Supporting Information for

Photoactivated Silicon-Oxygen and Silicon-Nitrogen Heterodehydrocoupling with a Commercially Available Iron Compound

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General Information

All reactions were prepared under purified a N_2 atmosphere in an M. Braun glovebox. Cyclopentadienyl dicarbonyl iron (II) dimer **1** was purified by sublimation. Alcohols and amines were distilled from CaH_2. Silanes were used without further purification. Benzene-d_6 was vacuum transferred from NaK alloy. NMR spectra were acquired on either a Varian 500 MHz spectrometer or a Bruker AXR 500 MHz spectrometer. Spectra recorded on both instruments were reported to TMS (δ 0.00) for ^{1}H and ^{29}Si NMR.

Catalytic Experiment Conditions

An oven-dried scintillation vial containing **1** (3.5 mg, 2.0 mol %) was charged with silane, followed by excess alcohol, 0.5 mL benzene-d_6, and TMS. A similar method was performed with amine coupling, however, loading of **1** was determined by substrates. Mixtures were transferred to a J-Young type polytetrafluoroethylene-valved NMR tube and subsequently placed under visible-light irradiation. Reactions were subjected to a cycle of freeze-pump-thaw after 1 and 2 h of irradiation. All reactions were performed at ambient temperature under irradiation in the visible spectrum using a 40 W LED bulb.

Figure S.1 LED Reactor for Photocatalysis

Table S1. Experimental and Literature NMR Characterization Data for Silyl Ethers.

Entry	**Compound**	**^{1}H NMR (*Lit*)**	**^{29}Si NMR (*Lit*)**	**References**
1	$PhSi(O^{n}Pr)_3$	3.79[a] (*3.84*)[b]	-57.99[a]	1
2	$PhSi(OBn)_3$	4.84[a] (*4.855*)[a]	-56.24[a] (*-56.4*)[a]	2, 3
3	$PhSiH(O^{i}Pr)_2$	5.28[a] (*5.19*)[a]	-34.52[a] (*-34.8*)[a]	4
4	$PhSi(O^{i}Pr)_3$	4.32[a] (*4.30-4.22*)[b]	-61.79[a] (*-61.8*)[a]	5, 3
5	$PhMeSi(O^{n}Pr)_2$	3.67[a]	-18.11[a]	
6	$PhMeSi(OBn)_2$	4.71[a] (*4.91-4.82*)[b]	-15.48[a]	6
7	$PhMeSiH(O^{i}Pr)$	5.21[a]	-6.65[a]	
8	$PhMeSi(O^{i}Pr)_2$	4.02[a]	-21.83[a]	
9	$Ph_2SiH(O^{n}Pr)$	5.63[a]	N/A	
10	$Ph_2Si(O^{n}Pr)_2$	3.72[a]	-32.20[a]	
11	$Ph_2Si(OBn)_2$	4.79[a] (*4.75*)[a]	-29.89[a] (*-30.82*)[a]	7, 3
12	$Ph_2SiH(O^{i}Pr)$	5.64[a] (*5.70*)[a]	-14.74[a] (*-14.81*[a])	3
13	$PhMe_2Si(O^{n}Pr)$	3.47[a]	6.66[a]	
14	$PhMe_2Si(OBn)$	4.56[a] (*4.77*)[b]	9.03[a] (*8.9*)[b]	6, 8
15	$PhMe_2Si(O^{i}Pr)$	4.01[a] (*4.111-4.030*)[b]	4.21[a]	9

[a] in C_6D_6. [b] in $CDCl_3$. N.R. = Not Reported.

Table S2. Experimental and Literature NMR Characterization Data for Silamines.

Entry	**Compound**	**^{1}H NMR (*Lit*)**	**^{29}Si NMR (*Lit*)**	**Reference**
16	$PhSiH_2(HN^{n}Pr)$	5.08[a]	-29.83[a]	
17	$PhSiH(HN^{n}Pr)_2$	5.17[a] (*4.87*)[a]	-26.57[a] (-*24.13*)	[10]
18	$PhSiH_2(HN^{t}Bu)$	5.09[a] (*5.12*)[a]	-37.95[a] (-*37.36*)[a]	[11]
19	$PhSiH(HN^{t}Bu)_2$	5.45a (*5.23*-*5.22*)[a]	N/A (-*30.61*)[a]	[12]
20	$PhSiH_2(HNPh)$	4.99[a]	-36.77[a]	
21	$PhSiH_2(HN^{i}Pr)$	5.20[a] (*5.19*)[a]	-30.8[a] (-*38.22*)[a]	[13]
22	$PhSiH_2(NEt_2)$	5.13[a] (*5.10*)[a]	-25.20[a] (-*25.44*)[a]	[14]
23	$PhSiH(NEt_2)_2$	5.11[a] (*5.13*)[a]	-18.95[a] (-*19.18*)[a]	[14]
24	$PhMeSiH(HN^{n}Pr)$	5.12[a] (*5.15*)[a]	-14.61[a] (-*14.23*)[a]	[13]
25	$PhMeSiH(HN^{t}Bu)$	5.20[a] (*5.23*)[a]	-21.35[a] (-*21.33*)[a]	[13]
26	$PhMeSiH(HN^{i}Pr)$	5.14[a] (*5.16*)[a]	-16.95[a] (-*16.82*)[a]	[13]
27	$PhMeSiH(NEt_2)$	5.09[a] (*5.08*)[a]	-11.07[a] (-*10.98*)[a]	[14]
28	$Ph_2SiH(HN^{n}Pr)$	5.57[a] (*5.61*)[a]	-17.78[a] (-*17.29*)[a]	[13]
29	$Ph_2SiH(HN^{t}Bu)$	5.68[a] (*5.70*)[a]	-25.06[a] (-*24.86*)[a]	[14]
30	$Ph_2SiH(HN^{i}Pr)$	5.60[a] (*5.63*)[a]	-20.14[a] (-*20.26*)[a]	[12]
31	$Ph_2SiH(NEt_2)$	5.55[a] (*5.55*)[a]	-14.35[a] (-*14.27*)[a]	[14]

[a] in C_6D_6. N.R. = Not Reported.

Spectroscopic Intermediates

$PhSiH_3$ and 1. An oven-dried scintillation vial containing 1 (35.3 mg, 0.1 mmol) was charged with an equivalent of $PhSiH_3$ (12.5 µL, 11.0 mg, 0.1 mmol), followed by 1.0 mL benzene-*d*$_6$. The mixture was transferred to a J-Young type polytetrafluoroethylene-valved NMR tube and subsequently placed under visible-light irradiation. After a ^1H NMR spectrum was taken after 24 h, an equimolar amount of ^nPrOH (7.5 µL, 6.0 mg, 0.1 mmol) was added, and the mixture was irradiated for an additional 24 h.

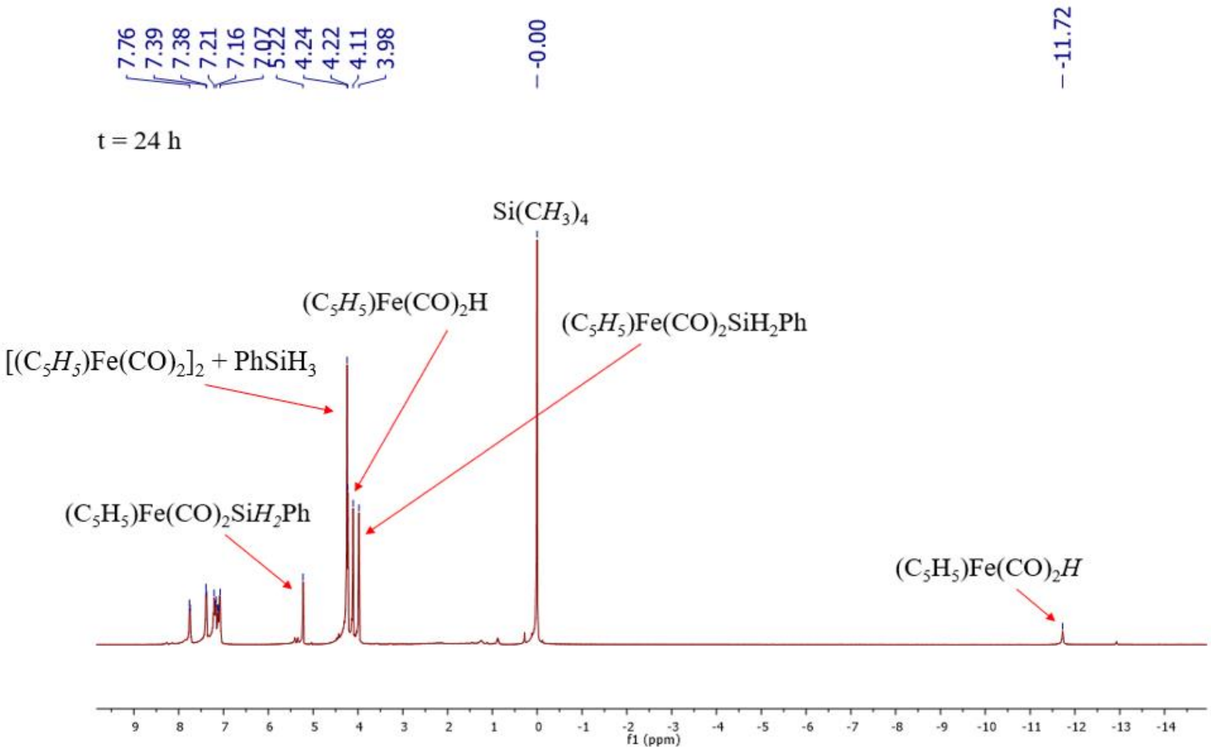

Figure S.2 ^1H NMR spectrum of the stoichiometric reaction between $PhSiH_3$ and **1** (benzene-*d*$_6$, 500 MHz)

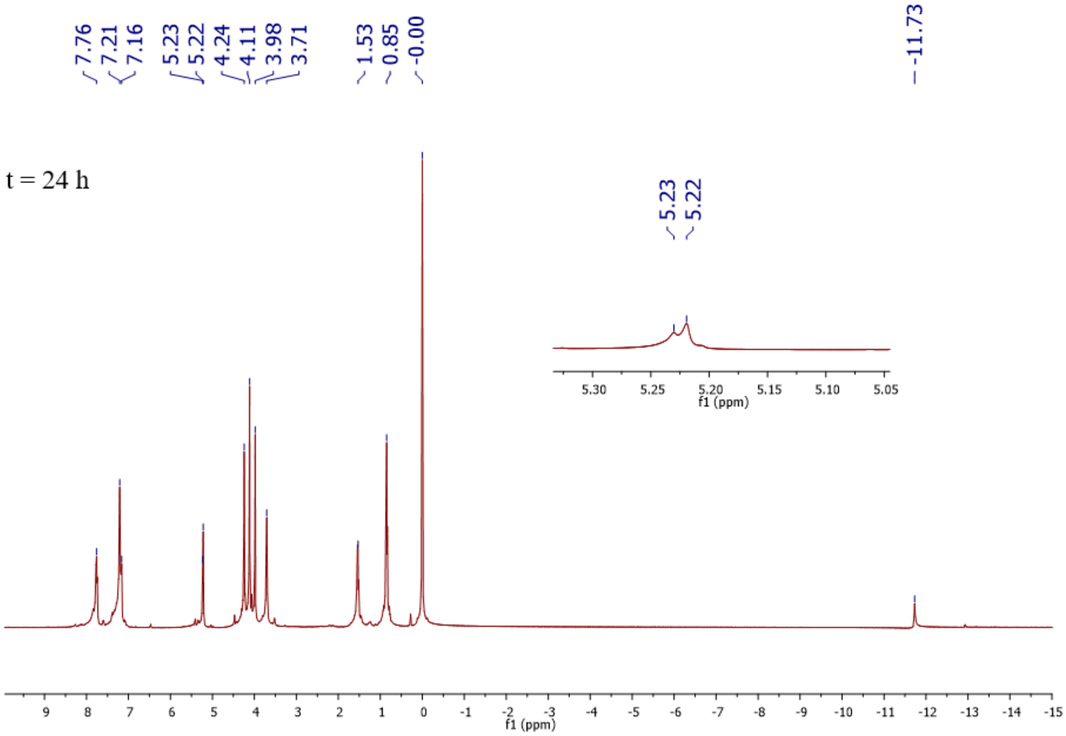

Figure S.3 ^{1}H NMR spectrum of the stoichiometric reaction between $PhSiH_3$ and **1** after added ^{n}PrOH (benzene-d_6, 500 MHz)

^{n}PrOH and 1 under H_2. An oven-dried scintillation vial containing 1 (35.3 mg, 0.1 mmol) was charged with an equivalent of ^{n}PrOH (7.5 µL, 6.0 mg, 0.1 mmol), followed by 0.5 mL benzene-d_6. The mixture was transferred to a J-Young type polytetrafluoroethylene-valved NMR tube and subsequently subjected to a cycle of freeze-pump-thaw. After an initial ^{1}H NMR spectrum was taken, the mixture was placed under hydrogen. After 1 h, an equimolar amount of $PhSiH_3$ (12.5 µL, 11.0 mg, 0.1 mmol) was added and the mixture was left to react for 15 h.

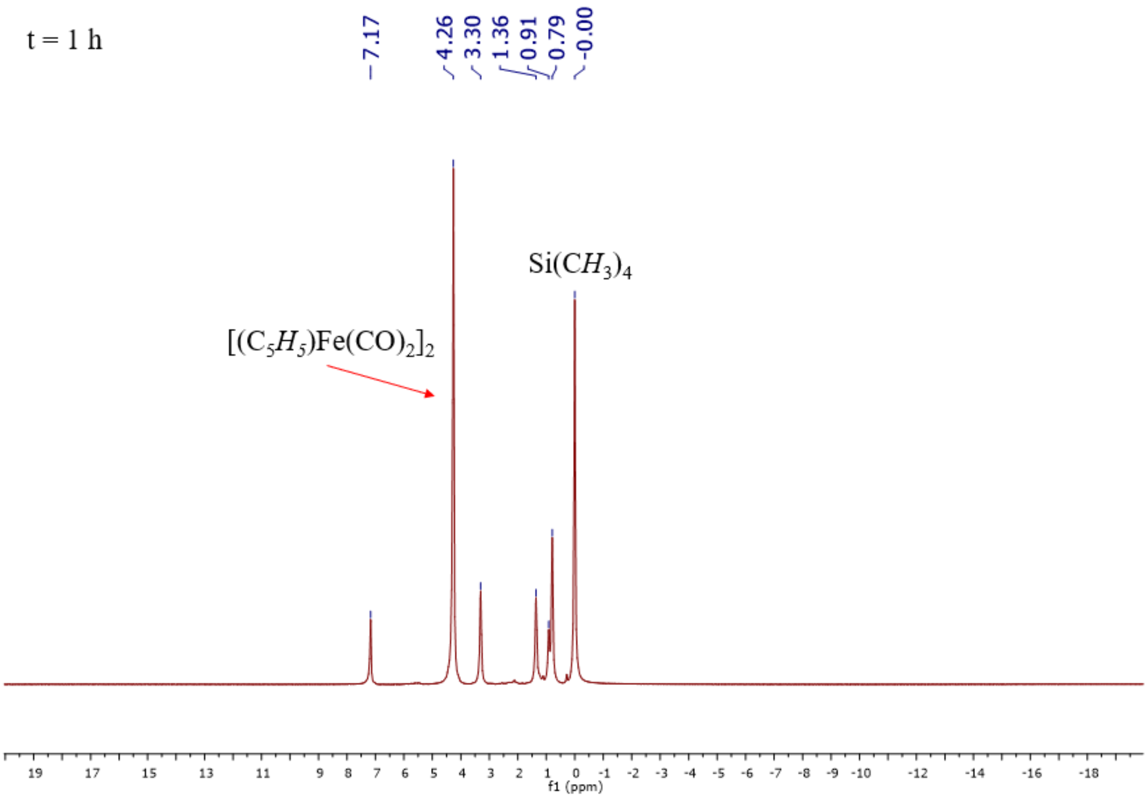

Figure S.4 ^{1}H NMR spectrum of the stoichiometric reaction between ^{n}PrOH and **1** under H_2 (benzene-d_6, 500 MHz)

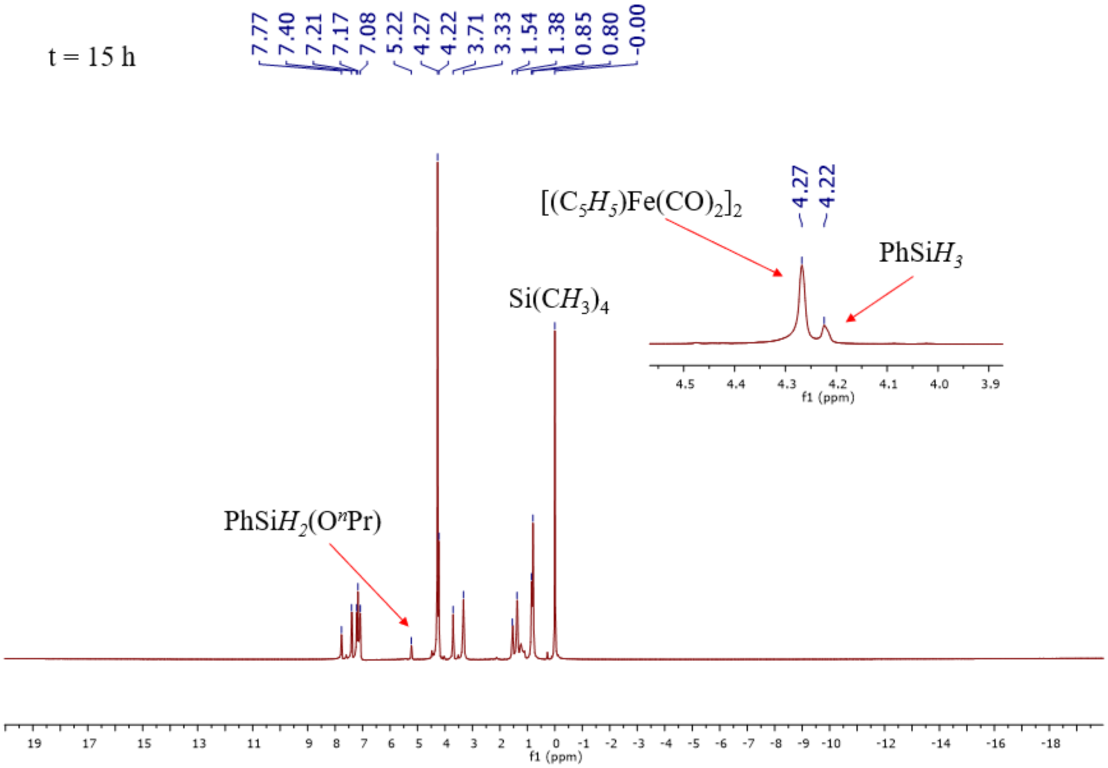

Figure S.5 ^{1}H NMR spectrum of the stoichiometric reaction between ^{n}PrOH and **1** under H_2 after added $PhSiH_3$ (benzene-d_6, 500 MHz)

***n*PrOH and 6.** An oven-dried scintillation vial containing **6** (64.1 mg, 2.3 mmol) was charged with an equivalent of ^{n}PrOH (17 µL, 13.6 mg, 2.3 mmol), followed by 0.5 mL benzene-*d*$_6$. The mixture was transferred to a J-Young type polytetrafluoroethylene-valved NMR tube.

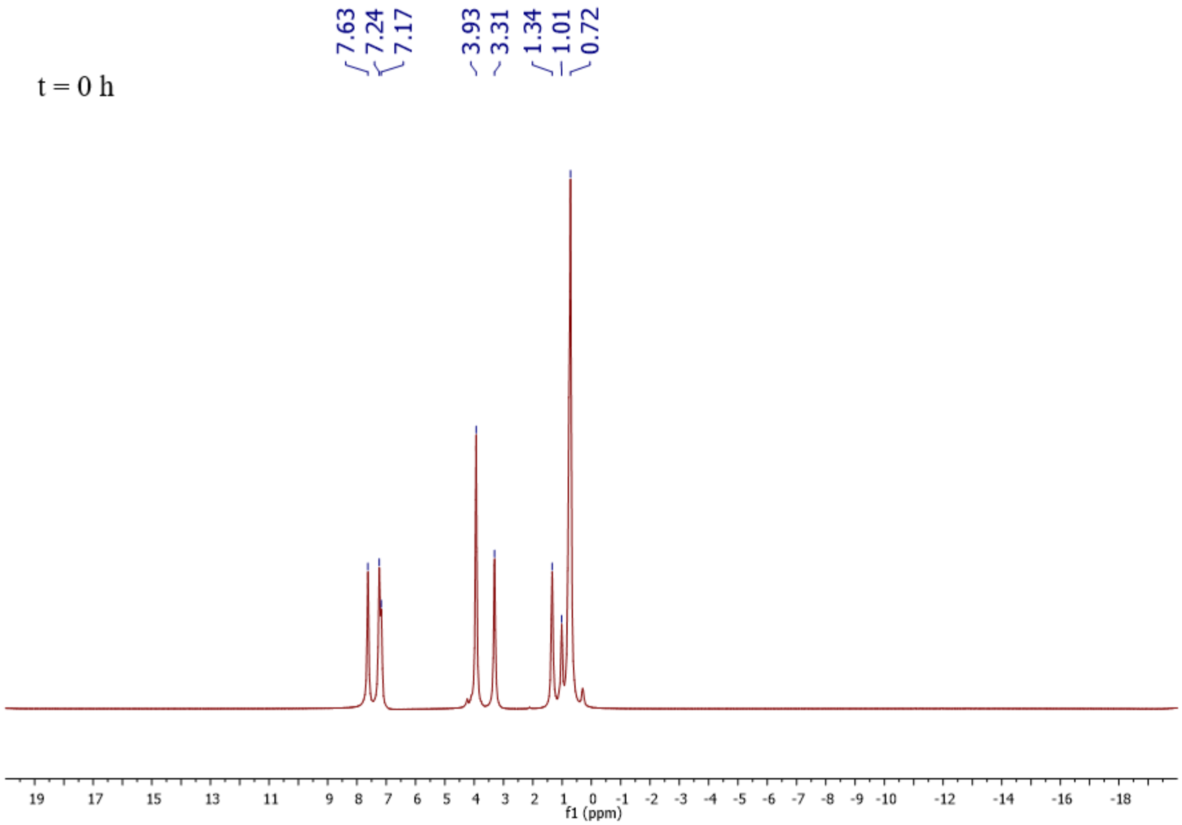

Figure S.6 ^{1}H NMR spectrum of the stoichiometric reaction between ^{n}PrOH and **6** (benzene-*d*$_6$, 99 MHz)

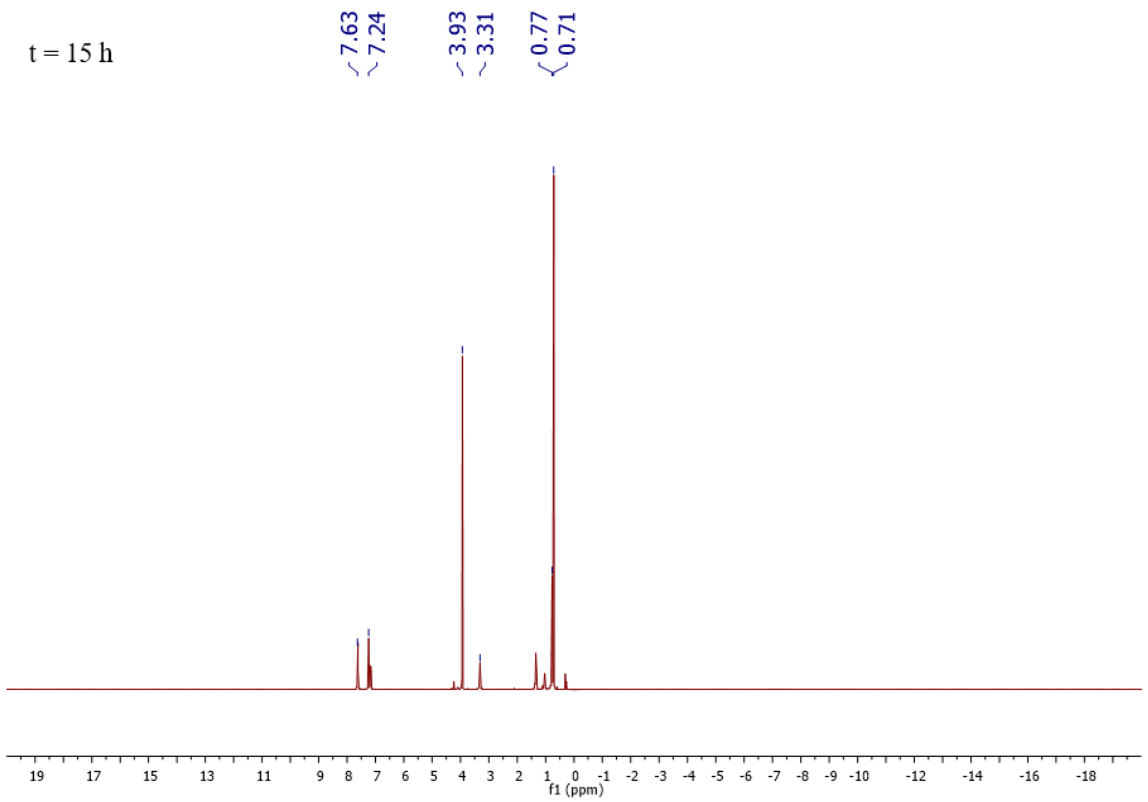

Figure S.7 ^{1}H NMR spectrum of the stoichiometric reaction between ^{n}PrOH and **6** (benzene-d_6, 99 MHz)

BnOH and $PhSiH_3$. An oven-dried scintillation vial containing **6** (3.1 mg, 2.0 mol %) was charged with $PhSiH_3$ (62.0 µL, 54.4 mg, 0.5 mmol), followed by 0.5 mL benzene-d_6, BnOH (208.0 µL, 216.3 mg, 2.0 mmol), and TMS (17.0 µL, 11.0 mg, 25.0 mol %).

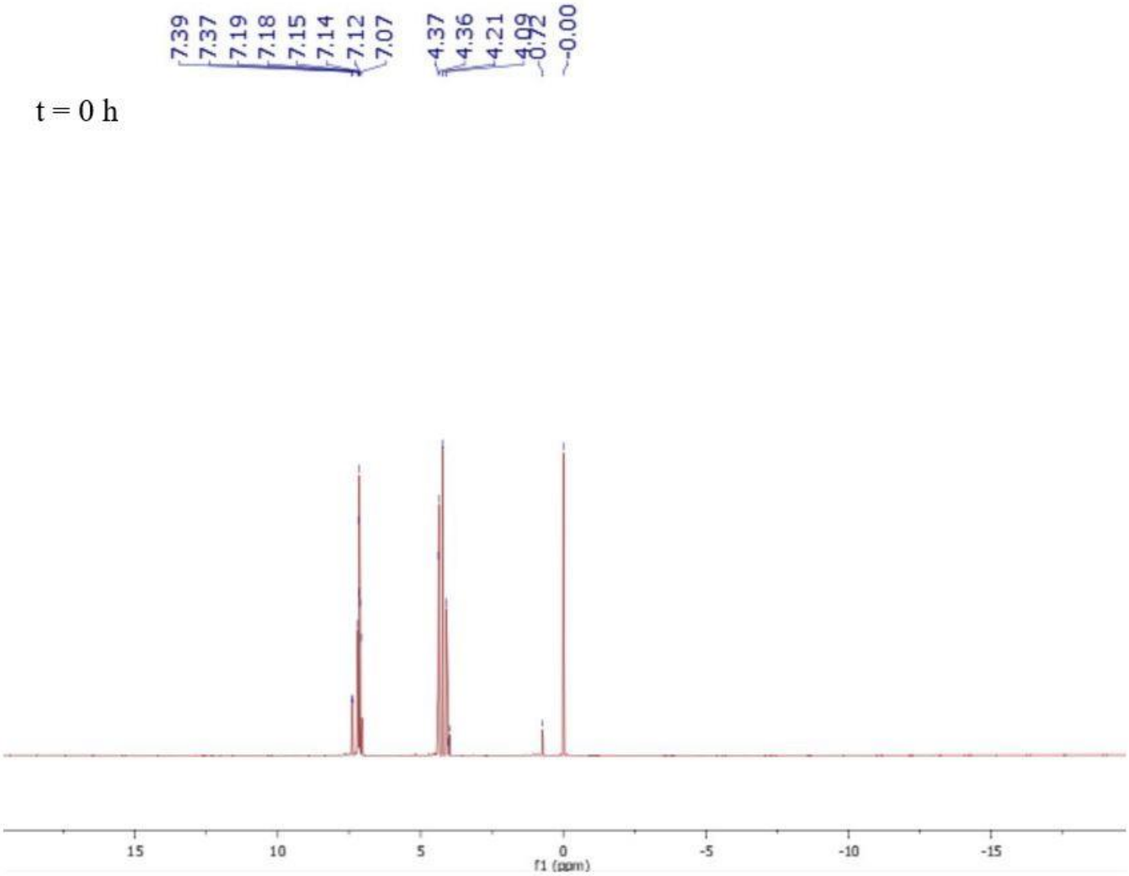

Figure S.8 ^{1}H NMR spectrum of the reaction between BnOH and $PhSiH_3$ catalyzed by **6** (benzene-d_6, 99 MHz)

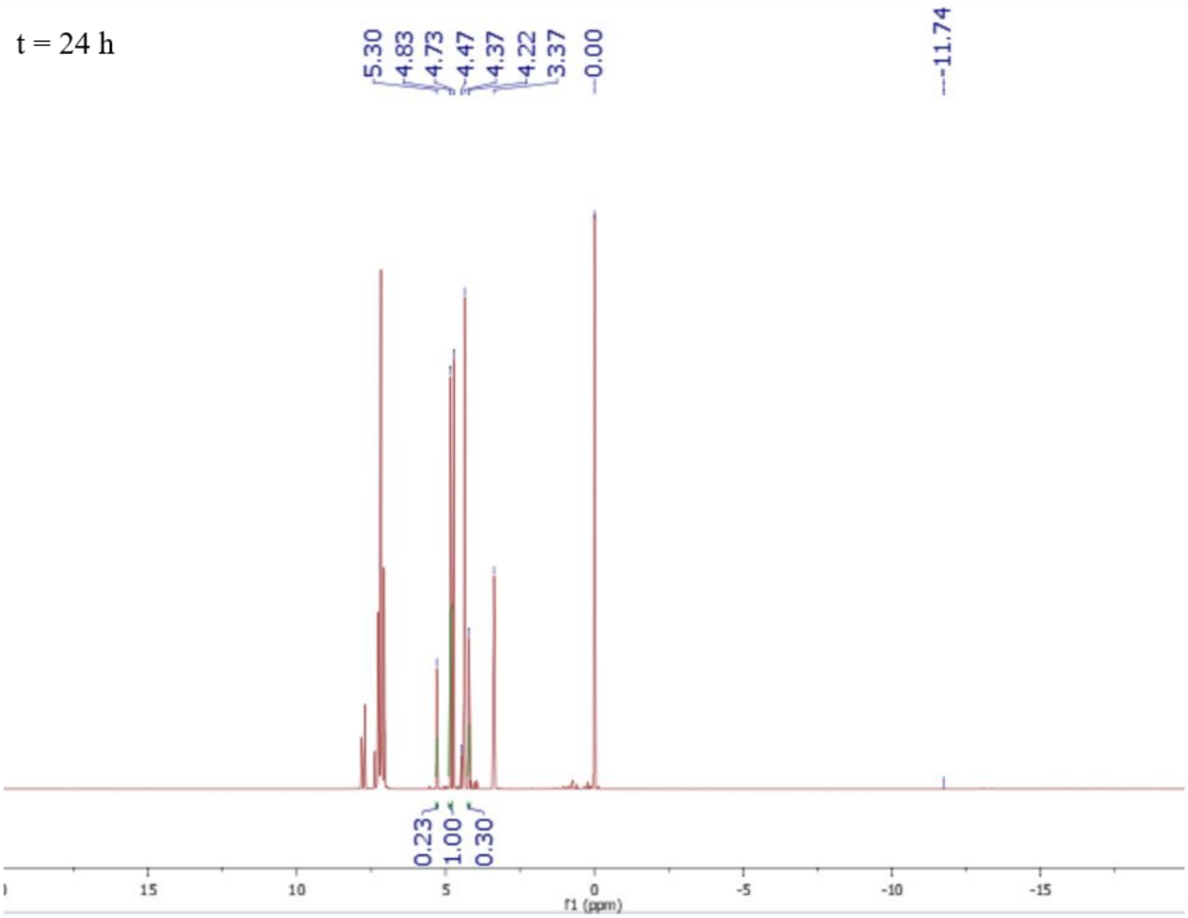

Figure S.9 ^{1}H NMR spectrum of the reaction between BnOH and $PhSiH_3$ catalyzed by **6** (benzene-*d*$_6$, 99 MHz)

Catalytic Silicon-Oxygen Heterodehydrocoupling

$PhSiH_3$ and ^{n}PrOH.[1] An oven-dried scintillation vial containing **1** (3.5 mg, 2.0 mol %) was charged with $PhSiH_3$ (61.5 µL, 54.0 mg, 0.5 mmol), followed by 0.5 mL benzene-*d*$_6$, ^{n}PrOH (150.0 µL, 120.4 mg, 2.0 mmol), and TMS (17.0 µL, 11.0 mg, 25.0 mol %). The mixture was transferred to a J-Young type polytetrafluoroethylene-valved NMR tube. After an initial ^{1}H NMR spectrum was collected, the reaction was irradiated under visible light. The reaction was subjected to a cycle of freeze-pump-thaw after 1 and 2 h of irradiation. After 24 h, the reaction showed 100% conversion to PhSi(O^{n}Pr)$_3$ as measured by ^{1}H NMR spectroscopy.

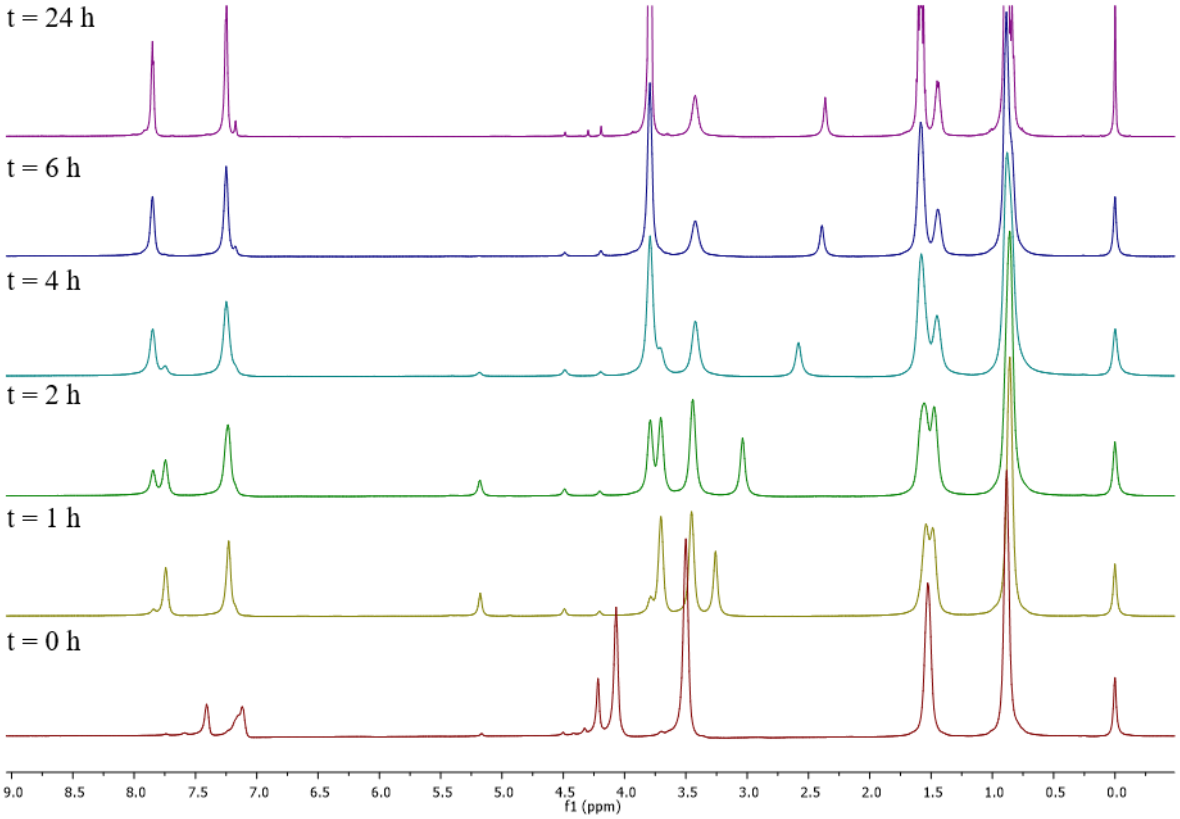

Figure S.10 Stacked ^{1}H NMR spectra of the reaction between $PhSiH_3$ and ^{n}PrOH catalyzed by **1** (benzene-*d*$_6$, 500 MHz)

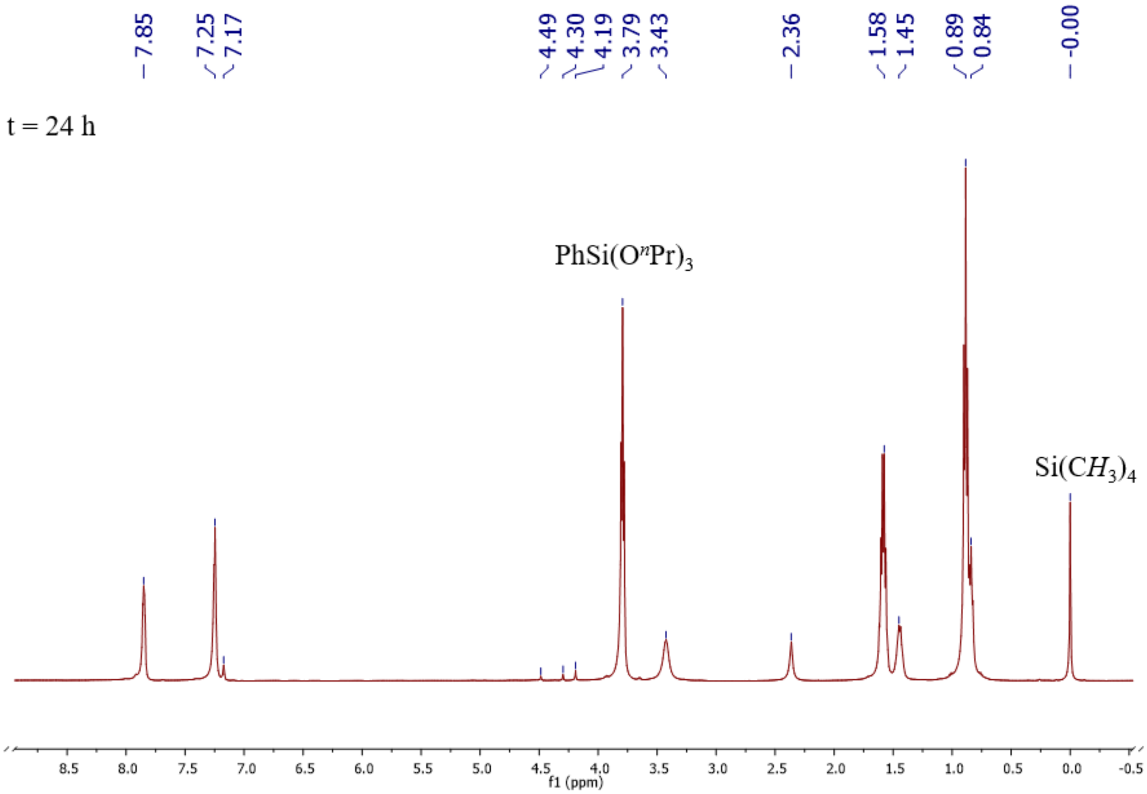

Figure S.11 Stacked ^{1}H NMR spectra of the reaction between PhSiH$_3$ and ^{n}PrOH catalyzed by **1** (benzene-d_6, 500 MHz)

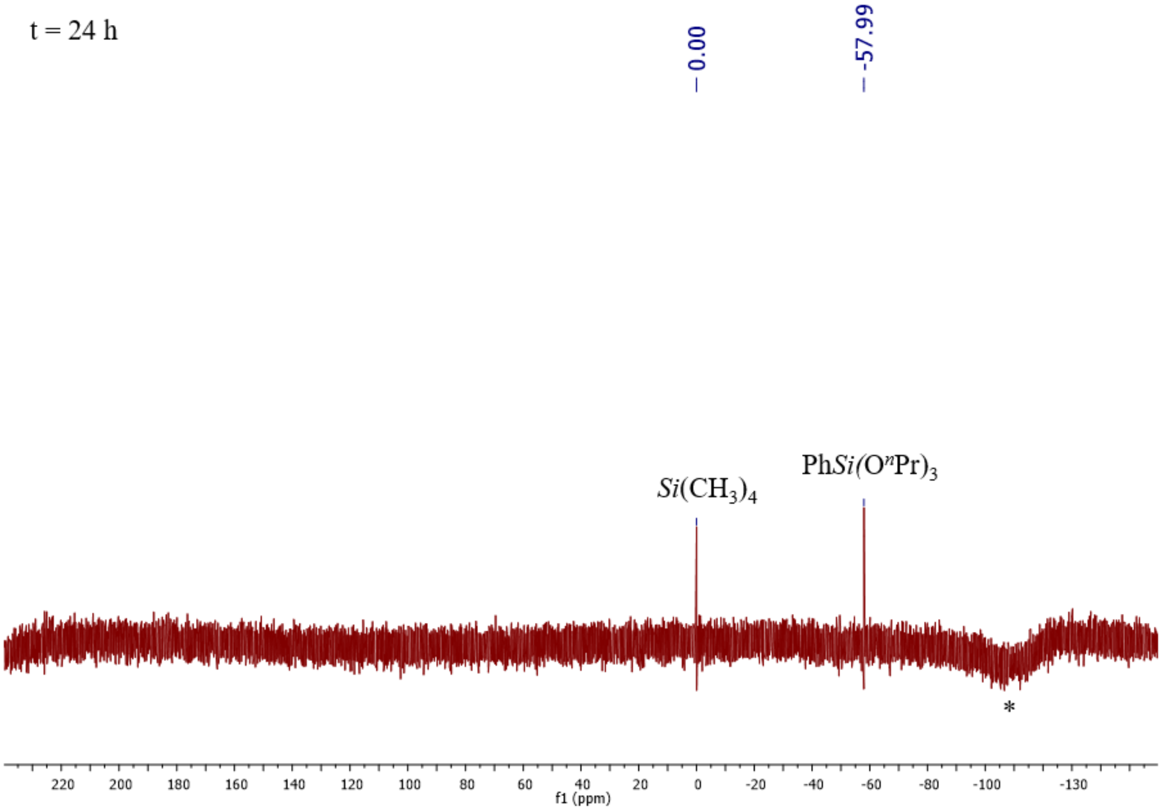

Figure S.12 $^{29}Si\{^{1}H\}$ NMR spectrum of the reaction between $PhSiH_3$ and $^{n}PrOH$ catalyzed by **1** (benzene-d_6, 99 MHz)

*This artefact is resultant from the ^{29}Si NMR probe and the borosilicate glass from the J-Young NMR tube

$PhSiH_3$ and BnOH.[2,3] An oven-dried scintillation vial containing **1** (3.5 mg, 2.0 mol %) was charged with $PhSiH_3$ (61.5 µL, 54.0 mg, 0.5 mmol), followed by 0.5 mL benzene-*d*$_6$, BnOH (210.0 µL, 219.2 mg, 2.0 mmol), and TMS (17.0 µL, 11.0 mg, 25.0 mol %). After 6 h of irradiation, the reaction showed 100% conversion to $PhSi(OBn)_3$ as measured by ^1H NMR spectroscopy.

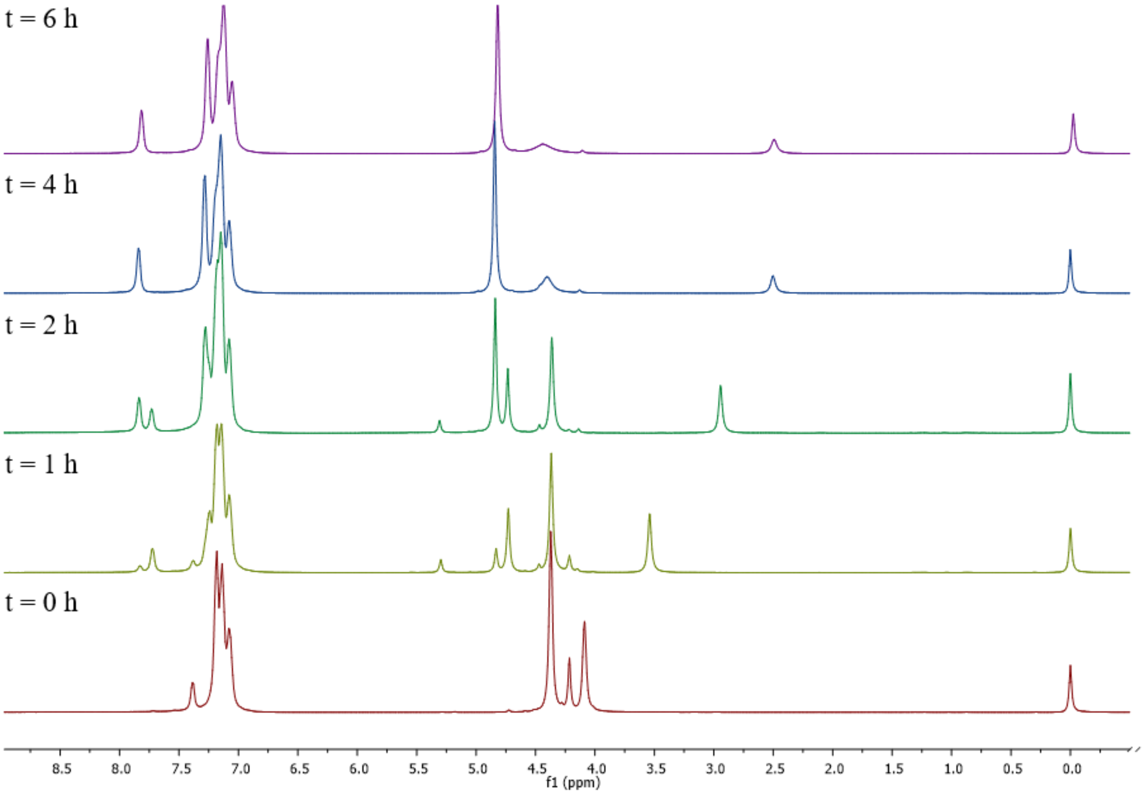

Figure S.13 Stacked ^1H NMR spectra of the reaction between $PhSiH_3$ and BnOH catalyzed by **1** (benzene-*d*$_6$, 500 MHz)

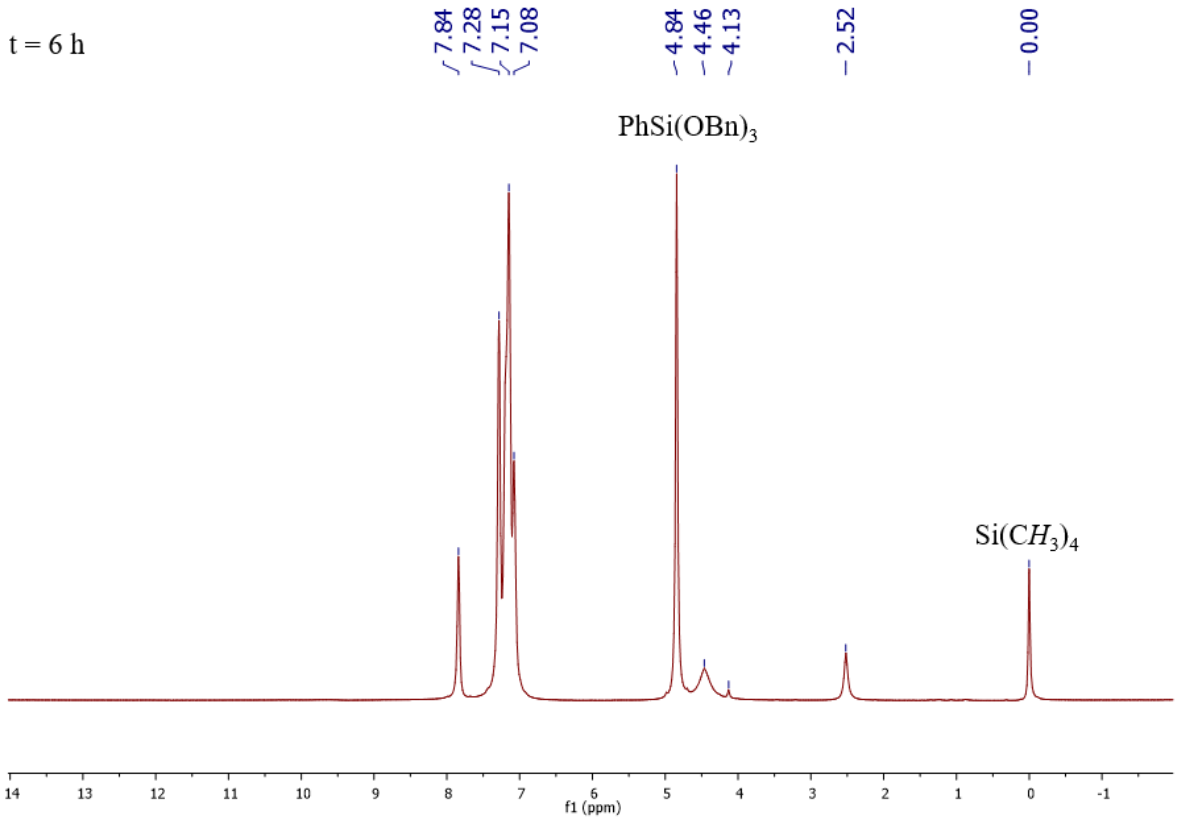

Figure S.14 Stacked ^{1}H NMR spectra of the reaction between $PhSiH_3$ and BnOH catalyzed by **1** (benzene-d_6, 500 MHz)

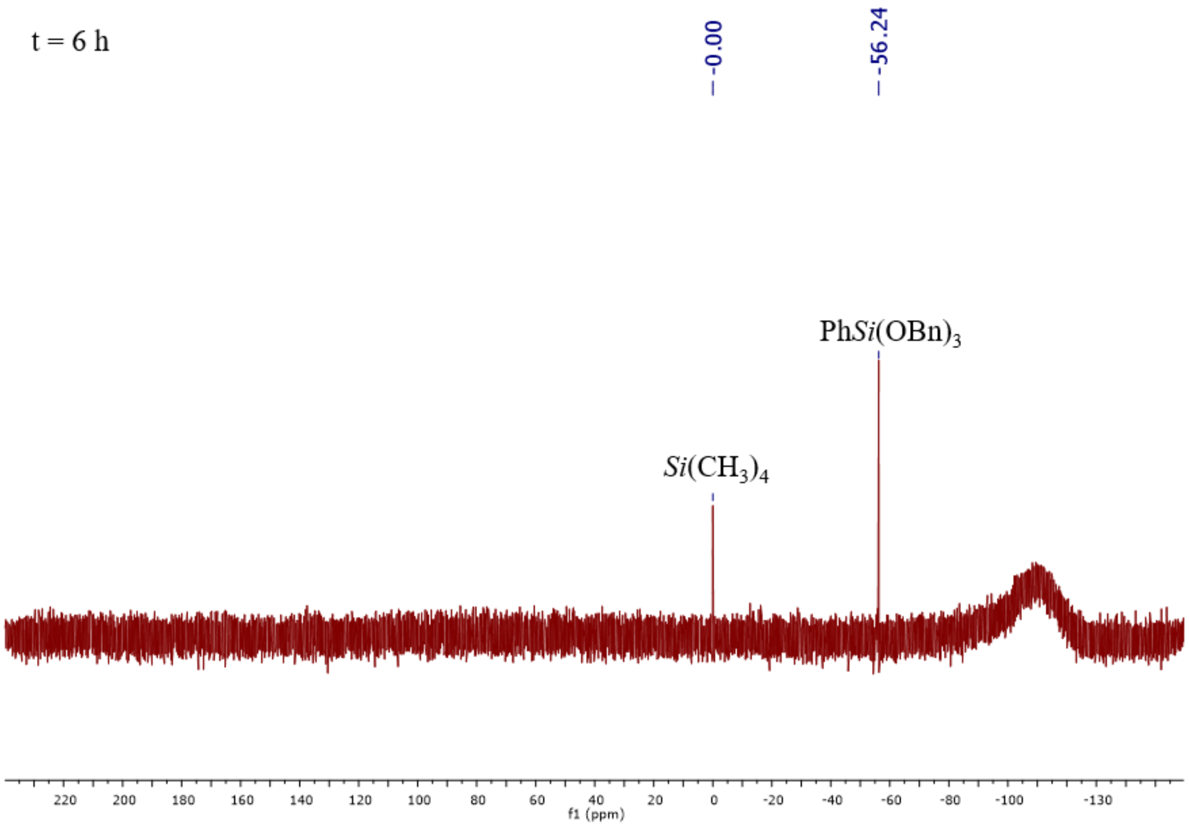

Figure S.15 ^{29}Si{^{1}H} NMR spectrum of the reaction between PhSiH$_3$ and BnOH catalyzed by **1** (benzene-d_6, 99 MHz)

$PhSiH_3$ and ^{i}PrOH.[4,3,5] An oven-dried scintillation vial containing **1** (3.5 mg, 2.0 mol %) was charged with $PhSiH_3$ (61.5 µL, 54.0 mg, 0.5 mmol), followed by 0.5 mL benzene-*d*$_6$, ^{i}PrOH (190.0 µL, 149.3 mg, 2.5 mmol), and TMS (17.0 µL, 11.0 mg, 25.0 mol %). After 24 h of irradiation, the reaction showed 100% conversion to $PhSi(O^{i}Pr)_3$ as measured by ^{1}H NMR spectroscopy.

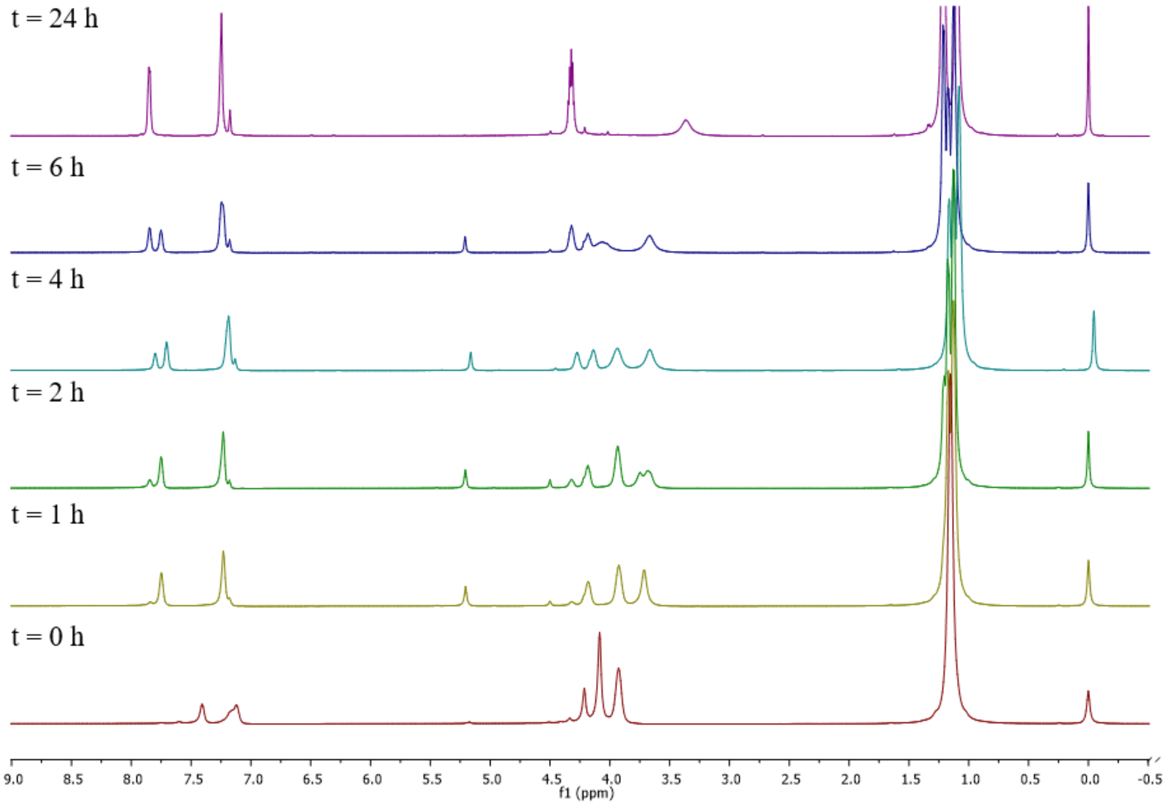

Figure S.16 Stacked ^{1}H NMR spectra of the reaction between $PhSiH_3$ and ^{i}PrOH catalyzed by **1** (benzene-*d*$_6$, 500 MHz)

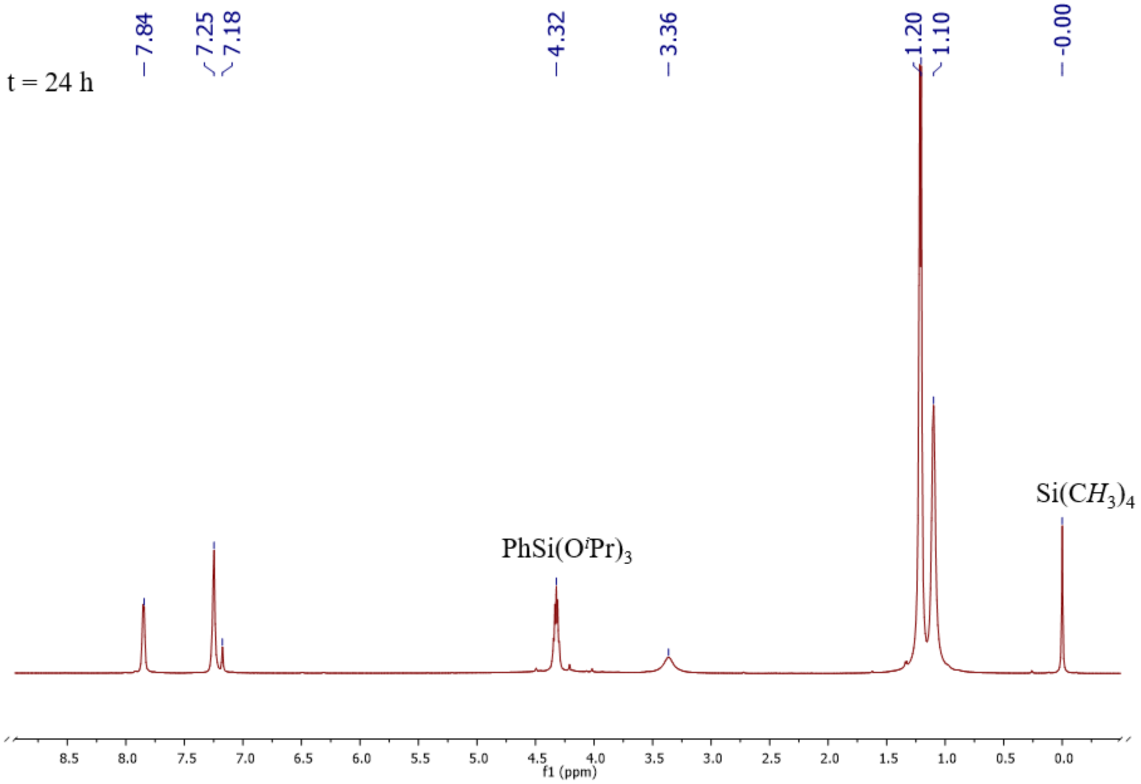

Figure S.17 ^{1}H NMR spectrum of the reaction between $PhSiH_3$ and ^{i}PrOH catalyzed by **1** (benzene-d_6, 500 MHz)

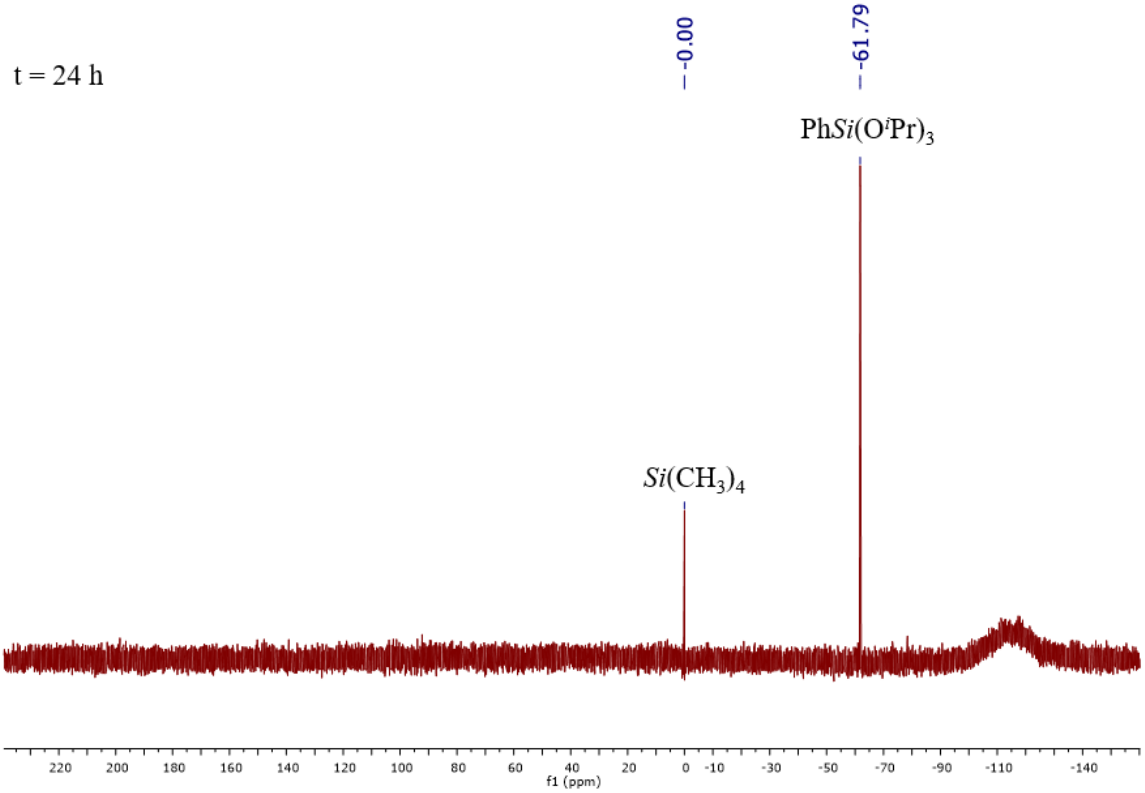

Figure S.18 ^{29}Si{^{1}H} NMR spectrum of the reaction between $PhSiH_3$ and ^{i}PrOH catalyzed by **1** (benzene-d_6, 99 MHz)

$PhMeSiH_2$ and ^{n}PrOH. An oven-dried scintillation vial containing **1** (3.5 mg, 2.0 mol %) was charged with $PhMeSiH_2$ (68.5 μL, 60.9 mg, 0.5 mmol), followed by 0.5 mL benzene-d_6, ^{n}PrOH (150.0 μL, 120.4 mg, 2.0 mmol), and TMS (11.5 μL, 7.4 mg, 16.9 mol %). After 24 h of irradiation, the reaction demonstrated 100% conversion from $PhMeSiH_2$ as measured by ^{1}H NMR spectroscopy. Although product isolation was unsuccessful, it was hypothesized that the resonance at δ 3.67 was $PhMeSi(O^nPr)_2$ and was produced in 100% conversion.

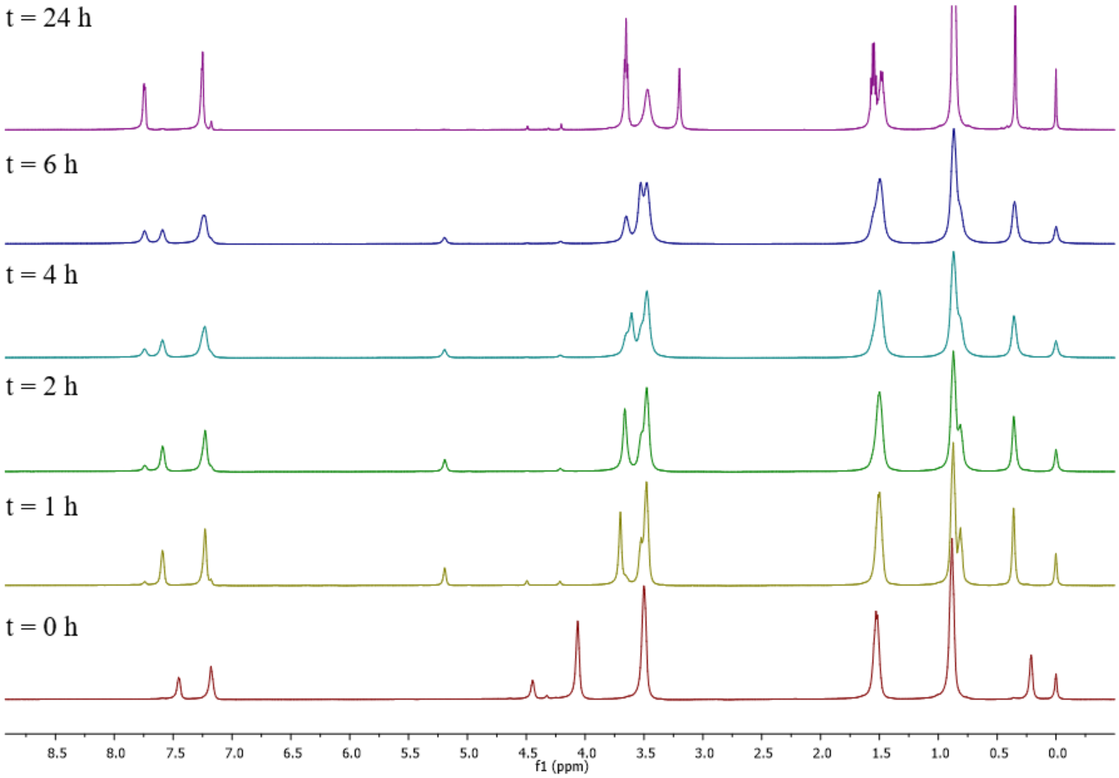

Figure S.19 Stacked ^{1}H NMR spectra of the reaction between $PhMeSiH_2$ and ^{n}PrOH catalyzed by **1** (benzene-d_6, 500 MHz)

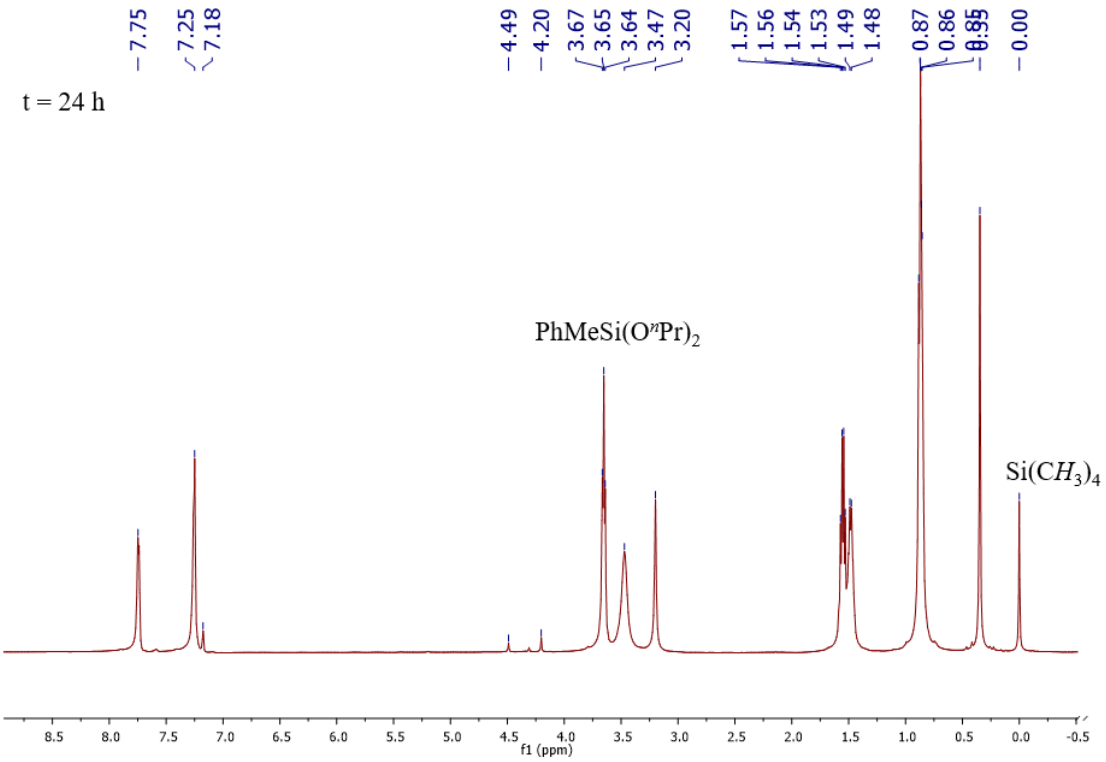

Figure S.20 ^{1}H NMR spectrum of the reaction between $PhMeSiH_2$ and ${}^{n}PrOH$ catalyzed by **1** (benzene-d_6, 500 MHz)

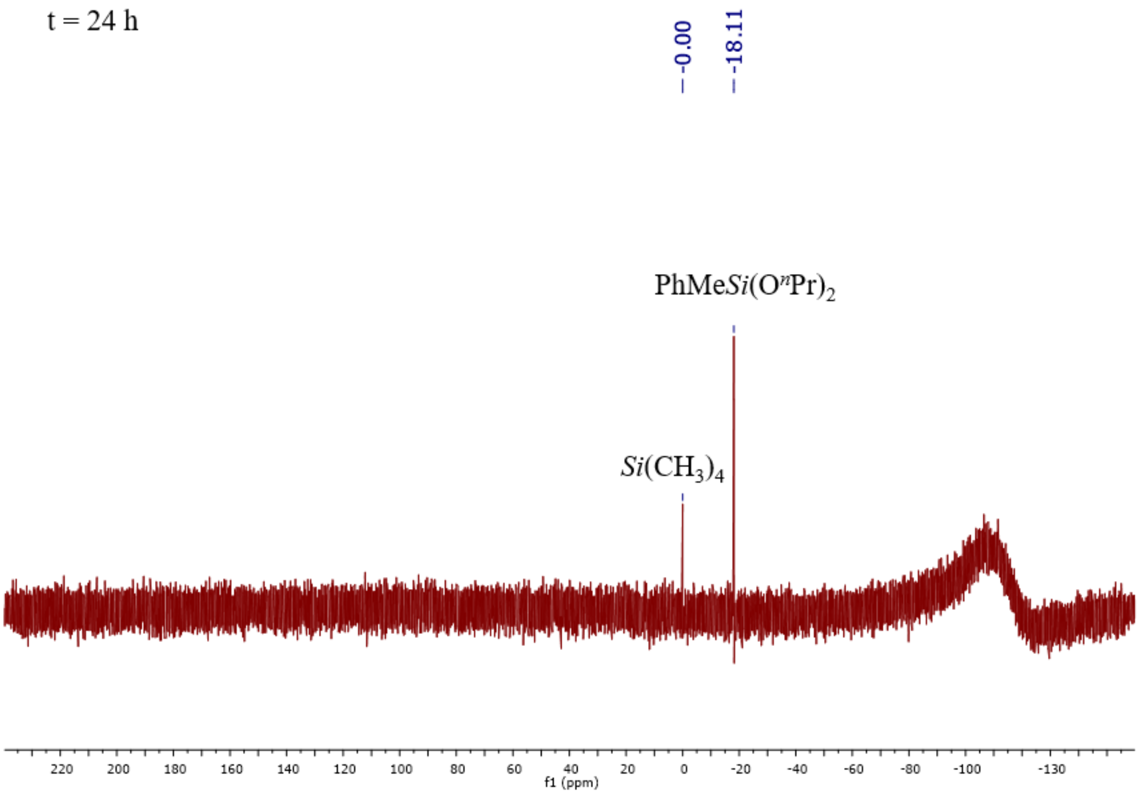

Figure S.21 $^{29}Si\{^{1}H\}$ NMR spectrum of the reaction between $PhMeSiH_2$ and $^{n}PrOH$ catalyzed by **1** (benzene-d_6, 99 MHz)

PhMeSiH$_2$ and BnOH.[6] An oven-dried scintillation vial containing **1** (3.5 mg, 2.0 mol %) was charged with PhMeSiH$_2$ (68.5 μL, 60.9 mg, 0.5 mmol), followed by 0.5 mL benzene-d_6, BnOH (210.0 μL, 219.2 mg, 2.0 mmol), and TMS (11.5 μL, 7.4 mg, 16.9 mol %). After 24 h of irradiation, the reaction showed 100% conversion to PhMeSi(OBn)$_2$ as measured by ^{1}H NMR spectroscopy.

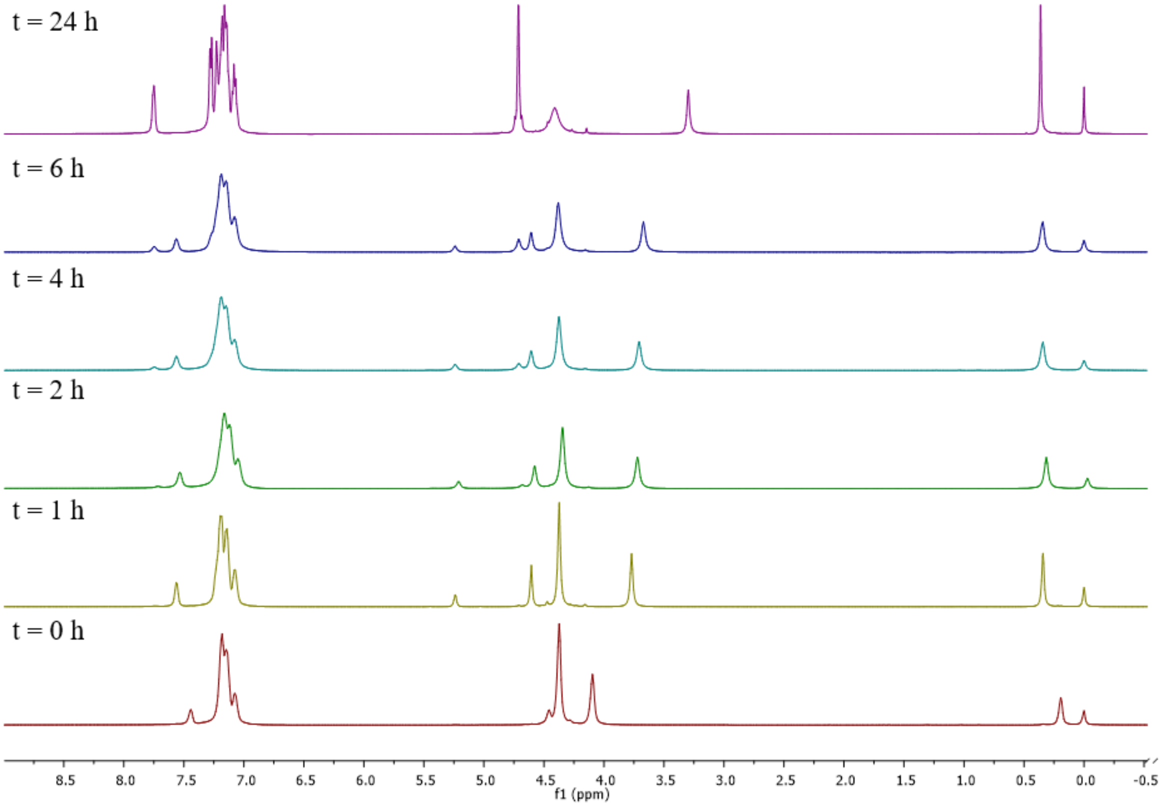

Figure S.22 Stacked ^{1}H NMR spectra of the reaction between PhMeSiH$_2$ and BnOH catalyzed by **1** (benzene-d_6, 500 MHz)

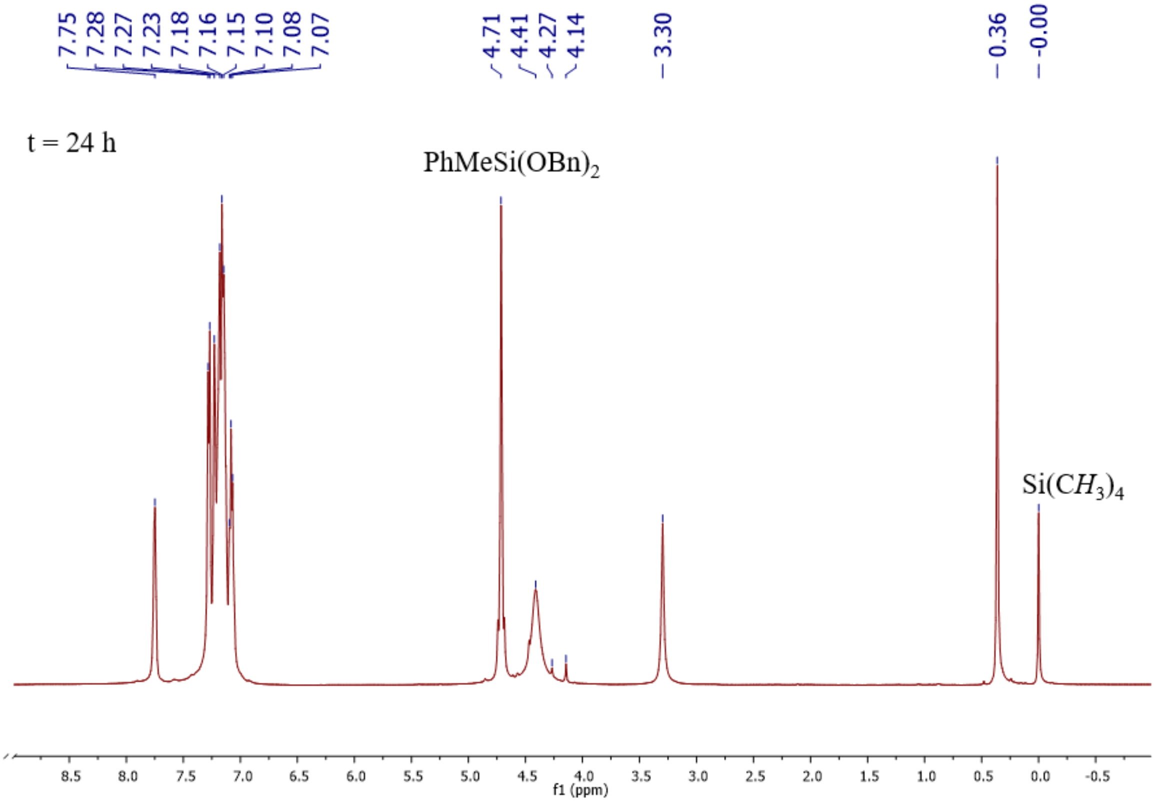

Figure S.23 ^{1}H NMR spectrum of the reaction between $PhMeSiH_2$ and BnOH catalyzed by **1** (benzene-d_6, 500 MHz)

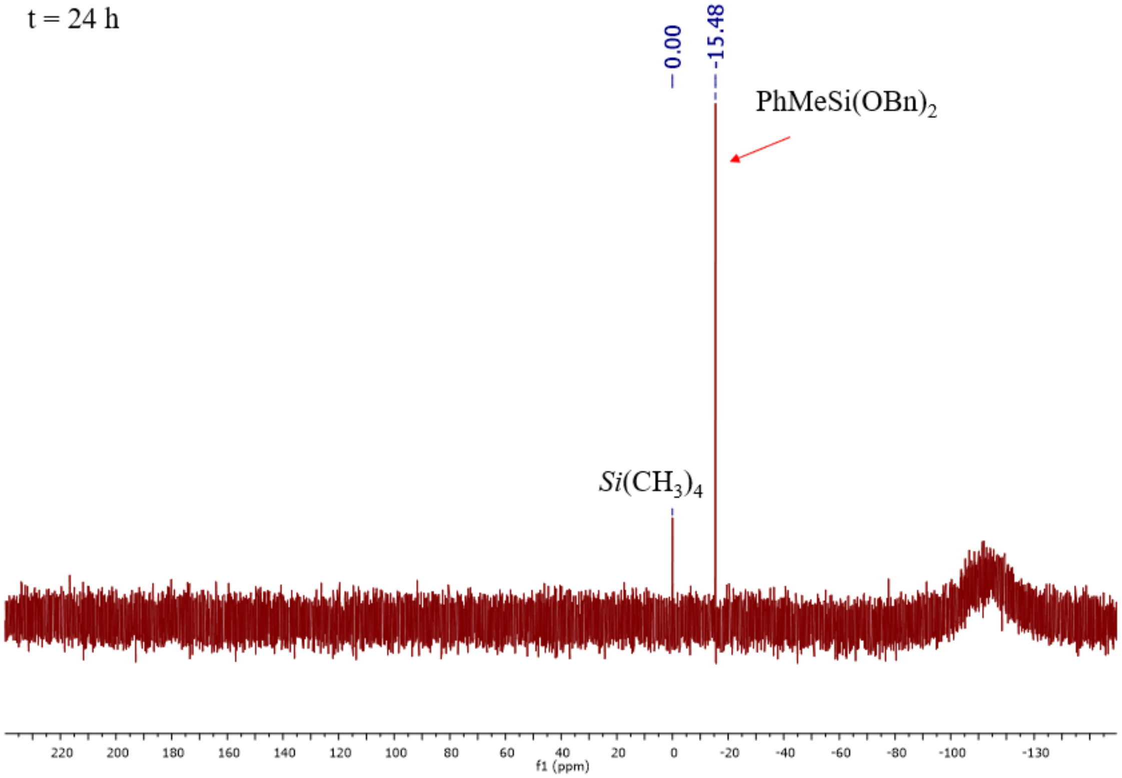

Figure S.24 ^{29}Si{^{1}H} NMR spectrum of the reaction between PhMeSiH$_2$ and BnOH catalyzed by **1** (benzene-*d*$_6$, 99 MHz)

PhMeSiH$_2$ and ^{i}PrOH. An oven-dried scintillation vial containing **1** (3.5 g, 2.0 mol %) was charged with PhMeSiH$_2$ (68.5 µL, 60.9 mg, 0.5 mmol), followed by 0.5 mL benzene-*d*$_6$, ^{i}PrOH (190.0 µL, 149.3 mg, 2.5 mmol), and TMS (11.5 µL, 7.4 mg, 16.9 mol %). Although product isolation was unsuccessful, it was hypothesized that the resonance at δ 5.20 corresponded to PhMeSiH(O^{i}Pr) and was produced in 9% conversion, while the resonance at δ 4.27 corresponded to the PhMeSi(O^{i}Pr)$_2$ and was produced in 91% yield, as measured by ^{1}H NMR spectroscopy.

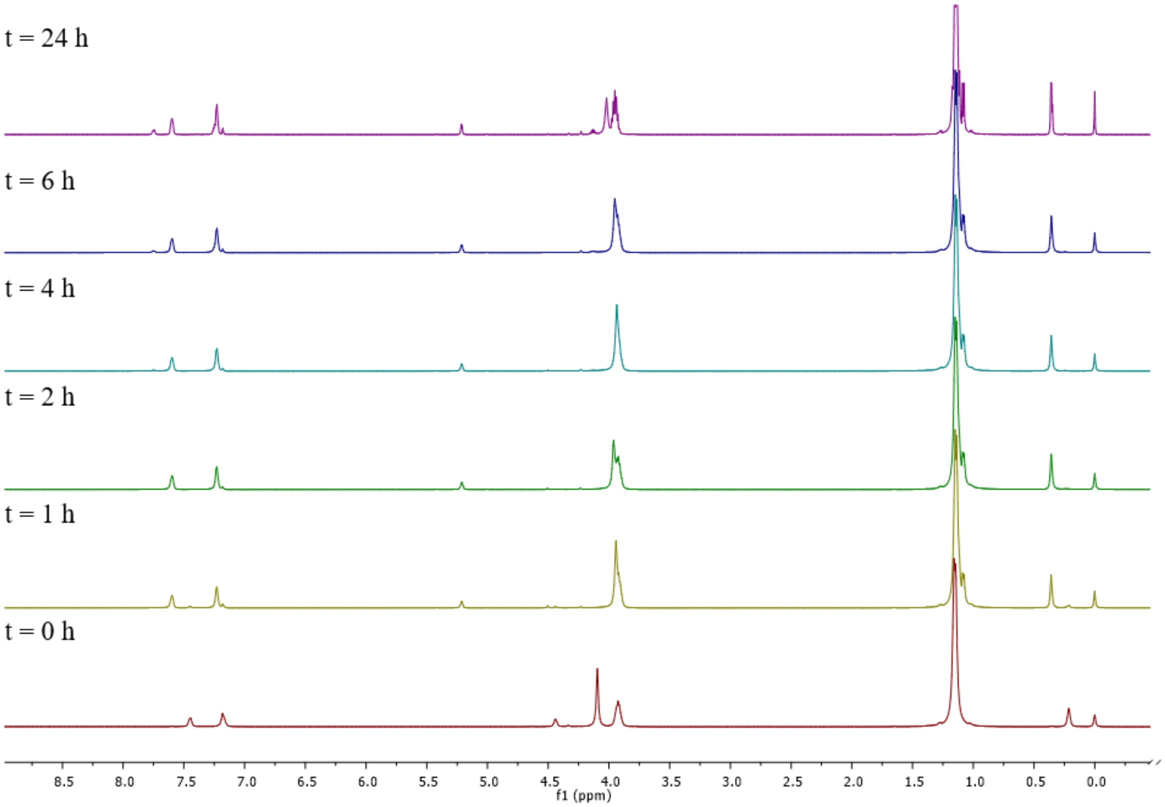

Figure S.25 Stacked ^{1}H NMR spectra of the reaction between PhMeSiH$_2$ and ^{i}PrOH catalyzed by **1** (benzene-*d*$_6$, 500 MHz)

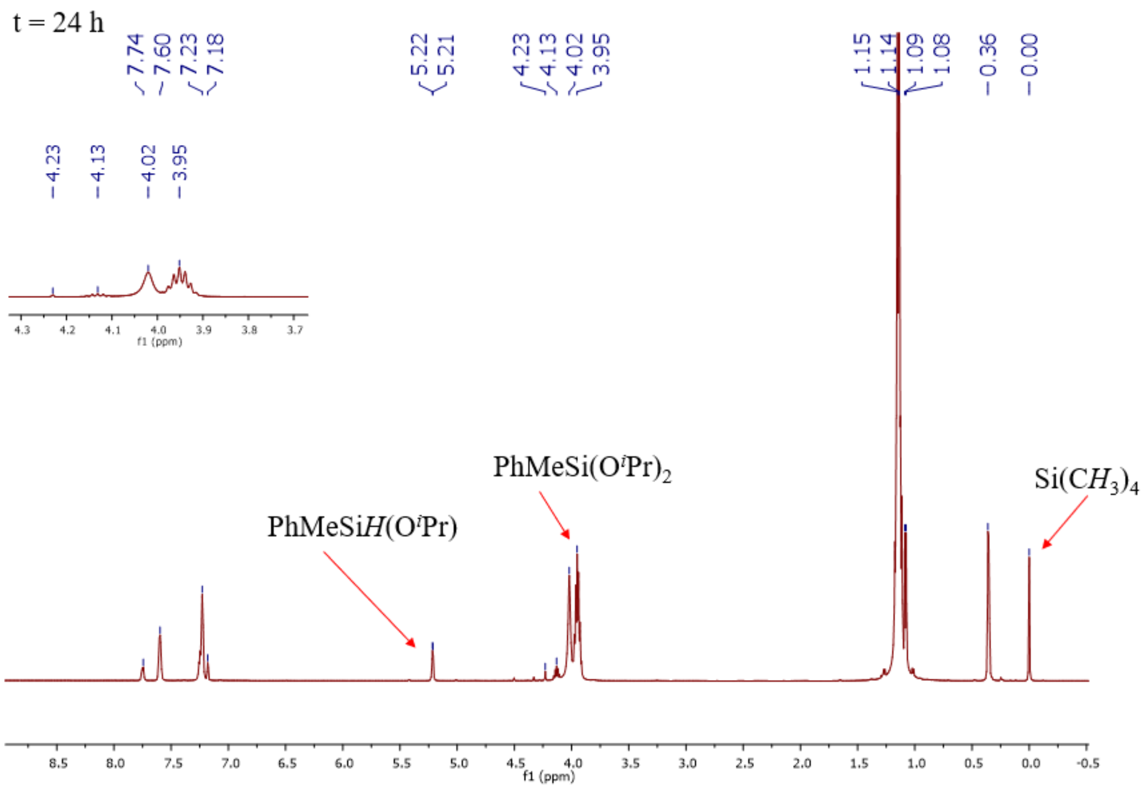

Figure S.26 ^{1}H NMR spectrum of the reaction between PhMeSiH$_2$ and ^{i}PrOH catalyzed by **1** (benzene-d_6, 500 MHz)

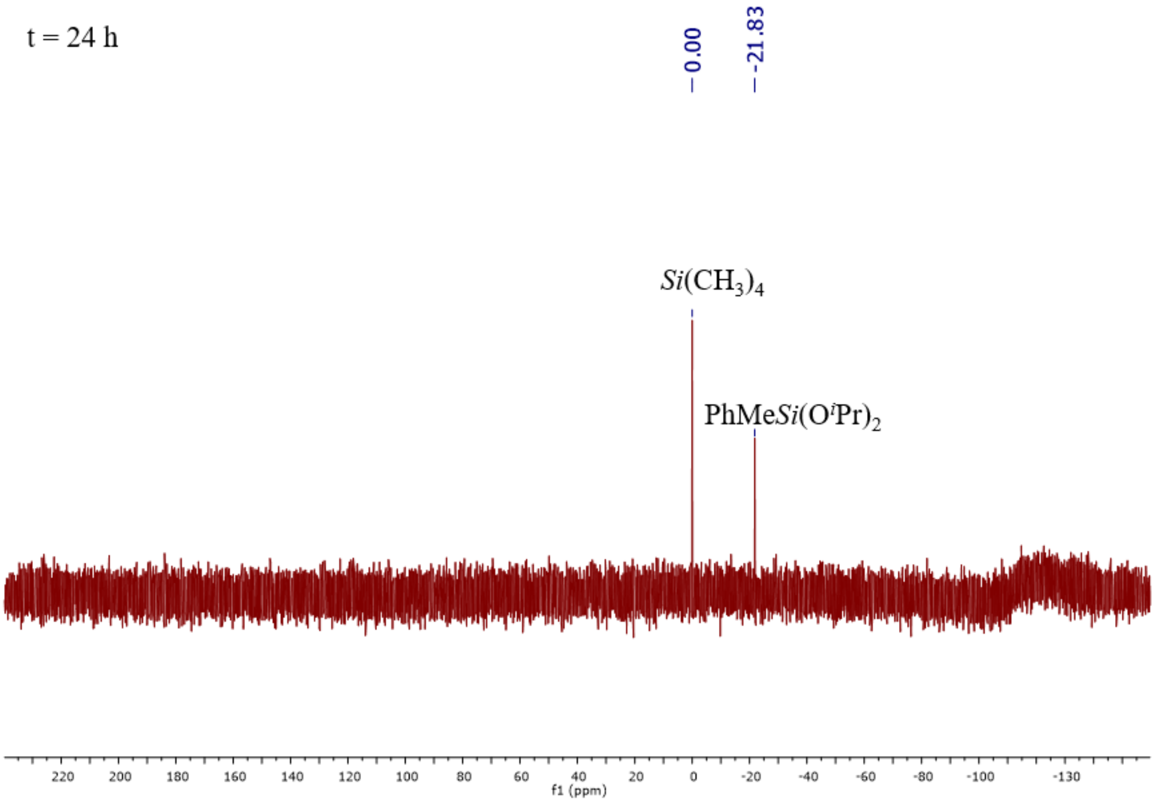

Figure S.27 $^{29}Si\{^{1}H\}$ NMR spectrum of the reaction between $PhMeSiH_2$ and $^{i}PrOH$ catalyzed by **1** (benzene-d_6, 99 MHz)

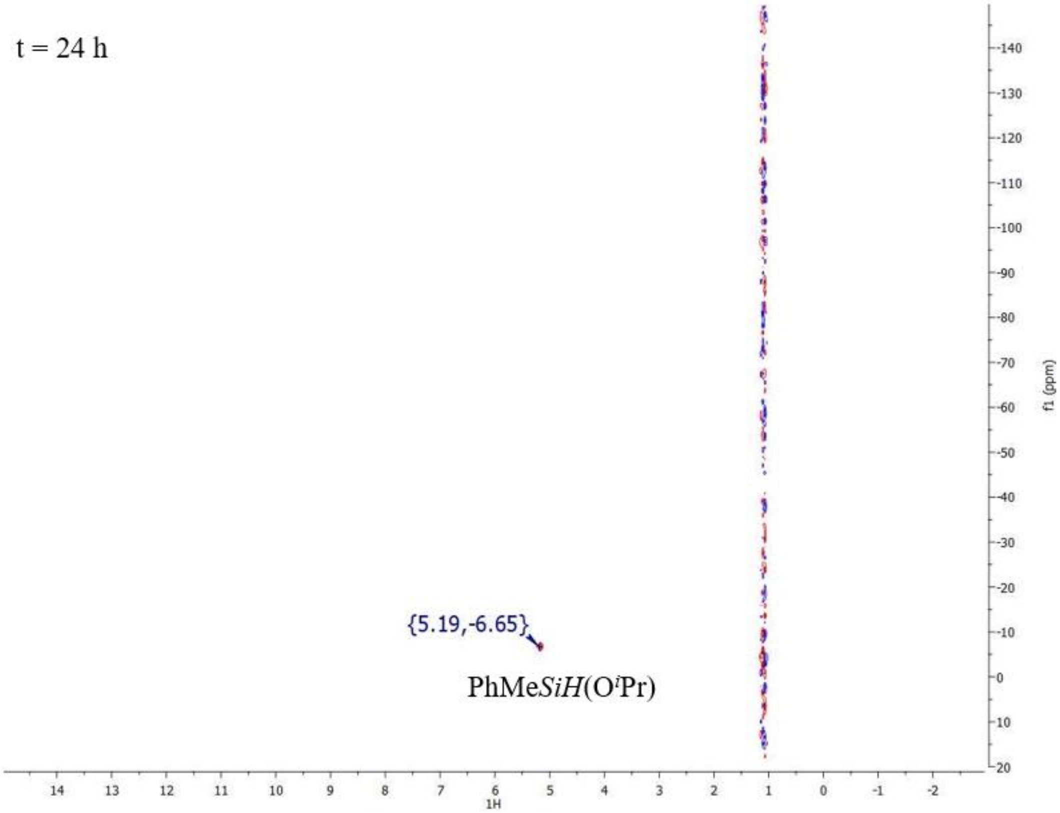

Figure S.28 ^{1}H-^{29}Si{^{1}H} HSQC spectrum of the reaction between $PhMeSiH_2$ and ^{i}PrOH catalyzed by **1** (benzene-d_6, 99 MHz)

Ph_2SiH_2 and ^nPrOH. An oven-dried scintillation vial containing **1** (3.5 mg, 2.0 mol %) was charged with Ph_2SiH_2 (93.0 μL, 92.3 mg, 0.5 mmol), followed by 0.5 mL benzene-d_6, ^{n}PrOH (150.0 μL, 120.4 mg, 2.0 mmol), and TMS (11.5 μL, 7.4 mg, 16.9 mol %). After 24 h of irradiation, the reaction reached 100% conversion from Ph_2SiH_2 according to ^{1}H NMR spectroscopy. Although product isolation was unsuccessful, it was hypothesized that the resonance at δ 3.72 corresponds to $Ph_2Si(O^nPr)_2$ and was produced in 100% conversion.

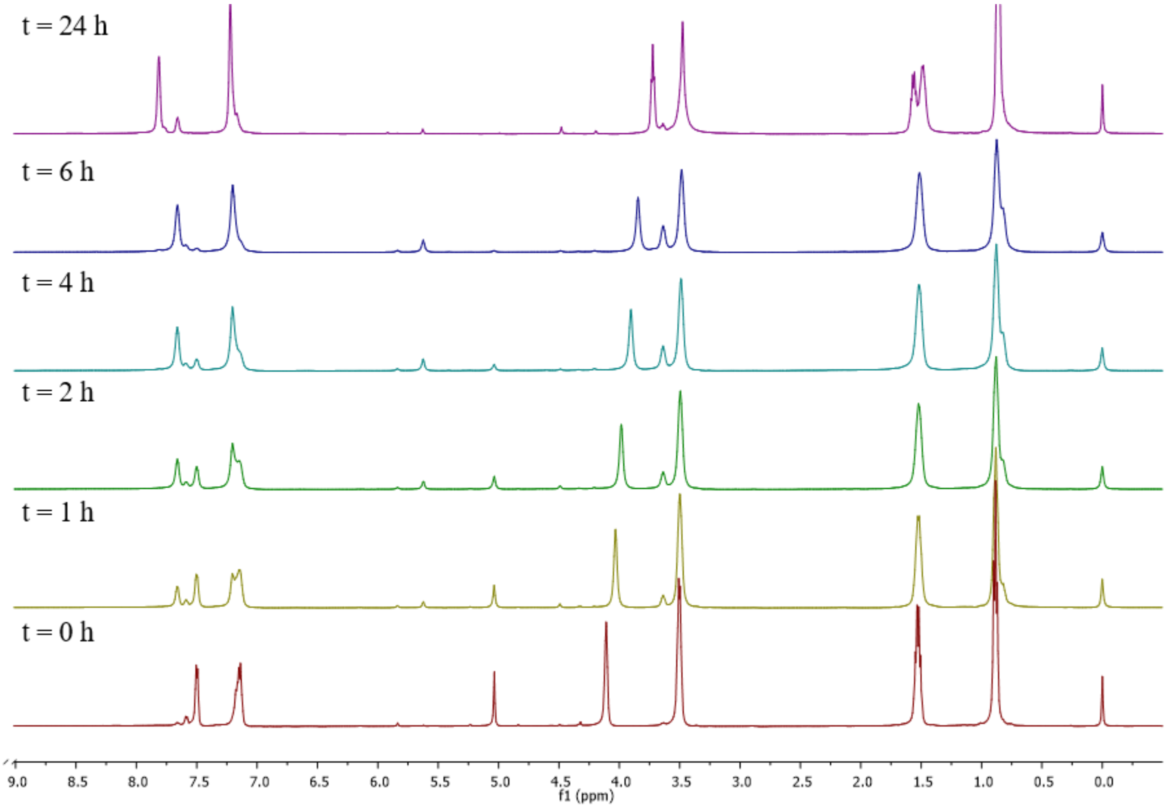

Figure S.29 Stacked ^{1}H NMR spectra of the reaction between Ph_2SiH_2 and ^{n}PrOH catalyzed by **1** (benzene-d_6, 500 MHz)

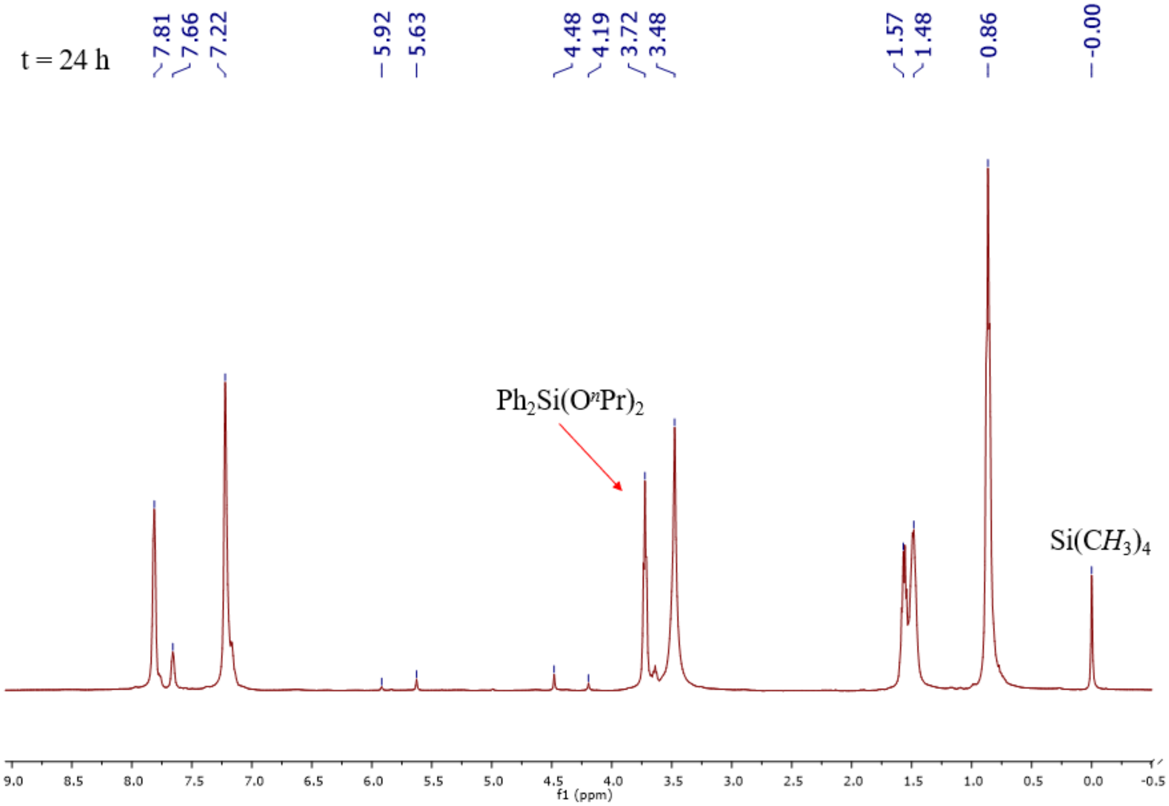

Figure S.30 ^{1}H NMR spectrum of the reaction between Ph_2SiH_2 and ^{n}PrOH catalyzed by **1** (benzene-d_6, 500 MHz)

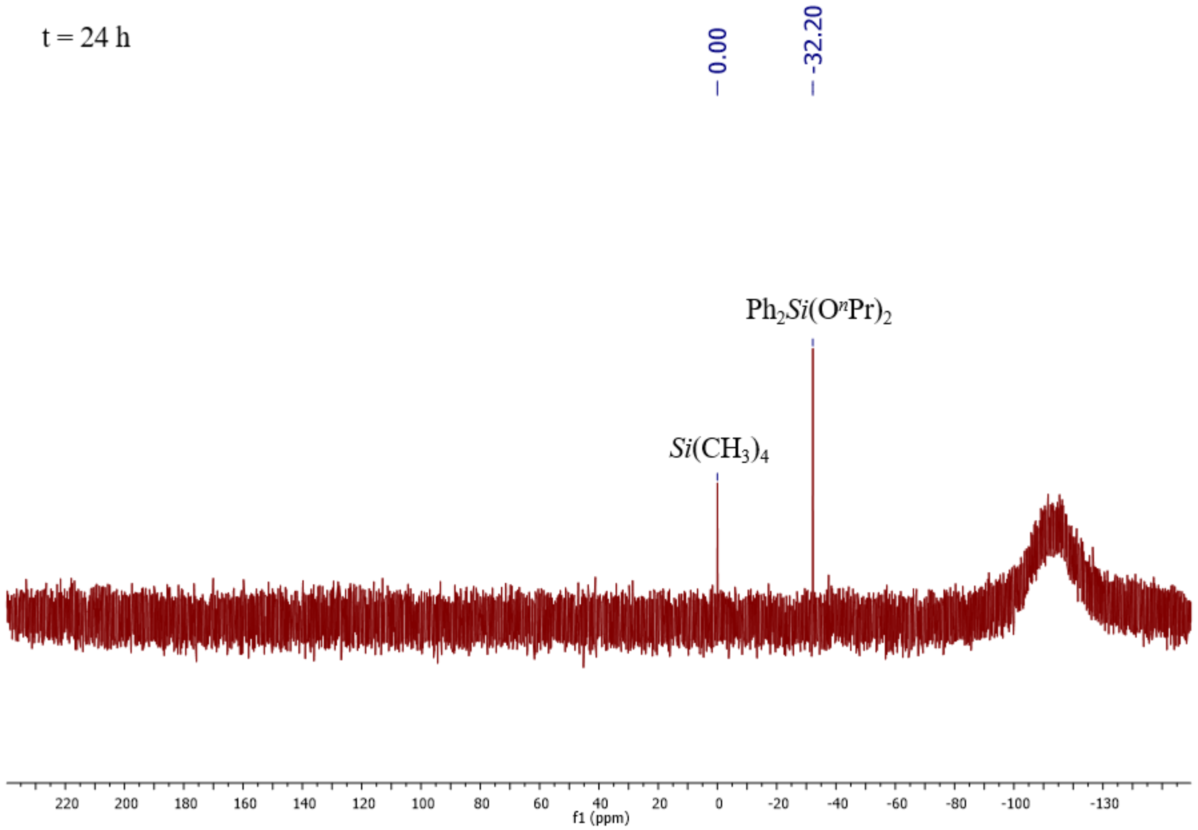

Figure S.31 $^{29}Si\{^1H\}$ NMR spectrum of the reaction between Ph_2SiH_2 and ^nPrOH catalyzed by **1** (benzene-d_6, 99 MHz)

Ph_2SiH_2 and BnOH.[7,3] An oven-dried scintillation vial containing **1** (3.5 mg, 2.0 mol %) was charged with Ph_2SiH_2 (93.0 µL, 92.3 mg, 0.5 mmol), followed by 0.5 mL benzene-*d*$_6$, BnOH (210.0 µL, 219.2 mg, 2.0 mmol), and TMS (11.5 µL, 7.4 mg, 16.9 mol %). After 24 h of irradiation, the reaction showed 100% conversion to $Ph_2Si(OBn)_2$ according to ^1H NMR spectroscopy.

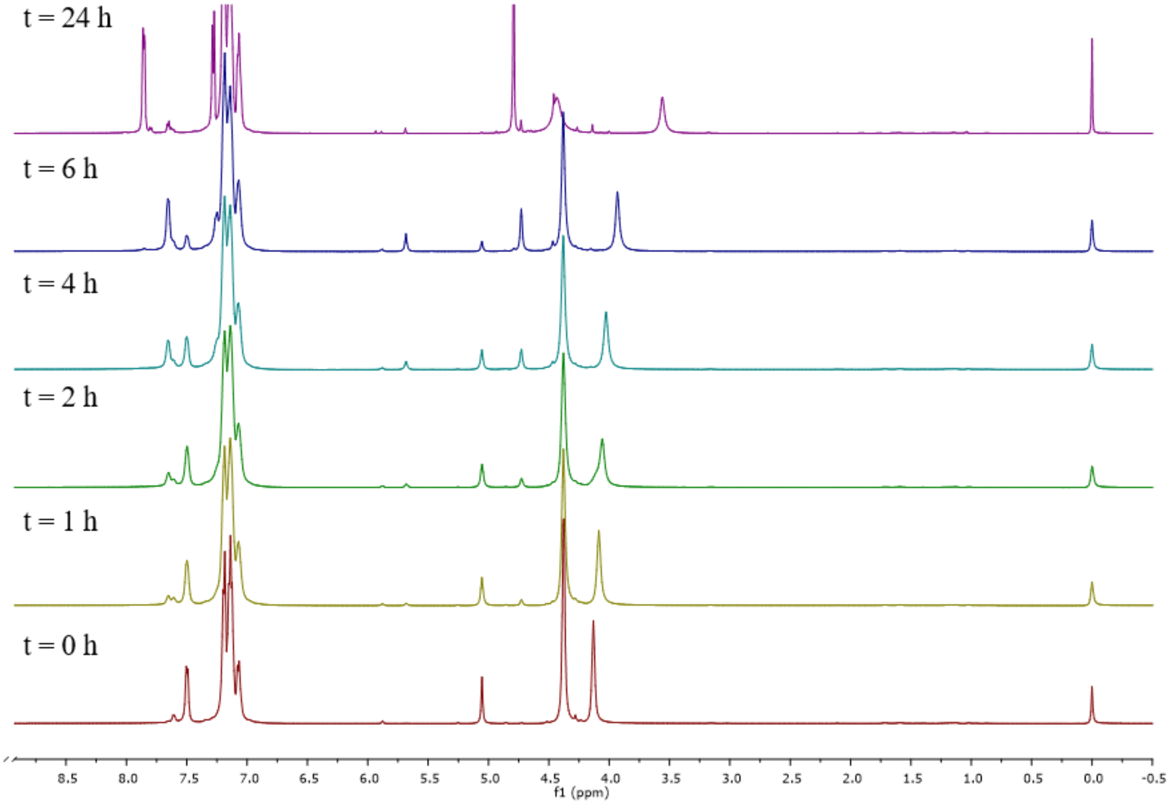

Figure S.32 Stacked ^1H NMR spectra of the reaction between Ph_2SiH_2 and BnOH catalyzed by **1** (benzene-*d*$_6$, 500 MHz)

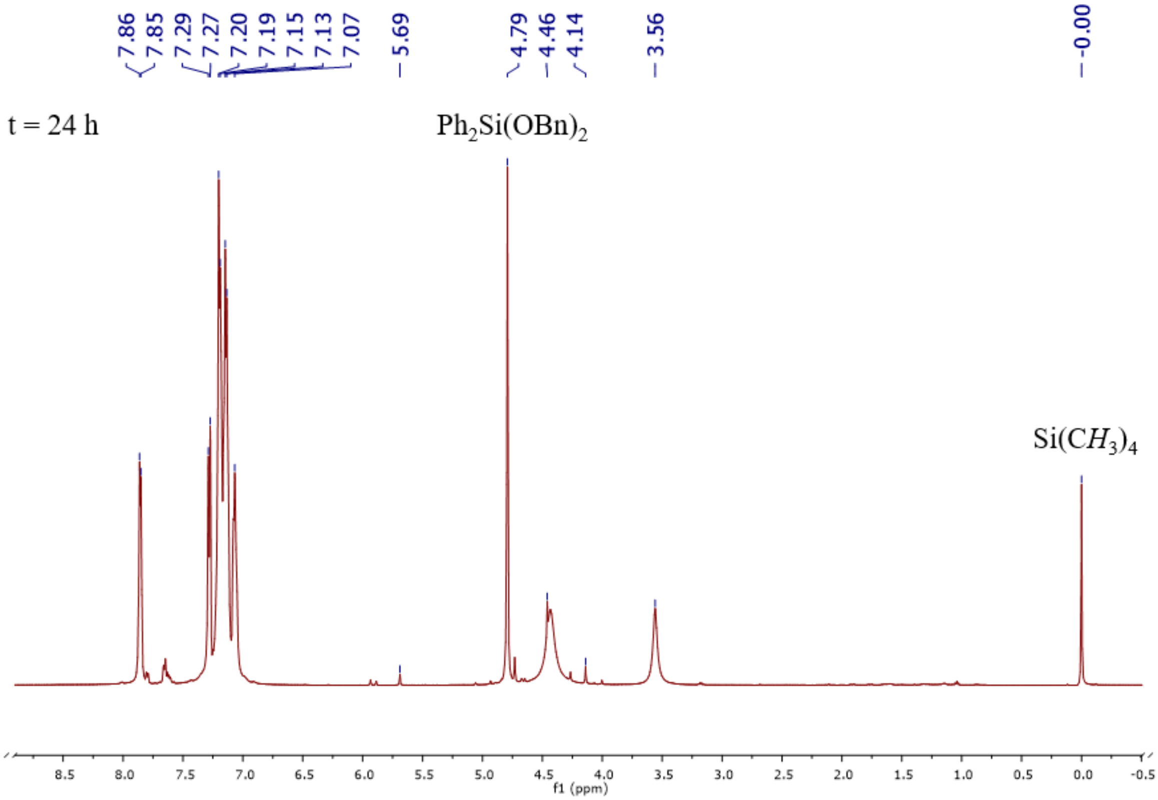

Figure S.33 ^{1}H NMR spectrum of the reaction between Ph_2SiH_2 and BnOH catalyzed by **1** (benzene-d_6, 500 MHz)

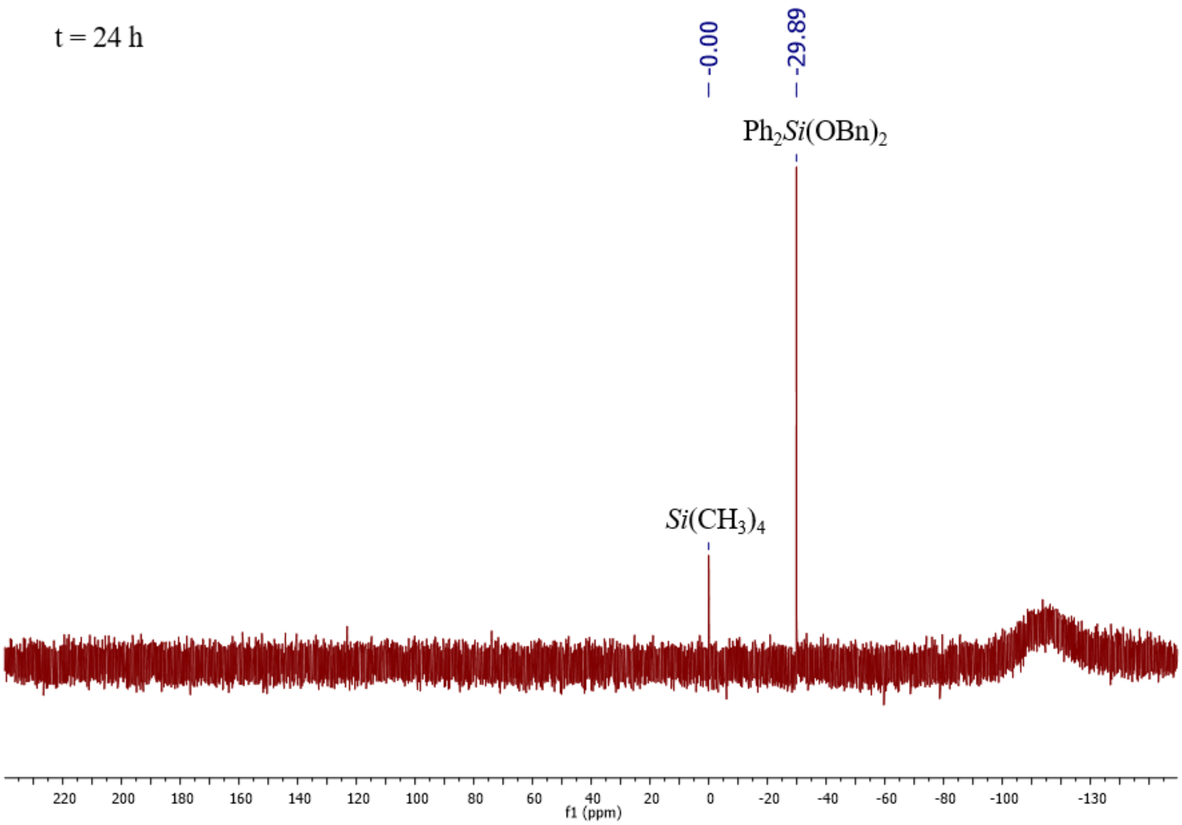

Figure S.34 $^{29}Si\{^1H\}$ NMR spectrum of the reaction between Ph_2SiH_2 and BnOH catalyzed by **1** (benzene-d_6, 99 MHz)

Ph_2SiH_2 and ^{i}PrOH.[3] An oven-dried scintillation vial containing **1** (3.5 mg, 2.0 mol %) was charged with Ph_2SiH_2 (93.0 µL, 92.3 mg, 0.5 mmol), followed by 0.5 mL benzene-*d*$_6$, ^{i}PrOH (190.0 µL, 149.3 mg, 2.5 mmol), and TMS (11.5 µL, 7.4 mg, 16.9 mol %). After 24 h of irradiation, the reaction showed 100% conversion to $Ph_2SiH(O^iPr)$ according to ^{1}H NMR spectroscopy.

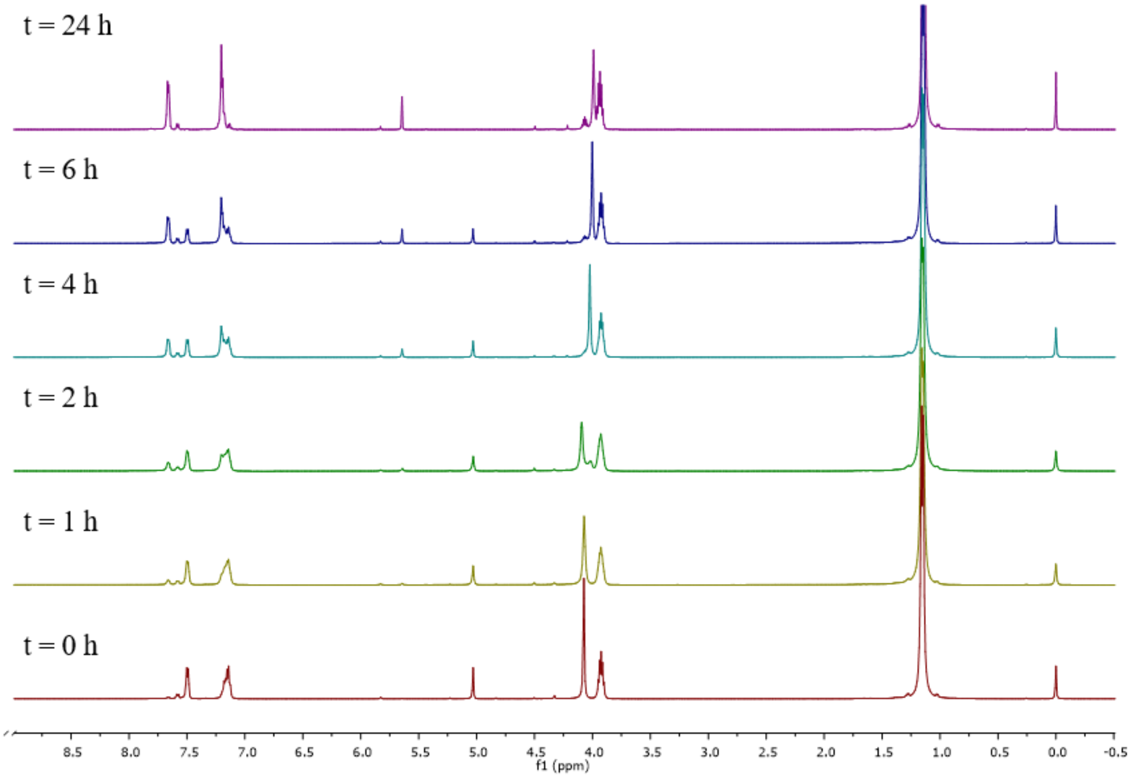

Figure S.35 Stacked ^{1}H NMR spectra of the reaction between Ph_2SiH_2 and ^{i}PrOH catalyzed by **1** (benzene-*d*$_6$, 500 MHz)

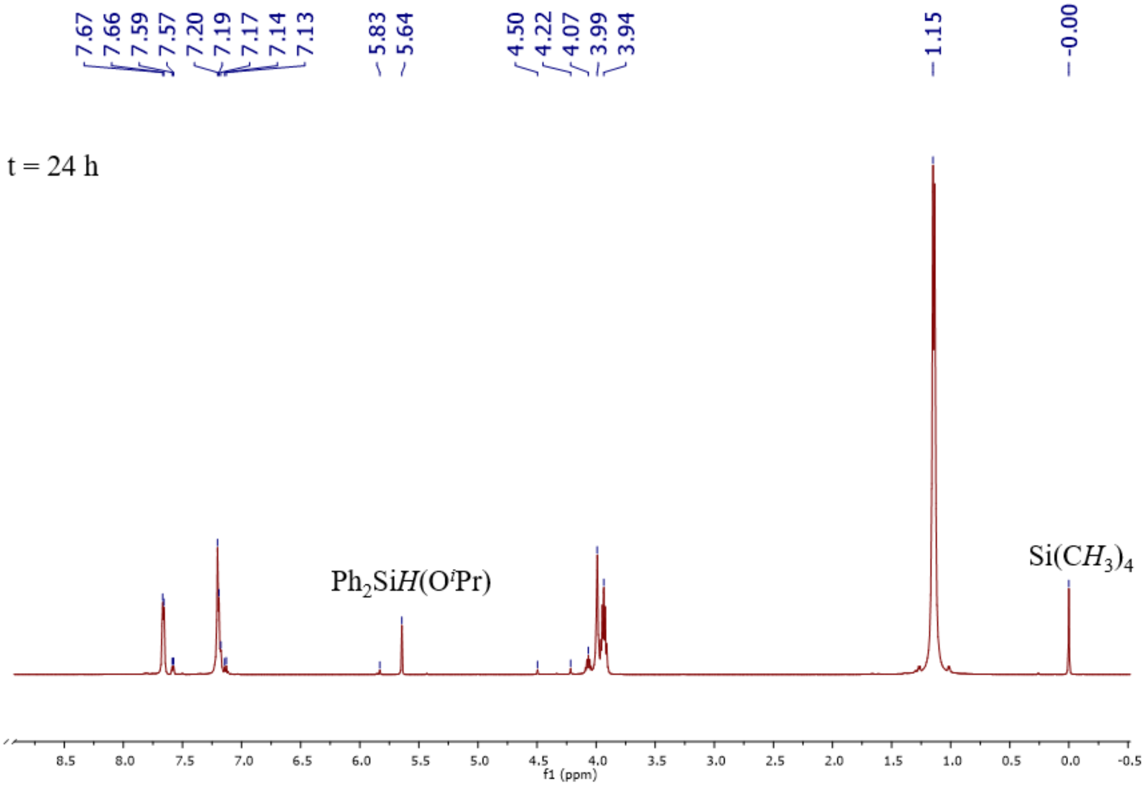

Figure S.36 ^{1}H NMR spectrum of the reaction between Ph_2SiH_2 and ^{i}PrOH catalyzed by **1** (benzene-d_6, 500 MHz)

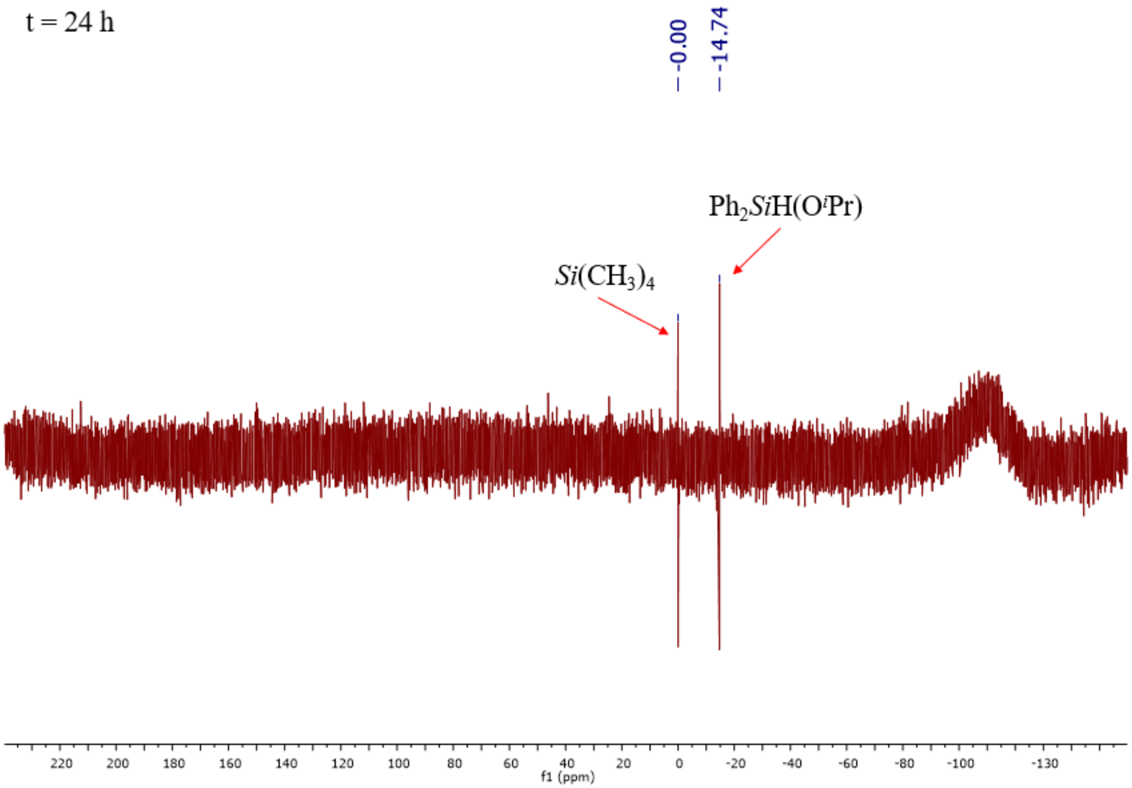

Figure S.37 $^{29}Si\{^1H\}$ NMR spectrum of the reaction between Ph_2SiH_2 and ^iPrOH catalyzed by **1** (benzene-d_6, 99 MHz)

$PhMe_2SiH$ and ^nPrOH. An oven-dried scintillation vial containing **1** (3.5 mg, 2.0 mol %) was charged with $PhMe_2SiH$ (76.5 µL, 68.0 mg, 0.5 mmol), followed by 0.5 mL benzene-*d*$_6$, ^nPrOH (150.0 µL, 150.2 mg, 2.5 mmol), and TMS (6.0 µL, 3.8 mg, 8.8 mol %). After 24 h of irradiation, the reaction showed partial disappearance of $PhMe_2SiH$ at δ 4.60 according to ^1H NMR spectroscopy. It was hypothesized that the peak at δ 3.47 was $PhMe_2Si(O^nPr)$ and was produced in 93% conversion.

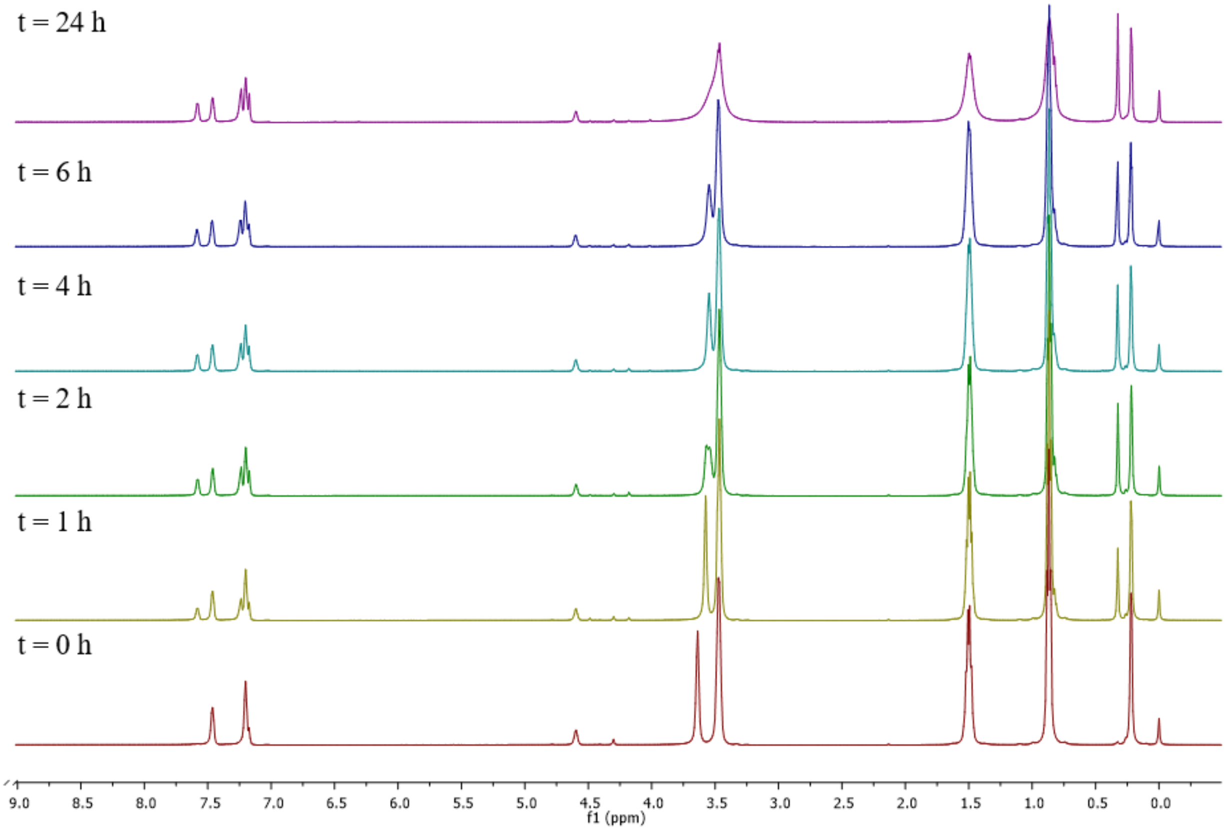

Figure S.38 Stacked ^1H NMR spectra of the reaction between $PhMe_2SiH$ and ^nPrOH catalyzed by **1** (benzene-*d*$_6$, 500 MHz)

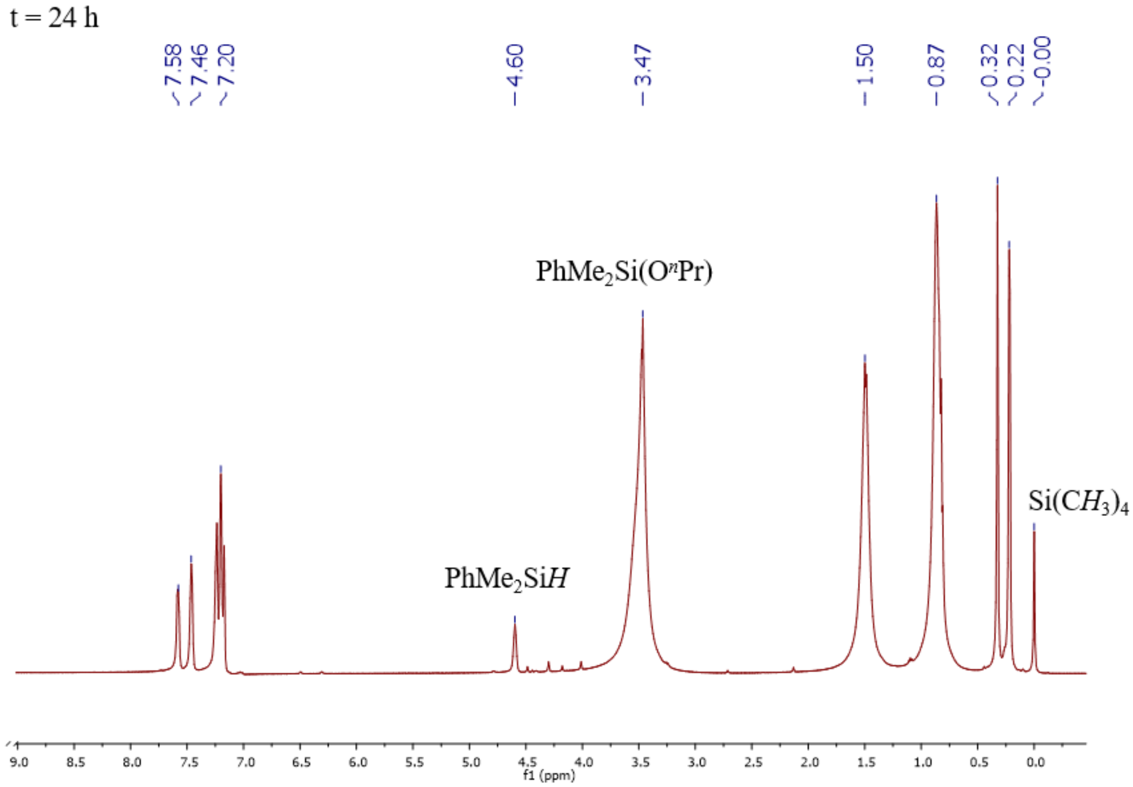

Figure S.39 ^{1}H NMR spectrum of the reaction between PhMe$_2$SiH and ^{n}PrOH catalyzed by **1** (benzene-d_6, 500 MHz)

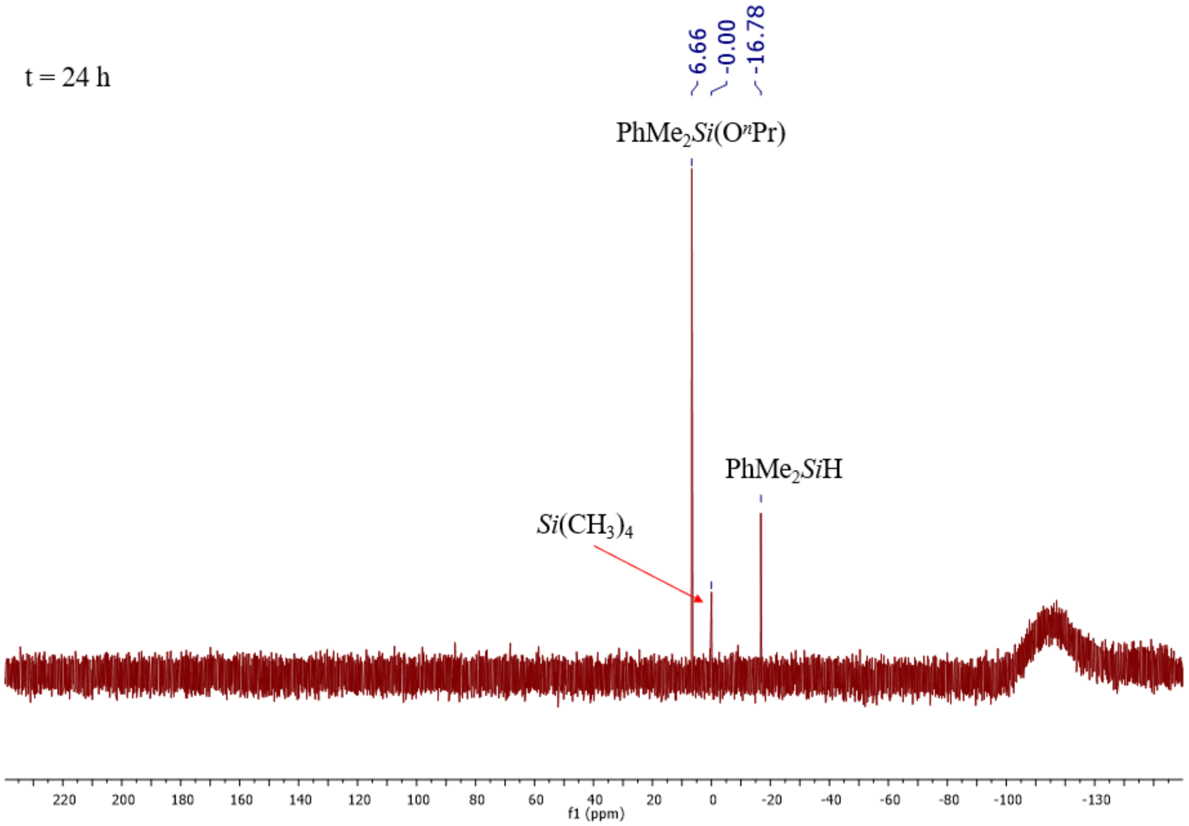

Figure S.40 ^{29}Si{^{1}H} NMR spectrum of the reaction between PhMe$_2$SiH and ^{n}PrOH catalyzed by **1** (benzene-d_6, 99 MHz)

$PhMe_2SiH$ and BnOH.[6,8] An oven-dried scintillation vial containing **1** (3.6 mg, 2.0 mol %) was charged with $PhMe_2SiH$ (76.5 μL, 68.0 mg, 0.5 mmol), followed by 0.5 mL benzene-*d*$_6$, BnOH (259.0 μL, 270.4 mg, 2.5 mmol), and TMS (6.0 μL, 3.8 mg, 8.8 mol %). After 2 h of irradiation, the reaction showed 100% conversion to $PhMe_2Si(OBn)$ according to ^1H NMR spectroscopy.

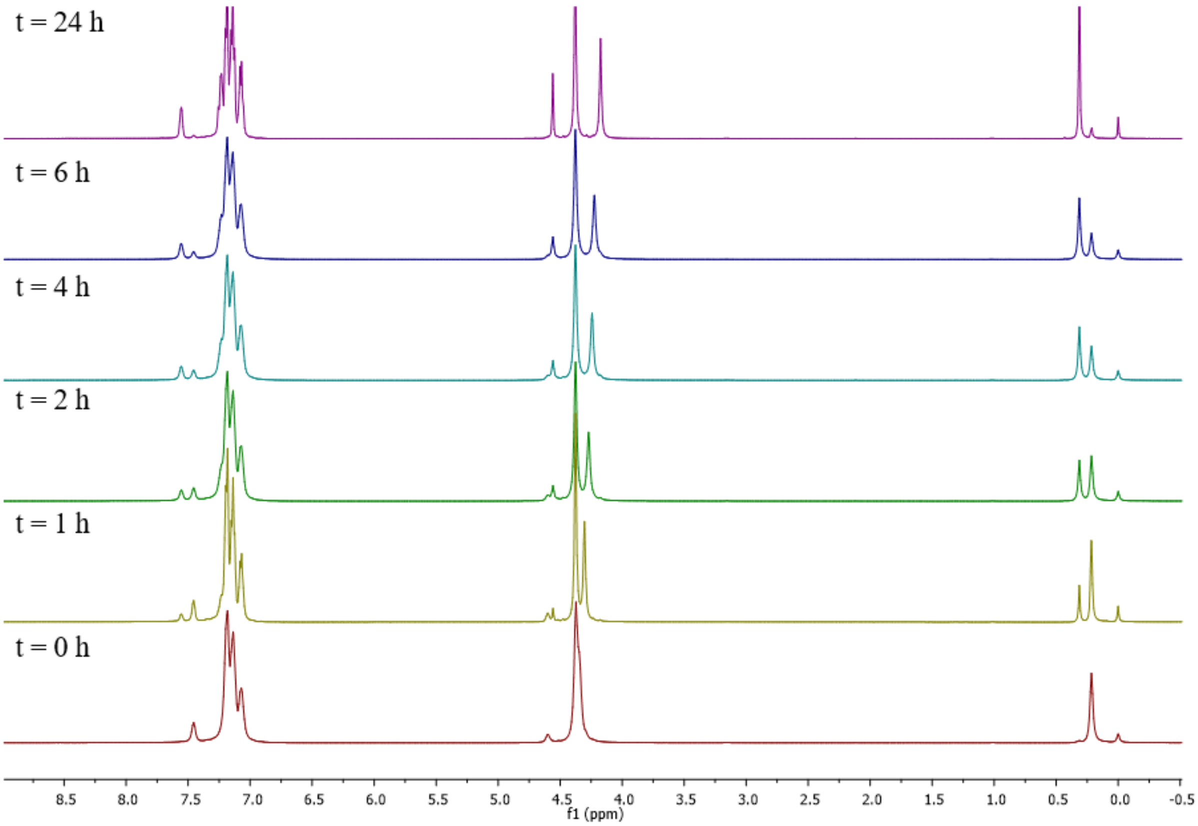

Figure S.41 Stacked ^1H NMR spectra of the reaction between $PhMe_2SiH$ and BnOH catalyzed by **1** (benzene-*d*$_6$, 500 MHz)

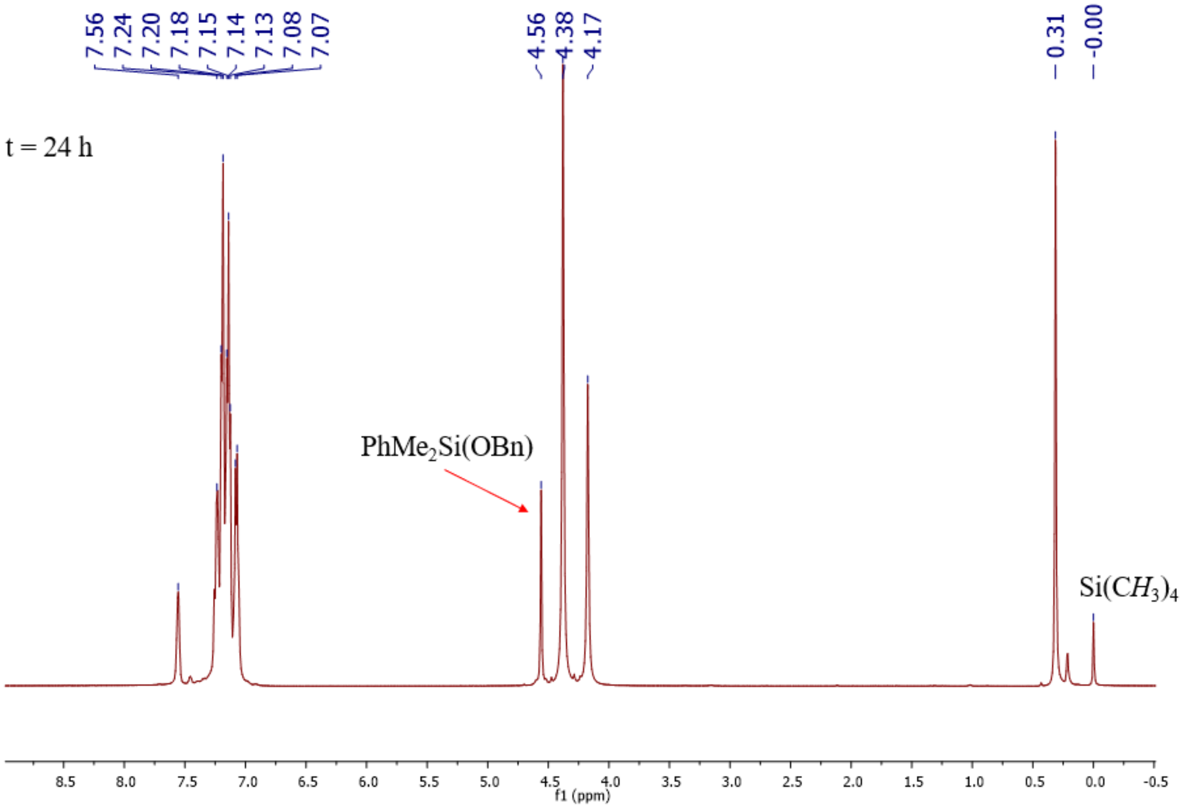

Figure S.42 ^{1}H NMR spectrum of the reaction between PhMe$_2$SiH and BnOH catalyzed by **1** (benzene-d_6, 500 MHz)

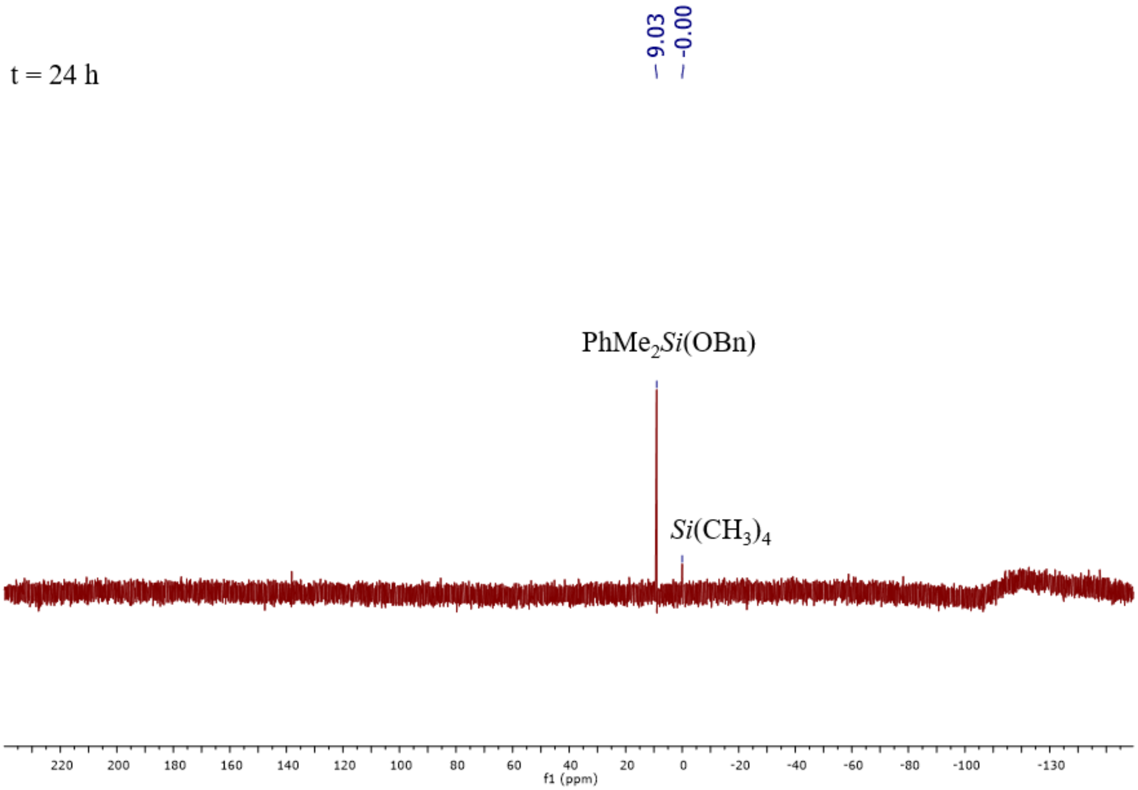

Figure S.43 ^{29}Si{^{1}H} NMR spectrum of the reaction between PhMe$_2$SiH and BnOH catalyzed by **1** (benzene-d_6, 99 MHz)

$PhMe_2SiH$ and $^{i}PrOH$.[9] An oven-dried scintillation vial containing **1** (3.6 mg, 2.0 mol %) was charged with $PhMe_2SiH$ (76.5 µL, 68.0 mg, 0.5 mmol), followed by 0.5 mL benzene-d_6, $^{i}PrOH$ (229.0 µL, 180.0 mg, 3.0 mmol), and TMS (6.0 µL, 3.8 mg, 8.8 mol %). After 24 h of irradiation, the reaction showed 93% conversion to $PhMe_2Si(O^{i}Pr)$ according to ^1H NMR spectroscopy.

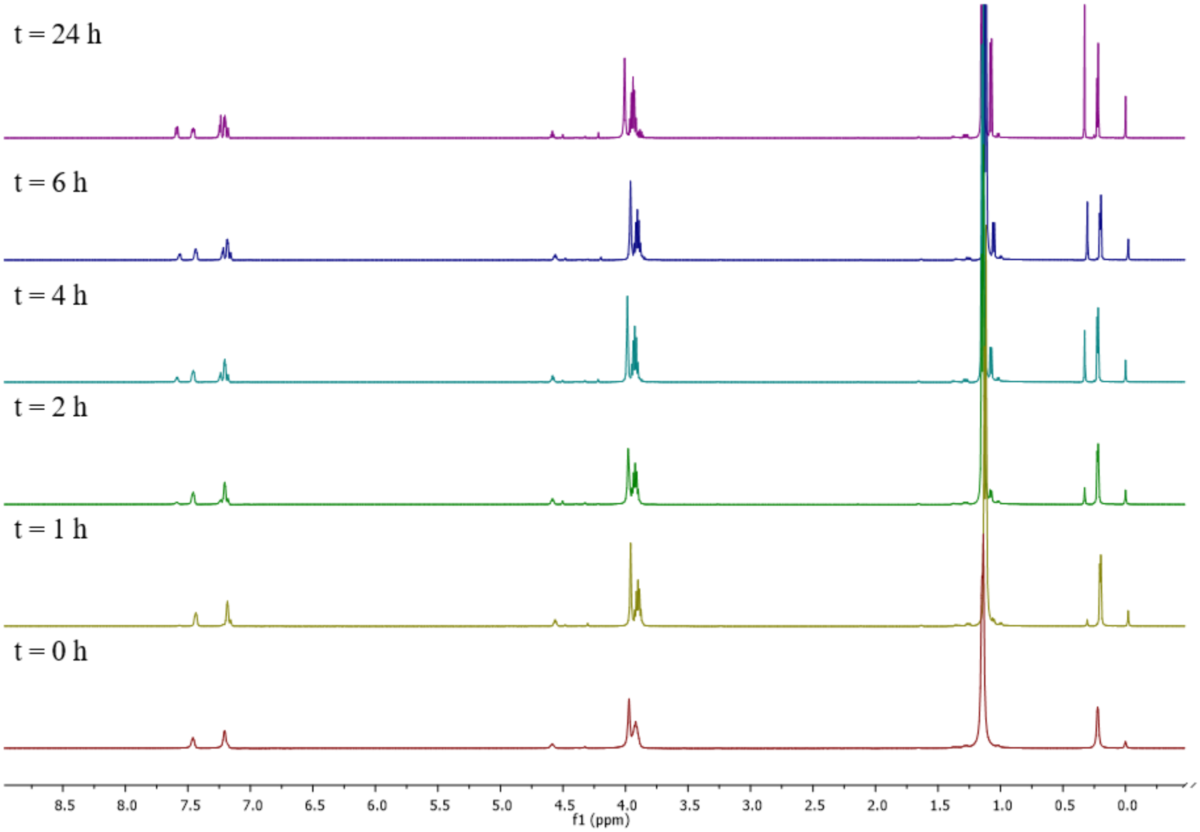

Figure S.44 Stacked ^1H NMR spectra of the reaction between $PhMe_2SiH$ and $^{i}PrOH$ catalyzed by **1** (benzene-d_6, 500 MHz)

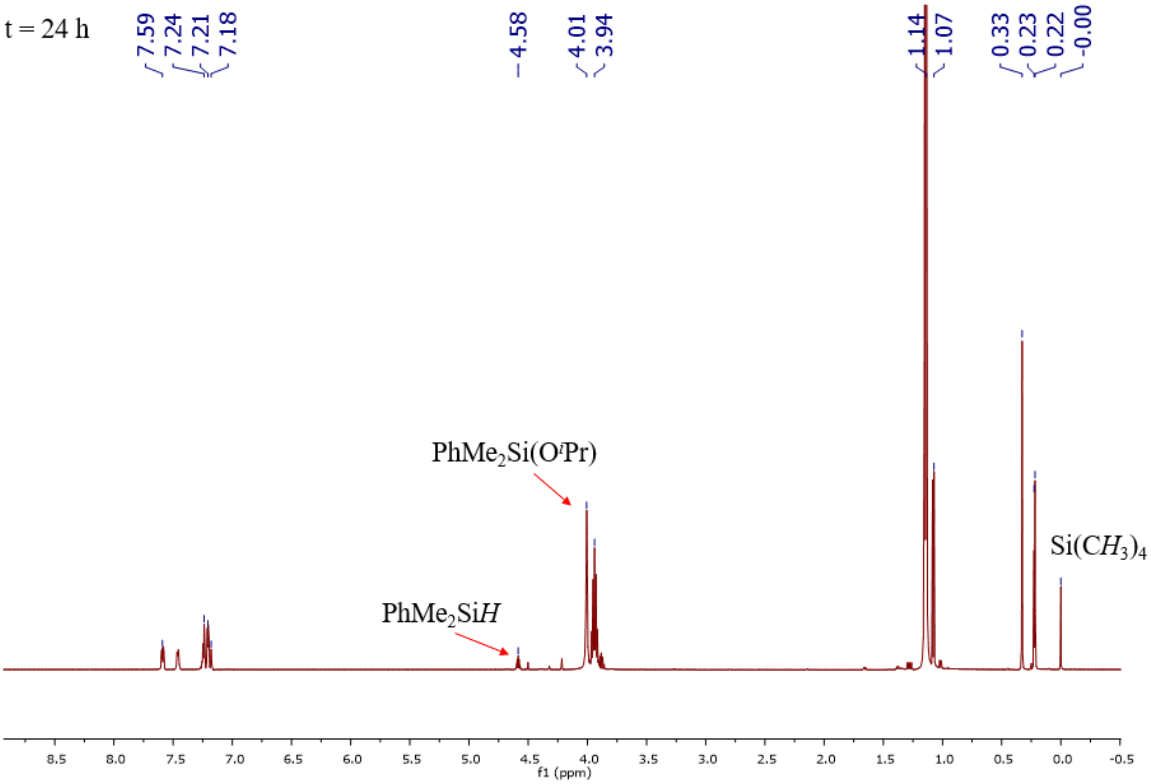

Figure S.45 ^{1}H NMR spectrum of the reaction between $PhMe_2SiH$ and ^{i}PrOH catalyzed by **1** (benzene-d_6, 500 MHz)

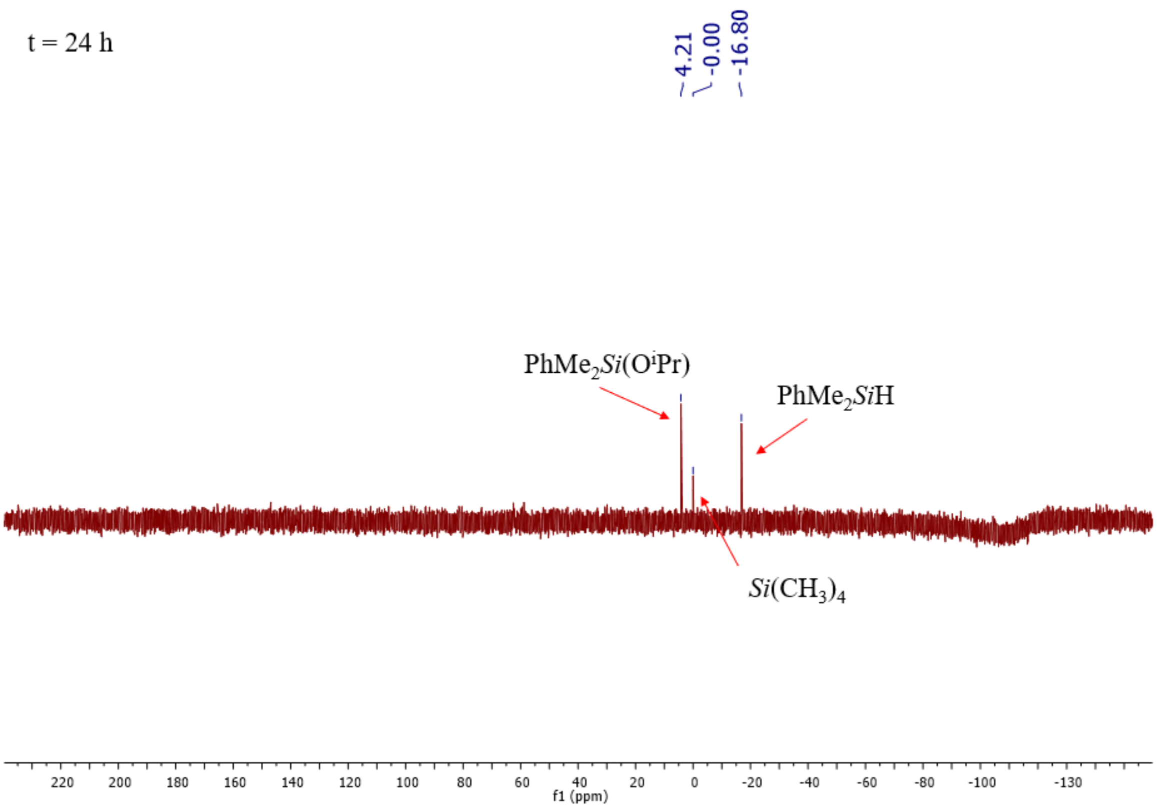

Figure S.46 ^{29}Si{^{1}H} NMR spectrum of the reaction between PhMe$_2$SiH and ^{i}PrOH catalyzed by **1** (benzene-d_6, 99 MHz)

Catalytic Silicon-Nitrogen Heterodehydrocoupling

$PhSiH_3$ and $^nPrNH_2$.[10] An oven-dried scintillation vial containing **1** (3.6 mg, 6.0 mol %) was charged with $PhSiH_3$ (18.7 mg, 0.2 mmol), followed by 0.5 mL benzene-d_6, $^nPrNH_2$ (41.8 mg, 0.7 mmol), and TMS (8.4 mg, 56.0 mol %). After 18 h of irradiation, it was hypothesized that the resonance at δ 5.08 was $PhSiH_2(HN^nPr)$ and was produced in 23% conversion, and the resonance at δ 5.17 was $PhSiH(HN^nPr)_2$ and was produced in 50% yield. A ^1H NMR spectrum was taken at 24 h and showed significant broadening to the point where resonances at δ 5.08 and δ 5.17 were indistinguishable.

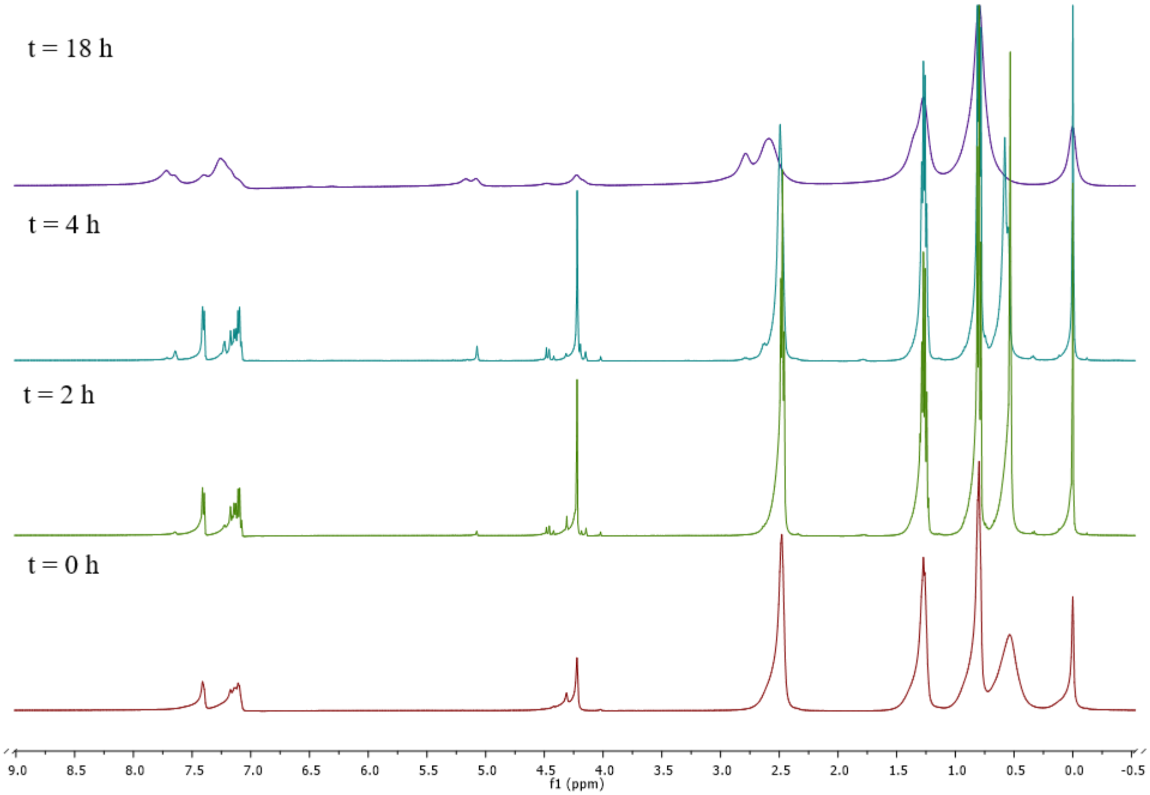

Figure S.47 Stacked ^1H NMR spectra of the reaction between $PhSiH_3$ and $^nPrNH_2$ catalyzed by **1** (benzene-d_6, 500 MHz)

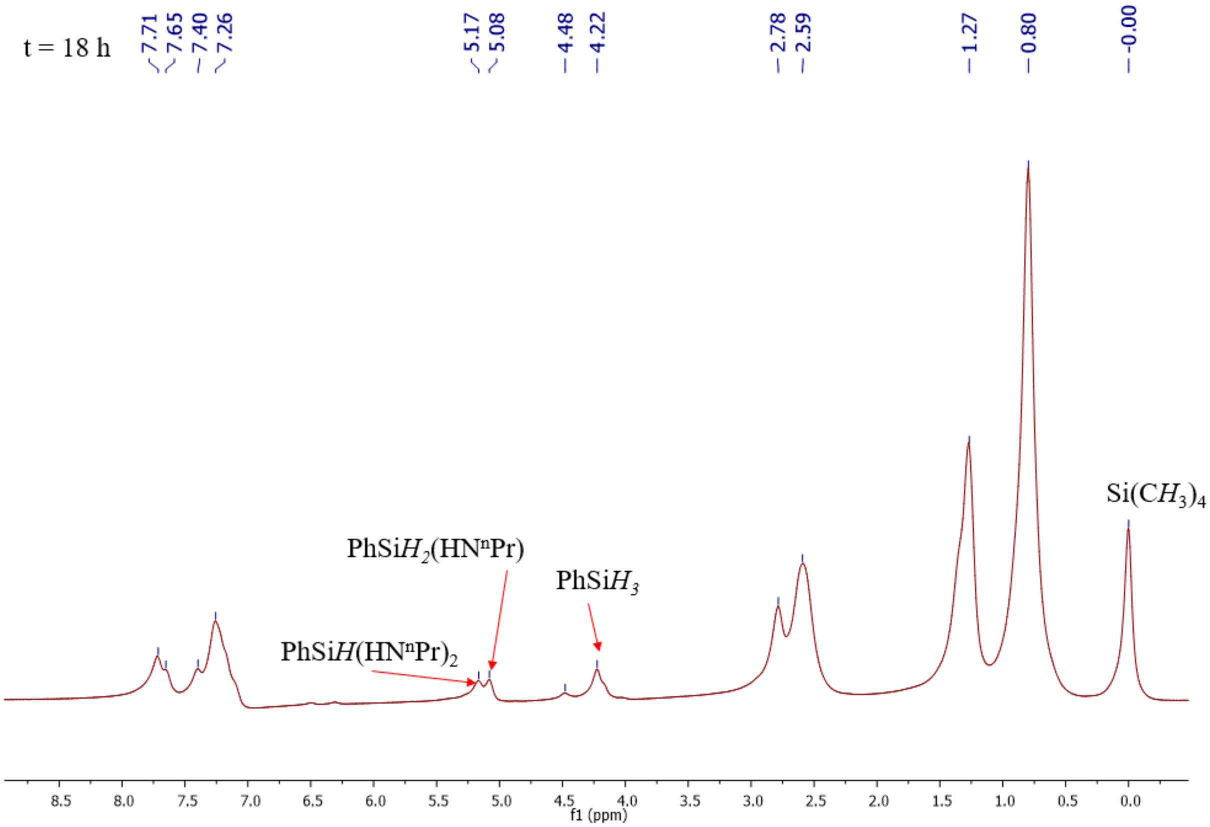

Figure S.48 ^{1}H NMR spectrum of the reaction between $PhSiH_3$ and $^{n}PrNH_2$ catalyzed by **1** (benzene-d_6, 500 MHz)

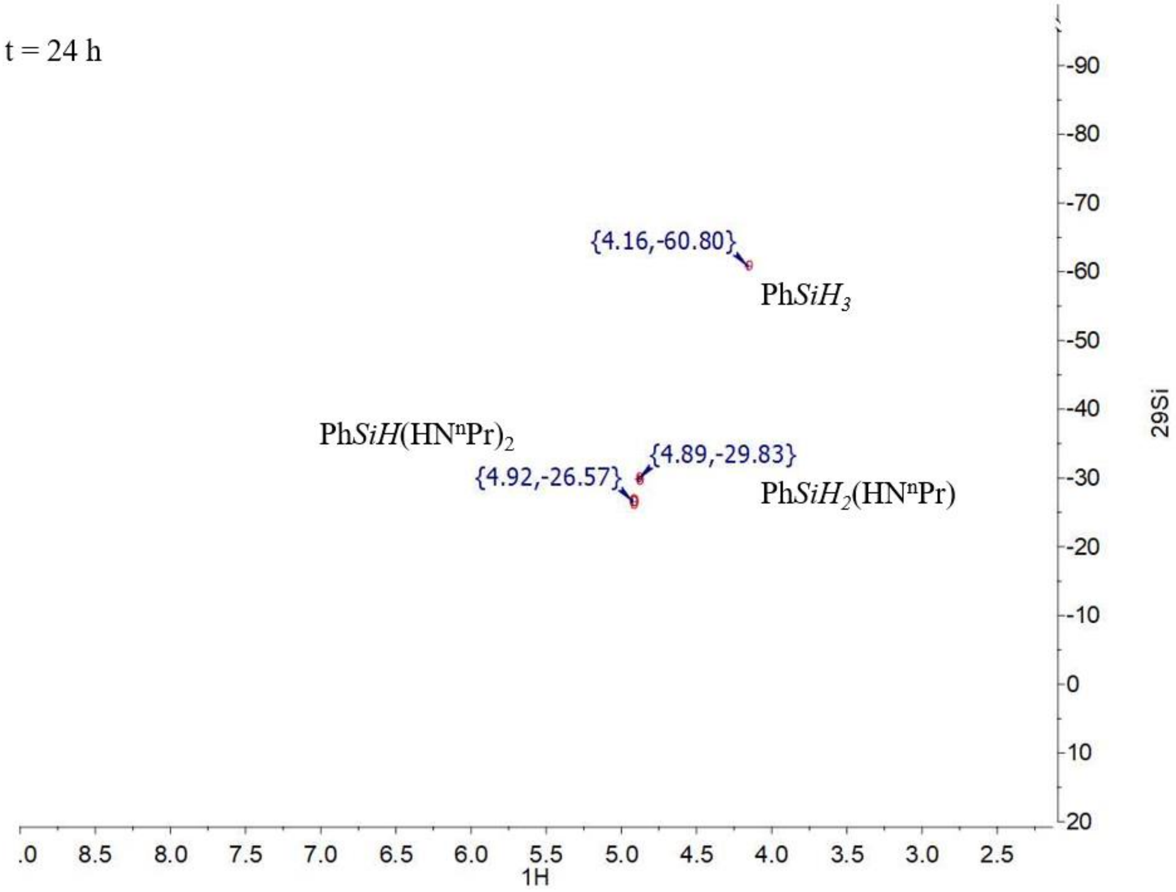

Figure S.49 ^{1}H-$^{29}Si\{^{1}H\}$ HSQC spectra of the reaction between $PhSiH_3$ and $^{n}PrNH_2$ catalyzed by **1** (benzene-d_6, 99 MHz)

$PhSiH_3$ and $^tBuNH_2$.[11,12] An oven-dried scintillation vial containing **1** (3.6 mg, 7.8 mol %) was charged with $PhSiH_3$ (14.3 mg, 0.1 mmol), followed by 0.5 mL benzene-d_6, $^tBuNH_2$ (42.2 mg, 0.6 mmol), and TMS (7.3 mg, 64.0 mol %). After 24 h of irradiation, the mixture showed 89% conversion to $PhSiH_2(HN^tBu)$ and 11% conversion to $PhSiH(HN^tBu)_2$ according to ^1H NMR spectroscopy.

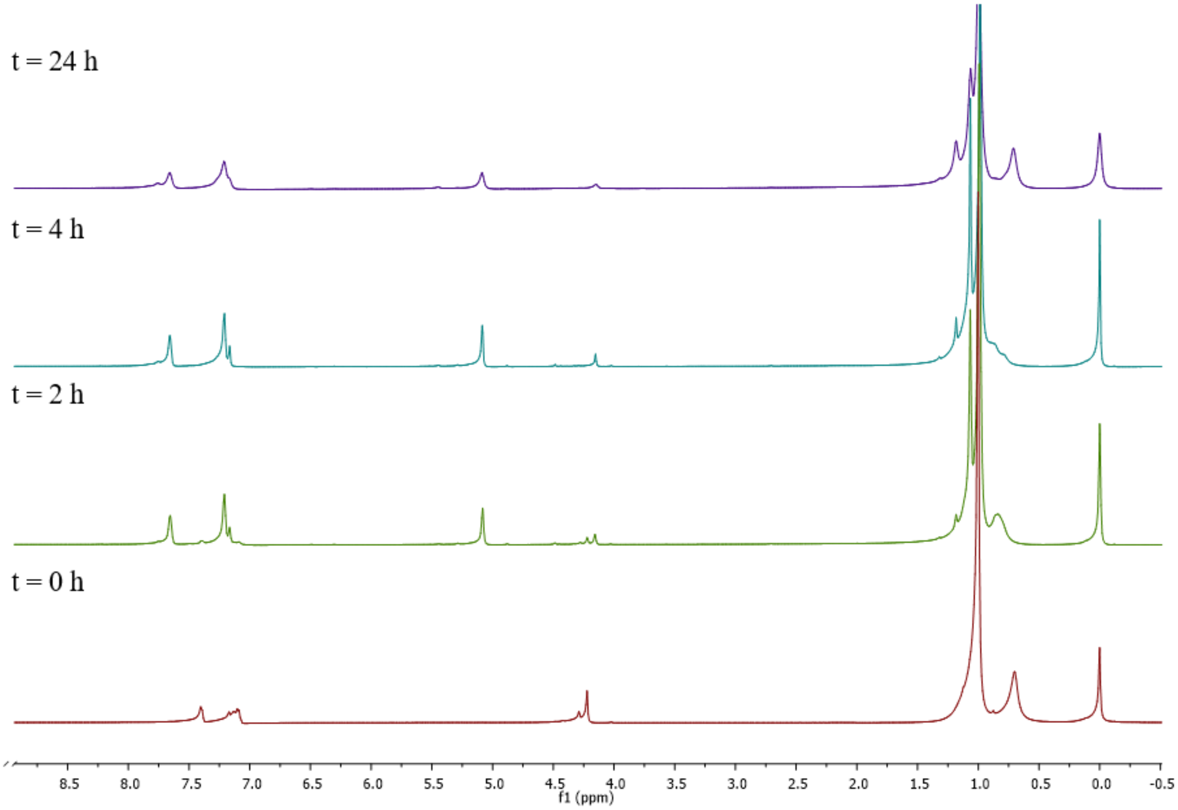

Figure S.50 Stacked ^1H NMR spectra of the reaction between $PhSiH_3$ and $^tBuNH_2$ catalyzed by **1** (benzene-d_6, 500 MHz)

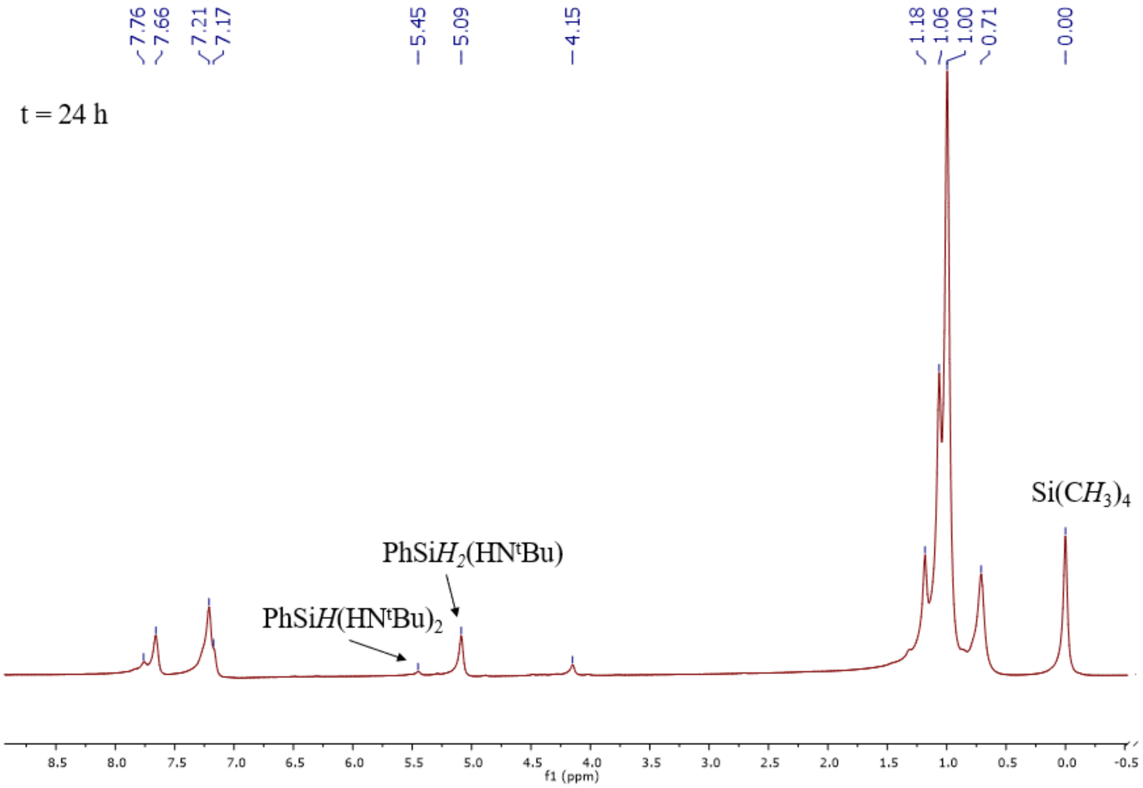

Figure S.51 ^{1}H NMR spectrum of the reaction between $PhSiH_3$ and $^{t}BuNH_2$ catalyzed by **1** (benzene-d_6, 500 MHz)

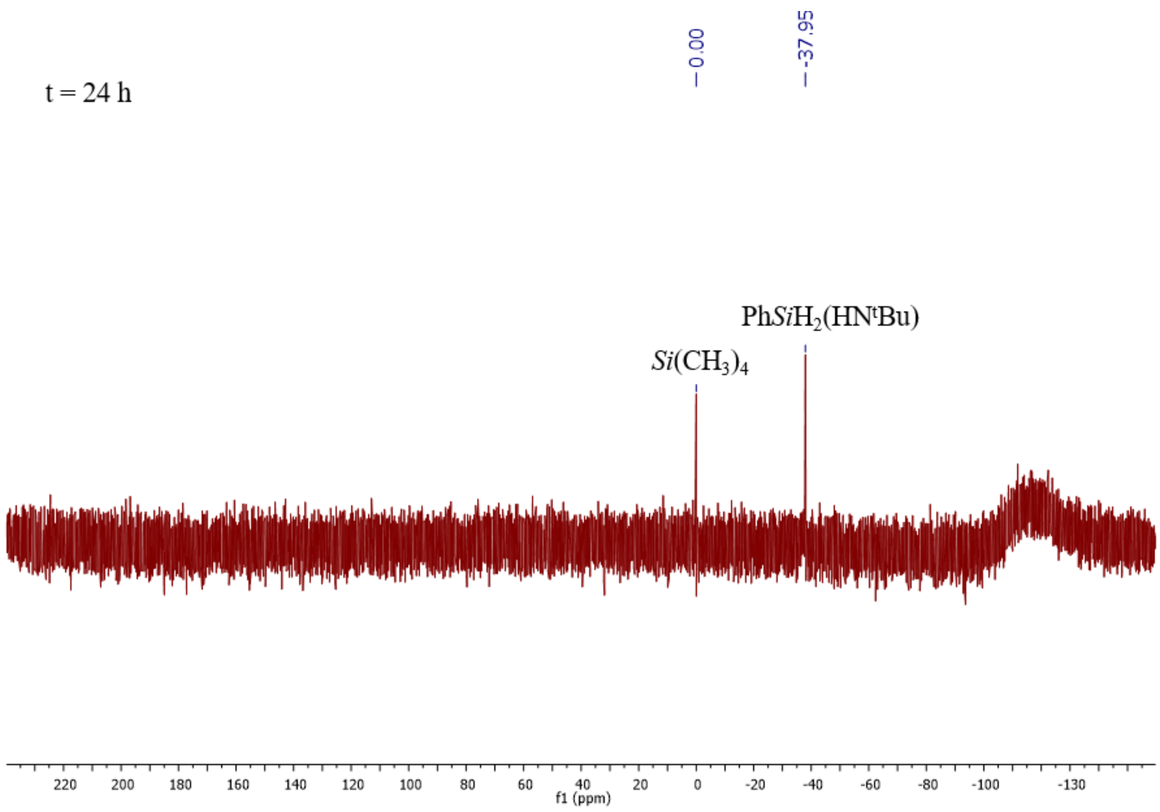

Figure S.52 $^{29}Si\{^{1}H\}$ NMR spectrum of the reaction between $PhSiH_3$ and $^{t}BuNH_2$ catalyzed by **1** (benzene-d_6, 99 MHz)

$PhSiH_3$ and $PhNH_2$. An oven-dried scintillation vial containing **1** (3.6 mg, 9.3 mol %) was charged with $PhSiH_3$ (11.9 mg, 0.1 mmol), followed by 0.5 mL benzene-*d*$_6$, $PhNH_2$ (47.0 mg, 0.5 mmol), and TMS (12.8 mg, 132.0 mol %). After 20 h of irradiation, it was hypothesized that the resonance at δ 5.07 was $PhSiH_2(HNPh)$ which was produced in 20% conversion according to ^1H NMR spectroscopy.

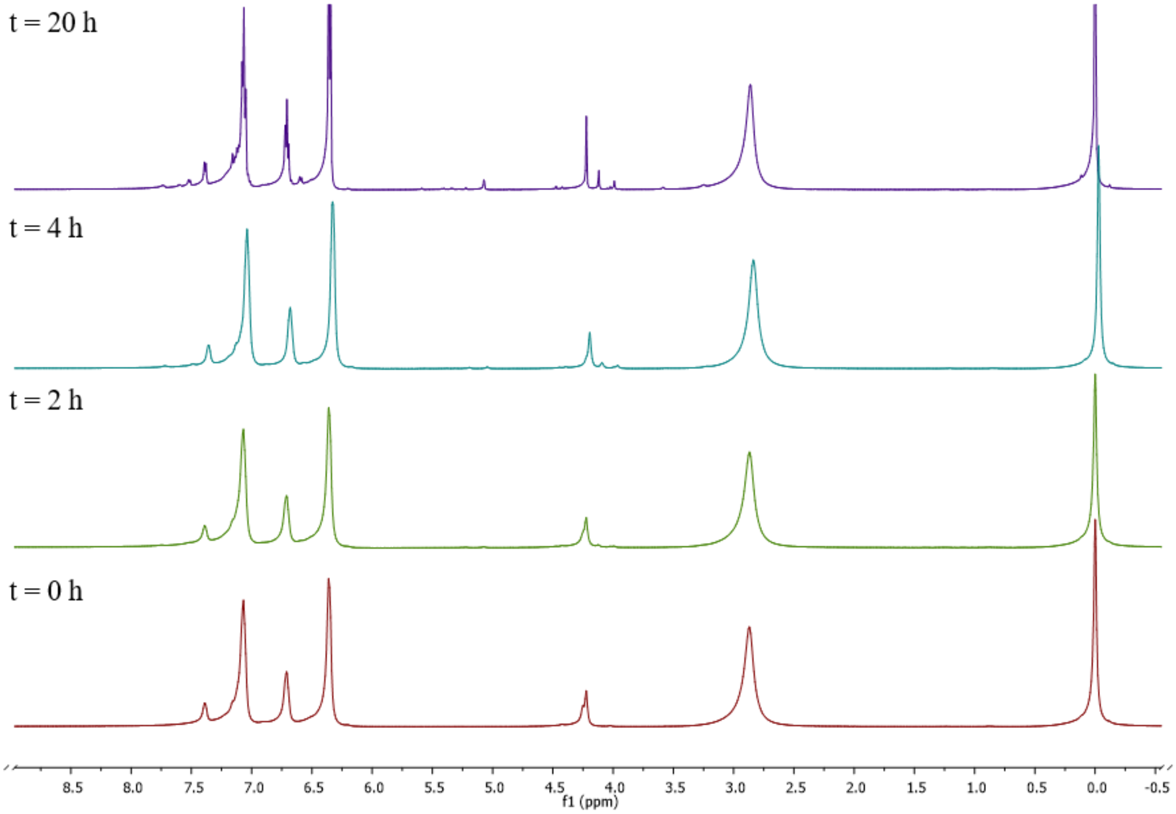

Figure S.53 Stacked ^1H NMR spectra of the reaction between $PhSiH_3$ and $PhNH_2$ catalyzed by **1** (benzene-*d*$_6$, 500 MHz)

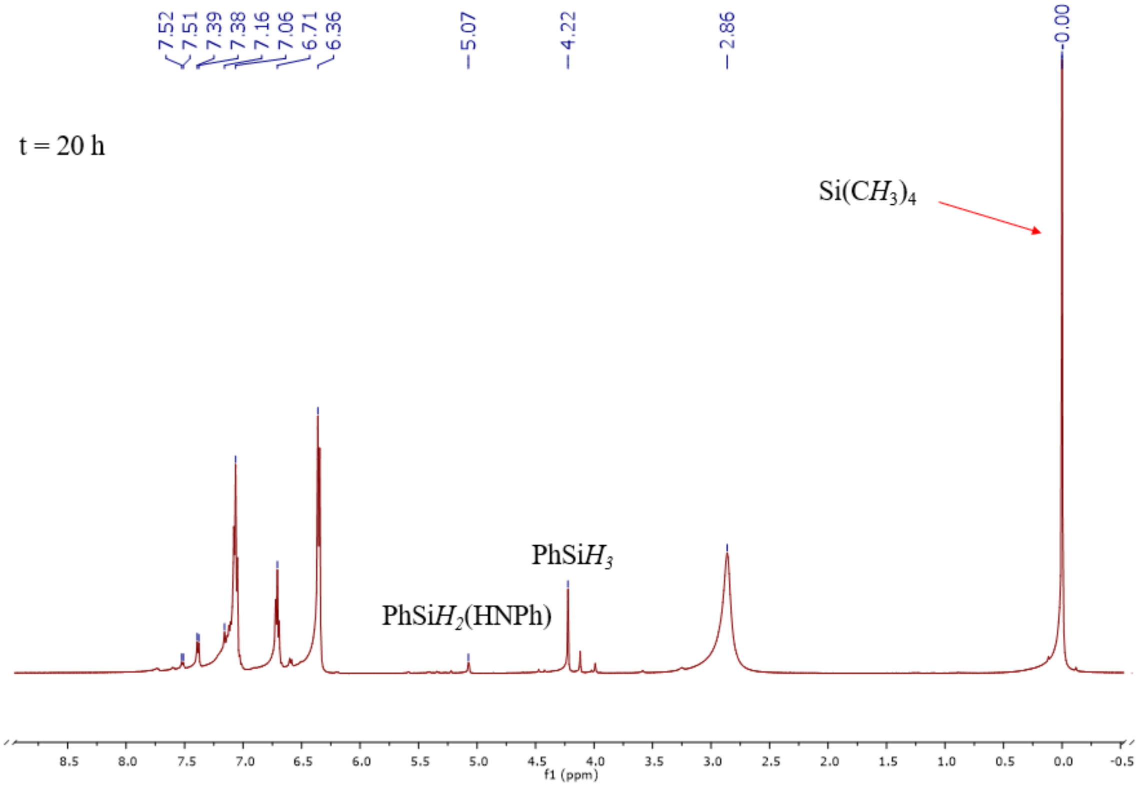

Figure S.54 ^{1}H NMR spectrum of the reaction between $PhSiH_3$ and $PhNH_2$ catalyzed by **1** (benzene-d_6, 500 MHz)

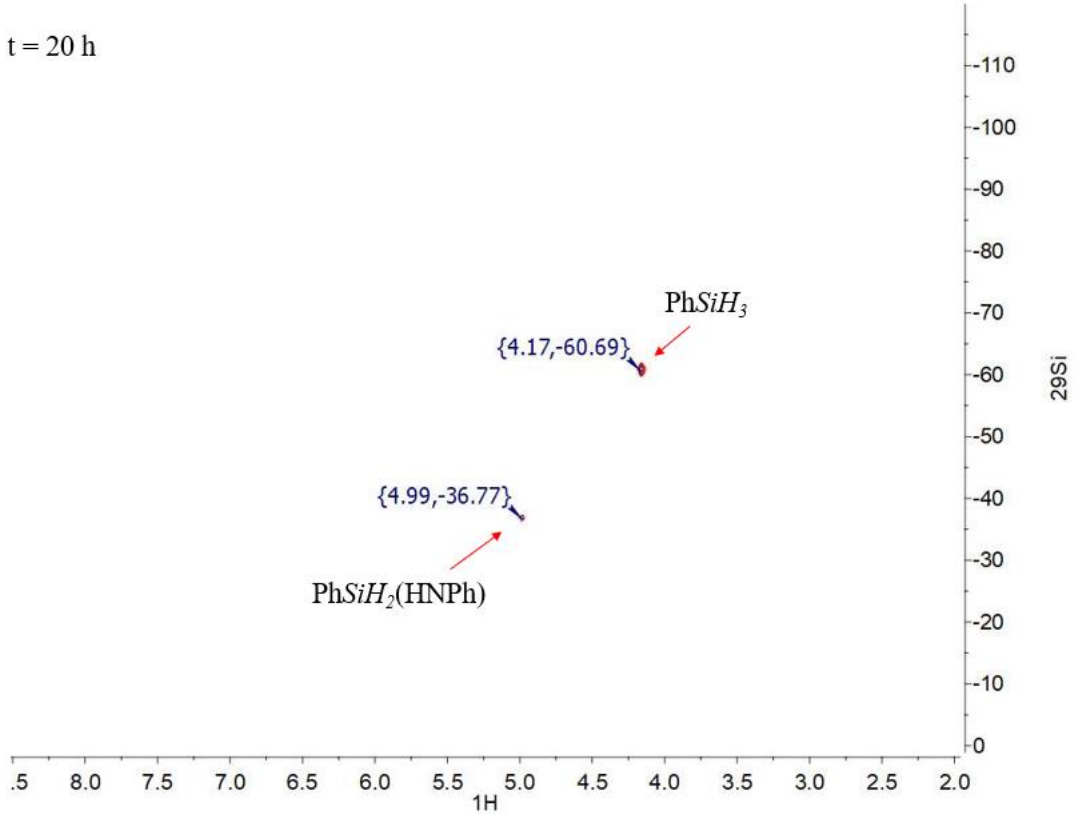

Figure S.55 ^{1}H-^{29}Si{^{1}H} HSQC spectra of the reaction between $PhSiH_3$ and $PhNH_2$ catalyzed by **1** (benzene-d_6, 99 MHz)

$PhSiH_3$ and $^iPrNH_2$.[13] An oven-dried scintillation vial containing **1** (3.6 mg, 8.5 mol %) was charged with $PhSiH_3$ (13.5 mg, 0.1 mmol), followed by 0.5 mL benzene-d_6, $^iPrNH_2$ (26.3 mg, 0.4 mmol), and TMS (4.2 mg, 40.0 mol %). After 20 h of irradiation, the mixture showed 100% conversion to $PhSiH_2(HN^iPr)$ according to ^1H NMR spectroscopy.

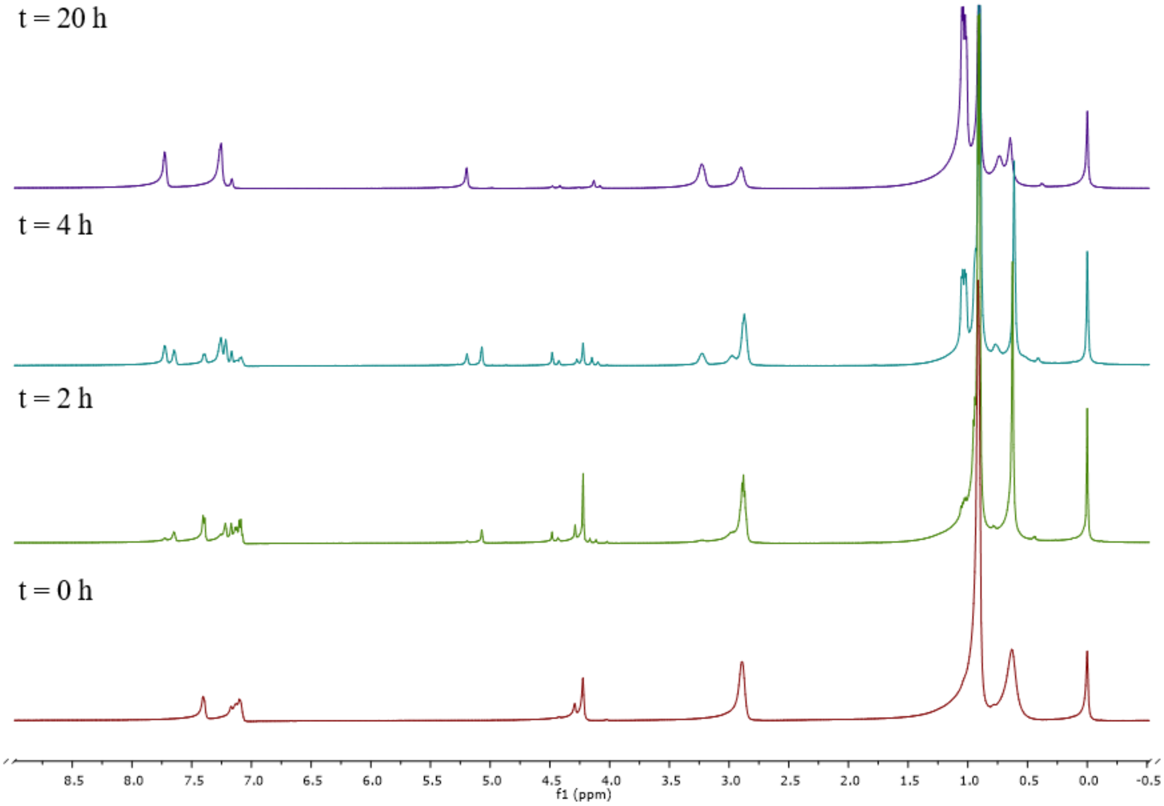

Figure S.56 Stacked ^1H NMR spectra of the reaction between $PhSiH_3$ and $^iPrNH_2$ catalyzed by **1** (benzene-d_6, 500 MHz)

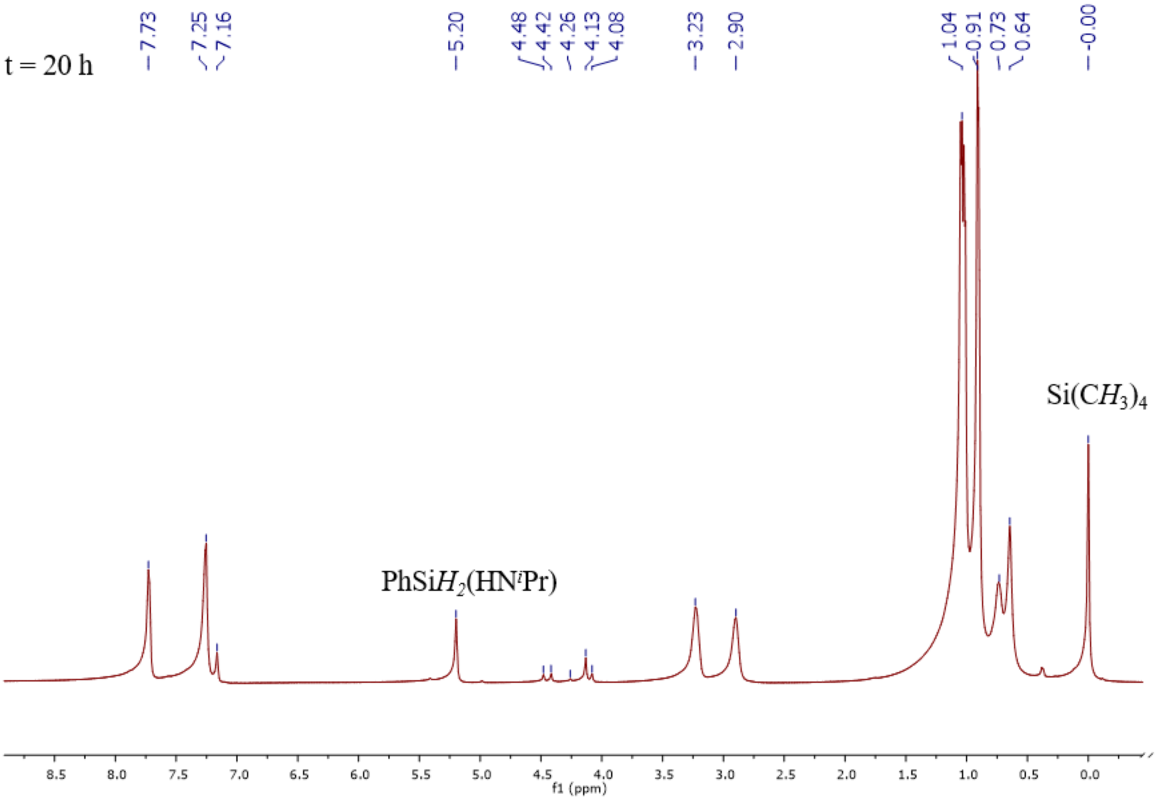

Figure S.57 ^{1}H NMR spectrum of the reaction between $PhSiH_3$ and ^{i}$PrNH_2$ catalyzed by **1** (benzene-d_6, 500 MHz)

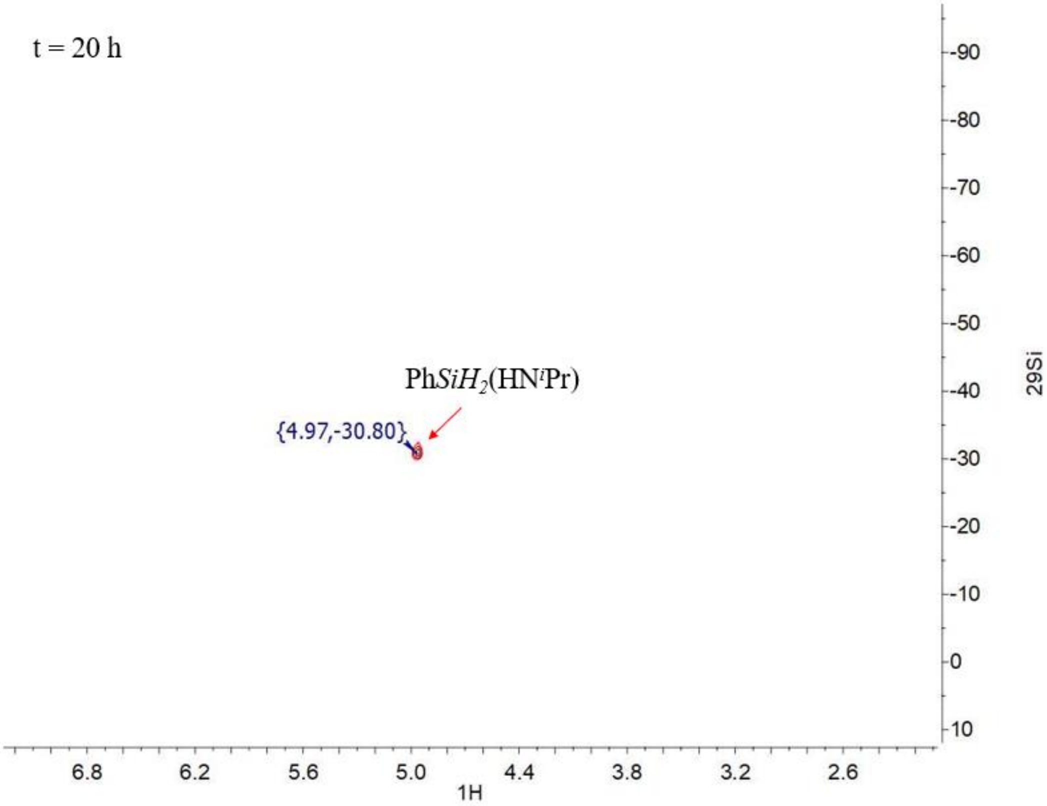

Figure S.58 ^{1}H-^{29}Si{^{1}H} HSQC spectra of the reaction between $PhSiH_3$ and ^{i}$PrNH_2$ catalyzed by **1** (benzene-d_6, 99 MHz)

$PhSiH_3$ and Et_2NH.[14] An oven-dried scintillation vial containing **1** (3.6 mg, 8.5 mol %) was charged with $PhSiH_3$ (12.8 mg, 0.1 mmol), followed by 0.5 mL benzene-*d*$_6$, Et_2NH (41.5 mg, 0.6 mmol), and TMS (5.0 mg, 47.2 mol %). After 4 h of irradiation, the mixture showed 29% conversion to $PhSiH_2(NEt_2)$ and 71% conversion to $PhSiH(NEt_2)_2$ according to ^1H NMR spectroscopy.

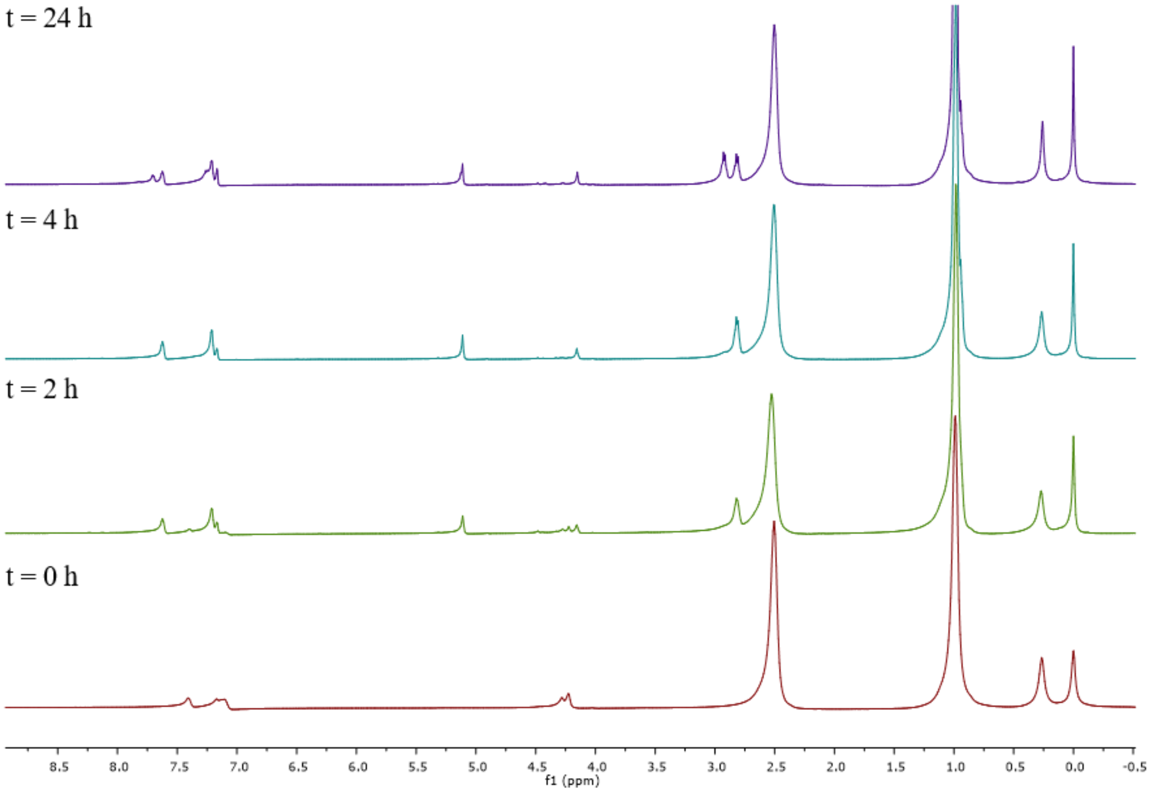

Figure S.59 Stacked ^1H NMR spectra of the reaction between $PhSiH_3$ and Et_2NH catalyzed by **1** (benzene-*d*$_6$, 500 MHz)

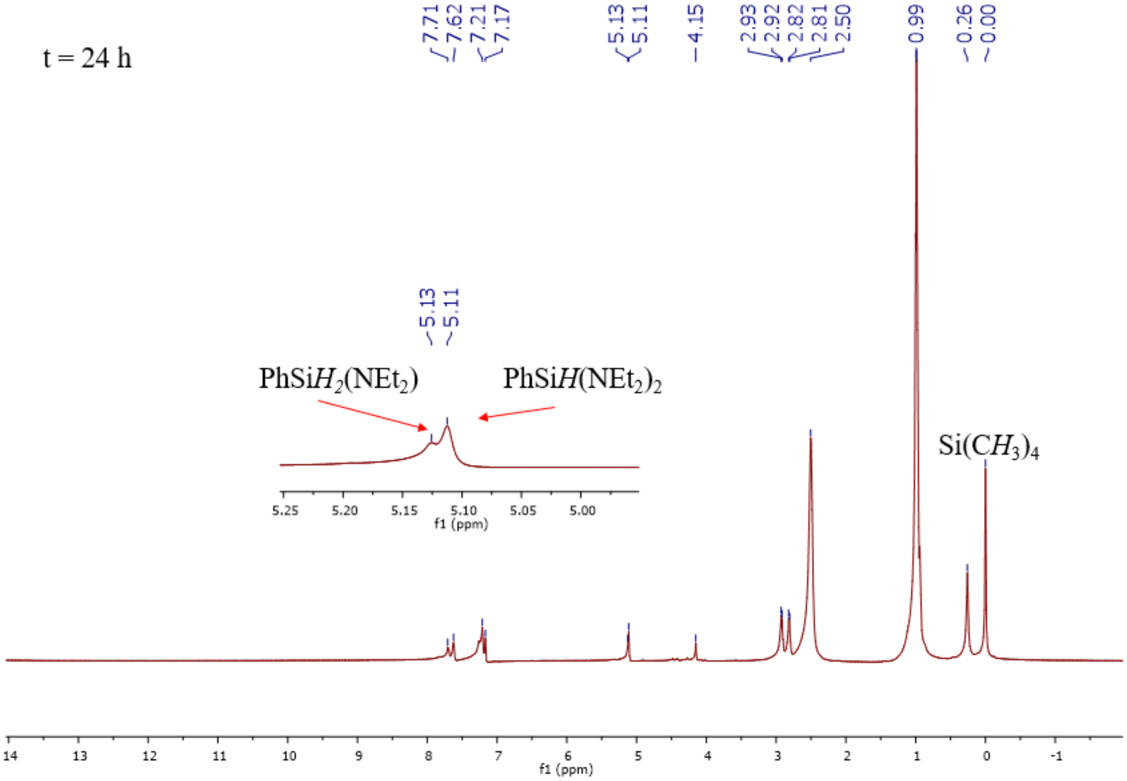

Figure S.60 ^{1}H NMR spectrum of the reaction between $PhSiH_3$ and Et_2NH catalyzed by **1** (benzene-d_6, 500 MHz)

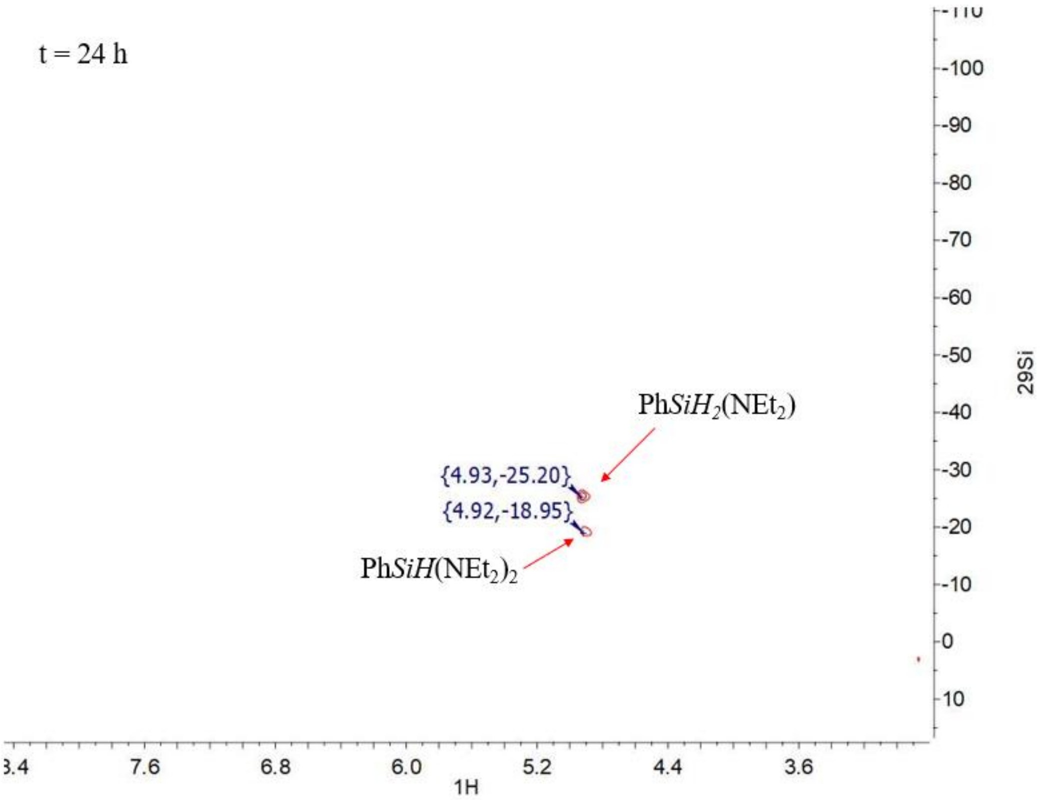

Figure S.61 ^{1}H-$^{29}Si\{^{1}H\}$ HSQC spectra of the reaction between $PhSiH_3$ and Et_2NH catalyzed by **1** (benzene-d_6, 99 MHz)

$PhMeSiH_2$ and $^nPrNH_2$.[13] An oven-dried scintillation vial containing **1** (3.6 mg, 9.3 mol %) was charged with $PhMeSiH_2$ (13.2 mg, 0.1 mmol), followed by 0.5 mL benzene-*d*$_6$, $^nPrNH_2$ (27.5 g, 0.5 mmol), and TMS (6.2 mg, 64.0 mol %). After 24 h of irradiation, the mixture showed 60% conversion to PhMeSiH(HN^{n}Pr) according to ^1H NMR spectroscopy.

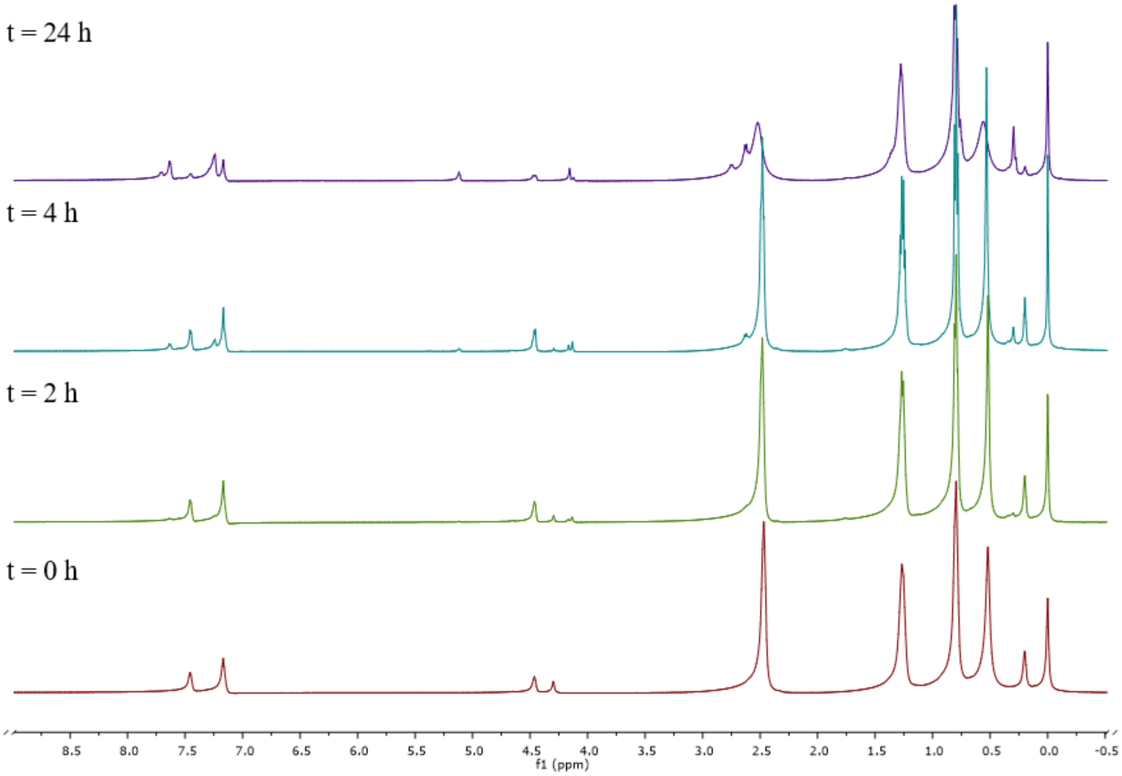

Figure S.62 Stacked ^1H NMR spectra of the reaction between $PhMeSiH_2$ and $^nPrNH_2$ catalyzed by **1** (benzene-*d*$_6$, 500 MHz)

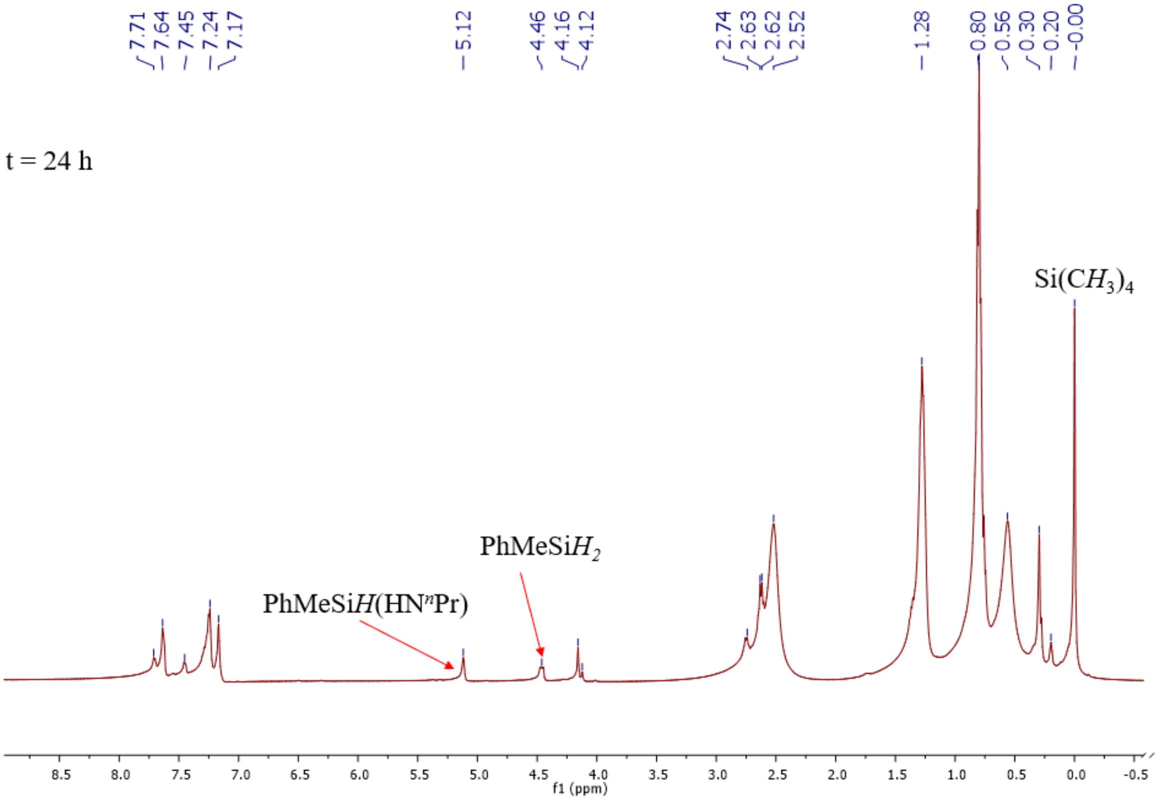

Figure S.63 ^{1}H NMR spectrum of the reaction between $PhMeSiH_2$ and ^{n}$PrNH_2$ catalyzed by **1** (benzene-d_6, 500 MHz)

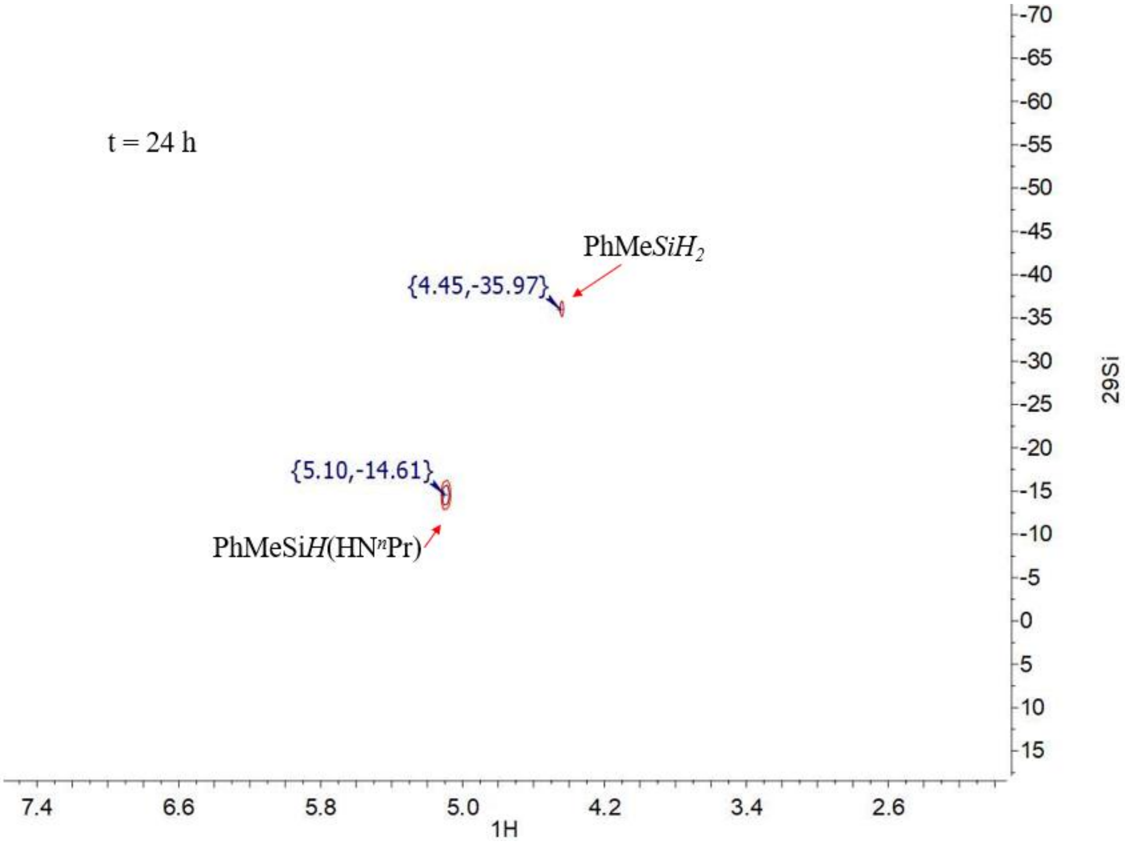

Figure S.64 ^{1}H-^{29}Si{^{1}H} HSQC spectra of the reaction between $PhMeSiH_2$ and $^{n}PrNH_2$ catalyzed by **1** (benzene-d_6, 99 MHz)

$PhMeSiH_2$ and ^{t}BuNH$_2$.[13] An oven-dried scintillation vial containing **1** (3.6 mg, 7.8 mol %) was charged with $PhMeSiH_2$ (15.7 mg, 0.1 mmol), followed by 0.5 mL benzene-d_6, ^{t}BuNH$_2$ (39.1 mg, 0.5 mmol), and TMS (5.3 mg, 46.2 mol %). After 24 h of irradiation, the reaction showed 100% conversion to PhMeSiH(HN^{t}Bu) according to ^{1}H NMR spectroscopy.

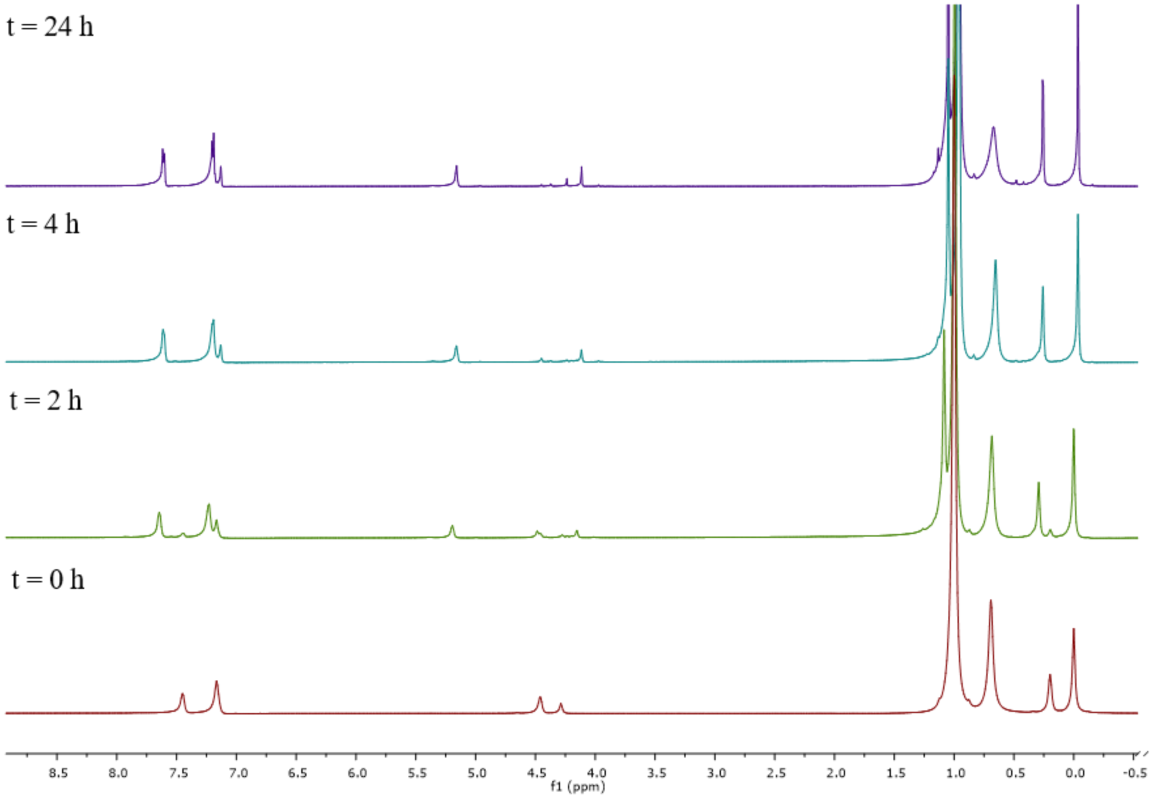

Figure S.65 Stacked ^{1}H NMR spectra of the reaction between $PhMeSiH_2$ and ^{t}BuNH$_2$ catalyzed by **1** (benzene-d_6, 500 MHz)

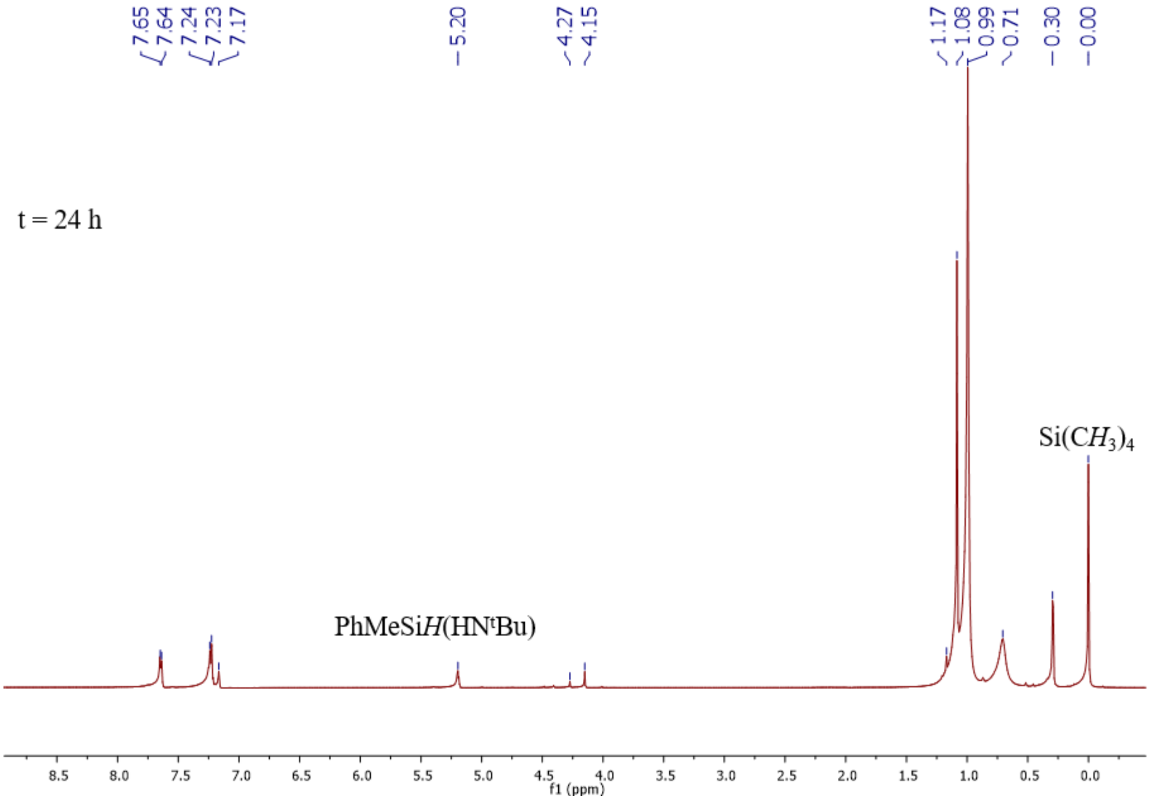

Figure S.66 ^{1}H NMR spectrum of the reaction between $PhMeSiH_2$ and ^{t}$BuNH_2$ catalyzed by **1** (benzene-d_6, 500 MHz)

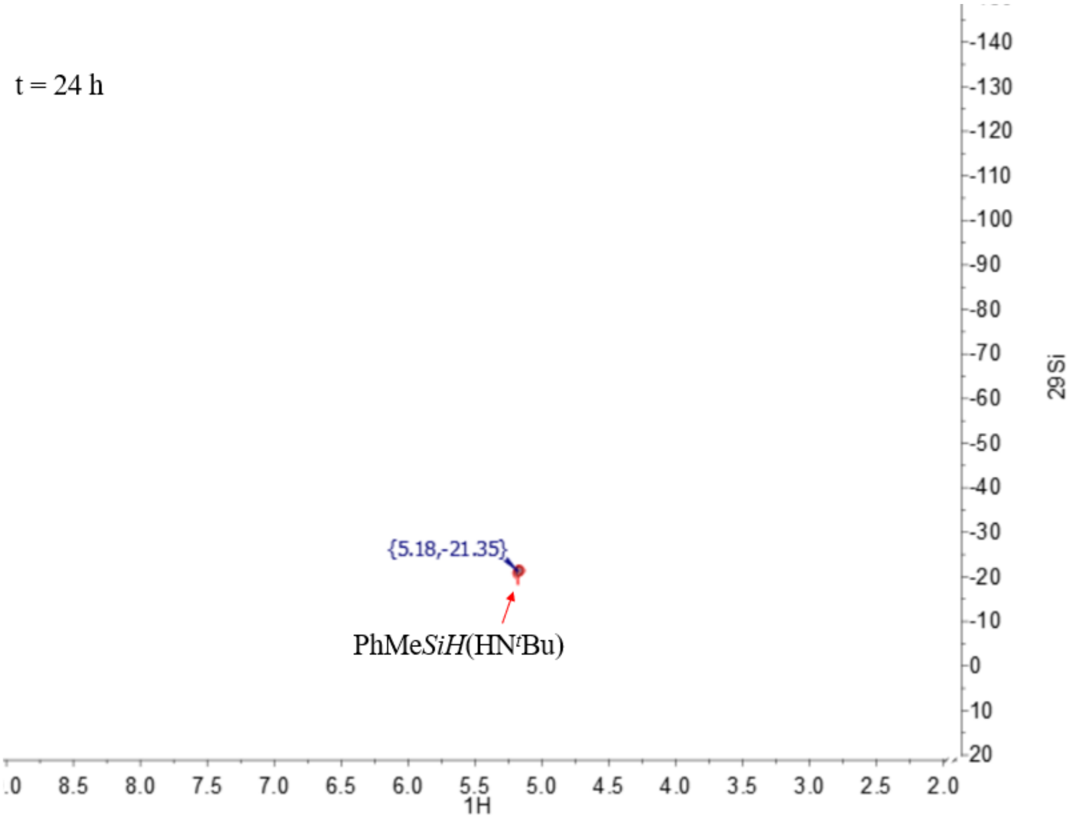

Figure S.67 ^{1}H-^{29}Si{^{1}H} HSQC spectra of the reaction between $PhMeSiH_2$ and $^{t}BuNH_2$ catalyzed by **1** (benzene-d_6, 99 MHz)

PhMeSiH$_2$ and ^{i}PrNH$_2$.[13] An oven-dried scintillation vial containing **1** (3.6 mg, 9.3 mol %) was charged with PhMeSiH$_2$ (13.5 g, 0.1 mmol) followed by 0.5 mL benzene-*d*$_6$, ^{i}PrNH$_2$ (26.3 mg, 0.4 mmol), and TMS (6.3 mg, 64.9 mol %). After 24 h of irradiation, it was hypothesized that the reaction reached 100% conversion from PhMeSiH$_2$ according to ^{1}H NMR spectroscopy.

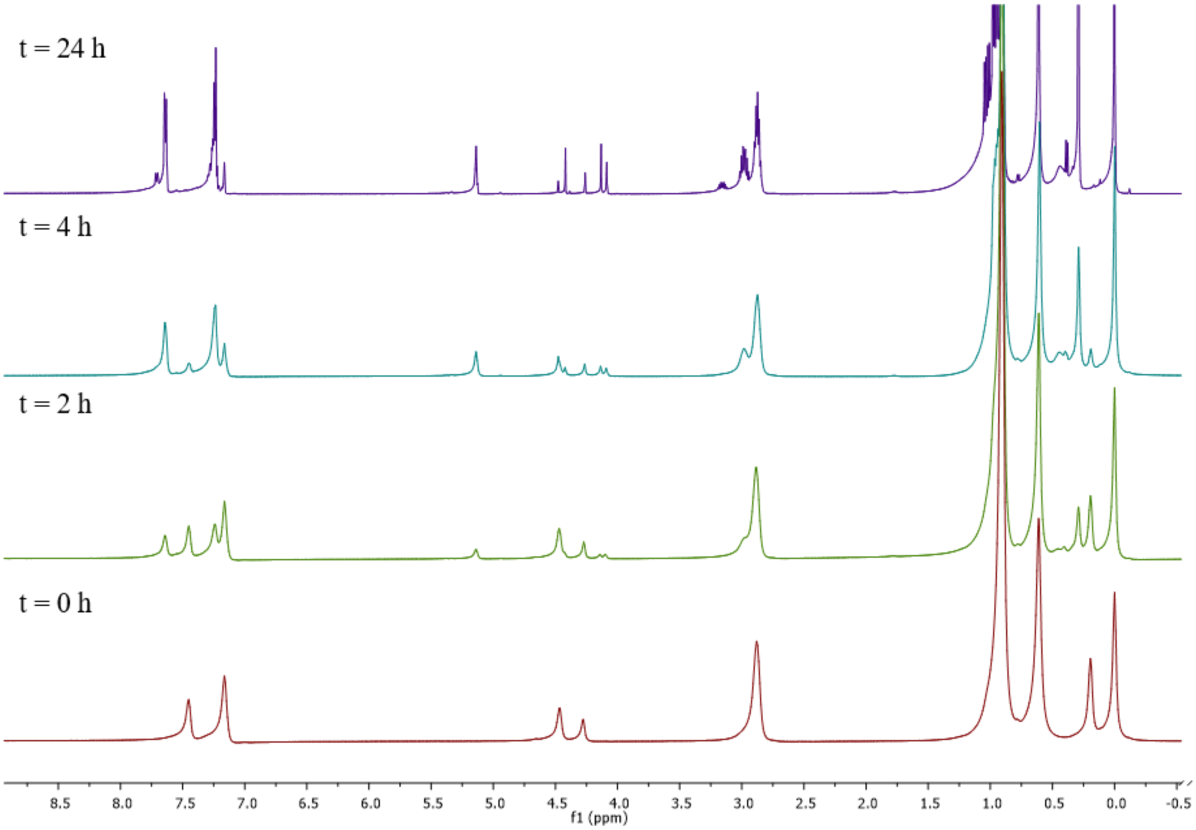

Figure S.68 Stacked ^{1}H NMR spectra of the reaction between PhMeSiH$_2$ and ^{i}PrNH$_2$ catalyzed by **1** (benzene-*d*$_6$, 500 MHz)

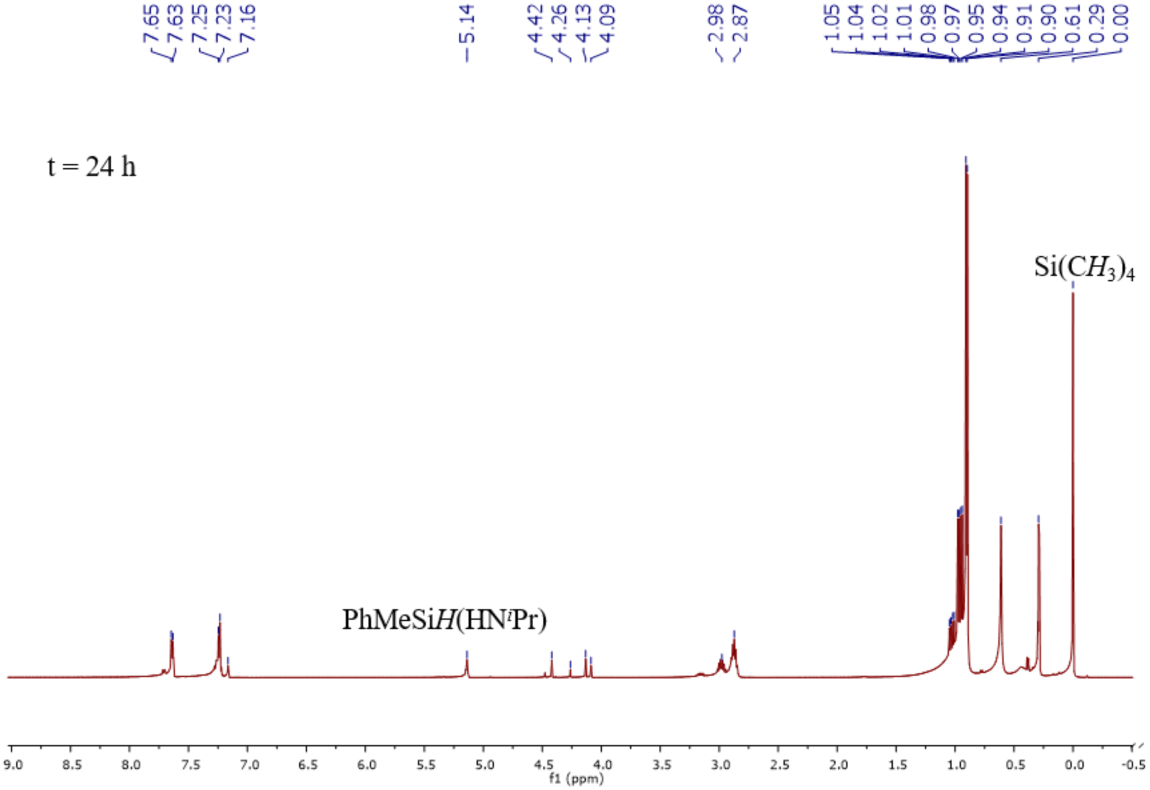

Figure S.69 ^{1}H NMR spectrum of the reaction between PhMeSiH$_2$ and ^{i}PrNH$_2$ catalyzed by **1** (benzene-d_6, 500 MHz)

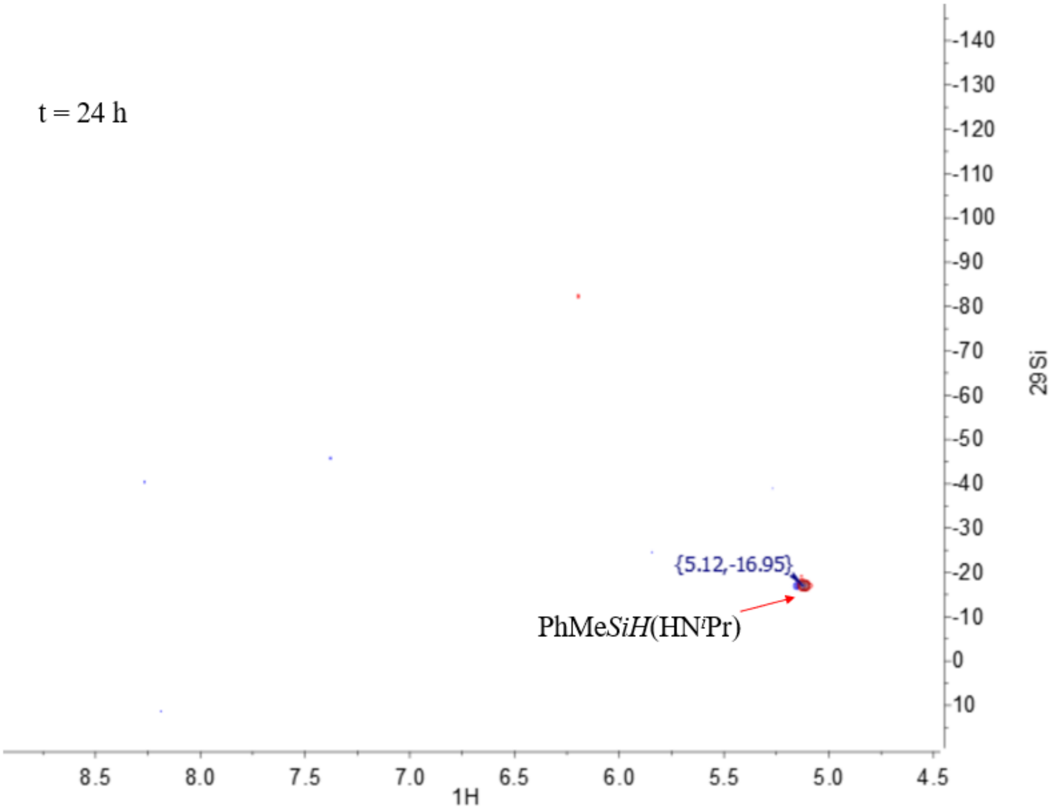

Figure S.70 ^{1}H-^{29}Si{^{1}H} HSQC spectra of the reaction between PhMeSiH_2 and ^{i}PrNH_2 catalyzed by **1** (benzene-*d*$_6$, 99 MHz)

$PhMeSiH_2$ and Et_2NH.[14] An oven-dried scintillation vial containing **1** (3.6 mg, 10.2 mol %) was charged with $PhMeSiH_2$ (12.8 mg, 0.1 mmol), followed by 0.5 mL benzene-*d*$_6$, Et_2NH (41.5 mg, 0.6 mmol), and TMS (4.8 mg, 54.4 mol %). After 24 h of irradiation, the reaction showed 100% conversion from $PhMeSiH_2$ according to ^1H NMR spectroscopy.

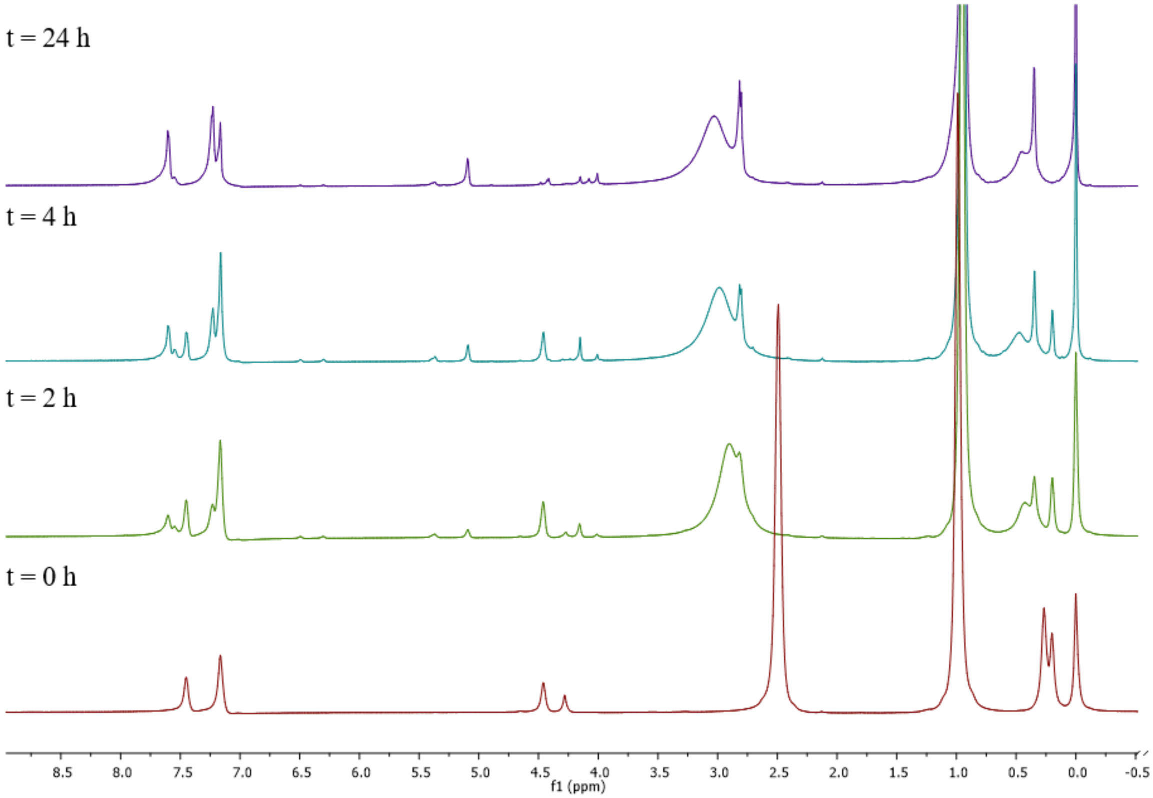

Figure S.71 Stacked ^1H NMR spectra of the reaction between $PhMeSiH_2$ and Et_2NH catalyzed by **1** (benzene-*d*$_6$, 500 MHz)

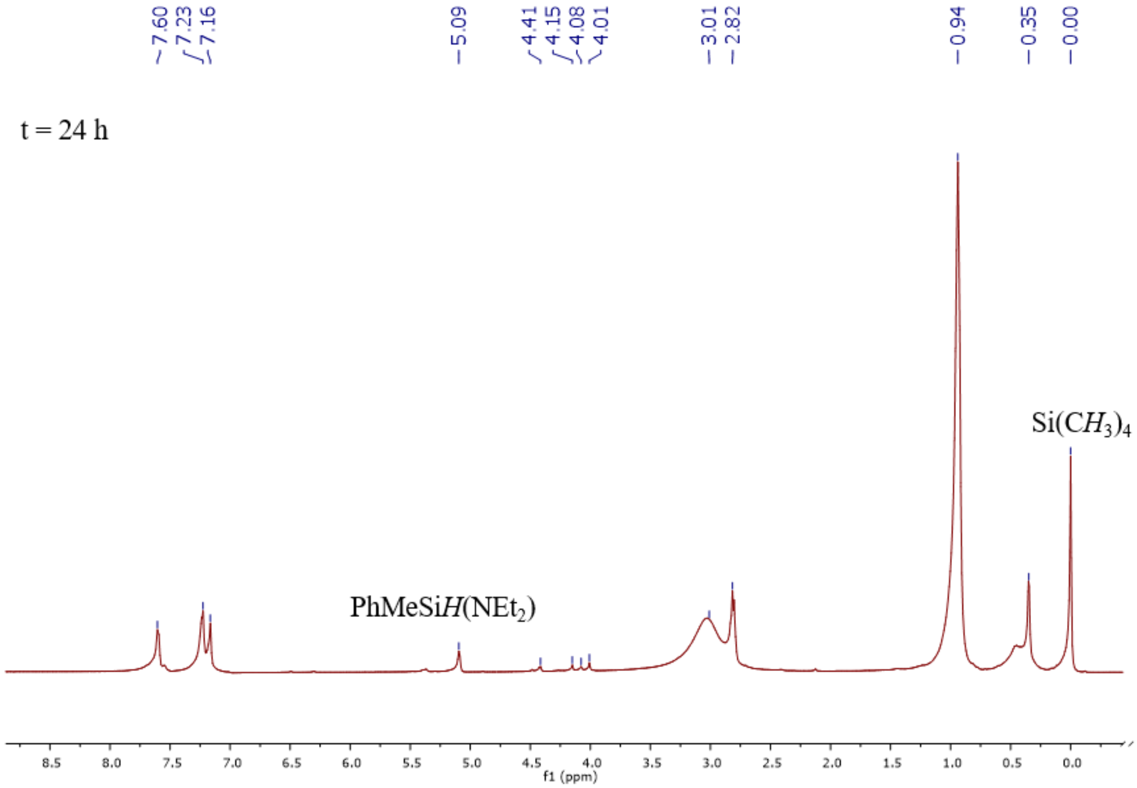

Figure S.72 ^{1}H NMR spectrum of the reaction between PhMeSiH$_2$ and Et$_2$NH catalyzed by **1** (benzene-d_6, 500 MHz)

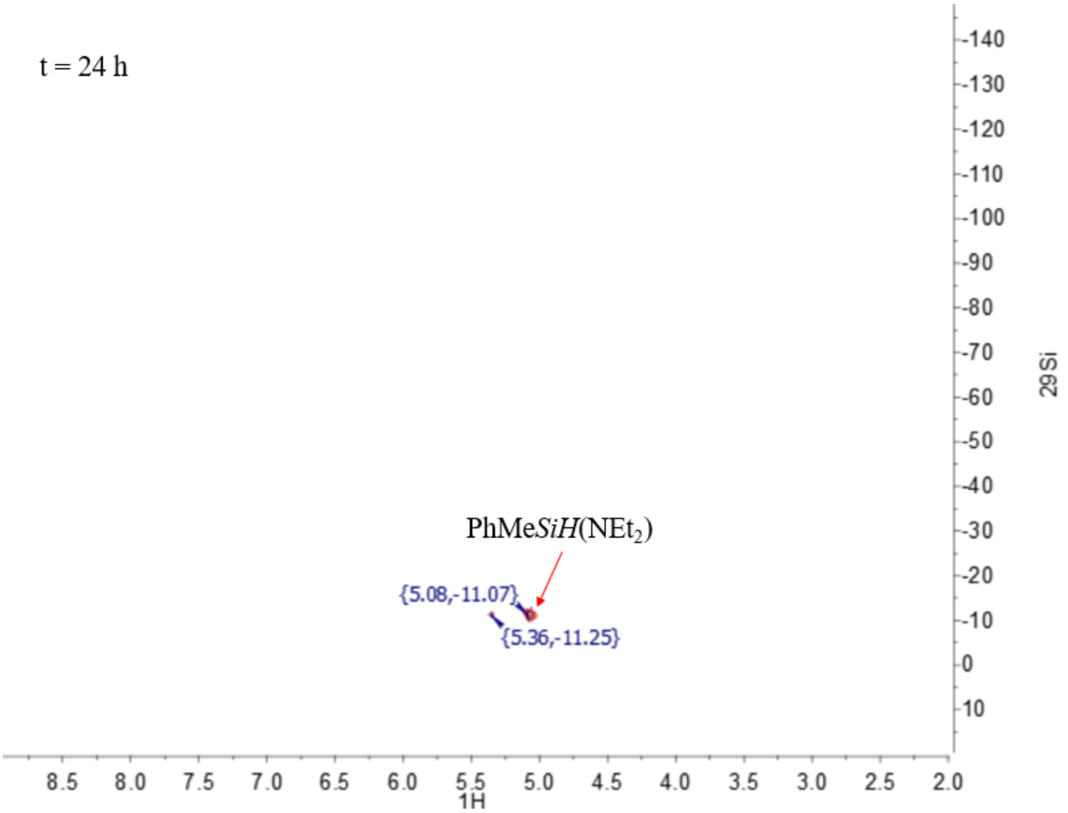

Figure S.73 ^{1}H-$^{29}Si\{^{1}H\}$ HSQC spectra of the reaction between $PhMeSiH_2$ and Et_2NH catalyzed by **1** (benzene-d_6, 99 MHz)

Ph_2SiH_2 and $^nPrNH_2$.[13] An oven-dried scintillation vial containing **1** (3.6 mg, 6.8 mol %) was charged with Ph_2SiH_2 (28.4 mg, 0.2 mmol), followed by 0.5 mL benzene-d_6, $^nPrNH_2$ (37.0 mg, 0.6 mmol), and TMS (5.2 mg, 39.3 mol %). After 24 h of irradiation, the reaction showed 74% conversion to $Ph_2SiH(HN^nPr)$ according to ^1H NMR spectroscopy.

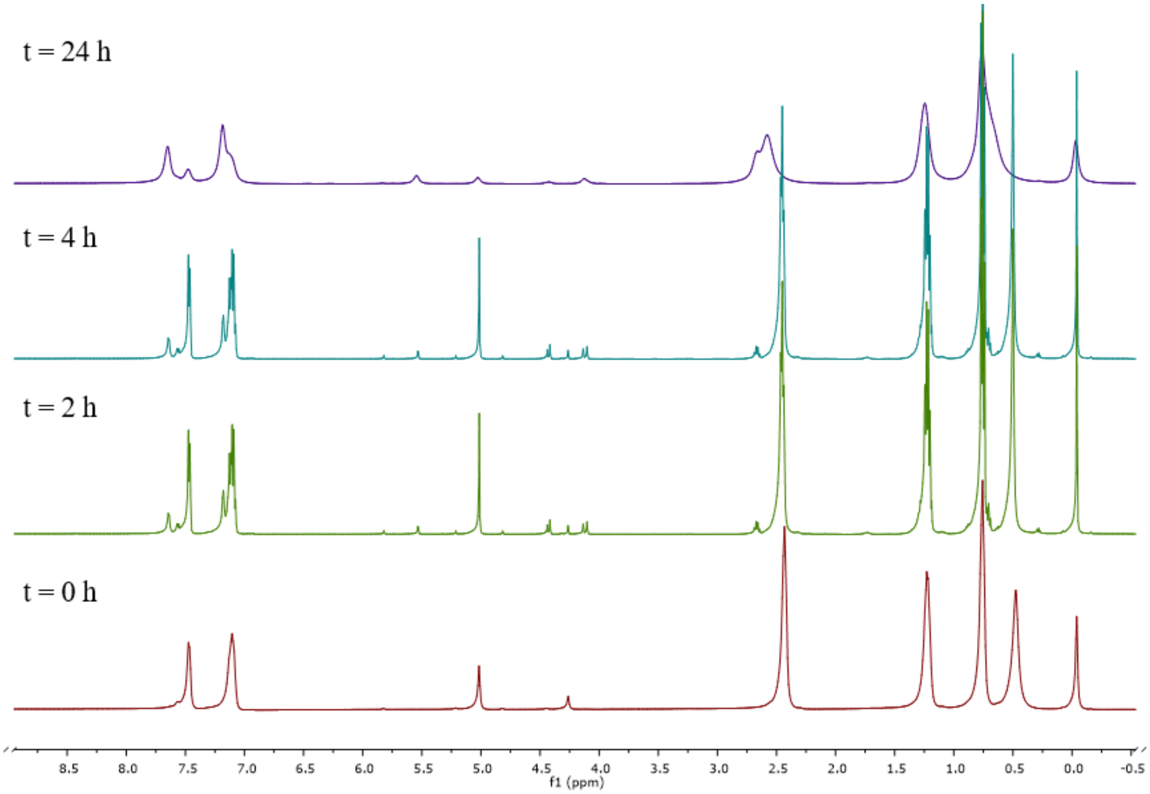

Figure S.74 Stacked ^1H NMR spectra of the reaction between Ph_2SiH_2 and $^nPrNH_2$ catalyzed by **1** (benzene-d_6, 500 MHz)

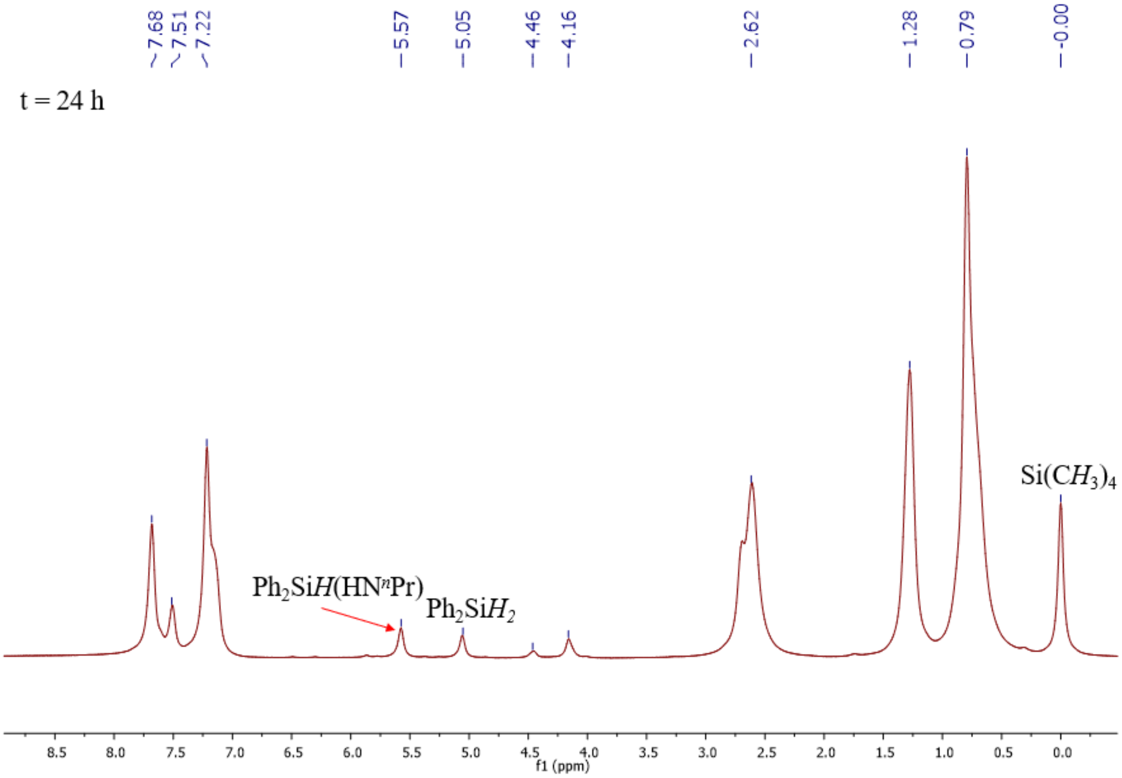

Figure S.75 ^{1}H NMR spectrum of the reaction between Ph_2SiH_2 and ^{n}PrNH$_2$ catalyzed by **1** (benzene-d_6, 500 MHz)

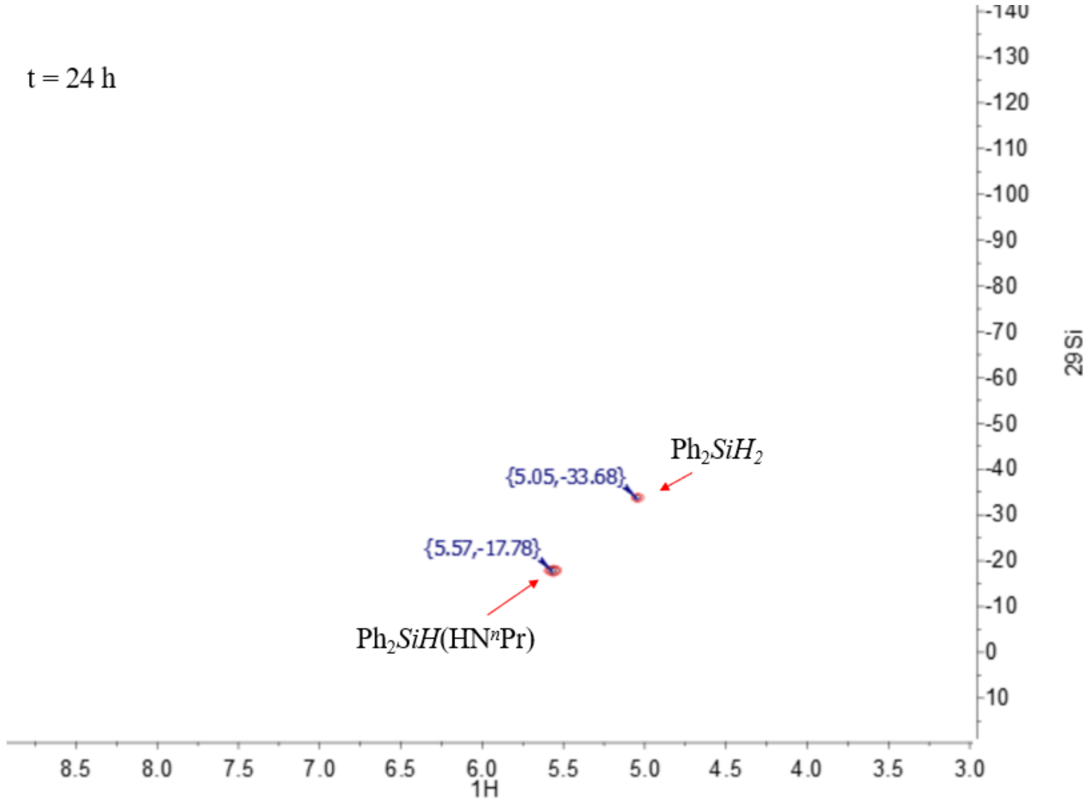

Figure S.76 ^{1}H-^{29}Si{^{1}H} HSQC spectra of the reaction between Ph_2SiH_2 and $^{n}PrNH_2$ catalyzed by **1** (benzene-d_6, 99 MHz)

Ph_2SiH_2 and ${}^tBuNH_2$.[14] An oven-dried scintillation vial containing **1** (4.0 mg, 8.1 mol %) was charged with Ph_2SiH_2 (25.1 mg, 0.1 mmol), followed by 0.5 mL benzene-*d*$_6$, ${}^tBuNH_2$ (45.8 mg, 0.6 mmol), and TMS (3.8 mg, 30.8 mol %). After 24 h of irradiation, the reaction showed 44% conversion to $Ph_2SiH(HN^tBu)$ according to ${}^1H$ NMR spectroscopy.

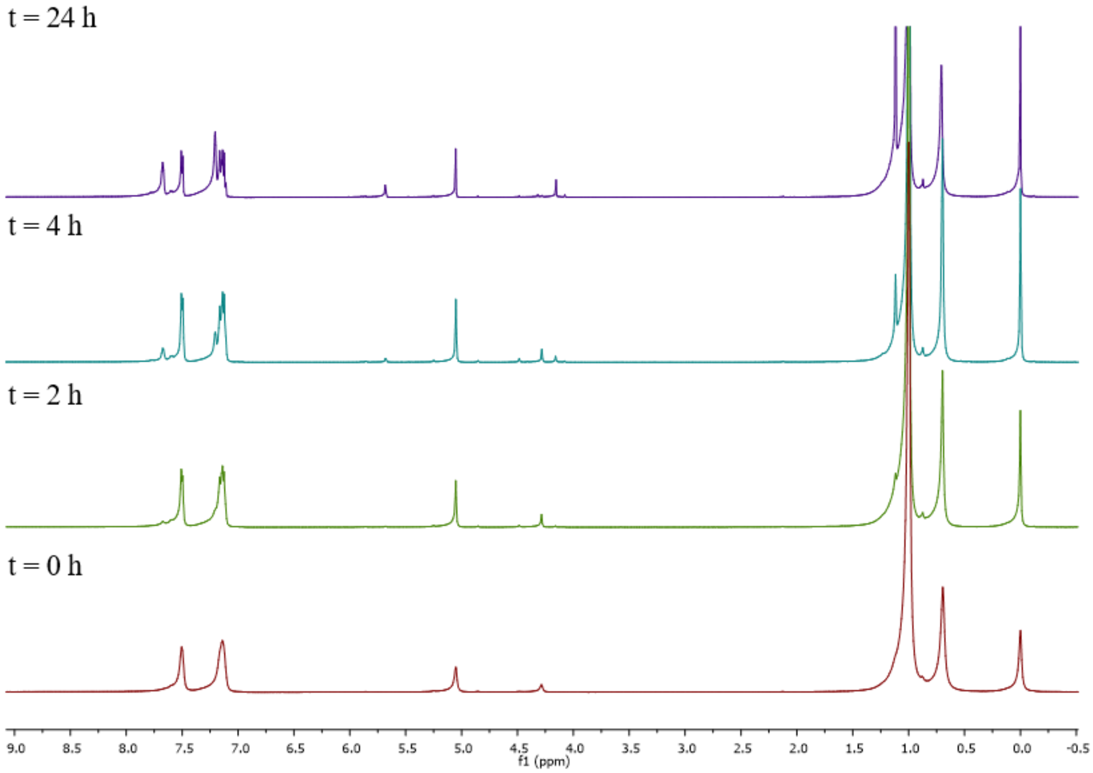

Figure S.77 Stacked ${}^1H$ NMR spectra of the reaction between Ph_2SiH_2 and ${}^tBuNH_2$ catalyzed by **1** (benzene-*d*$_6$, 500 MHz)

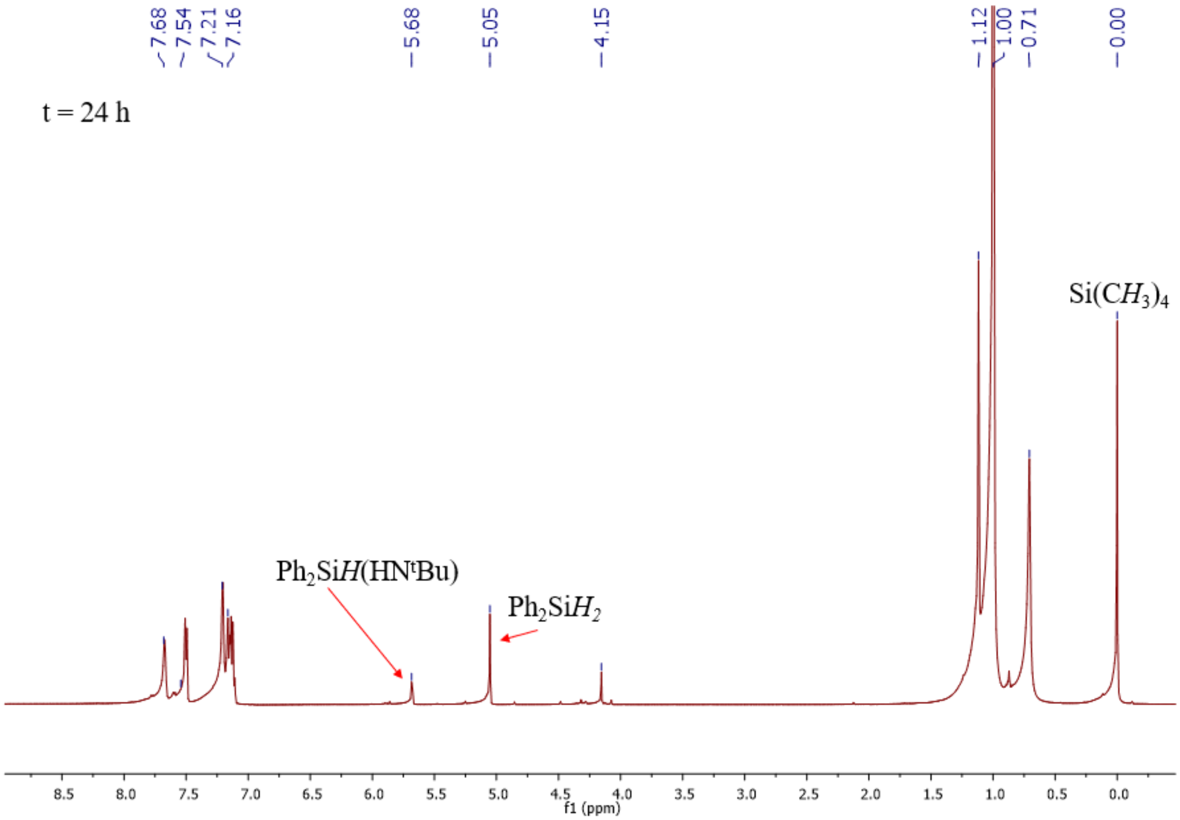

Figure S.78 ^{1}H NMR spectrum of the reaction between Ph_2SiH_2 and $^{t}BuNH_2$ catalyzed by **1** (benzene-d_6, 500 MHz)

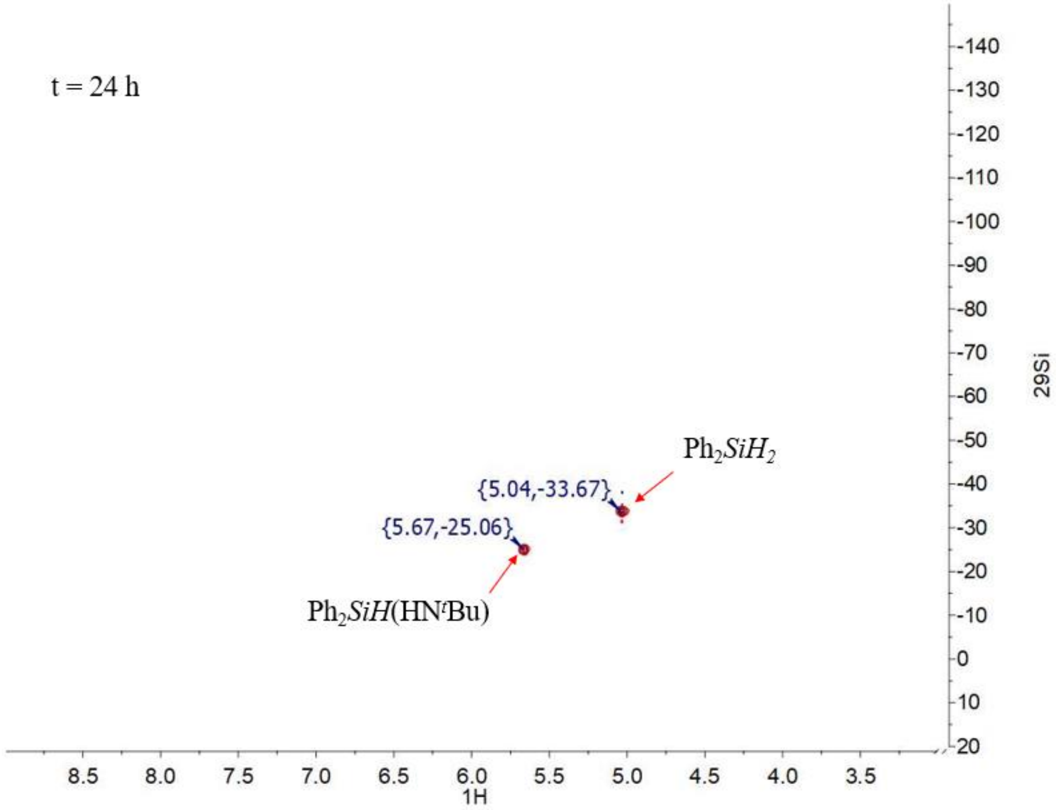

Figure S.79 ^{1}H-^{29}Si{^{1}H} HSQC spectra of the reaction between Ph$_2$SiH$_2$ and ^{t}BuNH$_2$ catalyzed by **1** (benzene-d_6, 99 MHz)

Ph_2SiH_2 and ^{i}PrNH$_2$.[12] An oven-dried scintillation vial containing **1** (3.6 mg, 7.8 mol %) was charged with Ph_2SiH_2 (23.3 mg, 0.1 mmol), followed by 0.5 mL benzene-*d*$_6$, ^{i}PrNH$_2$ (36.3 mg, 0.6 mmol), and TMS (5.5 mg, 48.0 mol %). After 24 h of irradiation, the reaction had reached 100% conversion from Ph_2SiH_2 according to ^{1}H NMR spectroscopy. However, in addition to $Ph_2SiH(HN^iPr)$ at δ -20.14 shown in ^{1}H-^{29}Si HSQC, a second signal appeared at δ -21.76. Although this was hypothesized to be $Ph_2Si(HN^iPr)_2$, the ^{29}Si NMR chemical shift does not match literature values.

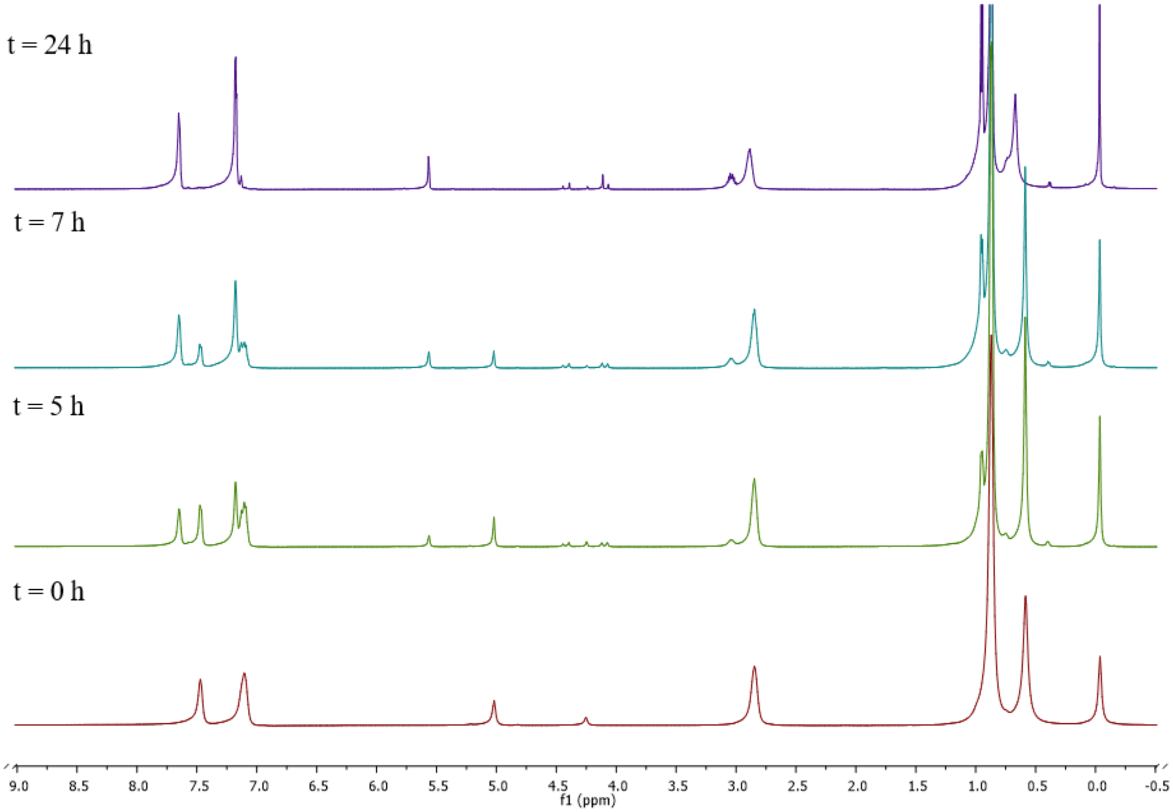

Figure S.80 Stacked ^{1}H NMR spectra of the reaction between Ph_2SiH_2 and ^{i}PrNH$_2$ catalyzed by **1** (benzene-*d*$_6$, 500 MHz)

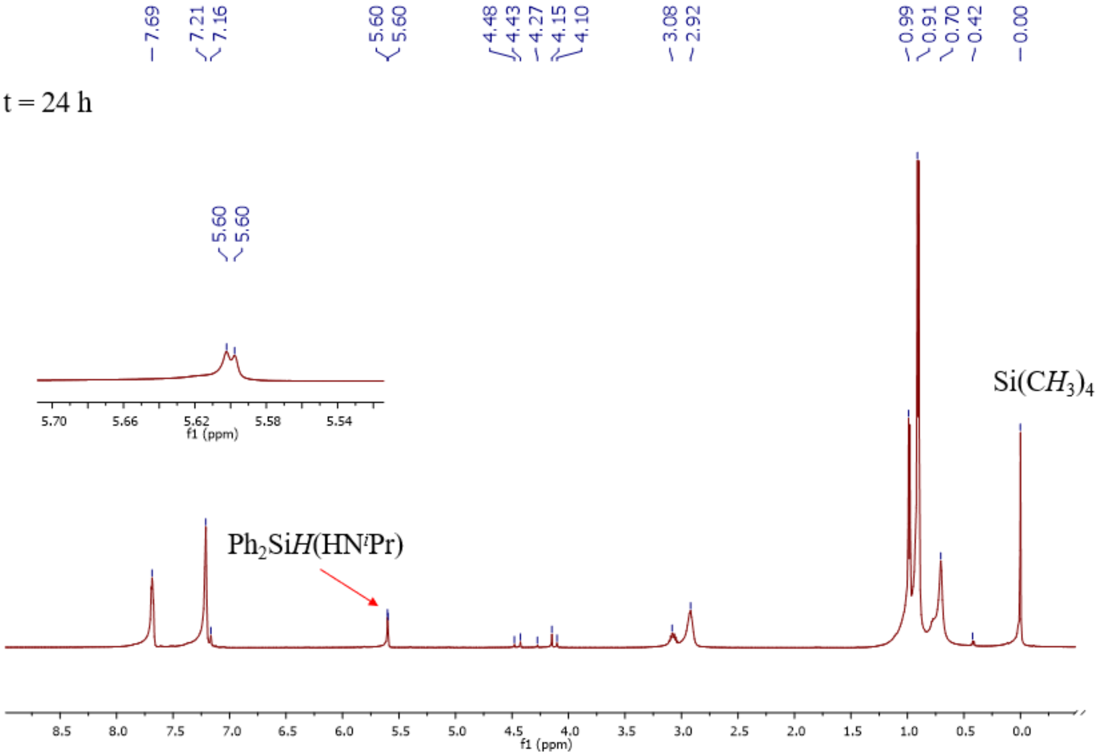

Figure S.81 ^{1}H NMR spectrum of the reaction between Ph_2SiH_2 and $^iPrNH_2$ catalyzed by **1** (benzene-d_6, 500 MHz)

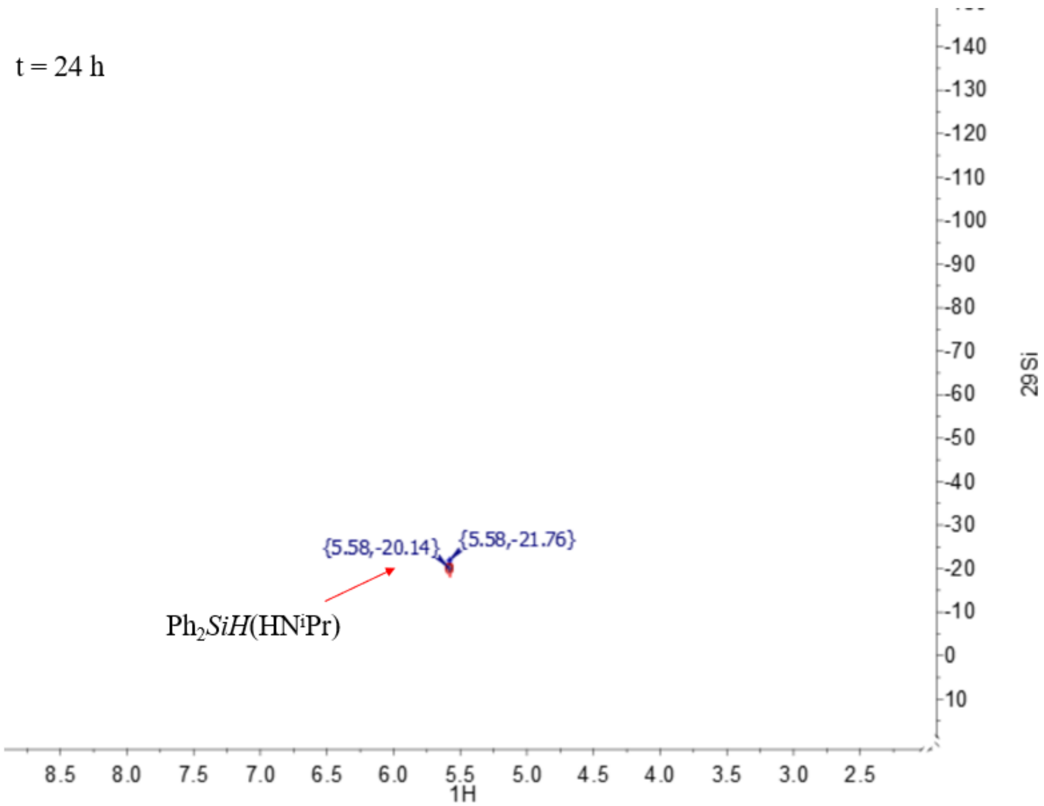

Figure S.82 ^{1}H-^{29}Si{^{1}H} HSQC spectra of the reaction between Ph_2SiH_2 and ^{i}PrNH$_2$ catalyzed by **1** (benzene-*d*$_6$, 99 MHz)

Ph_2SiH_2 and Et_2NH.[14] An oven-dried scintillation vial containing **1** (3.6 mg, 8.5 mol %) was charged with Ph_2SiH_2 (22.7 mg, 0.1 mmol) followed by 0.5 mL benzene-*d*$_6$, Et_2NH (47.5 mg, 0.7 mmol), and TMS (6.5 mg, 61.4 mol %). After 24 h of irradiation, the reaction showed 22% conversion to $Ph_2SiH(NEt_2)$ according to ^1H NMR spectroscopy.

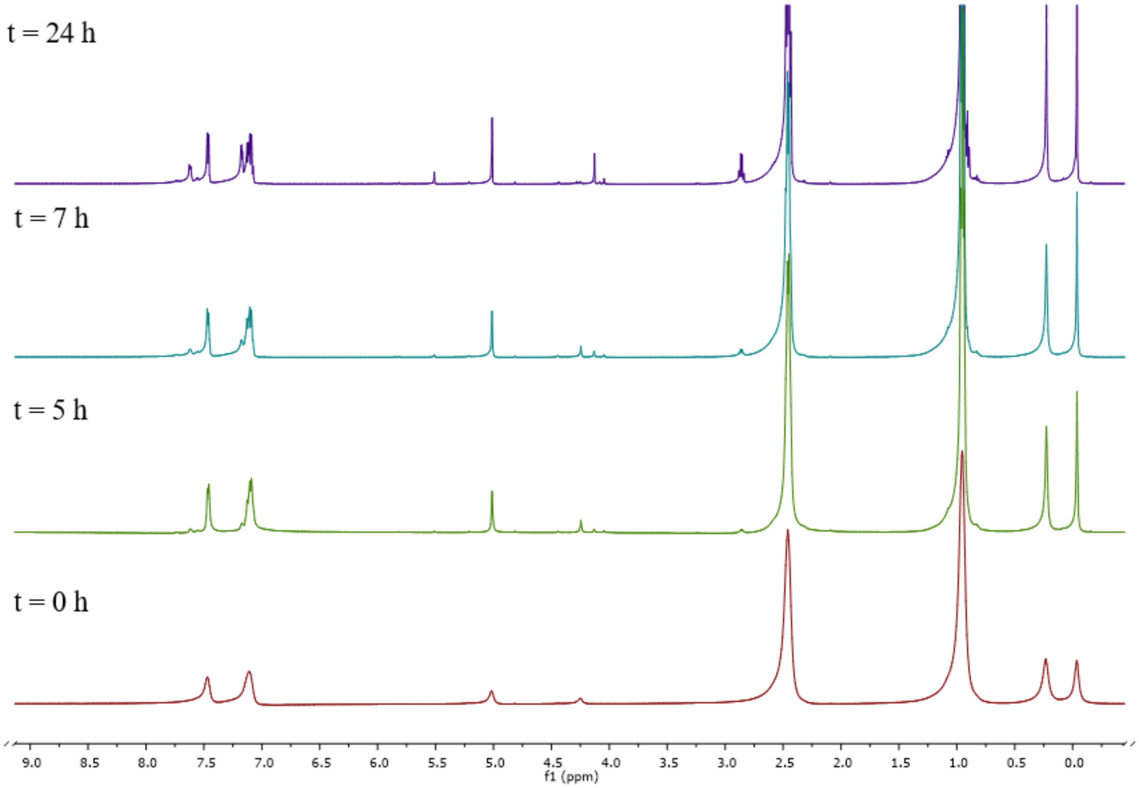

Figure S.83 Stacked ^1H NMR spectra of the reaction between Ph_2SiH_2 and Et_2NH catalyzed by **1** (benzene-*d*$_6$, 500 MHz)

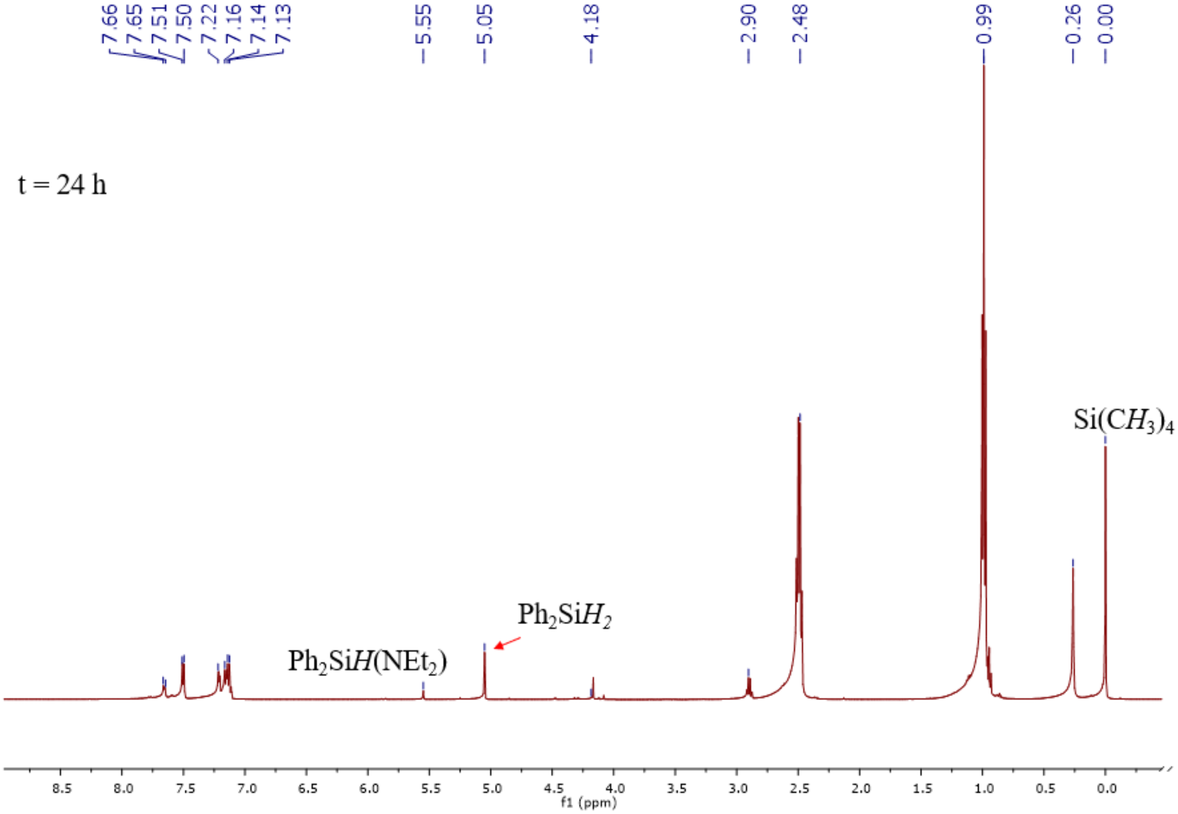

Figure S.84 ^{1}H NMR spectrum of the reaction between Ph_2SiH_2 and Et_2NH catalyzed by **1** (benzene-d_6, 500 MHz)

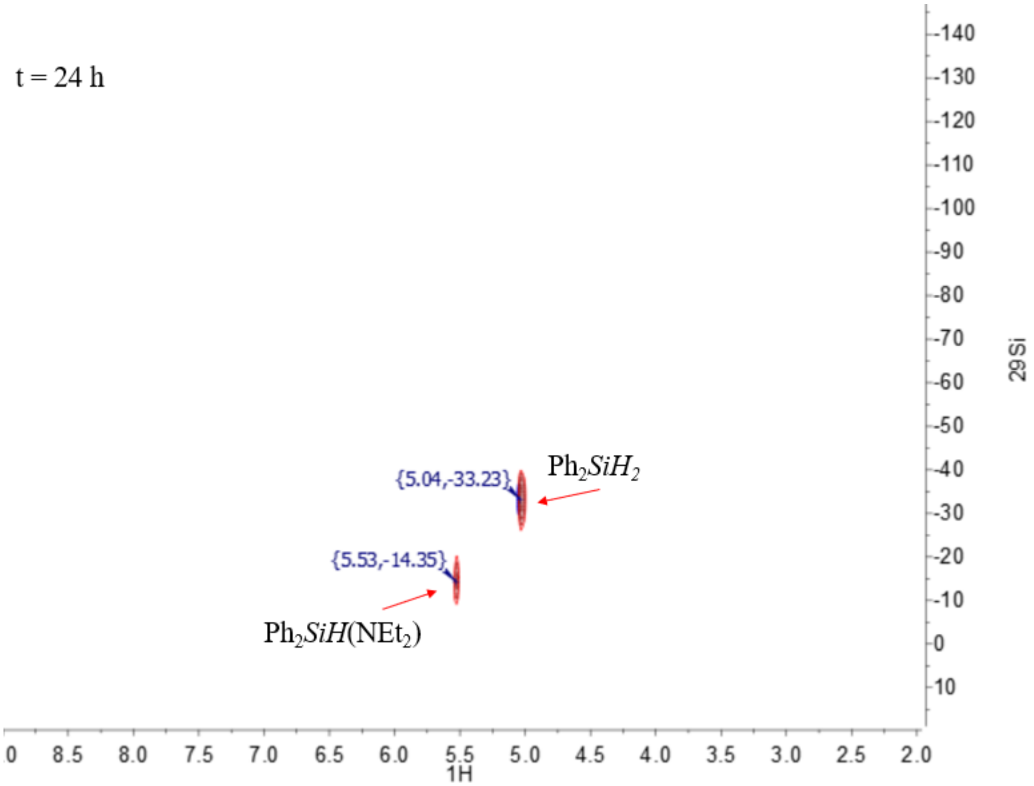

Figure S.85 ^{1}H-^{29}Si{^{1}H} HSQC spectra of the reaction between Ph_2SiH_2 and Et_2NH catalyzed by **1** (benzene-d_6, 99 MHz)

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