

*Electronic Supplementary Information*

**Manganese Catalysed Dehydrocoupling of Silanes and Siloxanes  
with Ammonia to Prepare Oligosilazanes and Polysiloxazanes**

Gautam K. Mehta, Thao T. Nguyen, Marco Flores and Ryan J. Trovitch\*

*School of Molecular Sciences, Arizona State University, Tempe, Arizona 85287, United States*

*\*e-mail: ryan.trovitch@asu.edu*

## EXPERIMENTAL DETAILS

**General Considerations:** All reactions were performed inside an MBraun glovebox under an atmosphere of purified nitrogen or on a high-vacuum manifold. Toluene, tetrahydrofuran, diethyl ether, and pentane were purchased from Sigma-Aldrich, purified using a Pure Process Technology solvent system, and stored in the glovebox over activated 4 Å molecular sieves and potassium in prior use. Benzene-*d*<sub>6</sub> was purchased from Oakwood Chemicals and dried over 4 Å molecular sieves and potassium prior to use. Celite was obtained from Oakwood Chemicals. Phenylsilane and diphenylsilane were acquired from Oakwood Chemical. Dimethylphenylsilane was obtained from Sigma-Aldrich. Methylphenylsilane was purchased from TCI America. Octylsilane, diisopropylsilane, diethylsilane, trimethylsilyl-terminated polymethylhydrosiloxane (TMS-*ter*-PMHS), phenyltris(dimethylsiloxy)silane, tris(trimethylsiloxy)silane, methyltris(dimethylsiloxy)silane, bis(trimethylsiloxy)methylsilane, 1,3,5,7-tetramethylcyclotetrasiloxane, heptamethylcyclotetrasiloxane, bis(diethylamino)silane, tetrakis(dimethylsiloxy)silane, and vinyltris(dimethylsiloxy)silane were obtained from Gelest. All liquid substrates were dried over 4 Å molecular sieves prior to catalyst screening. Dodecylsilane was prepared from dodecyltrichlorosilane according to modified procedure that involved refluxing a toluene and lithium aluminum hydride mixture followed by filtration under inert atmosphere.<sup>1</sup> [(<sup>2,6-iPr<sub>2</sub>Ph</sup>BDI)Mn(μ-H)]<sub>2</sub> (**1**) was synthesized according to the literature procedure.<sup>2</sup>

Solution nuclear magnetic resonance (NMR) spectra were recorded at room temperature on a Varian 400 MHz NMR spectrometer. All <sup>1</sup>H NMR and <sup>13</sup>C NMR chemical shifts (ppm) are reported relative to SiMe<sub>4</sub> using <sup>1</sup>H (residual) and <sup>13</sup>C chemical shifts of the solvent as secondary standards. <sup>29</sup>Si NMR chemical shifts (ppm) are reported relative to SiMe<sub>4</sub> using the absolute <sup>1</sup>H NMR frequency of an internal SiMe<sub>4</sub> standard.

**Thermogravimetric Analysis and Differential Scanning Calorimetry (TGA-DSC):** TGA-DSC was performed using a METTLER Toledo TGA/DSC1 STAR system. All solid samples were heated from 30-1000 °C at a rate of 10 °C per minute under a nitrogen or oxygen atmosphere.

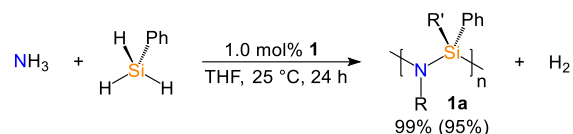
**Scanning Electron Microscope (SEM):** The oligosilazane **1a** was dip-coated onto copper tape and cured for 24 h in air prior to microscopic analysis. Scanning electron microscope (SEM) images of selected samples were collected on a Phenom XL desktop microscope operating at 5.0 kV acceleration voltage.

**General Procedure for Ammonia and Silane Dehydrocoupling Using 1 mol% **1**:** In the glove box under N<sub>2</sub> atmosphere, silane was added to a pre-weighed 20 mL scintillation vial with 5 mL of dry THF, a stir bar, and 1 mol% of [(<sup>2,6-iPr<sub>2</sub>Ph</sup>BDI)Mn(μ-H)]<sub>2</sub> to afford a light greenish-yellow solution. The mixture was then transferred to a 100 mL thick-walled glass bomb, sealed, and attached to the high vacuum line

outside the glove box. The gas from the headspace of the bomb was removed upon freezing the solution in liquid nitrogen, and subsequently, 1 atm of  $\text{NH}_3$  was added and condensed by liquid nitrogen. The bomb was disconnected from the vacuum line and allowed to warm to room temperature in a steel container and then set to stir. A freeze-pump-thaw cycle was performed after 2 h to release the  $\text{H}_2$  gas produced in the reaction. Again, the reaction was kept for stirring for 12 h and a freeze-pump-thaw was performed. After 24 h, a third freeze-pump-thaw cycle was performed and the extra ammonia was collected in a liquid nitrogen-cooled trap upon partial opening of the bomb to dynamic vacuum. The reaction mixture was transferred to the glove box and solvents were removed *in vacuo* to afford an oil or solid that was further characterized.  $^1\text{H}$  NMR spectroscopy was used to determine silane conversion and  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR data was collected for isolated samples. The theoretical yield for each oligomer was calculated assuming that the repeating unit features secondary amine and tertiary silane functionality (i.e., R and R' = H).

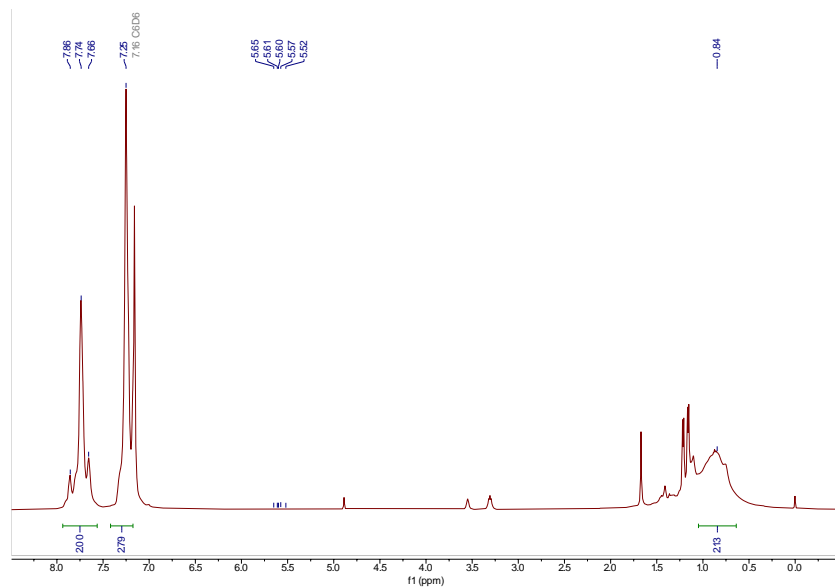
## PREPARATION OF OLIGOSILAZANES

### Ammonia and Phenylsilane Dehydrocoupling Using 1 mol% **1**:

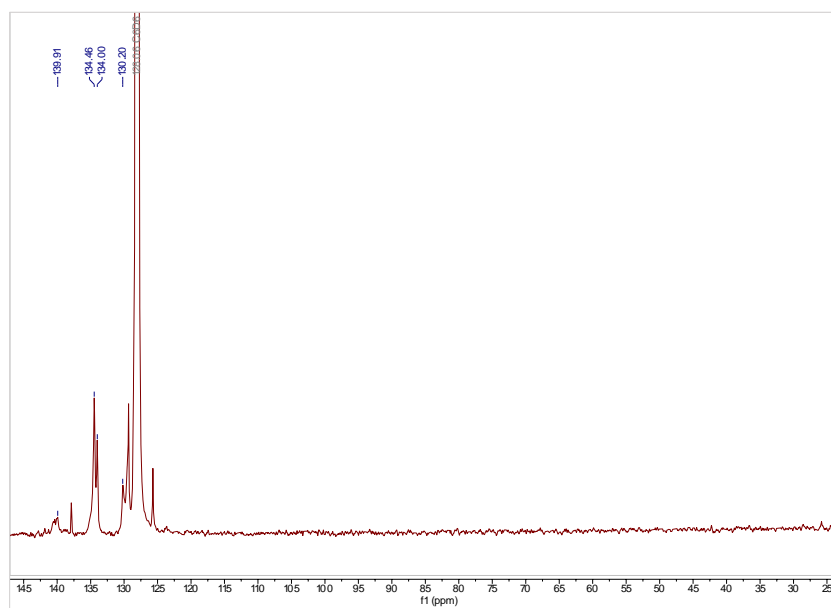


#### Scheme S1. Preparation of oligosilazane **1a**.

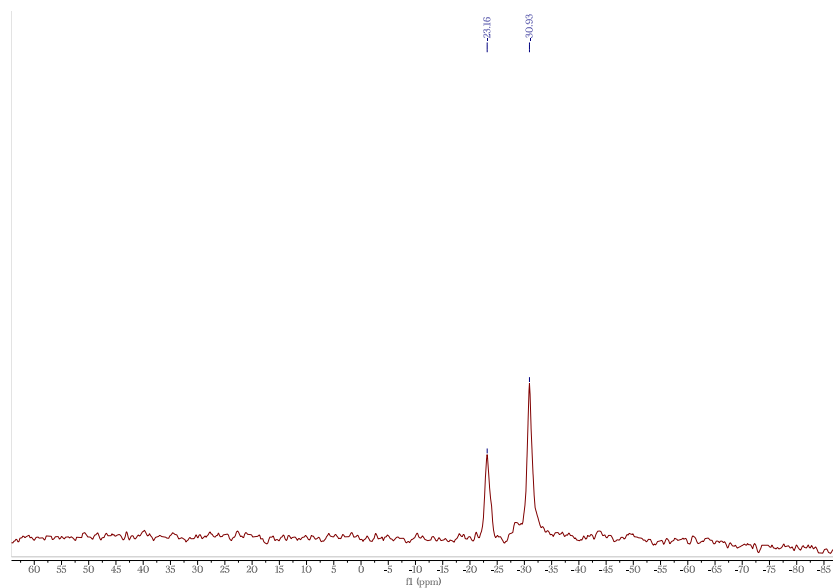
In the glove box under N<sub>2</sub> atmosphere, 0.490 g (4.528 mmol) of phenylsilane was charged to a pre-weighed 20 mL scintillation vial with 5 mL of dry THF, a stir bar, and 0.017 g (0.045 mmol) of **1** (light greenish-yellow color was observed). The mixture was then transferred to a 100 mL thick-walled glass bomb, sealed, and attached to the high vacuum line outside the glove box. The gas from the headspace of the bomb was removed upon freezing the solution with a liquid nitrogen trap, and subsequently, 1 atm of NH<sub>3</sub> was added. The bomb was disconnected from the vacuum line and allowed to warm to room temperature in a steel container and then set to stir. Freeze pump-thaw was performed after 2 h, 12 h, and 24 h to release the H<sub>2</sub> gas produced in the reaction. The extra ammonia was allowed to escape under a dynamic vacuum upon partial opening of the bomb and was collected in a trap cooled with liquid nitrogen. The reaction mixture was transferred to the glove box and solvents were removed *in vacuo* to afford a viscous oil. <sup>1</sup>H NMR spectroscopy revealed more than 99% conversion after 24 h and an isolated yield of 0.525 g (DOSY M<sub>w</sub> = 2,300 g/mol; 0.228 mmol oligomer; repeating units per oligomer = 18.8; 4.29 mmol of repeating unit; 95% isolated yield). <sup>1</sup>H NMR (400 MHz, benzene-*d*<sub>6</sub>): 7.86, 7.74, 7.66 (t, *m*-aryl), 7.25 (broad, *o*- & *p*-aryl), 5.65, 5.61, 5.60, 5.57, 5.52 (s, (NH)(NH)PhSiH, (NH)(NH<sub>2</sub>)PhSiH, (NH<sub>2</sub>)<sub>2</sub>PhSiH, (NH)PhSiH<sub>2</sub>, (NH<sub>2</sub>)PhSiH<sub>2</sub>), 0.84 (broad, NH, NH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, benzene-*d*<sub>6</sub>): 139.91 (NHSiC), 134.46 (*m*-Ph), 134.0 (*p*-Ph), 130.20 (*o*-Ph). <sup>29</sup>Si NMR (79 MHz, benzene-*d*<sub>6</sub>): 23.16 (NHSiNH), 30.93 (NH<sub>2</sub>SiNH). IR (KBr, cm<sup>-1</sup>): 3540-3170 (broad, N-H), 3030-2820 (broad, C-H), 850 (weak, Si-N).



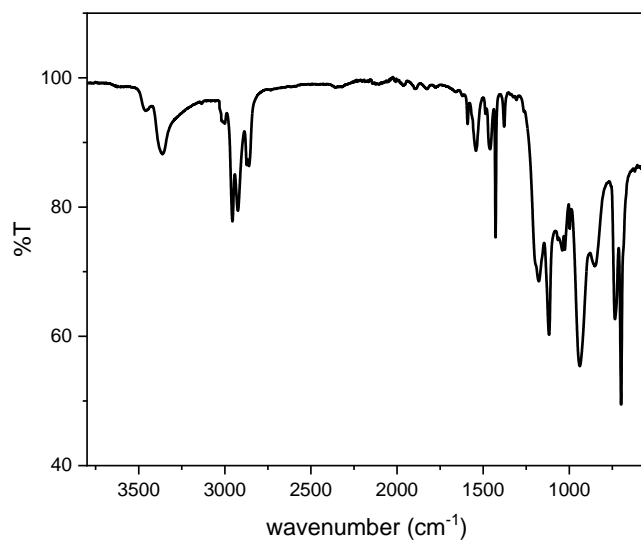
**Figure S1.**  $^1\text{H}$  NMR spectrum of **1a** in benzene- $d_6$ .



**Figure S2.**  $^{13}\text{C}$  NMR spectrum of **1a** in benzene- $d_6$ .

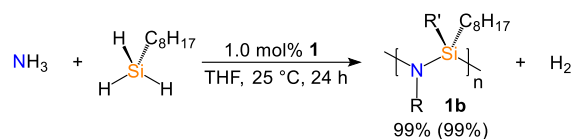


**Figure S3.**  $^{29}\text{Si}$  NMR spectrum of **1a** in benzene- $d_6$ .



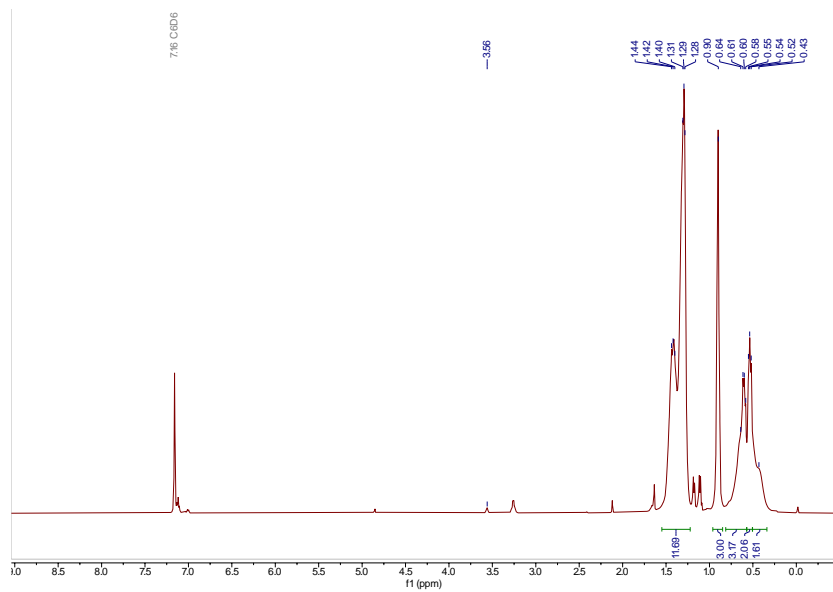
**Figure S4.** FT-IR spectrum of **1a**.

## Ammonia and Octylsilane Dehydrocoupling Using 1 mol% **1**:

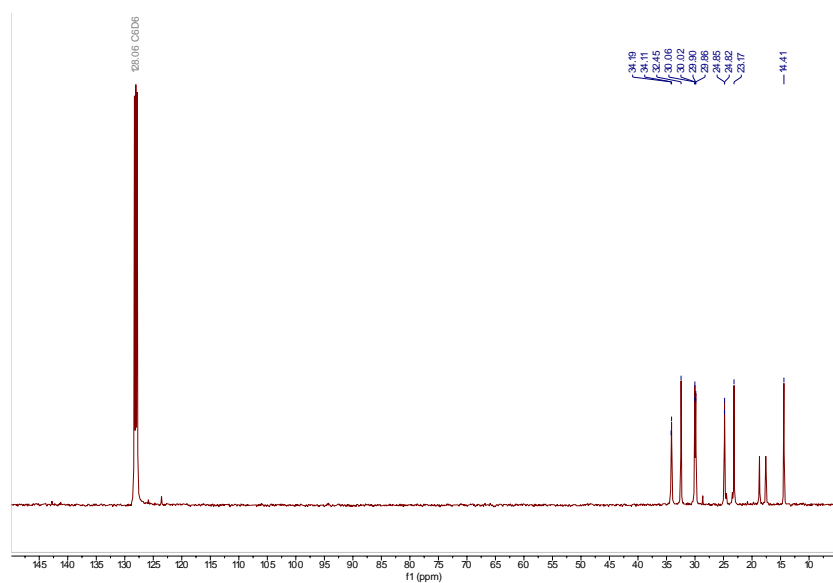


### Scheme S2. Preparation of oligosilazane **1b**.

In the glove box under N<sub>2</sub> atmosphere, 0.200 g (1.386 mmol) of octylsilane was charged to a pre-weighed 20 mL scintillation vial with 5 mL of dry THF, a stir bar, and 0.016 g (0.017 mmol) of **1** (light greenish-yellow color was observed). The mixture was then transferred to a 100 mL thick-walled glass bomb, sealed, and attached to the high vacuum line outside the glove box. The gas from the headspace of the bomb was removed upon freezing the solution with a liquid nitrogen trap, and subsequently, 1 atm of NH<sub>3</sub> was added. The bomb was disconnected from the vacuum line and allowed to warm to room temperature in a steel container and then set to stir. Freeze pump-thaw was performed after 2 h, 12 h, and 24 h to release the H<sub>2</sub> gas produced in the reaction. The extra ammonia was allowed to escape under a dynamic vacuum upon partial opening of the bomb and was collected in a trap cooled with liquid nitrogen. The reaction mixture was transferred to the glove box and solvents were removed *in vacuo* to afford a viscous oil. <sup>1</sup>H NMR spectroscopy revealed more than 99% conversion after 24 h and an isolated yield of 0.220 g (DOSY M<sub>w</sub> = 1,200 g/mol; 0.183 mmol oligomer; repeating units per oligomer = 7.5; 1.37 mmol of repeating unit; 99% isolated yield). <sup>1</sup>H NMR (400 MHz, benzene-*d*<sub>6</sub>): 1.44-1.40 (NHSiNH, NH<sub>2</sub>SiNH, Si(NH)<sub>3</sub>), 1.29 (broad, CH<sub>3</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>), 0.90 (s, CH<sub>3</sub>), 0.30-0.75 (SiCH<sub>2</sub>, SiCH<sub>2</sub>CH<sub>2</sub>, SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, CH<sub>3</sub>CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, benzene-*d*<sub>6</sub>): 34.19 (CH<sub>3</sub>CH<sub>2</sub>), 34.11 (SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 32.45 (SiCH<sub>2</sub>), 30.02, 29.90 (SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>), 24.85 (CH<sub>3</sub>CH<sub>2</sub>), 23.17 (SiCH<sub>2</sub>CH<sub>2</sub>), 14.41 (CH<sub>3</sub>). <sup>29</sup>Si NMR (79 MHz, benzene-*d*<sub>6</sub>): 20.56 (NHSiNH). IR (KBr, cm<sup>-1</sup>): 3510-3265 (broad, NH, NH<sub>2</sub>), 3000-2810 (strong, C-H), 821 (strong, Si-N).

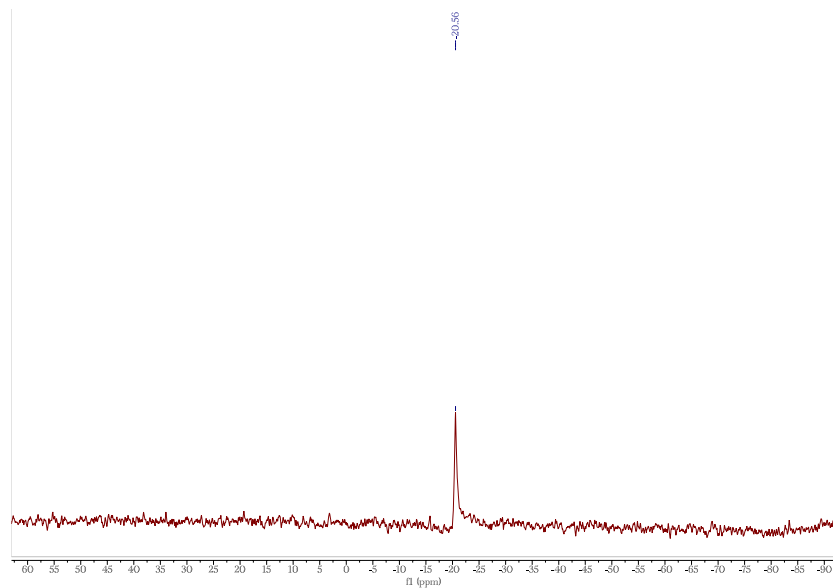


**Figure S5.** <sup>1</sup>H NMR spectrum of **1b** in benzene-*d*<sub>6</sub>.

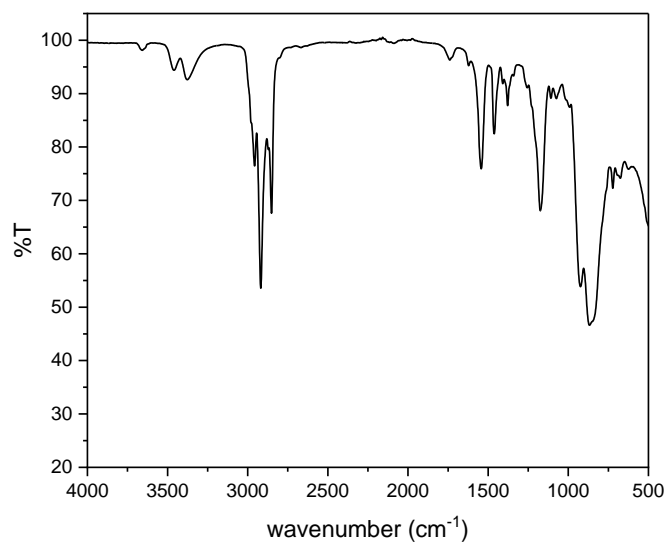


**Figure S6.** <sup>13</sup>C NMR spectrum of **1b** in benzene-*d*<sub>6</sub>.



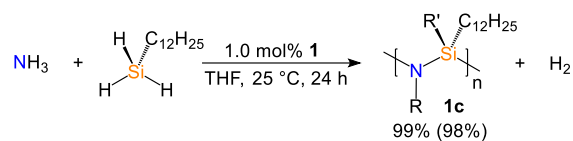


**Figure S7.**  $^{29}\text{Si}$  NMR spectrum of **1b** in benzene- $d_6$ .



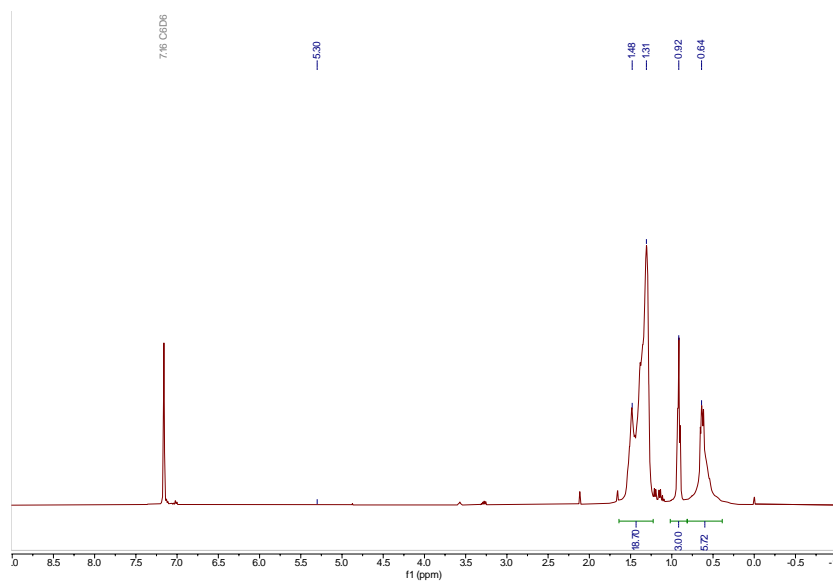
**Figure S8.** FT-IR spectrum of **1b**.

### Ammonia and Dodecylsilane Dehydrocoupling Using 1 mol% **1**:

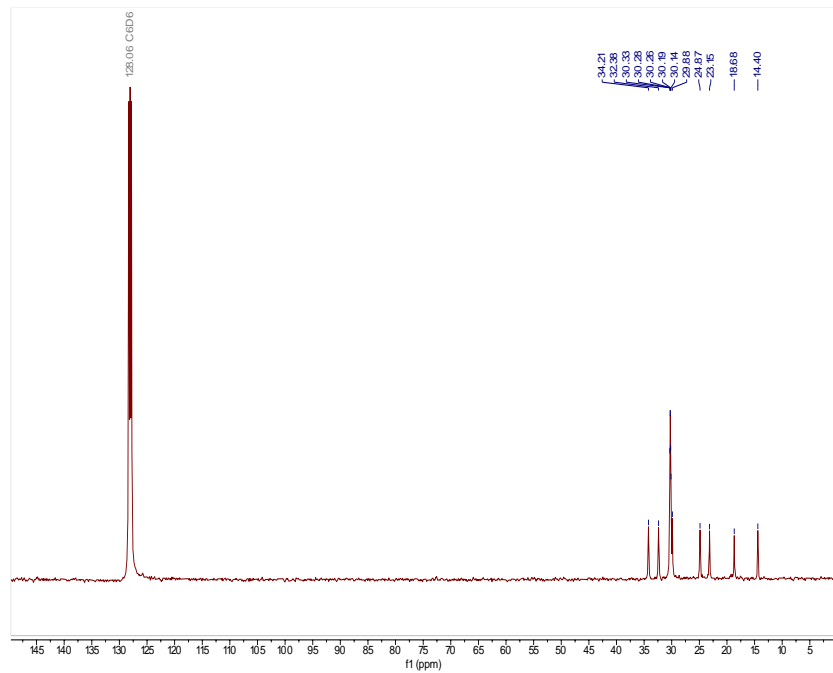


#### Scheme S3. Preparation of oligosilazane **1c**.

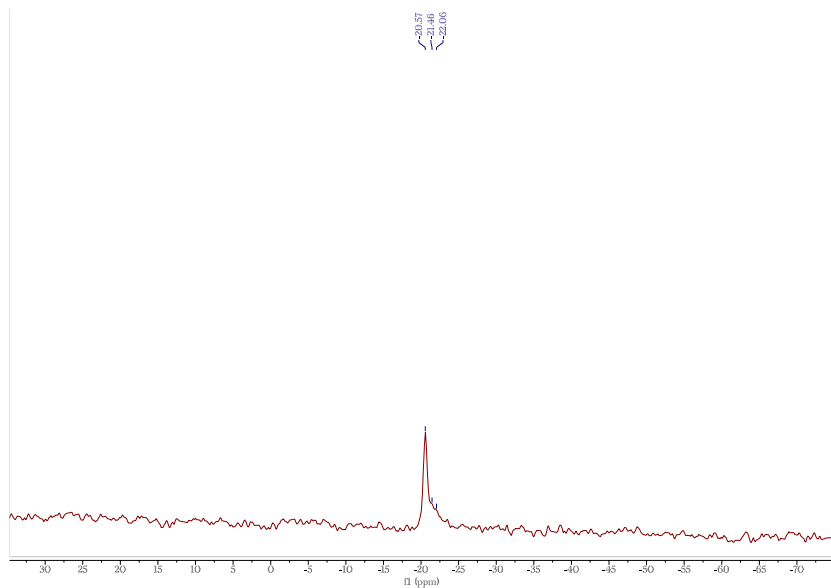
In the glove box under  $\text{N}_2$  atmosphere, 0.338 g (1.691 mmol) of dodecylsilane was charged to a pre-weighed 20 mL scintillation vial with 5 mL of dry THF, a stir bar, and 0.016 g (0.016 mmol) of **1** (light greenish-yellow color was observed). The mixture was then transferred to a 100 mL thick-walled glass bomb, sealed, and attached to the high vacuum line outside the glove box. The gas from the headspace of the bomb was removed upon freezing the solution with a liquid nitrogen trap, and subsequently, 1 atm of  $\text{NH}_3$  was added. The bomb was disconnected from the vacuum line and allowed to warm to room temperature in a steel container and then set to stir. Freeze pump-thaw was performed after 2 h, 12 h, and 24 h to release the  $\text{H}_2$  gas produced in the reaction. The extra ammonia was allowed to escape under a dynamic vacuum upon partial opening of the bomb and was collected in a trap cooled with liquid nitrogen. The reaction mixture was transferred to the glove box and solvents were removed *in vacuo* to afford colorless powder.  $^1\text{H}$  NMR spectroscopy revealed more than 99% conversion after 24 h and an isolated yield of 0.360 g (DOSY  $M_w = 900$  g/mol; 0.400 mmol oligomer; repeating units per oligomer = 4.1; 1.65 mmol of repeating unit; 98% isolated yield).  $^1\text{H}$  NMR (400 MHz, benzene- $d_6$ ): 5.30 (s, SiH), 1.23-1.60 (broad,  $\text{CH}_2$ ), 0.92 (t, NH,  $\text{NH}_2$ ), 0.64 (broad,  $\text{SiCH}_2$ ,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz, benzene- $d_6$ ): 34.21 ( $\text{Si}(\text{CH}_2)_2\text{CH}_2$ ), 32.28 ( $\text{CH}_3\text{CH}_2\text{CH}_2$ ), 30.29, 30.26, 30.19, 30.14 (internal  $\text{CH}_2$ ), 29.88 ( $\text{CH}_3\text{CH}_2\text{CH}_2$ ,  $\text{Si}(\text{CH}_2)_3\text{CH}_2$ ), 24.87 ( $\text{SiCH}_2$ ), 23.15 ( $\text{CH}_3\text{CH}_2$ ), 18.68 ( $\text{SiCH}_2\text{CH}_2$ ), 14.40 ( $\text{CH}_3$ ).  $^{29}\text{Si}$  NMR (79 MHz, benzene- $d_6$ ): -20.57 (NHSiNH), -21.46 (NHSiNH), -22.06 ( $\text{NH}_2\text{SiNH}$ ). IR (KBr,  $\text{cm}^{-1}$ ): 3480-3215 (broad, N-H), 2975-2790 (strong, C-H), 826 (weak, Si-N).



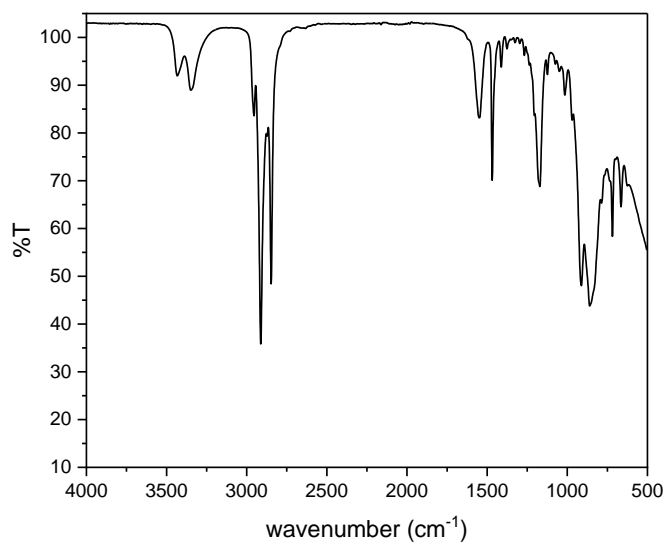
**Figure S9.**  $^1\text{H}$  NMR spectrum of **1c** in benzene- $d_6$ .



**Figure S10.**  $^{13}\text{C}$  NMR spectrum of **1c** in benzene- $d_6$ .

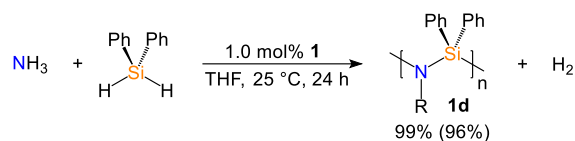


**Figure S11.**  $^{29}\text{Si}$  NMR spectrum of **1c** in benzene- $d_6$ .



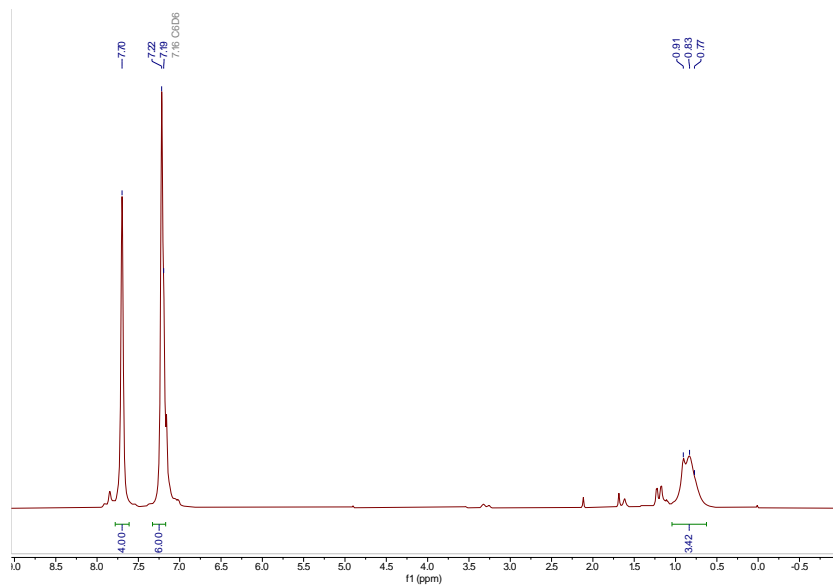
**Figure S12.** FT-IR spectrum of **1c**.

### Ammonia and Diphenylsilane Dehydrocoupling Using 1 mol% **1**:

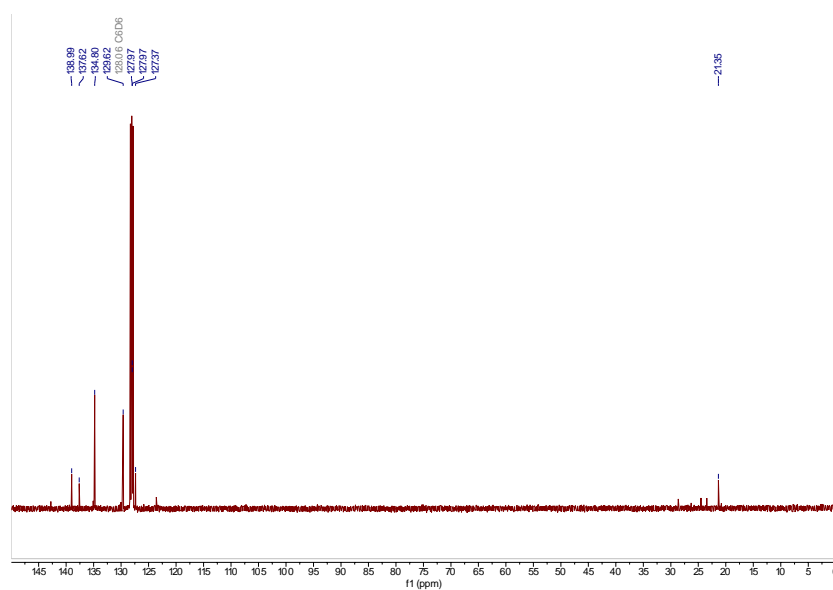


#### Scheme S4. Preparation of oligosilazane **1d**.

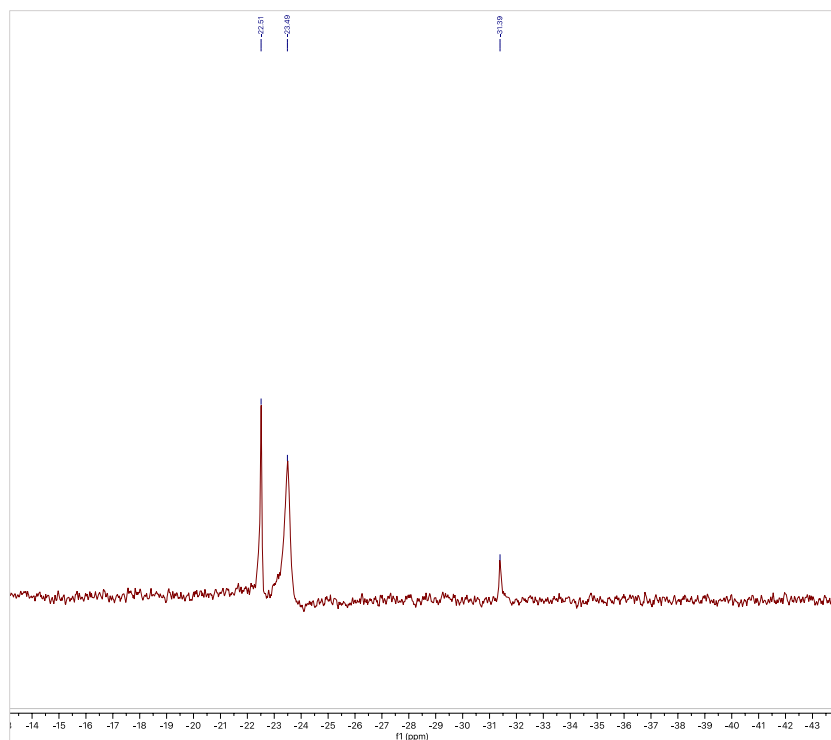
In the glove box under N<sub>2</sub> atmosphere, 0.322 g (1.749 mmol) of diphenylsilane was charged to a pre-weighed 20 mL scintillation vial with 5 mL of dry THF, a stir bar, and 0.016 g (0.017 mmol) of **1** (light greenish-yellow color was observed). The mixture was then transferred to a 100 mL thick-walled glass bomb, sealed, and attached to the high vacuum line outside the glove box. The gas from the headspace of the bomb was removed upon freezing the solution with a liquid nitrogen trap, and subsequently, 1 atm of NH<sub>3</sub> was added. The bomb was disconnected from the vacuum line and allowed to warm to room temperature in a steel container and then set to stir. Freeze pump-thaw was performed after 2 h, 12 h, and 24 h to release the H<sub>2</sub> gas produced in the reaction. The extra ammonia was allowed to escape under a dynamic vacuum upon partial opening of the bomb and was collected in a trap cooled with liquid nitrogen. The reaction mixture was transferred to the glove box and solvents were removed *in vacuo* to afford a viscous oil. <sup>1</sup>H NMR spectroscopy revealed more than 99% conversion after 24 h and an isolated yield of 0.336 g (DOSY M<sub>w</sub> = 700 g/mol; 0.480 mmol oligomer; repeating units per oligomer = 3.5; 1.66 mmol of repeating unit; 96% isolated yield). <sup>1</sup>H NMR (400 MHz, benzene-*d*<sub>6</sub>): 7.75-7.36 (broad, *m*-Ph), 7.25-7.12 (broad, *o*-Ph, *p*-Ph), 0.98-0.61 (broad, NH, NH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, benzene-*d*<sub>6</sub>): 138.99 (SiC), 134.80 (*o*-Ph), 129.62 (*p*-Ph), 127.97, 127.37 (*m*-Ph). <sup>29</sup>Si NMR (79 MHz, benzene-*d*<sub>6</sub>): 22.51 (Si(NH)<sub>2</sub>), 23.49 (Ph<sub>2</sub>HSi(NH)), 31.39 (Ph<sub>2</sub>Si(NH)(NSi<sub>2</sub>)). IR (KBr, cm<sup>-1</sup>): 3500-3250 (broad, N-H), 3000-2870 (strong, C-H), 810 (strong, Si-N).



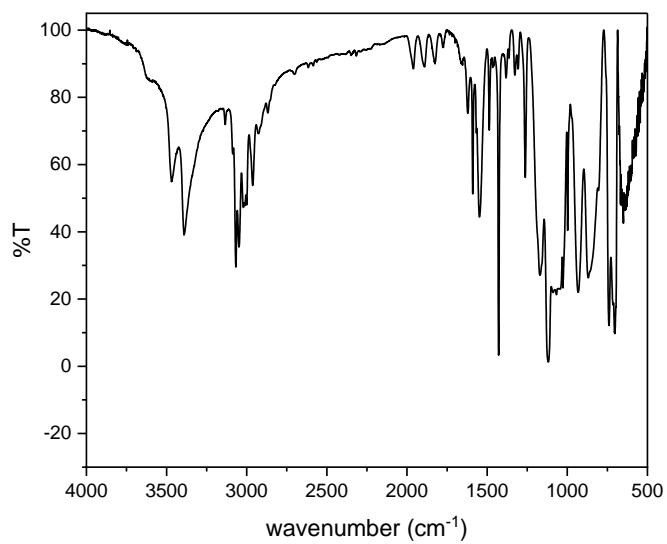
**Figure S13.**  $^1\text{H}$  NMR spectrum of **1d** in benzene- $d_6$ .



**Figure S14.**  $^{13}\text{C}$  NMR spectrum of **1d** in benzene- $d_6$ .



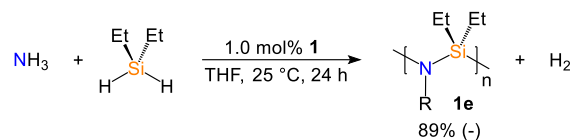
**Figure S15.**  $^{29}\text{Si}$  NMR spectrum of **1d** in benzene- $d_6$ .



**Figure S16.** FT-IR spectrum of **1d**.

## OBSERVATION OF OLIGOSILAZANES

### Ammonia and Diethylsilane Dehydrocoupling Using 1 mol% **1**:



#### Scheme S5. Observation of oligodiethylsilazane (**1e**).

In the glove box under N<sub>2</sub> atmosphere, 0.093 g (1.056 mmol) of diethylsilane was charged to a pre-weighed 20 mL scintillation vial with 5 mL of dry THF, a stir bar, and 0.010 g (0.010 mmol) of **1** (light greenish-yellow color was observed). The mixture was then transferred to a 100 mL thick-walled glass bomb, sealed, and attached to the high vacuum line outside the glove box. The gas from the headspace of the bomb was removed upon freezing the solution with a liquid nitrogen trap, and subsequently, 1 atm of NH<sub>3</sub> was added. The bomb was disconnected from the vacuum line and allowed to warm to room temperature in a steel container and then set to stir. Freeze pump-thaw was performed after 2 h, 12 h, and 24 h to release the H<sub>2</sub> gas produced in the reaction. The extra ammonia was allowed to escape under a dynamic vacuum upon partial opening of the bomb and was collected in a trap cooled with liquid nitrogen. The reaction mixture was transferred to the glove box and 89% conversion was observed by <sup>1</sup>H NMR spectroscopy. <sup>1</sup>H NMR (400 MHz, benzene-*d*<sub>6</sub>): 4.40 (s, Et<sub>2</sub>SiH<sub>2</sub>), 1.02-0.87 (m, CH<sub>3</sub>), 0.61-0.37 (m, CH<sub>2</sub>).

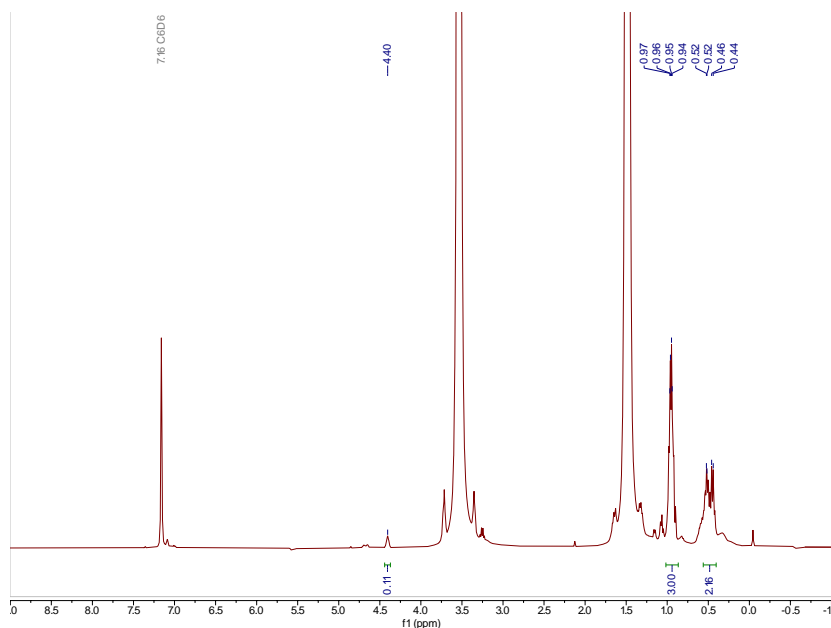
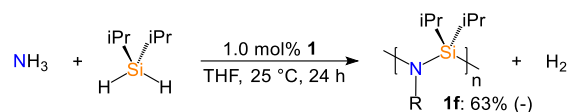


Figure S17. <sup>1</sup>H NMR spectrum showing conversion to **1e** in benzene-*d*<sub>6</sub>.



### Ammonia and Diisopropylsilane Dehydrocoupling Using 1 mol% **1**:



#### Scheme S6. Observation of oligodiisopropylsilazane (**1f**).

In the glove box under N<sub>2</sub> atmosphere, 0.084 g (0.528 mmol) of diisopropylsilane was added to a pre-weighed 20 mL scintillation vial with 5 mL of dry THF, a stir bar, and 0.005 g (0.005 mmol) of **1** (light greenish-yellow color was observed). The mixture was then transferred to a 100 mL thick-walled glass bomb, sealed, and attached to the high vacuum line outside the glove box. The gas from the headspace of the bomb was removed upon freezing the solution with a liquid nitrogen trap, and subsequently, 1 atm of NH<sub>3</sub> was added. The bomb was disconnected from the vacuum line and allowed to warm to room temperature in a steel container and then set to stir. Freeze pump-thaw was performed after 2 h, 12 h, and 24 h to release the H<sub>2</sub> gas produced in the reaction. The extra ammonia was allowed to escape under a dynamic vacuum upon partial opening of the bomb and was collected in a trap cooled with liquid nitrogen. The reaction mixture was transferred to the glove box and 63% conversion was observed by <sup>1</sup>H NMR spectroscopy. <sup>1</sup>H NMR (400 MHz, benzene-*d*<sub>6</sub>): 3.28 (s, iPr<sub>2</sub>SiH<sub>2</sub>), 1.67 (broad, NH, NH<sub>2</sub>), 1.15 (broad, CH<sub>3</sub>, (CH<sub>3</sub>)<sub>2</sub>CH).

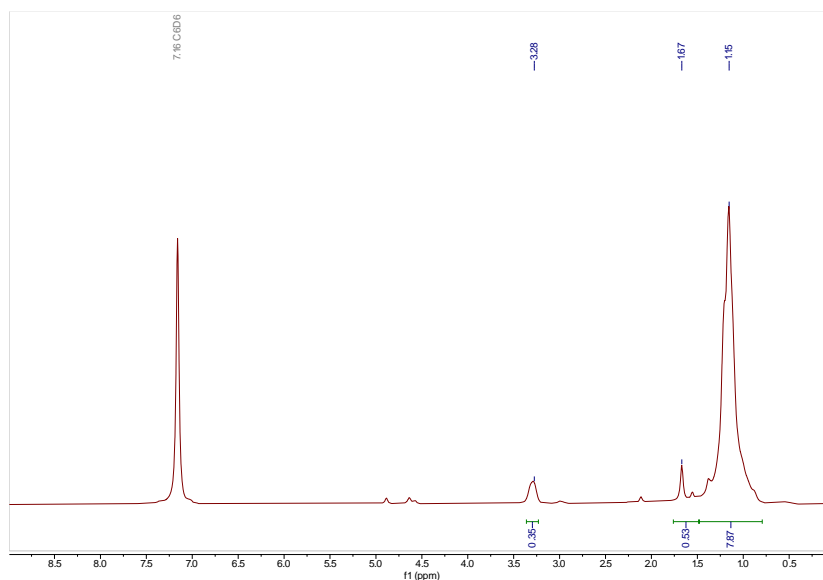
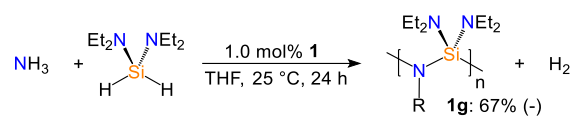


Figure S18. <sup>1</sup>H NMR spectrum showing conversion to **1f** in benzene-*d*<sub>6</sub>.

## Ammonia and Bis(diethylamino)silane Dehydrocoupling Using 1 mol% **1**:



### Scheme S7. Observation of oligobis(diethylamino)silazane (**1g**).

In the glove box under N<sub>2</sub> atmosphere, 0.092 g (0.528 mmol) of bis(diethylamino)silane was added to a pre-weighed 20 mL scintillation vial with 5 mL of dry THF, a stir bar, and 0.005 g (0.005 mmol) of **1** (light greenish-yellow color was observed). The mixture was then transferred to a 100 mL thick-walled glass bomb, sealed, and attached to the high vacuum line outside the glove box. The gas from the headspace of the bomb was removed upon freezing the solution with a liquid nitrogen trap, and subsequently, 1 atm of NH<sub>3</sub> was added. The bomb was disconnected from the vacuum line and allowed to warm to room temperature in a steel container and then set to stir. Freeze pump-thaw was performed after 2 h, 12 h, and 24 h to release the H<sub>2</sub> gas produced in the reaction. The extra ammonia was allowed to escape under a dynamic vacuum upon partial opening of the bomb and was collected in a trap cooled with liquid nitrogen. The reaction mixture was transferred to the glove box and 67% conversion was observed by <sup>1</sup>H NMR spectroscopy. <sup>1</sup>H NMR (400 MHz, benzene-*d*<sub>6</sub>): 4.74 (s, SiHNH), 4.67 (s, SiH<sub>2</sub>), 2.87 (broad, CH<sub>2</sub>), 0.99 (broad, CH<sub>3</sub>), 0.35 (broad, NH, NH<sub>2</sub>).

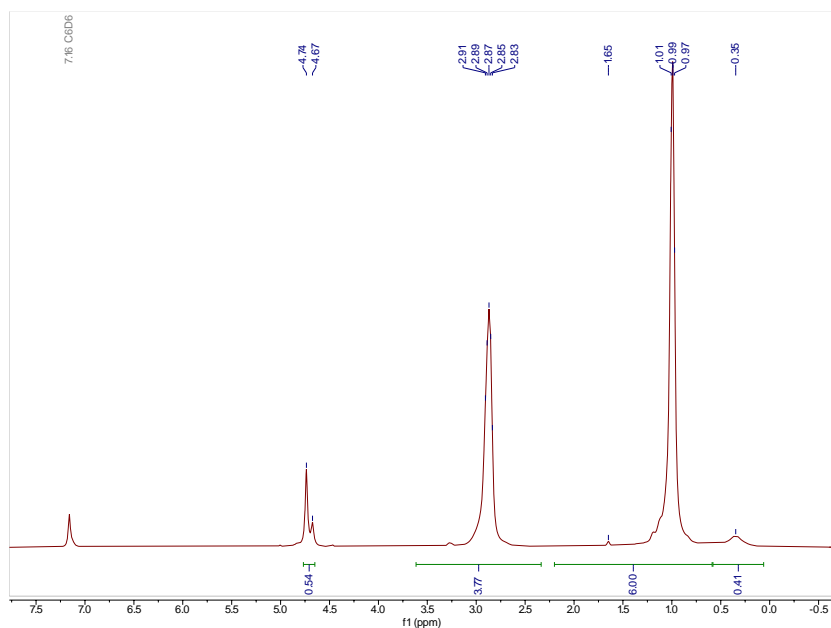
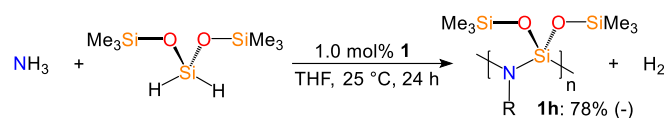


Figure S19. <sup>1</sup>H NMR spectrum showing conversion to **1g** in benzene-*d*<sub>6</sub>.

### Ammonia and Bis(trimethylsiloxy)silane Dehydrocoupling Using 1 mol% **1**:



#### Scheme S8. Observation of oligobis(trimethylsiloxy)silazane (**1h**).

In the glove box under  $\text{N}_2$  atmosphere, 0.176 g (0.845 mmol) of bis(trimethoxy)silane was added to a pre-weighed 20 mL scintillation vial with 5 mL of dry THF, a stir bar, and 0.008 g (0.008 mmol) of **1** (light greenish-yellow color was observed). The mixture was then transferred to a 100 mL thick-walled glass bomb, sealed, and attached to the high vacuum line outside the glove box. The gas from the headspace of the bomb was removed upon freezing the solution with a liquid nitrogen trap, and subsequently, 1 atm of  $\text{NH}_3$  was added. The bomb was disconnected from the vacuum line and allowed to warm to room temperature in a steel container and then set to stir. Freeze pump-thaw was performed after 2 h, 12 h, and 24 h to release the  $\text{H}_2$  gas produced in the reaction. The extra ammonia was allowed to escape under a dynamic vacuum upon partial opening of the bomb and was collected in a trap cooled with liquid nitrogen. The reaction mixture was transferred to the glove box and 78% conversion was observed by  $^1\text{H}$  NMR spectroscopy.  $^1\text{H}$  NMR (400 MHz, benzene- $d_6$ ): 4.65 (s, SiH), 0.22 (broad,  $\text{CH}_3$ ).

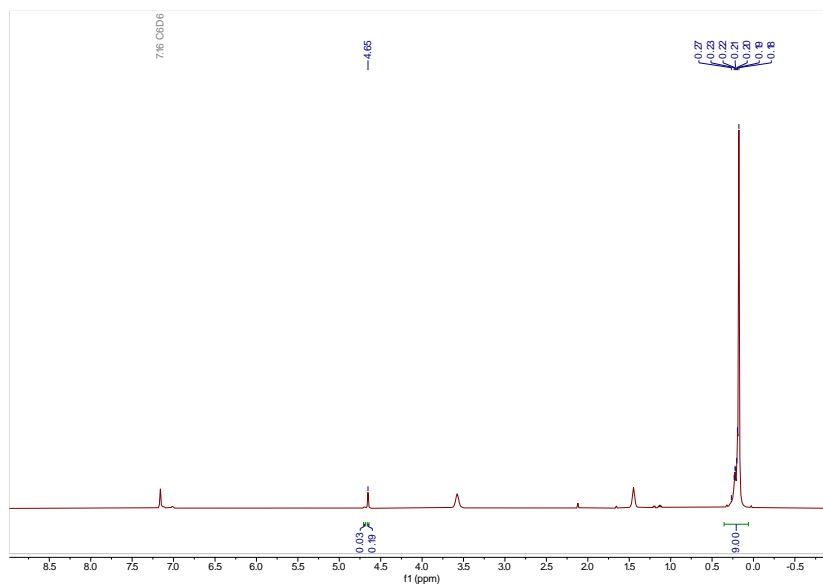
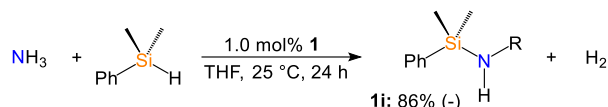


Figure S20.  $^1\text{H}$  NMR spectrum showing conversion to **1h** in benzene- $d_6$ .

## DEHYDROCOUPLING OF TERTIARY SILANES TO FORM AMINOSILANES

### Ammonia and Dimethylphenylsilane Dehydrocoupling Using 1 mol% **1**:



#### Scheme S9. Observation of aminated dimethylphenylsilane (**1i**).

In the glove box under N<sub>2</sub> atmosphere, 0.143g (1.056 mmol) of dimethylphenylsilane was added to a pre-weighed 20 mL scintillation vial with 5 mL of dry THF, a stir bar, and 0.010 g (0.010 mmol) of **1** (light greenish-yellow color was observed). The mixture was then transferred to a 100 mL thick-walled glass bomb, sealed, and attached to the high vacuum line outside the glove box. The gas from the headspace of the bomb was removed upon freezing the solution with a liquid nitrogen trap, and subsequently, 1 atm of NH<sub>3</sub> was added. The bomb was disconnected from the vacuum line and allowed to warm to room temperature in a steel container and then set to stir. Freeze pump-thaw was performed after 2 h, 12 h, and 24 h to release the H<sub>2</sub> gas produced in the reaction. The extra ammonia was allowed to escape under a dynamic vacuum upon partial opening of the bomb and was collected in a trap cooled with liquid nitrogen. The reaction mixture was transferred to the glove box and 86% conversion was observed by <sup>1</sup>H NMR spectroscopy. <sup>1</sup>H NMR (400 MHz, benzene-*d*<sub>6</sub>): 7.79-6.68 (broad, *aryl*), 0.88 (broad, *NH* and *NH*<sub>2</sub>), 0.50-0.02 (broad, *CH*<sub>3</sub>).

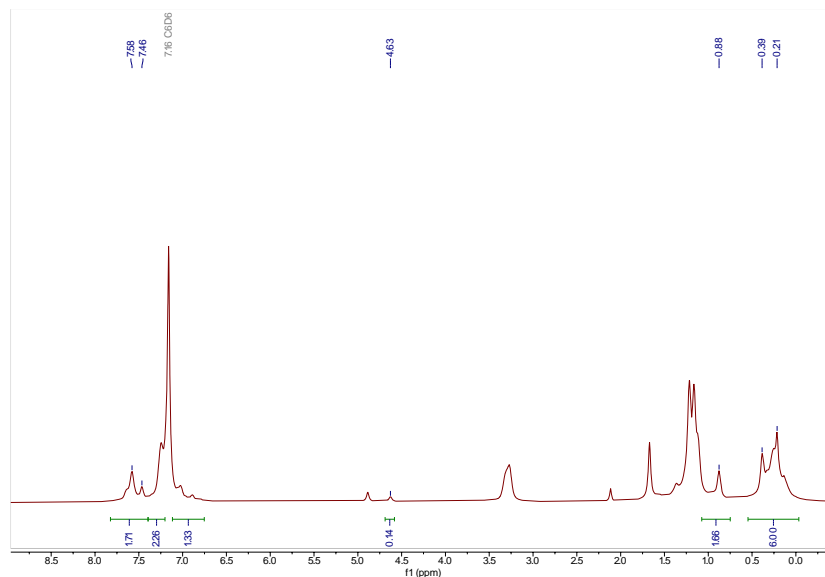
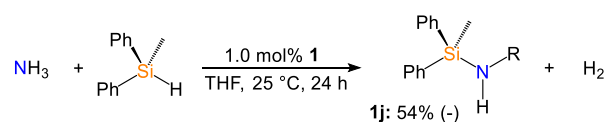


Figure S21. <sup>1</sup>H NMR spectrum showing conversion to **1i** in benzene-*d*<sub>6</sub>.

## Ammonia and Methylphenylsilane Dehydrocoupling Using 1 mol% **1**:



### Scheme S10. Observation of aminated methylphenylsilane (**1j**).

In the glove box under N<sub>2</sub> atmosphere, 0.209 g (1.056 mmol) of methylphenylsilane was added to a pre-weighed 20 mL scintillation vial with 5 mL of dry THF, a stir bar, and 0.010 g (0.010 mmol) of **1** (light greenish-yellow color was observed). The mixture was then transferred to a 100 mL thick-walled glass bomb, sealed, and attached to the high vacuum line outside the glove box. The gas from the headspace of the bomb was removed upon freezing the solution with a liquid nitrogen trap, and subsequently, 1 atm of NH<sub>3</sub> was added. The bomb was disconnected from the vacuum line and allowed to warm to room temperature in a steel container and then set to stir. Freeze pump-thaw was performed after 2 h, 12 h, and 24 h to release the H<sub>2</sub> gas produced in the reaction. The extra ammonia was allowed to escape under a dynamic vacuum upon partial opening of the bomb and was collected in a trap cooled with liquid nitrogen. The reaction mixture was transferred to the glove box and 54% conversion was observed by <sup>1</sup>H NMR spectroscopy. <sup>1</sup>H NMR (400 MHz, benzene-*d*<sub>6</sub>): 7.60 (broad, *p*-Ph), 7.51 (broad, *o*-Ph), 7.21 (broad, *m*-Ph), 5.14 (SiH), 0.88 (broad, NH, NH<sub>2</sub>), 0.48 (CH<sub>3</sub>).

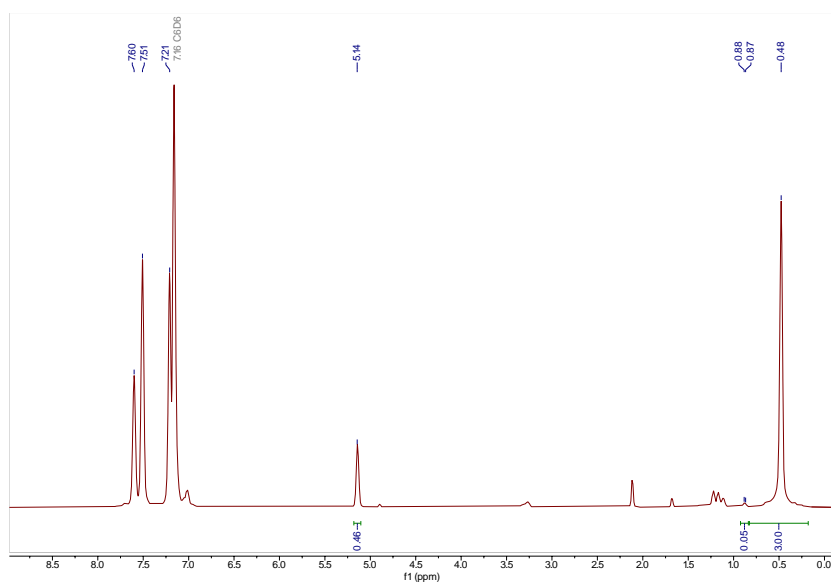
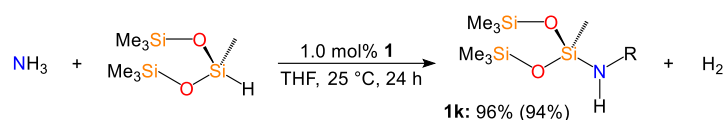


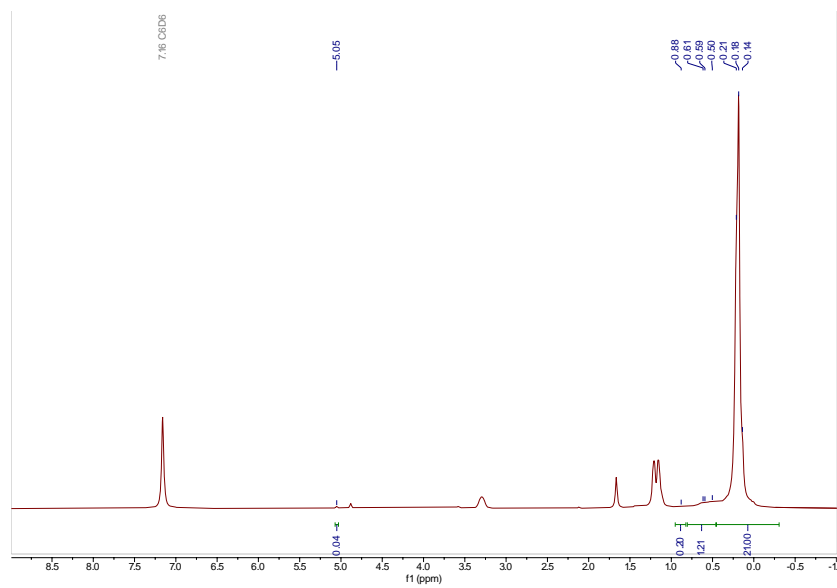
Figure S22. <sup>1</sup>H NMR spectrum showing conversion to **1j** in benzene-*d*<sub>6</sub>.

### Ammonia and Bis(trimethylsiloxy)methylsilane Dehydrocoupling Using 1 mol% **1**:

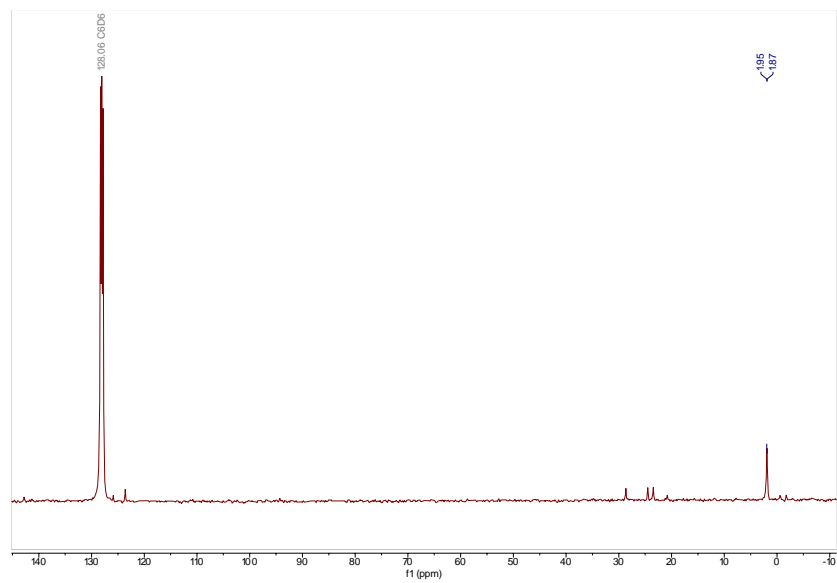


**Scheme S11.** Preparation of **1k** as a 12:1 mixture of disilylamine to silylamine.

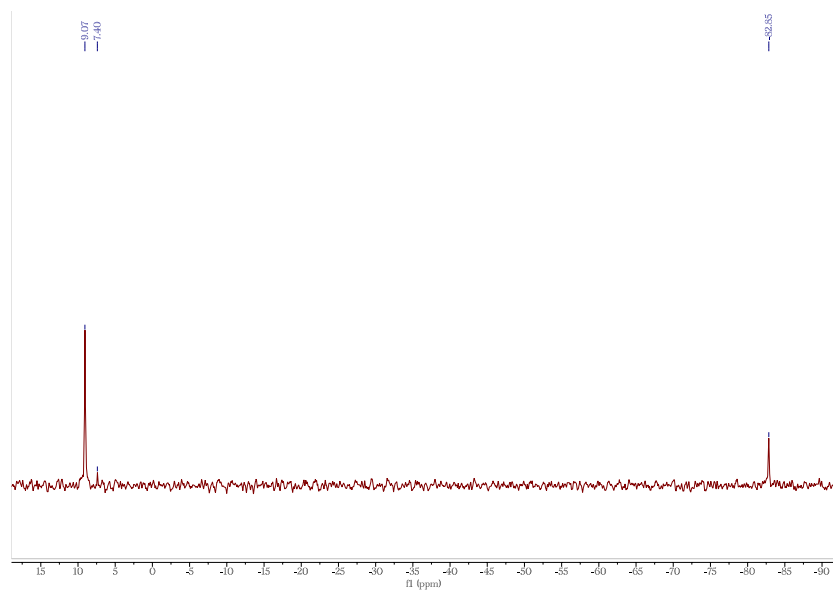
In the glove box under N<sub>2</sub> atmosphere, 0.235 g (1.056 mmol) of bis(trimethylsiloxy)methylsilane was charged to a pre-weighed 20 mL scintillation vial with 5 mL of dry THF, a stir bar, and 0.010 g (0.010 mmol) of **1** (light greenish-yellow color was observed). The mixture was then transferred to a 100 mL thick-walled glass bomb, sealed, and attached to the high vacuum line outside the glove box. The gas from the headspace of the bomb was removed upon freezing the solution with a liquid nitrogen trap, and subsequently, 1 atm of NH<sub>3</sub> was added. The bomb was disconnected from the vacuum line and allowed to warm to room temperature in a steel container and then set to stir. Freeze pump-thaw was performed after 2 h, 12 h, and 24 h to release the H<sub>2</sub> gas produced in the reaction. The extra ammonia was allowed to escape under a dynamic vacuum upon partial opening of the bomb and was collected in a trap cooled with liquid nitrogen. The reaction mixture was transferred to the glove box and solvents were removed *in vacuo* to afford a viscous oil. <sup>1</sup>H NMR spectroscopy revealed more than 96% conversion after 24 h and an isolated yield of 0.229 g (0.995 mmol, 94%) was obtained. <sup>1</sup>H NMR (400 MHz, benzene-*d*<sub>6</sub>): 5.05 (s, SiH), 0.88 (broad, NH<sub>2</sub>), 0.59 (broad, NH), 0.18 (broad, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, benzene-*d*<sub>6</sub>): 0.95-0.87 (broad, CH<sub>3</sub>). <sup>29</sup>Si NMR (79 MHz, benzene-*d*<sub>6</sub>): 9.07 (OSiCH<sub>3</sub>), -82.85 (SiNH, SiNH<sub>2</sub>). IR (KBr, cm<sup>-1</sup>): 3530 (broad, NH<sub>2</sub>), 3350 (broad, NH), 2975-2843 (strong, C-H), 2160 (broad, Si-H), 795 (weak, Si-N).



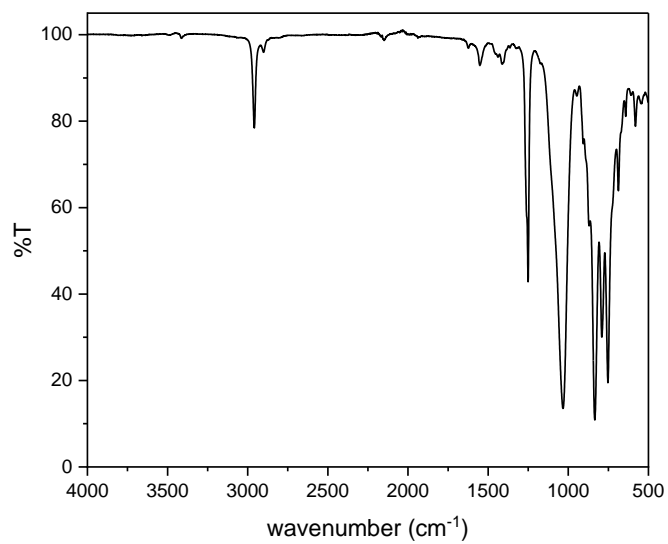
**Figure S23.**  $^1\text{H}$  NMR spectrum of **1k** in benzene- $d_6$ .



**Figure S24.**  $^{13}\text{C}$  NMR spectrum of **1k** in benzene- $d_6$ .



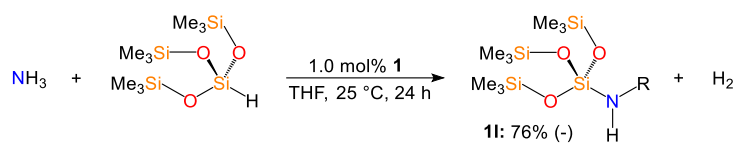
**Figure S25.**  $^{29}\text{Si}$  NMR spectrum of **1k** in benzene- $d_6$ .



**Figure S26.** FT-IR spectrum of **1k**.



## Ammonia and Tris(trimethylsiloxy)silane Dehydrocoupling Using 1 mol% **1**:



### Scheme S12. Observation of aminated tris(trimethylsiloxy)silane (**11**).

In the glove box under N<sub>2</sub> atmosphere, 0.333 g (1.05 mmol) of tris(trimethylsiloxy)silane was added to a pre-weighed 20 mL scintillation vial with 5 mL of dry THF, a stir bar and 0.010 g (0.010 mmol) of **1** (light greenish-yellow color was observed). The mixture was then transferred to a 100 mL thick-walled glass bomb, sealed, and attached to the high vacuum line outside the glove box. The gas from the headspace of the bomb was removed upon freezing the solution with a liquid nitrogen trap, and subsequently, 1 atm of NH<sub>3</sub> was added. The bomb was disconnected from the vacuum line and allowed to warm to room temperature in a steel container and then set to stir. Freeze pump-thaw was performed after 2 h, 12 h, and 24 h to release the H<sub>2</sub> gas produced in the reaction. The extra ammonia was allowed to escape under a dynamic vacuum upon partial opening of the bomb and was collected in a trap cooled with liquid nitrogen. The reaction mixture was transferred to the glove box and 76% conversion was observed by <sup>1</sup>H NMR spectroscopy. <sup>1</sup>H NMR (400 MHz, benzene-*d*<sub>6</sub>): 4.69 (s, SiH), 0.25-0.19 (broad, CH<sub>3</sub>).

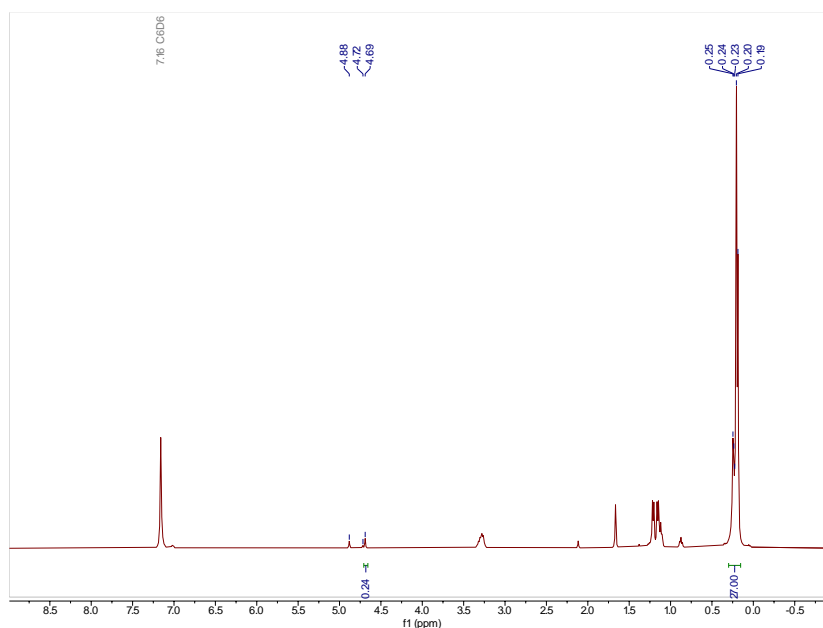
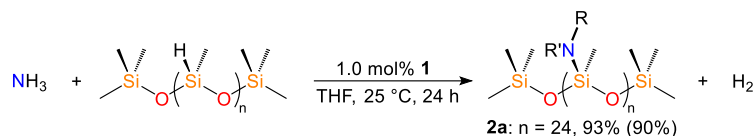


Figure S27. <sup>1</sup>H NMR spectrum showing conversion to **11** in benzene-*d*<sub>6</sub>.

## DEHYDROCOUPLING OF SILOXANES TO FORM POLYSILOXAZANE SOLIDS

### Ammonia and TMS-*ter*-PMHS (n = 24) Dehydrocoupling Using 1 mol% **1**:



### Scheme S13. Preparation of polysiloxazane **2a**.

In the glove box under N<sub>2</sub> atmosphere, 0.845 g (0.528 mmol) of TMS-*ter*-PMHS (n = 24) was charged to a pre-weighed 20 mL scintillation vial with 5 mL of dry THF, a stir bar, and 0.005 g (0.005 mmol) of **1** (light greenish-yellow color was observed). The mixture was then transferred to a 100 mL thick-walled glass bomb, sealed, and attached to the high vacuum line outside the glove box. The gas from the headspace of the bomb was removed upon freezing the solution with a liquid nitrogen trap, and subsequently, 1 atm of NH<sub>3</sub> was added. The bomb was disconnected from the vacuum line and allowed to warm to room temperature in a steel container and then set to stir. Freeze pump-thaw was performed after 2 h, 12 h, and 24 h to release the H<sub>2</sub> gas produced in the reaction. The extra ammonia was allowed to escape under a dynamic vacuum upon partial opening of the bomb and was collected in a trap cooled with liquid nitrogen. The reaction mixture was transferred to the glove box and solvents were removed *in vacuo* to afford a white solid identified as **2a**. The isolated yield was found to be 0.845 g (0.475 mmol, 90%). IR (KBr, cm<sup>-1</sup>): 3540-3320 (weak, N-H), 3010-2830 (strong, C-H), 2165 (broad, Si-H), 801 (strong, Si-N). TGA (N<sub>2</sub>): T<sub>-5%</sub> = 735 °C, total % wt. loss at 1000 °C = 9%. TGA (O<sub>2</sub>): T<sub>-5%</sub> = 495 °C, total % wt. loss at 1000 °C = 12%.

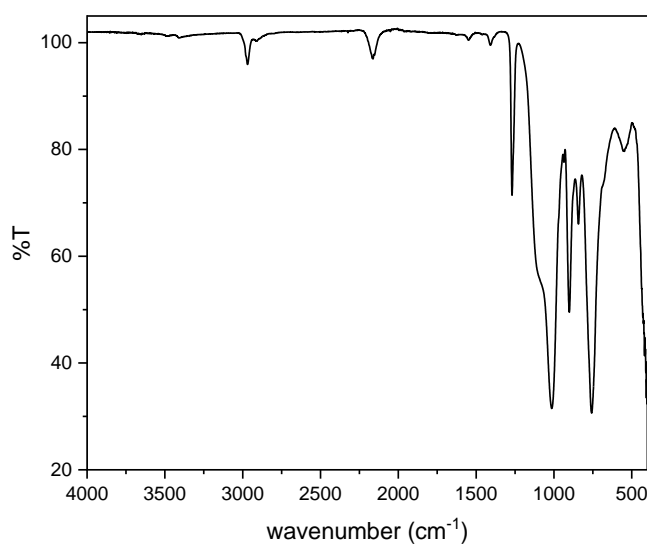
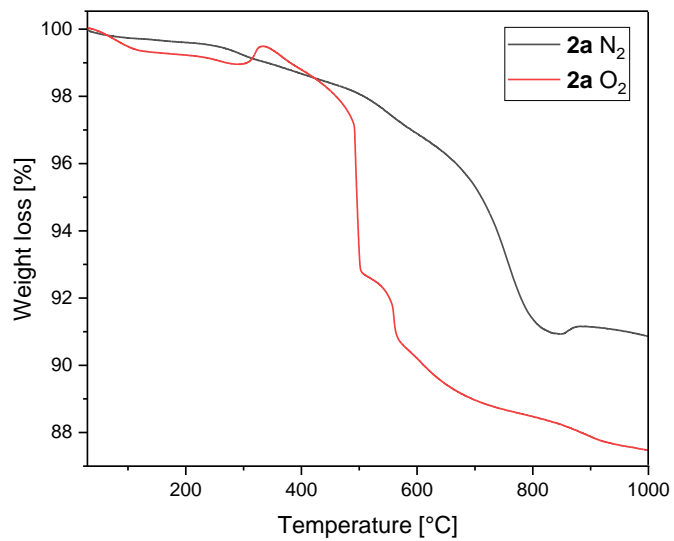
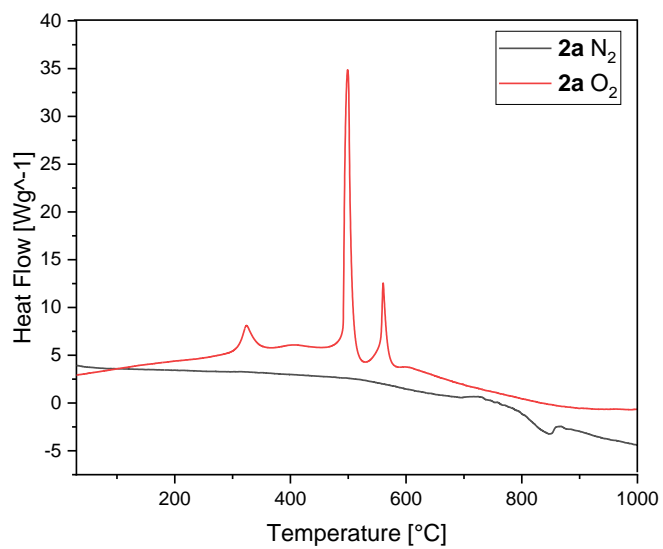


Figure S28. FT-IR spectrum of **2a**.

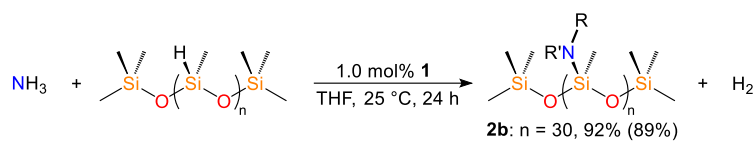


**Figure S29.** TGA thermogram of **2a** under N<sub>2</sub> and O<sub>2</sub>.



**Figure S30.** DSC thermogram of **2a** under N<sub>2</sub> and O<sub>2</sub>.

### Ammonia and TMS-*ter*-PMHS (n = 30) Dehydrocoupling Using 1 mol% **1**:



#### Scheme S14. Preparation of polysiloxazane **2b**.

In the glove box under N<sub>2</sub> atmosphere, 1.030 g (0.528 mmol) of TMS-*ter*-PMHS (n = 30) was charged to a pre-weighed 20 mL scintillation vial with 5 mL of dry THF, a stir bar, and 0.005 g (0.005 mmol) of **1** (light greenish-yellow color was observed). The mixture was then transferred to a 100 mL thick-walled glass bomb, sealed, and attached to the high vacuum line outside the glove box. The gas from the headspace of the bomb was removed upon freezing the solution with a liquid nitrogen trap and subsequently, 1 atm of NH<sub>3</sub> was added. The bomb was disconnected from the vacuum line and allowed to warm to room temperature in a steel container and further kept for stirring. Freeze pump-thaw was performed after 2 h, 12 h, and 24 h to release the H<sub>2</sub> gas produced in the reaction. The extra ammonia was allowed to escape under a dynamic vacuum upon partial opening of the bomb and was collected in a trap cooled with liquid nitrogen. The reaction mixture was transferred to the glove box and solvents were removed *in vacuo* to afford a white solid identified as **2b**. The isolated yield was found to be 1.027 g (0.472 mmol, 89%). IR (KBr, cm<sup>-1</sup>): 3535-3370 (weak, N-H), 3020-2830 (strong, C-H), 2168 (broad, Si-H), 816 (strong, Si-N). TGA (N<sub>2</sub>): T<sub>-5%</sub> = 596 °C, total % wt. loss at 1000 °C = 10%. TGA (O<sub>2</sub>): T<sub>-5%</sub> = 467 °C, total % wt. loss at 1000 °C = 12 %.

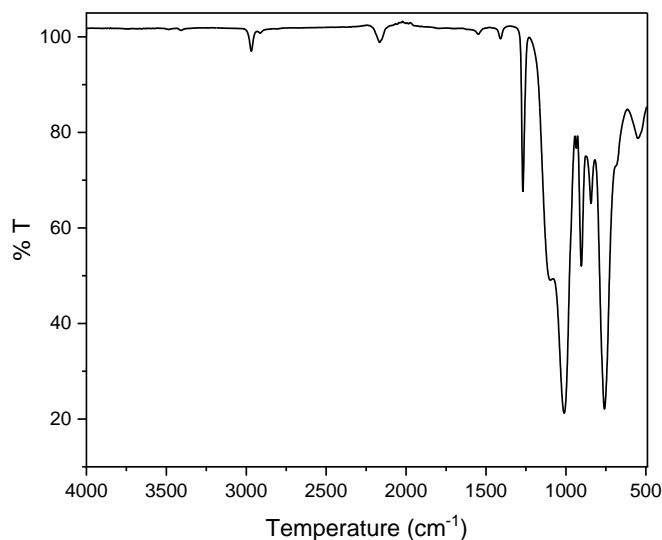
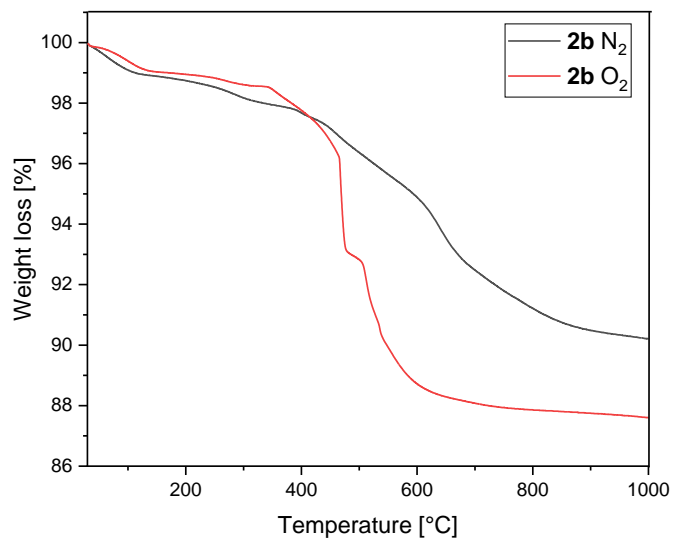
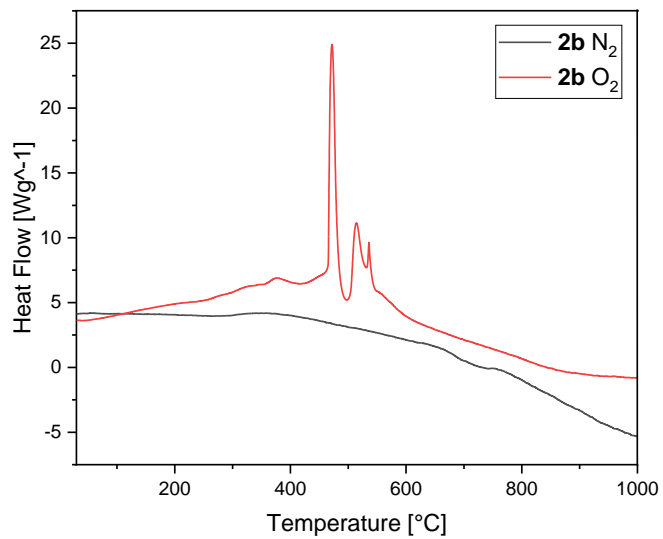


Figure S31. FT-IR spectrum of **2b**.

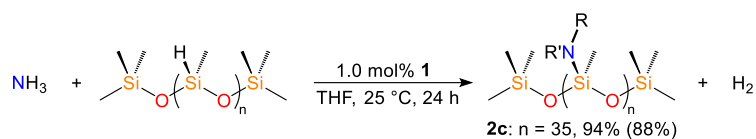


**Figure S32.** TGA thermogram of **2b** under N<sub>2</sub> and O<sub>2</sub>.



**Figure S33.** DSC thermogram of **2b** under N<sub>2</sub> and O<sub>2</sub>.

### Ammonia and TMS-*ter*-PMHS (n = 35) Dehydrocoupling Using 1 mol% **1**:



#### Scheme S15. Preparation of polysiloxazane **2c**.

In the glove box under N<sub>2</sub> atmosphere, 1.188 g (0.528 mmol) of TMS-*ter*-PMHS (n = 35) was charged to a pre-weighed 20 mL scintillation vial with 5 mL of dry THF, a stir bar and 0.005 g (0.005 mmol) of **1** (light greenish-yellow color was observed). The mixture was then transferred to a 100 mL thick-walled glass bomb, sealed, and attached to the high vacuum line outside the glove box. The gas from the headspace of the bomb was removed upon freezing the solution with a liquid nitrogen trap, and subsequently, 1 atm of NH<sub>3</sub> was added. The bomb was disconnected from the vacuum line and allowed to warm at room temperature in a steel container and then set to stir. Freeze pump-thaw was performed after 2 h, 12 h, and 24 h to release the H<sub>2</sub> gas produced in the reaction. The extra ammonia was allowed to escape under a dynamic vacuum upon partial opening of the bomb and was collected in a trap cooled with liquid nitrogen. The reaction mixture was transferred to the glove box and solvents were removed *in vacuo* to afford a white solid identified as **2c**. The isolated yield was found to be 1.171 g (0.466 mmol, 88%). IR (KBr, cm<sup>-1</sup>): 3536-3368 (weak, N-H), 3028-2843 (strong, C-H), 2165 (broad, Si-H), 808 (strong, Si-N). TGA (N<sub>2</sub>): T<sub>-5%</sub> = 740 °C, total % wt. loss at 1000 °C = 8%. TGA (O<sub>2</sub>): T<sub>-5%</sub> = 486 °C, total % wt. loss at 1000 °C = 11%.

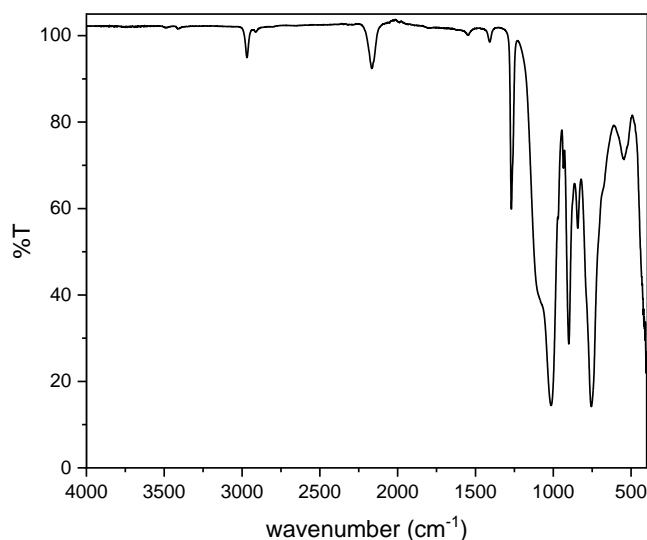
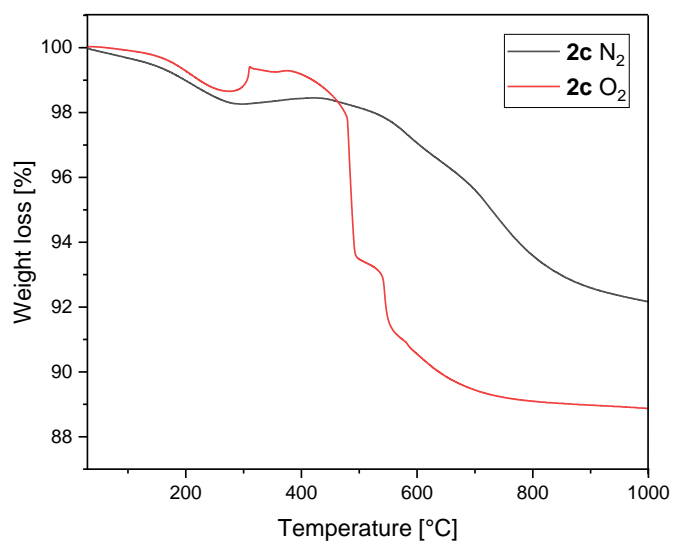
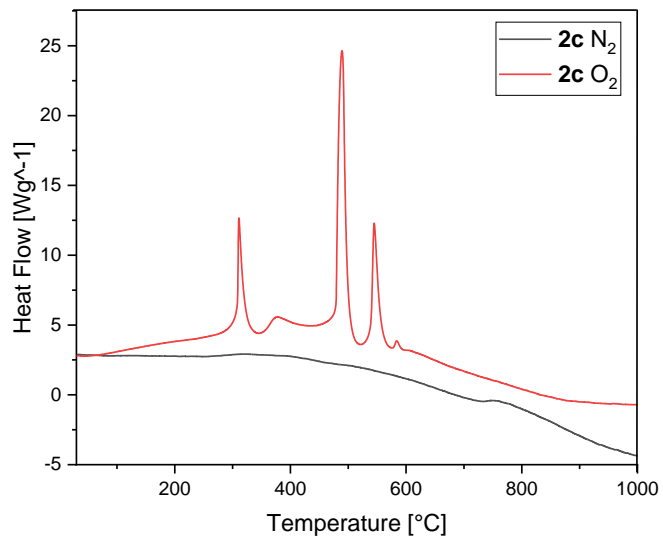


Figure S34. FT-IR spectrum of **2c**.

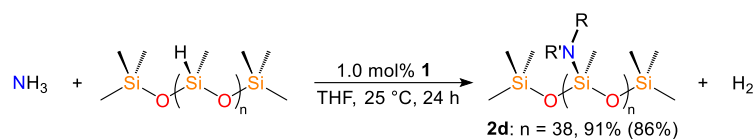


**Figure S35.** TGA thermogram of **2c** under N<sub>2</sub> and O<sub>2</sub>.



**Figure S36.** DSC thermogram of **2c** under N<sub>2</sub> and O<sub>2</sub>.

### Ammonia and TMS-*ter*-PMHS (n = 38) Dehydrocoupling Using 1 mol% **1**:



#### Scheme S16. Preparation of polysiloxazane **2d**.

In the glove box under N<sub>2</sub> atmosphere, 1.293 g (0.528 mmol) of TMS-*ter*-PMHS (n = 38) was charged to a pre-weighed 20 mL scintillation vial with 5 mL of dry THF, a stir bar, and 0.005 g (0.005 mmol) of **1** (light greenish-yellow color was observed). The mixture was then transferred to a 100 mL thick-walled glass bomb, sealed, and attached to the high vacuum line outside the glove box. The gas from the headspace of the bomb was removed upon freezing the solution with a liquid nitrogen trap, and subsequently, 1 atm of NH<sub>3</sub> was added. The bomb was disconnected from the vacuum line and allowed to warm to room temperature in a steel container and then set to stir. Freeze pump-thaw was performed after 2 h, 12 h, and 24 h to release the H<sub>2</sub> gas produced in the reaction. The extra ammonia was allowed to escape under a dynamic vacuum upon partial opening of the bomb and was collected in a trap cooled with liquid nitrogen. The reaction mixture was transferred to the glove box and solvents were removed *in vacuo* to afford a white solid identified as **2d**. The isolated yield was found to be 1.237 g (0.452 mmol, 86%). IR (KBr, cm<sup>-1</sup>): 3545-3375 (broad, N-H), 3015-2825 (strong, C-H), 2170 (broad, Si-H), 812 (strong, Si-N). TGA (N<sub>2</sub>): T<sub>-5%</sub> = 527 °C, total % wt. loss at 1000 °C = 12%. TGA (O<sub>2</sub>): T<sub>-5%</sub> = 430 °C, total % wt. loss at 1000 °C = 14%.

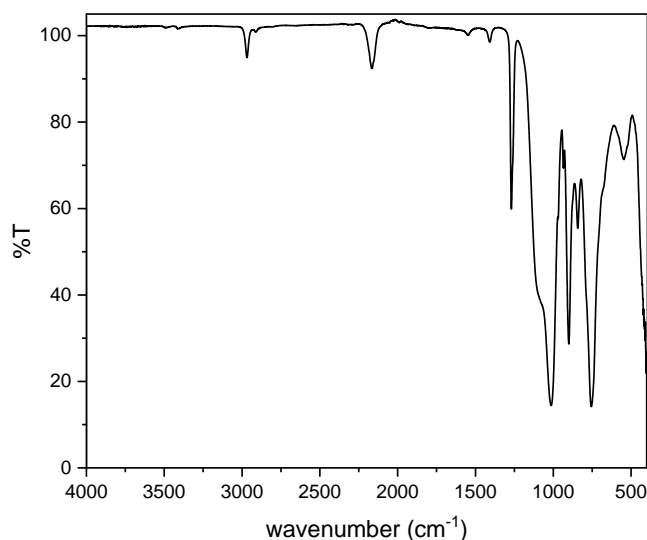
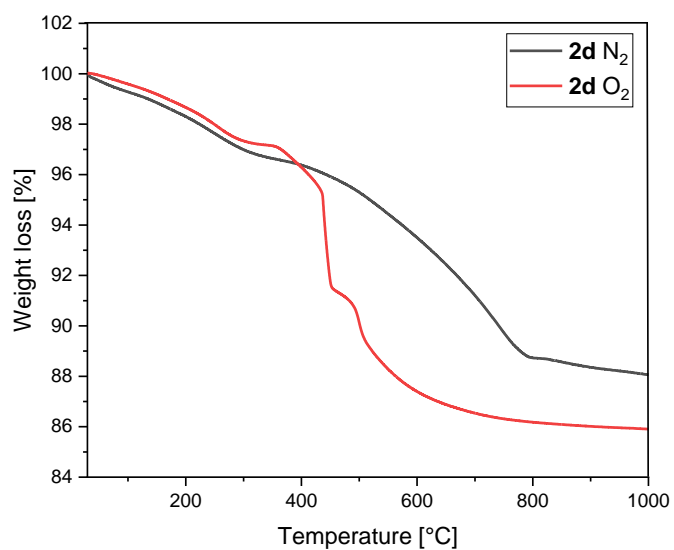
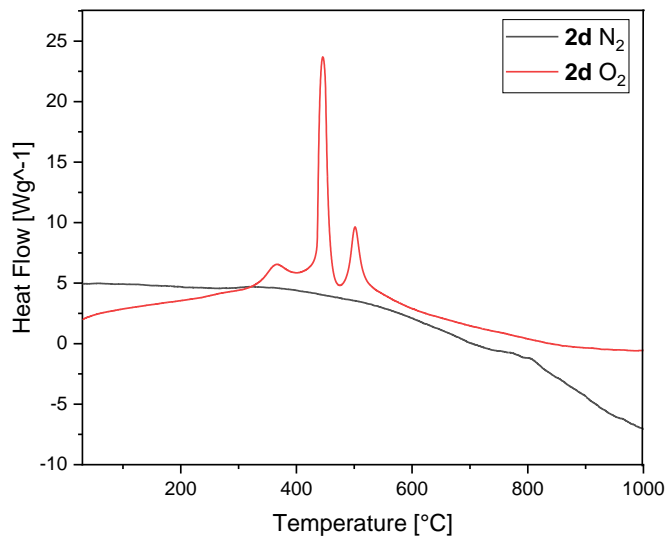


Figure S37. FT-IR spectrum of **2d**.





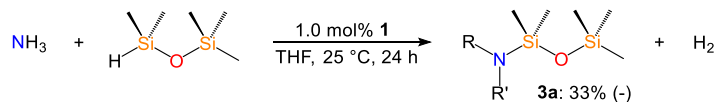
**Figure S38.** TGA thermogram of **2d** under N<sub>2</sub> and O<sub>2</sub>.



**Figure S39.** DSC thermogram of **2d** under N<sub>2</sub> and O<sub>2</sub>.

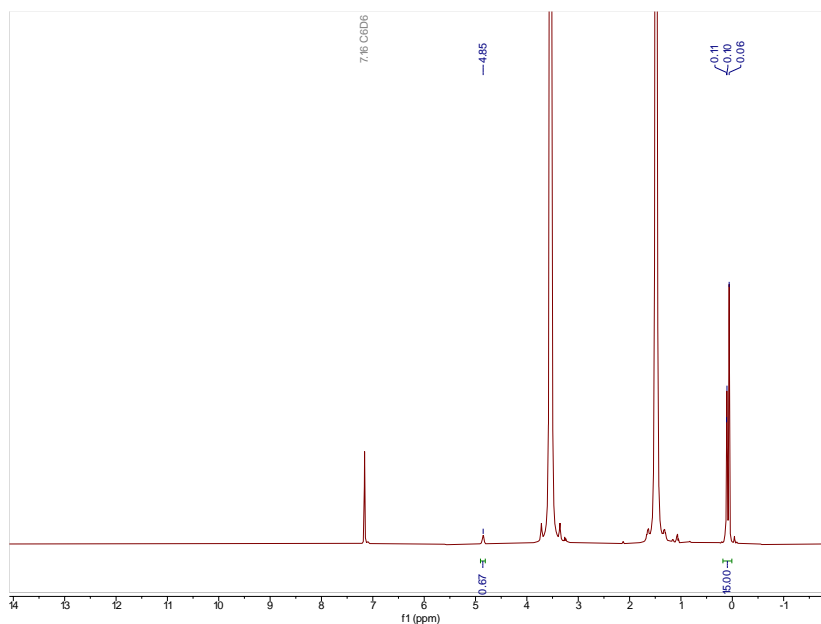
## DEHYDROCOUPLING OF DIMETHYLHYDROSILOXANES

### Ammonia and Dimethyl(trimethylsiloxy)silane Dehydrocoupling Using 1 mol% **1**:



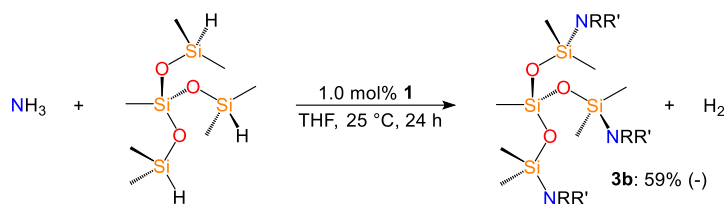
#### **Scheme S17.** Observation of aminated dimethyl(trimethylsiloxy)silane (**3a**).

In the glove box under N<sub>2</sub> atmosphere, 0.078 g (0.528 mmol) of dimethyl(trimethylsiloxy)silane was added to a pre-weighed 20 mL scintillation vial with 5 mL of dry THF, a stir bar, and 0.005 g (0.005 mmol) of **1** (light greenish-yellow color was observed). The mixture was then transferred to a 100 mL thick-walled glass bomb, sealed, and attached to the high vacuum line outside the glove box. The gas from the headspace of the bomb was removed upon freezing the solution with a liquid nitrogen trap, and subsequently, 1 atm of NH<sub>3</sub> was added. The bomb was disconnected from the vacuum line and allowed to warm to room temperature in a steel container and further kept for stirring. Freeze pump-thaw was performed after 2 h, 12 h, and 24 h to release the H<sub>2</sub> gas produced in the reaction. The extra ammonia was allowed to escape under a dynamic vacuum upon partial opening of the bomb and was collected in a trap cooled with liquid nitrogen. The reaction mixture was transferred to the glove box and <sup>1</sup>H NMR spectroscopy revealed 33% amination of the siloxane. <sup>1</sup>H NMR (400 MHz, benzene-*d*<sub>6</sub>): 4.85 (s, SiH), 0.11 (s, OSi(CH<sub>3</sub>)NH), 0.06 (OSi(CH<sub>3</sub>)<sub>3</sub>).



**Figure S40.** <sup>1</sup>H NMR spectrum showing conversion to **3a** in benzene-*d*<sub>6</sub>.

### Ammonia and Methyl(tris(dimethylsiloxy))silane Dehydrocoupling Using 1 mol% **1**:



#### Scheme S18. Observation of methyl(tris(dimethylsiloxy))silane amination (**3b**).

In the glove box under  $\text{N}_2$  atmosphere, 0.141 g (0.528 mmol) of methyl(tris(dimethylsiloxy))silane was added to a pre-weighed 20 mL scintillation vial with 5 mL of dry THF, a stir bar, and 0.005 g (0.005 mmol) of **1** (light greenish-yellow color was observed). The mixture was then transferred to a 100 mL thick-walled glass bomb, sealed, and attached to the high vacuum line outside the glove box. The gas from the headspace of the bomb was removed upon freezing the solution with a liquid nitrogen trap, and subsequently, 1 atm of  $\text{NH}_3$  was added. The bomb was disconnected from the vacuum line and allowed to warm to room temperature in a steel container and then set to stir. Freeze pump-thaw was performed after 2 h, 12 h, and 24 h to release the  $\text{H}_2$  gas produced in the reaction. The extra ammonia was allowed to escape under a dynamic vacuum upon partial opening of the bomb and was collected in a trap cooled with liquid nitrogen. The reaction mixture was transferred to the glove box and  $^1\text{H}$  NMR spectroscopy revealed 59% amination of the siloxane Si-H units.  $^1\text{H}$  NMR (400 MHz, benzene- $d_6$ ): 5.03 (s, SiH), 0.35-0.20 (broad,  $(\text{CH}_3)_2\text{Si}$ ,  $(\text{CH}_3)_3\text{Si}$ ).

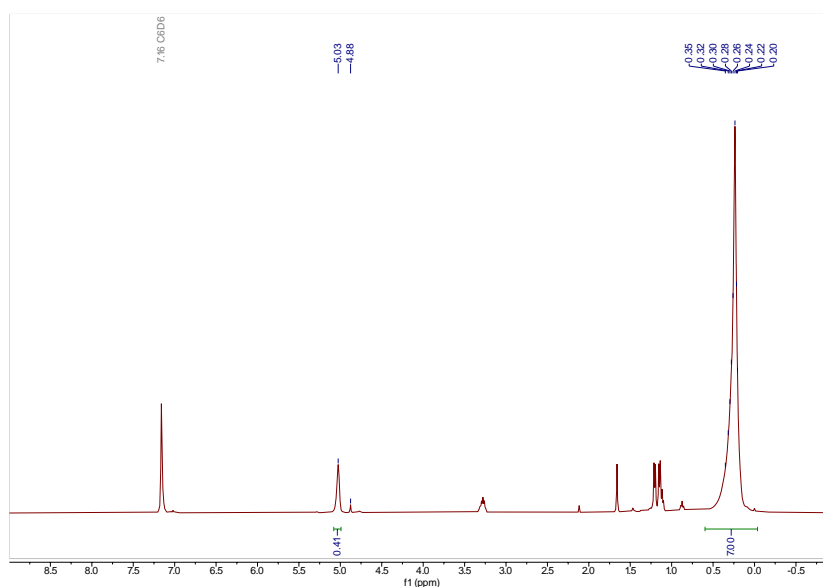
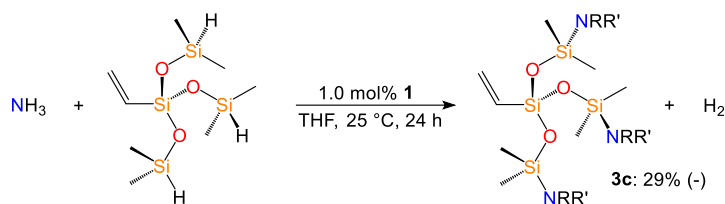


Figure S41.  $^1\text{H}$  NMR spectrum showing conversion to **3b** in benzene- $d_6$ .

### Ammonia and Vinyl(tris(dimethylsiloxy))silane Dehydrocoupling Using 1 mol% **1**:



#### Scheme S19. Observation of vinyl(tris(dimethylsiloxy))silane amination (**3c**).

In the glove box under  $\text{N}_2$  atmosphere, 0.148 g (0.528 mmol) of vinyl(tris(dimethylsiloxy))silane was added to a pre-weighed 20 mL scintillation vial with 5 mL of dry THF, a stir bar, and 0.005 g (0.005 mmol) of **1** (light greenish-yellow color was observed). The mixture was then transferred to a 100 mL thick-walled glass bomb, sealed, and attached to the high vacuum line outside the glove box. The gas from the headspace of the bomb was removed upon freezing the solution with a liquid nitrogen trap, and subsequently, 1 atm of  $\text{NH}_3$  was added. The bomb was disconnected from the vacuum line and allowed to warm to room temperature in a steel container and then set to stir. Freeze pump-thaw was performed after 2 h, 12 h, and 24 h to release the  $\text{H}_2$  gas produced in the reaction. The extra ammonia was allowed to escape under a dynamic vacuum upon partial opening of the bomb and was collected in a trap cooled with liquid nitrogen. The reaction mixture was transferred to the glove box and  $^1\text{H}$  NMR spectroscopy revealed 29% amination of the siloxane Si-H units.  $^1\text{H}$  NMR (400 MHz, benzene- $d_6$ ): 6.04-5.93 (m, *vinyl*), 4.99 (s, SiH), 0.20 (broad,  $\text{CH}_3$ ).

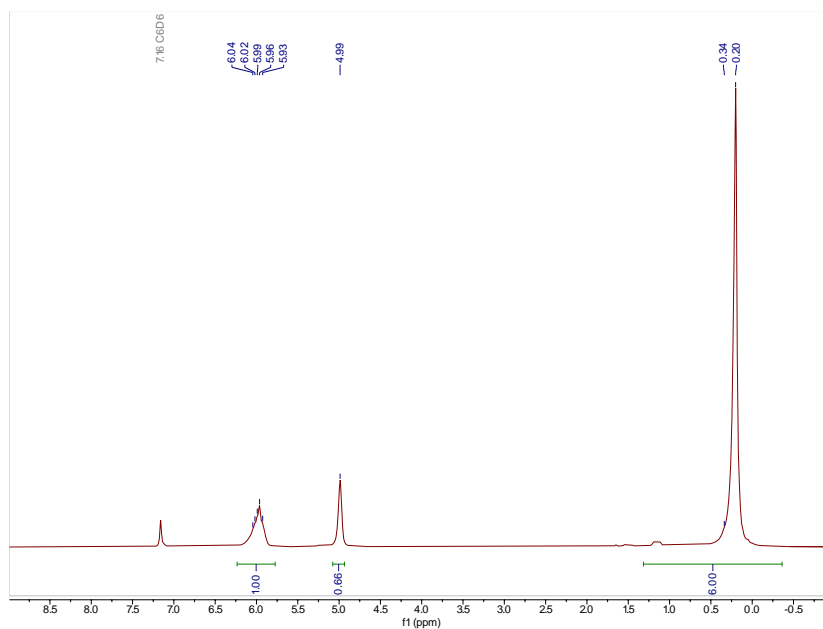
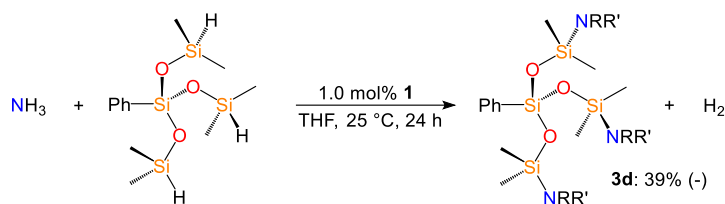


Figure S42.  $^1\text{H}$  NMR spectrum showing conversion to **3c** in benzene- $d_6$ .

### Ammonia and Phenyl(tris(dimethylsiloxy))silane Dehydrocoupling Using 1 mol% **1**:



#### Scheme S20. Observation of phenyl(tris(dimethylsiloxy))silane amination (**3d**).

In the glove box under  $\text{N}_2$  atmosphere, 0.174 g (0.528 mmol) of phenyl(tris(dimethylsiloxy))silane was added to a pre-weighed 20 mL scintillation vial with 5 mL of dry THF, a stir bar, and 0.005 g (0.005 mmol) of **1** (light greenish-yellow color was observed). The mixture was then transferred to a 100 mL thick-walled glass bomb, sealed, and attached to the high vacuum line outside the glove box. The gas from the headspace of the bomb was removed upon freezing the solution with a liquid nitrogen trap, and subsequently, 1 atm of  $\text{NH}_3$  was added. The bomb was disconnected from the vacuum line and allowed to warm to room temperature in a steel container and then set to stir. Freeze pump-thaw was performed after 2 h, 12 h, and 24 h to release the  $\text{H}_2$  gas produced in the reaction. The extra ammonia was allowed to escape under a dynamic vacuum upon partial opening of the bomb and was collected in a trap cooled with liquid nitrogen. The reaction mixture was transferred to the glove box and  $^1\text{H}$  NMR spectroscopy revealed 39% amination of the siloxane Si-H units.  $^1\text{H}$  NMR (400 MHz, benzene- $d_6$ ): 7.84-7.78 (broad, *aryl*), 7.25-7.20 (broad, *aryl*), 5.06 (s, SiH), 0.31-0.18 (broad, PhSi,  $(\text{CH}_3)_2\text{Si}$ ).

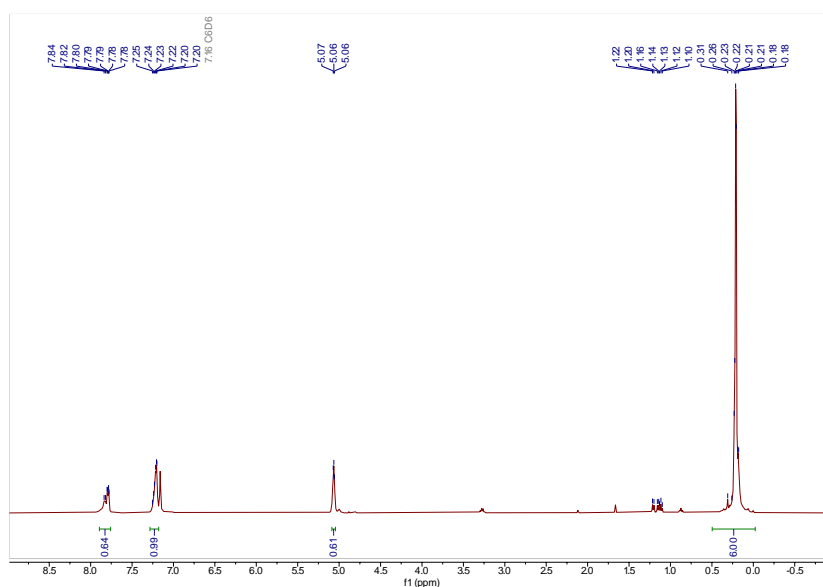
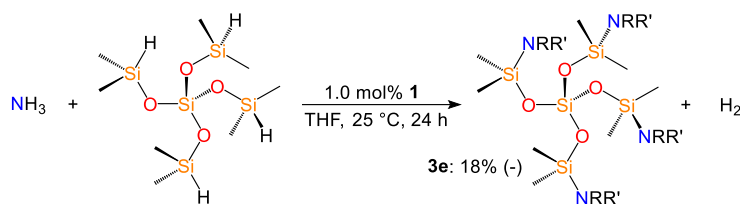


Figure S43.  $^1\text{H}$  NMR spectrum showing conversion to **3d** in benzene- $d_6$ .

### Ammonia and Tetrakis(dimethylsiloxy)silane Dehydrocoupling Using 1 mol% **1**:



#### Scheme S21. Observation of tetrakis(dimethylsiloxy)silane amination (**3e**).

In the glove box under  $\text{N}_2$  atmosphere, 0.173 g (0.528 mmol) of tetrakis(dimethylsiloxy)silane was added to a pre-weighed 20 mL scintillation vial with 5 mL of dry THF, a stir bar, and 0.005 g (0.005 mmol) of **1** (light greenish-yellow color was observed). The mixture was then transferred to a 100 mL thick-walled glass bomb, sealed, and attached to the high vacuum line outside the glove box. The gas from the headspace of the bomb was removed upon freezing the solution with a liquid nitrogen trap, and subsequently, 1 atm of  $\text{NH}_3$  was added. The bomb was disconnected from the vacuum line and allowed to warm to room temperature in a steel container and then set to stir. Freeze pump-thaw was performed after 2 h, 12 h, and 24 h to release the  $\text{H}_2$  gas produced in the reaction. The extra ammonia was allowed to escape under a dynamic vacuum upon partial opening of the bomb and was collected in a trap cooled with liquid nitrogen. The reaction mixture was transferred to the glove box and  $^1\text{H}$  NMR spectroscopy revealed 18% amination of the siloxane Si-H units.  $^1\text{H}$  NMR (400 MHz, benzene- $d_6$ ): 4.95 (SiH), 0.21 ( $(\text{CH}_3)_2\text{SiO}$ ).

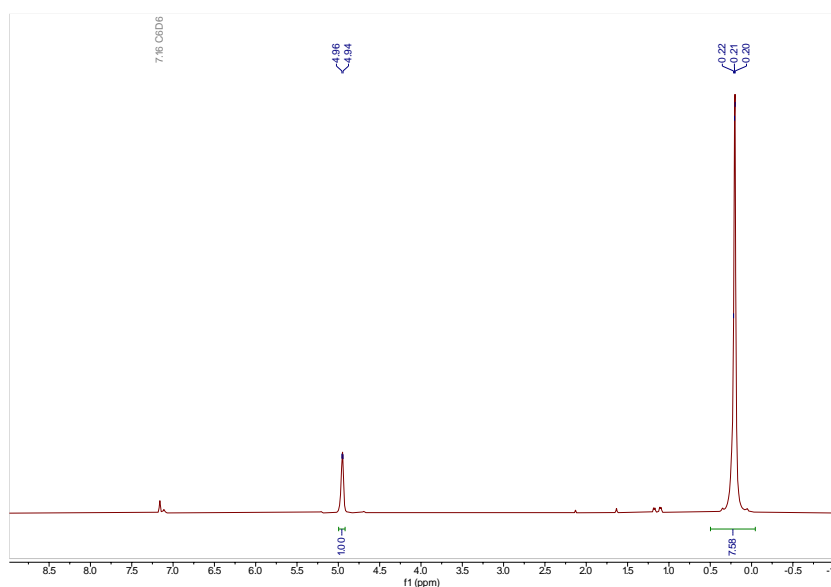
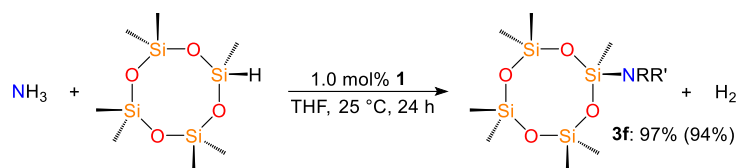


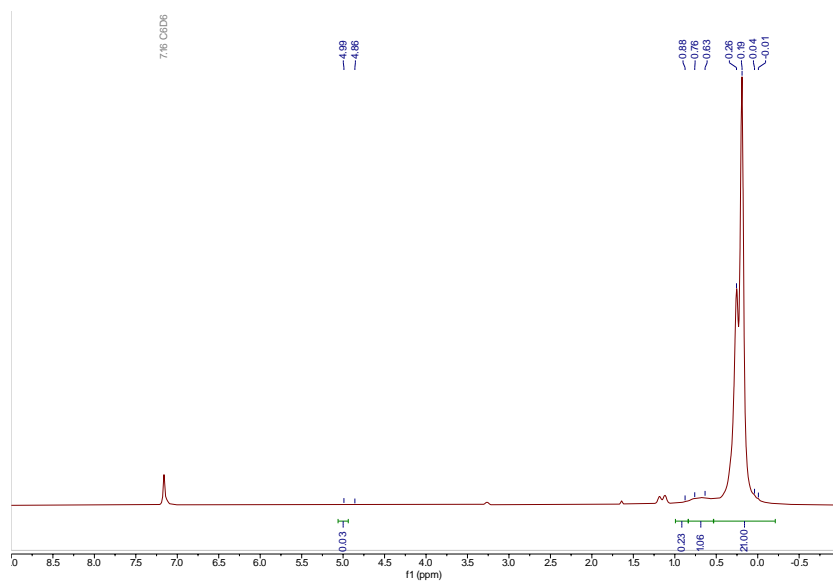
Figure S44.  $^1\text{H}$  NMR spectrum showing minimal conversion to **3e** in benzene- $d_6$ .

### Ammonia and 1,3,3,5,5,7,7-Heptamethyltetrasiloxane Dehydrocoupling Using 1 mol% **1**:

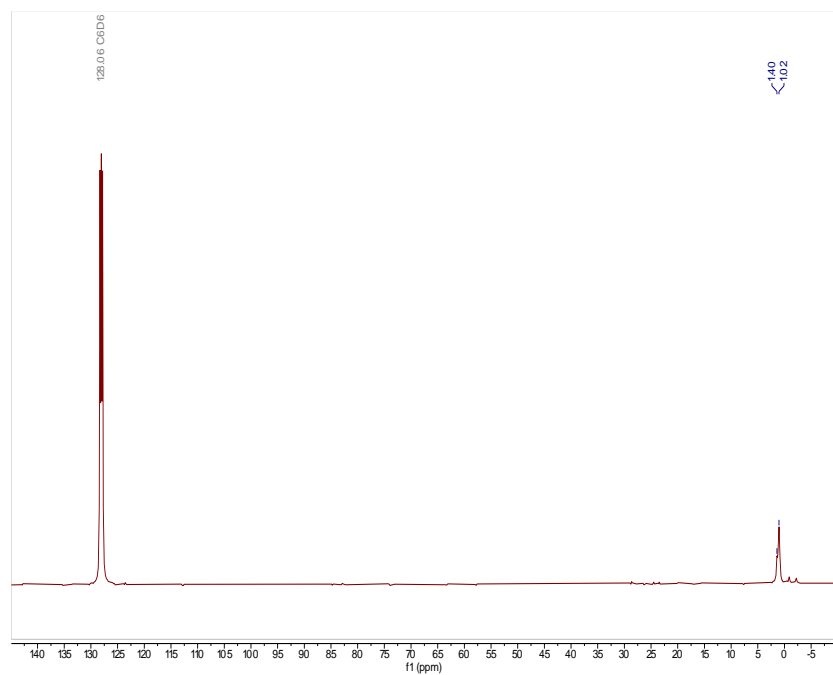


**Scheme S22.** Preparation of **3f** as a 9:1 mixture of disilylamine to silylamine.

In the glove box under N<sub>2</sub> atmosphere, 0.149 g (0.528 mmol) of 1,3,3,5,5,7,7-heptamethyltetrasiloxane was added to a pre-weighed 20 mL scintillation vial with 5 mL of dry THF, a stir bar, and 0.005 g (0.005 mmol) of **1** (light greenish-yellow color was observed). The mixture was then transferred to a 100 mL thick-walled glass bomb, sealed, and attached to the high vacuum line outside the glove box. The gas from the headspace of the bomb was removed upon freezing the solution with a liquid nitrogen trap, and subsequently, 1 atm of NH<sub>3</sub> was added. The bomb was disconnected from the vacuum line and allowed to warm to room temperature in a steel container and then set to stir. Freeze pump-thaw was performed after 2 h, 12 h, and 24 h to release the H<sub>2</sub> gas produced in the reaction. The extra ammonia was allowed to escape under a dynamic vacuum upon partial opening of the bomb and was collected in a trap cooled with liquid nitrogen. The reaction mixture was transferred to the glove box and solvents were removed *in vacuo* to afford a viscous oil. <sup>1</sup>H NMR spectroscopy revealed 97% amination of the siloxane Si-H units and the isolated yield was found to be 0.144 g (0.497 mmol, 94%). <sup>1</sup>H NMR (400 MHz, benzene-*d*<sub>6</sub>): 4.99 (s, SiH), 0.76-0.63 (broad, NH, NH<sub>2</sub>), 0.26 (broad, OSi(CH<sub>3</sub>)OSiNH), 0.19 (broad, OSi(CH<sub>3</sub>)). <sup>13</sup>C NMR (100 MHz, benzene-*d*<sub>6</sub>): 1.40 ((CH<sub>3</sub>)SiNH, (CH<sub>3</sub>)SiOSiNH), 1.02 (O(CH<sub>3</sub>)SiO). <sup>29</sup>Si NMR (79 MHz, benzene-*d*<sub>6</sub>): -19.48 (OSiNH), -19.83 (OSiNH<sub>2</sub>), -21.83 (OSiO, OSiOSiNH). IR (KBr, cm<sup>-1</sup>): 3550-3370 (broad, N-H), 2990-2825 (strong, C-H), 2110 (weak, Si-H), 801 (weak, Si-N overlapped with Si-O).

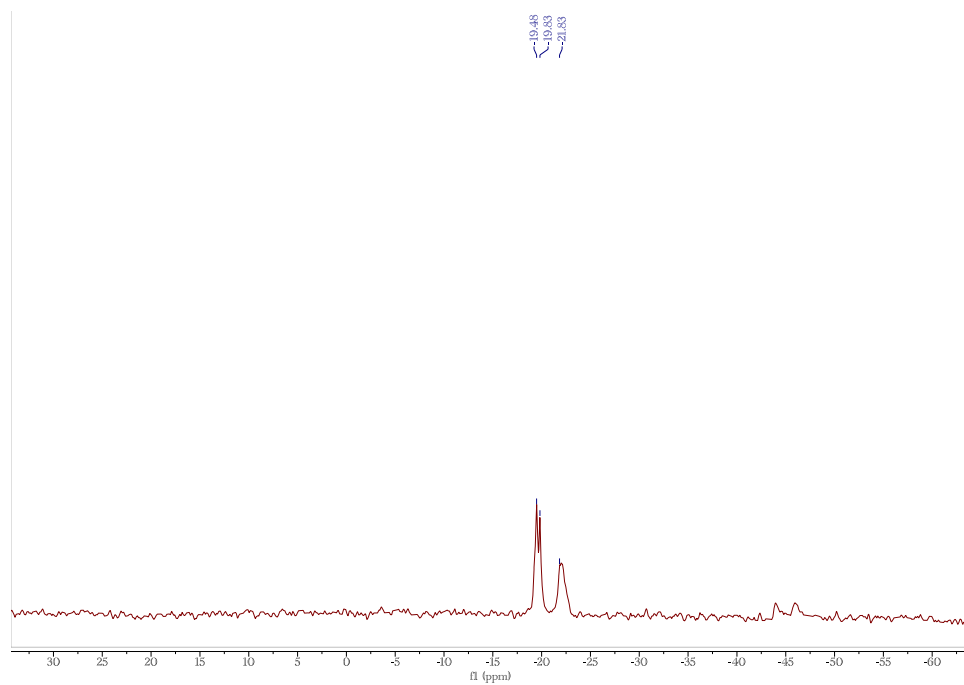


**Figure S45.** <sup>1</sup>H NMR spectrum of **3f** in benzene-*d*<sub>6</sub>.

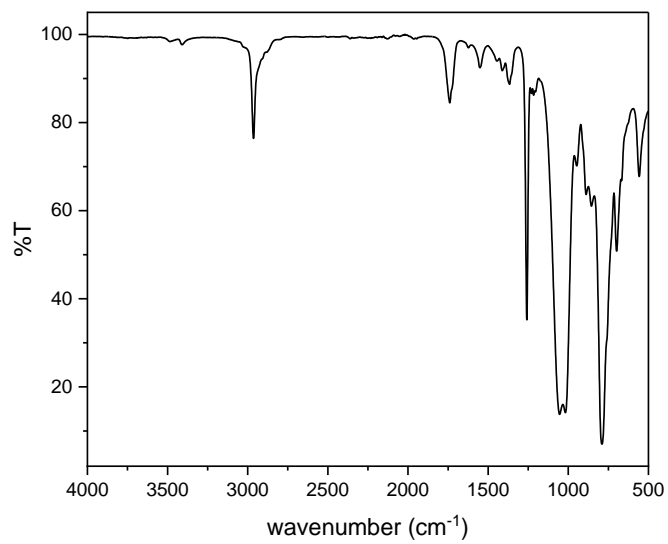


**Figure S46.** <sup>13</sup>C NMR spectrum of **3f** in benzene-*d*<sub>6</sub>.



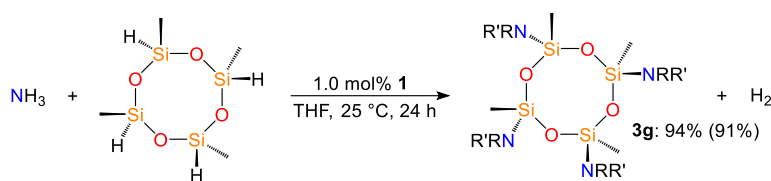


**Figure S47.**  $^{29}\text{Si}$  NMR spectrum of **3f** in benzene- $d_6$ .



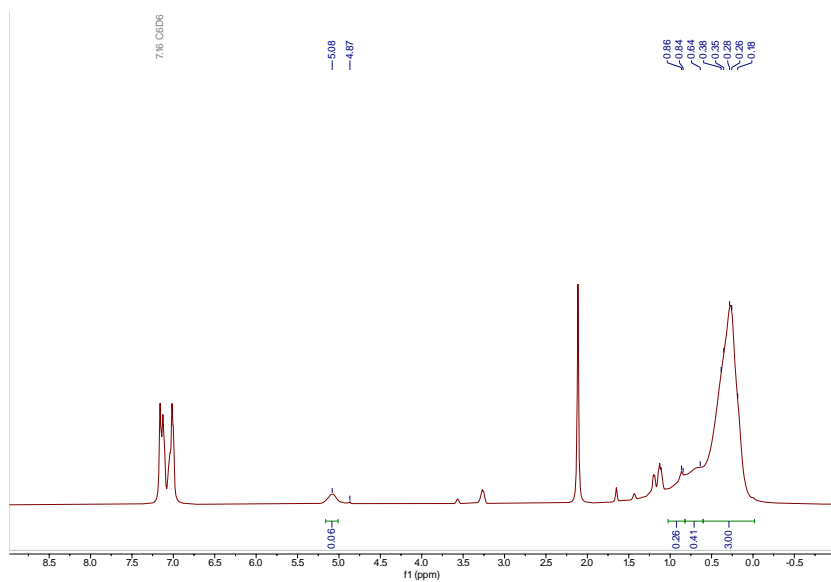
**Figure S48.** FT-IR spectrum of **3f**.

### Ammonia and 1,3,5,7-Tetramethylcyclotetrasiloxane Dehydrocoupling Using 1 mol% **1**:

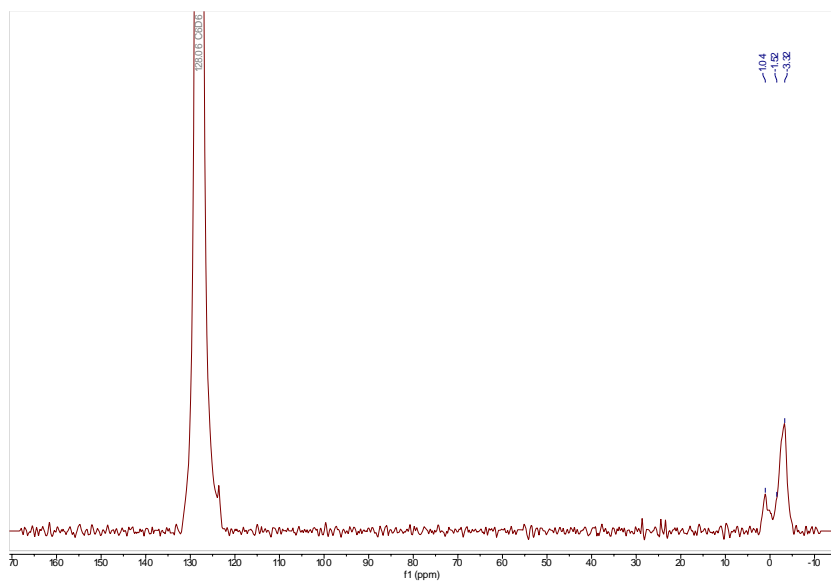


#### Scheme S23. Preparation of oligosiloxazane **3g**.

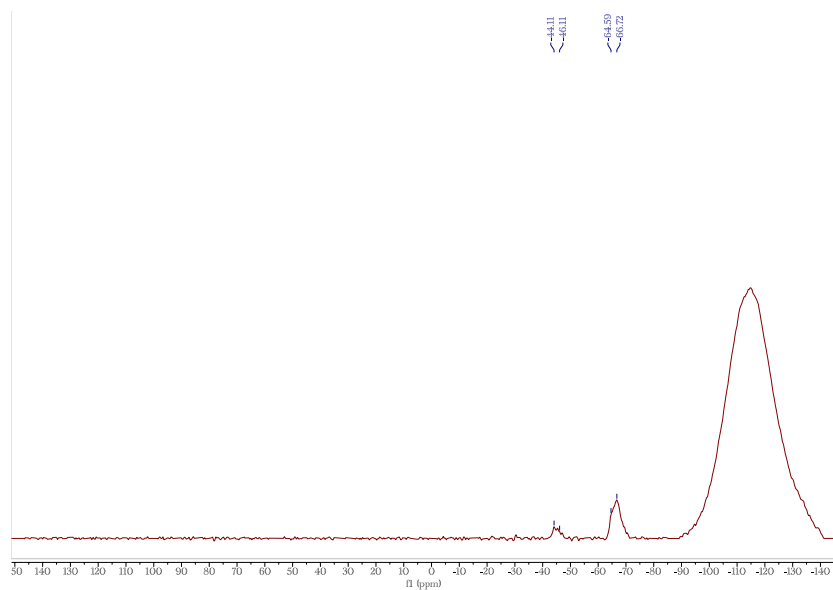
In the glove box under N<sub>2</sub> atmosphere, 0.254 g (1.06 mmol) of 1,3,5,7-tetramethylcyclotetrasiloxane was added to a pre-weighed 20 mL scintillation vial with 5 mL of dry THF, a stir bar, and 0.010 g (0.010 mmol) of **1** (light greenish-yellow color was observed). The mixture was then transferred to a 100 mL thick-walled glass bomb, sealed, and attached to the high vacuum line outside the glove box. The gas from the headspace of the bomb was removed upon freezing the solution with a liquid nitrogen trap, and subsequently, 1 atm of NH<sub>3</sub> was added. The bomb was disconnected from the vacuum line and allowed to warm to room temperature in a steel container and then set to stir. Freeze pump-thaw was performed after 2 h, 12 h, and 24 h to release the H<sub>2</sub> gas produced in the reaction. The extra ammonia was allowed to escape under a dynamic vacuum upon partial opening of the bomb and was collected in a trap cooled with liquid nitrogen. The reaction mixture was transferred to the glove box and solvents were removed *in vacuo* to afford a viscous oil. <sup>1</sup>H NMR spectroscopy revealed 94% amination of the siloxane Si–H units and the isolated yield was 0.256 g (DOSY M<sub>w</sub> = 4,300 g/mol; 0.060 mmol oligomer; repeating units per oligomer = 16.0; 0.96 mmol of repeating unit; 91% isolated yield). This product solidified 3 h after isolation to generate a solid, which allowed for TGA and DSC analysis. <sup>1</sup>H NMR (400 MHz, benzene-*d*<sub>6</sub>): 5.08 (broad, SiH), 0.9-0.6 (broad, NH, NH<sub>2</sub>), 0.28 (broad, OCH<sub>3</sub>SiONH, OCH<sub>3</sub>SiO). <sup>13</sup>C NMR (100 MHz, benzene-*d*<sub>6</sub>): 1.04 (broad, CH<sub>3</sub>OSiONH), 3.32 ((CH<sub>3</sub>)OSiO(NH<sub>2</sub>)). <sup>29</sup>Si NMR (79 MHz, benzene-*d*<sub>6</sub>): -46.11 to -44.11 (OSiO(CH<sub>3</sub>)NH<sub>2</sub>), -64.59 to -66.72 (OSiO(CH<sub>3</sub>)(NH<sub>2</sub>)). IR (KBr, cm<sup>-1</sup>): 3530-3370 (broad, N–H), 3000-2845 (strong, C–H), 2127 (weak, Si–H), 845 (strong, Si–N). TGA (N<sub>2</sub>): T<sub>-5%</sub> = 353 °C, total % wt. loss at 1000 °C = 16%. TGA (O<sub>2</sub>): T<sub>-5%</sub> = 356 °C, total % wt. loss at 1000 °C = 15%.



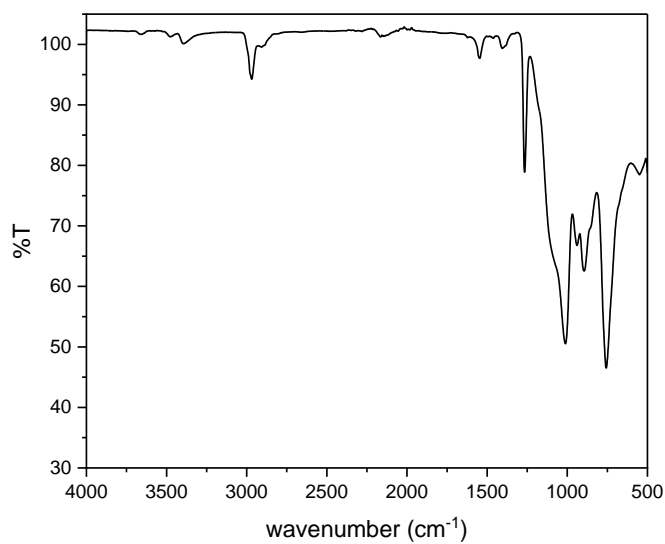
**Figure S49.** Representative  $^1\text{H}$  NMR spectrum of **3g** in benzene- $d_6$ .



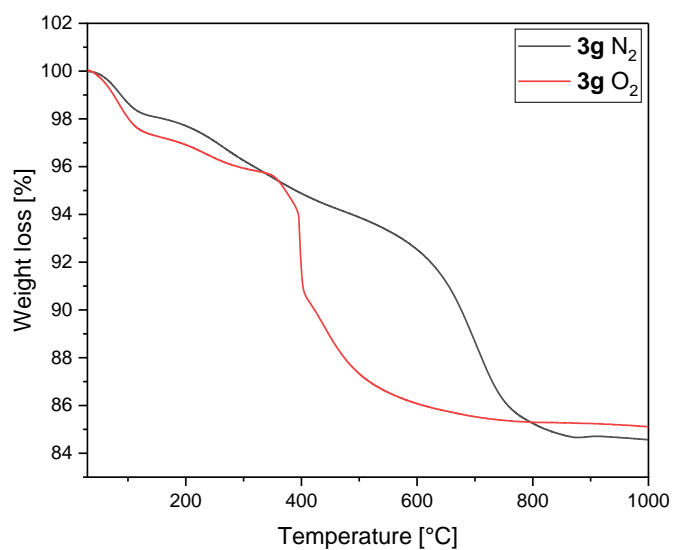
**Figure S50.** Representative  $^{13}\text{C}$  NMR spectrum of **3g** in benzene- $d_6$ .



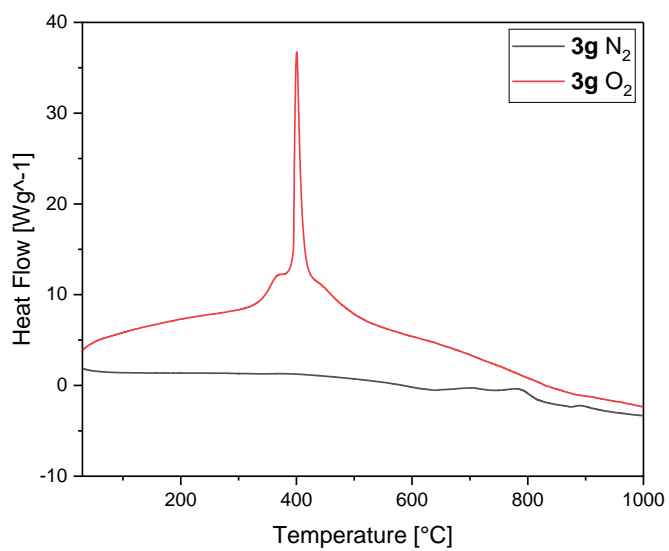
**Figure S51.**  $^{29}\text{Si}$  NMR spectrum of **3g** in benzene- $d_6$ . Since **3g** is relatively insoluble in benzene- $d_6$ , data was acquired over the course of 12 h and the large peak at -112 ppm is glass.



**Figure S52.** FT-IR spectrum of **3g**.

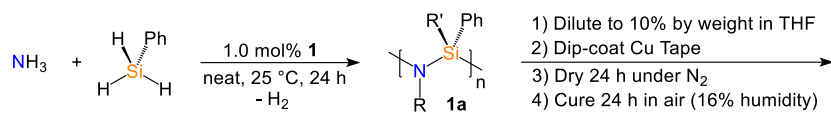


**Figure S53.** TGA thermogram of **3g** under N<sub>2</sub> and O<sub>2</sub>.

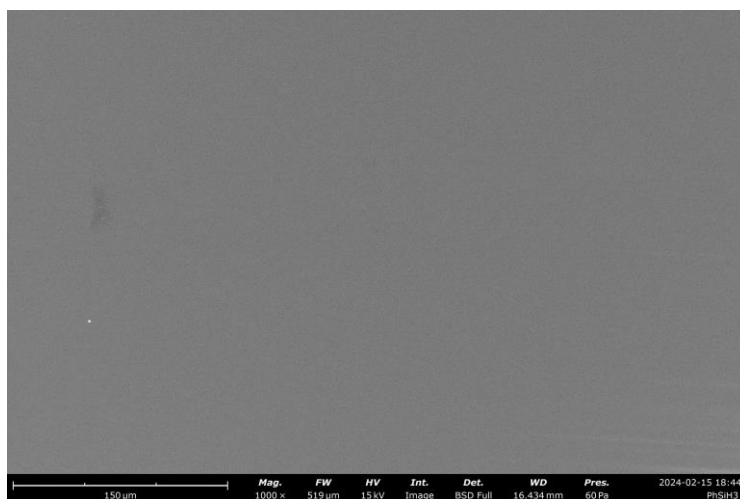


**Figure S54.** DSC thermogram of **3g** under N<sub>2</sub> and O<sub>2</sub>.

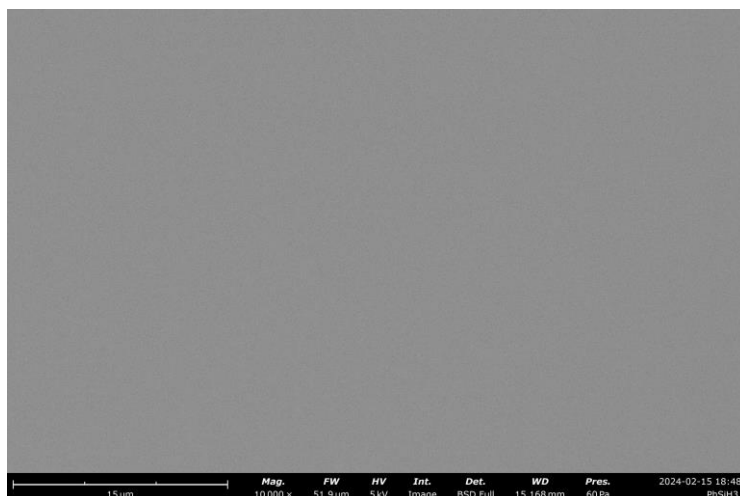
## APPLICATION OF COATINGS



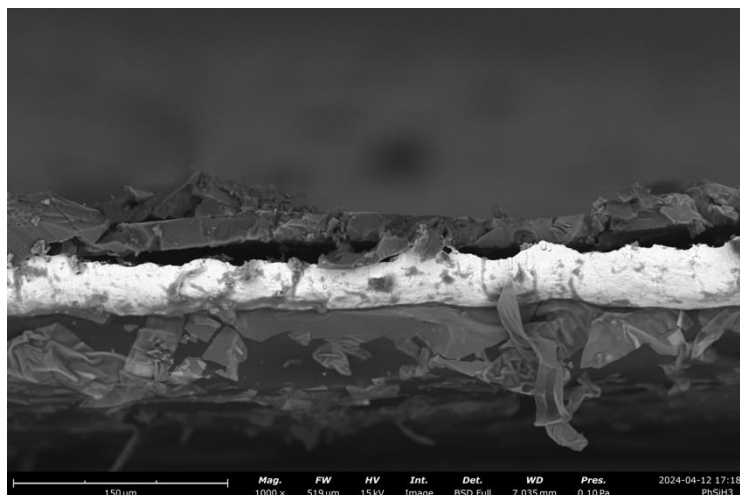
**Scheme S24.** Preparation of **1a** coating.



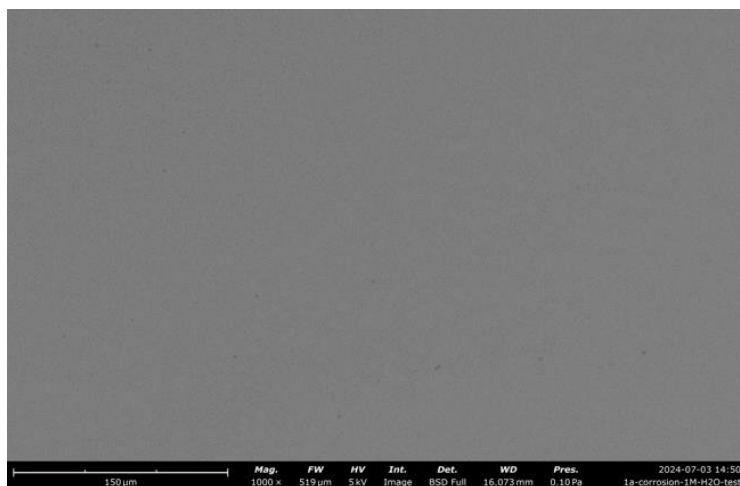
**Figure S55.** SEM image of **1a**-coated copper at 1,000× magnification after curing for 24 h at 25 °C (16% humidity).



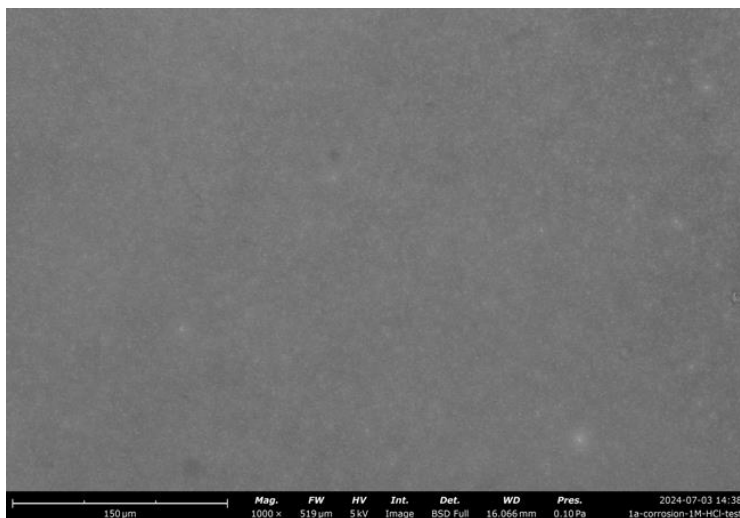
**Figure S56.** SEM image of **1a**-coated copper at 10,000× magnification after curing for 24 h at 25 °C (16% humidity).



**Figure S57.** SEM image showing the cross section of **1a**-coated copper tape at 1,000× magnification after curing in air for 24 h at 25 °C (16% humidity). The white strip across the center of the image is copper metal and the brittle coating of **1a** above it was found to be 20 μm thick. The material below copper is glue from carbon tape that was used to attach it to the sample holder.



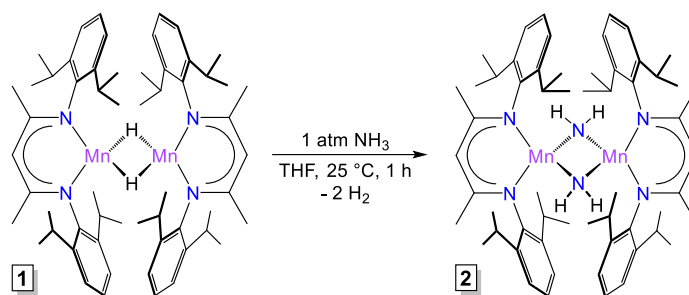
**Figure S58.** SEM image of **1a**-coated copper at 1,000× magnification after curing in air for 24 h, followed by submersion in deionized H<sub>2</sub>O for 24 h, followed by drying in air for 24 h at 25 °C.



**Figure S59.** SEM image of **1a**-coated copper at 1,000× magnification after curing in air for 24 h, followed by submersion in 1.0 M HCl for 24 h, followed by drying in air for 24 h at 25 °C.

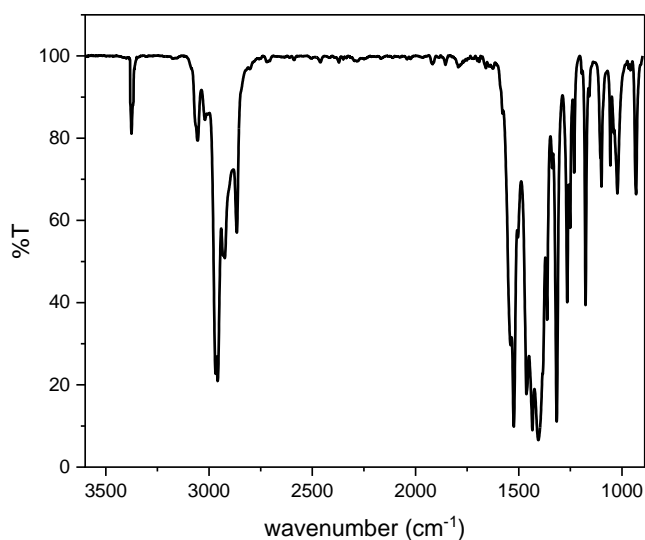


## INTERMEDIATE SYNTHESIS



**Scheme S25.** Preparation of  $[(^{2,6}\text{-iPr}_2\text{Ph})\text{BDI})\text{Mn}(\mu\text{-NH}_2)]_2$  (**2**).

Under  $\text{N}_2$  atmosphere, a 100 mL thick-walled glass bomb was charged with 0.2 g (0.2 mmol) of **1** in 5 mL THF. The bomb was sealed under  $\text{N}_2$  and attached to the vacuum line. The solution was frozen in liquid  $\text{N}_2$ , gas was removed from the head space under vacuum, and 1 atm of  $\text{NH}_3$  was introduced. The bomb was closed, disconnected from the vacuum line, and placed in a steel container to warm to room temperature in the back of an empty fume hood with the sash closed. The evolution of  $\text{H}_2$  gas and the formation of yellow precipitate were observed instantly. The reaction was allowed to occur at ambient temperature for 1 h. The bomb was then attached to the vacuum line and the solution was frozen in an ice-water bath, followed by  $\text{H}_2$  and  $\text{NH}_3$  removal. The bomb was brought into the glove box, the solid product was filtered, washed with THF and dried under vacuum to obtain a yellow powder identified as **2** (0.186 g, 90% yield). Crystals suitable for X-ray diffraction were grown from a low concentration THF solution at  $-35\text{ }^\circ\text{C}$ . Anal. for  $\text{C}_{58}\text{H}_{86}\text{Mn}_2\text{N}_6$ : Calcd. C, 71.29; H, 8.87; N, 8.60. Found: C, 71.65; H, 9.11; N, 8.30. Magnetic susceptibility (Gouy method,  $25\text{ }^\circ\text{C}$ ):  $\mu_{\text{eff}} = 6.24\ \mu_{\text{B}}$ . IR (KBr,  $\text{cm}^{-1}$ ): 3375 (broad, N–H), 3100–2790 (strong, C–H), 1540 (weak, C=N), 1524 (strong, C=C).

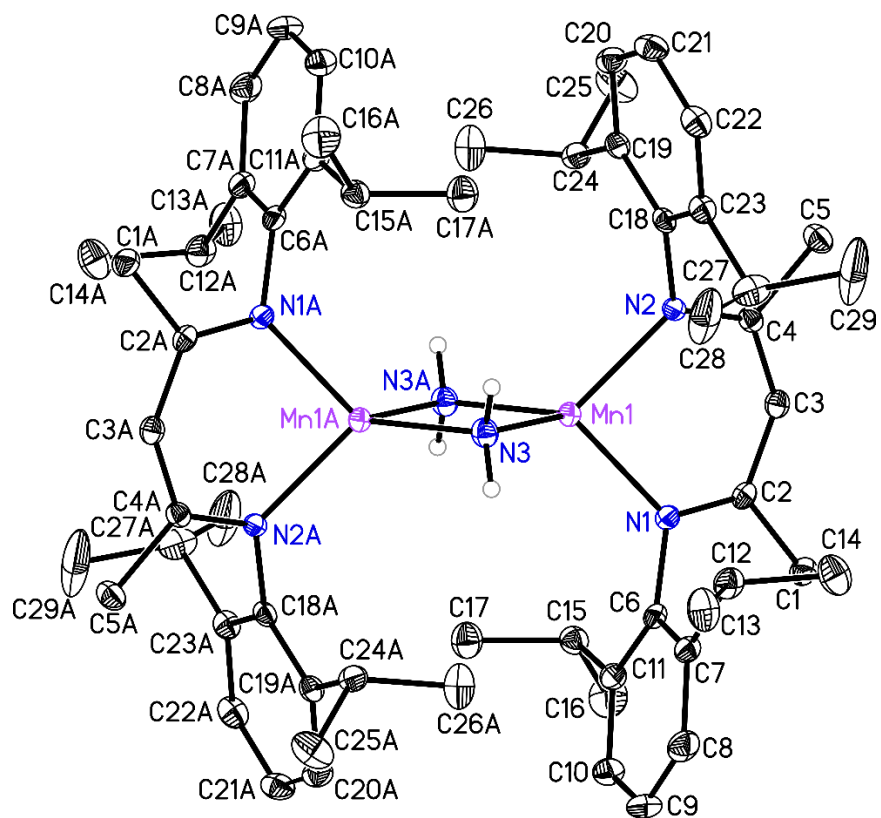


**Figure S60.** FT-IR spectrum of **2** in KBr.

## CRYSTALLOGRAPHIC TABLES

**Table S1.** Crystallographic Data for [(<sup>2,6-iPr<sub>2</sub>Ph</sup>BDI)Mn(μ-NH<sub>2</sub>)<sub>2</sub>] (**2**).

	<b>2</b>
chemical formula	C <sub>58</sub> H <sub>86</sub> Mn <sub>2</sub> N <sub>6</sub>
formula weight	977.20
crystal dimensions	0.295 × 0.159 × 0.151
crystal system	monoclinic
space group	C 1 2/c 1
a (Å)	22.875(10)
b (Å)	14.747(7)
c (Å)	16.257(7)
α (deg)	90
β (deg)	91.125(8)
γ (deg)	90
V (Å <sup>3</sup> )	5483.(4)
Z	4
T (°C)	123.0(1)
ρ <sub>calcd</sub> (g cm <sup>-3</sup> )	1.184
μ (mm <sup>-1</sup> )	0.502
reflections collected	22437
data/restraints/parameters	4996/0/308
R <sub>1</sub> [I > 2σ(I)]	0.0630
wR <sub>2</sub> (all data)	0.1273
Goodness-of-fit	1.051
Largest peak, hole (eÅ <sup>-3</sup> )	0.648, -0.347

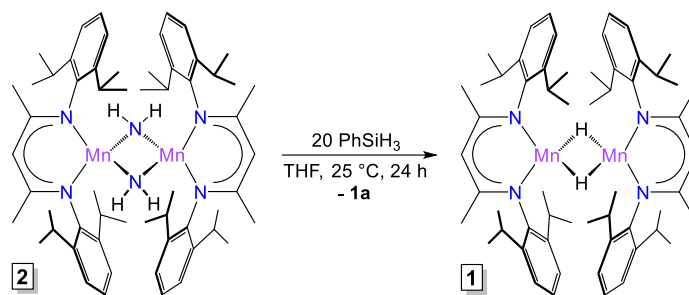


**Figure S61.** The molecular structure of **2** displayed at 30% probability ellipsoids. Hydrogen atoms, except those located on the bridging amido groups, are omitted for clarity.

**Table S2.** Bond lengths (Å) and angles (°) determined for **2**.

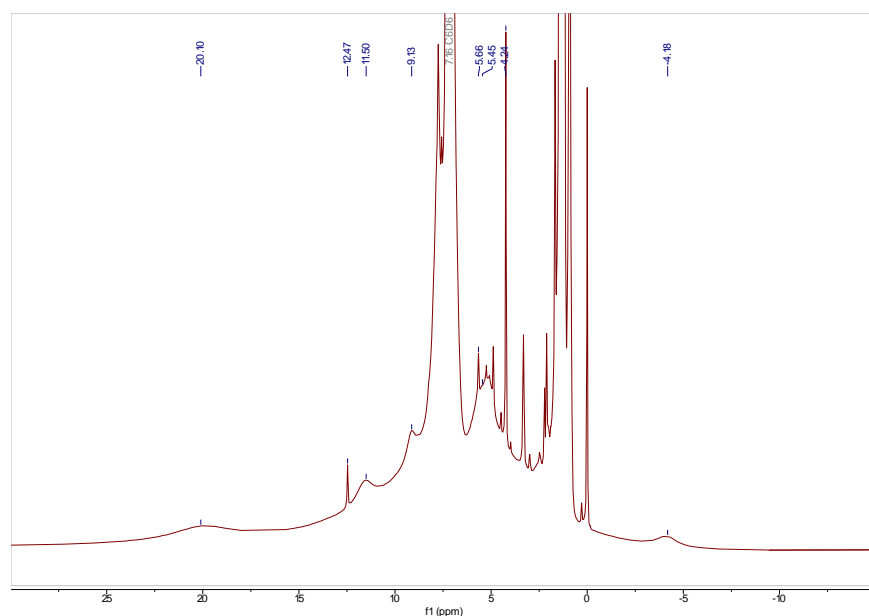
Mn1-N3	2.106(2)	C4-C5	1.514(3)	C18-C23	1.407(3)
Mn1-N1	2.111(2)	C6-C7	1.403(4)	C18-C19	1.410(3)
Mn1-N2	2.117(2)	C6-C11	1.405(4)	C19-C20	1.387(4)
Mn1-N3A	2.122(2)	C7-C8	1.399(4)	C19-C24	1.519(4)
Mn1-Mn1A	3.0423(12)	C7-C12	1.519(4)	C20-C21	1.377(4)
N1-C2	1.334(3)	C8-C9	1.381(4)	C21-C22	1.381(4)
N1-C6	1.446(3)	C9-C10	1.385(4)	C22-C23	1.390(4)
N2-C4	1.333(3)	C10-C11	1.391(4)	C23-C27	1.523(4)
N2-C18	1.440(3)	C11-C15	1.521(4)	C24-C26	1.515(4)
N3-Mn1A	2.122(2)	C12-C14	1.519(4)	C24-C25	1.524(4)
C1-C2	1.511(3)	C12-C13	1.529(4)	C27-C28	1.481(5)
C2-C3	1.399(3)	C15-C17	1.526(4)	C27-C29	1.501(5)
C3-C4	1.399(3)	C15-C16	1.534(4)		
N3-Mn1-N1	121.48(9)	C4-C3-C2	130.7(2)	C11-C15-C16	112.9(2)
N3-Mn1-N2	122.50(8)	N2-C4-C3	124.2(2)	C17-C15-C16	109.2(2)
N1-Mn1-N2	90.57(8)	N2-C4-C5	120.7(2)	C23-C18-C19	121.0(2)
N3-Mn1-N3A	87.98(9)	C3-C4-C5	115.0(2)	C23-C18-N2	119.2(2)
N1-Mn1-N3A	117.56(8)	C7-C6-C11	121.7(2)	C19-C18-N2	119.8(2)
N2-Mn1-N3A	119.96(8)	C7-C6-N1	117.8(2)	C20-C19-C18	117.9(2)
N3-Mn1-Mn1A	44.20(6)	C11-C6-N1	120.5(2)	C20-C19-C24	120.4(2)
N1-Mn1-Mn1A	133.18(6)	C8-C7-C6	118.0(2)	C18-C19-C24	121.7(2)
N2-Mn1-Mn1A	136.09(6)	C8-C7-C12	120.6(2)	C21-C20-C19	121.7(3)
N3A-Mn1-Mn1A	43.77(6)	C6-C7-C12	121.4(2)	C20-C21-C22	119.9(3)
C2-N1-C6	115.6(2)	C9-C8-C7	120.8(3)	C21-C22-C23	121.0(3)
C2-N1-Mn1	121.90(16)	C8-C9-C10	120.5(3)	C22-C23-C18	118.5(2)
C6-N1-Mn1	122.48(15)	C9-C10-C11	120.9(3)	C22-C23-C27	120.1(2)
C4-N2-C18	116.3(2)	C10-C11-C6	118.1(2)	C18-C23-C27	121.4(2)
C4-N2-Mn1	121.93(16)	C10-C11-C15	119.9(2)	C26-C24-C19	111.5(2)
C18-N2-Mn1	121.69(14)	C6-C11-C15	122.0(2)	C26-C24-C25	109.8(2)
Mn1-N3-Mn1	92.02(9)	C7-C12-C14	111.5(2)	C19-C24-C25	112.1(2)
N1-C2-C3	124.1(2)	C7-C12-C13	113.5(2)	C28-C27-C29	109.0(3)
N1-C2-C1	120.8(2)	C14-C12-C13	110.0(2)	C28-C27-C23	112.7(3)
C3-C2-C1	115.0(2)	C11-C15-C17	110.7(2)	C29-C27-C23	112.9(3)

## CATALYST REGENERATION



**Scheme S26.** Conversion of  $[(^{2,6}\text{-iPr}_2\text{PhBDI)Mn}(\mu\text{-NH}_2)]_2$  (**2**) to  $[(^{2,6}\text{-iPr}_2\text{PhBDI)Mn}(\mu\text{-H})]_2$  (**1**).

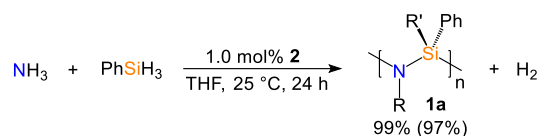
In the glove box under  $\text{N}_2$  atmosphere, 0.066 g (0.614 mmol) of phenylsilane was charged to a pre-weighed 20 mL scintillation vial with 5 mL of dry THF, a stir bar, and 0.030 g (0.030 mmol) of **2**, resulting in a yellow suspension. The reaction mixture was allowed to stir for 24 h and then solvents were removed in *vacuo* to afford a yellow solid previously identified as **1**.  $^1\text{H}$  NMR (400 MHz, benzene- $d_6$ ): 20.10 (peak width at half-height = 1854 Hz), 11.50 (557 Hz), 5.45 (728 Hz), -4.18 (715 Hz).



**Figure S62.**  $^1\text{H}$  NMR spectrum of **1** prepared from **2** and phenylsilane in benzene- $d_6$  at  $25\text{ }^\circ\text{C}$ .

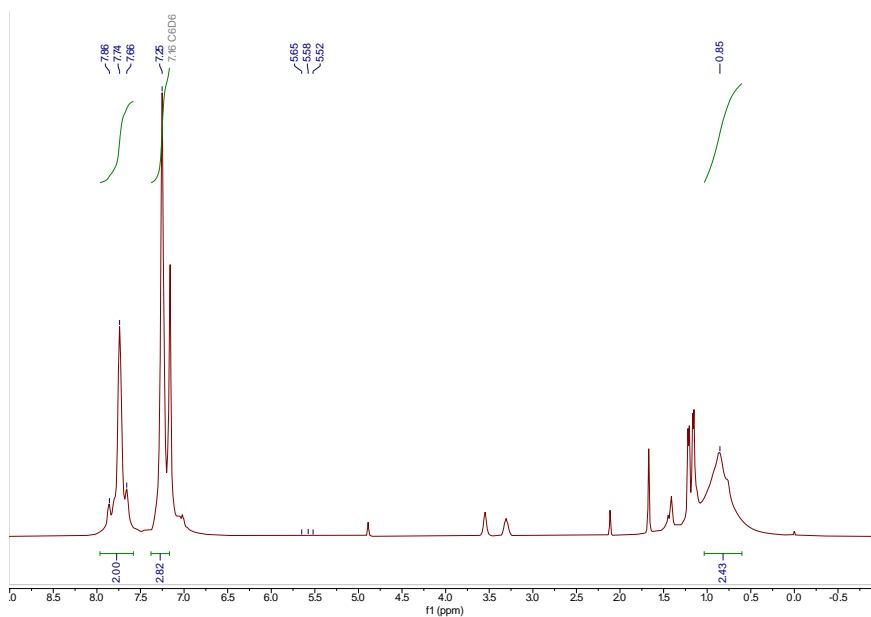
## PREPARATION OF OLIGOSILAZANE USING 2 AS A CATALYST

### Ammonia and Phenylsilane Dehydrocoupling Using 1 mol% 2:



#### Scheme S27. Preparation of oligosilazane **1a**.

In the glove box under  $\text{N}_2$  atmosphere, 0.101 g (0.933 mmol) of phenylsilane was charged to a pre-weighed 20 mL scintillation vial with 5 mL of dry THF, a stir bar, and 0.009 g (0.009 mmol) of **2** (a yellow suspension was observed). The mixture was then transferred to a 100 mL thick-walled glass bomb, sealed, and attached to the high vacuum line outside the glove box. The gas from the headspace of the bomb was removed upon freezing the solution with liquid nitrogen, and subsequently, 1 atm of  $\text{NH}_3$  was added. The bomb was disconnected from the vacuum line and allowed to warm to room temperature in a steel container and then set to stir. Freeze-pump-thaw cycles were performed after 2 h, 12 h, and 24 h to release the  $\text{H}_2$  gas produced in the reaction. The extra ammonia was allowed to escape under a dynamic vacuum upon partial opening of the bomb and was collected in a trap cooled with liquid nitrogen. The reaction mixture was transferred to the glove box and solvents were removed *in vacuo* to afford a viscous oil.  $^1\text{H}$  NMR spectroscopy revealed greater than 99% conversion after 24 h and 0.112 g of **1a** was obtained (DOSY  $M_w = 1,900$  g/mol; 0.058 mmol oligomer; repeating units per oligomer = 15.5; 0.91 mmol of repeating unit; 97% isolated yield).  $^1\text{H}$  NMR (400 MHz, benzene- $d_6$ ): 7.86, 7.74, 7.66 (t, *m*-aryl), 7.25 (broad, *o*- & *p*-aryl), 5.65, 5.58, 5.52 (s, (NH)(NH)PhSiH, (NH)(NH<sub>2</sub>)PhSiH, (NH<sub>2</sub>)<sub>2</sub>PhSiH, (NH)PhSiH<sub>2</sub>, (NH<sub>2</sub>)PhSiH<sub>2</sub>), 0.84 (broad, NH, NH<sub>2</sub>).



**Figure S63.**  $^1\text{H}$  NMR spectrum of **1a** prepared from **2** in benzene- $d_6$ .

## REFERENCES

1. M. Kamitani, K. Kanemitsu, K. Yujiri and H. Yuge, *Organometallics* 2023, **42**, 1839-1848.
2. T. K. Mukhopadhyay, M. Flores, T. L. Groy and R. J. Trovitch, *Chem. Sci.* 2018, **9**, 7673-7680.