Supporting Information

Formation of 1-Ethynyl-1H-Silole from Reaction of Silicon Atoms with Benzene: Matrix Infrared Spectroscopy and Quantum Chemical Calculations

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Table S1. Comparison of the observed and calculated harmonic vibrational frequencies, intensities (in Parentheses) of the Si[η^2(1,4)-C_6H_6] complex **(A)** and seven-membered ring cyc-SiC_6H_6 species **(B)**.

Si[η^2(1,4)-C_6H_6]				cyc-SiC_6H_6			
exptl	exptl [a]	calcd	calcd [a]	exptl	exptl [a]	calcd	calcd [a]
1600.2	1599.3	1653.2 (23)	1649.1 (22)	- - -	1475.9	1509.2 (88)	1508.9 (94)
1456.2	1465.5	1493.9 (9)	1492.9 (9)	1398.2	1389.3	1431.6 (91)	1428.2 (95)
1328.5	1338.3	1372.7 (13)	1367.9 (11)	613.6	618.5	633.2 (43)	629.0 (55)
1267.4 (site) 1262.6	1261.1	1289.8 (24)	1289.9 (26)	592.2	596.4	592.5 (56)	591.9 (56)
954.3	953.5	967.1 (39)	972.6 (45)				
925.7	924.6	931.6 (10)	931.7 (8)				
849.6	851.0	866.3 (59)	862.9 (64)				
836.5	836.8	847.2 (19)	846.8 (20)				
712.4	713.9	731.9 (29)	728.0 (32)				
503.7	502.8	492.9 (28)	492.9 (30)				

[a] The IR data previously observed by Reisenauer et al. in solid argon. [ref. 28] The calculated IR intensities are listed in parentheses in km/mol

Table S2. Calculated vibrational frequencies of species **A** and **B**. The calculated IR intensities are listed in parentheses in km/mol

A	**B**
3195.4 (20)	3154.4 (29)
3189.8 (14)	3133.7 (13)
3176.1 (10)	3097.1 (4)
3171.3 (5)	3095.8 (72)
3153.7 (1)	3068.5 (0)
3151.6 (17)	3067.3 (12)
1653.2 (23)	1638.8 (5)
1493.9 (9)	1594.5 (2)
1372.7 (13)	**1509.2 (88)**
1349.3 (6)	1502.7 (8)
1314.0 (0)	**1431.6 (91)**
1289.8 (24)	1415.5 (0)
1131.7 (2)	1319.8 (4)
1109.6 (0)	1284.5 (2)
1053.9 (1)	1252.6 (1)
1030.9 (1)	1069.8 (0)
1022.7 (2)	1061. 7 (2)
973.6 (0)	1051.7 (0)
967.1 (39)	1036.6 (0)
931.6 (10)	896.3 (1)
926.4 (0)	885.7 (3)
879.1 (3)	881.1 (1)
866.3 (59)	828.7 (0)
847.2 (19)	722.9 (13)
731.9 (29)	**633.2 (43)**
701.4 (3)	630.7 (4)
612.7 (0)	**592.5 (56)**
584.6 (0)	548.9 (0)
492.9 (28)	372.3 (0)
461.4 (1)	358.9 (0)
411.9 (0)	330.6 (4)
346.0 (0)	170.8 (0)
297.0 (3)	84.6 (1)

Table S3. Experimental and Calculated Harmonic Vibrational Frequencies, Intensities (in Parentheses), and Isotopic Frequency Ratios of the1-ethynyl-1H-silole (**C**).

	Exp					Cal				
	C_6H_6	$^{13}C_6H_6$	C_6D_6	$^{12}C/^{13}C$	H/D	C_6H_6	$^{13}C_6H_6$	C_6D_6	$^{12}C/^{13}C$	H/D
C	3313.2	3296.6	2611.5	1.0050	1.2687	3455.0 *(50)*	3436.5	2686.8	1.0054	1.2859
	2176.9	2177.2	1583.2	0.9999	1.3750	2214.4 *(94)*	2214.4	1592.7	1.0000	1.3903
	2053.8	1980.8	1927.3	1.0368	1.0656	2143.7 *(26)*	2066.9	1995.7	1.0372	1.0742
	866.3	849.9	725.3	1.0193	1.1944	872.1 *(59)*	853.9	731.5	1.0213	1.1922
	823.6	820.4	636.5	1.0039	1.2939	824.3 *(239)*	821.2	688.7	1.0038	1.1969
	723.9	716.5	602.8	1.0103	1.2009	725.8 *(35)*	718.9	576.4	1.0096	1.2592
	681.4	678.0	--	1.0050	--	695.3 *(104)*	691.4	541.3	1.0056	1.2845
	643.4	629.1	--	1.0227	--	638.4 *(60)*	625.1	584.5	1.0213	1.0922

Table S4. Comparison of the observed and calculated vibrational frequencies, intensities (in parentheses, w=weak, m=moderate, s=strong), and isotopic frequency of the1-ethynyl-1H-silole (**C**).

C_6H_6	$^{13}C_6H_6$	C_6D_6	Exptl
3455.0 (50)	**3436.5 (51)**	**2686.8 (14)**	**3313.2 (w)**
3204.3 (3)	3193.6 (2)	2375.8 (5)	
3203.1 (5)	3192.5 (5)	2372.3 (1)	
3151.1 (32)	3141.1 (32)	2324.7 (14)	
3136.6 (9)	3127.0 (9)	2314.8 (6)	
2214.4 (94)	**2214.3 (94)**	**1592.7 (59)**	**2176.9 (m)**
2143.7 (26)	**2066.9 (23)**	**1995.7 (42)**	**2053.8 (m)**
1617.5 (2)	1561.9 (2)	1563.4 (4)	
1541.6 (11)	1483.2 (10)	1519.3 (9)	
1368.4 (11)	1346.9 (11)	1186.5 (8)	
1315.9 (3)	1300.0 (4)	1071.0 (1)	
1118.7 (2)	1111.1 (1)	875.8 (19)	
1107.8 (10)	1105.6 (10)	797.4 (13)	
1009.2 (1)	1000.8 (1)	792.3 (4)	
1006.7 (0)	995.6 (0)	829.5 (0)	
941.5 (13)	916.1 (13)	837.2 (32)	
872.1 (59)	**853.9 (60)**	**731.5 (24)**	**866.3 (m)**
824.3 (239)	**821.2 (238)**	**688.7 (112)**	**823.6 (s)**
761.9 (0)	753.0 (0)	602.4 (0)	
756.2 (9)	738.3 (11)	639.4 (95)	
725.8 (35)	**719.0 (35)**	**576.4 (14)**	**723.9 (w)**
719.0 (41)	**712.3 (44)**	**565.6 (8)**	
697.8 (4)	691.8 (3)	522.6 (4)	
695.3 (104)	**691.4 (95)**	**541.3 (92)**	**681.4 (w)**
638.4 (60)	**625.1 (57)**	**584.5 (3)**	**643.3 (w)**
618.6 (3)	602.7 (3)	600.6 (5)	
489.8 (20)	481.2 (20)	451.0 (3)	
447.0 (6)	435.0 (5)	392.1 (10)	
391.5 (5)	378.5 (4)	366.0 (3)	
305.8 (9)	296.7 (8)	274.9 (6)	
252.7 (4)	244.7 (4)	230.0 (3)	
115.8 (1)	112.8 (1)	104.5 (0)	
91.4 (1)	89.2 (0)	84.6 (0)	

Table S5. Calculated vibrational frequencies, intensities (in Parentheses), and isotopic frequency of the 2-ethynyl-2H-silole Complexes (**C-isomer1**).

C_6H_6	$^{13}C_6H_6$	C_6D_6
3467.7 (100)	**3449.6 (96)**	**2691.1 (86)**
3201.8 (3)	3191.2 (3)	2371.8 (2)
3162.4 (18)	3152.2 (18)	2337.4 (9)
3143.1 (16)	3133.4 (16)	2319.5 (12)
2223.9 (90)	**2223.9 (90)**	**1607.4 (55)**
2220.4 (86)	**2220.4 (86)**	**1589.1 (56)**
2178.2 (21)	**2099.1 (20)**	**2042.0 (3)**
1608.4 (2)	1553.3 (2)	1562.0 (1)
1527.4 (5)	1469.8 (4)	1509.8 (5)
1357.2 (9)	1335.5 (9)	1190.9 (5)
1287.3 (3)	1271.7 (3)	1032.7 (1)
1181.0 (4)	1148.8 (3)	1150.0 (4)
1090.5 (9)	1075.8 (11)	862.4 (19)
1009.2 (0)	999.2 (1)	825.9 (0)
998.7 (5)	973.2 (9)	796.6 (1)
942.0 (90)	**940.9 (86)**	**687.6 (65)**
935.1 (11)	923.3 (13)	765.0 (0)
845.8 (74)	**830.9 (75)**	**715.2 (30)**
747.1 (84)	**741.6 (83)**	**585.0 (39)**
719.4 (8)	710.8 (5)	552.8 (12)
688.6 (19)	**681.9 (17)**	**570.2 (43)**
649.7 (43)	**644.5 (43)**	**513.0 (12)**
641.6 (44)	**635.9 (43)**	**490.6 (14)**
633.8 (1)	615.9 (2)	**612.7 (0)**
616.7 (2)	598.6 (3)	590.2 (0)
606.1 (11)	596.2 (13)	514.8 (6)
465.3 (19)	454.6 (18)	435.4 (24)
455.0 (6)	443.1 (5)	396.1 (12)
429.0 (3)	416.7 (2)	412.1 (0)
391.0 (1)	383.4 (1)	311.9 (1)
247.7 (2)	242.3 (2)	204.8 (1)
145.6 (1)	141.8 (1)	133.5 (1)
140.6 (1)	136.3 (1)	127.4 (1)

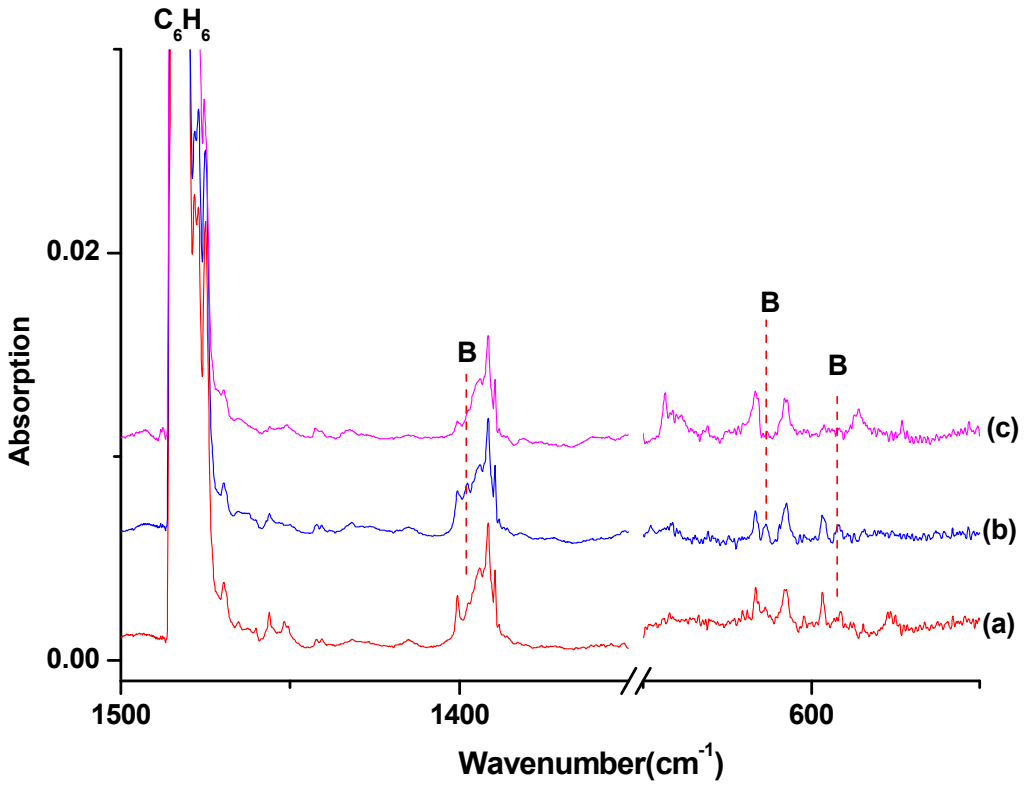


Figure S1 Infrared spectra in the 1500-1350 cm^{-1} and 650-550 region cm^{-1} from co-deposition of silicon atoms with 0.025 % benzene in solid neon. (a) afterwards annealing to 12 K, (b) after 15 min of UV−visible light (280 <λ< 580 nm) irradiation at 4K, (c) after 15 min of UV−visible light (250 <λ< 580 nm) irradiation at 4K.

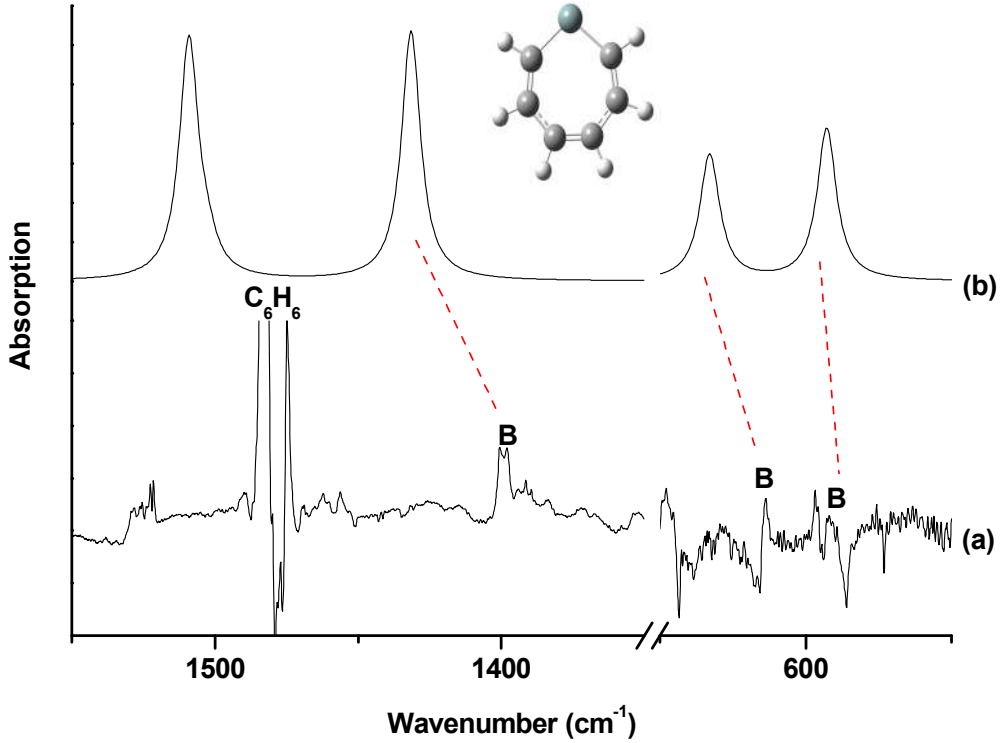


Figure S2. Infrared spectra in the 1550-1350 cm^{-1} and 650-550 cm^{-1} region from (a) spectra taken after 15 min full UV light irradiation minus spectrum after 15 min 280 <λ< 580 nm UV light irradiation; (b) calculated IR spectrum of 1-silacycloheptatrienylidene.

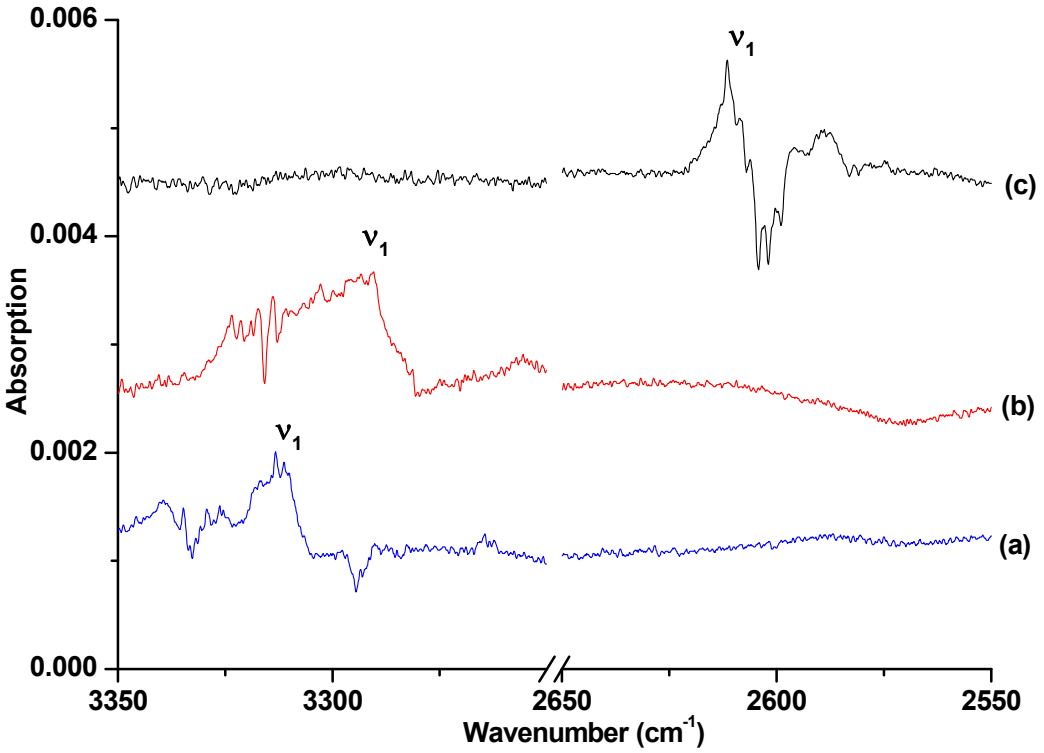
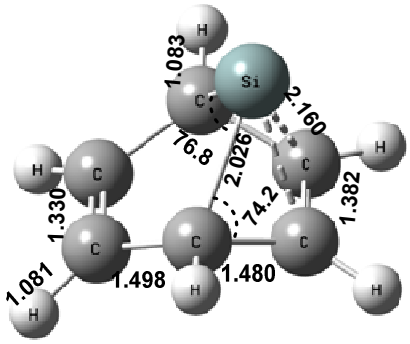
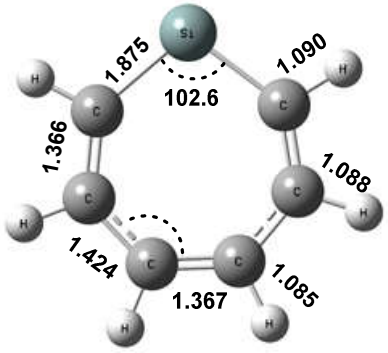


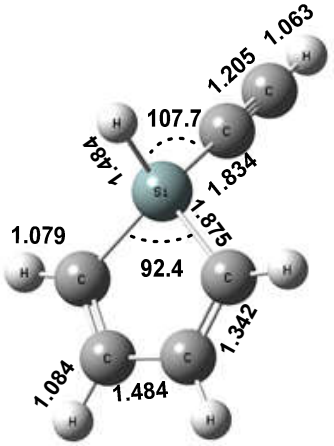
Figure S3. Infrared spectra in the 3350-3250 and 2650-2550 cm^{-1} regions from co-deposition of silicon with isotopic labeled benzene in solid neon (spectra taken after 15 min full UV light irradiation minus spectrum after annealing to 12 K): (a) Si+0.025 % C_6H_6, (b) Si +0.025 % $^{13}C_6H_6$, (d) Si +0.025 % C_6D_6.



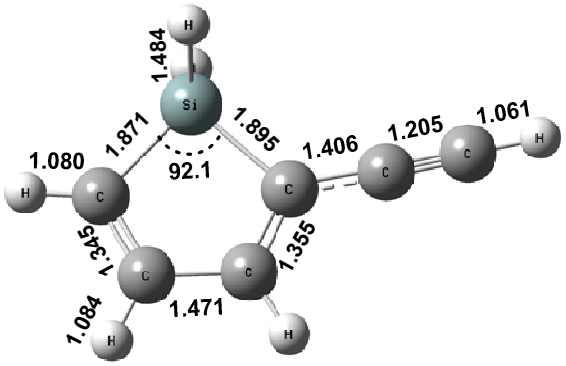
A, C_s, $^1A'$



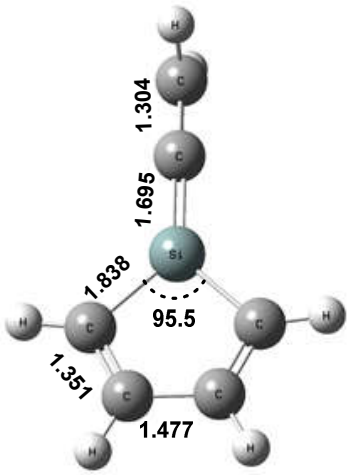
B, C_{2v}, $^1A_1$



C, C_s, $^1A'$
E=0 kJ mol^{-1}



C-isomer1, C_s, $^1A'$
E=23 kJ mol^{-1}



C-isomer2, C_{2v}, $^1A_1$
E=61 kJ mol^{-1}

Figure S4. Optimized structures and relative stabilities of singlet state species **A-C** and **C**-isomers at the B3LYP/aug-cc-pVTZ level. (bond lengths in angstrom and bond angles in degrees).

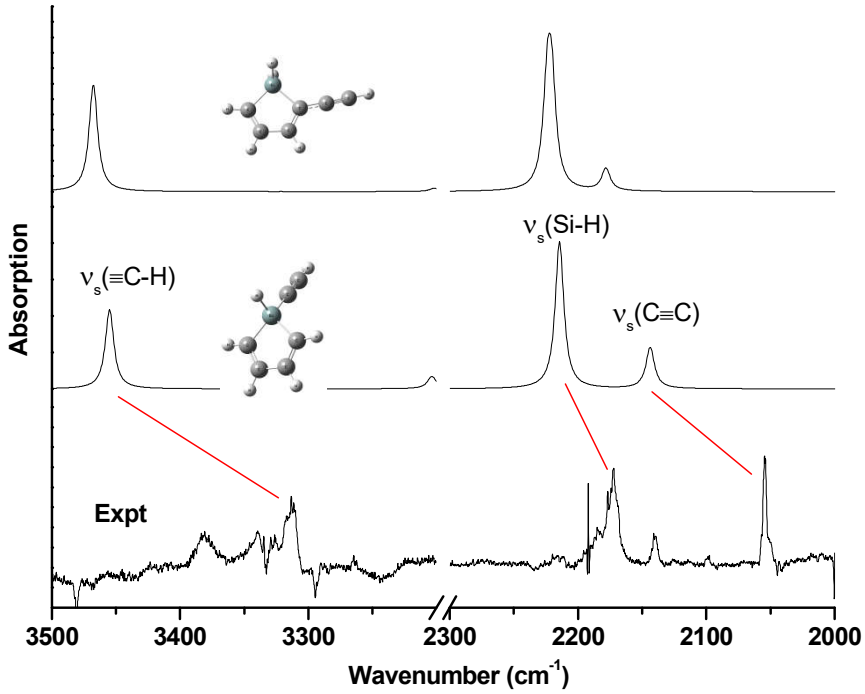


Figure S5. The experimental IR spectrum of 1-ethynyl-1H-silole in the solid neon matrix and its computed isomers spectrum (unscaled) in the 3500–3200 and 2300–2000 cm^{-1} range (ν_s- stretching vibration).

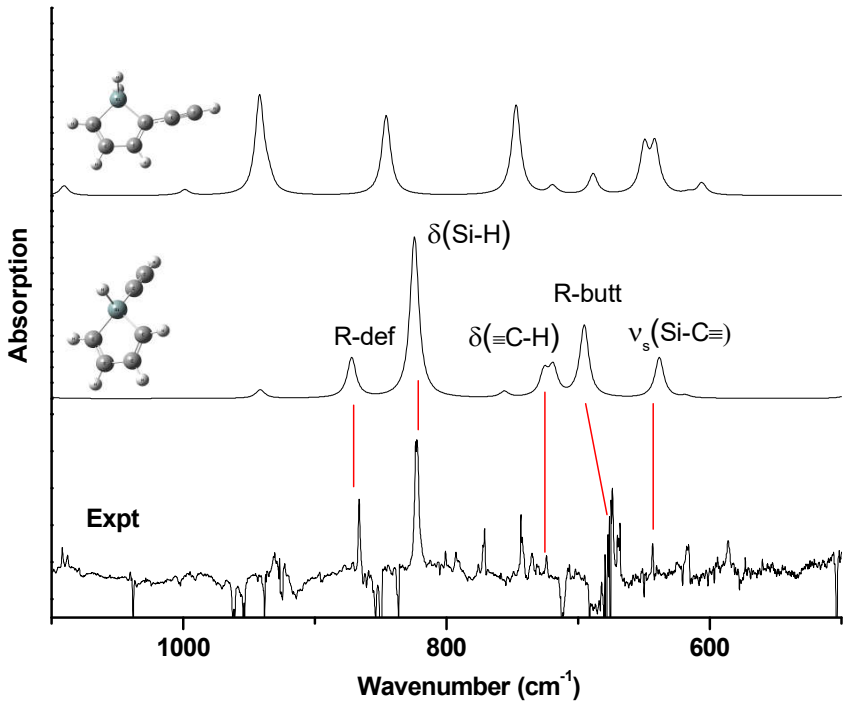
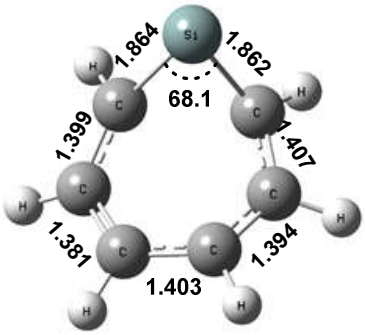
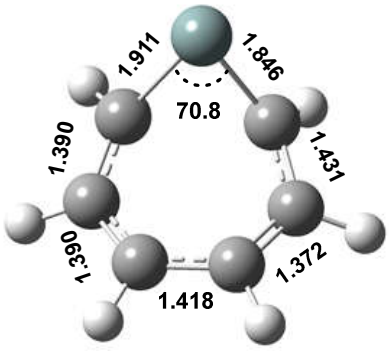


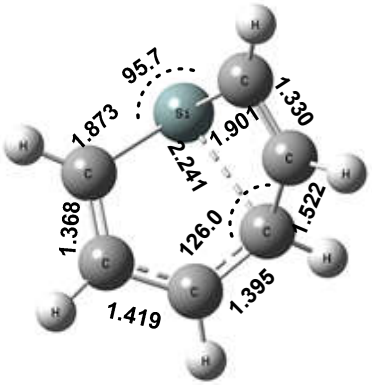
Figure S6. The experimental IR spectrum of 1-ethynyl-1H-silole in the solid neon matrix and its computed isomers spectrum (unscaled) in the 1100–500 cm^{-1} range (δ-wagging, ν_s- stretching vibration, R-ring, def-deformation, butt-butterfly).



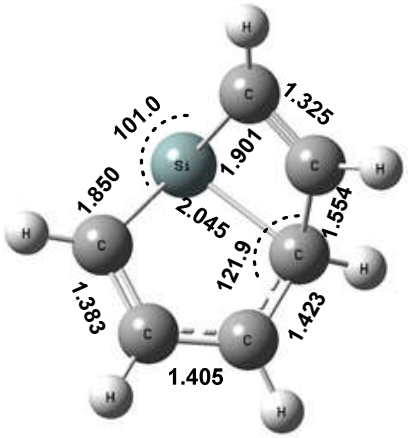
^{1}TS1, C_1, ^{1}A



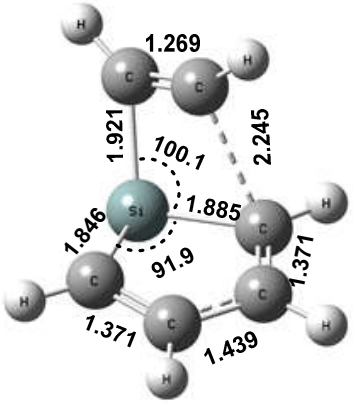
^{3}TS1, C_1, ^{3}A



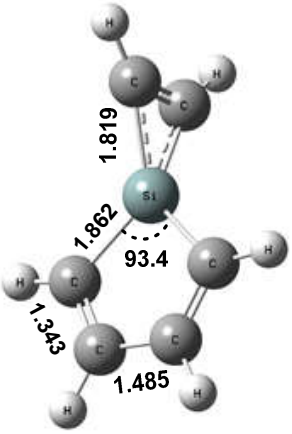
^{1}TS2, C_1, ^{1}A



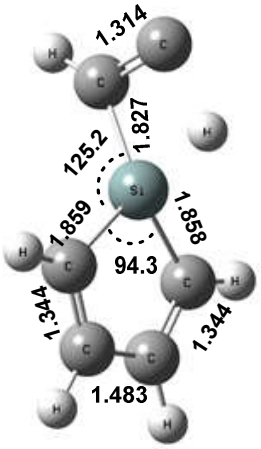
^{1}I1, C_1, ^{1}A



^{1}TS3, C_1, ^{1}A



^{1}I2, C_{2v}, ^{1}A$_1$



^{1}TS4, C_1, ^{1}A

Figure S7. Optimized structures of the intermediates and transition states involved in the reaction pathways are shown in Figure 6. Bond lengths in angstroms and bond angles in degrees.

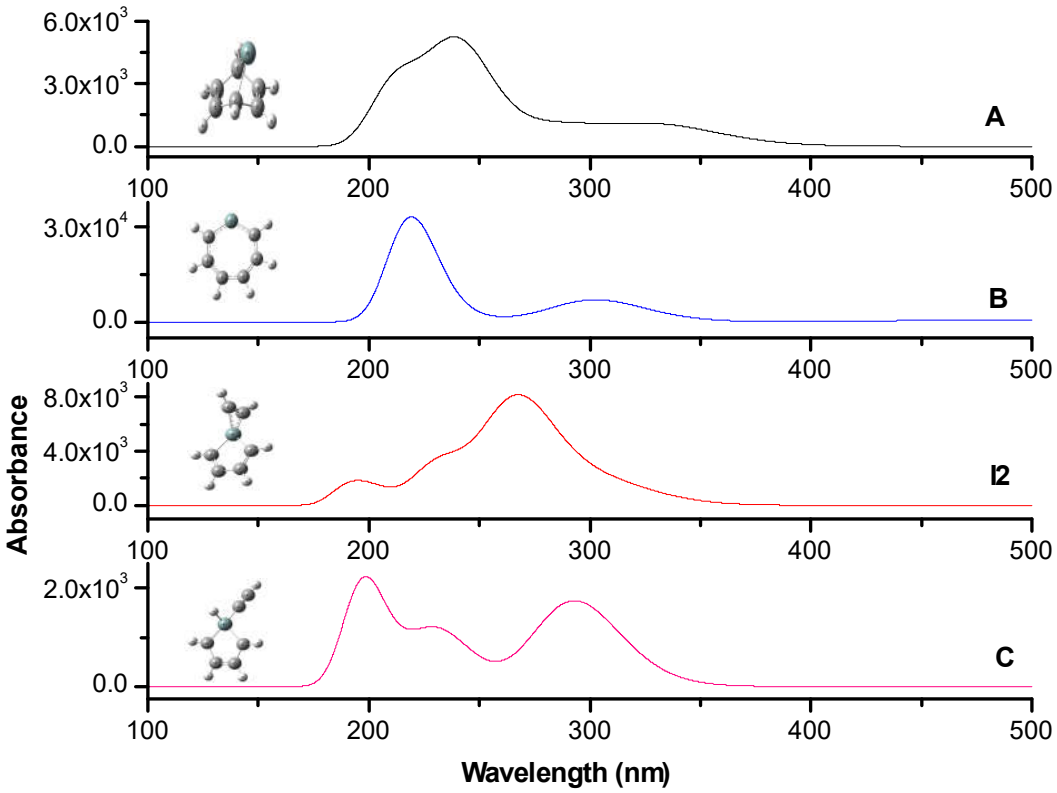


Figure S8. The calculated electronic absorptions spectra for the species **A**, **B**, **I2**, and **C** at the B3LYP/aug-cc-pVTZ level.

Table S6. Calculated atomic coordinates (in Angstroms) of SiC_6H_6 isomers **A-C** and **C-isomer1** at the B3LYP/aug-cc-pVTZ level.

A, (C_s, $^1A'$)

C	0.03677900	-1.56324000	0.66512900
C	0.03677900	-1.56324000	-0.66512900
C	0.03677900	-0.18705700	-1.25827400
C	-1.00418000	0.69951300	-0.69076900
C	-1.00418000	0.69951300	0.69076900
C	0.03677900	-0.18705700	1.25827400
H	-0.05386600	-2.44413500	1.28587900
H	-0.05386600	-2.44413500	-1.28587900
H	0.19562300	-0.09423100	-2.32512100
H	-1.62090400	1.36491100	-1.27901300
H	-1.62090400	1.36491100	1.27901300
H	0.19562300	-0.09423100	2.32512100
Si	1.00898300	1.06830900	0.00000000

B, (C_{2v}, $^1A_1$)

C	0.00000000	0.68331100	-1.73648700
C	0.00000000	-0.68331100	-1.73648700
C	0.00000000	-1.63486100	-0.67711800
C	0.00000000	1.63486100	-0.67711800
C	0.00000000	-1.46325800	0.67833800
C	0.00000000	1.46325800	0.67833800
H	0.00000000	2.66136800	-1.03882500
H	0.00000000	1.13144400	-2.72416100
H	0.00000000	-1.13144400	-2.72416100
H	0.00000000	-2.66136800	-1.03882500
H	0.00000000	-2.41146000	1.21644000
H	0.00000000	2.41146000	1.21644000
Si	0.00000000	0.00000000	1.85116400

C, (C_s, $^1A'$)

C	0.42120500	-0.70872000	1.35316500
C	0.42120500	-1.90373900	0.74204600
C	0.42120500	-1.90373900	-0.74204600
C	0.42120500	-0.70872000	-1.35316500
H	0.41970400	-0.60129100	2.42758100
H	0.41963700	-2.84892100	1.27414800
H	0.41963700	-2.84892100	-1.27414800
H	0.41970400	-0.60129100	-2.42758100
Si	0.46083100	0.58824900	0.00000000
C	-0.96725700	1.73872000	0.00000000
C	-1.90140200	2.50080700	0.00000000
H	-2.72627700	3.17101800	0.00000000
H	1.69899900	1.40626900	0.00000000

C-isomer1, (C_s, $^1A'$)

C	-0.66460700	-2.01003600	0.00000000
C	-1.67290300	-1.11888200	0.00000000
C	-1.31905000	0.30858300	0.00000000
C	0.00000000	0.61838200	0.00000000
H	-0.83467100	-3.07645800	0.00000000
H	-2.71954800	-1.40270900	0.00000000
H	-2.09643800	1.06357200	0.00000000
Si	0.93066400	-1.03216200	0.00000000
H	1.77162300	-1.22567300	1.20724200
H	1.77162300	-1.22567300	-1.20724200
C	0.53715300	1.91766700	0.00000000
C	1.05073700	3.00816800	0.00000000
H	1.49013300	3.97392100	0.00000000