Supplementary Information (SI) for Polymer Chemistry.

Supporting Information

Stereogenic-at-Silicon Hybrid Conjugated Polymers

Qifeng Jiang, Marissa G. Coschigano, Braden A. Mediavilla, Alexandra F. Gittens, Sophia J. Melvin and Rebekka S. Klausen*

Department of Chemistry, Johns Hopkins University, 3400 N. Charles St, Baltimore, MD, 21218

*klausen@jhu.edu

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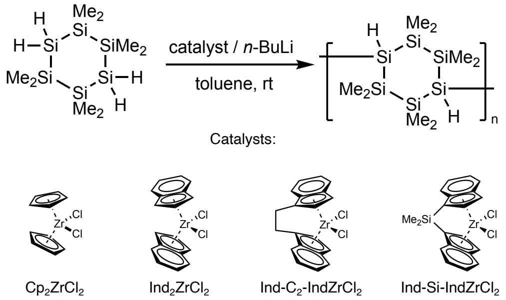
1. Supplemental Figures

Figure S1. Attempts of stereoselective dehydropolymerization of cyclosilane. Short oligomers were obtained using bulky catalysts.



Catalyst	M_n (Da)	M_w (Da)	M_w/M_n	Reaction Time
Cp_2ZrCl_2	2947	4104	1.39	1 day
Ind_2ZrCl_2	2479	3705	1.50	4 days
Ind-C_2-Ind$ZrCl_2$	448	529	1.12	2 days
Ind-Si-Ind$ZrCl_2$	555	662	1.14	10 days

Figure S2. Solubility characteristics of (left to right) **P1-P6** (0.5 mg polymer in 1 mL $CDCl_3$).

Figure S3. PS calibration curve in $CDCl_3$ for M_w prediction

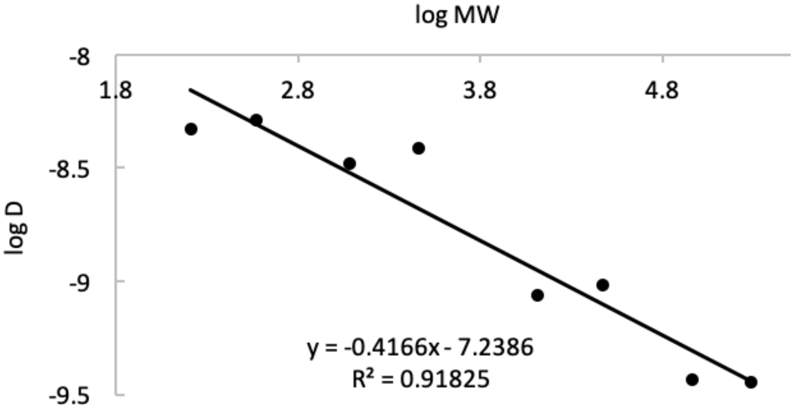
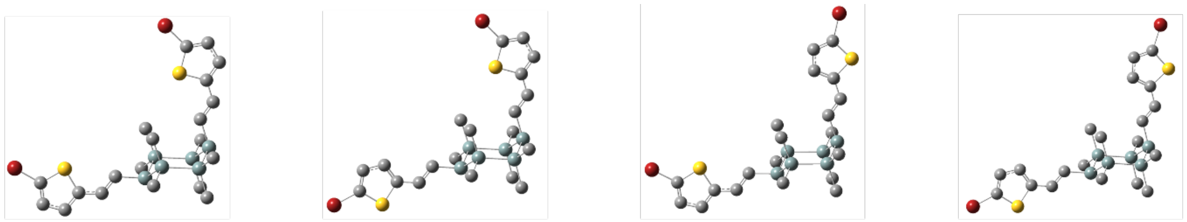


Figure S4. Rotational isomers for chair and twist-boat conformations of *cis*-**1**, calculated in the gas phase at the gas phase at the B3LYP-D3(BJ)/6-311++G(d,p) level of theory.

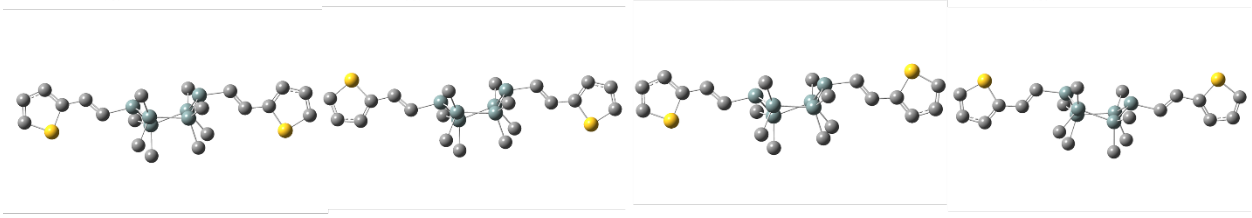


$\Delta\Delta G_{rel}$ = 0.00 kcal·mol^{-1} $\Delta\Delta G_{rel}$ = +1.58 kcal·mol^{-1} $\Delta\Delta G_{rel}$ = +1.84 kcal·mol^{-1} $\Delta\Delta G_{rel}$ = +3.47 kcal·mol^{-1}

$\Delta\Delta G_{rel}$ = +3.78 kcal·mol^{-1} $\Delta\Delta G_{rel}$ = +5.96 kcal·mol^{-1} $\Delta\Delta G_{rel}$ = +2.31 kcal·mol^{-1} $\Delta\Delta G_{rel}$ = +3.96 kcal·mol^{-1}

Figure S5. Rotational isomers for chair and twist-boat conformations of H-*cis*-**1**, calculated in the gas phase at the gas phase at the B3LYP-D3(BJ)/6-311++G(d,p) level of theory.

$\Delta\Delta G_{rel}$ = 0.00 kcal·mol^{-1} $\Delta\Delta G_{rel}$ = +1.40 kcal·mol^{-1} $\Delta\Delta G_{rel}$ = +1.58 kcal·mol^{-1} $\Delta\Delta G_{rel}$ = +2.98 kcal·mol^{-1}



$\Delta\Delta G_{rel}$ = +3.51 kcal·mol^{-1} $\Delta\Delta G_{rel}$ = +4.91 kcal·mol^{-1} $\Delta\Delta G_{rel}$ = +2.24 kcal·mol^{-1} $\Delta\Delta G_{rel}$ = +3.64 kcal·mol^{-1}

2. General Information

General Experimental Procedures

All experiments were performed under protection of dry argon with the rigid exclusion of air and moisture using standard Schlenk techniques or in a nitrogen glovebox. All glassware was oven-dried overnight in a 175 °C oven.

Materials

Unless otherwise specified, all chemicals were used as purchased without further purification. Solvents DCM (Fisher, HPLC grade), THF (Fisher, HPLC grade), and toluene (Fisher, certified ACS) were dried on a J. C. Meyer Solvent Dispensing System (SDS) using stainless steel columns packed with neutral alumina (except for toluene which is 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. Carbonylchlorohydridotris(triphenylphosphine)ruthenium(II) ($RuHCl(CO)(PPh_3)_3$), [1,3-Bis(diphenylphosphino)propane]dichloronickel(II) ($NiCl_2$dppp), isopropylmagnesium chloride (2.0M in THF), triphenylphosphine, and 2,5-dibromothiophene were purchased from Sigma Aldrich. Bis(indenyl)zirconium dichloride, rac-ethylenebis(indenyl)zirconium(IV) dichloride, and rac-dimethylsilylbis(1-indenyl)zirconium dichloride were purchased from Strem Chemicals. 1,2-dichloro-1,1,2,2-tetramethyldisilane was purchased from Gelest.

Instrumentation

^{1}H NMR, ^{13}C {^{1}H} NMR, ^{19}F {^{1}H} NMR and ^{29}Si {^{1}H} NMR spectra were recorded on either a Bruker Avance 300, 400 or III HD 400 MHz Spectrometer and chemical shifts are reported in parts per million (ppm). Spectra were recorded in benzene-d_6 or chloroform-d_1 with the residual solvent peak as the internal standard (^{1}H NMR: $CHCl_3$ $\delta = 7.26$, ^{13}C NMR: $CHCl_3$ $\delta = 77.16$). Chemical shifts of ^{29}Si {^{1}H} NMR spectra were calibrated by tris(Me_3Si)methane in $CDCl_3$. The temperature was room temperature unless otherwise specified. Multiplicities are as indicated: s (singlet), d (doublet), dd (doublet of doublets), m (multiplet) and br (broad). Coupling constants, J, are reported in Hertz, and integration is provided.

Solid-state $^1H\rightarrow^{29}Si$ and ^{13}C CPMAS spectra were recorded on a Bruker Ascend spectrometer (500 MHz) and chemical shifts were reported in parts per million (ppm). Chemical shifts of $^1H\rightarrow^{29}Si$ CPMAS spectra were calibrated by silicone rubber. Chemical shifts of $^1H\rightarrow^{13}C$ CPMAS spectra were calibrated by adamantane. In a glove box, 14 mg of polymer samples were packed into a sample rotor compatible with a 3.2 mm Phoenix HX probe. Spectral data was acquired at a spinning speed of 20 kHz.

All column chromatography was performed on a Teledyne ISCO Combiflash Rf+ using Redisep Rf silica columns. Fourier transformed infrared (FTIR) spectroscopy was performed on a Thermo NicoletNexus 670 FTIR spectrometer. Mass spectrometry and high-resolution mass spectrometry were performed in the Department of Chemistry at Johns Hopkins University using a VG Instruments VG70S/E magnetic sector mass spectrometer with electron ionization (EI) (70 eV). The samples for UV–vis spectroscopy were all prepared in the glove box and packed in sealed quartz cuvettes. UV–vis spectroscopy was performed on a Shimadzu UV-1800 UV–vis spectrophotometer. Molecular weights of polymers were measured by gel permeation chromatography (GPC) on a Tosoh Bioscience EcoSEC GPC workstation with UV detection at

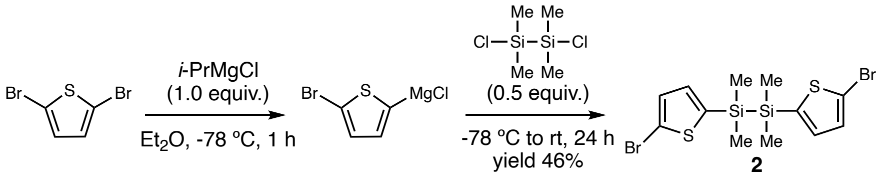
310 nm using butylated hydroxytoluene stabilized tetrahydrofuran (THF) as the eluent (0.35 mL min^{-1}, 40 °C) through TSKgel SuperMultipore HZ-M guard column (4.6 mm ID x 2.0 cm, 4 µm, Tosoh Bioscience) and a TSKgel SuperMultipore HZ-M column (4.6 mm ID x 15 cm, 4 µm, Tosoh Bioscience). Polystyrene 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 (0.5 mg mL^{-1}), filtered through syringe filters (Millex-FG Syringe Filter Unit, 0.20 µm, PTFE, EMD Millipore), and injected by an auto-sampler (10 µL).

3. Experimental Procedures and Tabulated Characterization Data

3.1 Isolation of *trans*-1 and *cis*-1

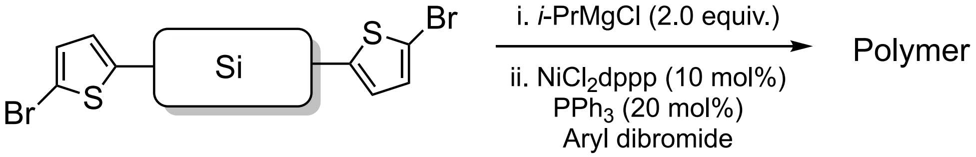
In a scintillation vial, 0.500 g of **1**[1] (dr 63:37 *trans:cis*) was dissolved in 2 mL of DCM and layered with 18 mL of dry methanol. The solution was allowed to sit overnight in a glove box and colorless crystals were found at the bottom. The mixture was filtered through a fritted funnel, washed with 5 mL of dry methanol and dried under vacuum. *trans*-**1** (dr 90:10 *trans:cis*) (0.270 g) was collected as a colorless crystal. The filtrate was collected and dried under vacuum, yielding a white powder *cis*-**1** (dr 20:80 *trans:cis*) (0.178 g).

3.2 Synthesis of 2



The procedure was adapted from literature.[2] On the Schlenk line, an oven-dried 100 mL Schlenk flask with a stir bar was charged with 2,5-dibromothiophene (1.0 equiv., 8.27 mmol, 2.00 g). Diethyl ether (50 mL) was added and the solution was cooled to -78 °C in an acetone/dry ice bath. With a syringe pump, *i*-PrMgCl (2 M in THF, 4.13 mL) was slowly added in 30 minutes and the reaction mixture was stirred for another 30 minutes. White precipitates were observed during the addition. 1,2-dichloro-1,1,2,2-tetramethyldisilane (0.5 equiv., 4.13 mmol, 0.774 g) was then added through syringe. The reaction mixture was allowed to warm up to room temperature and stirred for 24 hours. The reaction was quenched with 50 mL of DI water. The aqueous layer was separated from the organic layer and washed with diethyl ether (50 mL x 3). All the organic layers were combined, dried over anhydrous sodium sulfate, concentrated under vacuum and purified by silica column with 100 % hexanes. A colorless oil was isolated as **2** (0.83 g, 46%). NMR spectra were consistent with the literature.

3.3 Kumada polycondensation of di(bromothienyl)silane and aryl dibromide



In a glove box, an oven-dried 2-dram vial with stir bar was charged with di(bromothienyl)silane (1.0 equiv.) and THF (75 mM). *i*-PrMgCl (2.0 M in THF, 2.0 equiv.) was added by micro syringe. The solution was stirred at room temperature for 30 minutes, yielding a di-Grignard intermediate. NidpppCl$_2$ (0.1 equiv.), triphenylphosphine (0.2 equiv.) and aryl dibromide (1.5 equiv.) were weighed in a 2-dram vial with stir bar and dissolved in THF (0.3 mM). The di-Grignard solution was quickly added to the reaction mixture by pipette, yielding a dark red solution. Additional THF (0.3 mM) was used to rinse the vial and combined with the reaction mixture. The reaction was heated to 40 ˚C and allowed to stir for 24 hours in a glove box.

After 24 hours, in the glove box the reaction was quenched by adding the orange solution dropwise to 15 mL of dry methanol, which was stirred fast in a round bottom flask. Formation of precipitates was observed. The suspension was allowed to sit overnight, and the top clear yellow solution was decanted. 10 mL of methanol were added, and precipitates were washed sufficiently by stirring vigorously for 30 minutes. The suspension was allowed to sit until the precipitates settled at the bottom. The above washing procedure was repeated 2 more times. Then the suspension was filtered through a Buchner funnel with filter paper. The solid was washed with methanol and dried under vacuum, yielding hybrid polysilane products. Solid-state NMRs were reported due to the low solubility of the polysilanes in solvents.

Synthesis of P2: The polycondensation was set up at the scale of 0.045 mmol with *cis*-**1** (dr 20:80 *trans:cis*) and 2,5-dibromothiophene. Total volume of THF was 0.9 mL. Yield: 17 mg, 61%. M_w: 57620 Da.

Tabulated Characterization Data for ***P2***

δ_H (400 MHz, $CDCl_3$)	7.03 (br, 8H), 6.81 (br, 2H), 6.12 (br, 2H), 3.79 (br, 2H), 0.34 (br, 12H), 0.29 (br, 12H).
δ_C (126 MHz, CPMAS)	141.58, 134.03, 121.74, -6.89.
δ_{Si} (79 MHz, $CDCl_3$)	-40.11, -62.87, -64.83.

Synthesis of P3: The polycondensation was set up at the scale of 0.037 mmol with **1** (dr 65:35 *trans:cis*) and 2,5-dibromothiophene. Total volume of THF was 0.75 mL. Yield: 5 mg, 22%. M_w: 24280 Da.

Tabulated Characterization Data for ***P3***

δ_H (400 MHz, $CDCl_3$)	7.02 (br, 8H), 6.81 (br, 2H), 6.12 (br, 2H), 3.77 (br, 2H), 0.30 (br, 24H).
δ_C (126 MHz, CPMAS)	142.45, 135.40, 129.22, 124.11, 20.00, -6.97.
δ_{Si} (79 MHz, $CDCl_3$)	-39.86, -62.85, -64.77

Synthesis of P4: The polycondensation was set up at the scale of 0.227 mmol with **2** and 2,5-dibromothiophene. Total volume of THF was 3 mL. Yield: 55 mg, 66%. M_w: 81230 Da.

Tabulated Characterization Data for ***P4***

δ_H (400 MHz, $CDCl_3$)	7.22, (br, 3H), 7.07 (br, 3H), 0.44 (br, 12H).
δ_C (101 MHz, $CDCl_3$)	142.58, 137.52, 136.20, 135.43, 125.10, 124.45, -2.81, -2.87.
δ_{Si} (79 MHz, $CDCl_3$)	-24.43.

Synthesis of P5: The polycondensation was set up at the scale of 0.150 mmol with *trans*-**1** (dr 90:10 *trans:cis*) and 1,4-dibromo-2,5-((2-ethylhexyl)oxy)benzene. Total volume of THF was 3 mL. Yield: 30 mg, 24%. Solid-State NMRs were collected for low solubility in organic solvents.

Tabulated Characterization Data for ***P5***

δ_C (126 MHz, CPMAS)	206.56, 151.34, 145.73, 138.25, 127.47, 125.45, 50.68, 26.23, -3.97.
δ_{Si} (99 MHz, CPMAS)	17.82, -10.35, -30.57, -52.49.

Synthesis of P6: The polycondensation was set up at the scale of 0.037 mmol with **1** (dr 65:35 *trans:cis*) and 1,4-dibromo-2,5-((2-ethylhexyl)oxy)benzene. Total volume of THF was 0.75 mL. Yield: 11 mg, 35%. Solid-State NMRs were collected for low solubility in organic solvents.

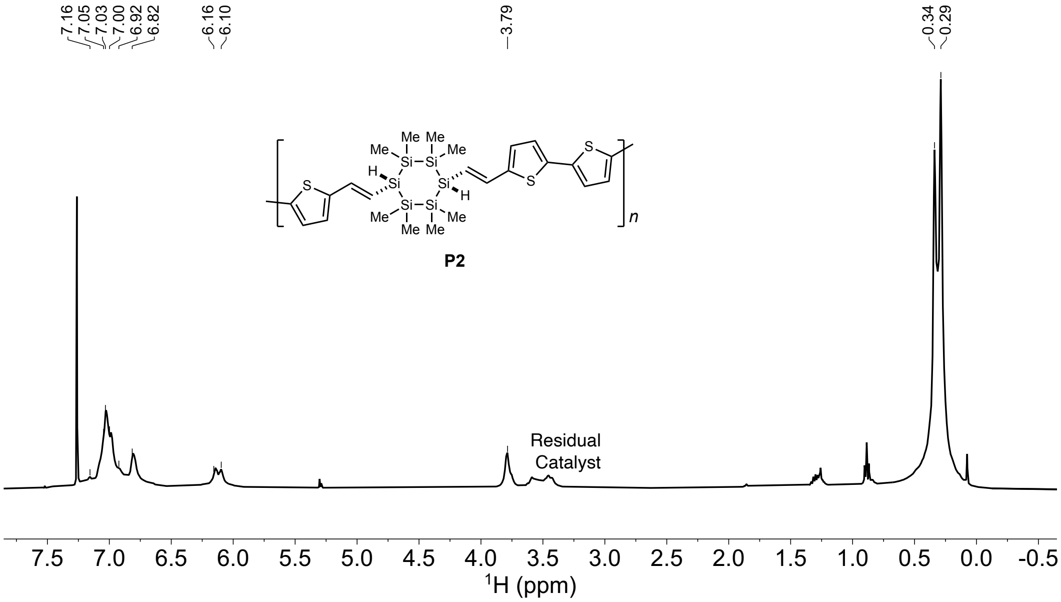
Tabulated Characterization Data for ***P6***

δ_C (126 MHz, CPMAS)	206.85, 150.62, 145.44, 137.68, 125.45, 51.11, 23.78, -3.97.
δ_{Si} (99 MHz, CPMAS)	7.82, -10.25, -30.85, -50.70.

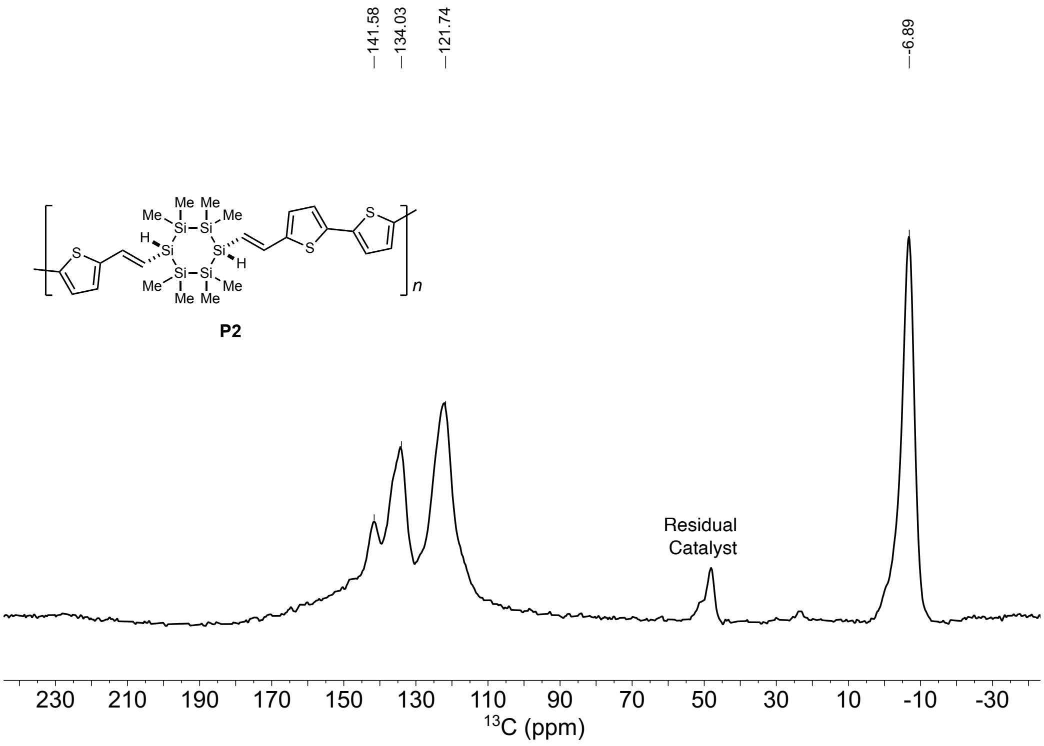
4. NMR Spectra

4.1 NMR Spectra of P2.

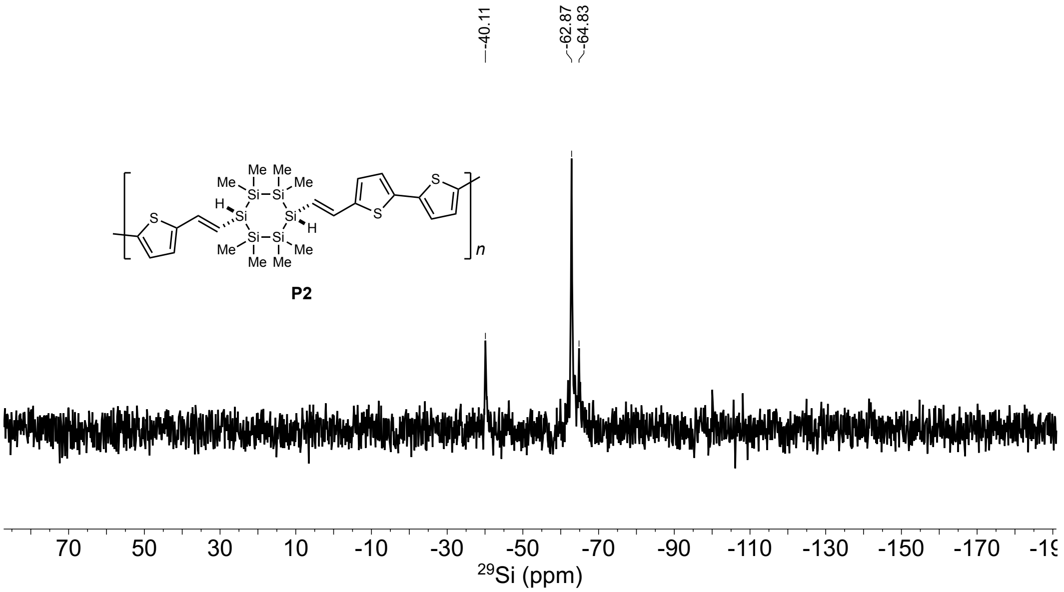
4.1.1 ^{1}H NMR Spectrum of **P2** (400 MHz, $CDCl_3$).



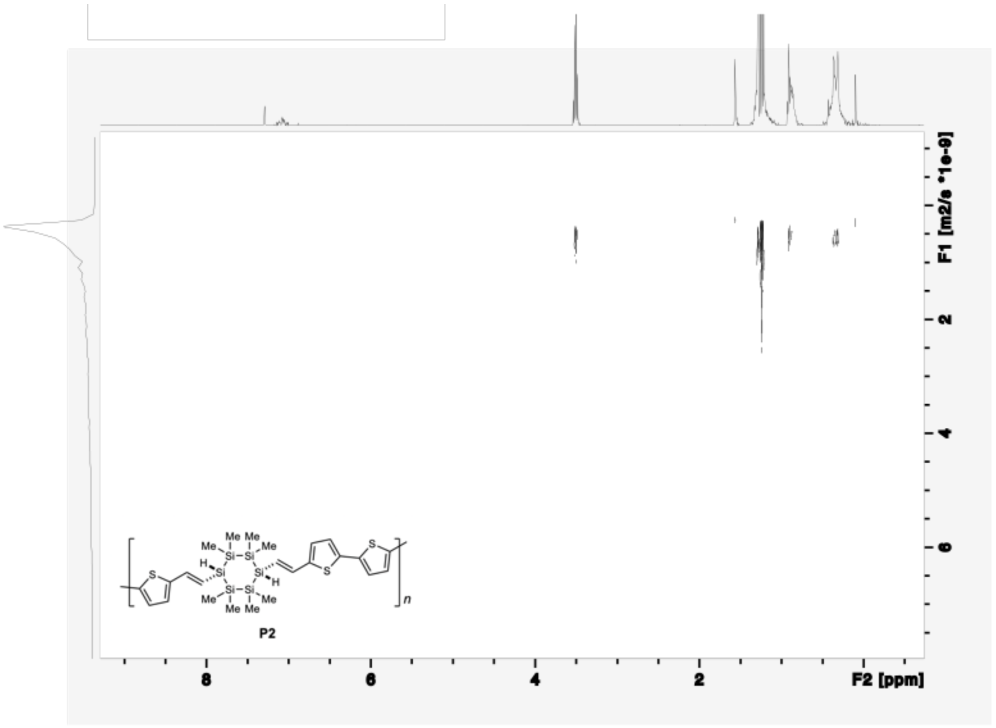
4.1.2 $^1H \rightarrow ^{13}C$ CPMAS spectrum of **P2**(126 MHz, CPMAS).



4.1.3 ^{29}Si{^{1}H} NMR Spectrum of **P2** (79 MHz, CDCl$_3$). $^{1}J_{\text{Si-H}}$ = 120 Hz.

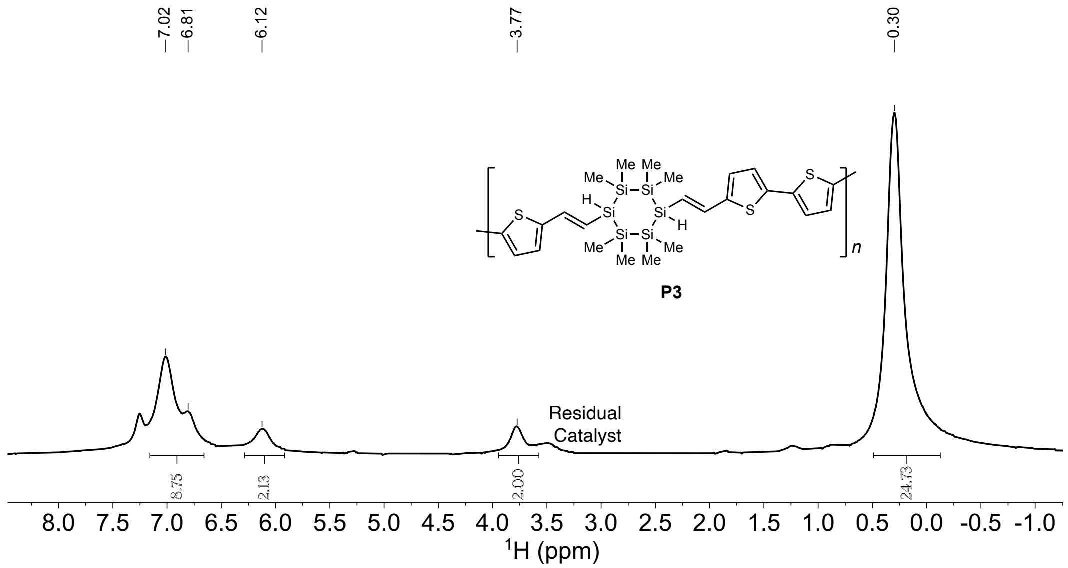


4.1.4 ^{1}H DOSY Spectrum of **P2** (400 MHz, CDCl$_3$, [**P2**] = 0.5 mg mL^{-1}). D = 6.0x10^{-10} m^{2}s^{-1}, M$_w$ = 57620 Da.

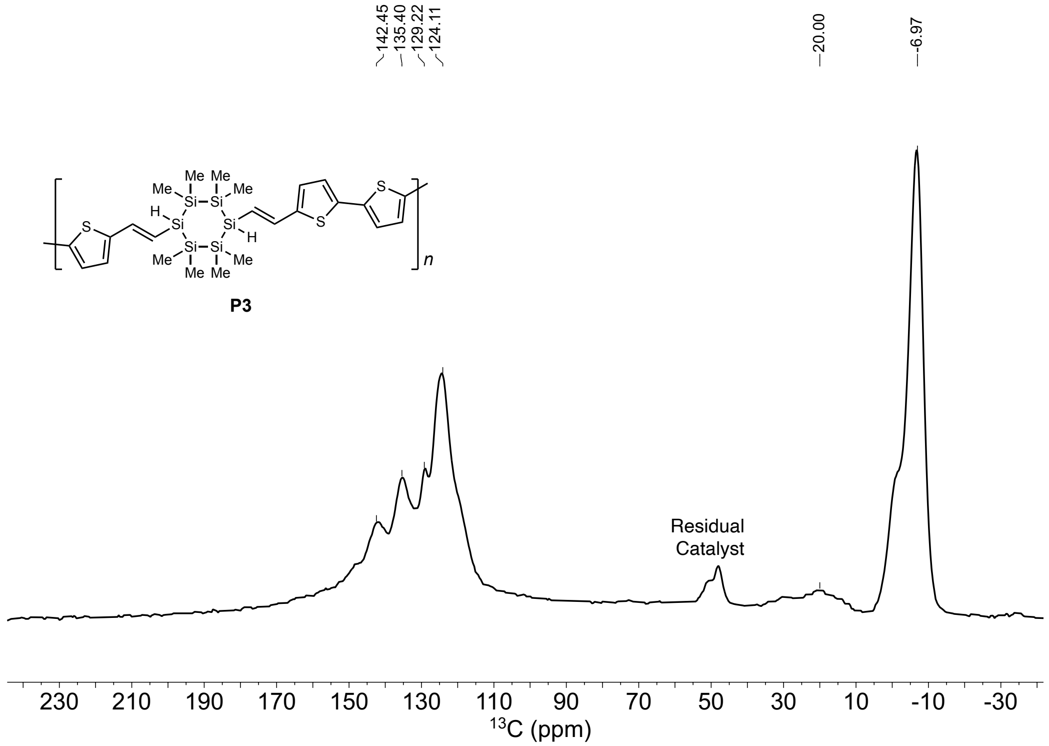


4.2 NMR Spectra of P3.

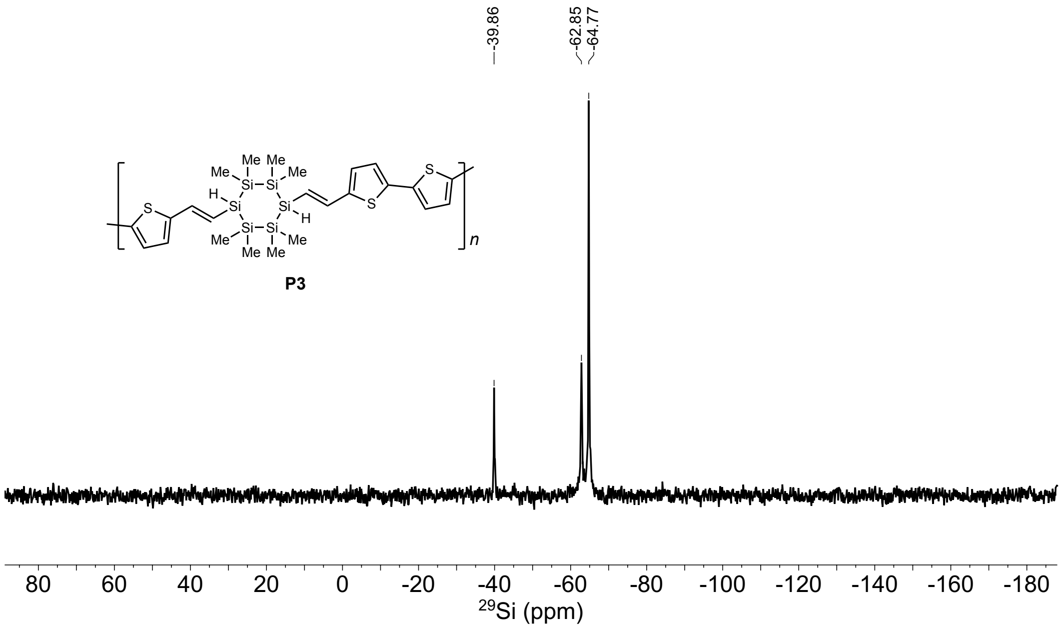
4.2.1 ^1H NMR Spectrum of **P3** (400 MHz, $CDCl_3$).



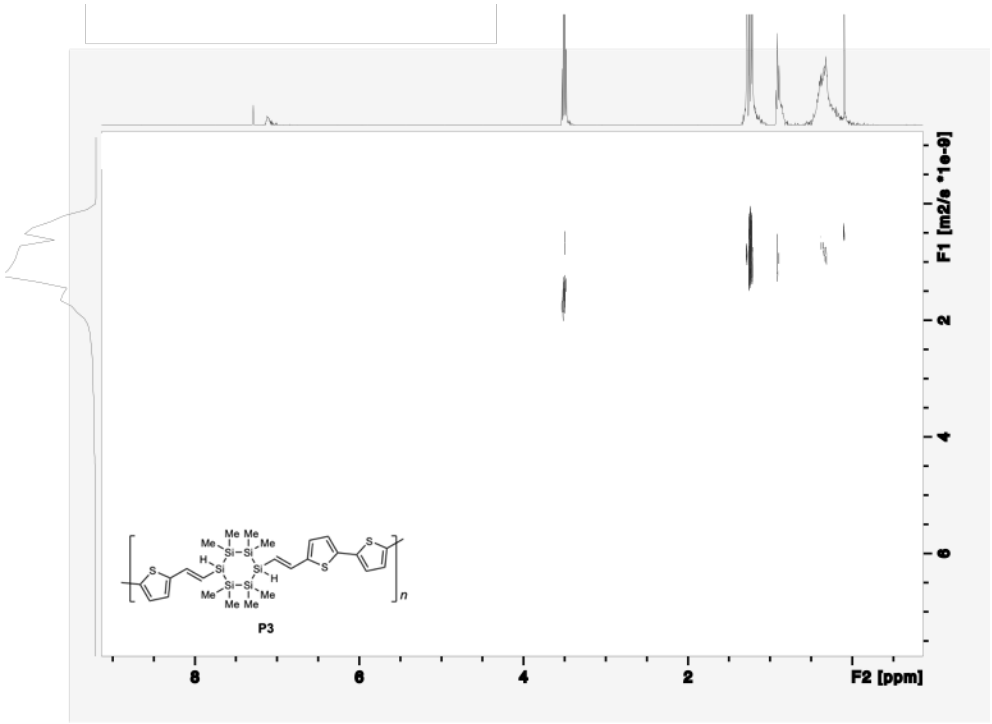
4.2.2 $^1H\rightarrow^{13}C$ CPMAS spectrum of **P3** (126 MHz, CPMAS).



4.2.3 $^{29}Si\{^1H\}$ NMR Spectrum of **P3** (79 MHz, $CDCl_3$). $^1J_{Si\text{-}H}$ = 120 Hz.

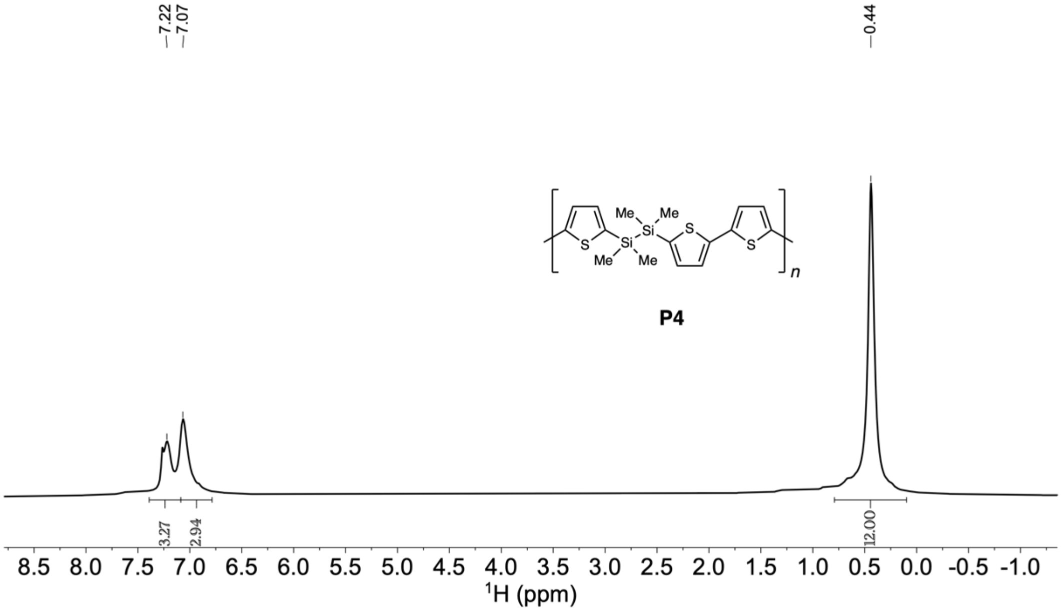


4.2.4 ^1H DOSY Spectrum of **P3** (400 MHz, $CDCl_3$, [**P3**] = 0.5 mg mL^{-1}). D = 8.6×10^{-10} m^2s^{-1}, M_w = 24280 Da.

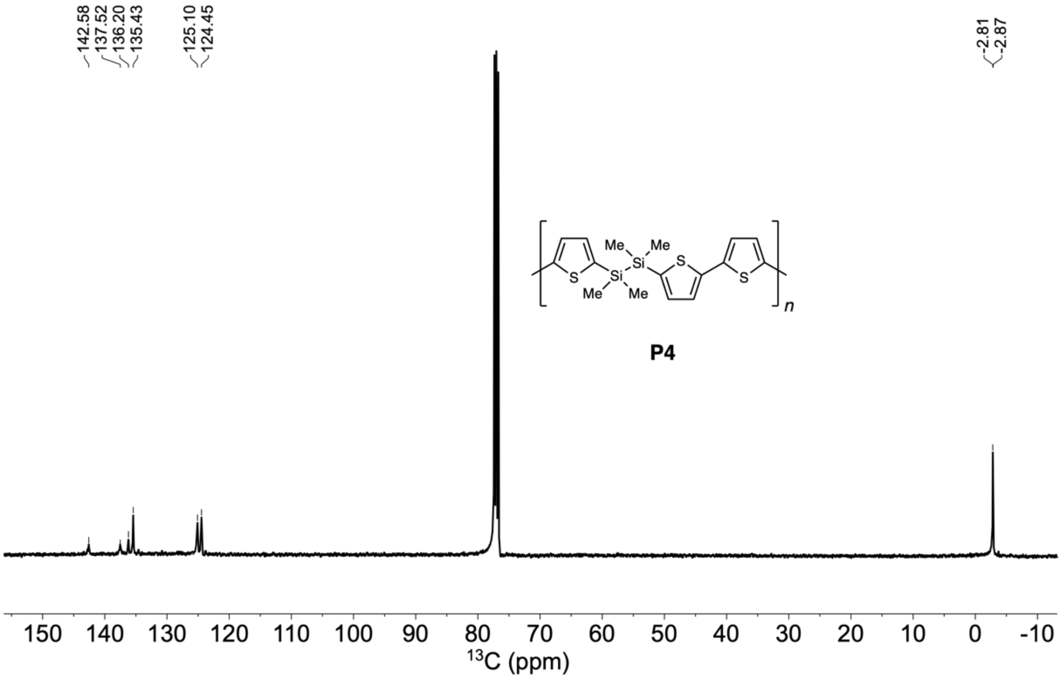


4.3 NMR Spectra of P4.

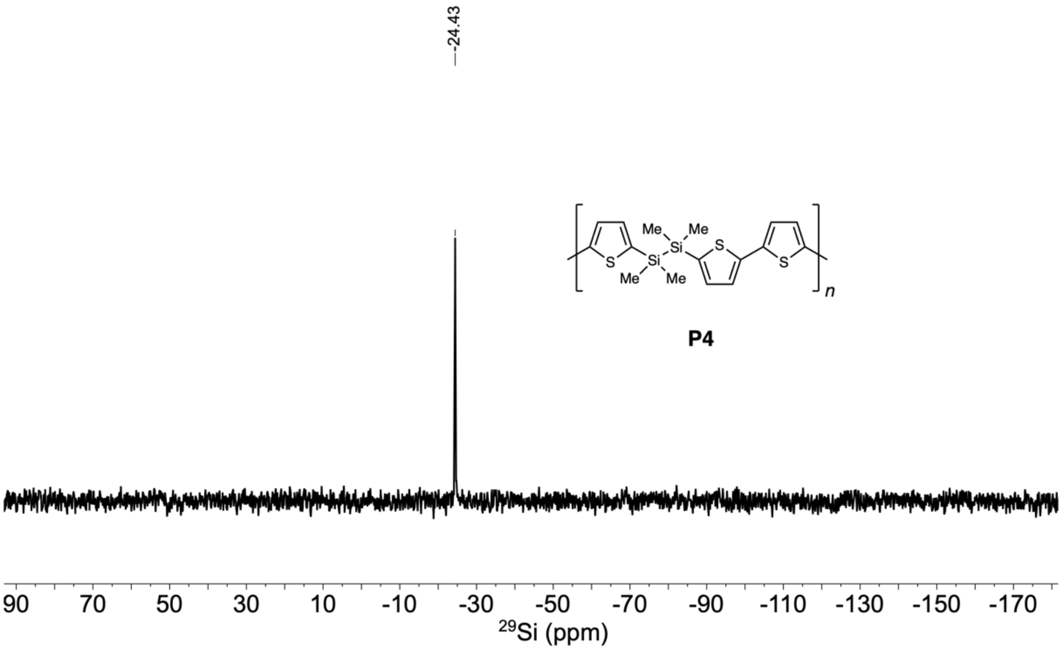
4.3.1 ¹H NMR Spectrum of **P4** (400 MHz, $CDCl_3$).



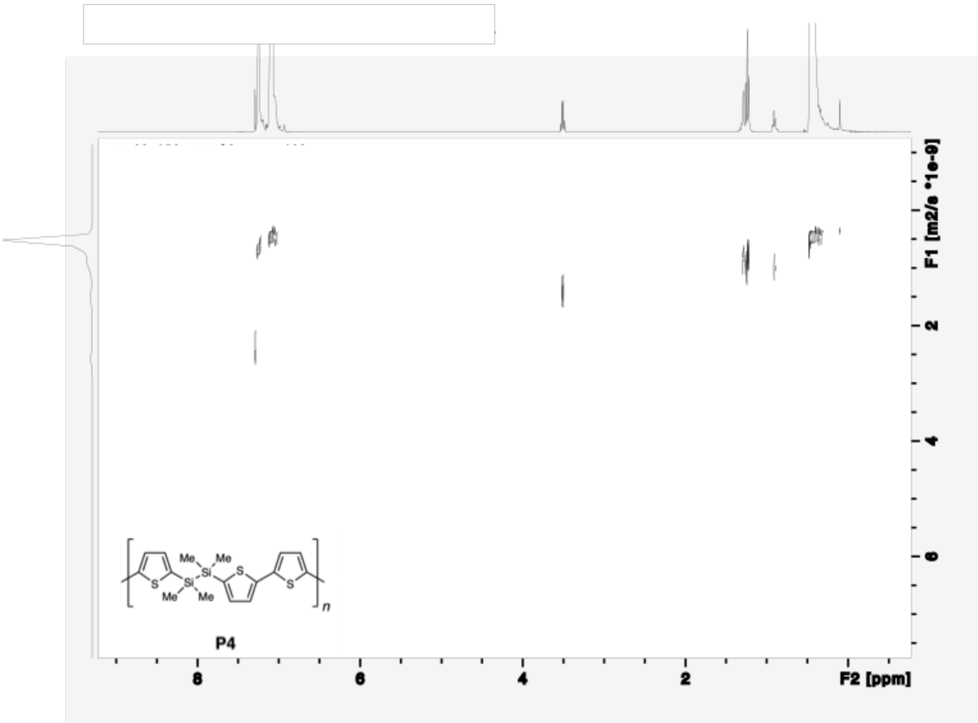
4.3.2 $^{13}C\{^1H\}$ NMR Spectrum of **P4** (101 MHz, $CDCl_3$).



4.3.3 $^{29}Si\{^1H\}$ NMR Spectrum of **P4** (79 MHz, $CDCl_3$). $^1J_{Si\text{-}H}$ = 7 Hz.

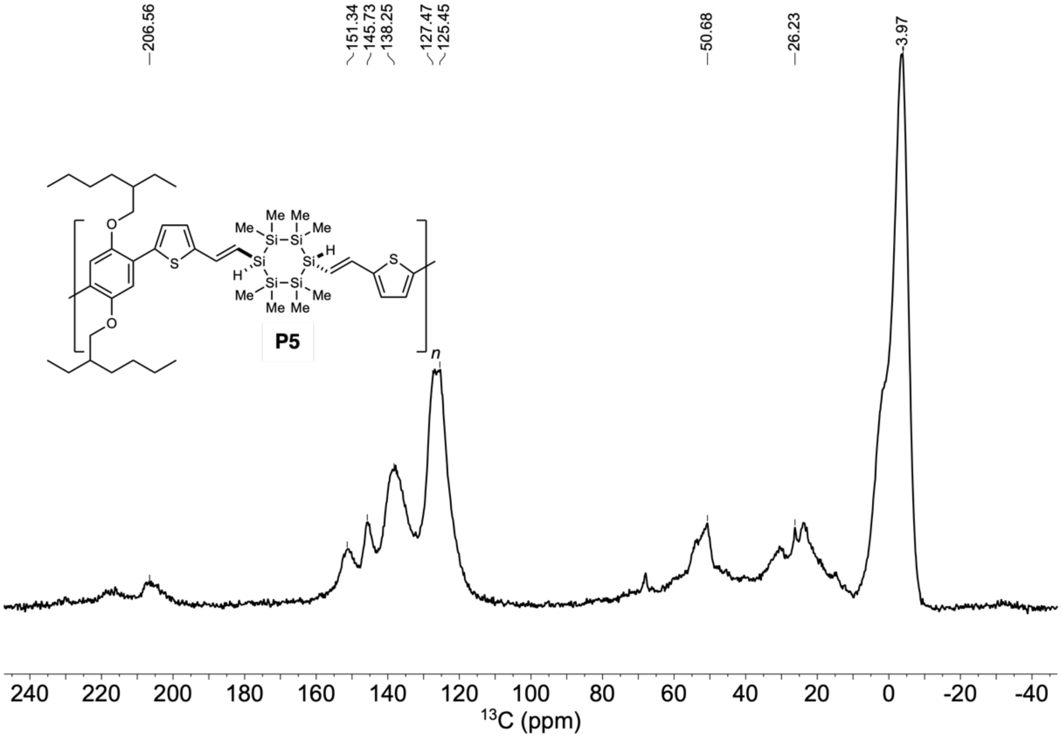


4.3.4 ^1H DOSY Spectrum of **P4** (400 MHz, $CDCl_3$, [**P4**] = 0.5 mg mL^{-1}). D = $5.2x10^{-10}$ m^2s^{-1}, M_w = 81230 Da.

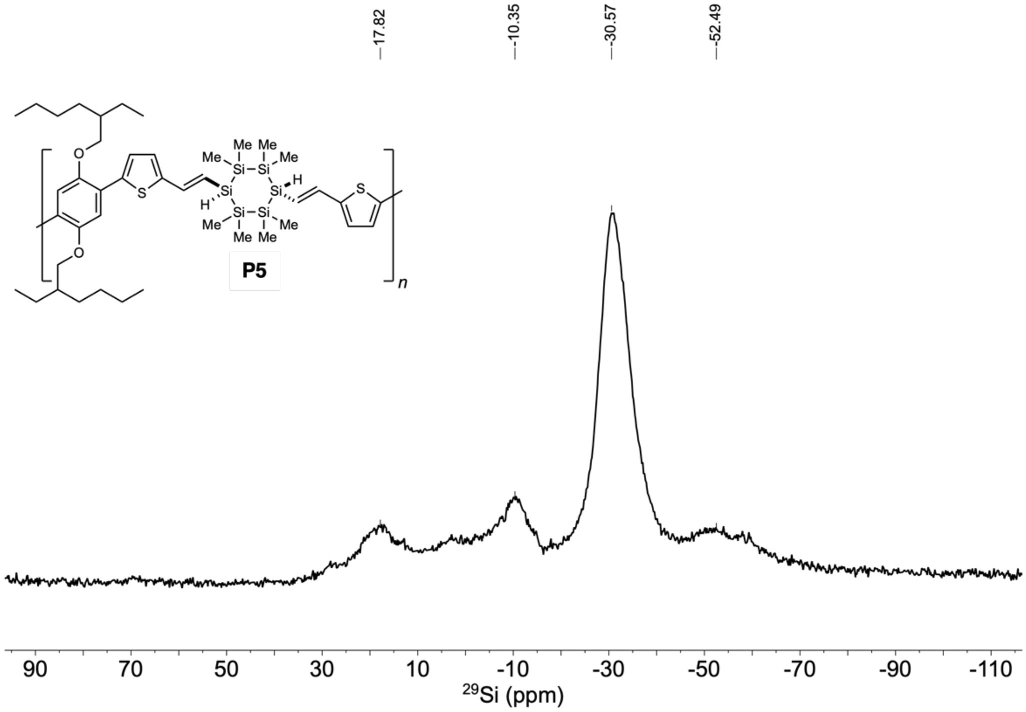


4.4 NMR Spectra of P5.

4.4.1 $^1H \rightarrow ^{13}C$ CPMAS spectrum of **P5** (126 MHz, CPMAS).

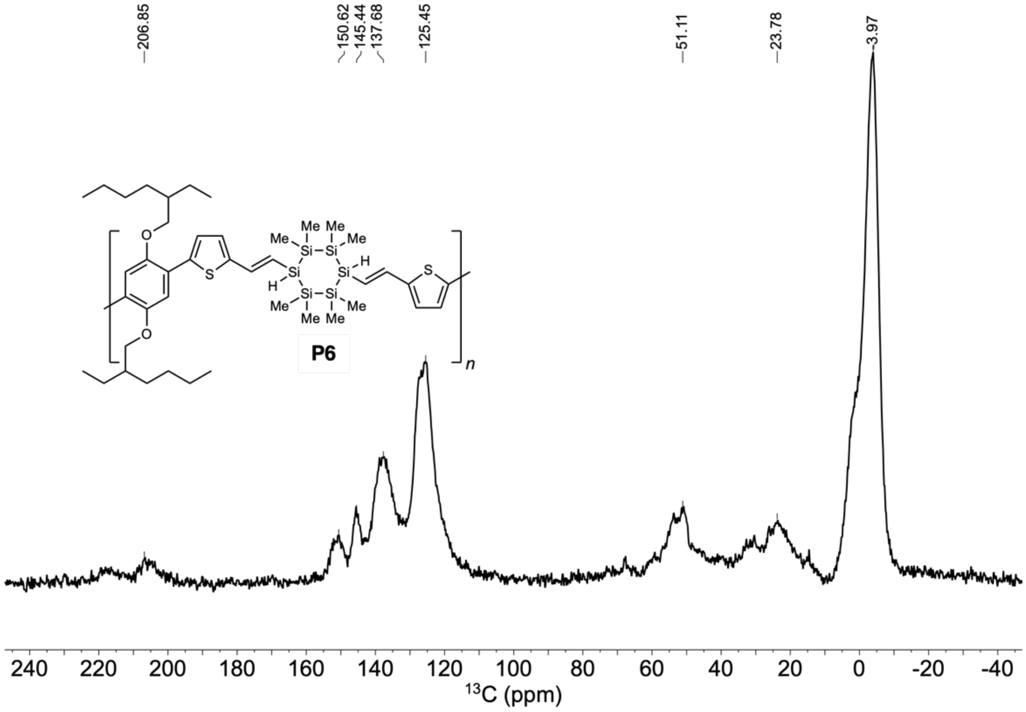


4.4.2 $^1H \rightarrow ^{29}Si$ CPMAS spectrum of **P5** (99 MHz, CPMAS).

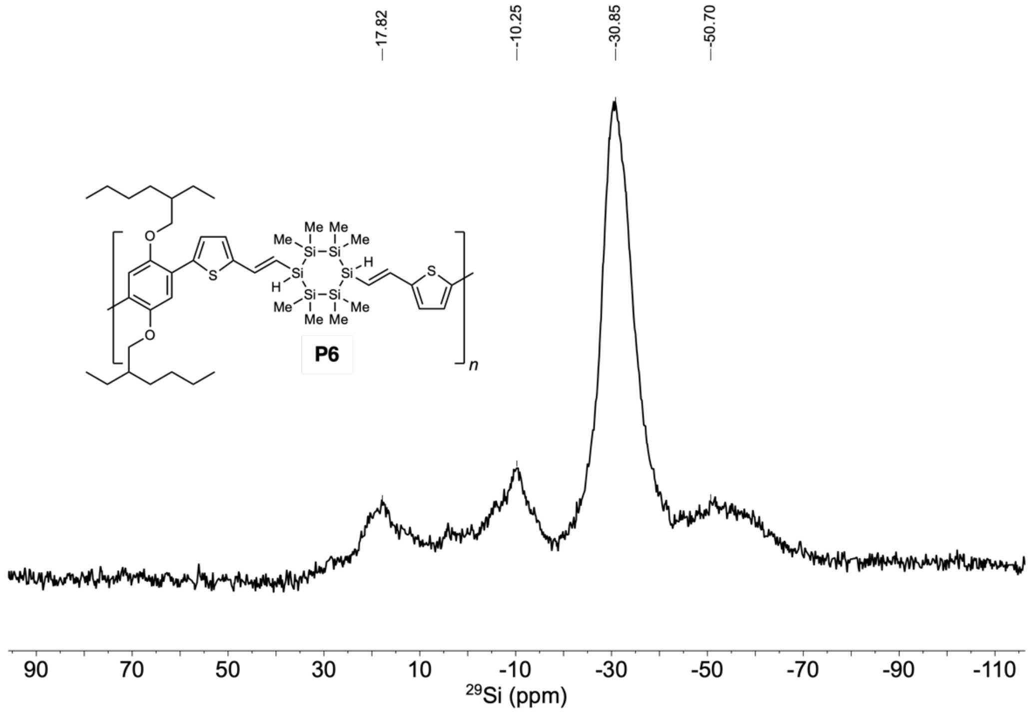


4.5 NMR Spectra of P6.

4.5.1 $^{1}H \rightarrow ^{13}C$ CPMAS spectrum of **P6** (126 MHz, CPMAS).



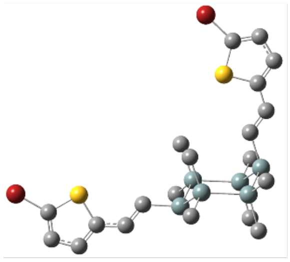
4.5.2 $^{1}H \rightarrow ^{29}Si$ CPMAS spectrum of **P6** (99 MHz, CPMAS).



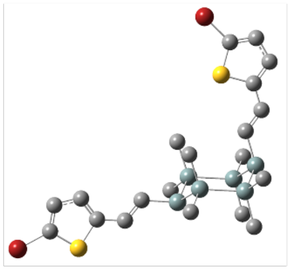
5. Computational Methods and Data

All calculations were performed in Gaussian 16. Geometry optimizations were done using the restricted B3LYP density functional, Grimme's D3 dispersion correction with Becke-Johnson damping, and the 6-311++G(d,p) basis set (B3LYP-D3(BJ)/6-311++G(d,p)). Harmonic frequency calculations were conducted analytically to confirm that optimized geometries had located minima on the potential energy surface. Single-point energies were calculated at the same level of theory for all optimized DFT geometries.

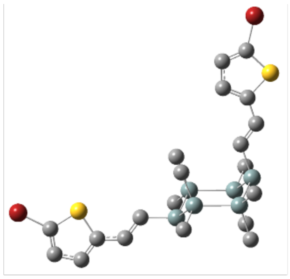
5.1 Rotational isomers of chair conformation *cis*-**1**



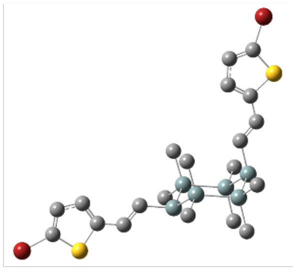
$\Delta\Delta G_{rel}$ = 0.00 kcal·mol^{-1}



$\Delta\Delta G_{rel}$ = +1.58 kcal·mol^{-1}

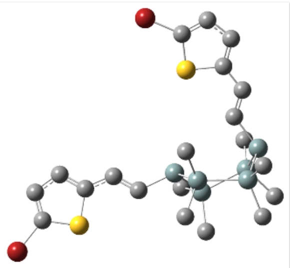


$\Delta\Delta G_{rel}$ = +1.84 kcal·mol^{-1}

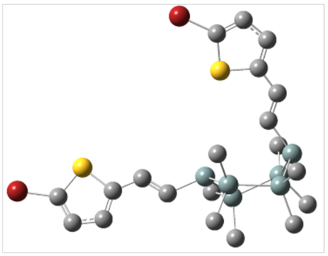


$\Delta\Delta G_{rel}$ = +3.47 kcal·mol^{-1}

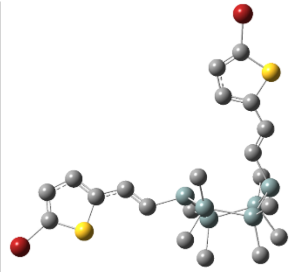
5.2 Rotational isomers of twist boat conformation *cis*-**1**



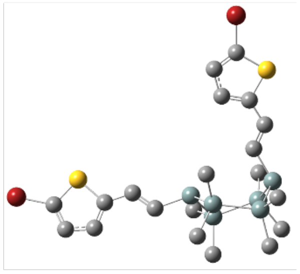
$\Delta\Delta G_{\mathrm{rel}} = +0.51\ \mathrm{kcal{\cdot}mol^{-1}}$



$\Delta\Delta G_{\mathrm{rel}} = +2.16\ \mathrm{kcal{\cdot}mol^{-1}}$

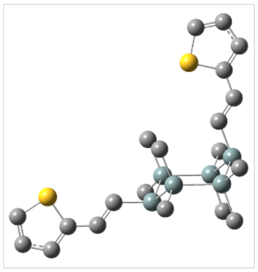


$\Delta\Delta G_{\mathrm{rel}} = +2.38\ \mathrm{kcal{\cdot}mol^{-1}}$

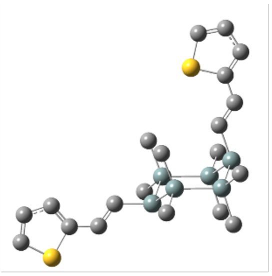


$\Delta\Delta G_{\mathrm{rel}} = +3.99\ \mathrm{kcal{\cdot}mol^{-1}}$

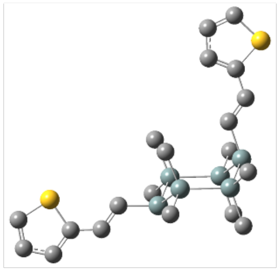
5.3 Rotational isomers of chair conformation H-*cis*-**1**



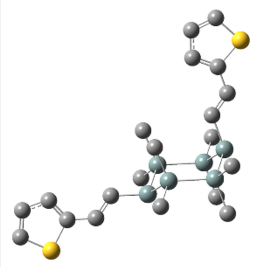
$\Delta\Delta G_{\mathrm{rel}} = 0.00\ \mathrm{kcal{\cdot}mol^{-1}}$



$\Delta\Delta G_{\mathrm{rel}} = +1.40\ \mathrm{kcal{\cdot}mol^{-1}}$

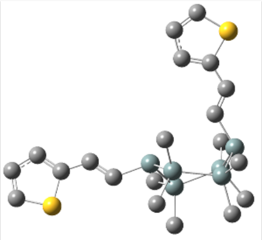


$\Delta\Delta G_{\mathrm{rel}} = +1.58\ \mathrm{kcal{\cdot}mol^{-1}}$

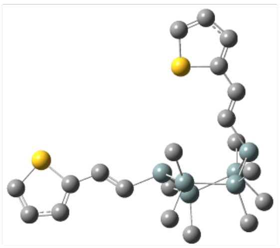


$\Delta\Delta G_{\mathrm{rel}} = +2.98\ \mathrm{kcal{\cdot}mol^{-1}}$

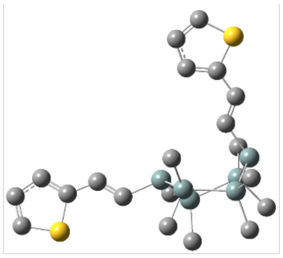
5.4 Rotational isomers of twist boat conformation H-*cis*-**1**



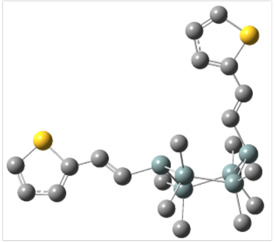
$\Delta\Delta G_{\mathrm{rel}} = +0.69\ \mathrm{kcal{\cdot}mol^{-1}}$



$\Delta\Delta G_{\mathrm{rel}} = +2.03\ \mathrm{kcal{\cdot}mol^{-1}}$



$\Delta\Delta G_{\mathrm{rel}} = +2.18\ \mathrm{kcal{\cdot}mol^{-1}}$



$\Delta\Delta G_{\mathrm{rel}} = +3.52\ \mathrm{kcal{\cdot}mol^{-1}}$

6. References

(1) Jiang, Q.; Gittens, A. F.; Wong, S.; Siegler, M. A.; Klausen, R. S. Highly Selective Addition of Cyclosilanes to Alkynes Enabling New Conjugated Materials. *Chem. Sci.* **2022**, *13* (25), 7587–7593. https://doi.org/10.1039/d2sc01690g.

(2) Wildeman, J.; Herrema, J. K.; Hadziioannou, G.; Schomaker, E. Synthesis of Poly[(Silanylene)Thiophene]S. *J. Inorg. Organomet. Polym.* **1991**, *1* (4), 567–580. https://doi.org/10.1007/BF00683517.