Supporting Information

Highly Selective Addition of Cyclosilanes to Alkynes Enabling New Conjugated Materials

Mr. Q. Jiang, Ms. A. F. Gittens, Ms. S. Wong, Dr. M. A. Siegler, Prof. R. 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. ^{1}H-^{29}Si HSQC NMR spectrum (400 MHz, C_6D_6) of **1a.** $^{1}J_{\text{Si-H}}$ = 120 Hz.

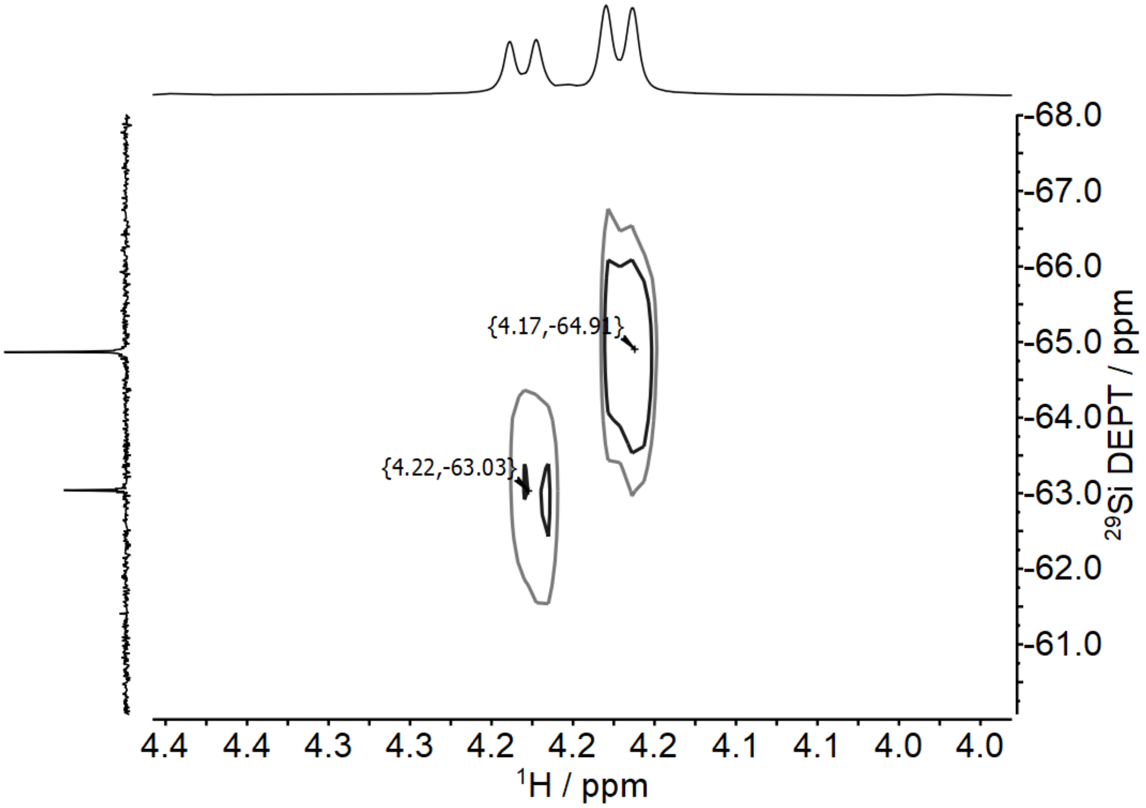


Figure S2. ^{29}Si INEPT+ NMR spectrum (79 MHz, C_6D_6) of *trans*-**1a**. The doublet (δ -64.84, $^{1}J_{\text{SiH}}$ = 169.8 Hz) was assigned to the *Si*H resonance. The experimentally measured coupling constant was consistent with typical one-bond coupling constants between silicon and proton.

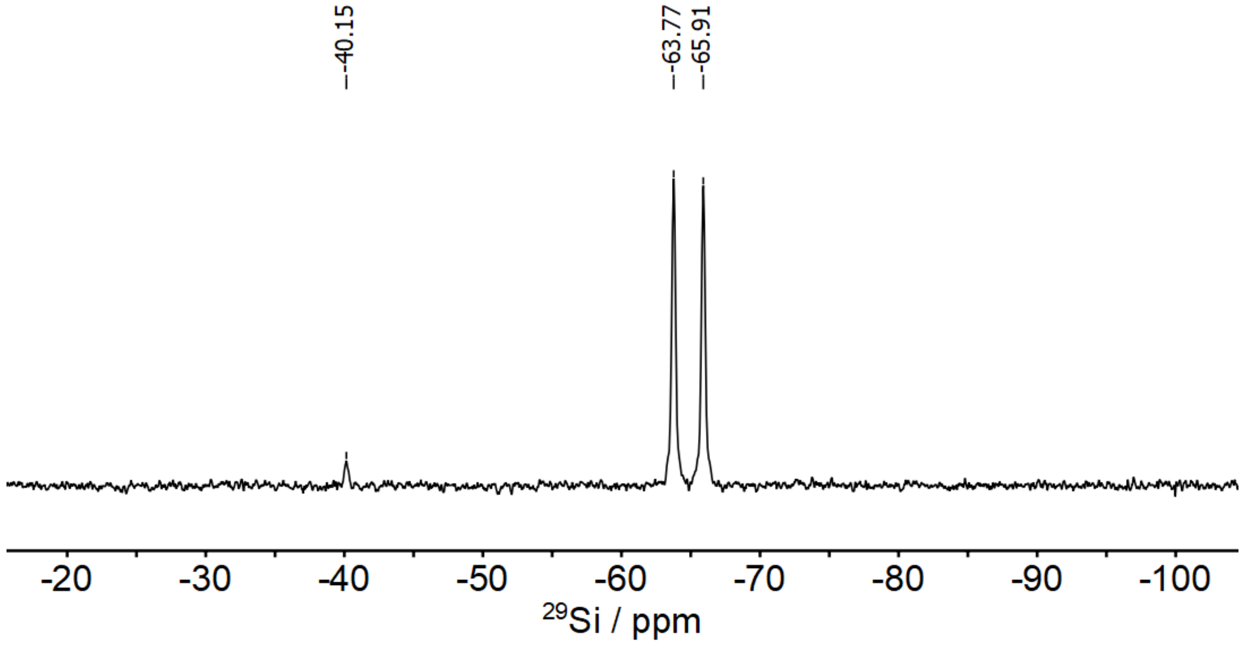


Figure S3. X-ray crystal structure of (a) *trans*-**1e** and (b) *trans*-**1j**. Blue = Si, black = C, pink = H, red = O, yellow = S, brown = Br. Hydrogens on methyl and aromatic groups are omitted for clarity.

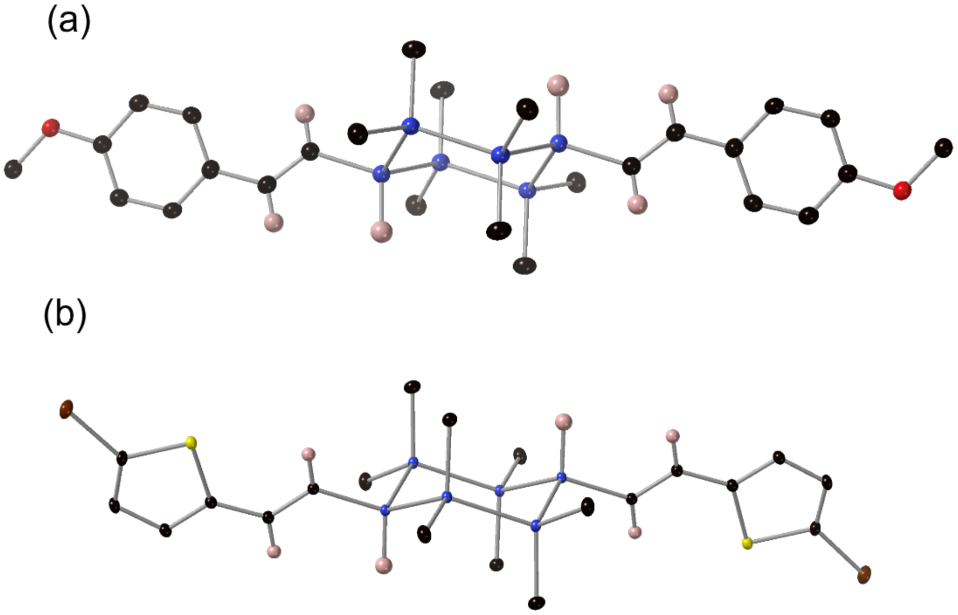


Figure S4. Cropped ^1H NMR spectra (400 MHz, C_6D_6) comparing Si*H* resonances of (top) **3a** and *trans*-$\mathbf{Si_{10}H_4}$ (bottom). Only a single Si*H* resonance was observed for 3a, indicating exclusive formation of a single diastereomer (see Figure 4 X-ray crystal structure for assignment).

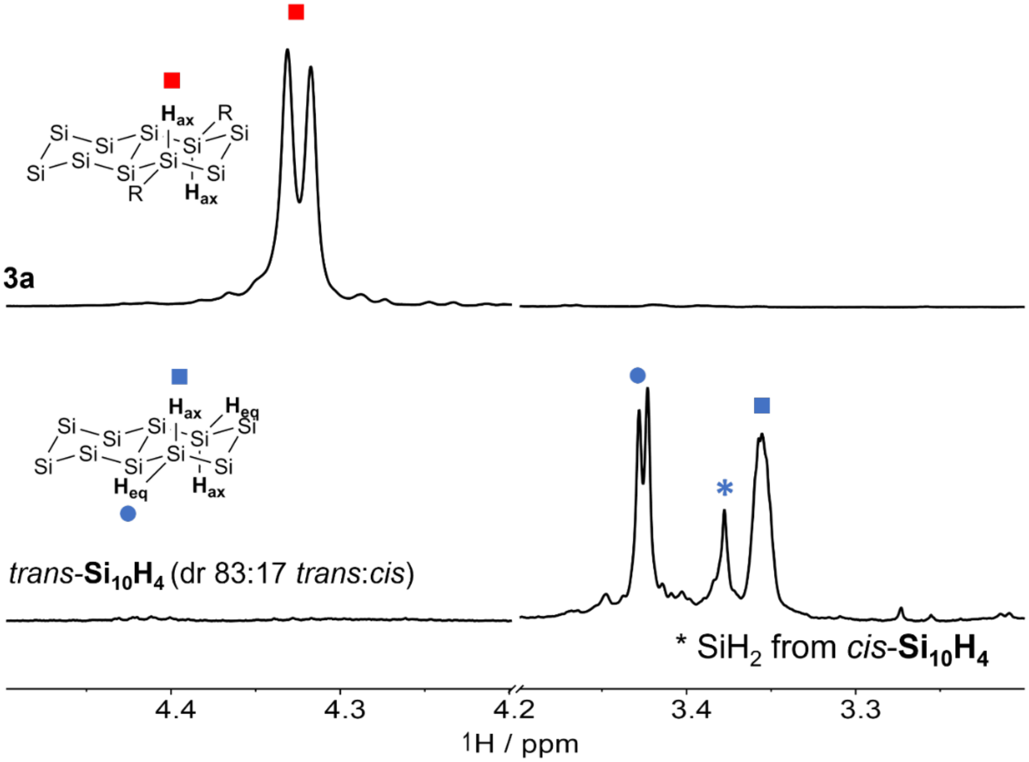


Figure S5. Calculated HOMO/LUMO orbital densities of *trans*-**1a**. B3YLP/6-31G(d). The HOMO is delocalized across both π- and σ-conjugated moieties.

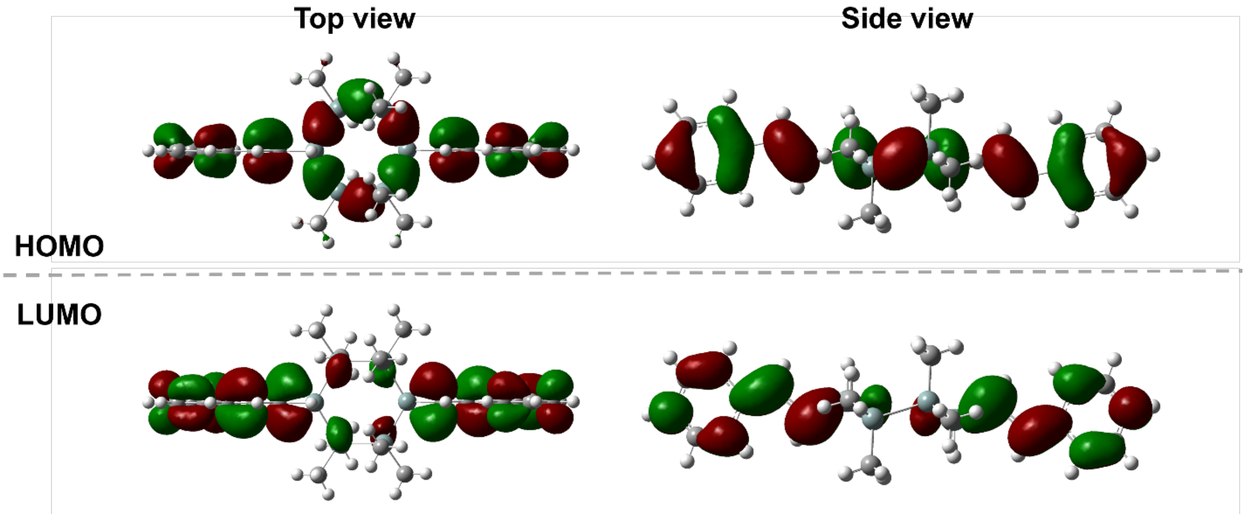


Figure S6. UV-vis Spectra. [compound] = 10^{-5} M, in *n*-pentane. (a) *trans*-**1b**. (b) **1c** (dr 62:38 *trans:cis*). (c) *trans*-**1e**. (d) **1g** (dr 65:35 *trans:cis*). (e) **1h** (dr 60:40 *trans:cis*).

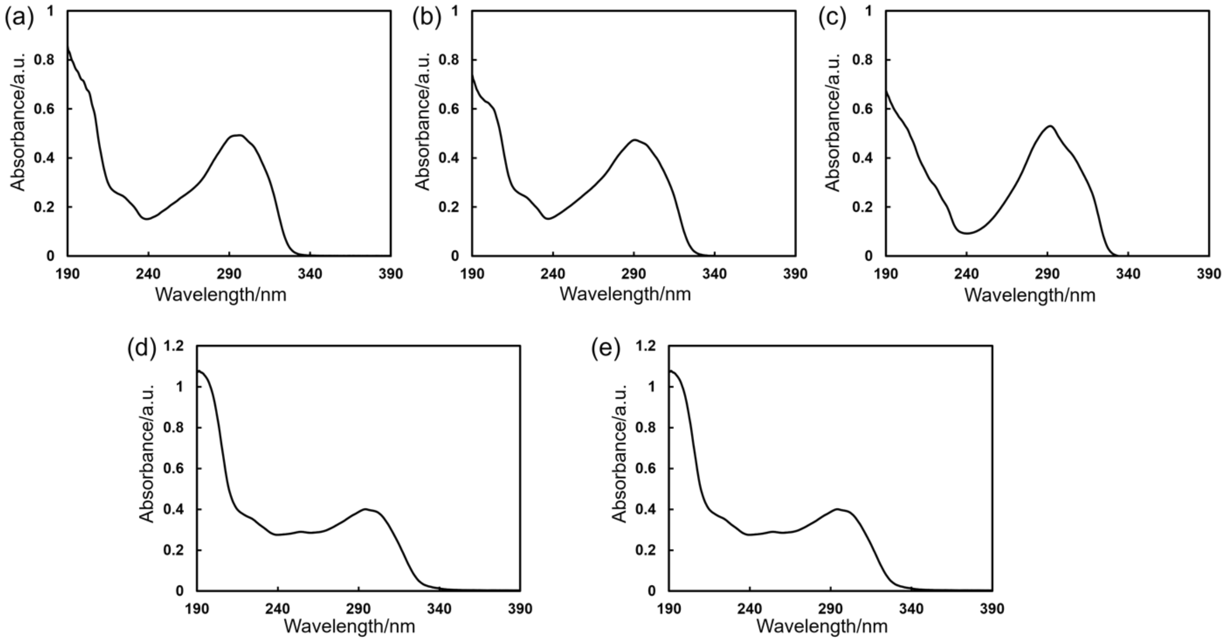
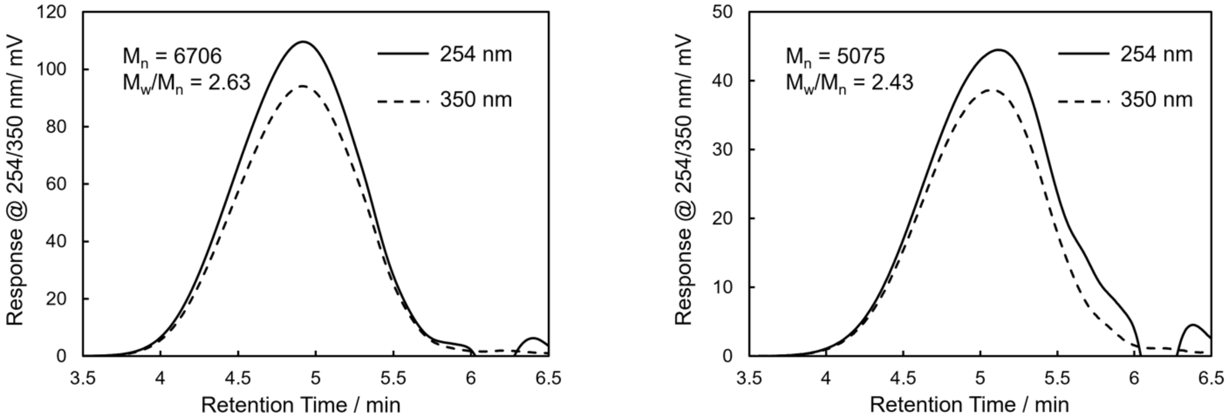


Figure S7. Size exclusion chromatograms of **P1 and P2** at 254 nm (solid line) and 350 nm (dotted line). Molecular weight determined relative to polystyrene standards at 254 nm (THF, [**P1**] or [**P2**] = 0.5 mg mL^{-1}, 40 °C, 0.35 mL min^{-1}, 10 µL injection)



2. General Information

General Experimental Procedures

All experiments were performed under protection of dry nitrogen or 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), pentane (Fisher, certified ACS), 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) ($NiCl_2dppp$), 1-chloro-4-ethynylbenzene, 4-ethynyl-N,N-dimethylaniline, 4-ethynylanisole, 1-ethynyl-4-(trifluoromethyl)benzene, methyl 4-ethynylbenzoate, isopropylmagnesium chloride (2.0M in THF), triphenylphosphine, 2-bromothiophene and 2,5-dibromothiophene were purchased from Sigma Aldrich. Tetrafunctional silanes (**1,4Si$_6$**[1], **1,3Si$_6$**[2] and *trans*-**Si$_{10}$H$_4$**[3]) and acetylenes (4-ethynylthioanisole[4], 4-ethynylbromobenzene[5] and 2-bromo-5-ethynylthiophene[6]) were prepared by adaptation of literature procedures.

Instrumentation

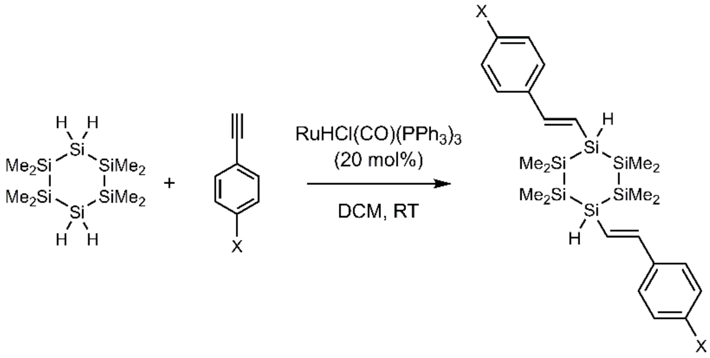
^1H NMR, $^{13}C\{^1H\}$ NMR, $^{19}F\{^1H\}$ NMR and $^{29}Si\{^1H\}$ NMR spectra were recorded on either a Bruker Avance 300, 400 or III HD 400 MHz Spectrometer and chemical shifts are reported in parts per million (ppm). Spectra were recorded in benzene-d$_6$ or chloroform-d$_1$ with the residual solvent peak as the internal standard (^1H NMR: C_6H_6 δ = 7.16; $CHCl_3$ δ = 7.26, ^{13}C NMR: C_6H_6 δ 128.06; $CHCl_3$ δ = 77.16). Chemical shifts of $^{19}F\{^1H\}$ NMR spectra were calibrated by 0.05% trifluorotoluene in C_6D_6. Chemical shifts of $^{29}Si\{^1H\}$ NMR spectra were calibrated by tris(Me_3Si)methane in $CDCl_3$, doped $Cr(acac)_3$. 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.

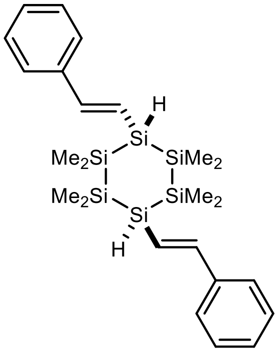
All column chromatography was performed on a Teledyne ISCO Combiflash Rf+ using Redisep Rf silica columns. Fourier transformed infrared (FTIR) spectroscopy was performed on a Thermo NicoletNexus 670 FTIR spectrometer. Mass spectrometry and high-resolution mass spectrometry were performed in the Department 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 254 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 Hydrosilation of acetylenes with 1,4Si$_6$



3.1.1 Synthesis of **1a**



In a glove box, an oven-dried scintillation vial with stir bar was charged with **1,4Si$_6$** (1.0 equiv., 1.71 mmol, 0.500 g) and RuHCl(CO)(PPh$_3$)$_3$ (0.2 equiv., 0.342 mmol, 0.325 g). DCM (10 mL) was added to dissolve the reagents. Phenylacetylene (2.5 equiv., 4.27 mmol, 0.47 mL) was added dropwise by syringe. After the addition was complete, the reaction mixture turned dark red and was stirred for 2 hours at room temperature. The solution was concentrated under vacuum, transferred to a silica gel cartridge, and then dried on it under vacuum. The cartridge was subjected to automated column chromatography with 100% hexanes to yield **1a** (dr 65:35 *trans:cis*) as a white solid (0.756 g, 89%).

Isolation of *trans*-**1a**: In a scintillation vial, 0.500 g of **1a** (dr 65:35 *trans:cis*) was dissolved in 3 mL of DCM and layered with 17 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*-**1a** (0.249 g, 77%) was collected as a colorless crystal. X-ray quality crystals were grown by liquid-liquid diffusion using THF as the solvent and methanol as the antisolvent.

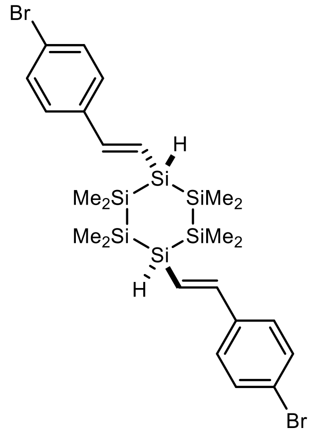
Enrichment of *cis*-**1a**: The filtrate was dried under vacuum yielding a white solid. The solid was determined as enriched *cis*-**1a** (dr 25:75 *trans:cis*) through ^{1}H NMR spectroscopy.

*Tabulated Characterization Data for **1a***

δ_H (400 MHz, C_6D_6)	*trans*-**1a**: 7.36 – 7.32 (m, 4H, Ar*H*), 7.25 (d, *J* = 18.8 Hz, 2H, vinyl), 7.15 – 7.09 (m, 4H, Ar*H*), 7.08 - 7.06 (m, 2H, Ar*H*), 6.63 (dd, *J* =

	18.7, 5.2 Hz, 2H, vinyl), 4.18 (d, *J* = 5.2 Hz, 2H, Si*H*), 0.42 (s, 12H, -C*H*$_3$), 0.39 (s, 12H, -C*H*$_3$). *cis*-**1a**: 7.36 – 7.32 (m, 4H, Ar*H*), 7.23 (d, *J* = 18.8 Hz, 2H, vinyl), 7.15 – 7.09 (m, 4H, Ar*H*), 7.08 - 7.06 (m, 2H, Ar*H*), 6.61 (dd, *J* = 18.7, 5.2 Hz, 2H, vinyl), 4.23 (d, *J* = 5.2 Hz, 2H, Si*H*), 0.42 (s, 12H, -C*H*$_3$), 0.38 (s, 12H, -C*H*$_3$).
δ_C (101 MHz, C_6D_6)	*trans*-**1a**: 147.62 (vinyl), 138.90 (*Ar*), 128.93 (*Ar*), 126.70 (*Ar*), 119.98 (vinyl), -4.54 (-*C*H$_3$), -4.56 (-*C*H$_3$). *cis*-**1a:** 147.68 (vinyl), 138.87 (*Ar*), 128.95 (*Ar*), 126.65 (*Ar*), 120.37 (vinyl), -4.28 (-*C*H$_3$), -4.43 (-*C*H$_3$).
δ_{Si} (79 MHz, C_6D_6)	*trans*-**1a**: -40.17 (*Si*Me$_2$), -64.88 (*Si*H). *cis*-**1a**: -40.36 (*Si*Me$_2$), -63.04 (*Si*H).
HRMS	Calcd. for $C_{24}H_{40}Si_6$: 496.1746. Found: 496.1738.
IR (cm^{-1})	2084 (SiH).
λ_{max} (pentane) /nm	*trans*-**1a**: 286 (*ε*/dm^3 mol^{-1} cm^{-1} 51900) *cis*-**1a**: 285 (*ε*/dm^3 mol^{-1} cm^{-1} 42400)

3.1.2 Synthesis of **1b**



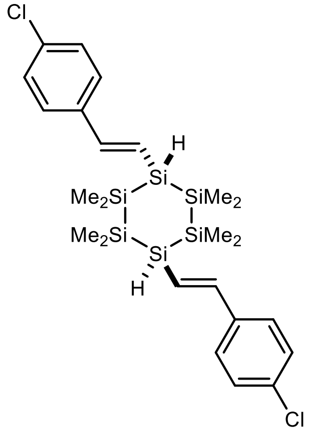
In a glove box, an oven-dried 2-dram vial with stir bar was charged with **1,4Si$_6$** (1.0 equiv., 0.342 mmol, 0.100 g) and RuHCl(CO)(PPh$_3$)$_3$ (0.2 equiv., 0.068 mmol, 0.0651 g). DCM (1 mL) was added to dissolve the reagents. 4-ethynylbromobenzene (2.5 equiv., 0.854 mmol, 0.155 g) was dissolved by 0.5 mL of DCM in a 1-dram vial and added dropwise into the reaction mixture by pipette. The vial was rinsed by 0.5 mL of DCM and the solution was added to the reaction as well. After the addition was complete, the reaction mixture turned dark red and was stirred for 2 hours at room temperature. The solution was transferred to a silica gel cartridge, and then dried on it under vacuum. The cartridge was subjected to automated column chromatography with 100% hexanes to yield **1b** (dr 65:35 *trans:cis*) as a white solid (0.179 g, 80%).

Isolation of *trans*-**1b**: In a scintillation vial, 0.500 g of **1a** (dr 65:35 *trans:cis*) was dissolved in 3 mL of DCM and layered with 17 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*-**1b** (0.233 g, 72%) was collected as a colorless crystal.

*Tabulated Characterization Data for **1b***

δ_H (400 MHz, C_6D_6)	*trans*-**1b**: 7.22 (t, *J* = 8.5 Hz, 4H, Ar*H*), 7.01 (d, *J* = 18.7 Hz, 2H, vinyl), 6.93 (d, *J* = 8.5 Hz, 4H, Ar*H*), 6.50 (dd, *J* = 18.7, 5.2 Hz, 2H, vinyl), 4.11 (d, *J* = 5.2 Hz, 2H, Si*H*), 0.4 (s, 12H, -C*H*$_3$), 0.38 (s, 12H, -C*H*$_3$). *cis*-**1b**: 7.22 (t, *J* = 8.5 Hz, 4H, Ar*H*), 7.03 (d, *J* = 18.7 Hz, 2H, vinyl), 6.93 (d, *J* = 8.5 Hz, 4H, Ar*H*), 6.48 (dd, *J* = 18.7, 5.2 Hz, 2H, vinyl), 4.11 (d, *J* = 5.2 Hz, 2H, Si*H*), 0.40 (s, 3H, -C*H*$_3$), 0.37 (s, 3H, -C*H*$_3$).
δ_C (101 MHz, C_6D_6)	*trans*-**1b**: 146.11 (vinyl), 137.55 (*Ar*), 132.05 (*Ar*), 122.24 (*Ar*), 121.19 (vinyl), -4.58 (-*C*H$_3$), -4.59 (-*C*H$_3$). *cis*-**1b:** 146.19 (vinyl), 137.49 (*Ar*), 132.08 (*Ar*), 122.29 (*Ar*), 121.59 (vinyl), -4.28 (-*C*H$_3$), -4.43 (-*C*H$_3$).
δ_{Si} (79 MHz, C_6D_6)	*trans*-**1b**: -40.10 (*Si*Me$_2$), -64.84 (*Si*H). *cis*-**1b**: -40.41 (*Si*Me$_2$), -63.00 (*Si*H).
HRMS	Calcd. for $C_{24}H_{38}Br_2Si_6$: 651.9956. Found: 651.9965.
IR (cm^{-1})	2068 (SiH).
λ_{max} (pentane) /nm	*trans*-**1b**: 296 (ε/dm^3 mol^{-1} cm^{-1} 49300)

3.1.3 Synthesis of **1c**

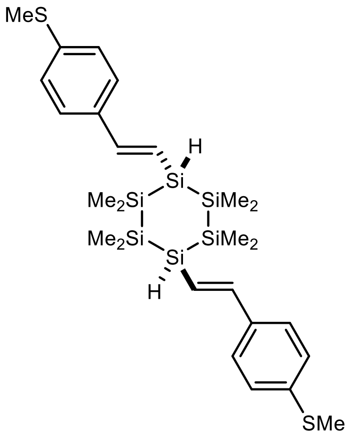


In a glove box, an oven-dried scintillation vial with stir bar was charged with **1,4Si$_6$** (1.0 equiv., 0.342 mmol, 0.100 g) and RuHCl(CO)(PPh$_3$)$_3$ (0.2 equiv., 0.068 mmol, 0.0651 g). DCM (1 mL) was added to dissolve the reagents. 4-ethynylchlorobenzene (2.5 equiv., 0.854 mmol, 0.117 g) was dissolved by 0.5 mL of DCM in a 1-dram vial and added dropwise into the reaction mixture by pipette. The vial was rinsed by 0.5 mL of DCM and the solution was added to the reaction as well. After the addition was complete, the reaction mixture turned dark red and was stirred for 2 hours at room temperature. The solution was transferred to a silica gel cartridge, and then dried on it under vacuum. The cartridge was subjected to automated column chromatography with 100% hexanes to yield **1c** (dr 62:38 *trans:cis*) as a white solid (0.145 g, 75%).

*Tabulated Characterization Data for **1c***

δ_H (400 MHz, C_6D_6)	*trans*-**1c**: 7.10 – 7.03 (m, 6H, Ar*H* and vinyl), 7.03 – 6.97 (m, 4H, Ar*H*), 6.49 (dd, *J* = 18.7, 5.2 Hz, 2H, vinyl), 4.13 (d, *J* = 5.2 Hz, 2H, Si*H*), 0.41 (s, 12H, -C*H*$_3$), 0.39 (s, 12H, -C*H*$_3$). *cis*-**1c**: 7.10 – 7.03 (m, 6H, Ar*H* and vinyl), 7.03 – 6.97 (m, 4H, Ar*H*), 6.47 (dd, *J* = 18.7, 5.2 Hz, 2H, vinyl), 4.18 (d, *J* = 5.2 Hz, 2H, Si*H*), 0.40 (s, 12H, -C*H*$_3$), 0.38 (s, 12H, -C*H*$_3$).
δ_C (101 MHz, C_6D_6)	*trans*-**1c**: 146.05 (vinyl), 137.17 (*Ar*), 134.00 (*Ar*), 129.12 (*Ar*), 129.09 (vinyl), -4.57 (-*C*H$_3$), -4.59 (-*C*H$_3$). *cis*-**1c:** 146.05 (vinyl), 137.17 (*Ar*), 134.00 (*Ar*), 129.09 (*Ar*), 120.99 (vinyl), -4.28 (-*C*H$_3$), -4.43 (-*C*H$_3$).
δ_{Si} (79 MHz, C_6D_6)	*trans*-**1c**: -40.09 (*Si*Me$_2$), -64.93 (*Si*H). *cis*-**1c**: -40.39 (*Si*Me$_2$), -63.06 (*Si*H).
HRMS	Calcd. for $C_{24}H_{40}Si_6$: 568.0907. Found: 568.0932.
IR (cm^{-1})	2061 (SiH).
λ_{max} (pentane) /nm	290 (ε/dm^3 mol^{-1} cm^{-1} 47400)

3.1.4 Synthesis of **1d**

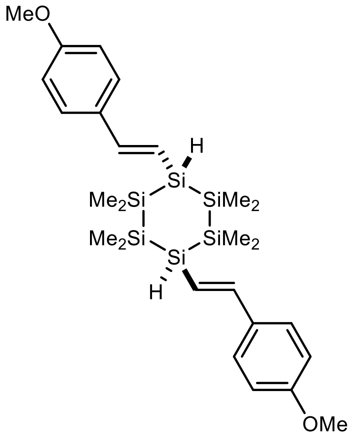


In a glove box, an oven-dried scintillation vial with stir bar was charged with **1,4Si$_6$** (1.0 equiv., 0.342 mmol, 0.100 g) and RuHCl(CO)(PPh$_3$)$_3$ (0.2 equiv., 0.068 mmol, 0.0651 g). DCM (1 mL) was added to dissolve the reagents. 4-ethynylmethylthiobenzene (2.5 equiv., 0.854 mmol, 0.127 g) was dissolved by 0.5 mL of DCM in a 1-dram vial and added dropwise into the reaction mixture by pipette. The vial was rinsed by 0.5 mL of DCM and the solution was added to the reaction as well. After the addition was complete, the reaction mixture turned dark red and was stirred for 2 hours at room temperature. The solution was transferred to a silica gel cartridge, and then dried on it under vacuum. The cartridge was subjected to automated column chromatography with 95% hexanes/5% ethyl acetate to yield **1d** (dr 66:34 *trans:cis*) as a white solid (0.167 g, 83%).

*Tabulated Characterization Data for **1d***

δ_H (400 MHz, C_6D_6)	*trans*-**1d**: 7.24 – 7.17 (m, 6H, Ar*H* and vinyl), 7.07 (d*, J* = 8.5 Hz, 4H, Ar*H*), 6.57 (dd*, J* = 18.7, 5.2 Hz, 2H, vinyl), 4.20 (d, J=5.2 Hz, 2H, Si*H*), 1.98 (s, 6H, -S*Me*), 0.44 (d*, J* = 0.5 Hz, 12H, -C*H*$_3$), 0.41 (s, 12H, -C*H*$_3$).
	cis-**1d**: 7.24 – 7.17 (m, 6H, Ar*H* and vinyl), 7.04 (d*, J* = 8.5 Hz, 4H, Ar*H*), 6.55 (dd*, J* = 18.7, 5.2 Hz, 2H, vinyl), 4.24 (d*, J* = 5.2 Hz, 2H, Si*H*), 1.98 (s, 6H, -S*Me*), 0.45 (s, 12H, -C*H*$_3$), 0.40 (s, 12H, -C*H*$_3$).
δ_C (101 MHz, C_6D_6)	*trans*-**1d**: 146.95 (vinyl), 139.26 (*Ar*), 135.74 (*Ar*), 128.87 (*Ar*), 127.11 (*Ar*), 126.88 (*Ar*), 118.98 (vinyl), 15.31 (-S*Me*), -4.50 (-*C*H$_3$), -4.52 (-*C*H$_3$).
	cis-**1d:** 147.03 (vinyl), 139.30 (*Ar*), 135.65 (*Ar*), 128.79 (*Ar*), 127.06 (*Ar*), 126.84 (*Ar*), 119.38 (vinyl), 15.26 (-S*Me*), -4.22 (-*C*H$_3$), -4.36 (-*C*H$_3$).
δ_{Si} (79 MHz, C_6D_6)	*trans*-**1d**: -40.15 (*Si*Me$_2$), -64.74 (*Si*H).
	cis-**1d**: -40.50 (*Si*Me$_2$), -62.87 (*Si*H).
HRMS	Calcd. for $C_{26}H_{44}S_2Si_6$: 588.1500. Found: 588.1492.
IR (cm^{-1})	2077 (SiH).

3.1.5 Synthesis of **1e**



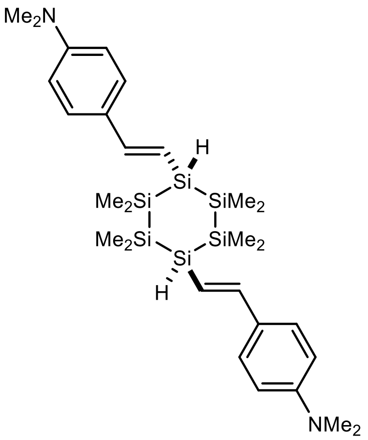
In a glove box, an oven-dried scintillation vial with stir bar was charged with **1,4Si$_6$** (1.0 equiv., 0.342 mmol, 0.100 g) and RuHCl(CO)(PPh$_3$)$_3$ (0.2 equiv., 0.068 mmol, 0.0651 g). DCM (2 mL) was added to dissolve the reagents. 4-ethynylanisole (2.5 equiv., 0.854 mmol, 0.11 mL) was added dropwise into the reaction mixture by syringe. After the addition was complete, the reaction mixture turned dark red and was stirred for 2 hours at room temperature. The solution was transferred to a silica gel cartridge, and then dried on it under vacuum. The cartridge was subjected to automated column chromatography with 90% hexanes/10% ethyl acetate to yield **1e** (dr 63:37 *trans:cis*) as a white solid (0.156 g, 82%). X-ray quality crystals were grown by liquid-liquid diffusion using THF as the solvent and methanol as the antisolvent.

*Tabulated Characterization Data for **1e***

δ_H (400 MHz, C_6D_6)	*trans*-**1e**: 7.42 –7.29 (m, 2H, Ar*H*), 7.25 (d*, J* = 18.7 Hz, 2H, vinyl), 7.08 – 7.01 (m, 2H, Ar*H*), 6.73 (t*, J* = 8.9 Hz, 4H, Ar*H*), 6.49 (dd*, J*

	= 18.7, 5.2 Hz, 2H, vinyl), 4.22 (d, *J* = 5.2 Hz, 2H, Si*H*), 3.28 (s, 6H, -O*Me*), 0.46 (s, 12H, -C*H*$_3$), 0.43 (s, 12H, -C*H*$_3$).
	cis-**1e**: 7.42 –7.29 (m, 2H, Ar*H*), 7.24 (d, *J* = 18.7 Hz, 2H, vinyl), 7.08 – 7.01 (m, 2H, Ar*H*), 6.73 (t, *J* = 8.9 Hz, 4H, Ar*H*), 6.47 (dd, *J* = 18.7, 5.2 Hz, 2H, vinyl), 4.27 (d, *J* = 5.2 Hz, 2H, Si*H*), 3.28 (s, 6H, -O*Me*), 0.47 (s, 12H, -C*H*$_3$), 0.41 (s, 12H, -C*H*$_3$).
δ_C (101 MHz, C_6D_6)	*trans*-**1e**: 160.25 (vinyl), 147.18 (*Ar*), 132.03 (*Ar*), 128.86 (*Ar*), 127.98 (*Ar*), 116.61(*Ar*), 114.40 (vinyl), 54.83 (-O*Me*), -4.46 (-*C*H$_3$), -4.49 (-*C*H$_3$).
	cis-**1e:** 160.25 (vinyl), 147.18 (*Ar*), 131.97 (*Ar*), 128.79 (*Ar*), 127.94 (*Ar*), 117.02 (*Ar*), 114.42 (vinyl), 54.81 (-O*Me*), -4.19 (-*C*H$_3$), -4.34 (-*C*H$_3$).
δ_{Si} (79 MHz, C_6D_6)	*trans*-**1e**: -40.24 (*Si*Me$_2$), -64.84 (*Si*H).
	cis-**1e**: -40.46 (*Si*Me$_2$), -63.01(*Si*H).
HRMS	Calcd. for $C_{26}H_{44}O_2Si_6$: 556.1957. Found: 556.1966.
IR (cm^{-1})	2064 (SiH).
λ_{max} (pentane) /nm	*trans*-**1e**: 292 (ε/dm^3 mol^{-1} cm^{-1} 53000)

3.1.6 Synthesis of **1f**

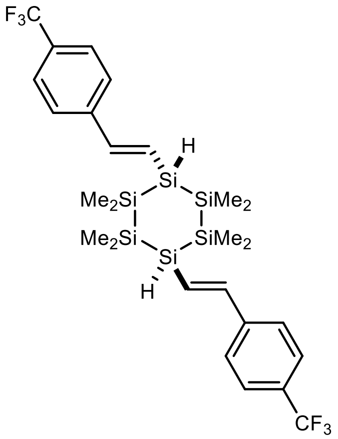


In a glove box, an oven-dried scintillation vial with stir bar was charged with **1,4Si$_6$** (1.0 equiv., 0.342 mmol, 0.100 g) and RuHCl(CO)(PPh$_3$)$_3$ (0.2 equiv., 0.068 mmol, 0.0651 g). DCM (1 mL) was added to dissolve the reagents. 4-ethynyl-N,N-dimethylanilline (2.5 equiv., 0.854 mmol, 0.124 g) was dissolved by 0.5 mL of DCM in a 1-dram vial and added dropwise into the reaction mixture by pipette. The vial was rinsed by 0.5 mL of DCM and the solution was added to the reaction as well. After the addition was complete, the reaction mixture turned dark red and was stirred for 2 hours at room temperature. The solution was transferred to a silica gel cartridge, and then dried on it under vacuum. The cartridge was subjected to automated column chromatography with 85% hexanes/15% ethyl acetate to yield **1f** (dr 62:38 *trans:cis*) as a white solid (0.137 g, 69%). The NMRs were collected at 50 ˚C for the poor solubility of the *trans* isomer at room temperature.

*Tabulated Characterization Data for **1f***

δ_H (400 MHz, C_6D_6)	*trans*-**1f**: 7.44 – 7.37 (m, 4H, Ar*H*), 7.30 (d, *J* = 18.6 Hz, 2H, vinyl), 6.53 (t, *J* = 8.3 Hz, 4H, Ar*H*), 6.44 (dd, *J* = 18.6, 5.2 Hz, 2H, vinyl), 4.25 (d, *J* = 5.2 Hz, 2H, Si*H*), 2.52 (s, 12H, -N*Me*$_2$), 0.47 (s, 12H, -C*H*$_3$), 0.45 (s, 12H, -C*H*$_3$). *cis*-**1f**: 7.44 – 7.37 (m, 4H, Ar*H*), 7.28 (d, *J* = 18.6 Hz, 2H, vinyl), 6.53 (t, *J* = 8.3 Hz, 4H, Ar*H*), 6.43 (dd, *J* = 18.6, 5.2 Hz, 2H, vinyl), 4.28 (d, *J* = 5.2 Hz, 2H, Si*H*), 2.52 (s, 12H, -N*Me*$_2$), 0.50 (s, 12H, -C*H*$_3$), 0.43 (s, 12H, -C*H*$_3$).
δ_C (101 MHz, C_6D_6)	*trans*-**1f**: 150.34 (vinyl), 147.57 (*Ar*), 113.30 (*Ar*), 112.88 (*Ar*), 112.29 (vinyl), 39.64 (-N*Me*$_2$), -4.77 (-*C*H$_3$), -4.81(-*C*H$_3$). *cis*-**1f:** 150.34 (vinyl), 147.62 (*Ar*), 112.88 (*Ar*), 112.27 (*Ar*), 39.64 (-N*Me*$_2$), -4.52 (-*C*H$_3$), -4.66 (-*C*H$_3$).
δ_{Si} (79 MHz, C_6D_6)	*trans*-**1f**: -40.30 (*Si*Me$_2$), -64.48 (*Si*H). *cis*-**1f**: -40.45 (*Si*Me$_2$), -62.86 (*Si*H).
HRMS	Calcd. for $C_{28}H_{50}N_2Si_6$: 582.2590. Found: 582.2593.
IR (cm^{-1})	2051 (SiH).

3.1.7 Synthesis of **1g**

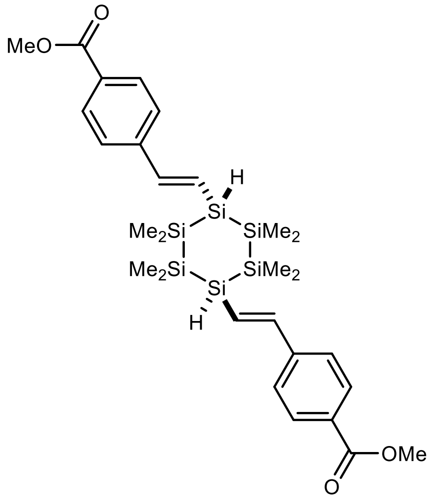


In a glove box, an oven-dried scintillation vial with stir bar was charged with **1,4Si$_6$** (1.0 equiv., 0.342 mmol, 0.100 g) and RuHCl(CO)(PPh$_3$)$_3$ (0.2 equiv., 0.068 mmol, 0.0651 g). DCM (1 mL) was added to dissolve the reagents. 4-ethynyltrifluoromethylbenzene (2.5 equiv., 0.854 mmol, 0.12 mL) was added dropwise into the reaction mixture by syringe. The vial was rinsed by 0.5 mL of DCM and the solution was added to the reaction as well. After the addition was complete, the reaction mixture turned dark red and was stirred for 2 hours at room temperature. The solution was transferred to a silica gel cartridge, and then dried on it under vacuum. The cartridge was subjected to automated column chromatography with 100% hexanes to yield **1g** (dr 65:35 *trans:cis*) as a white solid (0.154 g, 71%).

*Tabulated Characterization Data for **1g***

δ_H (400 MHz, C_6D_6)	*trans*-**1g**: 7.38 – 7.27 (m, 4H, Ar*H*), 7.12 - 7.05 (m, 6H, Ar*H* and vinyl), 6.61 (dd, *J* = 18.5, 5.4 Hz, 2H, vinyl), 4.14 (d, *J* = 5.4 Hz, 2H, Si*H*), 0.42 (s, 12H, -C*H*$_3$), 0.40 (s, 12H, -C*H*$_3$). *cis*-**1g**: 7.38 – 7.27 (m, 4H, Ar*H*), 7.12 - 7.05 (m, 6H, Ar*H* and vinyl), 6.60 (dd, *J* = 18.7, 5.4 Hz, 2H, vinyl), 4.18 (d, *J* = 5.4 Hz, 2H, Si*H*), 0.42 (s, 12H, -C*H*$_3$), 0.39 (s, 12H, -C*H*$_3$).
δ_C (101 MHz, C_6D_6)	*trans*-**1g**: 145.80 (vinyl), 141.71 (*Ar*), 126.72 (*Ar*), 125.89 (*Ar*), 124.00 (vinyl), -4.61 (-*C*H$_3$). *cis*-**1g:** 145.89 (vinyl), 141.71 (*Ar*), 126.65 (*Ar*), 125.86 (*Ar*), 124.36 (vinyl), -4.33 (-*C*H$_3$), -4.48 (-*C*H$_3$).
δ_F (376 MHz, C_6D_6)	*trans*-**1g**: -62.18 (-C*F*$_3$). *cis*-**1g**: -62.24 (-C*F*$_3$).
δ_{Si} (79 MHz, C_6D_6)	*trans*-**1g**: -39.98 (*Si*Me$_2$), -64.54 (*Si*H). *cis*-**1g**: -40.31 (*Si*Me$_2$), -62.73 (*Si*H).
HRMS	Calcd. for $C_{26}H_{38}F_6Si_6$: 632.1493. Found: 632.1499.
IR (cm^{-1})	2082 (SiH).
λ_{max} (pentane) /nm	294 (ε/dm^3 mol^{-1} cm^{-1} 40000)

3.1.8 Synthesis of **1h**

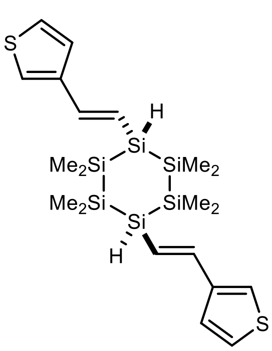


In a glove box, an oven-dried scintillation vial with stir bar was charged with **1,4Si$_6$** (1.0 equiv., 0.342 mmol, 0.100 g) and RuHCl(CO)(PPh$_3$)$_3$ (0.2 equiv., 0.068 mmol, 0.0651 g). DCM (1 mL) was added to dissolve the reagents. Methyl 4-ethynylbenzoate (2.5 equiv., 0.854 mmol, 0.137 g) was dissolved by 0.5 mL of DCM in a 1-dram vial and added dropwise into the reaction mixture by pipette. The vial was rinsed by 0.5 mL of DCM and the solution was added to the reaction as well. After the addition was complete, the reaction mixture turned dark red and was stirred for 2 hours at room temperature. The solution was transferred to a silica gel cartridge, and then dried on it under vacuum. The cartridge was subjected to automated column chromatography with 85% hexanes/15% ethyl acetate to yield **1h** (dr 60:40 *trans:cis*) as a white solid (0.168 g, 80%).

*Tabulated Characterization Data for **1h***

δ_H (400 MHz, C_6D_6)	*trans*-**1h**: 8.13 (d, *J* = 8.3 Hz, 4H, Ar*H*), 7.24 (d, *J* = 8.3 Hz, 4H, Ar*H*), 7.15 (d, *J* = 18.8 Hz, 2H, vinyl), 6.68 (dd, *J* = 18.8, 5.3 Hz, 2H, vinyl), 4.13 (d, *J* = 5.3 Hz, 2H, Si*H*), 3.50 (s, 6H, -COO*Me*), 0.41 (s, 12H, -C*H*$_3$), 0.37 (s, 12H, -C*H*$_3$). *cis*-**1h**: 8.10 (d, *J* = 8.3 Hz, 2H, Ar*H*), 7.24 (d, *J* = 8.3 Hz, 4H, Ar*H*), 7.15 (d, *J* = 18.8 Hz, 2H, vinyl), 6.65 (dd, *J* = 18.8, 5.3 Hz, 2H, vinyl), 4.13 (d, *J* = 5.3 Hz, 2H, Si*H*), 3.50 (s, 6H, -COO*Me*), 0.39 (s, 12H, -C*H*$_3$), 0.37 (s, 12H, -C*H*$_3$).
δ_C (101 MHz, C_6D_6)	*trans*-**1h**: 166.45 (*C*=O), 146.46 (vinyl), 142.51 (*Ar*), 130.46 (*Ar*), 130.20 (*Ar*), 126.47 (*Ar*), 124.30 (vinyl), 51.64 (-COO*Me*), -4.59 (-*C*H$_3$), -4.63 (-*C*H$_3$). *cis*-**1h**: 166.41 (*C*=O), 146.37 (vinyl), 142.57 (*Ar*), 130.44 (*Ar*), 130.18 (*Ar*), 126.55 (*Ar*), 123.91 (vinyl), 51.64 (-COO*Me*), -4.29 (-*C*H$_3$), -4.45 (-*C*H$_3$).
δ_{Si} (79 MHz, C_6D_6)	*trans*-**1h**: -39.88 (*Si*Me$_2$), -64.86 (*Si*H). *cis*-**1h**: -40.29 (*Si*Me$_2$), -62.90 (*Si*H).
HRMS	Calcd. for $C_{28}H_{44}O_4Si_6$: 612.1855. Found: 612.1843.
IR (cm^{-1})	1718 (C=O), 2073 (SiH).
λ_{max} (pentane) /nm	308 (ε/dm^3 mol^{-1} cm^{-1} 43100)

3.1.9 Synthesis of **1i**



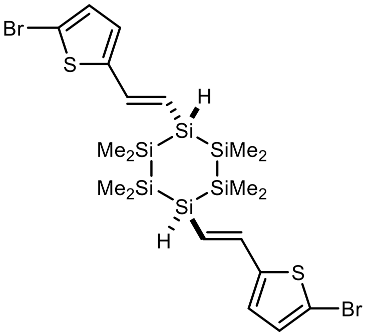
In a glove box, an oven-dried scintillation vial with stir bar was charged with **1,4Si$_6$** (1.0 equiv., 0.342 mmol, 0.100 g) and RuHCl(CO)(PPh$_3$)$_3$ (0.2 equiv., 0.068 mmol, 0.0651 g). DCM (1 mL) was added to dissolve the reagents. 3-ethynylthiophene (2.5 equiv., 0.854 mmol, 0.092 g) was diluted by 0.5 mL of DCM in a 1-dram vial and added dropwise into the reaction mixture by pipette. The vial was rinsed by 0.5 mL of DCM and the solution was added to the reaction as well. After the addition was complete, the reaction mixture turned dark red and was stirred for 30 minutes at room temperature. The solution was transferred to a silica gel cartridge, and then dried on it under vacuum. The cartridge was subjected to automated column chromatography with 100% hexanes to yield **1i** (dr 63:37 *trans:cis*) as a white solid (0.151 g, 87%).

*Tabulated Characterization Data for **1i***

δ_H (400 MHz, C_6D_6)	*trans*-**1i**: 7.14 (d, *J* = 18.7 Hz, 2H, vinyl), 7.06 (dt, *J* = 4.5, 2.1 Hz, 2H, thienyl), 6.79 – 6.74 (m, 4H, thienyl), 6.33 (dd, *J* = 18.7, 5.3

	Hz, 2H, vinyl), 4.11 (d, *J* = 5.3 Hz, 2H, Si*H*), 0.39 (s, 12H, -$\mathrm{C}H_3$), 0.37 (s, 12H, -$\mathrm{C}H_3$).
	cis-**1i**: 7.12 (d, *J* = 18.7 Hz, 2H, vinyl), 7.06 (dt, *J* = 4.5, 2.1 Hz, 2H, thienyl), 6.79 – 6.74 (m, 4H, thienyl), 6.31 (dd, *J* = 18.6, 5.3 Hz, 2H, vinyl), 4.16 (d, *J* = 5.3 Hz, 2H, Si*H*), 0.39 (s, 12H, -$\mathrm{C}H_3$), 0.36 (s, 12H, -$\mathrm{C}H_3$).
δ_C (101 MHz, C_6D_6)	*trans*-**1i**: 142.48 (vinyl), 141.38 (thienyl), 126.14 (thienyl), 125.05 (thienyl), 122.83 (thienyl), 119.18 (vinyl), -4.53 (-$C\mathrm{H}_3$), -4.55 (-$C\mathrm{H}_3$).
	cis-**1i:** 142.43 (vinyl), 141.45 (thienyl), 126.20 (thienyl), 124.96 (thienyl), 122.83 (thienyl), 119.61 (vinyl), -4.25 (-$C\mathrm{H}_3$), -4.42 (-$C\mathrm{H}_3$).
δ_{Si} (79 MHz, C_6D_6)	*trans*-**1i**: -40.28 (*Si*Me$_2$), -65.22 (*Si*H).
	cis-**1i**: -40.50 (*Si*Me$_2$), -63.32 (*Si*H).
HRMS	Calcd. for $C_{20}H_{36}S_2Si_6$: 508.0874. Found: 508.0871.
IR (cm^{-1})	2051, 2085 (SiH).

3.1.10 Synthesis of **1j**



In a glove box, an oven-dried scintillation vial with stir bar was charged with **1,4Si$_6$** (1.0 equiv., 1.708 mmol, 0.500 g) and RuHCl(CO)(PPh$_3$)$_3$ (0.2 equiv., 0.342 mmol, 0.325 g). DCM (8 mL) was added to dissolve the reagents. 2-bromo-5-ethynylthiophene (2.5 equiv., 4.269 mmol, 0.799 g) was diluted by 1 mL of DCM in a 1-dram vial and added dropwise into the reaction mixture by pipette. The vial was rinsed by 1 mL of DCM and the solution was added to the reaction as well. After the addition was complete, the reaction mixture turned dark red and was stirred for 30 minutes at room temperature. The solution was concentrated under vacuum, transferred to a silica gel cartridge, and then dried on it under vacuum. The cartridge was subjected to automated column chromatography with 100% hexanes to yield **1j** (dr 63:37 *trans:cis*) as a white solid (0.849 g, 75%).

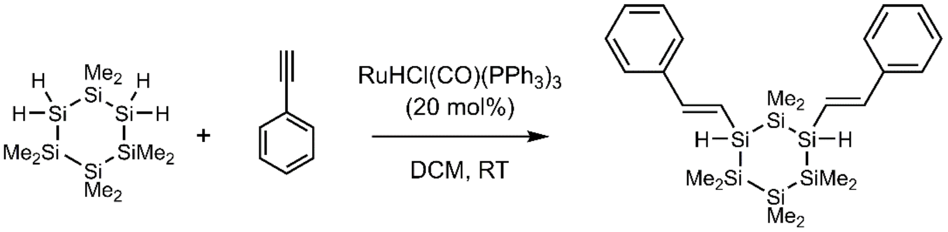
Isolation of *trans*-**1j**: In a scintillation vial, 0.500 g of **1j** (dr 63:37 *trans:cis*) was dissolved in 2 mL of DCM and layered with 18 mL of dry methanol. The solution was allowed to sit overnight in a glove box and colorless crystals were found at the bottom. The mixture was filtered through a fritted funnel, washed with 5 mL of dry methanol and dried under vacuum. *trans*-**1j** (dr 90:10 *trans:cis*) (0.270 g, 83%) was collected as a colorless crystal. X-ray quality crystals were grown by liquid-liquid diffusion using THF as the solvent and methanol as the antisolvent.

*Tabulated Characterization Data for **1j***

δ_H (400 MHz, C_6D_6)	*trans*-**1j**: 7.03 (d, *J* = 18.7 Hz, 2H, vinyl), 6.56 (d, *J* = 3.8 Hz, 2H, thienyl), 6.24 (dd, *J* = 18.7, 5.3 Hz, 2H, vinyl), 6.22 (d, *J* = 3.8 Hz, 2H, thienyl), 4.03 (d, *J* = 5.6 Hz, 2H, Si*H*), 0.33 (s, 12H, -C*H*$_3$), 0.33 (s, 12H, -C*H*$_3$). *cis*-**1j**: 7.01 (d, *J* = 18.7 Hz, 2H, vinyl), 6.56 (d, *J* = 3.8 Hz, 2H, thienyl), 6.22 (dd, *J* = 18.7, 5.3 Hz, 2H, vinyl), 6.22 (d, *J* = 3.8 Hz, 2H, thienyl), 4.08 (d, *J* = 5.6 Hz, 2H, Si*H*), 0.35 (s, 12H, -C*H*$_3$), 0.32 (s, 12H, -C*H*$_3$).
δ_C (101 MHz, C_6D_6)	*trans*-**1j**: 147.03 (vinyl), 138.90 (thienyl), 130.81 (thienyl), 125.90 (thienyl), 120.87 (thienyl), 112.31 (vinyl), -4.61 (-*C*H$_3$), -4.72 (-*C*H$_3$). *cis*-**1j:** 146.99 (vinyl), 138.99 (thienyl), 130.84 (thienyl), 125.92 (thienyl), 121.17 (thienyl), 112.38 (vinyl), -4.61 (-*C*H$_3$), -4.72 (-*C*H$_3$).
δ_{Si} (79 MHz, C_6D_6)	*trans*-**1j**: -40.23 (*Si*Me$_2$), -64.37 (*Si*H). *cis*-**1j**: -40.38 (*Si*Me$_2$), -62.85 (*Si*H).
HRMS	Calcd. for $C_{20}H_{34}Br_2S_2Si_6$: 663.9084. Found: 663.9064.
IR (cm^{-1})	2051, 2083 (SiH).
λ_{max} (pentane) /nm	*trans*-**1j**: 321 (ε/dm^3 mol^{-1} cm^{-1} 61100)
λ_{max} (THF) /nm	*trans*-**1j**: 323 (ε/dm^3 mol^{-1} cm^{-1} 51500)

3.2 Hydrosilation of acetylenes with 1,3Si$_6$

3.2.1 Synthesis of **2a**

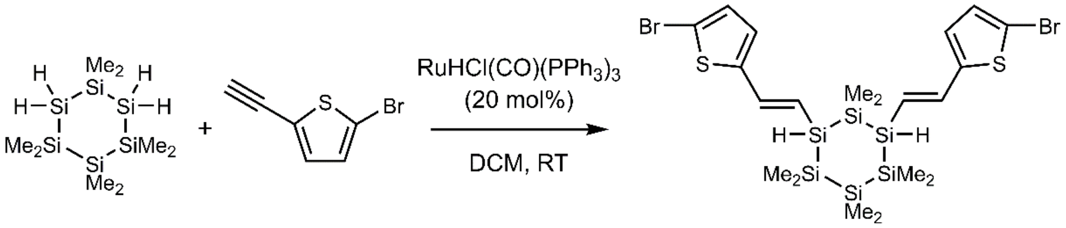


In a glove box, an oven-dried 2-dram vial with stir bar was charged with RuHCl(CO)(PPh$_3$)$_3$ (0.2 equiv., 0.068 mmol, 0.0651 g) and DCM (1.0 mL). **1,3Si$_6$** (1.0 equiv., 0.342 mmol, 0.100 g) was diluted by 1.0 mL of DCM added to the vial. Phenylacetylene (2.5 equiv., 0.854 mmol, 94 µL) was added dropwise into the reaction mixture by micro syringe. After the addition was complete, the reaction mixture turned dark red and was stirred for 2 hours at room temperature. The solution was transferred to a silica gel cartridge, and then dried on it under vacuum. The cartridge was subjected to automated column chromatography with 100% hexanes to yield **2a** (dr 55:45 *trans:cis*) as a white oily solid (0.152 g, 90%).

*Tabulated Characterization Data for **2a***

δ_H (400 MHz, C_6D_6)	*trans*-**2a**: 7.37 – 7.32 (m, 2H, Ar*H*), 7.33 – 7.26 (m, 2H, Ar*H*), 7.26 (d, *J* = 18.7 Hz, 2H, vinyl), 7.14 – 7.01 (m, 4H, Ar*H*), 6.62 (dd, *J* = 18.7, 5.1 Hz, 2H, vinyl), 4.22 (d, *J* = 5.1 Hz, 2H, Si*H*), 0.53 (s, 6H, -C*H*3), 0.40 (s, 12H, C*H*3), 0.29 (s, 6H, -C*H*3). *cis*-**2a**: 7.37 – 7.32 (m, 2H, Ar*H*), 7.33 – 7.26 (m, 2H, Ar*H*), 7.23 (d, *J* = 18.7 Hz, 2H, vinyl), 7.14 – 7.01 (m, 4H, Ar*H*), 6.61 (dd, *J* = 18.7, 5.1 Hz, 2H, vinyl), 4.27 (d, *J* = 5.3 Hz, 2H, Si*H*), 0.51 (s, 3H, -C*H*3), 0.50 (s, 3H, -C*H*3), 0.38 (s, 6H, -C*H*3), 0.37 (s, 6H, -C*H*3), 0.29 (s, 3H, -C*H*3), 0.28 (s, 3H, -C*H*3).
δ_C (101 MHz, C_6D_6)	*trans*-**2a**: 147.38 (vinyl), 138.42 (*Ar*), 128.53 (*Ar*), 126.35 (*Ar*), 119.75 (vinyl), -3.13 (-*C*H3), -4.57 (-*C*H3), -4.77 (-*C*H3). *cis*-**2a:** 147.37 (vinyl), 138.51 (*Ar*), 128.55 (*Ar*), 126.32 (*Ar*), 119.71 (vinyl), -2.54 (-*C*H3), -3.61 (-*C*H3), -6.43 (-*C*H3), -6.52 (-*C*H3).
δ_{Si} (79 MHz, C_6D_6)	*trans*-**2a**: -40.20 (*Si*Me2), -40.67 (*Si*Me2), -41.28 (*Si*Me2), -62.68 (*Si*H). *cis*-**2a**: -40.42 (*Si*Me2), -40.87 (*Si*Me2), -41.09 (*Si*Me2), -62.53 (*Si*H).
HRMS	Calcd. for $C_{24}H_{40}Si_6$: 496.1746. Found: 496.1763.
IR (cm^{-1})	2051, 2072 (SiH).
λ_{max} (pentane) /nm	284 (ε/dm^3 mol^{-1} cm^{-1} 38900)

3.2.2 Synthesis of **2b**



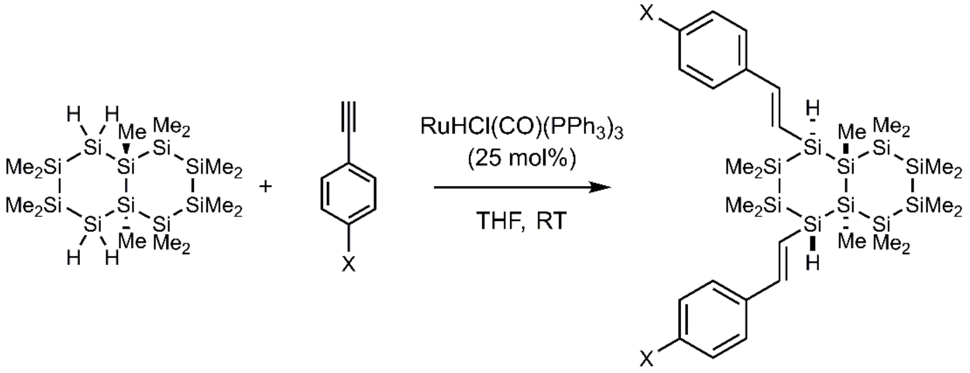
In a glove box, an oven-dried 2-dram vial with stir bar was charged with $RuHCl(CO)(PPh_3)_3$ (0.2 equiv., 0.068 mmol, 0.0651 g) and DCM (1.0 mL). **1,3Si$_6$** (1.0 equiv., 0.342 mmol, 0.100 g) was diluted by 0.5 mL of DCM added to the vial. 2-bromo-5-ethynylthiophene (2.5 equiv., 4.269 mmol, 0.160 g) was weighed in a 1-dram vial, diluted by 0.5 mL of DCM and added dropwise into the reaction mixture by pipette. The vial was rinsed by 0.5 mL of DCM and the solution was added to the reaction as well. After the addition was complete, the reaction mixture turned dark red and was stirred for 30 minutes at room temperature. The solution was transferred to a silica gel cartridge, and then dried on it under vacuum. The cartridge was subjected to automated column chromatography with 100% hexanes to yield **2b** (dr 50:50 *trans:cis*) as a pale yellow oil (0.188 g, 84%).

Tabulated Characterization Data for ***2b***

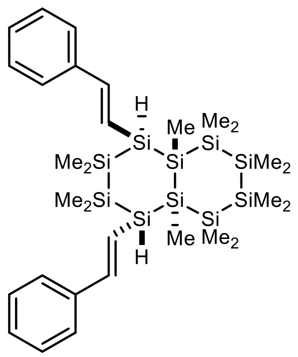
δ_H (400 MHz, C_6D_6)	*trans*-**2b**: 7.03 (d, *J* = 18.4 Hz, 2H, vinyl), 6.57 (d, *J* = 3.8 Hz, 2H, thienyl), 6.29 – 6.15 (m, 4H, vinyl and thienyl), 4.08 (d, *J* = 5.3 Hz,

	2H, Si*H*), 0.42 (s, 6H, -C*H*$_3$), 0.33 (s, 12H, -C*H*$_3$), 0.26 (s, 6H, -C*H*$_3$). *cis*-**2b**: 7.00 (d, *J* = 18.4 Hz, 2H, vinyl), 6.55 (d, *J* = 3.8 Hz, 2H, thienyl), 6.29 – 6.15 (m, 4H, vinyl and thienyl), 4.11 (d, *J* = 5.3 Hz, 2H, Si*H*), 0.41 (s, 6H, -C*H*$_3$), 0.31 (s, 12H, -C*H*$_3$), 0.24 (s, 6H, -C*H*$_3$).
δ_C (101 MHz, C_6D_6)	*trans*-**2b**: 146.99 (vinyl), 139.01 (thienyl), 130.81 (thienyl), 125.94 (thienyl), 120.87 (thienyl), 112.36 (vinyl), -2.95 (-*C*H$_3$), -4.28 (-*C*H$_3$), -4.33 (-*C*H$_3$), -4.54 (-*C*H$_3$), -4.56 (-*C*H$_3$). *cis*-**2b:** 146.94 (vinyl), 139.14 (thienyl), 130.79 (thienyl), 126.04 (thienyl), 120.82 (thienyl), 112.49 (vinyl), -2.37 (-*C*H$_3$), -3.35 (-*C*H$_3$), -6.08 (-*C*H$_3$), -6.15 (-*C*H$_3$), -6.21 (-*C*H$_3$).
δ_{Si} (79 MHz, C_6D_6)	*trans*-**2b**: 40.30 (*Si*Me$_2$), -40.78 (*Si*Me$_2$), -41.32 (*Si*Me$_2$), -62.54 (*Si*H). *cis*-**2b:** -40.37 (*Si*Me$_2$), -40.82 (*Si*Me$_2$), -41.14 (*Si*Me$_2$), -62.33 (*Si*H).
HRMS	Calcd. for $C_{20}H_{34}BrS_2Si_6$ ([M-^{79}Br]$^+$): 584.9901. Found: 584.9899.
IR (cm^{-1})	2051, 2062 (SiH).

3.3 Hydrosilation of acetylenes with *trans*-Si$_{10}$H$_4$



3.3.1 Synthesis of **3a**

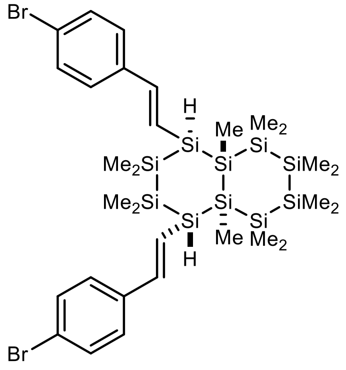


In a glove box, an oven-dried 2-dram vial with stir bar was charged with *trans*-**Si$_{10}$H$_4$** (dr 83:17 *trans*:*cis*, 1.0 equiv., 0.202 mmol, 0.100 g) and RuHCl(CO)(PPh$_3$)$_3$ (0.25 equiv., 0.051 mmol, 0.048 g). THF (1.0 mL) was added to dissolve the reagents. Phenylacetylene (4.0 equiv., 0.832 mmol, 0.085 g) was weighed in a 1-dram vial, diluted by 0.5 mL of THF and added dropwise to the reaction mixture by syringe. The vial was rinsed by 0.5 mL of THF, and the solution was added to the reaction as well. After the addition was complete, the reaction mixture turned dark red and was stirred for 24 hours at room temperature. The solution was transferred to a silica gel cartridge, and then dried on it under vacuum. The cartridge was subjected to automated column chromatography with 100% hexanes to yield **3a** as a white solid (0.102 g, 73%).

*Tabulated Characterization Data for **3a***

δ_H (400 MHz, C_6D_6)	7.38 – 7.34 (m, 4H, Ar*H*), 7.28 (d, *J* = 18.7, 2H, vinyl), 7.18 – 7.10 (m, 4H, Ar*H*), 7.08 – 7.03 (m, 2H, Ar*H*), 6.69 (dd, *J* = 18.7, 5.5, 2H, vinyl), 4.32 (d, *J* = 5.5, 2H, Si*H*), 0.57 (s, 6H, -C*H*$_3$), 0.49 (s, 6H, -C*H*$_3$), 0.44 (s, 6H, -C*H*$_3$), 0.42 (s, 6H, -C*H*$_3$), 0.33 (s, 6H, -C*H*$_3$), 0.26 (s, 6H, -C*H*$_3$), 0.21 (s, 6H, -C*H*$_3$).
δ_C (101 MHz, C_6D_6)	146.90 (vinyl), 138.96 (*Ar*), 128.97 (*Ar*), 126.69 (*Ar*), 121.54 (vinyl), -3.19 (-*C*H$_3$), -4.04 (-*C*H$_3$), -4.19 (-*C*H$_3$), -4.41 (-*C*H$_3$), -4.50 (-*C*H$_3$), -6.47 (-*C*H$_3$), -8.41 (-*C*H$_3$).
δ_{Si} (79 MHz, C_6D_6)	-36.12 (*Si*Me$_2$), -36.51 (*Si*Me$_2$), -39.96(*Si*Me$_2$), -67.78 (*Si*H), -75.89 (*Si*Si$_2$Me).
HRMS	Calcd. for $C_{30}H_{58}Si_{10}$: 698.2231. Found: 698.2194.
IR (cm^{-1})	2072 (SiH).
λ_{max} (pentane) /nm	298 (ε/dm^3 mol^{-1} cm^{-1} 29200), 294 (ε/dm^3 mol^{-1} cm^{-1} 29500)

3.3.2 Synthesis of **3b**



In a glove box, an oven-dried 2-dram vial with stir bar was charged with *trans*-**Si$_{10}$H$_4$** (dr 83:17 *trans*:*cis,* 1.0 equiv., 0.149 mmol, 0.074 g) and RuHCl(CO)(PPh$_3$)$_3$ (0.25 equiv., 0.042 mmol, 0.036 g). THF (0.75 mL) was added to dissolve the reagents. 4-Ethynylbromobenzene (4.0 equiv., 0.042 mmol, 0.108 g) was weighed in a 1-dram vial, diluted by 0.5 mL of THF and added dropwise to the reaction mixture by syringe. The vial was rinsed by 0.25 mL of THF, and the solution was added to the reaction as well. After the addition was complete, the reaction mixture turned dark red and was stirred for 24 hours at room temperature. The solution was transferred to a silica gel cartridge, and then dried on it under vacuum. The cartridge was subjected to automated column chromatography with 100% hexanes to yield **3b** as a white solid (0.072 g, 67%).

*Tabulated Characterization Data for **3b***

δ_H (400 MHz, C_6D_6)	7.25 (d, *J*=8.5, 4H, Ar*H*), 7.08 (d, *J* = 18.7, 2H, vinyl), 6.95 (d, *J* = 8.5, 4H, Ar*H*), 6.58 (dd, *J* = 18.7, 5.6, 2H, vinyl), 4.29 (d, *J* = 5.6, 2H, Si*H*), 0.56 (s, 6H, -CH_3), 0.48 (s, 6H, -CH_3), 0.44 (s, 6H, -CH_3), 0.41 (s, 6H, -CH_3), 0.30 (s, 6H, -CH_3), 0.27 (s, 6H, -CH_3), 0.22 (s, 6H, -CH_3).
δ_C (101 MHz, C_6D_6)	145.37 (vinyl), 137.60 (*Ar*), 132.12 (*Ar*), 122.79 (*Ar*), 122.26 (vinyl), 1.42 (-CH_3), -3.21 (-CH_3), -4.08 (-CH_3), -4.23 (-CH_3), -4.44 (-CH_3), -4.53 (-CH_3), -6.51 (-CH_3), -8.43 (-CH_3).
δ_{Si} (79 MHz, C_6D_6)	-36.08 (*Si*Me$_2$), -36.50 (*Si*Me$_2$), -39.89 (*Si*Me$_2$), -67.54 (*Si*H), -75.85 (*Si*Si$_2$Me).
HRMS	Calcd. for $C_{30}H_{56}Br_2Si_{10}$: 854.0441. Found: 854.0457.
IR (cm^{-1})	2065 (SiH).

3.4 Model reaction: Kumada cross-coupling of 1j and 2-bromothiophene

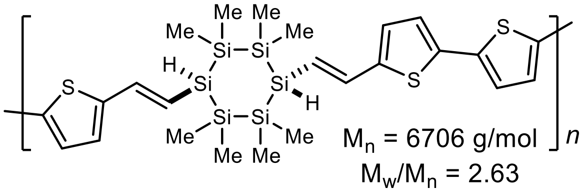
In a glove box, an oven-dried 2-dram vial with stir bar was charged with *trans*-**1j** (dr 90:10 *trans:cis*) (1.0 equiv., 0.075 mmol, 50.0 mg) and THF (1.0 mL). *i*-PrMgCl (2.0 M in THF) (75 µL) was added by micro syringe. The solution was stirred at room temperature for 30 minutes, yielding a di-Grignard intermediate. NidpppCl_2 (0.1 equiv., 0.007 mmol, 4.1 mg), triphenylphosphine (0.2 equiv., 0.014 mmol, 3.9 mg) and 2-bromothiophene (2.5 equiv., 0.187 mmol, 30.6 mg) were weighed in a 2-dram vial with stir bar and dissolved in THF (1.0 mL). The di-Grignard solution was quickly added to the reaction mixture by pipette, yielding a dark red solution. 0.5 mL of THF 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. The solution turned bright orange after 16 hours.

The reaction was cooled to room temperature and quenched by 0.1 mL of dry methanol. The solution was transferred to a silica gel cartridge, and then dried on it under vacuum. The cartridge was subjected to automated column chromatography with 100% hexanes to yield *trans*-**1k** (dr 90:10 *trans:cis*) as a yellow solid (43.5 mg, 86%).

*Tabulated Characterization Data for trans-**1k***

δ_H (400 MHz, C_6D_6)	7.21 (d, *J* = 18.3 Hz, 2H, vinyl), 6.98 (d, *J* = 3.6 Hz, 2H, thienyl), 6.84 (d, *J* = 3.7 Hz, 2H, thienyl), 6.69 (d, *J* = 5.2 Hz, 2H, thienyl), 6.65 – 6.58 (m, 2H, thienyl), 6.55 (d, *J* = 3.8 Hz, 2H, thienyl), 6.42 (dd, *J* = 18.4, 5.5 Hz, 2H, vinyl), 4.12 (d, *J* = 5.6 Hz, 2H, Si*H*), 0.39 (s, 12H, -CH_3), 0.38 (s, 12H, (thienyl)H_3).
δ_C (101 MHz, C_6D_6)	144.00 (vinyl), 139.23 (thienyl), 137.46 (thienyl), 136.84 (thienyl), 126.49 (thienyl), 124.39 (thienyl), 124.06 (thienyl), 123.83 (thienyl), 119.74 (vinyl), -4.93 (-CH_3), -5.01 (-CH_3).
δ_{Si} (79 MHz, C_6D_6)	-40.09 (*Si*Me$_2$), -64.57 (*Si*H).
HRMS	Calcd. for $C_{28}H_{40}S_4Si_6$: 672.0627. Found: 672.0623.
IR (cm^{-1})	2084 (SiH).
λ_{max} (THF) /nm	367 (ε/dm^3 mol^{-1} cm^{-1} 32600)

3.5 Synthesis of P1 via Kumada Polycondensation



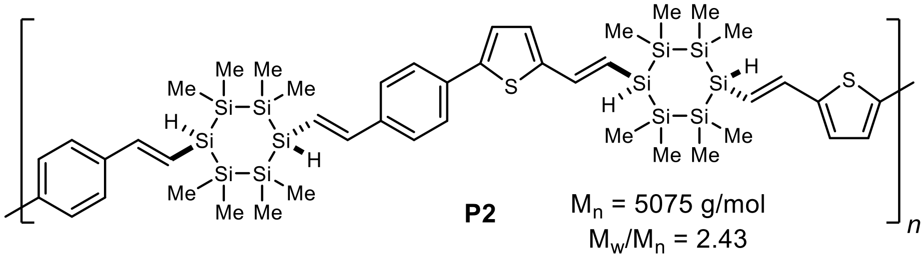
In a glove box, an oven-dried 2-dram vial with stir bar was charged with **1j** (dr 90:10 *trans:cis*) (1.0 equiv., 0.075 mmol, 50.0 mg) and THF (1.0 mL). *i*-PrMgCl (2.0 M in THF) (75 µL) was added by micro syringe. The solution was stirred at room temperature for 30 minutes, yielding a di-Grignard intermediate. 0.1 mL of reaction mixture was taken as an aliquot, quenched by methanol and dried under vacuum. The clean ^{1}H NMR spectrum of the quenched intermediate showed a full conversion of the starting cyclosilane. NidpppCl_2 (0.1 equiv., 0.007 mmol, 4.1 mg), triphenylphosphine (0.2 equiv., 0.014 mmol, 3.9 mg) and 2,5-dibromothiophene (1.5 equiv., 0.112 mmol, 27.2 mg) were weighed in a 2-dram vial with stir bar and dissolved in THF (1.0 mL). The di-Grignard solution was quickly added to the reaction mixture by pipette, yielding a dark red solution. 0.5 mL of THF 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. The solution turned bright orange after 16 hours.

After 24 hours, the reaction was quenched by adding the orange solution dropwise to 15 mL of dry methanol in a scintillation vial. Formation of orange precipitates was observed. The suspension was allowed to sit overnight, and the top clear yellow solution was removed. 10 mL of methanol were added, and precipitates were washed sufficiently by shaking the vial. 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 and the solid was dried under vacuum, yielding an orange powder (36.8 mg, 80%).

Tabulated Characterization Data for ***P1***

δ_H (400 MHz, $CDCl_3$)	7.03 (br, 4H, vinyl and thienyl), 6.82 (br, 2H, thienyl), 6.14 (br, 2H, vinyl), 3.77 (br, 2H, Si*H*), 0.31 (br, 24H, -C*H*$_3$).
δ_C (101 MHz, $CDCl_3$)	144.43 (vinyl), 138.64 (thienyl), 136.55 (thienyl), 136.24 (thienyl), 130.47 (thienyl), 126.36 (thienyl), 125.34 (thienyl), 124.56 (thienyl), 124.12 (thienyl), 120.92 (vinyl), 120.84 (vinyl), -4.35 (-*C*H$_3$), -4.59 (-*C*H$_3$), -4.67 (-*C*H$_3$).
δ_C (125.7 MHz, CPMAS)	141.58 (aromatic and vinyl), 134.03 (aromatic), 121.74 (aromatic and vinyl), -6.89 (-*C*H$_3$).
δ_{Si} (79 MHz, $CDCl_3$)	-39.88 (*Si*Me$_2$), -64.76 (*Si*H).
δ_{Si} (99.3 MHz, CPMAS)	-33.23 (*Si*Me$_2$), -62.68 (br, *Si*H)
IR (cm^{-1})	2051 (SiH).
λ_{max} (THF) /nm	433 (ε/dm^3 g^{-1} cm^{-1} 8.17), 418 (ε/dm^3 g^{-1} cm^{-1} 8.27)

3.6 Synthesis of P2 via Kumada Polycondensation



P2

M_n = 5075 g/mol
M_w/M_n = 2.43

In a glove box, an oven-dried 2-dram vial with stir bar was charged with **1j** (dr 90:10 *trans:cis*) (1.0 equiv., 0.075 mmol, 50.0 mg) and THF (1.0 mL). *i*-PrMgCl (2.0 M in THF) (75 µL) 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., 0.007 mmol, 4.1 mg), triphenylphosphine (0.2 equiv., 0.014 mmol, 3.9 mg) and *trans*-**1b** (1.1 equiv., 0.082 mmol, 54.0 mg) were weighed in a 2-dram vial with stir bar and dissolved in THF (1.0 mL). The di-Grignard solution was quickly added to the reaction mixture by pipette, yielding a dark red solution. 0.5 mL of THF 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. The solution turned dark red after 16 hours.

After 24 hours, the reaction was quenched by adding the orange solution dropwise to 15 mL of dry methanol in a scintillation vial. Formation of orange precipitates was observed. The suspension was allowed to sit overnight, and the top clear yellow solution was removed. 10 mL of methanol were added, and precipitates were washed sufficiently by shaking the vial. 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 and the solid was dried under vacuum, yielding a yellow powder (46.7 mg, 60%). Solid-state $^1H \rightarrow ^{29}Si$ and ^{13}C CPMAS spectra were recorded for its low solubility in $CDCl_3$. The broadness of peaks arises from the residual Ni catalyst.

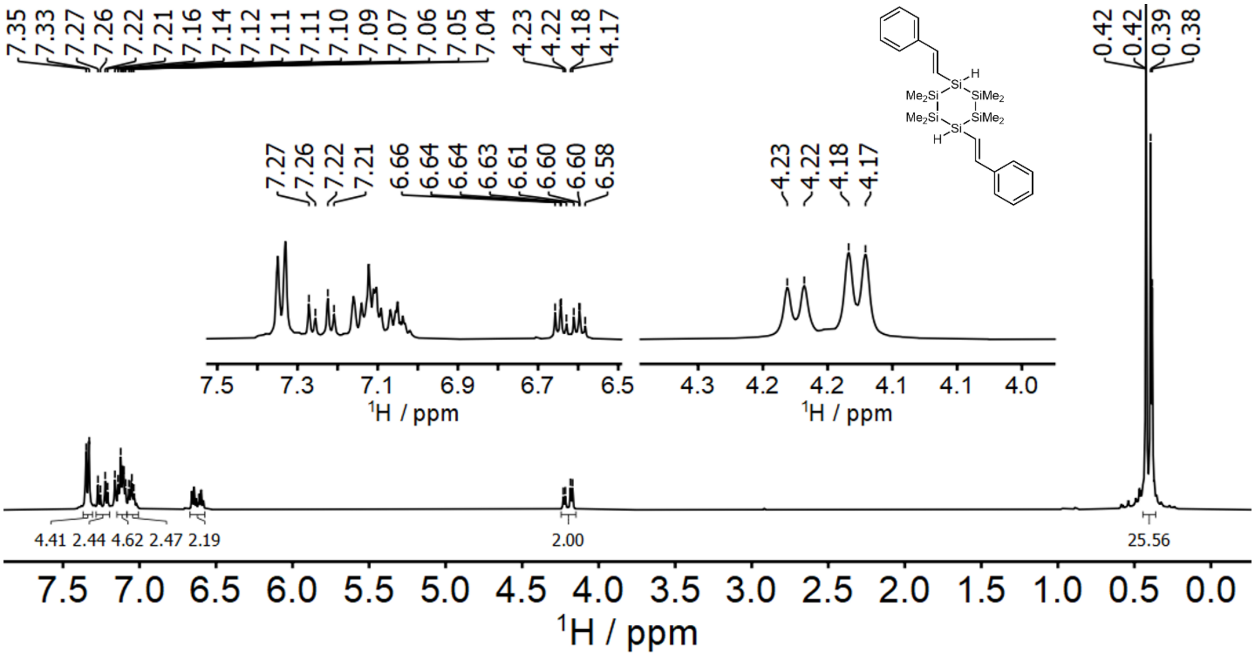
*Tabulated Characterization Data for **P2***

δ_H (400 MHz, $CDCl_3$)	7.70-7.65 (br, 4H, aromatic), 7.55-6.98 (br, 8H, vinyl and aromatic), 7.03-6.98 (br, 4H, vinyl and aromatic), 6.47 (br, 2H, vinyl), 6.20 (br, 2H, vinyl), 3.77 (br, 2H, Si*H*), 3.53 (br, 2H, Si*H*), 0.30 (br, 48H).
δ_C (125.7 MHz, CPMAS)	142.32 (aromatic and vinyl), 135.80 (aromatic), 128.93 (aromatic and vinyl), 124.61 (aromatic), -1.14 (-CH_3), -6.70 (-CH_3).
δ_{Si} (99.3 MHz, CPMAS)	-34.10 (*Si*Me_2), -65.98 (br, *Si*H)
IR (cm^{-1})	2064 (SiH).
λ_{max} (THF) /nm	311 (ε/dm^3 g^{-1} cm^{-1} 8.93)

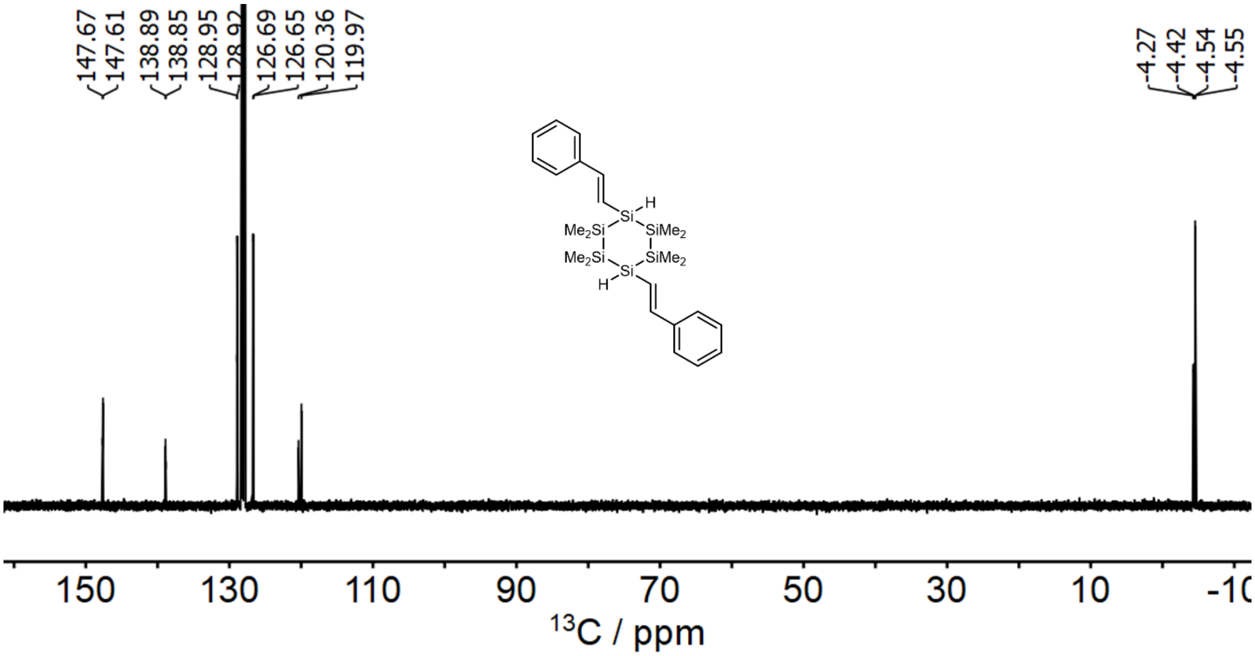
4. NMR Spectra

4.1 NMR Spectra of 1a

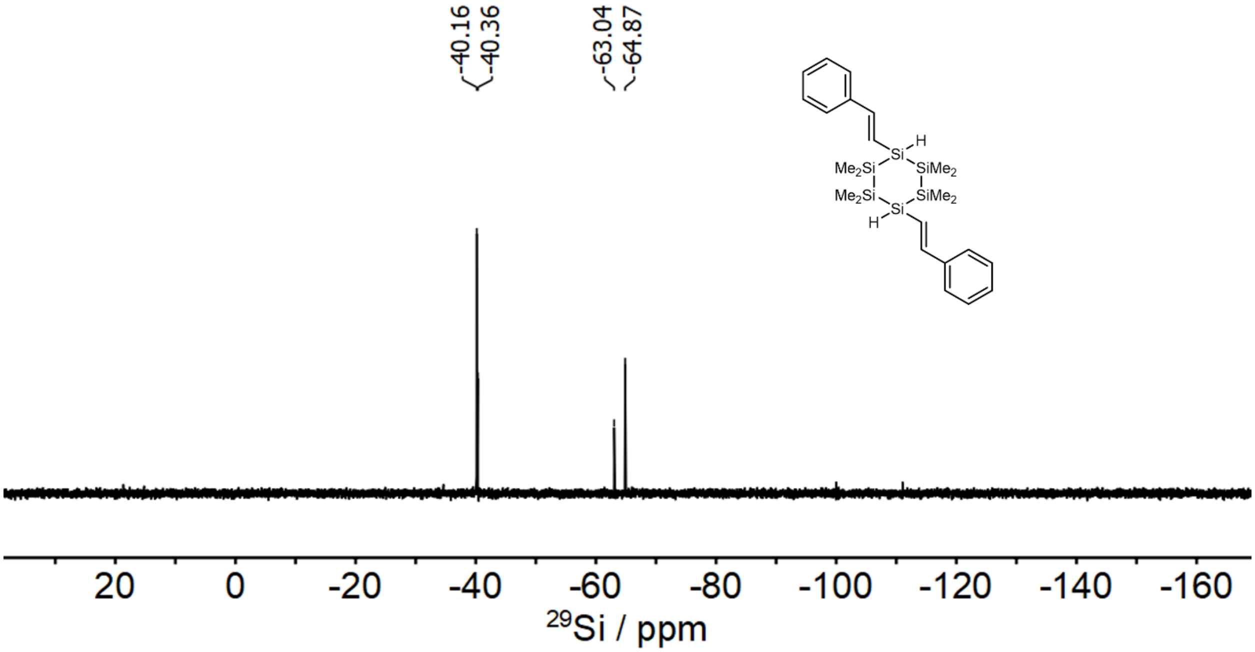
4.1.1 ^1H NMR Spectrum of **1a** (400 MHz, C_6D_6)



4.1.2 $^{13}C\{^1H\}$ NMR Spectrum of **1a** (101 MHz, C_6D_6)

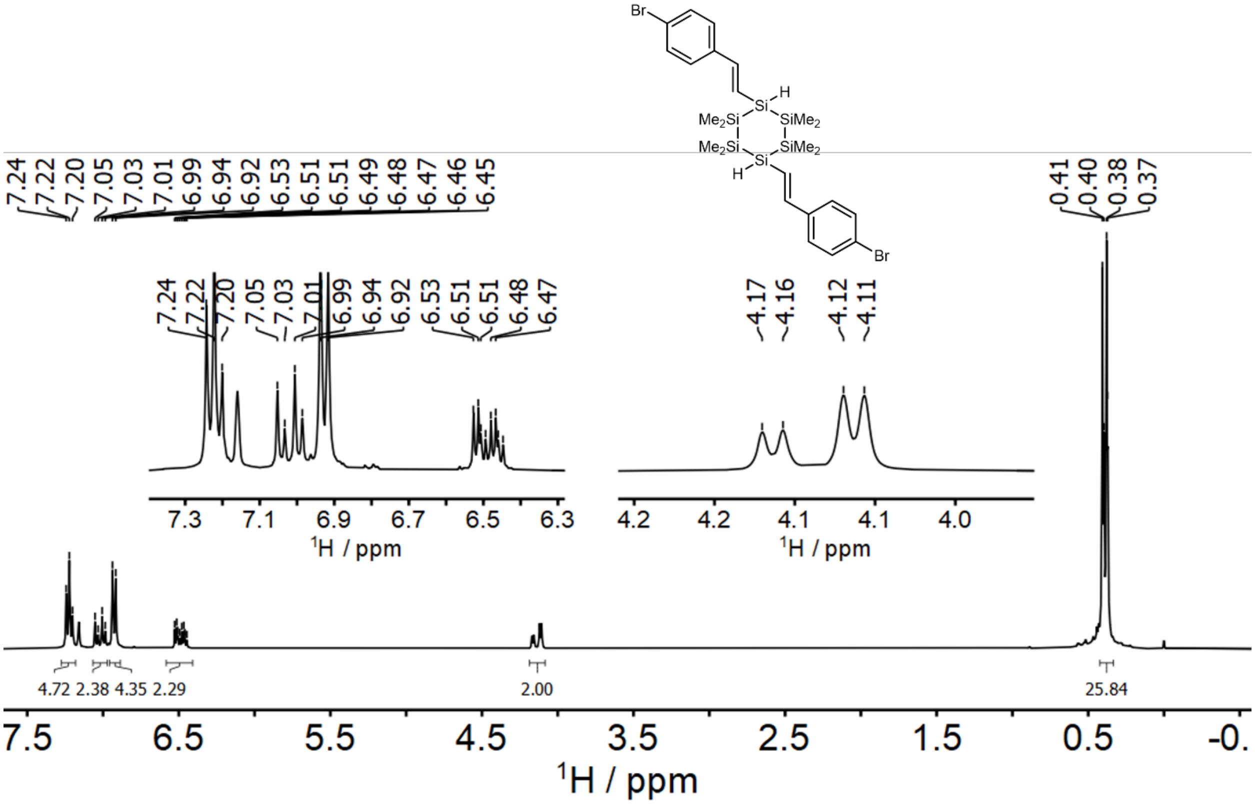


4.1.3 $^{29}Si\{^{1}H\}$ NMR Spectrum of **1a** (79 MHz, C_6D_6). $^{1}J_{Si\text{-}H}$ = 7 Hz.

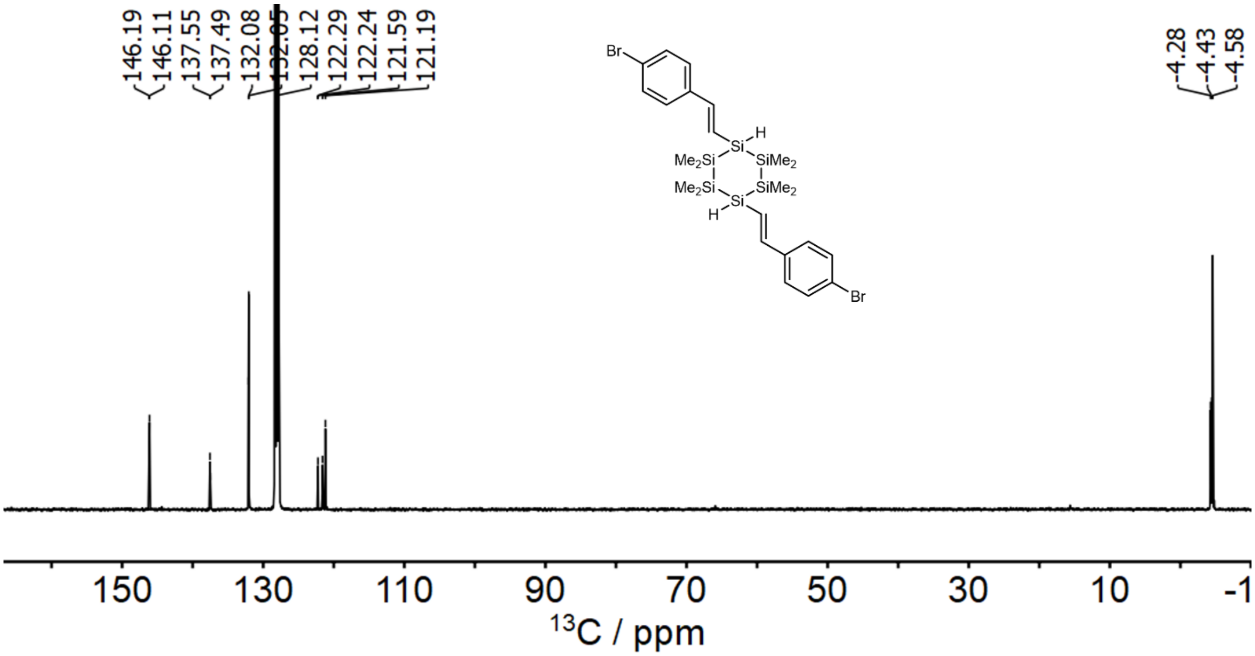


4.2 NMR Spectra of 1b

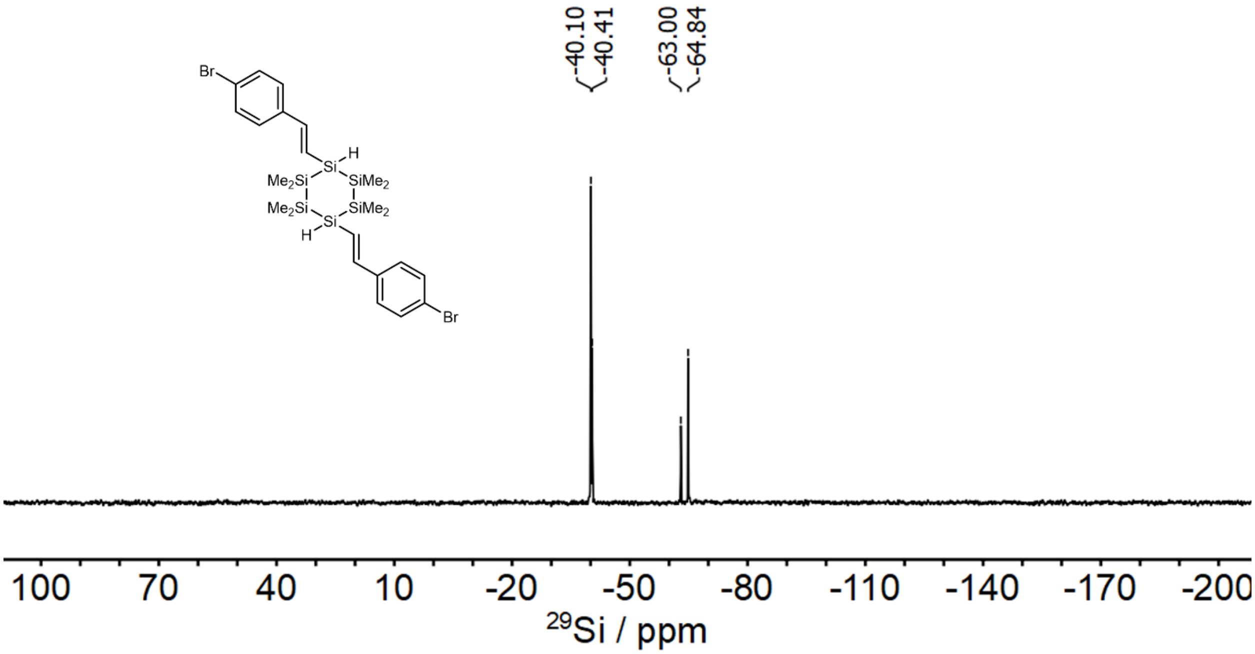
4.2.1 ^{1}H NMR Spectrum of **1b** (400 MHz, C_6D_6)



4.2.2 $^{13}C\{^{1}H\}$ NMR Spectrum of **1b** (101 MHz, C_6D_6)

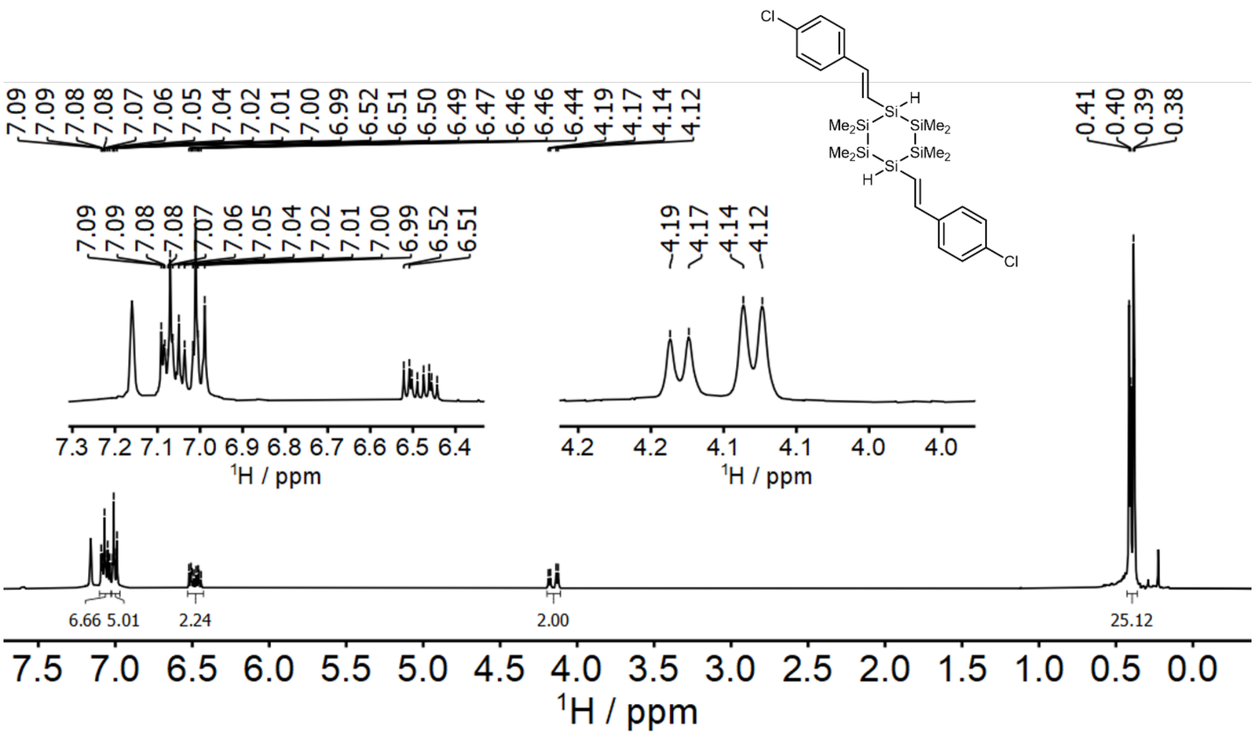


4.2.3 $^{29}Si\{^{1}H\}$ NMR Spectrum of **1b** (79 MHz, C_6D_6). $^{1}J_{Si\text{-}H}$ = 7 Hz.

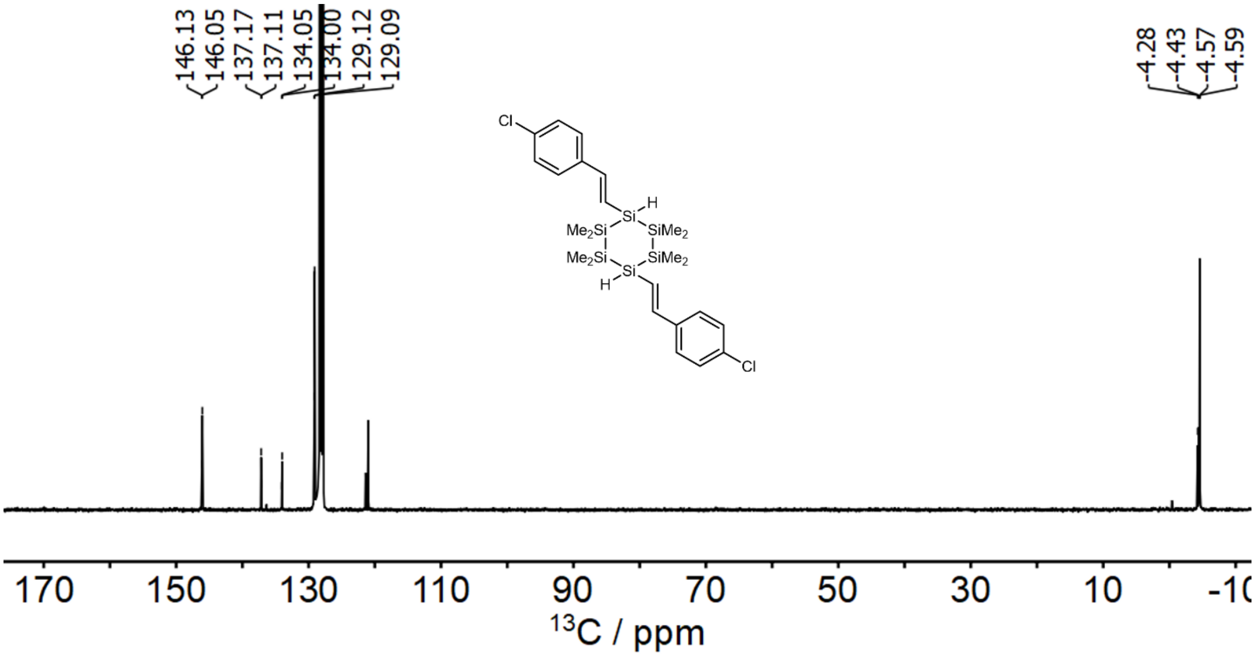


4.3 NMR Spectra of 1c

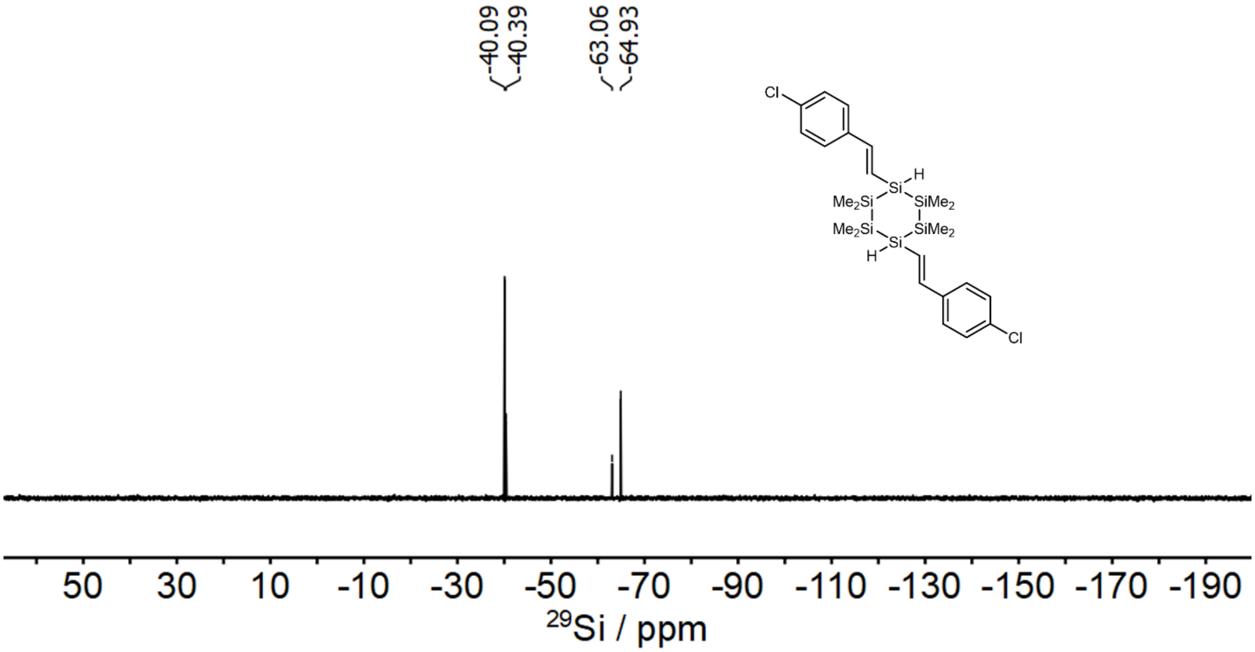
4.3.1 ^{1}H NMR Spectrum of **1c** (400 MHz, C_6D_6)



4.3.2 ^{13}C{^{1}H} NMR Spectrum of **1c** (101 MHz, C_6D_6)

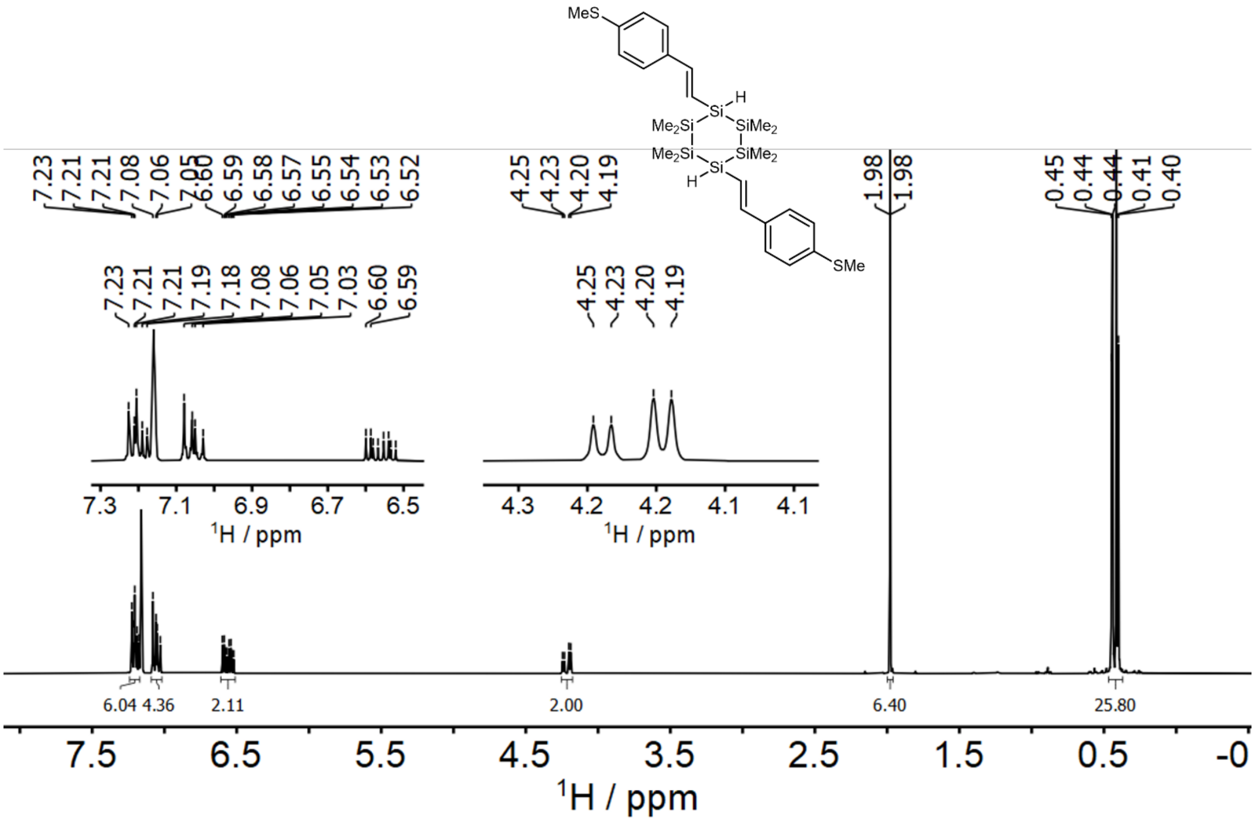


4.3.3 $^{29}Si\{^1H\}$ NMR Spectrum of **1c** (79 MHz, C_6D_6). $^1J_{Si\text{-}H}$ = 7 Hz.

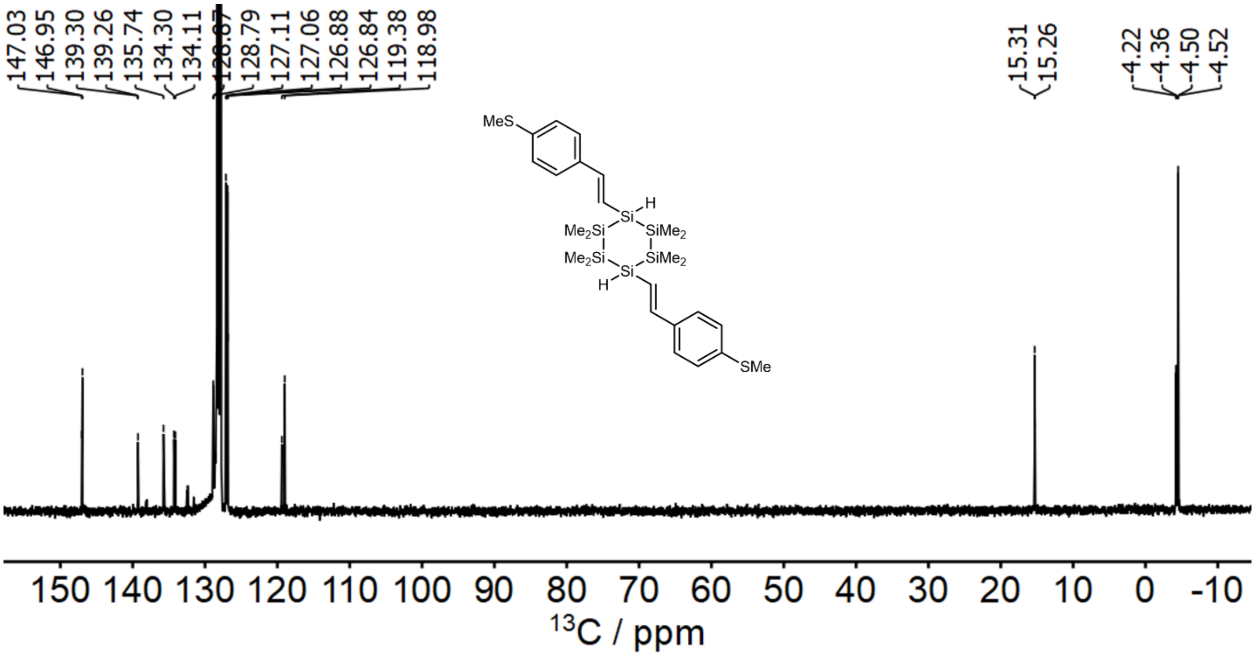


4.4 NMR Spectra of 1d

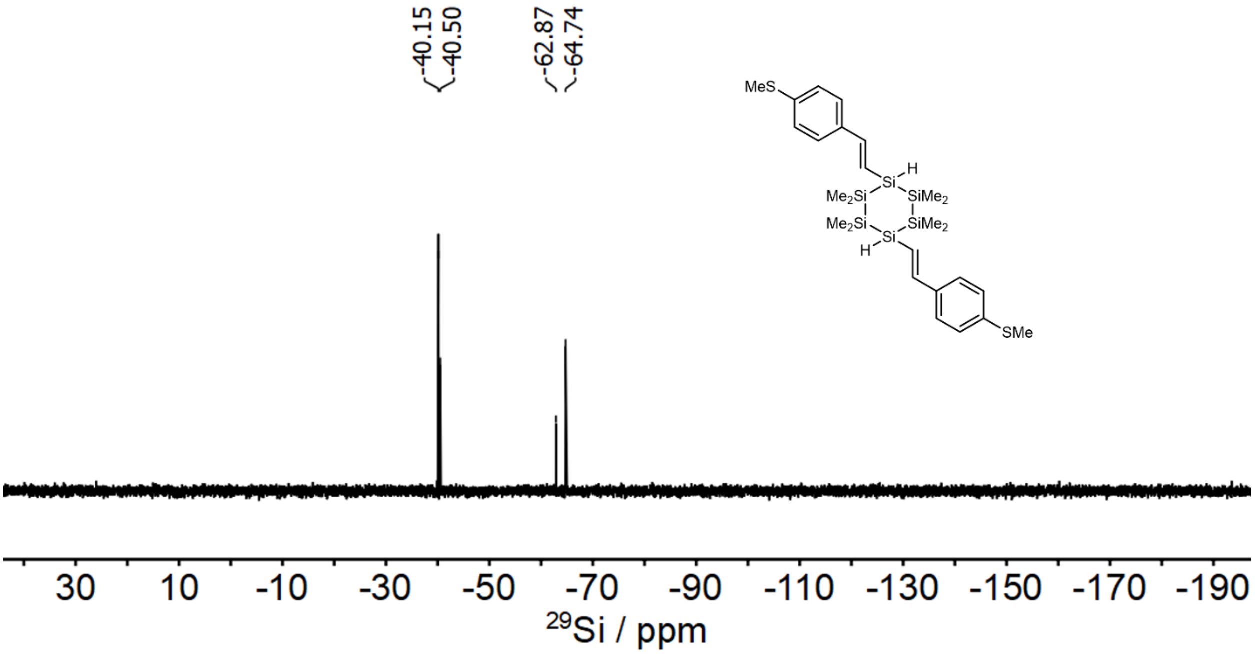
4.4.1 ^1H NMR Spectrum of **1d** (400 MHz, C_6D_6)



4.4.2 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR Spectrum of **1d** (101 MHz, C_6D_6)

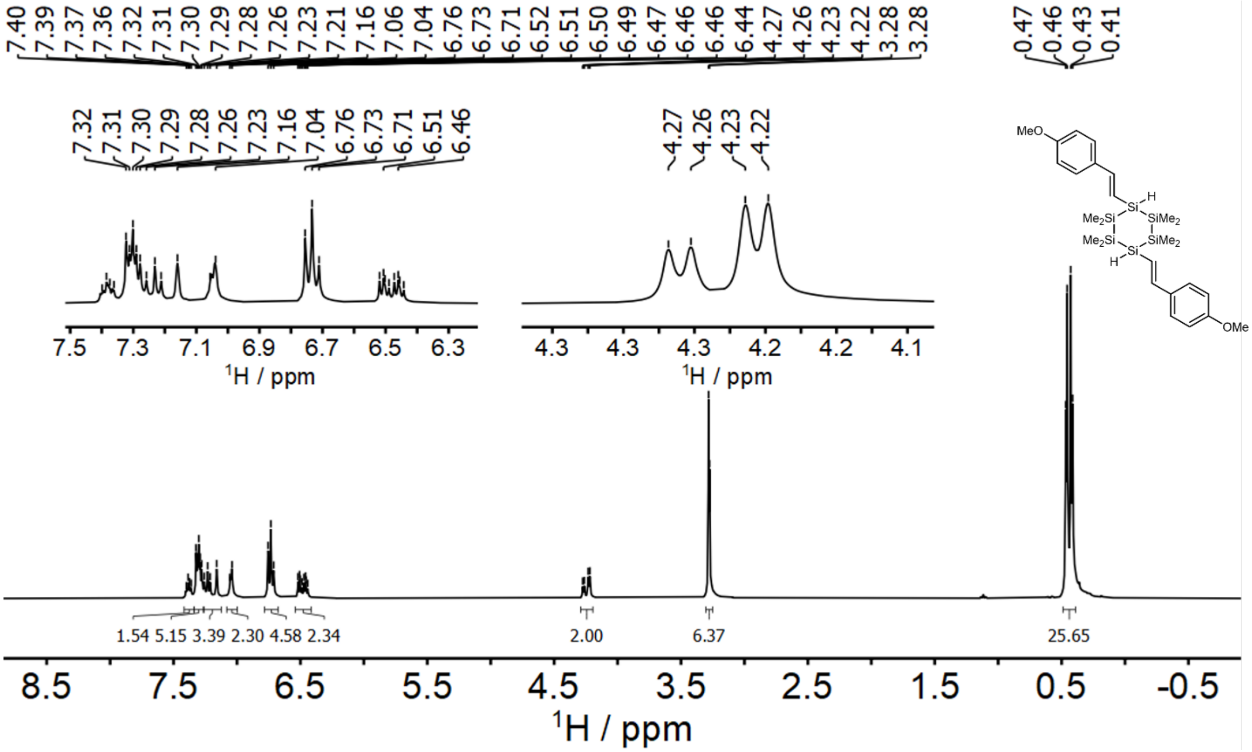


4.4.3 $^{29}\mathrm{Si}\{^{1}\mathrm{H}\}$ NMR Spectrum of **1d** (79 MHz, C_6D_6). $^{1}J_{\mathrm{Si\text{-}H}}$ = 7 Hz.

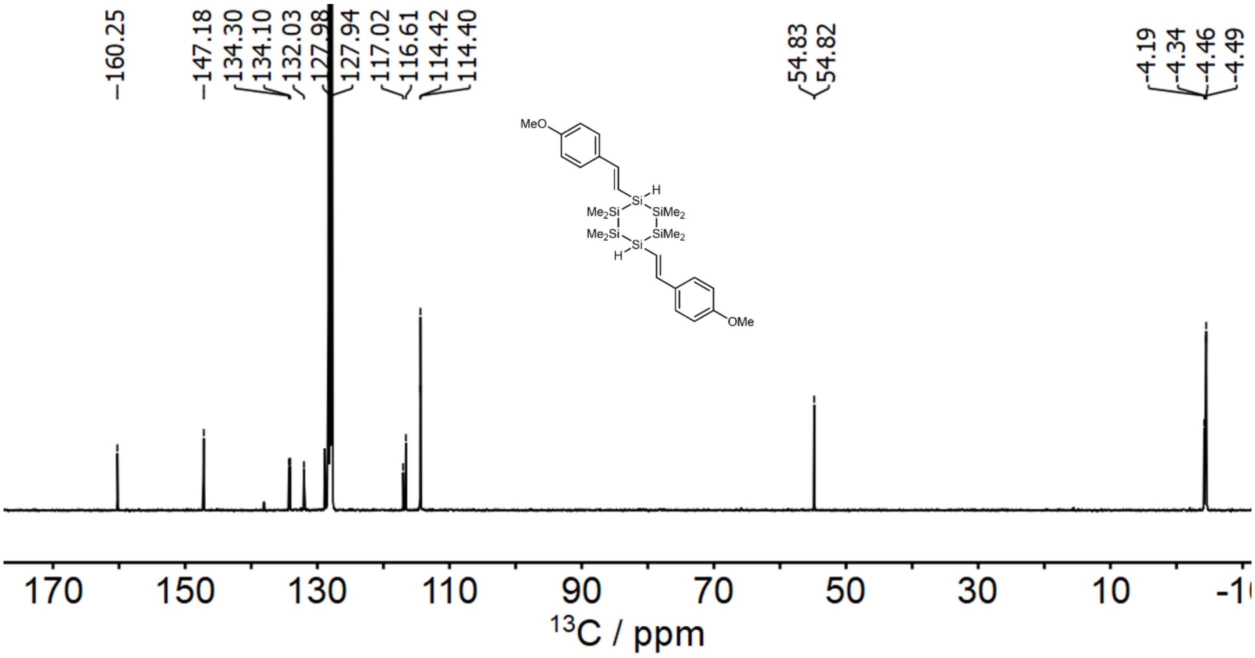


4.5 NMR Spectra of 1e

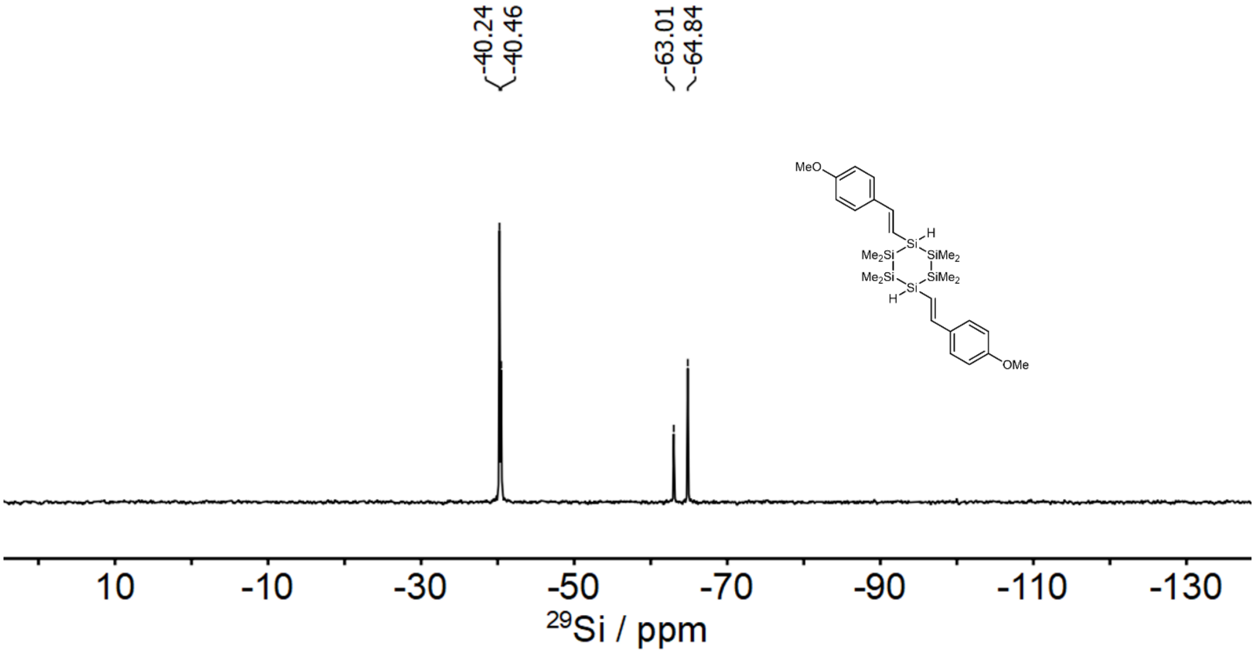
4.5.1 ^{1}H NMR Spectrum of **1e** (400 MHz, C_6D_6)



4.5.2 ^{13}C{^{1}H} NMR Spectrum of **1e** (101 MHz, C_6D_6)

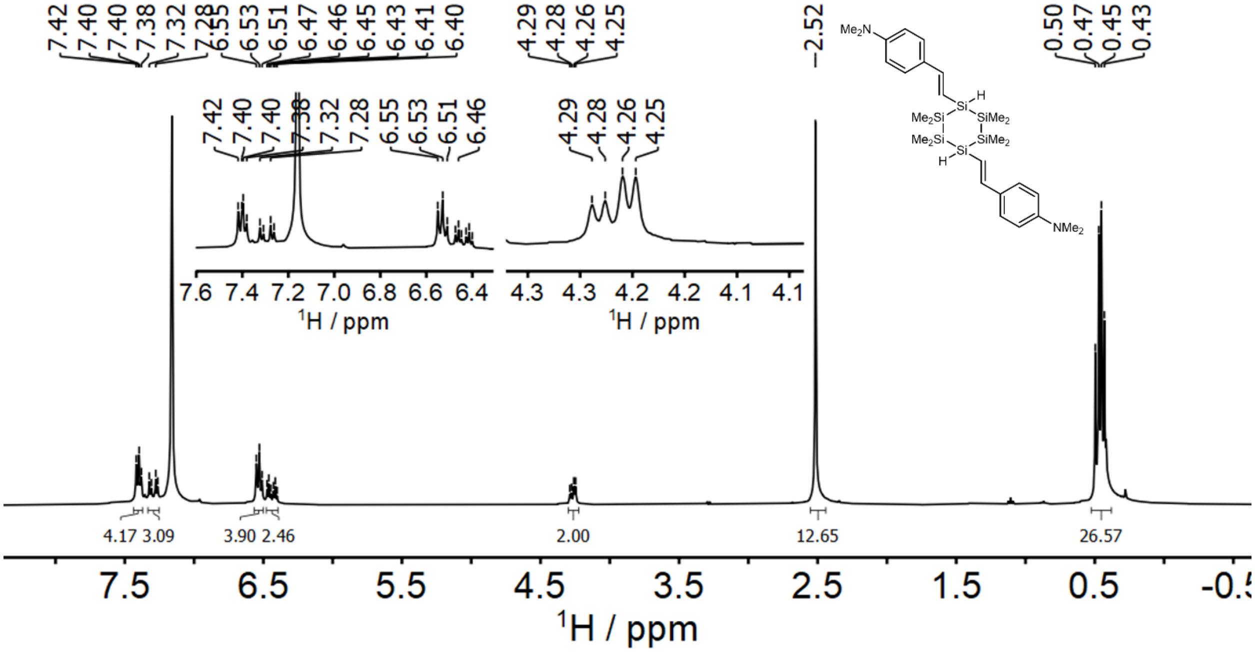


4.5.3 ^{29}Si{^{1}H} NMR Spectrum of **1e** (79 MHz, C_6D_6). $^{1}J_{\text{Si-H}}$ = 7 Hz.

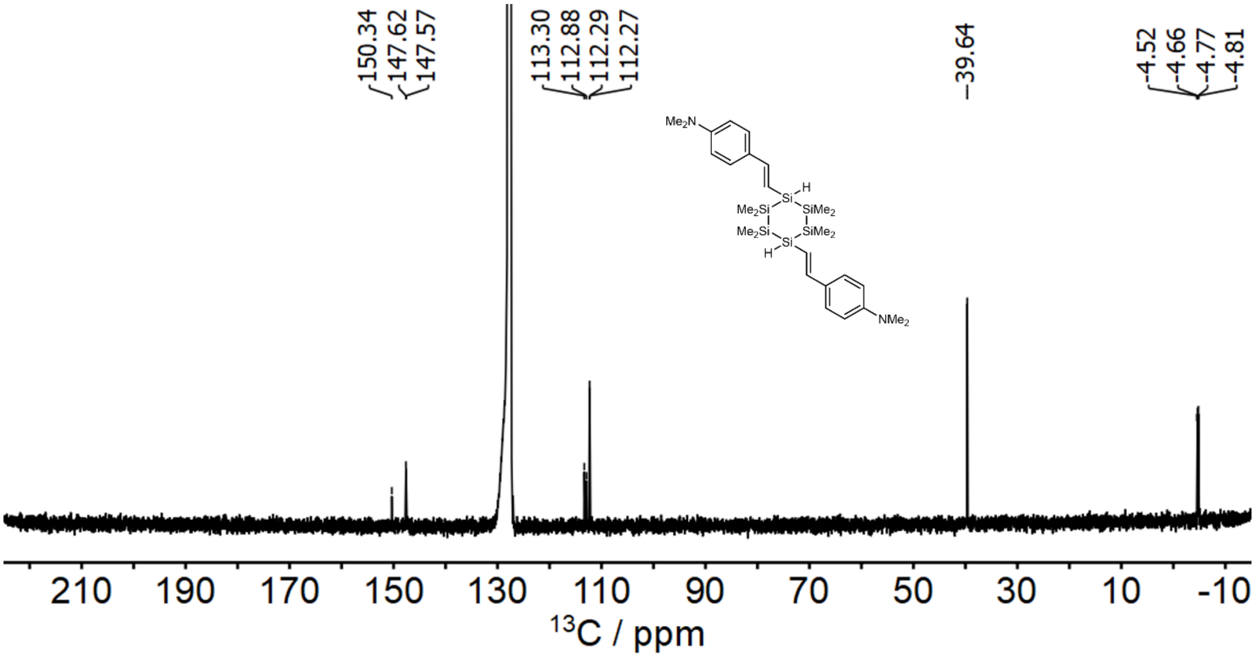


4.6 NMR Spectra of 1f

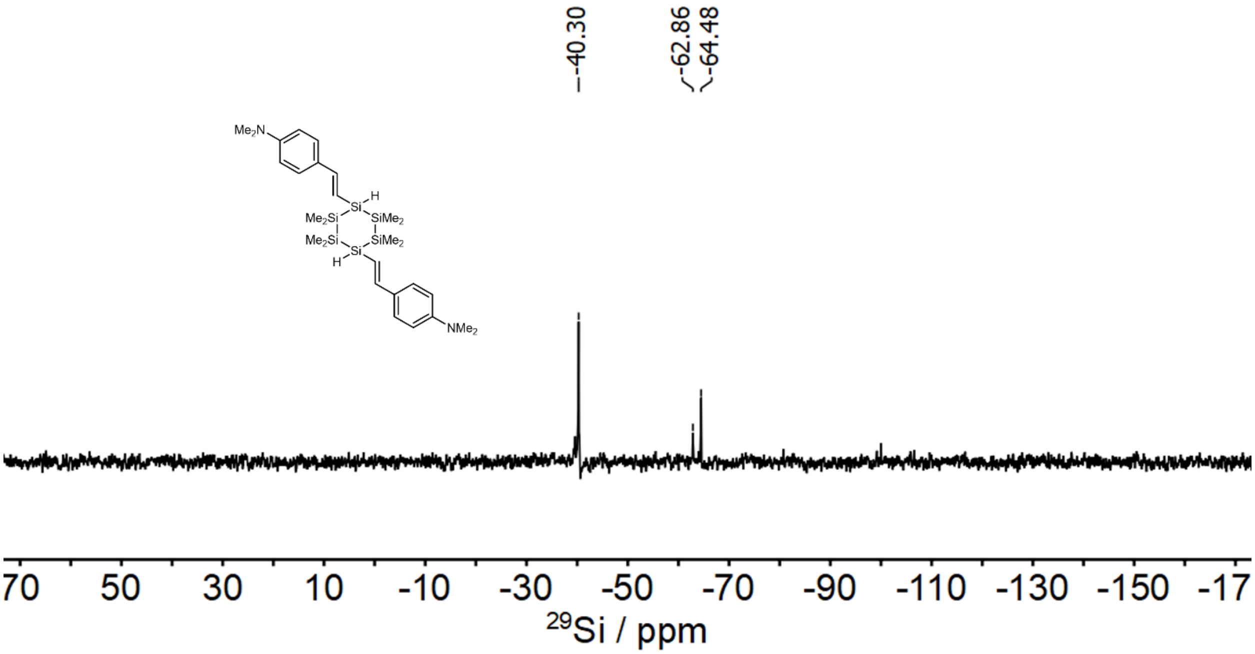
4.6.1 ^{1}H NMR Spectrum of **1f** (400 MHz, C_6D_6)



4.6.2 $^{13}C\{^{1}H\}$ NMR Spectrum of **1f** (101 MHz, C_6D_6)

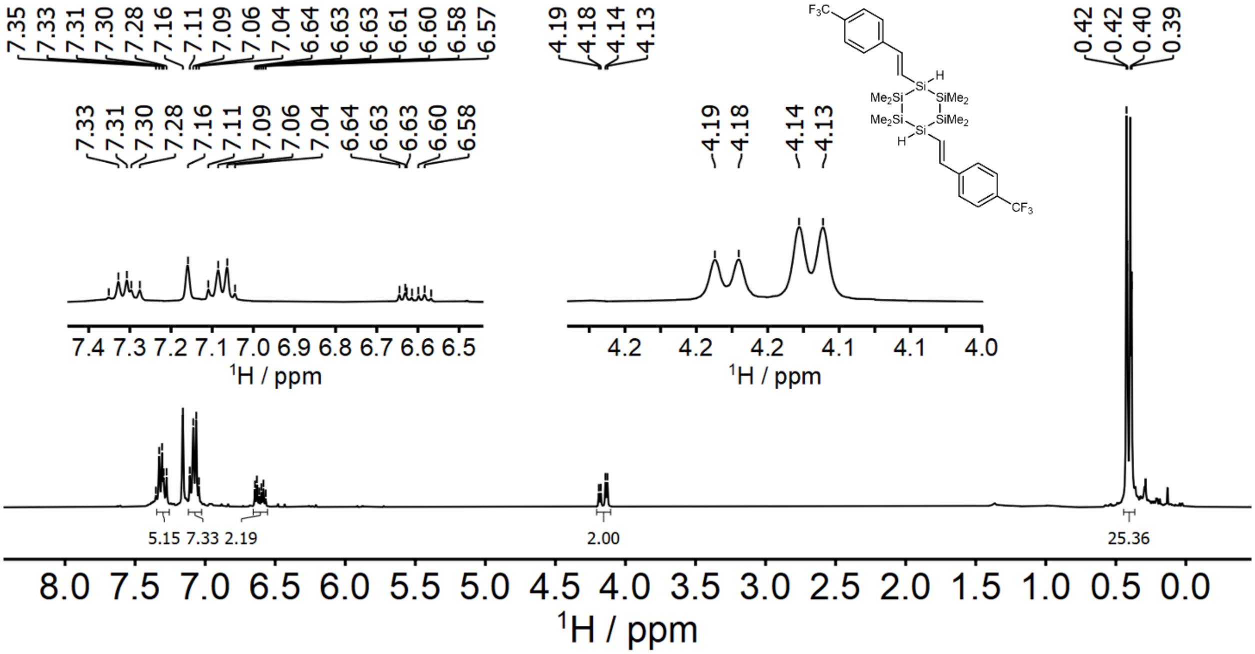


4.6.3 $^{29}Si\{^{1}H\}$ NMR Spectrum of **1f** (79 MHz, C_6D_6). $^{1}J_{Si\text{-}H}$ = 7 Hz.

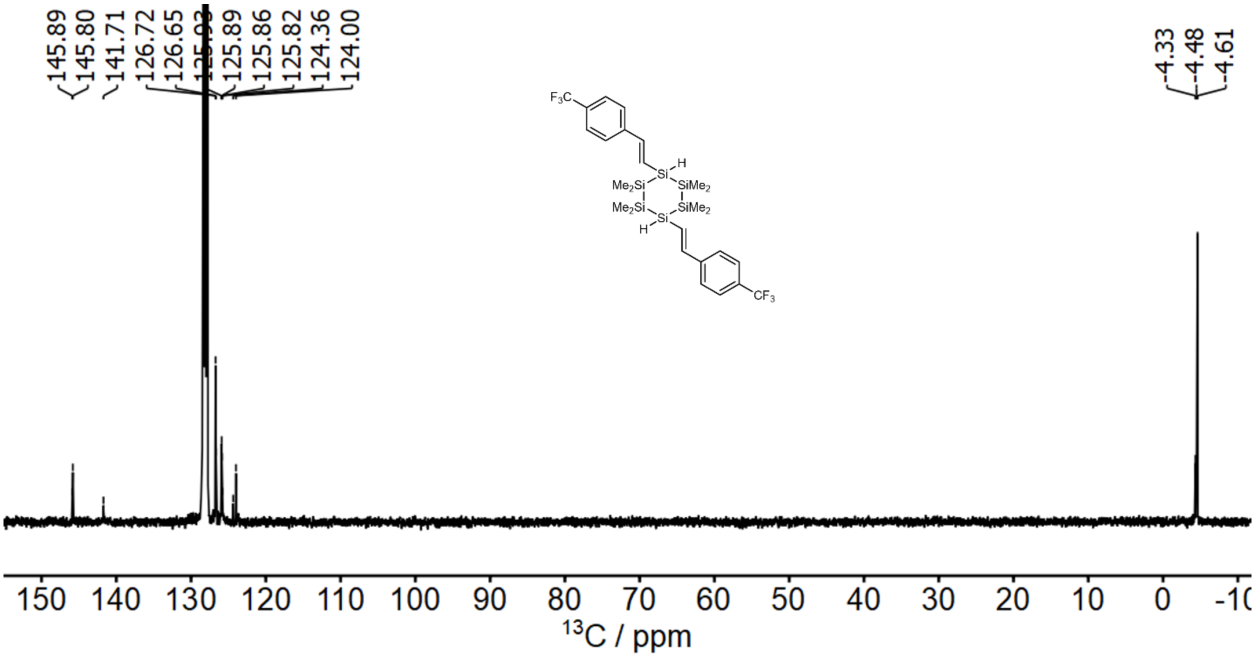


4.7 NMR Spectra of 1g

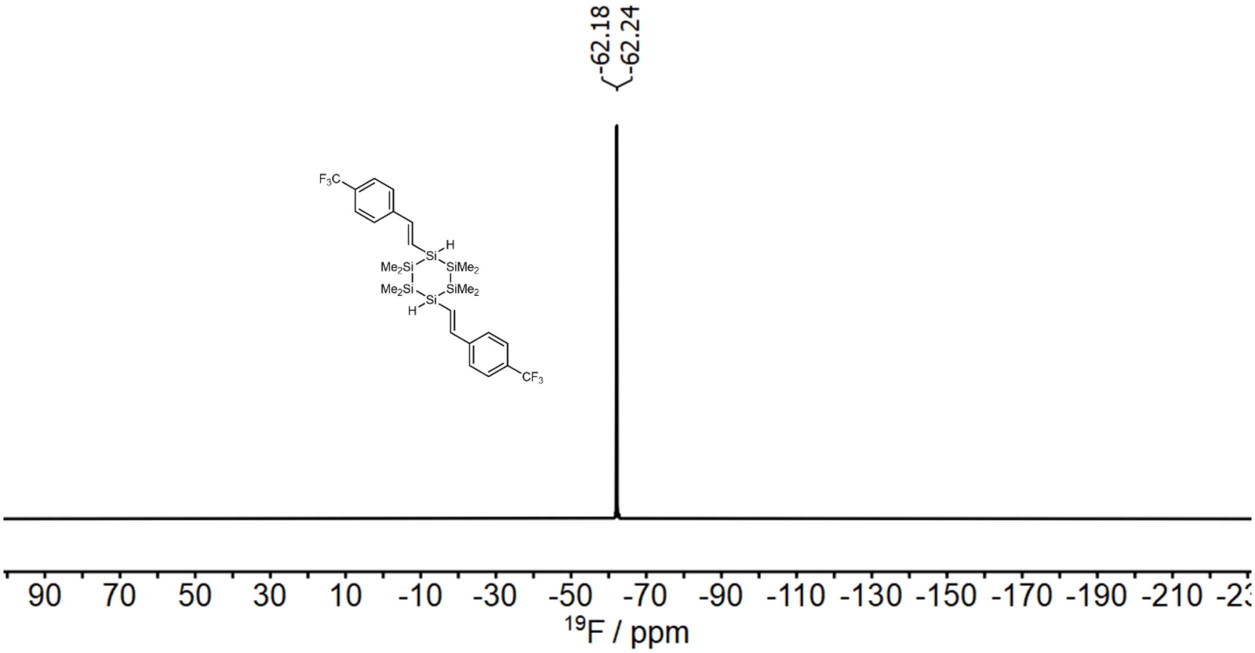
4.7.1 ^1H NMR Spectrum of **1g** (400 MHz, C_6D_6)



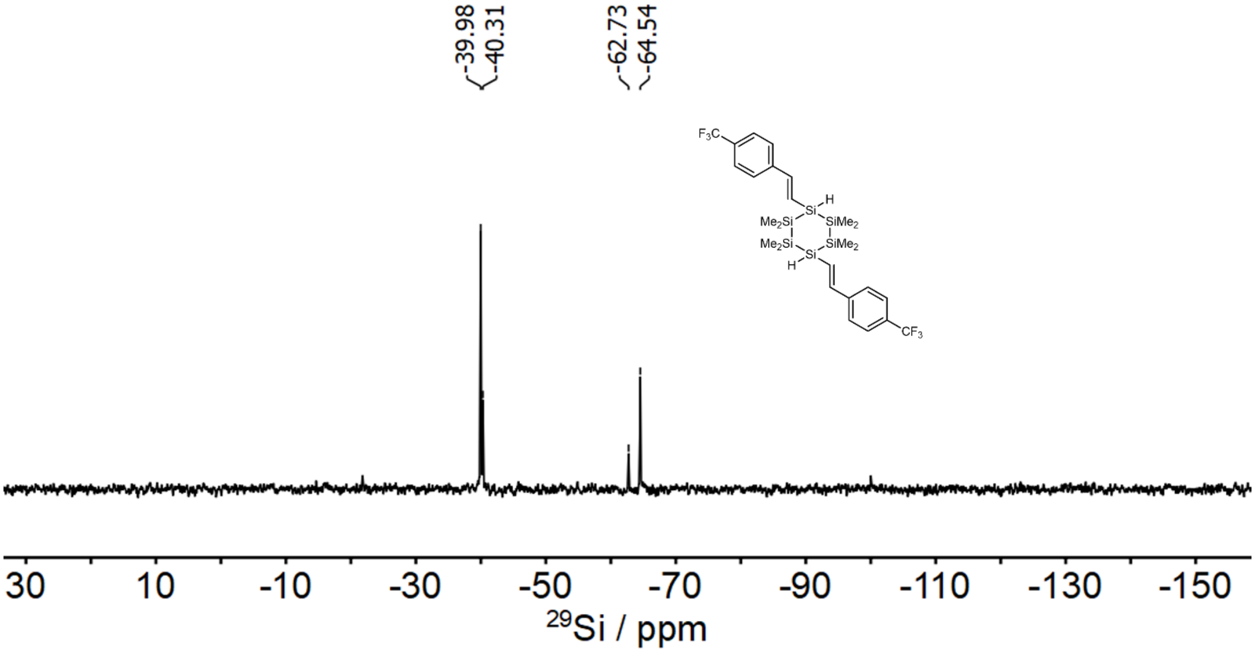
4.7.2 $^{13}C\{^1H\}$ NMR Spectrum of **1g** (101 MHz, C_6D_6)



4.7.3 $^{19}F\{^1H\}$ NMR Spectrum of **1g** (376 MHz, C_6D_6).

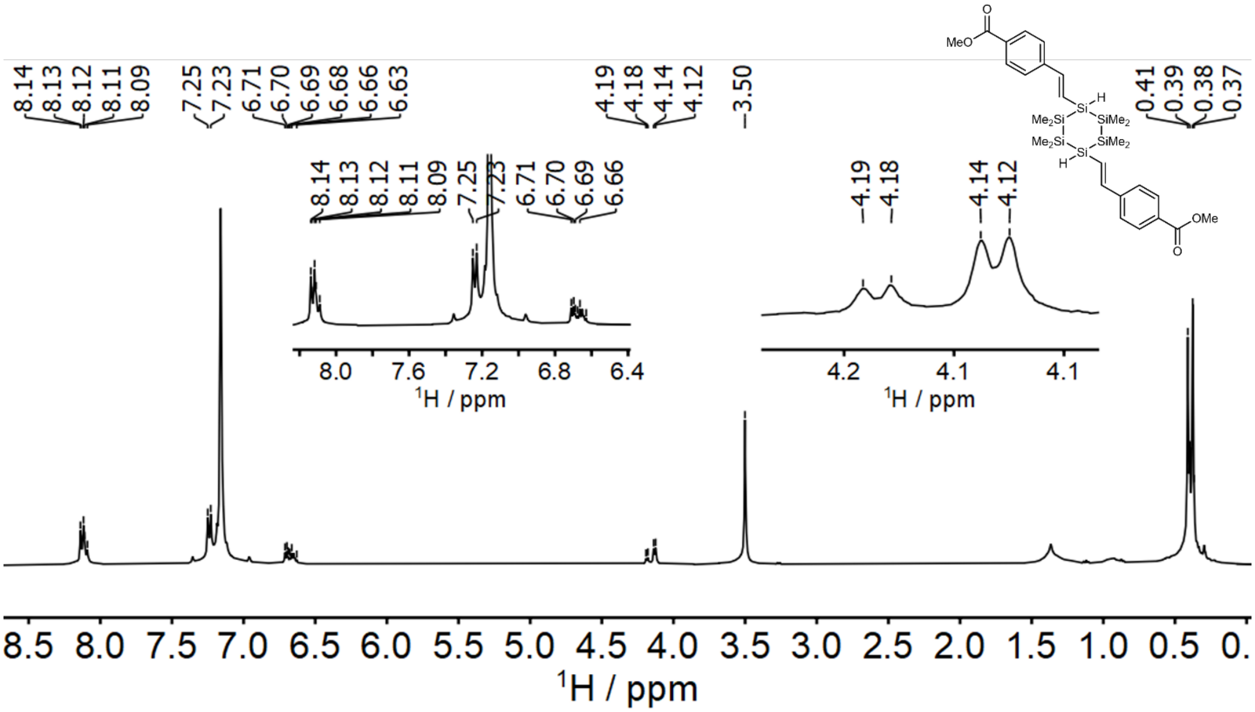


4.7.4 $^{29}Si\{^1H\}$ NMR Spectrum of **1g** (79 MHz, C_6D_6). $^1J_{Si\text{-}H}$ = 7 Hz.

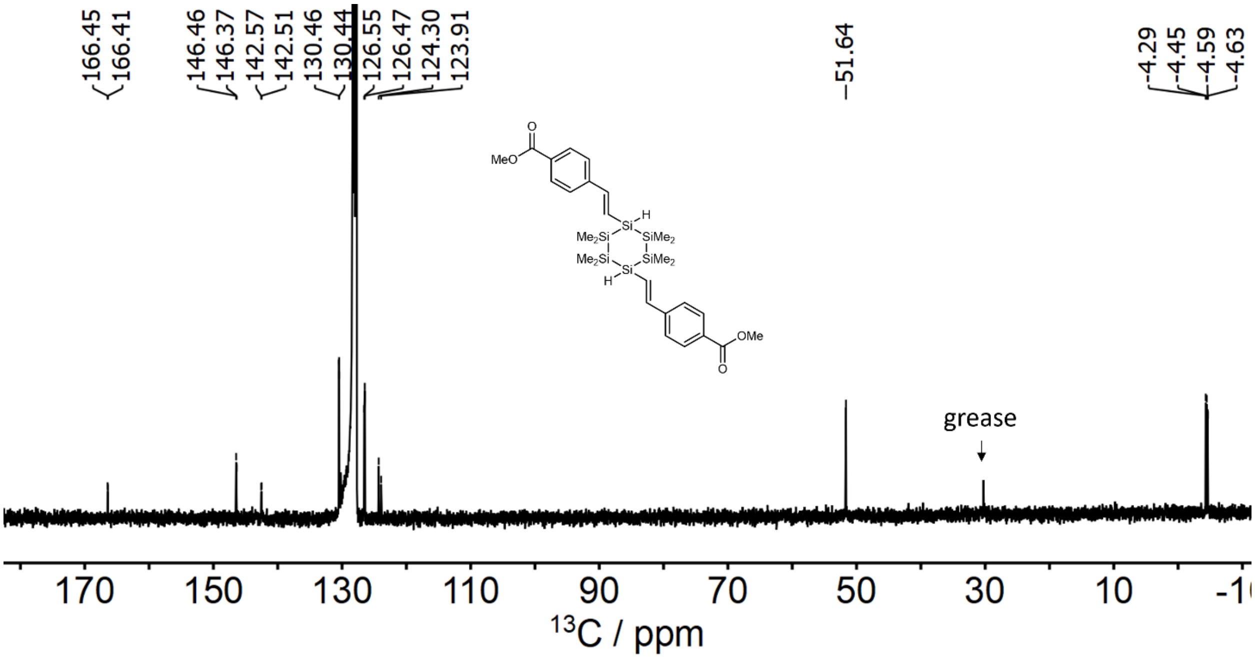


4.8 NMR Spectra of 1h

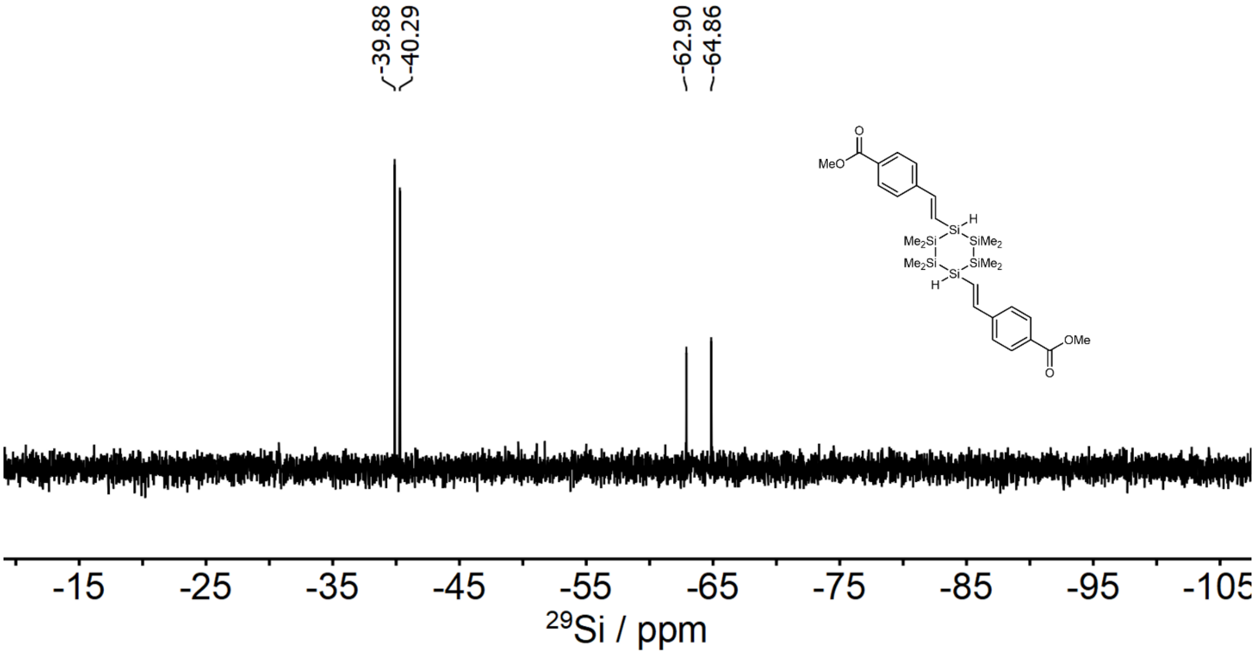
4.8.1 ^{1}H NMR Spectrum of **1h** (400 MHz, C_6D_6)



4.8.2 ^{13}C{^{1}H} NMR Spectrum of **1h** (101 MHz, C_6D_6)

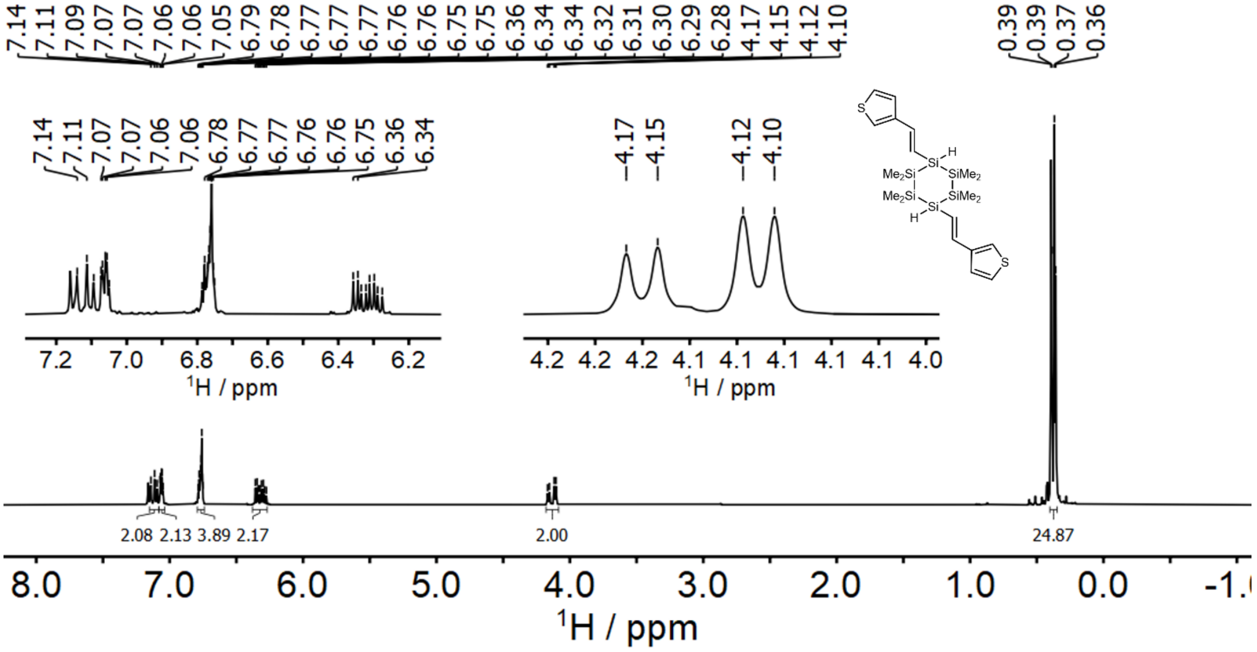


4.8.3 ^{29}Si{^{1}H} NMR Spectrum of **1h** (79 MHz, C_6D_6). $^{1}J_{Si\text{-}H}$ = 7 Hz.

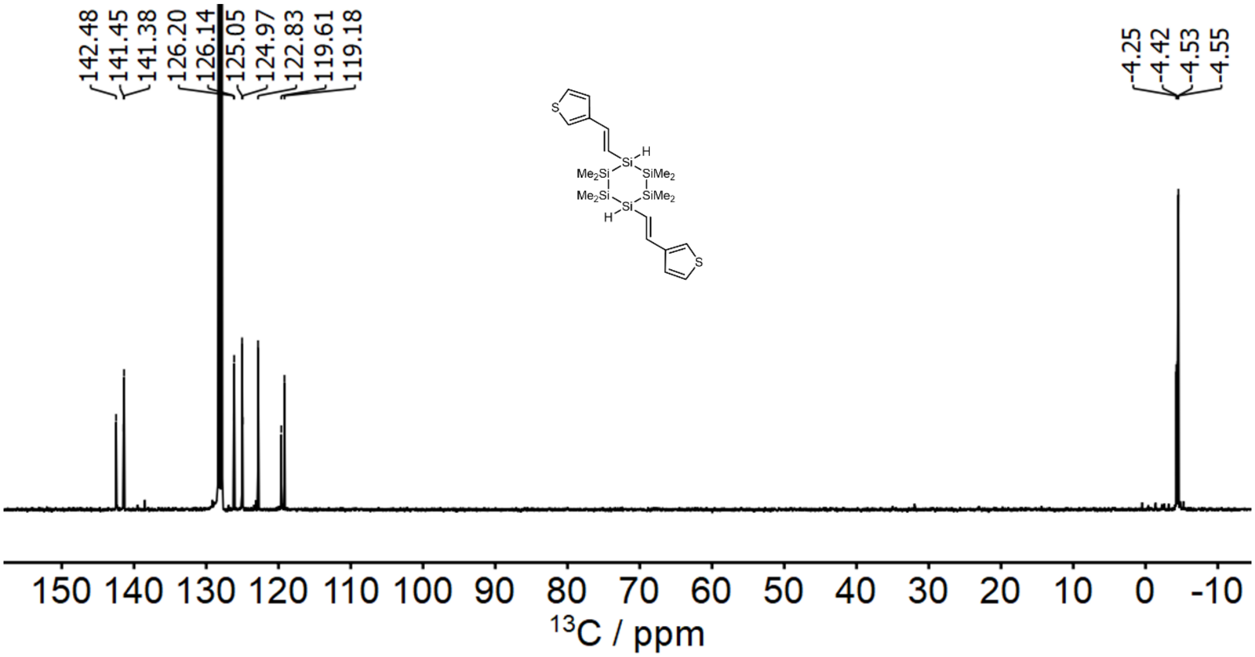


4.9 NMR Spectra of 1i

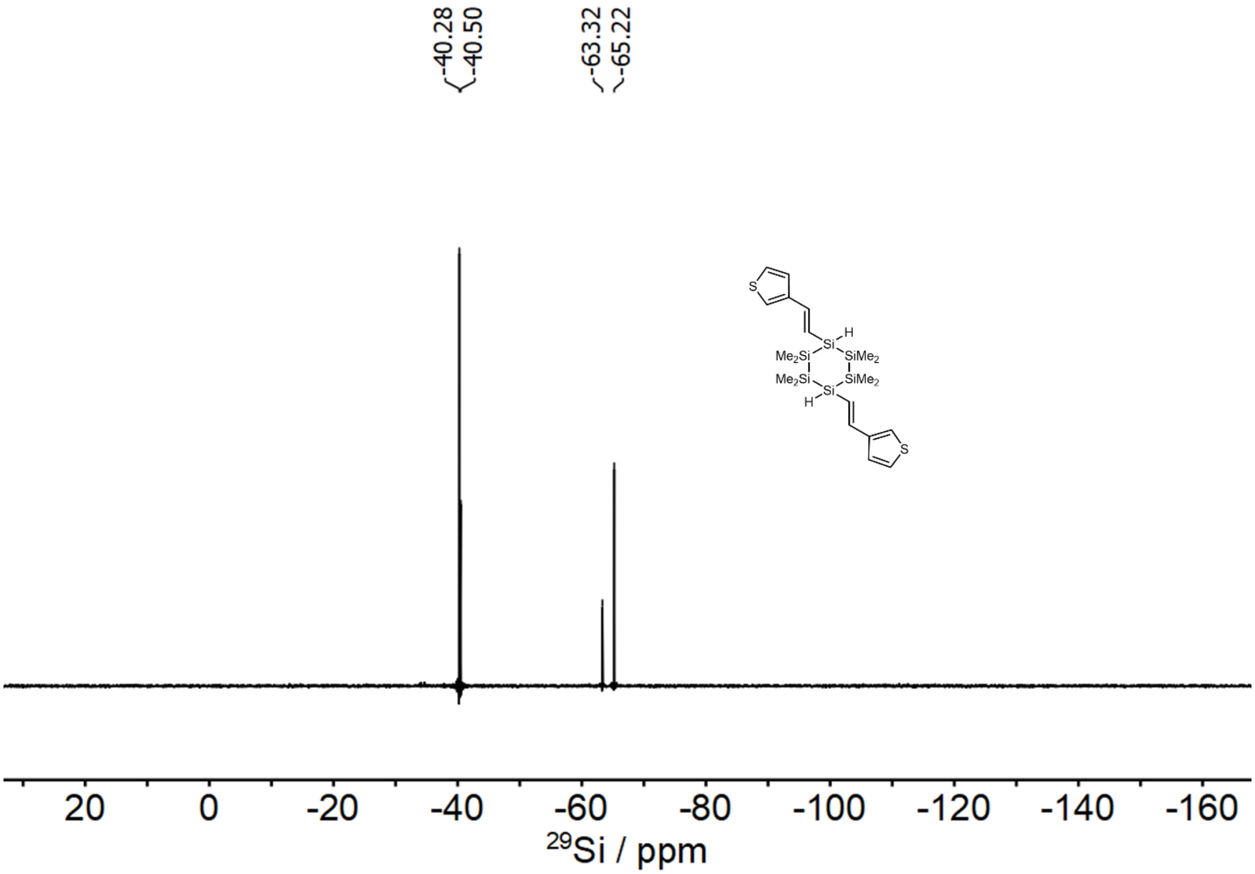
4.9.1 ^{1}H NMR Spectrum of **1i** (400 MHz, C_6D_6)



4.9.2 ^{13}C{^{1}H} NMR Spectrum of **1i** (101 MHz, C_6D_6)

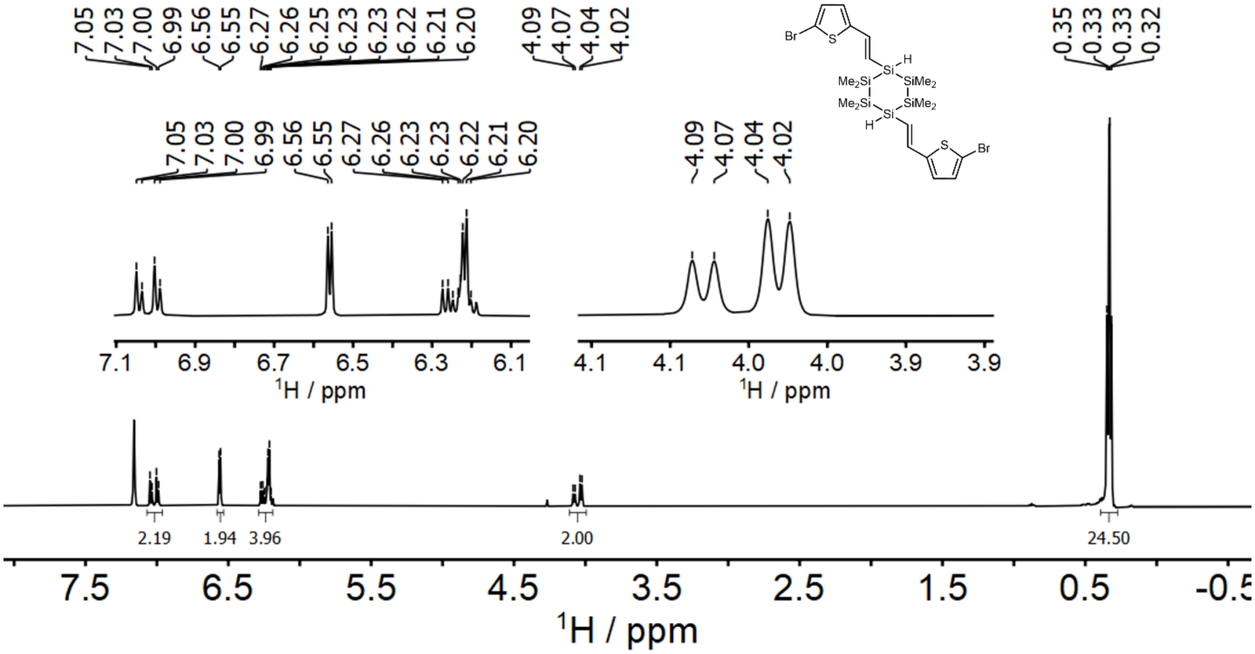


4.9.3 ^{29}Si{^{1}H} NMR Spectrum of **1i** (79 MHz, C_6D_6). $^{1}J_{\text{Si-H}}$ = 7 Hz.

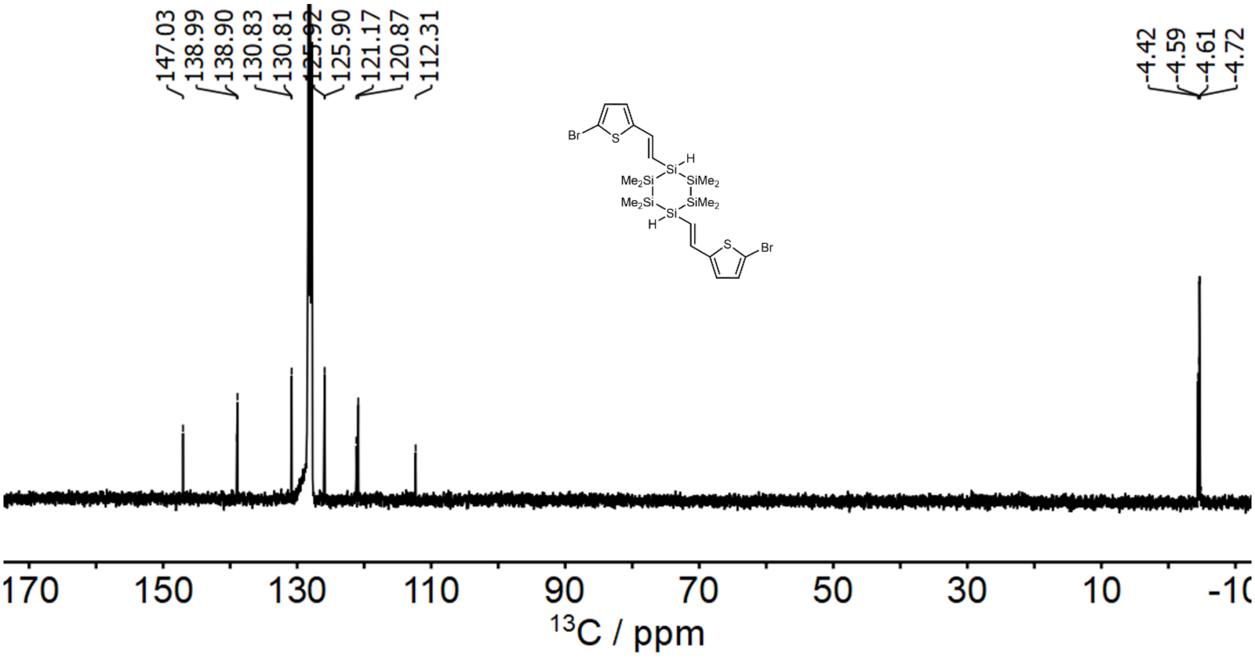


4.10 NMR Spectra of 1j

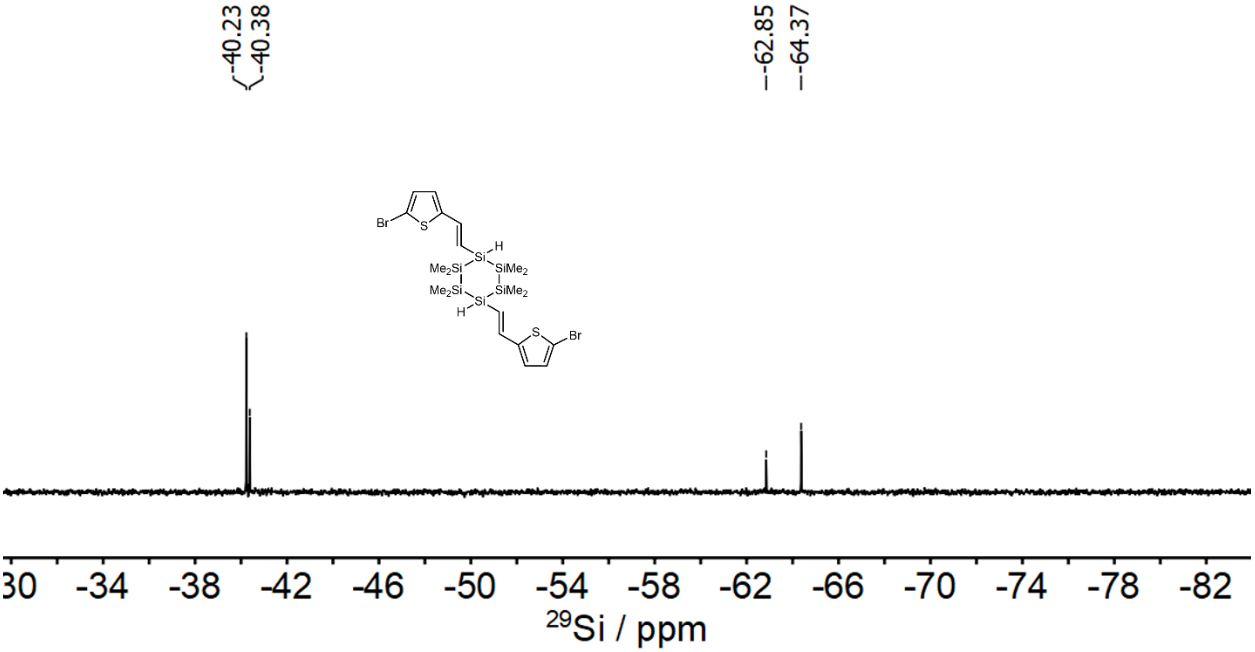
4.10.1 ^{1}H NMR Spectrum of **1j** (400 MHz, C_6D_6)



4.10.2 $^{13}C\{^1H\}$ NMR Spectrum of **1j** (101 MHz, C_6D_6)

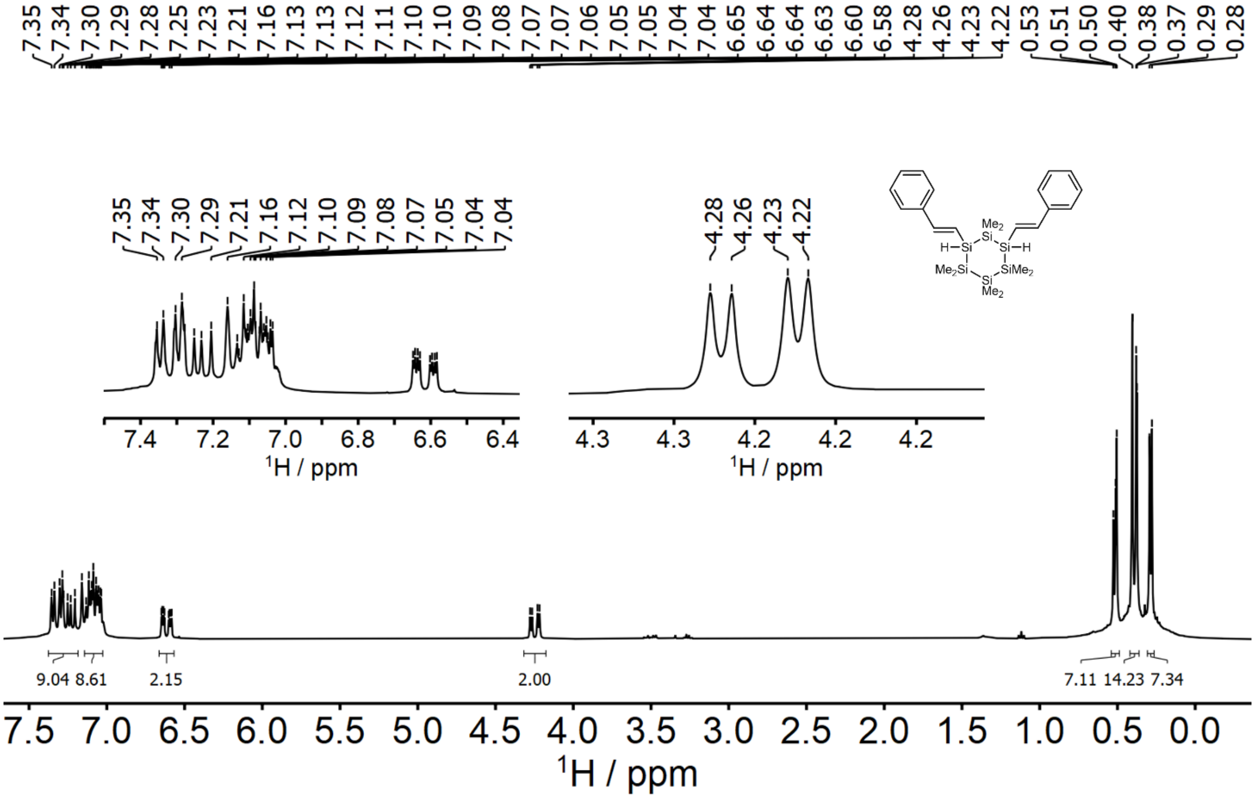


4.10.3 ^{29}Si{^{1}H} NMR Spectrum of **1j** (79 MHz, C_6D_6). $^{1}J_{\text{Si-H}}$ = 7 Hz.

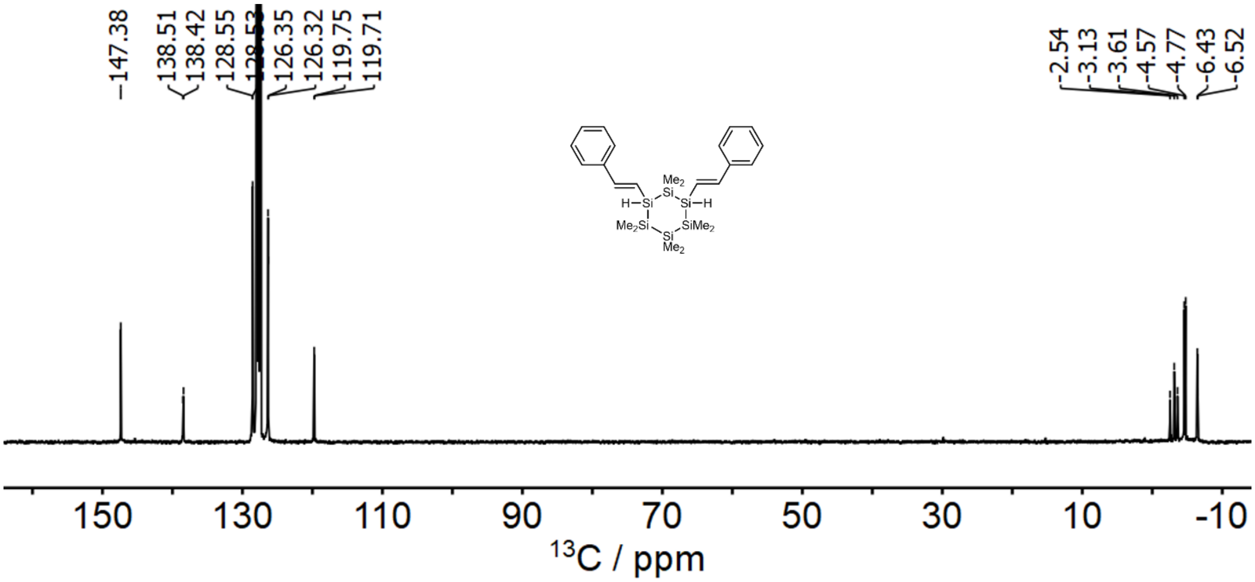


4.11 NMR Spectra of 2a

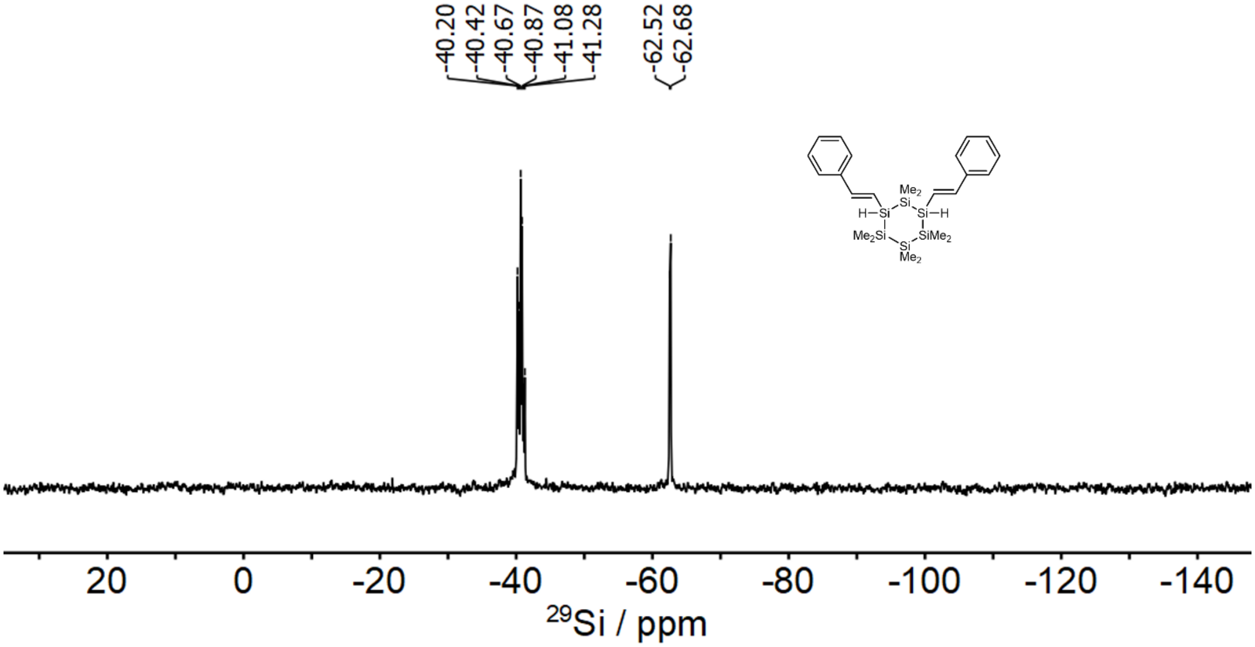
4.11.1 ^{1}H NMR Spectrum of **2a** (400 MHz, C_6D_6)



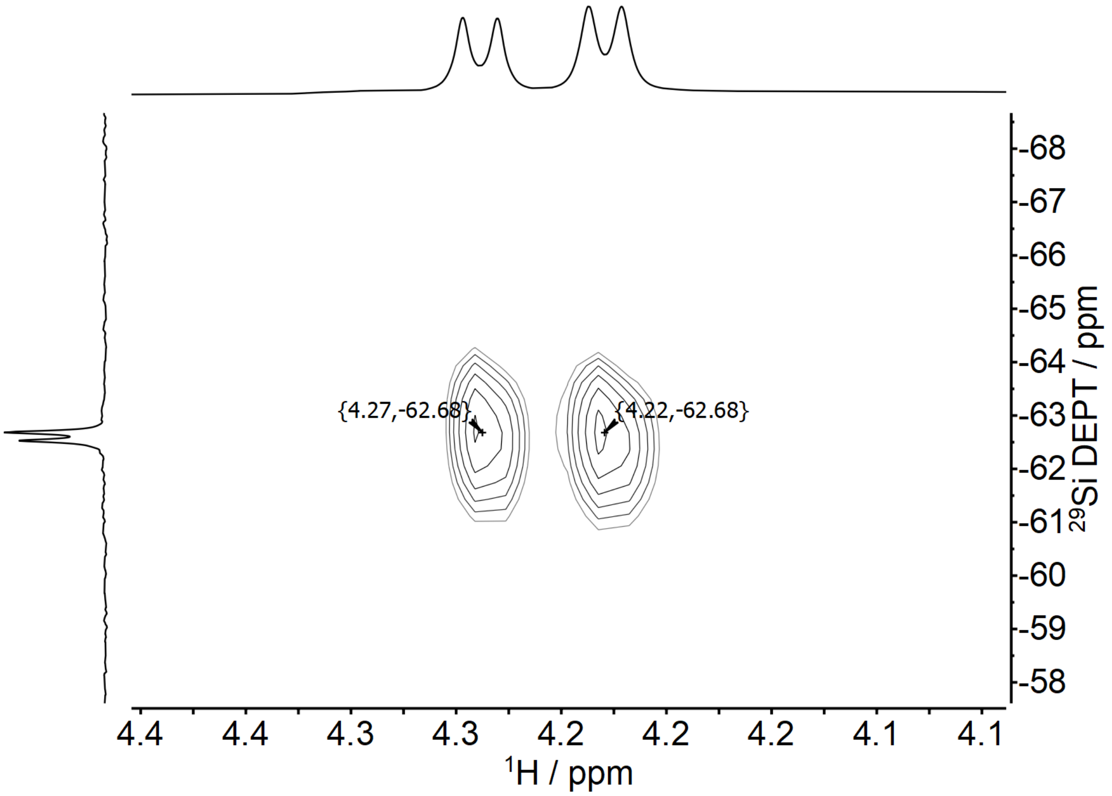
4.11.2 $^{13}C\{^1H\}$ NMR Spectrum of **2a** (101 MHz, C_6D_6)



4.11.3 $^{29}Si\{^1H\}$ NMR Spectrum of **2a** (79 MHz, C_6D_6). $^1J_{Si\text{-}H}$ = 7 Hz.

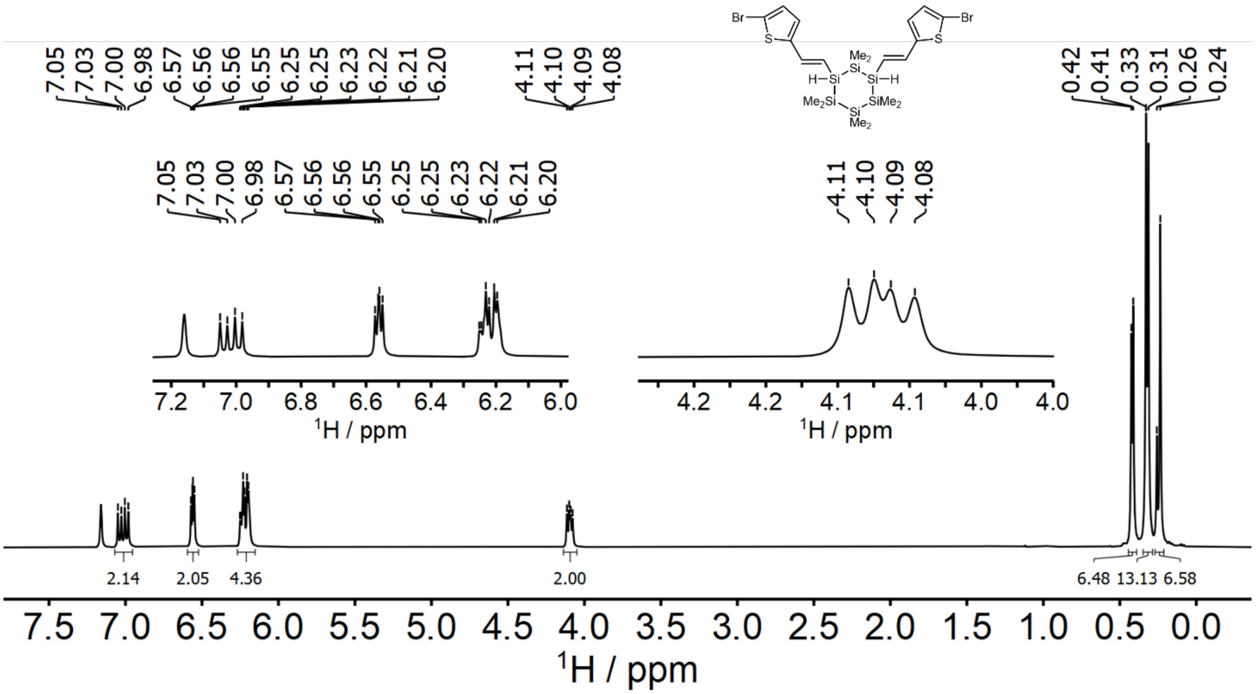


4.11.4 ^{1}H-^{29}Si HSQC NMR spectrum (400 MHz, C_6D_6) of **2a.** $^{1}J_{\text{Si-H}}$ = 120 Hz.

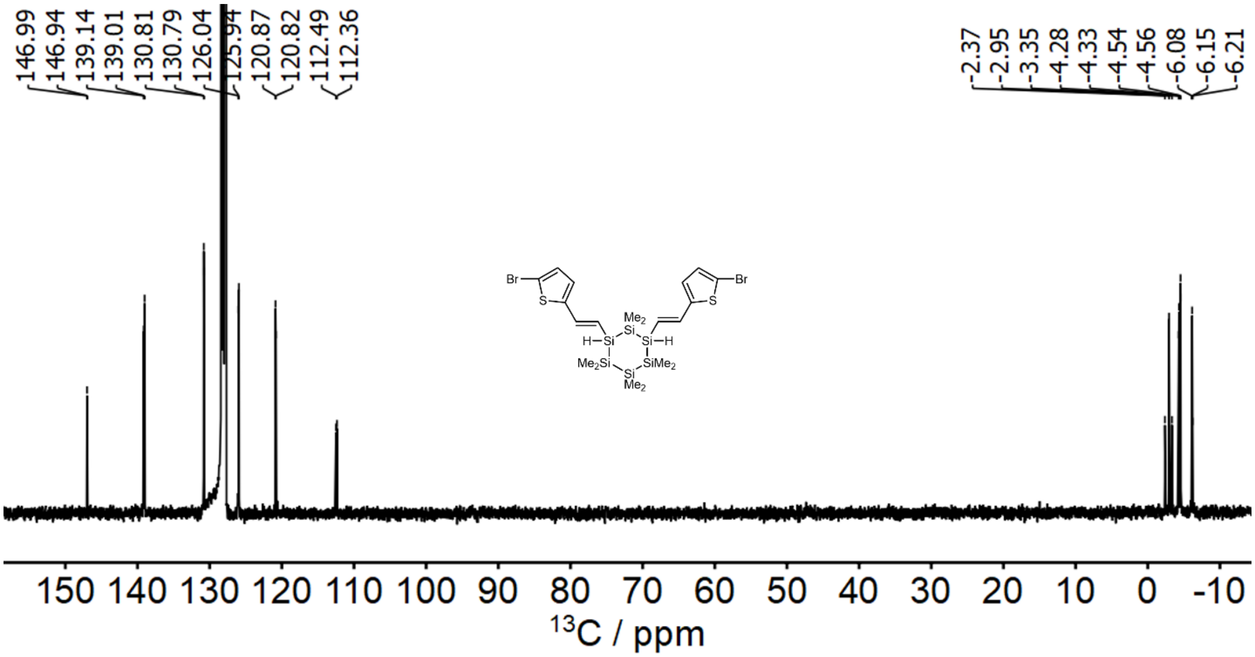


4.12 NMR Spectra of 2b

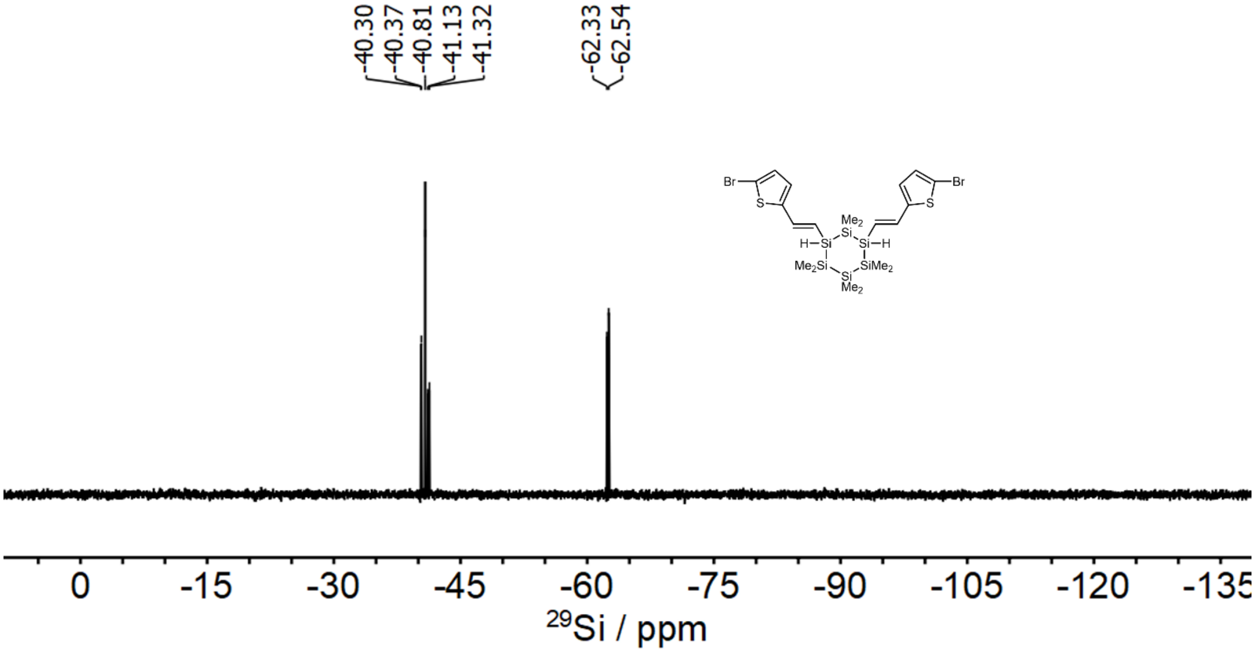
4.12.1 ^{1}H NMR Spectrum of **2b** (400 MHz, C_6D_6)



4.12.2 $^{13}C\{^{1}H\}$ NMR Spectrum of **2b** (101 MHz, C_6D_6)

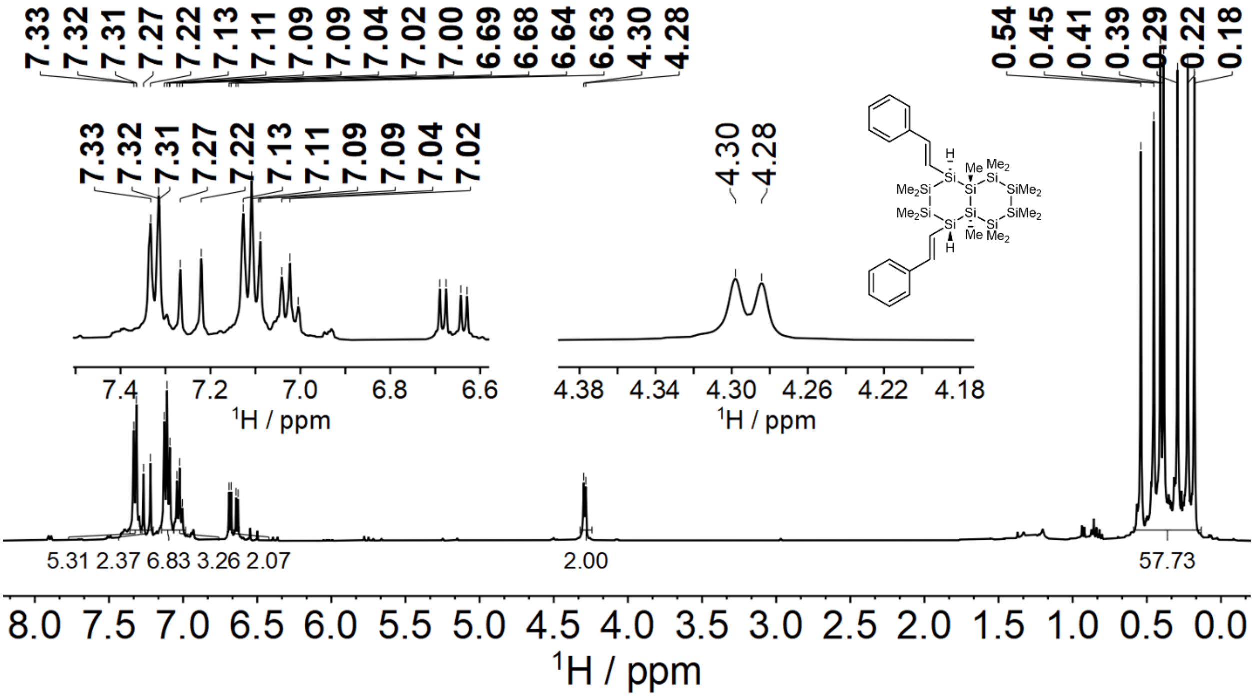


4.12.3 $^{29}Si\{^{1}H\}$ NMR Spectrum of **2b** (79 MHz, C_6D_6). $^{1}J_{Si\text{-}H}$ = 7 Hz.

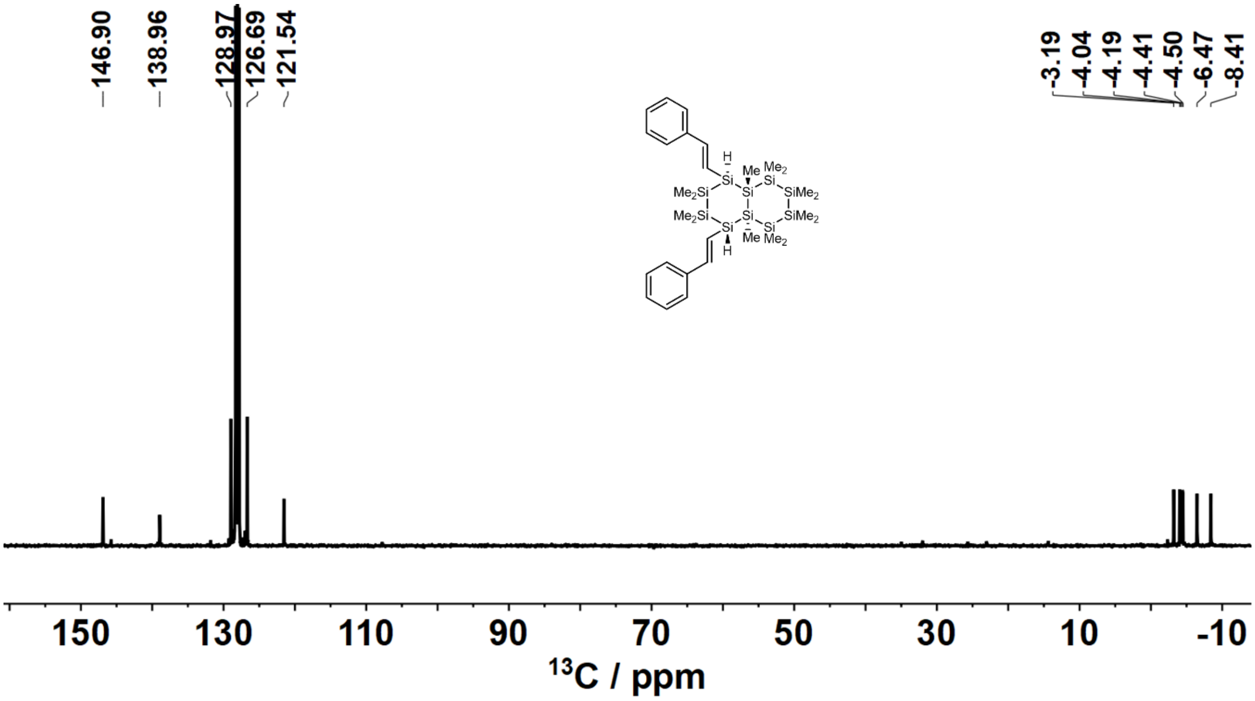


4.13 NMR Spectra of 3a

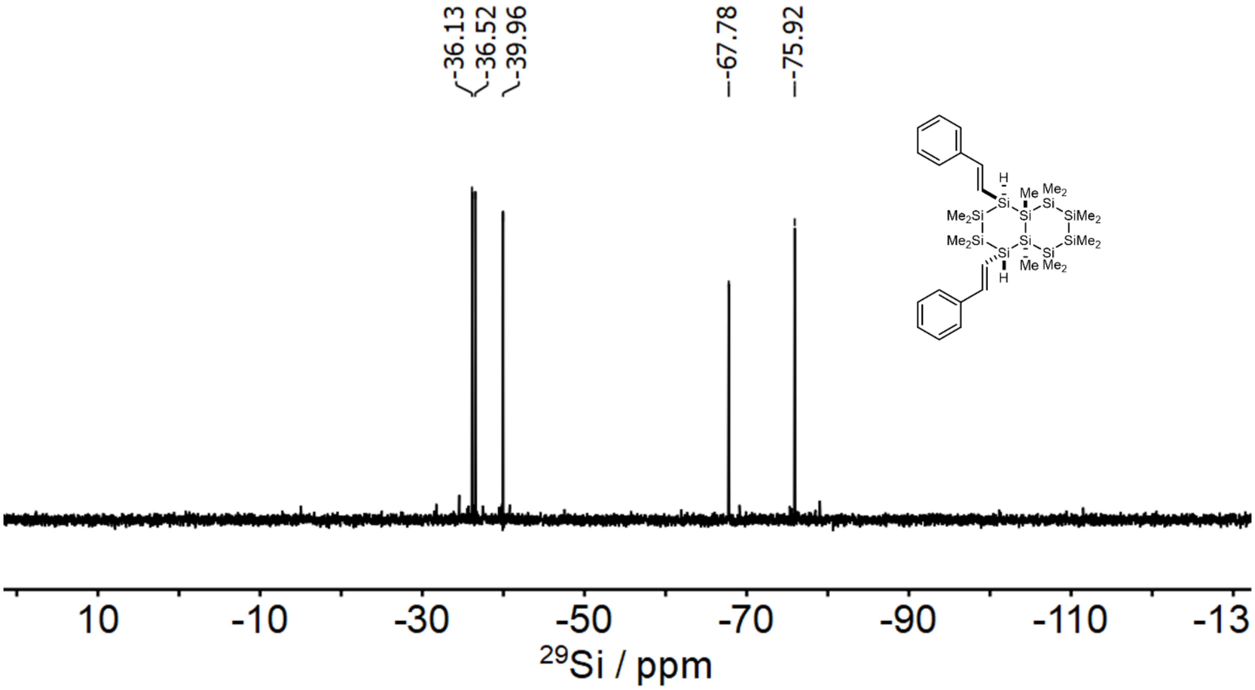
4.13.1 ^{1}H NMR Spectrum of **3a** (400 MHz, C_6D_6)



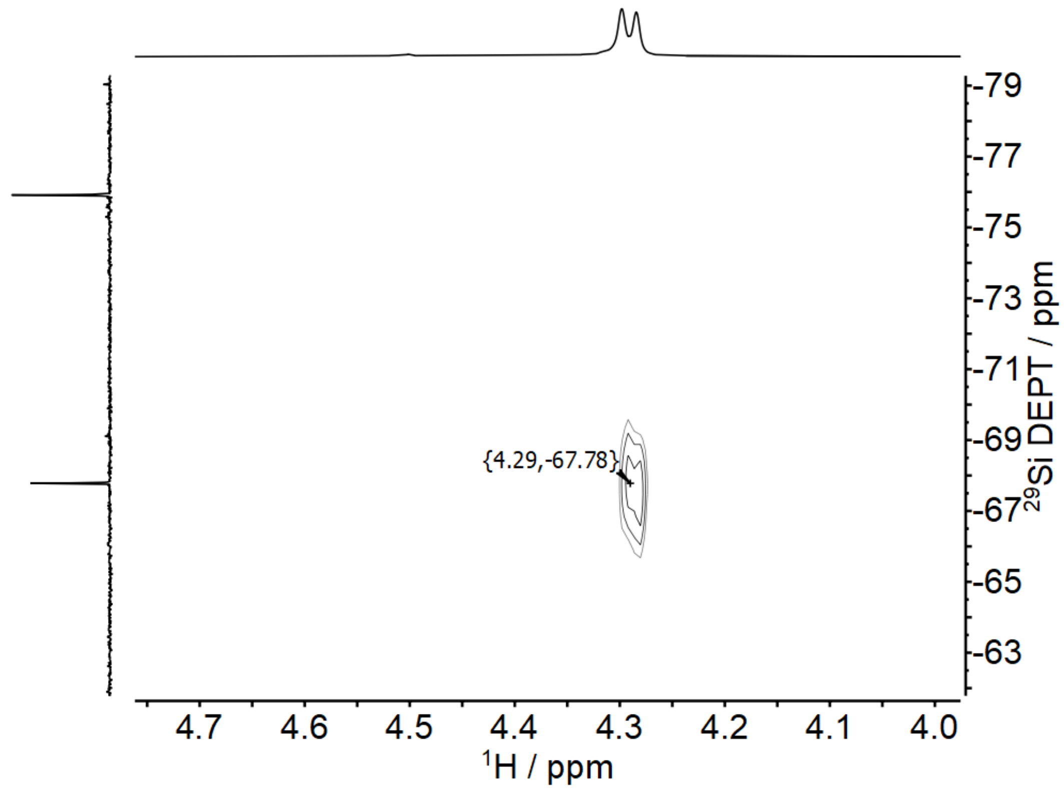
4.13.2 ^{13}C{^{1}H} NMR Spectrum of **3a** (101 MHz, C_6D_6)



4.13.3 ^{29}Si{^{1}H} NMR Spectrum of **3a** (79 MHz, C_6D_6). $^{1}J_{Si\text{-}H}$ = 7 Hz.

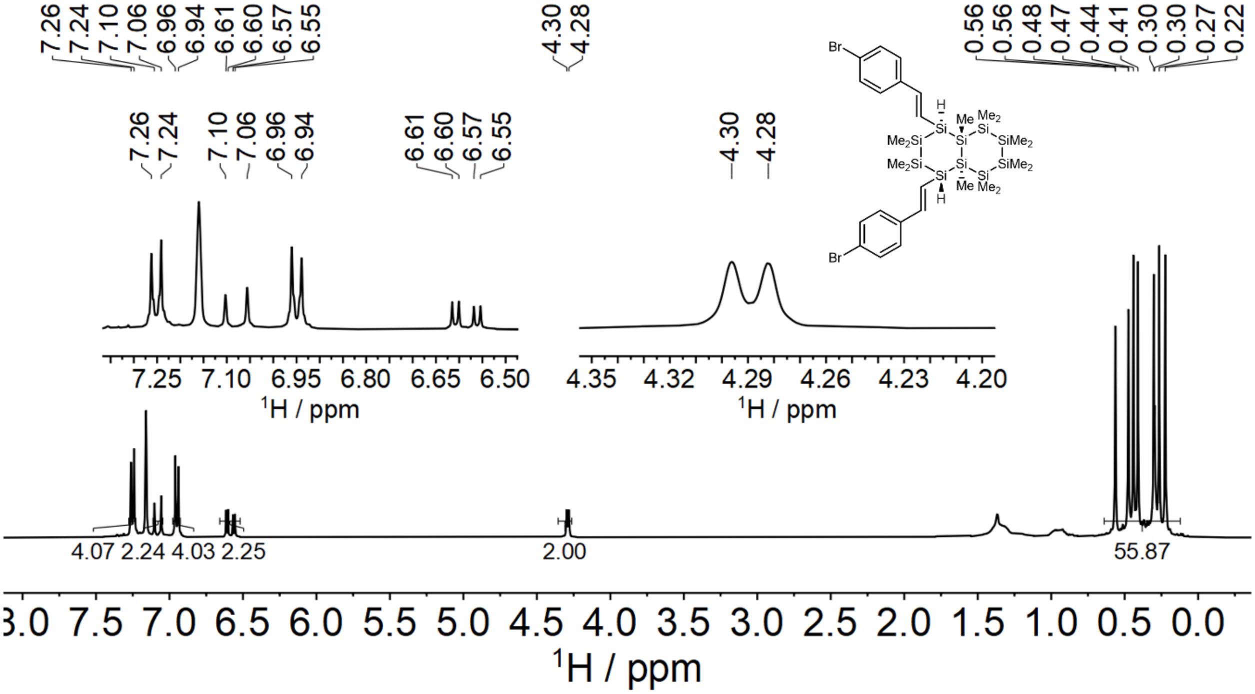


4.13.4 ^{1}H-^{29}Si HSQC NMR spectrum (400 MHz, C_6D_6) of **3a.** $^{1}J_{Si\text{-}H}$ = 120 Hz.

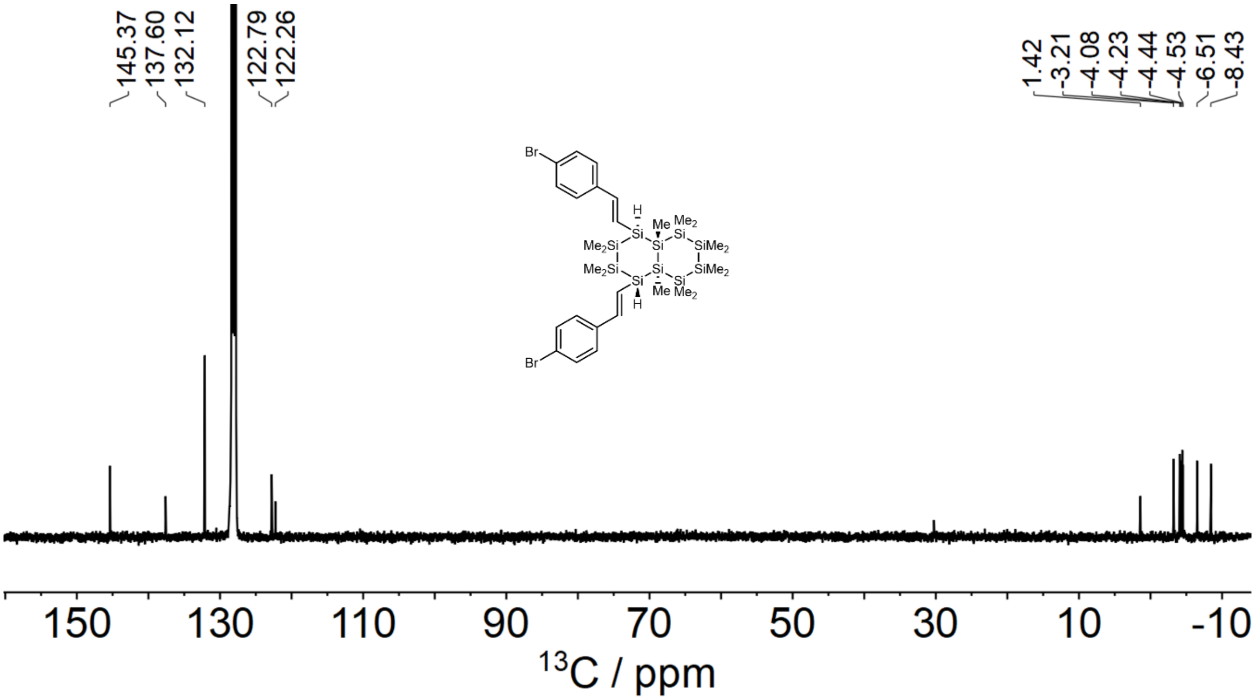


4.14 NMR Spectra of 3b

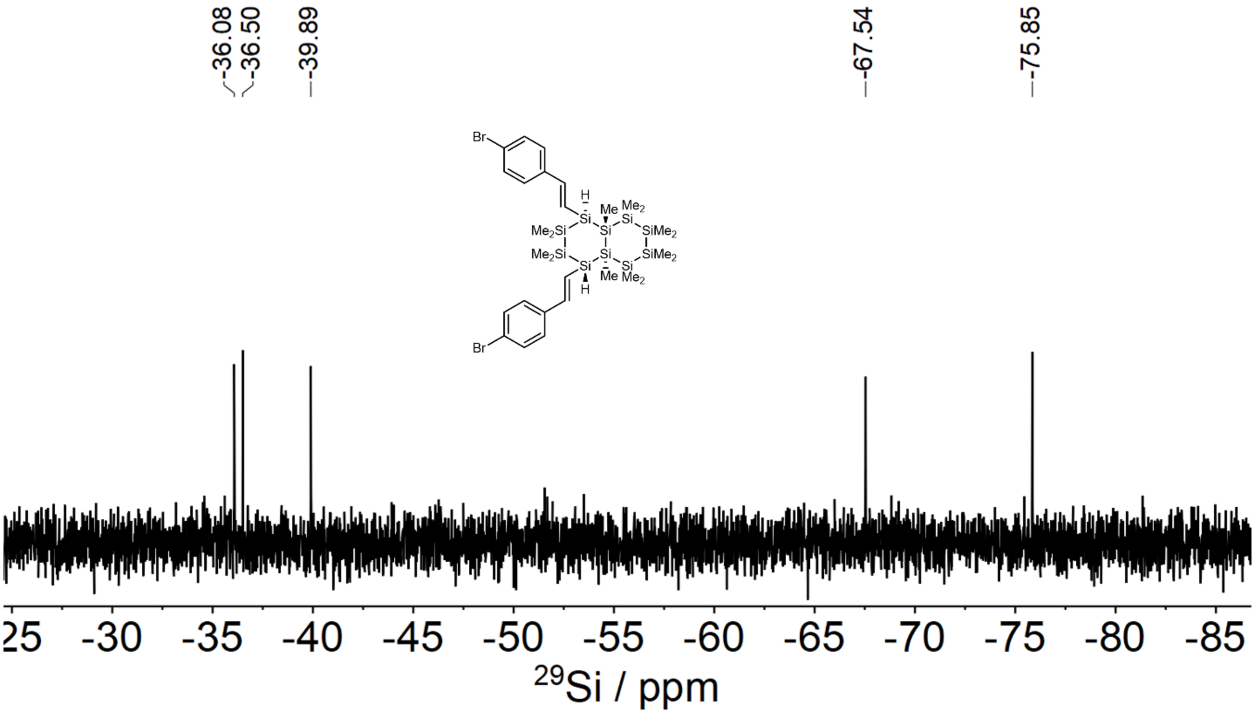
4.14.1 ^{1}H NMR Spectrum of **3b** (400 MHz, C_6D_6)



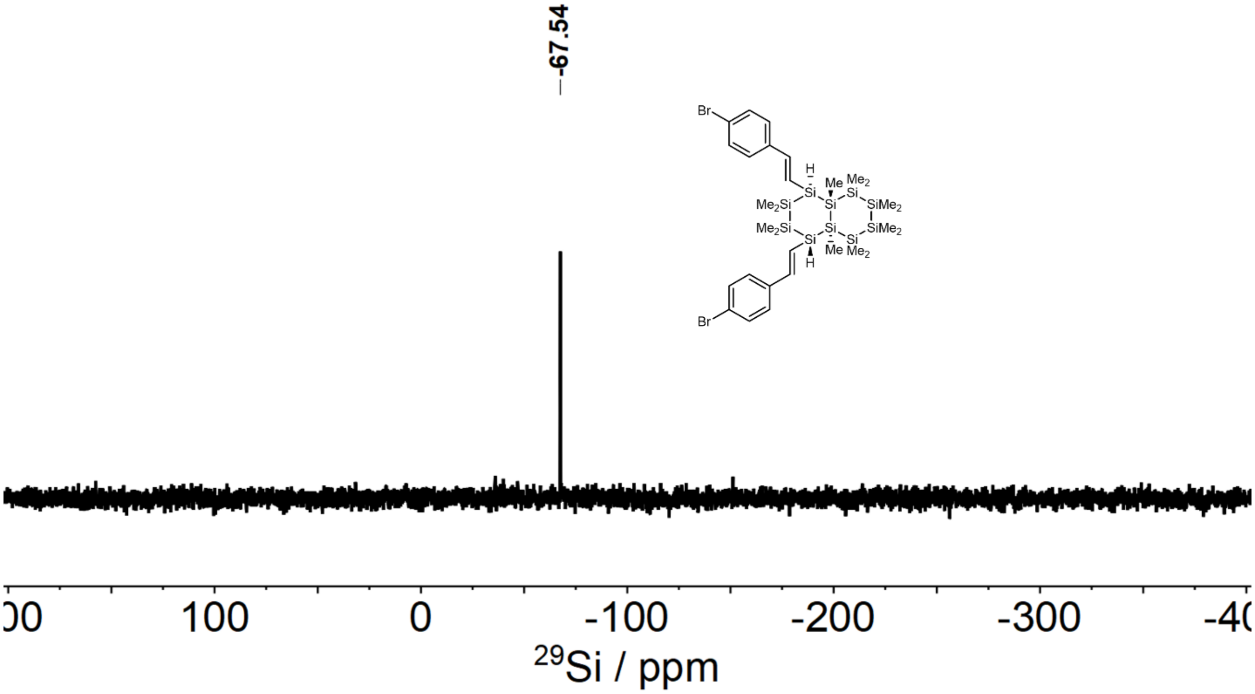
4.14.2 ^{13}C{^{1}H} NMR Spectrum of **3b** (101 MHz, C_6D_6)



4.14.3 ^{29}Si{^{1}H} NMR Spectrum of **3b** (79 MHz, C_6D_6). $^1J_{Si\text{-}H}$ = 7 Hz.

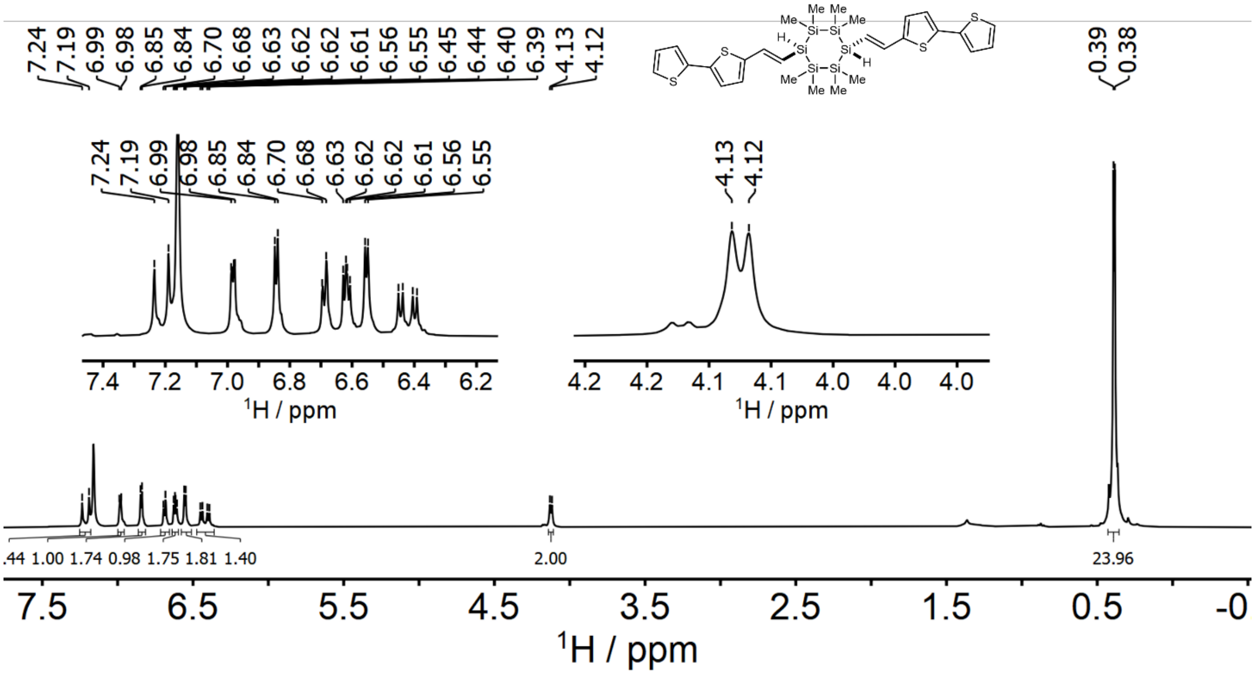


4.14.4 ^{29}Si{^{1}H} NMR Spectrum of **3b** (79 MHz, C_6D_6). $^1J_{Si\text{-}H}$ = 120 Hz.

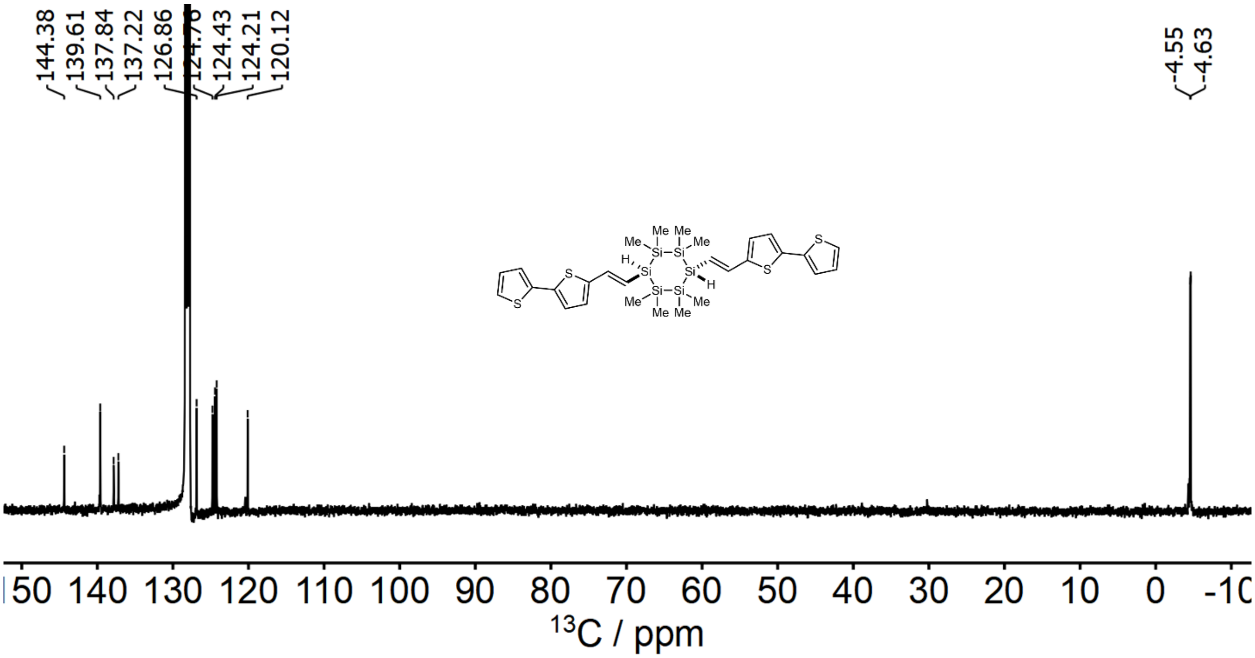


4.15 NMR Spectra of 1k

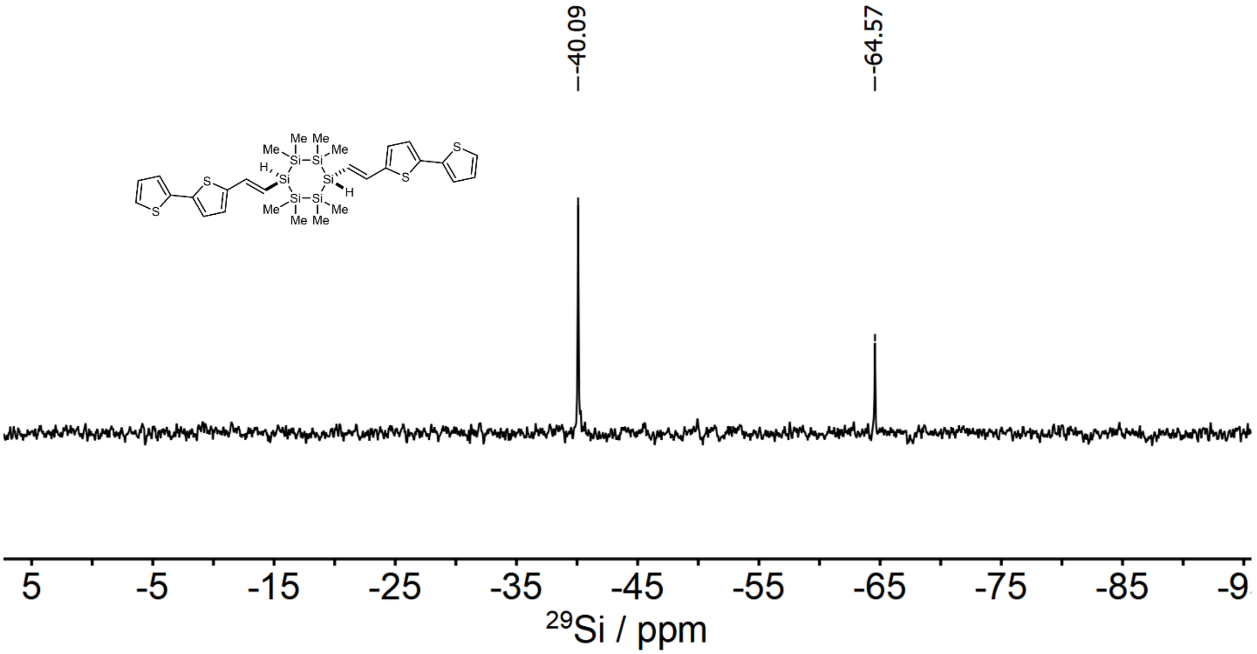
4.15.1 ^{1}H NMR Spectrum of **1k** (400 MHz, C_6D_6)



4.15.2 ^{13}C{^{1}H} NMR Spectrum of **1k** (101 MHz, C_6D_6)

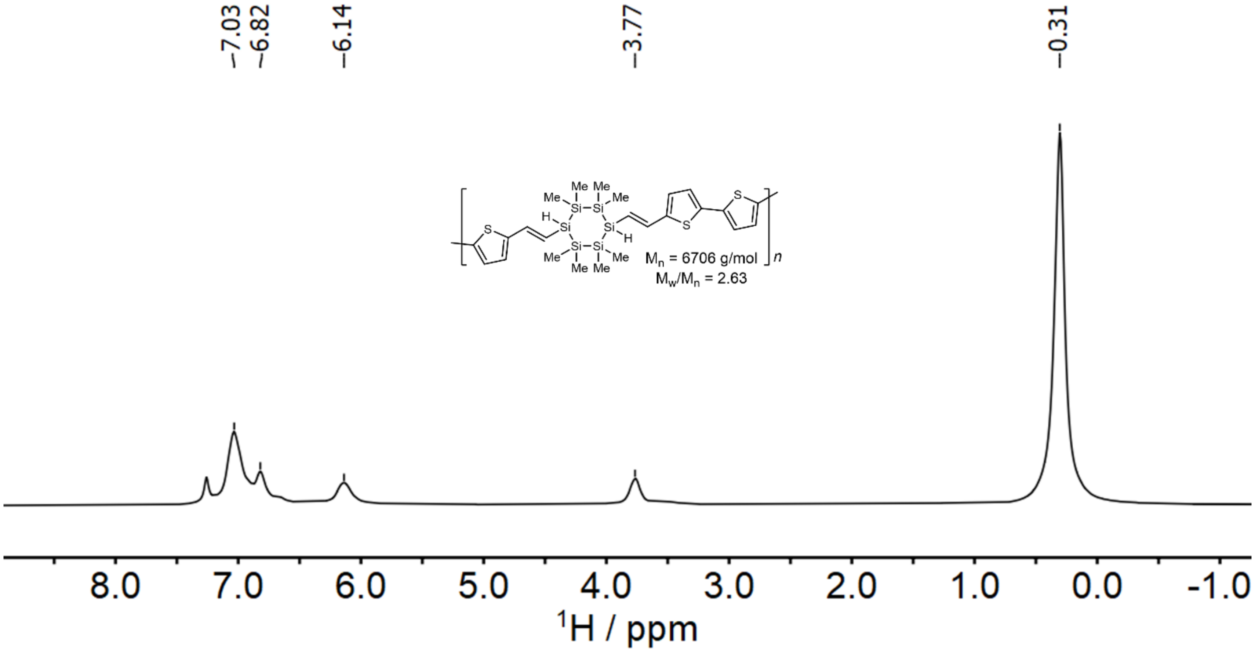


4.15.3 ^{29}Si{^{1}H} NMR Spectrum of **1k** (79 MHz, C_6D_6). $^{1}J_{Si\text{-}H}$ = 7 Hz.

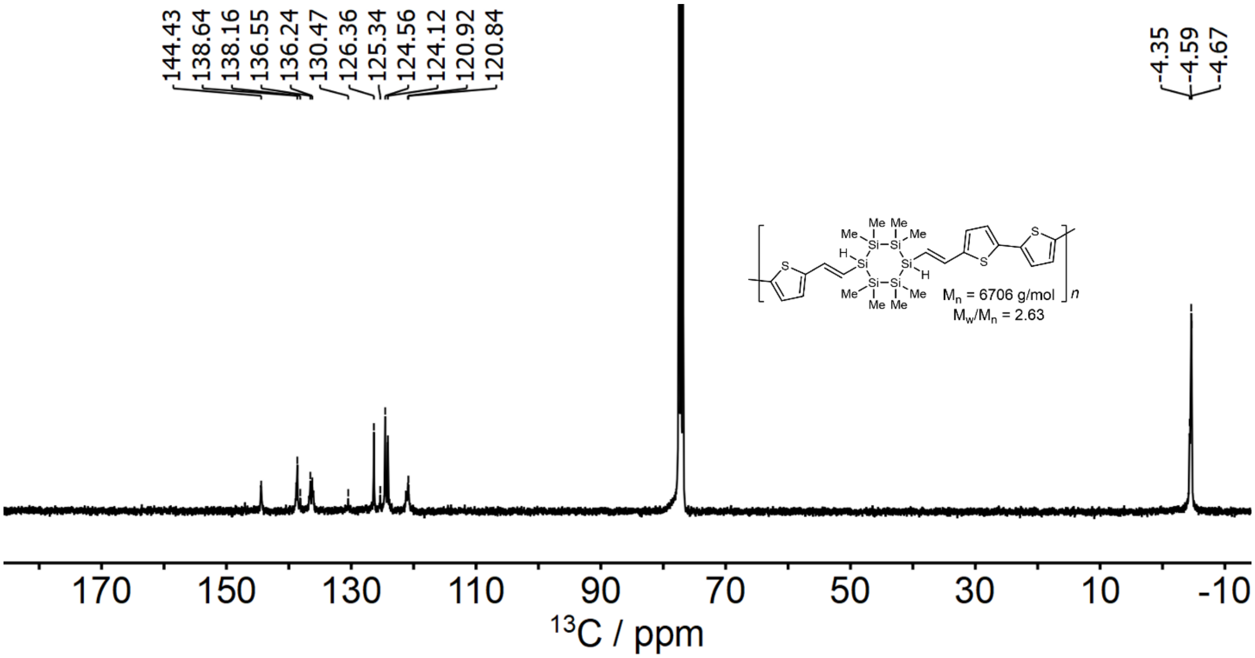


4.16 NMR Spectra of P1

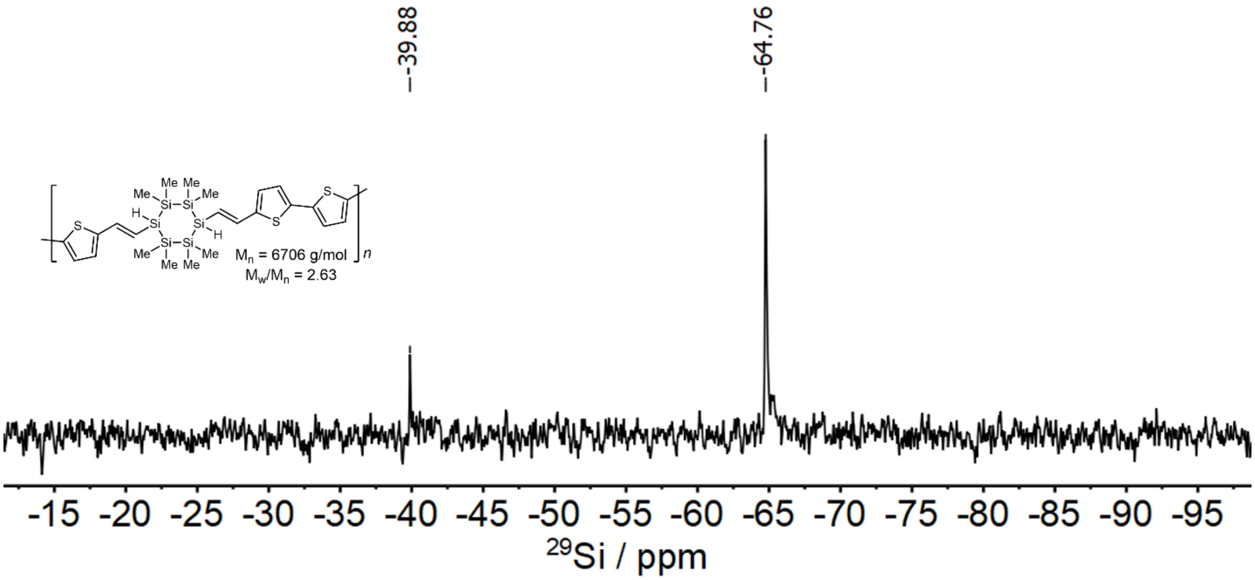
4.16.1 ^{1}H NMR Spectrum of **P1** (400 MHz, $CDCl_3$)



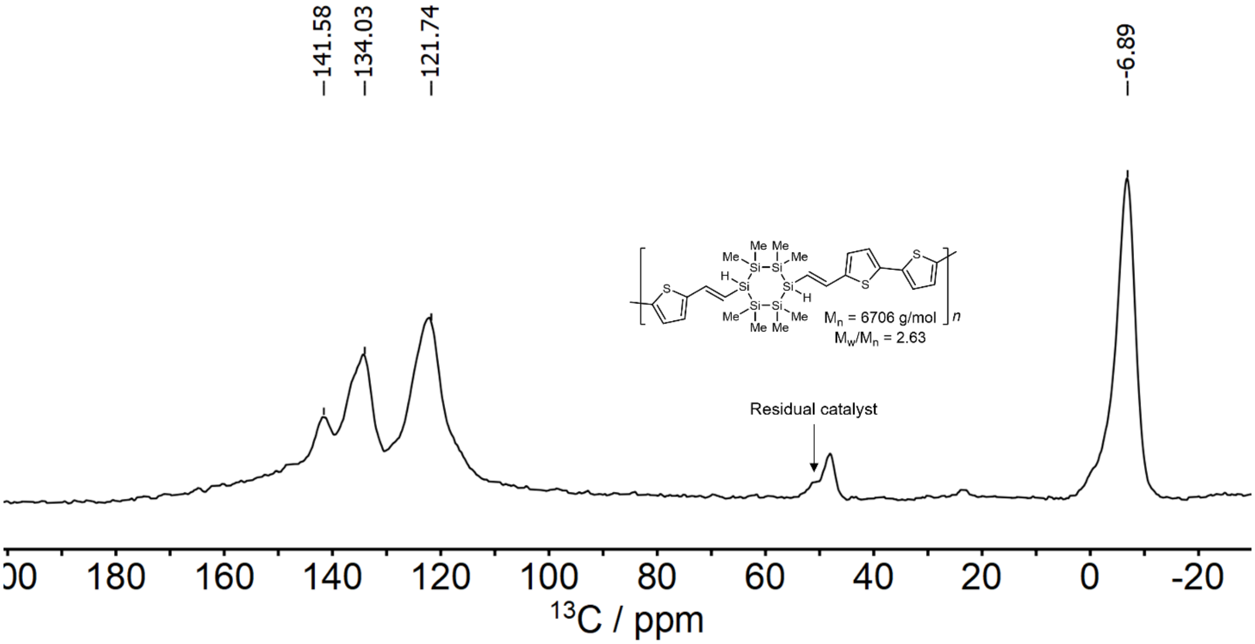
4.16.2 $^{13}C\{^1H\}$ NMR Spectrum of **P1** (101 MHz, $CDCl_3$)



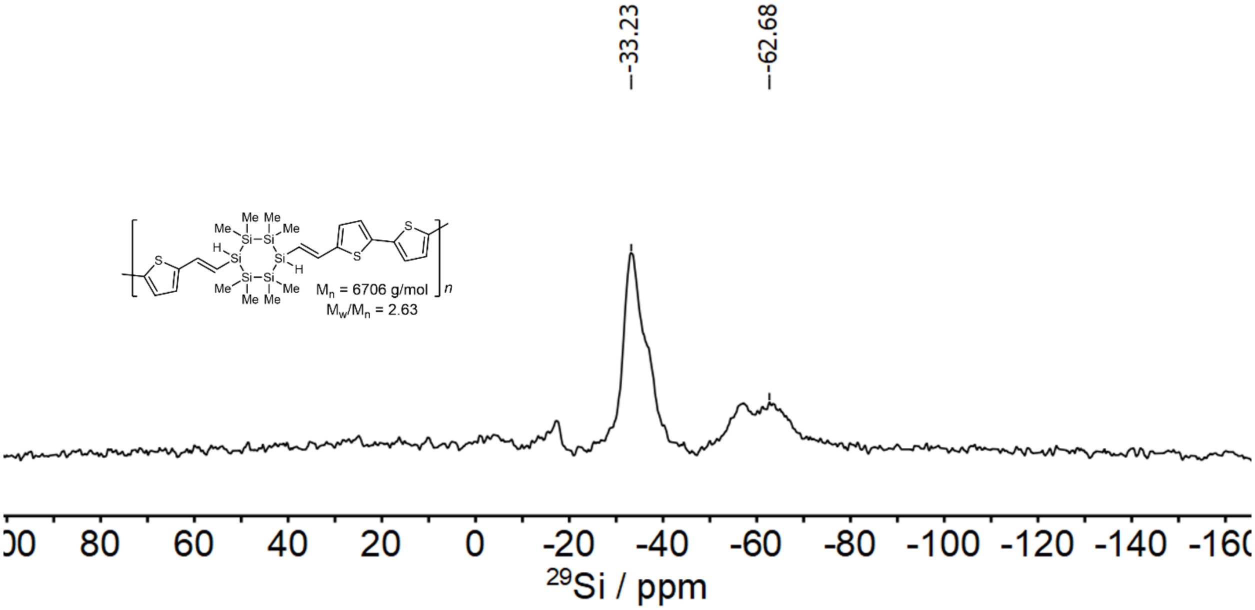
4.16.3 $^{29}Si\{^1H\}$ NMR Spectrum of **P1** (79 MHz, $CDCl_3$). $^1J_{Si\text{-}H}$ = 120 Hz.



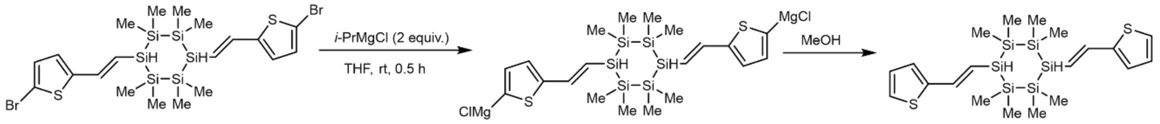
4.16.4 $^{1}H \rightarrow ^{13}C$ CPMAS spectrum of **P1** (126 MHz).



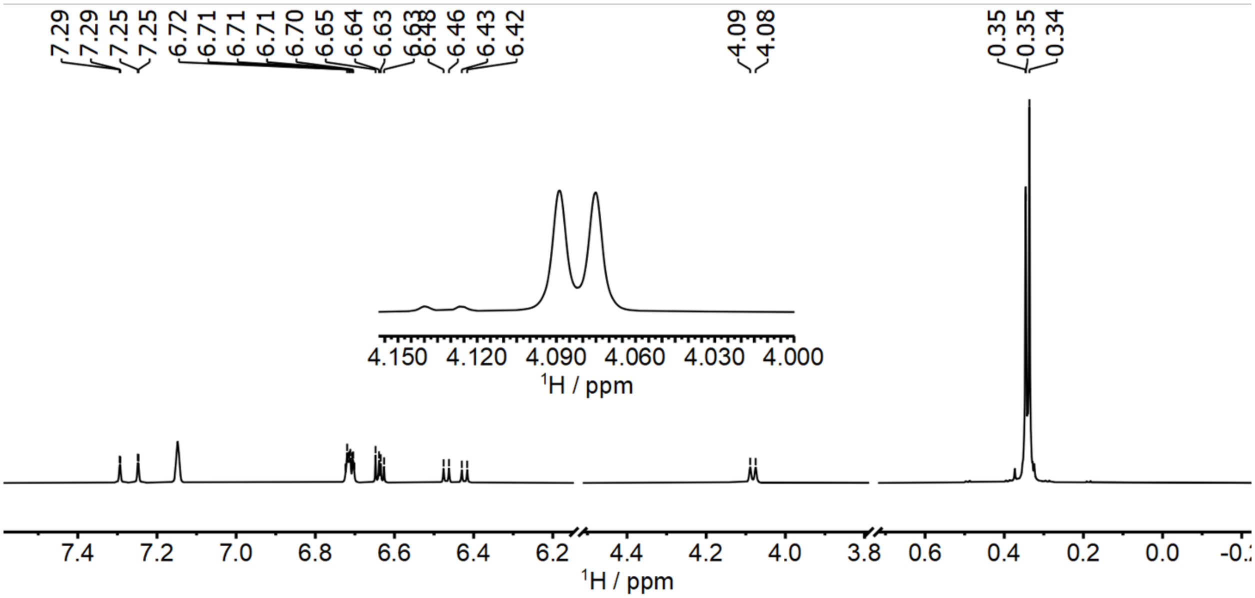
4.16.5 $^{1}H \rightarrow ^{29}Si$ CPMAS spectrum of **P1** (99 MHz).



4.16.6 ^{1}H NMR Spectrum of the quenched intermediate (400 MHz, C_6D_6).

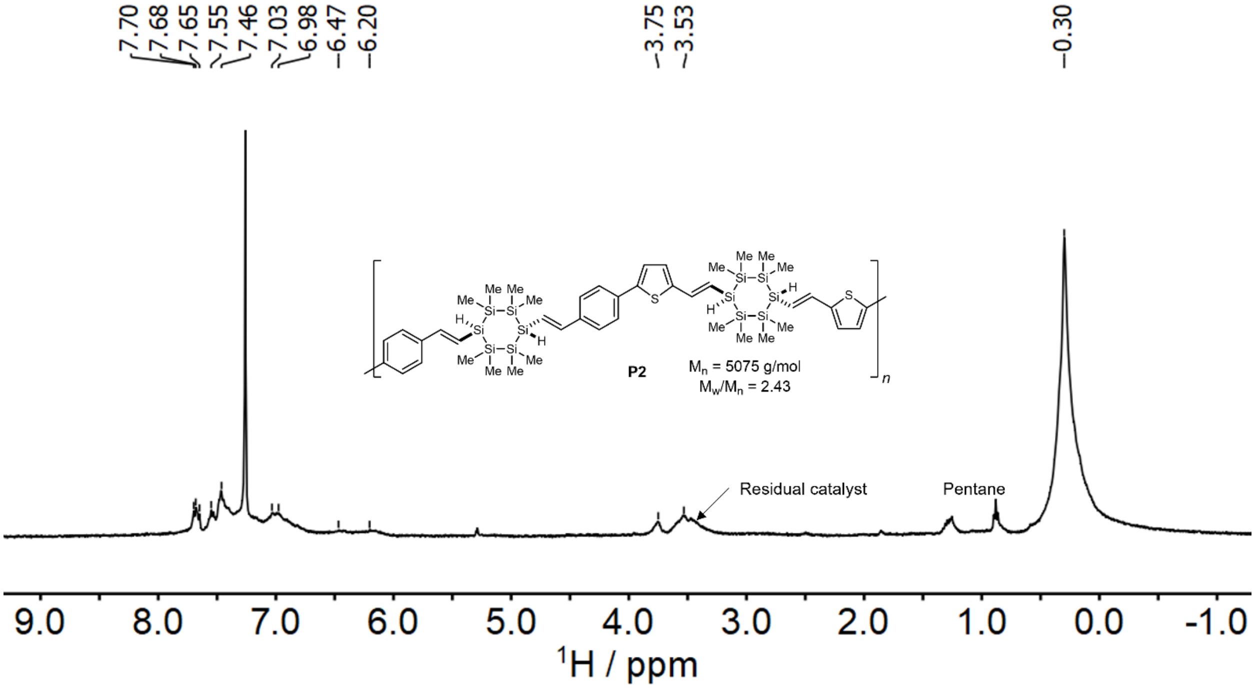


- 100 % conversion, clean NMR without purification

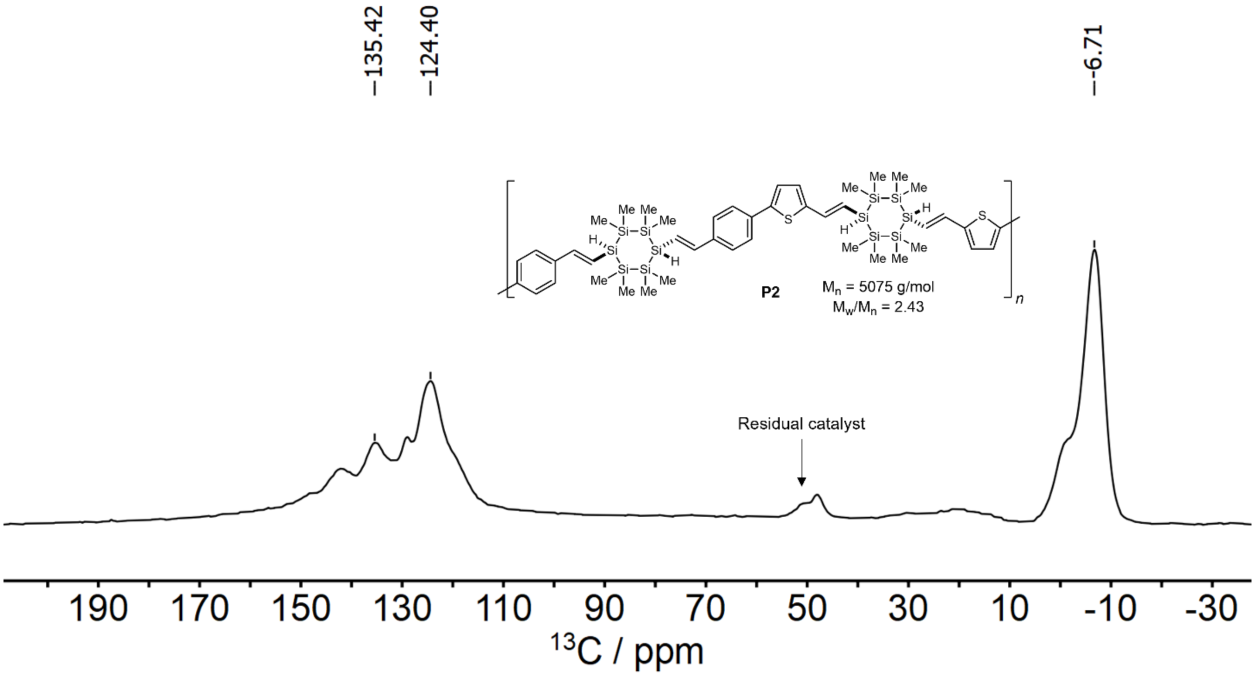


4.17 NMR Spectra of P2

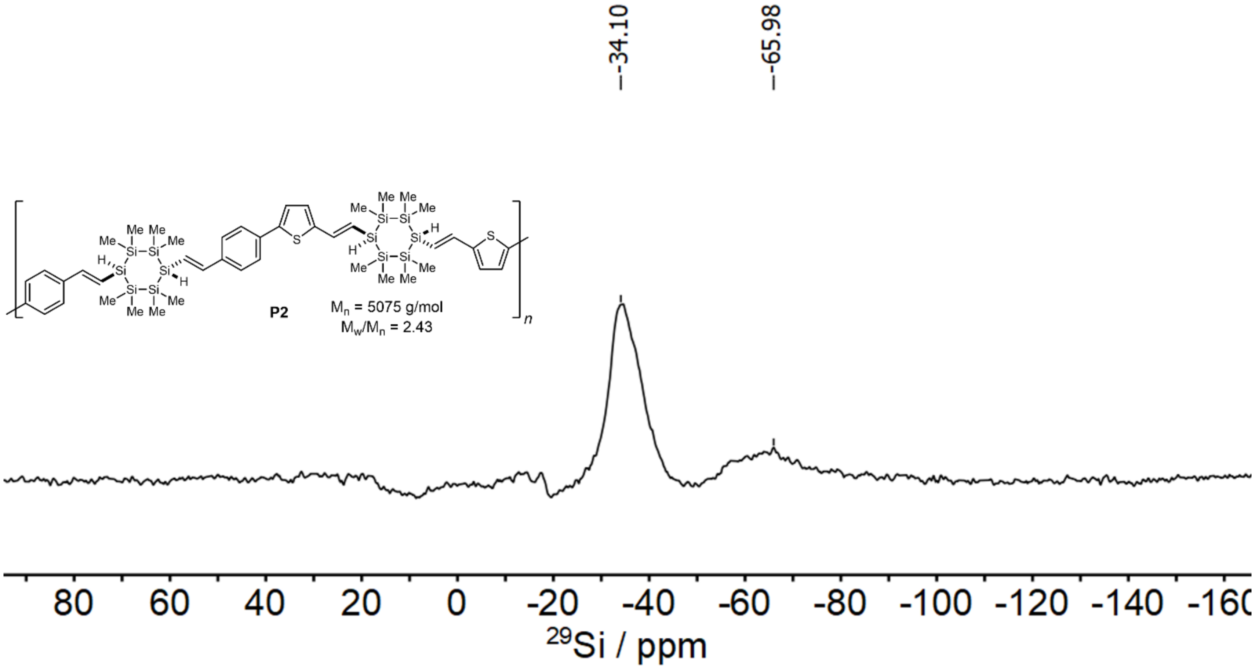
4.17.1 ^{1}H NMR Spectrum of **P2** (400 MHz, $CDCl_3$)



4.17.2 $^1H \rightarrow ^{13}C$ CPMAS spectrum of **P2** (126 MHz).



4.17.3 $^1H \rightarrow ^{29}Si$ CPMAS spectrum of **P2** (99 MHz).



5. Single Crystal X-Ray Crystallography

All reflection intensities were measured either at 110(2) K for **1a**, **1e** and **1j** or at 173 K for **3a** using a SuperNova diffractometer (equipped with Atlas detector) either with Mo *K*α radiation (λ = 0.71073 Å) for **1a** and **1j** or with Cu *K*α radiation (λ = 1.54178 Å) for **1e** and **3a** under the program CrysAlisPro (Version CrysAlisPro 1.171.39.29c, Rigaku OD, 2017). 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). Numerical absorption correction based on gaussian integration over a multifaceted crystal model was applied using CrysAlisPro for **1a** and **1j**. Analytical numeric absorption correction using a multifaceted crystal was applied using CrysAlisPro for **1e** and **3a**. The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). 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.

1a: The H atoms attached to Si1, Si4 and Si7 were found from difference Fourier maps, and their coordinates were refined freely. The structure is ordered. The asymmetric unit contains 1 + ½ crystallographically independent molecules. One of the two molecules is found at one site of inversion symmetry, and thus only one half is crystallographically independent.

1e/1j: The H atom attached to Si1 was found from difference Fourier map, and its coordinates were refined freely. The structure is ordered. The asymmetric unit contains ½ crystallographically independent molecule as it is found at one site of inversion symmetry.

3a: Some crystals were initially flashcooled from room temperature to 110 K, but these crystals cracked and the diffraction pattern was not of great quality. Another crystal was flashcooled from room temperature to 173 K, and the diffraction pattern was consistent with that of a single crystal. The H atoms attached to Si1, Si8, Si11 and Si18 were found from difference Fourier maps, and their coordinates were refined pseudofreely using the DFIX instruction in order to keep the Si–H within and acceptable range. The asymmetric unit contains two crystallographically independent molecules of the target compound. The C1A→C8A fragment is disordered over two orientations, and the occupancy factor of the major component of the disorder refines to 0.836(7).

Table S1 Crystallographic data for 1a

	1a
Crystal data	
Chemical formula	$C_{24}H_{40}Si_6$
M_r	497.10
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	110
a, b, c (Å)	36.3350 (8), 6.64881 (13), 18.7594 (4)
β (°)	95.565 (2)
V (Å^3)	4510.62 (16)
Z	6
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.29
Crystal size (mm)	0.54 × 0.35 × 0.14
Data collection	
Diffractometer	SuperNova, Dual, Cu at zero, Atlas
Absorption correction	Gaussian *CrysAlis PRO* 1.171.39.46 (Rigaku Oxford Diffraction, 2018) Numerical absorption correction based on gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.410, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	44126, 10362, 8191
R_{int}	0.037
(sin θ/λ)$_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.040, 0.095, 1.09
No. of reflections	10362
No. of parameters	427
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^-$	0.53, -0.26

^{3})	

Table S2 Crystallographic data for 1e

	1e
Crystal data	
Chemical formula	$C_{26}H_{44}O_2Si_6$
M_r	557.15
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	110
a, b, c (Å)	10.3662 (5), 11.2796 (6), 14.0764 (7)
β (°)	91.466 (4)
V (Å^3)	1645.37 (14)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	2.53
Crystal size (mm)	0.09 × 0.07 × 0.04
Data collection	
Diffractometer	SuperNova, Dual, Cu at zero, Atlas
Absorption correction	Analytical *CrysAlis PRO* 1.171.39.46 (Rigaku Oxford Diffraction, 2018) 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.
$T_{\min}$, $T_{\max}$	0.864, 0.917
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9929, 2958, 2235
R_{int}	0.054
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.598
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.051, 0.139, 1.04
No. of reflections	2958
No. of parameters	163
H-atom treatment	H atoms treated by a mixture of independent and constrained

	refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.92, -0.32

Table S3. Crystallographic data for 1j

	1j
Crystal data	
Chemical formula	$C_{20}H_{34}Br_2S_2Si_6$
M_r	666.95
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	110
a, *b*, *c* (Å)	22.2430 (8), 8.33206 (19), 18.2305 (6)
β (°)	113.890 (4)
V (Å^3)	3089.19 (19)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	3.00
Crystal size (mm)	0.33 × 0.25 × 0.10
Data collection	
Diffractometer	SuperNova, Dual, Cu at zero, Atlas
Absorption correction	Gaussian *CrysAlis PRO* 1.171.41.93a (Rigaku Oxford Diffraction, 2020) Numerical absorption correction based on gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.593, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	22208, 3551, 3249
R_{int}	0.027
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.020, 0.047, 1.02
No. of reflections	3551
No. of parameters	144

H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.53, -0.36

Table S4. Crystallographic data for 3a

	3a
Crystal data	
Chemical formula	$C_{30}H_{58}Si_{10}$
M_r	699.66
Crystal system, space group	Triclinic, *P*-1
Temperature (K)	173
a, *b*, *c* (Å)	8.8909 (3), 13.8639 (4), 37.0010 (12)
α, β, γ (°)	86.116 (2), 83.625 (2), 81.600 (2)
V (Å^3)	4477.9 (2)
Z	4
Radiation type	Cu *K*α
μ (mm^{-1})	2.90
Crystal size (mm)	0.27 × 0.16 × 0.06
Data collection	
Diffractometer	SuperNova, Dual, Cu at zero, Atlas
Absorption correction	Analytical *CrysAlis PRO* 1.171.41.93a (Rigaku Oxford Diffraction, 2020) 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}	0.555, 0.864
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	55290, 16062, 13297
R_{int}	0.046
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.598
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.068, 0.193, 1.10

No. of reflections	16062
No. of parameters	834
No. of restraints	261
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.86, -0.39

Computer programs: *CrysAlis PRO* 1.171.39.29c (Rigaku OD, 2017), *SHELXS2018*/3 (Sheldrick, 2018), *SHELXL2018*/3 (Sheldrick, 2018), *SHELXTL* v6.10 (Sheldrick, 2008).

References:

Sheldrick, G. M. (2015). Acta Cryst. C71, 3-8.

6. Computational methods

All DFT calculations were performed using the Gaussian 09 package[7]. Geometries were optimized using the B3LYP functional with the 6-31G(d) basis set starting from the crystal structure employing tight optimization parameters and an ultrafine integration grid. No symmetry restrictions were applied to geometry optimizations. Frequency calculations carried out at the same level of theory on fully optimized geometries showed no imaginary frequencies, confirming optimized geometries as local minima on their potential surfaces. Energy calculations carried out at the same level of theory and visualization of optimized geometries and molecular orbitals were performed using GaussView 5.0.9. Coordinates of the optimized structure can be found in the accompanying .xyz file.

7. Reference

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[2] E. A. Marro, E. M. Press, M. A. Siegler, R. S. Klausen, *J. Am. Chem. Soc.* **2018**, *140*, 5976–5986.

[3] E. A. Marro, C. P. Folster, E. M. Press, H. Im, J. T. Ferguson, M. A. Siegler, R. S. Klausen, *J. Am. Chem. Soc.* **2019**, *141*, 17926–17936.

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