

# Supporting Information for

## Si–N Heterodehydrocoupling with a Lanthanide Compound

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## General information

All manipulations were performed under a nitrogen atmosphere with dry, oxygen-free solvents using an M. Braun glovebox or standard Schlenk techniques. Benzene-*d*<sub>6</sub> was purchased from Cambridge Isotope Laboratory and then degassed and dried over NaK alloy. Tetrahydrofuran was dried over sodium and vacuum transferred. NMR spectra were recorded with a Bruker AXR 500 MHz or Varian 500 MHz spectrometer. Reported resonances are with reference to the residual solvent resonance ( $\delta$  7.16). ESI-mass spectra were collected on an AB-Sciex 4000 QTrap Hybrid Triple Quadrupole/Linear Ion trap mass spectrometer. IR data were collected on a Bruker Alpha FTIR spectrometer as neat samples. Phenylsilane (Oakwood Chemicals), methylphenylsilane (Sigma Aldrich), diphenylsilane (Acros Organics), and triphenylsilane (Gelest) were used as received. N-propylamine (Sigma Aldrich), isopropylamine (Alfa Aesar), tert-butylamine (Alfa Aesar), aniline (Sigma Aldrich), and diethylamine (Acros Organics) were dried by stirring over calcium hydride followed by distillation. Bis(trimethylsilyl)amine (Acros Organics) was used as received.

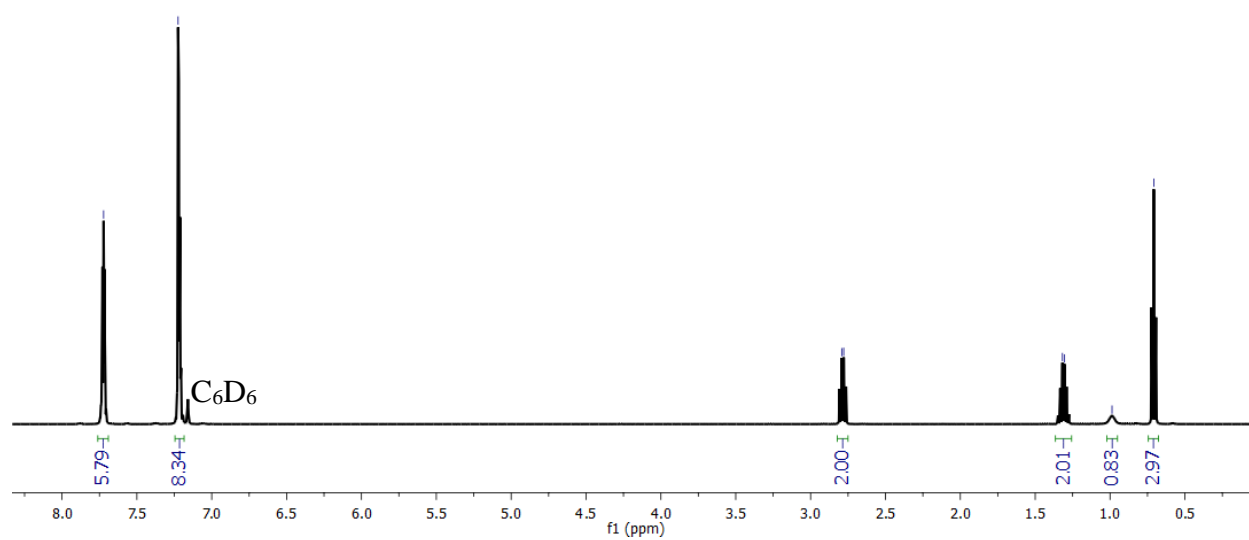
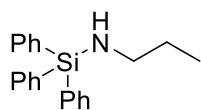
**Ph<sub>3</sub>Si(<sup>n</sup>PrNH):**

-7.72

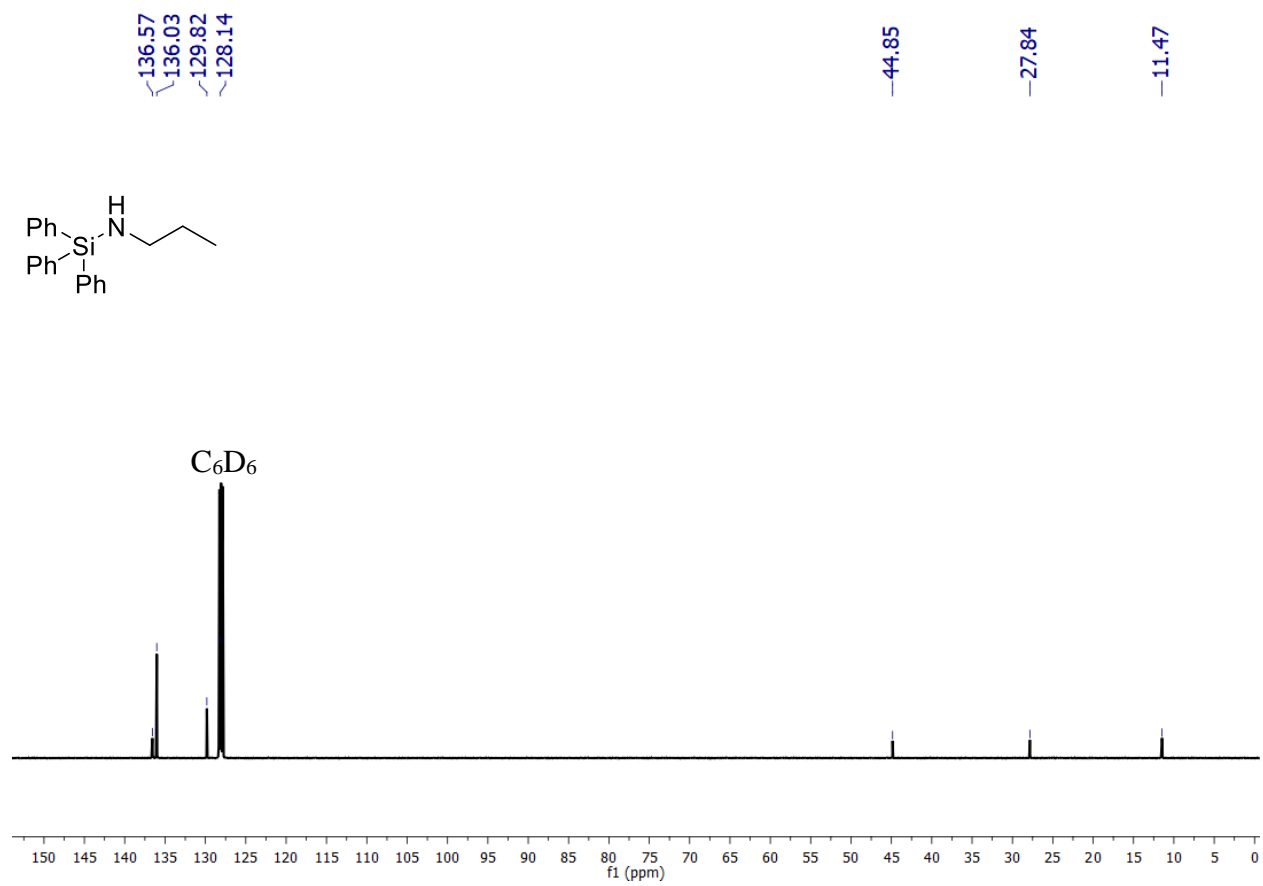
-7.22

2.79  
2.78

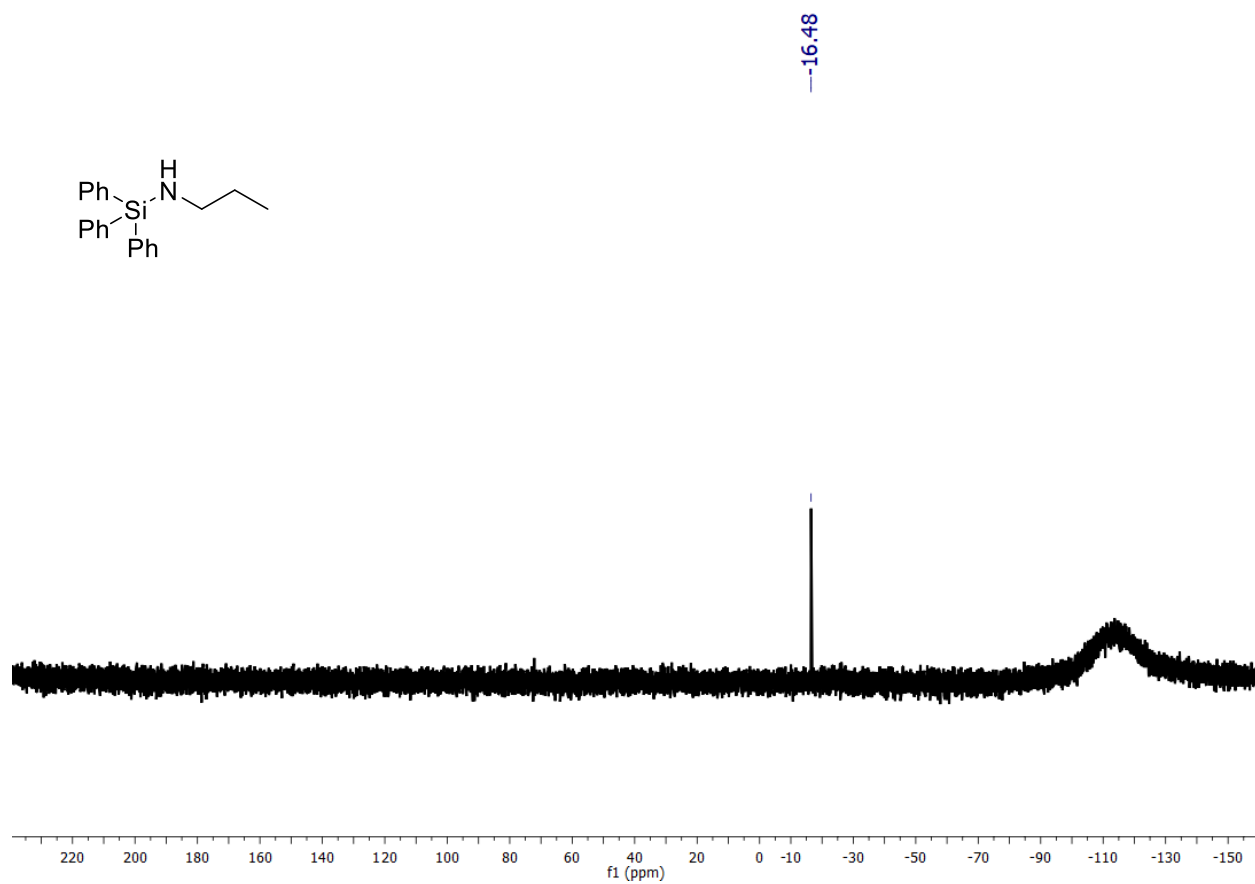
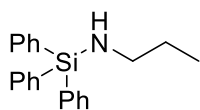
1.32  
1.30  
0.99  
0.71



<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz)



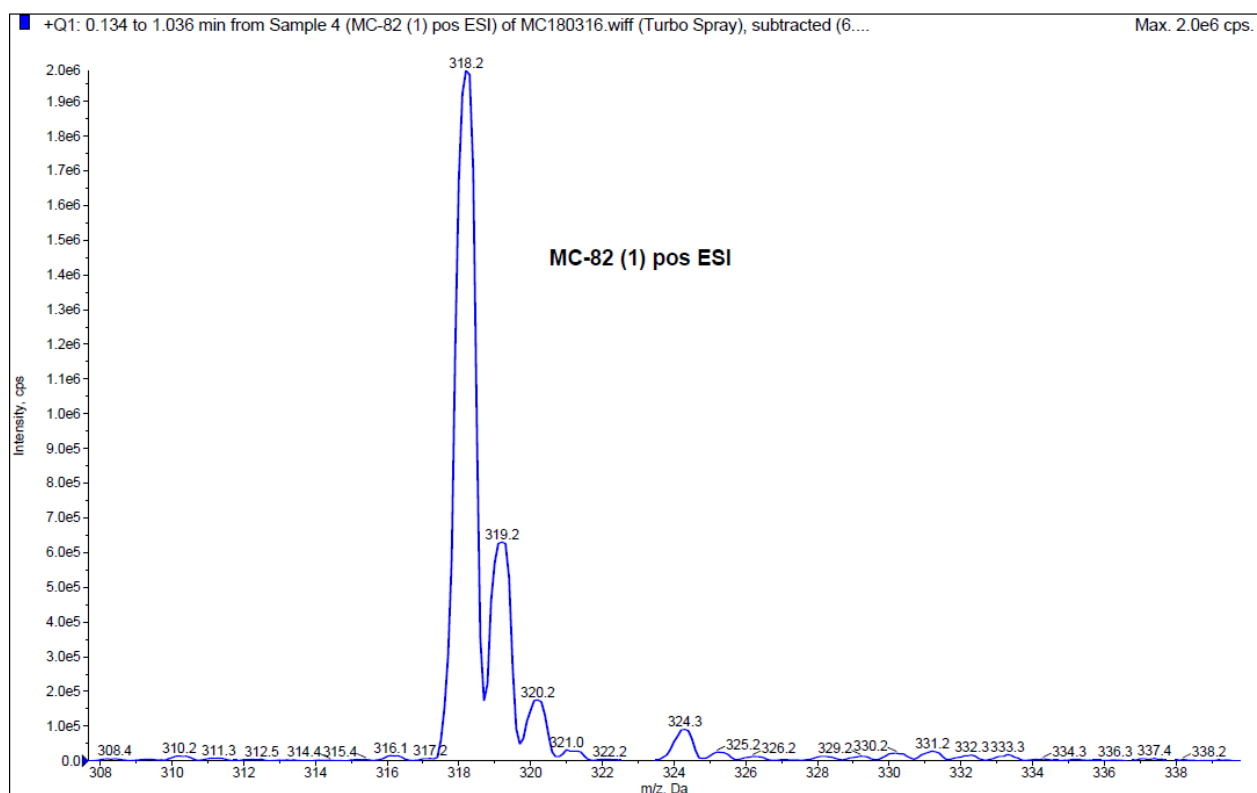
$^{13}\text{C}$  NMR (C<sub>6</sub>D<sub>6</sub>, 126 MHz)



$^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , 99 MHz)

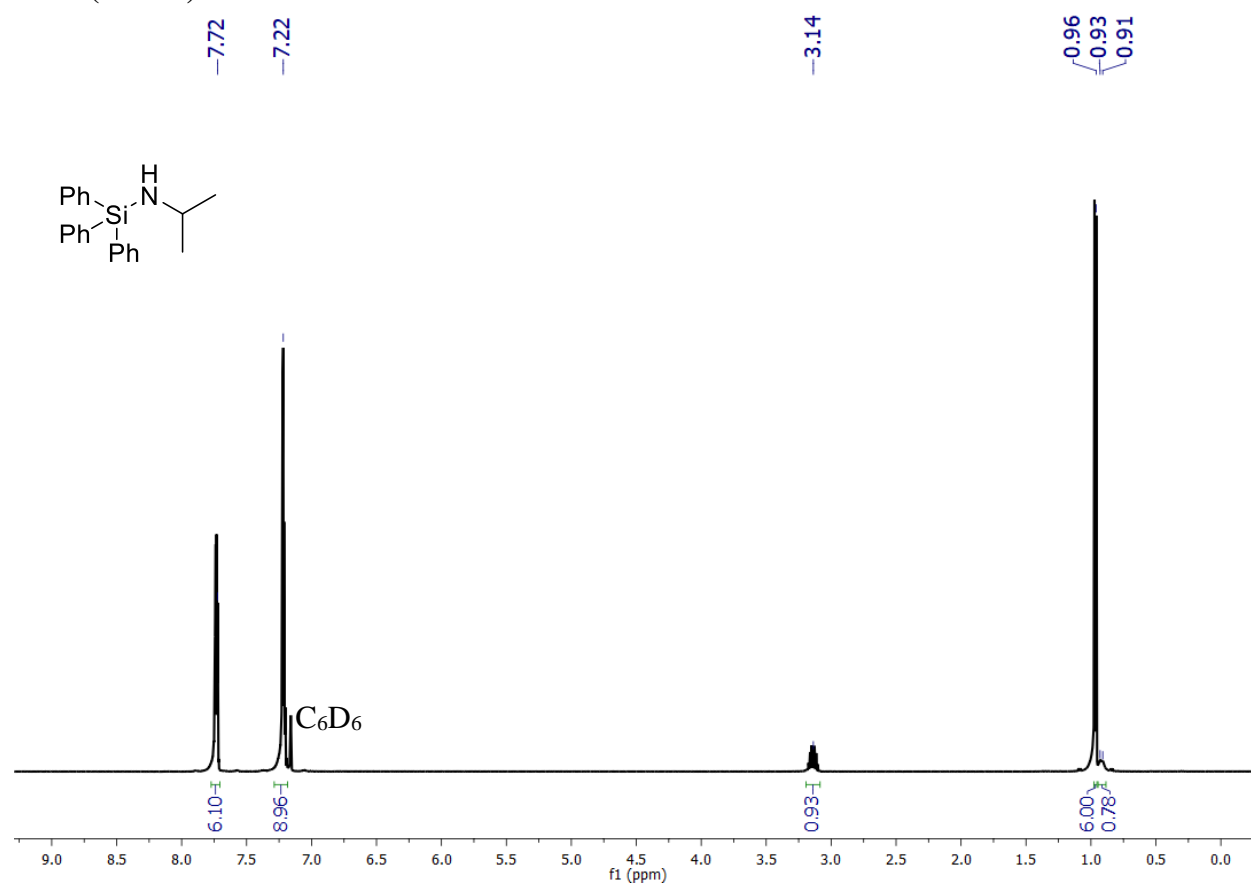


Infrared Spectroscopy (neat)

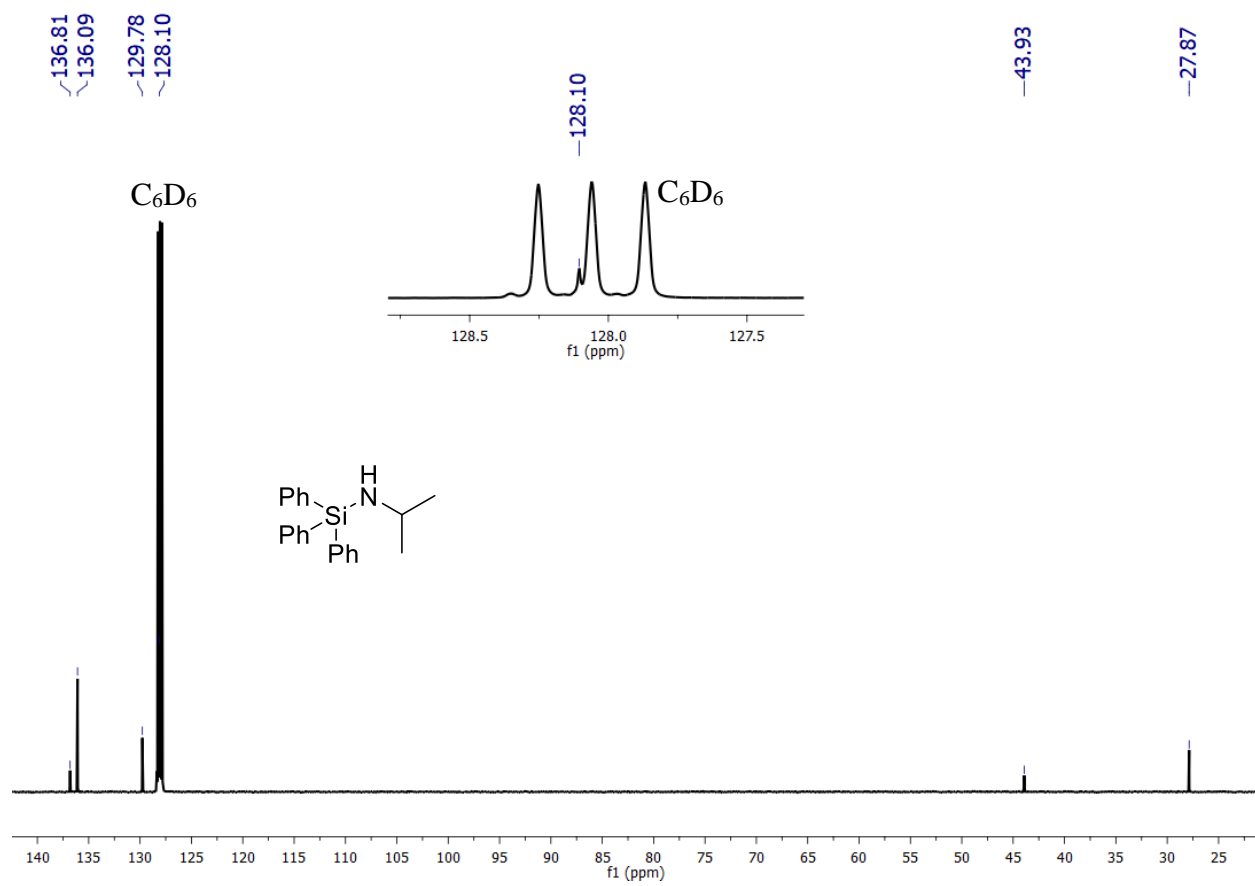


Mass Spectrometry (electron spray ionization)

**Ph<sub>3</sub>Si(<sup>i</sup>PrNH):**

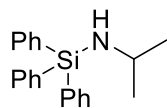


<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz)

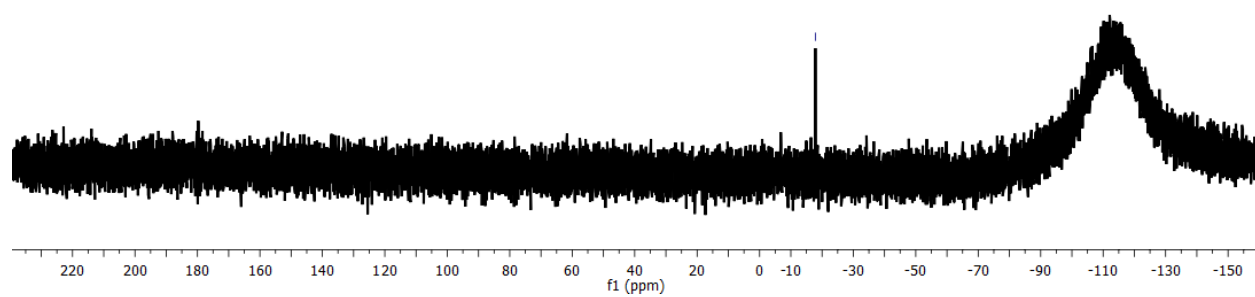


$^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 126 MHz)

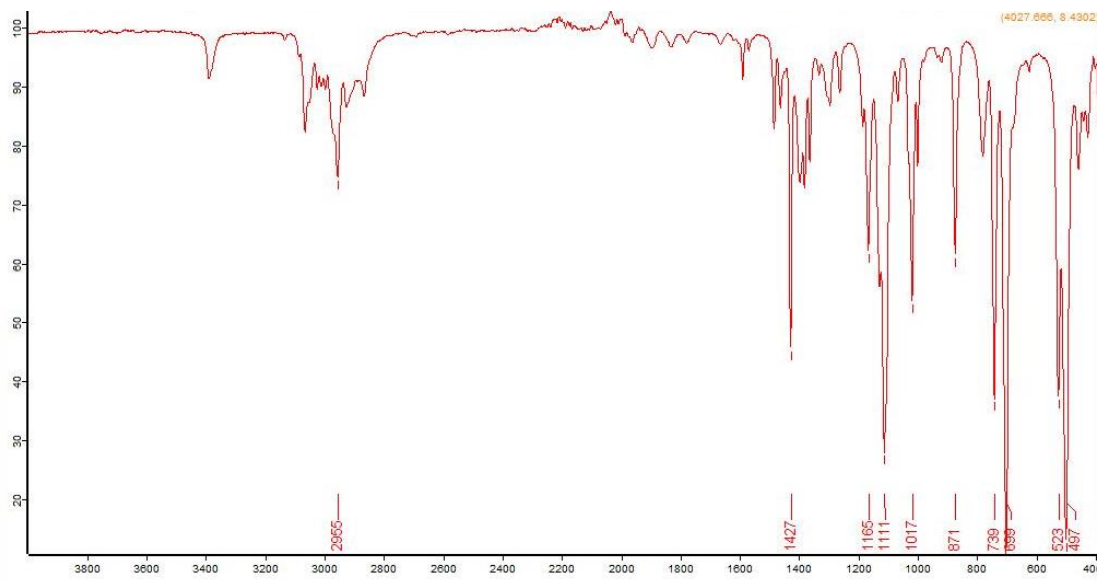




—17.86



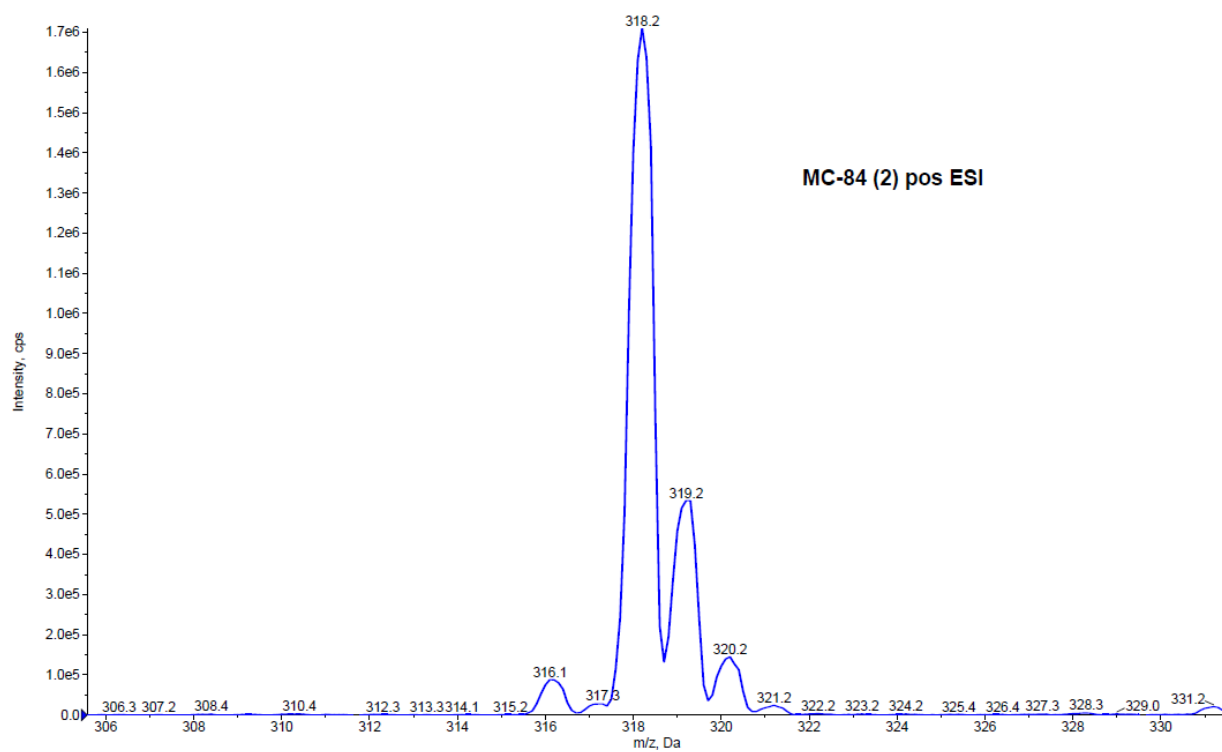
$^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , 99 MHz)



## Infrared Spectroscopy (neat)

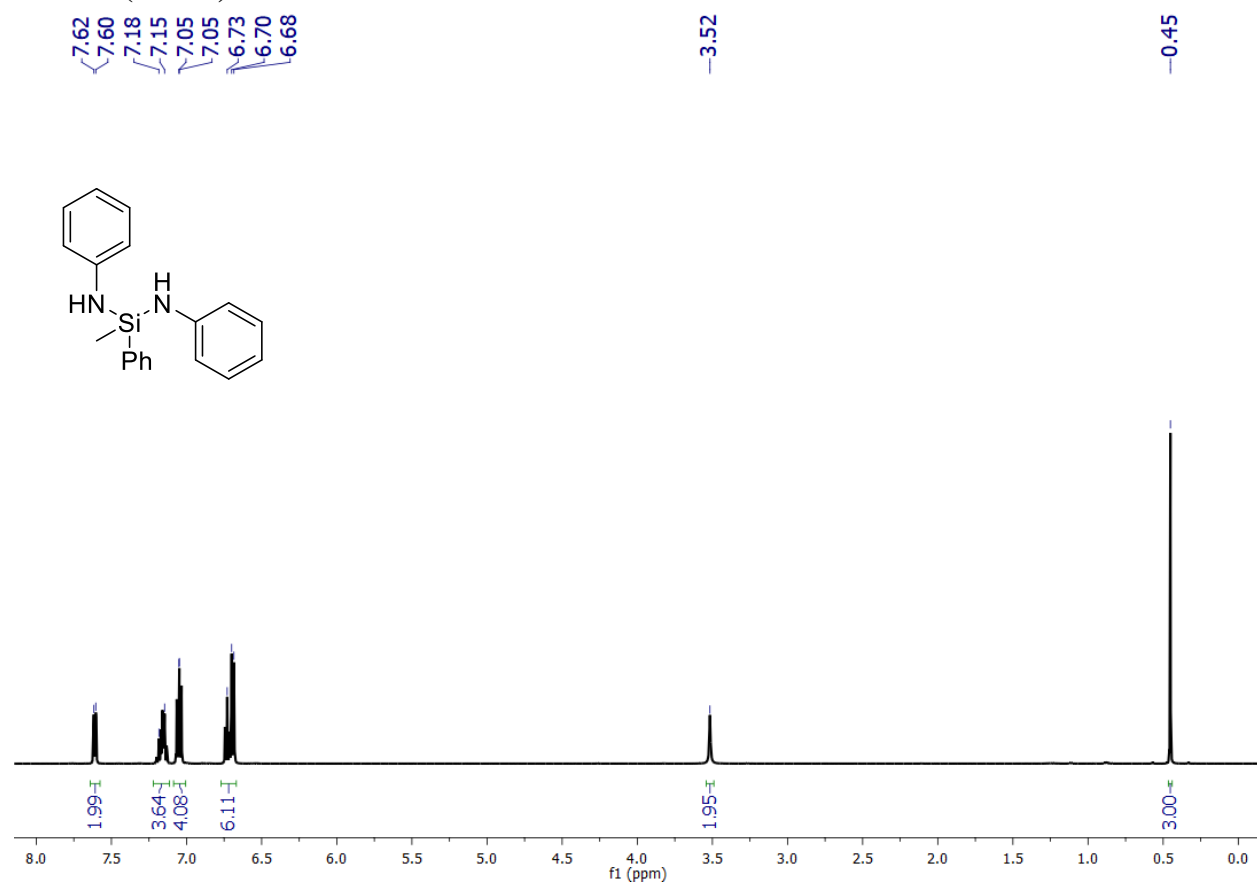
■ +Q1: 0.735 to 1.871 min from Sample 3 (MC-84 (2) pos ESI) of MC180316.wiff (Turbo Spray), subtracted (4....

Max. 1.7e6 cps

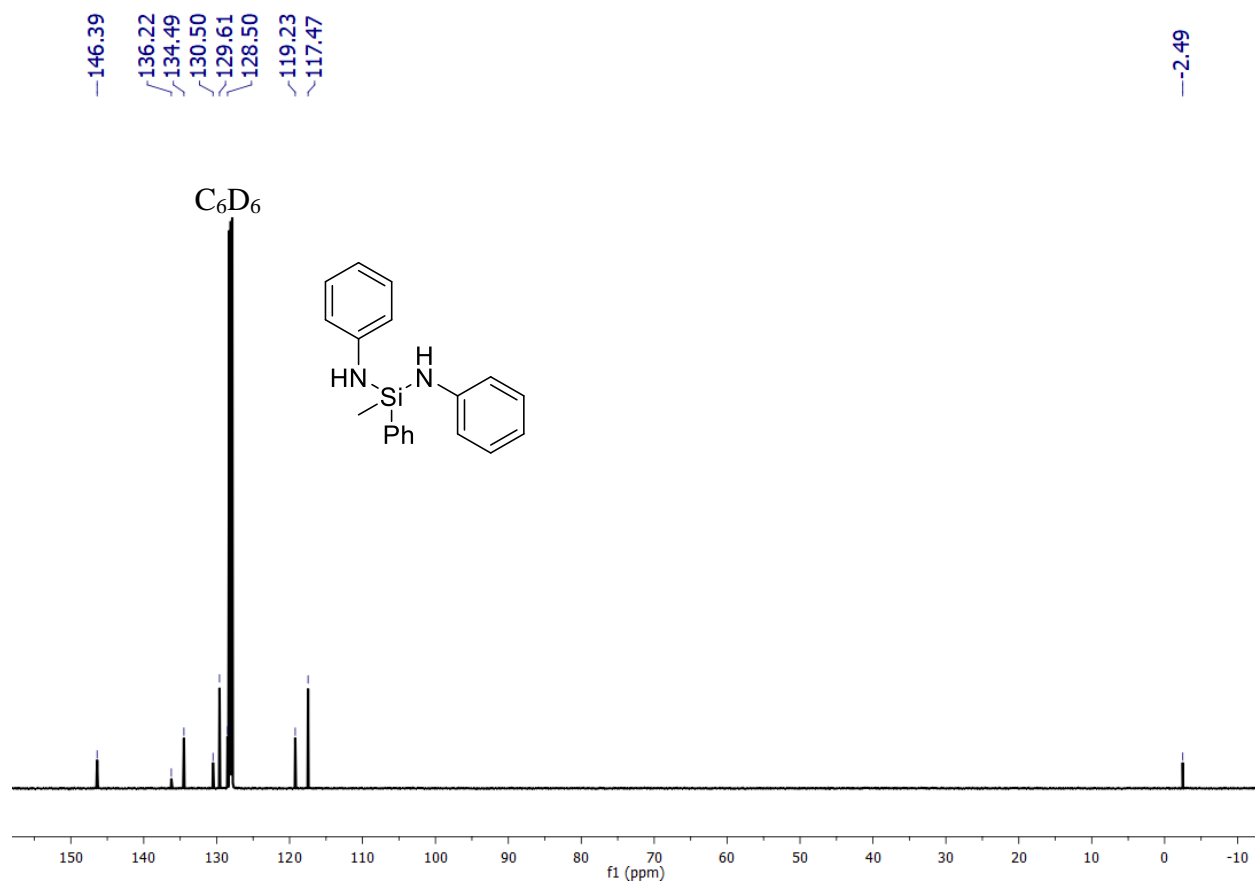


## Mass Spectrometry (electron spray ionization)

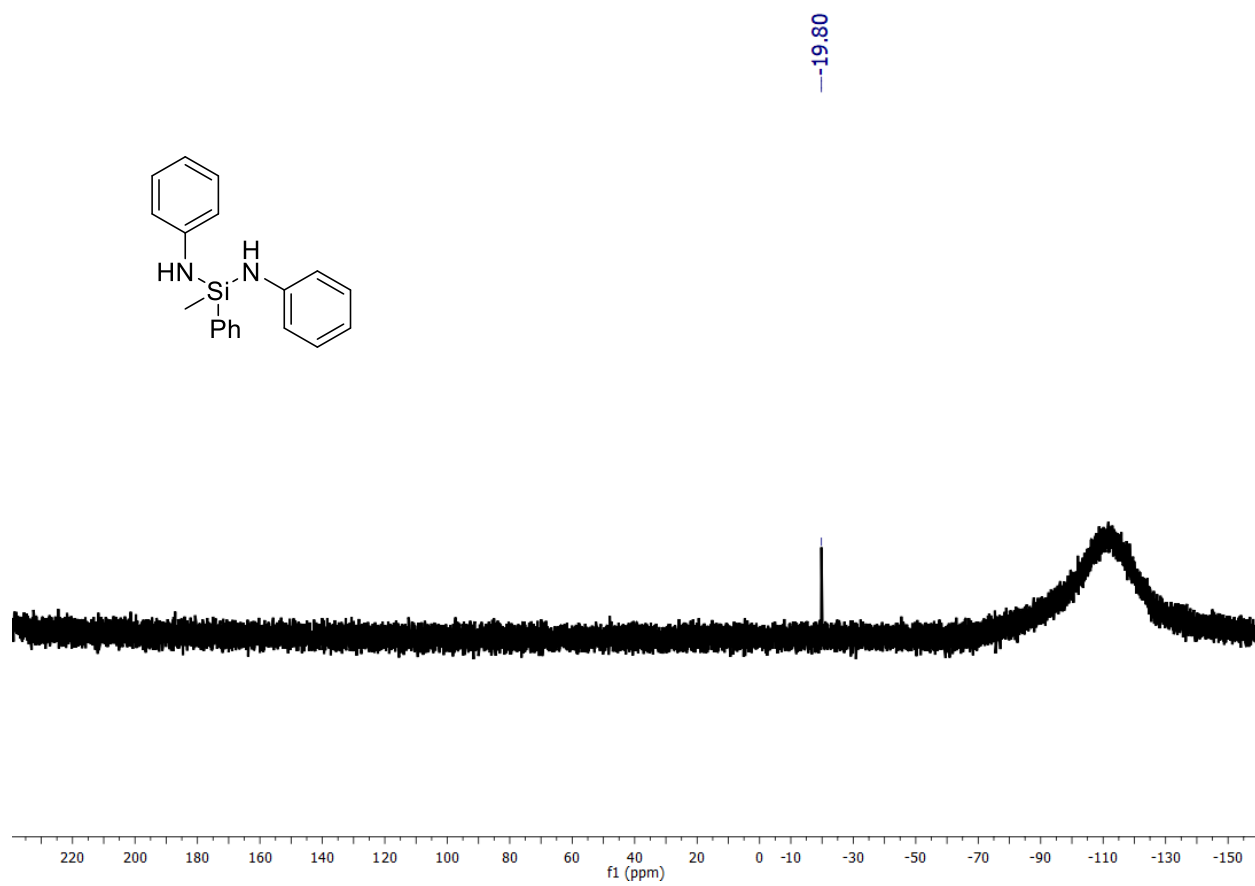
**MePhSi(PhNH)<sub>2</sub>:**



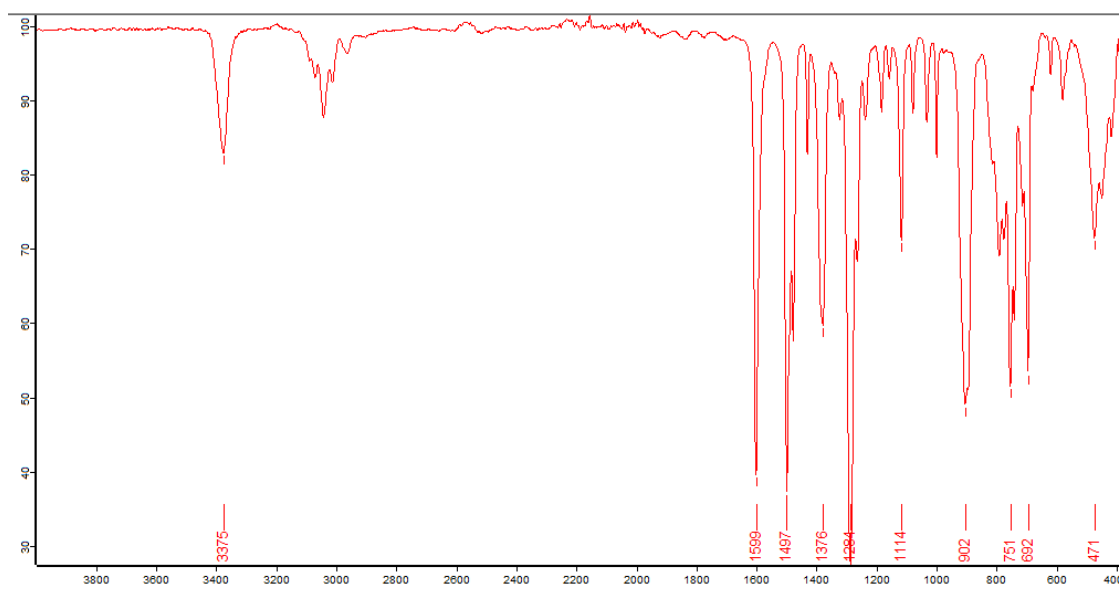
<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz) C<sub>6</sub>D<sub>6</sub> resonance is buried.



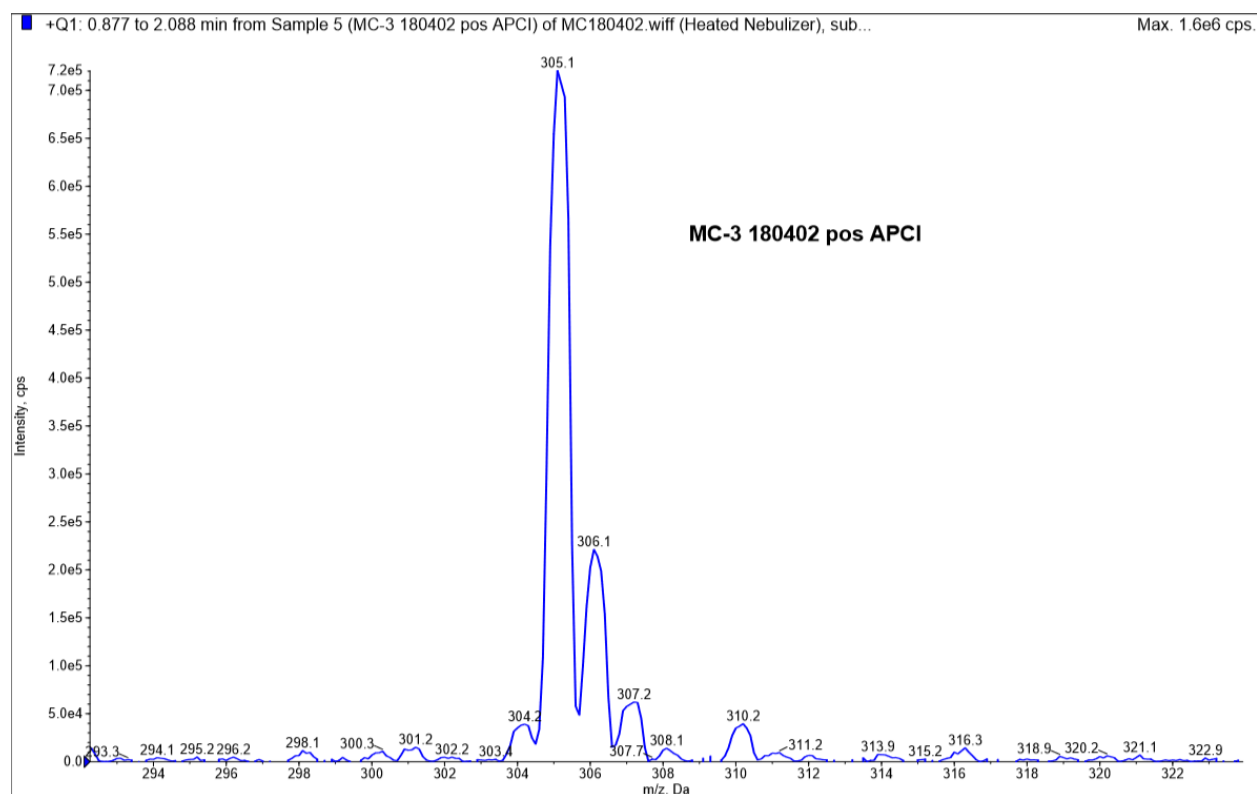
$^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 126 MHz)



$^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , 99 MHz)

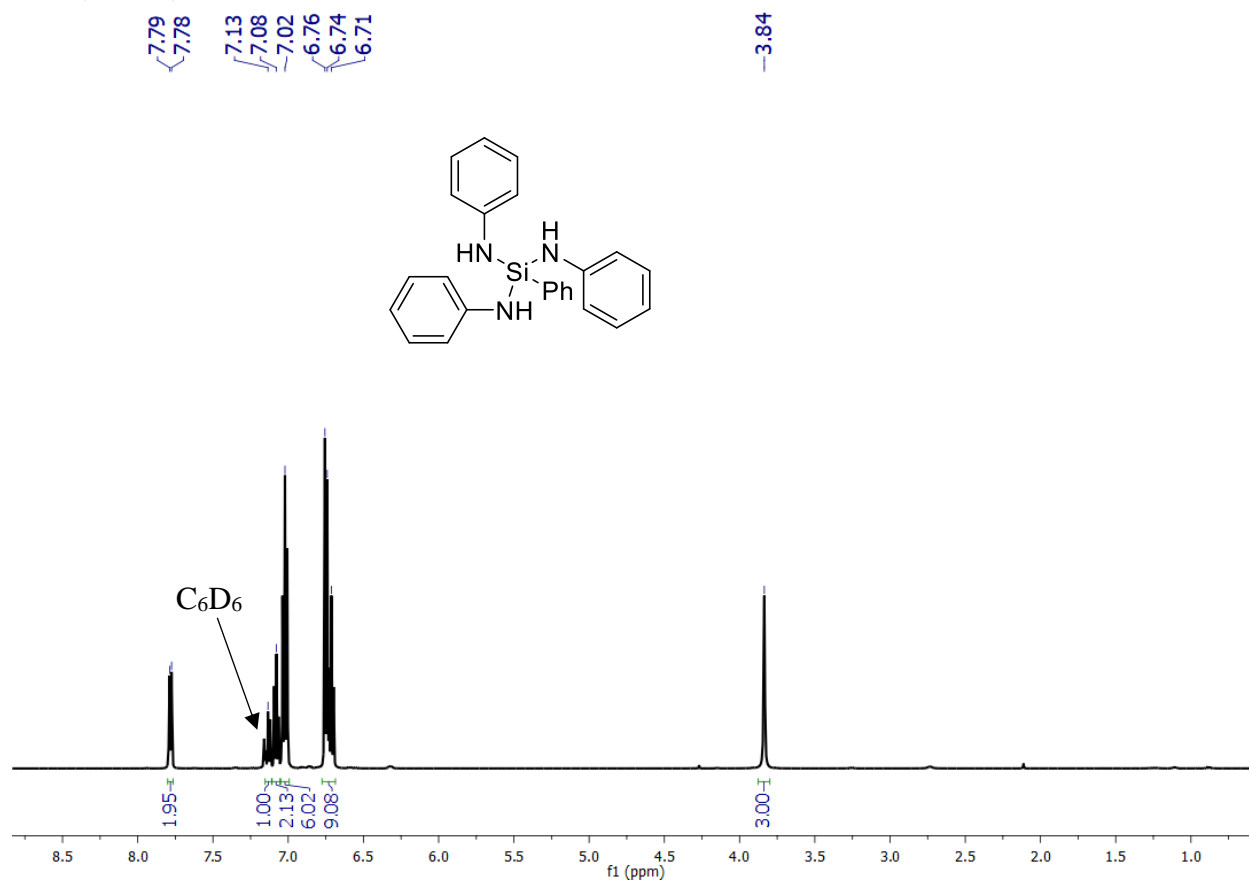


## Infrared Spectroscopy (neat)

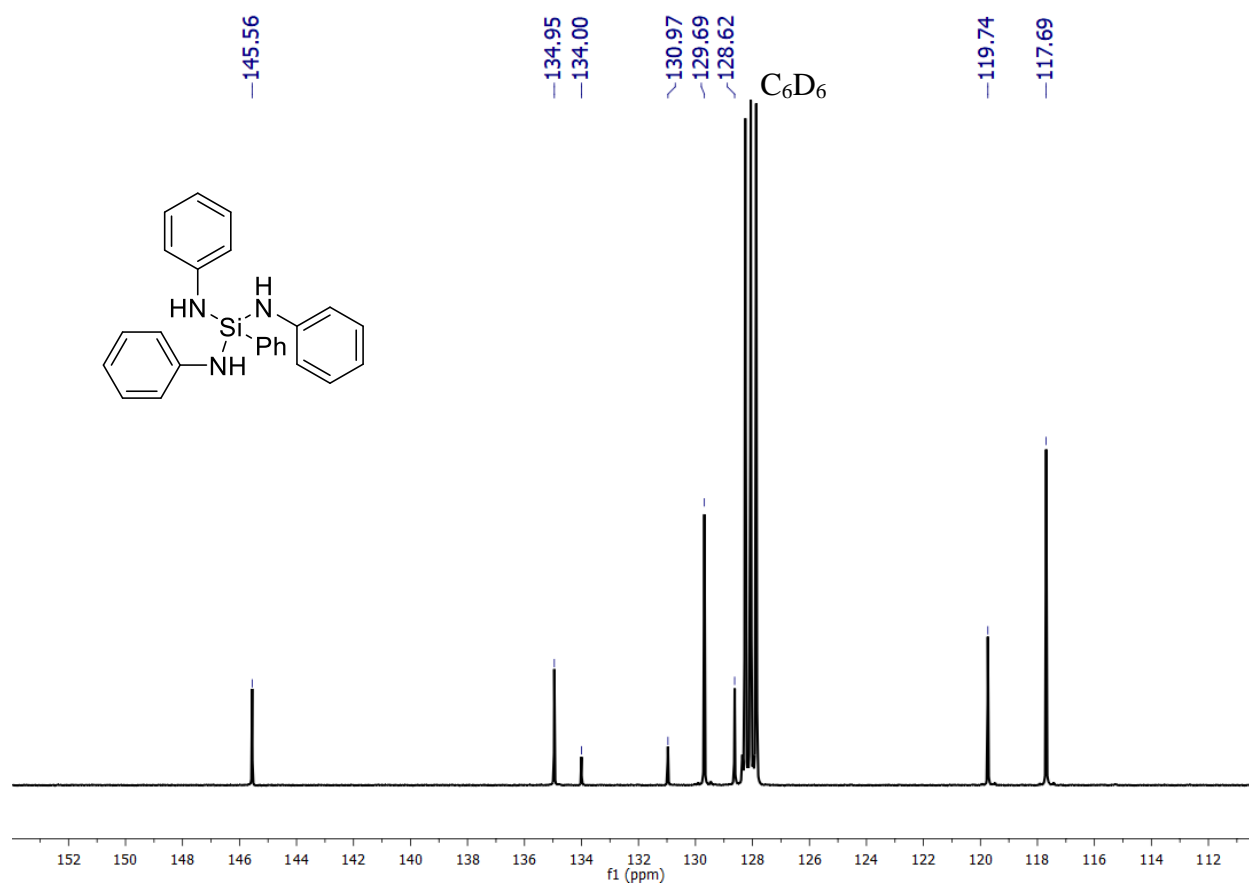


## Mass Spectrometry (electron spray ionization)

**PhSi(PhNH)<sub>3</sub>:**

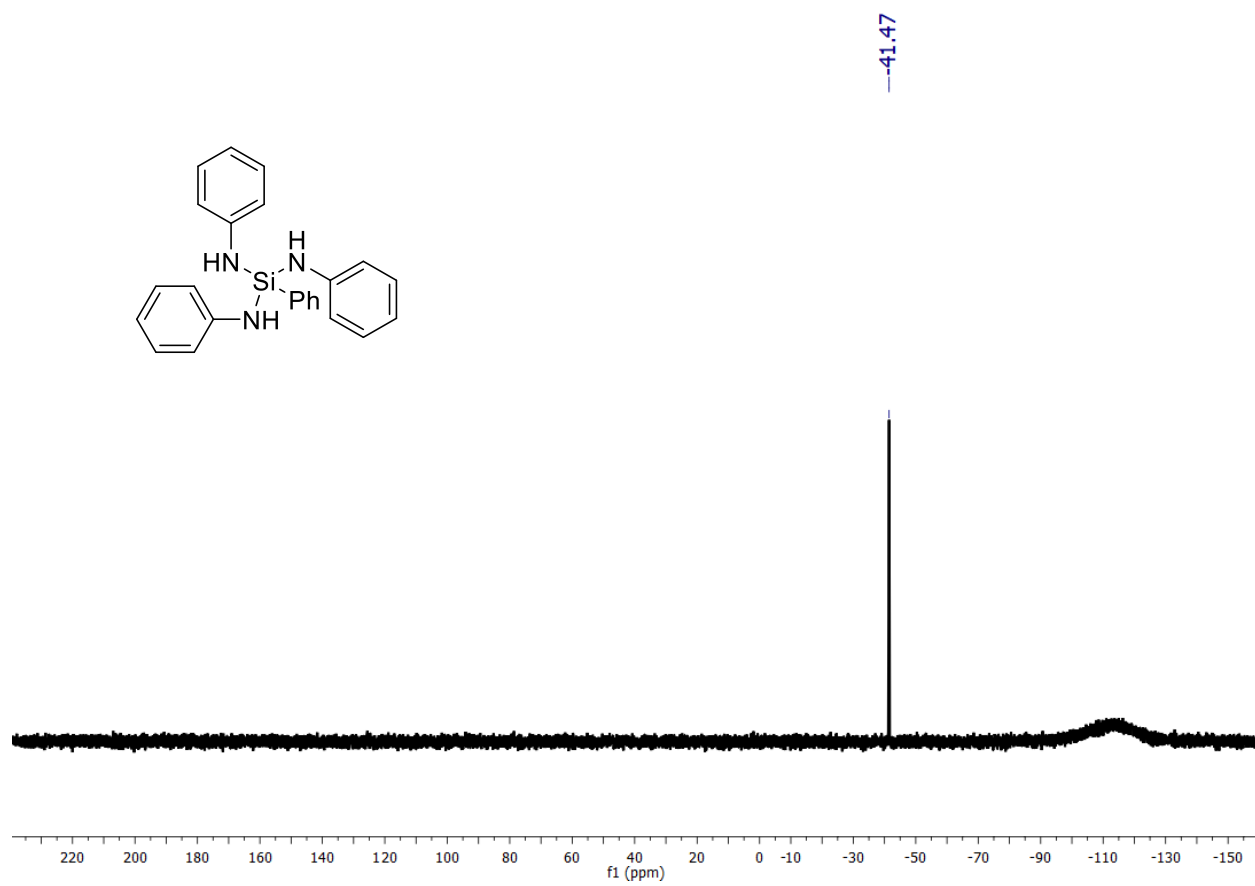


<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz)

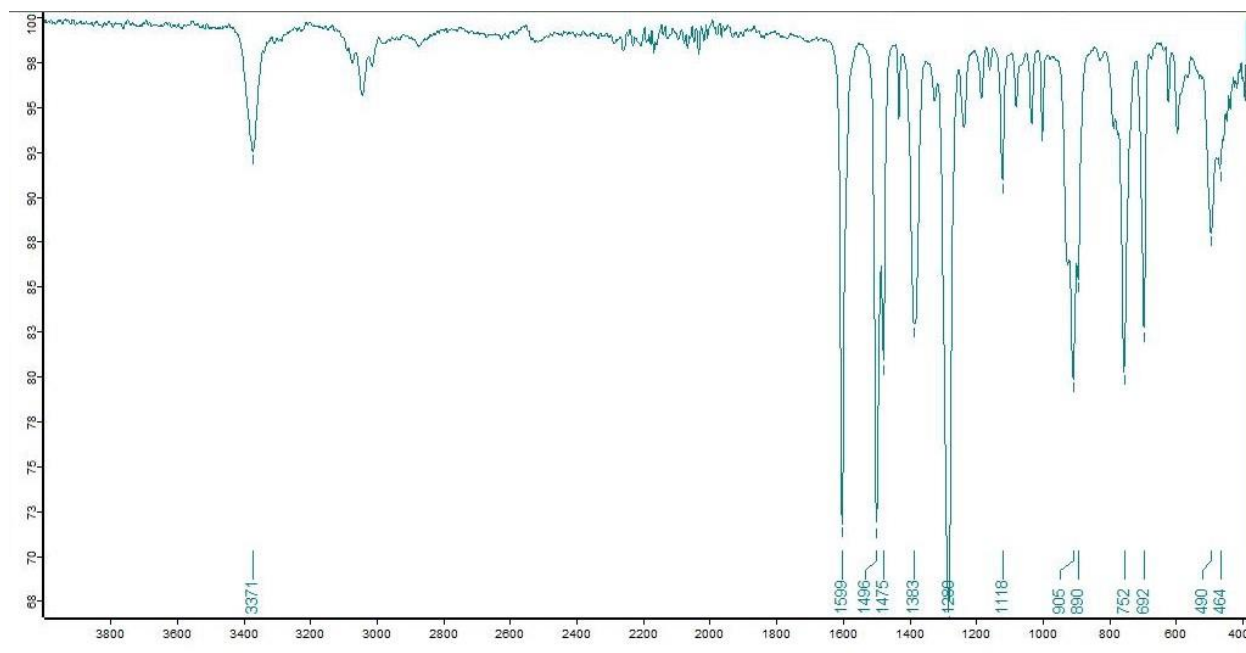


$^{13}\text{C}$  NMR (C<sub>6</sub>D<sub>6</sub>, 126 MHz)

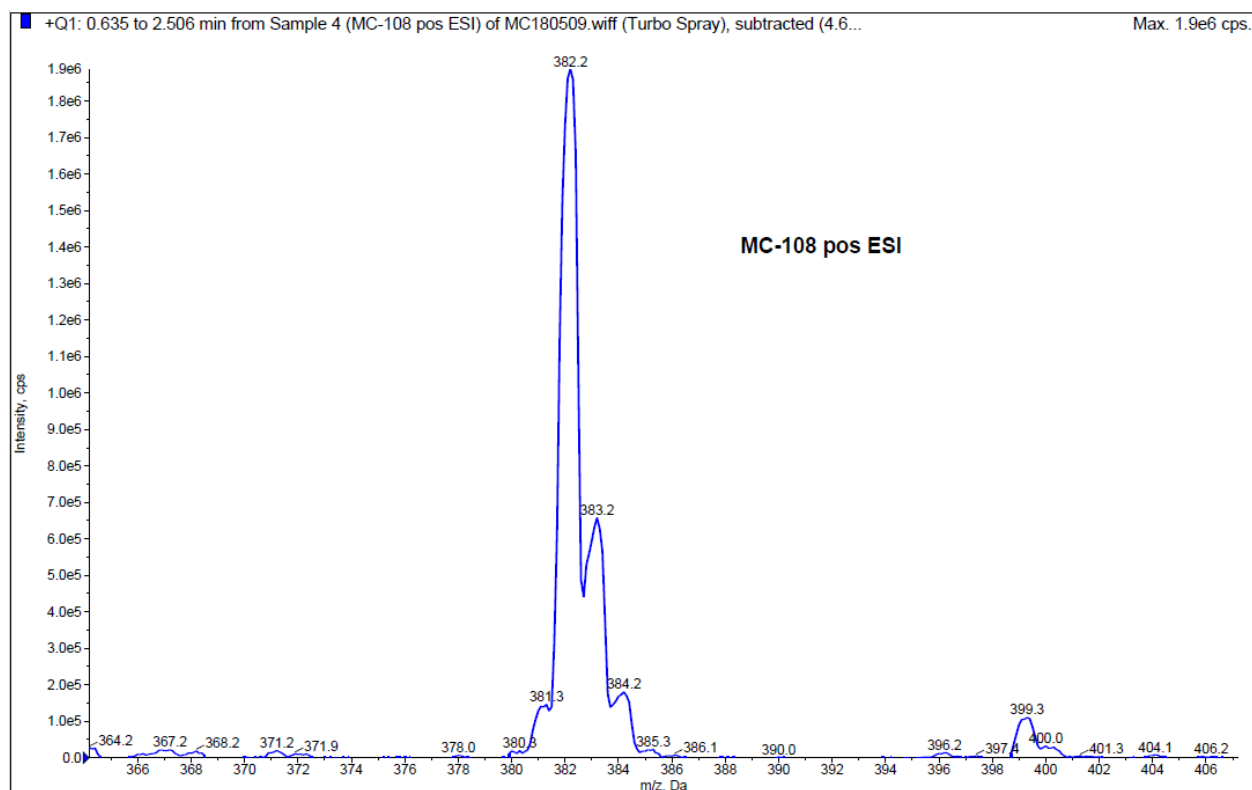




$^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , 99 MHz)



Infrared Spectroscopy (neat)



Mass Spectrometry (electron spray ionization)

***Catalytic experiments:***

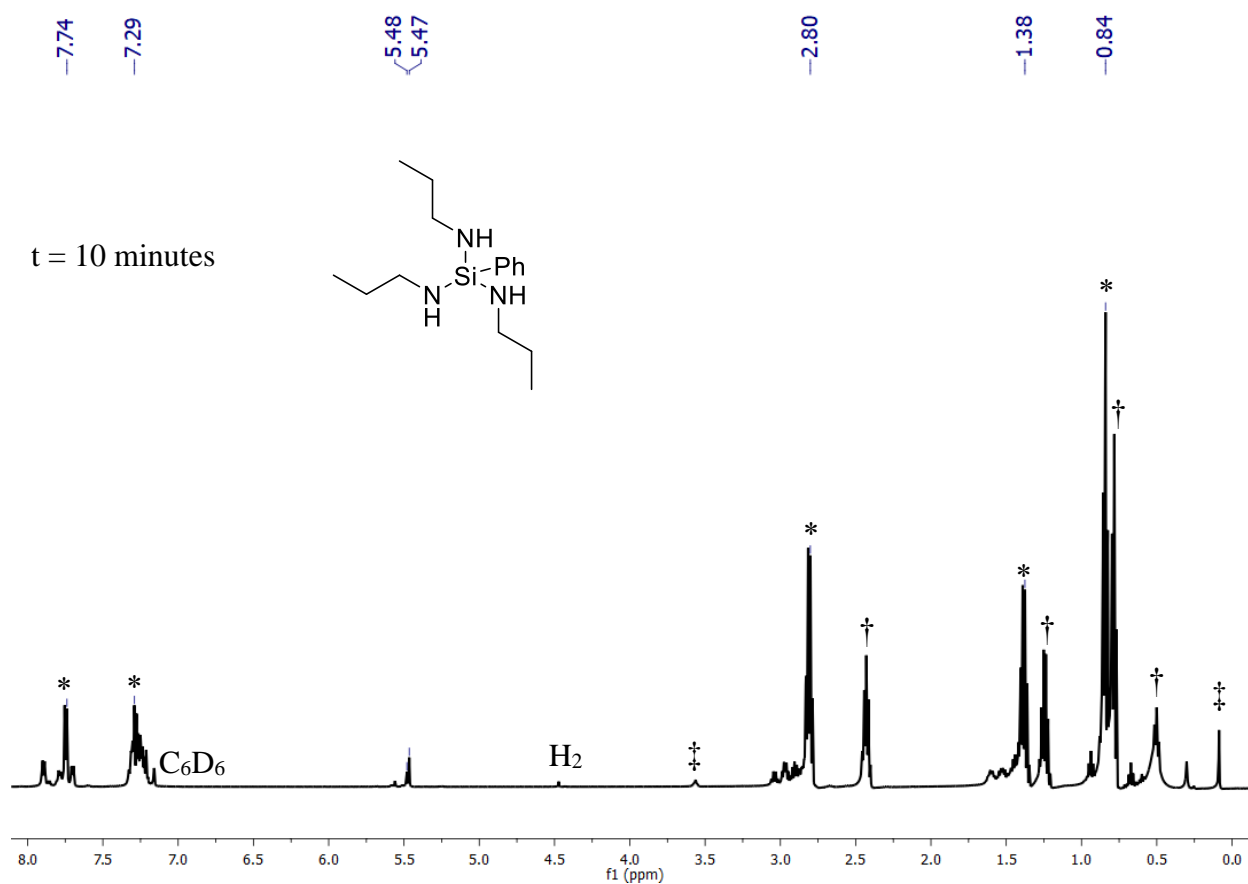
All reactions were conducted using a J-Young type polytetrafluoroethylene (PTFE)-valved NMR tube in benzene-*d*<sub>6</sub>. Upon obtaining an initial <sup>1</sup>H NMR, the solution was placed in an oil bath of the listed temperature. If no temperature is listed, the reaction was performed at ambient temperature. All NMR spectra were collected at 25 °C. The spectra below are of the reaction listed at a different time points to explicitly show the generation of product(s). Due to the solution bubbling, it was often difficult to obtain spectra immediately after addition. Typically, after 30 minutes it became possible to obtain a spectrum. Product isolation can be achieved by removal of solvent and volatiles followed by distillation under reduced pressure.

Product	*
Residual amine	†
Catalyst decomposition	‡

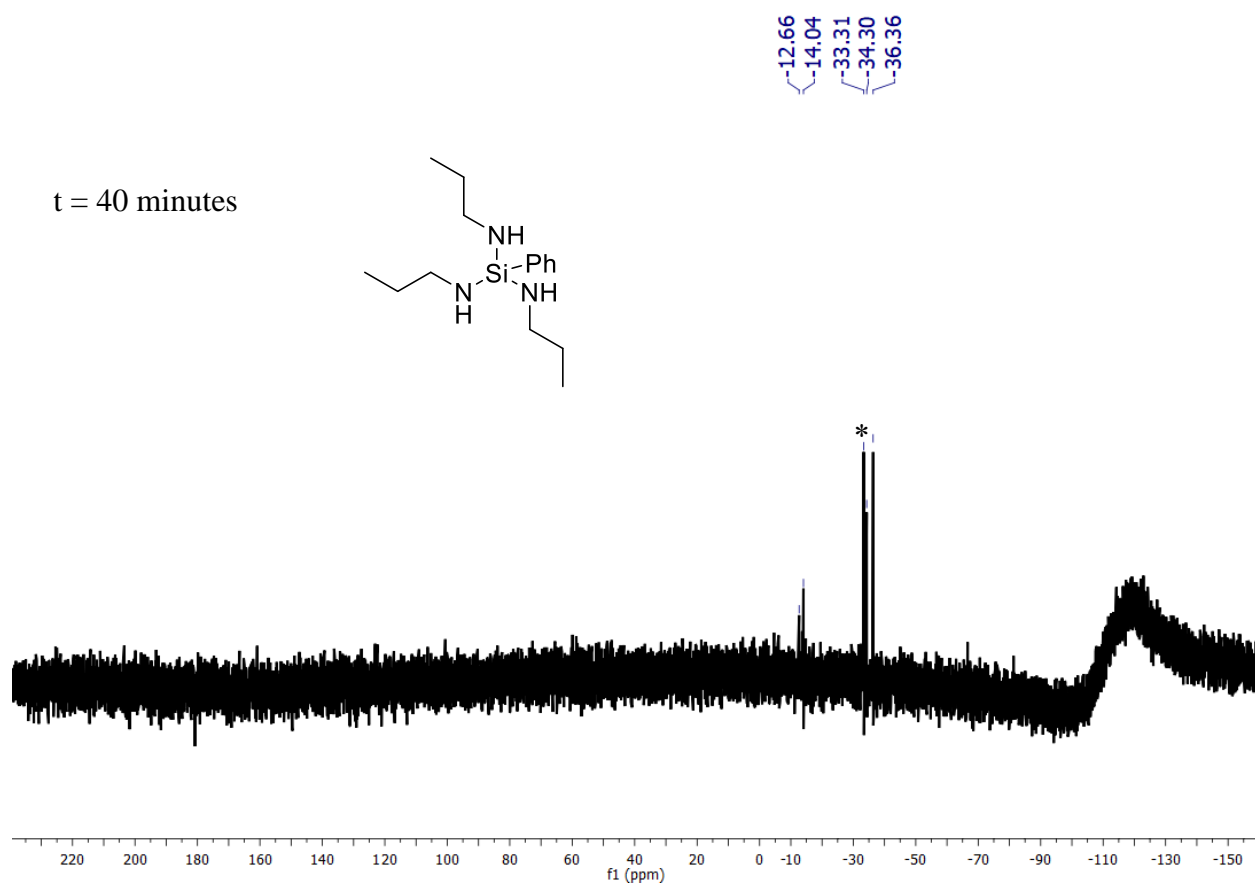
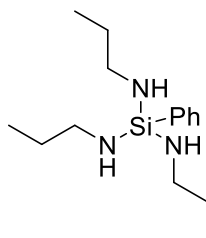
[La] catalyzed dehydrocoupling of reactions amine and silanes – general method as described with *n*-Propylamine and phenylsilane

### Reaction of *n*-propylamine and phenylsilane<sup>1</sup>

*n*-Propylamine (76.1 mg, 1.288 mmol) and phenylsilane (34.9 mg, 0.322 mmol) were mixed in ca. 0.5 mL benzene-*d*<sub>6</sub>. This solution was then pipetted into a vial containing **1** (2 mg, 2.6 x 10<sup>-3</sup> mmol). The mixture immediately began evolving gas. The bubbling solution was transferred into a J-Young type polytetrafluoroethylene (PTFE)-valved NMR tube as quickly as possible. PhSi(<sup>*n*</sup>PrNH)<sub>3</sub> was produced in 85 % yield by NMR. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 500 MHz): δ 7.74 (m, 2H), 7.29 (m, 3H), 2.80 (q, 6H), 1.38 (sextet, 6H), 0.84 (t, 9H), 0.76 (br s, 3H). <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>, 99 MHz): δ -33.31. Several ill-defined byproducts were observed. These are likely higher order silamines.



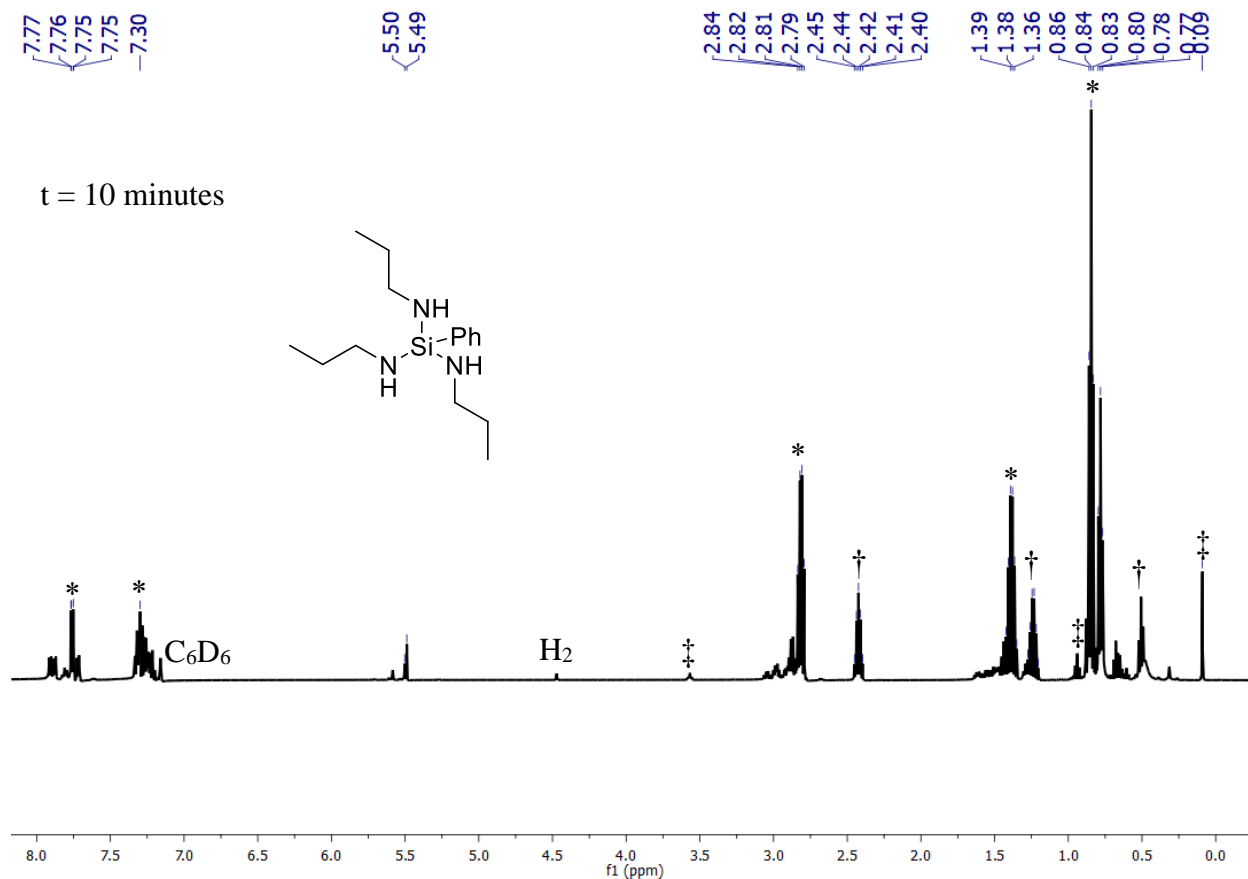
t = 40 minutes



$^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , 99 MHz)

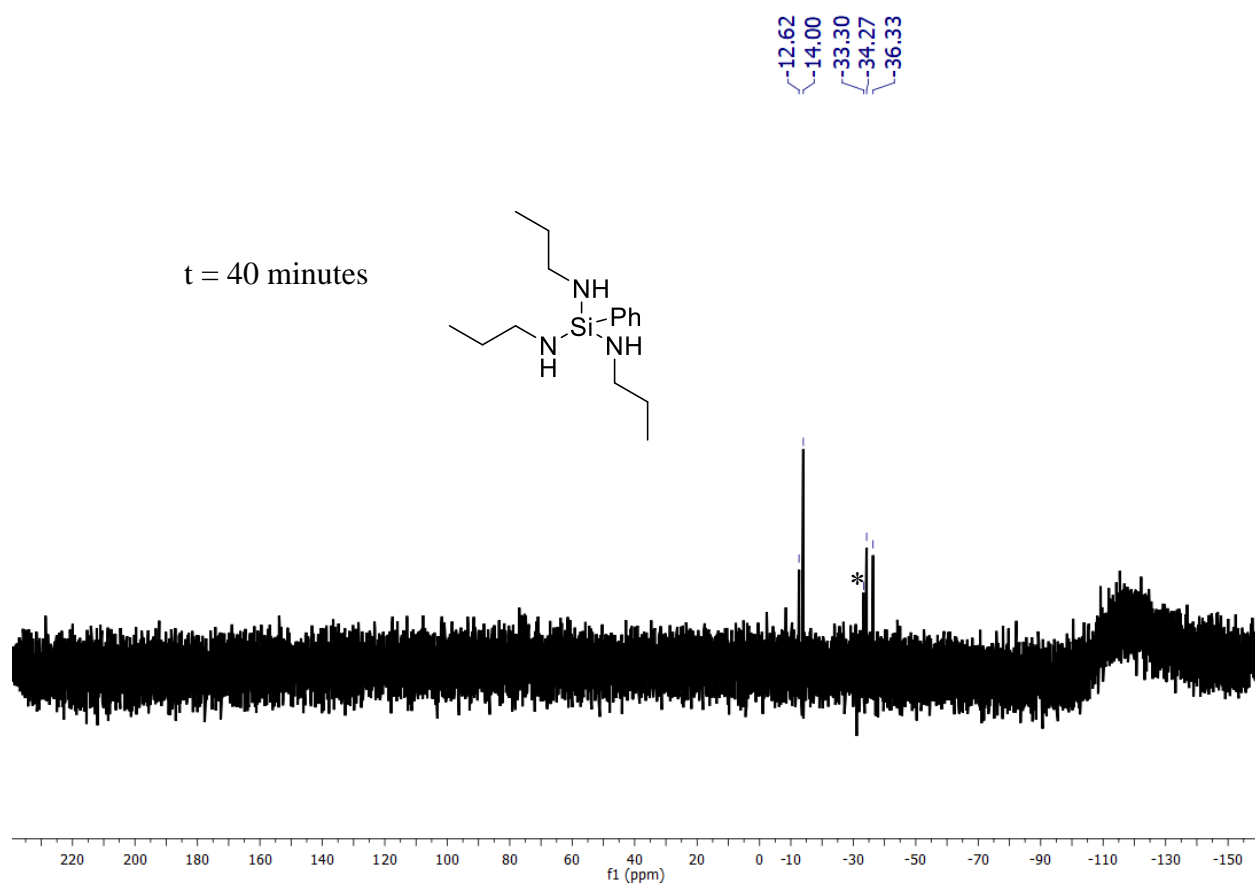
### Reaction of 3 *n*-propylamine and phenylsilane<sup>1</sup>

*n*-Propylamine (57.1 mg, 0.966 mmol) and phenylsilane (34.9 mg, 0.322 mmol) in 0.5 mL benzene-*d*<sub>6</sub> were added to **1** (2 mg, 2.6 × 10<sup>-3</sup> mmol). PhSi(<sup>*n*</sup>PrNH)<sub>3</sub> was produced in 45-60 % yield by NMR spectroscopy. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 500 MHz): δ 7.74 (m, 2H), 7.29 (m, 3H), 2.80 (q, 6H), 1.38 (sextet, 6H), 0.84 (t, 9H), 0.76 (br s, 3H). <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>, 99 MHz): δ -33.30. Several ill-defined byproducts were observed. These are likely higher order silamines.



<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz)

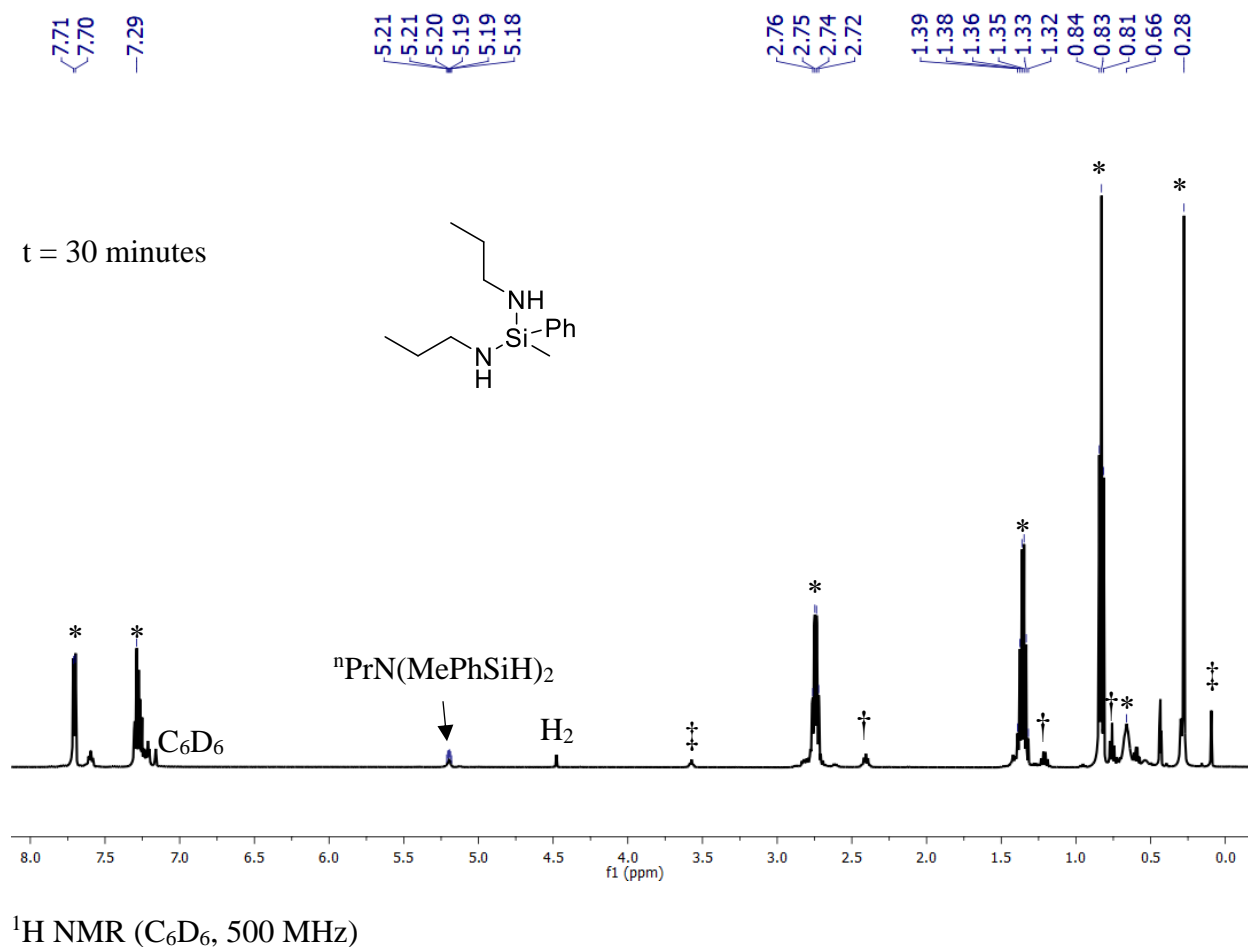
†



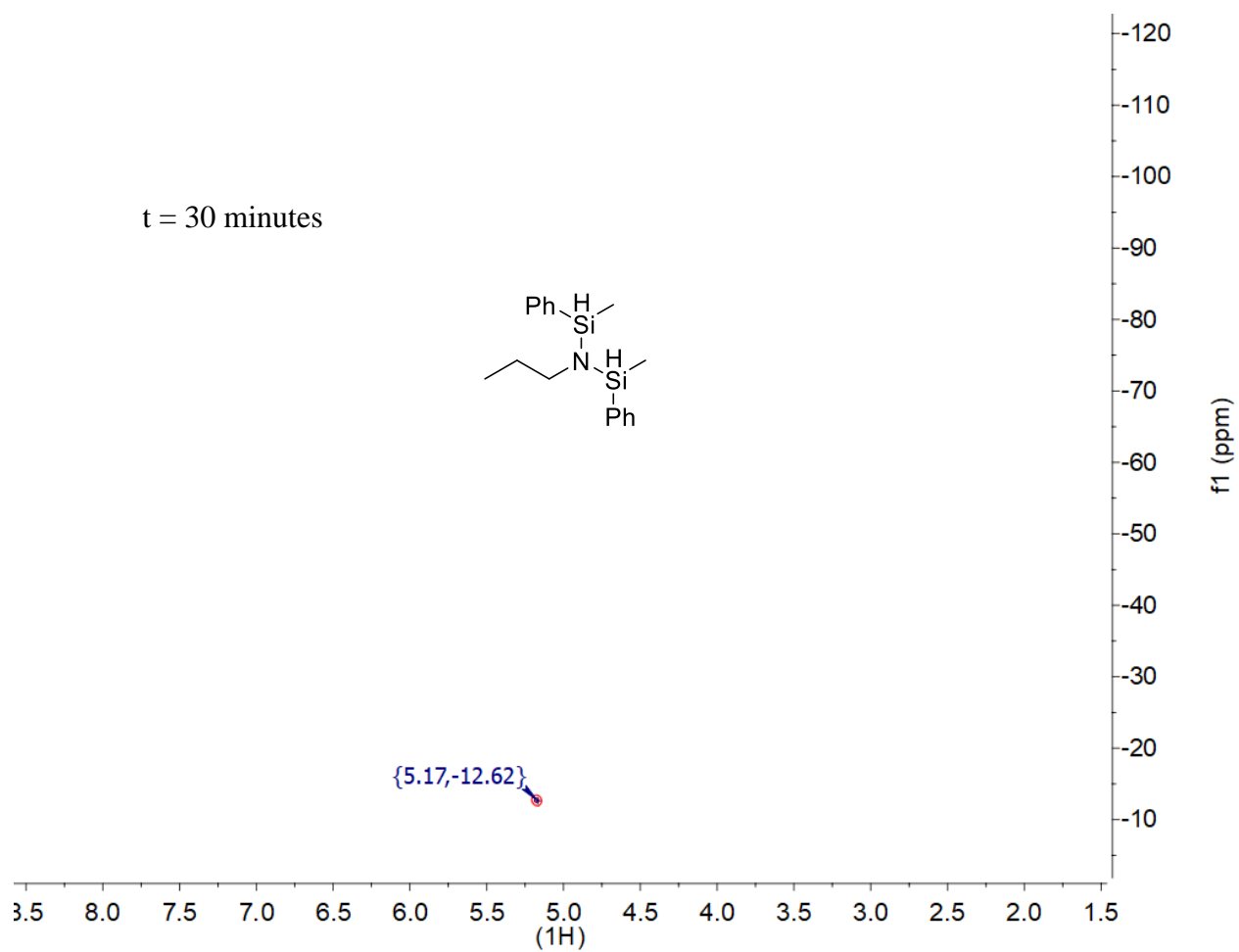
<sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, 99 MHz)

### Reaction of *n*-propylamine and methylphenylsilane<sup>1</sup>

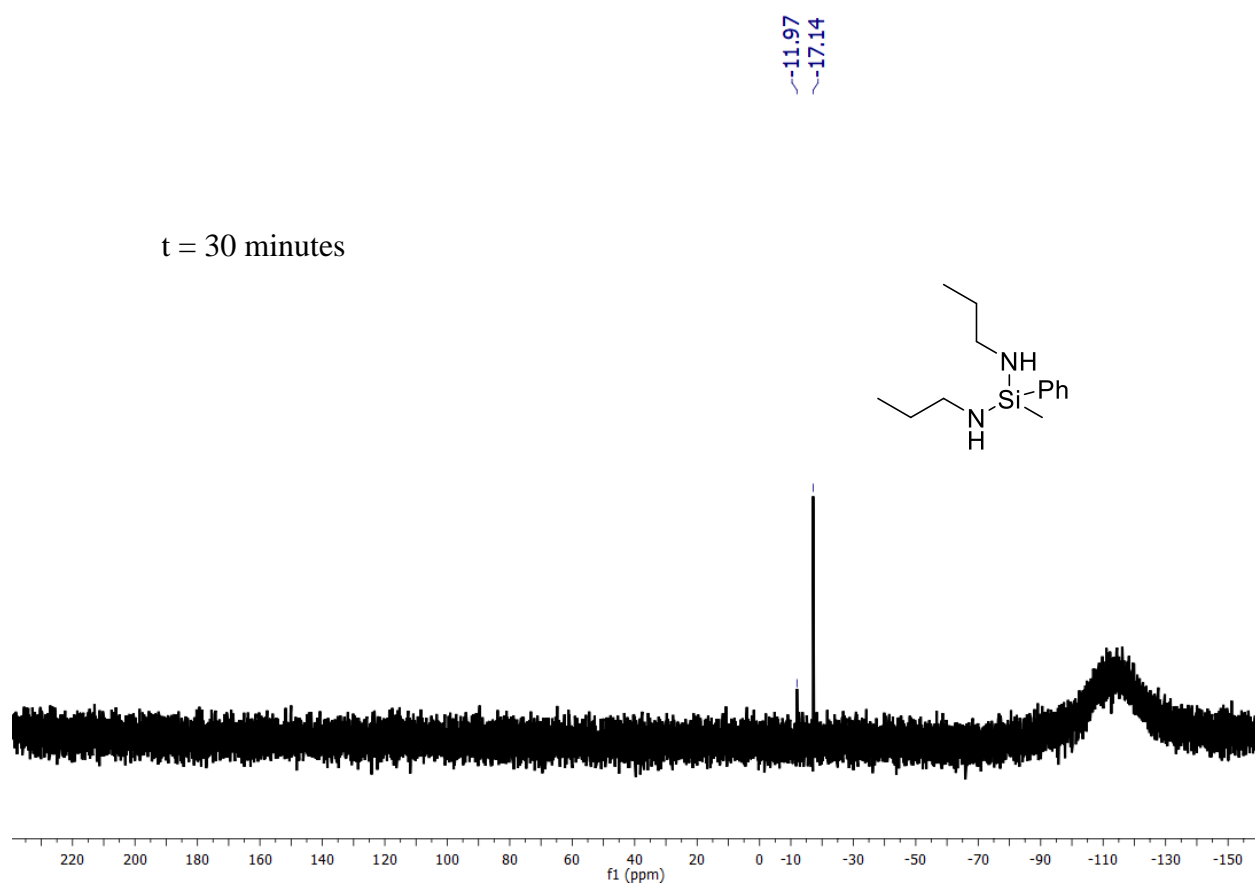
*n*-Propylamine (76.1 mg, 1.288 mmol) and methylphenylsilane (39.4 mg, 0.322 mmol) in 0.5 mL benzene-*d*<sub>6</sub> were added to **1** (2 mg, 2.6 × 10<sup>-3</sup> mmol). Over 30 minutes, MePhSi(<sup>*n*</sup>PrNH)<sub>2</sub> was produced in 96% yield. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 500 MHz): δ 7.70 (m, 2H), 7.29 (m, 3H), 2.74 (q, 4H), 1.35 (sextet, 4H), 0.83 (t, 6H), 0.66 (br s, 2H), 0.28 (s, 3H). <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>, 99 MHz): δ -17.14. A byproduct, presumed to be <sup>*n*</sup>PrN(MePhSiH)<sub>2</sub>, was produced in 4% yield. The isopropylamine analogue is known and exists as diastereomers, producing two overlapping quartets from the Si–H resonance at 5.23 ppm. A similar pattern is observed at for the byproduct at 5.19 ppm. <sup>1</sup>H-<sup>29</sup>Si HSQC NMR (benzene-*d*<sub>6</sub>) δ -12.62.







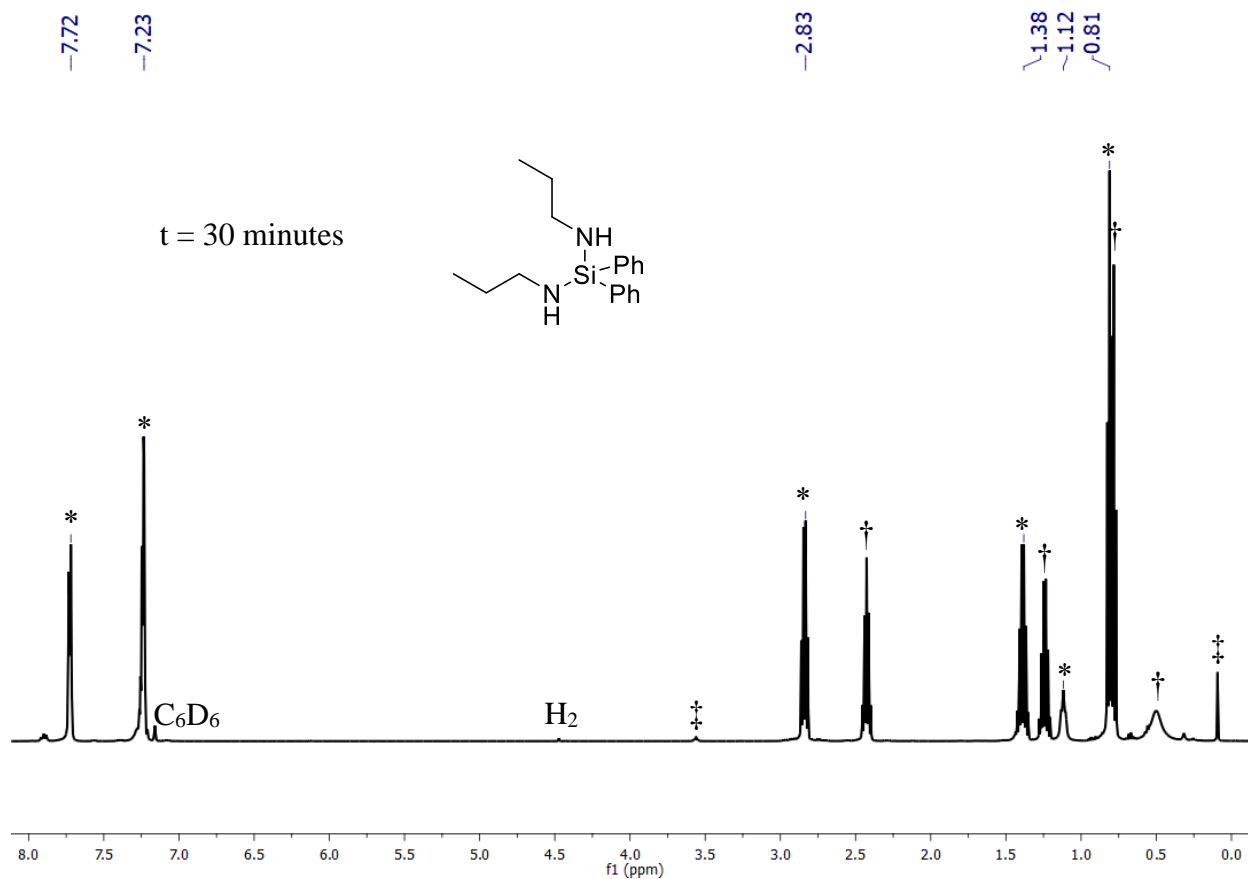
$^1\text{H}$ - $^{29}\text{Si}$  HSQC ( $\text{C}_6\text{D}_6$ )



$^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , 99 MHz)

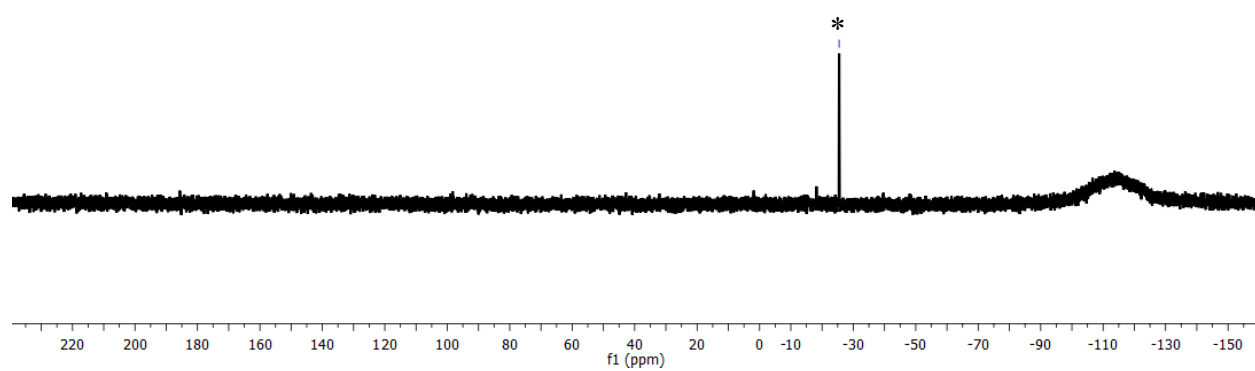
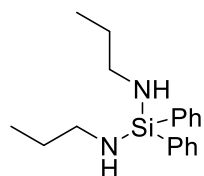
### Reaction of *n*-propylamine and diphenylsilane<sup>1</sup>

*n*-Propylamine (76.1 mg, 1.288 mmol) and diphenylsilane (59.3 mg, 0.322 mmol) in 0.5 mL benzene-*d*<sub>6</sub> were added to **1** (2 mg, 2.6 × 10<sup>-3</sup> mmol). Over 30 minutes, Ph<sub>2</sub>Si(<sup>*n*</sup>PrNH)<sub>2</sub> was produced in 100% yield. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 500 MHz): δ 7.72 (m, 4H), 7.23 (m, 6H), 2.83 (q, 4H), 1.38 (sextet, 4H), 1.12 (br, 2H) 0.81 (t, 6H). <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>, 99 MHz): δ -25.46.



<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz)

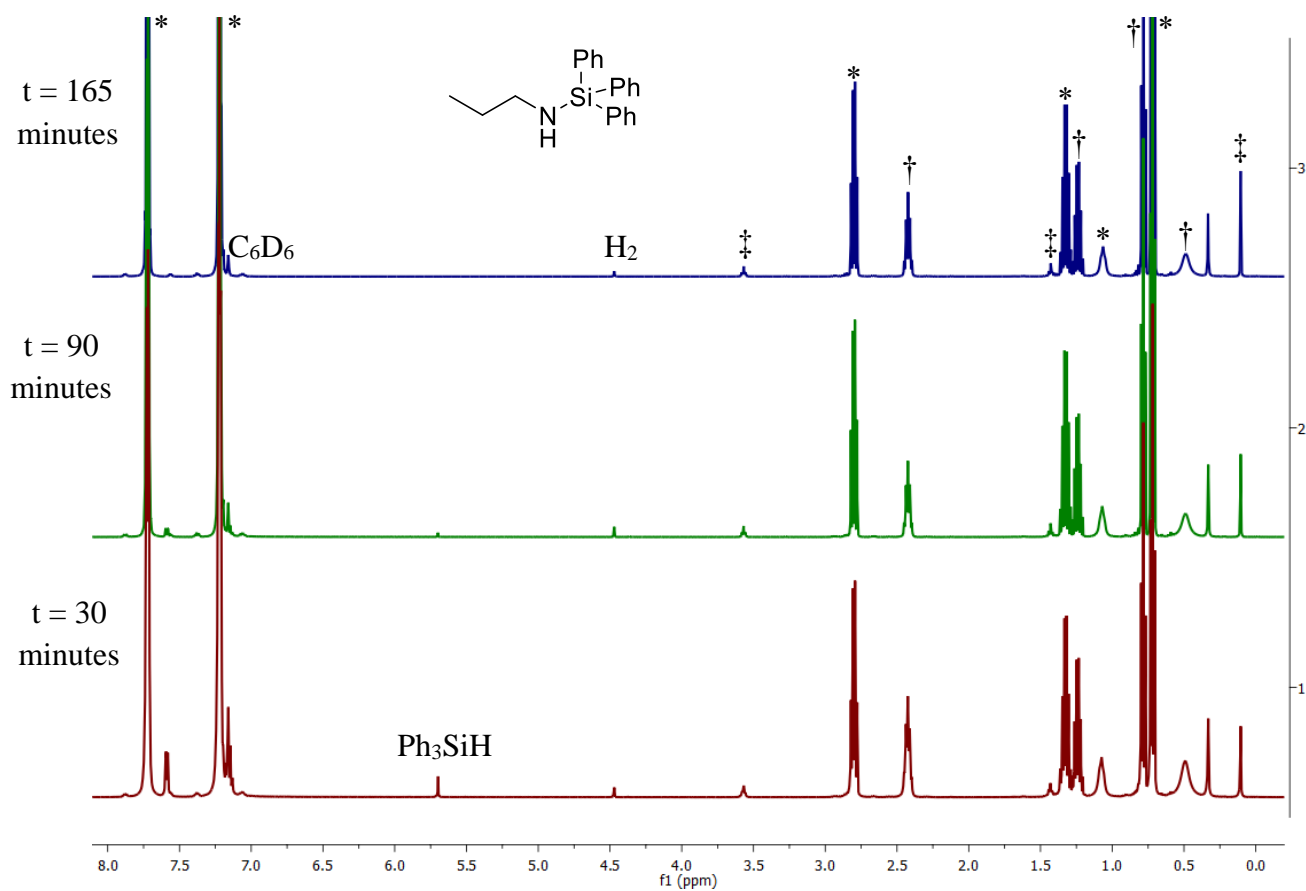
t = 30 minutes



$^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , 99 MHz)

### Reaction of *n*-propylamine and triphenylsilane

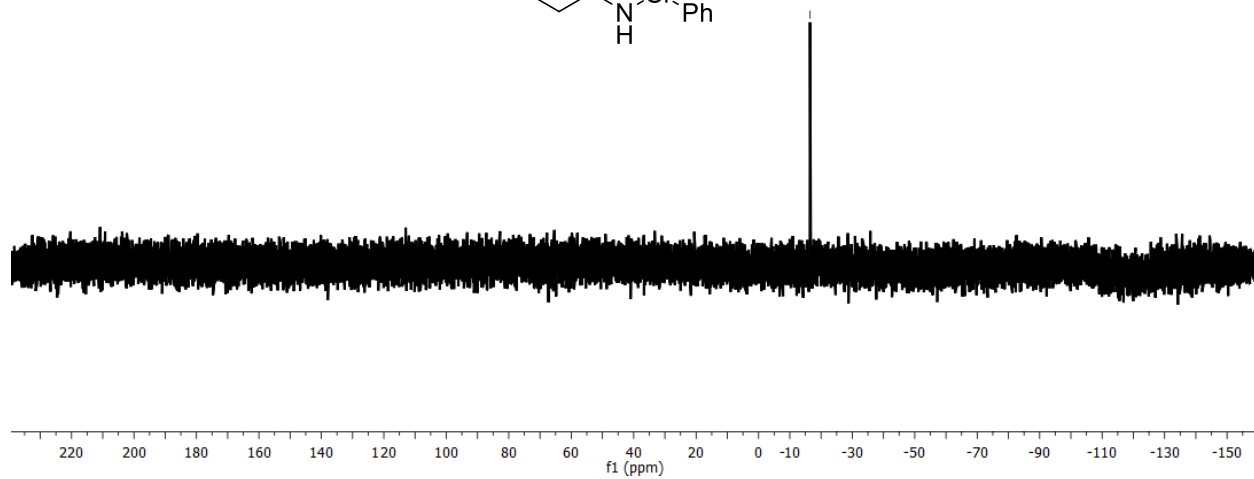
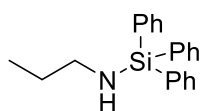
*n*-Propylamine (38.1 mg, 0.644 mmol) and triphenylsilane (83.9 mg, 0.322 mmol) in 0.5 mL benzene-*d*<sub>6</sub> were added to **1** (2 mg, 2.6 × 10<sup>-3</sup> mmol). The reaction was then heated at 60 °C. Over 2.75 hours, Ph<sub>3</sub>Si(<sup>*n*</sup>PrNH) was produced in 100% yield. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 500 MHz): δ 7.72 (m, 6H), 7.23 (m, 9H), 2.79 (q, 2H), 1.32 (sextet, 2H), 1.06 (br, 1H) 0.72 (t, 3H). <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>, 99 MHz): δ -16.48. The consumption of triphenylsilane can be observed by disappearance of the Si–H resonance at 5.71 ppm.



<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz)

t = 165  
minutes

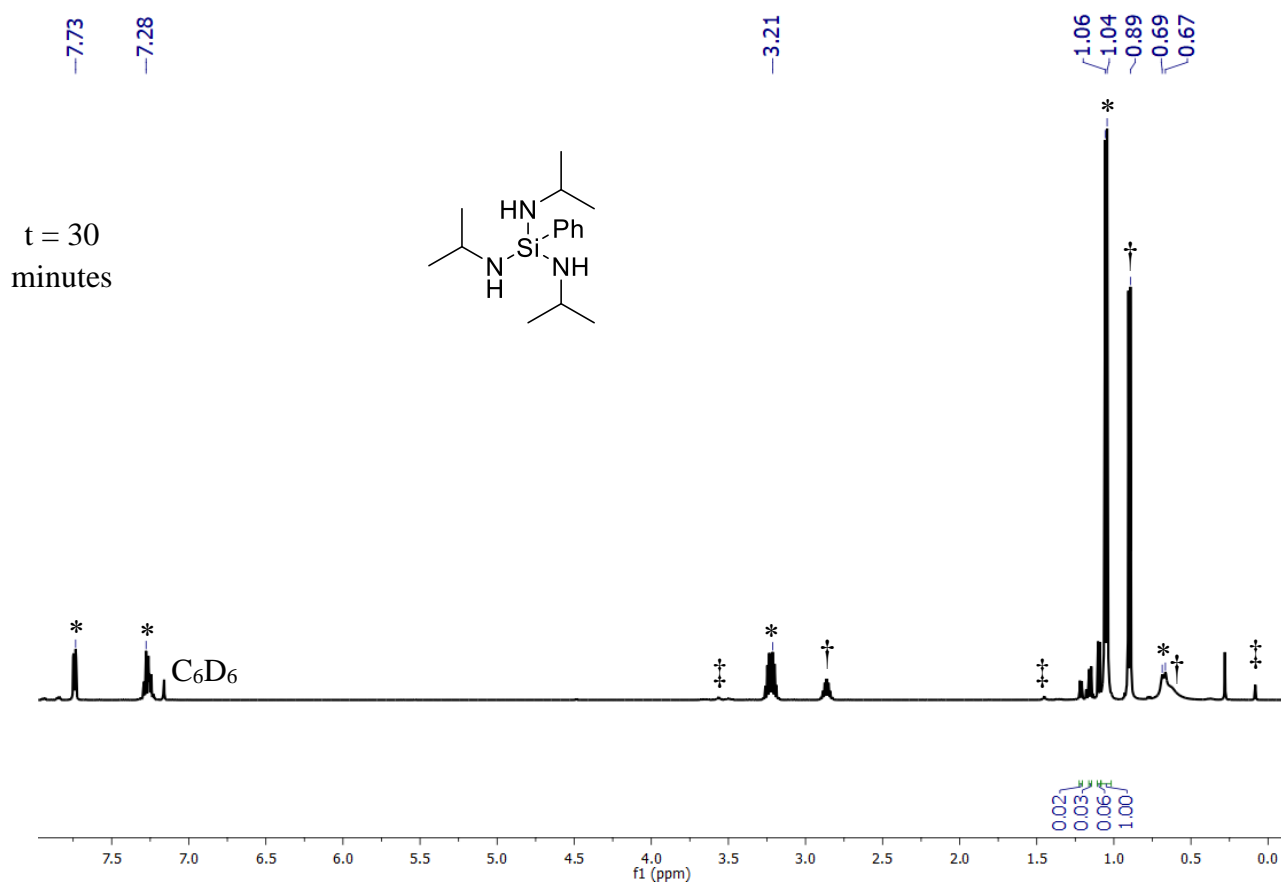
16.48



$^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , 99 MHz)

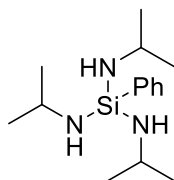
### Reaction of isopropylamine and phenylsilane<sup>2</sup>

Isopropylamine (114.2 mg, 1.932 mmol) and phenylsilane (34.9 mg, 0.322 mmol) in 0.5 mL benzene-*d*<sub>6</sub> were added to **1** (2 mg, 2.6 × 10<sup>-3</sup> mmol). Over 30 minutes, PhSi(<sup>*i*</sup>PrNH)<sub>3</sub> was produced in 90% yield. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 500 MHz): δ 7.73 (m, 2H), 7.28 (m, 3H), 3.21 (m, 3H), 1.06 (d, 18H), 0.65 (br d, 3H). <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>, 99 MHz): δ -37.39. Three byproducts can be observed with different isopropyl resonances at 1.09, 1.15 and 1.21 ppm in <sup>1</sup>H NMR and one Si resonance at -40.18 in <sup>29</sup>Si NMR.

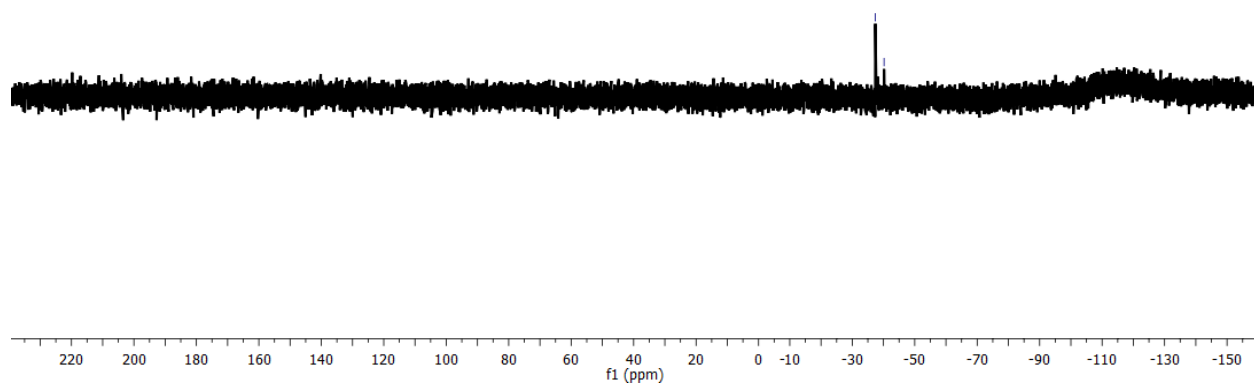


<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz)

t = 30  
minutes



37.39  
40.18

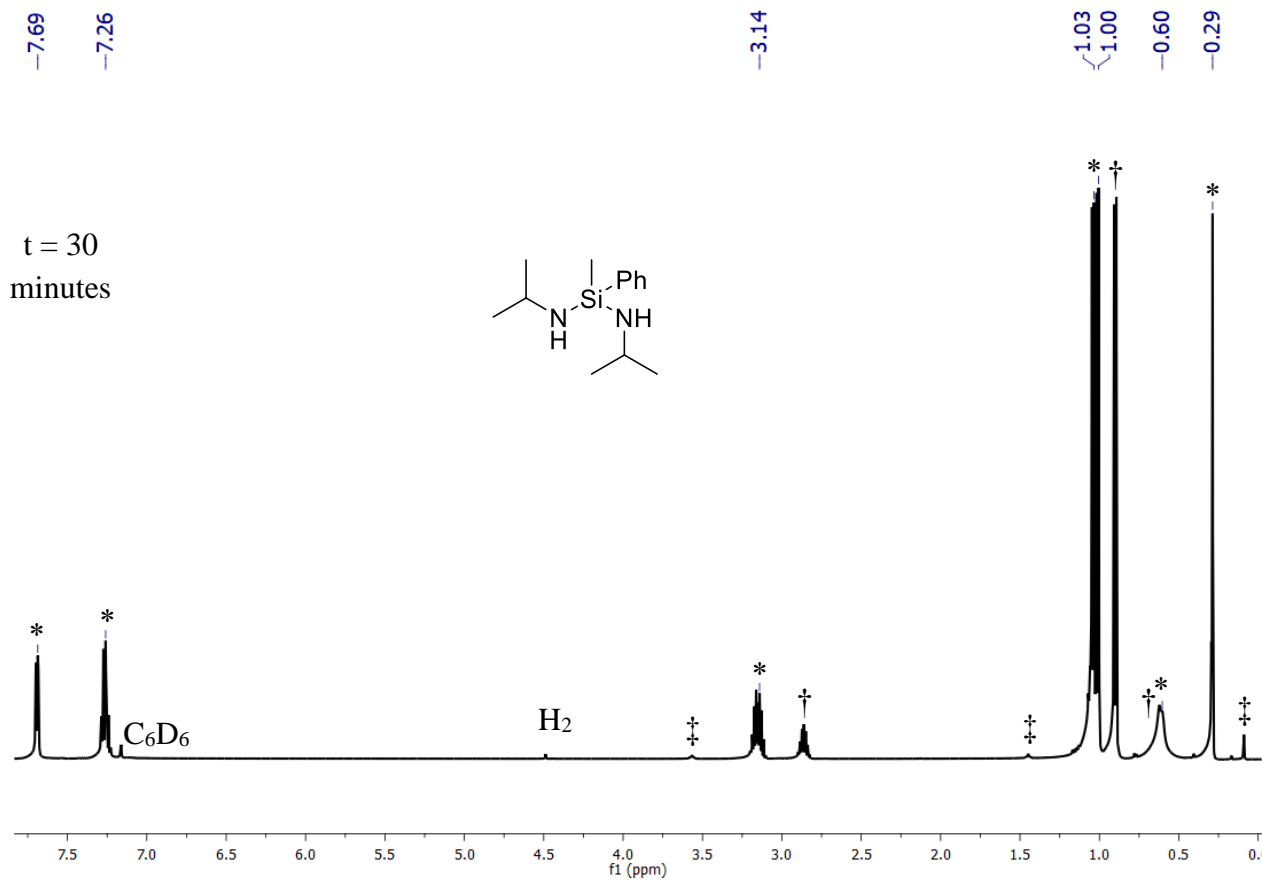


$^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , 99 MHz)

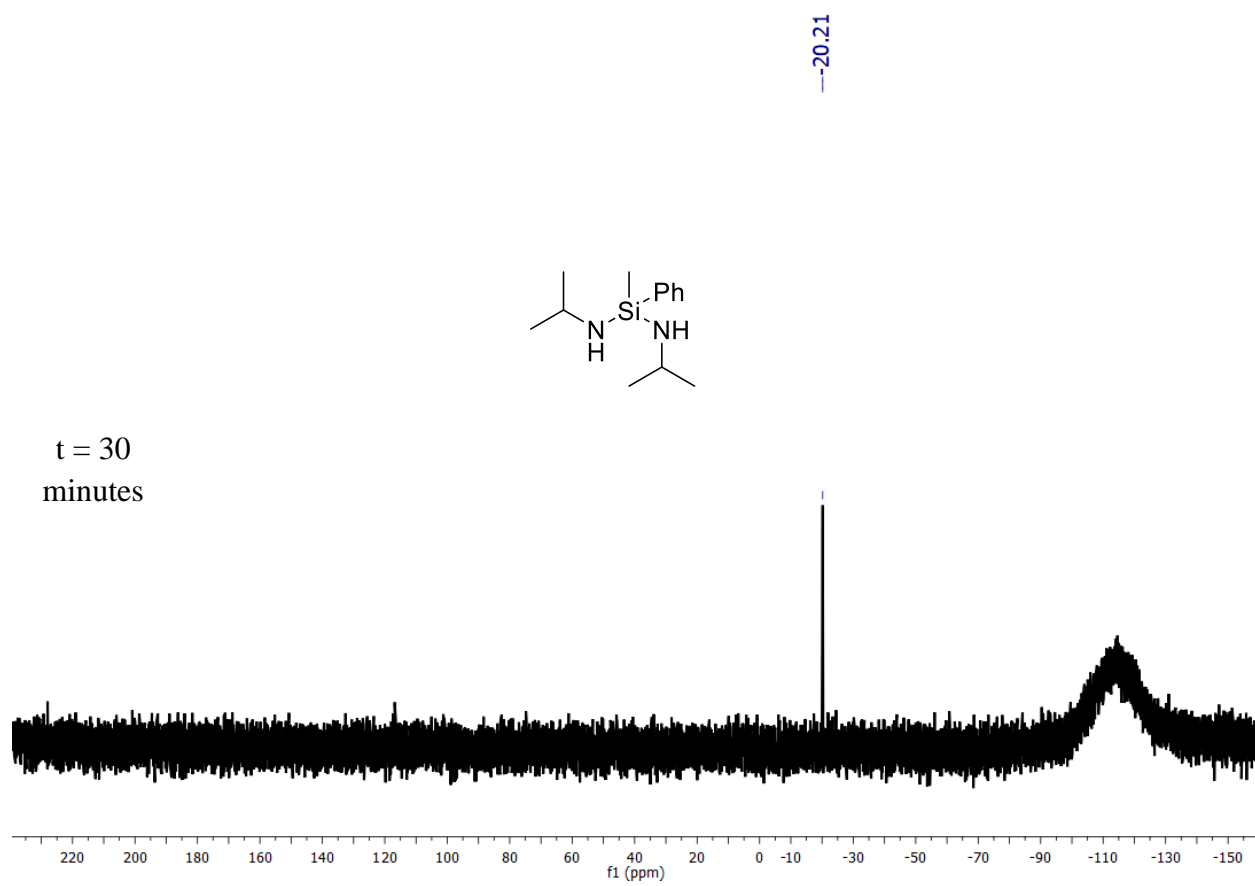


### Reaction of isopropylamine and methylphenylsilane<sup>3</sup>

Isopropylamine (76.1 mg, 1.288 mmol) and methylphenylsilane (39.4 mg, 0.322 mmol) in 0.5 mL benzene-*d*<sub>6</sub> were added to La[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>THF<sub>2</sub> (2 mg, 2.6 × 10<sup>-3</sup> mmol). Over 30 minutes, MePhSi(*i*PrNH)<sub>2</sub> was produced in 100% yield. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 500 MHz): δ 7.69 (m, 2H), 7.26 (m, 3H), 3.14 (m, 2H), 1.03 (d, 6H), 1.00 (d, 6H), 0.60 (br, 2H). <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>, 99 MHz): δ -20.21.



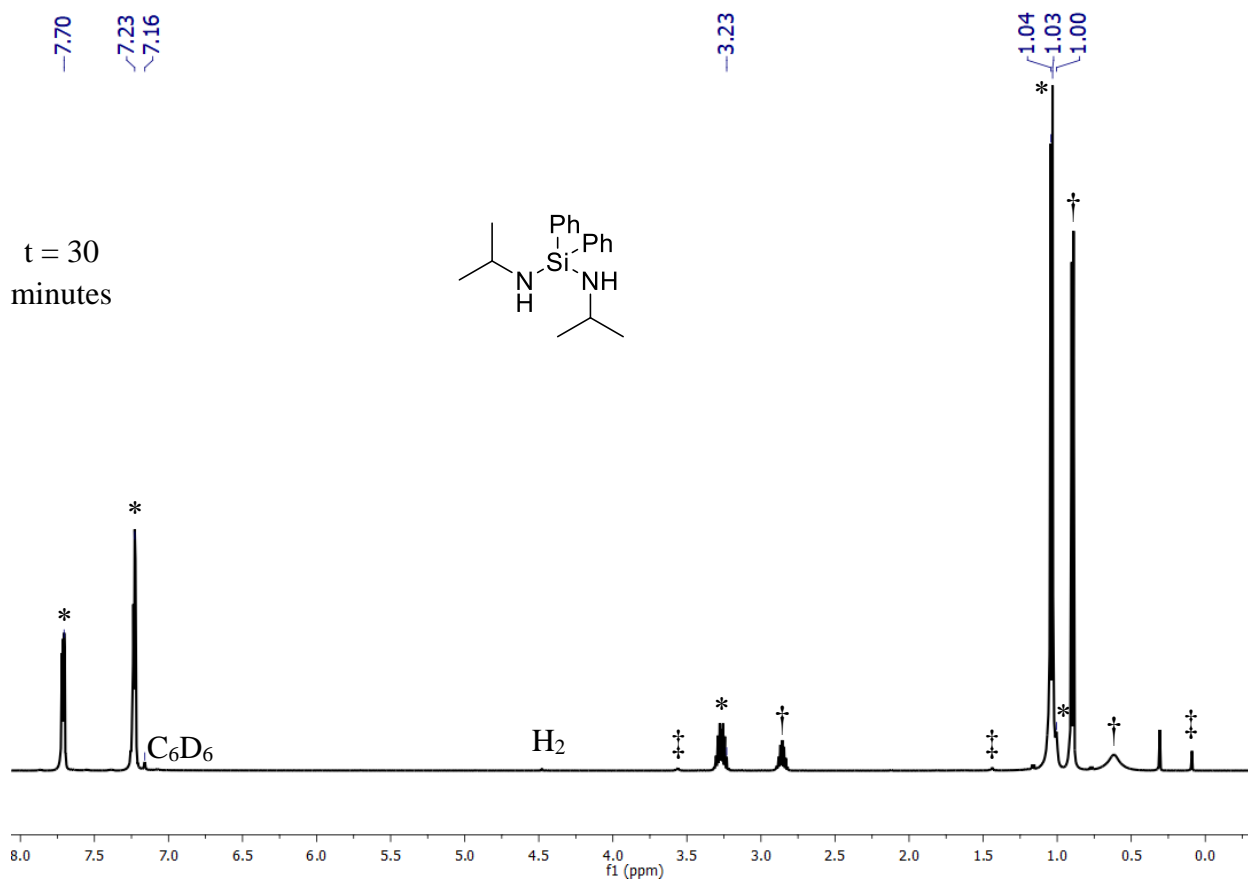
<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz)



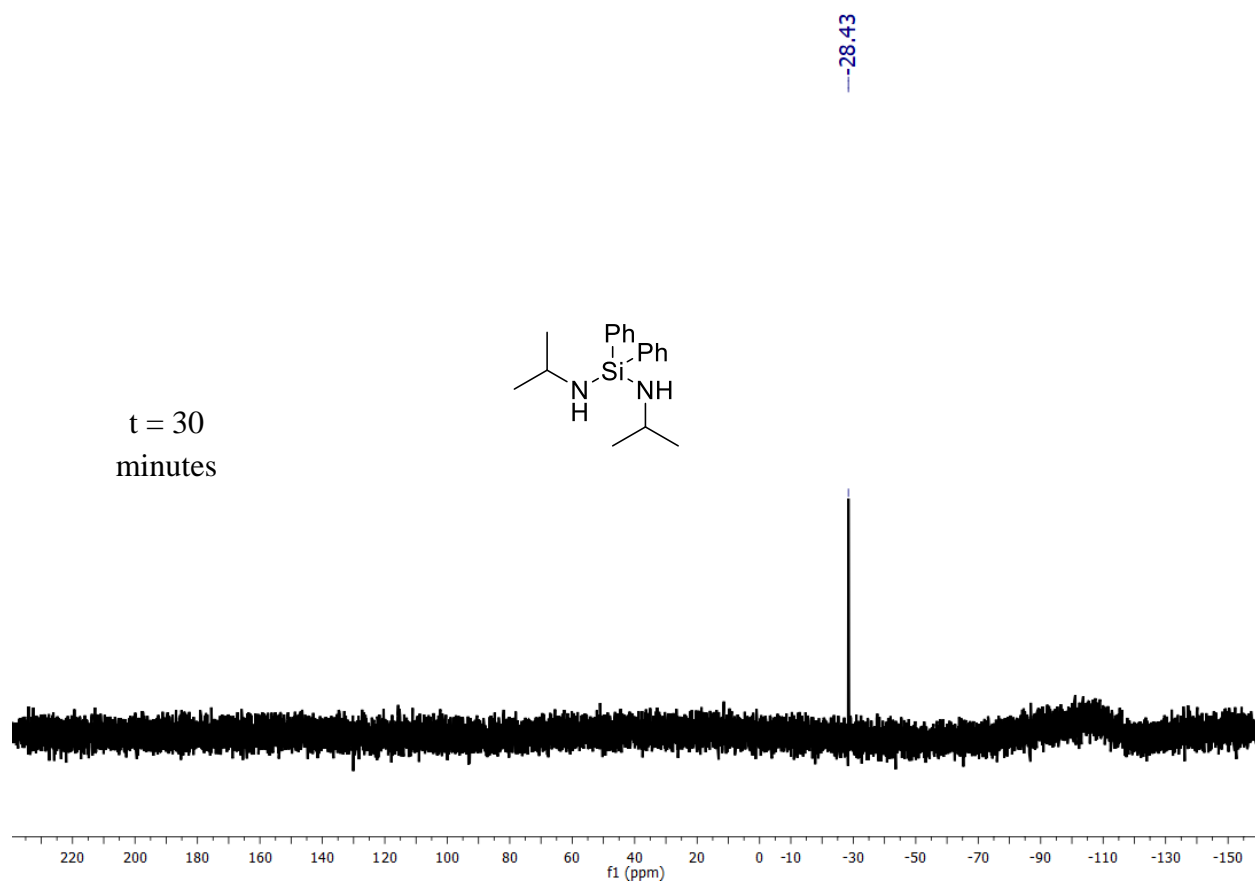
$^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , 99 MHz)

### Reaction of isopropylamine and diphenylsilane<sup>4</sup>

Isopropylamine (76.1 mg, 1.288 mmol) and diphenylsilane (59.3 mg, 0.322 mmol) in 0.5 mL benzene-*d*<sub>6</sub> were added to **1** (2 mg, 2.6 × 10<sup>-3</sup> mmol). Over 30 minutes, Ph<sub>2</sub>Si(<sup>*i*</sup>PrNH)<sub>2</sub> was produced in 100% yield. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 500 MHz): δ 7.70 (m, 4H), 7.23 (m, 6H), 3.23 (m, 2H), 1.03 (d, 12H), 1.00 (br s, 2H). <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>, 99 MHz): δ -28.43.



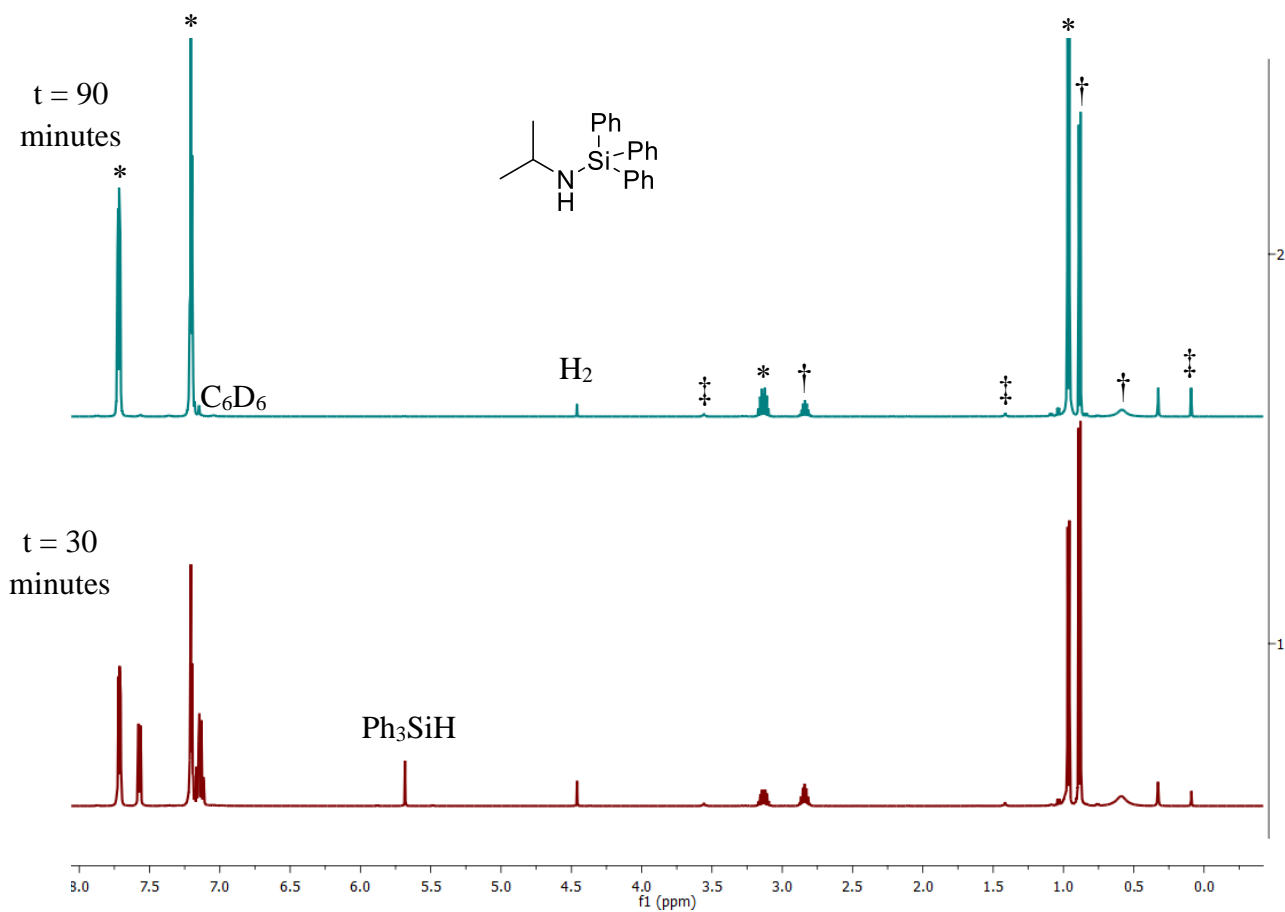
<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz)



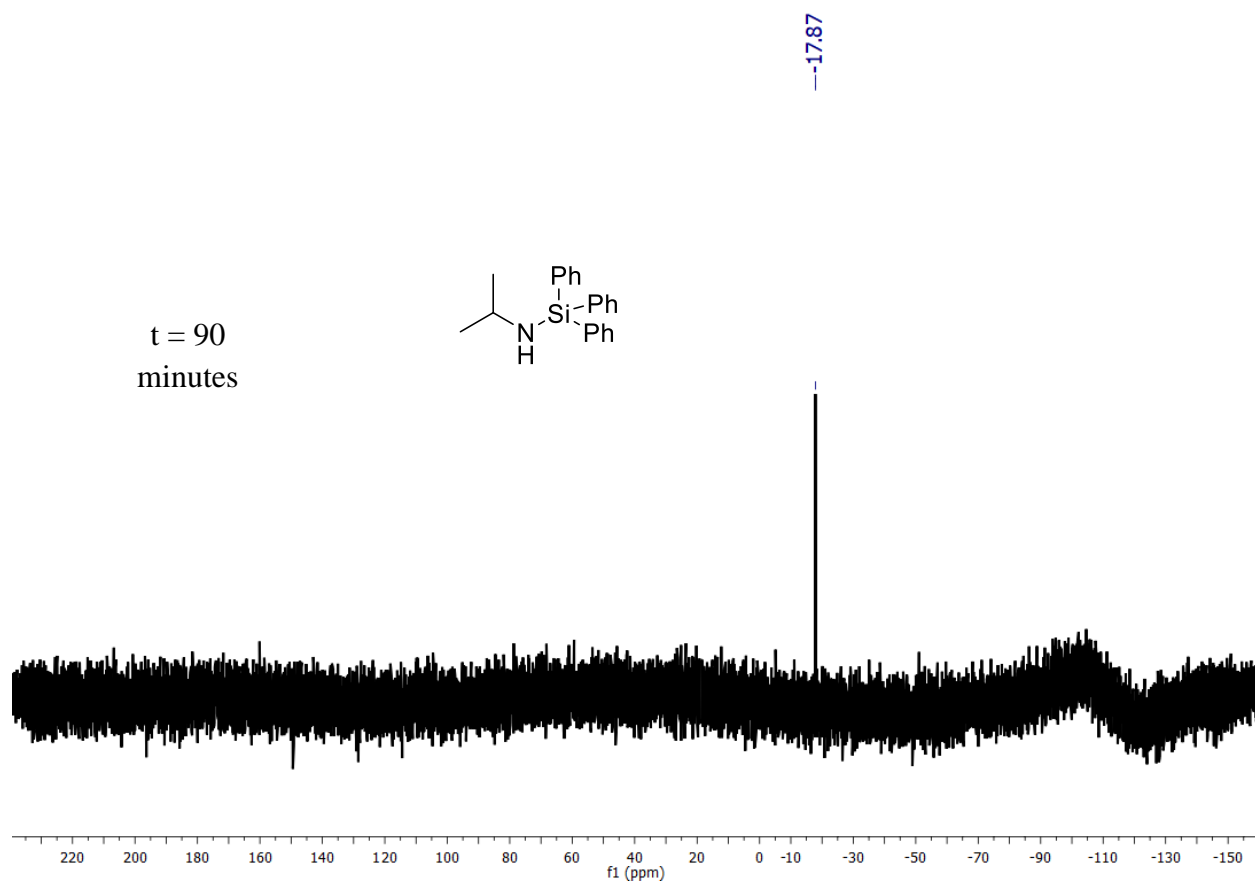
$^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , 99 MHz)

### Reaction of isopropylamine and triphenylsilane

Isopropylamine (38.1 mg, 0.644 mmol) and triphenylsilane (83.9 mg, 0.322 mmol) in 0.5 mL benzene- $d_6$  were added to **1** (2 mg,  $2.6 \times 10^{-3}$  mmol). The reaction was heated at 60 °C. Over 1.5 hours,  $\text{Ph}_3\text{Si}(\text{iPrNH})$  was produced in 100% yield.  $^1\text{H}$  NMR (benzene- $d_6$ , 500 MHz):  $\delta$  7.71 (m, 6H), 7.20 (m, 9H), 3.12 (m, 1H), 0.96 (d, 6H), 0.92 (br s, 1H).  $^{29}\text{Si}$  NMR (benzene- $d_6$ , 99 MHz):  $\delta$  -17.87. The consumption of triphenylsilane can be observed by disappearance of the Si-H resonance at 5.71 ppm.



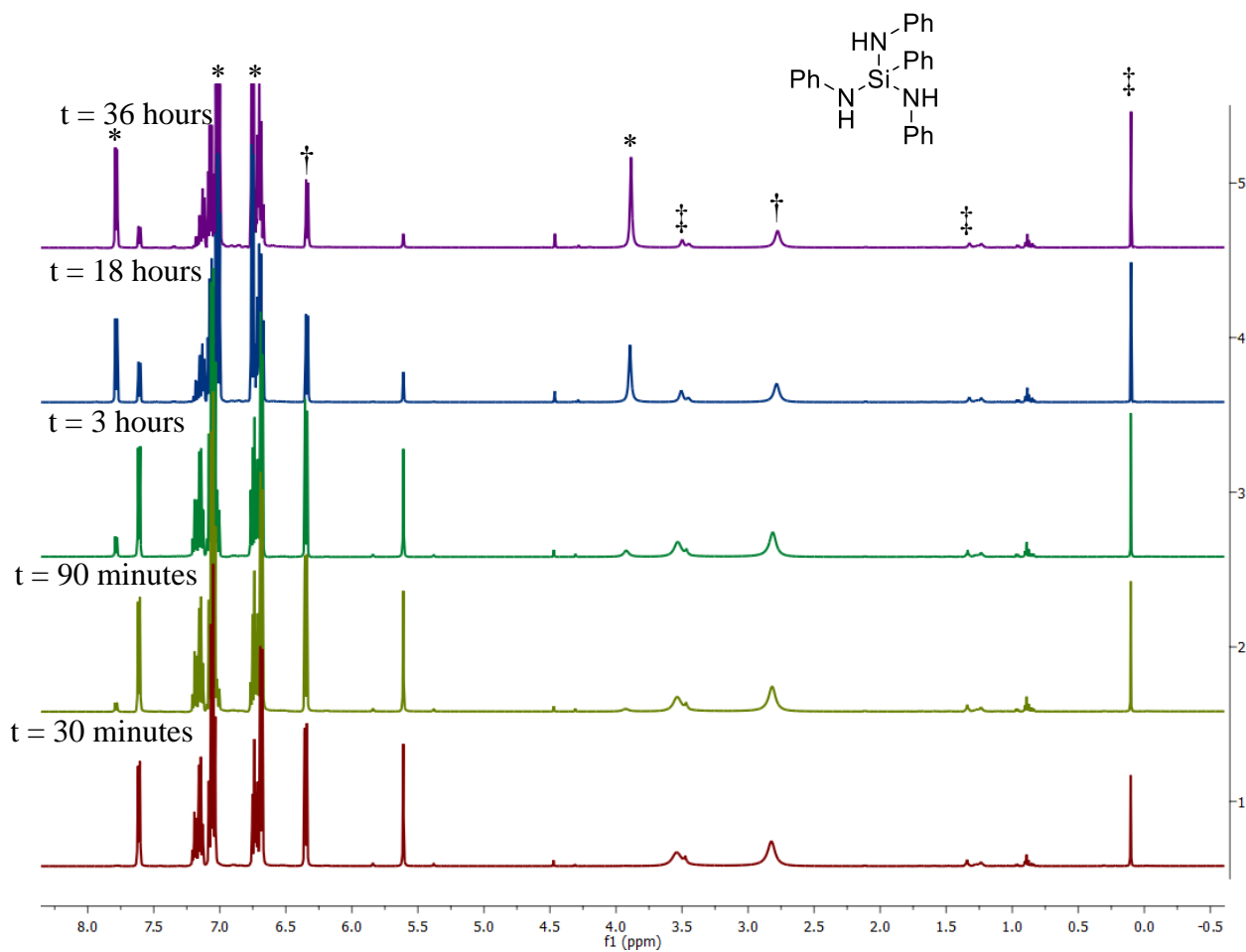
$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 500 MHz)



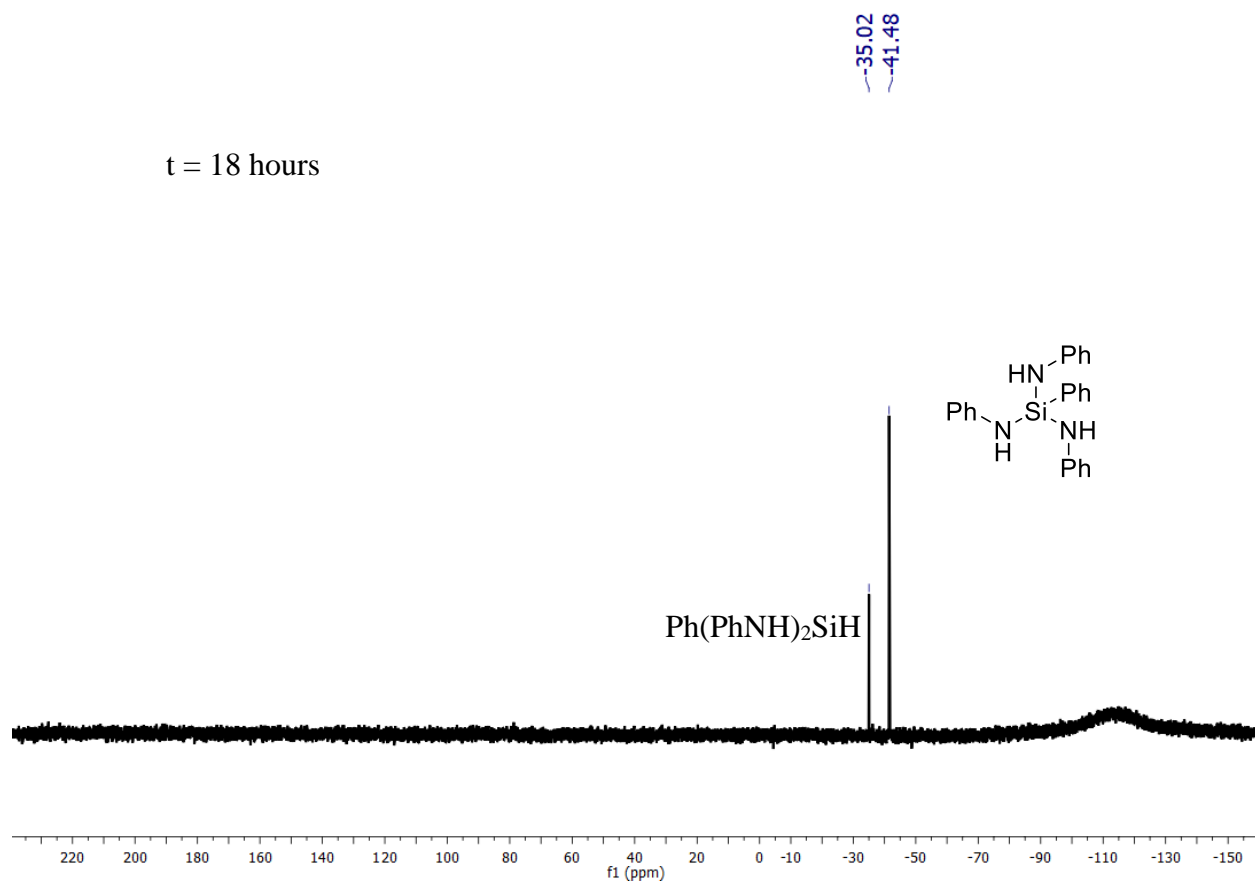
$^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , 99 MHz)

### Reaction of aniline and phenylsilane

Aniline (93.0 mg, 0.998 mmol) and phenylsilane (34.9 mg, 0.322 mmol) in 0.5 mL benzene- $d_6$  were added to **1** (2 mg,  $2.6 \times 10^{-3}$  mmol). Over 30 minutes,  $\text{Ph}(\text{PhNH})_2\text{SiH}$  was produced in 100% yield.  $^1\text{H}$  NMR (benzene- $d_6$ , 500 MHz):  $\delta$  7.60 (d, 2H), 7.14 (m, 3H), 7.05 (t, 4H), 6.74 (t, 2H), 6.68 (d, 4H), 5.61 (s, 1H), 3.54 (br s, 2H).  $^{29}\text{Si}$  NMR (benzene- $d_6$ , 99 MHz):  $\delta$  -35.02. Over 36 hours at 90 °C,  $\text{PhSi}(\text{PhNH})_3$  (\*) was produced in 85% yield. Spectroscopic information above.



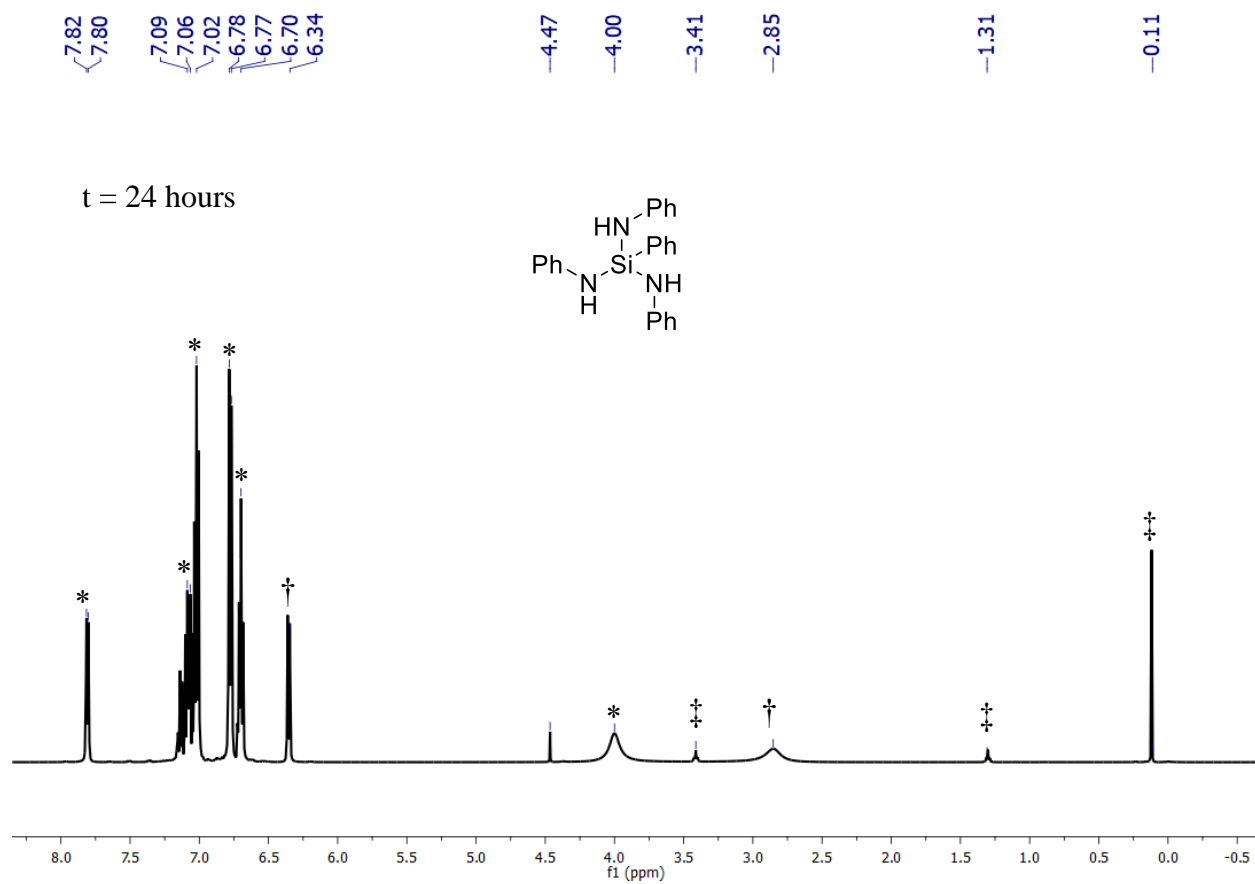
$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 500 MHz)  $\text{C}_6\text{D}_6$  resonance is buried.



<sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, 99 MHz)

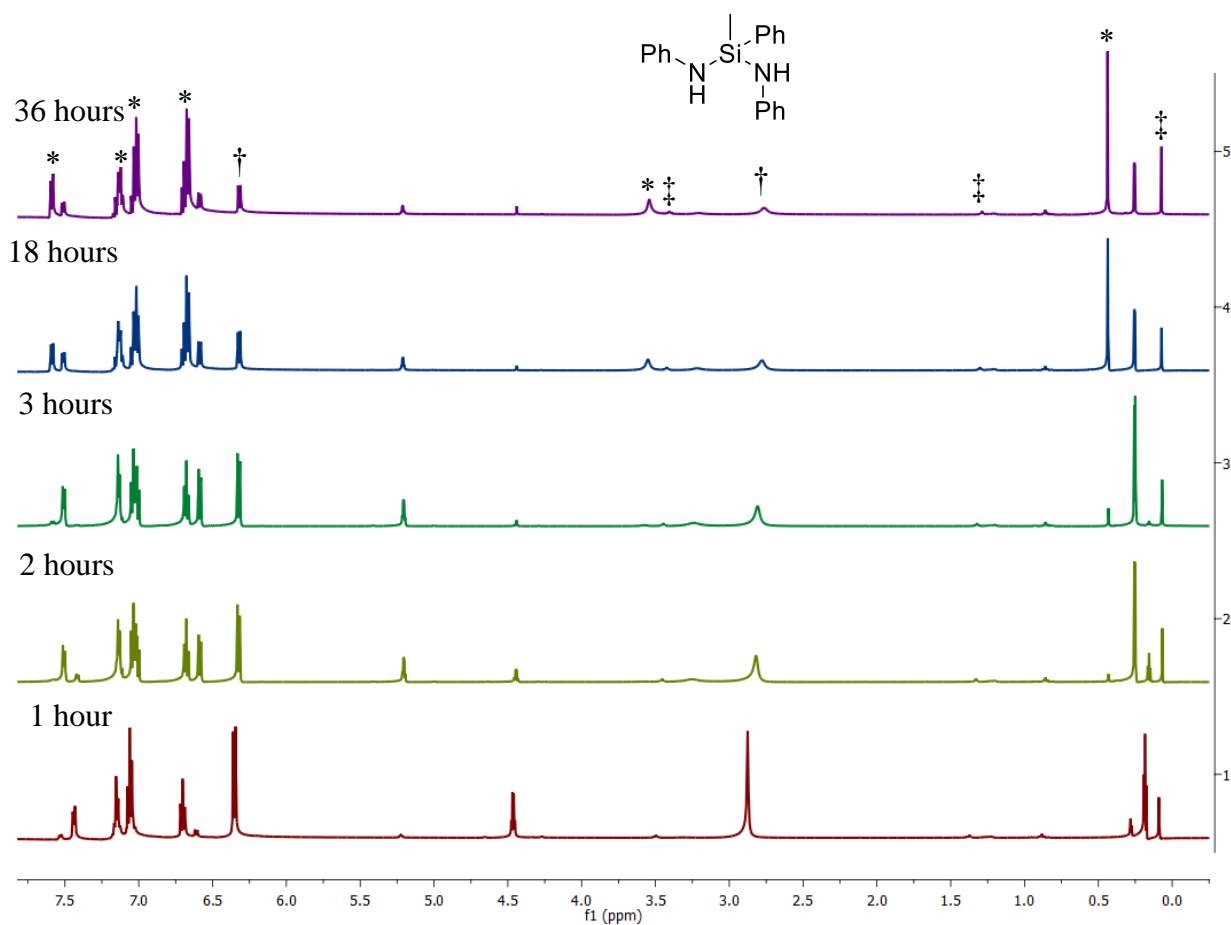
Aniline (389.9 mg, 4.19 mmol) and phenylsilane (113.3 mg, 1.05 mmol) in 0.5 mL benzene-*d*<sub>6</sub> were added to **1** (8 mg, 1.05 × 10<sup>-2</sup> mmol). The reaction was heated at 90 °C for 24 hours. PhSi(PhNH)<sub>3</sub> was produced in 100% yield. The product was isolated and characterized above. Below is a <sup>1</sup>H NMR of the reaction mixture after 24 hours.





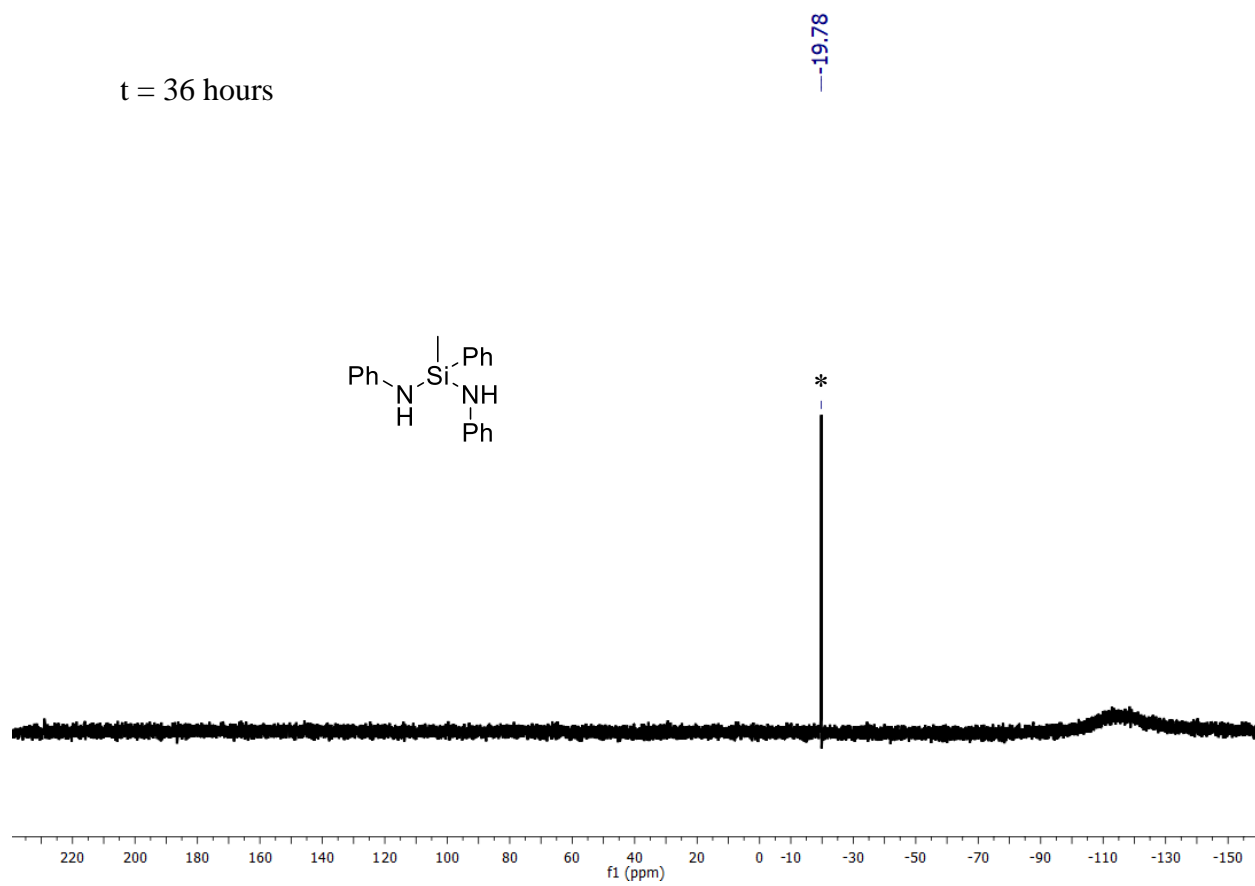
### Reaction of aniline and methylphenylsilane<sup>1</sup>

Aniline (63.1mg, 0.677 mmol) and methylphenylsilane (39.4 mg, 0.322 mmol) in 0.5 mL benzene-*d*<sub>6</sub> were added to **1** (2 mg, 2.6 x 10<sup>-3</sup> mmol). Over 3 hours, MePh(PhNH)SiH was produced in 100% yield. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 500 MHz): δ 7.53 (m, 2H), 7.15 (m, 3H), 7.05 (m, 2H), 6.70 (t, 1H), 6.61 (d, 2H), 5.22 (q, 1H), 3.26 (br s, 1H), 0.27 (d, 3H). <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>, 99 MHz): δ -19.87. Over the next 36 hours, MePhSi(PhNH)<sub>2</sub> (\*) is generated in 76% yield. MePhSi(PhNH)<sub>2</sub> is isolated and characterized above.



<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz) C<sub>6</sub>D<sub>6</sub> resonance is buried.

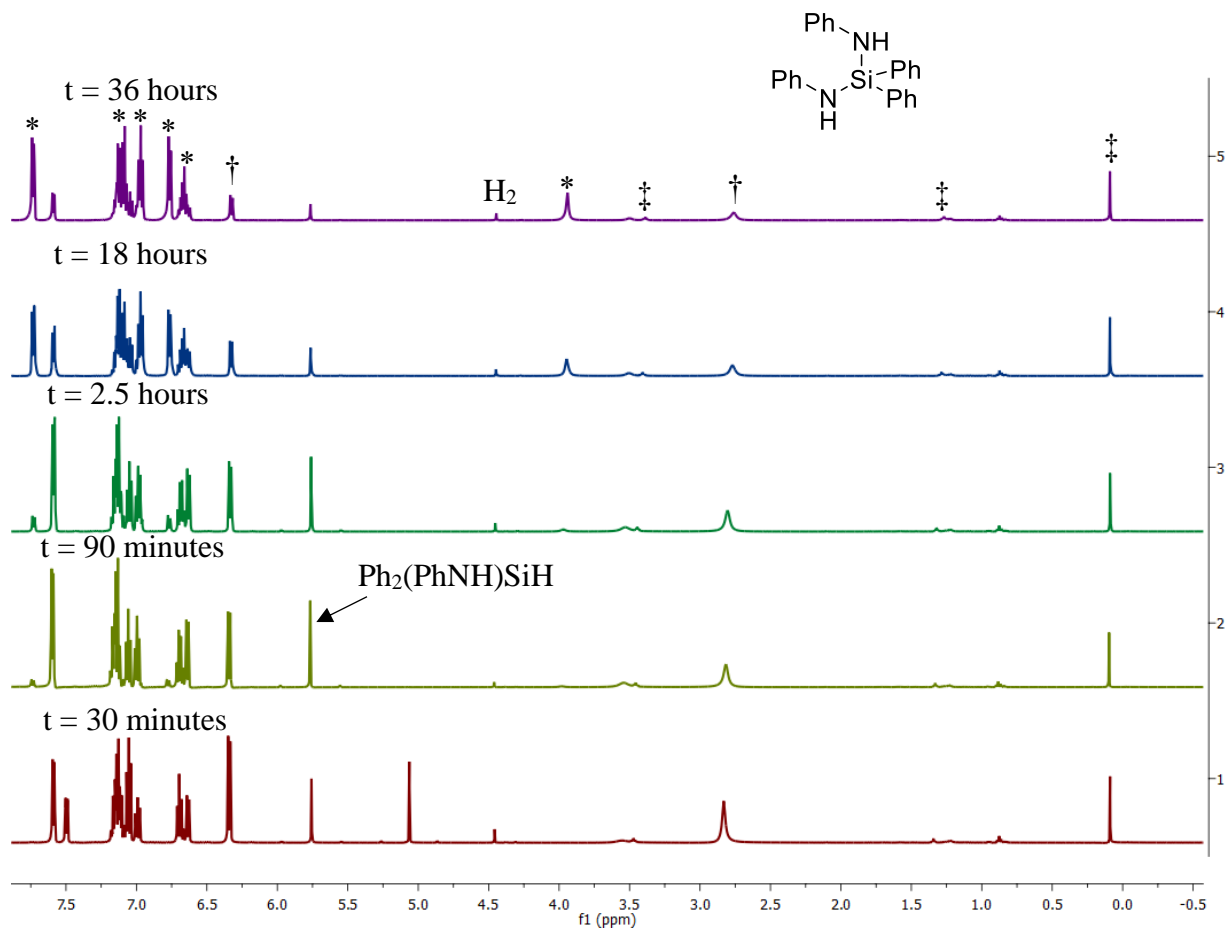
t = 36 hours



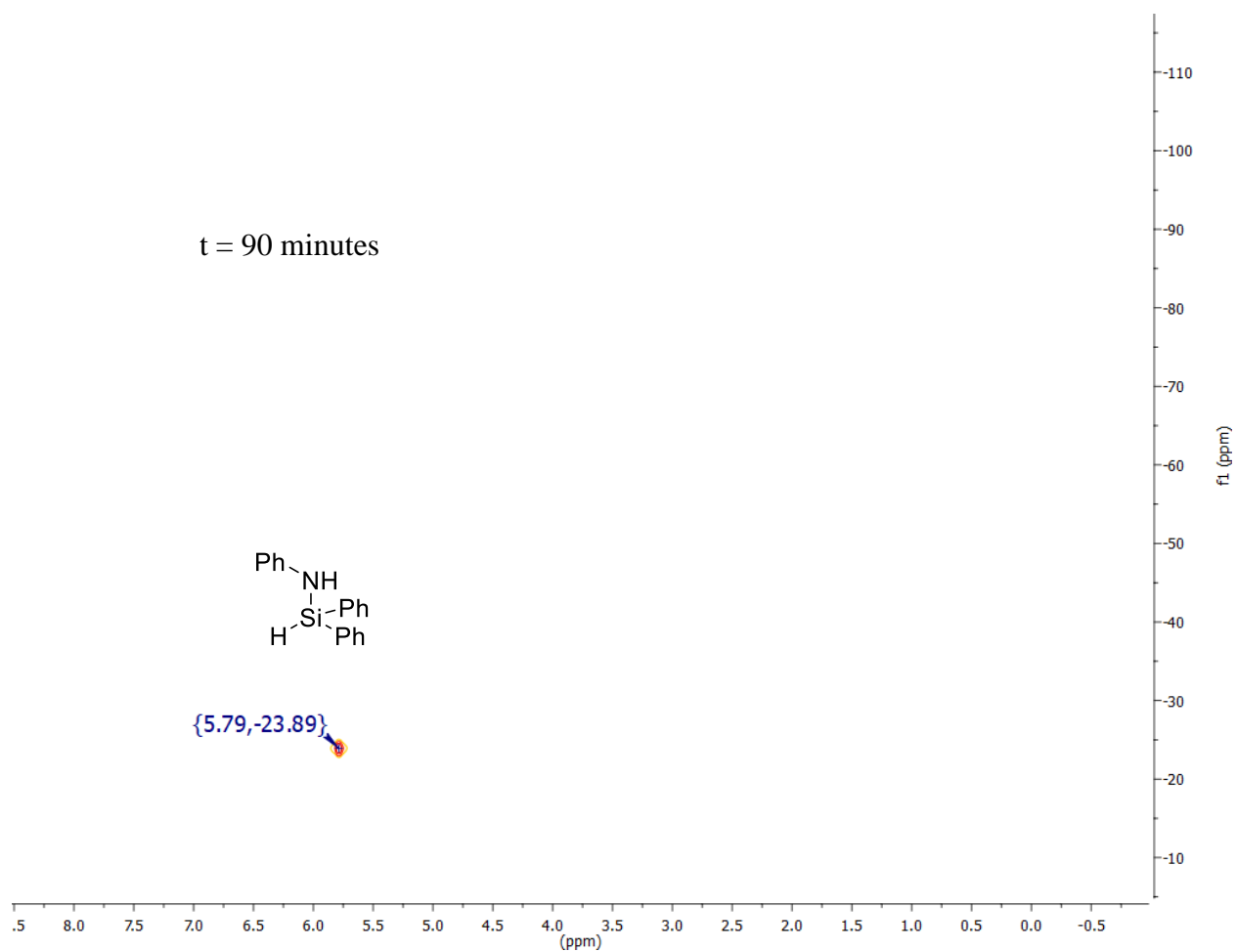
$^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , 99 MHz)

### Reaction of aniline and diphenylsilane<sup>1, 4</sup>

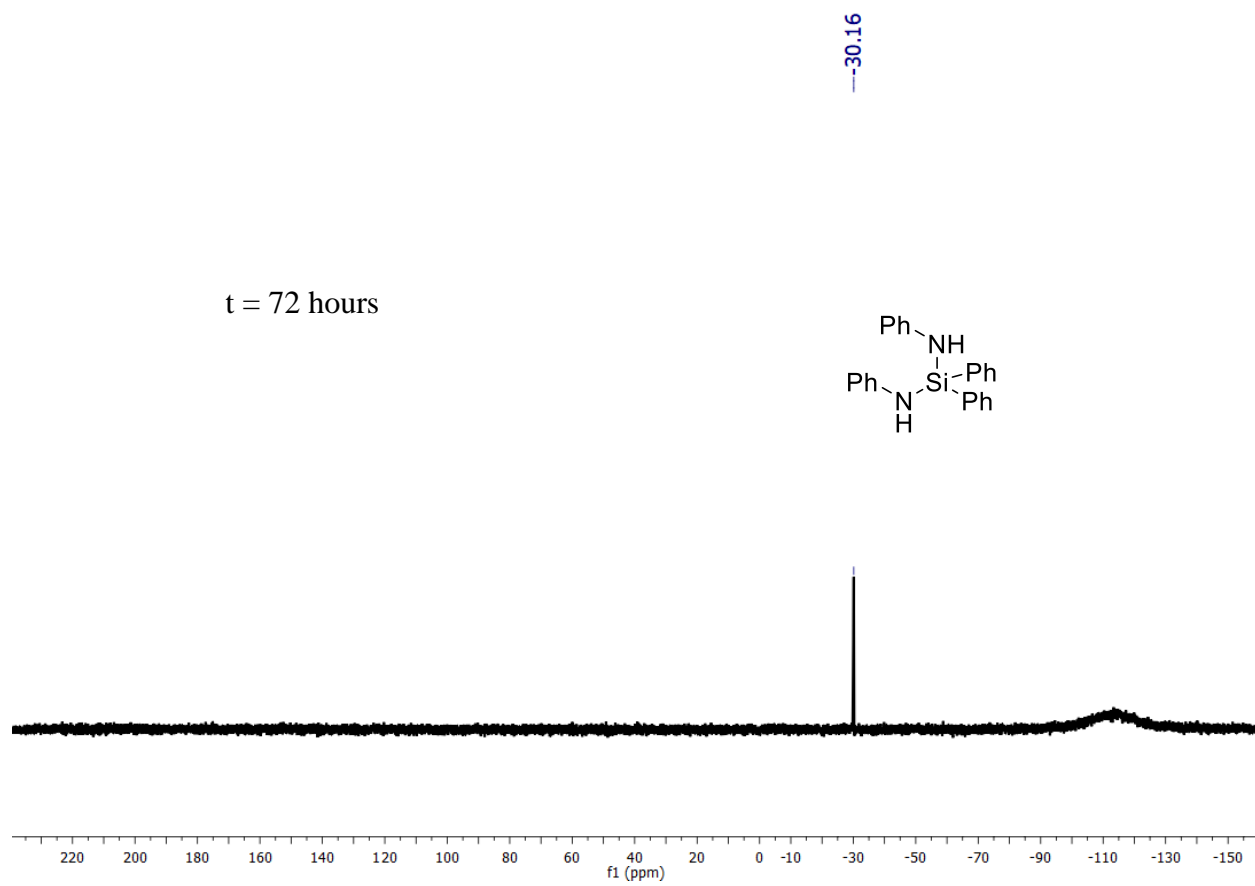
Aniline (63.1 mg, 0.677 mmol) and diphenylsilane (59.4 mg, 0.322 mmol) in 0.5 mL benzene-*d*<sub>6</sub> were added to **1** (2 mg, 2.6 × 10<sup>-3</sup> mmol). The reaction was heated at 60 °C. Over 1.5 hours, Ph<sub>2</sub>(PhNH)SiH was produced in 100% yield. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 500 MHz): δ 7.59 (m, 4H), 7.13 (m, 6H), 7.06 (t, 2H), 6.70 (t, 1H), 6.63 (d, 2H), 5.77 (s, 1H), 3.48 (br s, 1H). <sup>1</sup>H-<sup>29</sup>Si HSQC NMR (benzene-*d*<sub>6</sub>, 99 MHz): δ -23.89. After 72 hours, Ph<sub>2</sub>Si(PhNH)<sub>2</sub> was produced in 100% yield. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 500 MHz): δ 7.72 (m, 4H), 7.07-7.16 (m, 6H), 6.97 (m, 4H), 6.76 (d, 4H), 6.66 (m, 4H), 3.94 (br s, 2H). <sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>, 99 MHz): δ -30.16.



<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz) C<sub>6</sub>D<sub>6</sub> resonance is buried.



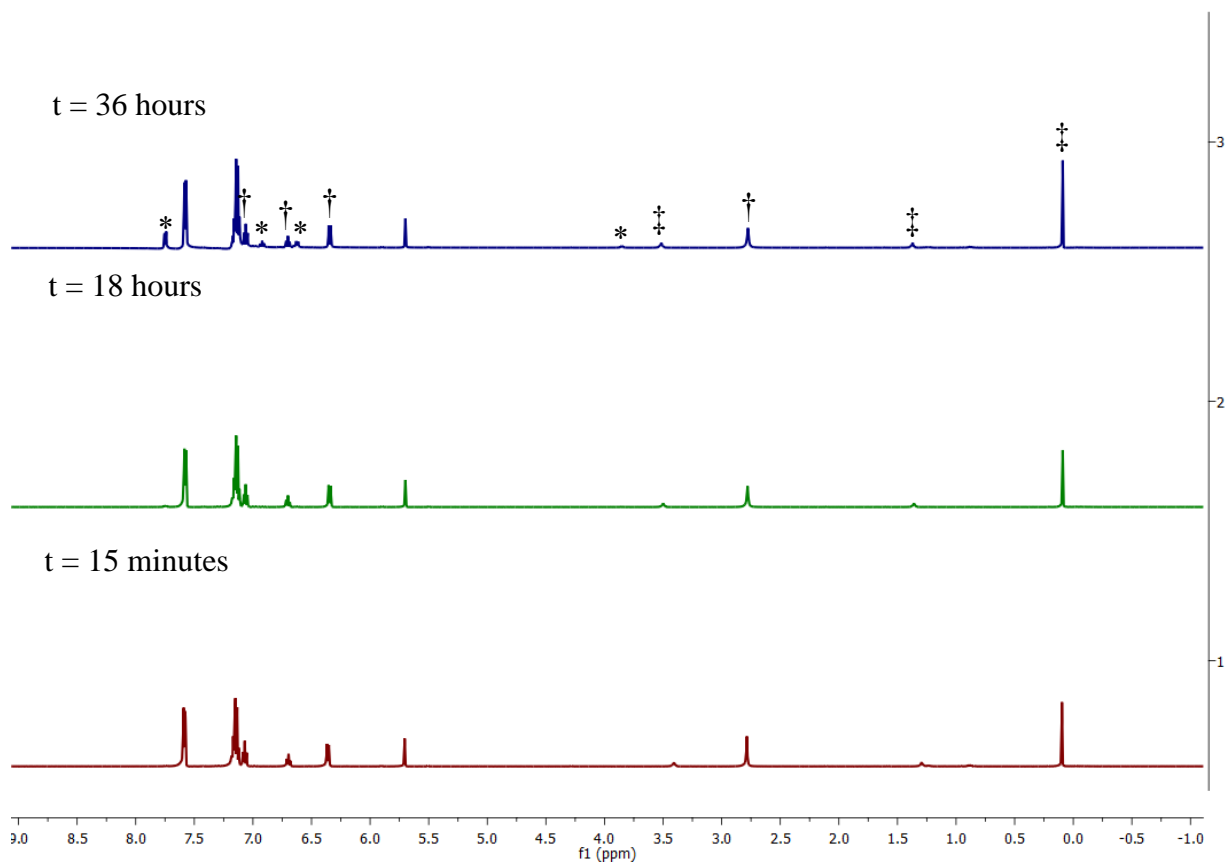
$^1\text{H}$ - $^{29}\text{Si}$  HSQC ( $\text{C}_6\text{D}_6$ )



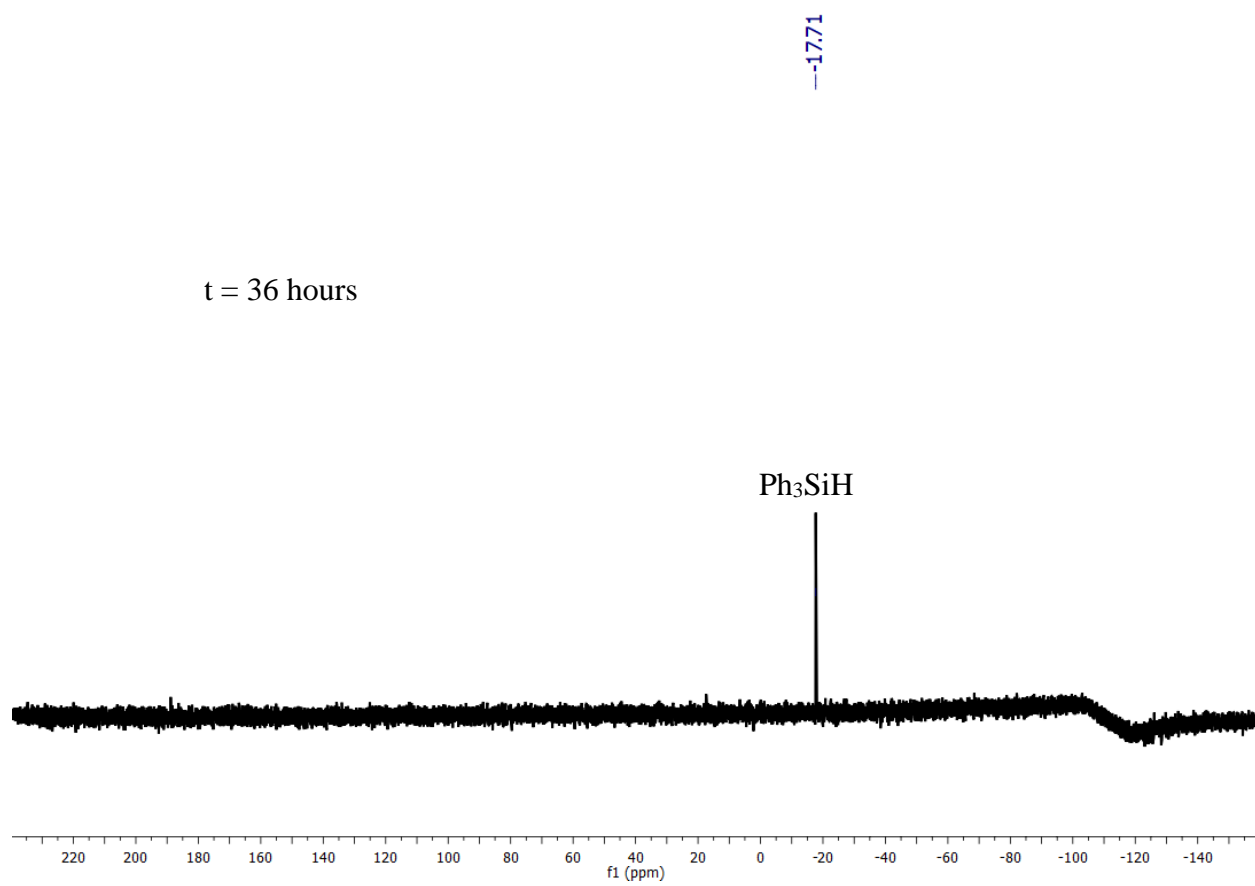
$^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , 99 MHz)

### Reaction of aniline and triphenylsilane

Aniline (6.6 mg, 0.071 mmol) and triphenylsilane (16.8 mg, 0.064 mmol) in 0.5 mL benzene- $d_6$  were added to **1** (2 mg,  $2.6 \times 10^{-3}$  mmol). The reaction was heated at 90 °C. Over 36 hours, several new aryl resonances observed. It is hypothesized that the product is  $\text{Ph}_3\text{Si}(\text{PhNH})$  and is produced in 16% yield. Due to the low yield, it wasn't possible to confirm the identity of the product.



$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 500 MHz)  $\text{C}_6\text{D}_6$  resonance is buried.

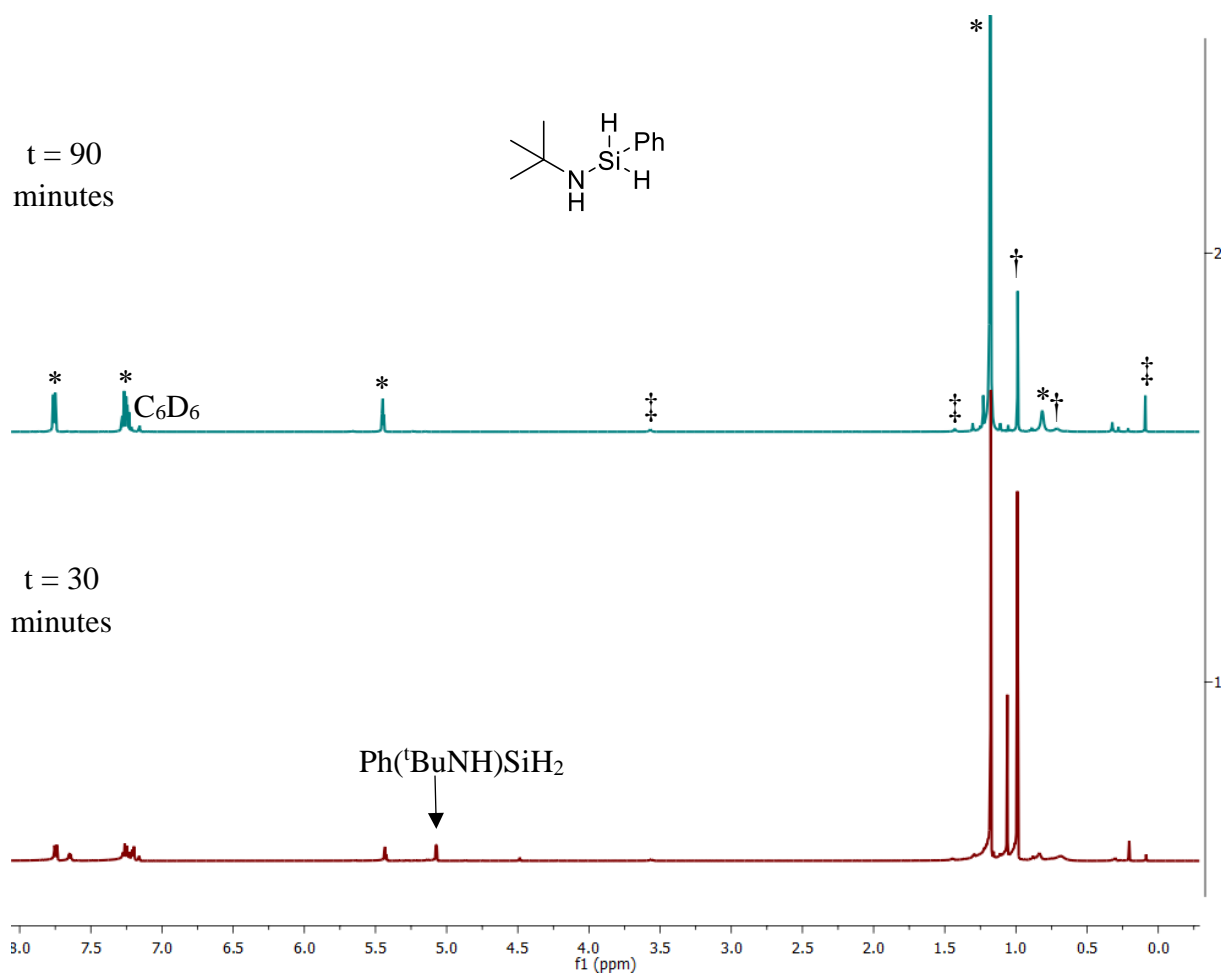


<sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, 99 MHz)



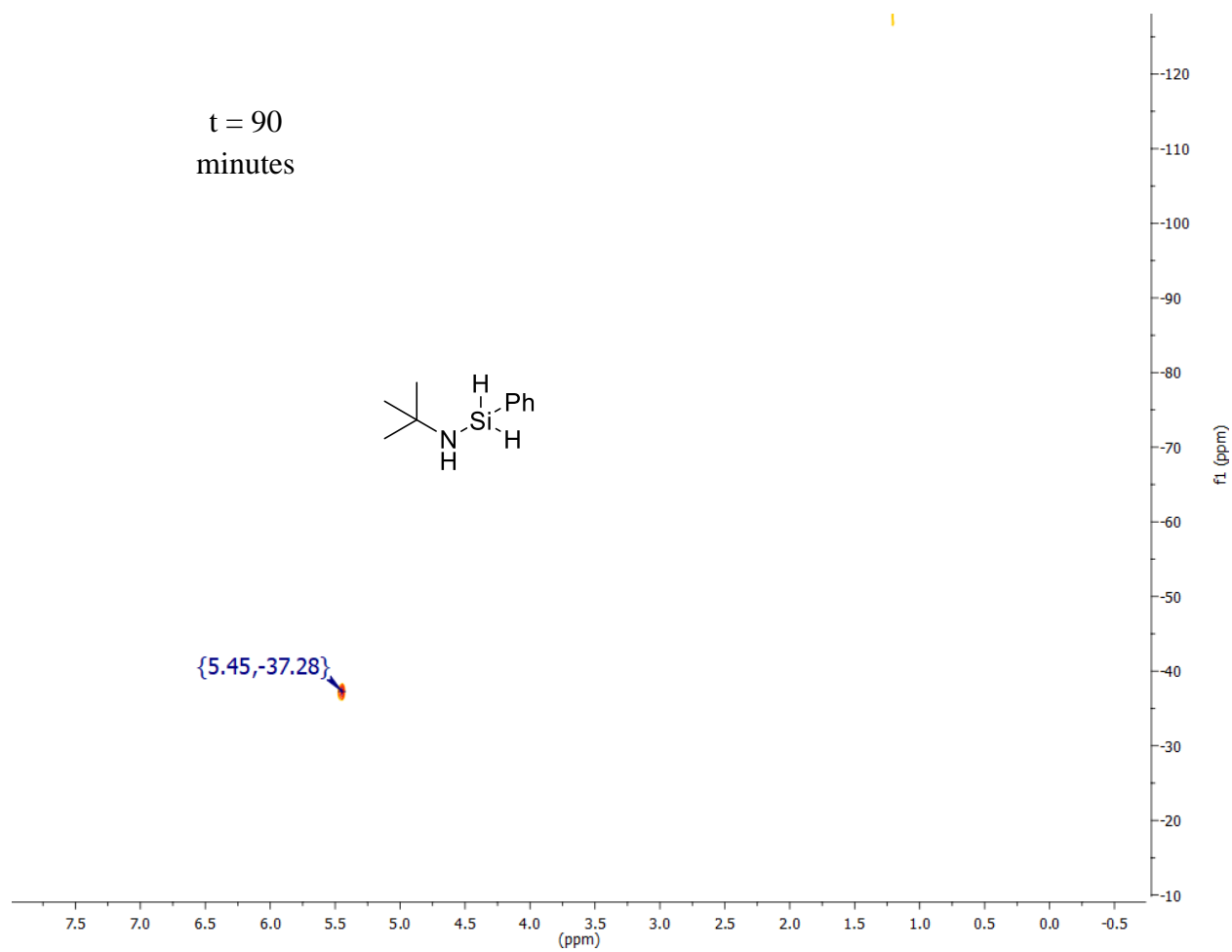
### Reaction of *tert*-butylamine and phenylsilane<sup>5</sup>

*Tert*-butylamine (73.14 mg, 0.967 mmol) and phenylsilane (34.9 mg, 0.322 mmol) in 0.5 mL benzene-*d*<sub>6</sub> were added to **1** (2 mg, 2.6 × 10<sup>-3</sup> mmol). Over 1.5 hours, Ph(<sup>*t*</sup>BuNH)<sub>2</sub>SiH was produced in 100% yield. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 500 MHz): δ 7.75 (m, 2H), 7.27 (m, 3H), 5.45 (t, 1H), 1.18 (s, 18H), 0.82 (br s, 2H). <sup>1</sup>H-<sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>, 99 MHz): δ -37.28. The generation and consumption of Ph(<sup>*t*</sup>BuNH)SiH<sub>2</sub> can be observed by appearance and disappearance of the Si-H and <sup>*t*</sup>Bu resonances at 5.07 (d, 2H) and 1.06 (s, 9H) ppm, respectively.



<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz)

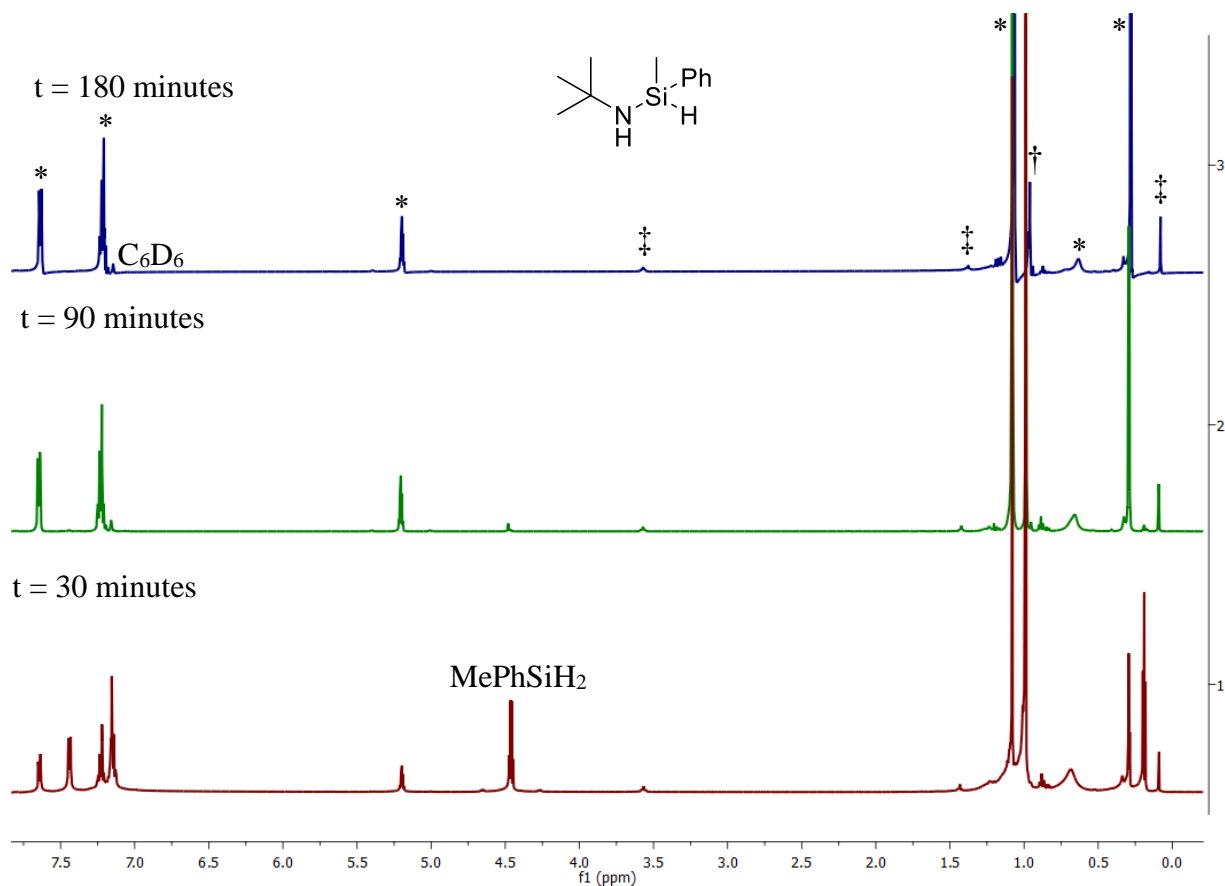
t = 90  
minutes



$^1\text{H}$ - $^{29}\text{Si}$  HSQC ( $\text{C}_6\text{D}_6$ )

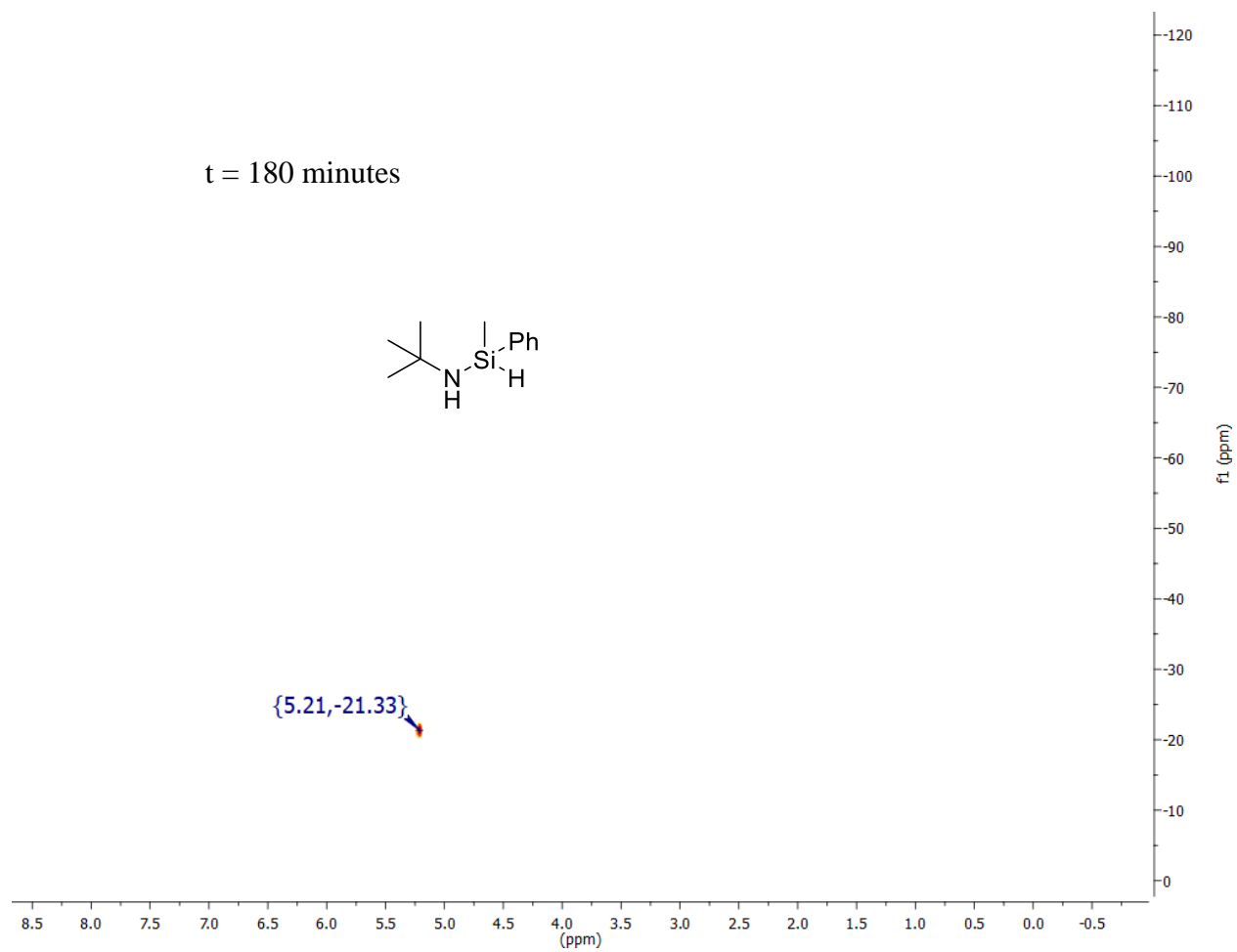
### Reaction of *tert*-butylamine and methylphenylsilane<sup>1</sup>

*Tert*-butylamine (49.5 mg, 0.676 mmol) and methylphenylsilane (34.9 mg, 0.322 mmol) in 0.5 mL benzene-*d*<sub>6</sub> were added to **1** (2 mg, 2.6 × 10<sup>-3</sup> mmol). The reaction was heated at 60 °C. Over 3 hours, MePh(*t*BuNH)SiH was produced in 100% yield. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 500 MHz): δ 7.64 (m, 2H), 7.22 (m, 3H), 5.21 (pentet, 1H), 1.08 (s, 9H), 0.64 (br s, 1H), 0.29 (d, 3H). <sup>1</sup>H-<sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>, 99 MHz): δ -21.33.



<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz)

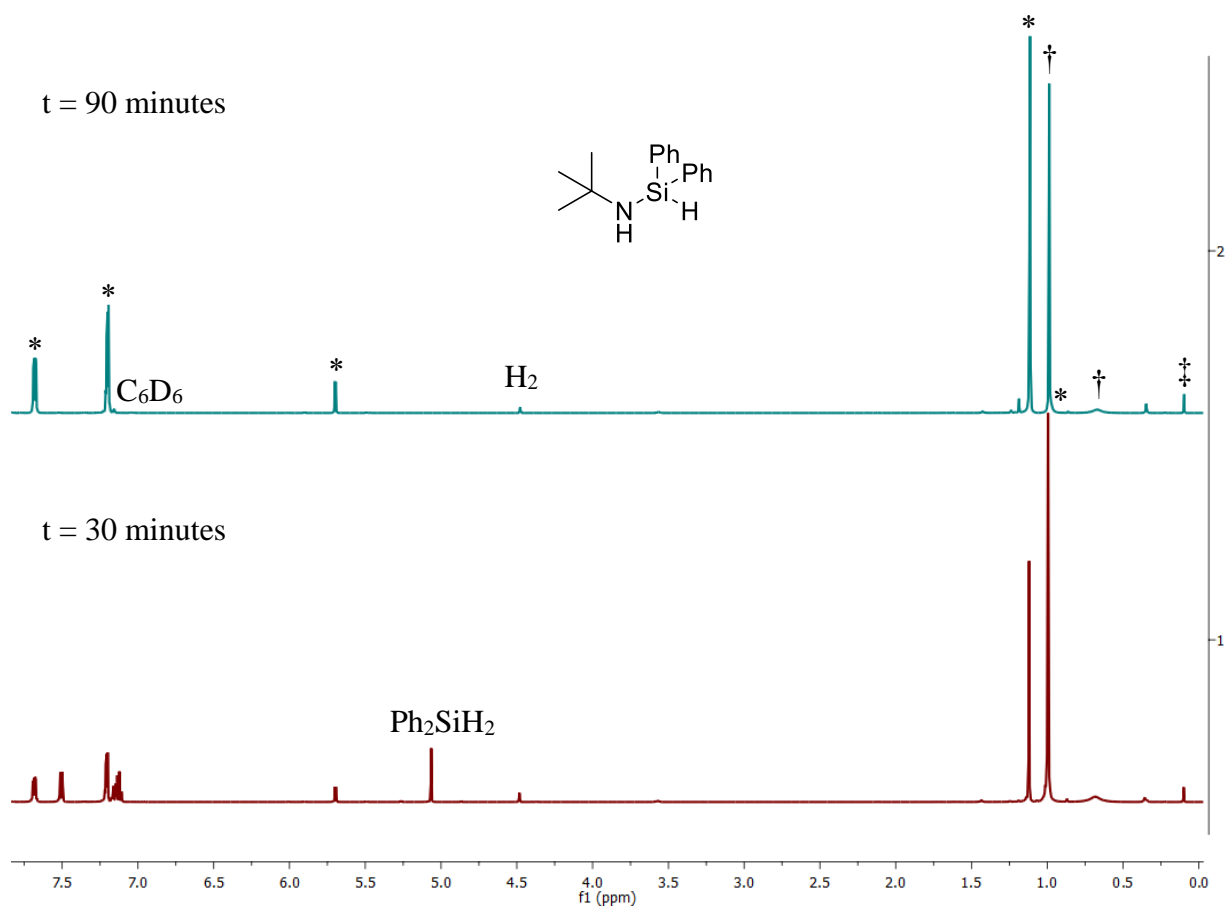
t = 180 minutes



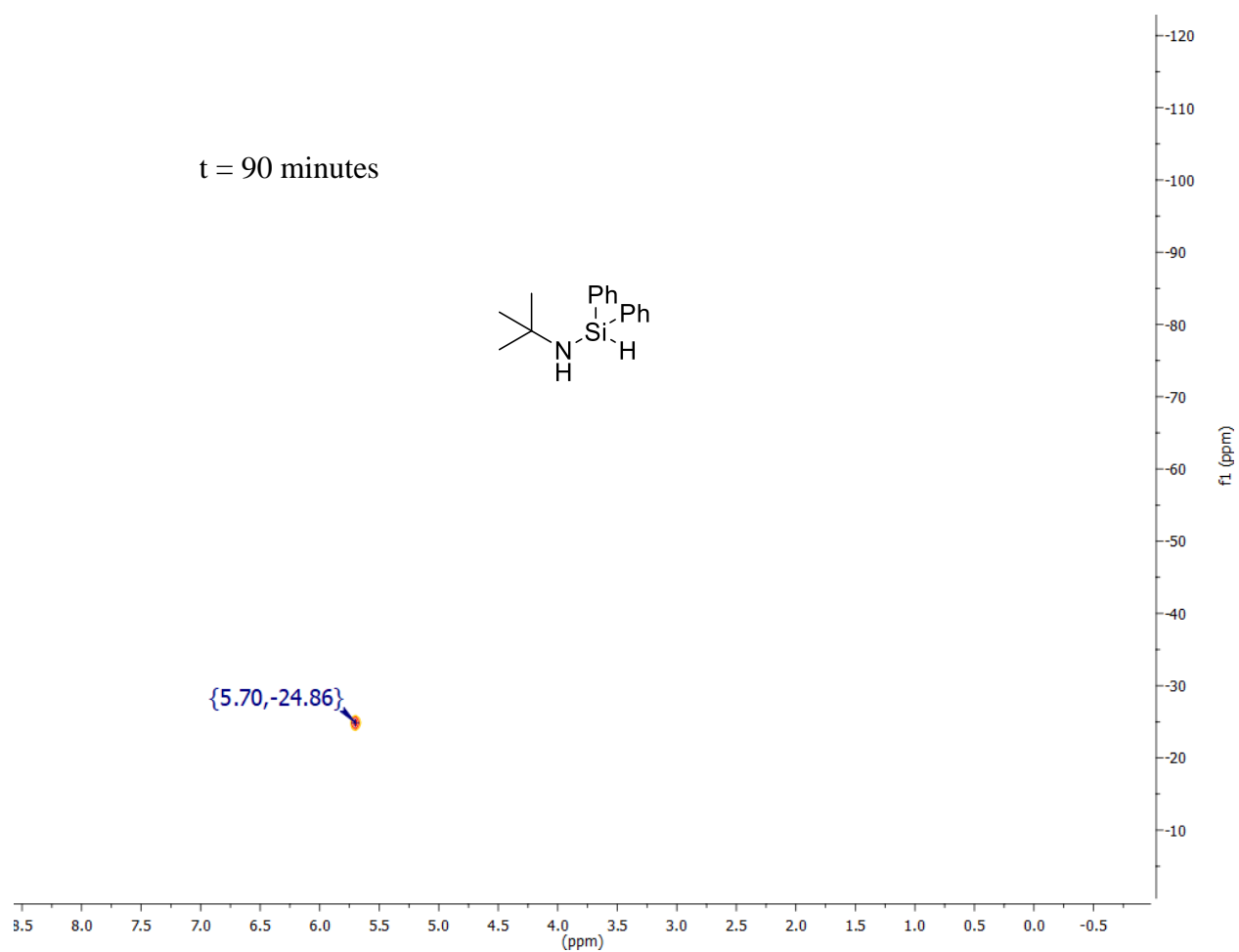
$^1\text{H}$ - $^{29}\text{Si}$  HSQC ( $\text{C}_6\text{D}_6$ )

### Reaction of *tert*-butylamine and diphenylsilane<sup>1</sup>

*Tert*-butylamine (49.5 mg, 0.676 mmol) and diphenylsilane (59.3 mg, 0.322 mmol) in 0.5 mL benzene-*d*<sub>6</sub> were added to **1** (2 mg, 2.6 × 10<sup>-3</sup> mmol). The reaction was heated at 60 °C. Over 1.5 hours, Ph<sub>2</sub>(*t*BuNH)SiH was produced in 100% yield. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 500 MHz): δ 7.68 (m, 4H), 7.20 (m, 6H), 5.70 (d, 1H), 1.12 (s, 9H), 0.97 (br s, 1H). <sup>1</sup>H-<sup>29</sup>Si NMR (benzene-*d*<sub>6</sub>, 99 MHz): -24.86.



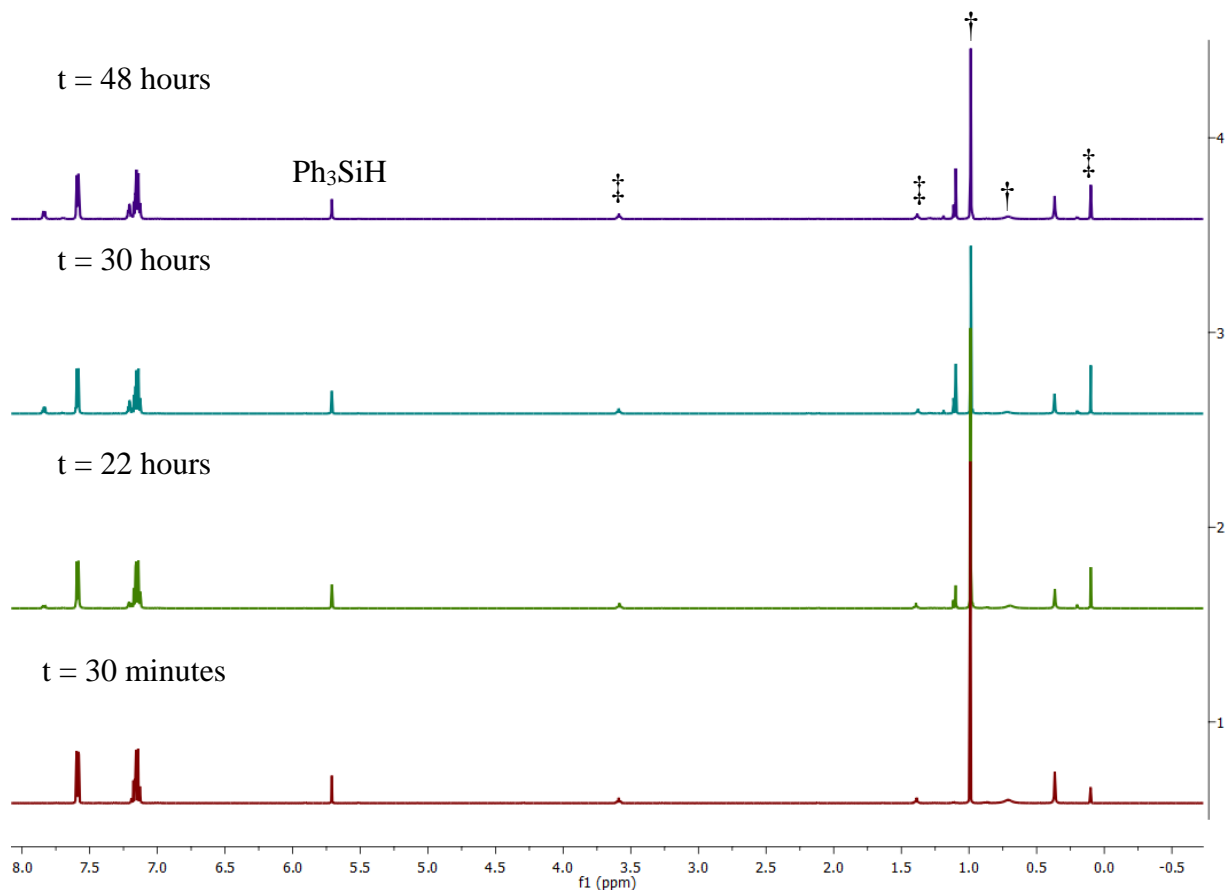
<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz)



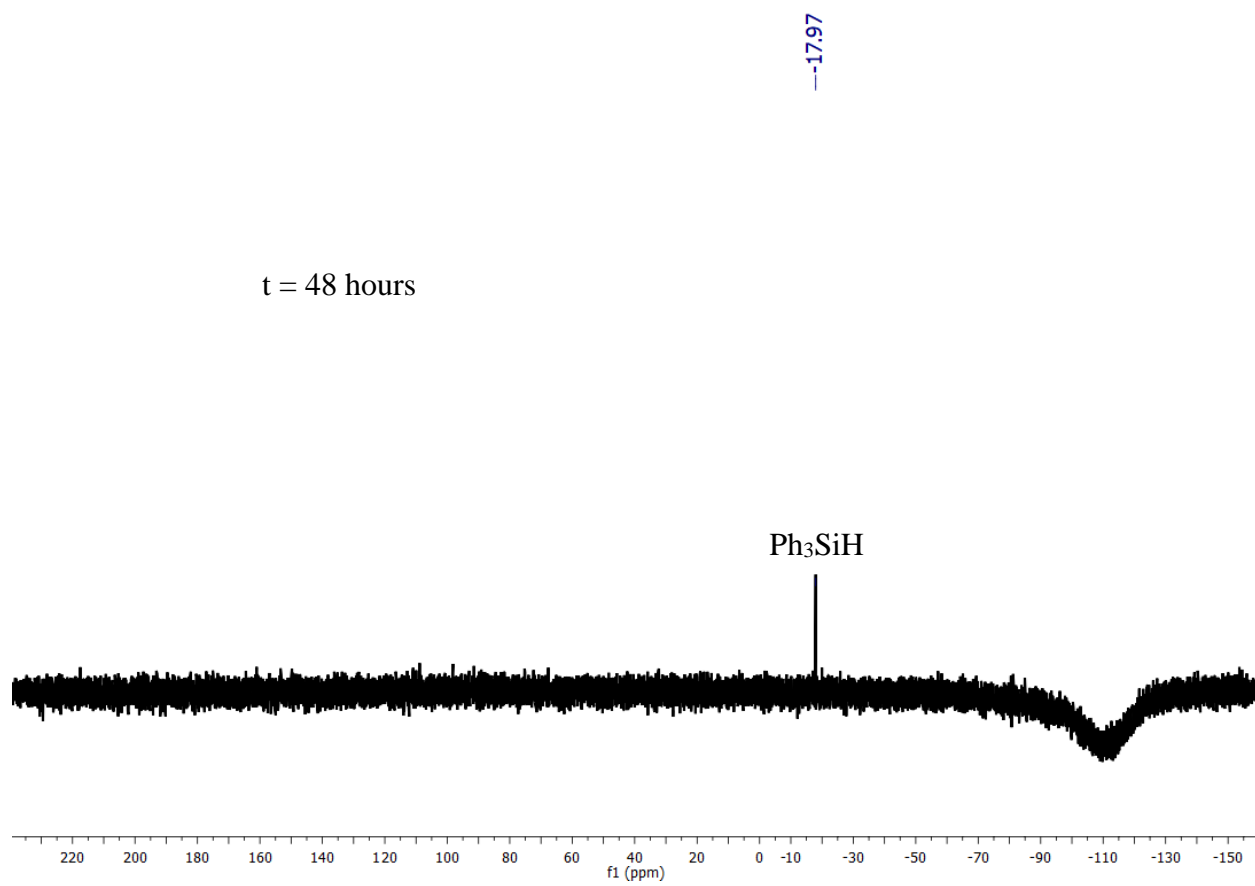
$^1\text{H}$ - $^{29}\text{Si}$  HSQC ( $\text{C}_6\text{D}_6$ )

### Reaction of *tert*-butylamine and triphenylsilane

*Tert*-butylamine (9.4 mg, 0.129 mmol) and triphenylsilane (16.8 mg, 0.064 mmol) in 0.5 mL benzene-*d*<sub>6</sub> were added to **1** (2 mg,  $2.6 \times 10^{-3}$  mmol). The reaction was heated at 90 °C. Over 48 hours, two new resonances, most likely <sup>t</sup>Bu resonances, appeared at 1.11 and 1.19 ppm. In addition, there were several new resonances in the phenyl region. It is likely that Ph<sub>3</sub>Si(<sup>t</sup>BuNH) was generated, but in less than 15% yield. The concentration of new species was too low to observe via <sup>29</sup>Si NMR.



<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz) C<sub>6</sub>D<sub>6</sub> resonance is buried.

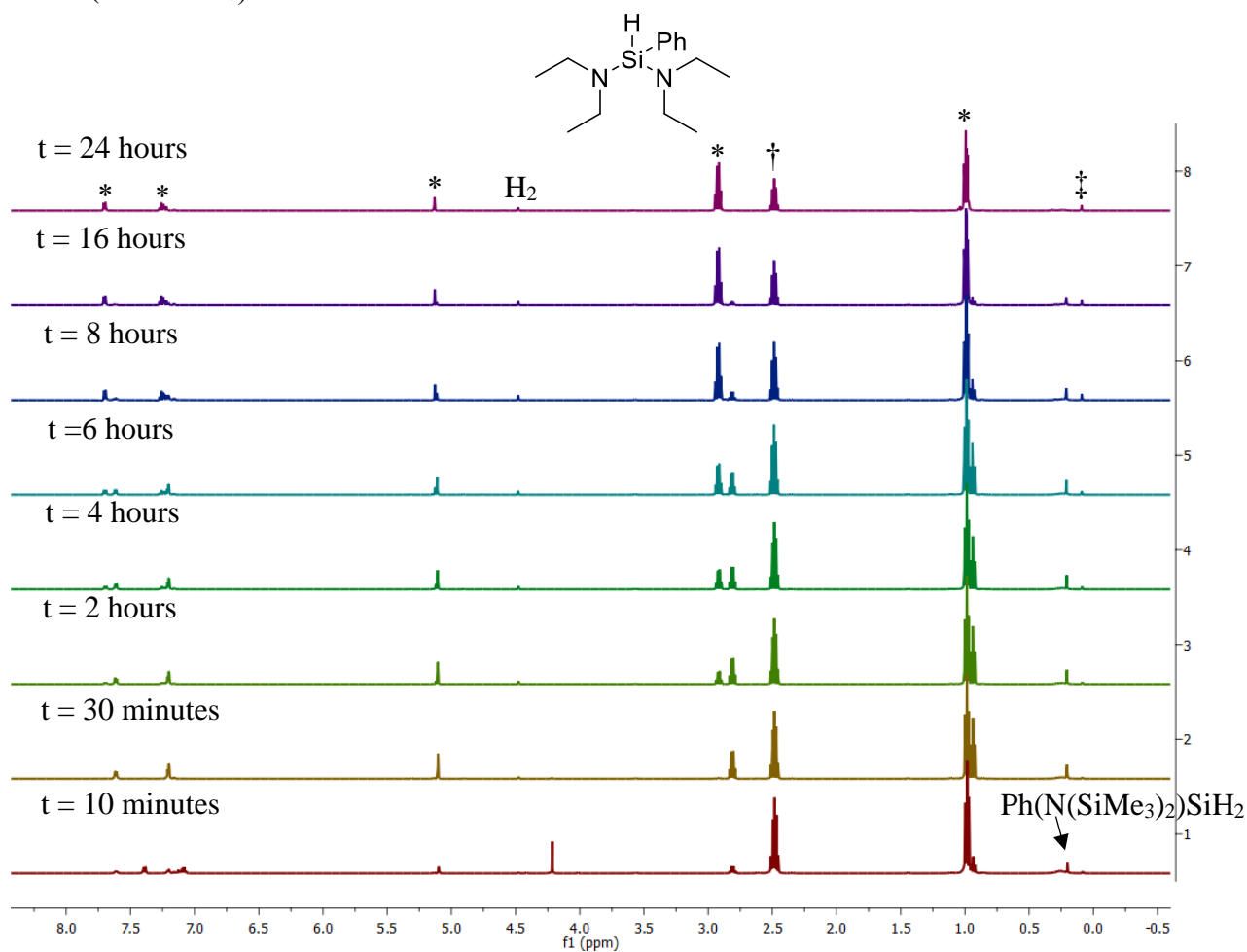


$^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , 99 MHz)

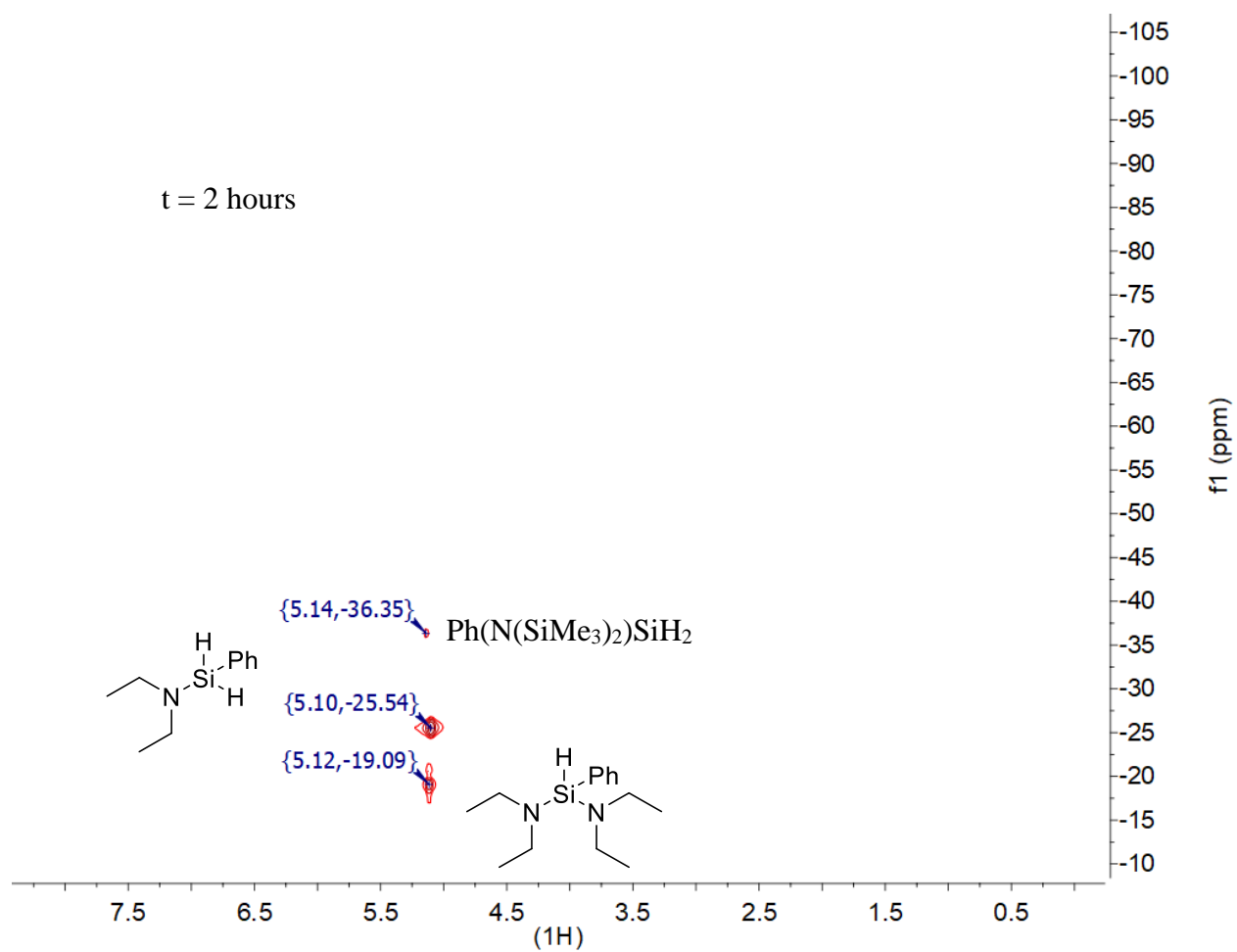


### Reaction of diethylamine and phenylsilane<sup>5</sup>

Diethylamine (73.0 mg, 0.998 mmol) and phenylsilane (34.9 mg, 0.322 mmol) in 0.5 mL benzene-*d*<sub>6</sub> were added to **1** (2 mg,  $2.6 \times 10^{-3}$  mmol). The reaction was heated at 60 °C. Over 30 minutes, Ph(Et<sub>2</sub>N)SiH<sub>2</sub> was produced in 97% yield. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 500 MHz): δ 7.60 (m, 2H), 7.19 (m, 3H), 5.10 (s, 2H), 2.80 (q, 4H), 0.94 (t, 6H). <sup>1</sup>H-<sup>29</sup>Si HSQC NMR (benzene-*d*<sub>6</sub>, 99 MHz): δ -25.44. After 24 hours, Ph(Et<sub>2</sub>N)<sub>2</sub>SiH was produced in 97% yield. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 500 MHz): δ 7.69 (m, 2H), 7.24 (m, 3H), 5.13 (s, 1H), 2.92 (q, 8H), 0.99 (t, 12). <sup>1</sup>H-<sup>29</sup>Si HSQC NMR (benzene-*d*<sub>6</sub>, 99 MHz): δ -19.18. The only byproduct is Ph(N(SiMe<sub>3</sub>)<sub>2</sub>)SiH<sub>2</sub> resulting from catalyst decomposition. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 500 MHz): δ 5.17 (s, 2H), 0.21 (s, 18H). <sup>1</sup>H-<sup>29</sup>Si HSQC NMR (benzene-*d*<sub>6</sub>): δ -36.35.

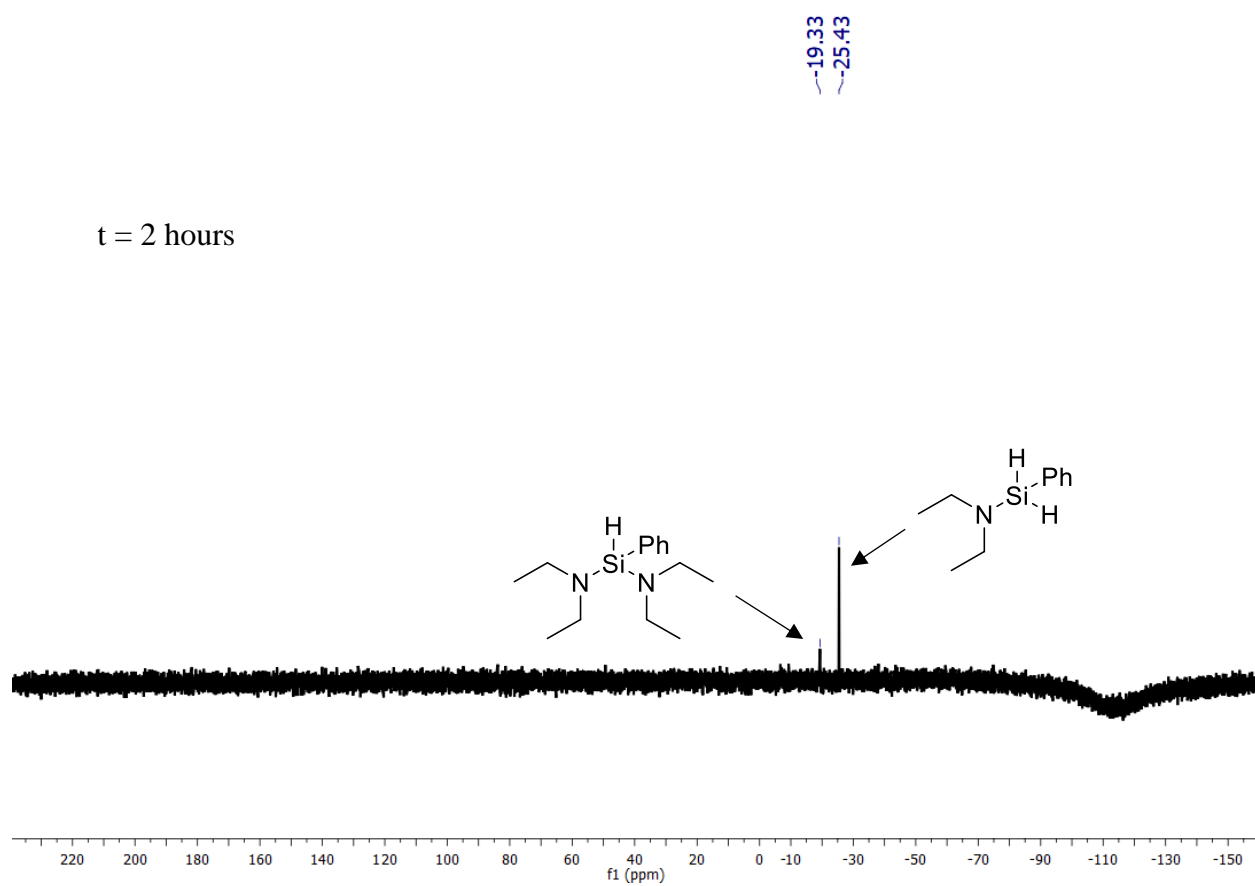


<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz) C<sub>6</sub>D<sub>6</sub> resonance is too small to observe.

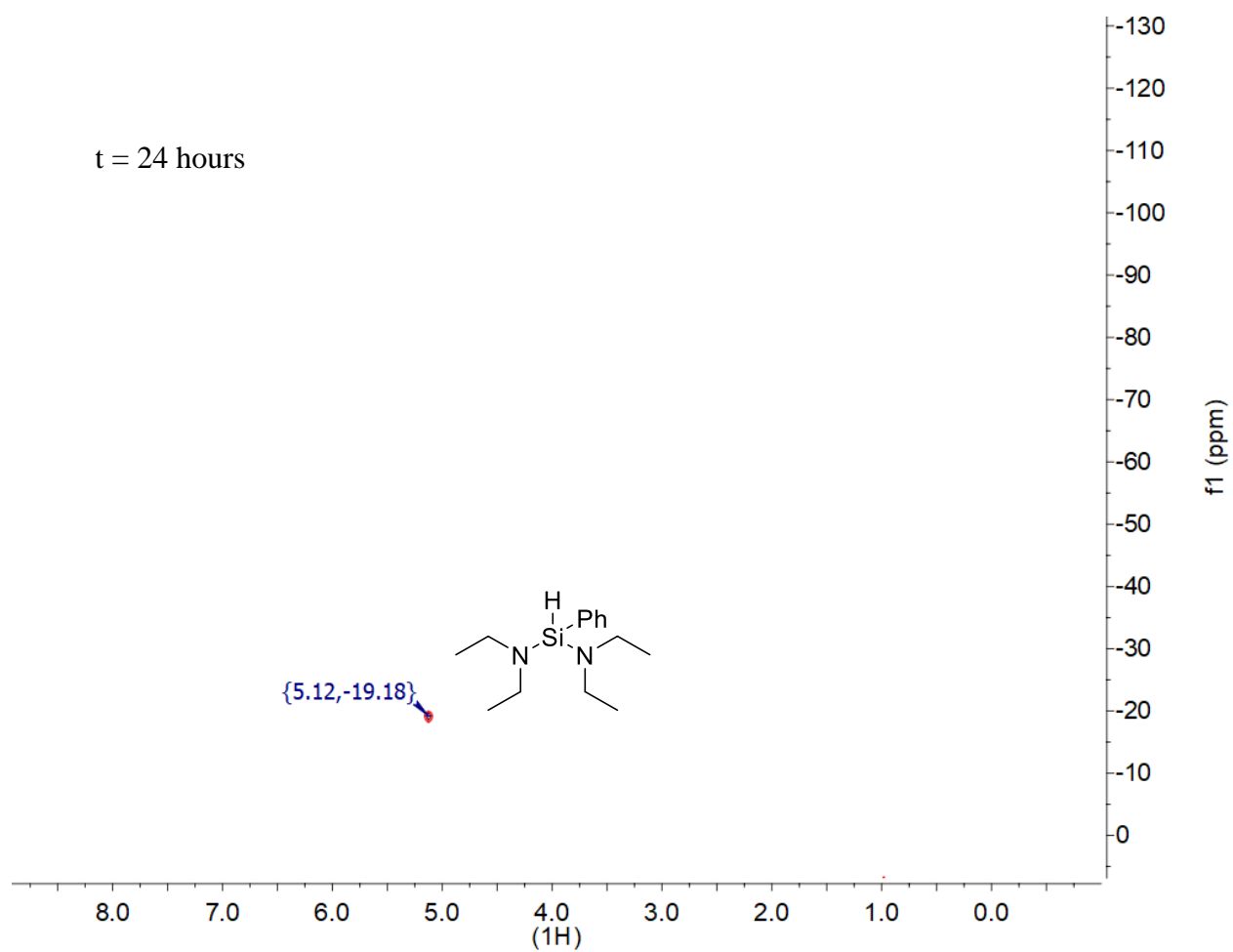


$^1\text{H}$ - $^{29}\text{Si}$  HSQC ( $\text{C}_6\text{D}_6$ )

t = 2 hours

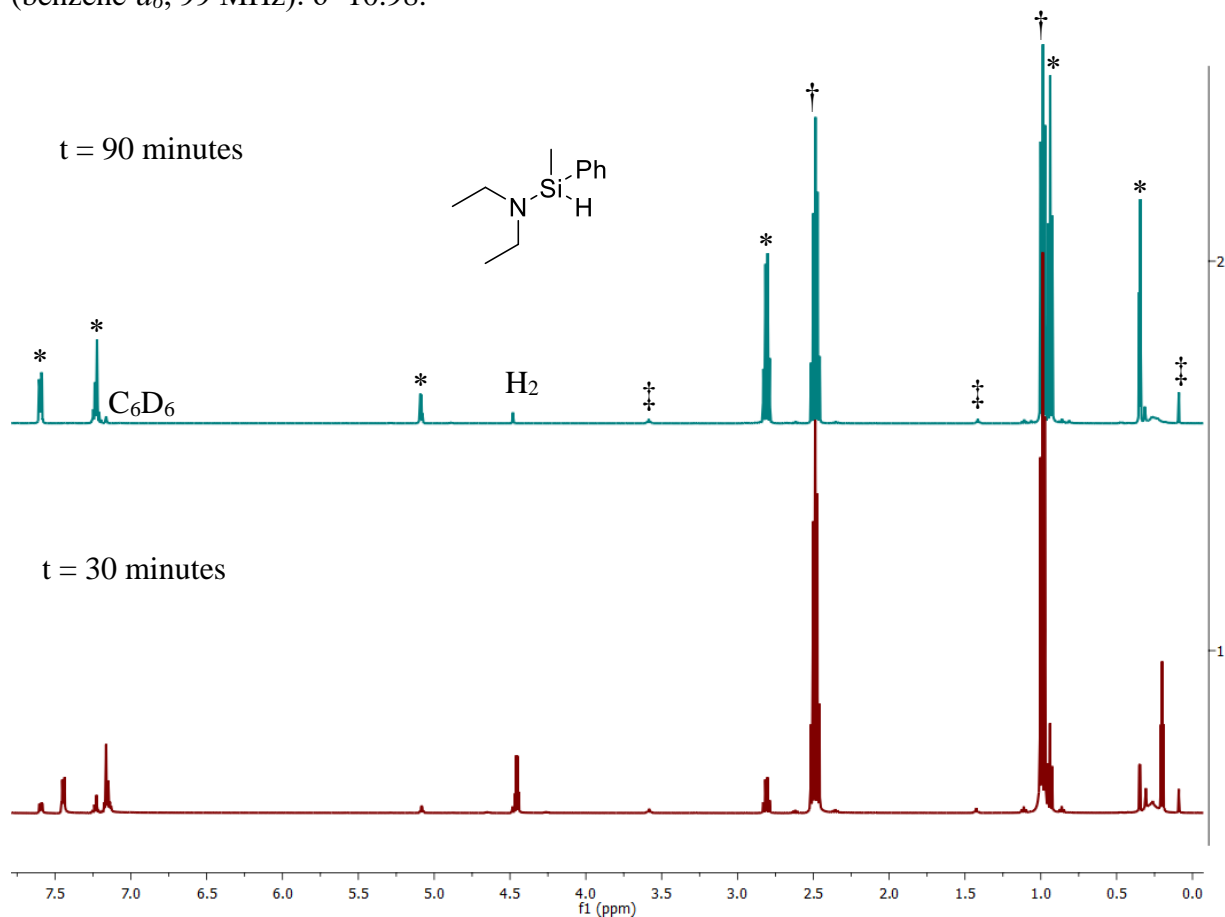


$^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , 99 MHz)

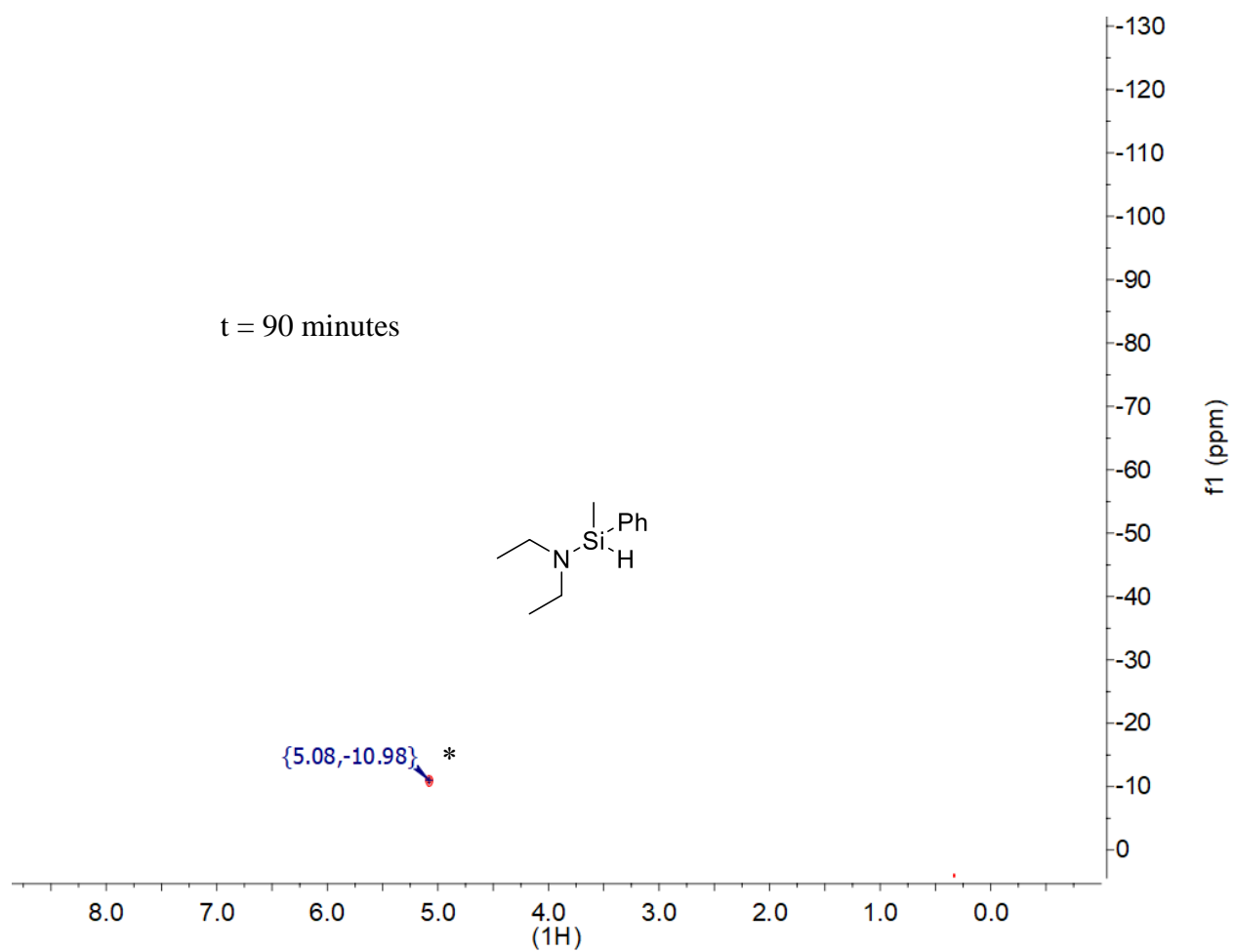


### Reaction of diethylamine and methylphenylsilane<sup>6,7</sup>

Diethylamine (70.6 mg, 0.966 mmol) and methylphenylsilane (39.4 mg, 0.322 mmol) in 0.5 mL benzene-*d*<sub>6</sub> were added to **1** (2 mg, 2.6 × 10<sup>-3</sup> mmol). The reaction was heated at 90 °C. Over 90 minutes, MePh(Et<sub>2</sub>N)SiH was produced in 100% yield. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 500 MHz): δ 7.59 (m, 2H), 7.22 (m, 3H), 5.08 (q, 1H), 2.80 (q, 4H), 0.94 (t, 6H), 0.35 (d, 3H). <sup>1</sup>H-<sup>29</sup>Si HSQC NMR (benzene-*d*<sub>6</sub>, 99 MHz): δ -10.98.

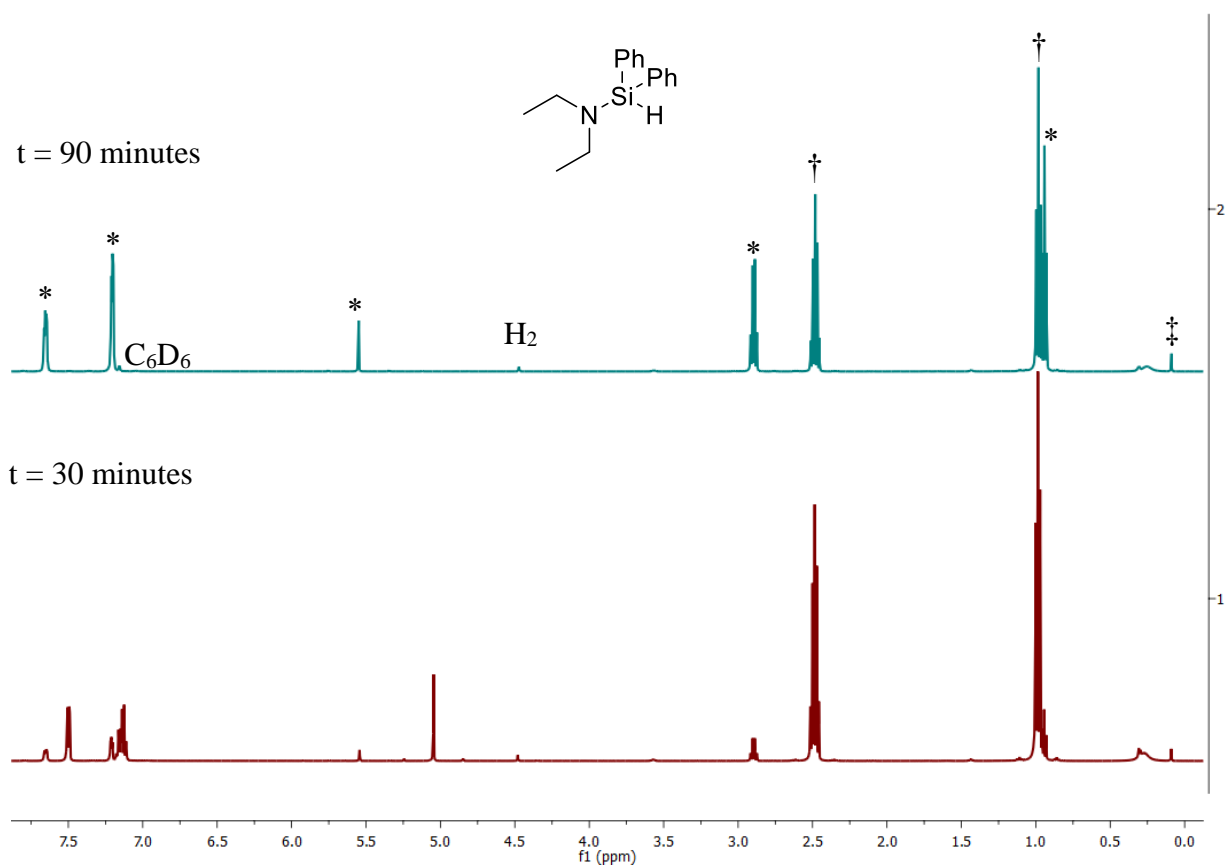


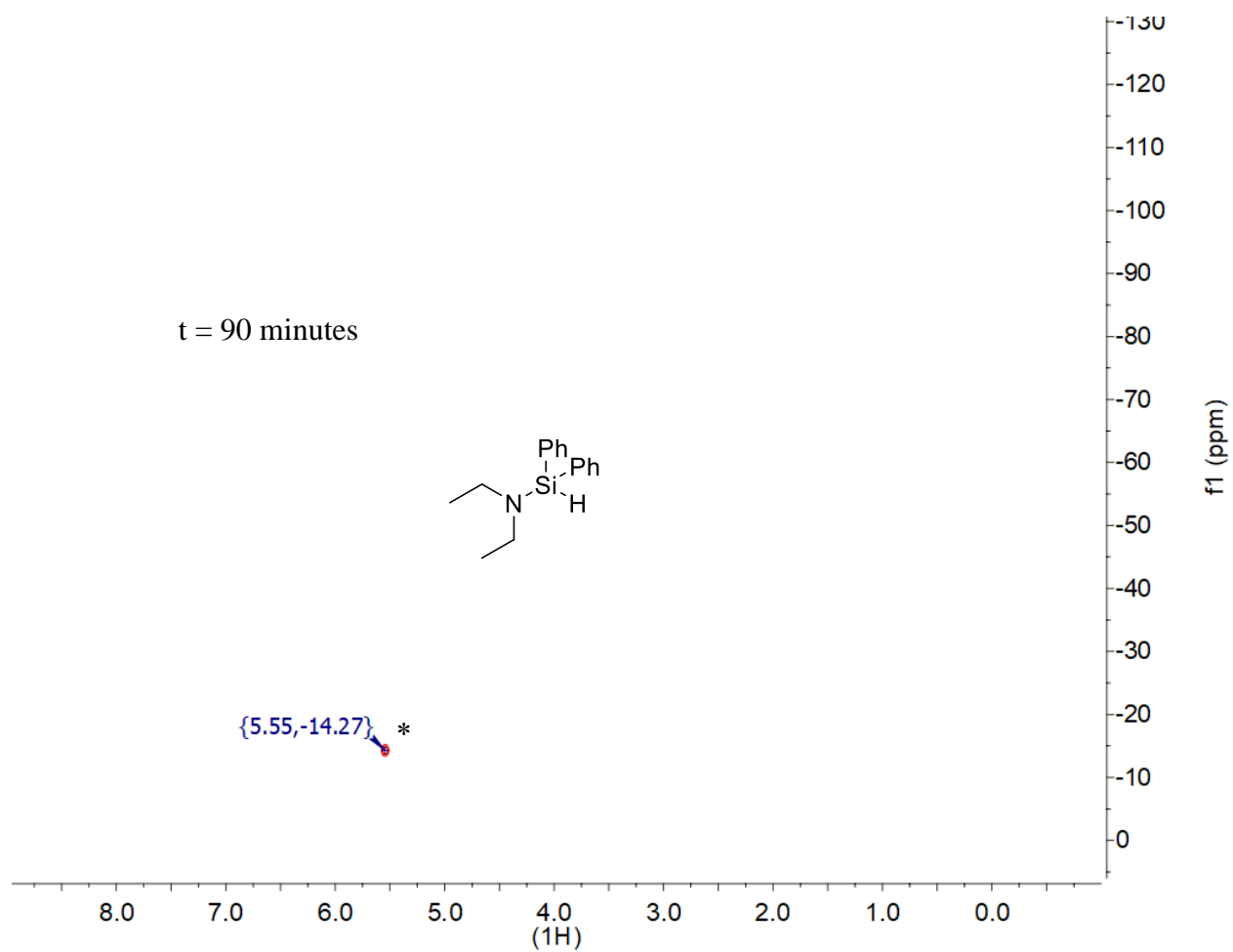
<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz) C<sub>6</sub>D<sub>6</sub>



### Reaction of diethylamine and diphenylsilane<sup>2</sup>

Diethylamine (70.6 mg, 0.966 mmol) and diphenylsilane (184.3 mg, 0.322 mmol) in 0.5 mL benzene-*d*<sub>6</sub> were added to **1** (2 mg, 2.6 × 10<sup>-3</sup> mmol). The reaction was heated at 90 °C. Over 90 minutes, MePh(Et<sub>2</sub>N)SiH was produced in 100% yield. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 500 MHz): δ 7.65 (m, 4H), 7.20 (m, 6H), 5.55 (s, 1H), 2.89 (q, 4H), 0.94 (t, 6H). <sup>1</sup>H-<sup>29</sup>Si HSQC NMR (benzene-*d*<sub>6</sub>, 99 MHz): δ -14.27.



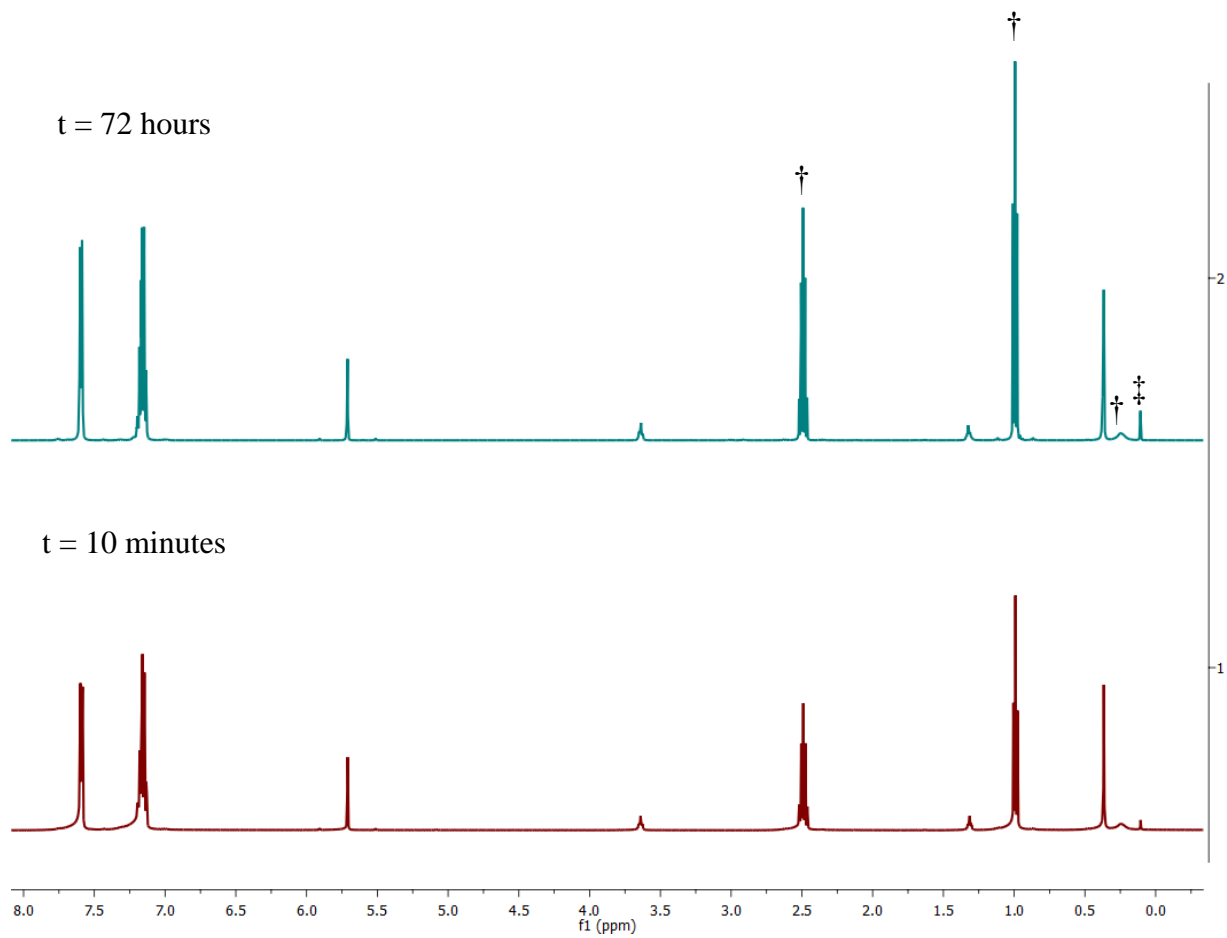


$^1\text{H}$ - $^{29}\text{Si}$  HSQC ( $\text{C}_6\text{D}_6$ )



### Reaction of diethylamine and triphenylsilane

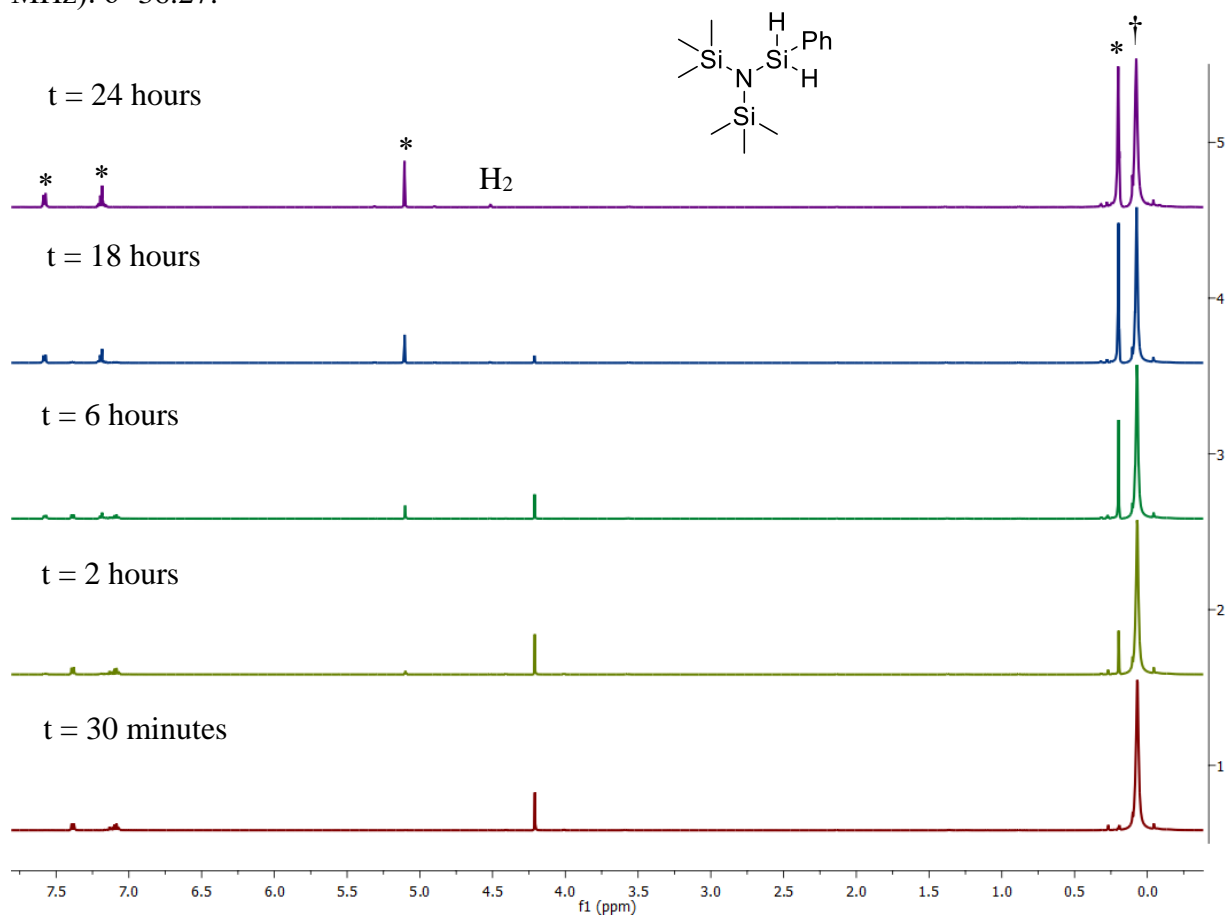
Diethylamine (10.4 mg, 0.142 mmol) and triphenylsilane (33.6 mg, 0.128 mmol) in 0.5 mL benzene- $d_6$  were added to **1** (4 mg,  $5.2 \times 10^{-3}$  mmol). The reaction was heated at 90 °C. Over 72 hours, no reaction was observed.



$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 500 MHz)  $\text{C}_6\text{D}_6$  resonance is buried.

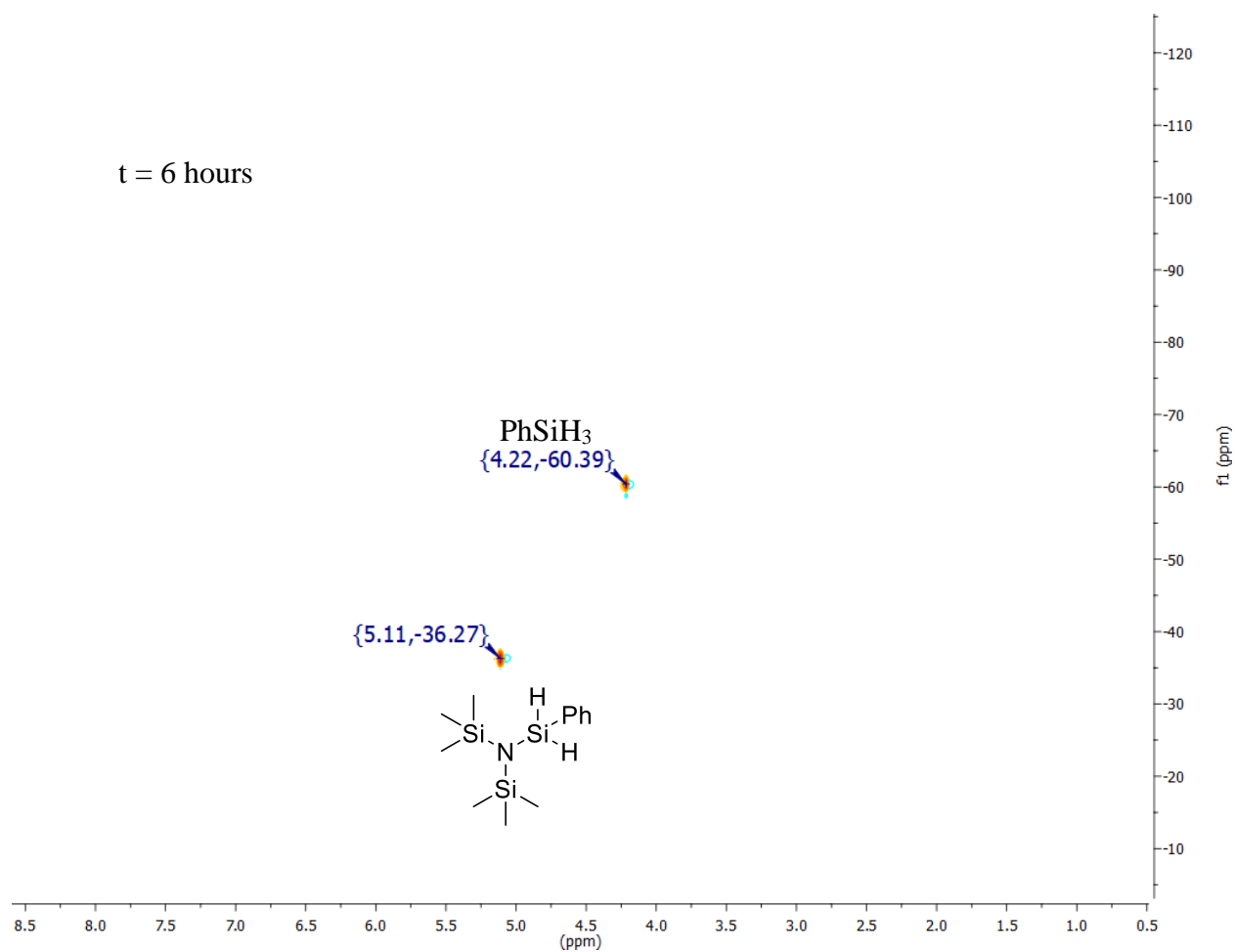
### Reaction of bis(trimethylsilyl)amine and phenylsilane<sup>6</sup>

Bis(trimethylsilyl)amine (161.40 mg, 0.999 mmol) and phenylsilane (34.9 mg, 0.322 mmol) in 0.5 mL benzene-*d*<sub>6</sub> were added to **1** (2 mg,  $2.6 \times 10^{-3}$  mmol) and the reaction was heated at 90 °C. Over 24 hours, Ph{N(SiMe<sub>3</sub>)<sub>2</sub>}SiH<sub>2</sub> was produced in 100% yield. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 500 MHz): δ 7.59 (m, 2H), 7.20 (m, 3H), 5.12 (s, 2H), 0.21 (s, 18H). <sup>1</sup>H-<sup>29</sup>Si HSQC NMR (benzene-*d*<sub>6</sub>, 99 MHz): δ -36.27.



<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz) C<sub>6</sub>D<sub>6</sub> resonance is buried.

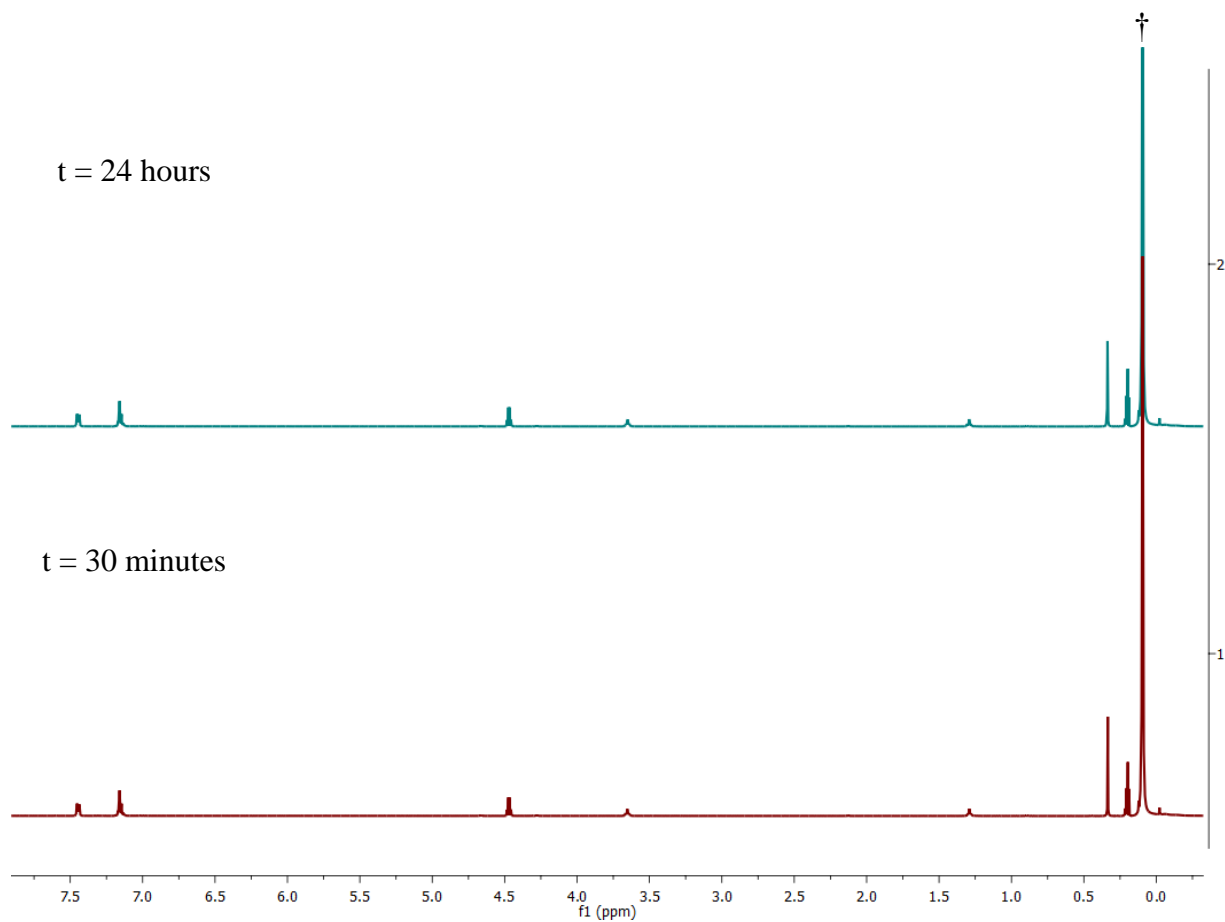
t = 6 hours



$^1\text{H}$ - $^{29}\text{Si}$  HSQC ( $\text{C}_6\text{D}_6$ )

### Reaction of bis(trimethylsilyl)amine and methylphenylsilane

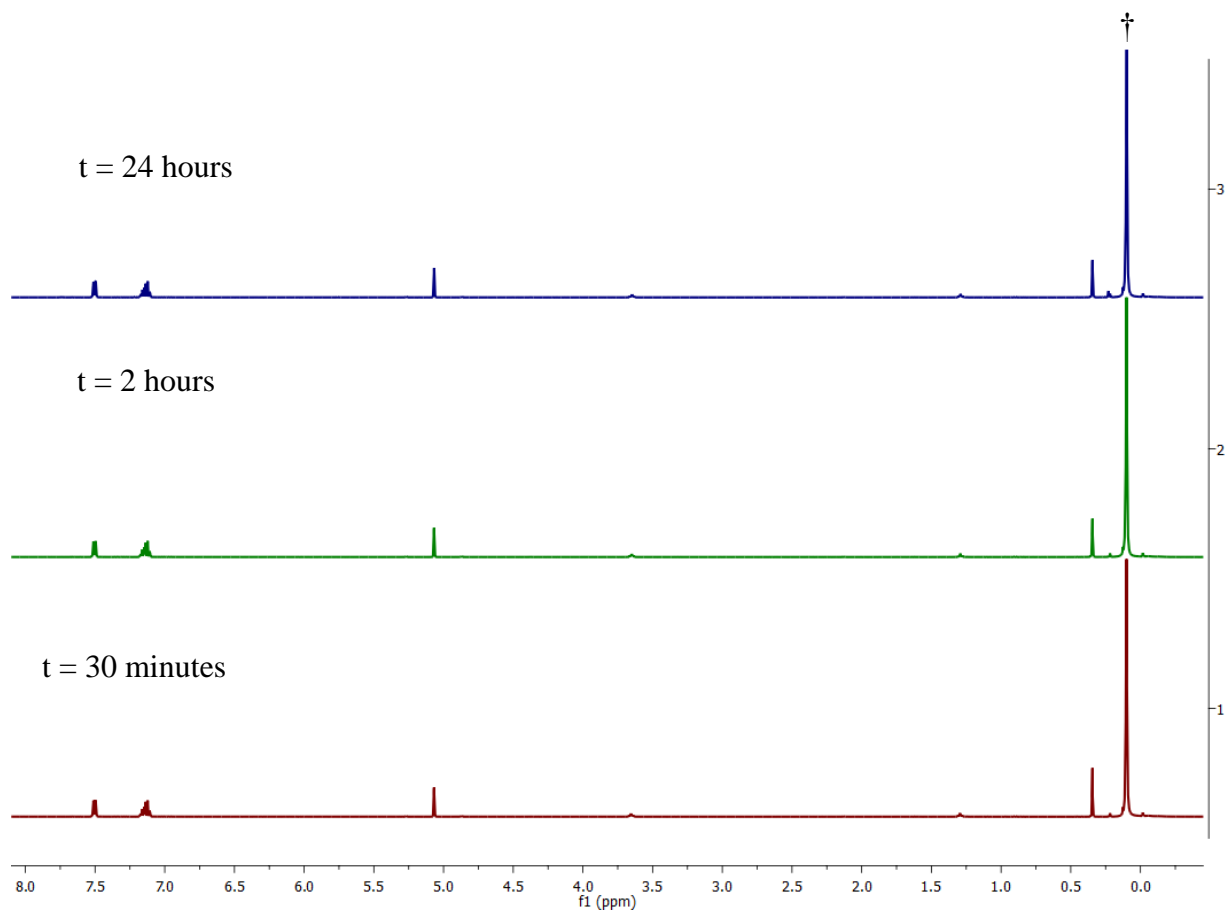
Bis(trimethylsilyl)amine (54.6 mg, 0.339 mmol) and methylphenylsilane (19.7 mg, 0.161 mmol) in 0.5 mL benzene-*d*<sub>6</sub> were added to **1** (5 mg,  $6.5 \times 10^{-3}$  mmol) and the reaction was heated at 90 °C. Over 24 hours, no reaction was observed.



<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz) C<sub>6</sub>D<sub>6</sub> resonance is buried.

### Reaction of bis(trimethylsilyl)amine and diphenylsilane

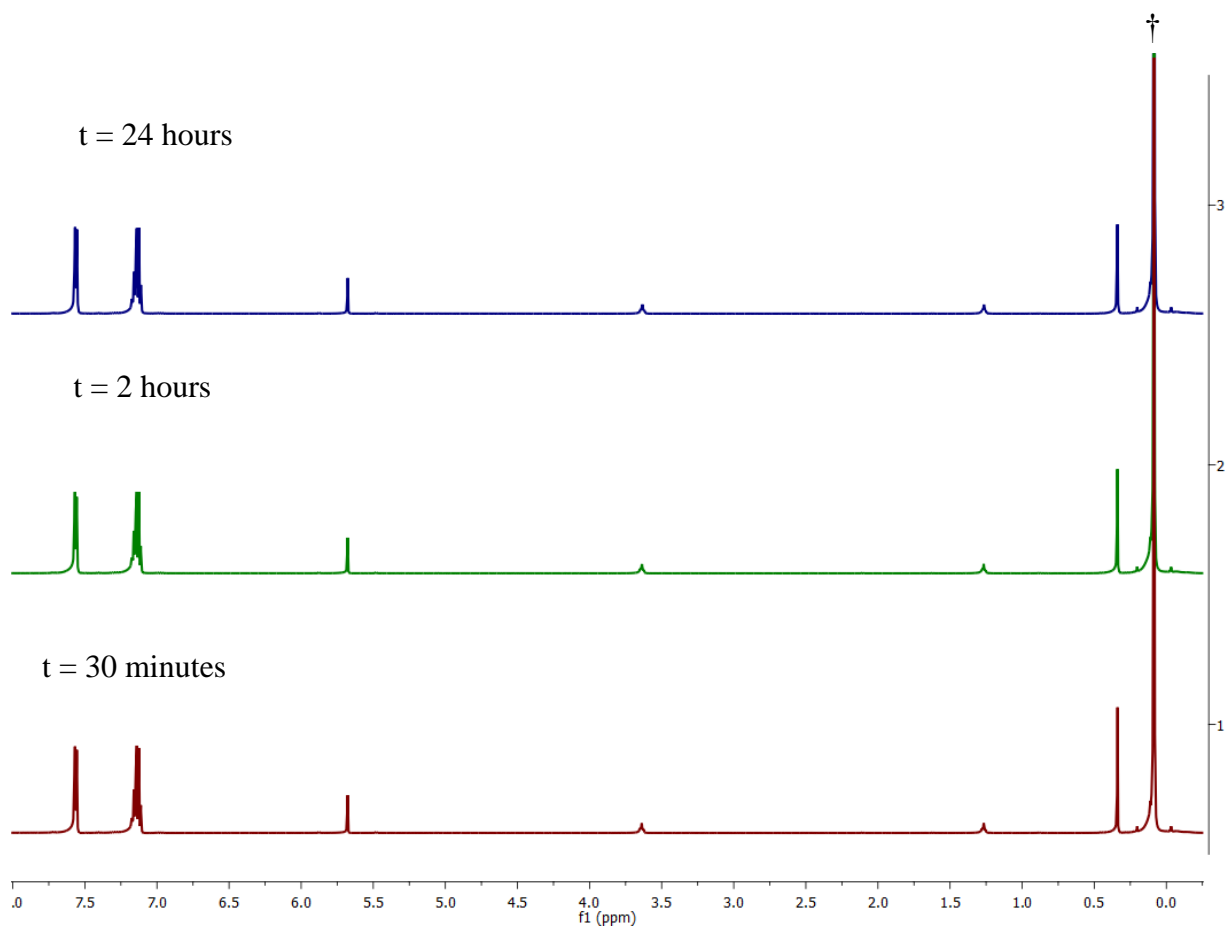
Bis(trimethylsilyl)amine (54.6 mg, 0.339 mmol) and diphenylsilane (29.7 mg, 0.161 mmol) in 0.5 mL benzene- $d_6$  were added to **1** (5 mg,  $6.5 \times 10^{-3}$  mmol) and the reaction was heated at 90 °C. Over 24 hours, no reaction was observed.



$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 500 MHz)  $\text{C}_6\text{D}_6$  resonance is buried.

### Reaction of bis(trimethylsilyl)amine and triphenylsilane

Bis(trimethylsilyl)amine (28.6 mg, 0.177 mmol) and triphenylsilane (42.0 mg, 0.161 mmol) in 0.5 mL benzene- $d_6$  were added to **1** (5 mg,  $6.5 \times 10^{-3}$  mmol) and the reaction was heated at 90 °C. Over 24 hours, no reaction was observed.



$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 500 MHz)  $\text{C}_6\text{D}_6$  resonance is buried.

## References:

1. Dunne, J. F.; Neal, S. R.; Engelkemier, J.; Ellern, A.; Sadow, A. D., Tris(oxazolinyl)boratomagnesium-Catalyzed Cross-Dehydrocoupling of Organosilanes with Amines, Hydrazine, and Ammonia. *J. Am. Chem. Soc.* **2011**, *133*, 16782-16785.
2. Pindwal, A.; Ellern, A.; Sadow, A. D., Homoleptic Divalent Dialkyl Lanthanide-Catalyzed Cross-Dehydrocoupling of Silanes and Amines. *Organometallics* **2016**, *35*, 1674-1683.
3. Wrackmeyer, B.; Stader, C.; Zhou, H.,  $^{13}\text{C}$ ,  $^{15}\text{N}$  and  $^{29}\text{Si}$  nuclear magnetic resonance studies of some aminosilanes and aminodisilanes. *Spectrochim. Acta A* **1989**, *45*, 1101-1111.
4. Eichhorn, B.; Nöth, H., New Diazasilaphosphetidines and their Precursors. *Z. Naturforsch. B Chem. Sci.* **2000**, *55*, 352-360.
5. Wang, J. X.; Dash, A. K.; Berthet, J. C.; Ephritikhine, M.; Eisen, M. S., Dehydrocoupling reactions of amines with silanes catalyzed by  $[(\text{Et}_2\text{N})_3\text{U}][\text{BPh}_4]$ . *J. Organomet. Chem.* **2000**, *610*, 49-57.
6. Xie, W.; Hu, H.; Cui, C.,  $[(\text{NHC})\text{Yb}\{\text{N}(\text{SiMe}_3)_2\}_2]$ -Catalyzed Cross-Dehydrogenative Coupling of Silanes with Amines. *Angew. Chem., Int. Ed.* **2012**, *51*, 11141-11144.
7. Baishya, A.; Peddarao, T.; Nembenna, S., Organomagnesium amide catalyzed cross-dehydrocoupling of organosilanes with amines. *Dalton Trans.* **2017**, *46*, 5880-5887.