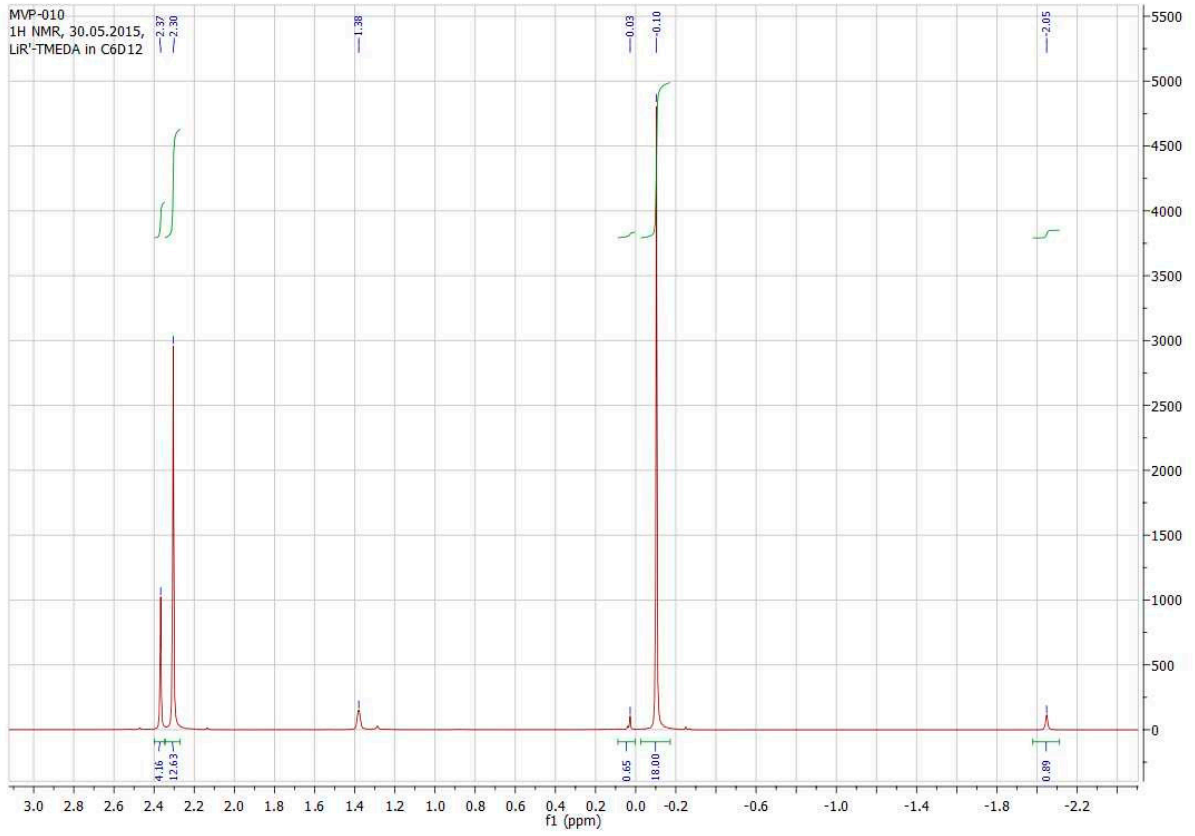


Figure S26: $^{1}H$ NMR of $LiCH(SiMe_3)_2$-TMEDA, **1b**, in $C_6D_{12}$

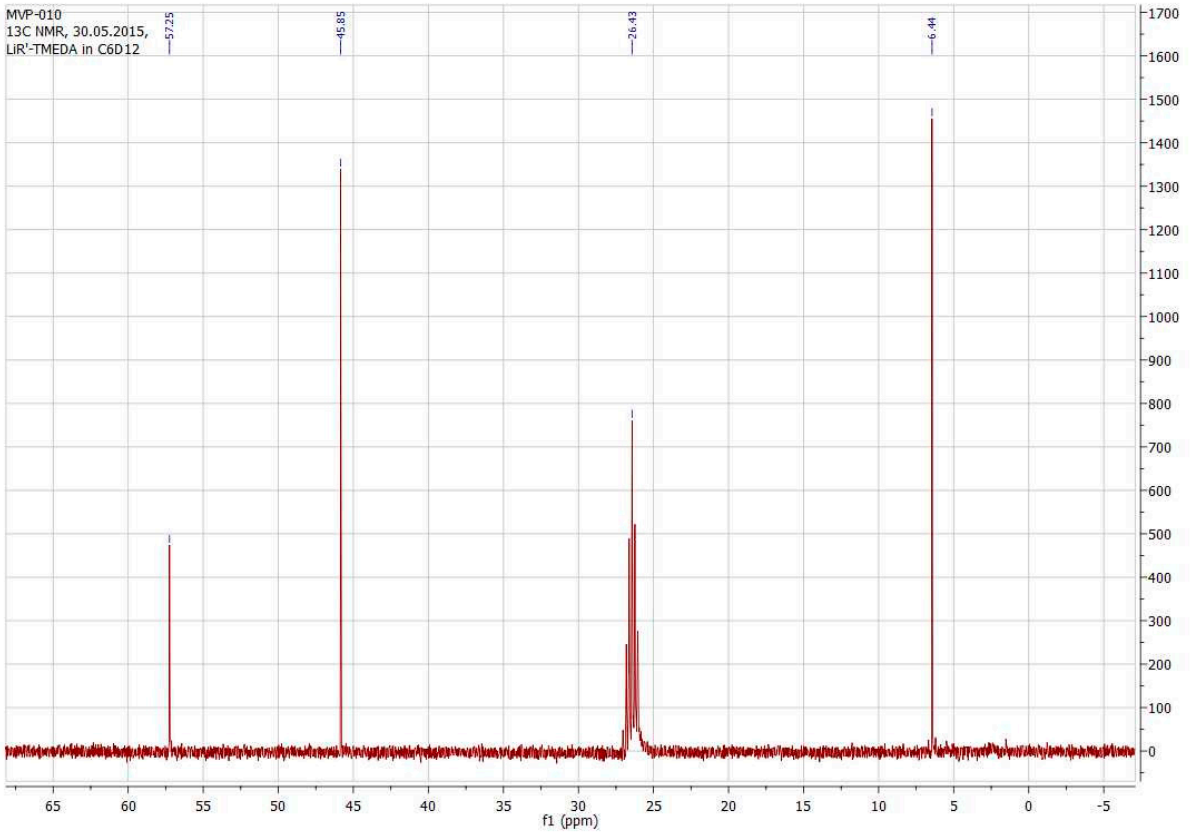


Figure S27: $^{13}C$ NMR of $LiCH(SiMe_3)_2$-TMEDA, **1b**, in $C_6D_{12}$

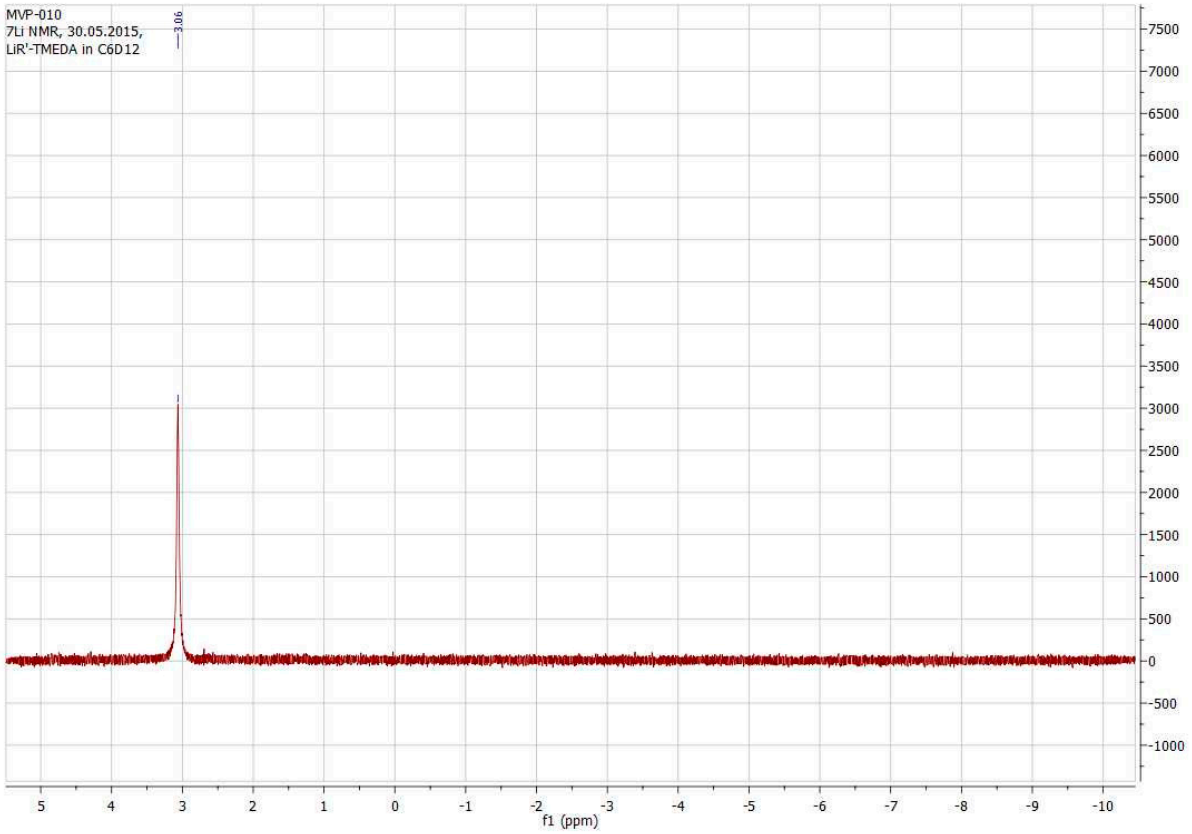


Figure S28: $^{7}Li$ NMR of $LiCH(SiMe_3)_2$-TMEDA, **1b**, in $C_6D_{12}$

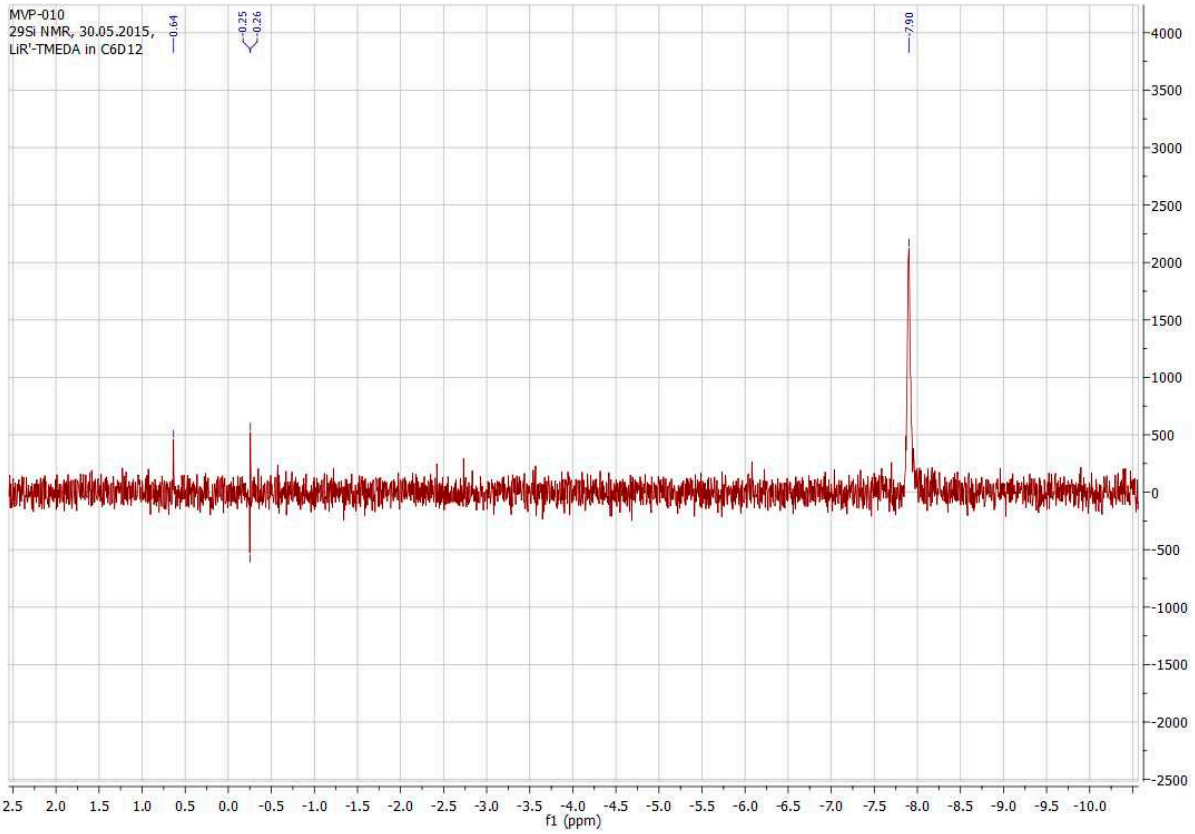


Figure S29: $^{29}$Si NMR of LiCH(SiMe$_3$)$_2$-TMEDA, **1b**, in $C_6D_{12}$

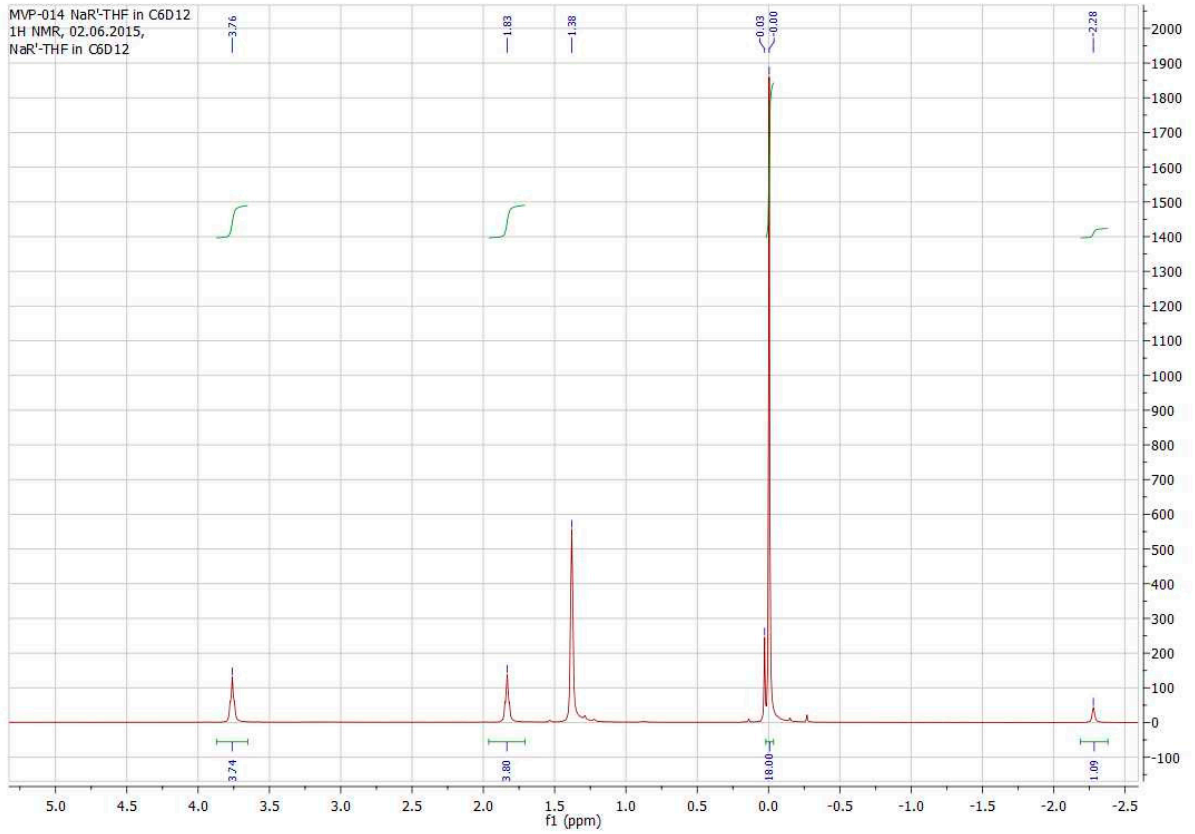


Figure S30: $^1$H NMR of NaCH(SiMe$_3$)$_2$-THF, **2a**, in $C_6D_{12}$

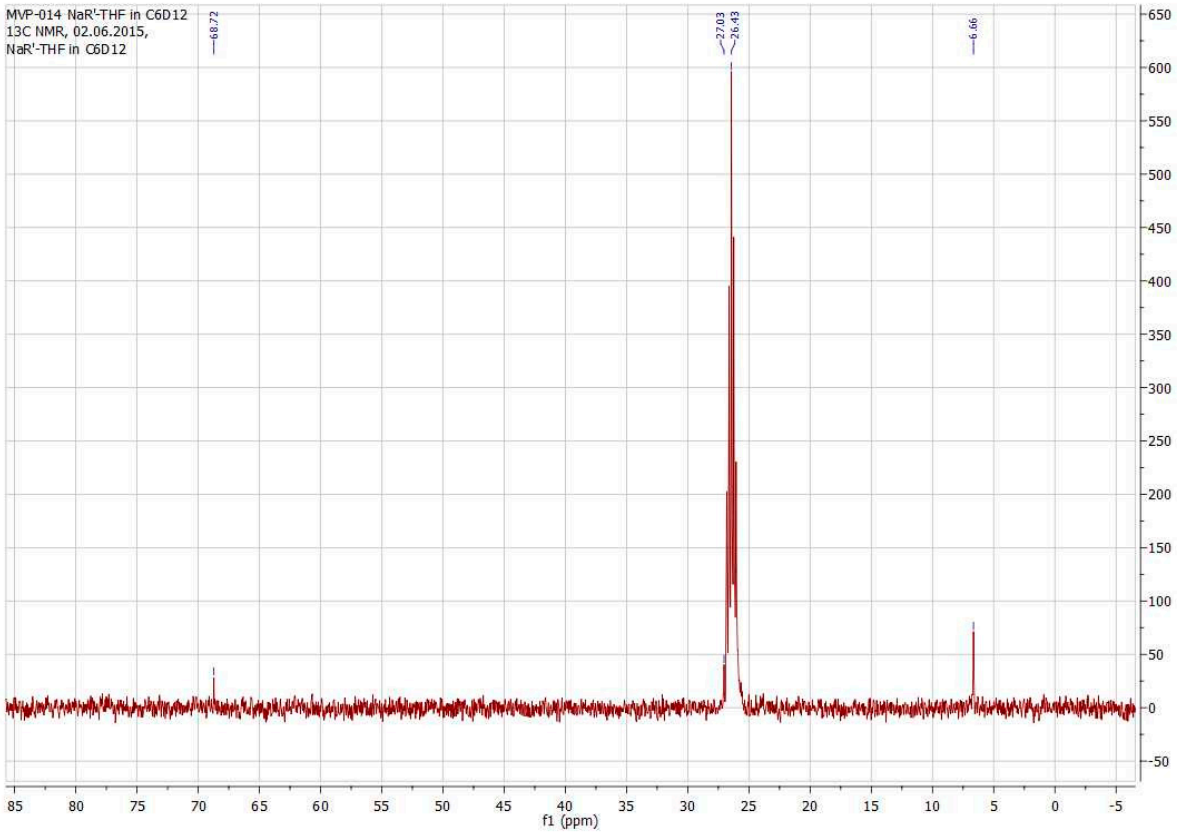


Figure S31: $^{13}C$ NMR of $NaCH(SiMe_3)_2$-THF, **2a**, in $C_6D_{12}$

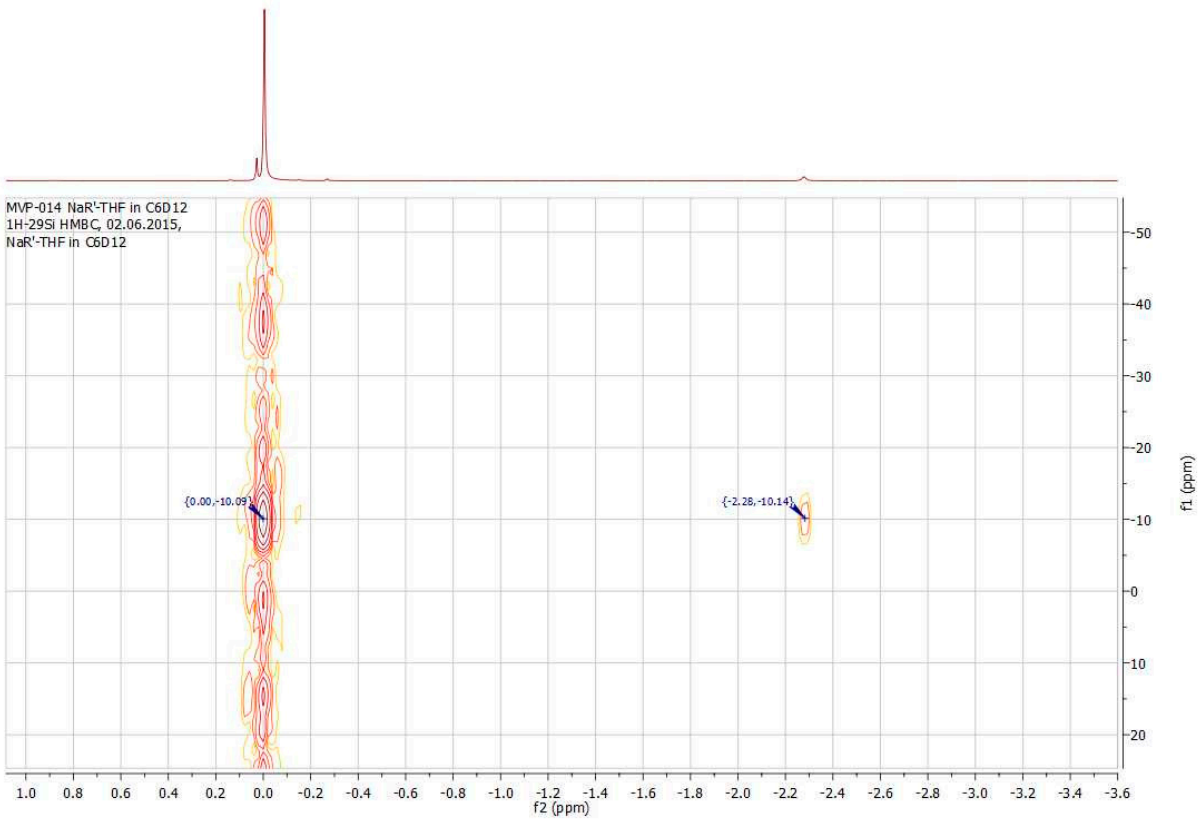


Figure S32: $^{1}H$-$^{29}Si$ HMBC NMR of $NaCH(SiMe_3)_2$-THF, **2a**, in $C_6D_{12}$

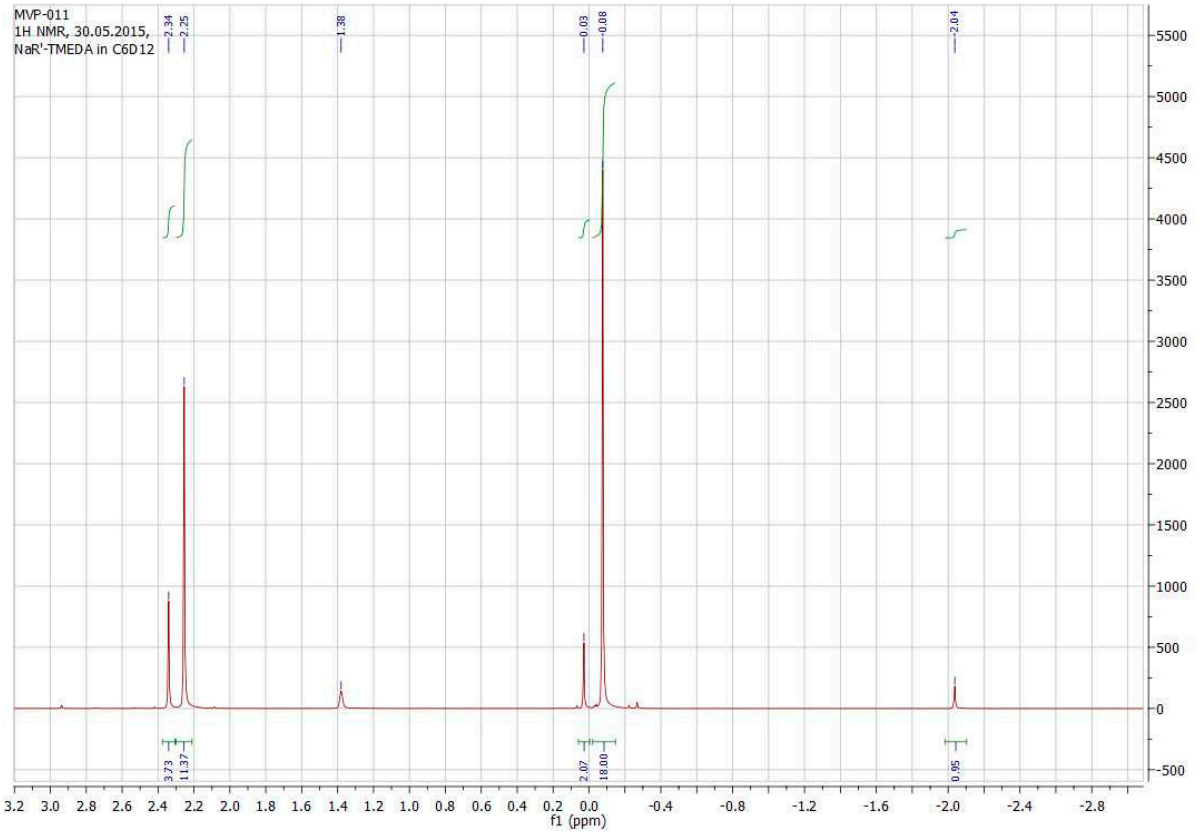


Figure S33: $^{1}H$ NMR of $NaCH(SiMe_3)_2$-TMEDA, **2b**, in $C_6D_{12}$

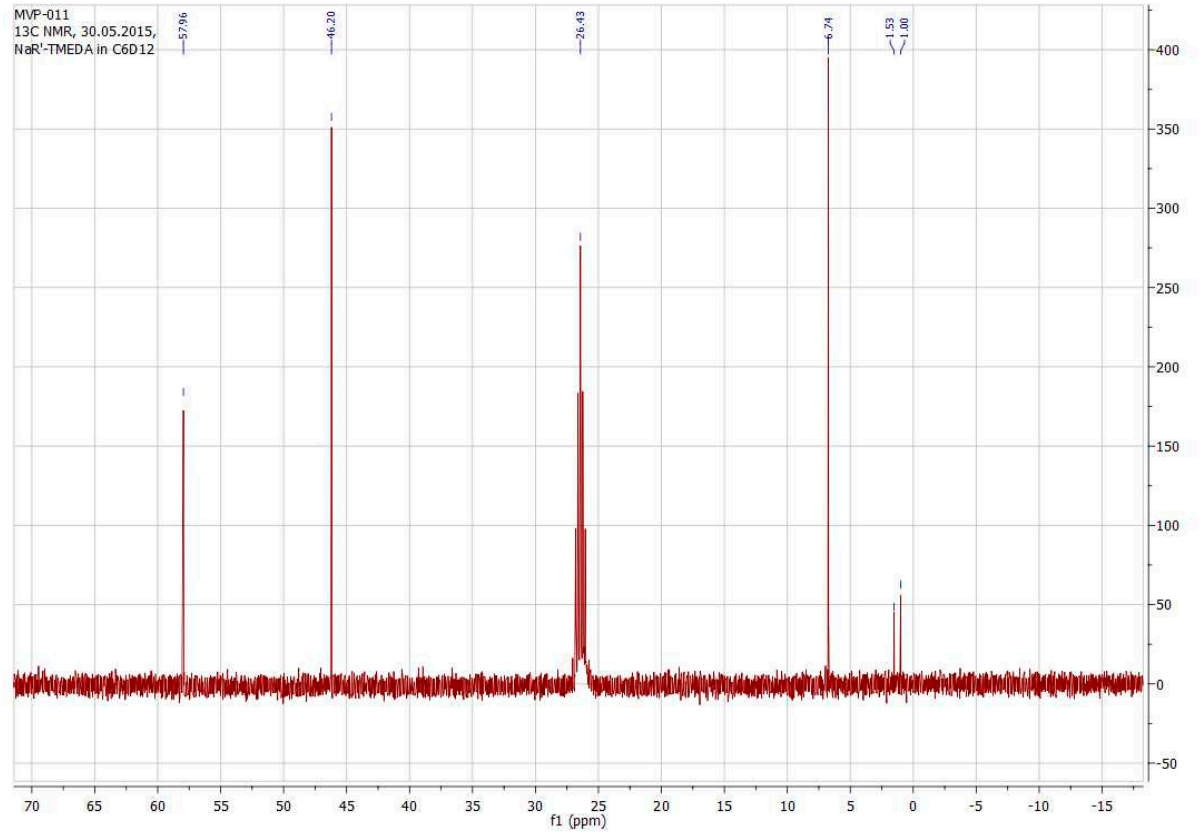


Figure S34: $^{13}C$ NMR of $NaCH(SiMe_3)_2$-TMEDA, **2b**, in $C_6D_{12}$

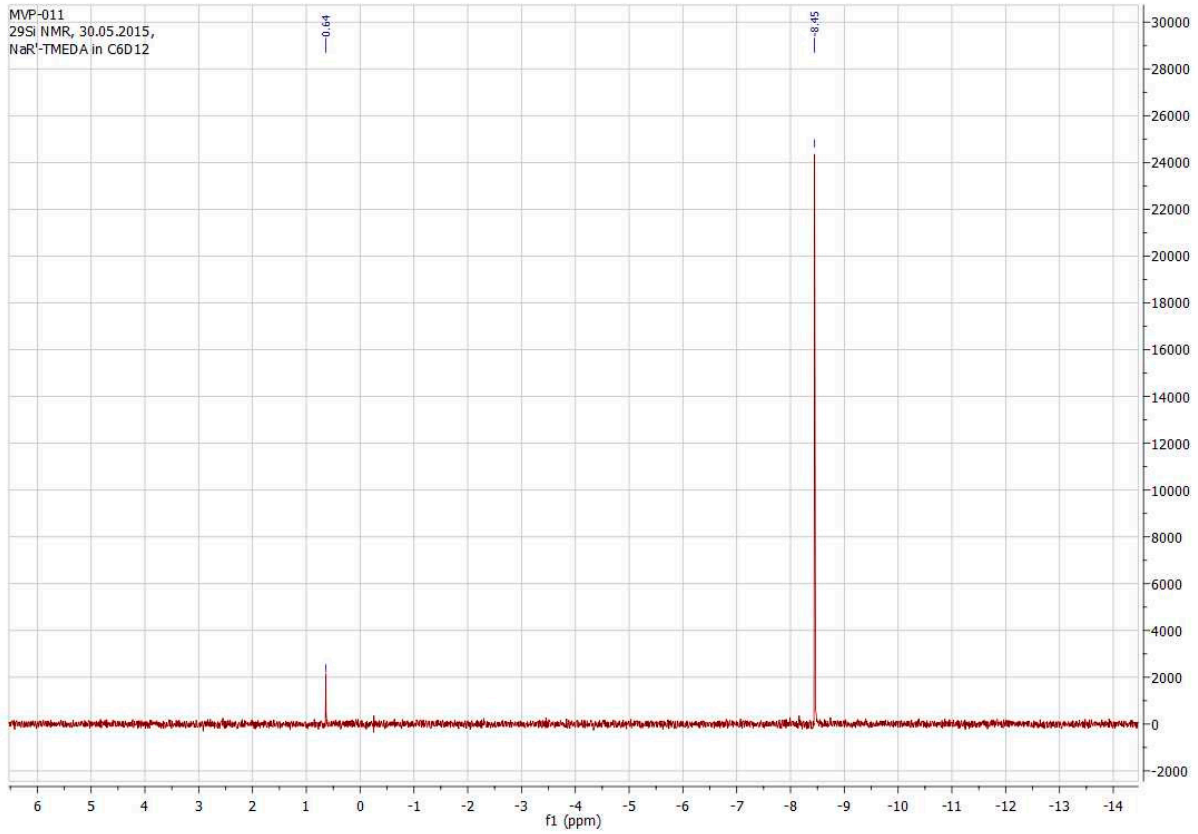


Figure S35: $^{29}$Si NMR of NaCH(SiMe$_3$)$_2$-TMEDA, **2b**, in $C_6D_{12}$

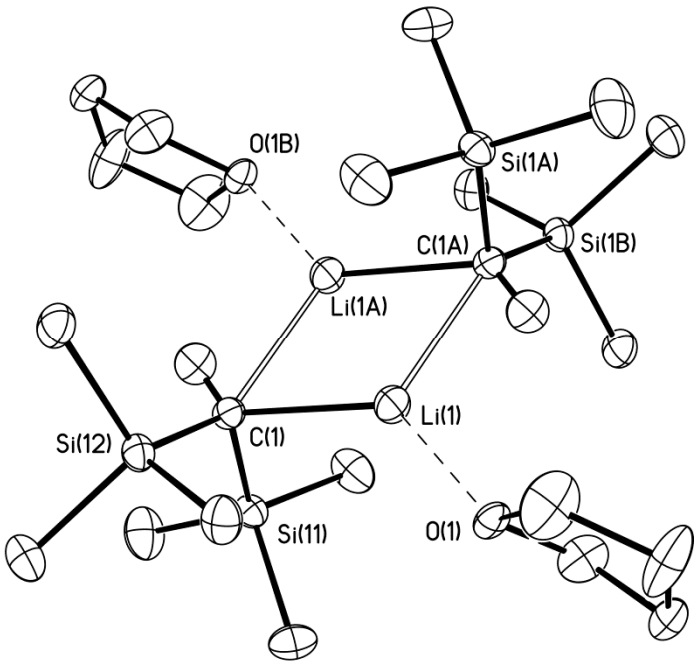


Figure S36: 30 % Displacement ellipsoid diagram of compound **1a**

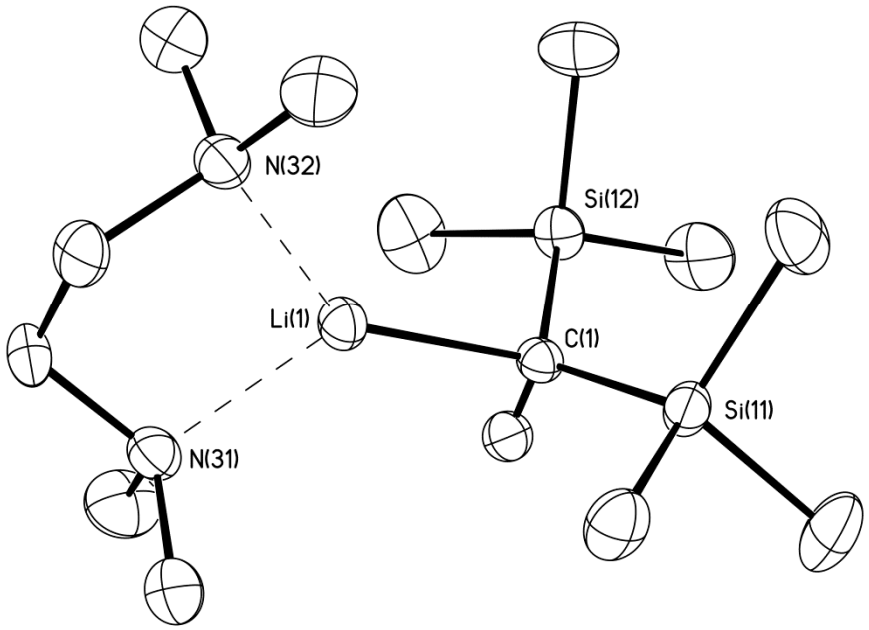


Figure S37: 30 % Displacement ellipsoid diagram of compound **1b**

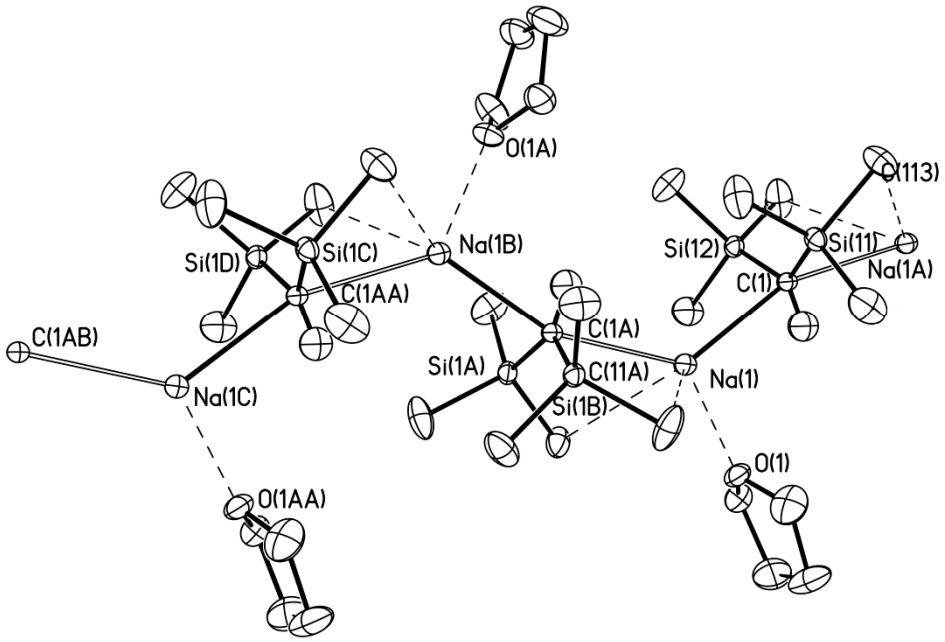


Figure S38: 30 % Displacement ellipsoid diagram of compound **2a**

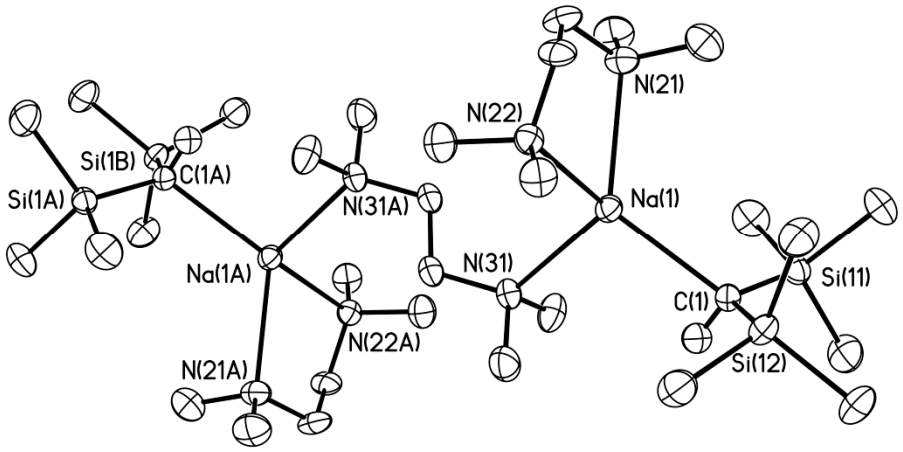


Figure S39: 30 % Displacement ellipsoid diagram of compound **2b**

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