Electronic Supplementary Information

Dearomative Cycloadditions of a Silylene with Pyrazine and Quinoxaline

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1. Experimental Details

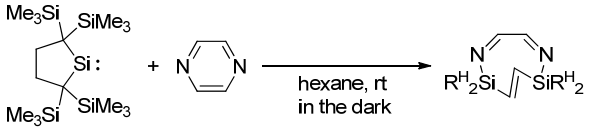
General Procedure

All reactions treating air-sensitive compounds were carried out under an inert atmosphere (N_2 or Ar) using a high-vacuum line and standard Schlenk techniques, or a glove box, as well as dry and oxygen-free solvents. NMR spectra were recorded on a Bruker Avance III 500 FT NMR spectrometer. The ^{1}H NMR chemical shifts were referenced to residual ^{1}H of the solvents; C_6D_6 (^{1}H δ 7.16).[S1] The ^{13}C and ^{29}Si NMR chemical shifts were relative to Me_4Si in ppm (δ 0.00). Sampling of air-sensitive compounds was carried out using a VAC NEXUS 100027 type glove box. Mass spectra were recorded on a Bruker Daltonics SolariX 9.4T. UV-vis spectra were recorded on a JASCO V-660 spectrometer. Measurement of melting point was measured on a SRS OptiMelt MPA100. Elemental analysis was performed with a J-SCIENCE LAB JM-11 at Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University.

Materials

Benzene and hexane were dried and deoxygenated with VAC-103991 type solvent purifiers. Benzene-d_6 (C_6D_6) was dried with molecular sieves (3A). Silylene **1** was prepared according to the published procedure.[S2] Pyrazine and quinoxaline were commercially available and used without further purification.

Reaction of Silylene 1 with Pyrazine (Synthesis of 2)



1 (= R^H_2Si:) **2**

In a screw vial (2 mL) equipped with a magnetic stir bar, pyrazine (8.0 mg, 100 μmol) and silylene **1** (55 mg, 150 μmol) were placed. Then, hexane (1 mL) was added to the vial. After stirring for 5 minutes in the dark condition, the volatiles were removed under reduced pressure. The residue was subjected to alumina column chromatography (eluent: hexane containing 2 vol% of Et_3N) and pure **2** was isolated in 50% yield (31 mg, 37 μmol).

2: purple crystals; mp. 158 °C (decomp.); ^{1}H NMR (500 MHz, C_6D_6, 297 K) δ 0.18 (s, 18H, $SiMe_3$), 0.30 (s, 18H, $SiMe_3$), 0.36 (s, 18H, $SiMe_3$), 0.39 (s, 18H, $SiMe_3$), 1.92–2.02 (m, 2H, CH_2CH_2), 2.02–2.09 (m, 2H, CH_2CH_2), 2.12–2.22 (m, 4H, CH_2CH_2), 8.54 (s, 2H, CH), 8.64 (s, 2H, CH); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 297 K) δ 3.5 ($SiMe_3$), 4.38 ($SiMe_3$), 4.43 ($SiMe_3$), 4.5 ($SiMe_3$), 11.3 (C) 11.8 (C), 33.0 (CH_2), 35.6 (CH_2), 169.3 (CH), 169.5 (CH); ^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 297 K) δ 0.2 (Si), 2.2 ($SiMe_3$), 2.9 ($SiMe_3$), 3.0 ($SiMe_3$), 3.7 ($SiMe_3$); HRMS (APCI) Calcd for $C_{36}H_{84}N_2Si_{10}$: 824.43217 (M^+); Found: 824.43216 (M^+); Elem. Anal. Calcd for $C_{36}H_{84}N_2Si_{10}$: C, 52.35; H, 10.25; N, 3.39%. Found: C, 52.38; H, 10.23; N, 3.39%; UV-vis (hexane) λ_{max}/nm (ε) 525 (59).

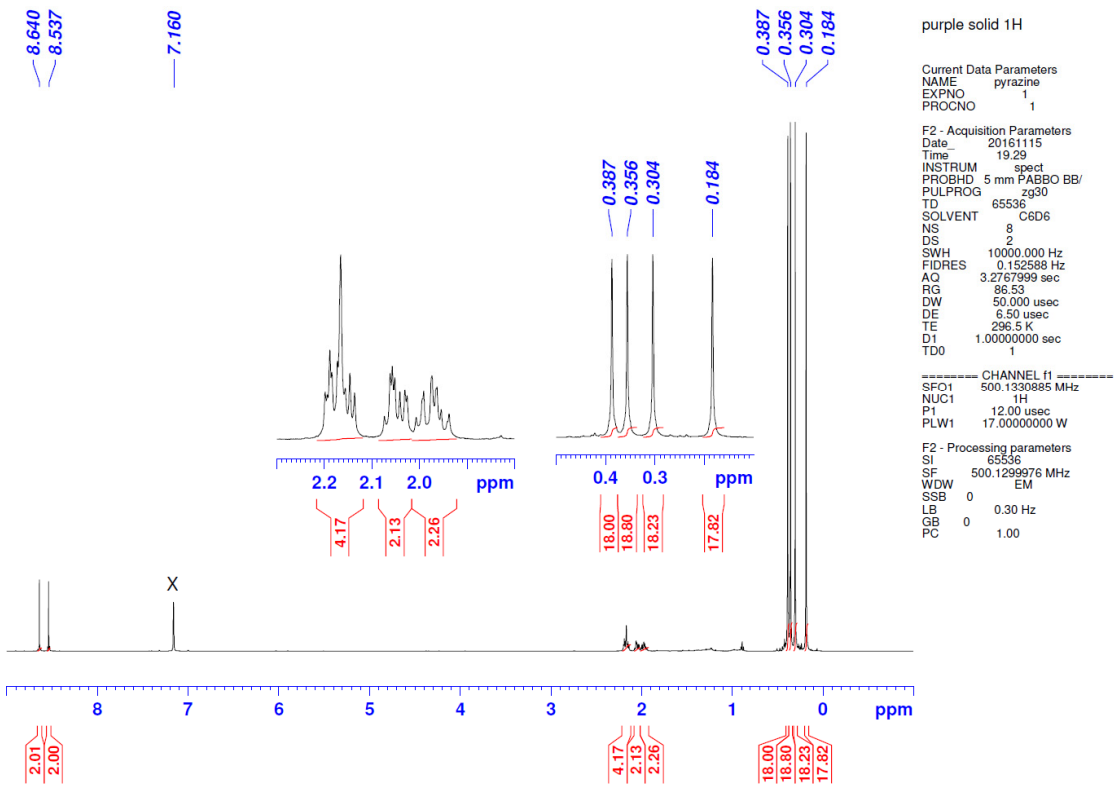


Fig. S1 ^{1}H NMR spectrum of **2** (in C_6D_6, 297 K). (× = C_6D_5H).

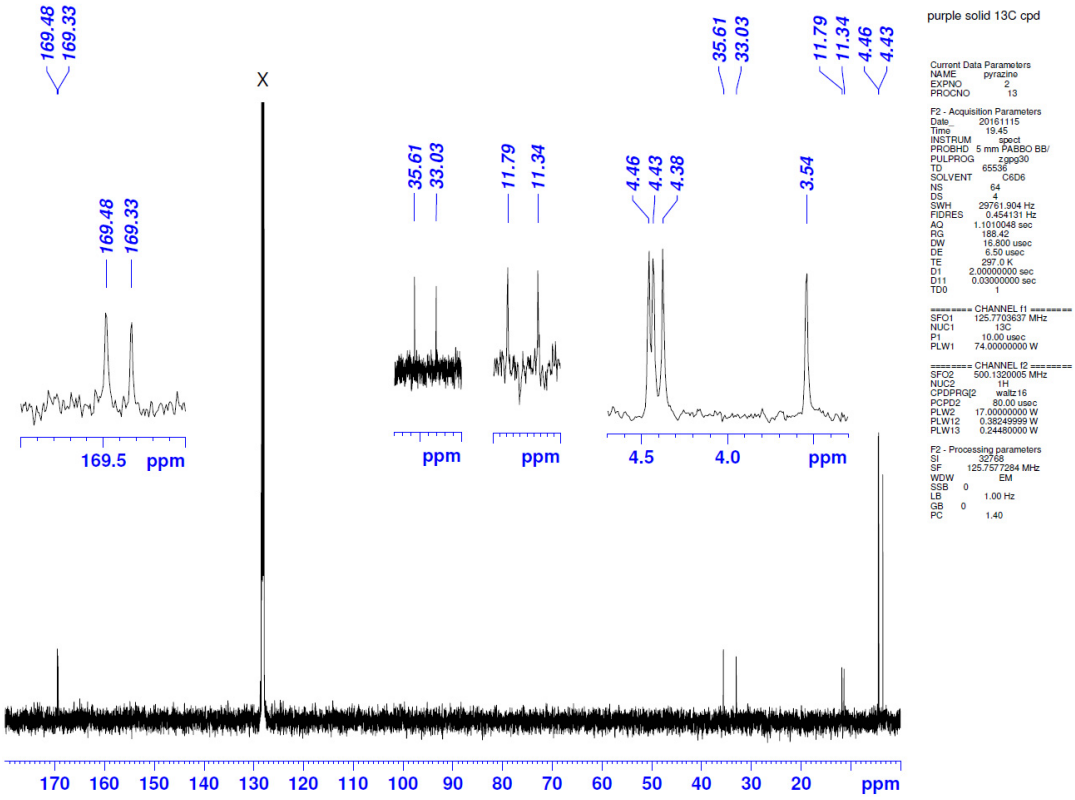


Fig. S2 $^{13}C\{^{1}H\}$ NMR spectrum of **2** (in C_6D_6, 297 K). (× = C_6D_6).

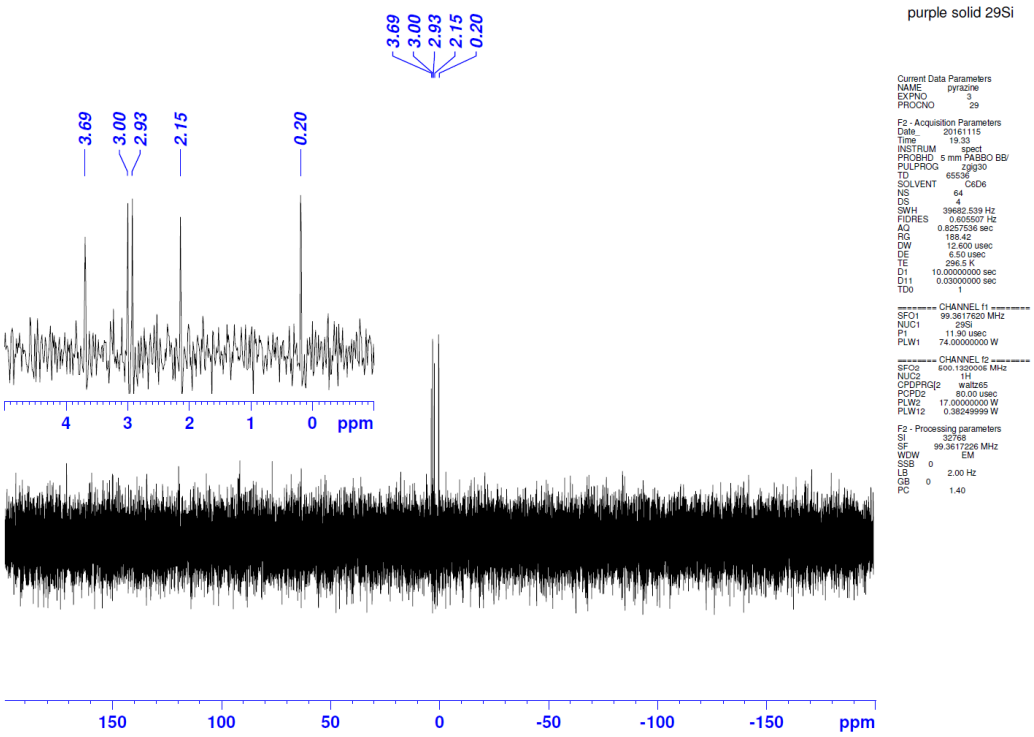


Fig. S3 $^{29}Si\{^{1}H\}$ NMR spectrum of **2** (in C_6D_6, 297 K).

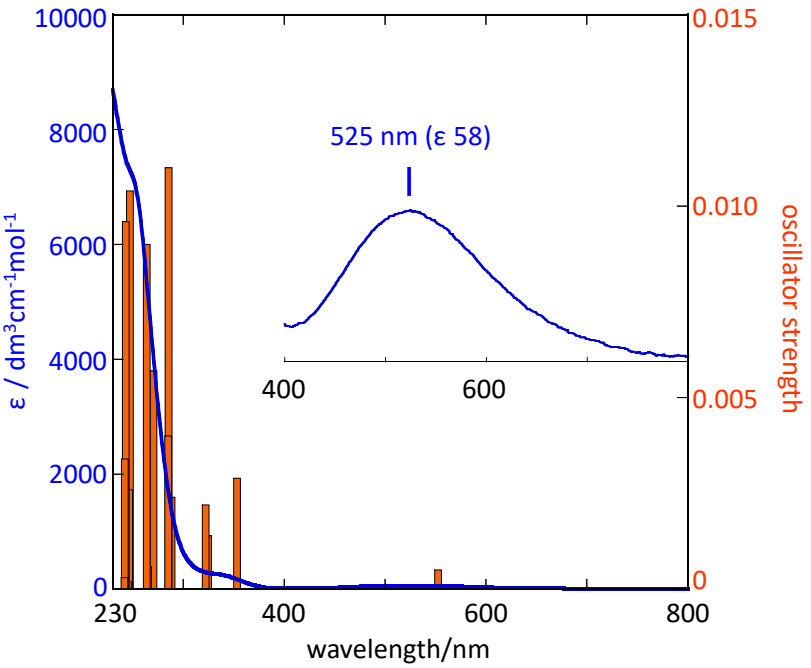
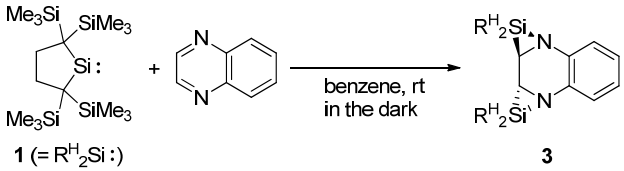


Fig. S4 UV-vis spectrum of **2** in hexane at room temperature. Superimposed vertical orange bars indicate band positions and oscillator strengths of $\mathbf{2}_{opt}$ calculated at the TD-B3PW91/6-311+G(d,p)//B3PW91/6-31G(d) level of theory.

Reaction of Silylene 1 with Quinoxaline (Synthesis of 3)



In a screw vial (2 mL) equipped with a magnetic stir bar, quinoxaline (7.0 mg, 54 µmol) and silylene **1** (38 mg, 100 µmol) were placed. Then, benzene (1.5 mL) was added to the vial. After stirring for 5 hours in the dark condition, the volatiles were removed under reduced pressure. Recrystallisation from hexane at −35 °C afforded pure **3** in 67% yield (30 mg, 34 µmol).

3: colorless crystals; mp. 231–233 °C; ^{1}H NMR (500 MHz, C_6D_6, 297 K) δ 0.10 (s, 18H, $SiMe_3$), 0.345 (s, 18H, $SiMe_3$), 0.354 (s, 18H, $SiMe_3$), 0.40 (s, 18H, $SiMe_3$), 1.82–1.90 (m, 2H, CH_2CH_2), 1.92–2.08 (m, 6H, CH_2CH_2), 2.77 (s, 2H, CH), 6.89-6.94 (AA'XX', 2H, CH), 7.16-7.20 (AA'XX', 2H, CH); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K) δ 2.88 ($SiMe_3$), 2.90 ($SiMe_3$), 3.8 ($SiMe_3$), 4.9 ($SiMe_3$), 5.5 (C), 6.5 (C), 31.6 (CH_2), 33.0 (CH_2), 33.7 (CH), 119.2 (CH), 120.7 (CH), 132.4 (C); ^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 297 K) δ −35.9 (Si), 3.0 ($SiMe_3$), 3.6 ($SiMe_3$), 3.8 ($SiMe_3$), 4.0 ($SiMe_3$); MS (EI, 70 eV) *m/z* (%) 874 (20, M^+), 859 (3, M^+−Me), 801 (7, M^+−$SiMe_3$), 502 (12, M^+−**1**), 73 (100); Elem. Anal. Calcd for $C_{40}H_{86}N_2Si_{10}$: C, 54.85; H, 9.90; N, 3.20%. Found: C, 55.05; H, 9.95; N, 3.26%.

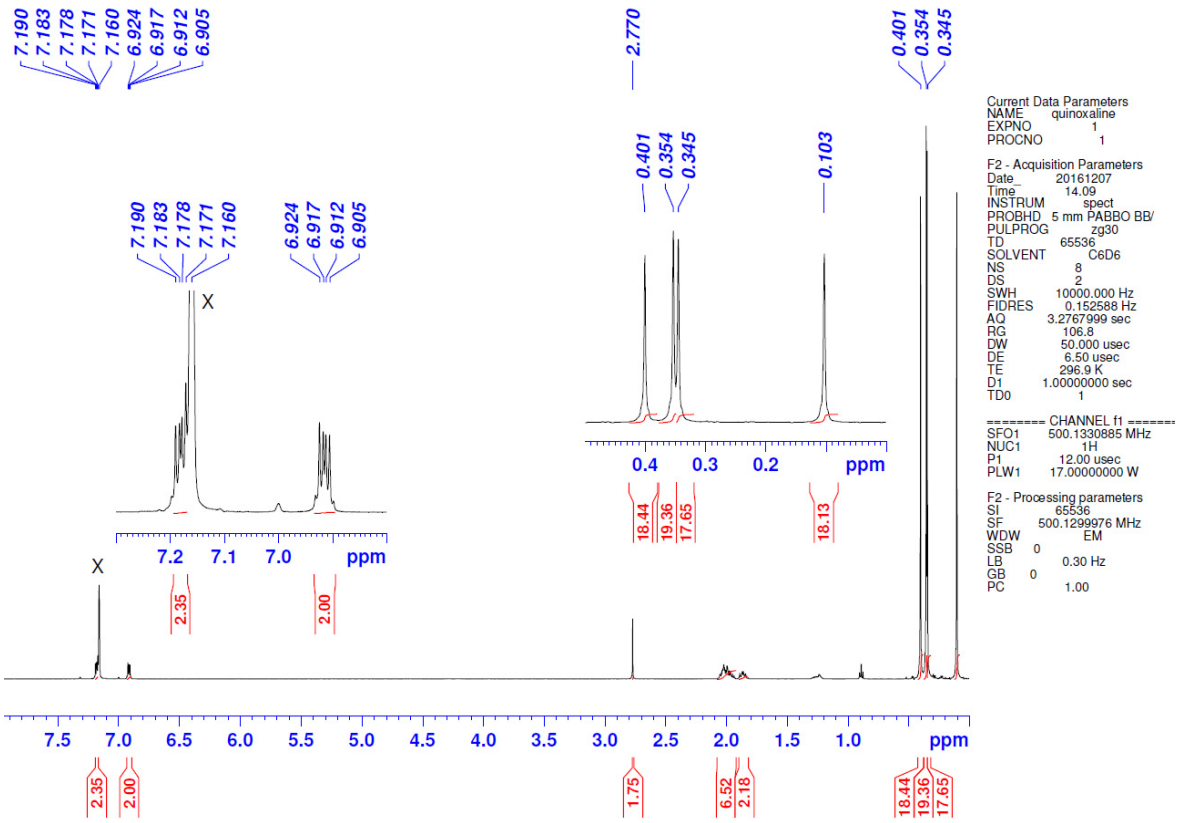


Fig. S5 ^{1}H NMR spectrum of **3** (in C_6D_6, 297 K). (× = C_6D_5H).

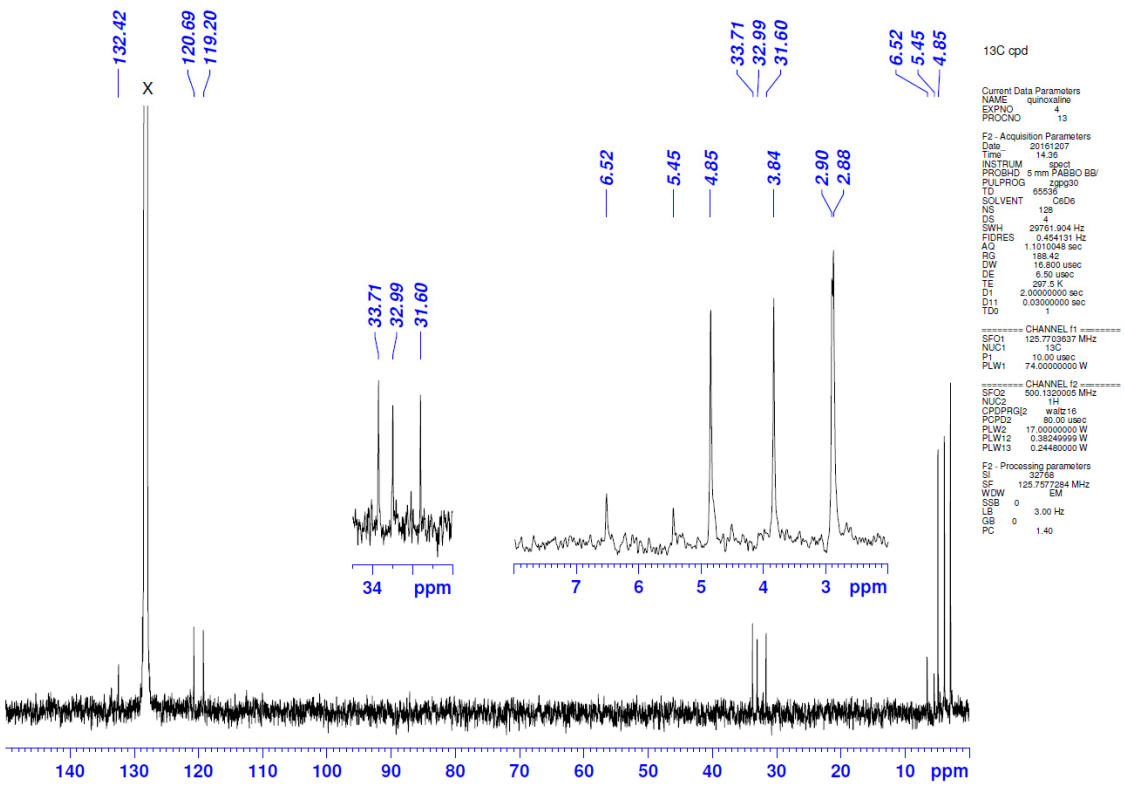


Fig. S6 $^{13}C\{^{1}H\}$ NMR spectrum of **3** (in C_6D_6, 298 K). (× = C_6D_6).

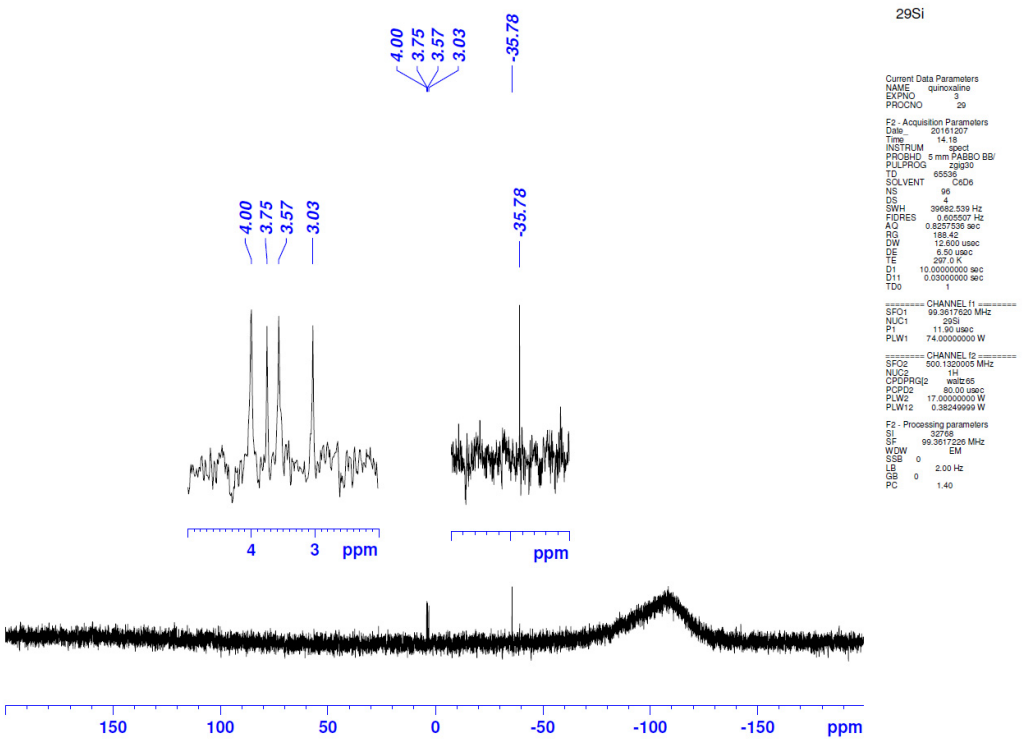


Fig. S7 $^{29}Si\{^{1}H\}$ NMR spectrum of **3** (in C_6D_6, 297 K).

2. Single Crystal X-ray Diffraction Analyses of 2 and 3

Single crystals suitable for X-ray diffraction study were obtained by recrystallisation from hexane at –35 °C for **2** and from toluene at –35 °C for **3**. The single crystals for data collection coated by Apiezon® grease was mounted on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer. X-ray diffraction data were collected on a Bruker AXS APEX II CCD diffractometer with graphite monochromated Mo-Kα radiation. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS[S3] and the structures were solved by direct methods and refined by full-matrix least squares against F^2 using all data (SHELEX-2014).[S4] Molecular structures ware analysed by Yadokari-XG[S5] software.

Crystal data for **2** (CCDC-1837160) (100 K): 0.10 mm × 0.10 mm × 0.10 mm; $C_{36}H_{84}N_2Si_{10}$; Formula weight 825.95; monoclinic; space group *C*2; a = 21.0673(7) Å, b = 9.5867(3) Å, c = 16.1406(5) Å, β = 129.5940(10)°, V = 2511.97(14) Å^3, Z = 2, D_{calcd} = 1.092 Mg m^{-3}, 7978 reflections measured, 4641 unique (R_{int} = 0.0213), which were used in all calculations; $R1$ = 0.0346 ($I > 2\sigma(I)$), $wR2$ = 0.0851 (all data), GOF = 1.061, max/min residual electron densities 0.563/–0.208 e/Å^3.

Crystal data for **3** (CCDC-1837161) (100 K): 0.20 mm × 0.20 mm × 0.10 mm; $C_{47}H_{94}N_2Si_{10}$; Formula weight 968.14; triclinic; space group *P*-1; a = 11.4668(3) Å, b = 13.4537(4) Å, c = 20.1191(6) Å, α = 77.1630(10)°, β = 84.5050(10)°, γ = 72.1030(10)°, V = 2878.52(14) Å^3, Z = 2, D_{calcd} = 1.117 Mg m^{-3}, 36402 reflections measured, 10714 unique (R_{int} = 0.0214), which were used in all calculations; $R1$ = 0.0301 ($I > 2\sigma(I)$), $wR2$ = 0.0765 (all data), GOF = 1.045, max/min residual electron densities 0.433/–0.226 e/Å^3.

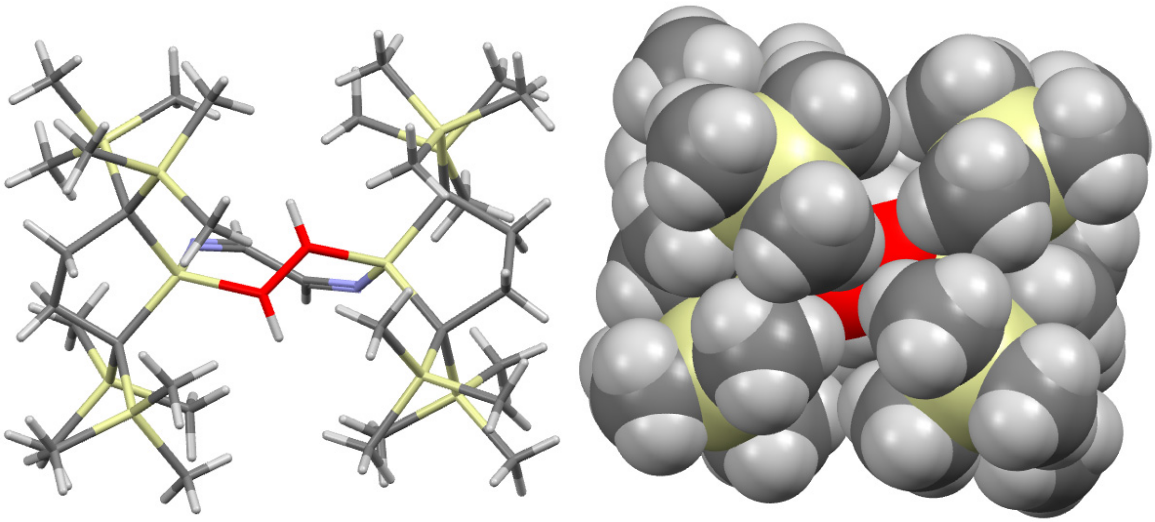
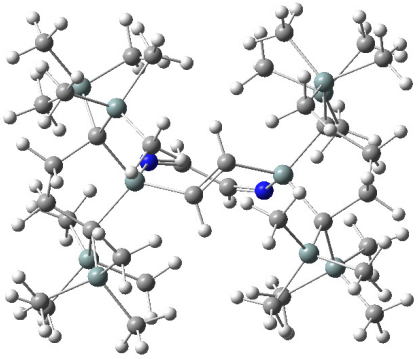


Fig. S8 Stick model (left) and space-filling model (right) of structure of **2**. Carbon atoms in red colour indicate *trans*-alkene moiety.

3. Theoretical Calculation

All theoretical calculations were performed using Gaussian 09[S6] and GRRM 14[S7] programs. Geometry optimisation and frequency analysis were carried out at the B3PW91/6-31G(d) level of theory for all compounds. Each TS was checked by IRC analysis. Atomic coordinates of the optimised structures were listed in Tables S1-S13. No imaginary frequencies were found in the equilibrium structures of all compounds and one imaginary frequencies were found in the transition states (TS1, TS2, TS3, TS4). Twenty excited states of $\mathbf{2}_{opt}$ and $\mathbf{2S}_{\mathbf{opt}}$ calculated at the TD-B3PW91/6-311+G(d,p) level of theory was summarised in Tables S14 and S15.

Table S1. Atomic Coordinates of $\mathbf{2}_{opt}$



Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
Si	5.658887207367	4.974728080809	4.060006640315
Si	8.104599454905	6.835310826350	2.993150702793
Si	8.504470687401	3.730340764485	3.143293184973
Si	3.050337616378	5.520508019652	2.280679705246
Si	3.491975714705	2.576882152093	3.229004777000
N	5.102691519292	6.603306665281	4.496222326468
C	5.092551888874	7.356691672262	5.513818264143
H	4.638331235568	8.361470179089	5.383357372445
C	5.901836745427	4.243346785363	5.778801308984
H	6.919112318732	4.268466145510	6.186722825009
C	7.194703990860	5.133093219563	2.921240975342
C	6.495065448109	4.983796700321	1.524745548443
H	6.067262370221	5.944582601128	1.219489520751
H	7.208437188239	4.705631788479	0.738243065269
C	5.360608089430	3.950931157076	1.590906373879
H	5.811045544424	2.951665234562	1.680246892446
H	4.807030349666	3.939865935522	0.641505993207
C	4.402504864968	4.232577183974	2.809446102581
C	7.054705527275	8.274392277628	2.346482886139
H	7.666897790957	9.184518325173	2.398022210185
H	6.153180523377	8.439587589288	2.941479252915
H	6.756509713673	8.147765149802	1.300247817563
C	9.628608412144	6.867073554880	1.857784316849
H	9.361538367368	6.651958394057	0.816326568306
H	10.426362628489	6.177760905623	2.149805272907
H	10.049946548941	7.880599880271	1.878570008523
C	8.676039432838	7.310320576652	4.740414552796
H	8.695009679902	8.403830100077	4.827192285328
H	9.685055110968	6.950133375753	4.962628339520
H	8.015879316452	6.933439377637	5.527832291570
C	9.357914218550	3.347713672313	1.490822777890
H	9.774032063060	4.225094141658	0.987594381231
H	8.677354438435	2.849339169320	0.790405243668
H	10.185236089860	2.652165302816	1.682042525811
C	9.850965190111	4.163511869967	4.407292560615
H	10.463344342829	3.268575761491	4.574513002891
H	9.444379130841	4.464298864881	5.378575060377
H	10.522070890077	4.959140070659	4.071030588972
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H	8.685340680027	1.378093713812	3.855189483320

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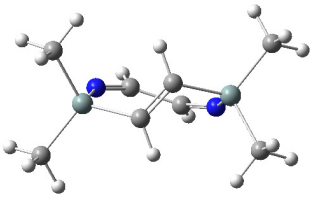
C	3.695640195399	7.002171248687	1.295202325718
H	2.836225447214	7.645776344111	1.064416389441
H	4.144030693430	6.711932363658	0.337914503627
H	4.416929993398	7.598417740506	1.856837194042
C	1.814717004603	4.745597818703	1.055209207511
H	1.143669725338	5.546750544898	0.717760196217
H	1.187807275097	3.950853460561	1.469786017330
H	2.312441271098	4.350962899058	0.161520453716
C	2.051049590015	6.203196061326	3.742983082155
H	2.411260287632	7.200569657533	4.010924615495
H	2.110385237545	5.580463557794	4.640164872260
H	0.991377957986	6.287725914386	3.471846410641
C	3.116048771754	1.615367311469	1.633395038837
H	4.033542818843	1.345343174598	1.098014278707
H	2.459781871133	2.135493302859	0.931433019773
H	2.622219297802	0.675753747165	1.913416808658
C	1.858725506627	2.797678298580	4.169194682425
H	1.379004171436	1.812462033708	4.233648739856
H	1.144290451972	3.480516072705	3.702058891586
H	2.023325992403	3.137225528730	5.197429481570
C	4.455336558405	1.327371679404	4.275261064960
H	4.835961092681	1.746192932584	5.209665314764
H	5.293206401814	0.874798577660	3.738945883841
H	3.760706816332	0.516372498436	4.531206477899
C	5.687438449473	7.356754379995	6.923674964464
Si	5.121292530730	4.974823589382	8.377610014620
Si	2.675425437603	6.835265014175	9.444371568055
Si	2.275806275274	3.730259013808	9.294358522977
Si	7.729800238607	5.520891020864	10.156921661071
Si	7.288389965328	2.577192361986	9.208731099416
N	5.677357891595	6.603424323101	7.941312183555
H	6.141576077390	8.361577396830	7.054082037103
C	4.878404711531	4.243339889294	6.658851879662
H	3.861128411617	4.268378367477	6.250926729092
C	3.585459120367	5.133125158157	9.516359619286
C	4.285103329641	4.983946465722	10.912865163387
H	4.712828719375	5.944779768215	11.218080617466
H	3.571750702774	4.705759712402	11.699377264663
C	5.419647233103	3.951171588735	10.846760023171
H	4.969297596707	2.951861005457	10.757475548665
H	5.973224200565	3.940206977279	11.796162007135
C	6.377729216055	4.232834280189	9.628206212717
C	3.725201069395	8.274455812151	10.090985773360
H	3.112940417464	9.184533153296	10.039401116860
H	4.626716093973	8.439689936319	9.495984898466
H	4.023401991321	8.147899552728	11.137227902960
C	1.151404487481	6.866942462980	10.579724176499
H	1.418487529653	6.651902499775	11.621194091199
H	0.353718928503	6.177538821405	10.287730505230
H	0.729970548527	7.880427832648	10.558886352879
C	2.103967375395	7.310159538914	7.697081165472
H	2.084995486453	8.403662640327	7.610228589382
H	1.094949541488	6.949958014741	7.474901381099
H	2.764117731534	6.933225190621	6.909681373081
C	1.422391601143	3.347625692692	10.946842386189
H	1.006195523246	4.224990073004	11.450034152208
H	2.102995600013	2.849340863354	11.647280842461
H	0.595131937609	2.651995884368	10.755650419228
C	0.929282561711	4.163283648065	8.030339835022
H	0.316973384231	3.268294641363	7.863145501908
H	1.335847773677	4.464070737003	7.059048501912
H	0.258111433951	4.958870044419	8.366570851396
C	2.948193799926	2.053786049455	8.727824967574
H	2.095124005368	1.377973100634	8.582546879254
H	3.596511125589	1.595221130676	9.481082520793
H	3.501357294670	2.092203191275	7.784983219037
C	7.084378498085	7.002544232811	11.142336804120
H	7.943741576238	7.646228765759	11.373093323472
H	6.636013659977	6.712309596031	12.099638055538
H	6.363038644668	7.598709049342	10.580679358305
C	8.965477042243	4.746122273384	11.382424998340
H	9.636463105640	5.547337622631	11.719847488510
H	9.592447597784	3.951409868109	10.967878916084
H	8.467778328658	4.351482885600	12.276125766100
C	8.729035289961	6.203593543003	8.694589555278
H	8.368738426558	7.200921402222	8.426596830149
H	8.669757804006	5.580811315399	7.797440026849
H	9.788697337260	6.288229801053	8.965726299818
C	7.664395478125	1.615780519643	10.804385113694
H	6.746929868018	1.345754188161	11.339810811355
H	8.320668137341	2.135963207554	11.506297720527
H	8.158246204543	0.676169224590	10.524397588088

C	8.921622778885	2.798064732645	8.268528551349
H	9.401403974542	1.812875674721	8.204104527794
H	9.636019029460	3.480960266499	8.735639002331
H	8.756997689264	3.137568122055	7.240283382735
C	6.325135211798	1.327540459750	8.162543145807
H	5.944506943537	1.746253225666	7.228091620242
H	5.487282303227	0.874954391426	8.698873542824
H	7.019826599387	0.516566370905	7.906684867640

Sum of electronic and zero-point Energies= -4424.968388878233

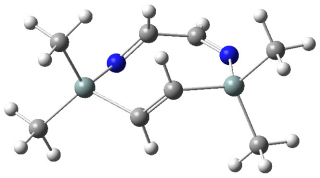
Table S2. Atomic Coordinates of **2m**



Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
Si	-2.094435077618	0.366757862187	0.026641255838
N	-1.682532984297	-1.304214066723	-0.344053560858
C	-0.713057688390	-2.114200147902	-0.280663289770
H	-0.902090870942	-3.146362940548	-0.641776027041
C	-0.479066875836	1.183169890740	0.475871129062
H	-0.158845559842	1.149680671983	1.523794911378
Si	2.094425741312	0.366755646021	-0.026609854654
N	1.682422012868	-1.304214524883	0.343990229356
C	0.712961985460	-2.114211757956	0.280530393923
H	0.902011201425	-3.146404787645	0.641550736763
C	0.479173734837	1.183600445586	-0.475569880741
H	0.159031941428	1.151266942448	-1.523544936634
C	3.325582972755	0.309903718268	-1.445883737593
H	3.696104623969	1.316801814627	-1.672216163670
H	4.184694017260	-0.321014469582	-1.194044840499
H	2.869610309357	-0.092655240107	-2.357291286746
C	2.867252917030	1.072278441208	1.533369461464
H	3.728349855878	0.466962520457	1.836377049797
H	3.211262846955	2.098671811887	1.360772830643
H	2.163495006526	1.090889014079	2.372232909714
C	-3.325763174100	0.309950826649	1.445762236959
H	-3.696105839899	1.316880795241	1.672200751384
H	-4.184970351309	-0.320753358129	1.193759591966
H	-2.869972889664	-0.092815467554	2.357159101064
C	-2.866971297621	1.072506754079	-1.533376736337
H	-3.728382142079	0.467566878403	-1.836255315248
H	-3.210484453683	2.099090317144	-1.360901476490
H	-2.163247047330	1.090652185928	-2.372280810130

Sum of electronic and zero-point Energies= -1002.498978211107

Table S3. Atomic Coordinates of **2m'**

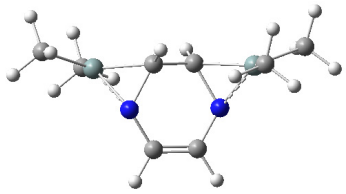


Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
Si	2.064111686065	0.386861510207	-0.034398645058
N	1.816594406412	-1.345432812167	0.323640853912
C	0.849887387680	-2.163404098866	0.300555378988
H	0.941372588038	-3.165284700691	0.741575754134
C	0.415993553064	1.116169134618	-0.567563299226
H	0.150479835477	0.917283055402	-1.614177141636
Si	-2.195678169944	0.262694078725	0.001770553340
N	-1.408138182376	-1.285933306769	0.462538155236
C	-0.456126059697	-1.675749552678	-0.282146687069
H	-0.345167832400	-1.396106295814	-1.349337948916

C	-0.605180295897	1.235234393772	0.311278974247	
H	-0.346168583565	1.374834289285	1.366925272528	
C	-3.594725254699	0.609830992992	1.199384059839	
H	-4.029351140979	1.601474897187	1.028767564944	
H	-4.395404721751	-0.131745647533	1.096741842621	
H	-3.235250331865	0.568852830276	2.233227092559	
C	-2.779919501896	0.342608040804	-1.788988485413	
H	-3.619296038205	-0.343718214272	-1.949569322154	
H	-3.123776402618	1.354496192522	-2.033802247793	
H	-1.994313784123	0.079112095505	-2.505526567966	
C	3.359425161441	0.455653001992	-1.394731597783	
H	3.655653002501	1.493590762471	-1.587127077487	
H	4.255326209779	-0.108637201688	-1.114520588569	
H	2.980085934472	0.037070242523	-2.333813291702	
C	2.693007190289	1.122998253588	1.573767769323	
H	3.597483475018	0.600735577698	1.903466129795	
H	2.934465976777	2.184464140190	1.444696581305	
H	1.951568237917	1.040355757183	2.375683927797	

Sum of electronic and zero-point Energies= -1002.488957049272

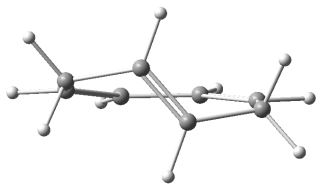
Table S4. Atomic Coordinates of **5m**



Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
Si	-2.347255787682	0.392588855298	-0.022175015805
N	-1.285749126021	-0.818380139361	0.622436638218
C	-0.627155867455	-1.991041223107	0.246939032444
H	-1.168650014538	-2.916335248880	0.421239785838
C	-0.566535937900	0.493149204986	0.507491862148
H	-0.300586160512	0.892343491609	1.490369600299
Si	2.347211537326	0.392623017390	0.022145262518
N	1.285654346587	-0.818358137068	-0.622323994996
C	0.627135640187	-1.991021242323	-0.246700448893
H	1.168697707323	-2.916301750471	-0.420859001425
C	0.566418772150	0.493206217978	-0.507297465452
H	0.300415443241	0.892379749075	-1.490170297997
C	3.773909423316	0.913220480135	-1.077132629532
H	4.097979132953	1.935044555039	-0.847680540916
H	4.638723646669	0.252125794359	-0.944230587649
H	3.473361829968	0.873218050313	-2.128390209364
C	2.750910988156	0.428471391404	1.856055408578
H	3.599394674064	-0.228762198097	2.080376375351
H	3.017829412868	1.438516470868	2.188894894142
H	1.895069129219	0.085303551753	2.445510377584
C	-3.774023466772	0.913484568619	1.076845065444
H	-4.097464807717	1.935563652617	0.847626004573
H	-4.639166496696	0.252913476281	0.943507394748
H	-3.473752424984	0.873016199381	2.128163438832
C	-2.750531233906	0.428201337813	-1.856186202445
H	-3.599091260898	-0.228906476174	-2.080594263609
H	-3.017146016465	1.438212901080	-2.189370994047
H	-1.894596376760	0.084683047871	-2.445305243350

Sum of electronic and zero-point Energies= -1002.467040533410

Table S5. Atomic Coordinates of **2c**

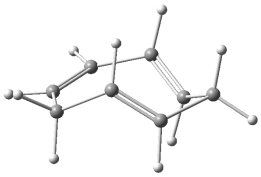


Atomic Type	Coordinates (Angstroms)		
	X	Y	Z

C	-0.734931408145	-1.501684530258	0.098290290287
C	0.736689973490	-1.501062001310	-0.098605949239
H	-1.058980778489	-2.533585172362	0.248405285458
H	1.061757733499	-2.532637433948	-0.248695423408
C	1.790405984482	-0.650191100878	-0.108797410692
H	2.761608271914	-1.124401297705	-0.268133416236
C	1.854678113219	0.851500159780	0.050011976731
H	2.637832191747	1.114809977411	0.774215366090
H	2.163065617714	1.292860450345	-0.911143108807
C	0.491797422992	1.300715650025	0.448966617204
H	0.245428631773	1.253347480191	1.510977908456
C	-1.789525191893	-0.651888469466	0.108504275748
H	-2.760176809626	-1.127151556995	0.268014026926
C	-0.493356374053	1.302301448590	-0.448018196719
H	-0.247084147225	1.259411076653	-1.510253355303
C	-1.855639790490	0.849865805128	-0.050222204121
H	-2.166366278111	1.290834510587	0.910344635455
H	-2.638498126233	1.111787148034	-0.775272652731

Sum of electronic and zero-point Energies= -310.505733005536

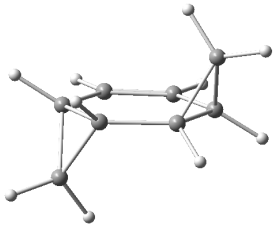
Table S6. Atomic Coordinates of **2c'**



Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
C	-1.435280010227	1.204398420632	0.003140264230
C	-0.033654968335	1.539644753741	0.326801861542
H	-2.204779208740	1.979405904022	0.029340006035
H	0.173055129573	1.823261141800	1.362469263610
C	0.955362866405	1.054463553185	-0.447655911271
H	0.688832211883	0.832192159552	-1.482638179247
C	2.100762049893	0.188702246250	0.067532501073
H	3.036378882019	0.248220399294	-0.496635300033
H	2.295144162521	0.365448556200	1.130397730244
C	1.302455162059	-1.089750044827	-0.191743622012
H	1.340136940479	-1.451171806825	-1.221459466655
C	-1.865942785429	-0.068777809480	-0.181951792324
H	-2.943656373071	-0.178360254036	-0.319576755758
C	0.184025944331	-1.286123084316	0.524006233321
H	0.152645864236	-0.822286050595	1.512451693874
C	-1.172653372877	-1.443429978635	-0.092778294962
H	-1.109116711053	-1.890680290479	-1.094819054381
H	-1.846271554408	-2.086330546019	0.492940111813

Sum of electronic and zero-point Energies= -310.460927237937

Table S7. Atomic Coordinates of **5c**

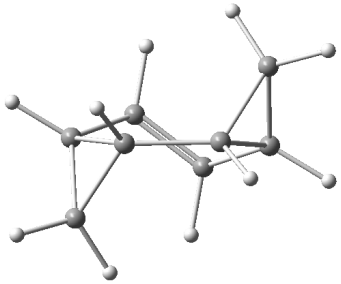


Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
C	-0.619508309519	1.498974065861	0.252420919690
C	0.619476645343	1.498634765402	-0.252339215046
H	-1.125417697684	2.441171815675	0.456927236826
H	1.126231797909	2.440554111852	-0.456100072054
C	1.366735123196	0.248437900459	-0.544721261299
H	2.026082135267	0.291535609689	-1.409665433803
C	1.842868592648	-0.625218859982	0.602767345731

H	2.800775025335	-1.130921101515	0.506289833423
H	1.606957159017	-0.280629154471	1.606273435762
C	0.700585088087	-1.074909455620	-0.268133374099
H	0.922936878633	-1.880722824398	-0.967913997968
C	-1.367616347975	0.248925231645	0.543731124040
H	-2.028192116461	0.292605967203	1.407710473379
C	-0.700650361693	-1.074639014649	0.269607186263
H	-0.923374533057	-1.879799996911	0.970014768222
C	-1.841999273732	-0.626101995976	-0.603280152340
H	-1.604647528562	-0.282690420104	-1.606862463459
H	-2.800055137748	-1.131567986149	-0.507299757307

Sum of electronic and zero-point Energies= -310.528414582582

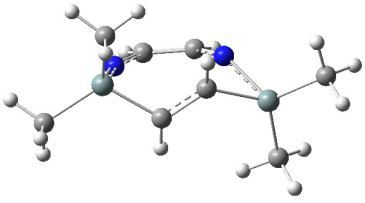
Table S8. Atomic Coordinates of **5c'**



Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
C	0.375652388432	-1.323872949129	0.567600331276
C	-0.377079143792	-1.324371245955	-0.567446739634
H	-0.153354882273	-1.351613756270	1.523468717965
H	0.150736890099	-1.354685207375	-1.523867065971
C	-1.458651365326	-0.326050080102	-0.568532102772
H	-2.158390857400	-0.283005376969	-1.402834435516
C	-1.829196477775	0.506618282639	0.637954297637
H	-2.793952956105	1.004281942076	0.578668925239
H	-1.585552661562	0.163391864697	1.637581762447
C	-0.720963431896	1.029536171977	-0.234658786536
H	-0.962758159872	1.842225580749	-0.917991646028
C	1.458439612546	-0.327048534828	0.568186836927
H	2.157895804327	-0.284679606397	1.402767795739
C	0.721466206626	1.028717944442	0.234382266061
H	0.963867755987	1.840670431438	0.918382091320
C	1.830153034264	0.505997869514	-0.637612882377
H	1.588618313954	0.164341408509	-1.638263682718
H	2.795024181756	1.003269786768	-0.576402921672

Sum of electronic and zero-point Energies= -310.437586077943

Table S9. Atomic Coordinates of **TS1**



Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
Si	2.237976650163	0.326565532164	-0.148905304395
N	1.620032261669	-1.171378050674	0.313930079143
C	0.681254829148	-2.023385440882	0.698312724290
H	0.901677677066	-3.093931353691	0.609099049908
C	0.552454832815	0.396179098687	-0.888203293491
H	0.335352856086	-0.276723804608	-1.717557020208
Si	-2.336414600855	0.316113467766	-0.178250049682
N	-1.179301604292	-0.460260125800	0.873130377891
C	-0.645940555936	-1.715421123801	0.936831276235
H	-1.359123690932	-2.537405655816	0.969904657555
C	-0.518675686537	0.718461205727	0.022806906410
H	-0.304871902441	1.521965268979	0.730463658259

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C           -3.587819273748     1.417824853015     0.669054114319
H           -3.935359584210     2.208705960887    -0.005426280289
H           -4.464598834138     0.844746123244     0.992761297601
H           -3.142428311366     1.885792916016     1.552122035341
C           -2.966724405592    -0.570876232404    -1.703884089656
H           -3.795314882358    -1.243378352421    -1.452577176406
H           -3.333174251380     0.141996535422    -2.451525954711
H           -2.171633077888    -1.169583428698    -2.159109611807
C            3.712178605882     0.228770294510    -1.306655916638
H            3.988695809515     1.221129748315    -1.683381545542
H            4.585896981773    -0.186328816903    -0.789669781637
H            3.493428338610    -0.417560199888    -2.162735193017
C            2.587770523696     1.582362555669     1.208799449801
H            3.493954567277     1.301542640872     1.759077075941
H            2.756195684124     2.580893349198     0.786047532856
H            1.768975236329     1.644288748843     1.932260359682 ------------------------------------------
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Sum of electronic and zero-point Energies=      -1002.436612986770
Imaginary Freq: -252.43410872
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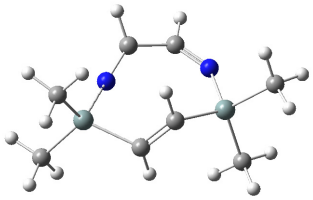
Table S10. Atomic Coordinates of **TS2**



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 Atomic Type             Coordinates (Angstroms)
                      X                 Y                 Z
---------------------------------------------------------------------
Si           2.164268668403    -0.288003437000    -0.017405428477
N            1.256762904134     1.155873210510     0.283064114333
C            0.486198588527     2.061347568166    -0.119053853135
H            0.757678709720     2.784869664174    -0.921707196245
C            0.607738846030    -1.340458790779     0.100775422288
H            0.341487974684    -1.647893992673     1.118498011263
Si          -2.018524144206    -0.420292244031    -0.052914190189
N           -1.828726800144     1.299828067903     0.331514306382
C           -0.951496057334     2.214796175839     0.328650687198
H           -1.263535126816     3.250240048284     0.557234126769
C           -0.405072438885    -1.066477225031    -0.750018087347
H           -0.133230737988    -0.682182141766    -1.742293683206
C           -3.425668892465    -0.475137902527    -1.299756612875
H           -3.676410337043    -1.513689372982    -1.547017580991
H           -4.323455557045     0.011648044415    -0.904165233761
H           -3.153934821794     0.031977416813    -2.232732524063
C           -2.495430723100    -1.252268869616     1.562592844895
H           -3.420778236683    -0.814100714028     1.951712417845
H           -2.663378753321    -2.324759430305     1.409736371706
H           -1.723482697592    -1.134380820476     2.329848941304
C            3.369686822363    -0.556773872740     1.394806992908
H            3.874025541646    -1.524685195061     1.292115813427
H            4.140918017123     0.221563841384     1.414693000729
H            2.853589016985    -0.542594430301     2.360478571333
C            3.034906146408    -0.373809887565    -1.685896574431
H            3.793709603818     0.412525945353    -1.773546583540
H            3.536102704532    -1.341491180073    -1.810860308830
H            2.332166809171    -0.253439854318    -2.517914668887 ------------------------------------------
------------------------
Sum of electronic and zero-point Energies=      -1002.486726950811
Imaginary Freq: -182.88276244
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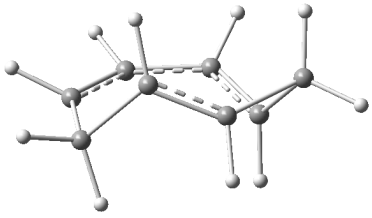
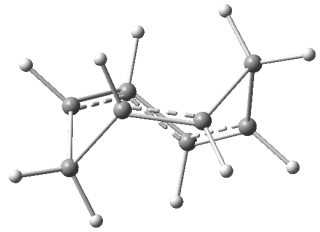
Table S11. Atomic Coordinates of **TS3**



Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
C	-0.975609563373	1.453729984067	0.105683928509
C	0.411952488684	1.586617173671	0.038267283981
H	-1.502115124996	2.295926884199	0.558313391736
H	0.853209944331	2.279137373647	0.757722412324
C	1.239327984448	0.595465529430	-0.538138687507
H	1.187224628821	0.437761631234	-1.611716015343
C	2.110163400777	-0.315795382320	0.262545033699
H	3.050931044018	-0.672431890572	-0.159758993755
H	2.196744171468	-0.030307214345	1.311802465944
C	0.885338959993	-1.121085737977	-0.092289105802
H	0.940281226419	-1.591853019537	-1.073550016889
C	-1.781149276273	0.308733904714	-0.002790968180
H	-2.729325124070	0.439788577032	0.521889954247
C	-0.343514693551	-1.286088836373	0.545245192058
H	-0.484804179309	-1.090487879206	1.605411613579
C	-1.532231662292	-1.137077628157	-0.354104871265
H	-1.272523221447	-1.339132924146	-1.398543672353
H	-2.409624759814	-1.734516739269	-0.087900045319

Sum of electronic and zero-point Energies= -310.443465166850

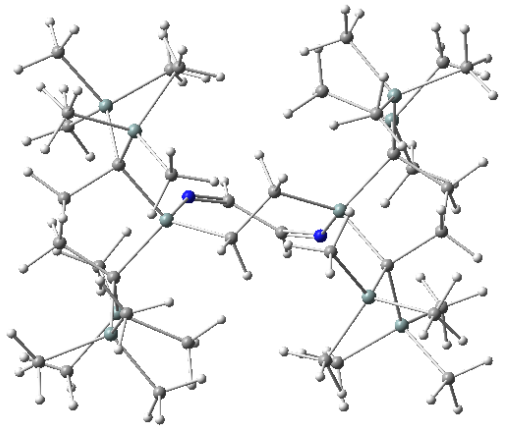
Table S12. Atomic Coordinates of **TS4**



Atomic Type	Coordinates (Angstroms)		
	X	Y	Z
C	-0.449979930771	-1.370537452750	-0.533399252063
C	0.450427102618	-1.370075295161	0.533805732364
H	-0.067160022432	-1.536436812575	-1.543621146741
H	0.067718552720	-1.536722563967	1.543896884885
C	1.512053114772	-0.443801496910	0.462511279592
H	2.173393170905	-0.347600530820	1.322594044216
C	1.776183405084	0.571532572843	-0.617132919180
H	2.765852178474	1.027450183924	-0.593780839883
H	1.467350261316	0.316674674229	-1.629603033745
C	0.681904458148	1.153113097716	0.224294667108
H	0.926327611313	1.606768222417	1.180228979084
C	-1.512119500539	-0.444267210753	-0.462747210894
H	-2.173151779527	-0.347968610197	-1.323099203467
C	-0.681826209889	1.153328280154	-0.223849800017
H	-0.925849232897	1.607618939730	-1.179551388797
C	-1.776578658170	0.571462211931	0.616609008781
H	-1.469256331341	0.316521863770	1.629479763587
H	-2.765983840986	1.027937628754	0.592366398266

Sum of electronic and zero-point Energies= -310.427888816353

Table S13. Atomic Coordinates of **$2S_{opt}$**



Atomic Type	Coordinates (Angstroms) X	Y	Z
Si	-2.120961144368	0.096743428756	-0.133420140720
Si	-3.567371622880	-2.014864493025	-2.139732584321
Si	-3.739827299273	-2.554771174295	0.931033286525
Si	-3.332247547464	3.028190848416	-0.624650208757
Si	-2.650898112401	2.303441869099	2.327850189372
N	-1.556413083366	0.633769451679	-1.718021574750
C	-0.613195816047	0.446773124105	-2.536650741216
H	-0.679332174252	0.946887640240	-3.524498848693
C	-3.555472969144	-1.166810007297	-0.404257985397
C	-4.782026736754	-0.195418776443	-0.298493577453
H	-4.928601510005	0.324268413765	-1.251093258795
H	-5.716764195300	-0.736369931658	-0.102501583081
C	-4.546628577459	0.857189210483	0.792807282859
H	-4.610235401063	0.359765716831	1.771111048802
H	-5.363969204409	1.591997288697	0.786022386021
C	-3.144059084542	1.550864288210	0.617323623021
C	-3.934413528224	-0.816284136150	-3.562596617687
H	-3.957697992226	-1.401551628897	-4.491430515332
H	-3.179298593604	-0.035361052538	-3.675700813835
H	-4.912313037210	-0.332537044577	-3.465257556326
C	-4.949149570477	-3.308709866352	-2.327692949694
H	-5.945258429014	-2.868828820602	-2.199751936051
H	-4.867649693263	-4.164152925146	-1.650697987336
H	-4.900272598072	-3.698972353394	-3.352780005707
C	-1.936700931808	-2.899093162799	-2.544558866329
H	-1.785581801098	-2.903200629846	-3.631281497709
H	-1.942915538194	-3.942048433329	-2.213248917297
H	-1.060314059123	-2.423518971910	-2.094540258829
C	-5.562563787410	-3.068641717670	1.086073665384
H	-6.063948532951	-3.254241255584	0.133129462689
H	-6.142851907484	-2.313325177997	1.629285682097
H	-5.614163437148	-3.994229139615	1.673874965113
C	-2.706430171554	-4.097928883196	0.545627630165
H	-2.754605184789	-4.769393137973	1.412119761436
H	-1.650317354814	-3.861035817584	0.376701719621
H	-3.062040219836	-4.660480513110	-0.322869633187
C	-3.281088256748	-2.131153763443	2.723490763653
H	-3.559421001773	-2.998796698933	3.336504897843
H	-3.836151290994	-1.272970817110	3.115103846726
H	-2.214058130634	-1.954077765066	2.884433771335
C	-4.324578189842	2.655151085121	-2.194276298200
H	-4.347558578156	3.574190622107	-2.795209441097
H	-5.366067286002	2.384192396517	-1.986135267300
H	-3.868723932990	1.870786375399	-2.800853522163
C	-4.353936975063	4.443252840161	0.144462925182
H	-4.491271707421	5.204987331442	-0.634602289723
H	-3.890438227774	4.938113200651	1.002902034314
H	-5.355843706027	4.114588317946	0.445237091526
C	-1.671006930101	3.768043331053	-1.169991390621
H	-1.435584008944	3.457276183322	-2.192192770169
H	-0.833620635722	3.467228234918	-0.534294231309
H	-1.717771900152	4.863823779621	-1.152344277652
C	-4.212176298132	2.895814976390	3.236371725290
H	-4.851322101831	2.051373472704	3.520305957487
H	-4.825932181522	3.601426879531	2.671139164257
H	-3.906780306491	3.393052196089	4.165961777911
C	-1.424927287201	3.748428771249	2.228095718566
H	-1.280576405281	4.140898404424	3.243040551953
H	-1.746302621836	4.580889716062	1.596484971877
H	-0.442506352477	3.419543331520	1.871247501689

C	-1.844962369999	1.133728874359	3.584492347579
H	-0.820575149996	0.859899911847	3.317823282209
H	-2.409606936260	0.216857133230	3.767257711344
H	-1.793397278129	1.676118490641	4.537846618789
C	0.613468544675	-0.445979924623	-2.536779488866
Si	2.121048228324	-0.096768093579	-0.133370596839
Si	3.567726734655	2.014756575134	-2.139529214422
Si	3.739651885696	2.554851699654	0.931133562671
Si	3.332246086462	-3.028247864263	-0.624643800500
Si	2.650640605296	-2.303557147397	2.327848898411
N	1.556607127378	-0.633356997496	-1.718146144323
H	0.679675312691	-0.945685971344	-3.524831988841
C	3.555602298530	1.166767634928	-0.404025427909
C	4.782176596641	0.195426170211	-0.298015112989
H	4.929095213720	-0.324145522720	-1.250627217602
H	5.716820628180	0.736410896387	-0.101672698936
C	4.546555982909	-0.857327343671	0.793110162837
H	4.610052601276	-0.360016660612	1.771480476324
H	5.363887910232	-1.592145872545	0.786334600680
C	3.143986921484	-1.550958535169	0.617370780503
C	3.934938768937	0.816263761699	-3.562420859473
H	3.958641538757	1.401676273455	-4.491152800912
H	3.179640553738	0.035568194374	-3.675858012030
H	4.912679141840	0.332236138566	-3.464886979177
C	4.949527053042	3.308608228161	-2.327342058589
H	5.945633718103	2.868714576829	-2.199415012189
H	4.868022905366	4.163985608437	-1.650279497511
H	4.900671289913	3.698946810574	-3.352395018082
C	1.937008393212	2.898907254879	-2.544495614058
H	1.784837366381	2.901110984542	-3.631066066754
H	1.943947573800	3.942457374193	-2.215029620072
H	1.060849377339	2.424522385770	-2.092773825913
C	5.562344947719	3.068777590840	1.086517142731
H	6.064028052785	3.254033091704	0.133666240059
H	6.142446379193	2.313629896894	1.630158157926
H	5.613793185481	3.994555403461	1.674026217185
C	2.706216033825	4.097863068541	0.545245994815
H	2.754326346299	4.769610625384	1.411516022792
H	1.650127023129	3.860846630937	0.376372760949
H	3.061780281550	4.660155933261	-0.323434767314
C	3.280644653669	2.131488106119	2.723583568691
H	3.558758233332	2.999284254651	3.336480130806
H	3.835833909052	1.273481749988	3.115413305717
H	2.213629594771	1.954246360398	2.884439773623
C	4.324684208322	-2.655037263647	-2.194156204198
H	4.347659842336	-3.573965668931	-2.795256714328
H	5.366166859486	-2.384152513850	-1.985882164458
H	3.868887311084	-1.870536663525	-2.800592491008
C	4.353833796508	-4.443287841838	0.144566131258
H	4.491441003412	-5.204982259467	-0.634488758458
H	3.890114170140	-4.938189074119	1.002856564025
H	5.355625647126	-4.114547184323	0.445630504210
C	1.671040197483	-3.768030407417	-1.170162427438
H	1.435300575273	-3.456627680019	-2.192095993056
H	0.833720545557	-3.467893931694	-0.534057379520
H	1.718100985983	-4.863814314017	-1.153288652025
C	4.211742819388	-2.896328221378	3.236430718785
H	4.851259582634	-2.052086595416	3.520111022548
H	4.825172484620	-3.602389934743	2.671408483998
H	3.906157904135	-3.393148431673	4.166183161007
C	1.424373186232	-3.748290325540	2.228057164621
H	1.279728538813	-4.140557119727	3.243038326653
H	1.745722750188	-4.580925799177	1.596662316185
H	0.442098768786	-3.419263232677	1.870941498479
C	1.844983452535	-1.133722348499	3.584582285736
H	0.820595044475	-0.859781860406	3.318082444985
H	2.409757894974	-0.216924164236	3.767255105781
H	1.793503383252	-1.676096397392	4.537941574630
C	-0.583396045871	-0.514523147446	0.795959126345
H	-0.292030834717	-1.450166795491	0.295046291630
H	-0.836043465742	-0.803078439358	1.819688935770
C	0.583456166954	0.514229573496	0.796129591431
H	0.292044964903	1.450052332007	0.295584717301
H	0.836107465126	0.802399047869	1.819960031923

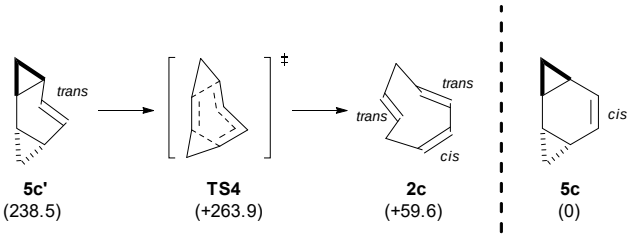
Sum of electronic and zero-point Energies= -4426.190392566788

Table S14. Transition Energy, Wavelength, and Oscillator Strengths of the Electronic Transition of $\mathbf{2}_{\mathbf{opt}}$.

```
Excited State   1:      Singlet-A      2.2443 eV
552.44 nm  f=0.0005  <S**2>=0.000
     227 -> 228        0.70392

Excited State   2:      Singlet-A      3.5090 eV
353.34 nm  f=0.0029  <S**2>=0.000
     227 -> 229        0.69501

Excited State   3:      Singlet-A      3.8169 eV
324.83 nm  f=0.0014  <S**2>=0.000
     219 -> 228       -0.37164
     221 -> 228        0.14016
     222 -> 228       -0.26455
     225 -> 228        0.29775
     227 -> 230        0.39425
     227 -> 231       -0.11573

Excited State   4:      Singlet-A      3.8464 eV
322.34 nm  f=0.0022  <S**2>=0.000
     226 -> 228        0.70075

Excited State   5:      Singlet-A      4.2983 eV
288.45 nm  f=0.0024  <S**2>=0.000
     222 -> 228        0.11190
     225 -> 228        0.58943
     227 -> 230       -0.35592

Excited State   6:      Singlet-A      4.3321 eV
286.20 nm  f=0.0575  <S**2>=0.000
     223 -> 228        0.56187
     224 -> 228        0.40571

Excited State   7:      Singlet-A      4.3454 eV
285.32 nm  f=0.0110  <S**2>=0.000
     223 -> 228       -0.41393
     224 -> 228        0.56949

Excited State   8:      Singlet-A      4.3512 eV
284.95 nm  f=0.0040  <S**2>=0.000
     222 -> 228        0.58011
     225 -> 228        0.12369
     227 -> 230        0.35566

Excited State   9:      Singlet-A      4.5798 eV
270.72 nm  f=0.0057  <S**2>=0.000
     219 -> 228        0.41265
     221 -> 228       -0.40317
     222 -> 228       -0.27035
     225 -> 228        0.19664
     227 -> 230        0.20726

Excited State  10:      Singlet-A      4.6190 eV
268.42 nm  f=0.0641  <S**2>=0.000
     223 -> 229        0.10661
     224 -> 229        0.10213
     226 -> 229        0.65922

Excited State  11:      Singlet-A      4.6740 eV
265.26 nm  f=0.0006  <S**2>=0.000
     219 -> 228        0.40812
     221 -> 228        0.55424
     227 -> 230        0.10472

Excited State  12:      Singlet-A      4.6990 eV
263.85 nm  f=0.0090  <S**2>=0.000
     220 -> 228        0.69718

Excited State  13:      Singlet-A      5.0175 eV
247.10 nm  f=0.0104  <S**2>=0.000
     225 -> 229        0.67818

Excited State  14:      Singlet-A      5.0379 eV
246.10 nm  f=0.0026  <S**2>=0.000
     213 -> 228       -0.13015
     217 -> 228        0.54634
     223 -> 229        0.33817
     224 -> 229        0.21921

Excited State  15:      Singlet-A      5.0471 eV
245.66 nm  f=0.0304  <S**2>=0.000
     217 -> 228       -0.39706
     223 -> 229        0.48037
     224 -> 229        0.27053
     226 -> 229       -0.12284

Excited State  16:      Singlet-A      5.0579 eV
245.13 nm  f=0.0002  <S**2>=0.000
     210 -> 228       -0.11909
     218 -> 228        0.68146

Excited State  17:      Singlet-A      5.1043 eV
242.90 nm  f=0.0096  <S**2>=0.000
     222 -> 229       -0.22572
     225 -> 229       -0.11487
     227 -> 230        0.14890
     227 -> 231        0.53993
     227 -> 234        0.29645

Excited State  18:      Singlet-A      5.1193 eV
242.19 nm  f=0.0034  <S**2>=0.000
     223 -> 229       -0.36769
     224 -> 229        0.59986

Excited State  19:      Singlet-A      5.1268 eV
241.84 nm  f=0.0003  <S**2>=0.000
     212 -> 228        0.27013
     216 -> 228        0.50695
     222 -> 229        0.36844
Excited State  20:      Singlet-A      5.1332 eV
241.53 nm  f=0.0000  <S**2>=0.000
     210 -> 228        0.16472
     215 -> 228        0.31813
     216 -> 228       -0.31210
     222 -> 229        0.44527
     227 -> 231        0.20153
```

Table S15. Transition Energy, Wavelength, and Oscillator Strengths of the Electronic Transition of **$2S_{opt}$**.

```
Excited State   1:       Singlet-A       2.3942 eV
517.86 nm  f=0.0006  <S**2>=0.000
     228 -> 229       0.70114

Excited State   2:       Singlet-A       3.6538 eV
339.33 nm  f=0.0010  <S**2>=0.000
     221 -> 229       0.18885
     222 -> 229       0.33025
     225 -> 229       0.30144
     227 -> 229       0.43129
     228 -> 230       0.24122

Excited State   3:       Singlet-A       4.2586 eV
291.14 nm  f=0.0155  <S**2>=0.000
     223 -> 229       0.20382
     224 -> 229       0.26260
     226 -> 229       0.61885

Excited State   4:       Singlet-A       4.2611 eV
290.97 nm  f=0.0009  <S**2>=0.000
     225 -> 229       0.50533
     227 -> 229      -0.47661

Excited State   5:       Singlet-A       4.2780 eV
289.82 nm  f=0.0659  <S**2>=0.000
     223 -> 229       0.31893
     224 -> 229       0.52713
     226 -> 229      -0.33430

Excited State   6:       Singlet-A       4.3524 eV
284.86 nm  f=0.0228  <S**2>=0.000
     223 -> 229       0.58509
     224 -> 229      -0.38503

Excited State   7:       Singlet-A       4.3912 eV
282.35 nm  f=0.0043  <S**2>=0.000
     222 -> 229       0.13873
     225 -> 229      -0.34470
     227 -> 229      -0.23378
     228 -> 230       0.52602
     228 -> 231      -0.11852

Excited State   8:       Singlet-A       4.4785 eV
276.84 nm  f=0.0089  <S**2>=0.000
     221 -> 229       0.12111
     222 -> 229       0.55478
     225 -> 229      -0.17464
     227 -> 229      -0.15904
     228 -> 230      -0.33507

Excited State   9:       Singlet-A       4.6330 eV
267.61 nm  f=0.0005  <S**2>=0.000
     221 -> 229       0.65643
     222 -> 229      -0.22623

Excited State  10:       Singlet-A       4.7064 eV
263.44 nm  f=0.0103  <S**2>=0.000
     220 -> 229       0.69731

Excited State  11:       Singlet-A       4.9697 eV
249.48 nm  f=0.0010  <S**2>=0.000
     216 -> 229       0.10999
     219 -> 229       0.68232

Excited State  12:       Singlet-A       5.0161 eV
247.17 nm  f=0.0032  <S**2>=0.000
     213 -> 229      -0.13151
     218 -> 229       0.68777

Excited State  13:       Singlet-A       5.0607 eV
244.99 nm  f=0.0001  <S**2>=0.000
     214 -> 229       0.17103
     217 -> 229       0.67174

Excited State  14:       Singlet-A       5.1083 eV
242.71 nm  f=0.0018  <S**2>=0.000
     211 -> 229       0.36756
     216 -> 229       0.56967
     219 -> 229      -0.11542

Excited State  15:       Singlet-A       5.1760 eV
239.54 nm  f=0.0049  <S**2>=0.000
     208 -> 229      -0.20538
     212 -> 229       0.48603
     213 -> 229       0.16865
     215 -> 229       0.42467

Excited State  16:       Singlet-A       5.2256 eV
237.26 nm  f=0.0280  <S**2>=0.000
     212 -> 229      -0.35097
     213 -> 229      -0.24368
     215 -> 229       0.54461

Excited State  17:       Singlet-A       5.2450 eV
236.39 nm  f=0.0097  <S**2>=0.000
     228 -> 230       0.14319
     228 -> 231       0.60746
     228 -> 234       0.29366

Excited State  18:       Singlet-A       5.2577 eV
235.81 nm  f=0.0003  <S**2>=0.000
     211 -> 229       0.40021
     214 -> 229       0.43622
     216 -> 229      -0.33636
     217 -> 229      -0.14675

Excited State  19:       Singlet-A       5.2984 eV
234.00 nm  f=0.0267  <S**2>=0.000
     210 -> 229       0.12975
     212 -> 229      -0.31470
     213 -> 229       0.59761
     218 -> 229       0.10760

Excited State  20:       Singlet-A       5.3188 eV
233.11 nm  f=0.0006  <S**2>=0.000
     211 -> 229      -0.41847
     214 -> 229       0.51836
     216 -> 229       0.19990
```



Scheme S1. Schematic energy diagrams of the reaction pathways from **5c'** to **2c**. Values in parentheses are relative energies (kJ mol^{-1}) to **5c**.

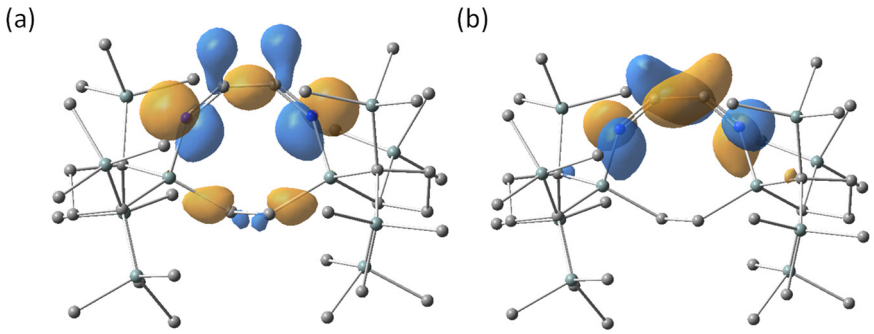


Fig. S9 Frontier Kohn-Sham orbitals of $\mathbf{2S_{opt}}$ calculated at the B3PW91/6-311G(d,p) level of theory (isosurface value = 0.05). Hydrogen atoms are omitted for clarity. (a) HOMO (–5.89 eV), (b) LUMO (–2.21 eV).

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