Supporting Information

Preparation of phenyl-substituted open-cage silsesquioxane-pendant polysiloxanes and their thermal and optical properties

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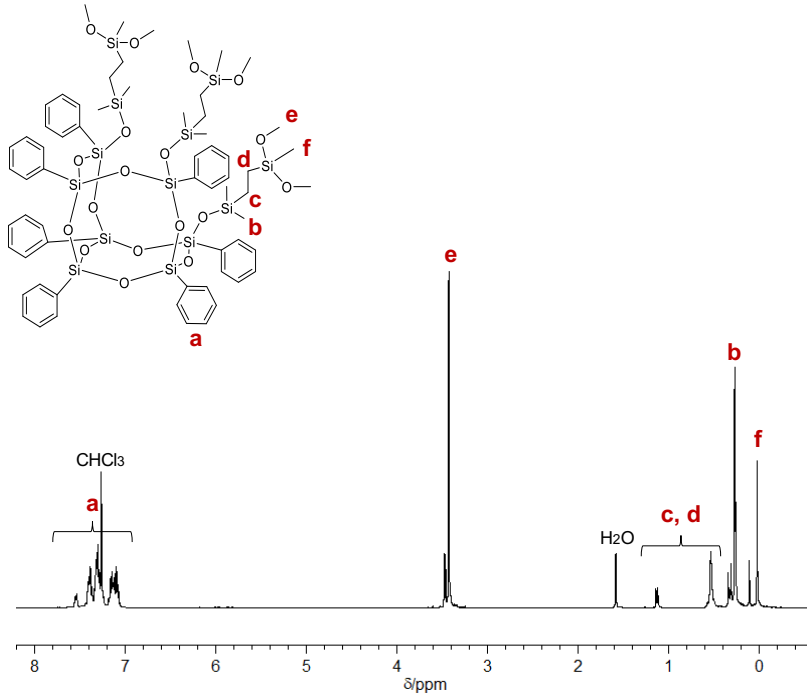
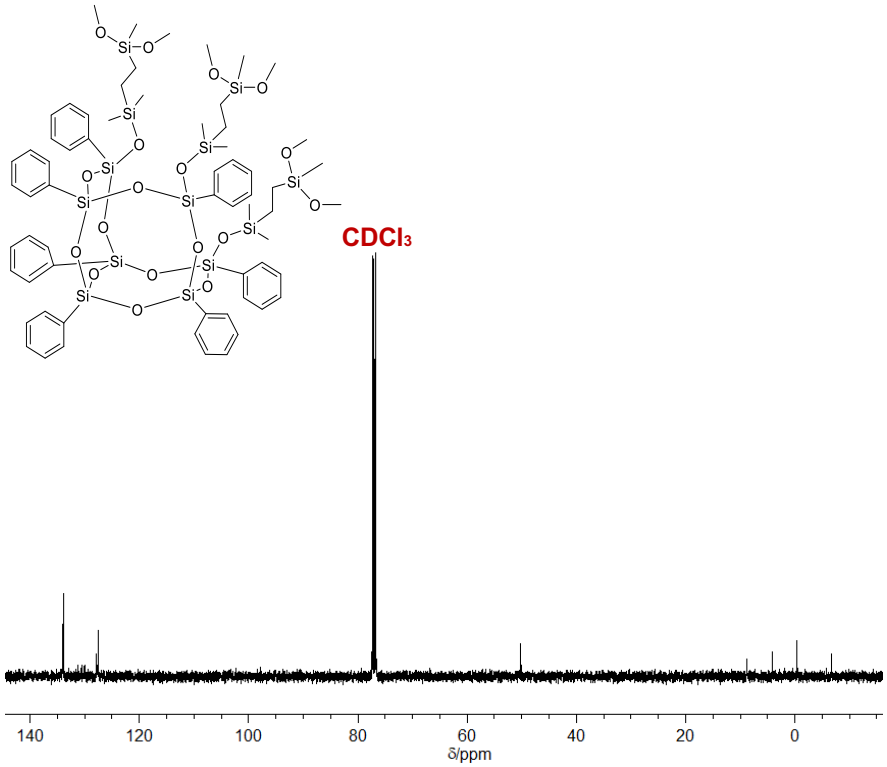
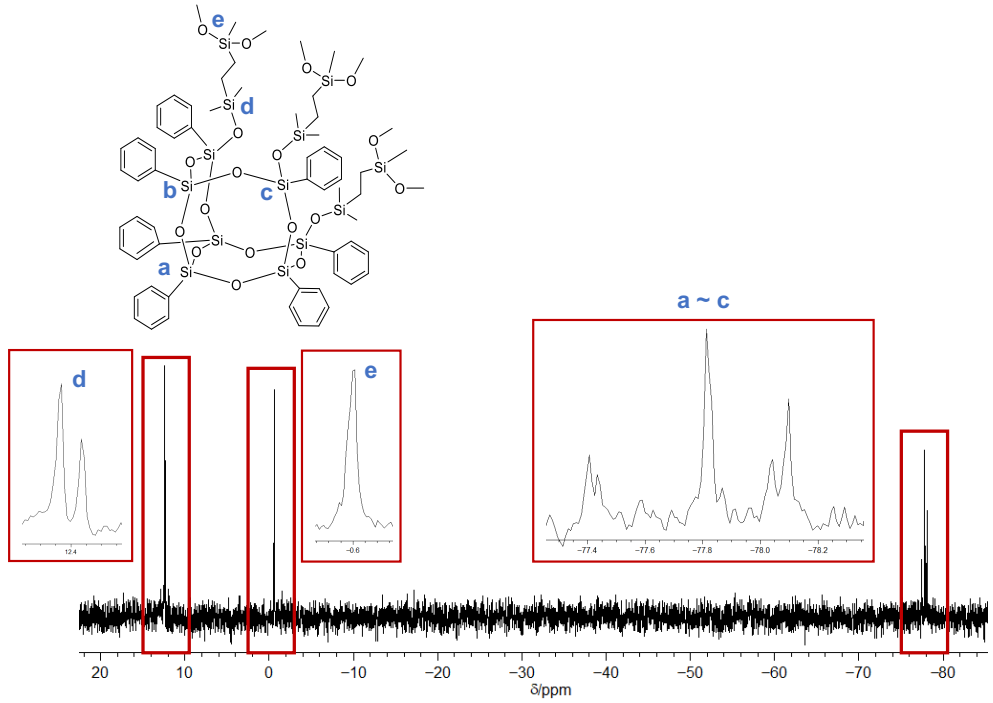
(a)


e
f
d
c
b
a
e
b
f
CHCl3
a
c, d
H2O
8
7
6
5
4
3
2
1
0
δ/ppm

(b)


CDCl3
140
120
100
80
60
40
20
0
δ/ppm

(c)



(d)

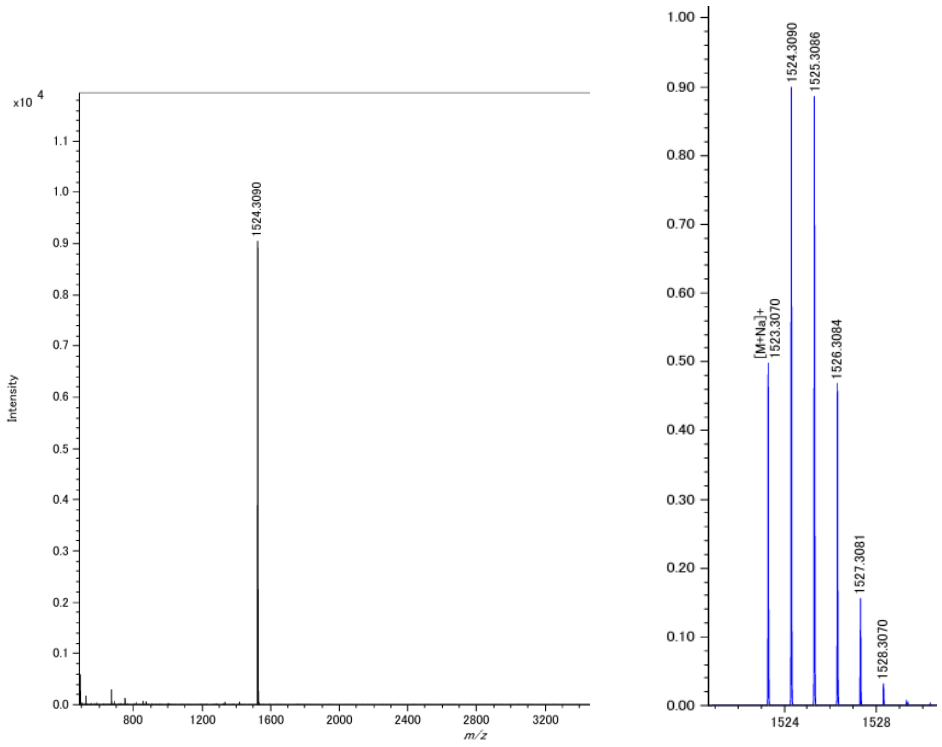
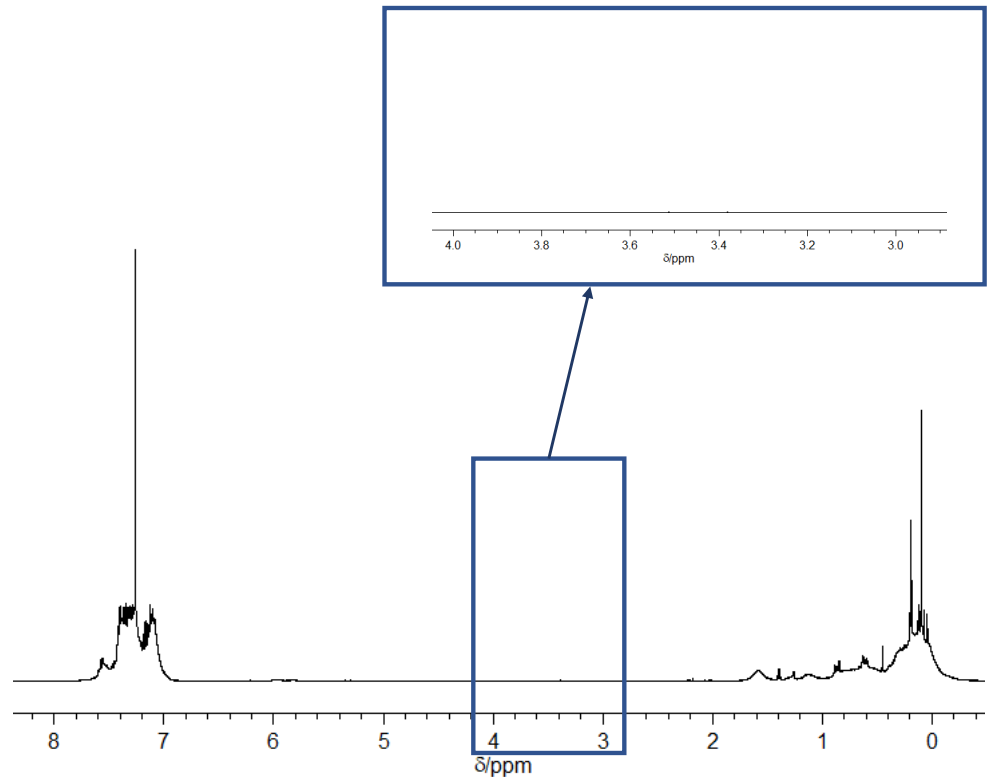


Figure S1 (a) ^{1}H-, (b) ^{13}C-, and (c) ^{29}Si-NMR spectra in $CDCl_3$ and (d) MALDI-TOF-MS spectrum of **Ph-H**.

(a)



(b)

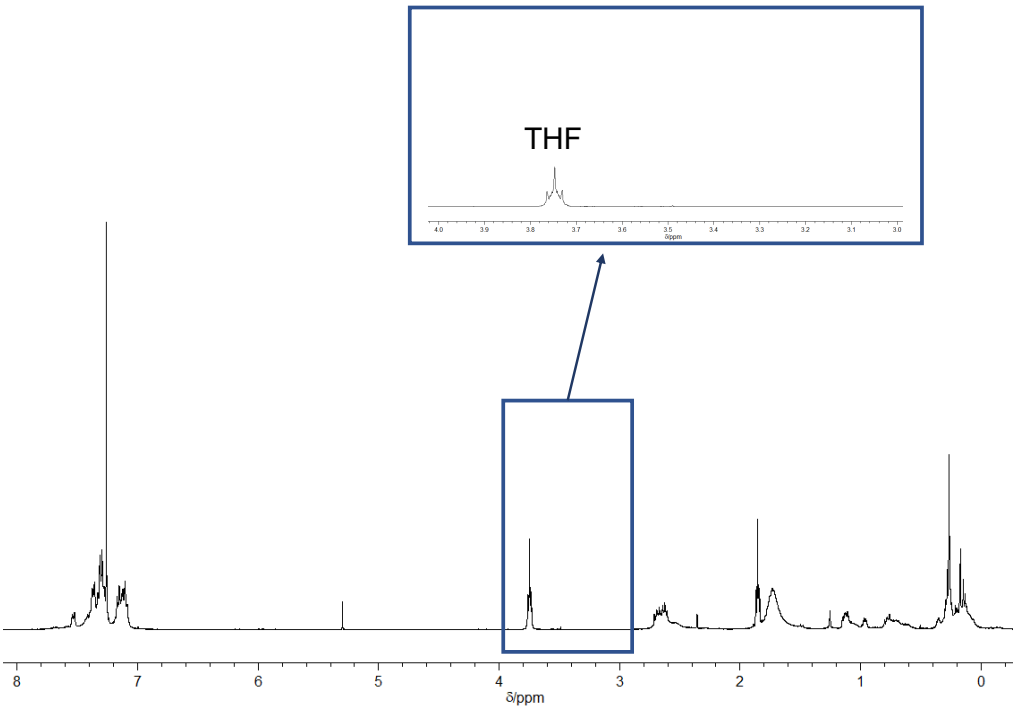


Figure S2 ^{1}H-NMR spectra of residual products in $CDCl_3$ after **Ph-H** (a) and **Ph-V** (b) were first hydrolyzed with 1 M HCl and concentrated.

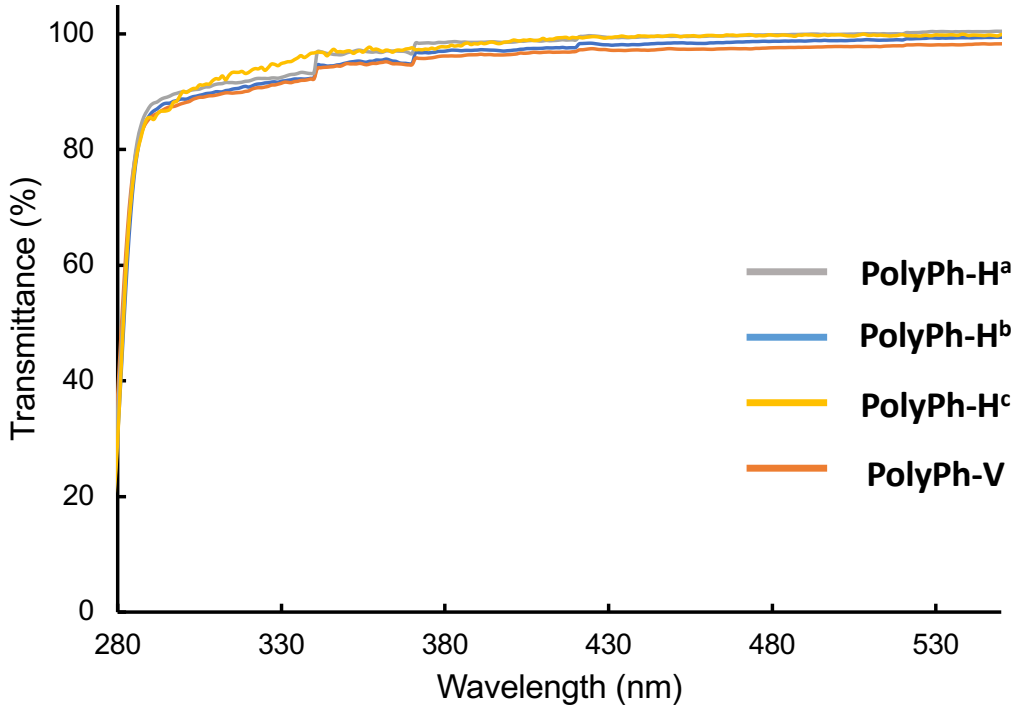


Figure S3 Transmittance spectra of **PolyPh-H^{a}**, **PolyPh-H^{b}**, **PolyPh-H^{c}**, and **PolyPh-V**.

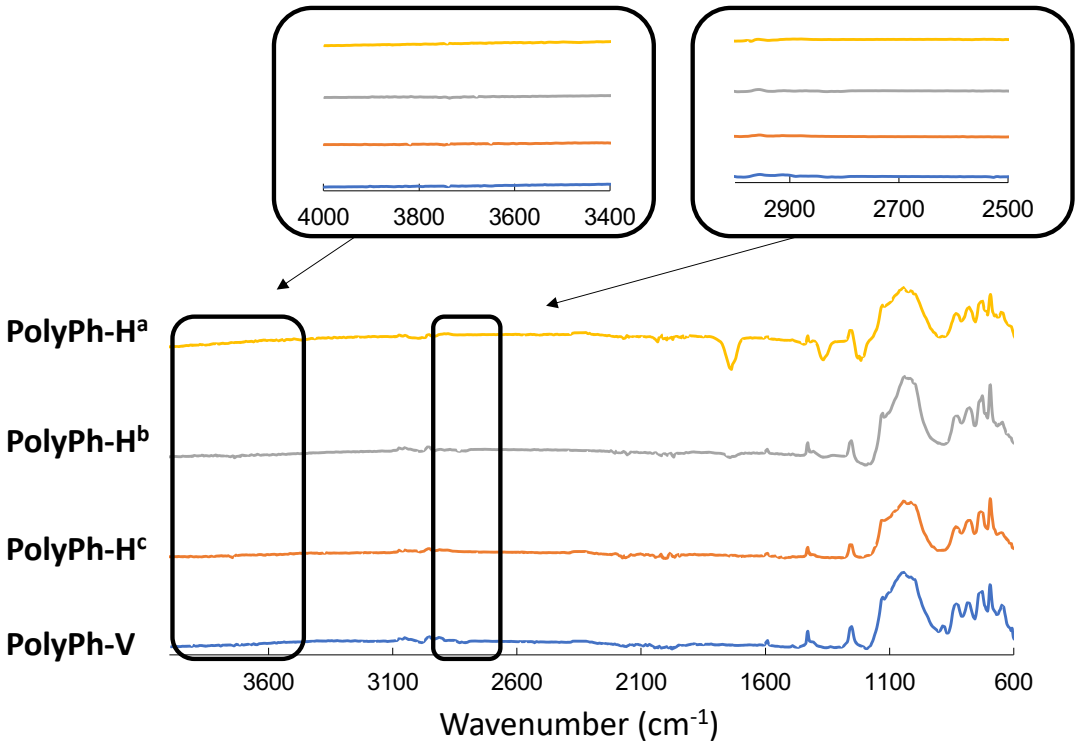


Figure S4 FT-IR spectra of **PolyPh-H^{a}**, **PolyPh-H^{b}**, **PolyPh-H^{c}**, and **PolyPh-V**.

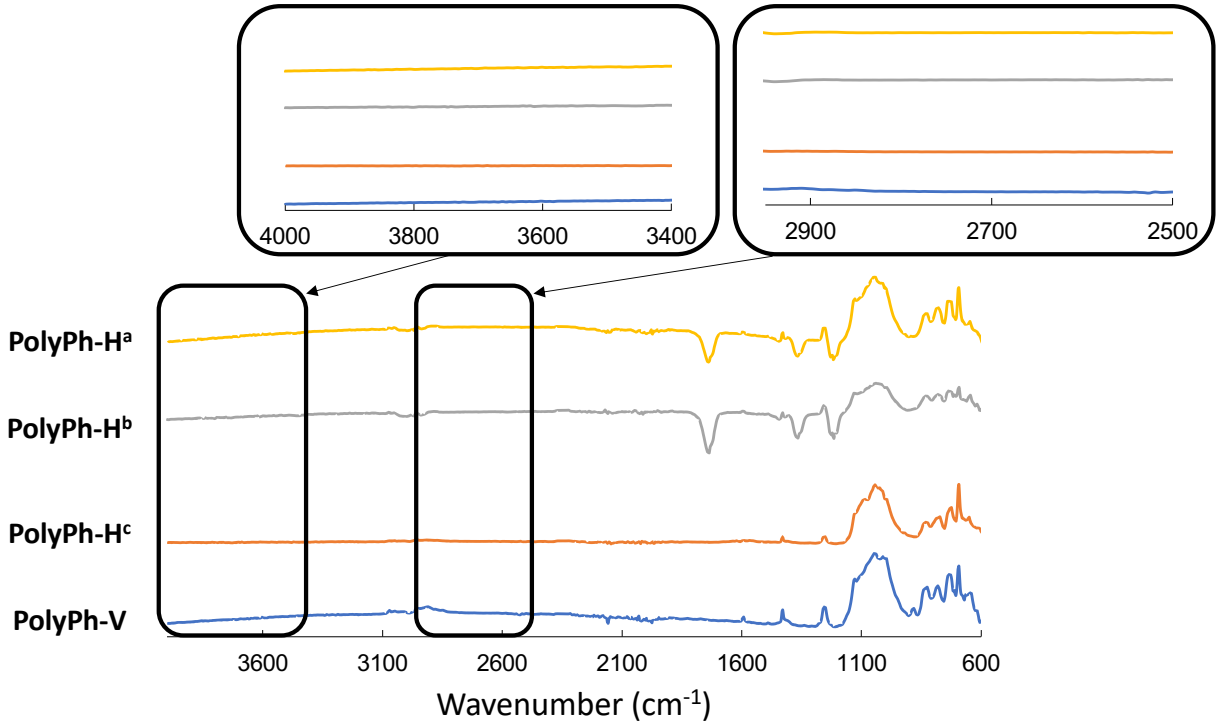
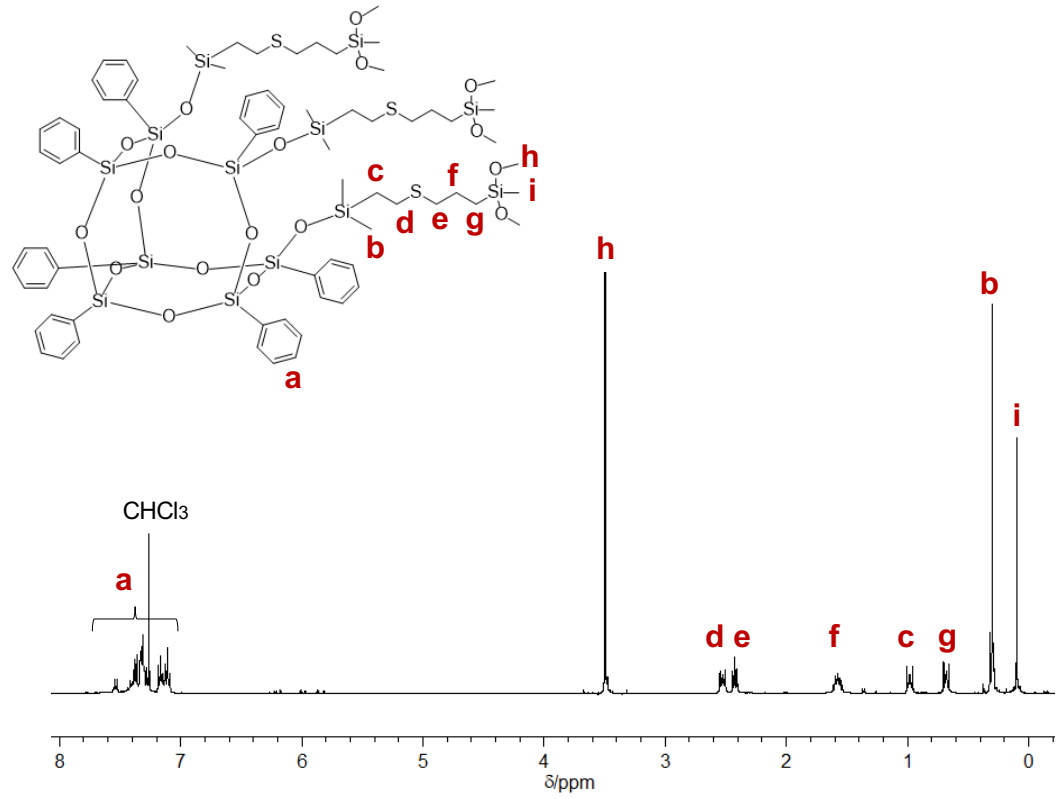
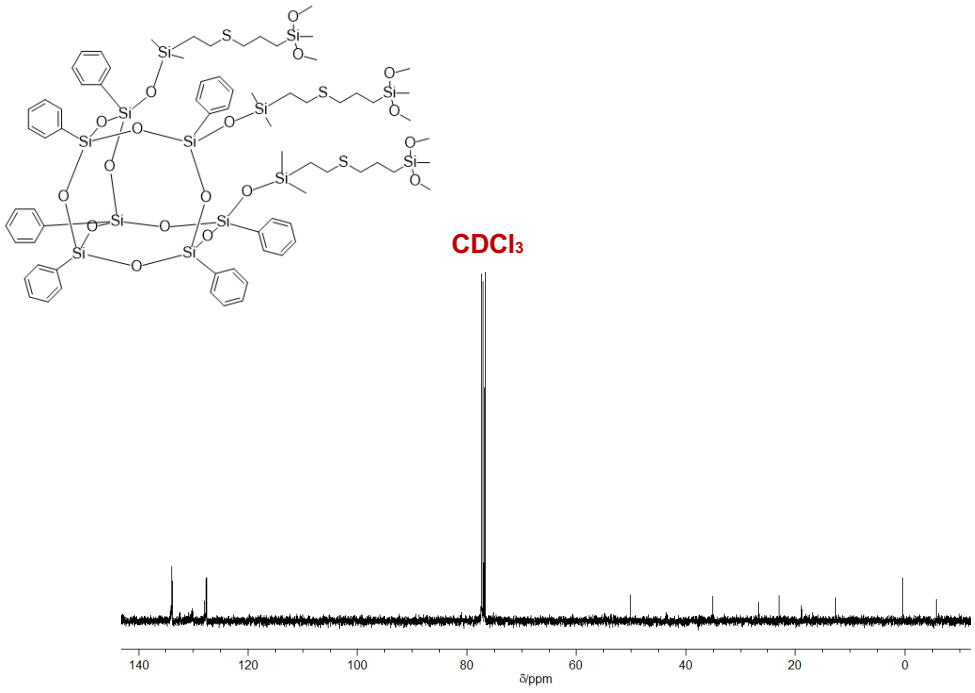


Figure S5 FT-IR spectra of **PolyPh-H^a**, **PolyPh-H^b**, **PolyPh-H^c**, and **PolyPh-V** after storage for three months at room temperature under air.

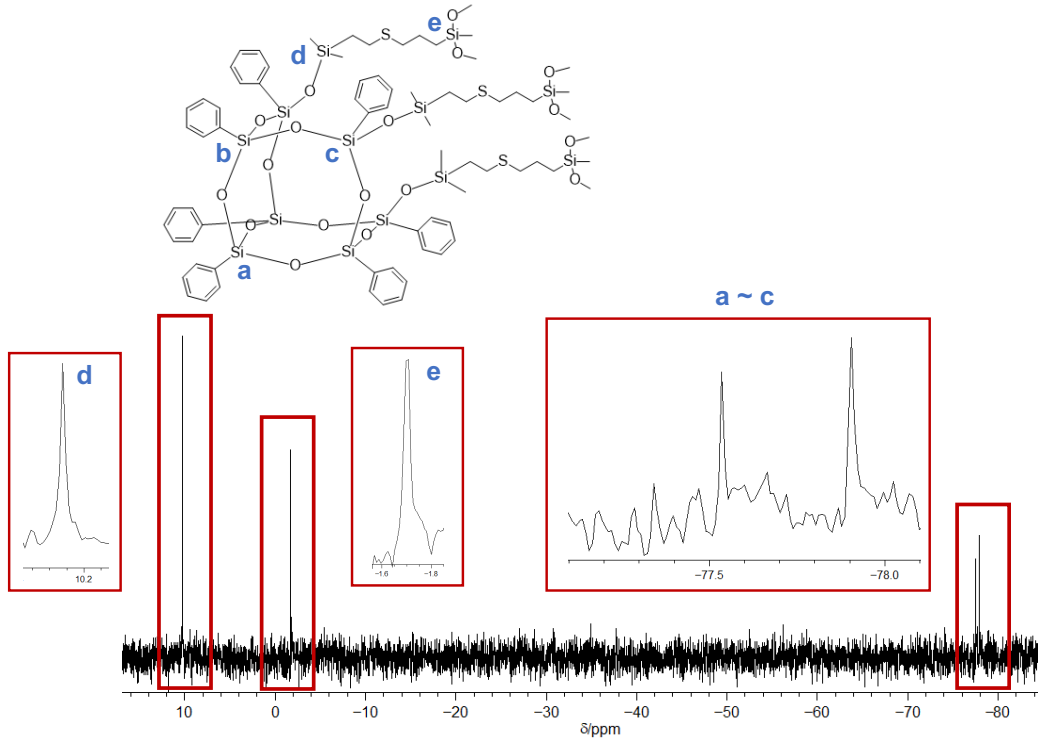
(a)



(b)



(c)



(d)

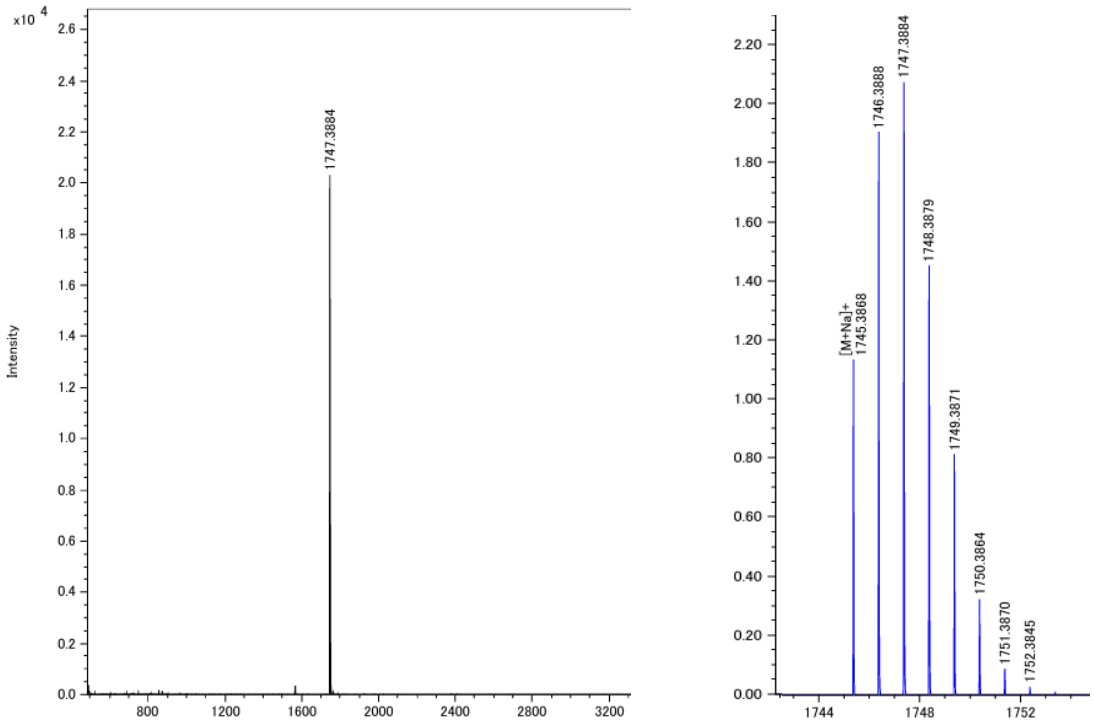


Figure S6 (a) ^{1}H-, (b) ^{13}C-, and (c) ^{29}Si-NMR spectra in $CDCl_3$ and (d) MALDI-TOF-MS spectrum of **Ph-V**.

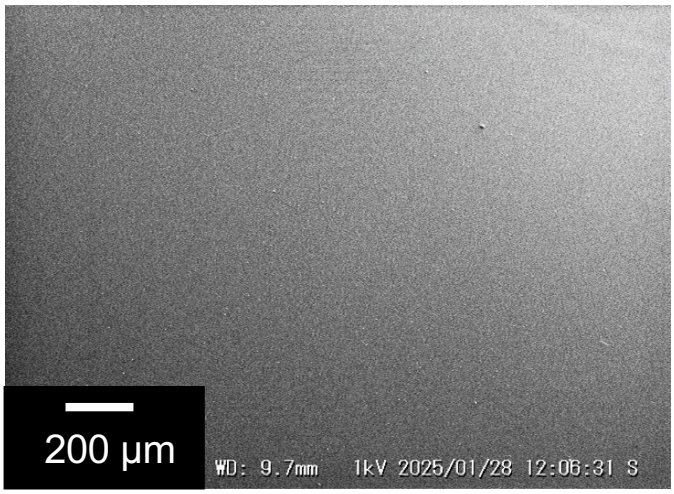


Figure S7 SEM image of the film of **PolyPh-V.**

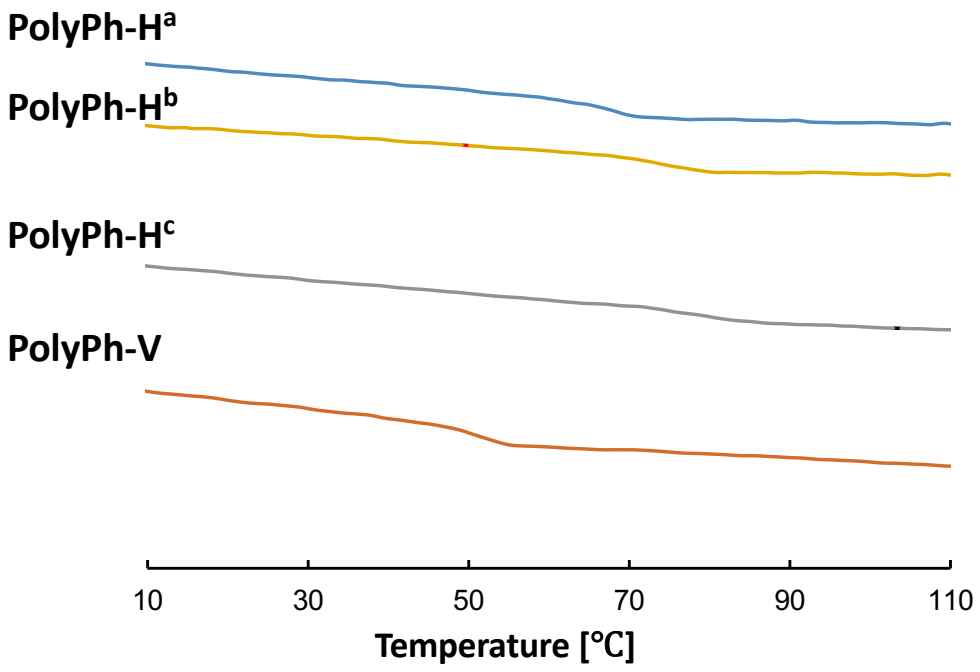


Figure S8 DSC analysis of **PolyPh-H^a**, **PolyPh-H^b**, **PolyPh-H^c**, and **PolyPh-V**.

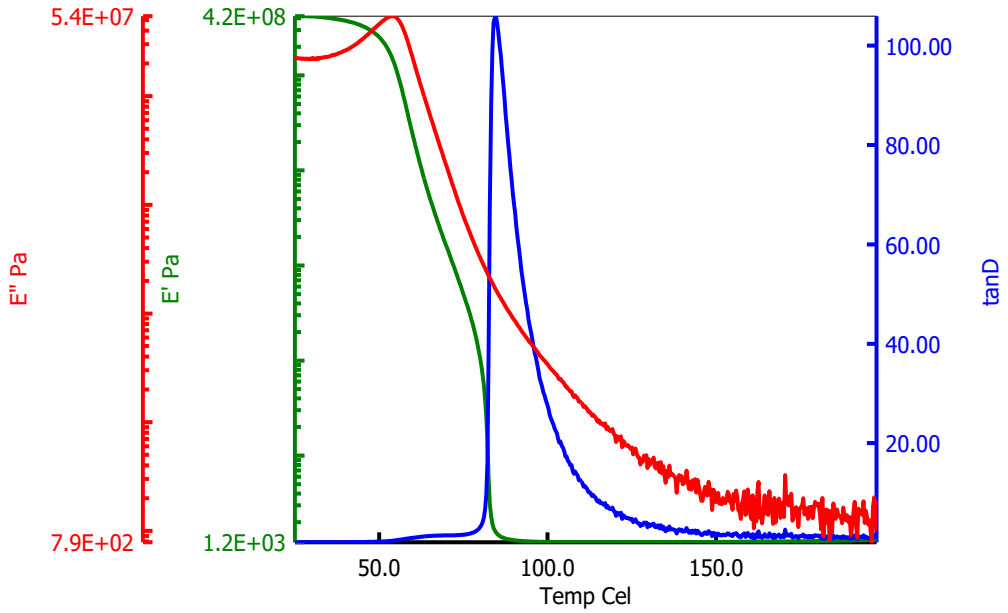


Figure S9 DMA thermograms for **PolyPh-H^{b}** at a frequency 1 Hz.

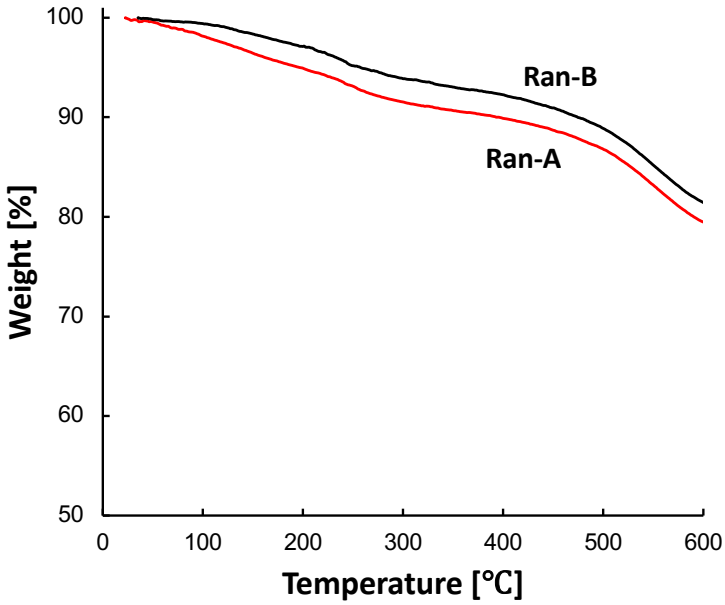


Figure S10. TGA thermograms of **Ran-A** and **Ran-B** at a heating rate of 10 °C min^{-1} in N_2 flow.

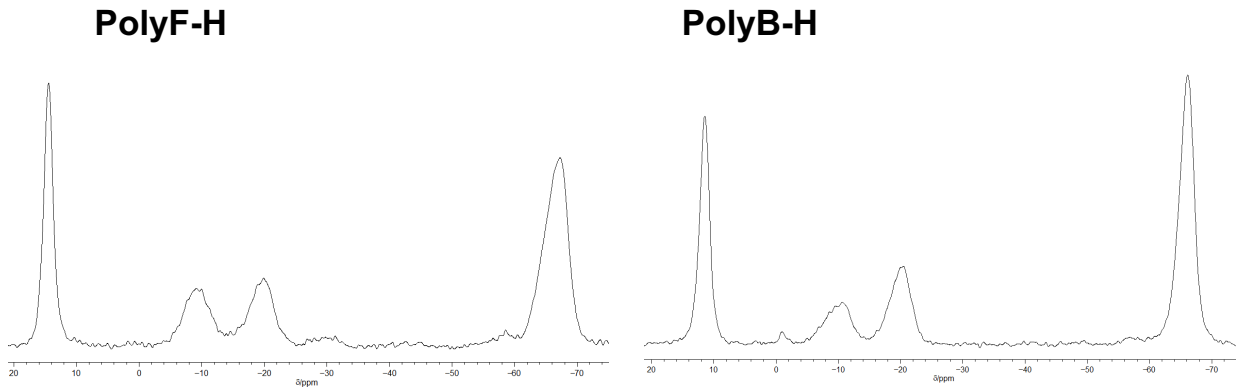


Figure S11 ^{29}Si CP-MAS (119 MHz) NMR spectra for **PolyF-H** and **PolyB-H**.

Dimethylmethoxyvinylsilane

To a MTHP (14.75 mL) solution of imidazole (5.02g, 73.77 mmol) under N_2, MeOH (4.49 mL, 110.65 mmol), and chlorodimethylvinylsilane (10.00 mL, 73.77 mmol) were added. The mixture was stirred at 0 °C for 0.5 h and at room temperature for 24 h. Distillation was carried out at 75 °C. After distillation, the resulting colorless liquid was concentrated, dried under vacuum (48 % yield, 4.15 g, 35.7 mmol).

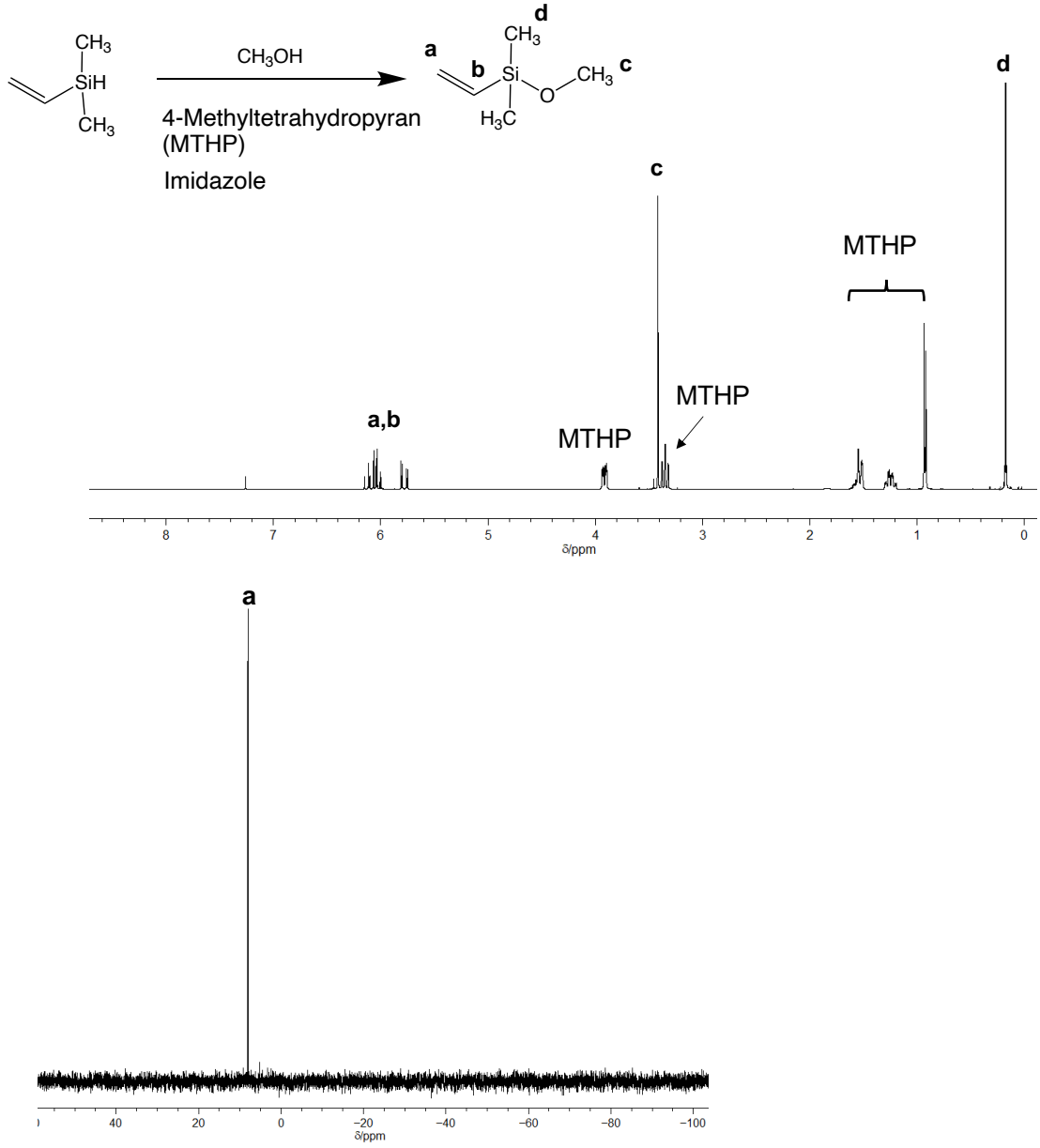


Figure S12 (a) ^{1}H-, and (b) ^{29}Si-NMR spectra of dimethylmethoxyvinylsilane in $CDCl_3$.

1-(Methyldimethoxysilyl)-2-(dimethylmethoxysilyl)ethane (MDME).

To dimethoxymethylsilane (0.90 mL, 7.30 mmol), dimethylmethoxyvinylsilane (0.99 mL, 7.30 mmol) and Pt(dvs) (2wt% in xylene, 73 µL) were added under N_2. SiliaMetS® triamine metal scavenger (0.175 g) was used to remove the catalyst. After filtration, the resulting colorless liquid (MDME) was concentrated and dried under vacuum.

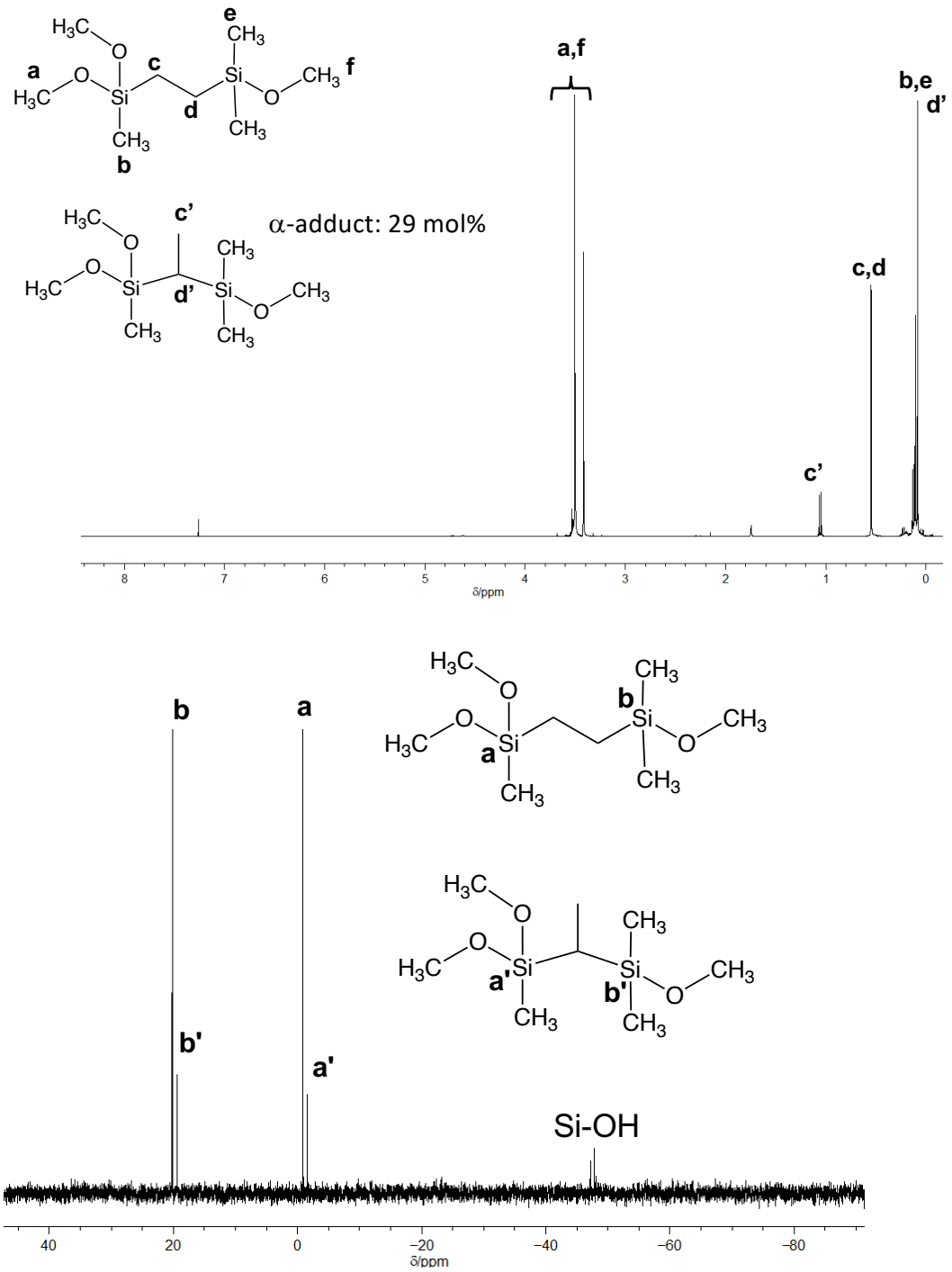


Figure S13 (a) ^{1}H-, and (b) ^{29}Si-NMR spectra of MDME in $CDCl_3$.