

*Electronic Supplementary Information*

**Formation of  $\alpha$ -[KSiH<sub>3</sub>] by hydrogenolysis of potassium triphenylsilyl**

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## General Experimental Remarks

All operations were performed under an inert atmosphere of dry argon using standard Schlenk line or glove box techniques. THF-*d*<sub>8</sub> was distilled under argon from sodium/benzophenone ketyl prior to use. THF and pentane were purified using a MB SPS-800 solvent purification system. <sup>t</sup>BuPh<sub>2</sub>SiCl, MeSiCl, Ph<sub>3</sub>SiCl, MePh<sub>2</sub>SiCl, K<sup>t</sup>OBu, hexamethylbenzene and tris(2-aminoethyl)amine (TREN) were purchased from Sigma Aldrich and purified by vacuum sublimation or distillation. Lithium and potassium were purchased from Sigma Aldrich and used without further purification. Hydrogen (99.999) and deuterium (99.8) were purchased from Praxair-Westfalen AG. Elemental analyses were performed on an *elementar vario EL* machine. MS spectra were recorded on a *Shimadzu GCMS-GP2010 Plus* machine. IR spectra were recorded on a *Nicolet, Avatar 360 FT-IR E.S.P.* spectrometer. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>29</sup>Si{<sup>1</sup>H} NMR spectra were recorded on a *Bruker Avance II 400* or a *Bruker Avance III HD 400* spectrometer at 25 °C in J. Young type NMR tubes. Chemical shifts for <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>29</sup>Si{<sup>1</sup>H} NMR spectra were referenced internally using the residual solvent resonance and are reported relative to tetramethylsilane. The resonances in <sup>1</sup>H and <sup>13</sup>C NMR spectra were assigned on the basis of two-dimensional NMR experiments (COSY, HSQC, HMBC). Ph<sub>3</sub>SiSiMe<sub>3</sub><sup>1</sup>, MePh<sub>2</sub>SiSiPh<sub>2</sub>Me<sup>2</sup> and tris(2-*N,N*-dimethylaminoethyl)amine (Me<sub>6</sub>TREN<sup>3</sup>) were prepared according to published procedures.

### Synthesis of <sup>t</sup>BuPh<sub>2</sub>SiSiMe<sub>3</sub>

<sup>t</sup>BuPh<sub>2</sub>SiCl (10.0 g, 0.04 mol) in THF (20 mL) was added at 0 °C to a stirred suspension of lithium (1.68 g, 0.24 mol) in THF (30 mL). The solution turned green and was stirred for 4 h at 0 °C. The solution was filtered and added to Me<sub>3</sub>SiCl (4 g, 0.04 mol) in THF (20 mL) slowly. The reaction solution was quenched with sulphuric acid (10%), the organic phases were extracted with Et<sub>2</sub>O (3×100 mL) and dried over MgSO<sub>4</sub>. Et<sub>2</sub>O was removed under reduced pressure, the product distilled under vacuum (160 °C, 5×10<sup>-2</sup> mbar and isolated as a colorless oil (10.2 g, 0.033 mol, 82%).

<sup>1</sup>H NMR (THF-D<sub>8</sub>, 400.1 MHz): δ<sub>H</sub> 0.17 (m, 9H, SiMe<sub>3</sub>), 1.14 (m, 9H, <sup>t</sup>Bu), 7.29-7.35 (m, 6H, *para/meta*-Ph), 7.54-7.59 (m, 4H, *ortho*-Ph) ppm.

<sup>13</sup>C{<sup>1</sup>H} NMR (THF-D<sub>8</sub>, 100.6 MHz): δ<sub>C</sub> 0.12 (SiMe<sub>3</sub>), 20.35 (C(CH<sub>3</sub>)<sub>3</sub>), 29.49 (C(CH<sub>3</sub>)<sub>3</sub>), 128.48 (*para*-Ph), 129.51 (*meta*-Ph), 136.96 (*ipso*-Ph), 137.20 (*ortho*-Ph) ppm.

$^{29}\text{Si}\{^1\text{H}\}$  NMR (THF- $\text{D}_8$ , 79.5 MHz):  $\delta_{\text{Si}}$  -19.43 ( $t\text{BuPh}_2\text{SiSiMe}_3$ ), -10.51 ( $t\text{BuPh}_2\text{SiSiMe}_3$ ) ppm.

Anal. calc. for  $\text{C}_{19}\text{H}_{28}\text{Si}_2$  (312.60  $\text{g}\cdot\text{mol}^{-1}$ ): C, 73.00; H, 9.03. Found: C, 72.83; H, 8.86%.

MS (70 eV):  $m/z = 312$  ( $\text{M}^+$ , 7%), 255 (100), 197 (29), 135 (45), 105 (10), 73 (13), 57 (3).

### Synthesis of $[\text{K}(\text{Me}_6\text{TREN})\text{SiPh}_3]$ (**1**)

A solution of KO $t$ Bu (112 mg, 1.00 mmol) in THF (2 mL) was added to  $\text{Ph}_3\text{SiSiMe}_3$  (333 mg, 1.00 mmol) in THF (2 mL) and stirred for 15 min at 25 °C.  $\text{Me}_6\text{TREN}$  (230 mg, 1.00 mmol) was added slowly and the reaction solution stirred for 16 h. The solvent was removed under reduced pressure and the product was washed with pentane (3 $\times$ 5 mL). After drying *in vacuo*,  $[\text{K}(\text{Me}_6\text{TREN})\text{SiPh}_3]$  (**1**) (387 mg, 0.73 mmol, 73%) was isolated as orange/brown powder. Single crystals of **1** suitable for X-ray diffraction were grown from THF at -30 °C over a period of 16 h.

$^1\text{H}$  NMR (THF- $\text{D}_8$ , 400.1 MHz):  $\delta_{\text{H}}$  2.14 (s, 18H, NCH<sub>3</sub>), 2.28 (d,  $^3J_{\text{H,H}} = 6.6$  Hz, 3H, CH<sub>2</sub>), 2.30 (d,  $^3J_{\text{H,H}} = 5.8$  Hz, 3H, CH<sub>2</sub>), 2.52 (d,  $^3J_{\text{H,H}} = 5.8$  Hz, 3H, CH<sub>2</sub>), 2.54 (d,  $^3J_{\text{H,H}} = 6.6$  Hz, 3H, CH<sub>2</sub>), 6.77-6.85 (m, 3H, *para*-Ph), 6.88-6.96 (m, 6H, *meta*-Ph), 7.29-7.37 (m, 6H, *ortho*-Ph) ppm.

$^{13}\text{C}\{^1\text{H}\}$  NMR (THF- $\text{D}_8$ , 100.6 MHz):  $\delta_{\text{C}}$  46.20 (CH<sub>3</sub>), 54.28 (CH<sub>2</sub>), 59.08 (CH<sub>2</sub>), 123.76 (*para*-Ph), 126.66 (*meta*-Ph), 136.91 (*ortho*-Ph), 158.63 (*ipso*-Ph) ppm.

$^{29}\text{Si}\{^1\text{H}\}$  NMR (THF- $\text{D}_8$ , 79.5 MHz):  $\delta_{\text{Si}}$  -7.38 (KSi) ppm.

Anal. calc. for  $\text{C}_{30}\text{H}_{45}\text{N}_4\text{KSi}$  (528.90  $\text{g}\cdot\text{mol}^{-1}$ ): C, 68.13; H, 8.58; N, 10.59. Found: C, 67.81; H, 8.55; N, 10.76%.

### Synthesis of $[\text{K}(\text{Me}_6\text{TREN})\text{Si}^t\text{BuPh}_2]$ (**5**)

A solution of KO $t$ Bu (224 mg, 2.00 mmol) in THF (4 mL) was added to  $t\text{BuPh}_2\text{SiSiMe}_3$  (626 mg, 2.00 mmol) in THF (4 mL) and stirred for 15 min at 25 °C.  $\text{Me}_6\text{TREN}$  (460 mg, 2.00 mmol) was added slowly and the reaction solution stirred for 72 h. The solvent was removed under reduced pressure and the product was washed with pentane (3 $\times$ 5 mL). After drying *in vacuo*,  $[\text{K}(\text{Me}_6\text{TREN})\text{Si}^t\text{BuPh}_2]$  (**5**) (708 mg, 1.40 mmol, 70%) was isolated as orange powder.

$^1\text{H}$  NMR (THF- $\text{D}_8$ , 400.1 MHz):  $\delta_{\text{H}}$  0.94 (s, 9H,  $\text{CH}_3$ ), 2.14 (s, 18H,  $\text{NCH}_3$ ), 2.29 (d,  $^3J_{\text{H,H}} = 6.5$  Hz, 3H,  $\text{CH}_2$ ), 2.31 (d,  $^3J_{\text{H,H}} = 5.7$  Hz, 3H,  $\text{CH}_2$ ), 2.53 (d,  $^3J_{\text{H,H}} = 5.7$  Hz, 3H,  $\text{CH}_2$ ), 2.56 (d,  $^3J_{\text{H,H}} = 6.5$  Hz, 3H,  $\text{CH}_2$ ), 6.71-6.84 (m, 2H, *para*-Ph), 6.85-6.97 (m, 4H, *meta*-Ph), 7.39-7.54 (m, 4H, *ortho*-Ph) ppm.

$^{13}\text{C}\{^1\text{H}\}$  NMR (THF- $\text{D}_8$ , 100.6 MHz):  $\delta_{\text{C}}$  20.62 ( $\text{C}(\text{CH}_3)_3$ ), 32.14 ( $\text{C}(\text{CH}_3)_3$ ), 46.23 ( $\text{NCH}_3$ ), 54.38 ( $\text{CH}_2$ ), 59.16 ( $\text{CH}_2$ ), 123.27 (*para*-Ph), 126.29 (*meta*-Ph), 137.50 (*ortho*-Ph), 160.47 (*ipso*-Ph) ppm.

$^{29}\text{Si}\{^1\text{H}\}$  NMR (THF- $\text{D}_8$ , 79.5 MHz):  $\delta_{\text{Si}}$  8.68 (KSi) ppm.

Anal. Calc. for  $\text{C}_{28}\text{H}_{49}\text{N}_4\text{KSi}$  (508.91  $\text{g}\cdot\text{mol}^{-1}$ ): C, 66.08; H, 9.71; N, 11.01. Found: C, 65.49; H, 9.99; N, 11.34%.

### Synthesis of $[\text{K}(\text{Me}_6\text{TREN})\text{SiMePh}_2]$ (6)

A solution of  $\text{MePh}_2\text{SiSiPh}_2\text{Me}$  (99 mg, 0.25 mmol) in THF- $\text{D}_8$  (1 mL) was added to potassium (30 mg, 0.77 mmol) and  $\text{Me}_6\text{TREN}$  (0.50 mmol) in THF- $\text{D}_8$  (1 mL) at 25 °C. The solution turned red and a  $^1\text{H}$  NMR spectrum was measured immediately. Isolation of the desired product failed due to fast decomposition.

$^1\text{H}$  NMR (THF- $\text{D}_8$ , 400.1 MHz):  $\delta_{\text{H}}$  0.35 (s, 3H,  $\text{CH}_3$ ), 2.18 (s, 18H,  $\text{NCH}_3$ ), 2.30 (d,  $^3J_{\text{H,H}} = 6.6$  Hz, 3H,  $\text{CH}_2$ ), 2.32 (d,  $^3J_{\text{H,H}} = 5.9$  Hz, 3H,  $\text{CH}_2$ ), 2.53 (d,  $^3J_{\text{H,H}} = 5.9$  Hz, 3H,  $\text{CH}_2$ ), 2.55 (d,  $^3J_{\text{H,H}} = 6.5$  Hz, 3H,  $\text{CH}_2$ ), 6.70-6.81 (m, 2H, *para*-Ph), 6.87-6.97 (m, 4H, *meta*-Ph), 7.35-7.42 (m, 4H, *ortho*-Ph) ppm.

### Synthesis of $\alpha$ - $[\text{KSiH}_3]$ (4)

A degassed solution of  $[\text{K}(\text{Me}_6\text{TREN})\text{SiPh}_3]$  (1) (264 mg, 0.50 mmol) in THF (3 mL) was charged with  $\text{H}_2$  (1 bar) in a glass autoclave and stirred for 7 d at 25 °C. The reaction mixture was layered with pentane (10 mL), the supernatant was decanted off and the product was washed with pentane (3×5 mL). The residual solvent was removed under reduced pressure and after drying *in vacuo*,  $\alpha$ - $[\text{KSiH}_3]$  (4) (32 mg, 0.46 mmol, 92 %) was isolated as grey powder.

$^1\text{H}$  NMR (THF- $\text{D}_8$ , 400.1 MHz):  $\delta_{\text{H}}$  1.22 (s, 3H,  $\text{SiH}$ ,  $^1J_{\text{SiH}} = 76.29$  Hz) ppm.

$^{29}\text{Si}\{^1\text{H}\}$  NMR (THF- $\text{D}_8$ , 79.5 MHz):  $\delta_{\text{Si}}$  -170.00 ( $\text{KSiH}_3$ ) ppm.

IR Absorptions:  $\nu_{\text{max}}/\text{cm}^{-1}$ : 1888sh ( $\text{SiH}$ ), 1842sh ( $\text{SiH}$ ), 1814s ( $\text{SiH}$ ), 977s ( $\text{SiH}$ ), 914s ( $\text{SiH}$ ).

The IR stretching frequencies are consistent with both the reported and calculated frequencies in the literature.<sup>4</sup>

### **Synthesis of $\alpha$ -[KSiD<sub>3</sub>] (4-D<sub>3</sub>)**

A degassed solution of [K(Me<sub>6</sub>TREN)SiPh<sub>3</sub>] (**1**) (264 mg, 0.50 mmol) in THF (3 mL) was charged with D<sub>2</sub> (1 bar) in a glass autoclave and stirred for 7 d at 25 °C. The reaction mixture was layered with pentane (10 mL), the supernatant was decanted off and the product was washed with pentane (3×5 mL). The residual solvent was removed under reduced pressure and after drying *in vacuo*,  $\alpha$ -[KSiD<sub>3</sub>] (**4-D<sub>3</sub>**) (36 mg, 0.49 mmol, 98 %) was isolated as grey powder.

IR Absorptions:  $\nu_{\max}/\text{cm}^{-1}$ : 1376sh (SiD), 1345sh (SiD), 1314s (SiD), 703s (SiD), 671s (SiD)

The IR stretching frequencies are consistent with both the reported and calculated frequencies in the literature.<sup>4</sup>

### ***in situ* Hydrogenation of alkali metal silyls**

The alkali metal silyl (56  $\mu\text{mol}$ ) and hexamethylbenzene (9 mg, 56  $\mu\text{mol}$ ) were dissolved in THF-D<sub>8</sub> (0.7 mL) in a J. Young's NMR tube. The solution was degassed, charged with H<sub>2</sub> (1 bar) and monitored by <sup>1</sup>H and <sup>29</sup>Si{<sup>1</sup>H} NMR spectroscopy for the period of time indicated.

*in situ*  $^1\text{H}$  and  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectra of the hydrogenation of  $[\text{K}(\text{Me}_6\text{TREN})\text{SiPh}_3]$  (1)

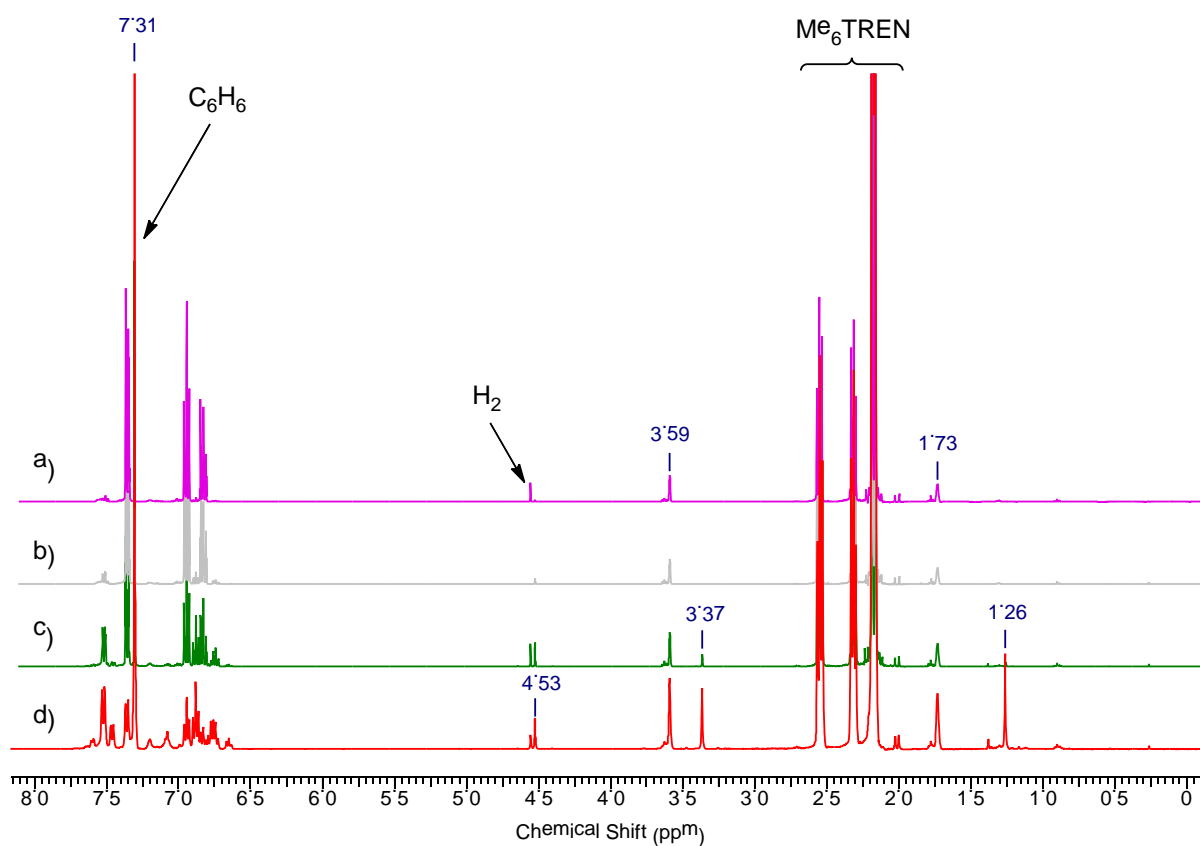


Figure S1. *in situ*  $^1\text{H}$  NMR spectra in THF- $\text{D}_8$  of the hydrogenation (1 bar of  $\text{H}_2$ ) of  $[\text{K}(\text{Me}_6\text{TREN})\text{SiPh}_3]$  at 25 °C after a) 12 h, b) 48 h, c) 72 h and d) 7 d.

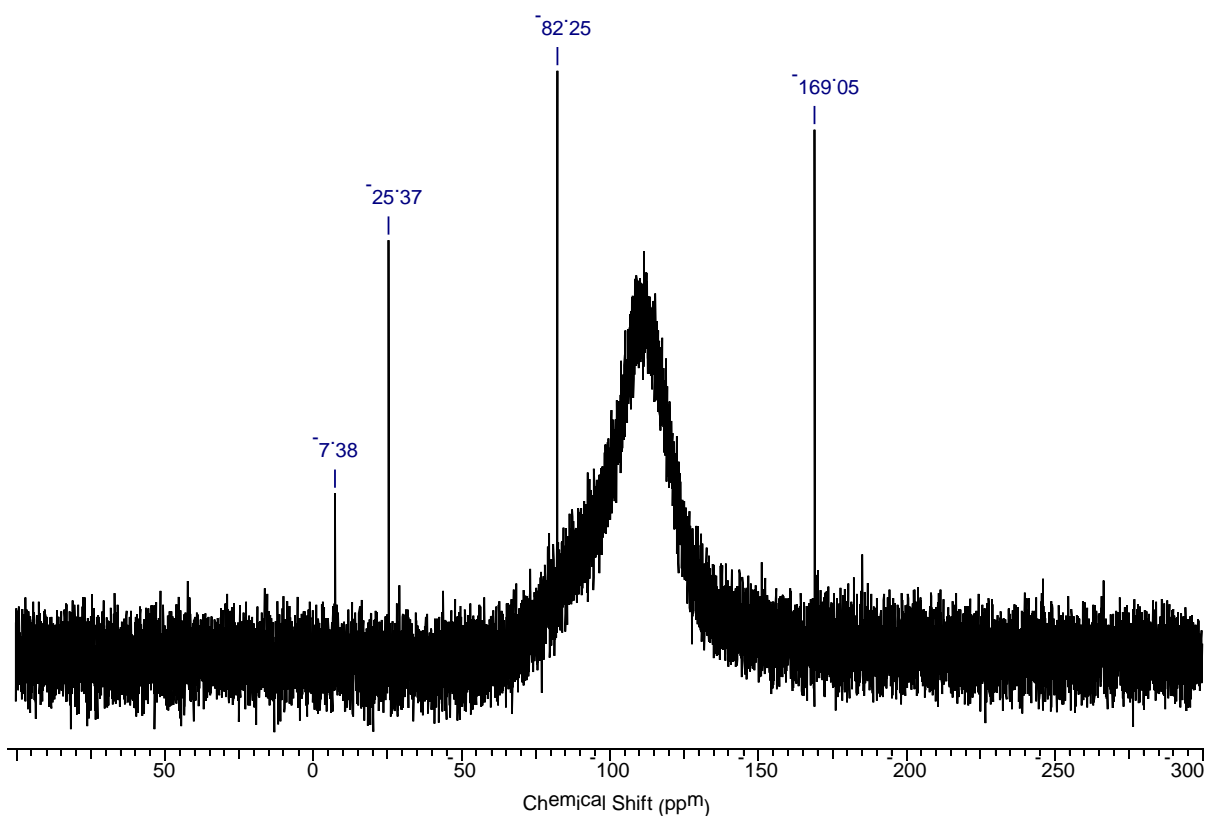


Figure S2. *in situ*  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum in THF- $\text{D}_8$  from the hydrogenation (1 bar of  $\text{H}_2$ ) of  $[\text{K}(\text{Me}_6\text{TREN})\text{SiPh}_3]$  at 25 °C after 7 d.

***in situ*  $^1\text{H}$  and  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectra of the hydrogenation of  $[\text{K}(\text{Me}_6\text{TREN})\text{Si}^i\text{BuPh}_2]$  (5)**

Table S1.  $^1\text{H}$  and  $^{29}\text{Si}\{^1\text{H}\}$  NMR chemical shifts in THF- $\text{D}_8$  at 25 °C of the silyl complexes

Entry	Complex	$\delta_{\text{H}}$ [ppm]					$^1J_{\text{Si-H}}$ [Hz]	$\delta_{\text{Si}}$ [ppm]
		<i>ortho</i> -Ph	<i>meta</i> -Ph	<i>para</i> -Ph	$\text{CH}_3$	<i>Si-H</i>		
<b>1</b>	$[\text{K}(\text{Me}_6\text{TREN})\text{Si}^i\text{BuPh}_2]$	7.37	6.92	6.78	0.95	–	–	8.69
<b>2</b>	$[\text{K}(\text{Me}_6\text{TREN})\text{SiH}^i\text{BuPh}]$	7.36	6.87	6.73	0.97	3.71	89.00	2.01
<b>3</b>	$[\text{K}(\text{Me}_6\text{TREN})\text{SiH}_2^i\text{Bu}]$	–	–	–	1.03	2.82	79.00	–46.09



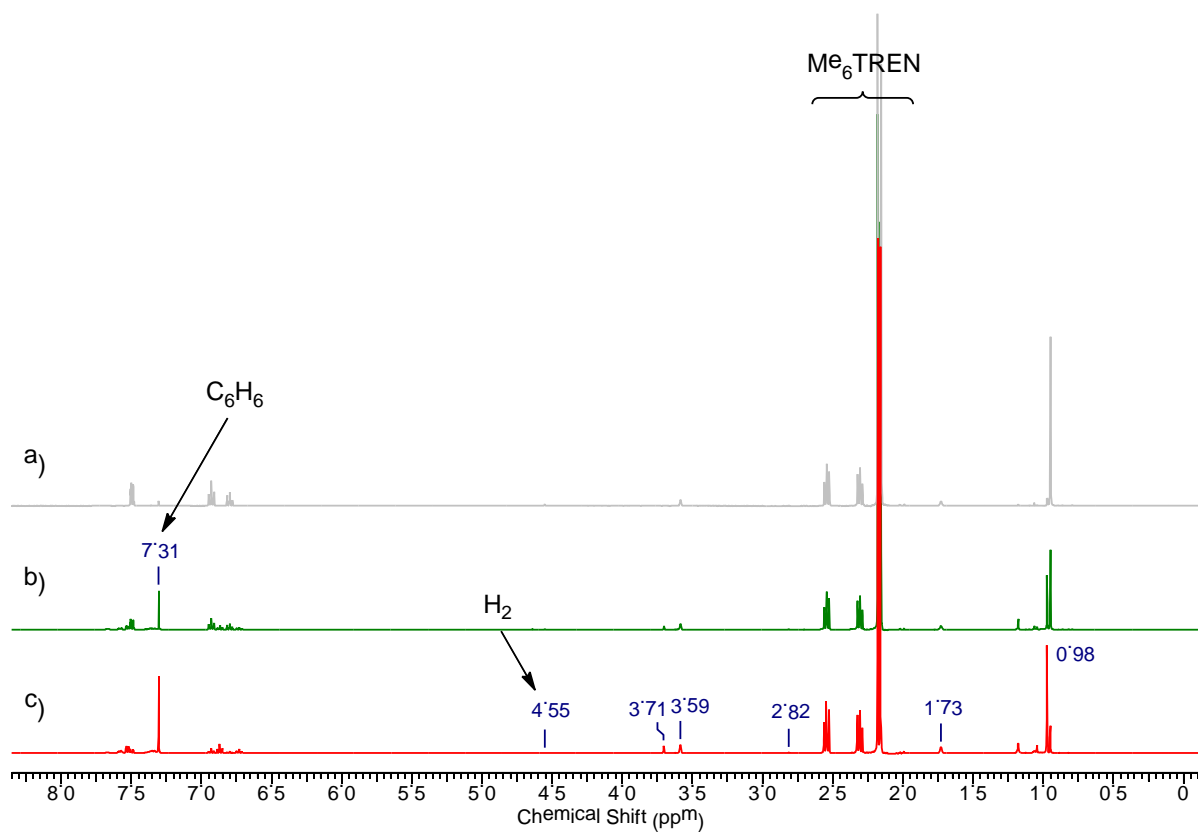


Figure S3. *in situ*  $^1\text{H}$  NMR spectra in  $\text{THF-D}_8$  of the hydrogenation (1 bar of  $\text{H}_2$ ) of  $[\text{K}(\text{Me}_6\text{TREN})\text{Si}'\text{BuPh}_2]$  at  $25\text{ }^\circ\text{C}$  after a) 4 h, b) 28 h and c) 48 h.

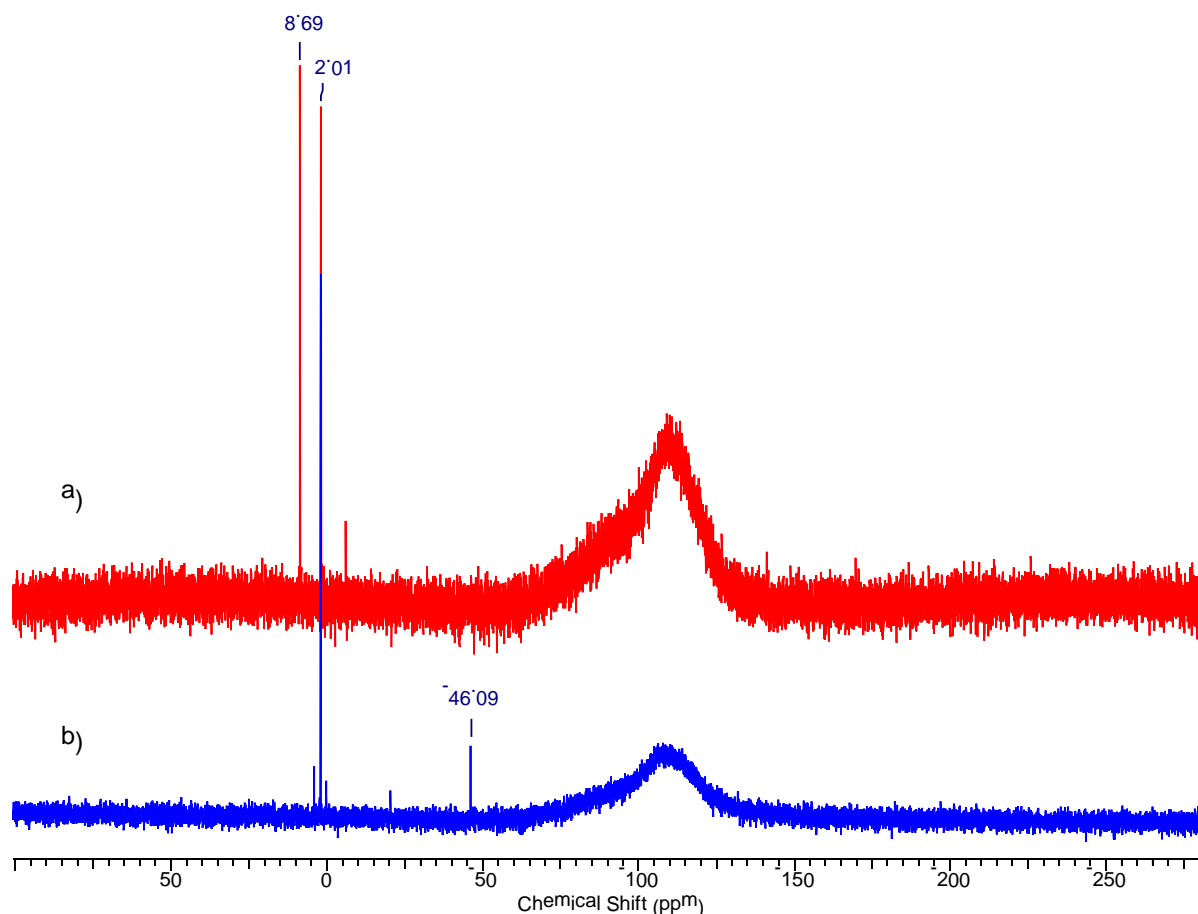


Figure S4. *in situ*  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectra in THF- $\text{D}_8$  of the hydrogenation (1 bar of  $\text{H}_2$ ) of  $[\text{K}(\text{Me}_6\text{TREN})\text{Si}'\text{BuPh}_2]$  at 25 °C after a) 28 h and b) 48 h.

## X-Ray Crystallography

### Crystal structure determination of $[\text{K}(\text{Me}_6\text{TREN})\text{SiPh}_3]$ (**1**)

X-ray diffraction data of **1** were collected at  $-173$  °C on a Bruker D8 goniometer with an APEX CCD area-detector in  $\omega$ -scan mode. Mo- $\text{K}\alpha$  radiation (multilayer optics,  $\lambda = 0.71073$  Å) from an Incoatec microsource was used. The SMART program package was used for the data collection and unit cell determination; processing of the raw frame data was performed using SAINT;<sup>4</sup> absorption corrections were applied with SADABS.<sup>5</sup> The structure of  $\text{C}_{30}\text{H}_{45}\text{KN}_4\text{Si}$  was solved in the orthorhombic space group *Pnma* (no. 62) with  $a = 18.0781(12)$  Å,  $b = 16.5653(11)$  Å,  $c = 10.2552(7)$  Å,  $V = 3071.1(4)$  Å<sup>3</sup>,  $Z = 8/2$ ,  $M = 528.89$  g·mol<sup>-1</sup>,  $\mu = 0.236$  mm<sup>-1</sup> by direct methods using SIR-92<sup>5</sup> using all 4800 independent reflections (of which 3888 were observed with  $I > 2\sigma(I)$ ,  $R_{\text{int}} = 0.0304$ ). The refinement was carried out against  $F^2$  with SHELXL-2013<sup>6</sup> as implemented in the WinGX program system.<sup>8</sup> The solution shows crystallographic mirror symmetry of the molecule with the atoms K1, Si1,

N3, C5, C9, C12, N3 located on special positions ( $x, \frac{1}{4}, z$ ) within a mirror plane. This crystallographically imposed symmetry leads to disorder of the Me<sub>6</sub>TREN ligand that could be resolved well with split positions for the atoms N1, N2, C1, C2, C3, C4, C6, C7 and C8 of equal multiplicity. All hydrogen atoms were included in idealized positions and treated as riding during the refinement leading to  $R1 = 0.0520$ ,  $wR2 = 0.1618$  ( $I > 2s(I)$ ) and  $R1 = 0.0673$ ,  $wR2 = 0.1695$  (all data). The program DIAMOND was used for the graphical representation.<sup>9</sup> CCDC reference number 1411710, these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

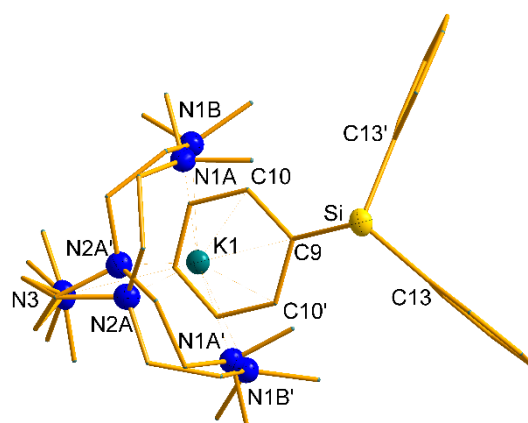


Figure S5. DIAMOND representation of the molecular structure of **1** showing the disorder of the Me<sub>6</sub>TACD ligand (hydrogen atoms are omitted for clarity).

### Powder X-ray diffraction

Powder X-ray diffraction patterns of **4** and **4-D<sub>3</sub>** were collected at room temperature on a Stoe&Cie STADI P diffractometer by means of an image plate employing Cu anode (40 kV, 30 mA) or Cu $\alpha$  ( $\lambda = 1.54059$  Å, equipped with a Johanson Ge monochromator radiation). Due to the air and moisture sensitivity of the compounds, they were sealed in 0.3 mm capillaries (Lindemann glass) in an argon glovebox. All diffractograms were examined using the MAUD software system.<sup>10</sup>

### Powder X-ray diffractogram of $\alpha$ -[KSiH<sub>3</sub>] (4)

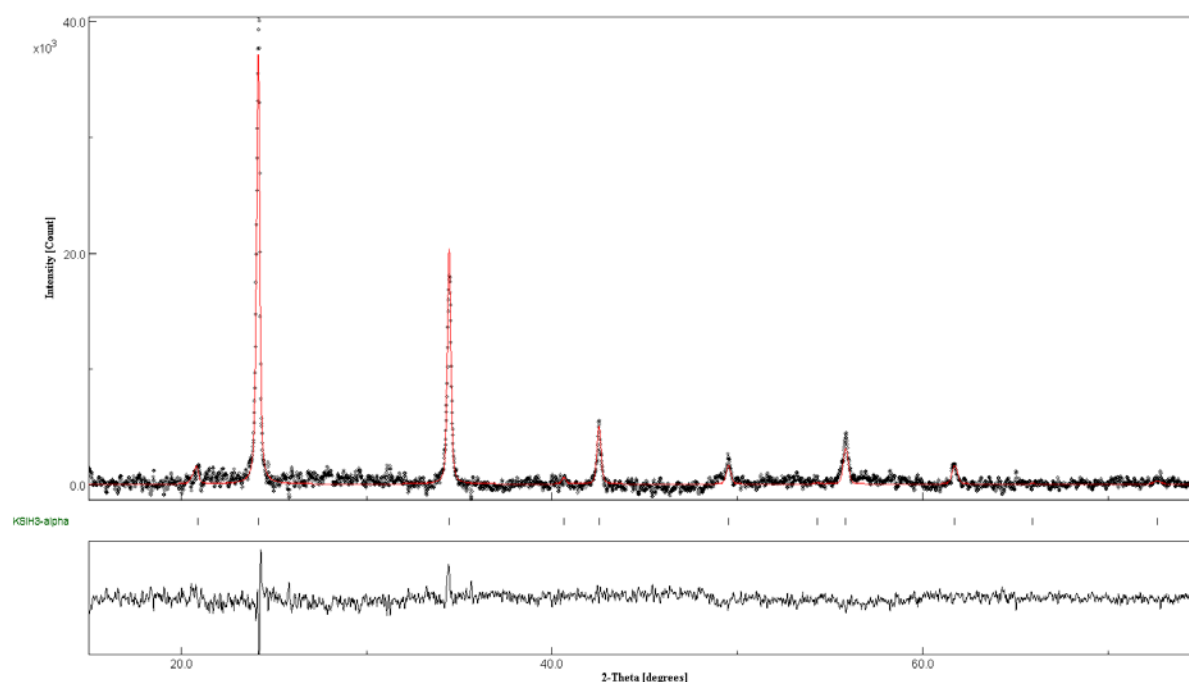


Figure S6. Measured powder X-ray diffraction patterns of  $\alpha$ -[KSiH<sub>3</sub>] (red), Rietveld refinement (black) and difference spectrum (below). Structure parameters:  $Fm\bar{3}m$ ,  $Z = 4$ ,  $a = 7.368(1) \text{ \AA}$ ,  $R_B = 2.7\%$ .

### Powder X-ray diffractogram of $\alpha$ -[KSiD<sub>3</sub>] (4-D<sub>3</sub>)

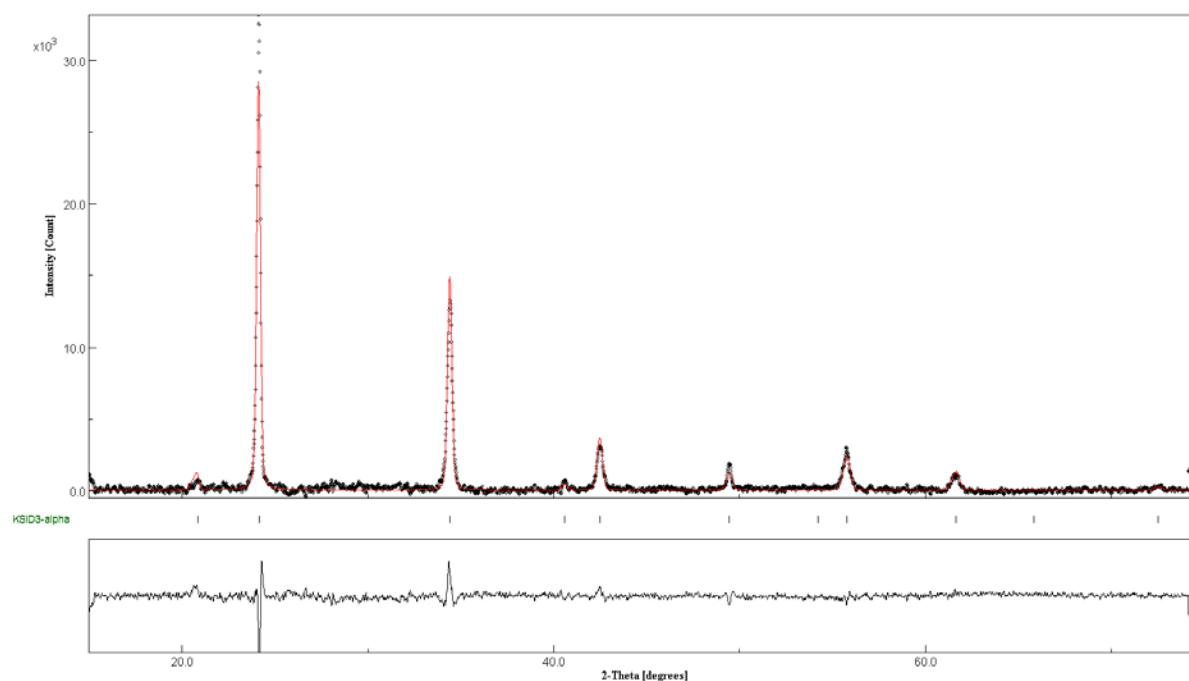


Figure S7. Measured powder X-ray diffraction patterns of  $\alpha$ -[KSiD<sub>3</sub>] (red), Rietveld refinement (black) and difference spectrum (below). Structure parameters:  $Fm\bar{3}m$ ,  $Z = 4$ ,  $a = 7.367(1) \text{ \AA}$ ,  $R_B = 6.7\%$ .



$^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectra of  $t\text{BuPh}_2\text{SiSiMe}_3$

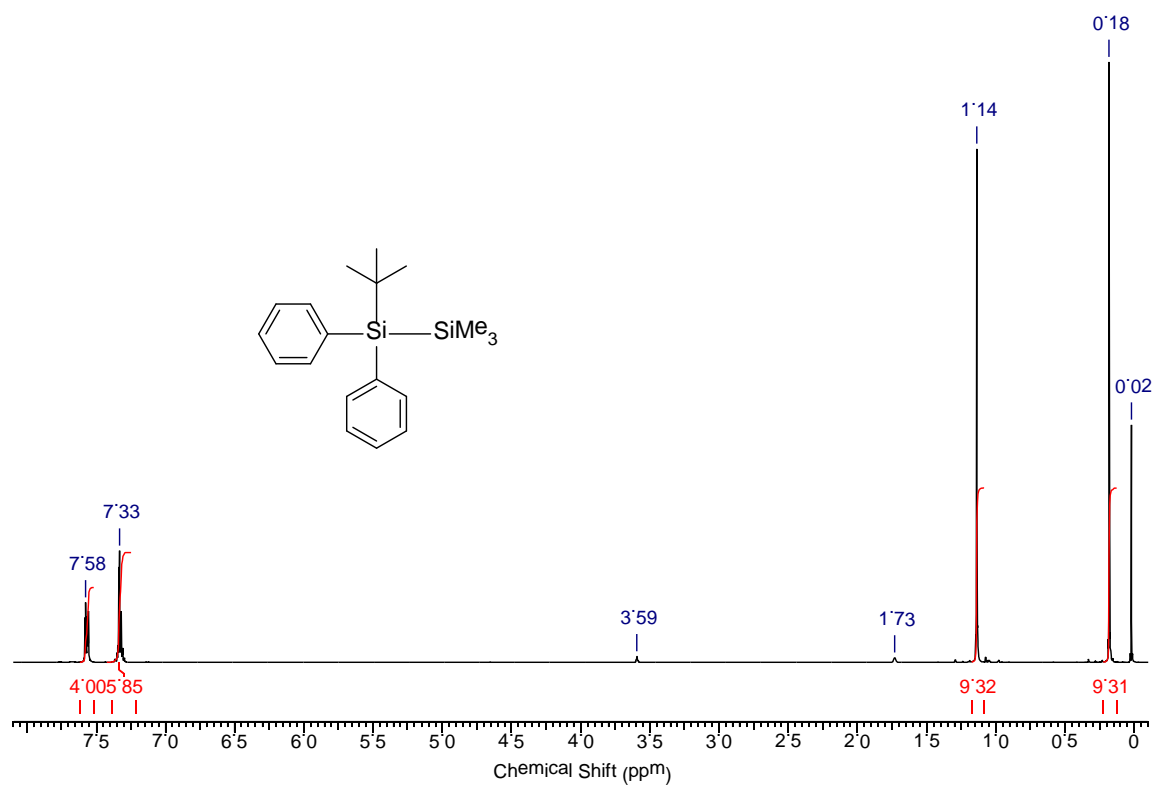


Figure S8.  $^1\text{H}$  NMR spectrum of  $t\text{BuPh}_2\text{SiSiMe}_3$  in  $\text{THF-D}_8$  at  $25\text{ }^\circ\text{C}$ .

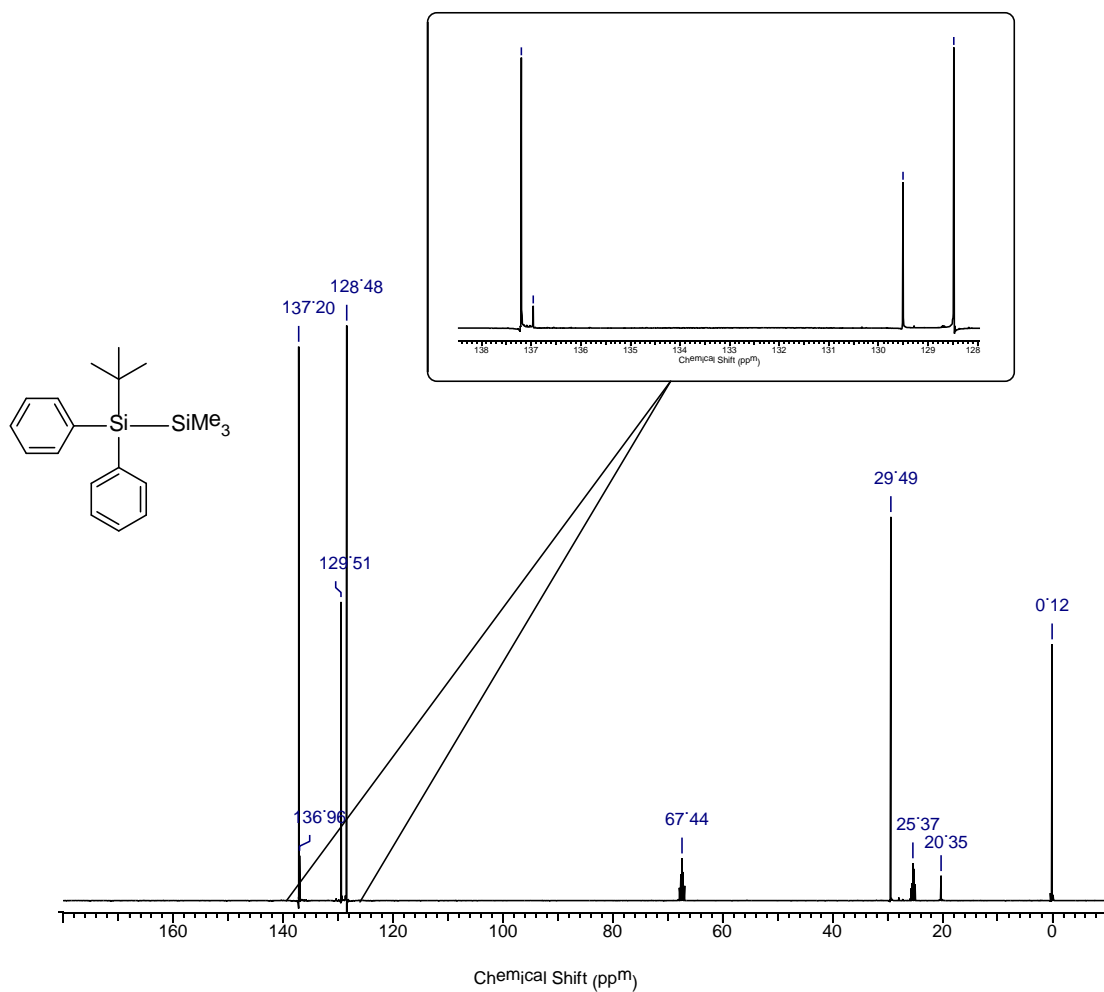


Figure S9.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $t\text{-BuPh}_2\text{SiSiMe}_3$  in THF- $\text{D}_8$  at 25 °C.

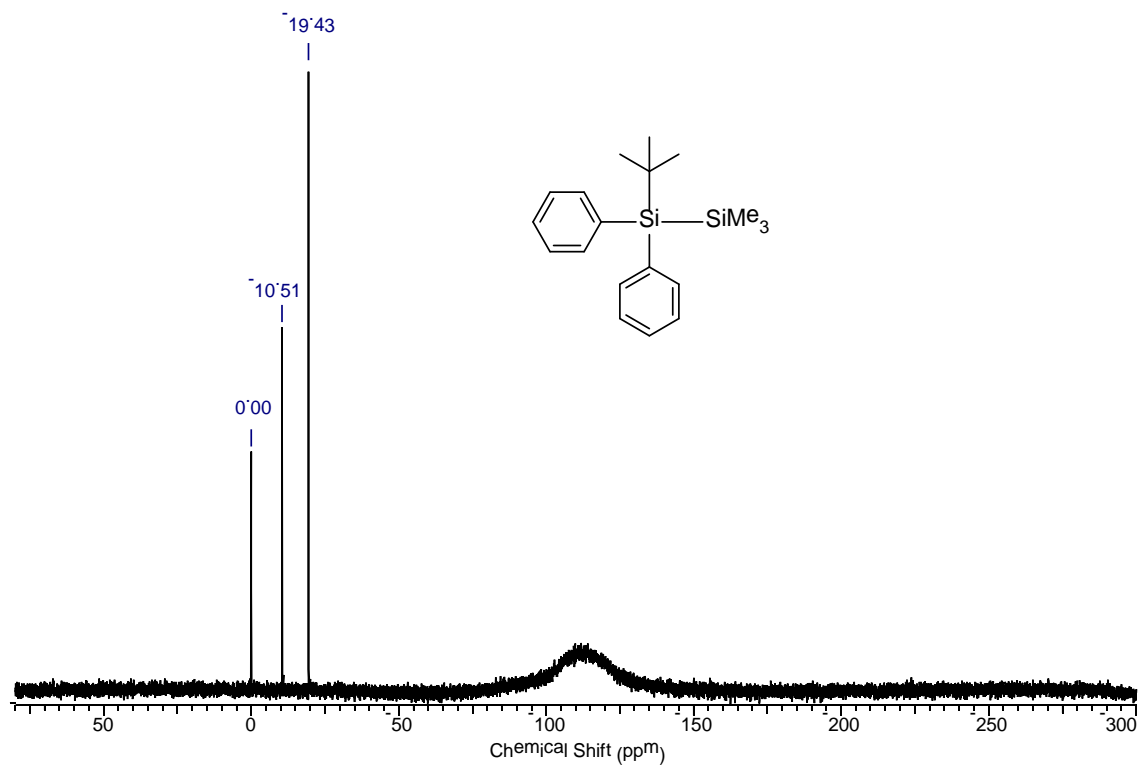


Figure S10.  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of  $t\text{-BuPh}_2\text{SiSiMe}_3$  in THF- $\text{D}_8$  at 25 °C.

$^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectra of  $[\text{K}(\text{Me}_6\text{TREN})\text{SiPh}_3]$  (1)

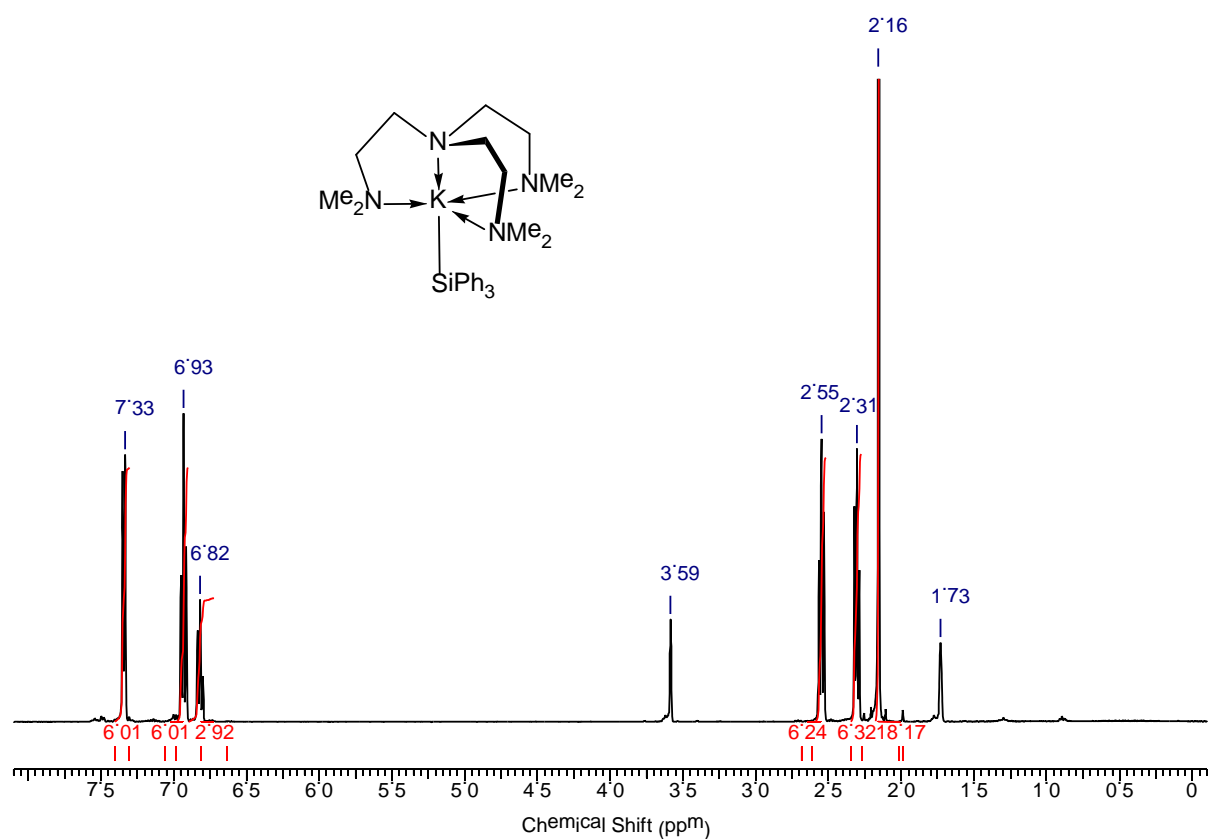


Figure S11.  $^1\text{H}$  NMR spectrum of  $[\text{K}(\text{Me}_6\text{TREN})\text{SiPh}_3]$  in THF-D<sub>8</sub> at 25 °C.

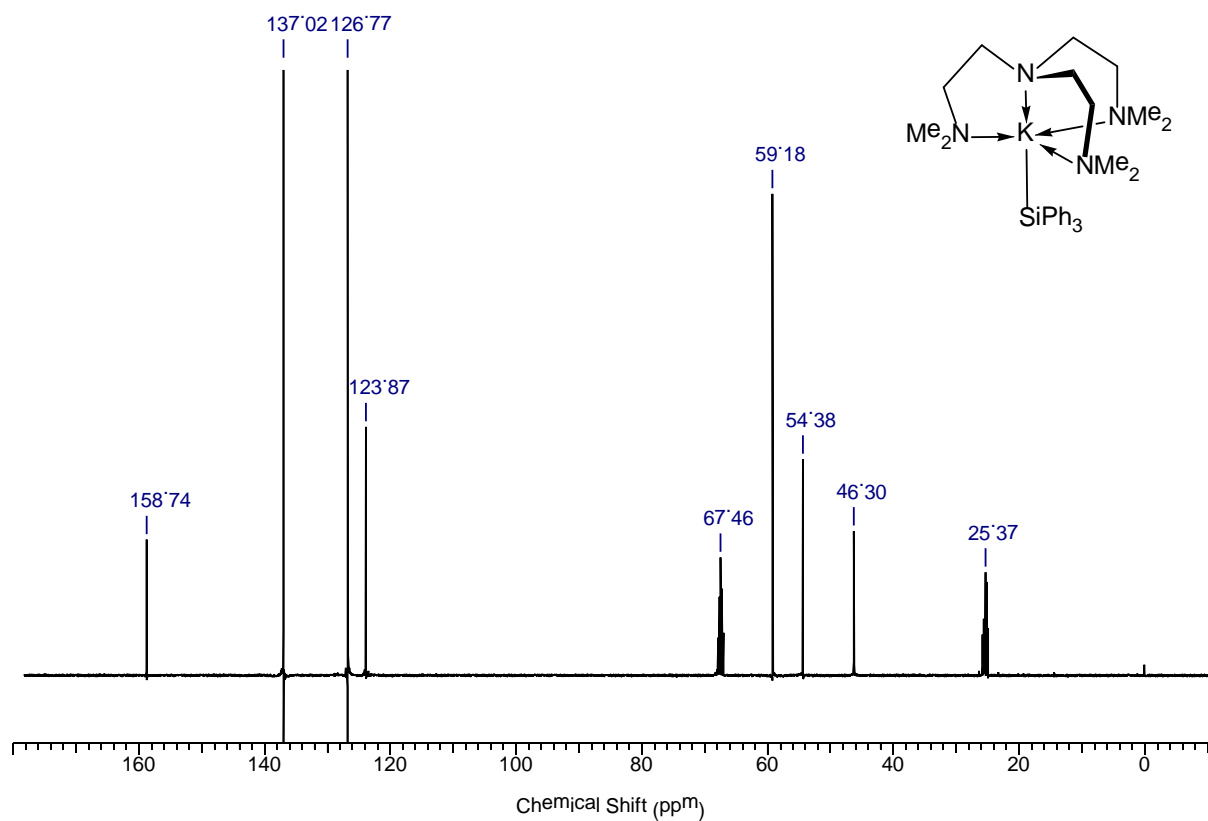


Figure S12.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[\text{K}(\text{Me}_6\text{TREN})\text{SiPh}_3]$  in THF-D<sub>8</sub> at 25 °C.



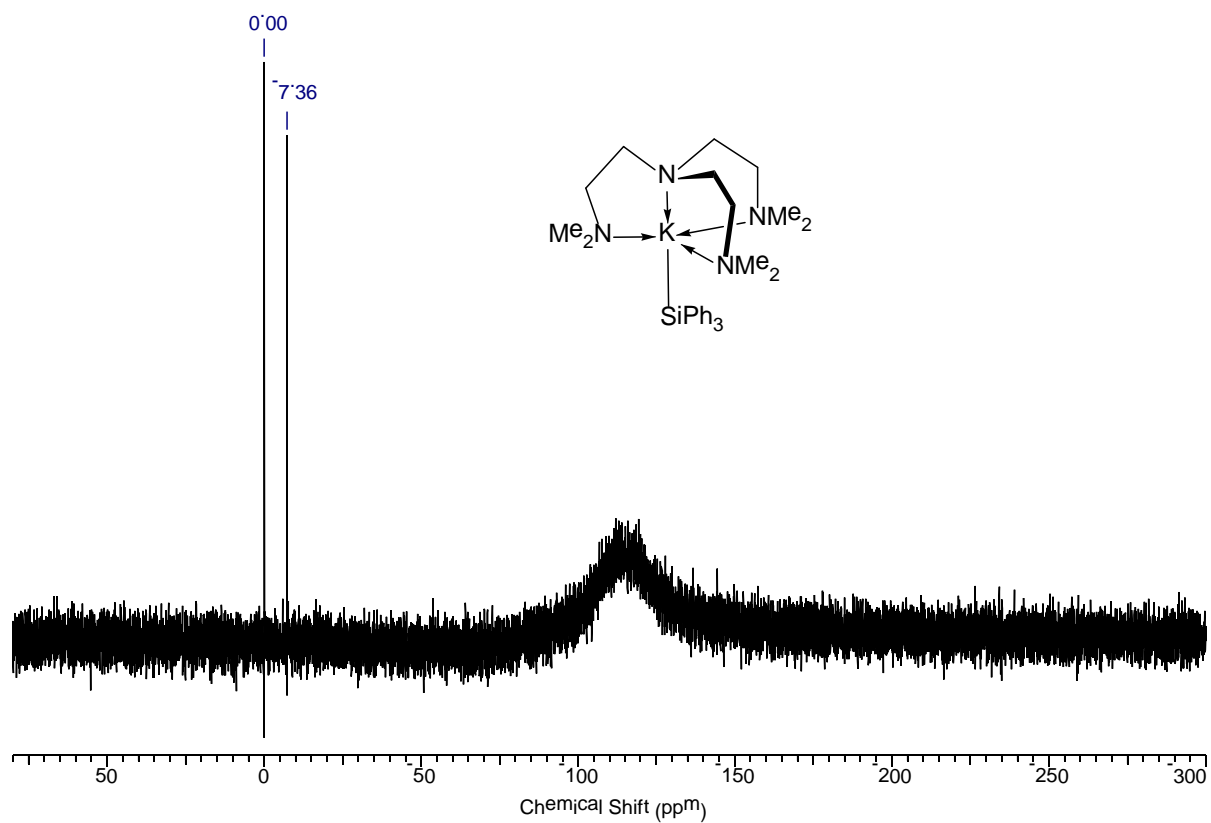


Figure S13.  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of  $[\text{K}(\text{Me}_6\text{TREN})\text{SiPh}_3]$  in  $\text{THF-D}_8$  at  $25\text{ }^\circ\text{C}$ .

## Variable temperature $^1\text{H}$ NMR spectra of $[\text{K}(\text{Me}_6\text{TREN})\text{SiPh}_3]$ (1)

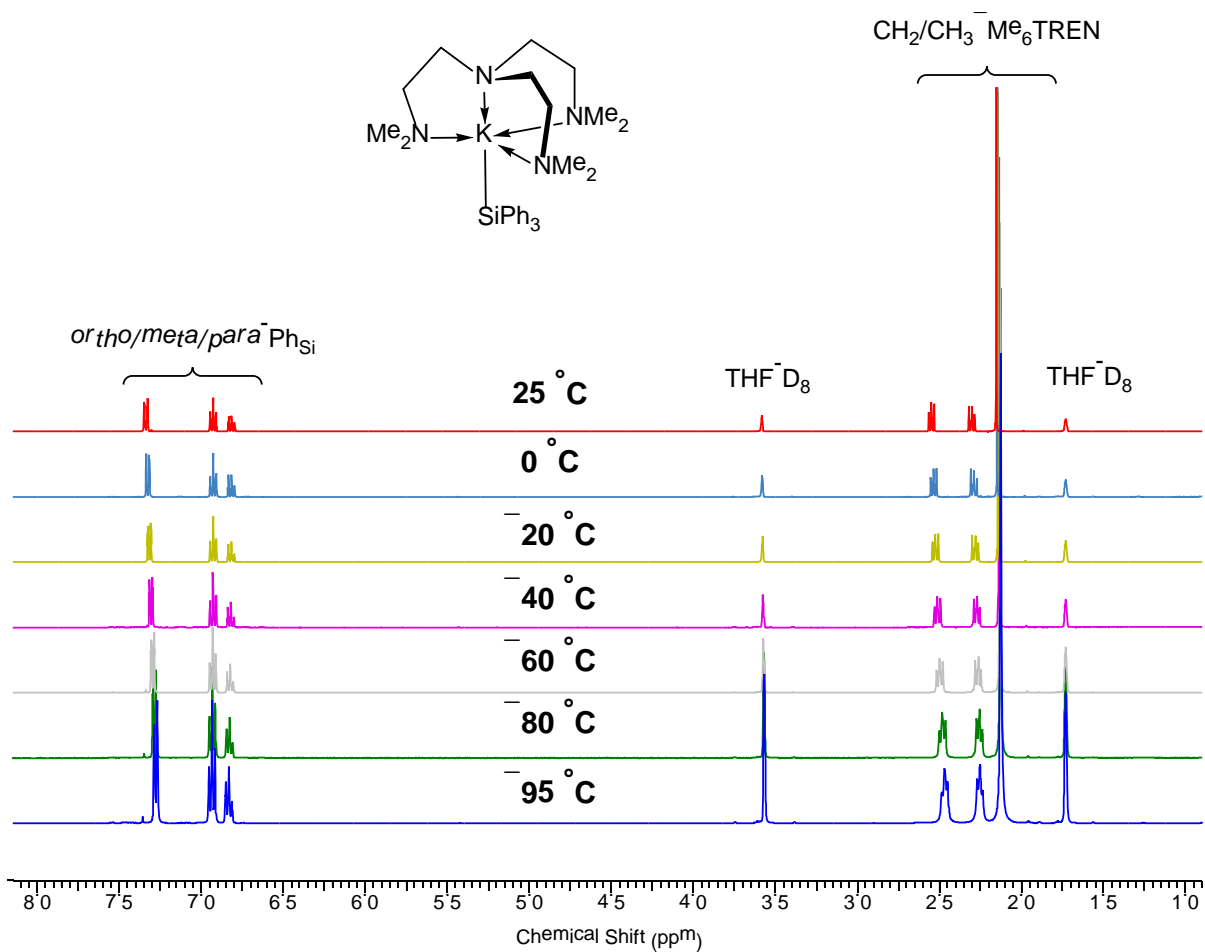


Figure S5. Variable temperature  $^1\text{H}$  NMR spectra of  $[\text{K}(\text{Me}_6\text{TREN})\text{SiPh}_3]$  (25 °C - -95 °C).

$^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectra of  $[\text{K}(\text{Me}_6\text{TREN})\text{Si}^i\text{BuPh}_2]$  (5)

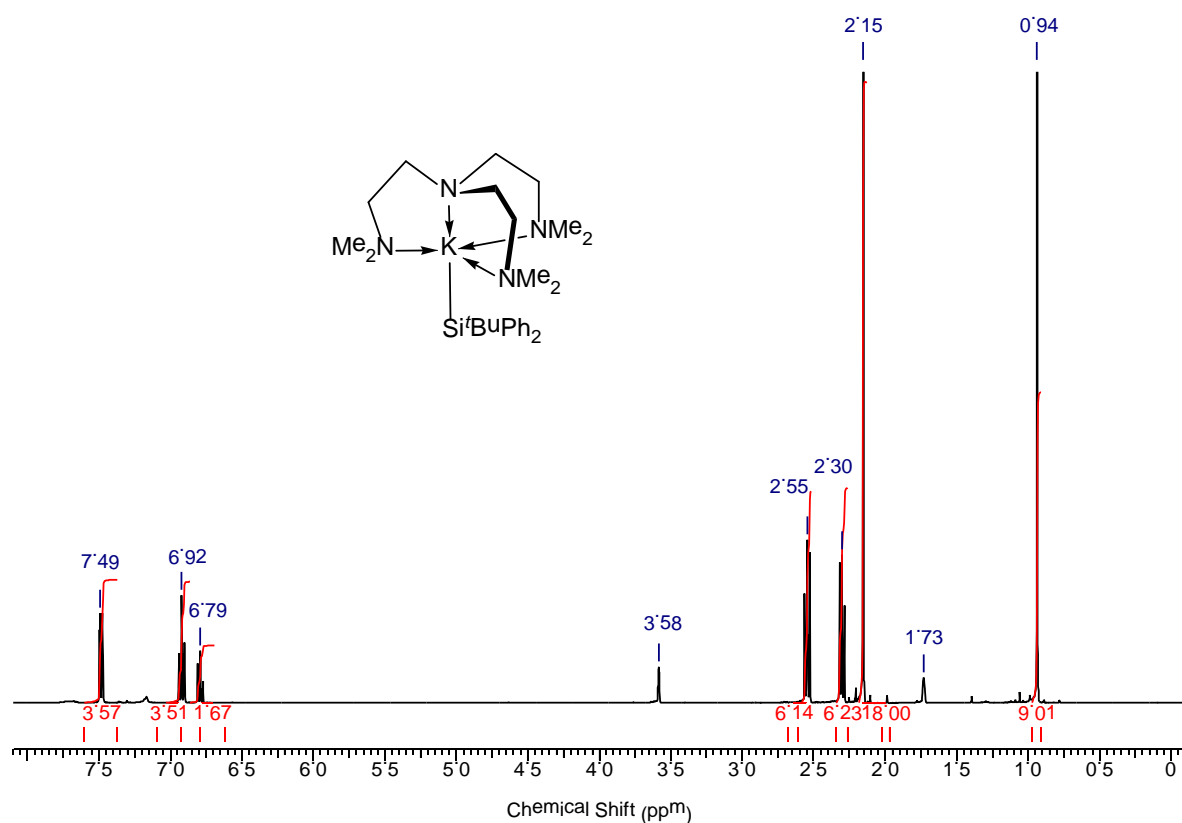


Figure S15.  $^1\text{H}$  NMR spectrum of  $[\text{K}(\text{Me}_6\text{TREN})\text{Si}^i\text{BuPh}_2]$  in  $\text{THF-D}_8$  at  $25\text{ }^\circ\text{C}$ .

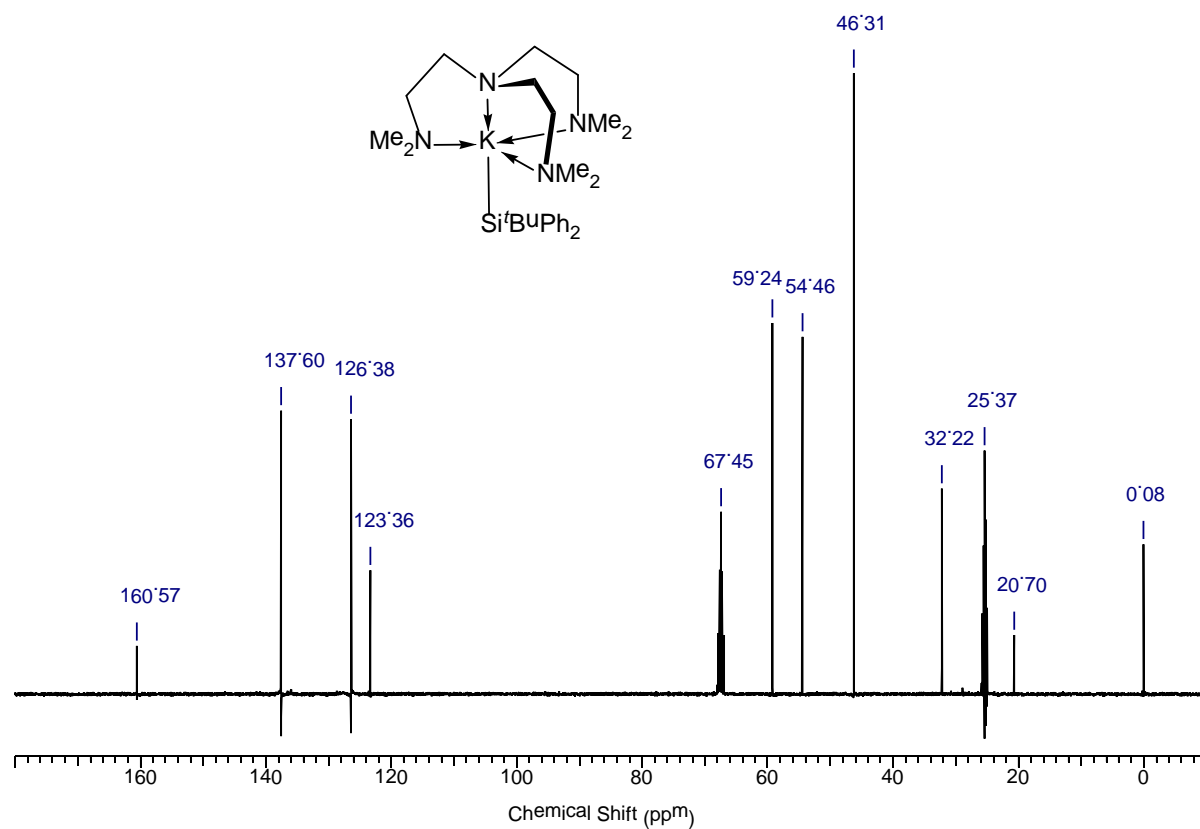


Figure S16.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[\text{K}(\text{Me}_6\text{TREN})\text{Si}^i\text{BuPh}_2]$  in  $\text{THF-D}_8$  at  $25\text{ }^\circ\text{C}$ .

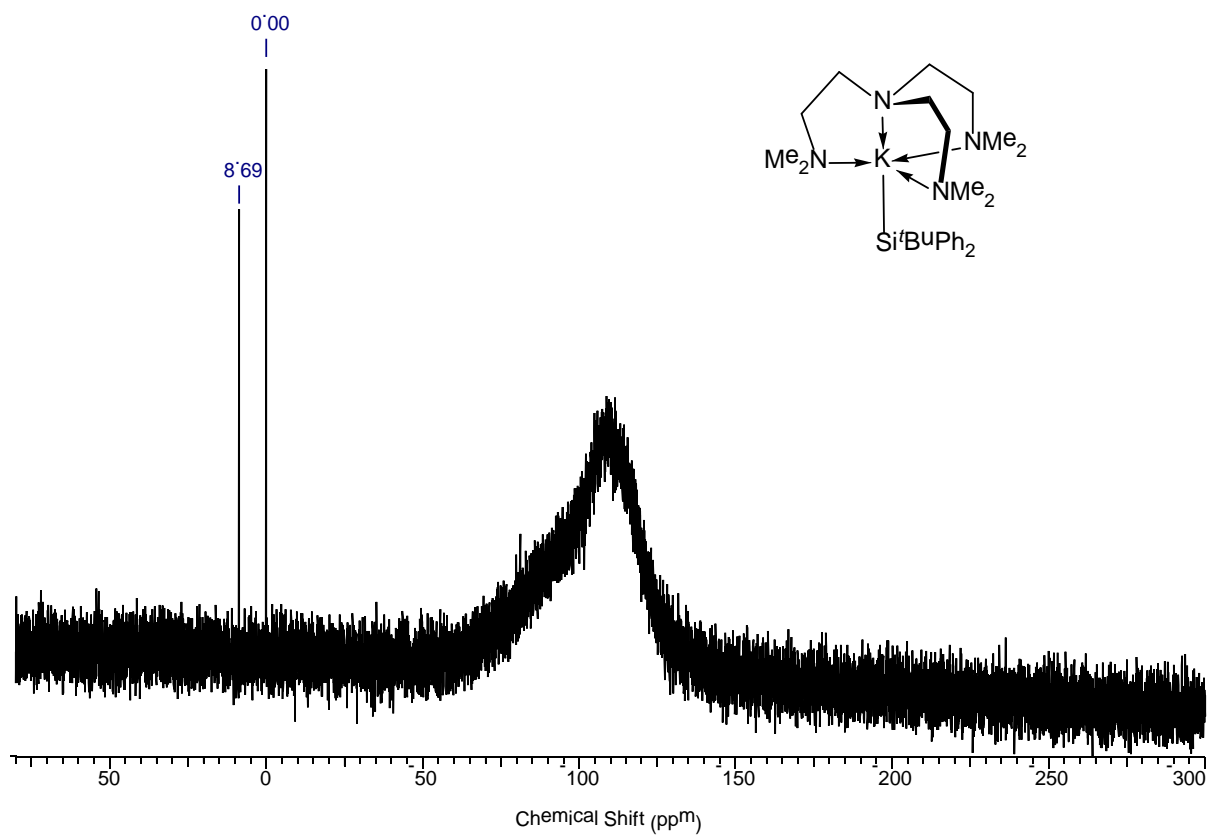


Figure S17.  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of  $[\text{K}(\text{Me}_6\text{TREN})\text{BuPh}_2]$  in  $\text{THF-D}_8$  at  $25\text{ }^\circ\text{C}$ .

**$^1\text{H}$  NMR spectrum of  $[\text{K}(\text{Me}_6\text{TREN})\text{SiMePh}_2]$  (**6**)**

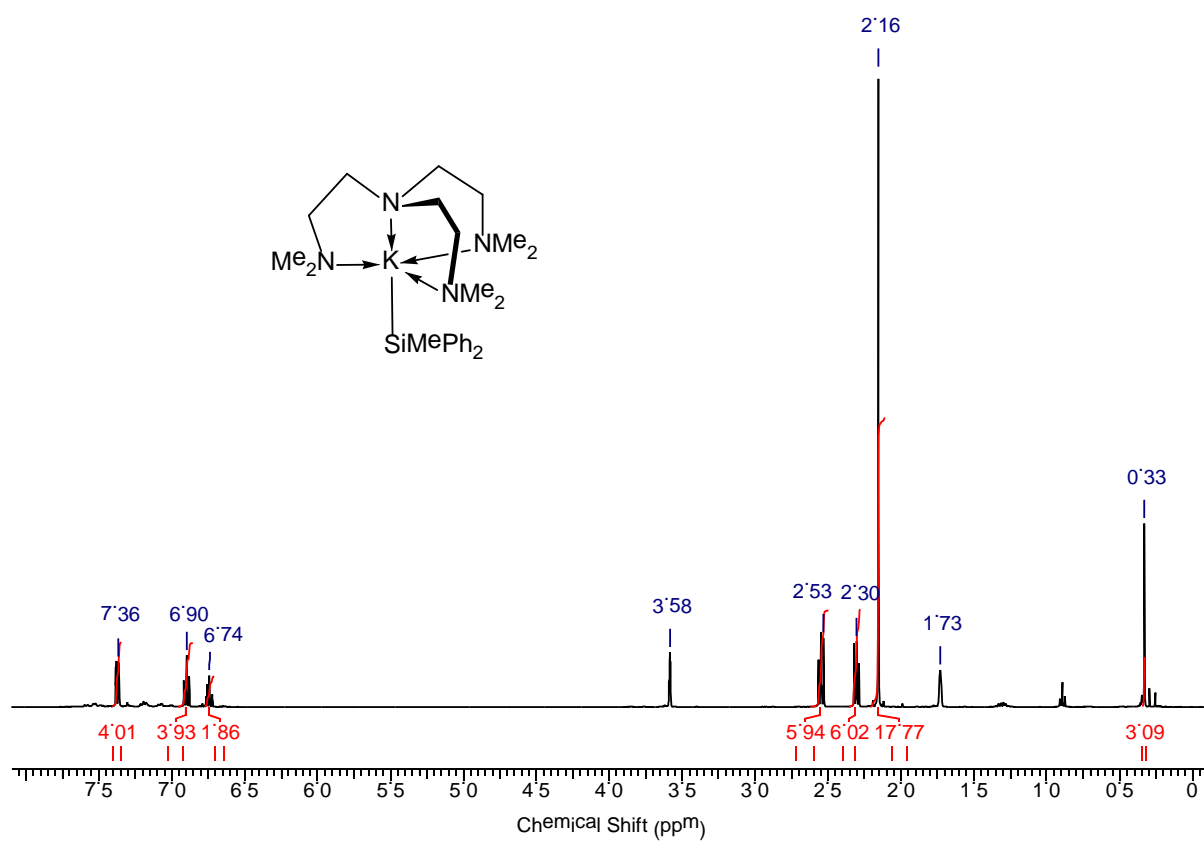


Figure S18.  $^1\text{H}$  NMR spectrum of  $[\text{K}(\text{Me}_6\text{TREN})\text{SiMePh}_2]$  in  $\text{THF-D}_8$  at  $25\text{ }^\circ\text{C}$ .

**$^1\text{H}$  and  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectra  $\alpha$ -[KSiH<sub>3</sub>] (4)**

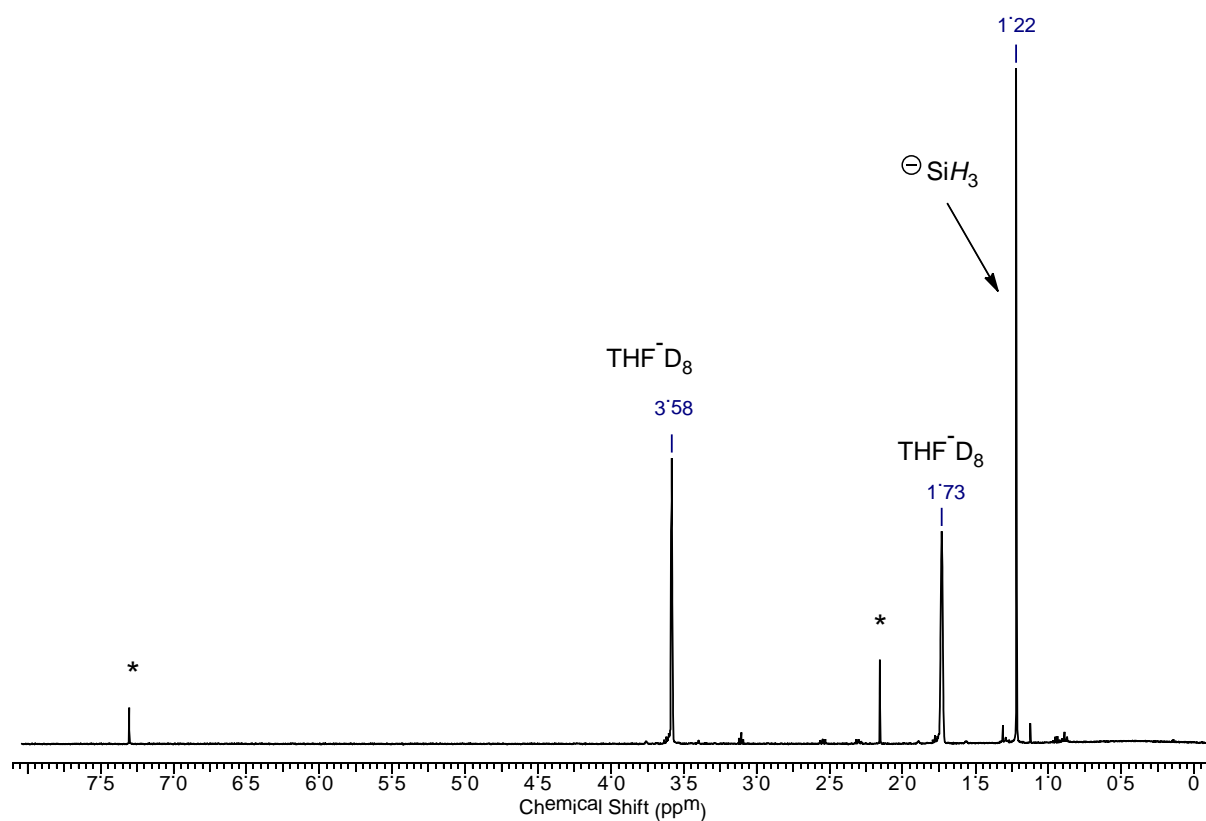


Figure S19.  $^1\text{H}$  NMR spectrum of  $\alpha$ -[KSiH<sub>3</sub>] in THF-D<sub>8</sub> at 25 °C. Traces of Me<sub>6</sub>TREN and benzene as impurity (\*).

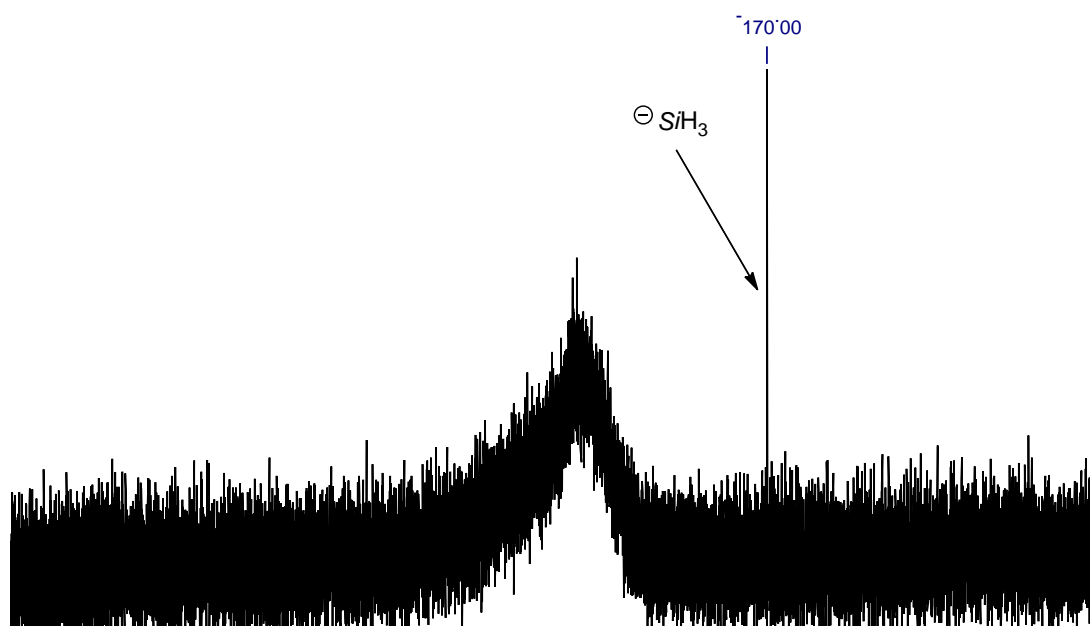


Figure S20.  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of  $\alpha$ -[KSiH<sub>3</sub>] in THF-D<sub>8</sub> at 25 °C.

### IR spectrum of $\alpha$ -[KSiH<sub>3</sub>] (4)

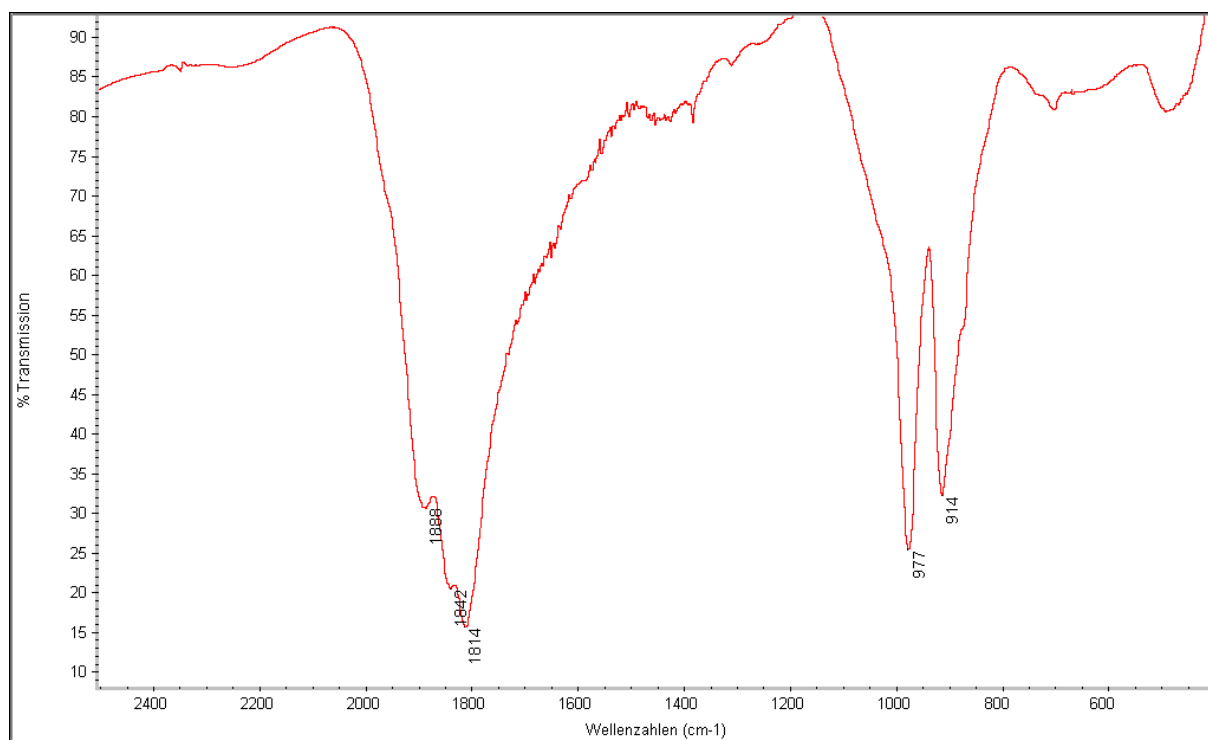


Figure S21. IR spectrum of  $\alpha$ -[KSiH<sub>3</sub>].

### IR spectrum of $\alpha$ -[KSiD<sub>3</sub>] (4-D<sub>3</sub>)

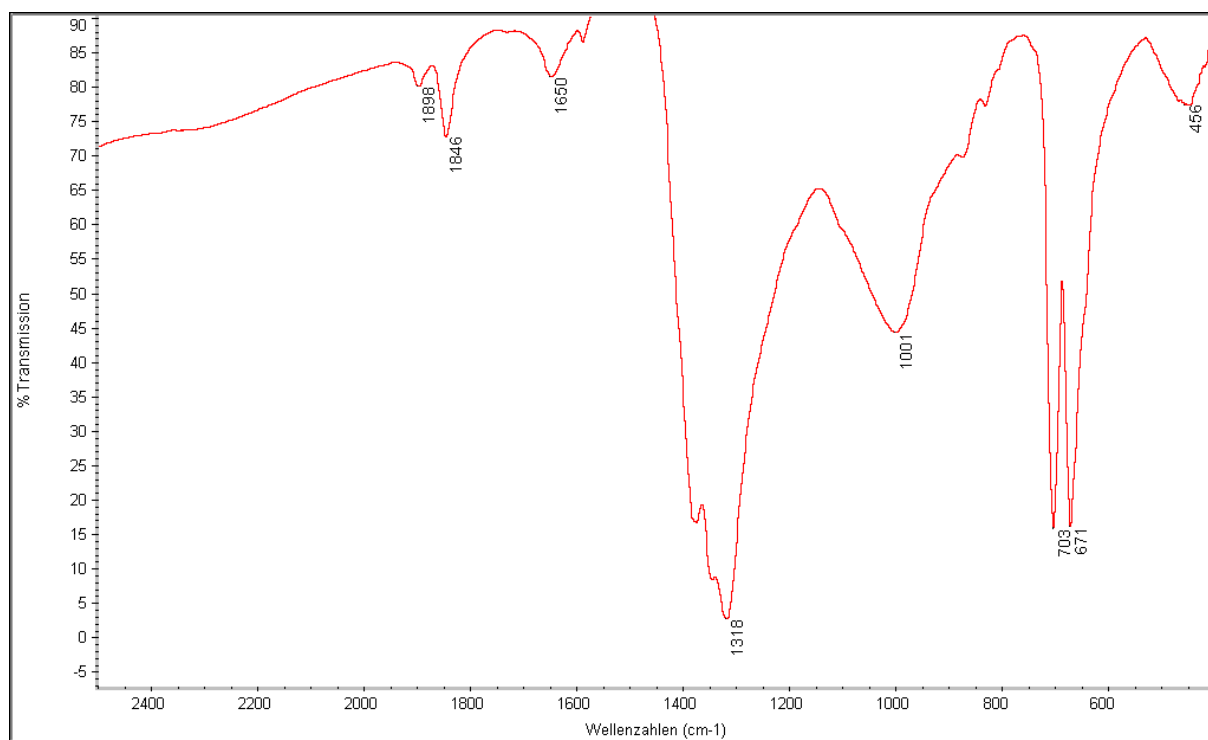
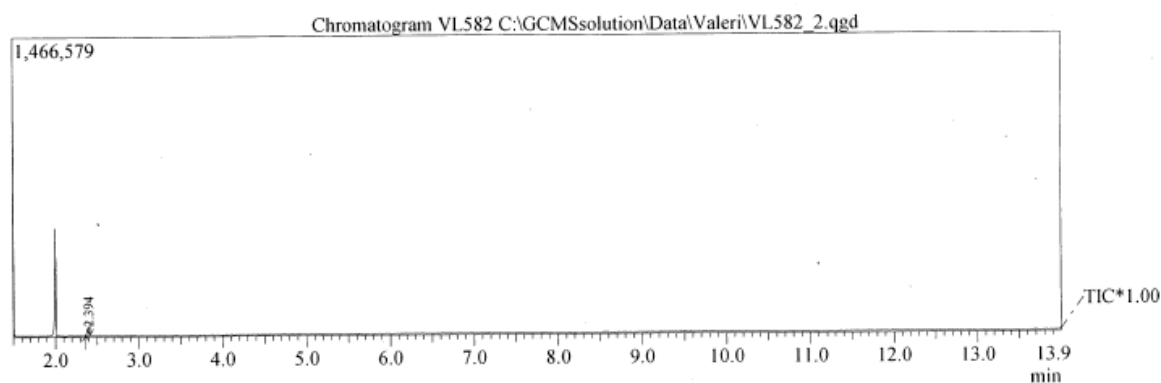


Figure S22. IR spectrum of  $\alpha$ -[KSiD<sub>3</sub>].

## GC/MS spectra of C<sub>6</sub>H<sub>6</sub> and C<sub>6</sub>H<sub>5</sub>D from reaction solution

Sample Information

Analyzed by : Admin  
 Analyzed : 22.04.2015 17:36:22  
 Sample Type : Unknown  
 Level # : 1  
 Sample Name : VL582  
 Sample ID : VL582  
 IS Amount : [1]-1  
 Sample Amount : 1  
 Dilution Factor : 1  
 Vial # : 5  
 Injection Volume : 1  
 Data File : C:\GCMSsolution\Data\Valeri\VL582\_2.qgd  
 Org Data File : C:\GCMSsolution\Data\Valeri\VL582\_2.qgd  
 Method File : C:\GCMSsolution\Data\Valeri\Valeri\_thf benzene hiflow sp40 33.qgm  
 Org Method File : C:\GCMSsolution\Data\Valeri\Valeri\_thf benzene hiflow sp40 33.qgm  
 Report File :  
 Tuning File : C:\GCMSsolution\System\Tune1\080912.qgt  
 Modified by : Admin  
 Modified : 22.04.2015 17:50:22



Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	2.394	2.363	2.413	59853	100.00	41059	100.00	1.46	MI	

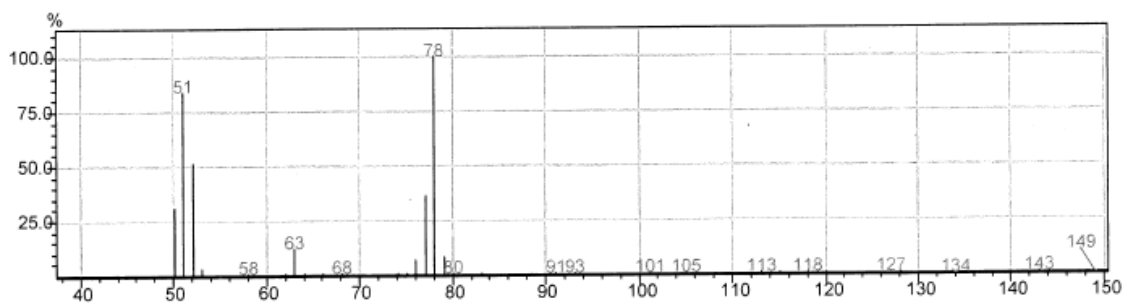
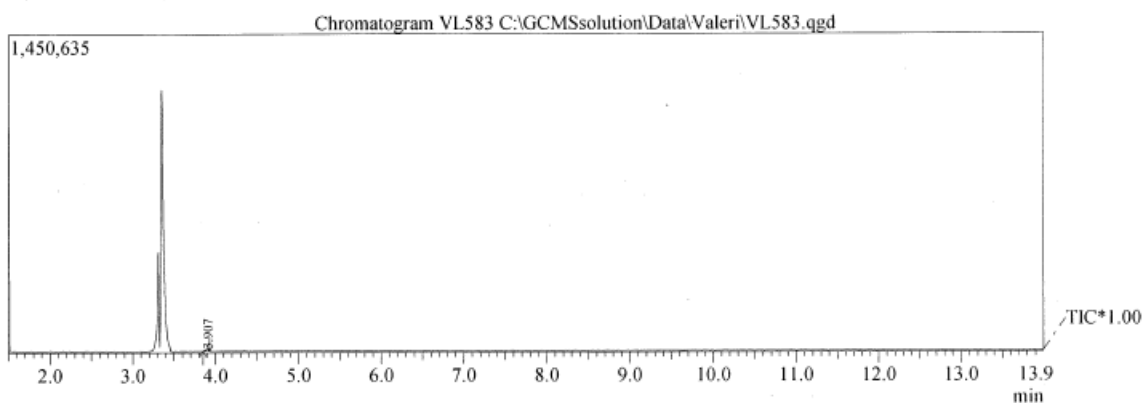


Figure S23. GC/MS spectrum of C<sub>6</sub>H<sub>6</sub> from hydrogenation reaction.



Sample Information

Analyzed by : Admin  
 Analyzed : 24.04.2015 09:22:19  
 Sample Type : Unknown  
 Level # : 1  
 Sample Name : VL583  
 Sample ID : VL583  
 IS Amount : [1]=1  
 Sample Amount : 1  
 Dilution Factor : 1  
 Vial # : 1  
 Injection Volume : 1  
 Data File : C:\GCMSsolution\Data\Valeri\VL583.qgd  
 Org Data File : C:\GCMSsolution\Data\Valeri\VL583.qgd  
 Method File : C:\GCMSsolution\Data\Valeri\Valeri\_thf benzene lowflow sp40 34.qgm  
 Org Method File : C:\GCMSsolution\Data\Valeri\Valeri\_thf benzene lowflow sp40 34.qgm  
 Report File :  
 Tuning File : C:\GCMSsolution\System1\Tune1\080912.qgt  
 Modified by : Admin  
 Modified : 24.04.2015 09:36:19



Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	3.907	3.850	3.929	21476	100.00	9543	100.00	2.25	MI	

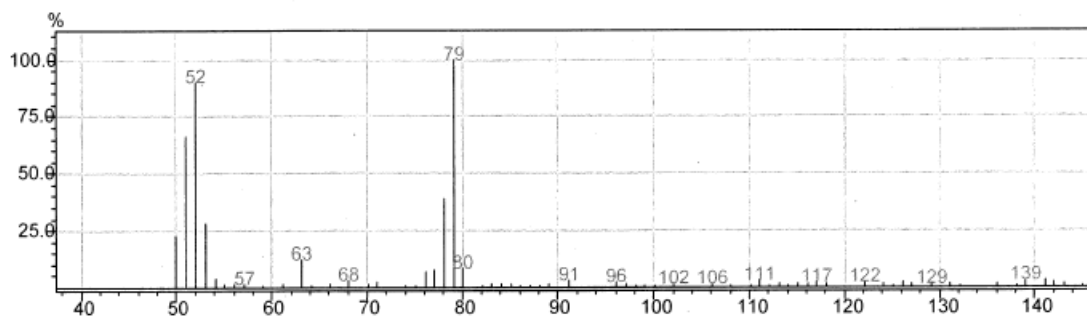


Figure S24. GC/MS spectrum of C<sub>6</sub>H<sub>5</sub>D from hydrogenation reaction.

## References

1. H. Gilman, D. J. Peterson and D. Wittenberg, *Chem. Ind.*, 1958, 1479-1480.
2. A. Fuerstner and H. Weidmann, *J. Organomet. Chem.*, 1988, **354**, 15-21.
3. M. Ciampolini and N. Nardi, *Inorg. Chem.*, 1966, **5**, 41-44.
4. V. F. Kranak, Y.-C. Lin, M. Karlsson, J. Mink, S. T. Norberg and U. Häussermann, *Inorg. Chem.*, 2015, **54**, 2300-2309.
5. A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1993, **26**, 343-350.
6. (a) G. M. Sheldrick, *TWINABS*, University of Göttingen: Göttingen, Germany, 2006; (b) G. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112-122.