Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Transformation of azulenes to bicyclic [4]dendralene and heptafulvene derivatives by photochemical cycloaddition of dialkylsilylene

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Contents

1. Experimental Details

General Procedures

All reactions treating air-sensitive compounds were carried out under inert atmosphere (N_2 or Ar) using a high-vacuum line, standard Schlenk techniques, a glove box, and dry and oxygen-free solvents. NMR spectra were recorded on a Bruker Avance III 500 FT NMR spectrometer. The ^{1}H NMR chemical shifts in C_6D_6 were referenced to residual C_6D_5H signal and the $^{13}C\{^1H\}$ NMR chemical shifts in C_6D_6 were referenced to the solvent signal (^{1}H δ 7.16 and ^{13}C δ 128.0). The $^{29}Si\{^1H\}$ NMR chemical shifts were relative to Me_4Si in ppm. 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. X-ray analysis was carried out using a Bruker AXS APEXII CCD diffractometer. UV-vis spectra were recorded on a JASCO V-660. Light at a wavelength of 440 ± 10 nm was provided from 150 W xenon lamp through a monochromater using a BUNKOUKEIKI SM-25ER.

Materials

Benzene-d_6, diethyl ether and hexane were dried in a tube covered with potassium mirror or over $LiAlH_4$, and then distilled prior to use by using a vacuum line. Azulene, guaiazulene and ferrocene were commercially available and used without further purification. Dialkylsilylene **1** was prepared according to the procedure described in the literature.[S1]

Reaction of Dialkylsilylene with Azulene

In a Schlenk tube-type flask (30 mL) equipped with a magnetic stir bar, dialkylsilylene **1** (22.7 mg, 0.061 mmol) and azulene (3.8 mg, 0.030 mmol) in hexane (20 mL) were placed. The mixture was irradiated for 10 hours at a wavelength of 440 nm ± 10 nm. This reaction performed three times in the same condition (total amount of materials: **1** (52.4 mg, 0.14 mmol), azulene (8.7 mg, 0.068 mmol)). After the resulting mixtures were combined and then concentrated in vacuo, recrystallization from diethyl ether at –30 °C gave **2** as yellow crystals (25.2 mg, 42%). mp 149-150 °C; δ_H (500 MHz, C_6D_6, 301 K) 0.10 (s, 9H, $SiMe_3$), 0.12 (s, 9H, $SiMe_3$), 0.18 (s, 9H, $SiMe_3$), 0.23 (s, 9H, $SiMe_3$), 0.32 (s, 9H, $SiMe_3$), 0.336 (s, 9H, $SiMe_3$), 0.340 (s, 9H, $SiMe_3$), 0.36 (s, 9H, $SiMe_3$), 1.73 (t, J = 6.0 Hz, 2H, CH_2), 1.86 (t, J = 6.0 Hz, 2H, CH_2), 2.08 (s, 4H, CH_2), 2.15 (dd, J = 5.0, 11 Hz, 1H, CH), 2.30 (dd, J = 6.5, 11 Hz, 1H, CH), 5.74 (dd, J = 5.0, 12 Hz, 1H, CH), 5.92 (d, J = 12 Hz, 1H, CH), 5.99 (dd, J = 2.5, 15 Hz, 1H, CH), 6.29 (d, J = 6.5 Hz, 1H, CH), 6.39 (s, 1H, CH), 6.97 (d, J = 15 Hz, 1H, CH); δ_C (125 MHz, C_6D_6) 2.95 ($SiMe_3$), 3.03 ($SiMe_3$), 3.8 ($SiMe_3$), 4.0 ($SiMe_3$), 4.5 ($SiMe_3$), 4.7 ($SiMe_3$), 4.8 ($SiMe_3$), 5.0 ($SiMe_3$), 11.5 (C), 13.3 (C), 26.8 (CH), 29.6 (CH), 32.2 (CH_2), 33.9 (CH_2), 34.1 (CH_2), 34.7 (CH_2), 123.9 (CH), 127.8 (CH), 132.0 (CH), 139.1 (CH), 145.1 (CH), 148.0 (C), 153.8 (CH); δ_{Si} (99 MHz, C_6D_6) –28.9 (Si), –6.9 (Si), 3.09 ($SiMe_3$), 3.17 ($SiMe_3$), 3.19 ($SiMe_3$), 3.3 ($SiMe_3$), 4.2 ($SiMe_3$),4.3 ($SiMe_3$), 5.6 ($SiMe_3$), 6.0 ($SiMe_3$); λ_{max}(hexane)/nm 287 (ε/dm^3 mol^{-1} cm^{-1}

42700), 371 (4260); Found: C, 57.68; H, 10.26%; M^+, 872.4575. Calc. for $C_{42}H_{88}Si_{10}$: C, 57.72; H, 10.15%; M^+, 872.4573. One ^{13}C resonance due to quaternary carbon nuclei in the dendralene moiety was not observed possibly because of overlapping with the resonance due to carbon nuclei of C_6D_6.

(NMR yield) In a Schlenk tube-type flask (30 mL) equipped with a magnetic stir bar, dialkylsilylene **1** (23.0 mg, 0.061 mmol) and azulene (4.1 mg, 0.030 mmol) in hexane (20 mL) were placed. The mixture was irradiated for 10 hours using light of wavelength of 440 nm. After the resulting mixtures were concentrated in vacuo, ferrocene (4.6 mg, 0.025 mmol) was added as an internal standard and NMR yield of **2** was estimated to be 68% by using the signal of the internal standard at 4.00 ppm.

Reaction of Dialkylsilylene with Guaiazulene

In a Schlenk tube-type flask (30 mL) equipped with a magnetic stir bar, dialkylsilylene **1** (15.0 mg, 0.040 mmol) and guaiazulene (5.6 mg, 0.028 mmol) in hexane (20 mL) were placed. The mixture was irradiated for 14 hours at a wavelength of 440 nm ± 10 nm. This reaction performed three times in the same condition (total amount of materials: **1** (45.2 mg, 0.12 mmol), guaiazulene (18.4 mg, 0.093 mmol)). After the resulting mixtures were combined and then concentrated in vacuo, recrystallization from hexane at –30 °C gave **3** as orange crystals (19.6 mg, 37%). mp 129-130 °C; δ_H (500 MHz, C_6D_6) δ 0.26 (s, 18H, $SiMe_3$), 0.29 (s, 18H, $SiMe_3$), 1.08 (d, J = 7.0 Hz, 6H, CH_3), 2.03 (s, 4H, CH_2), 2.15 (s, 3H, Me), 2.17 (s, 3H, Me), 2.34 (hept, J = 7.0 Hz, 1H, CH), 5.98 (d, J = 7.0 Hz, 1H, CH), 6.01 (d, J = 7.0 Hz, 1H, CH), 6.32 (s, 2H, CH), 6.54 (s, 1H, CH); δ_C (125 MHz, C_6D_6) 4.67 ($SiMe_3$), 4.74 ($SiMe_3$), 12.1 (C), 23.2 (Me), 26.8 (Me), 27.6 (Me), 34.3 (CH_2), 37.2 (CH), 125.3 (CH), 125.5 (CH), 126.6 (CH), 128.1 (CH), 135.3 (CH), 139.5 (C), 141.5 (C), 146.3 (C), 151.6 (C), 154.4 (C); δ_{Si} (99 MHz, C_6D_6) –6.4 (Si), 3.1 ($SiMe_3$, overlapped); λ_{max}(hexane)/nm 254 (ε/dm^3 mol^{-1} cm^{-1} 20400), 276sh (15200), 336 (5740), 380sh (2980); Found: C, 65.56; H, 10.39%; M^+, 570.3380. Calc. for $C_{31}H_{58}Si_5$: C, 65.18; H, 10.23; M^+, 570.3379.

(NMR yield) In a Schlenk tube-type flask (30 mL) equipped with a magnetic stir bar, dialkylsilylene **1** (12.6 mg, 0.034 mmol) and guaiazulene (5.0 mg, 0.025 mmol) in hexane (20 mL) were placed. The mixture was irradiated for 14 hours at a wavelength of 440 nm. After the resulting mixtures were concentrated in vacuo, ferrocene (2.5 mg, 0.013 mmol) was added as an internal standard and NMR yield of **3** was estimated to be 62% by using the signal of the internal standard at 4.00 ppm

2. NMR Spectra

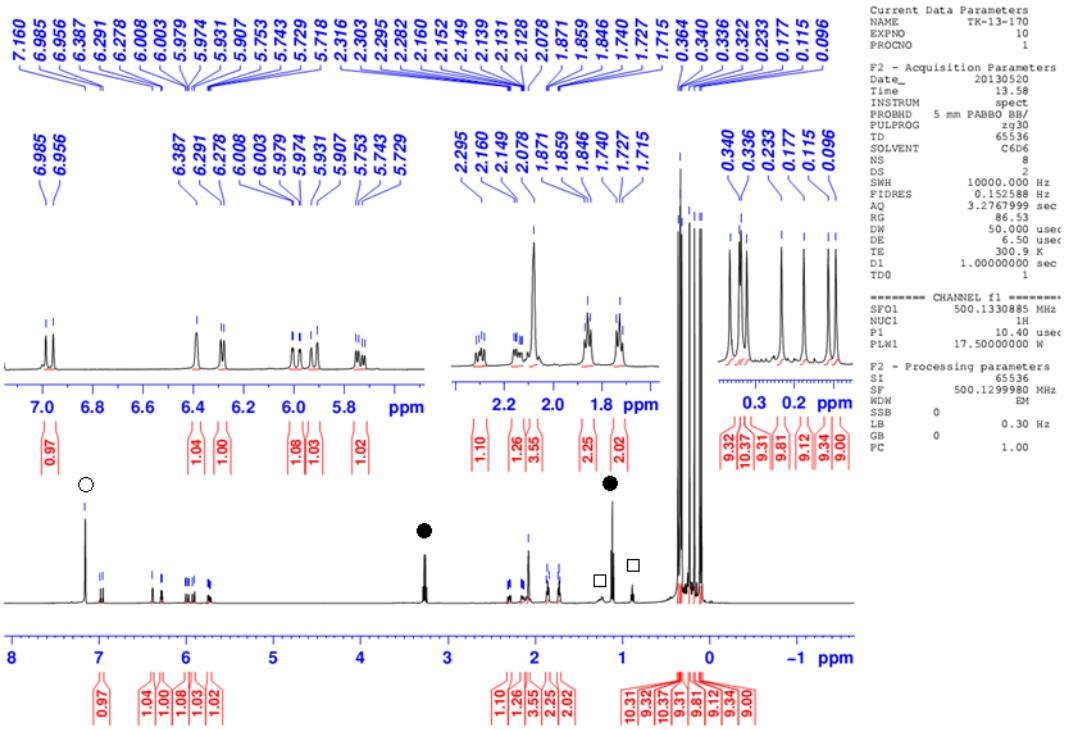


Figure S1. ^{1}H NMR spectrum of **2** in C_6D_6 at room temperature (○ = C_6D_5H, ● = Et_2O, □ = hexane).

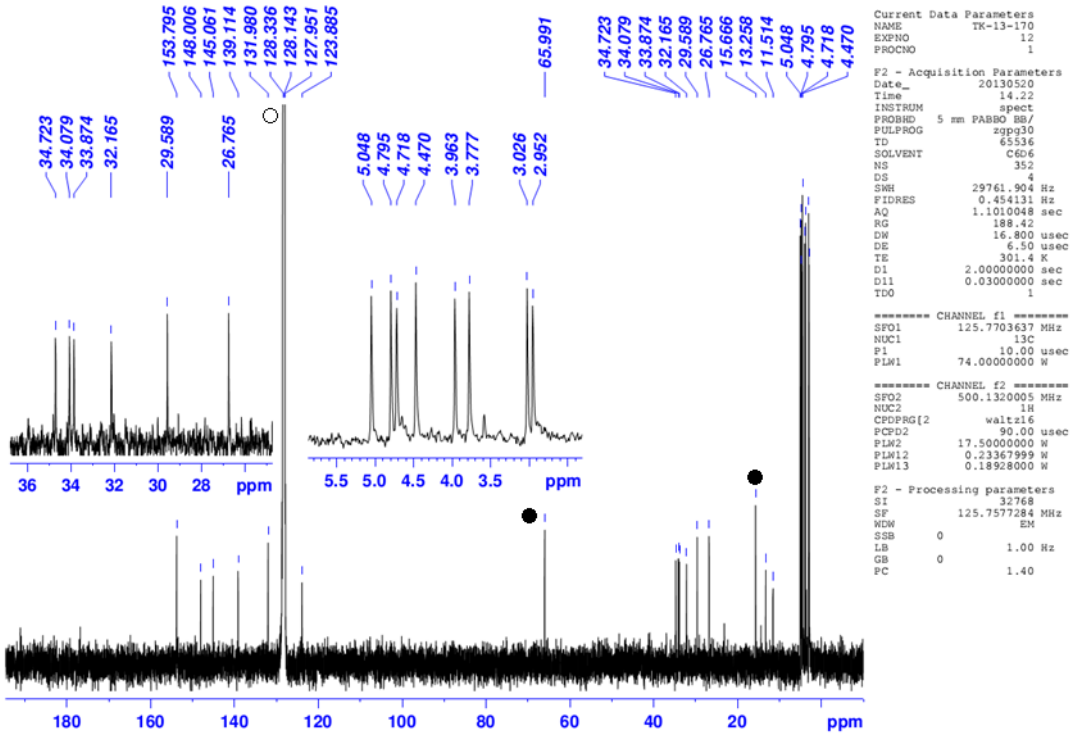


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **2** in C_6D_6 at room temperature (○ = C_6D_6, ● = Et_2O).

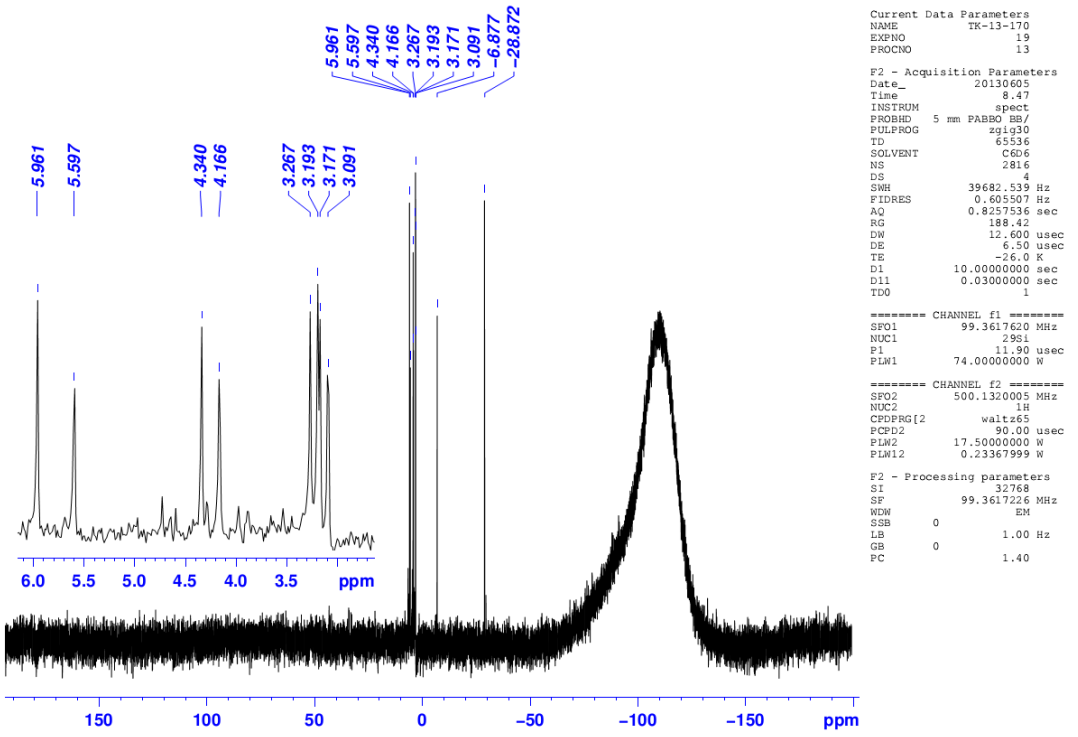


Figure S3. $^{29}Si\{^{1}H\}$ NMR spectrum of **2** in C_6D_6 at room temperature.

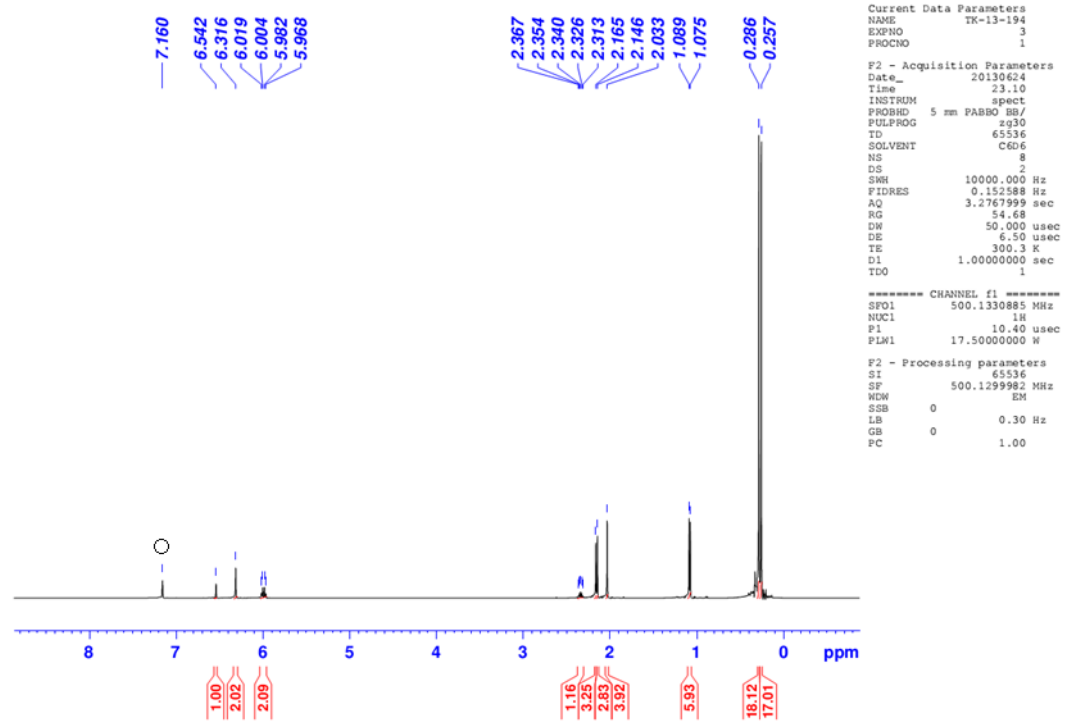


Figure S4. ^{1}H NMR spectrum of **3** in C_6D_6 at room temperature (○ = C_6D_5H).

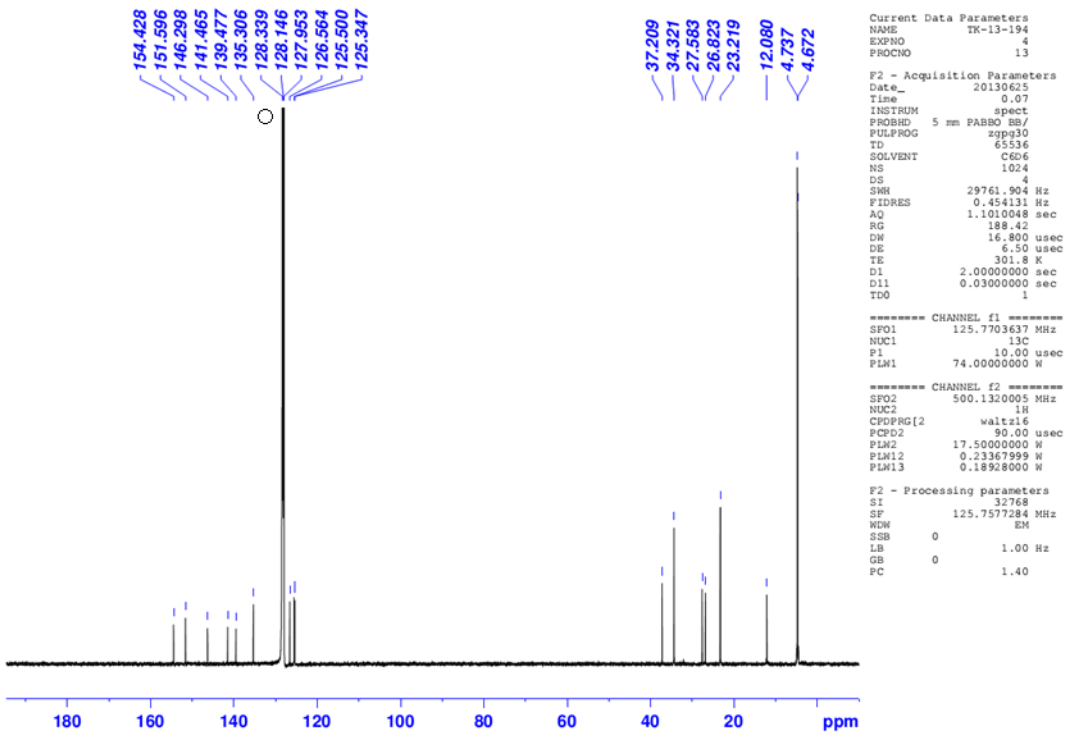


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in C_6D_6 at room temperature (○ = C_6D_6).

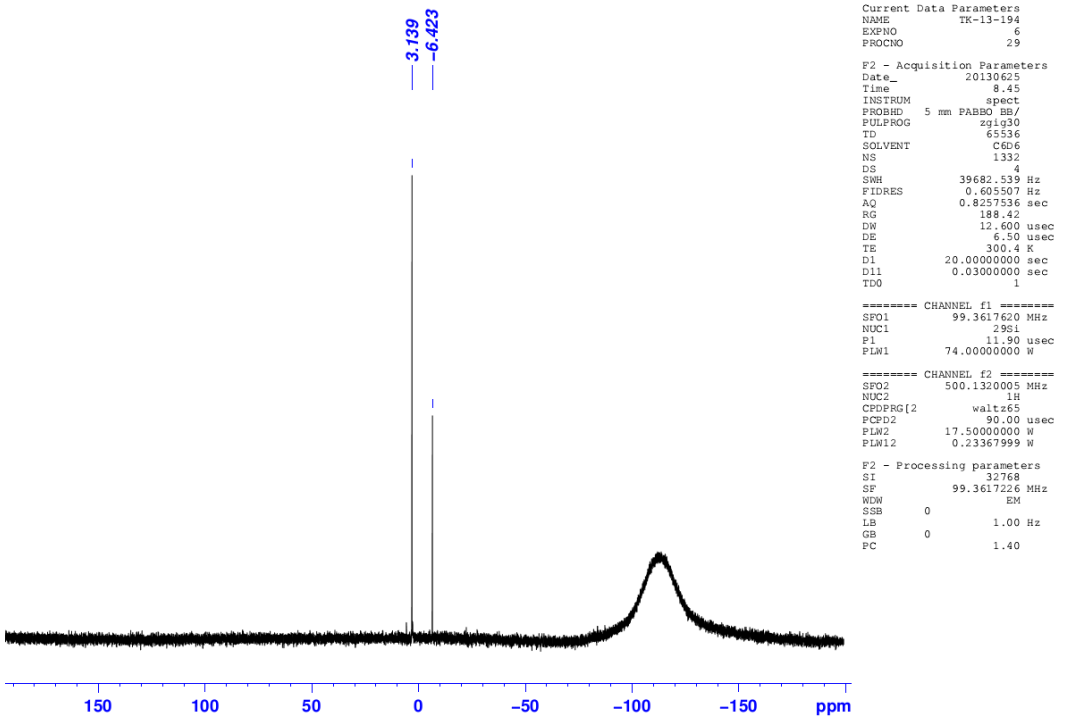


Figure S6. $^{29}Si\{^{1}H\}$ NMR spectrum of **3** in C_6D_6 at room temperature.

3. X-ray Analysis

Single crystals suitable for X-ray diffraction study were obtained by recrystallization in an inert atmosphere using following conditions; from Et_2O at –30 °C for **2** and from hexane at –30 °C for **3**. The single crystals for data collection coated by Apiezon® grease were 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-Kα radiation (λ 0.71073 Å). An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS and the structures were solved by direct methods and refined by full-matrix least squares against F^2 using all data (SHELXL-97).[S2] Molecular structure was analyzed by Yadokari-XG software.[S3] Details of crystal data were shown in Table S1.

Table S1. Crystal data of **2** and **3**.

	2·Et$_2$O	**3**
empirical formula	$C_{46}H_{98}OSi_{10}$	$C_{31}H_{58}Si_5$
formula weight	948.14	571.22
Temperature (K)	100(2)	100(2)
crystal system	Triclinic	Triclinic
space group	*P*-1	*P*-1
a (Å)	9.4329(13)	9.5864(15)
b (Å)	11.2567(16)	10.9534(17)
c (Å)	29.197(4)	18.638(3)
α (deg.)	85.049(2)	105.877(2)
β (deg.)	83.862(2)	92.815(2)
γ (deg.)	67.021(2)	110.499(2)
volume (Å^3)	2834.5(7)	1740.3(5)
Z	2	2
density (Mg/m^3)	1.111	1.090
absorption coefficient (mm^{-1})	0.263	0.223
F(000)	1044	628
Theta range for data collection(deg.)	1.40 to 25.00	1.15 to 25.00
Index ranges	-11<=h<=10,-13<=k<=13, 23<=l<=34	-11<=h<=11,-13<=k<=13,-22<=l<=22
Refrections collected	13273	16560
Independent reflections	9746 [*R*(int) = 0.0201]	6099 [*R*(int) = 0.0298]
Goodness-of-fit on F^2	1.074	1.043
Final *R* indices [$I>2\sigma(I)$]	0.0445	0.0348
R indices (all data)	0.1036	0.0980

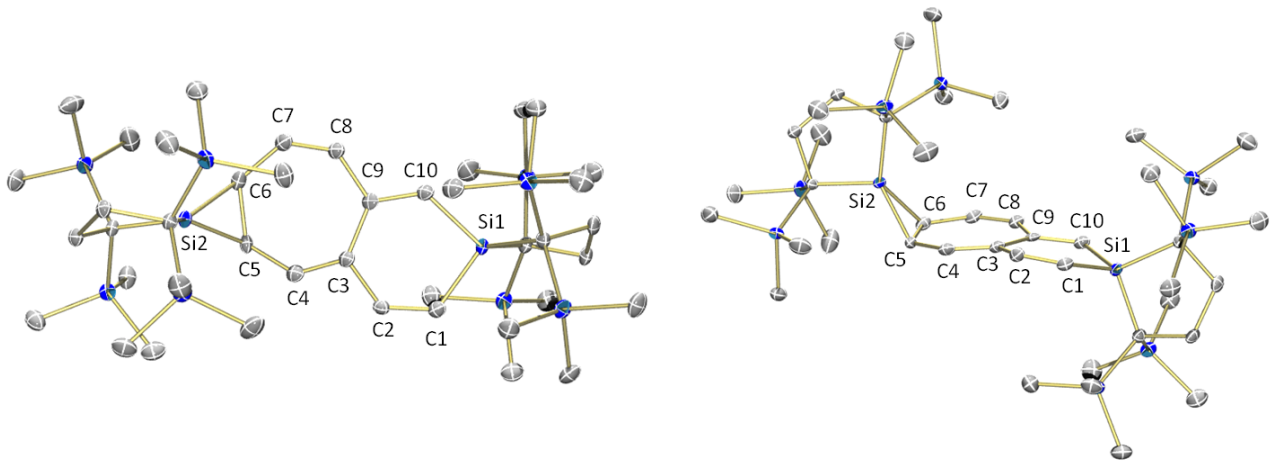


Figure S7. ORTEP drawings of **2·Et$_2$O**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1–C1 1.858(2), Si1–C10 1.871(2), Si2–C5 1.894(2), Si2–C6 1.898(2), C1–C2 1.343(4), C2–C3 1.477(3), C3–C4 1.357(4), C3–C9 1.490(3), C4–C5 1.467(4), C5-C6 1.546(3), C6-C7 1.463(4), C7-C8 1.337(4), C8-C9 1.479(3), C9-C10 1.354(4), C1-Si1-C10 98.13(11), C5–Si2–C6 48.13(10), Si2–C5–C6 66.06(13), Si2–C6–C5 65.81(12).

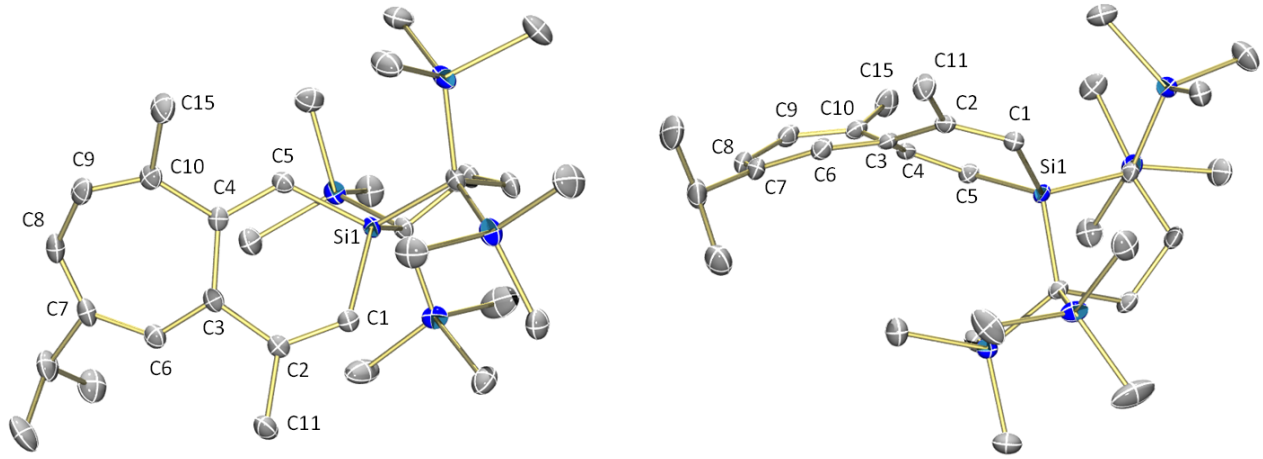
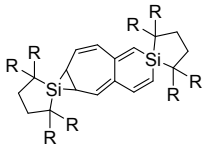


Figure S8. ORTEP drawings of **3**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angle (deg): Si1–C1 1.8545(15), Si1–C5 1.8486(16), C1–C2 1.345(2), C2–C3 1.489(2), C3–C4 1.492(2), C4–C5 1.355(2), C3–C6 1.363(2), C6–C7 1.439(2), C7–C8 1.349(2), C8–C9 1.437(2), C9–C10 1.349(2), C10–C4 1.488(2), C1–Si1–C5 97.83(7).

4. Theoretical Calculations

All theoretical calculations were performed using the Gaussian 09[S4] program and the GRRM14 program.[S5] Geometry optimization and frequency analysis for compounds **2'** and **3'** were carried out at the B3LYP/6-311G(d) level and those for dimethylsilylene (**1"**), azulene, **2"**, **4"** and **5"** were performed at the B3PW91/6-311G(d) level. The transition state between **4"** and **5"** (**TS(4"-5"**)) was found using the 2PSHS[S6] method in the GRRM14 program and confirmed using the IRC calculation. No imaginary frequencies were found in the optimized structures of all compounds except for **TS(4"-5"**). Atomic coordinates for **2', 3'**, **1"**, azulene, **2"**, **4", 5"** and **TS(4"-5"**) were summarized in Tables S2-S9. Thirty two excited states of **2'** and **3'** calculated at the TD-B3LYP/6-311++G(d,p) level were summarized in Tables S10 and S11. Kohn-Sham orbitals, their energy levels and assignment of absorption bands were shown in Figure S9. Energies for the reactions of silylene **1"** and azulene are summarized in Chart S1 and Figure S10.

Table S2. Atomic Coordinates of **2'** Calculated at the B3LYP/6-311G(d) Level.



2' (R = SiH_3)

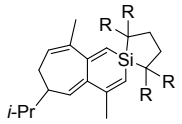
Atom	x	y	z
Si	3.30921700	-0.15309900	0.20541200
C	2.45233700	-0.39092300	1.82460700
H	2.95404600	-0.28532200	2.78341900
C	1.14720500	-0.72779500	1.85926900
H	0.69440200	-0.86536100	2.84097500
C	0.19754300	-0.95629700	0.75478600
C	-1.04600300	-1.32148700	1.18453600
H	-1.14009400	-1.39898300	2.26641500
C	-2.31935600	-1.63162100	0.54136100
H	-2.83393700	-2.43668500	1.06793200
C	-2.59109700	-1.66760500	-0.97813600
H	-3.19630900	-2.52707400	-1.26954100
C	-1.55216300	-1.35400100	-1.96578700
H	-1.90517900	-1.41887300	-2.99365400
C	-0.26646900	-0.99068800	-1.81889400
H	0.25125600	-0.80116800	-2.75543000
C	0.62307500	-0.79841800	-0.65787500
C	1.90809000	-0.46031600	-0.97634500
H	2.11243200	-0.36891300	-2.04167000
Si	-3.57807500	-0.34391900	-0.07048600
C	4.21281300	1.53372800	-0.02840500
C	5.58498500	1.12666200	-0.67057100
H	5.47702600	1.02485200	-1.75699500
H	6.35192000	1.89467500	-0.51764200
C	6.05204300	-0.22239100	-0.09080900
H	6.39797400	-0.06353100	0.93761000
H	6.92336900	-0.59387400	-0.64248500
C	4.86505000	-1.24964300	-0.11007700
Si	3.27772100	2.72868800	-1.15886000
Si	4.49546900	2.39162200	1.64075500
Si	5.10632600	-2.56194400	1.23343400
Si	4.78706000	-2.12192500	-1.79235200
C	-3.39040900	1.53917600	-0.13461700
C	-4.90176200	1.97196800	-0.25210200
H	-5.03988100	3.00522800	0.08272300
H	-5.21455700	1.95174000	-1.30251700
C	-5.81498100	1.02338600	0.55445200
H	-6.86624100	1.23205900	0.32865000
H	-5.68878900	1.23479800	1.62192800
C	-5.44662600	-0.47544300	0.25546400
Si	-2.44033100	2.24163900	-1.62476800
Si	-2.63785300	2.22500900	1.47687900
Si	-6.34484000	-1.09567800	-1.30040300
Si	-5.87363900	-1.57893000	1.73362200
H	6.09231900	-2.78380400	-2.06548500
H	3.71973800	-3.15287700	-1.82621000
H	4.53947800	-1.16470700	-2.90485600
H	5.26559500	-1.91365600	2.56219100
H	3.96715200	-3.51205300	1.29061900
H	6.34568400	-3.34576000	0.97050100
H	3.22700300	2.92670900	2.19663400
H	5.08856100	1.47483500	2.65134100
H	5.44549700	3.52302100	1.45775000
H	4.02095500	4.01397400	-1.28366900
H	3.15481900	2.15448400	-2.52548700
H	1.92112400	3.03508900	-0.63986900
H	-0.97713600	2.07113000	-1.48969700

H	-2.74463000	3.69599700	-1.70636400
H	-2.92014400	1.60426000	-2.87787200
H	-2.79464900	3.70439500	1.47709000
H	-3.35351100	1.69064600	2.66601200
H	-1.20341700	1.88273500	1.59178000
H	-7.81530900	-1.01862300	-1.09090600
H	-6.00197300	-0.26685300	-2.48533100
H	-5.97654100	-2.50423000	-1.59047200
H	-5.44375400	-2.98052100	1.49115100
H	-5.19422800	-1.07131400	2.95373700
H	-7.34048000	-1.57666800	1.97729400

E(RB3LYP) = -3605.22384019 A.U.

Zero-point correction = 0.494764 (Hartree/Particle)

Table S3. Atomic Coordinates of **3'** Calculated at the B3LYP/6-311G(d) Level.



3' (R = SiH_3)

Atom	x	y	z
Si	1.43405200	-0.05983600	0.13960300
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H	1.00735100	-0.82549600	2.58180700
C	-0.81689000	-0.15072200	1.84388700
C	-1.65223100	0.40743900	0.73914000
C	-1.01933200	1.28927000	-0.28097900
C	0.28407500	1.15586900	-0.64791000
H	0.65985600	1.85635100	-1.38739800
C	-2.95602000	-0.00648800	0.69906300
H	-3.22837500	-0.72061300	1.46779800
C	-4.02818400	0.26148800	-0.22284200
C	-4.08410200	1.36832200	-1.01228300
H	-4.99242800	1.51629700	-1.59284300
C	-3.12634900	2.42743400	-1.10611400
H	-3.51689700	3.34321200	-1.54571600
C	-1.80481100	2.44049700	-0.78998300
C	-1.51204900	-0.48500500	3.15146600
H	-0.77540700	-0.62264300	3.94386900
H	-2.08807000	-1.41448300	3.08837400
H	-2.20355000	0.30338100	3.45909400
C	-5.20705900	-0.71030500	-0.22137300
H	-5.89237500	-0.36945700	-1.00547000
C	-4.77561500	-2.14182400	-0.58406500
H	-4.10532800	-2.56762500	0.16830800
H	-4.25249700	-2.16717900	-1.54312200
H	-5.64704900	-2.79933200	-0.65681300
C	-5.99037400	-0.68355600	1.10391300
H	-6.32464300	0.32821100	1.34698500
H	-5.39099300	-1.04717400	1.94377300
H	-6.87464900	-1.32427700	1.03795100
C	-1.03373900	3.71812800	-1.04637200
H	-1.70960800	4.56471400	-1.17734300
H	-0.42055500	3.65035700	-1.95138400
H	-0.35209200	3.94123200	-0.22152800
C	1.89920800	-1.63479500	-0.87579900
C	3.43222200	-1.45606100	-1.16244300
H	3.93182200	-2.41704100	-1.33080100
H	3.58103300	-0.88005900	-2.08375000

C	4.09844200	-0.70319500	0.00551600
H	5.13075000	-0.43727900	-0.24928100
H	4.16694900	-1.37825900	0.86681700
C	3.24226100	0.55791600	0.37818100
Si	0.93147900	-1.74452300	-2.49894900
Si	1.60298400	-3.21598100	0.12656800
Si	3.60974200	1.11785800	2.14846100
Si	3.66248700	1.99587500	-0.78616000
H	-0.52992100	-1.85865500	-2.26514600
H	1.36522500	-2.94134000	-3.27397000
H	1.20038300	-0.54890300	-3.34039600
H	2.27468600	-3.16739000	1.45368400
H	0.15588200	-3.46113400	0.35043000
H	2.16679500	-4.38212600	-0.60836900
H	3.49556900	-0.03253400	3.08468400
H	2.68369800	2.19102800	2.59078200
H	5.00056100	1.64052500	2.25525700
H	3.22039700	1.74475400	-2.18448200
H	3.02619900	3.25955200	-0.33228300
H	5.13679900	2.19460300	-0.81305300

E(RB3LYP) = -2192.18839276 A.U.
Zero-point correction = 0.459901 (Hartree/Particle)

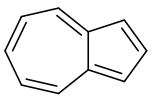
Table S4. Atomic Coordinates of **1"** Calculated at the B3PW91/6-311G(d) Level.

Me_2Si

Atom	x	y	z
Si	-0.093952545398	1.341455056303	-0.119411218460
C	0.654599034488	2.082053318480	1.473268344414
H	0.209102878699	3.038032690491	1.759958892205
H	0.629406377935	1.403990868893	2.334773780526
H	1.720503649291	2.276389840503	1.271989184655
C	0.604342196991	-0.425603286576	0.068308858781
H	-0.010292114937	-0.939638381802	0.824898140742
H	0.538461181064	-1.019293335498	-0.846986485196
H	1.634445711863	-0.460335480794	0.442866272322

ENERGY = -369.228186900267
Spin(**2) = 0.000000000000
ZPVE = 0.071250531780
SYMMETRY = C2

Table S5. Atomic Coordinates of azulene Calculated at the B3PW91/6-311G(d) Level.

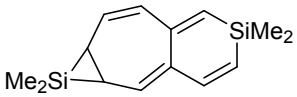


Atom	x	y	z
C	0.332363922414	1.020245458019	0.862295332550
C	1.725845520489	1.016383967623	0.861666823292
C	2.599211499509	2.102377130028	0.861689496743
C	-0.557650414531	2.092475037703	0.863109915027
C	2.307335667488	3.459294549731	0.862339541489
C	-0.276055387113	3.457340422694	0.863508715023
C	0.956231646576	4.095999364290	0.863197286793
H	-0.131608054454	0.035677140570	0.862119618148
H	2.193695983404	0.034976785628	0.861080496640
H	3.660150340505	1.854644677833	0.861117458052

H	-1.612354805951	1.828577194645	0.863477813503
H	-1.142465919817	4.117867115238	0.864153777836
C	3.241631904115	4.504137106847	0.862310150972
H	4.317564544313	4.380784479383	0.861772522182
C	2.547296772265	5.720397329129	0.863088947346
H	3.009561130178	6.701326214657	0.863249214469
C	1.167300826645	5.481659009083	0.863629759083
H	0.387262403965	6.232916316897	0.864270770849

ENERGY = -385.760830971915
Spin(**2) = 0.000000000000
ZPVE = 0.145920250399
SYMMETRY = C2v

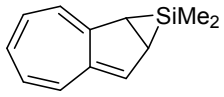
Table S6. Atomic Coordinates of **2"** Calculated at the B3PW91/6-311G(d) Level.



Atom	x	y	z
Si	1.260351513555	6.250025109647	2.631938148481
C	1.316786666332	6.494644827304	4.503957374144
C	0.564976416174	7.827574611544	1.862163330553
C	0.227147889401	4.774730855504	2.178859502671
C	2.894293034396	5.765867893804	1.920406313478
C	3.033715749775	4.579066554595	1.300784854037
C	2.047705127651	3.509157321329	1.070562243922
C	2.571211322334	2.431396678011	0.418284636095
C	2.078612002227	1.120983621591	0.017864312112
C	0.635999658523	0.612781029643	0.148611352034
C	-0.432532520156	1.436042261577	0.714110064679
C	-0.408760213914	2.653880451771	1.281773093312
C	0.642467747407	3.656911984690	1.517668298920
H	-0.829072844281	4.789376721244	2.454255846406
H	3.777657265527	6.401821669881	1.968654841407
H	4.017267099770	4.337027269611	0.893512851854
H	3.624118730884	2.537985444980	0.156517864179
H	2.561657608698	0.767705032377	-0.894222162786
H	0.317444524958	0.032928565675	-0.718435033080
H	-1.406990528797	0.948020281581	0.696335956738
H	-1.373757244835	2.990045838336	1.655913446868
H	1.958509239191	7.340577965915	4.773029010628
H	0.321090463838	6.699876932361	4.911406248549
H	1.707776915127	5.607028662262	5.008743092607
H	-0.438308510419	8.049911659257	2.240985368762
H	1.197580445143	8.691937498645	2.091223219583
H	0.499787786319	7.741859693275	0.774134109762
Si	1.853579669756	-0.284872956085	1.266893855857
C	1.862123001574	0.148435838457	3.080732758065
C	2.455028422071	-1.997097932533	0.801370833528
H	2.878096840146	0.159297510795	3.485619476154
H	1.427144527678	1.138162458219	3.235526563476
H	1.278136083449	-0.571331810219	3.662098141856
H	3.488048163269	-2.159768884246	1.123387501813
H	1.840050728785	-2.774551271552	1.265061491528
H	2.415873638447	-2.143880549307	-0.281096928240

ENERGY = -1124.340037057087
Spin(**2) = 0.000000000000
ZPVE = 0.296392673705
SYMMETRY = C1

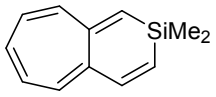
Table S7. Atomic Coordinates of **4"** Calculated at the B3PW91/6-311G(d) Level.



Atom	x	y	z
Si	1.159003259676	6.323075371430	2.466297673698
C	1.208304062541	5.384623033631	4.080508065547
C	0.539576783560	8.089422873978	2.568864828891
C	0.760288240878	5.441837442557	0.842088098843
C	2.262571025826	5.824967840842	1.043915716701
C	2.914129805400	4.506411427468	1.187532054965
C	2.047813903315	3.464521369404	1.058264790972
C	2.416555047217	2.068447867282	1.189482522562
C	1.657940755865	0.962493442682	1.017476950508
C	0.264569773694	0.847705291110	0.660790467505
C	-0.622672140287	1.845096568193	0.421212905517
C	-0.431748685132	3.268455677105	0.467188616811
C	0.695790968380	3.967269056779	0.767666329910
H	0.159631813992	6.012475583134	0.136765681182
H	2.718647347879	6.566022645167	0.386778257513
H	3.971732953956	4.395248425569	1.405434697041
H	3.460495460391	1.902557719778	1.451763073758
H	2.169468931240	0.012566070474	1.161770562796
H	-0.109102738573	-0.169780327403	0.574380901527
H	-1.633777511798	1.533015490717	0.165458955572
H	-1.319435739212	3.860591786855	0.252086758777
H	1.798792904262	5.917793489850	4.831855157154
H	0.202318475192	5.243275086307	4.486299882031
H	1.652444466628	4.397682718284	3.935598490704
H	-0.482641231965	8.135930896445	2.957108594468
H	1.168715594083	8.695833085778	3.227778324802
H	0.542782272125	8.560971987345	1.582548260801

ENERGY = -755.030984223648
Spin(**2) = 0.000000000000
ZPVE = 0.220920645983
SYMMETRY = C1

Table S8. Atomic Coordinates of **5"** Calculated at the B3PW91/6-311G(d) Level.

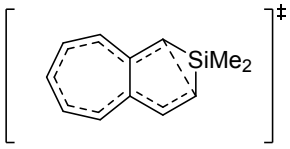


Atom	x	y	z
Si	1.253115657957	6.182058223341	2.647616456551
C	1.132400395111	6.400251770712	4.518540111009
C	0.966472585279	7.869229261460	1.851486725341
C	0.089567905351	4.895802387442	2.011533569321
C	2.875785564413	5.439513962795	2.137711916956
C	2.935546618566	4.261617036942	1.485493882381
C	1.840835308348	3.381825879958	1.069304250873
C	2.271646811084	2.251055263919	0.420274138702
C	1.603889911517	1.127074067840	-0.156728523518
C	0.273840592871	0.874954120900	-0.213057899881
C	-0.770221935534	1.701965700030	0.306585205876

C	-0.682811771410	2.888521388265	0.954171314069
C	0.429600803876	3.744999553105	1.356824384710
H	-0.980689047506	5.046822286999	2.161031308554
H	3.830265021615	5.923950984315	2.344986179093
H	3.920272435049	3.879185716427	1.213647696063
H	3.353324968339	2.187652369395	0.318209689792
H	2.264361874245	0.388140439392	-0.604216095251
H	-0.040399385504	-0.045148680182	-0.699845266909
H	-1.779195801243	1.322540412603	0.160156087218
H	-1.643174308316	3.310101825484	1.245545900553
H	1.867833988311	7.124759892510	4.884637082783
H	0.142953552188	6.767581444053	4.811511878761
H	1.304139733546	5.455645002252	5.041580793377
H	-0.025721694112	8.261100487449	2.099994689024
H	1.700719177376	8.604510850041	2.197962036925
H	1.037836828572	7.812800282544	0.761959127626

ENERGY = -755.054222397669
Spin(**2) = 0.000000000000
ZPVE = 0.221240596633
SYMMETRY = Cs

Table S9. Atomic Coordinates of **TS(4"-5")** Calculated at the B3PW91/6-311G(d) Level.



Atom	x	y	z
Si	1.230474870901	6.214055072440	2.588872195188
C	1.435995753934	5.396852002680	4.260793105783
C	0.724785063014	8.014538956689	2.719870718232
C	0.329109097243	5.338517332921	1.247038880363
C	2.428430982785	5.825157134316	1.262935435075
C	2.826853116909	4.459176408022	1.123078305845
C	1.886281415411	3.449985997458	1.111270437258
C	2.254204505829	2.076174872788	1.138765208531
C	1.522985027306	0.949019759226	0.868063586220
C	0.183067825499	0.849824289749	0.420097427217
C	-0.708293273960	1.861561699203	0.173710097506
C	-0.549921567288	3.253782536486	0.384781386121
C	0.499124742336	3.960260946413	0.927945843786
H	-0.423681161827	5.891616928387	0.683929433288
H	2.947255200212	6.579639974139	0.665996982283
H	3.874684276321	4.225439511341	0.941600691645
H	3.295896006375	1.900792180423	1.405856147971
H	2.052190523815	0.004649024654	0.972634085293
H	-0.171439624651	-0.159942981310	0.223709332594
H	-1.684730314467	1.561683126371	-0.199947283064
H	-1.431080181369	3.851946313251	0.154447229553
H	2.190279538730	5.912003013630	4.864315470396
H	0.496481034856	5.408263079896	4.822437771275
H	1.747579630944	4.355501652424	4.150051444441
H	-0.236872429017	8.121264334728	3.231654759590
H	1.459578356662	8.594589378252	3.286662120531
H	0.629411644763	8.472751116228	1.731722987209

ENERGY = -755.001550573164
Spin(**2) = 0.000000000000
ZPVE = 0.218606319133
SYMMETRY = C1

Table S10. Transition Energy, Wavelength, and Oscillator Strengths of Electronic Transitions of **2'** Calculated at the TD-B3LYP/6-311++G(d,p) Level (The 144th orbital is Highest Occupied Orbital Shown in Figure S9)

```
Excited State   1:      Singlet-A     3.1310 eV  395.99 nm  f=0.0380  <S**2>=0.000
    143 ->145         0.21492
    144 ->145         0.66696

 Excited State   2:      Singlet-A     3.8196 eV  324.60 nm  f=0.2088  <S**2>=0.000
    143 ->145         0.60709
    143 ->146         0.13963
    144 ->145        -0.16044
    144 ->146         0.26565

 Excited State   3:      Singlet-A     4.2319 eV  292.98 nm  f=0.4001  <S**2>=0.000
    143 ->145        -0.12871
    143 ->146        -0.36653
    144 ->145         0.10992
    144 ->146         0.56897

 Excited State   4:      Singlet-A     4.4767 eV  276.95 nm  f=0.7463  <S**2>=0.000
    142 ->145         0.19576
    143 ->145        -0.19424
    143 ->146         0.54443
    144 ->146         0.28986
    144 ->149         0.11080

 Excited State   5:      Singlet-A     4.5136 eV  274.69 nm  f=0.0001  <S**2>=0.000
    144 ->147         0.65292
    144 ->148        -0.11082
    144 ->149         0.13630
    144 ->150        -0.15386

 Excited State   6:      Singlet-A     4.7672 eV  260.08 nm  f=0.0114  <S**2>=0.000
    144 ->147         0.14958
    144 ->148         0.66257

 Excited State   7:      Singlet-A     4.8072 eV  257.91 nm  f=0.0510  <S**2>=0.000
    140 ->145         0.16850
    141 ->145         0.36945
    142 ->145         0.53469
    143 ->146        -0.13857

 Excited State   8:      Singlet-A     4.8556 eV  255.35 nm  f=0.0004  <S**2>=0.000
    141 ->145        -0.38888
    142 ->145         0.24009
    143 ->147         0.44832
    143 ->150        -0.16833
    144 ->149        -0.12152
    144 ->150        -0.11226

 Excited State   9:      Singlet-A     4.8631 eV  254.95 nm  f=0.0781  <S**2>=0.000
    141 ->145         0.42107
    142 ->145        -0.26648
    143 ->146         0.11406
    143 ->147         0.40543
    143 ->148        -0.11588
    143 ->149         0.11398
    144 ->149        -0.11728
```

```
Excited State  10:     Singlet-A     4.8948 eV  253.30 nm  f=0.0621  <S**2>=0.000
    143 ->147         0.17404
    144 ->147        -0.12973
    144 ->149         0.62738

Excited State  11:     Singlet-A     4.9364 eV  251.16 nm  f=0.0451  <S**2>=0.000
    143 ->147         0.16592
    144 ->147         0.12853
    144 ->148        -0.13303
    144 ->150         0.60629
    144 ->151         0.18011

Excited State  12:     Singlet-A     5.0478 eV  245.62 nm  f=0.0038  <S**2>=0.000
    143 ->148         0.14149
    144 ->150        -0.23006
    144 ->151         0.57055
    144 ->152        -0.17293
    144 ->153         0.17215

Excited State  13:     Singlet-A     5.0878 eV  243.69 nm  f=0.0114  <S**2>=0.000
    142 ->145         0.11577
    143 ->148        -0.16859
    143 ->149         0.55904
    143 ->150         0.22237
    144 ->151         0.10838
    144 ->152         0.14771
    144 ->154         0.10543

Excited State  14:     Singlet-A     5.1302 eV  241.68 nm  f=0.0034  <S**2>=0.000
    143 ->148         0.18899
    143 ->149        -0.10849
    144 ->152         0.61180
    144 ->153         0.19368

Excited State  15:     Singlet-A     5.1395 eV  241.24 nm  f=0.0021  <S**2>=0.000
    143 ->147         0.12877
    143 ->148         0.57973
    143 ->149         0.15906
    143 ->150         0.19932
    144 ->151        -0.14416
    144 ->153        -0.11567

Excited State  16:     Singlet-A     5.1744 eV  239.61 nm  f=0.0005  <S**2>=0.000
    140 ->145         0.32269
    144 ->151        -0.24405
    144 ->152        -0.12665
    144 ->153         0.41879
    144 ->154         0.31301

Excited State  17:     Singlet-A     5.1981 eV  238.52 nm  f=0.0067  <S**2>=0.000
    140 ->145         0.53564
    144 ->153        -0.36043
    144 ->155        -0.11308

Excited State  18:     Singlet-A     5.2563 eV  235.88 nm  f=0.0072  <S**2>=0.000
    139 ->145        -0.16718
    140 ->145        -0.21428
    143 ->149        -0.14686
    144 ->153        -0.21743
    144 ->154         0.52320
```

```
   144 ->155       -0.19646

Excited State  19:     Singlet-A     5.2734 eV  235.11 nm  f=0.0012  <S**2>=0.000
   139 ->145        0.53744
   143 ->147        0.11463
   143 ->149       -0.23248
   143 ->150        0.28742
   143 ->151        0.10566
   144 ->155       -0.15255

Excited State  20:     Singlet-A     5.2837 eV  234.65 nm  f=0.0018  <S**2>=0.000
   139 ->145       -0.38258
   143 ->147        0.13762
   143 ->148       -0.11975
   143 ->149       -0.14779
   143 ->150        0.45069
   143 ->151        0.17313
   144 ->154       -0.19566

Excited State  21:     Singlet-A     5.2912 eV  234.32 nm  f=0.0031  <S**2>=0.000
   143 ->153        0.11545
   144 ->153       -0.13089
   144 ->154        0.21795
   144 ->155        0.56810
   144 ->158        0.12158

Excited State  22:     Singlet-A     5.3742 eV  230.70 nm  f=0.0131  <S**2>=0.000
   143 ->150       -0.17247
   143 ->151        0.58243
   143 ->152       -0.15137
   143 ->154       -0.16101
   144 ->156       -0.17173

Excited State  23:     Singlet-A     5.4019 eV  229.52 nm  f=0.0057  <S**2>=0.000
   144 ->153       -0.12131
   144 ->156        0.49388
   144 ->157       -0.41685
   144 ->159        0.12024

Excited State  24:     Singlet-A     5.4206 eV  228.73 nm  f=0.0033  <S**2>=0.000
   143 ->151        0.15466
   143 ->154        0.13822
   144 ->155       -0.18444
   144 ->156        0.40144
   144 ->157        0.41035
   144 ->158        0.19935

Excited State  25:     Singlet-A     5.4756 eV  226.43 nm  f=0.0373  <S**2>=0.000
   143 ->151        0.17338
   143 ->152        0.32271
   143 ->153        0.31158
   143 ->154        0.36462
   143 ->155       -0.18181
   143 ->158       -0.10330
   144 ->158       -0.18151

Excited State  26:     Singlet-A     5.4781 eV  226.33 nm  f=0.0037  <S**2>=0.000
   143 ->152        0.38474
   143 ->153       -0.30721
   143 ->154       -0.16082
   144 ->155        0.12492
```

```
    144 ->156        0.10663
    144 ->157        0.20063
    144 ->158       -0.33581

 Excited State  27:     Singlet-A     5.4876 eV  225.94 nm  f=0.0104  <S**2>=0.000
    143 ->151        0.12776
    143 ->152        0.37798
    143 ->153       -0.18720
    144 ->157       -0.21747
    144 ->158        0.46282

 Excited State  28:     Singlet-A     5.5013 eV  225.37 nm  f=0.0136  <S**2>=0.000
    138 ->145        0.65946
    143 ->154        0.10197

 Excited State  29:     Singlet-A     5.5185 eV  224.67 nm  f=0.0114  <S**2>=0.000
    138 ->145        0.15632
    143 ->152        0.18990
    143 ->153        0.46790
    143 ->154       -0.35307
    143 ->155        0.16913

 Excited State  30:     Singlet-A     5.5660 eV  222.75 nm  f=0.0016  <S**2>=0.000
    144 ->157        0.12306
    144 ->158        0.13846
    144 ->159        0.64176
    144 ->161        0.10703

 Excited State  31:     Singlet-A     5.6160 eV  220.77 nm  f=0.0059  <S**2>=0.000
    143 ->155       -0.27054
    144 ->159        0.11132
    144 ->160        0.50619
    144 ->161       -0.13617
    144 ->162        0.11078
    144 ->163       -0.22257

 Excited State  32:     Singlet-A     5.6206 eV  220.59 nm  f=0.0031  <S**2>=0.000
    143 ->154        0.30334
    143 ->155        0.48088
    143 ->158        0.19453
    143 ->161       -0.10016
    144 ->160        0.21625
    144 ->163       -0.14396
    144 ->164        0.10745
```

Table S11. Transition Energy, Wavelength, and Oscillator Strengths of the Electronic Transition of **3'** Calculated at the TD-B3LYP/6-311++G(d,p) Level (The 109th orbital is Highest Occupied Orbital Shown in Figure S9)

```
Excited State   1:     Singlet-A     2.9174 eV  424.98 nm  f=0.0702  <S**2>=0.000
    109 ->110        0.69380

 Excited State   2:     Singlet-A     3.6786 eV  337.04 nm  f=0.1127  <S**2>=0.000
    108 ->110        0.30048
    109 ->111        0.62805

 Excited State   3:     Singlet-A     4.3692 eV  283.77 nm  f=0.3876  <S**2>=0.000
    105 ->110       -0.15098
    107 ->110       -0.12110
    108 ->110        0.58147
```

```
    108 ->111       -0.18427
    109 ->111       -0.23092

Excited State   4:     Singlet-A     4.5992 eV  269.58 nm  f=0.0061  <S**2>=0.000
    109 ->112        0.67685
    109 ->115       -0.13996

Excited State   5:     Singlet-A     4.7272 eV  262.28 nm  f=0.0274  <S**2>=0.000
    106 ->110       -0.28680
    108 ->111       -0.18889
    109 ->113       -0.32194
    109 ->114        0.39899
    109 ->115        0.22964
    109 ->116       -0.18897

Excited State   6:     Singlet-A     4.7316 eV  262.04 nm  f=0.0033  <S**2>=0.000
    106 ->110        0.49856
    107 ->110        0.39320
    109 ->113       -0.15873
    109 ->114        0.17400

Excited State   7:     Singlet-A     4.7797 eV  259.40 nm  f=0.1649  <S**2>=0.000
    106 ->110       -0.28267
    107 ->110        0.37597
    108 ->110        0.16882
    108 ->111        0.44965
    109 ->111       -0.13134
    109 ->113       -0.10103

Excited State   8:     Singlet-A     4.8998 eV  253.04 nm  f=0.0007  <S**2>=0.000
    109 ->112        0.13448
    109 ->114       -0.38118
    109 ->115        0.56105

Excited State   9:     Singlet-A     4.9066 eV  252.69 nm  f=0.0056  <S**2>=0.000
    109 ->113        0.54868
    109 ->114        0.33782
    109 ->115        0.23256

Excited State  10:     Singlet-A     4.9420 eV  250.88 nm  f=0.0708  <S**2>=0.000
    106 ->110        0.24281
    107 ->110       -0.38228
    108 ->111        0.44943
    109 ->113       -0.10450
    109 ->114        0.17535
    109 ->115        0.11236

Excited State  11:     Singlet-A     5.0528 eV  245.38 nm  f=0.0019  <S**2>=0.000
    105 ->110        0.12014
    109 ->113       -0.14919
    109 ->115        0.15890
    109 ->116        0.64033

Excited State  12:     Singlet-A     5.1398 eV  241.22 nm  f=0.0900  <S**2>=0.000
    105 ->110       -0.39609
    109 ->117        0.52704

Excited State  13:     Singlet-A     5.1568 eV  240.43 nm  f=0.1145  <S**2>=0.000
    105 ->110        0.45302
    107 ->111       -0.12209
    109 ->117        0.45439
```

```
    109 ->118       -0.12812

Excited State  14:     Singlet-A     5.1851 eV  239.12 nm  f=0.0220  <S**2>=0.000
    104 ->110        0.68175
    105 ->110        0.10322

Excited State  15:     Singlet-A     5.2860 eV  234.55 nm  f=0.0273  <S**2>=0.000
    109 ->118        0.64107
    109 ->119       -0.13747
    109 ->121       -0.15127

Excited State  16:     Singlet-A     5.3444 eV  231.99 nm  f=0.0004  <S**2>=0.000
    109 ->118        0.14778
    109 ->119        0.65761
    109 ->122        0.10693

Excited State  17:     Singlet-A     5.3608 eV  231.28 nm  f=0.0083  <S**2>=0.000
    103 ->110       -0.40478
    105 ->110        0.13993
    106 ->111        0.31497
    107 ->111        0.41592

Excited State  18:     Singlet-A     5.4074 eV  229.29 nm  f=0.0060  <S**2>=0.000
    103 ->110        0.43672
    106 ->111        0.28944
    107 ->111        0.20029
    109 ->119        0.10322
    109 ->120        0.34230
    109 ->121       -0.11964

Excited State  19:     Singlet-A     5.4091 eV  229.21 nm  f=0.0189  <S**2>=0.000
    103 ->110       -0.30257
    106 ->111       -0.19438
    109 ->120        0.54312
    109 ->122       -0.18032

Excited State  20:     Singlet-A     5.4643 eV  226.90 nm  f=0.0058  <S**2>=0.000
    106 ->111        0.15665
    109 ->118        0.13612
    109 ->120        0.15813
    109 ->121        0.56777
    109 ->122        0.22359
    109 ->123       -0.16297

Excited State  21:     Singlet-A     5.5096 eV  225.04 nm  f=0.0080  <S**2>=0.000
    109 ->120        0.12469
    109 ->121       -0.34403
    109 ->122        0.49818
    109 ->123       -0.27317

Excited State  22:     Singlet-A     5.5153 eV  224.80 nm  f=0.0300  <S**2>=0.000
    102 ->110       -0.14639
    106 ->111        0.43199
    107 ->111       -0.39298
    109 ->122       -0.23144
    109 ->123       -0.13602

Excited State  23:     Singlet-A     5.5517 eV  223.33 nm  f=0.0269  <S**2>=0.000
    107 ->111       -0.17190
    109 ->120        0.11890
    109 ->122        0.25916
```

```
   109 ->123       0.58594

Excited State  24:     Singlet-A     5.6549 eV  219.25 nm  f=0.0071  <S**2>=0.000
   102 ->110       0.21519
   105 ->111       0.23675
   109 ->124       0.55658
   109 ->125       0.20171
   109 ->128      -0.10756

Excited State  25:     Singlet-A     5.6741 eV  218.51 nm  f=0.0016  <S**2>=0.000
   102 ->110      -0.28931
   105 ->111      -0.26879
   109 ->124       0.37660
   109 ->125      -0.36665
   109 ->127       0.11035
   109 ->131      -0.10347

Excited State  26:     Singlet-A     5.7059 eV  217.29 nm  f=0.0115  <S**2>=0.000
   101 ->110       0.18169
   102 ->110      -0.10372
   105 ->111      -0.40011
   107 ->111       0.13754
   109 ->125       0.45982

Excited State  27:     Singlet-A     5.7693 eV  214.90 nm  f=0.0158  <S**2>=0.000
   101 ->110       0.12929
   102 ->110      -0.25518
   105 ->111       0.21590
   108 ->112       0.10045
   109 ->125       0.14120
   109 ->126       0.23849
   109 ->127       0.36376
   109 ->128      -0.30440

Excited State  28:     Singlet-A     5.7910 eV  214.10 nm  f=0.0045  <S**2>=0.000
   102 ->110       0.21845
   105 ->111      -0.21223
   108 ->112      -0.24641
   109 ->126       0.52211
   109 ->128      -0.11325

Excited State  29:     Singlet-A     5.8071 eV  213.50 nm  f=0.0145  <S**2>=0.000
    96 ->110      -0.10042
    99 ->110      -0.11064
   101 ->110       0.58651
   102 ->110       0.15662
   106 ->110       0.10413
   108 ->112      -0.13363
   109 ->125      -0.13492

Excited State  30:     Singlet-A     5.8224 eV  212.94 nm  f=0.0095  <S**2>=0.000
   101 ->110      -0.11292
   102 ->110       0.15345
   105 ->111      -0.16777
   108 ->112      -0.25619
   109 ->124      -0.10933
   109 ->126      -0.31803
   109 ->127       0.43312
   109 ->128      -0.15486

Excited State  31:     Singlet-A     5.8303 eV  212.65 nm  f=0.0006  <S**2>=0.000
```

```
    101 ->110       -0.12632
    104 ->111        0.63069
    105 ->111        0.14416
    108 ->112       -0.18059

Excited State  32:     Singlet-A     5.8556 eV  211.74 nm  f=0.0128  <S**2>=0.000
    102 ->110        0.23886
    104 ->111        0.18510
    105 ->111       -0.13287
    108 ->112        0.51789
    108 ->113       -0.10150
    108 ->116       -0.10575
    109 ->127        0.18623
```

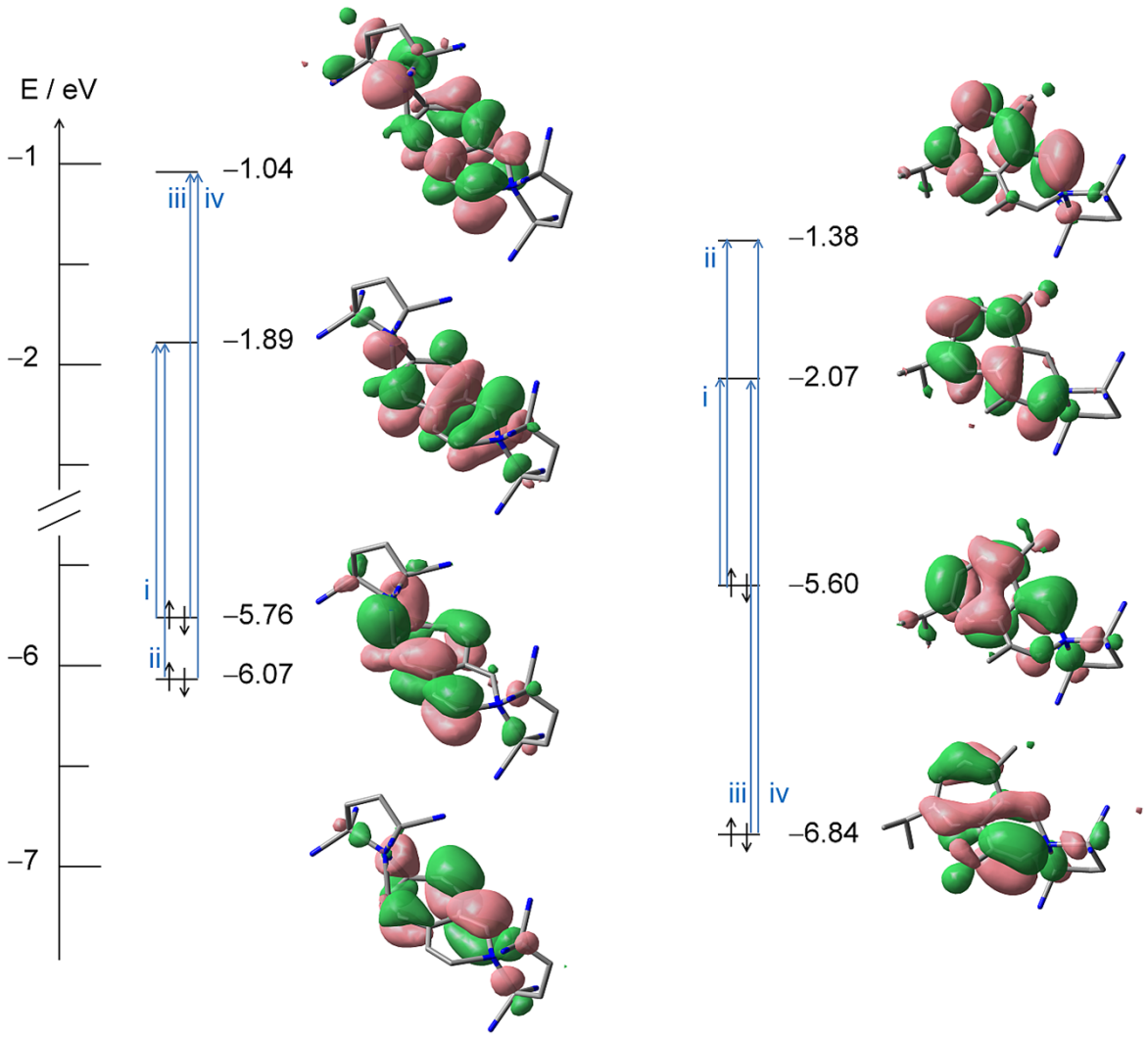
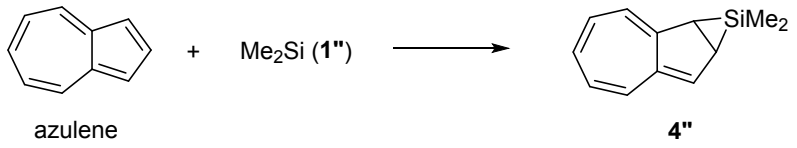


Figure S9. Frontier Kohn-Sham orbitals, their energy levels of **2'** (left) and **3'** (right) at the B3LYP/6-311++G(d,p)//B3LYP/6-311G(d) level. Transitions i-iv mainly contribute calculated absorption bands a-d shown in Figure 2 in the main text, respectively.

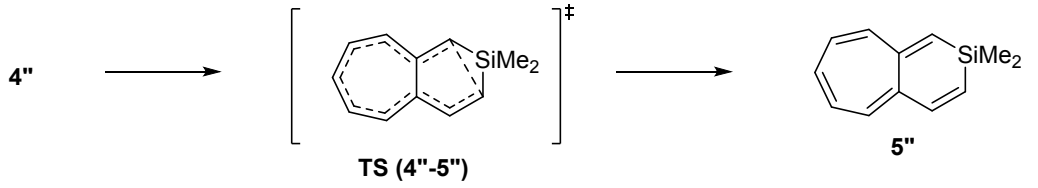
i) Addition of dimethylsilylene to azulene



azulene **4"**

ΔE = -100.3 kJ/mol
ΔG(298K) = -50.3 kJ/mol

ii) Isomerization of **4"** to **5"**

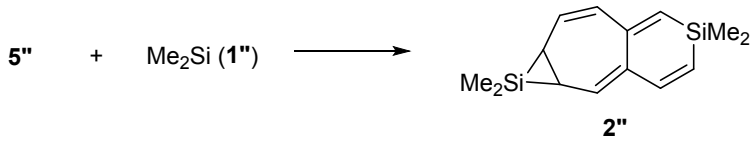


TS (4"-5") **5"**

ΔE = +71.2 kJ/mol
ΔG(298K) = +72.6 kJ/mol

ΔE = -60.2 kJ/mol
ΔG(298K) = -62.8 kJ/mol

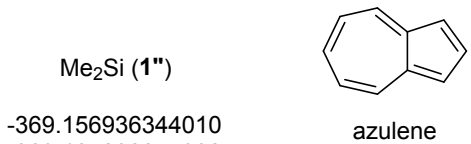
iii) Addition of dimethylsilylene to **5"**



2"

ΔE = -141.1 kJ/mol
ΔG(298K) = -87.5 kJ/mol

Figure S10. Calculated enthalpies and Gibbs energies at the B3PW91/6-311G(d) level.

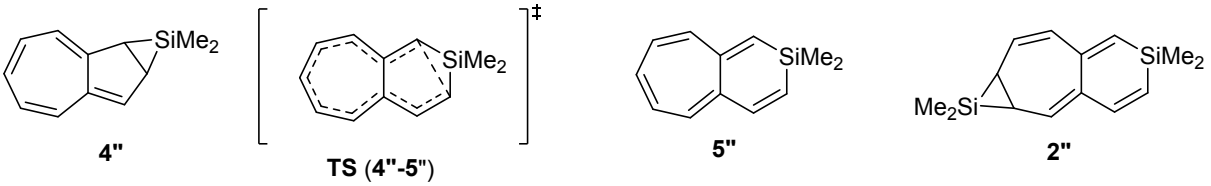


Me2Si (**1"**)

-369.156936344010
-369.184238874932

azulene

-385.614910671386
-385.645805851537



4" **TS** (**4"-5"**) **5"** **2"**

-754.810063501769	-754.782944178930	-754.832981725030	-1124.043644281558
-754.849338478524	-754.821675651563	-754.873270775312	-1124.090853164392

Chart S1. Calculated enthalpies (including a zero-point vibrational energy, upper) and Gibbs energies at 298 K (lower) at the B3PW91/6-311G(d) level. All geometries are optimized at the same level.

5. References

S1 M. Kira, S. Ishida, T. Iwamoto and C. Kabuto, *J. Am. Chem. Soc.* 1999, **121**, 9722.

S2 (a) G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997. (b) G. M. Sheldrick, SADABS, Empirical Absorption Correction Program; Göttingen, Germany, 1996.

S3 Yadokari-XG 2009, Release of Software for Crystal Structure Analyses, C. Kabuto, S. Akine, T. Nemoto and E. Kwon, *J. Cryst. Soc. Jpn.* 2009, **51**, 218.

S4 Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

S5 GRRM14: S. Maeda, Y. Harabuchi, Y. Osada, T. Taketsugu, K. Morokuma, K. Ohno, http://grrm.chem.tohoku.ac.jp/GRRM/index_e.html. See also, S. Maeda, K. Ohno and K. Morokuma, *Phys. Chem. Chem. Phys.*, 2013, **15**, 3683-3701.

S6 2PSHS: S. Maeda and K. Ohno, *Chem. Phys. Lett.*, 2005, **404**, 95-99.