

## Supporting Information

# Open-cage silsesquioxane necklace polymers having closed-cage silsesquioxane pendants

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## 1. Materials

Tetrahydrofuran (THF), toluene, triethylamine (NEt<sub>3</sub>), and magnesium sulfate anhydrous (MgSO<sub>4</sub>) were purchased from Nacalai Tesque (Kyoto, Japan). Distilled water was purchased from Wako Pure Chemical Industry (Osaka, Japan). Chlorodimethylvinylsilane, 1,1,3,3-tetramethyldisiloxane (**5b**) were purchased from Tokyo Chemical Industry (Tokyo, Japan). Xylene solution (0.1 M) of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (Pt(dvs)), 1,1,3,3,5,5-hexamethyltrisiloxane (**5a**), and 1,4-bis(dimethylsilyl)benzene (**5c**) were purchased from Sigma-Aldrich (Hattiesburg, Mississippi, US). Heptaphenyl trisilanol POSS (**1<sub>Ph</sub>**) and heptaisobutyl trisilanol POSS (**1<sub>iBu</sub>**) was purchased from Hybrid Plastics Inc (Hattiesburg, Mississippi, US). SiliaMetS(R) Thiol (40-63 μmol 60 Å, functionalized Silica) was purchased from SiliCycle, Inc. Dimethylvinylsilane-substituted heptaphenyl IC-POSS (**2<sub>Ph</sub>**) and heptaisobutyl IC-POSS (**2<sub>iBu</sub>**), and hydride-substituted heptaphenyl CC-POSS (**3<sub>Ph</sub>**) and heptaisobutyl CC-POSS (**3<sub>iBu</sub>**) were prepared by following the literatures.

## 2. Measurements

<sup>1</sup>H (400MHz) and <sup>13</sup>C (100MHz) nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DPX-400 spectrometer (Bruker Biospin GmbH, Rheinstetten, Germany) in CDCl<sub>3</sub> using Me<sub>4</sub>Si as an internal standard. The following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. Molecular weights were determined by size exclusion chromatography (SEC) of LC-6AD (Shimadzu, Kyoto, Japan) with Shodex KF-805L (Showa Denko, Tokyo, Japan), and then analysed by refractive index with RID-20A (Shimadzu, Kyoto, Japan). Preparative high-performance liquid chromatography (HPLC) for purification was performed on LC-6AD (Shimadzu, Kyoto, Japan) with a KF-2002 (for polymers, Showa Denko, Tokyo, Japan) or a tandem column system of two columns selected from Shodex KF-2001 and KF-2002 (for monomers, Showa Denko, Tokyo, Japan) using chloroform as an eluent. Matrix assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was recorded on a Bruker Autoflex II instrument (Bruker Daltonics, Billerica, MA, USA): *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) matrix (20 mg/mL in CHCl<sub>3</sub>) and sodium trifluoroacetate cationizing agents (1 mg/mL in THF). TGA and DSC measurements were performed by Shimadzu DTG-60 and DSC-60 Plus (Shimadzu, Kyoto, Japan), respectively, under nitrogen atmosphere at a heating rate of 10 °C/min. Transmittance spectra were recorded on a JASCO

spectrophotometer V-670 KNN (JASCO, Tokyo, Japan). Refractive index (RI) values were measured by Abbe's method with an Atago refractometer (Atago, Tokyo, Japan).

### 3. Synthetic procedure and characterization data

**Bis(dimethylvinylsilyloxy) heptaphenyl IC-POSS with heptaphenyl CC-POSS ( $4_{\text{Ph-Ph}}$ ).** A Toluene solution (8.4 mL) of  $2_{\text{Ph}}$  (1.00 g, 0.84 mmol),  $3_{\text{Ph}}$  (0.96 g, 1.00 mmol) and Pt(dvs) (0.1 M in xylene, 0.05 mL,  $5.0 \times 10^{-3}$  mmol) was stirred at 50 °C for 6 h under  $\text{N}_2$  atmosphere. The solvents were removed in *vacuo*, and the residue was subjected to preparative HPLC to give  $4_{\text{Ph-Ph}}$  (0.94 g, 0.44 mmol, 52%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.78-7.68 (m, 14H), 7.59-7.56 (m, 2H), 7.48-7.40 (m, 14H), 7.40-7.24 (m, 28H), 7.18-7.08 (m, 10H), 6.96-6.91 (t,  $J = 2.8\text{Hz}$ , 2H), 6.24-5.77 (m, 6H), 0.75 (s, 4H), 0.30-0.28 (m, 12H), 0.24-0.22 (m, 6H) ppm.  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  138.7, 134.4, 134.3, 134.2, 134.1, 134.0, 139.9, 132.9, 132.8, 132.6, 131.2, 130.8, 130.6, 130.5, 130.2, 130.1, 128.0, 127.7, 127.6, 9.1, 3.6, 0.5, -0.2 ppm.  $^{29}\text{Si-NMR}$  ( $\text{CDCl}_3$ , 80 MHz)  $\delta$  12.3, 0.1, -64.6, -77.4, -77.6, -77.8, -78.1, -78.2, -78.4, -78.7 ppm. MALDI-TOF MS ( $m/z$ ): calcd for  $\text{C}_{96}\text{H}_{98}\text{O}_{24}\text{Si}_{18}\text{Na}$  [ $\text{M}+\text{Na}$ ] $^+$ : 2161.2; found: 2161.2.

**Bis(dimethylvinylsilyloxy) heptaphenyl IC-POSS with heptaisobutyl CC-POSS ( $4_{\text{Ph-iBu}}$ ).** The same procedure as that of  $4_{\text{Ph-Ph}}$  using  $3_{\text{iBu}}$  instead of  $3_{\text{Ph}}$ . The isolated yield was 52%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.59-7.56 (m, 2H), 7.43-7.38 (m, 7H), 7.38-7.24 (m, 14H), 7.17-7.08 (m, 12H), 6.27-5.81 (m, 6H), 1.91-1.80 (m, 7H), 0.98-0.91 (m, 42H), 0.63-0.56 (m, 18H), 0.34-0.32 (m, 12H), 0.26-0.24 (m, 6H) ppm.  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  138.6, 134.1, 134.0, 133.9, 132.9, 132.8, 132.5, 132.9, 132.8, 132.5, 131.2, 130.7, 130.6, 130.1, 130.0, 129.9, 127.6, 127.5, 25.8, 25.7, 23.9, 22.6, 22.5, 8.9, 3.7, 0.4, -0.3 ppm.  $^{29}\text{Si-NMR}$  ( $\text{CDCl}_3$ , 80 MHz)  $\delta$  12.5, -0.2, -66.9, -67.5 -67.6, -67.8, -67.9, -77.3, -77.7, -77.8, -78.0, -78.1 ppm. MALDI-TOF MS ( $m/z$ ): calcd for  $\text{C}_{82}\text{H}_{126}\text{O}_{24}\text{Si}_{18}\text{Na}$  [ $\text{M}+\text{Na}$ ] $^+$ : 2021.4; found: 2021.4.

**Bis(dimethylvinylsilyloxy) heptaisobutyl IC-POSS with heptaphenyl CC-POSS ( $4_{\text{iBu-Ph}}$ ).** The same procedure as that of  $4_{\text{Ph-Ph}}$  using  $2_{\text{iBu}}$  instead of  $2_{\text{Ph}}$ . The isolated yield was 54%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.86-7.78 (m, 14H), 7.55-7.45 (m, 7H), 7.45-7.38 (m, 14H), 6.25-5.75 (m, 6H), 1.99-1.82 (m, 7H), 1.08-0.95 (m, 42H), 0.90-

0.75 (m, 4H), 0.67-0.57 (m, 14H), 0.26-0.24 (m, 12H), 0.20-0.18 (m, 6H) ppm.  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  139.1, 134.3, 134.2, 131.9, 130.8, 130.6, 130.4, 130.3, 130.2, 129.7, 127.9, 26.1, 26.0, 25.9, 25.7, 25.0, 24.1, 24.0, 23.9, 23.8, 22.5, 9.1, 3.7, 0.4, -0.3 ppm.  $^{29}\text{Si}$ -NMR ( $\text{CDCl}_3$ , 80 MHz)  $\delta$  9.8, -2.6, -64.3, -67.2, -67.6, -67.7, -67.8, -68.0, -77.8, -78.2, -78.3, -78.6 ppm. MALDI-TOF MS ( $m/z$ ): calcd for  $\text{C}_{82}\text{H}_{126}\text{O}_{24}\text{Si}_{18}\text{Na}$   $[\text{M}+\text{Na}]^+$ : 2021.4; found: 2021.4.

**Synthesis of polymer 6a.** A Toluene solution (0.3 mL) of **4<sub>Ph-Ph</sub>** (300 mg, 0.144 mmol), **5a** (29 mg, 0.14 mmol) and Pt(dvs) (0.1 M in xylene,  $8 \times 10^{-3}$  mL,  $8.0 \times 10^{-4}$  mmol) was stirred at 50 °C for 2 h under  $\text{N}_2$  atmosphere. The solvents were removed in *vacuo*, and the residue was subjected to preparative HPLC to give **5** (157 mg, 48%).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.89-7.80 (m, 14H), 7.70-7.65 (m, 2H), 7.56-7.46 (m, 14H), 7.46-7.32 (m, 28H), 7.27-7.16 (m, 10H), 7.05-6.97 (m, 2H), 0.85 (s, 4H), 0.64-0.47 (m, 8H), 0.42-0.34 (m, 18H), 0.24-0.02 (m, 18H) ppm.  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  134.3, 134.2, 134.1, 134.0, 133.9, 133.1, 132.8, 130.9, 130.6, 130.4, 130.2, 130.0, 130.0, 127.7, 127.6, 9.5, 9.1, 3.6, 1.5, -0.2, -0.5 ppm.  $^{29}\text{Si}$ -NMR ( $\text{CDCl}_3$ , 80 MHz)  $\delta$  12.7, 12.3, 8.3, -21.1, -64.5, -77.3, -77.6, -77.7, -78.0, -78.2, -78.5 ppm.

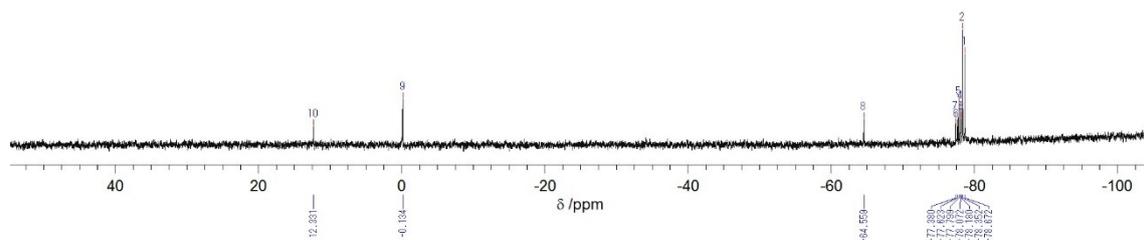
**Synthesis of polymer 6b.** The same procedure as that of **6a** using **5b** instead of **5a**. The isolated yield was 62%.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.95-7.82 (br, 14H), 7.74-7.68 (br, 2H), 7.60-7.53 (br, 14H), 7.53-7.34 (br, 28H), 7.29-7.18 (br, 10H), 7.09-7.01 (br, 2H), 0.92-0.84 (br, 4H), 0.65-0.47 (br, 8H), 0.47-0.35 (br, 18H), 0.20-0.01 (br, 12H) ppm.  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  134.4, 134.3, 134.2, 134.1, 134.0, 133.1, 132.8, 131.4, 131.3, 130.9, 130.8, 130.6, 130.5, 130.4, 130.2, 130.0, 128.0, 127.7, 9.6, 9.5, 9.1, 3.6, -0.2, -0.3 ppm.  $^{29}\text{Si}$ -NMR ( $\text{CDCl}_3$ , 80 MHz)  $\delta$  12.7, 12.4, 8.4, -64.4, -77.2, -77.6, -77.7, -77.9, -78.2, -78.2, -78.5 ppm.

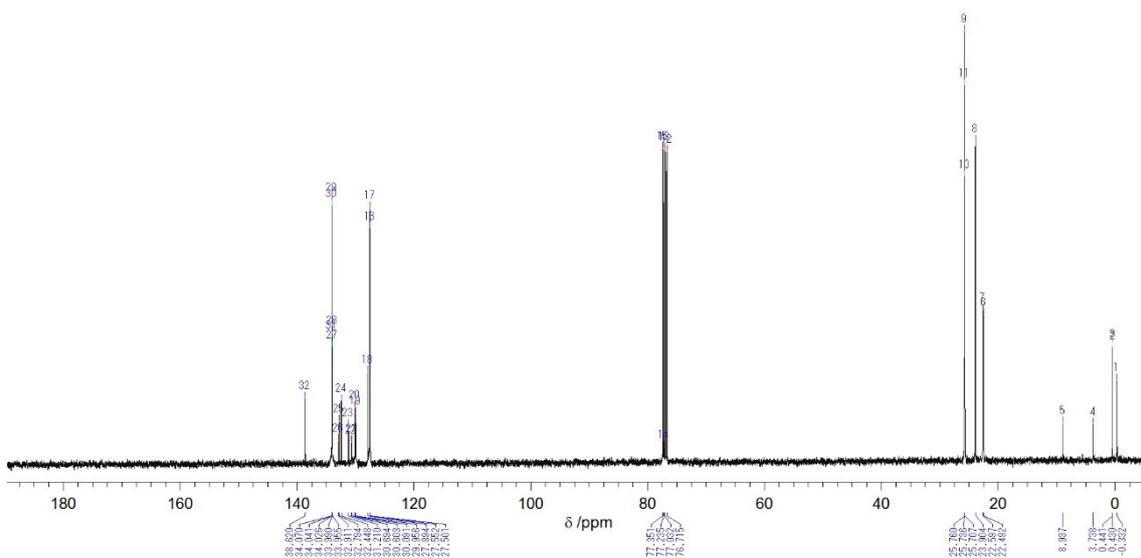
**Synthesis of polymer 6c.** The same procedure as that of **6a** using **5c** instead of **5a**. The isolated yield was 58%.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.94-7.85 (m, 14H), 7.74-7.70 (m, 2H), 7.60-7.53 (m, 14H), 7.53-7.36 (m, 32H), 7.30-7.19 (m, 10H), 7.12-7.05 (m, 2H), 0.92 (s, 4H), 0.83-0.64 (m, 8H), 0.47-0.37 (m, 18H), 0.34-0.26 (m, 12H) ppm.  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  134.4, 134.3, 134.2, 134.0, 133.1, 133.0, 132.9, 131.4, 131.3, 130.9, 130.8, 130.6, 130.5, 130.3, 130.2, 130.1, 128.0, 127.7, 10.3, 9.1, 7.0, 3.7, -0.1, -3.5 ppm.  $^{29}\text{Si}$ -NMR ( $\text{CDCl}_3$ , 80 MHz)  $\delta$  12.6, 12.4, -1.5, -64.4, -77.2, -77.5, -77.7, -77.9, -78.1, -78.5 ppm.

**Synthesis of polymer 7.** The same procedure as that of **6a** using **4<sub>Ph-tBu</sub>** instead of **4<sub>Ph-Ph</sub>**, and reaction time was changed from 2 h to 4 h. The isolated yield was 31 %. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.64-7.56 (m, 2H), 7.48-7.38 (m, 7H), 7.38-7.24 (m, 14H), 7.22-7.06 (m, 12H), 1.95-1.83 (m, 7H), 1.02-0.95 (m, 42H), 0.66-0.59 (m, 18H), 0.58-0.40 (m, 8H), 0.34-0.26 (m, 18H), 0.13-0.04 (m, 18H) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz) δ 134.0, 133.9, 133.0, 131.2, 130.1, 129.9, 127.9, 127.5, 25.8, 25.7, 23.9, 22.6, 22.5, 9.4, 8.9, 3.7, 1.2, 1.1, 1.0, -0.3, -0.6 ppm. <sup>29</sup>Si-NMR (CDCl<sub>3</sub>, 80 MHz) δ 12.6, 12.4, 8.1, -21.2, -67.0, -67.6, -67.8, -67.9, -77.4, -77.8, -78.1 ppm.

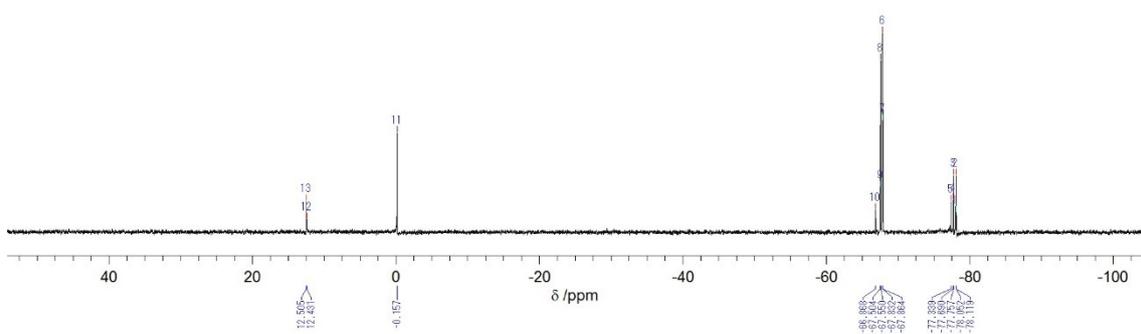
**Synthesis of polymer 8.** The same procedure as that of **6a** using **4<sub>tBu-Ph</sub>** instead of **4<sub>Ph-Ph</sub>**, and reaction time was changed from 2 h to 4 h. The isolated yield was 31 %. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.84-7.74 (m, 14H), 7.52-7.44 (m, 7H), 7.44-7.34 (m, 14H), 1.96-1.78 (m, 7H), 1.06-0.90 (m, 42H), 0.88-0.72 (m, 4H), 0.64-0.54 (m, 14H), 0.52-0.44 (m, 8H), 0.23-0.13 (m, 18H), 0.13-0.04 (m, 18H) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz) δ 134.3, 134.2, 130.7, 130.6, 130.4, 127.9, 26.1, 26.0, 25.9, 25.8, 25.7, 25.1, 25.0, 24.1, 24.0, 23.9, 23.8, 22.5, 9.5, 9.1, 3.6, 1.4, 1.3, 1.1, 0.4, 0.2, -0.4, -0.5 ppm. <sup>29</sup>Si-NMR (CDCl<sub>3</sub>, 80 MHz) δ 9.9, 9.7, 8.2, -2.6, -21.3, -64.4, -67.3, -67.6, -67.7, -67.8, -67.9, -68.1, -78.3, -78.6 ppm.







**Figure S5.**  $^{13}\text{C}$  NMR spectrum (100 MHz) of  $4_{\text{Ph-iBu}}$  in  $\text{CDCl}_3$ .



**Figure S6.**  $^{29}\text{Si}$  NMR spectrum (80 MHz) of  $4_{\text{Ph-iBu}}$  in  $\text{CDCl}_3$ .

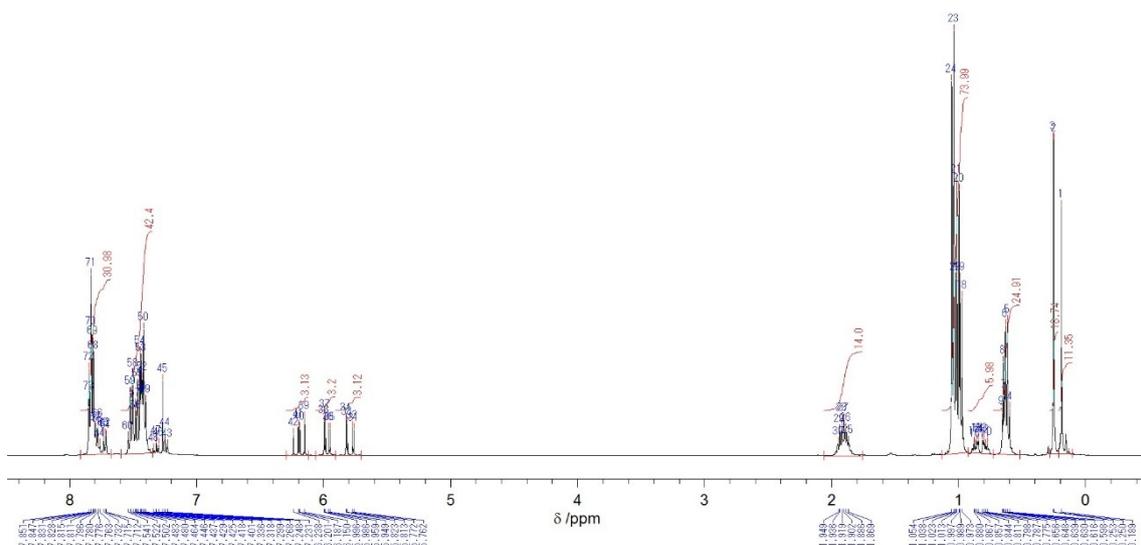


Figure S7.  $^1\text{H}$  NMR spectrum (400 MHz) of  $4i\text{Bu-Ph}$  in  $\text{CDCl}_3$ .

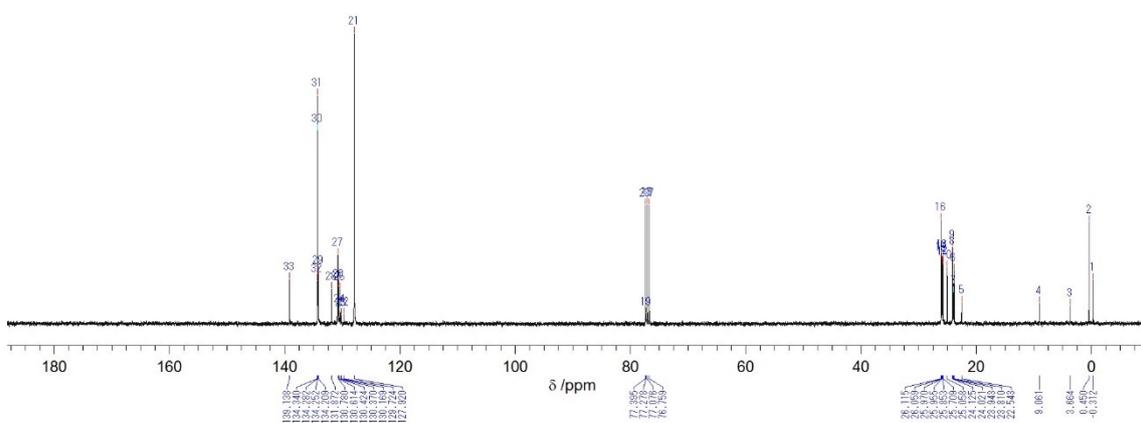
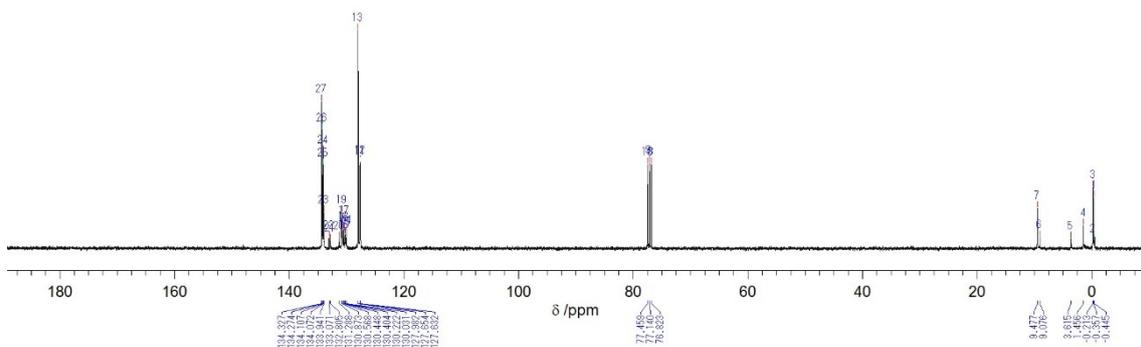
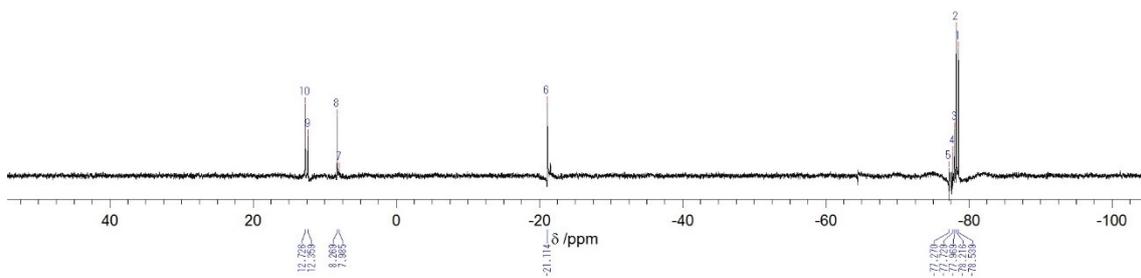


Figure S8.  $^{13}\text{C}$  NMR spectrum (100 MHz) of  $4i\text{Bu-Ph}$  in  $\text{CDCl}_3$ .

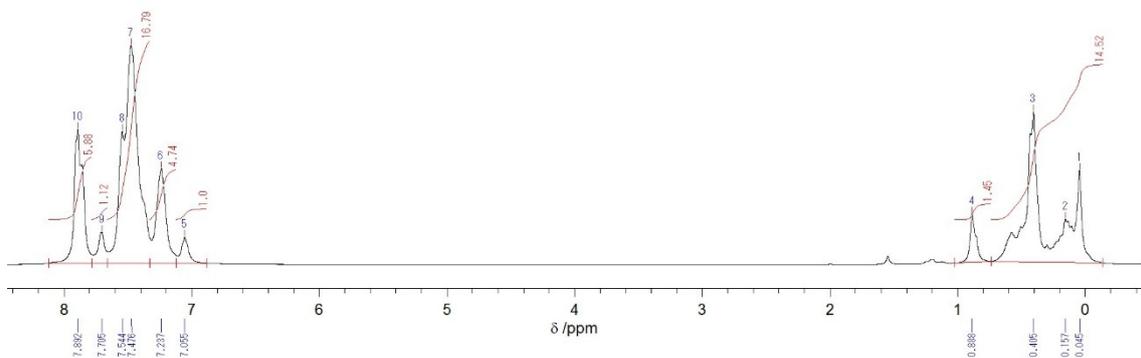




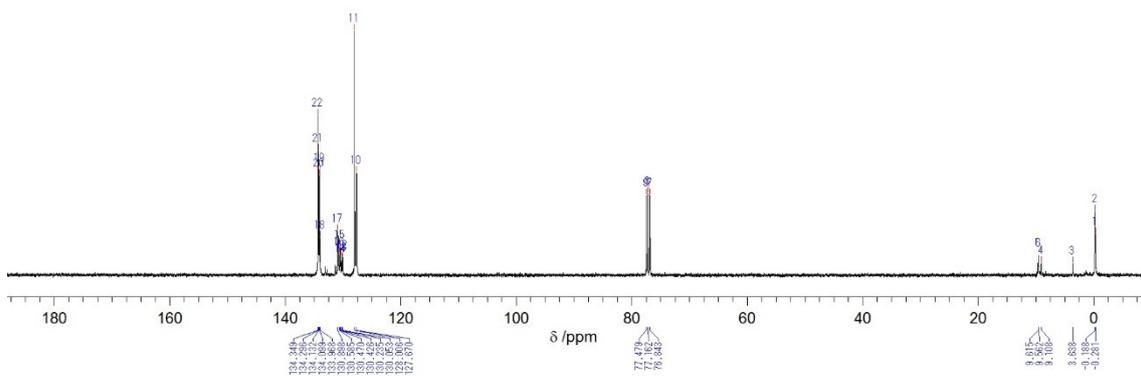
**Figure S11.**  $^{13}\text{C}$  NMR spectrum (100 MHz) of **6a** in  $\text{CDCl}_3$ .



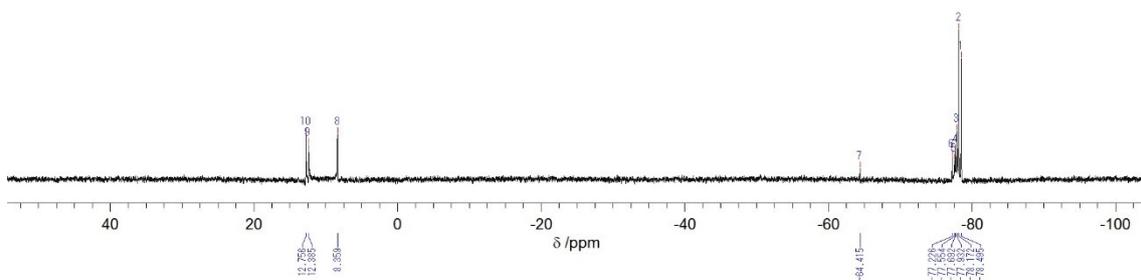
**Figure S12.**  $^{29}\text{Si}$  NMR spectrum (80 MHz) of **6a** in  $\text{CDCl}_3$ .



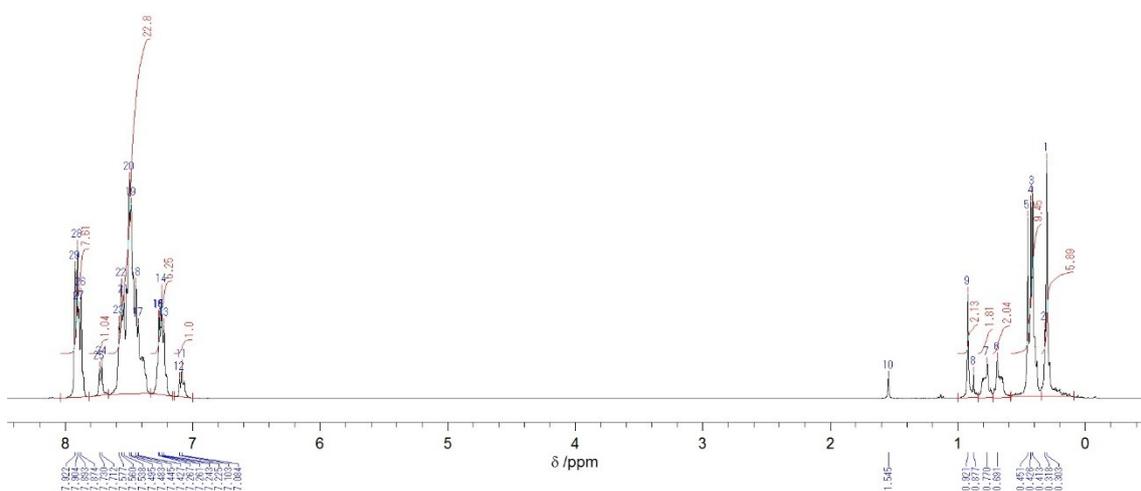
**Figure S13.**  $^1\text{H}$  NMR spectrum (400 MHz) of **6b** in  $\text{CDCl}_3$ .



**Figure S14.**  $^{13}\text{C}$  NMR spectrum (100 MHz) of **6b** in  $\text{CDCl}_3$ .

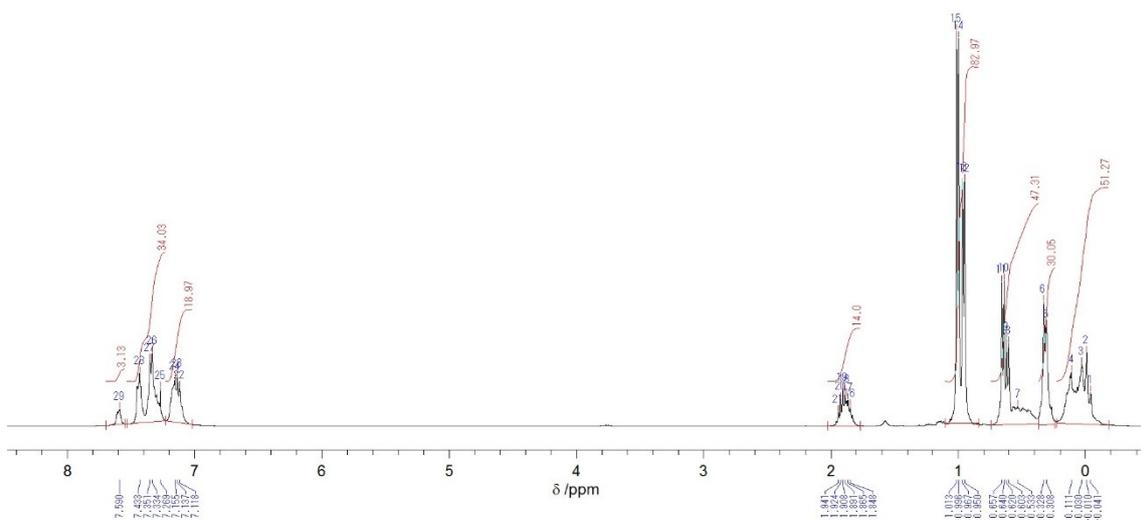


**Figure S15.**  $^{29}\text{Si}$  NMR spectrum (80 MHz) of **6b** in  $\text{CDCl}_3$ .

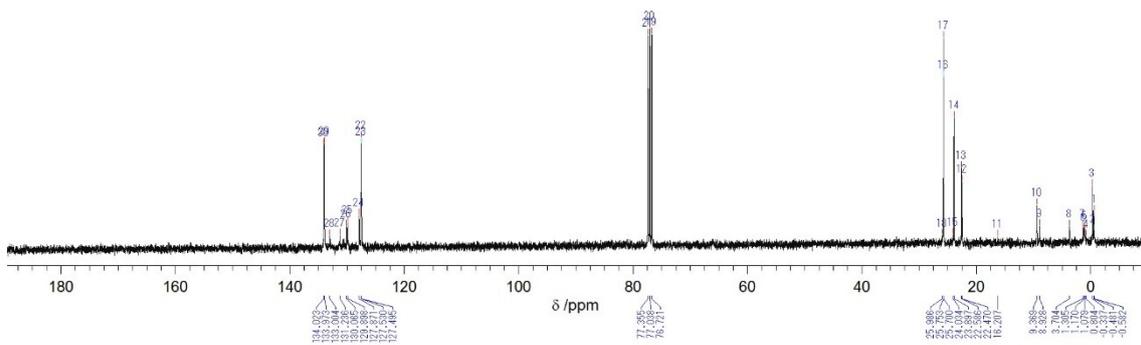


**Figure S16.**  $^1\text{H}$  NMR spectrum (400 MHz) of **6c** in  $\text{CDCl}_3$ .

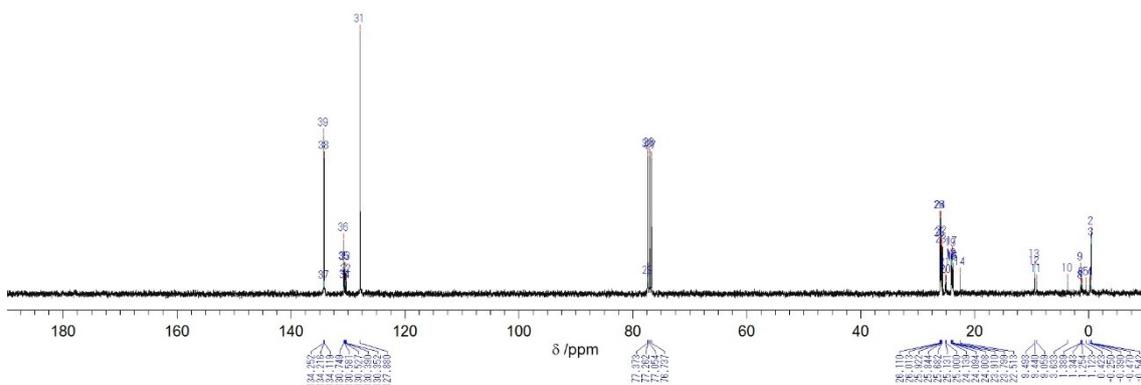




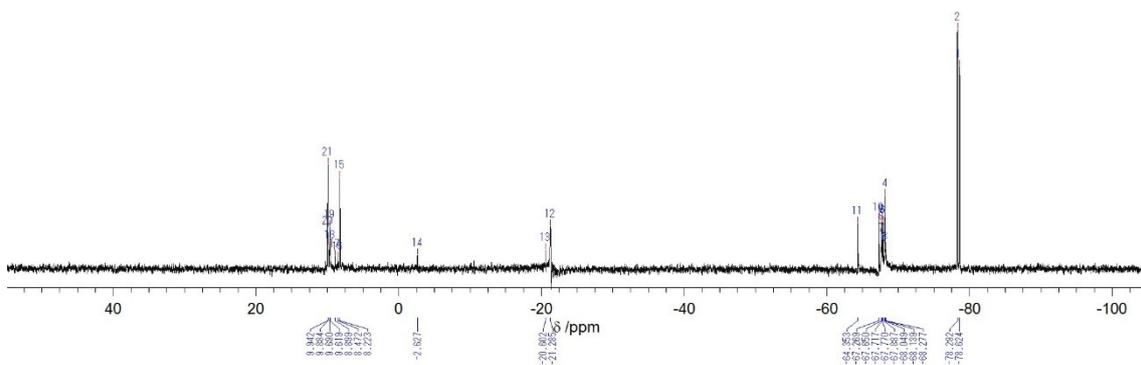
**Figure S19.**  $^1\text{H}$  NMR spectrum (400 MHz) of **6d** in  $\text{CDCl}_3$ .



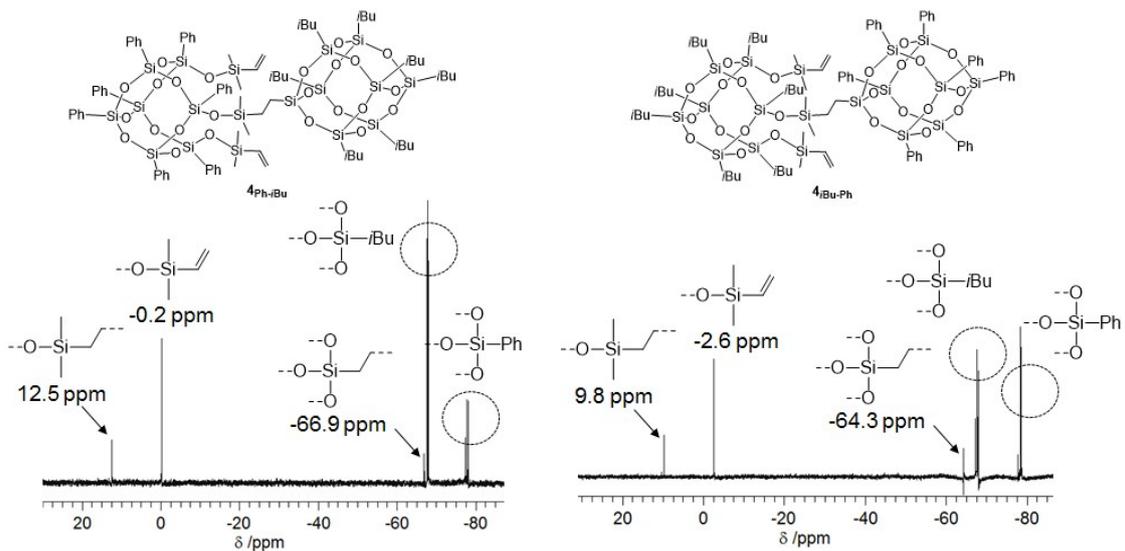




**Figure S23.**  $^{13}\text{C}$  NMR spectrum (100 MHz) of **6e** in  $\text{CDCl}_3$ .

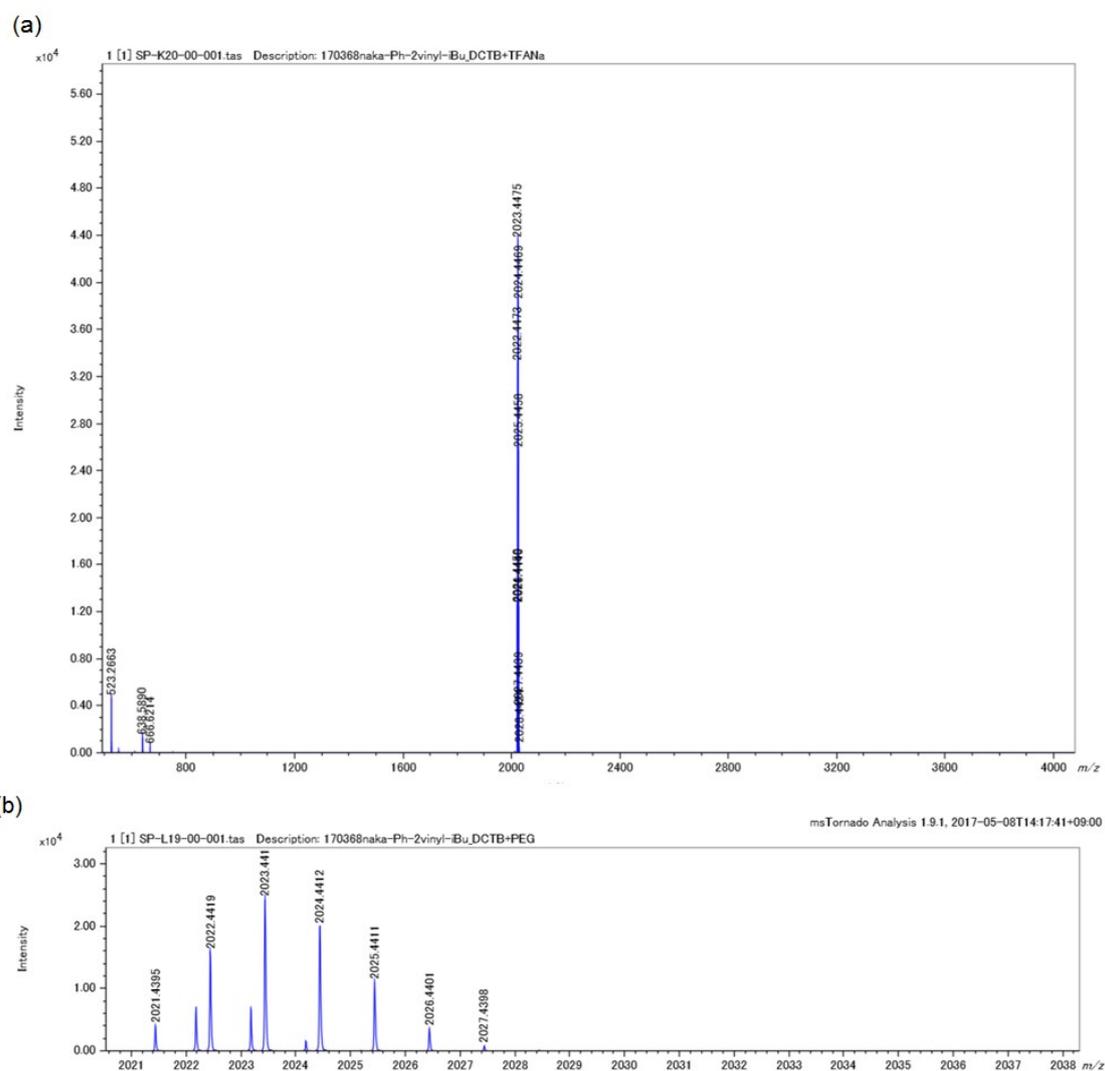


**Figure S24.**  $^{29}\text{Si}$  NMR spectrum (80 MHz) of **6e** in  $\text{CDCl}_3$ .

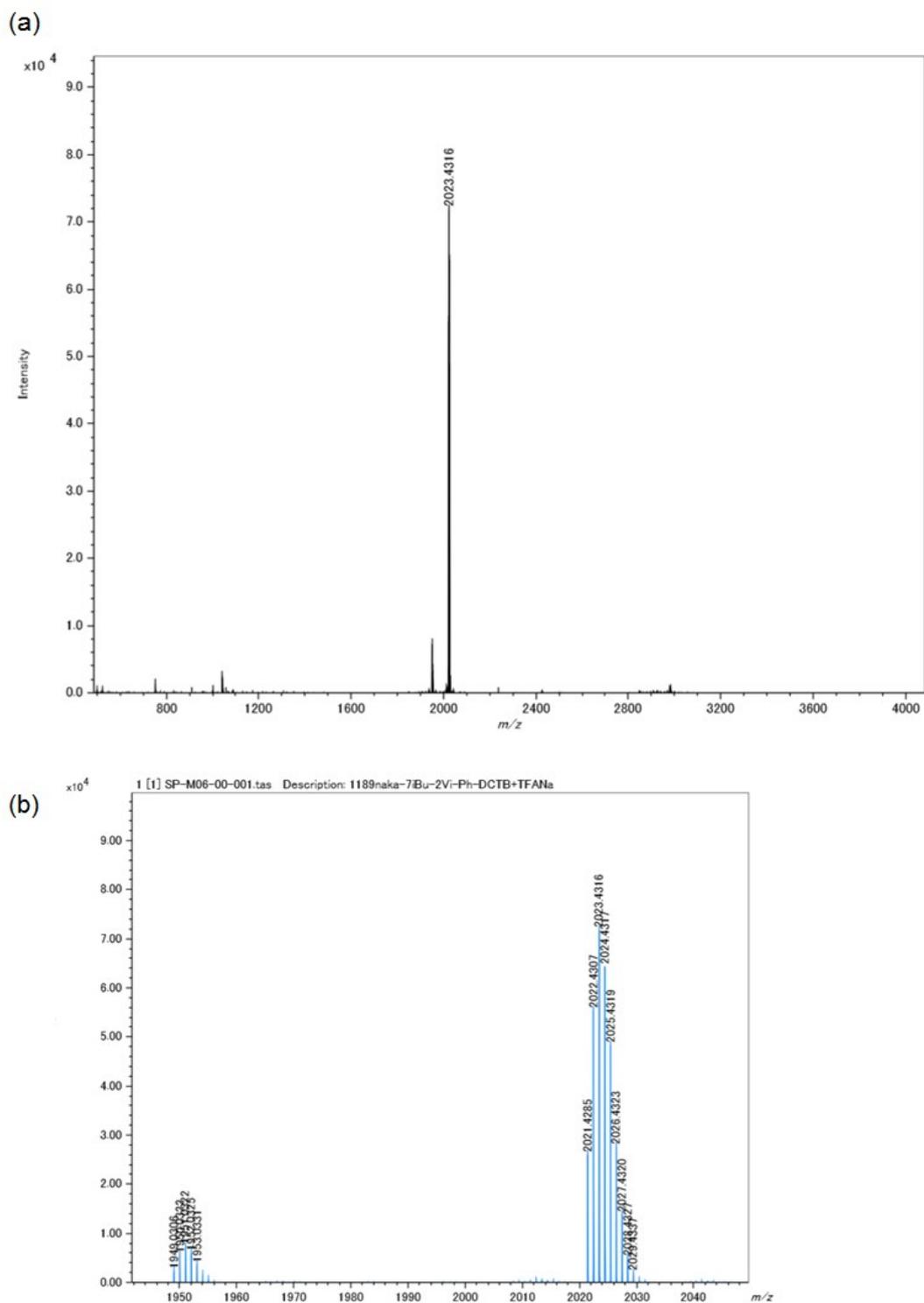


**Figure S25.**  $^{29}\text{Si}$  NMR spectra (80 MHz in  $\text{CDCl}_3$ ) and assignments of  $4_{\text{Ph-iBu}}$  and  $4_{\text{iBu-Ph}}$ .

## 5. MALDI-TOF-MASS spectra

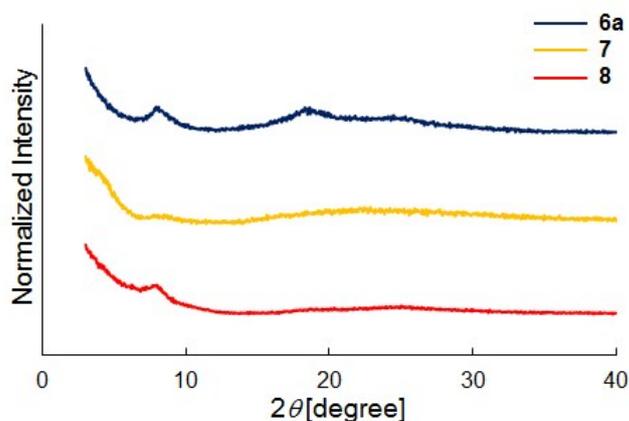


**Figure S26.** MALDI TOF MS spectrum of **4<sub>Ph-iBu</sub>**. Matrix: DCTB (20 mg/mL in CHCl<sub>3</sub>), cationizing agents: TFANa (1 mg/mL in THF). (a) Full spectrum and (b) expanded view.



**Figure S27.** MALDI TOF MS spectrum of **4<sub>i</sub>Bu-Ph**. Matrix: DCTB (20 mg/mL in CHCl<sub>3</sub>), cationizing agents: TFANa (1 mg/mL in THF).

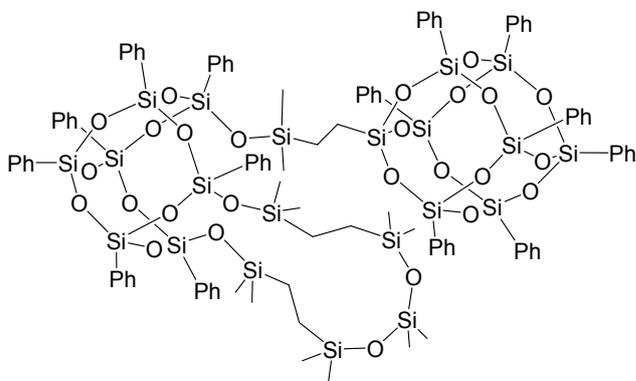
## 6. X-ray diffraction patterns



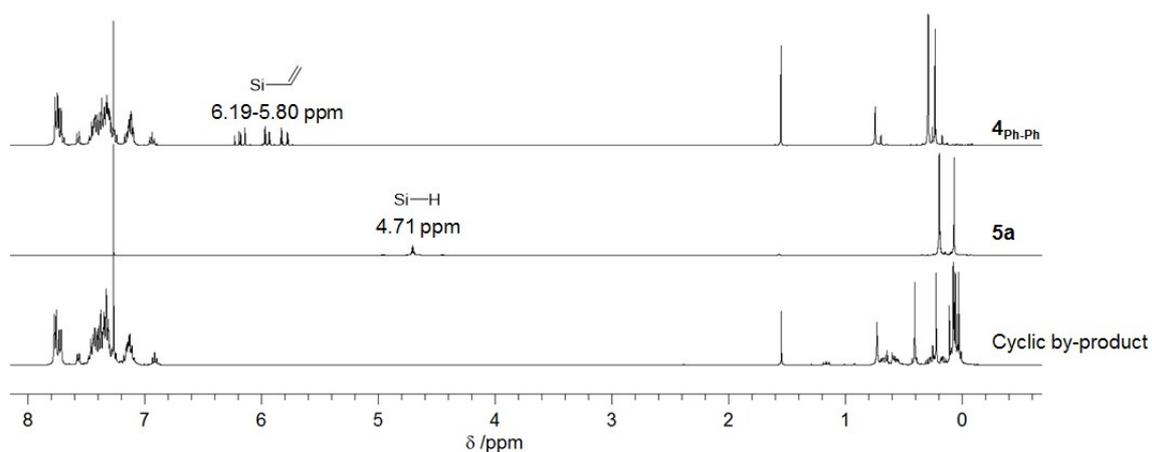
**Figure S28.** Powder X-ray diffraction patterns of **6a**, **7**, and **8**.

## 7. Detail of cyclic compound

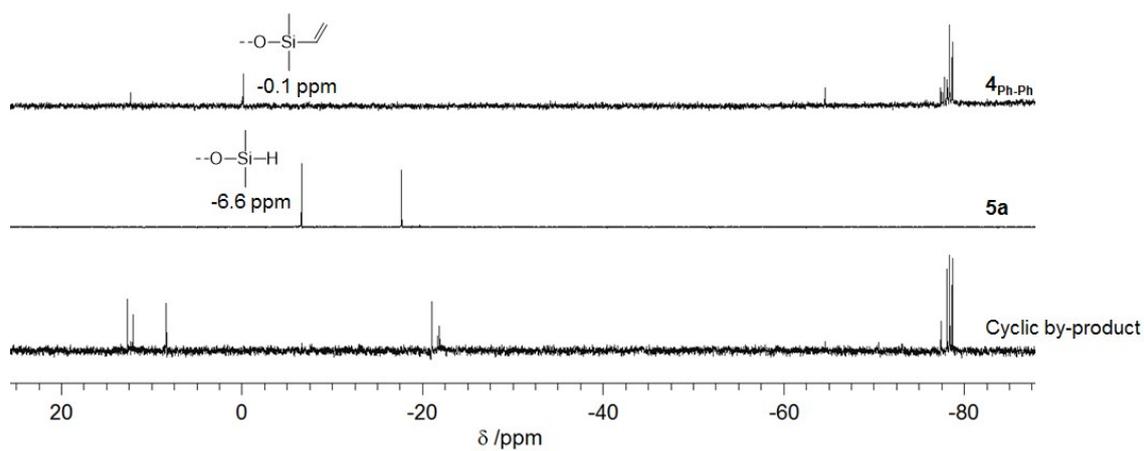
In the course of polymerization, low molecular weight by-products were observed in the SEC charts though the conversions of the monomers were approximately 100%. Thus, the by-product was isolated by preparative HPLC in the case of polymer **6a**. The  $^1\text{H-NMR}$  spectrum of the isolated by-product showed no signals due to vinyl (**4**<sub>Ph-Ph</sub>, 6.19-5.80 ppm) and Si-H (**5a**, 4.71 ppm) groups (Figure S29). In the  $^{29}\text{Si-NMR}$  spectrum, the signals due to dimethylvinylsilyl (**4a**, -0.1 ppm) and dimethylsilyl (**5a**, -6.6 ppm) groups also disappeared (Figure S30). The MALDI-TOF MS spectra showed a peak at 2369.3 Da ( $\text{C}_{102}\text{H}_{118}\text{O}_{26}\text{Si}_{21}\text{Na}$ :  $[\text{M}+\text{Na}]^+$  calcd. 2369.3) (Figure S31). These results indicate that the isolated by-product is cyclic compound as shown in Chart S1.



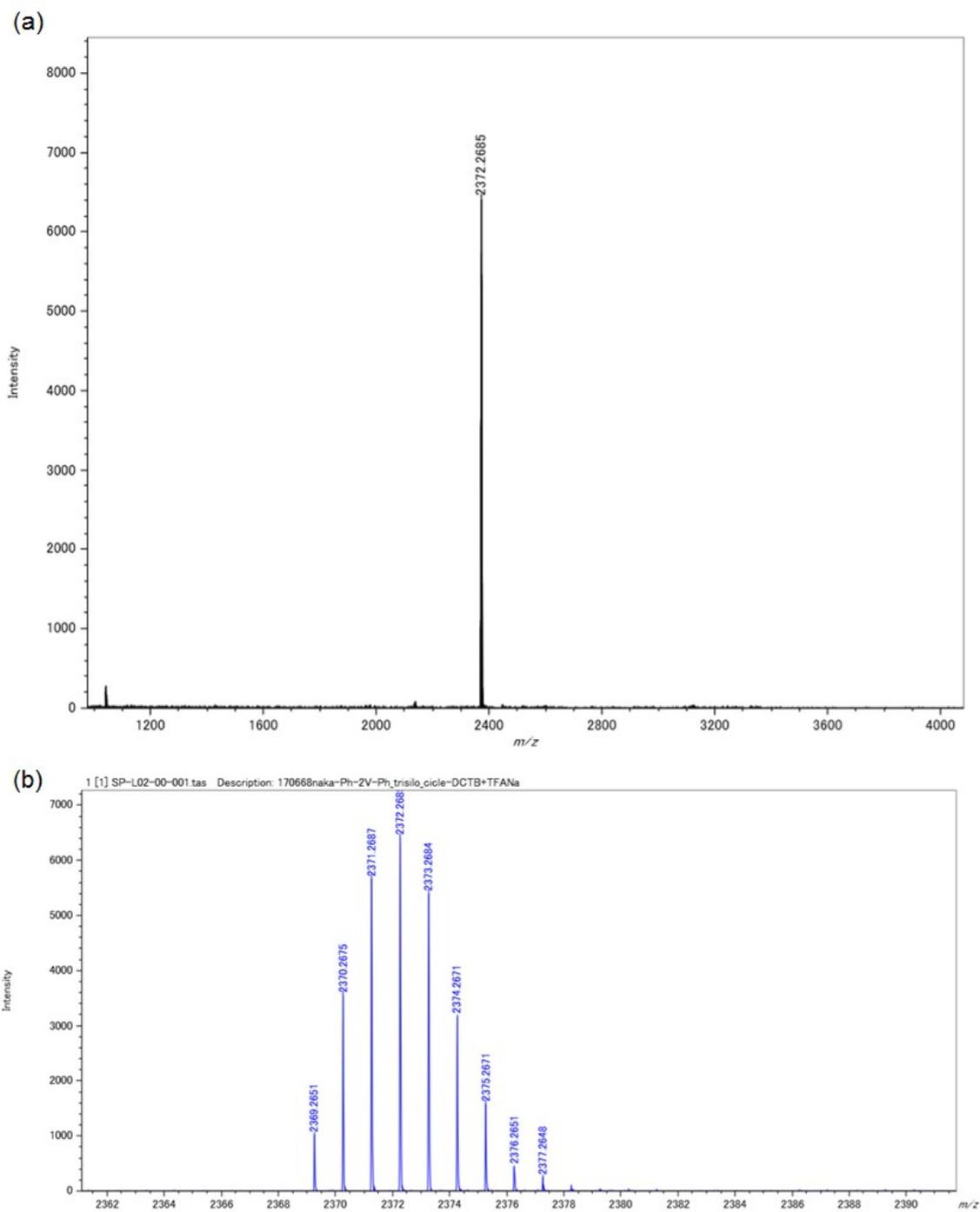
**Chart S1.** Chemical structure of the cyclic by-product.



**Figure S29.**  $^1\text{H}$ -NMR spectra (400 MHz in  $\text{CDCl}_3$ ) of **4<sub>Ph-Ph</sub>**, **5a**, and the cyclic by-product.



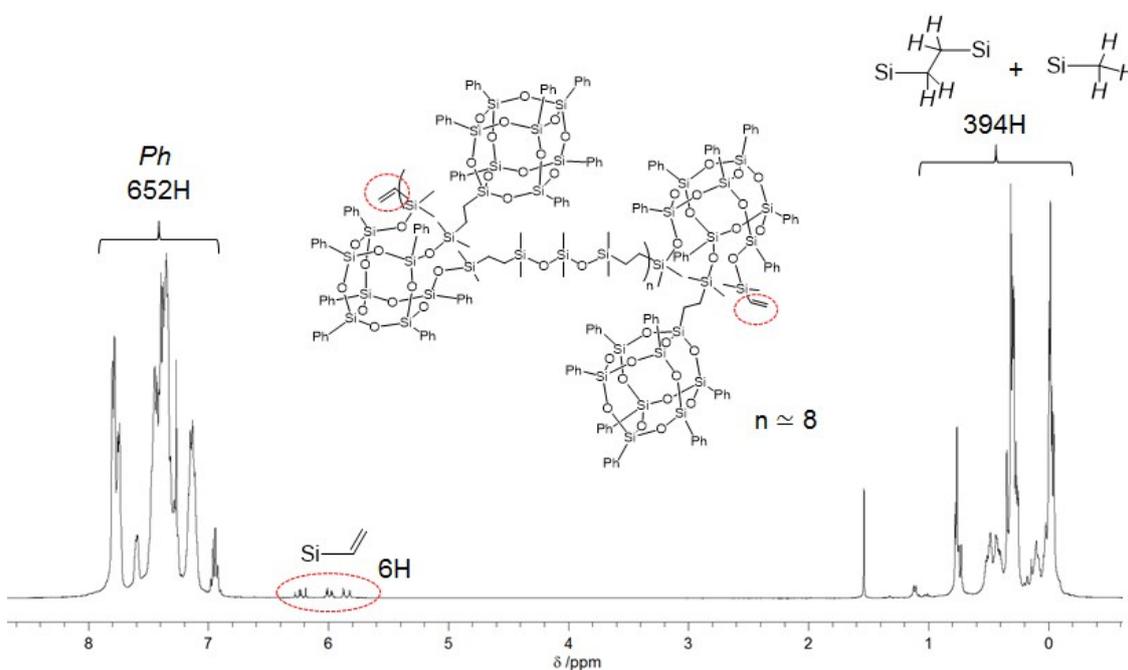
**Figure S30.**  $^{29}\text{Si}$ -NMR spectra (80 MHz in  $\text{CDCl}_3$ ) of **4<sub>Ph-Ph</sub>**, **5a**, and the cyclic by-product.



**Figure S31.** MALDI TOF MS spectrum of the cyclic by-product. Matrix: DCTB (20 mg/mL in  $\text{CHCl}_3$ ), cationizing agents: TFANa (1 mg/mL in THF).

## 8. Study on $M_n$ values

For the evaluation of  $M_n$  by  $^1\text{H-NMR}$  spectroscopy, vinyl groups were introduced to the end groups. That is, polymerization of 1.5 equivalent  $4_{\text{Ph-Ph}}$  with **5a** was carried out under the optimized condition (Run 4 in Figure 2). The low molecular weight molecules were removed by preparative HPLC (eluent: chloroform), and the obtained polymer products were subjected to  $^1\text{H-NMR}$  and SEC measurements. The  $^1\text{H-NMR}$  spectrum indicated that the  $M_n$  was approximately 21000 ( $n \approx 8$  in Figure S32), while the  $M_n$  estimated by the SEC was 7200. This result means that the molecular weight of the polymer was much underestimated using SEC.



**Figure S32.**  $^1\text{H-NMR}$  (400 MHz in  $\text{CDCl}_3$ ) of the end-labeled polymer.