# *Electronic Supplementary Information*

# Silane Diamine Copolymers: Efficient Synthesis, Solvent Absorption Capacity, and Limitations as Coatings

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## GENERAL CONSIDERATIONS

All reactions were performed inside an MBraun glovebox under an atmosphere of purified nitrogen. 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. Mesitylene was purchased from Sigma-Aldrich and dried over 4 Å molecular sieves. Celite and phenylsilane were obtained from Oakwood, while octylsilane was obtained from Gelest. Ethylenediamine, 1,4-diaminobutane, 1,6-diaminohexane, 1,12-diaminododecane, 2,2'-(ethylenedioxy)bis(ethylamine), and 4,7,10-trioxa-1,13-tridecanediamine were purchased from Oakwood Chemicals. All liquid substrates were dried over 4 Å molecular sieves prior to catalyst screening. $[(^{2,6\text{-}i\text{Pr}_2\text{Ph}}\text{BDI})\text{Mn}(\mu\text{-H})]_2$ (**1**) was synthesized according to literature procedure.[1]

**Nuclear Magnetic Resonance (NMR) Spectroscopy:** Solution NMR spectra were recorded at room temperature on a Varian 400 MHz or a Bruker 400 MHz NMR spectrometer. All $^1$H NMR chemical shifts were referenced to $SiMe_4$ using the residual $^1$H chemical shift of the solvent as a secondary standard.

**MALDI-TOF Mass Spectrometry:** Samples were analyzed on a Bruker microFlex LRF instrument (Billerica, MA, USA) with a 337 nm laser in positive mode scanning from 200 to 200,000 *m/z*. The ion source 1 voltage was 19.50 kV, ion source 2 voltage was 18.15 kV, the lens voltage was 7.00 kV, and ion suppression was off.

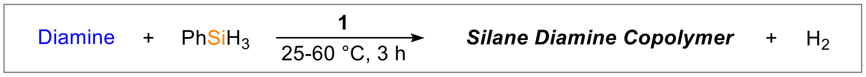
**Thermogravimetric Analysis and Differential Scanning Calorimetry (TGA-DSC):** TGA-DSC were performed using a METTLER Toledo TGA/DSC1 STAR system. All samples were heated from 30 °C to 1000 °C at a rate of 10 °C per minute under $N_2$ or $O_2$ atmosphere.

**Powder X-ray Diffraction (PXRD)**: PXRD patterns of all samples after TGA were collected on a Bruker D2 Phaser powder X-ray diffractometer with a Cu Kα radiation wavelength of 1.5406 Å at a scan speed of 1 second/step and a step size of 0.02°.

**Scanning Electron Microscopy and Energy-dispersive X-ray Analysis (SEM-EDX):** Solutions of lightly-cured silane diamine polymers were dip-coated on copper tape prior to microscopic analysis. Scanning electron microscopy (SEM) images of selected samples were collected on a FIB Zeiss Auriga microscope operating at 5.0 kV acceleration voltage. Energy-dispersive X-ray data was collected on the same unit at 20 kV acceleration voltage.

## DETERMINATION OF STANDARD REACTION CONDITIONS

**Table S1.** Optimization of **1**-catalyzed dehydrocoupling to prepare silane diamine copolymers.

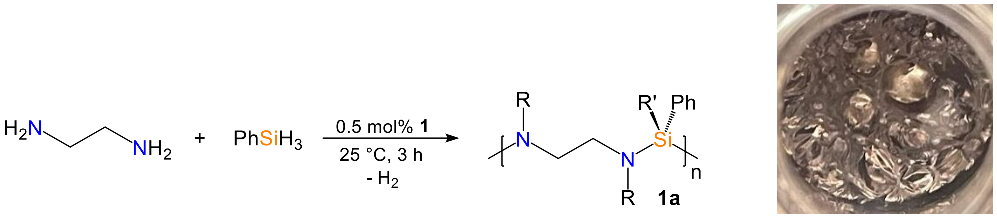


| Entry | Diamine | Solvent | Temperature | mol% | % Conversion |
|---|---|---|---|---|---|
| 1 | ethylenediamine | Neat | 25 °C | 1.0 | 99% |
| 2 | ethylenediamine | Neat | 25 °C | 0.5 | 99% |
| 3 | 1,6-diaminohexane | Neat | 25 °C | 0.5 | 68% |
| 4 | 1,6-diaminohexane | THF | 25 °C | 0.5 | 58% |
| 5 | 1,6-diaminohexane | Toluene | 25 °C | 0.5 | 66% |
| 6 | 1,6-diaminohexane | Pentane | 25 °C | 0.5 | 70% |
| 7 | 1,6-diaminohexane | Neat | 60 °C | 0.5 | 99% |

Percent conversion determined by $^1H$ NMR spectroscopy (integration of residual diamine against 1 mmol of mesitylene standard). For entries 4-6, 1 mL of solvent was added.

## PREPARATION OF SILANE DIAMINE NETWORKS

### Preparation of silane diamine 1a from phenylsilane and ethylenediamine using 0.5 mol% 1.



**Scheme S1.** Preparation and image of **1a**.

*Procedure for conversion determination:* In a $N_2$ filled glovebox, a 20 mL vial was weighed before adding 0.003 g (0.003 mmol) of **1**. Afterwards, 65 µL (0.53 mmol) of phenylsilane was added and no obvious color change was noted. Next, 44 µL (0.53 mmol) of ethylenediamine was added. Instantly, the evolution of hydrogen gas was observed, and the solution turned orange in color. The vial was kept uncapped under $N_2$ atmosphere for 3 h at ambient temperature to yield a dark brown solution. After 3 h, the catalyst was deactivated upon exposure to air and the solution was degassed under vacuum for 30 s. A $^1$H NMR spectrum of the wash in benzene-$d_6$ revealed more than 99% conversion of the starting diamine.

*Procedure for isolation and solid-state characterization:* In a $N_2$ filled glovebox, a 20 mL vial was weighed before adding 0.021 g (0.022 mmol) of catalyst **1**, followed by 550 µL (4.48 mmol) of phenylsilane. No obvious color change was noted. Next, 300 µL (4.48 mmol) of ethylenediamine was added. The formation of $H_2$ was observed and the solution turned orange in color. The reaction was kept uncapped at room temperature for 3 h to obtain a dark greenish-brown solid. Next, the vial was brought outside the glovebox and the catalyst was quickly deactivated upon exposure to air. The reaction was then brought back into the glovebox antechamber and degassed under vacuum for 30 s. The product was washed with pentane and ether to remove residual ligand and dried under vacuum to obtain 0.533 g (72% yield, assuming complete diamine dehydrocoupling) of a solid product identified as **1a**. MALDI-TOF of THF wash ($[M+H]^+$, m/z): 329.1 (n = 2), 696.0 (n = 4), 934.5 (n = 5 + 1 phenylsilane), 1166 (n = 7), 1455 (n = 8), 1694 (n = 10 + 1 diamine), 1977 (n = 12), 2257 (n = 13 + 1 phenylsilane), 2541 (n = 15 + 1 diamine), 2826 (n = 17 + 1 diamine), 3079 (n = 18 + 1 phenylsilane). IR (KBr, cm$^{-1}$): 3372 (broad, N–H), 3066-2848 (strong, C–H), 2119 (strong, Si–H), 830 (weak, Si–N). TGA ($N_2$): $T_{-5\%}$ = 173 °C, total % wt. loss at 1000 °C = 52%. TGA ($O_2$): $T_{-5\%}$ = 183 °C, total % wt.

loss at 1000 °C = 66%. $^1$H NMR of benzene-$d_6$ wash (500 MHz, benzene-$d_6$): 7.91 (broad, *aryl*), 7.72 (broad, *aryl*), 5.40 (s, $\mathrm{Si}H$), 5.34 (s, $\mathrm{Si}H_2$), 3.18 (broad, $\mathrm{C}H_2$), 2.96 (broad, $\mathrm{C}H_2$), 2.61 (broad, $\mathrm{C}H_2$), 0.88 (broad, $\mathrm{N}H$).

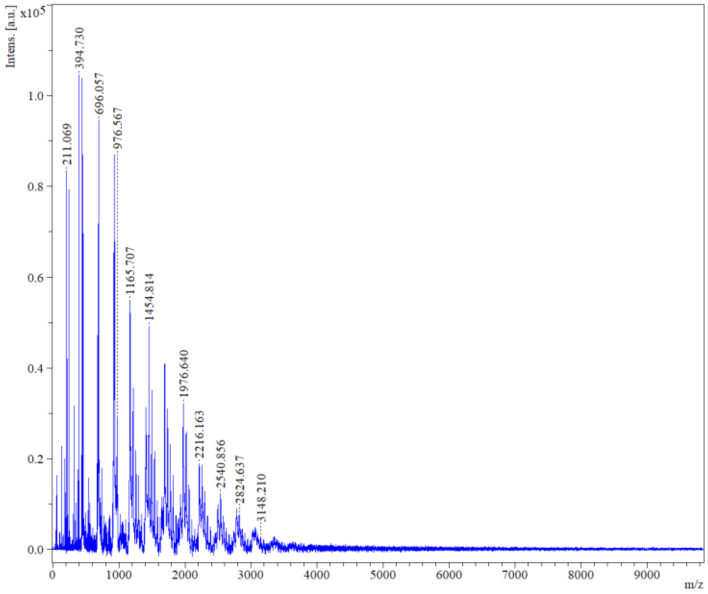


**Figure S1.** MALDI-TOF mass spectrum of **1a** THF wash.

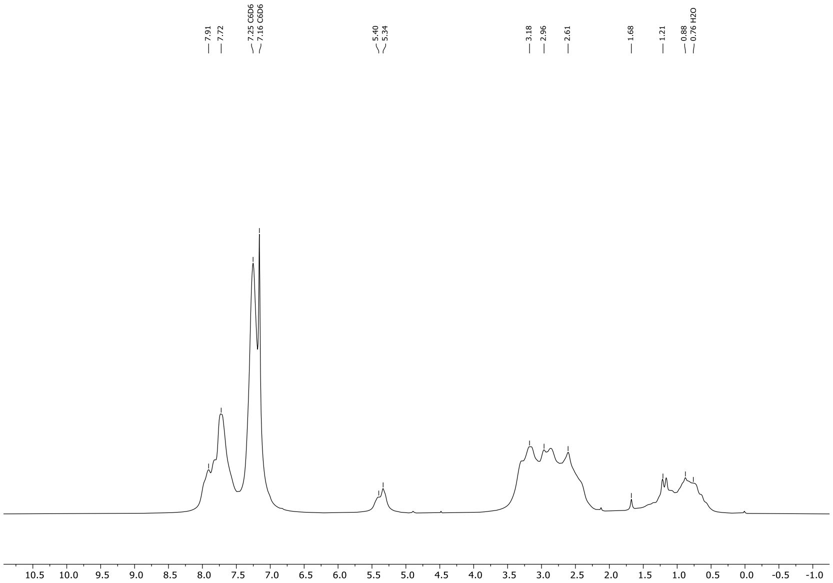


**Figure S2.** Representative $^1$H NMR spectrum of **1a** benzene-$d_6$ wash.

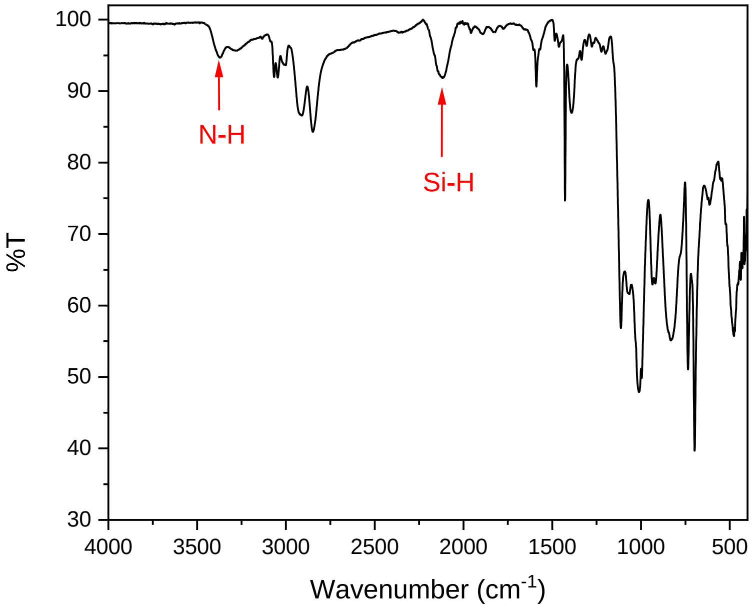


**Figure S3.** FT-IR spectrum of **1a** in KBr.

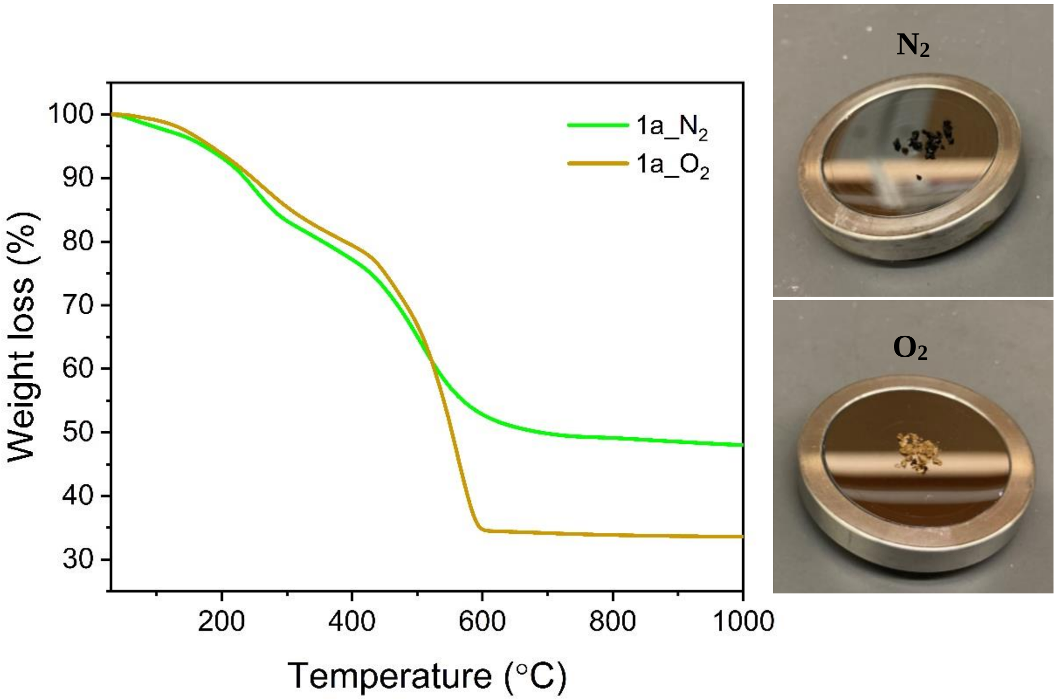


**Figure S4.** TGA thermogram of **1a** and photograph of product after TGA under $N_2$ and $O_2$.

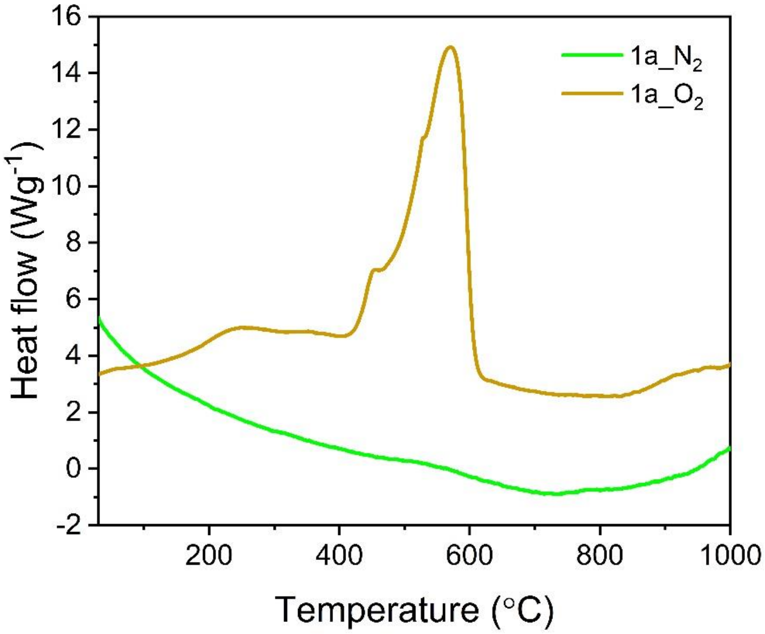


**Figure S5.** DSC thermogram of **1a** under $N_2$ and $O_2$.

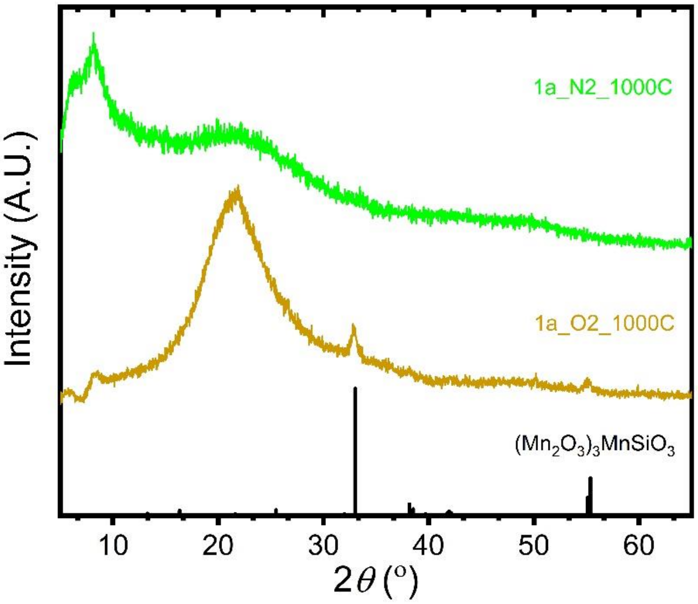
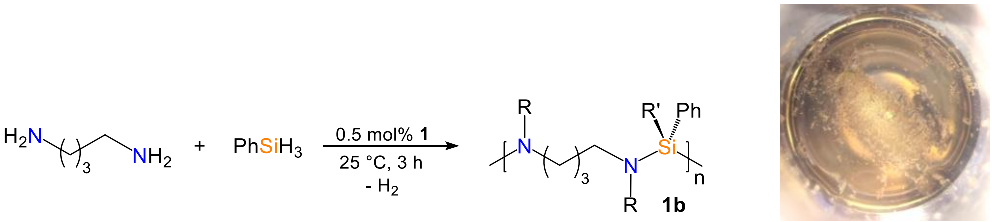


**Figure S6.** PXRD patterns of **1a** after TGA under $N_2$ and $O_2$, together with a simulated pattern of $(Mn_2O_3)_3MnSiO_3$.

**Preparation of 1b from phenylsilane and 1,4-diaminobutane using 0.5 mol% 1.**



**Scheme S2.** Preparation and image of **1b**.

*Procedure for conversion determination:* In a $N_2$ filled glovebox, a 20 mL vial was weighed before adding 0.002 g (0.002 mmol) of catalyst **1**. Afterwards, 39 µL (0.317 mmol) of phenylsilane was added and no obvious color change was noted. Next, 32 µL (0.317 mmol) of 1,4-diaminobutane in 2 mL of benzene-*d*$_6$ was added. Instantly, the evolution of hydrogen gas was observed, and the solution turned orange in color. The vial was kept uncapped under $N_2$ atmosphere for 3 h at ambient temperature to yield a dark brown solution. After 3 h, the catalyst was deactivated by quickly exposing to air and the solution was degassed under vacuum for 30 s. A $^1$H NMR spectrum of the wash in benzene-*d*$_6$ revealed greater than 99% conversion of the starting diamine.

*Procedure for isolation and solid-state characterization:* In a $N_2$ filled glovebox, a 20 mL vial was weighed before adding 0.021 g (0.023 mmol) of **1**, followed by 560 µL (4.6 mmol) of phenylsilane. No obvious color change was noted. Next, 0.422 g (4.6 mmol) of 1,4-diaminobutane in 2 mL toluene was added. The formation of $H_2$ was observed and the solution turned orange in color. The reaction was kept uncapped at room temperature for 3 h to obtain a dark brown solid. Next, the vial was brought outside the glovebox and the catalyst was deactivated upon exposure to air. The reaction was then brought back into the glovebox and degassed under vacuum for 30 s. The product was washed with pentane and ether to remove residual ligand and dried under vacuum to obtain 0.774 g (86% yield, assuming complete diamine dehydrocoupling) of a solid product identified as **1b**. IR (KBr, cm$^{-1}$): 3388-3290 (broad, N–H), 3057-2851 (strong, C–H), 2101 (strong, Si–H), 810 (weak, Si–N). MALDI-TOF of THF wash ($[M+H]^+$, m/z): 189.2 (n = 1), 393.8 (n = 2), 941.5 (n = 5), 1150 (n = 6), 1382 (n = 7), 1507 (n = 8). TGA ($N_2$): $T_{-5\%}$ = 273 °C, total % wt. loss at 1000 °C = 61%. TGA ($O_2$): $T_{-5\%}$ = 272 °C, total % wt. loss at 1000 °C = 70%.

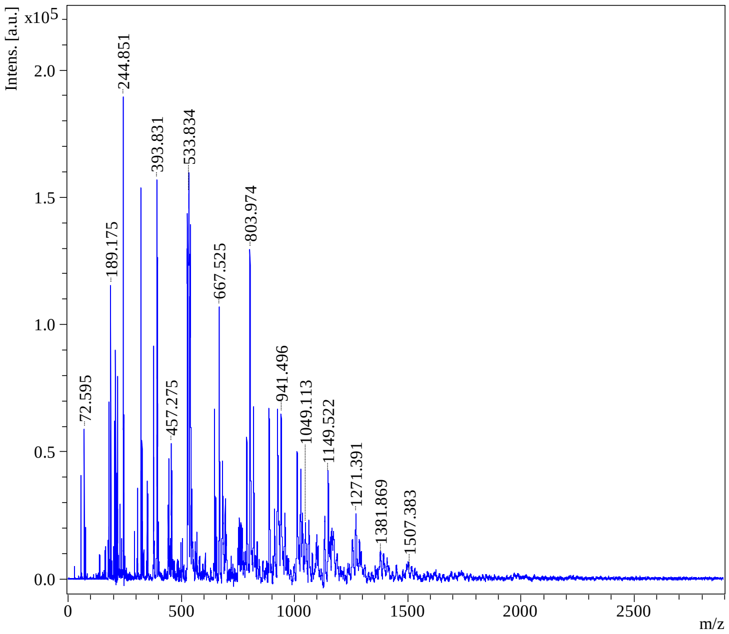


**Figure S7.** MALDI-MS spectrum of **1b** THF wash.

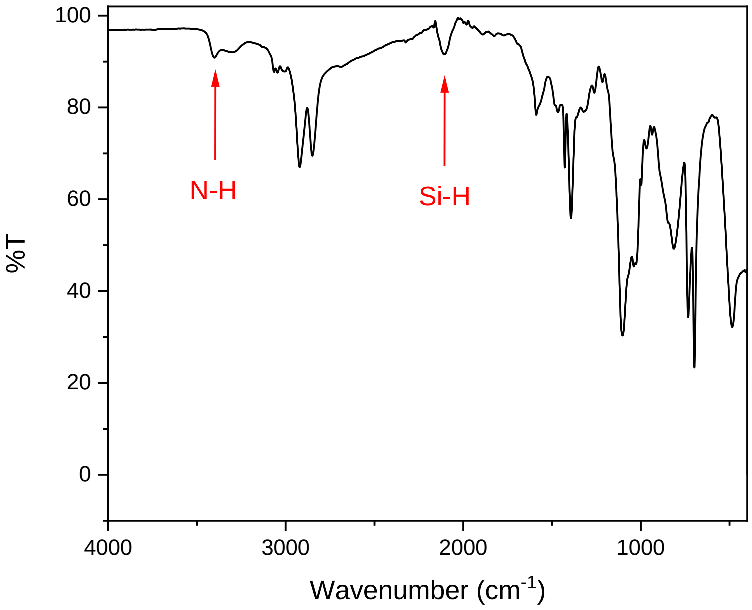


**Figure S8.** FT-IR spectrum of **1b** in KBr.

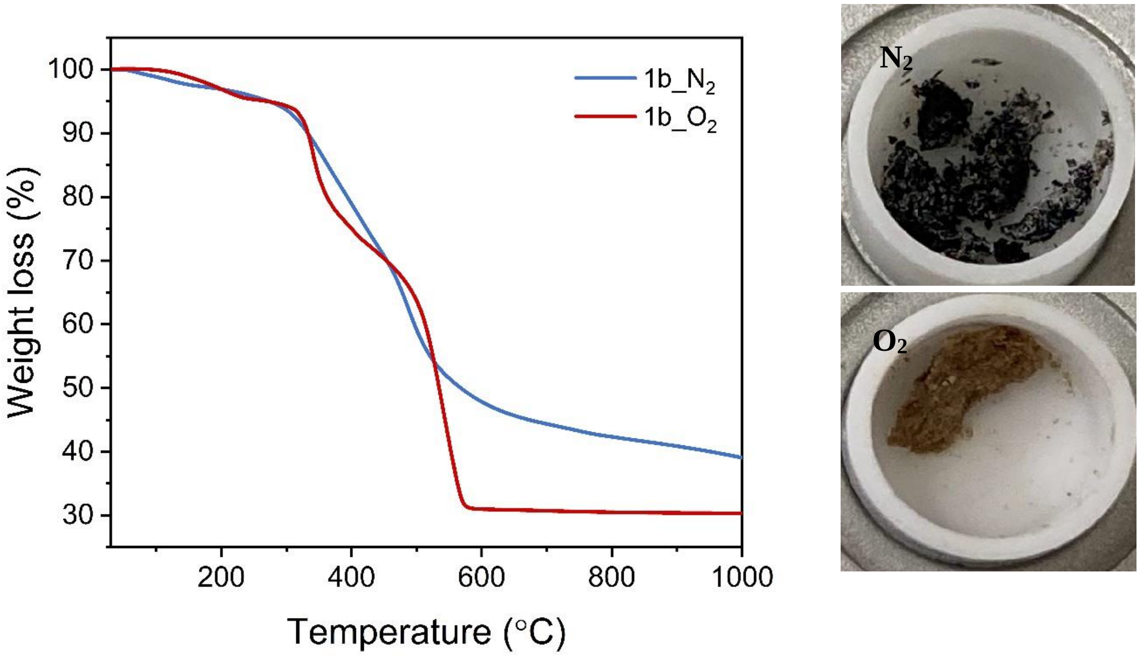


**Figure S9.** TGA thermogram of **1b** and photograph of product after TGA under N$_2$ and O$_2$.

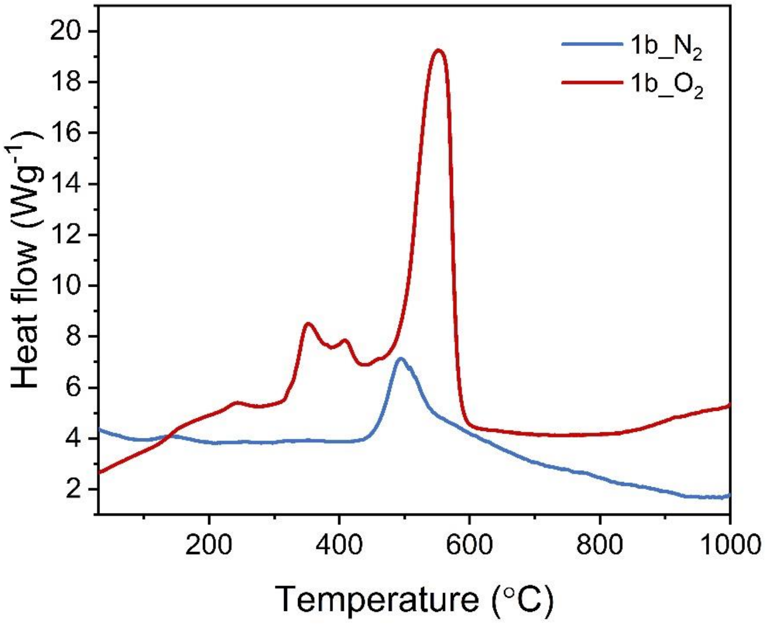


**Figure S10.** DSC thermogram of **1b** under N$_2$ and O$_2$.

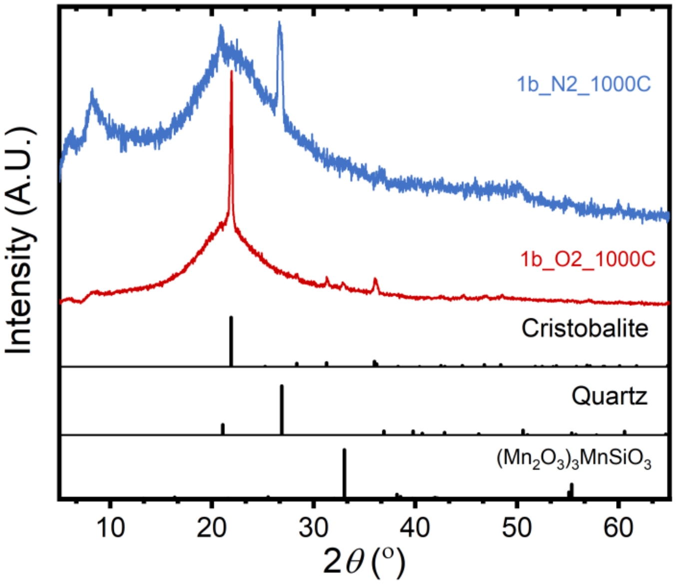
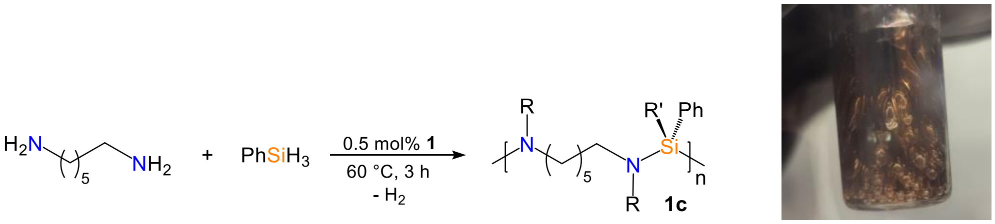


**Figure S11.** PXRD patterns of **1b** after TGA under $N_2$ and $O_2$, together with simulated patterns of cristobalite, quartz, and $(Mn_2O_3)_3MnSiO_3$.

### Preparation of 1c from phenylsilane and 1,6-diaminohexane using 0.5 mol% 1.



**Scheme S3.** Preparation and image of **1c**.

*Procedure for conversion determination:* In a $N_2$ filled glovebox, a 20 mL vial was weighed before adding 0.002 g (0.002 mmol) of catalyst **1**. Afterwards, 44 µL (0.36 mmol) of phenylsilane was added and no obvious color change was noted. Next, 0.041 g (0.36 mmol) of 1,6-diaminohexane in 2 mL benzene-$d_6$ was added. Instantly, the evolution of hydrogen gas was observed, and the solution turned orange in color. The vial was heated at 60 °C for 3 h to yield a dark brown solution. After 3 h, the catalyst was deactivated by exposing to air and the reaction was degassed under vacuum for 30 s. A $^1H$ NMR spectrum of the wash in benzene-$d_6$ revealed greater than 99% conversion of the starting diamine.

*Procedure for isolation and solid-state characterization:* In a $N_2$ filled glovebox, a 20 mL vial was weighed before adding 0.01 g (0.01 mmol) of catalyst **1**, followed by 260 µL (2.1 mmol) of phenylsilane. No obvious color change was noted. Next, 0.243 g (2.1 mmol) of 1,6-diaminohexane in 2 mL of toluene was added. The formation of $H_2$ was observed and the solution turned orange in color. The reaction was heated at 60 °C for 3 h to obtain an orangish-brown solid. Next, the vial was brought outside the glovebox and the catalyst was deactivated by exposing to air. The reaction was then brought back into the glovebox and degassed under vacuum for 30 s. The product was washed with pentane and ether to remove residual ligand and dried under vacuum to obtain 0.432 g (94% yield, assuming complete diamine dehydrocoupling) of a solid product identified as **1c**. MALDI-TOF of THF wash ($[M+H]^+$, m/z): 534.5 (n = 3 + phenylsilane), 805.8 (n = 3 + 1,6-diaminohexane), 928.1 (n = 4), 1049 (n = 4 + 1,6-diaminohexane). IR (KBr, $cm^{-1}$): 3401 (broad, N–H), 3065-2845 (strong, C–H), 2164-2094 (strong, Si–H), 850 (weak, Si–N). TGA ($N_2$): $T_{-5\%}$ = 96 °C, total % wt. loss at 1000 °C = 65%. TGA ($O_2$): $T_{-5\%}$ = 174 °C, total % wt. loss at 1000 °C = 68%.

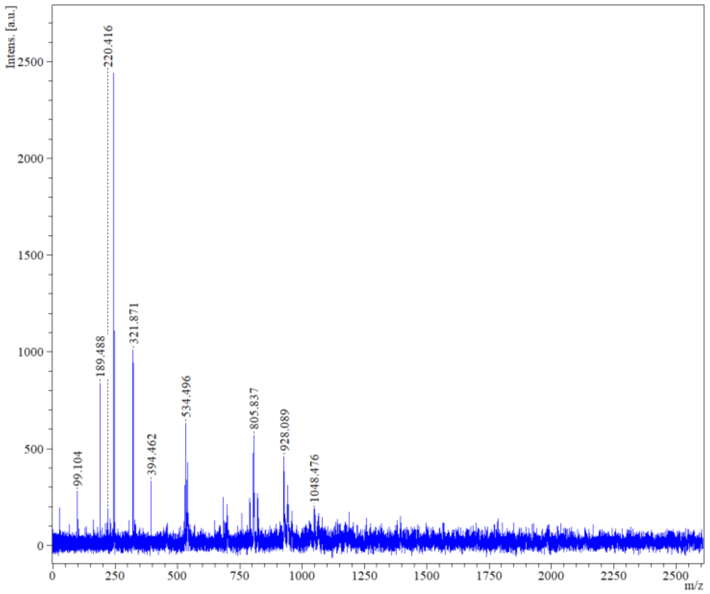


**Figure S12.** MALDI-TOF spectrum of **1c** THF wash.

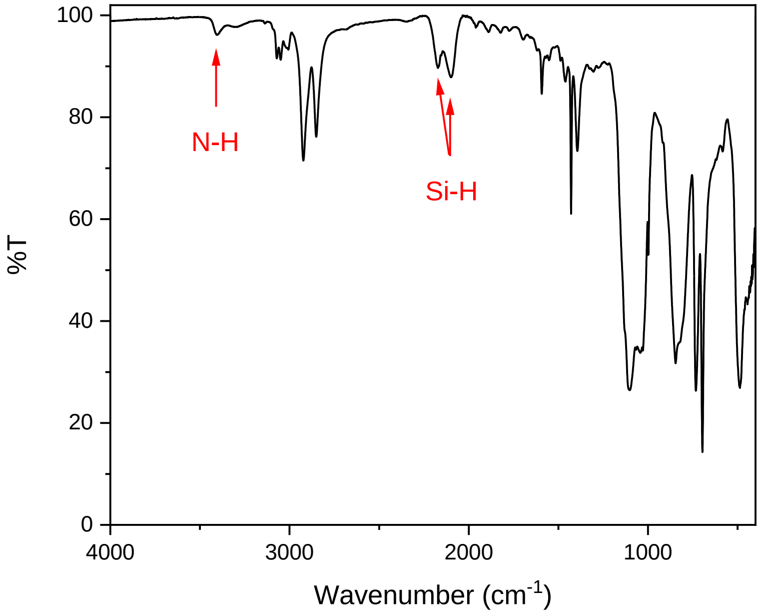


**Figure S13.** FT-IR spectrum of **1c** in KBr.

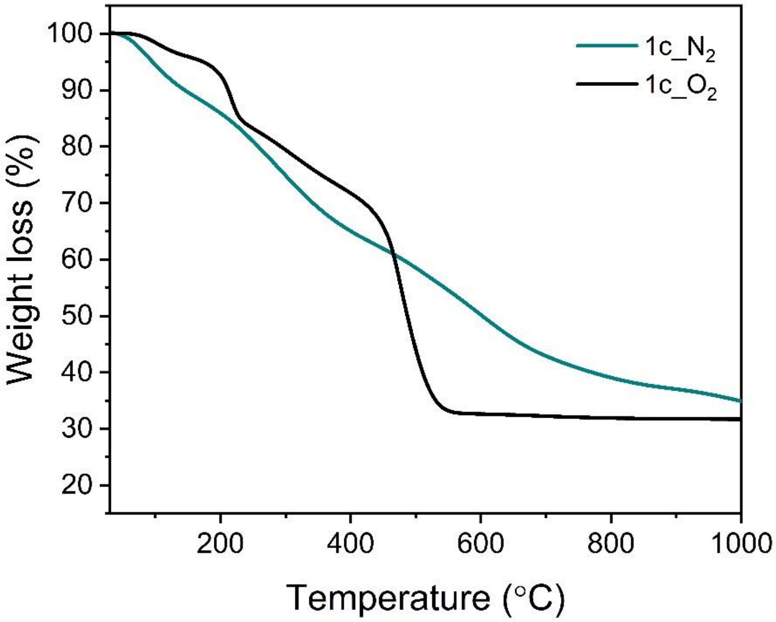


**Figure S14.** TGA thermogram of **1c** under $N_2$ and $O_2$.

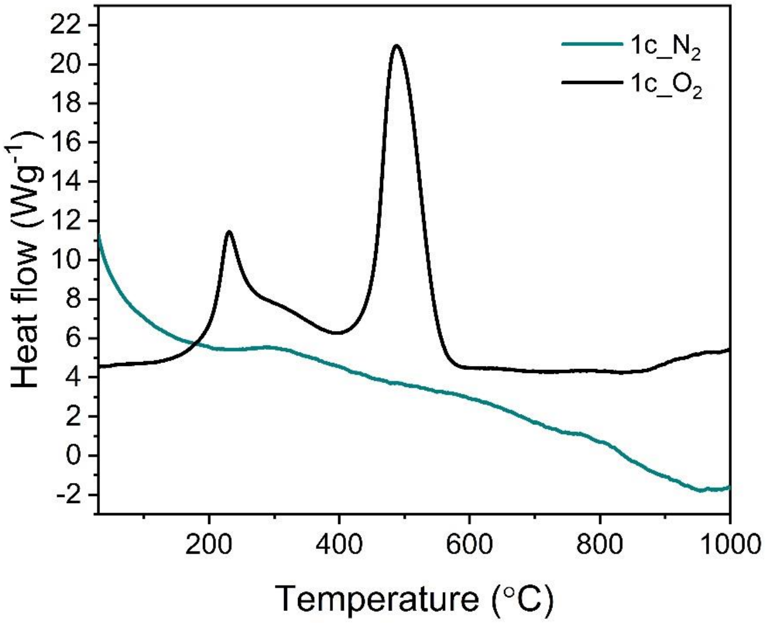


**Figure S15.** DSC thermogram of **1c** under $N_2$ and $O_2$.

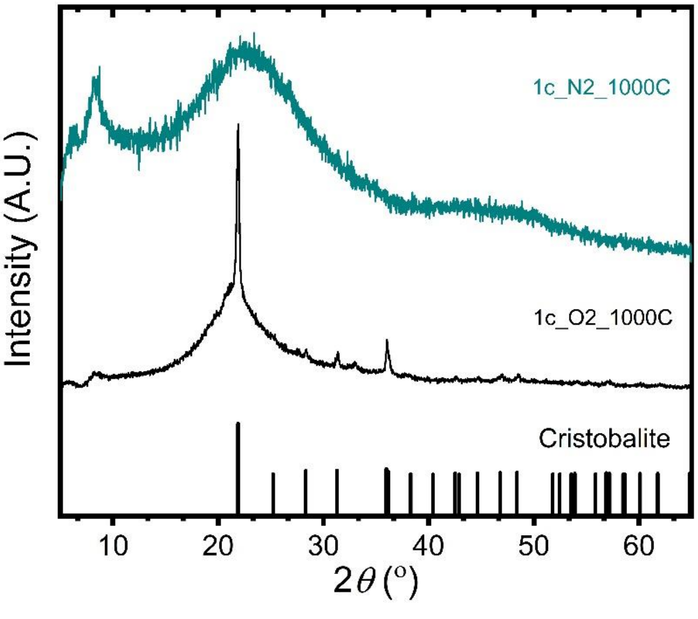
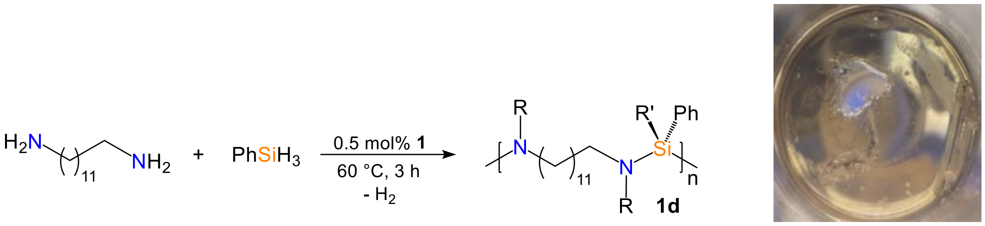


**Figure S16.** PXRD patterns of **1c** after TGA under $N_2$ and $O_2$, together with a simulated pattern of cristobalite.

**Preparation of 1d from phenylsilane and 1,12-diaminododecane using 0.5 mol% 1.**



**Scheme S4.** Preparation and image of **1d**.

*Procedure for conversion determination:* In a $N_2$ filled glovebox, a 20 mL vial was weighed before adding 0.001 g (0.001 mmol) of catalyst **1**. Afterwards, 18 µL (0.148 mmol) of phenylsilane was added and no obvious color change was noted. Next, 0.029 g (0.148 mmol) of 1,12-diaminododecane in 2 mL of benzene-$d_6$ was added. Instantly, the evolution of hydrogen gas was observed, and the solution turned orange in color. The vial was heated at 60 °C for 3 h to yield a brown solution. After 3 h, the catalyst was deactivated by exposing to air and the solution was degassed under vacuum for 30 s. A $^1$H NMR spectrum of the wash in benzene-$d_6$ revealed greater than 99% conversion of the starting diamine.

*Procedure for isolation and solid-state characterization:* In a $N_2$ filled glovebox, a 20 mL vial was weighed before adding 0.011 g (0.011 mmol) of **1**, followed by 300 µL (2.345 mmol) of phenylsilane, no obvious color change was noted. Next, 0.47 g (2.345 mmol) of 1,12-diaminododecane in 2 mL toluene was added. The formation of $H_2$ was observed and the solution turned orange in color. The reaction was heated at 60 °C for 3 h to obtain an orangish-brown solid. Next, the vial was brought outside the glovebox and the catalyst was deactivated by exposing to air. The reaction was then brought back into the glovebox and degassed under vacuum for 30 s. The product was washed with pentane and ether to remove residual ligand and dried under vacuum to obtain 0.659 g (91% yield, assuming complete diamine dehydrocoupling) of a solid product identified as **1d**. MALDI-TOF of THF wash ($[M+H]^+$, m/z): 1165 (n = 3 + 1 diamine), 1454 (n = 4 + 1 diamine), 1693 (n = 5 + 1 diamine), 1976 (n = 6 + 1 diamine), 2258 (n = 7 + 1 phenylsilane), 2541 (n = 8 + 1 phenylsilane), 2823 (n = 9 + 1 phenylsilane), 3080 (n = 10), 3397 (n = 11). IR (KBr, $cm^{-1}$): 3395 (broad, N–H), 2914-2840 (strong, C–H), 2109 (strong, Si–H), 835 (weak, Si–N). TGA ($N_2$): $T_{-5\%}$ = 375 °C, total % wt. loss at 1000 °C = 75%. TGA ($O_2$): $T_{-5\%}$ = 371 °C, total % wt. loss at 1000 °C = 81%.

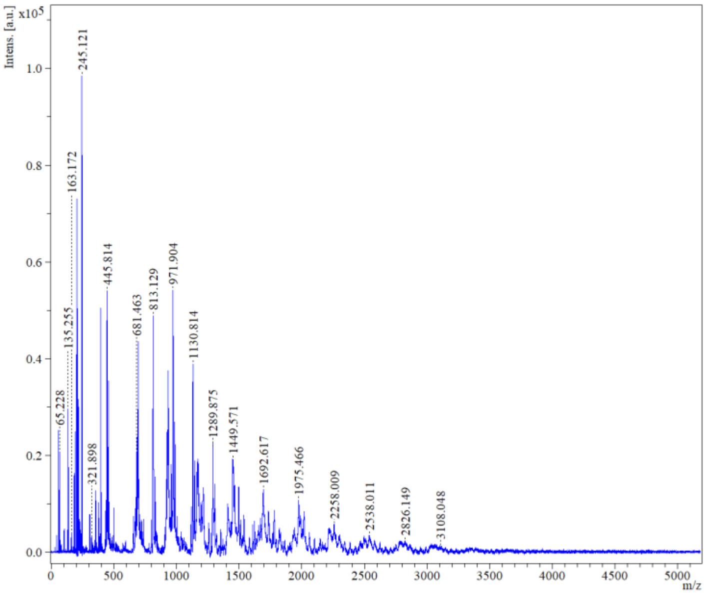


**Figure S17.** MALDI-TOF mass spectrum of **1d** THF wash.

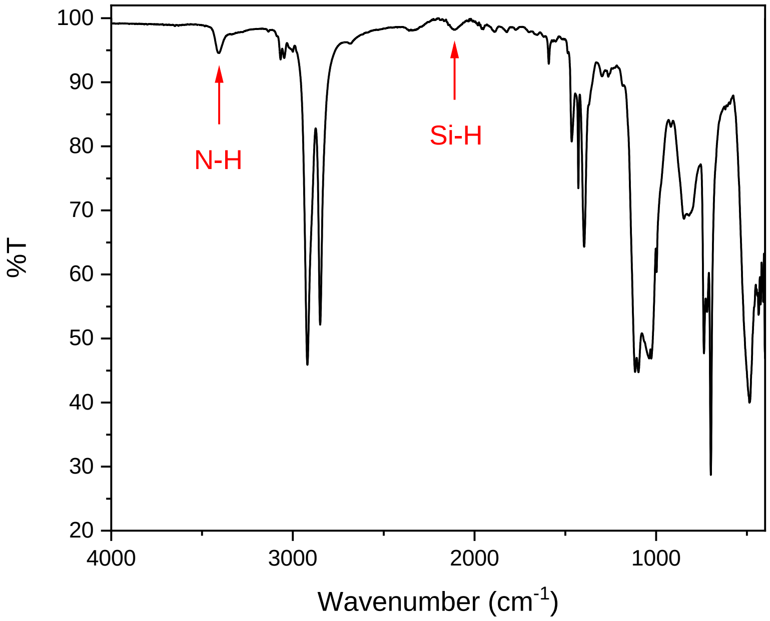


**Figure S18.** FT-IR spectrum of **1d** in KBr.

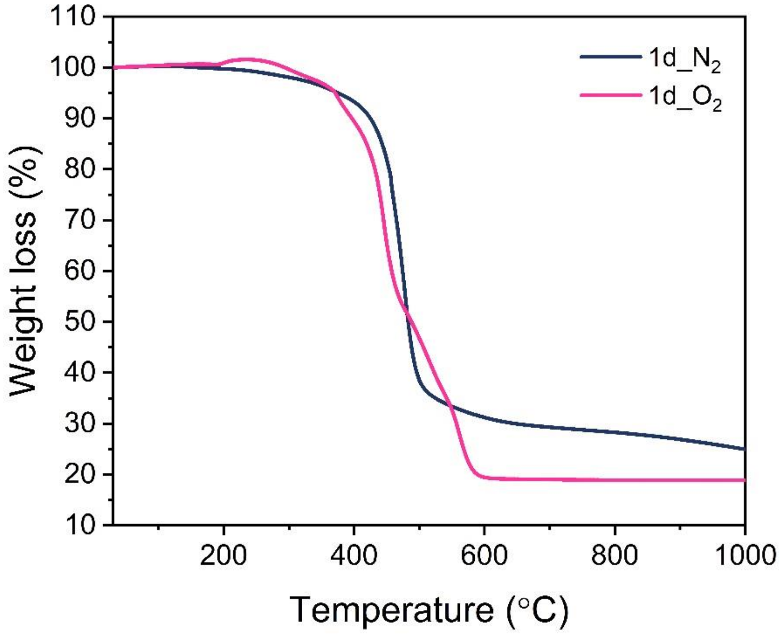


**Figure S19.** TGA thermogram of **1d** under $N_2$ and $O_2$.

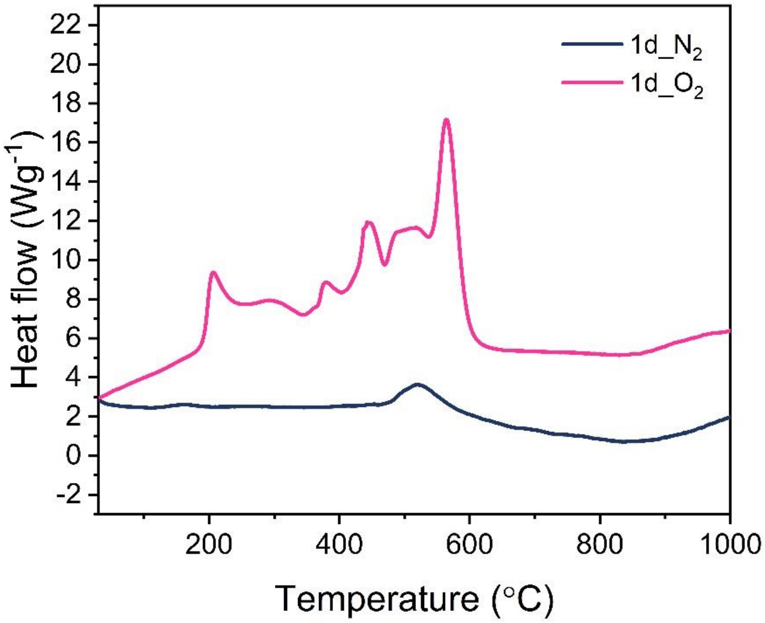


**Figure S20.** DSC thermogram of **1d** under $N_2$ and $O_2$.

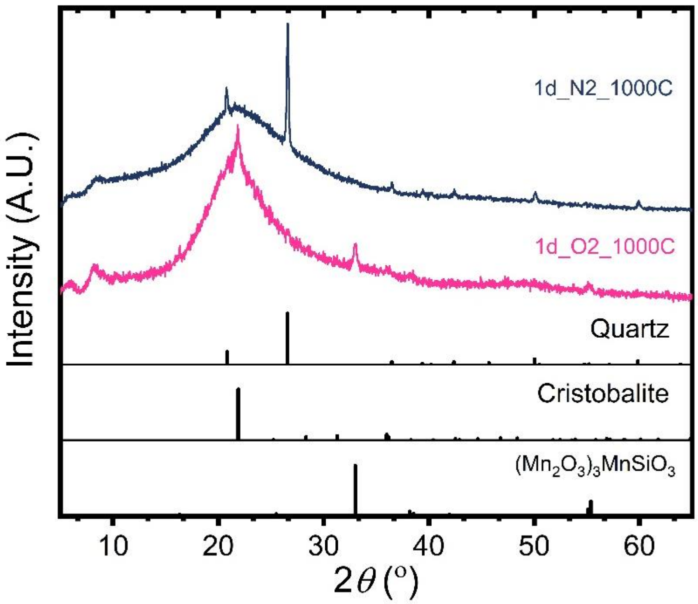
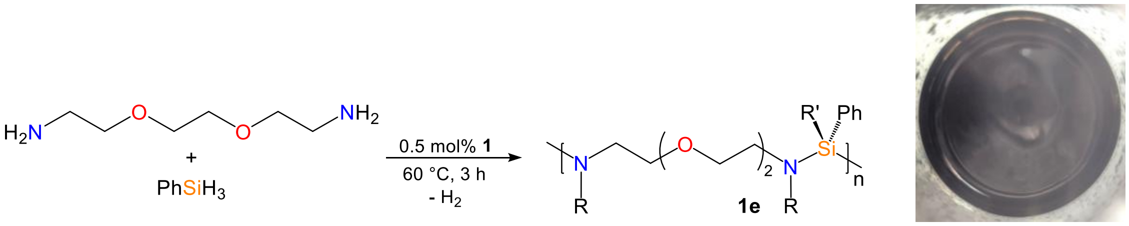


**Figure S21.** PXRD patterns of **1d** after TGA under $N_2$ and $O_2$, together with simulated patterns of quartz, cristobalite, and $(Mn_2O_3)_3MnSiO_3$.

### Preparation of 1e from phenylsilane and 2,2'-(ethylenedioxy)bis(ethylamine) using 0.5 mol% 1.



**Scheme S5.** Preparation and image of **1e**.

*Procedure for conversion determination:* In a $N_2$ filled glovebox, a 20 mL vial was weighed before adding 0.004 g (0.004 mmol) of catalyst **1**. Afterwards, 93 µL (0.76 mmol) of phenylsilane was added and no obvious color change was noted. Next, 111 µL (0.76 mmol) of 2,2'-(ethylenedioxy)bis(ethylamine) was added. Instantly, the evolution of hydrogen gas was observed and the solution turned orange in color. The vial was heated at 60 °C for 3 h to yield a brown solution. After 3 h, the catalyst was deactivated by exposing to air and the reaction was degassed under vacuum for 30 s. A $^1$H NMR spectrum of the wash in benzene-$d_6$ revealed greater than 99% conversion of the starting diamine.

*Procedure for isolated yield and solid-state characterization:* In a $N_2$ filled glovebox, a 20 mL vial was weighed before adding 0.012 g (0.013 mmol) of **1**, followed by 320 µL (2.62 mmol) of phenylsilane. No obvious color change was noted. Next, 400 µL (2.62 mmol) of 2,2'-(ethylenedioxy)bis(ethylamine) was added. The formation of $H_2$ was observed and the solution turned orange in color. The reaction was heated at 60 °C for 3 h to obtain a dark brown solid. Next, the vial was brought outside the glovebox and the catalyst was deactivated by exposing to air. The reaction was then brought back into the glovebox and degassed under vacuum for 30 s. The product was washed with pentane and ether to remove residual ligand and dried under vacuum to obtain 0.705 g (89% yield, assuming complete diamine dehydrocoupling) of a solid product identified as **1e**. MALDI-TOF of THF wash ($[M+H]^+$, m/z): 1172 (n = 4 +1 diamine), 1454 (n = 5 + 2 phenylsilane), 1694 (n = 6 + 1 diamine), 1977 (n = 7 + 2 phenylsilane), 2219 (n = 8 + 2 phenylsilane), 2513 (n = 10), 2792 (n = 10 + 2 diamine), 3110 (n = 12 + 1 phenylsilane). IR (KBr, cm$^{-1}$): 3374 (broad, N–H), 2934-2854 (strong, C–H), 830 (weak, Si–N). TGA ($N_2$): $T_{-5\%}$ = 157 °C, total % wt. loss at 1000 °C = 78%. TGA ($O_2$): $T_{-5\%}$ = 126 °C, total % wt. loss at 1000 °C = 80%.

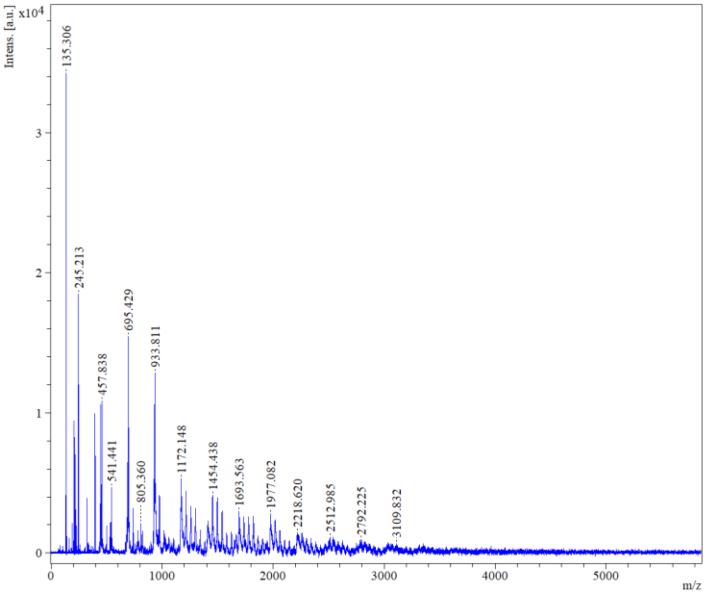


**Figure S22.** MALDI-TOF spectrum of **1e** THF wash.

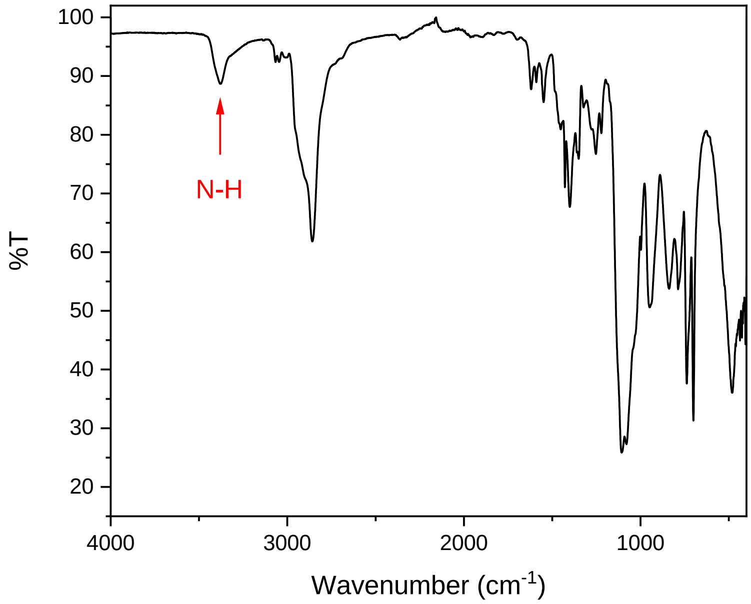


**Figure S23.** FT-IR spectrum of **1e** in KBr.

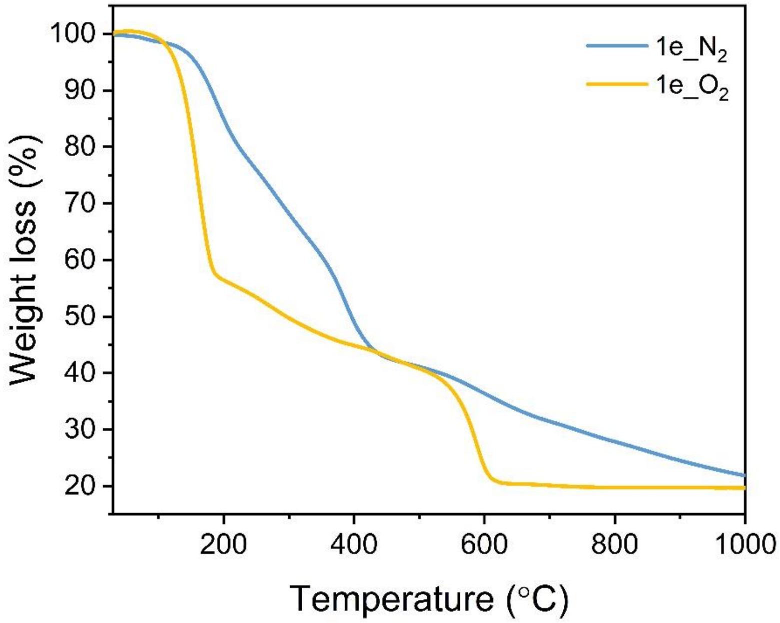


**Figure S24.** TGA thermogram of **1e** under $N_2$ and $O_2$.

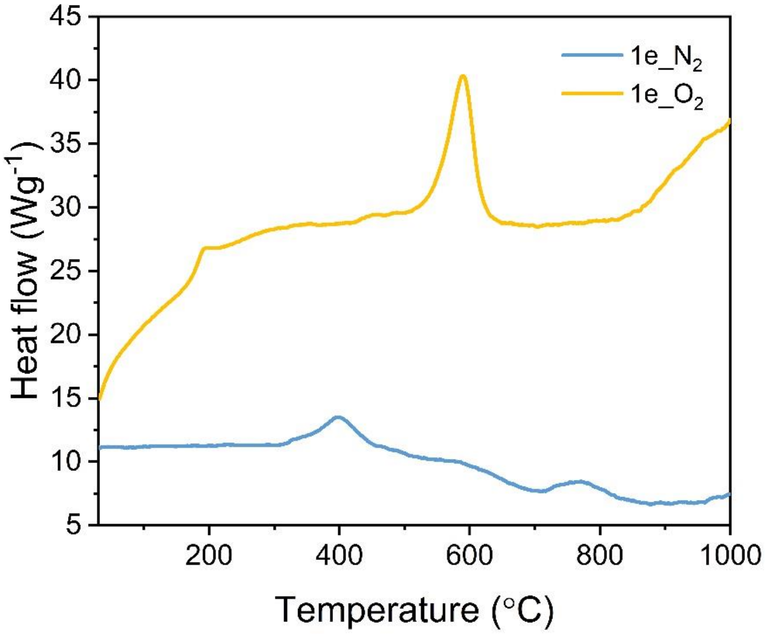


**Figure S25.** DSC thermogram of **1e** under N$_2$ and O$_2$.

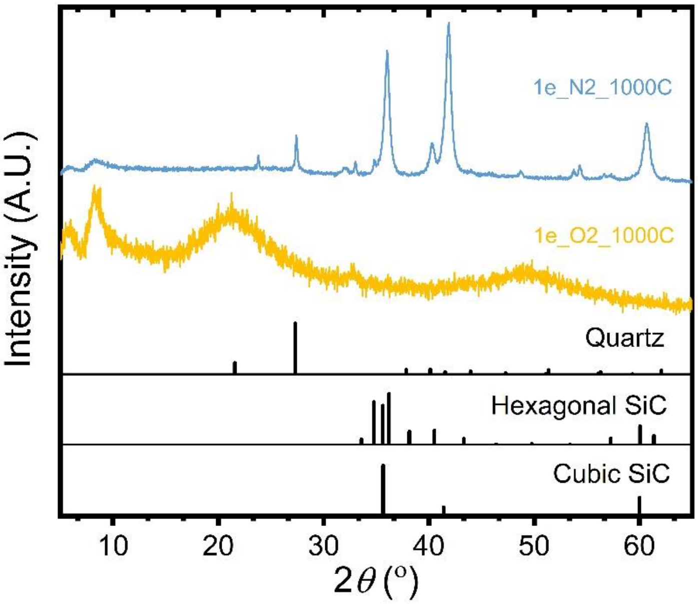
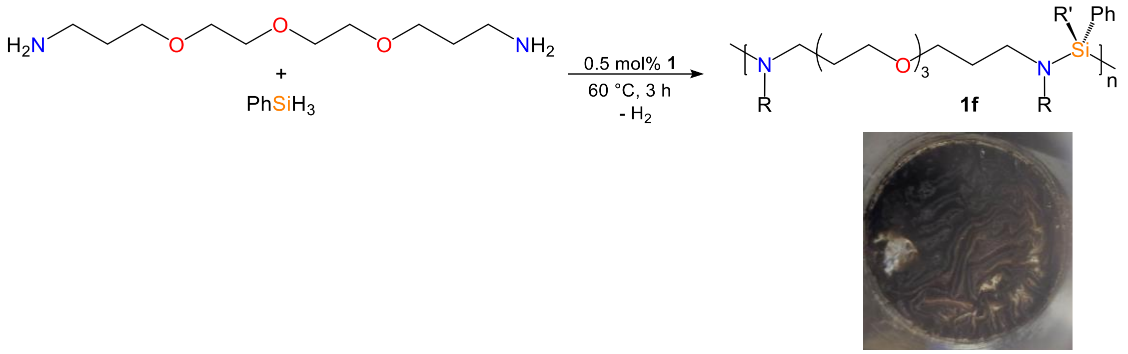


**Figure S26.** PXRD patterns of **1e** after TGA under N$_2$ and O$_2$, together with simulated patterns of quartz, hexagonal SiC, and cubic SiC.

## Preparation of 1f from phenylsilane and 4,7,10-trioxa-1,13-tridecanediamine using 0.5 mol% 1.



**Scheme S6.** Preparation and image of **1f**.

*Procedure for conversion determination:* In a $N_2$ filled glovebox, a 20 mL vial was weighed before adding 0.003 g (0.003 mmol) of catalyst **1**. Afterwards, 81 µL (0.66 mmol) of phenylsilane was added and no obvious color change was noted. Next, 139 µL (0.66 mmol) of 4,7,10-trioxa-1,13-tridecanediamine was added. Instantly, the evolution of hydrogen gas was observed, and the solution turned orange in color. The vial was heated at 60 °C for 3 h to yield a brown solution. After 3 h, the catalyst was deactivated by exposing to air and degassed under vacuum for 30 s. A $^1$H NMR spectrum of the wash in benzene-$d_6$ revealed greater than 99% conversion of the starting amine.

*Procedure for isolation and solid-state characterization:* In a $N_2$ filled glovebox, a 20 mL vial was weighed before adding 0.011 g (0.011 mmol) of **1**, followed by 300 µL (2.22 mmol) of phenylsilane, no obvious color change was noted. Next, 500 µL (2.22 mmol) of 4,7,10-trioxa-1,13-tridecanediamine was added. The formation of $H_2$ was observed and the solution turned orange in color. The reaction was heated at 60 °C for 3 h to obtain a dark brown solid. Next, the vial was brought outside the glovebox and the catalyst was deactivated by exposing to air. The reaction was then brought back into the glovebox and degassed under vacuum for 30 s. The product was washed with pentane and ether to remove residual ligand and dried under vacuum to obtain 0.662 g (92% yield, assuming complete diamine dehydrocoupling) of a solid product identified as **1f**. MALDI-TOF of THF wash ($[M+H]^+$, m/z): 933.9 (n = 3), 1172 (n = 3 + 2 phenylsilane), 1454 (n = 4 + 2 phenylsilane), 1779 (n = 5 + 1 phenylsilane), 1977 (n = 6), 2258 (n = 7), 2540 (n = 8), 2778 (n = 8 + 1 diamine), 3036 (n = 9 + 1 phenylsilane). IR (KBr, $cm^{-1}$):

3374 (broad, N–H), 2914-2845 (strong, C–H), 810 (weak, Si–N). TGA ($N_2$): $T_{-5\%}$ = 206 °C, total % wt. loss at 1000 °C = 76%. TGA ($O_2$): $T_{-5\%}$ = 262 °C, total % wt. loss at 1000 °C = 82%.

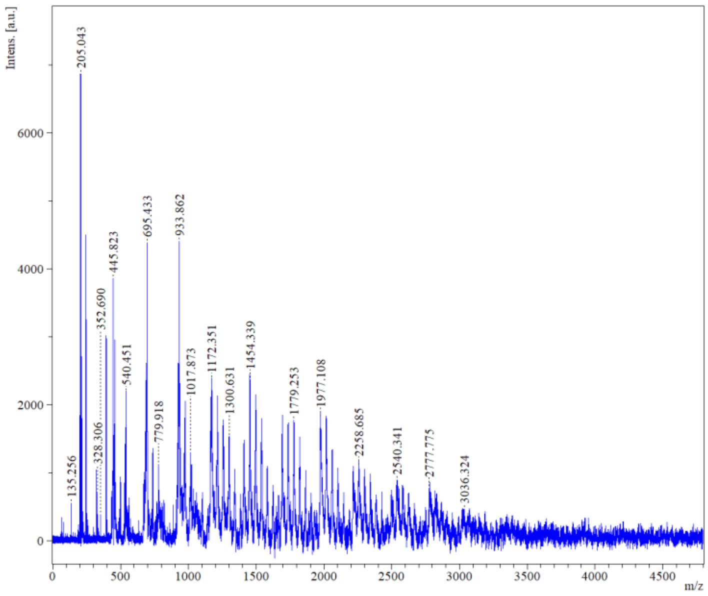


**Figure S27.** MALDI-TOF spectrum of **1f** THF wash.

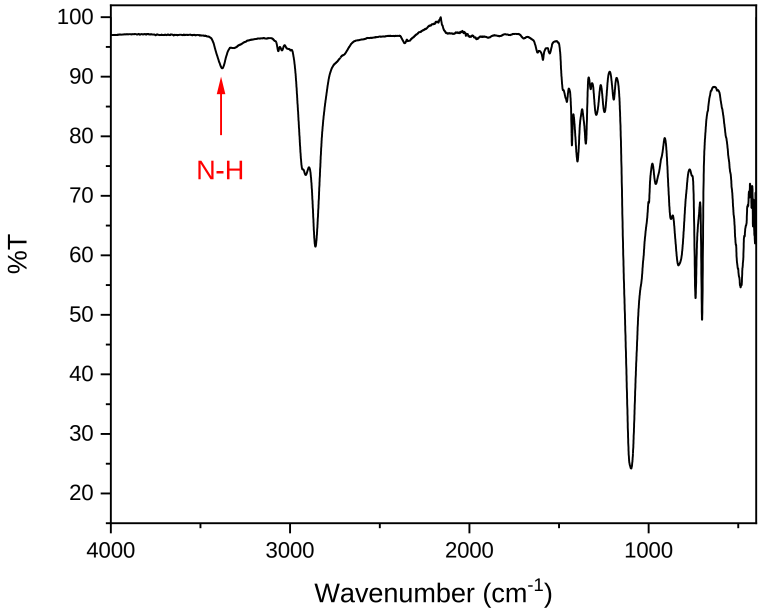


**Figure S28.** FT-IR spectrum of **1f** in KBr.

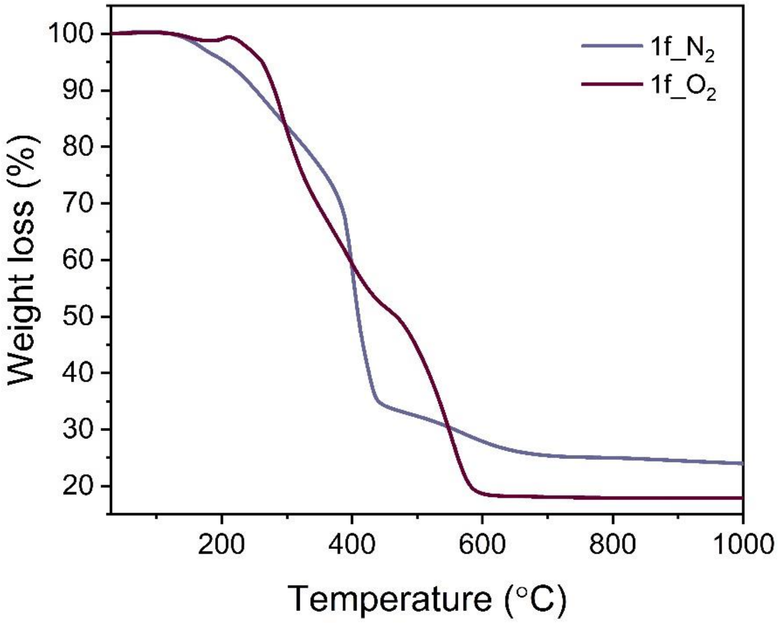


**Figure S29.** TGA thermogram of **1f** under $N_2$ and $O_2$.

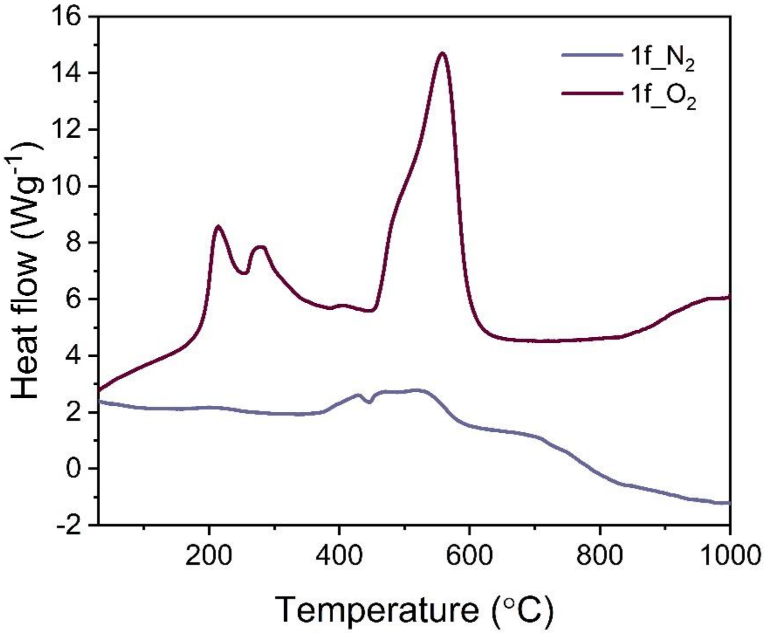


**Figure S30.** DSC thermogram of **1f** under $N_2$ and $O_2$.

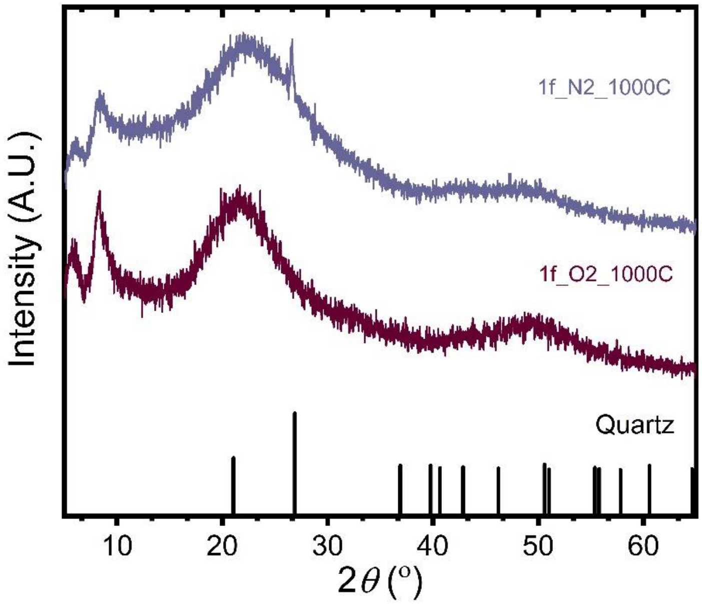
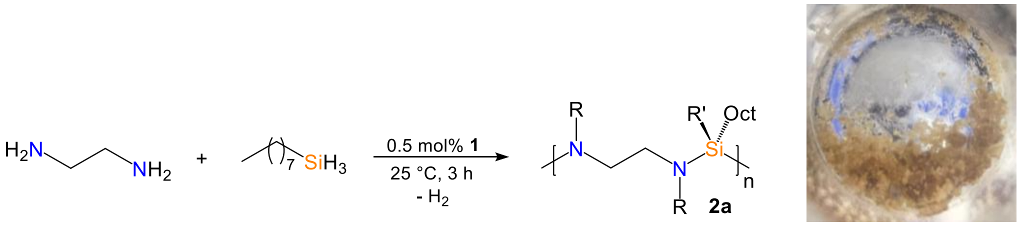


**Figure S31.** PXRD patterns of **1f** after TGA under $N_2$ and $O_2$, together with a simulated pattern of quartz.

### Preparation of 2a from octylsilane and ethylenediamine using 0.5 mol% 1.



**Scheme S7.** Preparation and image of **2a**.

*Procedure for conversion determination:* In a $N_2$ filled glovebox, a 20 mL vial was weighed before adding 0.005 g (0.005 mmol) of **1**. Afterwards, 188 µL (0.97 mmol) of octylsilane was added and no obvious color change was noted. Next, 65 µL (0.97 mmol) of ethylenediamine was added. Instantly, the evolution of hydrogen gas was observed, and the solution turned orange in color. The vial was kept uncapped under $N_2$ atmosphere for 3 h at ambient temperature to yield a dark brown solution. After 3 h, the catalyst was deactivated by exposing to air and the solution was degassed under vacuum for 30 s. A $^1$H NMR spectrum of the wash in benzene-$d_6$ revealed greater than 99% conversion of the starting diamine.

*Procedure for isolation and solid-state characterization:* In a $N_2$ filled glovebox, a 20 mL vial was weighed before adding 0.023 g (0.024 mmol) of **1**, followed by 900 µL (4.82 mmol) of octylsilane, no obvious color change was noted. Next, 320 µL (4.82 mmol) of ethylenediamine was added. The formation of $H_2$ was observed and the solution turned orange in color. The reaction was kept uncapped at room temperature for 3 h to obtain a brown solid. Next, the vial was brought outside the glovebox and the catalyst was deactivated upon exposing to air. The reaction was then brought back into the glovebox and degassed under vacuum for 30 s. The product was washed with pentane and ether to remove residual ligand and dried under vacuum to obtain 0.783 g (81% yield, assuming complete diamine dehydrocoupling) of a solid product identified as **2a**. MALDI-TOF of THF wash ($[M+H]^+$, m/z): 932.9 (n = 4 + 1 octylsilane), 1170 (n = 5 + 1 octylsilane), 1452 (n = 7 + 1 ethylenediamine), 1691 (n = 9), 1975 (n = 9 + 2 ethylenediamine), 2251 (n = 11 + 1 ethylenediamine). IR (KBr, cm$^{-1}$): 3404 (broad, N–H), 2924-2845 (strong, C–H), 2115 (strong, Si–H), 805 (weak, Si–N). TGA ($N_2$): $T_{-5\%}$ = 226 °C, total % wt. loss at 1000 °C = 68%. TGA ($O_2$): $T_{-5\%}$ = 206 °C, total % wt. loss at 1000 °C = 71%. $^1$H NMR of benzene-$d_6$ wash (500 MHz, benzene-$d_6$): 4.85 (s, Si*H*), 4.67 (s, Si$H_2$), 3.12 (broad, C$H_2$), 2.89 (broad, C$H_2$), 1.30 (broad, C$H_2$), 0.90 (broad, -C$H_3$).

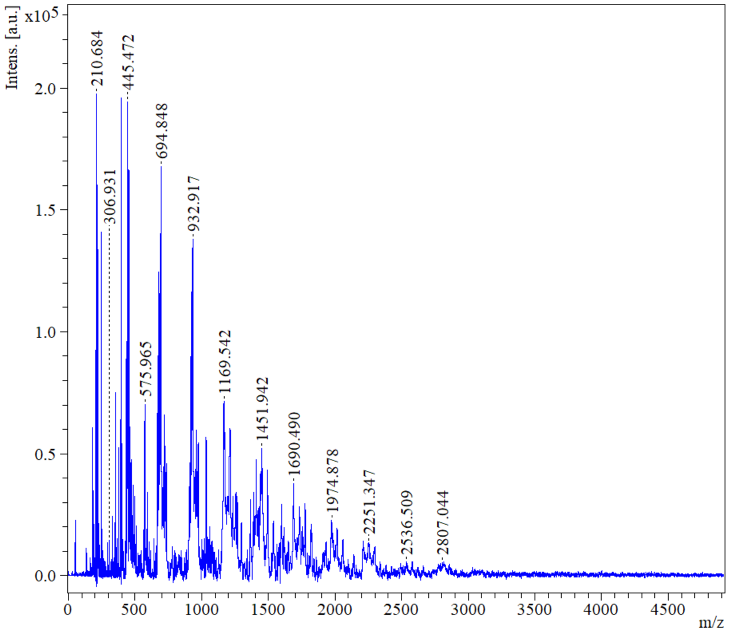


**Figure S32.** MALDI-TOF spectrum of **2a** THF wash.

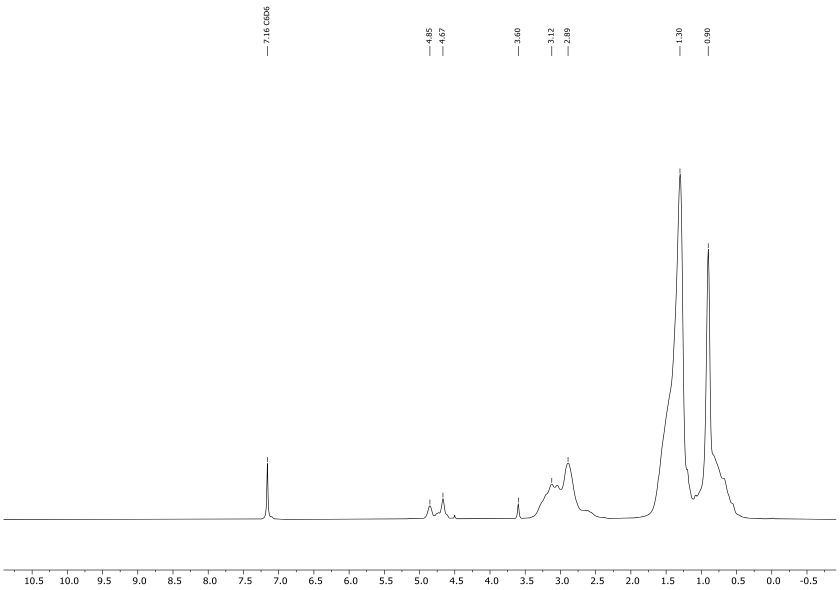


**Figure S33.** Representative $^{1}$H NMR spectrum of **2a** benzene-$d_6$ wash.

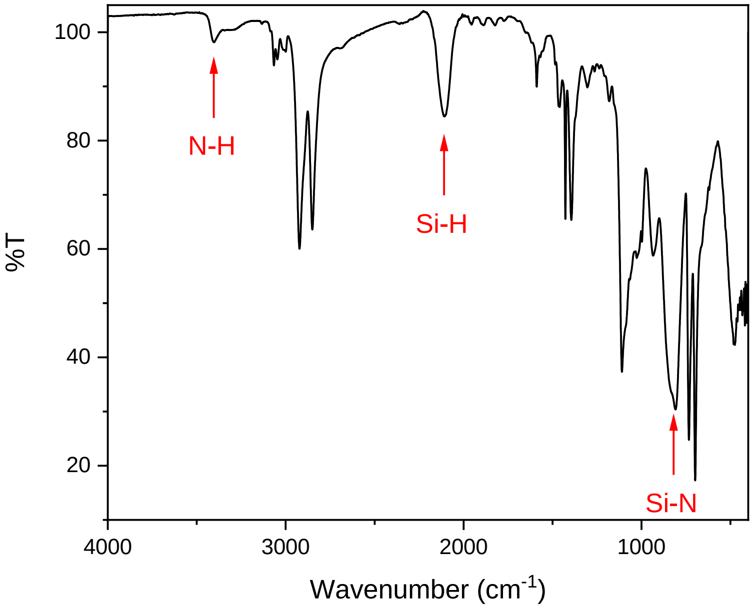


**Figure S34.** FT-IR spectrum of **2a** prepared in KBr.

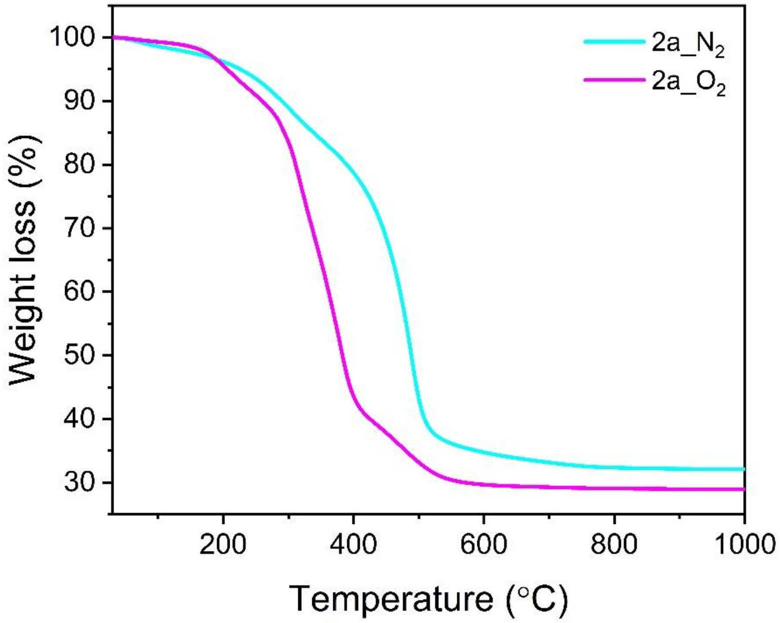


**Figure S35.** TGA thermogram of **2a** under $N_2$ and $O_2$.

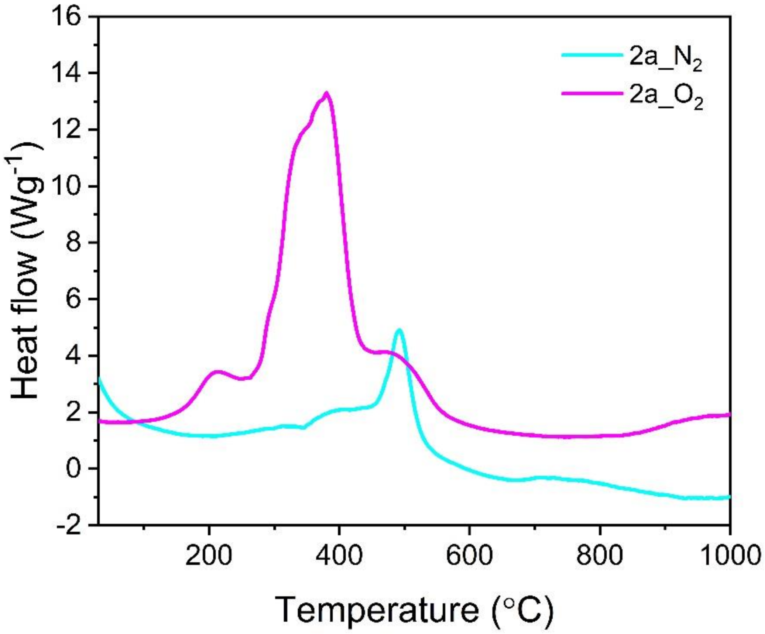


**Figure S36.** DSC thermogram of **2a** under $N_2$ and $O_2$.

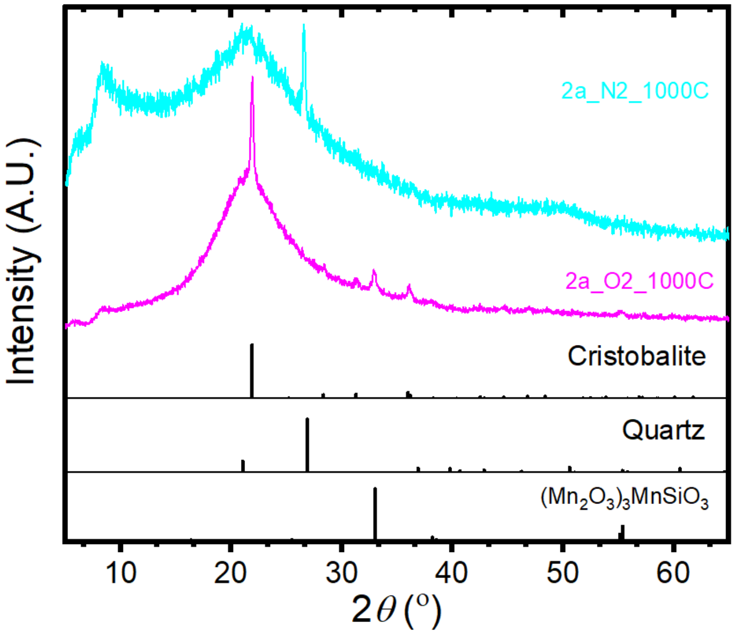
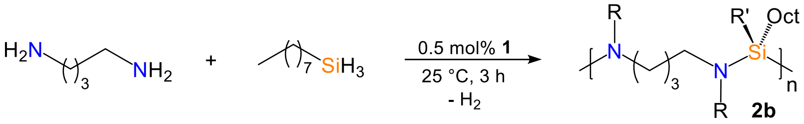


**Figure S37.** PXRD patterns of **2a** after TGA under $N_2$ and $O_2$, together with simulated patterns of cristobalite, quartz, and $(Mn_2O_3)_3MnSiO_3$.

**Preparation of 2b from octylsilane and 1,4-diaminobutane using 0.5 mol% 1.**



**Scheme S8.** Preparation and image of **2b**.

*Procedure for conversion determination:* In a $N_2$ filled glovebox, a 20 mL vial was weighed before adding 0.002 g (0.002 mmol) of **1**. Afterwards, 66 µL (0.338 mmol) of octylsilane was added and no obvious color change was noted. Next, 0.03 g (0.338 mmol) of 1,4-diaminobutane in 2 mL of benzene-$d_6$ was added. Instantly, the evolution of hydrogen gas was observed, and the solution turned orange in color. The vial was kept uncapped under $N_2$ atmosphere for 3 h at ambient temperature to yield a dark brown solution. After 3 h, the catalyst was deactivated by exposing to air and the solution was degassed under vacuum for 30 s. A $^1$H NMR spectrum of the wash in benzene-$d_6$ revealed greater than 99% conversion of the starting diamine.

*Procedure for isolation and solid-state characterization:* In a $N_2$ filled glovebox, a 20 mL vial was weighed before adding 0.005 g (0.005 mmol) of **1**, followed by 188 μL (0.972 mmol) of octylsilane, no obvious color change was noted. Next, 0.09 g (0.972 mmol) of 1,4-diaminobutane in 2 mL of toluene was added. The formation of $H_2$ was observed the solution turned orange in color. The reaction was kept uncapped at room temperature for 3 h to obtain a dark brown solid. Next, the vial was brought outside the glovebox and the catalyst was deactivated by exposing to air. The reaction was then brought back into the glovebox and degassed under vacuum for 30 s. The product was washed with pentane and ether to remove residual ligand and dried under vacuum to obtain 0.184 g (83% yield, assuming complete diamine dehydrocoupling) of a solid product identified as **2b**. MALDI-TOF of THF wash ($[M+H]^{+}$, m/z): 445.4 (n = 2), 694.9 (n = 3), 932.9 (n = 4), 1170 (n = 6 + 1 amine), 1694 (n = 7 + 1 amine). IR (KBr, cm$^{-1}$): 3414 (broad, N–H), 2919-2854 (strong, C–H), 2090 (strong, Si–H), 800 (weak, Si–N). TGA ($N_2$): $T_{-5\%}$ = 117 °C, total % wt. loss at 1000 °C = 77%. TGA ($O_2$): $T_{-5\%}$ = 180 °C, total % wt. loss at 1000 °C = 76%.

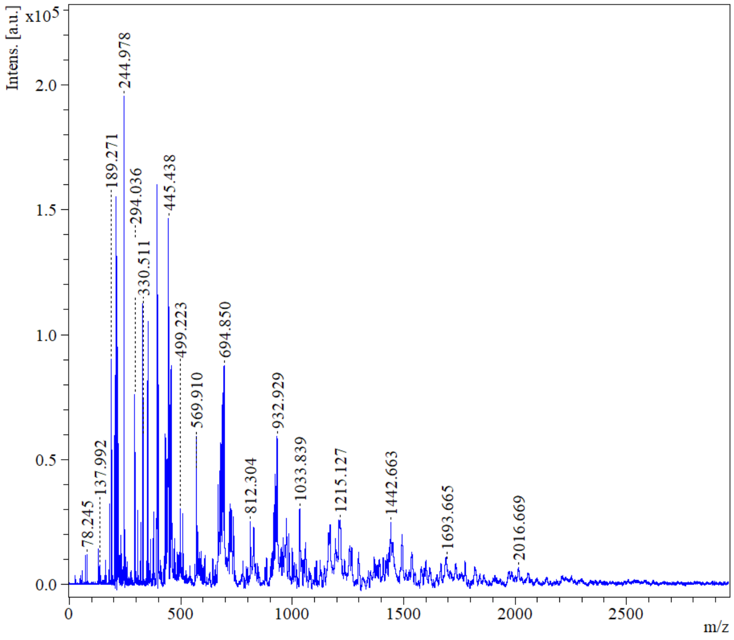


**Figure S38.** MALDI-TOF spectrum of **2b** THF wash.

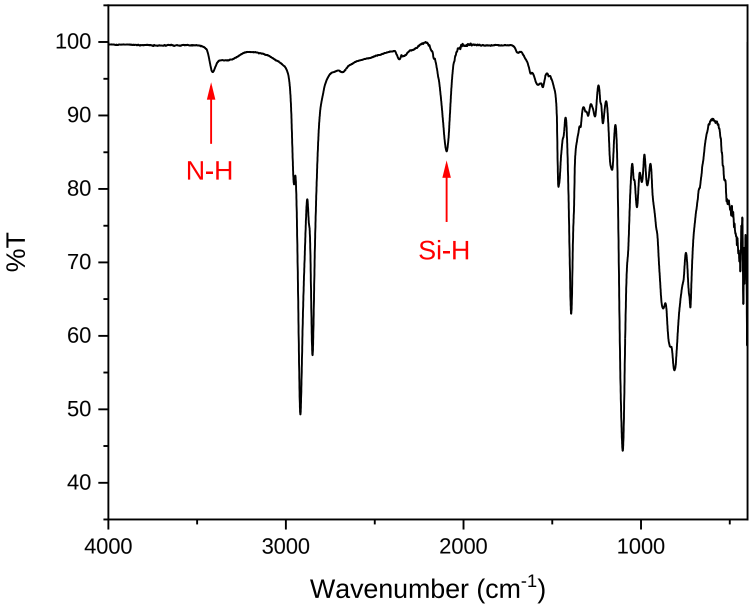


**Figure S39.** FT-IR spectrum of **2b** in KBr.

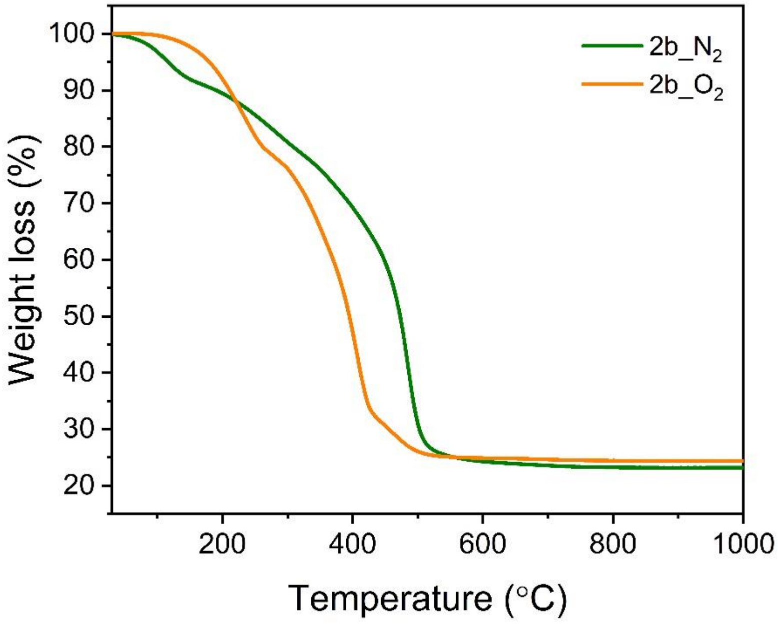


**Figure S40.** TGA thermogram of **2b** after TGA under $N_2$ and $O_2$.

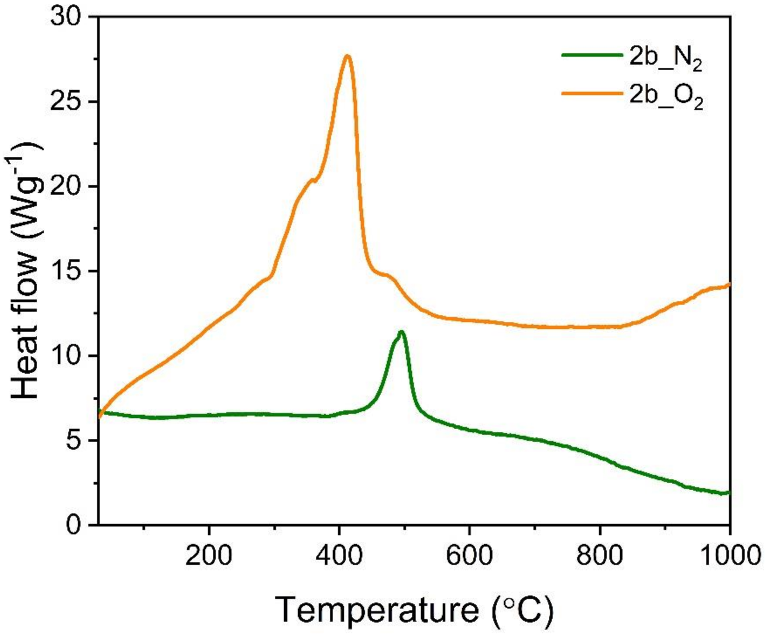


**Figure S41.** DSC thermogram of **2b** under $N_2$ and $O_2$.

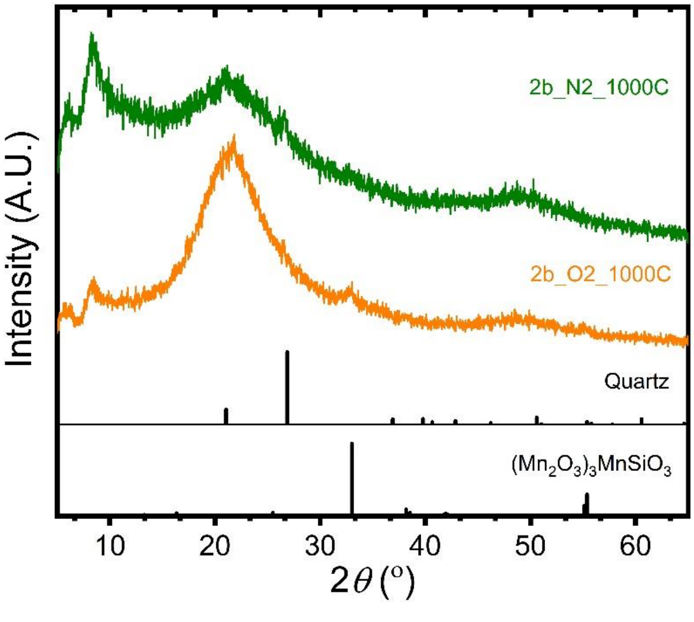
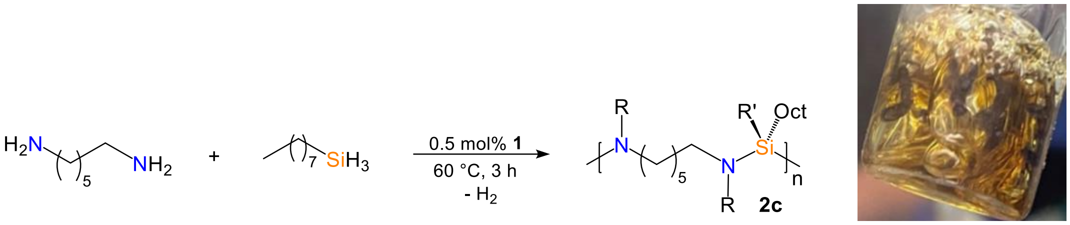


**Figure S42.** PXRD patterns of **2b** after TGA under $N_2$ and $O_2$, together with simulated patterns of quartz and $(Mn_2O_3)_3MnSiO_3$.

**Preparation of 2c from octylsilane and 1,6-diaminohexane using 0.5 mol% 1.**



**Scheme S9.** Preparation and image of **2c**.

*Procedure for conversion determination:* In a $N_2$ filled glovebox, a 20 mL vial was weighed before adding 0.006 g (0.006 mmol) of **1**. Afterwards, 233 µL (1.2 mmol) of octylsilane was added and no obvious color change was noted. Next, 0.14 g (1.2 mmol) of 1,6-diaminohexane in 2 mL of benzene-$d_6$ was added. Instantly, the evolution of hydrogen gas was observed, and the solution turned orange in color. The vial was heated at 60 °C for 3 h to yield a yellow solution. After 3 h, the catalyst was deactivated by exposing to air and the solution was degassed under vacuum for 30 s. A $^1$H NMR spectrum of the wash in benzene-$d_6$ revealed greater than 99% conversion of the starting diamine.

*Procedure for isolation and solid-state characterization:* In a $N_2$ filled glovebox, a 20 mL vial was weighed before adding 0.006 g (0.006 mmol) of catalyst **1**, followed by 249 µL (1.29 mmol) of octylsilane, no obvious color change was noted. Next, 0.15 g (1.29 mmol) of 1,6-diaminohexane in 2 mL of toluene was added. The formation of $H_2$ was observed and the solution turned orange in color. The reaction was heated at 60 °C for 3 h to obtain a yellow solid. Next, the vial was brought outside the glovebox and the catalyst was deactivated by exposing to air. The reaction was then brought back into the glovebox and degassed under vacuum for 30 s. The product was washed with pentane and ether to remove residual ligand and dried under vacuum to obtain 0.254 g (77% yield, assuming complete diamine dehydrocoupling) of a solid product identified as **2c**. MALDI-TOF of THF wash ($[M+H]^+$, m/z): 813.3 (n = 3), 986.5 (n = 3 + 2 1,6-diaminohexane), 1130 (n = 4 + 1 octylsilane), 1304 (n = 5), 1512 (n = 6). IR (KBr, cm$^{-1}$): 3404-3290 (broad, N–H), 2914-2835 (strong, C–H), 2099 (strong, Si–H), 805 (weak, Si–N). TGA ($N_2$): $T_{-5\%}$ = 289 °C, total % wt. loss at 1000 °C = 78%. TGA ($O_2$): $T_{-5\%}$ = 179 °C, total % wt. loss at 1000 °C = 79%.

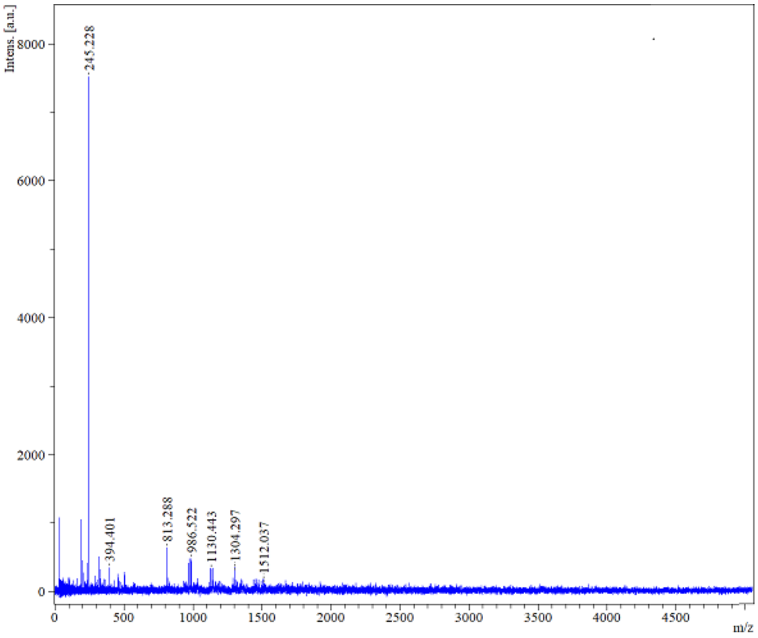


**Figure S43.** MALDI-TOF spectrum of **2c** THF wash.

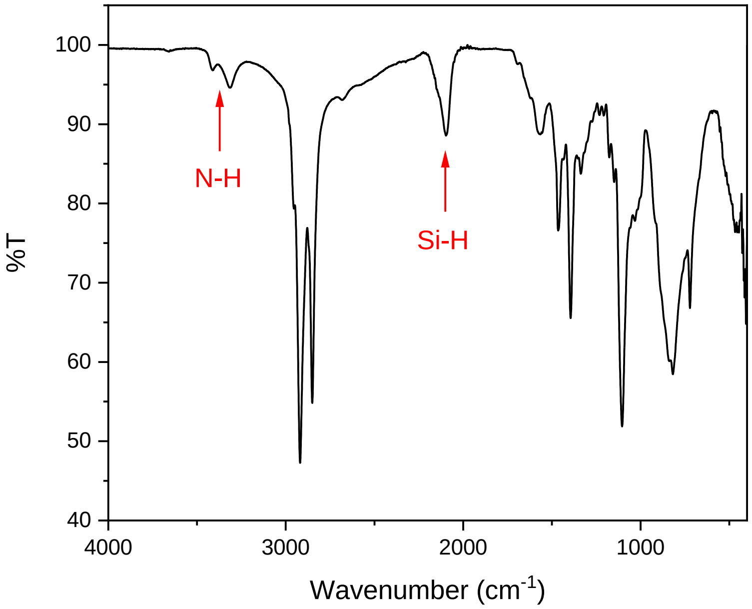


**Figure S44.** FT-IR spectrum of **2c** in KBr.

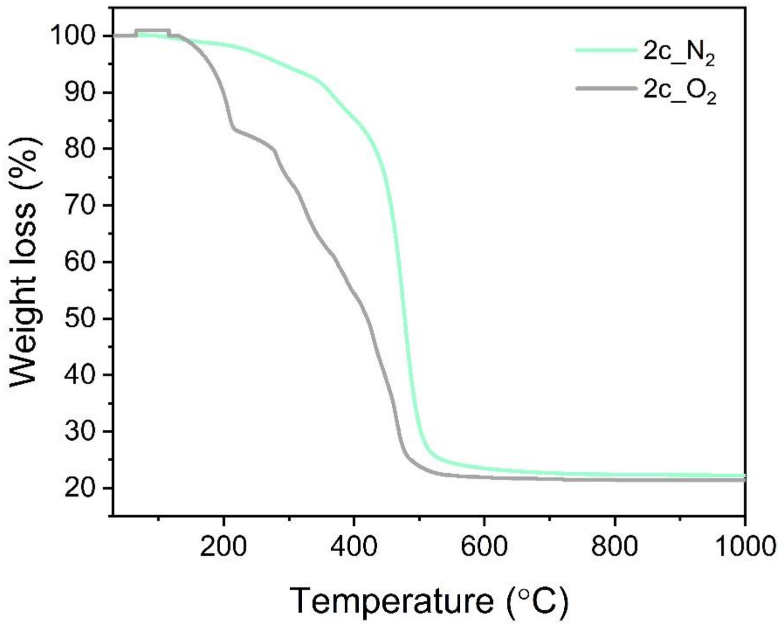


**Figure S45.** TGA thermogram of **2c** under $N_2$ and $O_2$.

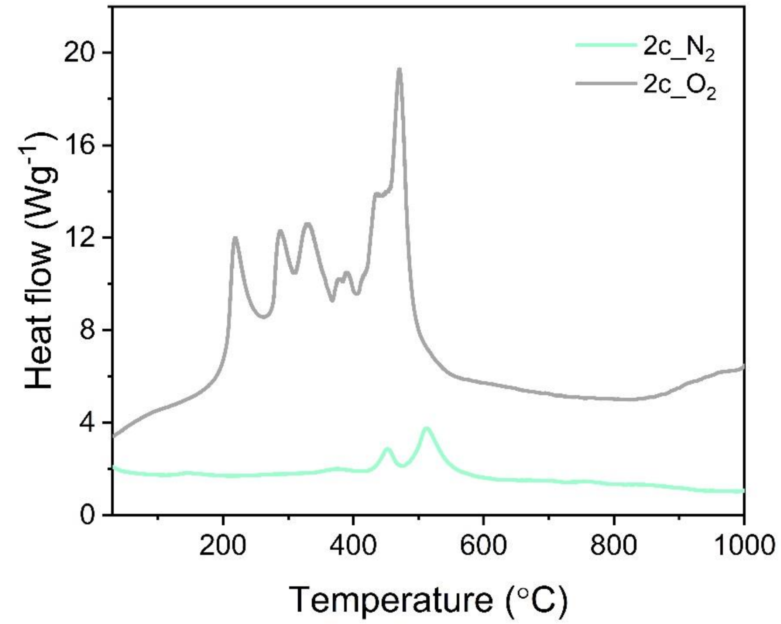


**Figure S46.** DSC thermogram of **2c** under $N_2$ and $O_2$.

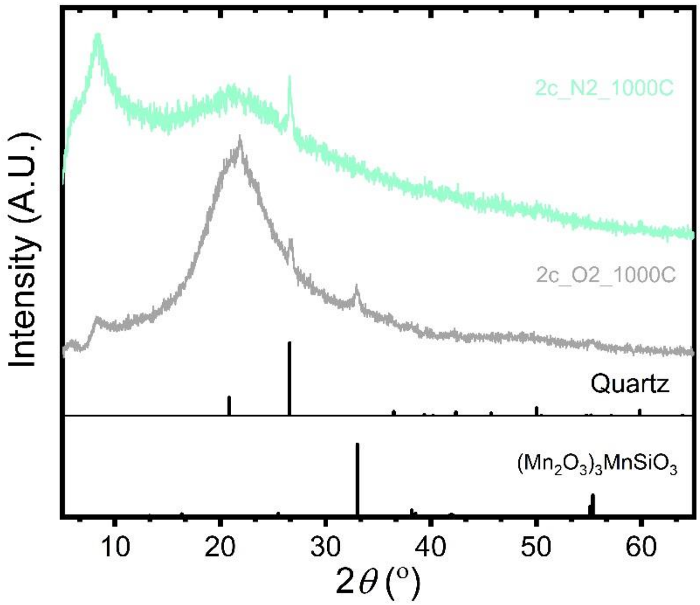
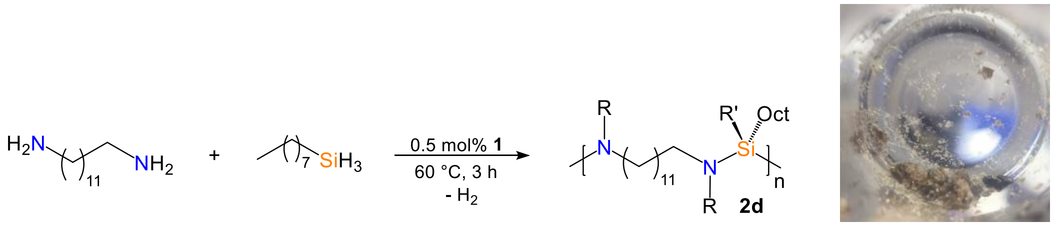


**Figure S47.** PXRD patterns of **2c** after TGA under $N_2$ and $O_2$, together with simulated patterns of quartz and $(Mn_2O_3)_3MnSiO_3$.

### Preparation of 2d from octylsilane and 1,12-diaminododecane using 0.5 mol% 1.



**Scheme S10.** Preparation and image of **2d**.

*Procedure for conversion determination:* In a $N_2$ filled glovebox, a 20 mL vial was weighed before adding 0.002 g (0.002 mmol) of **1**. Afterwards, 57 µL (0.296 mmol) of octylsilane was added and no obvious color change was noted. Next, 0.059 g (0.296 mmol) of 1,12-diaminododecane in 2 mL benzene-*d*₆ was added. Instantly, the evolution of hydrogen gas was observed, and the solution turned orange in color. The vial was heated at 60 °C for 3 h to yield a dark brown solution. After 3 h, the catalyst was deactivated by exposing to air and degassed under vacuum for 30 s. A $^1H$ NMR spectrum of the wash in benzene-$d_6$ revealed greater than 99% conversion of the starting diamine.

*Procedure for isolation and solid-state characterization:* In a $N_2$ filled glovebox, a 20 mL vial was weighed before adding 0.006 g (0.006 mmol) of **1**, followed by 254 µL (1.31 mmol) of octylsilane. No obvious color change was noted. Next, 0.262 g (1.31 mmol) of 1,12-diaminododecane in 2 mL of toluene was added. The formation of $H_2$ was observed and the solution turned orange in color. The reaction was heated at 60 °C for 3 h to obtain a dark brown solid. Next, the vial was brought outside the glovebox and the catalyst was deactivated by exposing to air. The reaction was then brought back into the glovebox and degassed under vacuum for 30 s. The product was washed with pentane and ether to remove residual ligand and dried under vacuum to obtain 0.406 g (90% yield, assuming complete diamine dehydrocoupling) of a solid product identified as **2d**. MALDI-TOF of THF wash ($[M+H]^{+}$, m/z): 681.5 (n = 2), 813.1 (n = 2 + 1 octylsilane), 971.9 (n = 2 + 2 octylsilane), 1131 (n = 3 + 1 octylsilane), 1450 (n = 4 + 1 octylsilane), 1693 (n = 5), 1976 (n = 5 + 2 octylsilane), 2258 (n = 6 + 1 octylsilane), 2538 (n = 7 + 1 octylsilane), 2826 (n = 8 + 1 octylsilane). IR (KBr, $cm^{-1}$): 3409-3309 (broad, N–H), 2909-2845 (strong, C–H), 2135 (strong, Si–H), 820 (weak, Si–N). TGA ($N_2$): $T_{-5\%}$ = 303 °C, total % wt. loss at 1000 °C = 83%. TGA ($O_2$): $T_{-5\%}$ = 314 °C, total % wt. loss at 1000 °C = 84%.

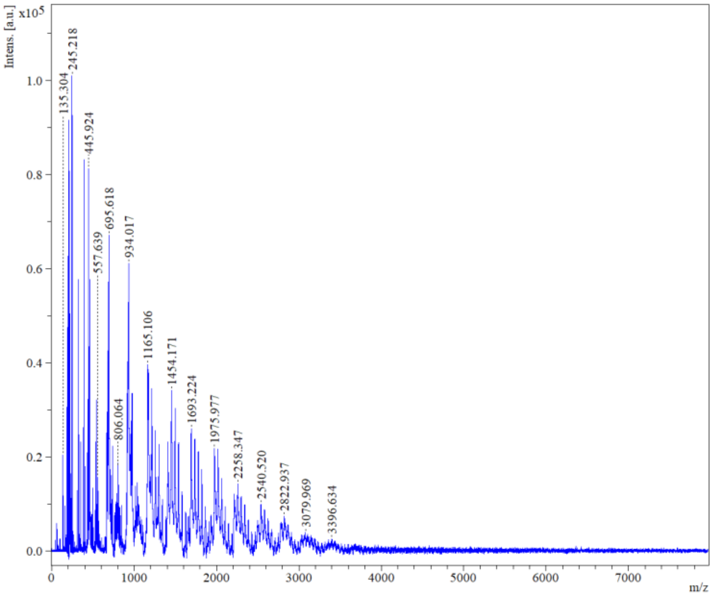


**Figure S48.** MALDI-TOF spectrum of **2d** THF wash.

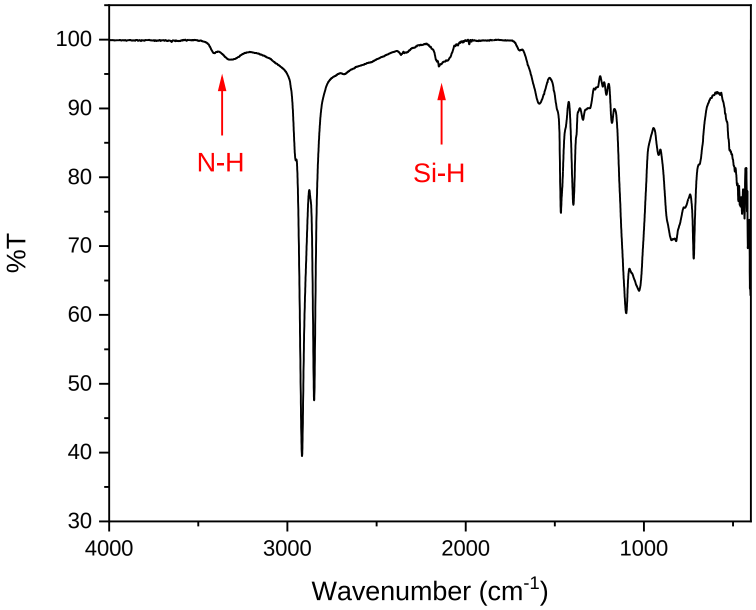


**Figure S49.** FT-IR spectrum of **2d** in KBr.

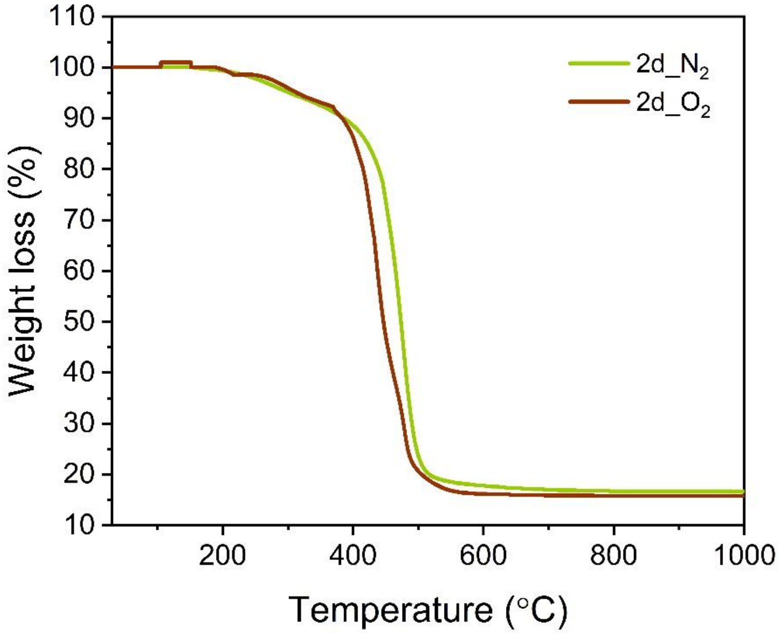


**Figure S50.** TGA thermogram of **2d** under $N_2$ and $O_2$.

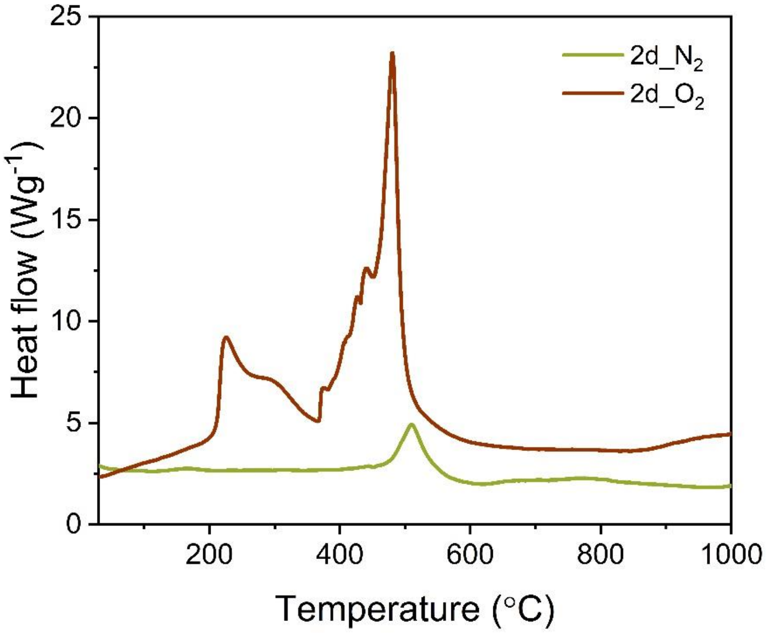


**Figure S51.** DSC thermogram of **2d** under $N_2$ and $O_2$.

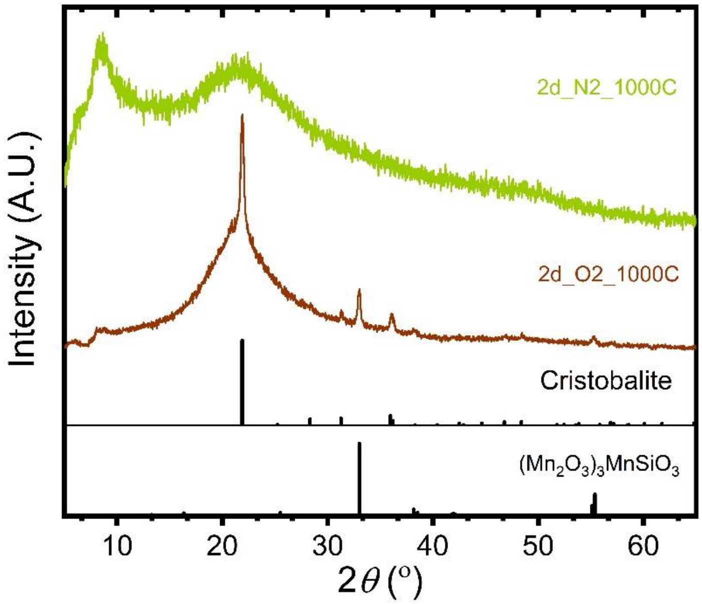
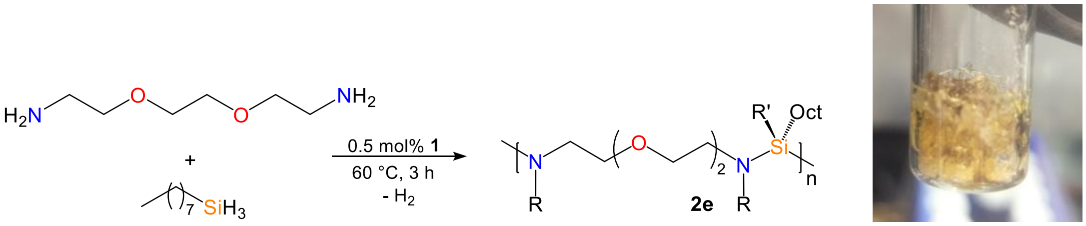


**Figure S52.** PXRD patterns of **2d** after TGA under $N_2$ and $O_2$, together with simulated patterns of cristobalite and $(Mn_2O_3)_3MnSiO_3$.

### Preparation of 2e from octylsilane and 2,2'-(ethylenedioxy)bis(ethylamine) using 0.5 mol% 1.



**Scheme S11.** Preparation and image of **2e**.

*Procedure for conversion determination:* In a $N_2$ filled glovebox, a 20 mL vial was weighed before adding 0.005 g (0.006 mmol) of **1**. Afterwards, 217 µL (1.12 mmol) of octylsilane was added and no obvious color change was noted. Next, 163 µL (1.12 mmol) of 2,2'-(ethylenedioxy)bis(ethylamine) was added. Instantly, the evolution of hydrogen gas was observed, and the solution turned orange in color. The vial was kept uncapped under $N_2$ atmosphere for 3 h at ambient temperature to yield a dark brown solution. After 3 h, the catalyst was deactivated by exposing to air and the solution was degassed under vacuum for 30 s. A $^1H$ NMR spectrum of the wash in benzene-$d_6$ revealed greater than 99% conversion of the starting diamine.

*Procedure for isolation and solid-state characterization:* In a $N_2$ filled glovebox, a 20 mL vial was weighed before adding 0.006 g (0.006 mmol) of **1**, followed by 245 µL (1.267 mmol) of octylsilane, no obvious color change was noted. Next, 185 µL (1.015 mmol) of 2,2'-(ethylenedioxy)bis(ethylamine) was added. The formation of $H_2$ was observed and the solution turned orange in color. The reaction was heated at 60 °C for 3 h to obtain a dark brown solid. Next, the vial was brought outside the glovebox, when the catalyst was deactivated by exposing to air. The reaction was then brought back into the glovebox and degassed under vacuum for 30 s. The product was washed with pentane and ether to remove residual ligand and dried under vacuum to obtain 0.344 g (94% yield, assuming complete diamine dehydrocoupling) of a solid product identified as **2e**. MALDI-TOF of THF wash ($[M+H]^+$, m/z): 1165 (n = 4), 1454 (n = 5), 1736 (n = 6), 2022 (n = 7), and 2230 (n = 8). IR (KBr, $cm^{-1}$): 3390 (broad, N–H), 2919-2840 (strong, C–H), 2104 (strong, Si–H), 835 (weak, Si–N). TGA ($N_2$): $T_{-5\%}$ = 157 °C, total % wt. loss at 1000 °C = 82%. TGA ($O_2$): $T_{-5\%}$ = 126 °C, total % wt. loss at 1000 °C = 80%.

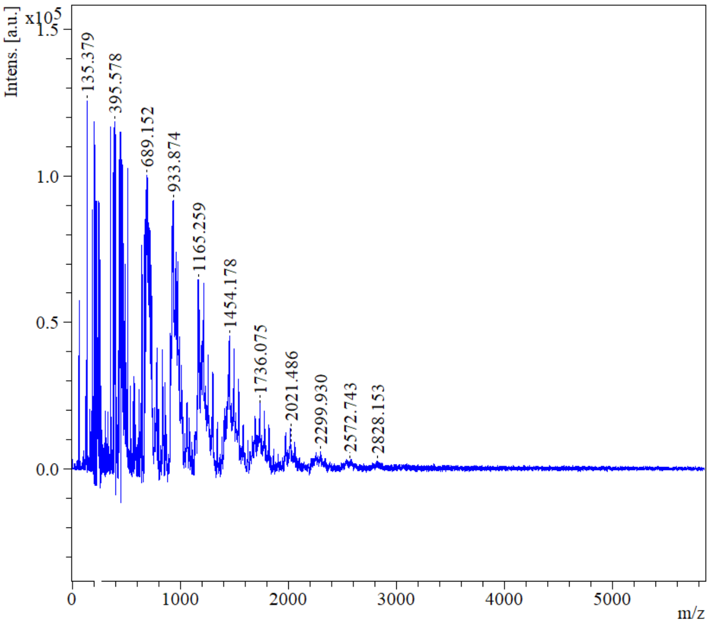


**Figure S53.** MALDI-TOF spectrum of **2e** THF wash.

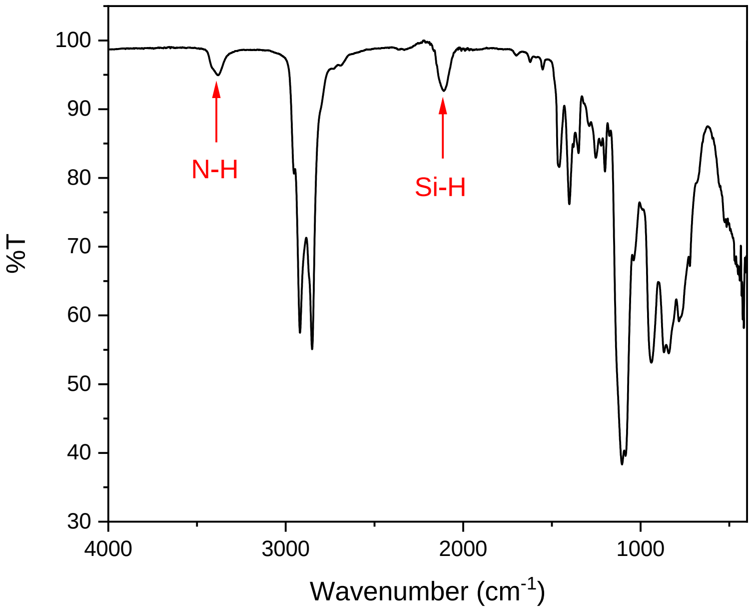


**Figure S54.** FT-IR spectrum of **2e** in KBr.

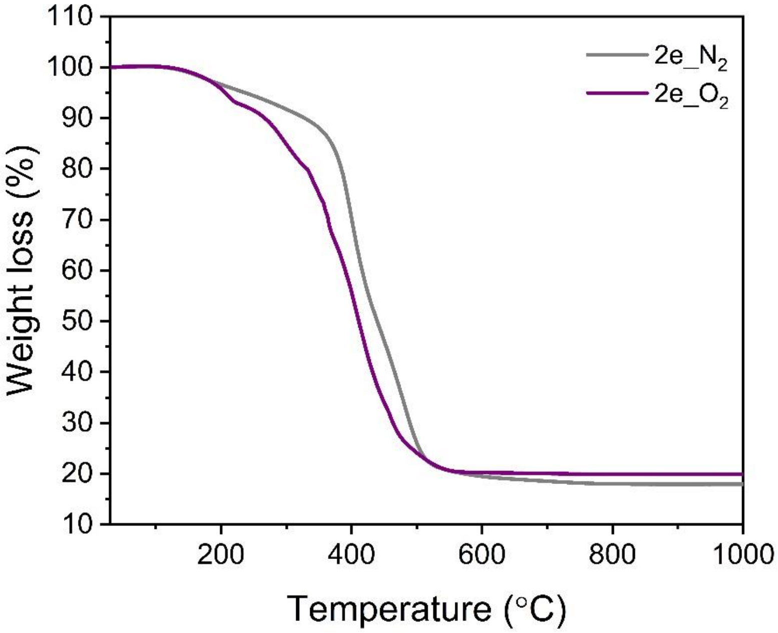


**Figure S55.** TGA thermogram of **2e** under $N_2$ and $O_2$.

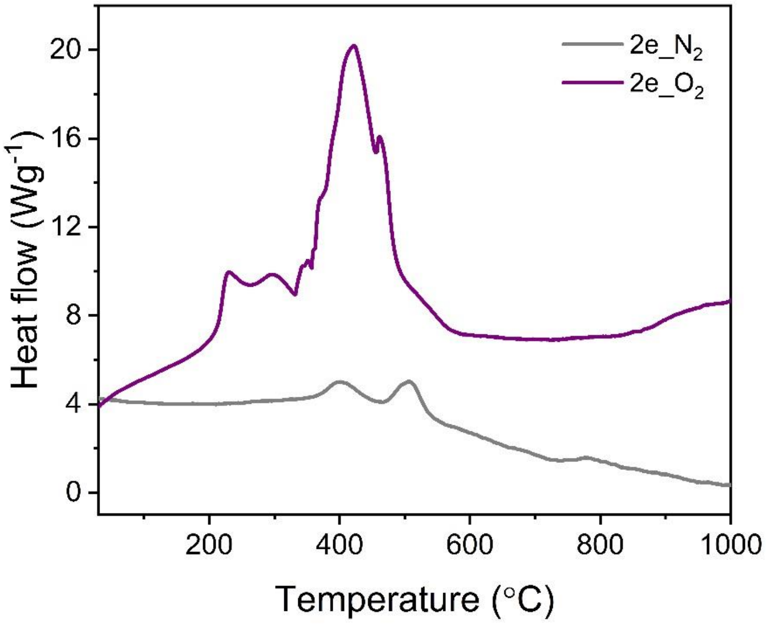


**Figure S56.** DSC thermogram of **2e** under $N_2$ and $O_2$.

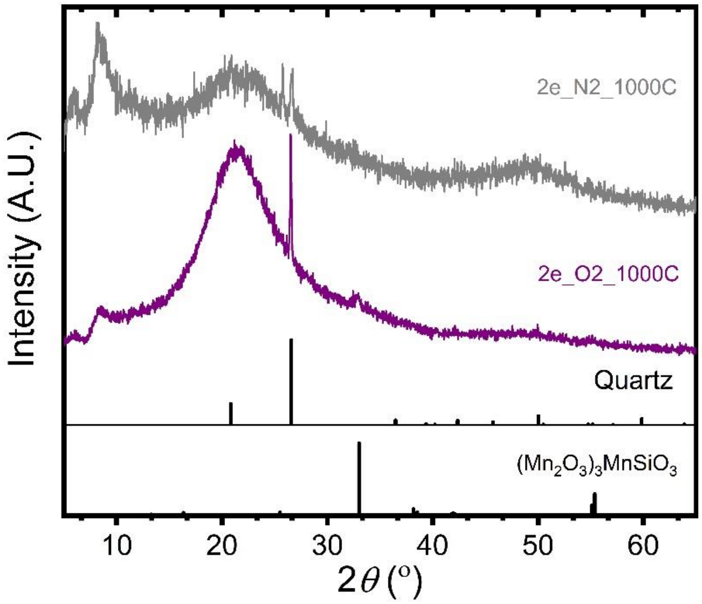
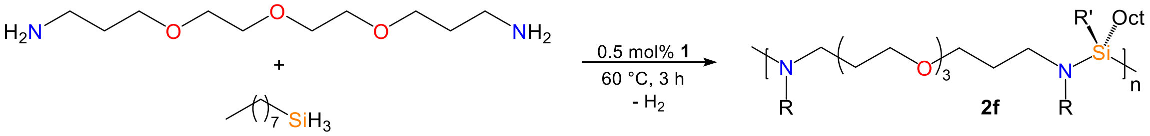
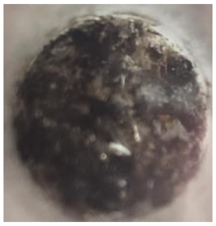


**Figure S57.** PXRD patterns of **2e** after TGA under $N_2$ and $O_2$, together with simulated patterns of quartz and $(Mn_2O_3)_3MnSiO_3$.

## Preparation of 2f from octylsilane and 4,7,10-trioxa-1,13-tridecanediamine using 0.5 mol% 1.



**2f**



**Scheme S12.** Preparation and image of **2f**.

*Procedure for conversion determination:* In a $N_2$ filled glovebox, a 20 mL vial was weighed before adding 0.005 g (0.005 mmol) of **1**. Afterwards, 188 µL (0.97 mmol) of octylsilane was added and no obvious color change was noted. Next, 206 µL (0.97 mmol) of 4,7,10-trioxa-1,13-tridecanediamine was added. Instantly, the evolution of hydrogen gas was observed, and the solution turned orange in color. The vial was kept uncapped under $N_2$ atmosphere for 3 h at ambient temperature to yield a dark brown solution. After 3 h, the catalyst was deactivated by exposing to air and degassed under vacuum for 30 s. A $^1$H NMR spectrum of the wash in benzene-$d_6$ showed greater than 99% conversion of the starting diamine.

*Procedure for isolation and solid-state characterization:* In a $N_2$ filled glovebox, a 20 mL vial was weighed before adding 0.005 g (0.005 mmol) of **1**, followed by 209 µL (1.08 mmol) of octylsilane. No obvious color change was noted. Next, 230 µL (1.08 mmol) of 4,7,10-trioxa-1,13-tridecanediamine was added. The formation of $H_2$ was observed and the solution turned orange in color. The reaction was heated at 60 °C for 3 h to obtain a dark brown solid. Next, the vial was brought outside the glovebox and the catalyst was deactivated by exposing to air. The reaction was then brought back into the glovebox and degassed under vacuum for 30 s. The product was washed with pentane and ether to remove residual ligand and dried under vacuum to obtain 0.342 g (88% yield, assuming complete diamine dehydrocoupling) of a solid product identified as **2f**. MALDI-TOF of THF wash ($[M+H]^+$, m/z): 933.3 (n = 2 + trioxadiamine), 1060 (n = 3), 1299 (n = 3 + trioxadiamine), 1539 (n = 4), 1821 (n = 5), 2060 (n = 5 + 2 octylsilane), 2314 (n = 6 + 1 octylsilane), 2625 (n = 6 + 2 trioxadiamine), and 2851 (n = 8). IR (KBr, cm$^{-1}$): 3391 (broad, N–H), 2928-2844 (strong, C–H), 2112 (strong, Si–H), 838 (weak, Si–N). TGA ($N_2$): $T_{-5\%}$ = 237 °C, total % wt. loss at 1000 °C = 89%. TGA ($O_2$): $T_{-5\%}$ = 206 °C, total % wt. loss at 1000 °C = 85%.

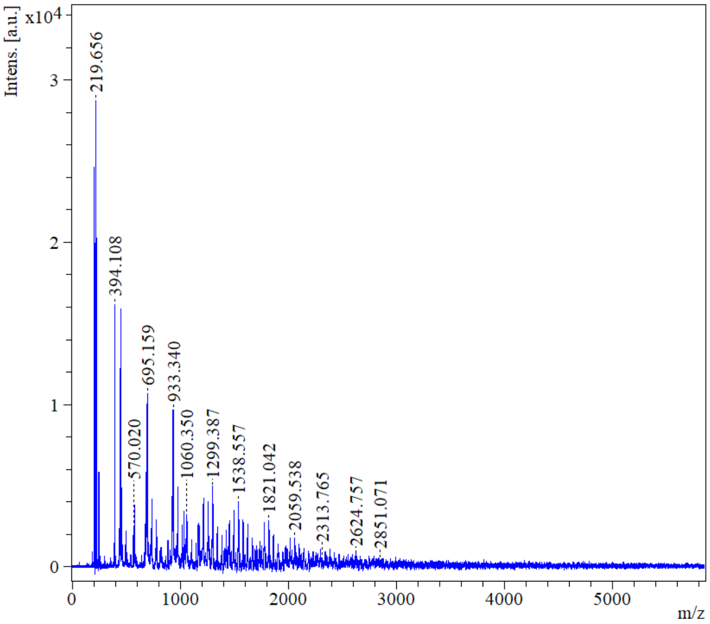


**Figure S58.** MALDI-TOF spectrum of **2f** THF wash.

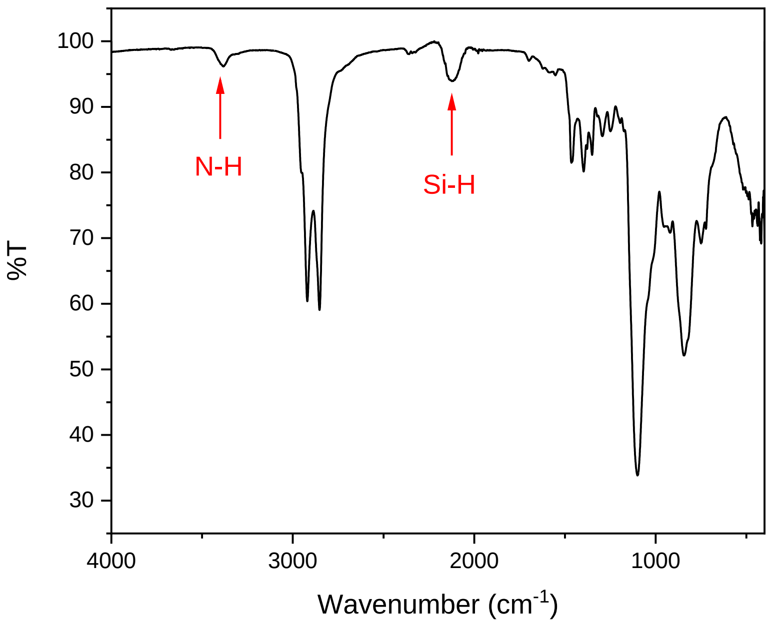


**Figure S59.** FT-IR spectrum of **2f** in KBr.

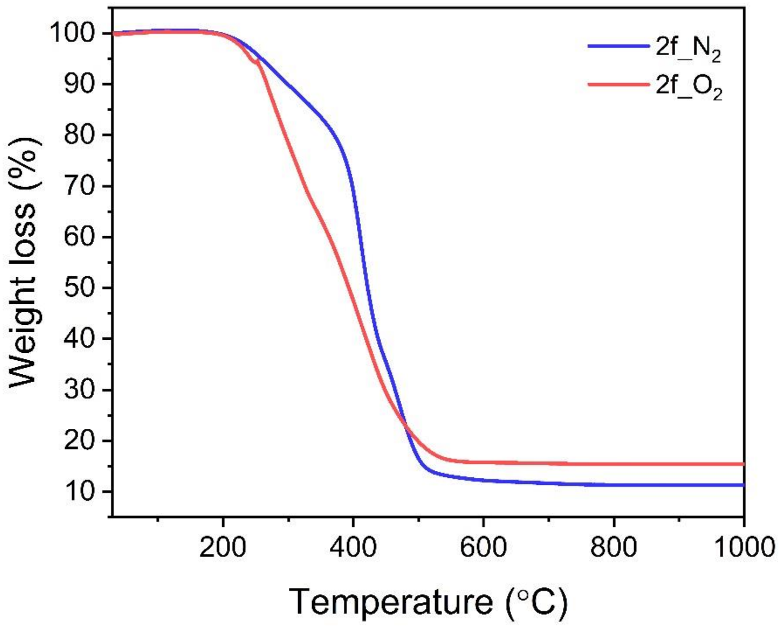


**Figure S60.** TGA thermogram of **2f** under $N_2$ and $O_2$.

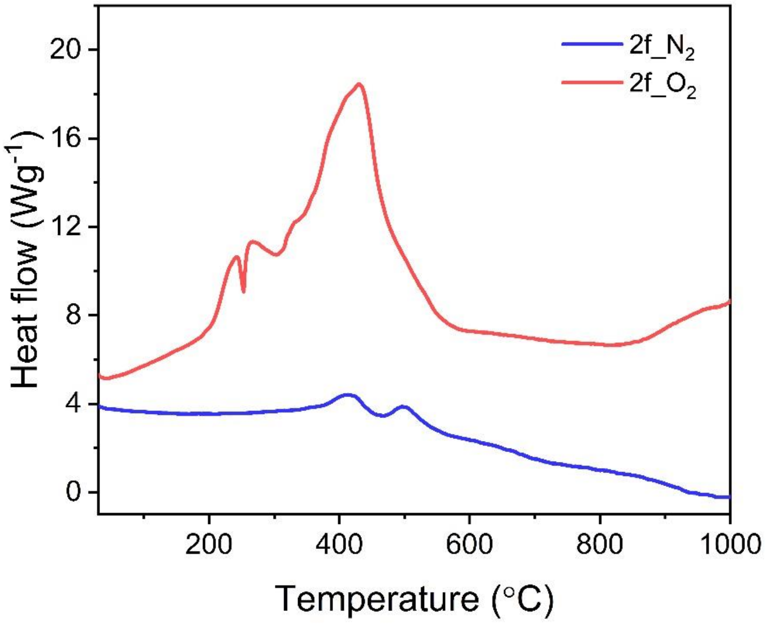


**Figure S61.** DSC thermogram of **2f** under $N_2$ and $O_2$.

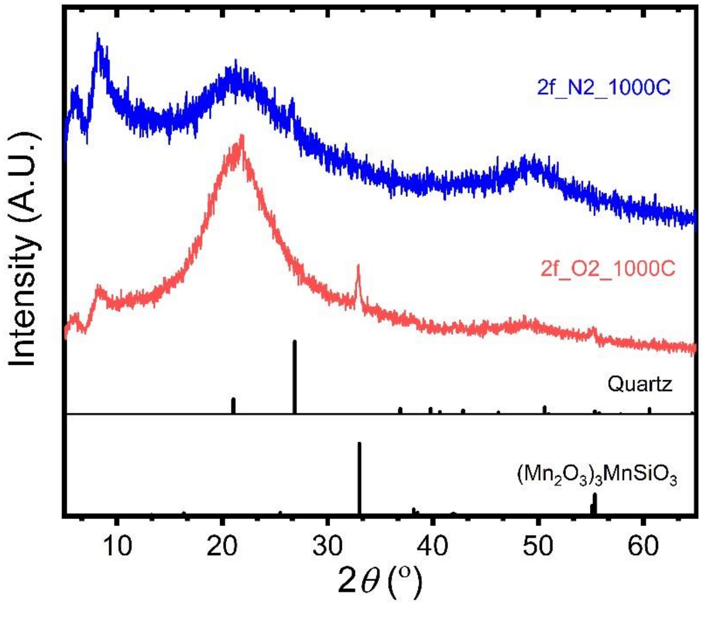


**Figure S62.** PXRD patterns of **2f** after TGA under $N_2$ and $O_2$, together with simulated patterns of quartz and $(Mn_2O_3)_3MnSiO_3$.

## SILANE DIAMINE COPOLYMER HYDROLYSIS

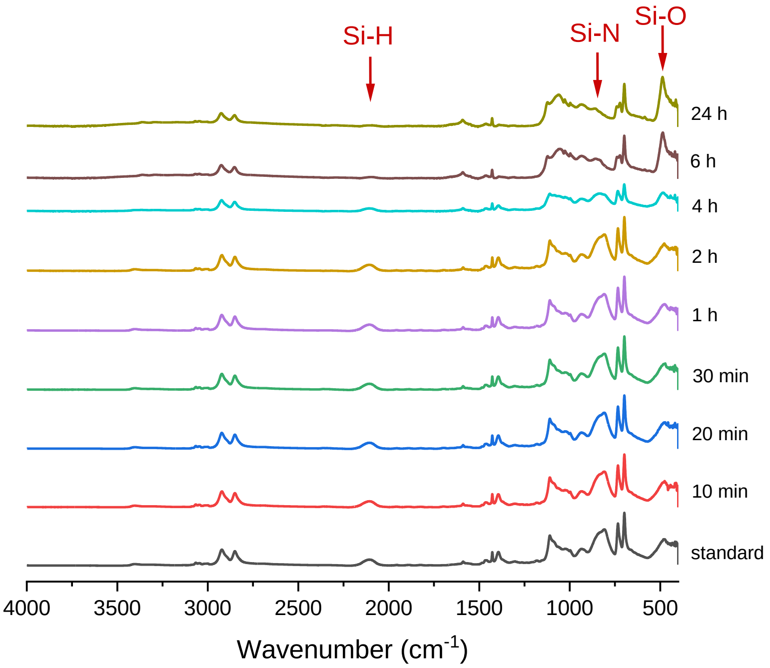
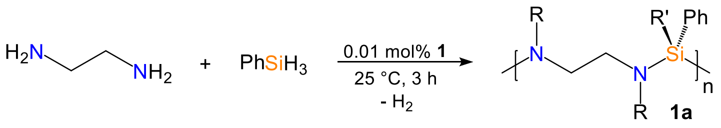


**Figure S63.** FT-IR spectra of **1a** collected before (black) and after exposure to air (23% humidity).

## TURNOVER FREQUENCY EXPERIMENT



In a $N_2$ filled glovebox, 0.005 g (0.005 mmol) of **1** was added to a 50 mL beaker. Then, 7.14 mL (58.11 mmol) of phenylsilane was added, followed by 2.5 mL of mesitylene and no obvious color change was noted. Next, 3.9 mL (58.11 mmol) of ethylenediamine was added. Instantly, the evolution of hydrogen gas was observed, and the solution turned from yellow to orange to dark brown in color over the course of 5 min. Aliquots of the reaction mixture were collected at regular intervals, and transferred to a vial that contained $I_2$ to deactivate the catalyst. The solution was then washed with benzene-$d_6$ and filtered through a microglass fiber for $^1$H NMR characterization. The percent conversion observed as a function of time is shown in Table S2.

**Table S2.** Percent conversion of the dehydrogenative coupling of ethylenediamine and phenylsilane using 0.01 mol% **1**.

| **Time** | **% Conversion** |
|---|---|
| 10 s | 30 |
| 30 s | 52 |
| 1 min | 79 |
| 5 min | 89 |
| 10 min | 91 |
| 30 min | 99 |

## PREPARATION OF LIGHTLY CROSSLINKED SOLUTIONS

**Preparation of 10% wt. solution of 1a:** Inside an inert glovebox atmosphere, a 20 mL scintillation vial was charged with 0.010 g (0.011 mmol) of **1**. To another vial, 0.14 mL (2.18 mmol) of ethylenediamine, 0.27 mL (2.18 mmol) of phenylsilane, and 3.3 mL of THF was added. The resulting mixture was then added to the vial containing **1** and the reaction slowly darkened in color. The mixture was then allowed to stir at room temperature for 1 h in a loosely capped vial to avoid any build-up of hydrogen gas. After 1 h, a piece of Cu tape was dip coated once into this solution for SEM analysis. *A similar procedure was followed to prepare 10% wt. solution of* ***2a****.*

**Preparation of 10% wt. solution of 1c:** Inside an inert glovebox atmosphere, a 20 mL scintillation vial was charged with 0.010 g (0.011 mmol) of **1**. To another vial, 0.251 g (2.18 mmol) of 1,6-diaminohexane, 0.27 mL (2.18 mmol) of phenylsilane, and 4.45 mL of THF was added. This resulting mixture was then added to the vial containing **1** and the reaction slowly darkened in color. The mixture was then allowed to stir at 60 °C for 1 h in a loosely capped vial to avoid any build-up of hydrogen gas. After 1 h, a piece of Cu tape was dip coated once into this solution for SEM analysis. *A similar procedure was followed to prepare 10% wt. solution of* ***2c****.*

**Preparation of 10% wt. solution of 1e:** Inside an inert glovebox atmosphere, a 20 mL scintillation vial was charged with 0.010 g (0.011 mmol) of **1**. To another vial, 0.32 mL (2.18 mmol) of 2,2'-(ethylenedioxy)bis(ethylamine), 0.27 mL (2.18 mmol) of phenylsilane, and 5.1 mL of THF was added. This resulting mixture was then added to the vial containing **1** and the reaction slowly darkened in color. The mixture was then allowed to stir at room temperature for 1 h in a loosely capped vial to avoid any build-up of hydrogen gas. After 1 h, a piece of Cu tape was dip coated once into this solution for SEM analysis. A *similar procedure was followed to prepare 10% wt. solution of **2e**.*

## ANALYSIS OF COATINGS

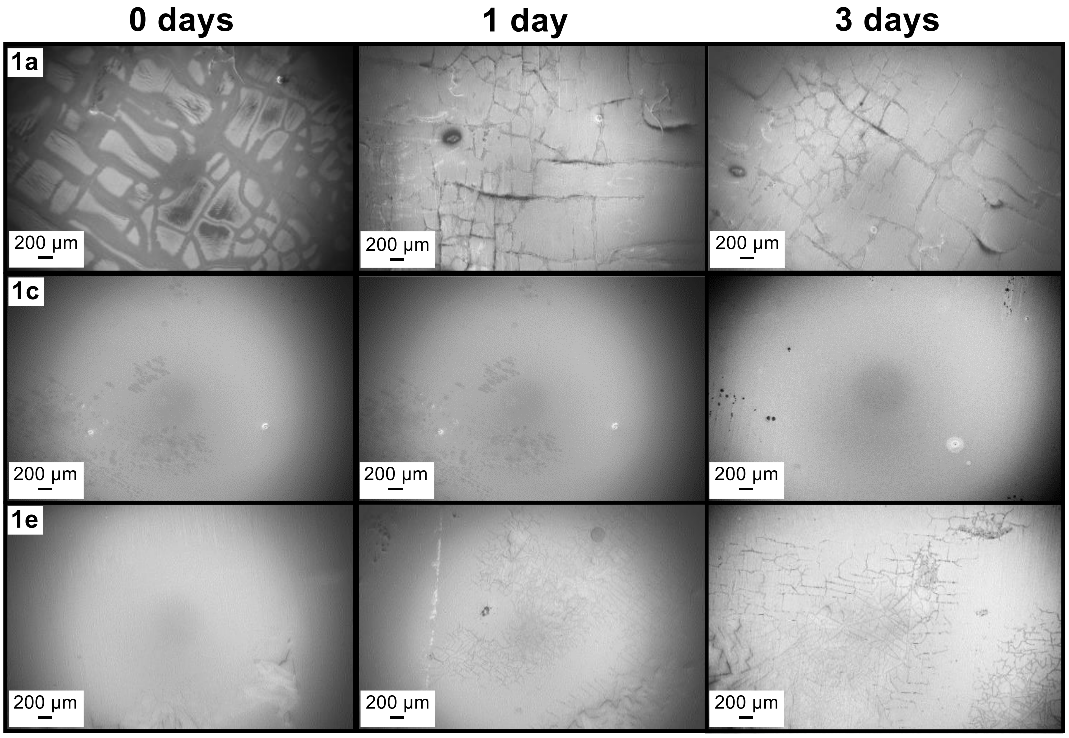


**Figure S64.** SEM images of copper tape dip-coated with **1a** (top), **1c** (middle), and **1e** (bottom) at 23× magnification and 0 days, 1 day, and 3 days of curing in air.

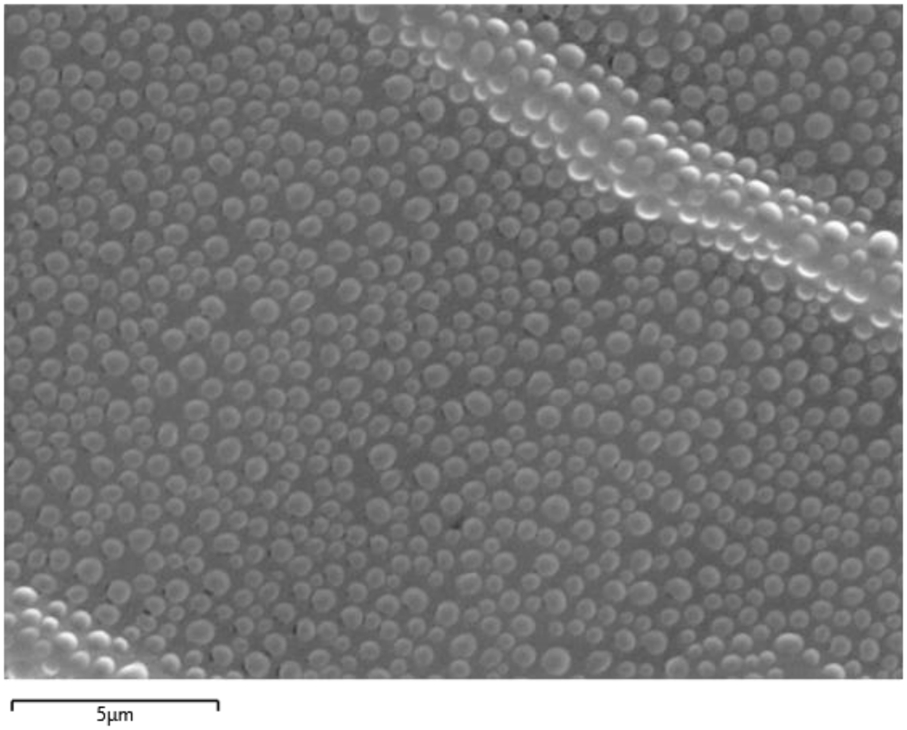


**Figure S65.** SEM image of copper tape dip-coated with **1a** at 1000× magnification and 0 days of curing in air.

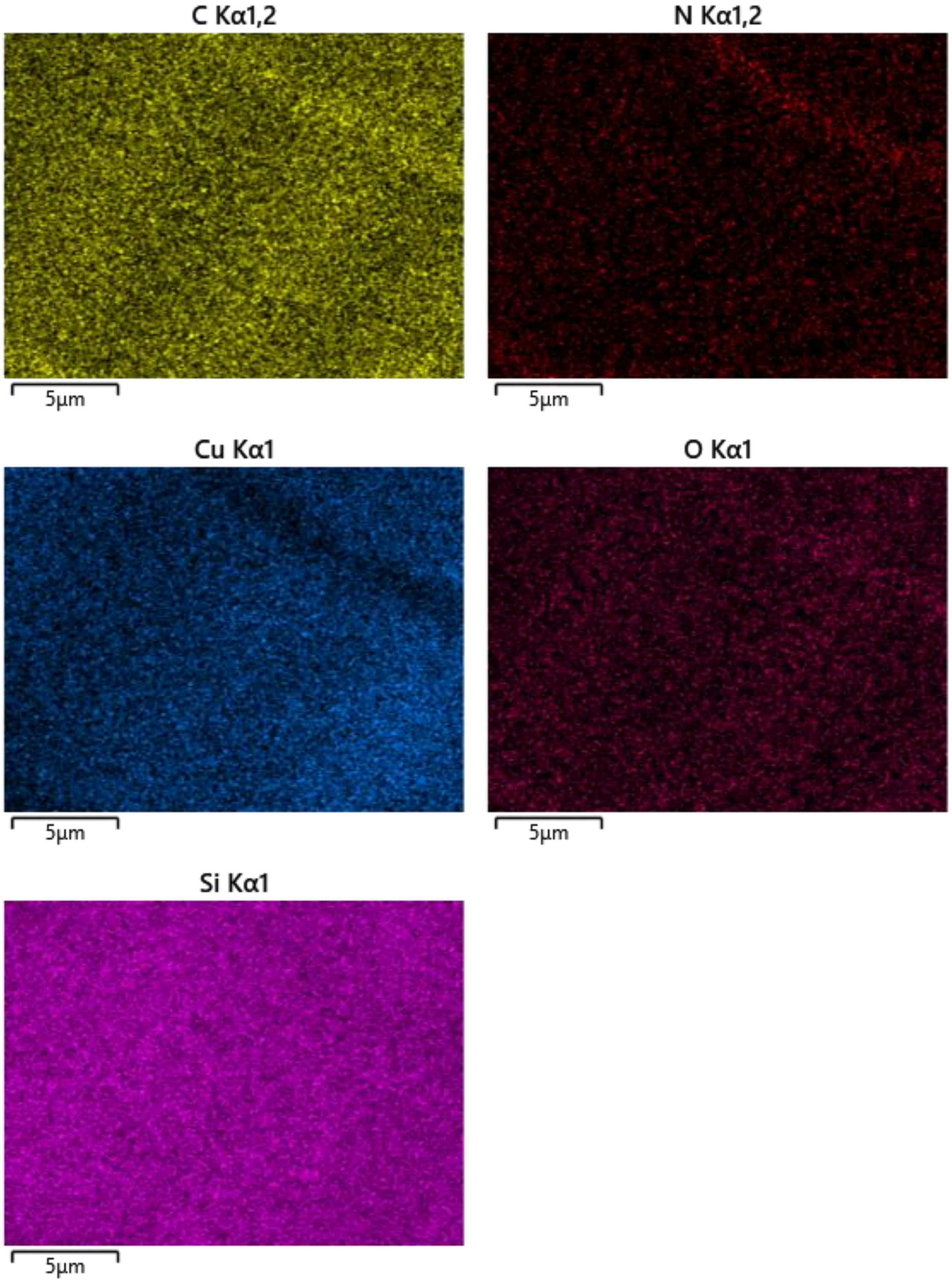


**Figure S66.** EDX analysis of copper tape dip-coated with **1a** at 1000× magnification and 0 days of curing in air (compare to **Figure S65**).

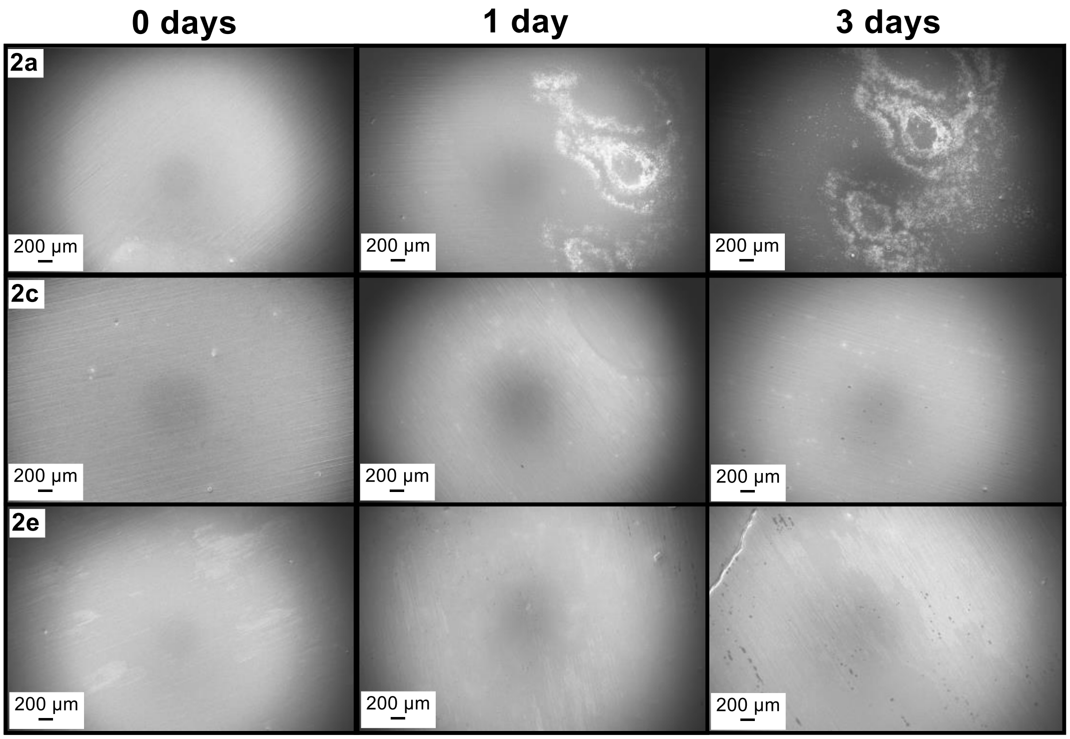


**Figure S67.** SEM images of copper tape dip-coated with **2a** (top), **2c** (middle), and **2e** (bottom) at 23× magnification after 0 days, 1 day, and 3 days of curing in air.

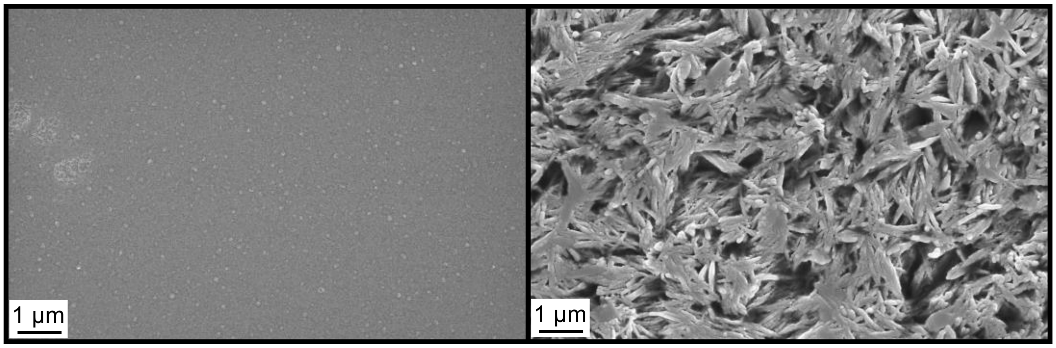


**Figure S68.** SEM images of Cu tape dip-coated once with 10% wt. solution of **1c** (left) and SEM image of Cu tape dip-coated three times with 20% wt. solution of **1c** (right) at 10,000× magnification.

## REFERENCES

1. T. K. Mukhopadhyay, M. Flores, T. L. Groy and R. J. Trovitch, *Chem. Sci.* 2018, **9**, 7673-7680.