Supporting Information

Directed Gas Phase Preparation of Singlet Ethylsilanediyl Carbene (HCCSiH; X^1A') - The Isovalent Counterpart of Triplet Propargylene (HCCCH; X^3B)

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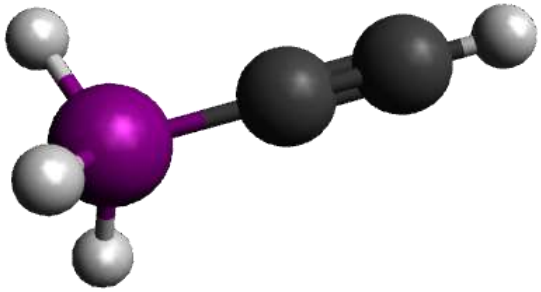
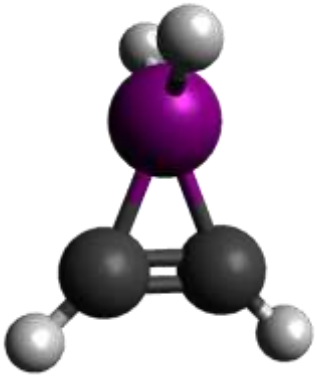
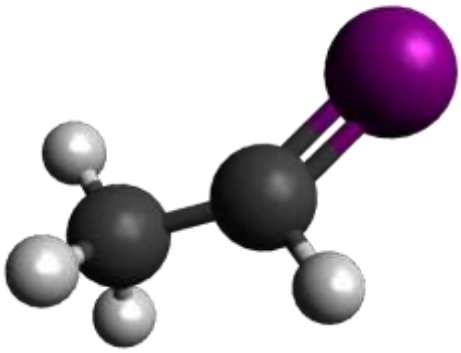
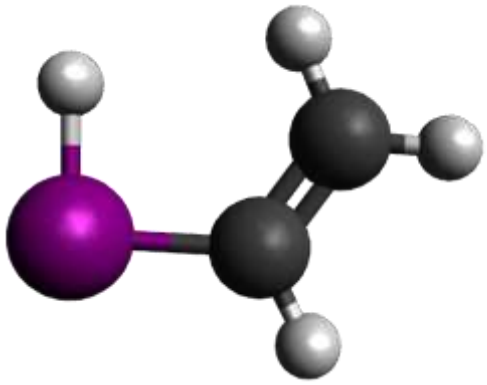
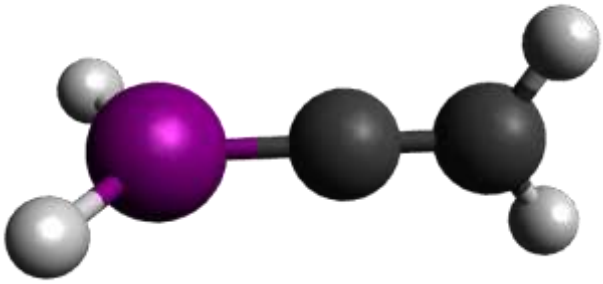
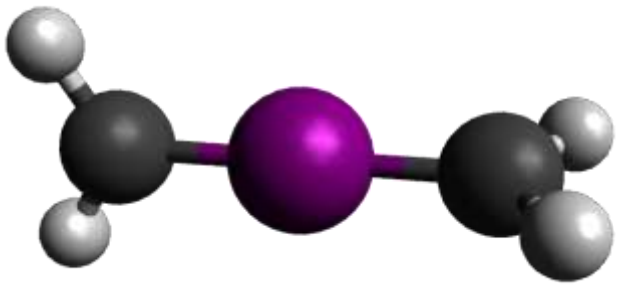
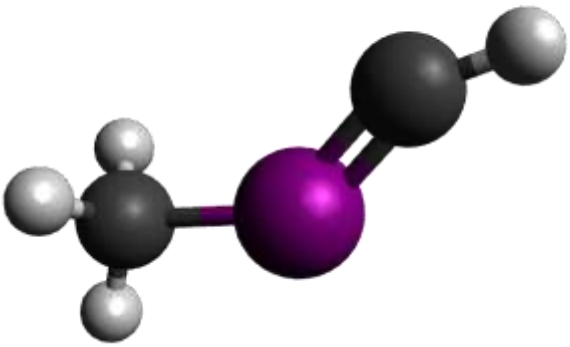
Table S1: Geometries of intermediates computed via ωB97M-V//def2-tzvpd. Relative energies are computed via sMP3: ωB97M-V//CBS.

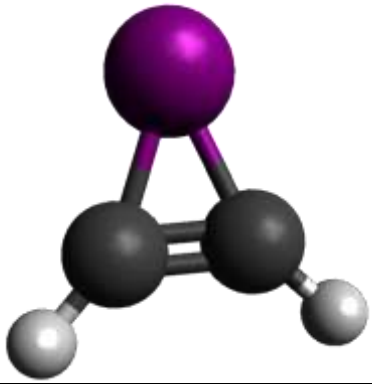
							
[i1]				[i2]			
C_{3v}				C_{2v}			
-619.3				-576.8			
Si	0.000000	0.000000	0.000000	Si	0.000000	0.000000	0.000000
C	-0.854274	-1.501931	-0.601048	C	-1.385740	0.665319	-0.947500
C	-1.416438	-2.489479	-0.997117	C	-1.385740	-0.665320	-0.947500
H	0.000000	0.000000	1.473943	H	-2.015172	1.431230	-1.377092
H	1.386926	0.000000	-0.499099	H	0.000000	0.000000	1.473717
H	-0.709797	1.191598	-0.498997	H	1.373606	0.000000	-0.534185
H	-1.914724	-3.362298	-1.347914	H	-2.015177	-1.431231	-1.377084
							

[i3]				[i4]			
C_s				C_s			
-543.2				-537.7			
Si	0.000000	0.000000	0.000000	Si	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.690359	H	0.000000	0.000000	1.521865
C	-0.807437	-0.001497	2.952639	C	1.873965	0.000000	-0.104193
H	1.102362	0.000000	1.849234	H	2.357030	0.000604	-1.080119
H	-1.875503	0.002242	2.737876	C	2.675269	-0.000729	0.966700
H	-0.589058	0.874483	3.567211	H	2.264814	-0.001335	1.970632
H	-0.594195	-0.882590	3.561763	H	3.759406	-0.000733	0.885808
							
[i5]				[i6]			
C_{2v}				D_{2d}			
-520.9				-462.8			
Si	0.000000	0.000000	0.000000	Si	0.000000	0.000000	0.000000
C	-1.435609	-0.005504	-0.870819	C	0.000000	0.000000	1.681602
C	-2.552493	-0.009442	-1.546599	C	-0.019317	0.012310	-1.681453
H	0.000000	0.000000	1.465207	H	0.923481	0.000000	2.242241
H	1.299293	0.000000	-0.677274	H	-0.924997	-0.006593	2.239877
H	-3.044370	0.912434	-1.846159	H	-0.016232	-0.907247	-2.248515
H	-3.040616	-0.934759	-1.841662	H	-0.023334	0.941160	-2.233305

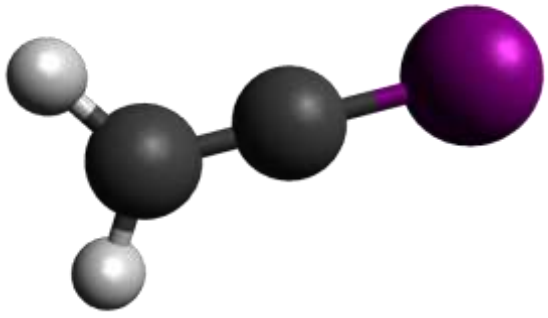


[i7]			
C_s			
-437.9			
Si	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.617522
C	-1.274405	0.000000	-1.368558
H	0.493160	0.000000	2.572365
H	-0.794681	0.008328	-2.344394
H	-1.902574	0.883529	-1.268852
H	-1.891939	-0.892100	-1.279003

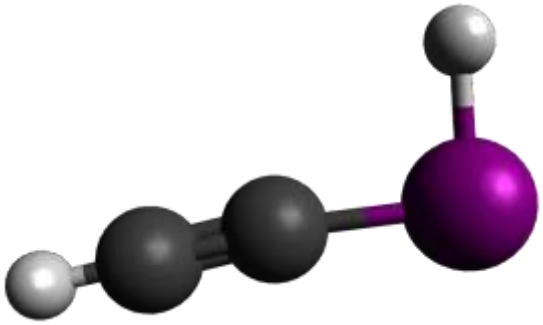
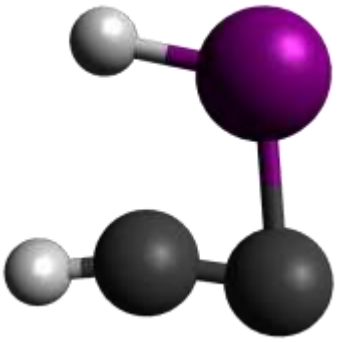
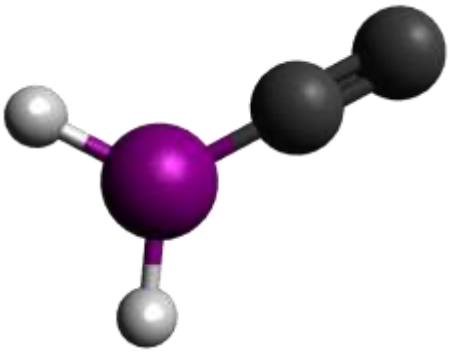
Table S2: Geometries of products computed via ωB97M-V//def2-tzvpd. Relative energies are computed via sMP3: ωB97M-V//CBS.



p1

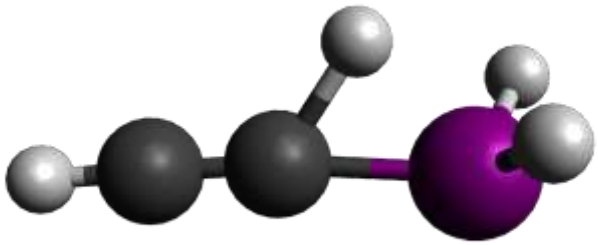
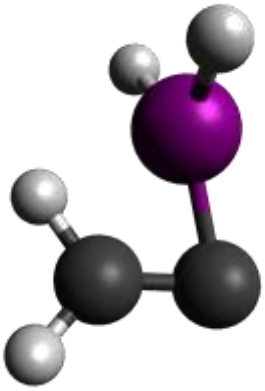


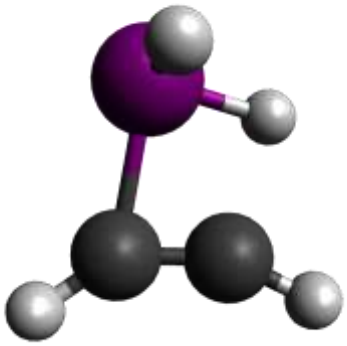
p2

C_{2v}				C_{2v}			
-486.9				-410.4			
Si	0.000000	0.000000	0.000000	Si	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.817019	C	0.000000	0.000000	1.688304
C	-1.244711	0.000000	1.323868	C	0.004466	0.000000	3.005001
H	0.422898	0.000000	2.812631	H	0.377646	-0.843751	3.581926
H	-2.234855	0.000000	1.759543	H	-0.364252	0.843412	3.585310
							
p3				p4			
C_s				C_s			
-406.0				-321.7			
Si	0.000000	0.000000	0.000000	Si	0.000000	0.000000	0.000000
C	1.837023	0.000000	-0.102990	C	1.860857	0.000000	-0.560224
C	3.030036	-0.000154	-0.306592	C	1.976322	0.000054	0.691721
H	0.000000	0.000000	1.516063	H	0.000000	0.000000	1.537499
H	4.082213	-0.000293	-0.471476	H	2.312622	0.000139	1.706620
							
p5				p6			
C_{2v}				C_{2v}			
-291.3				-263.8			

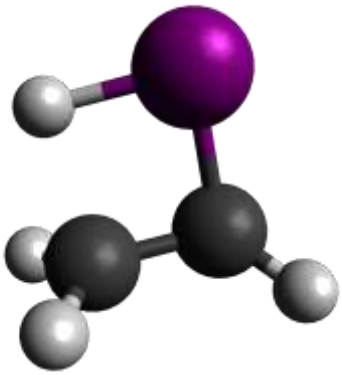
Si	0.000000	0.000000	0.000000	Si	-0.003946	0.000000	-0.002651
C	-1.389952	0.623924	-0.995810	C	-1.401693	0.000000	-0.933726
C	-1.389483	-0.626390	-0.995441	C	-2.453402	0.000000	-1.634145
H	0.000000	0.000000	1.471856	H	-0.001566	0.000000	1.464801
H	1.393799	0.000000	-0.472955	H	1.351148	0.000000	-0.565841

Table 3 :Geometries of transition states between intermediates computed via ωB97M-V//def2-tzvpd. Relative energies are computed via sMP3:ωB97M-V//CBS.

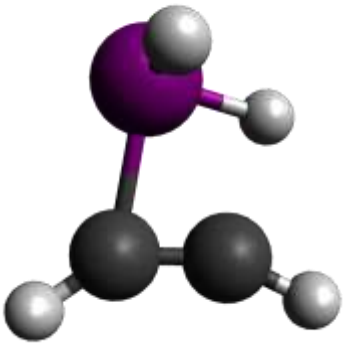
							
[i1] → [i2]				[i1] → [i5]			
C_s				C_1			
-341.2				-347.7			
Si	0.000000	0.000000	0.000000	Si	0.000000	0.000000	0.000000
C	-0.905563	-1.492108	-0.593622	C	-1.457613	-0.044499	-1.073976
C	-1.590068	-2.392332	-1.039303	C	-1.335073	-1.314056	-0.618213
H	0.231986	-1.635415	0.174963	H	0.000000	0.000000	1.472106
H	0.000000	0.000000	1.474913	H	1.378992	0.000000	-0.522256
H	1.363533	0.000000	-0.563492	H	-1.722817	-2.229280	-1.059793
H	-2.198545	-3.167641	-1.438338	H	-0.727597	-1.677895	0.324803



[i2] → [i4]			
C_1			
-418.8			
Si	0.000000	0.000000	0.000000
C	1.313987	-1.723682	-0.142780
C	0.094397	-1.932846	-0.360950
H	2.334544	-2.006755	0.017354
H	0.000000	0.000000	1.513813
H	1.517476	0.000000	-0.262374
H	-0.633836	-2.699740	-0.543994



[i3] → [i4]			
C_1			
-429.2			
Si	0.000000	0.000000	0.000000
C	1.727651	-0.335722	0.120605
C	1.711900	0.000000	1.491774
H	1.555887	-0.756931	2.250009
H	2.175947	0.910193	1.877335
H	0.000000	0.000000	1.592738
H	2.504449	-0.065333	-0.578511



[i4] → [i5]			
C_1			
-416.2			
Si	0.000000	0.000000	0.000000
C	0.733589	1.613930	-0.167785
C	1.300063	2.741027	-0.475919
H	0.000000	0.000000	1.503368
H	1.527111	0.000000	-0.300568

H	2.364349	2.901925	-0.357420
H	0.692702	3.558949	-0.848822

Table S4: Geometries of transition states between intermediates and products computed via ωB97M-V//def2-tzvpd. Relative energies are computed via sMP3: ωB97M-V//CBS.

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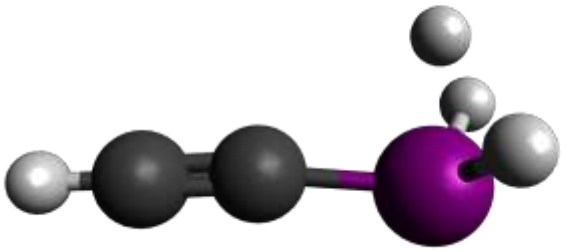
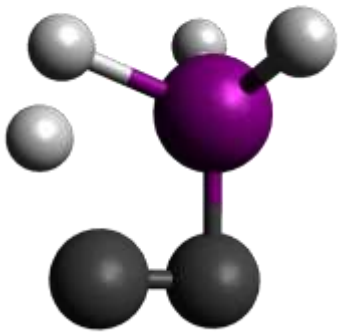
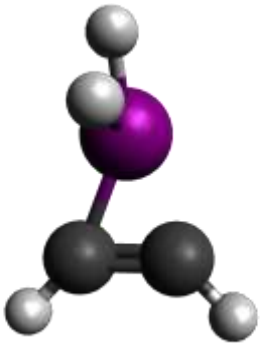
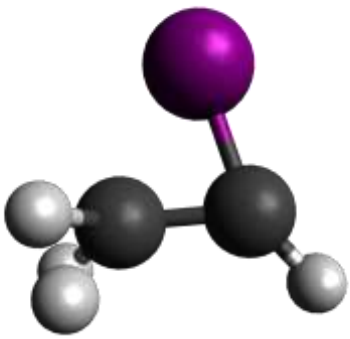
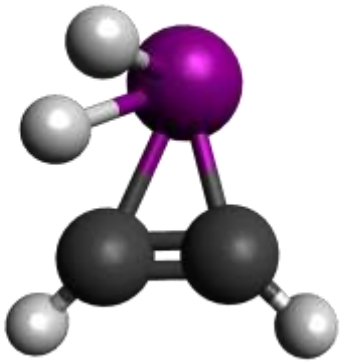
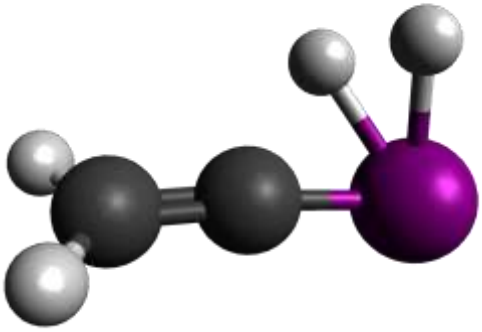
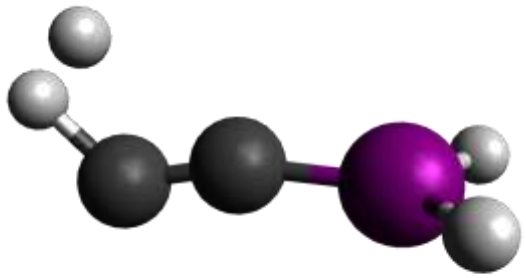
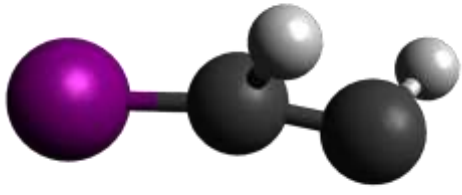
<tr><td colspan="4">  </td><td colspan="4">  </td></tr>
<tr><td colspan="4">[i1] → p3</td><td colspan="4">[i1] → p5</td></tr>
<tr><td colspan="4">C_1</td><td colspan="4">C_s</td></tr>
<tr><td colspan="4">-368.9</td><td colspan="4">-253.7</td></tr>
<tr><td>Si</td><td>0.000000</td><td>0.000000</td><td>0.000000</td><td>Si</td><td>0.000000</td><td>0.000000</td><td>0.000000</td></tr>
<tr><td>C</td><td>-0.888711</td><td>1.443961</td><td>-0.674208</td><td>C</td><td>-1.700902</td><td>0.398136</td><td>-1.123744</td></tr>
<tr><td>C</td><td>-1.572862</td><td>2.308346</td><td>-1.159266</td><td>C</td><td>-1.340547</td><td>-0.783616</td><td>-0.879820</td></tr>
<tr><td>H</td><td>1.352086</td><td>0.897109</td><td>0.216043</td><td>H</td><td>-0.075837</td><td>1.748386</td><td>-0.057228</td></tr>
<tr><td>H</td><td>0.000000</td><td>0.000000</td><td>1.474082</td><td>H</td><td>-0.823191</td><td>1.567615</td><td>-0.549988</td></tr>
<tr><td>H</td><td>1.433941</td><td>0.000000</td><td>-0.485603</td><td>H</td><td>0.000000</td><td>0.000000</td><td>1.466637</td></tr>
<tr><td>H</td><td>-2.167088</td><td>3.082572</td><td>-1.583384</td><td>H</td><td>1.345671</td><td>0.000000</td><td>-0.583354</td></tr>
<tr><td colspan="4">  </td><td colspan="4">  </td></tr>
</table>

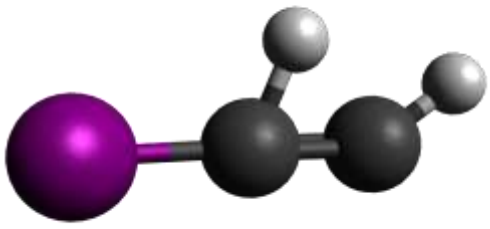
[i2] → p1				[i3] → p1			
C_s				C_1			
-270.6				-280.0			
Si	0.000000	0.000000	0.000000	Si	0.000000	0.000000	0.000000
C	0.873321	-0.667969	-1.436732	C	0.000000	0.000000	1.727005
C	0.873321	0.667972	-1.436731	C	-1.352955	-0.313896	1.391217
H	0.000000	0.000000	1.484863	H	0.462079	0.000000	2.701028
H	1.277116	-1.425052	-2.093433	H	-1.999840	-1.126497	1.695625
H	1.231419	0.000000	1.209189	H	-2.257603	0.632452	1.105559
H	1.277115	1.425055	-2.093431	H	-2.261452	0.664268	1.963708
							
[i4] → p1				[i4] → p2			
C_1				C_1			
-336.5				-353.9			
Si	0.000000	0.000000	0.000000	Si	0.000000	0.000000	0.000000
C	1.846216	0.769674	0.305676	C	1.371373	1.066785	0.262273
C	0.955823	1.657330	-0.043749	C	2.451987	1.807532	0.307760
H	0.000000	0.000000	1.665975	H	0.000000	0.000000	1.647367
H	2.922070	0.664101	0.289527	H	0.983695	0.000000	1.339072
H	0.971524	0.000000	1.359227	H	3.438883	1.383097	0.459499
H	0.998983	2.653771	-0.456962	H	2.390549	2.886186	0.199770



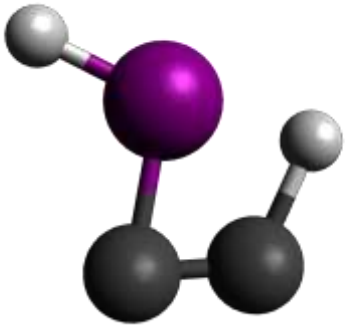
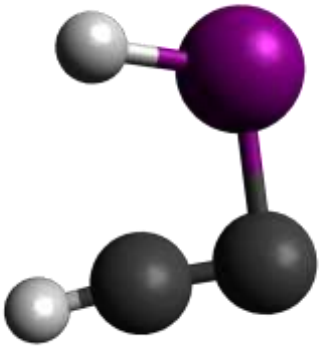
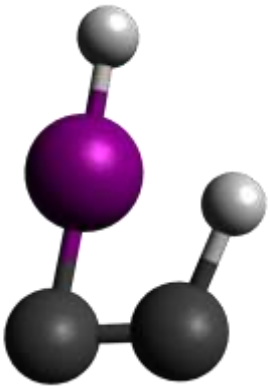
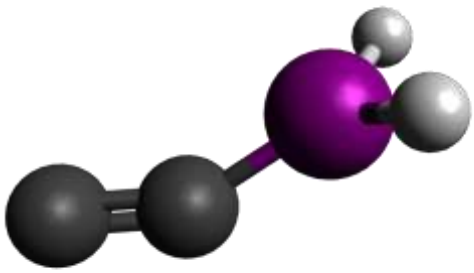
[i5] → p6			
C_s			
-170.8			
Si	0.000000	0.000000	0.000000
C	-1.431315	-0.094778	-0.881376
C	-2.510865	0.163091	-1.538868
H	0.000000	0.000000	1.465210
H	1.308865	0.000000	-0.658697
H	-3.333039	-0.693515	-2.030707
H	-2.886432	-1.389510	-1.763599

Table 5: Geometries of transition states between products computed via ωB97M-V//def2-tzvpd. Relative energies are computed via sMP3: ωB97M-V//CBS.





p1 → p2	p1 → p3
C_1	C_s

-121.0				-121.9			
Si	-0.062767	-0.086183	0.073070	Si	0.000000	0.000000	0.000000
C	0.026965	0.001523	1.814762	C	0.000000	0.000000	1.765972
C	-0.047514	0.261554	3.134472	C	-0.028708	0.001261	3.064140
H	1.121746	0.079120	2.282205	H	1.092270	0.000000	2.215600
H	-0.241059	-0.624165	3.756313	H	0.581793	-0.020638	3.953872
							
p1 → p5				p3 → p4			
C_s				C_1			
-94.1				-318.3			
Si	0.000000	0.000000	0.000000	Si	0.000000	0.000000	0.000000
C	-1.088881	0.079717	-1.633286	C	1.871756	0.000000	-0.406579
C	-1.739954	0.104904	-0.526823	C	2.162771	-0.583517	0.642726
H	0.000000	0.000000	1.479743	H	0.000000	0.000000	1.536241
H	0.343083	0.000000	-1.584918	H	2.504813	-1.034226	1.549757
							
p4 → p5				p5 → p6			
C_s				C_1			
-49.7				-263.9			
Si	0.000000	0.000000	0.000000	Si	0.000000	0.000000	0.000000

C	1.289444	0.000000	-1.444773	C	-1.397294	0.051727	-0.933125
C	-0.035347	0.000000	-1.769526	C	-2.318623	-0.563657	-1.541139
H	0.000000	0.000000	1.461972	H	0.000000	0.000000	1.468240
H	1.609119	0.000000	-0.059355	H	1.356377	0.000000	-0.562206

Table S6: RRKM reaction rate constants and imaginary frequencies of transition states

Reaction	k_f (s^{-1})	k_b (s^{-1})	ω_b (cm^{-1})
[i1] → [i2]	4.99E+10	1.20E+12	-888
[i1] → [i5]	4.98E+09	4.84E+10	-343
[i2] → [i4]	1.64E+12	1.34E+12	-814
[i3] → [i4]	1.76E+11	3.22E+11	-992
[i4] → [i5]	1.96E+12	9.63E+11	-874
[i1] → p3	1.10E+11		-1218
[i1] → p5	8.04E+08		-1000
[i2] → p1	1.72E+10		-1610
[i3] → p1	5.19E+09		-1445
[i4] → p1	6.70E+10		-1469
[i4] → p2	2.86E+11		-1318
[i5] → p6	1.80E+09		-1070

Table S7: RRKM reaction rate constants and imaginary frequencies of transition states for product rearrangement assuming maximum possible internal energy of **p3**.

Reaction	k_f (s^{-1})	k_b (s^{-1})	ω_b (cm^{-1})
p1→ p2	1.09E+10	3.72E+10	-718
p1 → p3	2.11E+11	2.62E+10	-1158
p1 → p5	1.82E+10	4.21E+10	-1581
p3 → p4	9.88E+11	1.10E+13	-335
p4 → p5	9.77E+08	1.62E+09	-1180
p5 → p6	1.35E+13	1.82E+12	-80

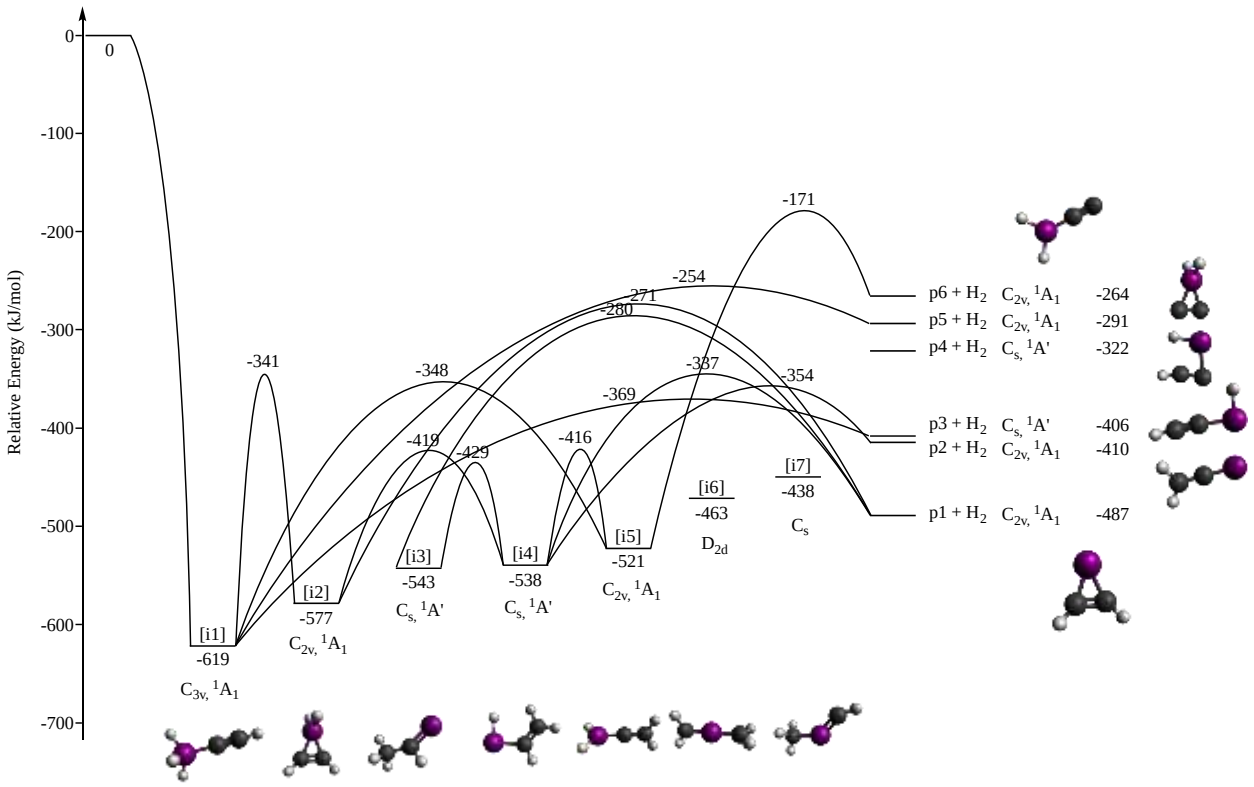


Figure S1: Complete potential energy surface of the reaction of C_2 + SiH_4 computed via sMP3: ωB97M-V//CBS. Relative energies are given in kJ mol^{-1}.

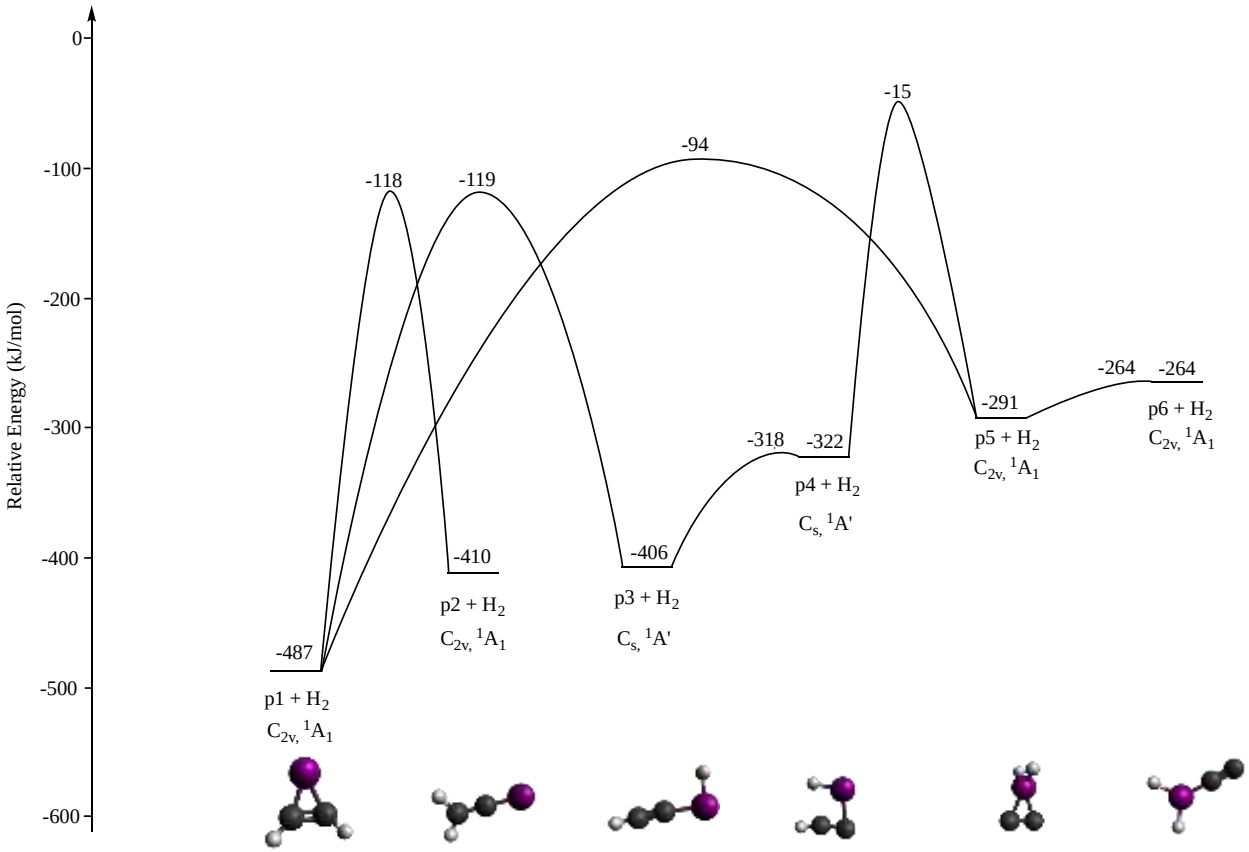


Figure S2: Potential energy surface of SiC_2H_2 isomerization computed via sMP3: ωB97M-V//CBS. Relative energies are given in kJ mol^{-1}.