Organocatalytic ring-opening polymerization of cyclotrisiloxanes using silanols as initiators for the precise synthesis of asymmetric linear polysiloxanes

Keita Fuchise,* Toshiaki Kobayashi, Kazuhiko Sato,* and Masayasu Igarashi*
Interdisciplinary Research Center for Catalytic Chemistry, National Institute of Advanced Industrial Science and Technology (AIST), Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan
E-mail: k-fuchise@aist.go.jp for K. F.; k.sato@aist.go.jp for K. S.; and masayasu-igarashi@aist.go.jp for M. I.

Electronic Supplementary Information (ESI)

Contents:

Experimental section

Materials.

Hexamethylcyclotrisiloxane (D3, Shin-Etsu Chemical), 1,3,5-trimethyl-1,3,5-trivinylcyclotrisiloxane (V3, Gelest, >95%, mixture of *cis* and *trans* isomers, *cis*/*trans* = 23/77) and triethylamine (Et$_3$N, FUJIFILM Wako, >99.0%) were purified by distillation from CaH_2 under a nitrogen atmosphere prior to use.

1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD, Tokyo Chemical Industry (TCI), >98.0%) and 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD, TCI, >95.0%) were dissolved in dry THF to prepare stock solutions, and these solutions were further dried over activated MS4Å prior to use.

Trimethylsilanol (Me$_3$SiOH, Aldrich, >97.5%), triethylsilanol (Et$_3$SiOH, TCI, >98%), triphenylsilanol (Ph$_3$SiOH, TCI, >98.0%), ethoxydimethylsilane (Me$_2$HSiOEt, Shin-Etsu Chemical, >99.8%), tris(trimethylsiloxy)silane ((TMSO)$_3$SiH, TCI, >98.0%), 1,1,1,3,5,5,5-heptamethyltrisiloxane (Me(TMSO)$_2$SiH, TCI, >98.0%), 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (V4, Gelest, 95–100%), Karstedt's catalyst (Pt(dvds), Gelest, 2.1–2.4% platinum concentration in toluene), chlorotrimethylsilane (Me$_3$SiCl, TCI, >98.0%), chlorodimethyl(phenyl)silane (Me$_2$PhSiCl, Gelest, >95%), chloro(methyl)diphenylsilane (MePh$_2$SiCl, Gelest, 95–100%), chlorodimethylsilane (Me$_2$HSiCl, TCI, >95.0%), chlorodimethyl(vinyl)silane (Me$_2$ViSiCl, TCI, >97.0%),

chloro(chloromethyl)dimethylsilane ($ClCH_2SiMe_2Cl$, TCI, >98.0%), chlorotriethoxysilane ($(EtO)_3SiCl$, Aldrich, 98%), acetic acid (FUJIFILM Wako, >99.7%), benzoic acid (Kanto, >99.5%), 4,4′-methylenebis(2,6-di-*tert*-butylphenol) (TCI, >98.0%), phenothiazine (TCI, >98.0%), acetamide (Aldrich, >98.0%), urea (TCI, >99.0%), ethylamine (TCI, 12 mol L^{-1} in THF), *n*-propylamine (TCI, >98.0%), *n*-butylamine (TCI, >99.0%), isobutylamine (FUJIFILM Wako, >98.0%), benzylamine (Aldrich, 99%), pyridine (FUJIFILM Wako, dehydrated, >99.5%), allyl methacrylate (TCI, >99.0%), potassium methacrylate (FUJIFILM Wako, >98.0%), tetra-*n*-butylphosphonium bromide (TCI, >99.0%), iodomethane (TCI, >99.5%, stabilized with copper chips), phenyllithium (TCI, 1.09 mol L^{-1} in cyclohexane/Et_2O), palladium 10% on carbon (Pd/C, wetted with ca. 55% water, TCI), *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, Aldrich, ≥98%), perfluorobenzoic acid (PFBA, TCI, >98.0%), sodium trifluoroacetate (TFANa, FUJIFILM Wako, >97.0%), silver trifluoroacetate (TFAAg, FUJIFILM Wako, >97.0%), sodium hydrogen carbonate ($NaHCO_3$, FUJIFILM Wako, 99.5–100.3%), sodium hydroxide (NaOH, FUJIFILM Wako, >97.0%), potassium hydroxide (KOH, FUJIFILM Wako, >85.0%), sodium sulfate (Na_2SO_4, FUJIFILM Wako, >99.0%), tetrahydrofuran (THF, FUJIFILM Wako, stabilizer free, >99.5%), 1,4-dioxane (FUJIFILM Wako, >99.5%), diethyl ether (Et_2O, FUJIFILM Wako, >99.0%), acetonitrile (MeCN, FUJIFILM Wako, >99.5%), 'dry' acetonitrile (FUJIFILM Wako, Super Dehydrated, >99.8%, water content <0.001%), 'dry' *N*,*N*-dimethylacetamide (DMF, FUJIFILM Wako, Super Dehydrated, >99.5%), cyclopentyl methyl ether (FUJIFILM Wako, Super Dehydrated, with stabilizer, >99.0%), *tert*-butyl methyl ether (FUJIFILM Wako, Super Dehydrated, >99.5%), cyclohexane (FUJIFILM Wako, Super Dehydrated, >99.5%), *m*-xylene (Aldrich, anhydrous, >99%), hexane (FUJIFILM Wako, deoxidized, water content <0.001%, >96.0%), di-*n*-butyl ether (nBu_2O, Aldrich, anhydrous, 99.3%), anisole (Aldrich, anhydrous, 99.7%), and ethyl acetate (FUJIFILM Wako, Super Dehydrated, >99.5%) were used as received.

Dimethylphenylsilanol ($Me_2PhSiOH$, TCI, >98.0%) was purified by distillation under a nitrogen atmosphere prior to use.

Diethyl carbonate (TCI, >98.0%), 4-methyltetrahydropyran (MTHP, TCI, >99.0%, stabilized with BHT), isobutyl acetate (^{i}BuOAc, TCI, >99.0%), hexamethyldisiloxane (HMDS, TCI, >98.0%), and 1,2-dimethoxyethane (DME, Aldrich, 99.5%) were dried over activated MS4Å prior to use.

'Dry' toluene (Kanto, dehydrated –Super Plus–, water content <0.001%), 'dry' dichloromethane (CH_2Cl_2, FUJIFILM Wako, Super Dehydrated, water content <0.001%), 'dry' diethyl ether (Et_2O, FUJIFILM Wako, Super Dehydrated, >99.5%), and 'dry' tetrahydrofuran (THF, Kanto, dehydrated –Super Plus–, water content <0.001%) were purified using a Glass Contour Solvent Dispensing System and used for the polymerization reactions.

1-Hydroxy-1,1,3,3,5,5,7,7,7-nonamethyltetrasiloxane (MeD4OH),[1] chloromethyldimethyl(ethoxy)silane,[2] propylenethiourea,[3] 1,3-diazacycloheptane-2-thione,[3] 2-methylthio-1,4,5,6-tetrahydropyrimidine hydroiodide,[4] 1-chloro-1,1,3,3,5,5,7,7-octamethyltetrasiloxane,[5] 1,2-trimethylene-3-propylguanidine (TMnPG),[6] and 1,2-trimethylene-3-isopropylguanidine (TMiPG)[6] were synthesized according to literature procedures.

Characterization.

NMR spectrocopy

^1H (600 MHz), $^{13}C\{^1H\}$ (150 MHz), and $^{29}Si\{^1H\}$ (119 MHz) NMR spectra were recorded using a BRUKER Biospin AVANCE III HD 600 NMR spectrometer with a CryoProbe. Chemical shifts are reported in δ (ppm) and

referenced to tetramethylsilane (0.00 ppm) for ^{1}H, ^{13}C, and ^{29}Si.

Size-exclusion chromatography (SEC)

Size-exclusion chromatography (SEC) was performed at 45 °C using a Waters ACQUITY Advanced Polymer Chromatography (APC) System consisting of a p-Isocratic Solvent Manager (Model AIS), Sample Manager pFTN (Model ASM), Column Manager-S (Model AZC), PDA TS Detector (Model ADT), and Refractive Index (RI) Detector (Model URI) equipped with a Waters APC™ XT45 column (linear, 4.6 mm × 150 mm; pore size, 4.5 nm; bead size, 1.7 μm; exclusion limit, 5000), a Waters APC™ XT200 column (linear, 4.6 mm × 150 mm; pore size, 20.0 nm; bead size, 2.5 μm; exclusion limit, 70 000), and a Waters APC™ XT450 column (linear, 4.6 mm × 150 mm; pore size, 45.0 nm; bead size, 2.5 μm; exclusion limit, 400 000) in toluene at a flow rate of 0.70 mL min^{-1}. The molar-mass dispersity ($Đ_M$) was determined based on a calibration curve prepared using polystyrene (PS) samples from a TSKgel® standard polystyrene oligomer kit (Tosoh) with weight-average molecular weights (M_w) and ($Đ_M$) values of 9.64×10^4 g mol^{-1} (1.01) and 5.9×10^2 g mol^{-1} (1.19), along with PS samples from a ReadyCal PS Kit for APC (Waters) with M_w ($Đ_M$) values of 6.25×10^4 g mol^{-1} (1.05), 4.23×10^4 g mol^{-1} (1.02), 3.40×10^4 g mol^{-1} (1.04), 2.75×10^4 g mol^{-1} (1.03), 2.12×10^4 g mol^{-1} (1.02), 1.55×10^4 g mol^{-1} (1.05), 8.90×10^3 g mol^{-1} (1.03), 4.71×10^3 g mol^{-1} (1.08), 3.46×10^3 g mol^{-1} (1.06), 2.25×10^3 g mol^{-1} (1.05), and 1.25×10^3 g mol^{-1} (1.12).

Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS)

MALDI-TOF MS of the obtained polymers was performed using a Bruker autoflex™ speed TOF/TOF system with a Smartbeam laser (Bruker Daltonics). Spectra were acquired in the positive linear or reflector mode by accumulating 200 to 2000 laser shots at a 19 kV acceleration voltage. External calibration was performed using Tosoh TSKgel® standard Polystyrene TS-502 (M_w = 2.63 kg mol^{-1}, $Đ_M$ = 1.05) and TS-521 (M_w = 5.06 kg mol^{-1}, $Đ_M$ = 1.02). In a typical measurement, a solution of the external standard was prepared by mixing TS-502 (12.5 μL, 10 mg mL^{-1} in THF), TS-521 (12.5 μL, 10 mg mL^{-1} in THF), the matrix (DCTB, 50 mg mL^{-1}, 20 μL), and the cationization agent (TFAAg, 2.2 mg mL^{-1}, 45 μL). Solution of the samples were prepared by mixing polysiloxane (30 mg mL^{-1} in THF, 10 μL), the matrix (DCTB for poly(dimethylsiloxane) (PDMS) and poly[methyl(vinyl)siloxane] (PMVS)), 50 mg mL^{-1}, 20 μL), and the cationization agent (TFAAg or TFANa, 2.2 mg mL^{-1}, 45 μL). Approximately 10 μL of the obtained mixture was spotted on a ground steel target plate and dried prior to measurements.

High-resolution mass spectrometry (HRMS)

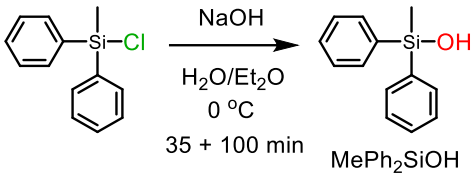
High-resolution electrospray ionization (ESI) mass spectra were obtained using a Bruker micrOTOF II.

Differential scanning calorimetry (DSC)

The melting points (m.p.) of the newly synthesized compounds in this study were measured using differential scanning calorimetry (DSC) on a Seiko Instruments DSC 7020. Approximately 3 mg of the sample was used for each measurement. The samples were heated from 25 °C to 140 °C at a heating rate of 2 °C min^{-1} under a nitrogen atmosphere. The m.p. was determined from the extrapolated onset temperature and the peak temperature of an endothermic peak in the first scan.

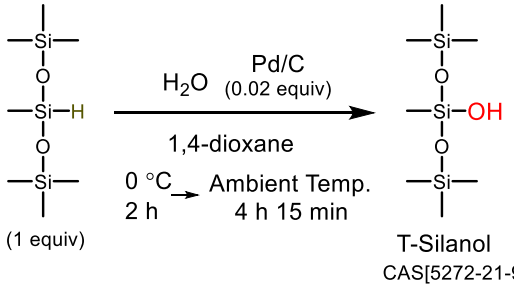
Synthesis of silanols

Methyldiphenylsilanol (MePh₂SiOH)[7]



Chloro(methyl)diphenylsilane (10.91 g, 46.87 mmol) was added dropwise to a vigorously stirred mixture of an aqueous solution of sodium hydroxide (80 mL, 1.0 mol L^{-1}, 80 mmol) and diethyl ether (160 mL) at 0 °C over 35 min. The reaction mixture was stirred for an additional 100 min, saturated with sodium chloride, and extracted three times with diethyl ether (80 mL). The combined organic phases were dried over $MgSO_4$ and concentrated by evaporating the ether under reduced pressure. The residue was distilled under reduced pressure using an oil bath to give $MePh_2SiOH$ as a highly viscous colorless liquid. Yield 8.19 g (81%). B.p. 112–115 °C / 0.24 mmHg. ^{1}H NMR (600 MHz, $CDCl_3$) 7.60–7.56 (m, 4H, aromatic meta), 7.42–7.34 (m, 6H, aromatic ortho and para), 2.42 (s, 1H, -O*H*), 0.64 (s, 3H, -CH_3). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) 137.03 (quaternary C), 133.96 (aromatic ortho), 129.88 (aromatic para), 127.91 (aromatic meta). ^{29}Si{^{1}H} NMR (100 MHz, $CDCl_3$) –2.52. HRMS (ESI) *m/z* calcd for $[C_{13}H_{14}OSiNa]^+$ $[M+Na]^+$ 237.0706, found 237.0706.

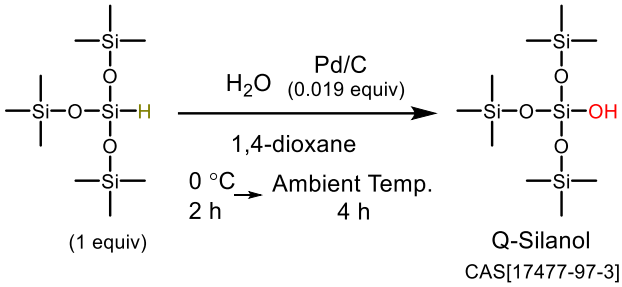
3-Hydroxy-1,1,1,3,5,5,5-heptamethylsilane (T-Silanol)



In a mixture of water (3.2 mL) and 1,4-dioxane (17 mL), 10% Pd/C on carbon (505.8 mg, ~213.9 µmol-Pd, wetted with ca. 55% water) was suspended under a N_2 atmosphere and cooled to 0 °C using an ice bath. Subsequently, a solution of $Me(TMSO)_2SiH$ (2.33 g, 10.5 mmol) in 1,4-dioxane (9.5 mL) was added dropwise over a period of 16 min. After 2 h of stirring, the ice bath was removed, and the solution was stirred for 4 h 15 min at ambient temperature. The reaction mixture was then filtered. Et_2O/H_2O (40 mL/25 mL) was added to the filtrate. The aqueous layer was separated and extracted with Et_2O (3 × 40 mL). The combined organic phases were washed with a saturated aqueous solution of NaCl (2 × 50 mL). The organic phase was dried over Na_2SO_4, filtered, and concentrated. The residue was distilled under reduced pressure to give T-Silanol as a colorless liquid. Yield 1.47 g (58.8%).

B.p. 71–72 °C / 6.8 mmHg (Lit. 76–78 °C / 17 mmHg).[8] ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.19 (s, 1H, O*H*), 0.12 (s, 18H, -OSi*Me*$_3$), 0.09 (s, 3H, -Si*Me*-OH). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 1.62 (-OSi*Me*$_3$), −2.99 (-Si*Me*-OH). ^{29}Si{^{1}H} NMR (119 MHz, $CDCl_3$): δ 8.69 (-O*Si*Me$_3$), −54.52 (-*Si*Me-OH). HR-MS (ESI) *m/z* calcd for $[C_7H_{22}O_3Si_3Na]^+$ $[M+Na]^+$ 261.0769, found 261.0769.

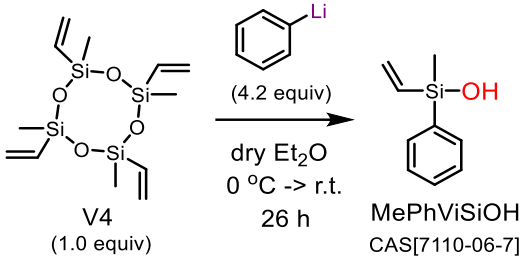
Tris(trimethylsiloxy)silanol (Q-Silanol)



In a mixture of water (3.5 mL) and 1,4-dioxane (17 mL), 10% Pd/C on carbon (496 mg, ~210 µmol-Pd, wetted with ca. 55% water) was suspended under a N_2 atmosphere and cooled to 0 °C using an ice bath. A solution of $(TMSO)_3SiH$ (3.28 g, 11.1 mmol) in 1,4-dioxane (8.3 mL) was then added dropwise over a period of 15 min. After 2 h of stirring, the ice bath was removed, and the solution was stirred for 4 h at ambient temperature. The reaction mixture was filtered, and Et_2O/H_2O (40 mL/25 mL) was added to the filtrate. The aqueous layer was separated and extracted with Et_2O (3 × 40 mL). The combined organic phases were then washed with a saturated aqueous solution of NaCl (2 × 50 mL). The organic phase was dried over Na_2SO_4, filtered, and concentrated. The residue was distilled under reduced pressure to give Q-Silanol as a colorless liquid. Yield 2.34 g (67.4%).

B.p. 71–72 °C / 0.75 mmHg (Lit. 64–65 °C / 0.75 mmHg).[8] ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.15 (br s, 1H, O*H*), 0.13 (s, 27H, Si*Me*$_3$). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 1.50 (Me). $^{29}Si\{^1H\}$ NMR (119 MHz, $CDCl_3$): δ 9.75 (*Si*Me$_3$), −96.15 (*Si*(OSiMe$_3$)$_3$). HRMS (ESI) *m/z* calcd for $[C_9H_{28}O_4Si_4Na]^+$ $[M+Na]^+$ 335.0957, found 335.0957.

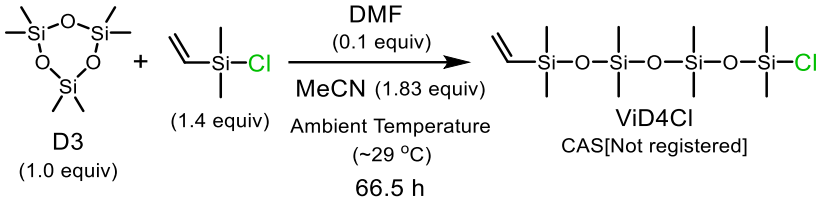
Methyl(phenyl)vinylsilanol (MePhViSiOH)[9]



Phenyllithium (58.5 mL, 63.8 mmol, 1.09 mol L^{-1} in cyclohexane/ Et_2O) was slowly added to a solution of V4 (5.24 g, 15.2 mmol) at 0 °C. The mixture was then stirred at ambient temperature for 26 h. Water (200 mL) was added to the reaction mixture at 0 °C. The organic phase was separated, and the aqueous phase was extracted with Et_2O (3 × 100 mL). The combined organic phase was dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by distillation in the presence of phenothiadine under reduced pressure to give MePhViSiOH as a colorless oil. Yield 2.63 g (26%).

B.p. 49–51 °C / 0.38 mmHg. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.63–7.57 (m, 2H, aromatic *meta*), 7.44–7.35 (m, 3H, aromatic *para* and *ortho*), 6.30 (dd, J = 14.8 Hz, J = 20.3 Hz, 1H, =C*H*Si-), 6.13 (dd, J = 3.7 Hz, J = 14.9 Hz, 1H, H^{trans}C=), 5.88 (dd, J = 3.7 Hz, J = 20.4 Hz, 1H, H^{cis}C=), 2.01 (br s, 1H, -O*H*), 0.47 (s, 3H, -SiCH_3). ^{13}C NMR (151 MHz, $CDCl_3$): δ 137.24 (quaternary C), 136.54 (=CH_2), 134.53 (-*C*H=CH_2), 133.62 (aromatic *ortho*), 129.79 (aromatic *para*), 127.88 (aromatic *meta*), –1.73 (-CH_3). $^{29}Si\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ –4.38. HRMS (ESI) *m/z* calcd for $[C_9H_{12}OSiNa]^+$ $[M+Na]^+$ 187.0550, found 187.0550.

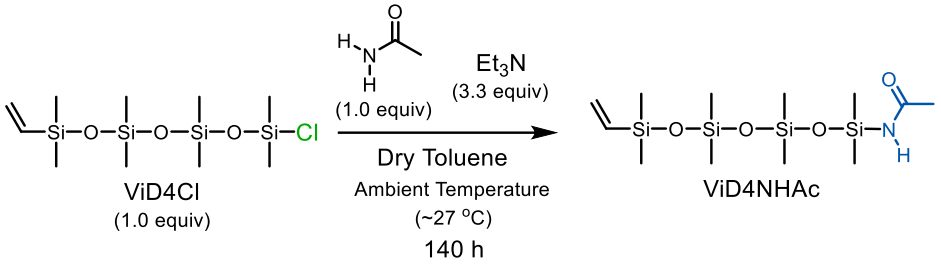
1-Chloro-1,1,3,3,5,5,7,7-octamethyl-7-vinyltetrasiloxane (ViD4Cl)[10]



D3 (17.22 g, 77.41 mmol) was placed in a flask under an argon atmosphere. $Me_2ViSiCl$ (13.10 g, 108.6 mmol) and dry MeCN (7.4 mL) were added to make a suspension. Dry DMF (565 mg, 7.73 mmol) was added to the suspension to initiate the reaction at ambient temperature (~29 °C). After 66.5 h, the reaction mixture was concentrated and purified by distillation under reduced pressure to obtain ViD4Cl as a colorless liquid. Yield: 14.80 g (43.13 mmol, 55.8%).

B.p. 88–93 °C / 24 mmHg (Lit. 61.5–63 °C / 1 mmHg).[10] ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.19 (dd, J = 14.9 Hz, 20.5 Hz, 1H, =C*H*-), 5.92 (dd, J = 3.8 Hz, 14.9 Hz, 1H, H^{trans}C(H)=), 5.78 (dd, J = 3.8 Hz, 20.5 Hz, 1H, H^{cis}C(H)=), 0.35 (s, 6H, SiMe_2-Cl), 0.21 (s, 6H, Vi-SiMe_2), 0.19 (s, 6H, SiMe_2O-SiMe$_2$-Cl), 0.17 (s, 6H, Vi-SiMe$_2$O-SiMe_2). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 139.38 (H_2C=), 132.08 (=*C*H-), 4.04 (SiMe_2Cl), 1.34 (Vi-SiMe_2), 1.11 (Vi-SiMe$_2$O-SiMe_2), 0.43 (SiMe_2O-SiMe$_2$Cl). ^{29}Si{^{1}H} NMR (119 MHz, $CDCl_3$): δ 3.68 (*Si*-Cl), −3.80 (Vi-*Si*), −19.16 (*Si*O-SiMe$_2$O-Cl), −20.40 (Vi-SiMe$_2$O-*Si*).

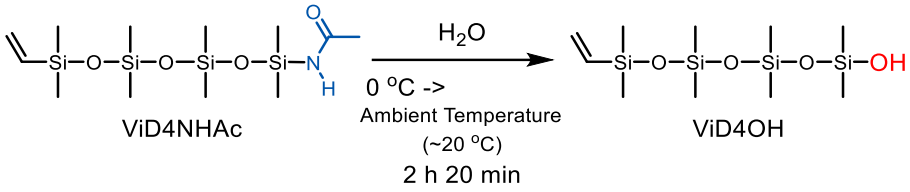
1-Acetylamino-1,1,3,3,5,5,7,7-octamethyl-7-vinyltetrasiloxane (ViD4NHAc)



ViD4Cl (3.54 g, 10.3 mmol) was added dropwise to a solution/suspension of acetamide (609 mg, 10.3 mmol) and Et_3N (3.46 g, 34.2 mmol) in dry toluene (21 mL) at ambient temperature (~27 °C) under an argon atmosphere. After 140 h of reaction, the precipitate was removed by filtration. The filtrate was concentrated to obtain MeD4NHAc as a pale orange and transparent liquid. Yield 3.53 g (93.6%). The obtained MeD4NHAc was used for the next reaction without further purification.

^{1}H NMR (600 MHz, $CDCl_3$): δ 6.13 (dd, J = 14.8 Hz, 20.4 Hz, 1H, =C*H*-), 5.95 (dd, J = 3.8 Hz, 14.9 Hz, 1H, H^{trans}C(H)=), 5.74 (dd, J = 3.9 Hz, 20.4 Hz, 1H, H^{cis}C(H)=), 5.15 (br s, 1H, N*H*), 2.01 (br, s, 3H, H_3CCO-), 0.30 (s, 6H, SiMe_2-NHAc), 0.17 (s, 6H, SiMe_2O-SiMe$_2$-NHAc), 0.10 (s, 6H, Vi-SiMe_2), 0.07 (s, 6H, Vi-SiMe$_2$O-SiMe_2). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 174.54 (*C*=O), 139.21 (H_2C=), 132.83 (=*C*H-), 25.11 (H_3CCO-), 1.16 (Vi-SiMe_2), 0.98 (Vi-SiMe$_2$O-SiMe_2), 0.32 (SiMe_2NHAc), 0.27 (SiMe_2O-SiMe$_2$NHAc). ^{29}Si{^{1}H} NMR (119 MHz, $CDCl_3$): δ −3.74 (Vi-*Si*), −8.69 (br s, *Si*-NHAc), −19.73 (br s, *Si*Me$_2$O-SiMe$_2$-NHAc), −20.43 (Vi-SiMe$_2$O-*Si*).

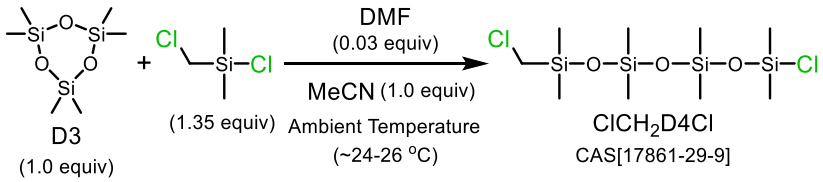
1-Hydroxy-1,1,3,3,5,5,7,7-octamethyl-7-vinyltetrasiloxane (ViD4OH)[10]



ViD4NHAc (3.21 g, 8.78 mmol) was added to a mixture of ice and water (30 g, 1.7 mol in total). The mixture was stirred for 2 h 20 min at ambient temperature (~20 °C). The reaction mixture was saturated with NaCl. The resulting aqueous solution was extracted with Et_2O (4 × 30 mL). The combined organic layer was washed with a saturated aqueous solution of NaCl (2 × 30 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by distillation under reduced pressure to give ViD4OH as a colorless liquid. Yield: 1.57 g (55.1%).

B.p. 47–49 °C / 0.23 mmHg. ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.13 (dd, J = 14.9 Hz, 20.3 Hz, 1H, =C*H*-), 5.95 (dd, J = 3.8 Hz, 14.8 Hz, 1H, H^{trans}C(H)=), 5.74 (dd, J = 3.8 Hz, 20.3 Hz, 1H, H^{cis}C(H)=), 2.30 (br s, 1H, -O*H*), 0.17 (s, 6H, Si(CH_3)$_2$), 0.14 (s, 6H, Si(CH_3)$_2$), 0.09 (s, 6H, Si(CH_3)$_2$), 0.08 (s, 6H, Si(CH_3)$_2$). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 139.23 (H_2C=), 131.88 (=*C*H-), 1.18 (Si*Me*$_2$), 1.02 (Si*Me*$_2$), 0.33 (Si*Me*$_2$), 0.23 (Si*Me*$_2$). ^{29}Si{^{1}H} NMR (119 MHz, $CDCl_3$): δ −3.54 (Vi-*Si*), −10.25 (*Si*-OH), −20.27 (Vi-SiMe$_2$O-*Si* or *Si*O-SiMe$_2$-OH), −20.73 (Vi-SiMe$_2$O-*Si* or *Si*O-SiMe$_2$-OH). HRMS (ESI) *m/z* calcd for $[C_{10}H_{28}O_4Si_4Na]^+$ $[M+Na]^+$ 347.0957, found 347.0957.

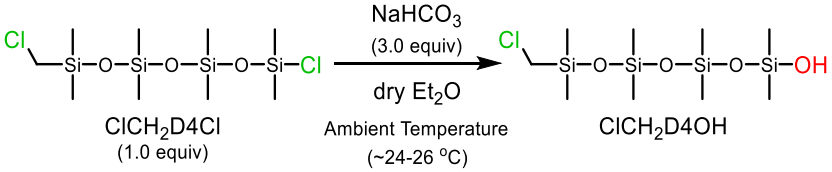
1-Chloro-7-chloromethyl-1,1,3,3,5,5,7,7-octamethyltetrasiloxane (ClCH$_2$D4Cl)



D3 (20.0 g, 89.9 mmol) was placed in a flask under an argon atmosphere. ClCH$_2$SiMe$_2$Cl (17.37 g, 121.4 mmol) and dry MeCN (4.7 mL) were added to make a suspension. Dry DMF (197 mg, 2.70 mmol) was added to the suspension to initiate the reaction at ambient temperature (~24–26 °C). After 19 h 30 min, the reaction mixture was purified by distillation under reduced pressure to obtain ClCH$_2$D4Cl as a colorless liquid. Yield: 18.28 g (50.01 mmol, 55.6%).

B.p. 78–81 °C / 1.05 mmHg. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.74 (s, 2H, ClCH_2-), 0.45 (s, 6H, -Si(CH_3)$_2$Cl), 0.22 (s, 6H, ClCH$_2$Si(CH_3)$_2$O-), 0.13 (s, 6H, Si(CH_3)$_2$OSi(CH$_3$)$_2$Cl), 0.10 (s, 6H, ClCH$_2$Si(CH$_3$)$_2$OSi(CH_3)$_2$O-). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 30.81 (Cl*C*H$_2$-), 4.07 (-Si(*C*H$_3$)$_2$Cl), 0.99 (Cl*C*H$_2$Si(CH$_3$)$_2$OSi(*C*H$_3$)$_2$-), 0.92 (-Si(*C*H$_3$)$_2$OSi(CH$_3$)$_2$Cl), −1.39 (ClCH$_2$Si(*C*H$_3$)$_2$-). ^{29}Si{^{1}H} NMR (100 MHz, $CDCl_3$): δ 3.82 (-*Si*Me$_2$Cl), 2.06 (ClCH$_2$*Si*-), −18.92 (-*Si*Me$_2$-OSiMe$_2$Cl), −19.61 (ClCH$_2$SiO-*Si*Me$_2$-).

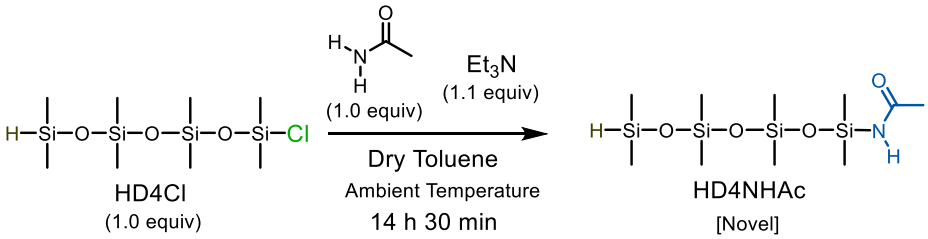
1-Chloromethyl-7-hydroxy-1,1,3,3,5,5,7,7-octamethyltetrasiloxane (ClCH$_2$D4OH)



ClCH$_2$D4Cl (9.14 g, 25.0 mmol) was added to a mixture of NaHCO$_3$ (6.30 g, 75.0 mmol) and Et$_2$O (35 mL) at ambient temperature under an argon atmosphere. After 43 h 45 min of reaction, distilled water (200 mL) was added to the reaction mixture. The aqueous phase was extracted with Et$_2$O (1 × 100 mL and 2 × 50 mL). The combined organic phases were washed with distilled water (3 × 100 mL). The organic phase was dried over Na$_2$SO$_4$, filtered, and concentrated. The residue was purified by Kugelrohr distillation at 0.23 mmHg and 79–87 °C to obtain ClCH$_2$D4OH as a colorless liquid. Yield: 7.99 g (23.0 mmol, 92.0%).

^{1}H NMR (600 MHz, CDCl$_3$): δ 2.75 (s, 2H, ClC*H*$_2$-), 0.23 (s, 6H, ClCH$_2$Si(C*H*$_3$)$_2$O-), 0.15 (s, 6H, -Si(C*H*$_3$)$_2$OH), 0.099 (s, 6H, Si(C*H*$_3$)$_2$OSi(CH$_3$)$_2$OH), 0.094 (s, 6H, ClCH$_2$Si(CH$_3$)$_2$OSi(C*H*$_3$)$_2$O-). ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$): δ 30.84 (Cl*C*H$_2$-), 1.04 (-Si(*C*H$_3$)$_2$OH), 1.01 (Cl*C*H$_2$Si(CH$_3$)$_2$OSi(*C*H$_3$)$_2$-), 0.34 (-Si(*C*H$_3$)$_2$OSi(CH$_3$)$_2$OH), −1.38 (ClCH$_2$Si(*C*H$_3$)$_2$-). ^{29}Si{^{1}H} NMR (100 MHz, CDCl$_3$): δ 2.18 (ClCH$_2$*Si*-), −10.29 (-*Si*Me$_2$OH), −19.75 (ClCH$_2$SiO-*Si*Me$_2$-), −20.69 (-*Si*Me$_2$-OSiMe$_2$Cl). HRMS (ESI) *m/z* calcd for [C$_9$H$_{27}$O$_4$Si$_4$ClNa]$^+$ [M+Na]$^+$ 369.0567, found 369.0570.

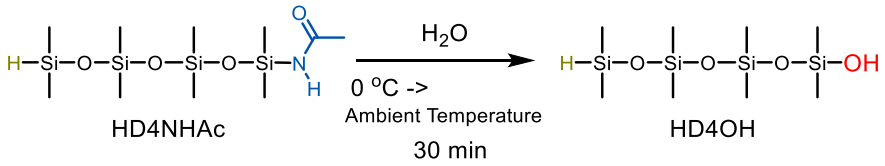
1-Acetylamino-1,1,3,3,5,5,7,7-octamethyltetrasiloxane



1-Chloro-1,1,3,3,5,5,7,7-octamethyltetrasiloxane (3.27 g, 10.3 mmol) was added dropwise to a solution/suspension of acetamide (609 mg, 10.3 mmol) and triethylamine (1.15 g, 11.3 mmol) in toluene (20.5 mL) at ambient temperature. After 14 h 30 min, the reaction mixture was filtered to remove triethylamine hydrochloride. The filtrate was concentrated to give 1-acetylamino-1,1,3,3,5,5,7,7-octamethyltetrasiloxane as a viscous liquid. Yield 3.12 g (89.1%).

^{1}H NMR (600 MHz, C$_6$D$_6$): δ 5.00 (sep, J = 2.7 Hz, 1H, Si*H*), 4.87 (br s, 1H, N*H*), 1.60 (br s, 3H, *H*$_3$CCO), 0.38 (br s, 6H, AcNH-Si(C*H*$_3$)$_2$O-), 0.24 (br s, 6H, AcNH-Si(CH$_3$)$_2$O- Si(C*H*$_3$)$_2$O-), 0.19 (d, J = 2.7 Hz, 6H, H-Si(C*H*$_3$)$_2$O-), 0.18 (br s, 6H, H-Si(CH$_3$)$_2$O- Si(C*H*$_3$)$_2$O-). ^{13}C{^{1}H} NMR (151 MHz, C$_6$D$_6$): δ 174.31 (*C*=O), 24.28 (H$_3$*C*-C=O), 0.92 (Si*Me*$_2$), 0.82 (Si*Me*$_2$), 0.58 (Si*Me*$_2$), 0.19 (Si*Me*$_2$). ^{29}Si{^{1}H} NMR (119 MHz, C$_6$D$_6$): δ −6.19 (*Si*H), −10.30 (*Si*NHAc), −19.15 (HSiMe$_2$-*Si*Me$_2$O-), −19.57 (AcNHSiMe$_2$-*Si*Me$_2$O-).

1-Hydroxy-1,1,3,3,5,5,7,7-octamethyltetrasiloxane (*HD4OH*)

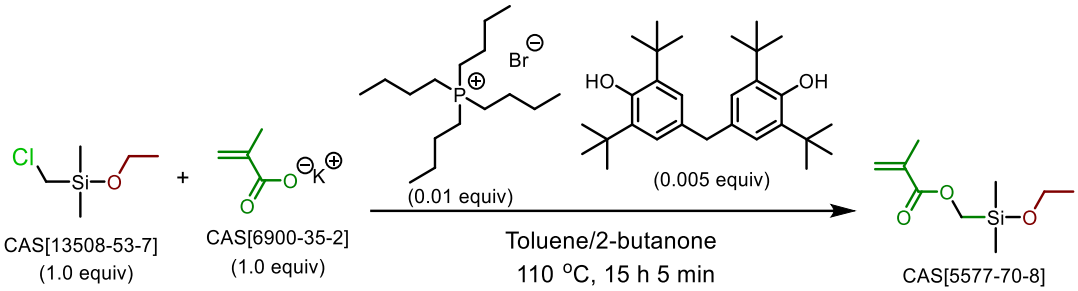


HD4NHAc (1.51 g, 4.45 mmol) was added to a mixture of ice and water (21 g, 1.7 mol, in total). The mixture was first stirred for 30 min at 0 °C, and then at ambient temperature. The reaction mixture was saturated with NaCl. The resulting aqueous solution was extracted with Et$_2$O (4 × 30 mL), and the combined organic layer was washed with a saturated aqueous solution of NaCl (4 × 20 mL). The organic layer was dried over Na$_2$SO$_4$, filtered, and

concentrated. The crude product was purified by distillation under reduced pressure to give HD4OH as a colorless liquid. Yield: 0.60 g (45%).

B.p. 36–37 °C / 0.4 mmHg. ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.71 (sep, J = 2.8 Hz, 1H, Si*H*), 2.24 (br s, 1H, -OH), 0.20 (d, J = 2.8 Hz, 6H, HSi(C*H*$_3$)$_2$-), 0.15 (s, 6H, HOSi(C*H*$_3$)$_2$), 0.10 (s, 6H, Si(C*H*$_3$)$_2$), 0.09 (Si(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 0.98 (Si*Me*$_2$), 0.85 (Si*Me*$_2$), 0.66 (Si*Me*$_2$), 0.32 (Si*Me*$_2$). ^{29}Si{^{1}H} NMR (119 MHz, $CDCl_3$): δ −6.27 (H*Si*), −10.14 (-*Si*Me$_2$OH), −19.20 (HSiMe$_2$-O-*Si*Me$_2$-O-SiMe$_2$- or HSiMe$_2$-O-SiMe$_2$-O-*Si*Me$_2$-), −20.55 (HSiMe$_2$-O-*Si*Me$_2$-O-SiMe$_2$- or HSiMe$_2$-O-SiMe$_2$-O-*Si*Me$_2$-). HRMS (ESI) calcd for $[C_8H_{26}O_4Si_4Na]^+$ $[M+Na]^+$ 321.0800, found 321.0802.

Methacryloyloxymethyl(dimethyl)ethoxysilane[11]

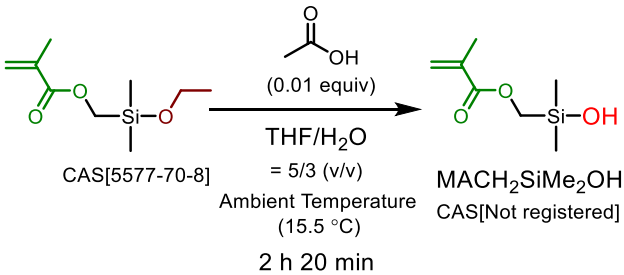


The synthesis was carried out following the experimental procedures reported by Pfeiffer's group.[11]

Potassium methacrylate (3.25 g, 26.2 mmol) was added to a solution of tetra-*n*-butylphosphonium bromide (89 mg, 0.26 mmol) and 4,4′-methylenebis(2,6-di-*tert*-butylphenol) (56.4 mg, 0.131 mmol) in toluene (1.5 mL) and 2-butanone (325 μL). Chloromethyldimethyl(ethoxy)silane (4.00 g, 26.2 mmol) was added to the reaction mixture. The reaction mixture was stirred for 15 h 5 min at 110 °C. The precipitated KCl was filtered out and washed with toluene. The products were purified by Kugelrohr distillation at 7.5 mmHg and 110–137 °C (Lit. b.p. 72–73 °C / 5 mmHg)[12] to obtain methacryloyloxymethyl(dimethyl)ethoxysilane as a colorless liquid. Yield: 3.41 g (64.3%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 6.09 (m, 1H, =C*H*^{cis}), 5.54 (m, 1H, =C*H*^{trans}), 3.87 (s, 2H, -OC*H*$_2$Si-), 3.74 (q, J = 7.0 Hz, 2H, -OC*H*$_2$CH$_3$), 1.95 (s, 3H, =CC*H*$_3$), 1.20 (t, J = 7.0 Hz, 2H, -CH$_2$C*H*$_3$), 0.21 (s, 6H, -Si(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 168.19 (*C*=O), 136.45 (H$_3$C*C*=), 125.17 (=*C*H$_2$), 58.88 (-O*C*H$_2$CH$_3$), 56.74 (-Si*C*H$_2$-), 18.47 (-CH$_2$*C*H$_3$ and =C*C*H$_3$ are overlapping), −3.14 (-Si*C*H$_3$). ^{29}Si{^{1}H} NMR (119 MHz, $CDCl_3$): δ 11.40. HRMS (ESI) *m/z* calcd for $[C_9H_{18}O_3SiNa]^+$ $[M+Na]^+$ 225.0917, found 225.0921.

Methacryloyloxymethyl(dimethyl)ethoxysilane (MACH$_2$SiMe$_2$OH)

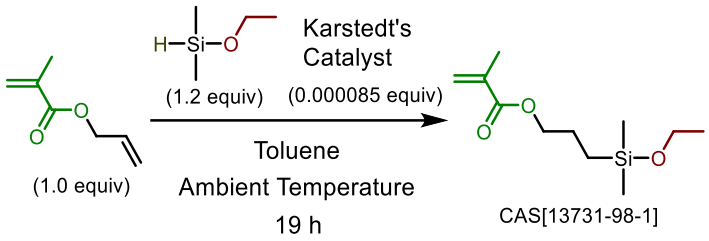


An aqueous solution of acetic acid (45 mL, 3.33 mmol L^{-1}, 0.15 mmol) was added to a solution of methacryloyloxymethyl(dimethyl)ethoxysilane (3.00 g, 14.8 mmol) in THF (74 mL) at ambient temperature (15.5 °C). After 2 h 20 min, NaCl (20.0 g) was added to the reaction mixture and the organic phase was separated.

The aqueous phase was extracted with Et_2O (2 × 40 mL). The combined organic phases were dried over Na_2SO_4 and filtered. The solvent was removed from the filtrate under reduced pressure. The residue was purified by distillation under reduced pressure in the presence of phenothiazine (3.2 mg) to give $MACH_2SiMe_2OH$ as a colorless liquid. Yield: 1.65 g (63.8%). The obtained $MACH_2SiMe_2OH$ was stored in a Teflon-coated vial at −30 °C.

B.p. 38–39 °C / 0.09 mmHg. ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.10 (m, 1H, =CH^{cis}), 5.59 (dq, 1H, =CH^{trans}), 3.85 (s, 2H, -OCH_2Si-), 3.07 (br s, 1H, -O*H*), 1.95 (m, 3H, =CCH_3), 0.21 (s, 6H, -Si(CH_3)$_2$). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 168.84 (*C*=O), 136.23 (H_3C*C*=), 125.57 (=*C*H$_2$), 59.14 (-Si*C*H$_2$-), 18.47 (=C*C*H$_3$), −1.67 (-Si*C*H$_3$). ^{29}Si{^{1}H} NMR (119 MHz, $CDCl_3$): δ 12.17. HRMS (ESI) *m*/*z* calcd for $[C_7H_{14}O_3SiNa]^+$ $[M+Na]^+$ 197.0604, found 197.0603.

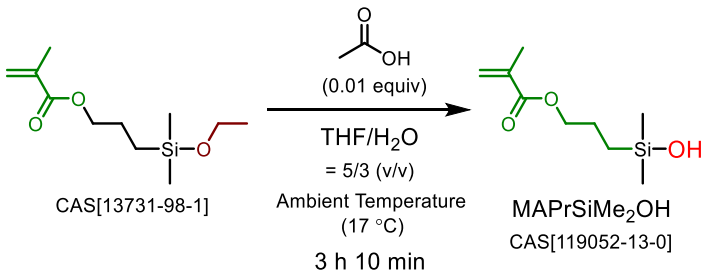
3-Methacryloyloxypropyldimethyl(ethoxy)silane



Ethoxydimethylsilane (3.26 g, 31.3 mmol) was added dropwise to a solution of allyl methacrylate (3.28 g, 26.0 mmol), phenothiazine (30 mg, 0.15 mmol), and Karstedt's catalyst (20 µL, 2.1–2.4 wt% in toluene, ~2.2 µmol) in toluene (5 mL) under a nitrogen atmosphere at ambient temperature. After 19 h, additional phenothiazine (50 mg, 0.25 mmol) was added to the reaction mixture. The reaction mixture was purified by Kugelrohr distillation at 90 °C and 0.23 mmHg to obtain 3-methacryloyloxypropyldimethyl(ethoxy)silane as a colorless liquid. Yield: 4.95 g (82.6%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 6.12–6.08 (m, 1H, =CH^{cis}), 5.56–5.53 (m, 1H, =CH^{trans}), 4.11 (t, J = 7.0 Hz, 2H, -COOCH_2-), 3.67 (q, J = 7.0 Hz, 2H, -CH_2CH$_3$), 1.96–1.93 (m, 3H, =CCH_3), 1.76–1.67 (m, 2H, -OCH$_2$CH_2-), 1.19 (t, J = 7.0 Hz, 3H, -CH$_2$CH_3), 0.67–0.59 (m, 2H, -CH_2Si), 0.12 (s, 6H, Si(CH_3)$_2$). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 167.51 (*C*=O), 136.55 (H_2*C*=), 125.18 (H_2C=*C*), 67.06 (-O*C*H$_2$CH$_2$-), 58.30 (-O*C*H$_2$CH$_3$), 22.59 (-OCH$_2$*C*H$_2$-), 18.55 (-OCH$_2$*C*H$_3$), 18.35 (=C*C*H$_3$), 12.30 (-*C*H$_2$Si), −2.16 (-Si(*C*H$_3$)$_2$). ^{29}Si{^{1}H} NMR (119 MHz, $CDCl_3$): δ 16.92. HRMS (ESI) *m*/*z* calcd for $[C_{11}H_{22}O_3SiNa]^+$ $[M+Na]^+$ 253.1230, found 253.1234.

(3-Methacryloloxypropyl)dimethylsilanol (MAPrSiMe$_2$OH)



An aqueous solution of acetic acid (52.0 mL, 3.33 mmol L^{-1}, 0.173 mmol) was added to a solution of 3-methacryloyloxypropyl(dimethyl)ethoxysilane (4.00 g, 17.4 mmol) in THF (87 mL) at ambient temperature (17 °C). After 3 h 10 min, NaCl (26.7 g) was added to the reaction mixture and the organic phase was separated. The aqueous

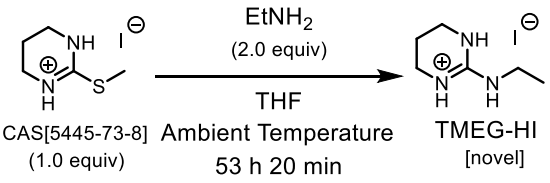
phase was extracted with Et_2O (1 × 30 mL and 2 × 55 mL). The combined organic phases were dried over Na_2SO_4 and filtered. The solvent was removed from the filtrate under reduced pressure. The residue was dissolved in toluene (80 mL), dried over Na_2SO_4, filtered, and concentrated. The residue was purified by distillation in the presence of phenothiazine (3.0 mg) under reduced pressure to give MAPrSiMe$_2$OH as a colorless liquid. Yield: 2.47 g (70.3%). The obtained MAPrSiMe$_2$OH was stored in a vial coated with Teflon at −30 °C.

B.p. 64–65.5 °C / 0.075 mmHg (Lit. 95–96 °C / 1 mmHg).[13] ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.12–6.08 (m, 1H, =CH^{cis}), 5.58–5.51 (m, 1H, =CH^{trans}), 4.13 (t, J = 7.0 Hz, 2H, -COOCH_2-), 2.27 (br s, 1H, -OH), 1.96–1.93 (m, 3H, =CCH_3), 1.79–1.70 (m, 2H, -OCH$_2$CH_2-), 0.66–0.60 (m, 2H, -CH_2Si), 0.15 (s, 6H, Si(CH_3)$_2$). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 167.67 (*C*=O), 136.50 (H$_2$*C*=), 125.36 (H$_2$C=*C*), 67.03 (-O*C*H$_2$-), 22.58 (-OCH$_2$*C*H$_2$-), 18.34 (=C*C*H$_3$), 13.67 (-*C*H$_2$Si), −0.34 (-Si(*C*H$_3$)$_2$). ^{29}Si{^{1}H} NMR (119 MHz, $CDCl_3$): δ 17.43. HRMS (ESI) *m*/*z* calcd for $[C_9H_{18}O_3SiNa]^+$ $[M+Na]^+$ 225.0917, found 225.0918.

Synthesis of guanidines

The 1,3-trimethylene-2-alkylguanidine hydroiodides were synthesized by modifying a typical procedure for the synthesis of guanidines.[14, 15]

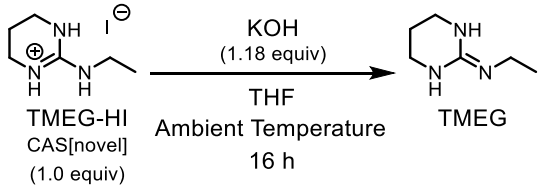
1,3-Trimethylene-2-ethylguanidine hydroiodide (TMEG-HI)



Ethylamine (3.60 mL, 12 mol L^{-1} in THF, 43 mmol) was added to a suspension of 2-methylthio-1,4,5,6-tetrahydropyrimidine hydroiodide (5.48 g, 21.3 mmol) in THF (32 mL, stabilizer-free) at ambient temperature. After 53 h 20 min of reaction, the reaction mixture was concentrated *in vacuo*. THF (32 mL, stabilizer-free) and ethylamine (1.86 mL, 12 mol L^{-1} in THF, 22 mmol) were added to the residue. After 18 h, the reaction mixture was concentrated *in vacuo*. The residue was washed with Et_2O (50 mL in total) at ambient temperature under air and dried *in vacuo* to give crude TMEG-HI as a pale-yellow solid. Yield: 4.67 g (77.6%).

M.p. 102 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 7.12 (br s, 2H, -NH(CH$_2$)$_3$NH-), 6.93 (br t, 1H, NHCH$_2$CH$_3$), 3.42 (t, J = 5.7 Hz, 4H, NCH_2CH$_2$CH_2N), 3.37 (dq, J = 5.2 Hz and 1.5 Hz, 3H, -CH_2CH$_3$), 1.98 (quintet, J = 5.8 Hz, 2H, NCH$_2$CH_2CH$_2$N), 1.28 (t, J = 7.3 Hz, 2H, CH$_2$CH_3). ^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6): δ 153.06 (*C*NCH$_2$CH$_3$), 38.50 (NH*C*H$_2$CH$_2$*C*H$_2$NH), 37.24 (-*C*H$_2$CH$_3$), 20.00 (NHCH$_2$*C*H$_2$CH$_2$NH), 14.11 (-*C*H$_3$). HRMS (ESI) *m*/*z* calcd for $[C_6H_{14}N_3]^+$ $[M-I]^+$ 128.1182, found 128.1181; calcd for $[I]^-$ $[M-TMEG-H]^-$ 126.9050, found 126.9047.

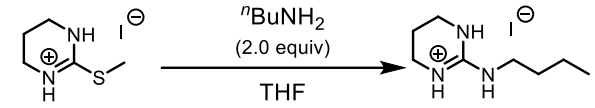
1,3-Trimethylene-2-ethylguanidine (TMEG)



KOH (260 mg, 4.63 mmol) was added to a solution of TMEG-HI (1.00 g, 3.92 mmol) in THF (10.0 mL) at ambient temperature. After 16 h, the reaction mixture was filtered using a SARTORIUS syringe filter (Mini Sarto SRP, pore size = 0.2 μm). The filtrate was concentrated under reduced pressure and dissolved in dry toluene (4 mL). The solution was concentrated under reduced pressure to obtain TMEG as a pale-yellow solid. The residue was dissolved in dry THF to prepare a stock solution of TMEG in THF (100 mg mL^{-1}). Yield: 267 mg (53.5%). Activated MS4Å was added to dehydrate the solution.

TMEG: *Hygroscopic*. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.28 (t, J = 5.8 Hz, 4H, NCH_2CH_2CH_2N), 3.10 (q, J = 7.2 Hz, 2H, -CH_2CH$_3$), 1.78–1.72 (m, 2H, NCH$_2$CH_2CH$_2$N), 1.12 (t, J = 7.2 Hz, 3H, -CH_3). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 153.09 (*C*NCH$_2$CH$_3$), 39.06 (NH*C*H$_2$CH$_2$*C*H$_2$NH), 36.28 (N*C*H$_2$CH$_3$), 20.70 (NHCH$_2$*C*H$_2$CH$_2$NH), 14.50 (-*C*H$_3$). HRMS (ESI) *m/z* calcd for $[C_6H_{14}N_3]^+$ $[M+H]^+$ 128.1182, found 128.1186.

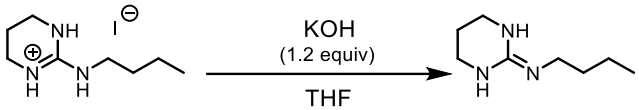
1,3-Trimethylene-2-isobutylguanidine hydroiodide (TMnBG-HI)



n-Butylamine (3.11 g, 42.5 mmol) was added to a suspension of 2-methylthio-1,4,5,6-tetrahydropyrimidine hydroiodide (5.48 g, 21.3 mmol) in THF (32 mL, stabilizer-free) at ambient temperature. After 23 h, the reaction mixture was concentrated *in vacuo*. The residue was washed with a total of 50 mL of Et_2O at ambient temperature under air and dried *in vacuo* to give crude TMnBG-HI as a yellow viscous liquid. Yield: 5.80 g (96.4%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.17 (br s, 2H, -N*H*(CH$_2$)$_3$N*H*-), 6.95 (br t, 1H, N*H*(CH$_2$)$_3$CH$_3$), 3.41 (t, J = 5.8 Hz, 4H, NCH_2CH_2CH_2N), 3.31 (dt, J = 7.0 Hz and 4.8 Hz, 2H, -CH_2CH$_2$CH$_2$CH$_3$), 1.97 (quintet, J = 5.9 Hz, 2H, NCH$_2$CH_2CH$_2$N), 1.62 (tt, J = 7.3 Hz, 2H, -CH$_2$CH_2CH$_2$CH$_3$), 1.45 (tq, J = 7.4 Hz, 2H, -CH$_2$CH$_2$CH_2CH$_3$), 0.93 (t, J = 7.3 Hz, 3H, -CH_3). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 153.22 (*C*N^{n}Bu), 42.03 (N*C*H$_2$CH$_2$CH$_2$CH$_3$), 38.48 (NH*C*H$_2$CH$_2$*C*H$_2$NH), 30.63 (NCH$_2$*C*H$_2$CH$_2$CH$_3$), 20.03 (NCH$_2$CH$_2$*C*H$_2$CH$_3$), 20.01 (NHCH$_2$*C*H$_2$CH$_2$NH), 13.73 (-*C*H$_3$). HRMS (ESI) *m/z* calcd for $[C_8H_{18}N_3]^+$ $[M–I]^+$ 156.1495, found 156.1498; calcd for $[I]^-$ $[M–TMnBG–H]^-$ 126.9050, found 126.9047.

1,3-Trimethylene-2-isobutylguanidine (TMnBG)[14]

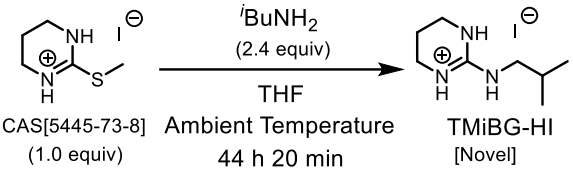


KOH (240 mg, 4.28 mmol) was added to a solution of TMnBG-HI (1.00 g, 3.53 mmol) in THF (10.0 mL) at ambient temperature. After 15 h 5 min, the reaction mixture was filtered using a SARTORIUS syringe filter (Mini Sarto SRP, pore size = 0.2 μm). The filtrate was concentrated under reduced pressure and dissolved in dry toluene (4 mL). The solution was concentrated under reduced pressure to obtain TMnBG as a pale-yellow solid. Yield: 281 mg (51.3%). The residue was dissolved in dry THF to prepare a stock solution of TMnBG in THF (100 mg mL^{-1}). Activated MS4Å was added to dehydrate the solution.

Hygroscopic. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.31 (t, J = 5.9 Hz, 4H, NCH_2CH_2CH_2N), 3.18 (t, J = 7.1 Hz, 2H, -

C*H*$_2$CH$_2$CH$_2$CH$_3$), 1.84 (quintet, *J* = 5.8 Hz, 2H, NCH$_2$C*H*$_2$CH$_2$N), 1.53 (tt, *J* = 7.3 Hz, 2H, -CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.39 (tq, *J* = 7.4 Hz, 2H, -CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.91 (t, *J* = 7.4 Hz, 3H, -C*H*$_3$). ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$): *δ* 152.32 (*C*N^{n}Bu), 41.33 (N*C*H$_2$CH$_2$CH$_2$CH$_3$), 41.27 (NH*C*H$_2$CH$_2$*C*H$_2$NH), 32.08 (NCH$_2$*C*H$_2$CH$_2$CH$_3$), 22.07 (NCH$_2$CH$_2$*C*H$_2$CH$_3$), 20.33 (NHCH$_2$*C*H$_2$CH$_2$NH), 13.92 (-*C*H$_3$). HRMS (ESI) *m/z* calcd for [C$_8$H$_{18}$N$_3$]$^+$ [M+H]$^+$ 156.1495, found 156.1492.

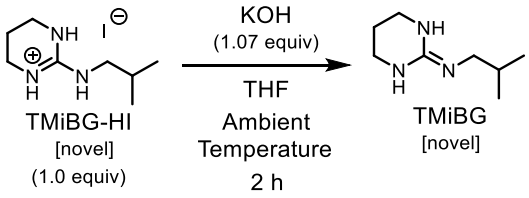
1,3-Trimethylene-2-isobutylguanidine hydroiodide (TMiBG-HI)



Isobutylamine (3.74 g, 51.1 mmol) was added to a suspension of 2-methylthio-1,4,5,6-tetrahydropyrimidine hydroiodide (5.49 g, 21.3 mmol) in THF (32 mL, with stabilizer) at ambient temperature. After 44 h 20 min at ambient temperature, the reaction mixture was concentrated under reduced pressure. The residue was dissolved in toluene (25 mL) and concentrated under reduced pressure, then dissolved again in toluene (25 mL) and concentrated under reduced pressure to obtain TMiBG-HI as an orange viscous liquid. Yield: 5.69 g (94.5%).

^{1}H NMR (600 MHz, CDCl$_3$): *δ* 7.20 (br s, 2H, -N*H*(CH$_2$)$_3$N*H*-), 6.93 (br t, *J* = 5.4 Hz, 1H, N*H*CH$_2$CH(CH$_3$)$_2$), 3.48–3.36 (m, 4H, NC*H*$_2$CH$_2$C*H*$_2$N), 3.15 (dd, *J* = 5.8 Hz and 6.7 Hz, 2H, -C*H*$_2$CH(CH$_3$)$_2$), 1.98–1.90 (m, 1H, -CH$_2$C*H*(CH$_3$)$_2$), 1.96 (quintet, *J* = 5.9 Hz, 2H, NCH$_2$C*H*$_2$CH$_2$N), 1.03 (d, *J* = 6.6 Hz, 6H, -C*H*$_3$). ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$): *δ* 153.33 (*C*NH^{i}Bu), 49.41 (N*C*H$_2$CH-), 38.49 (NH*C*H$_2$CH$_2$*C*H$_2$NH), 28.02 (NCH$_2$*C*H-), 20.26 (-*C*H$_3$), 20.02 (NHCH$_2$*C*H$_2$CH$_2$NH). HRMS (ESI) *m/z* calcd for [C$_8$H$_{18}$N$_3$]$^+$ [M−I]$^+$ 156.1495, found 156.1499; calcd for [I]$^-$ [M−TMiBG−H]$^-$ 126.9050, found 126.9046.

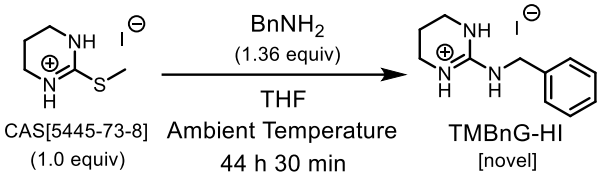
1,3-Trimethylene-2-isobutylguanidine (TMiBG)



KOH (21.8 mg, 389 μmol) was added to a solution of TMiBG-HI (103 mg, 364 μmol) in THF (10.0 mL) at ambient temperature. After 2 h, the reaction mixture was filtered using a SARTORIUS syringe filter (Mini Sarto SRP, pore size = 0.2 μm). The filtrate was concentrated under reduced pressure and dissolved in dry toluene (4 mL). The solution was concentrated under reduced pressure to obtain TMiBG as a pale-yellow solid. Yield: 48.9 mg (89.2%). The residue was dissolved in dry THF to prepare a stock solution of TMiBG in THF (50 mg mL^{-1}). Activated MS4Å was added to dehydrate the solution.

Hygroscopic. ^{1}H NMR (600 MHz, CDCl$_3$): *δ* 3.32 (t, *J* = 5.8 Hz, 4H, NC*H*$_2$CH$_2$C*H*$_2$N), 2.94 (t, *J* = 6.8 Hz, 2H, -NC*H*$_2$CH(CH$_3$)$_2$), 1.85–1.78 (m, 2H, NCH$_2$C*H*$_2$CH$_2$N), 1.83–1.74 (m, 1H, -C*H*(CH$_3$)$_2$), 0.95 (t, *J* = 6.6 Hz, 6H, -C*H*$_3$). ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$): *δ* 152.75 (*C*N^{i}Bu), 49.32 (N*C*H$_2$CH-), 40.38 (NH*C*H$_2$CH$_2$*C*H$_2$NH), 28.46 (NCH$_2$*C*H-), 21.46 (NHCH$_2$*C*H$_2$CH$_2$NH), 20.38 (-*C*H$_3$). HRMS (ESI) *m/z* calcd for [C$_8$H$_{18}$N$_3$]$^+$ [M+H]$^+$ 156.1495, found 156.1496.

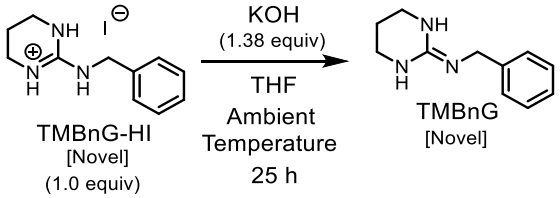
1,3-Trimethylene-2-benzylguanidine hydroiodide (TMBnG-HI)



Benzylamine (4.88 g, 45.5 mmol) was added to a suspension of 2-methylthio-1,4,5,6-tetrahydropyrimidine hydroiodide (8.65 g, 33.5 mmol) in THF (50 mL, with stabilizer). The reaction mixture was stirred for 44 h 30 min at ambient temperature (17 °C) and for 18 h 30 min at 50 °C. Then, the reaction mixture was concentrated under reduced pressure. The solid residue was washed with toluene (3 × 15 mL) and concentrated under reduced pressure to obtain TMBnG-HI as a white solid. Yield: 10.59 g (99.7%).

M.p. 119 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42 (br t, J = 5.9 Hz, 1H, N*H*Bn), 7.41–7.37 (m, 2H, aromatic *meta*), 7.35–7.24 (m, 3H, aromatic *ortho* and *para*), 7.20 (br s, 2H, -N*H*$(CH_2)_3$N*H*-), 4.49 (d, 2H, J = 5.6 Hz, NHC*H*$_2$Ph), 3.35–3.24 (m, 4H, NC*H*$_2$CH$_2$C*H*$_2$N), 1.87 (quintet, J = 5.9 Hz, 2H, NCH$_2$C*H*$_2$CH$_2$N). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 153.26 (*C*NHBn), 135.37 (aromatic quaternary), 128.91 (aromatic *meta*), 128.16 (aromatic *para*), 127.67 (aromatic *ortho*), 45.50 (N*C*H$_2$Ph), 38.44 (NH*C*H$_2$CH$_2$*C*H$_2$NH), 19.80 (NHCH$_2$*C*H$_2$CH$_2$NH). HRMS (ESI) *m*/*z* calcd for $[C_{11}H_{16}N_3]^+$ $[M-I]^+$ 190.1339, found 190.1340; calcd for $[I]^-$ $[M-TMBnG-H]^-$ 126.9050, found 126.9047.

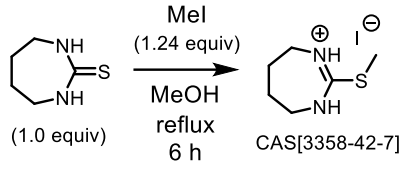
1,3-Trimethylene-2-benzylguanidine (TMBnG)



KOH (308.3 mg, 5.49 mmol) was added to a solution of TMBnG-HI (1.26 g, 3.97 mmol) in THF (10.0 mL) at ambient temperature. After 25 h, the reaction mixture was filtered using a SARTORIUS syringe filter (Mini Sarto SRP, pore size = 0.2 μm). The filtrate was concentrated under reduced pressure to obtain TMBnG as a white solid. Yield: 736.6 mg (97.9%). The residue was dissolved in dry THF to prepare a stock solution of TMBnG in THF (50 mg mL^{-1}). Activated MS4Å was added to dehydrate the solution.

Hygroscopic. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.32–7.27 (m, 4H, aromatic *ortho* and *meta*), 7.27–7.20 (m, 1H, aromatic *para*), 4.24 (s, 2H, NC*H*$_2$Ph), 3.25 (t, J = 5.8 Hz, 4H, NC*H*$_2$CH$_2$C*H*$_2$N), 1.79–1.67 (m, 2H, NCH$_2$C*H*$_2$CH$_2$N). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 151.98 (*C*NBn), 139.74 (aromatic quaternary), 128.52 (aromatic *meta*), 127.53 (aromatic *para*), 127.07 (aromatic *ortho*), 45.88 (N*C*H$_2$Ph), 41.22 (NH*C*H$_2$CH$_2$*C*H$_2$NH), 21.98 (NHCH$_2$*C*H$_2$CH$_2$NH). HRMS (ESI) *m*/*z* calcd for $[C_{11}H_{16}N_3]^+$ $[M+H]^+$ 190.1339, found 190.1337.

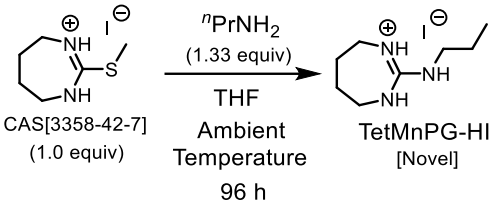
4,5,6,7-Tetrahydro-2-(methylthio)-1H-1,3-diazepine hydroiodide



The synthesis was carried out in a manner similar to that of 2-methylthio-1,4,5,6-tetrahydropyrimidine hydroiodide.[4] 1,3-Diazacycloheptane-2-thione (28.02 g, 215.2 mmol) and MeI (38.01 g, 267.8 mmol) were refluxed in MeOH (215 mL) for 6 h. Then, the MeOH was evaporated under reduced pressure to give 4,5,6,7-tetrahydro-2-(methylthio)-1*H*-1,3-diazepine hydroiodide as a yellow-orange solid. Yield: 57.01 g (97.3%).

^{1}H NMR (600 MHz, DMSO-d_6): δ 9.45 (br s, 2H, N*H*), 3.44 (br s, 4H, -NHC*H*$_2$-), 2.60 (s, 3H, -SC*H*$_3$), 1.76 (br quintet, J = 2.8 Hz, 4H, NHCH$_2$C*H*$_2$C*H*$_2$CH$_2$NH). ^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6): δ 170.60 (*C*SCH$_3$), 45.56 (NH*C*H$_2$), 25.29 (NCH$_2$*C*H$_2$), 14.78 (S*C*H$_3$). HRMS (ESI) *m*/*z* calcd for [C$_6$H$_{13}$N$_2$S]$^+$ [M−I]$^+$ 145.0794, found 145.0792; calcd for [I]$^-$ 126.9050, found 126.9048.

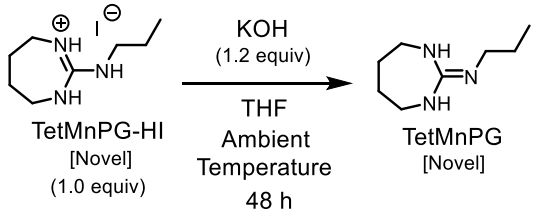
1,3-Tetramethylene-2-propylguanidine hydroiodide (TetMnPG-HI)



n-Propylamine (1.66 g, 28.1 mmol) was added to a suspension of 4,5,6,7-tetrahydro-2-(methylthio)-1*H*-1,3-diazepine hydroiodide (5.75 g, 21.1 mmol) in THF (55 mL, stabilizer-free) at ambient temperature. After 96 h, the reaction mixture was concentrated *in vacuo*. The residue was washed with a total of 30 mL of hexane at ambient temperature under air and dried *in vacuo* to give crude 1,2-tetramethylene-3-propylguanidine hydroiodide (TetMnPG-HI) as a pale-yellow solid. Yield: 6.00 g (~100%).

M.p. 72 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 7.56 (br s, 2H, -N*H*-), 3.16 (br s, 4H, NHC*H*$_2$ CH$_2$CH$_2$C*H*$_2$NH), 3.08 (br t, J = 7.1 Hz, 2H, -NHC*H*$_2$CH$_2$CH$_3$), 1.61–1.53 (m, 4H, NHCH$_2$C*H*$_2$C*H*$_2$CH$_2$NH), 1.47 (sextet, J = 7.3 Hz, 2H, C*H*$_2$CH$_3$), 0.87 (t, J = 7.4 Hz, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6): δ 160.30 (*C*NH^{n}Pr), 43.69 (NH*C*H$_2$CH$_2$CH$_2$*C*H$_2$NH), 43.38 (NH*C*H$_2$CH$_2$CH$_3$), 26.96 (NHCH$_2$*C*H$_2$*C*H$_2$CH$_2$NH), 21.95 (*C*H$_2$CH$_3$), 10.88 (*C*H$_3$). HRMS (ESI) *m*/*z* calcd for [C$_8$H$_{18}$N$_3$]$^+$ [M−I]$^+$ 156.1495, found 156.1492; calcd for [I]$^-$ [M−TetMnPG−H]$^-$ 126.9050, found 126.9048.

1,3-Tetramethylene-2-propylguanidine (TetMnPG)



KOH (0.30 g, 5.3 mmol) was added to a solution of TetMnPG-HI (1.28 g, 4.52 mmol) in THF (10.0 mL) at ambient temperature. After 48 h, the reaction mixture was filtered using a SARTORIUS syringe filter (Mini Sarto

SRP, pore size = 0.2 μm). The filtrate was concentrated under reduced pressure and dissolved in dry toluene (4 mL). Then, the solution was again filtered using a SARTORIUS syringe filter (Mini Sarto SRP, pore size = 0.2 μm). The filtrate was concentrated under reduced pressure to obtain TetMnPG as a pale-yellow solid. Yield: 523 mg (74.6%). The residue was dissolved in dry THF to prepare a stock solution of TetMnPG in THF (100 mg mL^{-1}). Activated MS4Å was added to dehydrate the solution.

Hygroscopic. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.12–3.04 (m, 4H, $NCH_2CH_2CH_2CH_2N$), 2.87 (t, J = 7.3 Hz, 2H, $CH_2CH_2CH_3$), 1.64–1.58 (m, 4H, $NCH_2CH_2CH_2CH_2N$), 1.56 (sextet, J = 7.4 Hz, 2H, CH_2CH_3), 0.93 (t, J = 7.4 Hz, 3H, CH_3). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 158.84 ($CN^{n}Pr$), 48.27 ($NCH_2CH_2CH_3$), 45.08 ($NHCH_2CH_2CH_2CH_2NH$), 29.94 ($NHCH_2CH_2CH_2CH_2NH$), 24.72 ($NCH_2CH_2CH_3$), 12.08 (CH_3). HRMS (ESI) m/z calcd for $[C_8H_{18}N_3]^+$ $[M+H]^+$ 156.1495, found 156.1494.

Homopolymerization of D3 (Tables 1–3)

Typically, polymerizations were conducted using the following procedures. A toluene solution of TMnPG (100 mg mL^{-1}, 16.0 μL, 11.3 μmol, 0.25 equiv) was added to a solution of D3 (252 mg, 1.13 mmol, 25 equiv) and MeD4OH (14.2 mg, 45.3 mmol, 1.0 equiv) in dry Et_2O (630 μL) in a glass vial or a flask under an argon atmosphere to initiate the polymerization at ambient temperature (24–26 °C). During the polymerization, an aliquot of the reaction mixture (~40 μL) was taken and mixed with a small amount of benzoic acid. The aliquot was analyzed by ^{1}H NMR to determine the conversion of the monomer and by SEC to analyze the molar-mass distribution of the crude product. After 2 h 21 min, dry pyridine (11.7 μL, 145 μmol, 3.2 equiv) was added as a hydrochloric acid scavenger, and $Me_2ViSiCl$ (12.2 μL, 90.7 μmol, 2.0 equiv) was added to end-cap the propagating polymers. The end-capping reaction was continued at least for 15 min and generally for longer than 12 h at ambient temperature to ensure quantitative end-capping. Then, the reaction mixture was concentrated under reduced pressure. The obtained oil was mixed/shaken with MeCN (3 mL) and the upper layer was removed; the washing procedure with MeCN was repeated four times. The solvent remaining in the product was thoroughly removed *in vacuo* to obtain α-trimethylsilyl-ω-dimethyl(vinyl)silyl-terminated PDMS ((Me_3SiO)-PDMS-$(OSiMe_2Vi)$) (156 mg, 57.8% yield, $M_{n,NMR}$ = 6.30 kDa, $Đ_M$ = 1.09$_0$) as a colorless liquid. ^{1}H NMR, $^{29}Si\{^{1}H\}$ NMR, and MALDI-TOF MS spectra of the product are shown in Fig. 3 and 4.

For the synthesis of PDMS with an ω-silanol group, rather than adding pyridine and chlorosilanes for the end-capping reaction, sufficient benzoic acid was added to the reaction mixture in order to terminate the polymerization by quenching the catalyst. The reaction mixture was then stirred for at least 5 min to completely neutralize the catalyst. Purification of the product was conducted using the same procedures as for end-capped PDMS. α-Trimethylsilyl-ω-dimethyl(hydroxy)silyl-terminated PDMS (Me_3SiO)-PDMS-OH (425 mg, 79.8% yield, $M_{n,NMR}$ = 5.74 kg mol^{-1}, $Đ_M$ = 1.10$_7$) was obtained from the polymerization of D3 (504 mg, 2.27 mmol, 25 equiv) using MeD4OH (28.3 mg, 90.7 mmol, 1 equiv), a toluene solution of TMnPG (100 mg mL^{-1}, 32.0 μL, 11.3 μmol, 0.25 equiv), and benzoic acid (27.2 mg, 0.223 mmol) in Et_2O (1.26 mL) at ambient temperature. ^{1}H and $^{29}Si\{^{1}H\}$ NMR spectra of the product are shown in Fig. S5.

The polymerization reactions of D3 using different catalysts and solvents under varying conditions were conducted using procedures similar to the typical procedures described above with THF solutions of the appropriate

guanidine (TMEG, TMiPG, TMnBG, TMiBG, TMBnG, TetMnPG, TBD, or MTBD) under the conditions listed in Tables 1 and 2.

Homopolymerization of V3 (Table 4)

Typically, polymerizations were conducted using the following procedures. A THF solution of TMEG (10.0 mg mL^{-1}, 16.0 μL, 1.26 μmol, 0.025 equiv) was added to a solution of V3 (328 mg, 1.27 mmol, 24.9 equiv) and MePhViSiOH (8.3 mg, 51 μmol, 1.0 equiv) in dry Et_2O (699 μL) in a glass vial under an argon atmosphere to initiate the polymerization at ambient temperature (24–26 °C). During the polymerization, an aliquot of the reaction mixture (~40 μL) was taken and mixed with a small amount of benzoic acid. The aliquot was analyzed by ^1H NMR to determine the conversion of monomer and by SEC to analyze the molar-mass distribution of the crude product. After 1 h 30 min, dry pyridine (13.0 μL, 161 μmol, 3.2 equiv) was added as a hydrochloric acid scavenger and $AllylSiMe_2Cl$ (13.6 μL, 101 μmol, 2.0 equiv) was added to end-cap the propagating polymers. The end-capping reaction was continued at least for 15 min and generally for longer than 12 h at ambient temperature to ensure quantitative end-capping. The mixture was concentrated under reduced pressure. The obtained oil was washed with $MeCN/H_2O$ (3 mL, 98/2 (v/v)) four times. The residual solvent was thoroughly removed from the product *in vacuo*. The residue was dissolved in toluene (3 mL) and again concentrated *in vacuo* to obtain α-methyl(phenyl)vinylsilyl-ω-allyl(dimethyl)silyl-terminated PMVS ((MePhViSiO)-PDMS-($OSiMe_2Allyl$)) (215 mg, 63.5% yield, $M_{n,NMR}$ = 6.45 kDa, $Đ_M = 1.10_9$) as a colorless liquid. ^1H NMR, $^{29}Si\{^1H\}$ NMR, and MALDI-TOF MS spectra of the product are shown in Fig. S22.

For the synthesis of PMVS with an ω-silanol group, rather than adding pyridine and chlorosilanes for the end-capping reaction, sufficient benzoic acid was added to the reaction mixture to terminate the polymerization by quenching the catalyst. The reaction mixture was then stirred for at least 5 min to completely neutralize the catalyst. Purification of the product was conducted using the same procedures as for end-capped PMVS. α-Trimethylsilyl-ω-hydroxy(methyl)vinylsilyl-terminated PMVS ((Me_3SiO)-PMVS-OH, 112 mg, 43.8% yield, $M_{n,NMR}$ = 5.66 kg mol^{-1}, $Đ_M = 1.12_1$) was obtained from the polymerization of V3 (244 mg, 0.943 mmol, 25 equiv) using MeD4OH (11.8 mg, 37.7 mmol, 1 equiv), a toluene solution of TMEG (5.0 mg mL^{-1}, 9.6 μL, 0.38 μmol, 0.010 equiv), and benzoic acid (11.2 mg, 91.7 μmol) in Et_2O (524 μL) at ambient temperature. ^1H NMR, $^{29}Si\{^1H\}$ NMR, and MALDI-TOF MS spectra of the product are shown in Fig. S19.

Block copolymerization of D3 and V3 (Table 4, entries 9a and 9b).

Typically, polymerizations were carried out as follows. A toluene solution of TMEG (10 mg mL^{-1}, 40.0 μL, 3.4 μmol, 0.075 equiv) was added to a solution of D3 (233 mg, 1.05 mmol) and MeD4OH (13.1 mg, 41.9 mL, 1 equiv) in dry Et_2O (582 μL) under an argon atmosphere to initiate the polymerization at ambient temperature (24–26 °C). Aliquots of the reaction mixture (approximately 70 mg each, 139 mg in total) were taken twice and mixed with a small amount of benzoic acid; the aliquots were subjected to ^1H NMR analysis to determine the conversion of monomer and to SEC to analyze the molar-mass distribution of the crude product. After 17 h 40 min, V3 (223 mg, 0.863 mmol) was added to the reaction mixture at ambient temperature. After 15 min, dry pyridine (10.8 μL, 134 μmol, 3.2 equiv) and $ClCH_2SiMe_2Cl$ (11.0 μL, 83.9 μmol, 2.0 equiv) were added to the reaction mixture to end-cap the propagating polymers. The reaction mixture was concentrated under reduced pressure. The obtained oil was

washed with MeCN (5 mL) four times. The residual solvent was thoroughly removed from the product *in vacuo*. The residue was dissolved in toluene (5 mL) and again concentrated *in vacuo* to obtain α-trimethylsilyl-ω-(chloromethyl)dimethylsilyl-terminated PDMS-*block*-PMVS (215 mg, 63.5% yield, $M_{n,NMR}$ = 9.81 kDa, $Đ_M$ = 1.10$_3$) as a colorless liquid. ^{1}H and ^{29}Si{^{1}H} NMR spectra of the product are shown in Fig. S26.

Determination of the height of the shoulder/peak in the high-molar-mass region (h_c) of the molar-mass distributions of the polysiloxanes (Tables 1–4)

A shoulder/peak was observed in the high-molar-mass region of the molar-mass distributions of the polysiloxanes obtained in this study. The chromatograms obtained by SEC were converted into graphs of the molar-mass distribution. The molar mass of standard polystyrenes (M_{PS}) calculated from the elution time was used as the *x*-axis. The observed RI value (Δn) divided by M_{PS} was used for the *y*-axis. The *y*-axis of the resulting curve was normalized so that the highest point of the molar-mass distribution was 100 mol%. The h_c value was determined as shown in the following example.

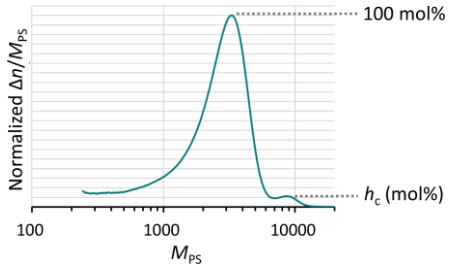


Fig. S1. Determination of h_c (mol%) for polysiloxanes from their molar-mass distributions, which were estimated from SEC measurements using toluene as the eluent, narrowly dispersed polystyrene standards, and an RI detector.

The apparent rate coefficient of condensation ($k_{c,app}$) for a given polymerization was calculated by dividing the h_c (mol%) value by the polymerization time (h).

Influence of the solvent on the polymerization kinetics of D3 using MeD4OH as the initiator and TMnPG as the catalyst (Table 1)

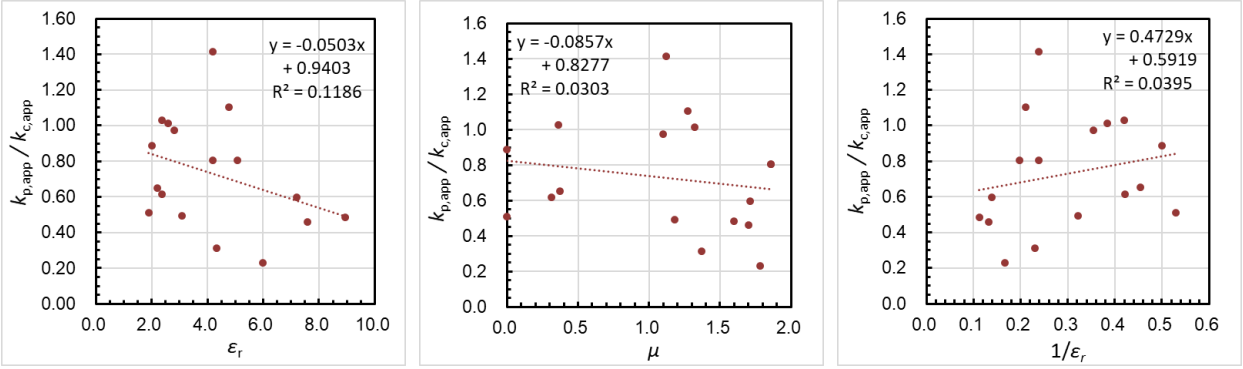


Fig. S2. Correlation of $k_{p,app}/k_{c,app}$ with the (a) relative permittivity (ε_r) of the solvents, (b) dipole moment of the solvents (μ), and (c) $1/\varepsilon_r$ values of the solvents in the polymerization of D3 using MeD4OH as the initiator and TMnPG as the catalyst.

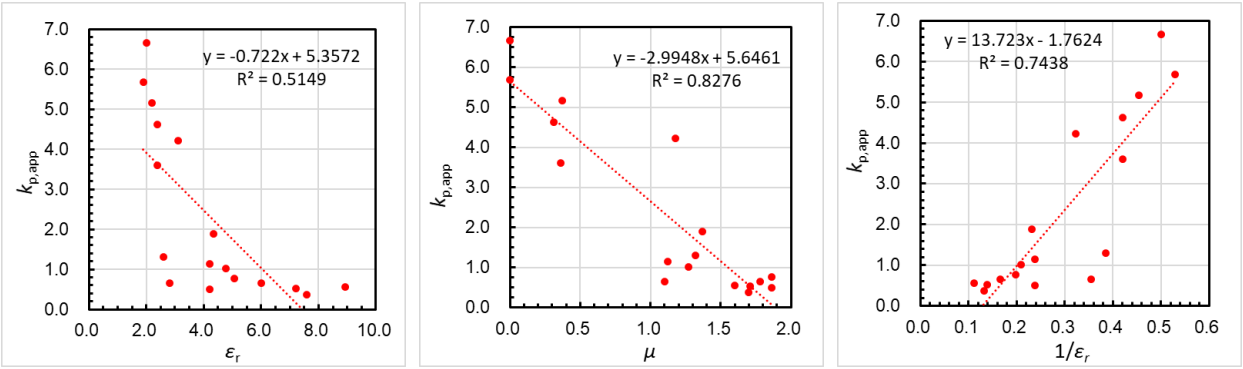


Fig. S3. Correlation of the apparent rate coefficients of propagation ($k_{p,app}$) with the (a) relative permittivity (ε_r) of the solvents, (b) dipole moment of the solvents (μ), and (c) $1/\varepsilon_r$ values of the solvents in the polymerization of D3 using MeD4OH as the initiator and TMnPG as the catalyst.

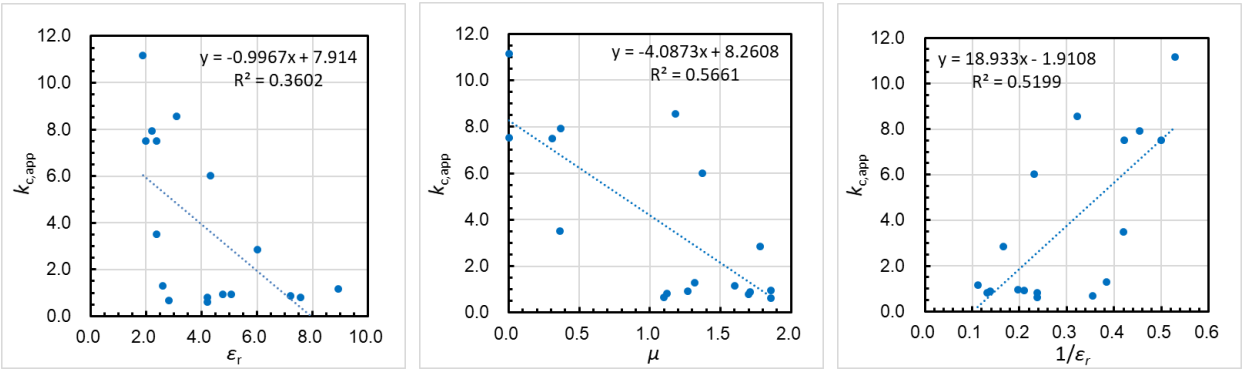


Fig. S4. Correlation of the apparent rate coefficients of condensation ($k_{c,app}$) with the (a) relative permittivity (ε_r) of the solvents, (b) dipole moment of the solvents (μ), and (c) $1/\varepsilon_r$ values of the solvents in the polymerization of D3 using MeD4OH as the initiator and TMnPG as the catalyst.

Determination of $M_{n,NMR}$ using ^{1}H NMR spectroscopy.

The M_n ($M_{n,NMR}$) values of the synthesized polysiloxanes were determined using ^{1}H NMR spectroscopy.

For Me_3SiO-PDMS-OH (Table 1–3), the integral values of peak h (I_h) and peaks a–g ($I_{a–g}$) in Fig. S5 were compared. $M_{n,NMR} = 74.154[(I_h + I_{a–g} - I_h/2) / I_h] + 90.20$

For Me_3SiO-PDMS-$OSiMe_2Vi$ (Table 3, Entries 1 and 3), the integral values of peak e (I_e) and peaks b–d ($I_{b–d}$) in Fig. 3 were compared. $M_{n,NMR} = 74.154(I_{b–d} / I_e) + 174.39$

For Et_3SiO-PDMS-$OSiMe_2Vi$ (Table 3, Entry 2), the integral values of peak b (I_b) and peaks c–e ($I_{c–e}$) in Fig. S6 were compared. $M_{n,NMR} = 74.154(I_{b–d} / I_e) + 216.47$

For Me_2PhSiO-PDMS-$OSiMe_2Vi$ (Table 3, Entry 4), the integral values of peak d (I_d) and peaks e–h ($I_{e–h}$) in Fig. S8 were compared. $M_{n,NMR} = 74.154(I_{e–h} / I_d) + 236.46$

For $MePh_2SiO$-PDMS-$OSiMe_2Vi$ (Table 3, Entry 5), the integral values of peak d (I_d) and peaks e–g ($I_{e–g}$) in Fig. S9 were compared. $M_{n,NMR} = 74.154(I_{e–g} / 2I_d) + 298.53$

For Ph_3SiO-PDMS-$OSiMe_2Vi$ (Table 3, Entry 6) the integral values of peak d (I_d) and peaks d–i ($I_{d–i}$) in Fig. S10 were compared. $M_{n,NMR} = 74.154(I_{d–i} / I_e) + 360.60$

For $(Me_3SiO)_2SiMeO$-PDMS-$OSiMe_2Vi$ (Table 3, Entry 7), the integral values of peak a (I_a) and peaks c–e ($I_{c–e}$) in Fig. S11 were compared. $M_{n,NMR} = 74.154(I_{c–e} / (I_a/3)) + 322.70$

For $(Me_3SiO)_3SiO$-PDMS-$OSiMe_2Vi$ (Table 3, Entry 8), the integral values of peak a (I_a) and peaks b–c ($I_{b–c}$) in Fig. S12 were compared. $M_{n,NMR} = 74.154(I_{b–c} / (2I_a/9)) + 396.85$

For $ViSiMe_2O$-PDMS-$OSiMe_2H$ (Table 3, Entry 9), the integral values of peak d (I_d) and peaks e–f ($I_{e–f}$) in Fig. S13 were compared. $M_{n,NMR} = 74.154(I_{e–f} / I_d) + 160.30$

For ViSiMePhO-PDMS-$OSiMe_2H$ (Table 3, Entry 10), the integral values of peak g (I_g) and peaks h–j ($I_{h–j}$) in Fig. S14 were compared. $M_{n,NMR} = 74.154(I_{h–j} / 2I_g) + 222.43$

For $ClCH_2SiMe_2O$-PDMS-$OSiMe_2H$ (Table 3, Entry 11), the integral values of peak b (I_b) and peaks c–d ($I_{c–d}$) in Fig. S15 were compared. $M_{n,NMR} = 74.154(I_{c–d} / I_b) + 182.79$

For $MACH_2SiMe_2O$-PDMS-$OSiMe_2CH_2Cl$ (Table 3, Entry 12), the integral values of peak e (I_e) and peaks f–h ($I_{f–h}$) in Fig. S16 were compared. $M_{n,NMR} = 74.154(I_{f–h} / I_e) + 280.90$

For $MAPrSiMe_2O$-PDMS-$OSiMe_2H$ (Table 3, Entry 13), the integral values of peak g (I_g) and peaks h–j ($I_{h–j}$) in Fig. S17 were compared. $M_{n,NMR} = 74.154(I_{h–j} / I_g) + 260.48$

For HSiMe2O-PDMS-OSiMe2Vi (Table 3, Entry 14), the integral values of peak b (I_b) and peaks c–d ($I_{c–d}$) in Fig. S18 were compared. $M_{n,NMR} = 74.154(I_{c–d} / I_b) + 160.30$

For Me_3SiO-$(SiMe_2O)_3$-PMVS-OH (Table 4, Entries 1 and 2), the integral values of peak a (I_a) and peaks e, i, and j ($I_{e,i,j}$) in Fig. S19 were compared. $M_{n,NMR} = 86.165(I_{e,i,j} / (I_a/3)) + 312.66$

For Me_3SiO-PMVS-OH (Table 4, Entries 1 and 2), the integral values of peak d (I_d) and peaks e, g, and h ($I_{e,g,h}$) in Fig. S20 were compared. $M_{n,NMR} = 86.165(I_{e,g,h} / (I_d/3)) + 90.20$

For Ph_3SiO-PMVS-OH (Table 4, Entry 4), the integral values of peak d (I_d) and peaks d–f, j, and k ($I_{d–f,j,k}$) in Fig. S21 were compared. $M_{n,NMR} = 86.165(I_{d–f,j,k} / I_d) + 276.41$

For MePhViSiO-PMVS-$SiMe_2$Allyl (Table 4, Entry 5), the integral values of peak g (I_g) and peak h (I_h) in Fig. S22 were compared. $M_{n,NMR} = 86.165(I_h / I_g) + 262.50$

For $ClCH_2SiMe_2O$-$(SiMe_2O)_3$-PMVS-$SiMe_2$CH2Cl (Table 4, Entry 6), the integral values of peaks b and j ($I_{b,j}$) and peaks f (I_f) in Fig. S23 were compared. $M_{n,NMR} = 86.165(I_f / (I_{b,j}/4)) + 453.73$

For $MACH_2SiMe_2O$-PMVS-$OSiMe_2CH_2Cl$ (Table 4, Entry 7), the integral values of peak j (I_j) and peak f (I_f) in Fig. S24 were compared. $M_{n,NMR} = 86.165(I_f / (I_j/2)) + 280.90$

For $MAPrSiMe_2O$-PMVS-$OSiMe_2CH_2Cl$ (Table 4, Entry 8), the integral values of peak g (I_g) and peak h (I_h) in Fig. S25 were compared. $M_{n,NMR} = 86.165(I_h / (I_g/2)) + 308.95$

For α-trimethylsilyl-ω-chloromethyldimethylsilyl-terminated PDMS-*block*-PMVS (Table 4, Entry 9b), the integral values of peak h (I_h), peaks a–c ($I_{a–c}$), and peak d (I_d) in Fig. S26 were compared. $M_{n,NMR} = 74.154(2I_{a–c} / I_h) + 86.165(2I_d / I_h) + 196.82$

Characterization of the obtained PDMS and PMVS

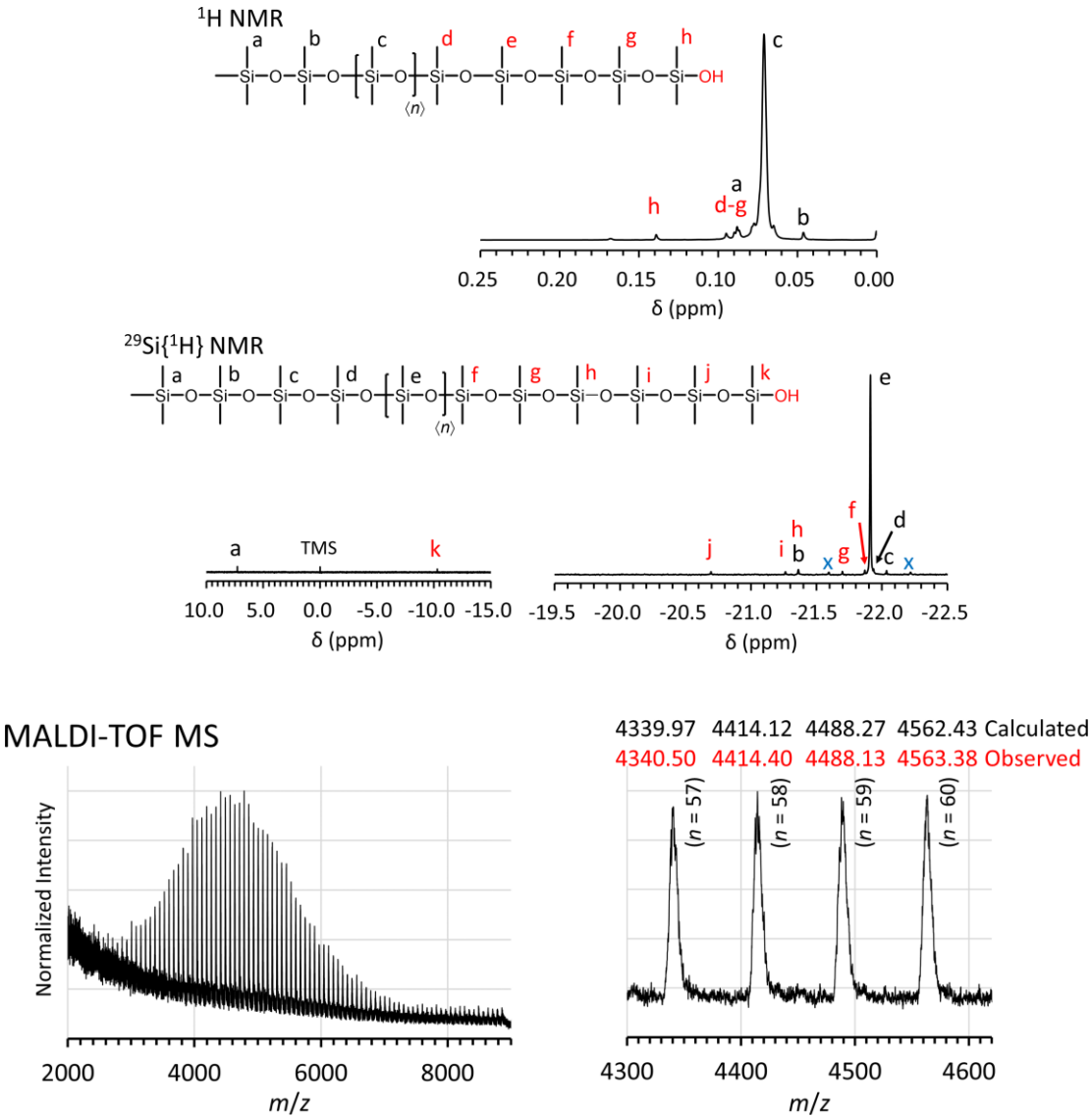


Fig. S5: ^{1}H NMR (600 MHz, in $CDCl_3$) and $^{29}Si\{^{1}H\}$ NMR (119 MHz, in $CDCl_3$) spectra of the PDMS ($M_{n,NMR}$ = 6.44 kg mol^{-1}, $Đ_M$ = 1.12$_6$) synthesized using D3 and MeD4OH.

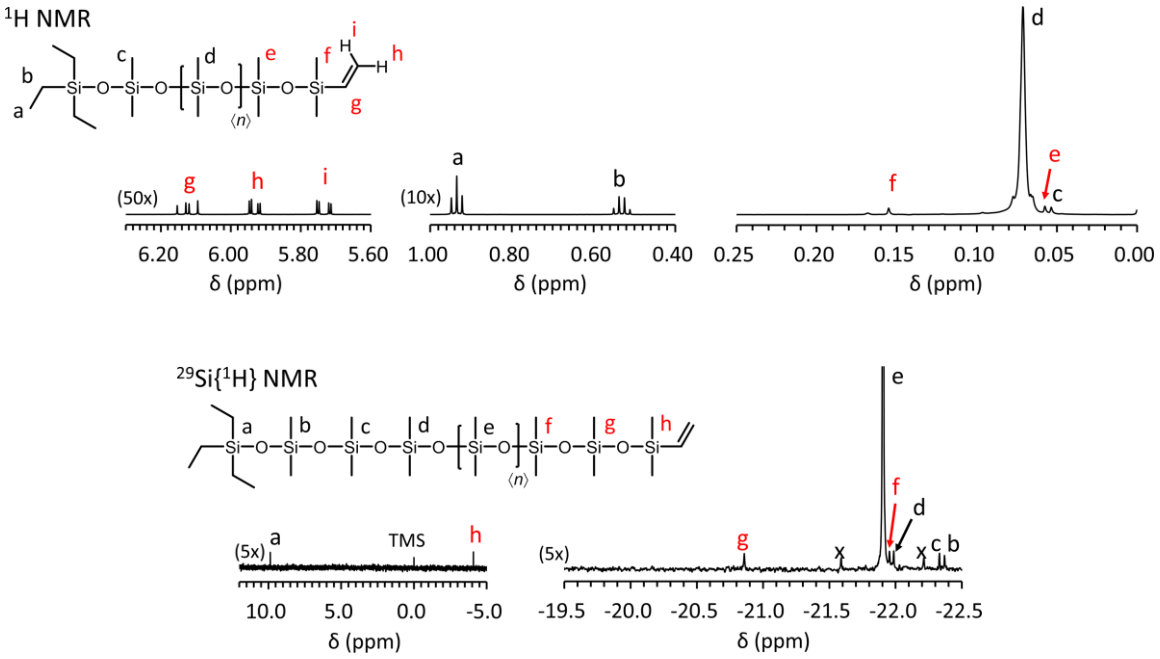


Fig. S6: ^{1}H NMR (600 MHz, in $CDCl_3$) and ^{29}Si{^{1}H} NMR (119 MHz, in $CDCl_3$) spectra of the PDMS ($M_{n,NMR}$ = 6.12 kg mol^{-1}, $Đ_M$ = 1.24$_5$) synthesized using D3, Et_3SiOH, and $Me_2ViSiCl$.

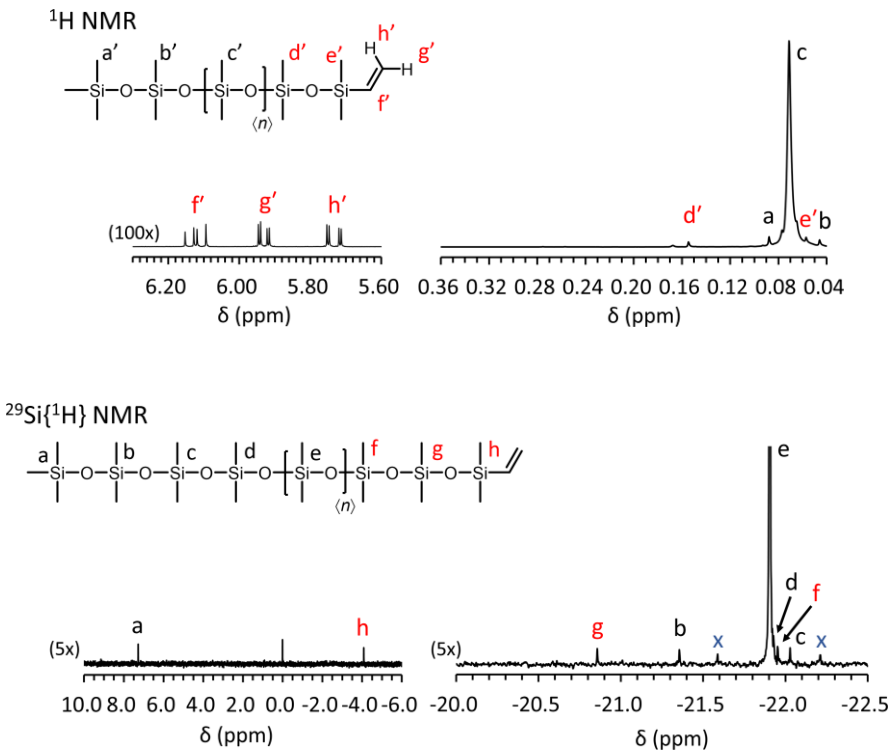


Fig. S7: ^{1}H NMR (600 MHz, in $CDCl_3$) and $^{29}Si\{^{1}H\}$ NMR (119 MHz, in $CDCl_3$) spectra of the PDMS ($M_{n,NMR}$ = 7.22 kg mol^{-1}, $Đ_M$ = 1.11$_1$) synthesized using D3, Et_3SiOH, and $Me_2ViSiCl$.

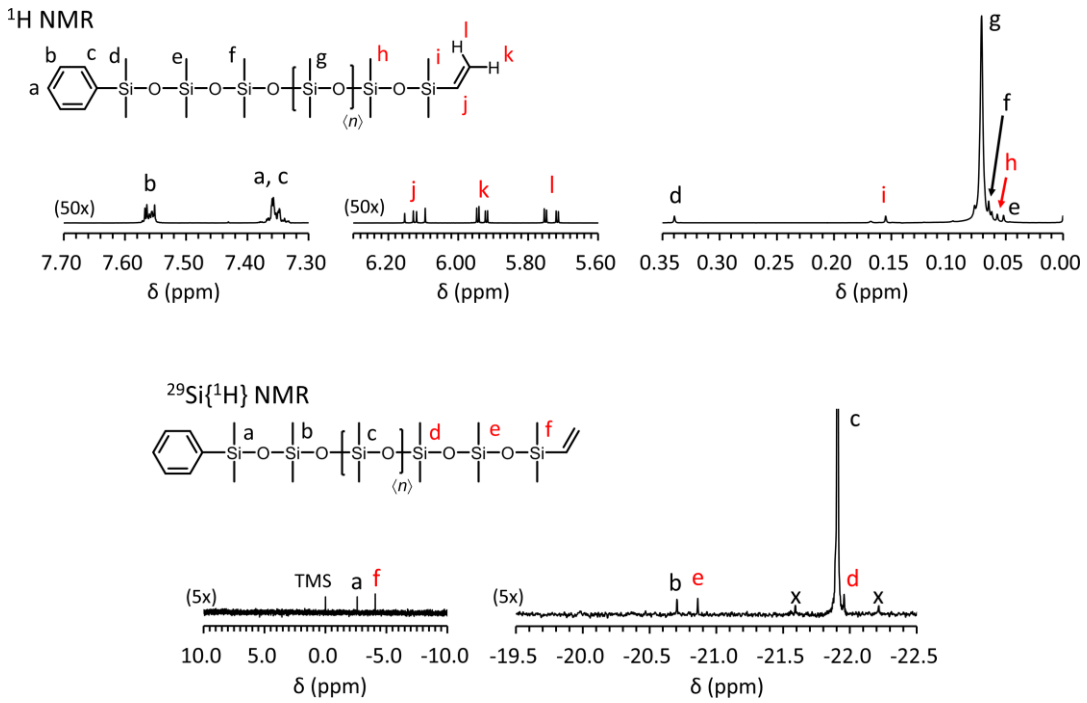


Fig. S8: ^{1}H NMR (600 MHz, in $CDCl_3$) and $^{29}Si\{^{1}H\}$ NMR (119 MHz, in $CDCl_3$) spectra of the PDMS ($M_{n,NMR}$ = 6.27 kg mol^{-1}, $Đ_M$ = 1.09$_0$) synthesized using D3, $Me_2PhSiOH$, and $Me_2ViSiCl$.

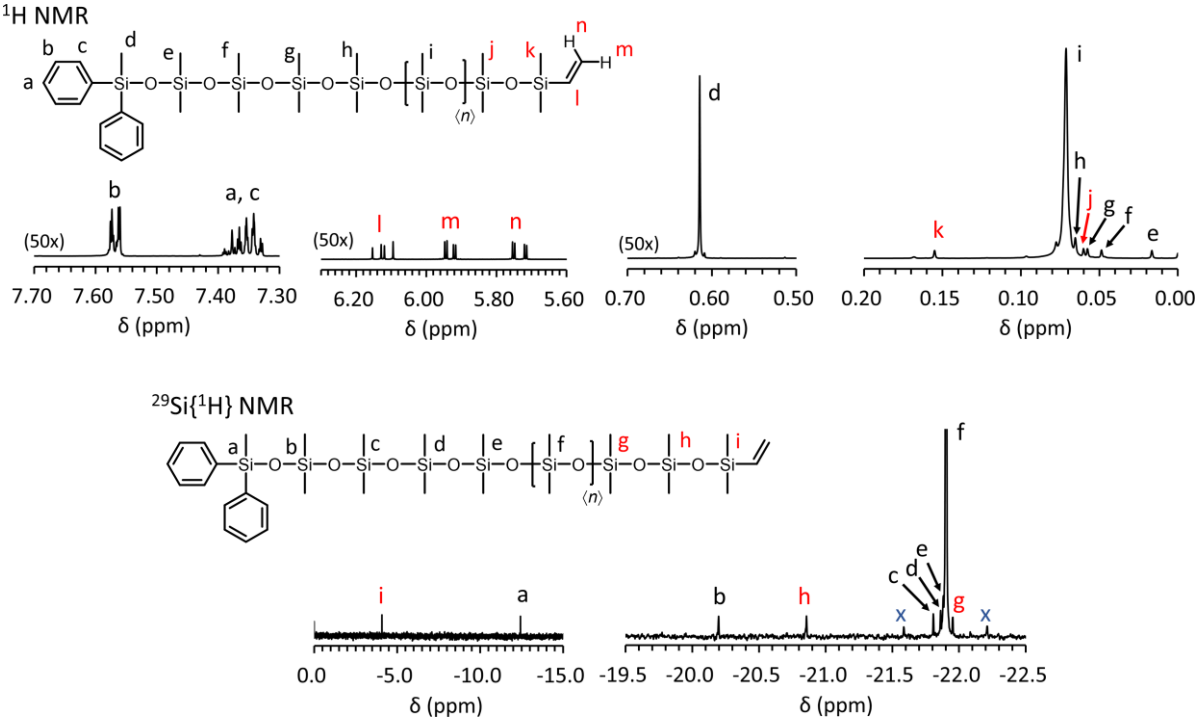


Fig. S9: ^{1}H NMR (600 MHz, in $CDCl_3$) and ^{29}Si{^{1}H} NMR (119 MHz, in $CDCl_3$) spectra of the PDMS ($M_{n,NMR}$ = 5.73 kg mol^{-1}, $Đ_M$ = 1.09$_5$) synthesized using D3, $MePh_2SiOH$, and $Me_2ViSiCl$.

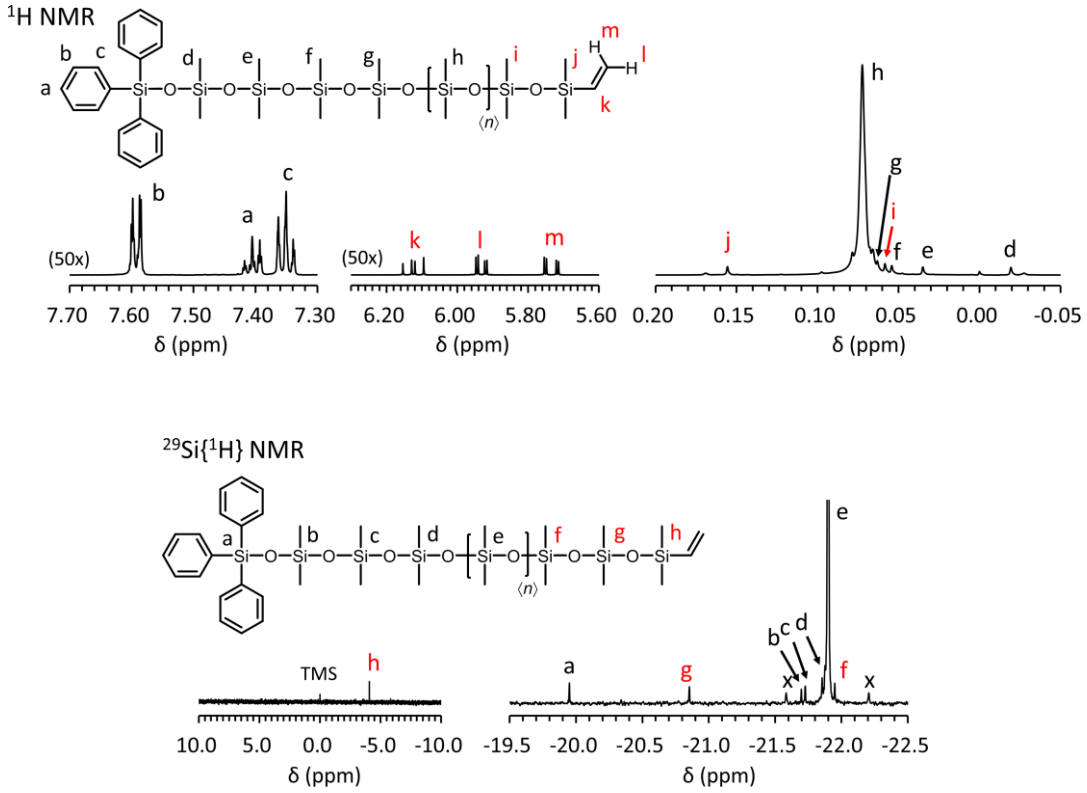


Fig. S10: ^{1}H NMR (600 MHz, in $CDCl_3$) and ^{29}Si{^{1}H} NMR (119 MHz, in $CDCl_3$) spectra of the PDMS ($M_{n,NMR}$ = 5.42 kg mol^{-1}, $Đ_M$ = 1.08$_1$) synthesized using D3, Ph_3SiOH, and $Me_2ViSiCl$.

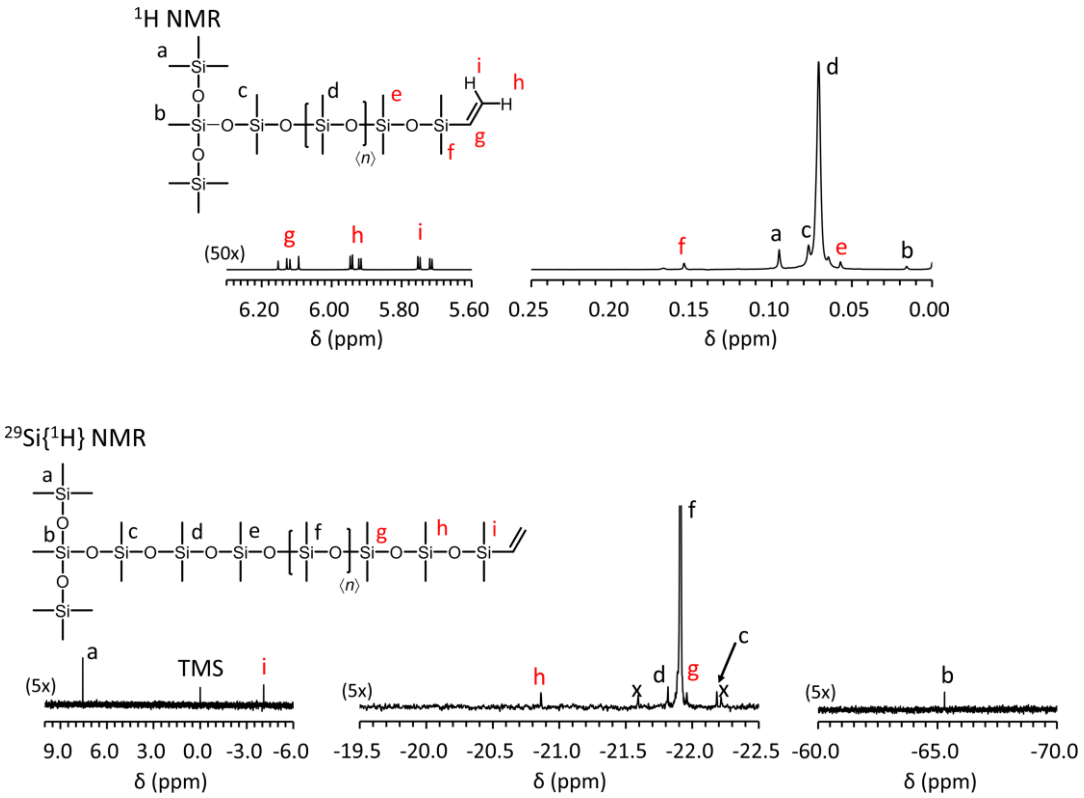


Fig. S11: H NMR (600 MHz, in $CDCl_3$) and $^{29}Si\{^1H\}$ NMR (119 MHz, in $CDCl_3$) spectra of the PDMS ($M_{n,NMR}$ = 5.95 kg mol^{-1}, $Đ_M$ = 1.11$_3$) synthesized using D3, T-Silanol, and $Me_2ViSiCl$.

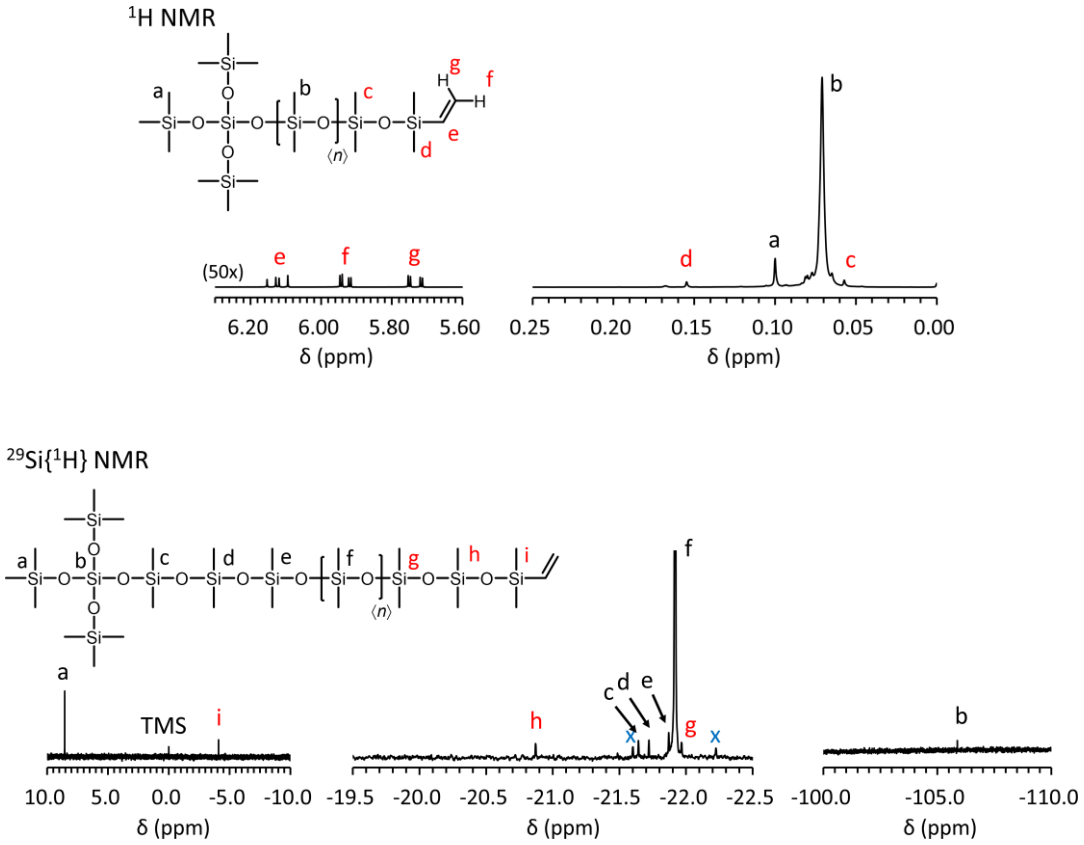


Fig. S12: ^{1}H NMR (600 MHz, in $CDCl_3$) and ^{29}Si{^{1}H} NMR (119 MHz, in $CDCl_3$) spectra of the PDMS ($M_{n,NMR}$ = 6.88 kg mol^{-1}, $Đ_M$ = 1.13$_3$) synthesized using D3, Q-Silanol, and $Me_2ViSiCl$.

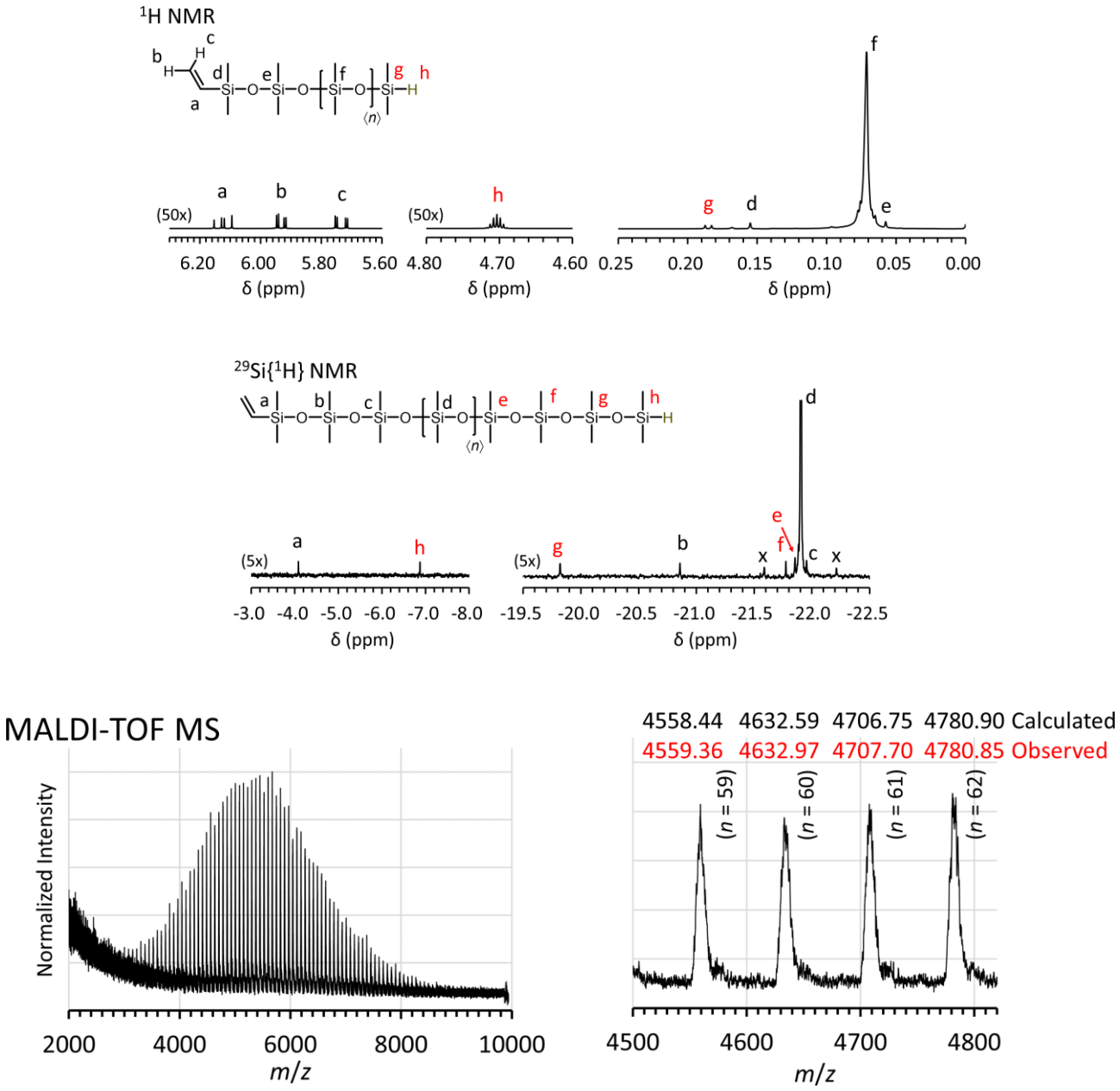


Fig. S13: ^{1}H NMR (600 MHz, in $CDCl_3$), $^{29}Si\{^{1}H\}$ NMR (119 MHz, in $CDCl_3$), and MALDI-TOF MS spectra (measured in linear mode using DCTB as the matrix and TFANa as the cationization agent) of the PDMS ($M_{n,NMR}$ = 6.50 kg mol^{-1}, $Đ_M$ = 1.12$_9$) synthesized using D3, ViD4OH, and Me_2HSiCl.

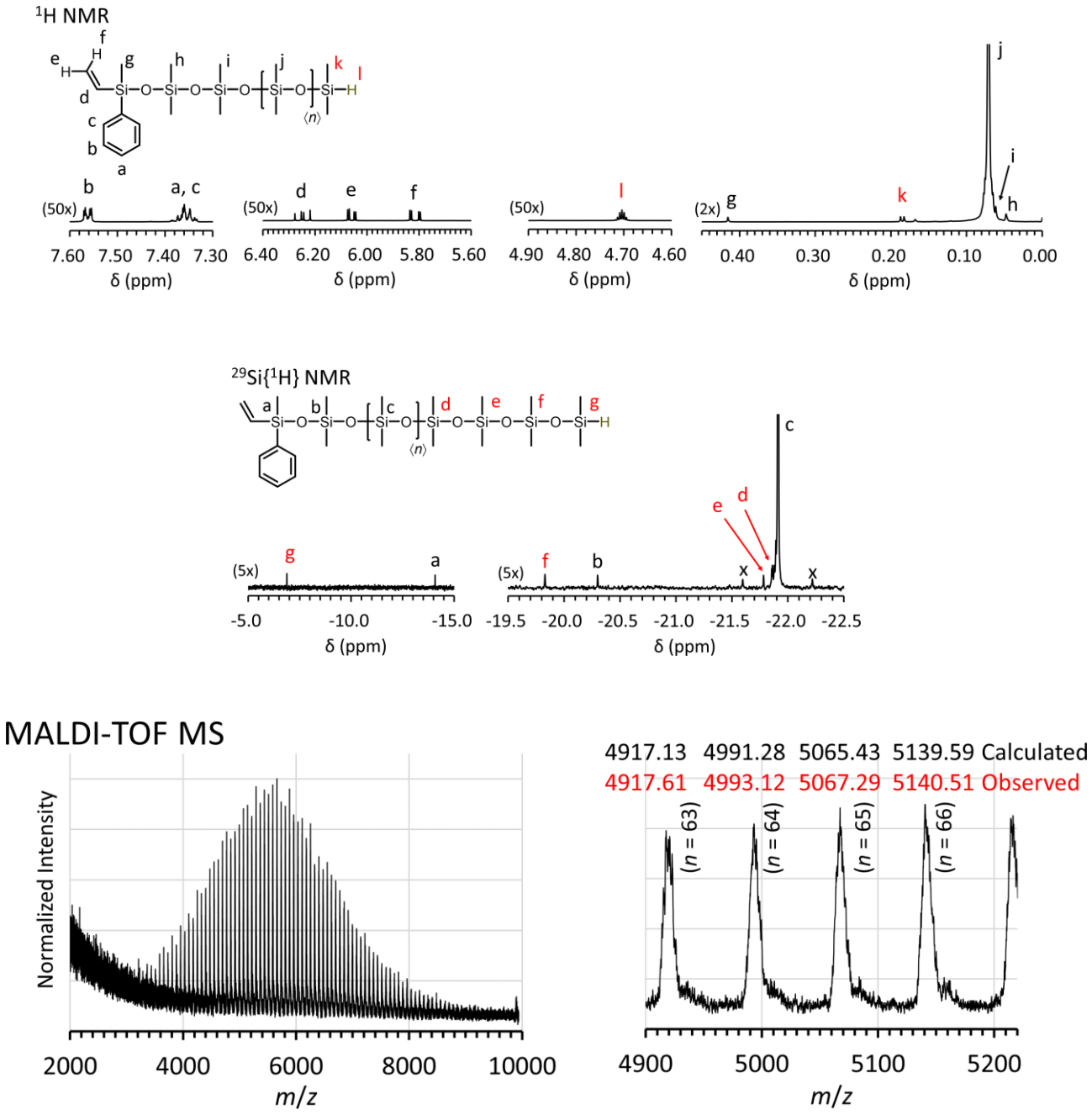


Fig. S14: ^{1}H NMR (600 MHz, in $CDCl_3$), ^{29}Si{^{1}H} NMR (119 MHz, in $CDCl_3$), and MALDI-TOF MS spectra (measured in linear mode using DCTB as the matrix and TFANa as the cationization agent) of the PDMS ($M_{n,NMR}$ = 6.62 kg mol^{-1}, $Đ_M$ = 1.10$_9$) synthesized using D3, MePhViSiOH, and Me_2HSiCl.

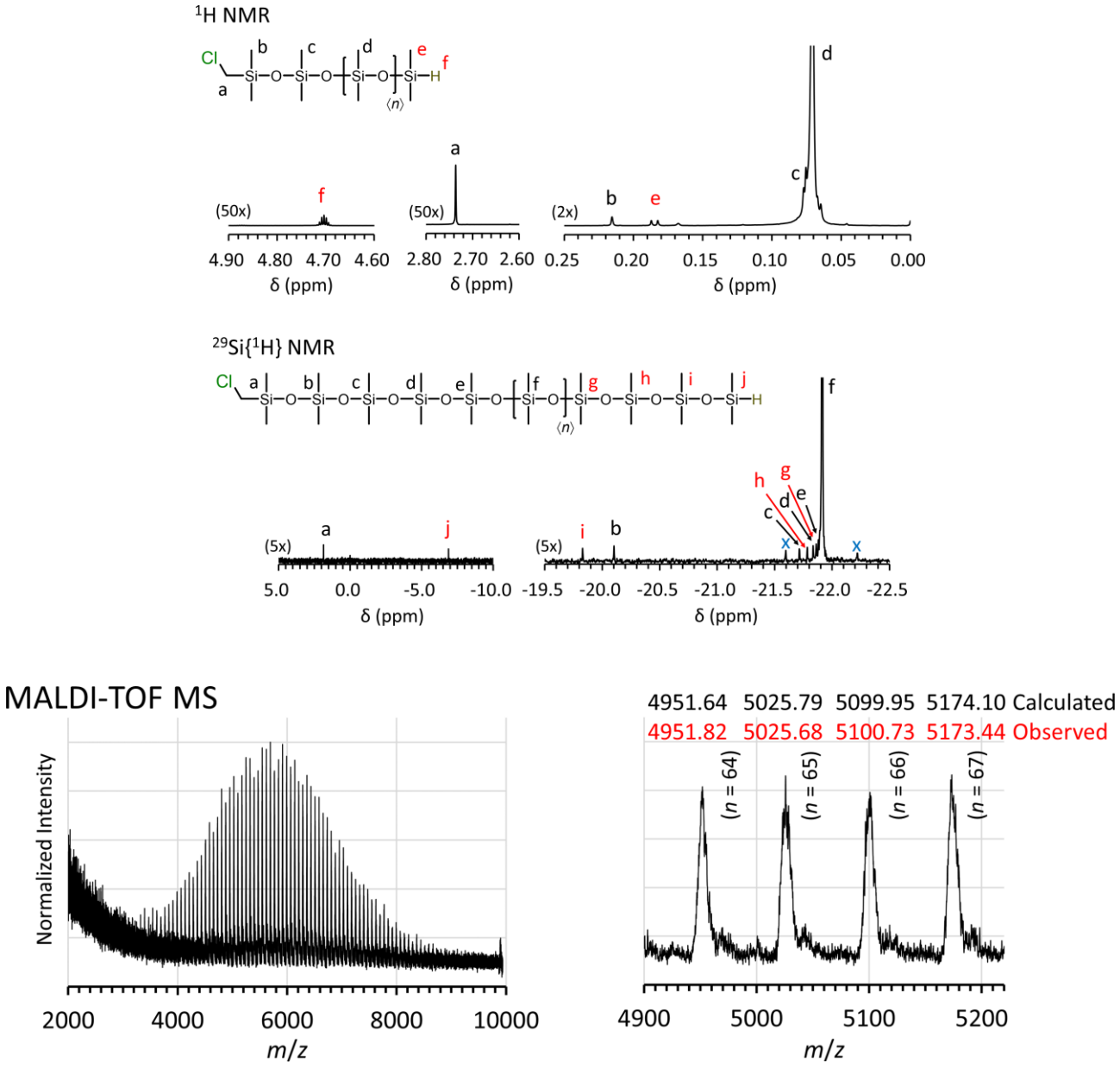


Fig. S15: ^{1}H NMR (600 MHz, in $CDCl_3$), ^{29}Si{^{1}H} NMR (119 MHz, in $CDCl_3$), and MALDI-TOF MS spectra (measured in linear mode using DCTB as the matrix and TFANa as the cationization agent) of the PDMS ($M_{n,NMR}$ = 7.06 kg mol^{-1}, $Đ_M$ = 1.12$_0$) synthesized using D3, $ClCH_2D4OH$, and Me_2HSiCl.

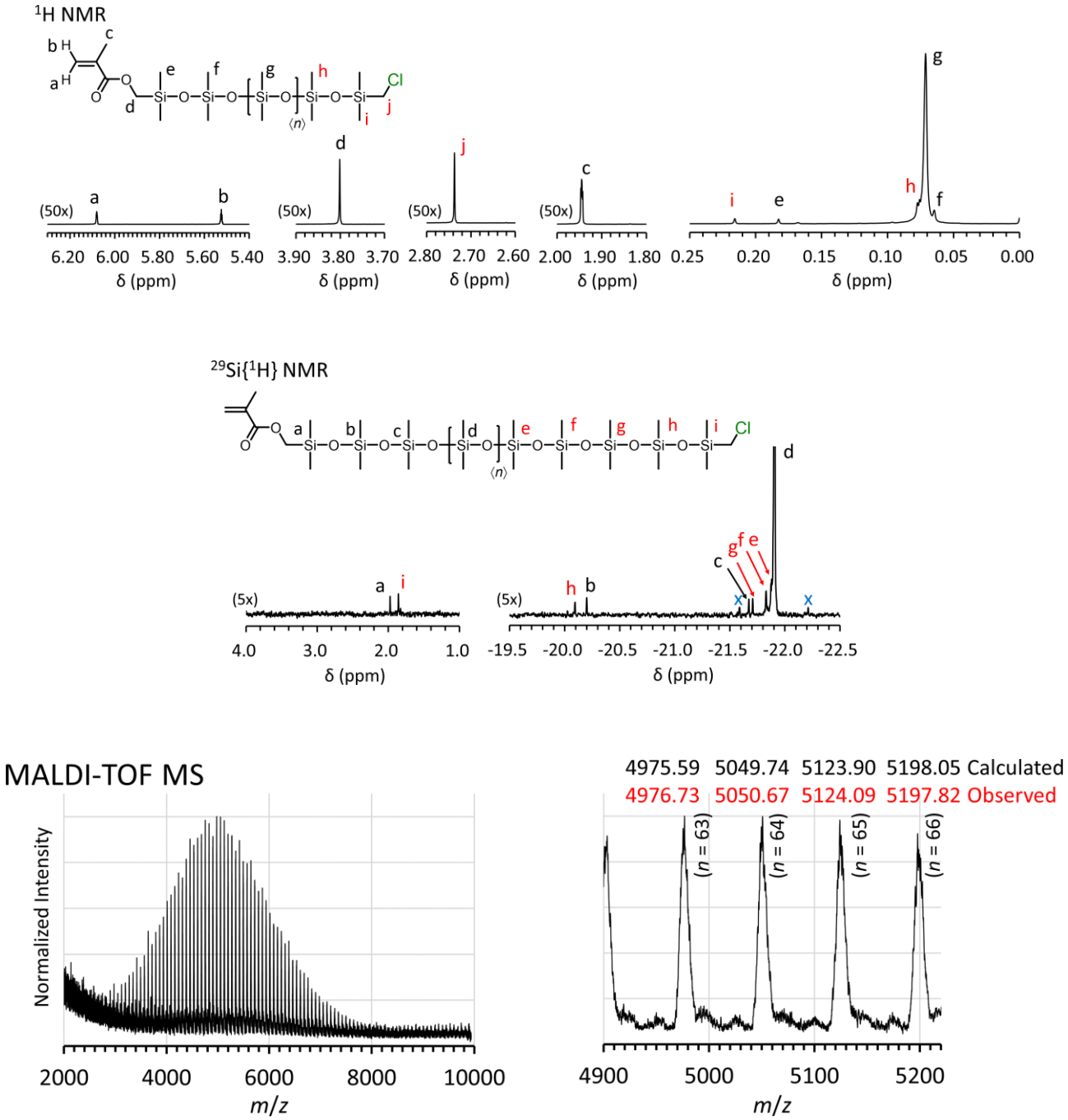


Fig. S16: ^{1}H NMR (600 MHz, in $CDCl_3$), $^{29}Si\{^{1}H\}$ NMR (119 MHz, in $CDCl_3$), and MALDI-TOF MS spectra (measured in linear mode using DCTB as the matrix and TFANa as the cationization agent) of the PDMS ($M_{n,NMR}$ = 5.70 kg mol^{-1}, $Đ_M$ = 1.18$_8$) synthesized using D3, $MACH_2SiMe_2OH$, and $ClCH_2SiMe_2Cl$.

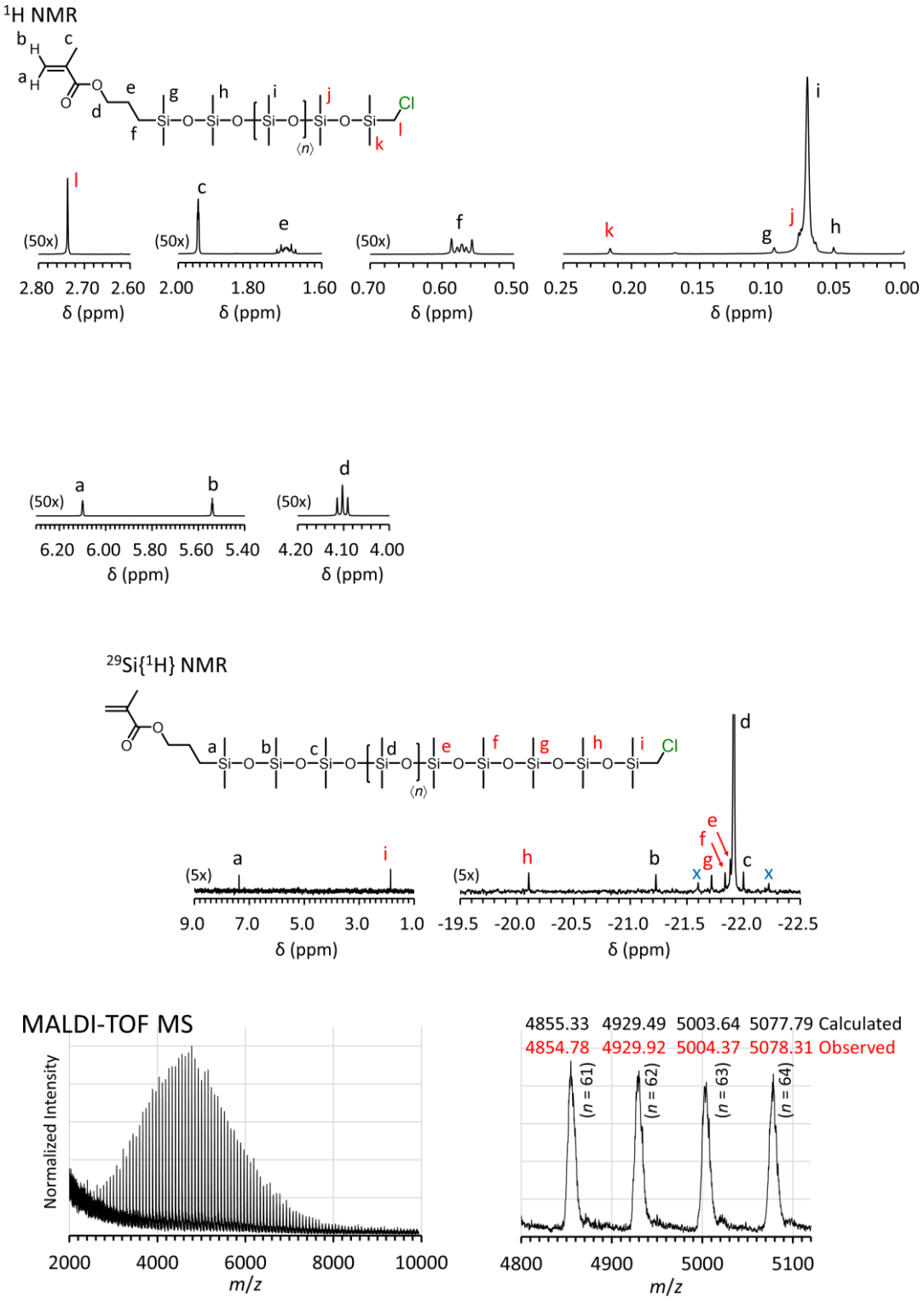


Fig. S17: ^{1}H NMR (600 MHz, in $CDCl_3$), ^{29}Si{^{1}H} NMR (119 MHz, in $CDCl_3$), and MALDI-TOF MS spectra (measured in linear mode using DCTB as the matrix and TFANa as the cationization agent) of the PDMS ($M_{n,NMR}$ = 5.37 kg mol^{-1}, $Đ_M$ = 1.10$_4$) synthesized using D3, MAPrSiMe$_2$OH, and Me$_2$HSiCl.

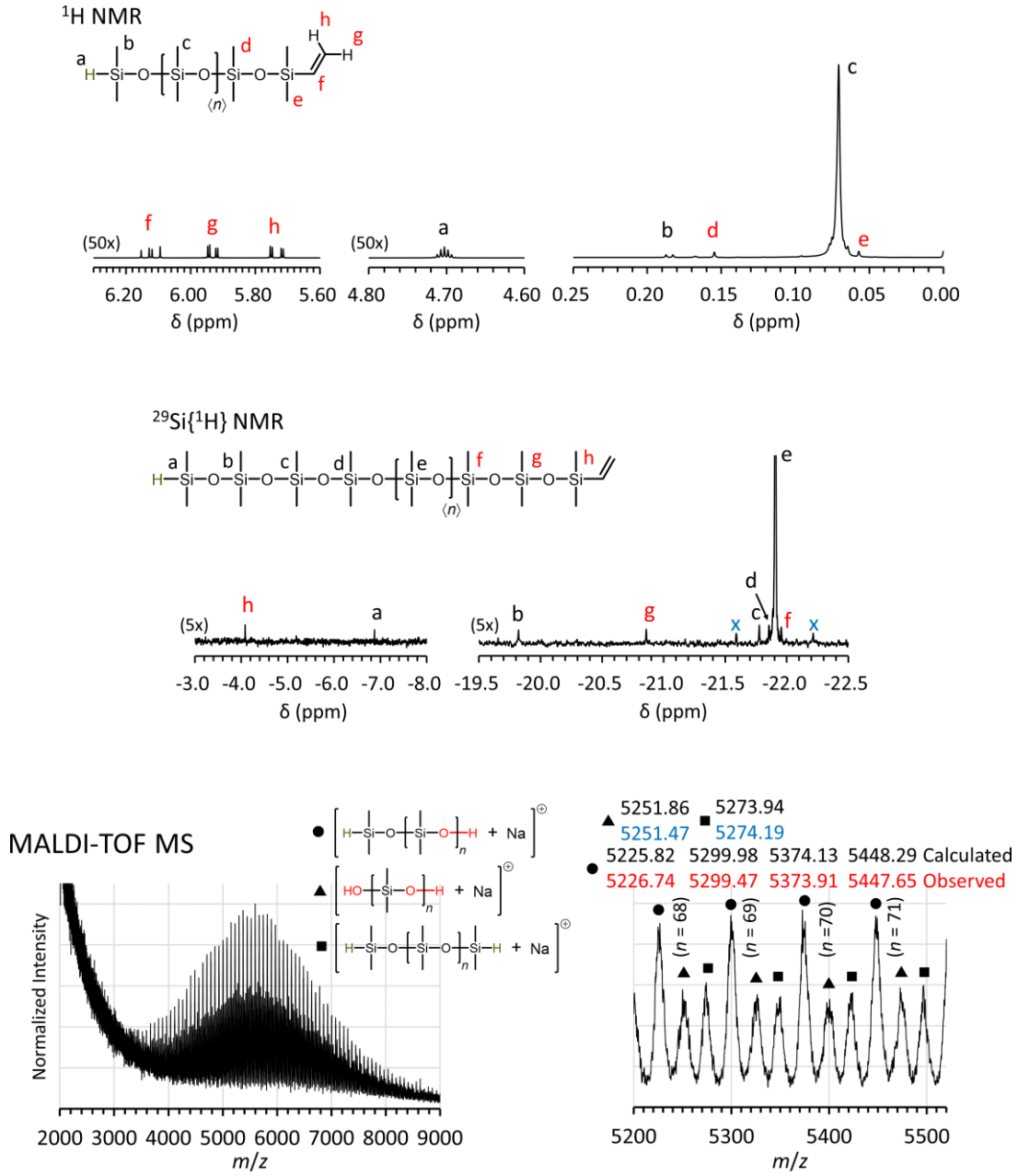


Fig. S18: ^{1}H NMR (600 MHz, in $CDCl_3$), ^{29}Si{^{1}H} NMR (119 MHz, in $CDCl_3$), and MALDI-TOF MS spectra (measured in linear mode using DCTB as the matrix and TFANa as the cationization agent) of the PDMS ($M_{n,NMR}$ = 6.41 kg mol^{-1}, $Đ_M$ = 1.09$_9$) synthesized using D3, HD4OH, and $Me_2ViSiCl$.

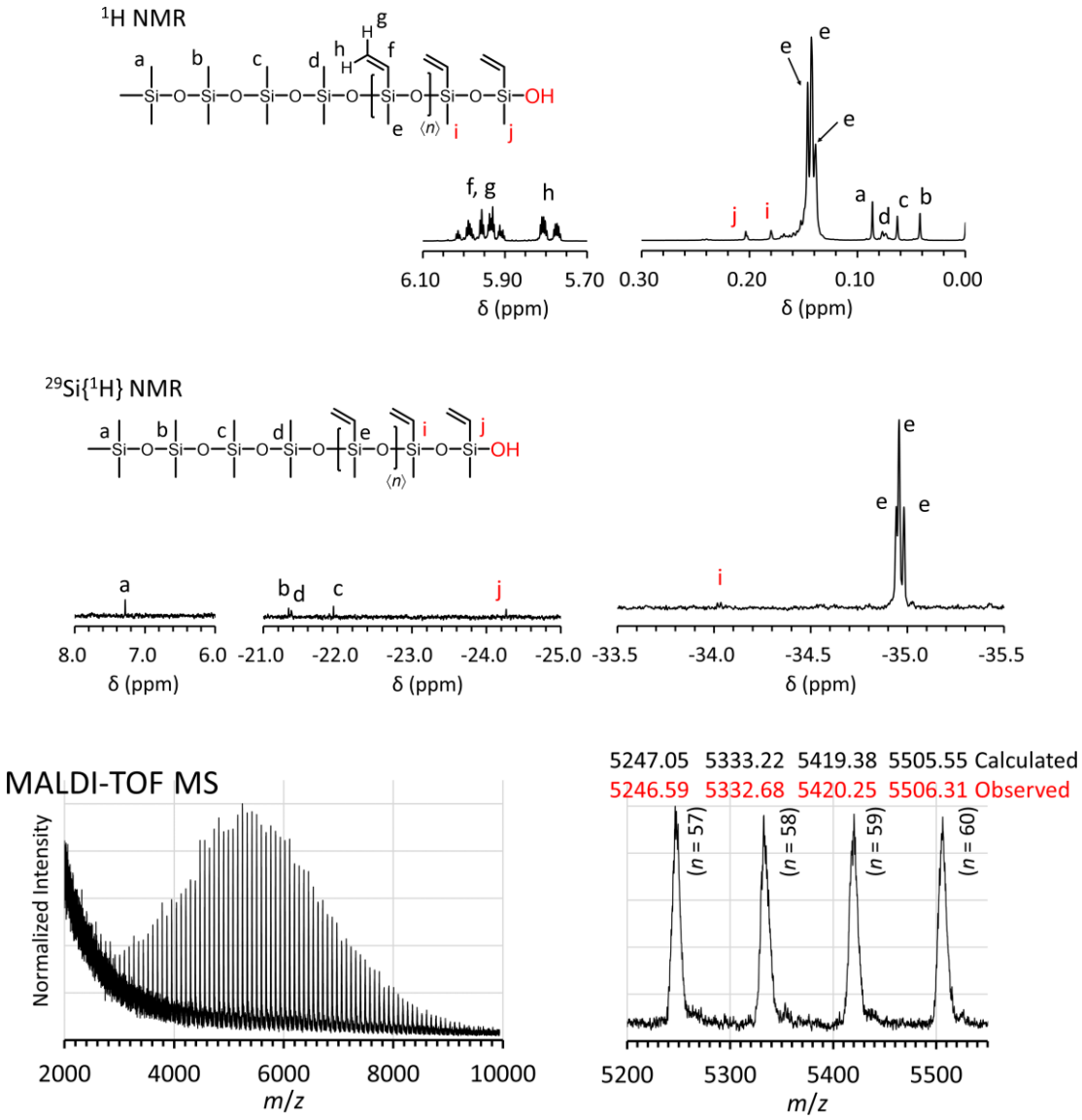


Fig. S19: ^{1}H NMR (600 MHz, in $CDCl_3$), ^{29}Si{^{1}H} NMR (119 MHz, in $CDCl_3$), and MALDI-TOF MS spectra (measured in linear mode using DCTB as the matrix and TFANa as the cationization agent) of the PMVS ($M_{n,NMR}$ = 5.66 kg mol^{-1}, $Đ_M$ = 1.12$_1$) synthesized using V3 and MeD4OH.

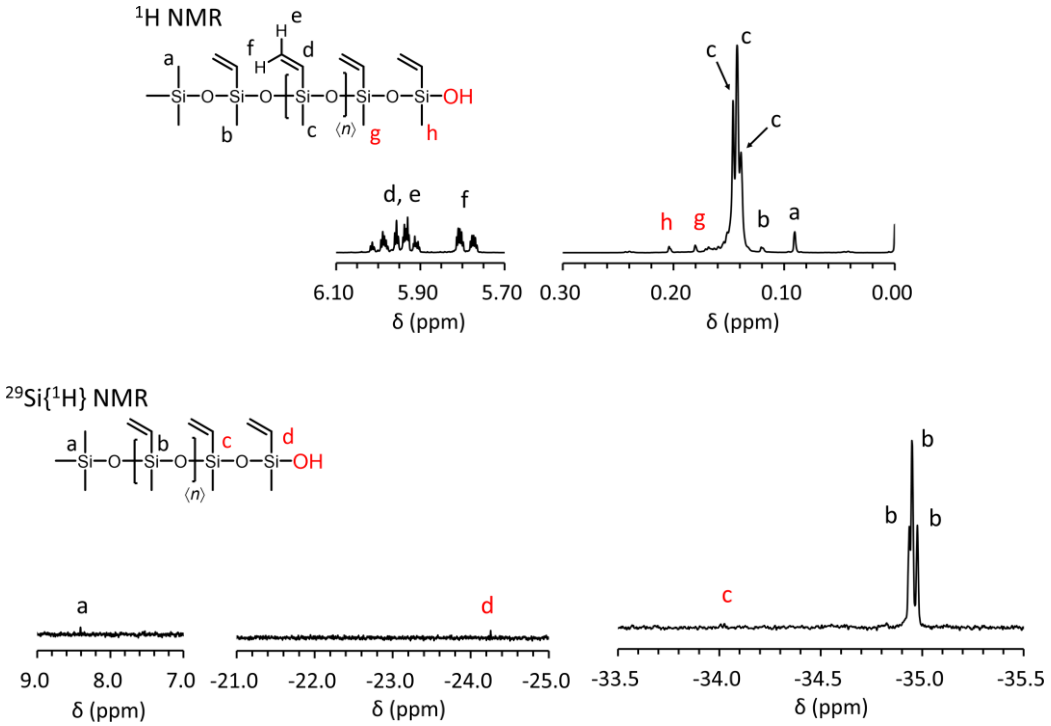


Fig. S20: ^{1}H NMR (600 MHz, in $CDCl_3$), ^{29}Si{^{1}H} NMR (119 MHz, in $CDCl_3$) of the PMVS ($M_{n,NMR}$ = 7.65 kg mol^{-1}, $Đ_M$ = 1.12$_2$) synthesized using V3 and Me_3SiOH.

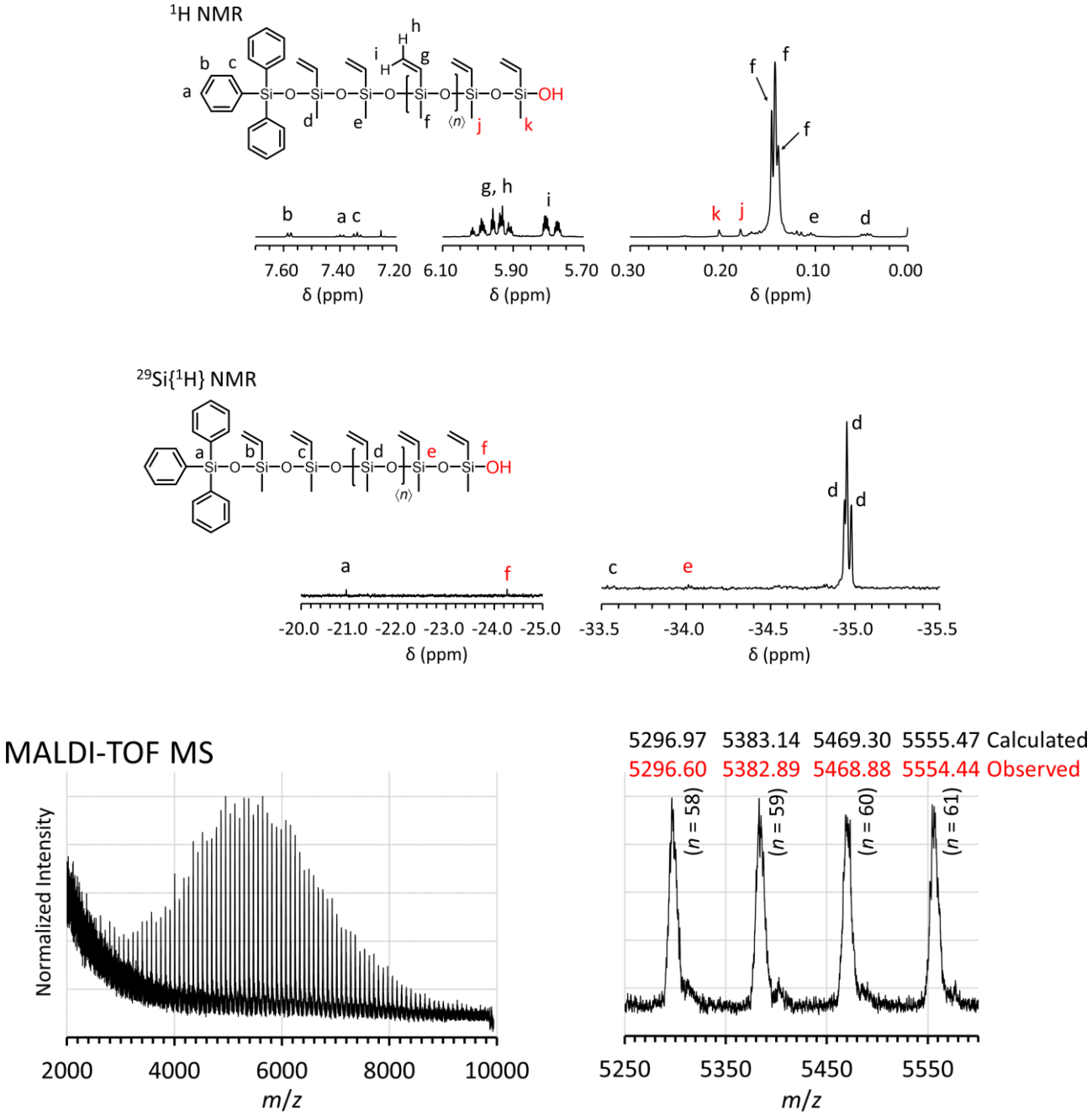


Fig. S21: ^{1}H NMR (600 MHz, in $CDCl_3$), ^{29}Si{^{1}H} NMR (119 MHz, in $CDCl_3$), and MALDI-TOF MS spectra (measured in linear mode using DCTB as the matrix and TFANa as the cationization agent) of the PMVS ($M_{n,NMR}$ = 6.76 kg mol^{-1}, $Đ_M$ = 1.09$_7$) synthesized using V3 and Ph_3SiOH.

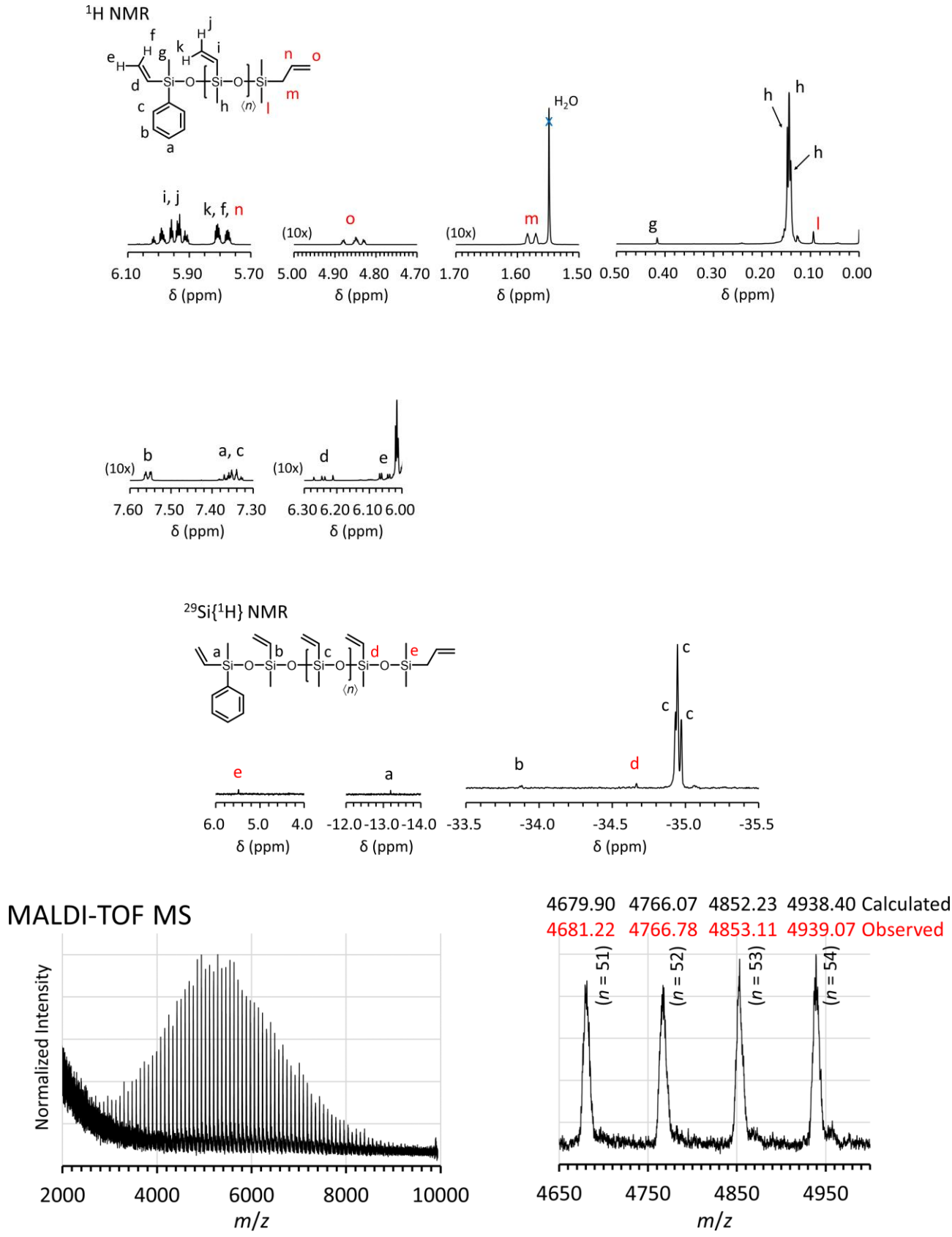


Fig. S22: ^{1}H NMR (600 MHz, in $CDCl_3$), ^{29}Si{^{1}H} NMR (119 MHz, in $CDCl_3$), and MALDI-TOF MS spectra (measured in linear mode using DCTB as the matrix and TFANa as the cationization agent) of the PMVS ($M_{n,NMR}$ = 6.45 kg mol^{-1}, $Đ_M$ = 1.10$_9$) synthesized using V3, MePhViSiOH, and AllylMe$_2$SiCl.

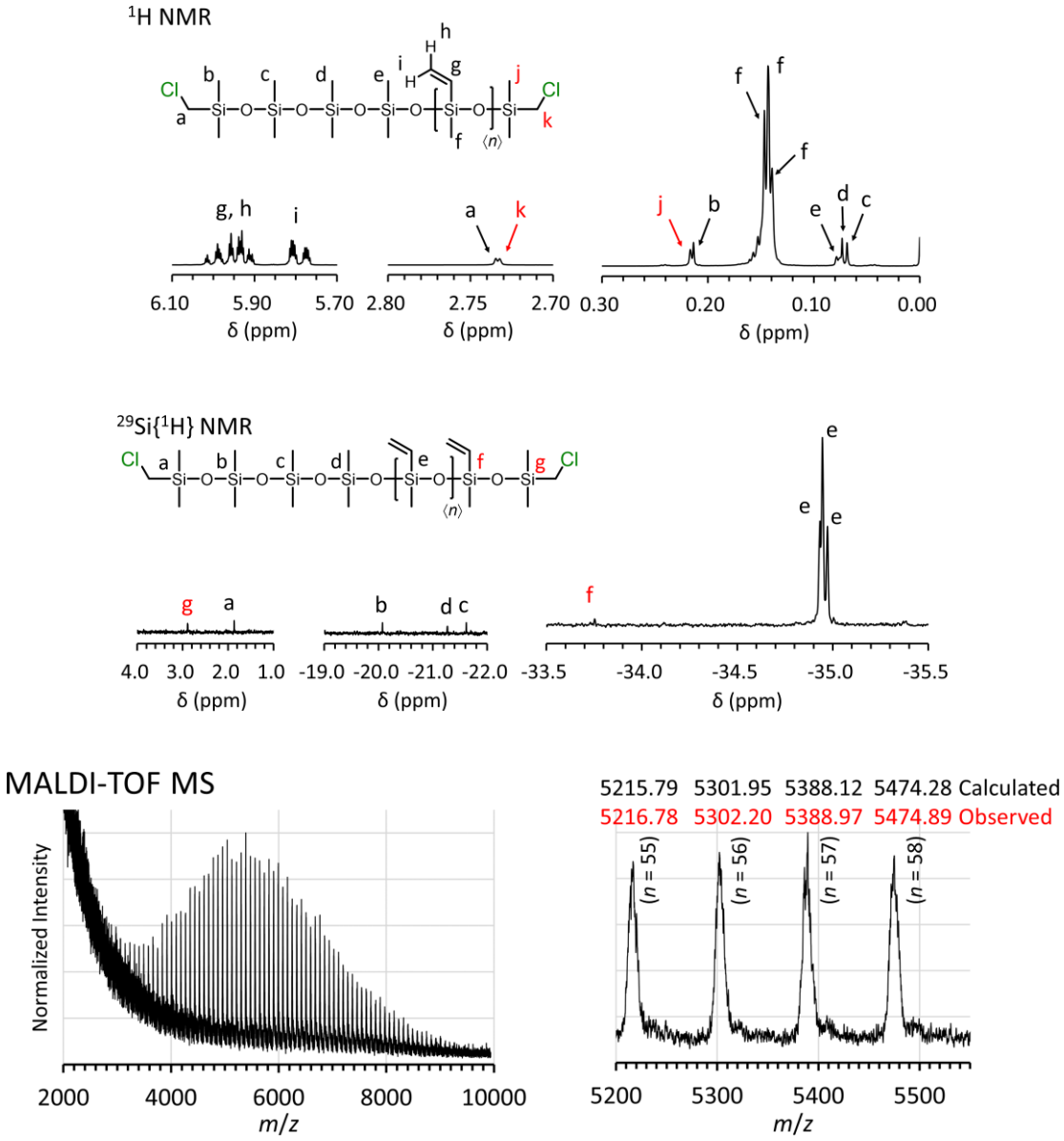


Fig. S23: ^{1}H NMR (600 MHz, in $CDCl_3$), ^{29}Si{^{1}H} NMR (119 MHz, in $CDCl_3$), and MALDI-TOF MS spectra (measured in linear mode using DCTB as the matrix and TFANa as the cationization agent) of the PMVS ($M_{n,NMR}$ = 6.74 kg mol^{-1}, $Đ_M$ = 1.10$_0$) synthesized using V3, $ClCH_2D4OH$, and $ClCH_2Me_2SiCl$.

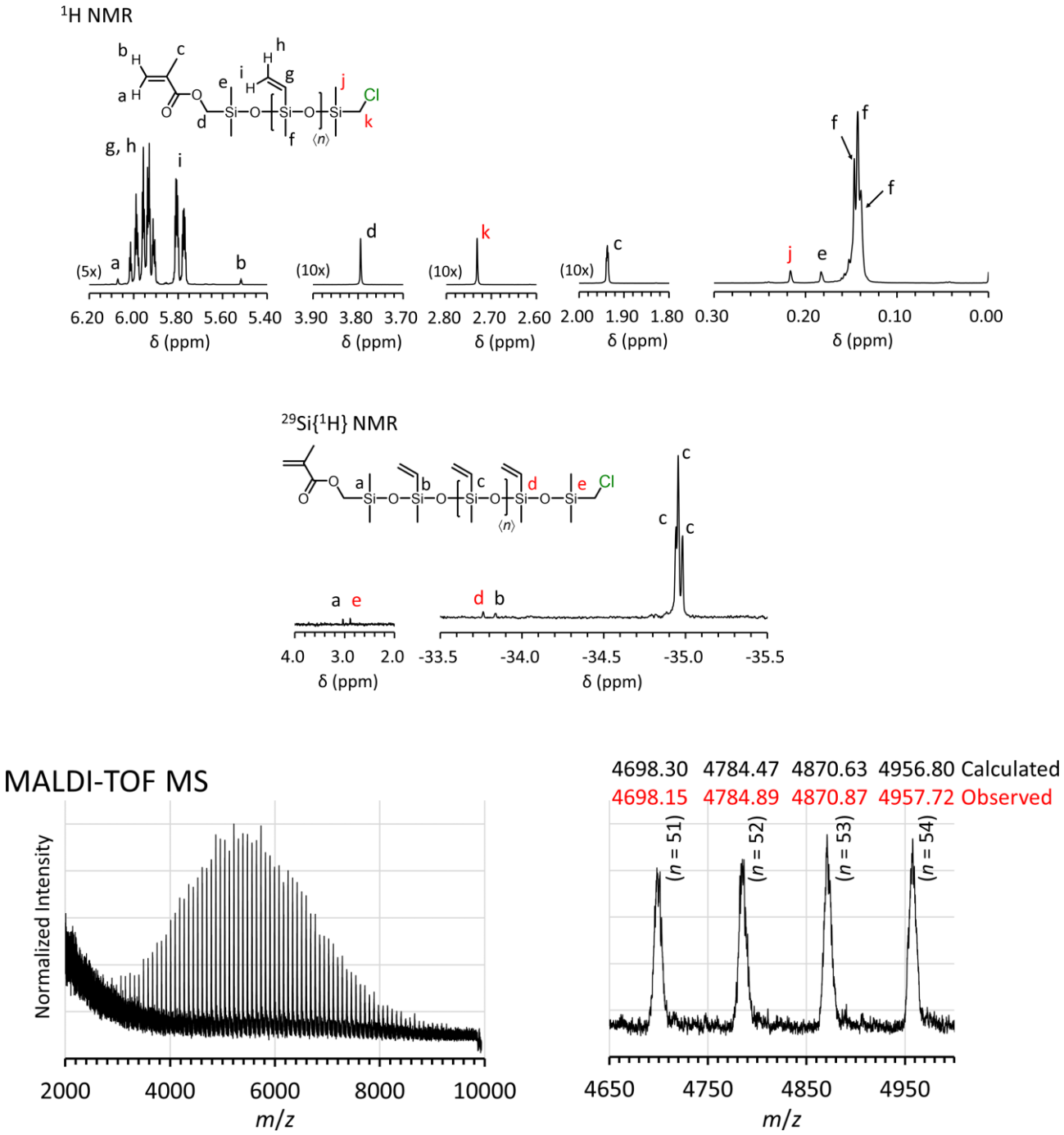


Fig. S24: ^{1}H NMR (600 MHz, in $CDCl_3$), $^{29}Si\{^{1}H\}$ NMR (119 MHz, in $CDCl_3$), and MALDI-TOF MS spectra (measured in linear mode using DCTB as the matrix and TFANa as the cationization agent) of the PMVS ($M_{n,NMR}$ = 6.67 kg mol^{-1}, $Đ_M$ = 1.10$_3$) synthesized using V3, $MACH_2SiMe_2OH$, and $ClCH_2Me_2SiCl$.

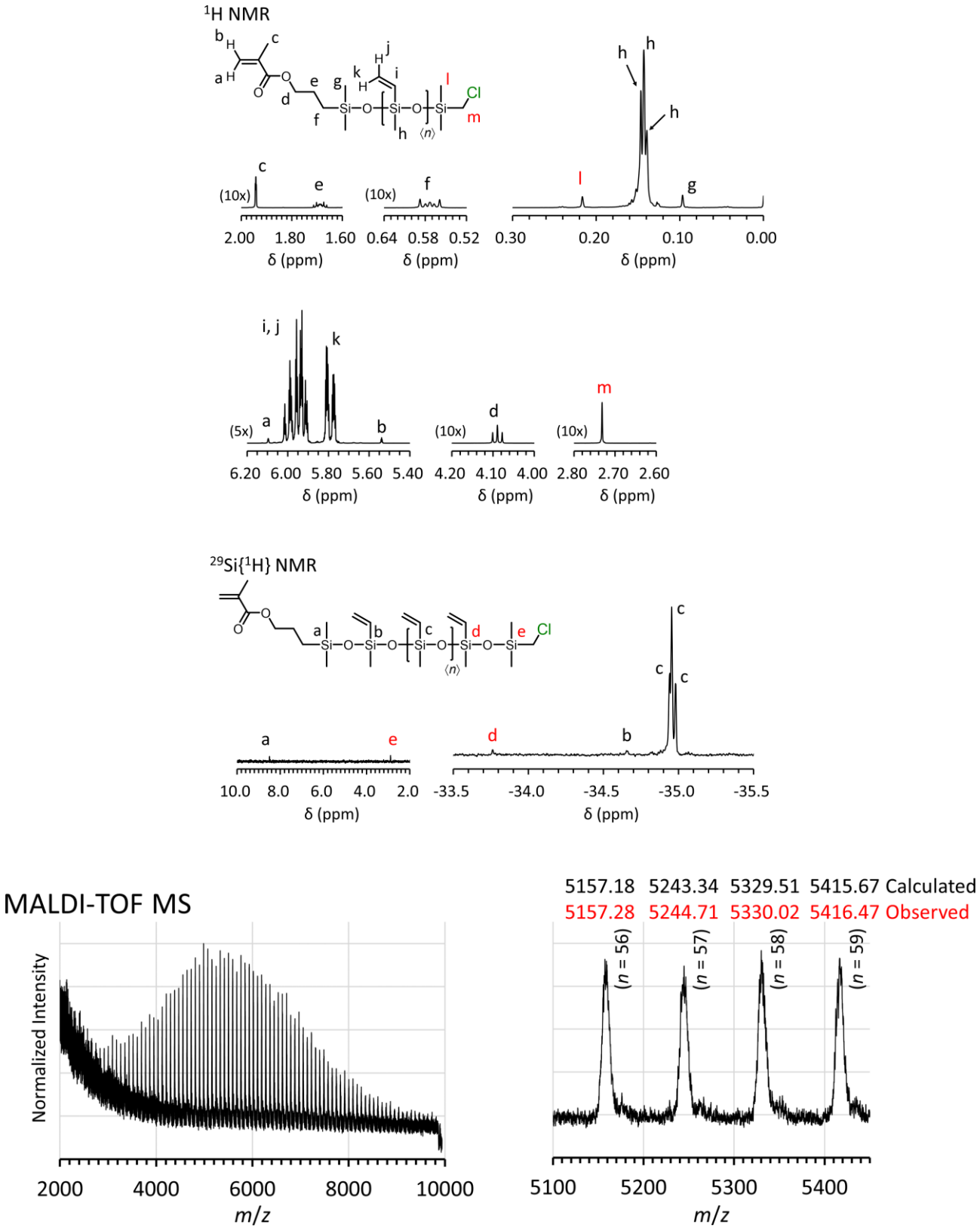


Fig. S25: ^{1}H NMR (600 MHz, in $CDCl_3$), ^{29}Si{^{1}H} NMR (119 MHz, in $CDCl_3$), and MALDI-TOF MS spectra (measured in linear mode using DCTB as the matrix and TFANa as the cationization agent) of the PMVS ($M_{n,NMR}$ = 6.48 kg mol^{-1}, $Đ_M$ = 1.11$_1$) synthesized using V3, MAPrSiMe$_2$OH, and ClCH$_2$Me$_2$SiCl.

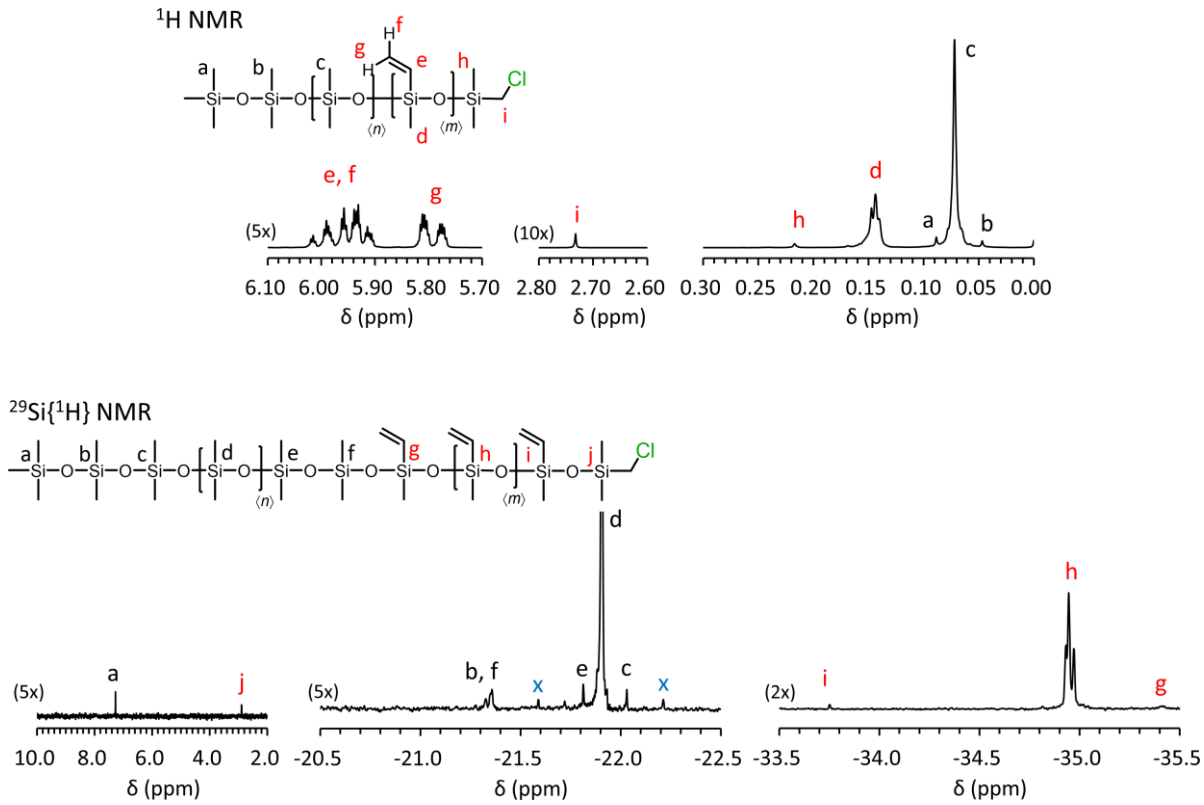


Fig. S26: ^{1}H NMR and ^{29}Si{^{1}H} NMR spectra of α-trimethylsilyl-ω-(chloromethyl)dimethylsilyl-terminated PDMS-*b*-PMVS (Table 4, Entry 11, $M_{n,NMR}$ = 9.81 kDa, $Đ_M$ = 1.10$_3$, h_c = 5.50 mol%) measured in $CDCl_3$.

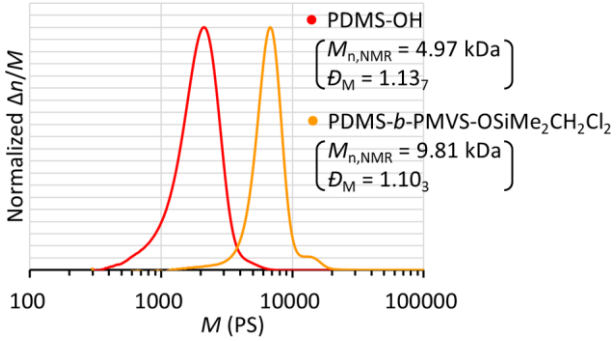
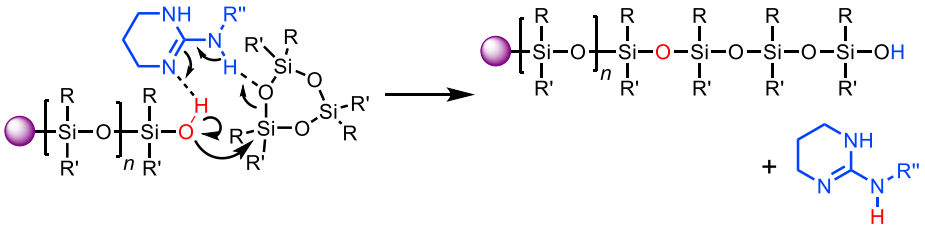


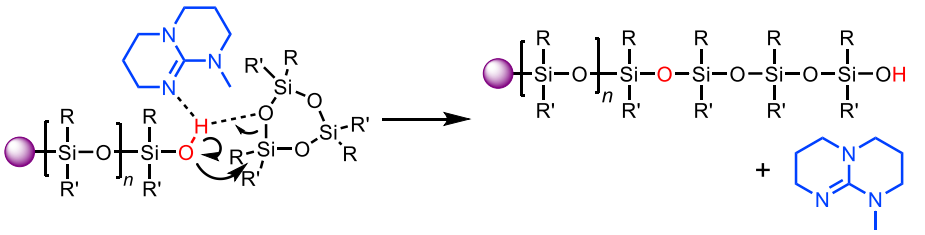
Fig. S27: Molar-mass distributions estimated for the products of the first polymerization (PDMS-OH, Table 4, Entry 9a) and the second polymerization (PDMS-*b*-PMVS-OSiMe$_2$CH$_2$Cl, Table 4, Entry 9b) in the consecutive polymerizations of D3 and V3 using MeD4OH and TMEG in Et_2O at ambient temperature (~24–26 °C) with $[D3]_0/[MeD4OH]_0/[TMnPG]_0$ = 25/1/0.075 and $[D3]_0$ = 1.80 mol L^{-1}. (Conditions for the SEC: toluene as the eluent, polystyrene standards, and an RI detector.)

Proton-shuttling mechanism for the initiation and propagation reactions

(a) ***Proton-shuttling mechanism*** catalyzed by guanidines with an N-H bond



(b) Proposed mechanism for catalysis by other bases (e.g., MTBD)



Scheme S1. Proposed mechanism for the ring-opening reaction of cyclotrisiloxanes in the propagation reaction catalyzed by (a) guanidines with an N-H bond on their amino groups and (b) other organic bases.

References

1 J. A. Cella and J. C. Carpenter, *J. Organomet. Chem.*, 1994, **480**, 23–26.

2 E. A. Kirichenko, A. I. Ermakov, N. I. Pimkin and V. M. Kopylov, *J. Gen. Chem. USSR*, 1980, **50**, 1280–1283.

3 C. F. H. Allen, C. O. Edens and J. Van Allan, *Org. Synth.*., 1946, **26**, 34–35.

4 M. Calas, M. Ouattara, G. Piquet, Z. Ziora, Y. Bordat, M. L. Ancelin, R. Escale and H. Vial, *J. Med. Chem.*, 2007, **50**, 6307–6315.

5 B. van Genabeek, B. F. M. de Waal, M. M. J. Gosens, L. M. Pitet, A. R. A. Palmans and E. W. Meijer, *J. Am. Chem. Soc.*, 2016, **138**, 4210–4218.

6 K. Fuchise, M. Igarashi, K. Sato and S. Shimada, *Chem. Sci.*, 2018, **9**, 2879–2891.

7 K. Hirabayashi, J.-i. Ando, J. Kawashima, Y. Nishihara, A. Mori and T. Hiyama, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 1409–1417.

8 A. V. Arzumanyan, I. K. Goncharova, R. A. Novikov, S. A. Milenin, K. L. Boldyrev, P. N. Solyev, Y. V. Tkachev, A. D. Volodin, A. F. Smol'yakov, A. A. Korlyukov and A. M. Muzafarov, *Green Chem.*, 2018, **20**, 1467–1471.

9 K. Hirabayashi, E. Takahisa, Y. Nishihara, A. Mori and T. Hiyama, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 2409–2417.

10 T. Suzuki, *Polymer*, 1989, **30**, 333–337.

11 S. Altmann and J. Pfeiffer, *Monatsh. Chem.*, 2003, **134**, 1081–1092.

12 K. A. Andrianov and A. K. Dabagova, *Dokl. Akad. Nauk SSSR*, 1958, **119**, 1149–1151.

13 Yu. T. Efimov, T. A. Tandura, V. M. Kopylov, S. I. Androsenko and M. I. Shkol'nik, *J. Gen. Chem. USSR*, 1991, **61**, 2083–2091.

14 N. Aoyagi and T. Endo, *Synth. Commun.* 2017, **47**, 442–448.

15 N. Aoyagi, Y. Furusho and T. Endo, *Synlett*, 2014, **25**, 983–986.