Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Treating Octasilanol $[Si_8O_{12}][OH]_8$ with Tetramethoxysilane and Trimethoxyvinylsilane: A Halogen-free Synthetic Route to Alkoxysilyl-substituted Double-four-ring Siloxanes

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1. General Information

^{1}H NMR (600 MHz), ^{13}C NMR (150 MHz), and ^{29}Si NMR (119 MHz) spectra were recorded at room temperature on a Bruker AVANCE III spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to an internal standard [Me_3Si-C_6H_5: 0.24 ppm (^{1}H NMR) and −1.1 ppm (^{13}C NMR), −4.0 ppm (^{29}Si NMR) for **4a**,**b** in CD_3CN (Figures S1-S6); 0.27 ppm (^{1}H NMR), −1.2 ppm (^{13}C NMR), and −4.2 ppm (^{29}Si NMR) for analysis of the reaction mixture in DMF-d_7 (Figures 1, S7)]. High-resolution time-of-flight (TOF) mass spectra (electrospray-ionization (ESI)) were recorded on a Bruker micrOTOF II spectrometer operating in negative-ion mode.

All manipulations were performed under an argon atmosphere using Schlenk-line techniques or an argon-filled glove box. $[Si_8O_{12}][OH]_8$ was prepared by our previously reported method.[1] QuadraPure^{TM} EDA was obtained from Aldrich Chemical Co. Tetramethoxysilane, trimethoxyvinylsilane, and trimethylphenylsilane were obtained from Tokyo Chemical Industry Co., Ltd. Tetramethoxysilane and trimethoxyvinylsilane were distilled before use. *N*,*N*-dimethylformamide (DMF; super dehydrated grade), hexane (super dehydrated grade), and conc. sulfuric acid (>95%) were obtained from FUJIFILM Wako Pure Chemical Co. Amberlyst^{TM} 15 (JS-HG·DRY) was obtained from ORGANO Co.

2. Experimental Details

H_2SO_4-catalyzed synthesis of $[Si_8O_{12}][OSi(OMe)_3]_8$ (4a). In a vial equipped with a magnetic stirring bar, $[Si_8O_{12}][OH]_8$(**3**)·11.46DMAc (29.0 mg, 0.0200 mmol) and tetramethoxysilane (100.1 mg, 0.658 mmol) were dissolved in DMF (0.3 mL). To the mixture, a DMF (0.1 mL) solution of H_2SO_4 (0.0020 mmol, 1.25 mol% based on the amount of SiOH moieties in **3**) was added. After stirring at room temperature for 24 h, Quadra Pure^{TM} EDA (5.0 mg, 4-8 eq. for H_2SO_4) was added and stirring was continued at room temperature for 5 min. Then, the reaction mixture was filtered to remove the Quadra Pure^{TM} EDA, before the solvent was removed from the filtrate *in vacuo*. The thus obtained solid was decantated with hexane to afford **4a** as a colorless solid (22.5 mg, 74.3%).

$[Si_8O_{12}][OSi(OMe)_3]_8$. ^{1}H NMR (600 MHz, CD_3CN): 3.55 (s, 72H, O*CH₃*); ^{13}C NMR (150 MHz, CD_3CN): 51.7 (O*Me*); ^{29}Si NMR (119 MHz, CD_3CN): −86.0 (SiO*Si*OMe), −110.3 (*Si*OSiOMe); HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{76}NO_{44}Si_{16}^+$ 1530.0043 $[M+NH_4]^+$, found 1530.0038.

Amberlyst^{TM} 15-catalyzed synthesis of $[Si_8O_{12}][OSi(OMe)_3]_8$ (4a). In a Schlenk tube equipped with a magnetic stirring bar, $[Si_8O_{12}][OH]_8$(**3**)·11.46DMAc (29.0 mg, 0.0200 mmol), tetramethoxysilane (98.7 mg, 0.648 mmol), and Amberlyst^{TM} 15 (JS-HG·DRY) (5.2 mg, 0.024 mmol, 15 mol% based on the amount of SiOH moieties in **3**) were added to DMF (0.5 mL). After stirring at 60 °C for 24 h, Amberlyst^{TM} 15 was separated from the reaction mixture by filtration, and the solvent was removed from the filtrate *in vacuo*. The thus obtained solid was decantated with hexane to afford **4a** as a colorless solid (27.8 mg, 91.8%).

Synthesis of [Si_8O_{12}][OSiVi(OMe)$_2$]$_8$ (4b). In a Schlenk tube equipped with a magnetic stirring bar, [Si_8O_{12}][OH]$_8$(**3**)·11.46DMAc (29.0 mg, 0.0200 mmol), trimethoxyvinylsilane (95.2 mg, 0.642 mmol), and Amberlyst™ 15 (JS-HG·DRY) (5.0 mg, 0.023 mmol, 14 mol% based on the amount of SiOH moieties in **3**) were added to DMF (0.5 mL). After stirring at 60 °C for 24 h, Amberlyst™ 15 was separated from the reaction mixture by filtration, and the solvent was removed from the filtrate *in vacuo*. The thus obtained solid was decantated with hexane to afford **4b** as a colorless solid (17.6 mg, 59.4%).

[Si_8O_{12}][OSiVi(OMe)$_2$]$_8$. ^{1}H NMR (600 MHz, CD_3CN): 3.52 (s, 48H, OCH_3), 5.88 (dd, 8H, ^3J = 19.0, 13.5 Hz, C*H*=CH$_2$), 6.01 (d, 8H, ^3J = 19.0 Hz, CH=CH_2), 6.15 (d, 8H, ^3J = 13.5 Hz, CH=CH_2); ^{13}C NMR (150 MHz, CD_3CN): 51.0 (O*Me*), 128.9 (SiCH=*CH$_2$*), 138.6 (Si*CH*=CH$_2$); ^{29}Si NMR (119 MHz, CD_3CN): −63.1 (SiO*Si*Vi(OMe)$_2$), −110.2 (*Si*OSiVi(OMe)$_2$); HRMS (ESI): *m*/*z* calcd. for $C_{32}H_{72}O_{36}Si_{16}Na^+$ 1503.0004 [M+Na]$^+$, found 1502.9990.

NMR spectra of 4a and 4b

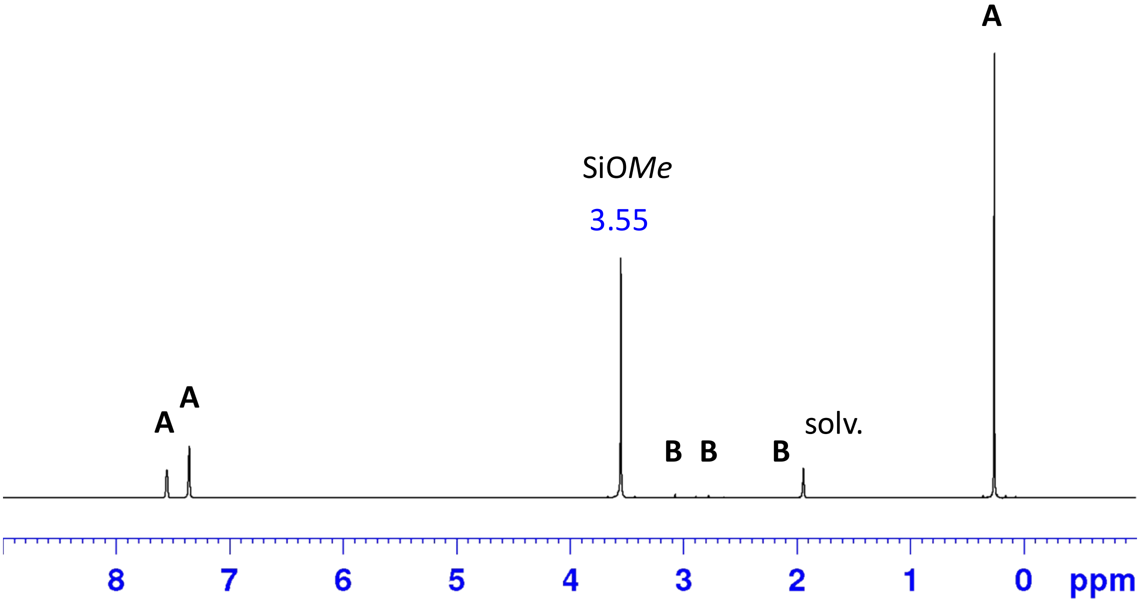

Figure S1. ^{1}H NMR spectrum of [Si_8O_{12}][OSi(OMe)$_3$]$_8$ (**4a**) in CD_3CN. **A**: signals corresponding to the internal standard trimethylsilylbenzene; **B**: signals corresponding to *N*,*N*-dimethylacetamide (DMAc).

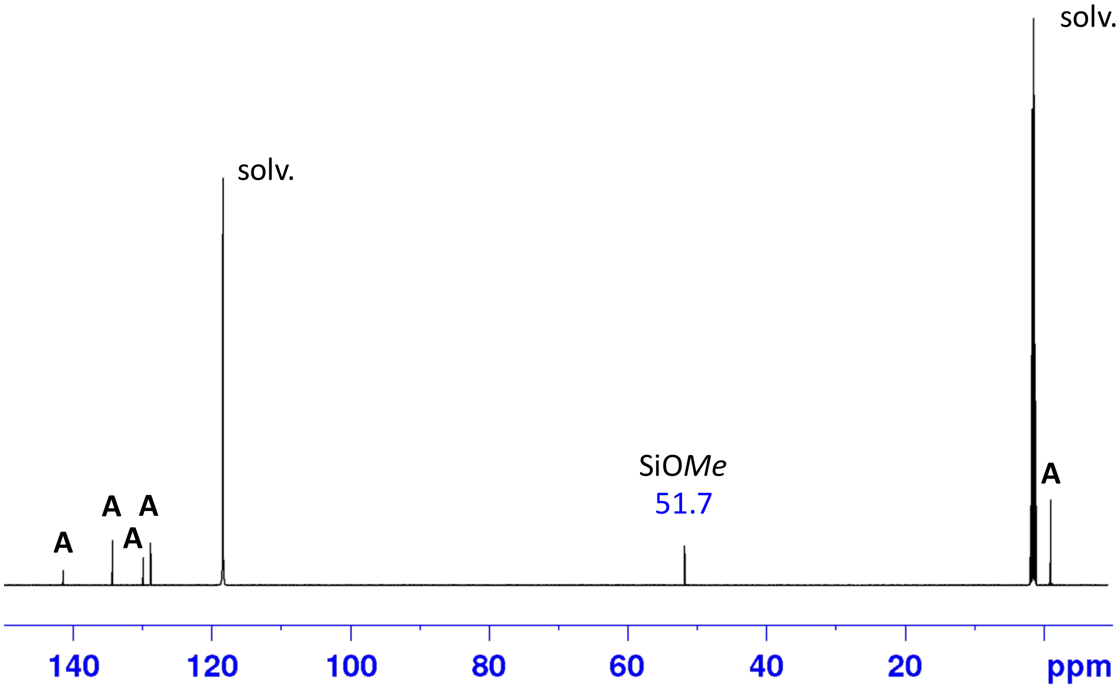

Figure S2. ^{13}C NMR spectrum of $[Si_8O_{12}][OSi(OMe)_3]_8$ (**4a**) in CD_3CN. **A**: signals corresponding to the internal standard trimethylsilylbenzene.

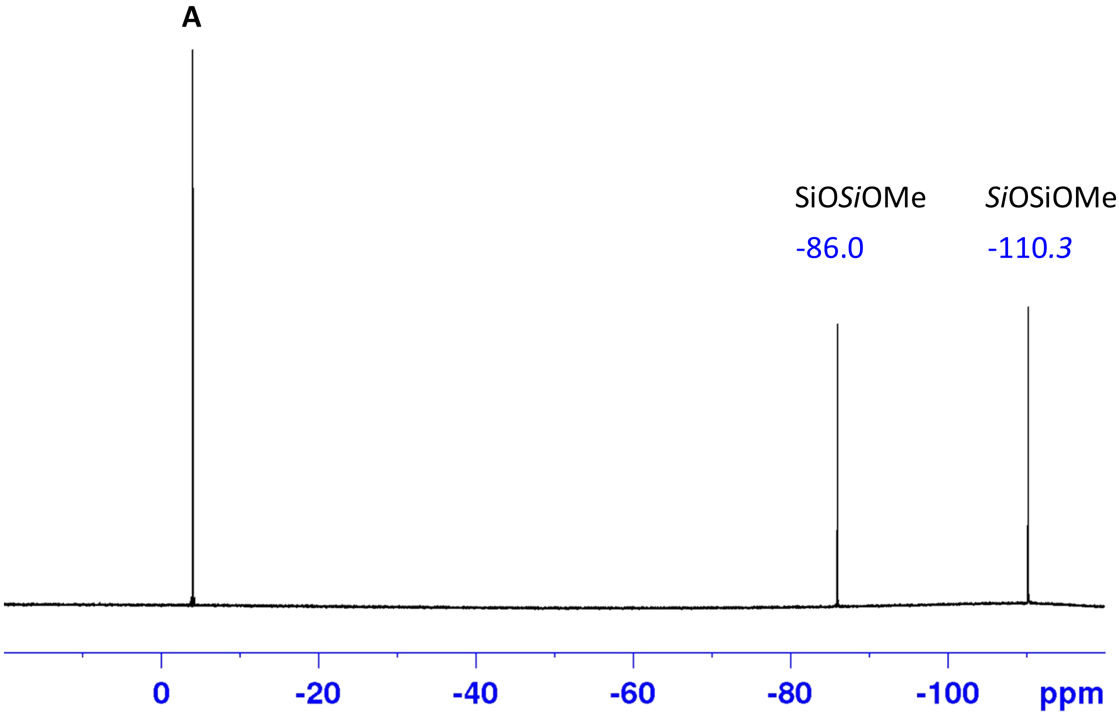

Figure S3. ^{29}Si NMR spectrum of $[Si_8O_{12}][OSi(OMe)_3]_8$ (**4a**) in CD_3CN. **A**: signals corresponding to the internal standard trimethylsilylbenzene.

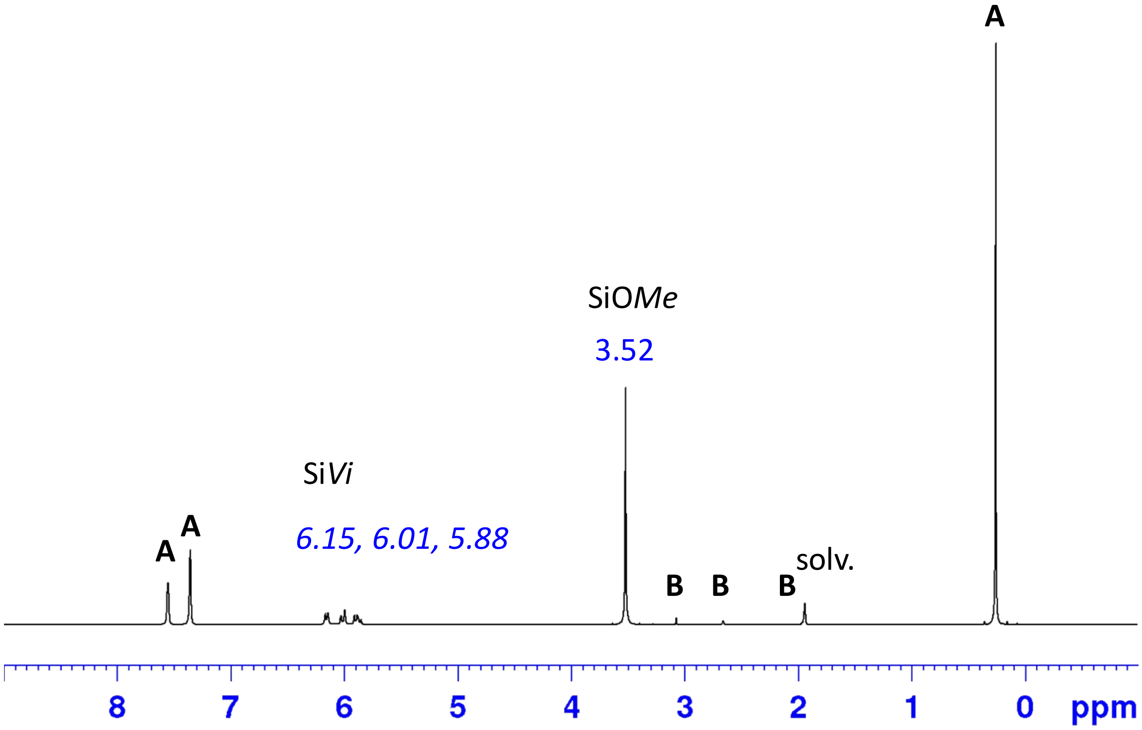

Figure S4. ^{1}H NMR spectrum of $[Si_8O_{12}][OSiVi(OMe)_2]_8$ (**4b**) in CD_3CN. **A**: signals corresponding to the internal standard trimethylsilylbenzene; B: signals corresponding to DMAc.

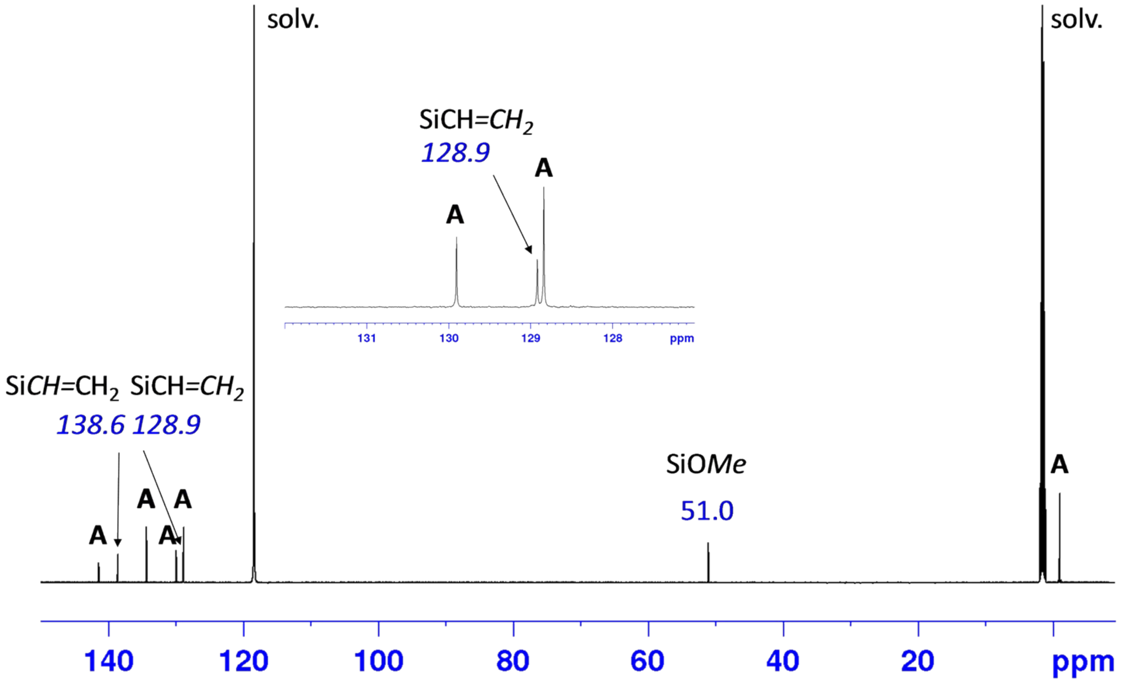

Figure S5. ^{13}C NMR spectrum of $[Si_8O_{12}][OSiVi(OMe)_2]_8$ (**4b**) in CD_3CN. **A**: signals corresponding to the internal standard trimethylsilylbenzene. Inset: magnification of the 127-132 ppm region.

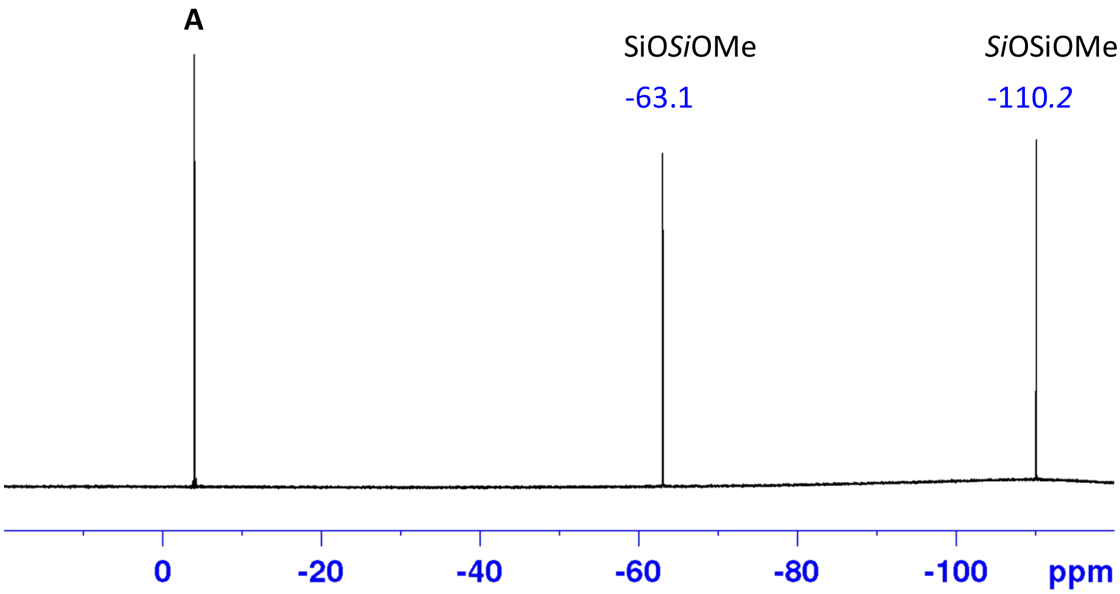

Figure S6. ^{29}Si NMR spectrum of $[Si_8O_{12}][OSiVi(OMe)_2]_8$ (**4b**) in CD_3CN. **A**: signals corresponding to the internal standard trimethylsilylbenzene.

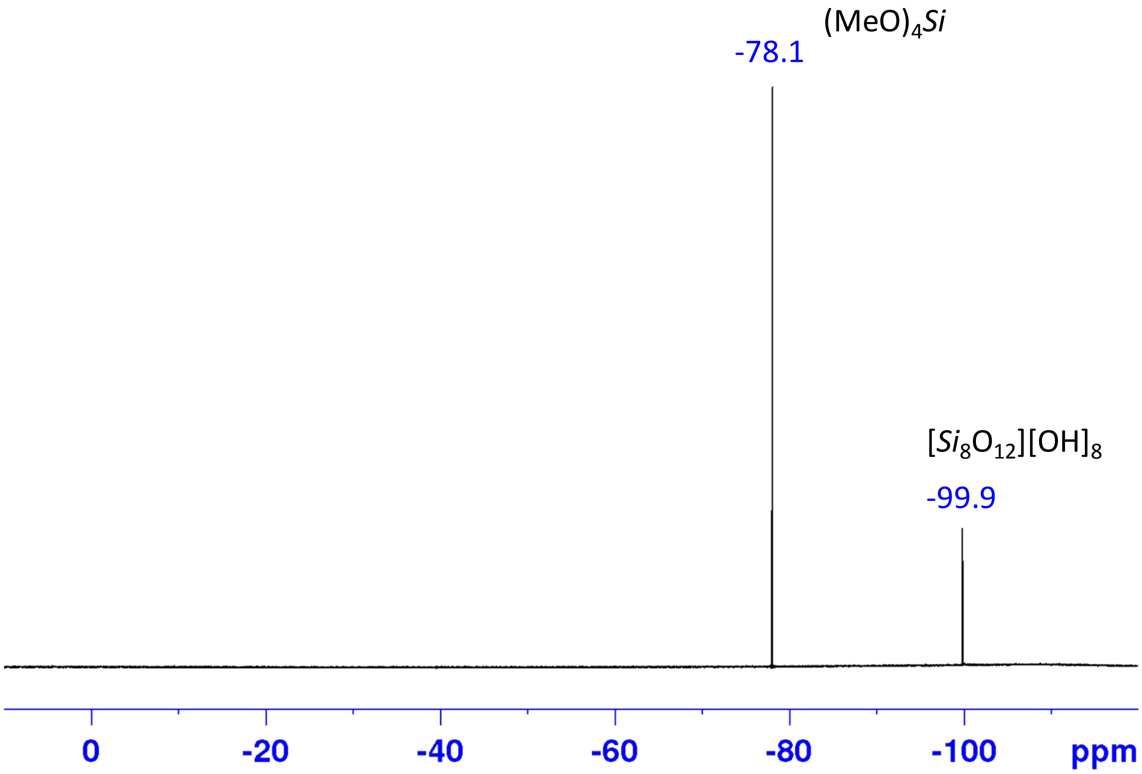

Figure S7. ^{29}Si NMR spectrum of the mixture of silanol $[Si_8O_{12}][OH]_8$(**3**) (0.02 mmol) and tetramethoxysilane (0.66 mmol) without an acidic catalyst in DMF-d_7 (after stirring for 24 h at RT). The starting materials remained unreacted.

3. Single-crystal X-ray diffraction analysis of $[Si_8O_{12}][OSi(OMe)_3]_8$ (4a)

Alkoxysilane **4a** (509 mg, 0.336 mmol) was dissolved in a mixture of toluene (1.5 mL) and hexane (0.5 mL). Keeping the solution at −30 °C for one day afforded single crystals of **4a**. X-ray diffraction data for **4a** were collected on a Rigaku XtaLAB P200 diffractometer with a Pilatus 200K detector using multi-layer mirror monochromatic Mo Kα radiation (λ = 0.71075 Å) under a stream of N_2 at 93 K. A thermal ellipsoid plot is shown in Figure 2, and the crystal data and structure-refinement parameters are listed in Table S1.

Data collection, cell refinement, and data reduction were conducted using the CrystalClear-SM Expert 2.0 software.[2] The structure was solved by direct methods using the program SHELXT-2015[3] and refined by full-matrix least-squares methods on F^2 using SHELXL-2015.[4] All materials for publication were prepared using the Olex2 software.[5] All non-hydrogen atoms were refined anisotropically. The H atoms were calculated geometrically and refined in riding mode using U_{iso}(H) values of $1.5U_{\mathrm{eq}}$(C).

Table S1. Crystal data and structure refinement parameters for **4a**

Moiety formula	$C_{24}H_{72}O_{44}Si_{16}$	
Sum formula	$C_{24}H_{72}O_{44}Si_{16}$	
Formula weight	1514.25	
Temperature	93 K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	*Cc*	
Unit cell dimensions	a = 14.713(3) Å	α = 90°
	b = 16.575(4) Å	β = 90.201(5)°
	c = 26.663(6) Å	γ = 90°
Volume	6503(2) Å^3	
Z	4	
Density (calculated)	1.547 Mg/m^3	
Absorption coefficient	0.413 mm^{-1}	
F(000)	3168	
Crystal size	0.23 × 0.14 × 0.04 mm^3	
Theta range for data collection	3.056 to 27.478°	
Index ranges	$-19 \le h \le 18$, $-21 \le k \le 21$, $-34 \le l \le 34$	
Reflections collected	40200	
Independent reflections	14534 [R(int) = 0.1161]	

Completeness to $\theta = 25.242°$	99.7%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14534 / 2 / 808
Goodness-of-fit on F^2	0.967
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0659$, $wR_2 = 0.1520$
R indices (all data)	$R_1 = 0.0965$, $wR_2 = 0.1664$
Largest diff. peak and hole	0.903 and –0.514 e.Å^{-3}

4. References

1 T. Nozawa, T. Matsumoto, F. Yagihashi, T. Beppu, K. Sato, M. Igarashi, *Chem. Lett.* 2018, **47**, 1530-1533.

2 *CrystalClear-SM Expert*: Rigaku Corporation, Tokyo, Japan, 2011.

3 *SHELXT–2015*: G. M. Sheldrick, Program for the Solution of Crystal Structures; *Acta Crystallogr. A* 2015, **71**, 3–8.

4 *SHELXL–2015*: G. M. Sheldrick, Program for the Refinement of Crystal Structures; *Acta Crystallogr. C* 2015, **71**, 3–8.

5 O. V. Dolomanov, L. J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, *OLEX2: A complete structure solution, refinement and analysis program*. *J. Appl. Cryst.* 2009, **42**, 339-341.