Electronic Supplementary Information

Interconversion between a planar 1,3-dichlorobicyclo[1.1.0]tetrasilane

and a (chloro)(chlorosilyl)cyclotrisilene

*Takumi Nukazawa and Takeaki Iwamoto**

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

Email: takeaki.iwamoto@tohoku.ac.jp

Contents

1. NMR spectra

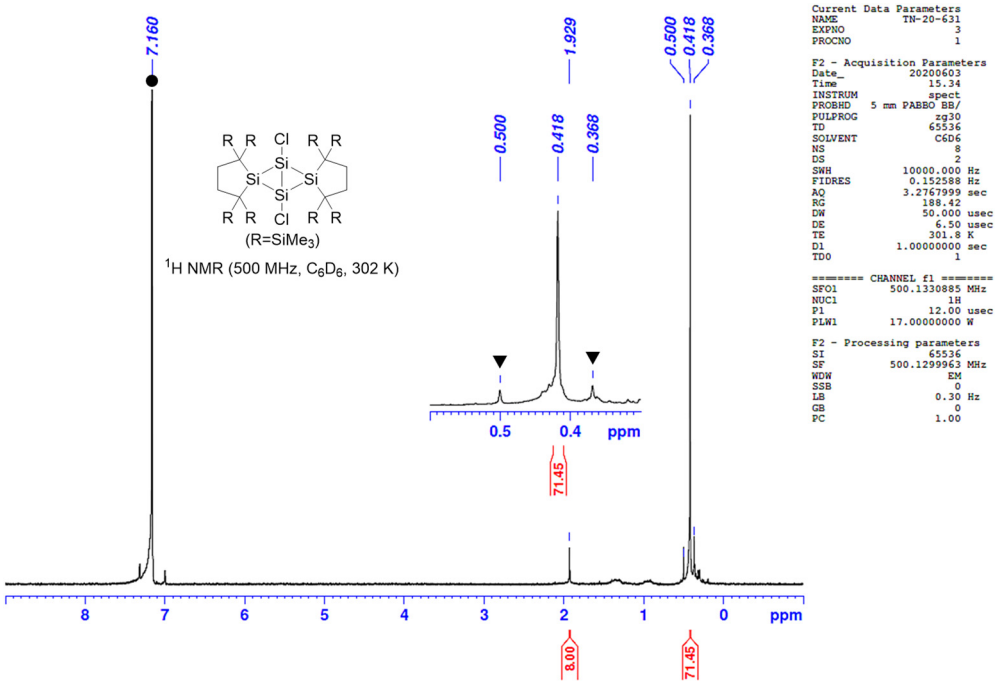


Figure S1. ^{1}H NMR spectrum of **4** in C_6D_6 at 302 K (● = C_6HD_5, ▼ = **6**).

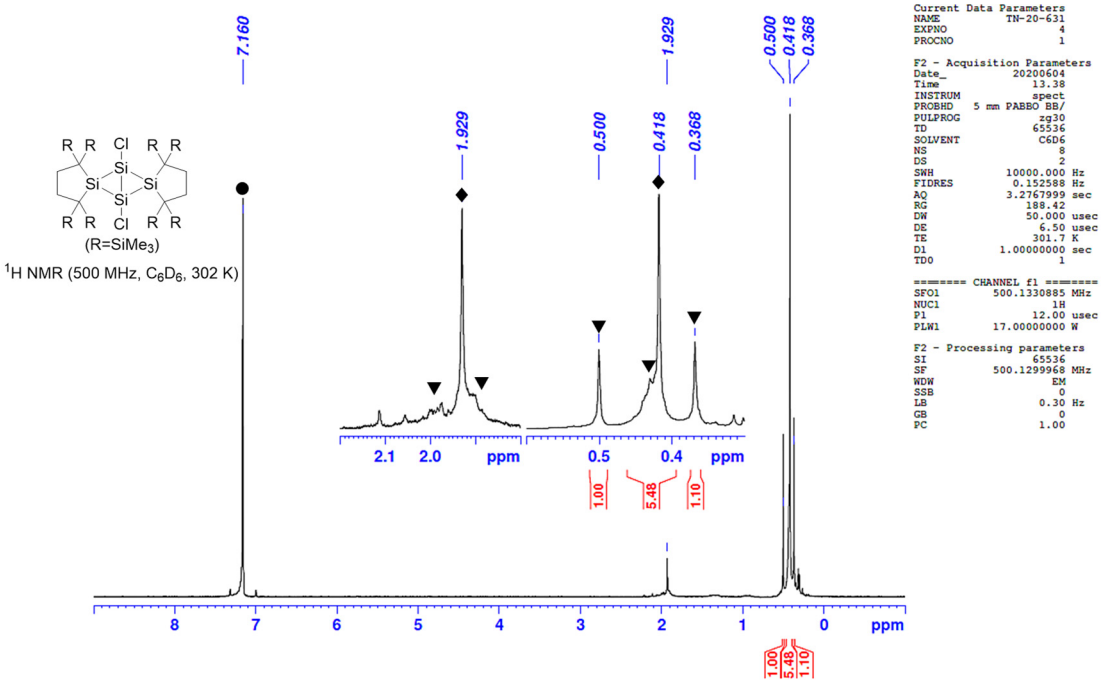


Figure S2. ^{1}H NMR spectrum of **4** in C_6D_6 at 302 K after 1 day (● = C_6HD_5, ♦ = **4**, ▼ = **6**).

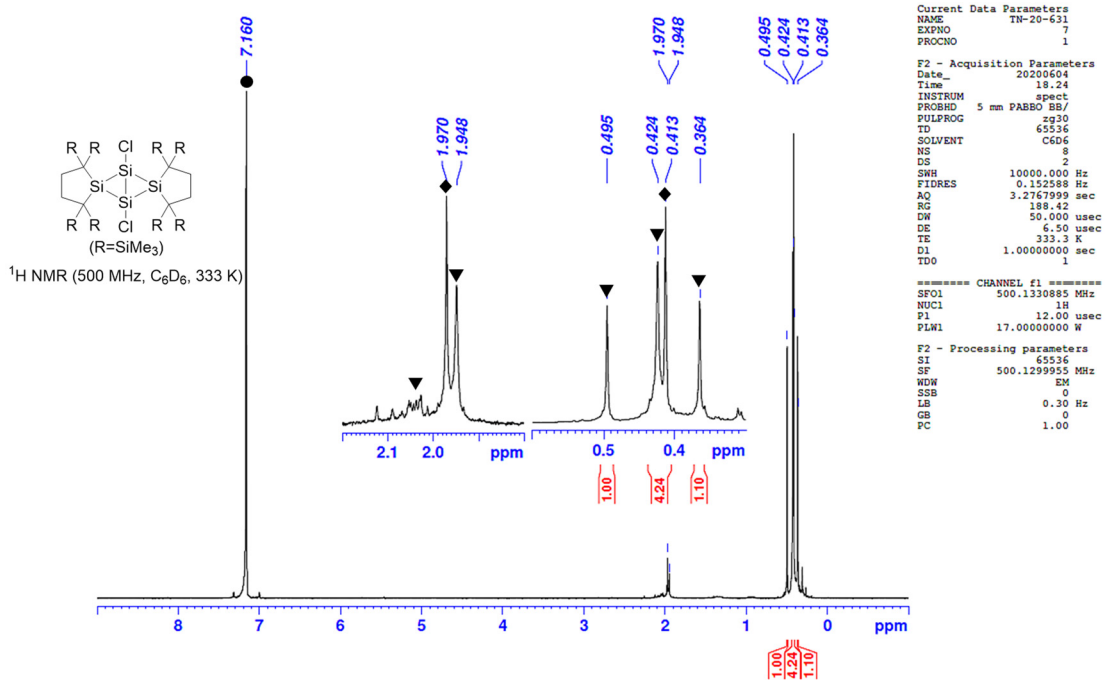


Figure S3. ^{1}H NMR spectrum of **4** in C_6D_6 at 333 K (● = C_6HD_5, ♦ = **4**, ▼ = **6**).

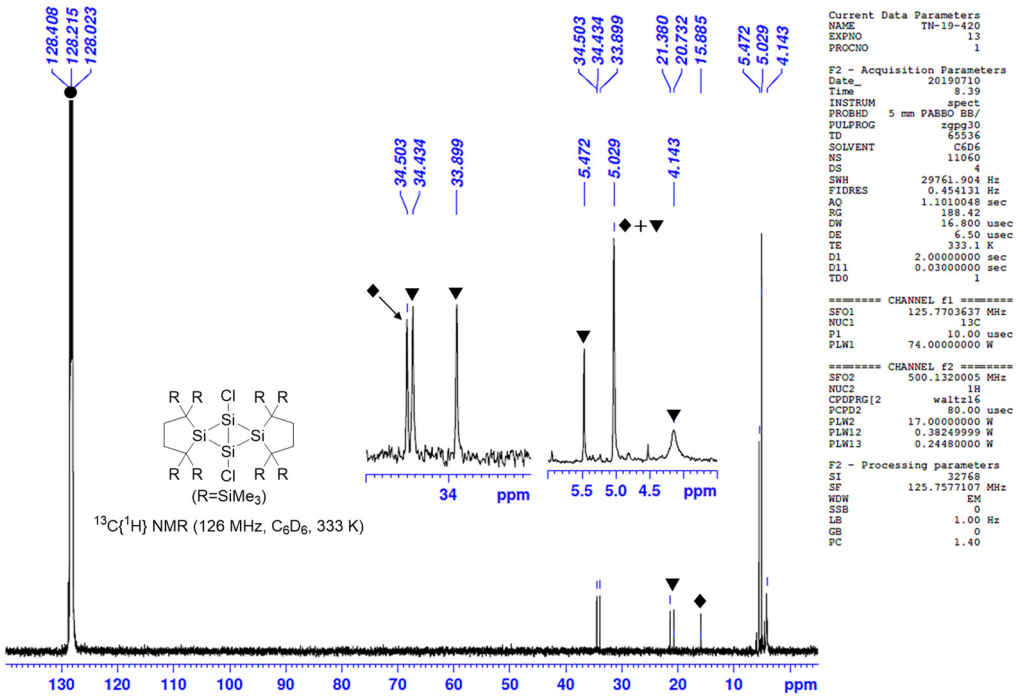


Figure S4. ^{13}C{^{1}H} NMR spectrum of **4** in C_6D_6 in 333 K (● = C_6D_6, ♦ = **4**, ▼ = **6**).

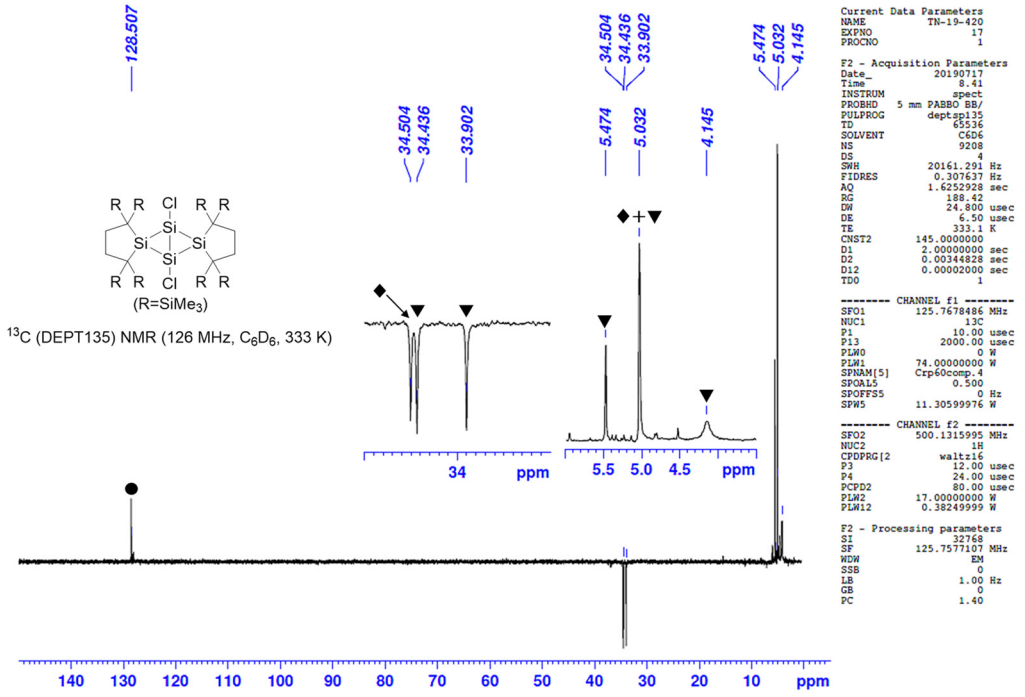


Figure S5. ^{13}C (DEPT135) NMR spectrum of **4** in C_6D_6 at 333 K (● = C_6D_6, ♦ = **4**, ▼ = **6**).

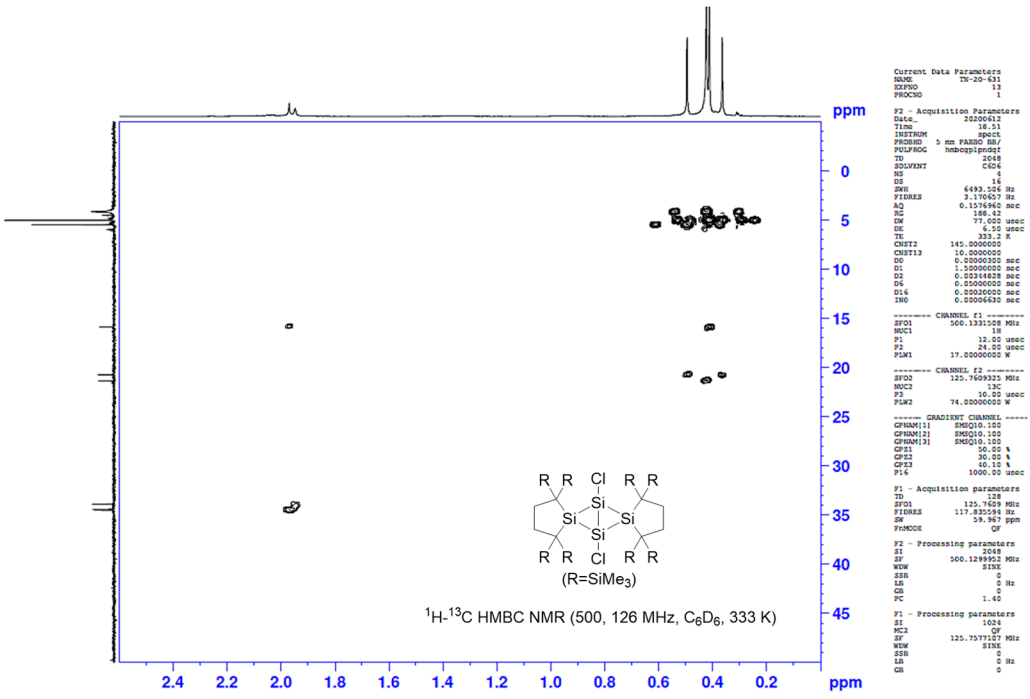


Figure S6. ^{1}H-^{13}C HMBC NMR spectrum of **4** in C_6D_6 at 333 K.

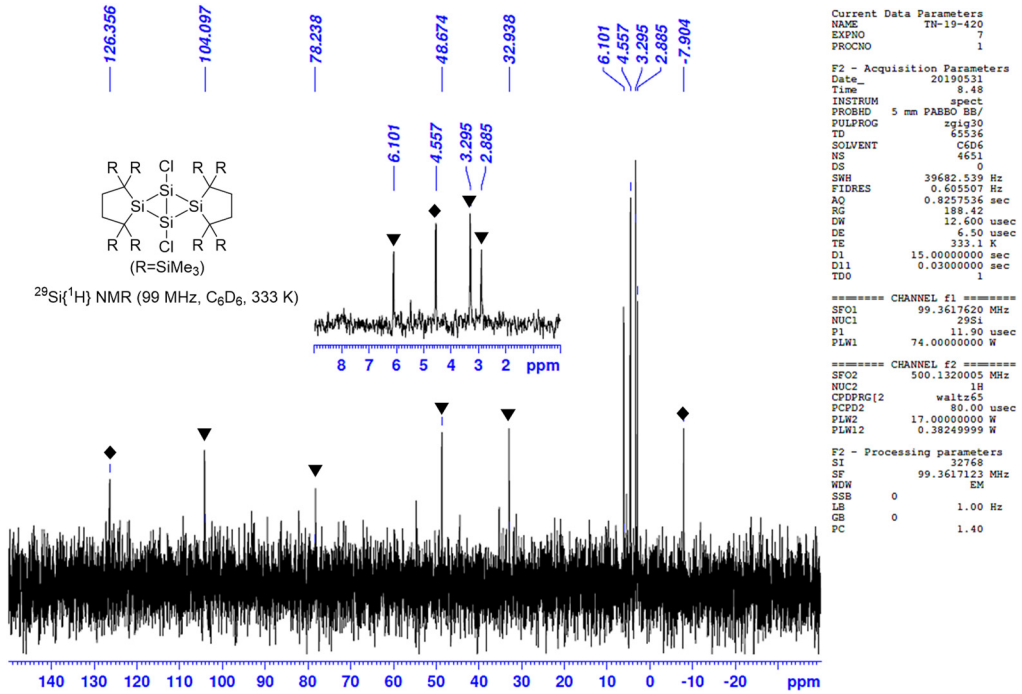


Figure S7. $^{29}Si\{^{1}H\}$ NMR spectrum of **4** in C_6D_6 at 333 K. (♦ = **4**, ▼ = **6**).

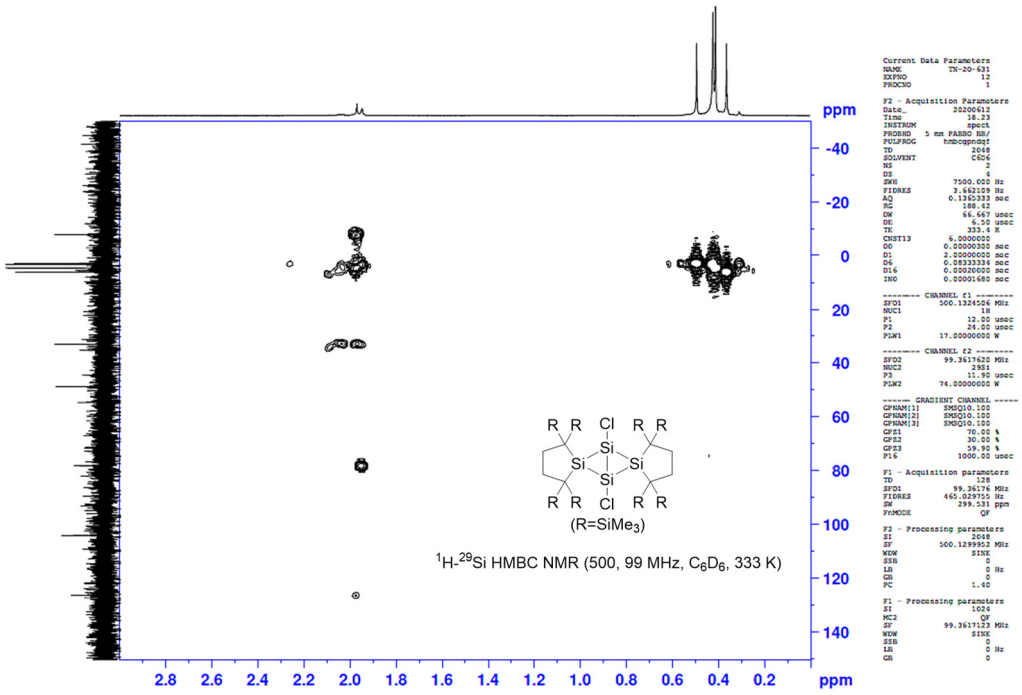


Figure S8. ^{1}H-^{29}Si HMBC NMR spectrum of **4** in C_6D_6 at 333 K.

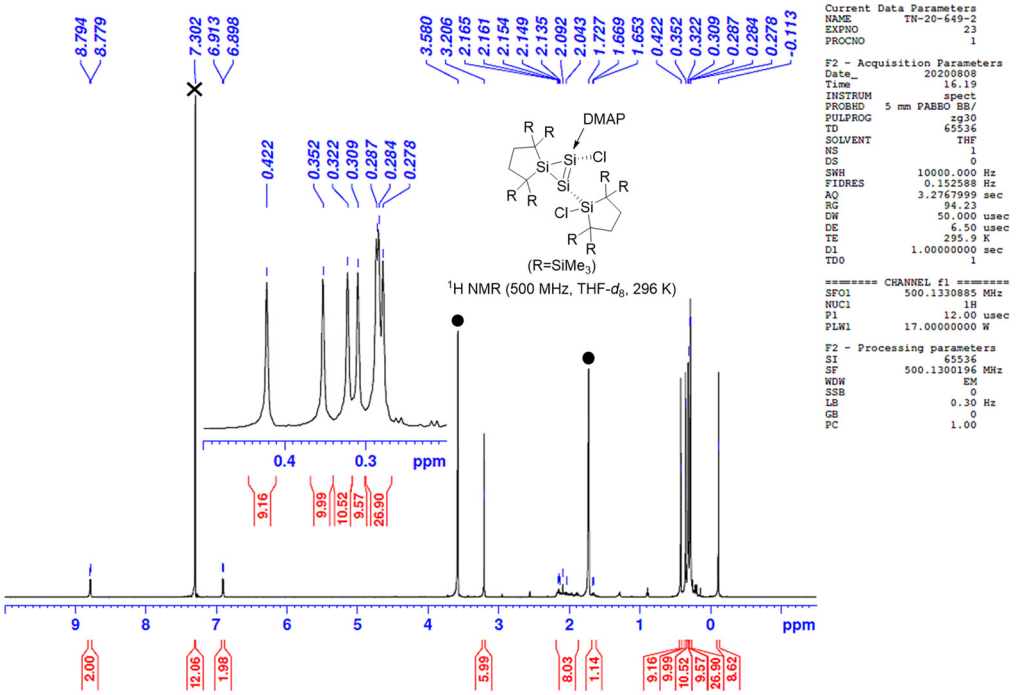


Figure S9. ^{1}H NMR spectrum of **7**·(benzene)$_2$ in THF-d_8 at 296 K (● = THF-d_8, × = benzene).

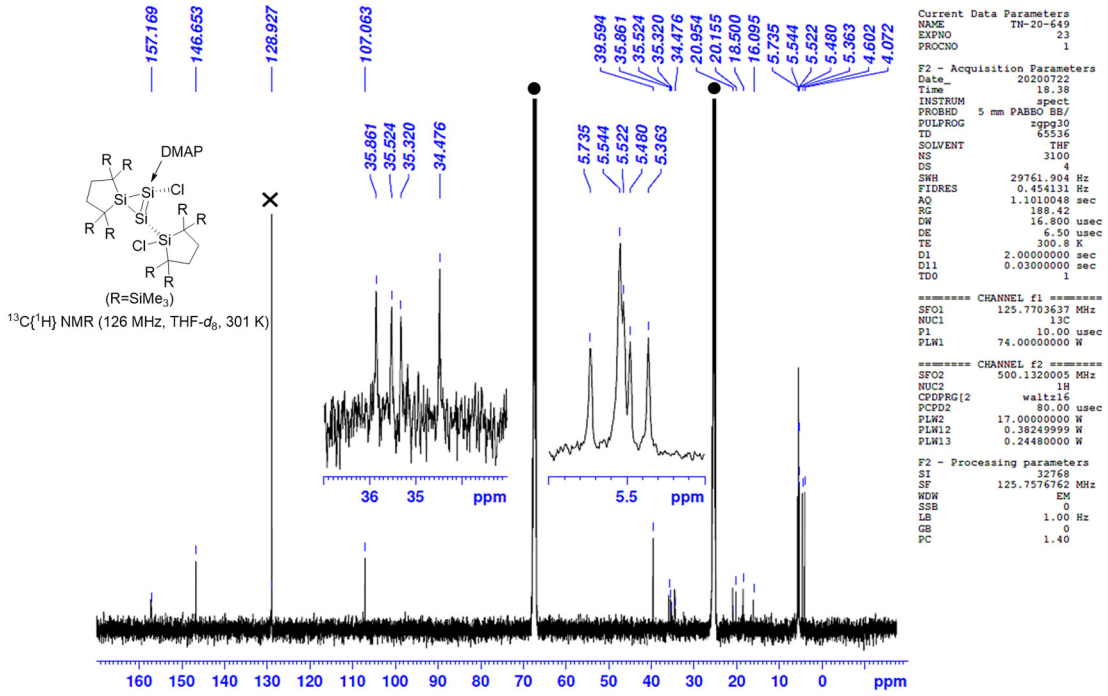


Figure S10. ^{13}C{^{1}H} NMR spectrum of **7**·(benzene)$_2$ in THF-d_8 in 301 K (● = THF-d_8, × = benzene).

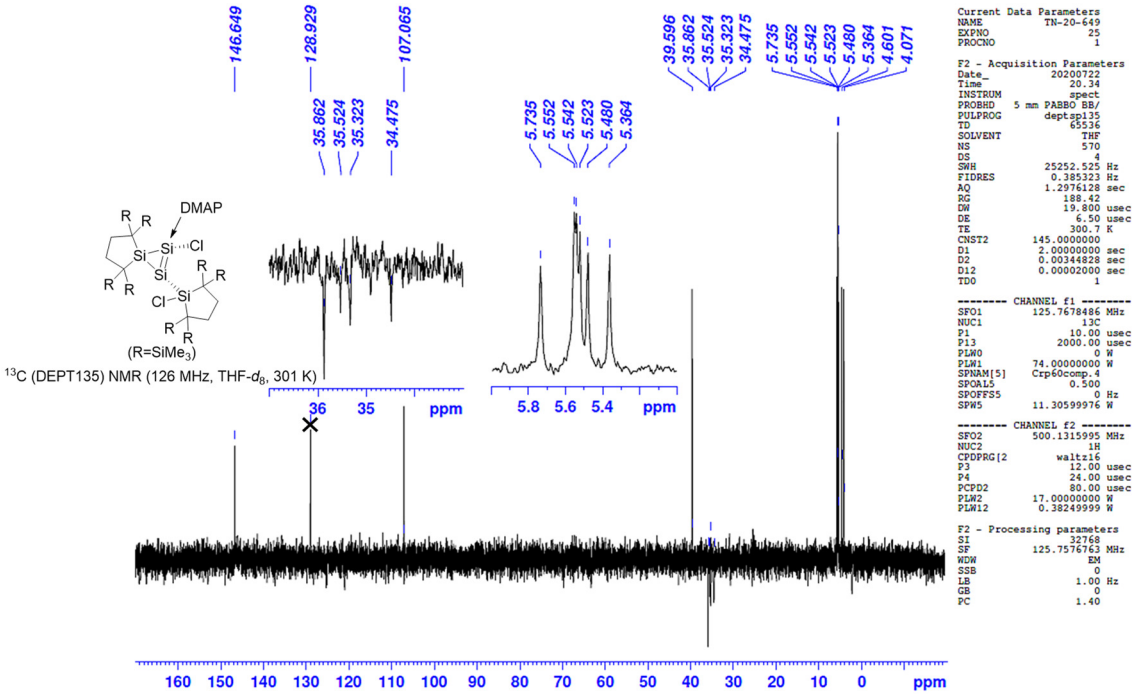


Figure S11. ^{13}C (DEPT135) NMR spectrum of **7**·(benzene)$_2$ in THF-d_8 at 301 K (× = benzene).

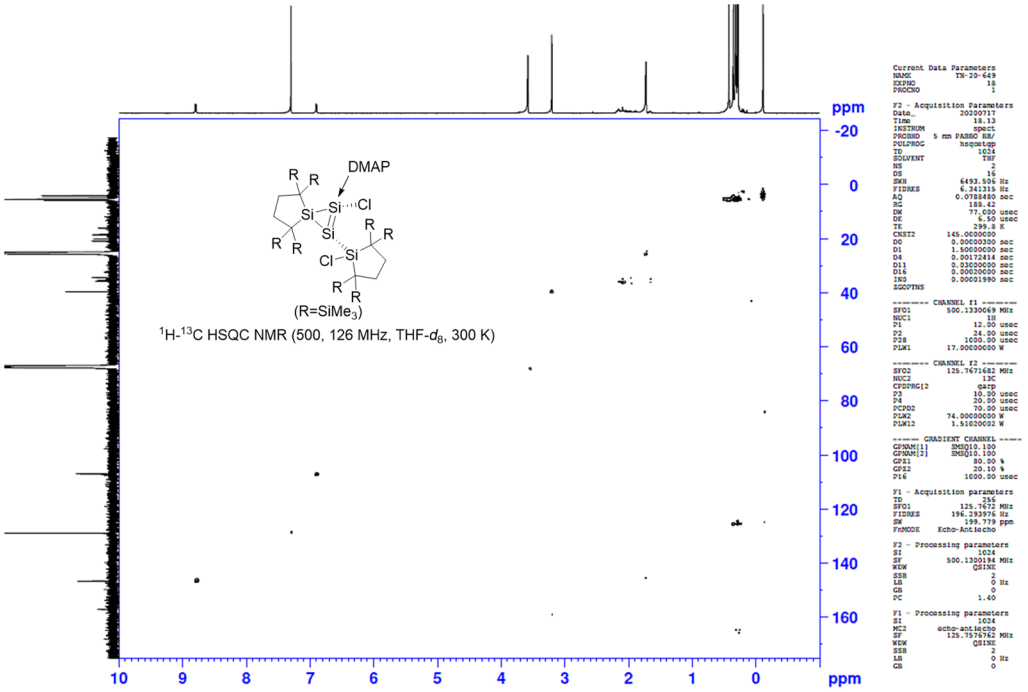


Figure S12. ^{1}H-^{13}C HSQC NMR spectrum of **7**·(benzene)$_2$ in THF-d_8 at 300 K.

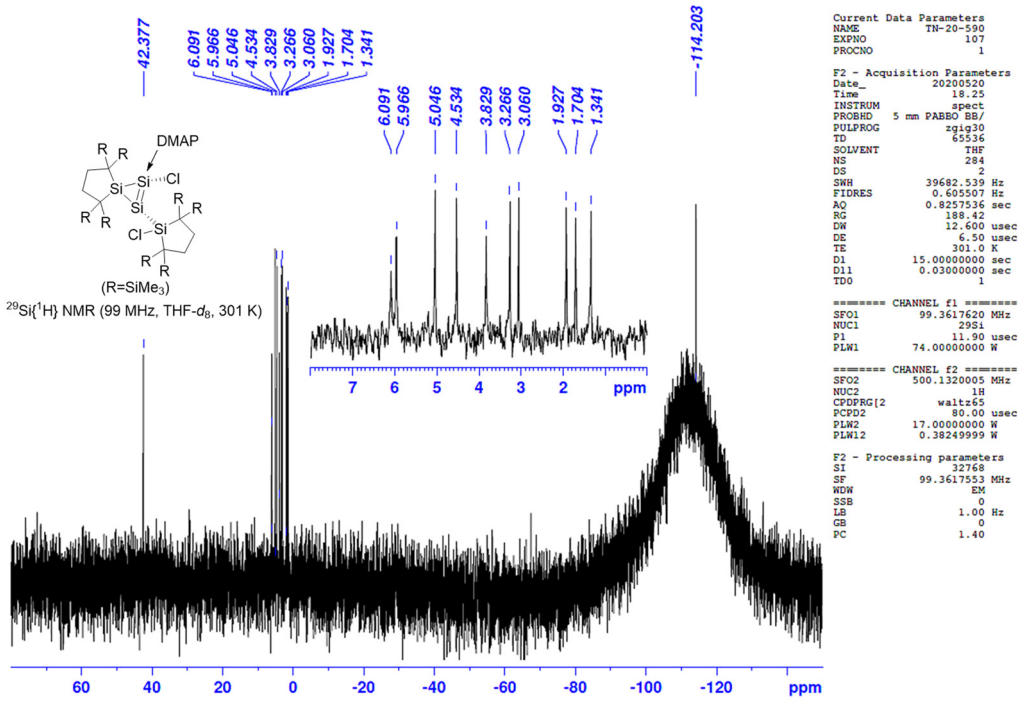


Figure S13. $^{29}Si\{^{1}H\}$ NMR spectrum of **7**·(benzene)$_2$ in THF-d_8 at 301 K.

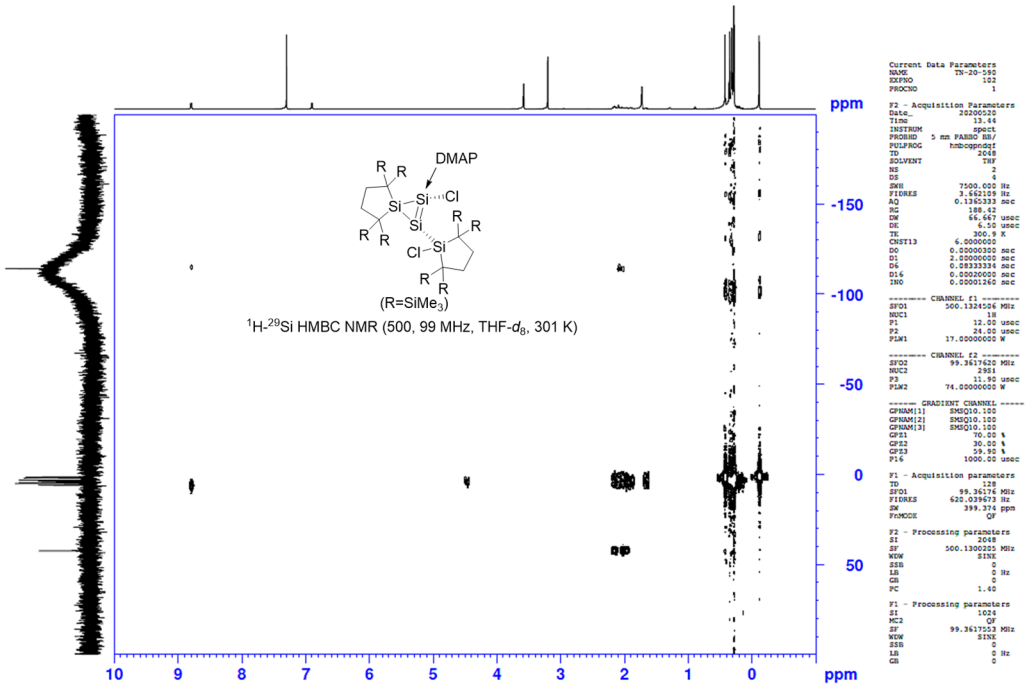


Figure S14. ^{1}H-^{29}Si HMBC NMR spectrum of **7**·(benzene)$_2$ in THF-d_8 at 301 K.

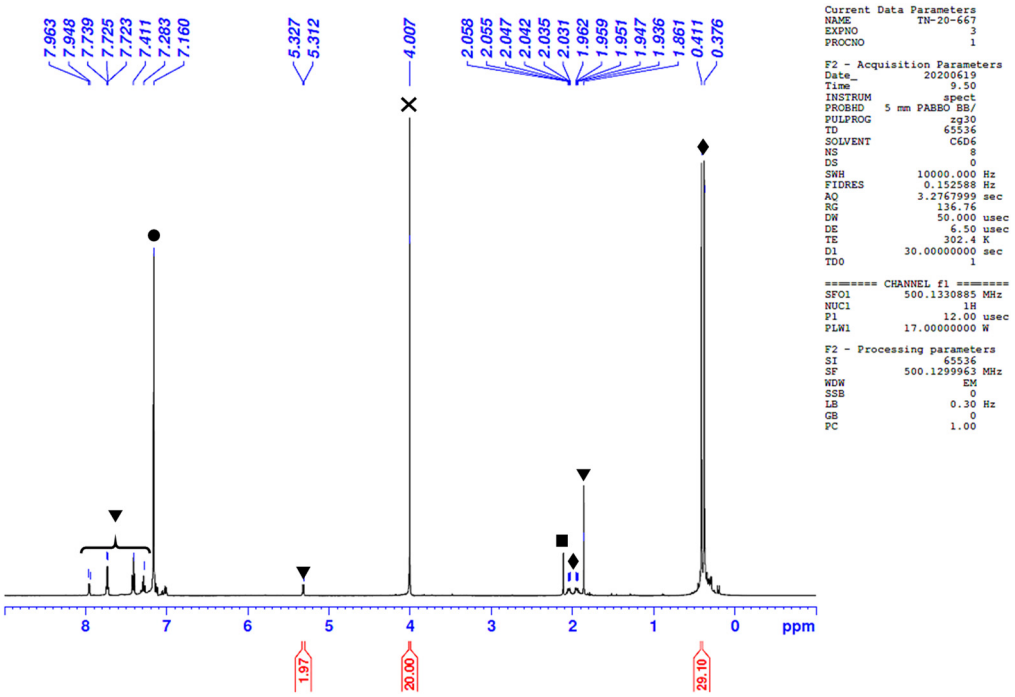


Figure S15. ^{1}H NMR spectrum of the reaction mixture of **7** with CCl_4 in the presence of BPh_3 in C_6D_6 at 302 K (● = C_6HD_5, ▼ = BPh_3•DMAP, ♦ = **3**, × = ferrocene, ■ = toluene).

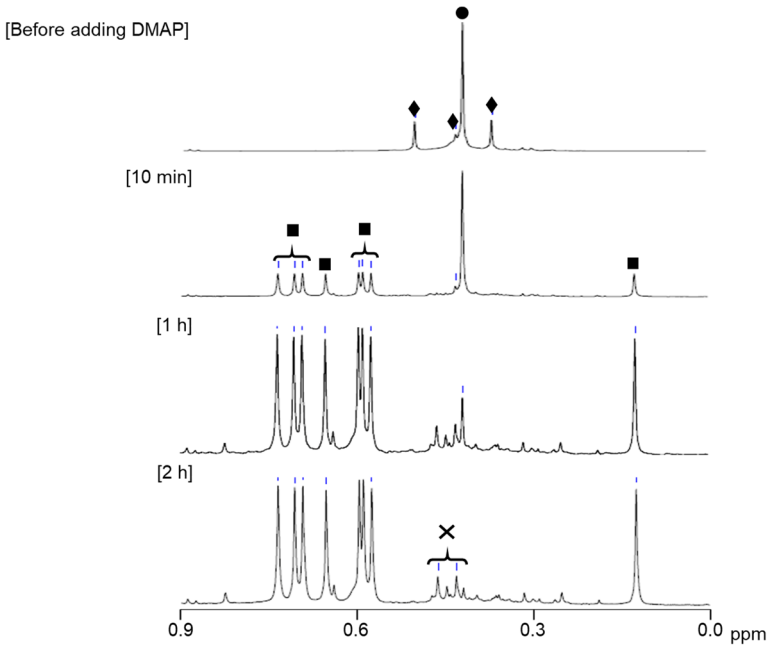


Figure S16. ^{1}H NMR spectra (TMS region) of the reaction mixture of **4**+**6** with DMAP in C_6D_6 at room temperature (● = **4**, ♦ = **6**, ■ = **7**, × = by products).

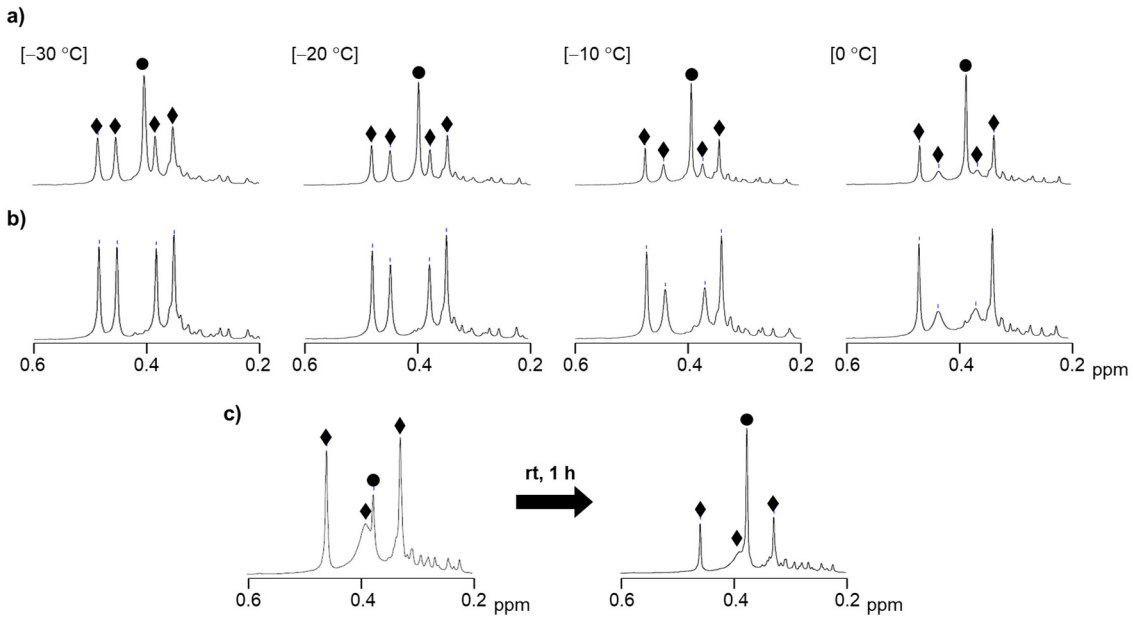


Figure S17. ^{1}H NMR spectra (TMS region) of a) the equilibrium mixture of **4**+**6** and b) the reaction mixture of **7** with BPh_3 in toluene-d_8 at variable temperature. c) ^{1}H NMR spectra (TMS region) of the reaction mixture of **7** with BPh_3 (left: just after warming up, right: after 1 hour) in toluene-d_8 at room temperature (● = **4**, ♦ = **6**).

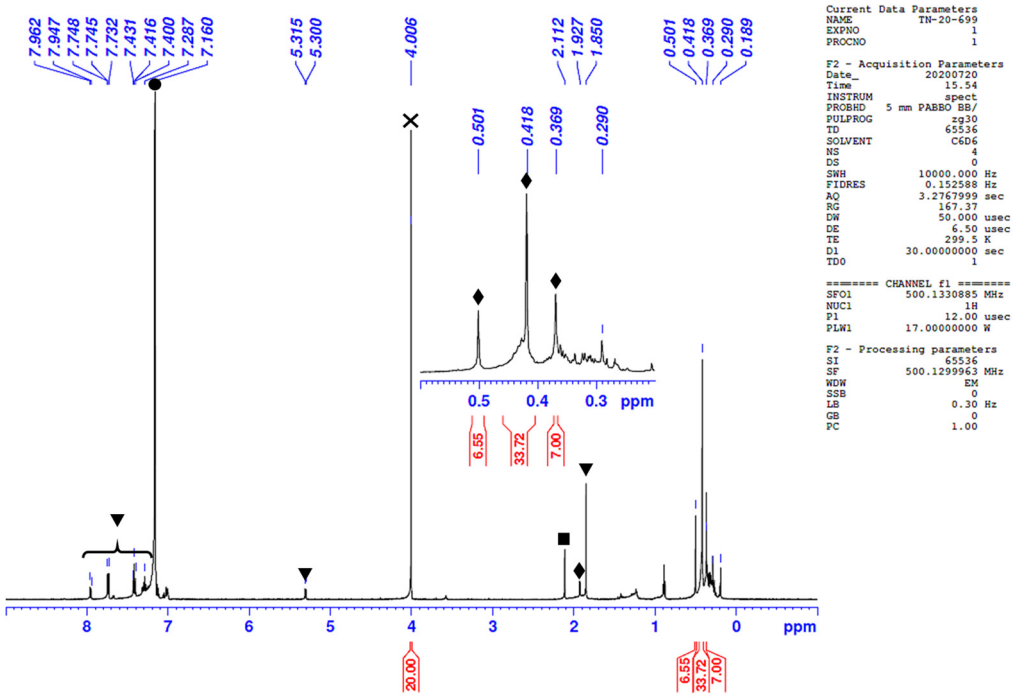


Figure S18. ^{1}H NMR spectrum of the reaction mixture of **7** with BPh_3 in C_6D_6 at 300 K (● = C_6HD_5, ▼ = BPh_3•DMAP, ♦ = **4+6**, × = ferrocene, ■ = toluene).

2. X-Ray diffraction analysis

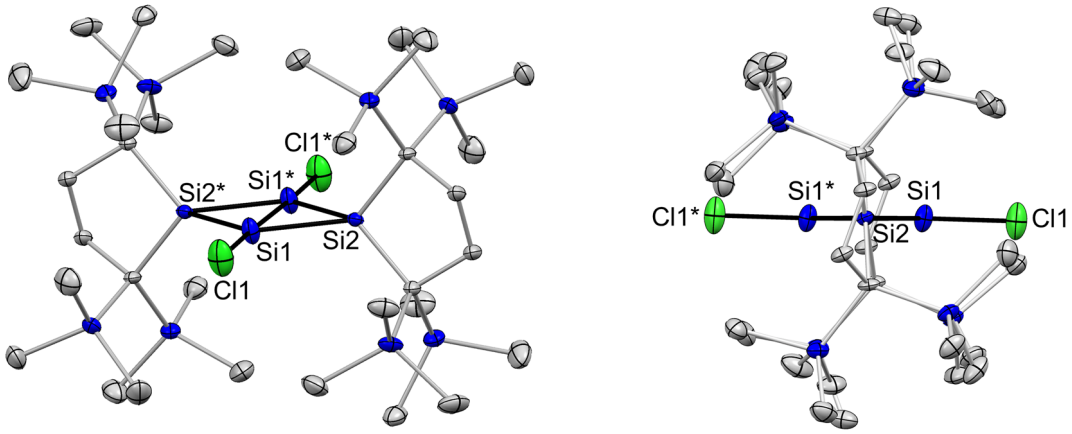


Figure S19. ORTEP drawings of **4**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms were omitted for clarity.

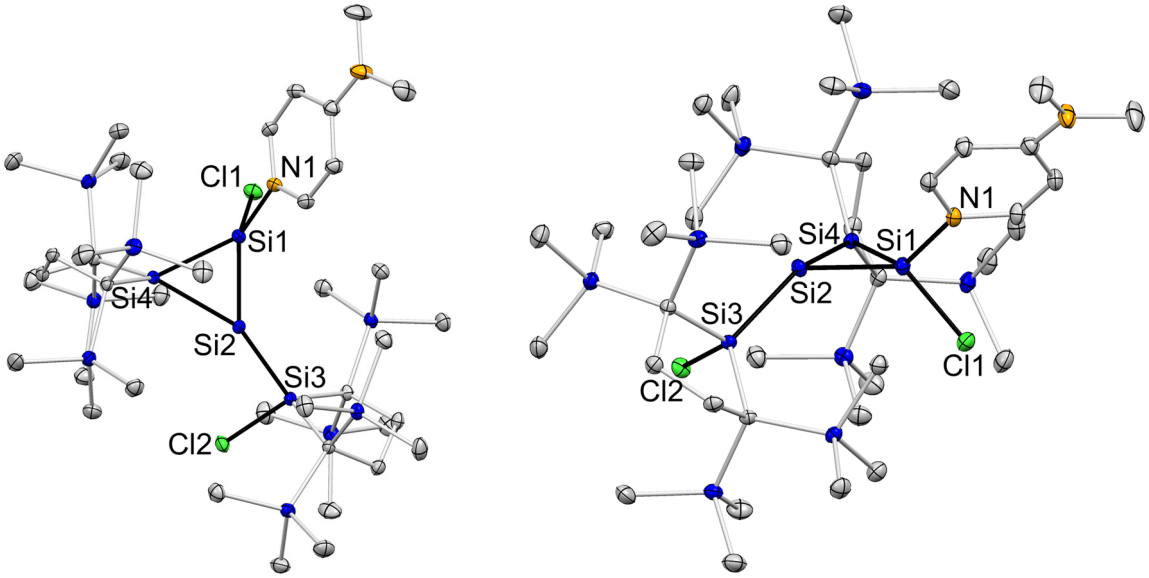


Figure S20. ORTEP drawings of **7**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms were omitted for clarity.

3. UV-vis absorption spectrum

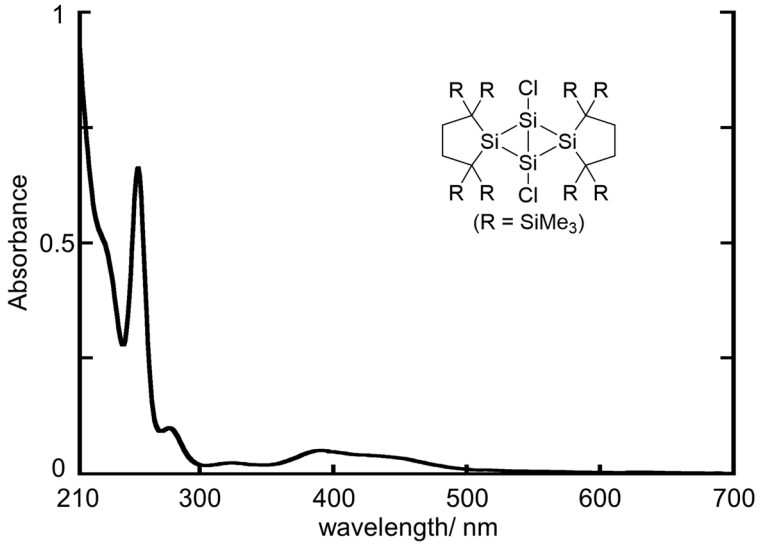


Figure S21. UV-Vis absorption spectrum of the equilibrium mixture of **4** and **6** in hexane at room temperature.

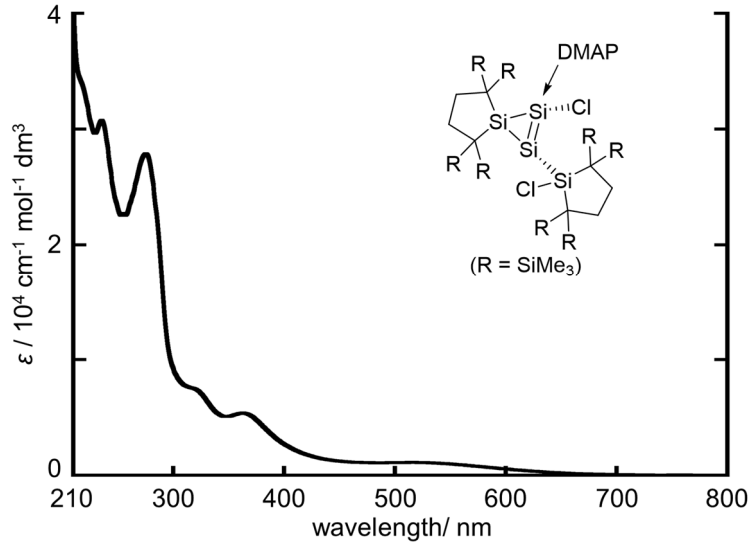


Figure S22. UV-Vis absorption spectrum of **7**·(benzene)$_2$ dissolved in hexane at room temperature.

Table S1. UV-vis Absorption Bands of **7**·(benzene)$_2$

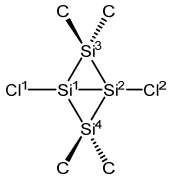
Absorption maximum / nm	ε / 10^4 cm^{-1} mol^{-1} dm^3
519	1,100
362	5,400
315 sh[a)]	7,600
275[b)]	28,000
236[b)]	31,000

a) sh = shoulder, b) the absorption bands of benzene involved the crystals of **7** should be overlapped.

4. Computational study

The atomic coordinates and energies of all equilibrium and transition structures are summarized in the file named "optimized_structures.xyz". The selected structural parameters of $\mathbf{4}_{opt}$, $\mathbf{4'}_{opt}$, $\mathbf{4''}_{opt}$, and $\mathbf{7}_{opt}$ are summarized in Table S2 and S3. Frontier Kohn-Sham orbitals and their energy levels of $\mathbf{4}_{opt}$ were shown in Figure S23. Isotropic chemical shielding tensors were calculated at the GIAO/M06L/6-311+G(2df,p) level of theory (Table S4 and S5). Absolute isotropic shielding tensors of ^{29}Si nucleus in tetramethylsilane were calculated to be 361.4 (GIAO/M06L/6-311+G(2df,p)). Excitation energies and oscillator strengths of $\mathbf{4}_{opt}$ and $\mathbf{6}_{opt}$ were calculated at the B3LYP/6-311G(d) level of theory (Tables S6 and S7). A possible reaction route between $\mathbf{4}_{opt}$ and $\mathbf{6}_{opt}$ calculated at the B3LYP-D3/B1 (basis B1: 6-311G(d) [core Si4Cl2], 6-31G(d) [carbon atoms in silacyclopentane rings], 3-21G* [others]) were shown in Figure S25.

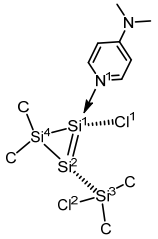
Table S2. Selected Structural Parameters of **4**, $\mathbf{4}_{opt}$, $\mathbf{4'}_{opt}$ and $\mathbf{4''}_{opt}$



Cpd	distance/Å							angle/°					$E^{b,c}$	$\Delta E^{c,e}$	note
	Si^1–Si^2	Si^1–Si^3	Si^1–Si^4	Si^2–Si^3	Si^2–Si^4	Si^1-Cl^1	Si^2-Cl^2	Cl^1-Si^1-Si^2	Cl^2-Si^2-Si^1	Si^1-Si^3-Si^2	Si^1-Si^4-Si^2	Si^3-Si^1-Si^2-Si^4	[ΔG]^{b,d}	[$\Delta\Delta G$]^{d,e}	(job name)
XRD															
4	2.581(2)	2.3249(17)	2.3361(17)	2.3361(17)	2.3249(17)	2.0690(18)	2.0690(18)	178.27(11)	178.27(11)	67.26(6)	67.26(6)	180.00	-	-	tn08a
DFT[a]															
$\mathbf{4}_{opt}$	2.58285	2.31823	2.33167	2.33167	2.31823	2.10926	2.10926	178.572	178.572	67.485	67.485	180.000	-5662.014735	0.0	TN74a
													[-5662.116181]	[0.0]	
$\mathbf{4'}_{opt}$	2.89287	2.39590	2.41124	2.45983	2.43874	2.14902	2.14000	109.187	113.787	73.121	73.233	-174.450	-5662.015099	-1.0	TN77_120
													[-5662.115585]	[1.6]	
$\mathbf{4''}_{opt}$	2.44338	2.32745	2.33875	2.33875	2.32745	2.10637	2.10637	160.679	160.679	63.152	63.152	-149.598	-5662.009600	13.5	TN84a
													[-5662.114172]	[5.3]	

a. optimized at the B3LYP-D3/6-311G(d) level of theory. b. in hartree. c. Zero-point vibrational energy corrections were included. d. at 298.15 K. e. in kJ mol^{-1}.

Table S3. Selected Structural Parameters of $\mathbf{7}_{opt}$



Cpd	distance/Å							angle/°			note
	Si^1–Si^2	Si^1–Si^4	Si^2–Si^3	Si^2–Si^4	Si^1-Cl^1	Si^3-Cl^2	Si^1-N^1	Si^1-Si^2-Si^4	Si^2-Si^1-Si^4	Si^1-Si^4-Si^2	(job name)
XRD											
7	2.2145(7)	2.2986(7)	2.3791(7)	2.3893(7)	2.1107(6)	2.1317(6)	1.8789(15)	59.76(2)	63.90(2)	66.98(3)	tn49a
DFT[a]											
$\mathbf{7}_{opt}$	2.21522	2.31830	2.38969	2.40381	2.14769	2.16048	1.94002	60.087	63.995	55.919	TN89aa

a. optimized at the B3LYP-D3/6-311G(d) level of theory.

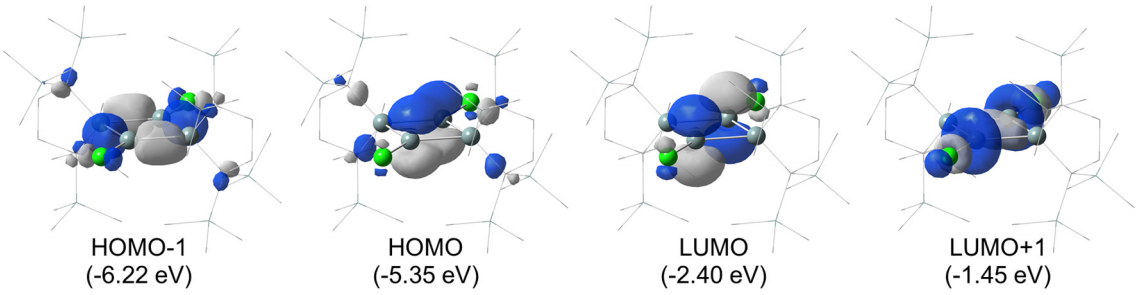


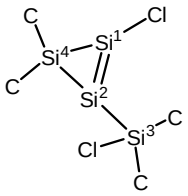
Figure S23. Frontier Kohn-Sham orbitals of $\mathbf{4}_{opt}$ at the B3LYP-D3/6-311G(d) level of theory.

Table S4. Experimental and Theoretical Isotropic ^{29}Si Chemical Shifts of **4**, $\mathbf{4}_{opt}$, $\mathbf{4'}_{opt}$ and $\mathbf{4''}_{opt}$

Compound	$SiMe_3$	Si (bridge)	Si (bridgehead)	note
4[a]	4.6	−7.9	126.4	TN420_7
$\mathbf{4}_{opt}$[b,c]	5.0 (356.4)[d]	−17.1 (378.5)	150.2 (211.2)	nmr2_TN74a
$\mathbf{4'}_{opt}$[b,c]	5.3 (356.1)[d]	139.5 (221.9)	−37.1 (398.3)	nmr2_TN77_120
		137.1 (224.3)	−49.9 (411.3)	
$\mathbf{4''}_{opt}$[b,c]	4.8 (356.6)[d]	−25.1 (386.5)	86.5 (274.8)	nmr_TN84a

a. Experimental ^{29}Si Chemical Shifts of **4** in benzene-d_6 at 333 K. b. GIAO/M06L/6-311+G(2df,p) level of theory. Absolute chemical shift for tetramethylsilane = 361.4. c. the absolute chemical shift is shown in the parentheses. d. average values.

Table S5. Experimental and Theoretical Isotropic ^{29}Si Chemical Shifts of $\mathbf{6}_{opt}$



	$SiMe_3$	Si^2=**Si^1**-Cl	**Si^2**=Si^1-Cl	Si^4 (Si_3 ring)	Si^3 (chlorosilyl)	Note
Experimental[a]	2.9, 3.3, 6.1	104.1	48.7	78.2	32.9	TN420_7
Theoretical[b,c]	4.2 (357.2)[d]	97.0 (264.4)	49.4 (311.9)	75.4 (286.0)	38.1 (323.3)	nmr2_TN82a

a. Experimental ^{29}Si Chemical Shifts of **6** in benzene-d_6 at 333 K. b. GIAO/M06L/6-311+G(2df,p) level of theory. Absolute chemical shift for tetramethylsilane = 361.4. c. the absolute chemical shift is shown in the parentheses. d. average values.

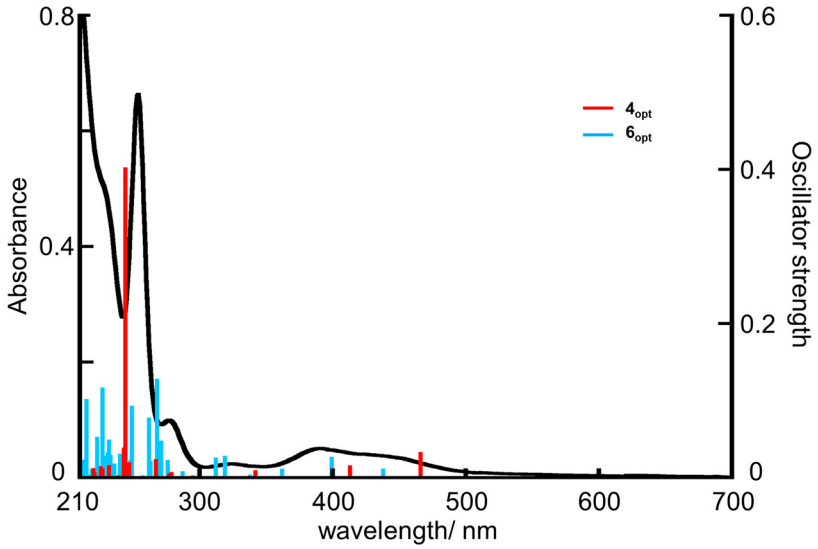


Figure S24. Experimental UV-vis absorption spectrum of the equilibrium mixture of **4** and **6** in hexane (black) and calculated band positions of $\mathbf{4}_{\mathbf{opt}}$ and $\mathbf{6}_{\mathbf{opt}}$ at the TD-B3LYP-D3/6-311G(d) level (red and blue).

Table S6. Transition Energy, Wavelength, and Oscillator Strengths of the Electronic Transition of $\mathbf{4_{opt}}$ (The 237th orbital is highest occupied orbital shown in Figure S23)

Excited State 1: Singlet-AU 2.6596 eV 466.17 nm f=0.0332
<S**2>=0.000
237 -> 238 0.67896
237 -> 239 -0.17174
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -5662.97431013
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-AG 2.8801 eV 430.48 nm f=0.0000
<S**2>=0.000
236 -> 238 0.70504

Excited State 3: Singlet-AU 3.0056 eV 412.51 nm f=0.0162
<S**2>=0.000
237 -> 238 0.16949
237 -> 239 0.67597

Excited State 4: Singlet-AU 3.6254 eV 341.99 nm f=0.0096
<S**2>=0.000
237 -> 240 0.68769

Excited State 5: Singlet-AG 3.7152 eV 333.72 nm f=0.0000
<S**2>=0.000
237 -> 241 0.70481

Excited State 6: Singlet-AG 3.8746 eV 319.99 nm f=0.0000
<S**2>=0.000
236 -> 239 0.69880

Excited State 7: Singlet-AG 4.1861 eV 296.18 nm f=0.0000
<S**2>=0.000
233 -> 238 -0.11200
235 -> 238 0.69584

Excited State 8: Singlet-AU 4.1991 eV 295.26 nm f=0.0026
<S**2>=0.000
234 -> 238 0.70535

Excited State 9: Singlet-AG 4.2735 eV 290.12 nm f=0.0000
<S**2>=0.000
233 -> 238 0.68739
235 -> 238 0.11840
236 -> 240 -0.10203

Excited State 10: Singlet-AU 4.3196 eV 287.03 nm f=0.0013
<S**2>=0.000
230 -> 238 -0.35899
231 -> 238 0.19538
232 -> 238 0.56102

Excited State 11: Singlet-AU 4.4516 eV 278.52 nm f=0.0074
<S**2>=0.000
230 -> 238 -0.30886
231 -> 238 0.49899
232 -> 238 -0.37371

Excited State 12: Singlet-AU 4.4717 eV 277.27 nm f=0.0059
<S**2>=0.000
230 -> 238 0.50949
231 -> 238 0.44481
232 -> 238 0.17234

Excited State 13: Singlet-AG 4.5559 eV 272.14 nm f=0.0000
<S**2>=0.000
229 -> 238 0.10870
233 -> 238 0.10925
236 -> 240 0.67874

Excited State 14: Singlet-AU 4.6516 eV 266.54 nm f=0.0240
<S**2>=0.000
236 -> 241 0.55902
237 -> 242 -0.42495

Excited State 15: Singlet-AG 4.6548 eV 266.36 nm f=0.0000
<S**2>=0.000
229 -> 238 0.69462
236 -> 240 -0.11101

Excited State 16: Singlet-AU 4.9319 eV 251.39 nm f=0.0005
<S**2>=0.000
228 -> 238 0.68938

Excited State 17: Singlet-AG 4.9464 eV 250.65 nm f=0.0000
<S**2>=0.000
226 -> 238 -0.10228
227 -> 238 0.68694

Excited State 18: Singlet-AU 5.0255 eV 246.71 nm f=0.0202
<S**2>=0.000
223 -> 238 0.40022
225 -> 238 0.52671
237 -> 242 0.11984

Excited State 19: Singlet-AG 5.0351 eV 246.24 nm f=0.0000
<S**2>=0.000
224 -> 238 -0.18600
226 -> 238 0.66703

Excited State 20: Singlet-AU 5.0715 eV 244.47 nm f=0.4028
<S**2>=0.000
225 -> 238 -0.25689
230 -> 240 -0.16019
236 -> 241 0.36213
237 -> 242 0.48343

Excited State 21: Singlet-AU 5.0853 eV 243.81 nm f=0.0392
<S**2>=0.000
219 -> 238 0.15226
223 -> 238 0.50704
225 -> 238 -0.37875
236 -> 241 -0.11926
237 -> 242 -0.16915

Excited State 22: Singlet-AG 5.1078 eV 242.74 nm f=0.0000
<S**2>=0.000
218 -> 238 -0.10510
221 -> 238 -0.11859
224 -> 238 0.66031
226 -> 238 0.16395

Excited State 23: Singlet-AG 5.1488 eV 240.80 nm f=0.0000
<S**2>=0.000
235 -> 239 0.69109

Excited State 24: Singlet-AU 5.1605 eV 240.26 nm f=0.0005
<S**2>=0.000
219 -> 238 -0.10107
234 -> 239 0.69475

Excited State 25: Singlet-AG 5.1750 eV 239.58 nm f=0.0000
<S**2>=0.000
218 -> 238 -0.19745
220 -> 238 -0.16010
221 -> 238 0.64258
226 -> 238 0.12372

Excited State 26: Singlet-AU 5.1898 eV 238.90 nm f=0.0031
<S**2>=0.000
219 -> 238 0.56210
222 -> 238 -0.37669

Excited State 27: Singlet-AU 5.1938 eV 238.72 nm f=0.0022
<S**2>=0.000
219 -> 238 0.33384
222 -> 238 0.56757
223 -> 238 -0.20751

Excited State 28: Singlet-AG 5.2111 eV 237.93 nm f=0.0000
<S**2>=0.000
218 -> 238 0.35523
220 -> 238 0.52265
221 -> 238 0.23219
233 -> 239 0.10324

Excited State 29: Singlet-AG 5.2177 eV 237.62 nm f=0.0000
<S**2>=0.000
220 -> 238 -0.12864
233 -> 239 0.42332
235 -> 239 0.13669
237 -> 244 -0.39387
237 -> 245 -0.29668
237 -> 246 -0.16483

Excited State 30: Singlet-AU 5.2547 eV 235.95 nm f=0.0003
<S**2>=0.000
216 -> 238 0.50300
217 -> 238 -0.45883

Excited State 31: Singlet-AG 5.2555 eV 235.91 nm f=0.0000
<S**2>=0.000
218 -> 238 0.48456
220 -> 238 -0.35848
233 -> 239 0.26227
237 -> 244 0.17618
237 -> 245 0.12631

Excited State 32: Singlet-AG 5.2592 eV 235.75 nm f=0.0000
<S**2>=0.000
218 -> 238 -0.27171
220 -> 238 0.20680
233 -> 239 0.47753
237 -> 244 0.29746
237 -> 245 0.20868
237 -> 246 0.11740

Excited State 33: Singlet-AU 5.3132 eV 233.35 nm f=0.0009
<S**2>=0.000
216 -> 238 0.45422
217 -> 238 0.51970

Excited State 34: Singlet-AU 5.3368 eV 232.32 nm f=0.0165
<S**2>=0.000
230 -> 239 -0.28837
232 -> 239 0.62008

Excited State 35: Singlet-AU 5.3509 eV 231.71 nm f=0.0007
<S**2>=0.000
230 -> 239 -0.13789
231 -> 239 0.67966

Excited State 36: Singlet-AU 5.4520 eV 227.41 nm f=0.0120
<S**2>=0.000
230 -> 239 0.30533
232 -> 239 0.13337
237 -> 243 0.60911

Excited State 37: Singlet-AG 5.4572 eV 227.19 nm f=0.0000
<S**2>=0.000
215 -> 238 0.69902

Excited State 38: Singlet-AU 5.4674 eV 226.77 nm f=0.0147
<S**2>=0.000
230 -> 239 0.53689
231 -> 239 0.15871
232 -> 239 0.24274
237 -> 243 -0.32682

Excited State 39: Singlet-AU 5.5349 eV 224.00 nm f=0.0018
<S**2>=0.000
214 -> 238 0.63465
219 -> 238 -0.10541
237 -> 247 -0.22362

Excited State 40: Singlet-AG 5.5714 eV 222.54 nm f=0.0000
<S**2>=0.000
237 -> 244 -0.44605
237 -> 245 0.46699
237 -> 246 0.22863
237 -> 251 -0.11452

Excited State 41: Singlet-AG 5.5938 eV 221.65 nm f=0.0000
<S**2>=0.000
229 -> 239 -0.20244
235 -> 240 0.40339
236 -> 242 0.52537

Excited State 42: Singlet-AU 5.6071 eV 221.12 nm f=0.0073
<S**2>=0.000
214 -> 238 0.20388
234 -> 240 0.39718
237 -> 247 0.49449
237 -> 250 0.12358

Excited State 43: Singlet-AG 5.6117 eV 220.94 nm f=0.0000
<S**2>=0.000
229 -> 239 0.66507
235 -> 240 0.16996
236 -> 242 0.12094

Excited State 44: Singlet-AU 5.6269 eV 220.34 nm f=0.0124
<S**2>=0.000
214 -> 238 -0.11933
234 -> 240 0.57325
237 -> 247 -0.36564

Excited State 45: Singlet-AG 5.6392 eV 219.86 nm f=0.0000
<S**2>=0.000
235 -> 240 0.54533
236 -> 242 -0.43265

Excited State 46: Singlet-AG 5.6920 eV 217.82 nm f=0.0000
<S**2>=0.000
213 -> 238 0.69754

Excited State 47: Singlet-AU 5.7024 eV 217.43 nm f=0.0012
<S**2>=0.000
212 -> 238 0.69660

Excited State 48: Singlet-AG 5.7406 eV 215.98 nm f=0.0000
<S**2>=0.000
233 -> 240 -0.45825
234 -> 241 0.52326

Table S7. Transition Energy, Wavelength, and Oscillator Strengths of the Electronic Transition of $\mathbf{6_{opt}}$ (The 237th orbital is highest occupied orbital)

Excited State 1: Singlet-A 2.8294 eV 438.21 nm f=0.0119
<S**2>=0.000
235 -> 238 -0.10313
237 -> 238 0.55576
237 -> 239 0.41018
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -5662.96653789
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.1085 eV 398.86 nm f=0.0270
<S**2>=0.000
235 -> 239 0.10704
236 -> 238 -0.11310
237 -> 238 -0.37316
237 -> 239 0.55405

Excited State 3: Singlet-A 3.4281 eV 361.67 nm f=0.0118
<S**2>=0.000
235 -> 238 -0.12710
236 -> 238 0.66975
237 -> 240 0.11911

Excited State 4: Singlet-A 3.6728 eV 337.57 nm f=0.0041
<S**2>=0.000
236 -> 238 -0.11450
236 -> 239 -0.21754
237 -> 240 0.64817

Excited State 5: Singlet-A 3.8813 eV 319.44 nm f=0.0282
<S**2>=0.000
235 -> 238 -0.47416
236 -> 238 -0.10104
236 -> 239 0.49811

Excited State 6: Singlet-A 3.9716 eV 312.17 nm f=0.0262
<S**2>=0.000
235 -> 238 0.44981
235 -> 239 -0.25459
236 -> 239 0.39936
237 -> 238 0.11617
237 -> 240 0.17884

Excited State 7: Singlet-A 4.3211 eV 286.92 nm f=0.0086
<S**2>=0.000
235 -> 239 0.13699
237 -> 241 0.68537

Excited State 8: Singlet-A 4.4902 eV 276.12 nm f=0.0230
<S**2>=0.000
232 -> 238 -0.11710
235 -> 239 -0.43612
236 -> 240 0.48258
237 -> 241 0.10130

Excited State 9: Singlet-A 4.5790 eV 270.77 nm f=0.0479
<S**2>=0.000
232 -> 238 0.12873
234 -> 238 0.59681
235 -> 239 0.13107
236 -> 240 0.28444

Excited State 10: Singlet-A 4.6190 eV 268.42 nm f=0.1284
<S**2>=0.000
231 -> 238 -0.15323
232 -> 238 -0.29016
234 -> 238 0.36315
235 -> 239 -0.27410
235 -> 240 0.15939
236 -> 240 -0.32784
236 -> 241 -0.11324

Excited State 11: Singlet-A 4.7169 eV 262.85 nm f=0.0219
<S**2>=0.000
232 -> 238 0.16718
233 -> 238 0.65947
235 -> 239 -0.10812

Excited State 12: Singlet-A 4.7404 eV 261.55 nm f=0.0779
<S**2>=0.000
232 -> 238 0.58426
233 -> 238 -0.22881
235 -> 239 -0.20115
236 -> 240 -0.11054
236 -> 241 -0.13784

Excited State 13: Singlet-A 4.8290 eV 256.75 nm f=0.0029
<S**2>=0.000
231 -> 238 0.66840
235 -> 239 -0.11868
236 -> 241 -0.12109

Excited State 14: Singlet-A 4.9788 eV 249.02 nm f=0.0933
<S**2>=0.000
229 -> 238 0.11948
230 -> 238 -0.31436
234 -> 239 -0.14263
235 -> 240 0.55196
236 -> 240 0.11793
237 -> 243 0.10112

Excited State 15: Singlet-A 4.9925 eV 248.34 nm f=0.0229
<S**2>=0.000
230 -> 238 0.58306
234 -> 239 0.14760
235 -> 240 0.31559

Excited State 16: Singlet-A 4.9980 eV 248.07 nm f=0.0014
<S**2>=0.000
230 -> 238 -0.19593
234 -> 239 0.67251

Excited State 17: Singlet-A 5.0894 eV 243.61 nm f=0.0030
<S**2>=0.000
229 -> 238 0.11075
233 -> 239 0.68518

Excited State 18: Singlet-A 5.1050 eV 242.87 nm f=0.0006
<S**2>=0.000
229 -> 238 0.59390
230 -> 238 0.11099
232 -> 239 -0.32523

Excited State 19: Singlet-A 5.1132 eV 242.48 nm f=0.0027
<S**2>=0.000
229 -> 238 0.31238
232 -> 239 0.61292

Excited State 20: Singlet-A 5.1707 eV 239.78 nm f=0.0312
<S**2>=0.000
231 -> 239 0.67103
236 -> 241 0.15682

Excited State 21: Singlet-A 5.2568 eV 235.85 nm f=0.0182
<S**2>=0.000
236 -> 241 -0.17062
237 -> 242 0.42620
237 -> 243 0.40154
237 -> 244 -0.14640
237 -> 245 0.18943
237 -> 246 -0.16629

Excited State 22: Singlet-A 5.3215 eV 232.99 nm f=0.0294
<S**2>=0.000
224 -> 238 0.11823
226 -> 238 -0.19520
227 -> 238 0.20345
228 -> 238 0.54467
236 -> 241 -0.25899

Excited State 23: Singlet-A 5.3579 eV 231.40 nm f=0.0493
<S**2>=0.000
222 -> 238 -0.13098
226 -> 238 0.17550
227 -> 238 -0.33953

228 -> 238 0.39113
230 -> 239 0.16730
236 -> 241 0.30798

Excited State 24: Singlet-A 5.3723 eV 230.78 nm f=0.0327
<S**2>=0.000
225 -> 238 0.24705
227 -> 238 0.43905
230 -> 239 0.34197
236 -> 241 0.20959
237 -> 242 0.15964

Excited State 25: Singlet-A 5.3798 eV 230.46 nm f=0.0175
<S**2>=0.000
225 -> 238 -0.24750
226 -> 238 -0.10062
227 -> 238 -0.18094
229 -> 239 -0.11187
230 -> 239 0.52751
236 -> 241 -0.21771

Excited State 26: Singlet-A 5.4182 eV 228.83 nm f=0.0225
<S**2>=0.000
225 -> 238 0.44183
226 -> 238 0.15461
227 -> 238 -0.10278
230 -> 239 0.17462
236 -> 241 -0.15071
237 -> 242 -0.29685
237 -> 243 0.20069
237 -> 245 -0.13121

Excited State 27: Singlet-A 5.4355 eV 228.10 nm f=0.0282
<S**2>=0.000
225 -> 238 -0.33763
226 -> 238 0.43156
227 -> 238 0.28293
230 -> 239 0.10945
237 -> 242 -0.15740
237 -> 243 0.18101
237 -> 244 -0.10193

Excited State 28: Singlet-A 5.4482 eV 227.57 nm f=0.1172
<S**2>=0.000
225 -> 238 0.12299
226 -> 238 0.40380
229 -> 239 -0.21172
236 -> 241 -0.17410
237 -> 242 0.20221
237 -> 243 -0.30213
237 -> 244 0.19641

Excited State 29: Singlet-A 5.4948 eV 225.64 nm f=0.0120
<S**2>=0.000
223 -> 238 0.26757
229 -> 239 0.57807
234 -> 240 0.18565
237 -> 243 -0.10711

Excited State 30: Singlet-A 5.5149 eV 224.82 nm f=0.0159
<S**2>=0.000
222 -> 238 -0.18300
223 -> 238 0.44787
224 -> 238 0.38222
226 -> 238 -0.11551
228 -> 238 -0.11574
229 -> 239 -0.15239
234 -> 240 -0.17387

Excited State 31: Singlet-A 5.5304 eV 224.19 nm f=0.0152
<S**2>=0.000
222 -> 238 -0.10745
223 -> 238 -0.36817
224 -> 238 0.51736
225 -> 238 -0.10285
229 -> 239 0.10611
234 -> 240 0.13521

Excited State 32: Singlet-A 5.5370 eV 223.92 nm f=0.0529
<S**2>=0.000
223 -> 238 0.13264
229 -> 239 -0.21542
234 -> 240 0.62294

Excited State 33: Singlet-A 5.5728 eV 222.48 nm f=0.0008
<S**2>=0.000
220 -> 238 -0.24675
221 -> 238 0.50277
222 -> 238 -0.34434
224 -> 238 -0.13720

Excited State 34: Singlet-A 5.5845 eV 222.02 nm f=0.0096
<S**2>=0.000
232 -> 240 -0.12341
235 -> 241 -0.11700
237 -> 243 0.31238
237 -> 244 0.44435
237 -> 246 0.29082
237 -> 248 0.17765

Excited State 35: Singlet-A 5.5998 eV 221.41 nm f=0.0016
<S**2>=0.000
220 -> 238 -0.19042
221 -> 238 0.29492
222 -> 238 0.53253
223 -> 238 0.15381
224 -> 238 0.16191

Excited State 36: Singlet-A 5.6259 eV 220.38 nm f=0.0035
<S**2>=0.000
219 -> 238 0.22338
220 -> 238 0.25045
231 -> 240 0.15327
232 -> 240 0.50023
233 -> 240 0.12924
237 -> 244 0.13905

Excited State 37: Singlet-A 5.6441 eV 219.67 nm f=0.0082
<S**2>=0.000
219 -> 238 0.61858
232 -> 240 -0.24289

Excited State 38: Singlet-A 5.6499 eV 219.45 nm f=0.0113
<S**2>=0.000
218 -> 238 -0.31698
219 -> 238 -0.13618
220 -> 238 0.46518
221 -> 238 0.27141
232 -> 240 -0.21428

Excited State 39: Singlet-A 5.6580 eV 219.13 nm f=0.0023
<S**2>=0.000
219 -> 238 -0.12110
235 -> 241 -0.21434
237 -> 242 -0.27924
237 -> 244 0.11091
237 -> 245 0.38376
237 -> 246 -0.33587
237 -> 247 0.11529
237 -> 248 0.11496
237 -> 250 0.11578

Excited State 40: Singlet-A 5.7148 eV 216.95 nm f=0.0042
<S**2>=0.000
215 -> 238 0.14424
216 -> 238 0.23376
218 -> 238 0.52346
219 -> 238 -0.12278
220 -> 238 0.23051
233 -> 240 -0.12144
237 -> 244 0.10391
237 -> 246 -0.12245

Excited State 41: Singlet-A 5.7232 eV 216.63 nm f=0.0030
<S**2>=0.000
217 -> 238 0.13852
232 -> 240 -0.19315
233 -> 240 0.61481
237 -> 246 -0.10804

Excited State 42: Singlet-A 5.7277 eV 216.46 nm f=0.0025
<S**2>=0.000

217 -> 238 -0.28535
218 -> 238 0.20137
220 -> 238 0.14849
233 -> 240 0.22360
237 -> 244 -0.26014
237 -> 245 0.26557
237 -> 246 0.32409

Excited State 43: Singlet-A 5.7377 eV 216.09 nm f=0.0006
<S**2>=0.000
215 -> 238 0.22025
217 -> 238 0.53744
237 -> 244 -0.11694
237 -> 245 0.22823
237 -> 246 0.21316

Excited State 44: Singlet-A 5.7490 eV 215.66 nm f=0.1020
<S**2>=0.000
225 -> 239 -0.13323
226 -> 239 -0.13273
228 -> 239 0.19045
235 -> 241 0.47476
237 -> 244 0.18679
237 -> 245 0.25687
237 -> 248 -0.13173

Excited State 45: Singlet-A 5.7659 eV 215.03 nm f=0.0003
<S**2>=0.000
215 -> 238 0.10807
216 -> 238 0.56521
217 -> 238 -0.15022
218 -> 238 -0.18423
220 -> 238 -0.10008
221 -> 238 -0.17573
228 -> 239 0.21036

Excited State 46: Singlet-A 5.7766 eV 214.63 nm f=0.0126
<S**2>=0.000
216 -> 238 -0.14718
218 -> 238 0.10519
228 -> 239 0.61731
231 -> 240 -0.11223
235 -> 241 -0.11925

Excited State 47: Singlet-A 5.7791 eV 214.54 nm f=0.0131
<S**2>=0.000
226 -> 239 -0.21446
227 -> 239 0.63865
235 -> 241 -0.11092

Excited State 48: Singlet-A 5.8101 eV 213.39 nm f=0.0236
<S**2>=0.000
215 -> 238 -0.13203
231 -> 240 0.61093
232 -> 240 -0.19066
237 -> 245 -0.10795

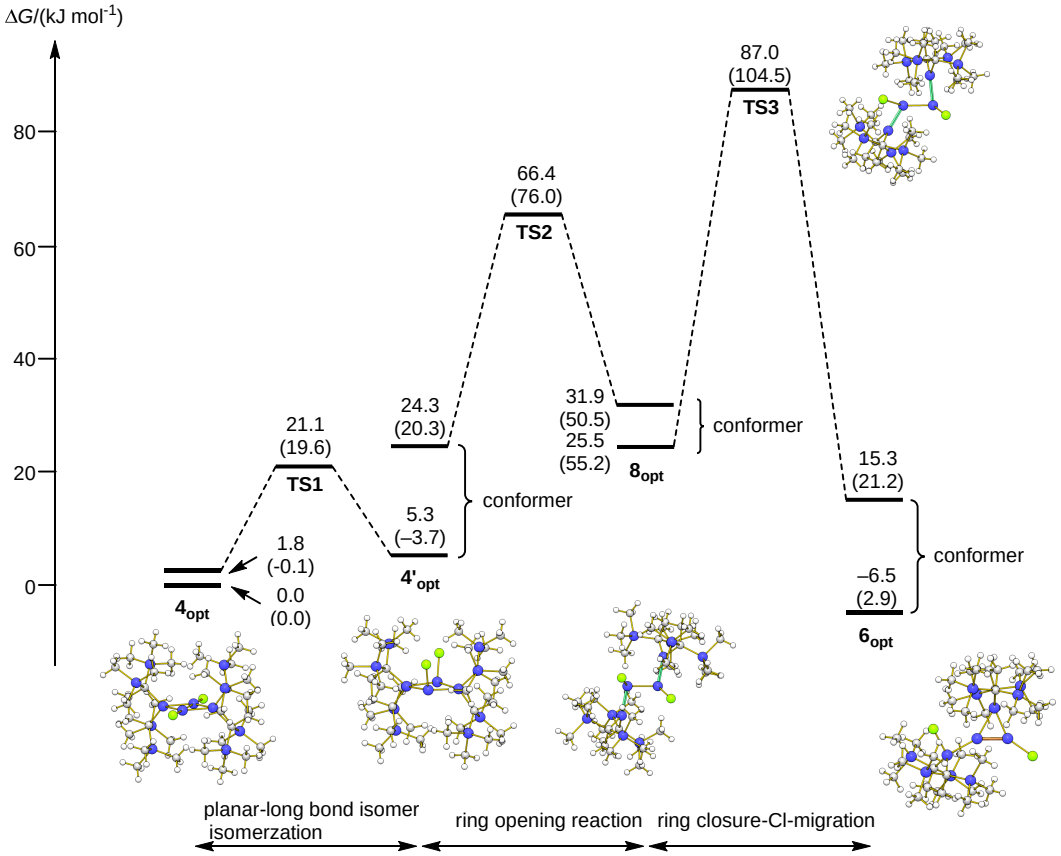


Figure S25. A possible reaction route between $\mathbf{4}_{opt}$ and $\mathbf{6}_{opt}$ calculated at the B3LYP-D3/B1 (basis B1: 6-311G(d) [core Si_4Cl_2], 6-31G(d) [carbon atoms in silacyclopentane rings], 3-21G* [others]).

5. Preliminary estimation of the thermodynamic parameters for the equilibrium between 4 and 6

In the ^{1}H NMR spectrum of a mixture of bicyclo[1.1.0]tetrasilane **4** and cyclotrisilene **6**, the signals due to four $SiMe_3$ groups (36 H) of **6** were substantially broadened and overlapped with that due to eight $SiMe_3$ groups (72H) of **4** (Figure S26). Assuming that only signals of **4** and **6** were overlapped in this region, the equilibrium constants K_{eq} (= [**6**]:[**4**]) were determined by using the integral ratio of the $SiMe_3$ signals of ^{1}H NMR spectra in C_6D_6 (Table S8). A plot of $\ln K_{eq}$ at various reciprocal temperatures are shown in Figure S27. The thermodynamic parameters for the isomerisation of **4** to **6** are calculated to be ΔH = +14.6 ± 2.9 kJ mol^{-1} and ΔS = +49 ± 9 J K^{-1} mol^{-1}.

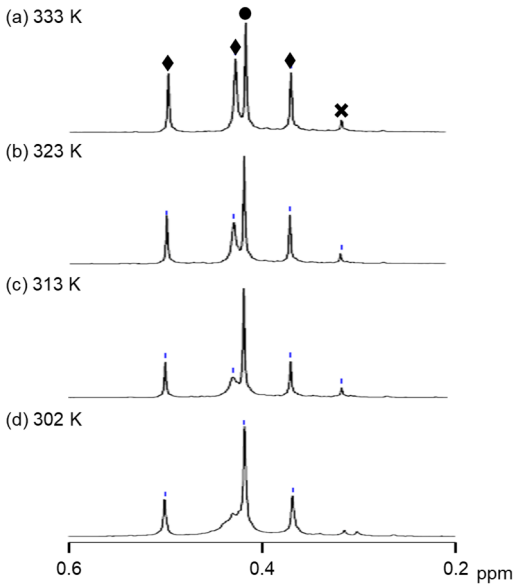


Figure S26. ^{1}H NMR spectra (TMS region) of a mixture of **4** and **6** in benzene-d_6 at (a) 333 K, (b) 323 K, (c) 313 K, and (d) 302 K (● = **4**, ♦ = **6**, × = **1**).

Table S8. The Equilibrium Constants K_{eq} (= [**6**]:[**4**]) in Benzene-d_6 at Various Temperatures

Temperature/K	Integral ratio ($SiMe_3$)		K_{eq} (=[**6**]:[**4**])[a]
	bicyclotetrasilane **4**	cyclotrisilene **6**	
333	2.11	4.00	1.90
323	2.36	4.00	1.69
313	3.24	4.00	1.23
302	3.48	4.00	1.15

a. Equilibrium constants (K_{eq}) were calculated using the integral ratio of $SiMe_3$ proton signals in the ^{1}H NMR spectrum.

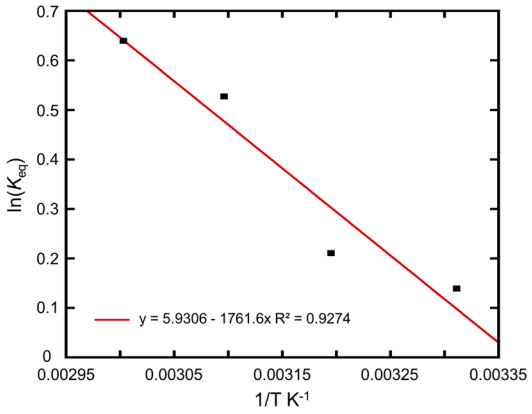


Figure S27. A plot of ln(K_{eq}) vs 1/T.