

Electronic Supplementary Information for: Homoleptic organolanthanide compounds supported by the bis(dimethylsilyl)benzyl ligand

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General. All manipulations were performed under a dry argon atmosphere using standard Schlenk techniques or under a nitrogen atmosphere in a glovebox unless otherwise indicated. Water and oxygen were removed from benzene, pentane, and THF solvents using an IT PureSolv system. Benzene-*d*₆ and toluene-*d*₈, were heated to reflux over Na/K alloy and chloroform-*d* was heated to reflux over CaH₂, and vacuum-transferred. LaI₃(THF)₄,^{1, 2} CeI₃(THF)₄,² PrI₃(THF)₃,³ and NdI₃(THF)₃^{1, 2} were prepared by reaction of Ln with Cl₂H₂ (La, Ce, Nd) and 1,2-C₂I₂H₄ according to the literature. α,α,α -Trichlorotoluene, α,α -dibromotoluene, and magnesium chips were purchased from Sigma-Aldrich, Alfa Aesar, and Strem Chemicals, respectively, and used as received. Dimethylchlorosilane was purchased from Gelest and distilled, and potassium tert-butoxide was purchased from Sigma-Aldrich and sublimed before use. Potassium benzyl was prepared according to the literature.⁴ ¹H, ¹³C{¹H}, and ²⁹Si{¹H} HMBC NMR spectra were collected on a Bruker DRX-400 spectrometer or a Bruker Avance III-600 spectrometer. Infrared spectra were measured on a Bruker Vertex 80, using KBr pellet (transmission mode) or Pike Miracle ATR (solution measurements). Elemental analyses were performed using a Perkin-Elmer 2400 Series II CHN/S. X-ray diffraction data was collected on a Bruker APEX II diffractometer.

HC(SiHMe₂)₂Ph (1). An oven-dried three-neck flask equipped with an addition funnel and a condenser was allowed to cool under vacuum. Mg turnings (6.00 g, 0.247 mol) were added to the flask under an Ar purge, and then THF (96 mL) was added. Me₂HSiCl (27.3 mL, 0.246 mol) was added to the flask through the addition funnel, which was subsequently rinsed with THF (36 mL). A THF solution of PhCHBr₂ (20.4 mL, 0.123 mol) was added in a dropwise fashion to initiate the reaction. Once the addition was complete, the reaction mixture was heated at reflux

for 2.5 h. The solution was filtered in air to remove salt byproducts, the filtrate was washed with water (3×200 mL), and the salt residue was further extracted with pentane. The filtrate and pentane extracts were combined and dried over MgSO_4 . The filtrate was concentrated under vacuum, and the resulting yellow liquid was distilled at 50 °C (3 mmHg) to yield $\text{HC}(\text{SiHMe}_2)_2\text{Ph}$ as a colorless product (18.2 g, 0.0874 mol, 70.9%) which contained only one peak in the chromatogram of a GC-MS with a m/z of 208.1 . ^1H NMR (benzene- d_6 , 600 MHz, 25 °C): δ 7.12 (t, 2 H, $^3J_{\text{HH}} = 7.7$ Hz, $m\text{-C}_6\text{H}_5$), 6.96 (d, 2 H, $o\text{-C}_6\text{H}_5$ and t, 1 H, $p\text{-C}_6\text{H}_5$ overlapped), 4.34 (v octet, 2 H, $^1J_{\text{SiH}} = 186$ Hz, SiHMe_2), 1.43 (t, 1 H, $^3J_{\text{HH}} = 4.0$ Hz, $\text{HC}(\text{SiHMe}_2)_2\text{Ph}$), 0.085 (d, 6 H, $^3J_{\text{HH}} = 3.7$ Hz, SiHMe_2), 0.035 (d, 6 H, $^3J_{\text{HH}} = 3.7$ Hz, SiHMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6 , 150 MHz, 25 °C): δ 142.42 (*ipso*- C_6H_5), 129.21 ($m\text{-C}_6\text{H}_5$), 129.15 ($p\text{-C}_6\text{H}_5$), 124.58 ($o\text{-C}_6\text{H}_5$), 24.68 ($\text{C}(\text{SiHMe}_2)_2$), -3.10 (SiHMe_2), -3.62 (SiHMe_2). $^{29}\text{Si}\{^1\text{H}\}$ NMR (benzene- d_6 , 119.3 MHz, 25 °C): δ -12.9 . IR (KBr, cm^{-1}): 3078 m, 3022 m, 2959 s, 2901 m, 2847 w, 2115 s (SiH), 1702 w, 1597 s, 1450 s, 1419 m, 1252 s, 1206 s, 1070 m, 1032 s, 896 s br, 836 s, 785 m, 699 s, 645 m, 537 m.

(TMEDA)K(C(SiHMe₂)₂Ph. THF solutions of $\text{HC}(\text{SiHMe}_2)_2\text{Ph}$ (1.32 g, 6.32 mmol, 5 mL) and KBn (0.823 g, 6.32 mmol, 15 mL) were cooled to -78 °C. The KBn solution was added to the cold, vigorously stirred $\text{HC}(\text{SiHMe}_2)_2\text{Ph}$ solution in a dropwise fashion to give a dark green solution. The reaction mixture was slowly warmed to room temperature and then was stirred for 17 h. The solvent was removed under vacuum, and the residue was washed with pentane (5×3 mL) and dried under vacuum overnight to yield $\text{K}(\text{SiHMe}_2)_2\text{Ph}$ as a dark brown oily THF adduct. TMEDA (2.3 mL, 15.3 mmol) was added, and the mixture was stirred in benzene (8 mL) for 2 h at room temperature. The solvent was evaporated under reduced pressure, and the residue was extracted with pentane (6×5 mL). The extracts were combined, concentrated in vacuo, and cooled at -30 °C to yield X-ray quality crystals (0.189 g, 0.521 mmol, 8.60%). ^1H NMR (benzene- d_6 , 400 MHz, 25 °C): δ 6.92 (t, 2 H, $^3J_{\text{HH}} = 7.7$ Hz, $m\text{-C}_6\text{H}_5$), 6.85 (d, 2 H, $^3J_{\text{HH}} = 7.4$ Hz, $o\text{-C}_6\text{H}_5$), 6.25 (t, 1 H, $^3J_{\text{HH}} = 6.9$ Hz, $p\text{-C}_6\text{H}_5$), 4.78 (m, 2 H, $^3J_{\text{HH}} = 3.6$ Hz, $^1J_{\text{SiH}} = 162$ Hz, SiHMe_2), 1.96 (s, 4 H, NCH_2), 1.88 (s, 12 H NMe), 0.56 (d, 12 H, $^3J_{\text{HH}} = 3.6$ Hz, SiHMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6 , 150 MHz, 25 °C): δ 158.58 (*ipso*- C_6H_5), 130.16 ($m\text{-C}_6\text{H}_5$), 121.19 ($o\text{-C}_6\text{H}_5$), 109.31 ($p\text{-C}_6\text{H}_5$), 57.82 (NCH_2), 45.95 ($\text{C}(\text{SiHMe}_2)_2$), 45.40 (NMe), 1.54 (SiHMe_2). $^{29}\text{Si}\{^1\text{H}\}$ NMR (benzene- d_6 , 119.3 MHz, 25 °C): δ -27.30 . $^{15}\text{N}\{^1\text{H}\}$ NMR (benzene- d_6 , 61 MHz,

25 °C): δ -361.9. IR (KBr, cm^{-1}): 3055 m, 2948 s, 2890 m, 2115 m (SiH), 1995 s (SiH), 1579 s, 1470 s, 1262 s br, 1187 m, 1150 m, 1080 m, 1026 m, 894 s br, 826 s, 756 s, 700 s, 632 m, 527 m. Anal. Calcd for $\text{C}_{17}\text{H}_{35}\text{KN}_2\text{Si}_2$: C, 56.29; H, 9.73; N, 7.72. Found: C, 56.18; H, 9.87; N, 7.26. mp 54 - 56 °C.

PhC(SiHMe₂)₃. This compound was previously synthesized from α,α,α -tribromotoluene, and its NMR spectra were previously reported in chloroform-*d*₁.⁵ We synthesized the compound starting from α,α,α -trichlorotoluene. An oven-dried three-neck flask equipped with a condenser and an addition funnel was cooled under vacuum. Mg turnings (12.0 g, 0.494 mol) were added to the flask. THF (180 mL) was added, and Me₂HSiCl (54.8 mL, 0.494 mol) was added through the addition funnel, which was then rinsed with THF (60 mL). PhCCl₃ (23.3 mL, 0.165 mol) was added to the flask in a dropwise fashion. The reaction mixture was heated at reflux for 4 h. Once the reflux was complete, the reaction mixture was cooled to room temperature and filtered in air to remove the salt byproducts. The filtrate was washed with water, and the salts were extracted with pentane. The filtrate and the pentane extracts were combined and dried over MgSO₄ for 15 min. The solution was filtered and concentrated under vacuum. The oily residue distilled at 87 °C under dynamic vacuum to yield the product as a colorless liquid (17.0 g, 0.0636 mol, 38.7%). GC-MS analysis revealed a single peak in the chromatograph corresponding to a *m/z* of 266.1 (expected 266.6). ¹H NMR (chloroform-*d*₁, 150 MHz, 25 °C): δ 7.29 (d, 2 H, ³*J*_{HH} = 7.8 Hz, *o*-C₆H₅), 7.24 (t, 2 H, ³*J*_{HH} = 7.7 Hz, *m*-C₆H₅), 7.08 (t, 1 H, ³*J*_{HH} = 7.2 Hz, *p*-C₆H₅), 4.33 (sept, 3 H, ³*J*_{HH} = 3.7 Hz, ¹*J*_{SiH} = 188 Hz, SiHMe₂), 0.20 (d, 18 H, ³*J*_{HH} = 3.6 Hz, SiHMe₂). ¹H NMR (benzene-*d*₆, 400 MHz, 25 °C): δ 7.39 (d, 2 H, ³*J*_{HH} = 7.8 Hz, *o*-C₆H₅), 7.12 (t, 2 H, ³*J*_{HH} = 7.4 Hz, *m*-C₆H₅), 6.95 (t, 1 H, ³*J*_{HH} = 7.4 Hz, *p*-C₆H₅), 4.56 (sept, 3 H, ³*J*_{HH} = 3.7 Hz, ¹*J*_{SiH} = 188 Hz, SiHMe₂), 0.22 (d, 18 H, ³*J*_{HH} = 3.8 Hz, SiHMe₂). ¹³C{¹H} NMR (benzene-*d*₆, 150 MHz, 25 °C): δ 142.78 (*ipso*-C₆H₅), 130.92 (*o*-C₆H₅), 129.08 (*m*-C₆H₅), 124.77 (*p*-C₆H₅), 15.47 (C(SiHMe₂)₂), -2.05 (SiHMe₂). ²⁹Si{¹H} NMR (benzene-*d*₆, 119.3 MHz, 25 °C): δ -13.08. IR (KBr, cm^{-1}): 3084 w, 3058 w, 2959 m, 2904 m, 2120 s (SiH), 1592 m, 1495 m, 1441 w, 1419 w, 1255 s, 1166 m, 1083 w, 1038 m, 916 s br, 882 s br, 844 s br, 756 w, 699 s, 644 m. *m/z* for C₁₃H₂₆Si₃: Calcd 266.61, Found 266.1.

KC(SiHMe₂)₂Ph (2). A THF solution of PhC(SiHMe₂)₃ (1.28 g, 4.79 mmol, 5 mL) was cooled to -78 °C. In a separate vessel, KO^tBu (0.510 g, 4.55 mmol) was dissolved in THF (15 mL) and cooled to -78 °C. This solution was slowly added to PhC(SiHMe₂)₃. The reaction mixture was stirred for 30 min at -78 °C and then slowly warmed to room temperature and stirred overnight. The solvent was removed under vacuum, and the residue was washed with pentane (3 × 3 mL). The residual pentane was removed under vacuum to yield the product as a brownish yellow powder (0.792 g, 3.21 mmol, 79.2%). ¹H NMR (benzene-*d*₆, 400 MHz, 25 °C): δ 6.75 (t, 2 H, ³*J*_{HH} = 7.6 Hz, *m*-C₆H₅), 6.58 (d, 2 H, ³*J*_{HH} = 8.0 Hz, *o*-C₆H₅), 6.08 (t, 1 H, ³*J*_{HH} = 6.9 Hz, *p*-C₆H₅), 4.57 (sept, 2 H, ³*J*_{HH} = 3.6 Hz, ¹*J*_{SiH} = 163 Hz, SiHMe₂), 0.42 (d, 12 H, ³*J*_{HH} = 3.6 Hz, SiHMe₂). ¹³C{¹H} NMR (benzene-*d*₆, 150 MHz, 25 °C): δ 157.90 (*ipso*-C₆H₅), 130.66 (*m*-C₆H₅), 120.51 (*o*-C₆H₅), 109.64 (*p*-C₆H₅), 45.97 (C(SiHMe₂)₂), 1.28 (SiHMe₂). ²⁹Si{¹H} NMR (benzene-*d*₆, 119.3 MHz, 25 °C): δ -27.53 . IR (KBr, cm⁻¹): 3055 m, 2940 s, 2889 m, 2493 w, 2118 m (SiH), 1995 s (SiH), 1583 s, 1532 m, 1472 s, 1263 s, 1252 s, 1187 m, 1081 w, 1010 s br, 898 s, 828 m, 800 m, 757 s, 700 s, 679 m, 630 m. Anal. Calcd for C₁₁H₁₉KSi₂: C, 53.59; H, 7.77. Found: C, 53.36; H, 8.00. mp 126 - 128 °C.

La{C(SiHMe₂)₂Ph}₃ (3). Method A. LaI₃(THF)₄ (0.0603 g, 0.0746 mmol) and (TMEDA)KC(SiHMe₂)₂Ph (0.0812 g, 0.224 mmol) were stirred in a mixture of pentane (2.5 mL) and benzene (2.5 mL) for 2 h at room temperature. The solvents were evaporated, and the solid residue was extracted with pentane (3 × 3 mL). The pentane was removed under vacuum to provide an analytically pure yellow sticky solid (0.0545 g, 0.0716 mmol, 95.9%). Recrystallization from pentane at -30 °C provided X-ray quality crystals.

Method B. LaI₃(THF)₄ (0.219 g, 0.270 mmol) and KC(SiHMe₂)₂Ph (0.200 g, 0.811 mmol) were stirred in benzene (8 mL) for 2 h at room temperature. La{C(SiHMe₂)₂Ph}₃ was isolated following the workup procedure described in Method A to obtain a yellow solid in high yield (0.193 g, 0.254 mmol, 93.9%). ¹H NMR (benzene-*d*₆, 600 MHz, 25 °C): δ 7.10 (t, 6 H, ³*J*_{HH} = 7.7 Hz, *m*-C₆H₅), 6.81 (t, 3 H, ³*J*_{HH} = 7.4 Hz, *p*-C₆H₅), 5.84 (d, 6 H, ³*J*_{HH} = 7.6 Hz, *o*-C₆H₅), 4.24 (septet, 6 H, ¹*J*_{SiH} = 144 Hz, ³*J*_{HH} = 3.5 Hz, SiHMe₂), 0.43 (d, 18 H, ³*J*_{HH} = 3.2 Hz, SiHMe₂), 0.32 (d, 18 H, ³*J*_{SiH} = 3.5 Hz, SiHMe₂). ¹H NMR (toluene-*d*₈, 125 MHz, -73 °C): δ 7.27 (3 H, *o*-C₆H₅, 3 H *m*-C₆H₅), 6.80 (3 H, *p*-C₆H₅, 3 H, *m*-C₆H₅), 4.68 (s br, 3 H, SiHMe₂), 4.15 (3 H, *o*-C₆H₅), 3.81 (s br, 3 H, SiHMe₂), 0.78, 0.68, (s br, 18 H La⁻HSiMe₂) 0.35, 0.08 (s br, 18 H, SiHMe₂).

$^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6 , 150 MHz, 25 °C): δ 149.66 (*ipso*-C₆H₅), 134.61 (*m*-C₆H₅), 129.96 (*o*-C₆H₅), 122.59 (*p*-C₆H₅), 56.29 (C(SiHMe₂)₂), 1.89 (SiHMe₂), 1.29 (SiHMe₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (toluene- d_8 , 150 MHz, -73 °C): δ 148.27 (*ipso*-C₆H₅), *m*-C₆H₅ and *o*-C₆H₅ overlap with toluene- d_8 , 122.26 (*p*-C₆H₅), 53.48 (C(SiHMe₂)₂), 2.33 (SiHMe₂), 1.47 (La⁻HSiMe₂), 0.89 (La⁻HSiMe₂), 0.41 (SiHMe₂). $^{29}\text{Si}\{^1\text{H}\}$ NMR (benzene- d_6 , 119.3 MHz, 25 °C): δ -18.0 (SiHMe₂). $^{29}\text{Si}\{^1\text{H}\}$ NMR (toluene- d_8 , 119.3 MHz, -73 °C): δ 1.80 (SiHMe₂), -12.97 (La⁻HSiMe₂). IR (KBr, cm⁻¹): 2954 m, 2111 m (SiH), 1859 m br (SiH), 1583 m, 1473 m, 1253 s, 1207 m, 1071 m, 888 s, 834 s, 767 m, 703 m, 462 m br. IR (ATR, pentane, cm⁻¹): 2106 m br (SiH), 1859 m br (SiH), 1585 m, 1474 m, 1256 m, 1248 m, 1209 s, 1033 m br, 930 s, 890 s, 834 s, 767 s, 708 m. Anal. Calcd for C₃₃H₅₇LaSi₆: C, 52.07; H, 7.55. Found: C, 52.48; H, 7.67. mp 119 °C.

Ce(C(SiHMe₂)₂Ph)₃ (4). **Method A.** CeI₃(THF)₄ (0.0682 g, 0.0843 mmol) and (TMEDA)KC(SiHMe₂)₂Ph (0.0917 g, 0.253 mmol) were stirred in a mixture of pentane (2.5 mL) and benzene (2.5 mL) for 5 h at room temperature. The color changed from dark red to orange. The solvents were evaporated, and the residue was extracted with pentane (3 × 3 mL). The pentane was removed under vacuum to yield an orange sticky solid (0.0599 g, 0.0786 mmol, 93.2%). Recrystallization from pentane at -30 °C afforded X-ray quality crystals.

Method B. CeI₃(THF)₄ (0.0750 g, 0.0928 mmol) and KC(SiHMe₂)₂Ph (0.0686 g, 0.278 mmol) were stirred in benzene (5 mL) for 5 h at room temperature. Ce{C(SiHMe₂)₂Ph}₃ was isolated following the workup procedure described in Method A to yield the product as an orange solid (0.0670 g, 0.0928 mmol, 94.8%). IR (KBr, cm⁻¹): 3024 s, 2959 s, 29254 s, 2853 s, 2115 m (SiH), 1648 m, 1598 m, 1493 m, 1459 m, 1398 br, 1256 s, 1206 m, 1155 m, 1092 m, 1028 s, 891 s, 837 s, 798 s. IR (ATR, pentane, cm⁻¹): 2958 s, 2923 s, 2874 s, 2115 w (SiH), 1865 w (SiH), 1461 m, 1380 m, 1248 w, 1208 w, 890 s br, 836 m, 766 m, 728 m. Anal. Calcd for C₃₃H₅₇CeSi₆: C, 51.99; H, 7.54. Found: C, 51.82 ; H, 7.45 . mp 118 °C.

Pr(C(SiHMe₂)₂Ph)₃ (5). **Method A.** PrI₃(THF)₃ (0.0657 g, 0.0890 mmol) and (TMEDA)KC(SiHMe₂)₂Ph (0.0969 g, 0.267 mmol) were stirred in a mixture of pentane (2.5 mL) and benzene (2.5 mL) overnight at room temperature. The color changed from dark red to greenish yellow. The solvents were removed under vacuum, and the residue was extracted with pentane (3 × 3 mL). The pentane was removed under vacuum to yield a yellow sticky solid

(0.0510 g, 0.0668 mmol, 75.1%). X-ray quality yellow crystals were obtained from recrystallization from a pentane solution cooled at $-30\text{ }^{\circ}\text{C}$.

Method B. $\text{PrI}_3(\text{THF})_3$ (0.0750 g, 0.102 mmol) and $\text{KC}(\text{SiHMe}_2)_2\text{Ph}$ (0.0751 g, 0.305 mmol) were stirred in benzene (5 mL) overnight at room temperature. $\text{Pr}\{\text{C}(\text{SiHMe}_2)_2\text{Ph}\}_3$ was isolated following the workup procedure described in Method A to yield the product as a yellow solid (0.0662 g, 0.0867 mmol, 85.3%). IR (KBr, cm^{-1}): 2955 s, 2926 s, 2854 s, 2113 s (SiH), 1868 br (SiH), 1595 m, 1492 m, 1473 m, 1415 br, 1251 s, 1207 s, 1030 s. IR (ATR, pentane, cm^{-1}): 2950 w, 2898 w, 2114 w br (SiH), 1870 w br (SiH), 1585 w, 1475 m, 1248 m, 1207 m, 1033 m br, 930 s, 888 s, 834 s, 768 s, 708 m, 677 w. Anal. Calcd for $\text{C}_{33}\text{H}_{57}\text{PrSi}_6$: C, 51.92 ; H, 7.54. Found: C, 51.81 ; H, 7.72. mp $123\text{ }^{\circ}\text{C}$.

Nd(C(SiHMe₂)₂Ph)₃. (6) Method A. $\text{NdI}_3(\text{THF})_3$ (0.0563 g, 0.0759 mmol) and (TMEDA) $\text{KC}(\text{SiHMe}_2)_2\text{Ph}$ (0.0827 g, 0.228 mmol) were stirred in a mixture of pentane (2.5 mL) and benzene (2.5 mL) overnight at room temperature. The color changed from dark red to green. The solvents were removed under vacuum, and the residue was extracted with pentane (3×3 mL). The pentane was removed under vacuum to yield a green sticky solid (0.0519 g, 0.0677 mmol, 89.1%). Green, X-ray quality crystals were obtained after recrystallization from pentane at $-30\text{ }^{\circ}\text{C}$.

Method B. $\text{NdI}_3(\text{THF})_3$ (0.0744 g, 0.100 mmol) and $\text{KC}(\text{SiHMe}_2)_2\text{Ph}$ (0.0742 g, 0.301 mmol) were stirred in benzene (5 mL) overnight at room temperature. The above procedure for isolation of $\text{Nd}\{\text{C}(\text{SiHMe}_2)_2\text{Ph}\}_3$ was followed to yield the product as a green solid (0.0681 g, 0.0888 mmol, 88.6%). ^1H NMR (benzene- d_6 , 600 MHz, $25\text{ }^{\circ}\text{C}$): δ 4.89, 1.36, -1.76 , -2.22 . IR (KBr, cm^{-1}): 2952 m, 2104 m (SiH), 1871 m br (SiH), 1583 m, 1473 m, 1252 s, 1209 m, 1071 m, 1032 m, 888 s, 832 s, 763 m, 704 m, 456 m br. IR (ATR, pentane, cm^{-1}): 2951 w, 2898 w, 2116 w br (SiH), 1869 m br (SiH), 1586 w, 1474 m, 1255 m, 1207 m, 1033 m br, 888 s, 834 s, 767 m, 708 m. Anal. Calcd for $\text{C}_{33}\text{H}_{57}\text{NdSi}_6$: C, 51.71; H, 7.50. Found: C, 51.96; H, 7.60; . mp $121\text{ }^{\circ}\text{C}$.

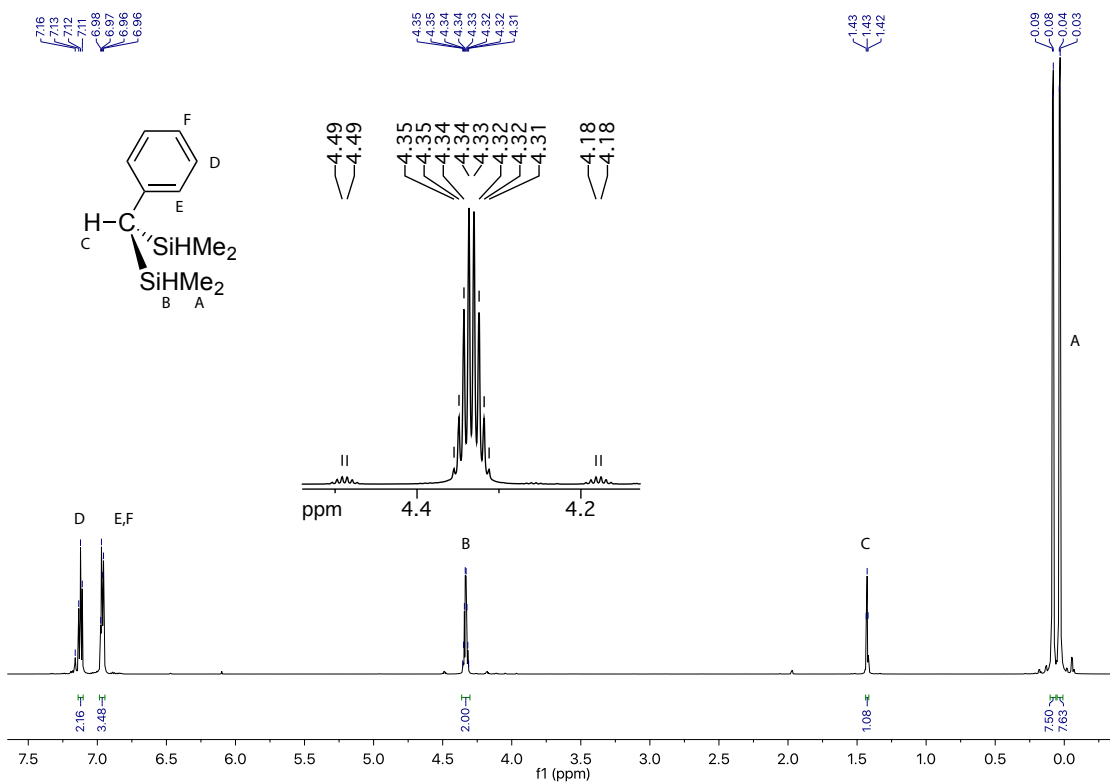


Figure S1. ^1H NMR spectrum of $\text{HC}(\text{SiHMe}_2)_2\text{Ph}$ (**1**) acquired in benzene- d_6 at room temperature.

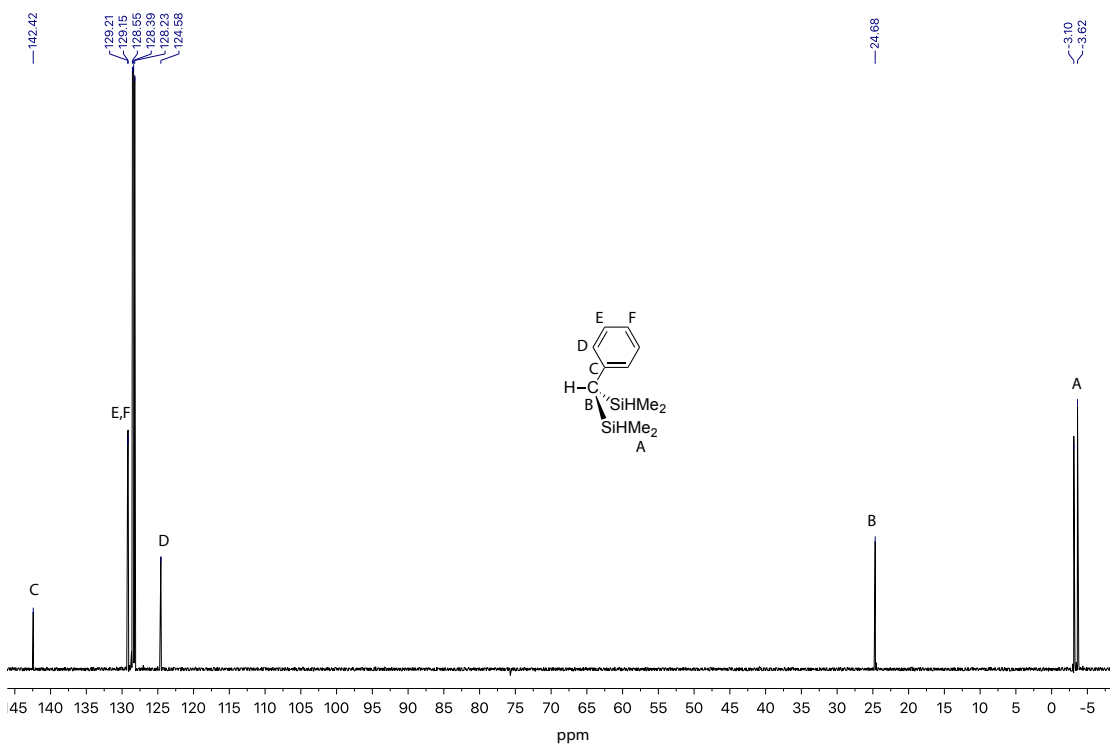


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{HC}(\text{SiHMe}_2)_2\text{Ph}$ (**1**) acquired in benzene- d_6 at room temperature.

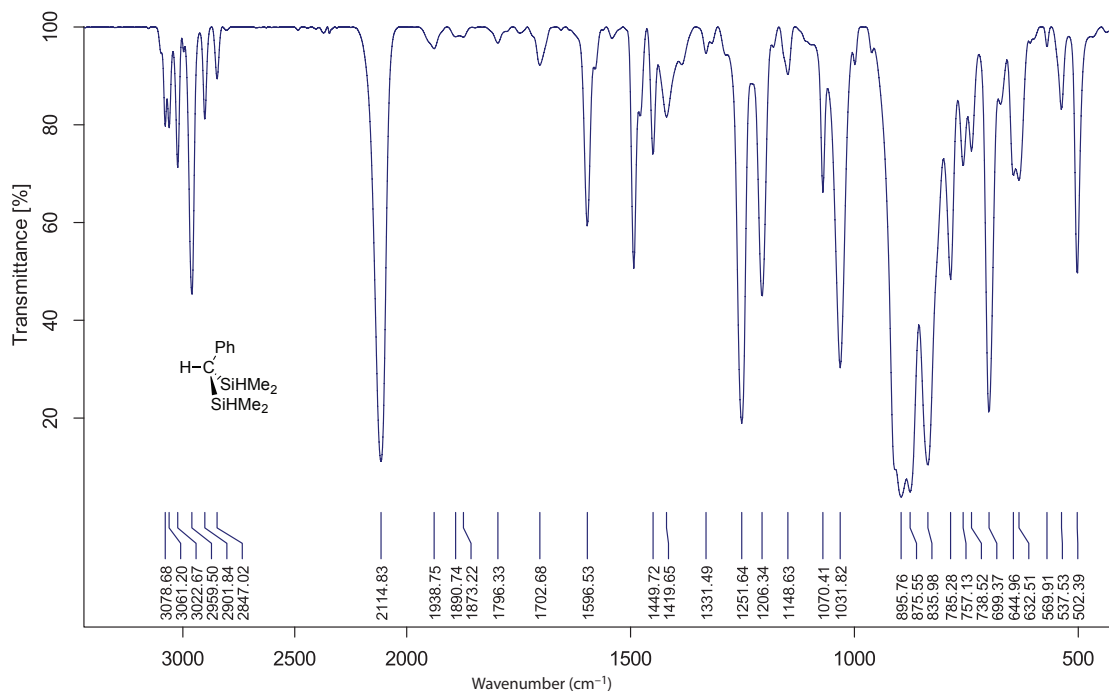


Figure S3. Infrared spectrum of $\text{HC}(\text{SiHMe}_2)_2\text{Ph}$ (**1**).

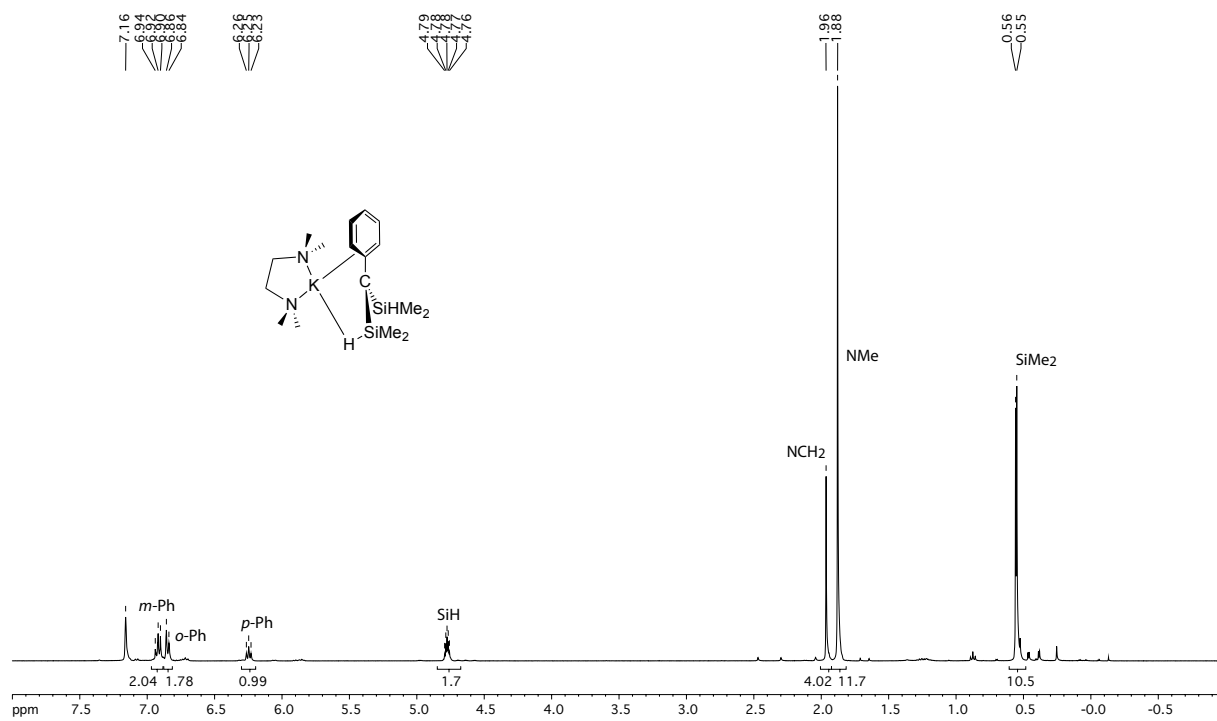


Figure S4. ¹H NMR spectrum of (TMEDA)KC(SiHMe₂)₂Ph (2·TMEDA).

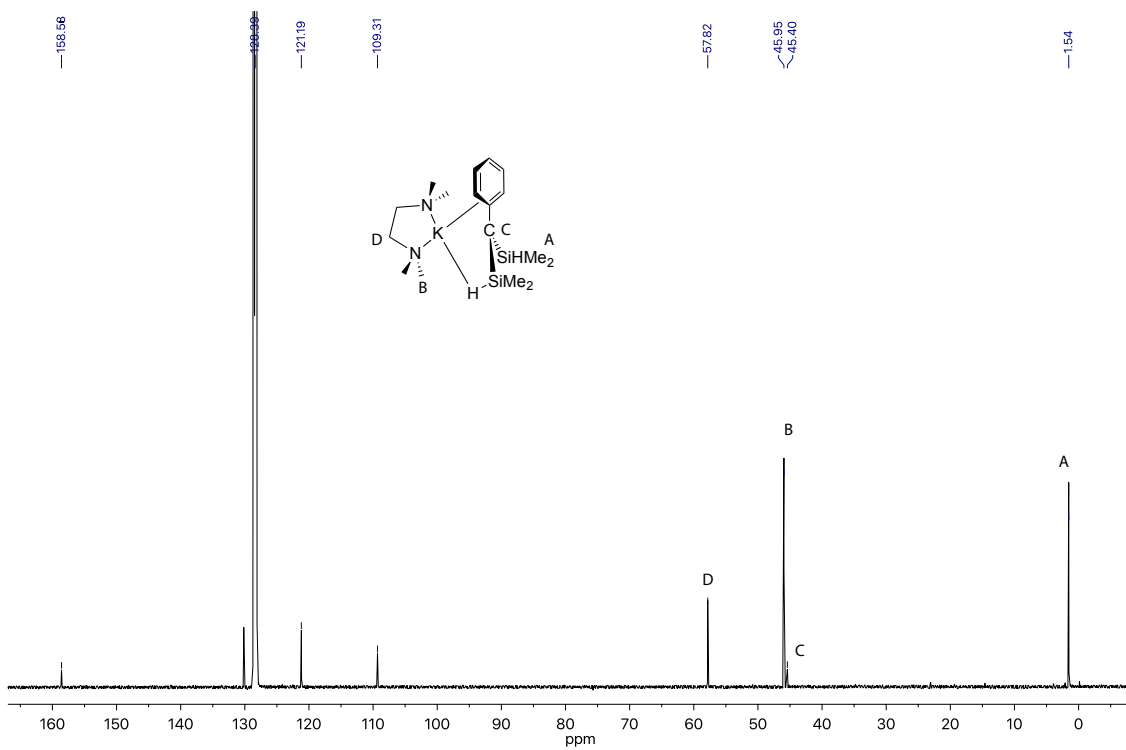


Figure S5. ¹³C{¹H} NMR spectrum of (TMEDA)KC(SiHMe₂)₂Ph (2·TMEDA).

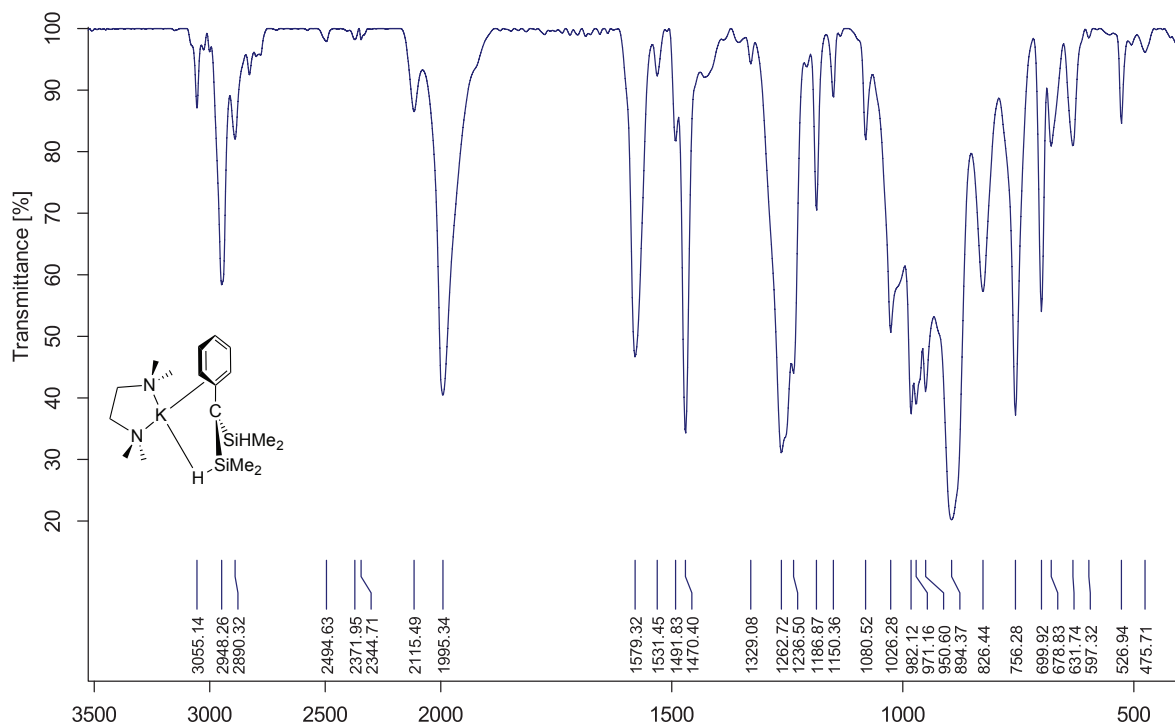


Figure S6. Infrared spectrum of (TMEDA)KC(SiHMe₂)₂Ph (2·TMEDA, KBr).

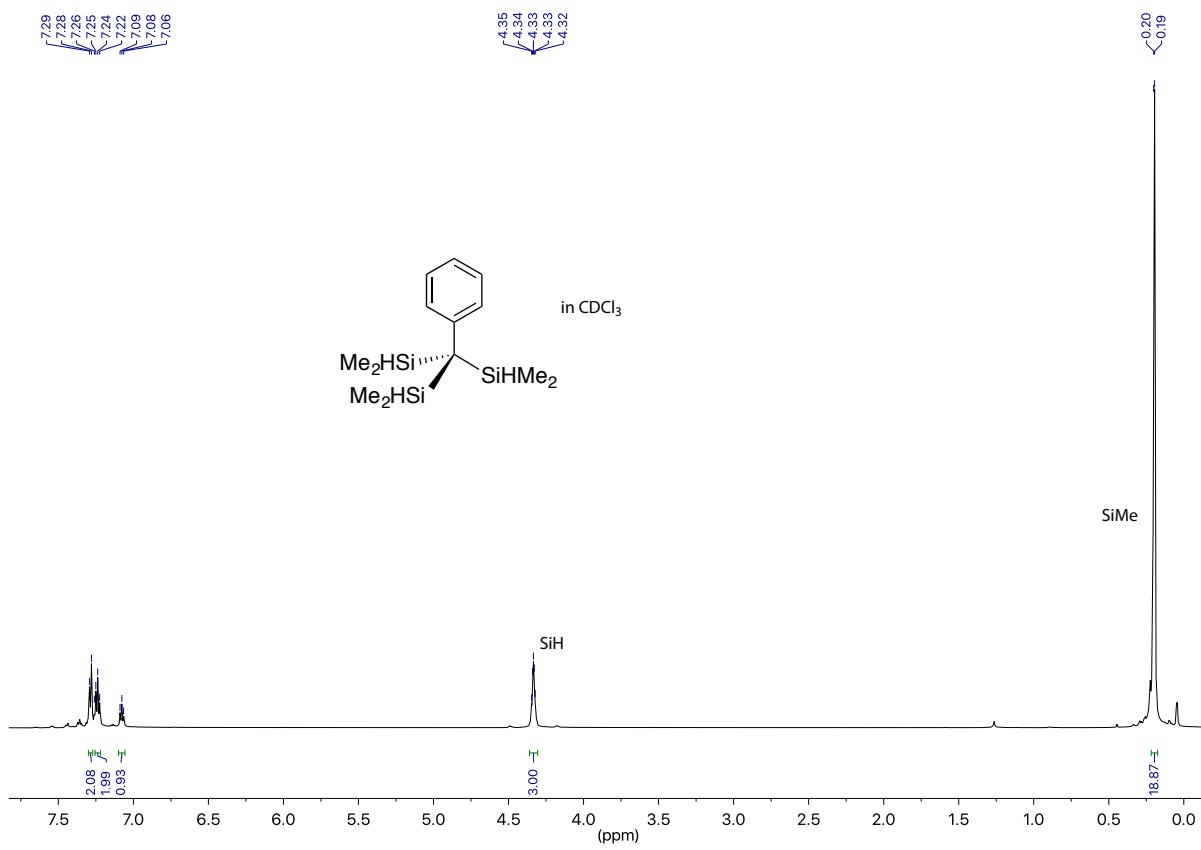


Figure S7. ^1H NMR spectrum of $\text{PhC}(\text{SiHMe}_2)_3$ in chloroform-*d*.

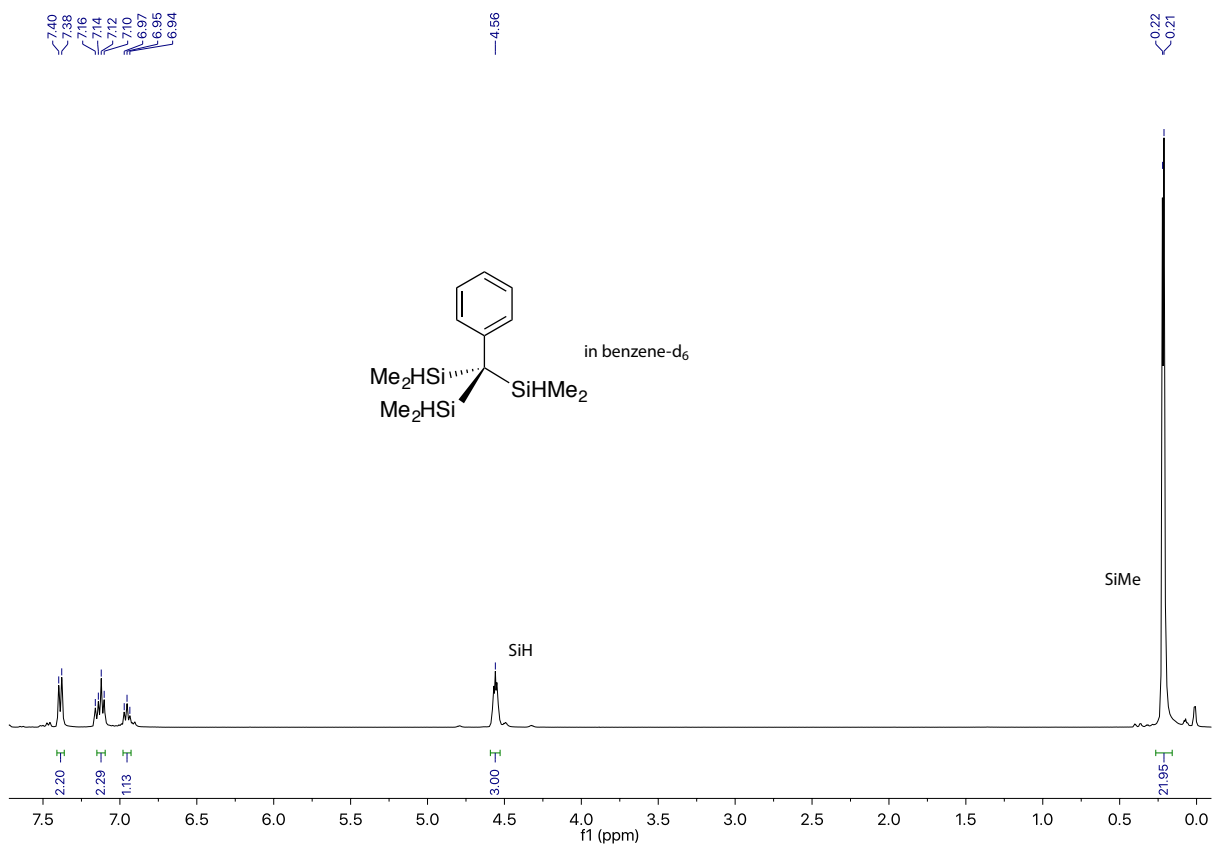


Figure S8. ^1H NMR spectrum of $\text{PhC}(\text{SiHMe}_2)_3$ in $\text{benzene-}d_6$.

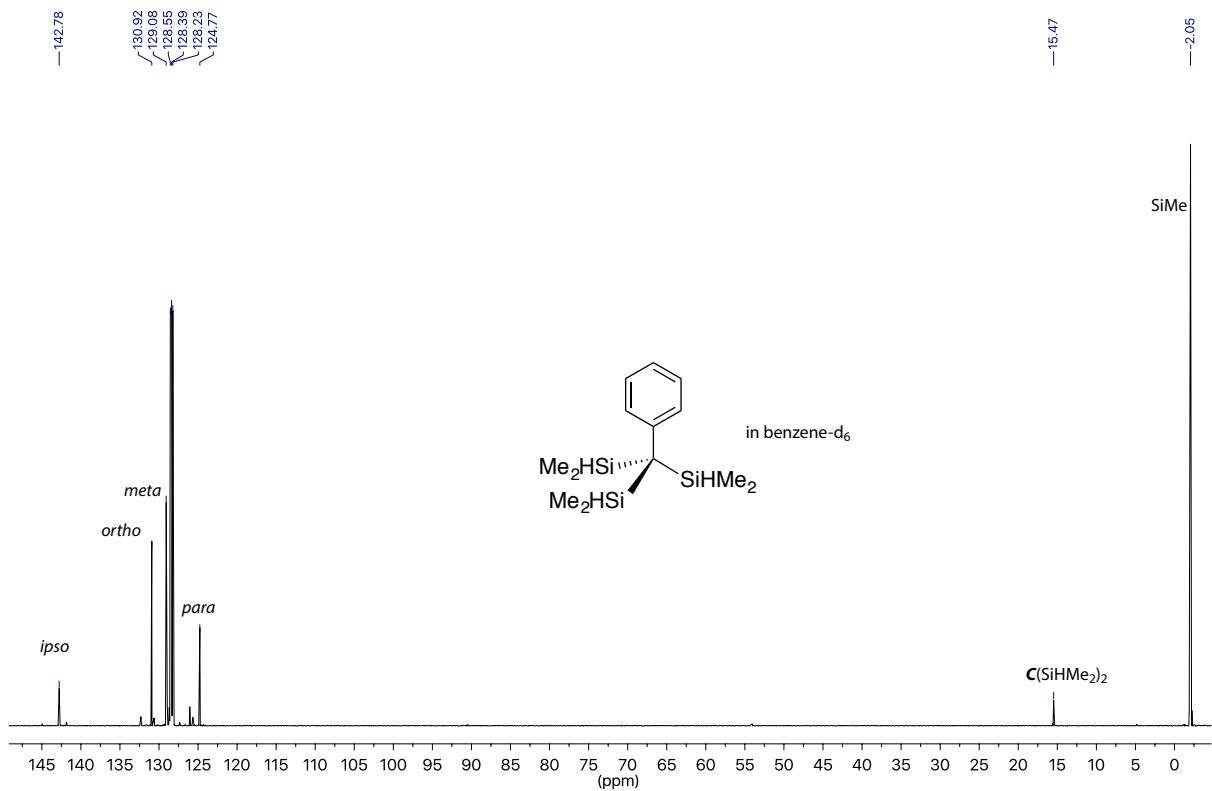


Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{PhC}(\text{SiHMe}_2)_3$ in benzene- d_6 .

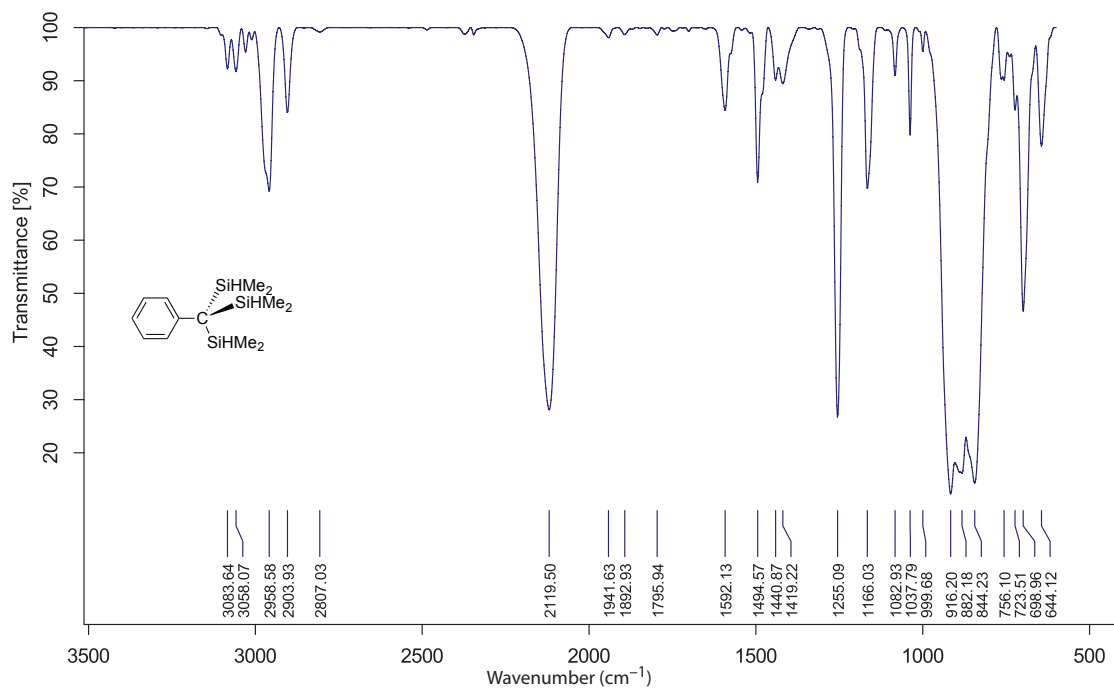


Figure S10. IR spectrum of $\text{PhC}(\text{SiHMe}_2)_3$ (KBr).

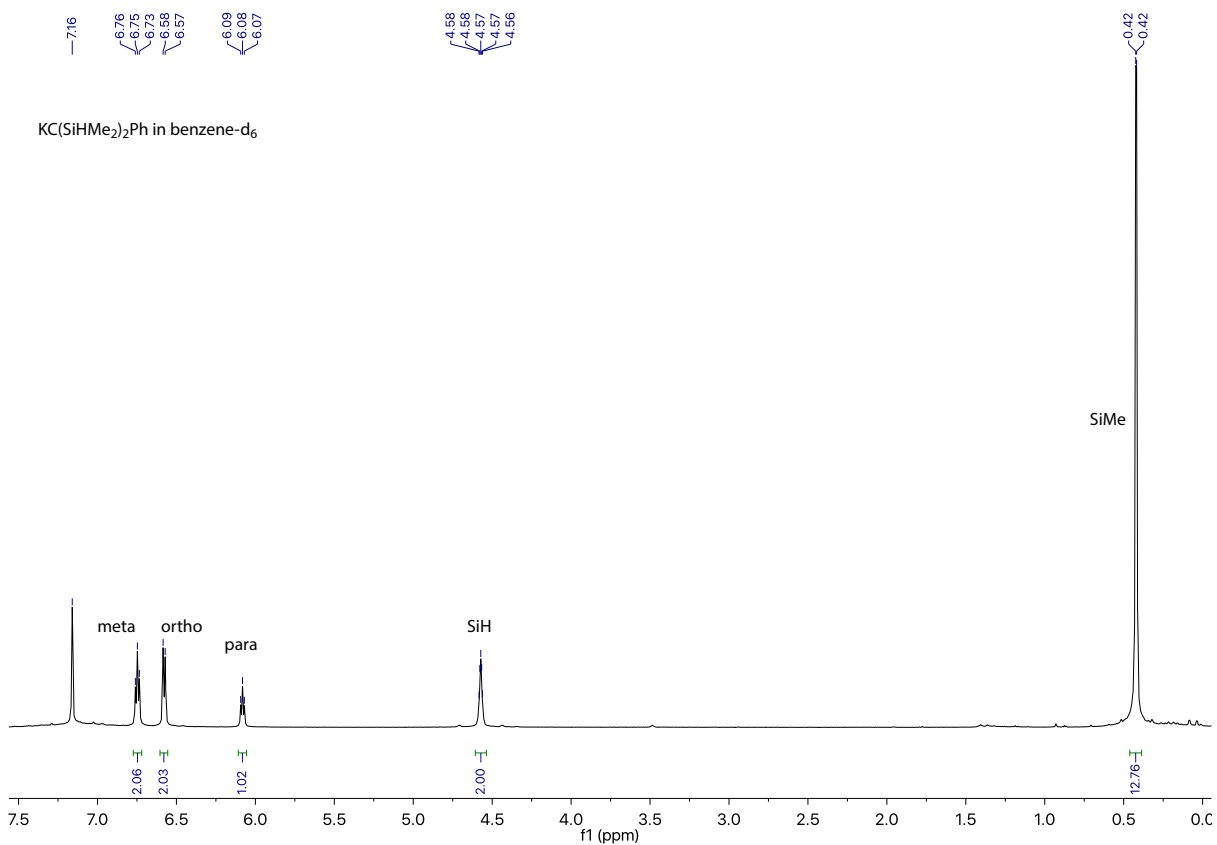


Figure S11. ^1H NMR spectrum of $\text{KC}(\text{SiHMe}_2)_2\text{Ph}$ dissolved in benzene- d_6 .

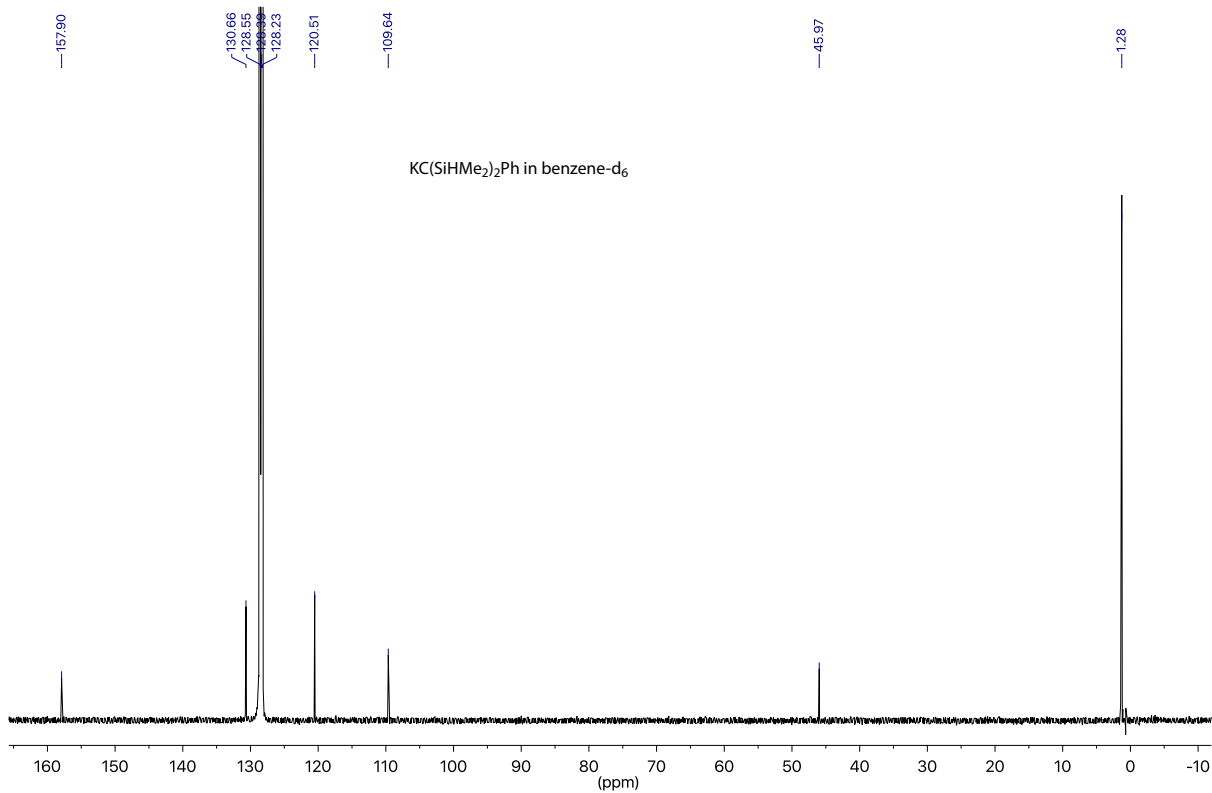


Figure S12. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{KC}(\text{SiHMe}_2)_2\text{Ph}$ dissolved in benzene-d_6 .

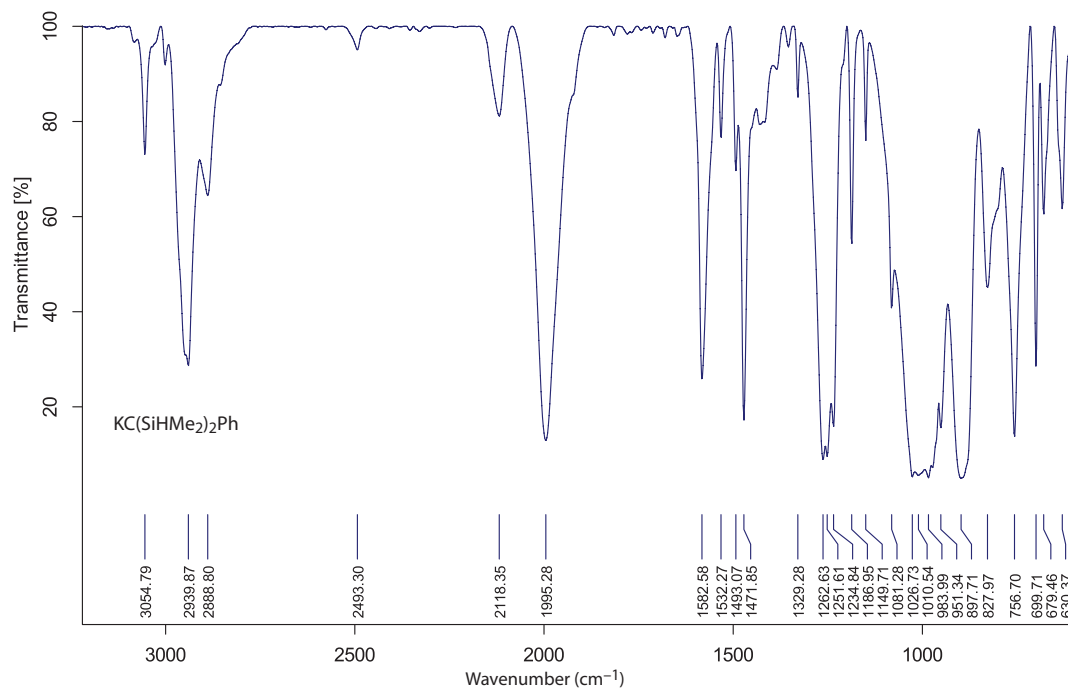


Figure S13. Infrared spectrum of $\text{KC}(\text{SiHMe}_2)_2\text{Ph}$ (2, KBr).

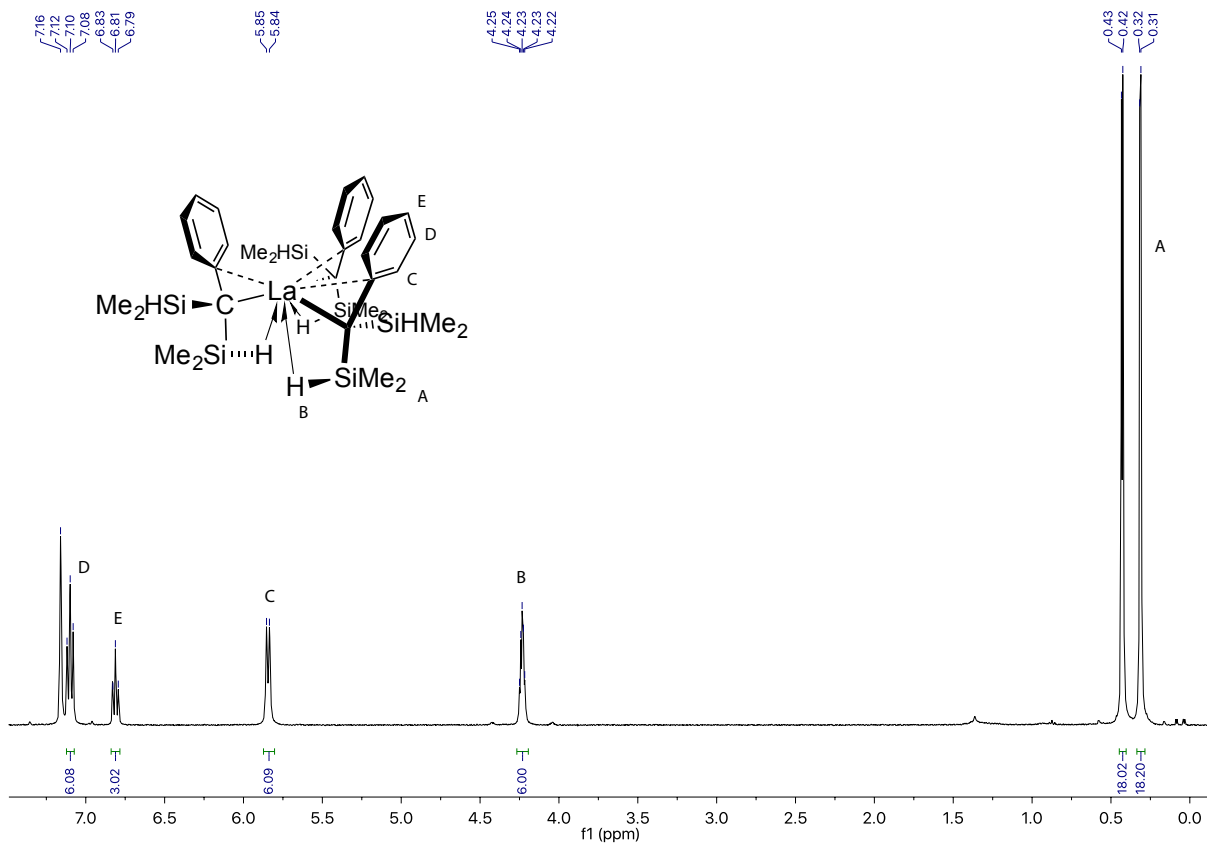


Figure S14. ^1H NMR spectrum of $\text{La}\{\text{C}(\text{SiHMe}_2)_2\text{Ph}\}_3$ (**3**) in benzene- d_6 at room temperature.

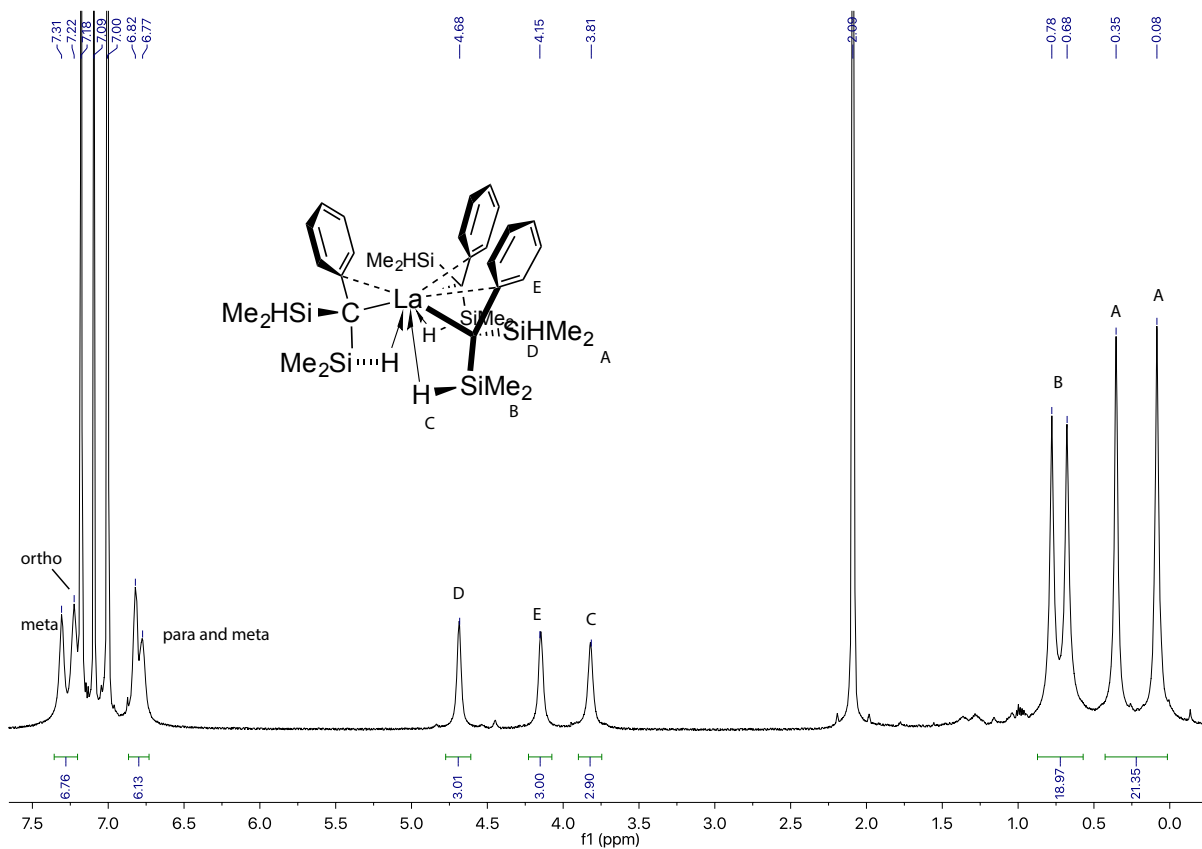


Figure S15. ^1H NMR spectrum of $\text{La}\{\text{C}(\text{SiHMe}_2)_2\text{Ph}\}_3$ (**3**) in $\text{toluene-}d_8$ and 200 K.

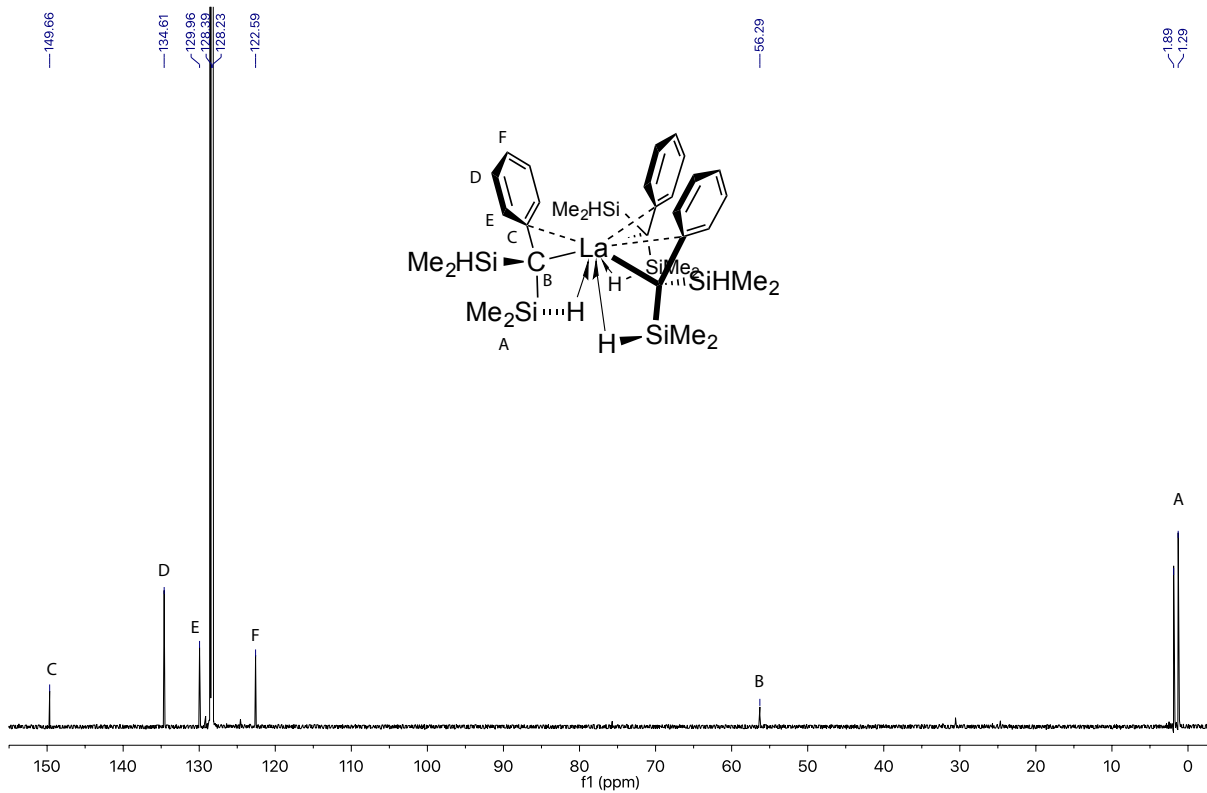


Figure S16. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{La}\{\text{C}(\text{SiHMe}_2)_2\text{Ph}\}_3$ (**3**) in $\text{benzene-}d_6$.

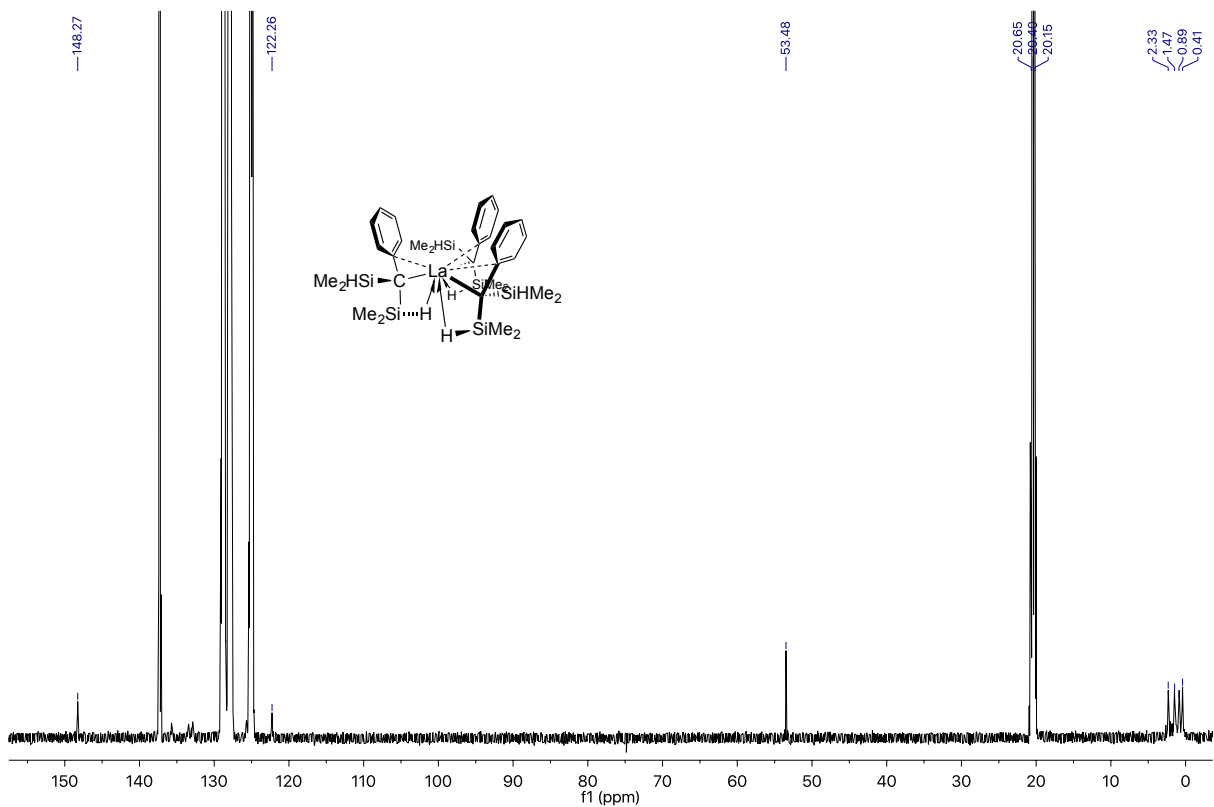


Figure S17. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{La}\{\text{C}(\text{SiHMe}_2)_2\text{Ph}\}_3$ (**3**) in $\text{toluene-}d_8$ at -200 K .

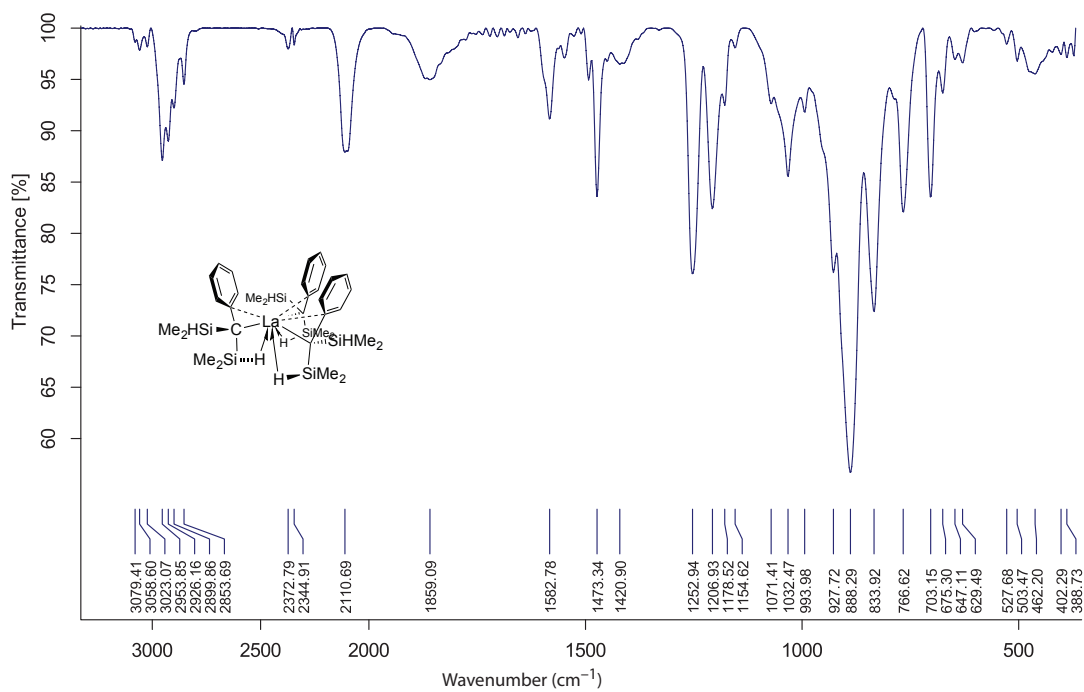


Figure S18. IR spectrum of $\text{La}\{\text{C}(\text{SiHMe}_2)_2\text{Ph}\}_3$ (**3**; KBr pellet).

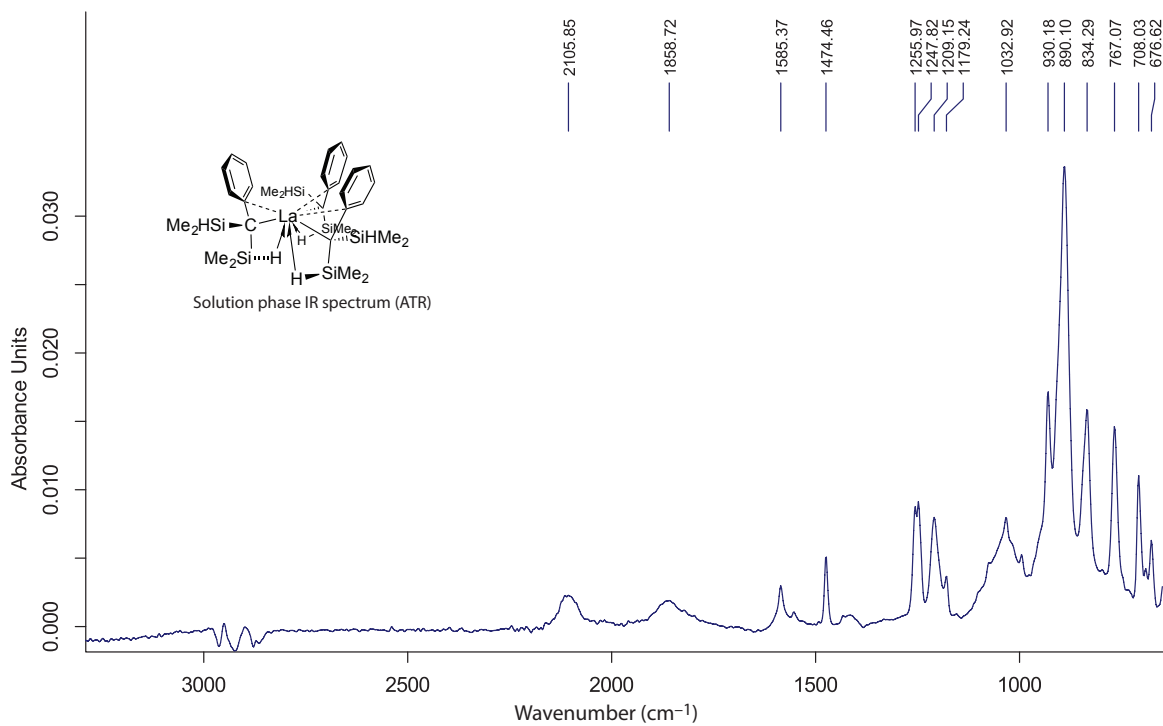


Figure S19. IR spectrum of $\text{La}\{\text{C}(\text{SiHMe}_2)_2\text{Ph}\}_3$ (**3**, ATR) dissolved in pentane.

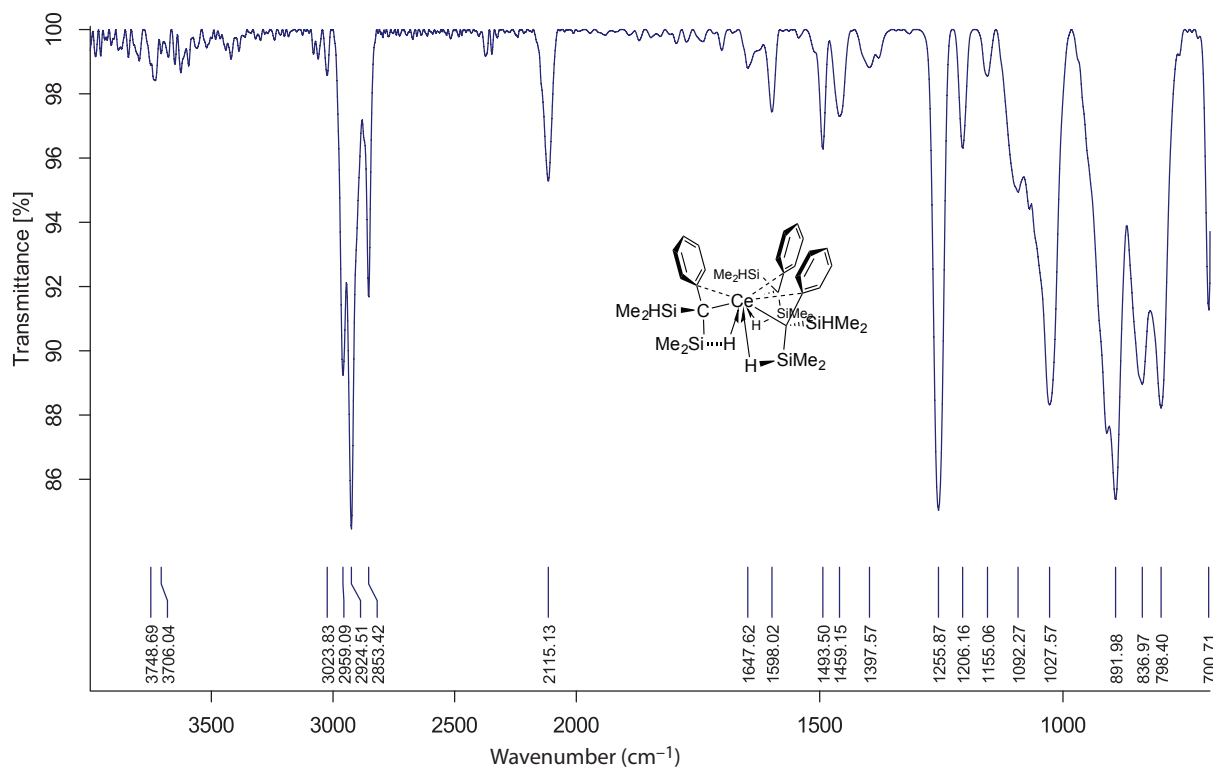


Figure S20. IR spectrum of $\text{Ce}\{\text{C}(\text{SiHMe}_2)_2\text{Ph}\}_3$ (**4**; KBr pellet).

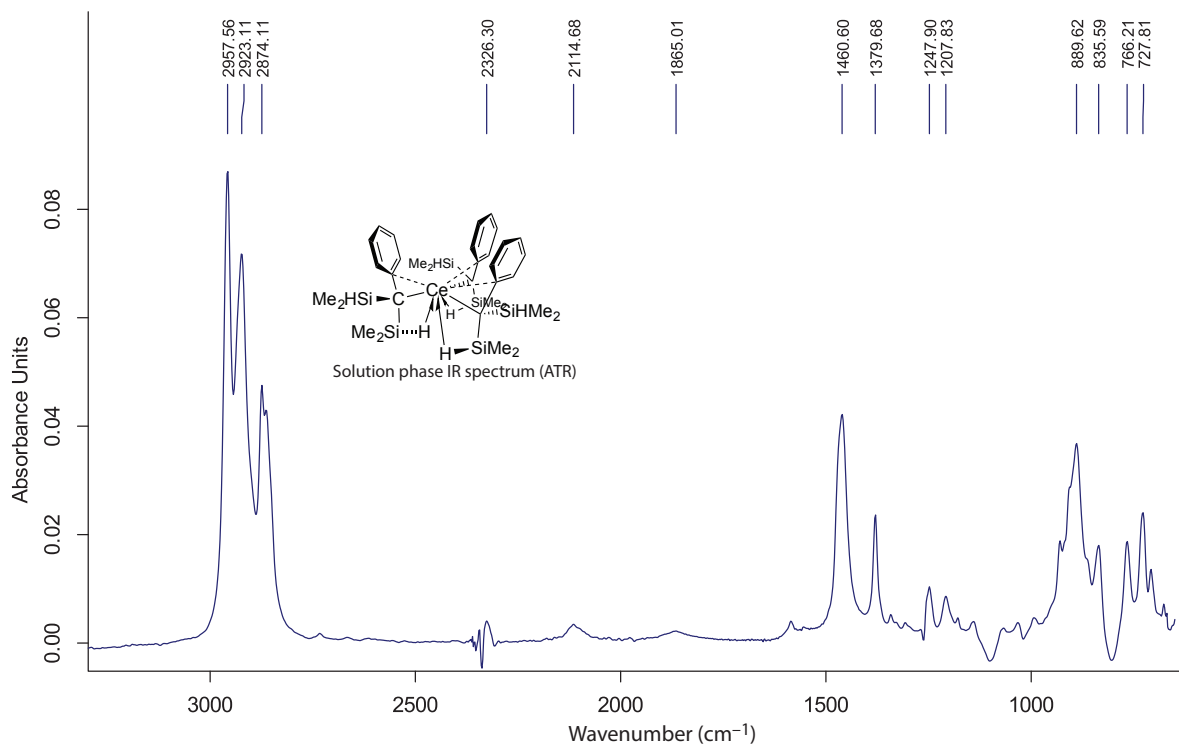


Figure S21. IR spectrum of Ce{C(SiHMe₂)₂Ph}₃ (**4**, ATR) dissolved in pentane.

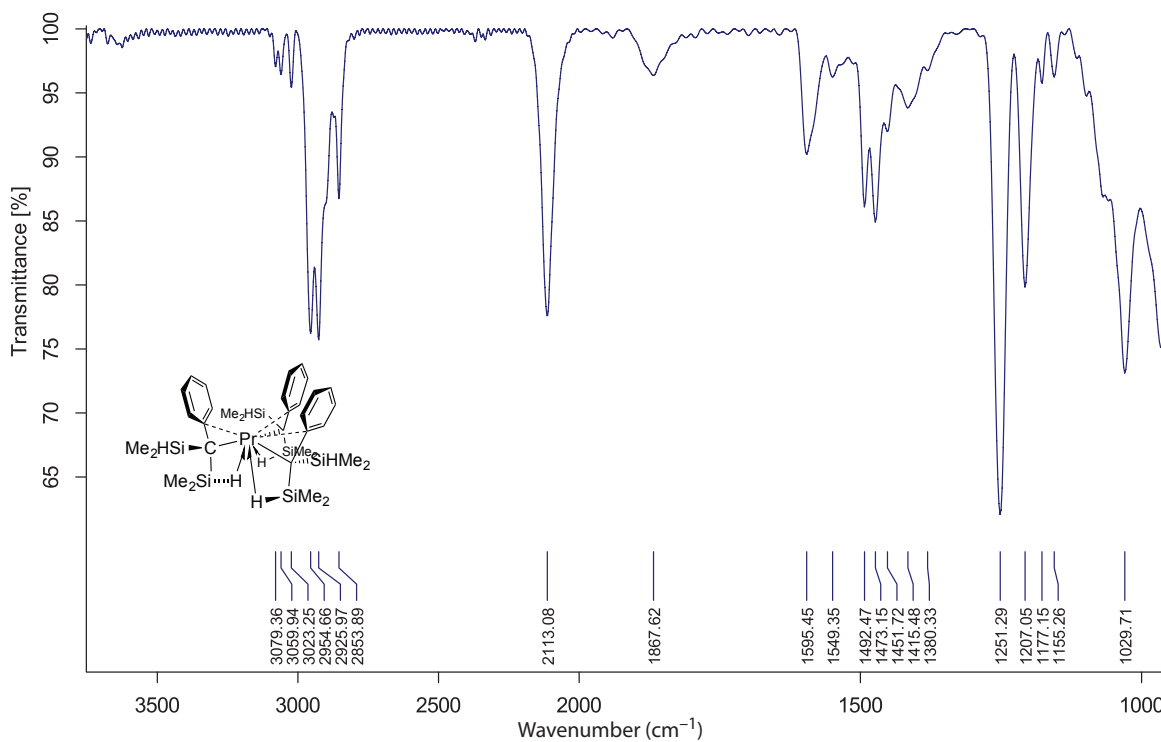


Figure S22. IR spectrum of Pr{C(SiHMe₂)₂Ph}₃ (**5**; KBr pellet).

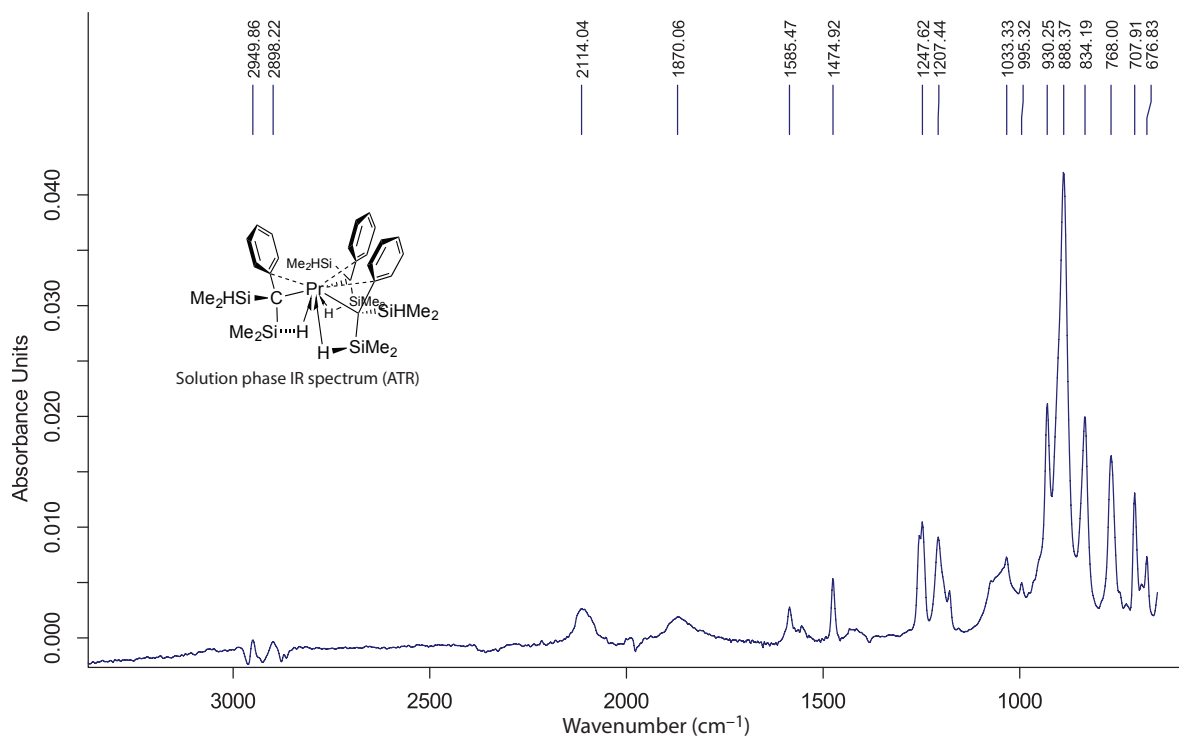


Figure S23. IR spectrum of Pr{C(SiHMe₂)₂Ph}₃ (**5**, ATR) dissolved in pentane.

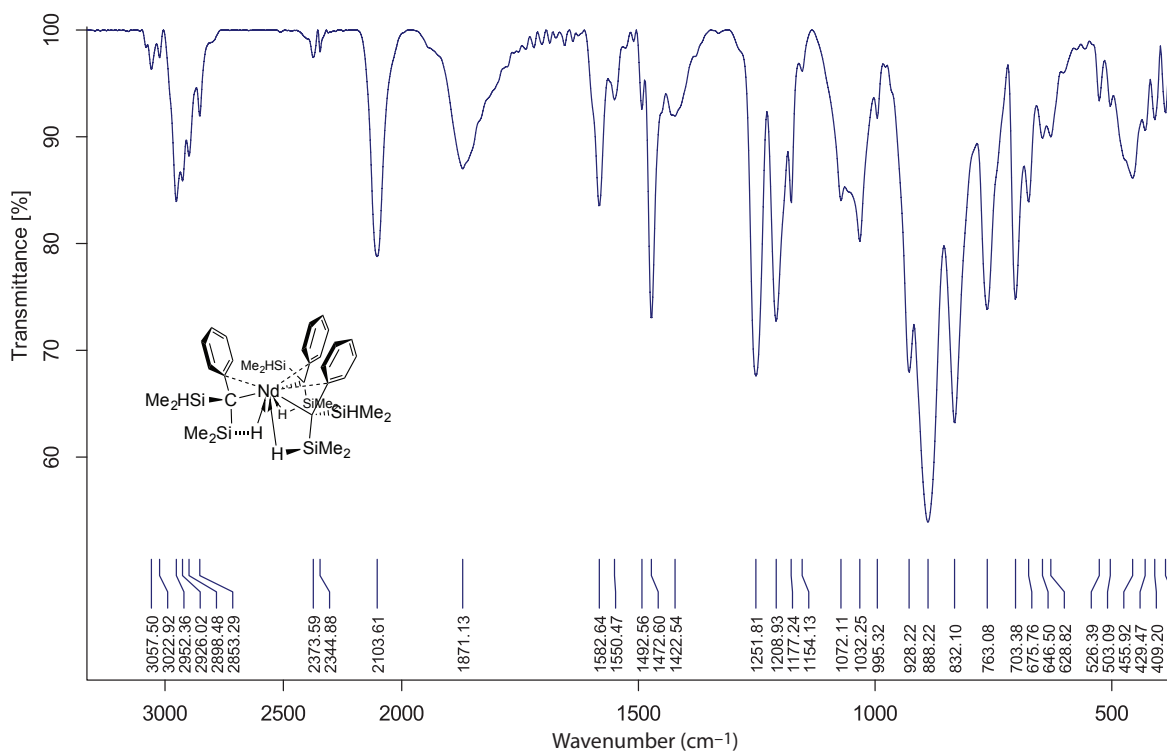


Figure S24. IR spectrum of Nd{C(SiHMe₂)₂Ph}₃ (**6**; KBr pellet).

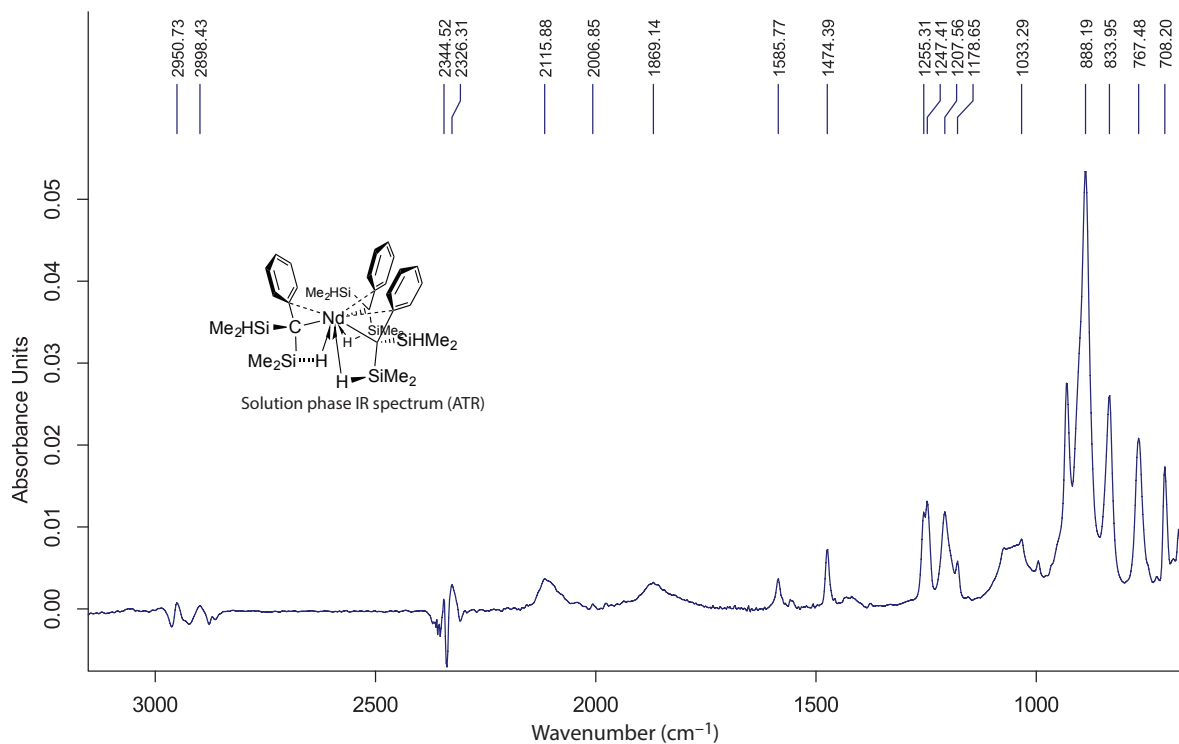


Figure S25. IR spectrum of Nd{C(SiHMe₂)₂Ph}₃ (**6**, ATR) dissolved in pentane.

References

1. G. B. Deacon, T. Feng, P. C. Junk, G. Meyer, N. M. Scott, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 2000, **53**, 853-865.
2. P. N. Hazin, J. C. Huffman and J. W. Bruno, *Organometallics*, 1987, **6**, 23-27.
3. D. G. Karraker, *Inorg. Chim. Acta*, 1987, **139**, 189-191.
4. M. Schlosser and J. Hartmann, *Angew. Chem. Int. Ed.*, 1973, **12**, 508-509.
5. L. H. Gade, C. Becker and J. W. Lauher, *Inorg. Chem.*, 1993, **32**, 2308-2314.