Supplemental Information
for
A Trifunctional Cyclohexasilane for Branched Poly(cyclosilane)

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Supplemental Figures:

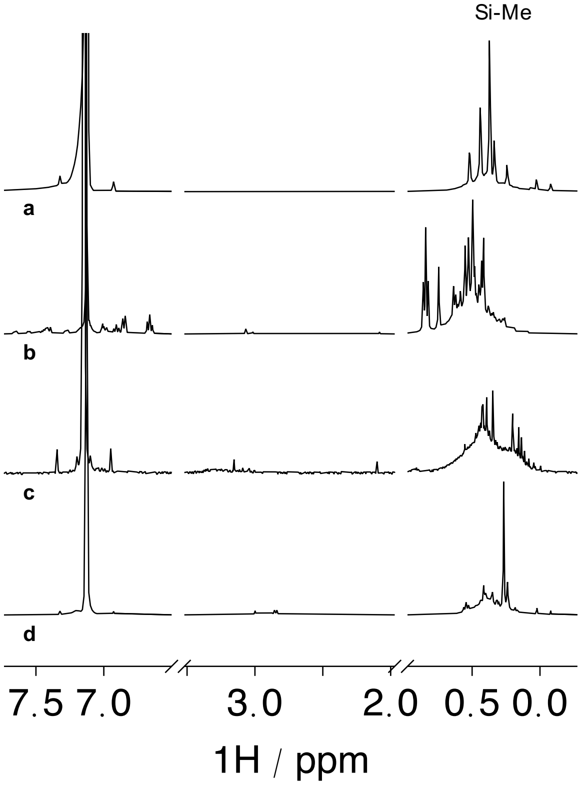


Figure S1. Cropped ^{1}H NMR spectra (400 MHz, C_6D_6) of silyltriflate intermediates illustrating decomposition occurring with excess TfOH used at higher temperatures. a. 6.6 equiv. of TfOH added to **3** at -78 ºC, b. 3.3 equiv. of TfOH added to **3** at 0 ºC followed consecutively by 4.5 equiv of TfOH added at -78 ºC, c. 4.5 equiv. of TfOH added to crude **4** at 0 ºC, d. 4.5 equiv. of TfOH added to crude **4** at -78 ºC.

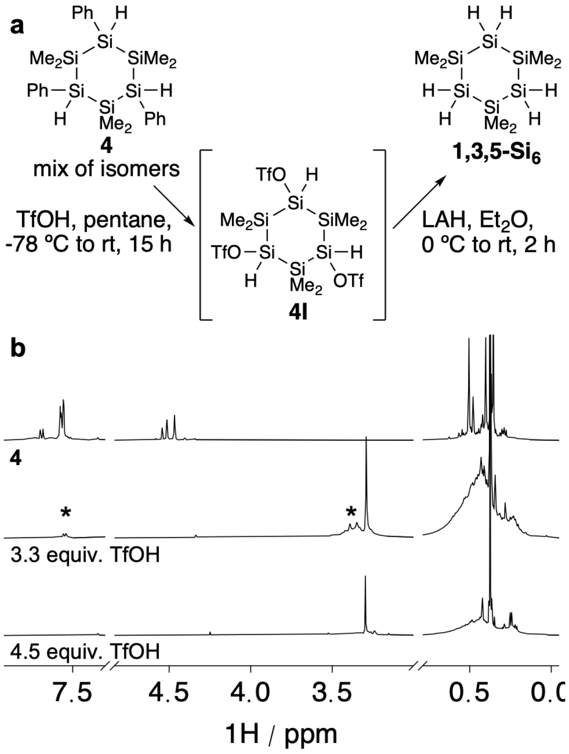


Figure S2. a. Reaction scheme of the partial dearylation and reduction of triphenyl cyclosilane **4** to form cyclosilane **1,3,5-Si₆** via silyl triflate intermediate **4I**. b. Cropped ^{1}H NMR spectra (400 MHz, C_6D_6) of **4** (upper) incomplete conversion of **4** using 3.3 equiv. TfOH, denoting partially dearylated structures with '*' (middle), and complete conversion of **4** using 4.5 equiv. TfOH (lower).

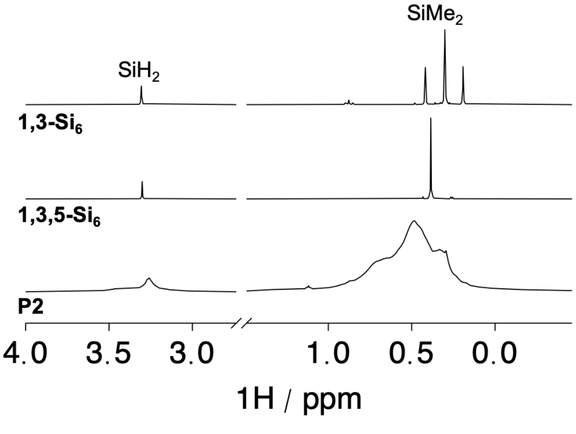


Figure S3. Cropped ^{1}H NMR spectra (400 MHz, C_6D_6) of **1,3-Si₆**, **1,3,5-Si₆**, and **P2** illustrating full consumption of both monomers during polymerization.

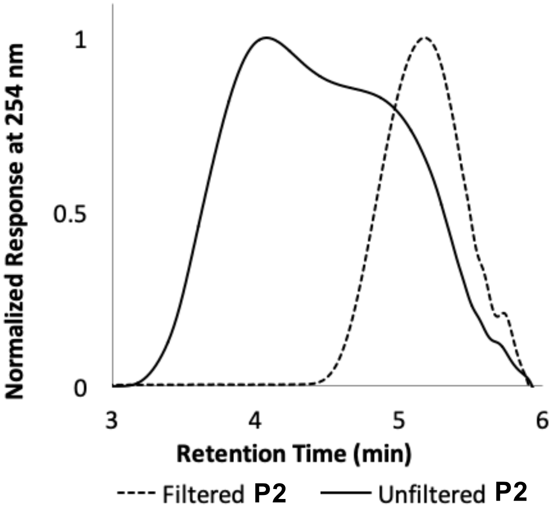


Figure S4. SEC trace of filtered and unfiltered **P2**. (THF, [polymer] = 1 mg mL^{-1}, 40 ºC, 0.35 mL min^{-1}, 10 μL injection).

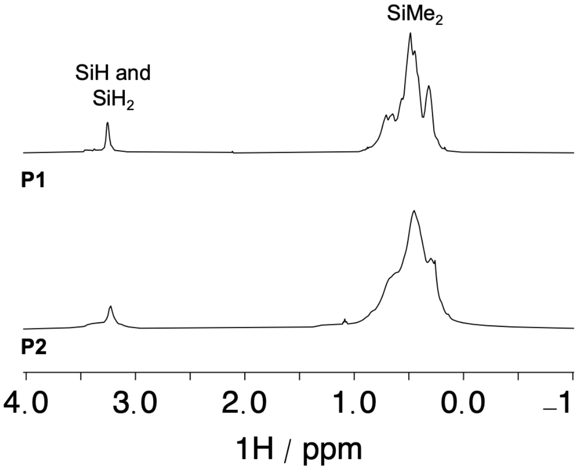


Figure S5. Cropped ^{1}H NMR spectra (500 MHz, C_6D_6) of **P1** (upper) and **P2** (lower) illustrating increased broadening of both SiH/SiH$_2$ peaks and SiMe$_2$ peaks with increasing mol % of trifunctional monomer.

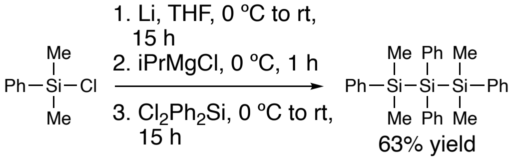
General Procedures: Unless otherwise specified, all chemicals were used as purchased without further purification. Solvents pentane (Fischer, certified ACS), diethyl ether (anhydrous, Fischer, certified ACS), tetrahydrofuran (Sigma Aldrich, OmniSolv®), and toluene (Sigma Aldrich, OmniSolv®), were dried on a J. C. Meyer Solvent Dispensing System (SDS) using stainless steel columns packed with neutral alumina (except for toluene, which was dried with neutral alumina and Q5 reactant, a copper(II) oxide oxygen scavenger), following the manufacturer's recommendations for solvent preparation and dispensation unless otherwise noted. Dichlorodiphenylsilane was purchased from Tokyo Chemical Industry (TCI);

trifluoromethanesulfonic acid was purchased from Oakwood Chemical; triethylamine hydrochloride was purchased from Thermo Fisher Scientific; chlorodimethylphenyl silane, lithium granules, isopropylmagnesium chloride (2.0 M in THF), lithium aluminum hydride, anhydrous ethyl acetate, Celite®, magnesium bromide ethyl etherate, bis(cyclopentadienyl)zirconium(IV) dichloride, and n-butyllithium solution (2.5 M in hexanes) were purchased from Sigma Aldrich; benzene-*d*$_6$ was purchased from Cambridge Isotope Laboratories. α,ω–dipotassiotrisilyl dianion 1 was synthesized according to an adaptation of the literature procedure.[1]

Instrumentation: Solution phase ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR were recorded on either a Bruker Avance 400, III HD 400 MHz, or Bruker Ascend Evo NEO 500 fit with helium-cooled BBFO cryoprobe Spectrometer and chemical shifts are reported in parts per million (ppm). Spectra were recorded in benzene-*d*$_6$ with the residual solvent peak as the internal standard (^{1}H NMR: C_6H_6 $\delta = 7.16$). Molecular weights were measured by size exclusion chromatography (SEC) on a Tosoh Bioscience EcoSEC GPC workstation with UV detection at 254 nm using butylated hydroxytoluene stabilized tetrahydrofuran (THF) as the eluent (0.35 mL min^{-1}, 40 ºC) through TSKgel SuperMultipore HZ-M guard column (4.6 mm ID $\times$2.0 cm, 4 μm, Tosoh Bioscience). Polystyrene standards (EasiVial PS-M, Agilent) were used to build a calibration curve. Processing was performed using EcoSEC Data Analysis software (Version 1.14, Tosoh Bioscience). The samples were dissolved in THF (1 mg mL^{-1}), filtered through syringe filters (Millex-FG Syringe Filter Unit, 0.20 μm, PTFE, EMD Millipore), and injected by an autosampler (10 μL). High Resolution Mass Spectrometry (HRMS) was performed in the Department of Chemistry at Johns Hopkins University using a VG Instruments VG70S/E magnetic sector mass spectrometer with EI (70 eV). The UNIlab Plus Glove Box by MBRAUN was maintained under nitrogen atmosphere. All column chromatography was performed on a Teledyne ISCO Combiflash Rf+ using Redisep Rf silica columns. IR spectra were collected on a Thermo Scientific Nicolet iS5 spectrometer equipped with iD5 ATR laminated diamond crystal attachment. Thermogravimetric analysis (TGA) was conducted using a TA Instruments SDT Q600 under flowing Ar at a heating rate of 5.0 ºC min^{-1} from 40 to 600 ºC.

Experimental Procedures:

Synthesis of Compound bis(dimethylphenylsilyl)diphenylsilane:

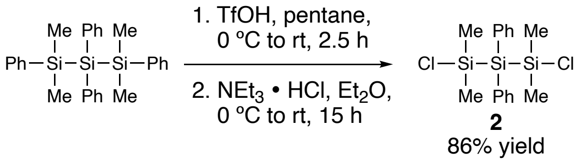


The synthesis of bis(dimethylphenylsilyl)diphenylsilane was adapted from previously published silane chain building procedures.[2,3]

An oven-dried 250 mL Schlenk flask equipped with a stir bar and an oven-dried 60 mL addition funnel fit with dummy flask were cooled under vacuum, then filled with argon. Under positive flow of argon, the Schlenk flask was charged with lithium granules (8.0 equiv., 480 mmol, 3.33 g), replacing the septum with the addition funnel. The setup was evacuated and backfilled three times. THF (107 mL) was added to the flask through the open addition funnel and the reaction mixture was cooled to 0 ºC via an ice/water bath. To the closed addition funnel was added chloro(dimethyl)phenyl silane (2.0 equiv., 120 mmol, 20.14 mL) and THF (38 mL). The reagent was added dropwise over an hour and the reaction color became dark red. After addition completion, the funnel was rinsed with 5 mL THF and was replaced with a septum. The reaction mixture stirred under argon overnight, allowing the ice bath to warm to room temperature.

The next day, an oven-dried 500 mL Schlenk flask, filter tube, and dummy flask were cooled under vacuum. The setup was evacuated and backfilled three times and under positive flow of argon the septum of the reaction flask was replaced with the filter tube. The reaction mixture was filtered over the filter tube into the new Schlenk flask. The filter tube was replaced with a septum, and the lithium was quenched. The reaction mixture was cooled to 0 ºC. Isopropylmagnesium chloride (2.2 equiv., 132 mmol, 66 mL, 2.0 M in THF) was added to the reaction flask, stirring for one hour. Still at 0 ºC, dichlorodiphenylsilane (1.0 equiv., 60 mmol, 12.62 mL) was added dropwise. The reaction mixture stirred under argon overnight, allowing the ice bath to warm to room temperature. After reaction completion, the mixture was cooled to 0 ºC and was quenched slowly with 80 mL each deionized water and saturated aqueous ammonium chloride, stirring for 30 minutes. The color changed from dark red to gray. The layers were separated and the aqueous layer was extracted 3 × 120 mL diethyl ether. The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The crude product, a yellow oil, was purified by automated column chromatography with 100% hexanes, then with a gradient to 10% ethyl acetate/90% hexanes to yield bis(dimethylphenylsilyl)diphenylsilane as a colorless oil after removal of solvent (yield: 17.09 g, 63%). ^{1}H NMR (400 MHz, C_6D_6, δ ppm) 7.56-7.54 (m, 5H), 7.37-7.35 (m, 5H), 7.14-7.11 (m, 10 H), 0.42 (s, 12H). ^{13}C NMR (100 MHz, C_6D_6, δ ppm) 136.39, 134.31, 128.65, -2.14. ^{29}Si NMR (80 MHz, C_6D_6, δ ppm) -19.48 (*Si*Me$_2$Ph), -40.40 (*Si*Ph$_2$). ^{29}Si NMR values match reported literature values.[4]

Synthesis of Compound 2:



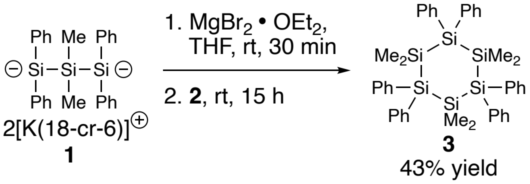
2
86% yield

The synthesis of bis(chlorodimethylsilyl)diphenylsilane **2** was adapted from previously published chlorination procedures.[5]

An oven-dried 250 mL Schlenk flask equipped with stir bar cooled under vacuum. The flask was charged with $Ph_4Me_4Si_3$ (1.0 equiv., 31.58 mmol, 14.30 g), then evacuated and backfilled three times. Pentane (66 mL) was added to the flask and the reaction mixture was cooled to 0 ºC. In an inert atmosphere glovebox, trifluoromethanesulfonic acid (2.0 equiv., 63.16 mmol, 5.58 mL) was added to closed addition funnel. The addition funnel was sealed and removed from the glovebox. Under positive flow of argon, the septum of the reaction flask was quickly replaced with the addition funnel and the trifluoromethanesulfonic acid was added dropwise. The funnel was rinsed with 6 mL pentane and replaced with a septum. After 30 minutes, the ice bath was removed and the reaction mixture was stirred for an additional two hours at room temperature. After two hours, the reaction mixture was concentrated under vacuum to remove volatiles. The resulting oil was dissolved in diethyl ether (73 mL) and the reaction mixture was cooled to 0 ºC. Under positive flow of argon, triethylamine hydrochloride (2.0 equiv., 63.16 mmol, 8.69 g) was added. After 30 minutes, the ice bath was removed and the biphasic reaction mixture was stirred under argon at room temperature overnight.

After reaction completion, stirring was stopped to allow the layers to separate. An oven-dried 250 mL 14/20 neck Schlenk flask was cooled under vacuum. The reaction mixture was cooled in a dry ice/acetone bath, freezing the lower ionic layer. The upper organic layer was decanted into the new Schlenk flask via syringe. The dry ice bath was removed and the ionic layer was thawed in a water bath. The ionic layer was extracted 3 × 15 mL diethyl ether, stirring for 15 minutes, freezing, and decanting between each extraction. The combined organic layers were concentrated under vacuum. The crude product, a reddish/brown oil, was purified by vacuum distillation at 160 ºC to yield **2** as a colorless oil, stored in the glovebox (yield: 10.09 g, 86%). ^{1}H NMR (400 MHz, C_6D_6, δ ppm) 7.69-7.68 (m, 4H), 7.15-7.14 (m, 6H), 0.51 (s, 12H). ^{13}C NMR (100 MHz, C_6D_6, δ ppm) 136.06, 129.49, 128.45, 3.37. ^{29}Si NMR (80 MHz, C_6D_6, δ ppm) 22.26 (*Si*Me_2Cl), -42.05 (*Si*Ph_2).

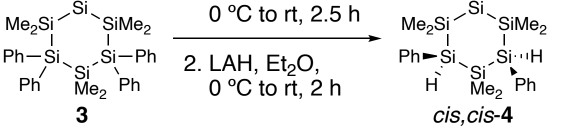
Synthesis of Compound 3:



α,ω–dipotassiotrisilyl dianion **1** was synthesized according to previous reports.[1]

In a glovebox, a 250 mL Schlenk flask containing dianion (1.0 equiv., 5.83 mmol, 6.02 g) was charged with THF (90 mL) and magnesium bromide ethyl etherate (1.1 equiv., 6.41 mmol, 1.66 g), stirring for 30 minutes. After 30 minutes, 2 was added dropwise (1.0 equiv., 5.83 mmol, 2.15 g massed via syringe). The reaction flask was sealed, removed from the glovebox, and attached to the Schlenk line. The reaction mixture stirred under argon at room temperature overnight. The colored changed from dark red to tan with addition of $MgBr_2•OEt_2$ and 2. After reaction completion, the mixture was quenched with 50 mL each deionized water and saturated aqueous ammonium chloride, stirring for 30 minutes. The layers were separated and the aqueous layer was extracted 3 × 100 mL hexanes. The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The crude product, a white solid, was purified by crystallization in hot toluene to yield **3** as a white crystalline solid (yield: 1.82 g, 43%). ^{1}H NMR (400 MHz, C_6D_6, δ ppm) 7.29-7.24 (m, 6H), 7.18-7.16 (m, 12H), 7.11-7.08 (m, 12H), 0.43 (s, 18H). ^{13}C NMR (100 MHz, C_6D_6, δ ppm) 137.04, 135.92, 128.45, 128.00, -3.15. ^{29}Si NMR (80 MHz, C_6D_6, δ ppm) -32.16 (*Si*Me_2), -41.34 (*Si*Ph_2). HRMS calcd. for $C_{42}H_{48}Si_6$: 720.2372. Found: 720.2354.

Synthesis of Compound *cis,cis*-4:

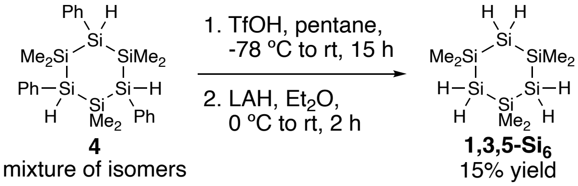


An oven-dried 100 mL Schlenk flask fit with stir bar was cooled under vacuum, then filled with argon and charged with **3** (1.0 equiv., 1.39 mmol, 1.00 g). The flask was evacuated and backfilled three times. Toluene (23 mL) was added to the flask to dissolve the starting material and the solution was cooled to 0 ºC. In an inert atmosphere glovebox, trifluoromethanesulfonic acid (3.3

equiv., 4.57 mmol, 0.4 mL) was added to closed addition funnel. The addition funnel was sealed and removed from the glovebox. Under positive flow of argon, the septum of the reaction flask was quickly replaced with the addition funnel and the trifluoromethanesulfonic acid was added dropwise. The funnel was rinsed with 5 mL toluene and replaced with a septum. After 30 minutes, the ice bath was removed and the reaction mixture was stirred for an additional two hours at room temperature. After two hours, the reaction mixture was concentrated under vacuum overnight in a water bath to remove volatiles. The tan solid silyl triflate intermediate was redissolved in diethyl ether (14 mL). The solution was cooled to 0 ºC and a suspension of lithium aluminum hydride (1.8 equiv., 2.50 mmol, 0.095 g in 14 mL diethyl ether) was added dropwise via cannula. After 30 minutes, the ice bath was removed and the reaction mixture was stirred for an additional 1.5 hours at room temperature.

After reaction completion, the reaction mixture was cooled to 0 ºC and was quenched with anhydrous ethyl acetate (1.1 mL), stirring for 30 minutes. The quenched reaction mixture was brought into the glovebox and was filtered over Celite, rinsing with diethyl ether. Solvent was removed under vacuum overnight. The resulting white solid was ground with a spatula and was suspended in toluene, stirring for six hours. The suspension was filtered (into a tared 100 mL schlenk flask if continuing to **1,3,5-Si$_6$**) and solvent was removed under vacuum overnight. The crude product, a white solid, was purified by crystallization in hot toluene to yield the single cis,*cis* isomer of **4** as a white crystalline solid (yield: 105 mg, 15%). ^{1}H NMR (400 MHz, C_6D_6, δ ppm) 7.59-7.57 (m, 6H), 7.19-7.17 (m, 9H), 4.48 (s, 3H), 0.52 (s, 9H), 0.38 (s, 9H). ^{13}C NMR (100 MHz, C_6D_6, δ ppm) 136.00, 132.79, 128.51, 128.20, -2.88, -3.89. ^{29}Si NMR (80 MHz, C_6D_6, δ ppm) -39.16 (*Si*Me$_2$), -58.01 (*Si*PhH). HRMS calcd. for $C_{24}H_{36}Si_6$: 492.1433. Found: 492.1445.

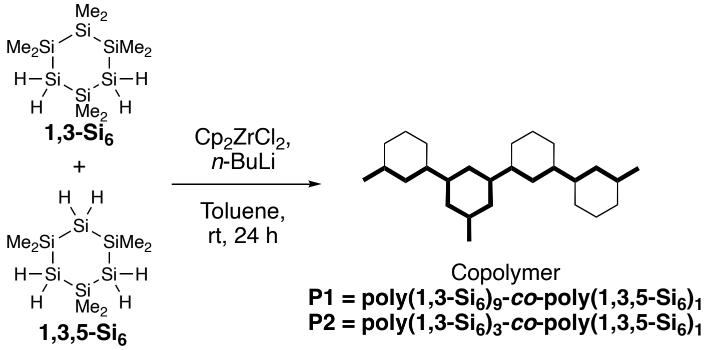
Synthesis of Compound 1,3,5-Si$_6$:



The 100 mL Schlenk flask containing crude **4** (1.0 equiv., 0.670 mmol, 0.33 g) was backfilled with argon and pentane (10 mL) was added to the flask to dissolve the starting material. The solution was cooled to -78 ºC via a dry ice/isopropanol bath. In a glovebox, trifluoromethanesulfonic acid (4.5 equiv., 3.01 mmol, 0.27 mL) was added to closed addition funnel. The addition funnel was sealed and removed from the glovebox. Under positive flow of argon, the septum of the reaction flask was quickly replaced with the addition funnel and the trifluoromethanesulfonic acid was added dropwise. The funnel was rinsed with 3.4 mL pentane and replaced with a septum. The reaction stirred under argon overnight, allowing the dry ice/isopropanol bath to warm to room temperature. After reaction completion, the reaction mixture was concentrated under vacuum for one hour to remove volatiles. The tan oil silyl triflate intermediate was redissolved in diethyl ether (7 mL). The solution was cooled to 0 ºC and a suspension of lithium aluminum hydride (1.8 equiv., 1.21 mmol, 0.046 g in 6.4 mL diethyl ether) was added dropwise via cannula. After 30 minutes, the ice bath was removed and the reaction mixture was stirred for an additional 1.5 hours at room temperature.

After reaction completion, the reaction mixture was cooled to 0 ºC and was quenched with anhydrous ethyl acetate (0.6 mL), stirring for 30 minutes. The quenched reaction mixture was brought into the glovebox and was filtered over Celite, rinsing with diethyl ether. Solvent was removed under vacuum overnight. The resulting white solid was ground with a spatula and was suspended in pentane, stirring for one hour. The suspension was filtered the and solvent was removed under vacuum. The crude product, a colorless oil, was purified by distillation under vacuum at 85 °C to yield **1,3,5-Si$_6$** as a clear, colorless oil (yield: 26 mg, 15%). ^{1}H NMR (400 MHz, C_6D_6, δ ppm) 3.30 (s, 6H), 0.39 (s, 18H). ^{13}C NMR (100 MHz, C_6D_6, δ ppm) -1.22. ^{29}Si NMR (80 MHz, C_6D_6, δ ppm) -41.31 (*Si*Me$_2$), -97.75 (*Si*H$_2$). HRMS calcd. for $C_6H_{24}Si_6$: 264.0494. Found: 264.0486.

General Polymerization Procedure:



1,3-Si$_6$ was synthesized according to previous reports.[6]

In a glovebox, a 2-dram vial fit with stir bar was charged with bis(cyclopentadienyl)zirconium(IV) dichloride (0.056 equiv., 0.013 mmol, 4 mg) and toluene (0.21 mL). The catalyst was activated with n-butyllithium solution (0.11 equiv., 0.025 mmol, 0.09 mL, 0.27 M in toluene), stirring for 30 minutes. To a separate vial was added **1,3-Si$_6$** and **1,3,5-Si$_6$** (0.227 mmol total) and 0.34 mL toluene. The monomer solution was added to the activated catalyst, rinsing 2 × 0.1 mL toluene. The reaction vial was sealed with a septum cap, vented with a needle, and stirred at room temperature for 24 hours.

After reaction completion, the polymer was dried under vacuum at room temperature for 1 hour and at 60 °C for at least 4 hours. No further purification was conducted.

Synthesis of Polymer P1:

The general procedure was followed using a feed ratio of 10% **1,3,5-Si$_6$** (0.1 equiv., 0.023 mmol, 6 mg) and 90% **1,3-Si$_6$** (0.9 equiv., 0.204 mmol, 60 mg). No further purification was conducted to yield a dark brown glassy solid. 100% conversion determined by ^{1}H NMR. ^{1}H NMR (500 MHz, C_6D_6, δ ppm) 3.26 (br), 0.90-0.19 (br). ^{13}C NMR (126 MHz, C_6D_6, δ ppm) 1.50, -0.77, -2.02, -2.61, -2.76, -5.63, -6.70. ^{29}Si NMR (80 MHz, C_6D_6, δ ppm) -31.85- -41.76 (*Si*Me$_2$), -111.22- -114.07 (*Si*H and *Si*H$_2$).

Synthesis of Polymer P2:

The general procedure was followed using a feed ratio of 25% **1,3,5-Si$_6$** (0.25 equiv., 0.057 mmol, 15 mg) and 75% **1,3-Si$_6$** (0.75 equiv., 0.170 mmol, 50 mg). No further purification was conducted to yield a dark brown glassy solid. 100% conversion determined by ^{1}H NMR. ^{1}H NMR (500 MHz, C_6D_6, δ ppm) 3.23 (br), 0.99-0.06 (br). ^{13}C NMR (126 MHz, C_6D_6, δ ppm) 1.50, -0.80, -2.65, -5.66, -6.69. ^{29}Si NMR (80 MHz, C_6D_6, δ ppm) -33.13- -40.77 (*Si*Me$_2$), -110.44- -114.00 (*Si*H and *Si*H$_2$).

Compound Characterization Spectra:

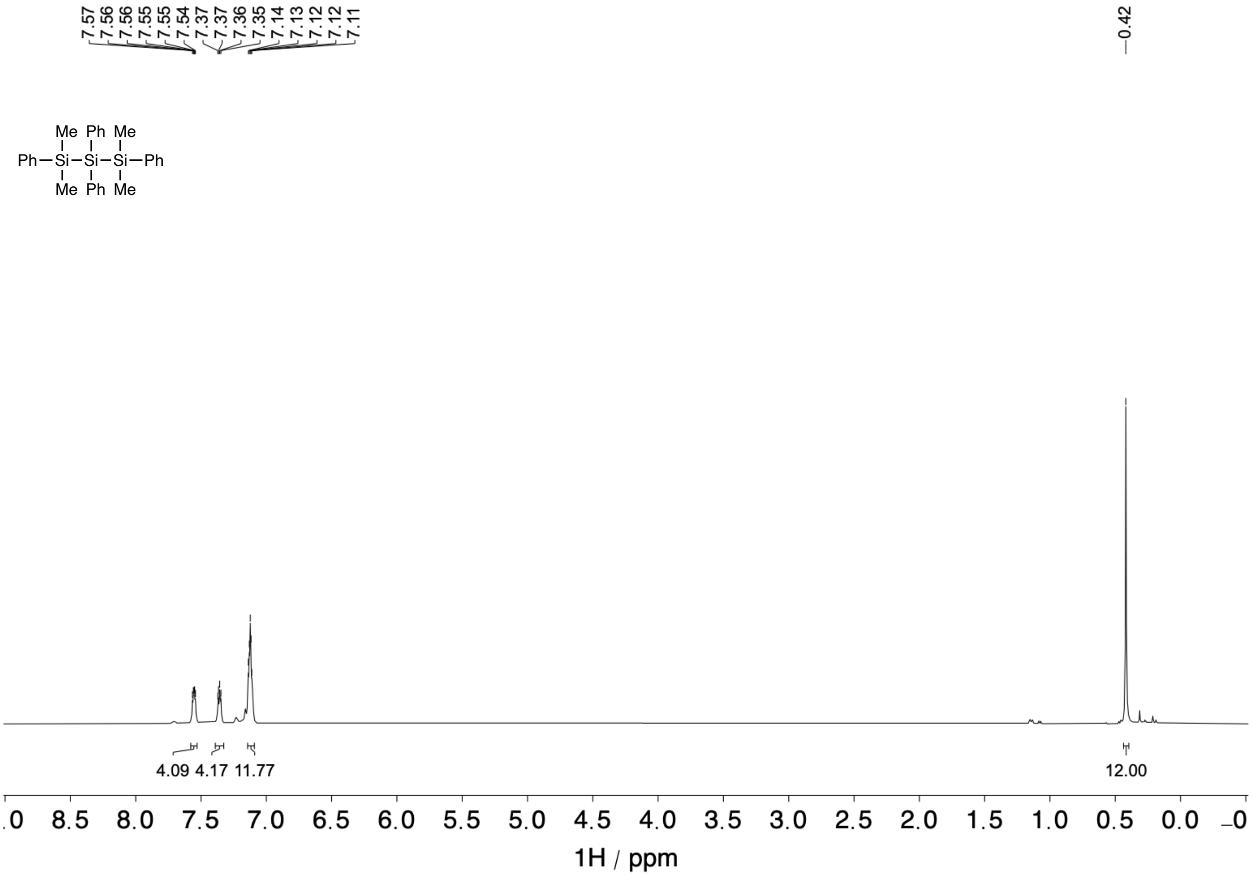


Figure S6. ^{1}H NMR (400 MHz, C_6D_6) spectrum of bis(dimethylphenylsilyl)diphenylsilane**.**

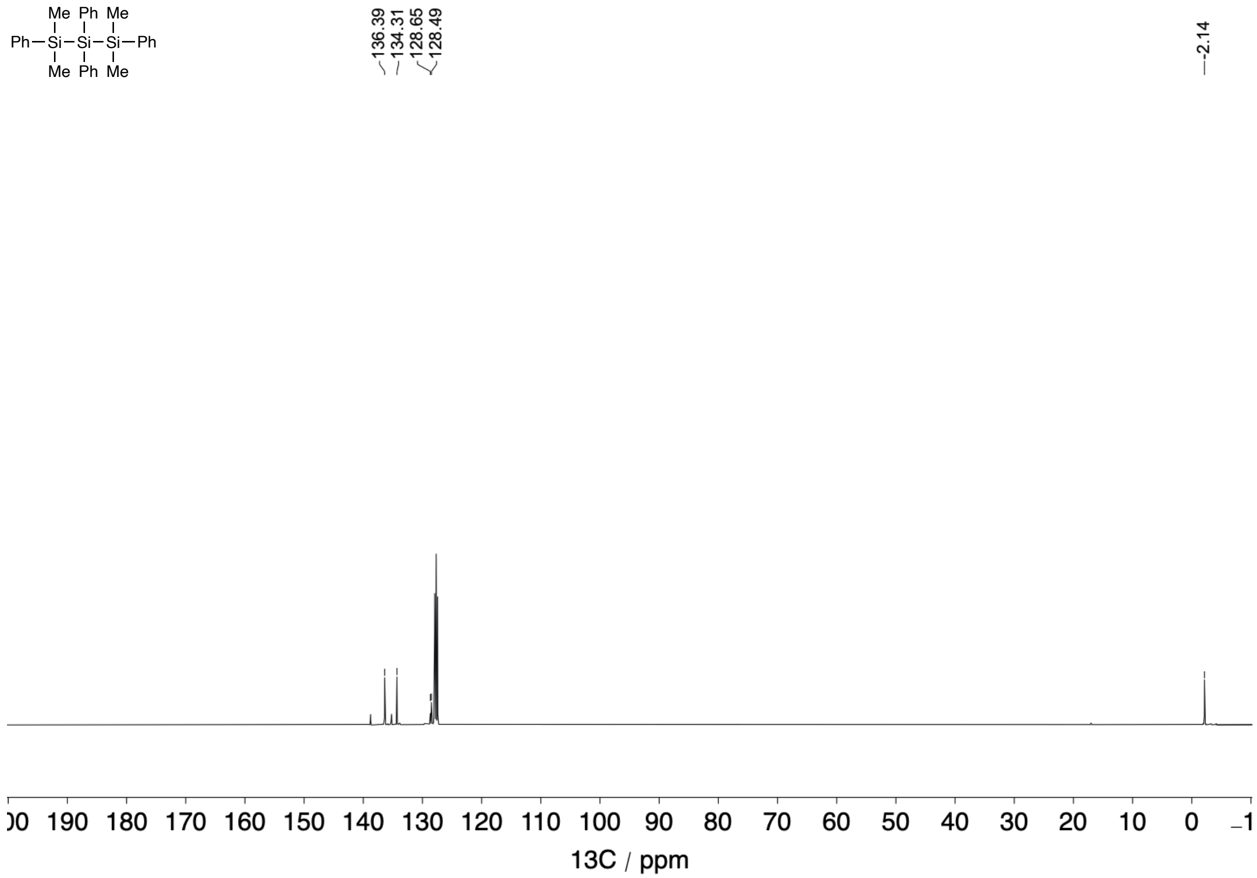


Figure S7. ^{13}C NMR (100 MHz, C_6D_6) spectrum of bis(dimethylphenylsilyl)diphenylsilane**.**

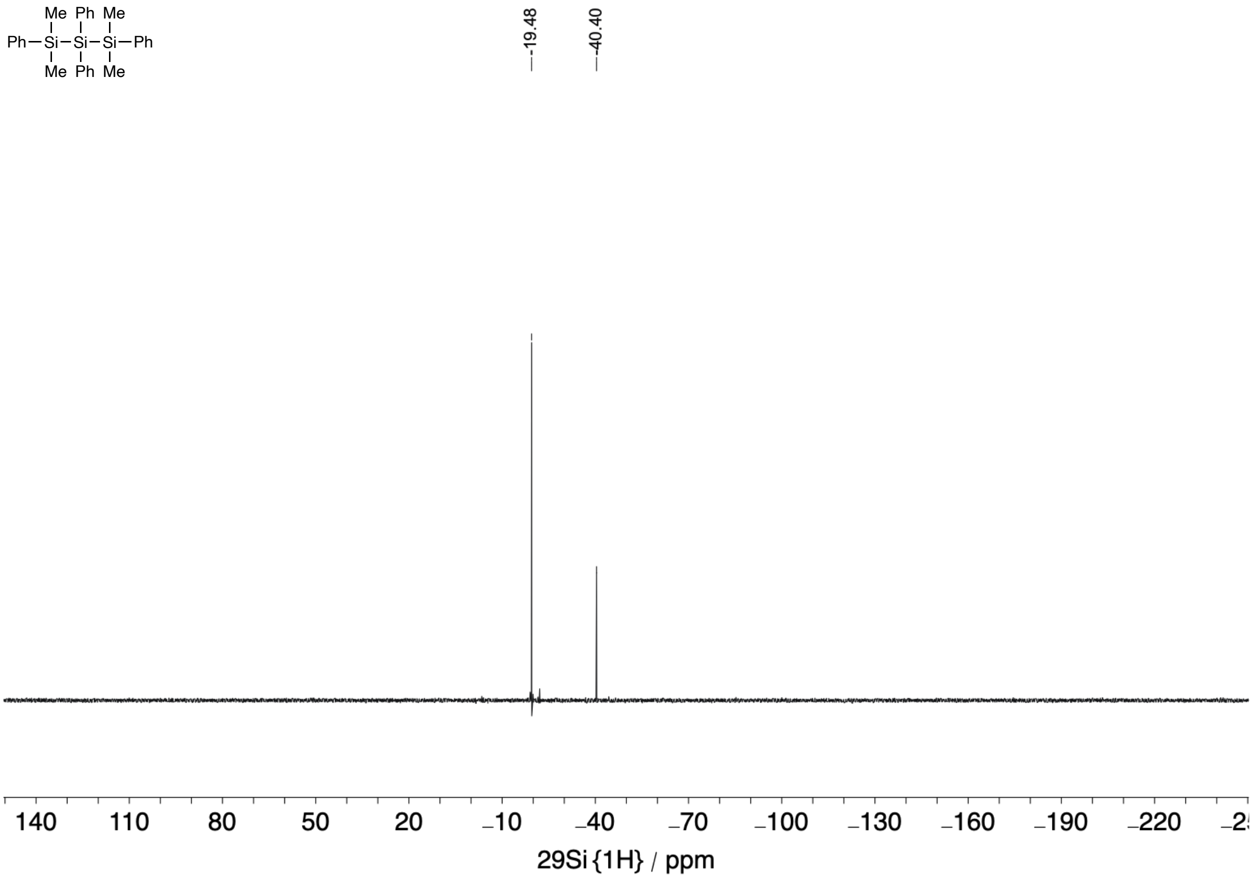


Figure S8. ^{29}Si NMR (80 MHz, C_6D_6) spectrum of bis(dimethylphenylsilyl)diphenylsilane**.**

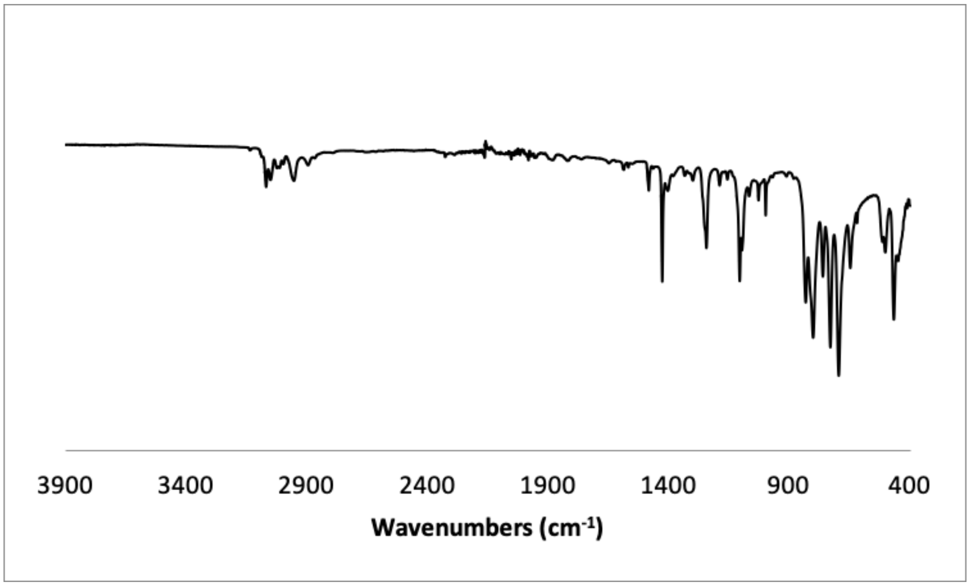


Figure S9. IR spectrum of bis(dimethylphenylsilyl)diphenylsilane**.**

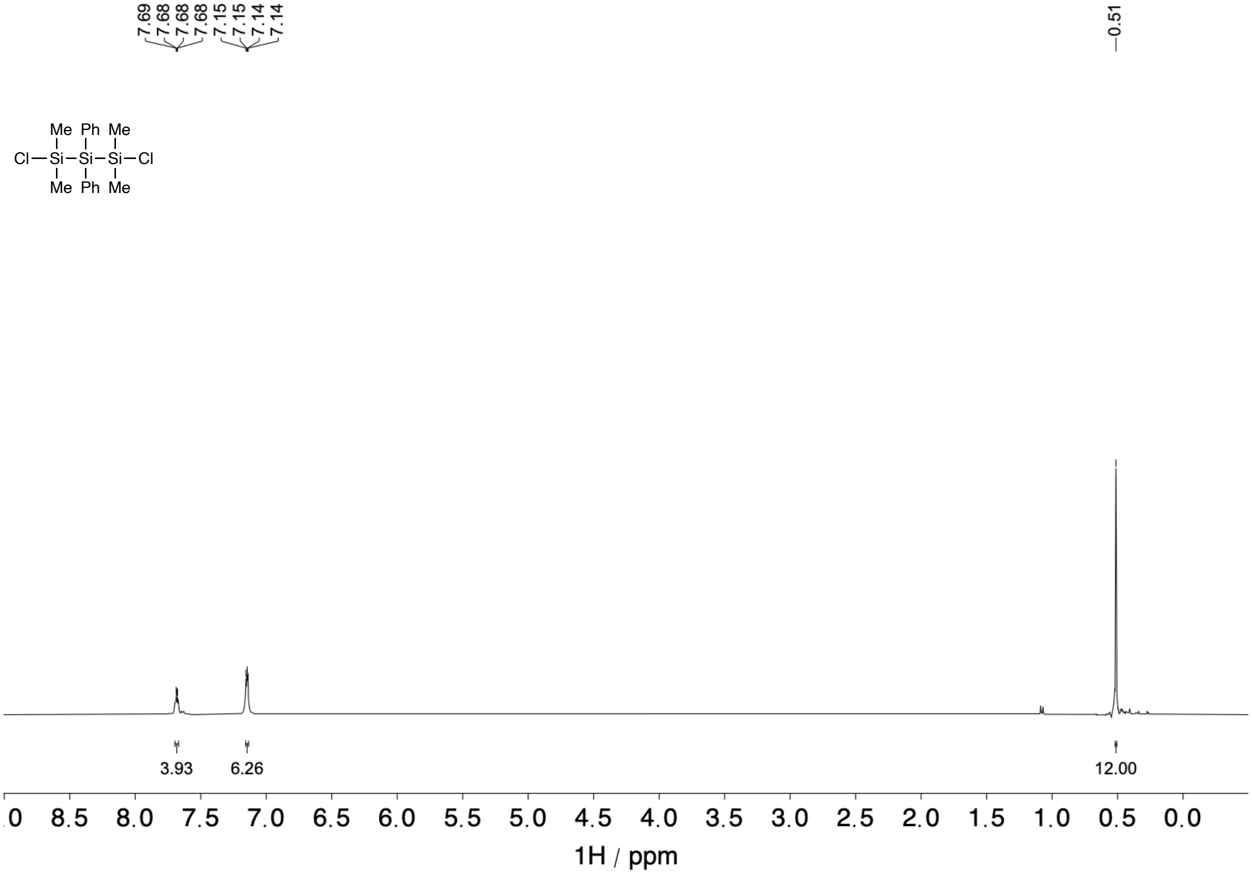


Figure S10. ^{1}H NMR (400 MHz, C_6D_6) spectrum of **2.**

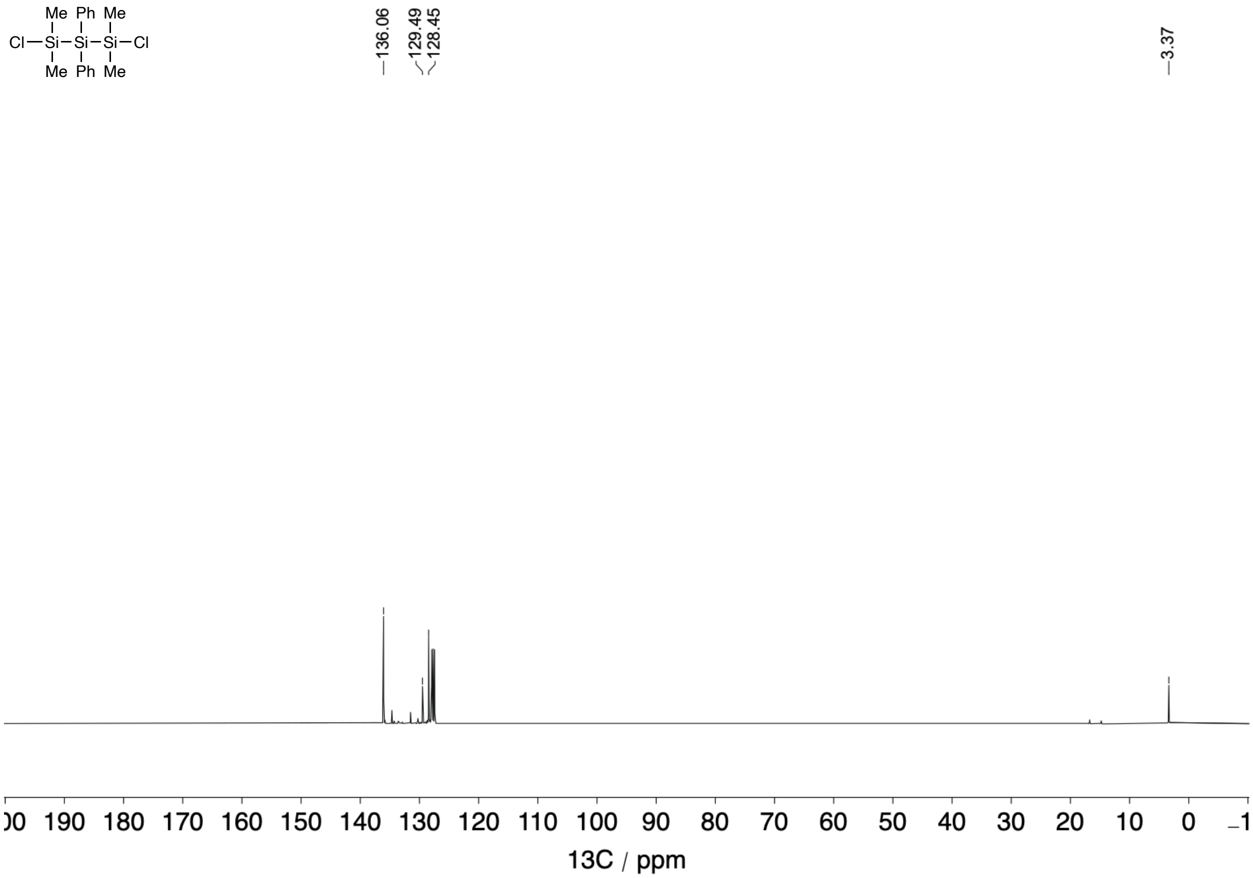


Figure S11. ^{13}C NMR (100 MHz, C_6D_6) spectrum of **2.**

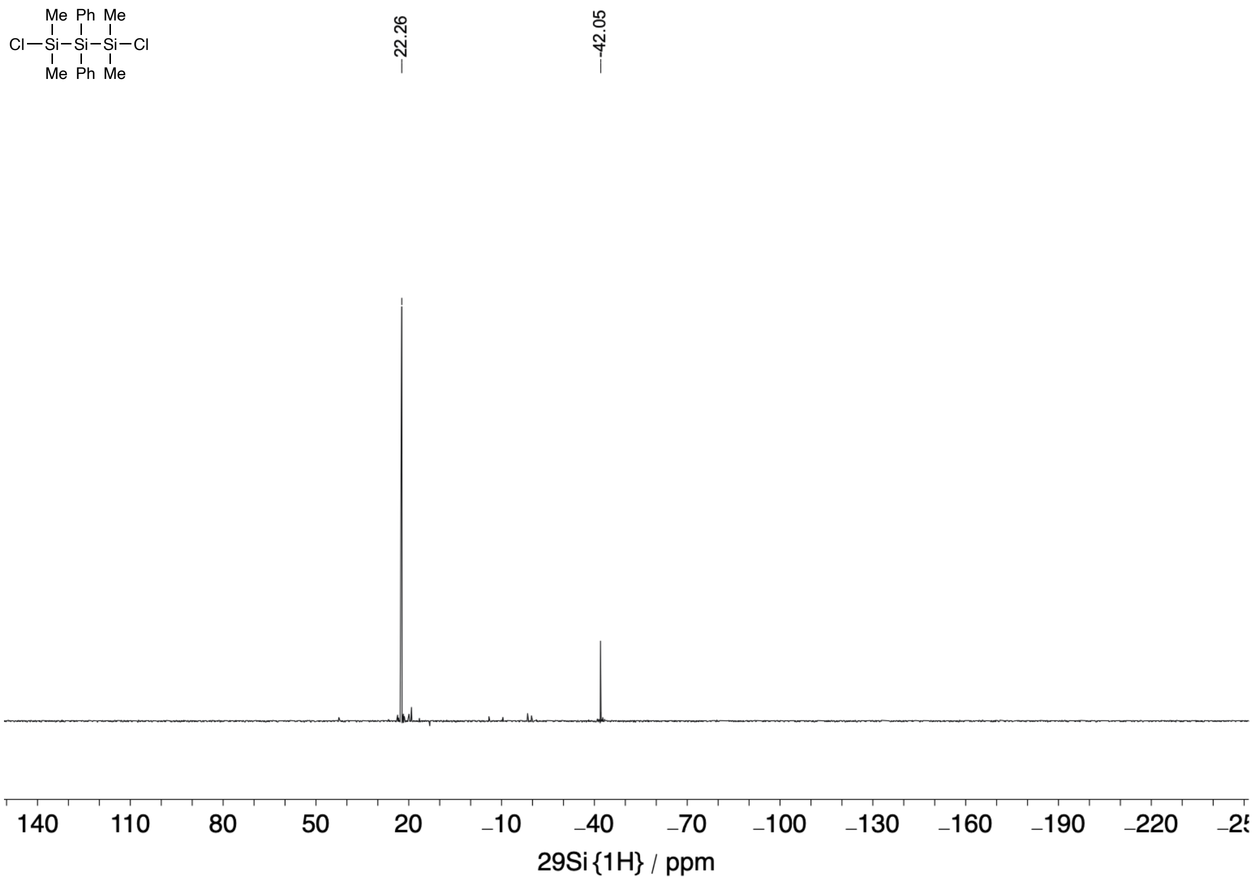


Figure S12. ^{29}Si NMR (80 MHz, C_6D_6) spectrum of **2.**

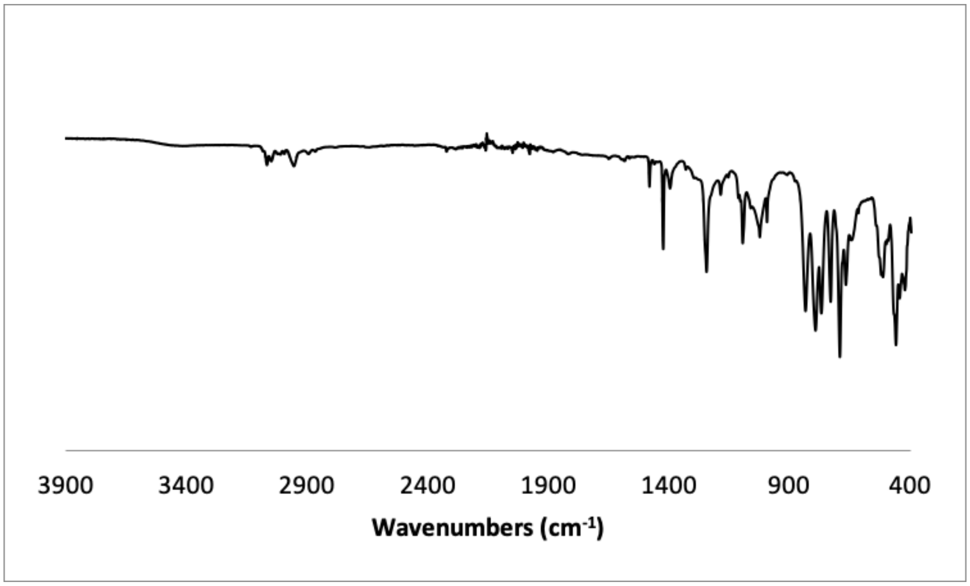


Figure S13. IR spectrum of **2.**

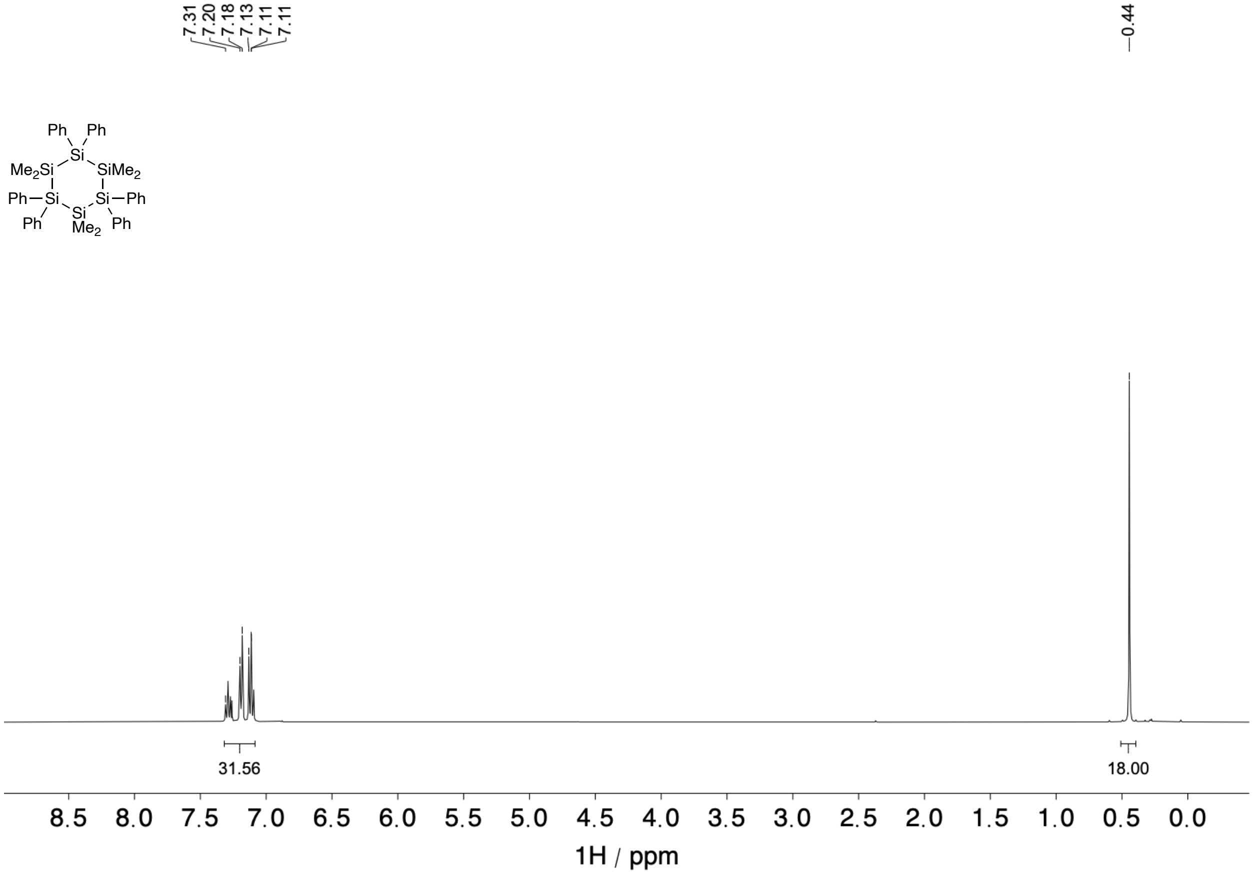


Figure S14. ^{1}H NMR (400 MHz, C_6D_6) spectrum of **3.**

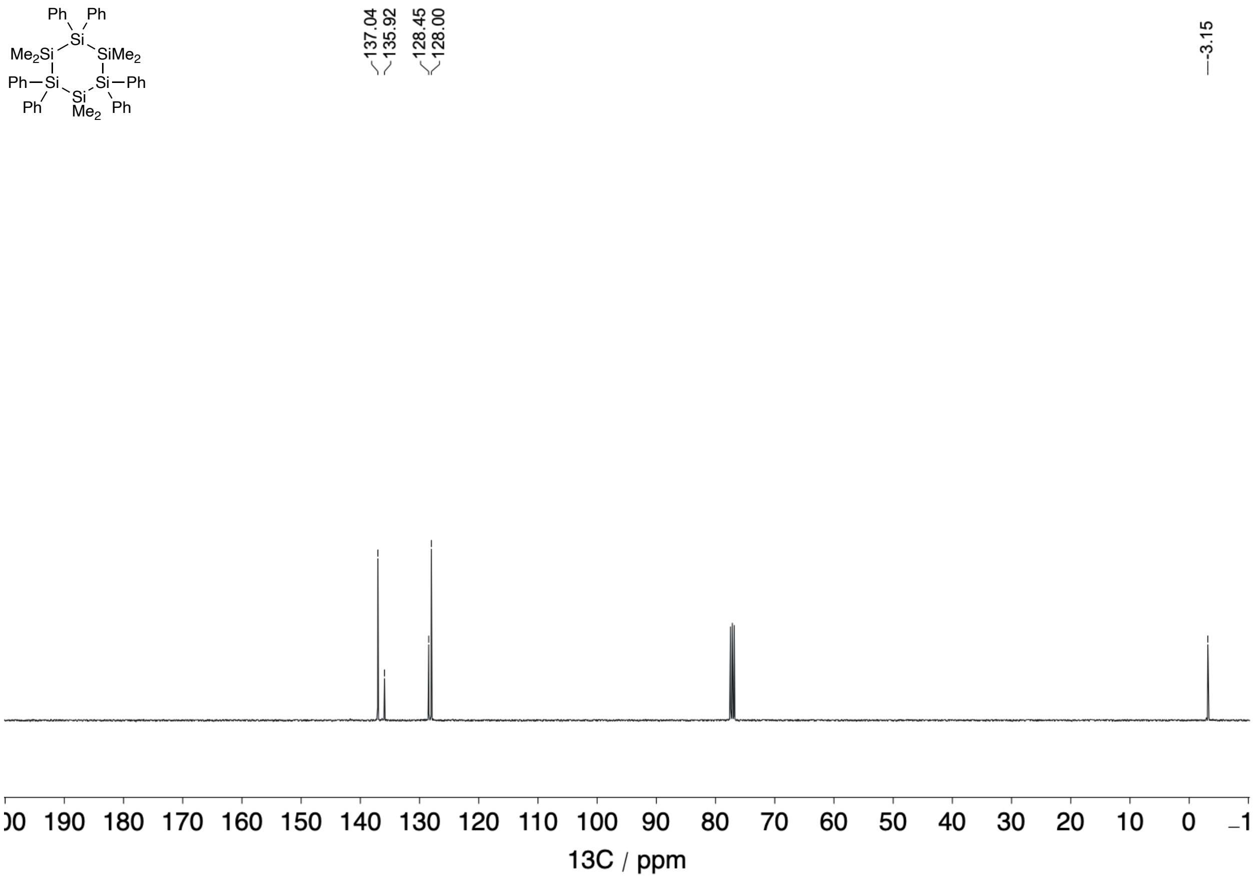


Figure S15. ^{13}C NMR (100 MHz, C_6D_6) spectrum of **3.**

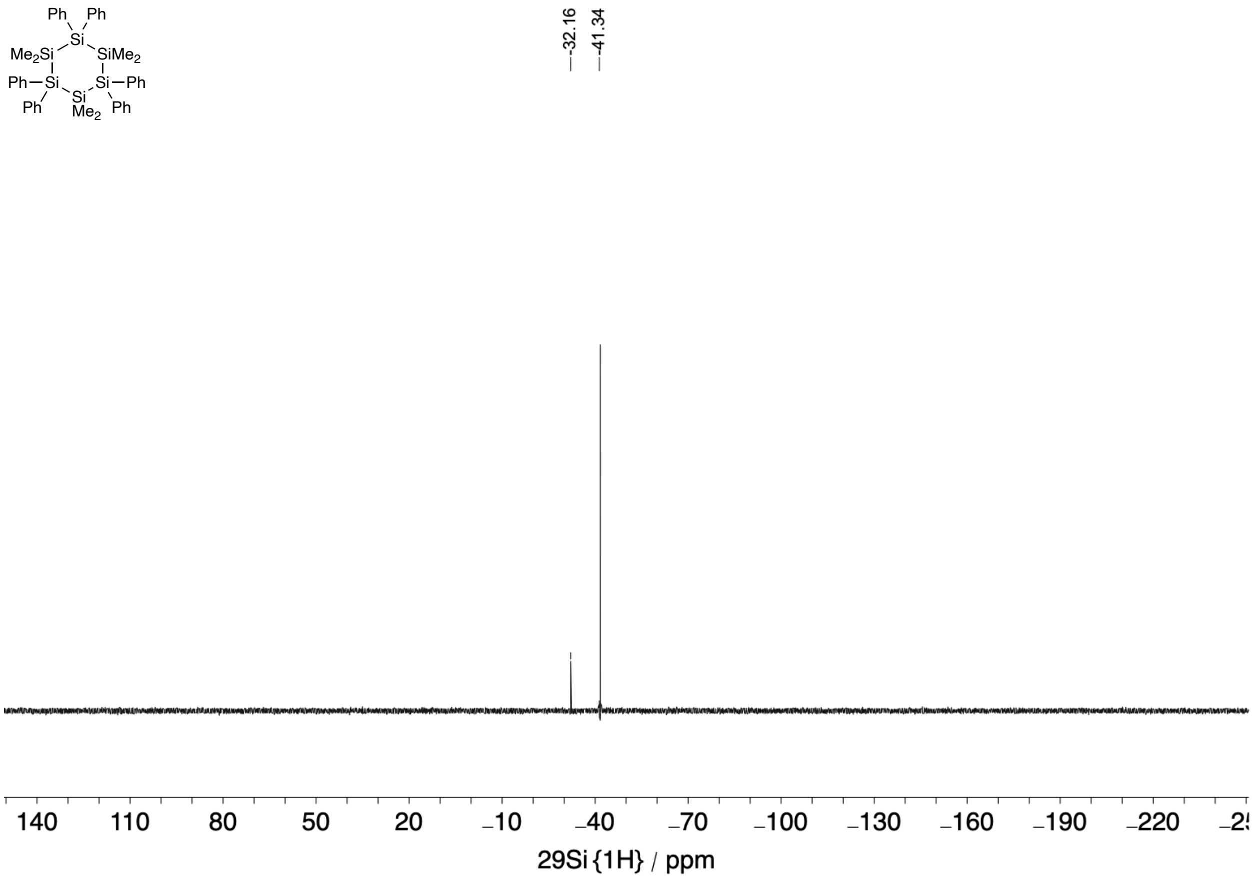


Figure S16. ^{29}Si NMR (80 MHz, C_6D_6) spectrum of **3.**

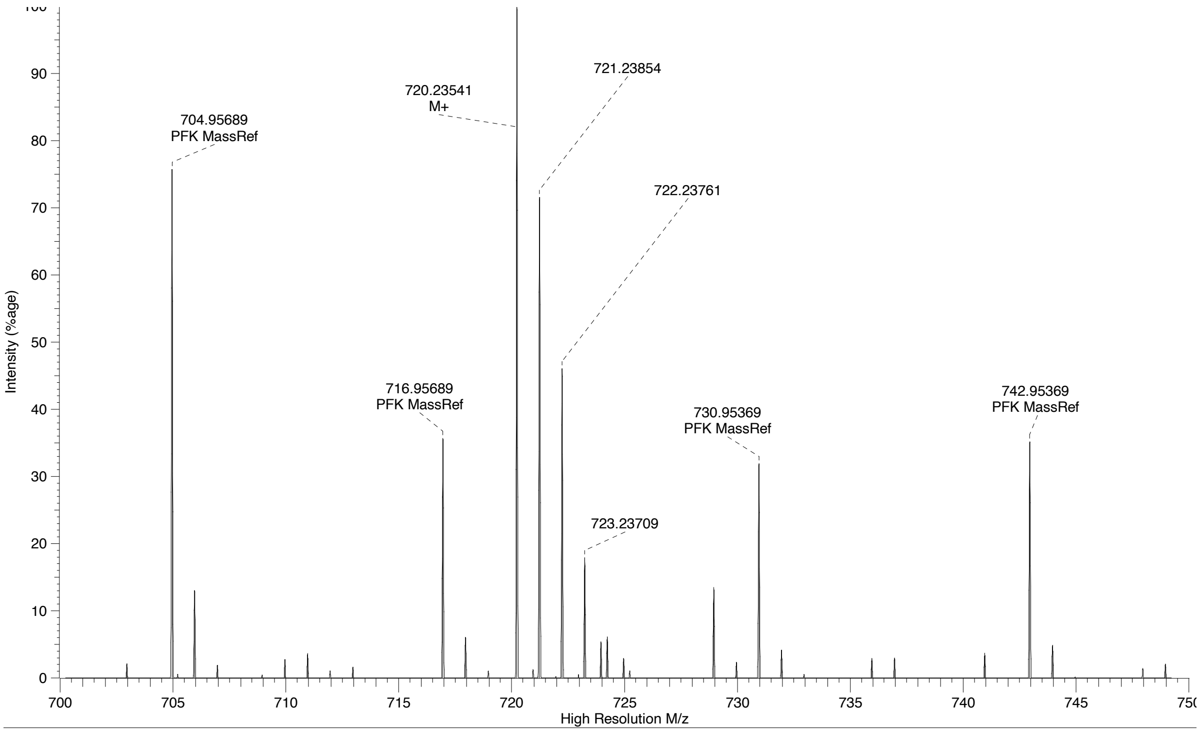


Figure S17. EI High Resolution Mass Spectrometry spectrum of **3.**

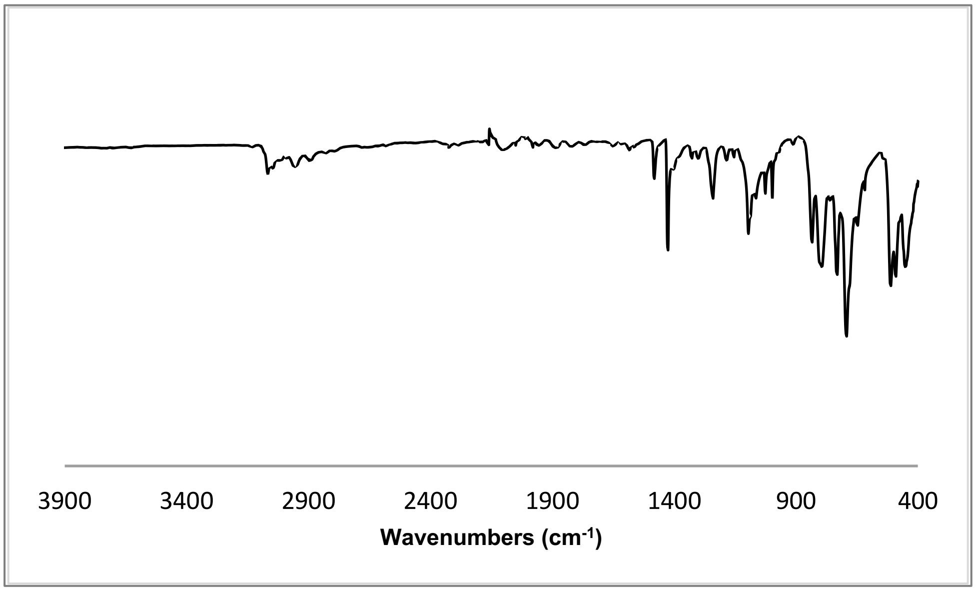


Figure S18. IR spectrum of **3.**

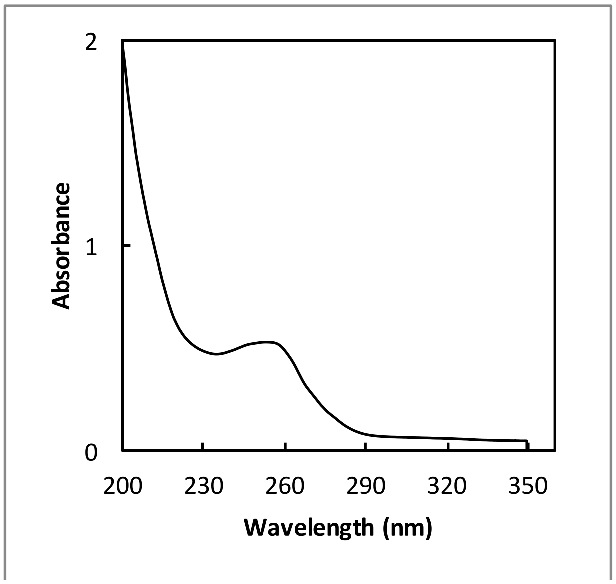


Figure S19. UV-vis spectrum of **3** ([compound] = 3.00×10^{-5} M, in pentane).

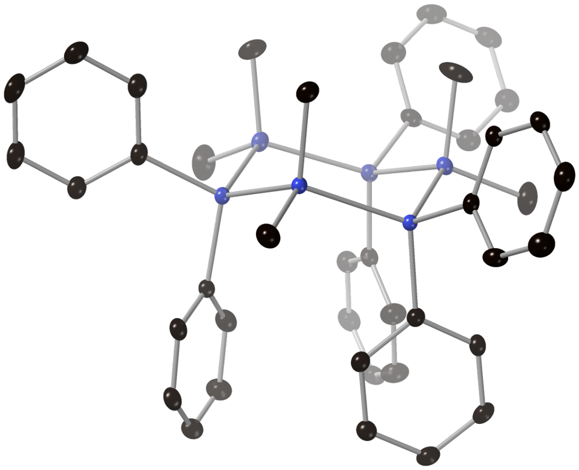


Figure S20. Displacement ellipsoid plot (50% probability level) of one of the two crystallographically independent molecules of **3** at 110 K. Hydrogens are omitted for clarity. Blue = silicon, black = carbon.

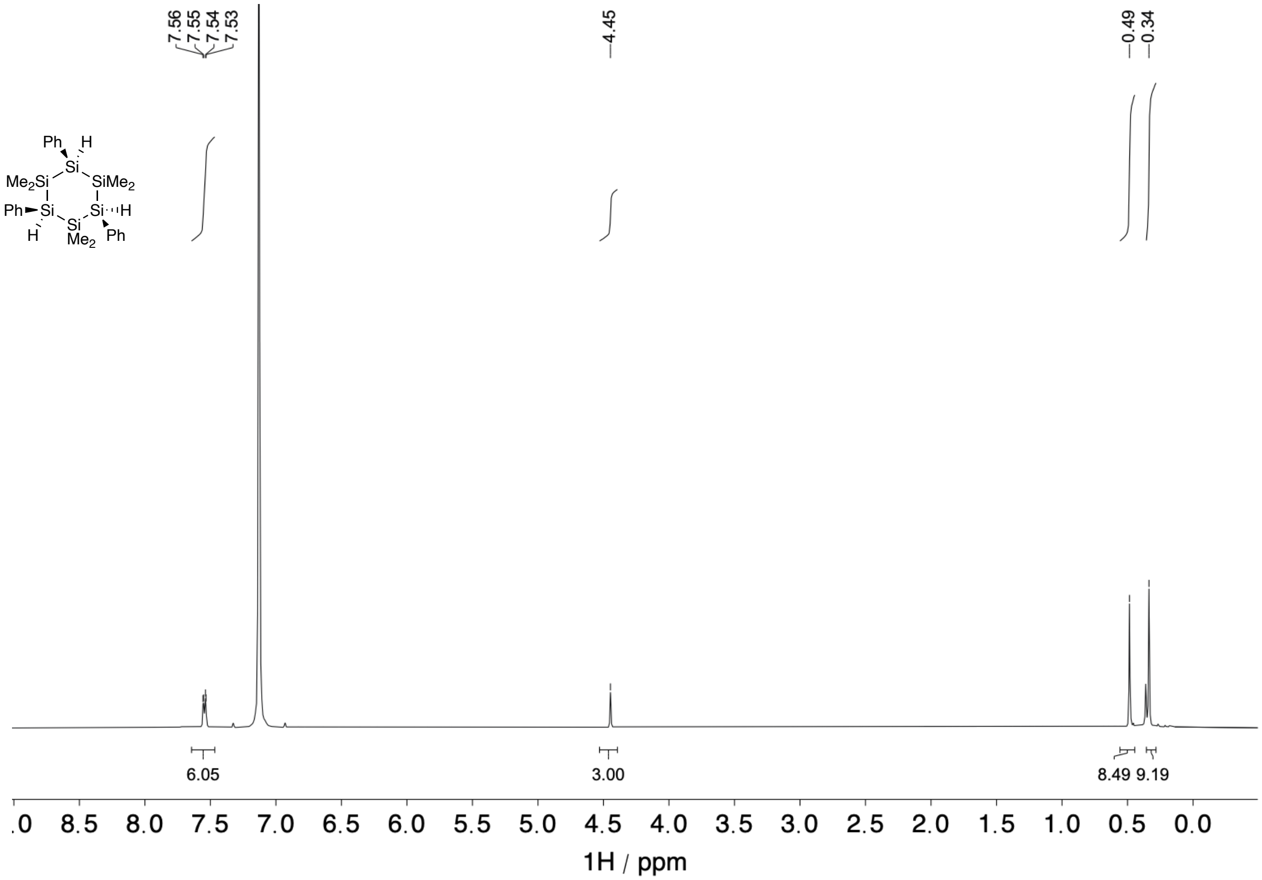


Figure S21. ^{1}H NMR (400 MHz, C_6D_6) spectrum of *cis,cis*-**4.**

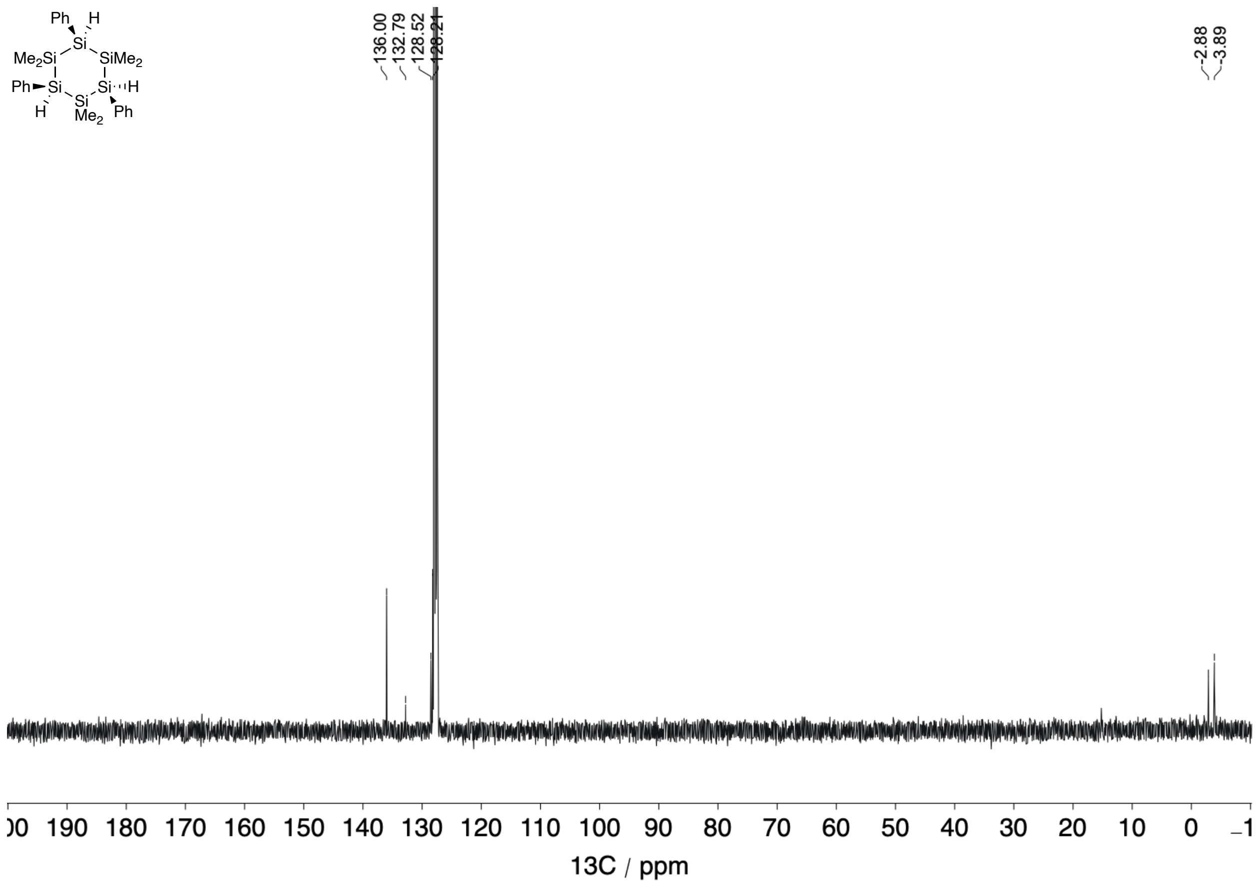


Figure S22. ^{13}C NMR (100 MHz, C_6D_6) spectrum of *cis,cis*-**4.**

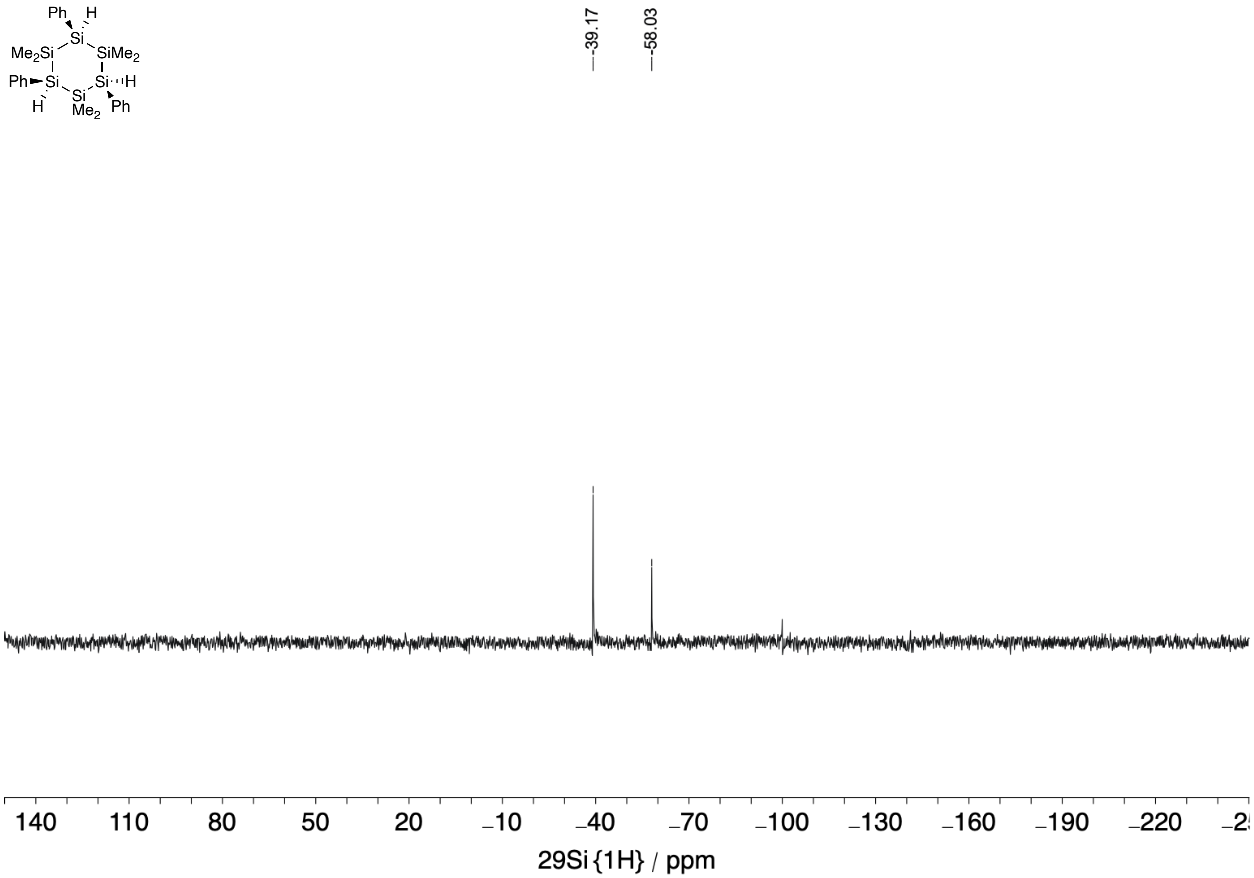


Figure S23. ^{29}Si NMR (80 MHz, C_6D_6) spectrum of *cis,cis*-**4.**

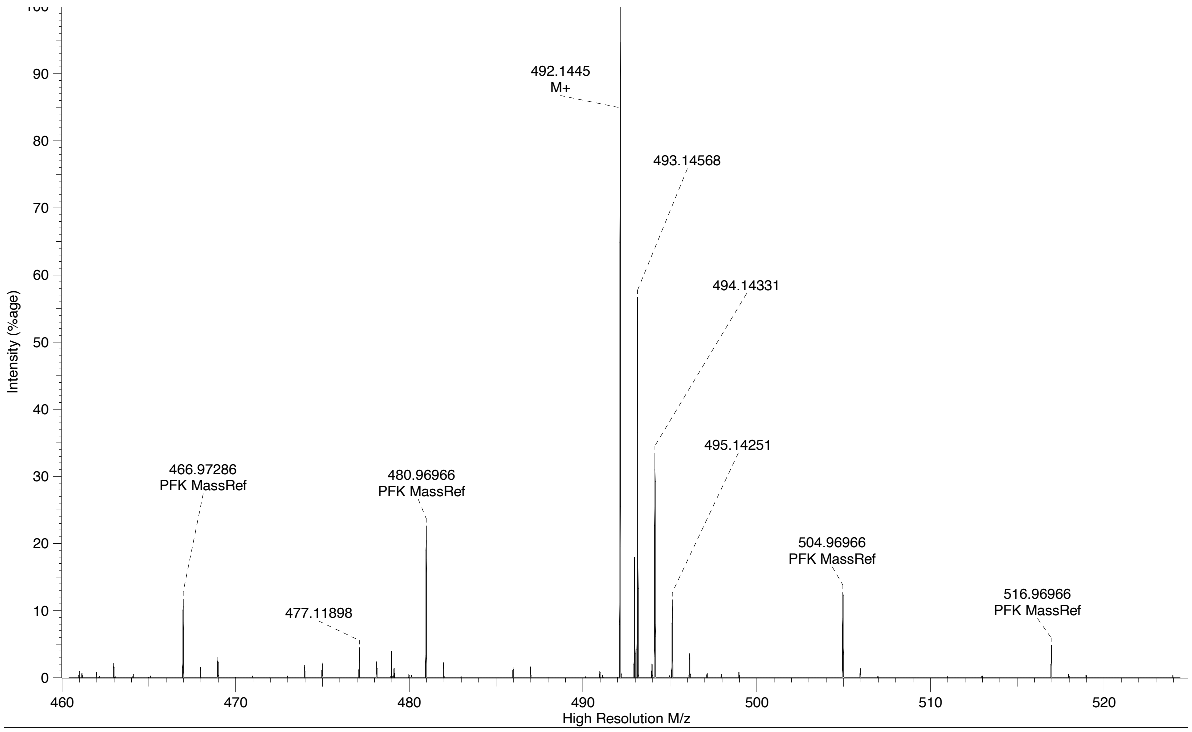


Figure S24. EI High Resolution Mass Spectrometry spectrum of **4.**

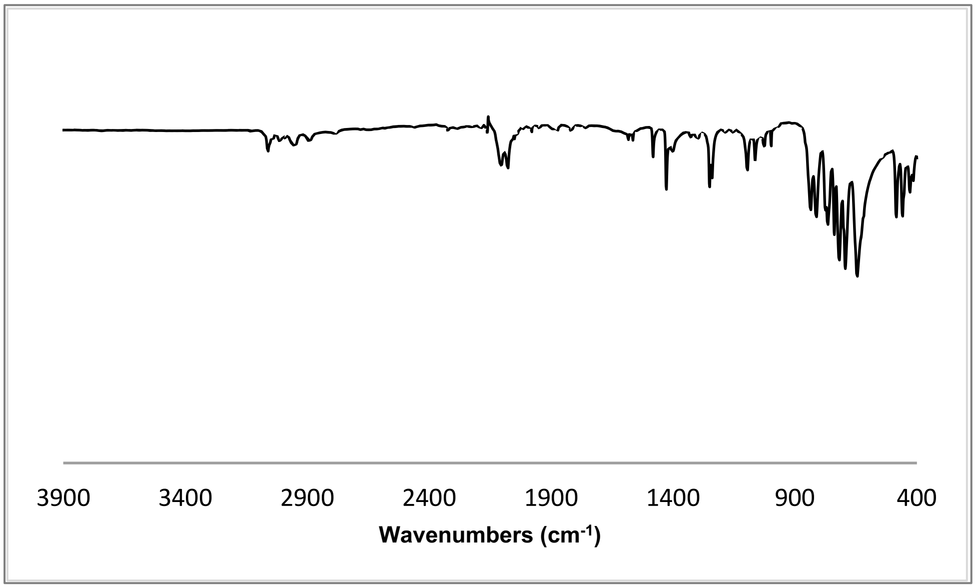


Figure S25. Full IR spectrum of *cis,cis*-**4.**

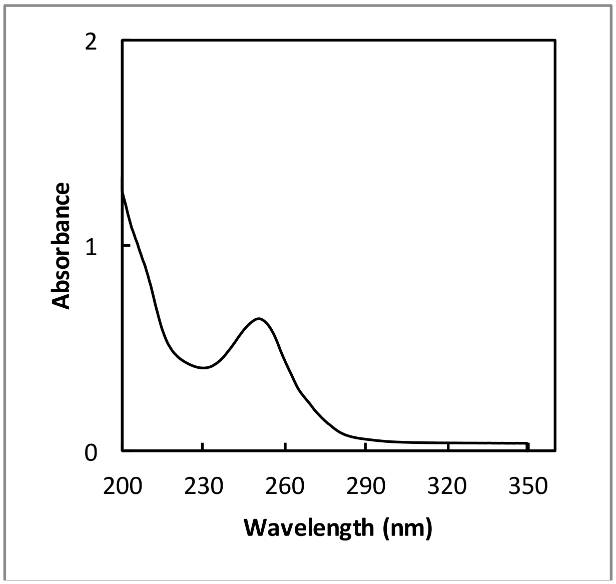


Figure S26. UV-vis spectrum of *cis,cis*-**4** ([compound] = 3.00×10^{-5} M, in pentane).

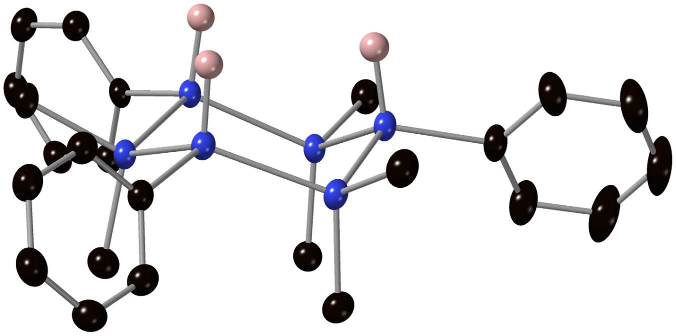


Figure S27. Displacement ellipsoid plot (50% probability level) of *cis,cis*-**4** at 110 K. Non-diagnostic hydrogen atoms are omitted for clarity. Blue = silicon, black = carbon, pink = hydrogen.

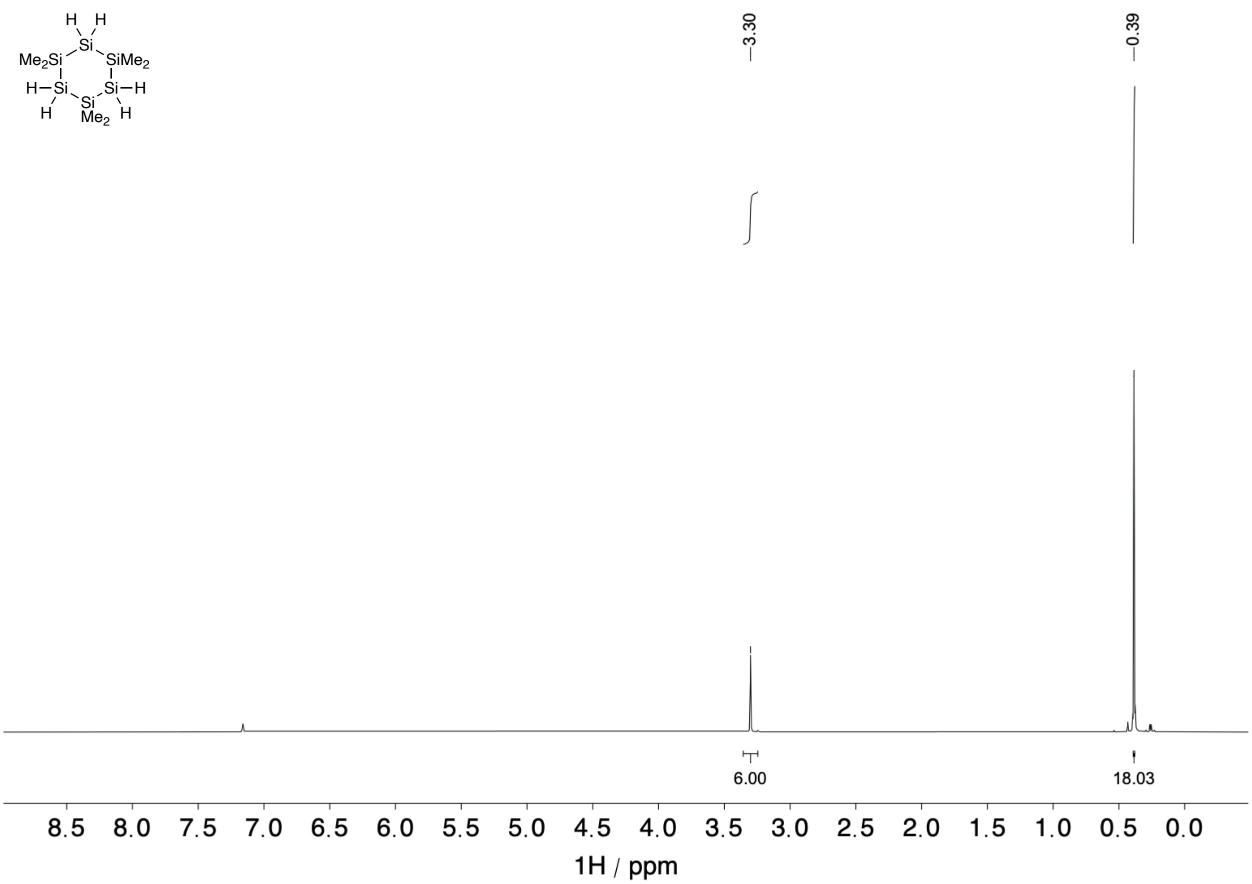


Figure S28. ^{1}H NMR (400 MHz, C_6D_6) spectrum of **1,3,5-Si$_6$.**

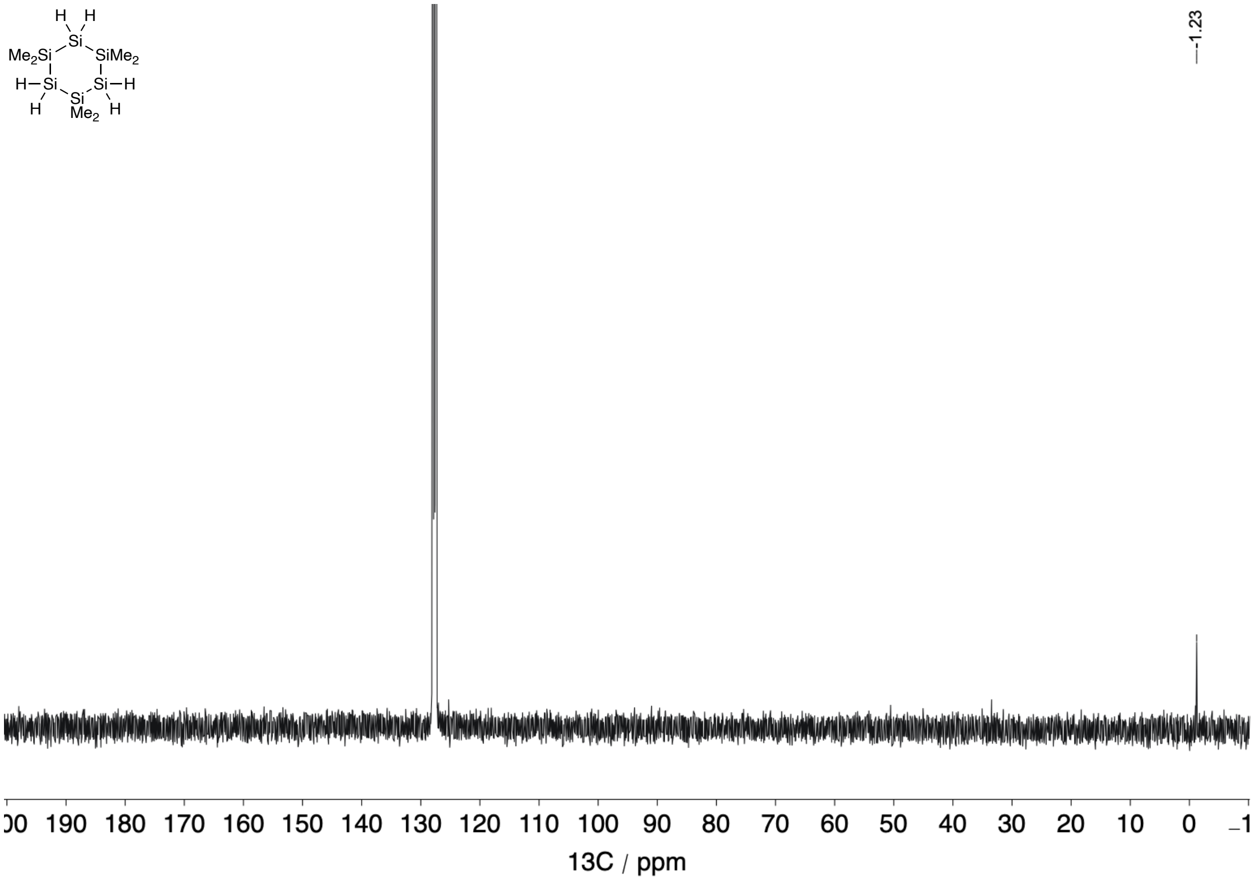


Figure S29. ^{13}C NMR (100 MHz, C_6D_6) spectrum of **1,3,5-Si$_6$.**

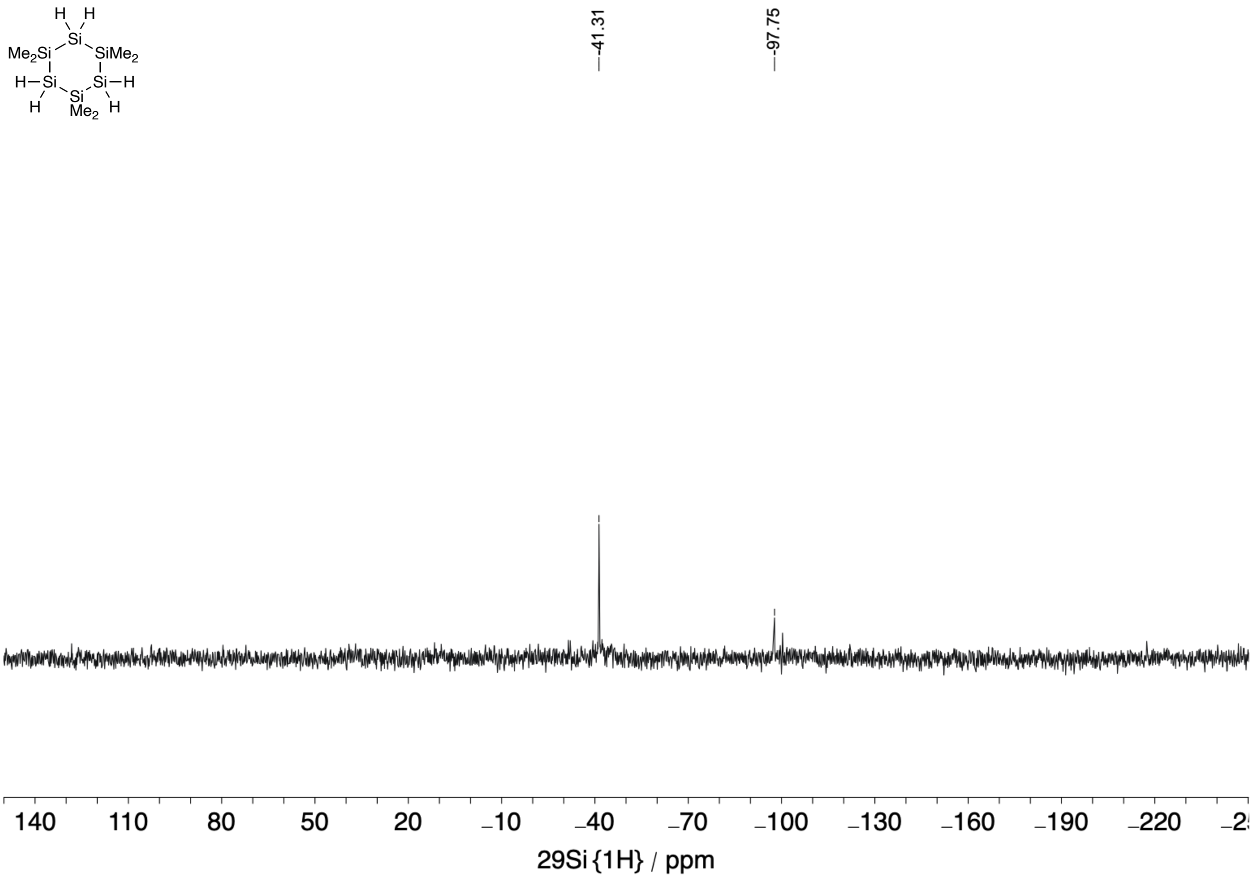


Figure S30. ^{29}Si NMR (80 MHz, C_6D_6) spectrum of **1,3,5-Si$_6$.**

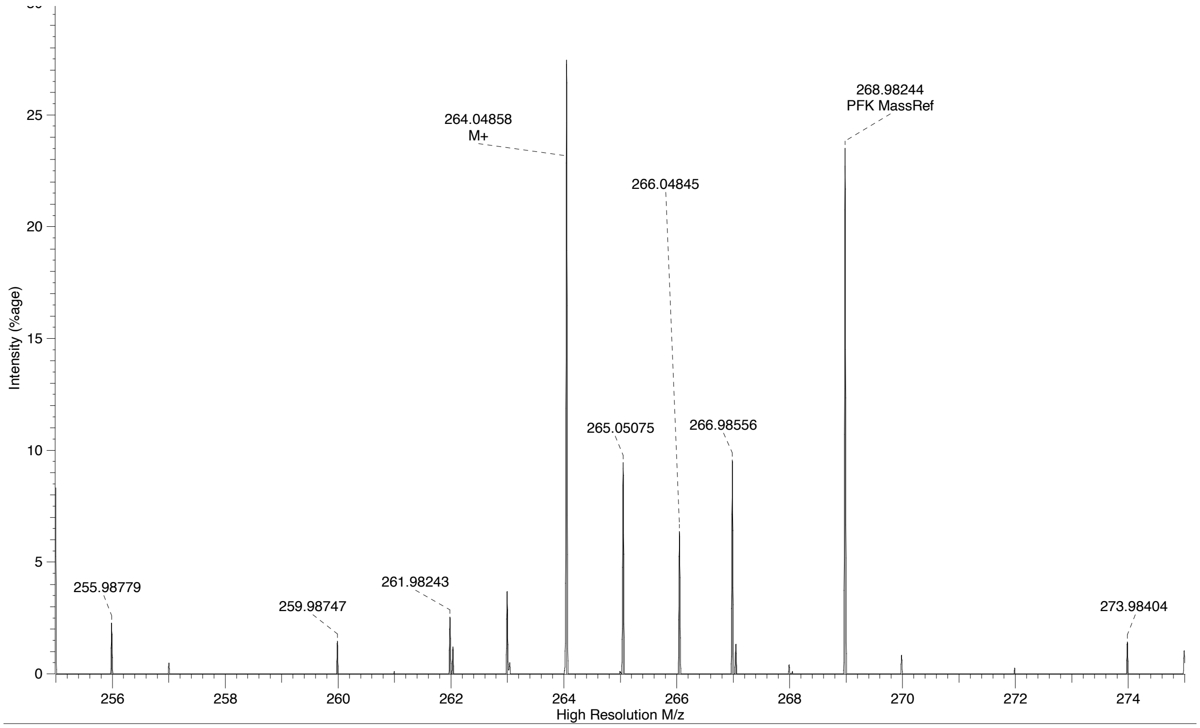


Figure S31. EI High Resolution Mass Spectrometry spectrum of **1,3,5-Si$_6$.**

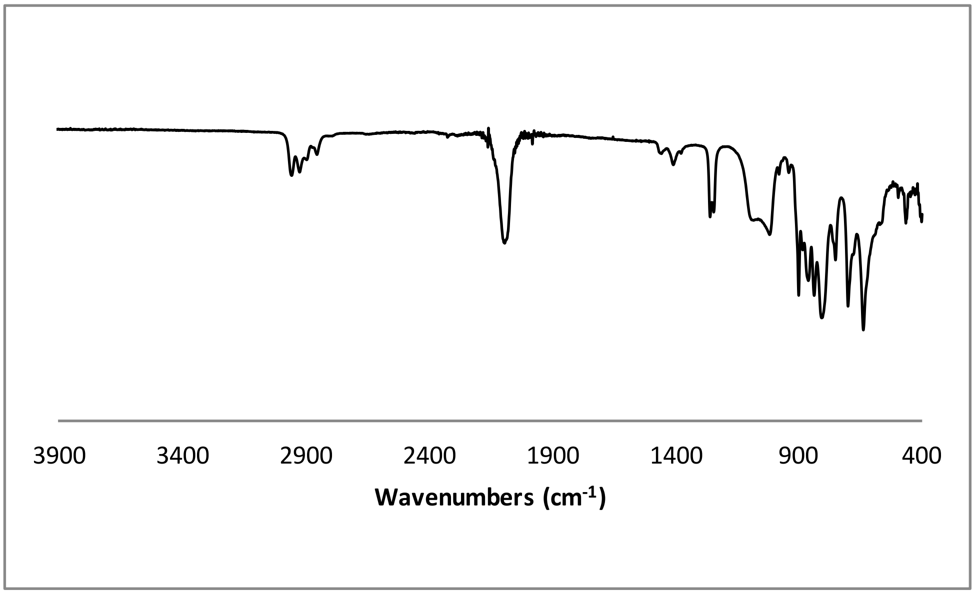


Figure S32. IR spectrum of **1,3,5-Si$_6$**.

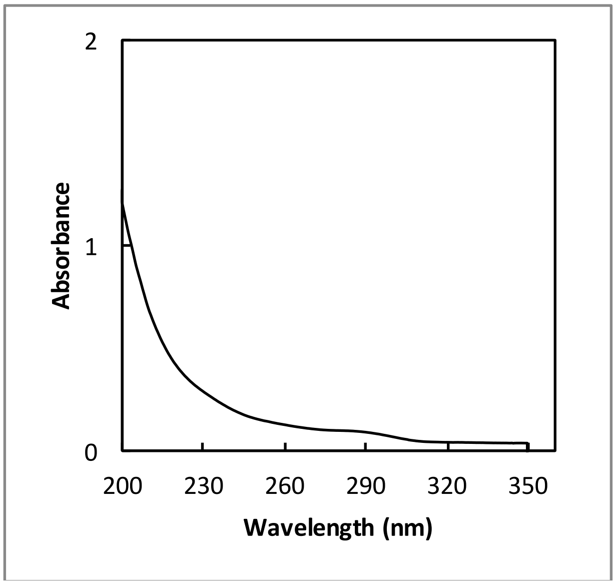


Figure S33. UV-vis spectrum of **1,3,5-Si$_6$** ([compound] = 3.00×10^{-5} M, in pentane).

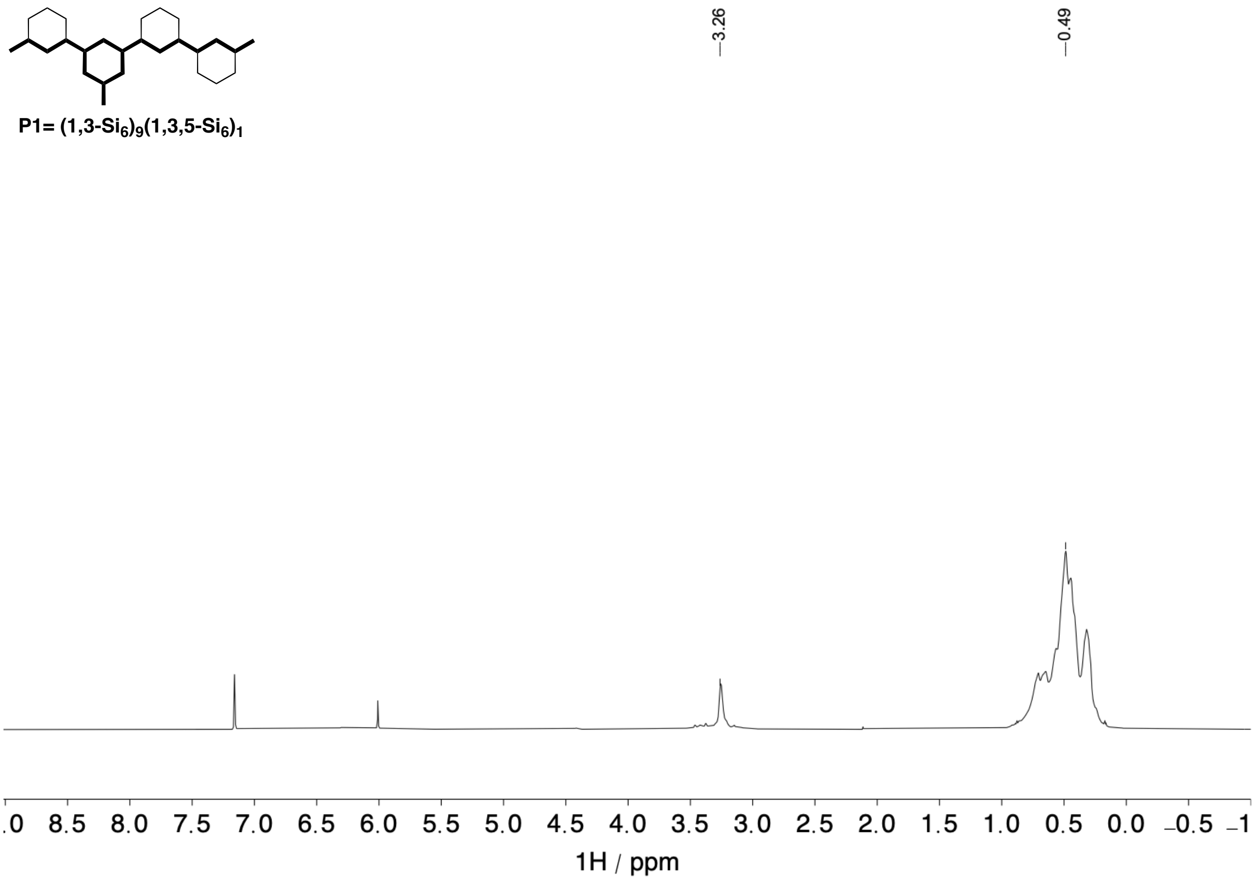


Figure S34. ^{1}H NMR (500 MHz, C_6D_6) spectrum of **P1**.

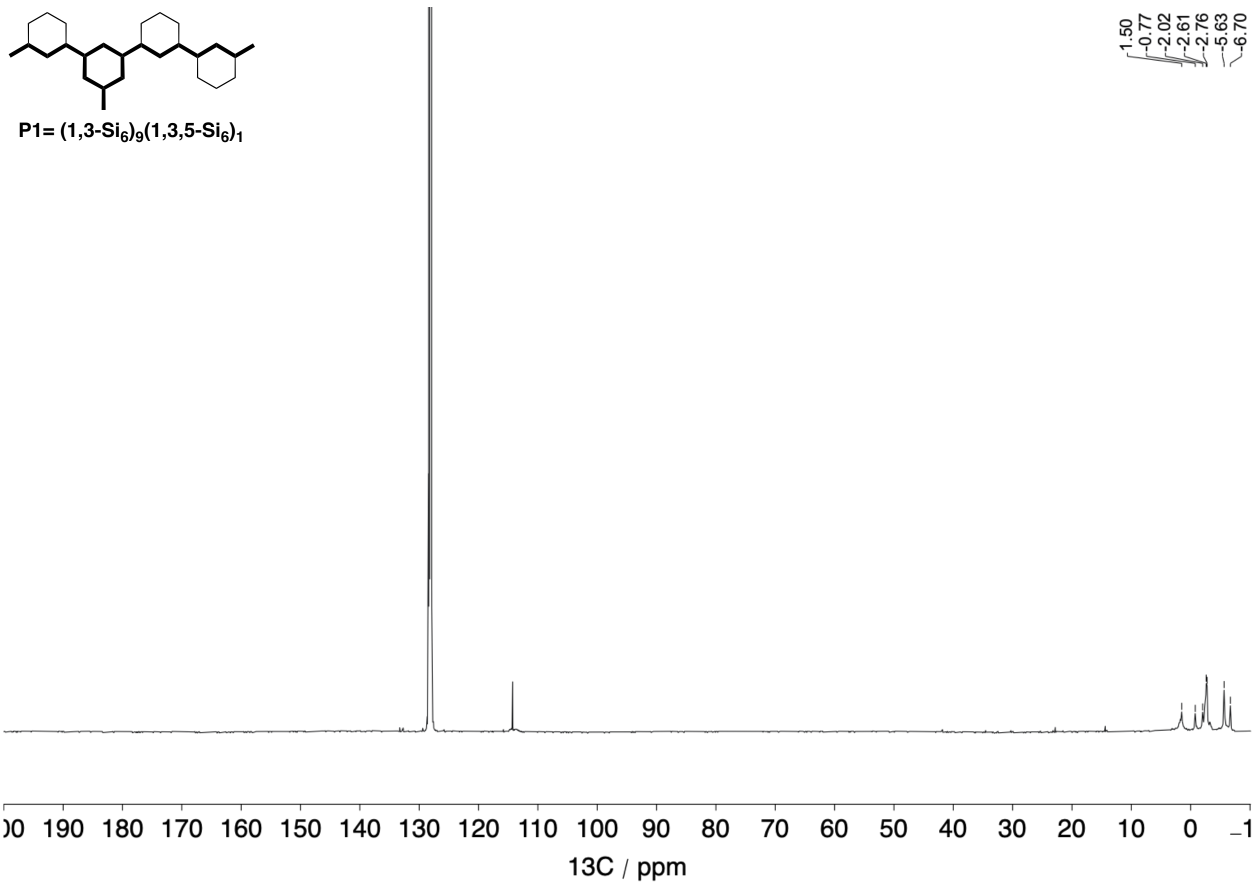


Figure S35. ^{13}C NMR (126 MHz, C_6D_6) spectrum of **P1.**

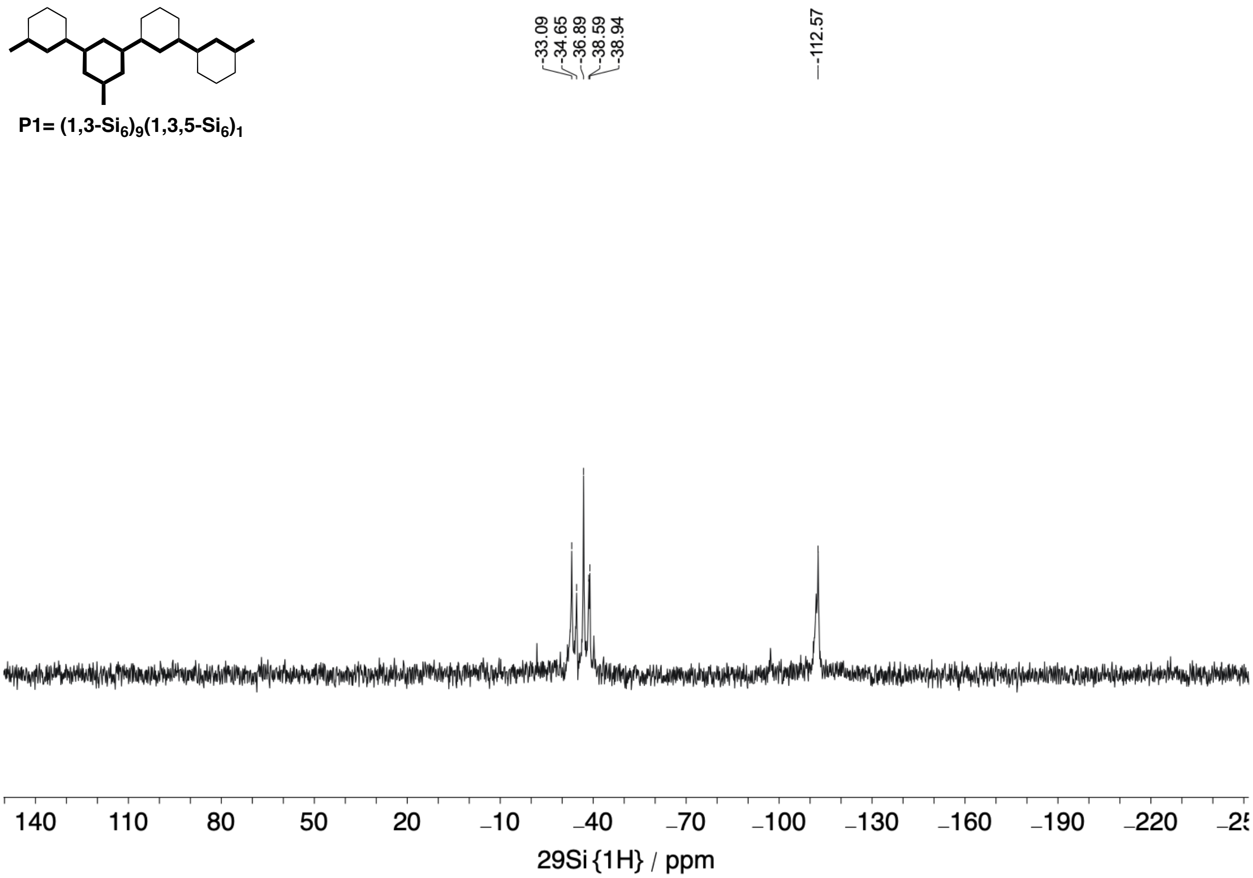


Figure S36. ^{29}Si NMR (80 MHz, C_6D_6) spectrum of **P1.**

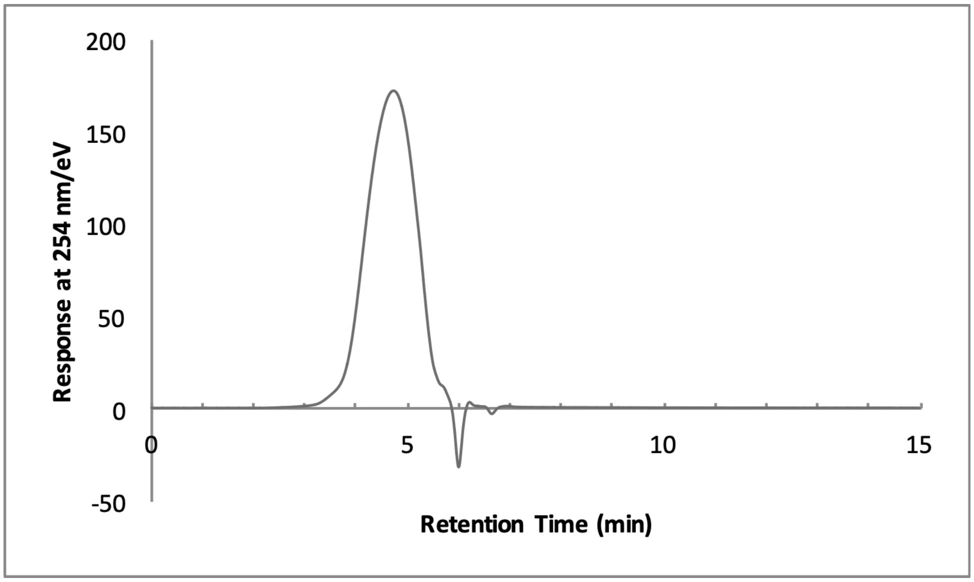


Figure S37. SEC trace of **P1** (THF, [polymer] = 1 mg mL^{-1}, 40 ºC, 0.35 mL min^{-1}, 10 μL injection).

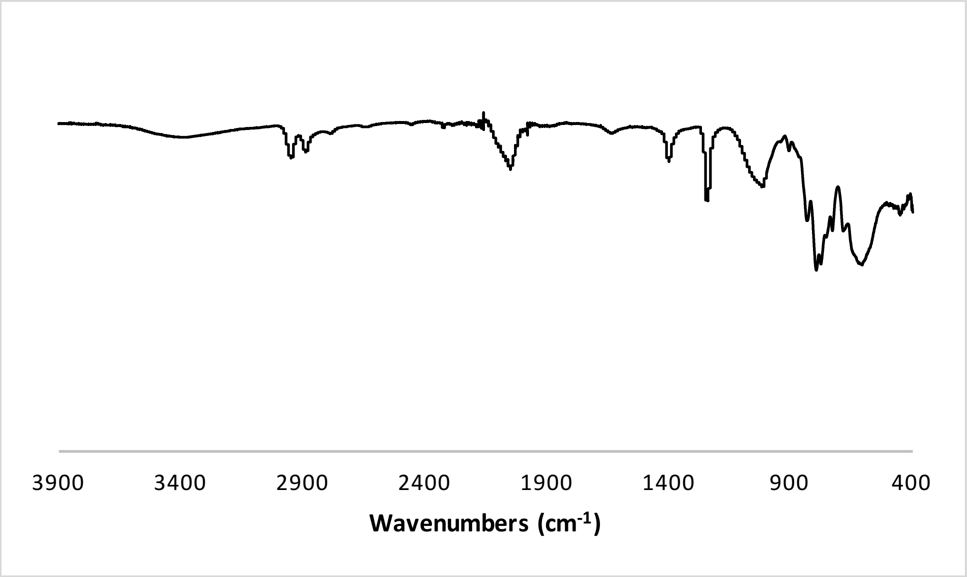


Figure S38. IR spectrum of **P1**.

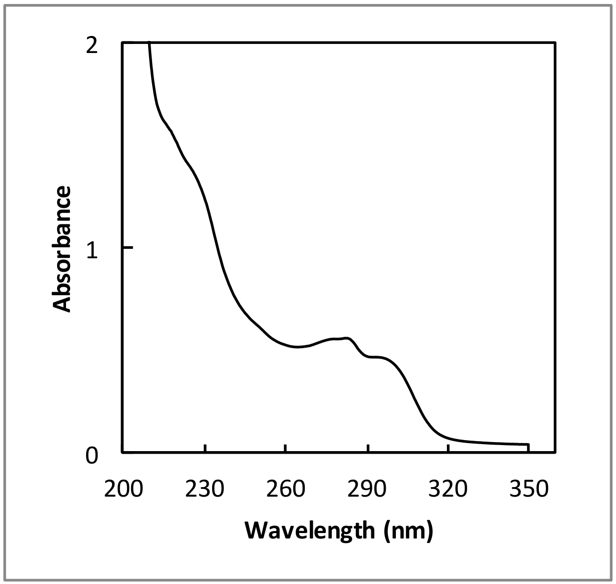


Figure S39. UV-vis spectrum of **P1** ([polymer] = 0.012 mg mL^{-1}, THF).

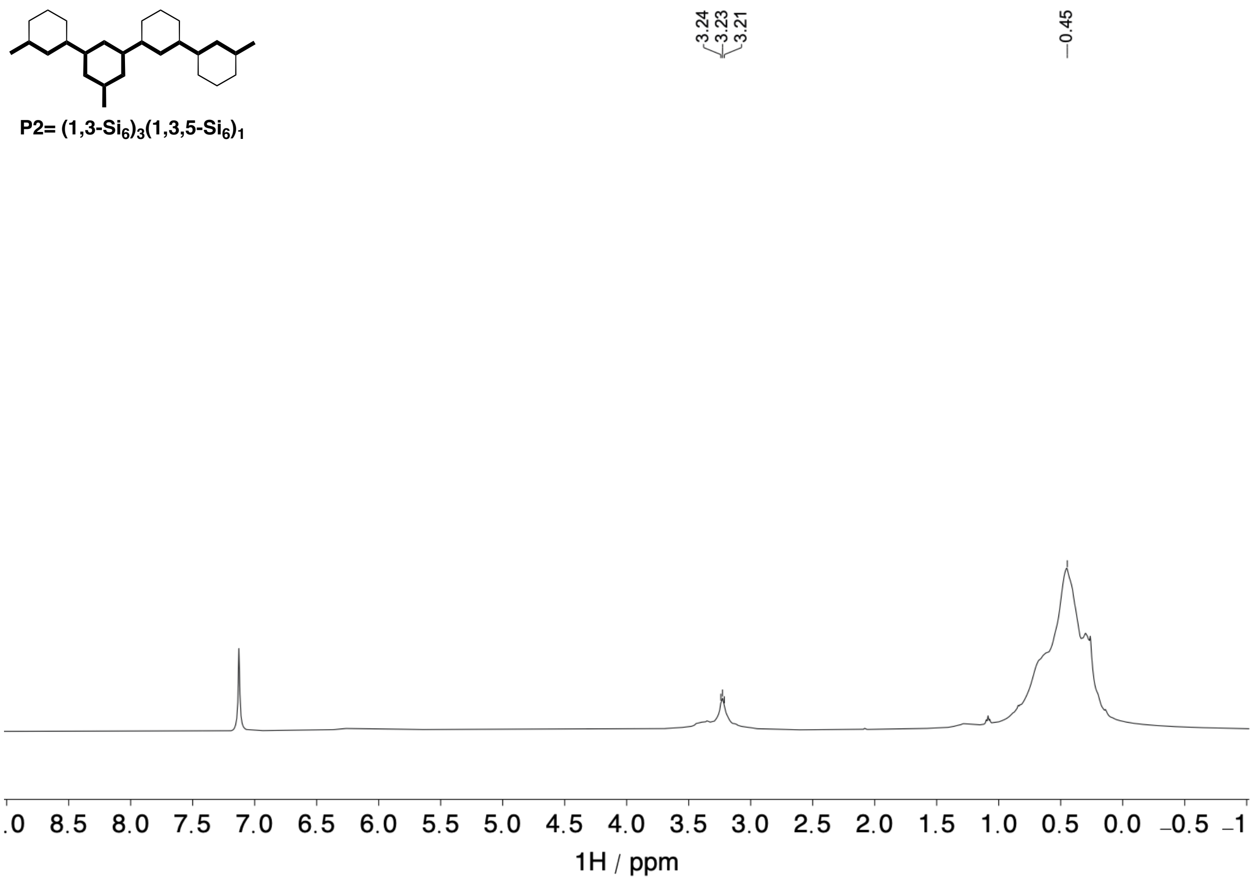
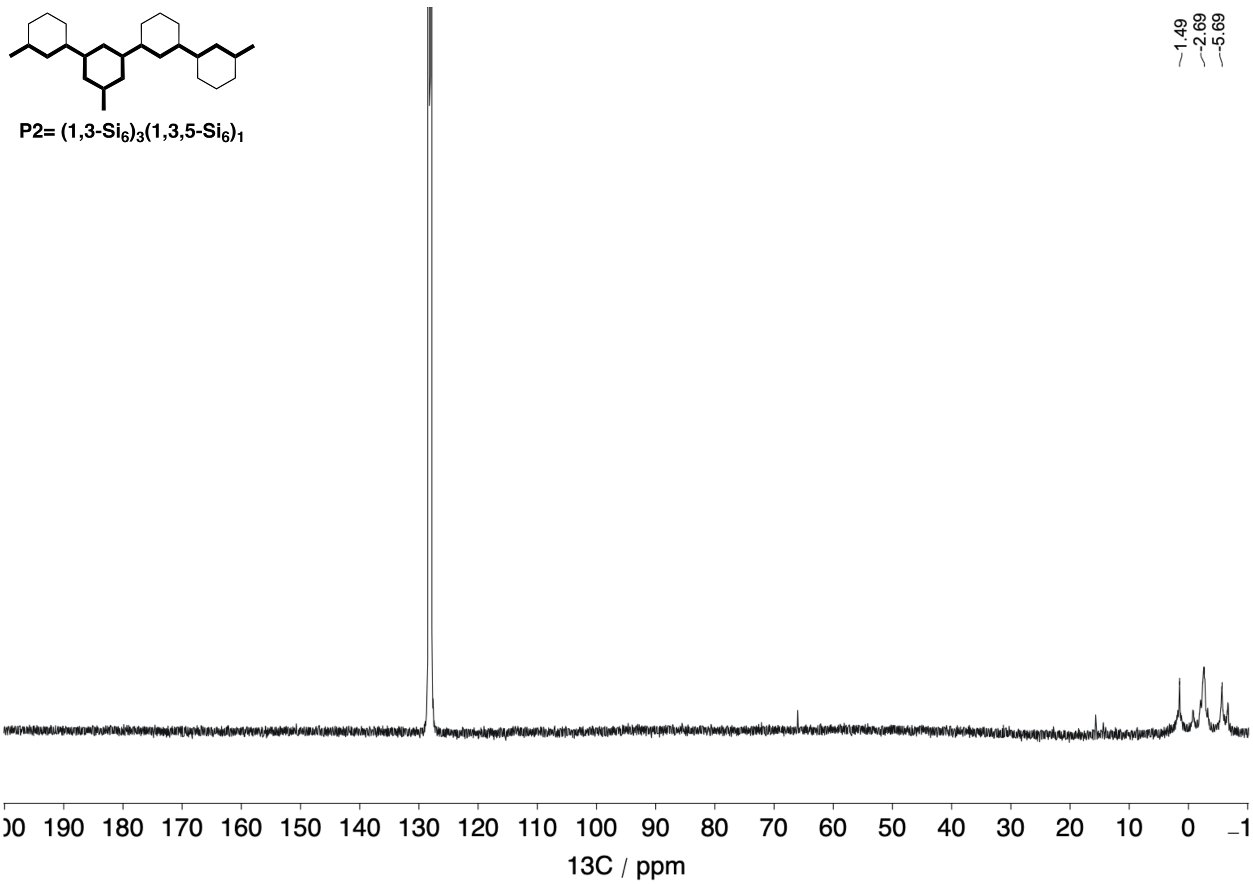


Figure S40. ^{1}H NMR (500 MHz, C_6D_6) spectrum of **P2.**



P2= $(1,3\text{-}Si_6)_3(1,3,5\text{-}Si_6)_1$

Figure S41. ^{13}C NMR (126 MHz, C_6D_6) spectrum of **P2.**

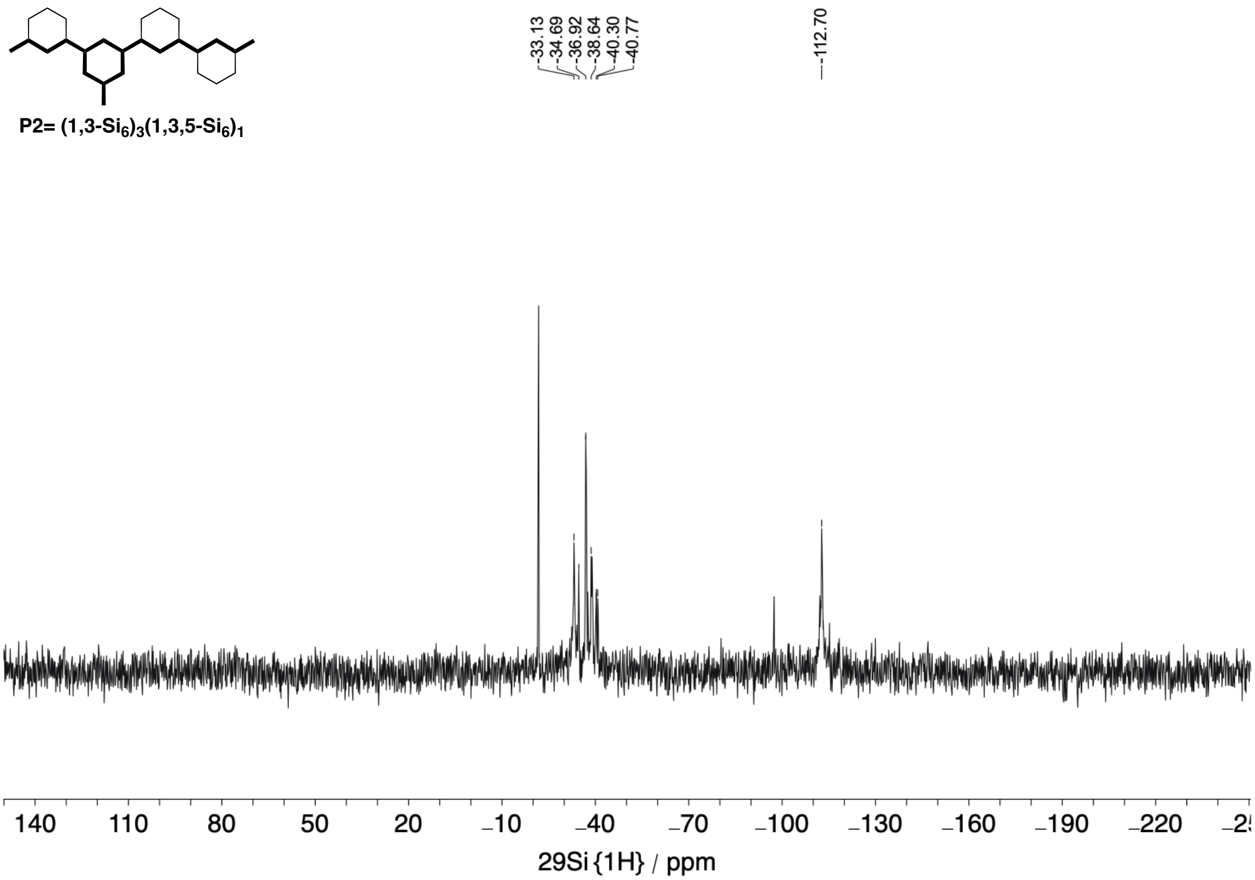


Figure S42. ^{29}Si NMR (80 MHz, C_6D_6) spectrum of **P2.**

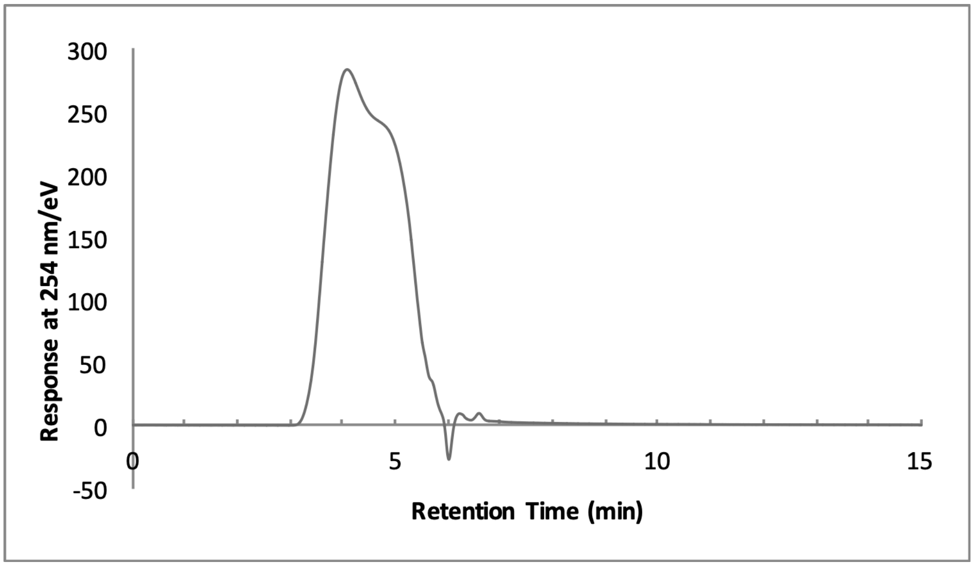


Figure S43. SEC trace of **P2** (THF, [polymer] = 1 mg mL^{-1}, 40 ºC, 0.35 mL min^{-1}, 10 μL injection).

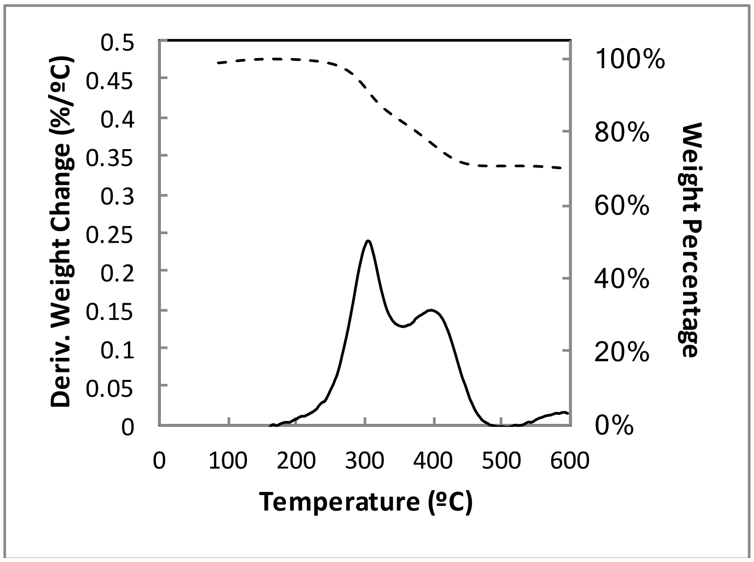


Figure S44. TGA curve of **P2**. Solid line: derivative weight change; dotted line: percentage weight change.

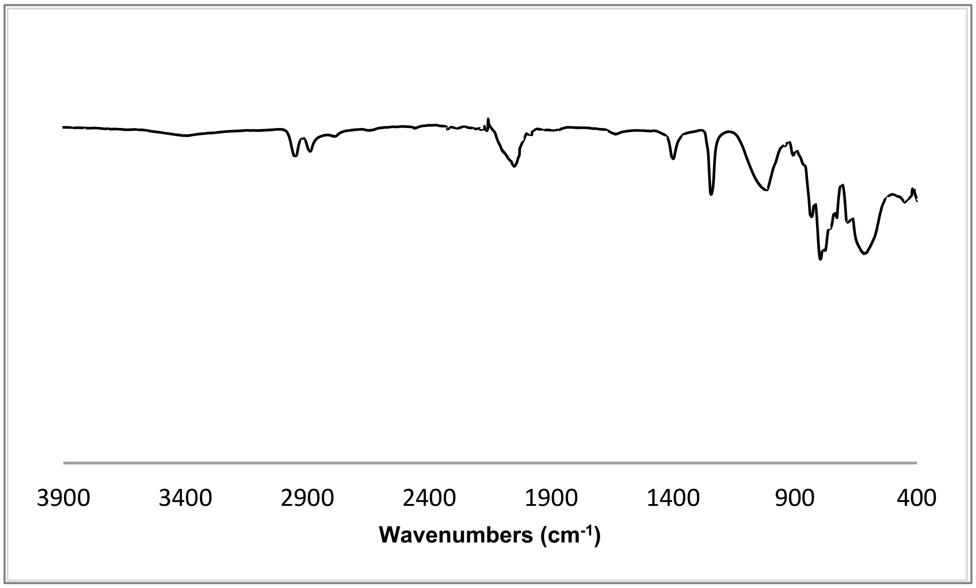


Figure S45. IR spectrum of **P2**.

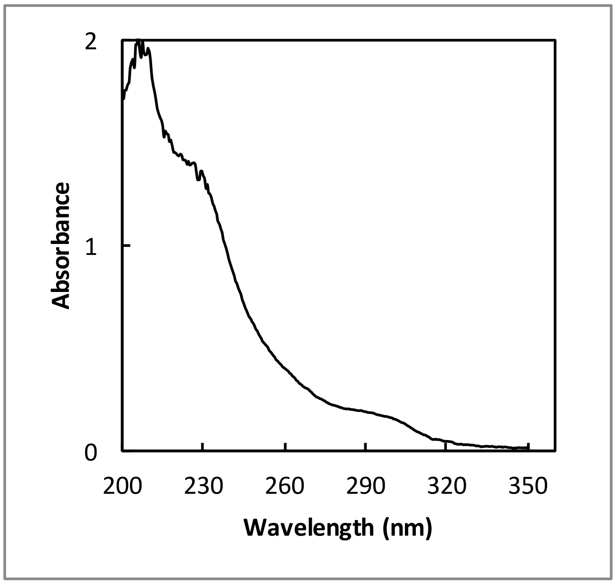


Figure S46. UV-vis spectrum of **P2** ([polymer] = 0.012 mg mL^{-1}, THF).

Single Crystal X-Ray Crystallography:

3: All reflection intensities were measured at 110(2) K using a SuperNova diffractometer (equipped with Atlas detector) with Cu *K*α radiation (λ = 1.54178 Å) under the program CrysAlisPro (Version CrysAlisPro 1.171.42.49, Rigaku OD, 2022). The same program was used to refine the cell dimensions and for data reduction. The structure was solved with the program SHELXS-2018/3 (Sheldrick, 2018) and was refined on F^2 with SHELXL-2018/3 (Sheldrick, 2018). Analytical numeric absorption correction using a multifaceted crystal model was applied using CrysAlisPro. The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms were placed at calculated positions using the instructions AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 U_{eq} of the attached C atoms.

The structure is ordered. The asymmetric unit contains two crystallographically independent molecules of the target compound. The crystal that was mounted on the diffractometer was non-merohedrally twinned, and the two twin components are related by a twofold axis along the **c** direction. The BASF scale factor refines to 0.2187(6).

Table S1. Crystallographic data for 3

	3
Crystal data	
Chemical formula	$C_{42}H_{48}Si_6$
M_r	721.34
Crystal system, space group	Triclinic, *P*-1
Temperature (K)	110
a, *b*, *c* (Å)	10.40544 (16), 11.84513 (16), 34.7565 (5)
α, β, γ (°)	90.4360 (11), 92.2033 (12), 106.3149 (13)
V (Å^3)	4107.57 (11)
Z	4

Radiation type	Cu *K*α
μ (mm^{-1})	2.11
Crystal size (mm)	0.33 × 0.18 × 0.09
Data collection	
Diffractometer	SuperNova, Dual, Cu at zero, Atlas
Absorption correction	Analytical *CrysAlis PRO* 1.171.42.49 (Rigaku Oxford Diffraction, 2022) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
$T_{\min}$, $T_{\max}$	0.590, 0.845
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	50229, 16679, 14937
R_{int}	0.028
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.106, 1.04
No. of reflections	16679
No. of parameters	878
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.36, -0.29

***Cis,cis*-4**: All reflection intensities were measured at 110.00(10) K using a Rigaku XtaLAB Synergy R (equipped with a rotating-anode X-ray source and HyPix-6000HE detector) with Cu *K*α radiation (λ = 1.54178 Å) under the program CrysAlisPro (Version CrysAlisPro 1.171.42.49, Rigaku OD, 2022). The same program was used to refine the cell dimensions and for data reduction. The structure was solved with the program SHELXS-2018/3 (Sheldrick, 2018) and was refined on F^2 with SHELXL-2018/3 (Sheldrick, 2018). Analytical numeric absorption correction using a multifaceted crystal was applied using CrysAlisPro. The temperature of the data collection was controlled using the system Cryostream 1000 from Oxford Cryosystems). The H atoms were placed at calculated positions (unless otherwise specified) using the instructions AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 U_{eq} of the attached C atoms. The H atoms attached to Si1, Si3 and Si5 were found from difference Fourier maps, and their coordinates were refined freely.

The structure is ordered. The crystal that was mounted on the diffractometer was non-merohedrally twinned, and the two twin components are related by a twofold rotation along [0.89 -0.00 0.45]. The BASF scale factor refines to 0.4345(9).

Table S2. Crystallographic data for *cis,cis*-4

	cis,cis-**4**
Crystal data	
Chemical formula	$C_{24}H_{36}Si_6$
M_r	493.07
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	110
a, *b*, *c* (Å)	20.9347 (4), 6.40525 (11), 23.5670 (5)
β (°)	114.011 (2)
V (Å^3)	2886.69 (10)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	2.77
Crystal size (mm)	0.08 × 0.08 × 0.02
Data collection	
Diffractometer	XtaLAB Synergy R, HyPix
Absorption correction	Analytical *CrysAlis PRO* 1.171.42.95a (Rigaku Oxford Diffraction, 2023) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.828, 0.947
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	32137, 6409, 5338
R_{int}	0.020
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.616
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.028, 0.078, 1.01
No. of reflections	6409
No. of parameters	287
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.36, -0.18

Computer programs: *CrysAlis PRO* 1.171.42.49 (Rigaku OD, 2022), *SHELXS2018*/3 (Sheldrick, 2018), *SHELXL2018*/3 (Sheldrick, 2018), *SHELXTL* v6.10 (Sheldrick, 2008).

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