Precise synthesis of linear polysiloxanes with a polar side-chain structure by organocatalytic controlled/living ring-opening polymerization of (3-cyanopropyl)pentamethylcyclotrisiloxane

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Electronic Supplementary Information (ESI)

Contents:

Experimental Section

Materials.

Hexamethylcyclotrisiloxane (D3, Kanto, 95%) was purified by distillation in the presence of CaH_2 under reduced pressure and a nitrogen atmosphere prior to use. 3-Cyanopropyl(dichloro)methylsilane ($CNPMeSiCl_2$, Gelest, 95-100%), chloro(3-cyanopropyl)dimethylsilane (TCI, >95.0%), triphenylsilanol (Ph_3SiOH, TCI, >98.0%), imidazole (Sigma-aldrich, 99.5%), benzoic acid (Kanto, >99.5%), pyridine (FUJIFILM Wako, dehydrated, >99.5%), sodium acetate (AcONa, Kishida, anhydrous, 98.5%), chlorodimethyl(vinyl)silane ($Me_2ViSiCl$, TCI, >97.0%), chlorodimethyl(phenyl)silane ($Me_2PhSiCl$, TCI, >96.0%), chlorodimethylsilane (HMe_2SiCl, Aldrich, 98%), chloro(chloromethyl)dimethylsilane ($ClCH_2SiMe_2Cl$, TCI, >98.0%), *n*-butyllithium (^{n}BuLi, Kanto, 1.58 mol L^{-1} in hexane), methylamine (TCI, 2.0 mol L^{-1} = 7.0 wt% in THF), sodium hydrogencarbonate ($NaHCO_3$, FUJIFILM Wako, 99.6–100.3%), potassium hydroxide (KOH, FUJIFILM Wako, >85.0%), sodium sulfate (Na_2SO_4, FUJIFILM Wako, >99.0%), hexane (FUJIFILM Wako, >97.0%), 'dry' diethyl ether (Et_2O, FUJIFILM Wako, Super Dehydrated, >99.5%), acetonitrile (MeCN, FUJIFILM Wako, >99.5%), 'dry' MeCN (FUJIFILM Wako, Super Dehydrated), 'dry' CH_2Cl_2 (FUJIFILM Wako, super dehydrated, water content < 0.001%), 'dry' toluene (Kanto, dehydrated –Super Plus–, water content < 0.001%), tetrahydrofuran (THF, stabilizer free, FUJIFILM Wako, >99.5%), and 'dry' THF (Kanto, dehydrated –Super Plus–, water content < 0.001%) were used as received.

Pentamethyl(vinyl)cyclotrisiloxane (VD2),[S1] 1,3-dihydroxy-1,1,3,3-tetramethyldisiloxane (HO-D2-OH),[S2] 1-hydroxy-1,1,3,3,5,5,7,7,7-nonamethyltetrasiloxane (MeD4OH),[S3] and 2-methylthio-1,4,5,6-tetrahydropyrimidine hydroiodide[S7] were synthesized as previously reported.

α,ω-Bis[dimethyl(vinyl)silyl]-terminated PDMS ($<X_{n,D}>$ = 62.2; $Đ_M$ = 1.09$_4$) for thermogravimetry analysis (TGA) was synthesized by the polymerization of D3 using water as an initiator, TMnPG as a catalyst, and $Me_2ViSiCl$ as an end-capping agent.

Measurements.

NMR

^1H (600 MHz), $^{13}C\{^1H\}$ (150 MHz), and $^{29}Si\{^1H\}$ (119 MHz) NMR spectra were recorded on a BRUKER Biospin AVANCE III HD 600 NMR spectrometer with a CryoProbe. Chemical shifts were reported in δ (ppm) and were referenced to tetramethylsilane (0.00 ppm) for ^1H, ^{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 number-average molar mass ($M_{n,SEC}$) and the molar-mass dispersity ($Đ_M$) were determined based on a calibration curve prepared using polystyrene (PS) samples from a TSKgel® standard polystyrene oligomer

kit (Tosoh) with weight-average molecular mass (M_w) and ($Đ_M$) values of 19.0×10^5 kDa (1.04), 9.64×10^4 g mol^{-1} (1.01), 3.79×10^4 g mol^{-1} (1.01), 1.74×10^4 g mol^{-1} (1.01), 1.02×10^4 g mol^{-1} (1.02), 5.06×10^3 g mol^{-1} (1.02), 2.63×10^3 g mol^{-1} (1.05), 1.01×10^3 g mol^{-1} (1.16), and 5.9×10^2 g mol^{-1} (1.19), along with PS samples from Chemco Co. with M_w ($Đ_M$) values of 17.0×10^5 g mol^{-1} (<1.06), 4.75×10^4 g mol^{-1} (1.06), 9.00×10^3 g mol^{-1} (1.04), and 4.00×10^3 g mol^{-1} (1.03).

High Resolution Mass Spectrometry (HR-MS)

The high-resolution atmospheric pressure chemical ionization (APCI) and electrospray ionization (ESI) mass spectra were obtained on a Bruker micrOTOF II.

Thermogravimetry analysis (TGA)

The samples were heated from 30 °C to 530 °C at the heating rate of 10 °C min^{-1} under a nitrogen flow at 200 mL min^{-1}.

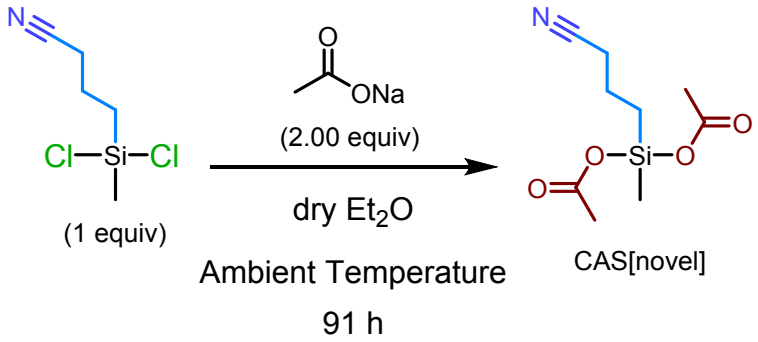
Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) was conducted with a Hitachi Hitech-Science DSC 7020.

Melting point (m.p.) was measured for 3-cyanopropylpentamethylcyclotrisiloxane (CNPD2). Approximately 5 mg of samples were used for the measurement. The sample was cooled to −70 °C at the cooling rate of 10 °C min^{-1} then heated to 50 °C at the heating rate of 2 °C min^{-1} under a nitrogen flow at 50 mL min^{-1}. The m.p. was determined from the extrapolated onset temperature and the peak temperature of an endothermic peak in the first scan.

Glass transition temperature (T_g) was measured for polysiloxanes. Approximately 5 mg of samples were used for each measurement. The samples were cooled to −150 °C at the cooling rate of 10 °C min^{-1} then heated to 100 °C at the heating rate of 10 °C min^{-1} under a nitrogen flow at 50 mL min^{-1}.

Synthesis of diacetoxy(3-cyanopropyl)methylsilane



3-Cyanopropyl(dichloro)methylsilane (10.00 g, 54.91 mmol) was added to a mixture of AcONa (9.03 g, 110 mmol) and dry Et_2O (55 mL). After 91 h, the solution was filtered through a glass filter. The filtrate was concentrated to obtain $CNPMeSi(OAc)_2$ as a yellow liquid. Yield: 10.91 g (47.61 mmol, 86.7%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 2.40 (t, J = 7.0 Hz, 2H, -CH_2CN), 2.12 (s, 6H, Si(COCH_3)$_2$), 1.87–1.77 (m, 2H, -CH_2CH$_2$CN), 1.14-1.07 (m, 2H, -SiCH_2CH$_2$), 0.52 (s, 3H, SiCH_3). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 170.80

(H_3CCO), 119.30 (*C*N), 22.49 (H_3CCO), 20.06 (-*C*H_2CN), 18.95(-*C*H_2CH_2CN), 14.34 (-Si*C*H_2CH_2), −2.88 (Si*C*H_3). $^{29}Si\{^1H\}$ NMR (119 MHz, $CDCl_3$): δ 2.33.

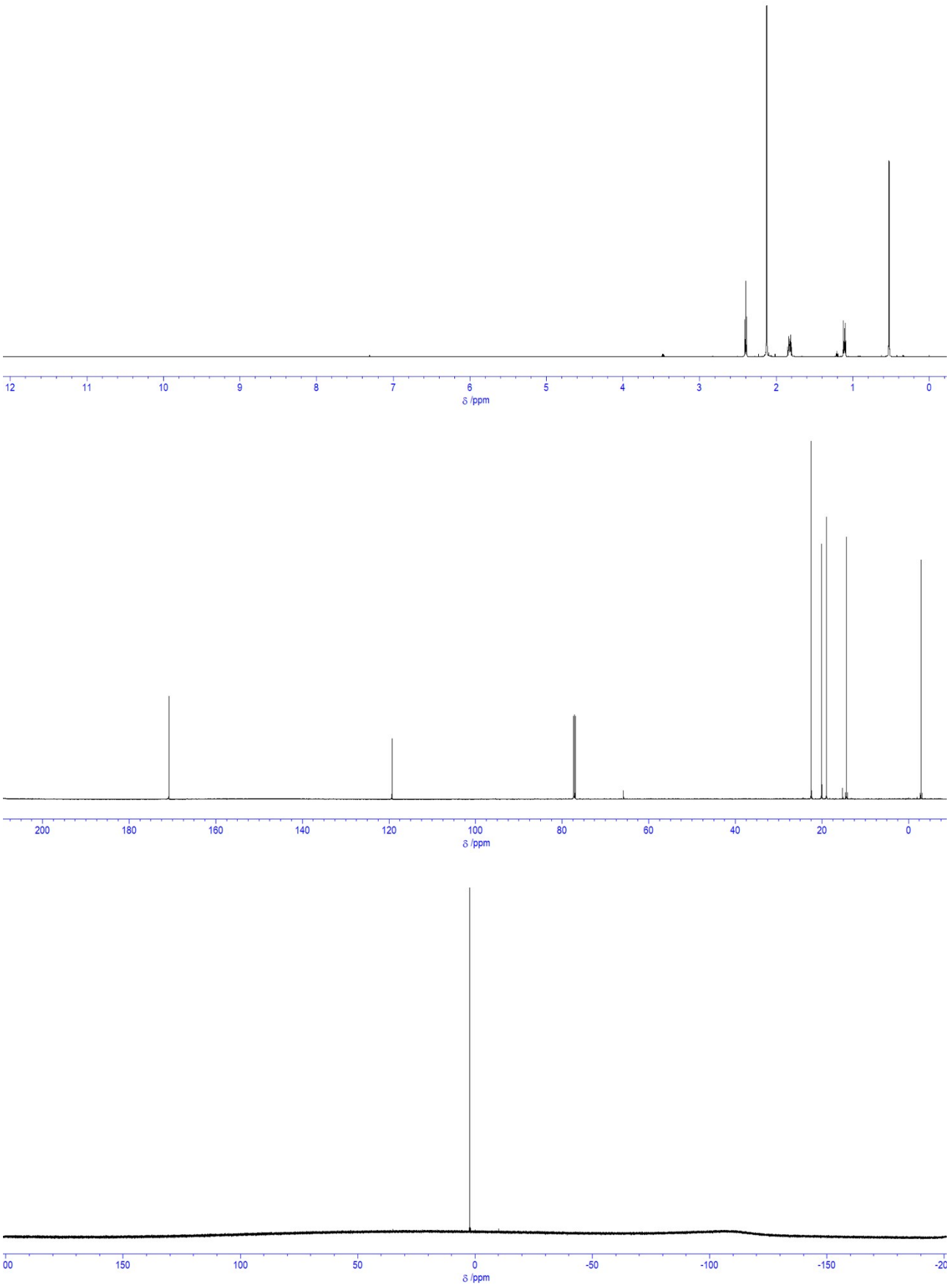
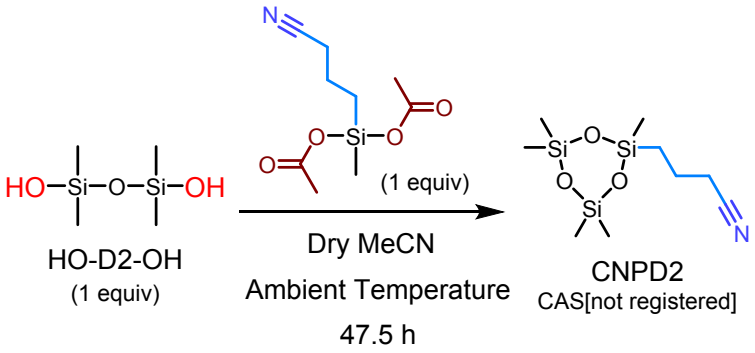


Fig. S1. (top) ^{1}H NMR, (middle) ^{13}C{^{1}H} NMR, and (bottom) ^{29}Si{^{1}H} NMR spectra of the obtained diacetoxy(3-cyanopropyl)methylsilane in $CDCl_3$.

Synthesis of 3-cyanopropylpentamethylcyclotrisiloxane (CNPD2)



$CNPMeSi(OAc)_2$ (41.30 g, 180.1 mmol) in dry MeCN (150 mL) was dropwise added to a solution of HO-D2-OH (30.00 g, 180.4 mmol) in dry MeCN (1.05 L) at ambient temperature. The reaction mixture was stirred for 47.5 h. Imidazole (73.73 g, 1.083 mol) was added to the reaction mixture. The reaction mixture was concentrated to a volume of around 300 mL. The MeCN phase was extracted with hexane (60 mL ×10). The hexane phase was concentrated to a volume of around 300 mL and washed with water (60 mL × 2) and brine (60 mL × 1), dried over Na_2SO_4, filtered, and concentrated. The residue was distilled under reduced pressure to give CNPD2[S4, S5] as a colorless liquid. Yield: 30.75 g (111.6 mmol, 62.0%).

M.p. 19–21 °C. B.p. 54–55 °C / 0.20 mmHg. ^{1}H NMR (600 MHz, $CDCl_3$): δ. 2.39 (t, 2H, J = 7.1 Hz, NCCH_2), 1.76 (m, 2H, -Si(CH_3)CH_2CH_2-), 0.76 (m, 2H, -Si(CH_3)C$H_2$$CH_2$-), 0.18 (s, 3H, Si(C$H_3$)$CH_2$$CH_2$-), 0.18 (s, 12H, -Si(C$H_3$)$_2$-). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 119.61 (-*C*N), 20.18 (-*C*H_2CN), 19.37 (-*C*$H_2$$CH_2$CN), 16.51 (-Si*C*$H_2$$CH_2$), 0.92 (-Si*C*$H_3$($CH_3$)-O-Si*C*$H_3$($CH_3$)-), 0.89 (-Si$CH_3$(*C*$H_3$)-O-Si$CH_3$(*C*$H_3$)-), −0.50 (-Si*C*$H_3$($CH_2$$CH_2$$CH_2$CN)). ^{29}Si{^{1}H} NMR (119 MHz, $CDCl_3$): δ −7.80 (*Si*(CH_3)$_2$-), −10.93 (*Si*(CH_3)$CH_2$$CH_2$-). HRMS (ESI in iPrOH) calcd for $[C_9H_{21}NO_3Si_3Na]^+$ $[M+Na]^+$ 298.0721, found 298.0720.

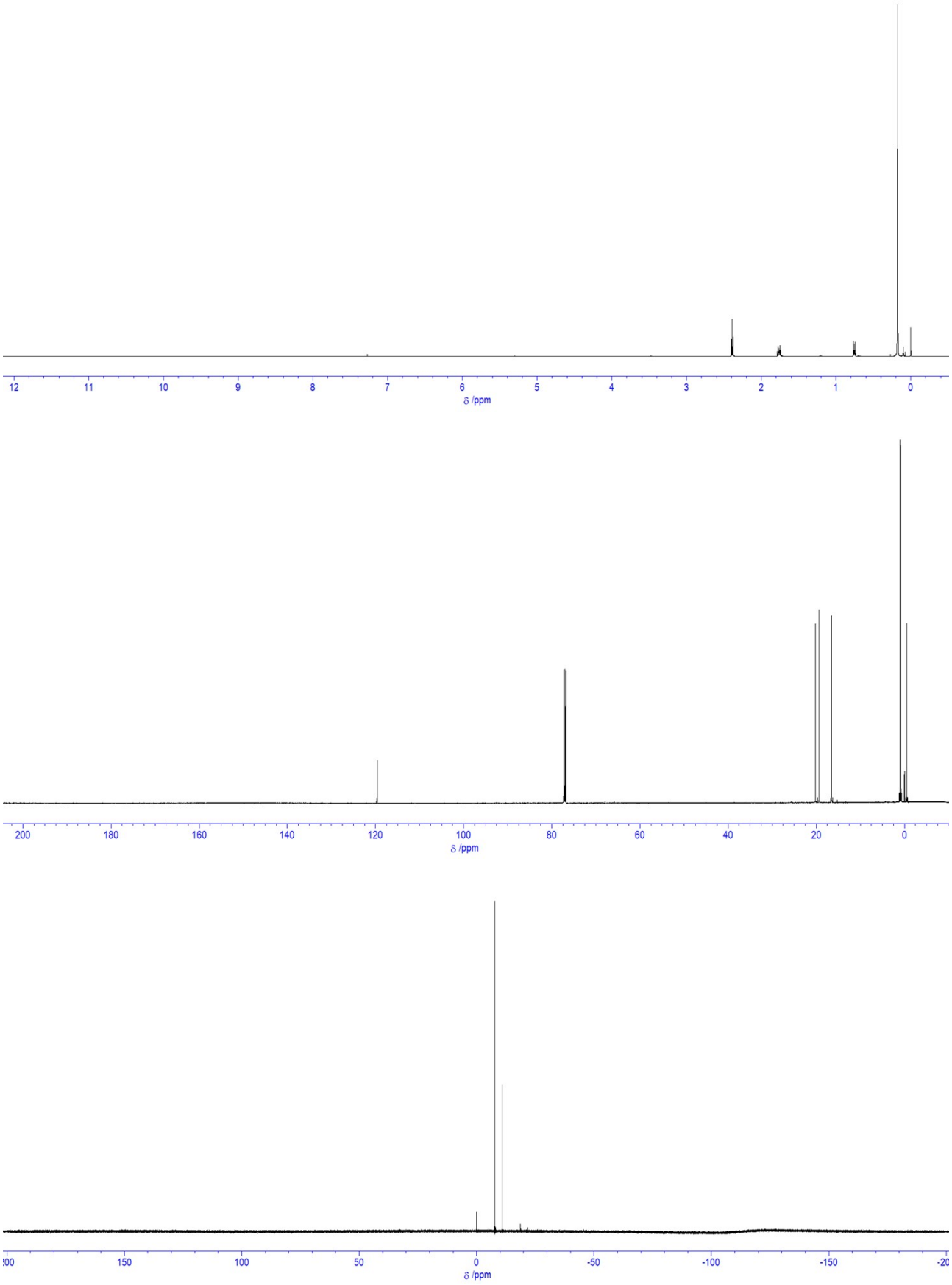
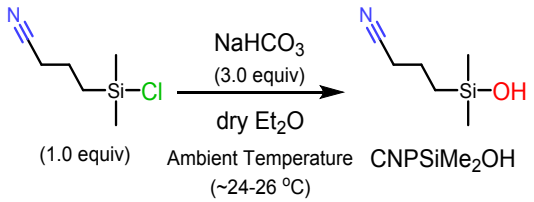


Fig. S2. (top) ^{1}H NMR, (middle) ^{13}C{^{1}H} NMR, and (bottom) ^{29}Si{^{1}H} NMR spectra of the obtained CNPD2 in $CDCl_3$.

Synthesis of 3-cyanopropyldimethylsilanol ($CNPSiMe_2OH$)



$NaHCO_3$ (11.69 g, 139.1 mmol) was gradually added to a mixture of chloro(3-cyanopropyl)dimethylsilane (7.50 g, 46.4 mmol) and dry Et_2O (65 mL) at ambient temperature under an argon atmosphere. After 26.5 h, the reaction mixture was filtered. The filtrate was concentrated under reduced pressure. The residue was purified by distillation under reduced pressure to obtain $CNPSiMe_2OH$ as a colorless liquid. Yield: 3.30 g (23.0 mmol, 42.0%).

B.p. 76–79 °C / 0.29 mmHg. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.14 (br s, 1H, -O*H*), 2.40 (t, J = 7.0 Hz, 2H, -CH_2CN), 1.79–1.70 (m, 2H, -CH_2CH$_2$CN), 0.78–0.70 (m, 2H, -SiCH_2-), 0.14 (s, 6H, -Si(CH_3)$_2$). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 119.82 (-*C*N), 20.51 (-*C*H$_2$CN), 19.88 (-*C*H$_2$CH$_2$CN), 17.30 (-Si*C*H$_2$CH$_2$), −0.36 (-Si(*C*H$_3$)$_2$). ^{29}Si{^{1}H} NMR (119 MHz, $CDCl_3$): δ 16.61. HRMS (ESI in MeOH) calcd for $[C_6H_{13}NOSiNa]^+$ $[M+Na]^+$ 166.0659, found 166.0655.

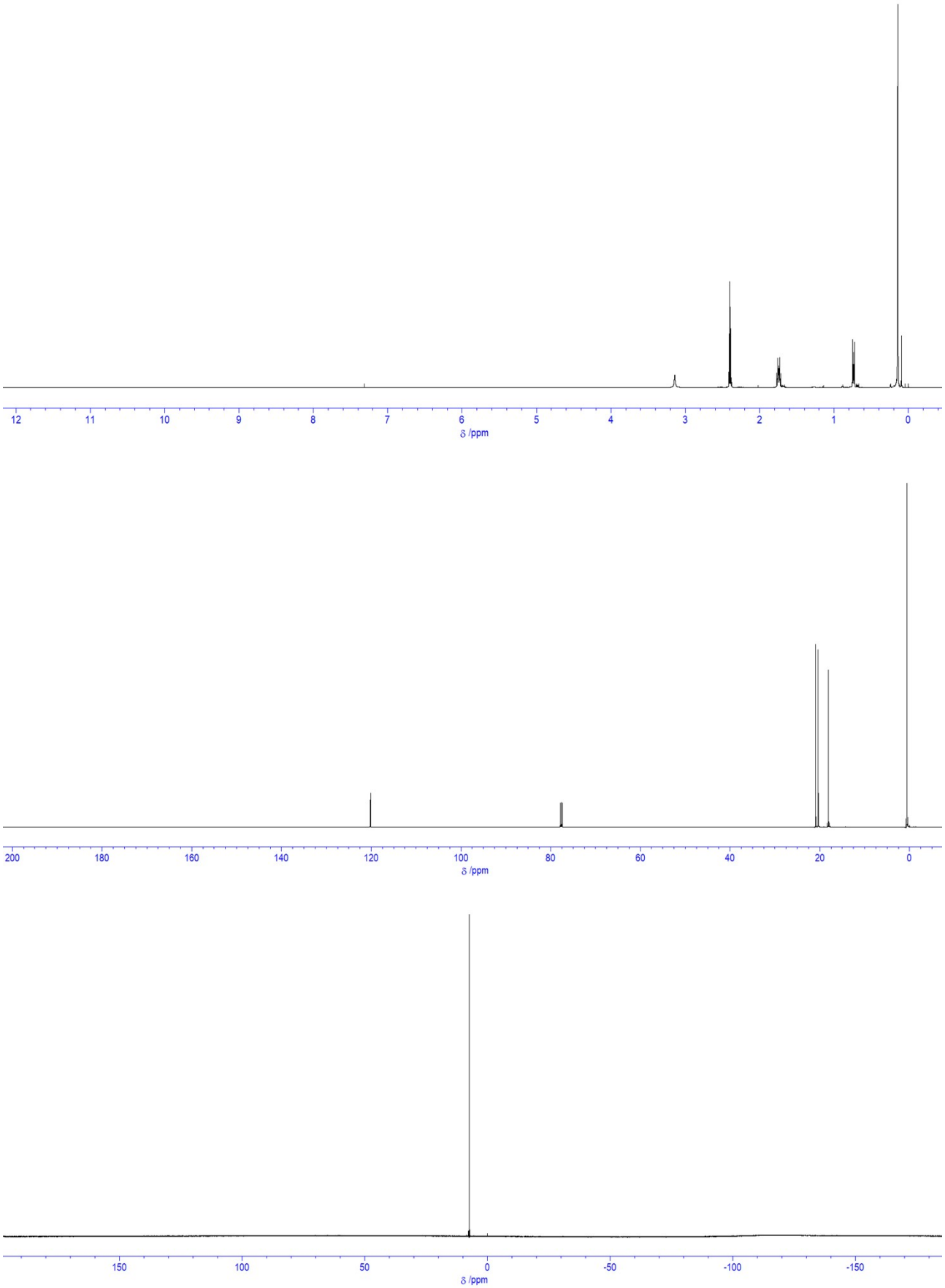
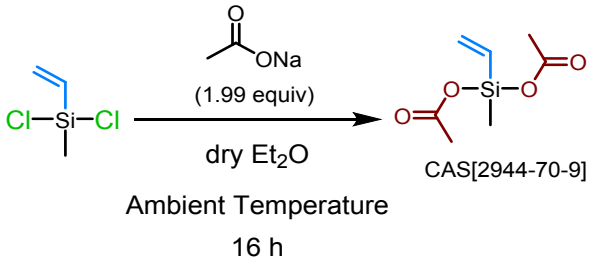


Fig. S3. (top) ^{1}H NMR, (middle) $^{13}C\{^{1}H\}$ NMR, and (bottom) $^{29}Si\{^{1}H\}$ NMR spectra of the obtained $CNPSiMe_2OH$ in $CDCl_3$.

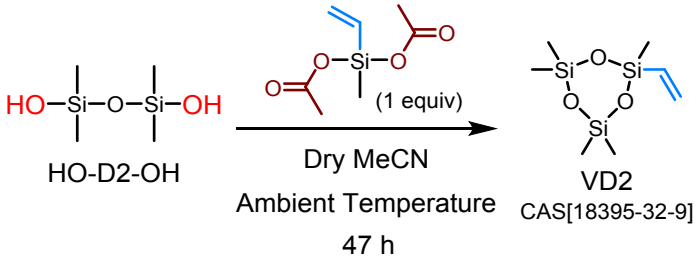
Synthesis of diacetoxy(methyl)vinylsilane (MeViSi(OAc)$_2$) [S8]



$MeViSiCl_2$ (26.00 g, 184.3 mmol) was added to a mixture of AcONa (30.02 g, 366.0 mmol) and dry Et_2O (184 mL). After 16 h, the solution was filtered through a glass filter. The filtrate was concentrated to obtain $MeViSi(OAc)_2$ as a colorless liquid. Yield: 24.78 g (131.6 mmol, 71.4%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 6.24–6.13 (m, 2H, vinyl), , 6.05 (dd, J = 4.7 Hz and 19.2 Hz, 1H, ^{cis}*H*C=CH-), 2.12 (s, 6H, H_3CCO), 0.60 (s, 3H, SiCH_3). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 170.70 (H_3C*C*O), 137.58 (H_2*C*=), 130.71 (=*C*H-), 22.56 (H_3*C*CO), −3.50 (Si*C*H$_3$). ^{29}Si{^{1}H} NMR (119 MHz, $CDCl_3$): δ −12.42.

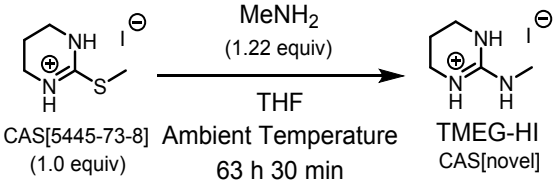
Synthesis of pentamethyl(vinyl)cyclotrisiloxane (VD2)



$MeViSi(OAc)_2$ (8.03 g, 42.6 mmol) in dry MeCN (40 mL) was dropwise added to a solution of HO-D2-OH (7.09 g, 42.6 mmol) in dry MeCN (173 mL) at ambient temperature. The reaction mixture was stirred for 47 h. Imidazole (17.40 g, 255.8 mmol) was added to the reaction mixture. The MeCN phase was extracted with hexane (50 mL ×4). The separated hexane phase was washed with water (200 mL × 3), dried over Na_2SO_4, filtered, and concentrated at 110 hPa. The residue was distilled under reduced pressure to give VD2 as a colorless liquid. Yield: 4.12 g (17.6 mmol, 41.3%).

M.p. 20–23 °C. B.p. 46–47.5 °C / 28.5 mmHg (Lit. 85 °C / 80 mmHg).[S9] (Lit. 45-50 °C / 14 mmHg).[S10] ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.09–6.00 (m, 2H, , vinyl), 5.88 (dd, 1H, J = 7.1 Hz, 17.0 Hz, Vi), 0.24 (s, 3H, Si*Me*Vi), 0.19_0 (s, 6H, Si*Me*$_2$), 0.17_6 (s, 6H, Si*Me*$_2$). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 135.88 (Vi), 134.03 (Vi), 0.95 (Si*Me*$_2$), 0.87 (Si*Me*$_2$), −0.77 (Si*Me*). ^{29}Si{^{1}H} NMR (119 MHz, $CDCl_3$): δ −7.71 (*Si*Me$_2$), −23.29 (*Si*Me). HRMS (APCI, in MeOH) calcd for $[C_7H_{19}O_3Si_3]^+$ $[M+H]^+$ 235.0637, found 235.0636.

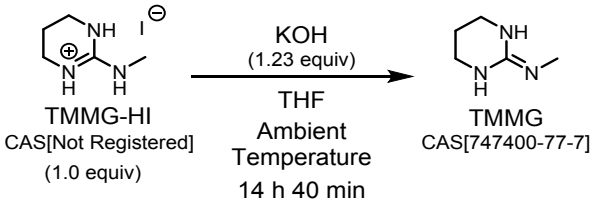
1,3-Trimethylene-2-methylguanidine hydroiodide (TMMG-HI)



Methylamine (4.19 g, 2.0 mol L^{-1} (7.0 wt%) in THF, 9.44 mmol) was added to a suspension of 2-methylthio-1,4,5,6-tetrahydropyrimidine hydroiodide (2.00 g, 7.75 mmol) in THF (7.0 mL, stabilizer-free) at ambient temperature. After 63 h 30 min of reaction, 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 TMMG-HI as a white solid. Yield: 1.87 g (~100%).

M.p. 65 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 7.71 (br s, 2H, -N*H*$(CH_2)_3$N*H*-), 7.14 (br s, 1H, N*H*CH_3), 3.24 (t, J = 5.7 Hz, 4H, NC*H*$_2$CH$_2$C*H*$_2$N), 2.68 (s, 3H, -C*H*$_3$), 1.81 (quintet, J = 5.8 Hz, 2H, NCH$_2$C*H*$_2$CH$_2$N). ^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6): δ 153.14 (*C*NCH$_3$), 37.95 (NH*C*H$_2$CH$_2$*C*H$_2$NH), 27.25 (-*C*H$_3$), 19.59 (NHCH$_2$*C*H$_2$CH$_2$NH). HRMS (ESI) calcd for $[C_5H_{12}N_3]^+$ $[M-I]^+$ 114.1026, found 114.1022; calcd for $[I]^-$ $[M-TMEG-H]^-$ 126.9050, found 126.9047.

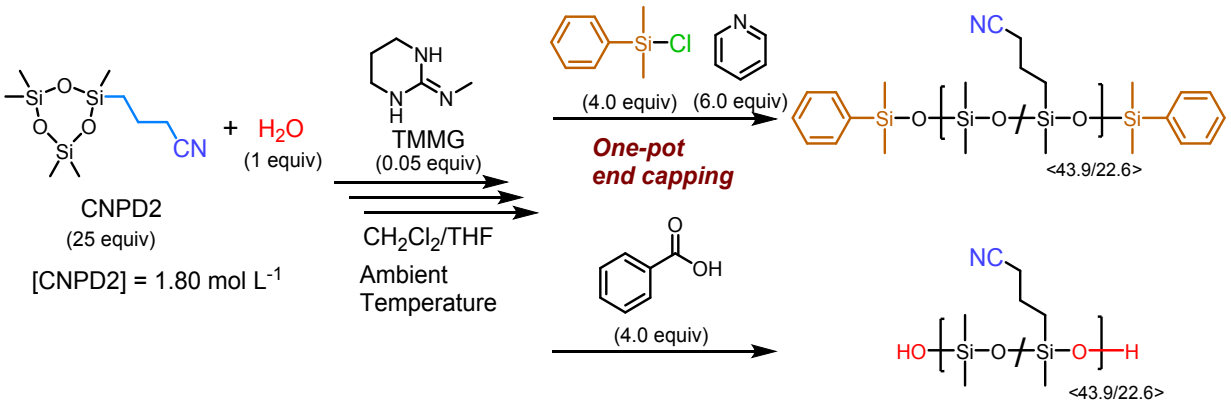
1,3-Trimethylene-2-methylguanidine (TMMG)



KOH (259 mg, 4.62 mmol) was added to a solution of TMMG-HI (0.90 g, 3.7 mmol) in THF (9.1 mL, stabilizer free) at ambient temperature. After 14 h 40 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 (6 mL). The solution was concentrated under reduced pressure. The residue was dissolved in THF (5.0 mL) and filtered using another SARTORIUS syringe filter (Mini Sarto SRP, pore size = 0.2 μm). The filtrate was concentrated under reduced pressure to obtain TMMG as a pale-yellow solid. The product was dissolved in dry THF to prepare a stock solution of TMMG in THF (60 mg mL^{-1}). Yield: 422 mg (~100%). Activated MS4Å was added to dehydrate the solution.

TMMG: *Hygroscopic*. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.30 (t, J = 5.8 Hz, 4H, NC*H*$_2$CH$_2$C*H*$_2$N), 2.72 (s, 3H, -C*H*$_3$), 1.82–1.75 (m, 2H, NCH$_2$C*H*$_2$CH$_2$N). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 153.24 (*C*NCH$_3$), 40.71 (NH*C*H$_2$CH$_2$*C*H$_2$NH), 28.25 (N*C*H$_3$), 21.68 (NHCH$_2$*C*H$_2$CH$_2$NH). HRMS (ESI) calcd for $[C_5H_{12}N_3]^+$ $[M+H]^+$ 114.1026, found 114.1021.

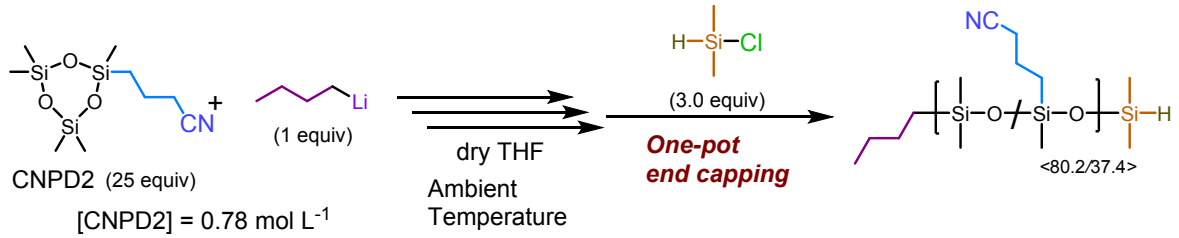
Polymerization of CNPD2



(Table 1, entry 2) CNPD2 (2.92 g, 10.6 mmol), dry CH_2Cl_2 (5.1 mL) and a THF solution of H_2O (1/99 (H_2O/THF, v/v), 764 μL, 424 μmol) was added to a flask equipped with a needle-valve under an argon atmosphere. A THF solution of TMMG (60 mg mL^{-1}, 40.0 μL, 21.2 μmol) was added to initiate the polymerization at ambient temperature (~25°C). The first-order kinetic plots for the polymerization showed linear relationship as shown in Fig. 1. After stirring for 5 h 19 min, the 1.56 g (around 15wt% of the initial reaction mixture) of the reaction mixture was taken in a vial and named as the mixture B. The residual reaction mixture was named as the mixture A. Pyridine (212 mg, 2.68 mmol, 6.3 equiv) as a scavenger of hydrochloric acid and $Me_2PhSiCl$ (292 mg, 1.71 mmol, 4.0 equiv) as an end-capping agent were added to the mixture A. The end-capping reaction was continued for 120 min at ambient temperature. Excess amount of benzoic acid against the amount of TMMG was added to the mixture B to quench the catalyst. The mixtures A and B were separately concentrated. The mixture A was repeatedly washed with MeCN/H_2O (in total 110 mL, 3/1, v/v). The residue was dissolved in 1,4-dioxane (10 <-12 mL) and concentrated *in vacuo* to obtain α,ω-bis[dimethyl(phenyl)silyl]-terminated P(DMS-*co*-CNPMS) (1.878 g, y. 72.6%, $M_{n,NMR}$ = 6.41 kg mol^{-1}, $\langle X_{n,D}/X_{n,CNP}\rangle$ = 43.9/22.6, $Đ_M$ = 1.06_7) as a colorless viscous. The mixture B was washed with MeCN/H_2O (3 mL, 2/1, v/v) eight times. The residue was dissolved in 1,4-dioxane (2 mL) and concentrated *in vacuo* to obtain α,ω-bis[dimethyl(phenyl)silyl]-terminated P(DMS-*co*-CNPMS) (320.5 mg, *y*. 72.9%, $M_{n,NMR}$ = 6.15 kg mol^{-1}, $\langle X_{n,D}/X_{n,CNP}\rangle$ = 43.9/22.6, $Đ_M$ = 1.06_7) as a colorless viscous liquid. ^1H and $^{29}Si\{^1H\}$ NMR spectra of the products are shown in Fig. 2 and S5.

The polymerizations initiated by silanols (Table 2) were conducted with the same procedures using the silanols, such as MeD4OH, Ph_3SiOH, and $CNPSiMe_2OH$ instead of the THF solution of H_2O.

Polymerization of CNPD2 initiated by ^{n}BuLi (Table 2, entry 4)



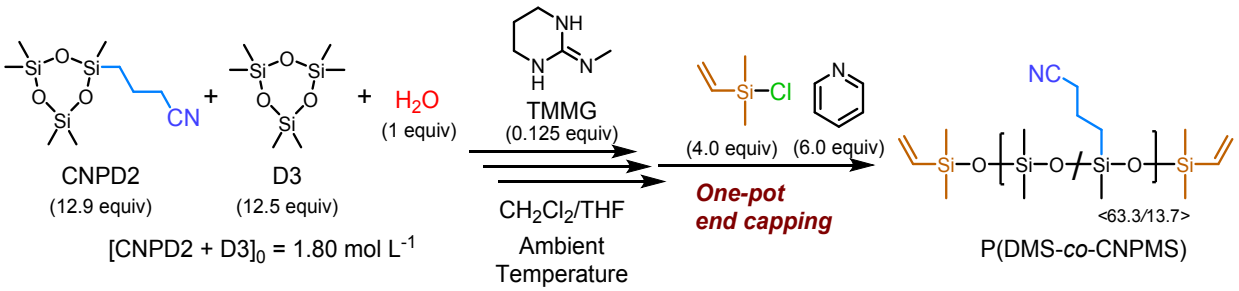
CNPD2 (292 mg, 1.06 mmol) and dry THF (1.37 mL) was added to a vial under an argon atmosphere. ^{n}BuLi (26.5 μL, 1.58 mol L^{-1} in hexane, 41.8 μmol) was added to initiate the polymerization at ambient temperature (~25°C). After stirring for 1 h 38 min, $HSiMe_2Cl$ (14.1 μL, 127 μmol, 3 equiv) as an end-capping agent was added

to the reaction mixture. The end-capping reaction was continued overnight at ambient temperature. The reaction mixture was concentrated, washed with MeCN/H_2O (4 mL, 7/3, v/v) five times. The residue was dissolved in 1,4-dioxane (2 mL) and concentrated *in vacuo* to obtain α-*n*-butyl-ω-dimethylsilyl-terminated P(DMS-*co*-CNPMS) (25 mg, y. 8.4%, $M_{n,NMR}$ = 11.0 kg mol^{-1}, $<X_{n,D}/X_{n,CNP}>$ = 80.2/37.4, $Đ_M$ = 1.22$_1$) as a colorless viscous liquid. Most of the product was soluble in MeCN/H_2O (7/3, v/v). ^{1}H, and ^{29}Si{^{1}H} NMR spectra of the product are shown in Fig. S10 and S11.

Statistical copolymerization of two different cyclotrisiloxanes (Table 3)

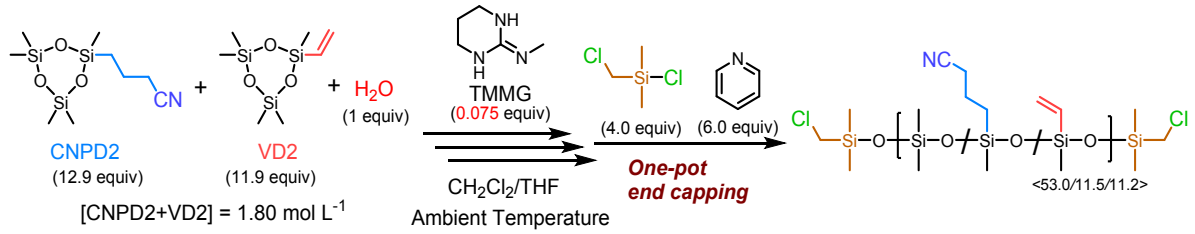
Typically, statistical copolymerizations of CNPD2 and another cyclotrisiloxane and D3 were conducted using the following procedures.

Statistical copolymerization of CNPD2 and D3 (Table 3, entry 1)



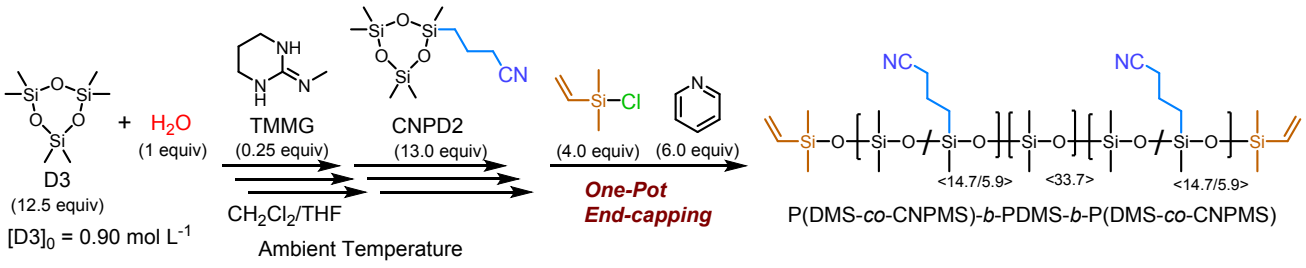
A THF solution of TMMG (60 mg mL^{-1}, 15.0 µL, 7.95 µmol, 0.125 equiv) was added to a solution of CNPD2 (227 mg, 824 µmol, 12.9 equiv), D3 (177 mg, 795 µmol, 12.5 equiv), and a THF solution of H_2O (1/99 (H_2O/THF, v/v), 115 µL, 63.6 µmol, 1.0 equiv) in dry CH_2Cl_2 (769 µL) in a glass vial or a flask 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 3 h 45 min, dry pyridine (30.8 µL, 382 µmol, 6.0 equiv) was added as a hydrochloric acid scavenger, and ViSiMe$_2$Cl (34.4 µL, 255 µmol, 4.0 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/H_2O (2/1 (v/v), 3 mL) and the upper layer was removed; the washing procedure with MeCN/H_2O was repeated in total 5 times. The residue was diluted with toluene (2 mL) and concentrated *in vacuo*. The solvent remaining in the product was thoroughly removed *in vacuo* to obtain α,ω-bis[dimethyl(vinyl)silyl]-terminated poly[dimethylsiloxane-*co*-3-cyanopropyl(methyl)siloxane] (P(DMS-*co*-CNPMS)) (249.8 mg, 60.1% yield, $M_{n,NMR}$ = 6.63 kDa ($<X_{n,D}/X_{n,CNP}>$ = 63.3/13.7), $Đ_M$ = 1.09$_9$) as a colorless liquid. ^{1}H NMR and ^{29}Si{^{1}H} NMR spectra of the product are shown in Fig. S12 and S13. (The sampling was conducted 5 times in this polymerization)

Statistical copolymerization of CNPD2 and VD2 (Table 3, entry 2)



A THF solution of TMMG (60 mg mL^{-1}, 8.0 μL, 4.2 μmol, 0.075 equiv) was added to a solution of CNPD2 (202 mg, 733 μmol, 12.9 equiv), VD2 (157 mg, 671 μmol, 11.9 equiv), and a THF solution of H_2O (H_2O/THF, 1/99 (v/v), 102 μL, 56.6 μmol, 1.0 equiv) in dry CH_2Cl_2 (684 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 46 min, dry pyridine (27.3 μL, 339 μmol, 6.0 equiv) was added as a hydrochloric acid scavenger, and $ClCH_2SiMe_2Cl$ (29.8 μL, 226 μmol, 4.0 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/H_2O (2/1 (v/v), 3 mL) and the upper layer was removed; the washing procedure with MeCN/H_2O was repeated in total eight times. The residue was diluted with toluene (2 mL) and concentrated *in vacuo*. The solvent remaining in the product was thoroughly removed *in vacuo* to obtain α,ω-bis[chloromethyldimethylsilyl]-terminated poly[dimethylsiloxane-*co*-methyl(vinyl)siloxane-*co*-3-cyanopropyl(methyl)siloxane] (P(DMS-*co*-MVS-*co*-CNPMS)) (240.0 mg, 64.5% yield, $M_{n,NMR}$ = 6.59 kDa ($\langle X_{n,D}/X_{n,CNP}/X_{n,V}\rangle$ = 53.0/11.5/11.2), $Đ_M$ = 1.09$_1$) as a colorless liquid. ^{1}H NMR and ^{29}Si{^{1}H} NMR spectra of the product are shown in Fig. S14 and S15. (The sampling was conducted three times in this polymerization)

Two-stage copolymerizations of D3 and CNPD2 (Table 3, entries 3 and 4)



A THF solution of TMMG (60 mg mL^{-1}, 17.0 μL, 9.02 μmol, 0.125 equiv) was added to a solution of D3 (201 mg, 902 μmol, 12.5 equiv) and a THF solution of H_2O (H_2O/THF, 1/99 (v/v), 130 μL, 72.1 μmol, 1.0 equiv) in dry CH_2Cl_2 (872 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. During the first-stage of the polymerization, 4.6wt% of the reaction mixture was taken to check the progress of the polymerization. After 4 h 0

min, CNPD2 (245 mg, 889 μmol, 13.0 equiv) was added to the reaction mixture. The second-stage of the polymerization was continue for 2 h 6 min. Dry pyridine (38.9 μL, 492 μmol, 7.15 equiv) was added as a hydrochloric acid scavenger, and $ViSiMe_2Cl$ (38.9 μL, 289 μmol, 4.2 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/H_2O (2/1 (v/v), 3 mL) and the upper layer was removed; the washing procedure with MeCN/H_2O was repeated in total four times. The residue was diluted with toluene (2 mL) and concentrated *in vacuo*. The solvent remaining in the product was thoroughly removed *in vacuo* to obtain α,ω-bis[dimethyl(vinyl)silyl]-terminated triblock poly[dimethylsiloxane-*co*-3-cyanopropyl(methyl)siloxane] (P(DMS-*co*-CNPMS)-*b*-PDMS-*b*-P(DMS-*co*-AMS)) (336.9 mg, 71.5% yield, $M_{n,NMR}$ = 6.37 kDa (Outer block: $<X_{n,D}/X_{n,CNP}>_{outer}$ = 14.7/5.9; Inner block: $<X_{n,D}>_{inner}$ = 33.7), $Đ_M$ = 1.09_8) as a colorless liquid. ^{1}H NMR and ^{29}Si{^{1}H} NMR spectra of the product are shown in Fig. S16 and S17. (The sampling was conducted four times in this polymerization)

Two-stage copolymerizations of D3 (25 equiv) and CNPD2 (31 equiv) with the same experimental procedures (Table 3, entry 4) produced P(DMS-*co*-CNPMS)-*b*-PDMS-*b*-P(DMS-*co*-AMS) with higher molar mass (336.9 mg, 71.5% yield, $M_{n,NMR}$ = 16.3 kDa, $<X_{n,D}/X_{n,CNP}>_{outer}$ = 44.8/17.2 and $<X_{n,D}>_{inner}$ = 69.3), $Đ_M$ = 1.09_8) as a colorless liquid. ^{1}H NMR and ^{29}Si{^{1}H} NMR spectra of the product are shown in Fig. S18 and S19.

Solubility test (Table 5)

The solubility of the synthesized p(DMS-*co*-CNPMS), p(DMS-*co*-CNPMS)-*b*-PDMS-*b*-p(DMS-*co*-CNPMS), and PDMS was quialitatively checked by adding 20–30 μL of solvents to 2 mg of polymers. The polymers were determined to be soluble, when the resulting mixture produces a homogeneous solution. The polymers were determined to be insoluble, when the resulting mixture produces separated two phases. The polymers were determined to be partly soluble, when the solvent dissolved an unignorable amount of polymers, in particular polymers with low molar mass.

For PDMS, the two expressions, ‘partly soluble (P)’ and ‘mostly insoluble (mX)’ were used to express the difference in the maximum molar mass of PDMS that the solvents can dissolve. As long as we have tested, acetone and 1,4-dioxane can dissolve PDMS with molar mass of up to 20000–40000. Methanol, acetonitrile, and *N*,*N*-dimethylformamide can dissolve PDMS with molar mass of up to 3000.

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 1–3)[S6]

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.

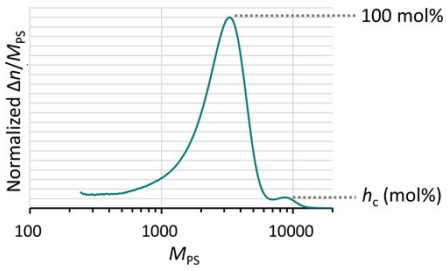


Fig. S4. Determination of h_c (mol%) for polysiloxanes from their molar-mass distributions, which were estimated from SEC measurements using toluene as the eluent, narrowly dispersed polystyrene standards, and an RI detector.

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).

Determination of number-average degree of polymerization (<X_n>) and $M_{n,NMR}$ of the polysiloxane using ^{1}H NMR spectroscopy.

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

Index 'Y' for $<X_{n,Y}>$ are defined as:

CNP = 3-cyanopropyl(methyl)siloxane units;

D = dimethylsiloxane units;

V = methyl(vinyl)siloxane units;

The integral values of peak x in ^{1}H NMR spectra are written as I_x.

For symmetrically terminated P(DMS-*co*-CNPMS) (Table 1, 3): The peaks in Fig. 2 and S12 were used for the calculation.

(α,ω-bis[dimethyl(phenyl)silyl]-P(DMS-*co*-CNPMS))

$<X_{n,CNP}> = (I_c/2) / (I_f/6)$

$<X_{n,D}> = ((I_{a+b} - 3I_c/2)/6) / (I_f/6)$

$M_{n,NMR} = 74.154<X_{n,D}> + 127.22<X_{n,CNP}> + M_{terminal}$

(α,ω-bis[dimethyl(phenyl)silyl] groups: $M_{terminal} = 286.52$, α,ω-bis[dimethyl(vinyl)silyl] groups: $M_{terminal} = 186.40$)

For asymmetrically terminated P(DMS-*co*-CNPMS) (Table 2): The peaks in Fig. S8 were used for the calculation.

(α-silyl-ω-[dimethyl(vinyl)silyl]-P(DMS-*co*-CNPMS))

$<X_{n,CNP}> = (I_c/2) / (I_{g+h+i}/3)$

$<X_{n,D}> = ((I_{a+b} - 3I_c/2)/6) / (I_{g+h+i}/3)$

$M_{n,NMR} = 74.154<X_{n,D}> + 127.22<X_{n,CNP}> + M_{α\text{-}end} + M_{ω\text{-}end}$

(α-[(3-cyanopropyl)dimethylsilyl] group, $M_{α\text{-}end} = 142.25$; α-[1,1,1,3,3,5,5,7,7-nonamethyltetrasiloxy] group, $M_{α\text{-}end} = 311.65$; α-triphenylsilyl group, $M_{α\text{-}end} = 275.40$)

(ω-[dimethyl(vinyl)silyl] group: $M_{ω\text{-}end} = 85.20$)

For P(DMS-*co*-MVS-*co*-CNPMS) with α,ω-bis[(chloromethyl)dimethylsilyl] groups (Table 2, entry 2): The peaks in Fig. S14 were used for the calculation.

$<X_{n,CNP}> = (I_g/2) / (I_j/6)$

$<X_{n,CNP}> = (I_{c+d+e}/3) / (I_j/6)$

$<X_{n,D}> = ((I_{a+f} - 3I_g/2)/6) / (I_j/6)$

$M_{n,NMR} = 74.154<X_{n,D}> + 86.165<X_{n,V}> + 127.22<X_{n,CNP}> + M_{terminal}$

(α,ω-bis[(chloromethyl)dimethylsilyl] groups: $M_{terminal} = 231.26$)

NMR spectra of the products

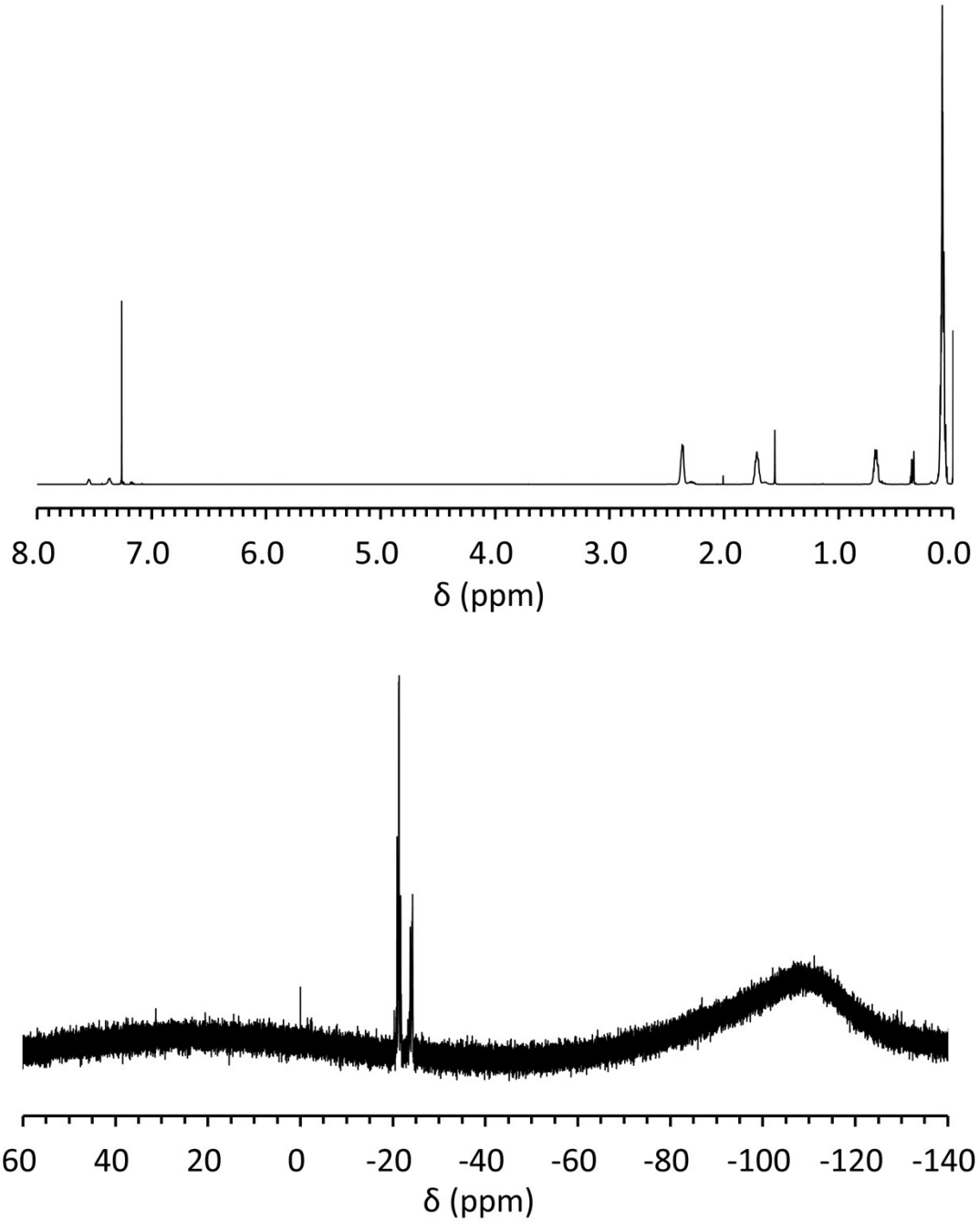


Fig. S5. Full ^{1}H and ^{29}Si{^{1}H} NMR spectra of α,ω-bis[dimethyl(phenyl)silyl]-terminated p(DMS-*co*-CNPMS) ($M_{n,NMR}$ = 6.41 kg mol^{-1}; $\langle X_{n,D}/X_{n,CNP}\rangle$ = 43.9/22.6; $Đ_M$ = 1.06$_7$, Table 1, entry 2) in $CDCl_3$.

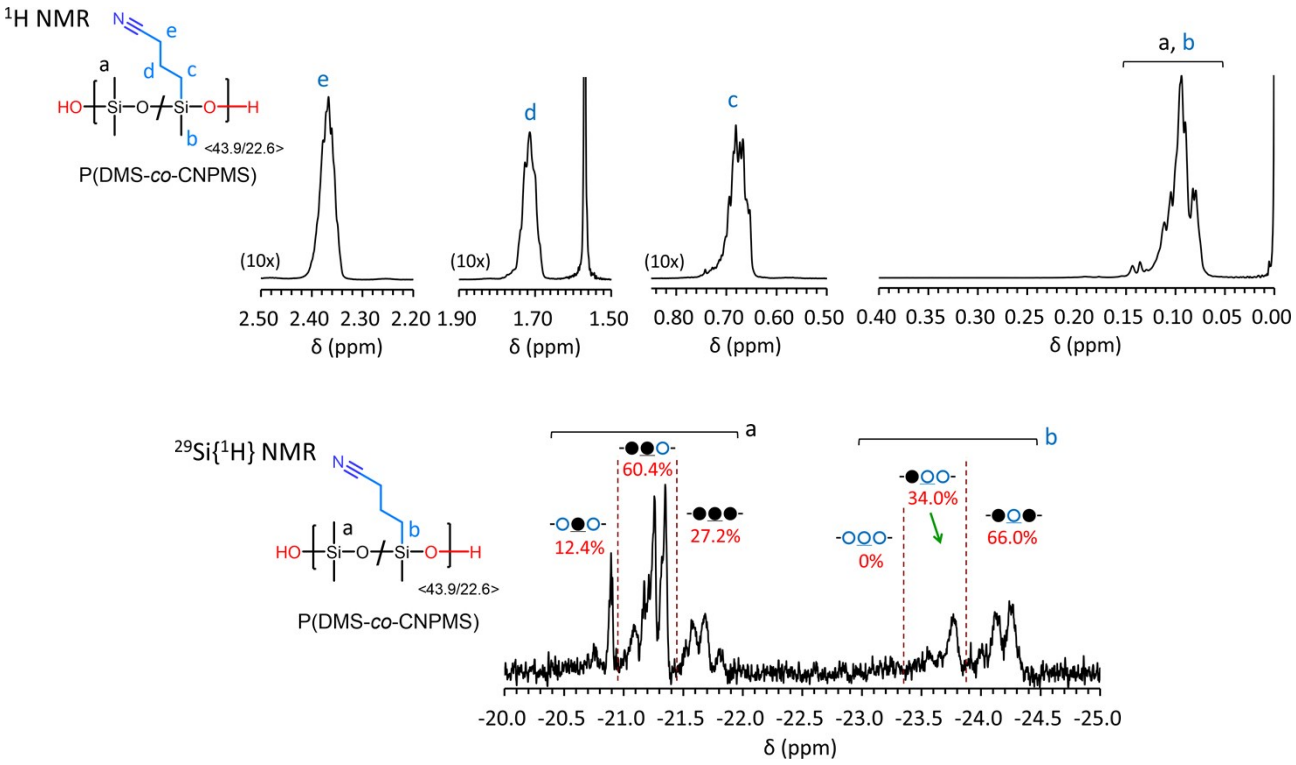


Fig. S6. ^{1}H NMR and ^{29}Si{^{1}H} NMR spectra of α,ω-silanol-terminated P(DMS-*co*-CNPMS) ($M_{n,NMR}$ = 6.14 kg mol^{-1}, $\langle X_{n,D}/X_{n,CNP}\rangle$ = 43.9/22.6, $Đ_M$ = 1.06$_7$) in $CDCl_3$.

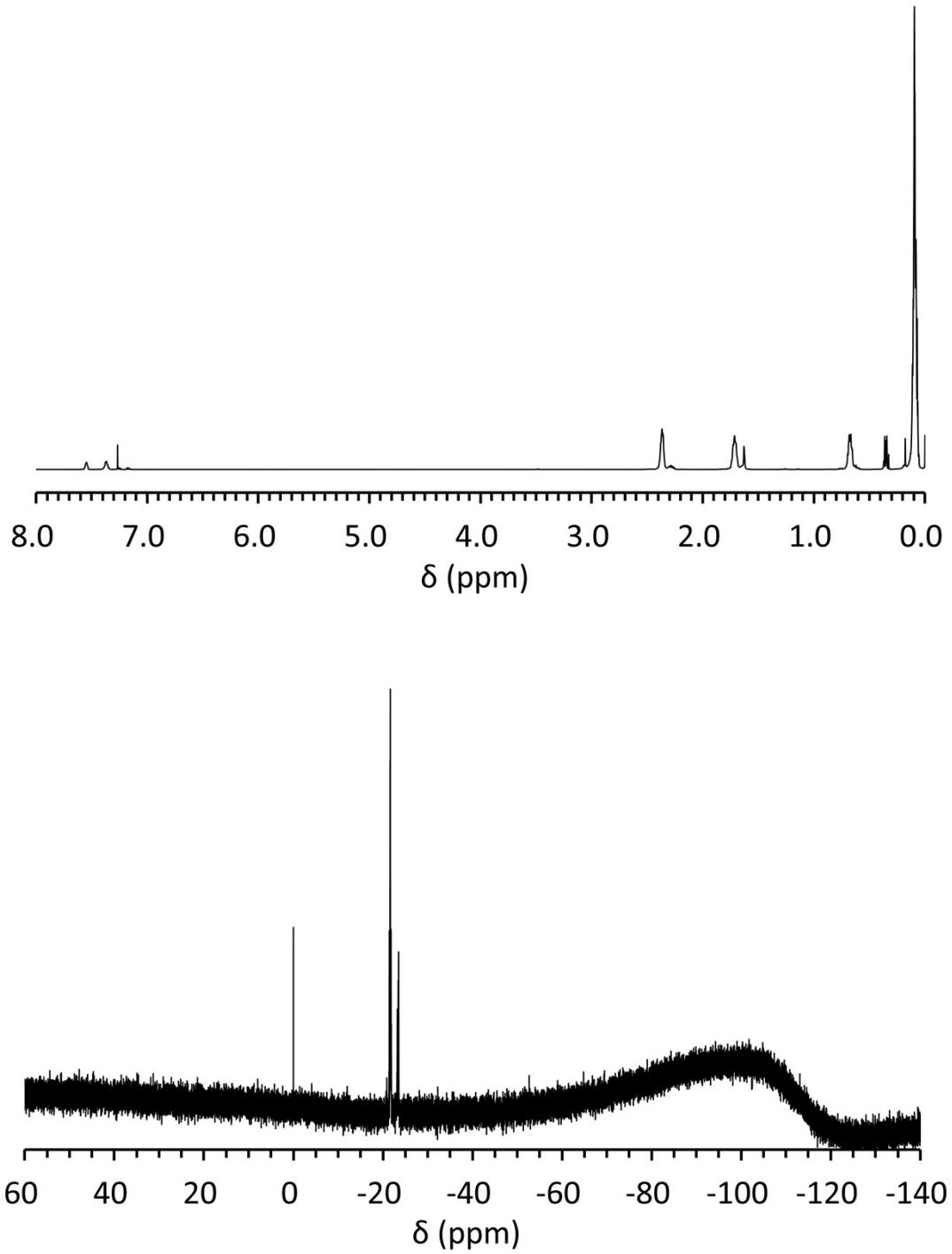


Fig. S7. Full ^{1}H and ^{29}Si{^{1}H} NMR spectra of α,ω-silanol-terminated P(DMS-*co*-CNPMS) ($M_{n,NMR}$ = 6.14 kg mol^{-1}, $<X_{n,D}/X_{n,CNP}>$ = 43.9/22.6, $Đ_M$ = 1.06$_7$) in $CDCl_3$.

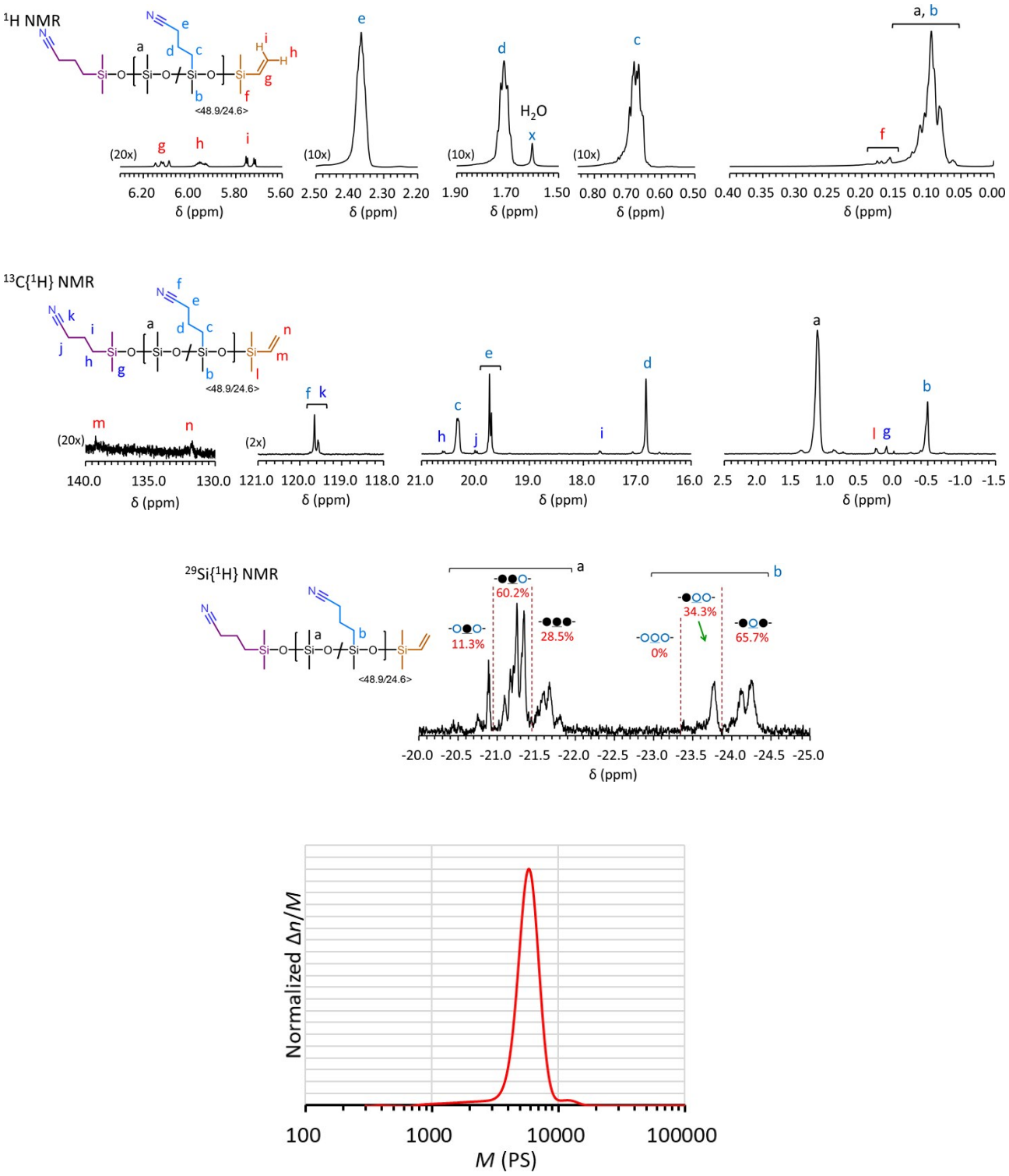


Fig. S8. ^{1}H NMR and ^{29}Si{^{1}H} NMR spectra of P(DMS-*co*-CNPMS) end-functionalized with a 3-cyanopropyldimethylsilyl and a dimethyl(vinyl)silyl group ($M_{n,NMR}$ = 6.99 kg mol^{-1}, $Đ_M$ = 1.10$_3$, Table 2, entry 3) in $CDCl_3$.

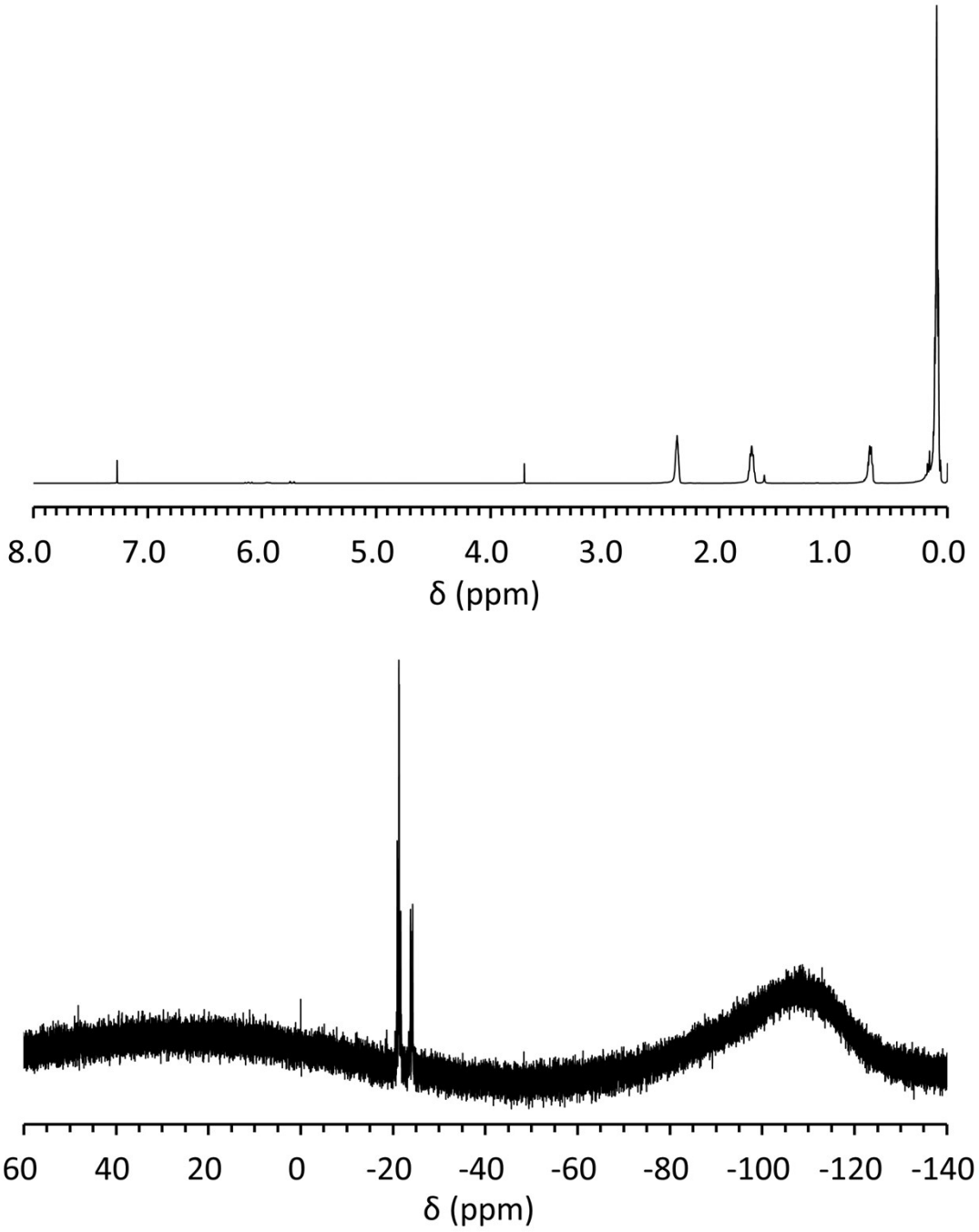


Fig. S9. Full ^{1}H and $^{29}Si\{^{1}H\}$ NMR spectra of P(DMS-*co*-CNPMS) end-functionalized with a 3-cyanopropyldimethylsilyl and a dimethyl(vinyl)silyl group ($M_{n,NMR}$ = 6.99 kg mol^{-1}, $Đ_M$ = 1.10$_3$, Table 2, entry 3) in $CDCl_3$.

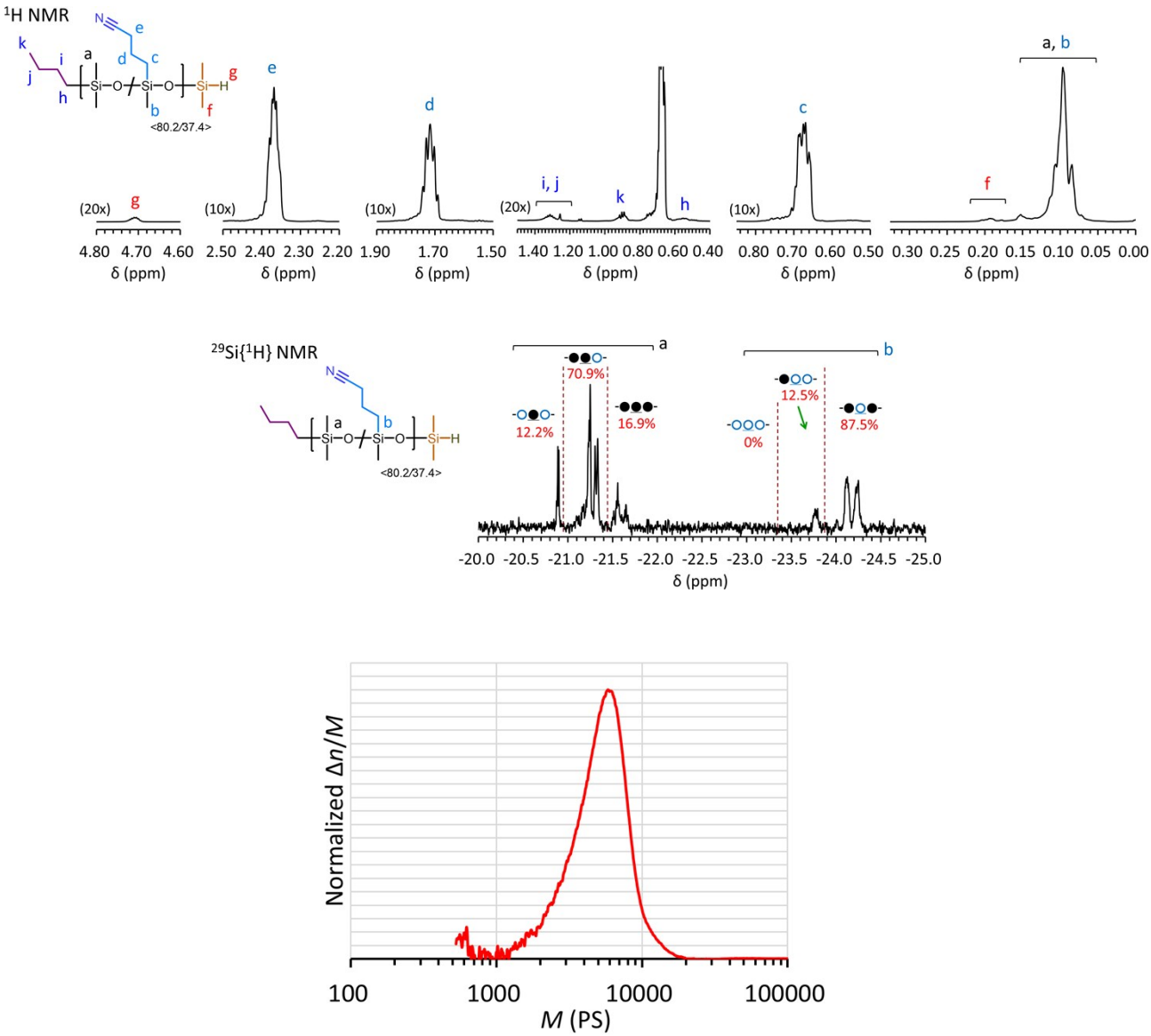


Fig. S10 ^{1}H NMR and ^{29}Si{^{1}H} NMR spectra of P(DMS-*co*-CNPMS) end-functionalized with an *n*-butyl and a dimethylsilyl group ($M_{n,NMR}$ = 11.0 kg mol^{-1}, $Đ_M$ = 1.22$_1$, Table 2, entry 4) in $CDCl_3$.

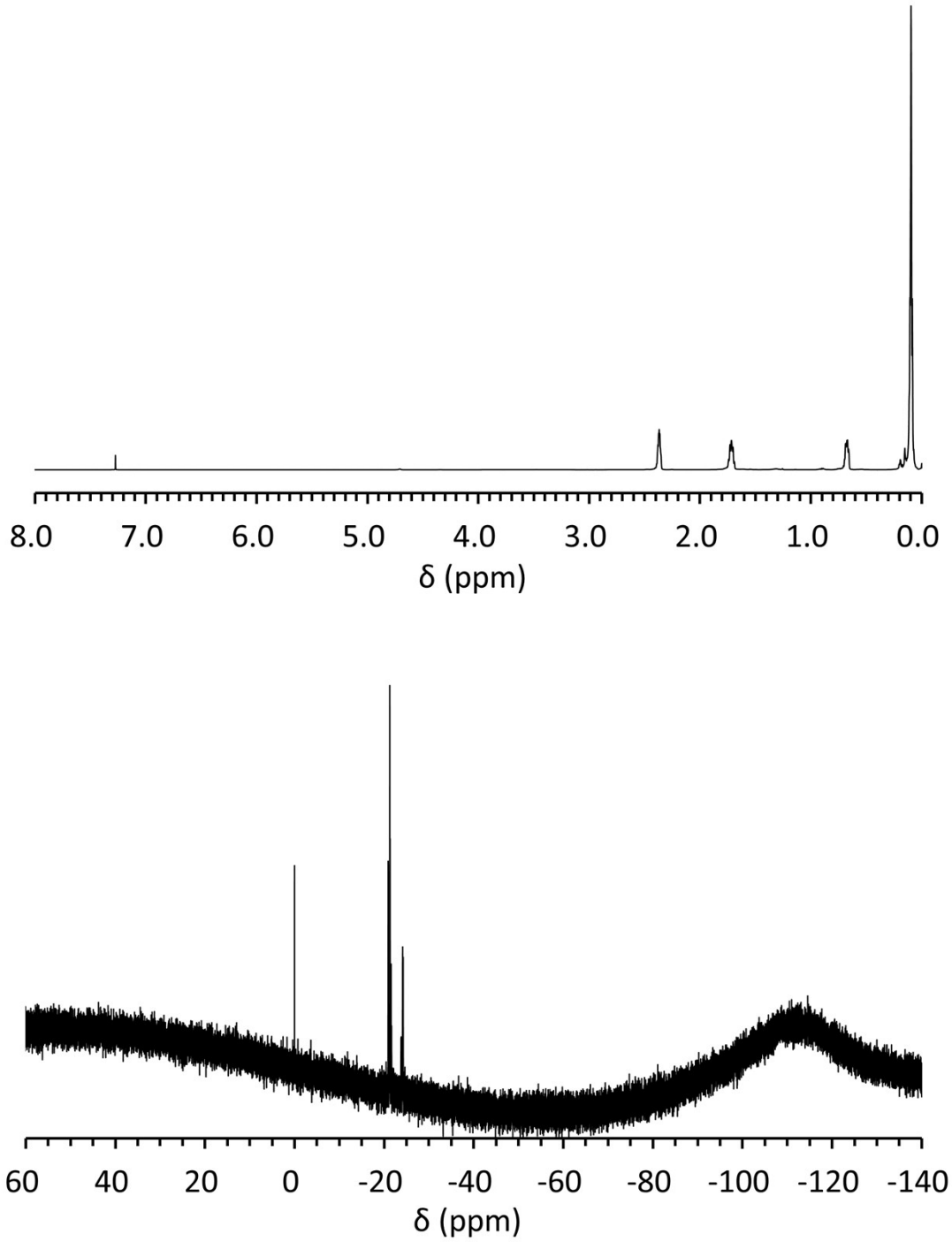


Fig. S11. Full ^{1}H and $^{29}Si\{^{1}H\}$ NMR spectra of P(DMS-*co*-CNPMS) end-functionalized with an *n*-butyl and a dimethylsilyl group ($M_{n,NMR}$ = 11.0 kg mol^{-1}, $Đ_M$ = 1.22$_1$, Table 2, entry 4) in $CDCl_3$.

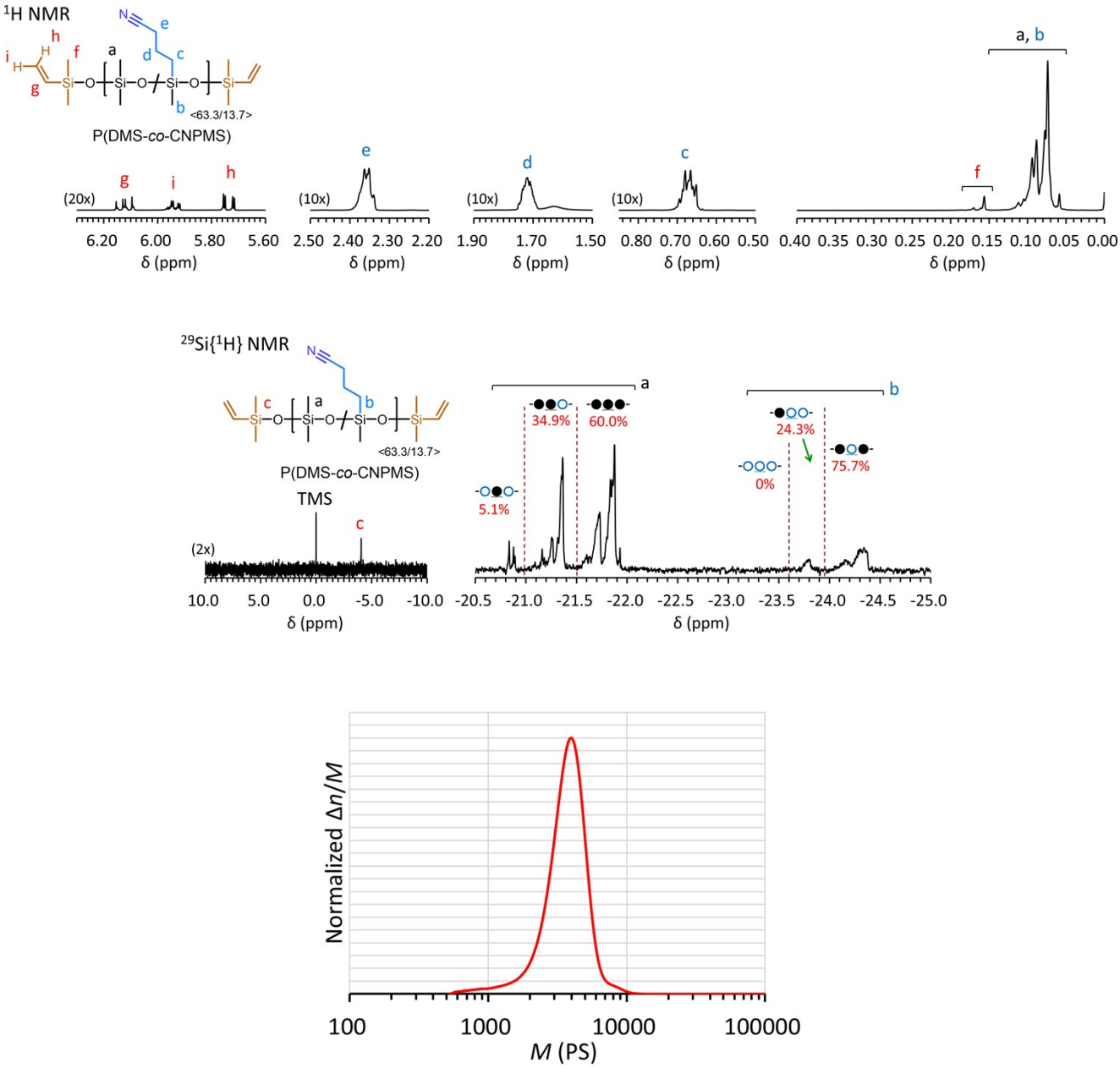


Fig. S12. ^{1}H NMR and ^{29}Si{^{1}H} NMR spectra of P(DMS-*co*-CNPMS) end-functionalized with (chloromethyl)dimethylsilyl groups ($M_{n,NMR}$ = 6.63 kg mol^{-1}, $Đ_M$ = 1.09$_9$, Table 3, entry 1) in $CDCl_3$.

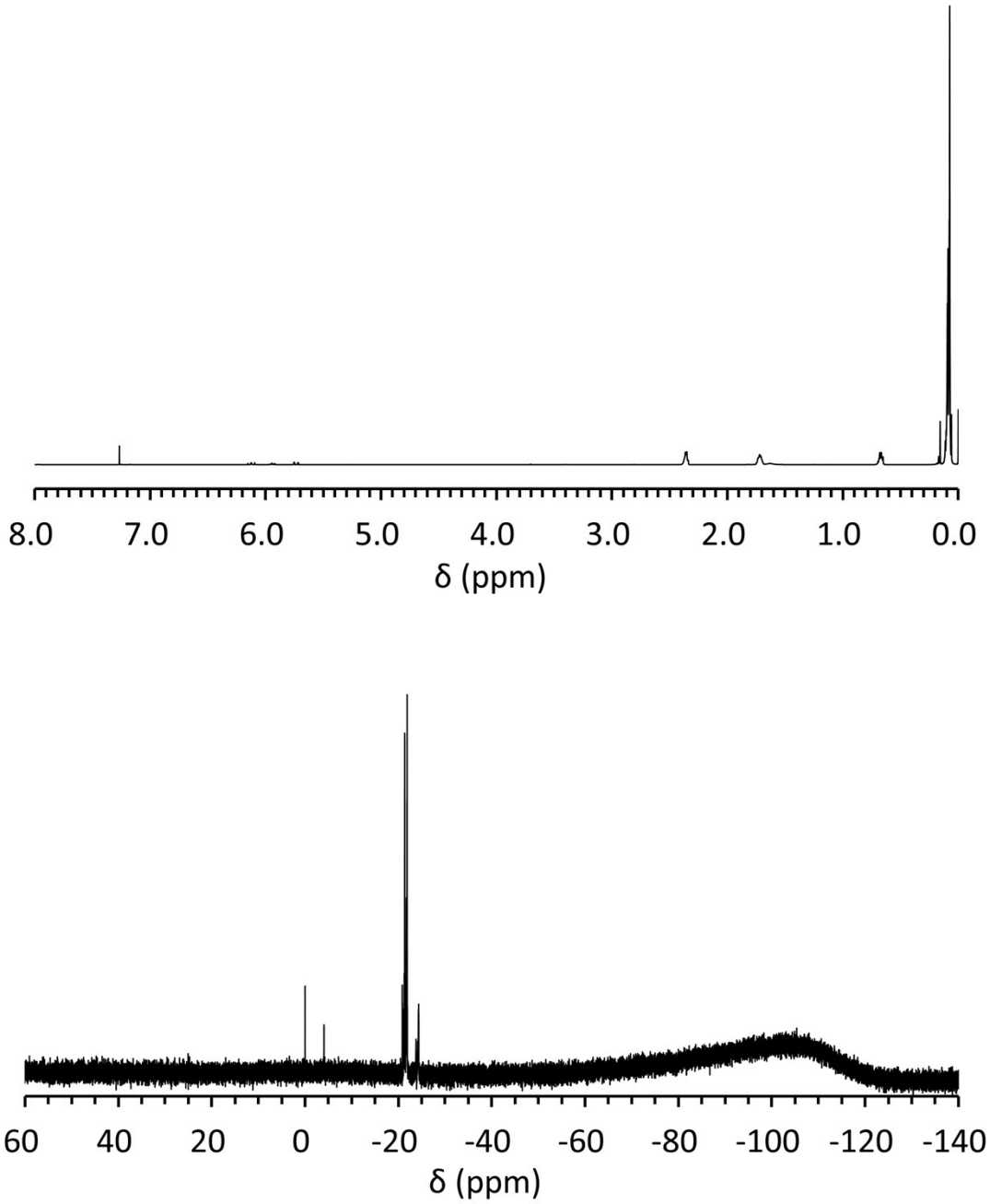


Fig. S13. Full ^{1}H and ^{29}Si{^{1}H} NMR spectra of P(DMS-*co*-CNPMS) end-functionalized with (chloromethyl)dimethylsilyl groups ($M_{n,NMR}$ = 6.63 kg mol^{-1}, $Đ_M$ = 1.09$_9$, Table 3, entry 1) in $CDCl_3$.

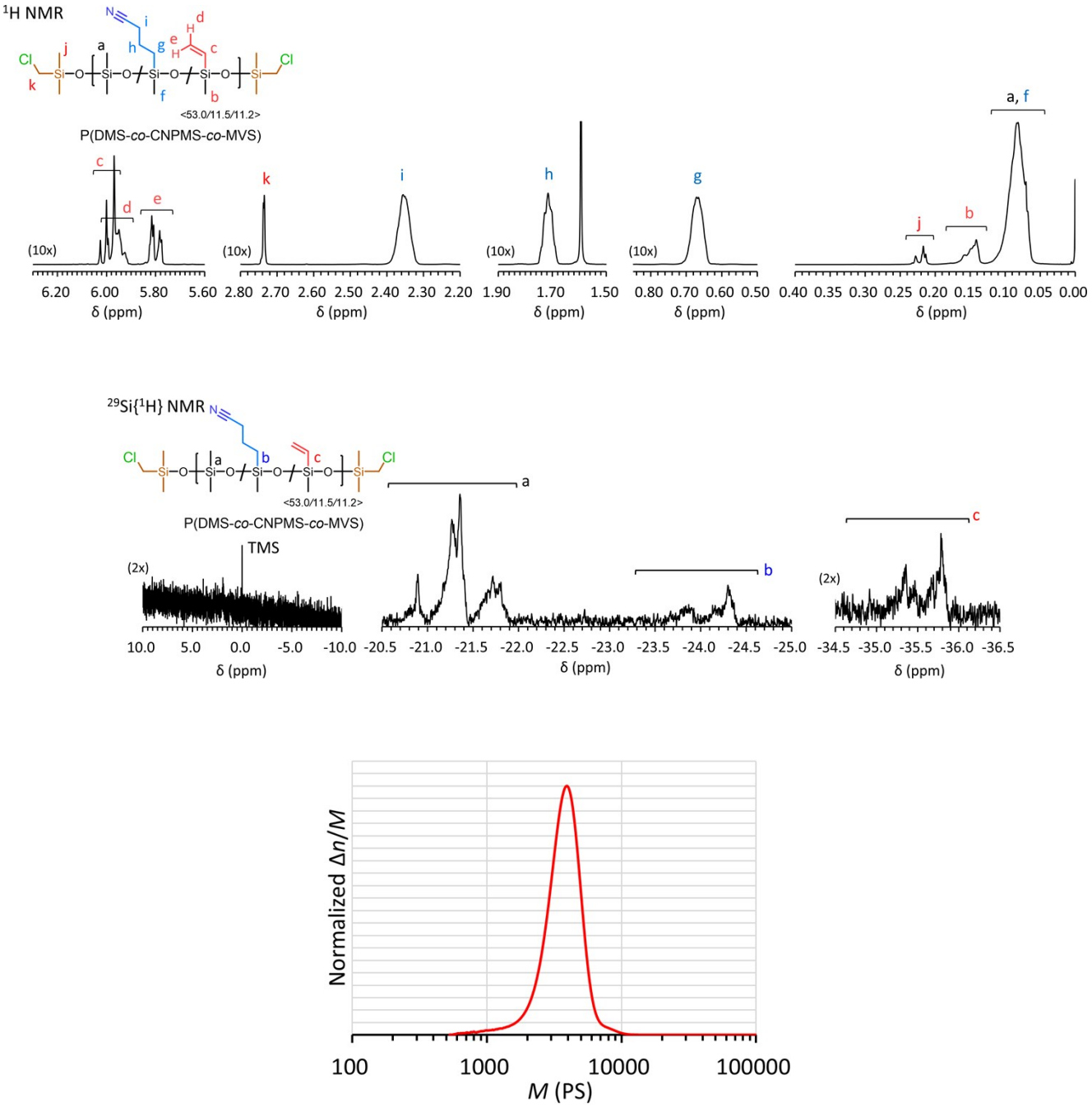


Fig. S14. ^{1}H NMR and ^{29}Si{^{1}H} NMR spectra of P(DMS-*co*-CNPMS-*co*-MVS) end-functionalized with (chloromethyl)dimethylsilyl groups ($M_{n,NMR}$ = 6.59 kg mol^{-1}, $Đ_M$ = 1.09$_1$, Table 3, entry 2) in $CDCl_3$.

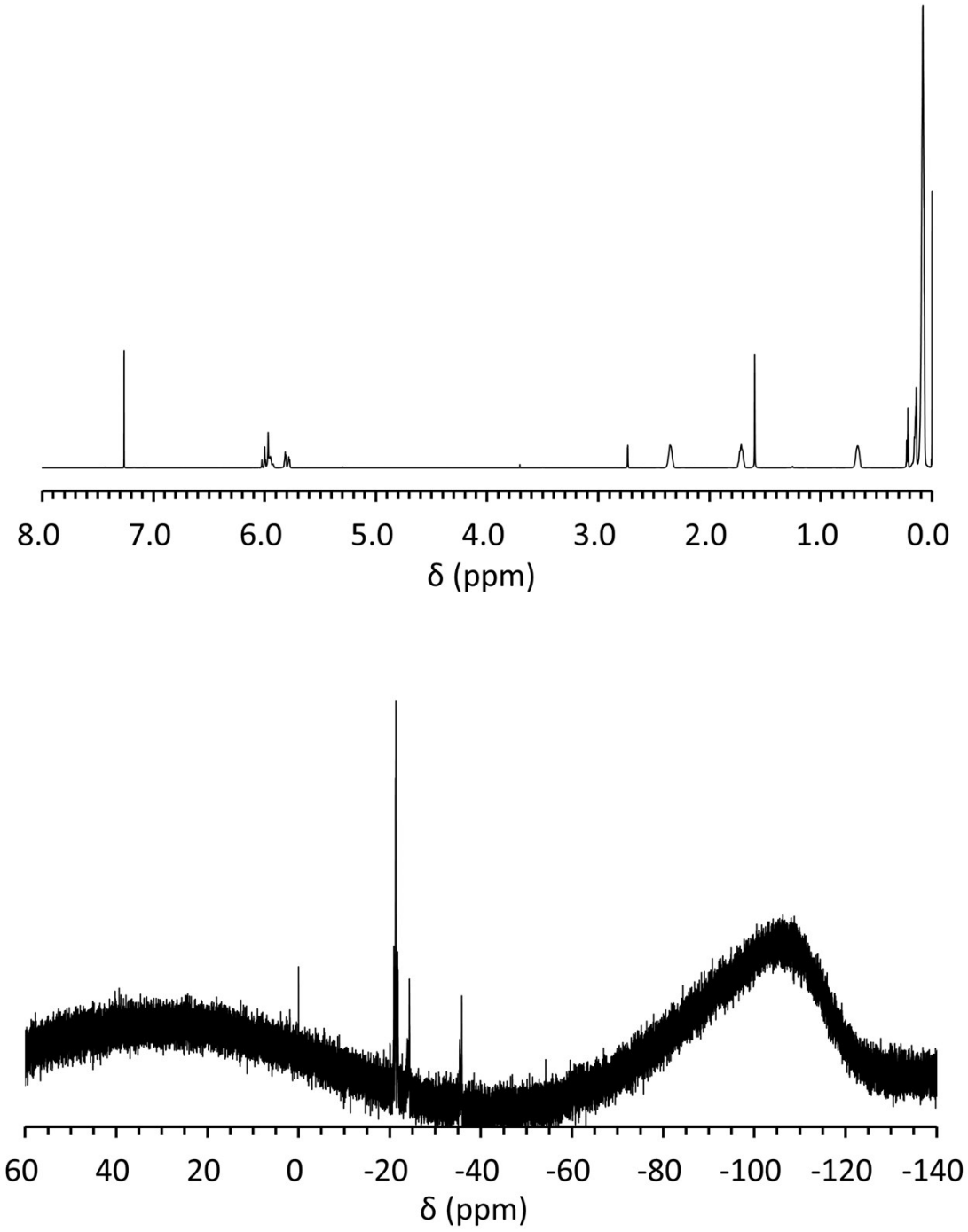


Fig. S15. Full ^{1}H and $^{29}Si\{^{1}H\}$ NMR spectra of P(DMS-*co*-CNPMS-*co*-MVS) end-functionalized with (chloromethyl)dimethylsilyl groups ($M_{n,NMR}$ = 6.59 kg mol^{-1}, $Đ_M$ = 1.09$_1$, Table 3, entry 2) in $CDCl_3$.

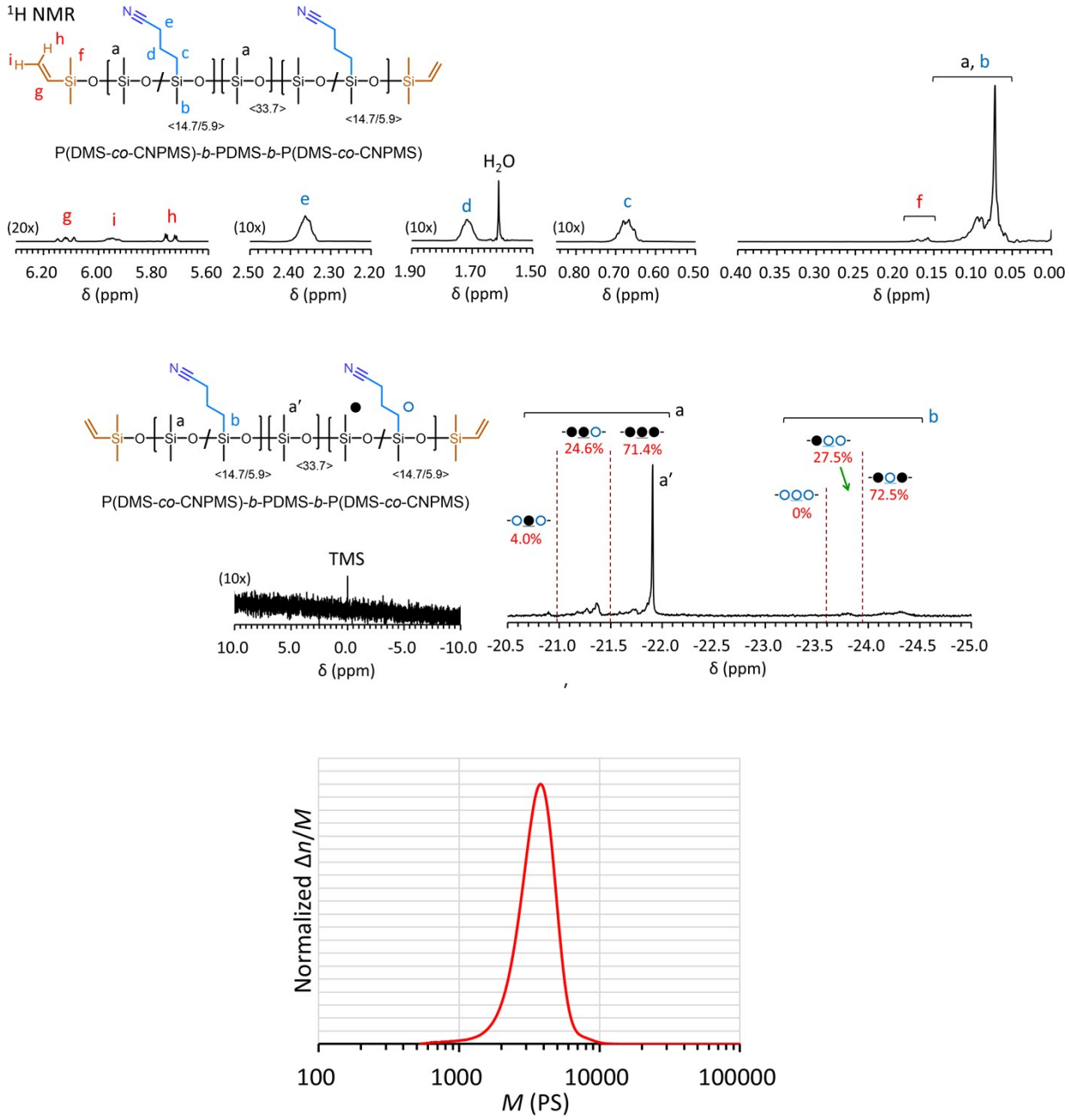


Fig. S16. ^{1}H NMR and ^{29}Si{^{1}H} NMR spectra of P(DMS-*co*-CNPMS)-*b*-PDMS-*b*-P(DMS-*co*-CNPMS) end-functionalized with (chloromethyl)dimethylsilyl groups ($M_{n,NMR}$ = 6.37 kg mol^{-1}, $Đ_M$ = 1.09$_8$, Table 3, entry 3) in $CDCl_3$.

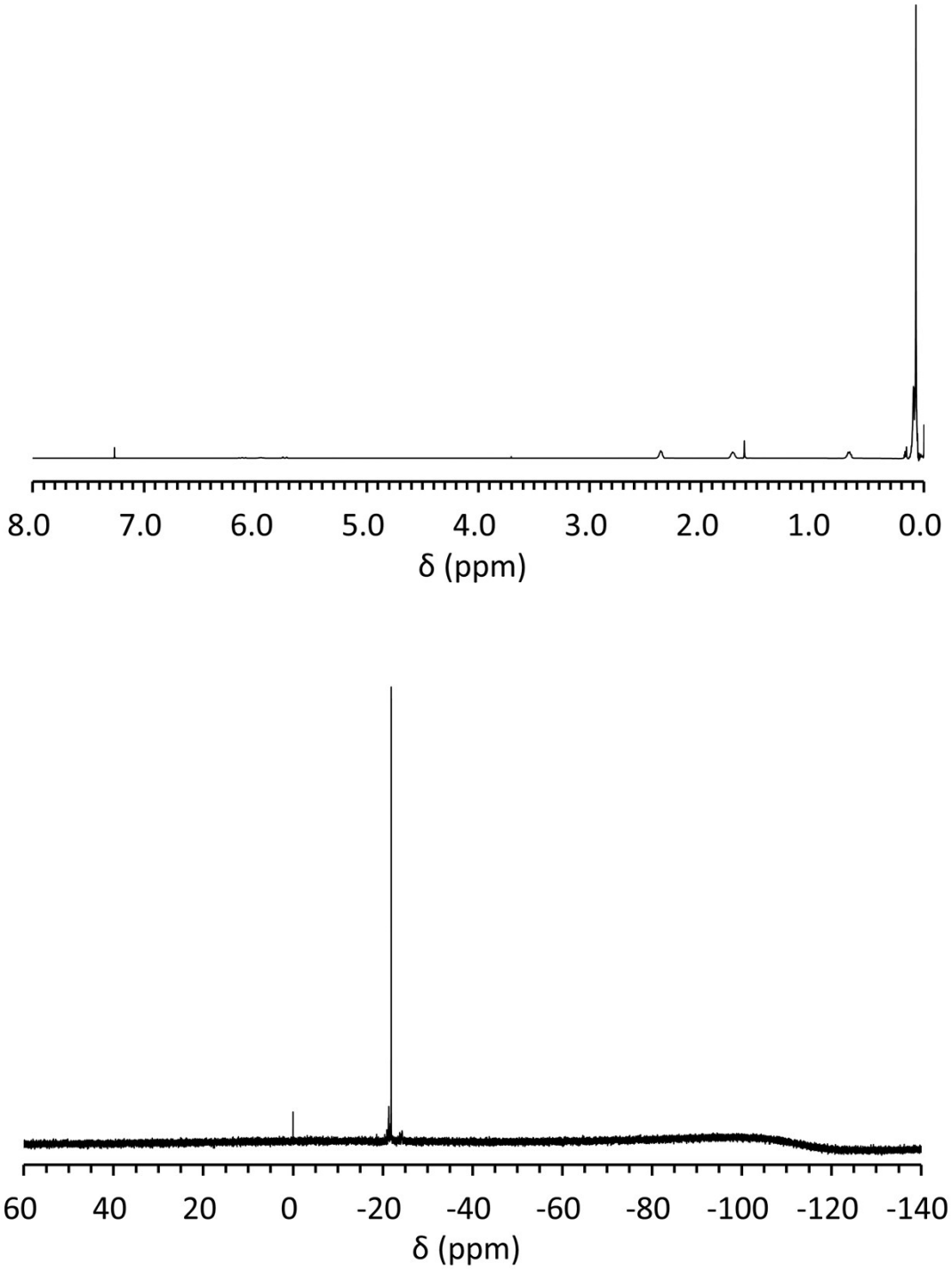


Fig. S17. Full ^{1}H and $^{29}Si\{^{1}H\}$ NMR spectra of P(DMS-*co*-CNPMS)-*b*-PDMS-*b*-P(DMS-*co*-CNPMS) end-functionalized with (chloromethyl)dimethylsilyl groups ($M_{n,NMR}$ = 6.37 kg mol^{-1}, $Đ_M$ = 1.09$_8$, Table 3, entry 3) in $CDCl_3$.

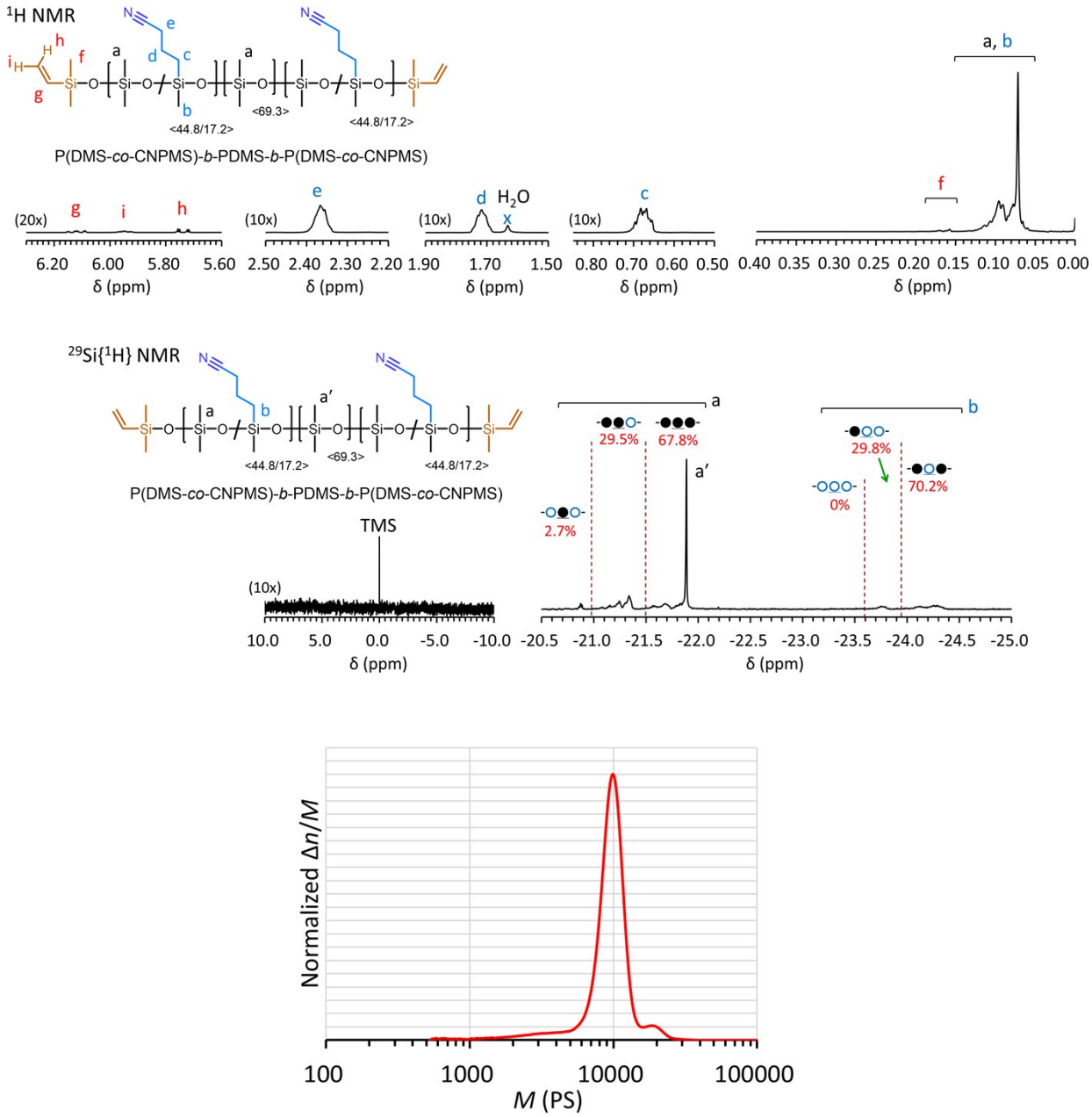


Fig. S18. ^{1}H NMR and ^{29}Si{^{1}H} NMR spectra of *α*,*ω*-bis[dimethyl(vinyl)silyl] P(DMS-*co*-CNPMS)-*b*-PDMS-*b*-P(DMS-*co*-CNPMS) ($M_{n,NMR}$ = 16.3 kg mol^{-1}, $Đ_M$ = 1.09$_8$, Table 3, entry 4) in $CDCl_3$.

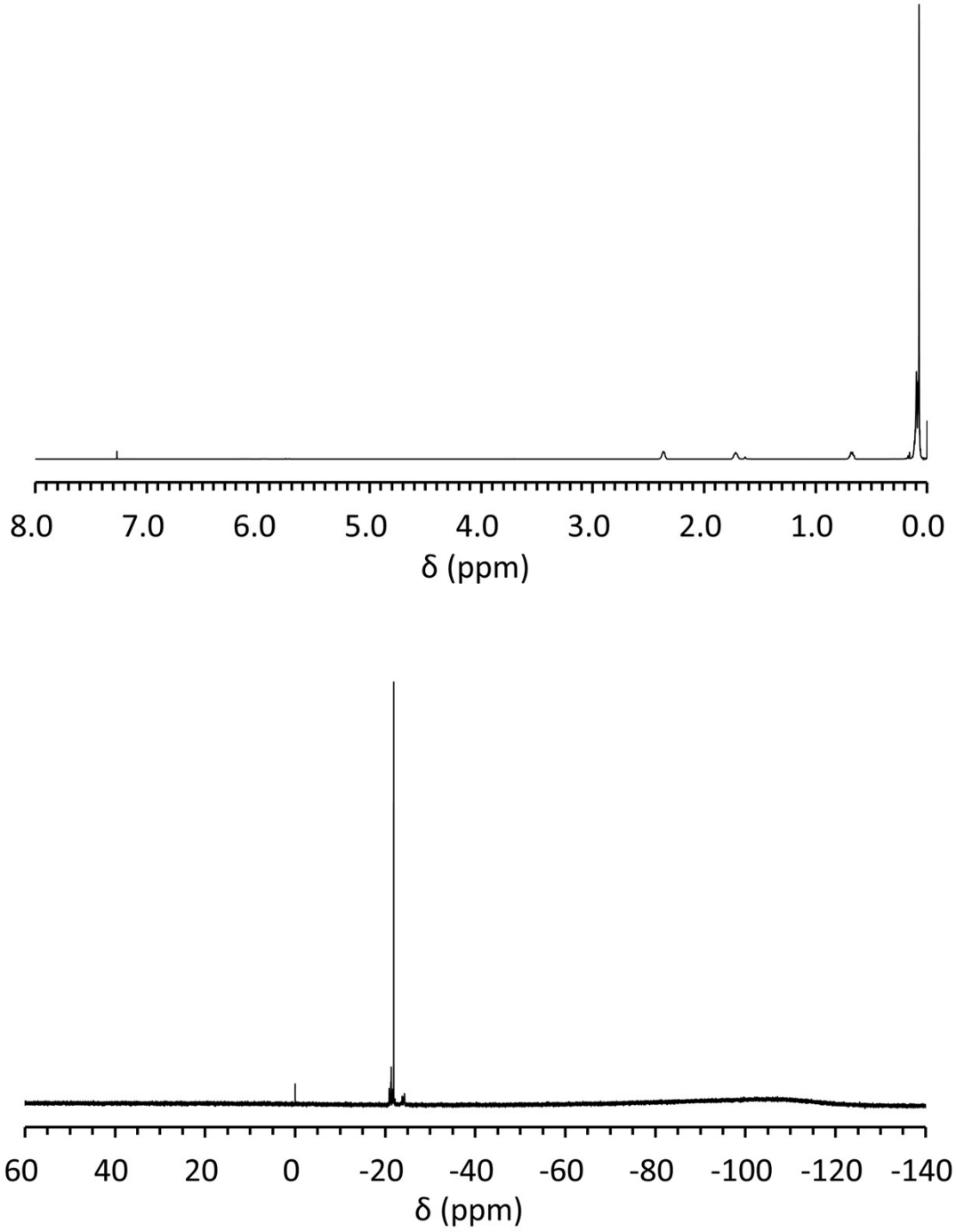


Fig. S19. Full ^{1}H and ^{29}Si{^{1}H} NMR spectra of α,ω-bis[dimethyl(vinyl)silyl] P(DMS-*co*-CNPMS)-*b*-PDMS-*b*-P(DMS-*co*-CNPMS) ($M_{n,NMR}$ = 16.3 kg mol^{-1}, $Đ_M$ = 1.09$_8$, Table 3, entry 4) in $CDCl_3$.

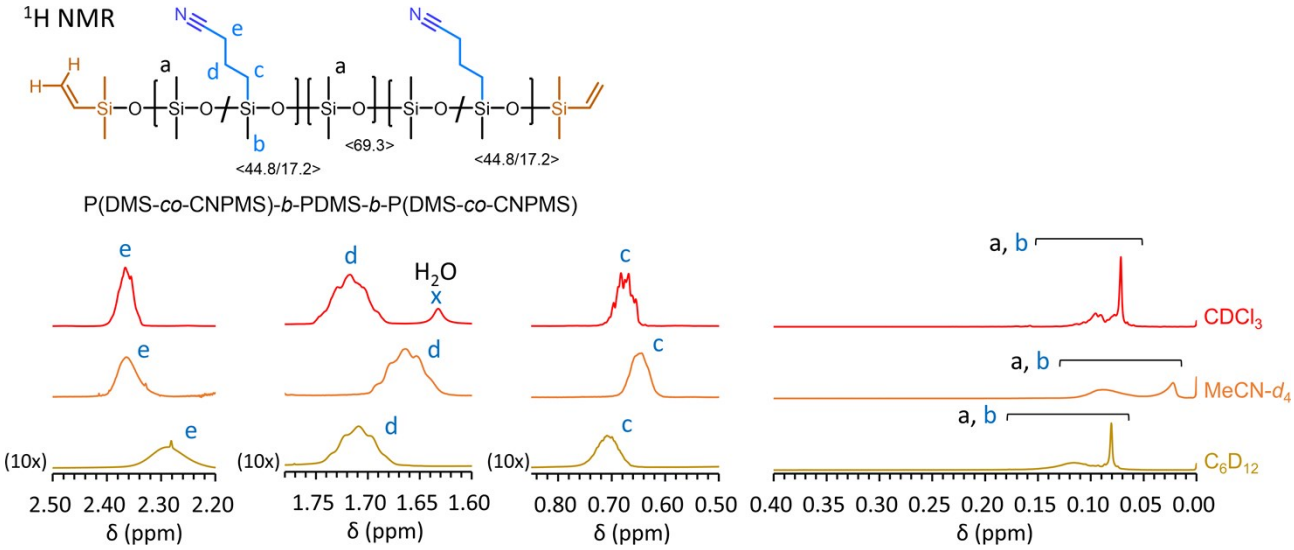


Fig. S20. ^{1}H NMR spectra of α,ω-bis[dimethyl(vinyl)silyl] P(DMS-*co*-CNPMS)-*b*-PDMS-*b*-P(DMS-*co*-CNPMS) ($M_{n,NMR}$ = 16.3 kg mol^{-1}, $Đ_M$ = 1.09$_8$, Table 3, entry 4) observed in $CDCl_3$, MeCN-d_4, and cyclohexane-d_{12} (C_6D_{12}).

Kinetics of the polymerizations

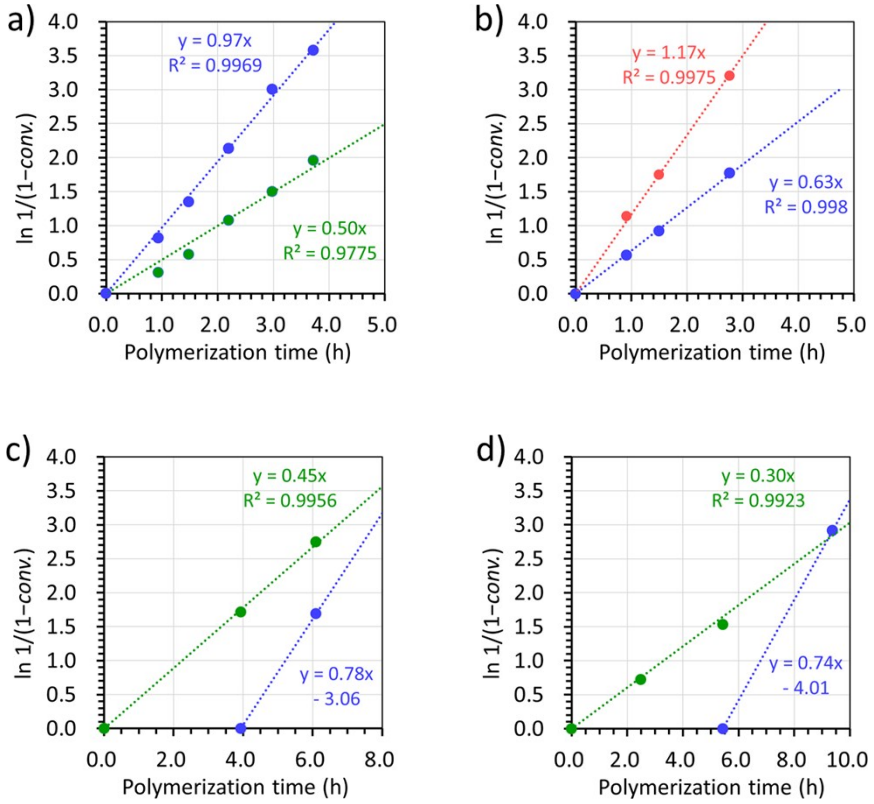


Fig. S21. First-order kinetic plots for the copolymerizations (Table 3) of:

(a) CNPD2 and D3 ($[CNPD2]_0/[D3]_0/[H_2O]_0/[TMMG]_0$ = 12.9/12.5/1/0.125, premix method, entry 1);

(b) CNPD2 and VD2 ($[CNPD2]_0/[VD2]_0/[H_2O]_0/[TMMG]_0$ = 12.9/11.9/1/0.075, premix method, entry 2);

(c) CNPD2 and D3 ($[CNPD2]_0/[D3]_0/[H_2O]_0/[TMMG]_0$ = 13.0/12.5/1/0.125, two-stage method, entry 3);.and

(d) CNPD2 and D3 ($[CNPD2]_0/[D3]_0/[H_2O]_0/[TMMG]_0$ = 31/25/1/0.30, two-stage method, entry 4).

The data for CNPD2, D3, and VD2 are indicated in blue, green, and red.

Method to simulate the monomeric unit sequences and chain-length distributions of the side-chain-functionalized polysiloxanes [S1]

Simulation A) for the products obtained via the polymerization of FnD2

This simulation uses the experimentally determined $M_{n,NMR}$, $Đ_M$, and molar ratios of the six possible monomer triads of P(DMS-*co*-FnMS), i.e., DDD/DDFn/FnDFn and FnFnFn/FnFnD/DFnD. The symbols D and Fn indicate a dimethylsiloxy unit and a methyl(organofunctional)siloxy unit, i.e. a (3-cyanopropyl)methylsiloxy unit.

- Ten polymer chains are generated.
- The numbers of monomeric units, $X_1 \ldots X_{10}$, for each polymer chain were determined from the normalized Gaussian distribution (Eq 1) using μ = [$M_{n,NMR}$ − (molar mass of terminal structure)])/M_{AV}, M_{AV} = (number-average molar mass of monomeric units in the polymer), and $\sigma = M_{n,NMR}/M_{AV} \times (Đ_M - 1)^{1/2}$. For P(DMS-*co*-CNPMS) with $<X_{n,D}>$ = 53.3 and $<X_{n,CNP}>$ = 27.0, M_{AV} = (74.154$<X_{n,D}>$ + 127.22$<X_{n,CNP}>$)/($<X_{n,D}>$ + $<X_{n,CNP}>$).

$$f(x) = \frac{1}{\sqrt{2\pi}\sigma} exp\left(\frac{-(x-\mu)^2}{2\sigma^2}\right) \quad (1)$$

- X_n was determined from the value that fulfills Eq 2:

$$\int_0^{X_n} f(x) = \frac{n}{11} \quad (n = 1, 2, 3, 4, 5, 6, 7, 8, 9, \text{and } 10) \qquad (2)$$

X_n was then rounded to the closest integer.

- First, two monomeric units were chosen for the 10 polymers. The probability of choosing each of the monomeric unit pairs *P*(DD), *P*(DFn), *P*(FnD), and *P*(FnFn) was calculated from the experimentally determined values of FnDFn/DDFn/DDD and FnFnFn/FnFnD/DFnD.

  For example, for FnDFn/DDFn/DDD = 0.071/0.695/0.234 and FnFnFn/FnFnD/DFnD = 0.000/0.399/0.601 (Table 4, Entry 6), the six values were calculated to be *P*(DDD) = 0.234/(2/3) = 0.156, *P*(DDFn) = 0.695/(2/3) = 0.463_3, *P*(FnDFn) = 0.071/(2/3) = 0.047_3, *P*(FnFnFn) = 0.000/(1/3) = 0.000, *P*(FnFnD) = 0.399/(1/3) = 0.133, and *P*(DFnD) = 0.601/(1/3) = 0.200_3.

  The first dyad sequence (DD/DFn/FnD/FnFn) was selected by comparing the following probabilities and a randomized number *RND* in the range of [0, 1):
  P(DD) = *P*(DDD) + *P*(DDFn)/2 = 0.387_{65}
  P(DFn) = *P*(DFnD) + *P*(FnFnD)/2 = 0.266_8
  P(FnD) = *P*(DDFn)/2 + *P*(FnDFn) = 0.278_{95}
  P(FnFn) = *P*(FnFnD)/2 + *P*(FnFnFn) = 0.066_5
- A single monomeric unit was repeatedly added to the previously generated sequences of monomeric units until the length of the polymer chain reached $X_1 \ldots X_{10}$ monomeric units.
  For the simulation of the polymerizations using water as an initiator, monomeric units were added to the left

and right of the generated monomeric sequence. For those using a silanol as an initiator, a monomeric unit was only added to the right. The monomeric unit was selected by comparing the following probabilities and a randomized number in the range of [0, 1):

Combination of terminal dyad and an incoming monomeric unit	Probability
…DD + D	P(DDD) × (2/3)
…DD + Fn	P(DDFn)/2 × (2/3)
…DFn + D	P(DFnD) × (1/3)
…DFn + Fn	P(FnFnD)/2 × (1/3)
…FnD + D	P(DDFn)/2 × (2/3)
…FnD + Fn	P(FnDFn)/2 × (2/3)
…FnFn + D	P(FnFnD)/2 × (1/3)
…FnFn + Fn	P(FnFnFn) × (1/3)

- The results of simulation A are shown in Fig. S11 and S12. The monomeric units of D and Fn are shown as ● and ○, respectively.

Simulation B) for the products in the copolymerizations

- The simulation uses the following parameters:
  (1) X_{M1} and X_{M2}, which are the initial molar ratios of the two monomers, M_1 (= FnD2) and M_2 (= D3 or Fn′D2), relative to the initiator;
  (2) $k_{p,app}$ and $Đ_M$, which are experimentally determined;
  (3) t_{exp}, which is the polymerization time in the actual experiments.
- Ten polymer chains were generated.
- The propagation reaction of the polymer chains was simulated. Condensation and intermolecular transfer of a terminal siloxy group (Scheme S1) were ignored in this simulation.
- For example, the values X_{M1} = 7.5, X_{M2} = 17.5, k_{p,app_M1} = 0.83, k_{p,app_M2} = 0.85, $Đ_M$ = 1.095, and t_{exp} = 2.6 [h] were used for the simulation of the copolymerization of AD2 (M1) and D3 (M2) shown in Table 3, Entry 6.
- The values of the expected numbers of monomeric units, $X_1 \ldots X_{10}$, in each polymer chain were determined from Eq 1 and Eq 2 using $\mu = X_{M1} \times [1 - \exp(-k_{p,app\_M1} \times t_{exp})] + X_{M2} \times [1 - \exp(-k_{p,app\_M2} \times t_{exp})]$ and $\sigma = \mu(Đ_M - 1)^{1/2}$.
- The overall polymerization was divided into Y stages. The propagation reactions in each stage were simulated for each polymer chain to generate sequences of monomeric units. This process was repeated Y times. The initial value of the time, t, was set to 0. After one round of the process, t_{step} (= t_{exp}/Y) was added to t for the next round. A Y value of 20 was used in this study.
- The following equations gave the numbers of monomers reacting with each polymer between t and $t+t_{step}$:

$$N_{M1} = X_n \times [X_{M1}/(X_{M1}+X_{M2})] \times [\{1 - \exp[-k_{p,app\_M1} \times (t + t_{step})]\} - [1 - \exp(-k_{p,app\_M1} \times t)]] \quad (3)$$

$N_{M2} = X_n \times [X_{M2}/(X_{M1}+X_{M2})] \times [\{1 - \exp[-k_{p,app\_M2} \times (t + t_{step})]\} - [1 - \exp(-k_{p,app\_M2} \times t)]]$ (4)

- Additionally, the following values were calculated:

  $N_{total} = N_{M1} + N_{M2} + N_{residual}$ (5)

  ($N_{residual}$ is the decimal part of N_{total} in the previous round of the process. Zero is used for $N_{residual}$ in the first round of the process.)

  $r_{M2} = N_{M2}/(N_{M1} + N_{M2})$ (6)

  N_{total_int} was calculated by rounding off N_{total}. (7)

- If $N_{total} \geq 1$, the polymer chain reacts with M1 or M2 N_{total_int} times. M1 or M2 was selected by comparing r_{M2} and a randomized number, *RND*, within the range of [0, 1). Namely, if $RND < r_{M2}$, a triad sequence was randomly selected from among FnDD (○●●), DFnD (●○●), or DDFn (●●○). The selected triad was used as the first triad sequence of the polymer chain or randomly added to the left or the right of the already generated polymer chain. If $RND \geq r_{M2}$ and M2 was D3, a triad sequence from D3, i.e., DDD (●●●), was used as the first triad sequence or randomly added to the left or right of the already generated polymer chain. If M2 was Fn′D2, a triad sequence was randomly selected from among Fn′DD (△●●), DFn′D (●△●), or DDFn′ (●●△) instead of DDD.
- The decimal part of N_{total} was used as $N_{residual}$ for the next round of the process.
- Triad sequences were randomly selected in this simulation because we found that statistical propagation was predominant in the actual polymerization experiments.
- The results of simulation A are shown in Fig. S11 and S12. The monomeric units D, Fn, and Fn′ are shown as ●, ○, and △, respectively.

Determination of the expected ratio of triad monomeric sequences in the products obtained in the copolymerizations of FnD2 and D3 proceeding via statistical propagation.

- The values shown in Table 4, Entries 4 and 5 were determined by the following process.
- A sufficiently long sequence of ● (= D) and ○ (= Fn) was randomly generated by combining the four possible triad sequences, i.e., ●●●/○●●/●○●/●●○. The ratio of each triad to be used was determined from the molar ratio of D3 and FnD2 used in the polymerization.
- For example, in a polymerization using D3/FnD2 = 5/5, the ratio of the four triad sequences would be:
  ●●●/○●●/●○●/●●○ = 0.5000/0.1667/0.1667/0.1667
- In a polymerization using D3/FnD2 = 3/7, the ratio of the four triad sequences would be:
  ●●●/○●●/●○●/●●○ = 0.7/0.1/0.1/0.1
- The numbers of each of the six triad sequences, i.e., ●<u>●</u>●/●<u>●</u>○/○<u>●</u>○ and ○<u>○</u>○/○<u>○</u>●/●<u>○</u>●, in the resultant sequence were counted to determine the theoretical ratio.

Simulation of the monomeric unit sequences and chain-length distributions of the side-chain-functionalized polysiloxanes[S1]

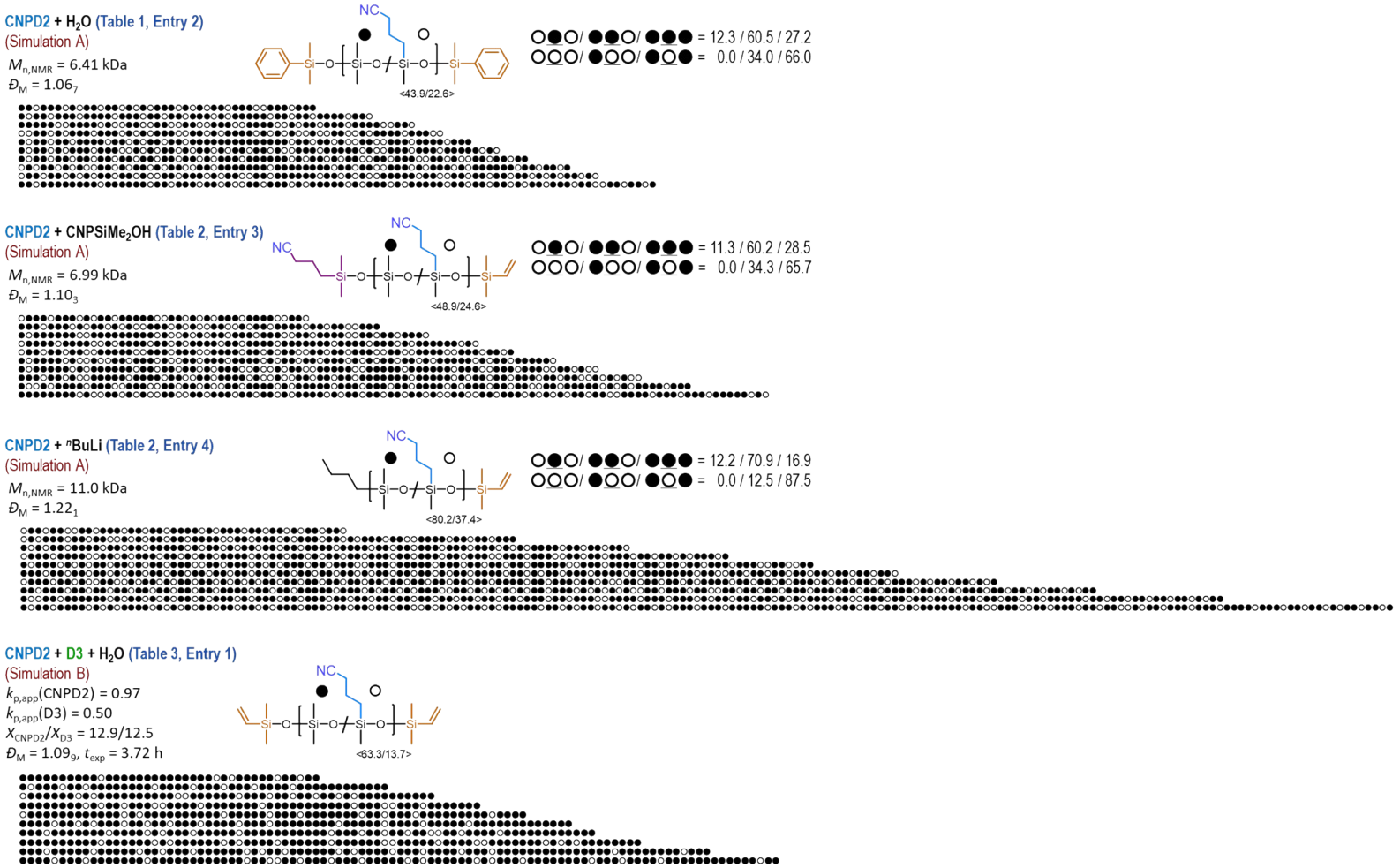


Fig. S22. Simulated results for the sequence of monomeric units and distribution of chain length of P(DMS-*co*-CNPMS) synthesized with different methods. The simulation method and the parameters used for each polymer are indicated in the figures.

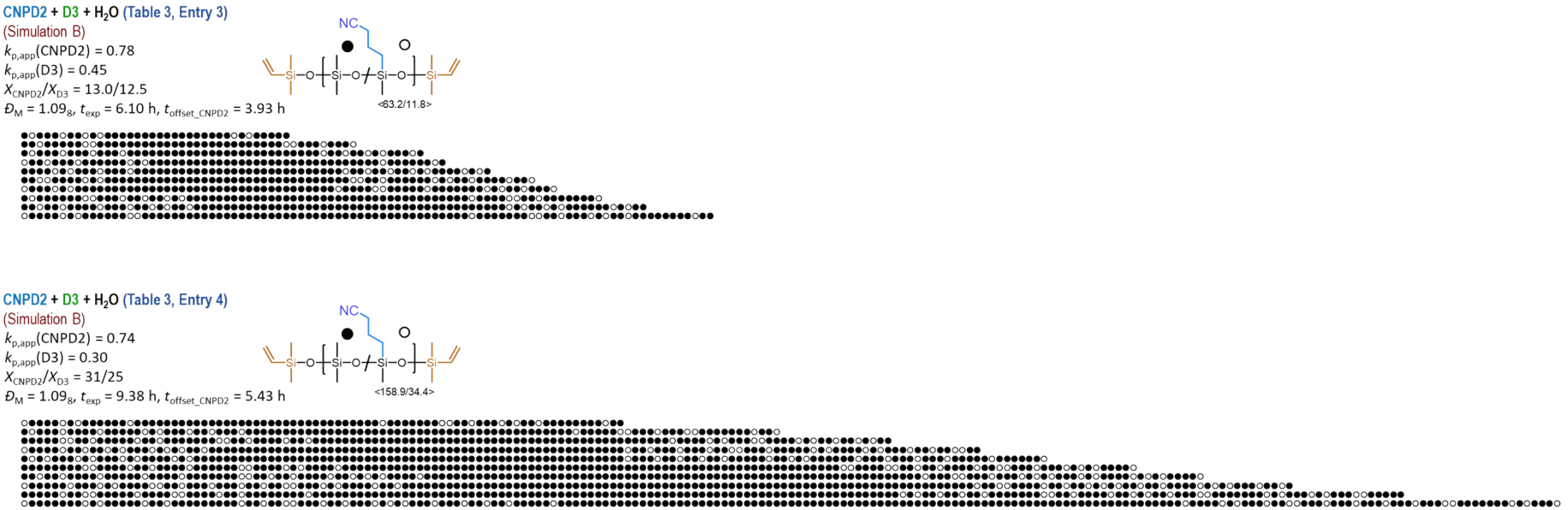


Fig. S22. (continued). Simulated results for the sequence of monomeric units and distribution of chain length of P(DMS-*co*-CNPMS) synthesized with different methods. The simulation method and the parameters used for each polymer are indicated in the figures.

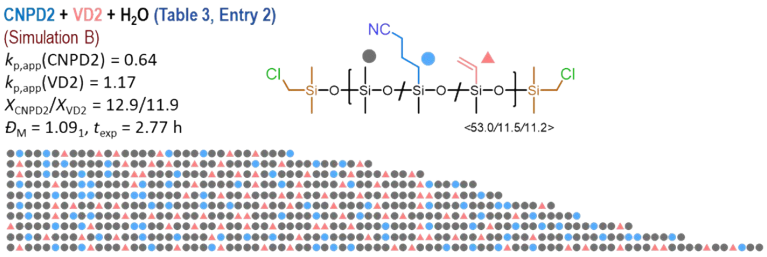
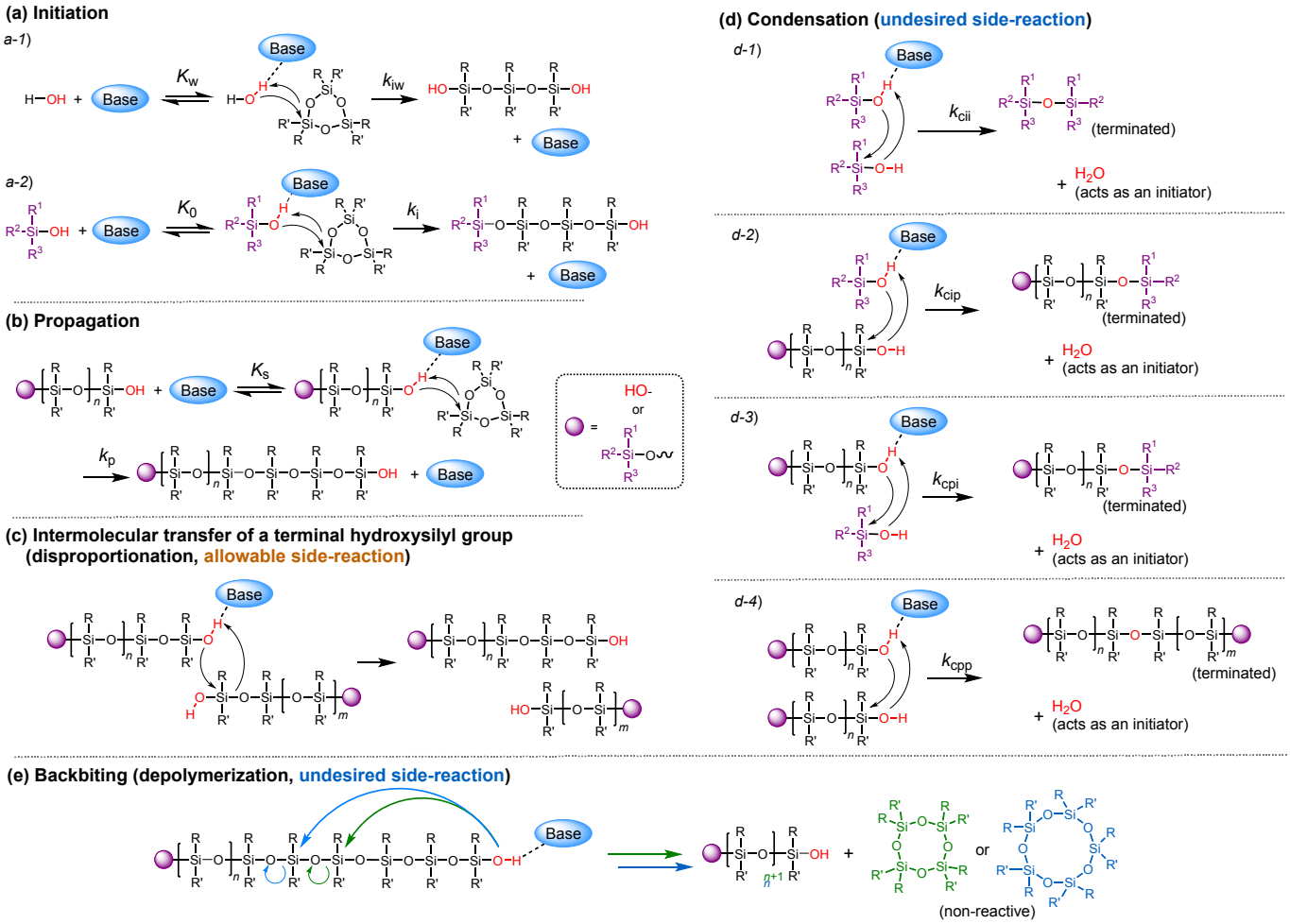


Fig. S23. Simulated results for the sequence of monomeric units and distribution of chain length of P(DMS-*co*-CNPMS-*co*-MVS) synthesized with different methods. The method and the parameters used for each polymer are indicated in the figures.



Scheme S1. Possible and plausible elementary reactions in the polymerization of cyclotrisiloxanes using a water or a silanol as an initiator and a strong organic base as a catalyst.[S6]

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