

Supporting Information for:

Grignard Reagents as Simple Precatalysts for the Dehydrocoupling of Amine and Silanes

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S1. General Methods

All manipulations were conducted under a positive pressure of N₂ in a M. Braun glovebox or using standard Schlenk techniques. Dry, oxygen-free solvents, reagents, and solid support were used throughout experimentation and stored inside the glovebox. Benzene-*d*₆ (C₆D₆) was distilled from CaH₂ and stored over activated 3Å molecular sieves for at least 48 h prior to use. 3Å molecular sieves were dried between 180-200 °C under dynamic vacuum for at least 1 d.

Methyl magnesium bromide and 2-mesitylmagnesium bromide (MesMgBr) were obtained from chemical vendors as solutions in tetrahydrofuran (THF). Dimethylmagnesium was synthesized according to a modified literature procedure followed by filtration.¹ For catalysis, these reagents were titrated thrice with I₂ and 0.5 M LiCl in THF. Amines were distilled under dynamic N₂ from CaH₂ and stored over 3Å molecular sieves. PhSiH₃ was distilled under dynamic N₂ and stored over 3Å molecular sieves while Ph₂SiH₂ and PhMeSiH₂ were distilled under dynamic vacuum and stored over 3Å molecular sieves. Ph₃SiH was recrystallized from hexanes solution at -40 °C. Hexamethylbenzene (C₆Me₆) was sublimed at 150 °C under dynamic vacuum.

Glassware was cleaned by sequential washings of base (5% KOH/10% ⁱPrOH/85% H₂O), acid (10% HNO₃/90% H₂O), and deionized water. Glassware was oven dried at 140 °C for at least 1 h, which was either transferred to the antechamber of an M. Braun glovebox or placed under dynamic vacuum connected to a Schlenk line. Catalytic reactions were conducted in PTFE-sealed J-Young NMR tubes, which were cleaned and dried by the methods mentioned above.

Nuclear magnetic resonance (NMR) spectra were recorded at ambient temperature on a Bruker AXR 500 MHz spectrometer. Chemical shifts (δ) are reported in parts per million (ppm). ¹H NMR spectra were referenced to an internal standard of C₆Me₆ (δ = 2.13).

S2. Catalytic Experiments

S2.1. General Procedure for Catalytic Experiments:

In an M. Braun glovebox, a 20 mL scintillation vial was charged with 0.5 mL of benzene-*d*₆, followed by 50 μL 0.4 M C₆Me₆ in benzene-*d*₆, silane, amine, and catalyst. The solution was quickly transferred to a PTFE-sealed J-Young NMR tube via a glass pipette and left to react at ambient temperature unless otherwise specified.






Icon	Meaning
	Aminosilane
	Silane
	Hydrogen Gas
	C ₆ Me ₆
	Methane

Figure S.1. List of icons and identifiers

S2.2. PhSiH₃ and ⁿBuNH₂

PhSiH₃ (41.0 μL, 3.36 × 10⁻¹ mmol), ⁿBuNH₂ (201.0 μL, 20.16 × 10⁻¹ mmol, 6.0 equiv.), and MeMgBr (15.0 μL, 1.68 × 10⁻² mmol, 5.0 mol %) were reacted together in 0.5 mL of benzene-*d*₆ in the presence of C₆Me₆ standard (50.0 μL, 0.4 M in benzene-*d*₆). Complete consumption of PhSiH₃ was observed after 0.5 h. The appearance of multiplet centered at δ = 2.87 in the ¹H NMR spectrum indicates 98% conversion to PhSi(NHⁿBu)₃ after 0.5 h at ambient temperature.

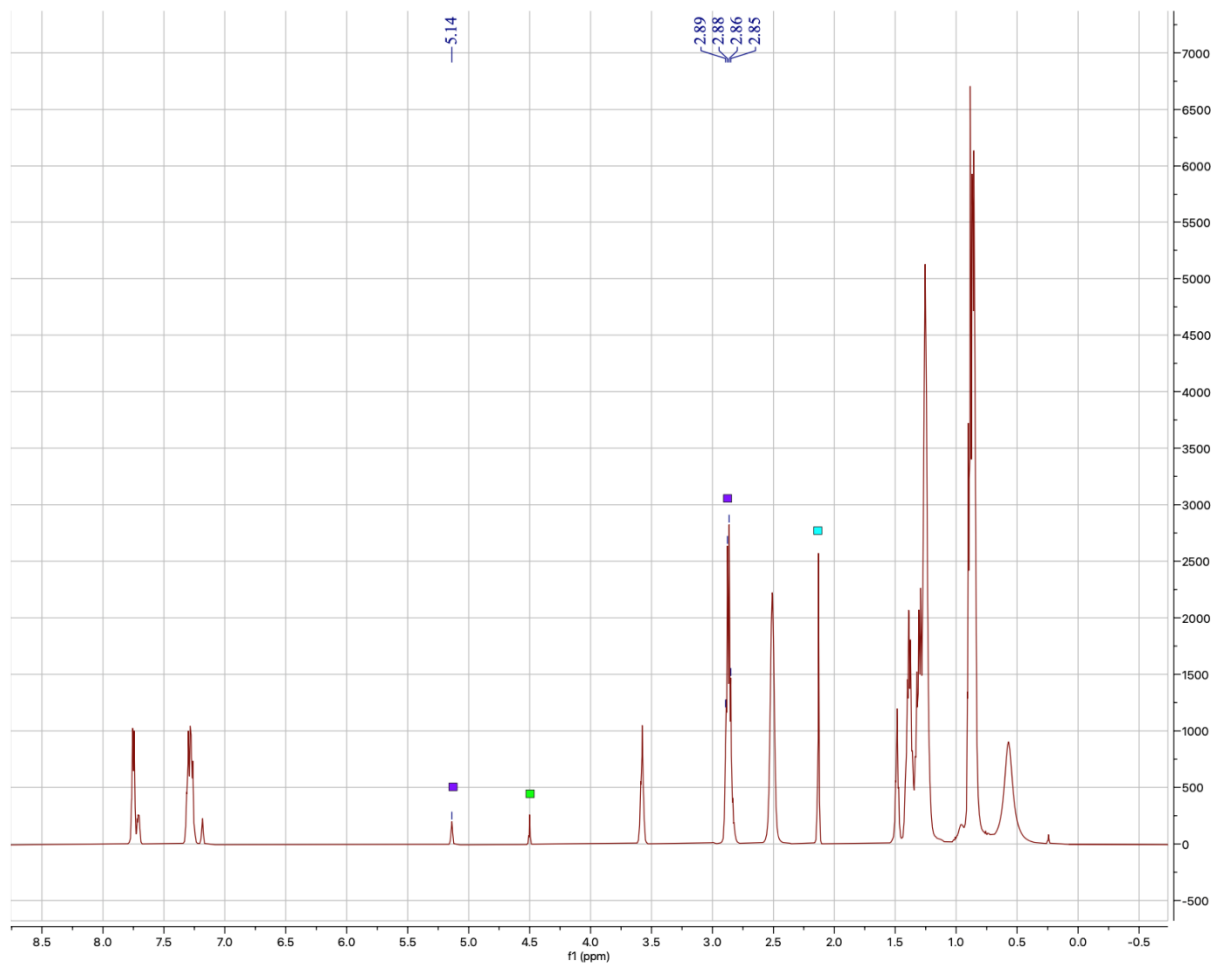


Figure S.2. ^1H NMR spectrum of the reaction between PhSiH_3 and $t\text{BuNH}_2$ catalyzed by MeMgBr in benzene- d_6 after 0.5 h.

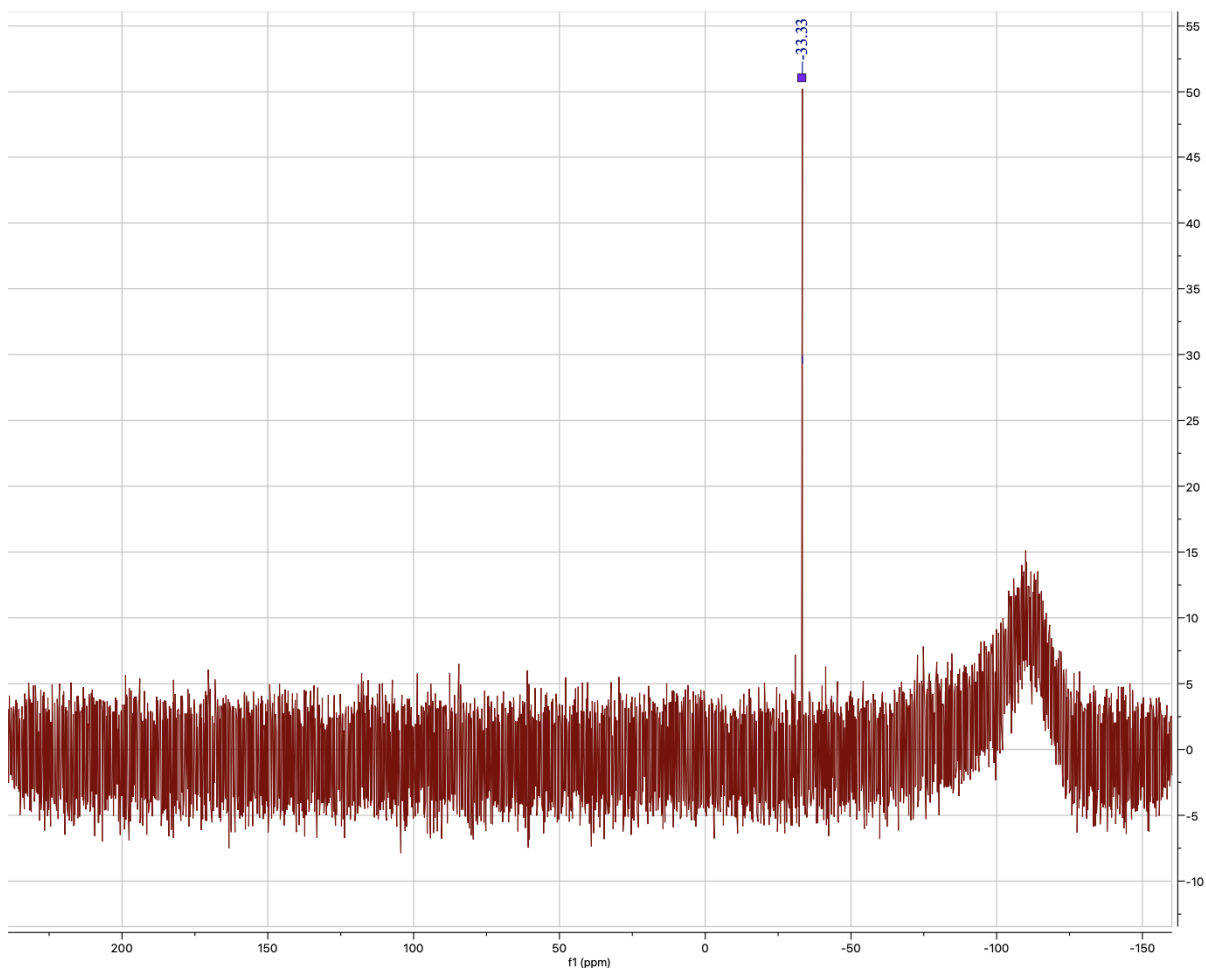


Figure S.3. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of the reaction between PhSiH_3 and $^t\text{BuNH}_2$ catalyzed by MeMgBr in benzene- d_6 after 0.5 h.

S2.3. PhSiH_3 and $^t\text{BuNH}_2$

PhSiH_3 (41.0 μL , 3.36×10^{-1} mmol), $^t\text{BuNH}_2$ (212.0 μL , 20.16×10^{-1} mmol, 6.0 equiv.), and MeMgBr (15.0 μL , 1.68×10^{-2} mmol, 5.0 mol %) were reacted together in 0.5 mL of benzene- d_6 in the presence of C_6Me_6 standard (50.0 μL , 0.4 M in benzene- d_6). The appearance of a diagnostic triplet centered at $\delta = 5.42$ in the ^1H NMR spectrum indicates 9% conversion to $\text{PhSiH}(\text{NH}^t\text{Bu})_2$ after 1 h at ambient temperatures while the appearance of a diagnostic doublet centered between $\delta = 5.06$ and $\delta = 5.07$ in the ^1H NMR spectrum indicates 91% conversion to $\text{PhSiH}_2(\text{NH}^t\text{Bu})$ after 1 h at ambient temperatures. Spectra were consistent with previous reports of this compound.^{2,3}

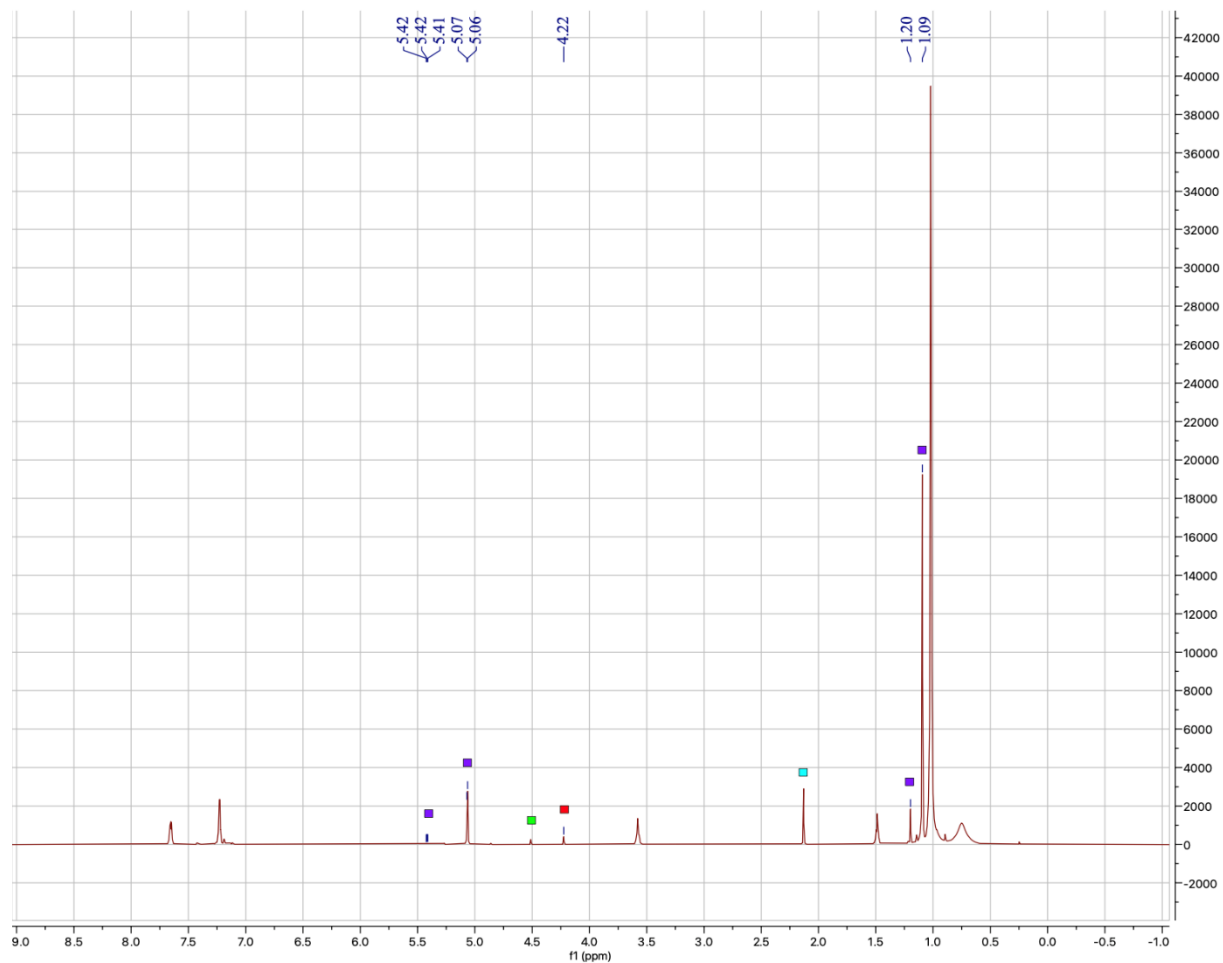


Figure S.4. ^1H NMR spectrum of the reaction between PhSiH_3 and $t\text{BuNH}_2$ catalyzed by MeMgBr in benzene- d_6 after 1 h.

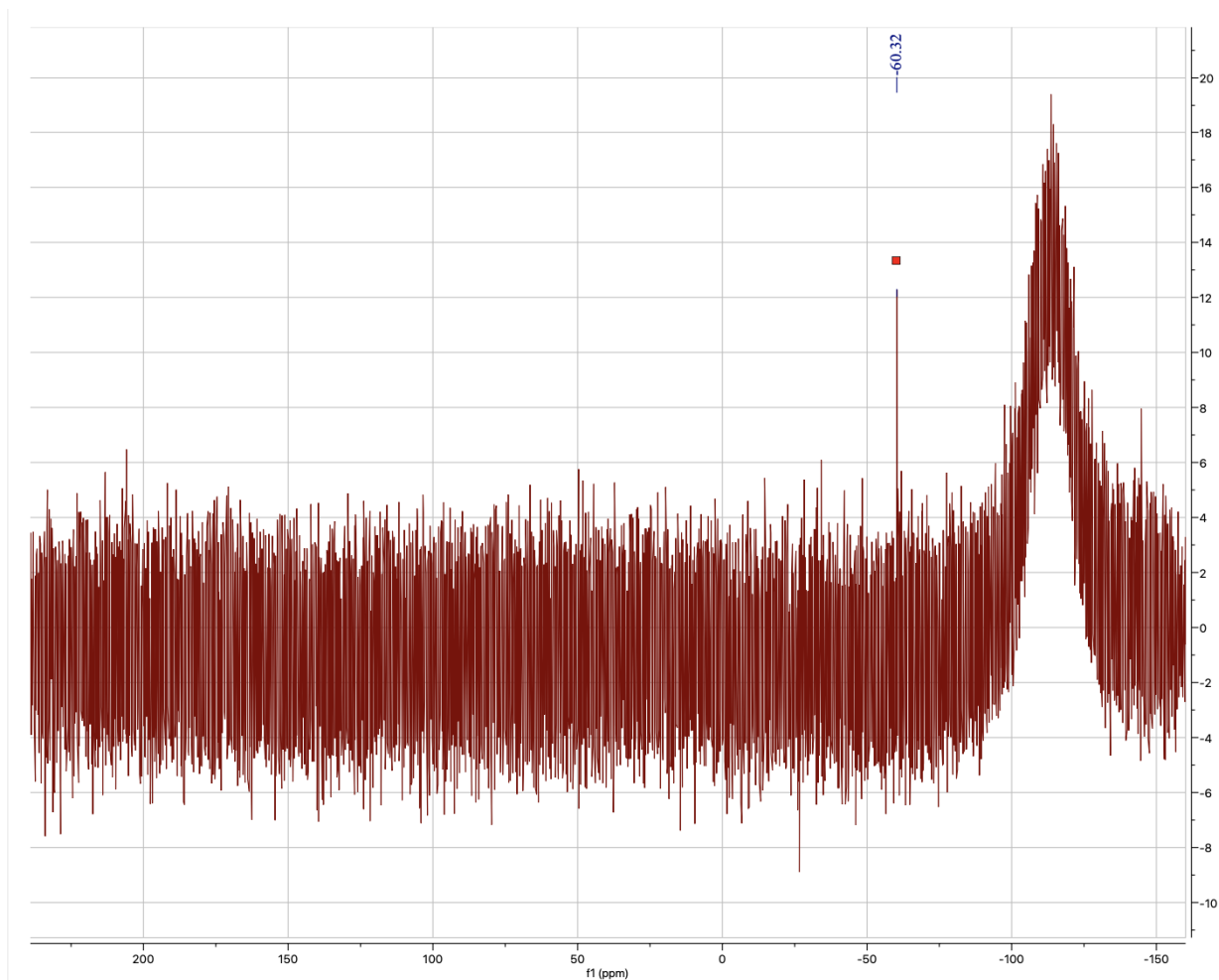


Figure S.5. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of the reaction between PhSiH_3 and $^t\text{BuNH}_2$ catalyzed by MeMgBr in benzene- d_6 after 1 h.

S2.4. PhSiH_3 and $^t\text{BuNH}_2$

PhSiH_3 (41.0 μL , 3.36×10^{-1} mmol), $^t\text{BuNH}_2$ (204.0 μL , 20.16×10^{-1} mmol, 6.0 equiv.), and MeMgBr (15.0 μL , 1.68×10^{-2} mmol, 5.0 mol %) were reacted together in 0.5 mL of benzene- d_6 in the presence of C_6Me_6 standard (50.0 μL , 0.4 M in benzene- d_6). Complete consumption of PhSiH_3 was observed after 1 h. The appearance of a multiplet centered at $\delta = 2.97$ and a multiplet centered at $\delta = 5.20$ in the ^1H NMR spectrum indicates 70% conversion to $\text{PhSi}(\text{NH}^t\text{Bu})_3$ after 1 h at ambient temperature.

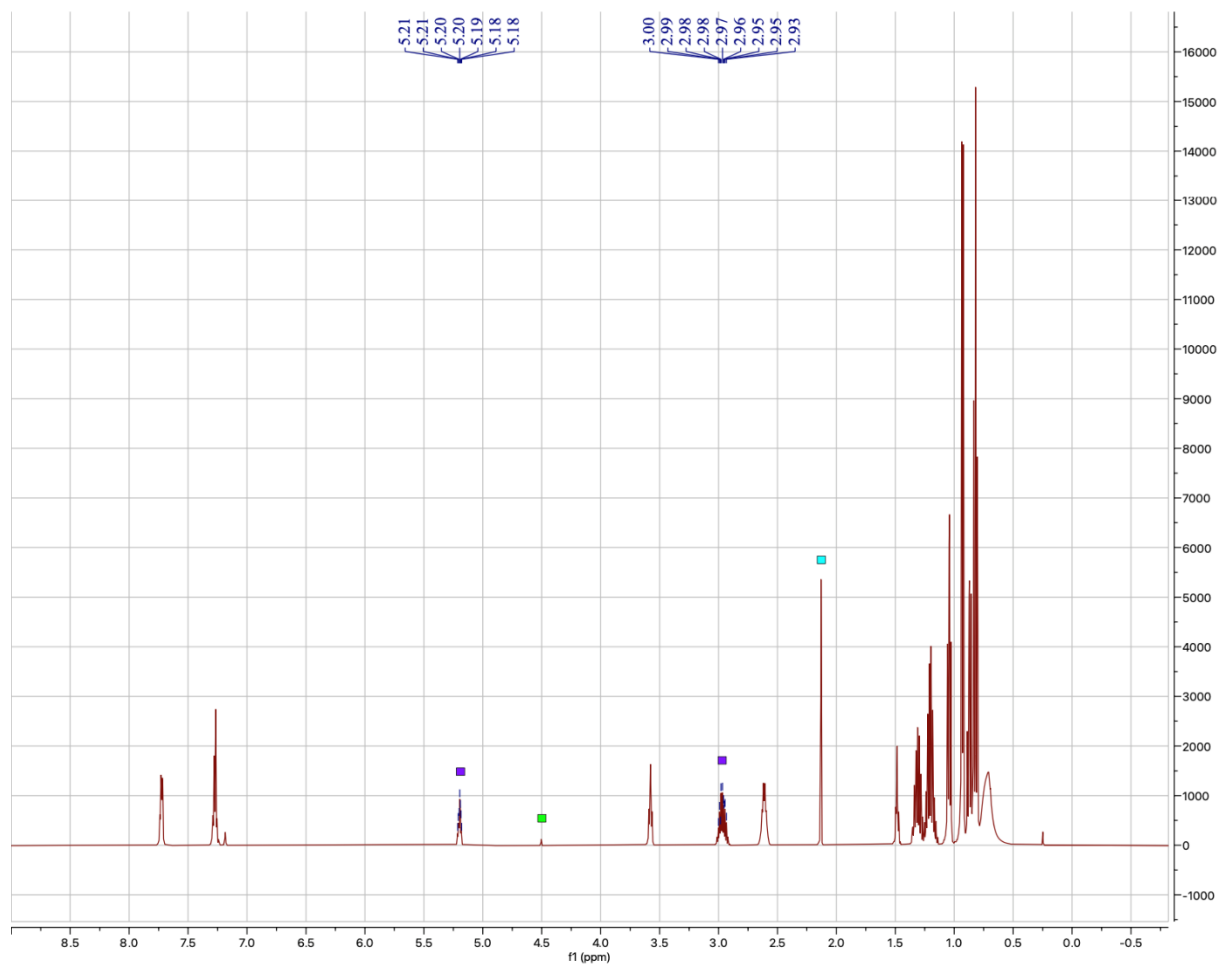


Figure S.6. ^1H NMR spectrum of the reaction between PhSiH_3 and $^s\text{BuNH}_2$ catalyzed by MeMgBr in benzene- d_6 after 1 h.

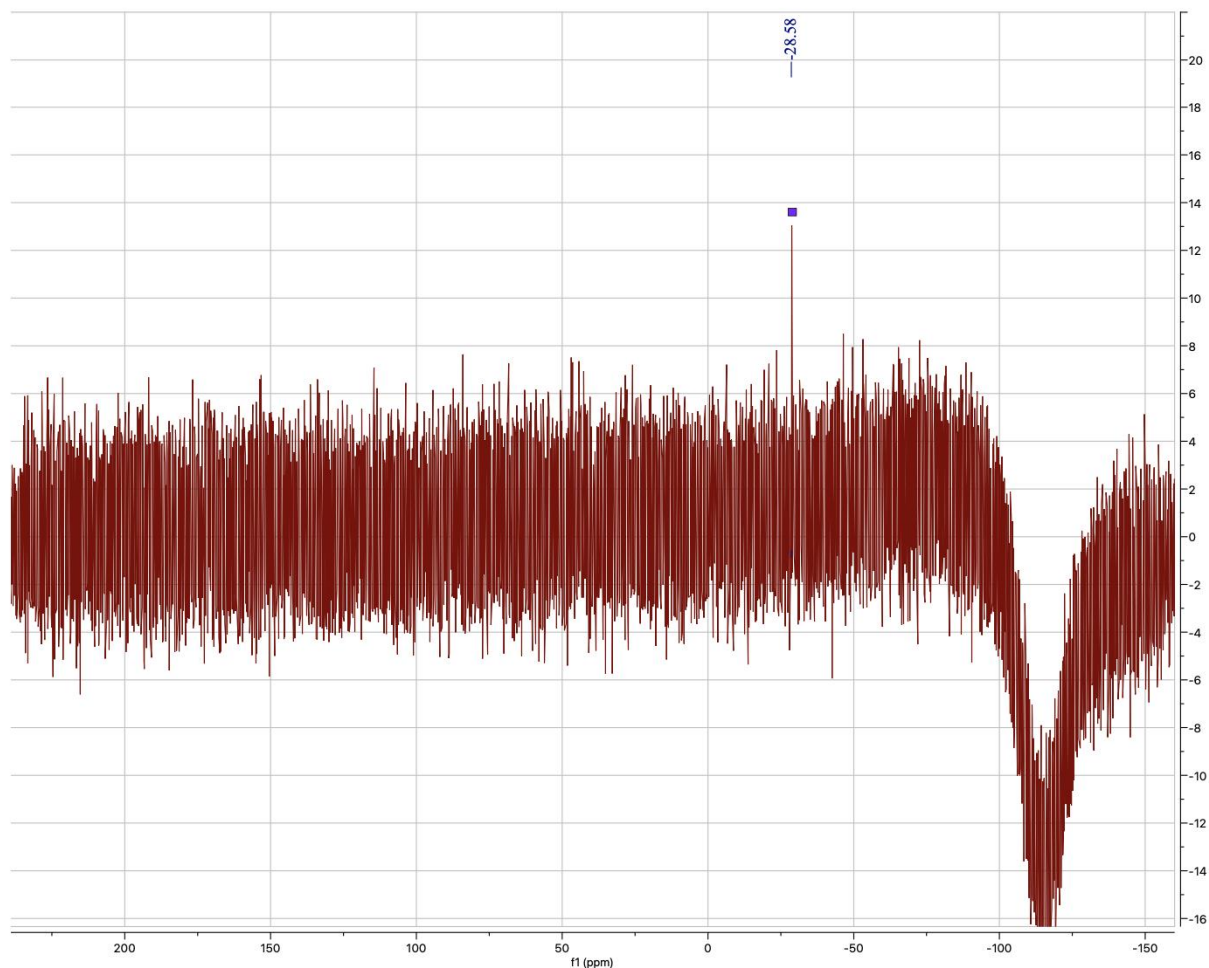


Figure S.7. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of the reaction between PhSiH_3 and $^s\text{BuNH}_2$ catalyzed by MeMgBr in benzene- d_6 after 1 h.

S2.5. PhSiH_3 and $^n\text{HeNH}_2$

PhSiH_3 (41.0 μL , 3.36×10^{-1} mmol), $^n\text{HeNH}_2$ (266.0 μL , 20.16×10^{-1} mmol, 6.0 equiv.), and MeMgBr (15.0 μL , 1.68×10^{-2} mmol, 5.0 mol %) were reacted together in 0.5 mL of benzene- d_6 in the presence of C_6Me_6 standard (50.0 μL , 0.4 M in benzene- d_6). Complete consumption of PhSiH_3 was observed after 1 h. The appearance of a multiplet centered at $\delta = 2.88$ in the ^1H NMR spectrum indicates 98% conversion to $\text{PhSi}(\text{NH}^n\text{He})_3$ after 1 h at ambient temperature.

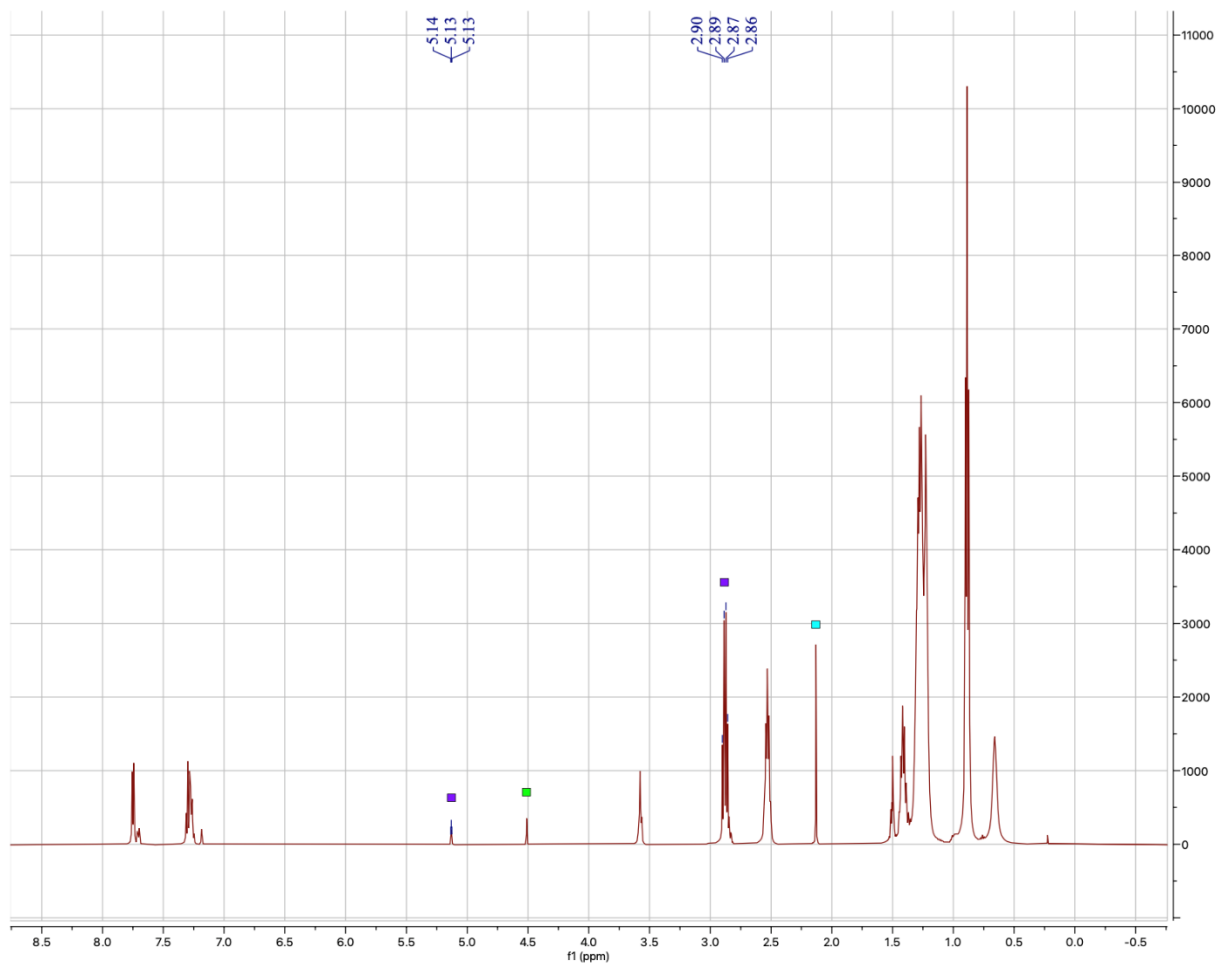


Figure S.8. ^1H NMR spectrum of the reaction between PhSiH_3 and $^3\text{HeNH}_2$ catalyzed by MeMgBr in benzene- d_6 after 1 h.

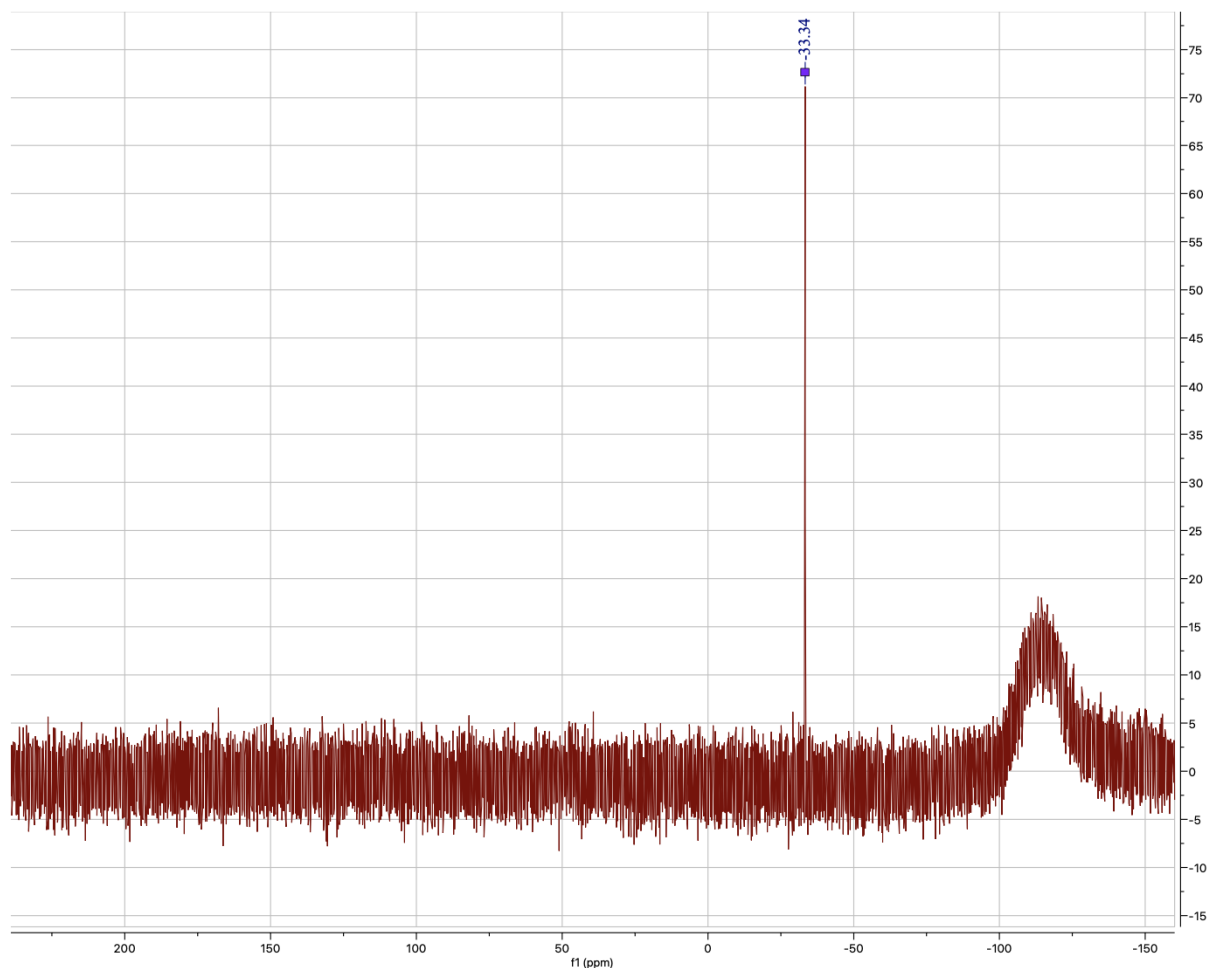


Figure S.9. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of the reaction between PhSiH_3 and $n\text{HeNH}_2$ catalyzed by MeMgBr in benzene- d_6 after 1 h.

S2.6. PhSiH_3 and $i\text{PrNH}_2$

PhSiH_3 (41.0 μL , 3.36×10^{-1} mmol), $i\text{PrNH}_2$ (173.0 μL , 20.16×10^{-1} mmol, 6.0 equiv.), and MeMgBr (15.0 μL , 1.68×10^{-2} mmol, 5.0 mol %) were reacted together in 0.5 mL of benzene- d_6 in the presence of C_6Me_6 standard (50.0 μL , 0.4 M in benzene- d_6). Complete consumption of PhSiH_3 was observed after 1 h. The appearance of a multiplet centered at $\delta = 3.23$ in the ^1H NMR spectrum indicates 70% conversion to $\text{PhSi}(\text{NH}^i\text{Pr})_3$ after 1 h at ambient temperature. Spectra were consistent with previous reports of this compound.^{2,4}

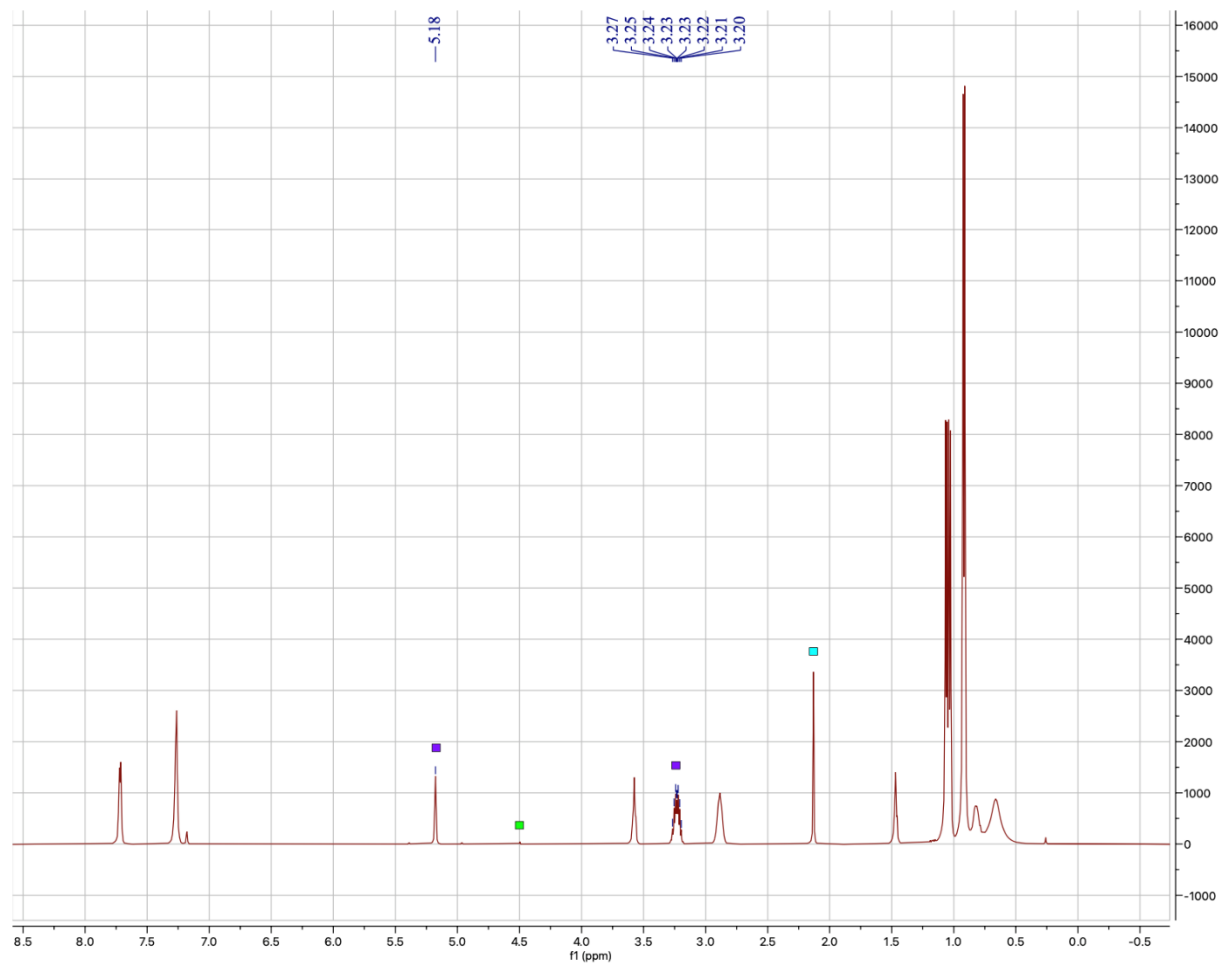


Figure S.10. ^1H NMR spectrum of the reaction between PhSiH_3 and $i\text{PrNH}_2$ catalyzed by MeMgBr in benzene- d_6 after 1 h.

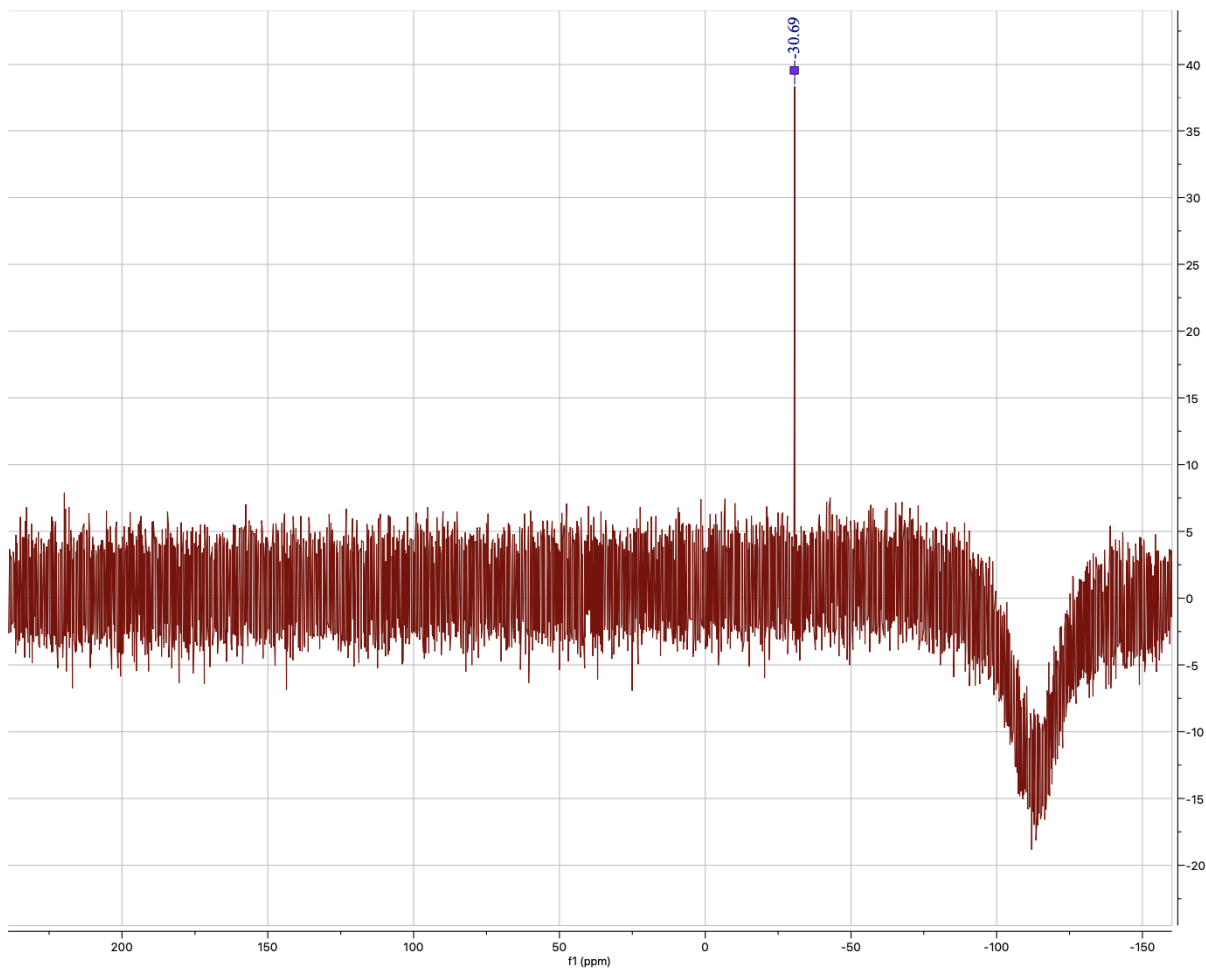


Figure S.11. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of the reaction between PhSiH_3 and $i\text{PrNH}_2$ catalyzed by MeMgBr in benzene- d_6 after 1 h.

S2.7. PhSiH_3 and Et_2NH

PhSiH_3 (41.0 μL , 3.36×10^{-1} mmol), Et_2NH (209.0 μL , 20.16×10^{-1} mmol, 6.0 equiv.), and MeMgBr (15.0 μL , 1.68×10^{-2} mmol, 5.0 mol %) were reacted together in 0.5 mL of benzene- d_6 in the presence of C_6Me_6 standard (50.0 μL , 0.4 M in benzene- d_6). Complete consumption of PhSiH_3 was observed after 1 h. The appearance of two multiplets, one centered between $\delta = 2.92$ and $\delta = 2.93$ and the second centered between $\delta = 2.83$ and $\delta = 2.84$ in the ^1H NMR spectrum, indicates 44% conversion to $\text{PhSiH}(\text{NEt}_2)_2$ and 56% conversion to $\text{PhSiH}_2(\text{NEt}_2)$ after 1 h at ambient temperature. Spectra were consistent with previous reports of this compound.^{2,5,6}

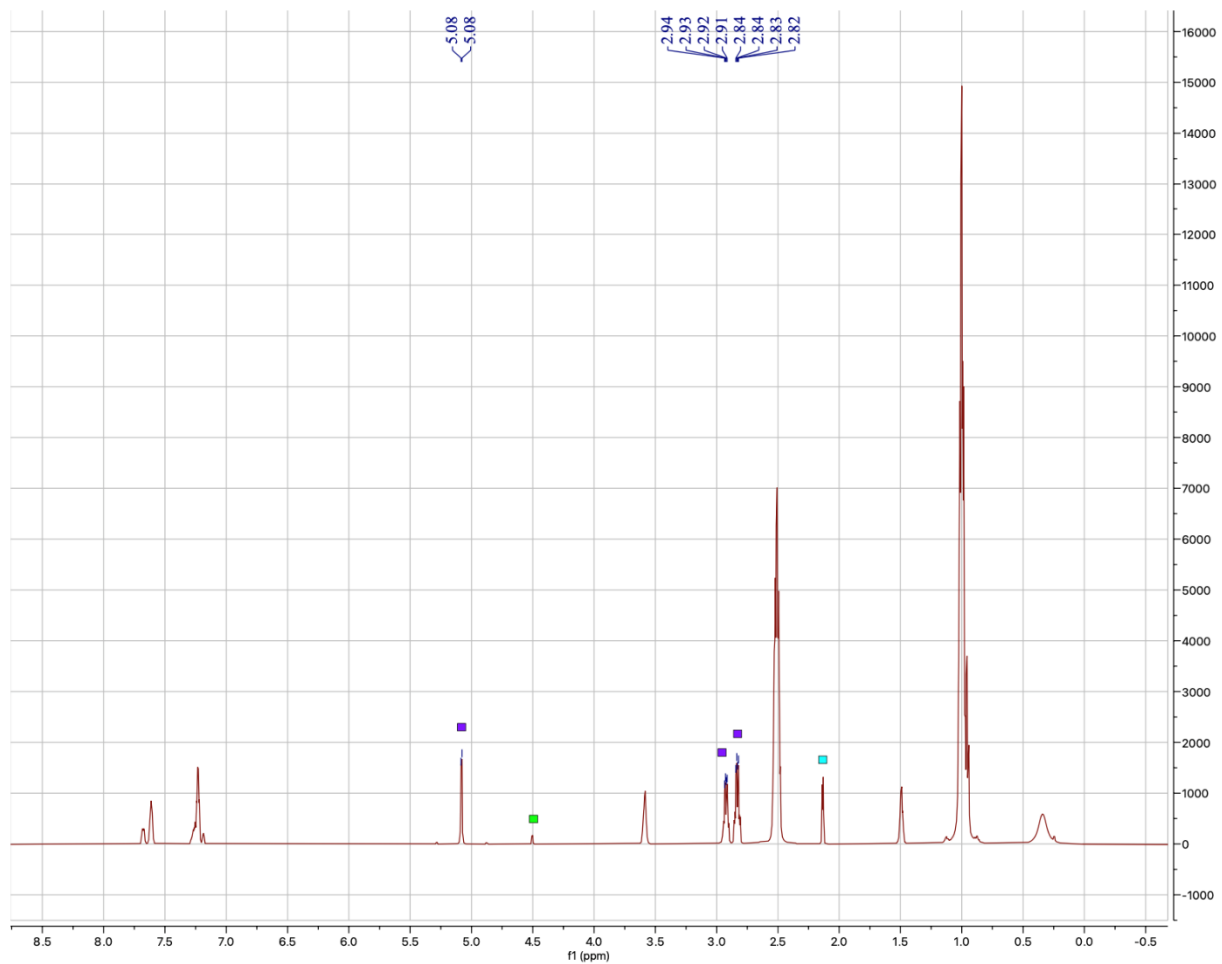


Figure S.12. ^1H NMR spectrum of the reaction between PhSiH_3 and Et_2NH catalyzed by MeMgBr in benzene- d_6 after 1 h.

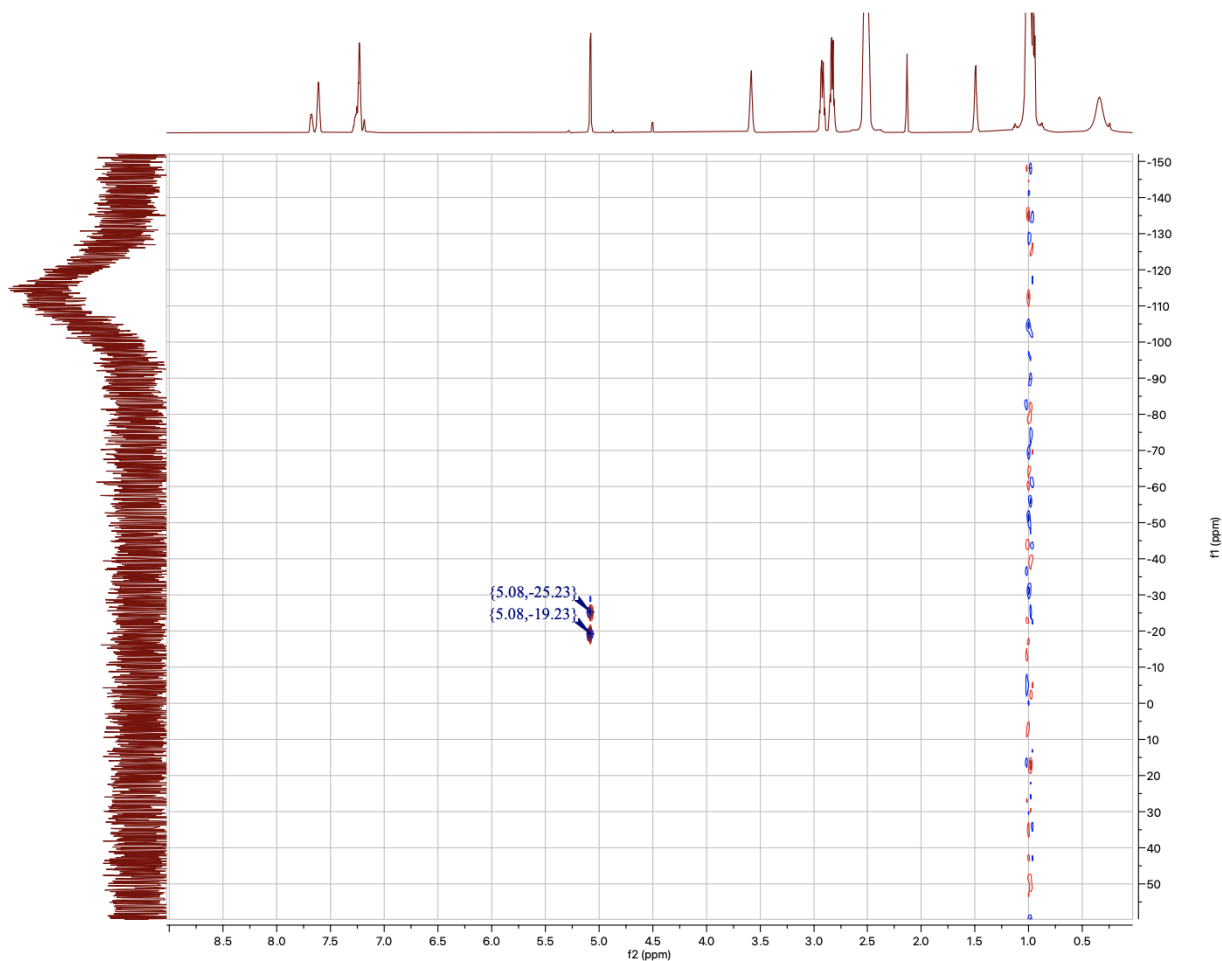


Figure S.13. ^1H - $^{29}\text{Si}\{^1\text{H}\}$ HSQC NMR spectrum of the reaction between PhSiH_3 and Et_2NH catalyzed by MeMgBr in benzene- d_6 after 1 h.

S2.8. PhSiH_3 and PyNH

PhSiH_3 (41.0 μL , 3.36×10^{-1} mmol), PyNH (168.0 μL , 20.16×10^{-1} mmol, 6.0 equiv.), and MeMgBr (15.0 μL , 1.68×10^{-2} mmol, 5.0 mol %) were reacted together in 0.5 mL of benzene- d_6 in the presence of C_6Me_6 standard (50.0 μL , 0.4 M in benzene- d_6). Complete consumption of PhSiH_3 was observed after 1 h. The appearance of a multiplet centered at $\delta = 3.05$ and a peak at $\delta = 5.27$ in the ^1H NMR spectrum, indicates 100% conversion to $\text{PhSiH}(\text{NPy})_2$ after 1 h at ambient temperature.

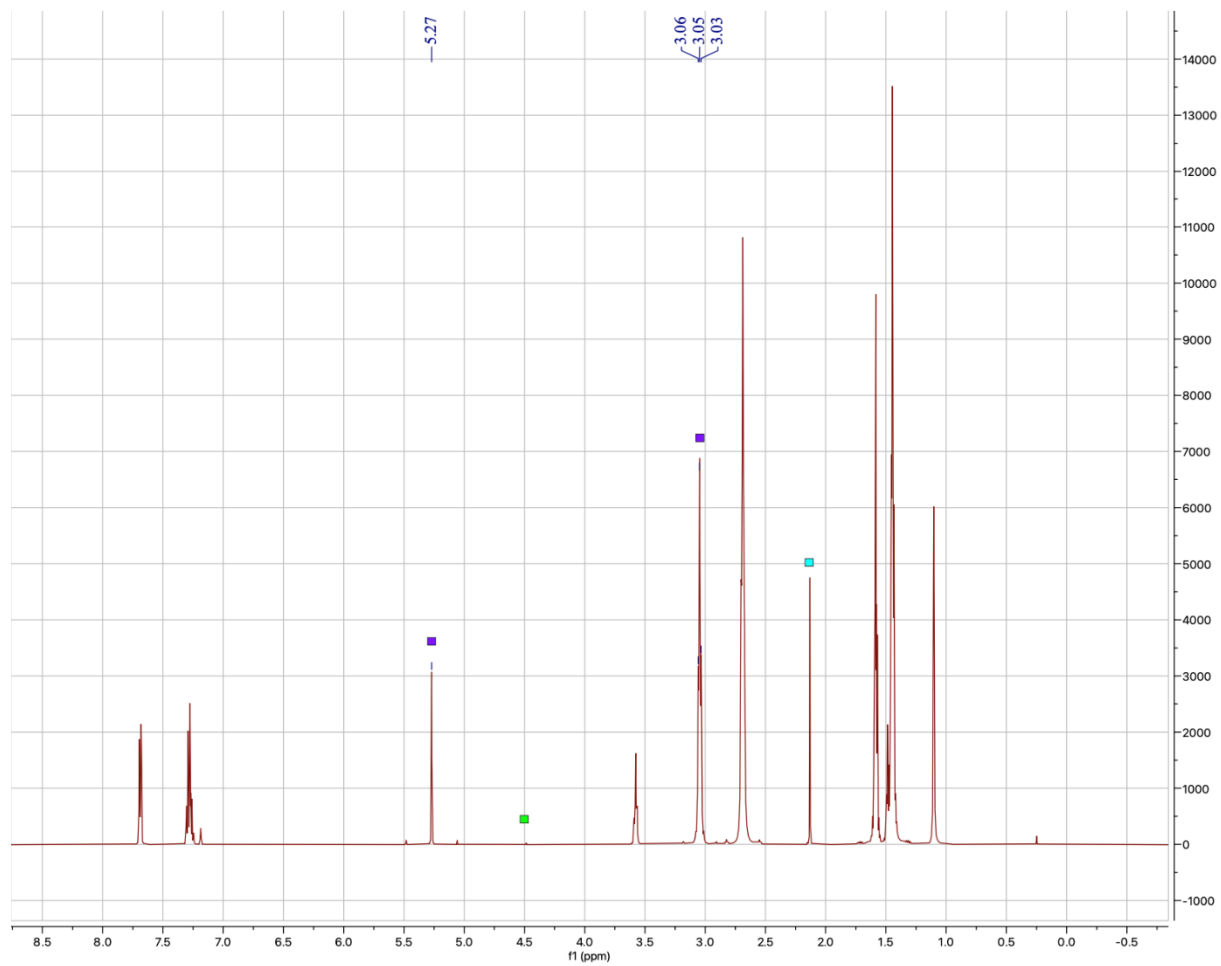


Figure S.14. ¹H NMR spectrum of the reaction between PhSiH₃ and PyNH catalyzed by MeMgBr in benzene-*d*₆ after 1 h.

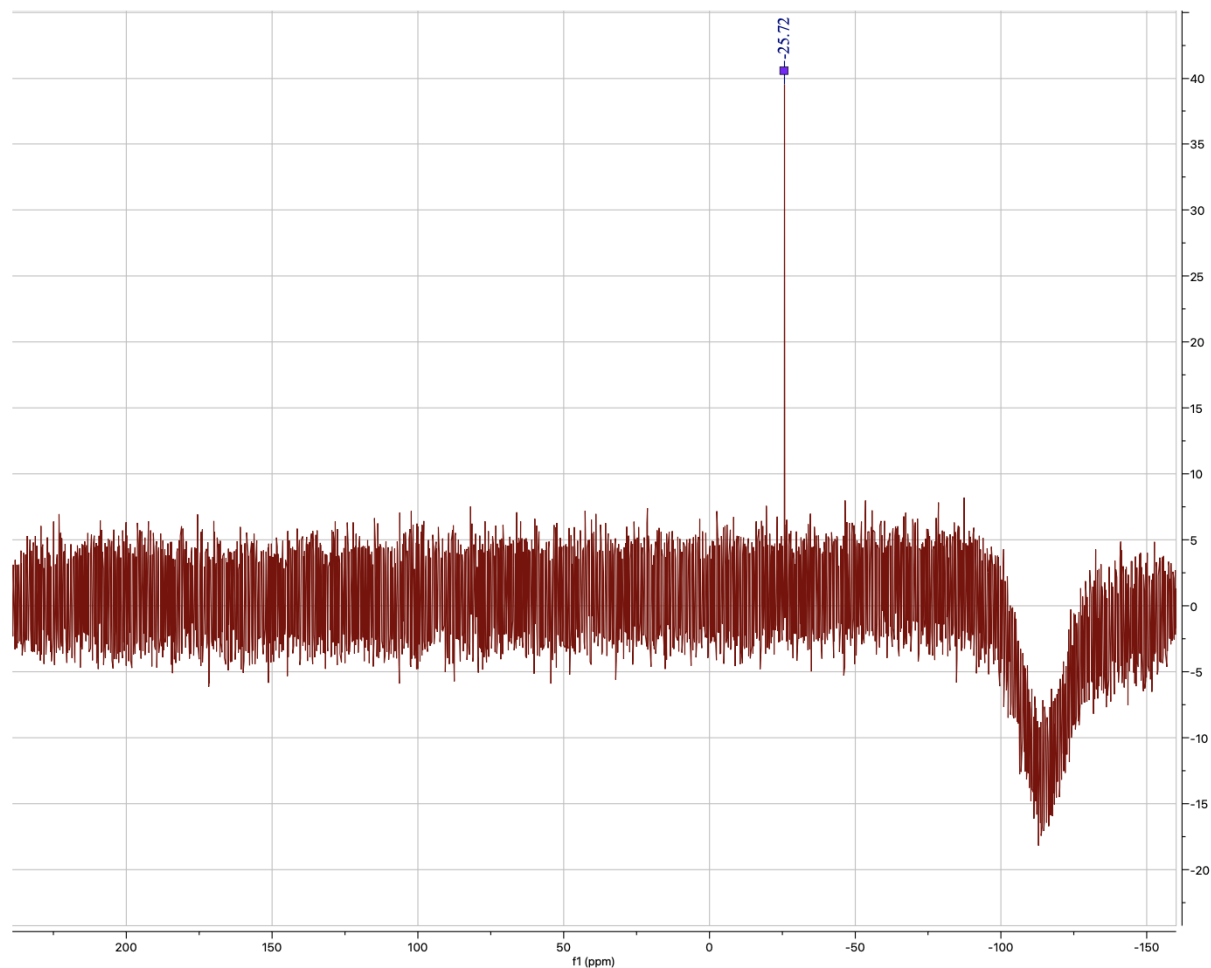


Figure S.15. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of the reaction between PhSiH_3 and PyNH catalyzed by MeMgBr in benzene- d_6 after 1 h.

S2.9. PhSiH_3 and PhNH_2

PhSiH_3 (41.0 μL , 3.36×10^{-1} mmol), PhNH_2 (188.2 μL , 20.16×10^{-1} mmol, 6.0 equiv.), and MeMgBr (15.0 μL , 1.68×10^{-2} mmol, 5.0 mol %) were reacted together in 0.5 mL of benzene- d_6 in the presence of C_6Me_6 standard (50.0 μL , 0.4 M in benzene- d_6). Lack of formation of hydrogen gas and no new peaks in the ^1H NMR spectrum indicate no reactivity.

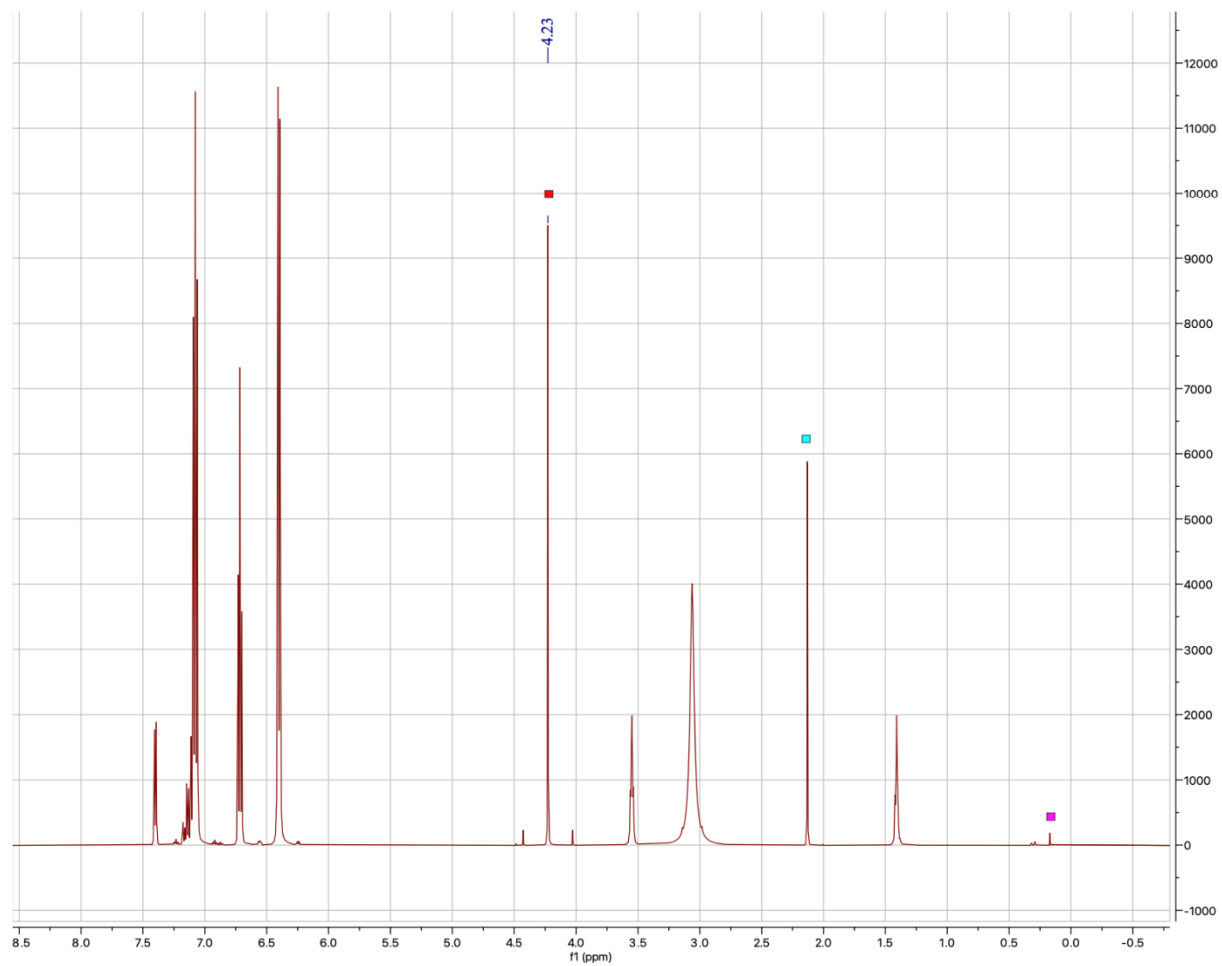


Figure S.16. ^1H NMR spectrum of the reaction between PhSiH_3 and PhNH_2 catalyzed by MeMgBr in benzene- d_6 after 1 h.

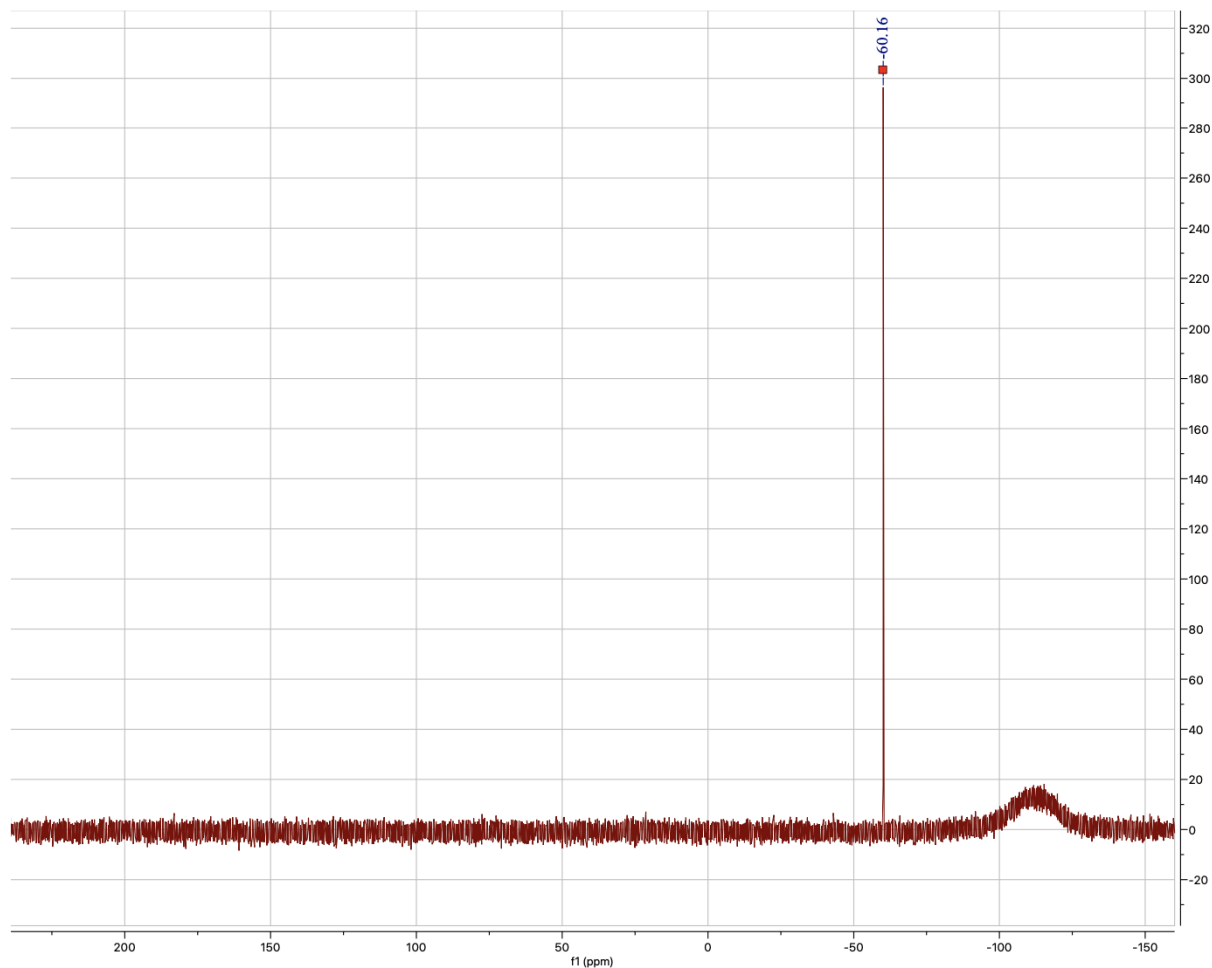


Figure S.17. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of the reaction between PhSiH_3 and PhNH_2 catalyzed by MeMgBr in benzene- d_6 after 1 h.

S2.10. Ph_2SiH_2 and $n\text{BuNH}_2$

Ph_2SiH_2 (62.4 μL , 3.36×10^{-1} mmol), $n\text{BuNH}_2$ (134.2 μL , 13.44×10^{-1} mmol, 4.0 equiv.), and MeMgBr (14.7 μL , 1.68×10^{-2} mmol, 5.0 mol %) were reacted together in 0.5 mL of benzene- d_6 in the presence of C_6Me_6 standard (50.0 μL , 0.4 M in benzene- d_6). Complete consumption of Ph_2SiH_2 was observed after 1 h. After 1 h at ambient temperature, the appearance of a multiplet centered at $\delta = 2.91$ in the ^1H NMR spectrum indicates 20% conversion to $\text{Ph}_2\text{Si}(\text{NH}^n\text{Bu})_2$ and the appearance of a multiplet centered between at $\delta = 2.76$ and $\delta = 2.77$ and a doublet centered at $\delta = 5.56$ in the ^1H NMR spectrum, indicates 80% conversion to $\text{Ph}_2\text{SiH}(\text{NH}^n\text{Bu})$.

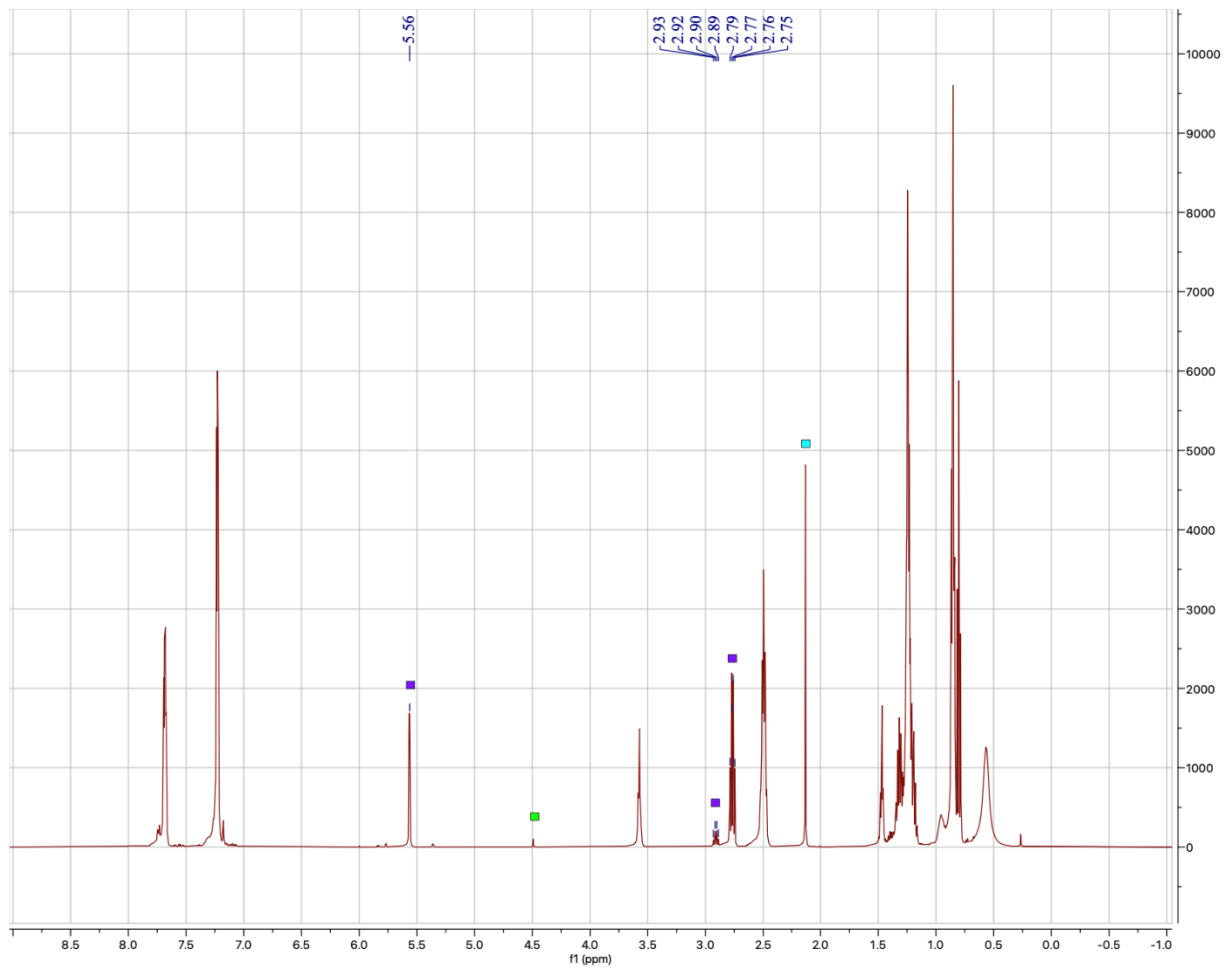


Figure S.18. ¹H NMR spectrum of the reaction between Ph₂SiH₂ and ⁿBuNH₂ catalyzed by MeMgBr in benzene-*d*₆ after 1 h.

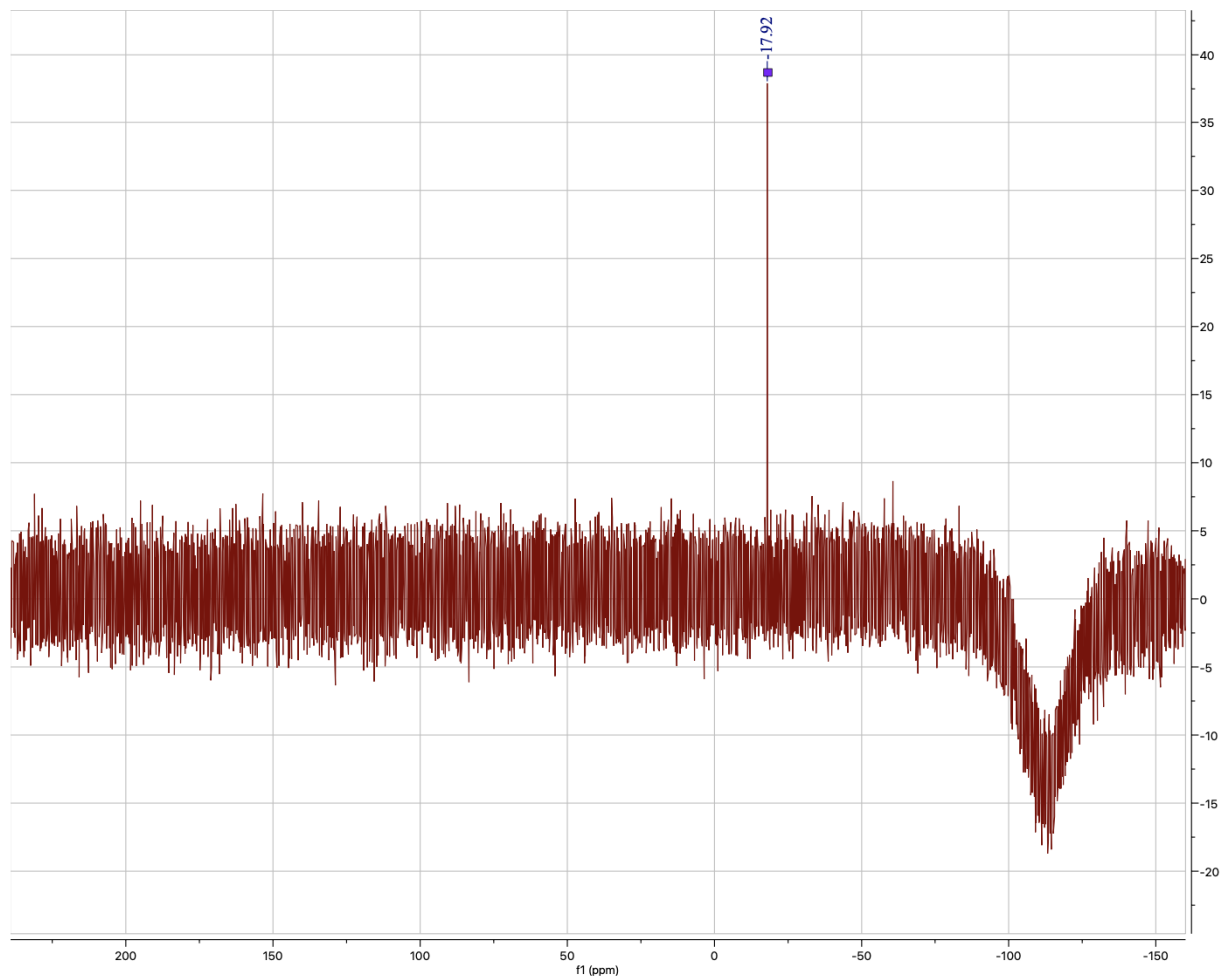


Figure S.19. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of the reaction between Ph_2SiH_2 and $^t\text{BuNH}_2$ catalyzed by MeMgBr in benzene- d_6 after 1 h.

S2.11. Ph_2SiH_2 and $^t\text{BuNH}_2$

Ph_2SiH_2 (62.4 μL , 3.36×10^{-1} mmol), $^t\text{BuNH}_2$ (141.2 μL , 13.44×10^{-1} mmol, 4.0 equiv.), and MeMgBr (14.7 μL , 1.68×10^{-2} mmol, 5.0 mol %) were reacted together in 0.5 mL of benzene- d_6 in the presence of C_6Me_6 standard (50.0 μL , 0.4 M in benzene- d_6). Incomplete consumption of Ph_2SiH_2 was observed after 1 h, as determined by the presence of the SiH peak at $\delta = 5.05$ in the ^1H NMR spectrum. After 1 h at ambient temperature, the appearance of a peak at $\delta = 1.13$ in the ^1H NMR spectrum indicates 50% conversion to $\text{Ph}_2\text{SiH}(\text{NH}^t\text{Bu})$. Spectra were consistent with previous reports of these compounds.^{2,7}

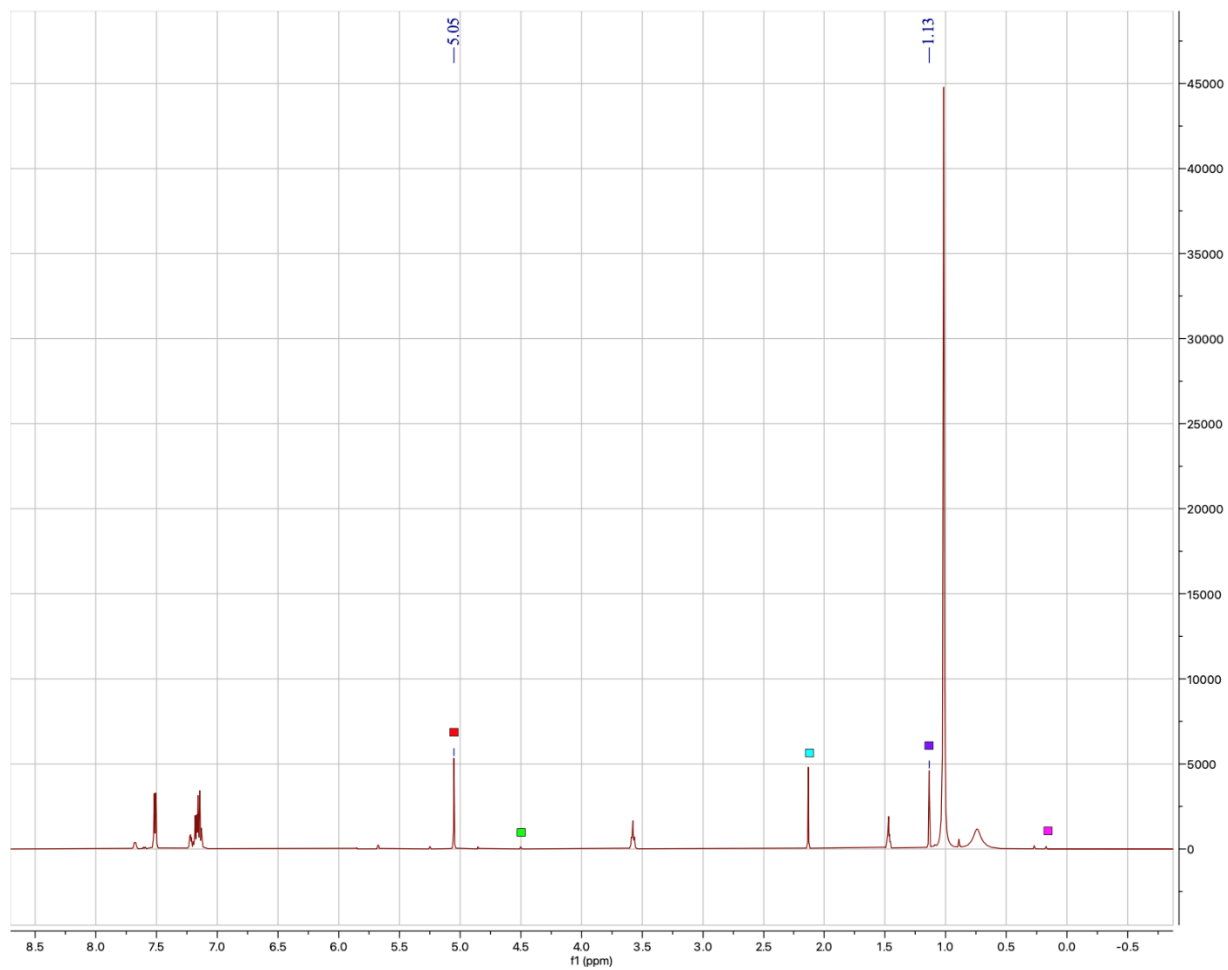


Figure S.20. ¹H NMR spectrum of the reaction between Ph₂SiH₂ and ^tBuNH₂ catalyzed by MeMgBr in benzene-*d*₆ after 1 h.

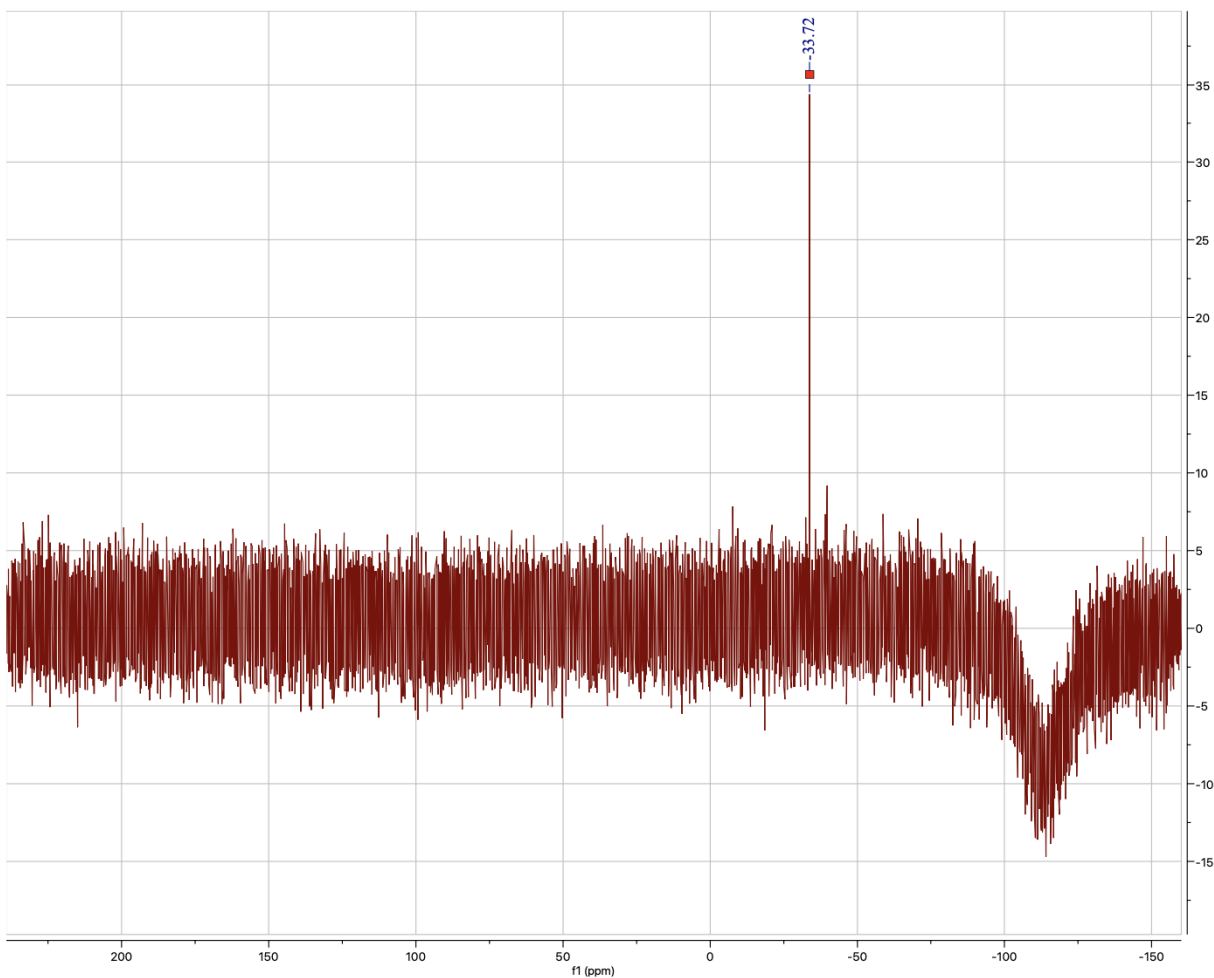


Figure S.21. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of the reaction between Ph_2SiH_2 and $t\text{BuNH}_2$ catalyzed by MeMgBr in benzene- d_6 after 1 h.

S2.12. Ph_2SiH_2 and PyNH

Ph_2SiH_2 (62.4 μL , 3.36×10^{-1} mmol), PyNH (112.2 μL , 13.44×10^{-1} mmol, 4.0 equiv.), and MeMgBr (14.7 μL , 1.68×10^{-2} mmol, 5.0 mol %) were reacted together in 0.5 mL of benzene- d_6 in the presence of C_6Me_6 standard (50.0 μL , 0.4 M in benzene- d_6). Complete consumption of Ph_2SiH_2 was observed after 1 h. The appearance of a multiplet centered at $\delta = 3.01$ and a peak at $\delta = 5.60$ in the ^1H NMR spectrum, indicates 100% conversion to $\text{Ph}_2\text{SiH}(\text{NPy})$ after 1 h at ambient temperature.

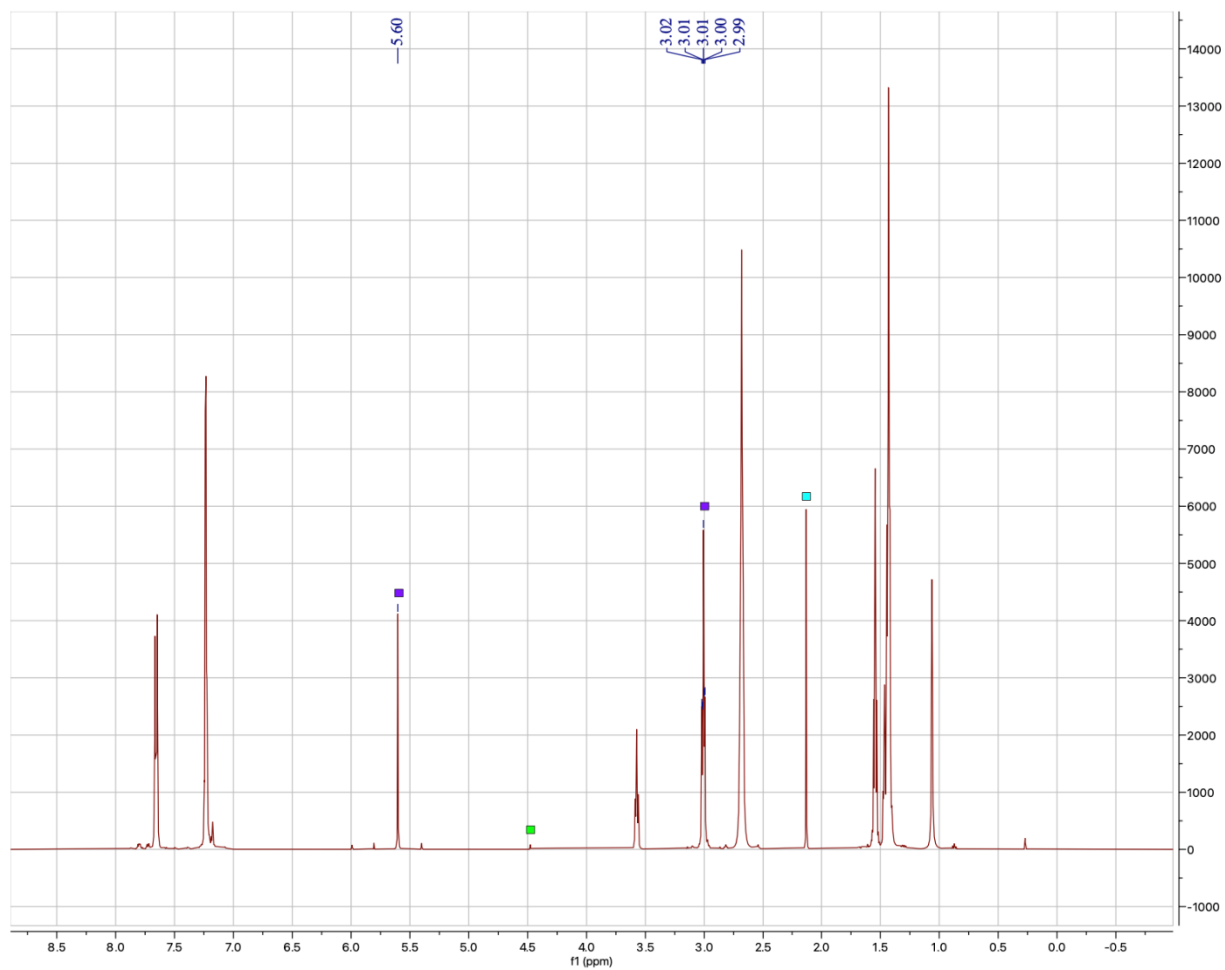


Figure S.22. ^1H NMR spectrum of the reaction between Ph_2SiH_2 and PyNH catalyzed by MeMgBr in benzene- d_6 after 1 h.

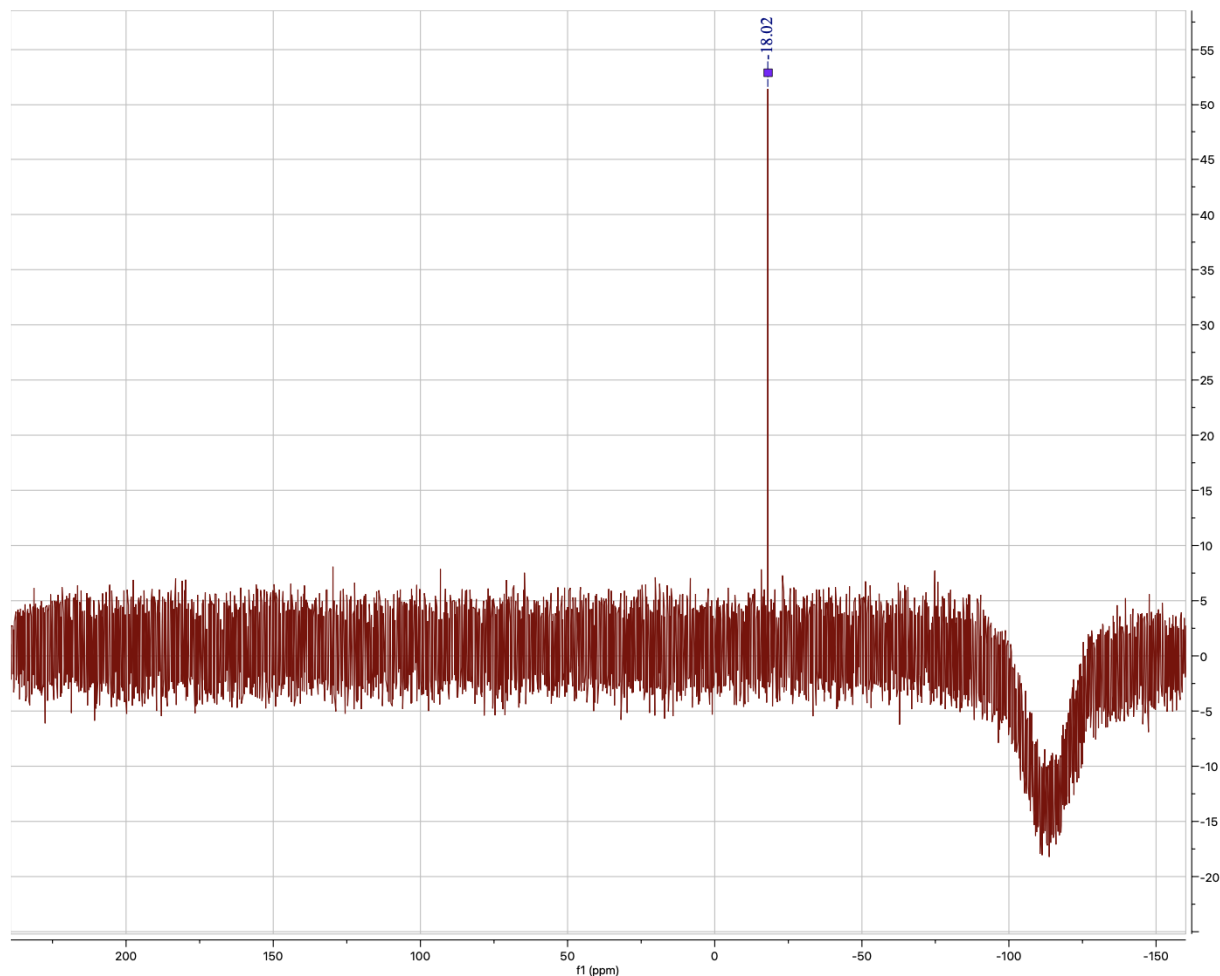


Figure S.23. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of the reaction between Ph_2SiH_2 and PyNH catalyzed by MeMgBr in benzene- d_6 after 1 h.

S2.13. Ph_2SiH_2 and Et_2NH

Ph_2SiH_2 (62.4 μL , 3.36×10^{-1} mmol), Et_2NH (139.0 μL , 13.44×10^{-1} mmol, 4.0 equiv.), and MeMgBr (14.7 μL , 1.68×10^{-2} mmol, 5.0 mol %) were reacted together in 0.5 mL of benzene- d_6 in the presence of C_6Me_6 standard (50.0 μL , 0.4 M in benzene- d_6). Incomplete consumption of Ph_2SiH_2 was observed after 1 h, as determined by the presence of the SiH peak at $\delta = 5.05$ in the ^1H NMR spectrum. The appearance of a diagnostic quartet centered between $\delta = 2.90$ and $\delta = 2.91$ in the ^1H NMR spectrum indicates 27% conversion to $\text{Ph}_2\text{SiH}(\text{NEt}_2)$ after 1 h at ambient temperature. Spectra were consistent with previous reports of this compound.^{2,6}

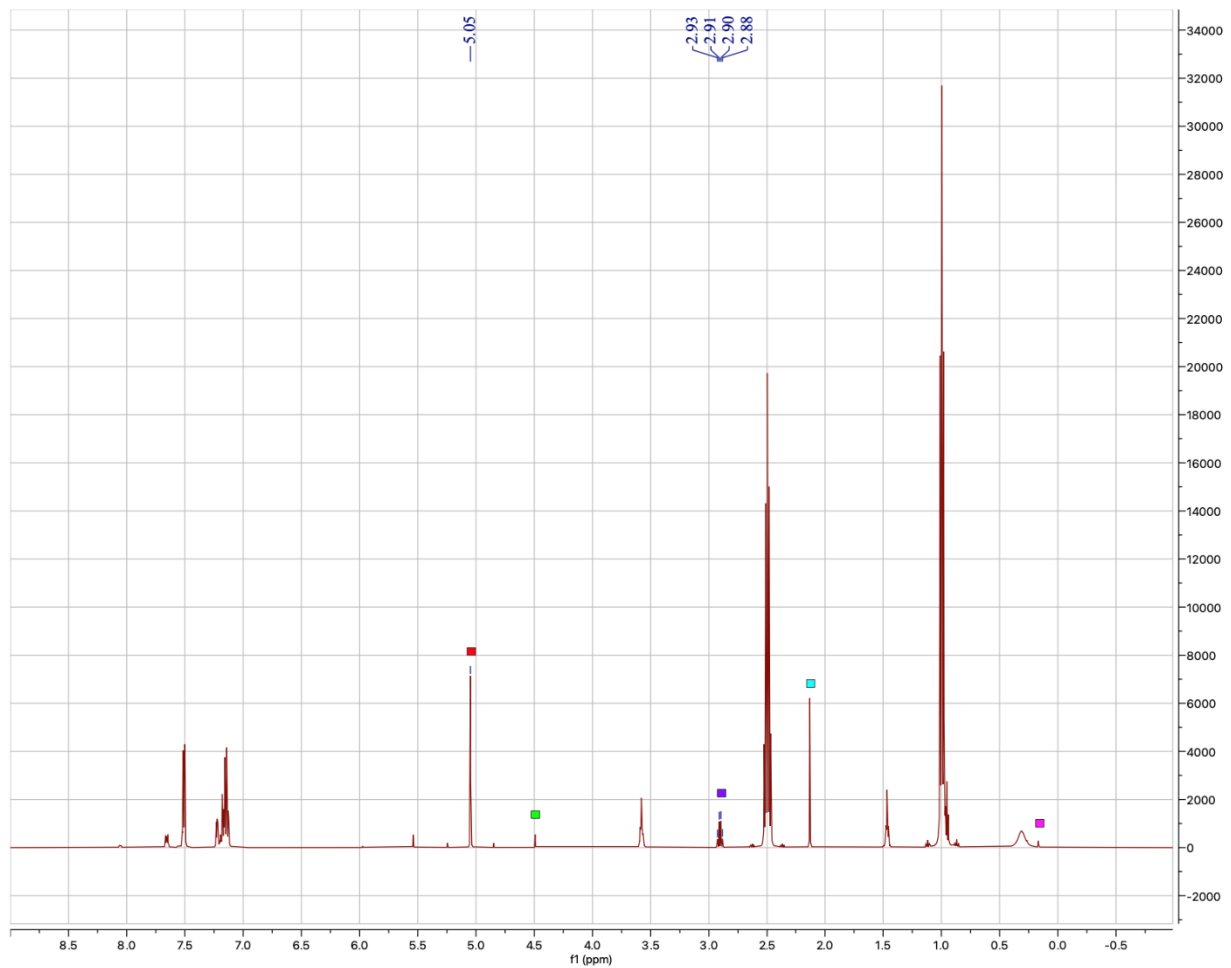


Figure S.24. ^1H NMR spectrum of the reaction between Ph_2SiH_2 and Et_2NH catalyzed by MeMgBr in benzene- d_6 after 1 h.

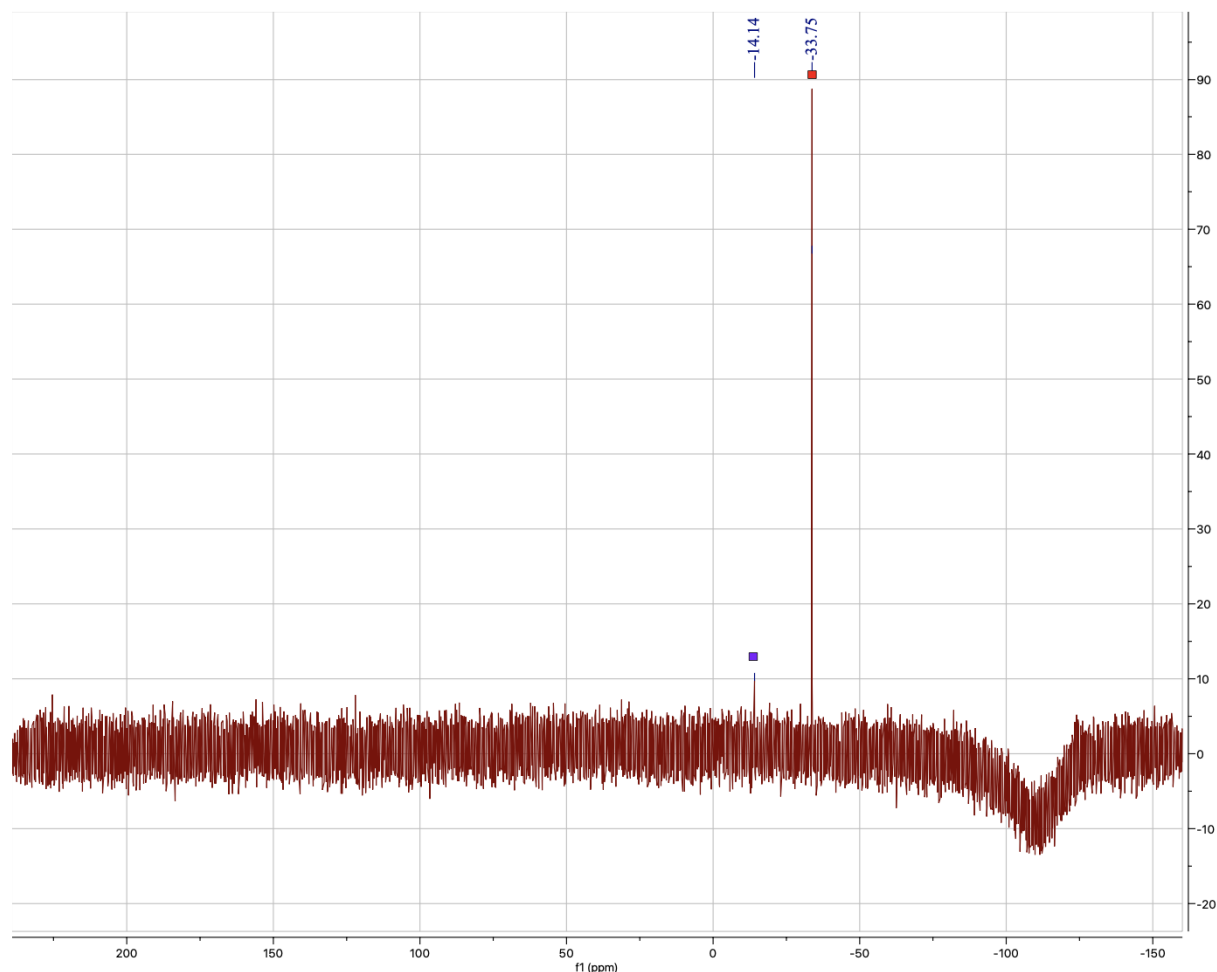


Figure S.25. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of the reaction between Ph_2SiH_2 and Et_2NH catalyzed by MeMgBr in benzene- d_6 after 1 h.

S2.14. PhMeSiH_2 and $n\text{BuNH}_2$

PhMeSiH_2 ($46.1 \mu\text{L}$, $3.36 \times 10^{-1} \text{ mmol}$), $n\text{BuNH}_2$ ($134.2 \mu\text{L}$, $13.44 \times 10^{-1} \text{ mmol}$, 4.0 equiv.), and MeMgBr ($14.7 \mu\text{L}$, $1.68 \times 10^{-2} \text{ mmol}$, 5.0 mol %) were reacted together in 0.5 mL of benzene- d_6 in the presence of C_6Me_6 standard ($50.0 \mu\text{L}$, 0.4 M in benzene- d_6). Complete consumption of PhMeSiH_2 was observed after 1 h. The appearance of a multiplet centered at $\delta = 2.81$ and a quartet centered at $\delta = 2.69$ in the ^1H NMR spectrum indicates 45% conversion to $\text{PhMeSi}(\text{NH}n\text{Bu})_2$ and 55% conversion to $\text{PhMeSiH}(\text{NH}n\text{Bu})$ after 1 h at ambient temperature.

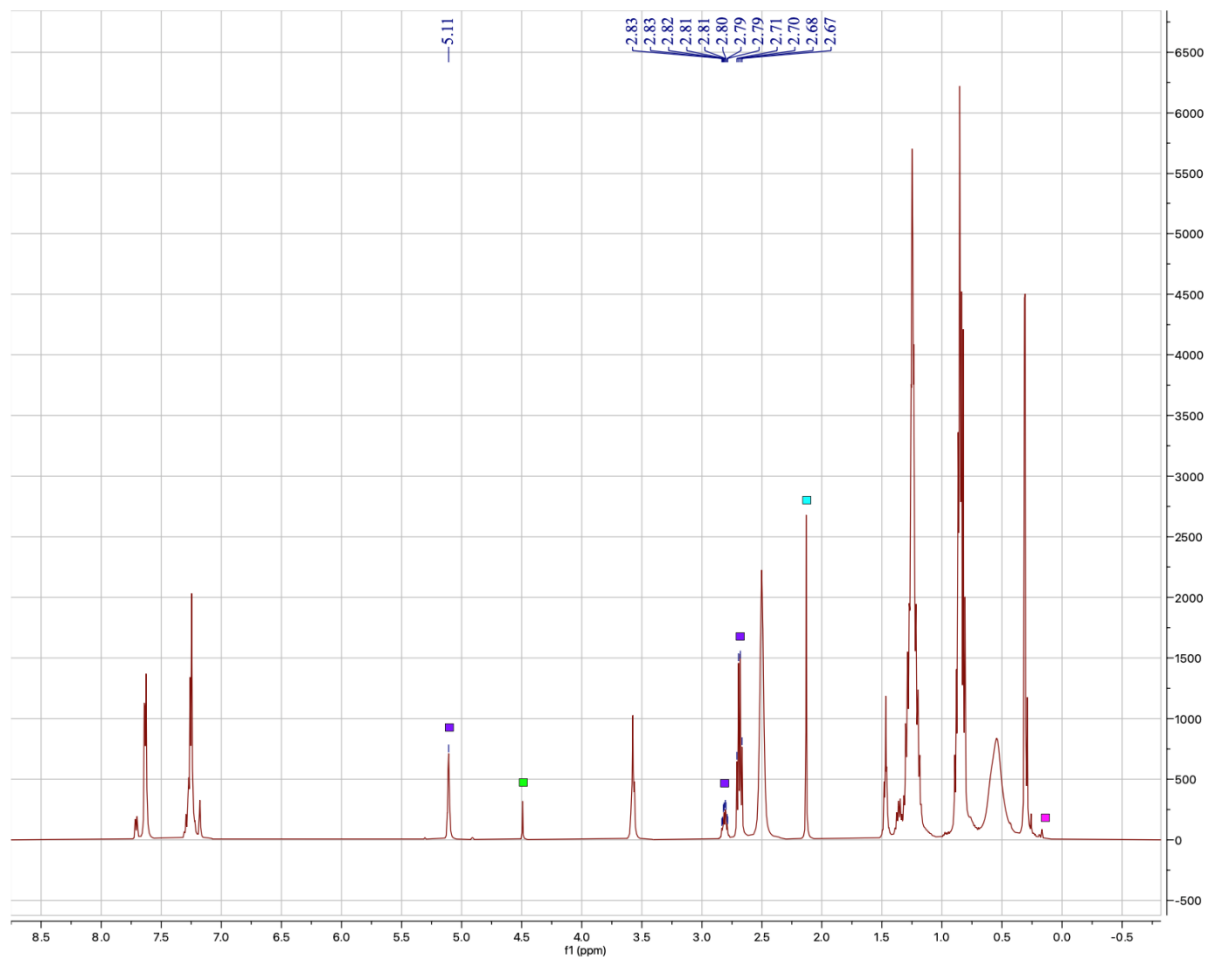


Figure S.26. ^1H NMR spectrum of the reaction between PhMeSiH_2 and $t\text{BuNH}_2$ catalyzed by MeMgBr in benzene- d_6 after 1 h.

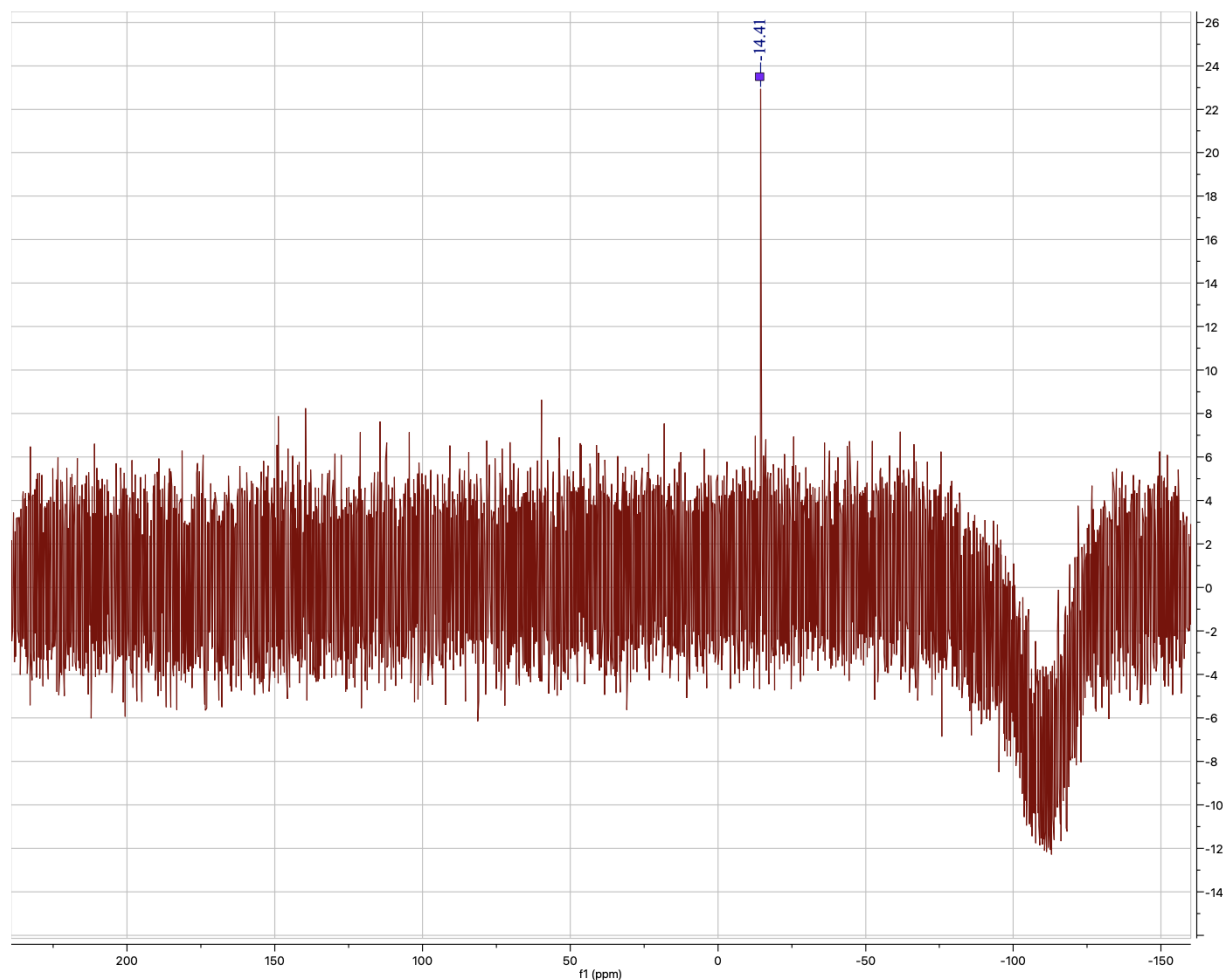


Figure S.27. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of the reaction between PhMeSiH_2 and $t\text{BuNH}_2$ catalyzed by MeMgBr in benzene- d_6 after 1 h.

S2.15. PhMeSiH_2 and $t\text{BuNH}_2$

PhMeSiH_2 ($46.1 \mu\text{L}$, $3.36 \times 10^{-1} \text{ mmol}$), $t\text{BuNH}_2$ ($141.2 \mu\text{L}$, $13.44 \times 10^{-1} \text{ mmol}$, 4.0 equiv.), and MeMgBr ($14.7 \mu\text{L}$, $1.68 \times 10^{-2} \text{ mmol}$, 5.0 mol %) were reacted together in 0.5 mL of benzene- d_6 in the presence of C_6Me_6 standard ($50.0 \mu\text{L}$, 0.4 M in benzene- d_6). Incomplete consumption of PhMeSiH_2 was observed after 1 h, as determined by the presence of the SiH peak at $\delta = 4.45$ in the ^1H NMR spectrum. After 1 h at ambient temperature, the appearance of a peak at $\delta = 1.10$ in the ^1H NMR spectrum indicates 29% conversion to $\text{PhMeSiH}(\text{NH}t\text{Bu})$. Spectra were consistent with previous reports of these compounds.^{2,7}

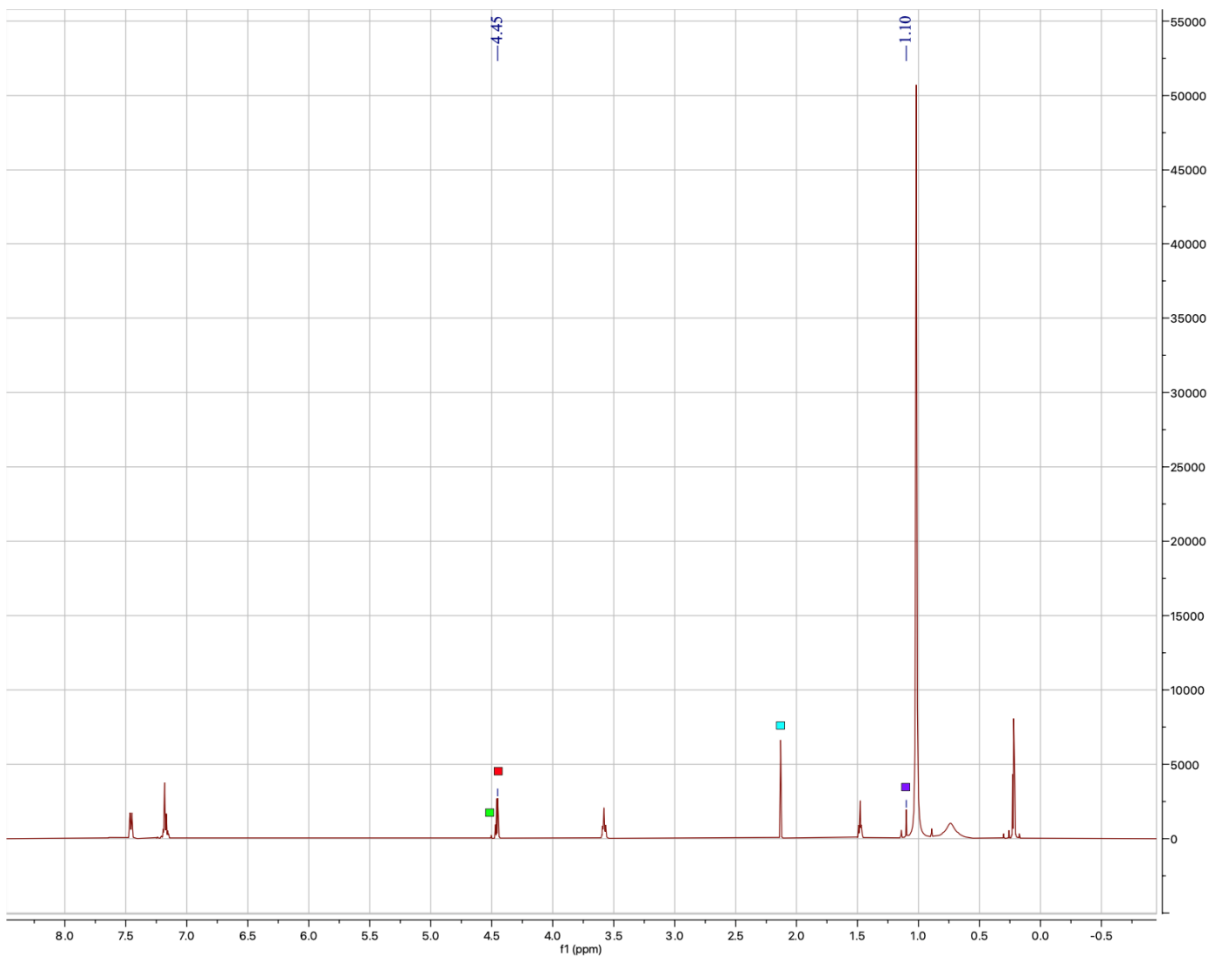


Figure S.28. ^1H NMR spectrum of the reaction between PhMeSiH_2 and $t\text{BuNH}_2$ catalyzed by MeMgBr in benzene- d_6 after 1 h.

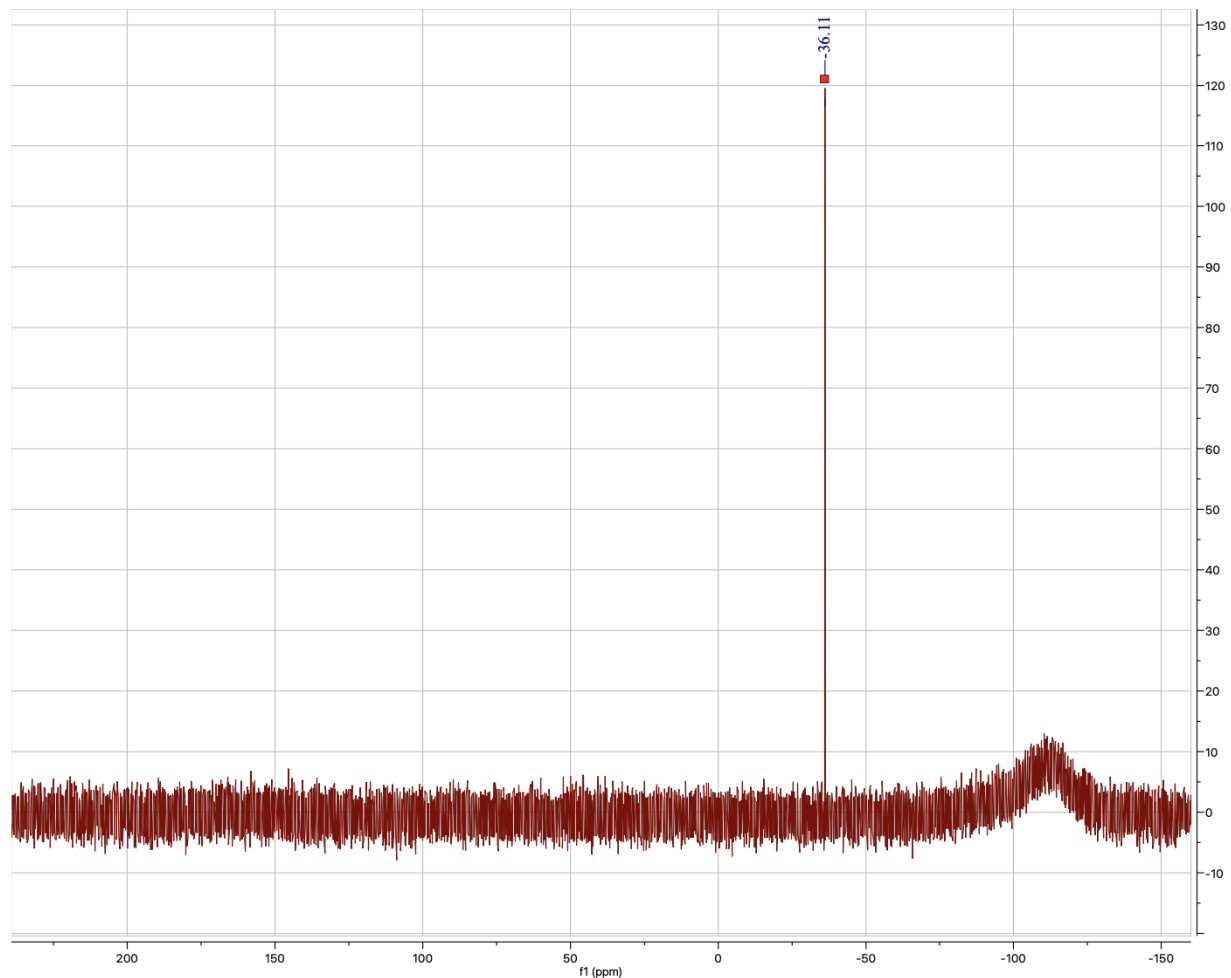


Figure S.29. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of the reaction between PhMeSiH_2 and $^t\text{BuNH}_2$ catalyzed by MeMgBr in benzene- d_6 after 1 h.

S2.16. PhMeSiH_2 and PyNH

PhMeSiH_2 (46.1 μL , 3.36×10^{-1} mmol), PyNH (112.2 μL , 13.44×10^{-1} mmol, 4.0 equiv.), and MeMgBr (14.7 μL , 1.68×10^{-2} mmol, 5.0 mol %) were reacted together in 0.5 mL of benzene- d_6 in the presence of C_6Me_6 standard (50.0 μL , 0.4 M in benzene- d_6). Complete consumption of PhMeSiH_2 was observed after 1 h. The appearance of a multiplet centered between $\delta = 2.93$ and $\delta = 2.94$ and a quartet centered between $\delta = 5.13$ and $\delta = 5.14$ in the ^1H NMR spectrum, indicates 100% conversion to $\text{PhMeSiH}(\text{NPy})$ after 1 h at ambient temperature.

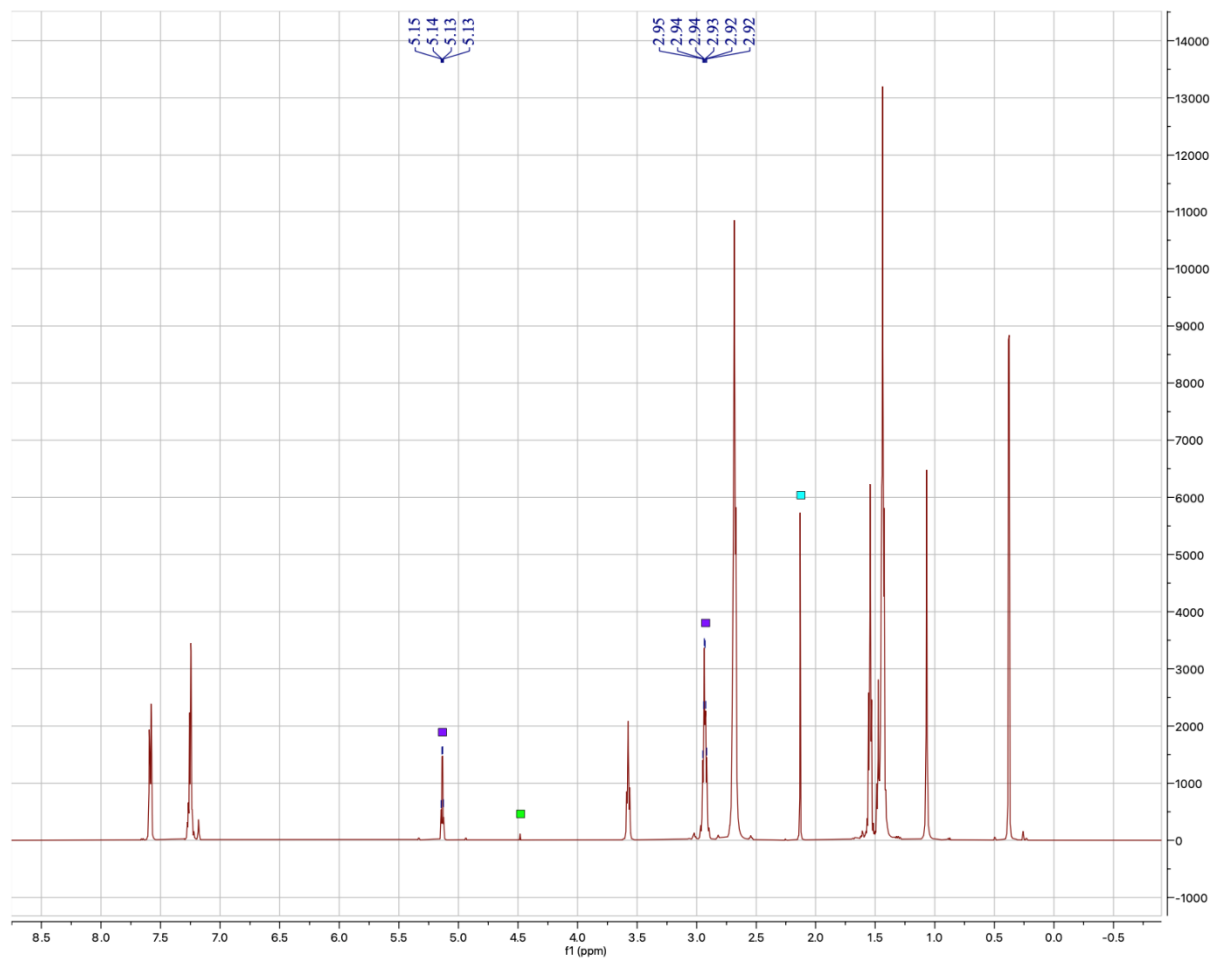


Figure S.30. ^1H NMR spectrum of the reaction between PhMeSiH_2 and PyNH catalyzed by MeMgBr in benzene- d_6 after 1 h.

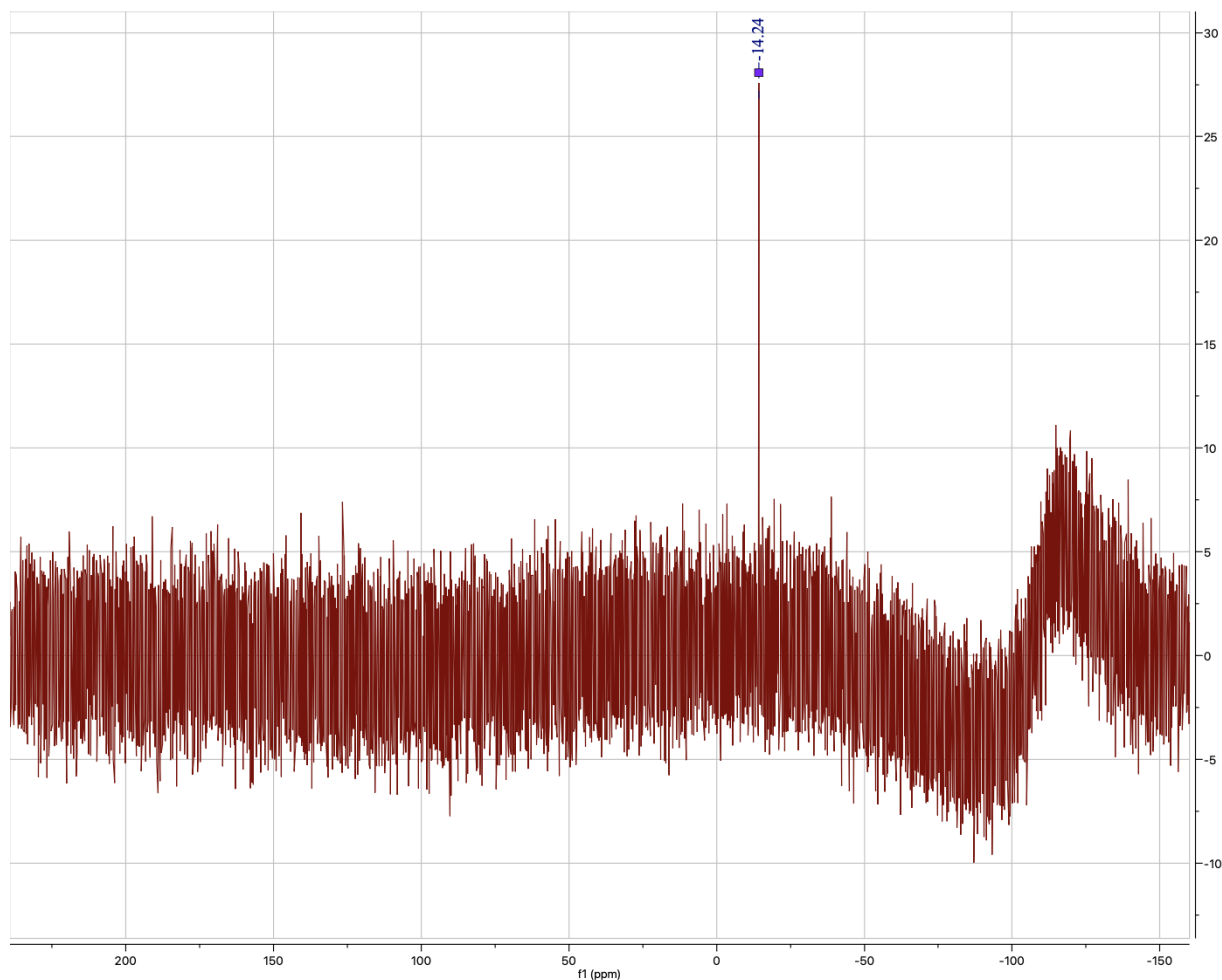


Figure S.31. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of the reaction between PhMeSiH_2 and PyNH catalyzed by MeMgBr in benzene- d_6 after 1 h.

S2.17. PhMeSiH_2 and Et_2NH

PhMeSiH_2 ($46.1 \mu\text{L}$, 3.36×10^{-1} mmol), Et_2NH ($139.0 \mu\text{L}$, 13.44×10^{-1} mmol, 4.0 equiv.), and MeMgBr ($14.7 \mu\text{L}$, 1.68×10^{-2} mmol, 5.0 mol %) were reacted together in 0.5 mL of benzene- d_6 in the presence of C_6Me_6 standard ($50.0 \mu\text{L}$, 0.4 M in benzene- d_6). Incomplete consumption of PhMeSiH_2 was observed after 1 h, as determined by the presence of the SiH peak at $\delta = 4.45$ in the ^1H NMR spectrum. The appearance of a diagnostic quartet centered between $\delta = 2.81$ and $\delta = 2.82$ in the ^1H NMR spectrum indicates 60% conversion to $\text{PhMeSiH}(\text{NEt}_2)$ after 1 h at ambient temperature. Spectra were consistent with previous reports of this compound.^{2,6}

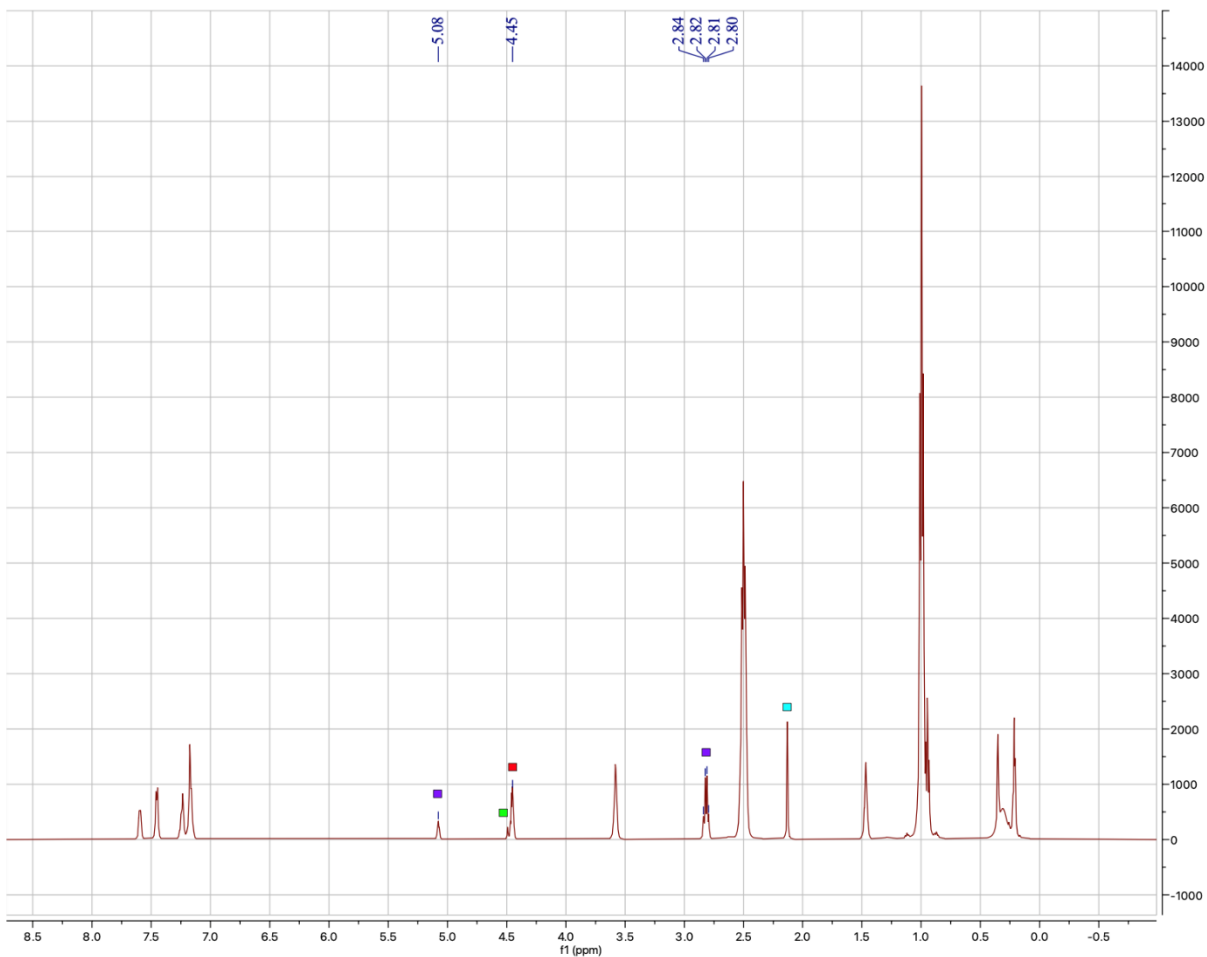


Figure S.32. ¹H NMR spectrum of the reaction between PhMeSiH₂ and Et₂NH catalyzed by MeMgBr in benzene-*d*₆ after 1 h.

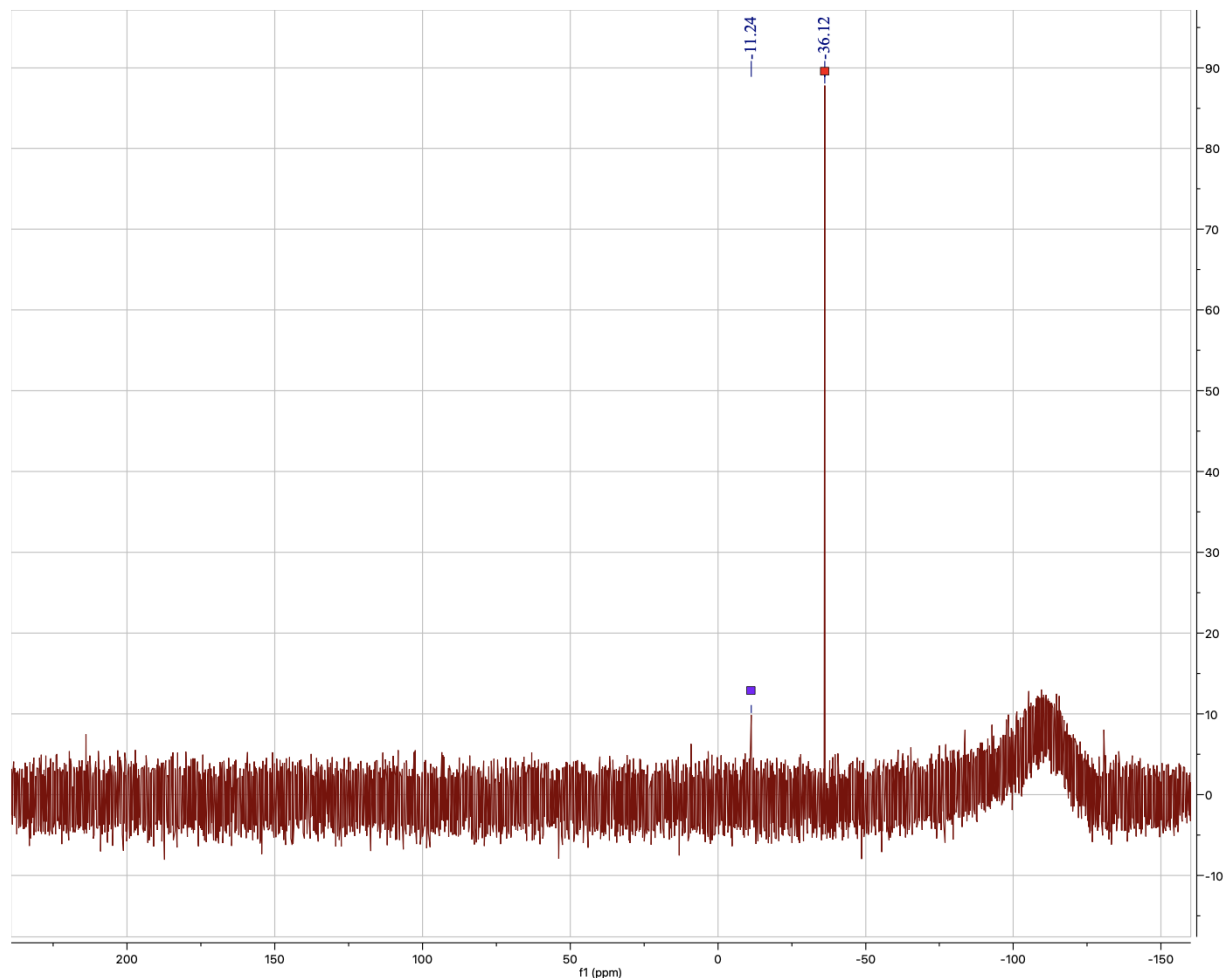


Figure S.33. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of the reaction between PhMeSiH_2 and Et_2NH catalyzed by MeMgBr in benzene- d_6 after 1 h.

S2.18. Ph_3SiH and $^t\text{BuNH}_2$

Ph_3SiH (100 μL , 3.36 M in benzene- d_6 , 3.36×10^{-1} mmol), $^t\text{BuNH}_2$ (70.6 μL , 6.72×10^{-1} mmol, 2.0 equiv.), and MeMgBr (14.7 μL , 1.68×10^{-2} mmol, 5.0 mol %) were reacted together in 0.5 mL of benzene- d_6 in the presence of C_6Me_6 standard (50.0 μL , 0.4 M in benzene- d_6). Lack of formation of hydrogen gas and no new peaks in the ^1H NMR spectrum indicate no reactivity despite heating overnight at 40 $^\circ\text{C}$.

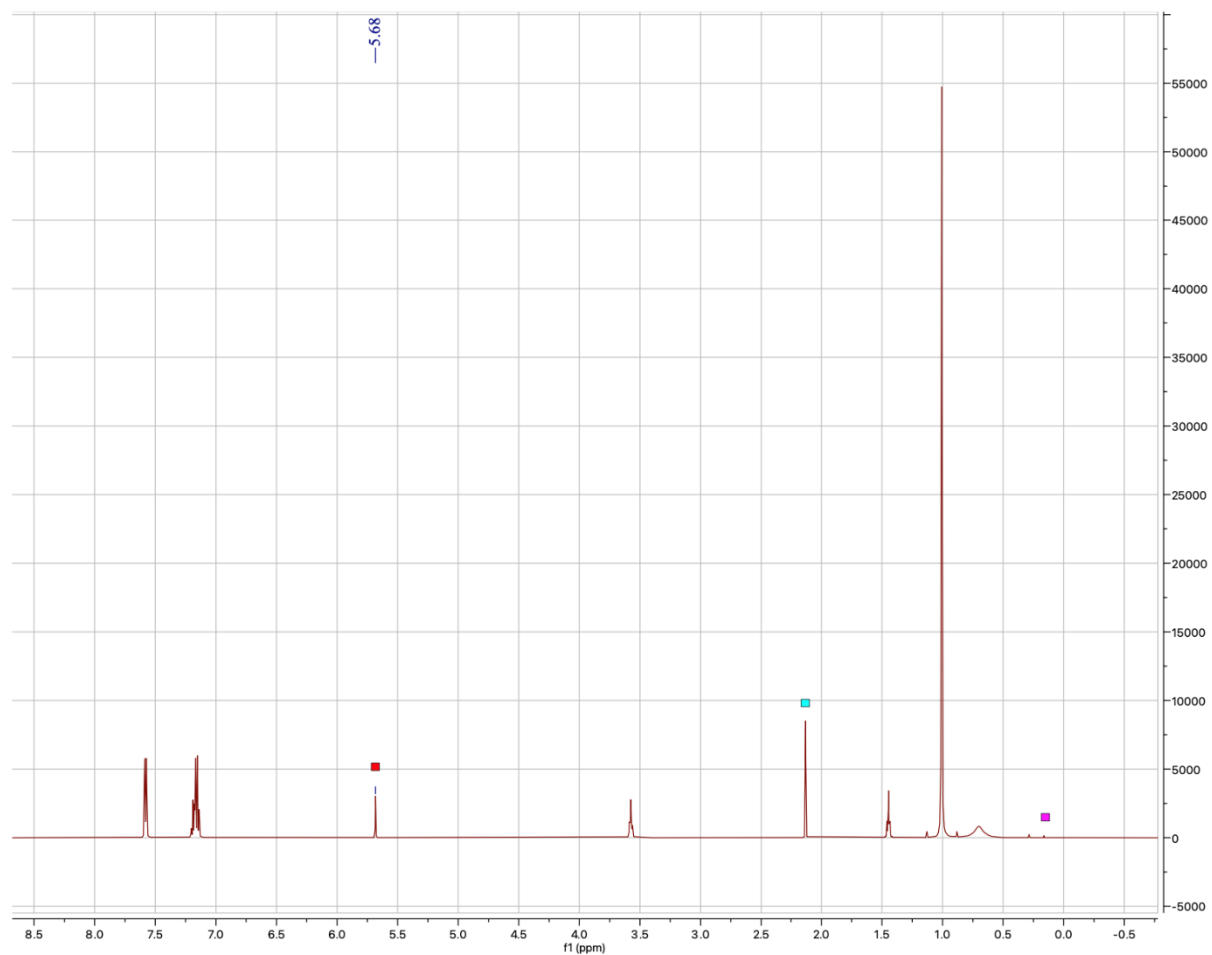


Figure S.36. ^1H NMR spectrum of the reaction between Ph_3SiH and $t\text{BuNH}_2$ catalyzed by MeMgBr in benzene- d_6 after overnight heating at $40\text{ }^\circ\text{C}$.

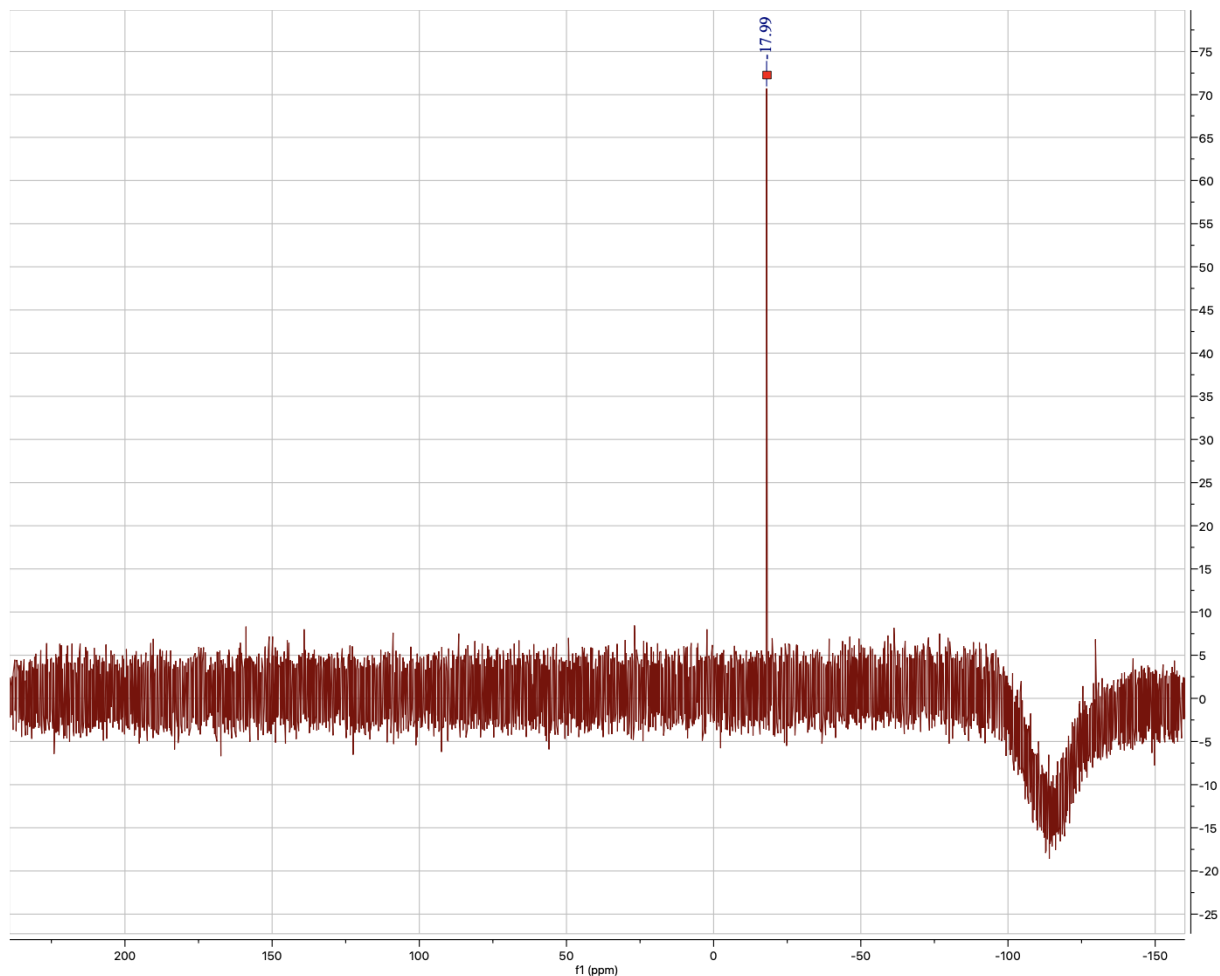


Figure S.37. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of the reaction between Ph_3SiH and $^t\text{BuNH}_2$ catalyzed by MeMgBr in benzene- d_6 after overnight heating at $40\text{ }^\circ\text{C}$.

S2.19. Ph_3SiH and $^t\text{BuNH}_2$

Ph_3SiH ($100\ \mu\text{L}$, $3.36\ \text{M}$ in benzene- d_6 , $3.36 \times 10^{-1}\ \text{mmol}$), $^t\text{BuNH}_2$ ($67.0\ \mu\text{L}$, $6.72 \times 10^{-1}\ \text{mmol}$, 2.0 equiv.), and MeMgBr ($14.7\ \mu\text{L}$, $1.68 \times 10^{-2}\ \text{mmol}$, 5.0 mol %) were reacted together in $0.5\ \text{mL}$ of benzene- d_6 in the presence of C_6Me_6 standard ($50.0\ \mu\text{L}$, $0.4\ \text{M}$ in benzene- d_6). Incomplete consumption of Ph_3SiH was observed after overnight heating to $40\text{ }^\circ\text{C}$, as determined by the presence of the SiH peak at $\delta = 5.68$ in the ^1H NMR spectrum. The appearance of a diagnostic quartet centered at $\delta = 2.85$ in the ^1H NMR spectrum indicates 63% conversion to $\text{Ph}_3\text{Si}(\text{NH}^t\text{Bu})$ after overnight heating at $40\text{ }^\circ\text{C}$. Spectra were consistent with previous reports of this compound.^{2,8}

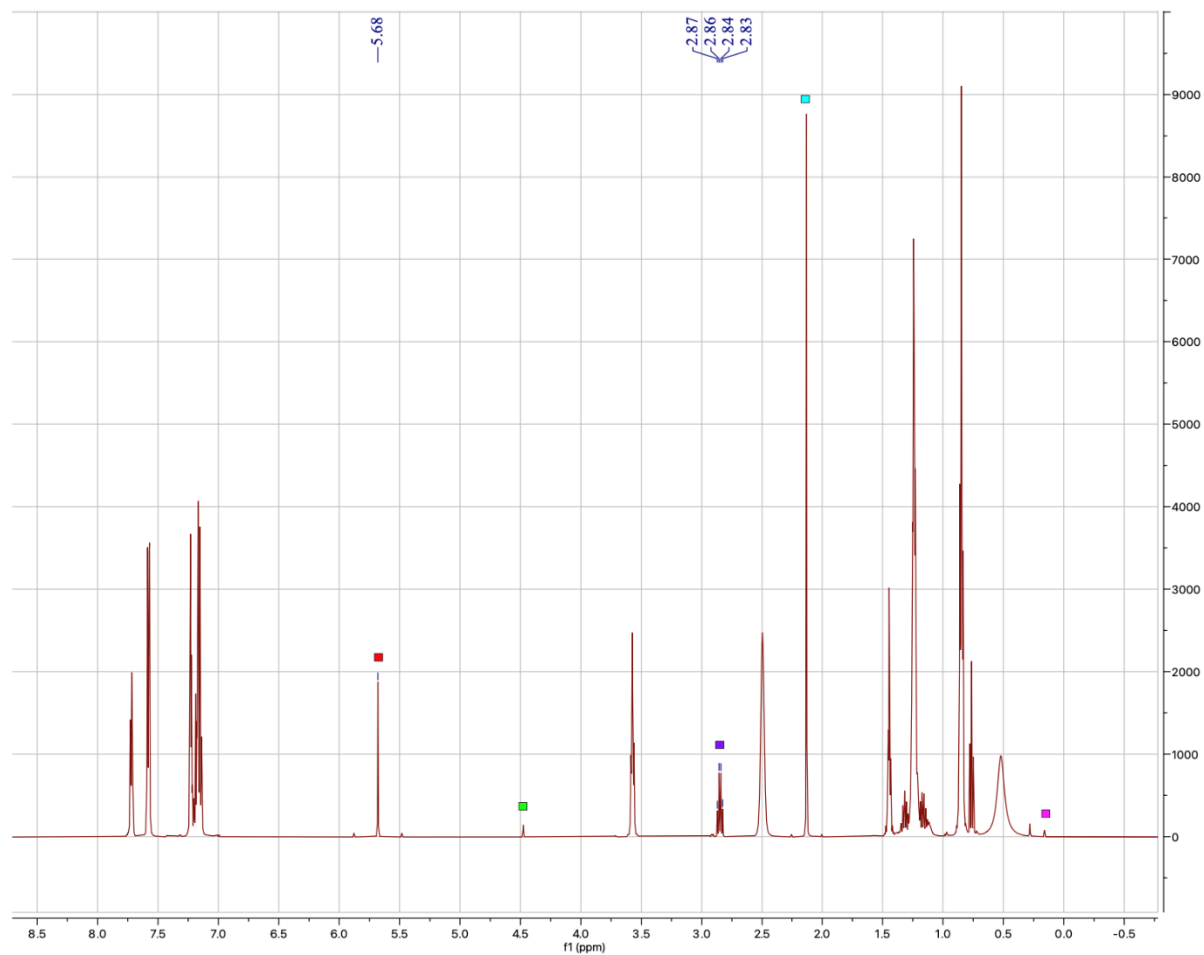


Figure S.38. ^1H NMR spectrum of the reaction between Ph_3SiH and $n\text{BuNH}_2$ catalyzed by MeMgBr in benzene- d_6 after overnight heating at 40°C .

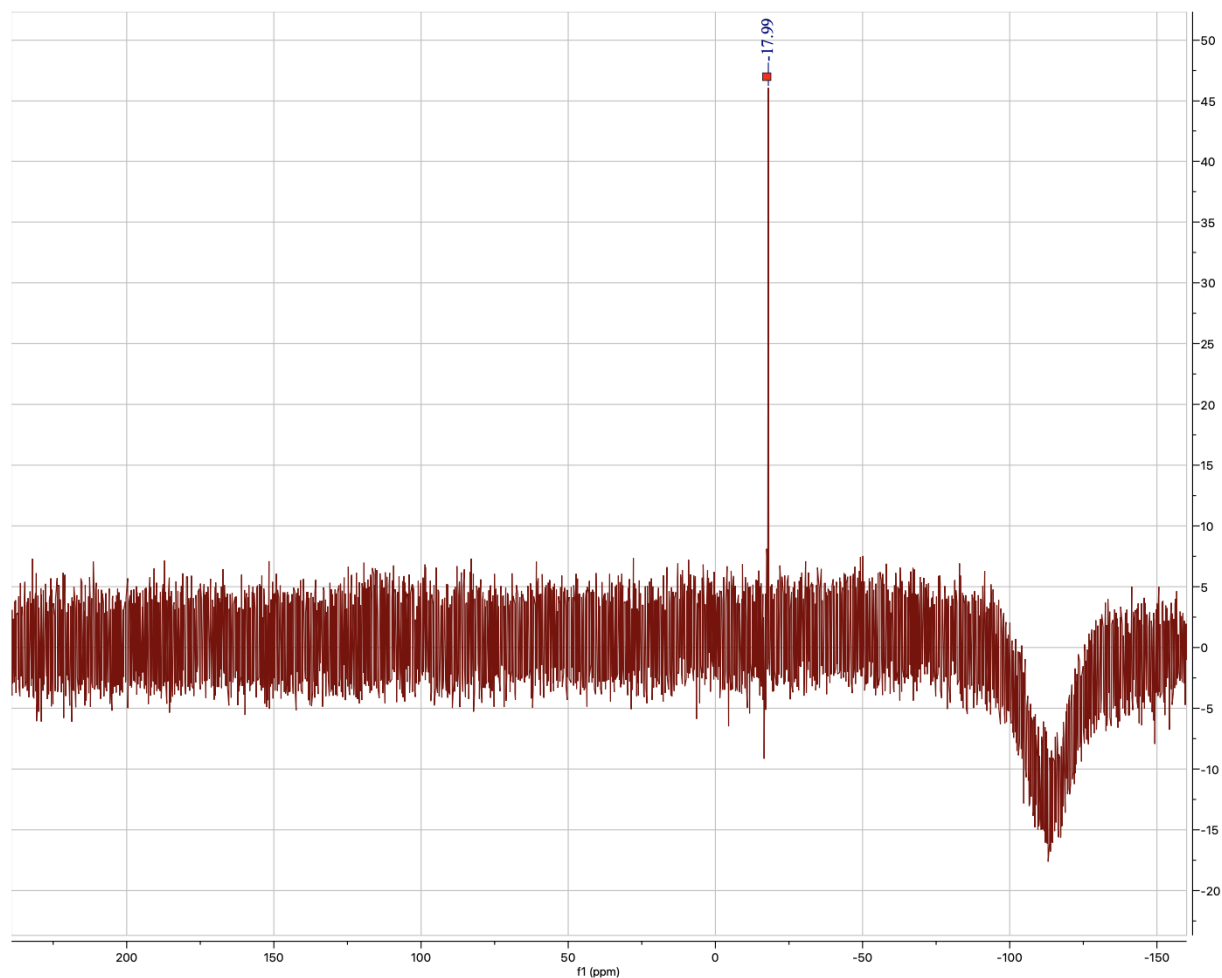


Figure S.39. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of the reaction between Ph_3SiH and $n\text{BuNH}_2$ catalyzed by MeMgBr in benzene- d_6 after overnight heating at $40\text{ }^\circ\text{C}$.

S2.20. Ph_3SiH and PyNH

Ph_3SiH ($100\text{ }\mu\text{L}$, 3.36 M in benzene- d_6 , $3.36 \times 10^{-1}\text{ mmol}$), PyNH ($56.0\text{ }\mu\text{L}$, $6.72 \times 10^{-1}\text{ mmol}$, 2.0 equiv.), and MeMgBr ($14.7\text{ }\mu\text{L}$, $1.68 \times 10^{-2}\text{ mmol}$, 5.0 mol %) were reacted together in 0.5 mL of benzene- d_6 in the presence of C_6Me_6 standard ($50.0\text{ }\mu\text{L}$, 0.4 M in benzene- d_6). Incomplete consumption of Ph_3SiH was observed after overnight heating to $40\text{ }^\circ\text{C}$, as determined by the presence of the SiH peak at $\delta = 5.68$ in the ^1H NMR spectrum. The appearance of a diagnostic multiplet centered at $\delta = 3.09$ in the ^1H NMR spectrum indicates 51% conversion to $\text{Ph}_3\text{Si}(\text{NPy})$ after overnight heating at $40\text{ }^\circ\text{C}$. Spectra were consistent with previous reports of this compound.^{2,9}

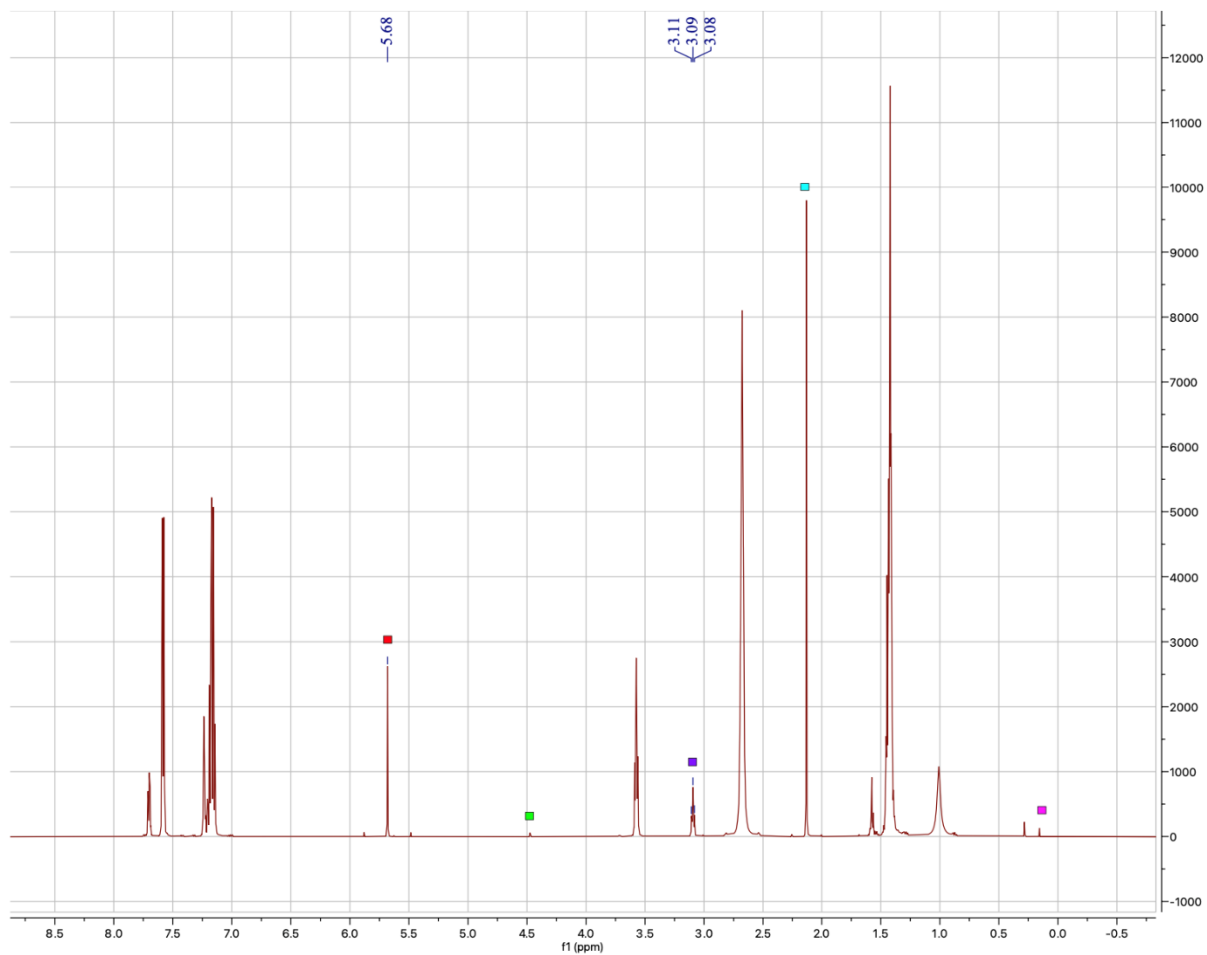


Figure S.40. ^1H NMR spectrum of the reaction between Ph_3SiH and PyNH catalyzed by MeMgBr in benzene- d_6 after overnight heating at $40\text{ }^\circ\text{C}$.

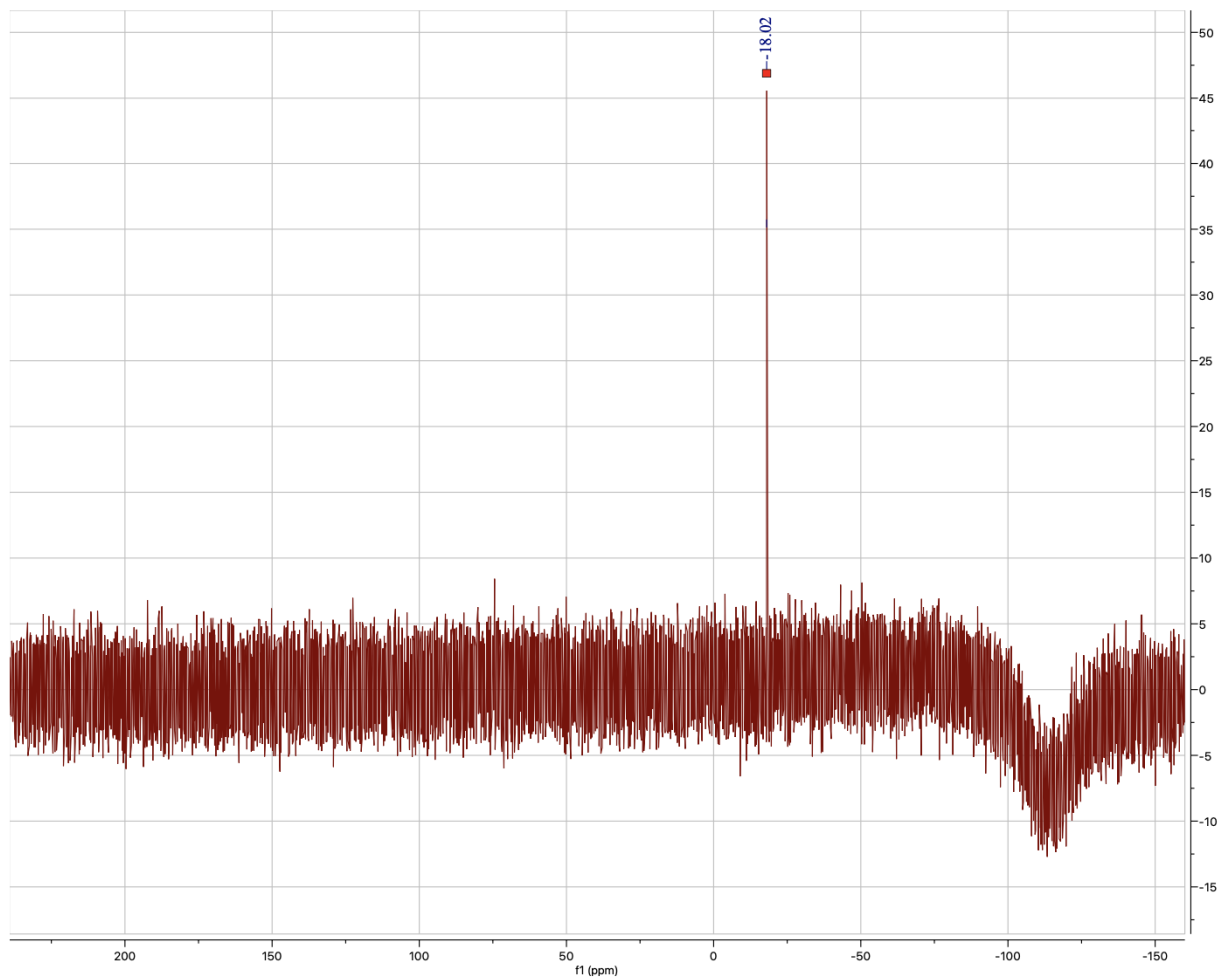


Figure S.41. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of the reaction between Ph_3SiH and PyNH catalyzed by MeMgBr in benzene- d_6 after overnight heating at 40°C .

S3. Mechanistic Investigations

S3.1. Stoichiometric PhSiH₃ and MeMgBr

PhSiH₃ (41.0 μL, 3.36 × 10⁻¹ mmol, 1.0 equiv.) and MeMgBr (247.1 μL, 3.36 × 10⁻¹ mmol, 1.0 equiv.) were reacted together in 0.5 mL of benzene-*d*₆ in the presence of C₆Me₆ standard (50.0 μL, 0.4 M in benzene-*d*₆). The appearance of a multiplet at δ = 4.43 in the ¹H NMR spectrum and a peak at δ = -36.16 in the ²⁹Si{¹H} NMR spectrum is indicative of formation of PhMeSiH₂.

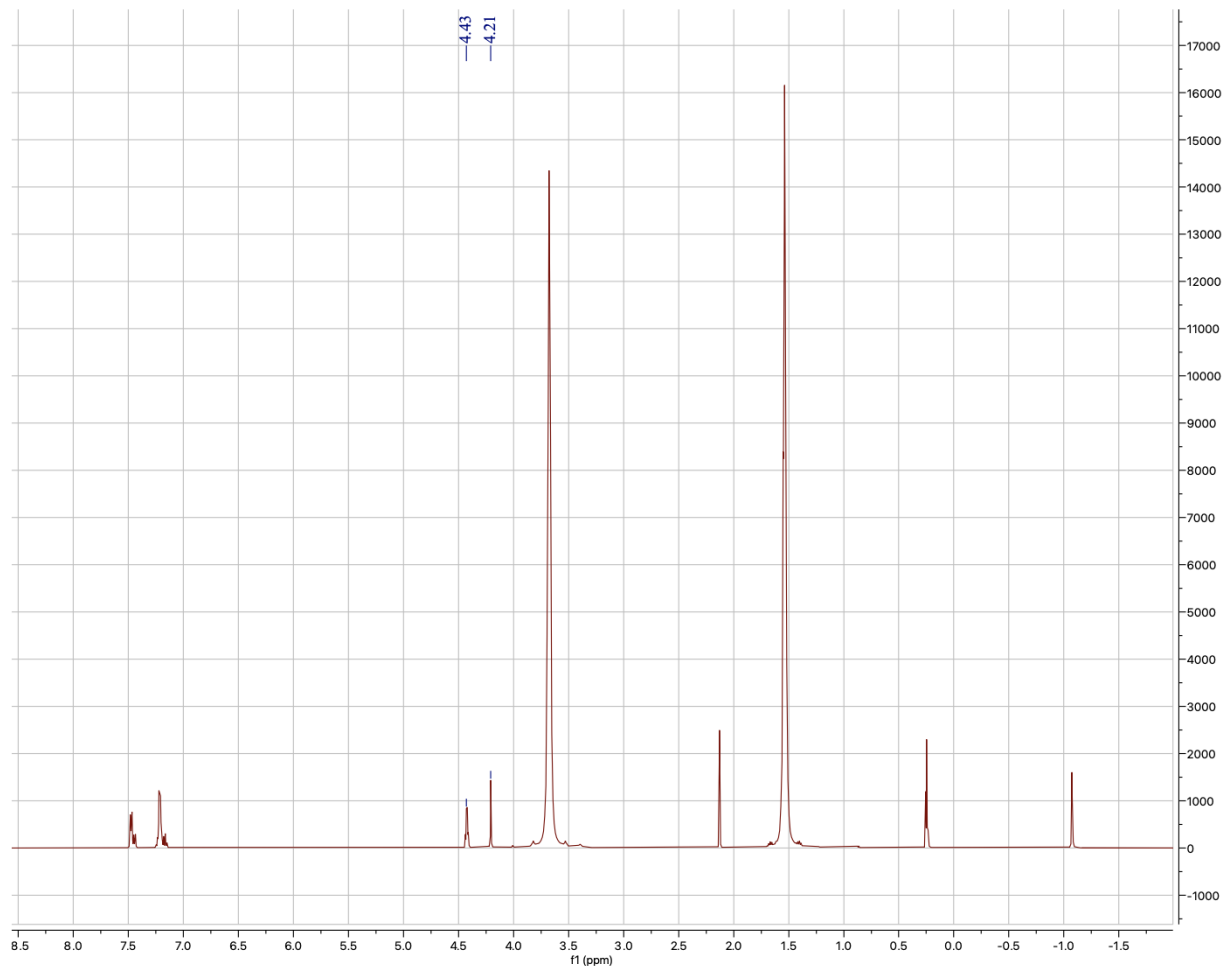


Figure S.42. ¹H NMR spectrum of the stoichiometric reaction between PhSiH₃ and MeMgBr in benzene-*d*₆.

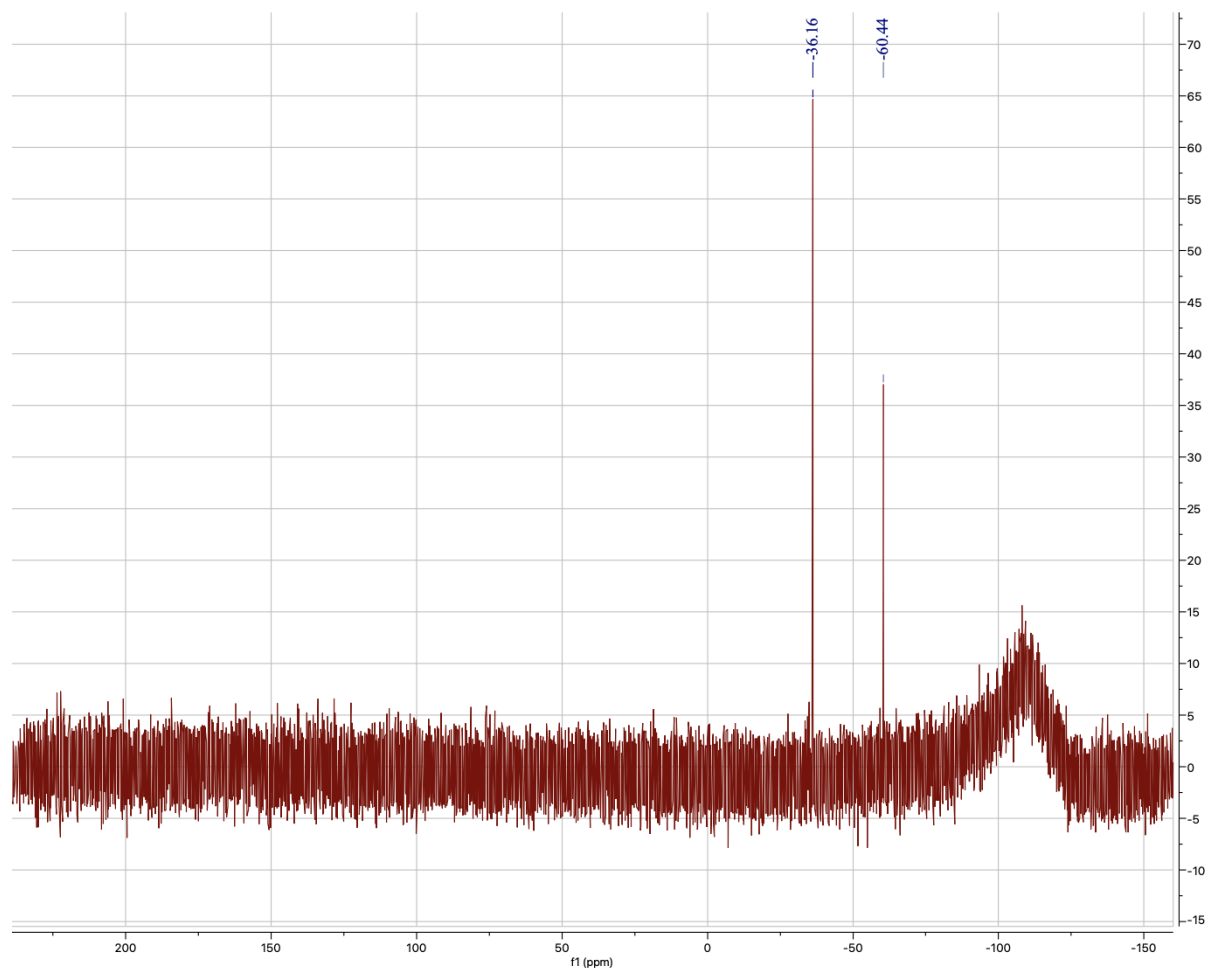


Figure S.43. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of the stoichiometric reaction between PhSiH_3 and MeMgBr in benzene- d_6 .

S3.2. Stoichiometric $n\text{BuNH}_2$ and MeMgBr

$n\text{BuNH}_2$ ($33.5 \mu\text{L}$, 3.36×10^{-1} mmol, 1.0 equiv.) and MeMgBr ($247.1 \mu\text{L}$, 3.36×10^{-1} mmol, 1.0 equiv.) were reacted together in 0.5 mL of benzene- d_6 in the presence of C_6Me_6 standard ($50.0 \mu\text{L}$, 0.4 M in benzene- d_6). The appearance of a peak at $\delta = 0.16$ in the ^1H NMR spectrum is indicative of formation of methane while the peak at $\delta = -0.50$, multiplet centered between $\delta = 0.98$ and $\delta = 0.99$, and the peak at $\delta = 2.97$ suggests formation of $n\text{BuN(H)MgBr}$.

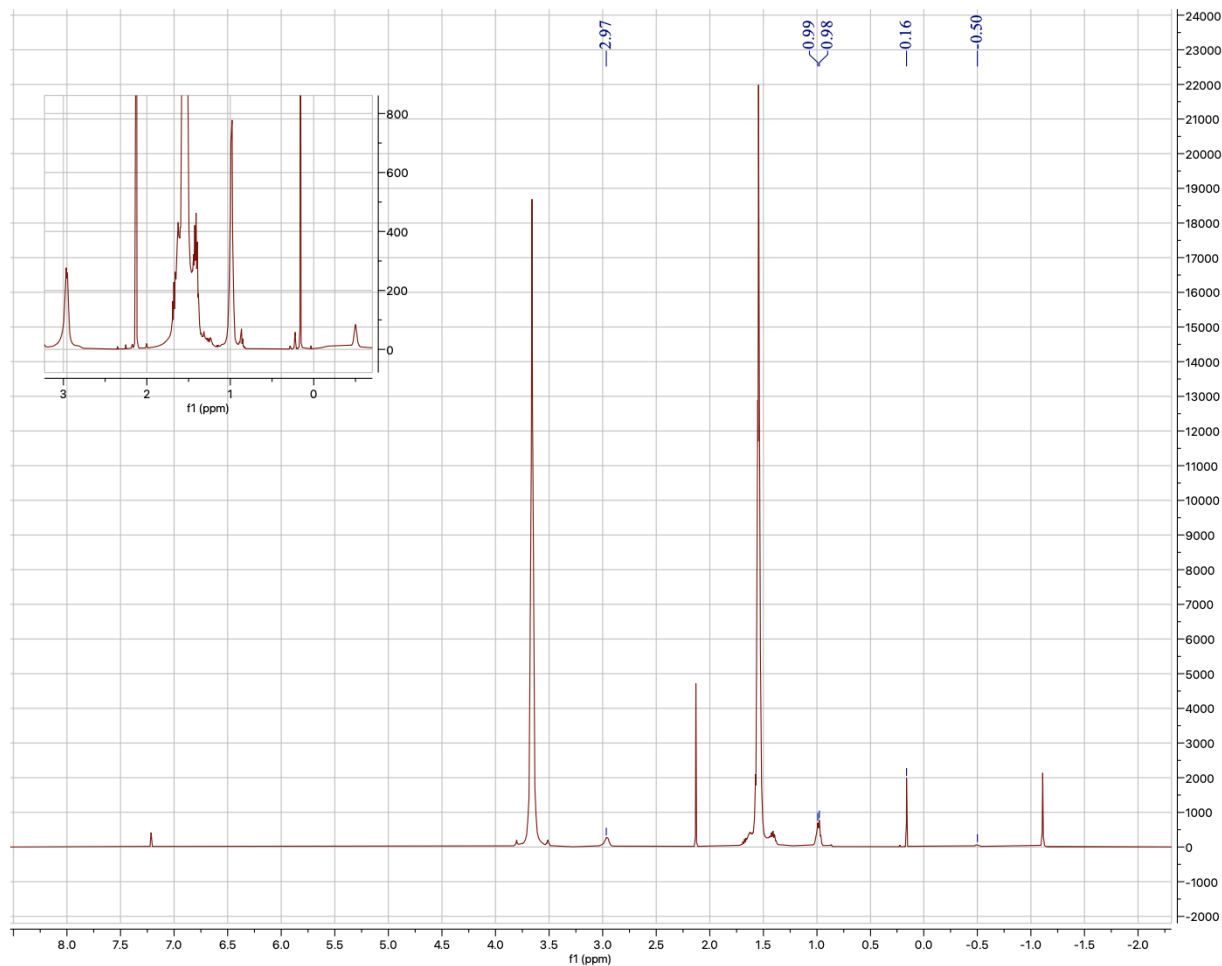


Figure S.44. ¹H NMR spectrum of the stoichiometric reaction between ⁿBuNH₂ and MeMgBr in benzene-*d*₆.

S3.3. PhSiH₃ and ⁿBuNH₂ with MesMgBr

PhSiH₃ (41.0 μL, 3.36 × 10⁻¹ mmol), ⁿBuNH₂ (201.0 μL, 20.16 × 10⁻¹ mmol, 6.0 equiv.), and MesMgBr (18.7 μL, 1.68 × 10⁻² mmol, 5.0 mol %) were reacted together in 0.5 mL of benzene-*d*₆ in the presence of C₆Me₆ standard (50.0 μL, 0.4 M in benzene-*d*₆). Complete consumption of PhSiH₃ was observed after 1 h. The appearance of multiplet centered at δ = 2.87 in the ¹H NMR spectrum indicates 97% conversion to PhSi(NHⁿBu)₃ after 1 h at ambient temperature.

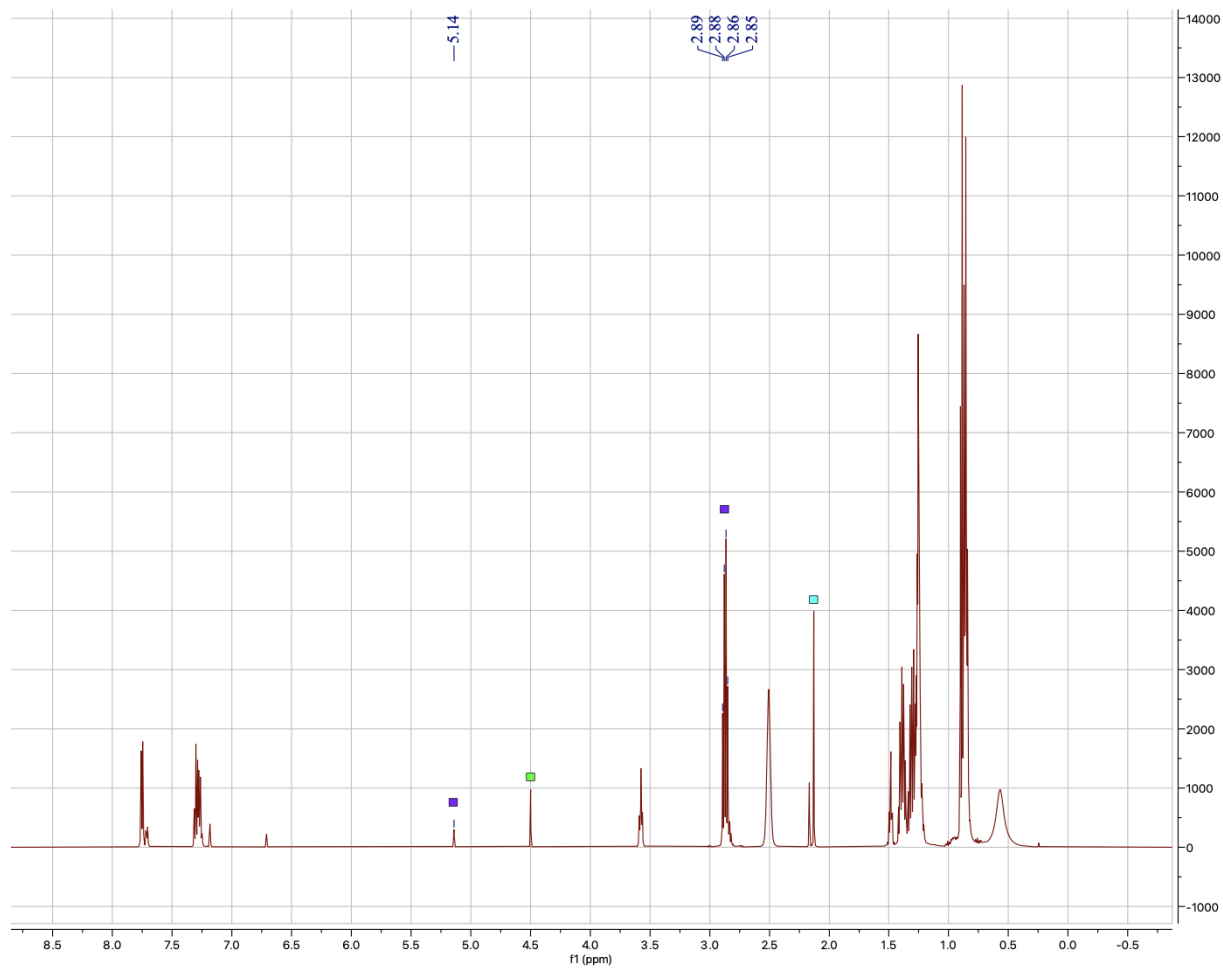


Figure S.45. ^1H NMR spectrum of the reaction between PhSiH_3 and $n\text{BuNH}_2$ catalyzed by MesMgBr in $\text{benzene-}d_6$ after 1 h.

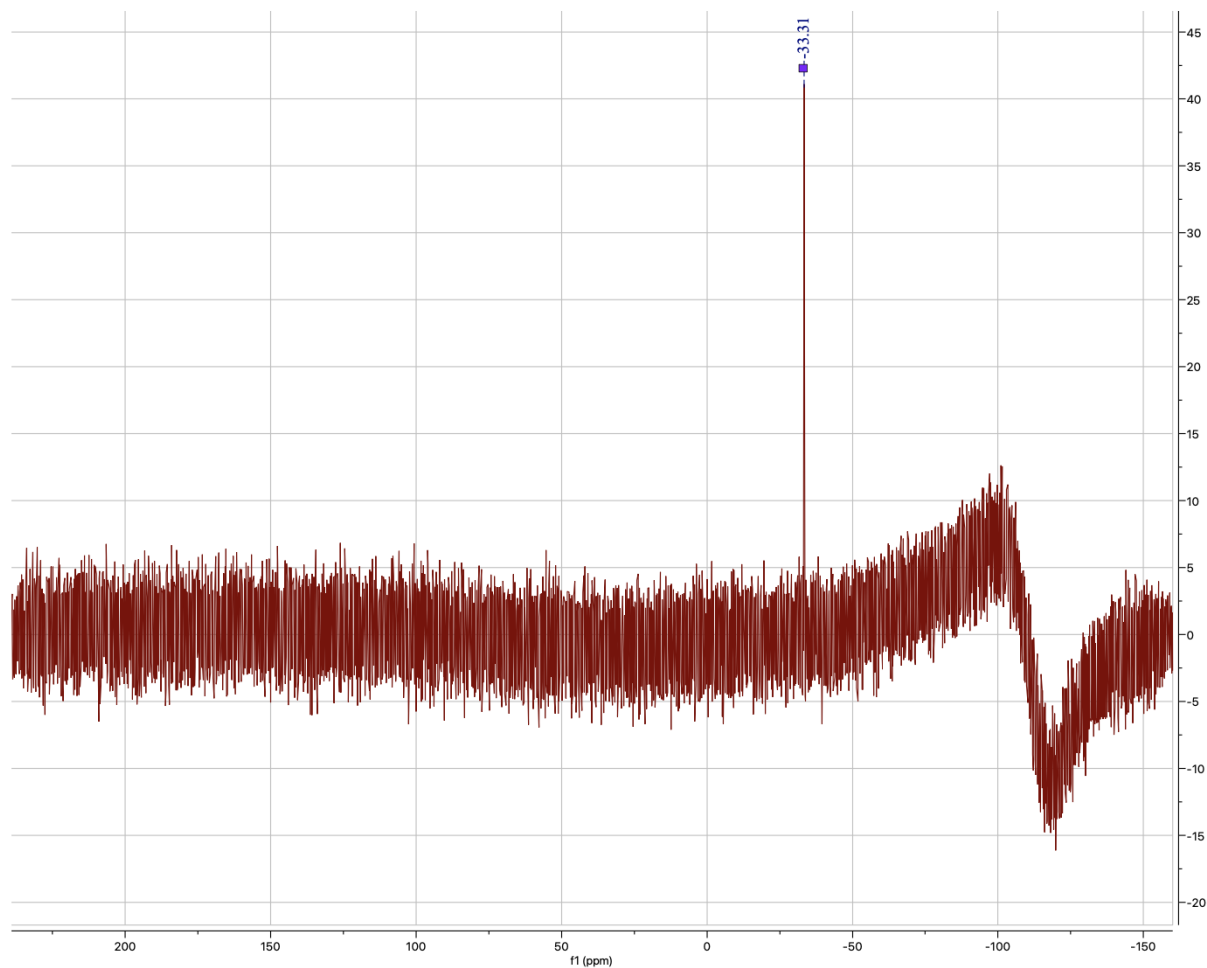


Figure S.46. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of the reaction between PhSiH_3 and $n\text{BuNH}_2$ catalyzed by MesMgBr in benzene- d_6 after 1 h.

S3.4. PhSiH_3 and $n\text{BuNH}_2$ with Me_2Mg

PhSiH_3 (41.0 μL , 3.36×10^{-1} mmol), $n\text{BuNH}_2$ (201.0 μL , 20.16×10^{-1} mmol, 6.0 equiv.), and Me_2Mg (32.0 μL , 1.68×10^{-2} mmol, 5.0 mol %) were reacted together in 0.5 mL of benzene- d_6 in the presence of C_6Me_6 standard (50.0 μL , 0.4 M in benzene- d_6). Complete consumption of PhSiH_3 was observed after 1 h. The appearance of multiplet centered at $\delta = 2.85$ in the ^1H NMR spectrum indicates 91% conversion to $\text{PhSi}(\text{NH}n\text{Bu})_3$ after 1 h at ambient temperature.

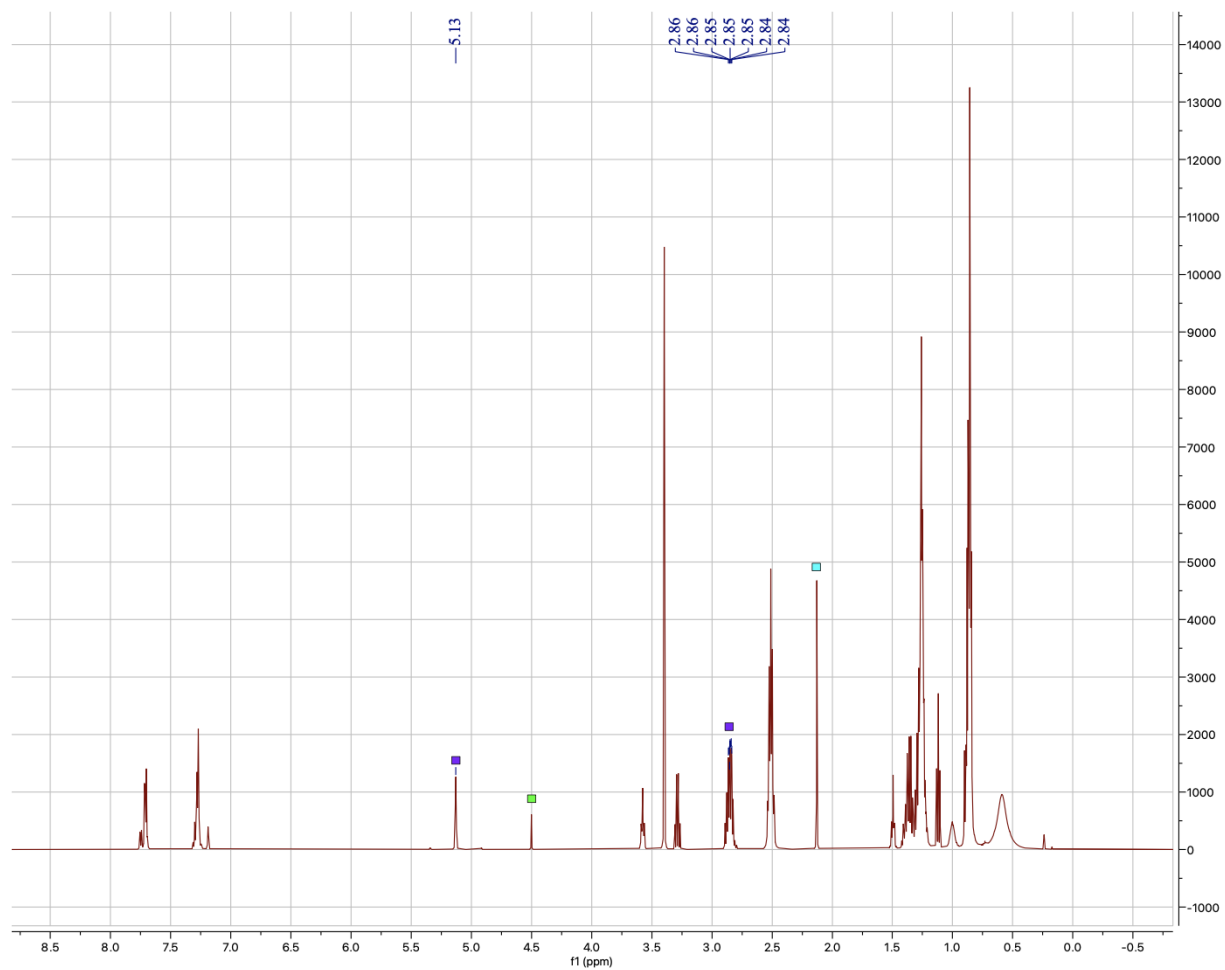


Figure S.47. ^1H NMR spectrum of the reaction between PhSiH_3 and $n\text{BuNH}_2$ catalyzed by Me_2Mg in benzene- d_6 after 1 h.

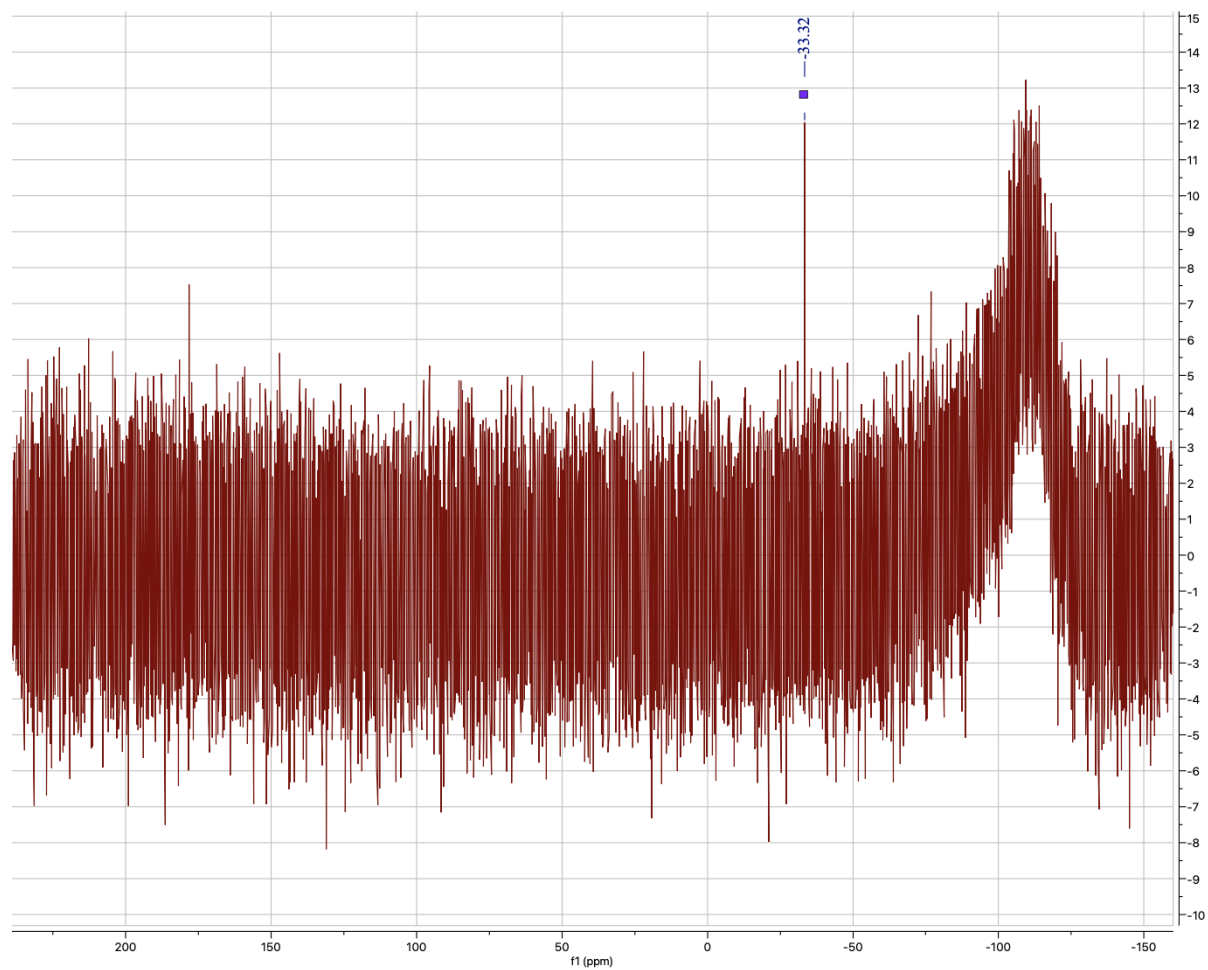


Figure S.48. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of the reaction between PhSiH_3 and $n\text{BuNH}_2$ catalyzed by Me_2Mg in benzene- d_6 after 1 h.

S4. References

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