

## Ladder Distyrylbenzenes with Silicon and Chalcogen Bridges: Synthesis, Structures, and Properties

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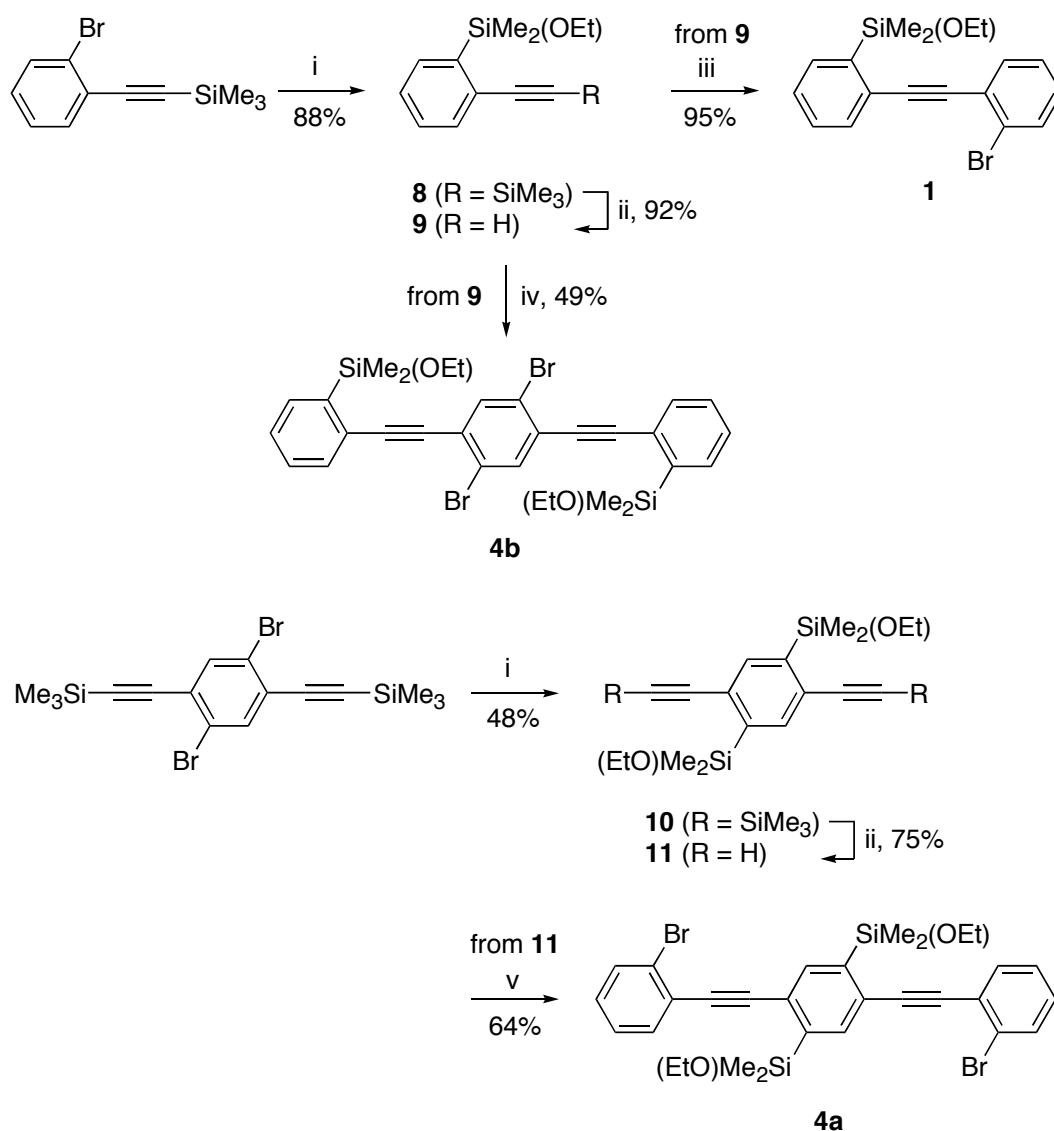
### Experimental Section

**General.** Melting point (mp) determination was performed using a Yanaco MP-S3 instrument.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured with a JEOL A-400 spectrometer. UV-visible absorption and fluorescence spectra were measured with a Shimadzu UV-3150 spectrometer and a F-4500 Hitachi spectrometer, respectively, in degassed spectral grade THF. Cyclic voltammograms were recorded on a CHI600A instrument. Thin layer chromatography (TLC) was performed on plates coated with 0.25 mm thick silica gel 60F-254 (Merck). Column chromatography was performed using a Fuji Silysia silica gel PSQ60B (60  $\mu\text{m}$ ). All reactions were carried out under argon atmosphere.

### Starting Materials Synthesis.

**1-(Ethoxydimethylsilyl)-2-(trimethylsilylethynyl)benzene (8).** To a solution of (2-bromophenyl)trimethylsilylacetylene (15g, 60 mmol) in  $\text{Et}_2\text{O}$  was added a hexane solution of *n*-BuLi (1.6 M, 37.5 mL, 60 mmol) dropwise at  $-78\text{ }^\circ\text{C}$ . After stirring the mixture for 2.5 h,  $(\text{Et}_2\text{N})\text{Me}_2\text{SiCl}$  (13.2 g, 80 mmol) was added via syringe at the same temperature. The reaction mixture was allowed to warm to room temperature and stirred for 9 h. EtOH (60 mL, 1 mol) and  $\text{NH}_4\text{Cl}$  (6.7 g, 126 mmol) were added and the mixture was stirred at room temperature for 5 h. The reaction mixture was filtered and the filtrate was concentrated under reduced pressure. After passing the resulting mixture through a silica gel column (hexane/AcOEt 20/1,  $R_f = 0.46$ ), distillation under reduced pressure afforded 14.6 g (53

# **Scheme S1**



*Reagents and conditions:* i, 1) *n*-BuLi, Et<sub>2</sub>O; 2) (Et<sub>2</sub>N)Me<sub>2</sub>SiCl; 3) EtOH, cat. NH<sub>4</sub>Cl; ii, K<sub>2</sub>CO<sub>3</sub>, THF/EtOH; iii, 1-bromo-2-iodobenzene, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, CuI, Et<sub>3</sub>N; iv, 1,4-dibromo-2,5-diiodobenzene, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, CuI, 1/1 Et<sub>3</sub>N/THF; v, 1-bromo-2-iodobenzene, Pd(PPh<sub>3</sub>)<sub>4</sub>, CuI, 1/4 (*i*-Pr)<sub>2</sub>NH/THF.

mmol) of **8** in 88% yield as colorless liquid (62–69 °C, 0.2 mmHg): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.64–7.60 (m, 1H), 7.51–7.46 (m, 1H), 7.33–7.29 (m, 2H), 3.78 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.47 (s, 6H), 0.25 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 141.17, 134.14, 132.82, 129.09, 127.69, 127.67, 106.47, 96.92, 58.80, 18.54, –0.26, –1.29. HRMS(EI): 276.1375. Calcd for C<sub>15</sub>H<sub>24</sub>OSi<sub>2</sub>: 276.1336.

**1-(Ethoxydimethylsilyl)-2-ethynylbenzene (9).** To a solution of **8** in 100 mL of THF was

added  $\text{K}_2\text{CO}_3$  (0.73 g, 5.3 mmol) and EtOH (100 mL, 1.7 mol) and the mixture was stirred at room temperature for 22 h. After filtration, the filtrate was concentrated under reduced pressure. The resulting mixture was subjected to a silica gel column chromatography (hexane/AcOEt 20/1,  $R_f$  = 0.48) to afford 9.9 g of **9** (49 mmol) in 92% yield as pale yellow liquid:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.65–7.61 (m, 1H), 7.55–7.50 (m, 1H), 7.37–7.31 (m, 2H), 3.77 (q,  $J$  = 7.1 Hz, 2H), 3.21 (s, 1H), 1.25 (t,  $J$  = 7.1 Hz, 3H), 0.48 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  141.29, 134.24, 133.27, 129.21, 127.95, 126.71, 84.86, 79.95, 58.83, 18.47, –1.25. HRMS(EI): 204.0969. Calcd for  $\text{C}_{12}\text{H}_{16}\text{OSi}$ : 204.0970.

**[2-(Ethoxydimethylsilyl)phenyl](2-bromophenyl)acetylene (1).** To a mixture of 2-bromoiodobenzene (2.8 g, 10 mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (140 mg, 0.2 mmol), and CuI (0.78 mg, 0.4 mmol) in  $\text{Et}_3\text{N}$  (15 mL) was added a  $\text{Et}_3\text{N}$  (10 mL) solution of **9** (2.1 g, 11 mmol) at room temperature. The reaction mixture was stirred at the same temperature for 10 h. After filtration through Celite, the filtrate was concentrated under reduced pressure. The resulting mixture was subjected to a silica gel column chromatography (hexane/AcOEt 20/1,  $R_f$  = 0.28) to afford 3.4 g (9.5 mmol) of **10** in 95% yield as pale yellow liquid:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.68–7.55 (m, 4H), 7.39–7.36 (m, 2H), 7.30 (t,  $J$  = 7.3 Hz, 1H), 7.19 (t,  $J$  = 7.3 Hz, 1H), 3.79 (q,  $J$  = 7.1 Hz, 2H), 1.24 (t,  $J$  = 7.1 Hz, 3H), 0.53 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  140.63, 134.32, 133.18, 132.95, 132.51, 129.35, 129.32, 127.83, 127.52, 127.06, 125.62, 125.29, 95.15, 90.41, 58.83, 18.51, –0.97. HRMS(EI): 358.0381. Calcd for  $\text{C}_{18}\text{H}_{19}\text{BrOSi}$ : 358.0389.

**1,4-Dibromo-2,5-bis{[2-(ethoxydimethylsilyl)phenyl]ethynyl}benzene (4b).** To a mixture of 1,4-dibromo-2,5-diiodobenzene (24 g, 50 mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (702 mg, 1.0 mmol), and CuI (380 mg, 2.0 mmol) in a 1/1  $\text{Et}_3\text{N}$ /THF mixed solvent (250 mL) was added a solution of **9** (21 g, 103 mmol) in a 1/1  $\text{Et}_3\text{N}$ /THF mixed solvent. The mixture was then stirred at room temperature for 10 h. After filtration through Celite, the filtrate was concentrated under reduced pressure. Recrystallization of the resulting mixture from AcOEt afforded 15.8 g (25 mmol) of **4b** in 49% yield as white solid: mp. 135–137 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.77 (s, 2H), 7.69–7.63 (m, 4H), 7.43–7.36 (m, 4H), 3.78 (q,  $J$  = 7.1 Hz, 4H), 1.25 (t,  $J$  = 7.1 Hz, 6H), 0.52 (s, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  140.95, 136.08, 134.43, 133.15, 129.38, 128.30, 126.89, 126.66, 123.47, 97.91, 89.14, 58.85, 18.51, –0.96. HRMS (FAB): 638.0319. Calcd for  $\text{C}_{30}\text{H}_{42}\text{Br}_2\text{O}_2\text{Si}_2$ : 638.0308.

**1,4-Bis(ethoxydimethylsilyl)-2,5-bis[(trimethylsilyl)ethynyl]benzene (10).** To a solution of 1,4-dibromo-2,5-[(trimethylsilyl)ethynyl]benzene (11.8 g, 27.6 mmol) in  $\text{Et}_2\text{O}$  (100 mL)

was added a hexane solution of *n*-BuLi (1.6 M, 38 mL, 61 mmol) dropwise at  $-78\text{ }^{\circ}\text{C}$ . After stirring for 1 h,  $(\text{Et}_2\text{N})\text{Me}_2\text{SiCl}$  (11.4 g, 69 mmol) was added at the same temperature. The mixture was allowed to warm to room temperature, followed by stirring for 19 h. EtOH (30 mL, 0.5 mol) and  $\text{NH}_4\text{Cl}$  (7.4 g, 138 mmol) were added to the mixture, followed by stirring for 5 h. The reaction mixture was filtered and the filtrate was concentrated under reduced pressure. Recrystallization of the resulting mixture from AcOEt afforded 6.3 g (3.3 mmol) of **10** in 48% yield as white solid: mp.  $130\text{--}132\text{ }^{\circ}\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.70 (s, 2H), 3.77 (q,  $J = 6.8\text{ Hz}$ , 4H), 1.25 (t,  $J = 6.8\text{ Hz}$ , 6H), 0.46 (s, 12H), 0.25 (s, 18H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  141.94, 138.38, 126.76, 106.49, 98.87, 58.88, 18.52,  $-0.29$ ,  $-1.41$ . HRMS (EI): 474.2252. Calcd for  $\text{C}_{24}\text{H}_{42}\text{O}_2\text{Si}_4$ : 474.2262.

**1,4-Bis(ethoxydimethylsilyl)-2,5-diethynylbenzene (11).** To a solution of **10** (5.0 g, 11 mmol) in 30 mL of THF was added  $\text{K}_2\text{CO}_3$  (0.28 g, 2.1 mmol) and EtOH (30 mL, 0.43 mol). The reaction mixture was stirred at room temperature for 30 h, and then filtered. After concentration of the filtrate under reduced pressure,  $\text{Et}_2\text{O}$  was added and the organic layer was washed with brine, dried over  $\text{MgSO}_4$ , filtered, and concentrated. The resulting mixture was subjected to a silica gel column chromatography ( $\text{CH}_2\text{Cl}_2$ ,  $R_f = 0.43$ ) to give 2.6 g (7.8 mmol) of **11** in 75% yield as white solid: mp.  $91\text{--}93\text{ }^{\circ}\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.75 (s, 2H), 3.76 (q,  $J = 7.1\text{ Hz}$ , 4H), 3.30 (s, 2H), 1.24 (t,  $J = 7.1\text{ Hz}$ , 6H), 0.47 (s, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  142.29, 138.90, 126.14, 84.83, 81.58, 58.93, 18.46,  $-1.38$ . HRMS (EI): 330.1472. Calcd for  $\text{C}_{18}\text{H}_{26}\text{O}_2\text{Si}_2$ : 330.1471.

**1,4-Bis(2-bromo-1-phenyl)ethynyl-2,5-bis(ethoxydimethylsilyl)benzene (4a).** To a mixture of 2-bromiodobenzene (3.4 g, 12 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (140 mg, 0.12 mmol), and CuI (46 mg, 0.24 mmol) in a 1/4 (*i*-Pr) $_2$ NH/THF mixed solvent (10 mL) was added a solution of **11** (2.0 g, 6.0 mmol) in 2.5 mL of a 1/4 (*i*-Pr) $_2$ NH/THF mixed solvent dropwise at room temperature. The reaction mixture was stirred for 48 h. After filtration through Celite, the filtrate was concentrated under reduced pressure. The resulting mixture was passed thorough a silica gel column ( $\text{CH}_2\text{Cl}_2$ ), and purified by recrystallization from AcOEt to give 2.5 g (3.9 mmol) of **4a** in 64% yield as white solid: mp.  $135\text{--}137\text{ }^{\circ}\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.91 (s, 2H), 7.63 (dd,  $J = 8.0\text{ Hz}$ ,  $J = 1.2\text{ Hz}$ , 2H), 7.57 (dd,  $J = 7.8\text{ Hz}$ ,  $J = 1.7\text{ Hz}$ , 2H), 7.33–7.29 (m, 2H), 7.22–7.18 (m, 2H), 3.81 (q,  $J = 7.1\text{ Hz}$ , 4H), 1.25 (t,  $J = 7.1\text{ Hz}$ , 6H), 0.54 (s, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  141.59, 138.61, 133.24, 132.54, 129.53, 127.11, 126.66, 125.42, 125.28, 95.20, 92.17, 58.99, 18.52,  $-1.13$ . HRMS (FAB): 638.0300. Calcd for  $\text{C}_{30}\text{H}_{42}\text{Br}_2\text{O}_2\text{Si}_2$ : 638.0308.

### A Typical Procedure of Cascade-Type Anionic Cyclization

**Compound 5a.** To a solution of compound **4a** (640 mg, 1.0 mmol) in THF (20 mL) was added a pentane solution of *t*-BuLi (1.57 M, 2.6 mL, 4.0 mmol) dropwise at  $-78\text{ }^{\circ}\text{C}$ . After stirred for 1 h, sulfur ( $\text{S}_8$ ) (64 mg, 2.0 mmol) was added as a powder under a stream of argon. The mixture was kept at the same temperature for 10 min and then was allowed to warm to room temperature with stirring over 3 h. After addition of a saturated  $\text{NH}_4\text{Cl}$  aqueous solution, the mixture was extracted with  $\text{CHCl}_3$ . The organic layer was washed with brine, dried over  $\text{MgSO}_4$ , filtered, and concentrated under reduced pressure. The resulting mixture was successively washed with ethanol and hexane to give 180 mg (0.40 mmol) of **5a** in 40% yield as bright yellow powder: mp.  $>300\text{ }^{\circ}\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.91 (d,  $J = 7.8$  Hz, 2H), 7.76 (d,  $J = 7.8$  Hz, 2H), 7.71 (s, 2H), 7.41–7.37 (m, 2H), 7.33–7.29 (m, 2H), 0.58 (s, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.54, 143.58, 143.13, 142.84, 141.93, 137.08, 125.37, 124.83, 123.98, 123.96, 123.20,  $-3.50$ . HRMS (EI): 454.0696. Calcd for  $\text{C}_{26}\text{H}_{22}\text{S}_2\text{Si}_2$ : 454.0702.

**Compound 5b.** This compound was prepared in 68% yield essentially in the same manner as described for **5a**: mp.  $>300\text{ }^{\circ}\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.20 (s, 2H),  $\delta$  7.60 (d,  $J = 7.1$  Hz, 2H), 7.52 (d,  $J = 7.1$  Hz, 2H), 7.44–7.40 (m, 2H), 7.30–7.28 (m, 2H), 0.56 (s, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 156.73, 143.92, 141.33, 140.85, 139.24, 136.42, 132.31, 130.23, 127.34, 121.66, 117.77,  $-3.44$ . HRMS (EI): 454.0701. Calcd for  $\text{C}_{26}\text{H}_{22}\text{S}_2\text{Si}_2$ : 454.0702.

**Compound 5c.** This compound was prepared in 30% yield essentially in the same manner as described for **5a** using selenium powder instead of sulfur powder: mp.  $>300\text{ }^{\circ}\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.23 (s, 2H), 7.59 (d,  $J = 6.8$  Hz, 2H), 7.43–7.39 (m, 4H), 7.31–7.27 (m, 2H), 0.56 (s, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.63, 145.91, 142.24, 141.47, 140.43, 139.72, 132.04, 130.35, 127.29, 122.78, 122.58,  $-3.40$ . HRMS (EI): 549.9595. Calcd for  $\text{C}_{26}\text{H}_{22}\text{Se}_2\text{Si}_2$ : 549.9590.

### Oxidation of Si,S-Bridged Distyrylbenzene

**Compound 6a.** To a solution of **5a** (100 mg, 0.22 mmol) in  $\text{CH}_2\text{Cl}_2$  (30 mL) was added mCPBA (190mg, 1.1 mmol). The mixture was stirred at room temperature for 10 h. After addition of a saturated  $\text{NaHSO}_3$  aqueous solution, the mixture was extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with brine, dried over  $\text{MgSO}_4$ , filtered, and concentrated under reduced pressure. Recrystallization from DMSO afforded 20 mg (0.040 mmol) of **6a** in 18%

yield as yellow solid: mp. >300 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.97 (s, 2H), 7.76 (d, *J* = 7.1 Hz, 2H), 7.60–7.56 (m, 2H), 7.52–7.48 (m, 2H), 7.34 (d, *J* = 7.1 Hz, 2H), 0.62 (s, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 153.06, 143.67, 143.56, 139.74, 138.18, 133.84, 132.40, 129.71, 127.29, 125.49, 121.94, –4.24. HRMS (EI): 518.0495. Calcd for C<sub>26</sub>H<sub>22</sub>O<sub>4</sub>S<sub>2</sub>Si<sub>2</sub>: 518.0498.

**Compound 6b.** This compound was prepared in 45% yield essentially in the same manner as described for **6a**: mp. >300 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.75 (d, *J* = 7.3 Hz, 2H), 7.66 (d, *J* = 7.3 Hz, 2H), 7.61 (s, 2H), 7.53–7.50 (m, 2H), 7.45–7.43 (m, 2H), 0.62 (s, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 154.83, 144.63, 140.99, 140.19, 137.17, 134.18, 133.34, 130.92, 129.69, 123.57, 118.25, –4.17. HRMS (EI): 518.0474. Calcd for C<sub>26</sub>H<sub>22</sub>O<sub>4</sub>S<sub>2</sub>Si<sub>2</sub>: 518.0498.

## X-Ray Crystallography

**X-Ray Crystal Structure Analysis of Compound 5a.** Single crystals of **5a** suitable for X-ray crystal analysis were obtained by recrystallization from a chloroform/ethanol mixed solvent. Intensity data were collected at 103 K on a Rigaku Single Crystal CCD X-ray Diffractometer (Saturn 70 with MicroMax-007) with Mo Kα radiation (λ = 0.71073 Å) and graphite monochromator. A total of 8827 reflections were measured at a maximum 2θ angle of 55.0°, of which 2583 were independent reflections (*R*<sub>int</sub> = 0.0234). The structure was solved by direct methods (SHELXS-97<sup>1</sup>) and refined by the full-matrix least-squares on *F*<sup>2</sup> (SHELXL-97<sup>1</sup>). All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: C<sub>26</sub>H<sub>22</sub>S<sub>2</sub>Si<sub>2</sub>; FW = 454.74, crystal size 0.20 × 0.20 × 0.10 mm<sup>3</sup>, monoclinic, *P*2<sub>1</sub>/c, *a* = 8.9171(15) Å, *b* = 10.8286(17) Å, *c* = 11.756(2) Å, β = 94.3574(7)°, *V* = 1131.9(3) Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 1.334 g cm<sup>–3</sup>. The refinement converged to *R*<sub>1</sub> = 0.0280, *wR*<sub>2</sub> = 0.0741 (*I* > 2σ(*I*)), GOF = 1.053.

**X-Ray Crystal Structure Analysis of Compound 5b.** Single crystals of **5b** suitable for X-ray crystal analysis were obtained by recrystallization from toluene/dichloromethane. Intensity data were collected at 173 K on a Rigaku Single Crystal CCD X-ray Diffractometer (Saturn 70 with MicroMax-007) with Mo Kα radiation (λ = 0.71073 Å) and graphite monochromator. A total of 7138 reflections were measured at a maximum 2θ angle of 50.0°, of which 2005 were independent reflections (*R*<sub>int</sub> = 0.0361). The structure was solved by direct methods (SHELXS-97<sup>2</sup>) and refined by the full-matrix least-squares on *F*<sup>2</sup> (SHELXL-97<sup>2</sup>). All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: C<sub>26</sub>H<sub>22</sub>S<sub>2</sub>Si<sub>2</sub>;

FW = 454.74, crystal size  $0.15 \times 0.10 \times 0.05 \text{ mm}^3$ , monoclinic,  $P2_1/c$ ,  $a = 11.383(3) \text{ \AA}$ ,  $b = 6.8442(18) \text{ \AA}$ ,  $c = 15.037(4) \text{ \AA}$ ,  $\beta = 93.264(4)^\circ$ ,  $V = 1169.6(5) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 1.291 \text{ g cm}^{-3}$ . The refinement converged to  $R_1 = 0.0309$ ,  $wR_2 = 0.0827$  ( $I > 2\sigma(I)$ ), GOF = 0.997.

**X-Ray Crystal Structure Analysis of Compound 5c.** Single crystals of **5c** suitable for X-ray crystal analysis were obtained by recrystallization from a chloroform/ethanol mixed solvent. Intensity data were collected at 123 K on a Rigaku Single Crystal CCD X-ray Diffractometer (Saturn 70 with MicroMax-007) with Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and graphite monochromator. A total of 14669 reflections were measured at a maximum  $2\theta$  angle of  $50.0^\circ$ , of which 4035 were independent reflections ( $R_{\text{int}} = 0.0316$ ). The structure was solved by direct methods (SHELXS-97<sup>1</sup>) and refined by the full-matrix least-squares on  $F^2$  (SHELXL-97<sup>1</sup>). All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows:  $\text{C}_{26}\text{H}_{22}\text{Se}_2\text{Si}_2$ ; FW = 548.54, crystal size  $0.15 \times 0.10 \times 0.05 \text{ mm}^3$ , monoclinic,  $P2_1/n$ ,  $a = 8.8891(16) \text{ \AA}$ ,  $b = 9.8528(18) \text{ \AA}$ ,  $c = 26.162(5) \text{ \AA}$ ,  $\beta = 90.8205(10)^\circ$ ,  $V = 2291.1(7) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_c = 1.590 \text{ g cm}^{-3}$ . The refinement converged to  $R_1 = 0.0282$ ,  $wR_2 = 0.0652$  ( $I > 2\sigma(I)$ ), GOF = 1.080.

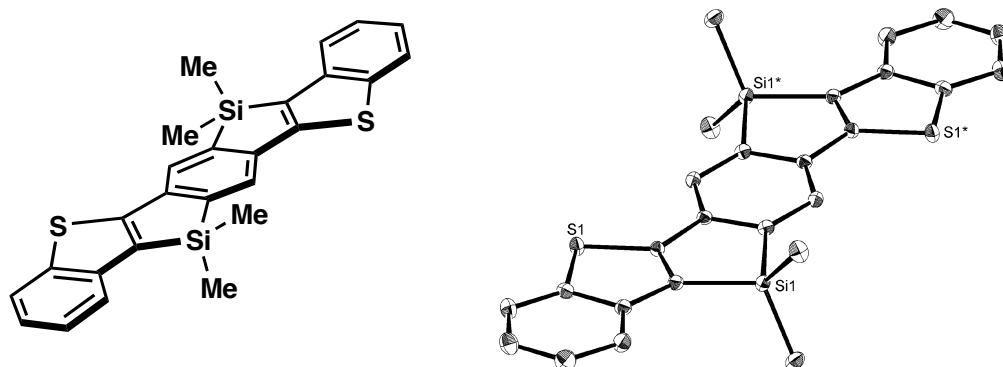
**X-Ray Crystal Structure Analysis of Compound 6a.** Single crystals of **6a** suitable for X-ray crystal analysis were obtained by recrystallization from DMSO. Intensity data were collected at 173 K on a Rigaku Single Crystal CCD X-ray Diffractometer (Saturn 70 with MicroMax-007) with Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and graphite monochromator. A total of 8017 reflections were measured at a maximum  $2\theta$  angle of  $50.0^\circ$ , of which 2197 were independent reflections ( $R_{\text{int}} = 0.0549$ ). The structure was solved by direct methods (SHELXS-97<sup>1</sup>) and refined by the full-matrix least-squares on  $F^2$  (SHELXL-97<sup>1</sup>). All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows:  $\text{C}_{26}\text{H}_{22}\text{O}_4\text{S}_2\text{Si}_2$ ; FW = 518.74, crystal size  $0.12 \times 0.10 \times 0.03 \text{ mm}^3$ , monoclinic,  $P2_1/a$ ,  $a = 13.042(4) \text{ \AA}$ ,  $b = 6.878(2) \text{ \AA}$ ,  $c = 14.555(5) \text{ \AA}$ ,  $\beta = 106.6984(14)^\circ$ ,  $V = 1250.5(7) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 1.378 \text{ g cm}^{-3}$ . The refinement converged to  $R_1 = 0.0523$ ,  $wR_2 = 0.1107$  ( $I > 2\sigma(I)$ ), GOF = 1.128.

**X-Ray Crystal Structure Analysis of Compound 6b.** Single crystals of **6b** suitable for X-ray crystal analysis were obtained by recrystallization from a chloroform/ethanol mixed solvent. Intensity data were collected at 103 K on a Rigaku Single Crystal CCD X-ray Diffractometer (Saturn 70 with MicroMax-007) with Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and graphite monochromator. A total of 8117 reflections were measured at a maximum  $2\theta$  angle of  $50.0^\circ$ , of which 2159 were independent reflections ( $R_{\text{int}} = 0.0607$ ). The structure was

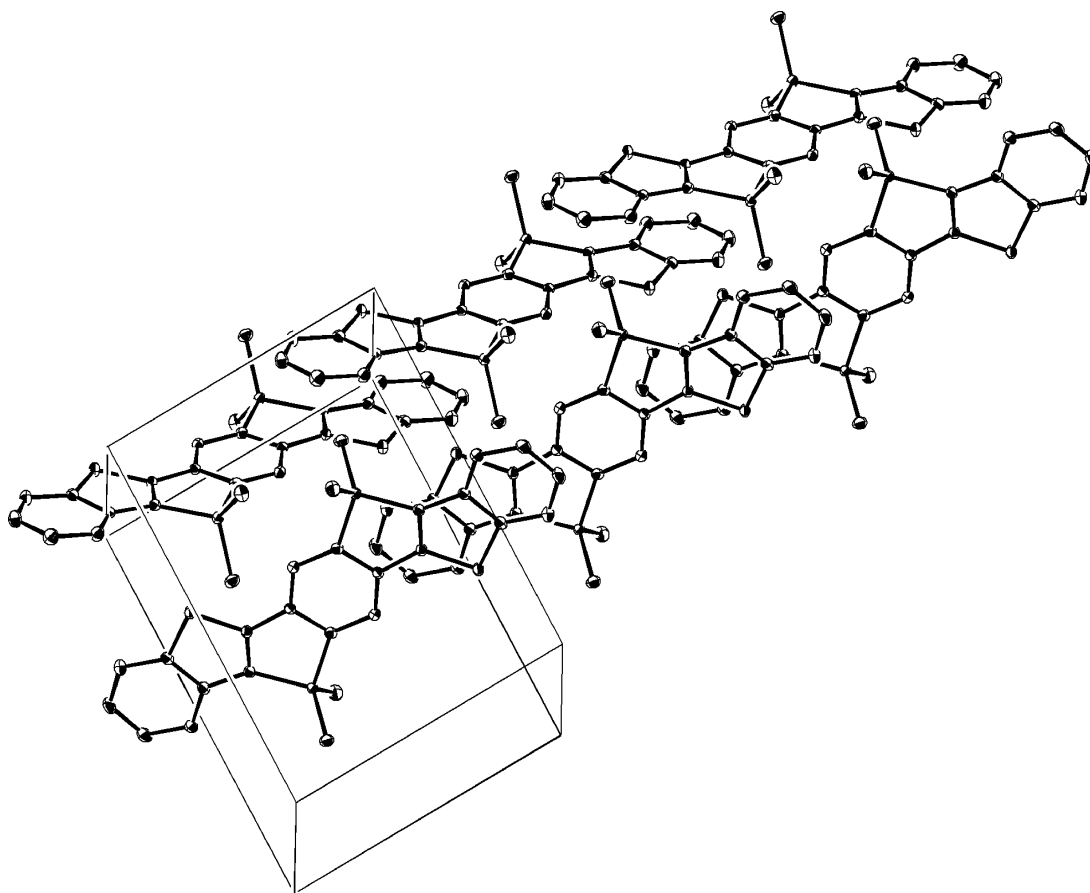
solved by direct methods (SHELXS-97<sup>1</sup>) and refined by the full-matrix least-squares on  $F^2$  (SHELXL-97<sup>1</sup>). All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows:  $C_{26}H_{22}O_4S_2Si_2$ ; FW = 518.74, crystal size  $0.15 \times 0.10 \times 0.05 \text{ mm}^3$ , monoclinic,  $P2_1/n$ ,  $a = 9.057(3) \text{ \AA}$ ,  $b = 13.776(4) \text{ \AA}$ ,  $c = 10.813(4) \text{ \AA}$ ,  $\beta = 113.9271(11)^\circ$ ,  $V = 1233.2(7) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 1.397 \text{ g cm}^{-3}$ . The refinement converged to  $R_1 = 0.0498$ ,  $wR_2 = 0.1139$  ( $I > 2\sigma(I)$ ), GOF = 1.115.



a)

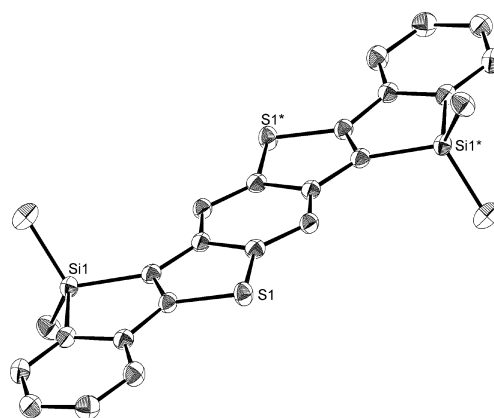
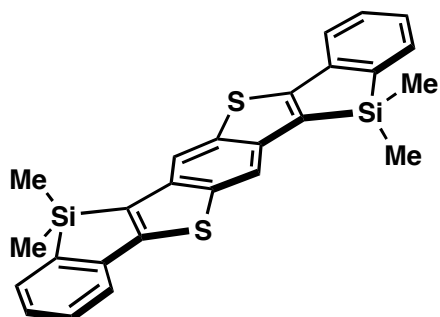


b)

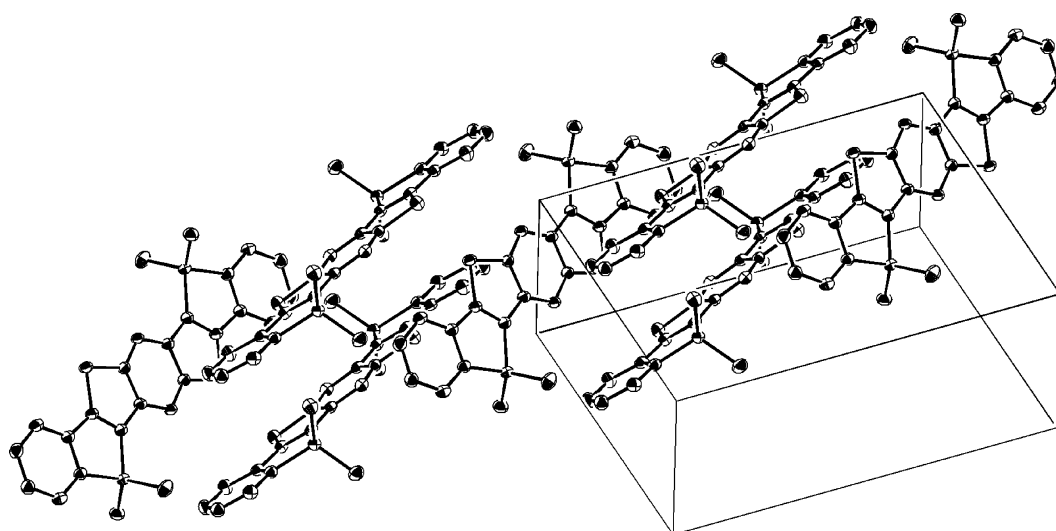


**Figure S1.** ORTEP drawing of **5a** (50% probability for thermal ellipsoids): a) a perspective view and b) a packing structure. Hydrogen atoms are omitted for clarity.

a)

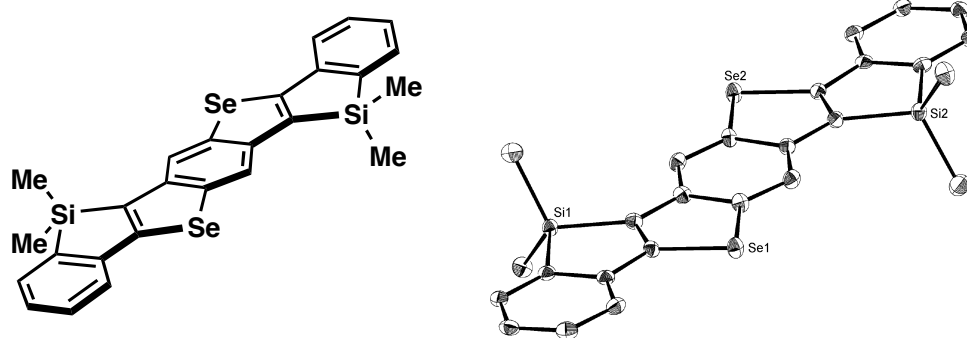


b)

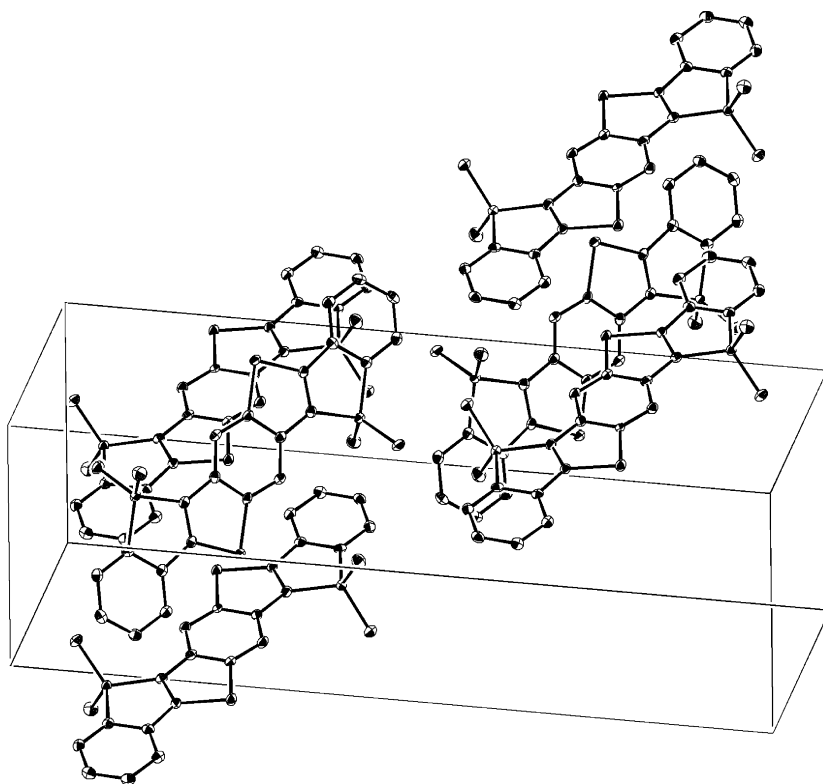


**Figure S2.** ORTEP drawing of **5b** (50% probability for thermal ellipsoids): a) a perspective view and b) a packing structure. Hydrogen atoms are omitted for clarity.

a)

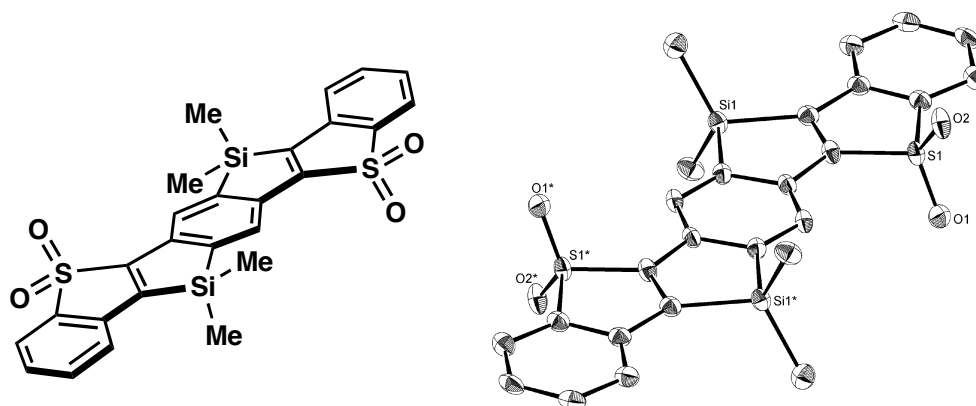


b)

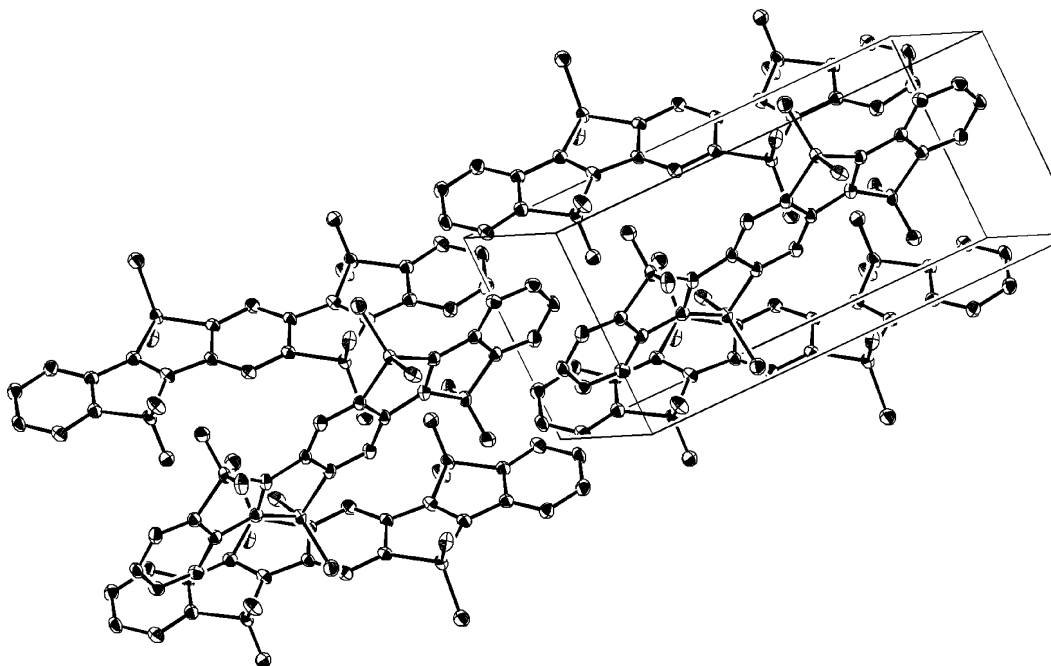


**Figure S3.** ORTEP drawing of **5c** (50% probability for thermal ellipsoids): a) a perspective view and b) a packing structure. Hydrogen atoms are omitted for clarity.

a)

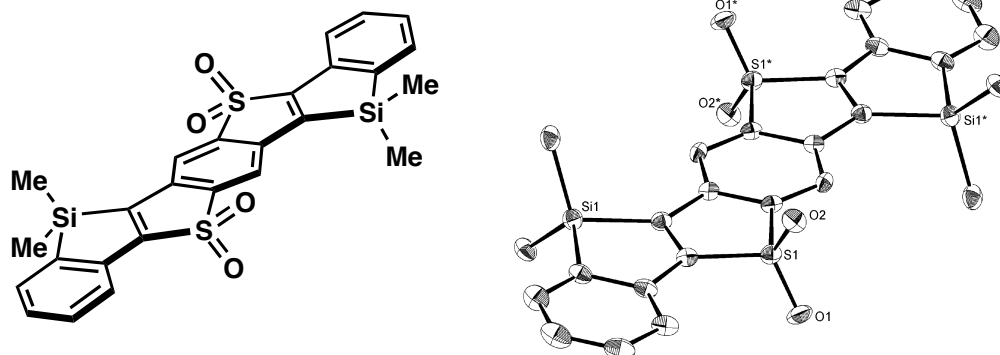


b)

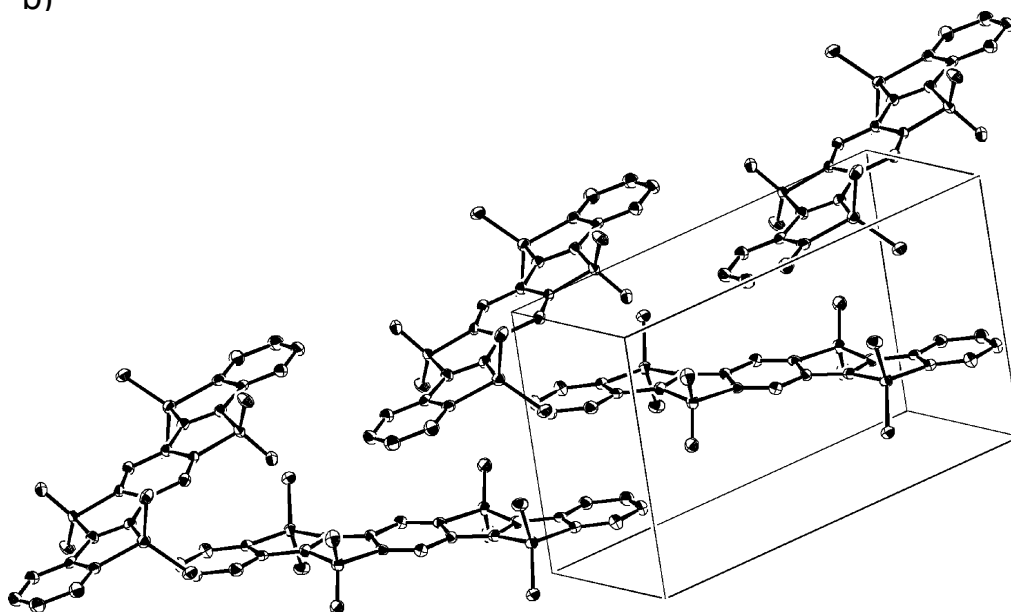


**Figure S4.** ORTEP drawing of **6a** (50% probability for thermal ellipsoids): a) a perspective view and b) a packing structure. Hydrogen atoms are omitted for clarity.

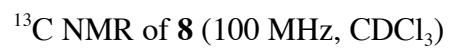
a)



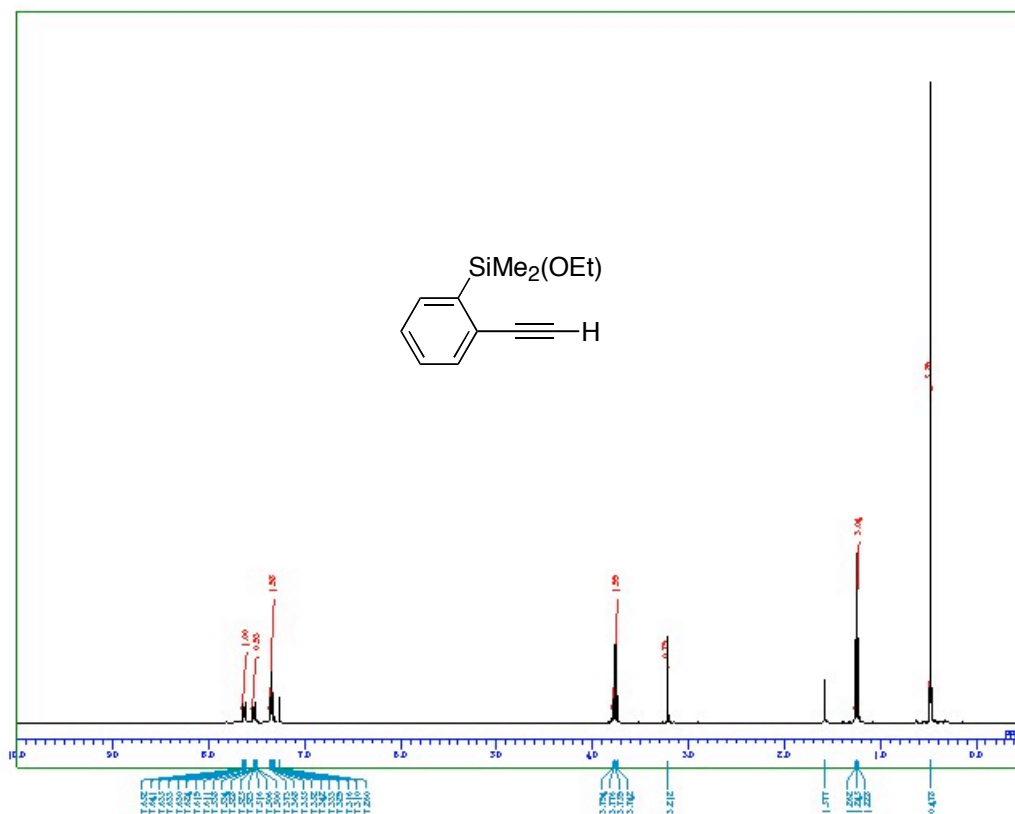
b)



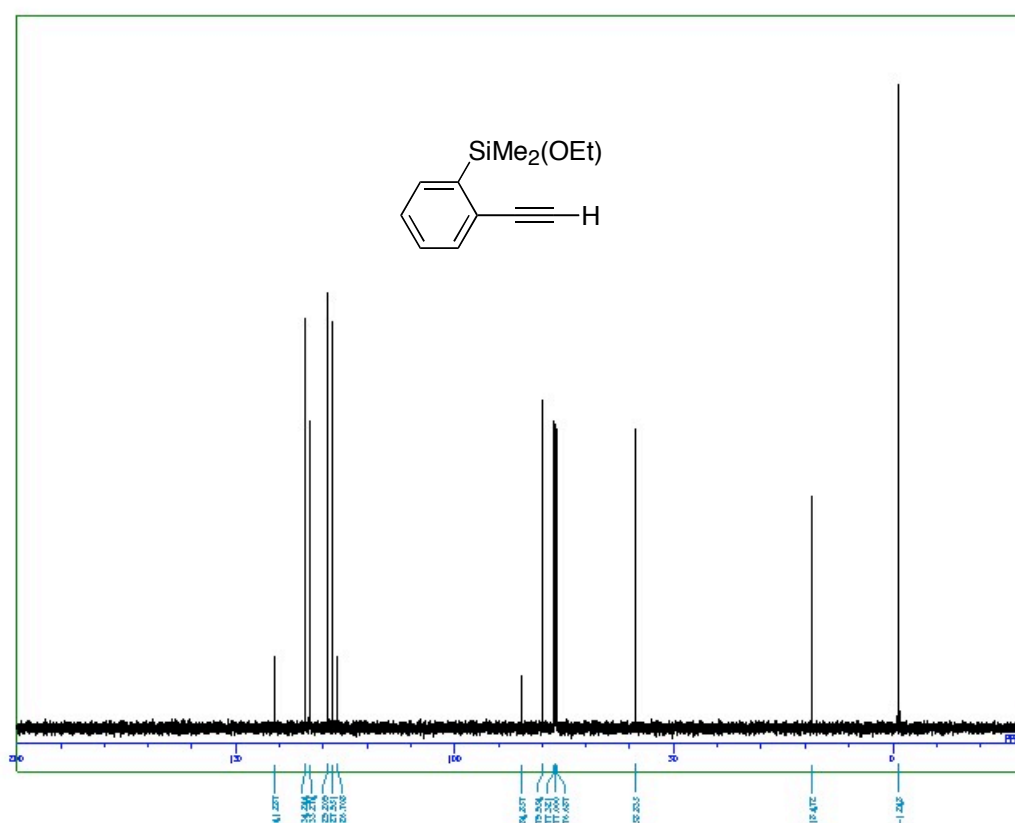
**Figure S5.** ORTEP drawing of **6b** (50% probability for thermal ellipsoids): a) a perspective view and b) a packing structure. Hydrogen atoms are omitted for clarity.

<sup>1</sup>H NMR of **8** (400 MHz, CDCl<sub>3</sub>)

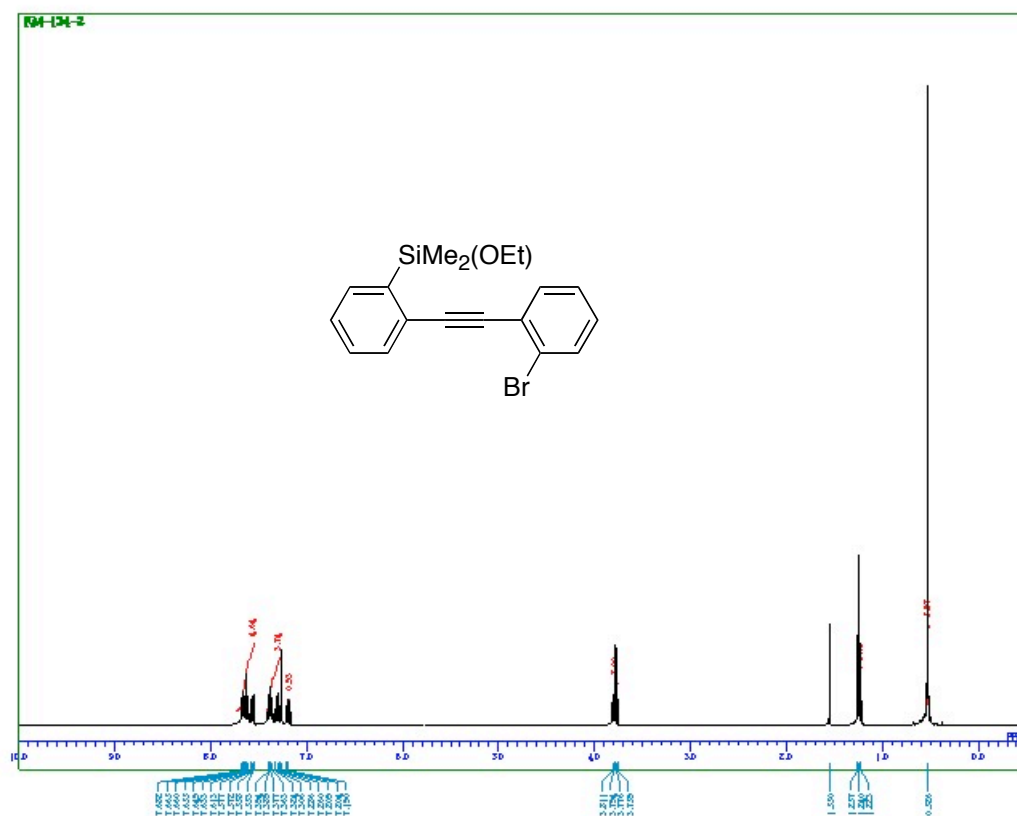
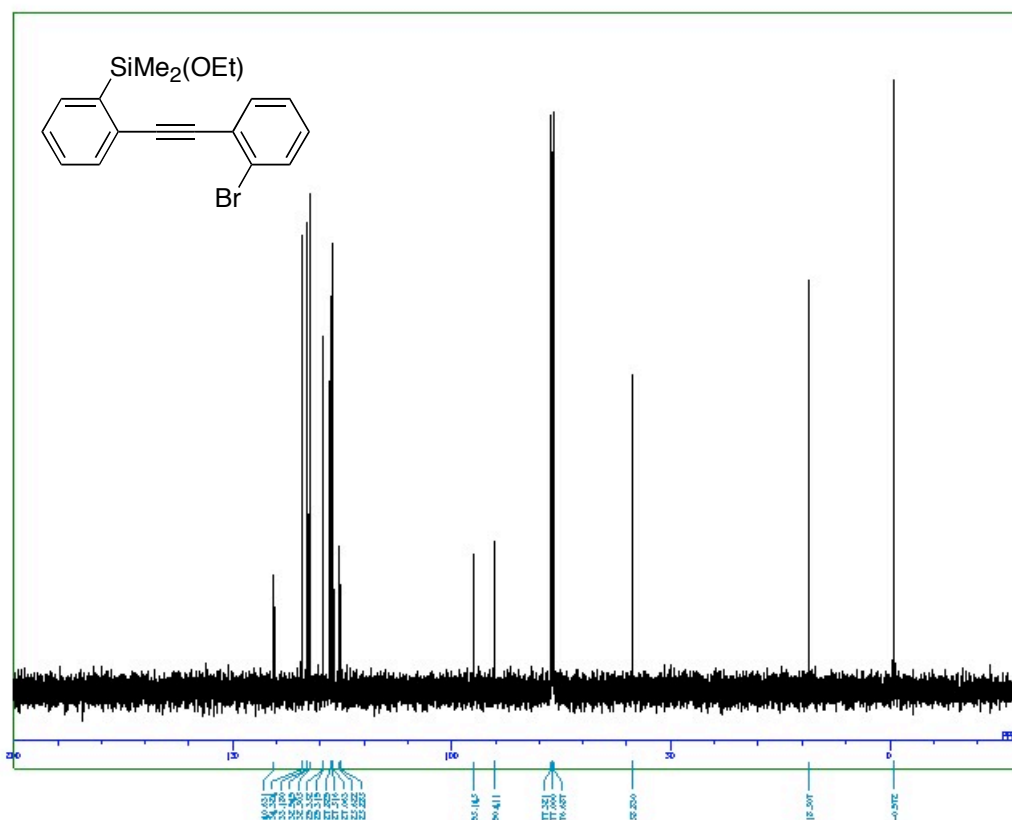
$^1\text{H}$  NMR of **9** (400 MHz,  $\text{CDCl}_3$ )



$^{13}\text{C}$  NMR of **9** (100 MHz,  $\text{CDCl}_3$ )

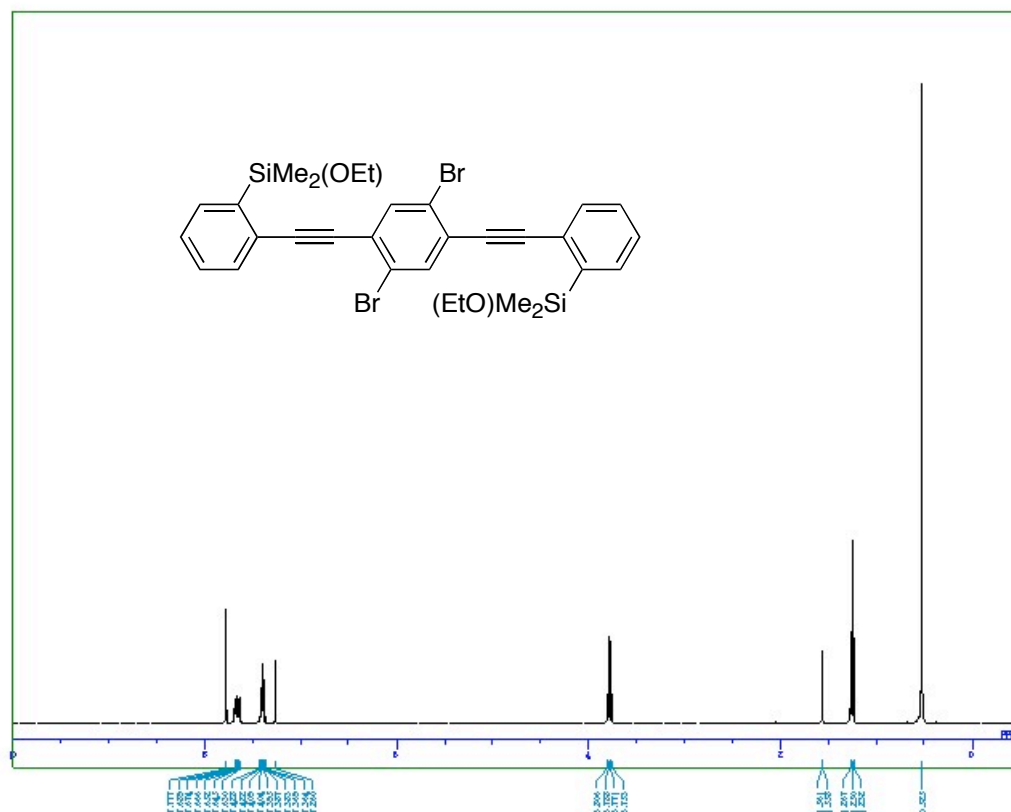


<sup>1</sup>H NMR of **1** (400 MHz, CDCl<sub>3</sub>)

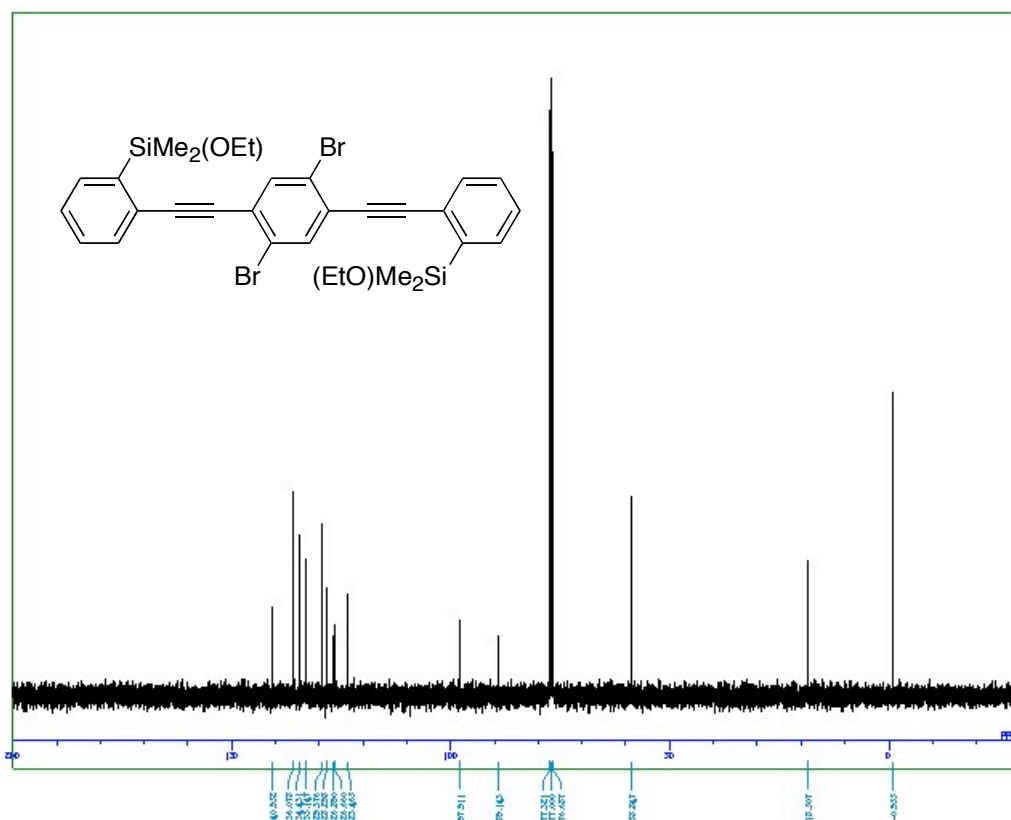
 $^{13}\text{C}$  NMR of **1** (100 MHz,  $\text{CDCl}_3$ )



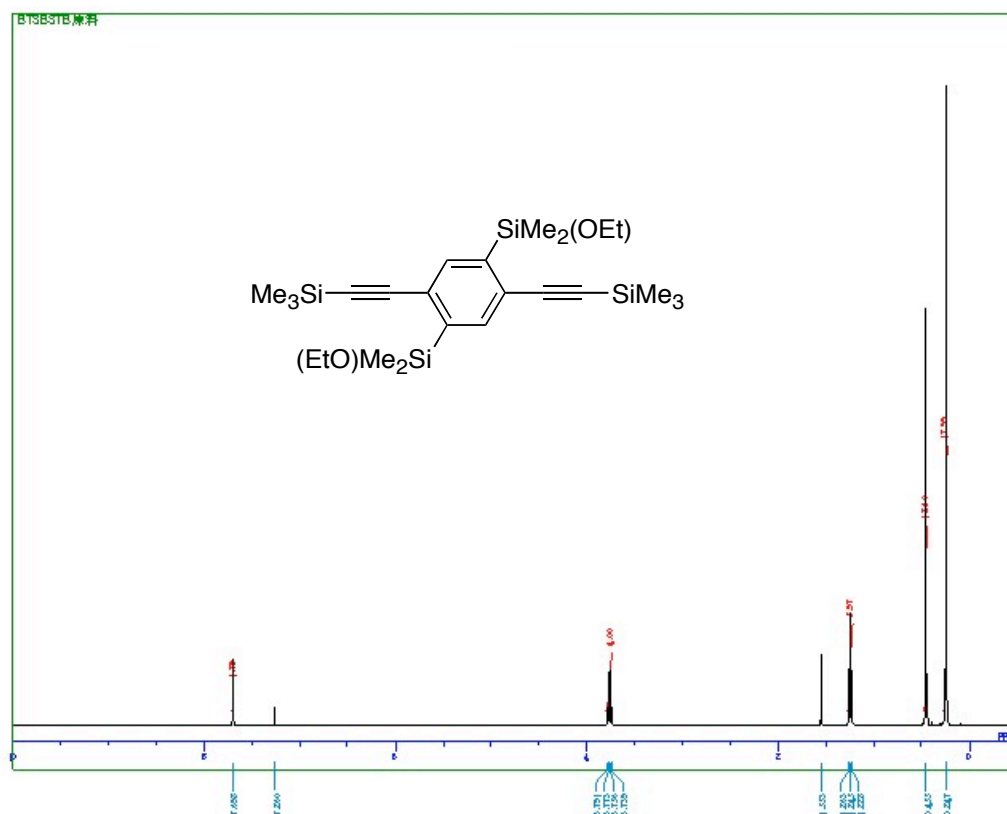
$^1\text{H}$  NMR of **4b** (400 MHz,  $\text{CDCl}_3$ )



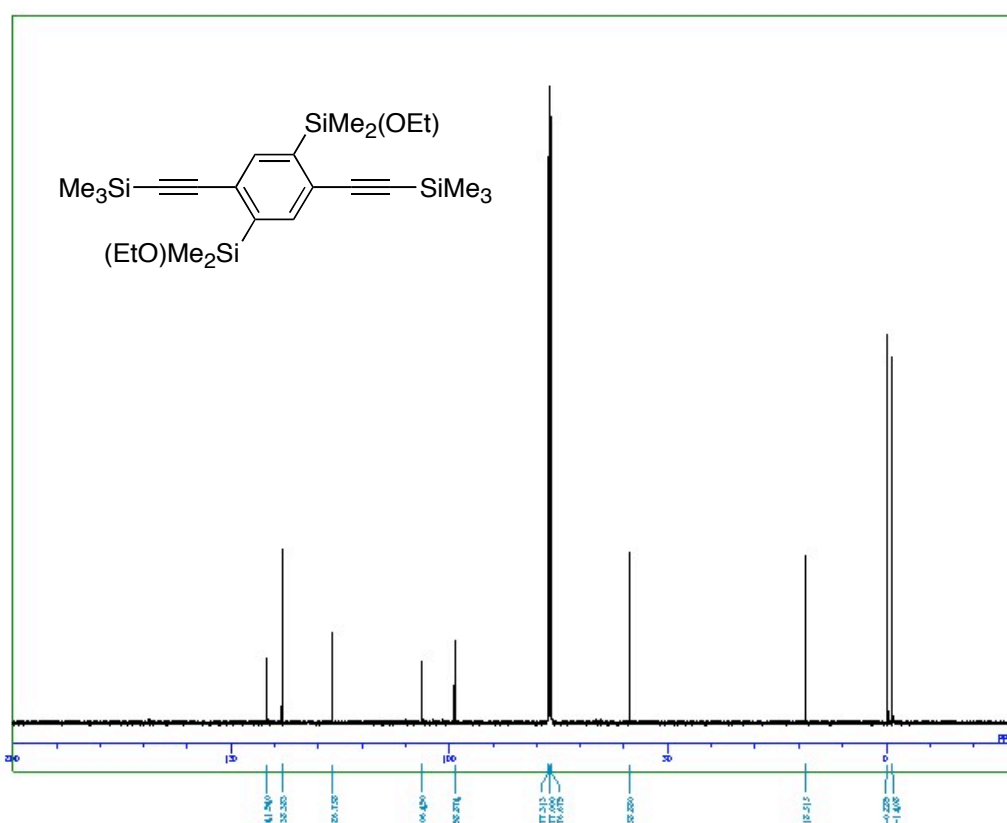
$^{13}\text{C}$  NMR of **4b** (100 MHz,  $\text{CDCl}_3$ )



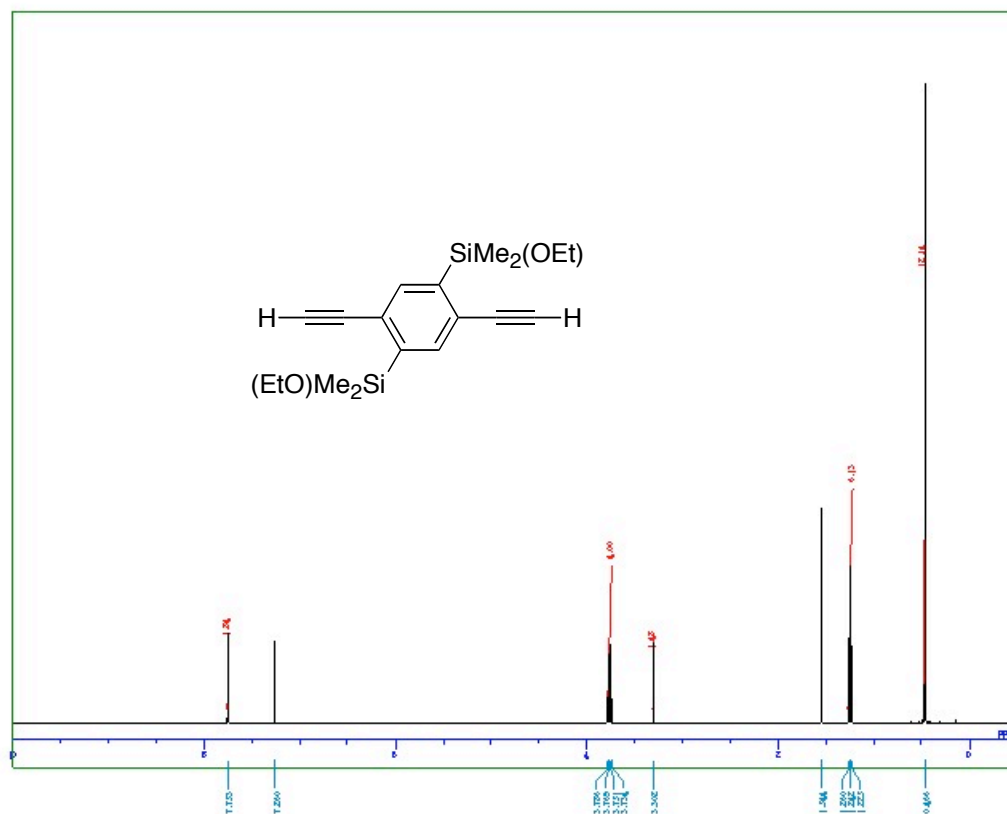
$^1\text{H}$  NMR of **10** (400 MHz,  $\text{CDCl}_3$ )



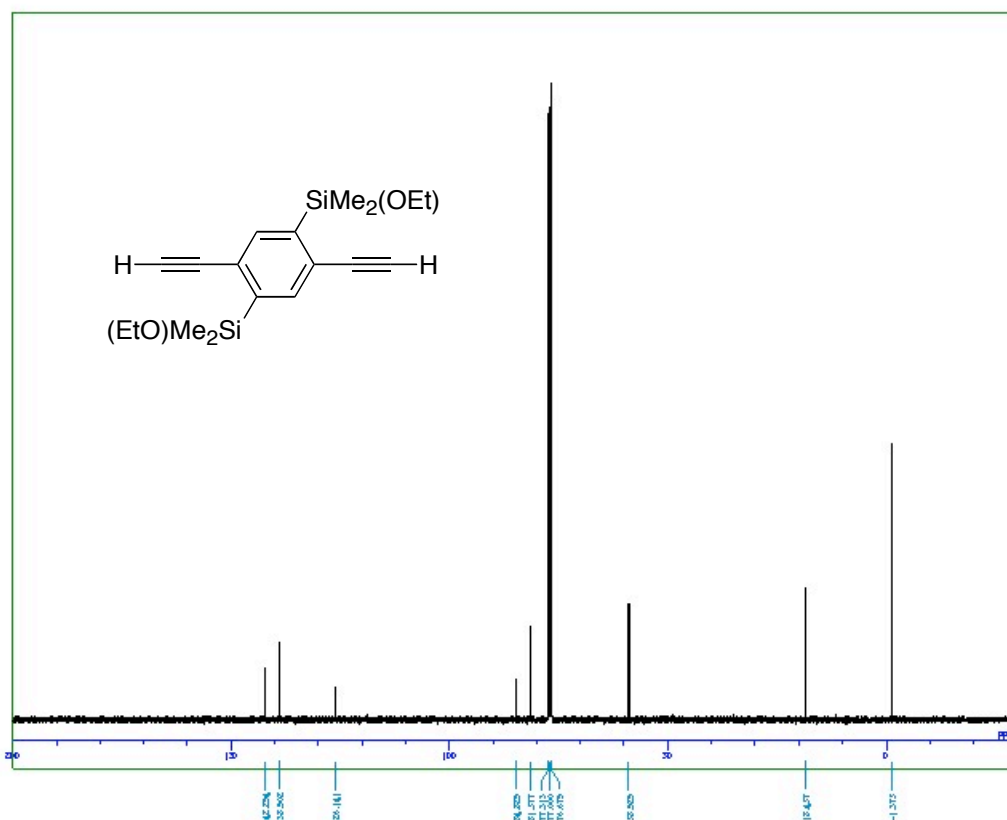
$^{13}\text{C}$  NMR of **10** (100 MHz,  $\text{CDCl}_3$ )



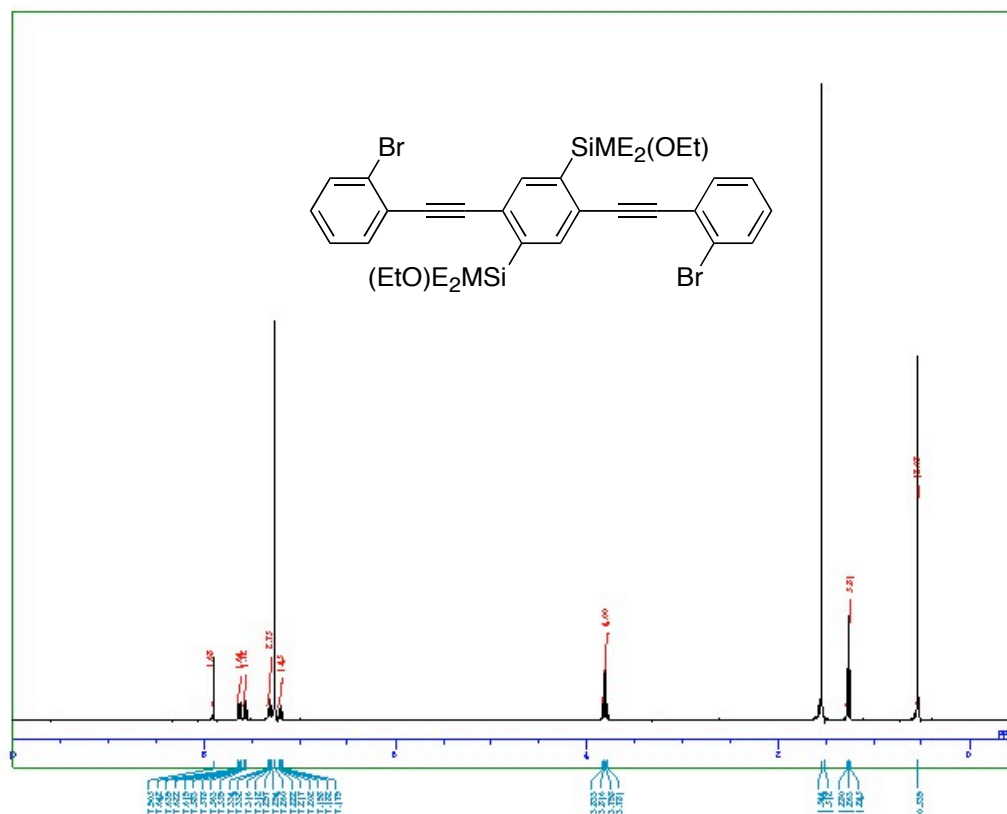
$^1\text{H}$  NMR of **11** (400 MHz,  $\text{CDCl}_3$ )



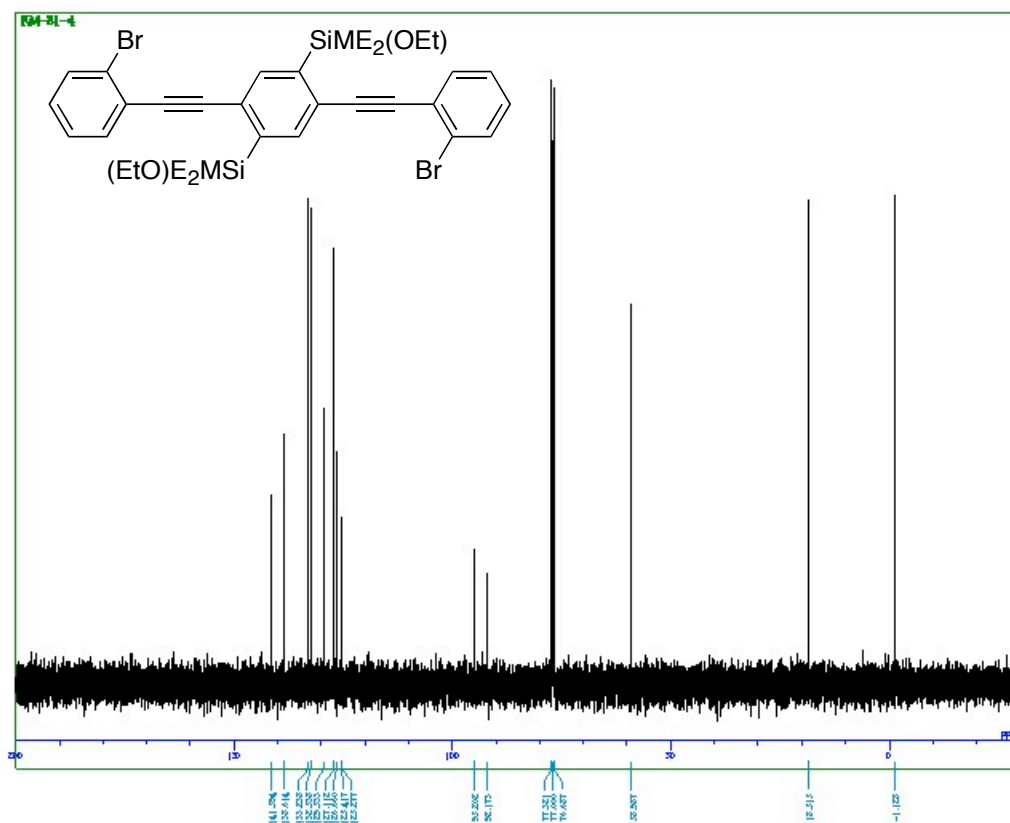
$^{13}\text{C}$  NMR of **11** (100 MHz,  $\text{CDCl}_3$ )



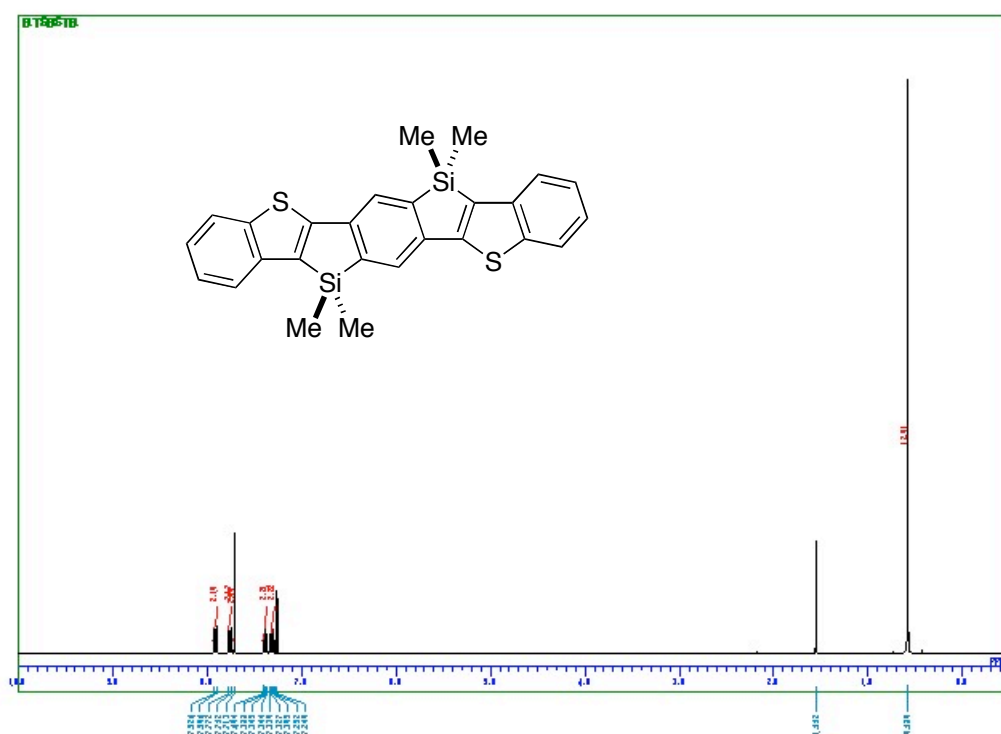
$^1\text{H}$  NMR of **4a** (400 MHz,  $\text{CDCl}_3$ )



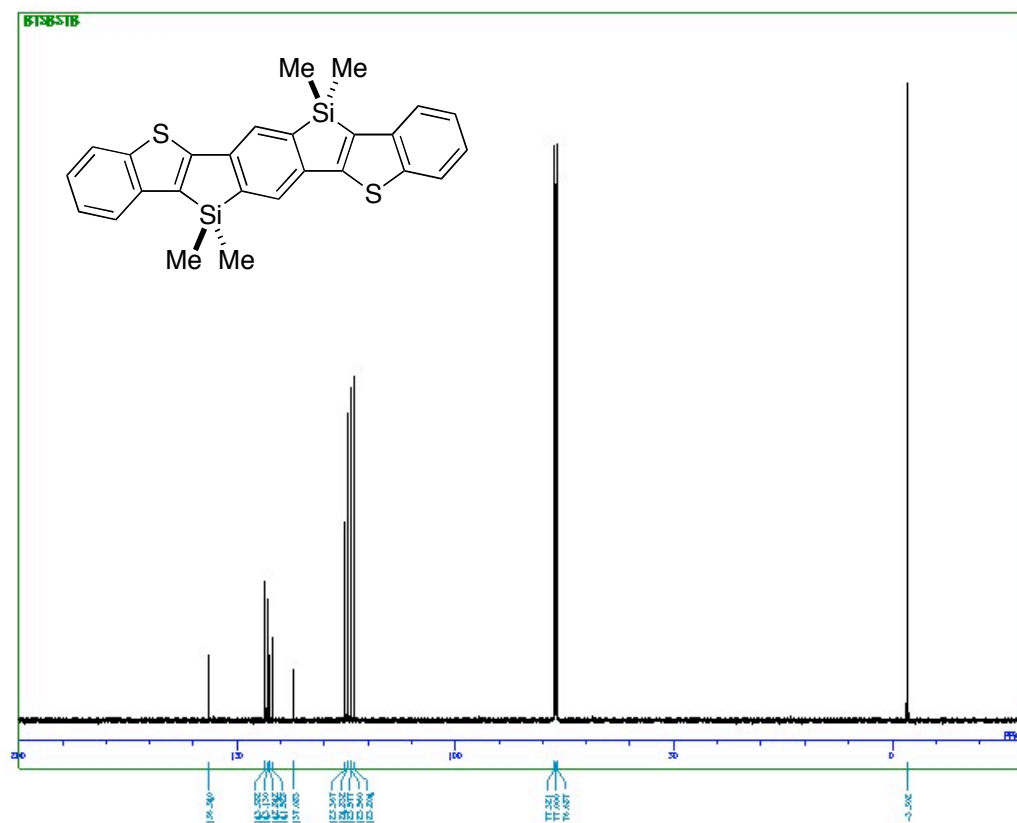
$^{13}\text{C}$  NMR of **4a** (100 MHz,  $\text{CDCl}_3$ )



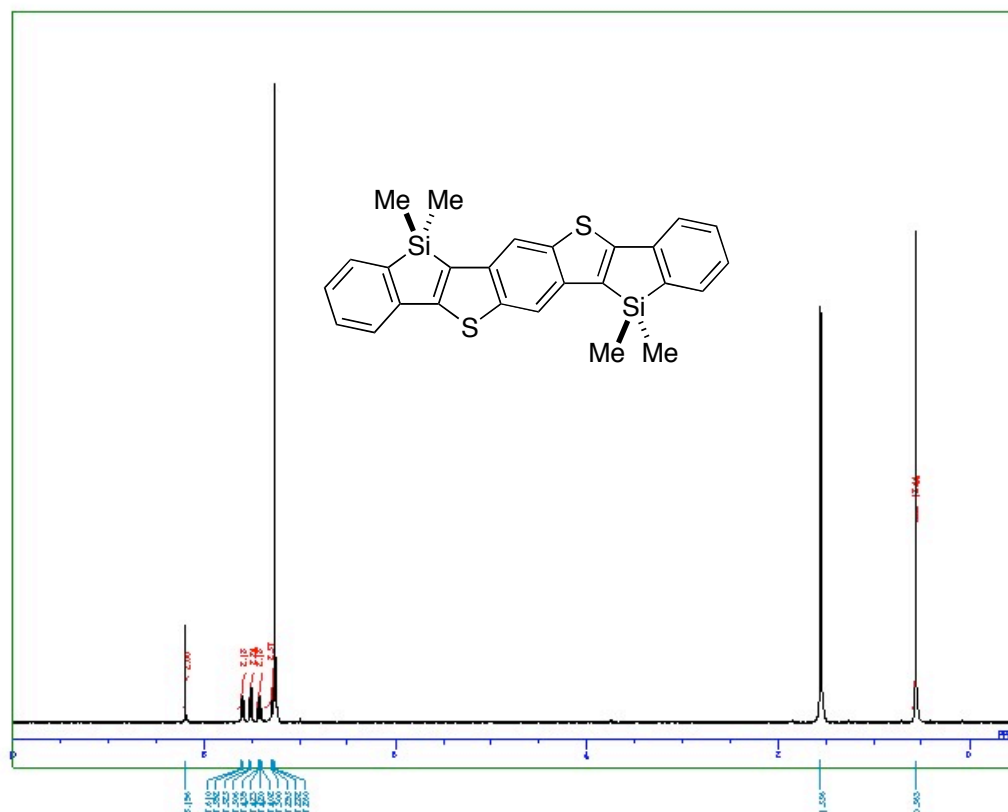
$^1\text{H}$  NMR of **5a** (400 MHz,  $\text{CDCl}_3$ )



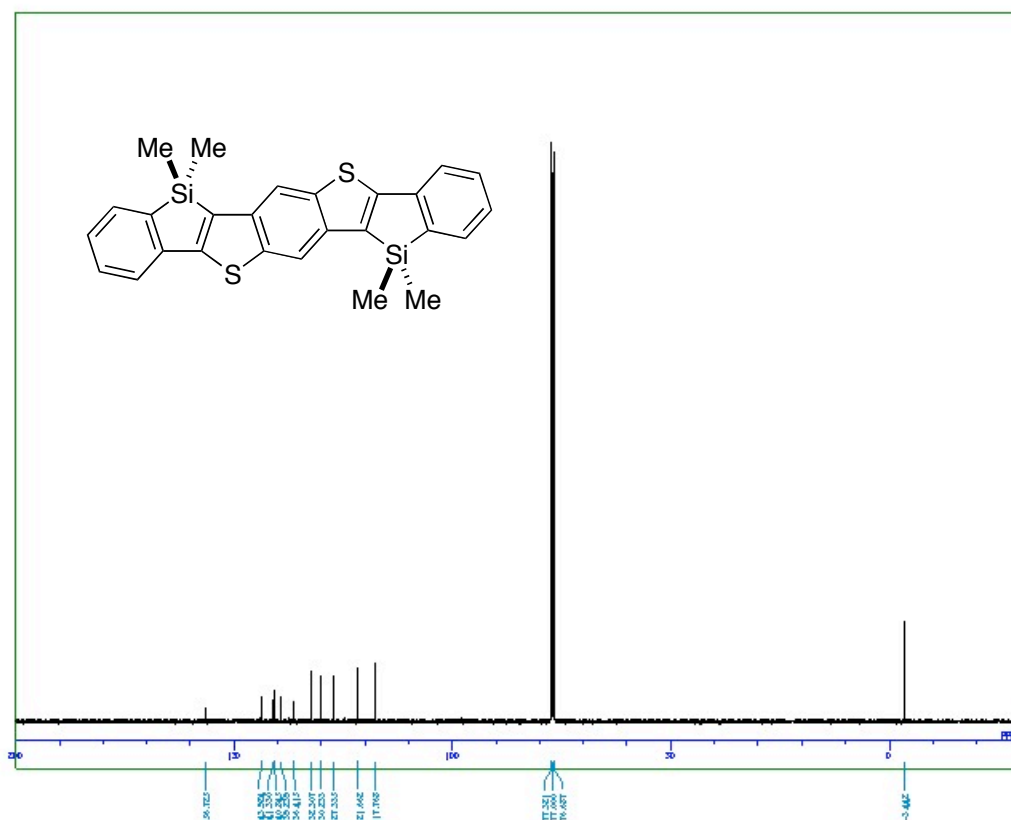
$^{13}\text{C}$  NMR of **5a** (100 MHz,  $\text{CDCl}_3$ )

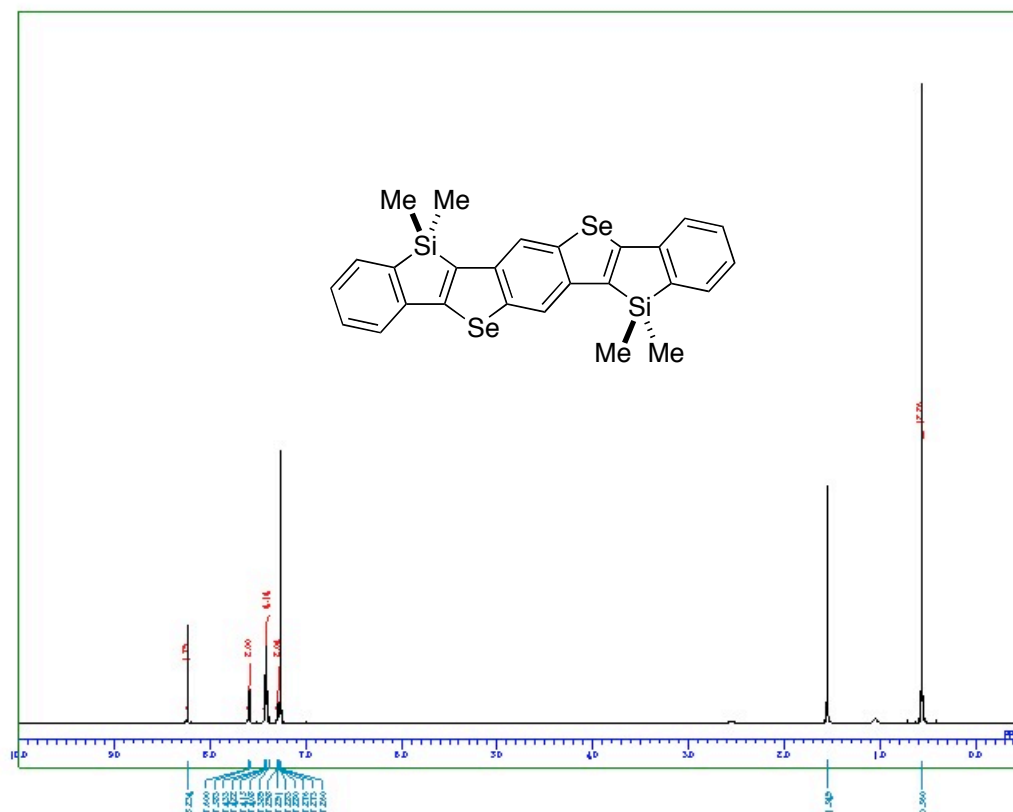
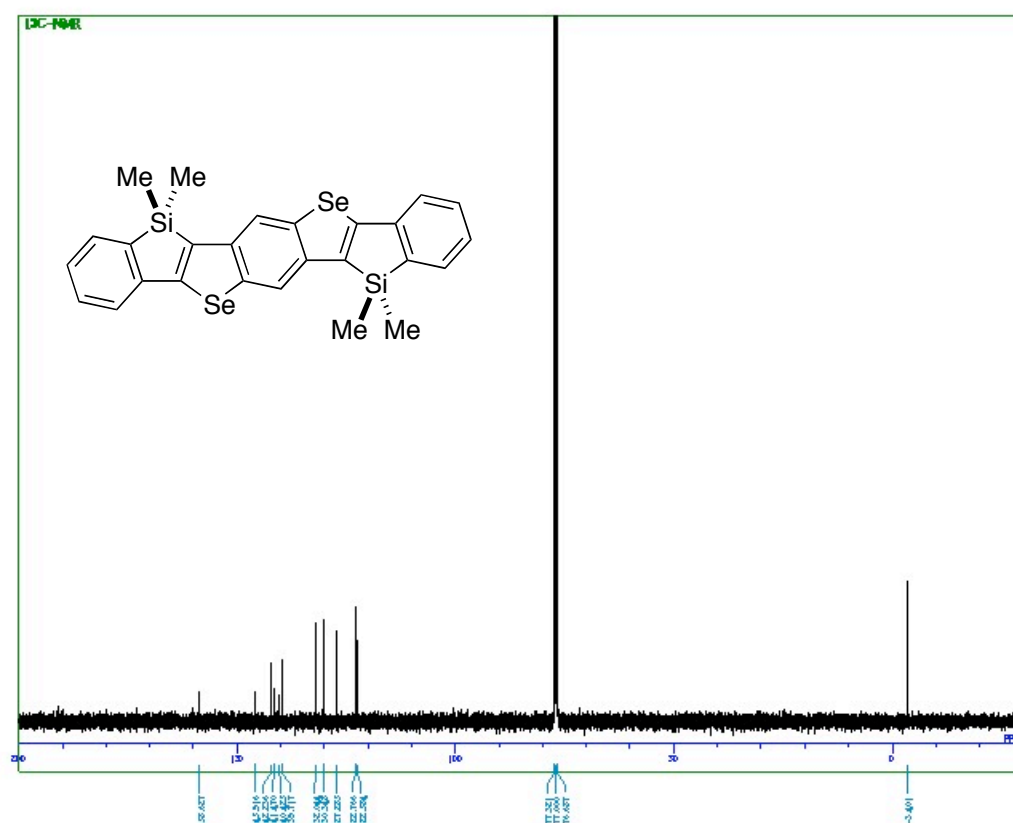


$^1\text{H}$  NMR of **5b** (400 MHz,  $\text{CDCl}_3$ )

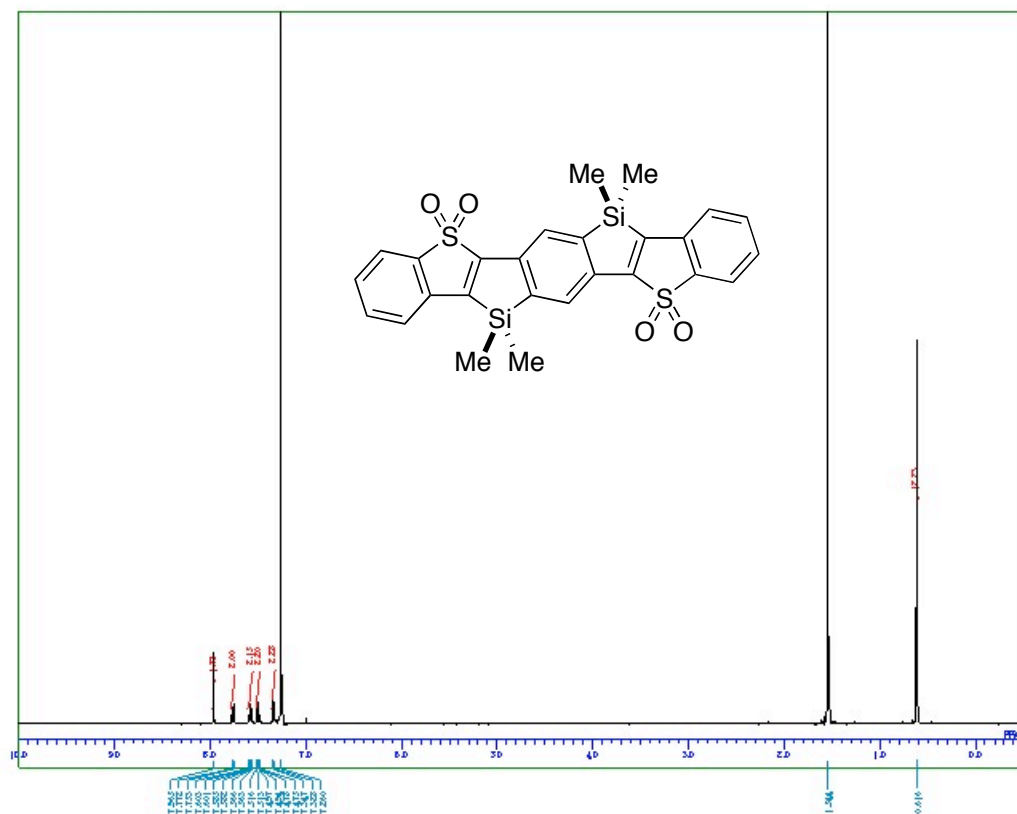


$^{13}\text{C}$  NMR of **5b** (100 MHz,  $\text{CDCl}_3$ )

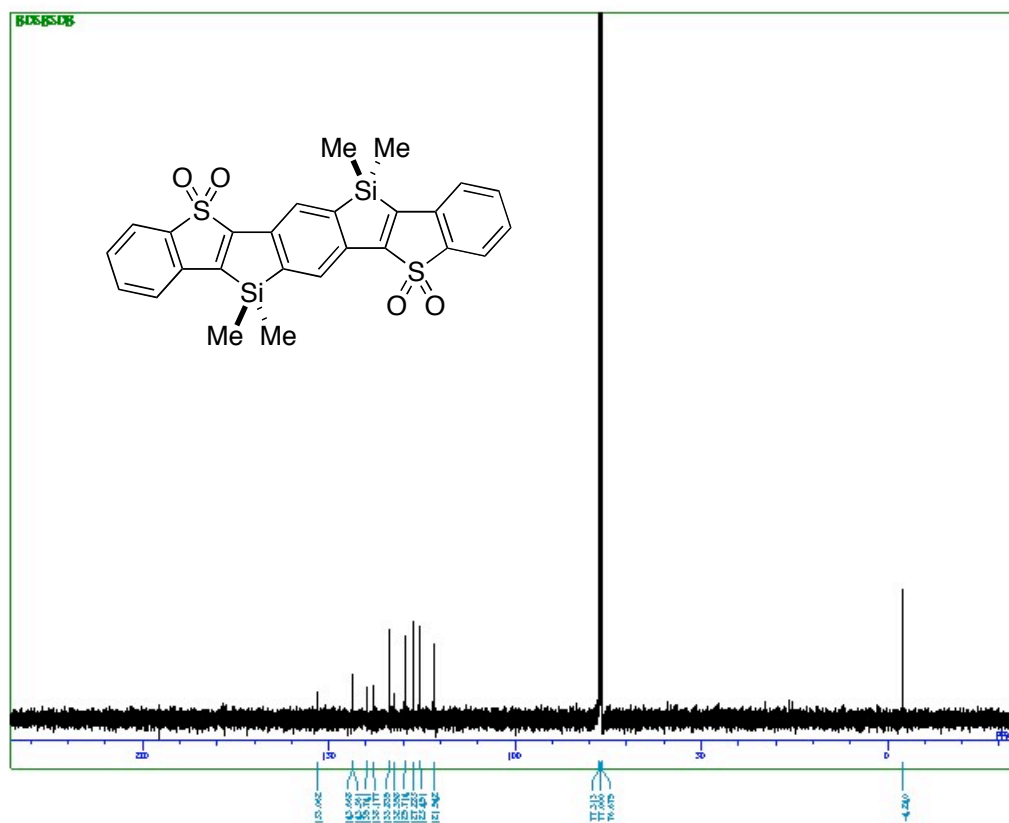


<sup>1</sup>H NMR of **5c** (400 MHz, CDCl<sub>3</sub>) $^{13}\text{C}$  NMR of **5c** (100 MHz,  $\text{CDCl}_3$ )

$^1\text{H}$  NMR of **6a** (400 MHz,  $\text{CDCl}_3$ )

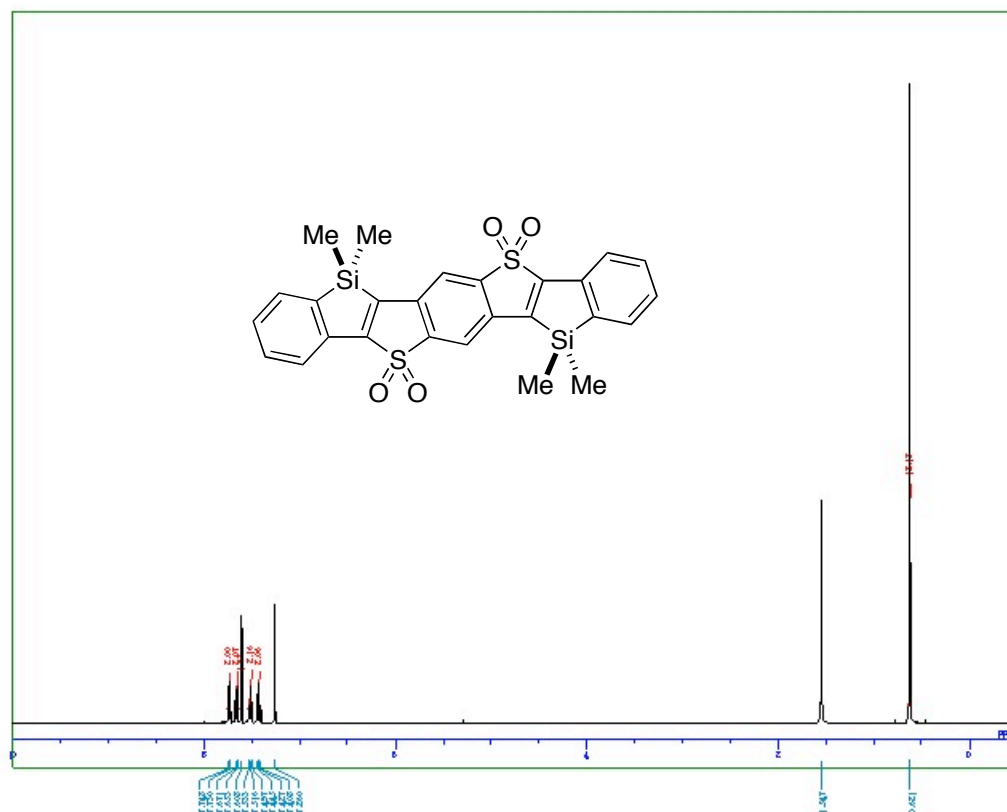


$^{13}\text{C}$  NMR of **6a** (100 MHz,  $\text{CDCl}_3$ )





$^1\text{H}$  NMR of **6b** (400 MHz,  $\text{CDCl}_3$ )



$^{13}\text{C}$  NMR of **6b** (100 MHz,  $\text{CDCl}_3$ )

