

Electronic Supplementary Information

Twisted push-pull disilenes obtained by direct 1,2-hydro/chloroborylation of a silylone

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1. Experimental Details

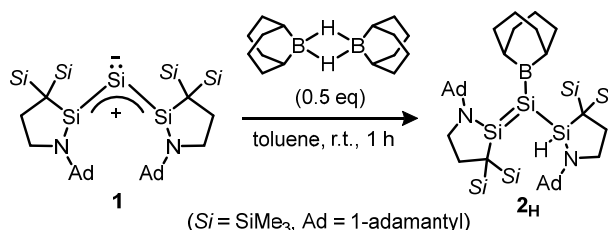
General Procedures

All reactions treating air-sensitive compounds were carried out under Ar atmosphere using a high-vacuum line, standard Schlenk techniques, or a glovebox, as well as dry and oxygen-free solvents. ^1H , ^{13}C and ^{29}Si nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Biospin Avance 500 FT NMR spectrometer at room temperature (r.t.) unless otherwise noted. ^1H NMR chemical shifts were referenced to the peaks of residual protons of benzene- d_6 (δ 7.16) or toluene- d_8 (δ 7.09).¹ ^{13}C and ^{29}Si NMR chemical shifts in C_6D_6 or toluene- d_8 were relative to SiMe_4 in ppm. Data are reported as follows: chemical shift, multiplicity (s = singlet, t = triplet, m = multiplet), coupling constant in hertz (Hz), and an integration value. Melting points (mp) were measured by an OptiMelt MAP100. High-resolution mass spectra were performed on a Bruker Daltonics solarix 9.4T FT-ICR spectrometer using an APCI method. Elemental analysis was performed on a J-SCIENCE LAB JM-11 for CHN elements at Research and Analytical Center for Giant Molecules (Graduate School of Science, Tohoku University). The reactions were performed under dry argon atmosphere unless otherwise noted. Sampling of air-sensitive compounds was carried out using a VAC NEXUS 100027 type glovebox. UV-vis spectra were recorded on a JASCO V-770 spectrometer. X-ray analysis was carried out using a Bruker AXS APEXII CCD diffractometer.

Materials

Dry and degassed hexane and toluene were prepared using a VAC 103991 solvent purifier. Et_2O , heptane and hexamethyldisiloxane were distilled over lithium aluminum hydride and degassed prior to use. Acetonitrile was degassed and dried by $\text{MS } 3\text{ \AA}$ and CaH_2 prior to use. Benzene- d_6 (C_6D_6) was degassed and dried by $\text{MS } 4\text{ \AA}$ prior to use. Toluene- d_8 (C_7D_8) was degassed and preserved in the presence of potassium mirror prior to use. Cyclic (alkyl)(amino)silylene (CAASi)-coordinated silylone **1**² and 9-borabicyclo[3.3.1]nonane chloride³ were prepared according to the published procedures. All other chemicals were of reagent grade and used without further purification.

Synthesis of Disilene **2_H**

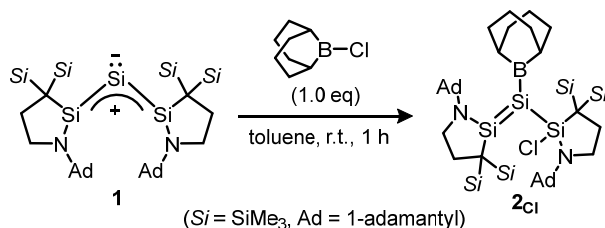


In a screw-top vial (10 mL) equipped with a magnetic stir bar, silylone **1** (71 mg, 0.094 mmol) and 9-BBN hydride dimer (11 mg, 0.047 mmol) were dissolved in toluene (1.0 mL) under argon atmosphere. The color of the reaction mixture immediately changed from dark purple to dark blue. After stirring for 1 hour, the volatiles were removed in vacuo and the resulting blue solids were washed with 0.5 mL of hexane three times to afford disilene **2_H** (61 mg, 0.069 mmol) as a blue powder in 73% yield.

2_H: a blue powder; mp 143 °C (decomp.); ^1H NMR (500 MHz, C_7D_8 , 296 K) 0.36 (s, 18H, SiMe_3), 0.47 (s, 18H, SiMe_3), 1.57-1.67 (m, 2H, 9-BBN), 1.67-1.74 (m, 6H, Ad), 1.75-1.82 (m, 6H, Ad), 1.91-2.32 (m, 4H+18H+10H, CH_2 +Ad+9-BBN overlapping with solvent signals), 2.57 (brs, 2H, 9-BBN), 2.95-3.08 (m, 4H, CH_2), 5.83 (s with satellites due to ^{29}Si [$^1J(^1\text{H}, ^{29}\text{Si}) = 95.7\text{ Hz}$], 1H, SiH); ^1H NMR (500 MHz, C_7D_8 , 213 K) 0.26 (s, 9H, SiMe_3), 0.38 (s, 9H, SiMe_3), 0.45 (s, 9H, SiMe_3), 0.68 (brs, 9H, SiMe_3), 1.58-2.44 (m, 4H+30H+12H, CH_2 +Ad+9-BBN overlapping with solvent signals), 2.56 (brs, 1H, CHH), 2.66 (brs, 1H, CHH), 2.70-2.81 (m, 2H, 9-BBN), 2.86 (brs, 1H, CHH), 3.01 (brs, 1H, CHH), 5.81 (s with satellites due to ^{29}Si [$^1J(^1\text{H}, ^{29}\text{Si}) = 195.4\text{ Hz}$], 1H, SiH); ^{13}C NMR (125 MHz, C_7D_8 , 297 K) 2.0 (CH_3), 2.5 (CH_3), 23.3 (CH_2), 30.3 (CH_2), 30.5 (CH), 33.5 (CH), 34.3 (CH_2), 34.9 (CH_2), 37.0 (CH_2), 44.1 (CH_2), 45.1 (CH_2), 55.3 (C) (the signal for the $\text{C}(\text{SiMe}_3)_2$ carbon nuclei was not observed probably due to overlap with solvent signals); ^{29}Si NMR (99 MHz, C_7D_8 , 296 K) -53.7 (SiB), 2.0 (SiMe_3), 3.1 (SiMe_3) (the signal for the (alkyl)(amino)Si nuclei was not observed); ^1H - ^{29}Si HMBC NMR (99 MHz, C_6D_6 , 213 K) -57.0 (SiB), -20.1 (SiH), 180.3 [(alkyl)(amino)Si=Si]; no ^{11}B NMR signals were observed; HRMS (APCI) (m/z): Calcd for $\text{C}_{46}\text{H}_{90}\text{BN}_2\text{OSi}_7$ [$\text{M}^+ + \text{OH}$] 893.55256, Found 893.55251 (Numerous attempts of HRMS measurements failed due to the extreme sensitivity of **2_H** toward oxygen and moisture); Elem. Anal. (%): Calcd for $\text{C}_{46}\text{H}_{89}\text{BN}_2\text{Si}_7$, C, 62.95; H, 10.22; N, 3.19, Found. C, 62.76; H, 10.29; N, 3.15.

*Note: **2_H** gradually decomposes in both solid state and in solution under storage above -25 °C.

Synthesis of Disilene **2_{Cl}**

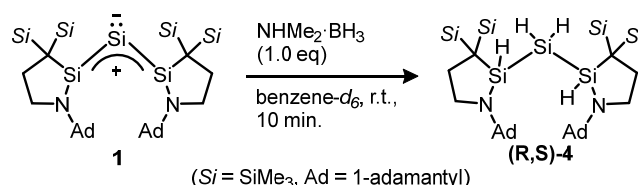


In a screw-top vial (10 mL) equipped with a magnetic stir bar, silylone **1** (76 mg, 0.10 mmol) and 9-BBN chloride (8.0 mg, 0.050 mmol) were dissolved in toluene (1.0 mL) under argon atmosphere. The color of the reaction mixture immediately changed from dark purple to dark blue. After stirring for 1 hour, the volatiles were removed in vacuo and the resulting blue solids were washed with 0.5 mL of hexane three times to afford disilene **2_{Cl}** (69 mg, 0.075 mmol) as a blue powder in 75% yield.

2_{Cl}: a blue powder; mp 161 °C (decomp.); ¹H NMR (500 MHz, C₇D₈, 297 K) 0.46 (brs, 18H, SiMe₃), 0.50 (brs, 18H, SiMe₃), 1.59-1.65 (m, 2H, 9-BBN), 1.68-1.74 (m, 6H, Ad), 1.75-1.83 (m, 6H, Ad), 1.95-2.32 (m, 4H+18H+10H, CH₂+Ad+9-BBN overlapping with solvent signals), 2.53 (brs, 2H, 9-BBN), 2.97-3.13 (m, 4H, CH₂); ¹³C NMR (125 MHz, C₇D₈, 299 K) 2.4 (CH₃), 3.2 (CH₃), 22.2 (C), 23.2 (CH₂), 29.8 (CH₂), 30.5 (CH), 32.4 (CH), 34.3 (CH₂), 34.8 (CH₂), 36.9 (CH₂), 44.3 (CH₂), 45.2 (CH₂), 56.5 (C); ²⁹Si NMR (99 MHz, C₇D₈, 296 K) -34.3 (SiB), 2.0 (SiMe₃), 3.6 (SiMe₃), 92.9 [(alkyl)(amino)Si]; ²⁹Si NMR (CP MAS, 293 K) -35.0 (SiB), -27.2 (SiB), 1.8 (SiMe₃), 4.2 (SiMe₃), 7.8 (SiCl), 8.8 (SiCl), 175.2 [(alkyl)(amino)Si=Si], 178.6 [(alkyl)(amino)Si=Si]; ¹¹B NMR (CP MAS, 293 K) 82.3 (9-BBN), 87.9 (9-BBN); HRMS (APCI) (*m/z*): Calcd for C₄₆H₈₉BClN₂OSi₇ [M⁺ + OH] 927.51359, Found 927.51346 (Numerous attempts of HRMS measurements failed due to the extreme sensitivity of **2_{Cl}** toward oxygen and moisture); Elem. Anal. (%): Calcd for C₄₆H₈₈BClN₂Si₇, C, 60.58; H, 9.73; N, 3.07, Found. C, 60.35; H, 9.94; N, 3.13.

*Note: **2_{Cl}** gradually decomposes in both solid state and in solution under storage above -25 °C.

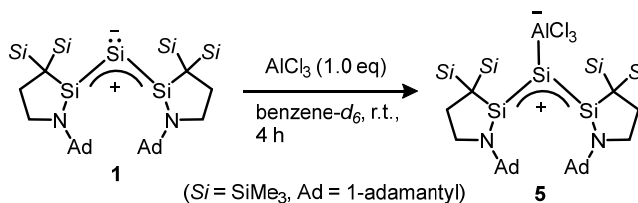
Synthesis of Trisilane (R,S)-4



In a J. Young NMR tube, a mixture of silylone **1** (41 mg, 0.054 mmol), NHMe₂·BH₃ (3.2 mg, 0.054 mmol) and benzene-*d*₆ (0.45 mL) was placed under argon atmosphere. The color of the reaction mixture immediately changed from dark purple to pale yellow. After 1 h, the volatiles were removed in vacuo and the resulting pale-yellow oil was recrystallized from an acetonitrile : hexamethyldisiloxane = 1 : 1 solution (0.5 mL) at -27 °C overnight to afford a pale-yellow solid. After removal of the solution, the pale-yellow solid was recrystallized from Et₂O (0.1 mL) at -27 °C overnight to afford trisilane (R,S)-**4** (27 mg, 0.036 mmol) as a white crystalline solid in 67% yield.

(R,S)-**4**: a white crystalline solid; mp 176-178 °C; ¹H NMR (500 MHz, C₆D₆, 296 K) 0.28 (s, 18H, SiMe₃), 0.34 (s, 18H, SiMe₃), 1.57-1.64 (m, 6H, Ad), 1.65-1.71 (m, 6H, Ad), 1.93-2.12 (m, 4H+18H, CH₂+Ad), 2.87 (t, ³J(H,H) = 6.3 Hz, 4H, CH₂), 3.69 (dd, ³J(H,H) = 4.0 Hz, 1H, SiHH), 3.77 (dd, ³J(H,H) = 4.0 Hz, 1H, SiHH), 5.62 (t with satellites due to ²⁹Si [¹J(¹H, ²⁹Si) = 195.0 Hz], ³J(H,H) = 3.7 Hz, 2H, (alkyl)(amino)SiH); ¹³C NMR (125 MHz, C₆D₆, 297 K) 1.5 (CH₃), 2.9 (CH₃), 7.8 (C), 30.5 (CH₂), 30.6 (CH), 37.2 (CH₂), 43.8 (CH₂), 44.5 (CH₂), 52.6 (C); ²⁹Si NMR (99 MHz, C₆D₆, 296 K) -95.6 (SiH₂), -17.3 [(alkyl)(amino)Si], 3.5 (SiMe₃), 4.1 (SiMe₃); HRMS (APCI) (*m/z*): Calcd for C₃₈H₇₈N₂Si₇ [M⁺] 758.45444, Found 758.45456; Elem. Anal. (%): Calcd for C₃₈H₇₈N₂Si₇, C, 60.08; H, 10.35; N, 3.69, Found. C, 60.01; H, 10.27; N, 3.68.

Synthesis of Silylone-AlCl₃ Complex 5

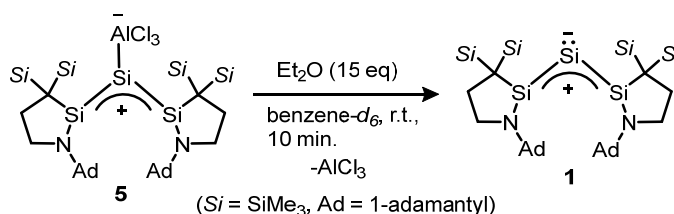


In a screw-top vial (10 mL), silylone **1** (55 mg, 0.073 mmol) and AlCl₃ (9.6 mg, 0.072 mmol) were dissolved in benzene-*d*₆ (0.45 mL) under argon atmosphere. The color of the reaction mixture gradually changed from dark purple to orange with the concomitant precipitation of an orange solid. After 4 h, the volatiles were removed in vacuo and the resulting orange solid was washed with 0.5 mL of hexane three times to afford silylone-AlCl₃ complex **5** (58 mg, 0.065 mmol) as an orange powder in 89% yield.

5: orange powder; mp 158-160 °C; ¹H NMR (500 MHz, C₆D₆, 303 K) 0.36 (brs, 9H, SiMe₃), 1.55-1.80 (m, 12H, Ad), 1.90 (brs, 4H, CH₂), 2.08 (brs, 18H, Ad), 2.81 (brs, 4H, CH₂); ¹³C {¹H} NMR (125 MHz, C₆D₆, 297 K) 2.7 (CH₃), 19.7 (C), 29.7 (CH₂), 30.4 (CH), 36.8 (CH₂), 44.2 (CH₂), 45.3 (CH₂), 56.5 (C); ²⁹Si {¹H} NMR (99 MHz, C₆D₆, 296 K) 2.9 (SiMe₃) (no other signals could be observed due to signal broadening); (Numerous attempts of HRMS measurements failed due to the extreme sensitivity of **5** toward oxygen and moisture); Elem. Anal. (%): Calcd for C₃₈H₇₄AlCl₃N₂Si₇, C, 51.34; H, 8.39; N, 3.15, Found. C, 51.21; H, 8.13; N, 3.01.

*Note: **5** is extremely sensitive to solvents other than benzene, especially ethereal solvents, and regenerates **1**.

Reaction of Silylone-AlCl₃ Complex 5 with Et₂O



To an orange suspension of silylone-AlCl₃ complex **5** (11 mg, 0.014 mmol) in benzene-*d*₆ (0.45 mL in a J. Young NMR tube), Et₂O (10.4 mg, 0.14 mmol) was treated under argon atmosphere. The color of the reaction mixture immediately changed from orange to dark purple with the loss of precipitates. The formation of **1** (82% yield) was confirmed by NMR spectra.² Yields were determined by ¹H NMR integrals using 1,3,5-tri-*tert*-butylbenzene as an internal standard.

2. NMR Spectra

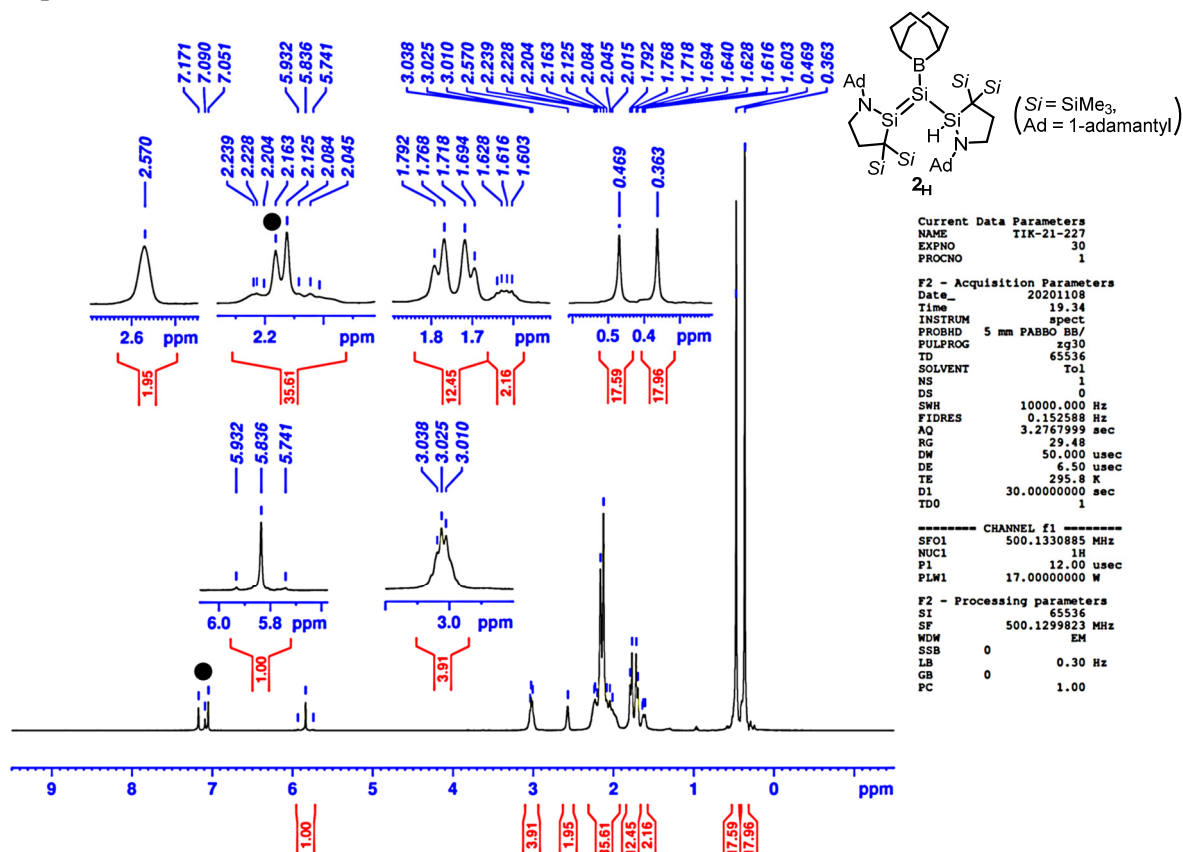


Figure S1. ^1H NMR spectrum of disilene **2_H** in C_7D_8 at 296 K (● = $\text{C}_7\text{D}_7\text{H}$).

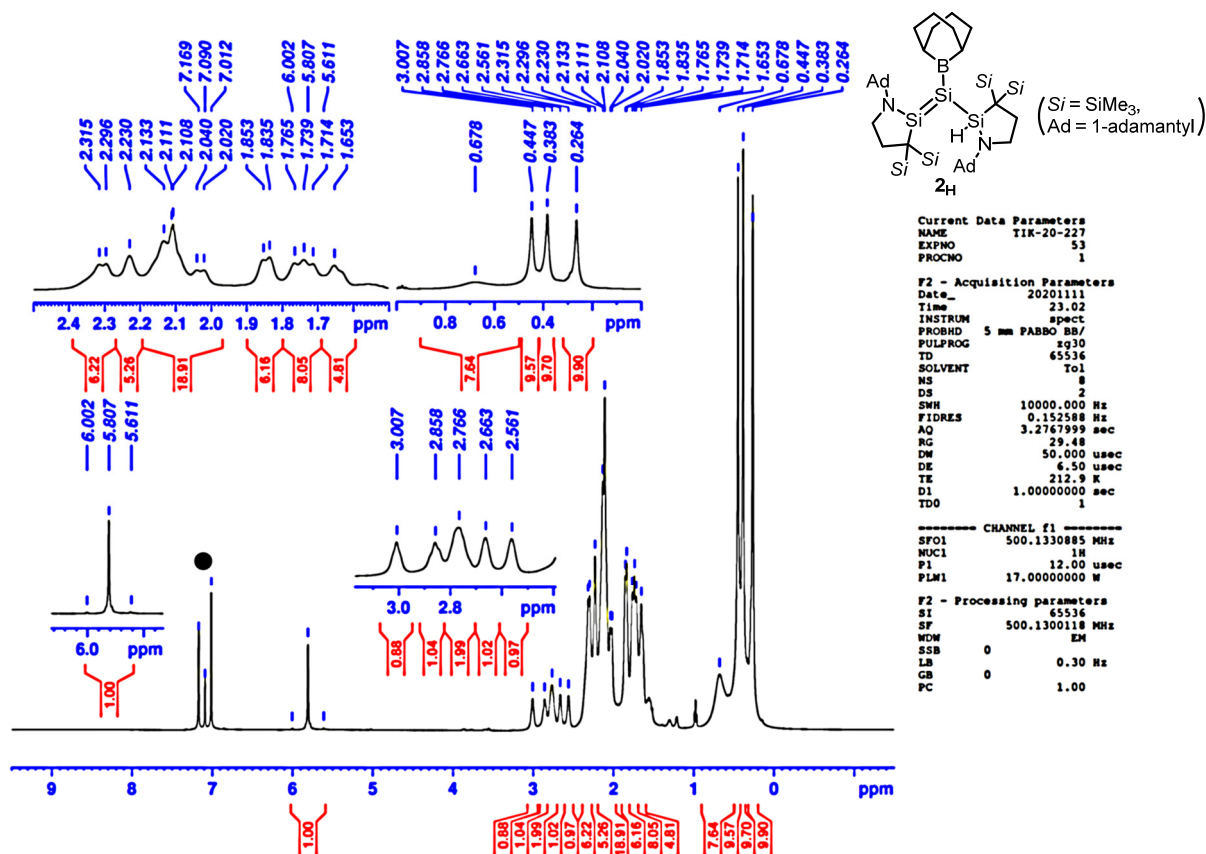


Figure S2. ^1H NMR spectrum of disilene **2_H** in C_7D_8 at 213 K (● = $\text{C}_7\text{D}_7\text{H}$).

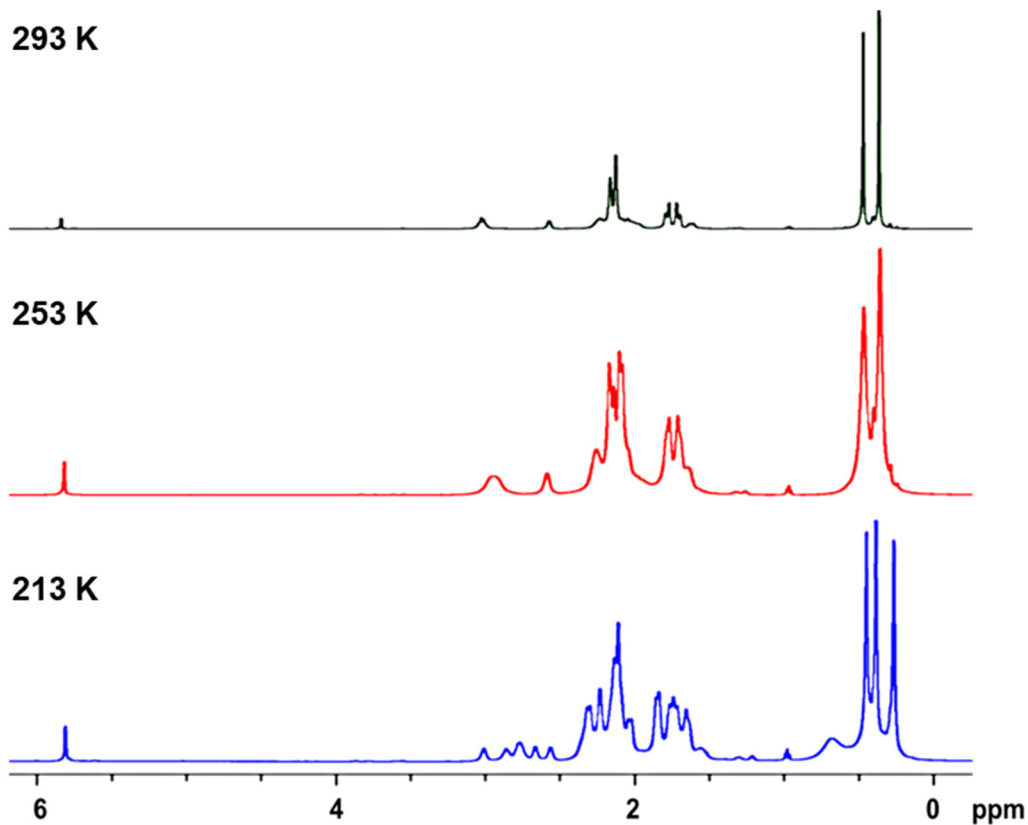


Figure S3. ^1H NMR spectra of disilene 2_{H} in C_7D_8 at various temperatures.

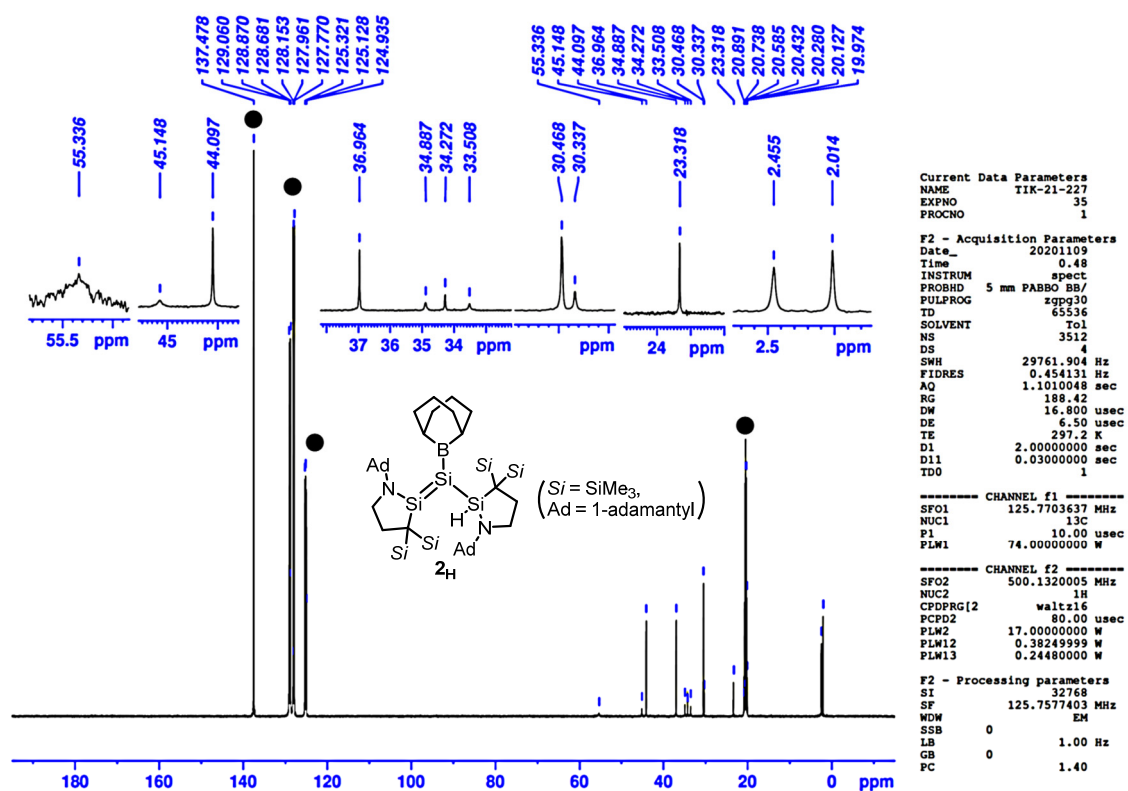


Figure S4. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of disilene 2_{H} in C_7D_8 at 297 K (● = C_7D_8).

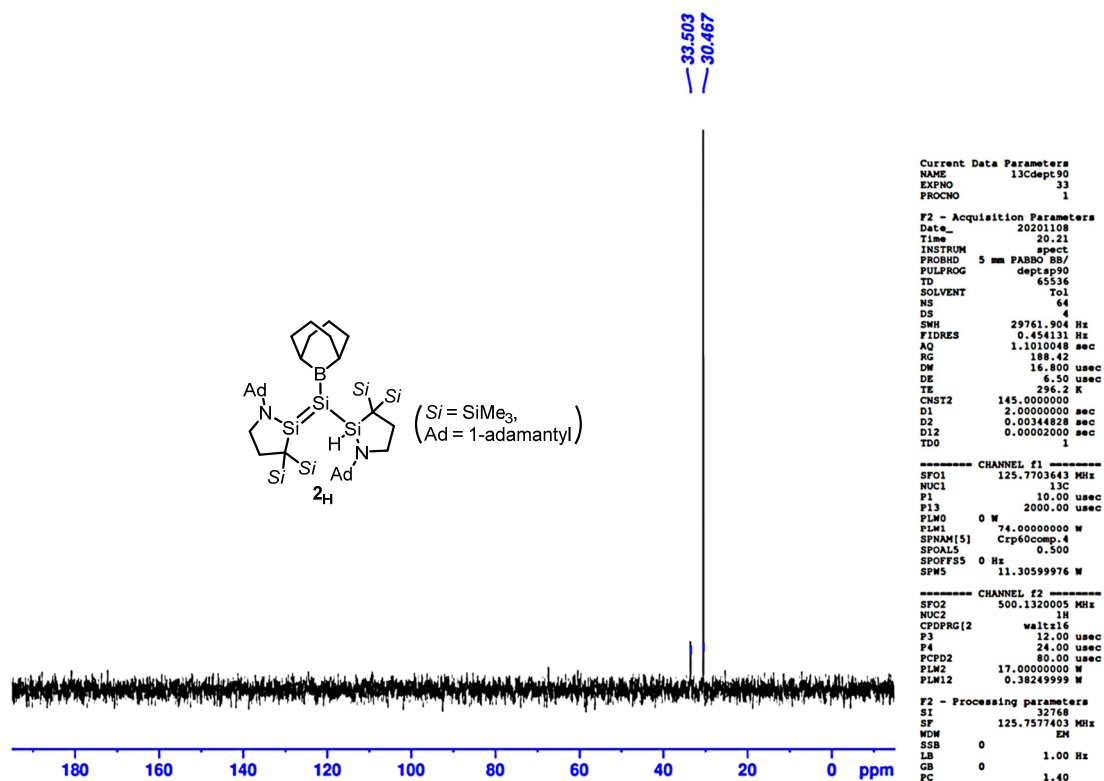


Figure S5. ¹³C{¹H} (DEPT90) NMR spectrum of disilene **2H** in C₇D₈ at 296 K.

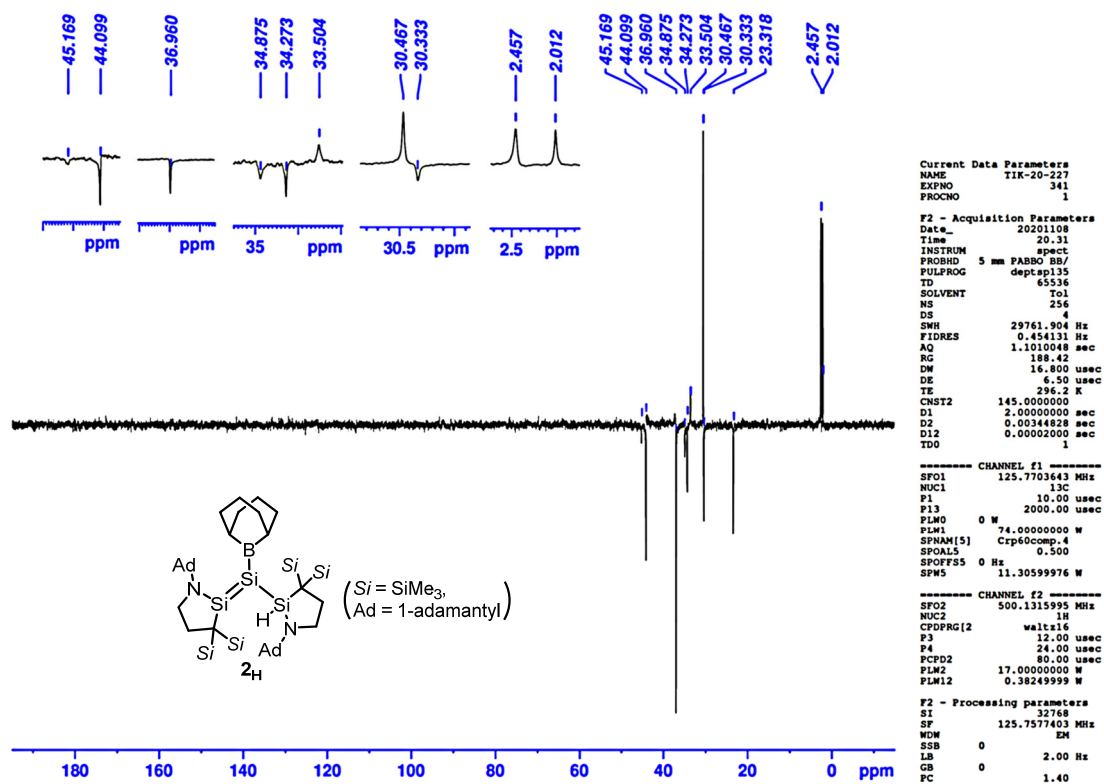


Figure S6. ¹³C{¹H} (DEPT135) NMR spectrum of disilene **2H** in C₇D₈ at 296 K.

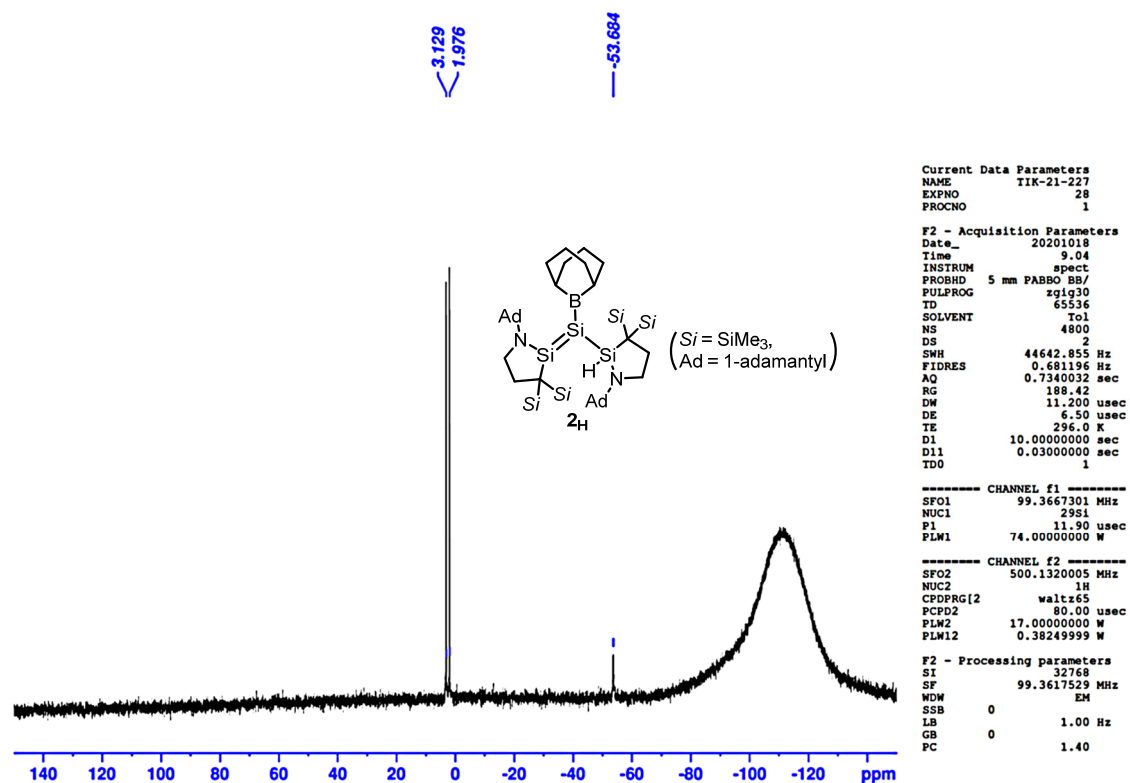


Figure S7. $^{29}Si\{^1H\}$ NMR spectrum of disilene **2H** in C_7D_8 at 296 K.

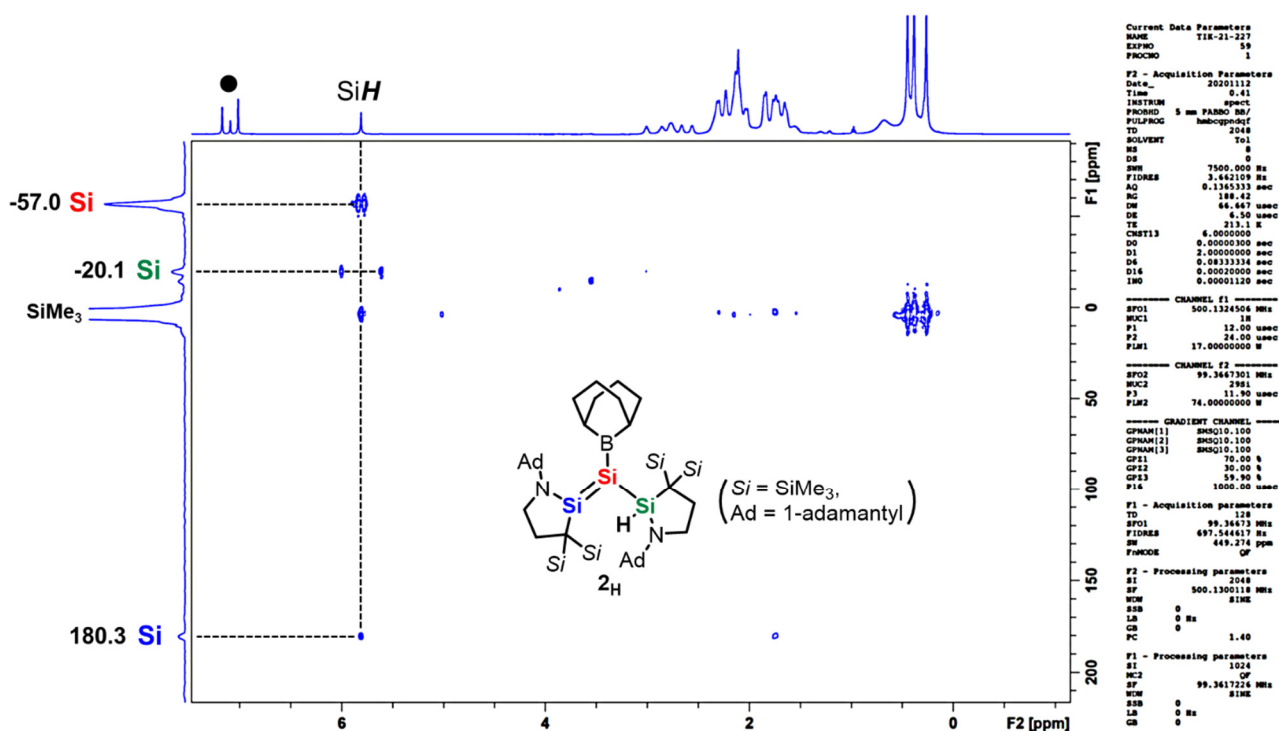


Figure S8. 1H - ^{29}Si HMBC NMR spectrum of disilene **2H** in C_7D_8 at 213 K (● = C_7D_7H).

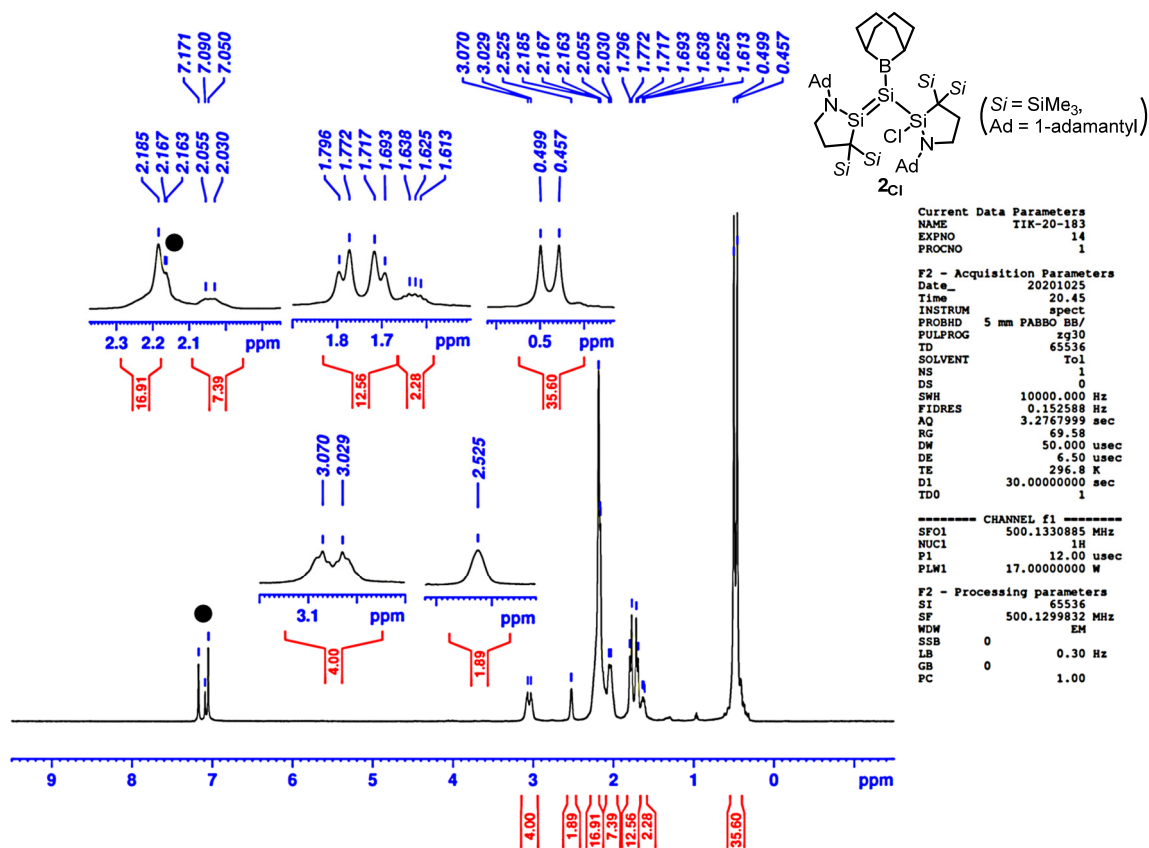


Figure S9. ^1H NMR spectrum of disilene **2Cl** in C_7D_8 at 297 K (● = $\text{C}_7\text{D}_7\text{H}$).

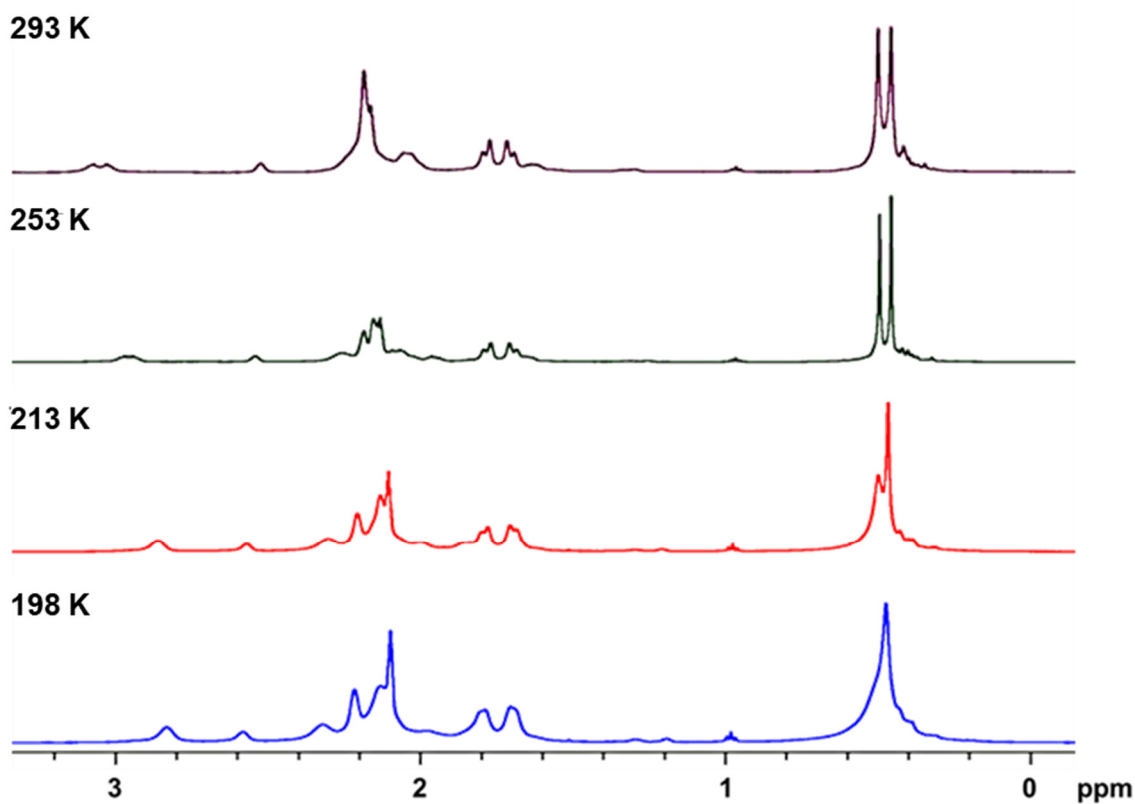


Figure S10. ^1H NMR spectrum of disilene **2Cl** in C_7D_8 at various temperatures.

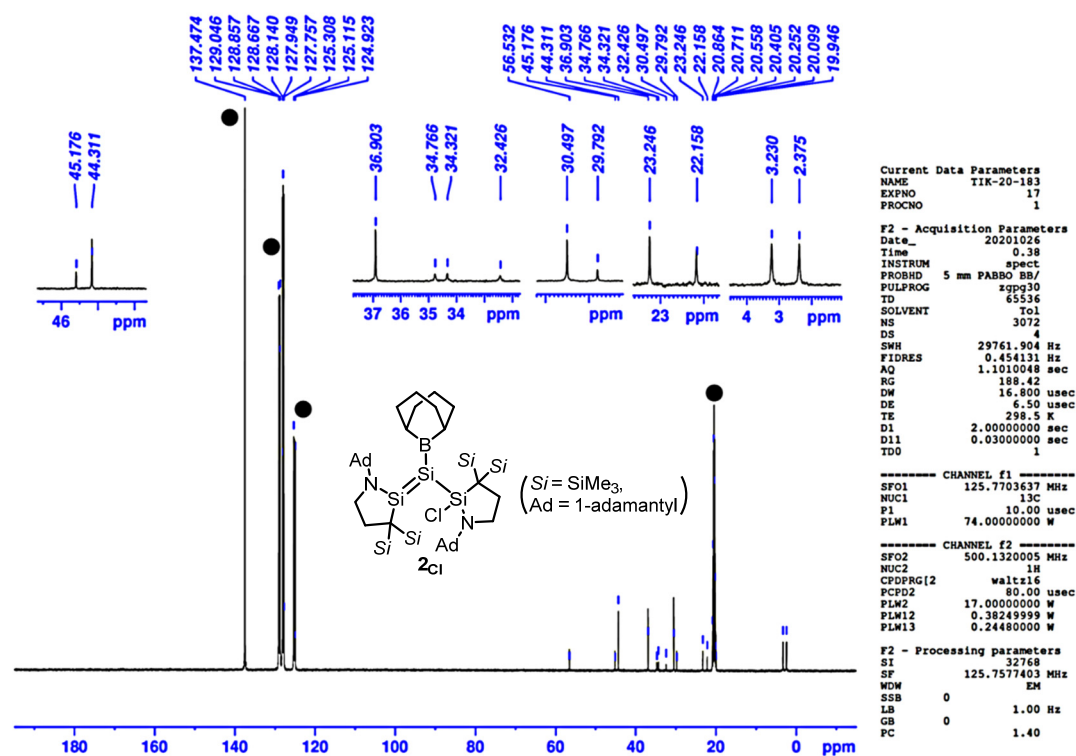


Figure S11. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of disilene **2Cl** in C_7D_8 at 299 K (● = C_7D_8).

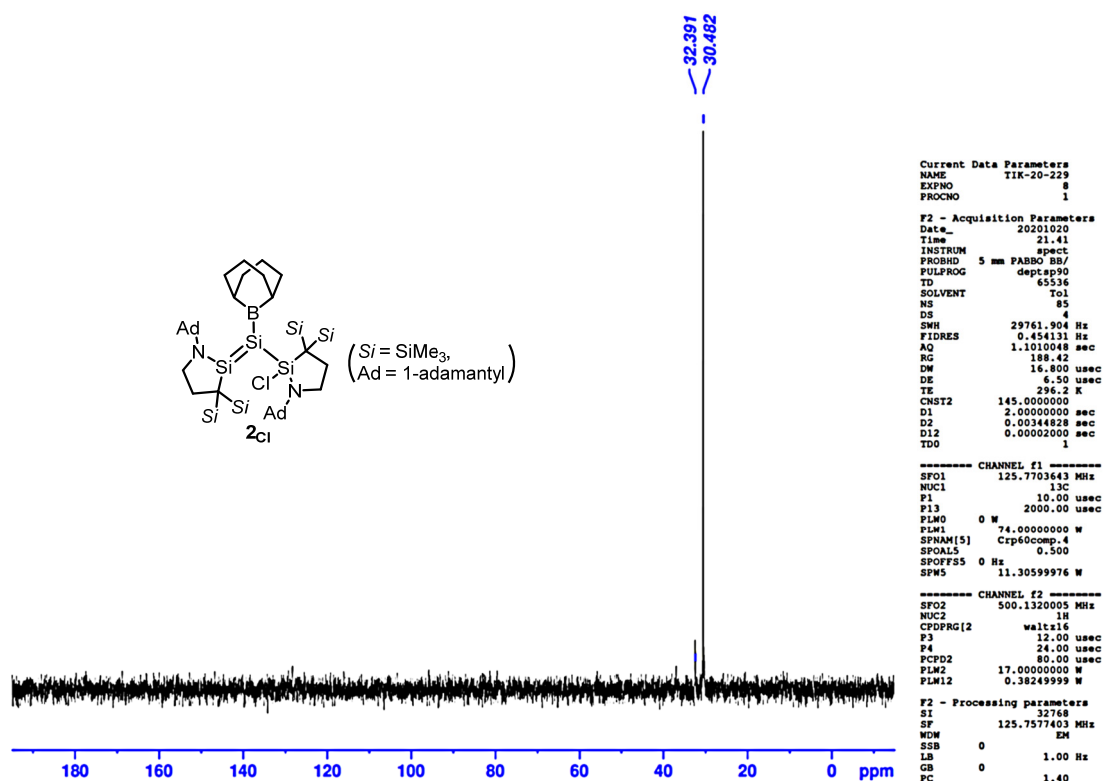


Figure S12. $^{13}\text{C}\{^1\text{H}\}$ (dept90) NMR spectrum of disilene **2Cl** in C_7D_8 at 296 K.

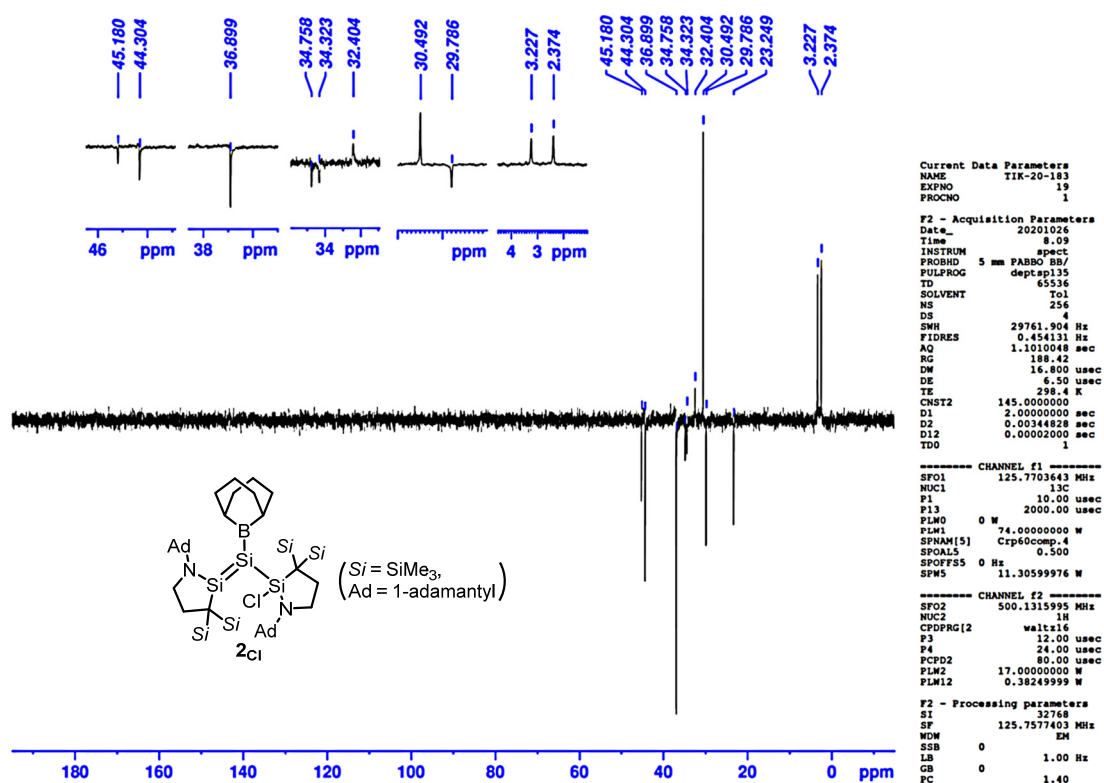


Figure S13. $^{13}\text{C}\{^1\text{H}\}$ (dept135) NMR spectrum of disilene 2Cl in C_7D_8 at 298 K.

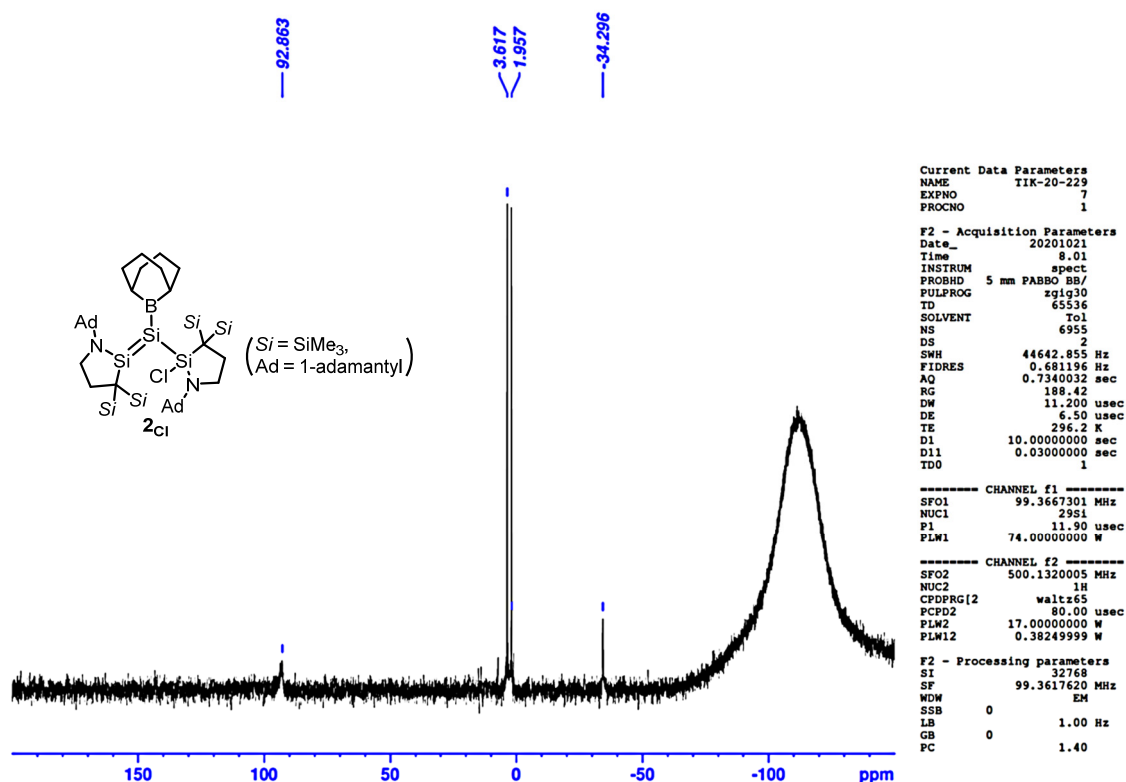


Figure S14. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of disilene 2Cl in C_7D_8 at 296 K.

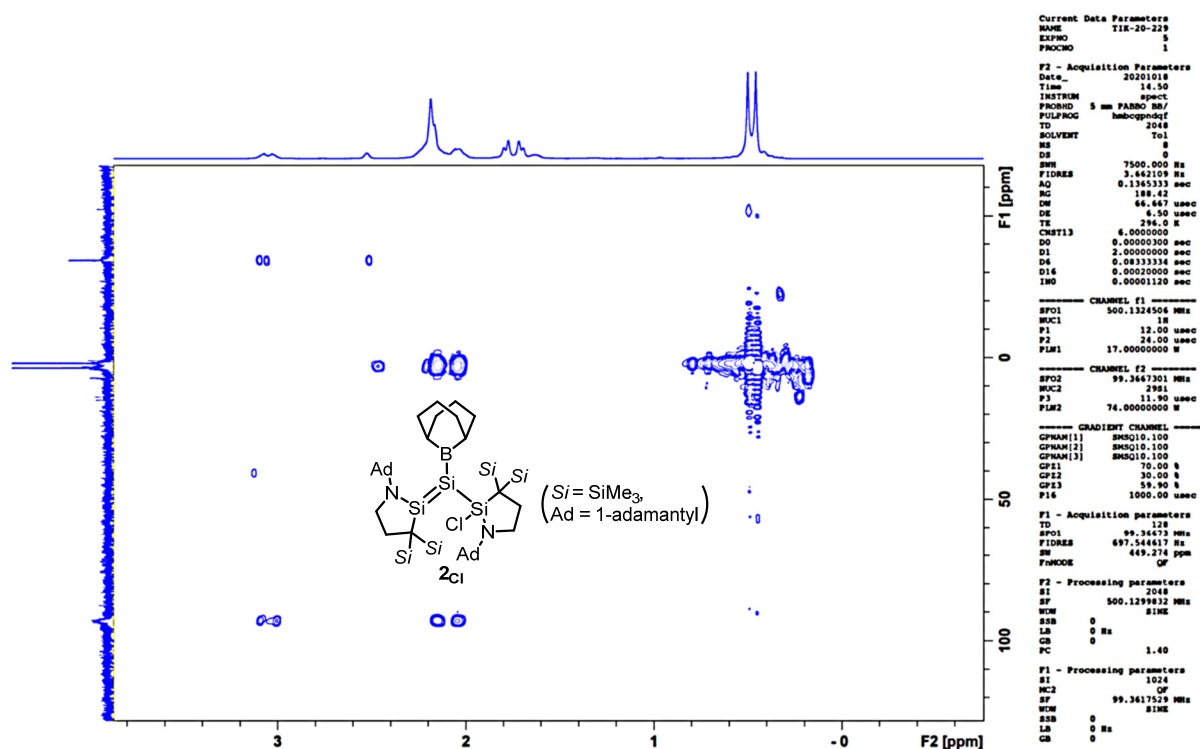


Figure S15. ^1H - ^{29}Si HMBC NMR spectrum of disilene 2Cl in C_7D_8 at 296 K.

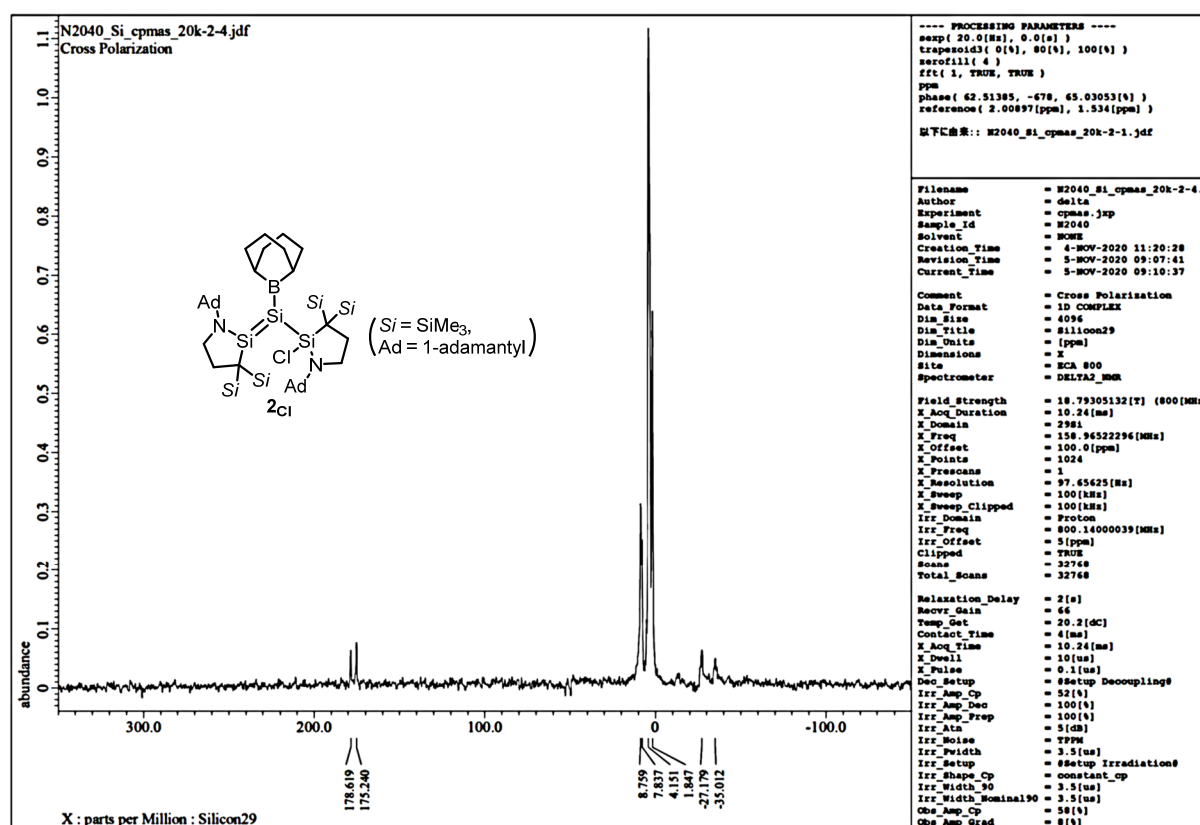


Figure S16. ^{29}Si CP MAS NMR spectrum of disilene 2Cl at 293 K.

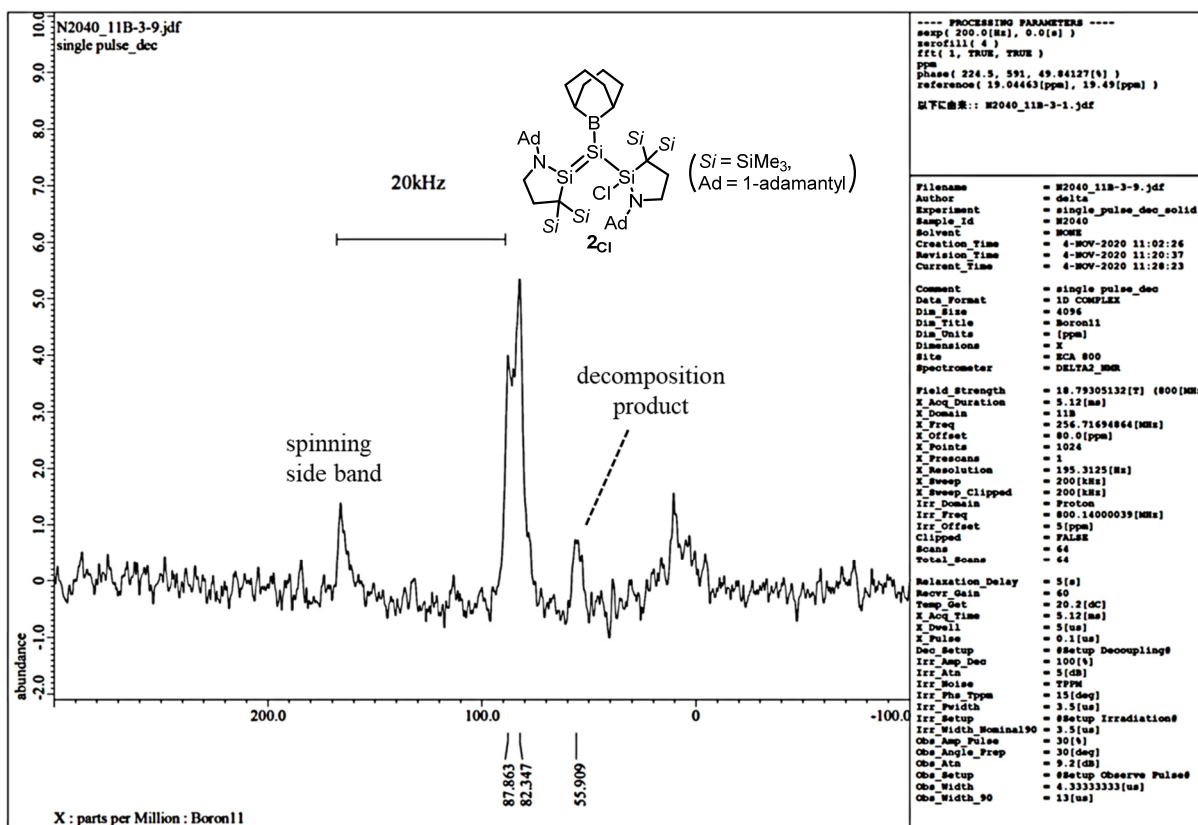


Figure S17. ^{11}B CP MAS NMR spectrum of disilene **2_{Cl}** at 293 K.

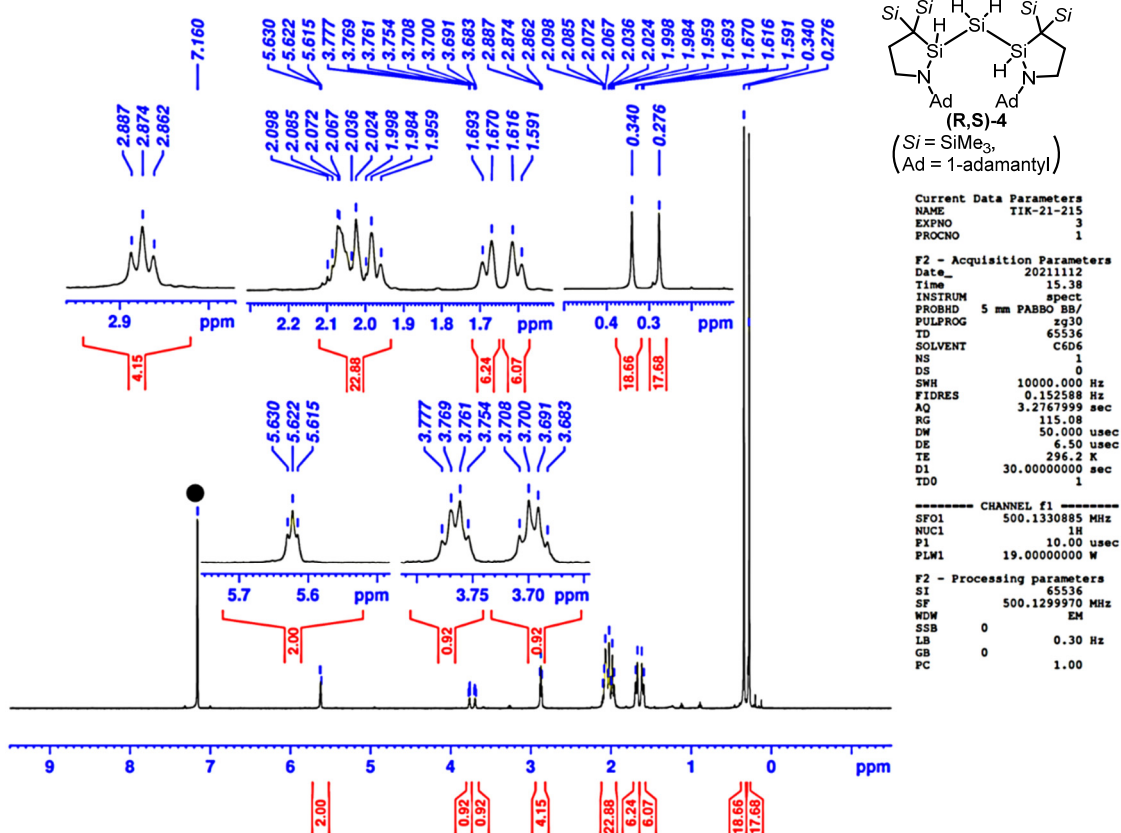


Figure S18. ^1H NMR spectrum of trisilane (R,S)-**4** in C_6D_6 at 296 K (● = $\text{C}_6\text{D}_5\text{H}$).

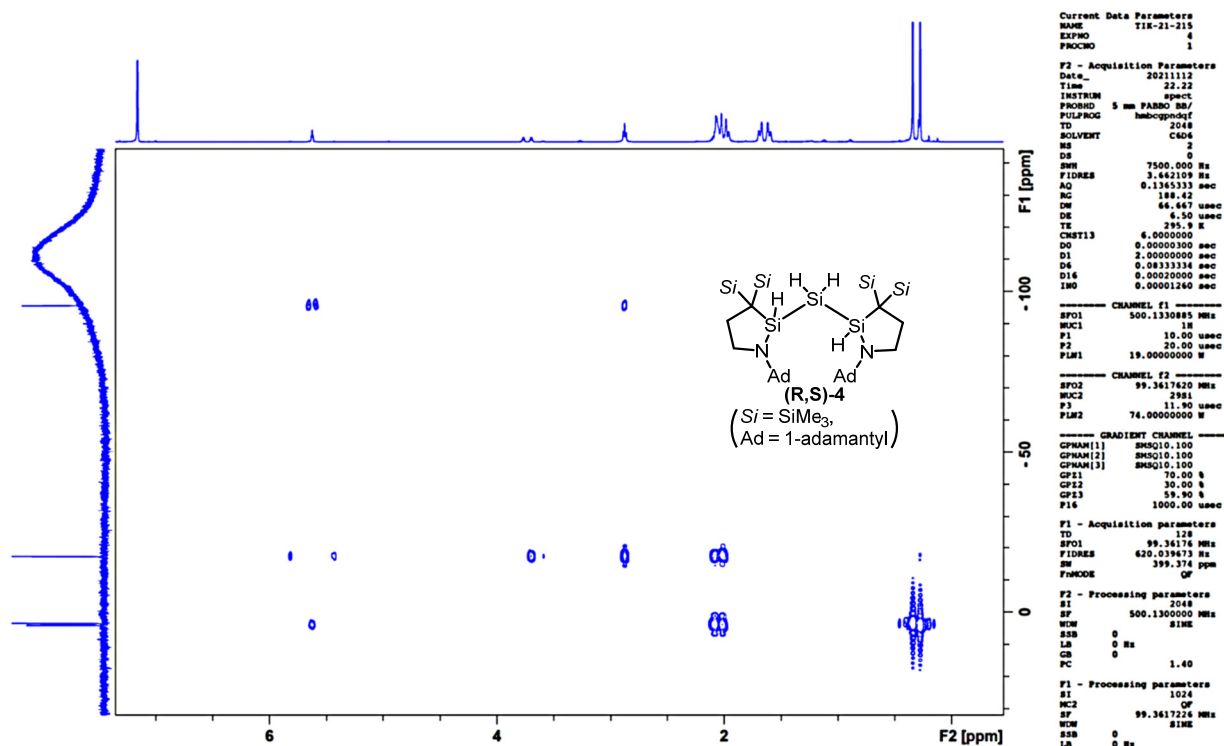


Figure S23. ^1H - ^{29}Si HMBC NMR spectrum of trisilane (R,S)-4 in C_6D_6 at 296 K.

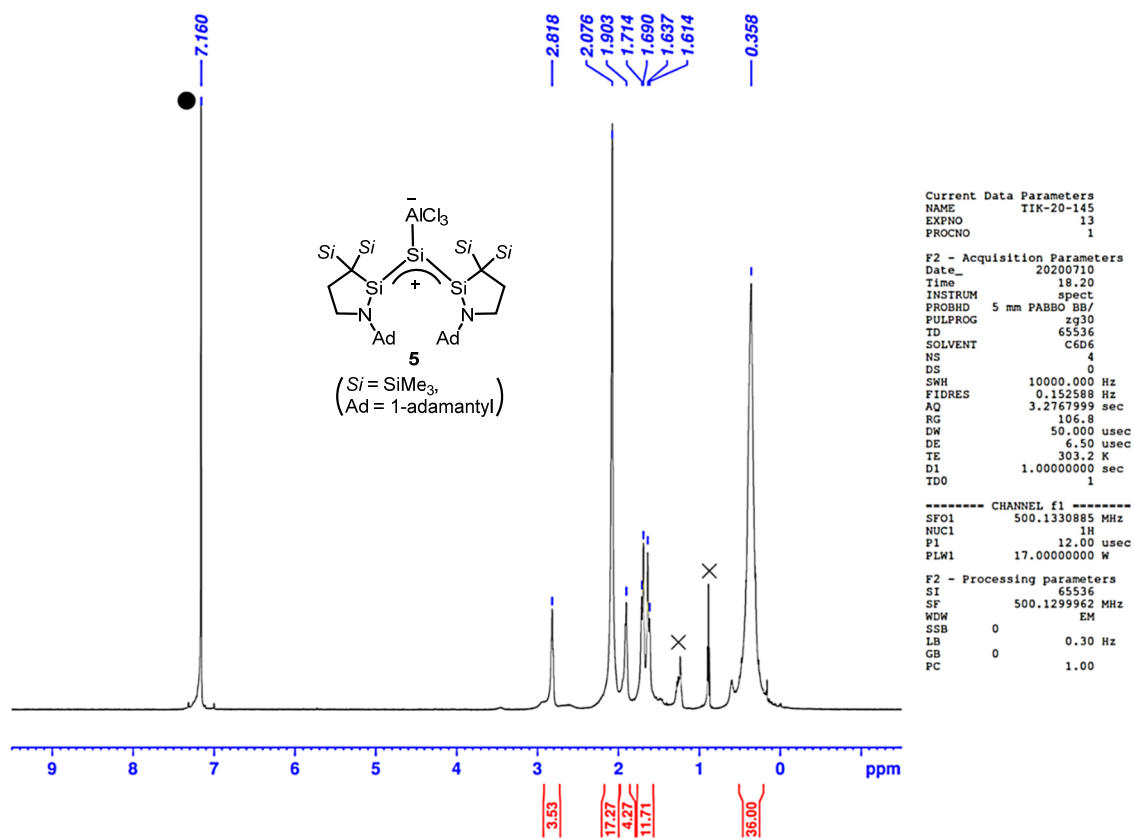


Figure S24. ^1H NMR spectrum of silylone- AlCl_3 complex 5 in C_6D_6 at 303 K (● = $\text{C}_6\text{D}_5\text{H}$, × = trace residual hexane).

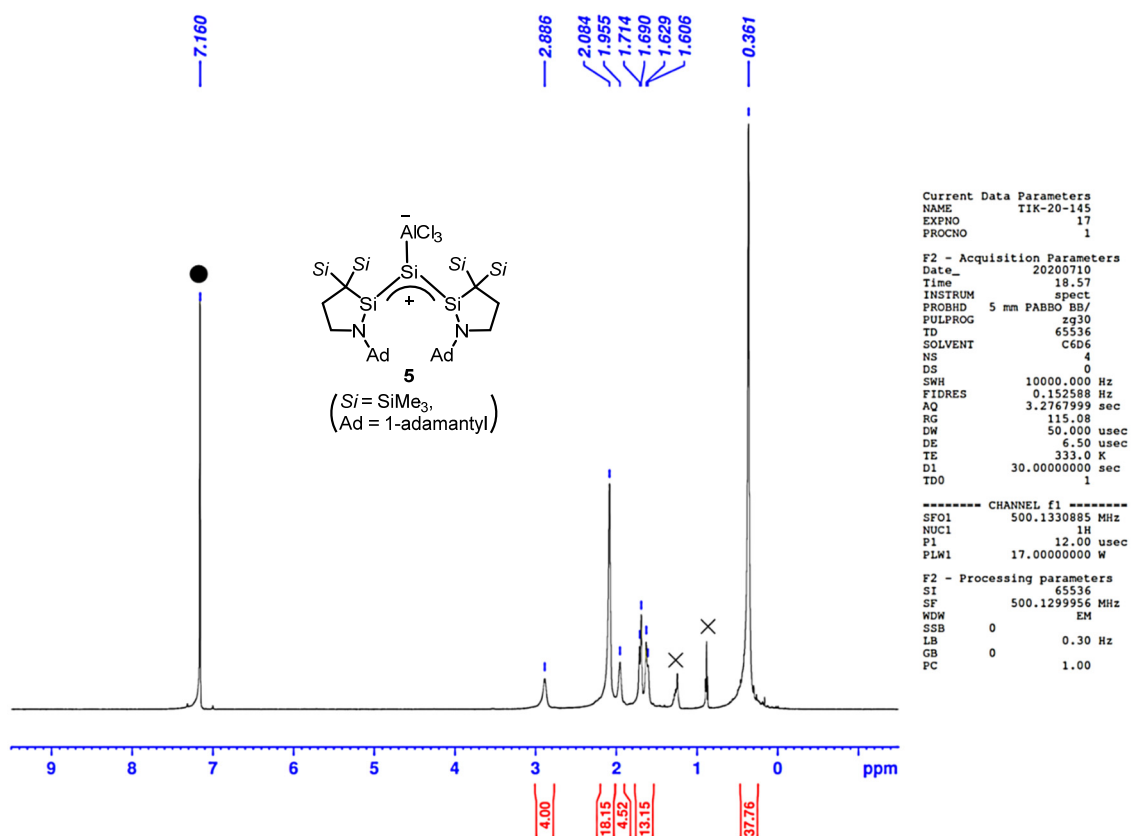


Figure S25. 1H NMR spectrum of silylone- $AlCl_3$ complex 5 in C_6D_6 at 333 K (● = C_6D_5H , × = trace residual hexane).

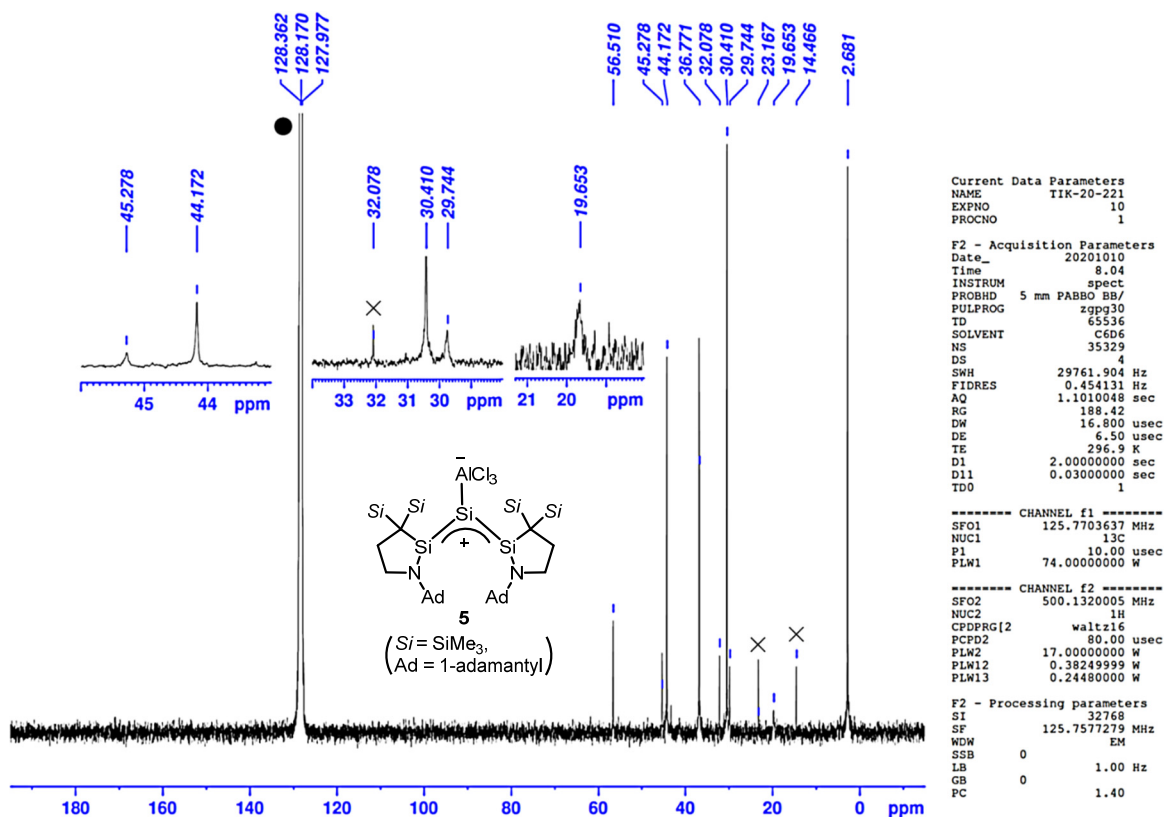


Figure S26. $^{13}C\{^1H\}$ NMR spectrum of silylone- $AlCl_3$ complex 5 in C_6D_6 at 297 K (● = C_6D_6 , × = trace residual hexane).

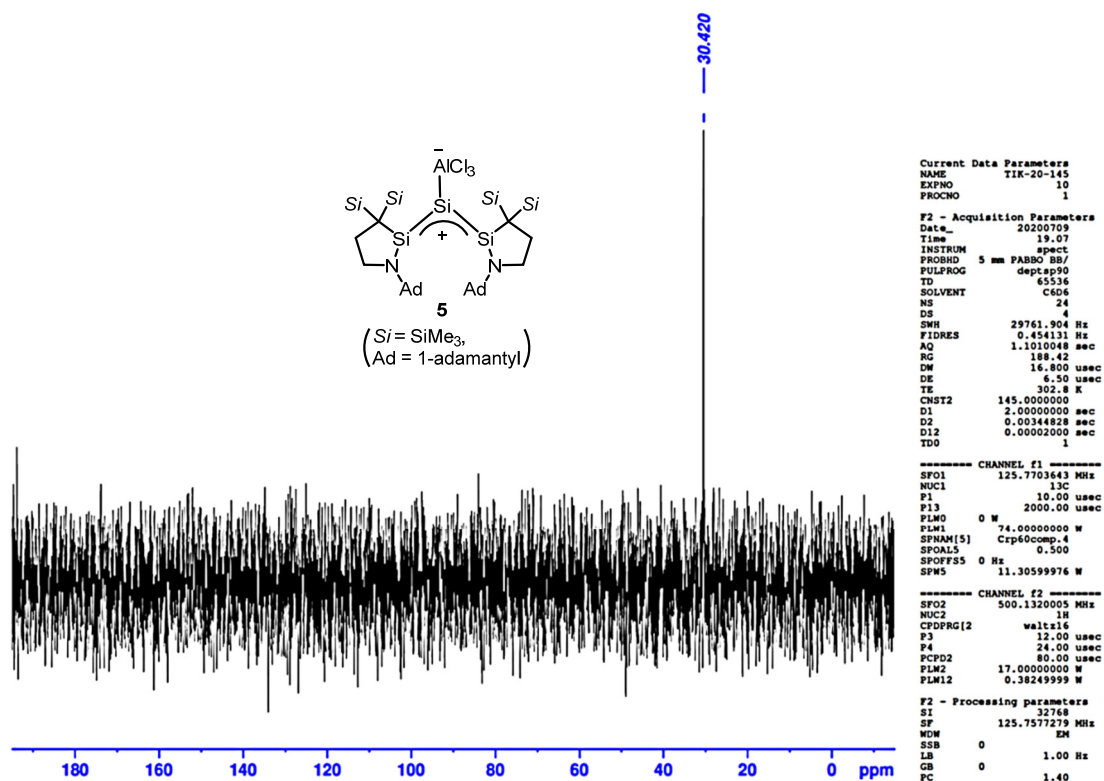


Figure S27. $^{13}\text{C}\{^1\text{H}\}$ (DEPT90) NMR spectrum of silylone- AlCl_3 complex 5 in C_6D_6 at 303 K.

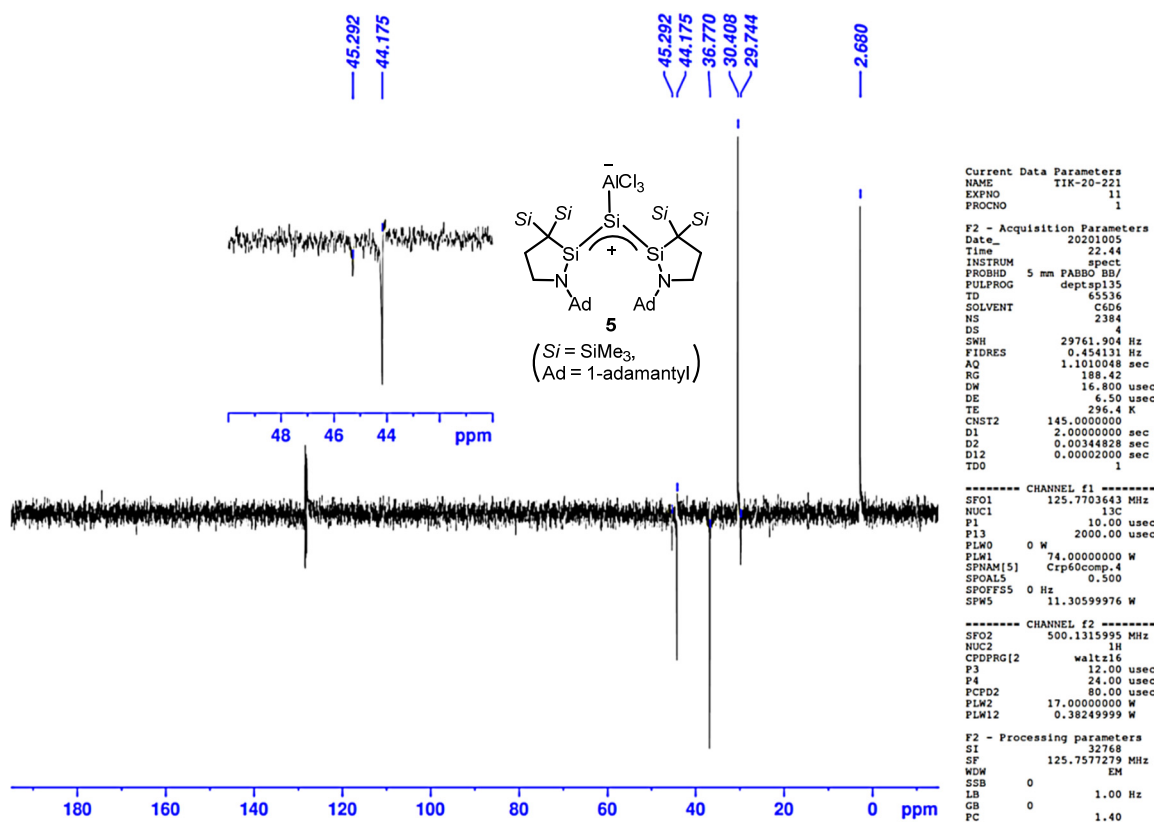


Figure S28. $^{13}\text{C}\{^1\text{H}\}$ (DEPT135) NMR spectrum of silylone- AlCl_3 complex 5 in C_6D_6 at 296 K.

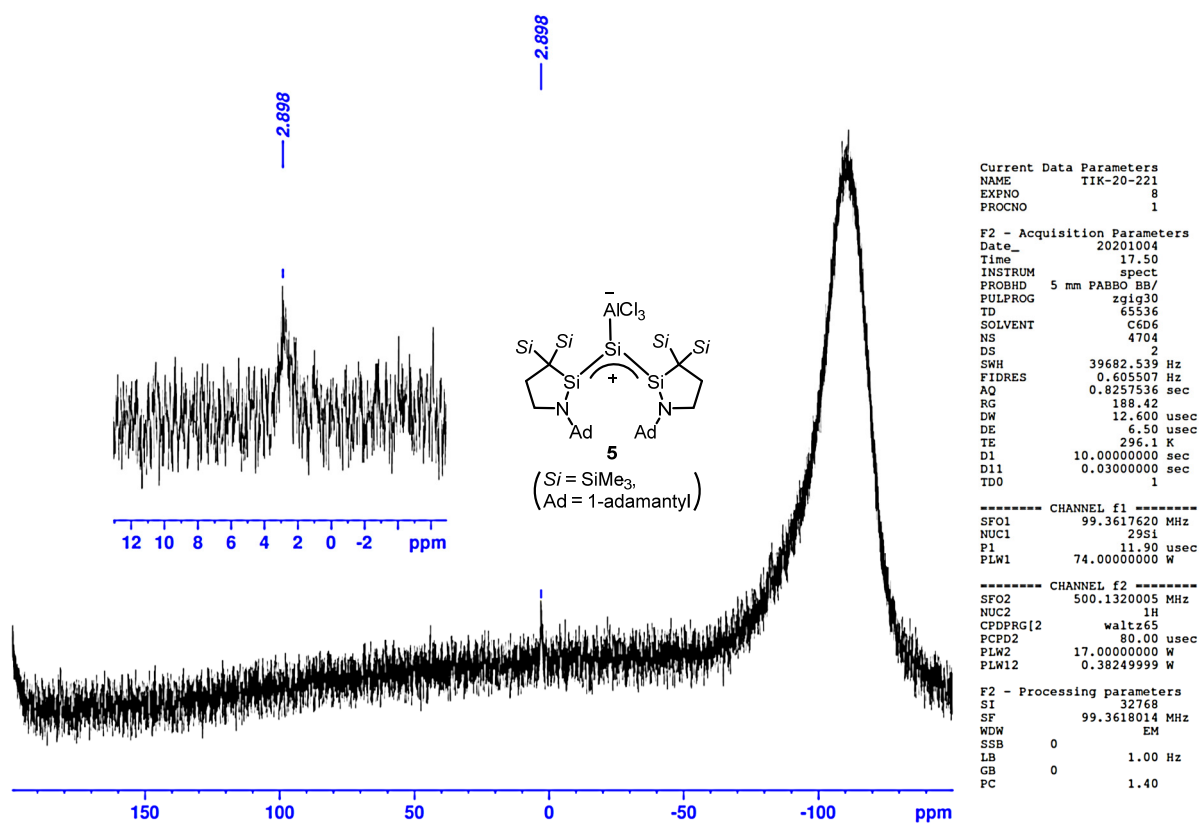


Figure S29. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of silylone- AlCl_3 complex **5** in C_6D_6 at 296 K.

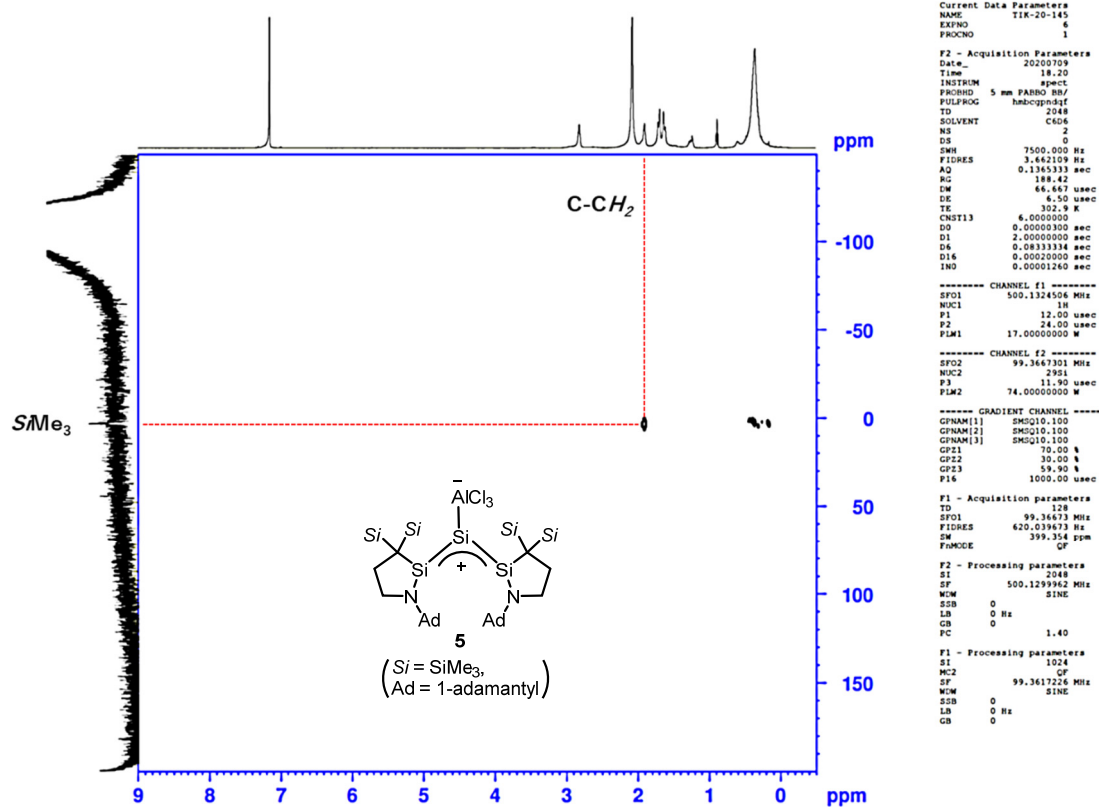


Figure S30. ^1H - ^{29}Si HMBC NMR spectrum of silylone- AlCl_3 complex **5** in C_6D_6 at 303 K.

3. X-ray Analysis

Single crystals suitable for X-ray diffraction study were obtained by recrystallization in an inert atmosphere using the following conditions; from toluene at $-27\text{ }^{\circ}\text{C}$ for disilene **2_H**, from heptane at $-27\text{ }^{\circ}\text{C}$ for disilene **2_{Cl}**, from hexane at $-27\text{ }^{\circ}\text{C}$ for trisilane (R,S)-**4**. The single crystals for data collection were coated by Apiezon® grease and mounted on the glass fiber and then transferred to the cold gas stream of the diffractometer. X-ray diffraction data were collected on a Bruker AXS APEX II CCD diffractometer with graphite monochromated Mo-K α radiation. An empirical absorption correction based on the multiple measurements of equivalent reflections was applied using the program SADABS.⁴ All of the structures were solved by direct methods and refined by full-matrix least squares against F^2 using all data (SHELXL-2018).⁵ Molecular structures were analyzed by Yadokari-XG software.⁶

Crystal data of **2_H** (CCDC-2166052) (100 K): $\text{C}_{113}\text{H}_{202}\text{B}_2\text{N}_4\text{Si}_{14}$; Fw 2031.65; triclinic; $P\bar{1}$, $a = 12.1655(7)\text{ \AA}$, $b = 12.3858(7)\text{ \AA}$, $c = 22.4816(12)\text{ \AA}$, $\alpha = 84.3400(10)^{\circ}$, $\beta = 85.9620(10)^{\circ}$, $\gamma = 61.9680(10)^{\circ}$, $V = 2974.4(3)\text{ \AA}^3$, $Z = 1$, $R1 = 0.0586$ ($I > 2\sigma(I)$), $wR2 = 0.1229$ (all data), GOF = 1.052.

Crystal data of **2_{Cl}** (CCDC-2166503) (100 K): $\text{C}_{46}\text{H}_{88}\text{BClN}_2\text{Si}_7$; Fw 912.07; triclinic; $P\bar{1}$, $a = 12.786(2)\text{ \AA}$, $b = 13.133(2)\text{ \AA}$, $c = 18.193(3)\text{ \AA}$, $\alpha = 74.073(4)^{\circ}$, $\beta = 70.697(4)^{\circ}$, $\gamma = 66.021(4)^{\circ}$, $V = 2599.4(8)\text{ \AA}^3$, $Z = 2$, $R1 = 0.0485$ ($I > 2\sigma(I)$), $wR2 = 0.1280$ (all data), GOF = 1.025.

Crystal data of (R,S)-**4** (CCDC-2166504) (100 K): $\text{C}_{38}\text{H}_{78}\text{N}_2\text{Si}_7$; Fw 759.65; monoclinic; $P2_1/c$, $a = 12.6423(5)\text{ \AA}$, $b = 15.0411(6)\text{ \AA}$, $c = 23.2504(9)\text{ \AA}$, $\beta = 92.9190(10)^{\circ}$, $V = 4415.4(3)\text{ \AA}^3$, $Z = 4$, $R1 = 0.0355$ ($I > 2\sigma(I)$), $wR2 = 0.0911$ (all data), GOF = 1.049.

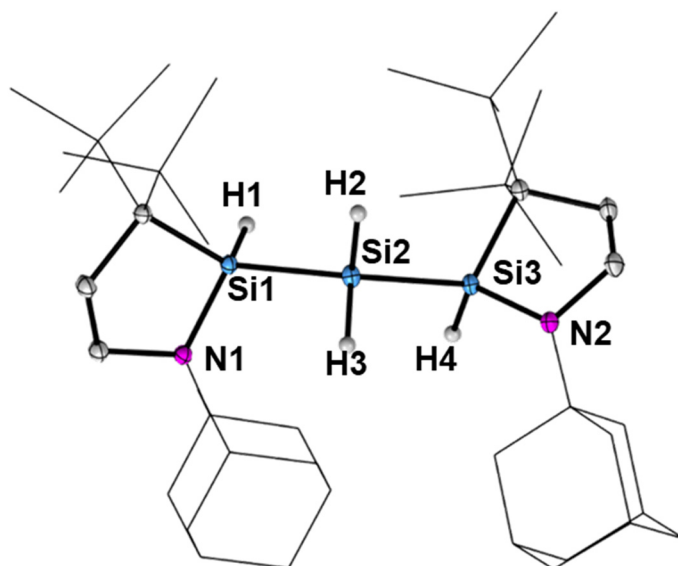


Figure S32. Molecular structure of **4** with thermal ellipsoids set at 50% probability. H atoms except for H1-H4 are omitted for clarity.

4. UV-Vis Absorption Spectra

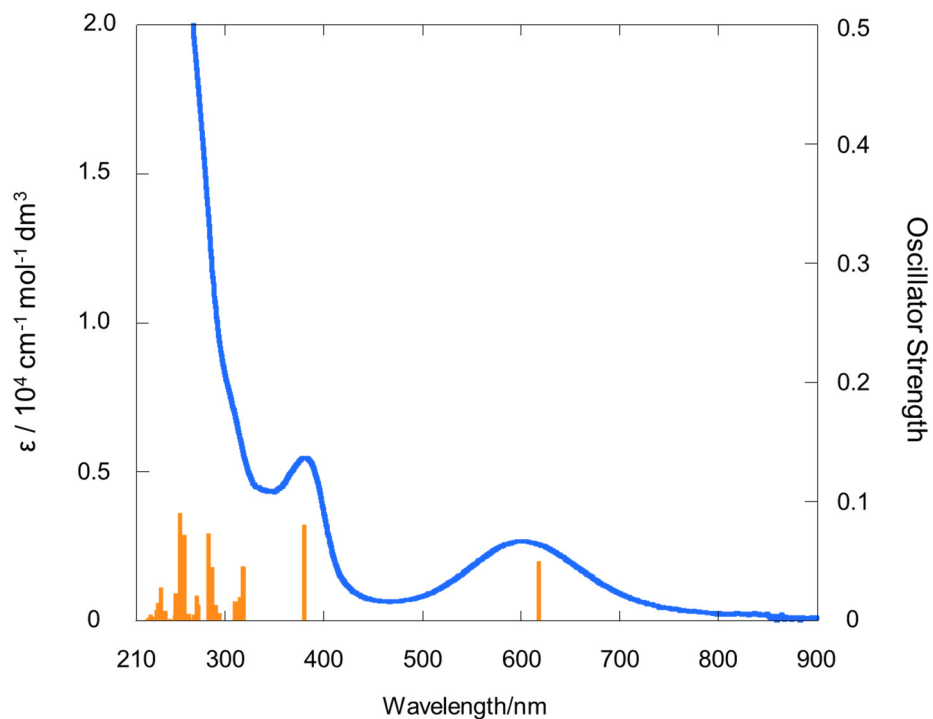


Figure S33. UV-Vis absorption spectrum of **2_H** in hexane at 297 K and band positions of **2_{H,opt}** calculated at the M06-2X/B2 (B2: 6-311+G(3d) [Cl,Si,N,B], 6-31+G(d) [C,H])//B3LYP-D3/B1 (B1: 6-311G(d) [Cl,Si,N,B], 6-31G(d) [C,H]) level of theory (vertical orange bars).

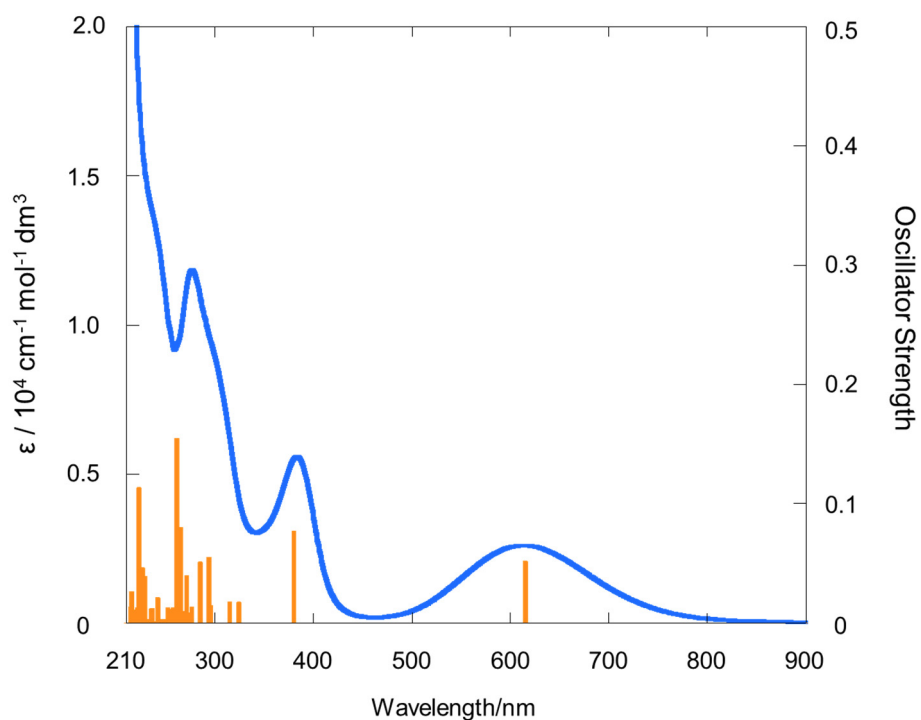


Figure S34. UV-Vis absorption spectrum of **2_{Cl}** in hexane at 297 K and band positions of **2_{Cl,opt}** calculated at the M06-2X/B2//B3LYP-D3/B1 level of theory (vertical orange bars).

5. Computational Studies

All theoretical calculations were performed using the Gaussian 09,⁷ GRRM 14⁸ or NBO 7.0⁹ program. Geometry optimization and frequency analysis for **2_{H,opt}**, **2_{Cl,opt}**, **3_{a-d}**, **6_{a-b}**, **7_{a-b}**, **8_{a-b}** and **D_{opt}** were performed at the B3PW91-D3/B1 (B1= 6-311G(d) [Cl,Si,N,B] & 6-31G(d) [C,H]) level of theory. In the case of mechanistic studies of the 1,3-migration reactions, geometry optimization and frequency analysis for **2_{H,opt}**, **2_{H,opt'}**, **2_{Cl,opt}**, **2_{Cl,opt'}**, **TS1_H**, **TS1_{Cl}**, **INT_{H,singlet}**, **INT_{H,triplet}**, **INT_{Cl,singlet}** and **INT_{Cl,triplet}** were performed at the (U)B3PW91-D3/6-31G(d) level of theory. Imaginary frequencies were not found in any of the optimized equilibrium structures. Atomic coordinates and energies for all compounds are summarized in a xyz file (tik_coordinates.xyz). Selected structural parameters of the optimized disilenes are summarized in Table S1. Excitation energies and oscillator strengths of **2_{H,opt}** and **2_{Cl,opt}** were calculated at the M06-2X/B2 (B2: 6-311+G(3d) [Cl,Si,N,B], 6-31+G(d) [C,H])/B3PW91-D3/B1 level of theory and are summarized in Tables S2-S3. Selected Kohn-Sham orbitals of **2_{H,opt}** and **2_{Cl,opt}** calculated at the M06-2X/B2//B3PW91-D3/B1 level of theory are shown in Figures S36-S37. Natural Bonding Orbital (NBO) analysis of **2_{H,opt}**, **2_{Cl,opt}** and **D_{opt}** were conducted with the NBO 7.0 program.

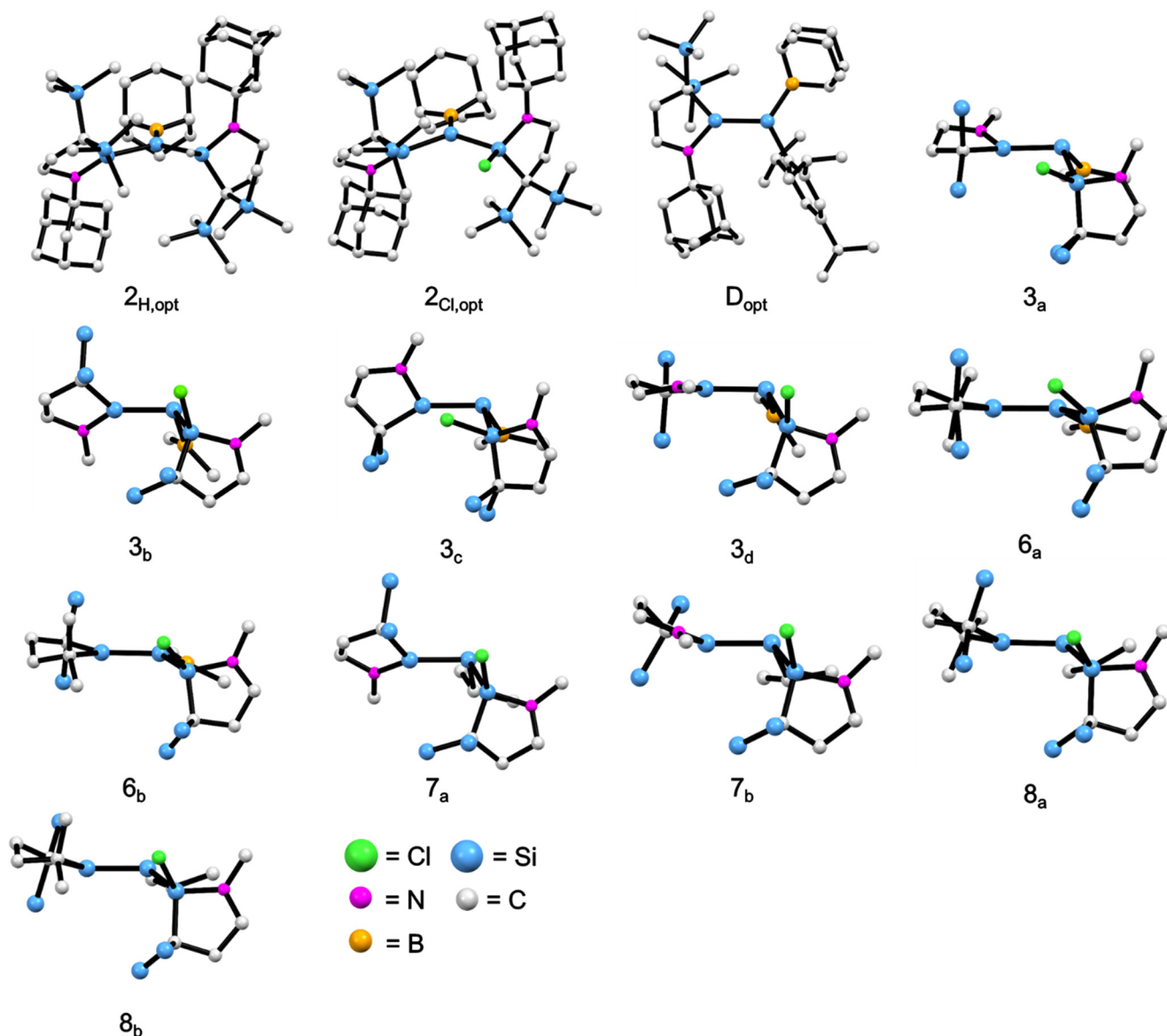
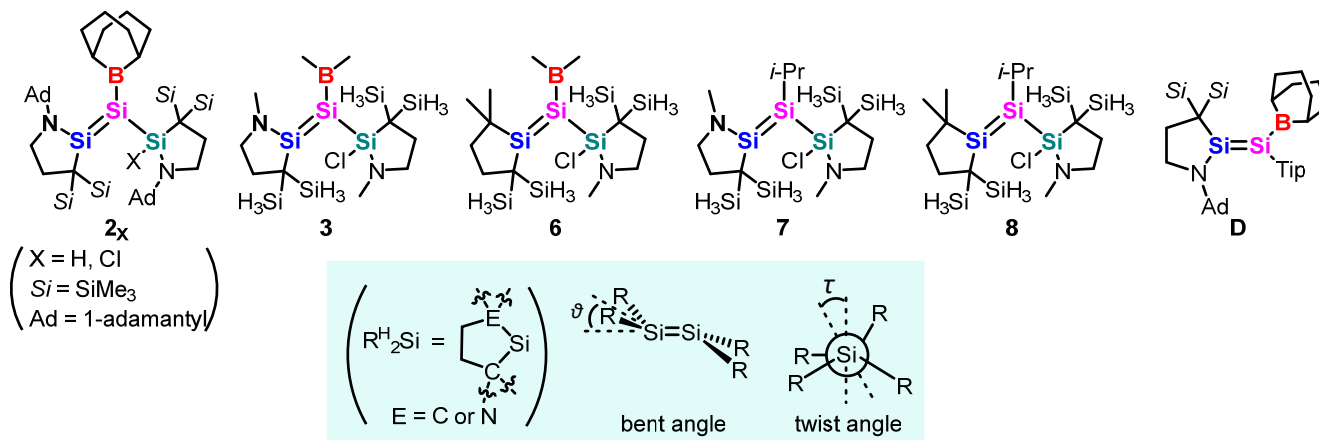


Figure S35. Molecular structures of various disilenes optimized at the B3PW91-D3/B1 level of theory. Hydrogen atoms except for the H-Si of **2_{H,opt}** are omitted for clarity.

Table S1. Selected Structural Parameters of Various Disilenes Calculated at the B3PW91-D3/B1 Level of Theory as well as the Crystal Structures of **2_H** and **2_{Cl}**.



Compound	Distance [Å]				Angles [°]					Relative Gibbs Energy (kJ mol ⁻¹ , 298.15 K)
					Si=Si Twist Angle (τ)	Bent Angle (θ)		Sum of Angles		
	Si=Si	Si-B	N-Si	Si-N		R ^H ₂ Si=Si	Si=SiR(SiR ^H ₂ Cl)	R ^H ₂ Si=Si	Si=SiR(SiR ^H ₂ Cl)	
2 _{H,opt}	2.211	1.929	1.720	1.755	52.1	8.2	4.4	359.0	359.8	-
2 _H ^a	2.2184(11)	1.935(3)	1.699(2)	1.744(2)	48.1	9.2	10.4	358.7	359.1	-
2 _{Cl,opt}	2.250	1.941	1.722	1.736	56.7	16.5	13.7	355.9	358.2	-
2 _{Cl} ^a	2.2541(10)	1.931(3)	1.702(2)	1.726(2)	60.9	13.0	6.5	357.5	359.6	-
3 _a	2.237	2.007	1.711	1.723	8.5	13.5	57.9	357.0	323.3	0.0
3 _b	2.226	2.008	1.709	1.724	41.0	10.4	65.2	358.3	318.1	+1.9
3 _c	2.274	1.993	1.701	1.722	92.4	2.9	61.9	359.8	318.2	+10.1
3 _d	2.220	2.003	1.708	1.725	0.6 (179.4)	0.9	63.9	360.0	319.5	+1.9
6 _a	2.183	1.993	-	1.722	6.5 (173.5)	5.3	21.8	359.6	355.0	+6.6
6 _b	2.184	2.000	-	1.723	3.6	5.1	25.2	359.6	353.2	0.0
7 _a	2.260	-	1.712	1.724	52.0	19.2	69.4	354.3	309.9	0.0
7 _b	2.252	-	1.712	1.729	2.1	19.2	59.9	354.2	319.1	+6.4
8 _a	2.193	-	-	1.727	7.7	16.6	39.6	355.8	340.8	+4.8
8 _b	2.192	-	-	1.726	4.5 (175.5)	16.2	38.1	356.1	343.3	0.0
D _{opt}	2.214	1.933	1.735	-	24.6	11.9	1.9	357.8	360.0	-

[a] Structure obtained by XRD analysis.

Table S2. Transition Energy, Wavelength, and Oscillator Strengths of the Electronic Transition of 2_{H,opt}. The 241st Orbital is the Highest Occupied Orbital (HOMO) (tik65en_enan.log).

Excited State <S**2>=0.000	1:	Singlet-A	2.0049 eV	618.40 nm	f=0.0498	241 -> 248	-0.18802
						241 -> 249	-0.33317
241 -> 242		0.68685				241 -> 250	0.46609
Excited State <S**2>=0.000	2:	Singlet-A	3.2612 eV	380.18 nm	f=0.0811	241 -> 251	0.17755
						241 -> 274	0.11203
239 -> 242		-0.12355				Excited State	12:
241 -> 242		-0.10406				<S**2>=0.000	Singlet-A
241 -> 246		-0.14086				4.5728 eV	271.13 nm
241 -> 247		0.55747				f=0.0209	
241 -> 250		0.10766				241 -> 248	0.49461
241 -> 252		-0.24993				241 -> 249	0.20959
						241 -> 250	0.17300
Excited State <S**2>=0.000	3:	Singlet-A	3.8968 eV	318.17 nm	f=0.0454	241 -> 251	0.23004
						241 -> 252	0.10363
239 -> 242		0.15525				241 -> 255	0.11647
240 -> 242		0.46329				241 -> 273	0.10382
241 -> 244		-0.11070				Excited State	13:
241 -> 248		0.11144				<S**2>=0.000	Singlet-A
241 -> 260		-0.27641				4.6249 eV	268.08 nm
241 -> 267		0.16054				f=0.0048	
						241 -> 248	-0.20346
Excited State <S**2>=0.000	4:	Singlet-A	3.9299 eV	315.49 nm	f=0.0200	241 -> 249	0.47676
						241 -> 250	0.26991
238 -> 242		-0.10954				241 -> 251	-0.16503
240 -> 242		0.37329				241 -> 252	0.28210
241 -> 243		-0.37074				241 -> 255	-0.10587
241 -> 260		0.30257				Excited State	14:
241 -> 267		-0.15746				<S**2>=0.000	Singlet-A
						4.7026 eV	263.65 nm
Excited State <S**2>=0.000	5:	Singlet-A	3.9950 eV	310.35 nm	f=0.0161	f=0.0016	
						241 -> 247	0.15714
240 -> 242		0.24518				241 -> 248	-0.20025
241 -> 243		0.55710				241 -> 250	-0.18834
241 -> 246		0.11325				241 -> 251	0.50163
241 -> 247		0.11273				241 -> 252	0.25764
241 -> 260		0.14522				Excited State	15:
						<S**2>=0.000	Singlet-A
Excited State <S**2>=0.000	6:	Singlet-A	4.2187 eV	293.89 nm	f=0.0067	4.7183 eV	262.77 nm
						f=0.0059	
239 -> 242		0.12103				238 -> 242	0.14517
241 -> 243		-0.11263				240 -> 247	0.18193
241 -> 244		0.39524				241 -> 244	0.22469
241 -> 246		0.44296				241 -> 248	0.12046
241 -> 247		0.13516				241 -> 250	0.26058
						241 -> 255	0.12984
Excited State <S**2>=0.000	7:	Singlet-A	4.2529 eV	291.53 nm	f=0.0064	241 -> 256	-0.13896
						241 -> 260	0.11229
239 -> 242		-0.17779				241 -> 270	0.13201
241 -> 244		-0.30089				241 -> 274	-0.20371
241 -> 245		0.46597				241 -> 277	0.13799
241 -> 246		0.29815				241 -> 278	-0.15198
241 -> 252		-0.10930				Excited State	16:
						<S**2>=0.000	Singlet-A
Excited State <S**2>=0.000	8:	Singlet-A	4.2801 eV	289.68 nm	f=0.0132	4.7586 eV	260.55 nm
						f=0.0046	
241 -> 244		0.37264				241 -> 247	0.24403
241 -> 245		0.40912				241 -> 249	-0.23163
241 -> 246		-0.33137				241 -> 251	-0.30520
241 -> 251		-0.10004				241 -> 252	0.40284
						241 -> 254	0.15012
Excited State <S**2>=0.000	9:	Singlet-A	4.3343 eV	286.06 nm	f=0.0452	241 -> 255	0.10788
						241 -> 266	0.10475
238 -> 242		0.22349				241 -> 272	0.13755
239 -> 242		0.48237				Excited State	17:
239 -> 247		-0.10395				<S**2>=0.000	Singlet-A
241 -> 244		-0.15010				4.8058 eV	257.99 nm
241 -> 245		0.23039				f=0.0722	
241 -> 246		-0.13322				236 -> 242	-0.14801
241 -> 247		0.12411				236 -> 247	0.10124
						237 -> 242	-0.13607
Excited State <S**2>=0.000	10:	Singlet-A	4.3769 eV	283.27 nm	f=0.0732	238 -> 242	0.27116
						238 -> 247	-0.10215
239 -> 242		0.15186				239 -> 247	0.14913
241 -> 243		-0.10169				240 -> 242	0.14582
241 -> 245		-0.10758				240 -> 247	0.31915
241 -> 246		0.14892				240 -> 252	-0.14305
241 -> 248		-0.25059				241 -> 274	0.12537
241 -> 249		0.16418				Excited State	18:
241 -> 252		-0.19177				<S**2>=0.000	Singlet-A
241 -> 255		0.17795				4.8753 eV	254.31 nm
241 -> 266		0.15520				f=0.0902	
241 -> 272		0.28591				237 -> 242	0.59147
241 -> 273		0.16037				238 -> 242	0.31038
241 -> 276		-0.11743				Excited State	19:
						<S**2>=0.000	Singlet-A
Excited State <S**2>=0.000	11:	Singlet-A	4.5622 eV	271.76 nm	f=0.0134	4.9391 eV	251.03 nm
						f=0.0046	
239 -> 242		0.15186				236 -> 242	-0.10416
241 -> 243		-0.10169				237 -> 242	-0.12497
241 -> 245		-0.10758				241 -> 253	0.37434
241 -> 246		0.14892				241 -> 254	0.19070
241 -> 248		-0.25059				241 -> 255	0.34013
241 -> 249		0.16418				241 -> 258	-0.17460
241 -> 252		-0.19177				241 -> 263	-0.10446
241 -> 255		0.17795					
241 -> 266		0.15520					
241 -> 272		0.28591					
241 -> 273		0.16037					
241 -> 276		-0.11743					

Excited State <S**2>=0.000	20:	Singlet-A	4.9667 eV	249.63 nm	f=0.0231	240 -> 269	-0.10045				
234 -> 242		-0.10622				Excited State <S**2>=0.000	29:	Singlet-A	5.3054 eV	233.69 nm	f=0.0118
236 -> 242		0.28798				240 -> 243		0.29450			
237 -> 242		0.13510				240 -> 244		0.45413			
238 -> 242		-0.17890				240 -> 246		0.19473			
238 -> 247		0.14944				240 -> 247		0.10406			
239 -> 242		0.17962				240 -> 248		0.19631			
239 -> 247		0.27822				240 -> 255		0.10197			
239 -> 252		-0.12595				Excited State <S**2>=0.000	30:	Singlet-A	5.3457 eV	231.93 nm	f=0.0151
240 -> 247		0.19935				241 -> 258		0.10478			
241 -> 253		0.14217				241 -> 260		0.12605			
Excited State <S**2>=0.000	21:	Singlet-A	4.9824 eV	248.84 nm	f=0.0041	241 -> 261		0.24542			
241 -> 253		0.27792				241 -> 263		0.36235			
241 -> 254		0.27758				241 -> 265		0.16907			
241 -> 255		-0.18236				241 -> 266		0.10860			
241 -> 256		0.30384				241 -> 268		0.21024			
241 -> 257		0.12874				241 -> 272		-0.25425			
241 -> 258		0.32478				241 -> 286		-0.10621			
Excited State <S**2>=0.000	22:	Singlet-A	4.9927 eV	248.33 nm	f=0.0009	241 -> 296		-0.10491			
241 -> 253		0.42723				Excited State <S**2>=0.000	31:	Singlet-A	5.3771 eV	230.58 nm	f=0.0026
241 -> 254		-0.30354				241 -> 260		-0.21070			
241 -> 255		-0.19076				241 -> 261		0.53200			
241 -> 256		-0.20783				241 -> 262		-0.18127			
241 -> 257		-0.15032				241 -> 268		-0.11007			
241 -> 258		0.13695				241 -> 272		0.19817			
241 -> 259		-0.16275				Excited State <S**2>=0.000	32:	Singlet-A	5.4071 eV	229.30 nm	f=0.0092
241 -> 260		0.11484				236 -> 242		0.23167			
Excited State <S**2>=0.000	23:	Singlet-A	5.0326 eV	246.36 nm	f=0.0006	239 -> 242		-0.12334			
241 -> 254		0.40909				239 -> 247		-0.21543			
241 -> 255		-0.29321				240 -> 247		0.18937			
241 -> 256		-0.40690				240 -> 260		0.10182			
241 -> 258		-0.12912				241 -> 255		-0.11510			
Excited State <S**2>=0.000	24:	Singlet-A	5.0636 eV	244.85 nm	f=0.0009	241 -> 262		0.29846			
241 -> 255		0.12570				241 -> 263		-0.21053			
241 -> 256		-0.15828				241 -> 265		0.18709			
241 -> 257		0.56648				241 -> 266		0.12720			
241 -> 259		-0.27989				Excited State <S**2>=0.000	33:	Singlet-A	5.4142 eV	229.00 nm	f=0.0032
Excited State <S**2>=0.000	25:	Singlet-A	5.0830 eV	243.92 nm	f=0.0014	236 -> 242		-0.22549			
241 -> 253		-0.15909				239 -> 242		0.13397			
241 -> 255		0.19675				239 -> 247		0.19945			
241 -> 256		-0.25751				240 -> 247		-0.15279			
241 -> 257		-0.21281				240 -> 260		-0.15506			
241 -> 258		0.50309				241 -> 261		0.15993			
241 -> 263		-0.12484				241 -> 262		0.32540			
Excited State <S**2>=0.000	26:	Singlet-A	5.1418 eV	241.13 nm	f=0.0004	241 -> 263		-0.15547			
241 -> 254		-0.12672				241 -> 265		0.17415			
241 -> 256		-0.15745				241 -> 266		0.10094			
241 -> 257		0.23877				Excited State <S**2>=0.000	34:	Singlet-A	5.4506 eV	227.47 nm	f=0.0025
241 -> 259		0.55381				241 -> 260		0.19049			
241 -> 260		-0.10889				241 -> 261		-0.11299			
Excited State <S**2>=0.000	27:	Singlet-A	5.1883 eV	238.97 nm	f=0.0080	241 -> 262		-0.39644			
233 -> 242		-0.12509				241 -> 263		-0.13096			
234 -> 242		-0.15572				241 -> 265		0.39796			
236 -> 242		0.19976				241 -> 267		0.19550			
237 -> 242		-0.19242				241 -> 272		0.12275			
238 -> 242		0.28224				Excited State <S**2>=0.000	35:	Singlet-A	5.4762 eV	226.41 nm	f=0.0017
238 -> 247		0.11731				241 -> 262		0.13171			
239 -> 242		-0.18840				241 -> 263		0.20514			
239 -> 247		0.11303				241 -> 264		0.44160			
240 -> 242		0.13247				241 -> 265		0.22789			
240 -> 243		0.11243				241 -> 266		-0.18534			
240 -> 247		-0.18638				241 -> 267		-0.28810			
240 -> 260		-0.17839				241 -> 269		0.12798			
241 -> 259		-0.14043				Excited State <S**2>=0.000	36:	Singlet-A	5.5024 eV	225.33 nm	f=0.0038
Excited State <S**2>=0.000	28:	Singlet-A	5.2724 eV	235.16 nm	f=0.0283	241 -> 260		0.25133			
239 -> 247		0.19182				241 -> 262		0.15650			
240 -> 247		-0.18962				241 -> 263		0.26876			
240 -> 252		0.14321				241 -> 265		-0.11241			
240 -> 260		0.36193				241 -> 267		0.36399			
240 -> 261		0.11136				241 -> 268		-0.30964			
240 -> 263		-0.14145				241 -> 269		-0.10642			
240 -> 265		-0.10826				241 -> 271		0.14238			
240 -> 267		-0.19158									

Excited State 37: <S**2>=0.000	Singlet-A	5.5297 eV	224.22 nm	f=0.0050	Excited State 39: <S**2>=0.000	Singlet-A	5.5806 eV	222.17 nm	f=0.0028
241 -> 263	-0.19423				241 -> 261	0.16343			
241 -> 264	0.44401				241 -> 264	-0.13470			
241 -> 265	-0.22112				241 -> 268	-0.34609			
241 -> 266	0.13637				241 -> 269	0.45555			
241 -> 267	0.17737				241 -> 271	-0.10668			
241 -> 268	0.12709				241 -> 272	-0.19206			
241 -> 270	-0.12329								
241 -> 272	-0.11454				Excited State 40: <S**2>=0.000	Singlet-A	5.6243 eV	220.44 nm	f=0.0011
241 -> 285	-0.12878				240 -> 243	0.37838			
241 -> 286	-0.10657				240 -> 245	0.22597			
					240 -> 246	-0.26602			
Excited State 38: <S**2>=0.000	Singlet-A	5.5542 eV	223.23 nm	f=0.0005	240 -> 248	-0.33626			
241 -> 261	-0.10450				240 -> 249	-0.13489			
241 -> 266	0.40584				240 -> 250	0.13556			
241 -> 267	-0.27479								
241 -> 268	-0.31589								
241 -> 269	-0.23490								
241 -> 272	-0.13518								

Table S3. Transition Energy, Wavelength, and Oscillator Strengths of the Electronic Transition of **2Cl_{opt}**. The 249th orbital is the Highest Occupied Orbital (HOMO) (tik62en1b.log)

Excited State 1: <S**2>=0.000	Singlet-A	2.0161 eV	614.98 nm	f=0.0519	Excited State 9: <S**2>=0.000	Singlet-A	4.5159 eV	274.55 nm	f=0.0084
249 -> 250	0.69039				249 -> 252	0.24726			
Excited State 2: <S**2>=0.000	Singlet-A	3.2614 eV	380.16 nm	f=0.0768	249 -> 253	0.42426			
247 -> 250	-0.13980				249 -> 254	-0.14801			
249 -> 252	0.49646				249 -> 255	0.38253			
249 -> 253	-0.18180								
249 -> 254	-0.28919				Excited State 10: <S**2>=0.000	Singlet-A	4.5766 eV	270.91 nm	f=0.0399
249 -> 255	-0.24322				246 -> 250	0.13854			
					247 -> 252	0.12140			
Excited State 3: <S**2>=0.000	Singlet-A	3.8261 eV	324.04 nm	f=0.0175	248 -> 252	0.17509			
248 -> 250	0.25576				248 -> 254	-0.10347			
249 -> 256	-0.13440				249 -> 253	0.26552			
249 -> 261	-0.22748				249 -> 255	-0.25580			
249 -> 264	0.14744				249 -> 256	0.10561			
249 -> 267	-0.12834				249 -> 261	-0.10984			
249 -> 268	0.30363				249 -> 273	-0.11027			
249 -> 269	0.23686				249 -> 276	0.11392			
249 -> 270	-0.19652				249 -> 277	0.10172			
249 -> 271	0.13885				249 -> 278	-0.21354			
					249 -> 282	0.10596			
Excited State 4: <S**2>=0.000	Singlet-A	3.9376 eV	314.87 nm	f=0.0176	249 -> 283	-0.11904			
246 -> 250	-0.15249								
248 -> 250	0.60189				Excited State 11: <S**2>=0.000	Singlet-A	4.6281 eV	267.89 nm	f=0.0097
249 -> 268	-0.14830				246 -> 250	-0.14764			
					247 -> 252	-0.12869			
Excited State 5: <S**2>=0.000	Singlet-A	4.1903 eV	295.88 nm	f=0.0149	248 -> 252	-0.15812			
246 -> 250	-0.11003				249 -> 254	0.31000			
247 -> 250	-0.29054				249 -> 255	-0.24351			
249 -> 251	0.56786				249 -> 256	0.27038			
					249 -> 258	-0.16222			
Excited State 6: <S**2>=0.000	Singlet-A	4.2173 eV	293.99 nm	f=0.0554	249 -> 259	0.14069			
246 -> 250	0.12548				249 -> 282	-0.13005			
247 -> 250	0.40497				249 -> 284	-0.15464			
249 -> 251	0.32535								
249 -> 252	0.10439				Excited State 12: <S**2>=0.000	Singlet-A	4.6820 eV	264.81 nm	f=0.0803
249 -> 253	0.19513				245 -> 250	0.53389			
249 -> 255	-0.19563				246 -> 250	0.37859			
Excited State 7: <S**2>=0.000	Singlet-A	4.3431 eV	285.48 nm	f=0.0511	Excited State 13: <S**2>=0.000	Singlet-A	4.7520 eV	260.91 nm	f=0.1548
246 -> 250	-0.11254				245 -> 250	0.10974			
247 -> 250	-0.29036				246 -> 250	-0.14933			
249 -> 251	-0.11045				247 -> 252	-0.18129			
249 -> 252	-0.14033				247 -> 254	0.10964			
249 -> 253	0.36351				248 -> 250	-0.11015			
249 -> 255	-0.23618				248 -> 252	-0.23538			
249 -> 256	-0.15626				248 -> 254	0.13714			
249 -> 268	0.11482				248 -> 255	0.10550			
249 -> 278	0.12780				249 -> 257	0.11638			
					249 -> 258	0.25895			
Excited State 8: <S**2>=0.000	Singlet-A	4.4857 eV	276.40 nm	f=0.0135	249 -> 278	-0.15826			
249 -> 252	0.35473				249 -> 282	0.13733			
249 -> 254	0.47990				249 -> 283	-0.12898			
249 -> 255	0.13594				249 -> 284	0.14455			
249 -> 256	-0.16646								
					Excited State 14: <S**2>=0.000	Singlet-A	4.8143 eV	257.53 nm	f=0.0068
					249 -> 254	-0.11262			
					249 -> 256	-0.35731			

249 -> 257	-0.24521					249 -> 266	0.17965			
249 -> 259	0.40294					249 -> 267	0.10450			
249 -> 264	-0.10751									
249 -> 268	-0.12919					Excited State 22:	Singlet-A	5.1929 eV	238.76 nm	f=0.0002
249 -> 284	-0.10440					<S**2>=0.000				
						249 -> 261	0.41511			
Excited State 15:	Singlet-A	4.8291 eV	256.75 nm	f=0.0130		249 -> 262	-0.12988			
<S**2>=0.000						249 -> 263	-0.33488			
249 -> 256	-0.31740					249 -> 264	-0.30167			
249 -> 257	0.48515					249 -> 268	0.15731			
249 -> 260	0.27269					249 -> 269	0.15127			
						249 -> 271	0.10639			
Excited State 16:	Singlet-A	4.8659 eV	254.80 nm	f=0.0027		Excited State 23:	Singlet-A	5.2293 eV	237.10 nm	f=0.0005
<S**2>=0.000						<S**2>=0.000				
244 -> 250	-0.21818					249 -> 261	0.31361			
245 -> 250	-0.21503					249 -> 262	0.46696			
245 -> 252	0.10901					249 -> 264	0.18754			
246 -> 250	0.23685					249 -> 265	-0.18783			
246 -> 252	-0.15465					249 -> 271	-0.10431			
247 -> 250	-0.14511									
247 -> 252	-0.20478					Excited State 24:	Singlet-A	5.2503 eV	236.15 nm	f=0.0122
247 -> 254	0.12221					<S**2>=0.000				
247 -> 255	0.10126					244 -> 250	-0.15488			
249 -> 257	-0.21489					247 -> 252	0.12099			
249 -> 258	0.15962					248 -> 252	-0.15907			
249 -> 259	-0.15488					249 -> 261	0.14448			
						249 -> 262	-0.34919			
Excited State 17:	Singlet-A	4.8989 eV	253.09 nm	f=0.0117		249 -> 264	0.38763			
<S**2>=0.000						249 -> 266	0.10542			
244 -> 250	0.10012					249 -> 268	-0.10134			
245 -> 250	0.10939									
247 -> 252	0.11606					Excited State 25:	Singlet-A	5.2529 eV	236.03 nm	f=0.0116
249 -> 256	-0.12516					<S**2>=0.000				
249 -> 257	-0.26074					241 -> 250	0.11993			
249 -> 258	0.15074					242 -> 250	0.14534			
249 -> 259	-0.27230					244 -> 250	0.27762			
249 -> 260	0.36692					247 -> 250	-0.12253			
249 -> 266	-0.14743					247 -> 252	-0.20694			
249 -> 284	-0.13286					247 -> 254	0.11862			
						248 -> 252	0.19187			
Excited State 18:	Singlet-A	4.9109 eV	252.47 nm	f=0.0129		248 -> 253	-0.11969			
<S**2>=0.000						249 -> 261	0.16357			
249 -> 253	-0.12072					249 -> 262	-0.11095			
249 -> 256	0.14565					249 -> 264	0.25980			
249 -> 258	0.53926									
249 -> 259	0.19719					Excited State 26:	Singlet-A	5.2822 eV	234.72 nm	f=0.0004
249 -> 260	-0.13379					<S**2>=0.000				
249 -> 263	-0.14644					249 -> 261	0.21110			
249 -> 282	-0.10535					249 -> 263	0.32741			
						249 -> 265	0.40140			
Excited State 19:	Singlet-A	5.0122 eV	247.37 nm	f=0.0033		249 -> 266	-0.32316			
<S**2>=0.000						249 -> 267	-0.10062			
249 -> 255	0.14964					249 -> 268	0.10192			
249 -> 256	0.12802									
249 -> 257	-0.13497					Excited State 27:	Singlet-A	5.3308 eV	232.58 nm	f=0.0006
249 -> 259	0.33855					<S**2>=0.000				
249 -> 260	0.41832					249 -> 264	-0.14717			
249 -> 263	0.12424					249 -> 265	0.36097			
249 -> 266	0.15764					249 -> 266	0.46185			
249 -> 269	0.10123					249 -> 267	-0.12585			
249 -> 271	0.12908					249 -> 268	-0.13679			
249 -> 284	0.11218					249 -> 275	-0.11343			
Excited State 20:	Singlet-A	5.1165 eV	242.32 nm	f=0.0213		Excited State 28:	Singlet-A	5.3801 eV	230.45 nm	f=0.0029
<S**2>=0.000						<S**2>=0.000				
239 -> 250	0.13021					249 -> 265	0.21311			
241 -> 250	0.15921					249 -> 267	0.58112			
242 -> 250	0.15939					249 -> 268	0.20222			
244 -> 250	0.13638									
245 -> 250	-0.24025					Excited State 29:	Singlet-A	5.4175 eV	228.86 nm	f=0.0391
246 -> 250	0.29022					<S**2>=0.000				
246 -> 252	0.10916					248 -> 251	0.11681			
247 -> 250	-0.19544					248 -> 252	0.12406			
247 -> 252	0.13010					248 -> 253	0.35454			
248 -> 250	0.16621					248 -> 254	-0.21005			
248 -> 252	-0.23449					248 -> 256	-0.29260			
248 -> 253	0.10403					248 -> 261	0.10190			
248 -> 254	0.12479					248 -> 263	0.10194			
248 -> 255	0.10397					248 -> 268	0.13890			
						248 -> 273	0.11264			
Excited State 21:	Singlet-A	5.1341 eV	241.49 nm	f=0.0011		248 -> 278	0.15011			
<S**2>=0.000										
249 -> 256	0.10386					Excited State 30:	Singlet-A	5.4900 eV	225.84 nm	f=0.0462
249 -> 258	0.12500					<S**2>=0.000				
249 -> 259	-0.13169					249 -> 266	0.13382			
249 -> 261	0.12231					249 -> 267	-0.11521			
249 -> 262	-0.25414					249 -> 270	0.17636			
249 -> 263	0.42954					249 -> 272	0.14393			
249 -> 264	-0.15460					249 -> 275	0.32307			
249 -> 265	-0.26419									

249 -> 282	-0.23297					Excited State 38:	Singlet-A	5.6925 eV	217.80 nm	f=0.0110
249 -> 283	-0.12410					<S**2>=0.000				
249 -> 286	-0.11455					244 -> 250	-0.13369			
249 -> 288	0.19273					246 -> 252	0.10976			
249 -> 292	-0.11299					248 -> 251	0.21409			
249 -> 294	0.10907					248 -> 253	0.12218			
						248 -> 254	-0.16272			
Excited State 31:	Singlet-A	5.5674 eV	222.70 nm	f=0.1136		248 -> 255	0.10469			
<S**2>=0.000						248 -> 278	-0.10844			
240 -> 250	0.24511					249 -> 269	-0.13458			
248 -> 251	0.12613					249 -> 270	-0.17396			
248 -> 257	0.11740					249 -> 271	0.12310			
248 -> 261	-0.20394					249 -> 272	0.15732			
248 -> 267	-0.11609					249 -> 274	-0.19714			
248 -> 268	0.24503					249 -> 275	0.22445			
248 -> 269	0.18830					249 -> 277	-0.13553			
248 -> 270	-0.15304									
249 -> 268	-0.10488					Excited State 39:	Singlet-A	5.7197 eV	216.77 nm	f=0.0266
249 -> 269	0.14896					<S**2>=0.000				
						248 -> 251	0.22052			
Excited State 32:	Singlet-A	5.5841 eV	222.03 nm	f=0.0075		248 -> 253	0.12074			
<S**2>=0.000						248 -> 254	-0.15125			
240 -> 250	-0.16105					248 -> 255	0.12974			
249 -> 268	-0.22006					248 -> 268	-0.14482			
249 -> 269	0.46351					248 -> 276	0.10498			
249 -> 270	0.17446					248 -> 278	-0.11246			
249 -> 274	-0.23098					249 -> 269	0.13588			
249 -> 275	0.12597					249 -> 272	-0.21699			
249 -> 278	0.13049					249 -> 273	0.13999			
						249 -> 274	0.30671			
Excited State 33:	Singlet-A	5.6189 eV	220.66 nm	f=0.0127		249 -> 278	-0.13267			
<S**2>=0.000										
232 -> 250	0.10764					Excited State 40:	Singlet-A	5.7310 eV	216.34 nm	f=0.0136
240 -> 250	0.51159					<S**2>=0.000				
241 -> 250	0.10866					239 -> 250	-0.13575			
249 -> 268	-0.10811					241 -> 250	-0.15222			
249 -> 271	0.19231					242 -> 250	-0.11236			
249 -> 273	-0.12002					244 -> 250	0.41692			
						244 -> 252	0.11801			
Excited State 34:	Singlet-A	5.6315 eV	220.16 nm	f=0.0011		245 -> 252	0.11511			
<S**2>=0.000						246 -> 252	-0.13021			
240 -> 250	-0.16857					249 -> 273	-0.16158			
249 -> 268	-0.15713					249 -> 274	-0.16679			
249 -> 270	0.22296									
249 -> 271	0.39822									
249 -> 273	-0.30400									
249 -> 274	0.14899									
249 -> 275	-0.10138									
Excited State 35:	Singlet-A	5.6475 eV	219.54 nm	f=0.0103						
<S**2>=0.000										
235 -> 250	-0.12419									
236 -> 250	0.10623									
239 -> 250	0.24706									
241 -> 250	0.26408									
242 -> 250	0.21509									
244 -> 252	0.12123									
245 -> 250	0.16356									
245 -> 252	0.10951									
246 -> 250	-0.18639									
246 -> 252	-0.18796									
246 -> 254	0.10300									
249 -> 274	-0.10724									
Excited State 36:	Singlet-A	5.6590 eV	219.09 nm	f=0.0034						
<S**2>=0.000										
249 -> 268	0.12119									
249 -> 269	0.17693									
249 -> 270	0.13480									
249 -> 272	0.48950									
249 -> 274	0.22659									
249 -> 275	-0.17853									
249 -> 277	0.10924									
249 -> 278	0.20896									
249 -> 280	0.10770									
Excited State 37:	Singlet-A	5.6768 eV	218.41 nm	f=0.0032						
<S**2>=0.000										
249 -> 267	-0.10784									
249 -> 268	0.23238									
249 -> 270	0.42642									
249 -> 271	-0.18195									
249 -> 272	-0.13277									
249 -> 274	-0.24628									
249 -> 275	-0.14931									
249 -> 276	0.11617									
249 -> 278	-0.11037									
249 -> 280	0.11677									

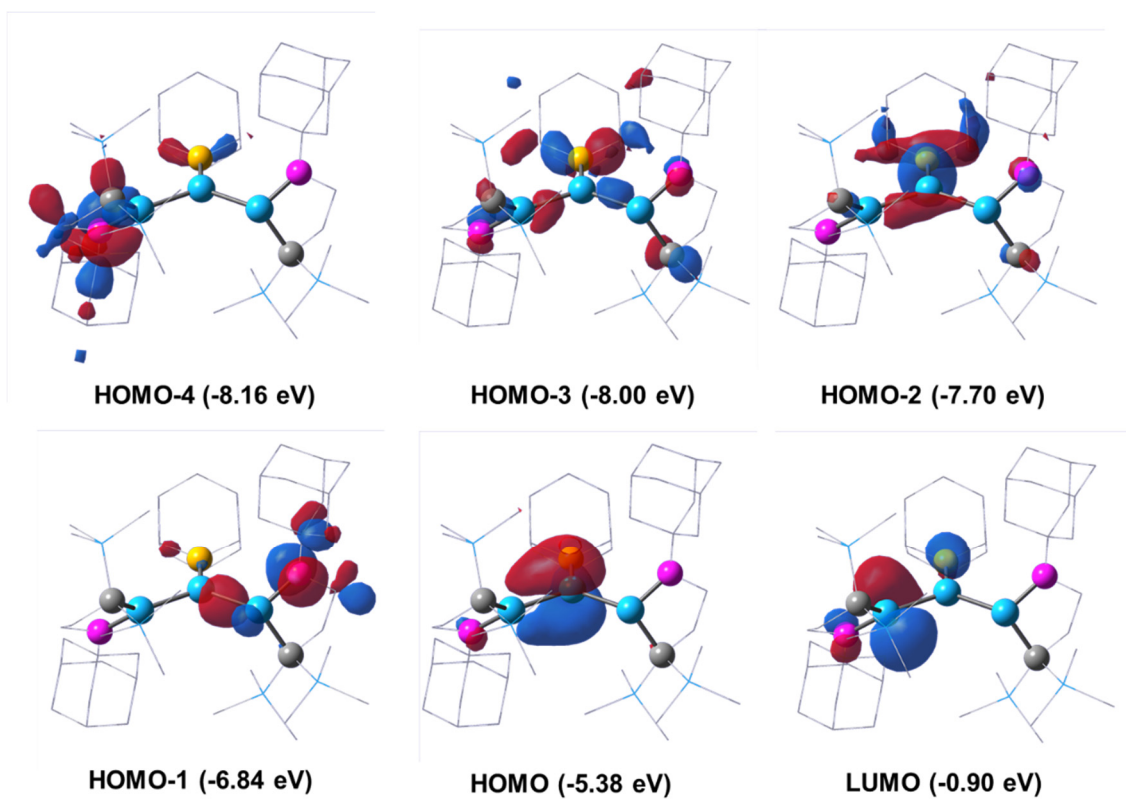


Figure S36. Selected Kohn-Sham Orbitals of $2_{H,opt}$ calculated at the M06-2X/B2//B3PW91-D3/B1 level of theory (isosurface value $0.05 \text{ e}^- \text{ a.u.}^{-3}$).

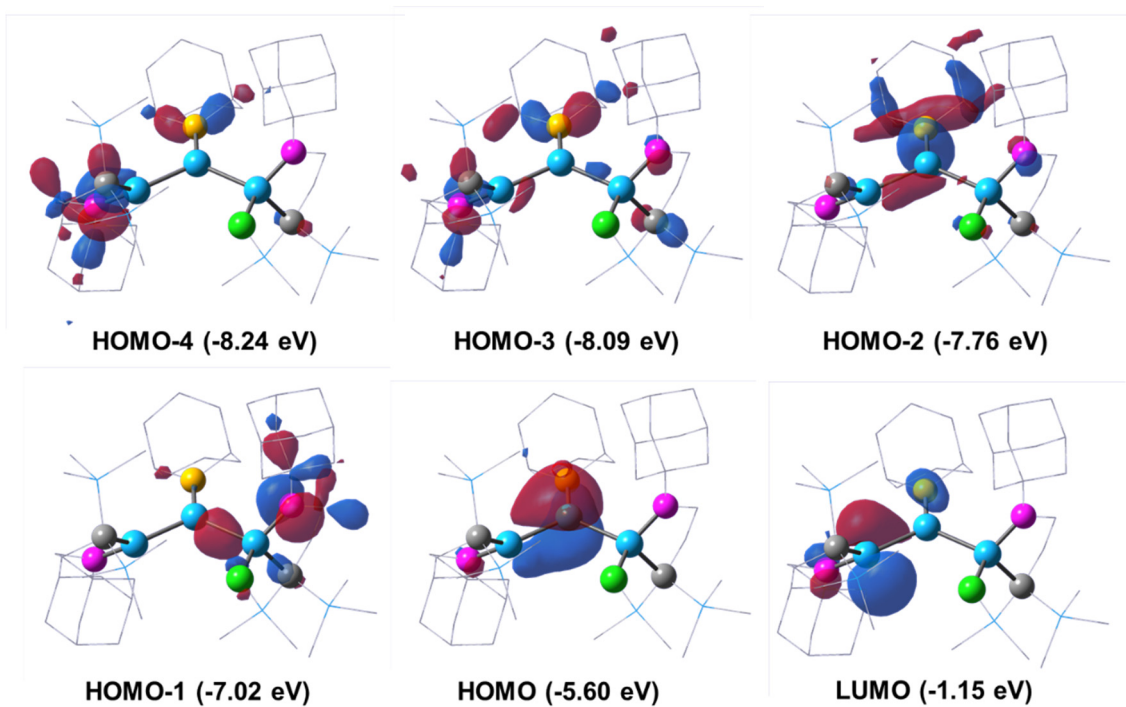


Figure S37. Selected Kohn-Sham Orbitals of $2_{Cl,opt}$ calculated at the M06-2X/B2//B3PW91-D3/B1 level of theory (isosurface value $0.05 \text{ e}^- \text{ a.u.}^{-3}$).

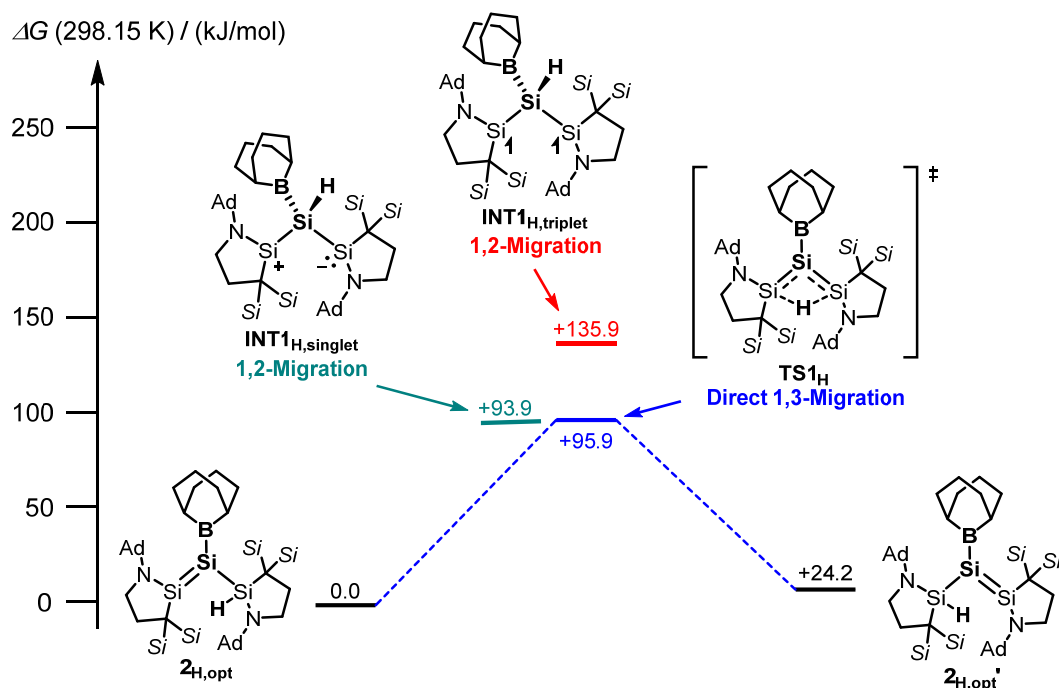


Figure S38. Possible transition states and intermediates in the reversible 1,3-hydride migration of **2_{H,opt}** calculated at the (U)B3PW91-D3/6-31G(d) level of theory.

The Gibbs energy of the 1,2-migrated isomer of **2_{H,opt}** (**INT1_{H,singlet}**) was 93.9 kJ mol⁻¹ which was comparable to that of **TS1_H**. Thus, the possibility of competing 1,2-migration cannot be ruled out, though unlikely.

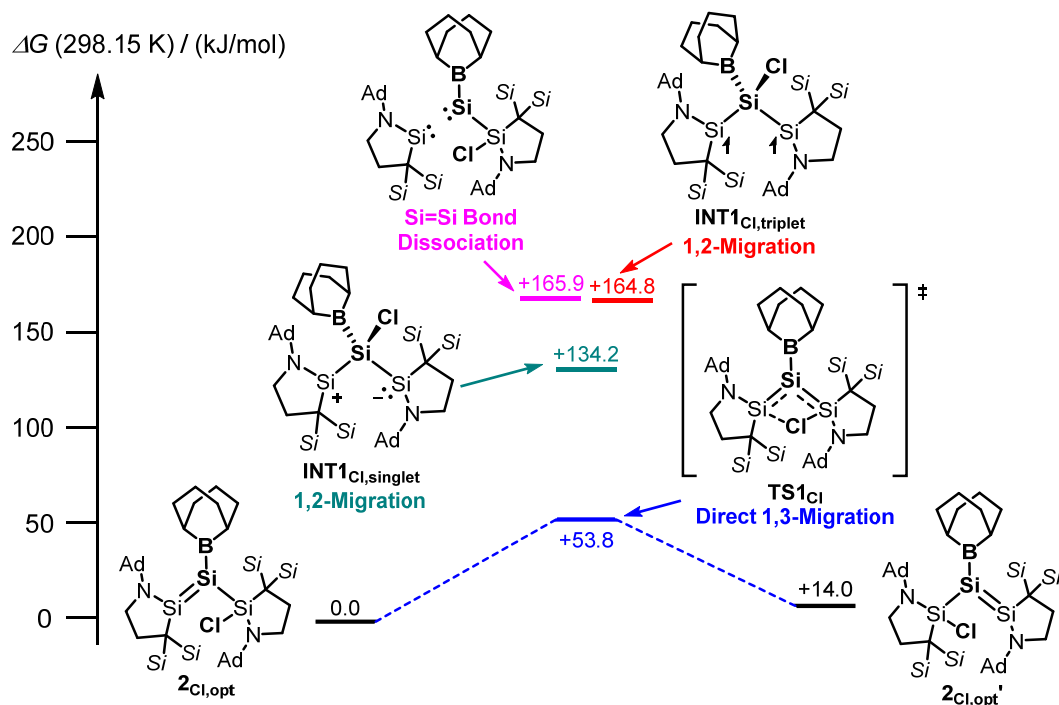


Figure S39. Possible transition states and intermediates in the reversible 1,3-chloride migration of **2_{Cl,opt}** calculated at the (U)B3PW91-D3/6-31G(d) level of theory.

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