

Supporting Information

Mechanism for Si—Si Bond Rupture in Single Molecule Junctions

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I. General Information

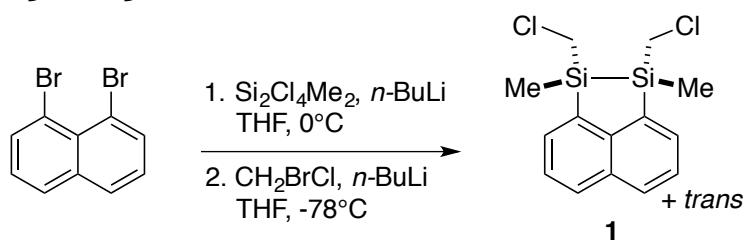
All reactions were carried out in flame-dried glassware with magnetic stirring unless otherwise indicated. The flasks were fitted with rubber septa and reactions were conducted under a positive pressure of nitrogen unless otherwise noted. Degassed solvents were purified by passage through an activated alumina column.

Materials. Commercial reagents were used without further purification unless otherwise noted. All reagents were purchased from Sigma-Aldrich, with the following exceptions. 1,1,2,2-tetrachlorodisilane was purchased from TCI. 1,8-dibromonaphthalene was purchased from Ark Pharm, Inc.

Instrumentation. ^1H , ^{13}C , and ^{29}Si NMR spectra were recorded on a Bruker DPX-400 (400 MHz) or a Bruker DPX-500 (500 MHz) spectrometer. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent (CDCl_3 = 7.26 ppm). Chemical shifts for carbon are reported in parts per million downfield from CDCl_3 internal standard (77.23 ppm). Chemical shifts for silicon are reported in parts per million downfield from tetramethylsilane and referenced to the silicon resonance of tetramethylsilane (TMS δ 0.0). The silicon NMR resonances were determined with a DEPT pulse sequence. Data are based on apparent multiplicities and are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, m = multiplet), coupling constants in Hertz, and integration. The mass spectroscopic data were obtained at the Columbia University mass spectrometry facility using a Waters XEVO G2XS QToF mass spectrometer with a UPC₂ SFC inlet, electrospray ionization (ESI) probe, atmospheric pressure chemical ionization (APCI) probe, and atmospheric solids analysis probe (ASAP). Infrared spectra were recorded on a Perkin Elmer Paragon 1000 FT-IR spectrometer. HPLC analyses for compounds **2a** and **2b** were performed on an Agilent 1200 Series HPLC, UV detection monitored at 254 nm, using a Luna silica column (3 Å) or a Chiralcel IB-3 column (25 cm).

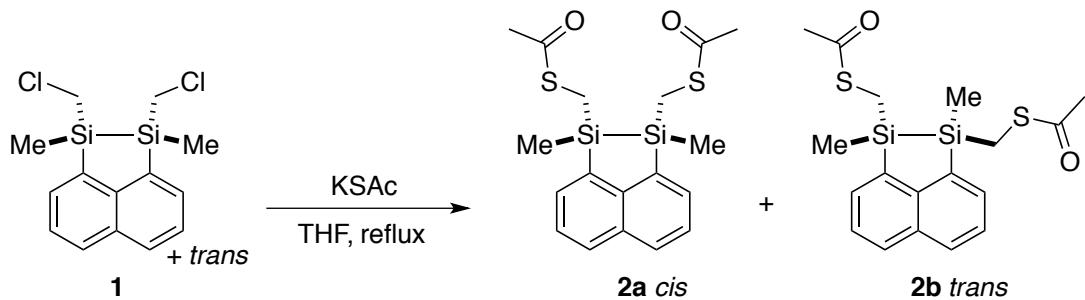
II. Synthetic procedures and characterization of compounds

Synthesis of dithiol **3a** and **3b**



The synthesis of **1** was adapted from Li, Su *et al.*¹ To a cooled (0 °C) solution of dibromonaphthalene (500 mg, 1.75 mmol) in THF (9 mL) was added *n*-butyllithium (1.47 mL, 2.5 M in THF, 3.67 mmol). After 10 min, the dilithiate was added by cannula into a cooled (-78 °C) solution of 1,1,2,2-tetrachlorodimethyldisilane (314 μL , 1.75 mmol) in THF (35 mL). The reaction

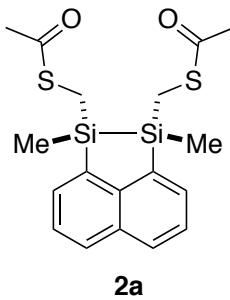
mixture was allowed to warm to room temperature over 1 h. To the reaction mixture was added bromochloromethane (239 μ L, 3.67 mmol). The reaction mixture was cooled to -78 °C, submerging it deeply into the dry ice-acetone bath to ensure the sides of the glass were cold. To the reaction mixture was added *n*-butyllithium (1.47 mL, 2.5 M in THF, 3.67 mmol) dropwise over 30 min down the side of the flask. The reaction mixture was warmed to room temperature overnight and quenched by the addition of saturated aqueous NH₄Cl (20 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with brine, dried (Na₂SO₄), filtered, and concentrated. Purification of the residue by silica gel flash chromatography (1% to 2% EtOAc/hexanes) afforded bis(chloromethyl)disilane **1** as a clear, colorless oil (242 mg, 0.778 mmol, 44% over two steps, 1.2:1 mixture of isomers, as judged by ¹H NMR spectroscopy). IR (thin film) 3047, 2956, 2923, 1483, 1440, 1394, 1335, 1309, 1250, 1221, 1174, 1156, 881, 798, 711, 642, 616 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.89 (m, 4H), δ 7.53 (m, 2H), δ 3.21 (s) and δ 3.12 (d, *J* = 3.7 Hz, 4H total), δ 0.67 and δ 0.63 (s, 6H total); ¹³C NMR (126 MHz, CDCl₃) δ 146.0, 138.4, 133.0, 132.8, 130.1, 125.8, 29.4, 29.3, -6.5, -6.8; ²⁹Si NMR (60 MHz, CDCl₃) δ -19.4, -19.5. HRMS predicted for C₁₄H₁₇Si₂Cl₂ (ASAP+): calcd 311.0245 ([M+H]⁺), observed 311.0246 ([M+H]⁺).



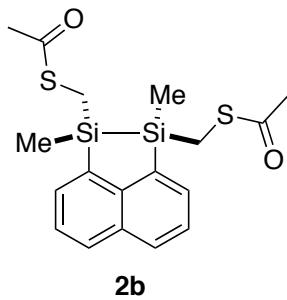
To a solution of bis(chloromethyl)disilane **1** (193 mg, 0.619 mmol) in THF (6 mL) was added potassium thioacetate (155 mg, 1.36 mmol). The reaction mixture was heated at reflux for 4 h. The reaction mixture was cooled to room temperature and quenched by the addition of saturated aqueous NH₄Cl (10 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine, dried (Na₂SO₄), filtered, and concentrated. Purification of the residue by silica gel flash chromatography (5% to 15% EtOAc/hexanes) afforded bis(thioacetate)disilane as a 1.2:1 mixture of *trans/cis* isomers (150 mg, 0.384 mmol, 62%).

The assignment of stereochemistry for **2a** and **2b** was made as follows: the *trans/cis* isomeric mixture was separated by analytical HPLC using a Luna silica column (3 Å) to isolate pure isomers. The *trans/cis* mixture was then analyzed using a Chiralcel IB-3 column (25 cm). The chromatogram showed three peaks, two of which integrated in a 50:50 ratio. Compound **2b** (the first to elute off of the Luna silica column) was then analyzed using this chiral HPLC assay and showed the two peaks in a 50:50 ratio. Compound **2b** is therefore assigned as the *trans* diastereomer, which is chiral (*dl*). Analysis of compound **2a** (the second to elute off of the Luna silica column) using the same chiral HPLC assay revealed a single peak, and this allowed the

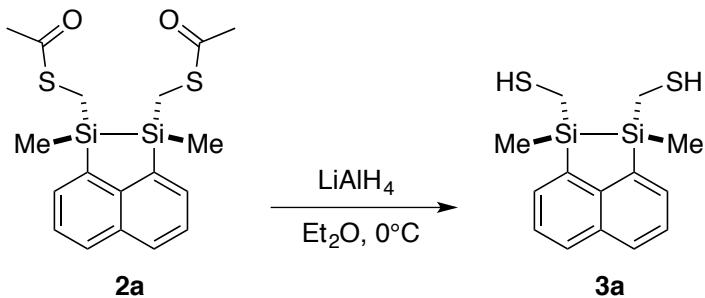
assignment of **2a** as the *cis* diastereomer, which is achiral (*meso*). All HPLC conditions and traces are included below.



Odorous, pale yellow oil. IR (thin film) 3046, 2953, 2924, 2894, 2851, 1687, 1482, 1413, 1352, 1308, 1250, 1138, 1104, 954, 878, 797, 780, 719, 625 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.88 (dd, J = 8.3, 1.2 Hz, 2H), δ 7.82 (dd, J = 6.6, 1.3 Hz, 2H), δ 7.51 (dd, J = 8.2, 6.6 Hz, 2H), δ 2.52 (d, J = 2.0 Hz, 4H), δ 2.32 (s, 6H), δ 0.50 (s, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 196.5, 145.8, 139.8, 132.7, 132.5, 129.9, 125.8, 30.2, 12.0, -5.3; ^{29}Si NMR (60 MHz, CDCl_3) δ -19.8. HRMS predicted for $\text{C}_{18}\text{H}_{23}\text{O}_2\text{S}_2\text{Si}_2$ (ASAP+): calcd 391.0678 ($[\text{M}+\text{H}]^+$), observed 391.0676 ($[\text{M}+\text{H}]^+$).

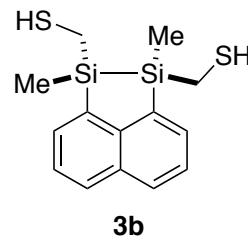


Odorous, pale yellow oil. IR (thin film) 3046, 2954, 2920, 2895, 2851, 1686, 1482, 1406, 1352, 1308, 1247, 1137, 1102, 1017, 953, 879, 799, 785, 728, 697, 623 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.88 (dd, J = 8.3, 1.2 Hz, 2H), δ 7.80 (dd, J = 6.7, 1.3 Hz, 2H), δ 7.52 (dd, J = 8.2, 6.6 Hz, 2H), δ 2.45 (s, 4H), δ 2.30 (s, 6H), δ 0.55 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.4, 145.8, 139.7, 132.7, 132.5, 129.8, 125.7, 30.1, 12.1, -5.3; ^{29}Si (60 MHz, CDCl_3) δ -19.8. HRMS predicted for $\text{C}_{18}\text{H}_{23}\text{O}_2\text{S}_2\text{Si}_2$ (ASAP+): calcd 391.0678 ($[\text{M}+\text{H}]^+$), observed 391.0676 ($[\text{M}+\text{H}]^+$).



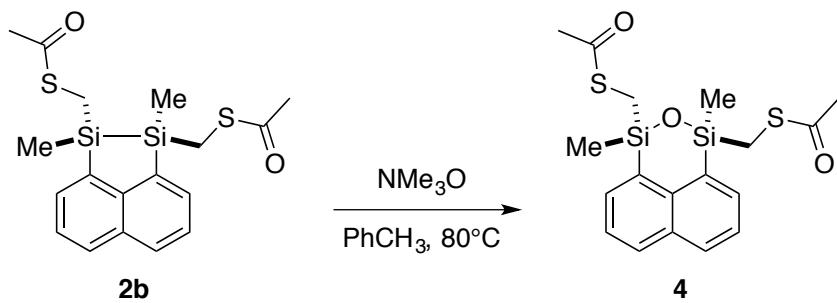
Cis and *trans* bis(methylthiol)disilane **3a** and **3b** were synthesized with a method adapted from Li, Su et al.¹ Lithium aluminum hydride (14.8 mg, 0.389 mmol) was added to a flame-dried flask. Et_2O (1 mL) was added and the flask was cooled to 0 °C. To the flask was added a solution of *cis* bis(thioacetate)disilane **2a** (30.5 mg, 0.0782 mmol) in Et_2O (1 mL). The reaction mixture was stirred at 0 °C for 10 minutes, and quenched by the addition of 1 M HCl (1 mL) at 0 °C. The reaction mixture was stirred at room temperature for 10 minutes and filtered over celite. 2 mL of H_2O was added, the layers were separated and the aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated to yield a colorless oil **3a** (23.5 mg, 0.0766 mmol, 98%). IR (thin film) 3045, 2952, 2922, 2894, 2851, 1482, 1334, 1308, 1249, 1156, 877, 796, 789, 779, 713, 553, 434 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.89 (dd, J = 8.3, 1.3 Hz, 2H), δ 7.84 (dd, J = 6.6, 1.3 Hz, 2H), δ 7.53 (dd, J = 8.2, 6.6 Hz, 2H), δ 2.14 (m, 4H), δ 1.37 (dd, J = 7.9, 6.7 Hz, 2H), δ 0.56 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.1, 140.0, 132.8, 132.4, 129.8, 125.8,

6.0, -5.7; ^{29}Si NMR (60MHz, CDCl_3) δ -16.9. HRMS predicted for $\text{C}_{14}\text{H}_{17}\text{S}_2\text{Si}_2$ (ASAP-): calcd 305.0310 ($[\text{M}-\text{H}]^-$), observed 305.0297 ($[\text{M}-\text{H}]^-$).

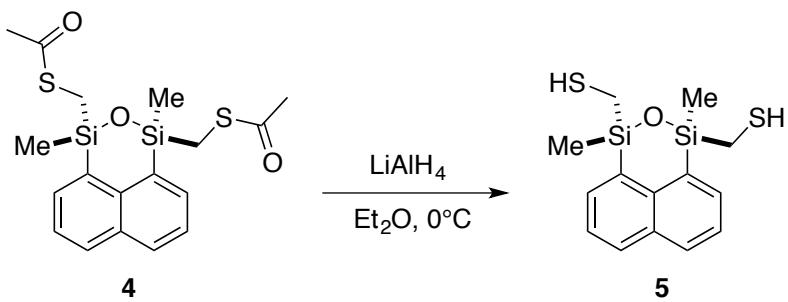


3b was synthesized using the same general procedure with **2b** as the reactant. Colorless oil (2.3 mg, 97%). IR (thin film) 3045, 2954, 2921, 2895, 2850, 1557, 1482, 1438, 1386, 1333, 1308, 1248, 1156, 1015, 878, 784, 725, 691, 609, 554 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.90 (dd, J = 8.3, 1.3 Hz, 2H), δ 7.82 (dd, J = 6.6, 1.3 Hz, 2H), δ 7.53 (dd, J = 8.2, 6.6 Hz, 2H), δ 2.01 (d, J = 7.3 Hz, 4H), δ 1.19 (t, J = 7.3 Hz, 2H), δ 0.65 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.2, 139.8, 132.7, 132.3, 129.8, 125.8, 6.1, -5.9; ^{29}Si NMR (60MHz, CDCl_3) δ -16.8. HRMS predicted for $\text{C}_{14}\text{H}_{17}\text{S}_2\text{Si}_2$ (ASAP-): calcd 305.0310 ($[\text{M}-\text{H}]^-$), observed 305.0306 ($[\text{M}-\text{H}]^-$).

Synthesis of siloxane dithiol **5**

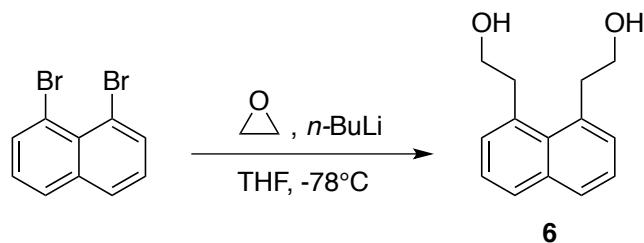


The synthesis of **4** was adapted from Klausen *et al.*² To a solution of bis(thioacetate)disilane **2b** (27.6 mg, 0.0706 mmol) in toluene (0.7 mL) was added trimethylamine N-oxide (10.6 mg, 0.141 mmol). The reaction mixture was stirred at 80 °C for 4 hours. The reaction mixture was concentrated and the residue was purified by silica gel flash chromatography (10% EtOAc/Hexanes) to give a clear oil (20.0 mg, 0.0492 mmol, 70%). IR (thin film) 3053, 2958, 2897, 2851, 1687, 1489, 1354, 1254, 1139, 996, 892, 804, 624 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.92 (dd, J = 8.3, 1.4 Hz, 2H), δ 7.65 (dd, J = 6.7, 1.4 Hz, 2H), δ 7.51 (dd, J = 8.2, 6.7 Hz, 2H), δ 2.39 (m, 4H), δ 2.24 (s, 6H), δ 0.57 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.0, 141.1, 133.2, 133.0, 132.8, 131.4, 125.0, 30.1, 15.4, -0.3; ^{29}Si NMR (60MHz, CDCl_3) δ 0.15. HRMS predicted for $\text{C}_{18}\text{H}_{23}\text{O}_3\text{S}_2\text{Si}_2$ (ASAP+): calcd 407.0627 ($[\text{M}+\text{H}]^+$), observed 407.0623 ($[\text{M}+\text{H}]^+$).

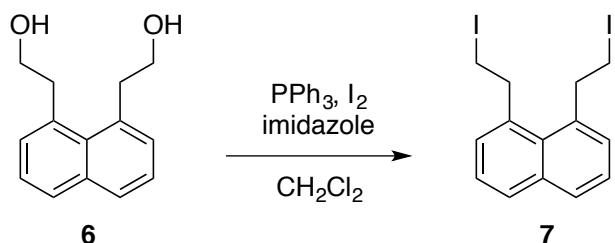


Lithium aluminum hydride (4.7 mg, 0.123 mmol) was added to a flame-dried flask. Et₂O (1 mL) was added and the flask was cooled to 0 °C. To the flask was added a solution of *cis* bis(thioacetate)siloxane **4** (10.0 mg, 0.0246 mmol) in Et₂O (0.5 mL). The reaction mixture was stirred at 0 °C for 10 minutes, and quenched by the addition of 1 M HCl (1 mL) at 0 °C. The reaction mixture was stirred at room temperature for 10 minutes and filtered over celite. 2 mL of H₂O was added, the layers were separated and the aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated to yield a colorless oil **5** (7.1 mg, 0.022 mmol, 89%). IR (thin film) 3052, 2956, 2921, 2898, 2851, 1589, 1561, 1489, 1450, 1383, 1307, 1253, 1158, 996, 892, 800, 780, 737, 595, 527, 467 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.93 (dd, *J* = 8.3, 1.4 Hz, 2H), δ 7.67 (dd, *J* = 6.7, 1.4 Hz, 2H), δ 7.52 (dd, *J* = 8.2, 6.7 Hz, 2H), δ 1.98 – 1.81 (m, 4H), δ 1.10 (dd, *J* = 8.4, 6.2 Hz, 2H), δ 0.63 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 141.7, 133.4, 132.9, 132.9, 131.3, 125.1, 9.3, -0.8; ²⁹Si NMR (60 MHz, CDCl₃) δ 0.28. HRMS predicted for C₁₄H₁₇OSi₂ (ASAP-): calcd 321.0259 ([M-H]⁺), observed 321.0259 ([M-H]⁺).

Synthesis of disulfide 8

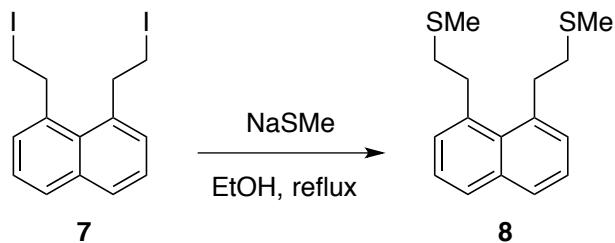


To a cooled (0 °C) solution of dibromonaphthalene (250 mg, 0.874 mmol) in THF (4.4 mL) was added *n*-butyllithium (0.735 mL, 2.5 M in THF, 1.84 mmol). After 10 min of stirring at 0 °C, a solution of ethylene oxide was added (0.735 mL, 2.5 M in THF, 1.84 mmol). The reaction mixture was allowed to warm to room temperature over 4 h and quenched by the addition of 1 M HCl (5 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with brine, dried (Na₂SO₄), filtered, and concentrated. Purification of the residue by silica gel flash chromatography (100% EtOAc) afforded naphthyl diol **6** as a white solid (58.4 mg, 0.270 mmol, 31%). Spectral data matches previous characterization.³



To a solution of naphthyl diol **6** (58.4 mg, 0.270 mmol) in CH_2Cl_2 (3 mL) was added imidazole (91.9 mg, 1.35 mmol), then iodine (274 mg, 1.08 mmol), then triphenylphosphine (283 mg, 1.08 mmol). The reaction mixture was stirred at room temperature for 6 hours and quenched with H_2O (10 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3 x

15 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), filtered, and concentrated. Purification of the residue by silica gel flash chromatography (1% to 5% EtOAc/hexanes) afforded naphthyl diiodide **7** as a golden oil (43.2 mg, 0.0991 mmol, 37%). IR (thin film) 3034, 2955, 2922, 2852, 1597, 1579, 1508, 1424, 1380, 1300, 1207, 1166, 1118, 821, 808, 773, 698, 553 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.83 (m, 2H), δ 7.39 (m, 4H), δ 3.63 (t, J = 7.2 Hz, 4H), δ 3.29 (t, J = 7.2 Hz, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 136.5, 136.3, 130.4, 129.8, 129.6, 125.4, 41.6, 5.0. HRMS predicted for $\text{C}_{12}\text{H}_{11}\text{I}_2$ (ASAP+): calcd 436.9263 ($[\text{M}+\text{H}]^+$), observed 436.9260 ($[\text{M}+\text{H}]^+$).



To a solution of naphthyl diiodide **7** (14.1 mg, 0.0323 mmol) in ethanol (1 mL) was added sodium thiomethoxide (4.99 mg, 0.0711 mmol). The reaction mixture was heated at reflux for 6 hours. The reaction mixture was cooled to room temperature and quenched by the addition of saturated aqueous NH_4Cl (5 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), filtered, and concentrated. Purification of the residue by silica gel flash chromatography (1% to 5% EtOAc/hexanes) afforded naphthyl disulfide **8** as a clear oil (6.96 mg, 0.0252 mmol, 78%). IR (thin film) 3033, 2915, 2850, 1598, 1579, 1429, 1378, 1313, 1221, 1166, 810, 774, 644, 610, 564 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.76 (m, 2H), δ 7.37 (m, 4H), δ 3.43 (t, J = 7.2 Hz, 4H), δ 2.75 (t, J = 7.2 Hz, 4H), δ 2.15 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 136.7, 136.1, 130.4, 130.1, 129.2, 125.1, 37.5, 36.7, 15.9. HRMS predicted for $\text{C}_{16}\text{H}_{21}\text{S}_2$ (ASAP+): calcd 277.1085 ($[\text{M}+\text{H}]^+$), observed 277.1084 ($[\text{M}+\text{H}]^+$).

III. STM-Break Junction experiment details

We measured the conductance of single molecules bound to gold electrodes using a home-built modified Scanning Tunneling Microscope (STM). We used a 0.25 mm diameter gold wire (99.998%, Alfa Aesar) as the STM tip and a gold-coated (99.999%, Alfa Aesar) mica surface as the substrate. A commercially available single-axis piezoelectric positioner (Nano-P15, Mad City Labs) was used to achieve sub-angstrom level control of the tip-substrate distance. The STM was controlled using a custom written program in IgorPro (Wavemetrics, Inc.) and operated in ambient conditions at room temperature. The gold substrate was cleaned using UV/Ozone for 15 minutes prior to use. For each measurement, 1000 traces were first collected prior to adding molecular solutions to ensure that the gold was clean. Solutions of the target molecules at 1 mM concentration in 1,2,4-trichlorobenzene (Sigma-Aldrich or Alfa Aesar, 99% purity) were added to the substrate for molecular conductance measurements. The applied bias was 225 mV, and the substrate was displaced at a speed of 19 nm/s for all measurements. The current and voltage data were acquired at 40 kHz. For each molecule, we collected over 10,000 traces to create 1D conductance histograms without data selection (Figure 1 in the main text).

IV. Additional Figures

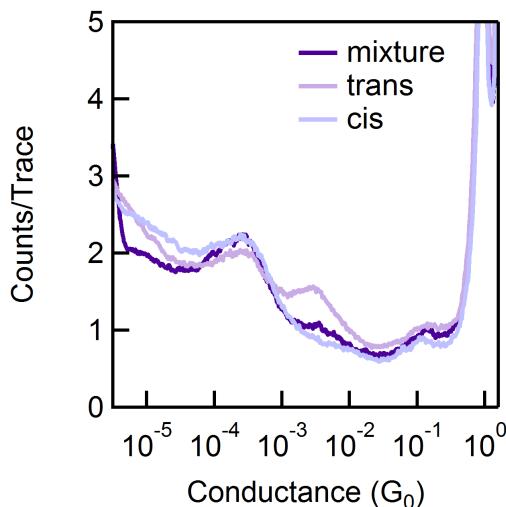


Figure S1. (a) 1D conductance histograms of mixture (dark purple), trans isomer (light purple) and cis isomer (light blue) of **Si2Naph**.

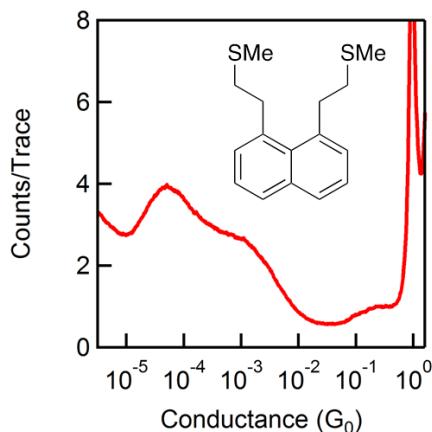


Figure S2. 1D Conductance histograms of molecule **8** naphthyl disulfide with the structure shown inside.

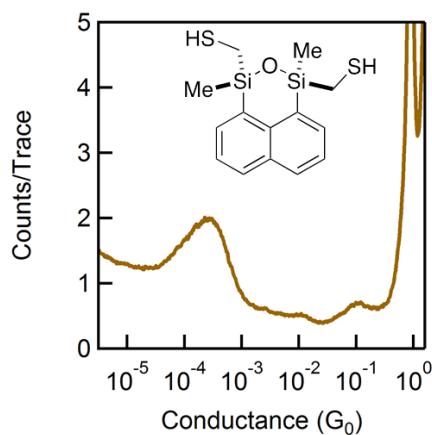


Figure S3. 1D Conductance histograms of molecule **5** siloxane dithiol with the structure shown inside.

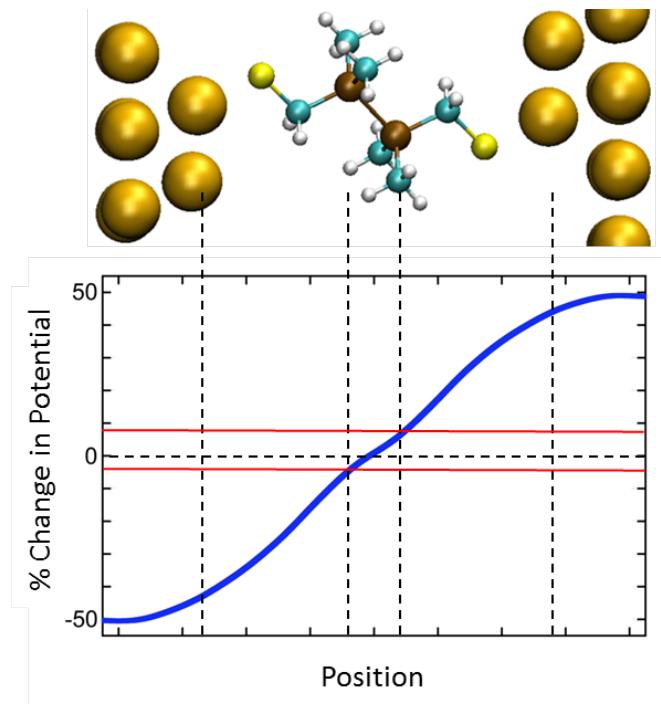


Figure S4. 3D structure of **Si2** molecular junction with electrodes and calculated voltage drop across the **Si2** junction.

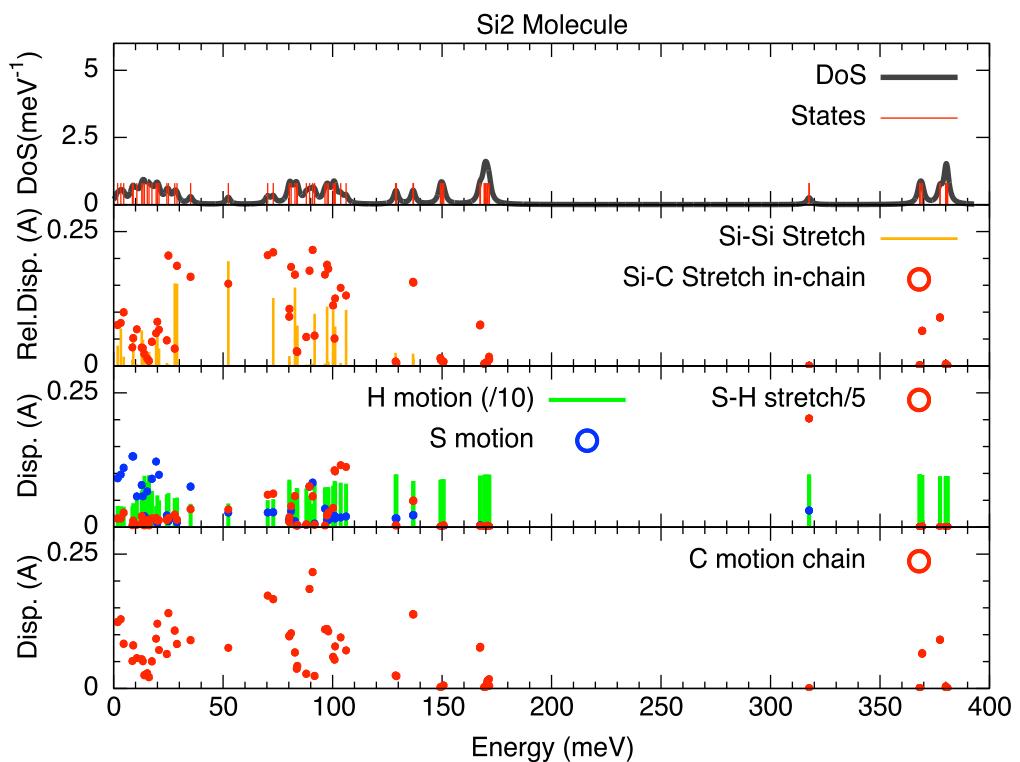


Figure S5. Calculated phonon modes and modes decomposition for **Si2**.

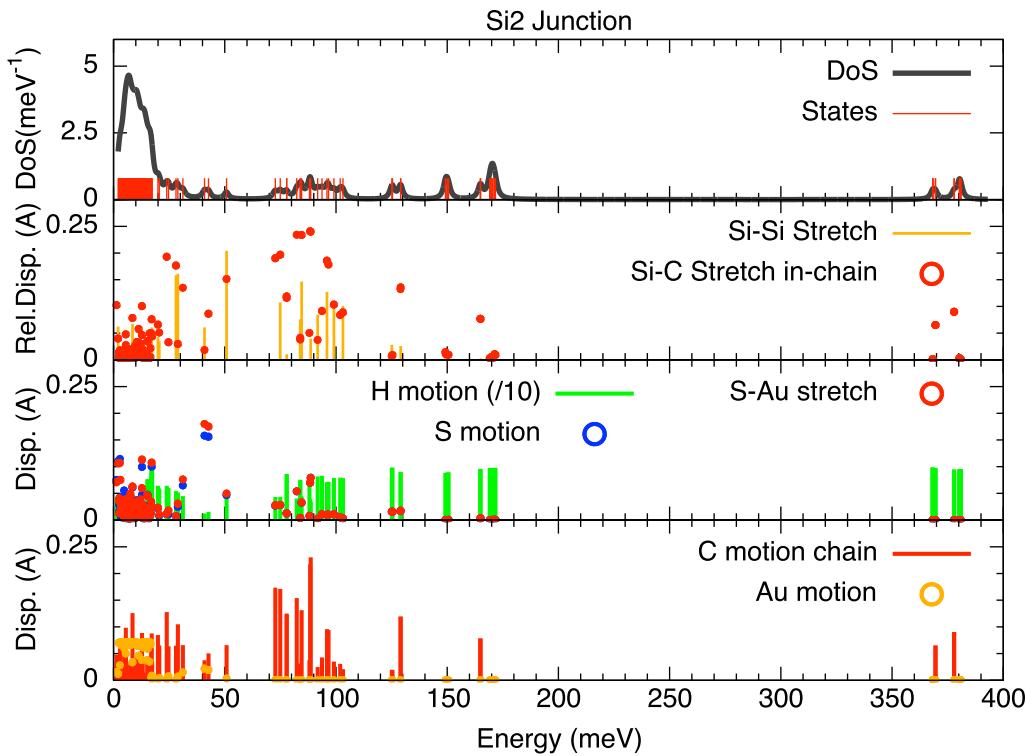


Figure S6. Calculated phonon modes and modes decomposition for Au-**Si2**-Au junction.

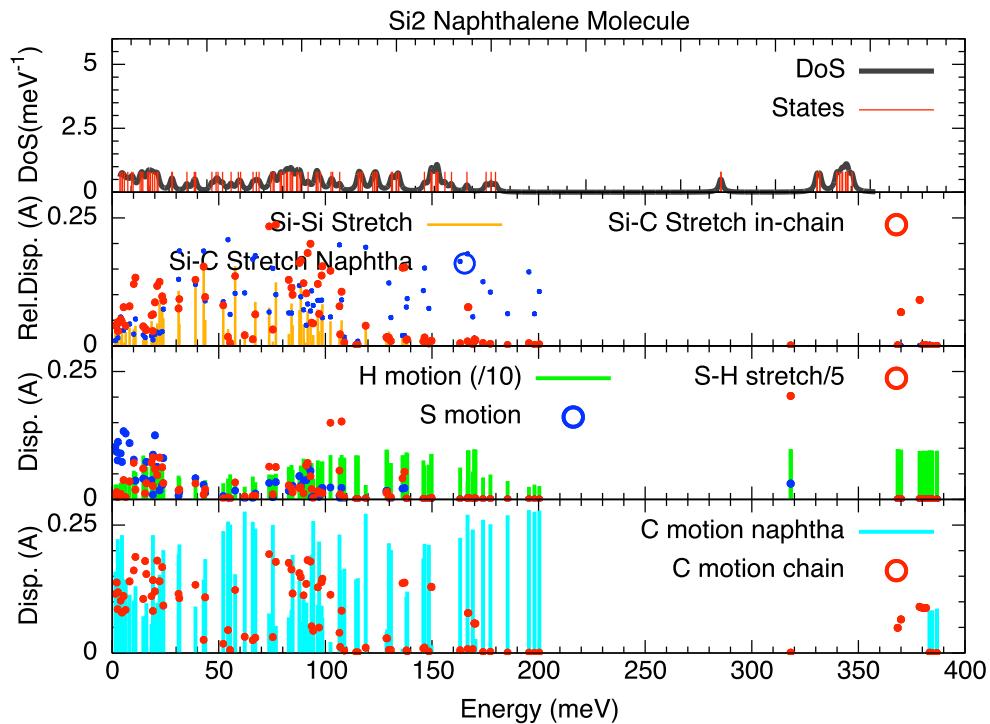


Figure S7. Calculated phonon modes and modes decomposition for **Si2Naph**.

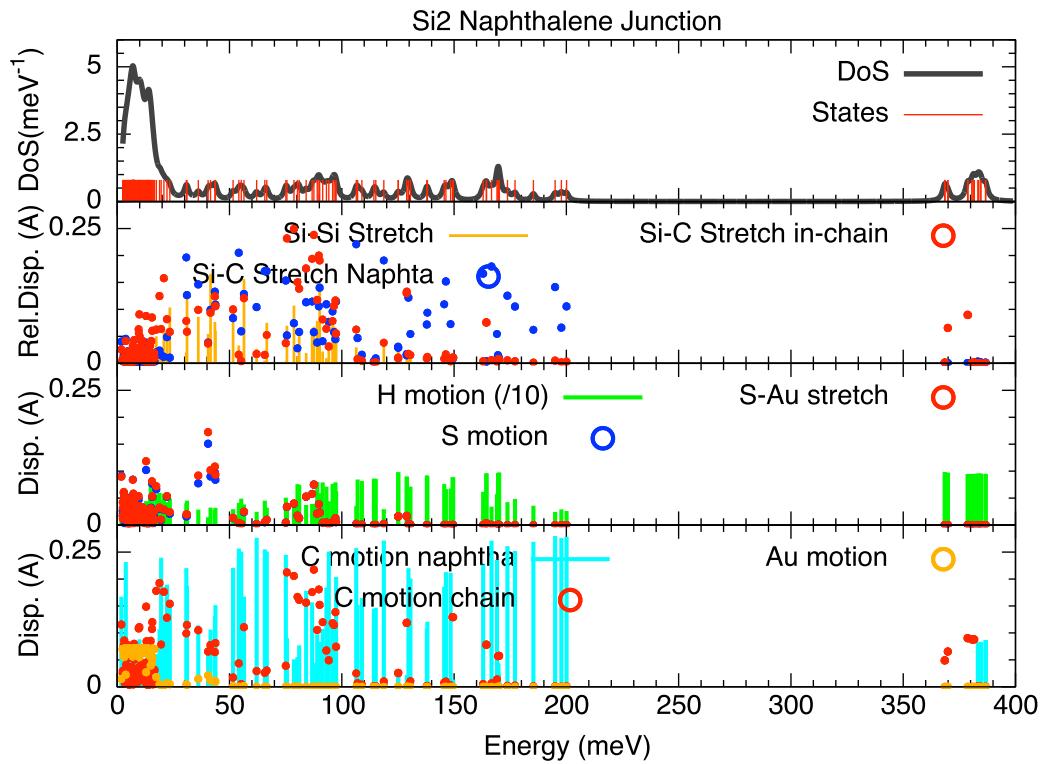


Figure S8. Calculated phonon modes and modes decomposition for Au-**Si2Naph**-Au junction.

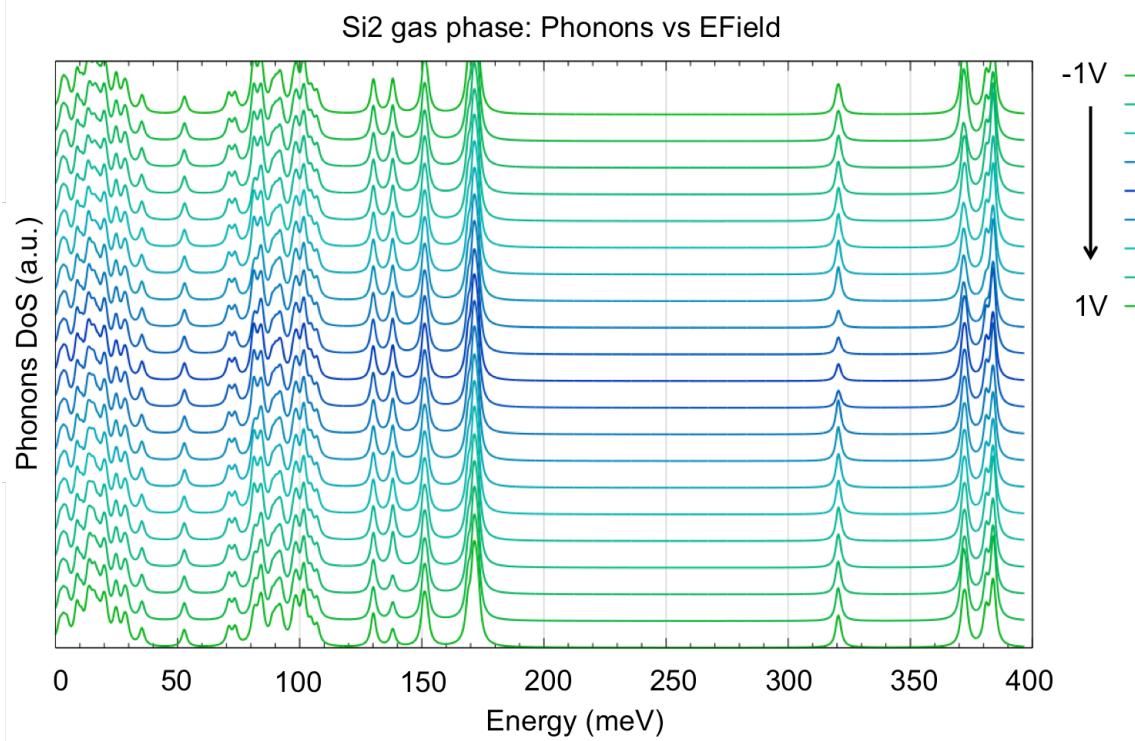


Figure S9. Calculated vibrational modes for gas phase **Si2** as a function of applied voltage.

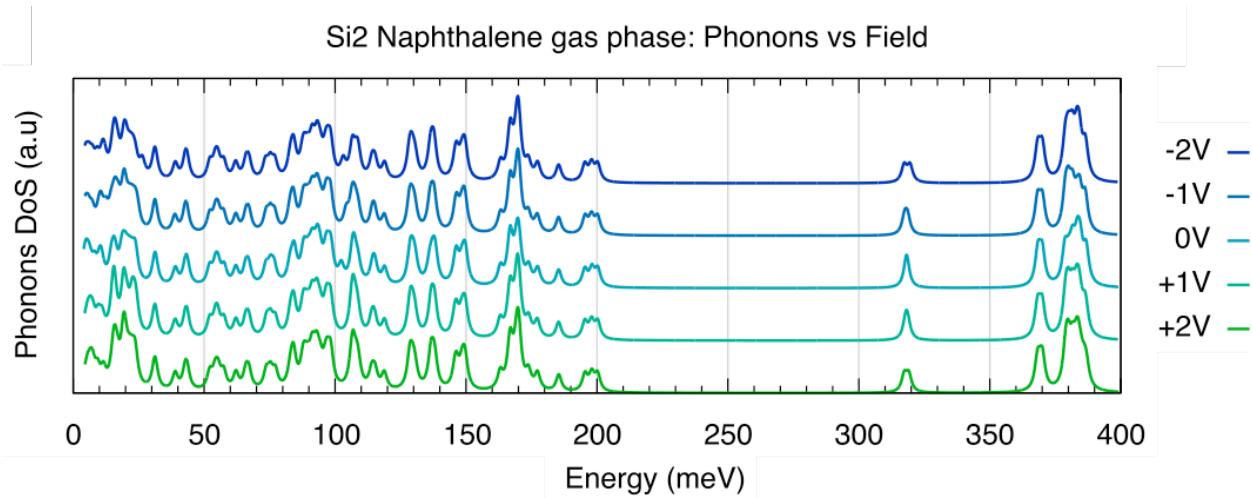


Figure S10. Calculated vibrational modes for gas phase **Si2Naph** as a function of applied voltage.

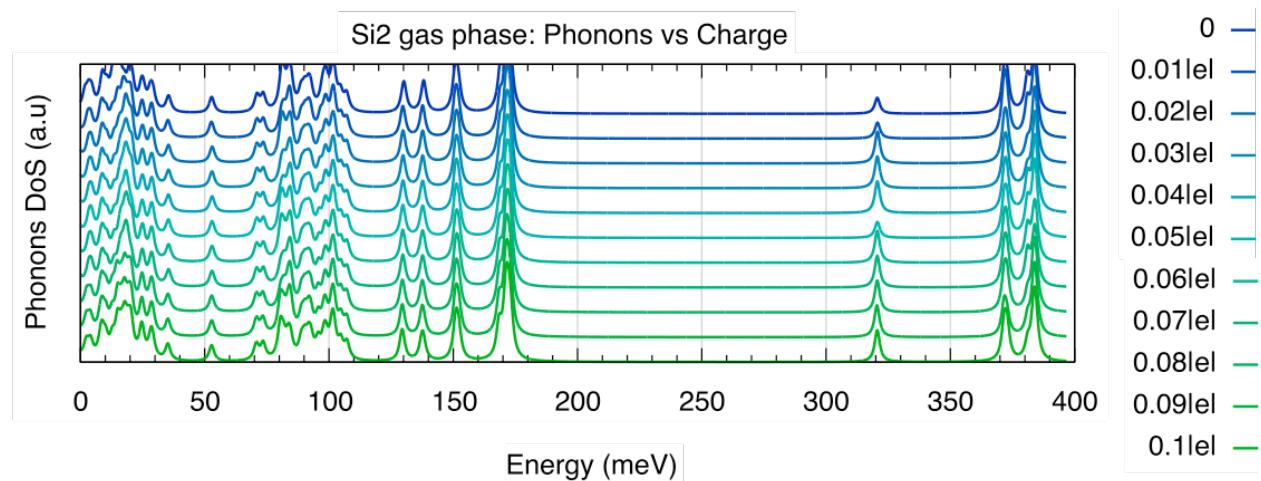


Figure S11. Calculated vibrational modes for gas phase **Si2** as a function of charge.

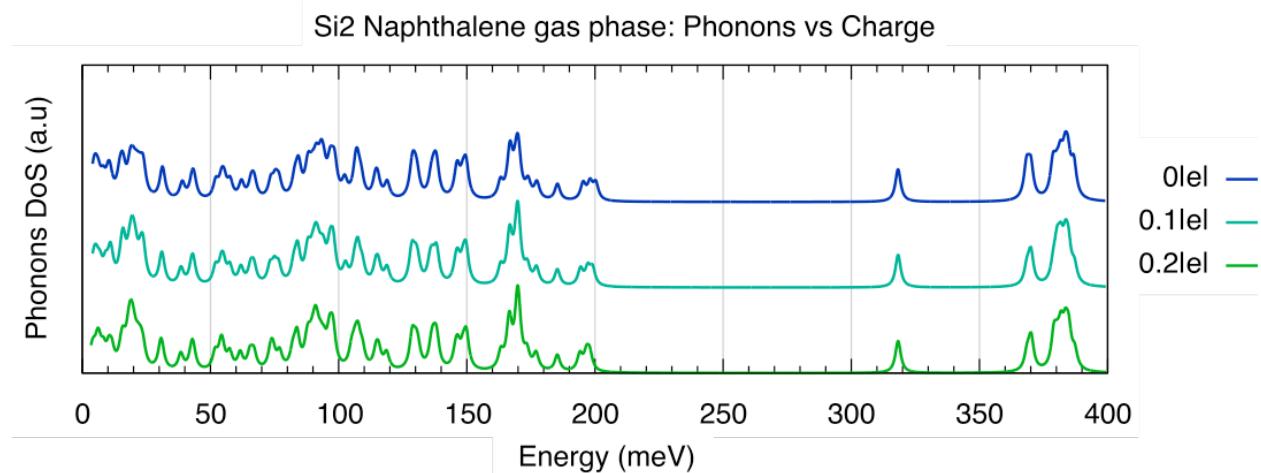


Figure S12. Calculated vibrational modes for gas phase **Si2Naph** as a function of charge.

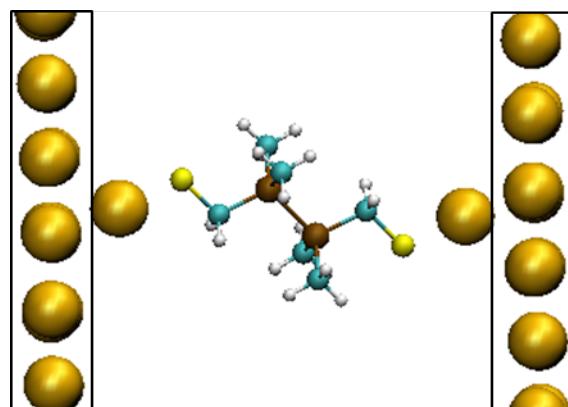
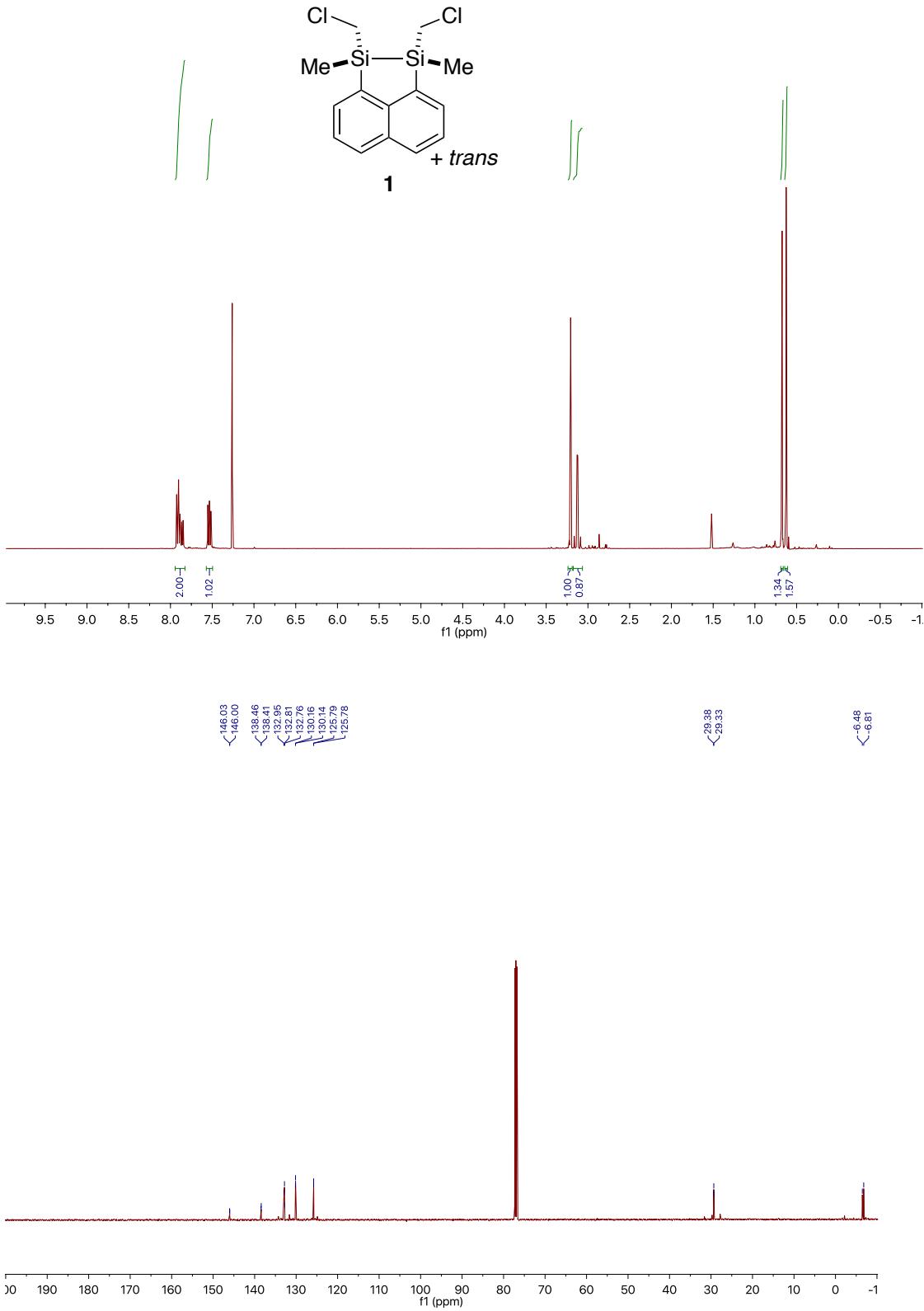
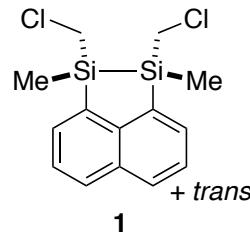
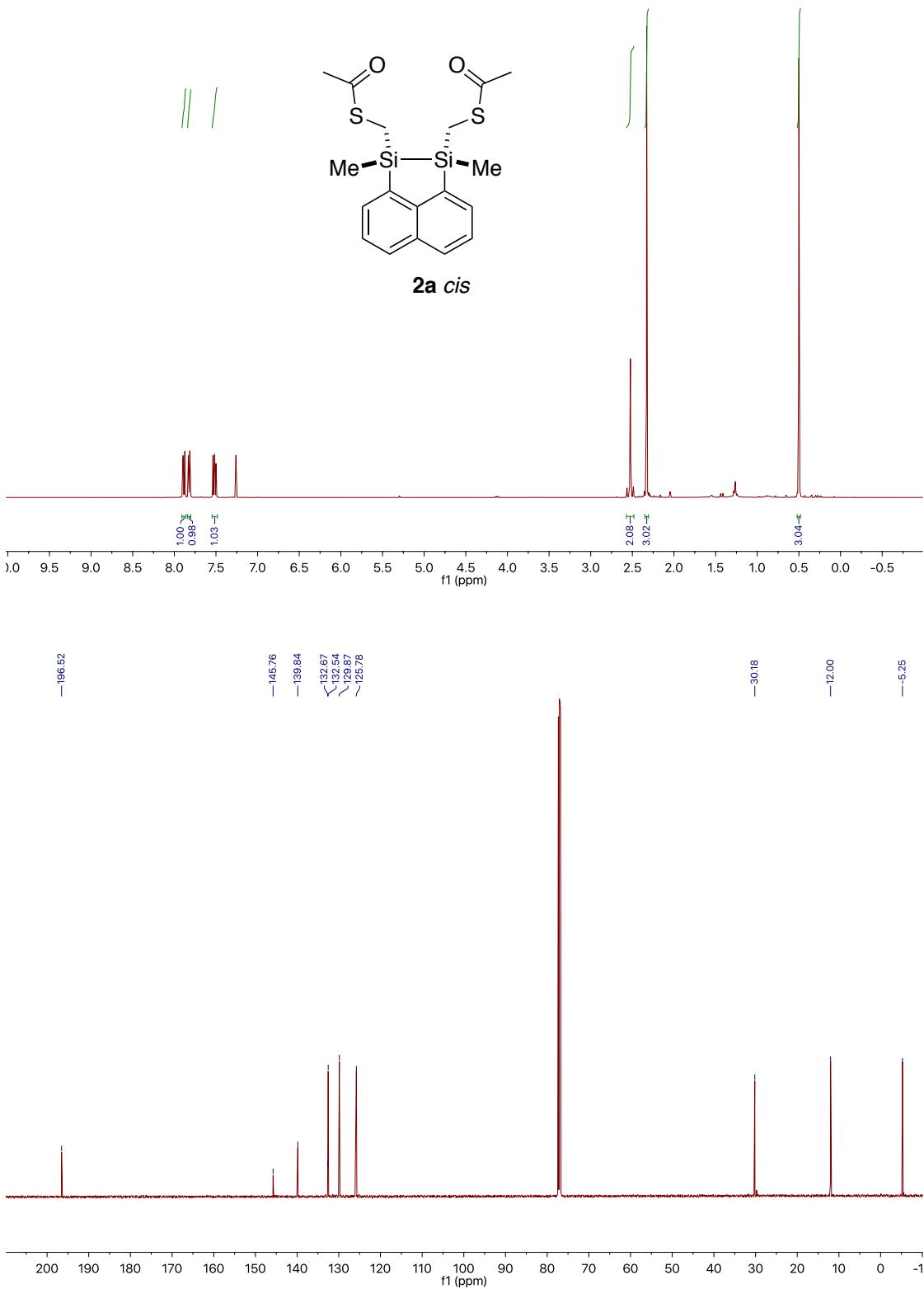


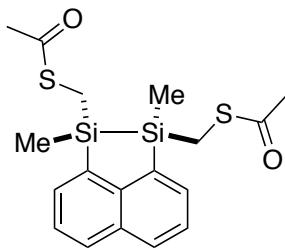
Figure S13. Example 3D structure of molecular junction of **Si2** used for MD simulations. The Au atoms in the box are fixed, and the rest are allowed to move.

V. NMR spectra

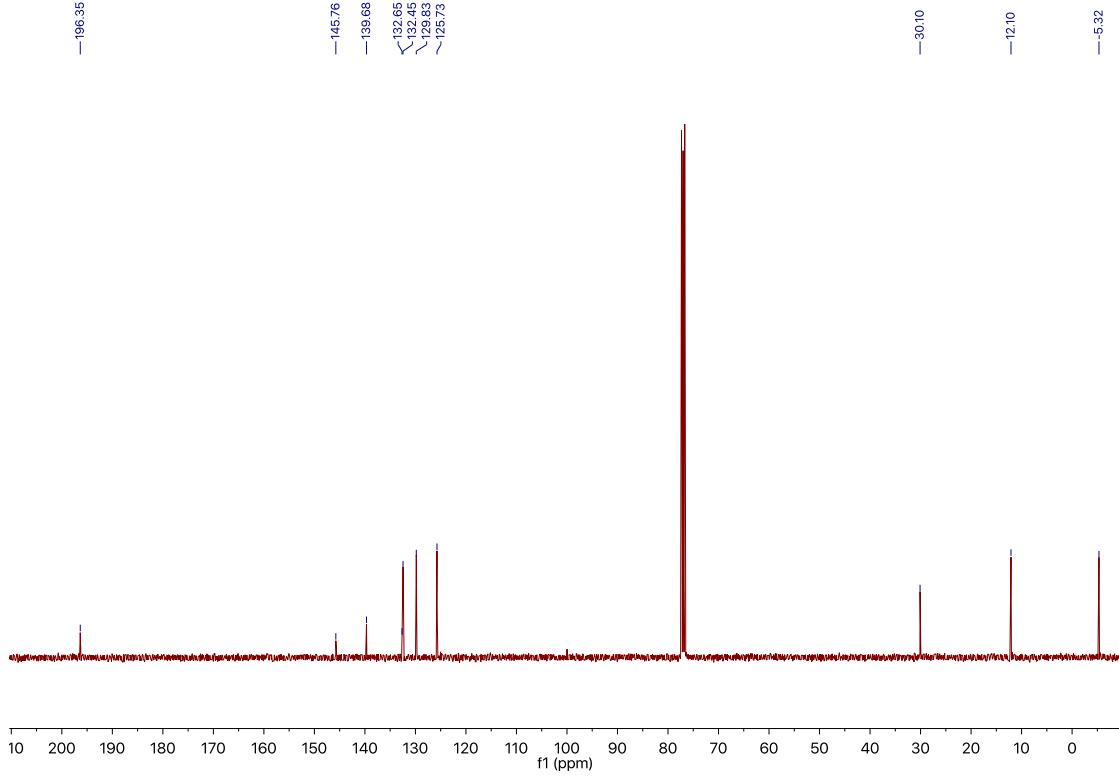
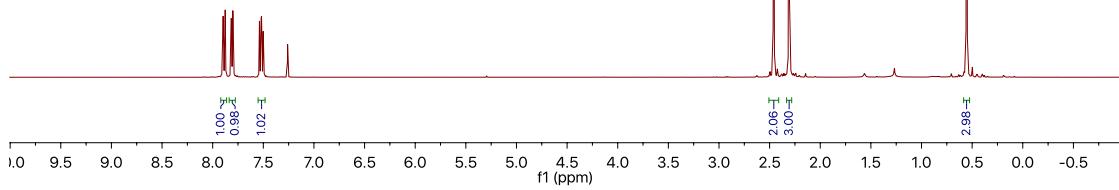




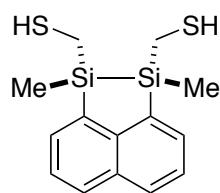
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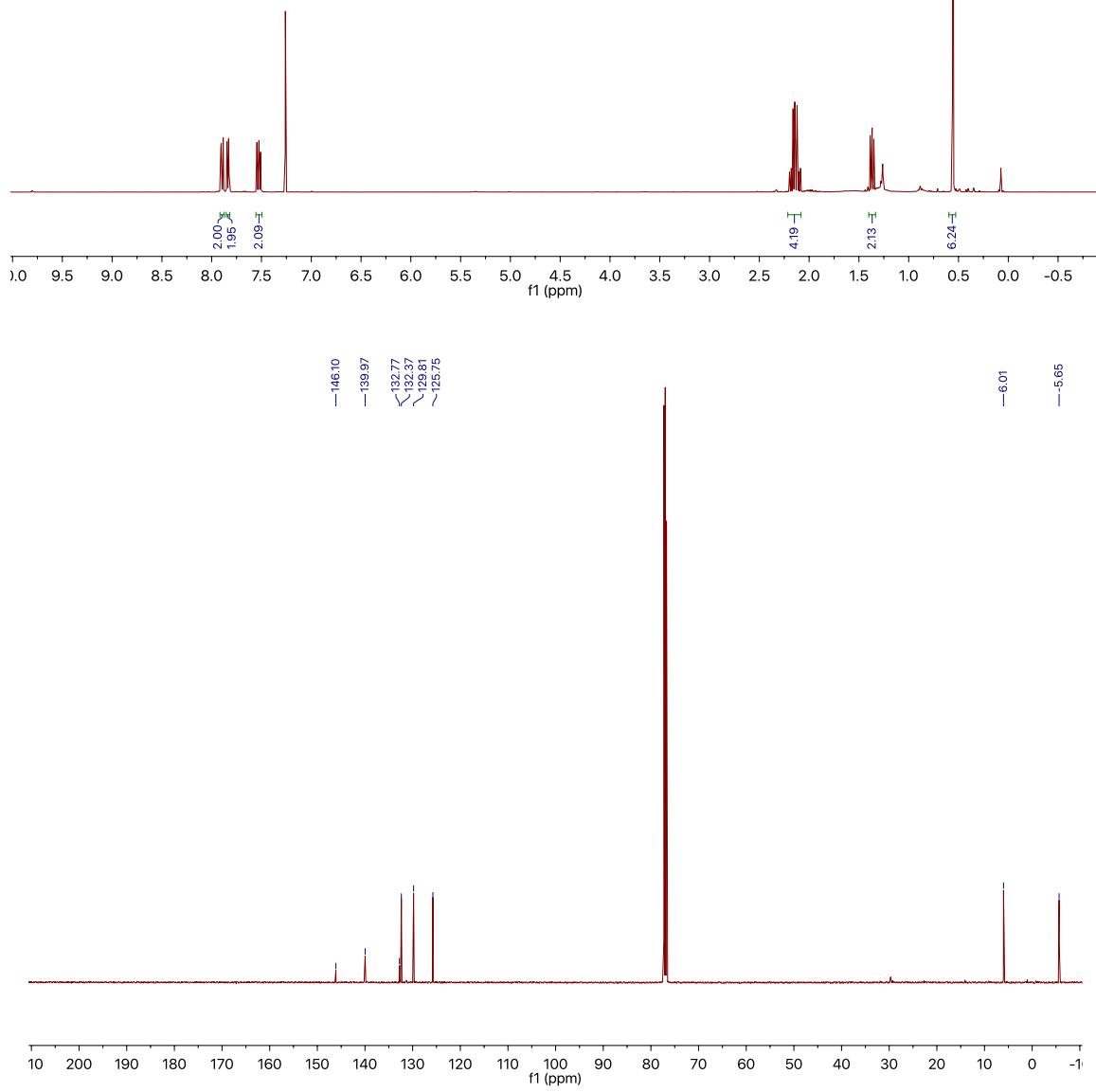
2b *trans*

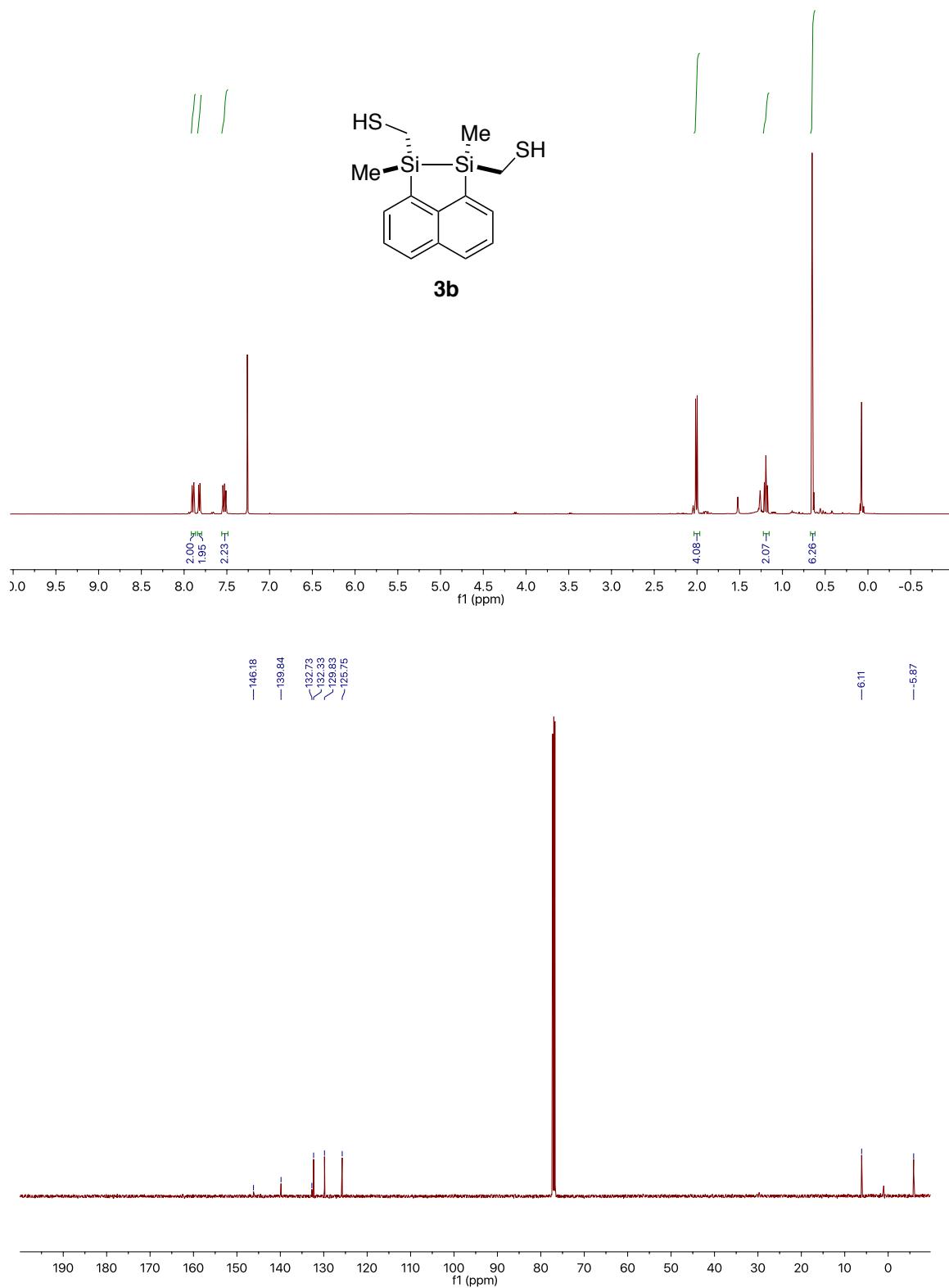


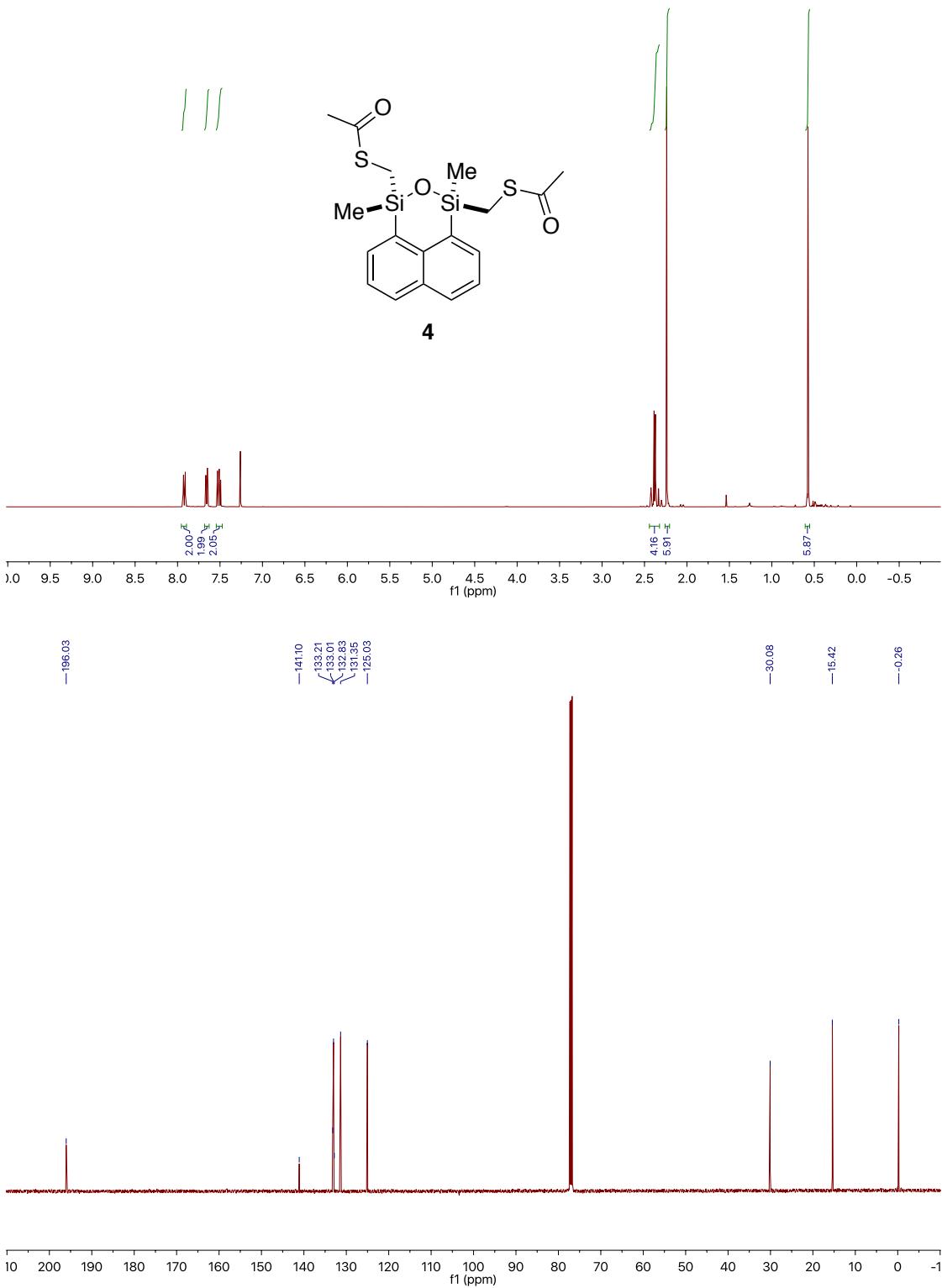
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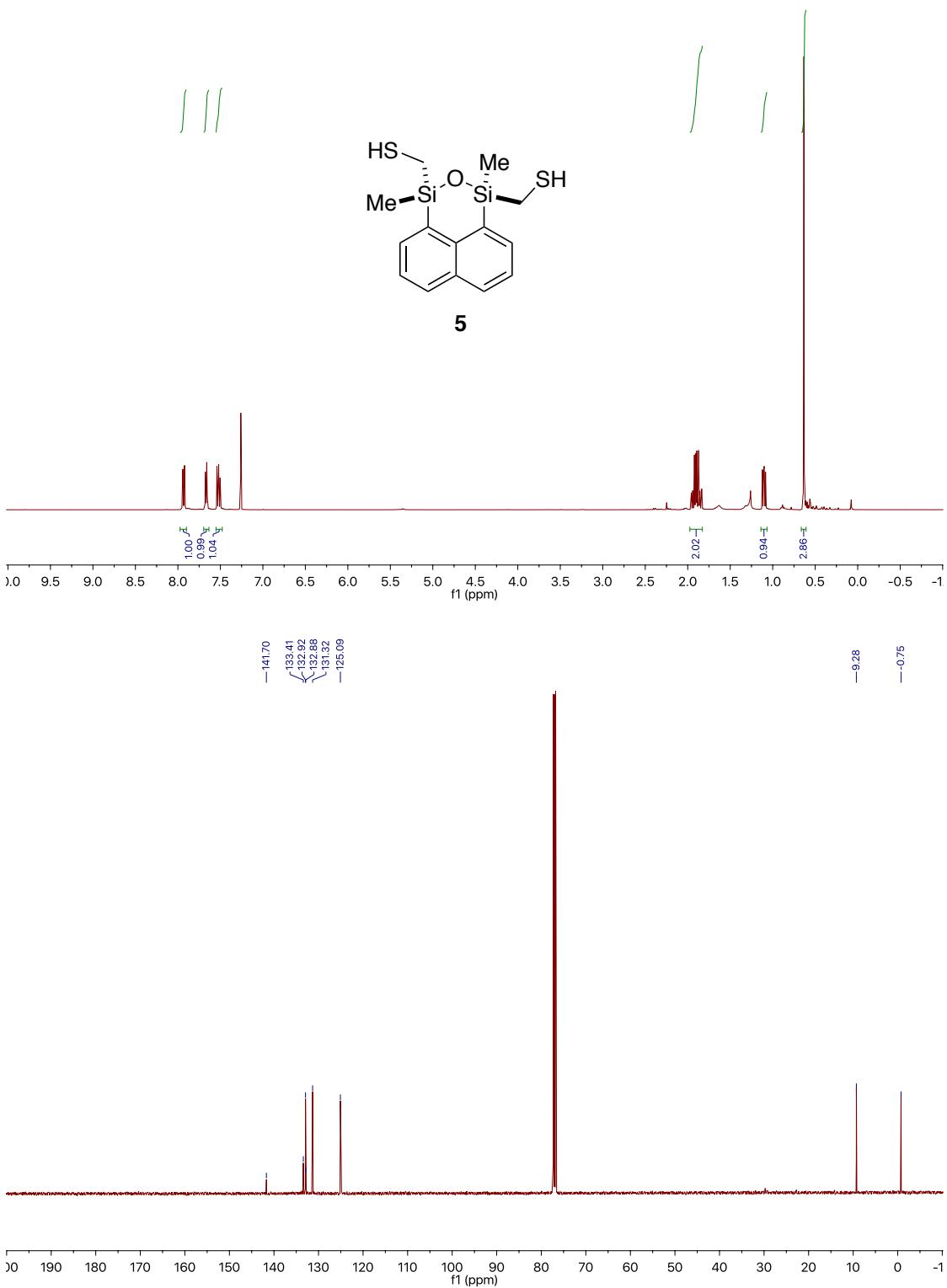


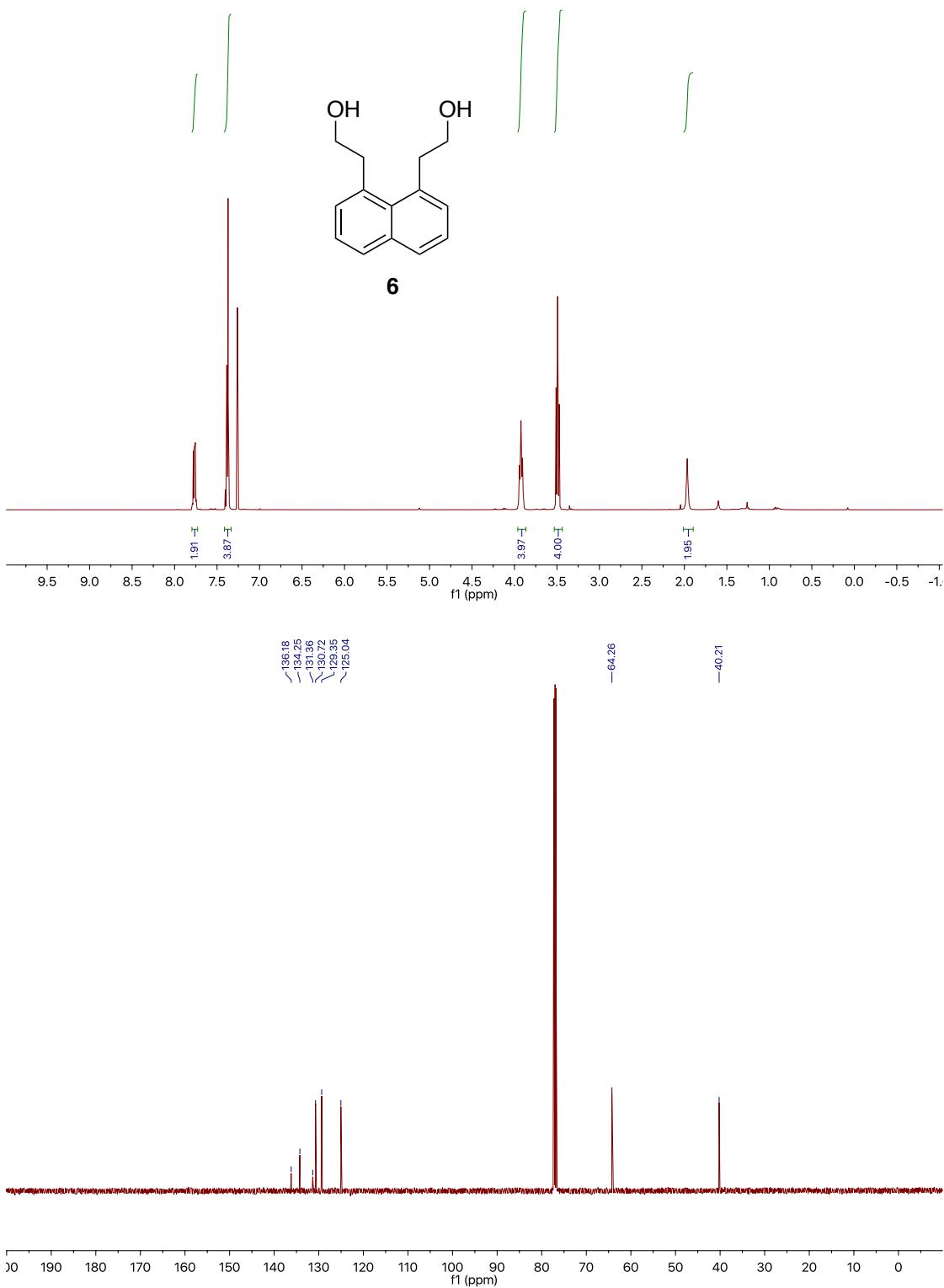
3a

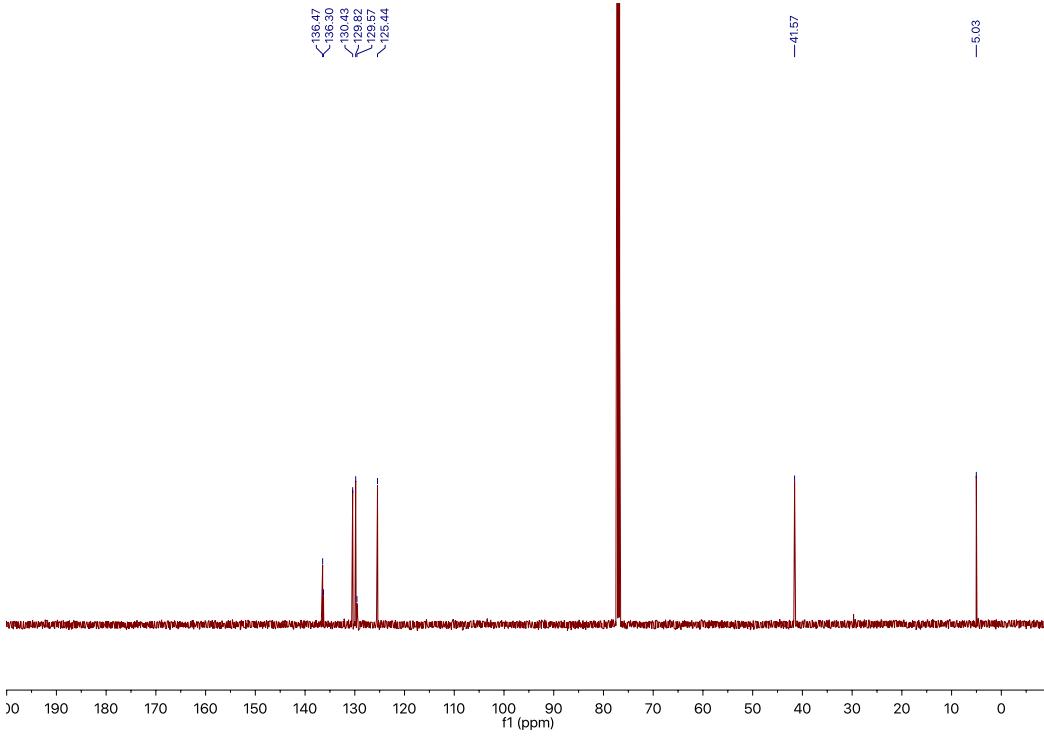
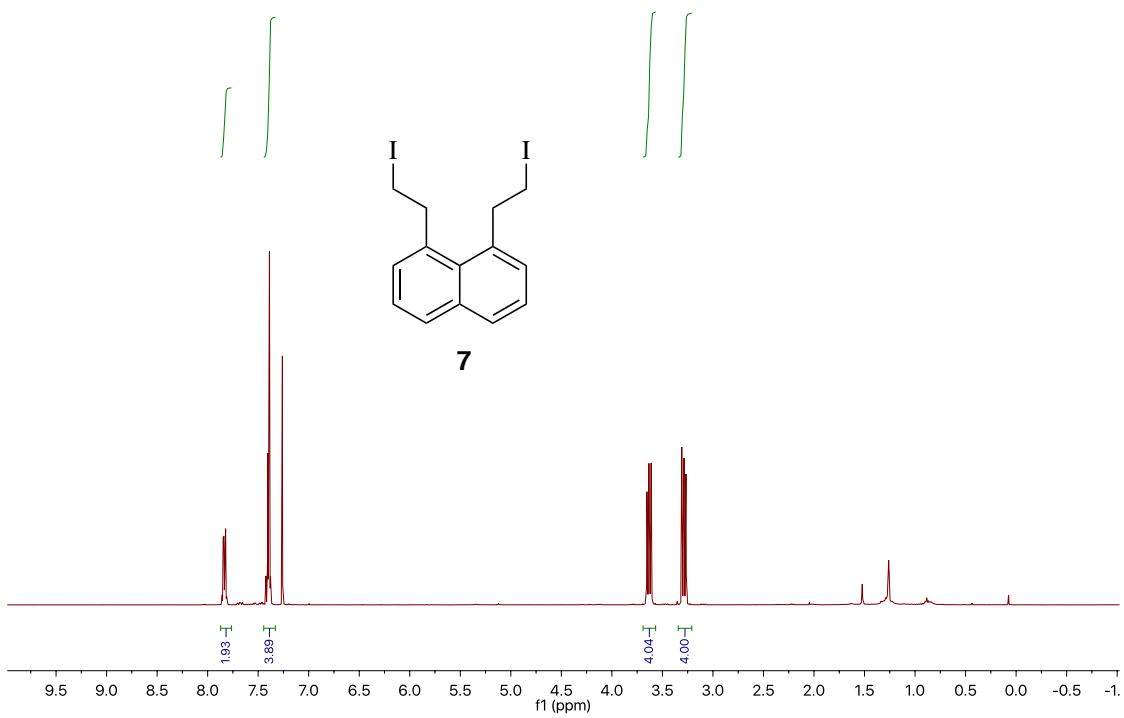


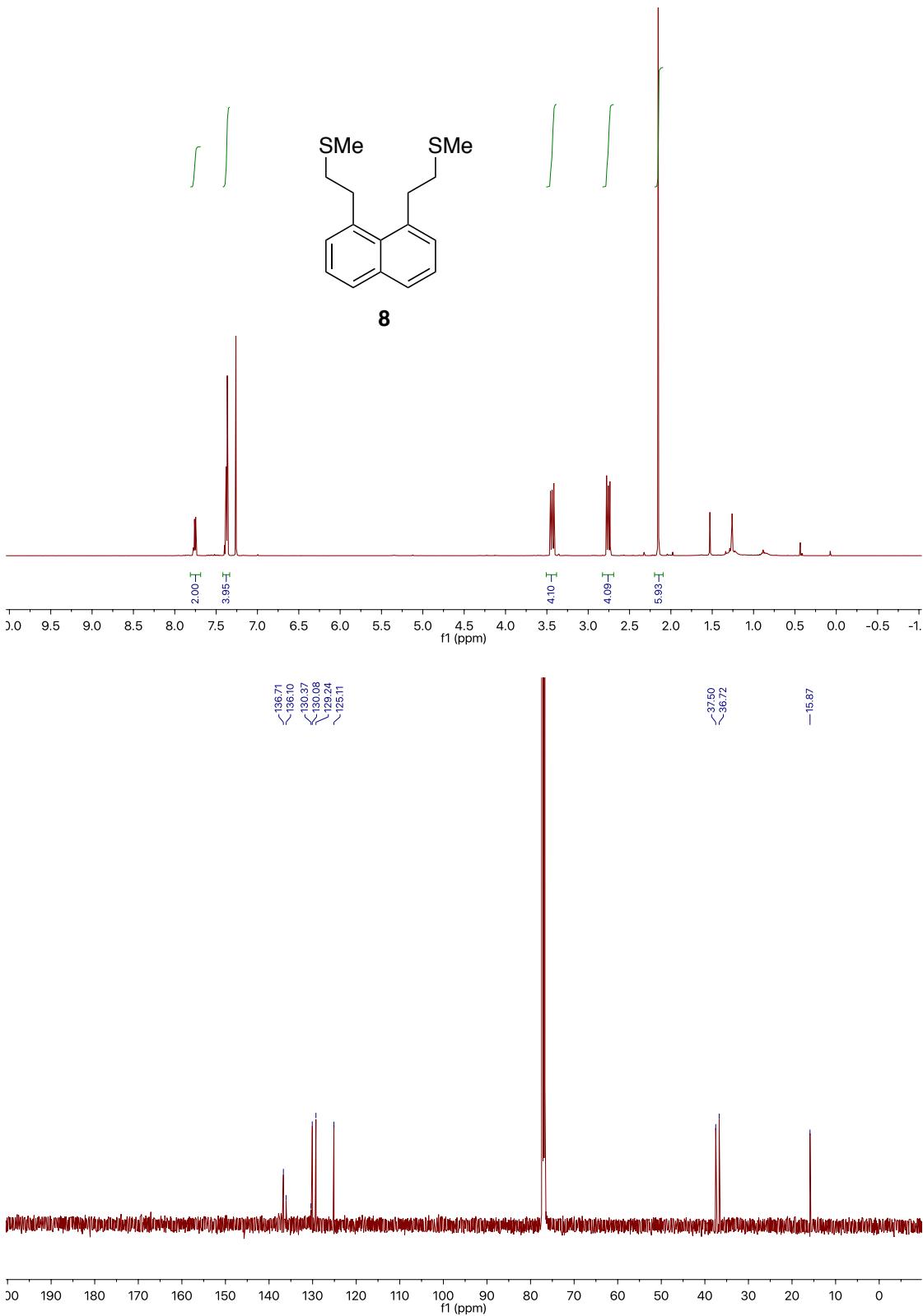




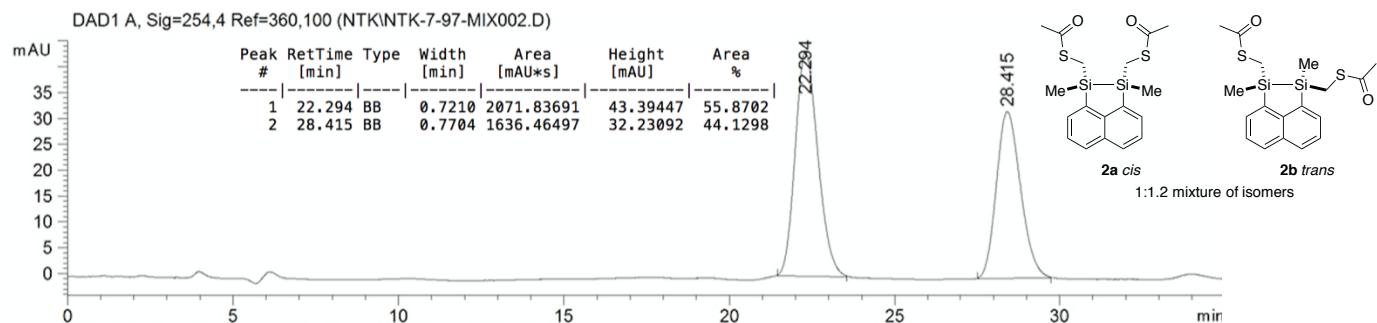




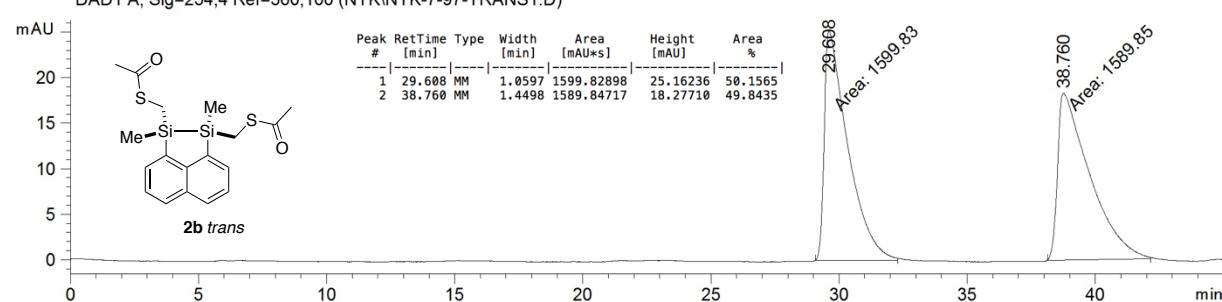
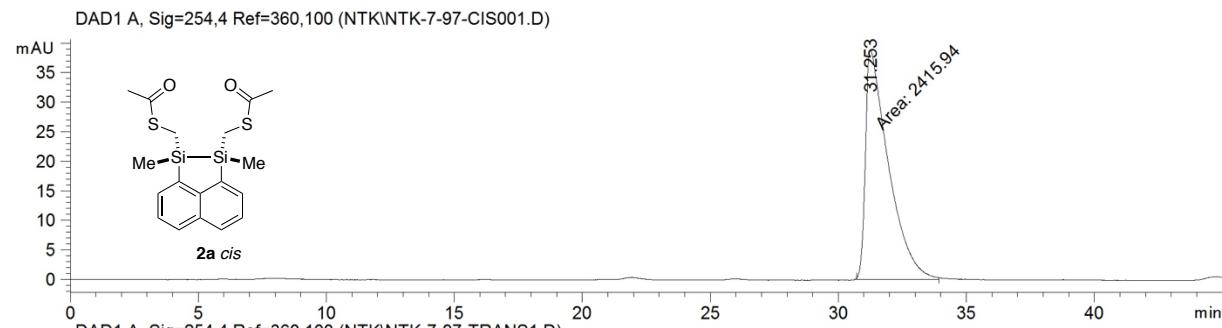
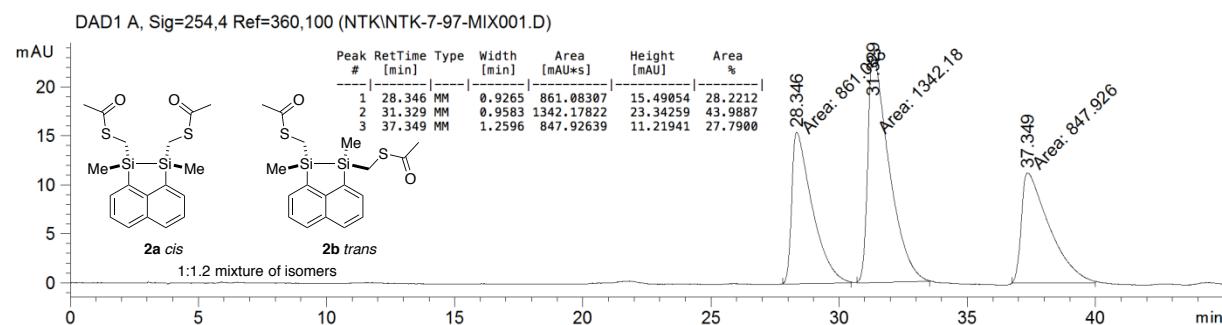




VI. HPLC chromatograms of dithioacetate **2a** and **2b**
 Luna 3Å silica column, 100% dichloromethane, 1 mL/min



Chiralcel IB-3 column, 5% dichloromethane in hexanes, 1 mL/min



1. Li, H.; Su, T. A.; Zhang, V.; Steigerwald, M. L.; Nuckolls, C.; Venkataraman, L. *J. Am. Chem. Soc.* **2015**, 137, (15), 5028-33.
2. Klausen, R. S.; Widawsky, J. R.; Steigerwald, M. L.; Venkataraman, L.; Nuckolls, C. *J. Am. Chem. Soc.* **2012**, 134, (10), 4541-4.
3. Xu, J.; Vasella, A. *Helv. Chim. Acta* **1999**, 82, (10), 1728-1752.