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Supporting Information for:

Commercially Available Organolithiums as Simple, Effective Precatalysts for Silicon–Nitrogen Heterodehydrocoupling

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S1. General and Experimental Information

S1.1. General Methods

All manipulations were conducted under a positive pressure of N_2 in either an 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. Solvents such as *n*-pentane, hexanes, and toluene were degassed with argon, dried by passing through columns of alumina and Q5, and subsequently stored over 3Å molecular sieves. Tetrahydrofuran (THF) was dried over Na/benzophenone, and subsequently distilled and stored in a 1 L PTFE-sealed Strauss flask. Benzene-*d*$_6$ (C_6D_6) was distilled from CaH_2 and stored over activated 3Å molecular sieves for at least 48 h prior to use. Celite and 3Å molecular sieves were dried between 180-200°C under dynamic vacuum for at least 1 d.

Organolithium reagents were obtained from chemical vendors as solutions: methyl lithium (MeLi) in 1,2-dimethoxyethane, ethyl lithium (EtLi) in dibutyl ether, trimethylsilylmethyl lithium (Me_3SiCH_2Li) in hexanes, *normal*-butyl lithium (^{n}BuLi) in hexanes, *secondary*-butyl lithium (^{s}BuLi) in cyclohexane, *tertiary*-butyl lithium (^{t}BuLi) in pentane, and phenyl lithium (PhLi) in dibutyl ether. For catalysis, these reagents were filtered through Celite inside the glovebox, titrated thrice with *N*-benzylbenzamide in 2-3 mL of THF (Section S1.3., *vide infra*), and stored at -40°C prior to use. Me_3SiCH_2Li was isolated as a solid by filtering the received hexanes solution through Celite inside the glovebox and recrystallizing from a saturated solution at -40°C. Amines were distilled under dynamic N_2 from CaH_2 and stored over 3Å molecular sieves. $PhSiH_3$ and $PhMeSiH_2$ were distilled under dynamic N_2 and stored over 3Å molecular sieves. Ph_2SiH_2 was distilled under dynamic vacuum and stored over 3Å molecular sieves. $PhMe_2SiH$ and Ph_2MeSiH were received, transferred to the glovebox, and stored over 3Å molecular sieves. Ph_3SiH was recrystallized from hexanes at -40°C. Hexamethylbenzene (C_6Me_6) was sublimed at 150 °C under dynamic vacuum. Reagents such as tertiary

silanes (*p*-X-C_6H_4)Ph_2SiH for Hammett competition experiments were synthesized and purified by literature methods.[1]

Glassware was cleaned by sequential washings of base (5% KOH/10% ^{i}PrOH/85% H_2O), acid (10% HNO_3/90% H_2O), 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. Electron paramagnetic resonance (EPR) measurements were collected at ambient temperature on a Bruker EMXplus Spectrometer.

S1.2. Abbreviations

Table S1. Common and Uncommon Abbreviations and their Associated Indicators

Abbreviation	Full Name (Formula)	Abbreviation	Full Name (Formula)
Me	Methyl (κ^1-CH_3)	^{s}Bu	*s*-Butyl [κ^1-CH(Et)(Me)]
Et	Ethyl (κ^1-CH_2Me)	^{t}Bu	*t*-Butyl [κ^1-$C(Me)_3$]
^{n}Pr	*n*-Propyl (κ^1-CH_2CH_2Me)	^{n}Pe	*n*-Pentyl [κ^1-$CH_2(CH_2)_3Me$]
^{i}Pr	*i*-Propyl [κ^1-$CH(Me)_2$]	^{n}He	*n*-Hexyl [κ^1-$CH_2(CH_2)_4Me$]
^{n}Bu	*n*-Butyl [κ^1-$CH_2(CH_2)_2Me$]	Ph	Phenyl (η^1-C_6H_5)
^{i}Bu	*i*-Butyl [κ^1-$CH_2CH(Me)_2$]	NPy	Pyrrolidine (η^1-NC_4H_8)

S1.3. Sample Procedure for Titration with *N*-Benzylbenzamide

In the glovebox, *N*-Benzylbenzamide was added to a 20 mL glass scintillation vial equipped with a microstir bar and dissolved in 2-3 mL of THF. RLi was slowly added via a 1 mL syringe until the solution turned a consistent dark purple. The molarity of RLi was found using Eq. 1. These reactions were run in triplicate.

$$M = \frac{moles\ of\ N{-}Benzylbenzamide}{L\ of\ added\ RLi} \quad (1)$$

Table S2. Titration results for lithiated reagents

Entry	RLi	*M* from Vendor	*M* after Filtration
1	Me	3.10	2.80
2	Et	1.70	1.50
3	Me_3SiCH_2	0.70	---[a]
4	^{n}Bu	2.40	2.50[b]
5	^{s}Bu	1.30	1.40[b]
6	^{t}Bu	1.60	1.50
7	Ph	2.00	1.70

[a]Isolated as a solid (*vide supra*). [b]The increased M of these solutions is attributed to the loss of stock solution solvent under dynamic vacuum during filtration.

S2. Hammett Competition Experiments

S2.1. General Information

Stock solutions of (*p*-X-C_6H_4)Ph_2SiH (X = CF_3, H, Me, OMe) were prepared inside the glovebox to a concentration of 1.0 M in benzene-d_6. These solutions were stored at -40 °C and unfrozen only immediately prior to the start of experimentation.

S2.2. General Procedure for Hammett Competition Experiments

In the glovebox, Ph_3SiH (188.5 μL, 1.8 × 10^{-1} mmol, 1.0 M in benzene-d_6), (*p*-X-C_6H_4)Ph_2SiH (188.5 μL, 1.8 × 10^{-1} mmol, 1.0 M in benzene-d_6), C_6Me_6 (52.5 μL, 0.4 M in benzene-d_6) and ^{t}BuNH$_2$ (79.5 μL, 7.5 × 10^{-1} mmol) were added to 0.5 mL of benzene-d_6 in a 20 mL glass scintillation. After the addition of **1** (14.5 μL, 3.7 × 10^{-2} mmol, 11.1 mol %, 2.9 M in hexanes), the effervescent solution was quickly transferred to a PTFE-sealed J-Young NMR tube via a glass pipette. The solution was allowed to react for 1 h at ambient temperature before ^{1}H NMR spectra were acquired. These reactions were run in triplicate.

S2.3. Data Refinement and Analysis

Spectra were referenced to an internal standard of C_6Me_6 (i.e., δ = 2.13). Integrations were determined from diagnostic ^{t}Bu peaks, with $Ph_3Si(NH^tBu)$ normalized to 1.00. The full listing of raw and refined data is presented in Table S2.1, where red values indicate omitted data points. Logarithmic mean values of k_H/k_D were plotted against the substituent constant for the corresponding *p*-substituted silane, which were obtained from the literature.[2]

Table S2.1. Data for Hammett analysis between Ph_3SiH and (p-X-C_6H_4)Ph_2SiH

		k_X/k_H			$\log(k_X/k_H)$				
X	**Hammett Parameter**	**1**	**2**	**3**	**1**	**2**	**3**	**Mean**	**σ**
CF_3	0.54	2.89	3.60	3.49	0.45	0.56	0.54	1.10	0.01
H	0.00	1.00	1.00	1.00	0.00	0.00	0.00	0.00	0.00
Me	-0.17	0.98	0.99	0.99	-0.01	0.00	0.00	-0.02	0.00
OMe	-0.27	0.81	0.83	0.85	-0.09	-0.08	-0.07	-0.24	0.01

S3. Catalytic Experiments

S3.1. General Procedure

In an M. Braun glovebox, a 20 mL scintillation vial was charged with 0.5 mL of benzene-d_6, followed by silane, amine, and **1**. The vigorously bubbling solution was quickly transferred to a PTFE-sealed J-Young NMR tube via glass pipette and left to react at ambient temperature for 1 h, unless otherwise specified.

Table 3.1. List of icons and identifiers

Icon	Meaning	Note(s)
●	Aminosilane	Desired Product
■	Silane	Reagent
♦	Hydrogen Gas	By-product
▲	C_6Me_6	Internal Standard
▼	Benzene-d_6	Solvent (i.e., residual C_6H_6)
‡	Borosilicate Glass Peak	From NMR tube

S3.2. $PhSiH_3$ and 6.0 equiv. of $^nPrNH_2$

$PhSiH_3$ (46.5 μL, 3.7×10^{-1} mmol), $^nPrNH_2$ (186.0 μL, 22.6×10^{-1} mmol, 6.0 equiv.), and **1** (14.5 μL, 3.7×10^{-2} mmol, 2.6 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6 in the presence of C_6Me_6 standard (52.5 μL, 0.4 M in benzene-d_6). Complete consumption of $PhSiH_3$ was observed after 1 h, as determined by the absence of the Si*H* peak at $\delta = 4.22$ in the ^{1}H NMR spectrum. The appearance of a diagnostic peak at $\delta = 2.82$ in the ^{1}H NMR spectrum indicated 66% conversion to $PhSi(NH^nPr)_3$ after 1 h at ambient temperature. Additional peaks contributed to the lowered conversion. Spectra were consistent with previous reports of this compound.[3]

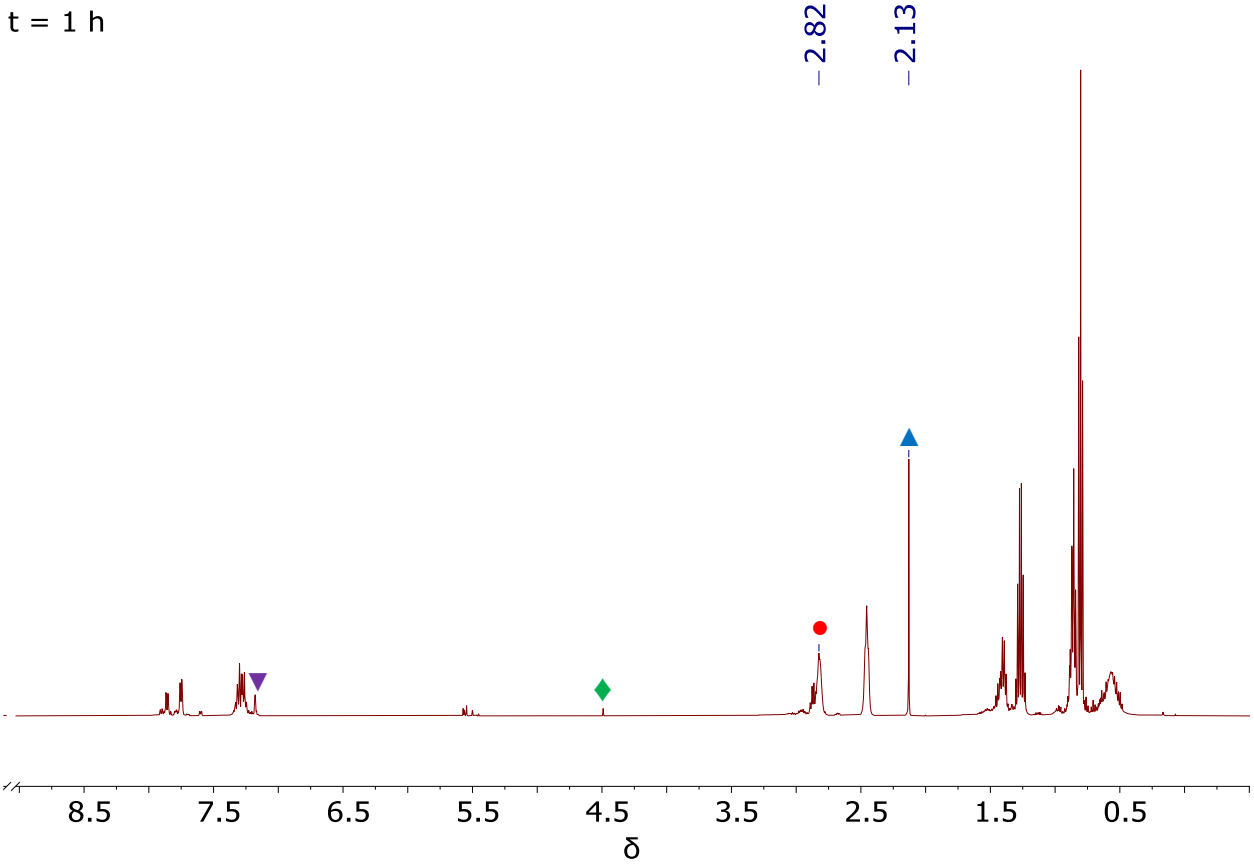

Figure S3.1. ^{1}H NMR spectrum of the reaction between $PhSiH_3$ and $^nPrNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

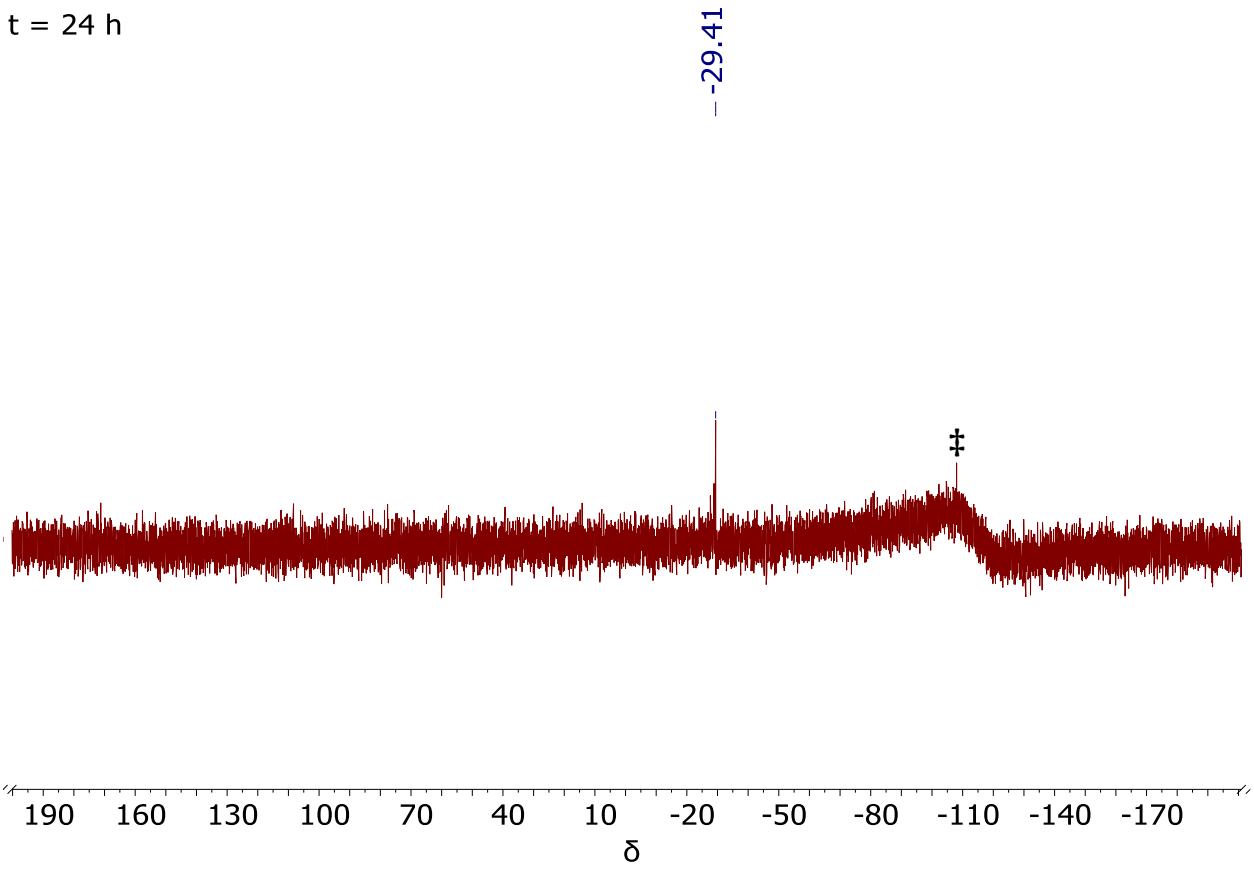

Figure S3.2. $^{29}Si\{^{1}H\}$ NMR spectrum of the reaction between $PhSiH_3$ and $^{n}PrNH_2$ catalyzed by **1** in benzene-d_6 after 24 h.

S3.3. $PhSiH_3$ and 6.0 equiv. of $^{i}PrNH_2$

$PhSiH_3$ (46.5 μL, 3.7×10^{-1} mmol), $^{i}PrNH_2$ (194.0 μL, 22.6×10^{-1} mmol, 6.0 equiv.), and **1** (14.5 μL, 3.7×10^{-2} mmol, 2.6 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6 in the presence of C_6Me_6 standard (52.5 μL, 0.4 M in benzene-d_6). Complete consumption of $PhSiH_3$ was observed after 1 h. The appearance of a diagnostic septet centered at $\delta = 3.24$ in the ^{1}H NMR spectrum indicated 85% conversion to $PhSi(NH^{i}Pr)_3$ after 1 h at ambient temperature. The appearance of additional ^{i}Pr peaks, which are likely oligomeric products, contributed to the lowered conversion. Spectra were consistent with previous reports of this compound.[4]

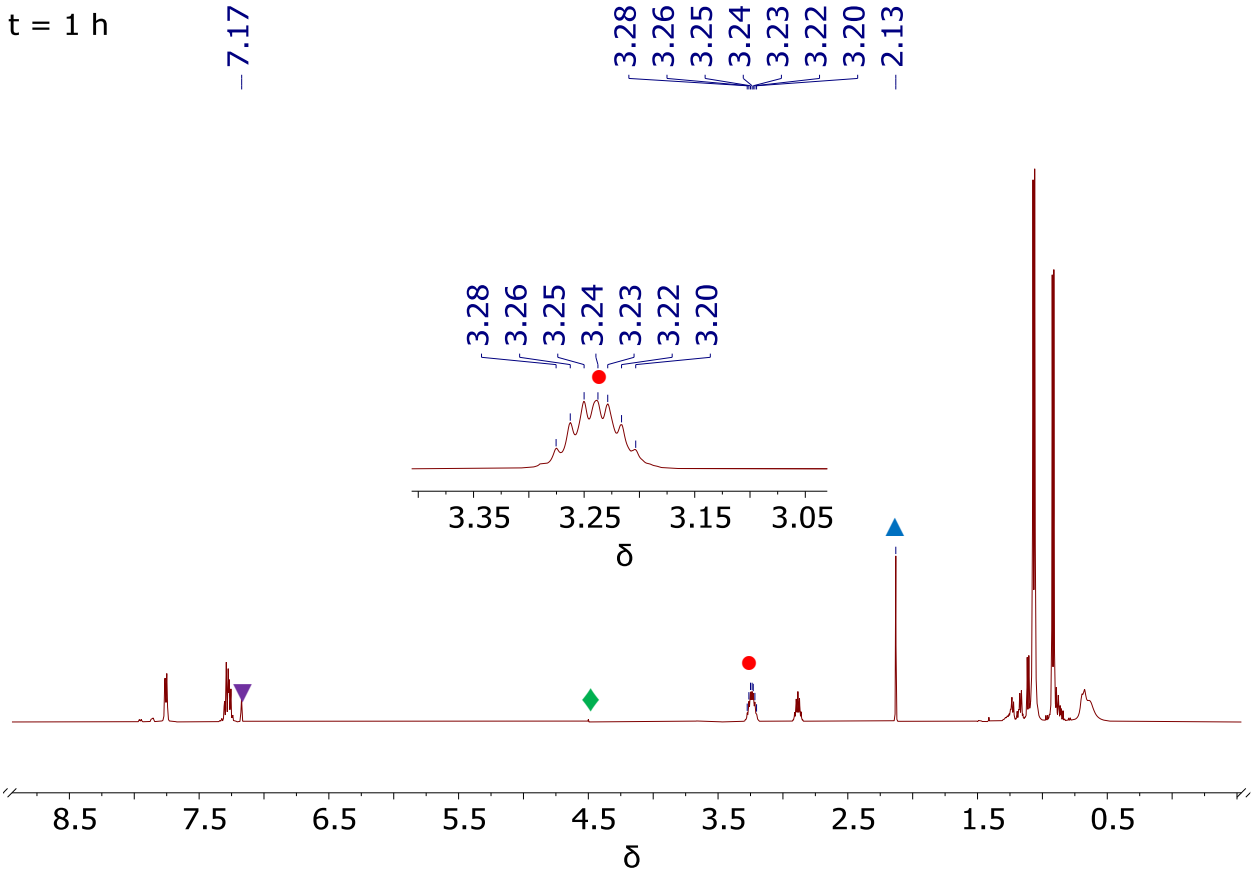

Figure S3.3. ^{1}H NMR spectrum of the reaction between $PhSiH_3$ and $^{i}PrNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

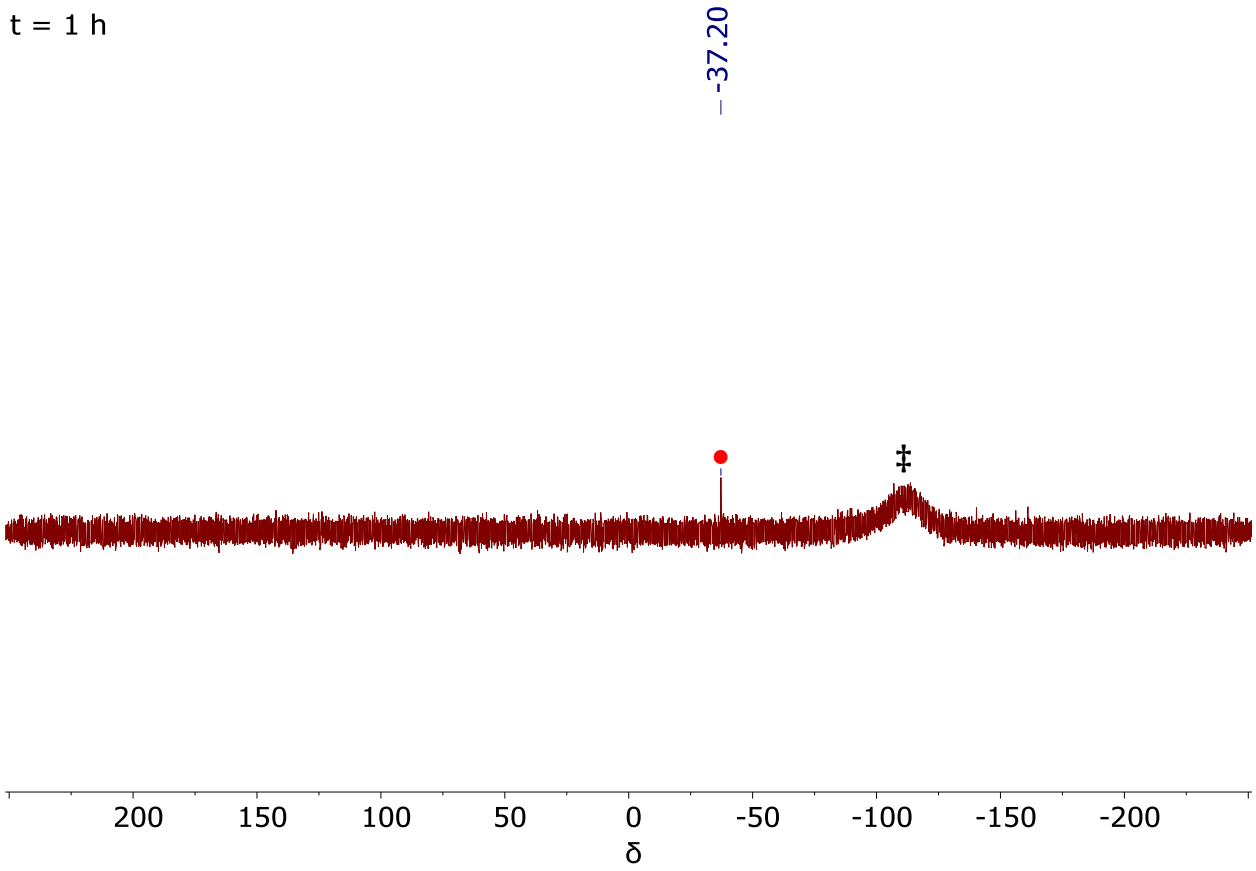

Figure S3.4. $^{29}Si\{^{1}H\}$ NMR spectrum of the reaction between $PhSiH_3$ and $^{i}PrNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

S5.4. $PhSiH_3$ and 6.0 equiv. of $^tBuNH_2$

$PhSiH_3$ (46.5 μL, 3.7 × 10^{-1} mmol), $^tBuNH_2$ (238.0 μL, 22.6 × 10^{-1} mmol, 6.0 equiv.), and **1** (14.5 μL, 3.7 × 10^{-2} mmol, 2.6 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6. Complete consumption of $PhSiH_3$ was observed after 1 h. The appearance of a diagnostic triplet centered at δ = 5.41 in the ^{1}H NMR spectrum indicated 98% conversion to $PhSiH(NH^tBu)_2$ after 1 h at ambient temperature. An additional peak in the ^{1}H-^{29}Si{^{1}H} NMR HSQC spectrum was observed, which was not consistent with $PhSiH_2NH^tBu$,[3] $(PhSiH_2)_2N^tBu$,[4] or $[PhHSi\text{-}\mu\text{-}(N^tBu)]_2$.[5] Spectra were consistent with previous reports of this compound.[3, 6]

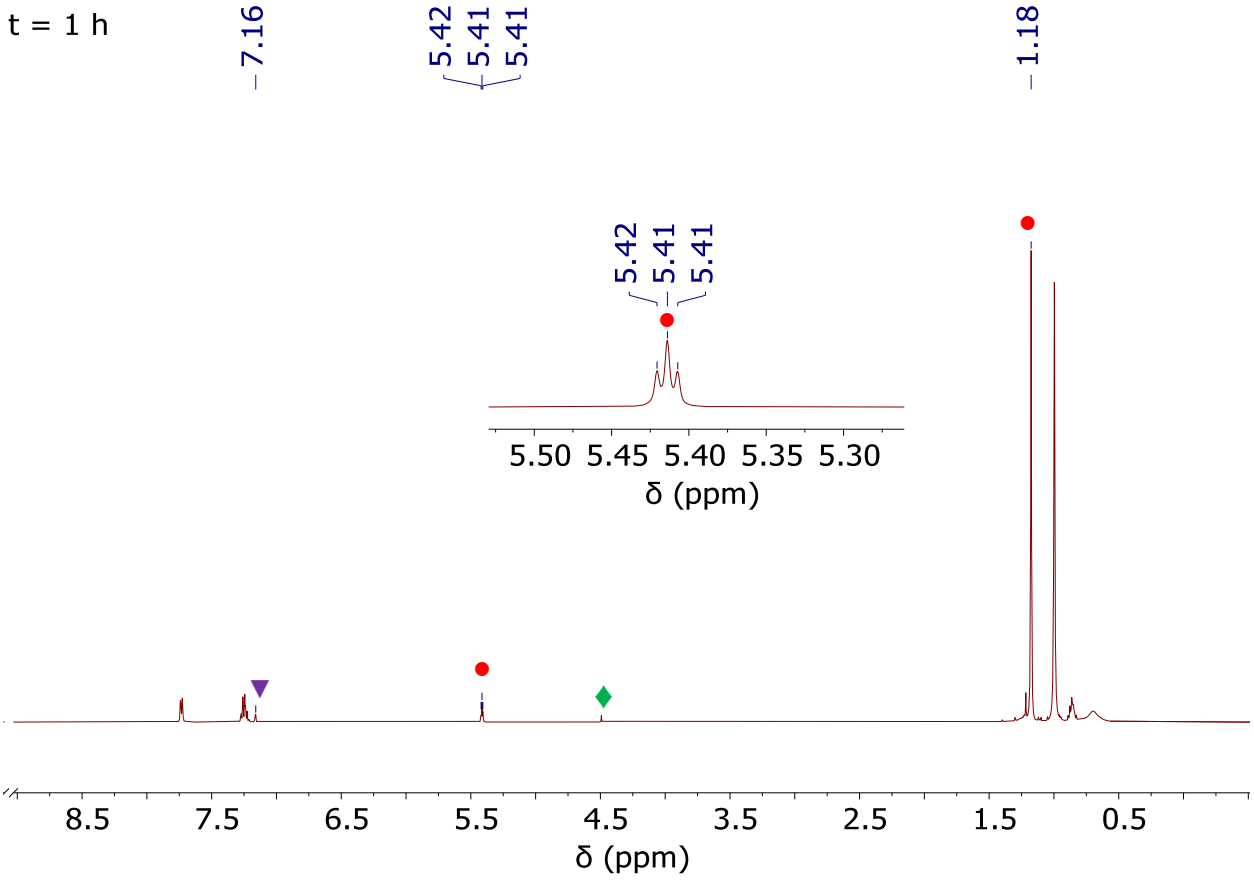

Figure S3.5. ^{1}H NMR spectrum of the reaction between $PhSiH_3$ and $^tBuNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

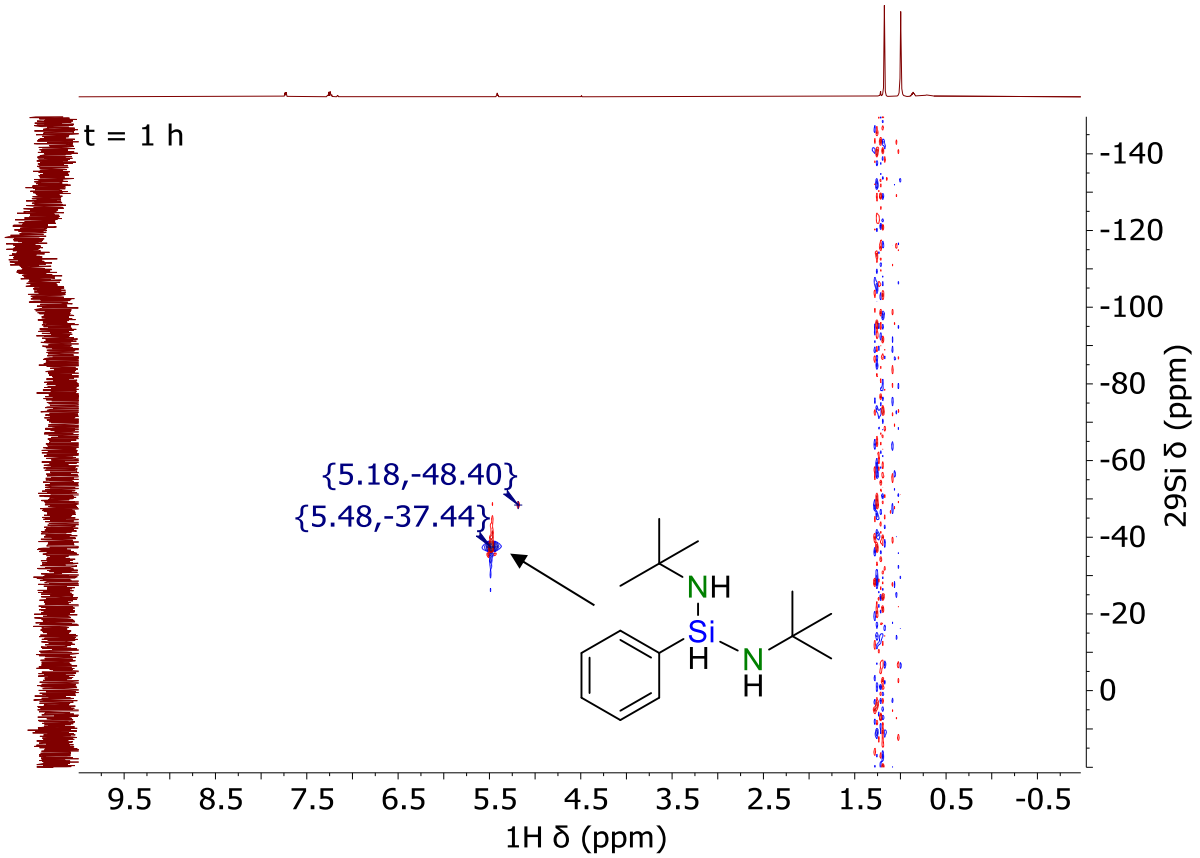

Figure S3.6. ^{1}H-$^{29}Si\{^{1}H\}$ HSQC NMR spectrum of the reaction between $PhSiH_3$ and $^{t}BuNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

S5.5. $PhSiH_3$ and 6.0 equiv. $PhNH_2$

$PhSiH_3$ (46.5 μL, 3.7 × 10^{-1} mmol), $PhNH_2$ (204.5 μL, 22.6 × 10^{-1} mmol, 6.0 equiv.), and **1** (16.5 μL, 3.7 × 10^{-2} mmol, 2.3 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6. Complete consumption of $PhSiH_3$ was observed after 1 h. The bis- and tris(aminosilane) products $PhSiH(NHPh)_2$ and $PhSi(NHPh)_3$ were formed in approximately 90% and 10% conversion, respectively. A peak at δ = -40.43 in the ^{1}H-^{29}Si{^{1}H} HSQC NMR spectrum, which is indistinguishable in the ^{1}H NMR spectrum, may be consistent with residual $PhSiH_2(NHPh)$. Spectra were consistent with previous reports of these compounds.[6, 7]

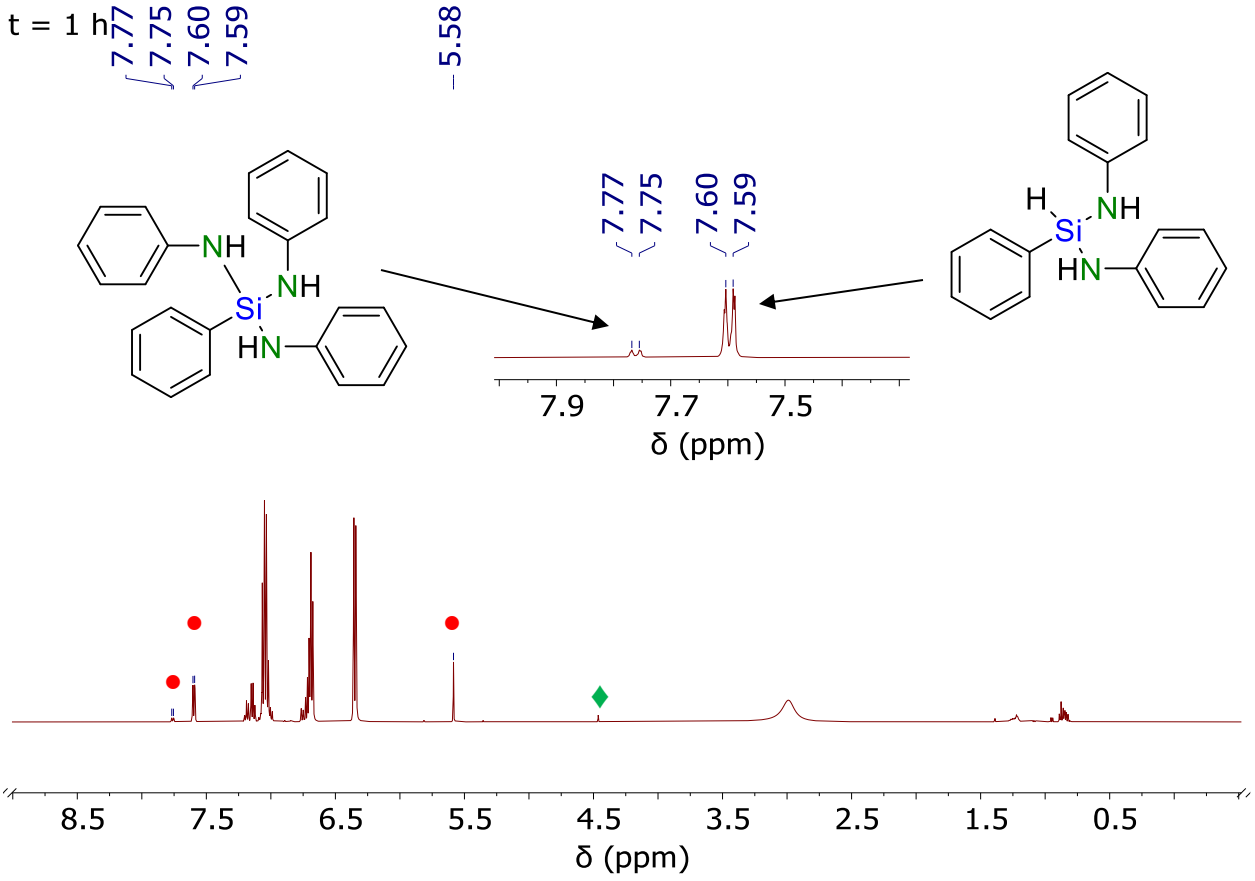

Figure S3.7. ^{1}H NMR spectrum of the reaction between $PhSiH_3$ and $PhNH_2$ catalyzed by **1** in benzene-d_6 after 1 h. Residual solvent was buried by product aryl peaks.

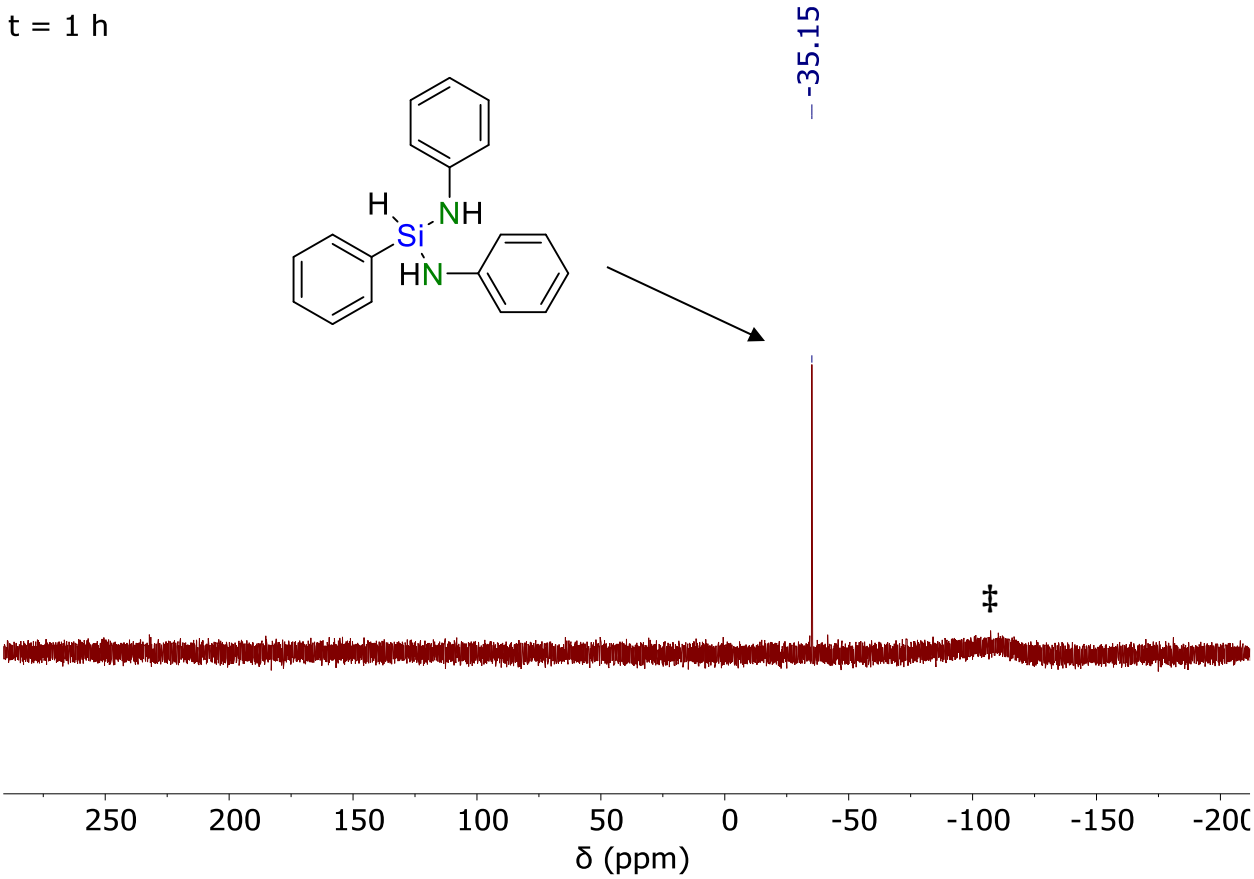

Figure S3.8. $^{29}Si\{^{1}H\}$ NMR spectrum of the reaction between $PhSiH_3$ and $PhNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

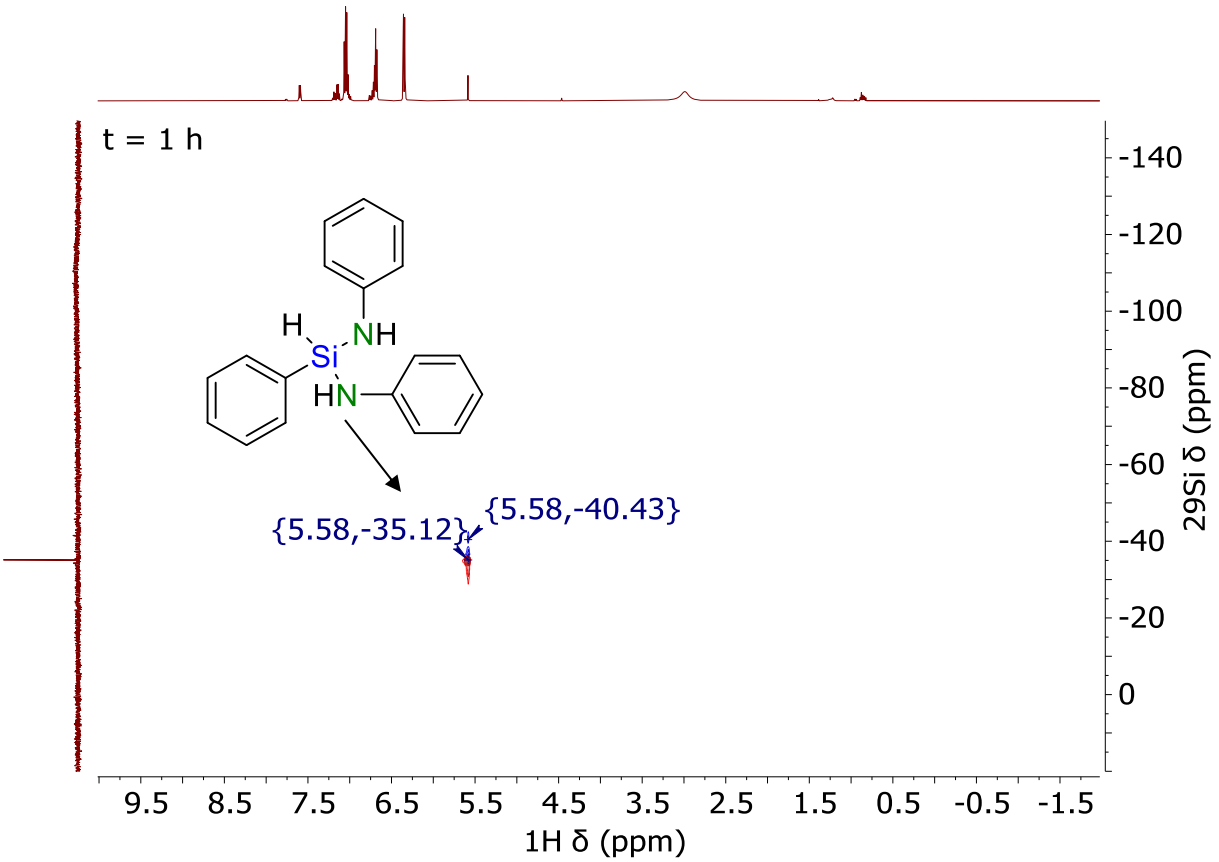

Figure S3.9. $^{29}Si\{^{1}H\}$ NMR spectrum of the reaction between $PhSiH_3$ and $PhNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

S5.6. $PhSiH_3$ and 6.0 equiv. of PyNH

$PhSiH_3$ (46.5 μL, 3.7 × 10^{-1} mmol), PyNH (186.0 μL, 22.6 × 10^{-1} mmol, 6.0 equiv.), and **1** (14.5 μL, 3.7 × 10^{-2} mmol, 2.6 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6. Complete consumption of $PhSiH_3$ was observed after 0.5 h. The appearance of a multiplet centered at δ = 3.10 in the ^{1}H NMR spectrum indicated 100% conversion to $PhSi(NPy)_3$ after 0.5 h at ambient temperature.

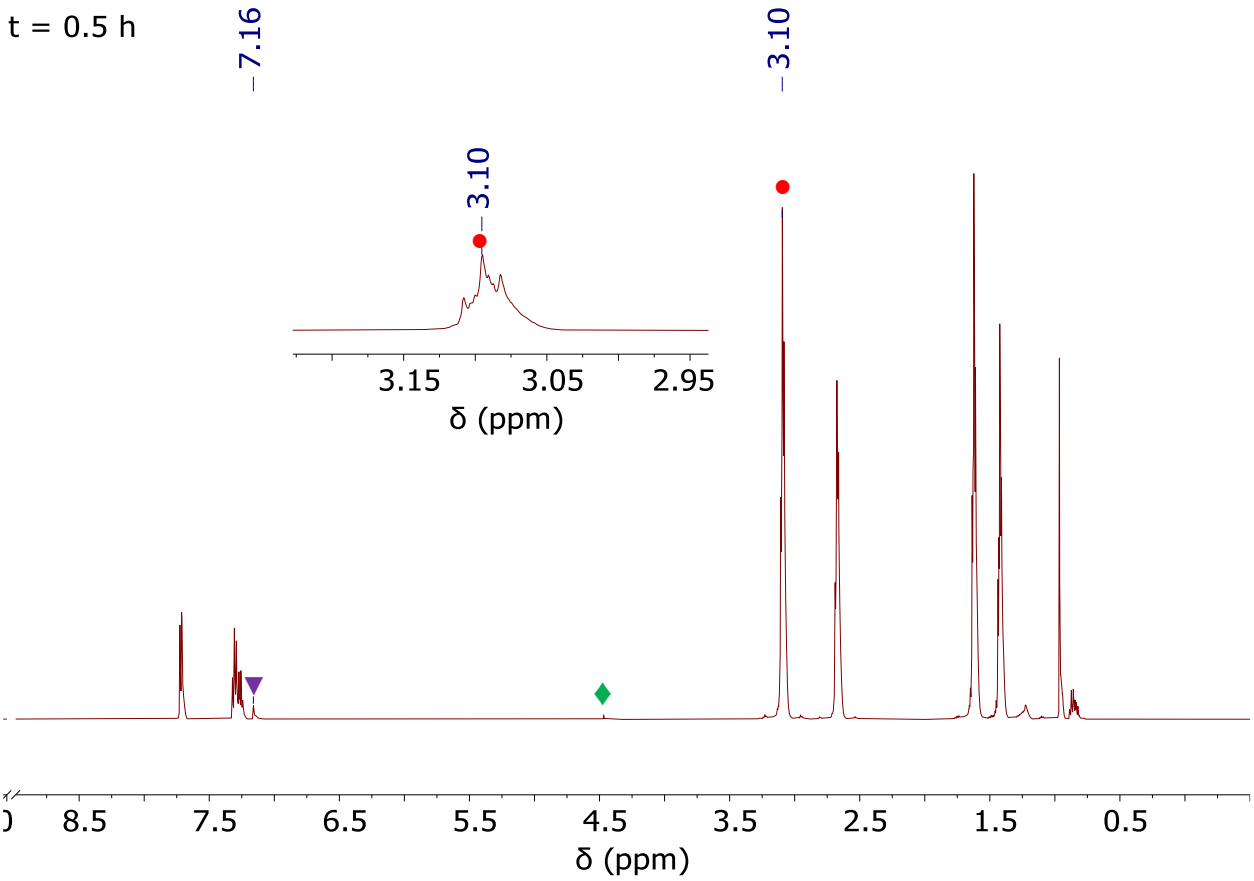

Figure S3.10. ^{1}H NMR spectrum of the reaction between $PhSiH_3$ and PyNH catalyzed by **1** in benzene-d_6 after 0.5 h.

S5.7. $PhSiH_3$ and 6.0 equiv. of Et_2NH

$PhSiH_3$ (46.5 μL, 3.7 × 10^{-1} mmol), Et_2NH (234.0 μL, 22.6 × 10^{-1} mmol, 6.0 equiv.), and **1** (14.5 μL, 3.7 × 10^{-2} mmol, 2.6 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6. Complete consumption of $PhSiH_3$ was observed after 1 h. The appearance of two diagnostic quartets, one centered between δ = 2.91 and δ = 2.90 and the second centered between δ = 2.81 and δ = 2.80 in the ^{1}H NMR spectrum, indicated 52% conversion to $PhSiH(NEt_2)_2$ and 48% conversion to $PhSiH_2(NEt_2)$ after 1 h at ambient temperature. The reaction was subsequently ended, due to the cessation of gas evolution. Spectra were consistent with previous reports of these compounds.[6, 8]

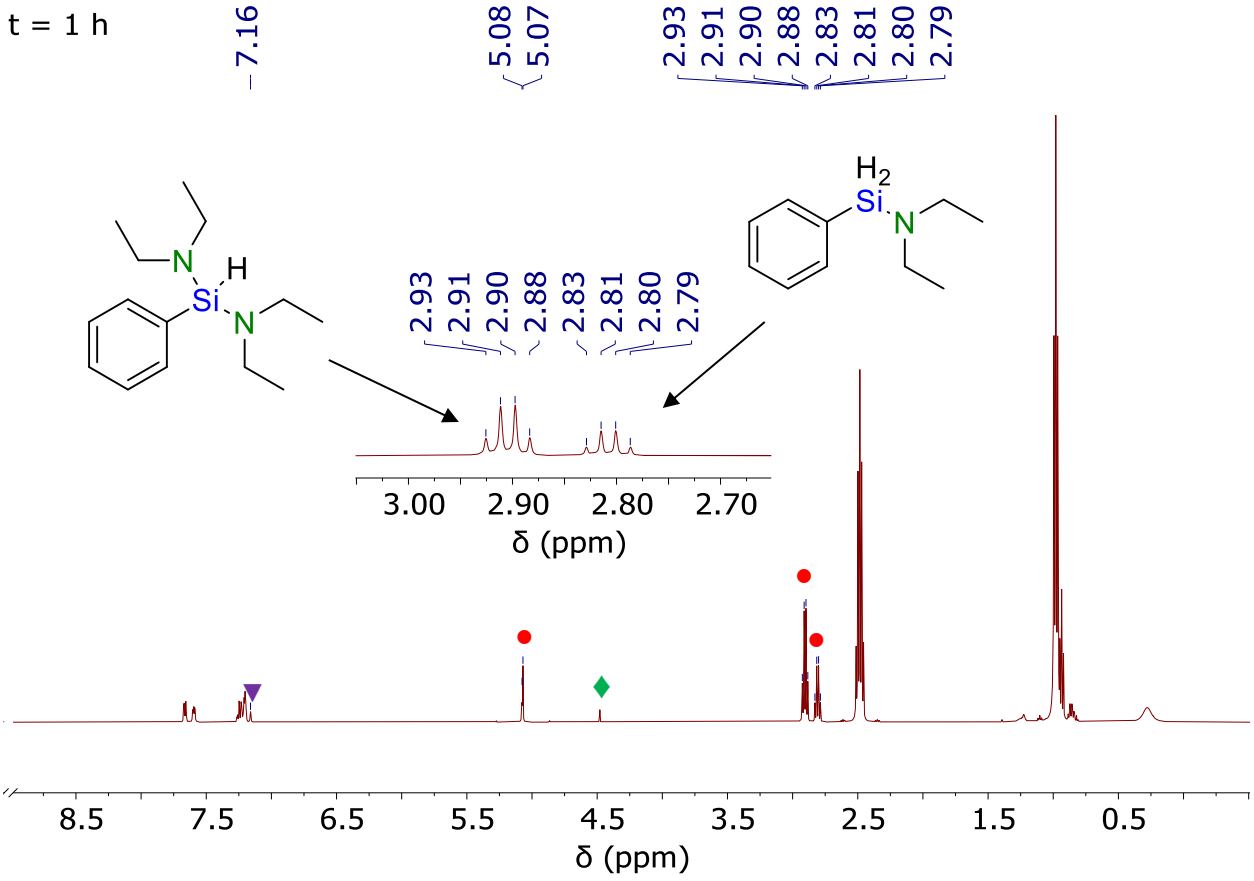

Figure S3.11. ^{1}H NMR spectrum of the reaction between $PhSiH_3$ and Et_2NH catalyzed by **1** in benzene-d_6 after 1 h.

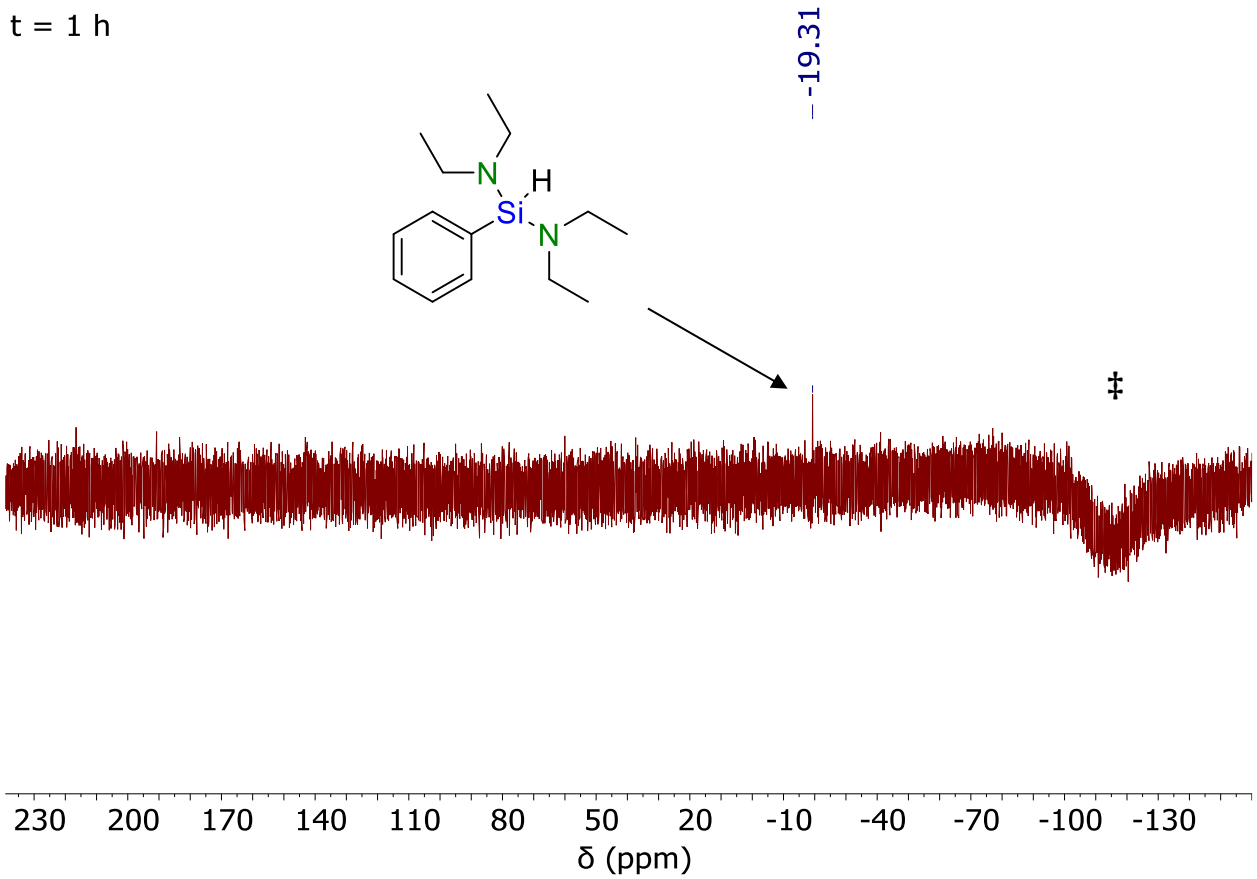

Figure S3.12. $^{29}Si\{^{1}H\}$ NMR spectrum of the reaction between $PhSiH_3$ and Et_2NH catalyzed by **1** in benzene-d_6 after 1 h.

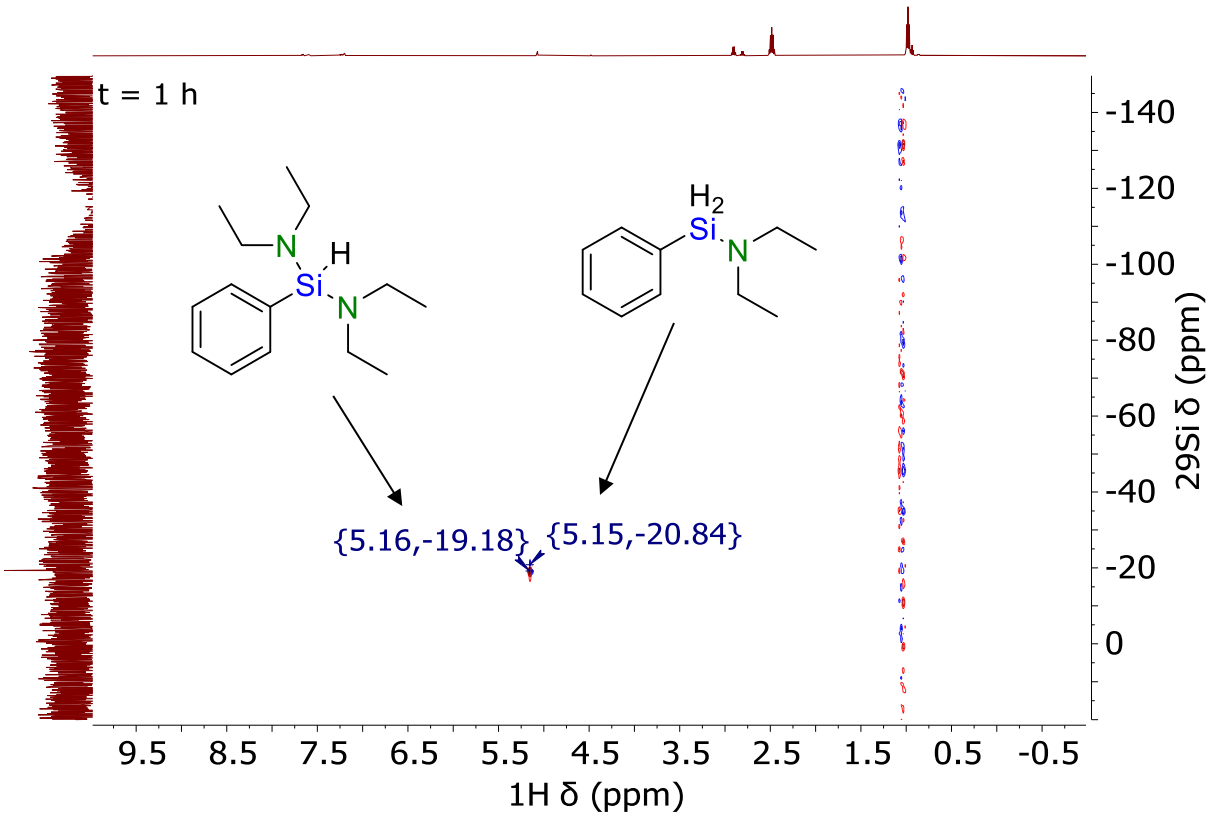

Figure S3.13. ^{1}H-$^{29}Si\{^{1}H\}$ HSQC NMR spectrum of the reaction between $PhSiH_3$ and Et_2NH catalyzed by **1** in benzene-d_6 after 1 h.

S5.8. $PhMeSiH_2$ and 4.0 equiv. of $^{n}PrNH_2$

$PhMeSiH_2$ (51.5 μL, 3.7×10^{-1} mmol), $^{n}PrNH_2$ (123.5 μL, 15.0×10^{-1} mmol, 4.0 equiv.), and **1** (14.5 μL, 3.7×10^{-2} mmol, 2.6 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6 in the presence of C_6Me_6 standard (52.5 μL, 0.4 M in benzene-d_6). Complete consumption of $PhMeSiH_2$ was observed after 1 h, as determined by the disappearance of the Si*H* peak at $\delta = 4.46$ in the ^{1}H NMR spectrum. The appearance of a diagnostic peak at $\delta = 2.76$ in the ^{1}H NMR spectrum, and a single peak in the ^{29}Si{^{1}H} NMR spectrum at $\delta = -17.17$, indicated 100% conversion to $PhMeSi(NH^{n}Pr)_2$ after 1 h at ambient temperature. Spectra were consistent with previous reports of this compound.[7]

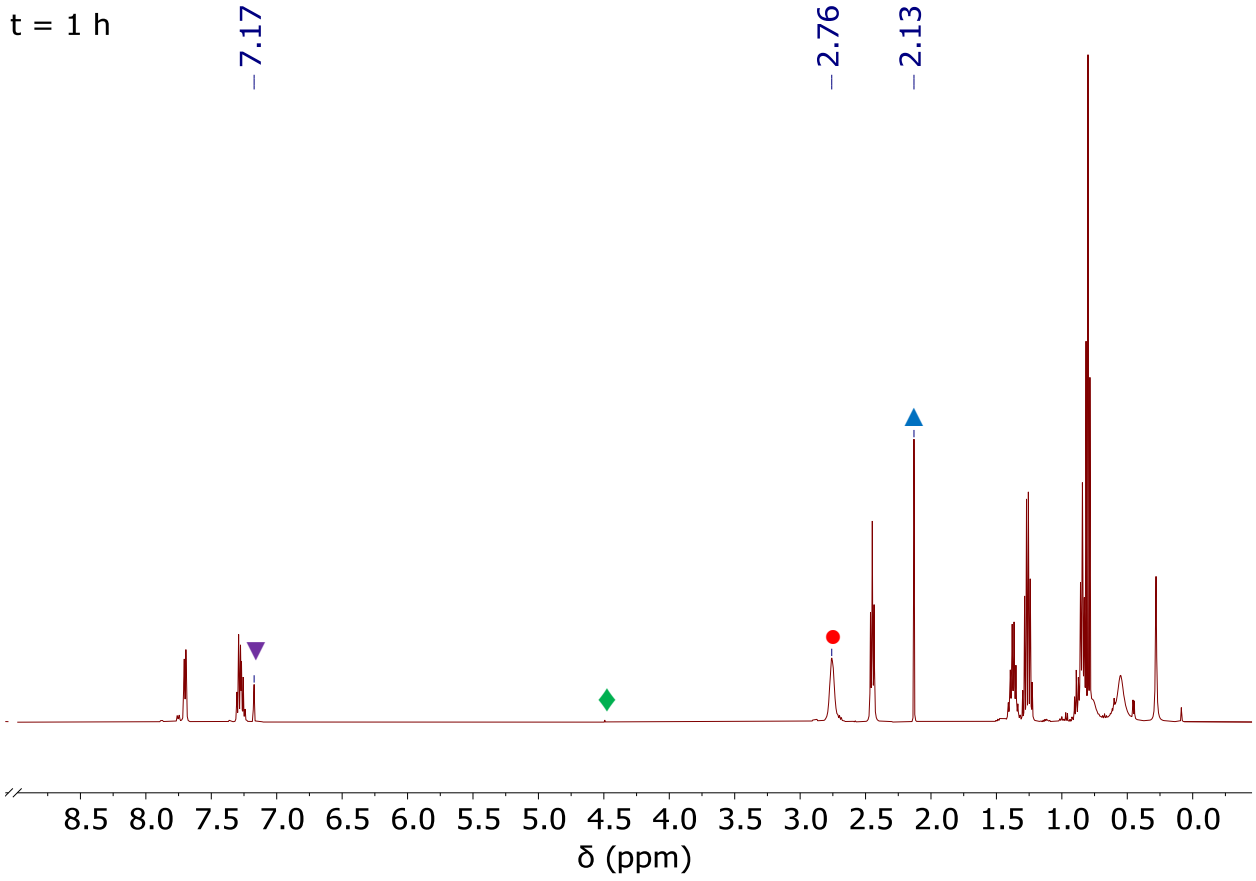

Figure S3.14. ^{1}H NMR spectrum of the reaction between $PhMeSiH_2$ and $^{n}PrNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

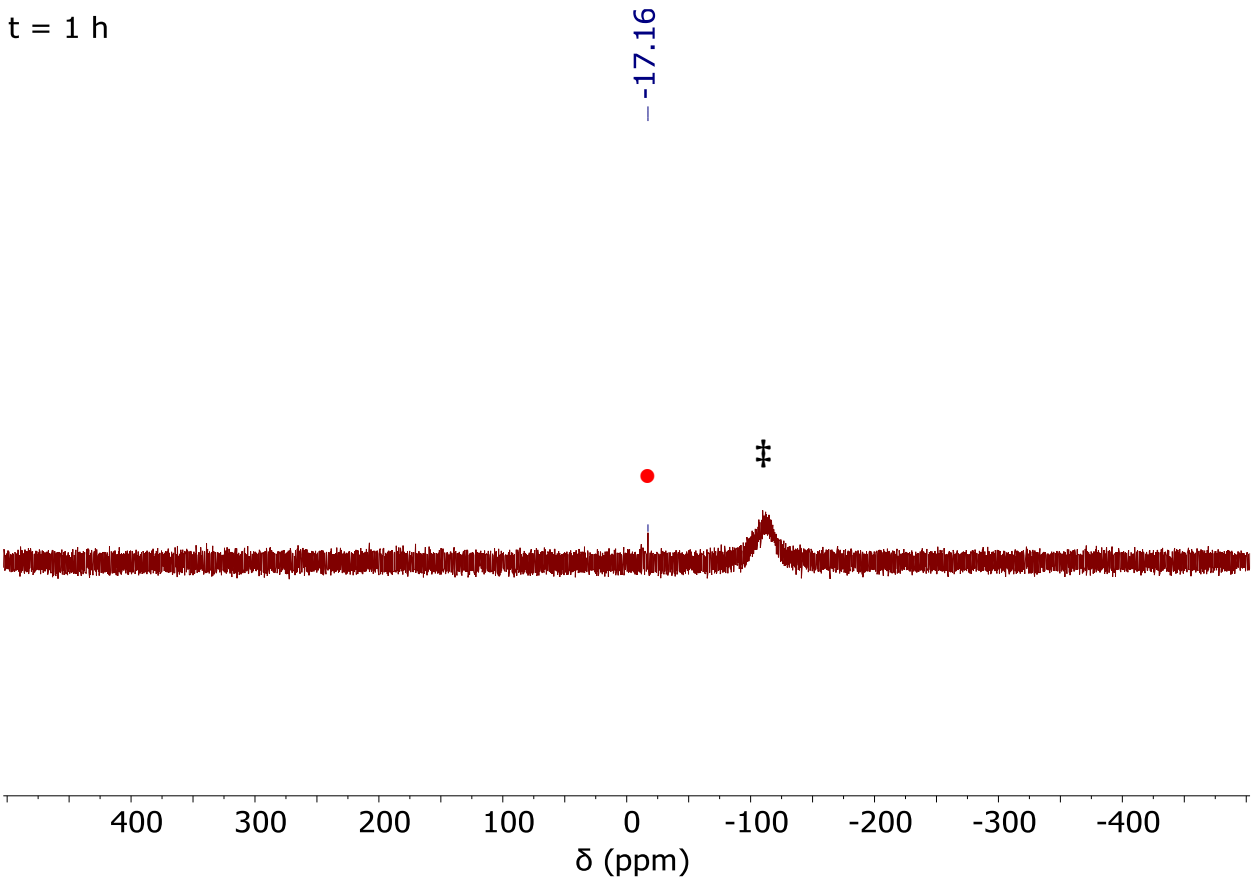

Figure S3.15. $^{29}Si\{^{1}H\}$ NMR spectrum of the reaction between $PhMeSiH_2$ and $^{n}PrNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

S5.9. $PhMeSiH_2$ and 4.0 equiv. of $^{i}PrNH_2$

$PhMeSiH_2$ (51.5 μL, 3.7×10^{-1} mmol), $^{i}PrNH_2$ (128.5 μL, 15.0×10^{-1} mmol, 4.0 equiv.), and **1** (14.5 μL, 3.7×10^{-2} mmol, 2.6 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6 in the presence of C_6Me_6 standard (52.5 μL, 0.4 M in benzene-d_6). Complete consumption of $PhMeSiH_2$ was observed after 1 h. The appearance of a diagnostic multiplet centered at δ = 3.16 in the ^{1}H NMR spectrum, and a single peak at δ = -20.21 in the $^{29}Si\{^{1}H\}$ NMR spectrum, indicated 100% conversion to $PhMeSi(NH^{i}Pr)_2$ after 1 h at ambient temperature. Spectra were consistent with previous reports of this compound.[6, 9]

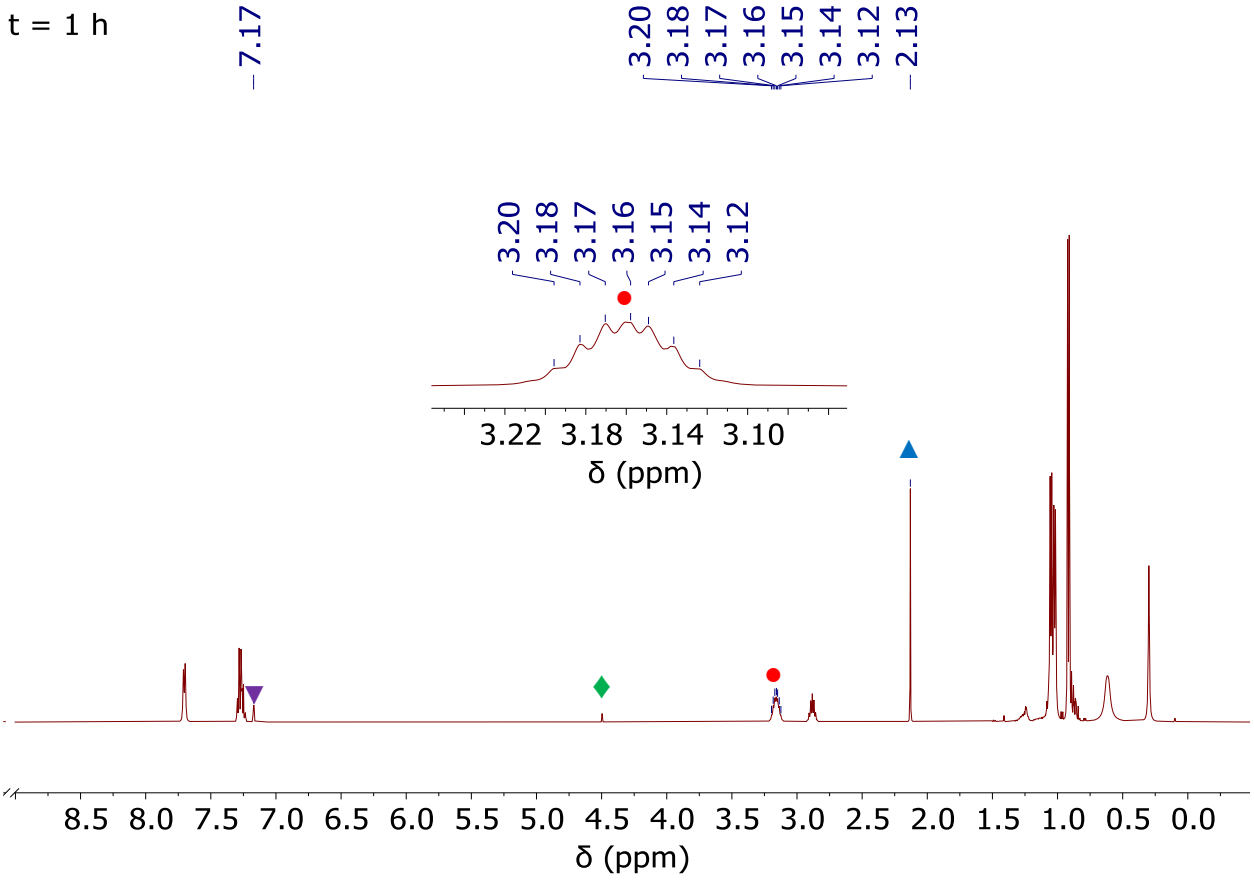

Figure S3.16. ^{1}H NMR spectrum of the reaction between $PhMeSiH_2$ and $^{i}PrNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

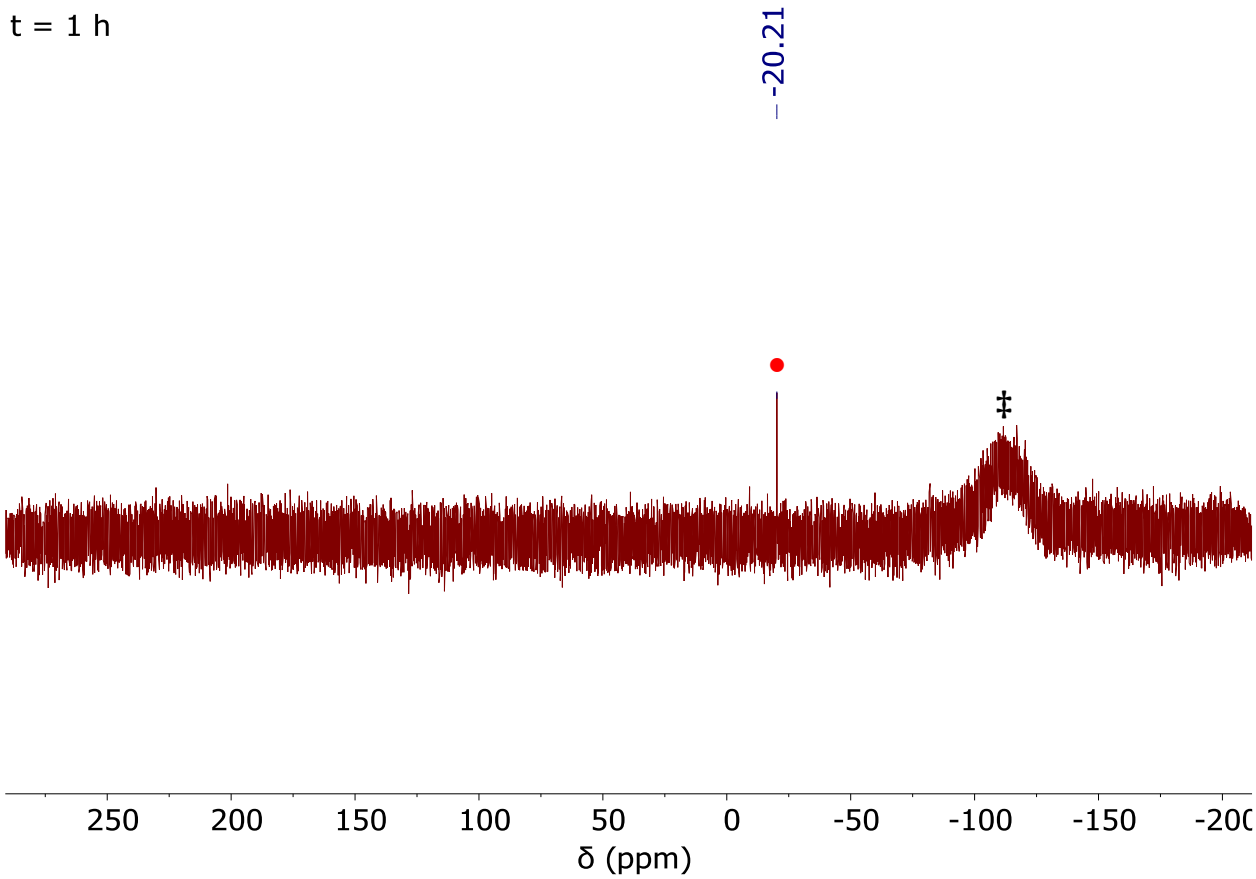

Figure S3.17. $^{29}Si\{^{1}H\}$ NMR spectrum of the reaction between $PhMeSiH_2$ and $^{i}PrNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

S5.10. $PhMeSiH_2$ and 4.0 equiv. of $^tBuNH_2$

$PhMeSiH_2$ (52.0 μL, 3.7×10^{-1} mmol), $^tBuNH_2$ (159.5 μL, 15.0×10^{-1} mmol, 4.0 equiv.), and **1** (16.5 μL, 3.7×10^{-2} mmol, 2.3 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6 in the presence of C_6Me_6 (52.5 μL, 0.4 M in benzene-d_6). Complete consumption of $PhMeSiH_2$ was observed after 1 h. The appearance of a quintet centered at δ = 1.08, and a diagnostic signal at δ = -21.50 in the ^1H-$^{29}Si\{^1H\}$ HSQC NMR spectrum, indicated at least 96% conversion to $PhMeSiH(NH^tBu)$ after 1 h at ambient temperature. The appearance of two additional Me peaks contributed to lower aminosilane conversions. Spectra were consistent with previous reports of this compound.[7]

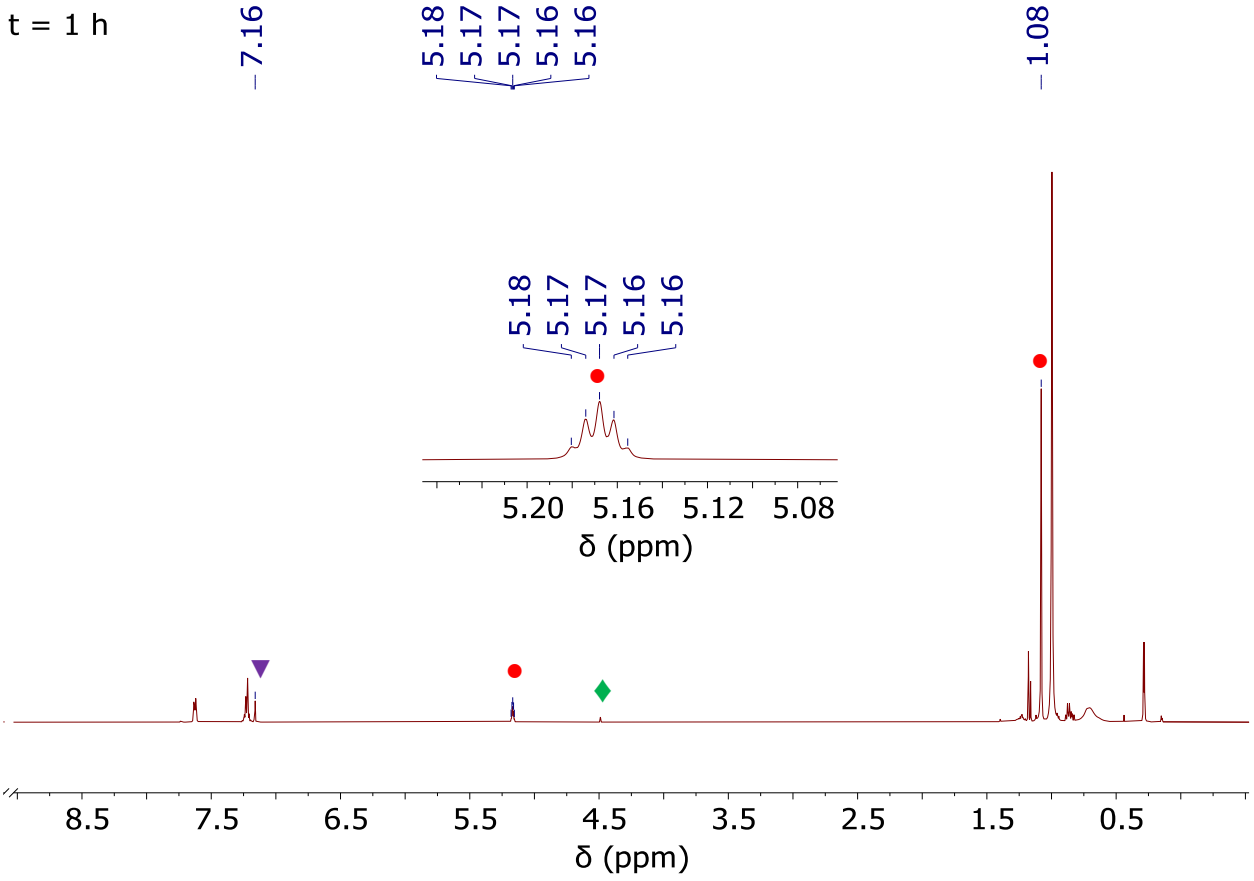

Figure S3.18. ^1H NMR spectrum of the reaction between $PhMeSiH_2$ and $^tBuNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

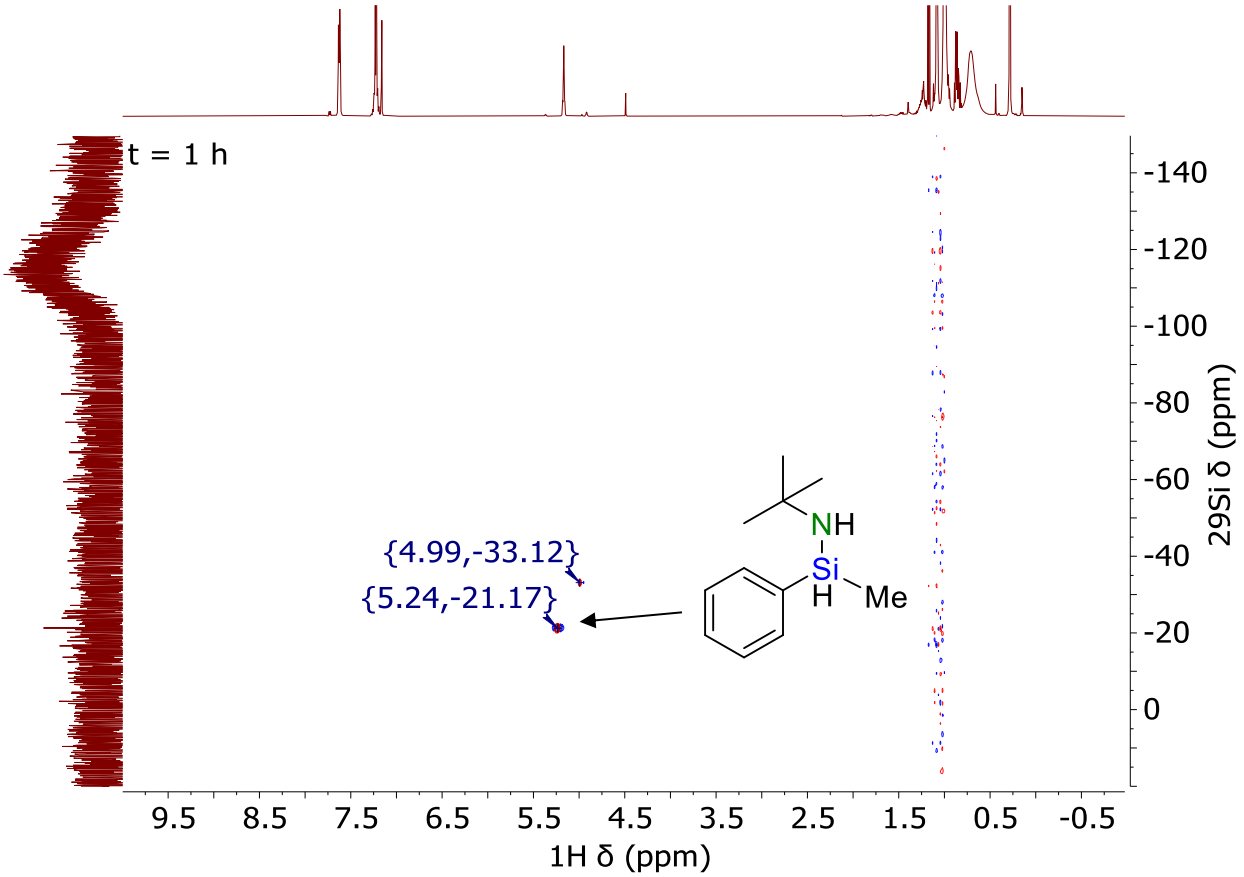

Figure S3.19. ^{1}H-^{29}Si{^{1}H} HSQC NMR spectrum of the reaction between $PhMeSiH_2$ and $^{t}BuNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

S5.11. $PhMeSiH_2$ and 4.0 equiv. of $PhNH_2$

$PhMeSiH_2$ (52.0 μL, 3.7×10^{-1} mmol), $PhNH_2$ (137.0 μL, 15.0×10^{-1} mmol, 4.0 equiv.), and **1** (16.5 μL, 3.7×10^{-2} mmol, 2.3 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6 in the presence of C_6Me_6 (52.5 μL, 0.4 M in benzene-d_6). Incomplete consumption of $PhMeSiH_2$ was observed after 1 h. Based on the relative integrations of product peak at δ = 0.29 to reagent peak at δ = 0.20, PhMeSiH(NHPh) was formed in 53% conversion after 1 h at ambient temperature. Spectra were consistent with previous reports of this compound.[7]

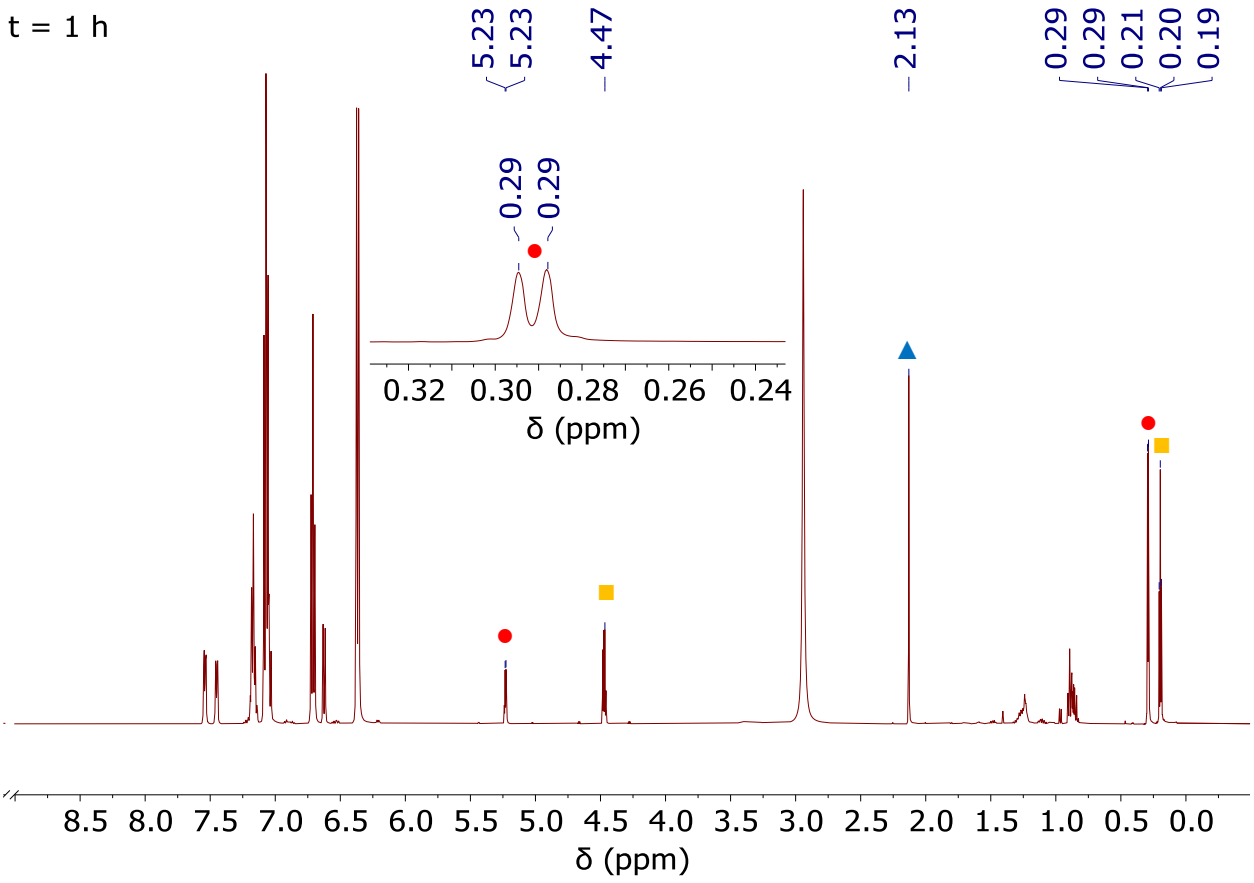

Figure S3.20. ^{1}H NMR spectrum of the reaction between $PhMeSiH_2$ and $PhNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

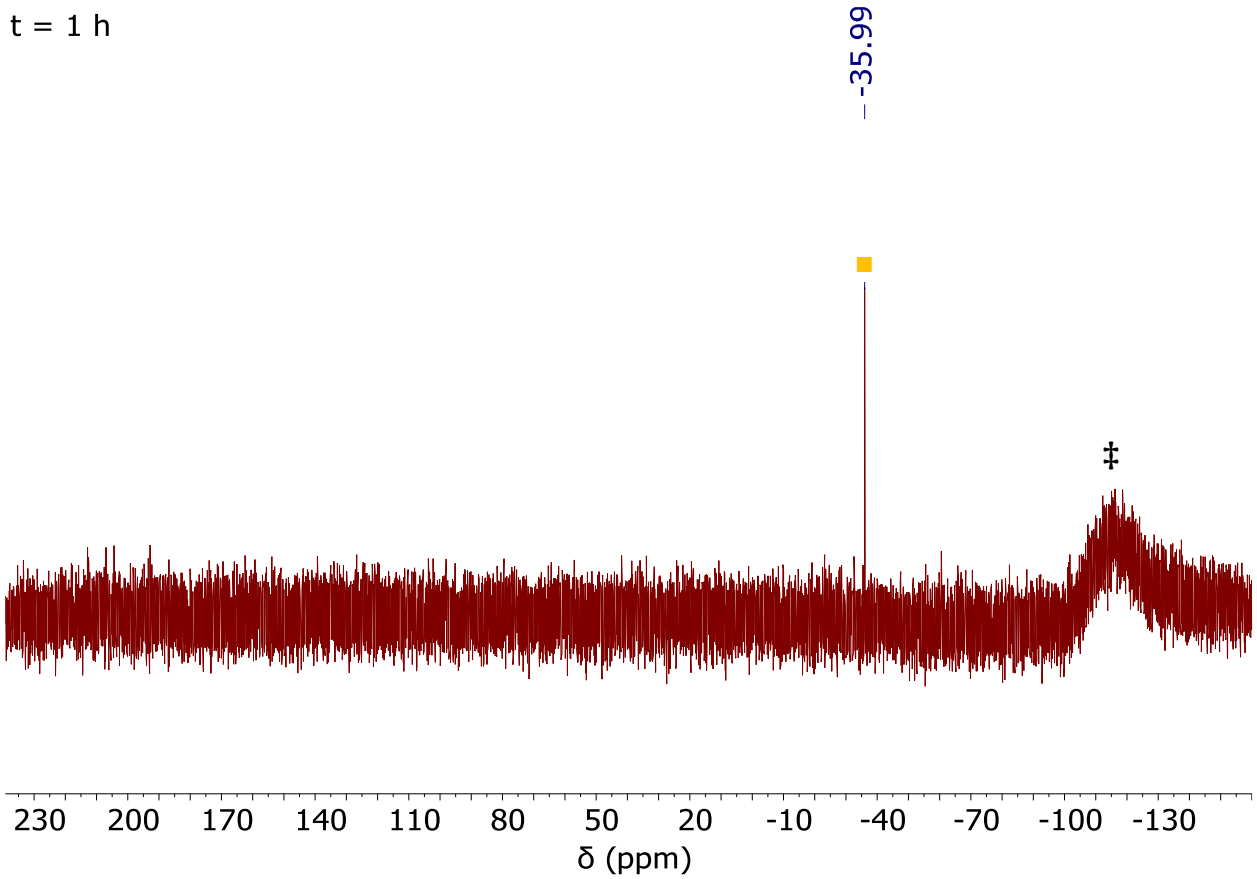

Figure S3.21. $^{29}Si\{^{1}H\}$ NMR spectrum of the reaction between $PhMeSiH_2$ and $PhNH_2$ catalyzed by **1** in benzene-d_6 after 1 h. The peak at δ = -35.99 is $PhMeSiH_2$.

S5.12. $PhMeSiH_2$ and 4.0 equiv. of PyNH

$PhMeSiH_2$ (52.0 μL, 3.7×10^{-1} mmol), PyNH (159.5 μL, 15.0×10^{-1} mmol, 4.0 equiv.), and **1** (16.5 μL, 3.7×10^{-2} mmol, 2.3 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6. Complete consumption of $PhMeSiH_2$ was observed after 0.5 h. The appearance of a diagnostic multiplet centered at $\delta = 3.01$ in the ^{1}H NMR spectrum indicated 100% conversion to $PhMeSi(NPy)_2$ after 0.5 h at ambient temperature.

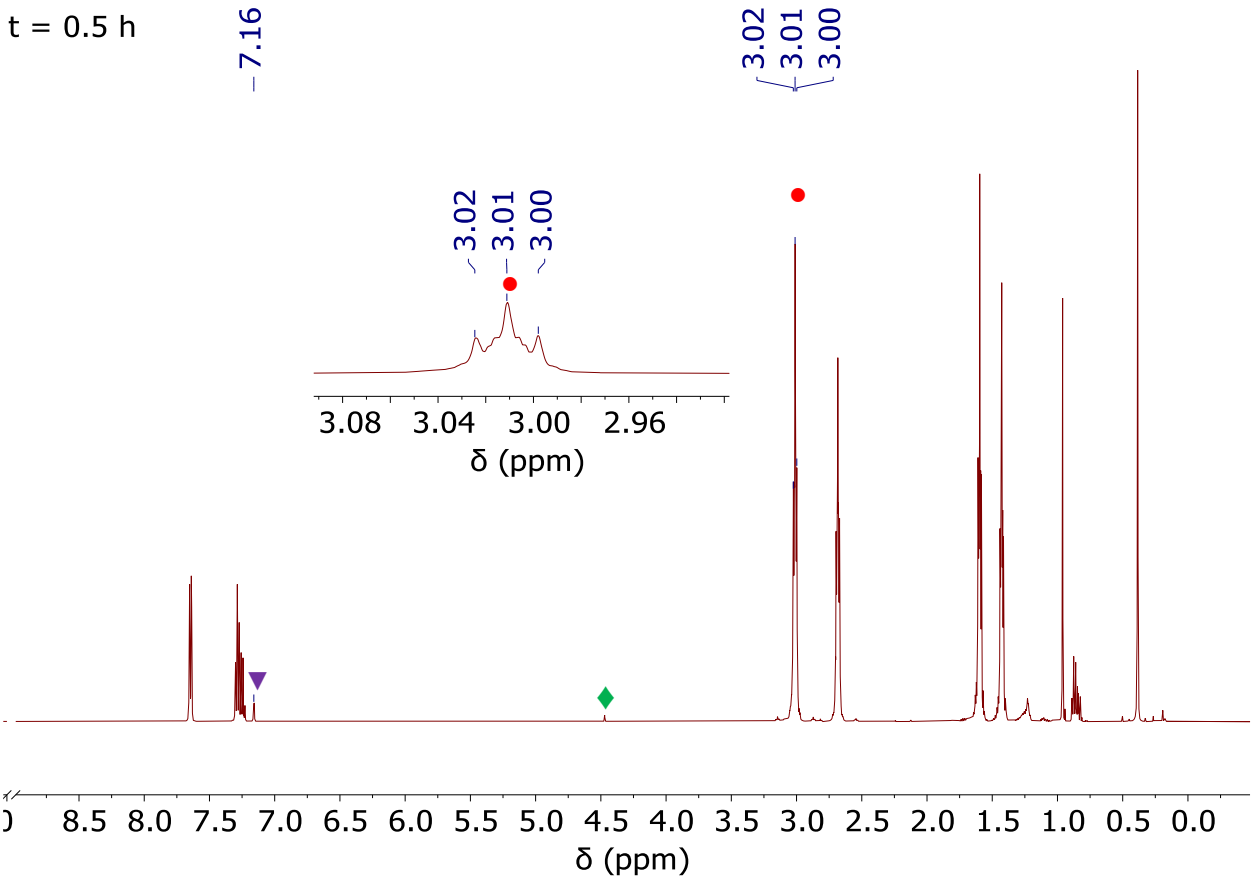

Figure S3.22. ^{1}H NMR spectrum of the reaction between $PhMeSiH_2$ and PyNH catalyzed by **1** in benzene-d_6 after 0.5 h.

S5.13. $PhMeSiH_2$ and 4.0 equiv. of Et_2NH

$PhMeSiH_2$ (51.5 μL, 3.7 × 10^{-1} mmol), Et_2NH (155.0 μL, 15.0 × 10^{-1} mmol, 4.0 equiv.), and **1** (14.5 μL, 3.7 × 10^{-2} mmol, 2.6 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6. Complete consumption of $PhMeSiH_2$ was observed after 1 h. The appearance of a diagnostic quartet centered between δ = 2.81 and δ = 2.80 in the ^{1}H NMR spectrum, and a single peak at δ = -11.19 in the ^{29}Si{^{1}H} NMR spectrum, indicated 100% conversion to $PhMeSiH(NEt_2)$ after 1 h at ambient temperature. The reaction was subsequently ended, due to the cessation of gas evolution. Spectra were consistent with previous reports of this compound.[6]

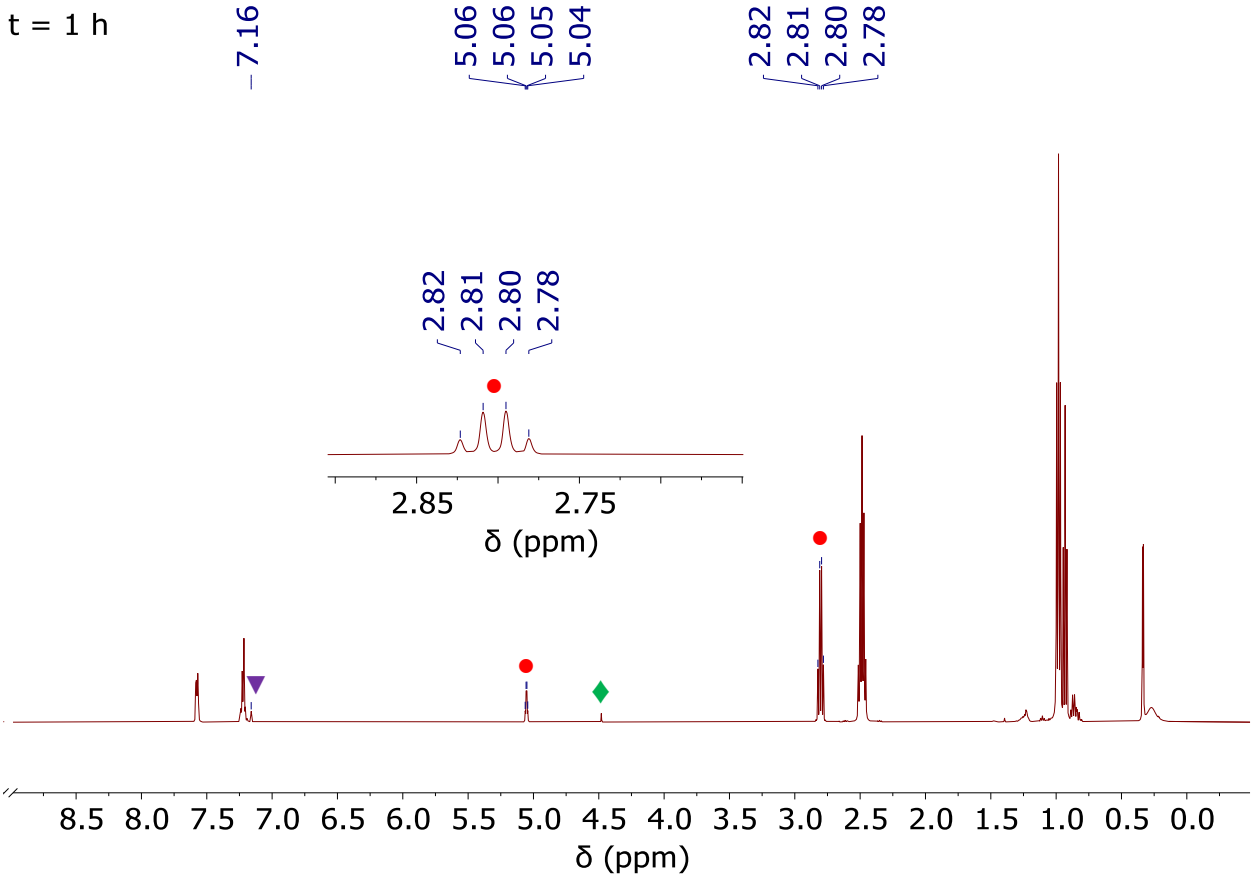

Figure S3.23. ^{1}H NMR spectrum of the reaction between $PhMeSiH_2$ and Et_2NH catalyzed by **1** in benzene-d_6 after 1 h.

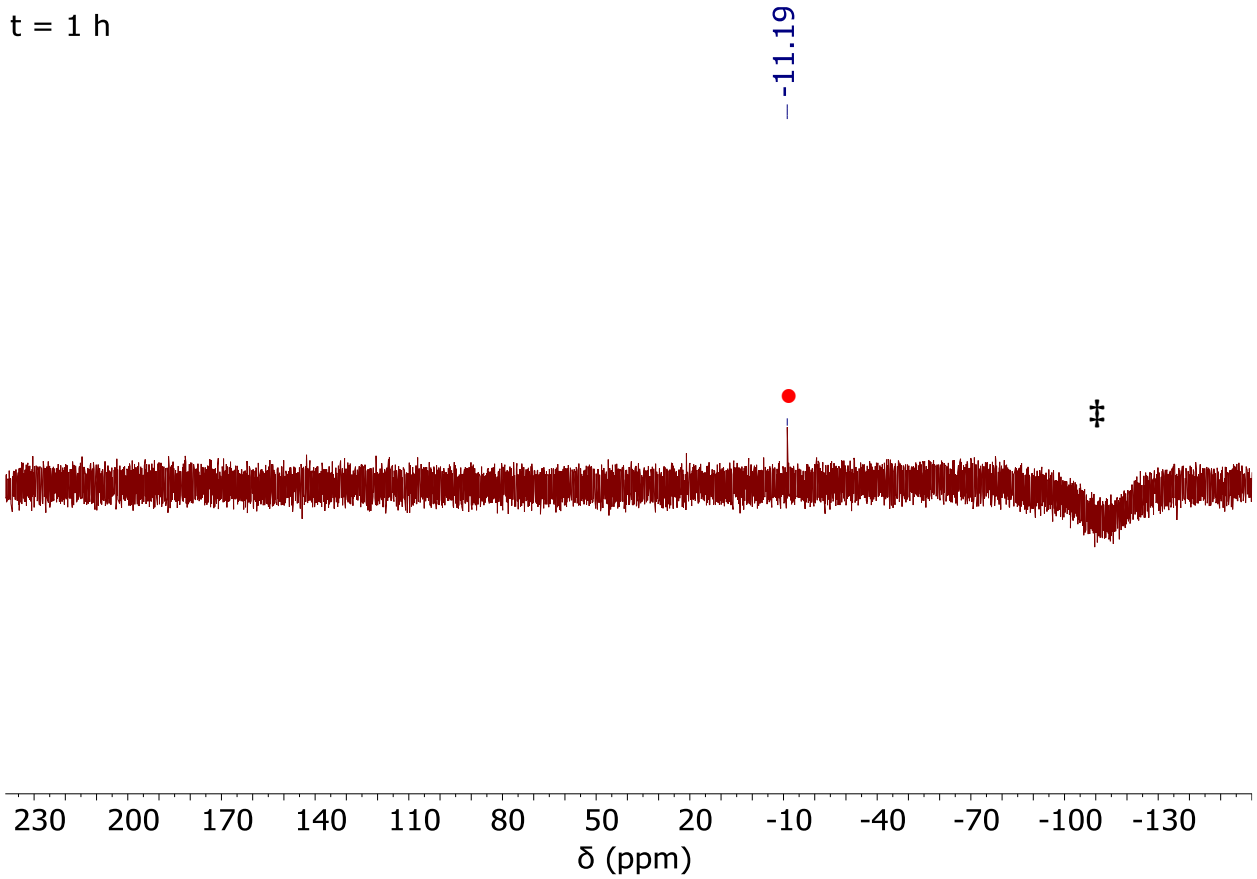

Figure S3.24. ^{29}Si NMR spectrum of the reaction between $PhMeSiH_2$ and Et_2NH catalyzed by **1** in benzene-d_6 after 1 h.

S5.14. Ph_2SiH_2 and 4.0 equiv. of $^nPrNH_2$

Ph_2SiH_2 (70.0 μL, 3.7×10^{-1} mmol), $^nPrNH_2$ (123.5 μL, 15.0×10^{-1} mmol, 4.0 equiv.), and **1** (14.5 μL, 3.7×10^{-2} mmol, 2.6 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6 in the presence of C_6Me_6 standard (52.5 μL, 0.4 M in benzene-d_6). Complete consumption of Ph_2SiH_2 was observed after 1 h, as determined by the disappearance of the Si*H* peak at δ = 5.08 in the ^{1}H NMR spectrum. The appearance of a diagnostic quartet centered between δ = 2.84 and δ = 2.85 in the ^{1}H NMR spectrum, and a single peak at δ = -25.50 in the ^{29}Si{^{1}H} NMR spectrum, indicated 99% conversion to $Ph_2Si(NH^nPr)_2$ after 1 h at ambient temperature. Spectra were consistent with previous reports of this compound.[7]

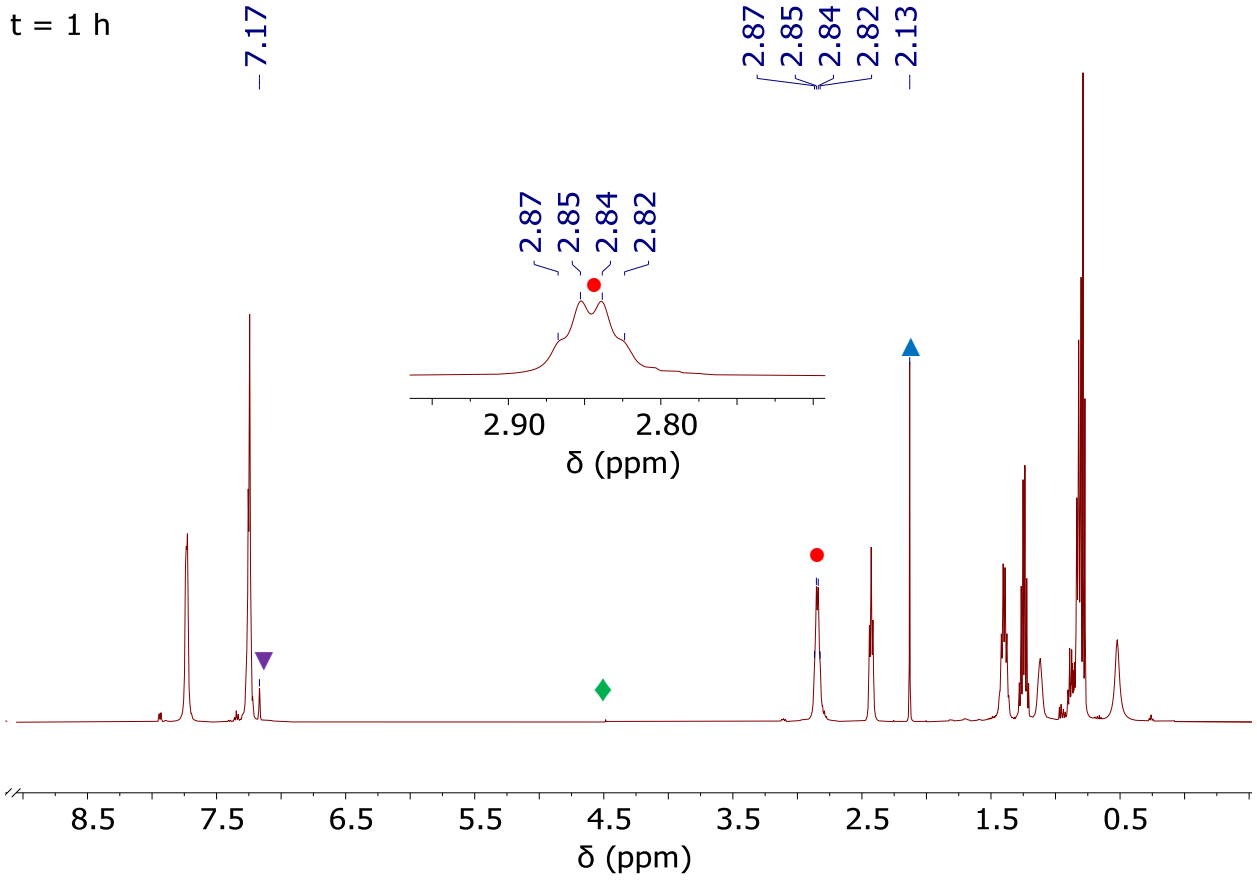

Figure S3.25. ^{1}H NMR spectrum of the reaction between Ph_2SiH_2 and $^nPrNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

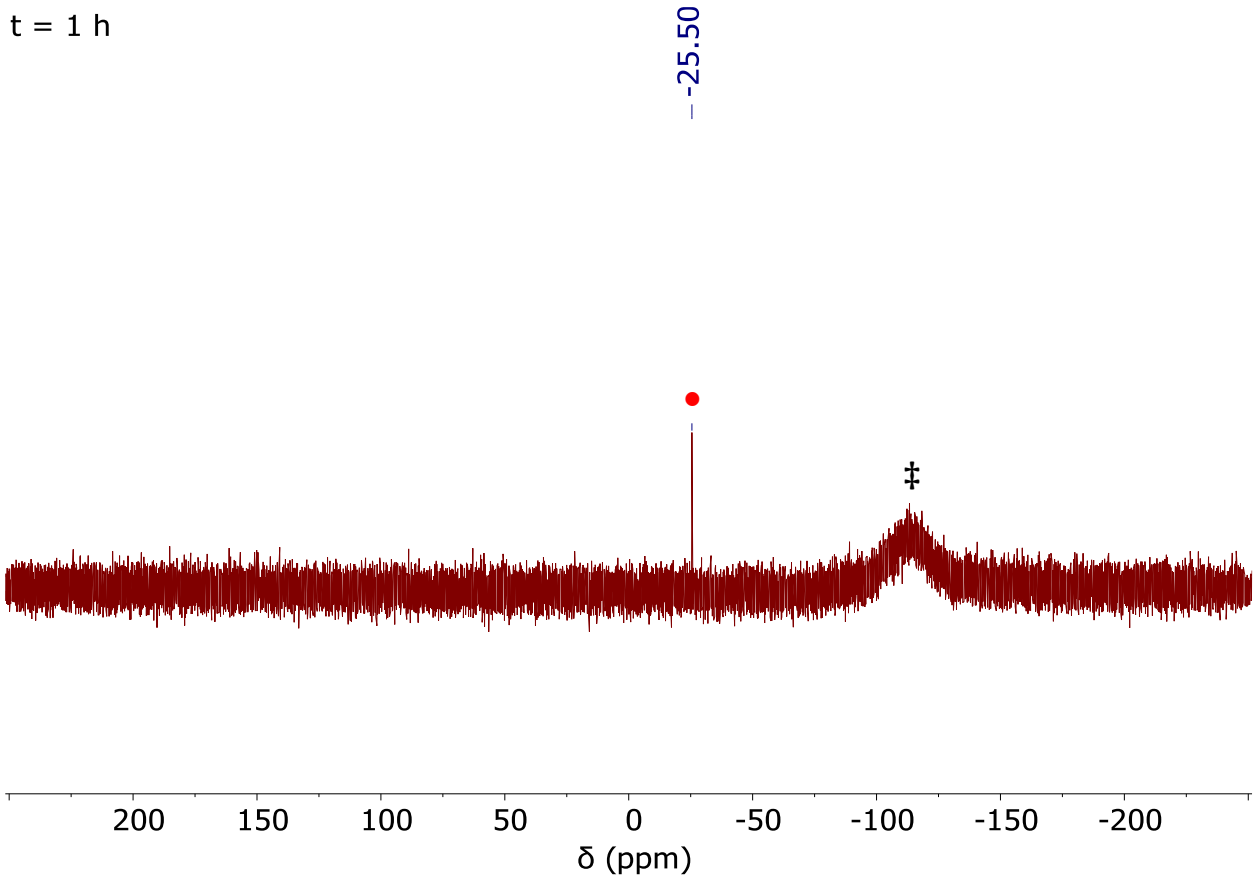

Figure S3.26. $^{29}Si\{^{1}H\}$ NMR spectrum of the reaction between Ph_2SiH_2 and $^{n}PrNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

S5.15. Ph_2SiH_2 and 4.0 equiv. of $^iPrNH_2$

Ph_2SiH_2 (70.5 μL, 3.7 × 10^{-1} mmol), $^iPrNH_2$ (130.0 μL, 15.0 × 10^{-1} mmol, 4.0 equiv.), and **1** (14.5 μL, 3.7 × 10^{-2} mmol, 2.6 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6 in the presence of C_6Me_6 standard (52.5 μL, 0.4 M in benzene-d_6). Complete consumption of Ph_2SiH_2 was observed after 1 h. The appearance of a diagnostic multiplet centered at δ = 3.27 in the ^{1}H NMR spectrum, and a single peak at δ = -28.44 in the ^{29}Si{^{1}H} NMR spectrum, indicated 100% conversion to $Ph_2Si(NH^iPr)_2$ after 1 h at ambient temperature. Spectra were consistent with previous reports of this compound.[6]

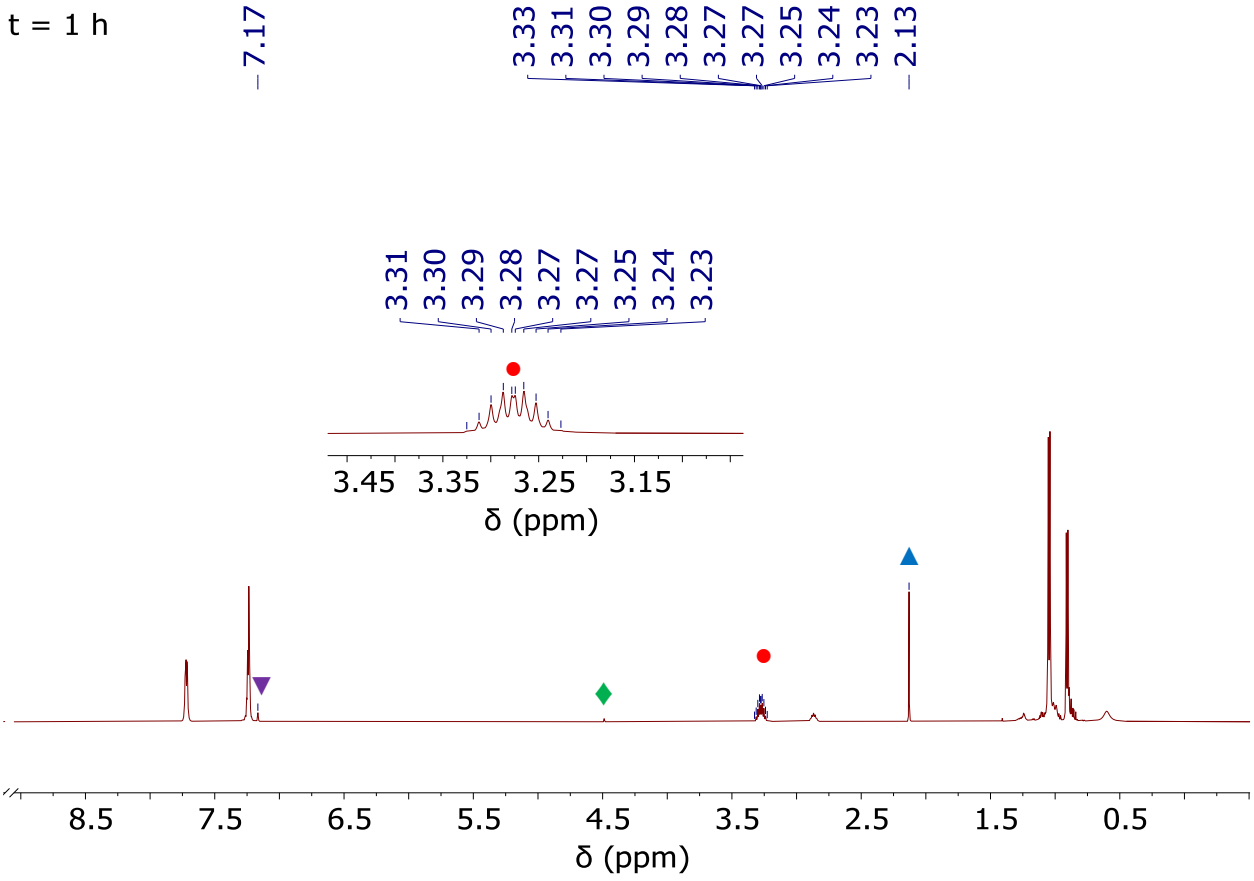

Figure S3.27. ^{1}H NMR spectrum of the reaction between Ph_2SiH_2 and $^iPrNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

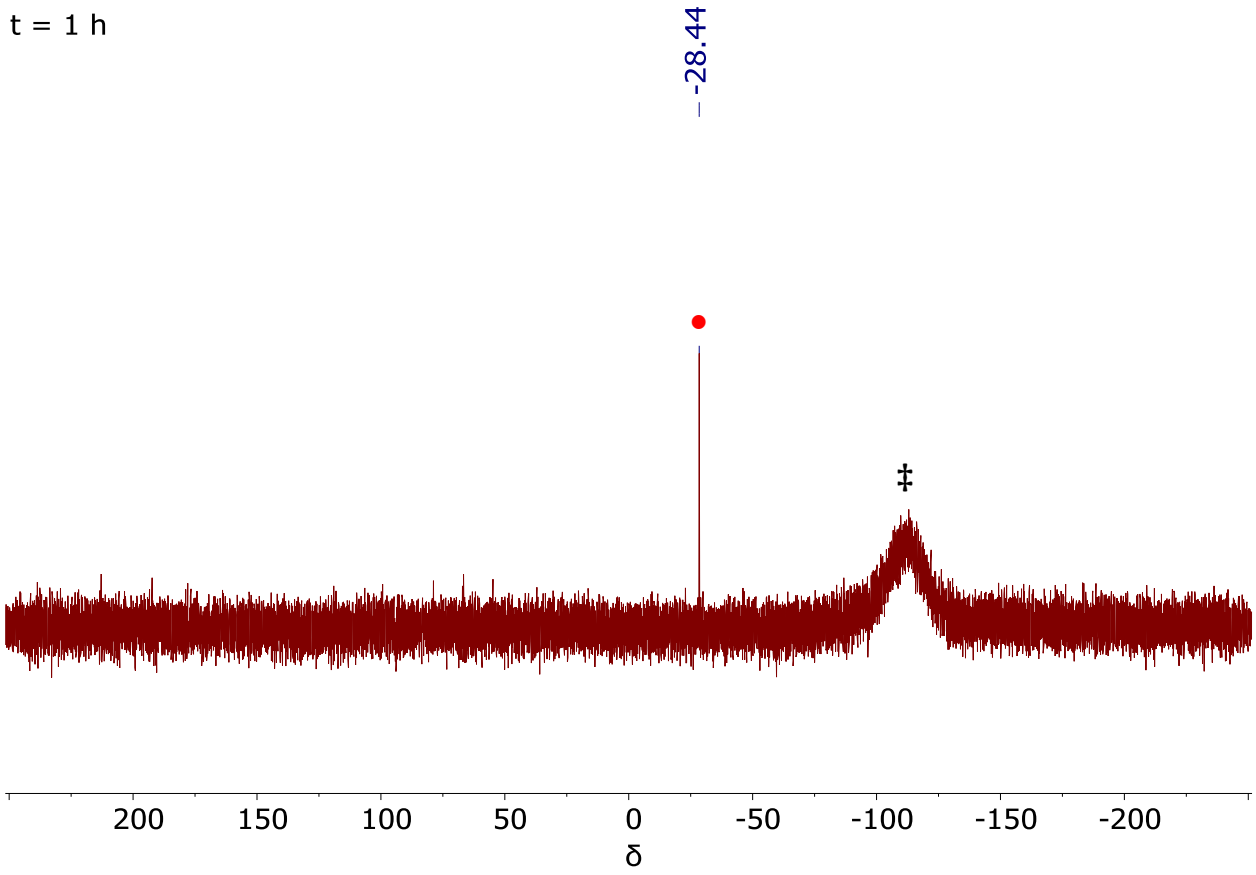

Figure S3.28. $^{29}Si\{^{1}H\}$ NMR spectrum of the reaction between Ph_2SiH_2 and $^{i}PrNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

S5.16. Ph_2SiH_2 and 4.0 equiv. of $^tBuNH_2$

Ph_2SiH_2 (70.0 μL, 3.7 × 10^{-1} mmol), $^tBuNH_2$ (158.0 μL, 15.0 × 10^{-1} mmol, 4.0 equiv.), and **1** (14.5 μL, 3.7 × 10^{-1} mmol, 2.6 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6. Complete consumption of Ph_2SiH_2 was observed after 1 h. After 1 h at ambient temperature, $Ph_2SiH(NH^tBu)$ and $Ph_2Si(NH^tBu)_2$ were formed in approximately 97% and 3% conversion. Spectra were consistent with previous reports of these compounds.[7, 10]

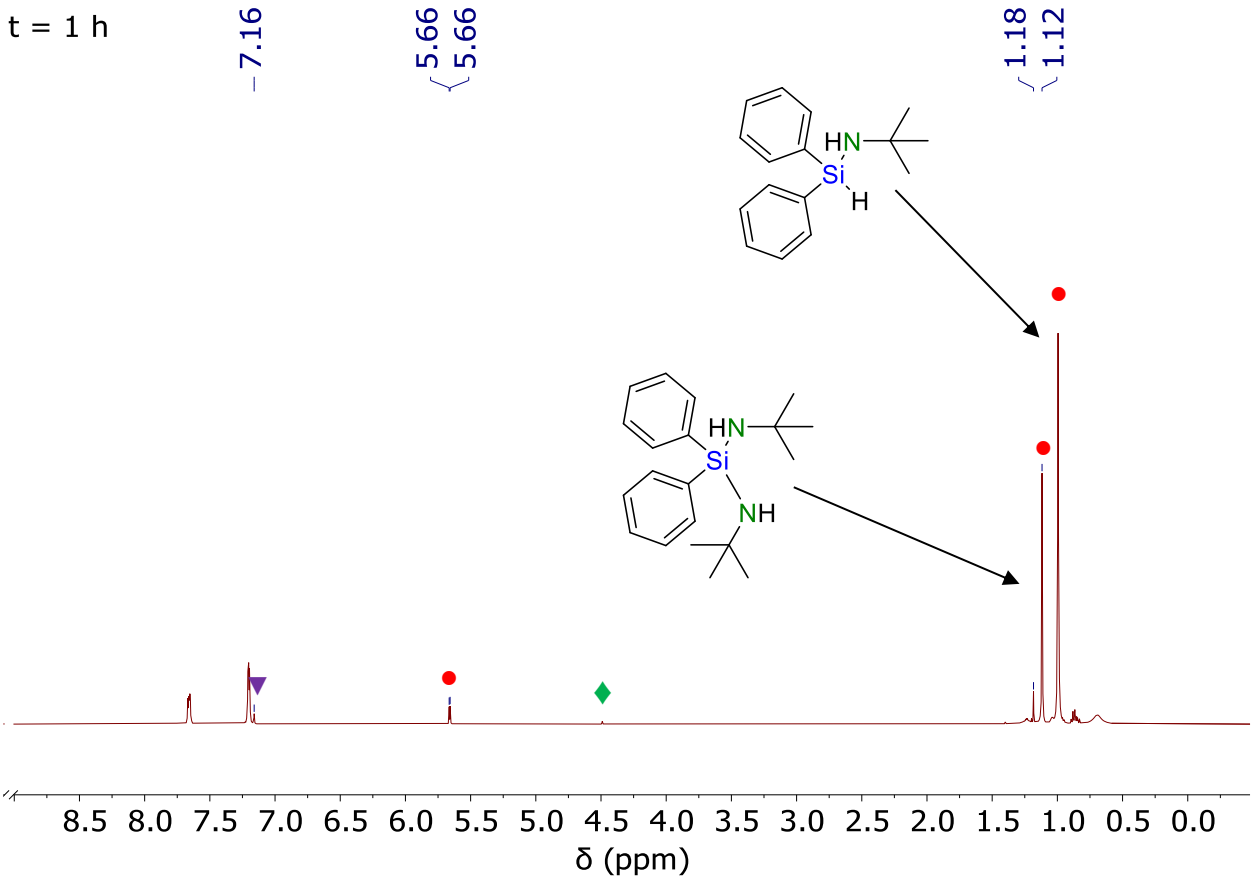

Figure S3.29. ^{1}H NMR spectrum of the reaction between Ph_2SiH_2 and $^tBuNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

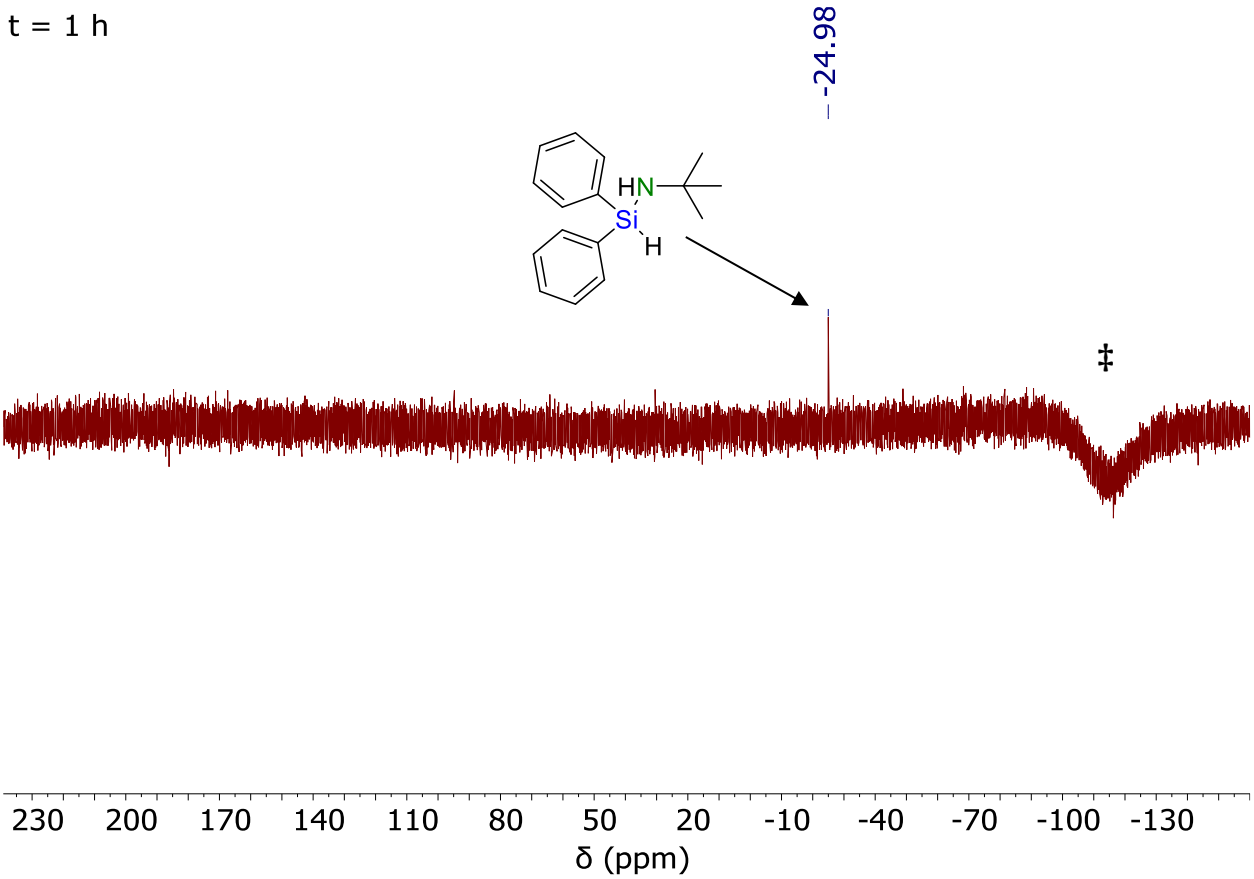

Figure S3.30. $^{29}Si\{^{1}H\}$ NMR spectrum of the reaction between Ph_2SiH_2 and $^{t}BuNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

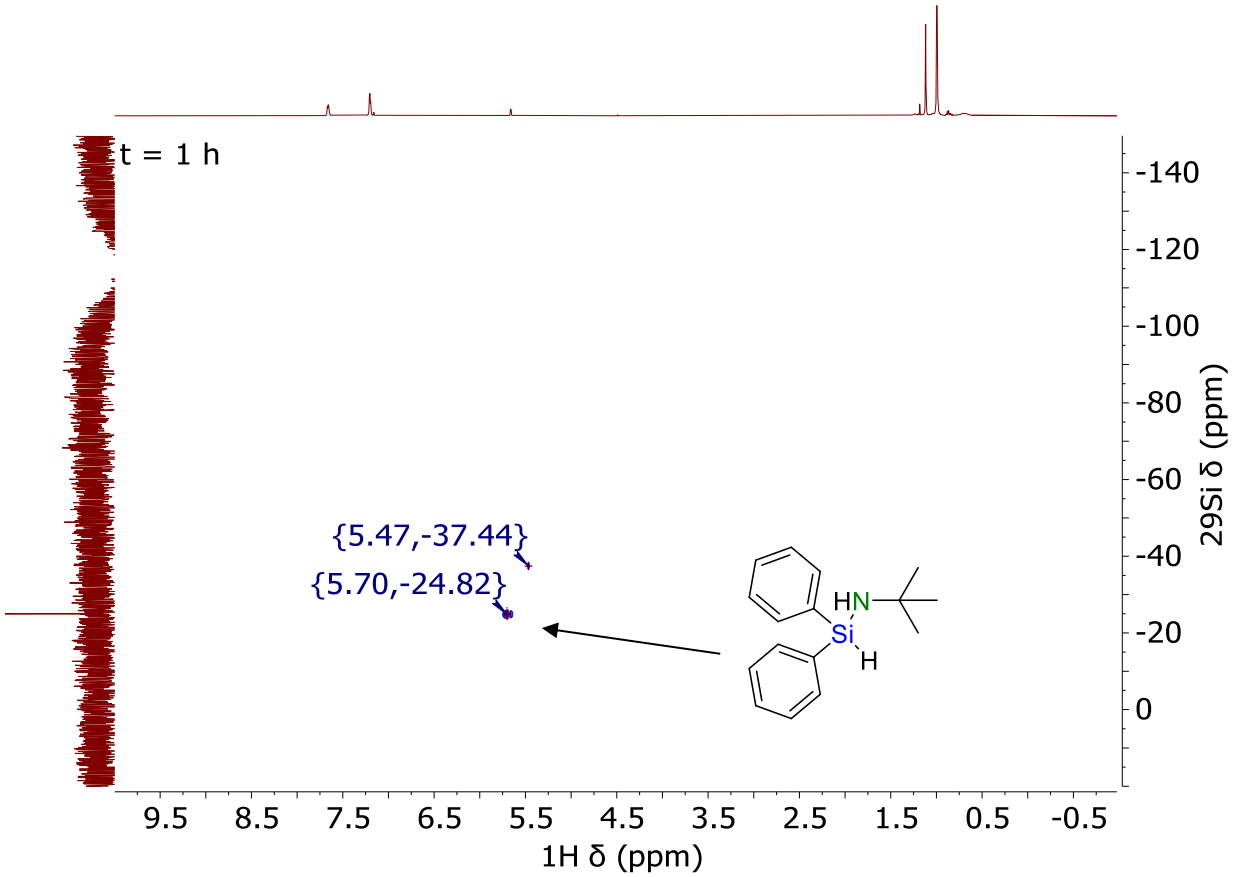

Figure S3.31. ^{1}H-$^{29}Si\{^{1}H\}$ HSQC NMR spectrum of the reaction between Ph_2SiH_2 and $^{t}BuNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

S5.17. Ph_2SiH_2 and 4.0 equiv. of $PhNH_2$

Ph_2SiH_2 (70.5 μL, 3.7 × 10^{-1} mmol), $PhNH_2$ (137.5 μL, 15.2 × 10^{-1} mmol, 4.0 equiv.), and **1** (16.5 μL, 3.7 × 10^{-1} mmol, 2.3 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6. Complete consumption of Ph_2SiH_2 was observed after 1 h. After 1 h at ambient temperature, $Ph_2SiH(NHPh)$ and $Ph_2Si(NHPh)_2$ were formed in approximately 99% and 1% conversion. Spectra were consistent with previous reports of these compounds.[6, 7]

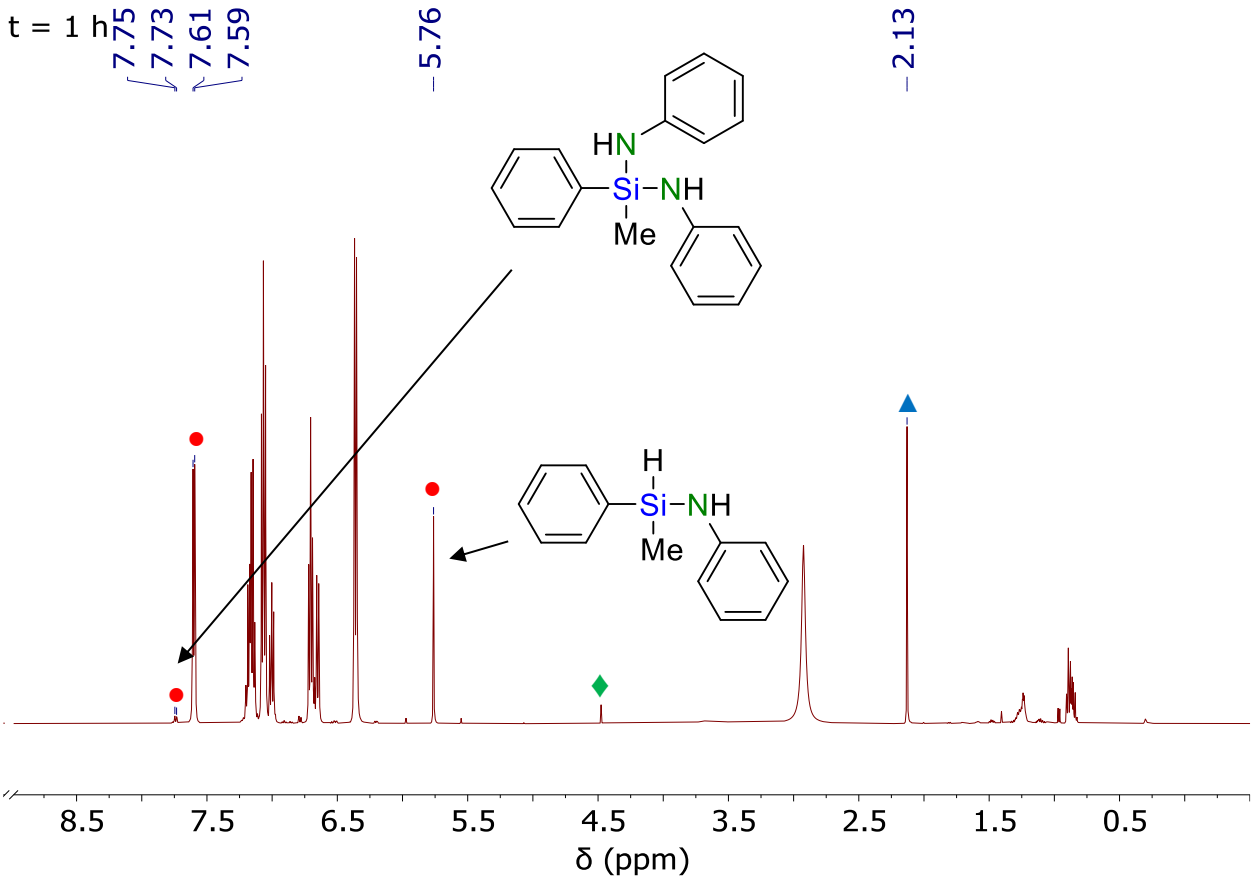

Figure S3.32. ^{1}H NMR spectrum of the reaction between Ph_2SiH_2 and $PhNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

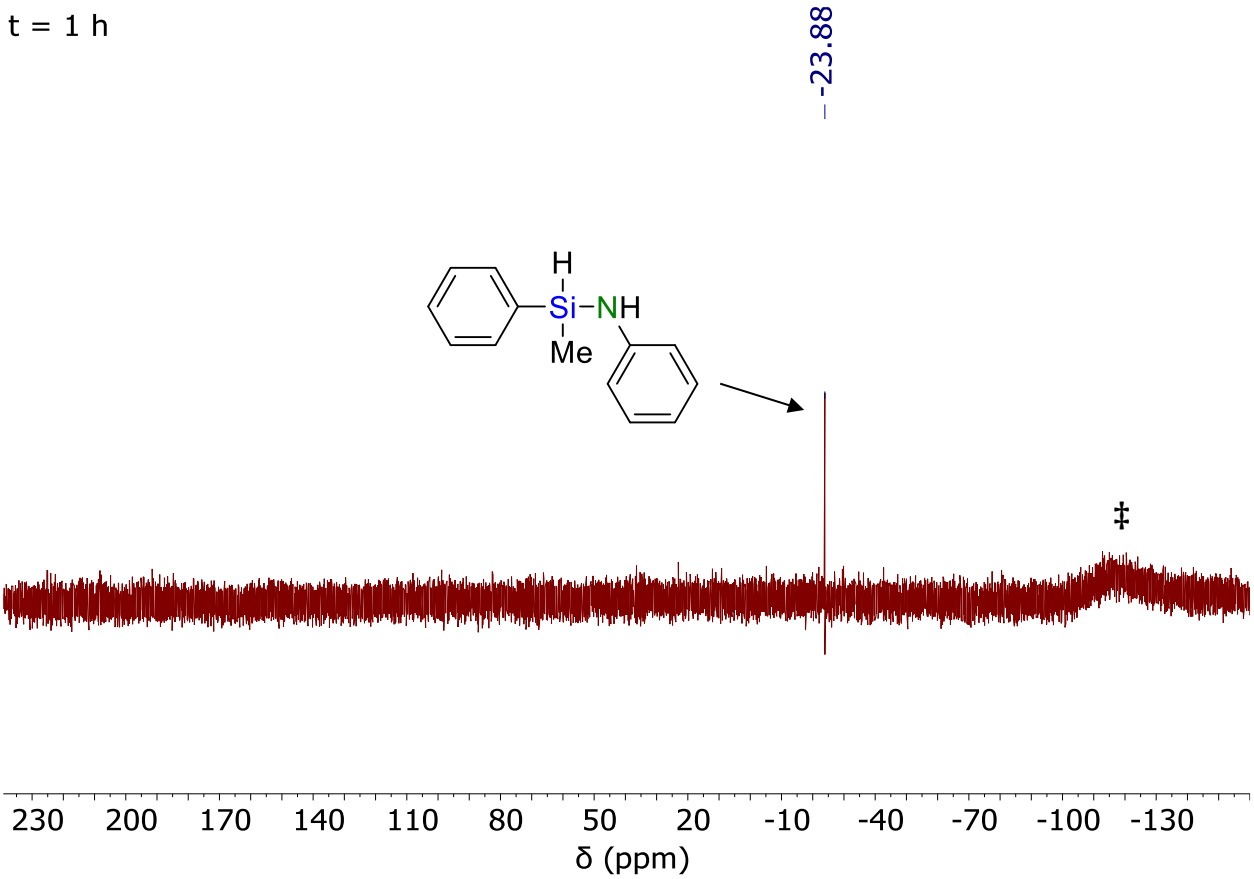

Figure S3.33. $^{29}Si\{^{1}H\}$ NMR spectrum of the reaction between Ph_2SiH_2 and $PhNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

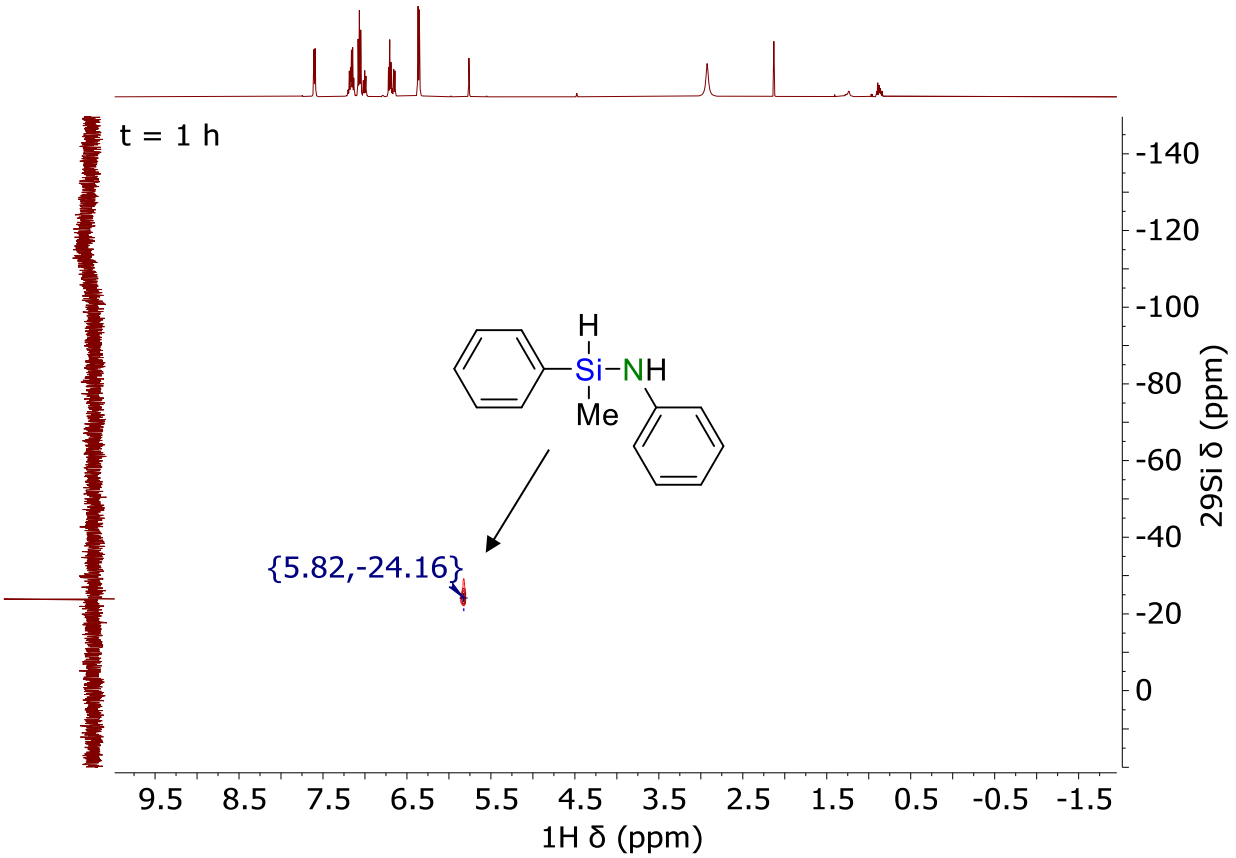

Figure S3.34. ^{1}H-$^{29}Si\{^{1}H\}$ HSQC NMR spectrum of the reaction between Ph_2SiH_2 and $PhNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

S5.18. Ph_2SiH_2 and 4.0 equiv. of PyNH

Ph_2SiH_2 (70.0 μL, 3.7 × 10^{-1} mmol), PyNH (123.5 μL, 15.0 × 10^{-1} mmol, 4.0 equiv.), and **1** (15.0 μL, 3.7 × 10^{-2} mmol, 2.5 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6. Complete consumption of Ph_2SiH_2 was observed after 0.5 h. The appearance of a diagnostic multiplet centered at δ = 3.10 in the ^{1}H NMR spectrum indicated 100% conversion to $Ph_2Si(NPy)_2$ after 0.5 h at ambient temperature.

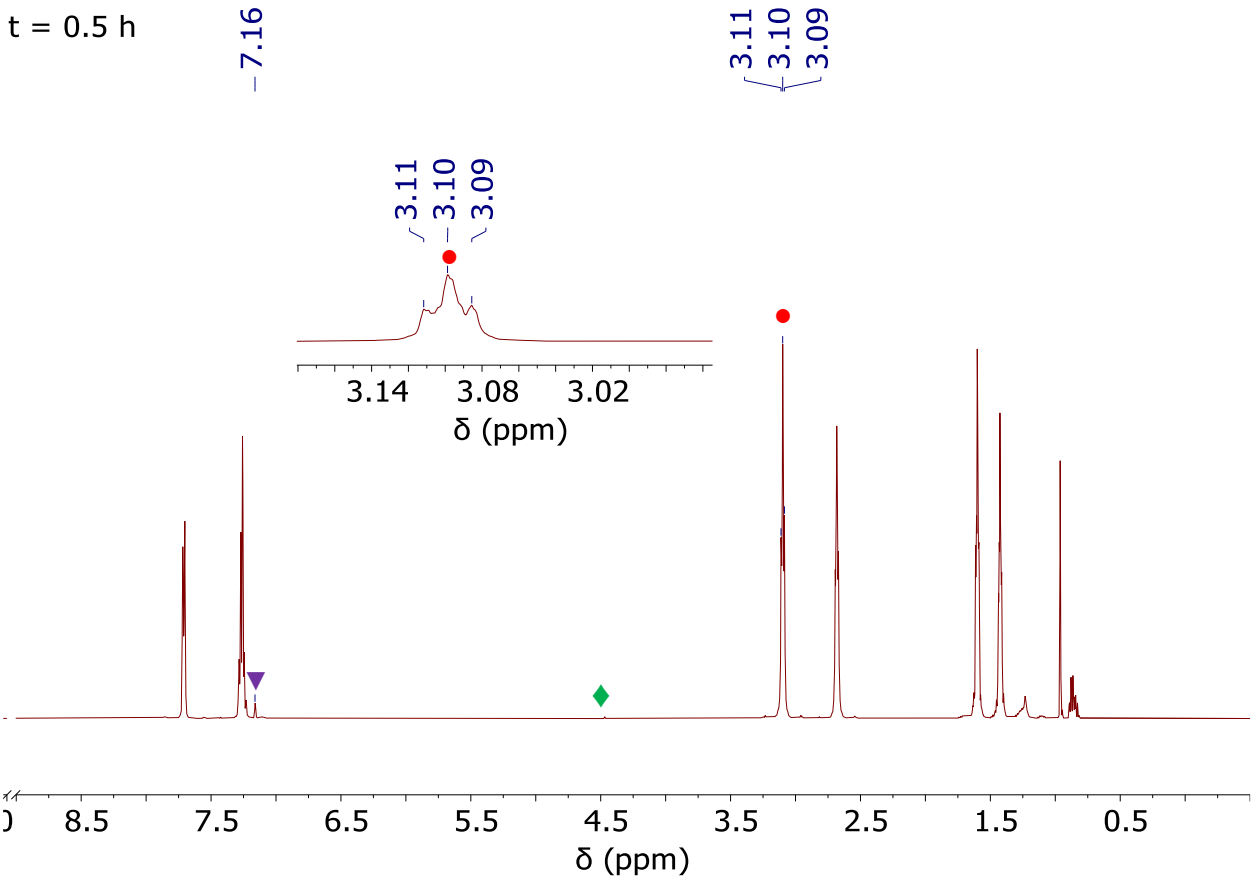

Figure S3.35. ^{1}H NMR spectrum of the reaction between Ph_2SiH_2 and PyNH catalyzed by **1** in benzene-d_6 after 0.5 h.

S5.19. Ph_2SiH_2 and 4.0 equiv. of Et_2NH

Ph_2SiH_2 (70.0 μL, 3.7×10^{-1} mmol), Et_2NH (155.5 μL, 15.0×10^{-1} mmol, 4.0 equiv.), and **1** (14.5 μL, 3.7×10^{-2} mmol, 2.6 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6. Incomplete consumption of Ph_2SiH_2 was observed after 1 h, as determined by the presence of the Si*H* peak at δ = 5.02 in the ^{1}H NMR spectrum. The appearance of a diagnostic quartet centered between δ = 2.89 and δ = 2.88 in the ^{1}H NMR spectrum indicated 69% conversion to $Ph_2SiH(NEt_2)$ after 1 h at ambient temperature. The reaction was subsequently ended, due to the cessation of gas evolution. Spectra were consistent with previous reports of this compound.[6]

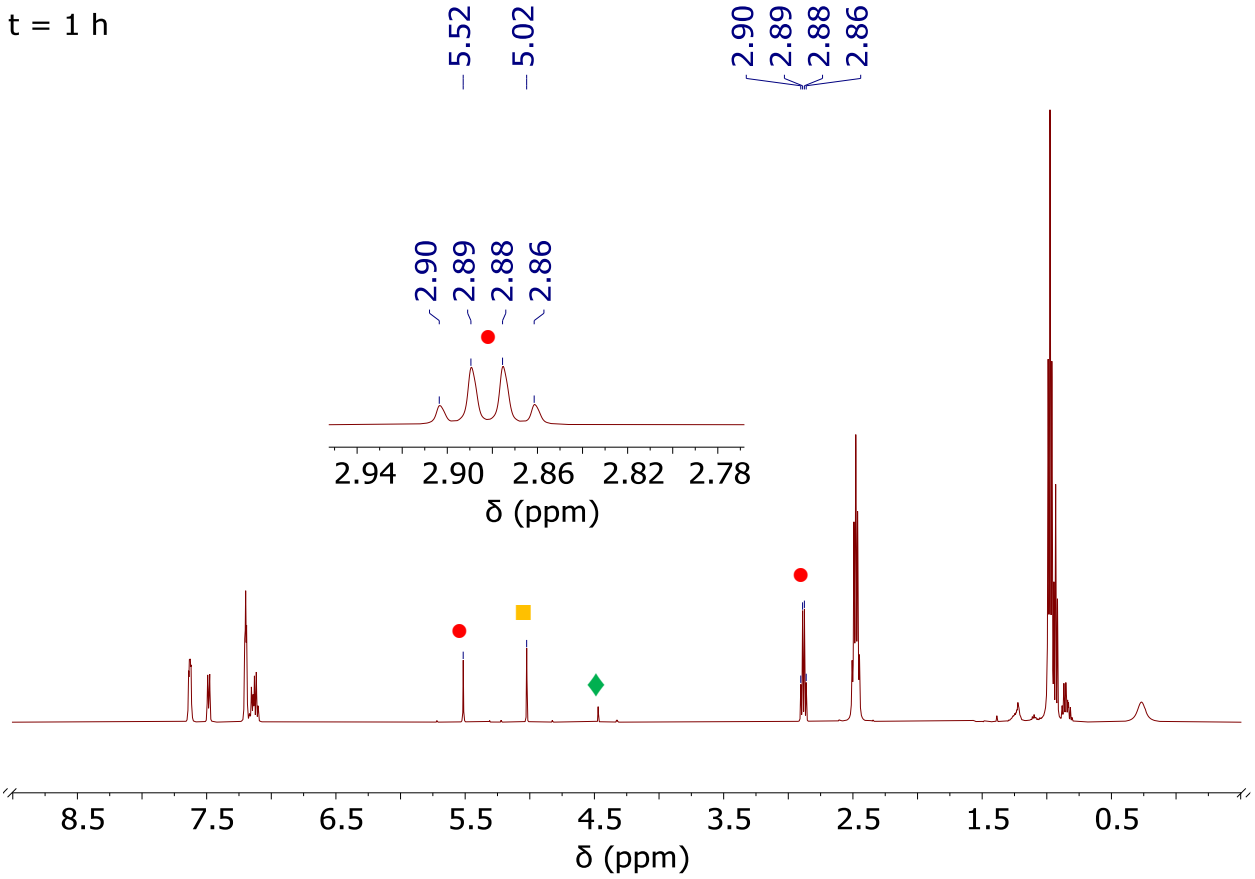

Figure S3.36. ^{1}H NMR spectrum of the reaction between Ph_2SiH_2 and Et_2NH catalyzed by **1** in benzene-d_6 after 1 h. Residual solvent is buried by aryl peaks.

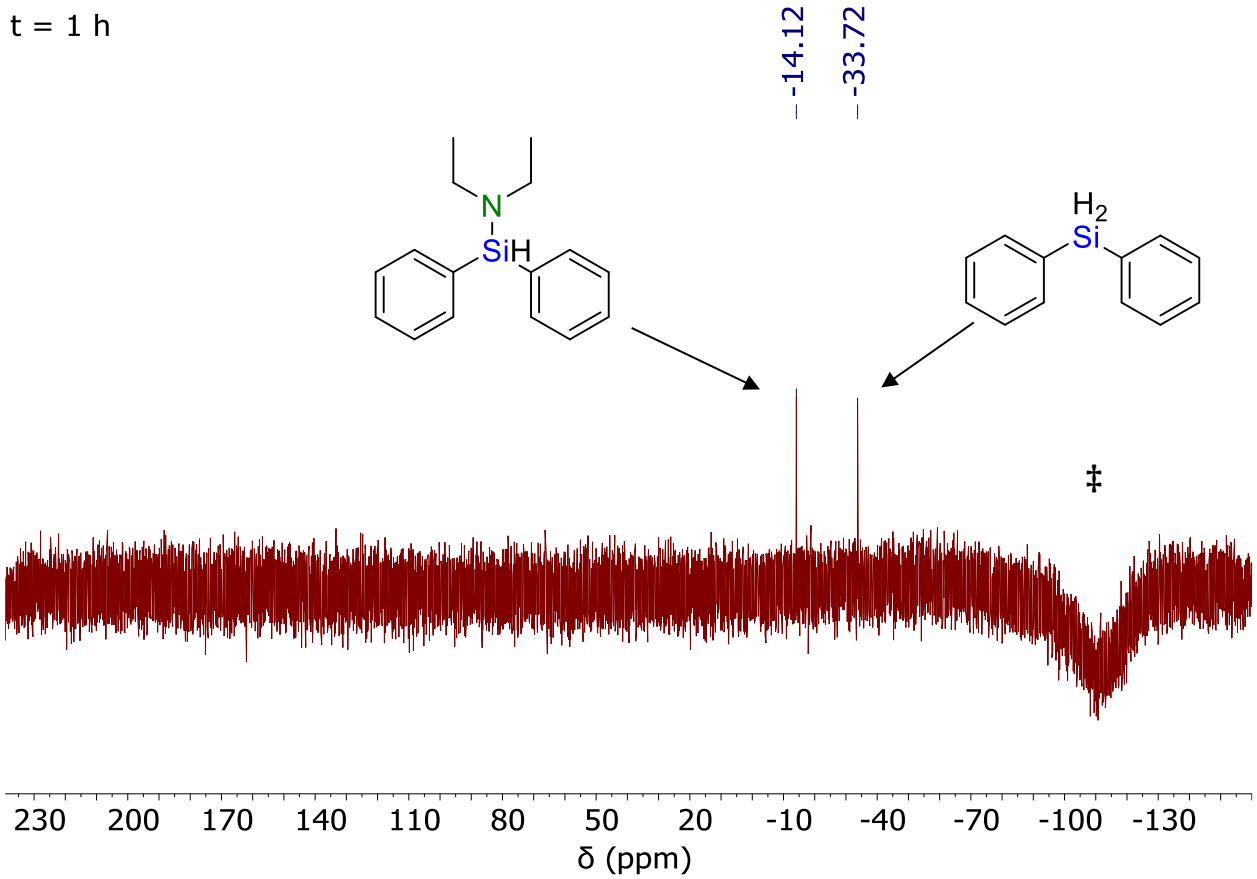

Figure S3.37. $^{29}Si\{^{1}H\}$ NMR spectrum of the reaction between Ph_2SiH_2 and Et_2NH catalyzed by **1** in benzene-d_6 after 1 h. The peak at δ = -33.72 is Ph_2SiH_2.

S5.20. $PhMe_2SiH$ and 2.0 equiv. of $^nPrNH_2$

$PhMe_2SiH$ (57.5 μL, 3.7×10^{-1} mmol), $^nPrNH_2$ (61.5 μL, 7.5×10^{-1} mmol, 2.0 equiv.), and **1** (14.5 μL, 3.7×10^{-2} mmol, 2.6 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6. Complete consumption of $PhMe_2SiH$ was observed after 1 h, as determined by the disappearance of the Si*H* peak at δ = 4.60 in the ^{1}H NMR spectrum. The appearance of a broad, quartet centered between δ = 2.60 and δ = 2.59 in the ^{1}H NMR spectrum indicated 100% conversion to $PhMe_2Si(NH^nPr)$ after 1 h at ambient temperature.

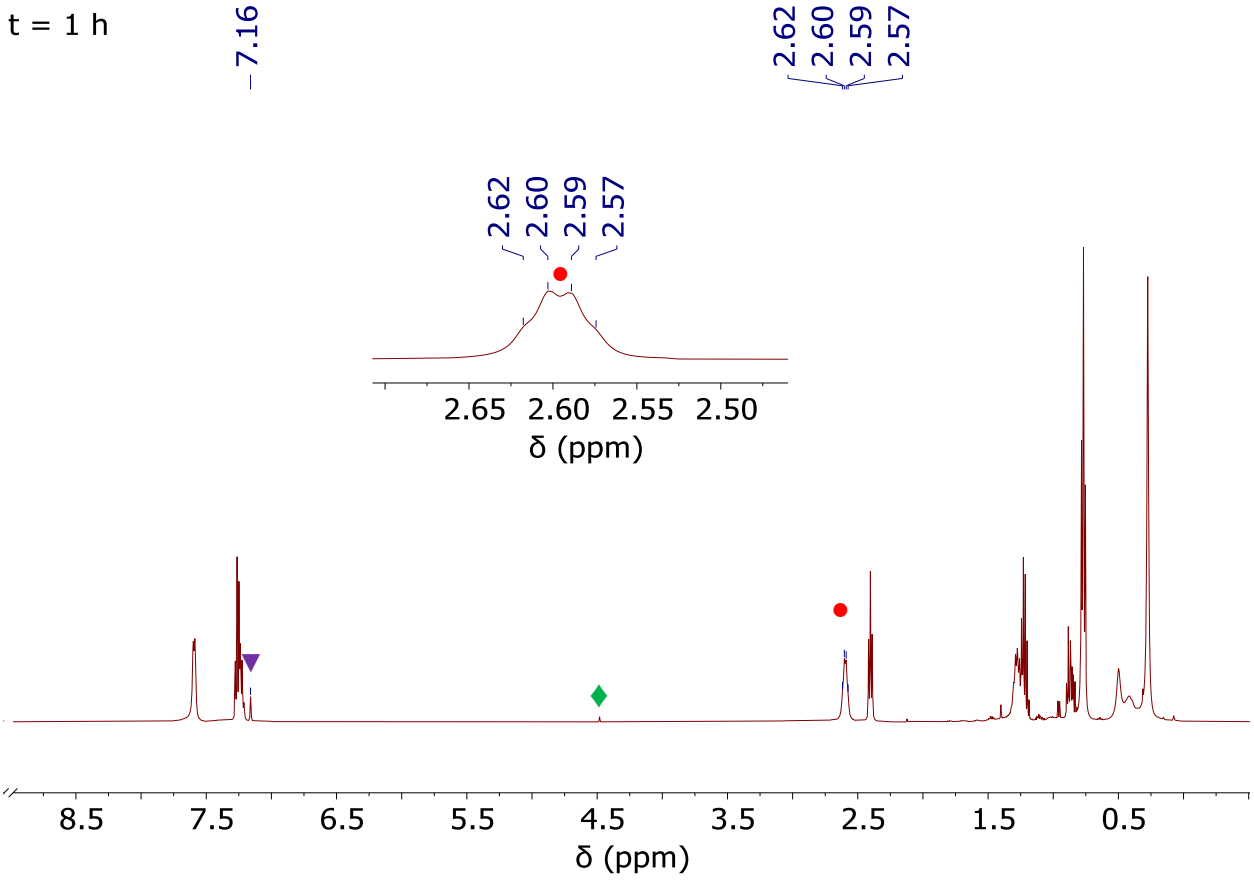

Figure S3.38. ^{1}H NMR spectrum of the reaction between $PhMe_2SiH$ and $^nPrNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

S5.21. $PhMe_2SiH$ and 2.0 equiv. of $^{i}PrNH_2$

$PhMe_2SiH$ (57.5 μL, 3.7×10^{-1} mmol), $^{i}PrNH_2$ (64.0 μL, 7.5×10^{-1} mmol, 2.0 equiv.), and **1** (14.5 μL, 3.7×10^{-2} mmol, 2.6 M in hexanes, 10.0 mol%) were reacted together in 0.5 mL of benzene-d_6. Complete consumption of $PhMe_2SiH$ was observed after 1 h. The appearance of a diagnostic septet centered δ = 2.93 in the ^{1}H NMR spectrum, and a single peak at δ = -6.41 in the $^{29}Si\{^{1}H\}$ NMR spectrum, indicated 100% conversion to $PhMe_2Si(NH^{i}Pr)$ after 1 h at ambient temperature. Spectra were consistent with previous reports of this compound.[9, 11]

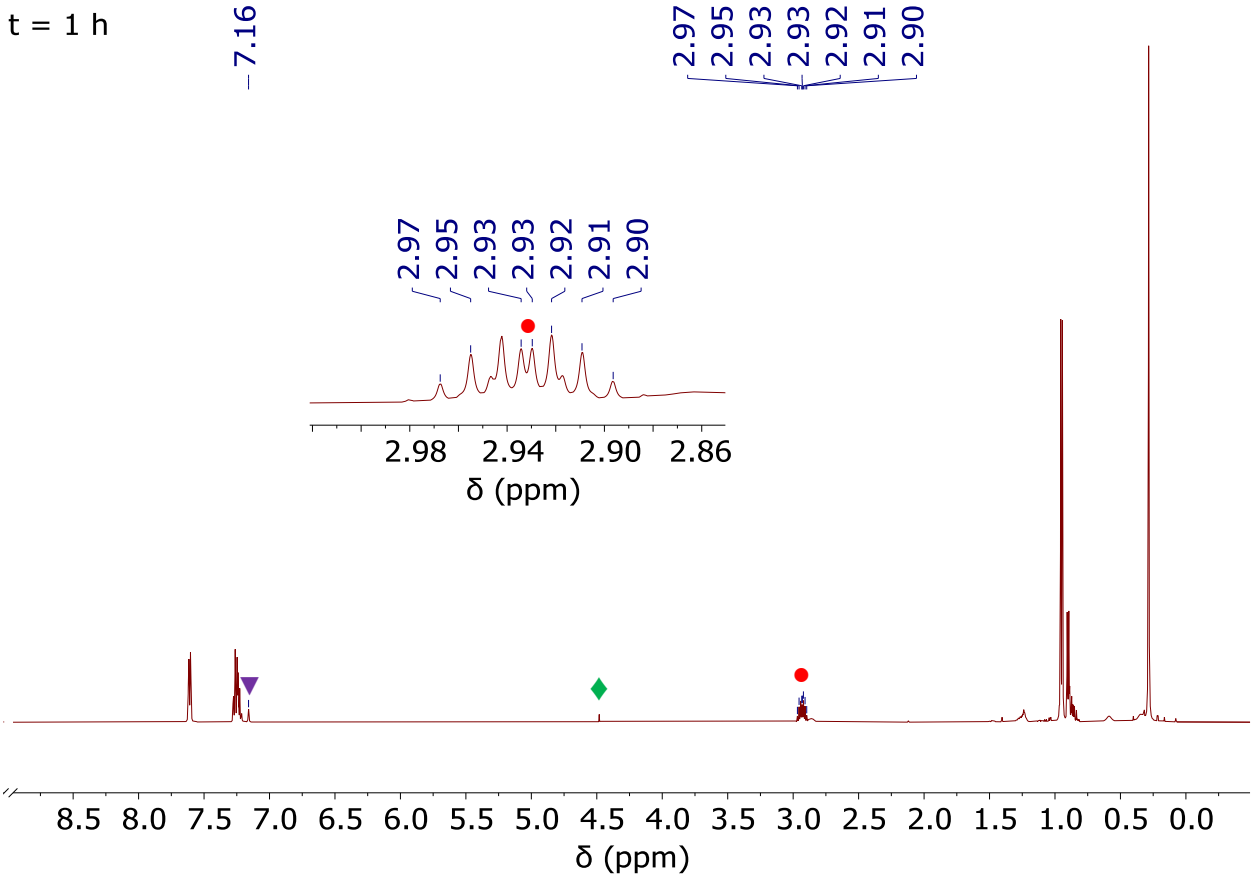

Figure S3.39. ^{1}H NMR spectrum of the reaction between $PhMe_2SiH$ and $^{i}PrNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

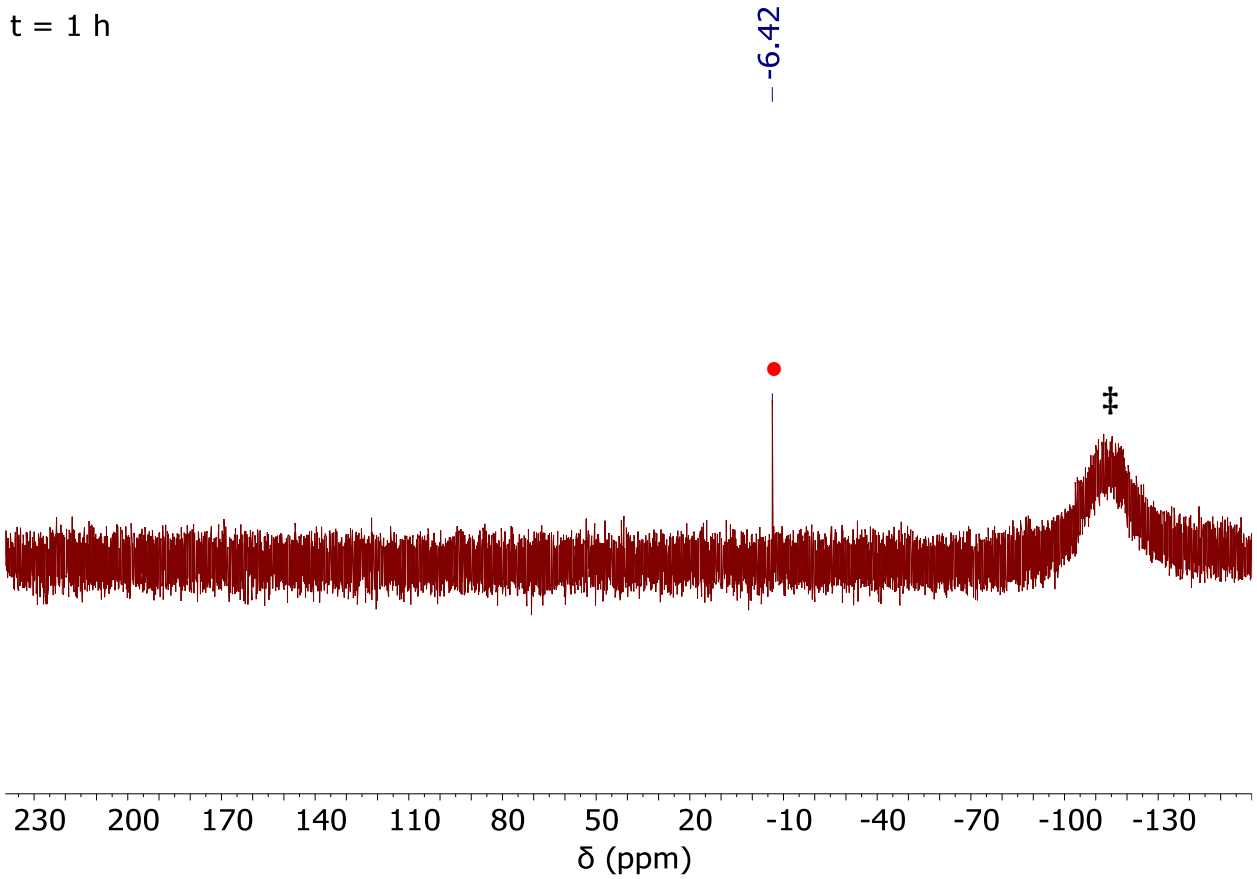

Figure S3.40. $^{29}Si\{^{1}H\}$ NMR spectrum of the reaction between $PhMe_2SiH$ and $^{i}PrNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

S5.22. $PhMe_2SiH$ and 2.0 equiv. of $PhNH_2$

$PhMe_2SiH$ (58.0 μL, 3.7×10^{-1} mmol), $PhNH_2$ (68.5 μL, 7.5×10^{-1} mmol, 2.0 equiv.), and **1** (16.5 μL, 3.7×10^{-2} mmol, 2.3 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6. After 1 h, no reaction occurred.

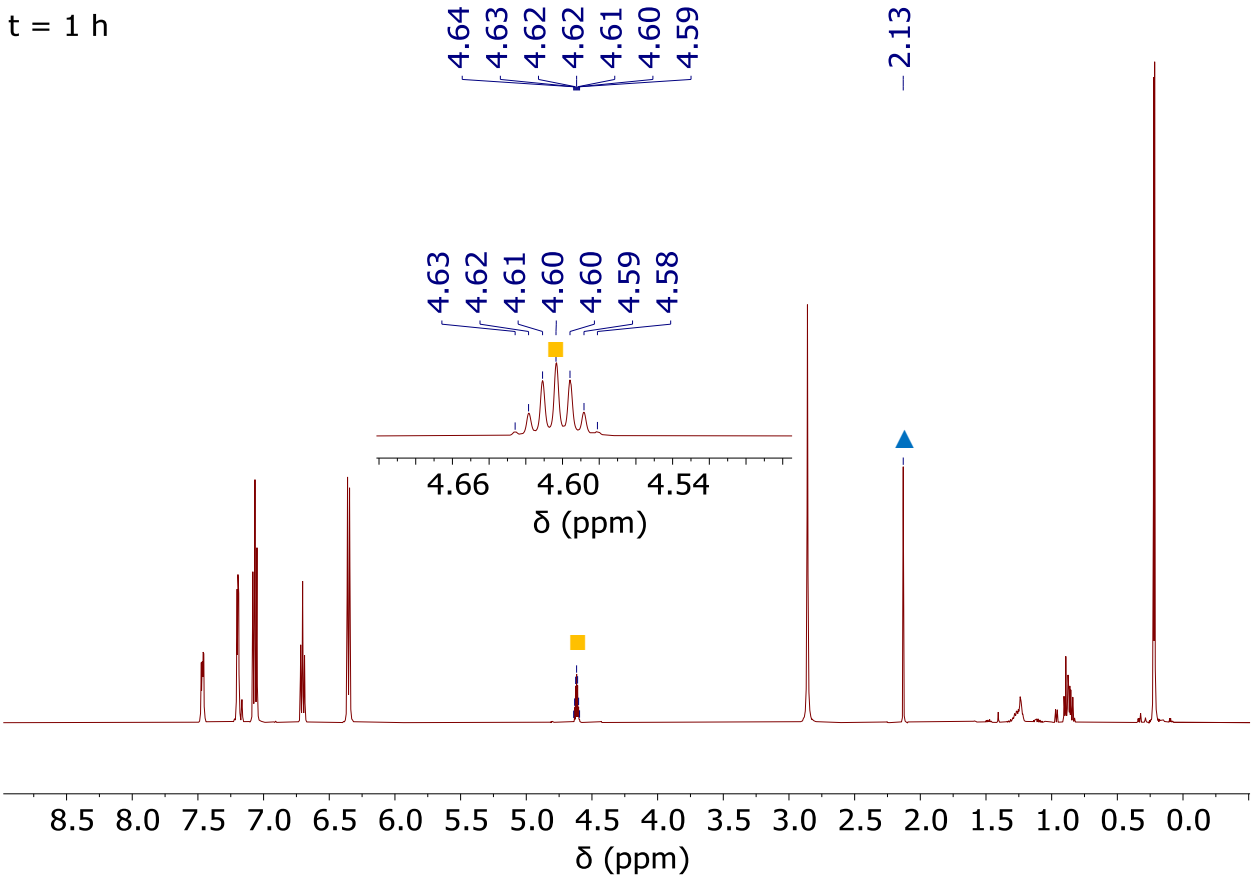

Figure S3.41. ^{1}H NMR spectrum of the reaction between $PhMe_2SiH$ and $PhNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

S5.24. $PhMe_2SiH$ and 2.0 equiv. of Et_2NH

$PhMe_2SiH$ (57.5 μL, 3.7×10^{-1} mmol), Et_2NH (77.5 μL, 7.5×10^{-1} mmol, 2.0 equiv.), and **1** (14.5 μL, 3.7×10^{-2} mmol, 2.6 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6. Incomplete consumption of $PhMe_2SiH$ was observed after 1 h, as determined by the presence of the Si*H* peak at δ = 4.59 in the ^{1}H NMR spectrum. The appearance of a diagnostic quartet centered between δ = 2.78 and δ = 2.77 in the ^{1}H NMR spectrum indicated 48% conversion to $PhMe_2Si(NEt_2)$ after 1 h at ambient temperature. The reaction was ended after 1 h, due to the cessation of gas evolution. Spectroscopic data was consistent with previous reports of this compound.[12]

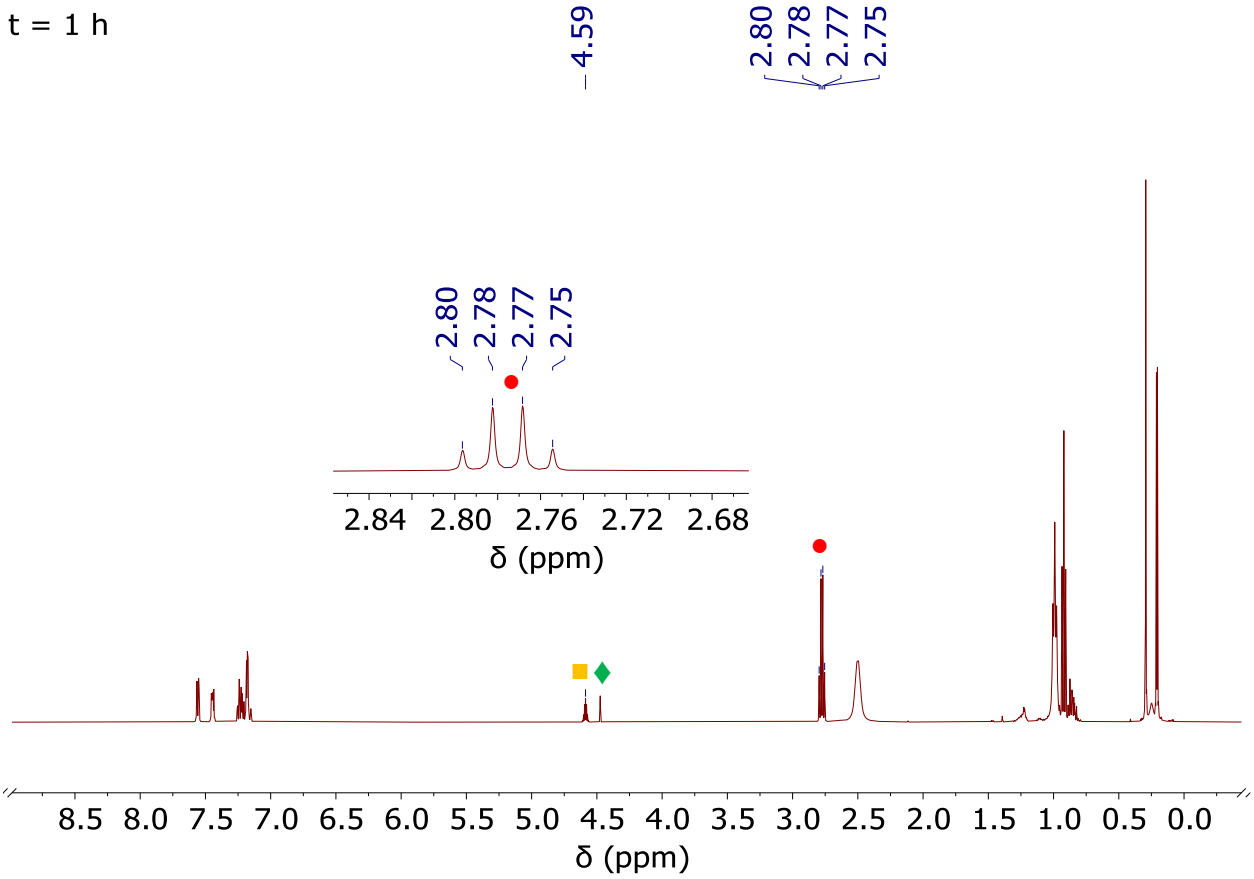

Figure S3.42. ^{1}H NMR spectrum of the reaction between $PhMe_2SiH$ and Et_2NH catalyzed by **1** in benzene-d_6 after 1 h. Residual solvent is buried by aryl peaks.

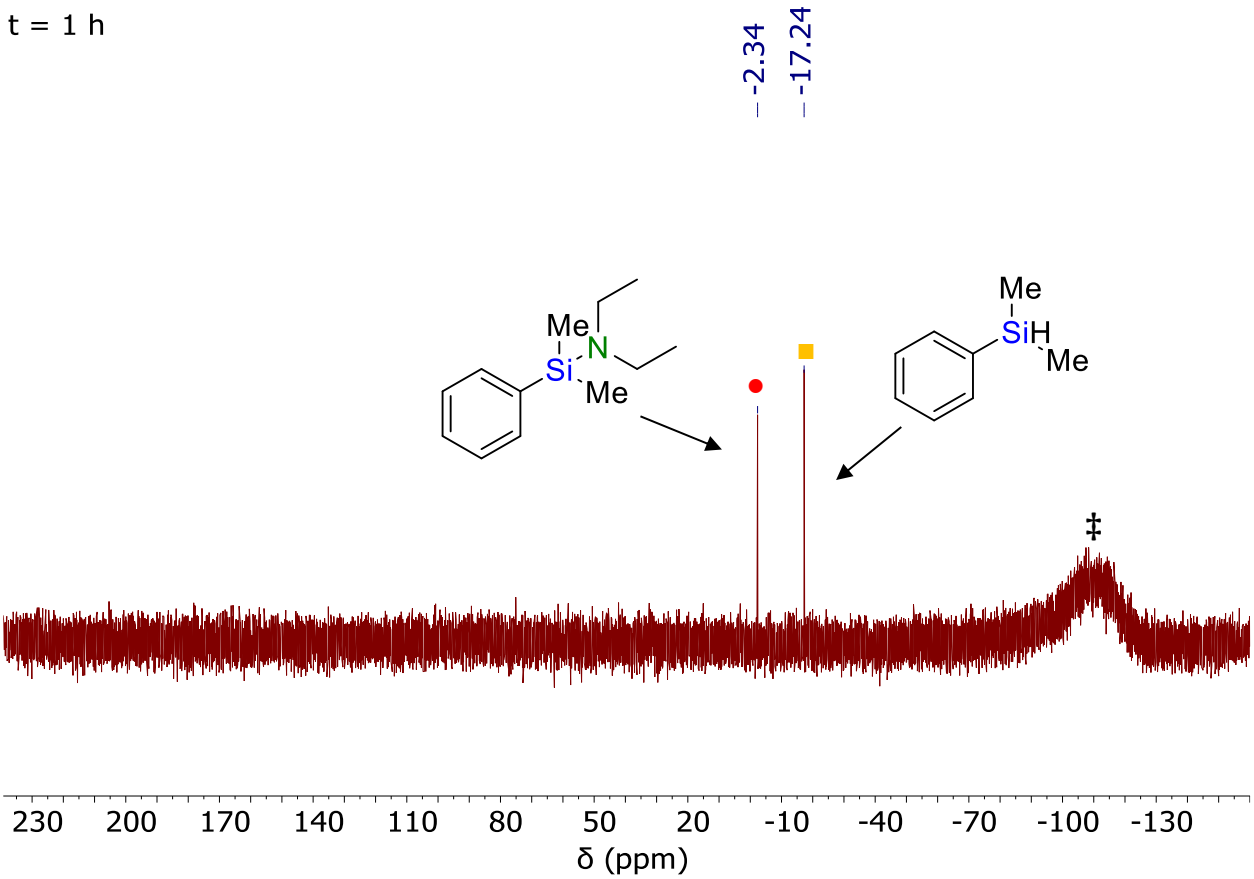

Figure S3.43. $^{29}Si\{^{1}H\}$ NMR spectrum of the reaction between $PhMe_2SiH$ and Et_2NH catalyzed by **1** in benzene-d_6 after 1 h.

S5.26. Ph_2MeSiH and 2.0 equiv. of Et_2NH

Ph_2MeSiH (75.0 μL, 3.7×10^{-1} mmol), Et_2NH (78.0 μL, 7.5×10^{-1} mmol, 2.0 equiv.), and **1** (14.5 μL, 3.7×10^{-2} mmol, 2.6 M in hexanes, 10.0 mol%) were reacted together in 0.5 mL of benzene-d_6. Incomplete consumption of Ph_2MeSiH was observed after 1 h, as determined by the presence of the Si*H* peak at δ = 5.10 in the ^{1}H NMR spectrum. The appearance of a multiplet centered between δ = 2.86 and δ = 2.85 in the ^{1}H NMR spectrum indicated 57% conversion to $Ph_2MeSi(NEt_2)$ after 1 h at ambient temperature, which was supported by the presence of a peak at δ = -7.15 in the ^{29}Si{^{1}H} NMR spectrum. The reaction was ended after 1 h, due to the slow progression of gas evolution. Spectroscopic data was consistent with previous reports of this compound.[13, 14]

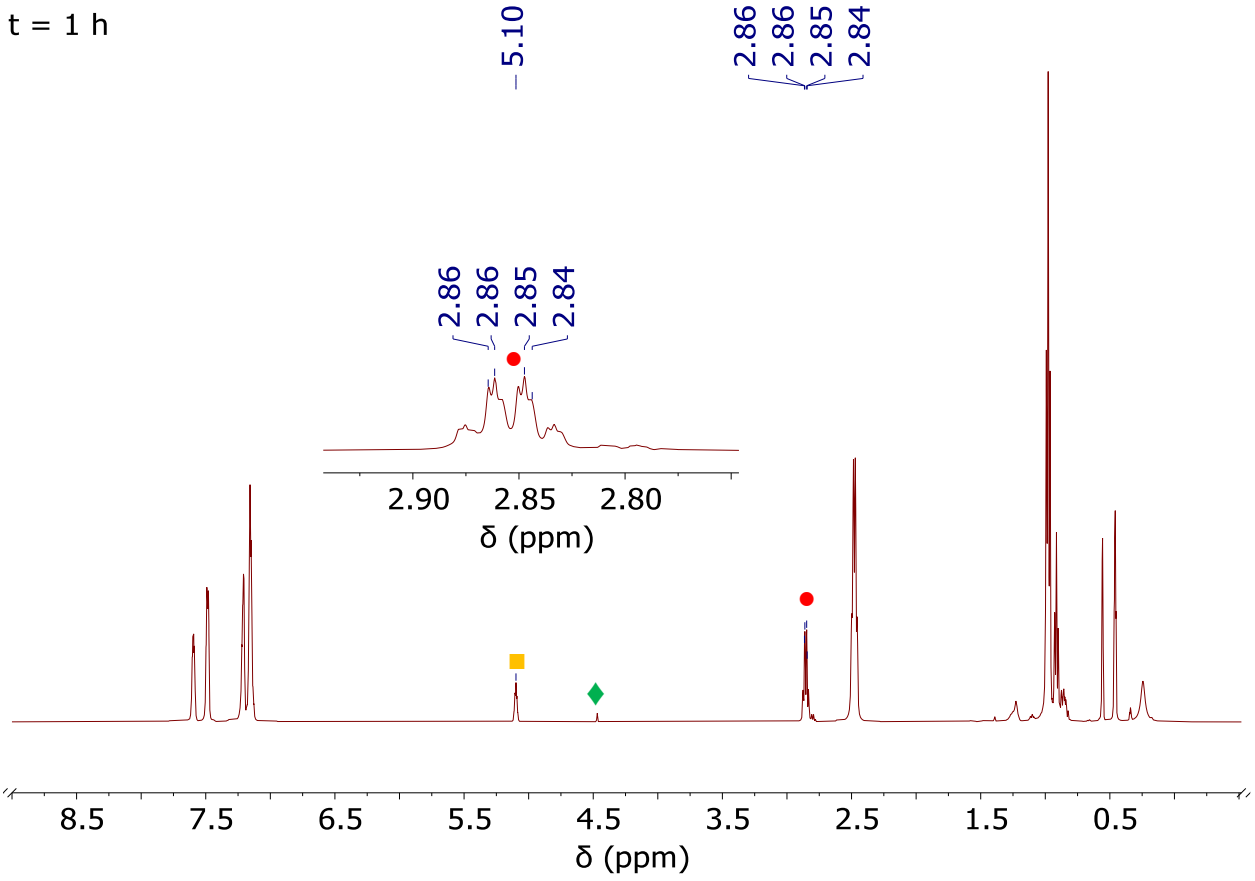

Figure S3.44. ^{1}H NMR spectrum of the reaction between Ph_2MeSiH and Et_2NH catalyzed by **1** in benzene-d_6 after 1 h. Residual solvent is buried by aryl peaks.

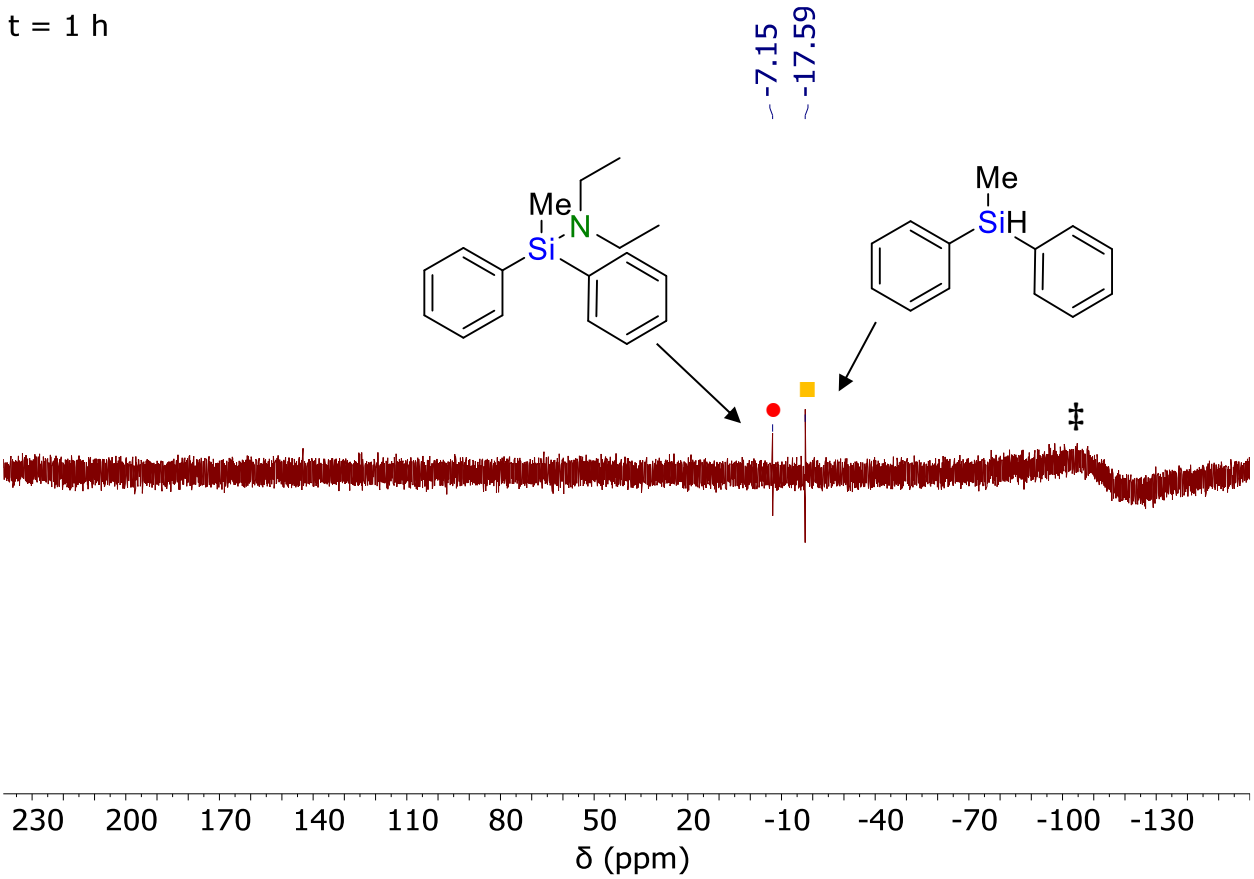

Figure S3.45. $^{29}Si\{^{1}H\}$ NMR spectrum of the reaction between Ph_2MeSiH and Et_2NH catalyzed by **1** in benzene-d_6 after 1 h.

S5.27. Ph_3SiH and 2.0 equiv. of $^nPrNH_2$

Ph_3SiH (98.0 mg, 3.7×10^{-1} mmol), $^nPrNH_2$ (62.0 μL, 7.5×10^{-1} mmol, 2.0 equiv.), and **1** (14.5 μL, 3.7×10^{-2} mmol, 2.6 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6 in the presence of C_6Me_6 standard (52.5 μL, 0.4 M in benzene-d_6). Complete consumption of Ph_3SiH was observed after 1 h, as determined by the disappearance of the Si*H* peak at δ = 5.69 in the ^1H NMR spectrum. The appearance of a diagnostic quartet centered between δ = 2.80 and δ = 2.79, and a single peak in the $^{29}Si\{^1H\}$ NMR spectrum at δ = -16.46, indicated 100% conversion to $Ph_3Si(NH^nPr)$ after 1 h at ambient temperature. Spectra were consistent with previous reports of this compound.[6]

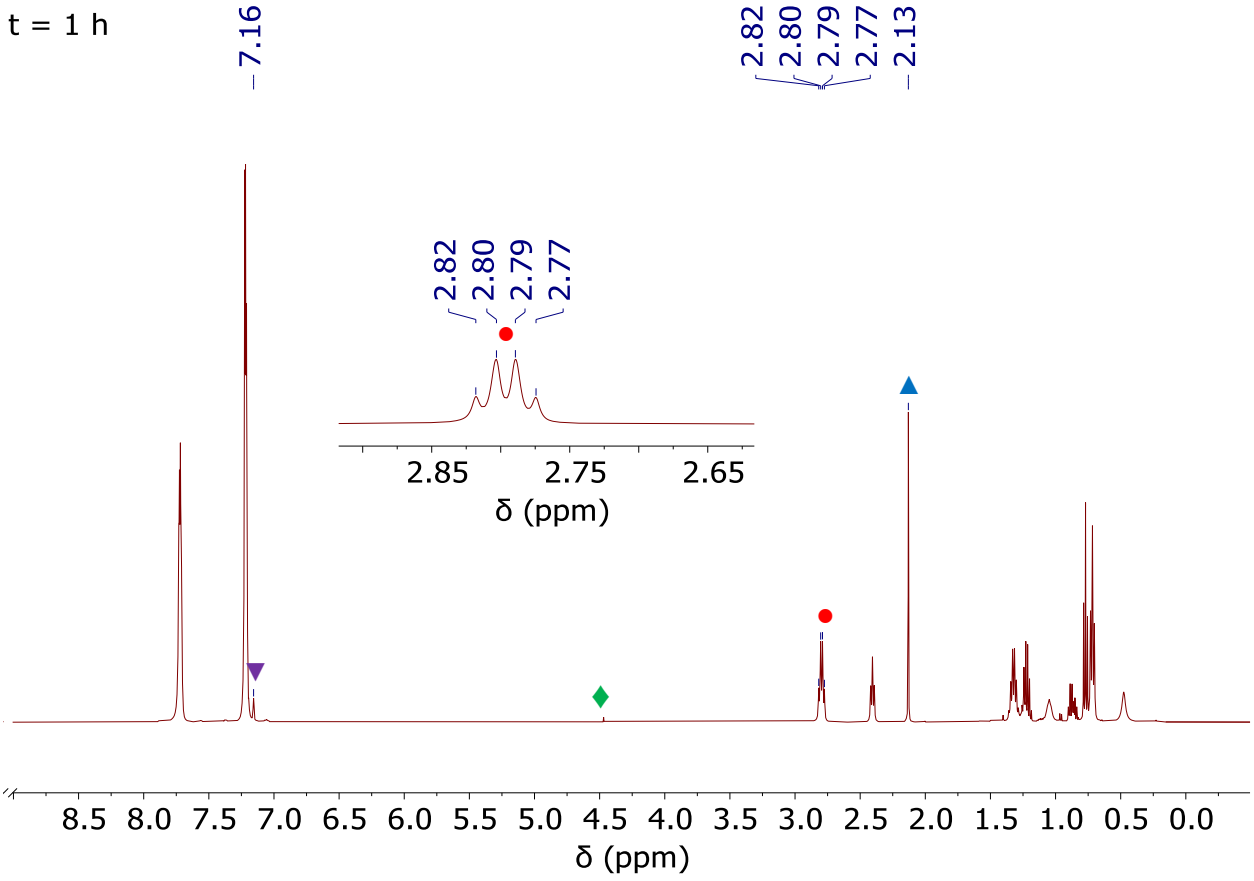

Figure S3.46. ^1H NMR spectrum of the reaction between Ph_3SiH and $^nPrNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

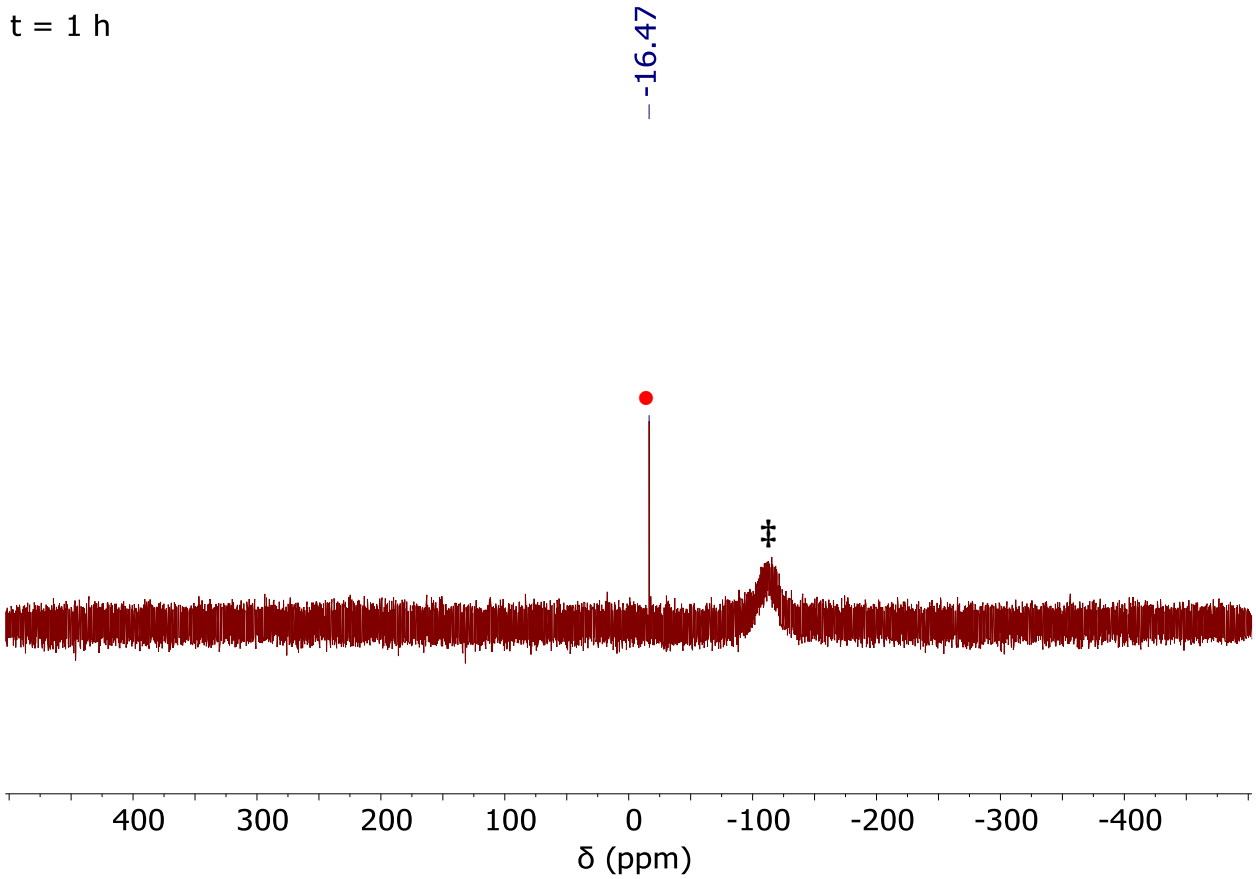

Figure S3.47. $^{29}Si\{^{1}H\}$ NMR spectrum of the reaction between Ph_3SiH and $^{n}PrNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

S5.28. Ph_3SiH and 2.0 equiv. of $^iPrNH_2$

Ph_3SiH (98.0 mg, 3.7×10^{-1} mmol), $^iPrNH_2$ (64.5 μL, 7.5×10^{-1} mmol, 2.0 equiv.), and **1** (14.5 μL, 3.7×10^{-2} mmol, 2.6 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6 in the presence of C_6Me_6 standard (52.5 μL, 0.4 M in benzene-d_6). Complete consumption of Ph_3SiH was observed after 1 h. The appearance of a diagnostic septet centered between at δ = 3.15-3.14 in the ^1H NMR spectrum, and a single peak in the $^{29}Si\{^1H\}$ NMR spectrum at δ = -17.85, indicated 100% conversion to $Ph_3Si(NH^iPr)$ after 1 h at ambient temperature. Spectra were consistent with previous reports of this compound.[6]

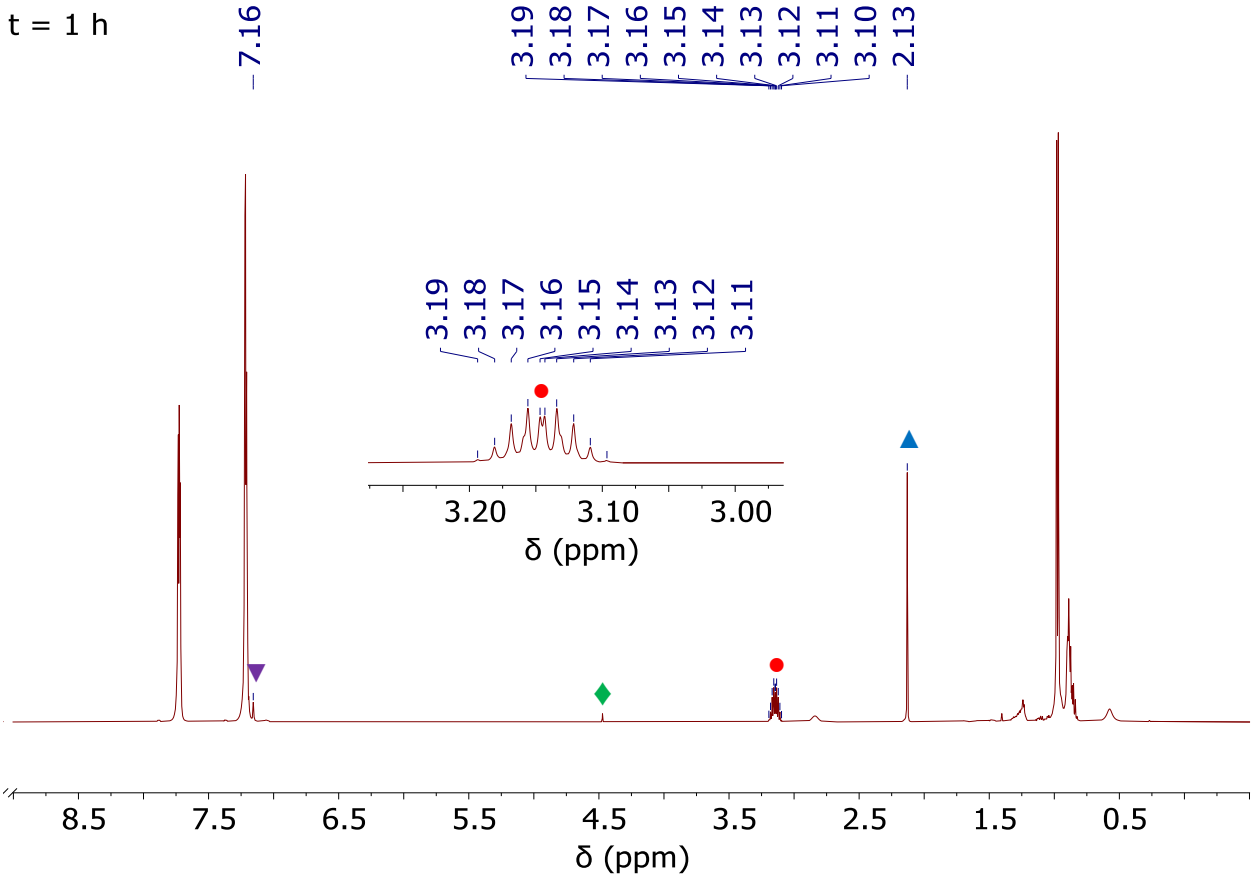

Figure S3.48. ^1H NMR spectrum of the reaction between Ph_3SiH and $^iPrNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

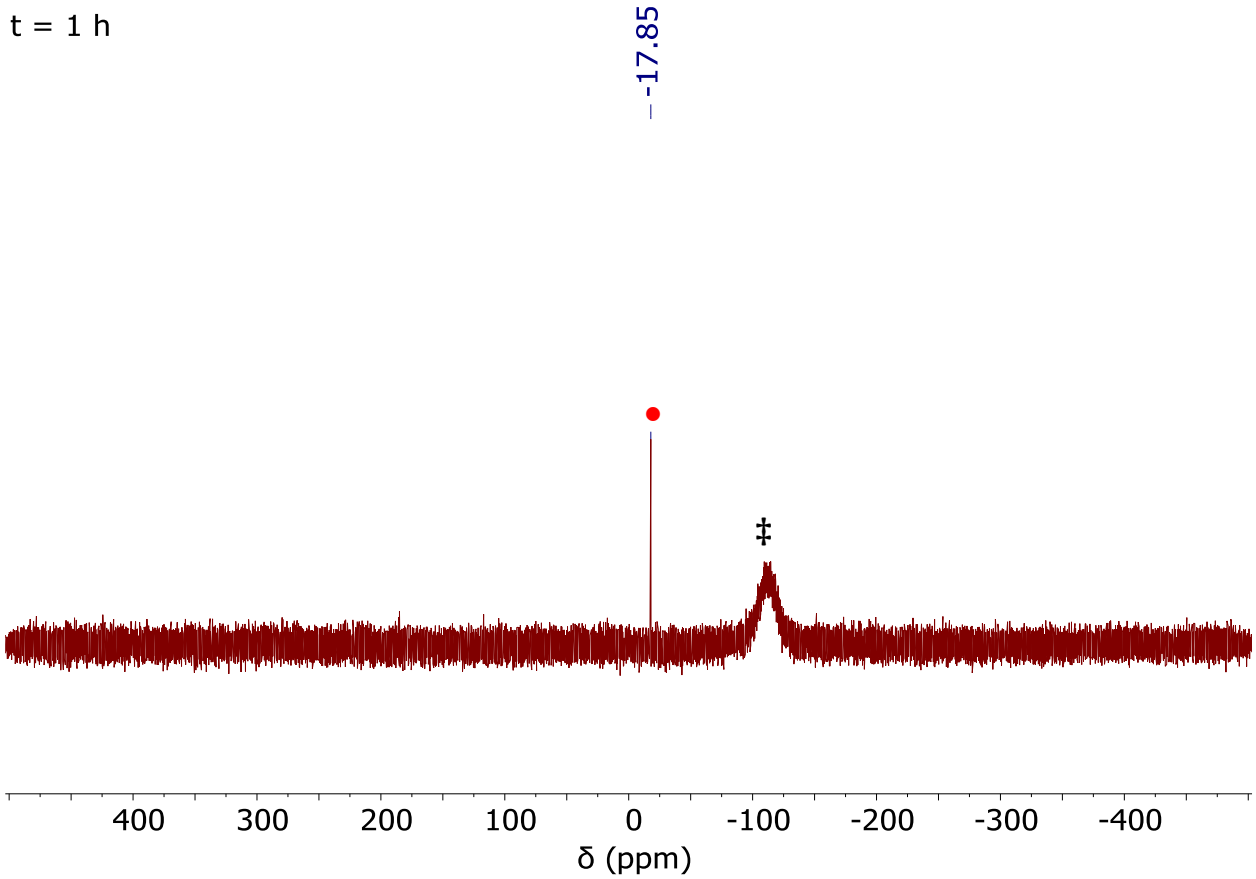

Figure S3.49. $^{29}Si\{^{1}H\}$ NMR spectrum of the reaction between Ph_3SiH and $^{i}PrNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

S5.29. Ph_3SiH and 2.0 equiv. of $^{n}BuNH_2$

Ph_3SiH (98.0 mg, 3.7×10^{-1} mmol), $^{n}BuNH_2$ (75.0 μL, 7.5×10^{-1} mmol, 2.0 equiv.), and **1** (14.5 μL, 3.7×10^{-2} mmol, 2.6 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6 in the presence of C_6Me_6 standard (52.5 μL, 0.4 M in benzene-d_6). Complete consumption of Ph_3SiH was observed after 1 h. The appearance of a diagnostic quartet centered between δ = 2.86 and δ = 2.84 in the ^1H NMR spectrum, and a single peak in the $^{29}Si\{^1H\}$ NMR spectrum at δ = -16.50, indicated 100% conversion to $Ph_3Si(NH^{n}Bu)$ after 1 h at ambient temperature. Spectra were consistent with previous reports of this compound.[15]

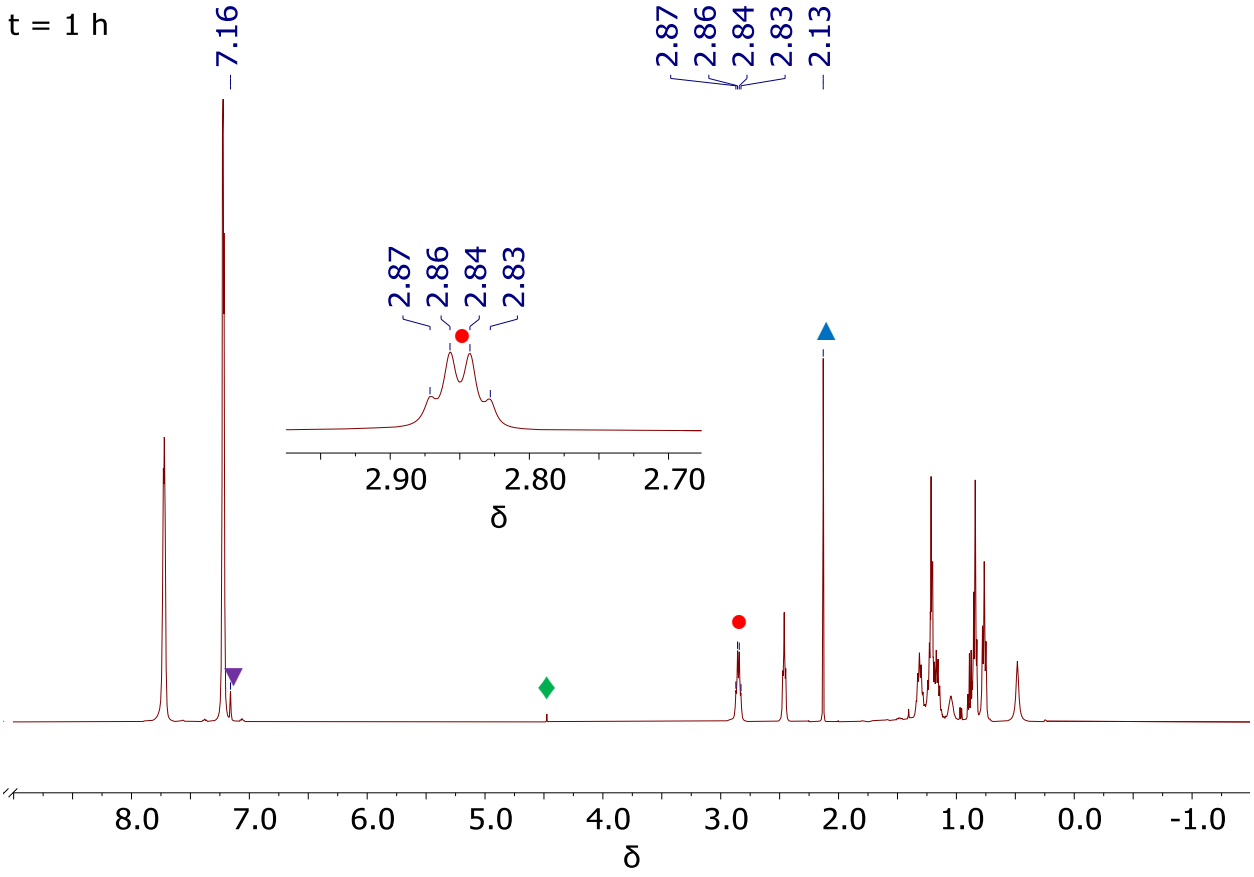

Figure S3.50. ^1H NMR spectrum of the reaction between Ph_3SiH and $^{n}BuNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

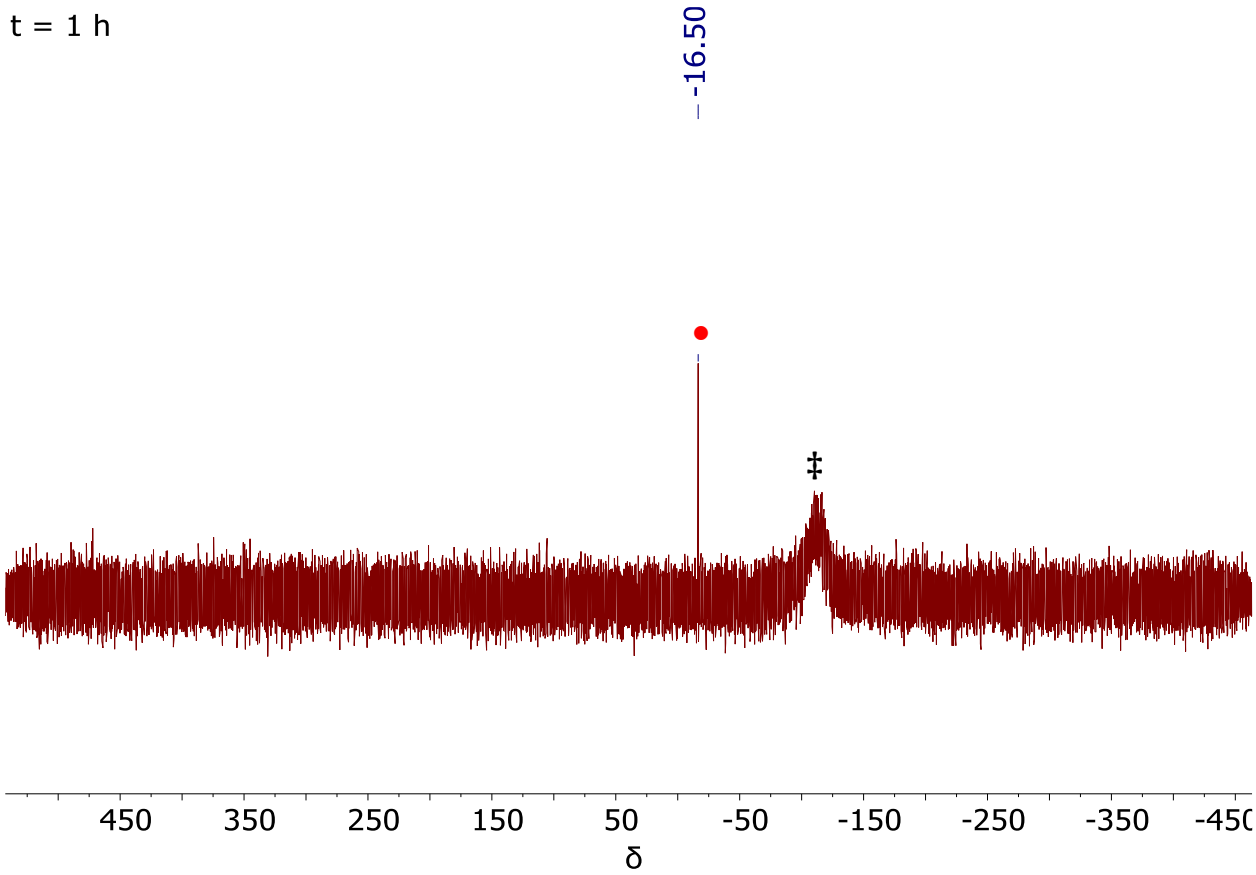

Figure S3.51. $^{29}Si\{^{1}H\}$ NMR spectrum of the reaction between Ph_3SiH and $^{n}BuNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

S5.30. Ph_3SiH and 2.0 equiv. of $^tBuNH_2$

Ph_3SiH (98.0 mg, 3.7×10^{-1} mmol), $^tBuNH_2$ (79.5 μL, 7.5×10^{-1} mmol, 2.0 equiv.), and **1** (15.0 μL, 3.7×10^{-2} mmol, 2.5 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6. After 1 h at ambient temperature, 80% conversion to $Ph_3Si(NH^tBu)$ was observed. The reaction was subsequently run to completion.

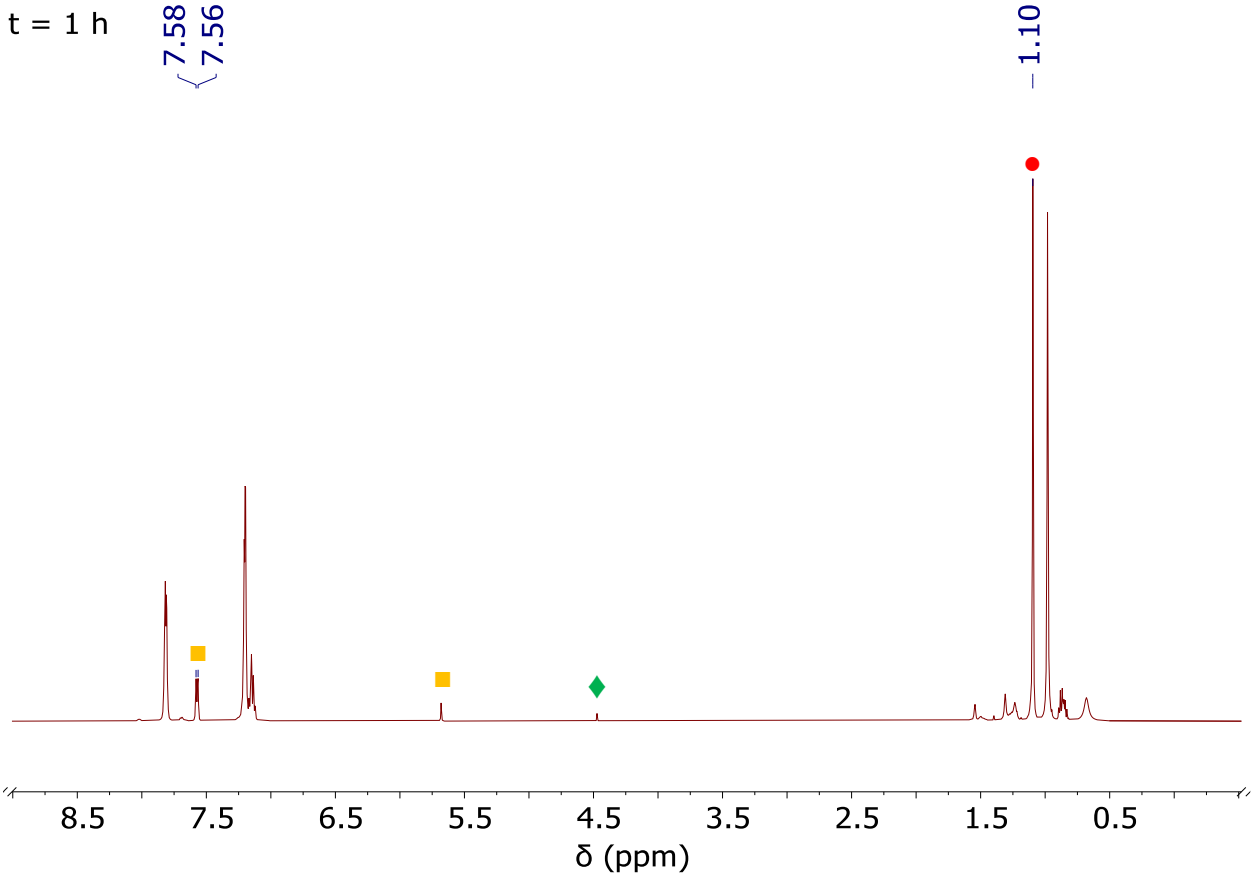

Figure S3.52. ^1H NMR spectrum of the reaction between Ph_3SiH and $^tBuNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

S5.31. Ph_3SiH and 2.0 equiv. of $^nPeNH_2$

Ph_3SiH (98.0 mg, 3.7×10^{-1} mmol), $^nPeNH_2$ (87.5 μL, 7.5×10^{-1} mmol, 2.0 equiv.), and **1** (14.5 μL, 3.7×10^{-2} mmol, 2.6 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL benzene-d_6 in the presence of C_6Me_6 standard (52.5 μL, 0.4 M in benzene-d_6). Complete consumption of Ph_3SiH was observed after 1 h. The appearance of a diagnostic quartet centered between δ = 2.86 and δ = 2.84 in the ^1H NMR spectrum, and a single peak in the $^{29}Si\{^1H\}$ NMR spectrum at δ = -16.51, indicated 100% conversion to $Ph_3Si(NH^nPe)$ after 1 h at ambient temperature. Spectra were consistent with previous reports of this compound.[16]

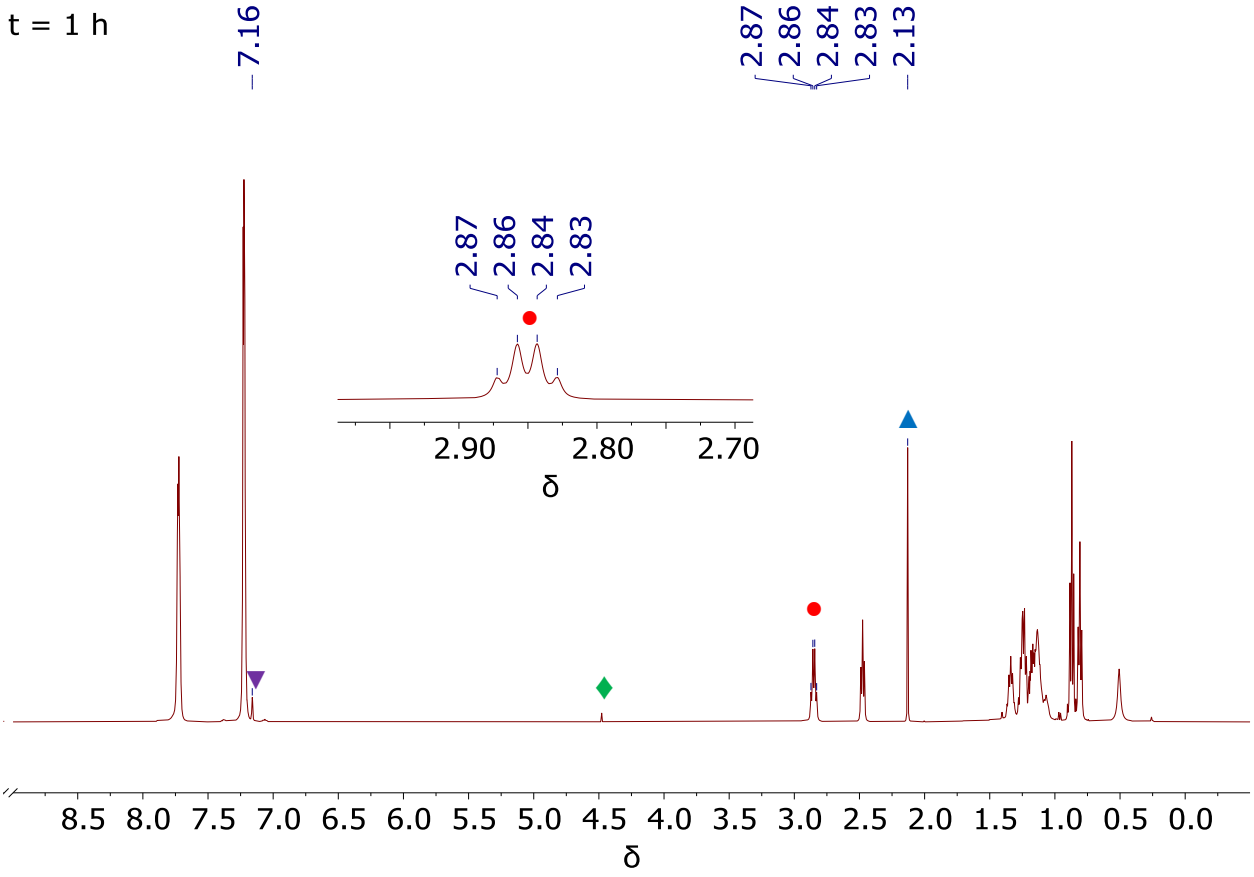

Figure S3.53. ^1H NMR spectrum of the reaction between Ph_3SiH and $^nPeNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

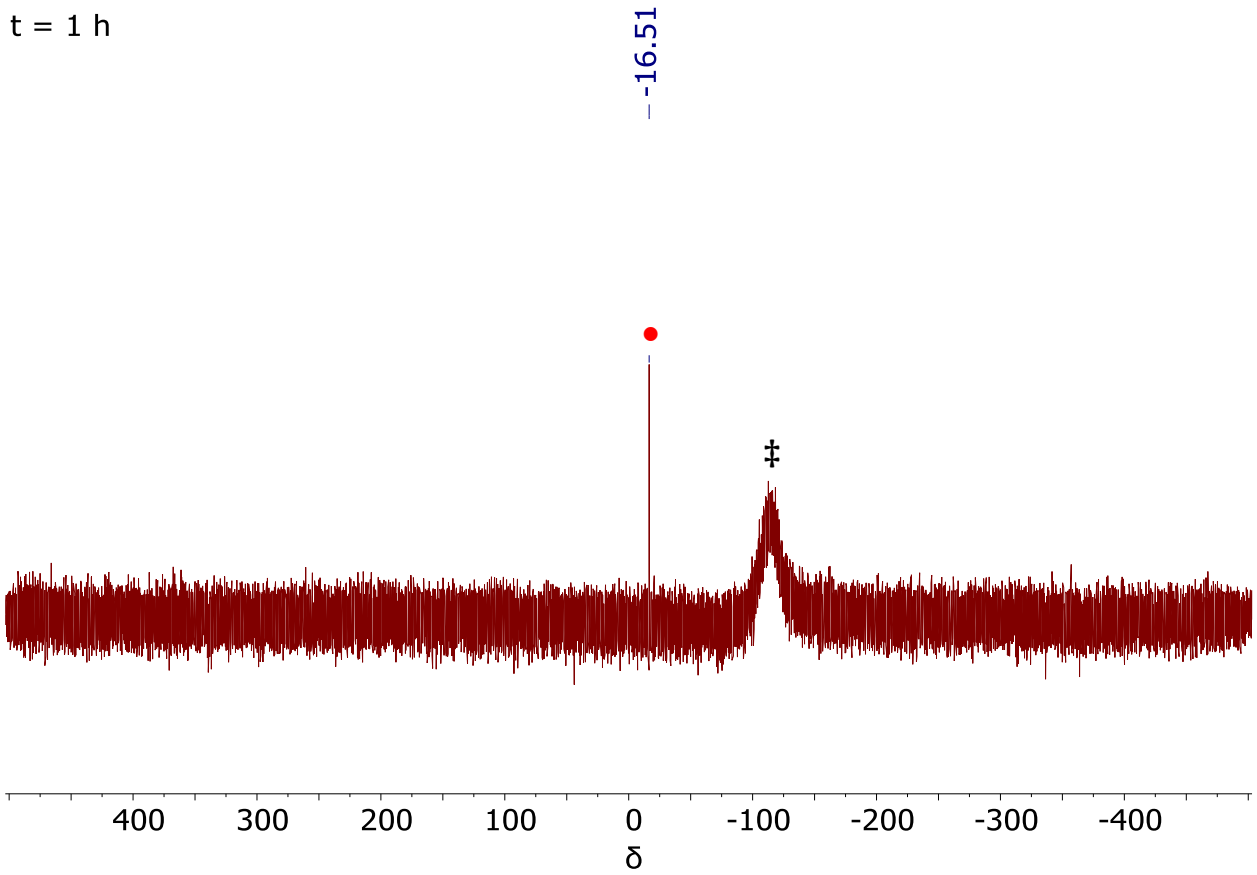

Figure S3.54. $^{29}Si\{^{1}H\}$ NMR spectrum of the reaction between Ph_3SiH and $^{n}PeNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

S5.32. Ph_3SiH and 2.0 equiv. of $^{n}HeNH_2$

Ph_3SiH (98.0 mg, 3.7×10^{-1} mmol), $^{n}HeNH_2$ (99.0 μL, 7.5×10^{-1} mmol, 2.0 equiv.), and **1** (14.5 μL, 3.7×10^{-2} mmol, 2.6 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6 in the presence of C_6Me_6 standard (52.5 μL, 0.4 M in benzene-d_6). Complete consumption of Ph_3SiH was observed after 1 h. The appearance of a diagnostic quartet centered between δ = 2.87 and δ = 2.85 in the ^1H NMR spectrum, and a single peak in the $^{29}Si\{^1H\}$ NMR spectrum at δ = -16.50, indicated 100% conversion to $Ph_3Si(NH^{n}He)$ after 1 h at ambient temperature. Spectra were consistent with previous reports of this compound.[16]

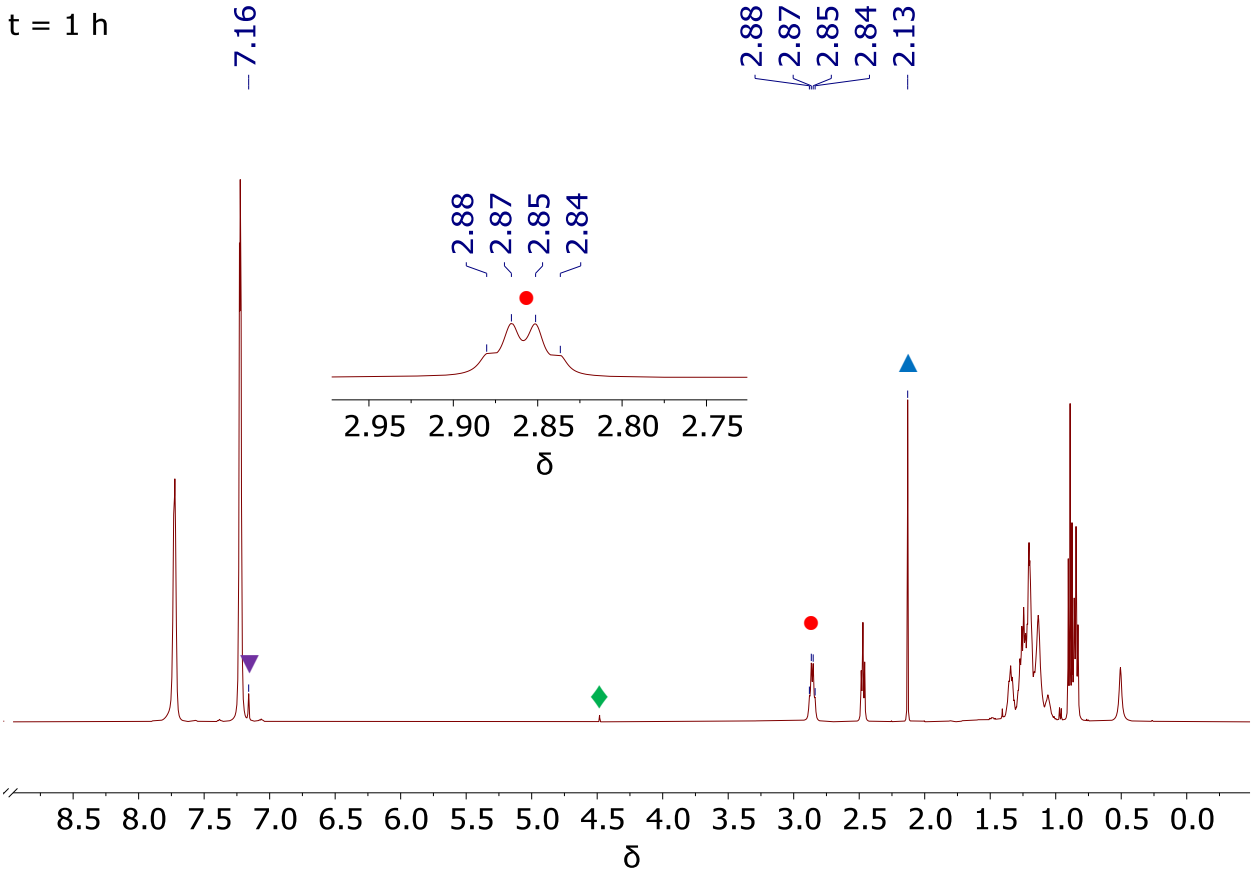

Figure S3.55. ^1H NMR spectrum of the reaction between Ph_3SiH and $^{n}HeNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

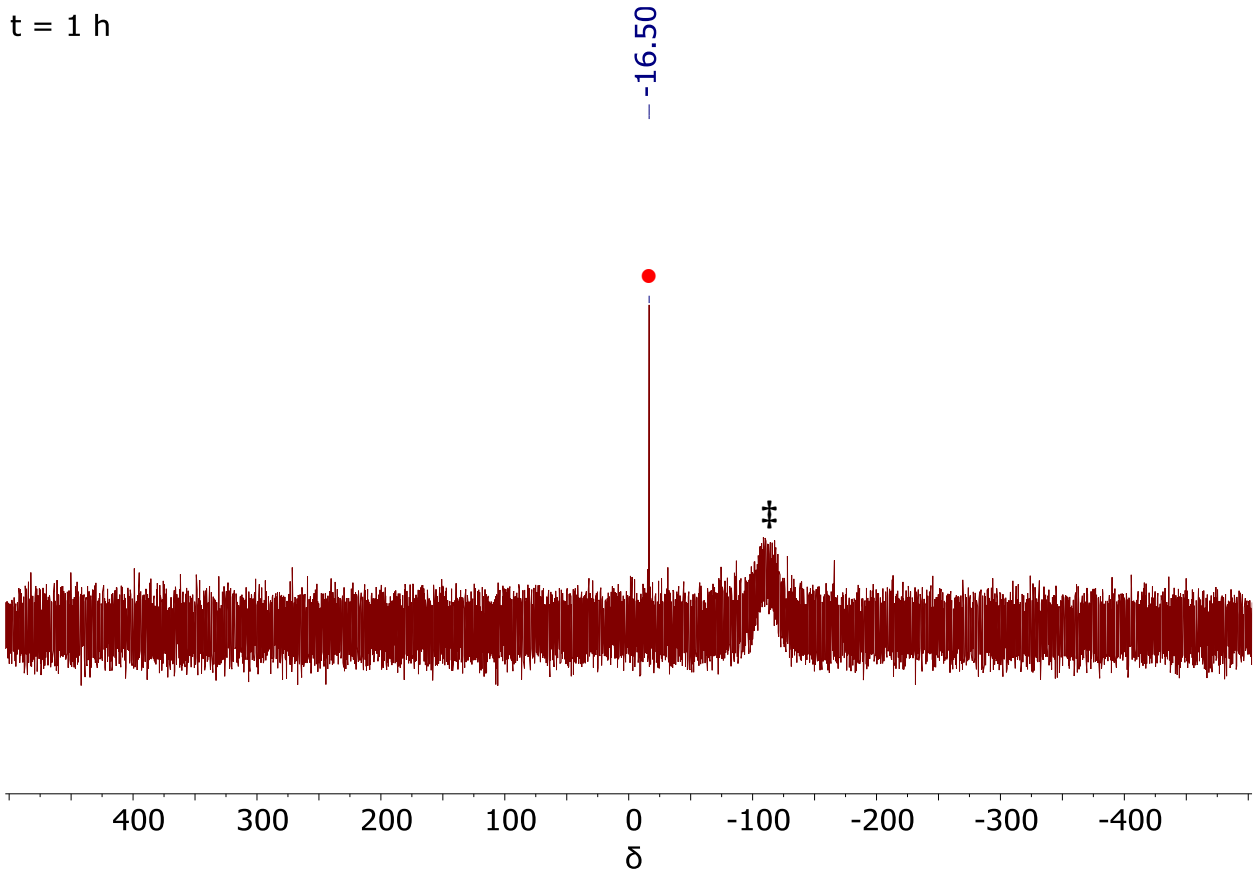

Figure S3.56. $^{29}Si\{^{1}H\}$ NMR spectrum of the reaction between Ph_3SiH and $^{n}HeNH_2$ catalyzed by **1** in benzene-d_6 after 1 h.

S5.33. Ph_3SiH and 2.0 equiv. of $PhNH_2$

Ph_3SiH (98.0 mg, 3.7×10^{-1} mmol), $PhNH_2$ (68.0 μL, 7.5×10^{-1} mmol, 2.0 equiv.), and **1** (16.5 μL, 3.7×10^{-2} mmol, 2.3 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6. After 1 h, no reaction occurred.

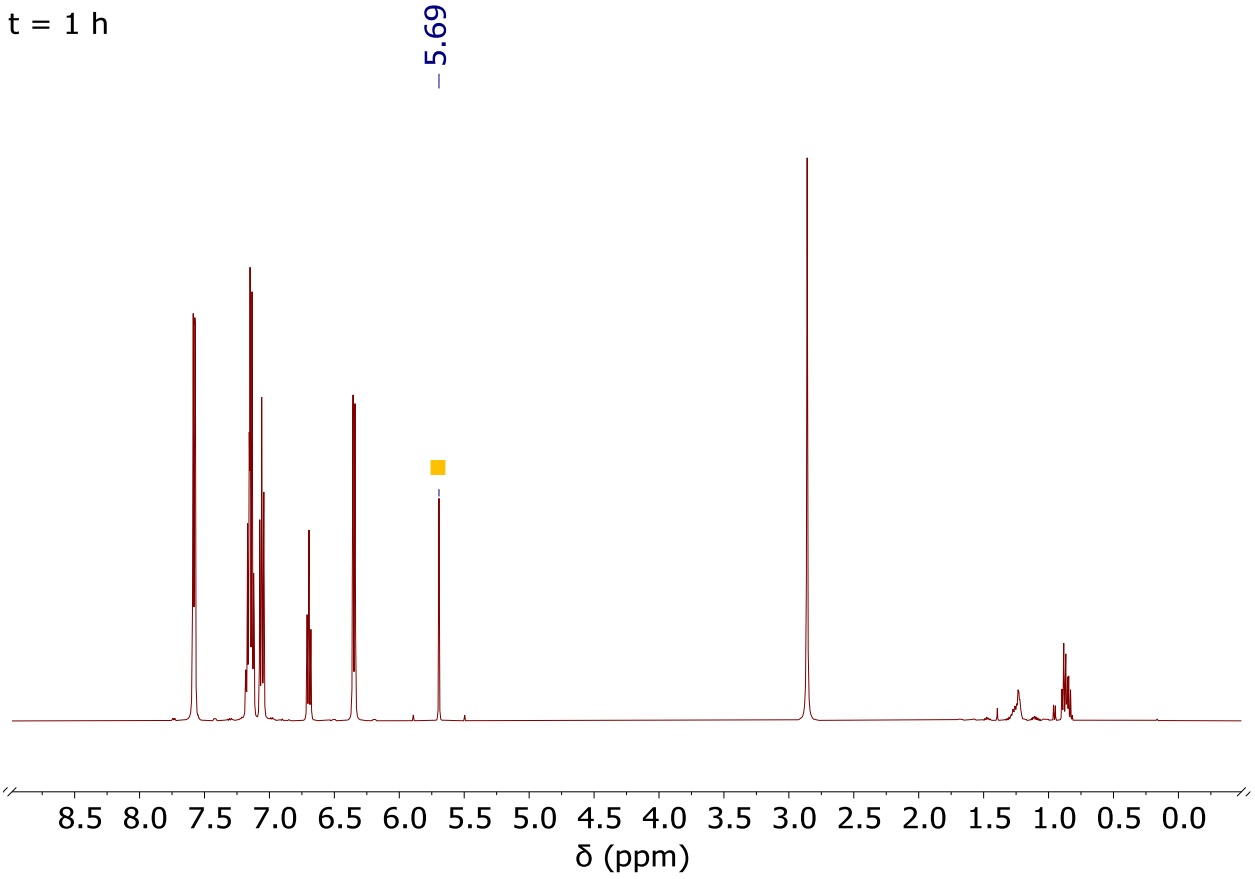

Figure S3.57. ^1H NMR spectrum of the reaction between Ph_3SiH and $PhNH_2$ catalyzed by **1** in benzene-d_6 after 1 h. The peak at -5.69 is Ph_3SiH.

S5.34. Ph_3SiH and 2.0 equiv. of PyNH

Ph_3SiH (98.0 mg, 3.7×10^{-1} mmol), PyNH (62.0 μL, 7.5×10^{-1} mmol, 2.00 equiv.), and **1** (15.0 μL, 3.7×10^{-2} mmol, 2.5 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6. Complete consumption of Ph_3SiH was observed after 0.5 h. The appearance of a diagnostic multiplet centered at δ = 3.10 in the ^{1}H NMR spectrum indicated 100% conversion to $Ph_3Si(NPy)$ after 0.5 h at ambient temperature. Spectra were consistent with previous reports of this compound.[17]

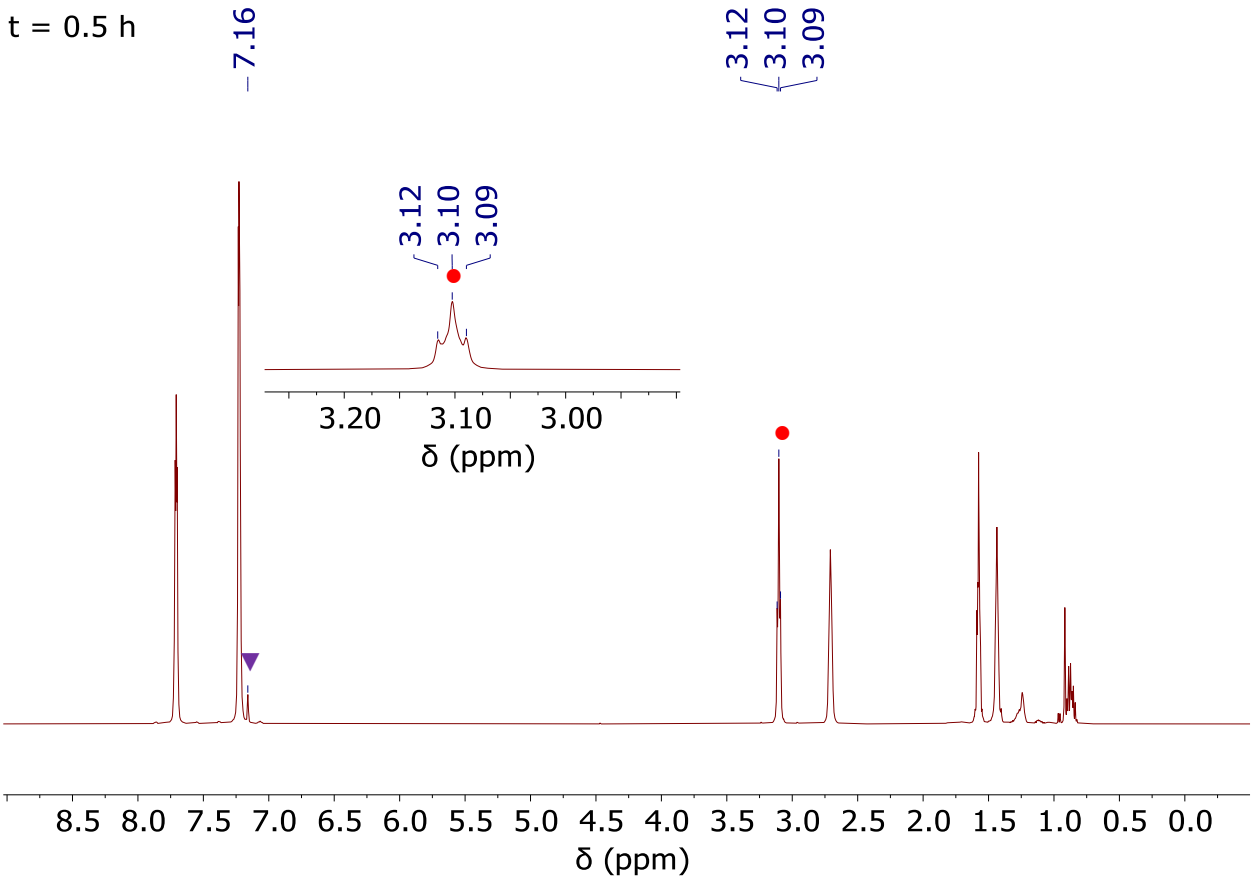

Figure S3.58. ^{1}H NMR spectrum of the reaction between Ph_3SiH and PyNH catalyzed by **1** in benzene-d_6 after 0.5 h.

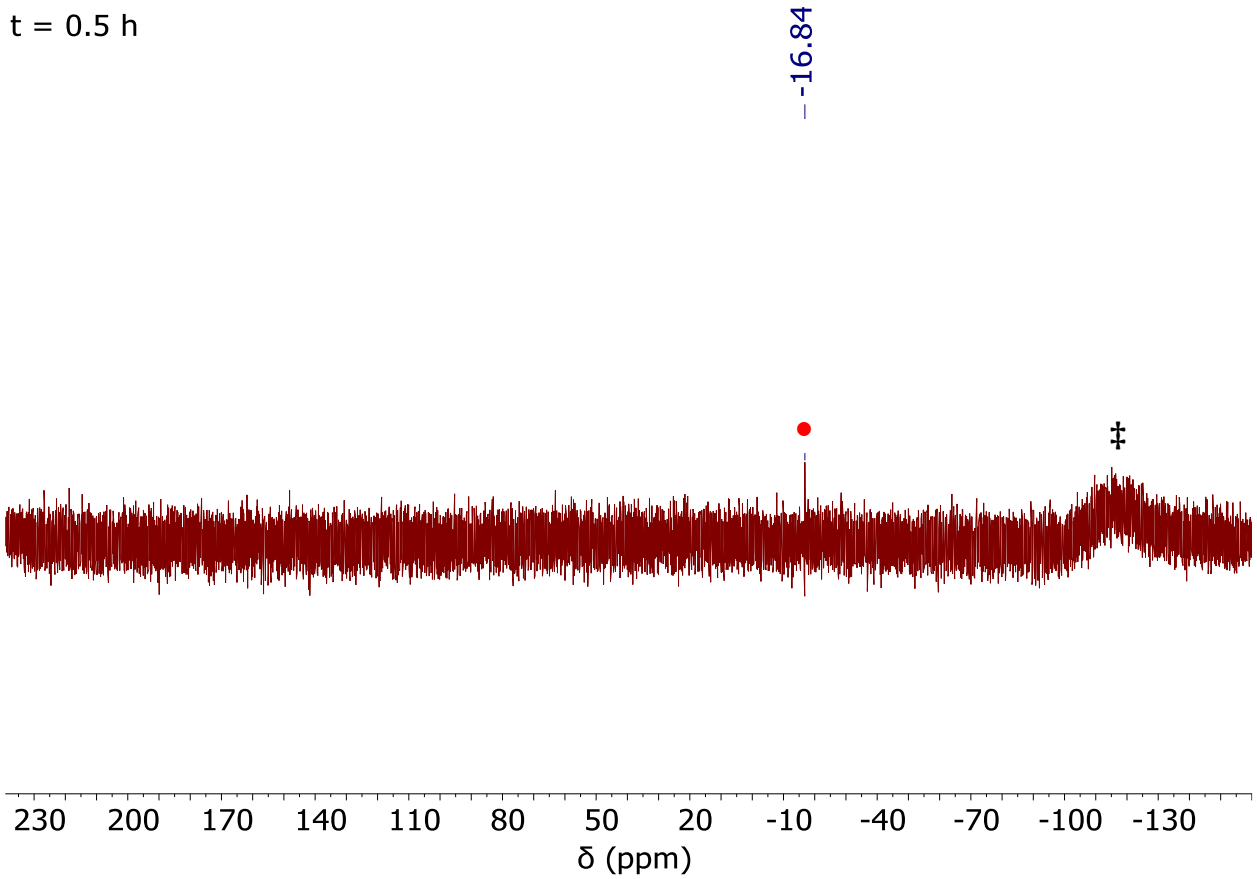

Figure S3.59. $^{29}Si\{^{1}H\}$ NMR spectrum of the reaction between Ph_3SiH and PyNH catalyzed by **1** in benzene-d_6 after 1 h.

S5.35. Ph_3SiH and 2.0 equiv. of Et_2NH

Ph_3SiH (98.0 mg, 3.7×10^{-1} mmol), Et_2NH (78.0 μL, 7.5×10^{-1} mmol, 2.0 equiv.), and **1** (15.0 μL, 3.7×10^{-2} mmol, 2.5 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6. After 1 h at ambient temperature, 88% conversion to $Ph_3Si(NEt_2)$. The reaction was run to completion.

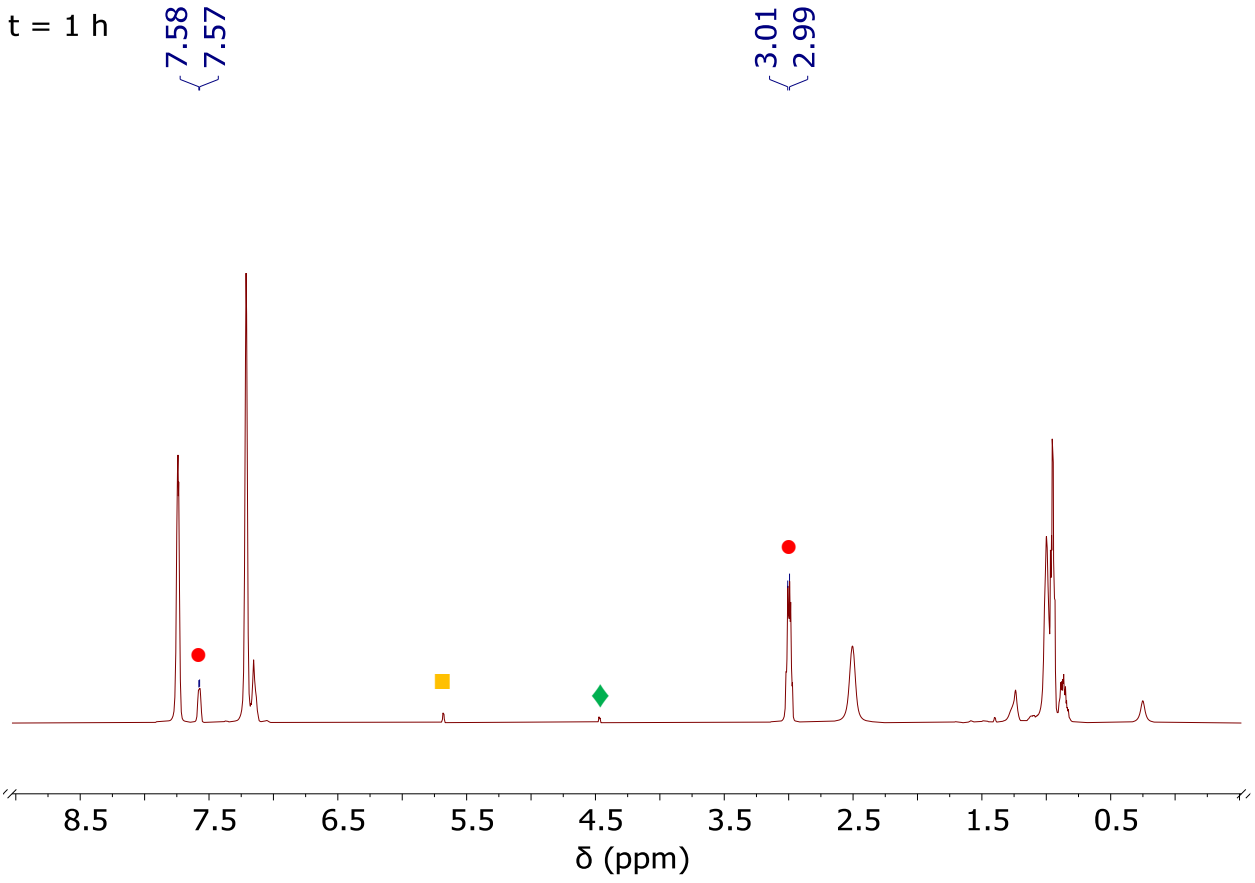

Figure S3.60. ^1H NMR spectrum of the reaction between Ph_3SiH and Et_2NH catalyzed by **1** in benzene-d_6 after 1 h.

S5.36. (*p*-MeO-C$_6$H$_4$)Ph$_2$SiH and 2.0 equiv. of ^{t}BuNH$_2$

(*p*-MeO-C$_6$H$_4$)Ph$_2$SiH (116.6 mg, 4.0 × 10^{-1} mmol), ^{t}BuNH$_2$ (84.5 μL, 8.0 × 10^{-1} mmol, 2.0 equiv.), and **1** (16.0 μL, 4.0 × 10^{-2} mmol, 2.5 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-*d*$_6$. After 1 h at ambient temperature, (*p*-MeO-C$_6$H$_4$)Ph$_2$Si(NH^{t}Bu) was formed in approximately 72% conversion. The reaction was subsequently run to completion.

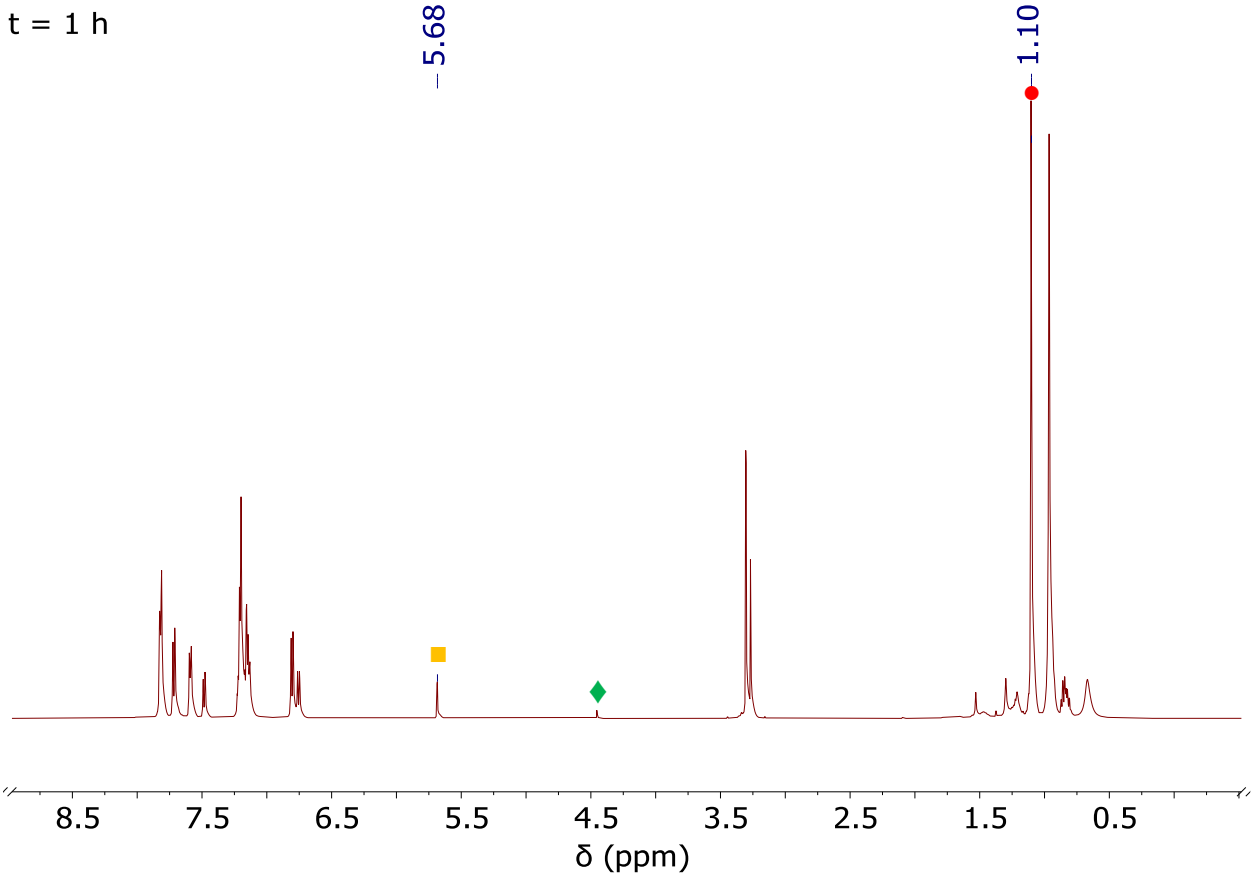

Figure S3.61. ^{1}H NMR spectrum of the reaction between (*p*-MeO-C$_6$H$_4$)Ph$_2$SiH and ^{t}BuNH$_2$ catalyzed by **1** in benzene-*d*$_6$ after 1 h. Residual solvent is buried by aryl peaks.

S5.37. (*p*-Me-C_6H_4)Ph_2SiH and 2.0 equiv. of $^tBuNH_2$

(*p*-Me-C_6H_4)Ph_2SiH (95.0 mg, 3.5×10^{-1} mmol), $^tBuNH_2$ (72.5 μL, 7.0×10^{-1} mmol, 2.0 equiv.), and **1** (14.0 μL, 3.5×10^{-2} mmol, 2.5 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6. After 1 h at ambient temperature, (*p*-Me-C_6H_4)$Ph_2Si(NH^tBu)$ was formed in approximately 77% conversion. The reaction was subsequently run to completion.

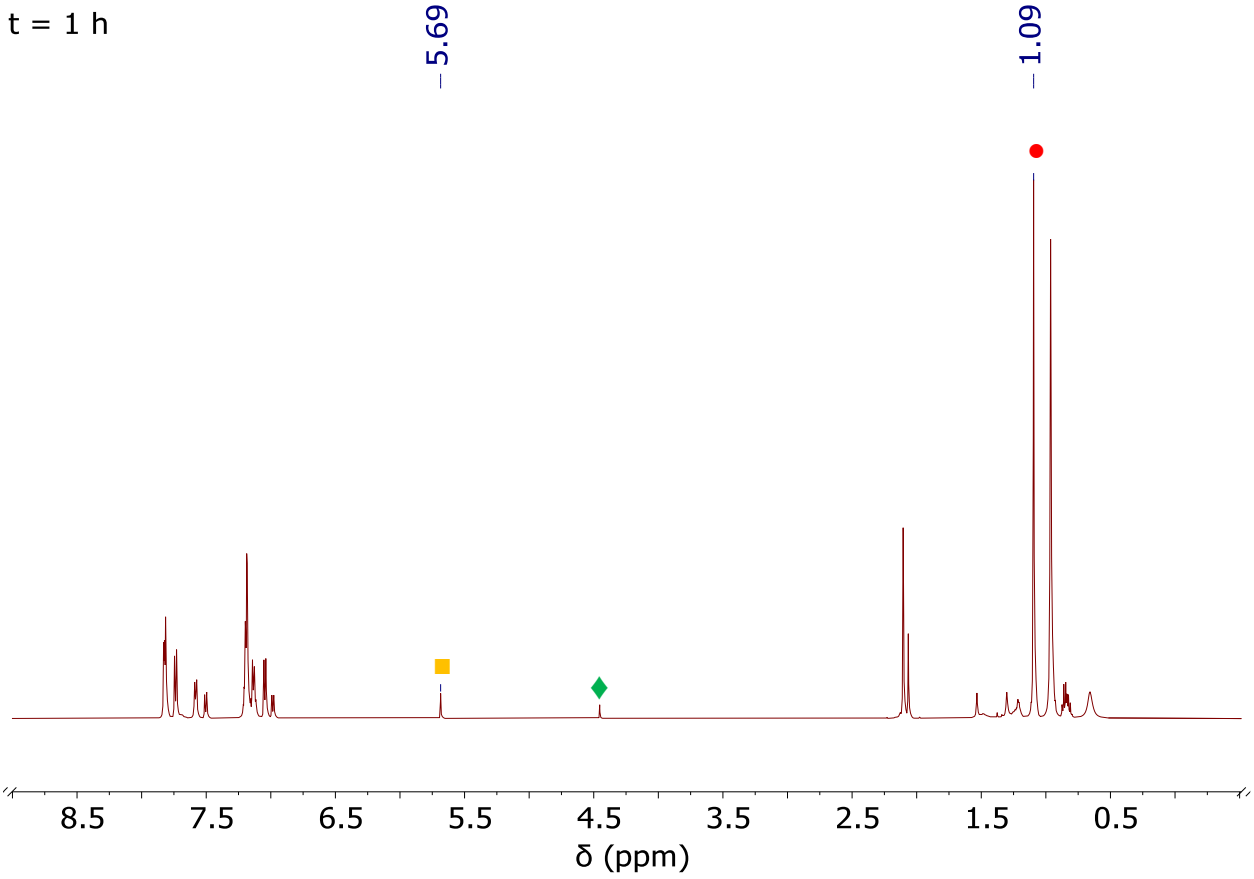

Figure S3.62. ^1H NMR spectrum of the reaction between (*p*-Me-C_6H_4)Ph_2SiH and $^tBuNH_2$ catalyzed by **1** in benzene-d_6 after 1 h. Residual solvent is buried by aryl peaks.

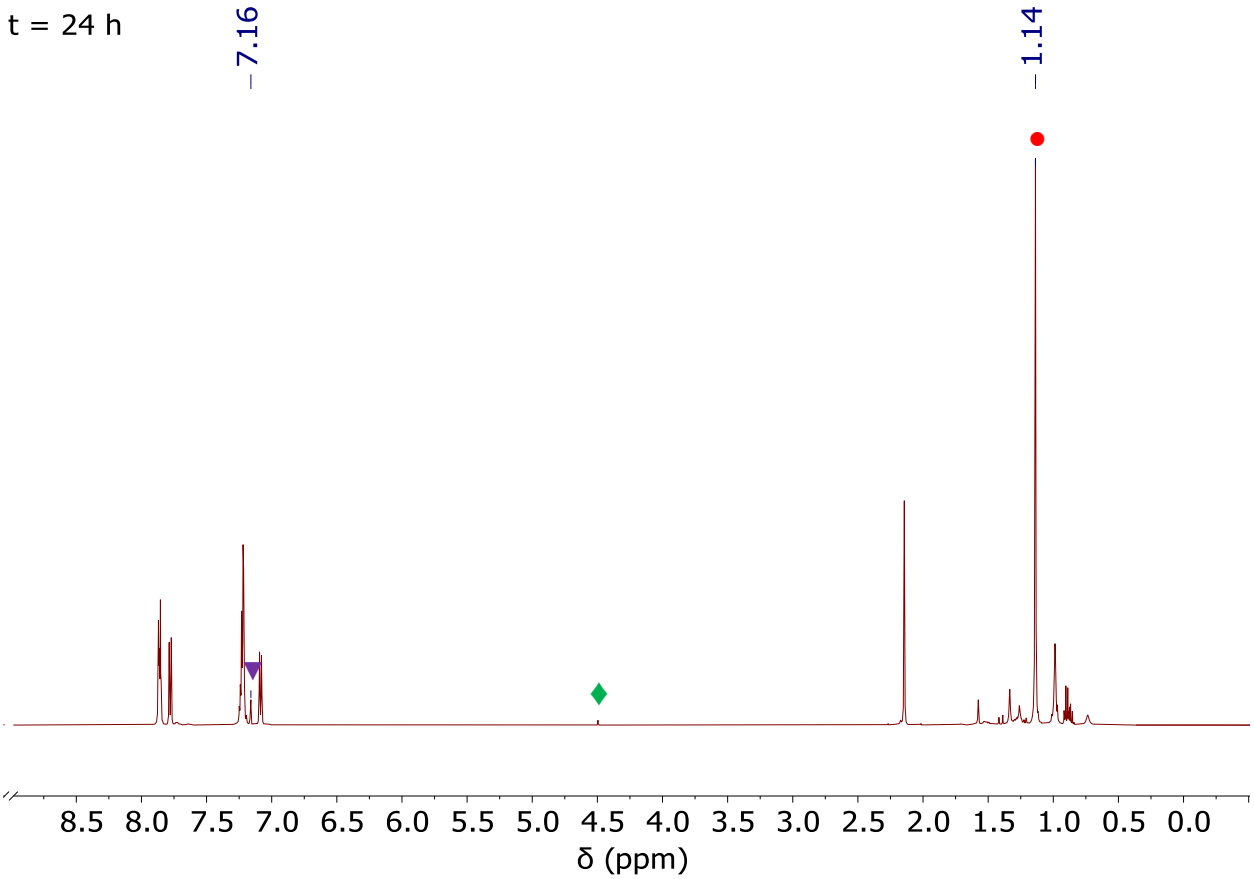

Figure S3.63. ^{1}H NMR spectrum of the reaction between (*p*-Me-C_6H_4)Ph_2SiH and ^{t}BuNH_2 catalyzed by **1** in benzene-d_6 after 24 h.

S5.38. (p-F_3C-C_6H_4)Ph_2SiH and 2.0 equiv. of $^tBuNH_2$

(p-F_3C-C_6H_4)Ph_2SiH (146.1 mg, 4.4×10^{-1} mmol), $^tBuNH_2$ (93.5 µL, 8.8×10^{-1} mmol, 2.0 equiv.), and **1** (18.0 µL, 4.5×10^{-2} mmol, 2.5 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6. After 1 h at ambient temperature, (p-F_3C-C_6H_4)$Ph_2Si(NH^tBu)$ was formed in approximately 54% conversion. The reaction was subsequently run to completion.

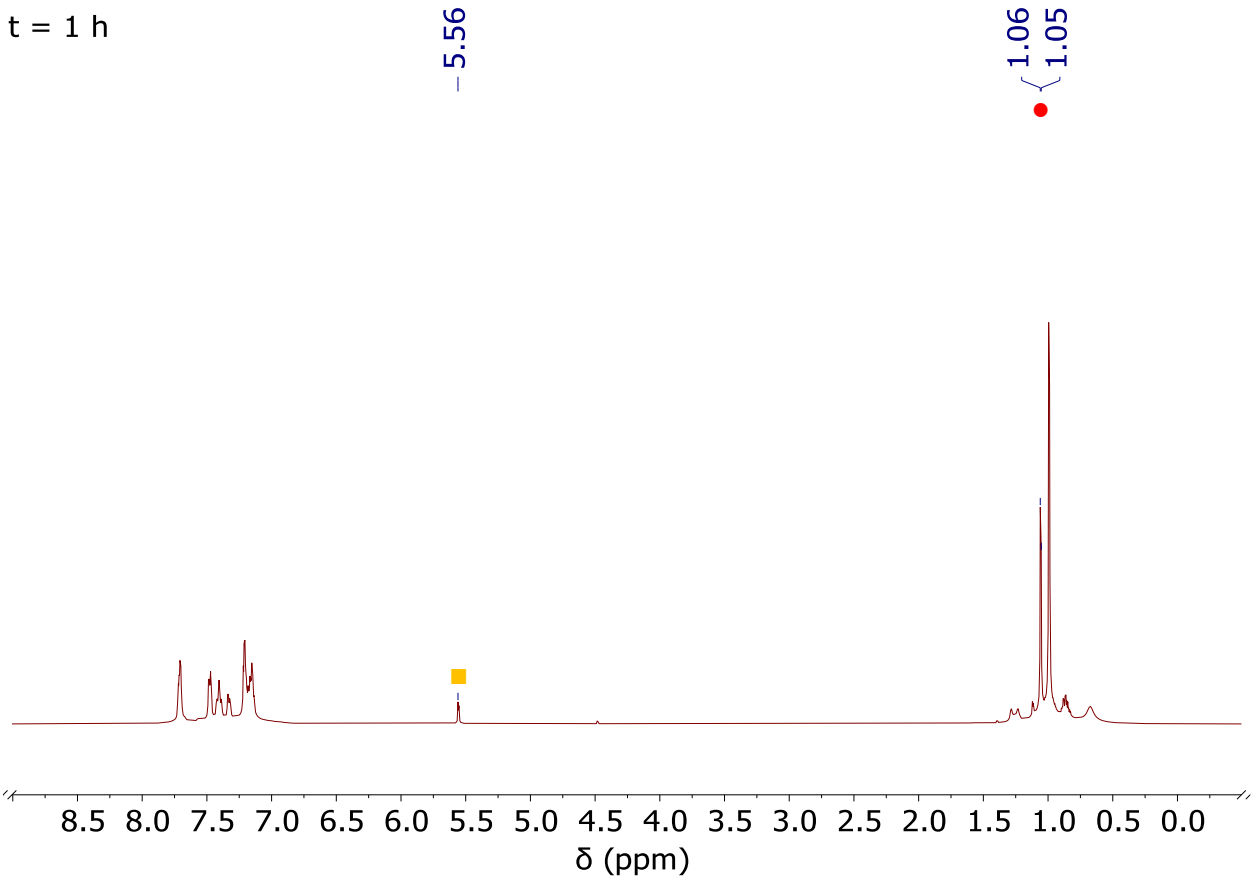

Figure S3.64. ^1H NMR spectrum of the reaction between (p-F_3C-C_6H_4)Ph_2SiH and $^tBuNH_2$ catalyzed by **1** in benzene-d_6 after 1 h. Residual solvent is buried by aryl peaks.

S5.39. Et_3SiH and 2.0 equiv. of PyNH

Et_3SiH (60.5 μL, 44.0 mg, 3.7×10^{-1} mmol), PyNH (62.5 μL, 7.6×10^{-1} mmol, 2.0 equiv.), and **1** (16.5 μL, 3.7×10^{-2} mmol, 2.3 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6. After 1 h at ambient temperature, Et_3Si(NPy) was formed in approximately 93% conversion.

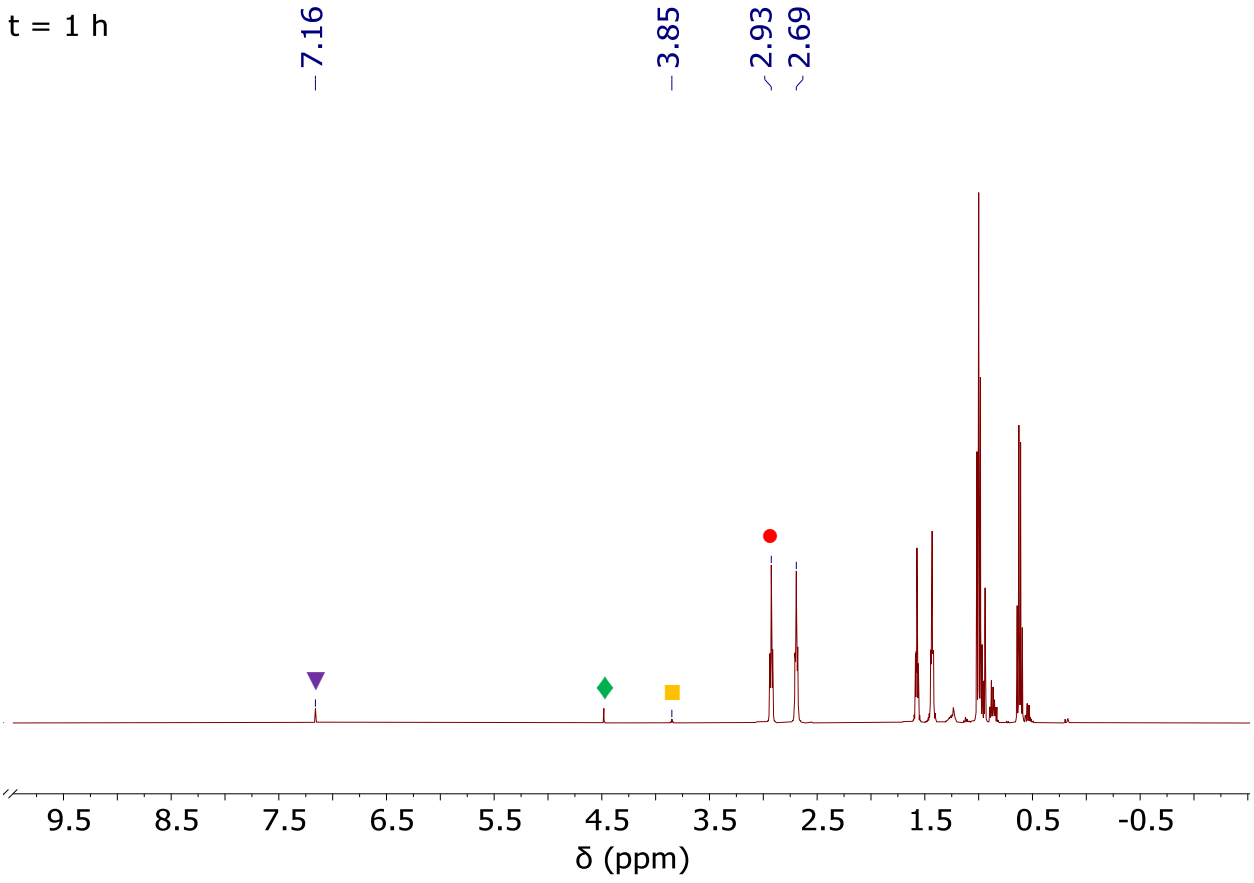

Figure S3.65. ^{1}H NMR spectrum of the reaction between Et_3SiH and PyNH catalyzed by **1** in benzene-d_6 after 1 h.

S5.40. Et_3SiH and 2.0 equiv. of Ph_2NH

Et_3SiH (79.0 μL, 4.9×10^{-1} mmol), Ph_2NH (168.0 mg, 9.9×10^{-1} mmol, 2.0 equiv.), and **1** (15.0 μL, 4.9×10^{-2} mmol, 2.3 M in hexanes, 10.0 mol %) were reacted together in 0.5 mL of benzene-d_6. After 1 h at ambient temperature, no reaction occurred.

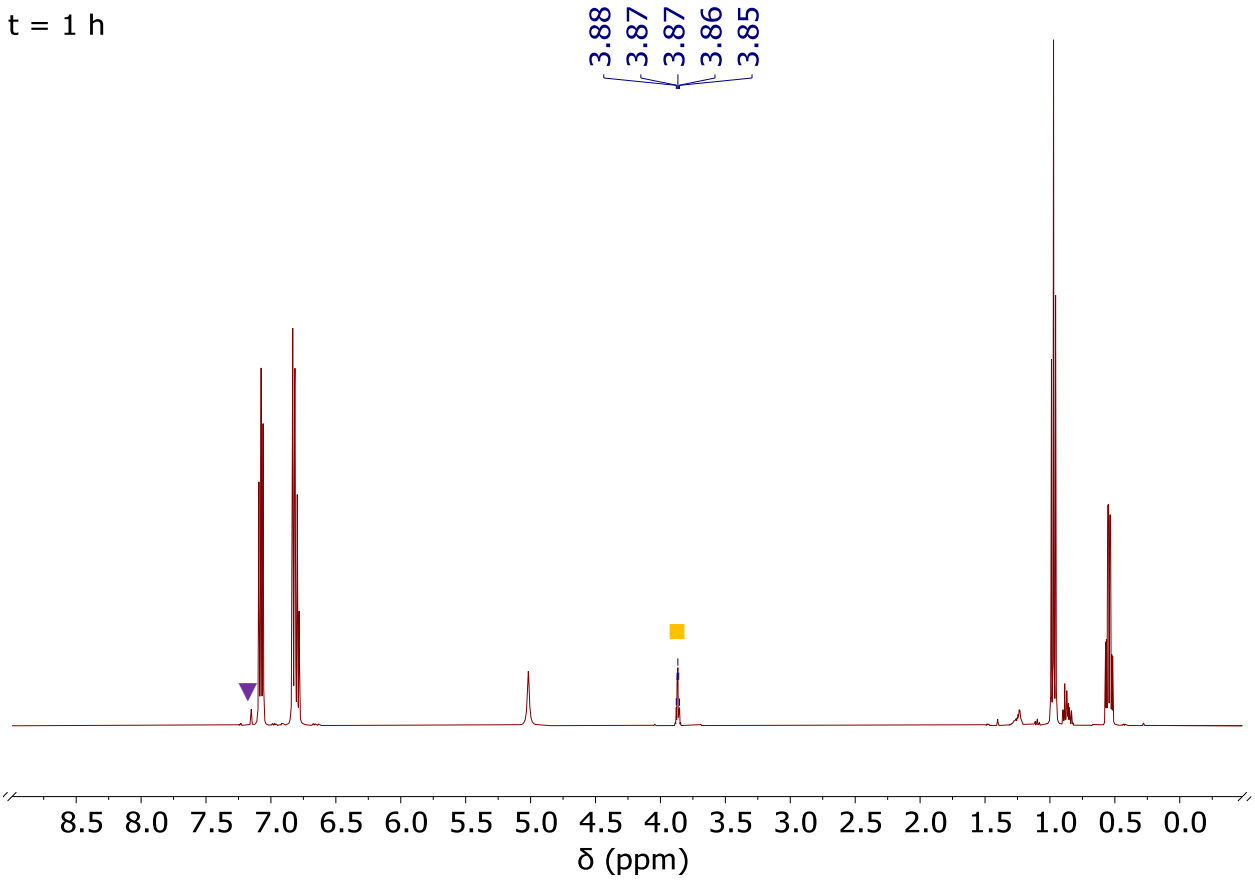

Figure S3.66. ^{1}H NMR spectrum of the reaction between Et_3SiH and Ph_2NH catalyzed by **1** in benzene-d_6 after 1 h. The peak centered at δ = 3.87 is Et_3SiH.

S4. EPR Acquisition

S4.1. General Procedure

Ph_3SiH (96.0 mg, 3.7×10^{-1} mmol), $^tBuNH_2$ (77.0 μL, 7.4×10^{-1} mmol, 2.0 equiv.), and **1** (14.0 μL, 3.7×10^{-2} mmol) were reacted together in a PTFE-sealed J-Young Quartz NMR tube. After 5 min, EPR measurements were acquired at ambient temperature.

S4.2. EPR Spectrum

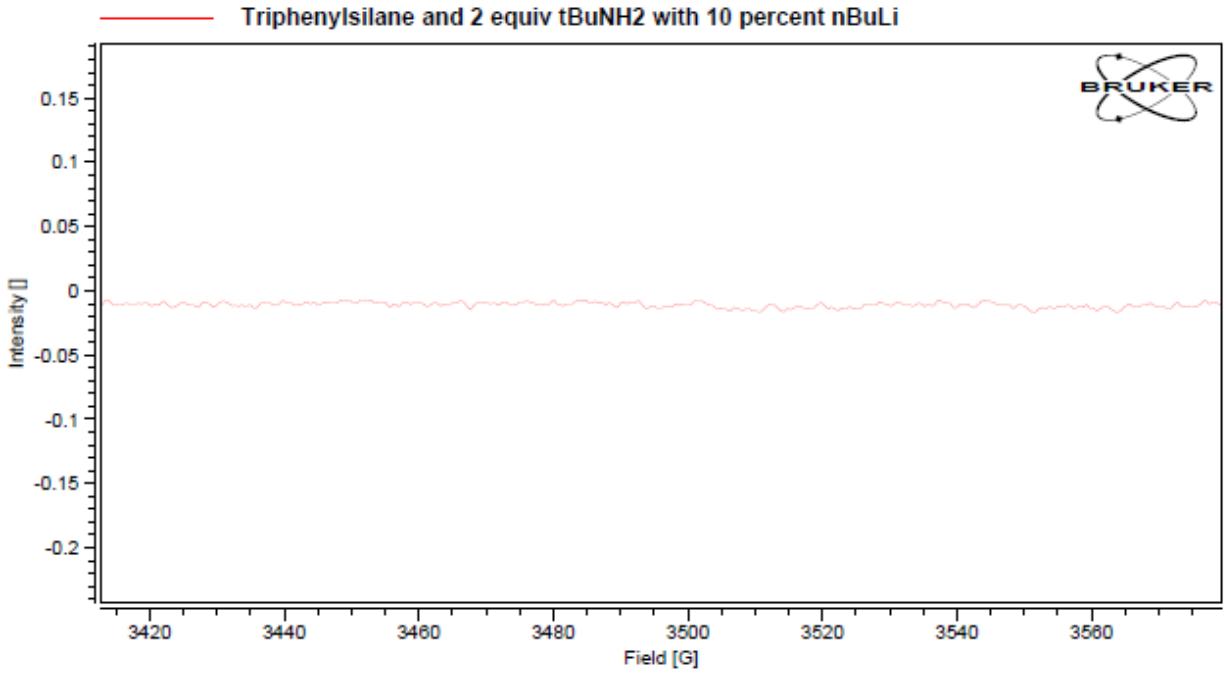

Figure S4.1. EPR Spectrum of the reaction between Ph_3SiH and 2.0 equiv. of $^tBuNH_2$ with **1**

Conditions: microwave frequency = 98.5×10^{-1} GHz; microwave power = 632.5×10^{-3} mW; modulation amplitude = 1.0 G; modulation frequency = 100.0 kHz; time constant = 1.0×10^{-2} ms; conversion time = 90.0 ms

S5. Workup and Characterization Details

S5.1. General Workup for Isolating Aminosilanes

After completion of the reaction, the desired aminosilane was purified either by vacuum distillation or vacuum distillation.

For aminosilanes $PhSi(NPy)_3$, (*p*-MeO-C_6H_4)$Ph_2Si(NH^tBu)$, (*p*-Me-C_6H_4)$Ph_2Si(NH^tBu)$, and (*p*-F_3C-C_6H_4)$Ph_2Si(NH^tBu)$, the NMR tube was opened to air, the solution added to a 20 mL scintillation vial to quench reactive intermediates, and the contents subsequently transferred to a W-shaped, bulb-to-bulb distillation apparatus via glass pipette. The contents were carefully reduced under dynamic vacuum to afford an oil, which was subsequently distilled over, using consistent and even heating from a heat gun. The W distillation apparatus was brought into the glovebox and the oil was characterized.

For aminosilanes $Ph_3Si(NH^tBu)$ and $Ph_3Si(NEt_2)$, the NMR tube was opened to air, and the contents quickly transferred to a Schlenk tube under dynamic N_2. The tube was sealed with a glass stopper and the contents were reduced to either an oil or a solid under dynamic vacuum. The stopper was subsequently switched for a water-cooled cold finger and the contents heated under dynamic vacuum until solid had sublimed. The sublimator was brought into the glovebox and the pure solid was characterized.

S5.2. PhSi(NPy)$_3$

Colorless oil (Yield: 52 mg, 44%). ^{1}H NMR (benzene-d_6, 500 MHz): 7.77 (d, J = 7.9 Hz, 2H), 7.41-7.19 (m, 3H), 3.13 (s, 12H), 1.63 (s, 12 H). ^{13}C{^{1}H} NMR (benzene-d_6, 126 MHz): 137.88 (s), 135.37 (s), 129.17 (s), 47.49 (s), 27.22 (s). ^{29}Si{^{1}H} (benzene-d_6, 99Hz): -34.67. HRMS (ESI) $[M+H]^+$ for $C_{18}H_{30}N_3Si^+$; calc'd: 316.2204, found: 316.2197.

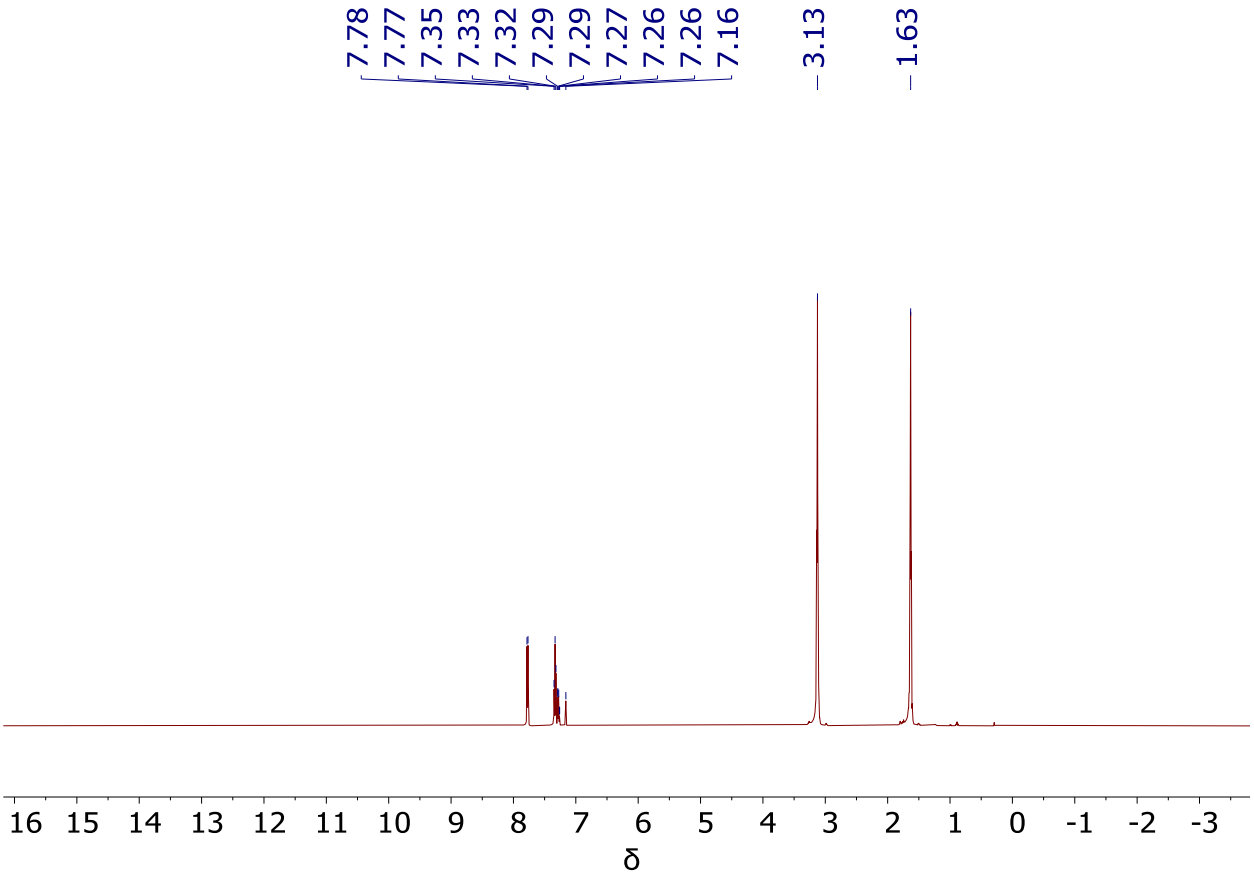

Figure S5.1. ^{1}H NMR spectrum for PhSi(NPy)$_3$.

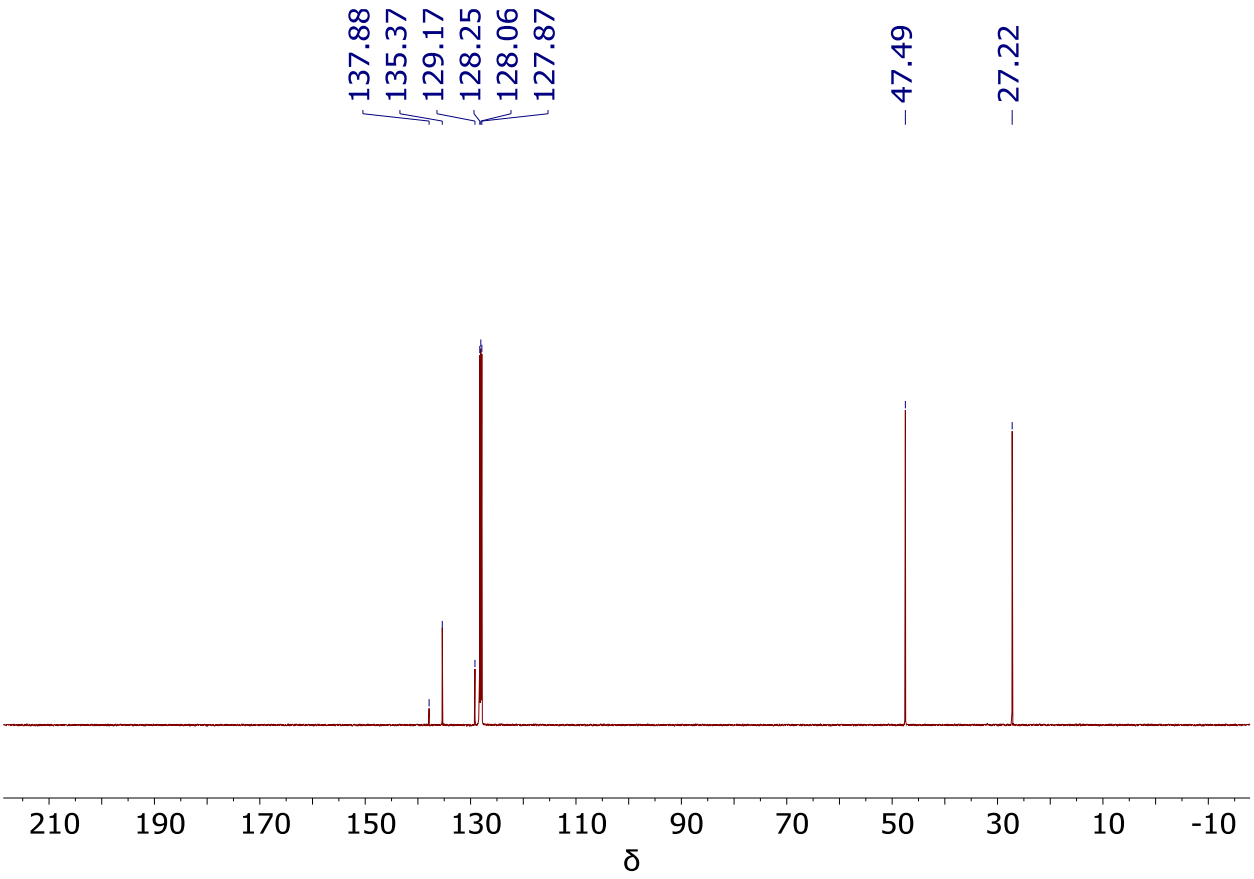

Figure S5.2. $^{13}C\{^{1}H\}$ NMR spectrum for $PhSi(NPy)_3$.

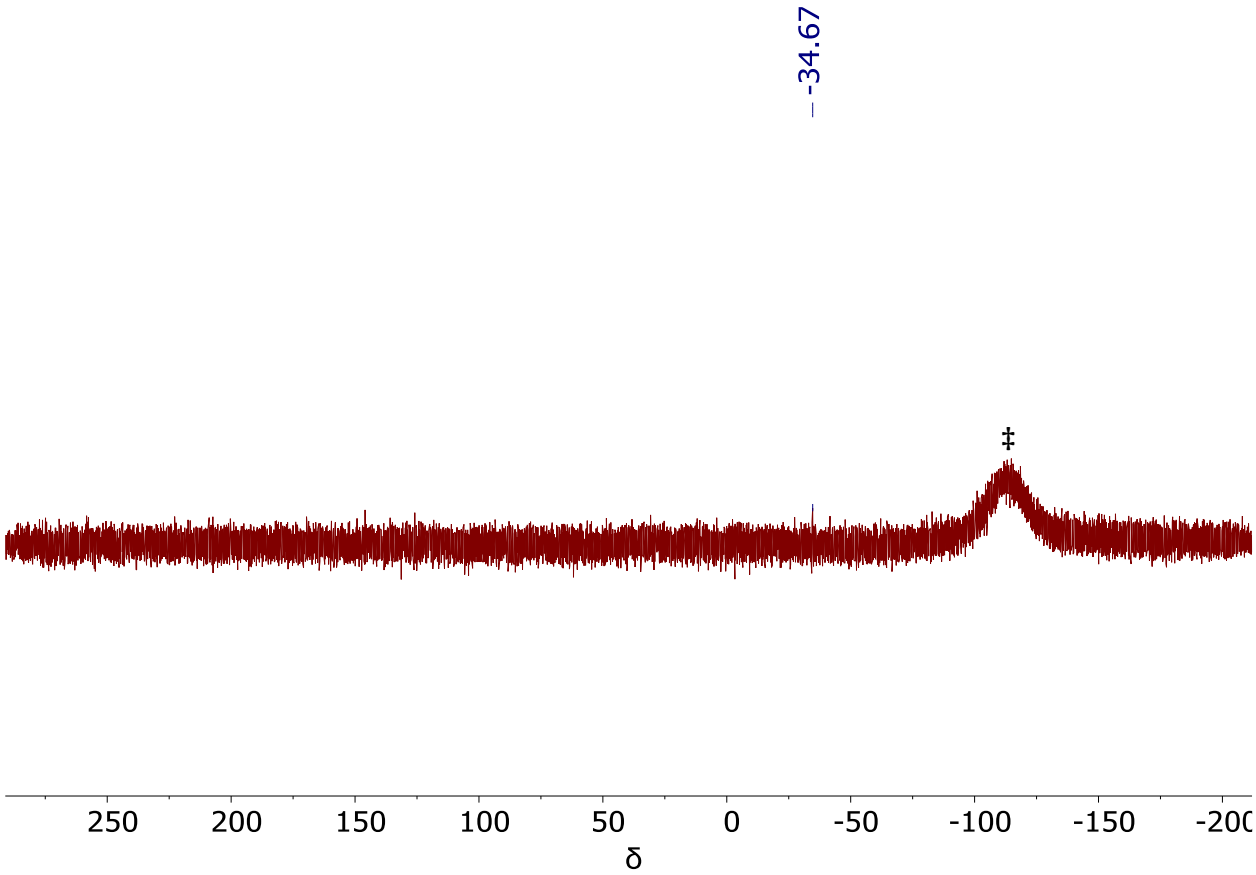

Figure S5.3. $^{29}Si\{^{1}H\}$ NMR spectrum for $PhSi(NPy)_3$.

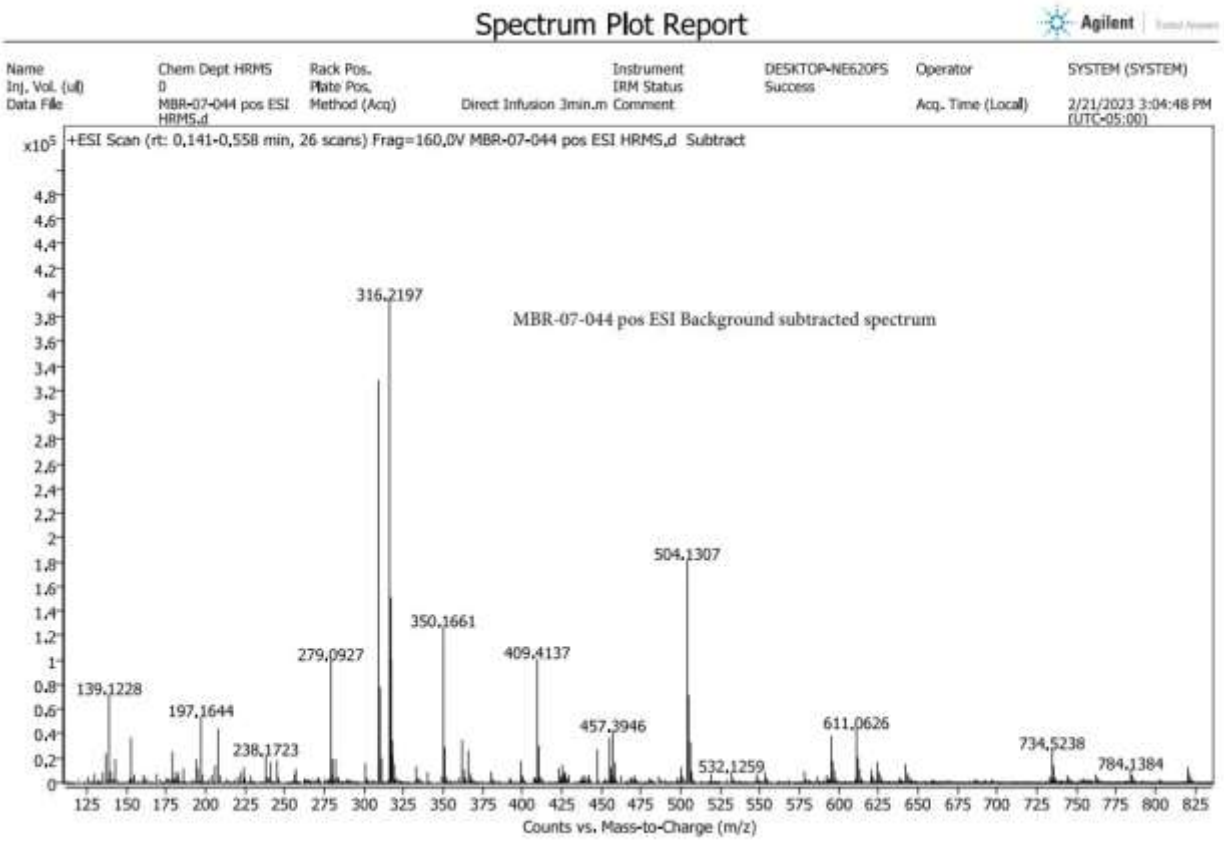

Figure S5.4. Full HRMS fragmentation spectrum for $[PhSi(NPy)_3+H]^+$.

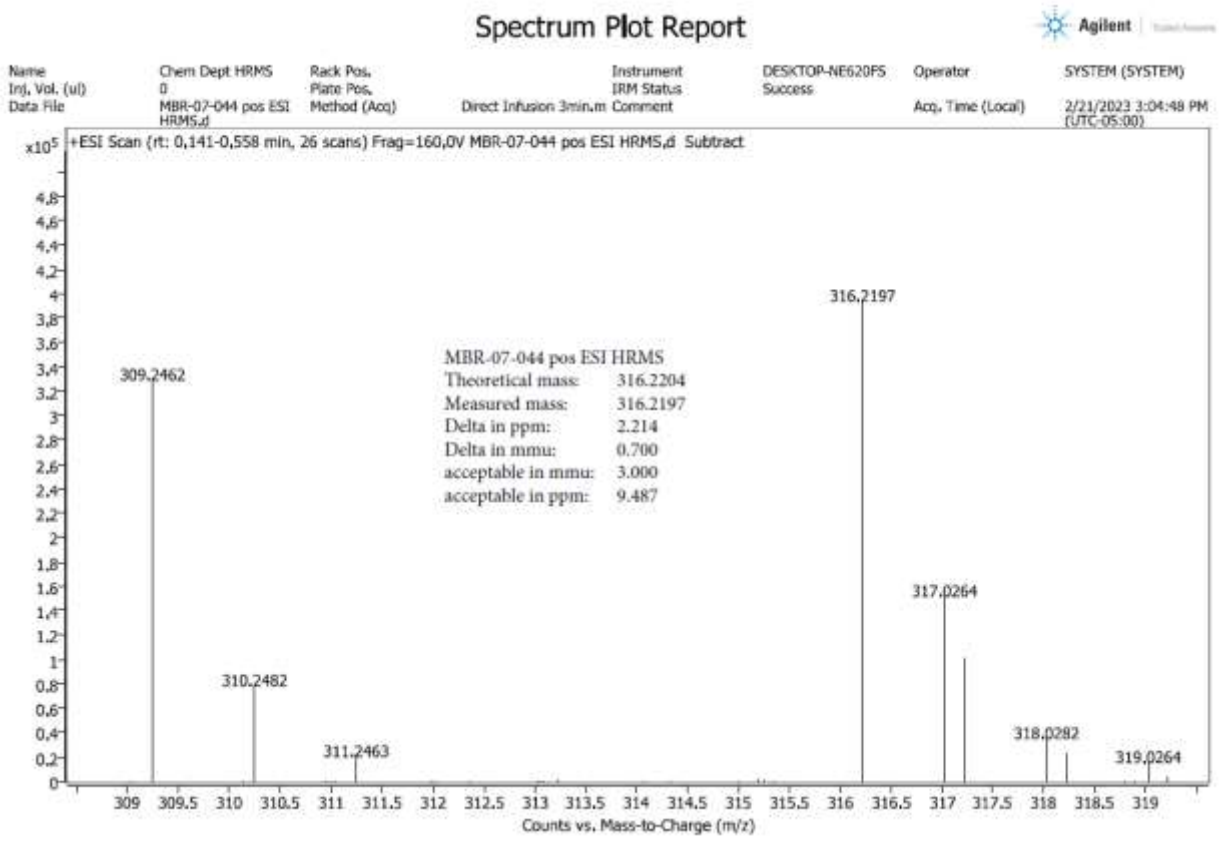

Figure S5.5. Background-subtracted HRMS fragmentation spectrum for $[PhSi(NPy)_3+H]^+$.

S5.3. $Ph_3Si(NH^tBu)$

White solid (14.9 mg, 12% yield). ^1H NMR (benzene-d_6, 500 MHz): 7.88-7.79 (m, 6H), 7.21 (dd, J = 5.0, 1.9 Hz), 1.28 (s, 1H), 1.09 (s, 9H). $^{13}C\{^1H\}$ NMR (benzene-d_6, 126 MHz): 137.38, 135.89, 129.30, 33.54, 1.09. $^{29}Si\{^1H\}$ NMR (benzene-d_6, 99 MHz): -20.93. HRMS (ESI) $[M+H]^+$ for $C_{22}H_{26}NSi^+$; calc'd: 332.1819, found: 332.1819.

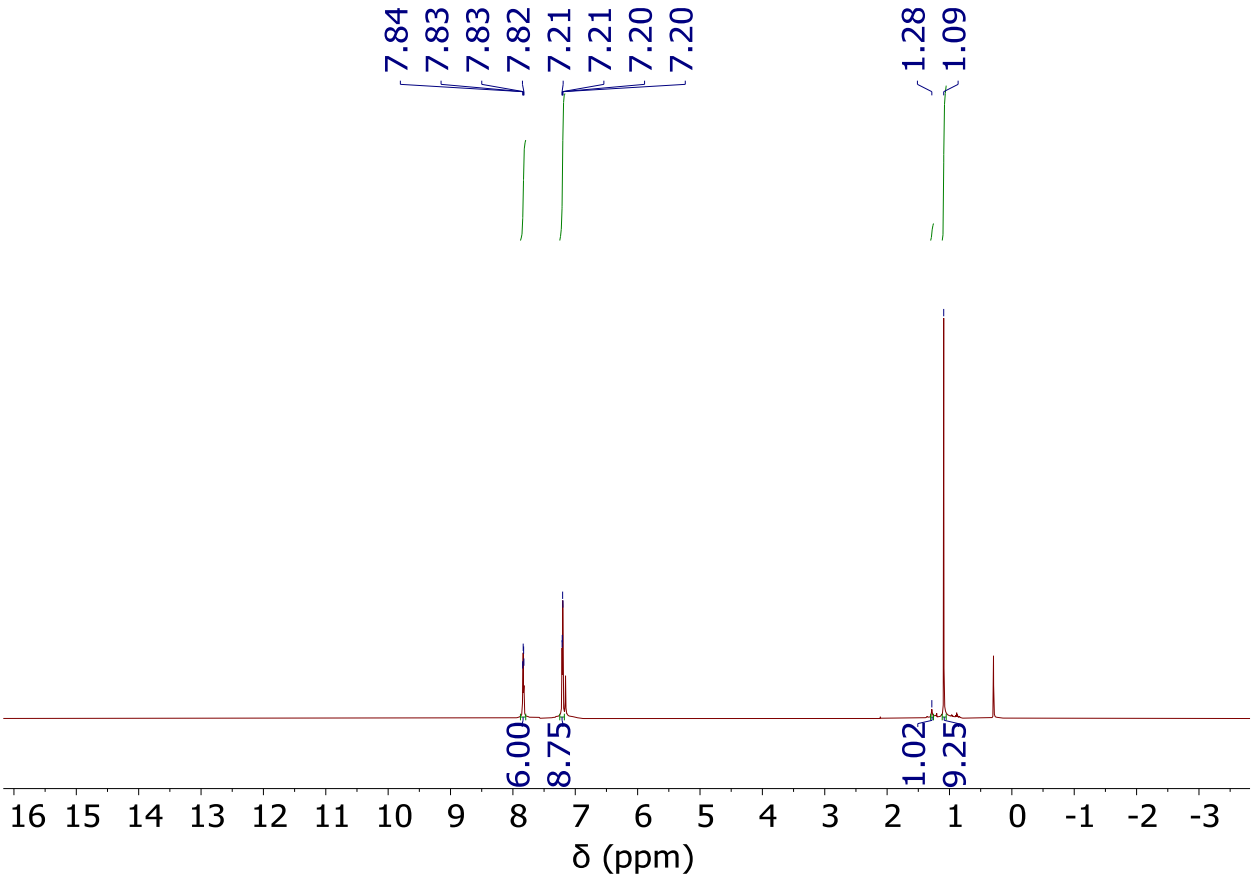

Figure S5.6. ^1H NMR spectrum for $Ph_3Si(NH^tBu)$.

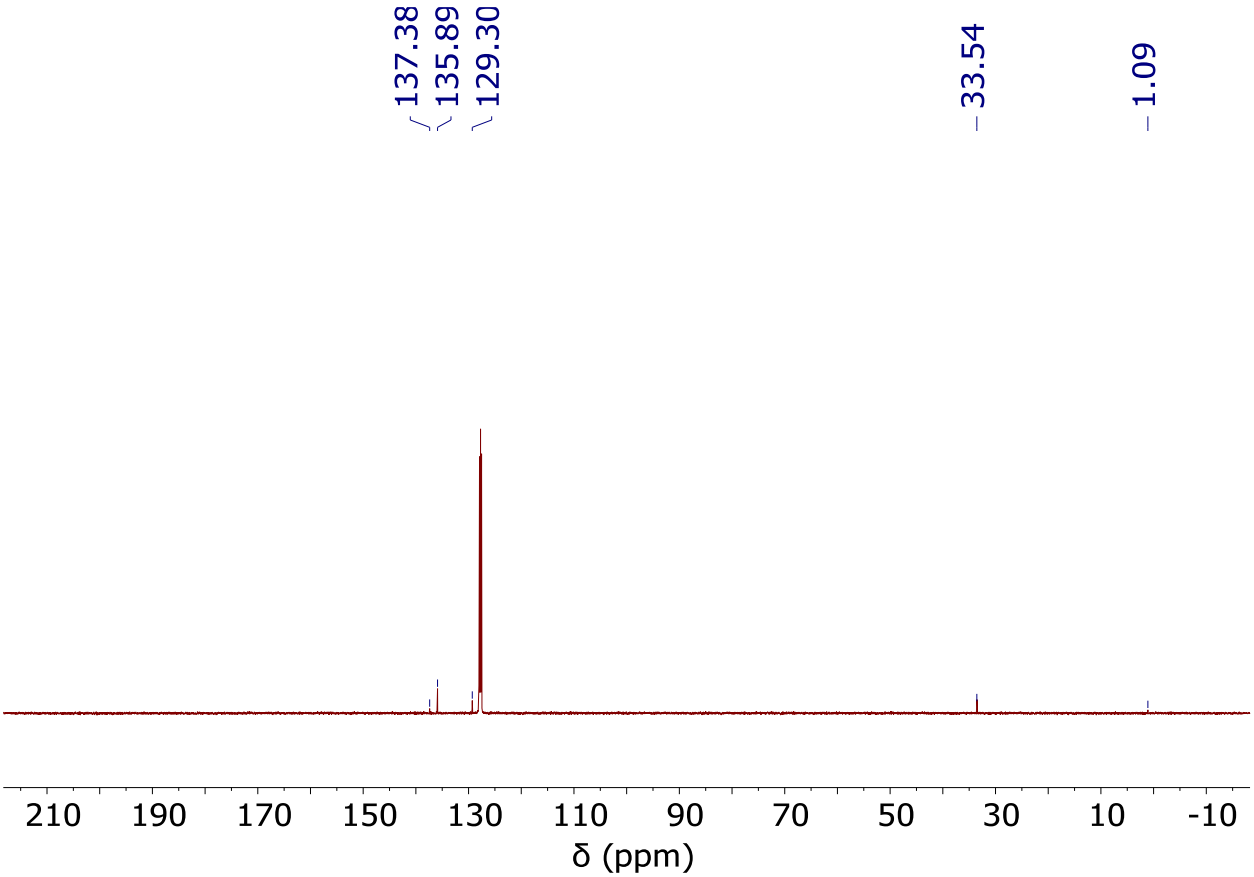

Figure S5.7. $^{13}C\{^{1}H\}$ NMR spectrum for $Ph_3Si(NH^tBu)$.

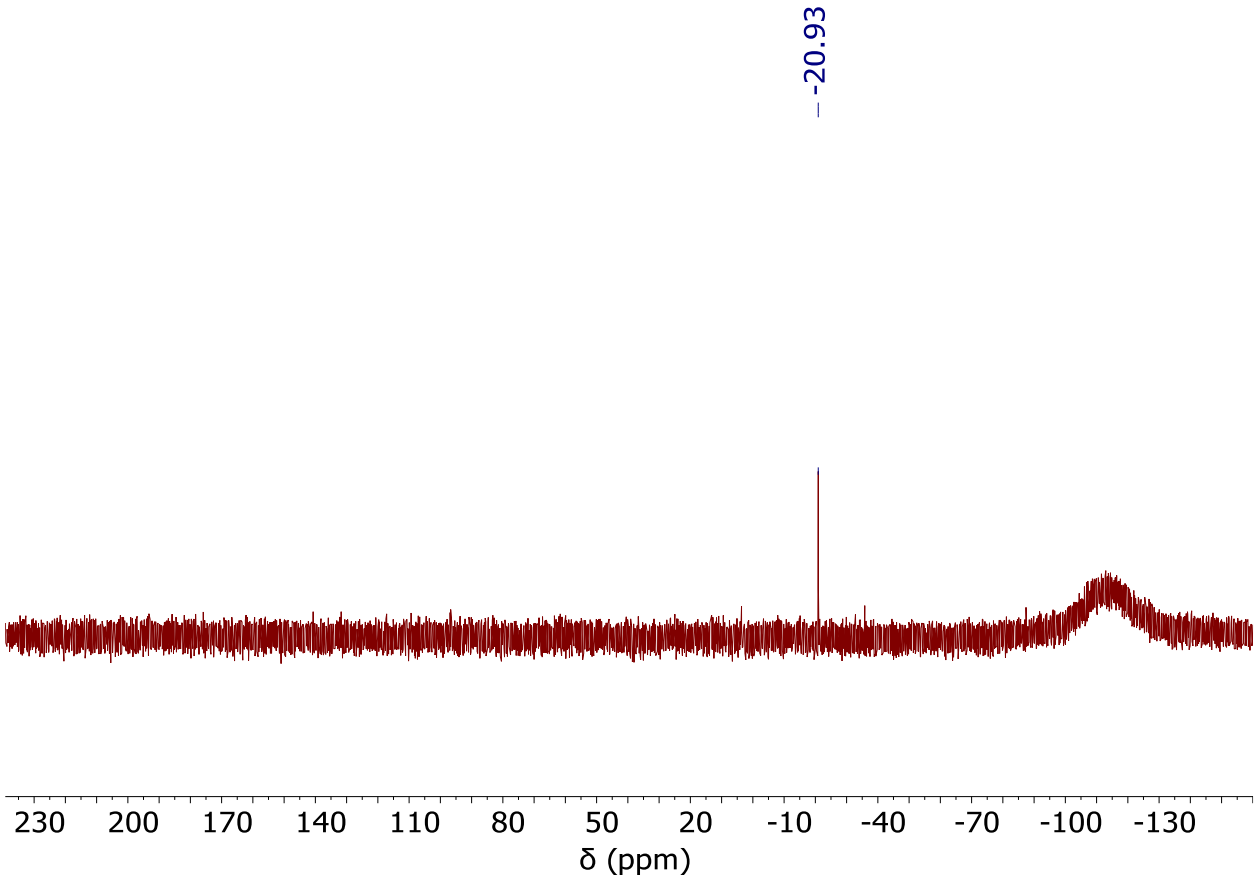

Figure S5.8. $^{29}Si\{^{1}H\}$ NMR spectrum for $Ph_3Si(NH^tBu)$.

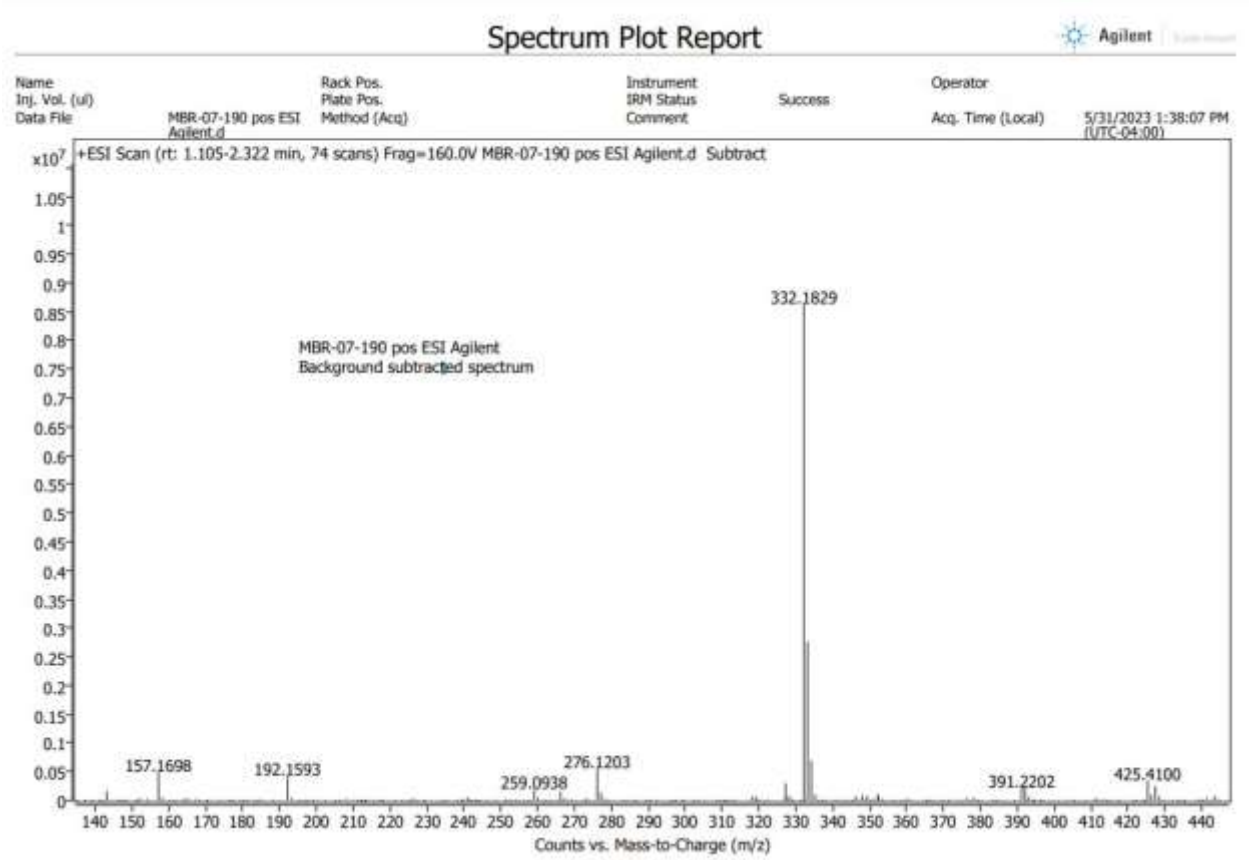

Figure S5.8. Full HRMS fragmentation spectrum for $[Ph_3Si(NH^tBu)+H]^+$.

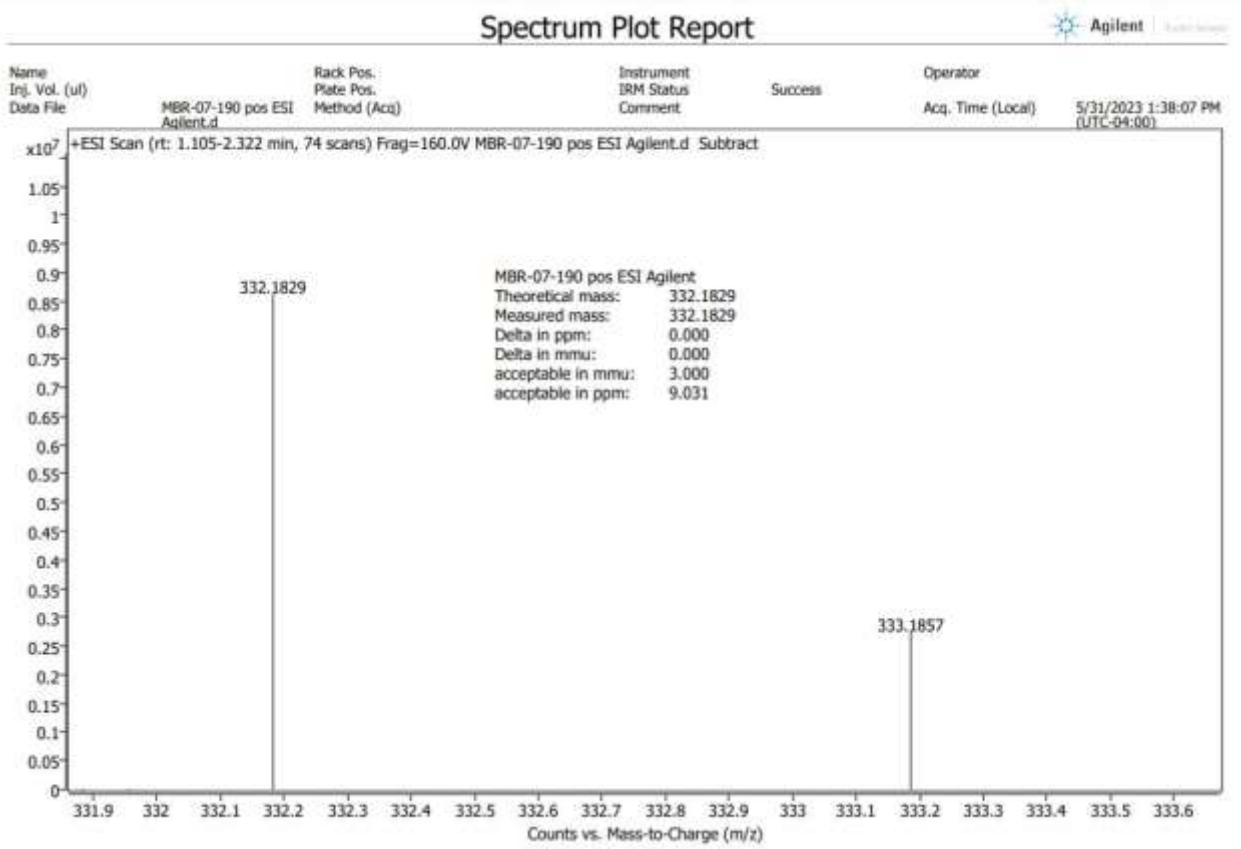

Figure S5.9. Background-subtracted HRMS fragmentation spectrum for $[Ph_3Si(NH^tBu)+H]^+$.

S5.3. (*p*-MeO-C_6H_4)$Ph_2Si(NH^tBu)$

Opaque oil (85.1 mg, 59% Yield). ^{1}H NMR (benzene-d_6, 500 MHz): 7.87 (dd, J = 7.6, 1.9 Hz, 4H), 7.76 (d, J = 8.7 Hz, 2H), 7.23 (d, J = 7.5 Hz, 6H), 6.84 (d, J = 8.7 Hz, 2H), 3.30 (s, 3H), 1.30 (s, 1H), 1.13 (s, 9H). ^{13}C{^{1}H} NMR (benzene-d_6, 126 MHz): 161.01, 137.85, 137.46, 135.81, 129.18, 113.59, 54.18, 49.80, 33.55. ^{29}Si{^{1}H} NMR (benzene-d_6, 99 MHz): -20.95. HRMS (ESI) $[M+H]^+$ for $C_{23}H_{28}NOSi^+$; calc'd: 362.1935, found: 362.1935.

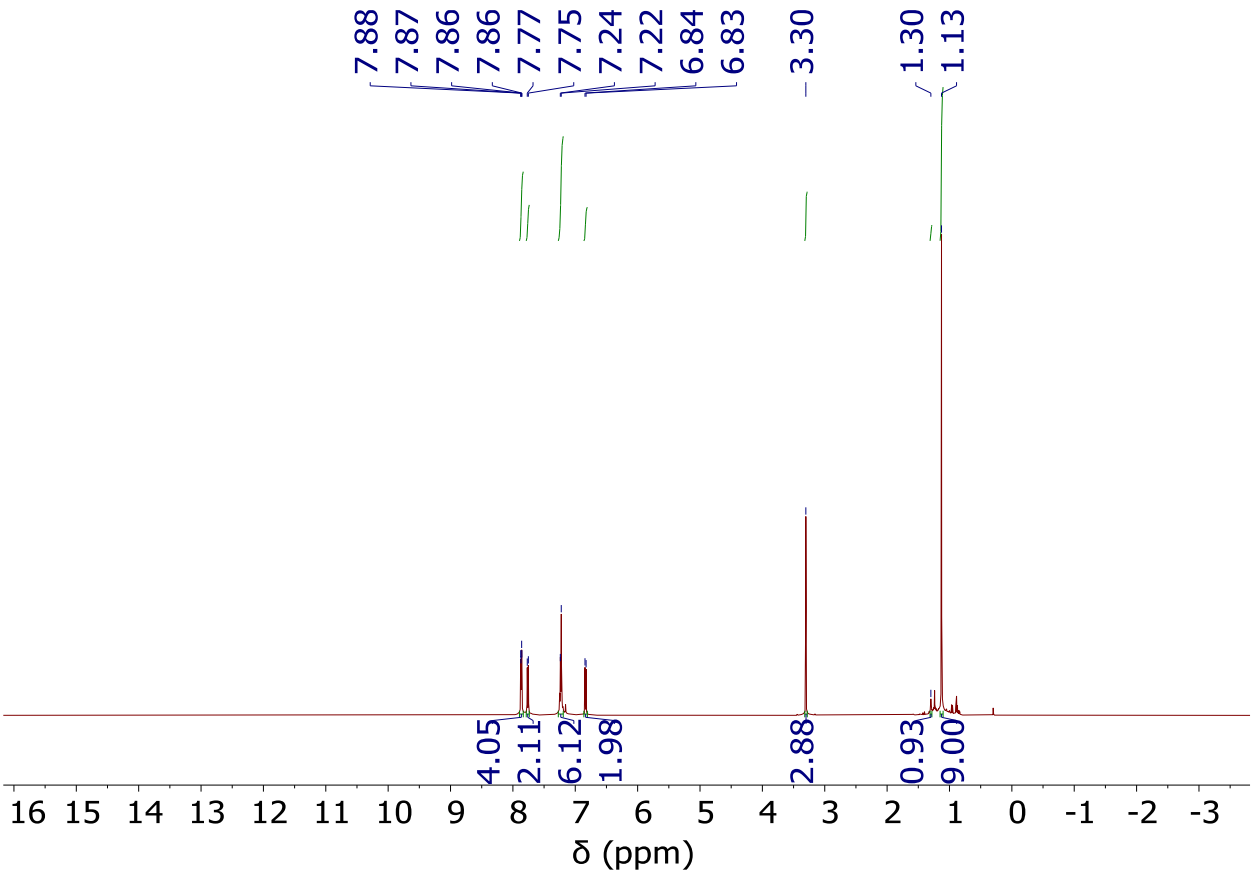

Figure S5.10. ^{13}C{^{1}H} NMR spectrum for (*p*-MeO-C_6H_4)$Ph_2Si(NH^tBu)$.

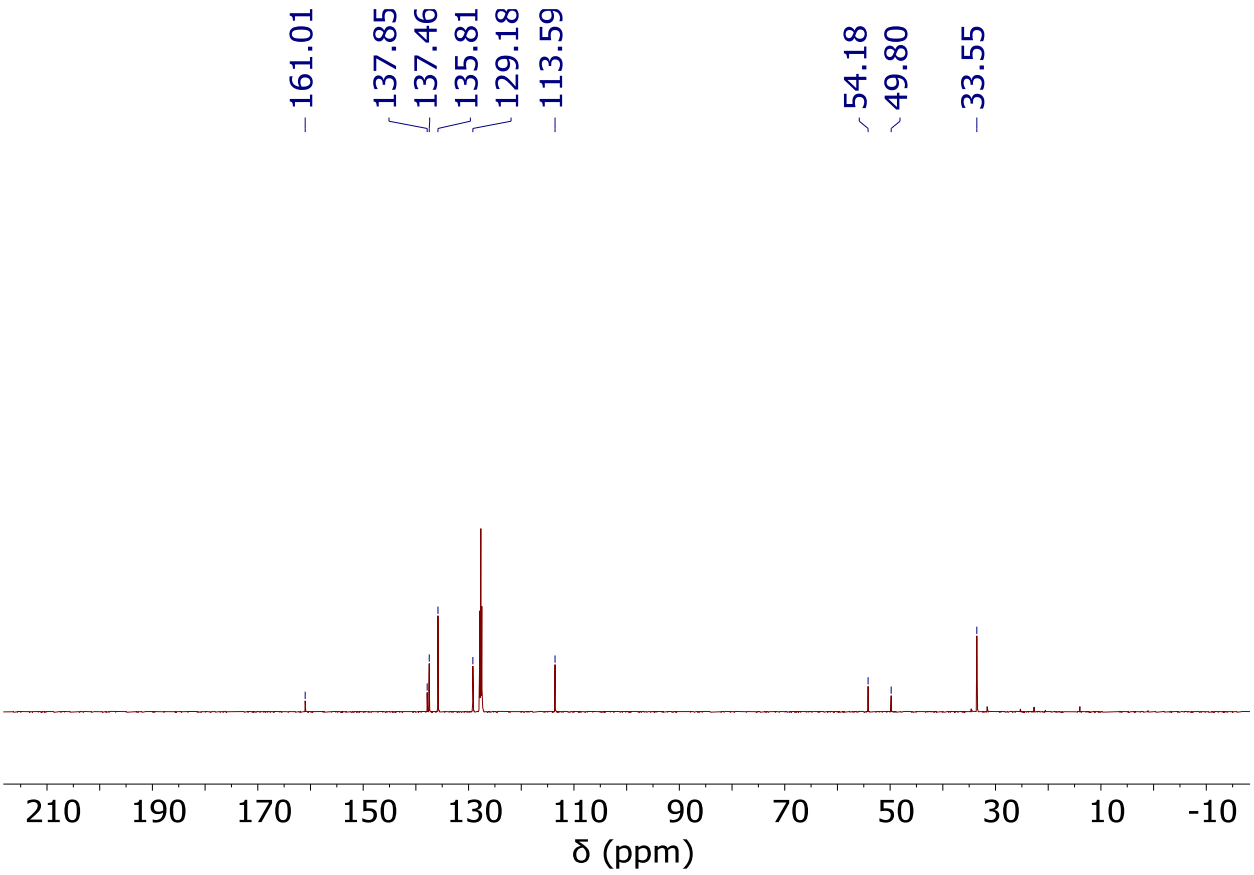

Figure S5.11. $^{13}C\{^{1}H\}$ NMR spectrum for (*p*-MeO-C_6H_4)Ph_2Si(NH^{t}Bu).

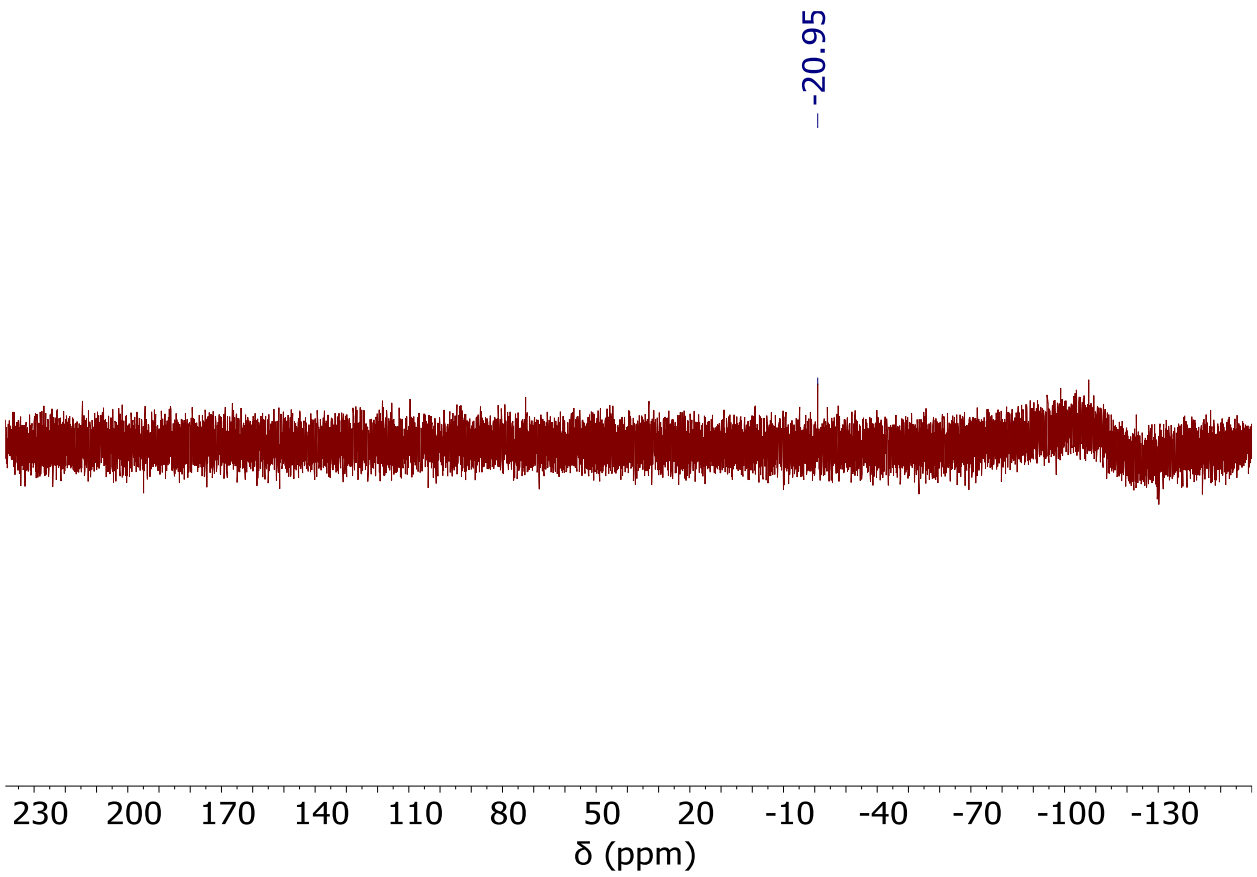

Figure S5.12. $^{29}Si\{^{1}H\}$ NMR spectrum for (*p*-MeO-C_6H_4)$Ph_2Si(NH^tBu)$.

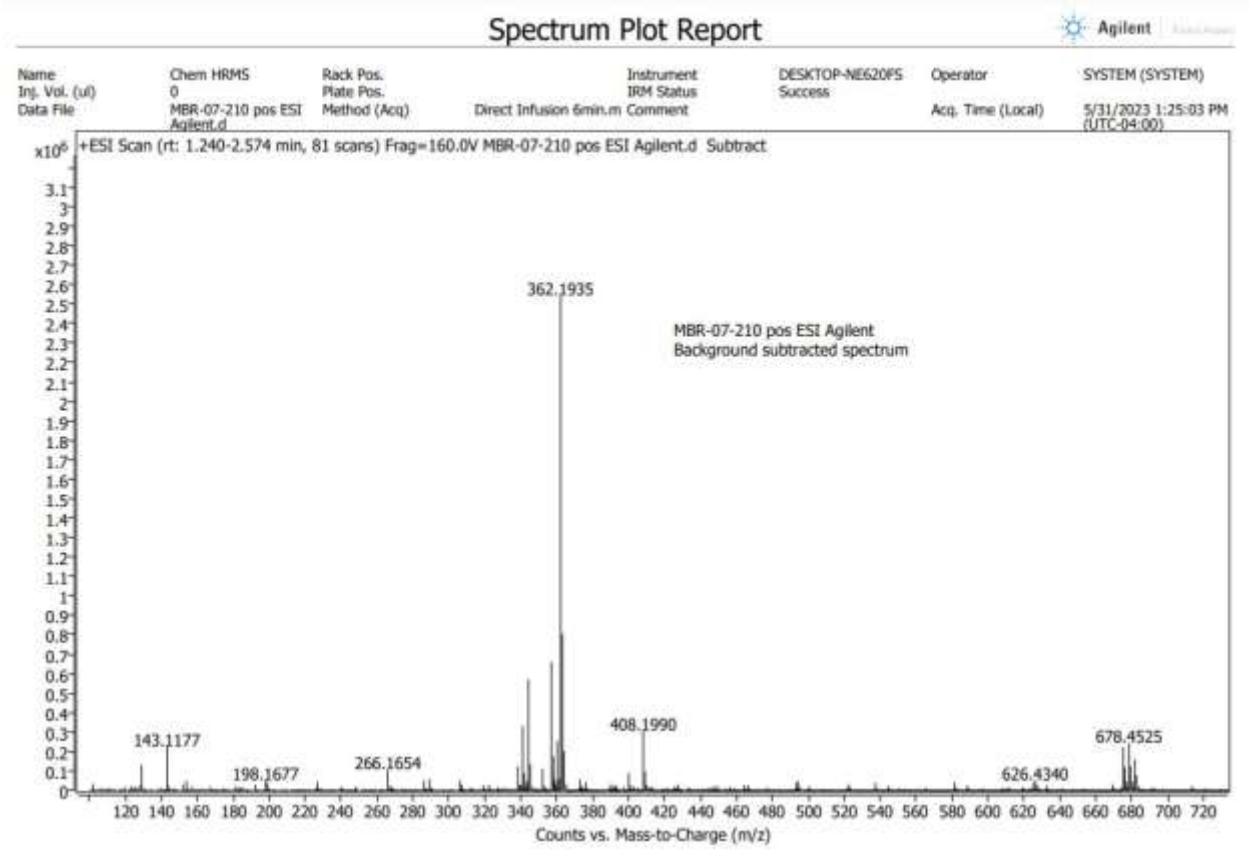

Figure S5.13. Full HRMS fragmentation spectrum for $[(p\text{-MeO-}C_6H_4)Ph_2Si(NH^tBu)+H]^+$.

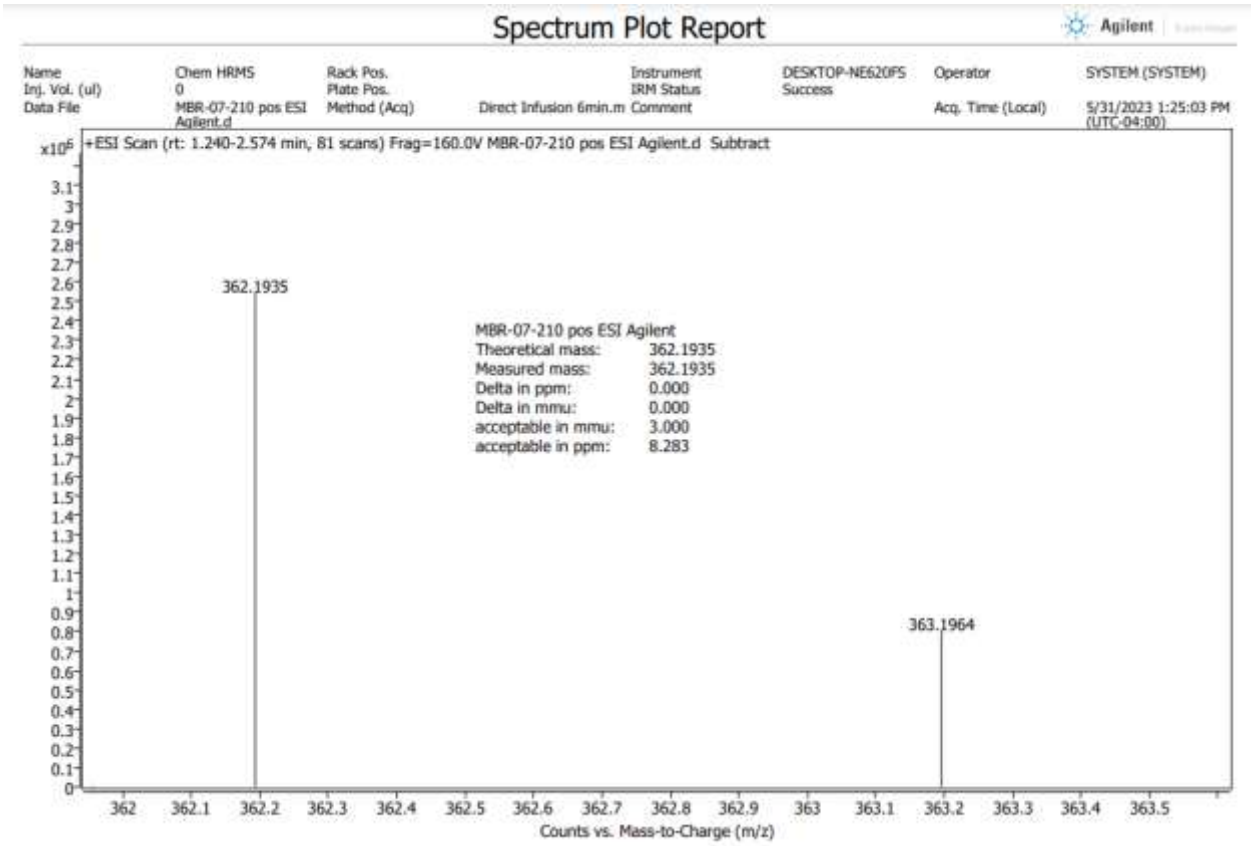

Figure S5.14. Background-subtracted HRMS fragmentation spectrum for [(*p*-MeO-C_6H_4)Ph_2Si(NH^{t}Bu)+H]$^+$.

S5.4. (p-Me-C_6H_4)$Ph_2Si(NH^tBu)$

Opaque oil (17.9 mg, 15% Yield). ^{1}H NMR (benzene-d_6, 500 MHz): 7.86 (dd, J = 6.9, 2.5 Hz, 4H), 7.78 (d, J = 8.1 Hz, 2H), 7.30-7.17 (m, 6H), 7.07 (d, J = 7.5 Hz, 2H), 2.12 (s, 3H), 1.31 (s, 1H), 1.12 (s, 9H). ^{13}C{^{1}H} NMR (benzene-d_6, 126 MHz): 139.33, 138.04, 136.40, 136.22, 134.08, 129.59, 128.95, 50.20, 33.92, 21.49. ^{29}Si{^{1}H} NMR (benzene-d_6, 99 MHz): -20.26. HRMS (ESI) $[M+H]^+$ for $C_{23}H_{28}NSi^+$; calc'd: 346.1986, found: 346.1987.

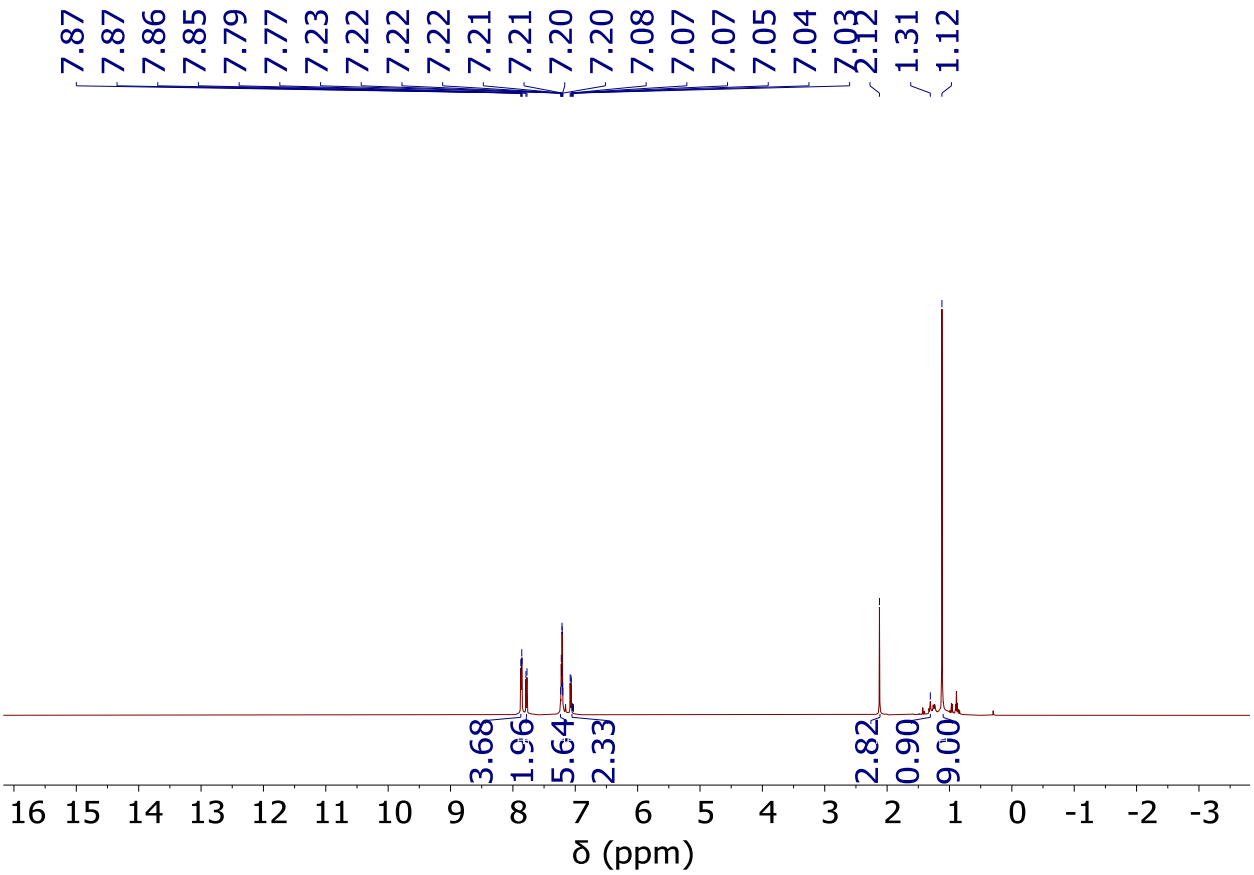

Figure S5.15. ^{1}H NMR spectrum for (p-Me-C_6H_4)$Ph_2Si(NH^tBu)$.

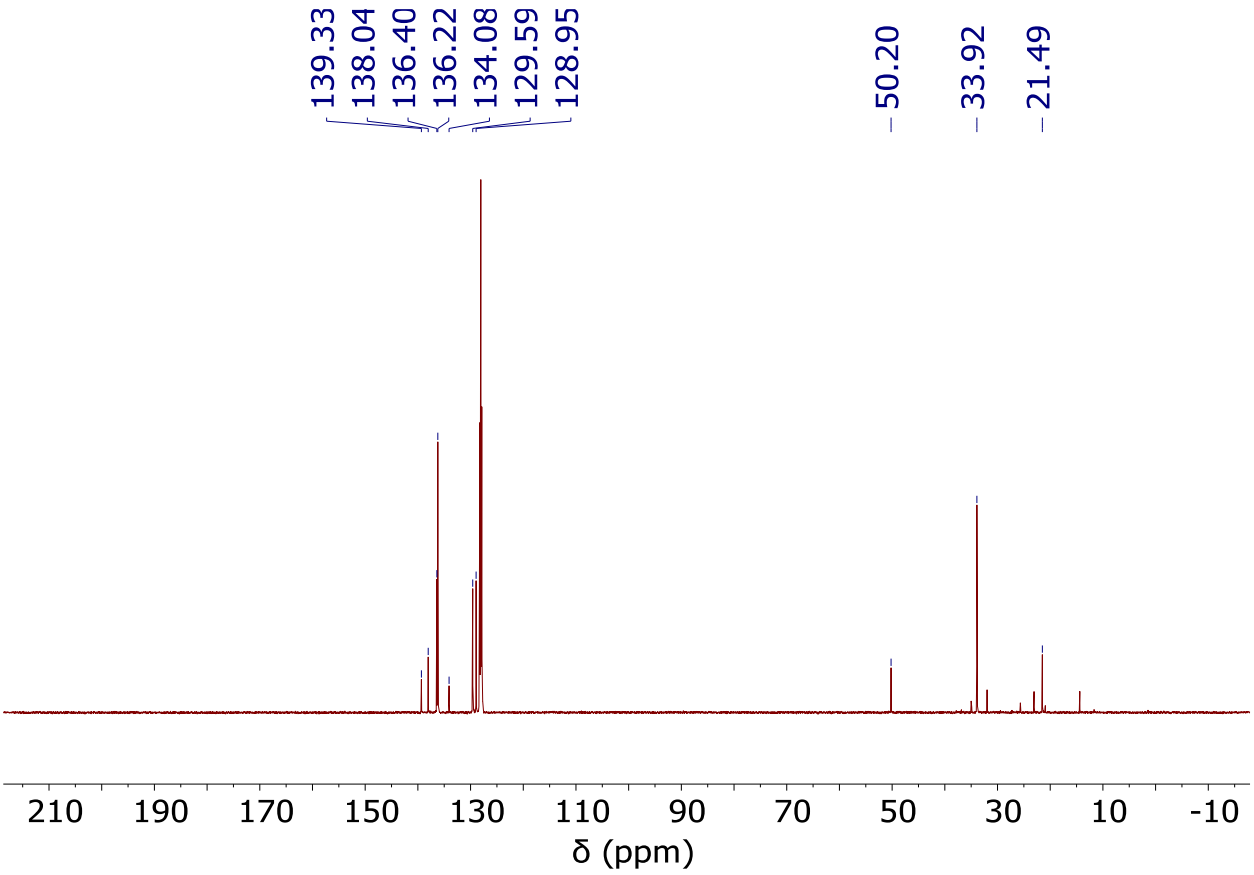

Figure S5.16. $^{13}C\{^{1}H\}$ NMR spectrum for (*p*-Me-C_6H_4)$Ph_2Si(NH^tBu)$.

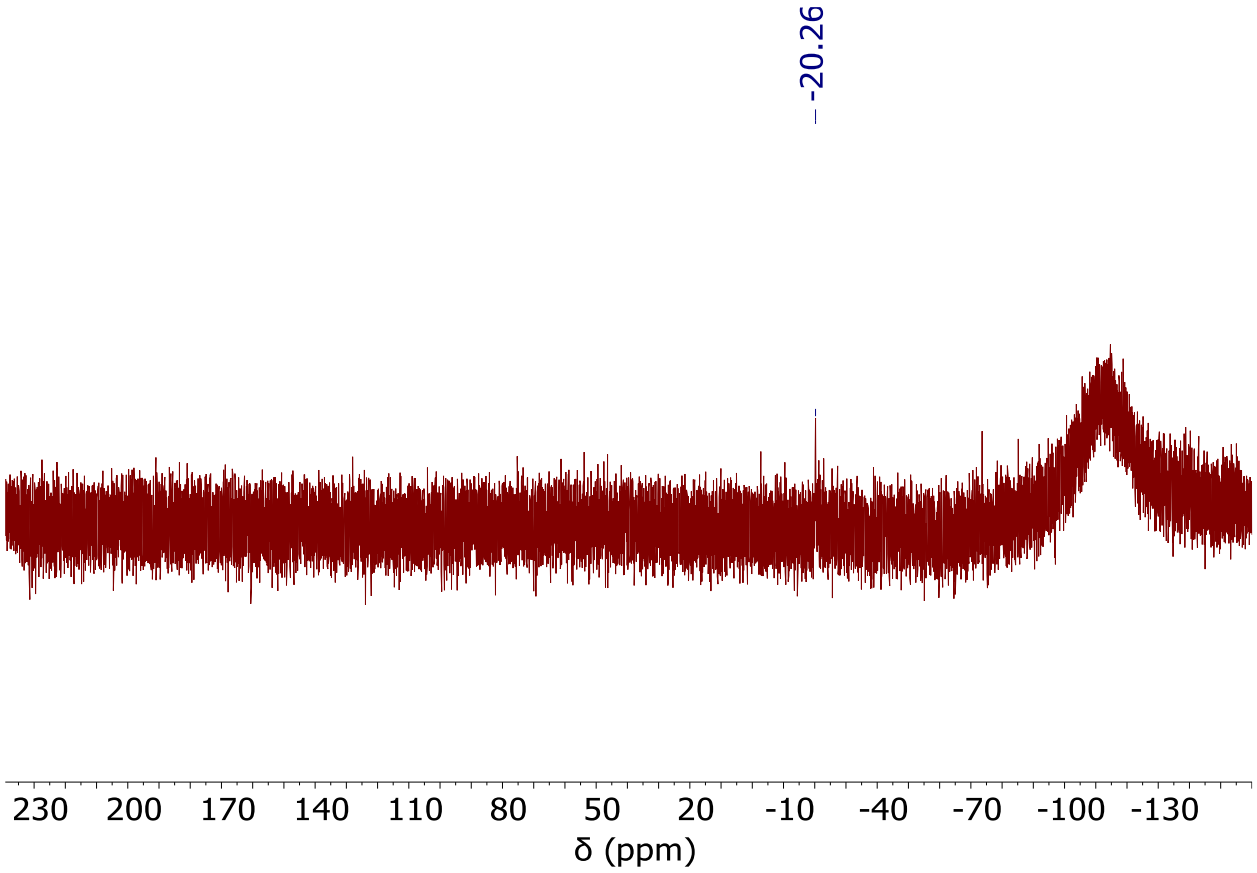

Figure S5.17. $^{29}Si\{^{1}H\}$ NMR spectrum for (*p*-Me-C_6H_4)$Ph_2Si(NH^tBu)$.

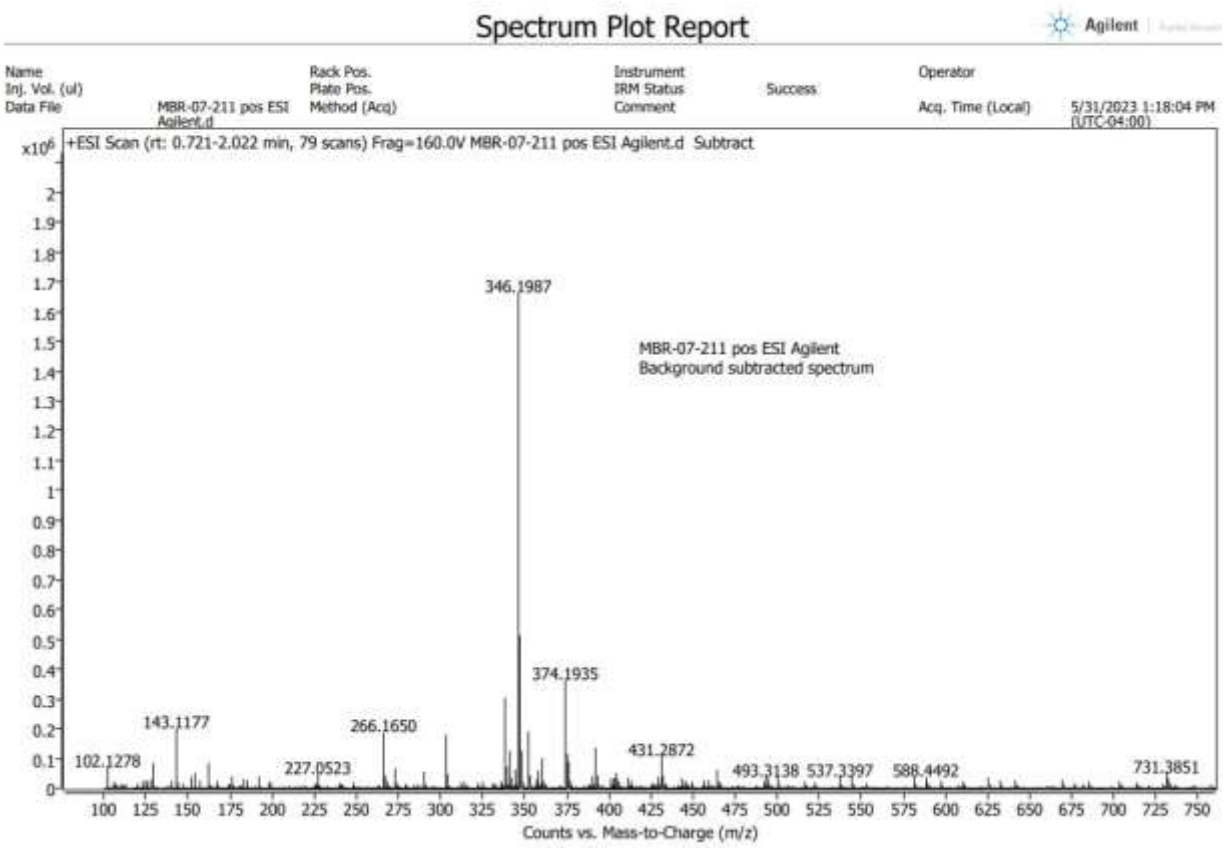

Figure S5.18. Full HRMS fragmentation spectrum for [(*p*-Me-C_6H_4)$Ph_2Si(NH^tBu)$+H]$^+$.

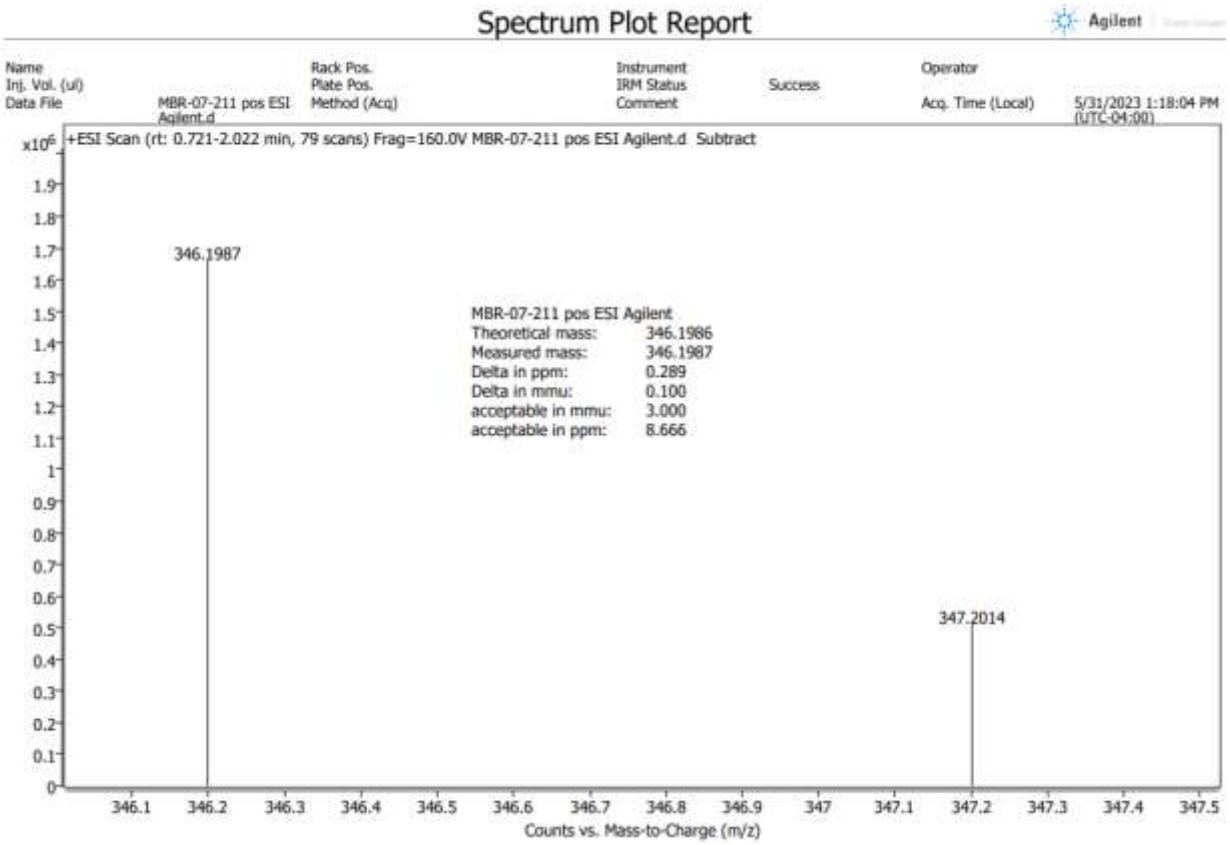

Figure S5.19. Background-subtracted HRMS fragmentation spectrum for [(*p*-Me-C_6H_4)$Ph_2Si(NH^tBu)+H]^+$.

S5.5. (p-F_3C-C_6H_4)$Ph_2Si(NH^tBu)$

Opaque oil (92.9 mg, 82% Yield). ^1H NMR (benzene-d_6, 500 MHz): 7.75-7.67 (m, 6H), 7.38 (d, J = 8.2 Hz, 2H), 7.24-7.17 (m, 6H), 1.36 (s, 1H), 1.05 (s, 9H). $^{13}C\{^1H\}$ NMR (benzene-d_6, 126 MHz): 142.46, 136.29, 136.03, 135.68, 129.60, 124.12, 49.87, 33.41. $^{19}F\{^1H\}$ NMR (benzene-d_6, 471 MHz): -61.34. $^{29}Si\{^1H\}$ NMR (benzene-d_6, 99 MHz): -21.42. HRMS (ESI) $[M+H]^+$ for $C_{23}H_{25}F_3NSi^+$; calc'd: 500.1703, found: 400.1706.

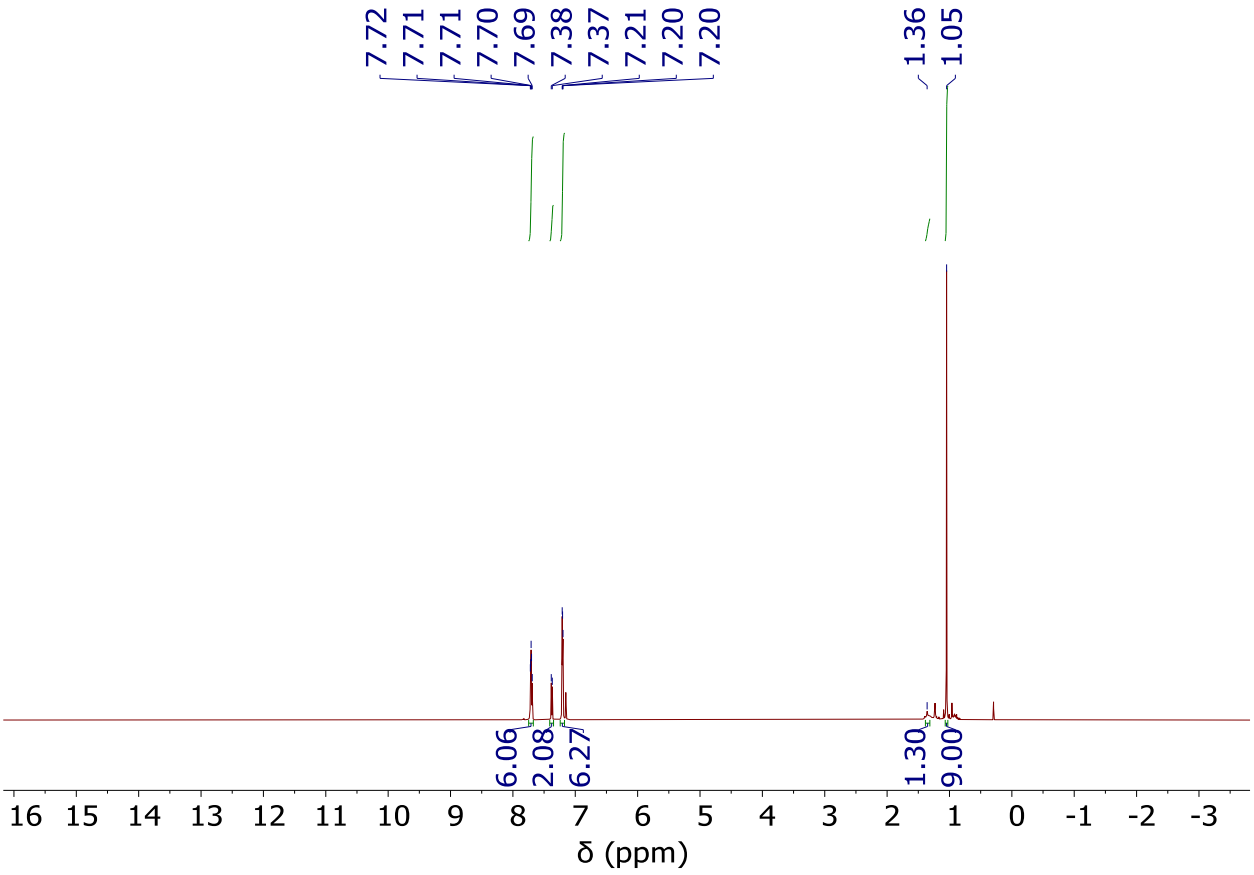

Figure S5.20. ^1H NMR spectrum for (p-F_3C-C_6H_4)$Ph_2Si(NH^tBu)$.

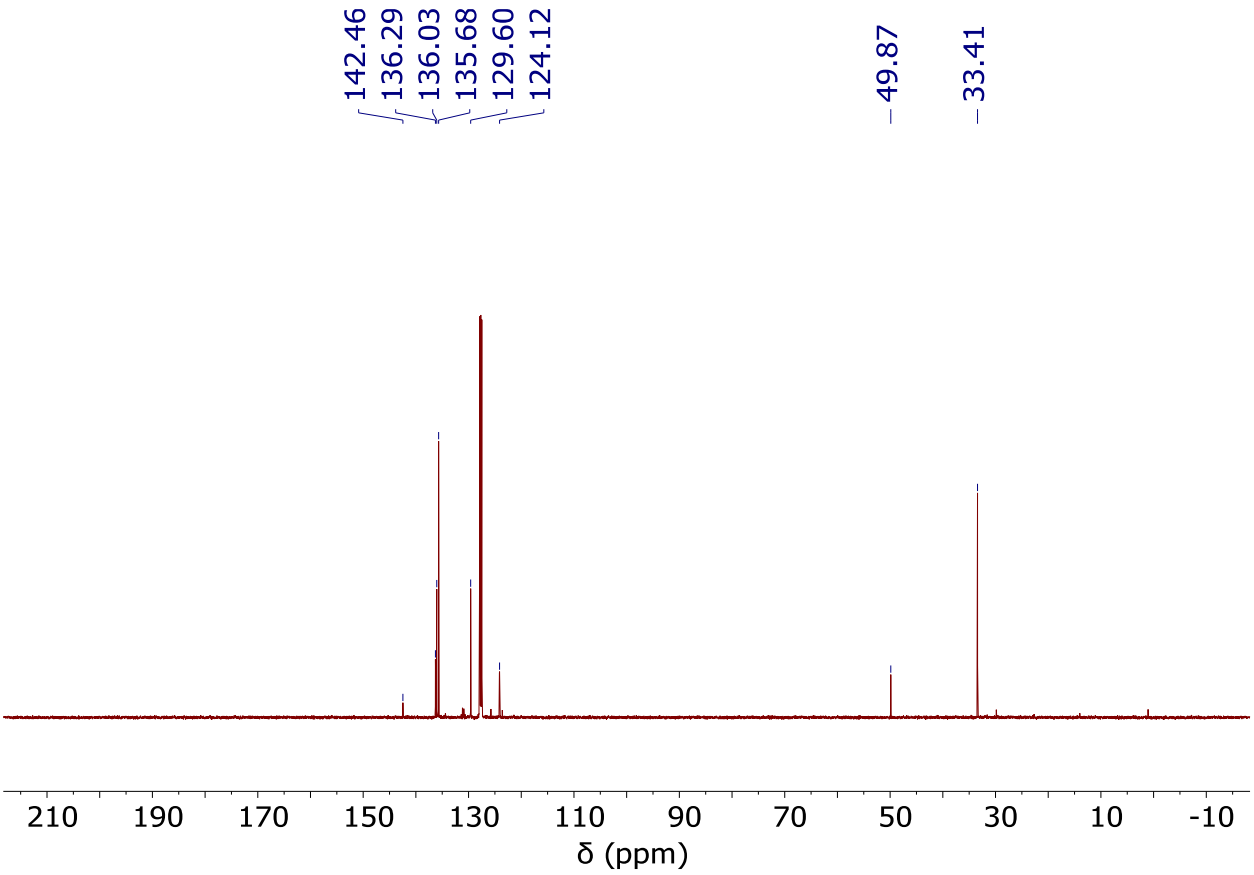

Figure S5.21. $^{13}C\{^{1}H\}$ NMR spectrum for (*p*-F_3C-C_6H_4)$Ph_2Si(NH^tBu)$.

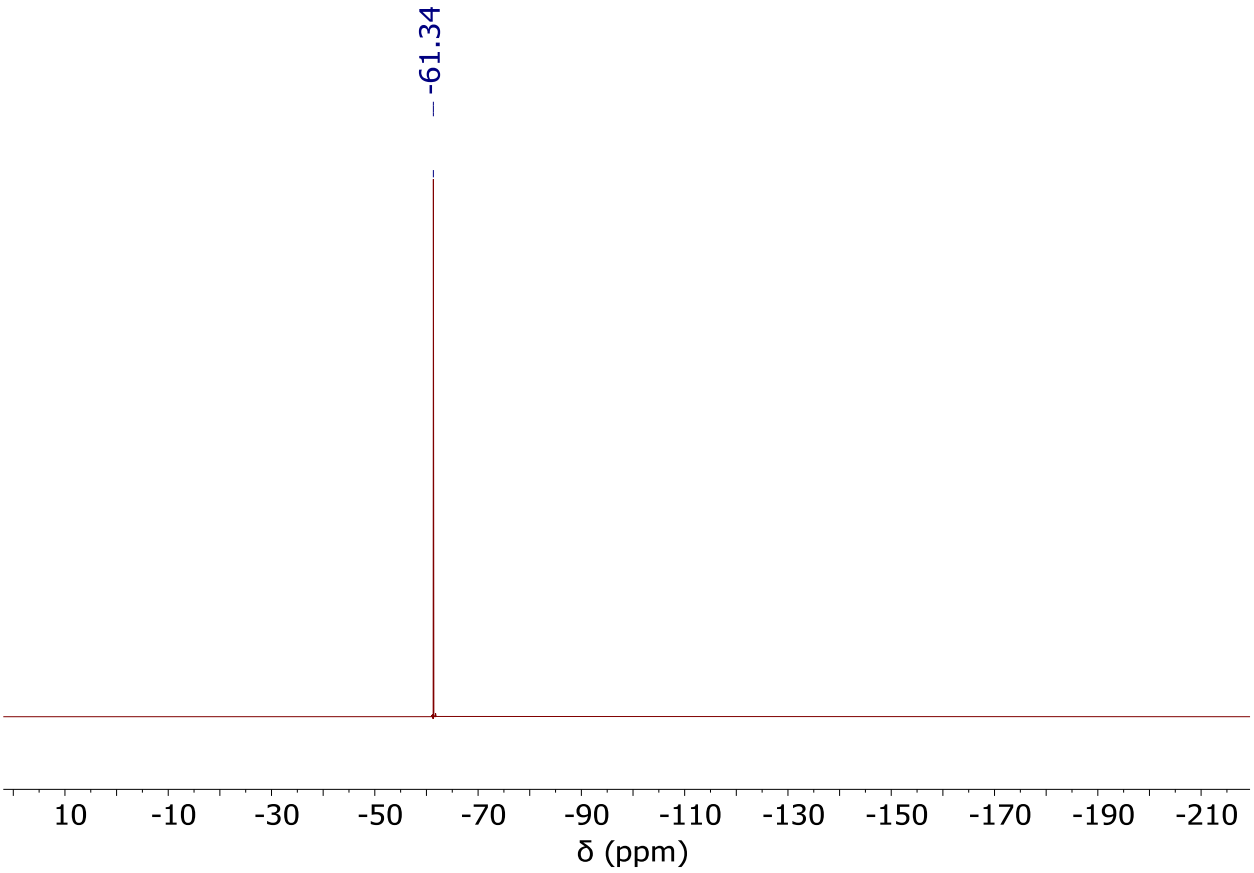

Figure S5.22. $^{19}F\{^{1}H\}$ NMR spectrum for (*p*-F_3C-C_6H_4)$Ph_2Si(NH^tBu)$.

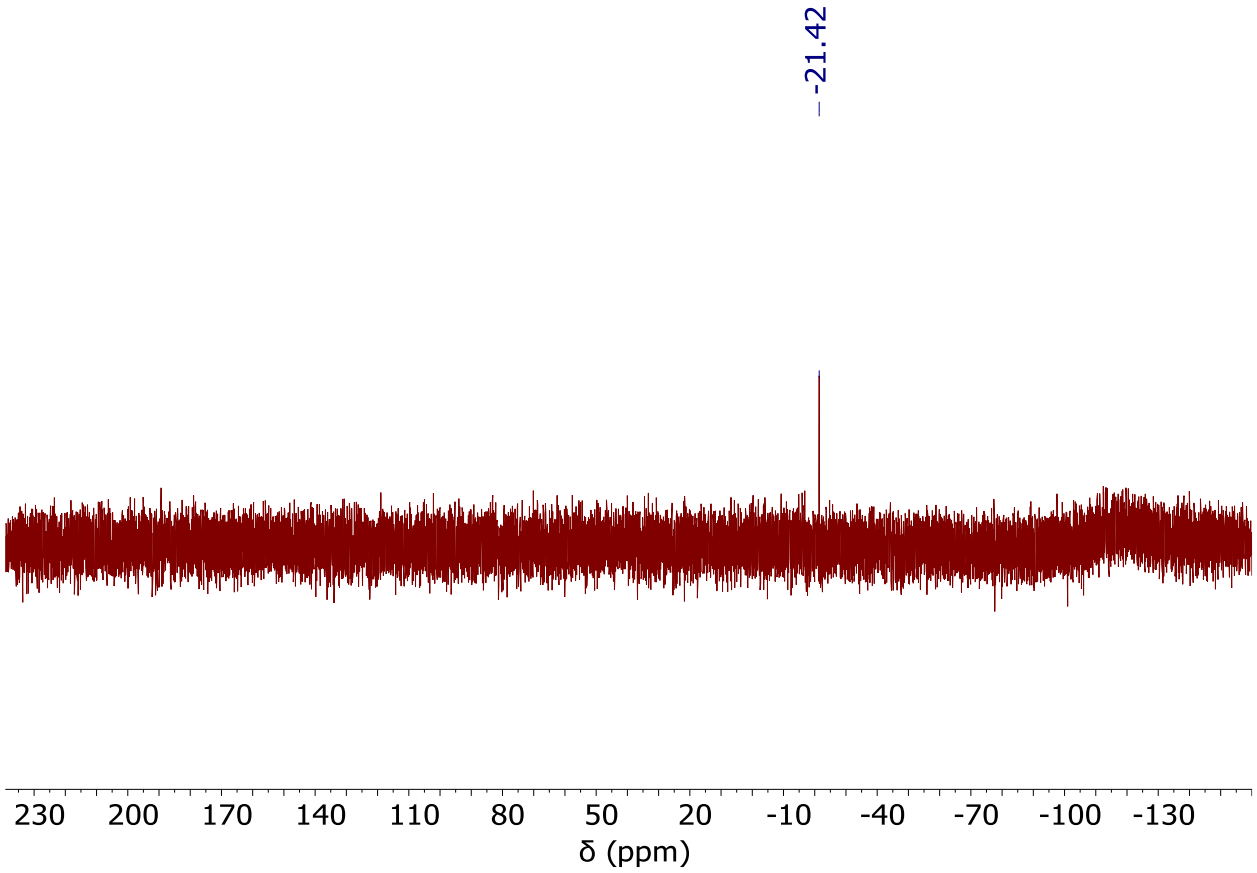

Figure S5.23. $^{29}Si\{^{1}H\}$ NMR spectrum for (*p*-F_3C-C_6H_4)$Ph_2Si(NH^tBu)$.

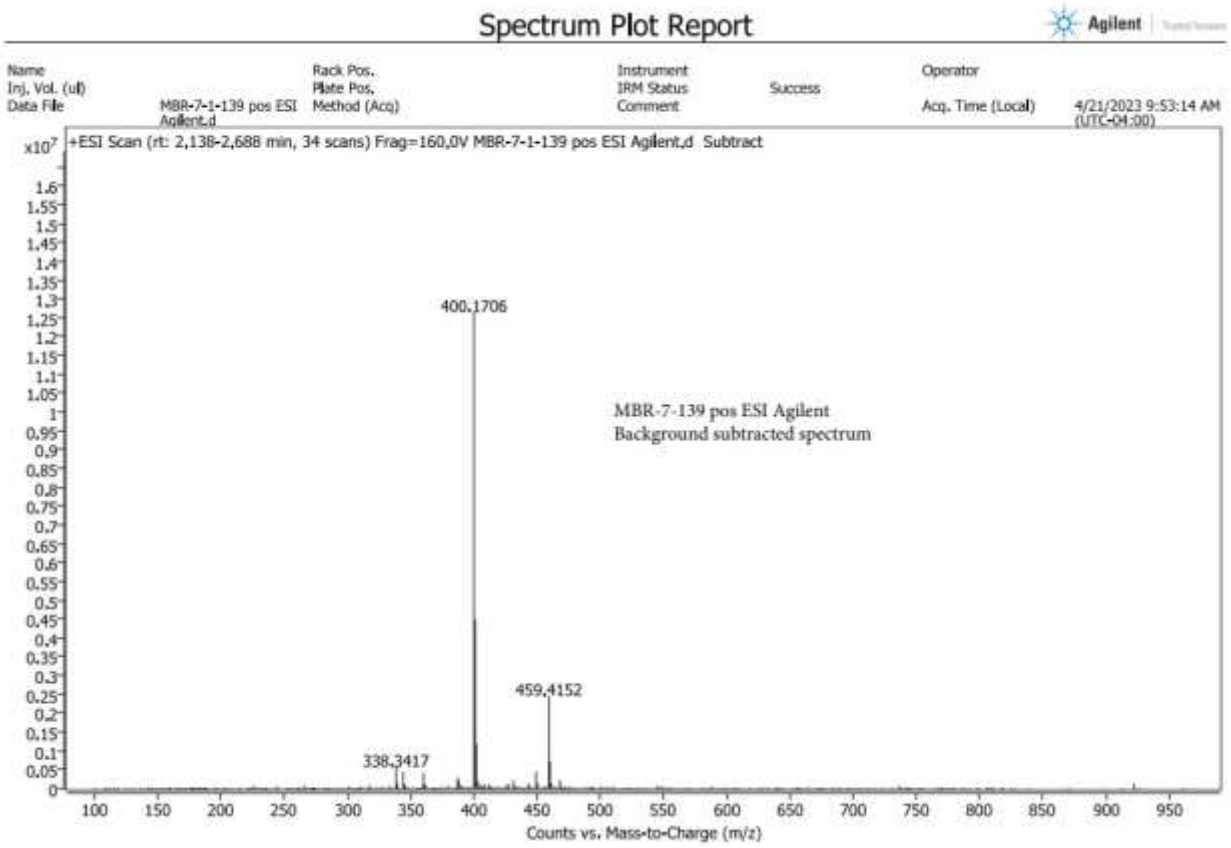

Figure S5.24. Full HRMS fragmentation spectrum for $[(p\text{-}F_3C\text{-}C_6H_4)Ph_2Si(NH^tBu)+H]^+$.

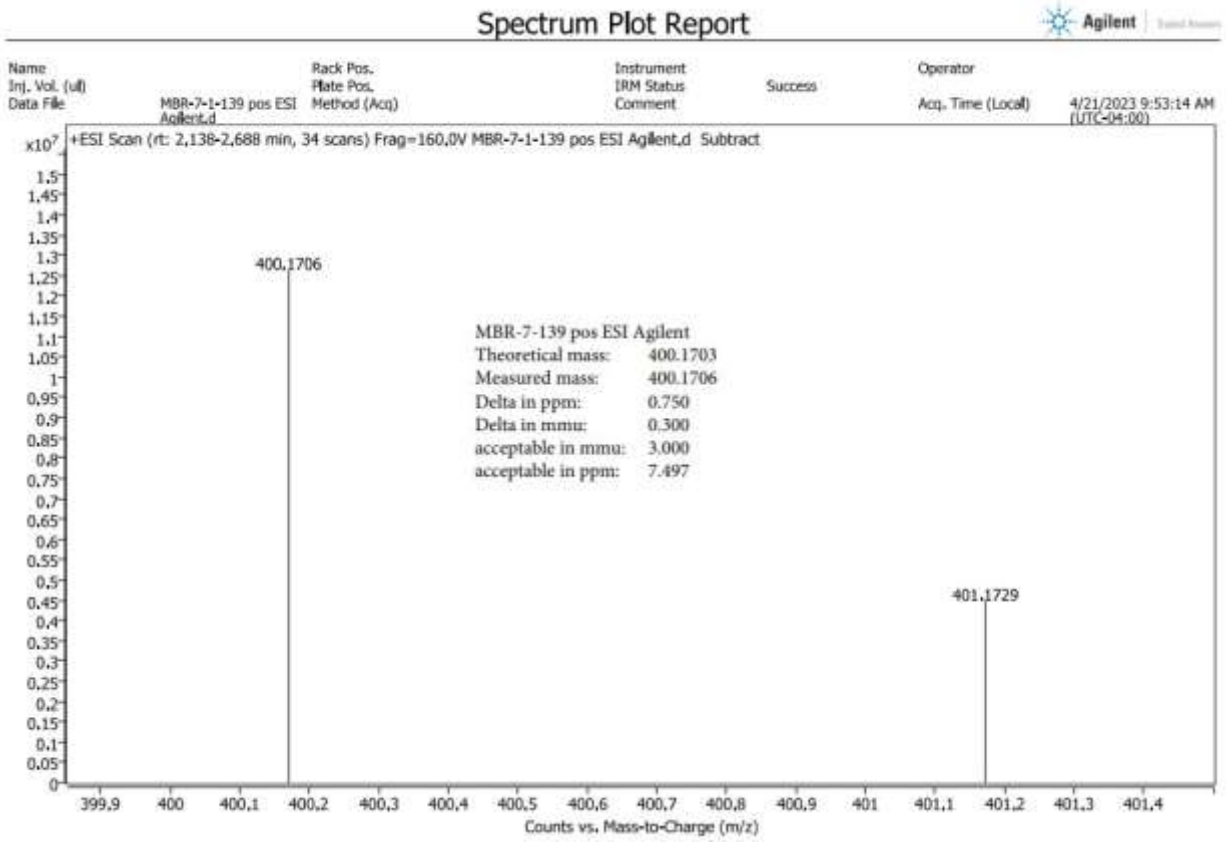

Figure S5.25. Background-subtracted HRMS fragmentation spectrum for [(*p*-F_3C-C_6H_4)Ph_2Si(NH^{t}Bu)+H]$^+$.

S5.6. $Ph_3Si(NEt_2)$

White solid (84.4 mg, 68% yield). ^{1}H NMR (benzene-d_6, 500 MHz): 7.78-7.76 (m, 6H), 7.22-7.21 (m, 9H), 3.03-2.98 (q, J = 7.1 Hz, 4H), 0.96 (t, J = 7.0 Hz, 6H). ^{13}C{^{1}H} NMR (benzene-d_6, 126 MHz): 136.18, 129.45, 127.80, 40.50, 15.06. ^{29}Si{^{1}H} NMR (benzene-d_6, 99 MHz): -12.45. HRMS (ESI) $[M+H]^+$ for $C_{22}H_{26}NSi^+$; calc'd: 332.1829, found: 332.1831.

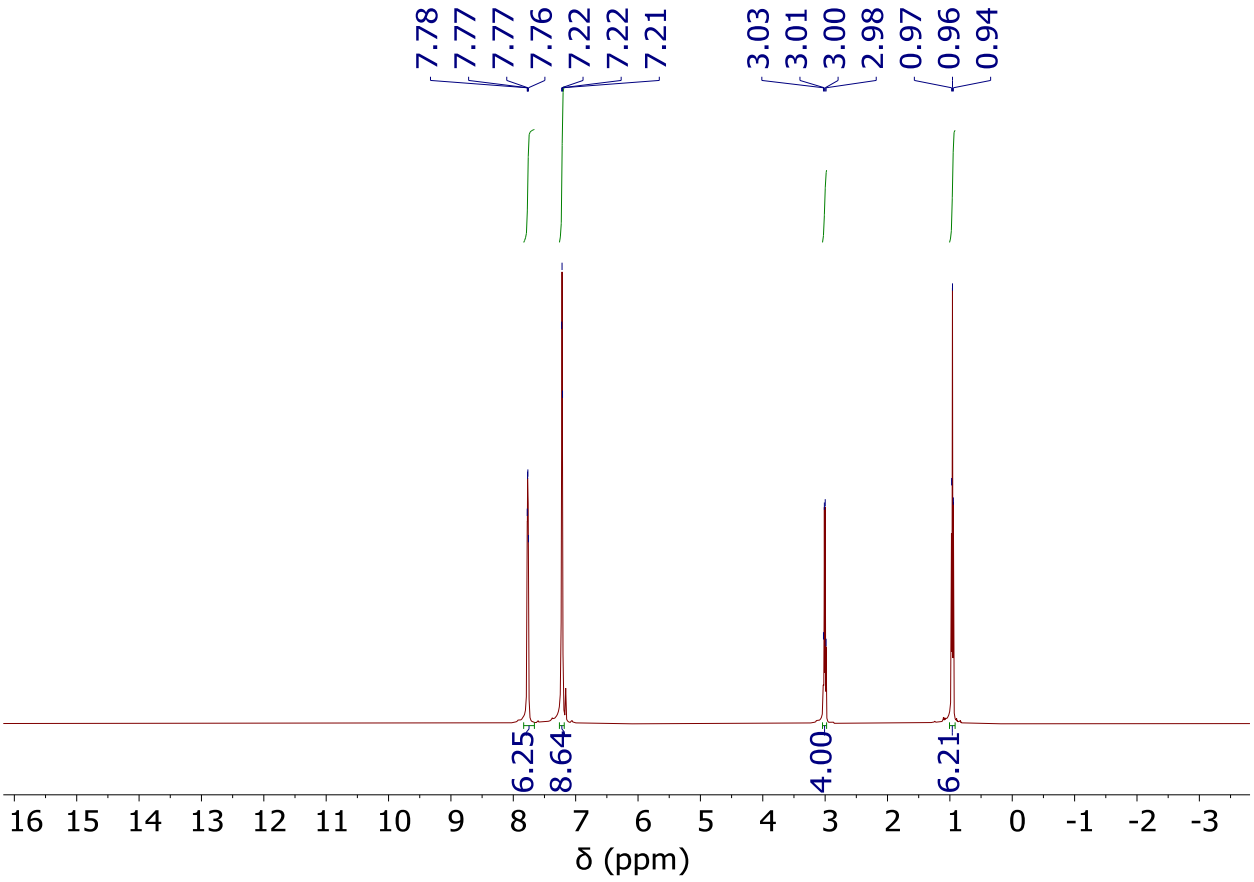

Figure S5.26. ^{1}H NMR spectrum for $Ph_3Si(NEt_2)$.

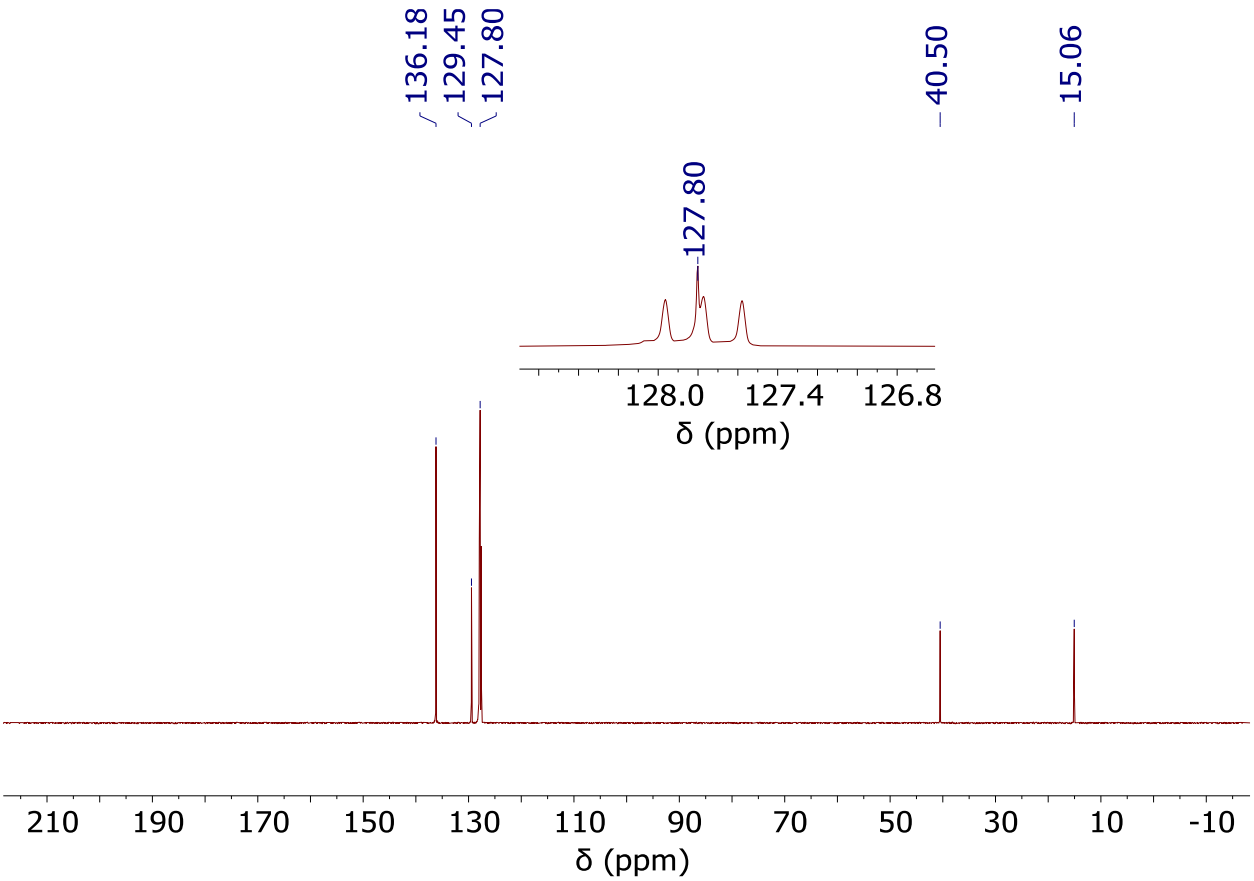

Figure S5.27. $^{13}C\{^{1}H\}$ NMR spectrum for $Ph_3Si(NEt_2)$.

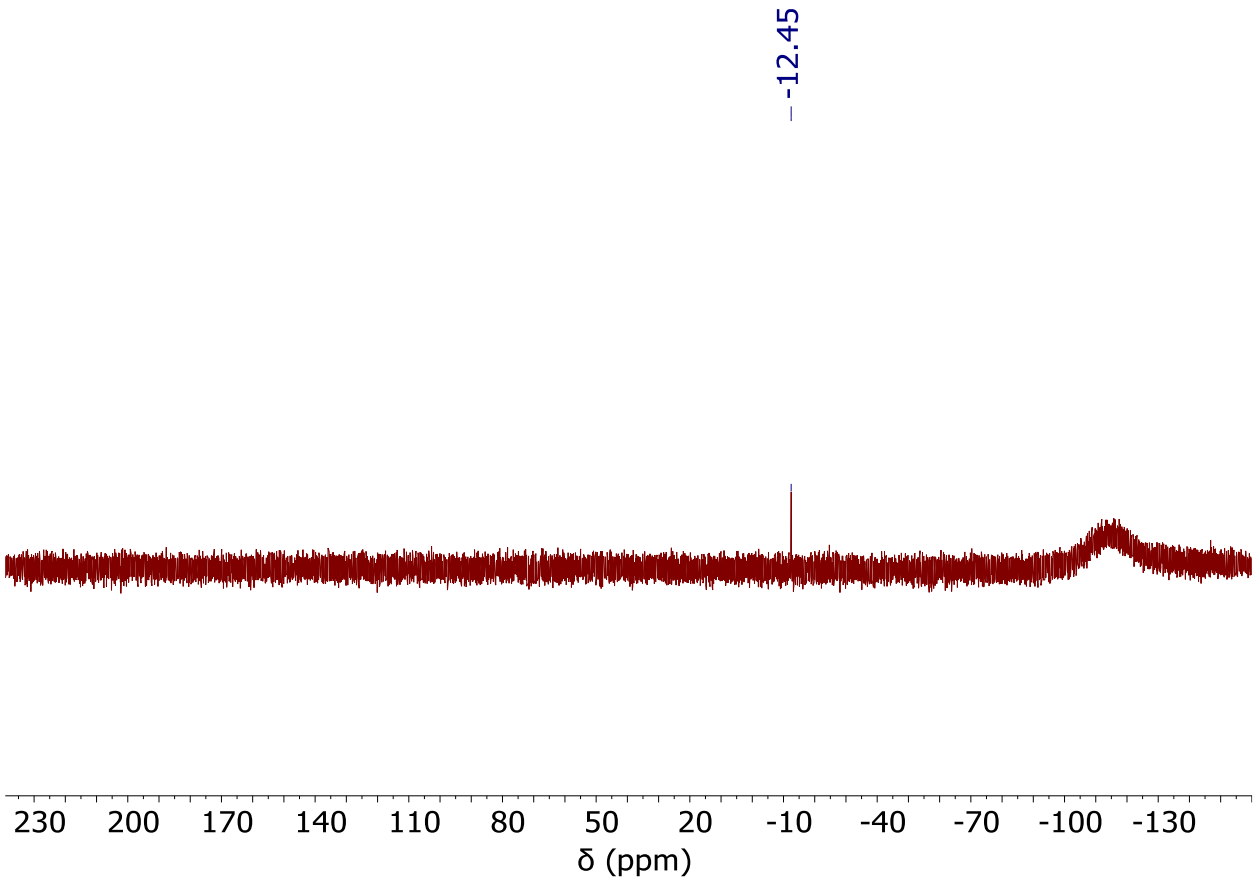

Figure S5.28. $^{29}Si\{^{1}H\}$ NMR spectrum for $Ph_3Si(NEt_2)$.

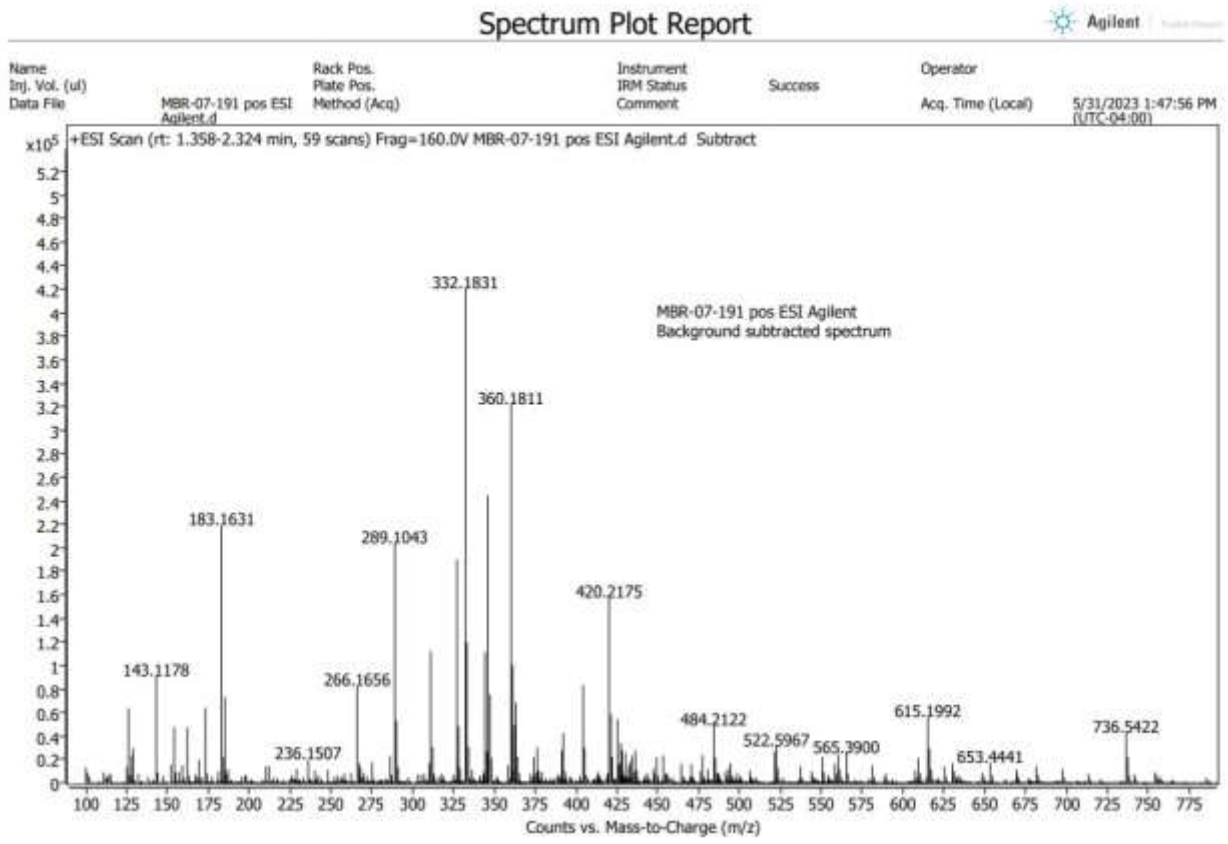

Figure S5.29. Full HRMS fragmentation spectrum for $[Ph_3Si(NEt_2)+H]^+$.

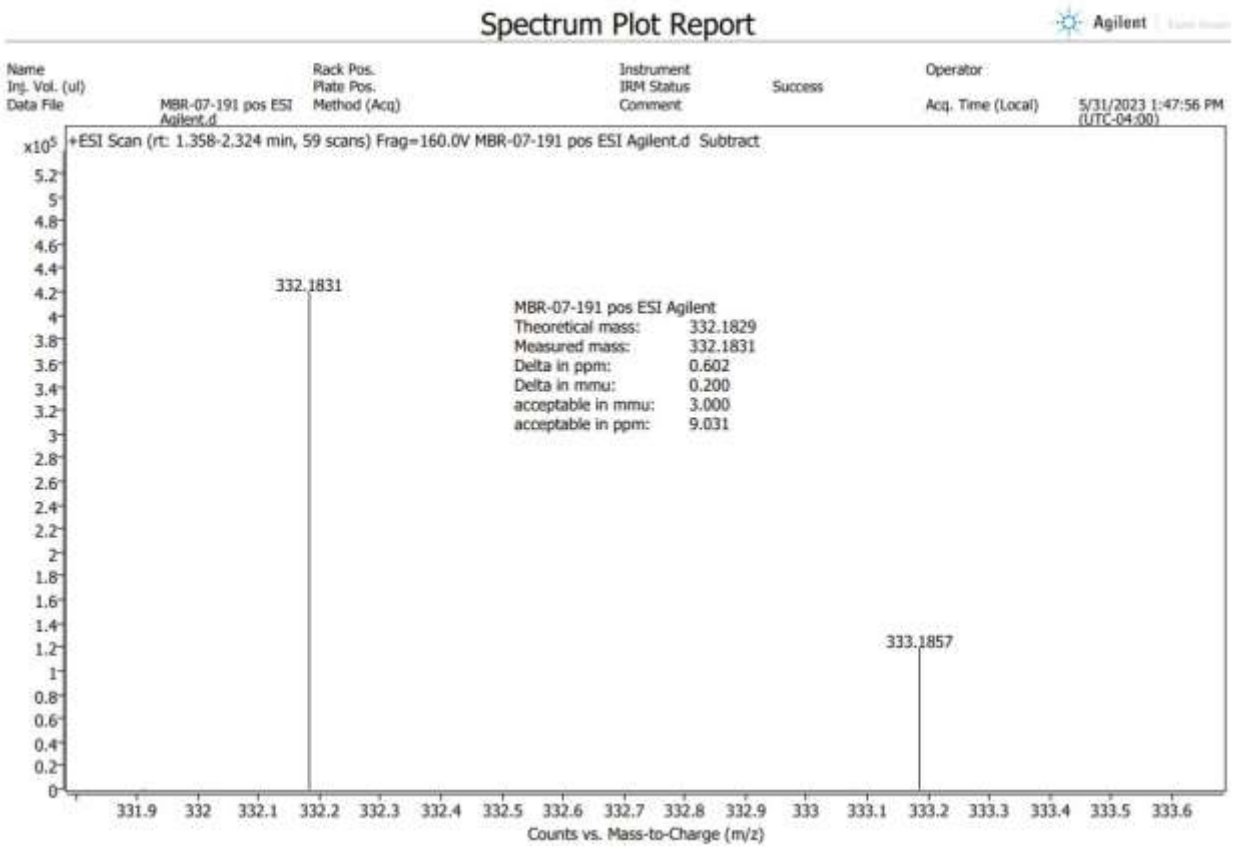

Figure S5.30. Background-subtracted HRMS fragmentation spectrum for $[Ph_3Si(NEt_2)+H]^+$.

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