Thiol-Triggered Deconstruction of Bifunctional Silyl Ether Terpolymers via an S_NAr-Triggered Cascade

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Supplementary Figures

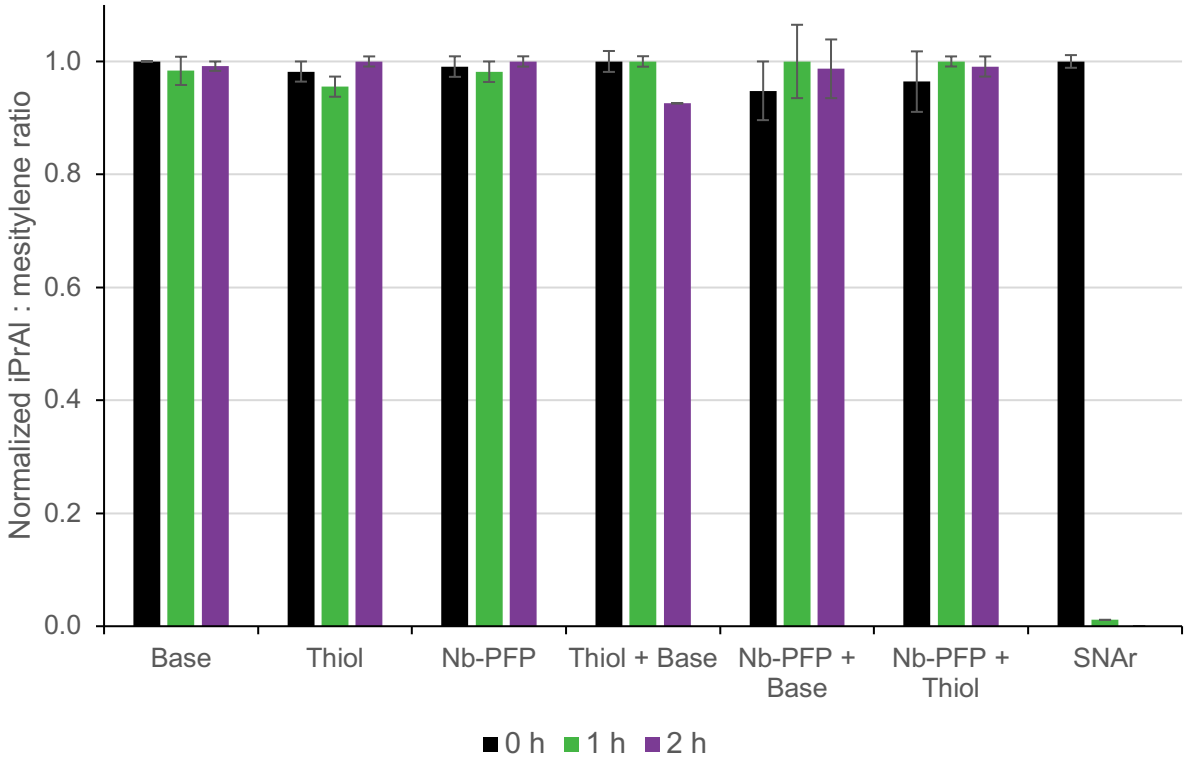


Fig. S1. Bar chart comparing the ratio of **iPrAl** to a mesitylene internal standard (10 mol%) from GC-MS runs. **iPrAl** reacted with either K_2CO_3 (base), **Nb-PFP**, 1-dodecanethiol (thiol), or combinations of the above in DMF for 2 h at 25 °C. Time points at 0 h (black), 1 h (green), and 2 h (purple). Ratios calculated using peak integration, and averaged over three runs. Error bars show standard deviation.

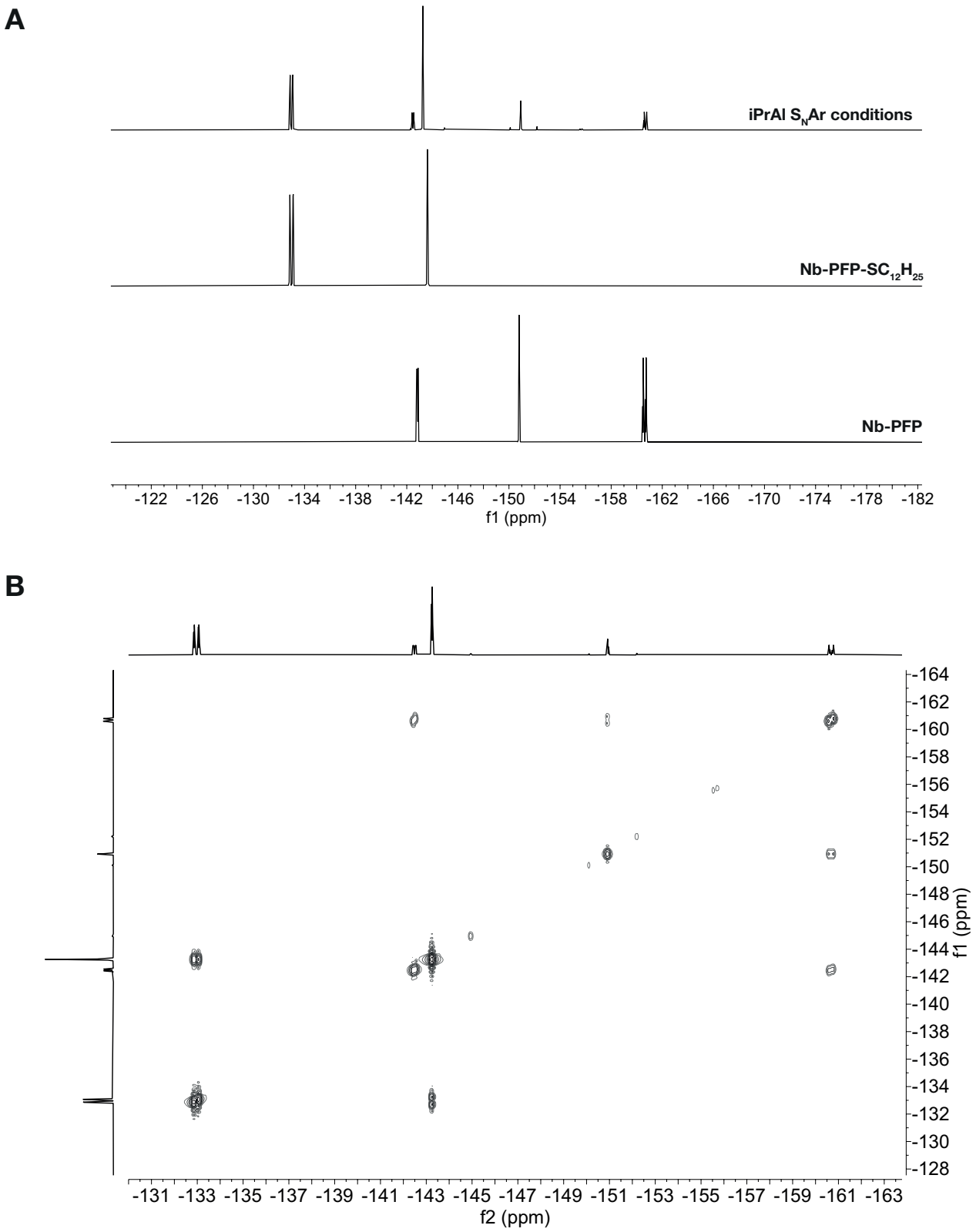


Fig. S2. A) ^{19}F NMR spectra (565 MHz, $CDCl_3$. 25 °C) comparing the reaction mixture of the S_NAr conditions **iPrAl**, 1-dodecanethiol, **Nb-PFP** and K_2CO_3 in DMF (top) to monomer **Nb-PFP-SC$_{12}$H$_{25}$** (middle) and synthesized S_NAr product **Nb-PFP** (bottom). B) ^{19}F–^{19}F COSY NMR experiment of the S_NAr mixture (565 MHz, $CDCl_3$, 25 °C).

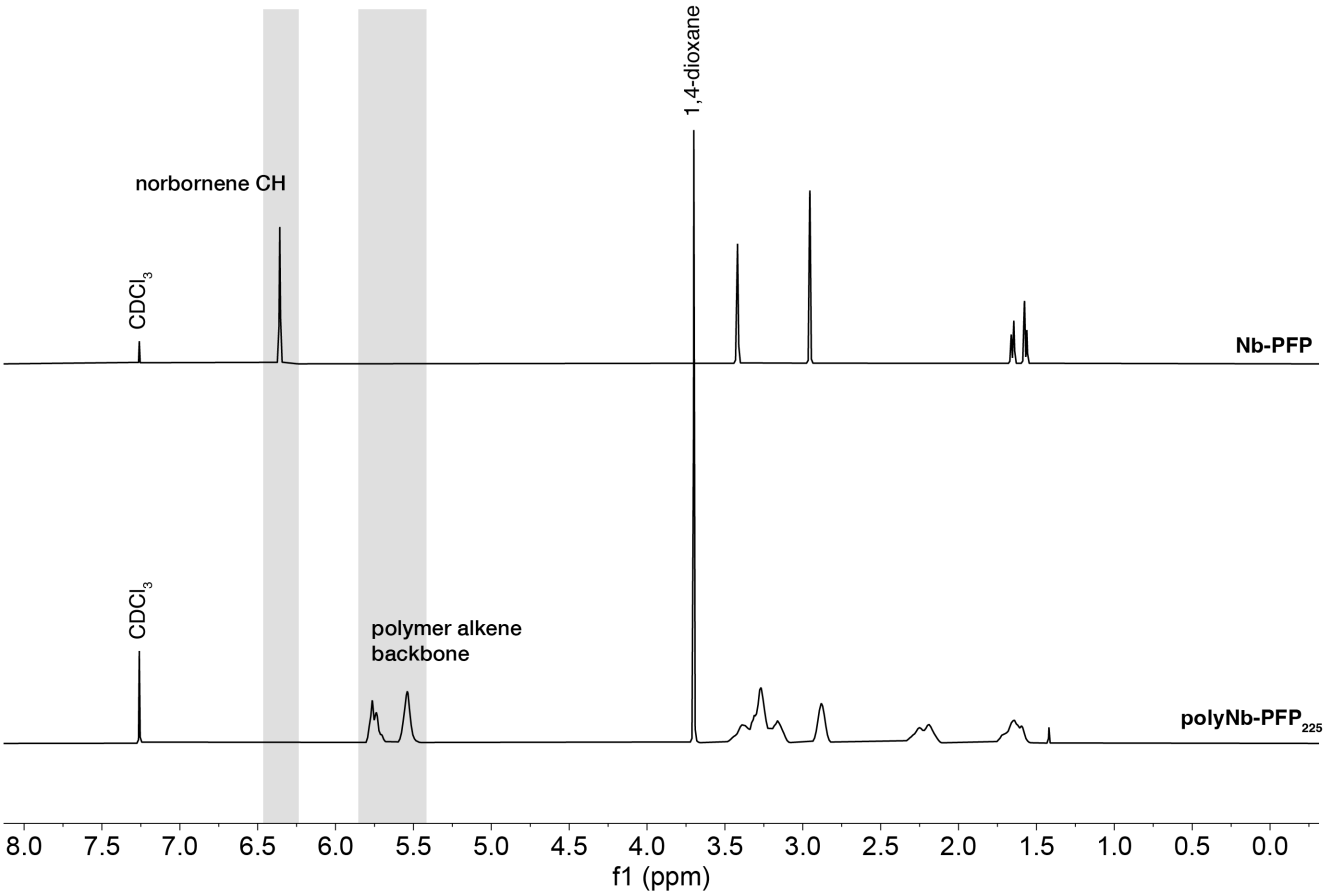


Fig. S3. ^{1}H NMR spectra comparing **Nb-PFP** (top) to polymerized **polyNb-PFP** (bottom) (600 MHz, $CDCl_3$. 25 °C).

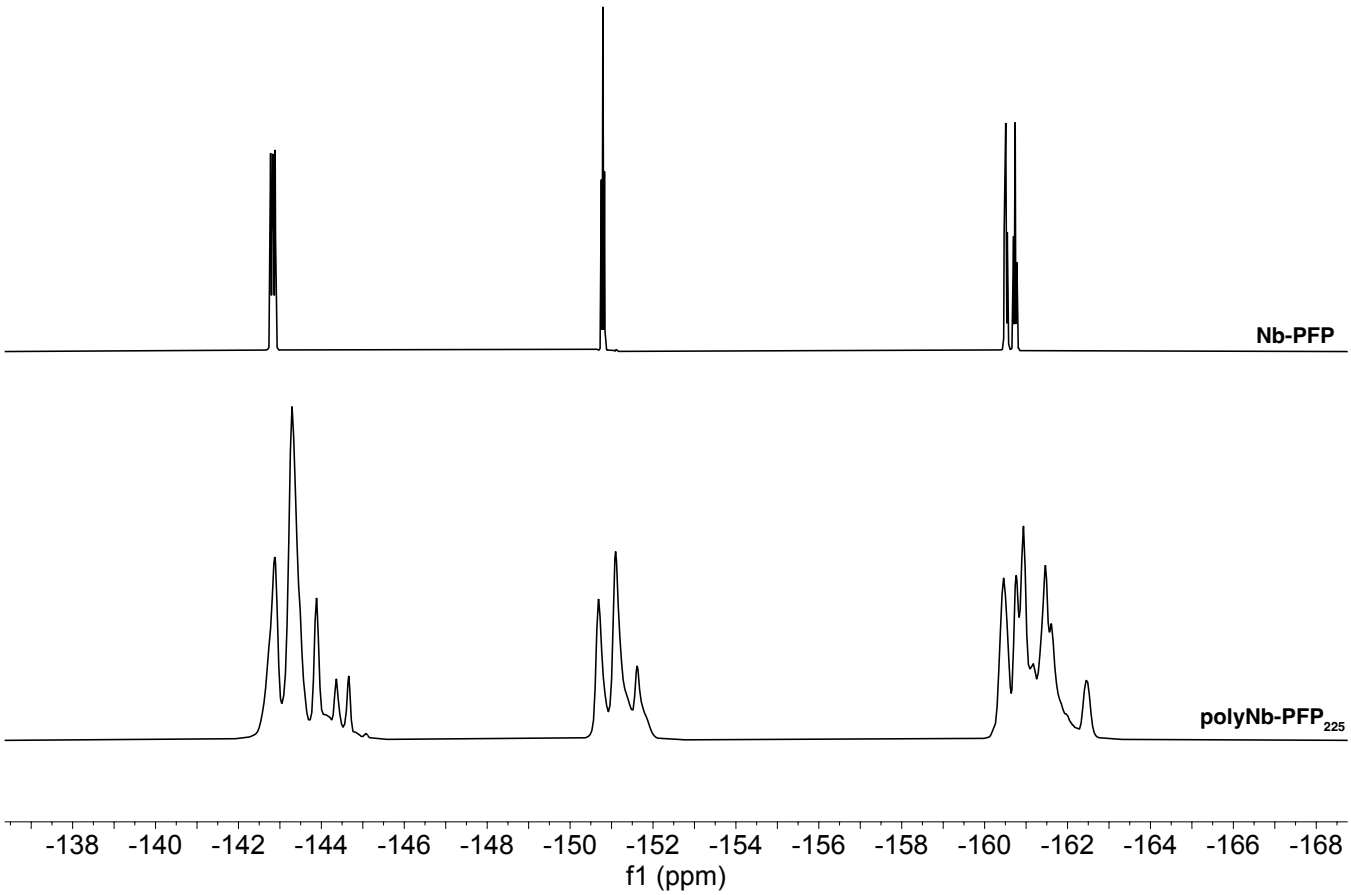


Fig. S4. ^{19}F NMR spectra comparing **Nb-PFP** (top) to polymerized **polyNb-PFP** (bottom) (565 MHz, $CDCl_3$. 25 °C).

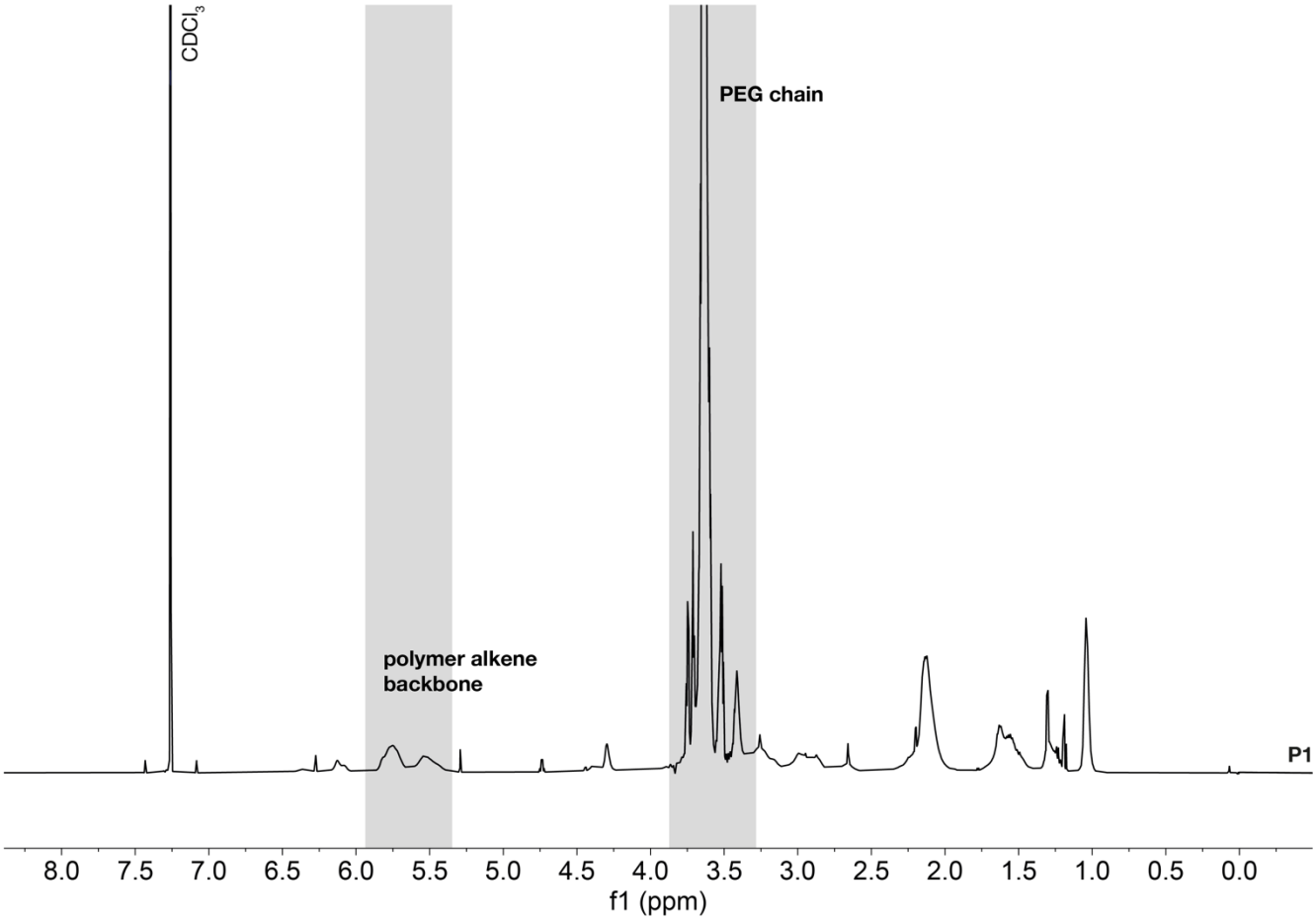


Fig. S5. ^{1}H NMR spectrum of **P1** (600 MHz, $CDCl_3$. 25 °C).

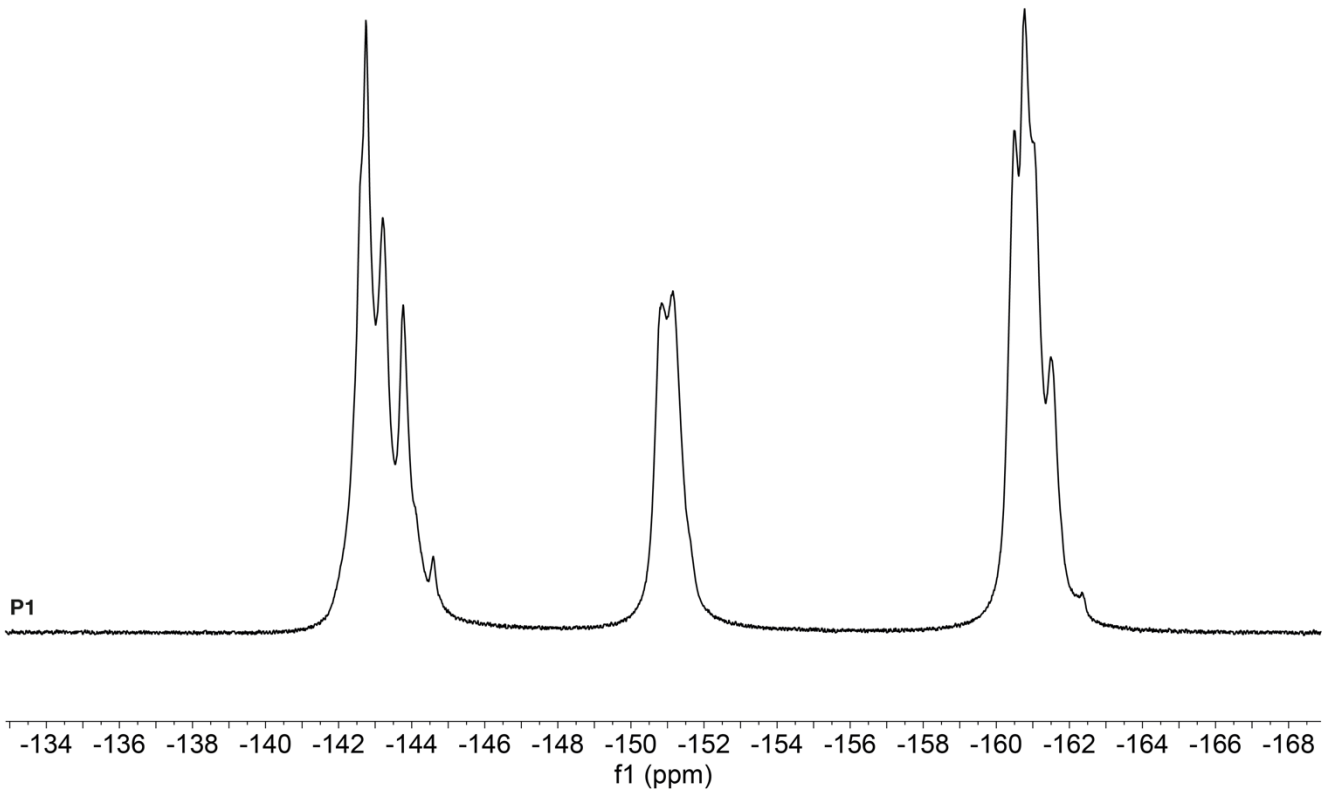


Fig. S6. ^{19}F NMR spectrum of **P1** (565 MHz, $CDCl_3$. 25 °C).

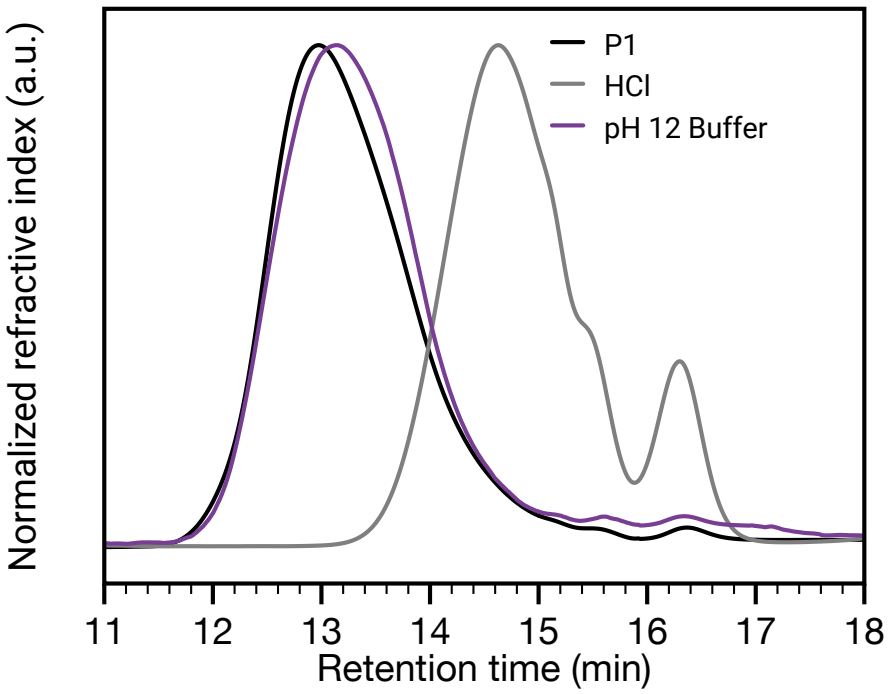


Fig. S7. GPC traces (DMF mobile phase) comparing the parent terpolymer **P1** (black) and the HCl hydrolysis product (grey), to the control experiment where **P1** is exposed to only a pH 12 Na_2HPO_4/NaOH buffer solution (purple).

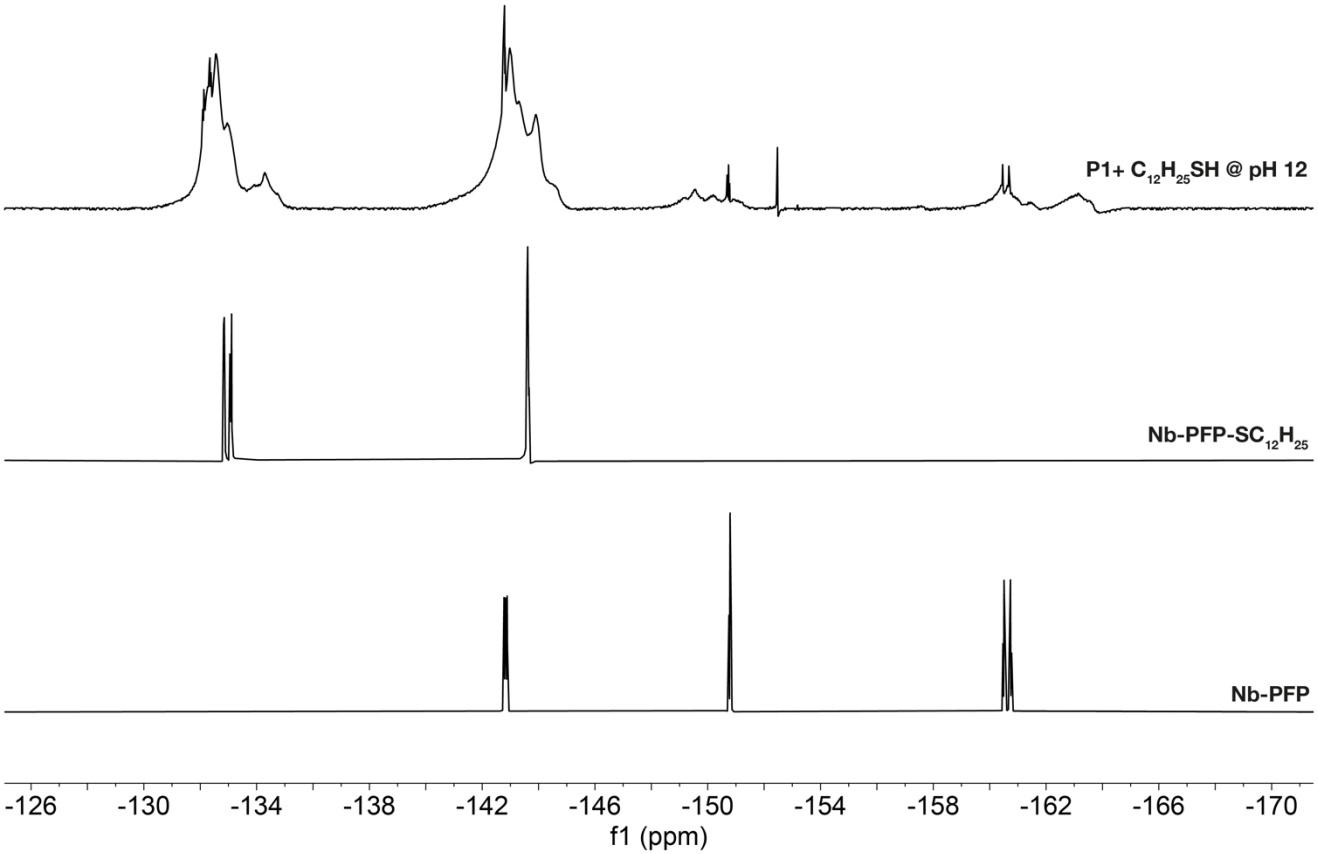


Fig. S8. ^{19}F NMR spectra comparing the S_NAr deconstruction products from the reaction of **P1** with 1-dodecanethiol in pH 12 buffer (top), to **Nb-PFP-SC$_{12}$H$_{25}$** (middle), and **Nb-PFP** (bottom) (565 MHz, $CDCl_3$. 25 °C).

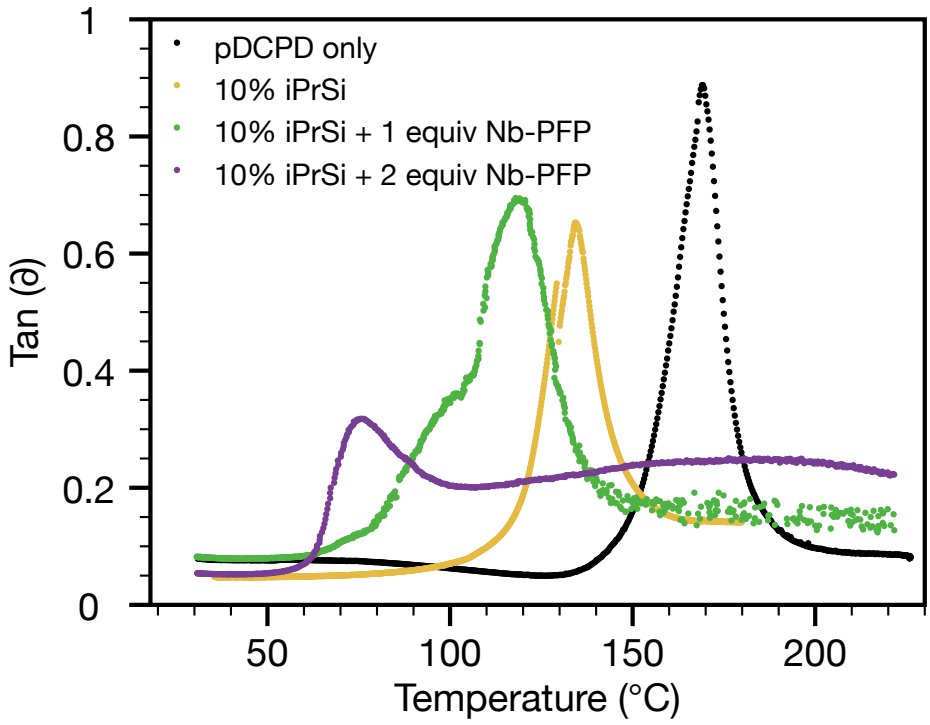


Fig. S9. Dynamic mechanical analysis (DMA) of thermoset materials containing: only pDCPD (black); 10% **iPrSi8** (yellow, **T2**); 10% i**PrSi8** + 1.0 equiv **Nb-PFP** (green); and 10% **iPrSi8** + 2.0 equiv **Nb-PFP** (**T1**).

Table S1. Glass transition temperatures (Tg) of thermoset materials calculated via DMA.

Sample	**Tg (°C)**
pDCPD only	169
10% iPrSi8 (**T2**)	134
10% iPrSi8 + 1.0 equiv Nb-PFP	118
10% iPrSi8 + 2.0 equiv Nb-PFP (**T1**)	67

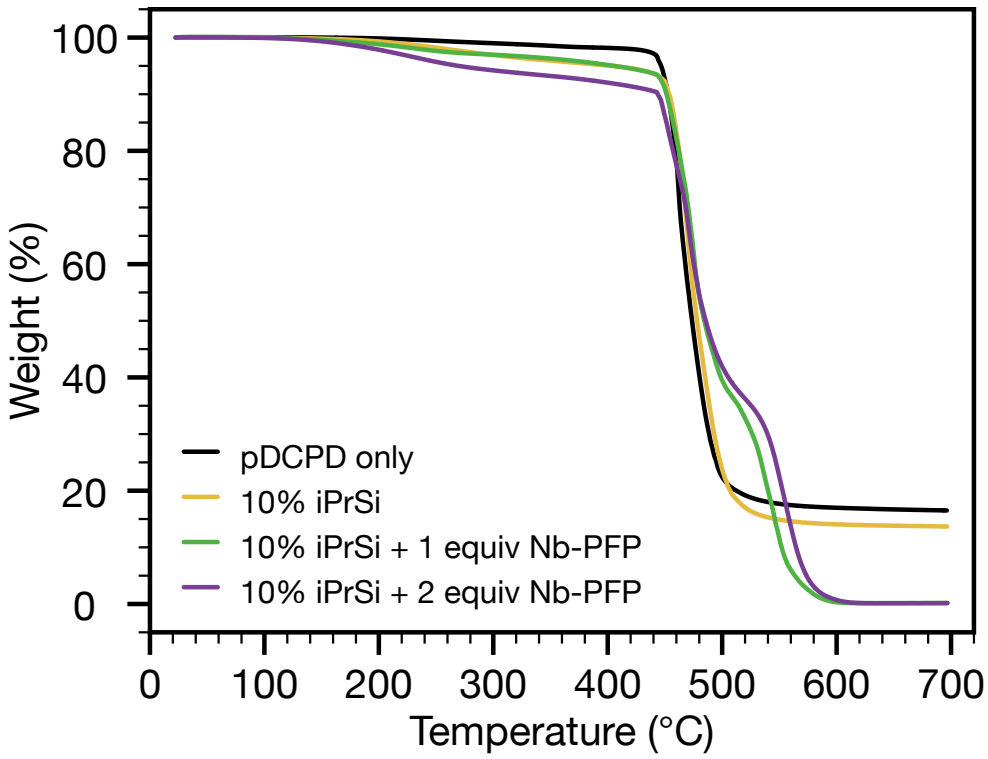


Fig. S10. Thermogravimetic analysis (TGA) of thermoset materials containing: only pDCPD (black); 10% **iPrSi8** (yellow, **T2**); 10% i**PrSi8** + 1.0 equiv **Nb-PFP** (green); and 10% **iPrSi8** + 2.0 equiv **Nb-PFP** (**T1**).

Table S2. Decomposition temperatures of thermoset materials calculated via TGA.

Sample	**Decomposition Temperature (°C)**
pDCPD only	453
10% iPrSi8 (**T2**)	464
10% iPrSi8 + 1.0 equiv Nb-PFP	458 (550)[1]
10% iPrSi8 + 2.0 equiv Nb-PFP (**T1**)	454 (547)[1]

[1] Secondary shoulder due to decomposition of **Nb-PFP** additive.

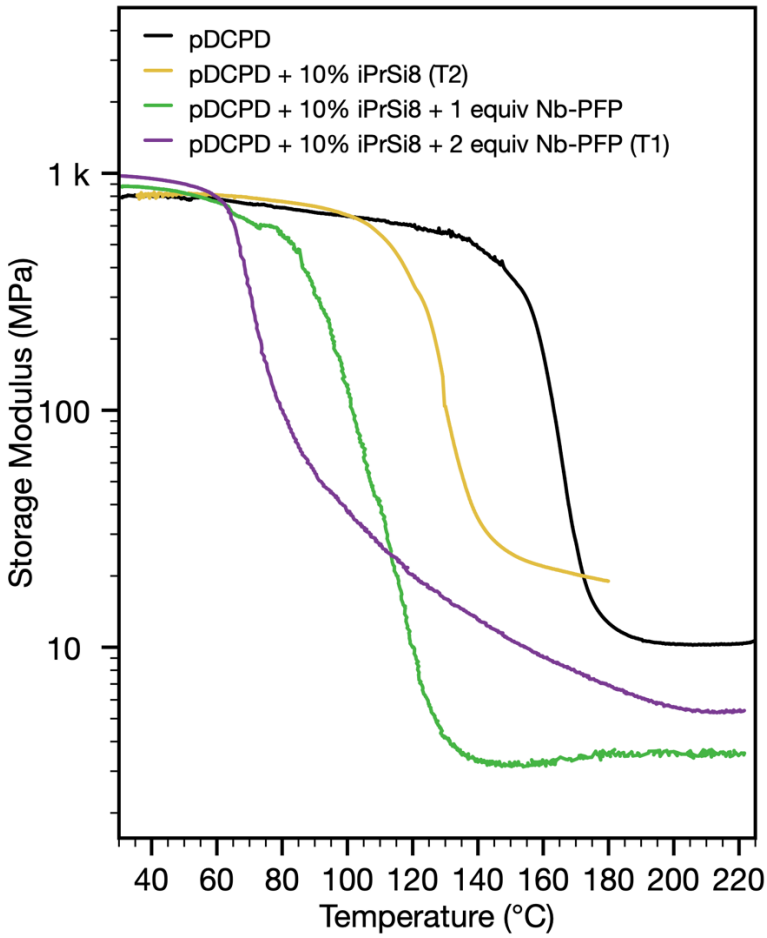


Fig. S11. Storage moduli calculated by DMA for thermoset materials containing: only pDCPD (black); 10% **iPrSi8** (yellow, **T2**); 10% i**PrSi8** + 1.0 equiv **Nb-PFP** (green); and 10% **iPrSi8** + 2.0 equiv **Nb-PFP** (**T1**).

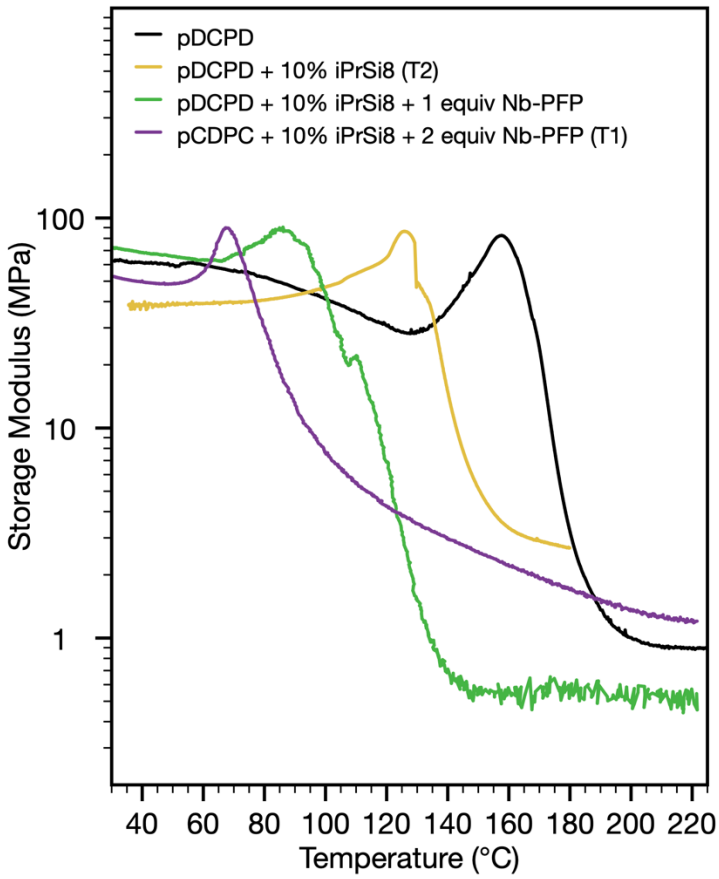


Fig. S12. Loss moduli calculated by DMA for thermoset materials containing: only pDCPD (black); 10% **iPrSi8** (yellow, **T2**); 10% i**PrSi8** + 1.0 equiv **Nb-PFP** (green); and 10% **iPrSi8** + 2.0 equiv **Nb-PFP** (**T1**).

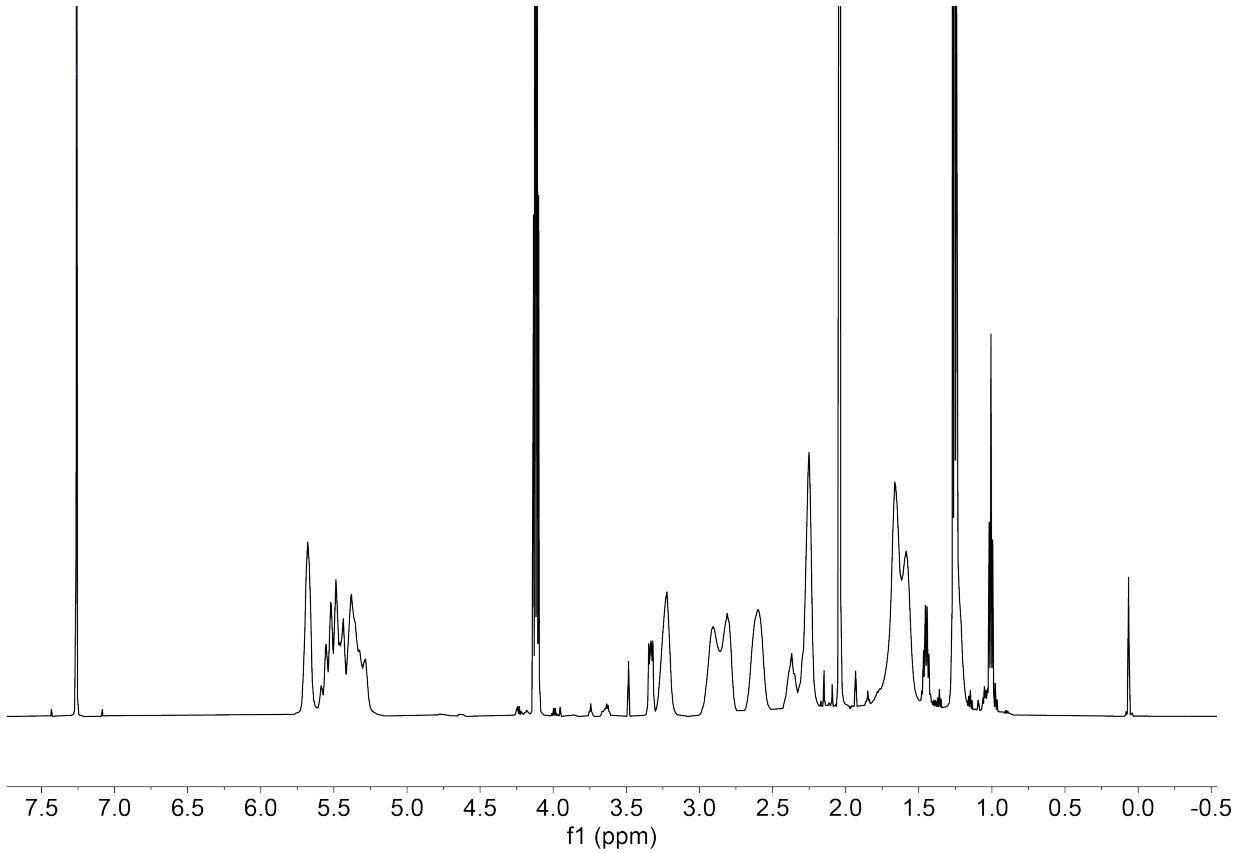


Fig. S13. ^{1}H NMR spectrum of **T1** fragments when exposed to TBAF (600 MHz, $CDCl_3$, 25 °C).

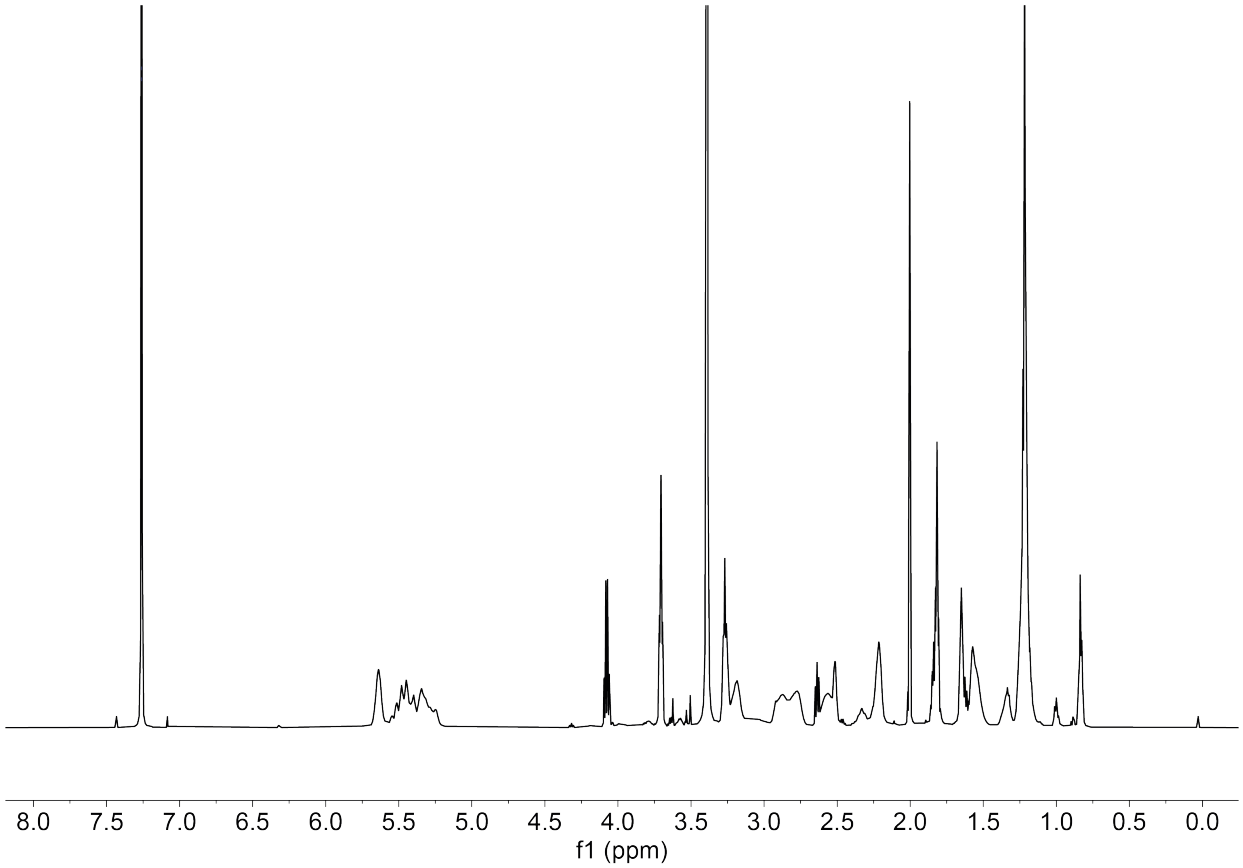


Fig. S14. ^{1}H NMR spectrum of **T1** deconstruction fragments generated from S_NAr conditions with 1-dodecanethiol and DBU (600 MHz, $CDCl_3$, 25 °C).

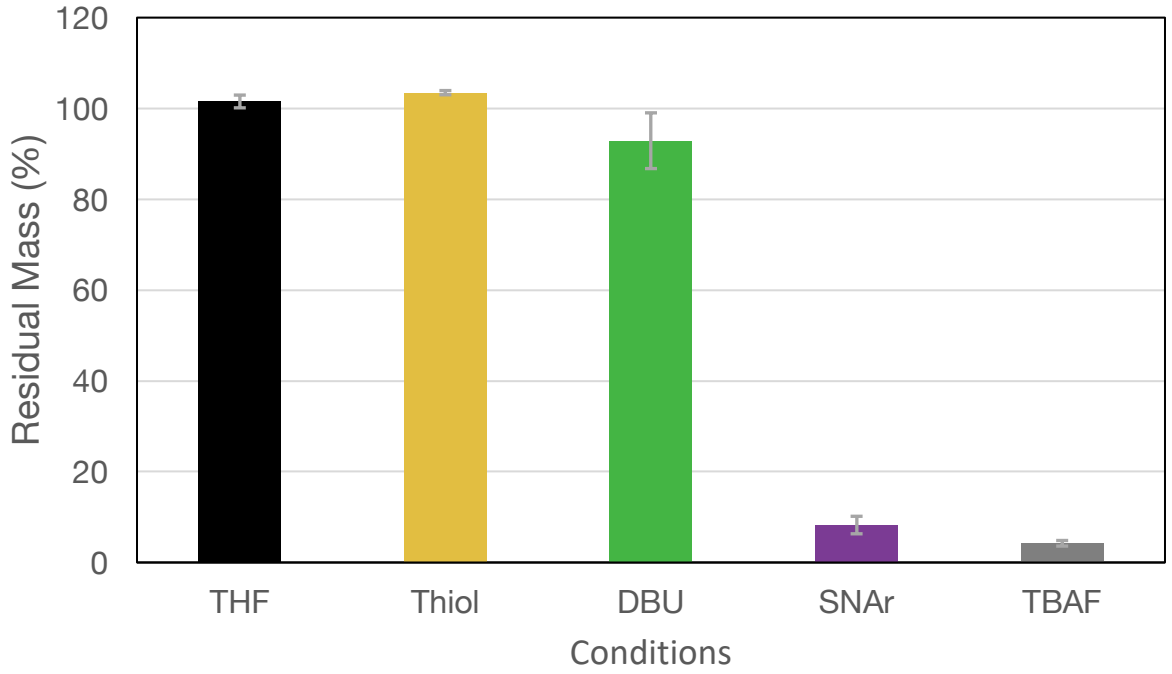


Fig. S15. Residual mass of **T1** after 3 h reaction with THF (as a negative control, *black*); THF and 1-dodecanethiol (2.0 equiv with respect to PFP, *yellow*); THF and DBU (2.0 equiv with respect to PFP, *green*); THF, 1-dodecanethiol (2.0 equiv with respect to PFP), and DBU (2.0 equiv with respect to PFP, S_NAr conditions, *purple*); and 0.2 M TBAF (as a positive control, *grey*). Error bars show standard deviation.

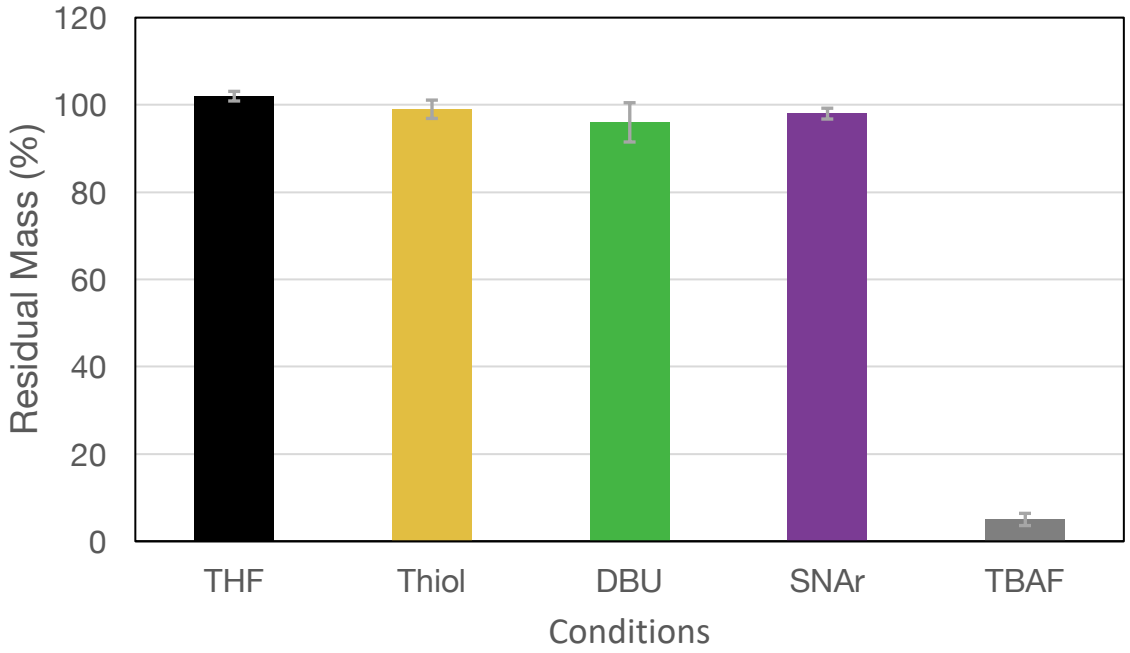


Fig. S16. Residual mass of **T2** after 3 h reaction with THF (as a negative control, *black*); THF and 1-dodecanethiol (2.0 equiv with respect to PFP, *yellow*); THF and DBU (2.0 equiv with respect to PFP, *green*); THF, 1-dodecanethiol (2.0 equiv with respect to PFP), and DBU (2.0 equiv with respect to PFP, S_NAr conditions, *purple*); and 0.2 M TBAF (as a positive control, *grey*). Error bars show standard deviation.

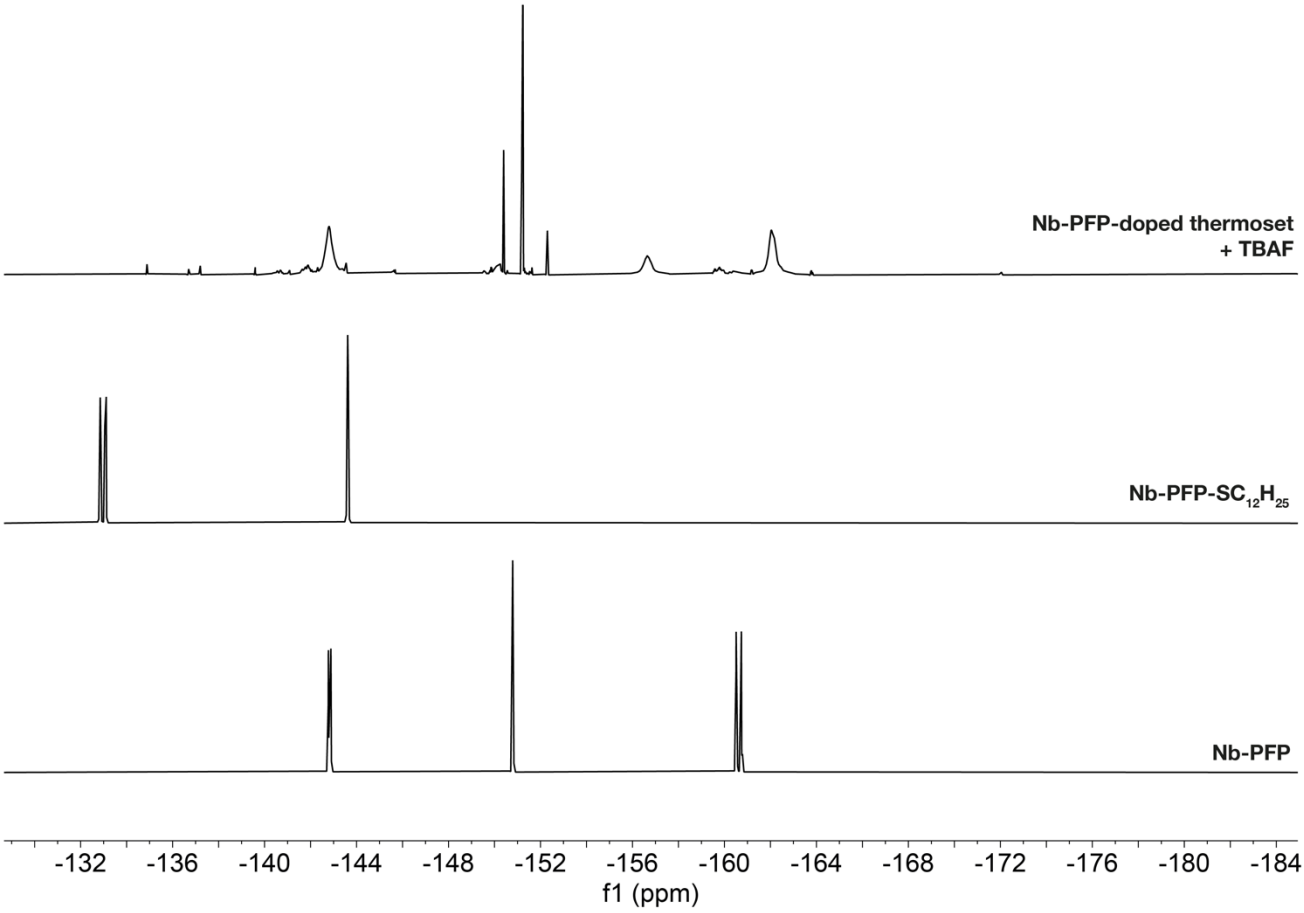


Fig. S17. ^{19}F NMR spectra of **T1** deconstruction fragments generated from TBAF (top) compared to **Nb-PFP-SC$_{12}$H$_{25}$** (middle), and **Nb-PFP** (bottom) (565 MHz, $CDCl_3$. 25 °C).

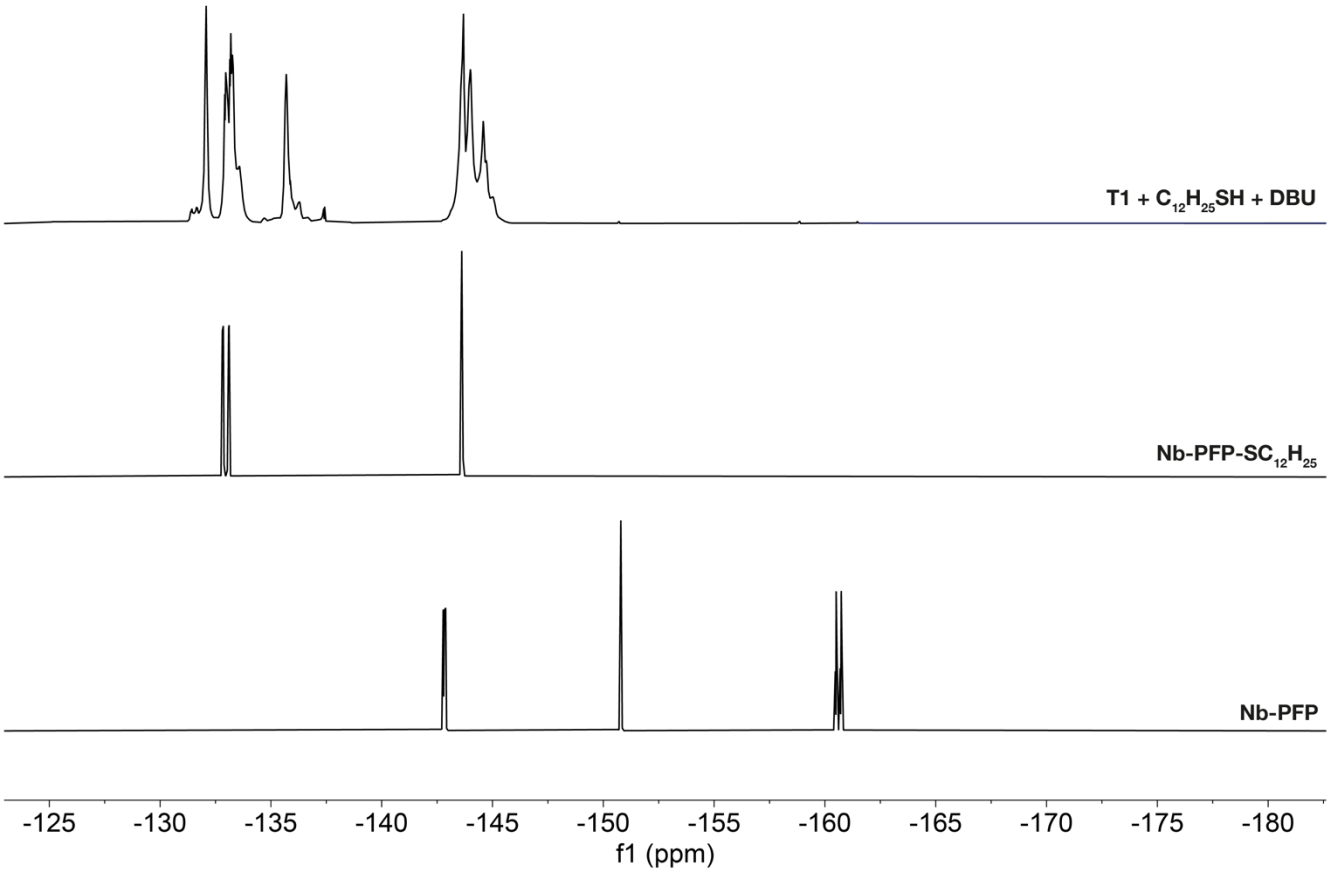


Fig. S18. ^{19}F NMR spectra of **T1** deconstruction fragments generated from S_NAr conditions of 1-dodacenethiol and DBU (top) compared to **Nb-PFP-SC$_{12}$H$_{25}$** (middle), and **Nb-PFP** (bottom) (565 MHz, $CDCl_3$. 25 °C).

Materials and Methods

Materials

Solvents were purchased from Millipore Sigma and were used as received unless otherwise noted. Dry solvents were used when available. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. and used as received. **iPrSi8**;[1] **Nb-PFP**;[2] **PEG-MM**,[3] and Grubbs' 3rd Generation catalyst[4] were prepared as per the literature.

Nuclear magnetic resonance spectroscopy (NMR)

^{1}H, $^{19}F\{^{1}H\}$, $^{13}C\{^{1}H\}$ and $^{13}C\{^{1}H\}\{^{19}F\}$ NMR spectra and 2D NMR experiments (^{1}H–^{1}H COSY, ^{19}F–^{19}F COSY, ^{1}H–$^{13}C\{^{19}F\}$ HSQC, ^{1}H–$^{13}C\{^{19}F\}$ HMBC, ^{19}F–^{13}C HSQC, and ^{19}F–^{13}C HMBC) were recorded using a 600 MHz Bruker AVANCE NMR spectrometer at 25 °C. The NMR spectra were referenced to the relevant residual protonated solvent peak. Chemical shifts are reported as parts per million (ppm) and splitting patters are designated as follows: s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet), and br (broad).

High-resolution mass spectrometry (HR-MS)

High resolution mass spectrometry (HR-MS) measurements were recorded using a JEOL AccuTOF 4G LC-plus system equipped with an ionSense DART (Direct Analysis in Real Time) source.

Gas chromatography-mass spectrometry (GC-MS)

GC-MS was conducted using a nominal mass Agilent 5977B mass spectrometer attached to a 7890B gas chromatograph fitted with an autosampler. The GC uses a J&W HP-5MS Ultra Inert column, 30 m x 0.25 mm x 0.25 μm. ChemStation is used as the acquisition software, and MassHunter as the data analysis software. Helium was used as the carrier gas at a gas flow rate of 1.2 mL/min, and an injector temperature and detector temperature of 250 °C. The column temperature operated from 45 to 315 °C using the following method: hold at 45 °C for 2 min; 45 to 250 °C at a rate of 25 °C/min; 250 to 315 °C at a rate of 50 °C/min; hold at 315 °C for 1 min. Retention times: mesitylene = 5.045 min; **iPrAl** = 6.897 min; $C_{12}H_{25}SH$ = 8.559 min; **Nb-PFP** = 9.885 min.

Size Exclusion Chromatography (SEC)

Chloroform ($CHCl_3$)

GPC analyses of **polyNb-PFP** polymers were performed on a Tosoh EcoSEC HLC-8320 system, equipped with three TSKgel Super HZ columns, each with 6 mm inner diameter, 150 mm length, and 3 μm pore size. $CHCl_3$ with 0.75% EtOH stabilizer is used as the mobile phase, and heated to 40 °C.

N,N-Dimethylformamide (DMF)

GPC analyses of polyethylene glycol (PEG)-containing polymers were performed on an Agilent 1260 Infinity system with dual Agilent PL1110-6500 columns and a 0.025 M LiBr in DMF mobile phase at 60 °C. The differential refractive index (dRI) of each compound was monitored using a Wyatt Optilab T-rEX detector.

*Note. The Mn values for DMF SEC traces can merely be used as a comparison and have little meaning as we do not know the dn/dc values for these modified polymers, which will change after deconstruction. There are no standards that could be used to gain accurate values. Herein, we use the PEG dn/dc standard of 0.0566 mL/g.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was carried out on 2–3 mg samples of pDCPD materials. Analyses were performed on a TA Instrument Discovery 5500 system. Studies were performed under a constant stream of nitrogen gas at a temperature ramp of 15 °C/min. Experiments were performed at the MIT Institute for Soldier Nanotechnologies.

Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis was carried out on a TA Discovery DMA 850 system. Samples with dimensions ca. 2.2 × 1.5 × 8–10 mm (w × t × l) were tested in tension mode. Temperature sweeps were conducted from 30–220 °C at a heating rate of 3 °C/min. A preload force of 0.01 N and 125.0% force tracking was applied during the measurements with a data sampling interval of 3 s/pt. Strain was applied at a frequency of 1 Hz and an amplitude of 10 μm. Data were collected using Trios software and exported to Microsoft Excel for analysis. Experiments were performed at the MIT Institute for Soldier Nanotechnologies. For T_g calculations, the temperature of the highest tan delta peak was used.

Sample Preparation for Dynamic Mechanical Analysis

A neat mixture of dicyclopentadiene (DCPD) and the relevant comonomers (**iPrSi8** and/or **Nb-PFP**) were added to a vial containing finely powered Grubbs' 2nd generation catalyst (2 mg/mL) and vortexed until homogenous. The resulting mixture was added into a silicone mold with dimensions of ca. 12 × 3 × 3 mm (approximately 300 μL per mold). The mold was prepared using MoldMax 60 (Reynolds Advanced Materials), poured over a dish containing 1-inch bars cut from a zinc-galvanized low-carbon steel bar (1/8" thick, 1/8" wide, 3 ft. long, McMaster-Carr). The samples were heated at 120 °C for 30 min, then taken out of the oven and cut out of the mold. The samples were further sanded before measurement by DMA to ensure suitable size.

Small Molecule Syntheses

Previously reported compounds

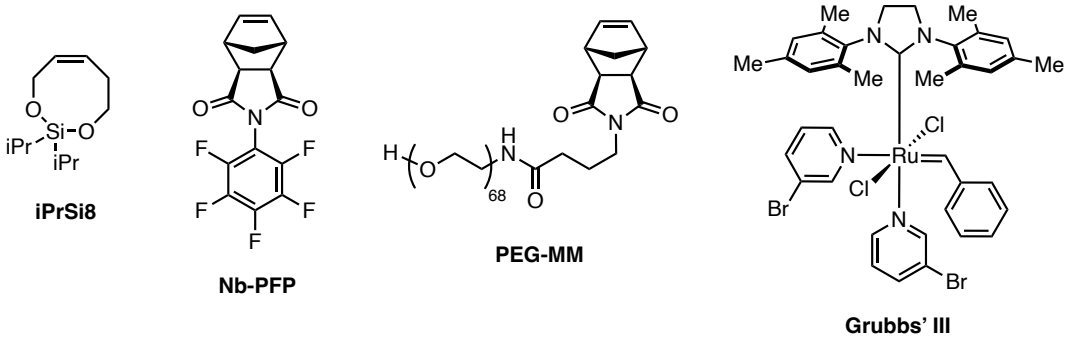
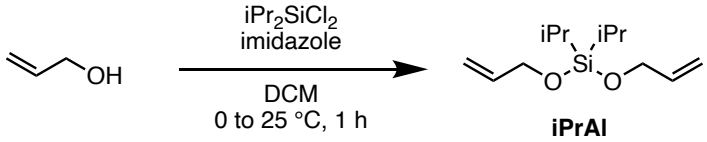


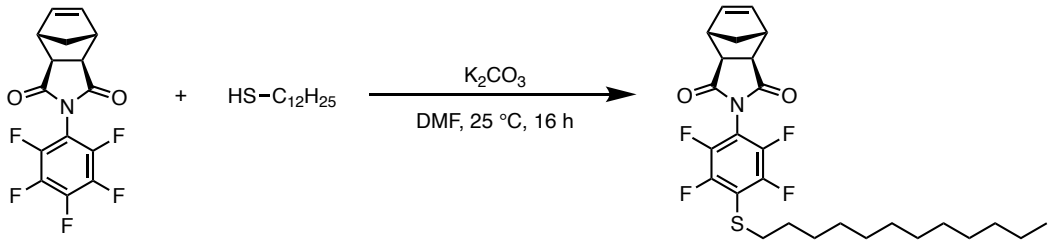
Chart S1. Previously reported compounds used in this study: **iPrSi8**;[1] **Nb-PFP**;[2] **PEG-MM**,[3] Grubbs' 3rd generation (Grubbs' III).[4]

Synthesis of bis(allyloxy)diisopropylsilane (**iPrAl**)



Imidazole (0.408 g, 6.00 mmol, 2.0 equiv) and allyl alcohol (0.407 mL, 6.00 mmol, 2.0 equiv) were dissolved in 10 mL of DCM and the solution cooled to 0 °C. Dichlorodiisopropylsilane (0.541 mL, 3.00 mmol, 1.0 equiv) was then added dropwise to the solution with stirring, where a white precipitate immediately formed. The reaction was allowed to warm to room temperature and stir for 1 h. The mixture was then filtered and the resulting solution concentrated under vacuum. The resulting mixture was diluted with hexanes (10 mL) and washed with H_2O (3 × 10 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give pure **iPrAl** as a colourless oil (0.390 g, 1.71 mmol, 57% yield). ^{1}H NMR ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.94 (ddt, *J* = 17.1, 10.4, 4.5 Hz, 1H), 5.31 (dq, *J* = 17.1, 1.9 Hz, 1H), 5.10 (dq, *J* = 10.5, 1.8 Hz, 1H), 4.30 (dt, *J* = 4.6, 1.9 Hz, 2H), 1.15 – 0.96 (m, 8H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 137.2, 114.1, 63.7, 17.5, 1238. HR-MS (DART): Calculated for $C_{12}H_{25}O_2Si$ $[M+H]^+$: 229.1624, found 229.1629.

Synthesis of (3a*R*,4*R*,7*S*,7a*S*)-2-(4-(dodecylthio)-2,3,5,6-tetrafluorophenyl)-3a,4,7,7a-tetrahydro-1*H*-4,7-methanoisoindole-1,3(2*H*)-dione (**Nb-PFP-SC$_{12}$H$_{25}$**)

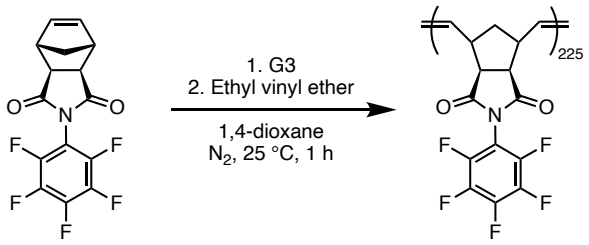


Nb-PFP-SC$_{12}$H$_{25}$

A round-bottomed flask was charged with **Nb-PFP** (0.422 g, 1.08 mmol, 1.0 equiv), $C_{12}H_{25}SH$ (0.390 mL, 1.62 mmol, 1.5 equiv) and K_2CO_3 (0.297 g, 2.15 mmol, 2.0 equiv) and dissolved in DMF (50 mL). The solution was heated to reflux for 16 h. Following cooling, the DMF was removed *in vacuo*, and the crude mixture dissolved in CH_2Cl_2 (50 mL). The organic layer was washed with H_2O (3 × 50 mL) and brine (1 × 50 mL), dried with Mg_2SO_4, filtered, and the CH_2Cl_2 removed. The crude compound was purified *via* column chromatography (silica gel, 100% hexanes to 9:1 hexanes:EtOAc gradient) to give pure **Nb-PFP-SC$_{12}$H$_{25}$** as a white powder (0.375 g, 0.730 mmol, 68% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.36 (t, *J* = 1.9 Hz, 2H), 3.42 (t, *J* = 1.9 Hz, 2H), 3.01 – 2.91 (m, 4H), 1.68 – 1.55 (m, 4H), 1.40 (p, *J* = 5.9 Hz, 2H), 1.26 (d, *J* = 7.8 Hz, 16H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ –132.96 (ddd, *J* = 136.8, 24.4, 10.8 Hz), –143.63 (m). ^{13}C{^{1}H}{^{19}F} NMR (151 MHz, $CDCl_3$) δ 175.0, 147.1 (d, *J* = 20.4 Hz), 143.1 (d, *J* = 34.3 Hz), 138.0, 117.6, 110.7, 48.6, 46.0, 43.1, 34.8, 32.0, 30.0, 29.8, 29.7, 29.6, 29.5, 29.2, 28.6, 22.8, 14.3. DART-MS (m/z) calculated for $C_{27}H_{34}F_4NO_2S$: 512.22464; found 512.22534 $[M+H]^+$.

Polymer Syntheses

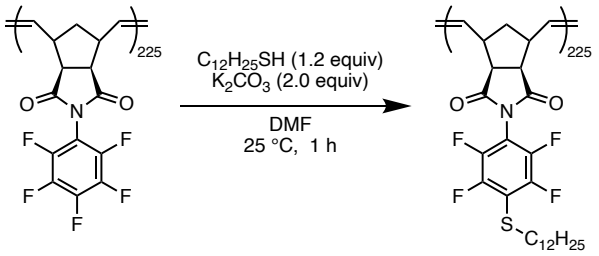
Synthesis of homopolymer **polyNb-PFP**



polyNb-PFP$_{225}$

In a N_2 glovebox, to a 1 dram vial containing **Nb-PFP** (0.276 g, 0.838 mmol) was added 1,4-dioxane (1.70 mL) to give a 0.5 M **Nb-PFP** solution. To this was added 300 µL Grubbs' 3rd generation catalyst in 1,4-dioxane (3.31 mg, 3.74 µmol, 0.012 M), for a target DP of 225. The reaction stirred at room temperature for 1 h, removed from the glovebox, and quenched with a drop of ethyl vinyl ether (EVE). The polymer was analyzed using NMR spectroscopy and $CHCl_3$ GPC.

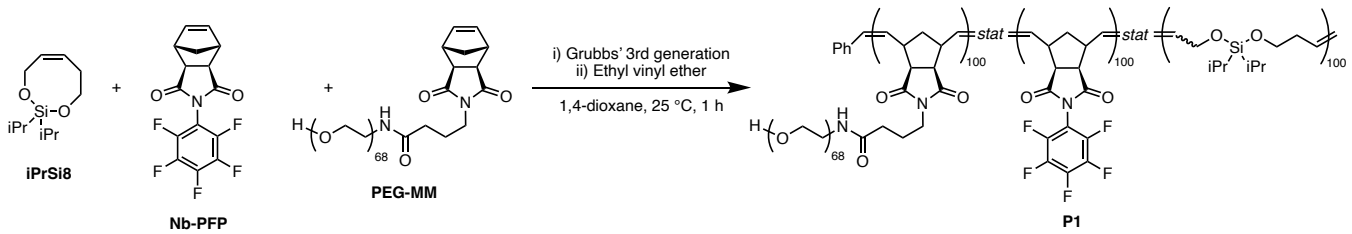
Synthesis of **polyNb-PFP-SC$_{12}$H$_{25}$** using S_NAr



polyNb-PFP **polyNb-PFP-SC$_{12}$H$_{25}$**

To a 1 dram vial was added **polyNb-PFP** (15 mg, 45.6 µmol, 1.0 equiv) as a 0.5 M 1,4-dioxane solution, 1-dodecanethiol (13 µL, 54.7 µmol, 1.2 equiv) and K_2CO_3 (12.6 mg, 91.1 µmol, 2.0 equiv), and DMF (500 µL). The reaction mixture was then stirred at 25 °C for 1 h. The solvent was removed *in vacuo*, $CDCl_3$ added, and the solution filtered over a 0.2 µm PTFE membrane filter. The polymer was analyzed using NMR spectroscopy and GPC ($CHCl_3$ mobile phase).

Synthesis of bottlebrush terpolymer **P1**



In a N_2 glovebox, to a 1 dram vial containing a stir bar was added 980 µL of a 1 M **PEG-MM** 1,4-dioxane solution (245 mg, 98.0 µmol, 100 equiv), 196 µL of a 0.5 M 1,4-dioxane solution of **Nb-PFP** (32 mg, 98.0 µmol,

100 equiv), and 98 µL of a 1.0 M 1,4-dioxane solution of **iPrSi8** (21 mg, 98.0 µmol, 100 equiv). To this was added 98 µL of a 0.01 M 1,4-dioxane solution of Grubbs' 3rd generation catalyst (0.87 mg, 0.98 µmol, 1 equiv) to a give a target DP = 300. The vial was sealed, and the reaction was stirred at room temperature for 1 h. Following this, the vial was removed from the glovebox, and the reaction quenched with a drop of EVE. The reaction mixture was used directly for deconstruction experiments as described in the "Deconstruction Studies" section. The polymer was analyzed using NMR spectroscopy and GPC (DMF mobile phase).

Small Molecule GC-MS Studies

The following stock solutions were prepared in DMF: **iPrSi8** (100 mg/mL); **Nb-PFP** (100 mg/mL); 1-dodecanethiol (100 mg/mL); mesitylene (20 mg/mL). Total reaction volume was 1 mL. Timepoints were prepared as follows: 2 µL of the reaction solution was diluted with 1.8 mL of HPLC-grade DCM, and filtered through a 0.2 µm PTFE filter. Instrumental conditions for the GC-MS experiments can be found in the "Materials and Methods" section.

Procedure for small molecule GC-MS studies of **iPrAl** + K_2CO_3

To a 1 dram vial containing a stir bar was added 114 µL **iPrAl** stock solution (11.4 mg, 0.050 mmol, 1.0 equiv), 30 µL mesitylene stock solution (0.60 mg, 0.005 mmol, 0.1 equiv) and 856 µL DMF. Time point t = 0 h was taken. K_2CO_3 (33 mg, 0.10 mmol, 2.0 equiv) was then added, and the vial was sealed with a PTFE lid and reacted for 2 h. Time points were taken at t = 0, 1 and 2 h.

Procedure for small molecule GC-MS studies of **iPrAl** + 1-dodecanethiol

To a 1 dram vial containing a stir bar was added 114 µL **iPrAl** stock solution (11.4 mg, 0.050 mmol, 1.0 equiv), 30 µL mesitylene stock solution (0.60 mg, 0.005 mmol, 0.1 equiv) and 704 µL DMF. Time point t = 0 h was taken. 152 µL of 1-dodecanethiol stock solution (15.2 mg, 0.075 mmol, 1.5 equiv) was then added, and the vial was sealed with a PTFE lid and reacted for 2 h. Time points were taken at t = 0, 1 and 2 h.

Procedure for small molecule GC-MS studies of **iPrAl** + **Nb-PFP**

To a 1 dram vial containing a stir bar was added 114 µL **iPrAl** stock solution (11.4 mg, 0.050 mmol, 1.0 equiv), 30 µL mesitylene stock solution (0.60 mg, 0.005 mmol, 0.1 equiv) and 562 µL DMF. Time point t = 0 h was taken. K_2CO_3 (33 mg, 0.10 mmol, 2.0 equiv) and 294 µL of **Nb-PFP** stock solution (29.4 mg, 0.075 mmol, 1.5 equiv) were then added, and the vial was sealed and reacted for 2 h. Time points were taken at t = 0, 1 and 2 h.

Procedure for small molecule GC-MS studies of **iPrAl** + 1-dodecanethiol + K_2CO_3

To a 1 dram vial containing a stir bar was added 114 µL **iPrAl** stock solution (11.4 mg, 0.050 mmol, 1.0 equiv), 30 µL mesitylene stock solution (0.60 mg, 0.005 mmol, 0.1 equiv) and 704 µL DMF. Time point t = 0 h was taken. 152 µL of 1-dodecanethiol stock solution (15.2 mg, 0.075 mmol, 1.5 equiv) and K_2CO_3 (33 mg, 0.10 mmol, 2.0 equiv) were then added, and the vial was sealed with a PTFE lid and reacted for 2 h. Time points were taken at t = 0, 1 and 2 h.

Procedure for small molecule GC-MS studies of **iPrAl** + **Nb-PFP** + K_2CO_3

To a 1 dram vial containing a stir bar was added 114 µL **iPrAl** stock solution (11.4 mg, 0.050 mmol, 1.0 equiv), 30 µL mesitylene stock solution (0.60 mg, 0.005 mmol, 0.1 equiv) and 562 µL DMF. Time point t = 0 h

was taken. K_2CO_3 (33 mg, 0.10 mmol, 2.0 equiv) and 294 µL of **Nb-PFP** stock solution (29.4 mg, 0.075 mmol, 1.5 equiv) were then added, and the vial was sealed with a PTFE lid and reacted for 2 h. Time points were taken at t = 0, 1 and 2 h.

Procedure for small molecule GC-MS studies of **iPrAl** + **Nb-PFP** + 1-dodecanethiol

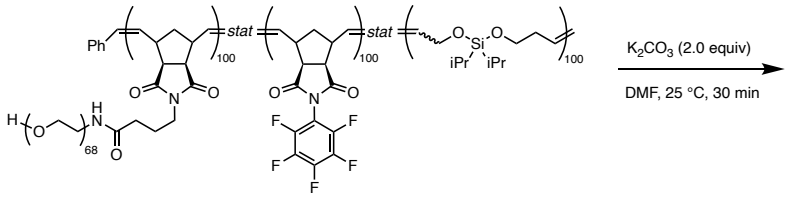
To a 1 dram vial containing a stir bar was added 114 µL **iPrAl** stock solution (11.4 mg, 0.050 mmol, 1.0 equiv), 30 µL mesitylene stock solution (0.60 mg, 0.005 mmol, 0.1 equiv) and 410 µL DMF. Time point t = 0 h was taken. 152 µL of 1-dodecanethiol stock solution (15.2 mg, 0.075 mmol, 1.5 equiv) and 294 µL of **Nb-PFP** stock solution (29.4 mg, 0.075 mmol, 1.5 equiv) were then added, and the vial was sealed with a PTFE lid and reacted for 2 h. Time points were taken at t = 0, 1 and 2 h.

Procedure for small molecule GC-MS studies of **iPrAl**+ 1-dodecanethiol + **Nb-PFP +** K_2CO_3

To a 1 dram vial containing a stir bar was added 114 µL **iPrAl** stock solution (11.4 mg, 0.050 mmol, 1.0 equiv), 30 µL mesitylene stock solution (0.60 mg, 0.005 mmol, 0.1 equiv) and 410 µL DMF. Time point t = 0 h was taken. K_2CO_3 (33 mg, 0.10 mmol, 2.0 equiv), 294 µL of **Nb-PFP** stock solution (29.4 mg, 0.075 mmol, 1.5 equiv) and 152 µL of 1-dodecanethiol stock solution (15.2 mg, 0.075 mmol, 1.5 equiv) were then added, and the vial was sealed with a PTFE lid and reacted for 2 h. Time points were taken at t = 0, 1 and 2 h.

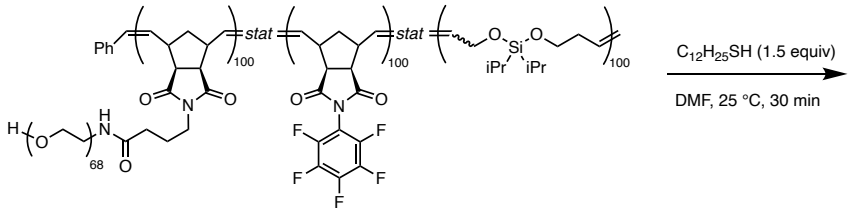
Deconstruction Studies

Control study of **P1** with K_2CO_3 in DMF



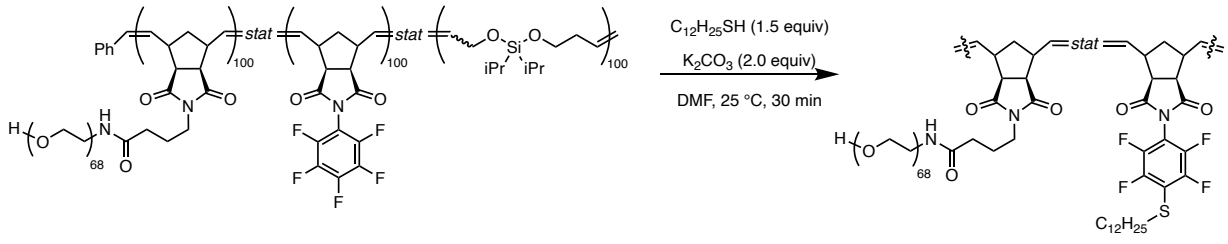
100µL of **P1** (21.7 mg) in a 1,4-dioxane stock solution was added to a dry 1 dram vial with a stir bar. The solution was diluted with dry DMF (500 µL). To this was added K_2CO_3 (2.0 mg, 14.6 µmol, 2.0 equiv with respect to Nb-PFP in the polymer), and the reaction stirred at room temperature for 30 min. Undissolved K_2CO_3 was removed by passing the solution through a 0.2 µm nylon filter, and the DMF removed *in vacuo*. The residue was dissolved in DCM and passed through a 0.2 µm PTFE filter to remove any residual K_2CO_3, and the solution dried under reduced pressure. The residue was analyzed via GPC (DMF mobile phase) and NMR experiments.

Control study of **P1** with 1-dodecanethiol in DMF



100µL of **P1** (21.7 mg) in a 1,4-dioxane stock solution was added to a dry 1 dram vial with a stir bar. The solution was diluted with dry DMF (500 µL). To this was added 1-dodecanethiol (2.2 mg, 2.6 µL, 11.0 µmol, 1.5 equiv with respect to Nb-PFP in the polymer), and the reaction stirred at room temperature for 30 min. The DMF was removed under reduced pressure. The residue was analyzed via GPC (DMF mobile phase) and NMR experiments.

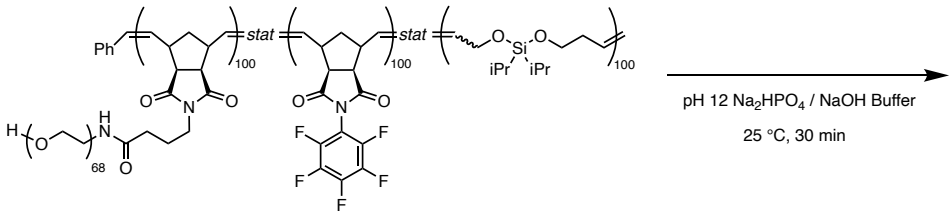
S_NAr of **P1** with 1-dodecanethiol and K_2CO_3 in DMF



100µL of **P1** (21.7 mg) in a 1,4-dioxane stock solution was added to a dry 1 dram vial with a stir bar. The solution was diluted with dry DMF (500 µL). To this was added K_2CO_3 (2.0 mg, 14.6 µmol, 2.0 equiv with respect to Nb-PFP in the polymer), and 1-dodecanethiol (2.2 mg, 2.6 µL, 11.0 µmol, 1.5 equiv with respect to Nb-PFP in the polymer), and the reaction stirred at room temperature for 30 min. Undissolved K_2CO_3 was removed by passing

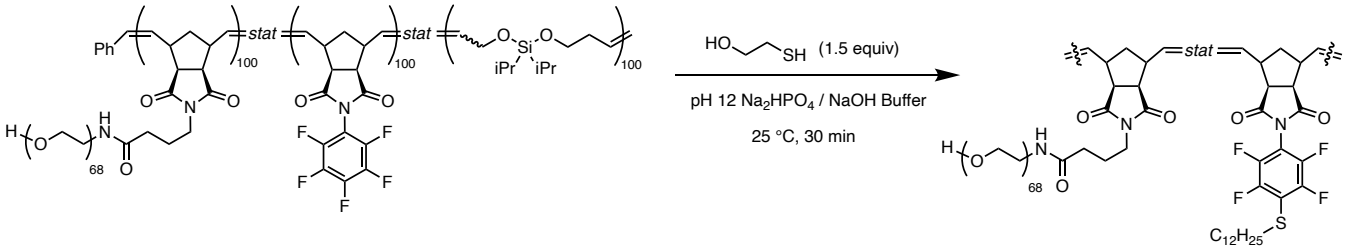
the solution through a 0.2 µm nylon filter, and the DMF removed *in vacuo*. The residue was dissolved in DCM and passed through a 0.2 µm PTFE filter to remove any residual K_2CO_3, and the solution dried under reduced pressure. The residue was analyzed via GPC (DMF mobile phase) and NMR experiments.

Control study of **P1** in pH 12 Na_2HPO_4/NaOH buffer solution



100µL of **P1** (21.7 mg) in a 1,4-dioxane stock solution was added to a dry 1 dram vial with a stir bar. The solution was diluted with pH 12 Na_2HPO_4/NaOH buffer solution (1000 µL) and stirred at room temperature for 30 min. The solution was dried under reduced pressure, dissolved in DCM, and passed through a 0.2 µm PTFE filter to remove any solids, following which the solution was dried under reduced pressure. The residue was analyzed via GPC (DMF mobile phase).

S_NAr of **iPrSi–Nb-PFP–PEG** with 2-mercaptoethanol in pH 12 Na_2HPO_4/NaOH buffer solution



100µL **P1** (21.7 mg) in a 1,4-dioxane stock solution was added to a dry 1 dram vial with a stir bar. The solution was diluted with pH 12 Na_2HPO_4/NaOH buffer solution (500 µL). To this was added 2-mercaptoethanol (0.86 mg, 0.80 µL, 11.0 µmol, 1.5 equiv with respect to Nb-PFP in the polymer), and the reaction stirred at room temperature for 30 min. The solution was dried under reduced pressure, dissolved in DCM, and passed through a 0.2 µm PTFE filter to remove any solids, following which the solution was dried under reduced pressure. The residue was analyzed via GPC (DMF mobile phase) and NMR experiments.

Thermoset Materials

Synthesis of Comonomer-Containing pDCPD

Nb-PFP (1.2286 g, 3.73 mmol, 2.0 equiv) was added to a 20 mL vial and dissolved in 4 mL DCM. Next, dicyclopentadiene (DCPD, 3600 µL, 26.7 mmol, 14.4 equiv) and **iPrSi8** (400 µL, 1.86 mmol, 1.0 equiv) were added to the mixture, and vortexed. DCM was slowly removed under rotary evaporator at 400 torr and 40 °C over 20 min, being careful not to also remove DCPD. Once DCM was removed, the mixture was added to a vial containing finely powdered Grubbs' 2nd generation catalyst (8.0 mg, 9.42 µmol, 0.005 equiv). The resulting mixture was added as 200 mg portions into 1 mL glass vials, and heated at 120 °C for 30 minutes to cure. The vials were then broken to release the samples.

Deconstruction and Mass Analysis of pDCPD Resin

pDCPD samples prepared at 10% v/v **iPrSi8** (relative to DCPD only) and **Nb-PFP** (2.0 equiv) were prepared, weighed, and added to preweighed 20 mL scintillation vials. Samples were then incubated in triplicate using the following conditions: (A) 5 mL THF (negative control); (B) 5 mL THF + 1-dodecanethiol (2.0 equiv); (C) 5 mL THF + 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 2.0 equiv); (D) 5 mL THF + 1-dodecanethiol (2.0 equiv) + DBU (2.0 equiv); (E) 5 mL 0.2 M tetrabutylammonium fluoride (TBAF) in THF (positive control).

Samples (A), (B), and (C), left behind cohesive pDCPD resin pucks. Liquids were removed by pipette, then samples were resuspended in fresh THF (2 x 3 mL), which was immediately removed again to wash any deposited solids from the vials, leaving behind swollen pDCPD pucks. For samples (D) and (E) – where residual solids were small skin-like fragments which could not be easily avoided by pipette – solids were filtered onto pre-weighed filter paper, then rinsed by THF (3 x 3 mL). Vials and weigh papers were then dried under vacuum at 60 °C for 72 h, then reweighed to determine the mass of remaining solids, which was calculated as a percentage.

Nuclear Magnetic Resonance (NMR) Spectra

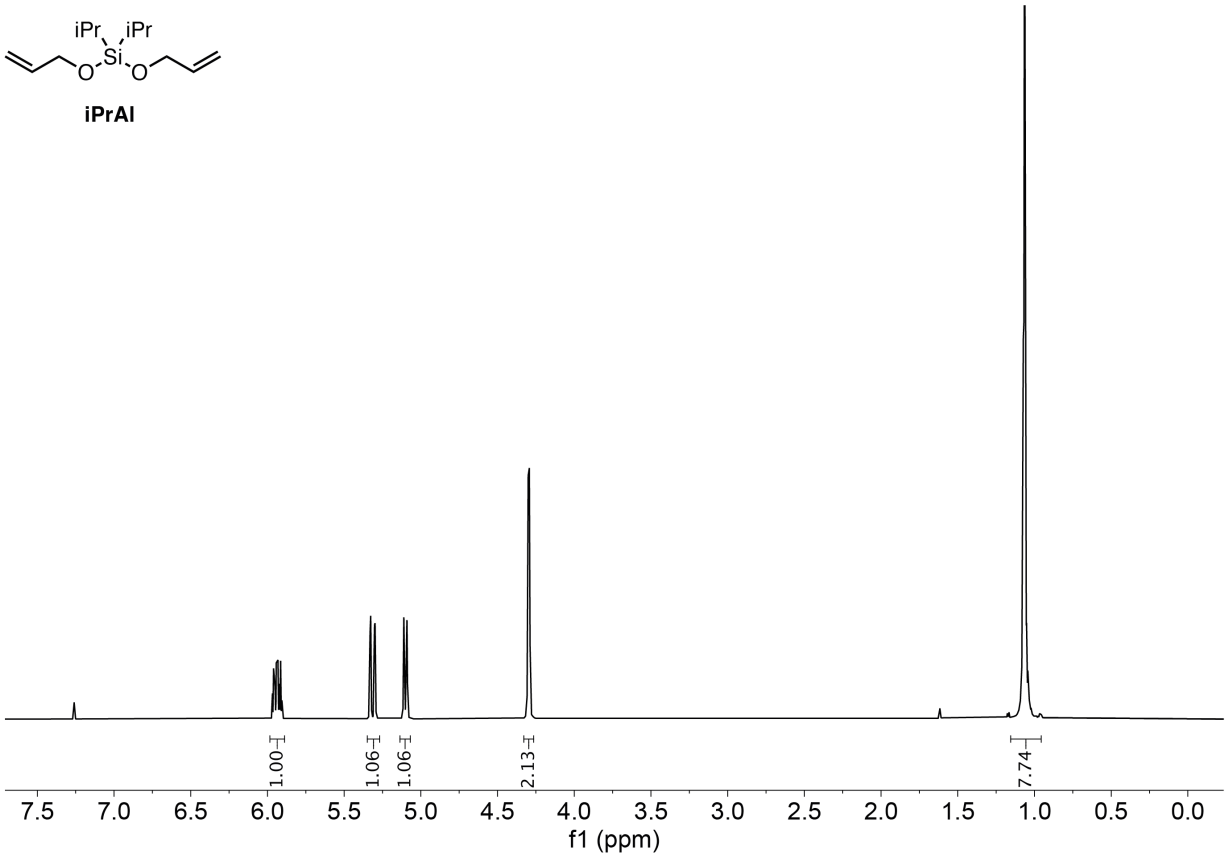


Fig. S19. ^{1}H NMR of **iPrAl** (600 MHz, $CDCl_3$. 25 °C).

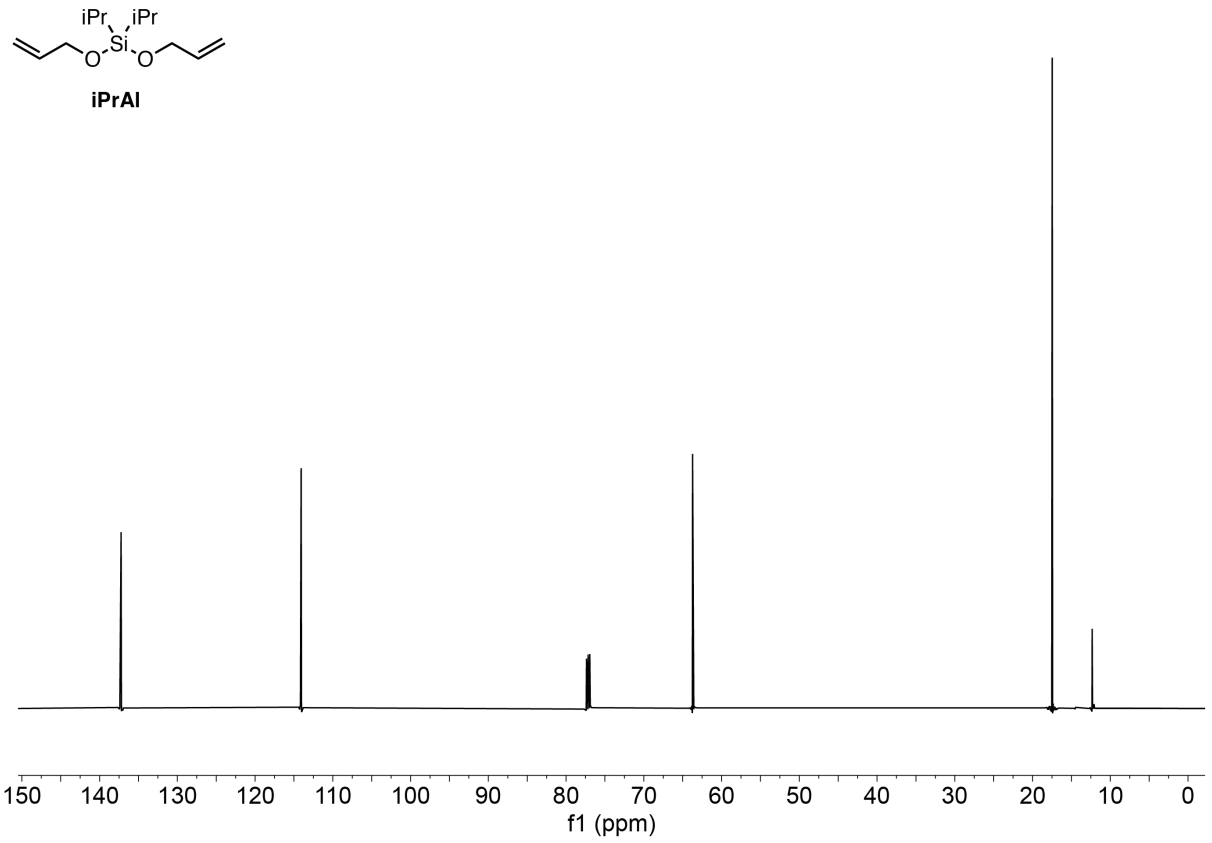


Figure S20. $^{13}C\{^{1}H\}$ NMR of **iPrAl** (151 MHz, $CDCl_3$. 25 °C).

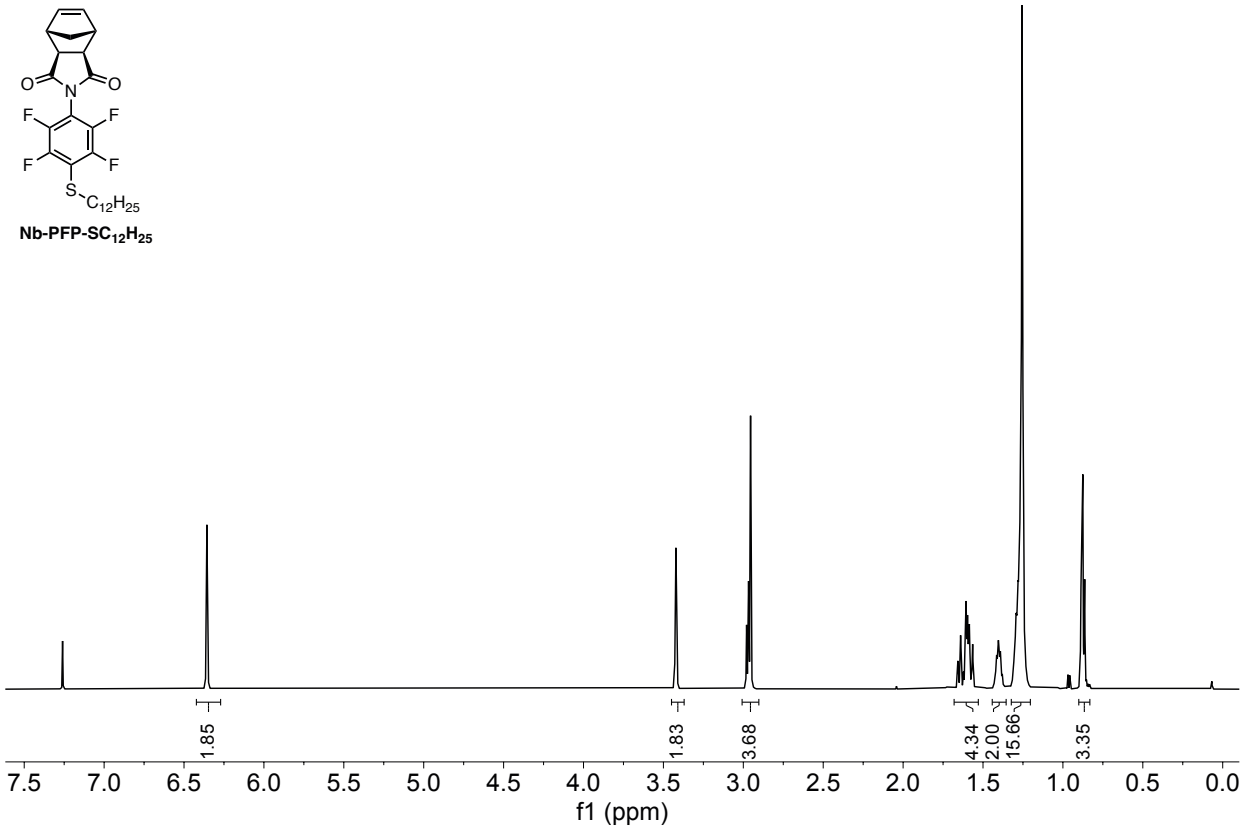


Figure S21. ^{1}H NMR of **Nb-PFP-SC$_{12}$H$_{25}$** (600 MHz, $CDCl_3$. 25 °C).

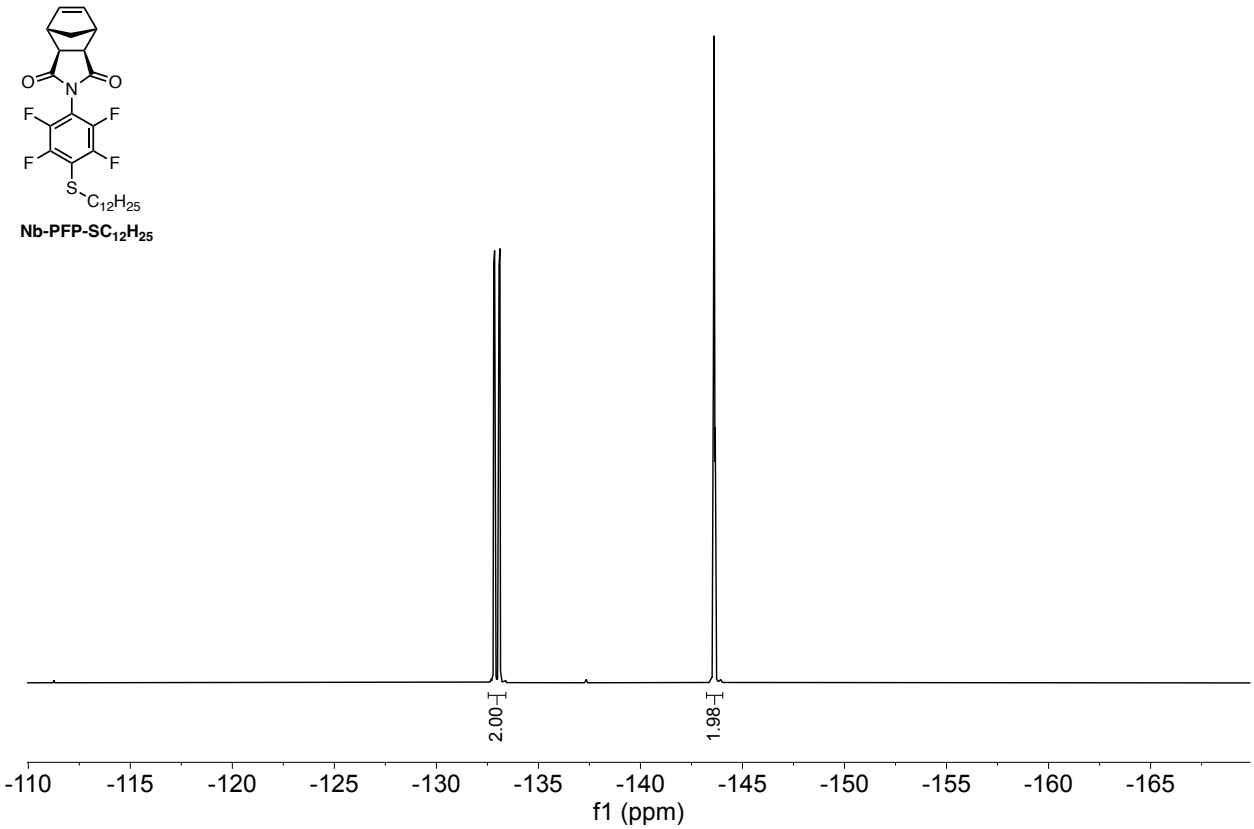


Figure S22. ^{19}F NMR of **Nb-PFP-SC$_{12}$H$_{25}$** (565 MHz, $CDCl_3$. 25 °C).

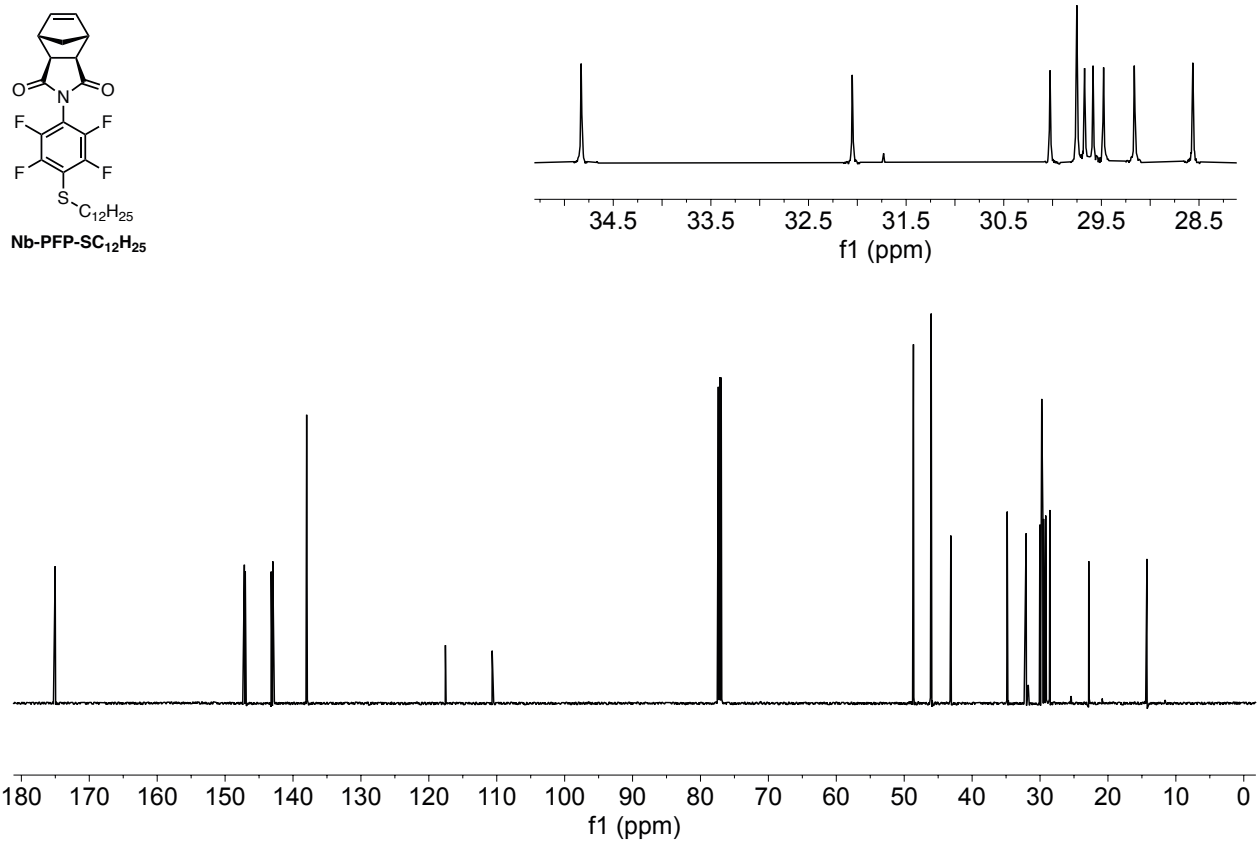


Figure S23. $^{13}C\{^1H\}\{^{19}F\}$ NMR of **Nb-PFP-SC$_{12}$H$_{25}$** (151 MHz, $CDCl_3$. 25 °C).

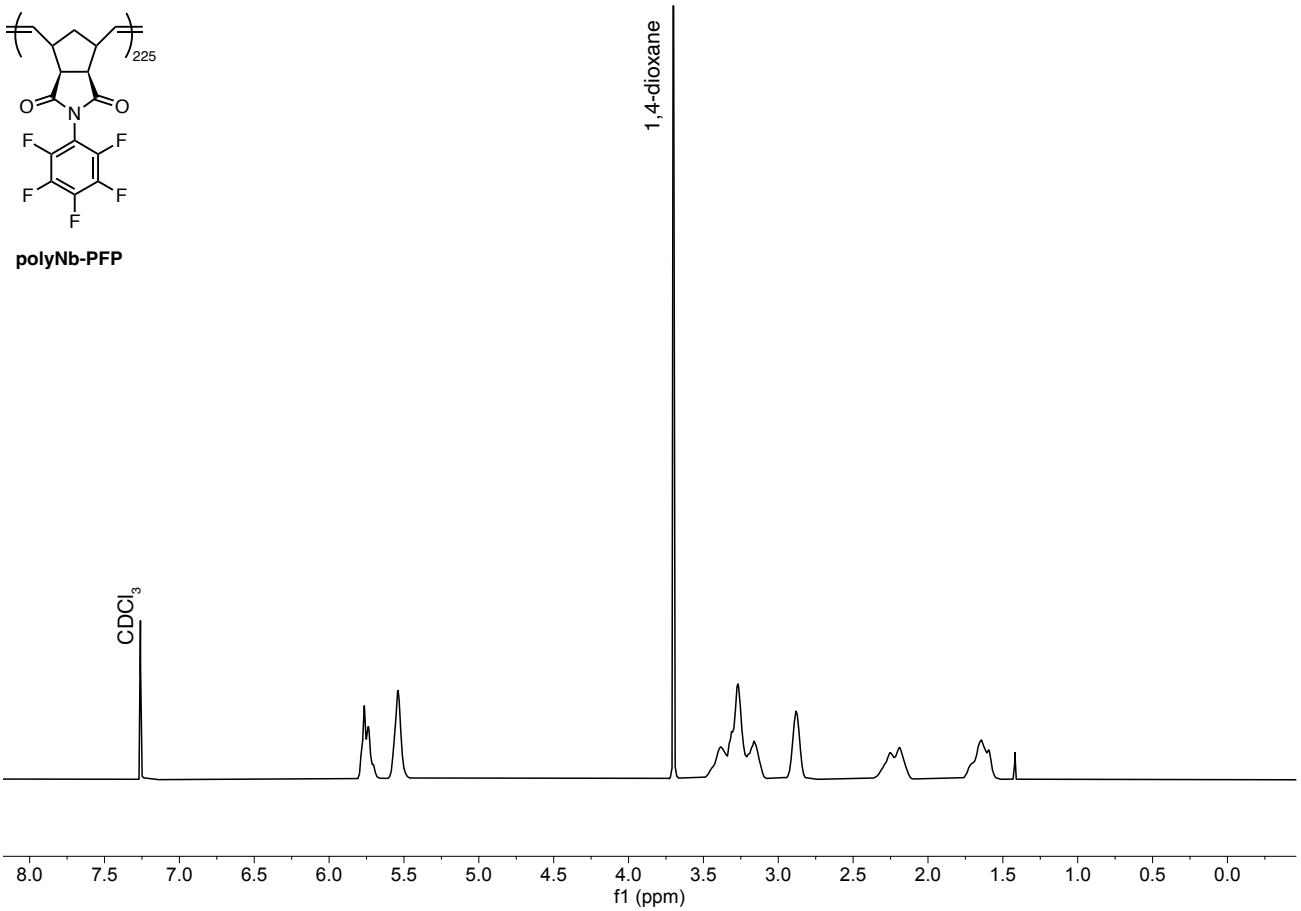


Figure S24. ^{1}H NMR of **polyNb-PFP** (600 MHz, $CDCl_3$. 25 °C).

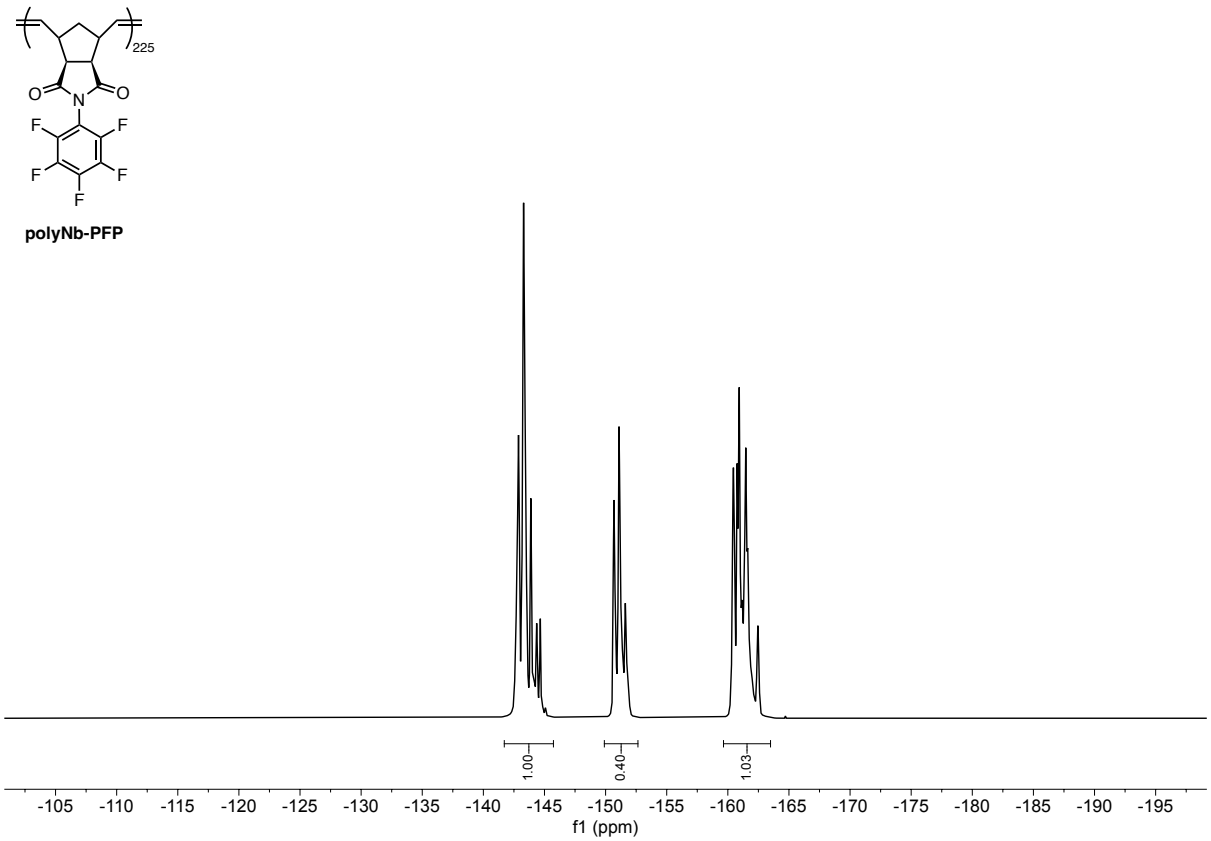


Figure S25. ^{19}F NMR of **polyNb-PFP** (565 MHz, $CDCl_3$. 25 °C).

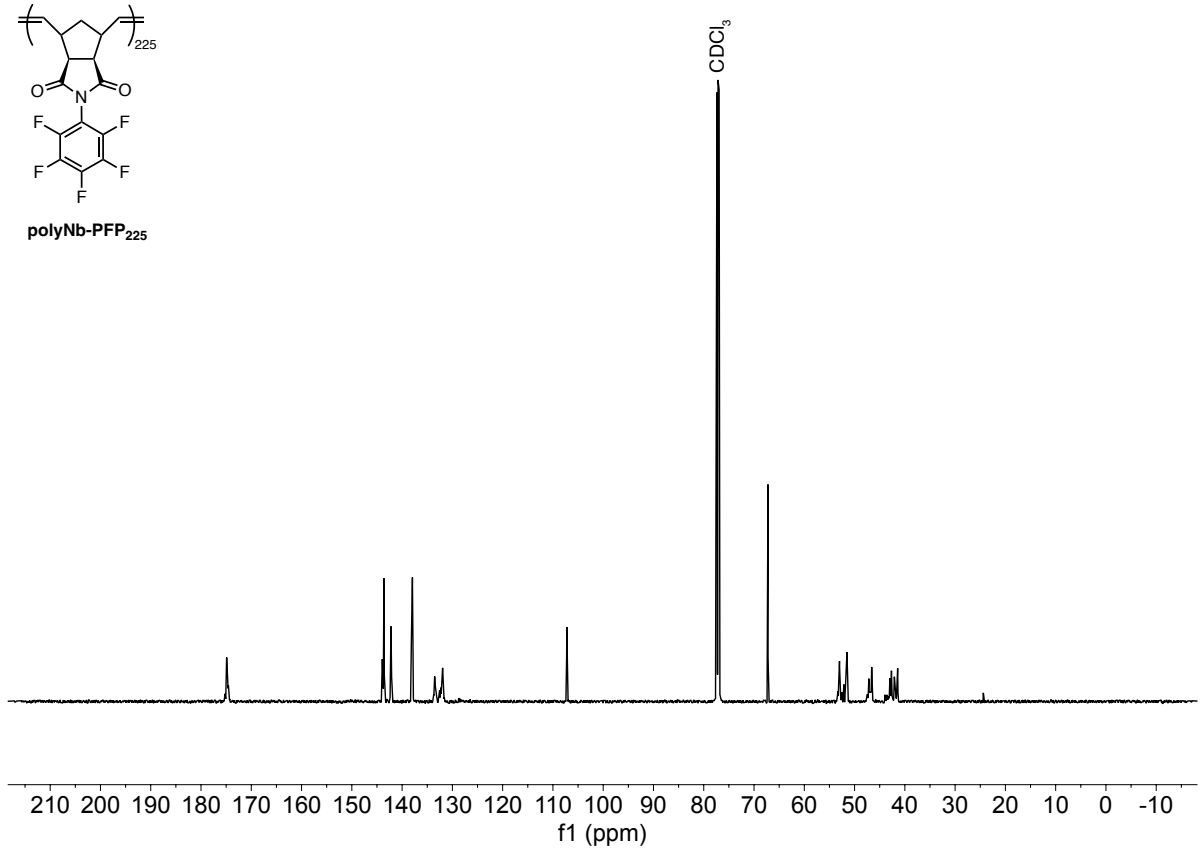


Figure S26. $^{13}C\{^{1}H\}\{^{19}F\}$ NMR of **polyNb-PFP** (151 MHz, $CDCl_3$. 25 °C).

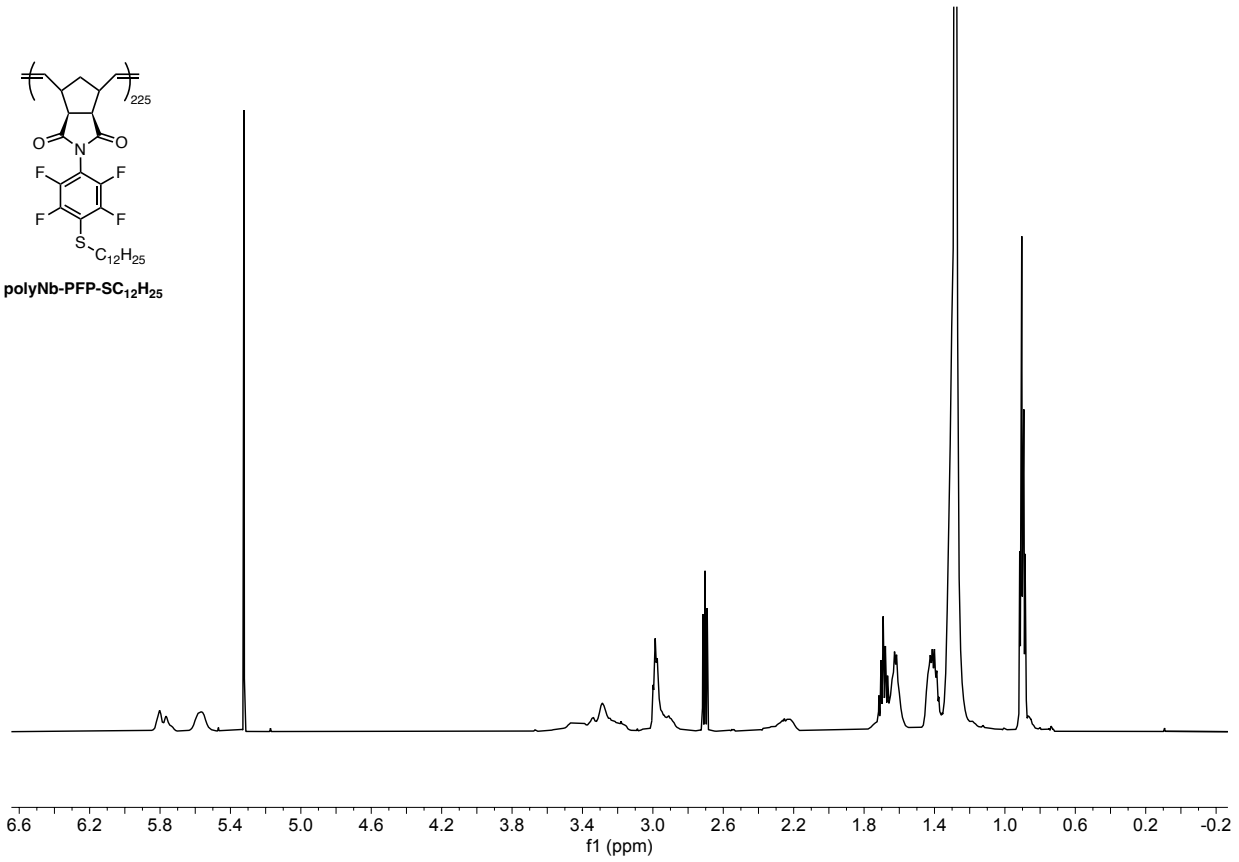


Figure S27. ^{1}H NMR of **polyNb-PFP-SC$_{12}$H$_{25}$** (600 MHz, $CDCl_3$. 25 °C).

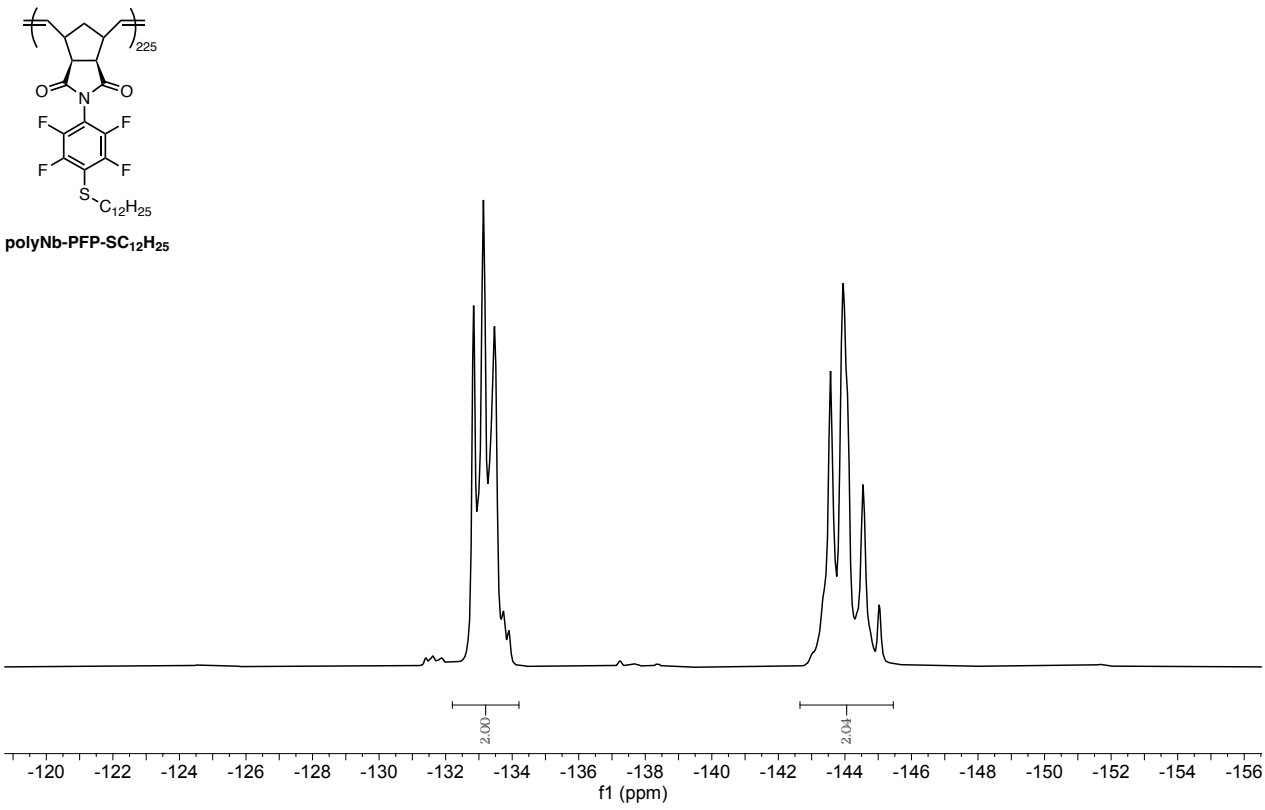


Figure S28. ^{119}F NMR of **polyNb-PFP-SC$_{12}$H$_{25}$** (565 MHz, $CDCl_3$. 25 °C).

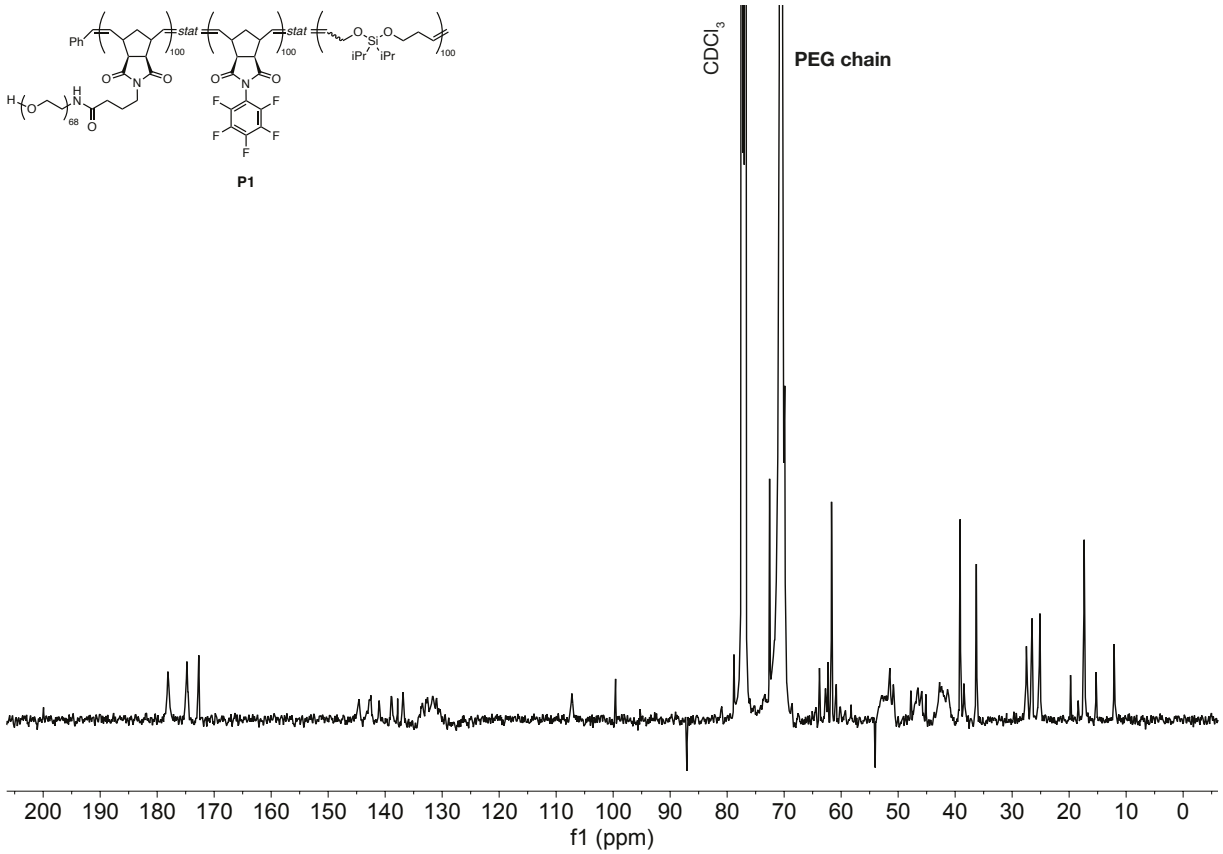


Figure S29. $^{13}C\{^{1}H\}$ NMR of **P1** (126 MHz, $CDCl_3$. 25 °C).

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