

## Supporting Information

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## 1. Computational details

All structures were optimized in gas phase by Minnesota hybrid meta density functional theory method of Zhao and Truhlar M06-2X,<sup>1</sup> using the 6-311G(d,p) basis set<sup>2</sup> with an ultrafine grid. Frequency calculations were performed at the same level of theory to identify all stationary points as minima (zero imaginary frequency and one imaginary frequency for transition state). Reliability of DFT calculations was consolidated when  $\Delta E$ s at M06-2X was compared with the single-point CCSD(T)<sup>3</sup> calculated  $\Delta E$  using the same basis set for the following changes (from Figure 1): **1-H**→**2-H** (34.7 vs 36.5 kcal mol<sup>-1</sup>), **1-CH<sub>3</sub>**→**2-CH<sub>3</sub>** (41.0 vs 43.3 kcal mol<sup>-1</sup>), **1-SiH<sub>3</sub>**→**2-SiH<sub>3</sub>** (27.8 vs 31.7 kcal mol<sup>-1</sup>), **1-SiF<sub>3</sub>**→**2-SiF<sub>3</sub>** (24.6 vs 28.7 kcal mol<sup>-1</sup>), **1-F**→**2-F** (62.5 vs 63.2 kcal mol<sup>-1</sup>), and **1-BH<sub>2</sub>**→**2-BH<sub>2</sub>** (11.4 vs 14.8 kcal mol<sup>-1</sup>). Stable singlet state character of the species was confirmed through checking the wavefunction stability, and comparing singlet-triplet energy, following the procedure described by Massimiliano Arca and co-workers.

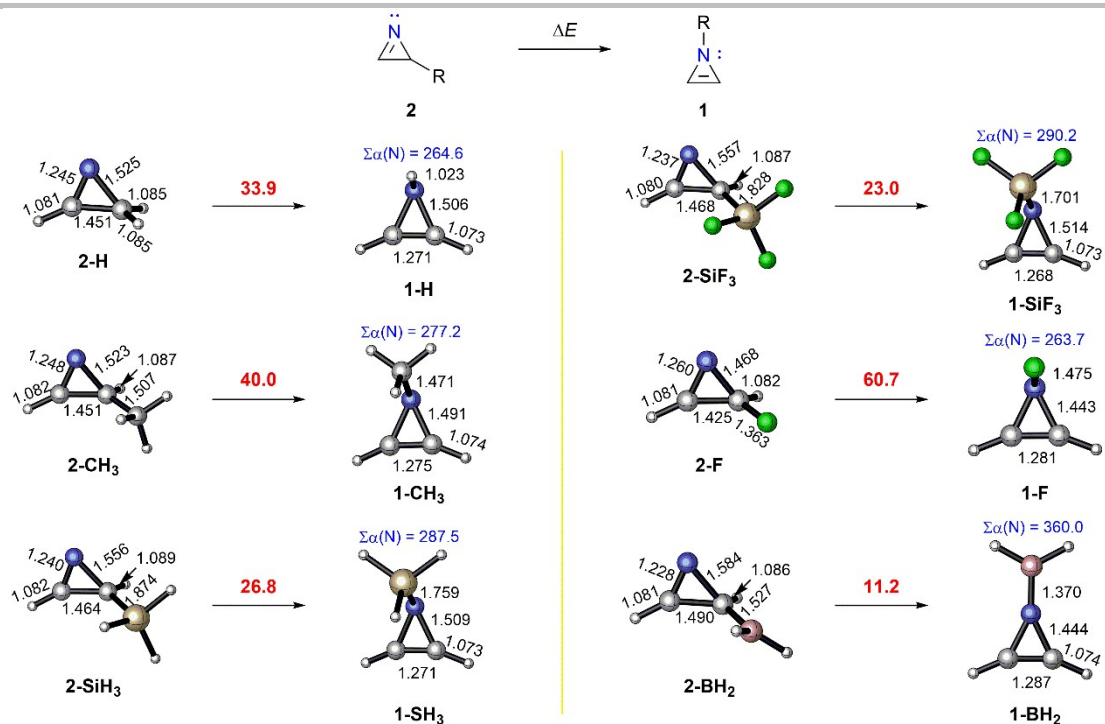
We applied the synchronous transit-guided quasi-Newton (STQN) method to calculate transition states (TSs), developed by H. B. Schlegel and coworkers.<sup>5</sup> It uses a linear synchronous transit or quadratic synchronous transit approach to get closer to the quadratic region around the TS and then uses a quasi-Newton or eigenvector-following algorithm to complete the optimization. For energy minimizations, it uses redundant internal coordinates by default to perform optimizations. Using an empirical estimate of the Hessian and suitable starting structures, this method will converge efficiently to the actual TS. The STQN method is requested with the "QST2" and "QST3" options to the "Opt" keyword. As its input, QST2 requires two molecule specifications, i.e., reactant and product. However, QST3 requires three molecule specifications, (in the order of) reactant, product, and an initial structure for the TS. Here, we employed QST2 keyword. After getting a suitable transition state (TS), its connection with the corresponding reactant, product, and/or intermediate was confirmed through intrinsic reaction coordinate (IRC) calculations.<sup>6</sup> Both reaction path directions (forward and backward) were followed requiring initial force constants from TS calculations.

In order to estimate aromaticity of azirine rings, we calculated nucleus-independent chemical shifts (NICS) using the gauge including atomic orbitals (GIAO) method<sup>7</sup> at 6-311G(d,p) basis set. Realizing small size of azirine, we decided to consider NICS(1)<sub>zz</sub>, one of the best NICS methods employed to estimate aromaticity.<sup>8</sup> Another aromaticity index, Harmonic oscillator model of heterocyclic electron delocalization (HOMED) index,<sup>9</sup> formulated to determine aromaticity of heterocycles was also considered. HOMED values were acquired by using formula described below.

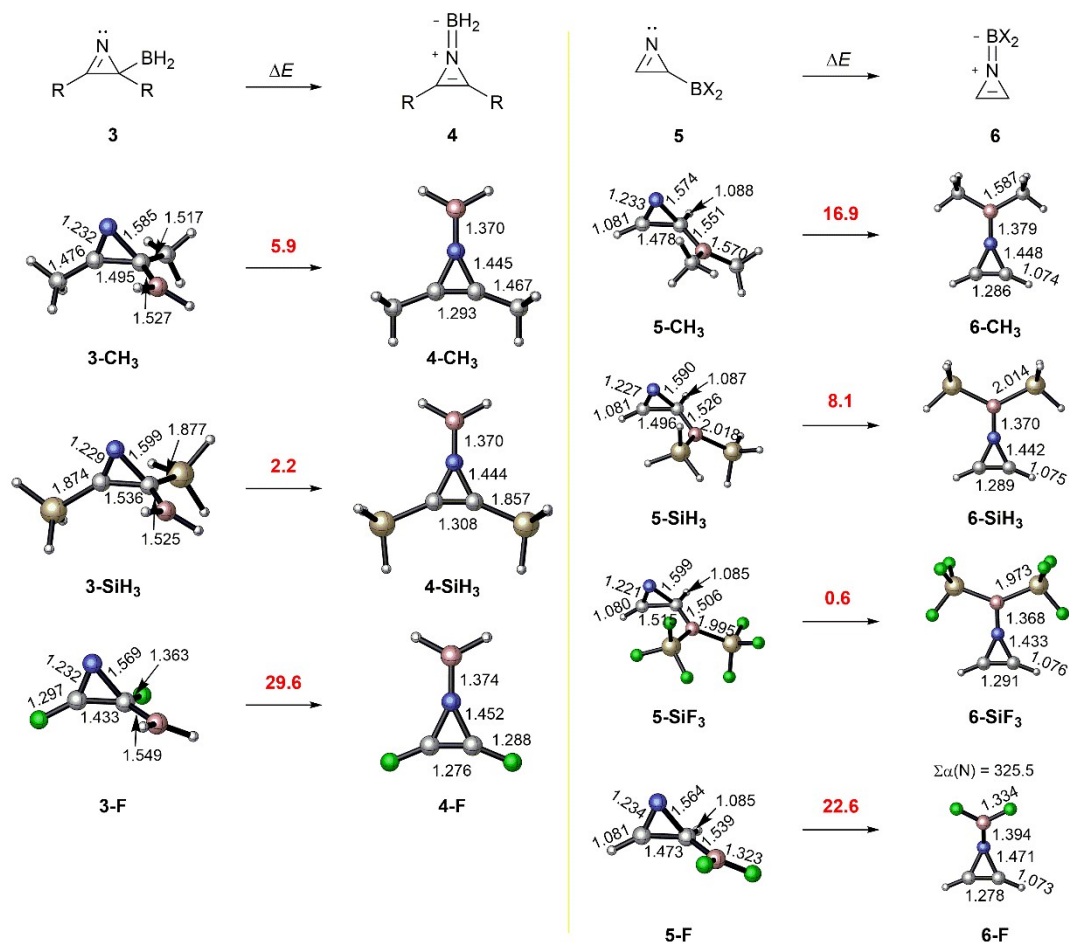
$$HOMA = 1 - \frac{\alpha}{n} \sum_{i=1}^n (R_{opt} - R_i)^2$$

Where  $\alpha = 78.6/87.4$  (CC/CN bond, respectively),  $n$  = number of bonds taken into summation,  $R_{opt} = 1.387/1.339$  Å (i.e., optimal CC/CN bond length, respectively) and  $R_i$  values give the CC/CN bond lengths of the ring segment considered. We employed Multiwfn program<sup>10</sup> to calculate HOMED values. Positive HOMA values point to aromaticity and negative HOMA values indicate antiaromaticity or reduced aromatic character. All calculations were executed with Gaussian09 (G09) program,<sup>11</sup> except HOMED.

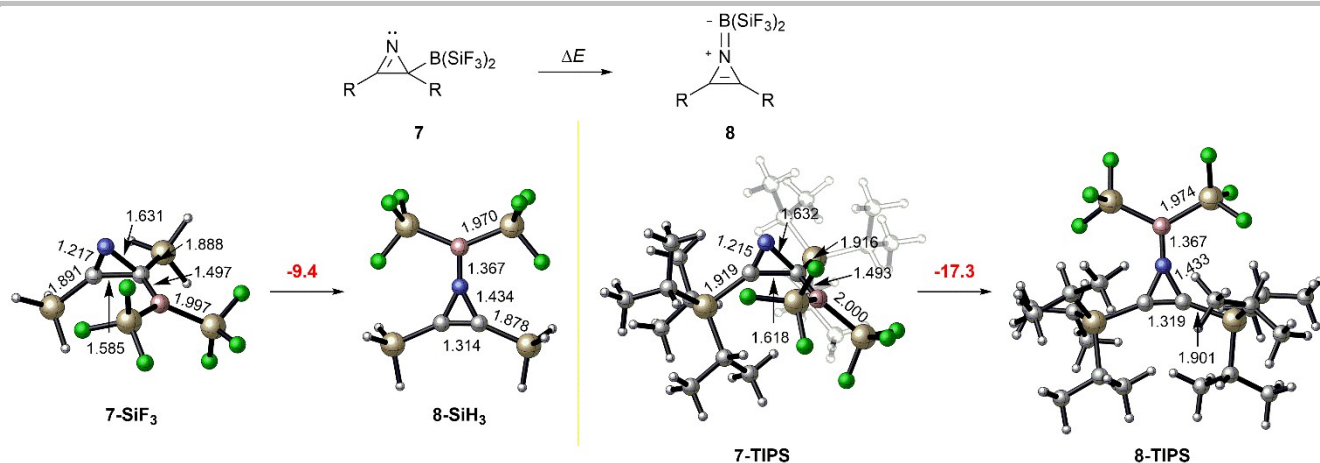
## 2. Geometries, and free isomerization energies of 2H-azirines (2, 3, 5 and 7) to 1H-azirines (1, 4, 6 and 8)



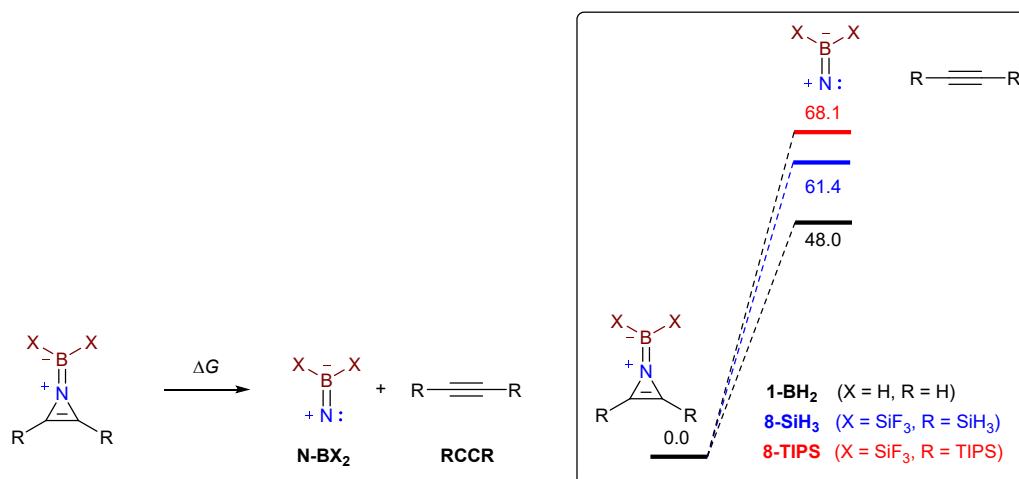
**Scheme S1.** Geometries and isomerization free energies of 2H-azirines (**2**) to 1H-azirines (**1**). Bond lengths, bond angles, and relative free energies are given in Å, degree (°) and kcal mol<sup>-1</sup>, respectively. Color code of 3D-structures; white: hydrogen, grey: carbon, blue: nitrogen, pink: boron, golden: silicon, green: fluorine.



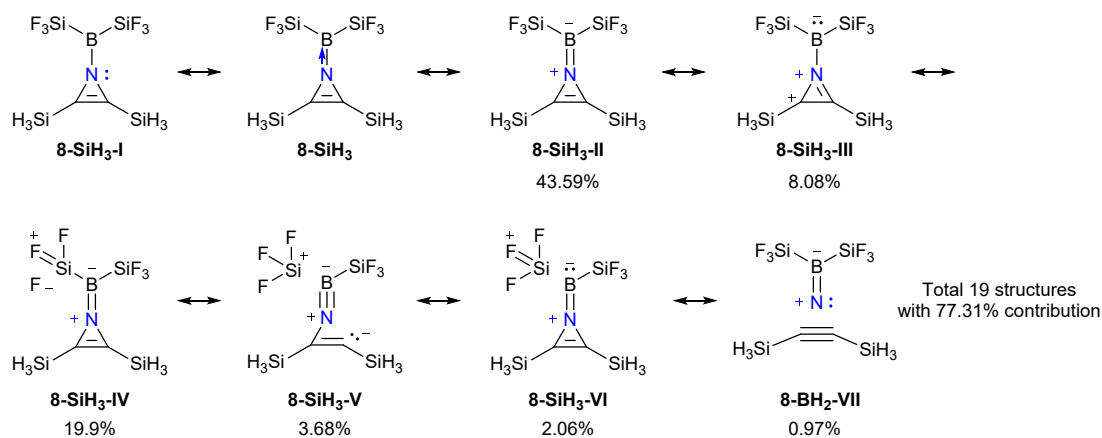
**Scheme S2.** Geometries and isomerization free energies of 2H-azirines (**3** and **5**) to 1H-azirines (**4** and **6**). Bond lengths and relative free energies are given in Å and kcal mol<sup>-1</sup>, respectively. Color code of 3D-structures; white: hydrogen, grey: carbon, blue: nitrogen, pink: boron, golden: silicon, green: fluorine.



**Scheme S3.** Geometries and isomerization energies of *2H*-azirines (**7**) to *1H*-azirines (**8**). Bond lengths, bond angles and relative energies are given in Å, degree (°) and kcal mol<sup>-1</sup>, respectively. Color code of 3D-structures; white: hydrogen, grey: carbon, blue: nitrogen, pink: boron, golden: silicon, green: fluorine. Isopropyl groups of TIPS (on right side) are sent to background for clarity.



**Scheme S4.** Decomposition of the selected boryl-substituted *1H*-azirines to the corresponding nitrenes (in T1 state, as S0 state is unstable), and acetylenes. Relative free energies are given in kcal mol<sup>-1</sup>.



**Scheme S5.** Natural resonance theory analysis (NRT) of **8-SiH<sub>3</sub>**, with limitation of one percent.

### 3. Correlations between Isomerization energies ( $\Delta G$ s) and other properties of *1H*- and *2H*-azirines

**Table S1.** Various (structural, and electronic) properties of 1*H*- and 2*H*-azirines. The  $\Delta G$ s are given in kcal mol<sup>-1</sup>, HOMO-LUMO energies and gaps are provided in eV, bond lengths are given in Å, and NICS(1)<sub>zz</sub> are provided in ppm.

Sr. No.	1 <i>H</i> -Azirines											2 <i>H</i> -Azirines							
	Compd	X	R	$\Delta G$	C=C	C-N	C-X (B.O.)	HOMO	LUMO	Gap	BDE (N-R)	$\Delta BDE$ (N-R - N-C)	C-C	C=N	C-N	HOMO	LUMO	Gap	BDE (N-C)
1	1-H	H	H	33.9	1.271	1.506	0.88	-7.34	1.01	8.35	79.6	33.5	1.451	1.245	1.525	-9.38	-0.64	8.74	113.1
2	1-CH <sub>3</sub>	CH <sub>3</sub>	H	40	1.275	1.491	1	-7.16	0.94	8.1	70.2	42.1	1.451	1.248	1.523	-8.78	0.8	9.58	112.2
3	1-SiH <sub>3</sub>	SiH <sub>3</sub>	H	26.8	1.271	1.509	0.74	-6.92	0.52	7.44	64.8	29.1	1.464	1.24	1.556	-9.12	0.42	9.54	93.9
4	1-SiF <sub>3</sub>	SiF <sub>3</sub>	H	23	1.268	1.514	0.7	-7.88	0.01	7.89	82.5	25.2	1.468	1.237	1.557	-10.06	-0.13	9.93	107.7
5	1-F	F	H	60.7	1.281	1.443	0.78	-9.06	0.26	9.32	61.2	62.2	1.425	1.26	1.468	-9.48	0.2	9.68	123.4
6	1-BH <sub>2</sub>	BH <sub>2</sub>	H	11.2	1.287	1.444	1.28	-7.22	0.29	7.51	104.2	20.2	1.49	1.228	1.584	-9.38	-0.64	8.74	124.4
7	4-CH <sub>3</sub>	BH <sub>2</sub>	CH <sub>3</sub>	5.9	1.293	1.445	1.3	-6.6	1.08	7.68	105.4	17.1	1.495	1.232	1.585	-8.59	-0.42	8.17	122.4
8	4-SiH <sub>3</sub>	BH <sub>2</sub>	SiH <sub>3</sub>	2.2	1.308	1.444	1.27	-7.06	-0.63	6.43	105.4	15.2	1.536	1.229	1.599	-8.85	-0.81	8.04	120.6
9	4-F	BH <sub>2</sub>	F	29.6	1.276	1.452	1.26	-7.6	1.21	8.81	99.2	22.9	1.433	1.232	1.569	-10.14	-1.54	8.6	122.1
10	6-CH <sub>3</sub>	B(CH <sub>3</sub> ) <sub>2</sub>	H	16.9	1.286	1.448	1.18	-6.87	0.45	7.32	95.5	23.7	1.478	1.233	1.574	-9.09	0.18	9.27	120.2
11	6-SiH <sub>3</sub>	B(SiH <sub>3</sub> ) <sub>2</sub>	H	8.1	1.289	1.442	1.3	-7.74	-0.2	7.54	103.1	17.6	1.496	1.227	1.59	-8.64	-1.5	7.14	120.7
12	6-F	BF <sub>2</sub>	H	22.6	1.278	1.471	1.02	-7.4	0.29	7.69	93.8	28.2	1.473	1.234	1.564	-9.7	0.1	9.8	129.6
13	6-SiF <sub>3</sub>	B(SiF <sub>3</sub> ) <sub>2</sub>	H	0.6	1.291	1.433	1.38	-8.84	-0.92	7.92	120.1	9.6	1.515	1.221	1.599	-10.46	-2.87	7.59	122.0
14	8-SiH <sub>3</sub>	B(SiF <sub>3</sub> ) <sub>2</sub>	SiH <sub>3</sub>	-9.4	1.314	1.434	1.38	-8.4	-1.36	7.04	127.5	6.6	1.585	1.217	1.631	-9.65	-2.67	6.98	134.1
15	8-TIPS	B(SiF <sub>3</sub> ) <sub>2</sub>	TIPS	-17.3	1.319	1.433	1.38	-7.84	-0.8	7.04	133.5	10.3	1.618	1.215	1.632	-8.58	-2.27	6.31	143.8

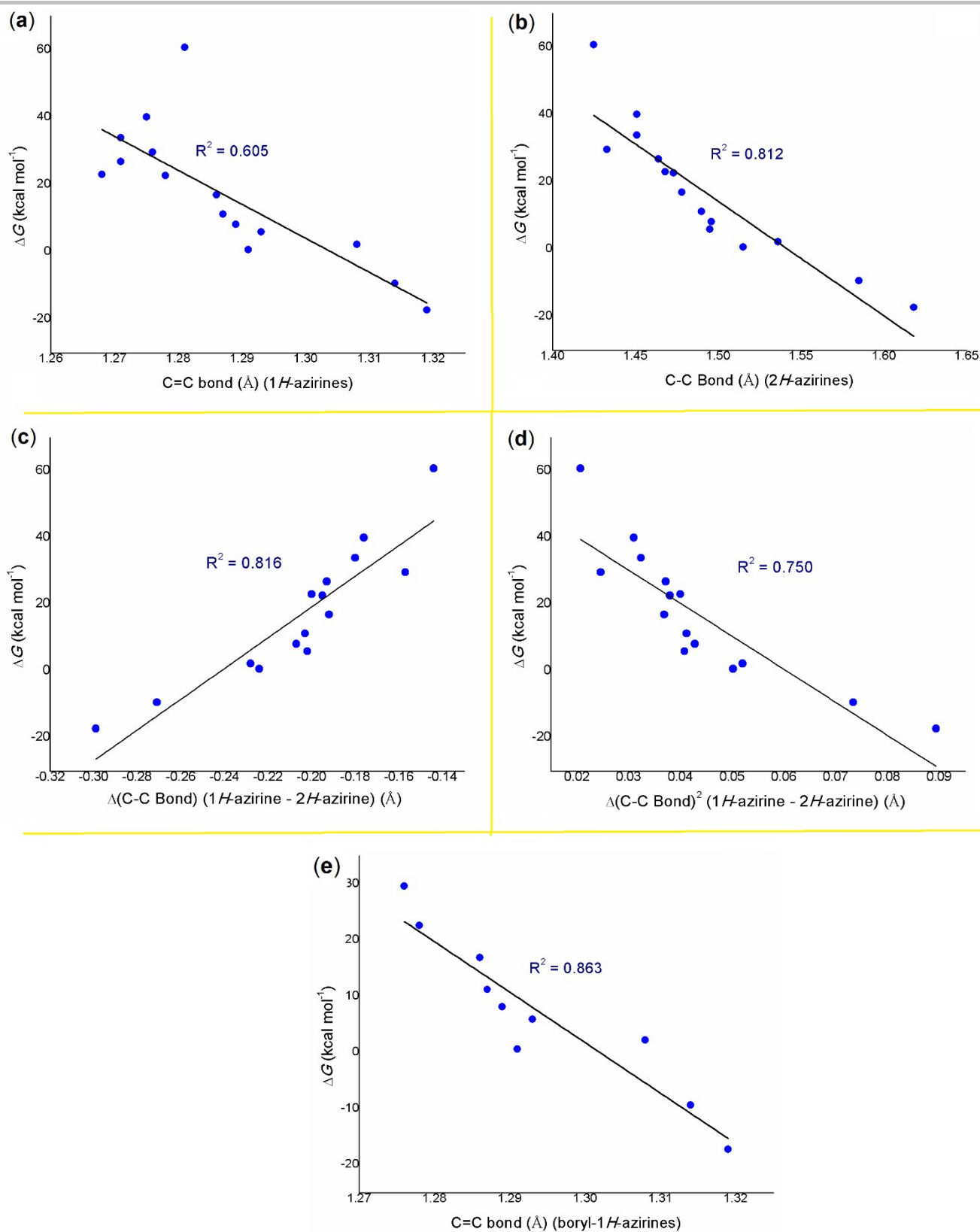
**Table S2.** The  $\Delta G$ , and aromaticity indices (NICS(1)<sub>zz</sub>, and HOMHED) values of 1*H*- and 2*H*-azirines. The  $\Delta G$ s are given in kcal mol<sup>-1</sup>, and NICS(1)<sub>zz</sub> are provided in ppm.

Sr. No.	1 <i>H</i> -Azirines							2 <i>H</i> -Azirines		
	Compd	X	R	$\Delta G$	NICS(1) <sub>zz</sub>	HOMHED	$\Delta$ HOMHED	NICS(1) <sub>zz</sub>	HOMHED	
1	1-H	H	H	33.9	-7.2	-0.968	-0.598	-20	-0.37	
2	1-CH <sub>3</sub>	CH <sub>3</sub>	H	40	-7.1	-0.683	-0.343	-19.1	-0.34	
3	1-SiH <sub>3</sub>	SiH <sub>3</sub>	H	26.8	0.6	-1.046	-0.237	-17.8	-0.809	
4	1-SiF <sub>3</sub>	SiF <sub>3</sub>	H	23	-2.5	-1.153	-0.298	-20.2	-0.855	
5	1-F	F	H	60.7	-19	0.071	-0.224	-22.1	0.295	
6	1-BH <sub>2</sub>	BH <sub>2</sub>	H	11.2	-0.2	0.099	1.486	-18.8	-1.387	
7	4-CH <sub>3</sub>	BH <sub>2</sub>	CH <sub>3</sub>	5.9	-4.9	0.166	1.566	-18.7	-1.4	
8	4-SiH <sub>3</sub>	BH <sub>2</sub>	SiH <sub>3</sub>	2.2	-2.3	0.2	2.102	-17.3	-1.902	
9	4-F	BH <sub>2</sub>	F	29.6	3.2	-0.063	0.862	-16.6	-0.925	
10	6-CH <sub>3</sub>	B(CH <sub>3</sub> ) <sub>2</sub>	H	16.9	2.4	0.045	1.201	-20.8	-1.156	
11	6-SiH <sub>3</sub>	B(SiH <sub>3</sub> ) <sub>2</sub>	H	8.1	-1.6	0.138	1.649	-19.1	-1.511	
12	6-F	BF <sub>2</sub>	H	22.6	0.5	-0.332	0.651	-21.2	-0.983	
13	6-SiF <sub>3</sub>	B(SiF <sub>3</sub> ) <sub>2</sub>	H	0.6	-5.4	0.25	2.053	-20	-1.803	
14	8-SiH <sub>3</sub>	B(SiF <sub>3</sub> ) <sub>2</sub>	SiH <sub>3</sub>	-9.4	-7.9	0.33	3.273	-17.8	-2.943	
15	8-TIPS	B(SiF <sub>3</sub> ) <sub>2</sub>	TIPS	-17.3	-10.2	0.339	3.669	-17.4	-3.33	

As most of the 1*H*-azirines (except boryl substituted 1-BH<sub>2</sub>) and all 2*H*-azirines in Scheme 2 (Scheme S1) possess nonplanar geometries, a thermodynamic explanation based on NICS(1)<sub>zz</sub> will be unreasonable here. For instance, highly unstable 1*H*-azirines 1-F display highly negative NICS(1)<sub>zz</sub> value (Scheme 2). The hyperconjugative aromaticity explanation for 2*H*-azirines could not lead to any conclusion as azirine is a small 3-membered ring (3-MR), and substituent size could greatly affect NICS values. For instance, 2-SiH<sub>3</sub> and 2-SiF<sub>3</sub> display lower stabilities (-27.8 and -24.6 kcal/mol, respectively) compared to the parent azirine 1-H (-34.7 kcal/mol), however, the corresponding ED SiH<sub>3</sub> group and EW SiF<sub>3</sub> group lead to higher and lower negative NICS(1)<sub>zz</sub> values (-17.8 and -20.2 ppm, respectively) than 1-H (-20.0 ppm). Besides thermodynamic stability mismatches, small changes in NICS(1)<sub>zz</sub> with respect to electronic effects is in accordance with the P. v. R. Schlyer's findings (Main Text Paragraph).<sup>12</sup> For instance, a slight increase in negative NICS(1)<sub>zz</sub> value is observed when  $\sigma$ -EWG is present at sp<sup>3</sup> carbon (for instance, 2-SiF<sub>3</sub>, and 2-F compared to the unsubstituted 2-H) and on the other hand, ED groups slightly increase electron density at the ipso carbon and, as a result, slightly reduce negative NICS(1)<sub>zz</sub> (Scheme 2). Further, NICS(1)<sub>zz</sub> values of all 2*H*-azirines display a very small change when subjected to substitution.

On the other hand, HOMHED displays more negative values for the high energy 1*H*-azirines, except 1-F, and 1-BH<sub>2</sub>, and less negative values for the 2*H*-azirines, except 2-F; these exceptions show positive values. Further, 1*H*-azirines with the planar geometry, like boryl-substituted 1*H*-azirines, including the more stabilized 1*H*-azirines display higher HOMHED values compared to the corresponding 2*H*-azirines (Table S2). Further, relative HOMHED (i.e.,  $\Delta$ HOMHED) correspond well to the relative free energy change ( $\Delta G$ ) (Figure S3), because HOMHED considers geometry changes.

HOMHED is linked to geometry, therefore, it displays better relation with  $\Delta G$  (as discussed above). For instance, in 1*H*-azirines, C=C bond changes from shorter CC bond to slightly longer CC bond (i.e., from localization to delocalization) with decreasing  $\Delta G$  (i.e., increasing stability) (Figure S1a). In the case of 2*H*-azirines, the C-C single bond moves to C=C double bond with the decreasing  $\Delta G$ . Interestingly, the difference between the CC bonds of two azirines (i.e.,  $\Delta(C-C \text{ bond}) = C-C \text{ bond}_{1H\text{-azirine}} - C-C \text{ bond}_{2H\text{-azirine}}$ ) displays a good correlation with  $\Delta G$  ( $R^2 = 0.816$ ) (Fig. S1c). However,  $\Delta G$  vs square of the difference of the bond lengths of the 1*H*- and 2*H*-azirines indicates a poor correlation ( $R^2 = 0.750$ ). An increase/decrease in the C-N/C=N bond lengths (respectively) is observed in 2*H*-azirines as the  $\Delta G$  decreases (Fig. S2,  $R^2 = 0.918/0.866$ ). It means longer bonds C-N, and shorter C=N bonds bring localization to 2*H*-azirines, thereby, decreasing their stability, and allowing them to convert to 1*H*-azirine with ease.



**Fig. S1.** Correlation between the isomerization free energies ( $\Delta G$ s) of 2H-azirines to 1H-azirines and C=C bonds of 1H-azirines (a), and 2H-azirines (b);  $\Delta G$ s vs  $\Delta(\text{C-C bond})$  (c),  $\Delta G$ s vs  $\Delta(\text{C-C bond})^2$  (d); where  $\Delta(\text{C-C bond}) = \text{C-C bond}_{1H\text{-azirine}} - \text{C-C bond}_{2H\text{-azirine}}$ ;  $\Delta G$ s vs C=C bonds of only boryl-substituted 1H-azirines (e).

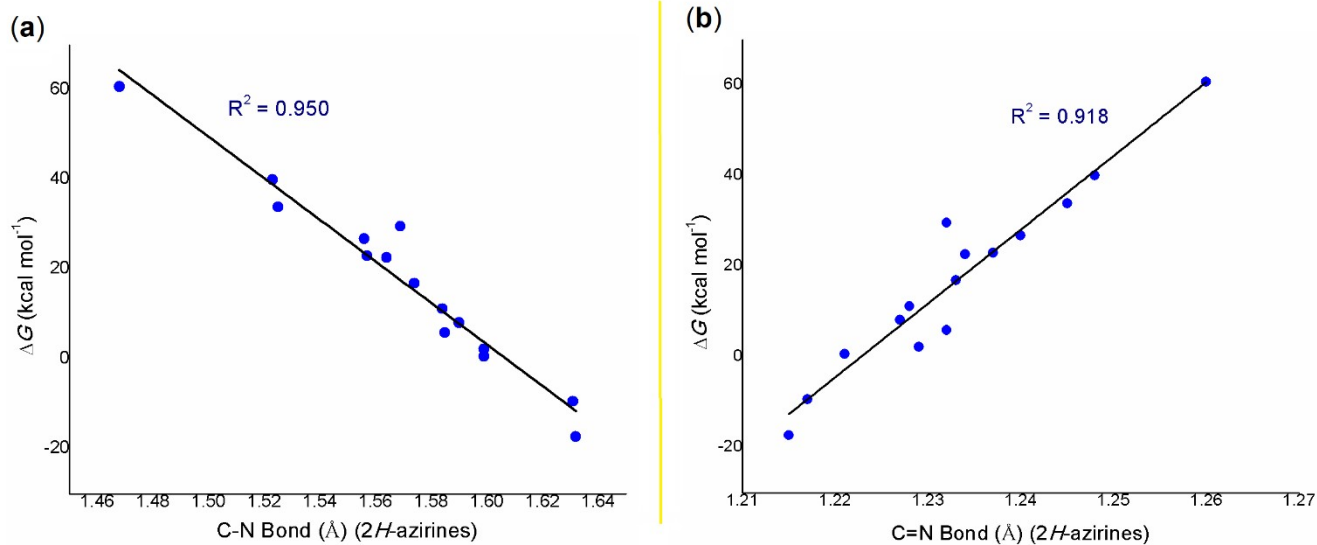


Fig. S2. Correlation between the isomerization free energies ( $\Delta G$ s) of 2H-azirines to 1H-azirines and C-N (a), and C=N bonds (b) of 2H-azirines.

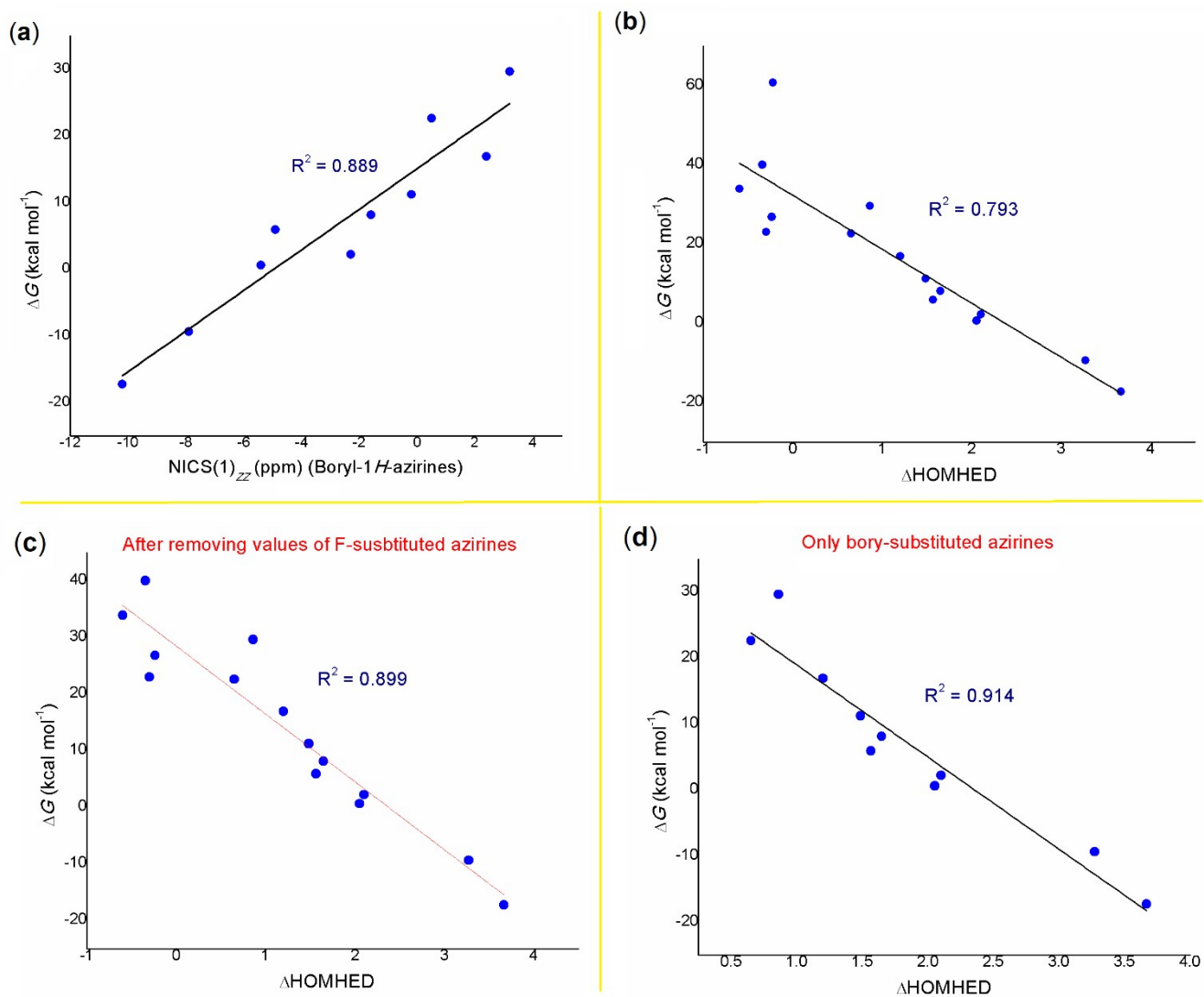


Fig. S3. Correlation between  $\Delta G$ s and NICS (1)<sub>zz</sub> of only boryl-substituted 1H-azirines, and  $\Delta$ HOMHED (b),  $\Delta$ HOMHED (excluding F-substituted azirines; where  $\Delta$ HOMHED = HOMHED<sub>(1H-azirine)</sub> - HOMHED<sub>(2H-azirine)</sub>) (c), and  $\Delta$ HOMHED (including only boryl-substituted azirines) (d).

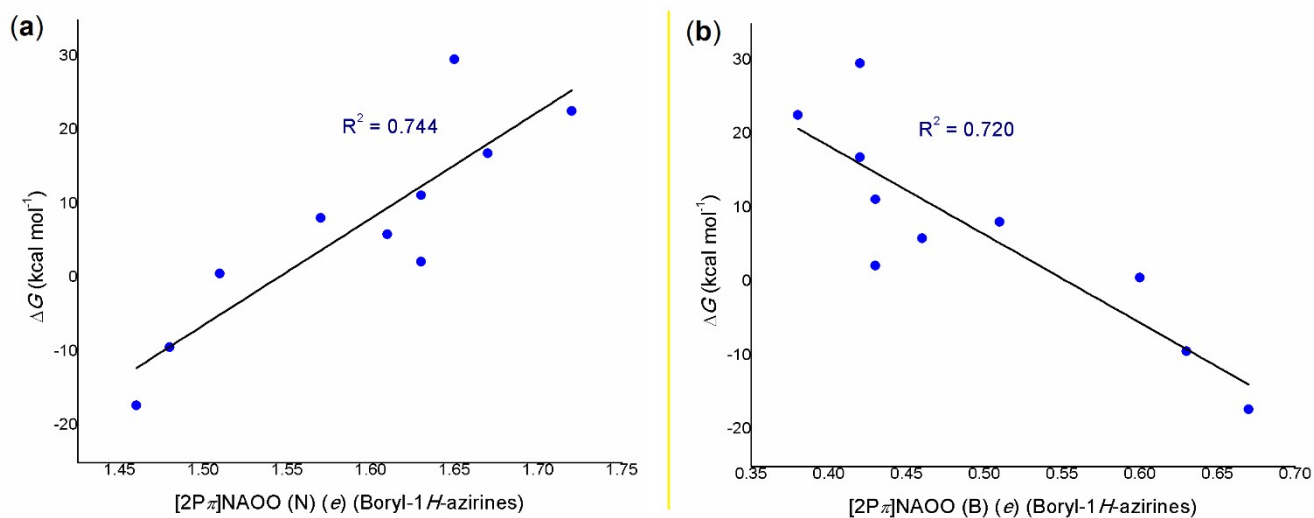


Fig. S4. Correlation between the  $\Delta G$ s and [2P $\pi$ ] natural atomic orbital occupancies [2P $\pi$ ]NAO of N (a) and B (b) atoms in the N=B bond of only boryl-substituted 1H-azirines.

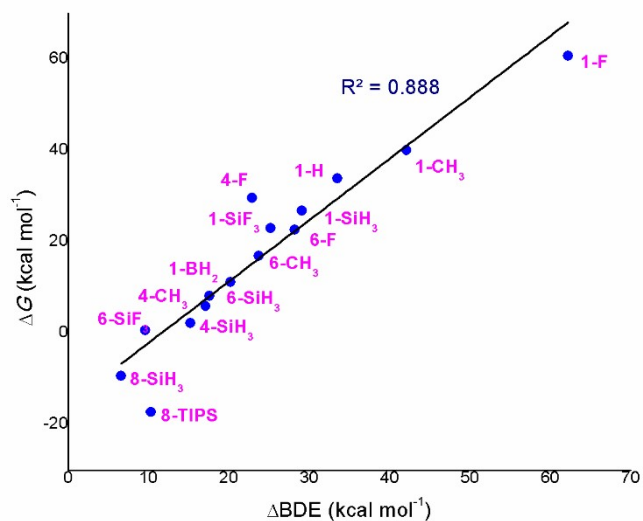


Fig. S5. Correlation between the  $\Delta G$  and difference of the two BDEs ( $\Delta BDE = BDE_{(C-R)} - BDE_{(N-R)}$ ) (data is taken from Schemes 2–6).



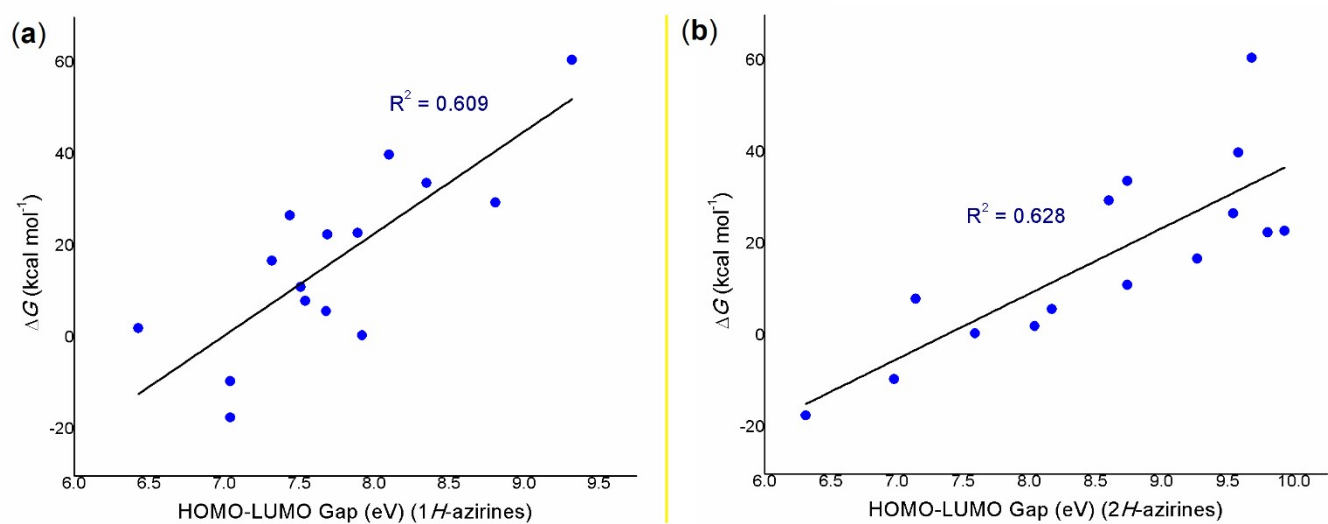


Fig. S6. Correlation between the  $\Delta G$ s and HOMO-LUMO gaps of the 1*H*- (a) and 2*H*-azirines.

#### 4. Frontier molecular orbitals of species involved in reactions energy profiles of 1*H*-azirine formation

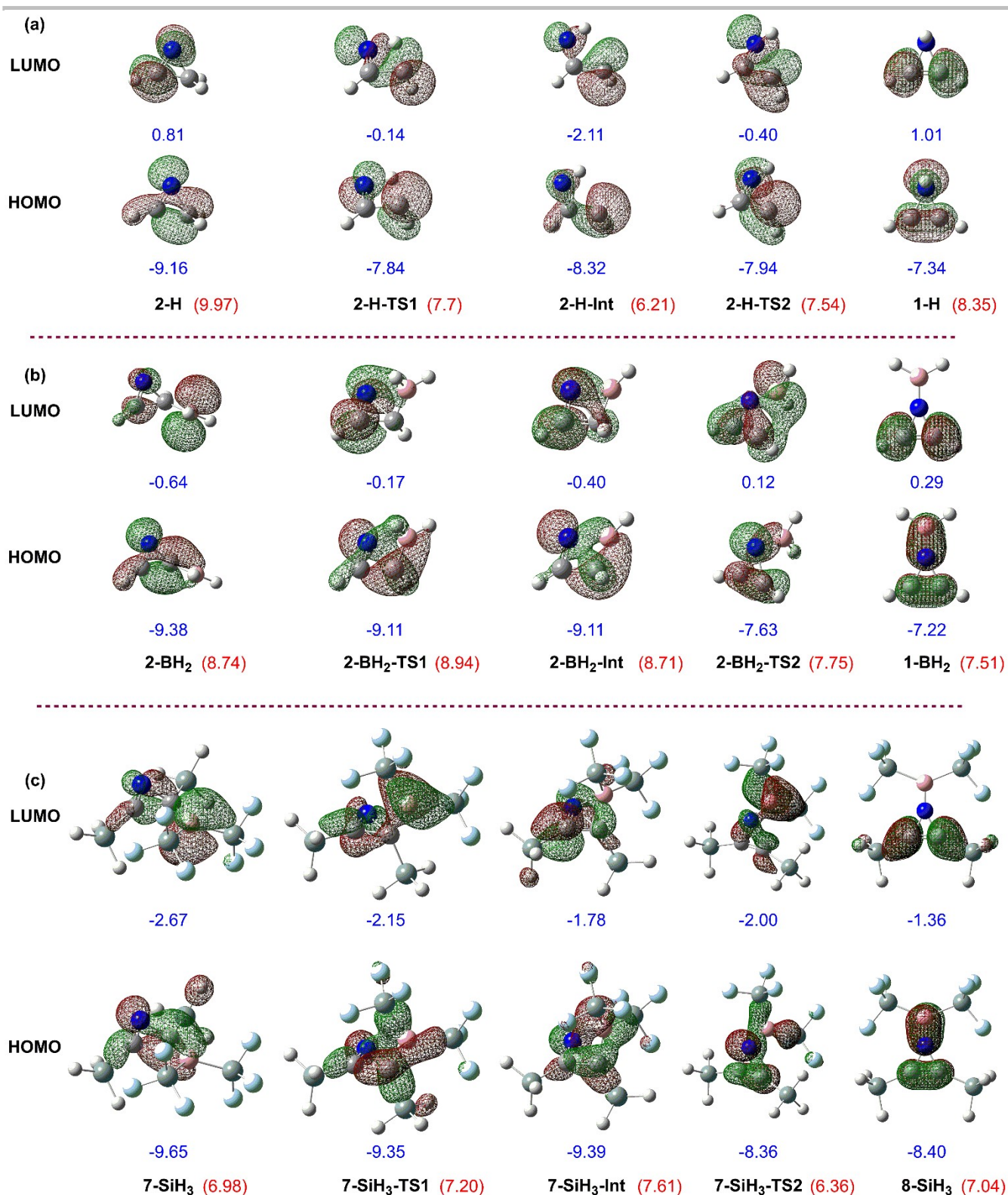


Fig. S7. Frontier molecular orbitals are provided for the species involved in the reaction mechanism of 2-H→1-H, 2-BH<sub>2</sub>→1-BH<sub>2</sub>, and 7-SiH<sub>3</sub>→8-SiH<sub>3</sub>. HOMO, LUMO (blue), and HOMO-LUMO gap (red) energies are given in eV. Reaction mechanisms are presented in Fig. 1 and Scheme 5. Color code of 3D-structures; white: hydrogen, grey: carbon, blue: nitrogen, pink: boron, teal (blue-green): silicon, cyan: fluorine.

## 5. Trend of various properties with stability of boryl (BX<sub>2</sub>) substituted 1H-azirines (6–8)

It is of worth mentioning here that the stability of BX<sub>2</sub> substituted 1H-azirines (mentioned in Tables S1 and S2) find correlation with their aromaticity (Fig. S3). For most of the 1H-azirines (Fig. S8), the following parameters change systematically with their increasing stability.

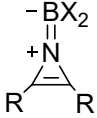
	6-F	6-CH <sub>3</sub>	1-BH <sub>2</sub>	6-SiH <sub>3</sub>	6-SiF <sub>3</sub>	8-SiH <sub>3</sub>	8-TIPS
$\Delta G$	22.6	16.9	11.2	8.1	0.6	-9.4	-17.3
Stability increasing	→						
NICS(1) <sub>zz</sub>	0.5	2.5	-0.2	-1.6	-5.4	-7.9	-10.2
HOMHED	-0.332	0.045	0.099	0.138	0.250	0.330	0.339
Aromaticity increasing	→						
C=C bond length	1.278	1.286	1.287	1.289	1.291	1.314	1.319
Increasing	→						
C-N bond length	1.471	1.448	1.444	1.442	1.432	1.434	1.433
Decreasing	→						
B-N bond length	1.394	1.379	1.370	1.370	1.368	1.367	1.367
Decreasing	→						
[2p $\pi$ ] NAOO (N)	1.72	1.67	1.63	1.57	1.51	1.48	1.46
Decreasing	→						
[2p $\pi$ ] NAOO (B)	0.38	0.42	0.43	0.51	0.60	0.63	0.67
Increasing	→						

Fig. S8. Stabilities of (selected boryl-substituted) 1H-azirines are correlated with various parameters. The  $\Delta G$  is described in kcal mol<sup>-1</sup>, NICS(1)<sub>zz</sub> in ppm, bond length in Å, and NAOO in e.

## 7. Cartesian Coordinates and Absolute Energies (Es)

Absolute energies and Cartesian coordinates are provided separately in .xyz file.

## 8. References

- (a) Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* 2008, **120**, 215; (b) Y. Zhao, D. G. Truhlar, *Acc. Chem. Res.* 2008, **41**, 157.
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## 9. Author Contributions

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A.M.R. conceived the project, performed theoretical calculations, and drafted the manuscript, and J.Z. supervised and revised it. Both authors discussed the results and commented on the manuscript.