

Supporting information

# Synthesis of a series of octaalkoxy-substituted cage silsesquioxanes catalyzed by zinc acetate

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## 1. Synthesis

### *Procedure for octamethoxy-POSS (8MeO-POSS).*

8MeO-POSS was synthesized by reacting 8H-POSS with methanol in the presence of  $\text{Zn}(\text{OAc})_2$  as a catalyst. 8H-POSS (0.20 g, 0.47 mmol) and  $\text{Zn}(\text{OAc})_2$  (0.0026 g, 0.014 mmol) was added in 50 mL flask and purge to  $\text{N}_2$  atmosphere. THF (12 mL: 1 L per 40 mmol of 8H-POSS) was added into the flask and stirred at 25 °C. MeOH (1.51 g, 47.1 mmol) were added into the flask and stirred at 25 °C. The 8H-POSS / methanol /  $\text{Zn}(\text{OAc})_2$  molar ratio was 1:100:0.03. Then the mixture was heated to 60 °C and stirred for 3 h under a  $\text{N}_2$  atmosphere, after which the mixture was stirred 18 h at 25 °C. Then an acetic acid (20 mg, 0.33 mmol) was added. The mixture was dried under vacuum pressure to give a colorless solid. The crude product was purified by extract using chloroform (50 mL) and filtration. The solution was evaporated and dried under vacuum pressure for 18 h at 40 °C. Product was gained as white solid (0.31 mg).

$^1\text{H-NMR}$  (in  $\text{CD}_3\text{CN}$ , 400 MHz):  $\delta = 3.38$  (s) ppm for SiOMe.  $^{29}\text{Si-NMR}$  (in  $\text{CD}_3\text{CN}$ , 80 MHz):  $\delta = -101.4$  ppm for  $(\text{SiO})_3\text{SiOMe}$ ,  $-92.7$  ppm for  $(\text{SiO})_2\text{Si}(\text{OR})_2$  (R = Me or H). MALDI-TOF-MS (m/z.  $[\text{M}+\text{Na}]^+$ ): 686.9 (calculated), 685.9 (observed).

### *Procedure for octaethoxy-POSS (8EtO-POSS).*

8EtO-POSS was synthesized by reacting 8H-POSS with methanol in the presence of  $\text{Zn}(\text{OAc})_2$  as a catalyst. 8H-POSS (0.20 g, 0.47 mmol) and  $\text{Zn}(\text{OAc})_2$  (0.0026 g, 0.014 mmol) was added in 50 mL flask and purge to  $\text{N}_2$  atmosphere. THF (12 mL: 1 L per 40 mmol of 8H-POSS) was added into the flask and stirred at 25 °C. EtOH (2.17 g, 47.1 mmol) were added into the flask and stirred at 25 °C. The 8H-POSS / ethanol /  $\text{Zn}(\text{OAc})_2$  molar ratio was 1:100:0.03. Then the mixture was heated to 60 °C and stirred for 3 h under a  $\text{N}_2$  atmosphere, after which the mixture was stirred 18 h at 25 °C. Then an acetic acid (20 mg, 0.33 mmol) was added. The mixture was dried under vacuum pressure to give a colorless solid. The crude product was purified by extract using chloroform (50 mL) and filtration. The solution was evaporated and dried under vacuum pressure for 18 h at 40 °C. Product was gained as white solid (NMR yield: >99%, isolated yield: 99% (0.36 mg)).

$^1\text{H-NMR}$  (in  $\text{CDCl}_3$ , 400 MHz):  $\delta = 1.24$  (t, 3H) ppm, 3.89 (m, 2H) ppm.  $^{29}\text{Si-NMR}$

(in CDCl<sub>3</sub>, 80 MHz):  $\delta = -102.7$  ppm. MALDI-TOF-MS (m/z. [M+Na]<sup>+</sup>): 799.0 (calculated), 799.5 (observed).

*Procedure for octaisopropoxy-POSS (8iPrO-POSS).*

8iPrO-POSS was synthesized by reacting 8H-POSS with methanol in the presence of Zn(OAc)<sub>2</sub> as a catalyst. 8H-POSS (0.20 g, 0.47 mmol) and Zn(OAc)<sub>2</sub> (0.0026 g, 0.014 mmol) was added in 50 mL flask and purge to N<sub>2</sub> atmosphere. THF (12 mL: 1 L per 40 mmol of 8H-POSS) was added into the flask and stirred at 25 °C. isopropanol (2.83 g, 47.1 mmol) were added into the flask and stirred at 25 °C. The 8H-POSS / isopropanol / Zn(OAc)<sub>2</sub> molar ratio was 1:100:0.03. Then the mixture was heated to 60 °C and stirred for 3 h under a N<sub>2</sub> atmosphere, after which the mixture was stirred 18 h at 25 °C. Then an acetic acid (20 mg, 0.33 mmol) was added. The mixture was dried under vacuum pressure to give a colorless solid. The crude product was purified by extract using chloroform (50 mL) and filtration. The solution was evaporated and dried under vacuum pressure for 18 h at 40 °C. Product was gained as white solid (NMR yield: >99%, isolated yield: >99% (0.42 mg)). <sup>1</sup>H-NMR (in CDCl<sub>3</sub>, 400 MHz):  $\delta = 1.23$  (d, 6H) ppm, 4.29 (m, 1H). <sup>29</sup>Si-NMR (in CDCl<sub>3</sub>, 80 MHz):  $\delta = -103.8$  ppm. MALDI-TOF-MS (m/z. [M+Na]<sup>+</sup>): 911.2 (calculated), 911.7 (observed).

*Procedure for octa-tert-butoxy-POSS (8tBuO-POSS).*

8tBuO-POSS was synthesized by reacting 8H-POSS with methanol in the presence of Zn(OAc)<sub>2</sub> as a catalyst. 8H-POSS (0.20 g, 0.47 mmol) and Zn(OAc)<sub>2</sub> (0.0026 g, 0.014 mmol) was added in 50 mL flask and purge to N<sub>2</sub> atmosphere. THF (12 mL: 1 L per 40 mmol of 8H-POSS) was added into the flask and stirred at 25 °C. *tert*-Butanol (1.75 g, 47.1 mmol) were added into the flask and stirred at 25 °C. The 8H-POSS / *tert*-butanol / Zn(OAc)<sub>2</sub> molar ratio was 1:100:0.03. Then the mixture was heated to 60 °C and stirred for 3 h under a N<sub>2</sub> atmosphere, after which the mixture was stirred 18 h at 25 °C. Then an acetic acid (20 mg, 0.33 mmol) was added. The mixture was dried under vacuum pressure to give a colorless solid. The crude product was purified by extract using chloroform (50 mL) and filtration. The solution was evaporated and dried under vacuum pressure for 18 h at 40 °C. Product was gained as white solid (NMR yield: 55% (0.22 g)). <sup>1</sup>H-NMR (in CDCl<sub>3</sub>, 400 MHz):  $\delta = 1.36$  (s) ppm for SiO*t*Bu, 4.25 ppm for SiH. <sup>29</sup>Si-NMR (in CDCl<sub>3</sub>, 80 MHz):  $\delta = -108.8$  ppm for SiO*t*Bu, -84.4 ppm for SiH.

*Dehydration and condensation of 8MeO-POSS*

Typical procedure is as follow. 8MeO-POSS (0.050 g, 0.072 mmol) and pure H<sub>2</sub>O (0.087 g, 4.8 mmol) in toluene (1.4 mL) was stirred at 25 °C for 10 min. 0.1 mol/L of hydrochloric acid aqueous solution (0.051 mL, 0.0051 mmol) was added to the solution, and stirred for 1 h at 60 °C (first step). After that the temperature was raised to 100 °C for dehydration condensation (second step), and then the mixture was stirred for 1 h at 100 °C to remove alcohol and water. The solvent was removed under reduced pressure to obtain a target product. For base-treated hydrolysis, 1 wt% of triethylamine (Et<sub>3</sub>N) aqueous solution (0.051 g, 0.0051 mmol) was used instead of hydrochloric acid aqueous solution.

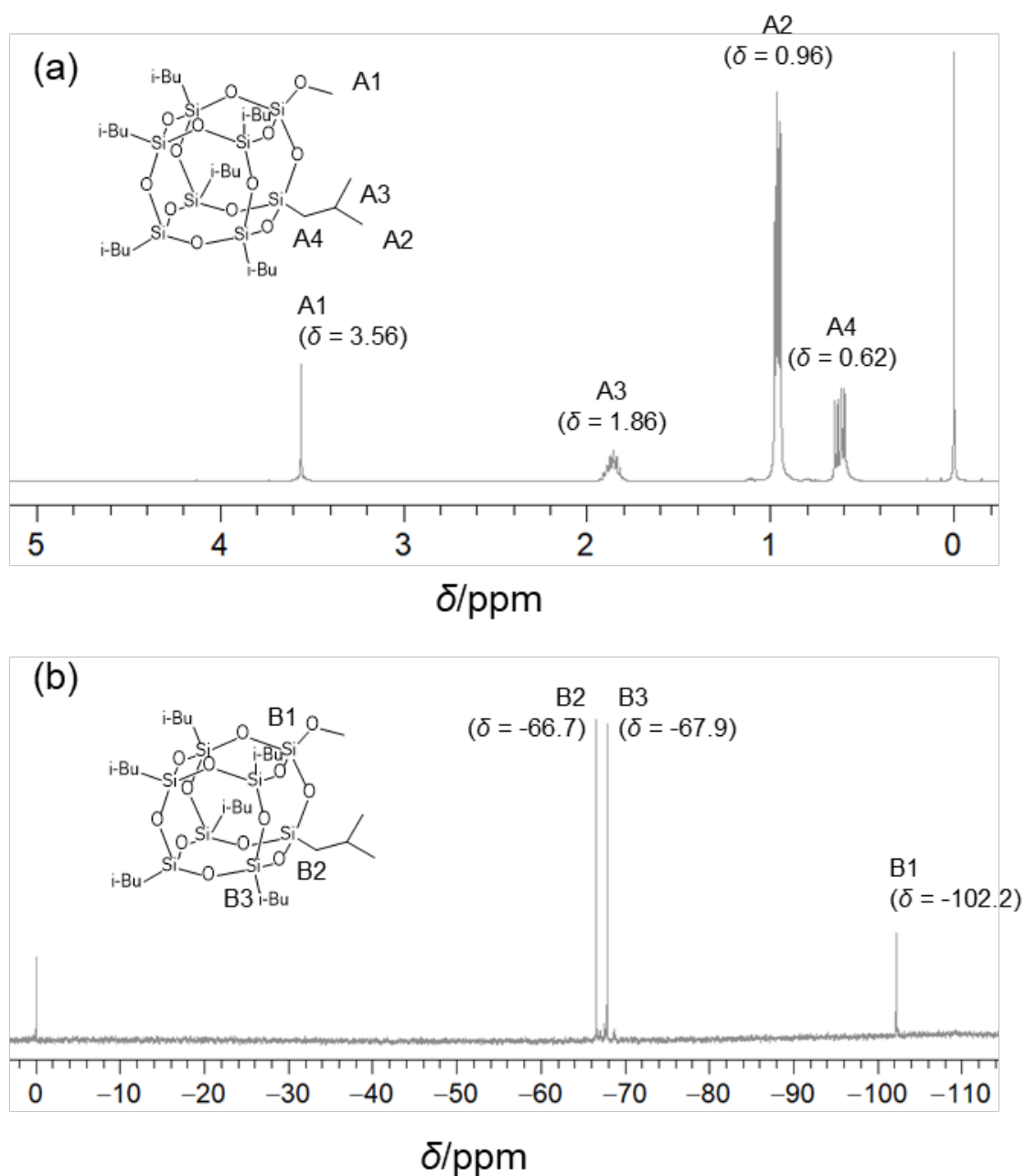
#### *Dehydration and condensation of 8EtO-POSS*

Typical procedure is as follow. 8EtO-POSS (0.050 g, 0.064 mmol) and pure H<sub>2</sub>O (0.077 g, 4.3 mmol) in toluene (1.3 mL) was stirred at 25 °C for 10 min. 0.1 mol/L of hydrochloric acid aqueous solution (0.045 mL, 0.0045 mmol) was added to the solution, and stirred for 1 h at 60 °C (first step). After that the temperature was raised to 100 °C for dehydration condensation (second step), and then the mixture was stirred for 1 h at 100 °C to remove alcohol and water. The solvent was removed under reduced pressure to obtain a target product. For base-treated hydrolysis, 1 wt% of triethylamine (Et<sub>3</sub>N) aqueous solution (0.046 g, 0.0045 mmol) was used instead of hydrochloric acid aqueous solution.

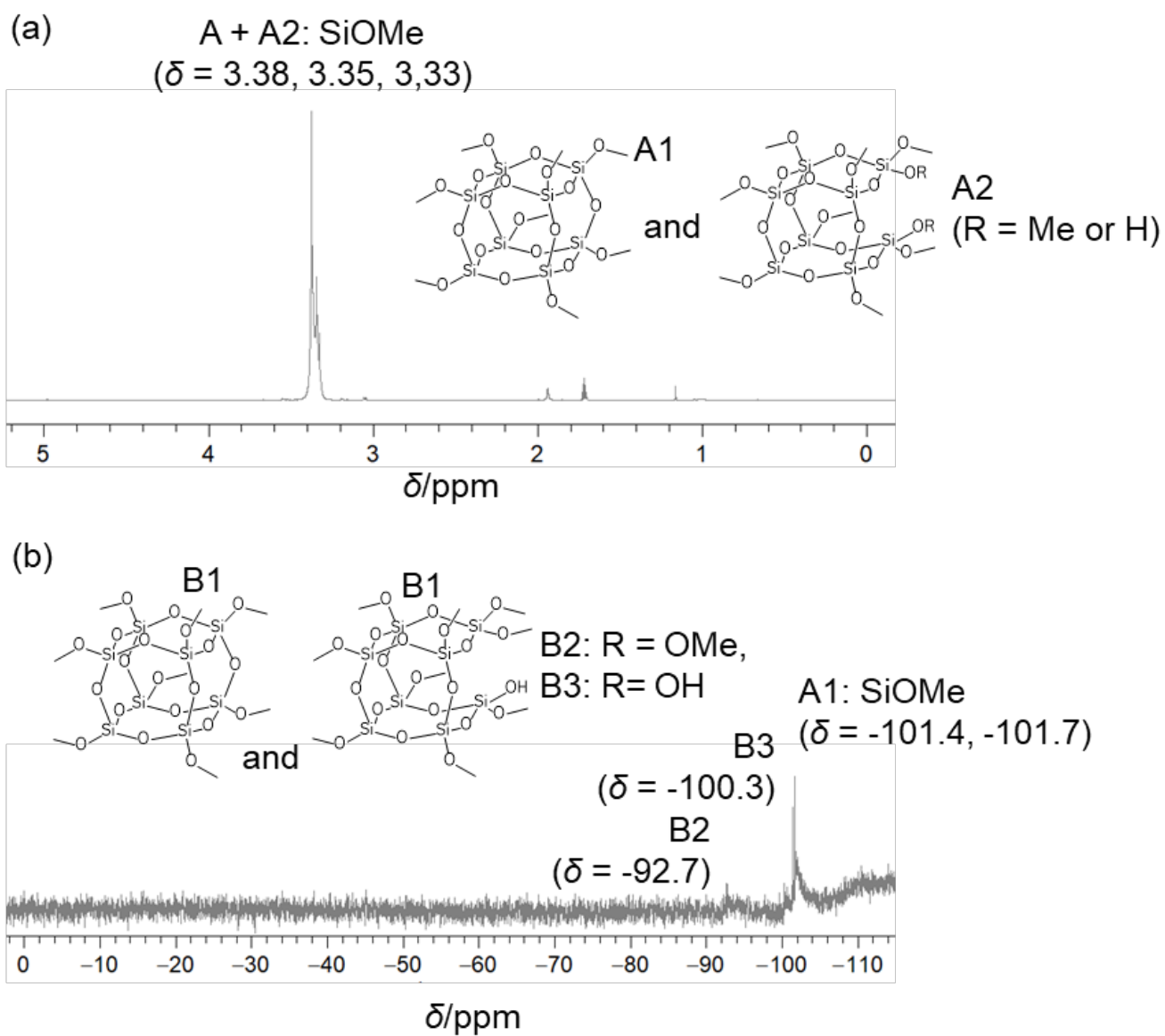
#### *Dehydration and condensation of 8iPrO-POSS*

Typical procedure is as follow. 8iPrO-POSS (0.050 g, 0.057 mmol) and pure H<sub>2</sub>O (0.068 g, 3.8 mmol) in toluene (1.1 mL) was stirred at 25 °C for 10 min. 0.1 mol/L of hydrochloric acid aqueous solution (0.040 mL, 0.0040 mmol) was added to the solution, and stirred for 1 h at 60 °C (first step). After that the temperature was raised to 100 °C for dehydration condensation (second step), and then the mixture was stirred for 1 h at 100 °C to remove alcohol and water. The solvent was removed under reduced pressure to obtain a target product. For base-treated hydrolysis, 1 wt% of triethylamine (Et<sub>3</sub>N) aqueous solution (0.040 g, 0.0039 mmol) was used instead of hydrochloric acid aqueous solution.

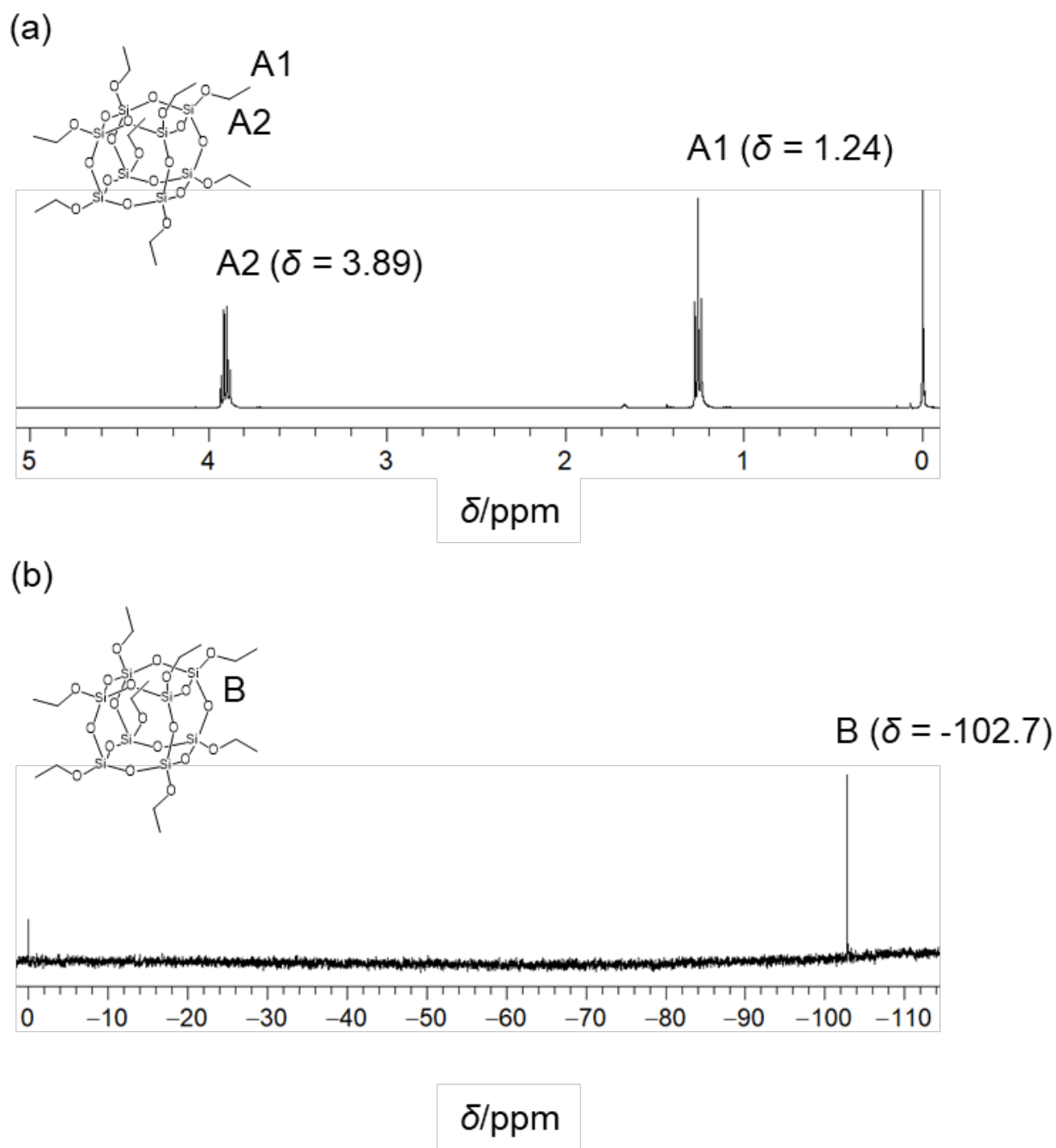
## 2. NMR spectra



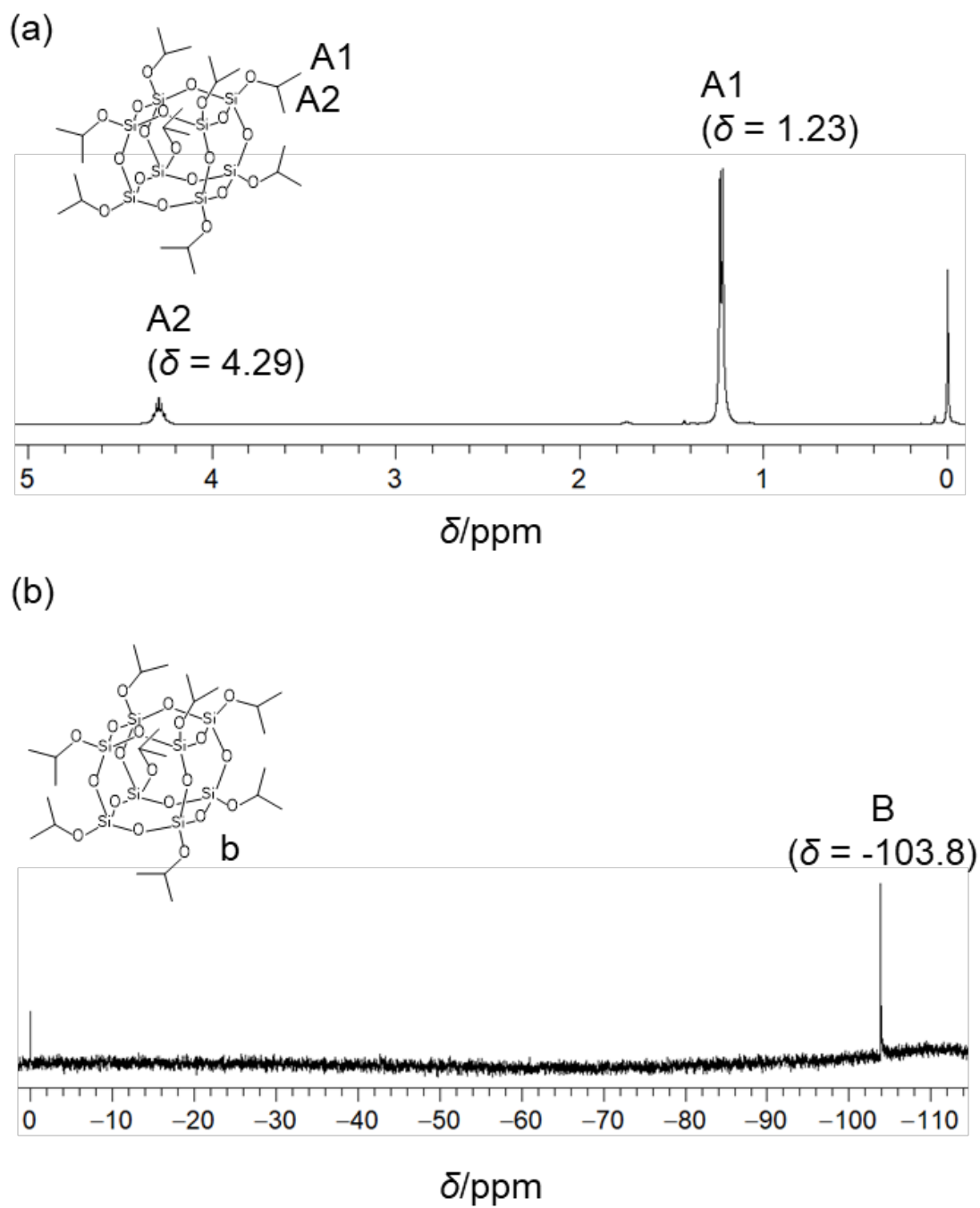
**Fig. S1.** (a) <sup>1</sup>H (400 MHz) and (b) <sup>29</sup>Si (80 MHz) NMR spectra of 7*i*Bu1MeO-POSS obtained by entry 4 in Table 1 via Zn(OAc)<sub>2</sub> catalyzed reaction between 7*i*Bu1H-POSS and MeOH. The spectra were recorded in CDCl<sub>3</sub>.



**Fig. S2.** (a)  $^1\text{H}$  and (b)  $^{29}\text{Si}$  NMR spectra of 8MeO-POSS via  $\text{Zn}(\text{OAc})_2$  catalyzed reaction between 8H-POSS and methanol. The spectra were recorded in acetonitrile- $d_3$ .

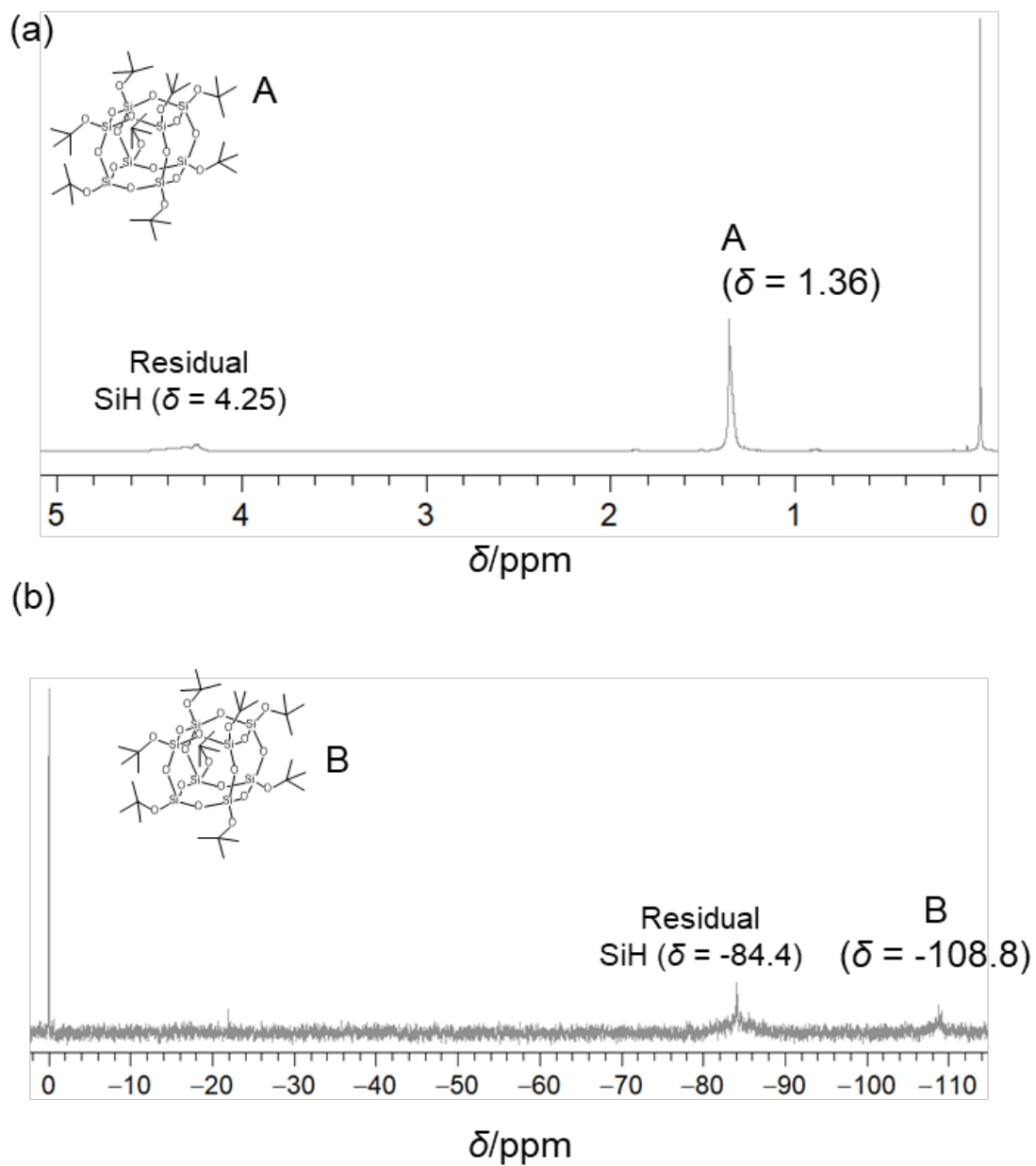


**Fig. S3.** (a)  $^1\text{H}$  and (b)  $^{29}\text{Si}$  NMR spectra of 8EtO-POSS via  $\text{Zn}(\text{OAc})_2$  catalyzed reaction between 8H-POSS and ethanol. The spectra were recorded in  $\text{CDCl}_3$ .



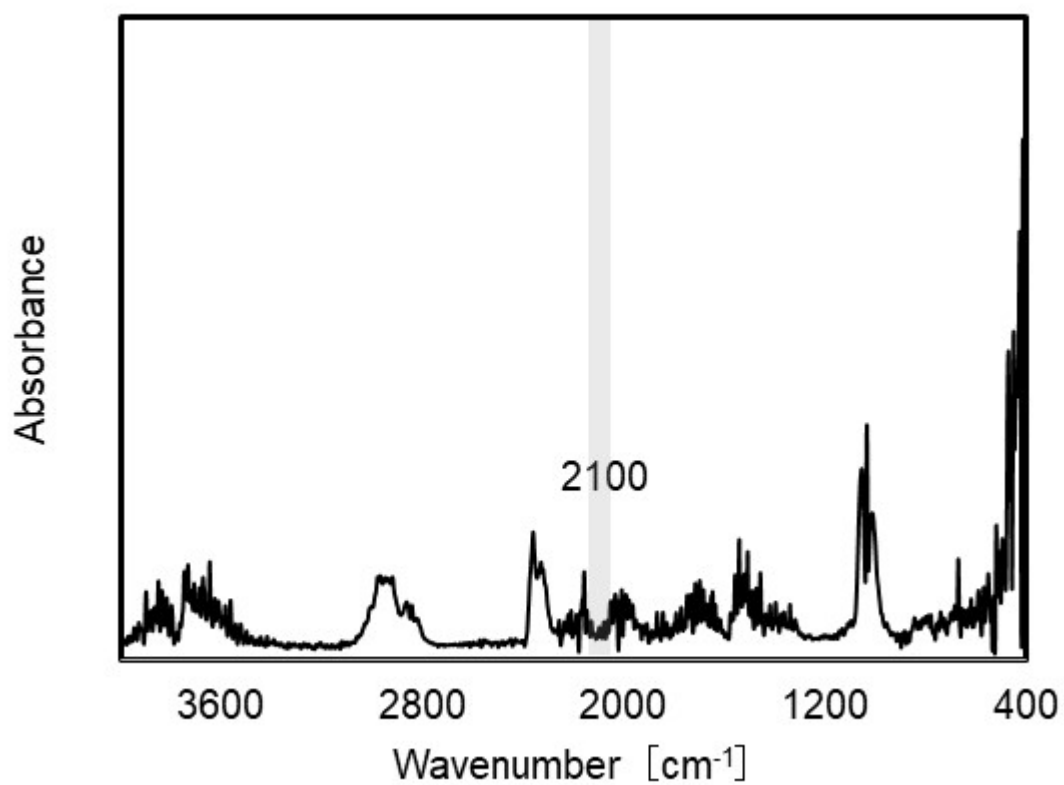
**Fig. S4.** (a)  $^1\text{H}$  and (b)  $^{29}\text{Si}$  NMR spectra of 8*i*PrO-POSS via  $\text{Zn}(\text{OAc})_2$  catalyzed reaction between 8H-POSS and isopropanol. The spectra were recorded in  $\text{CDCl}_3$ .





**Fig. S5.** (a)  $^1\text{H}$  and (b)  $^{29}\text{Si}$  NMR spectra of 8*t*BuO-POSS via  $\text{Zn}(\text{OAc})_2$  catalyzed reaction between 8H-POSS and *tert*-butanol. The spectra were recorded in  $\text{C}_6\text{D}_6$ .

### 3. FT-IR spectra



**Fig. S6.** FT-IR spectrum of colorless solid during methoxylation from 8H-POSS without acetic acid addition.

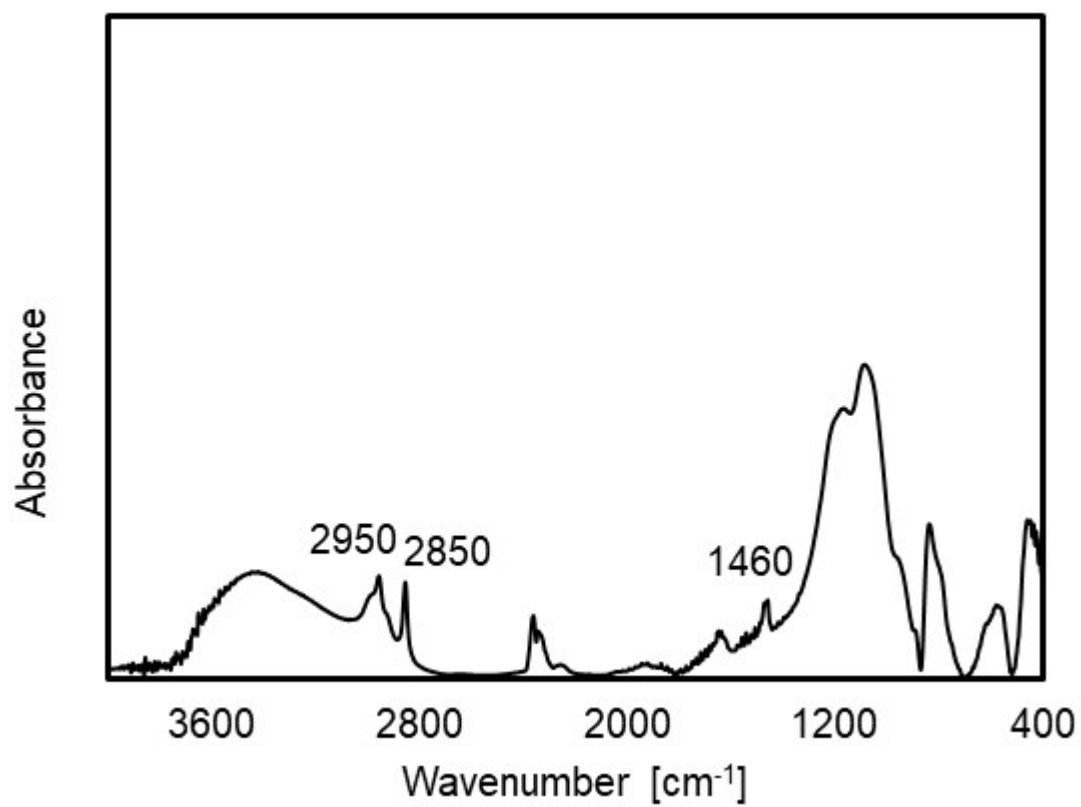


Fig. S7. FT-IR spectrum of 8MeO-POSS.

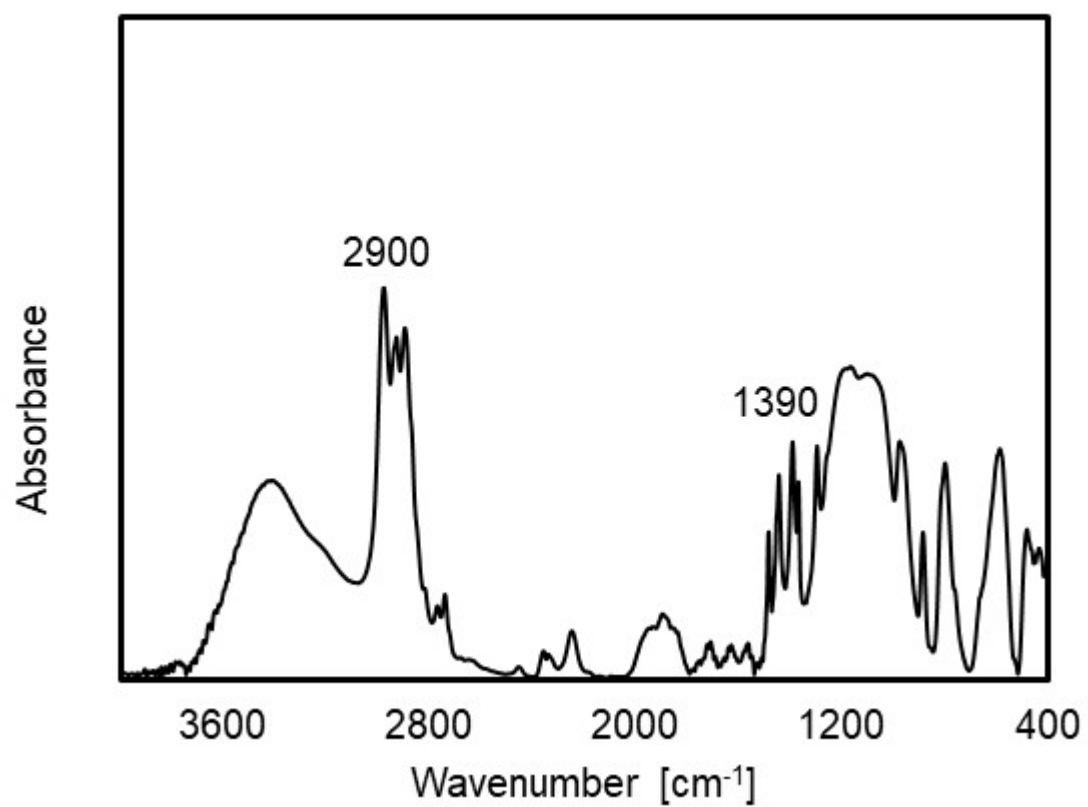
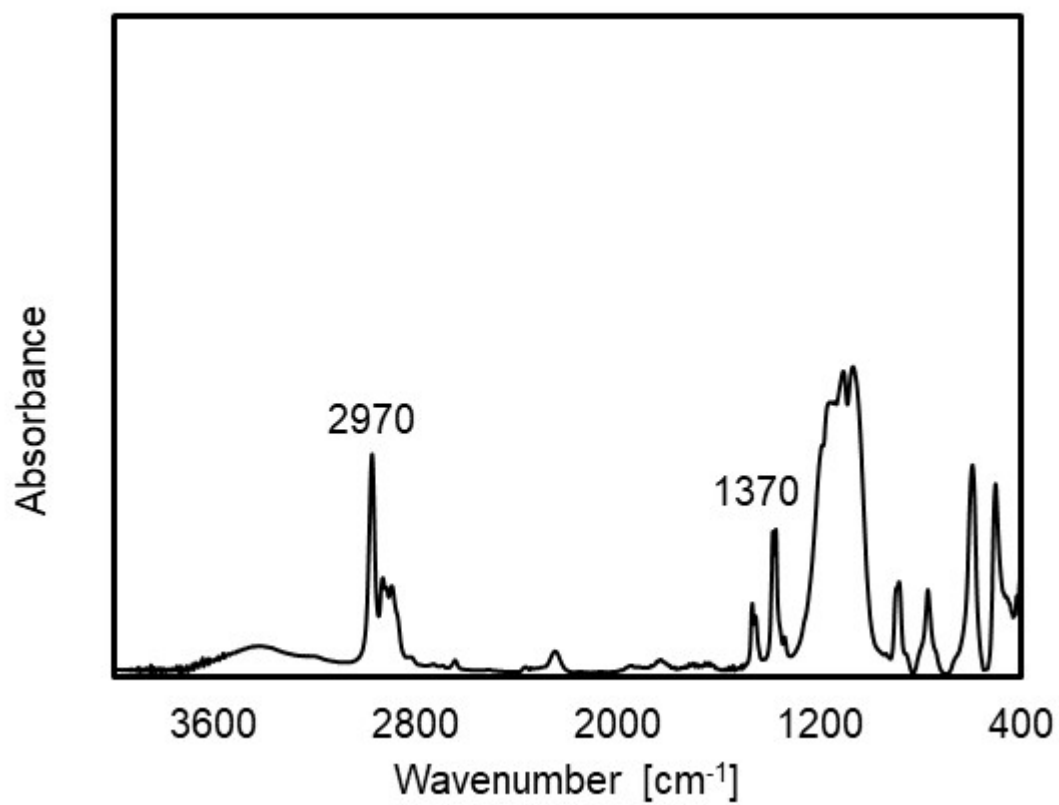
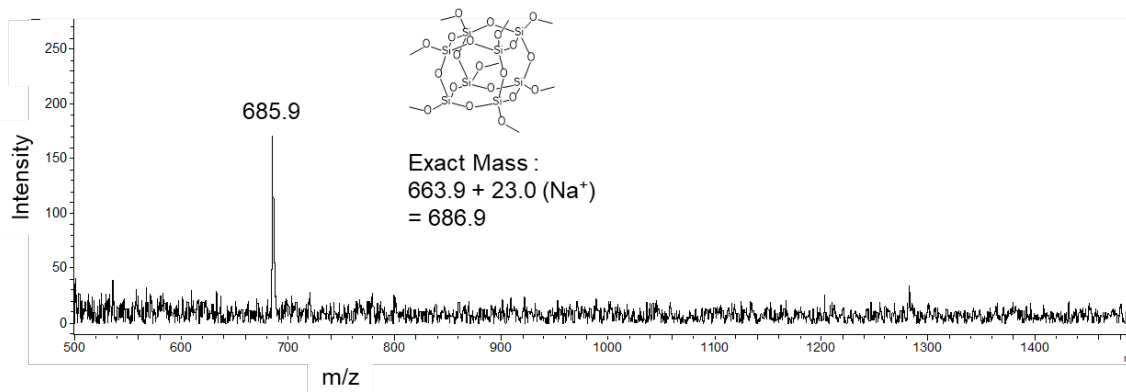


Fig. S8. FT-IR spectrum of 8EtO-POSS.

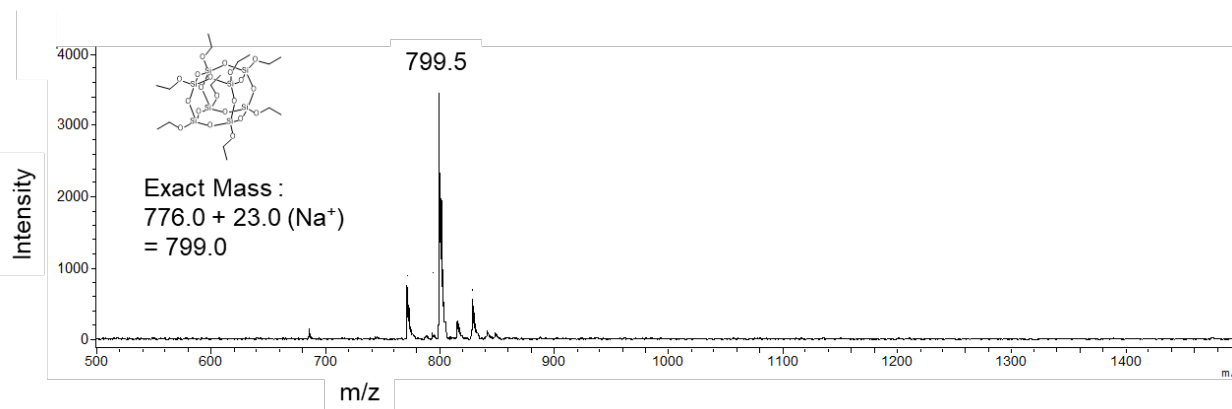


**Fig. S9.** FT-IR spectrum of 8*i*PrO-POSS.

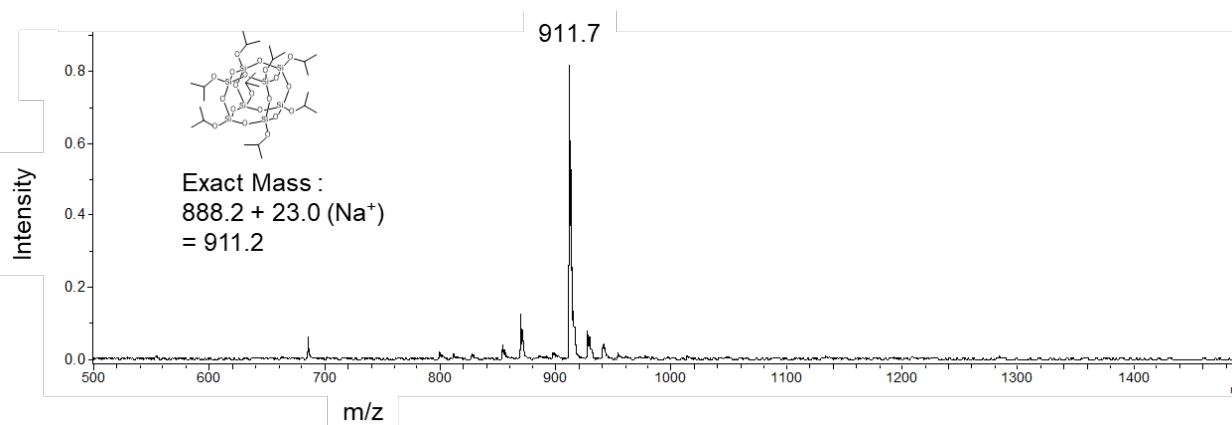
#### 4. MALDI-TOF-MS spectra



**Fig. S10.** MALDI-TOF-MS spectrum of 8MeO-POSS via Zn(OAc)<sub>2</sub> catalyzed reaction between 8H-POSS and methanol.



**Fig. S11.** MALDI-TOF-MS spectrum of 8EtO-POSS via Zn(OAc)<sub>2</sub> catalyzed reaction between 8H-POSS and ethanol.



**Fig. S12.** MALDI-TOF-MS spectrum of 8*i*PrO-POSS via Zn(OAc)<sub>2</sub> catalyzed reaction between 8H-POSS and isopropanol.

## 5. Effect of acetic acid addition

**Table S1.** Addition of acetic acid for reaction mixture of 8H-POSS and alcohol.<sup>a</sup>

Entry	Alcohol	Acid	Acid (molar ratio)	Yield <sup>b</sup> [%]	Yield <sup>c</sup> [%]
1	MeOH	None	0	N.D.	0
2	MeOH	CH <sub>3</sub> CO <sub>2</sub> H	0.7	>99	94
3	IPA	None	0	N.D.	2
4	IPA	CH <sub>3</sub> CO <sub>2</sub> H	0.7	>99	99

<sup>a</sup>Reaction conditions: 8H-POSS / alcohol / Zn(OAc)<sub>2</sub> molar ratio was 1:100:0.030. THF (40 mmol/L for 8H-POSS). <sup>b</sup>NMR yield. <sup>c</sup>Isolated yield

## 6. Solubility

**Table S2.** Solubility test results of POSS.

Solvent	8 <i>t</i> Bu-POSS <sup>a</sup>	8EtO-POSS	8 <i>i</i> PrO-POSS
<i>n</i> -Hexane	P	P	P
Diethyl ether	P	P	P
Toluene	P-	P	P-
Ethyl acetate	F	P	P-
Chloroform	P	P	P
THF	P	P	P
Acetone	F+	P	P
Acetonitrile	F	P	F
DMF	F	P	F+
DMSO	F	F	F

a) A. J. Guenther *et al.*, *Ind. Eng. Chem. Res.* 2012, *51*, 12282-12293.

Test concentration: 1 mg/mL

P: Complete dissolution within 2 min.

P-: Complete dissolution within 1 h but not within 2 min.

F+: Significant but incomplete dissolution occurred.

F: Little or no dissolution was observed.