Supporting Information for

Polynorbornene with Silicon Cluster Pendant Groups

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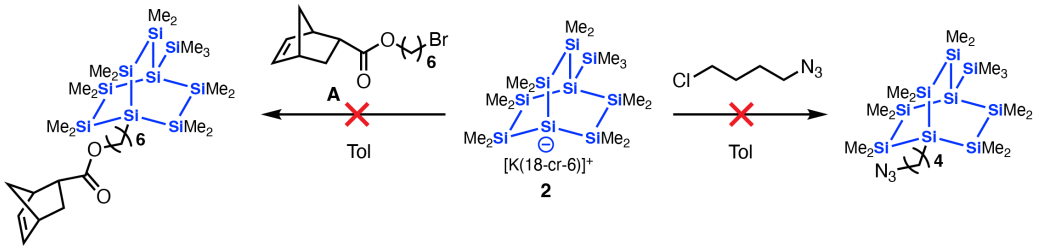
Supporting Schemes, Figures, and Tables from Main Text



Scheme S1. Initial unsuccessful routes to functionalize cluster silanide **2** directly with norbornene endgroups (left) and azide endgroups (right). Reaction of **2** with α,ω-bromo(norbornenyl)alkane **A**. led to an intractable mixture of products and disappearance of the norbornene ^{1}H NMR shifts previously seen for **A**, suggesting side reactivity between the soft silanide nucleophile and the strained norbornene double bond. Next, we sought to selectively displace the chloride in 1,4-azidochlorobutane that we could subsequently deprotect to an amino group for amide coupling with *exo*-5-norbornenecarboxylic acid. However, we found **2** reacted at the azide, leading to N_2 evolution upon silanide addition and an intractable mixture of products.

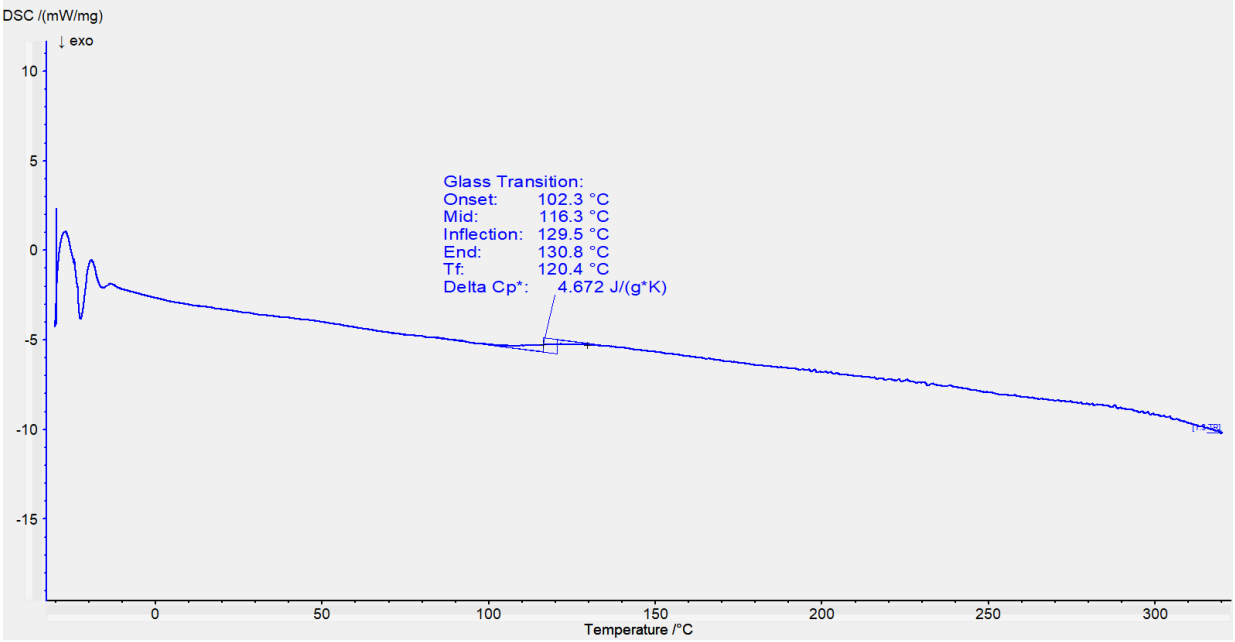


Figure S1. Differential scanning calorimetry trace of **PNB-Si[2.2.2]** at 10°C/min rate over full temperature range.

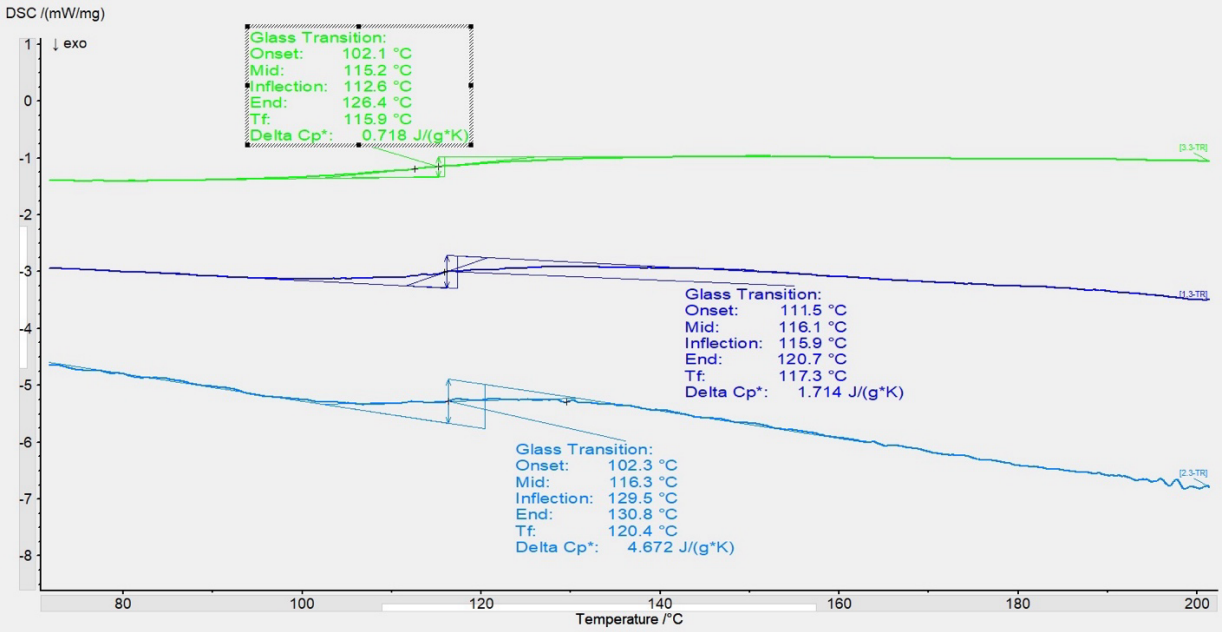


Figure S2. Differential scanning calorimetry traces of **PNB-Si[2.2.2]** at 30 ˚C/min (top), 20 ˚C/min (middle), 10˚C/min (bottom) zoomed at T_g region.

Table S1. Summary of molecular weight (Mw, Mn), polydispersity (PDI), degree of polymerization (DP) of **PNB-C**.

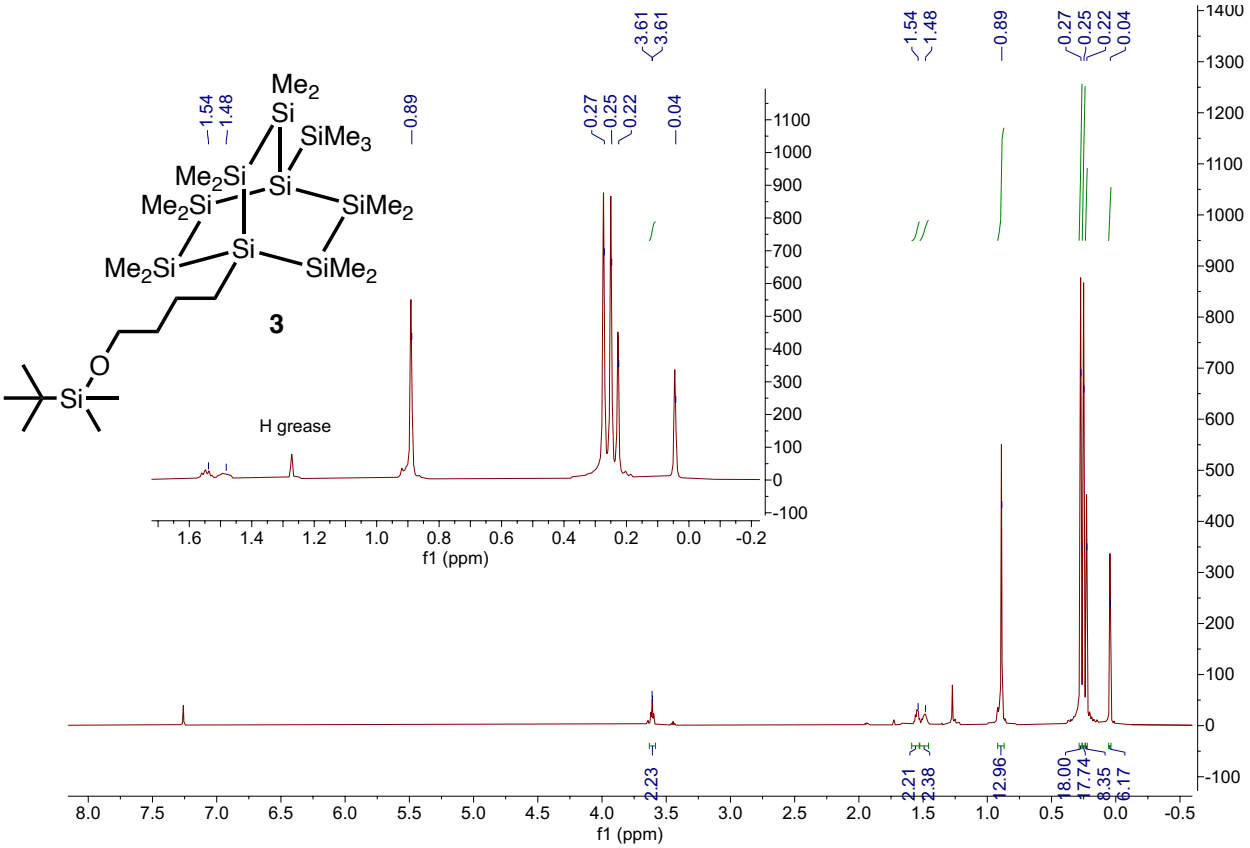
Entry	$[M]_0/[I]$	yield (%)	M_n (kg mol^{-1})[a]	M_w (kg mol^{-1})[a]	M_w/M_n[a]	DP[b]
1	500:1	90	716	763	1.07	4206

[a]Determined by SEC relative to 128 kDA polystyrene standard (THF, [**PNB-C** = 10 mg mL^{-1}], 1 mL min^{-1}, 20 μL injection).
[b]Degree of polymerization (DP), determined by dividing the M_n (Da) value obtained by SEC for repeating unit mass (RU = 170.23 g/mol).

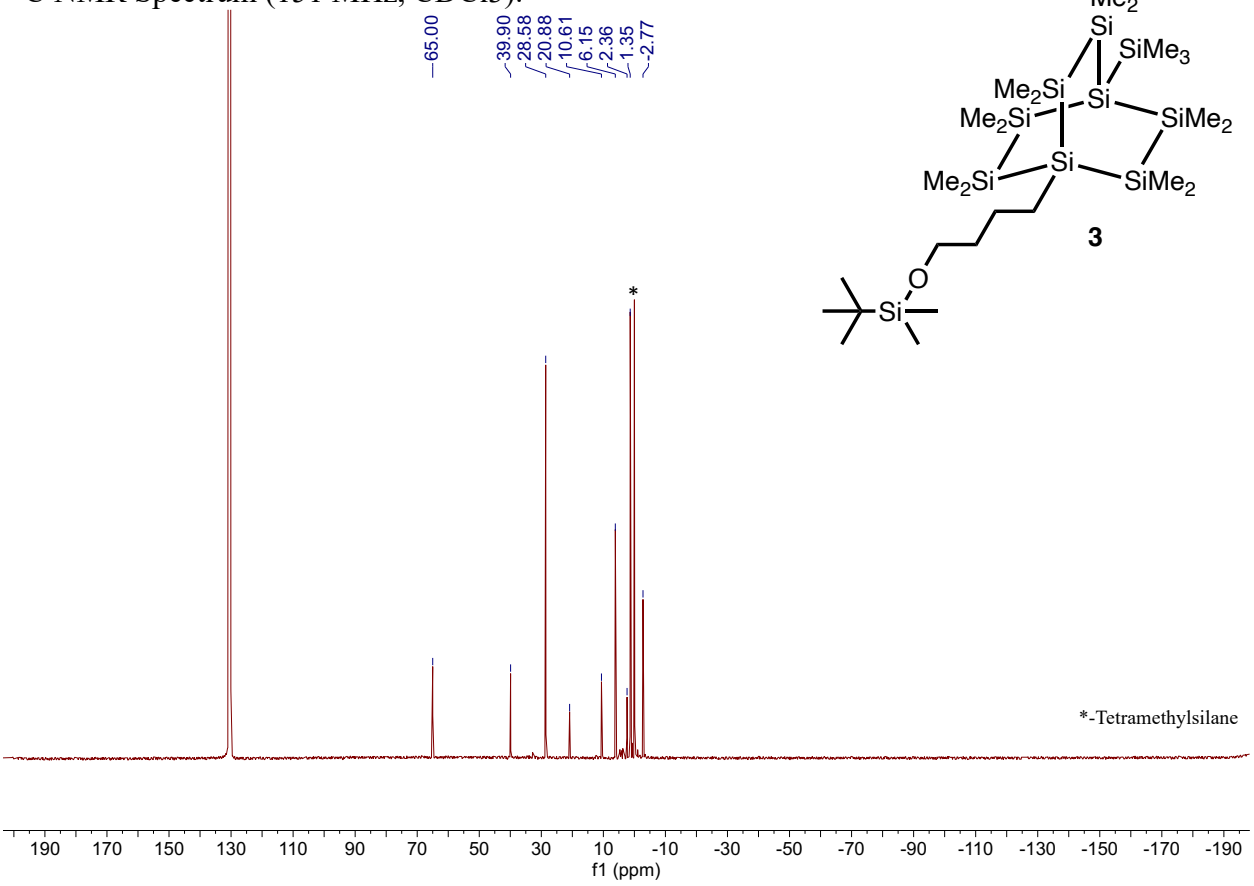
NMR Spectra

NMR Spectra of **3**

^{1}H NMR Spectrum (600 MHz, CDCl3):

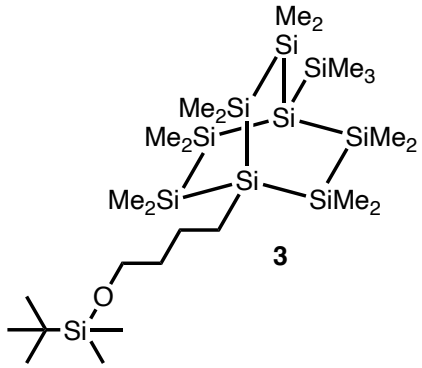


^{13}C NMR Spectrum (151 MHz, CDCl3):



3

^{29}Si-DEPT NMR Spectrum (119 MHz, CDCl3):

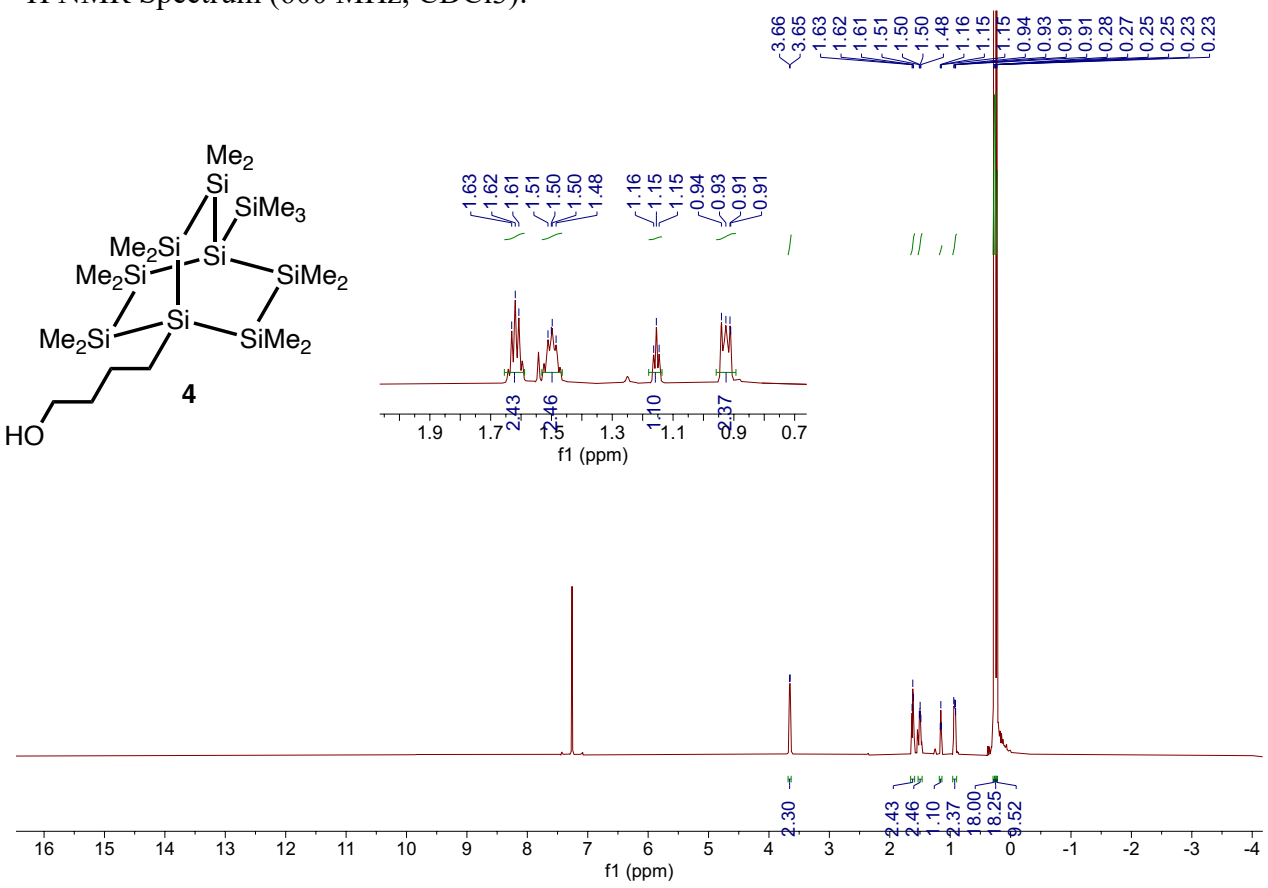


3

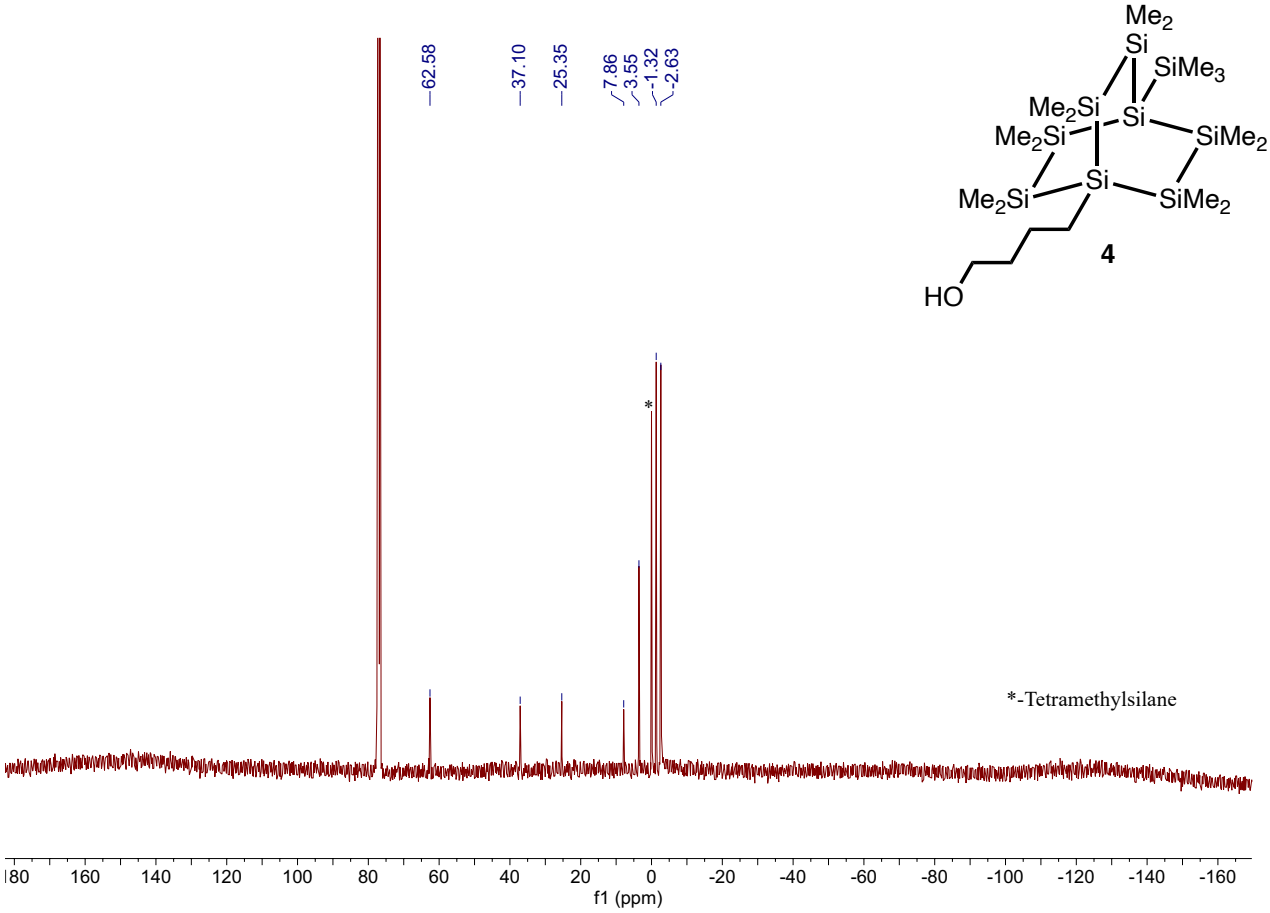
*-Tetramethylsilane

NMR Spectra of **4**

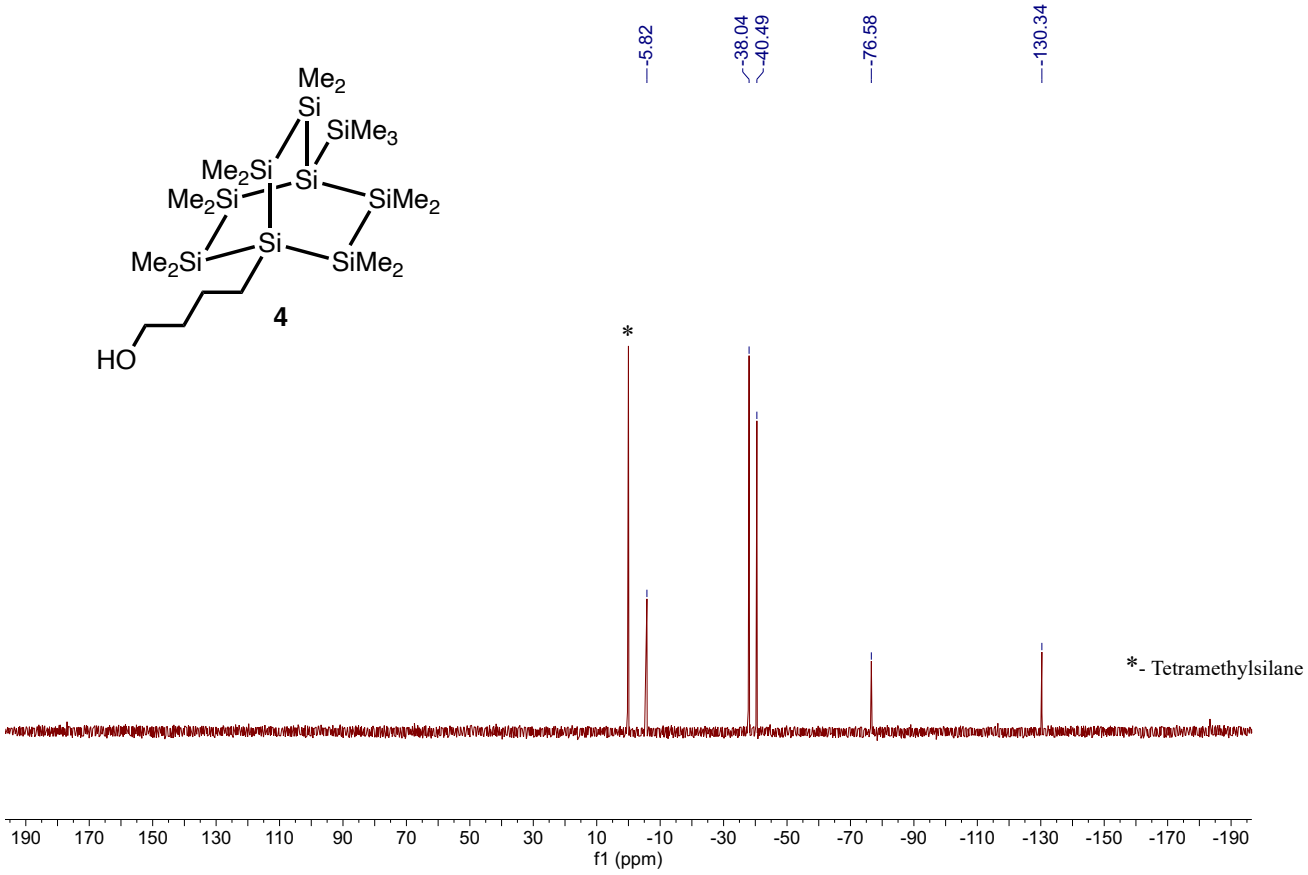
^{1}H NMR Spectrum (600 MHz, CDCl3):



^{13}C NMR Spectrum (101 MHz, $CDCl_3$):

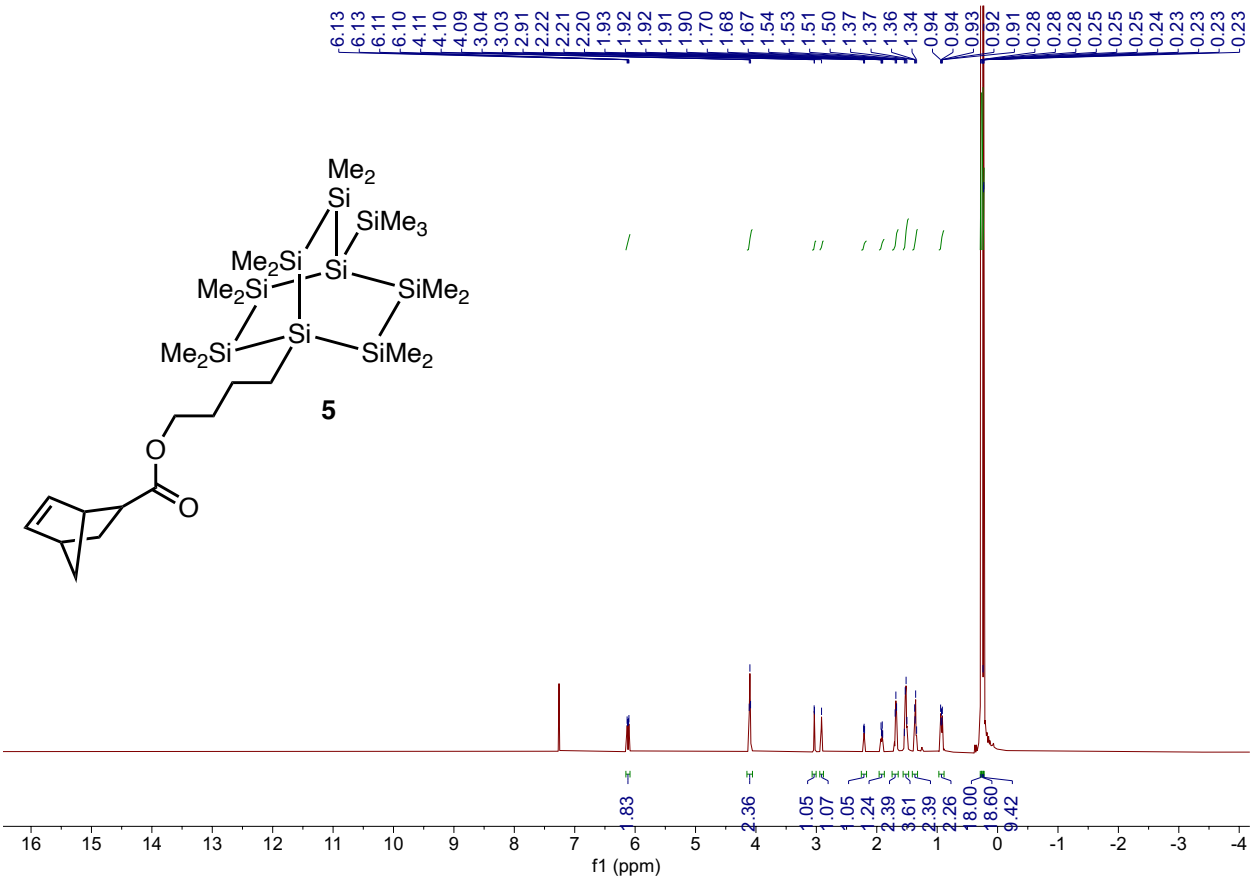


^{29}Si NMR Spectrum (119 MHz, CDCl3):

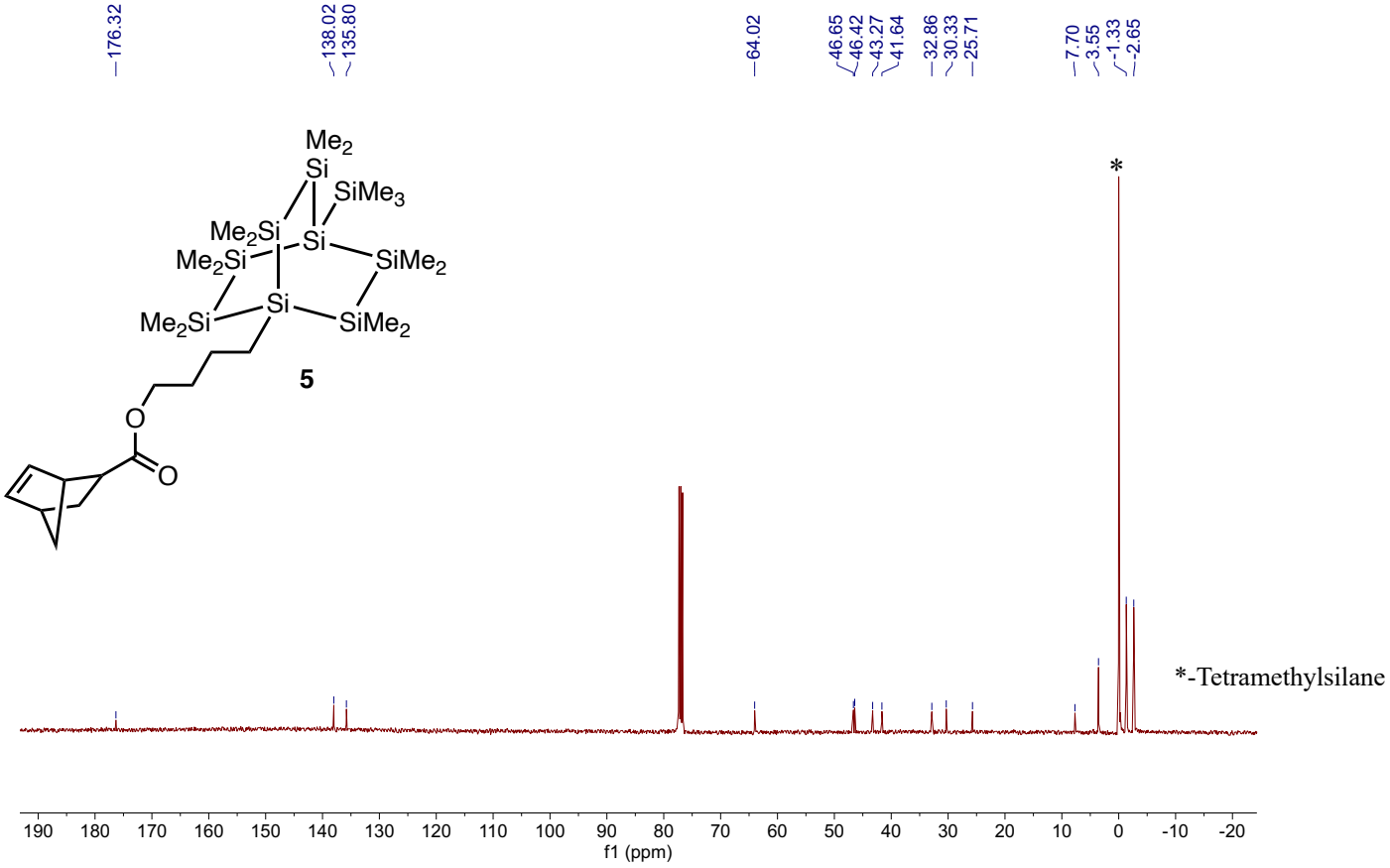


NMR Spectra of **5**

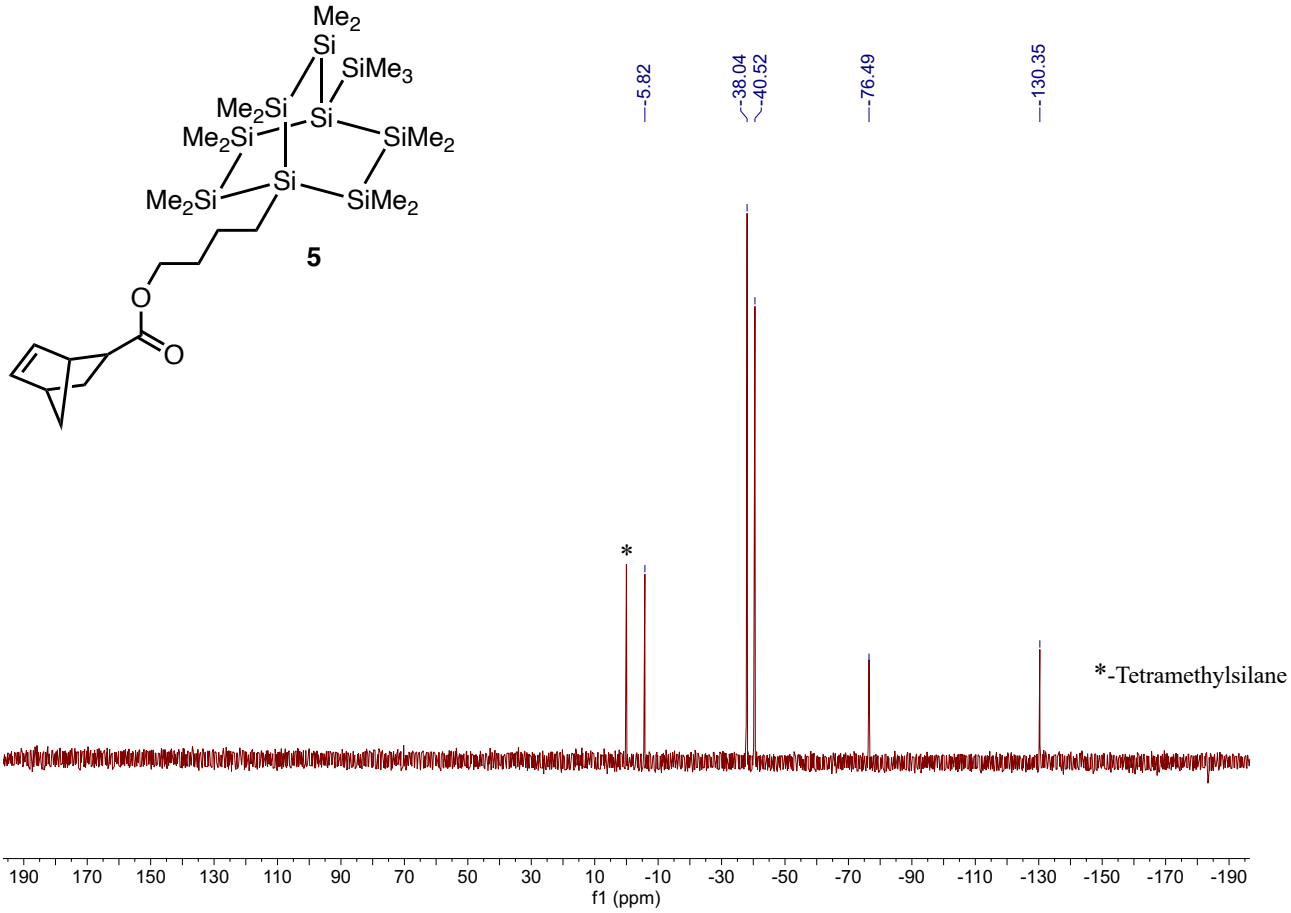
^{1}H NMR Spectrum (600 MHz, $CDCl_3$):



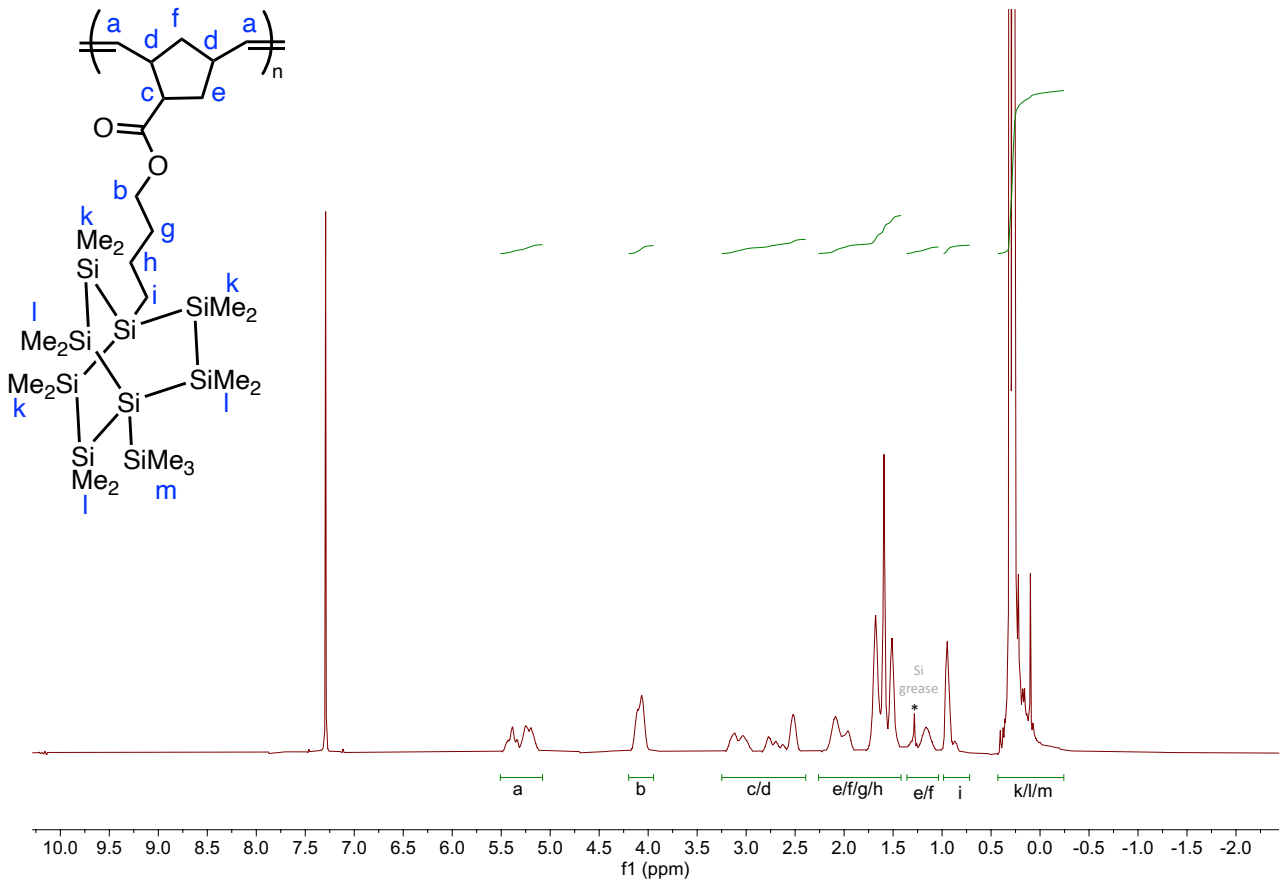
^{13}C NMR Spectrum (101 MHz, $CDCl_3$):



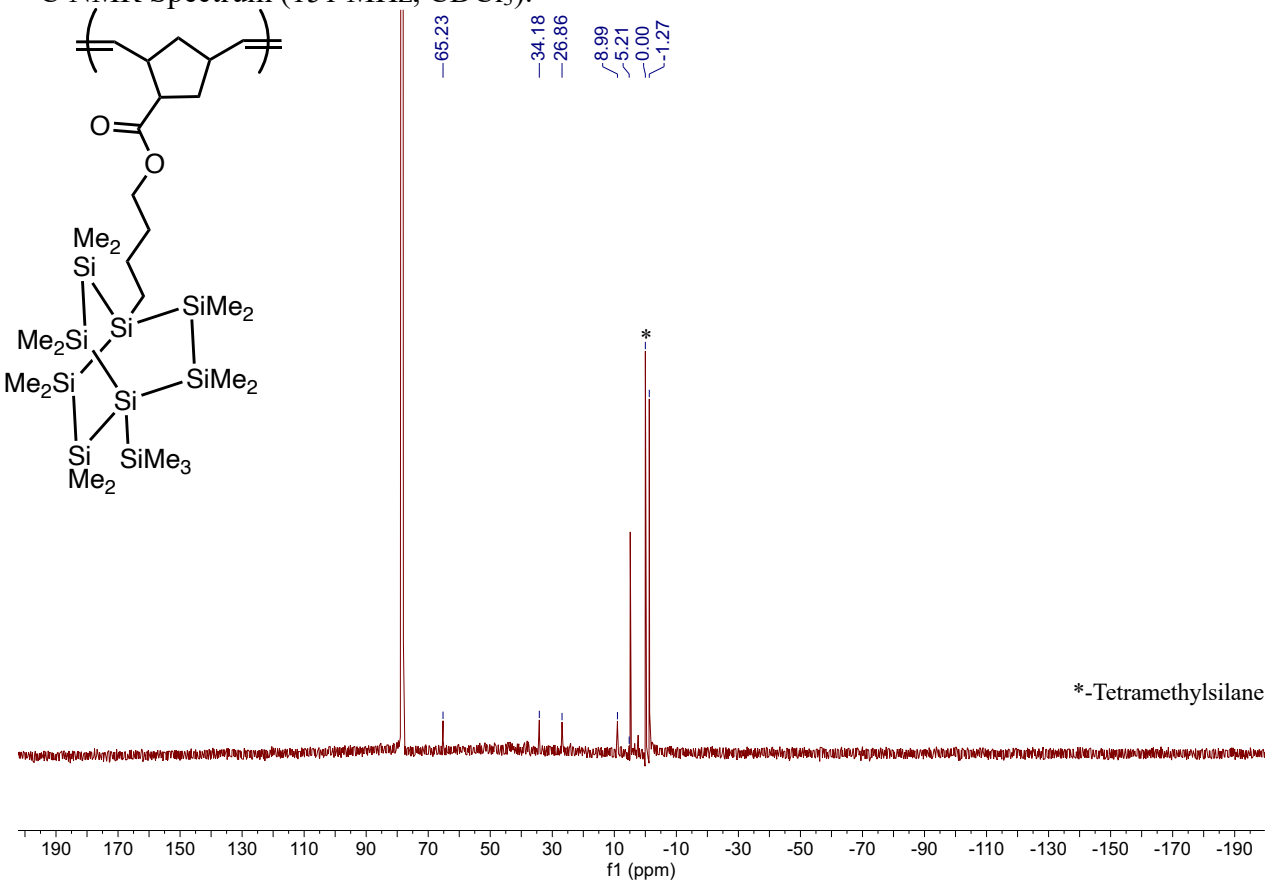
^{29}Si NMR Spectrum (79 MHz, $CDCl_3$):



NMR Spectra of **PNB-Si[2.2.2]** (2000:1 M:I ratio)
^{1}H NMR Spectrum (600 MHz, $CDCl_3$):



^{13}C NMR Spectrum (151 MHz, $CDCl_3$):



^{29}Si NMR Spectrum (79 MHz, $CDCl_3$):