

Electronic Supplementary Information

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

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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 prior to use. Benzene-*d*₆ was purchased from Oakwood Chemicals and dried over 4 Å molecular sieves and potassium prior to use. Celite, phenylsilane, and diphenylsilane were acquired from Oakwood Chemical. Dimethylphenylsilane was obtained from Sigma-Aldrich. Methyldiphenylsilane 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 a modified procedure that involved refluxing a toluene and lithium aluminum hydride mixture followed by filtration under inert atmosphere.¹ [(^{2,6}-iPr₂PhBDI)Mn(μ-H)]₂ (**1**) was synthesized according to the literature procedure.²

Solution nuclear magnetic resonance (NMR) spectra were recorded at room temperature on a Varian 400 MHz NMR spectrometer. All ¹H NMR and ¹³C NMR chemical shifts (ppm) are reported relative to SiMe₄ using ¹H (residual) and ¹³C chemical shifts of the solvent as secondary standards. ²⁹Si NMR chemical shifts (ppm) are reported relative to SiMe₄ using the absolute ¹H NMR frequency of an internal SiMe₄ 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.

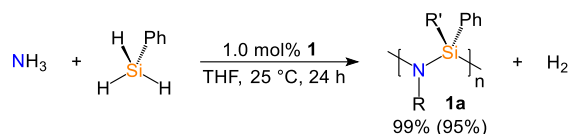
Scanning Electron Microscope (SEM): The oligosilazane **1a** was dip-coated onto copper tape and cured for 24 h in air prior to microscopic analysis. Scanning electron microscope (SEM) images of selected samples were collected on a Phenom XL desktop microscope operating at 5.0 kV acceleration voltage.

General Procedure for Ammonia and Silane Dehydrocoupling Using 1 mol% **1:** In the glove box under N₂ 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 [(^{2,6}-iPr₂PhBDI)Mn(μ-H)]₂ 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, 2 atm of 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 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. ^1H NMR spectroscopy was used to determine silane conversion and ^1H , ^{13}C and ^{29}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_2 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, 2 atm of 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 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. ^1H NMR spectroscopy revealed more than 99% conversion after 24 h and a yield of 0.525 g was obtained (DOSY $M_w = 2,300$ g/mol; 0.228 mmol oligomer; repeating units per oligomer = 18.8; 4.29 mmol of repeating unit; 95% isolated yield). ^1H NMR (400 MHz, benzene- d_6): 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)(NH₂)PhSiH, (NH₂)₂PhSiH, (NH)PhSiH₂, (NH₂)PhSiH₂), 0.84 (broad, NH, NH₂). ^{13}C NMR (100 MHz, benzene- d_6): 139.91 (NHSiC), 134.46 (*m*-Ph), 134.0 (*p*-Ph), 130.20 (*o*-Ph). ^{29}Si NMR (79 MHz, benzene- d_6): 23.16 (NHSiNH), 30.93 (NH₂SiNH). IR (KBr, cm^{-1}): 3540-3170 (broad, N-H), 3030-2820 (broad, C-H), 850 (weak, Si-N).

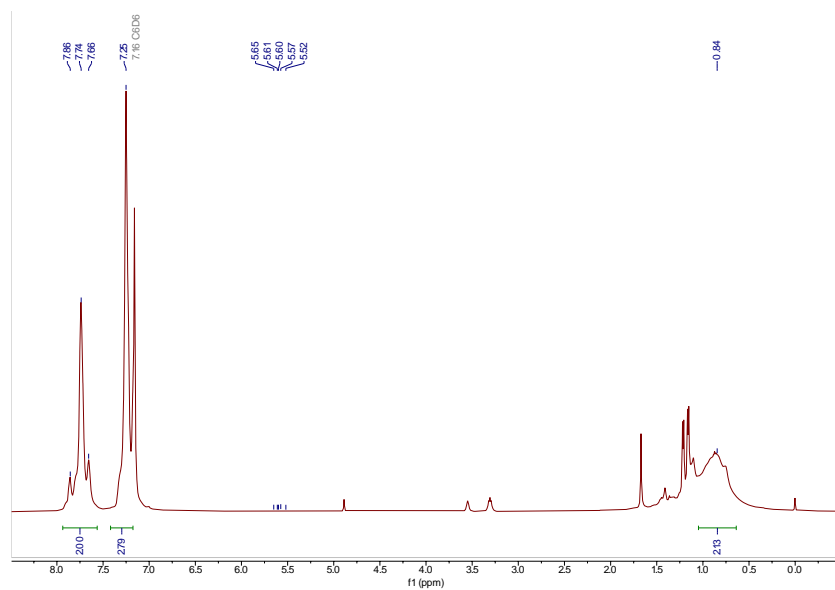


Figure S1. ¹H NMR spectrum of **1a** in benzene-*d*₆.

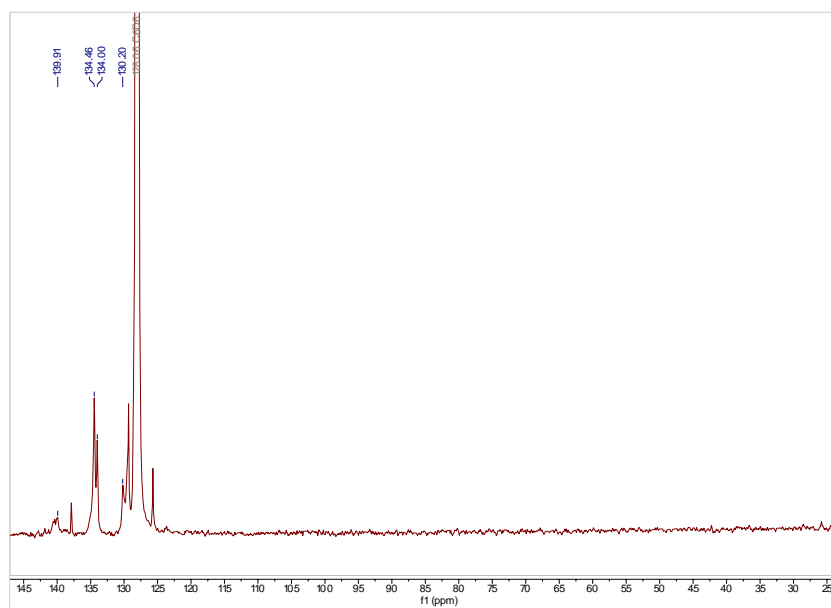


Figure S2. ¹³C NMR spectrum of **1a** in benzene-*d*₆.

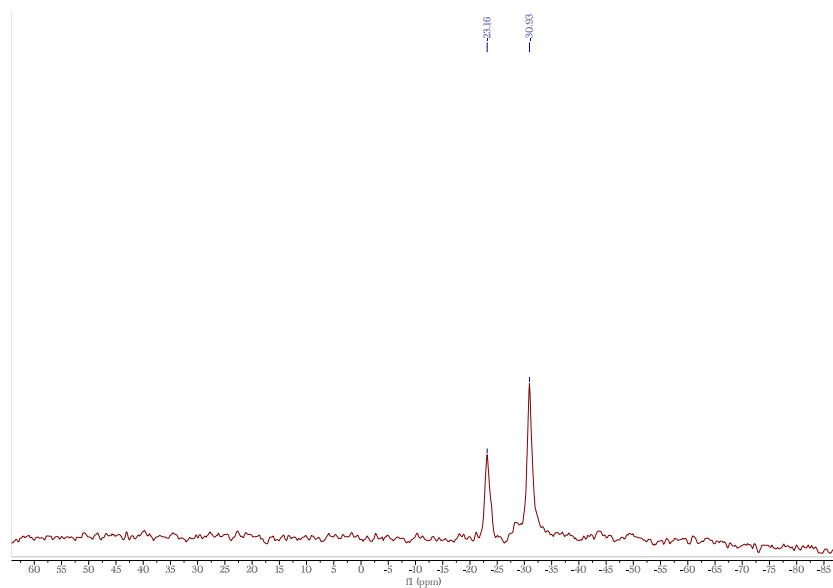


Figure S3. ^{29}Si NMR spectrum of **1a** in benzene- d_6 .

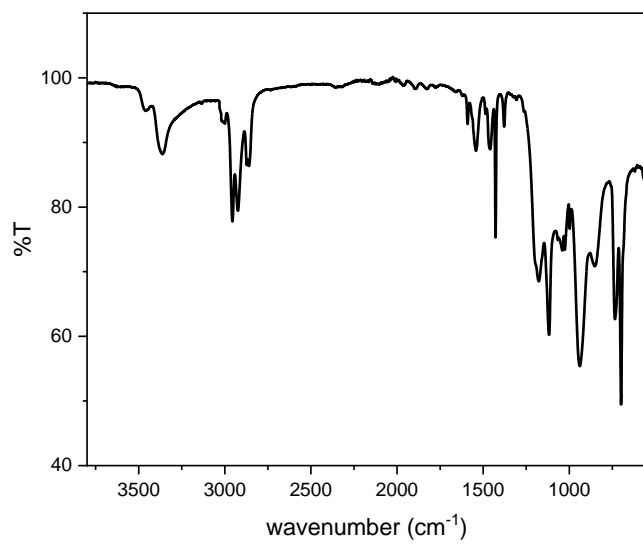
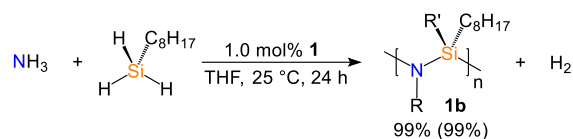


Figure S4. FT-IR spectrum of **1a**.

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



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

In the glove box under N₂ 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, 2 atm of NH₃ 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 H₂ 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. ¹H NMR spectroscopy revealed more than 99% conversion after 24 h and a yield of 0.220 g was obtained (DOSY M_w = 1,200 g/mol; 0.183 mmol oligomer; repeating units per oligomer = 7.5; 1.37 mmol of repeating unit; 99% isolated yield). ¹H NMR (400 MHz, benzene-*d*₆): 1.44-1.40 (NH₂SiNH, NH₂SiNH, Si(NH)₃), 1.29 (broad, CH₃CH₂(CH₂)₃), 0.90 (s, CH₃), 0.30-0.75 (SiCH₂, SiCH₂CH₂, SiCH₂CH₂CH₂, CH₃CH₂). ¹³C NMR (100 MHz, benzene-*d*₆): 34.19 (CH₃CH₂), 34.11 (SiCH₂CH₂CH₂), 32.45 (SiCH₂), 30.02, 29.90 (SiCH₂CH₂CH₂(CH₂)₂), 24.85 (CH₃CH₂), 23.17 (SiCH₂CH₂), 14.41 (CH₃). ²⁹Si NMR (79 MHz, benzene-*d*₆): 20.56 (NH₂SiNH). IR (KBr, cm⁻¹): 3510-3265 (broad, NH, NH₂), 3000-2810 (strong, C-H), 821 (strong, Si-N).

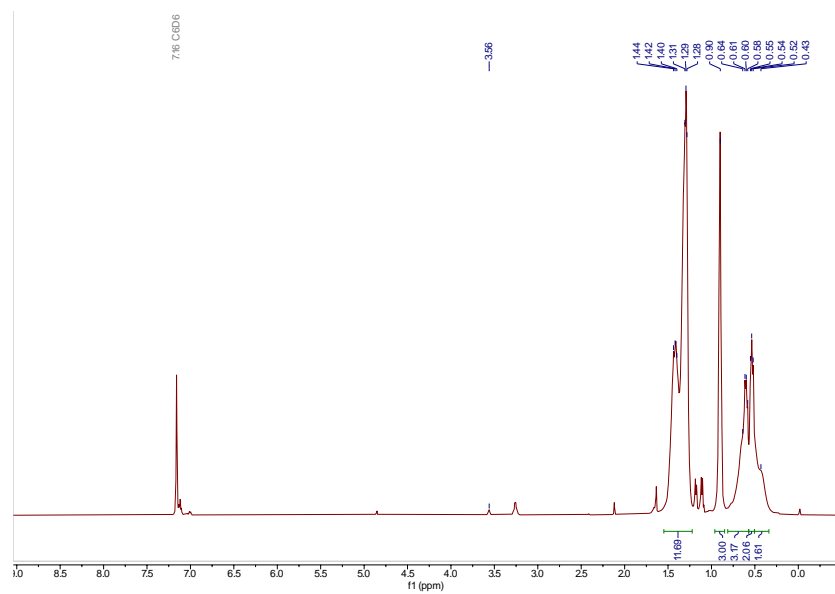


Figure S5. ^1H NMR spectrum of **1b** in benzene- d_6 .

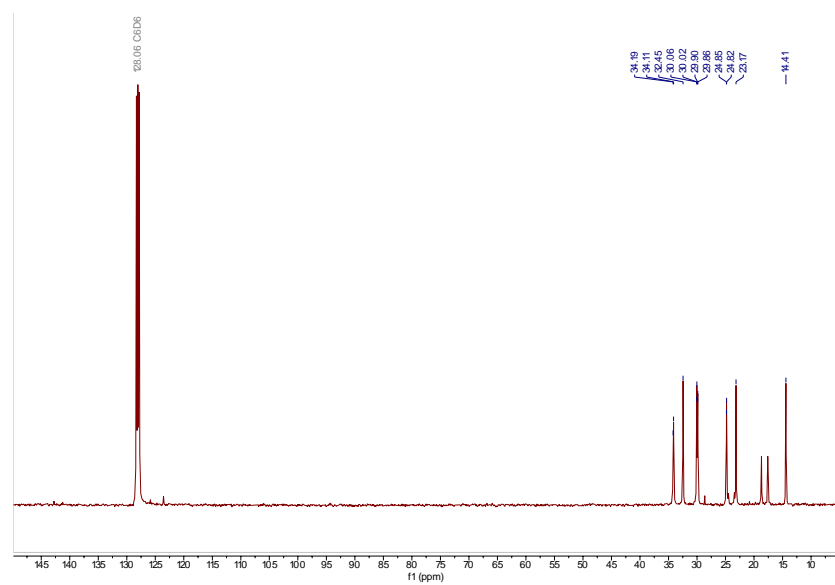


Figure S6. ^{13}C NMR spectrum of **1b** in benzene- d_6 .

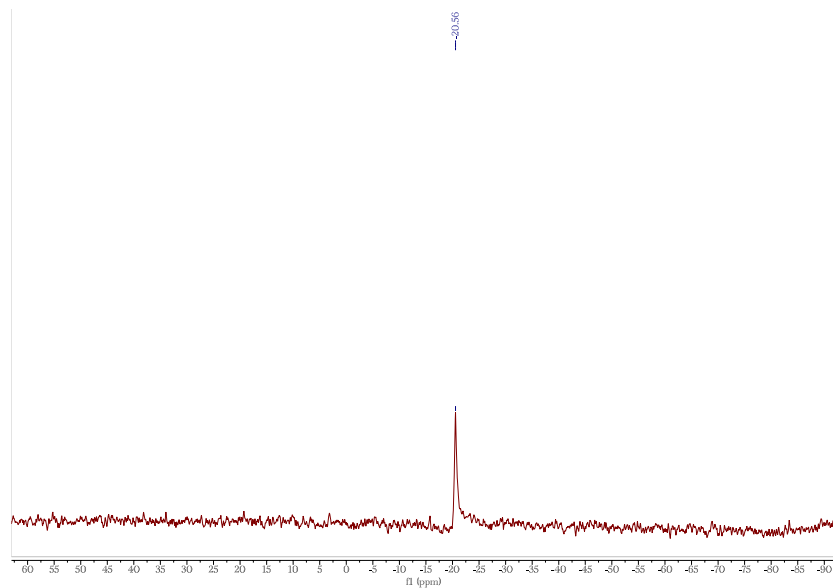


Figure S7. ^{29}Si NMR spectrum of **1b** in benzene- d_6 .

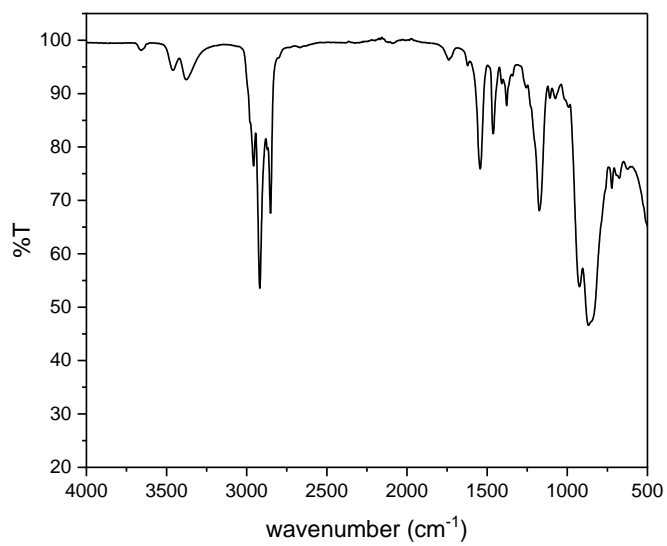
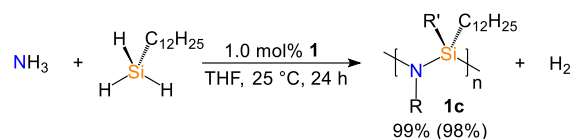


Figure S8. FT-IR spectrum of **1b**.

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



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

In the glove box under N₂ 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, 2 atm of NH₃ 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 H₂ 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. ¹H NMR spectroscopy revealed more than 99% conversion after 24 h and a yield of 0.360 g was obtained (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). ¹H NMR (400 MHz, benzene-*d*₆): 5.30 (s, SiH), 1.23-1.60 (broad, CH₂), 0.92 (t, NH, NH₂), 0.64 (broad, SiCH₂, CH₃). ¹³C NMR (100 MHz, benzene-*d*₆): 34.21 (Si(CH₂)₂CH₂), 32.28 (CH₃CH₂CH₂), 30.29, 30.26, 30.19, 30.14 (internal CH₂), 29.88 (CH₃CH₂CH₂, Si(CH₂)₃CH₂), 24.87 (SiCH₂), 23.15 (CH₃CH₂), 18.68 (SiCH₂CH₂), 14.40 (CH₃). ²⁹Si NMR (79 MHz, benzene-*d*₆): -20.57 (NHSiNH), -21.46 (NHSiNH), -22.06 (NH₂SiNH). IR (KBr, cm⁻¹): 3480-3215 (broad, N-H), 2975-2790 (strong, C-H), 826 (weak, Si-N).

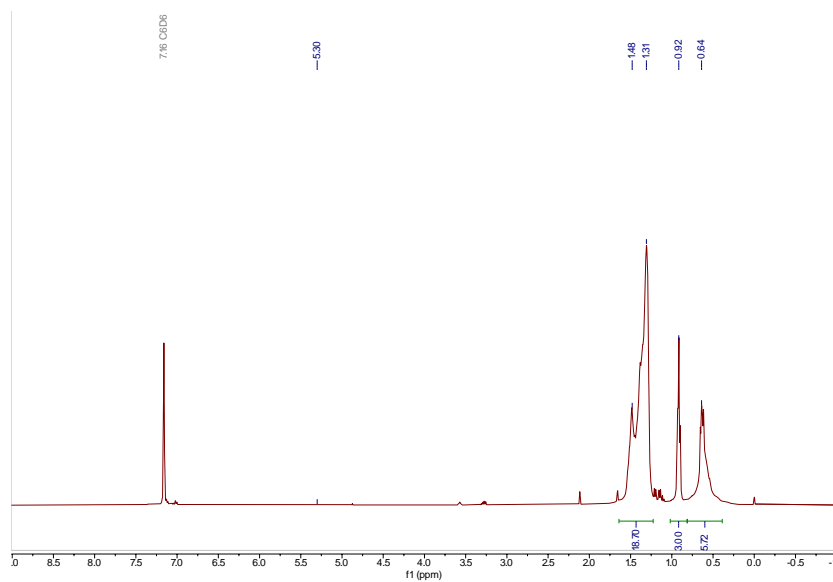


Figure S9. ^1H NMR spectrum of **1c** in benzene- d_6 .

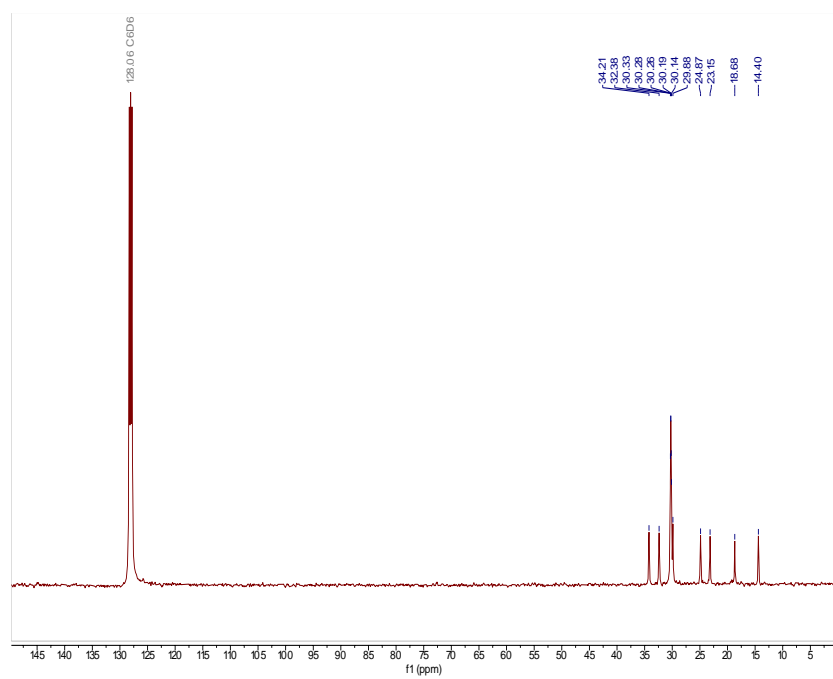


Figure S10. ^{13}C NMR spectrum of **1c** in benzene- d_6 .

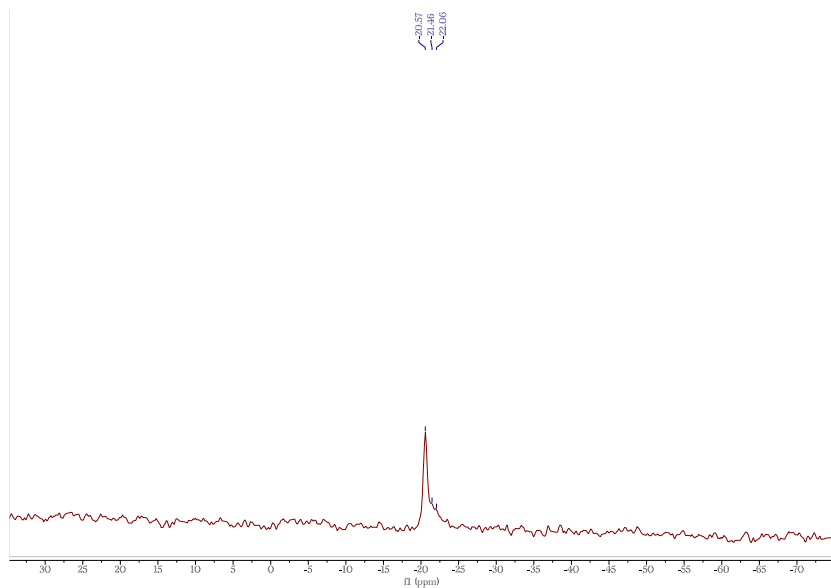


Figure S11. ^{29}Si NMR spectrum of **1c** in benzene- d_6 .

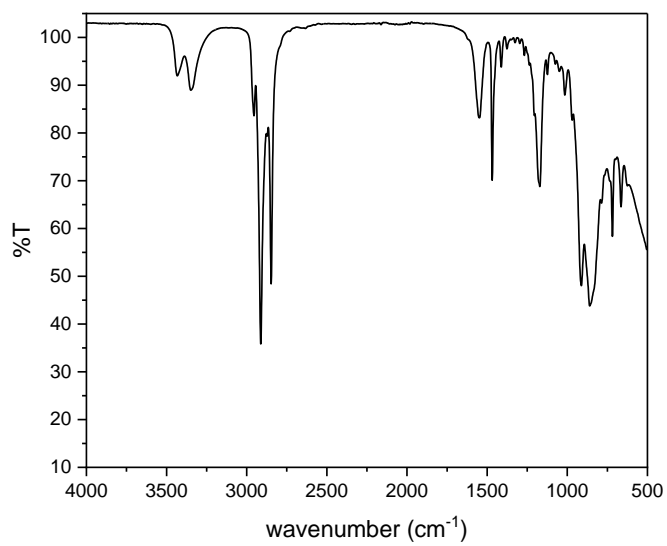
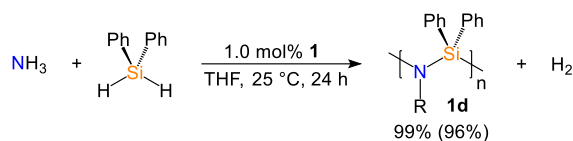


Figure S12. FT-IR spectrum of **1c**.

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



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

In the glove box under N₂ 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, 2 atm of NH₃ 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 H₂ 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. ¹H NMR spectroscopy revealed more than 99% conversion after 24 h and a yield of 0.336 g was obtained (DOSY M_w = 700 g/mol; 0.480 mmol oligomer; repeating units per oligomer = 3.5; 1.66 mmol of repeating unit; 96% isolated yield). ¹H NMR (400 MHz, benzene-*d*₆): 7.75-7.36 (broad, *m*-Ph), 7.25-7.12 (broad, *o*-Ph, *p*-Ph), 0.98-0.61 (broad, NH, NH₂). ¹³C NMR (100 MHz, benzene-*d*₆): 138.99 (SiC), 134.80 (*o*-Ph), 129.62 (*p*-Ph), 127.97, 127.37 (*m*-Ph). ²⁹Si NMR (79 MHz, benzene-*d*₆): 22.51 (Si(NH)₂), 23.49 (Ph₂HSi(NH)), 31.39 (Ph₂Si(NH)(NSi₂)). IR (KBr, cm⁻¹): 3500-3250 (broad, N-H), 3000-2870 (strong, C-H), 810 (strong, Si-N).

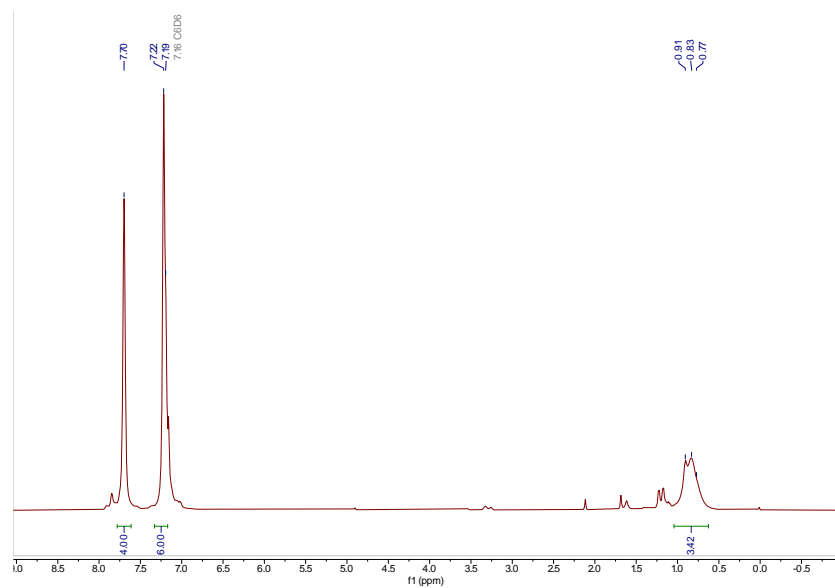


Figure S13. ¹H NMR spectrum of **1d** in benzene-*d*₆.

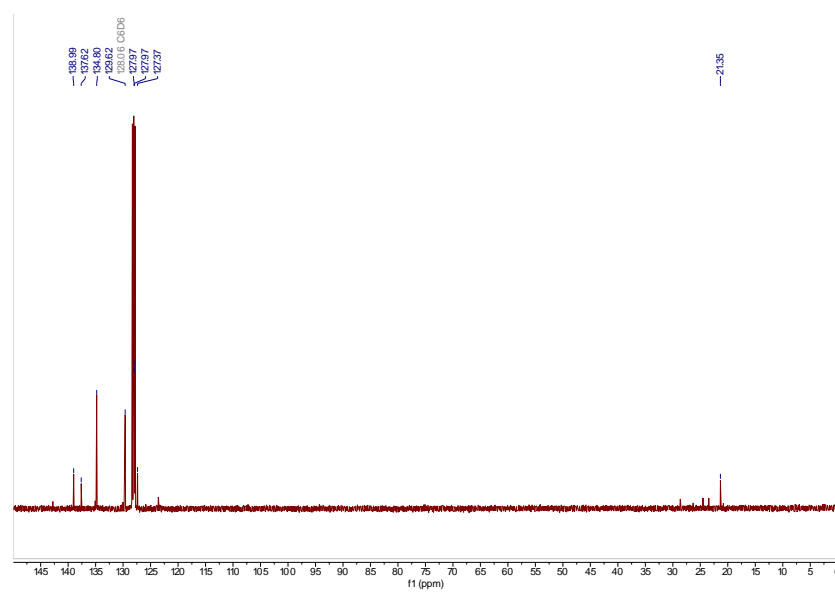


Figure S14. ¹³C NMR spectrum of **1d** in benzene-*d*₆.

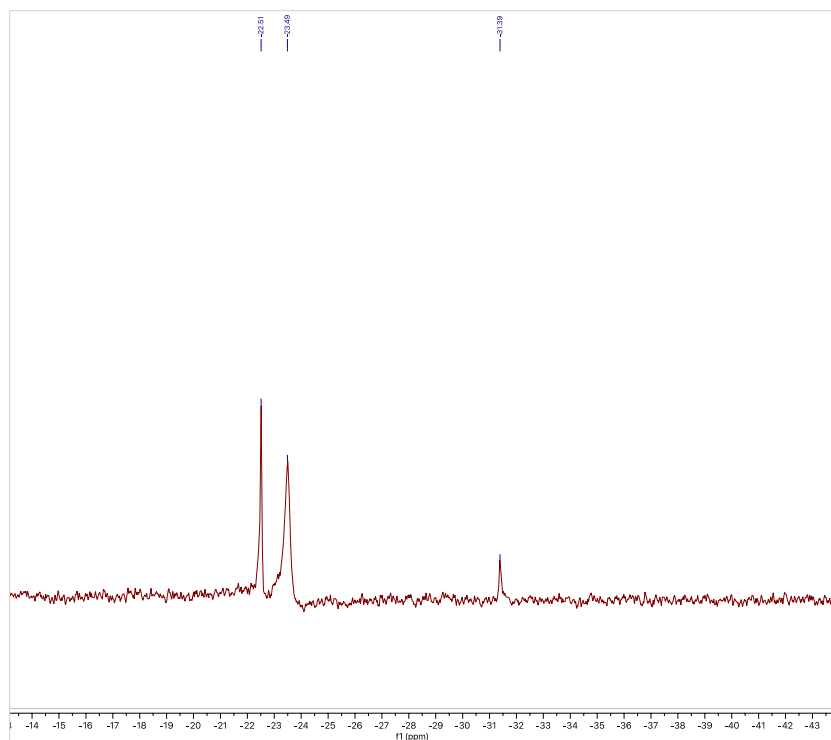


Figure S15. ^{29}Si NMR spectrum of **1d** in benzene- d_6 .

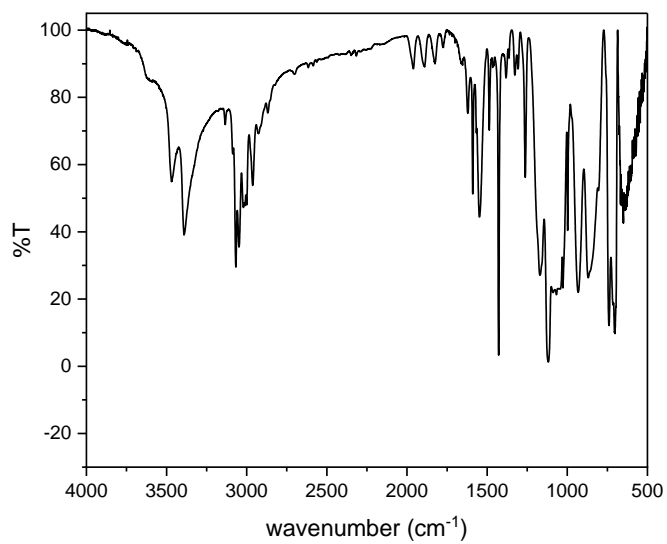
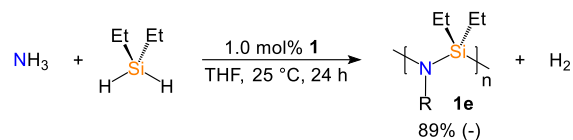


Figure S16. FT-IR spectrum of **1d**.

OBSERVATION OF OLIGOSILAZANES

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



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

In the glove box under N₂ 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, 2 atm of NH₃ 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 H₂ 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 ¹H NMR spectroscopy. ¹H NMR (400 MHz, benzene-*d*₆): 4.40 (s, Et₂SiH₂), 1.02-0.87 (m, CH₃), 0.61-0.37 (m, CH₂).

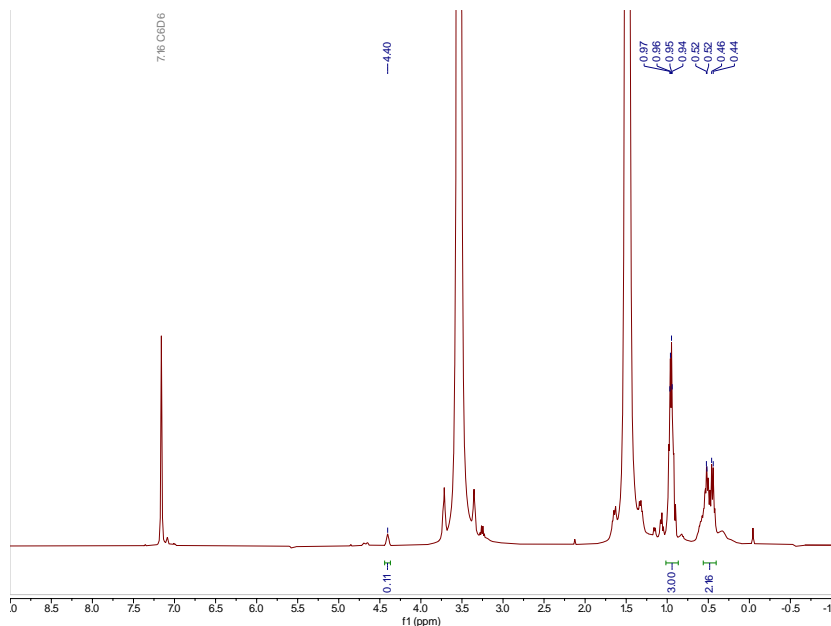
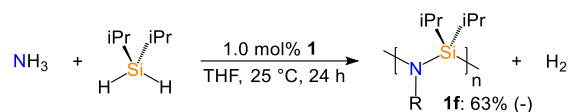


Figure S17. ¹H NMR spectrum showing conversion to **1e** in benzene-*d*₆.

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



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

In the glove box under N₂ 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, 2 atm of NH₃ 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 H₂ 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 ¹H NMR spectroscopy. ¹H NMR (400 MHz, benzene-*d*₆): 3.28 (s, iPr₂SiH₂), 1.67 (broad, NH, NH₂), 1.15 (broad, CH₃, (CH₃)₂CH).

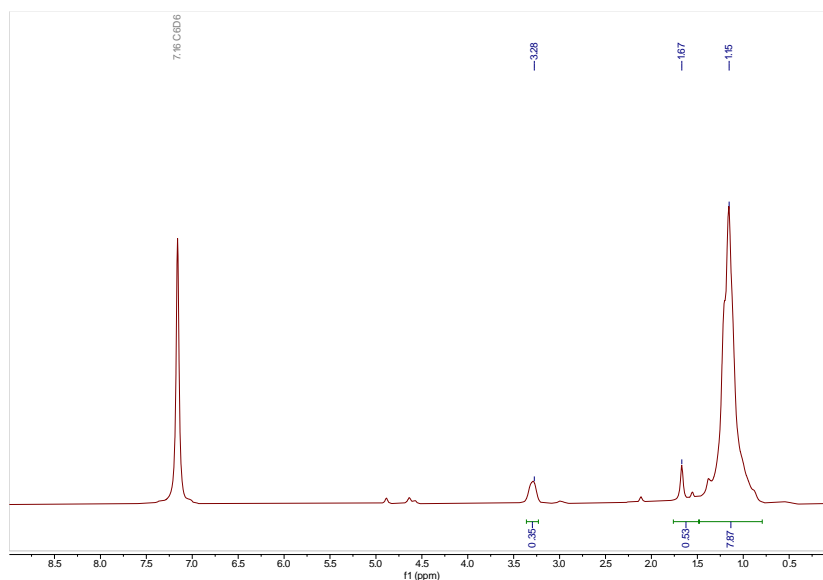
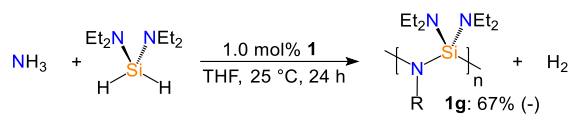


Figure S18. ¹H NMR spectrum showing conversion to **1f** in benzene-*d*₆.

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



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

In the glove box under N₂ 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, 2 atm of NH₃ 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 H₂ 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 ¹H NMR spectroscopy. ¹H NMR (400 MHz, benzene-*d*₆): 4.74 (s, SiHNH), 4.67 (s, SiH₂), 2.87 (broad, CH₂), 0.99 (broad, CH₃), 0.35 (broad, NH, NH₂).

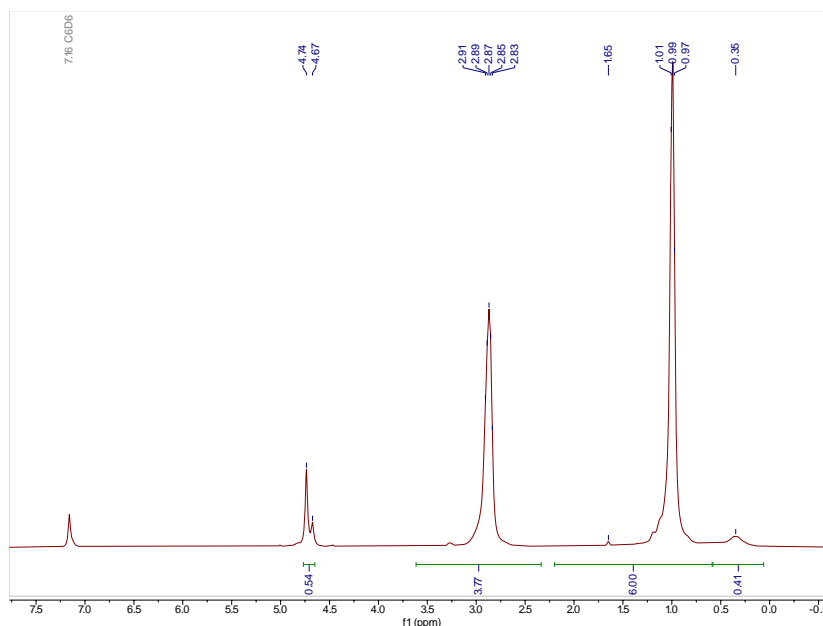
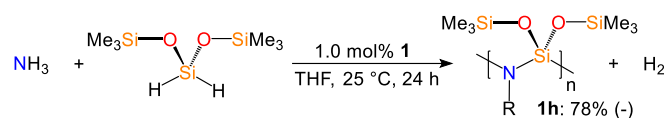


Figure S19. ¹H NMR spectrum showing conversion to **1g** in benzene-*d*₆.

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



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

In the glove box under N₂ 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, 2 atm of NH₃ 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 H₂ 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 ¹H NMR spectroscopy. ¹H NMR (400 MHz, benzene-*d*₆): 4.65 (s, SiH), 0.22 (broad, CH₃).

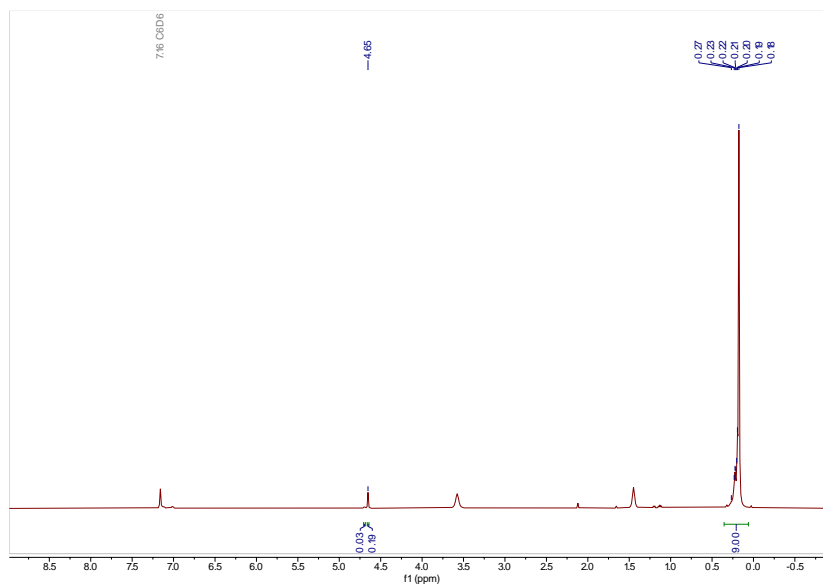
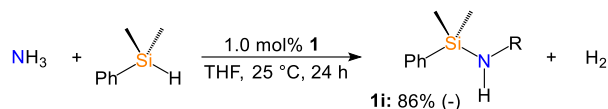


Figure S20. ¹H NMR spectrum showing conversion to **1h** in benzene-*d*₆.

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 N₂ atmosphere, 0.143 g (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, 2 atm of NH₃ 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 H₂ 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 ¹H NMR spectroscopy. ¹H NMR (400 MHz, benzene-*d*₆): 7.79-6.68 (broad, *aryl*), 0.88 (broad, *NH* and *NH*₂), 0.50-0.02 (broad, *CH*₃).

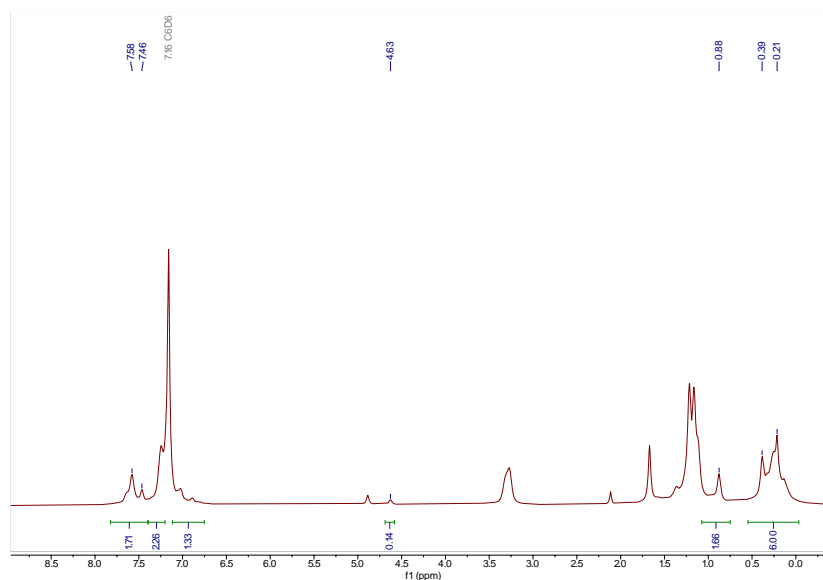
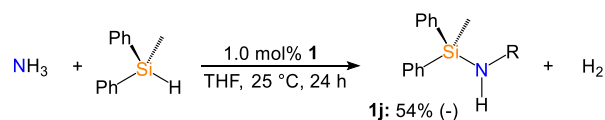


Figure S21. ¹H NMR spectrum showing conversion to **1i** in benzene-*d*₆.

Ammonia and Methyldiphenylsilane Dehydrocoupling Using 1 mol% **1**:



Scheme S10. Observation of aminated methyldiphenylsilane (**1j**).

In the glove box under N₂ atmosphere, 0.209 g (1.056 mmol) of methyldiphenylsilane 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, 2 atm of NH₃ 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 H₂ 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 ¹H NMR spectroscopy. ¹H NMR (400 MHz, benzene-*d*₆): 7.60 (broad, *p*-Ph), 7.51 (broad, *o*-Ph), 7.21 (broad, *m*-Ph), 5.14 (SiH), 0.88 (broad, NH, NH₂), 0.48 (CH₃).

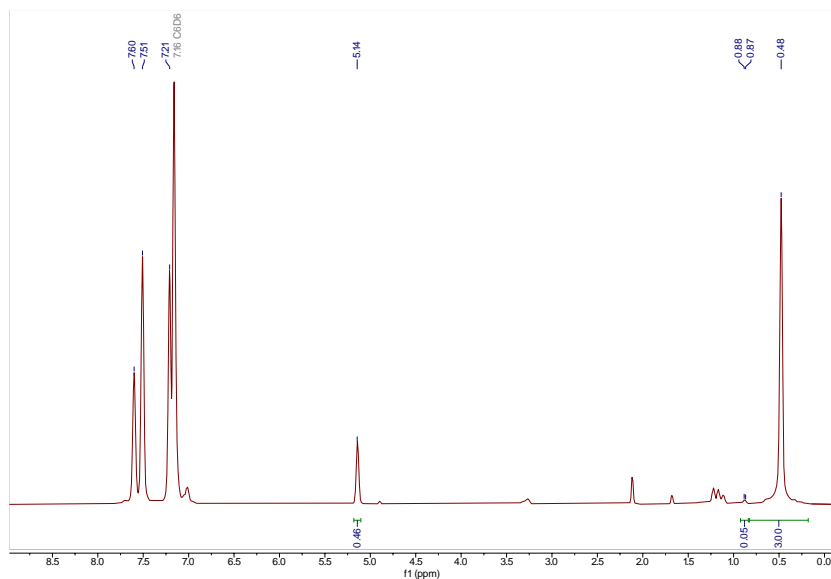
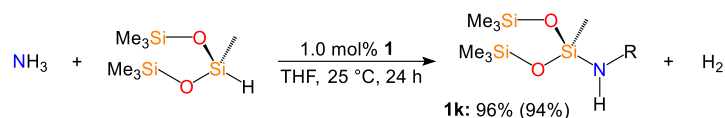


Figure S22. ¹H NMR spectrum showing conversion to **1j** in benzene-*d*₆.

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_2 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, 2 atm of 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 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. ^1H NMR spectroscopy revealed more than 96% conversion after 24 h and a yield of 0.229 g (0.995 mmol, 94%) was obtained. ^1H NMR (400 MHz, benzene- d_6): 5.05 (s, SiH), 0.88 (broad, NH_2), 0.59 (broad, NH), 0.18 (broad, CH_3). ^{13}C NMR (100 MHz, benzene- d_6): 0.95-0.87 (broad, CH_3). ^{29}Si NMR (79 MHz, benzene- d_6): 9.07 (OSiCH_3), -82.85 (SiNH , SiNH_2). IR (KBr, cm^{-1}): 3530 (broad, NH_2), 3350 (broad, NH), 2975-2843 (strong, C-H), 2160 (broad, Si-H), 795 (weak, Si-N).

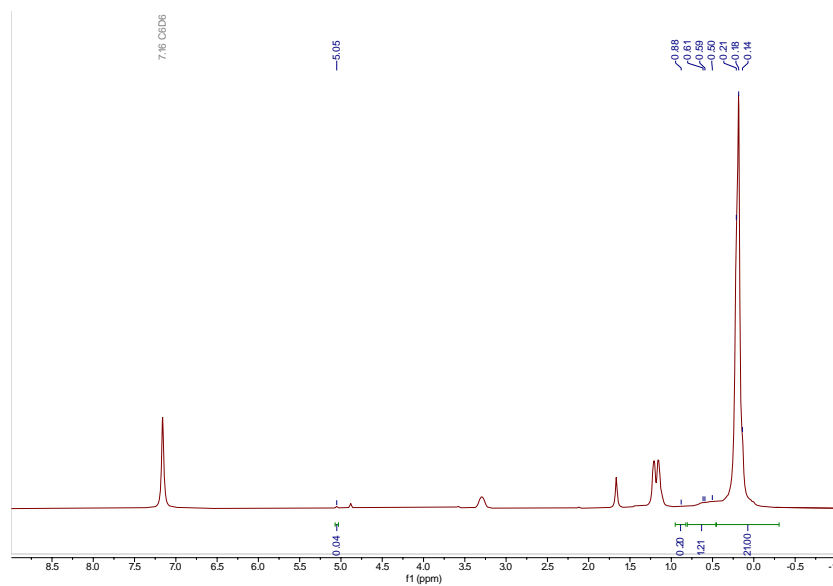


Figure S23. ^1H NMR spectrum of **1k** in benzene- d_6 .

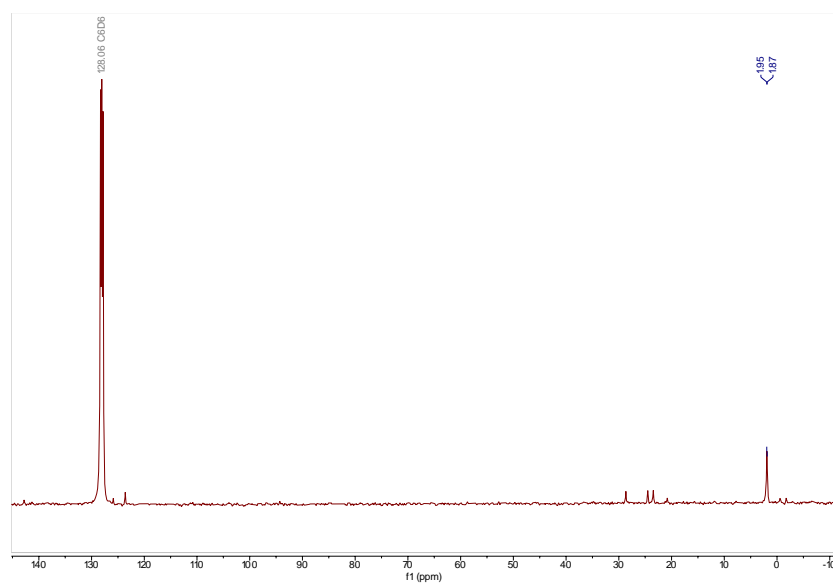


Figure S24. ^{13}C NMR spectrum of **1k** in benzene- d_6 .

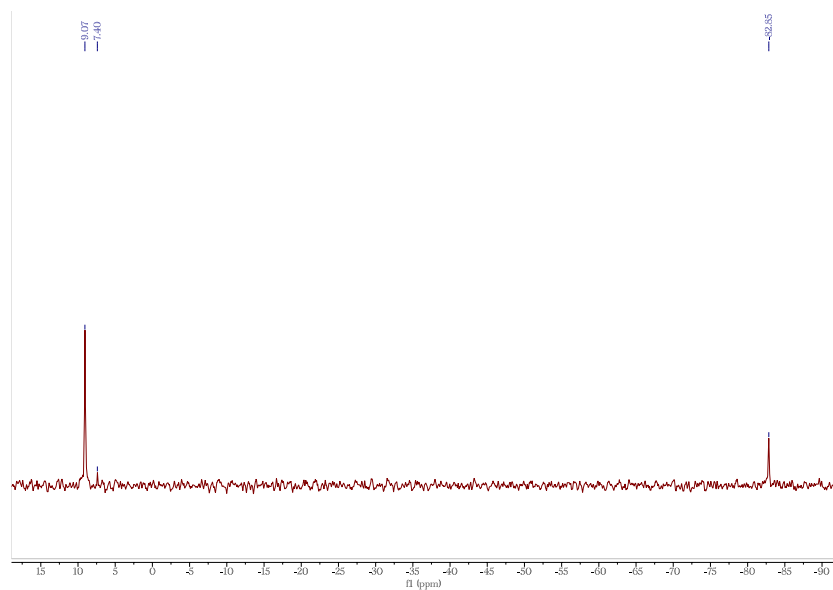


Figure S25. ^{29}Si NMR spectrum of **1k** in benzene- d_6 .

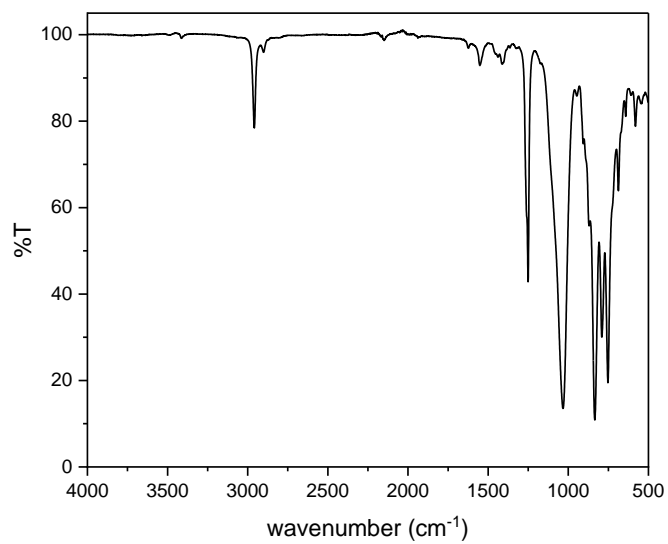
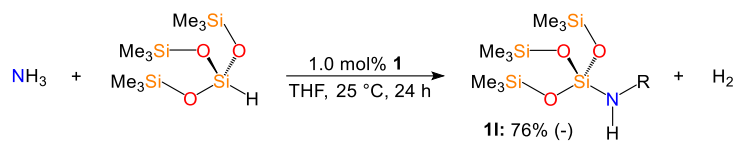


Figure S26. FT-IR spectrum of **1k**.

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



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

In the glove box under N₂ 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, 2 atm of NH₃ 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 H₂ 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 ¹H NMR spectroscopy. ¹H NMR (400 MHz, benzene-*d*₆): 4.69 (s, SiH), 0.25-0.19 (broad, CH₃).

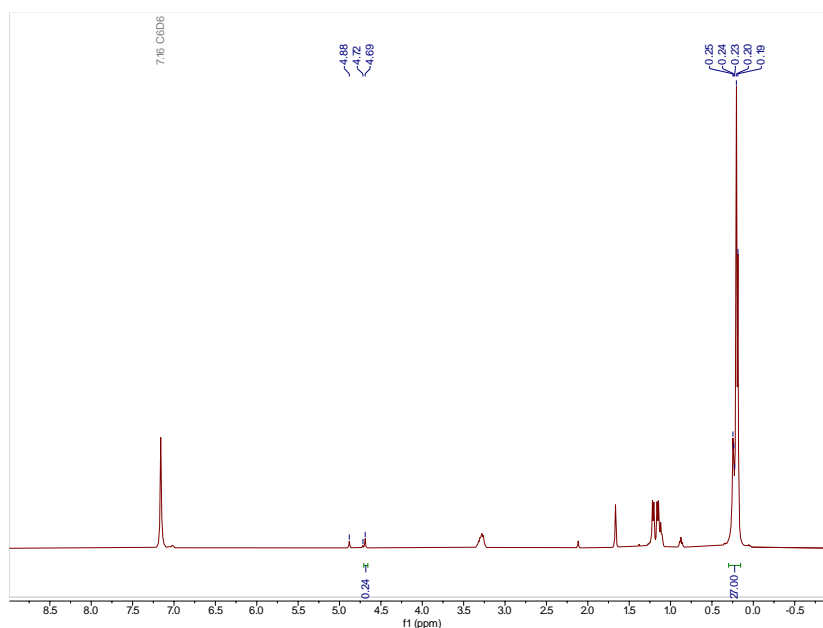
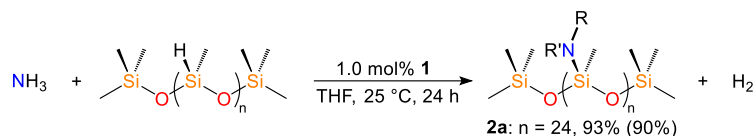


Figure S27. ¹H NMR spectrum showing conversion to **11** in benzene-*d*₆.

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_2 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, 2 atm of 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 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 white solid identified as **2a**. The isolated yield was found to be 0.845 g (0.475 mmol, 90%). IR (KBr, cm^{-1}): 3540-3320 (weak, N-H), 3010-2830 (strong, C-H), 2165 (broad, Si-H), 801 (strong, Si-N). TGA (N_2): $T_{-5\%} = 735\text{ }^\circ\text{C}$, total % wt. loss at $1000\text{ }^\circ\text{C} = 9\%$. TGA (O_2): $T_{-5\%} = 495\text{ }^\circ\text{C}$, total % wt. loss at $1000\text{ }^\circ\text{C} = 12\%$.

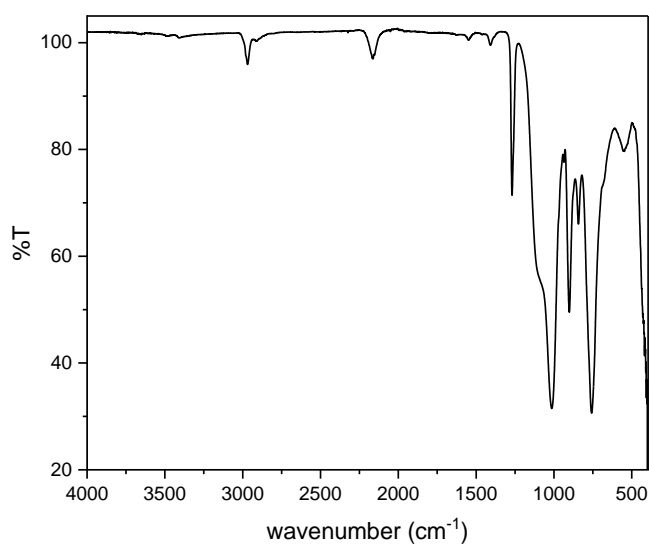


Figure S28. FT-IR spectrum of **2a**.

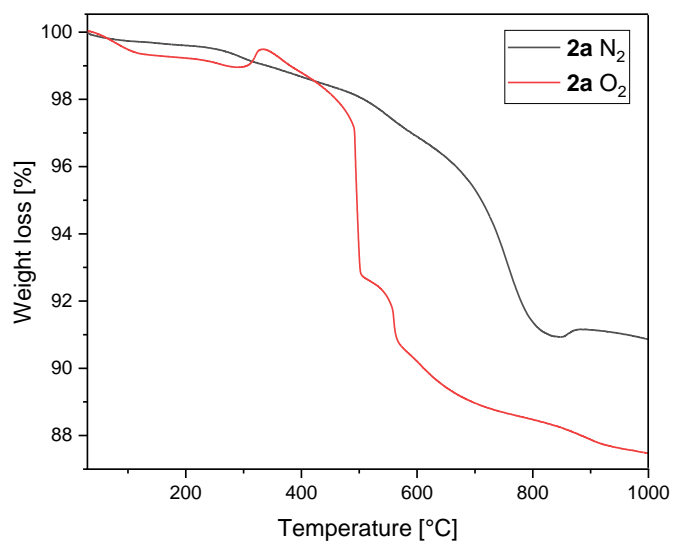


Figure S29. TGA thermogram of **2a** under N₂ and O₂.

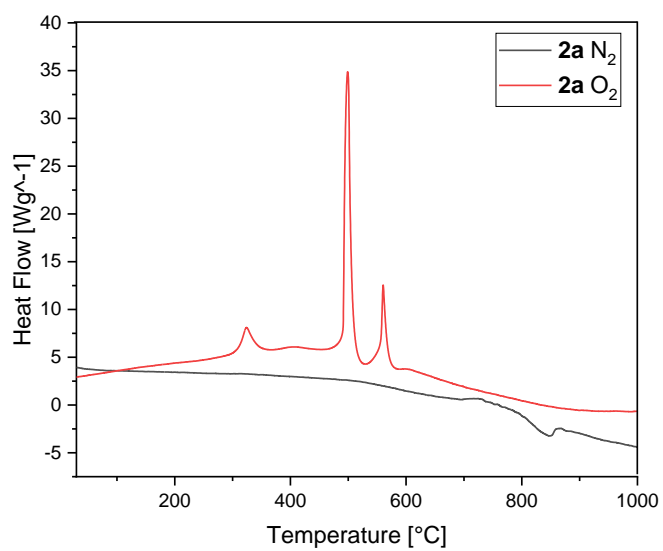
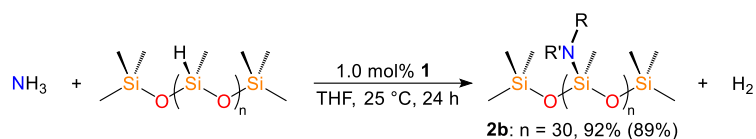


Figure S30. DSC thermogram of **2a** under N₂ and O₂.

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



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

In the glove box under N_2 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, 2 atm of NH_3 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_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 white solid identified as **2b**. The isolated yield was found to be 1.027 g (0.472 mmol, 89%). IR (KBr, cm^{-1}): 3535-3370 (weak, N–H), 3020-2830 (strong, C–H), 2168 (broad, Si–H), 816 (strong, Si–N). TGA (N_2): $T_{-5\%} = 596\text{ }^\circ\text{C}$, total % wt. loss at $1000\text{ }^\circ\text{C} = 10\%$. TGA (O_2): $T_{-5\%} = 467\text{ }^\circ\text{C}$, total % wt. loss at $1000\text{ }^\circ\text{C} = 12\%$.

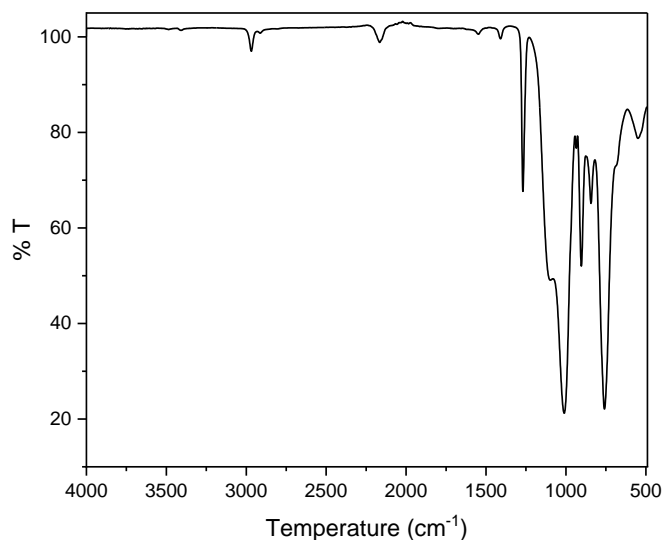


Figure S31. FT-IR spectrum of **2b**.

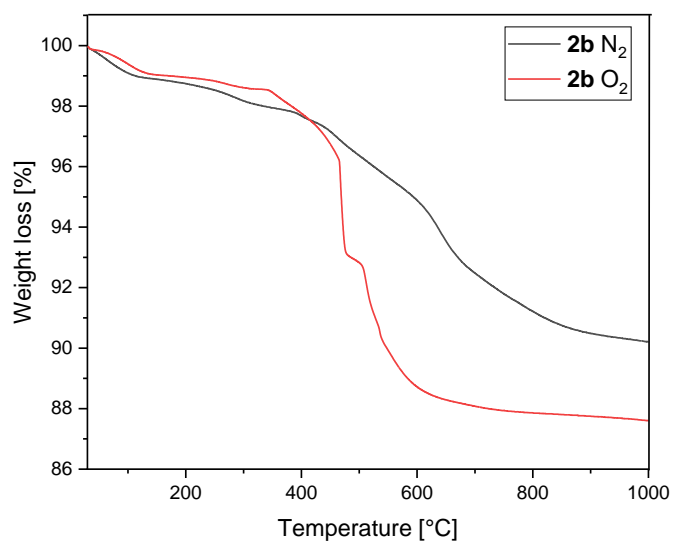


Figure S32. TGA thermogram of **2b** under N₂ and O₂.

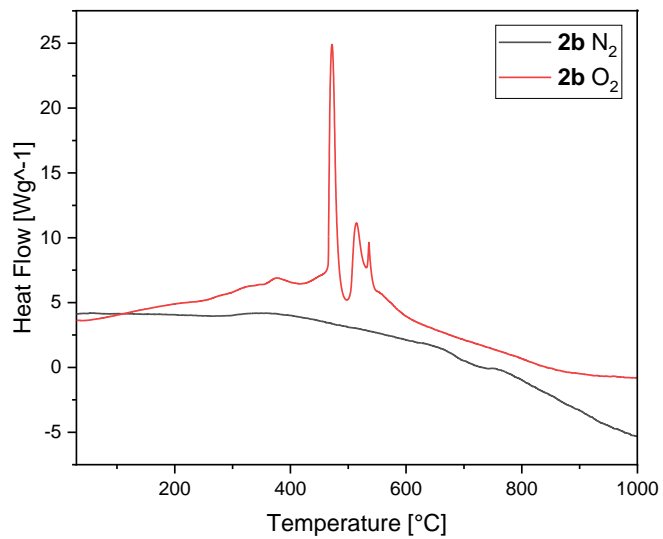
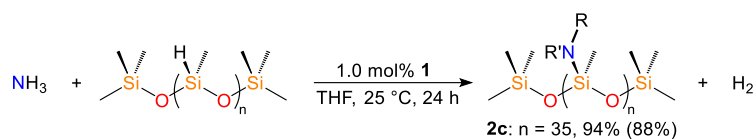


Figure S33. DSC thermogram of **2b** under N₂ and O₂.

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



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

In the glove box under N₂ 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, 2 atm of NH₃ 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 H₂ 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⁻¹): 3536-3368 (weak, N-H), 3028-2843 (strong, C-H), 2165 (broad, Si-H), 808 (strong, Si-N). TGA (N₂): T_{-5%} = 740 °C, total % wt. loss at 1000 °C = 8%. TGA (O₂): T_{-5%} = 486 °C, total % wt. loss at 1000 °C = 11%.

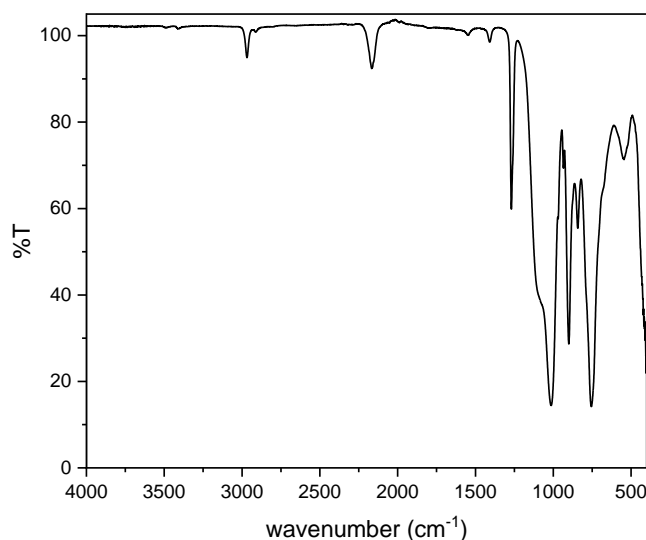


Figure S34. FT-IR spectrum of **2c**.

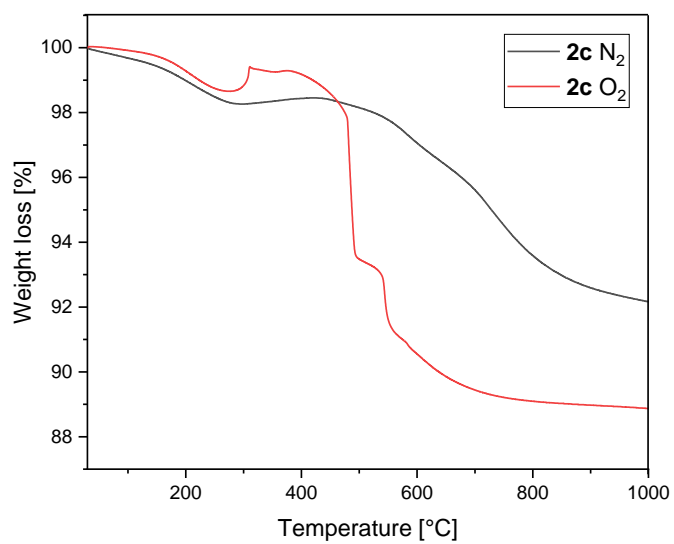


Figure S35. TGA thermogram of **2c** under N_2 and O_2 .

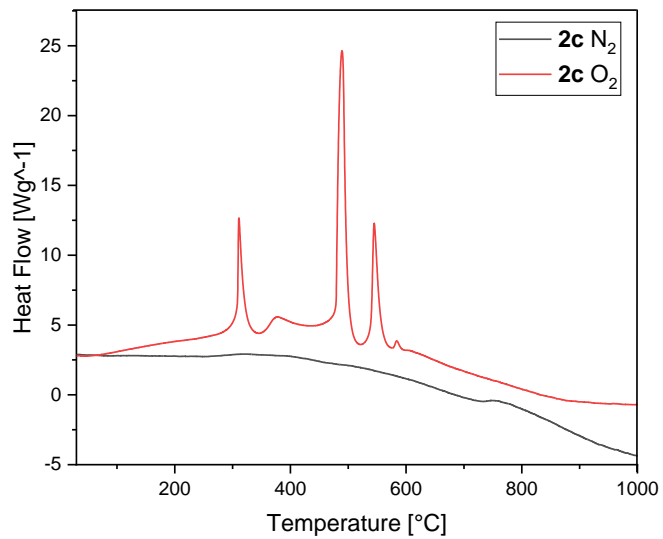
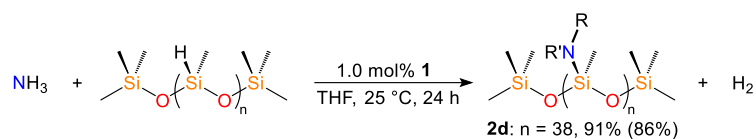


Figure S36. DSC thermogram of **2c** under N_2 and O_2 .

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



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

In the glove box under N₂ 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, 2 atm of NH₃ 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 H₂ 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⁻¹): 3545-3375 (broad, N-H), 3015-2825 (strong, C-H), 2170 (broad, Si-H), 812 (strong, Si-N). TGA (N₂): T_{-5%} = 527 °C, total % wt. loss at 1000 °C = 12%. TGA (O₂): T_{-5%} = 430 °C, total % wt. loss at 1000 °C = 14%.

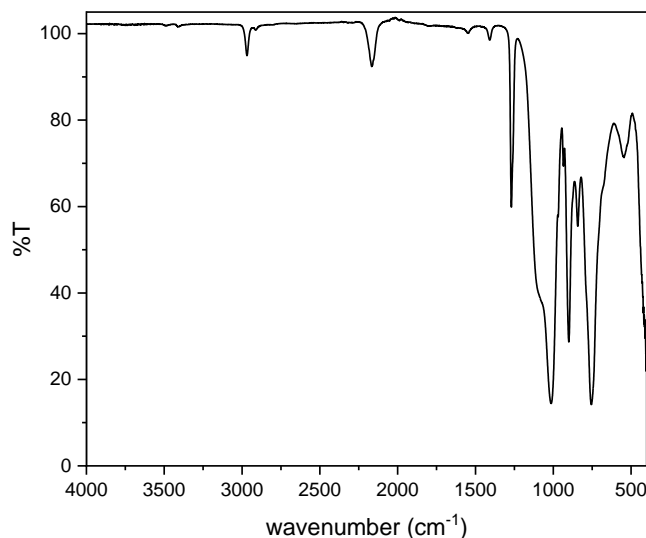


Figure S37. FT-IR spectrum of **2d**.

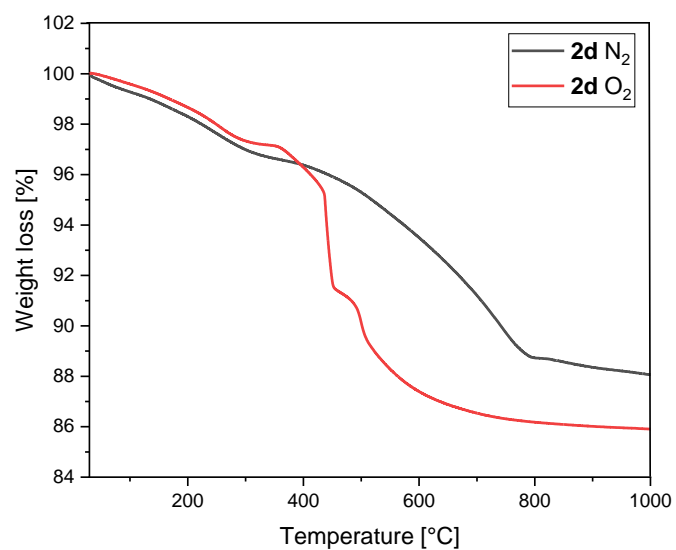


Figure S38. TGA thermogram of **2d** under N₂ and O₂.

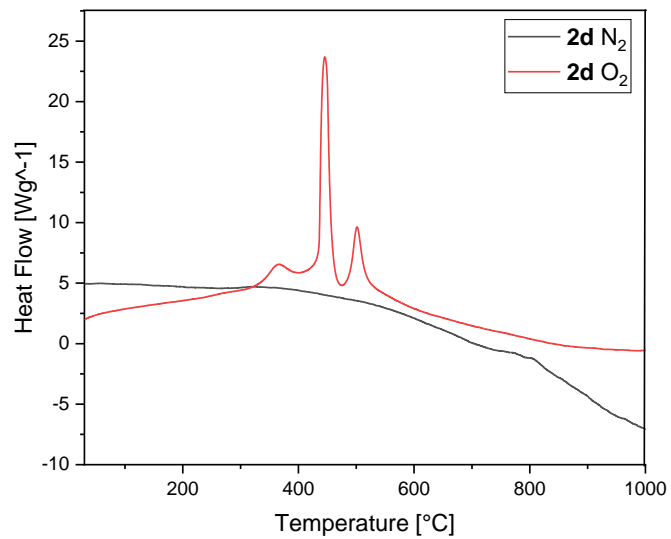
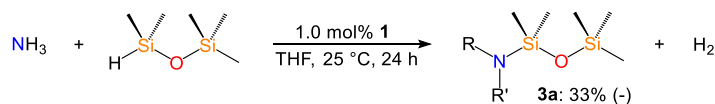


Figure S39. DSC thermogram of **2d** under N₂ and O₂.

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 N₂ 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, 2 atm of NH₃ 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 H₂ 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 ¹H NMR spectroscopy revealed 33% amination of the siloxane. ¹H NMR (400 MHz, benzene-*d*₆): 4.85 (s, SiH), 0.11 (s, OSi(CH₃)NH), 0.06 (OSi(CH₃)₃).

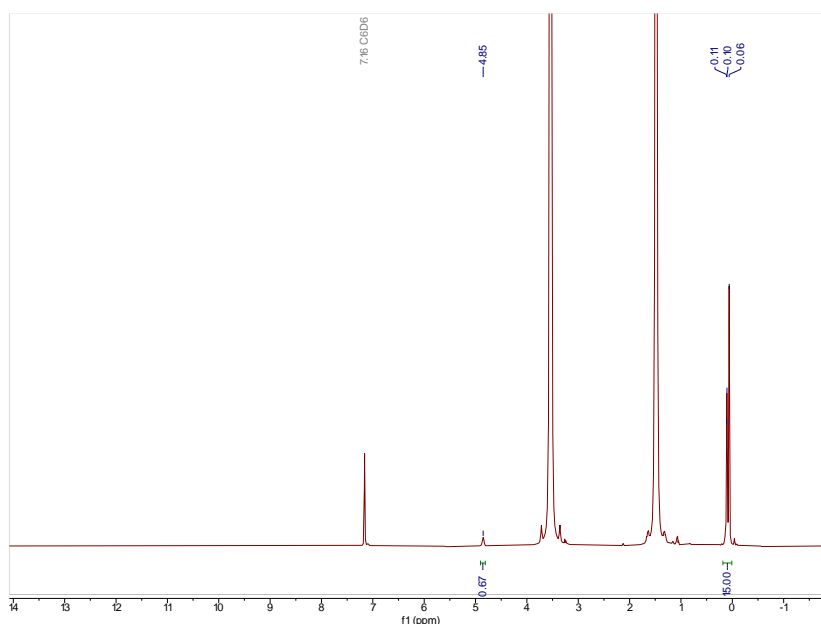
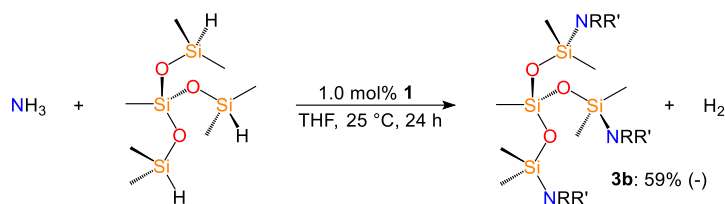


Figure S40. ¹H NMR spectrum showing conversion to **3a** in benzene-*d*₆.

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



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

In the glove box under N₂ atmosphere, 0.141 g (0.528 mmol) of methyl(tris(dimethylsiloxyl)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, 2 atm of NH₃ 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 H₂ 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 ¹H NMR spectroscopy revealed 59% amination of the siloxane Si–H units. ¹H NMR (400 MHz, benzene-*d*₆): 5.03 (s, SiH), 0.35-0.20 (broad, (CH₃)Si, (CH₃)₂Si).

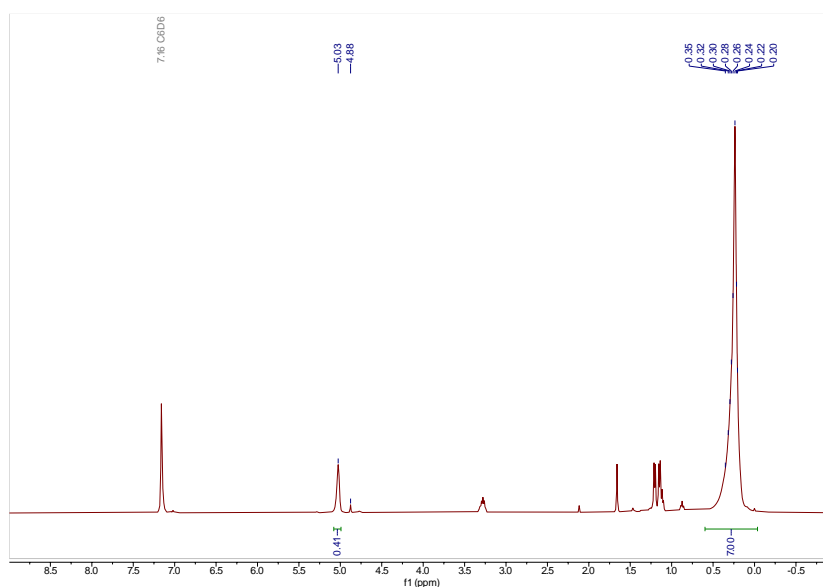
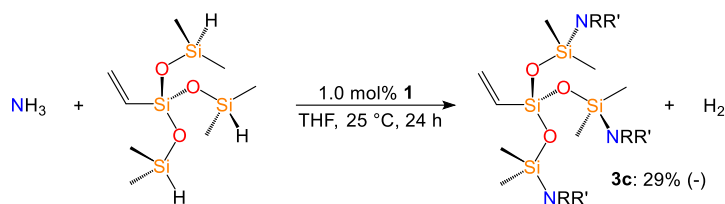


Figure S41. ¹H NMR spectrum showing conversion to **3b** in benzene-*d*₆.

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 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, 2 atm of 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 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 ^1H NMR spectroscopy revealed 29% amination of the siloxane Si-H units. ^1H NMR (400 MHz, benzene- d_6): 6.04-5.93 (m, *vinyl*), 4.99 (s, SiH), 0.20 (broad, CH_3).

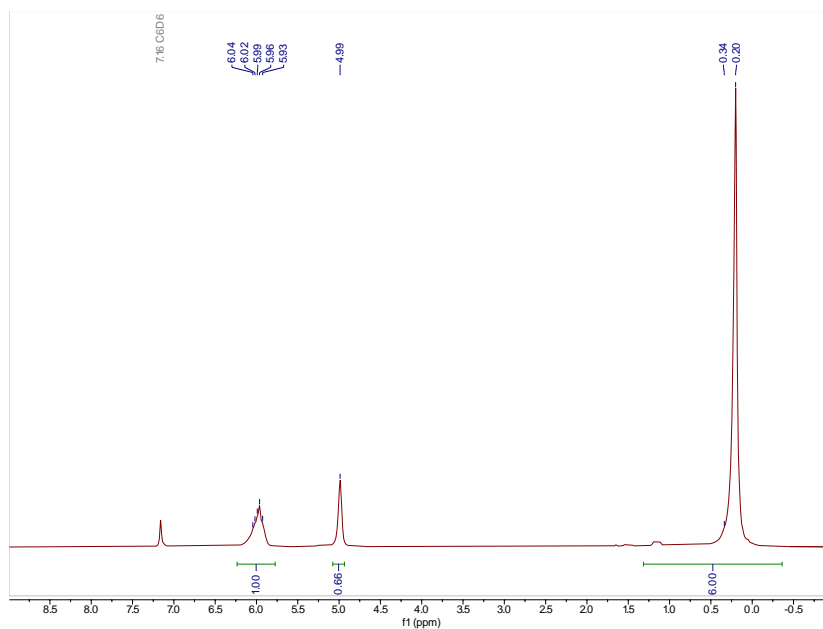
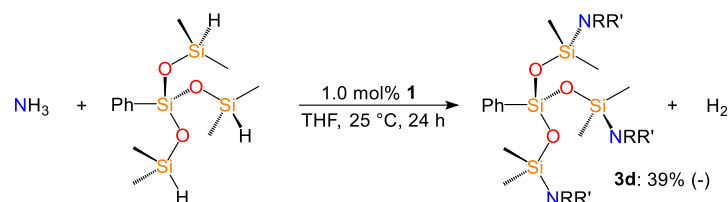


Figure S42. ^1H NMR spectrum showing conversion to **3c** in benzene- d_6 .

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 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, 2 atm of 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 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 ^1H NMR spectroscopy revealed 39% amination of the siloxane Si-H units. ^1H 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, $(\text{CH}_3)_2\text{Si}$).

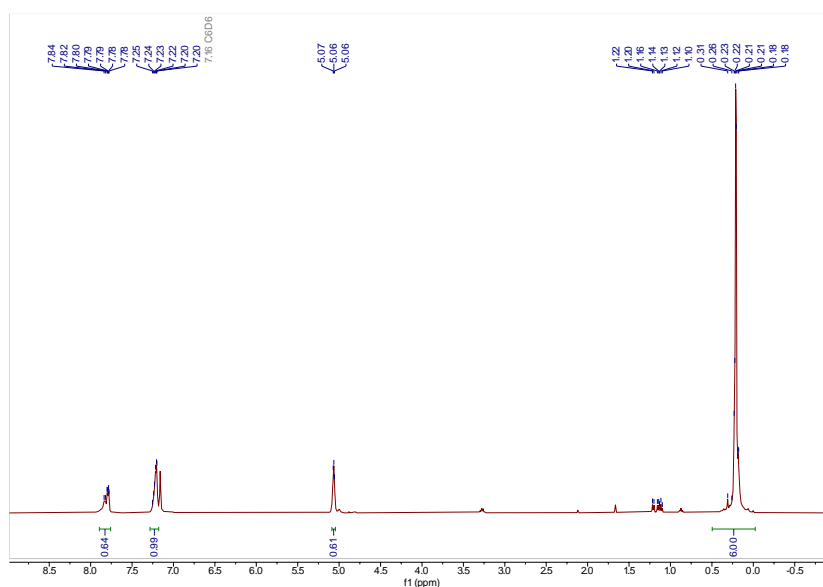
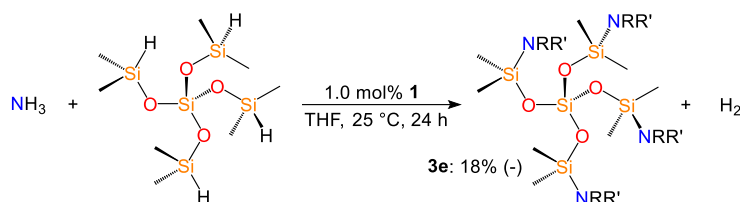


Figure S43. ^1H NMR spectrum showing conversion to **3d** in benzene- d_6 .

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



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

In the glove box under N_2 atmosphere, 0.173 g (0.528 mmol) of tetrakis(dimethylsiloxo)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, 2 atm of 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 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 ^1H NMR spectroscopy revealed 18% amination of the siloxane Si-H units. ^1H NMR (400 MHz, benzene- d_6): 4.95 (SiH), 0.21 ($(\text{CH}_3)_2\text{SiO}$).

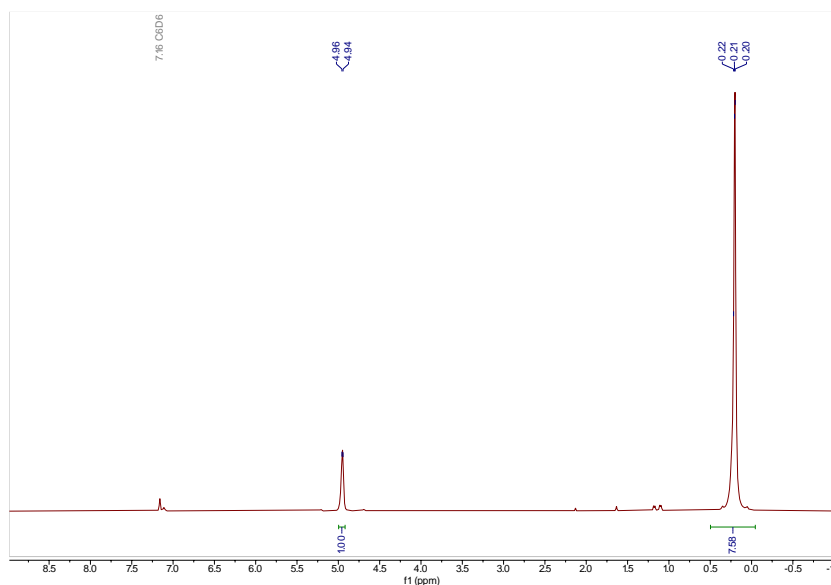
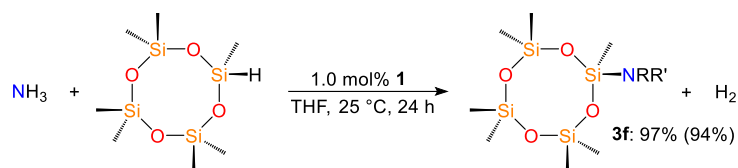


Figure S44. ^1H NMR spectrum showing minimal conversion to **3e** in benzene- d_6 .

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 N₂ 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, 2 atm of NH₃ 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 H₂ 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. ¹H 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%). ¹H NMR (400 MHz, benzene-*d*₆): 4.99 (s, SiH), 0.76–0.63 (broad, NH, NH₂), 0.26 (broad, OSi(CH₃)OSiNH), 0.19 (broad, OSi(CH₃)). ¹³C NMR (100 MHz, benzene-*d*₆): 1.40 ((CH₃)SiNH, (CH₃)SiOSiNH), 1.02 (O(CH₃)SiO). ²⁹Si NMR (79 MHz, benzene-*d*₆): -19.48 (OSiNH), -19.83 (OSiNH₂), -21.83 (OSiO, OSiOSiNH). IR (KBr, cm⁻¹): 3550–3370 (broad, N–H), 2990–2825 (strong, C–H), 2110 (weak, Si–H), 801 (weak, Si–N overlapped with Si–O).

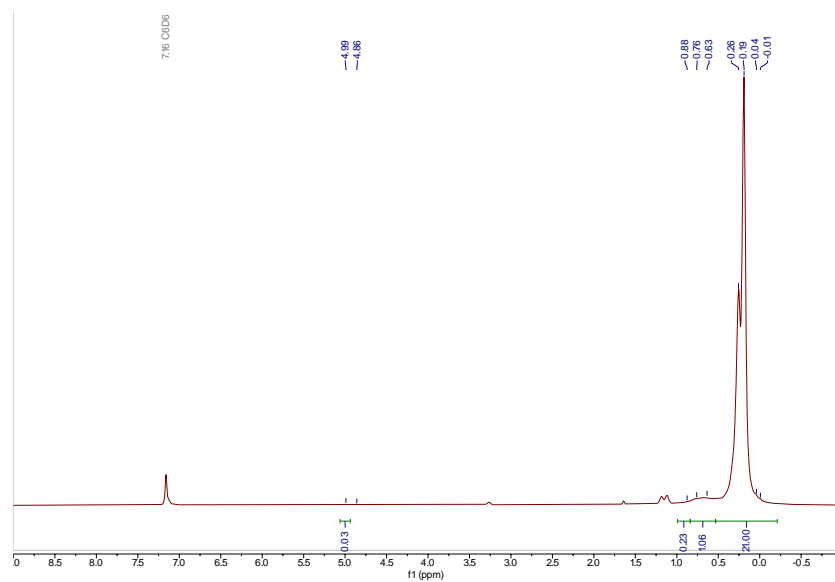


Figure S45. ^1H NMR spectrum of **3f** in benzene- d_6 .

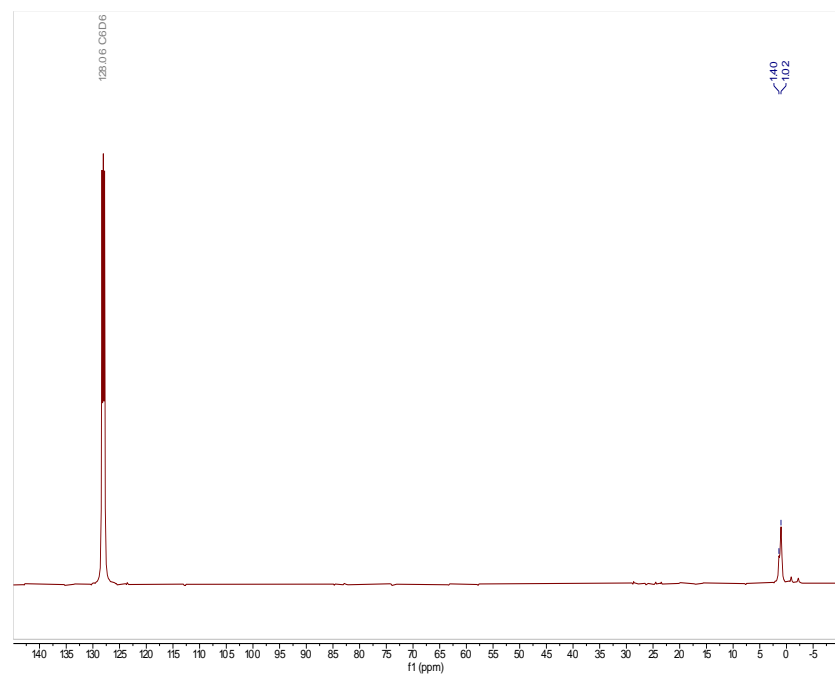


Figure S46. ^{13}C NMR spectrum of **3f** in benzene- d_6 .

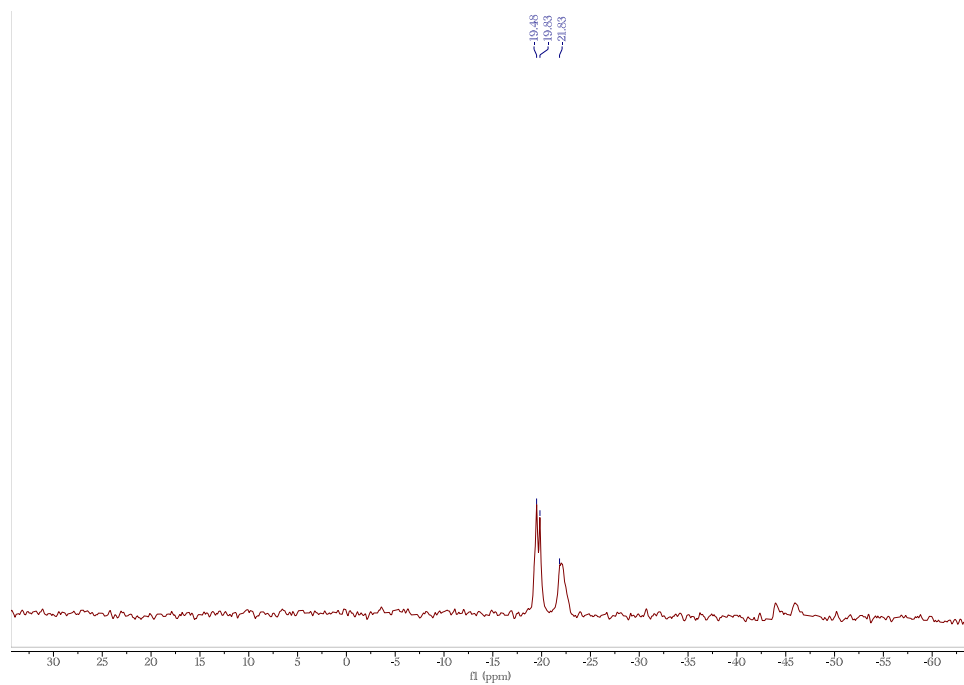


Figure S47. ^{29}Si NMR spectrum of **3f** in benzene- d_6 .

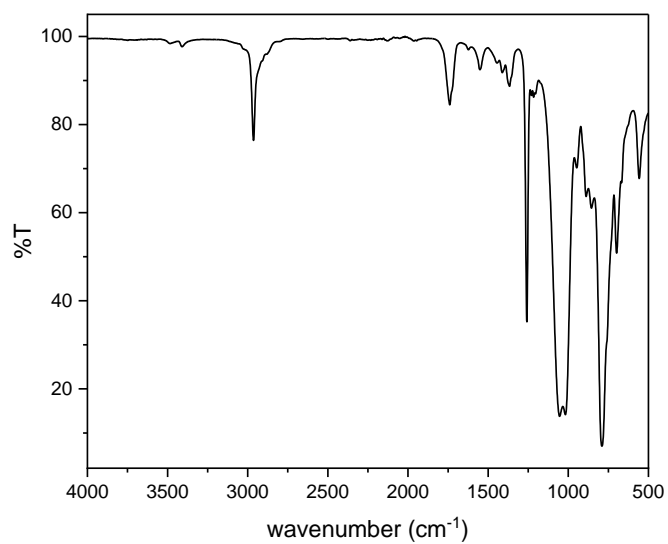
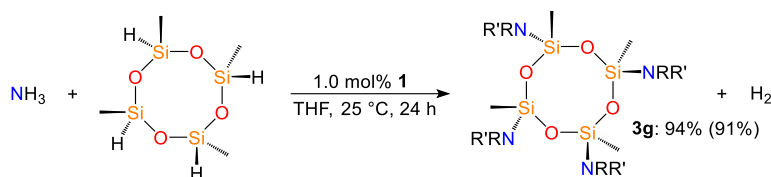


Figure S48. FT-IR spectrum of **3f**.

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



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

In the glove box under N₂ 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, 2 atm of NH₃ 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 H₂ 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. ¹H NMR spectroscopy revealed 94% amination of the siloxane Si–H units and the yield was 0.256 g (DOSY M_w = 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 facilitated TGA and DSC analysis. ¹H NMR (400 MHz, benzene-*d*₆): 5.08 (broad, SiH), 0.9–0.6 (broad, NH, NH₂), 0.28 (broad, OCH₃SiONH, OCH₃SiO). ¹³C NMR (100 MHz, benzene-*d*₆): 1.04 (broad, CH₃OSiONH), 3.32 ((CH₃)OSiO(NH₂)). ²⁹Si NMR (79 MHz, benzene-*d*₆): -46.11 to -44.11 (OSiO(CH₃)NH₂), -64.59 to -66.72 (OSiO(CH₃)(NH₂)). IR (KBr, cm⁻¹): 3530–3370 (broad, N–H), 3000–2845 (strong, C–H), 2127 (weak, Si–H), 845 (strong, Si–N). TGA (N₂): T_{-5%} = 353 °C, total % wt. loss at 1000 °C = 16%. TGA (O₂): T_{-5%} = 356 °C, total % wt. loss at 1000 °C = 15%.

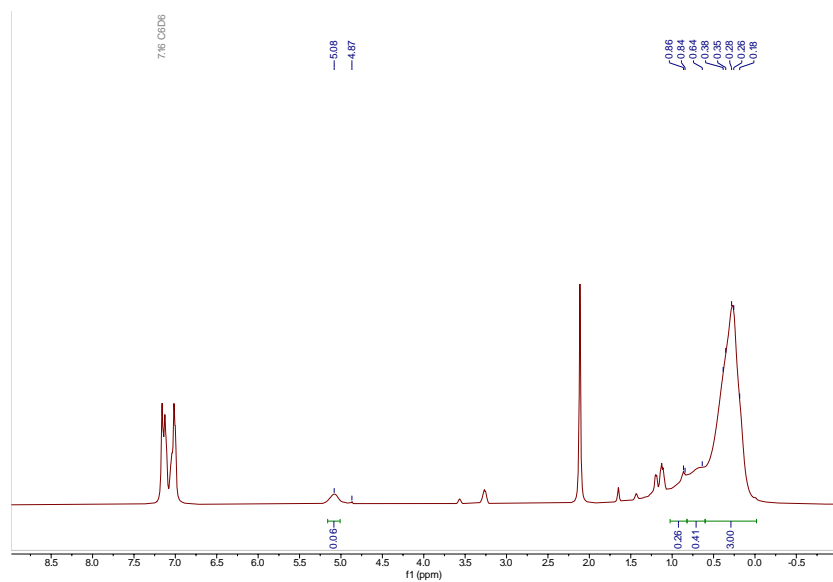


Figure S49. Representative ^1H NMR spectrum of **3g** in benzene- d_6 .

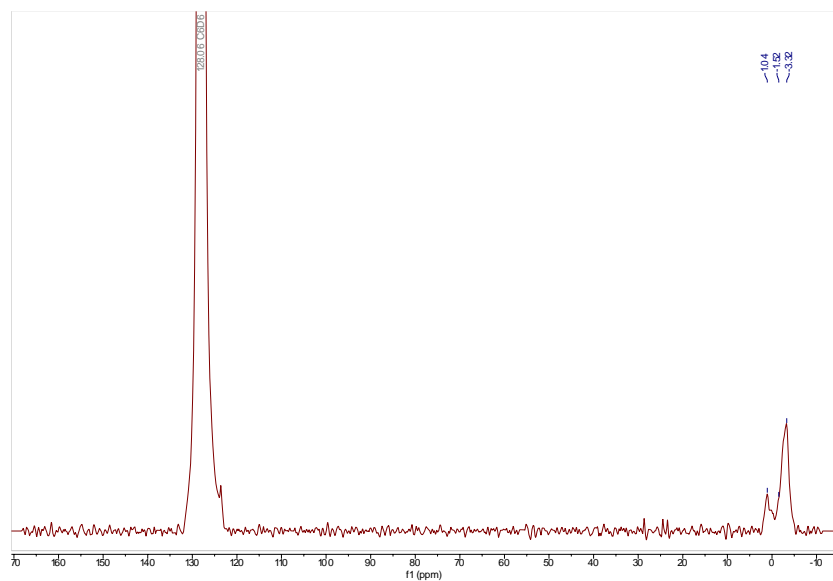


Figure S50. Representative ^{13}C NMR spectrum of **3g** in benzene- d_6 .

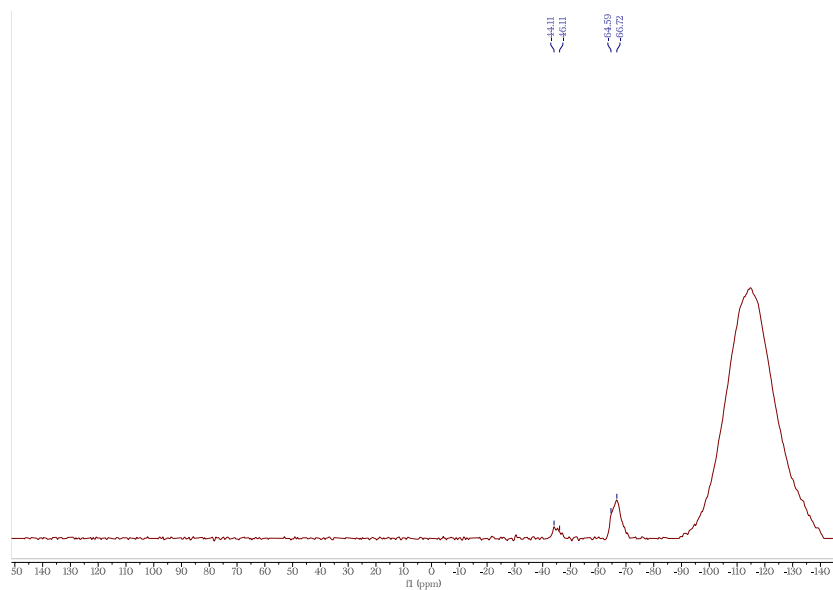


Figure S51. ^{29}Si NMR spectrum of **3g** in benzene- d_6 . Data was acquired over the course of 12 h and the large peak at -112 ppm is glass.

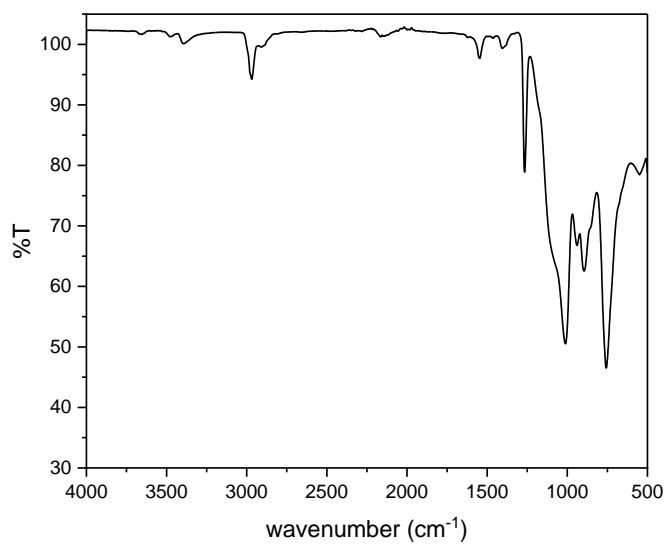


Figure S52. FT-IR spectrum of **3g**.

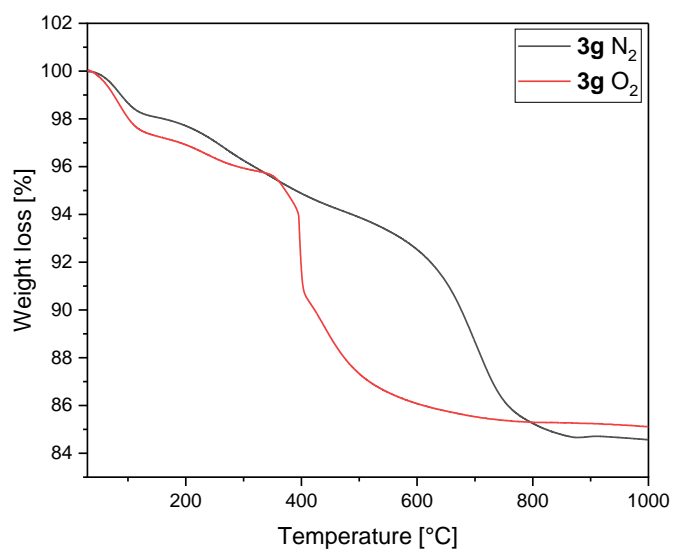


Figure S53. TGA thermogram of **3g** under N_2 and O_2 .

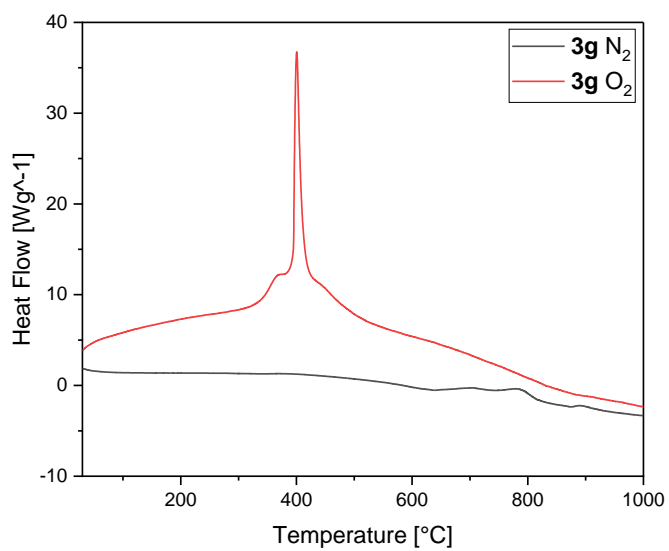
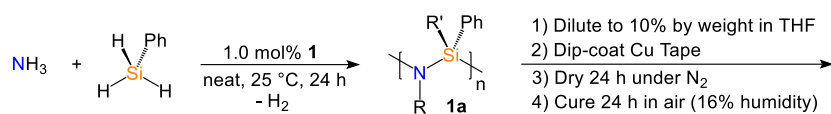


Figure S54. DSC thermogram of **3g** under N_2 and O_2 .

APPLICATION OF COATINGS



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

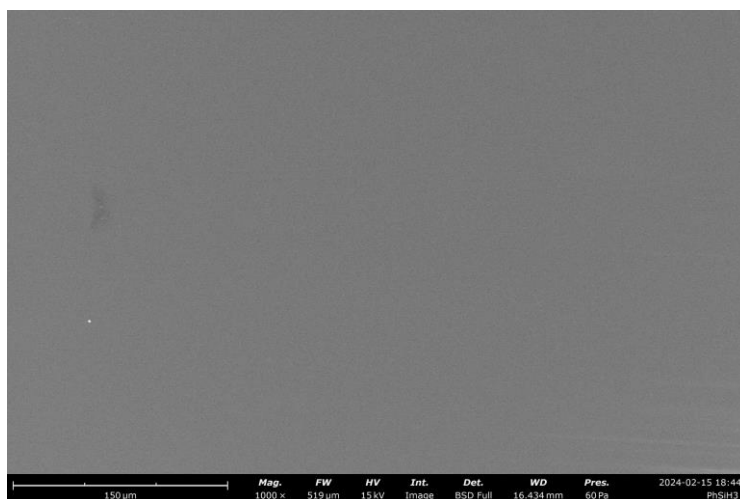


Figure S55. SEM image of **1a**-coated copper at 1,000× magnification after curing for 24 h at 25 °C (16% humidity).

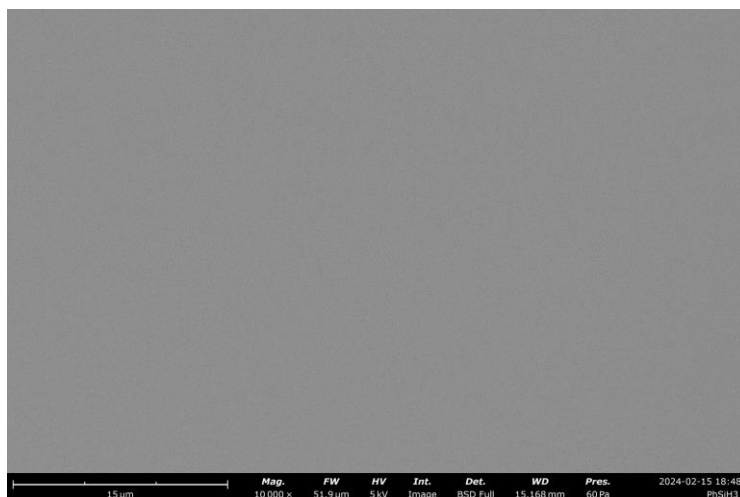


Figure S56. SEM image of **1a**-coated copper at 10,000× magnification after curing for 24 h at 25 °C (16% humidity).

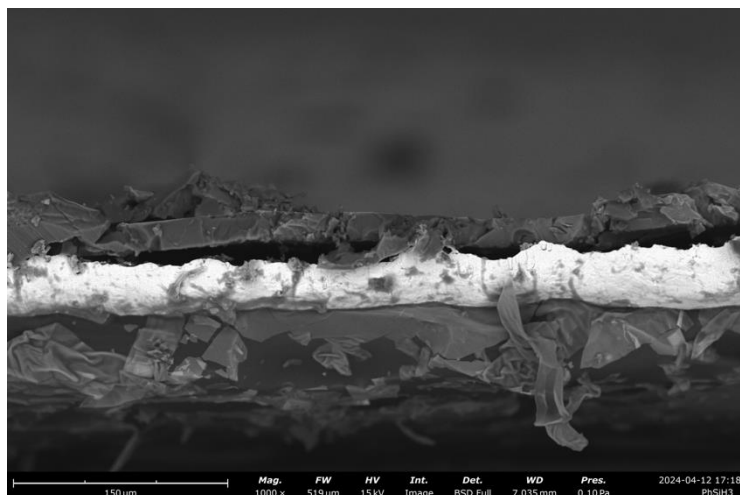


Figure S57. SEM image showing the cross section of **1a**-coated copper tape at 1,000× magnification after curing in air for 24 h at 25 °C (16% humidity). The white strip across the center of the image is copper metal and the brittle coating of **1a** above it was found to be 20 μm thick. The material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

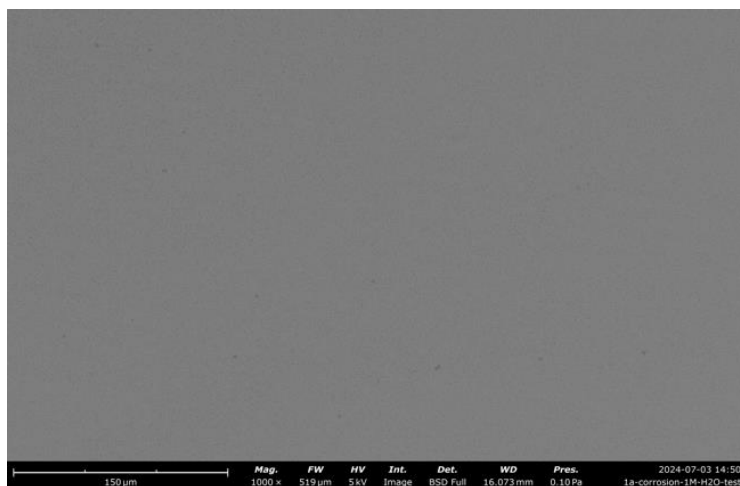


Figure S58. SEM image of **1a**-coated copper at 1,000× magnification after curing in air for 24 h, followed by submersion in deionized H₂O for 24 h, followed by drying in air for 24 h at 25 °C.

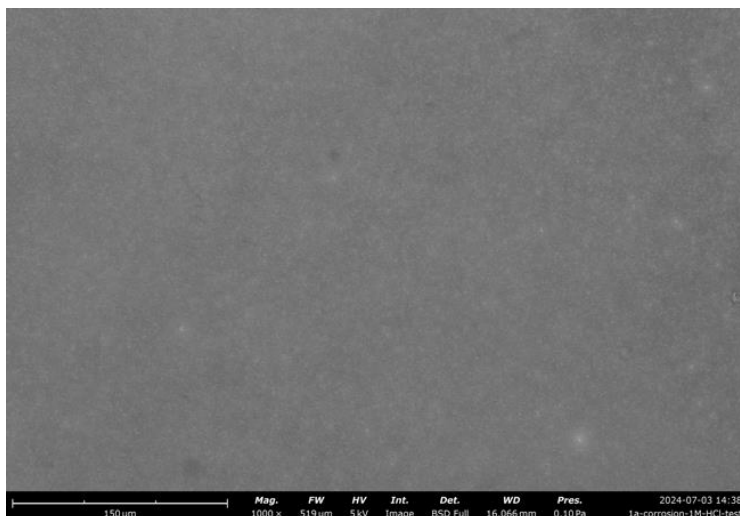
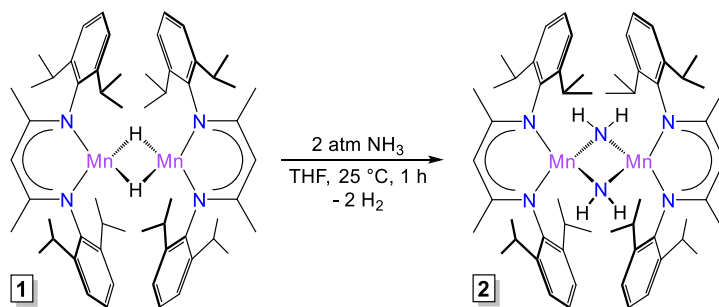


Figure S59. SEM image of **1a**-coated copper at 1,000 \times magnification after curing in air for 24 h, followed by submersion in 1.0 M HCl for 24 h, followed by drying in air for 24 h at 25 °C.

INTERMEDIATE SYNTHESIS



Scheme S25. Preparation of [(^{2,6}-iPr₂PhBDI)Mn(μ-NH₂)]₂ (**2**).

Under N₂ 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 N₂ and attached to the vacuum line. The solution was frozen in liquid N₂, gas was removed from the head space under vacuum, and 2 atm of NH₃ 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 H₂ 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 H₂ and NH₃ 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 °C. Anal. for C₅₈H₈₆Mn₂N₆: 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 °C): μ_{eff} = 6.24 μ_B. IR (KBr, cm⁻¹): 3375 (broad, N-H), 3100-2790 (strong, C-H), 1540 (weak, C=N), 1524 (strong, C=C).

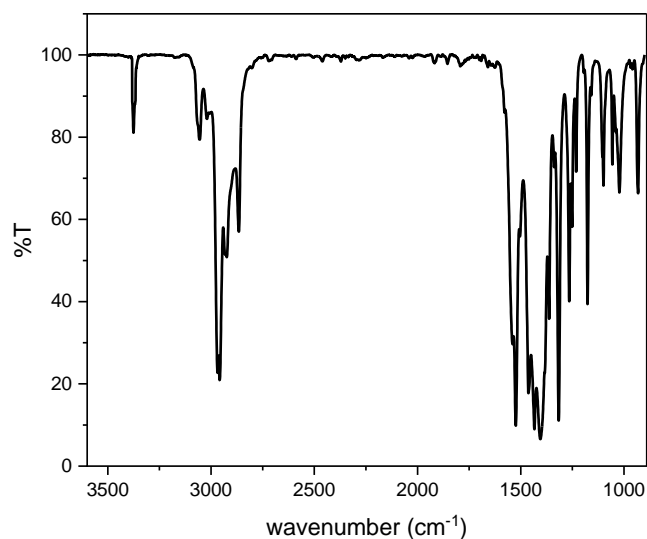


Figure S60. FT-IR spectrum of **2** in KBr.

CRYSTALLOGRAPHIC TABLES

Table S1. Crystallographic Data for $[(^{2,6}\text{-iPr}_2\text{PhBDI})\text{Mn}(\mu\text{-NH}_2)]_2$ (**2**).

	2
chemical formula	$\text{C}_{58}\text{H}_{86}\text{Mn}_2\text{N}_6$
formula weight	977.20
crystal dimensions	$0.295 \times 0.159 \times 0.151$
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 ³)	5483.(4)
Z	4
T (°C)	123.0(1)
ρ_{calcd} (g cm ⁻³)	1.184
μ (mm ⁻¹)	0.502
reflections collected	22437
data/restraints/parameters	4996/0/308
R ₁ [$I > 2\sigma(I)$]	0.0630
wR ₂ (all data)	0.1273
Goodness-of-fit	1.051
Largest peak, hole (eÅ ⁻³)	0.648, -0.347

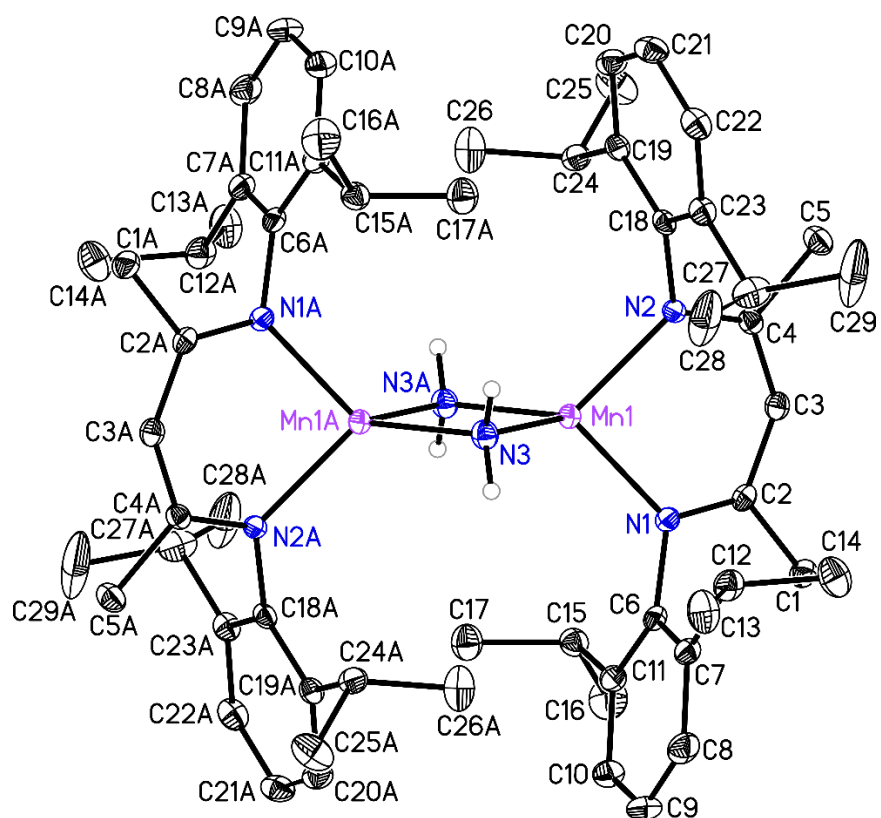
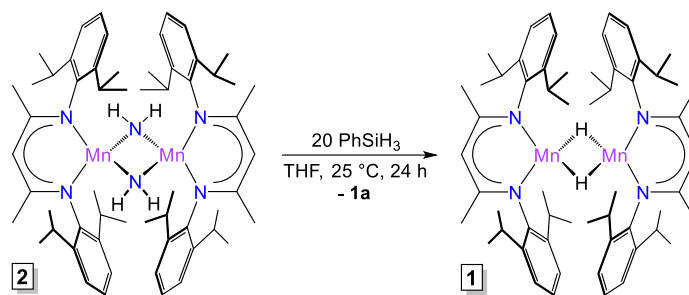


Figure S61. The molecular structure of **2** displayed at 30% probability ellipsoids. Hydrogen atoms, except those located on the bridging amido groups, are omitted for clarity.

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

In the glove box under 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**.² ^1H 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).

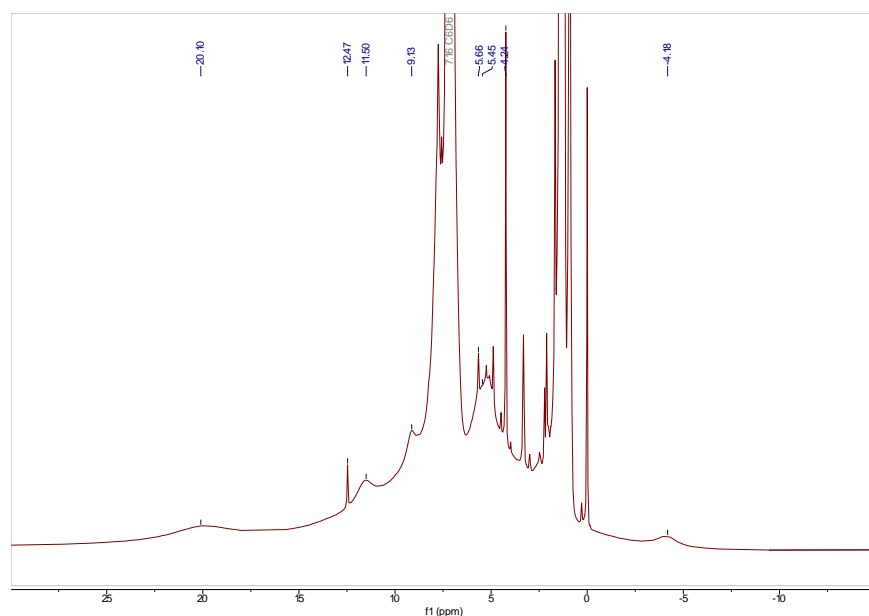
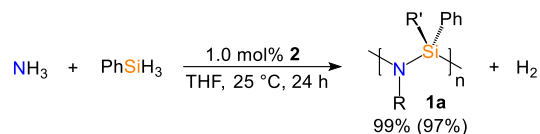


Figure S62. ^1H NMR spectrum of **1** prepared from **2** and phenylsilane in benzene- d_6 at 25 °C.

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 N₂ 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, 2 atm of NH₃ 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 H₂ 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. ¹H 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). ¹H 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)(NH₂)PhSiH, (NH₂)₂PhSiH, (NH)PhSiH₂, (NH₂)PhSiH₂), 0.84 (broad, NH, NH₂).

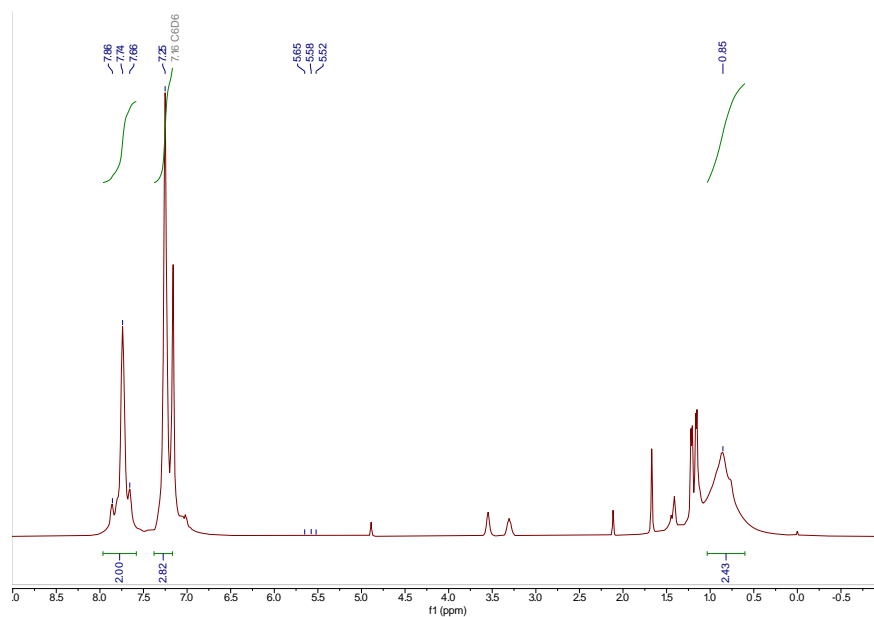


Figure S63. ^1H NMR spectrum of **1a** prepared from **2** in benzene- d_6 .

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