Electronic supplementary information

Photochemical formation of the elusive Dewar isomers of aromatic systems: why are substituted azaborines different?

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1. Complementary CASPT2 calculations

In order to assess whether the shapes of the S_1 PESs in Fig. 6 of the main text, as predicted by TD-DFT (TD-CAM-B3LYP/cc-pVTZ//TD-CAM-B3LYP/cc-pVDZ), are qualitatively accurate, the energies of the key points on these PESs were also obtained by performing single-point calculations at the MS-CASPT2/cc-pVTZ level of theory. The resulting energies are compared to the TD-DFT ones in Fig. S1, with the former given in red color and the latter in black color. Encouragingly, even though the actual S_1 energies relative to the S_0 state differ between the two methodologies, the shapes that MS-CASPT2 predicts for the S_1 PESs are consistent with those that TD-DFT provides. Specifically, MS-CASPT2 corroborates all the key findings by TD-DFT discussed in the main text: (a) that the S_0/S_1 CI lies *above* the S_1 FC point for the benzenes but *below* for the azaborines, (b) that the S_0/S_1 CI for the unsubstituted azaborine is reached in a barrierless fashion, and (c) that the minimum on the S_1 PES of 1-silyl-2-chloroazaborine is separated from the S_0/S_1 CI by a very small barrier.

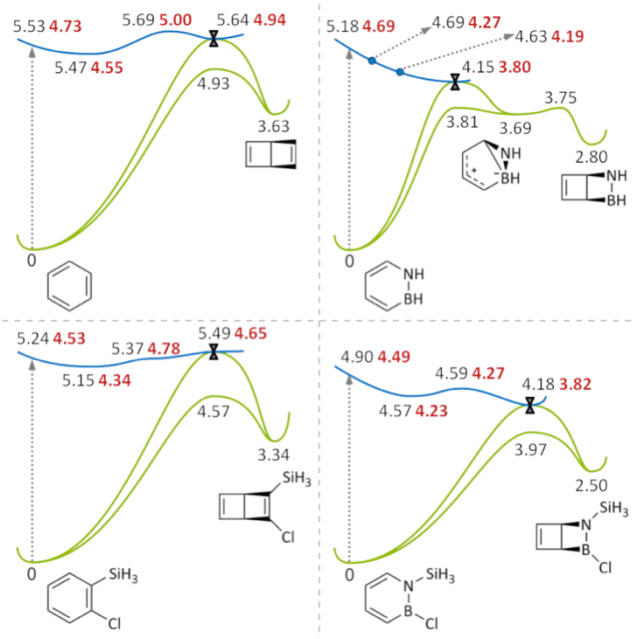

Fig. S1 Calculated S_0 (green) and S_1 (blue) PESs of benzene (top left), azaborine (top right), 1-silyl-2-chlorobenzene (bottom left) and 1-silyl-2-chloroazaborine (bottom right), with dashed vertical lines indicating photoexcitation to the respective S_1 FC point and local maxima corresponding to transition structures (TSs). S_1/S_0 CIs are indicated with hourglass symbols. For each system, TD-DFT/MS-CASPT2 electronic energies of the relevant structures (stationary points, the S_1 FC point, and the S_1/S_0 CI) are given in eV in black/red color relative to the corresponding S_0 global minimum. For the unsubstituted azaborine, the calculations consider two additional S_1 structures, as described in the caption for Fig. 8 of the main text.

2. Geometries of optimized conical intersections

The geometries of the optimized minimum-energy S_1/S_0 CIs in Fig. 6 of the main text are shown in Fig. S2. Although it is common for methods used to perform such optimizations to employ both of the gradient-difference and non-adiabatic coupling vectors spanning the so-called "branching space" in which the S_1/S_0 degeneracy is lifted,[1] the CI geometries in Fig. S2 were optimized with an implementation of a penalty-function method in the SHARC 2.0 package[2] that only requires calculation of the former vector.[1] Accordingly, for each CI geometry, Fig. S2 plots (in blue color) this vector, but not the non-adiabatic coupling vector. Furthermore, while the branching space is multidimensional,[3] Fig. S2 also highlights (in red color) the distances at the CI geometries between the two C atoms that subsequently form a bond in the S_0 Dewar isomers, and how these distances evolve from the S_0 parent species to the S_0 Dewar isomers.

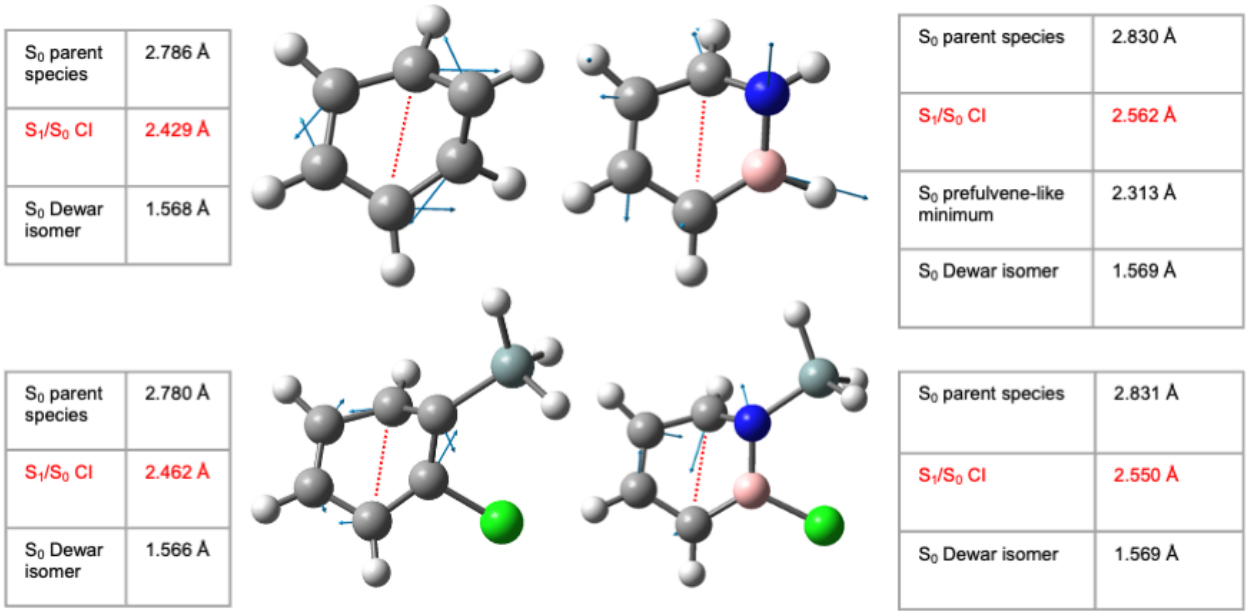

Fig. S2 Geometries of the optimized minimum-energy S_1/S_0 CIs of benzene (top left), azaborine (top right), 1-silyl-2-chlorobenzene (bottom left) and 1-silyl-2-chloroazaborine (bottom right) in Fig. 6 of the main text, with C, H, B, N, Si and Cl atoms shown in grey, light-grey, pink, blue, dark-turquoise and green colors, respectively. For each CI geometry, shown in blue color is also the gradient-difference vector and in red color the distance between the two C atoms that form a bond in the corresponding S_0 Dewar isomer.

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1 B. G. Levine, J. D. Coe and T. J. Martínez, Optimizing conical intersections without derivative coupling vectors: Application to multistate multireference second-order perturbation theory (MS-CASPT2), *J. Phys. Chem. B*, 2008, **112**, 405–413.

2 S. Mai, P. Marquetand and L. González, Nonadiabatic dynamics: the SHARC approach, *WIREs Comput. Mol. Sci.*, 2018, **8**, e1370.

3 F. Bernardi, M. Olivucci and M. A. Robb, Potential energy surface crossings in organic photochemistry, *Chem. Soc. Rev.*, 1996, **25**, 321–328.

3. Reaction dynamics following internal conversion

As discussed in connection to Fig. 6 of the main text, three different reaction channels are of particular interest for the S_0 dynamics of the unsubstituted azaborine following IC from the S_1 state. These channels are illustrated in Fig. S3a, using blue color for the formation of the Dewar isomer through the prefulvene-like minimum, green color for the back-reaction forming the parent azaborine through the prefulvene-like minimum, and red color for the direct back-reaction to the parent azaborine. Fig. S3b, in turn, plots calculated NAMD trajectories that describe these three cases, as differentiated by how the B–C_6 distance changes during the simulations. From these plots, it can be seen that the trajectories evolve very similarly from the S_1 FC point (at time t = 0) to the instance when IC takes place (at $t \approx 100$ fs), which is indicated with dotted vertical lines. However, following IC, the trajectories become distinctly different, with that for the direct back-reaction (red color) not spending any time in the region of the prefulvene-like minimum (where B–$C_6 \approx 1.8$ Å). In sharp contrast, the trajectories for the formation of the Dewar isomer (blue color) and the indirect back-reaction (green color) do populate this region for some 150 and 100 fs, respectively.

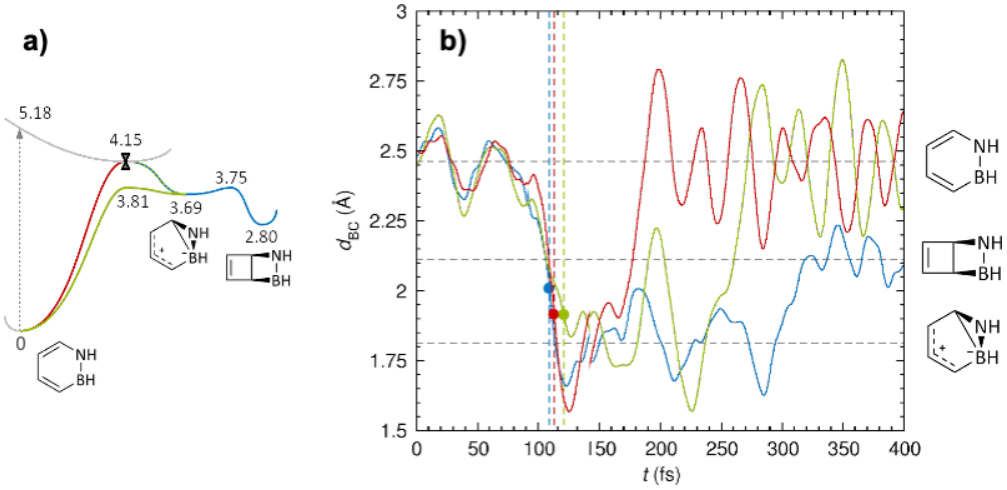

Fig. S3 a) Different reaction channels for the S_0 dynamics of the unsubstituted azaborine following IC from the S_1 state, here illustrated based on the corresponding S_0 PES derived from Fig. 6 of the main text. b) Changes in B–C_6 distance during three different NAMD trajectories that describe these reaction channels. No relevant changes in this distance occur beyond 400 fs.

4. Reaction pathways for the formation of other (than Dewar) photoproducts

Fig. 7 of the main text presents the portions of the S_0 PES of azaborine that are relevant for comparing different reaction pathways starting from the prefulvene-like minimum formed upon IC at the S_1/S_0 CI. Fig. S4, in turn, shows the optimized geometries of the potential-energy minima along these pathways.

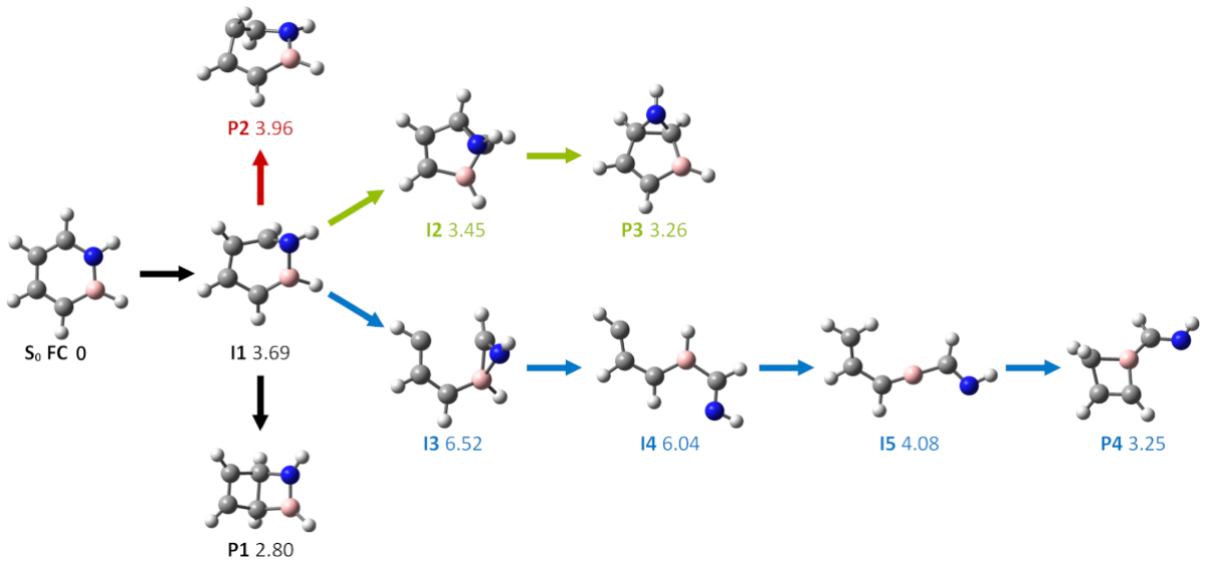

Fig. S4 Optimized geometries of different minima on the S_0 PES of azaborine connected to the **I1** prefulvene-like minimum formed upon IC at the S_1/S_0 CI, with C, H, B and N atoms shown in grey, light-grey, pink and blue colors, respectively. The electronic energies of the minima are given in eV relative to the S_0 global minimum (labeled **S_0 FC**).

5. Cartesian coordinates and total electronic energies of optimized geometries

Each geometry is identified by referring to the relative electronic energy or label it is associated with in a specific Figure of the main text, as indicated below. Coordinates are given in Å (CAM-B3LYP/cc-pVDZ). Total electronic energies (*E*) of S_0 and S_1 states are given in a.u. (CAM-B3LYP/cc-pVTZ). For geometries corresponding to transition structures (TSs), the imaginary vibrational frequency is given in cm^{-1}. For all structures expect TSs, all vibrational frequencies were found to be real.

5.1. Azaborine

S_0 geometry with relative electronic energy 0 eV in Fig. 6 of the main text
E(S_0) = -235.623975093 a.u.
E(S_1) = -235.433699513 a.u.

N	1.273663	0.488102	0.000012
B	0.227011	1.462547	0.000019
C	-1.172761	0.890697	0.000005
C	-1.330928	-0.472218	-0.000012
C	-0.215798	-1.357402	-0.000017
C	1.052600	-0.857468	-0.000005
H	2.245466	0.774387	0.000020
H	0.539892	2.624712	0.000034
H	-2.071615	1.512402	0.000009
H	-2.330550	-0.919300	-0.000022
H	-0.362886	-2.437257	-0.000031
H	1.930313	-1.506044	-0.000009

S_1 geometry with relative electronic energy 4.69 eV in Fig. 8 of the main text
E(S_0) = -235.545739479 a.u.
E(S_1) = -235.451559412 a.u.

N	1.432180	0.143724	-0.390203
B	0.561774	1.255778	0.132164
C	-0.936227	1.121592	0.046102
C	-1.468041	-0.178992	-0.129730
C	-0.566094	-1.221591	0.036688
C	0.832113	-0.939403	0.190815
H	2.428071	0.208513	-0.207117
H	1.136920	2.142151	0.718579
H	-1.618865	1.967154	0.160299
H	-2.526118	-0.375463	-0.314006
H	-0.885239	-2.264425	0.110770
H	1.460597	-1.652528	0.738835

S_1 geometry with relative electronic energy 4.63 eV in Fig. 8 of the main text
E(S_0) = -235.502160480 a.u.
E(S_1) = -235.453642259 a.u.

N	1.438683	0.040985	-0.456762
B	0.633177	1.179110	0.128310
C	-0.868969	1.155243	0.058869
C	-1.478817	-0.114089	-0.129289
C	-0.637528	-1.190461	0.025605

C	0.768202	-0.902488	0.267135
H	2.432892	0.068663	-0.247117
H	1.290273	2.025014	0.684026
H	-1.493064	2.037923	0.213504
H	-2.539123	-0.246723	-0.358736
H	-0.957973	-2.232768	-0.046594
H	1.333002	-1.523782	0.976781

S_1/S_0 CI geometry with relative electronic energy 4.15 eV in Fig. 6 of the main text
$E(S_0)$ = -235.472572300 a.u.
$E(S_1)$ = -235.470217258 a.u.

N	-1.413079	-0.073253	-0.485176
B	-0.701169	1.145913	0.097533
C	0.785104	1.179686	0.091383
C	1.474508	-0.054323	-0.122968
C	0.697838	-1.162058	-0.016282
C	-0.708463	-0.884905	0.360570
H	-2.408557	-0.067174	-0.281268
H	-1.427421	2.023412	0.481811
H	1.365046	2.091748	0.235798
H	2.538615	-0.110478	-0.354971
H	1.038212	-2.180828	-0.207917
H	-1.202422	-1.443865	1.158895

S_0 geometry with relative electronic energy 3.69 eV labeled **I1** in Fig. 7 of the main text
$E(S_0)$ = -235.488482780 a.u.

N	-1.456578	-0.278704	-0.497359
B	-0.728841	1.066362	-0.053805
C	0.751308	1.152218	0.039985
C	1.505994	-0.069713	-0.130848
C	0.694970	-1.137977	0.020057
C	-0.616470	-0.654416	0.502542
H	-2.429384	-0.188788	-0.197355
H	-1.488878	1.919984	0.319135
H	1.262903	2.081303	0.315581
H	2.548460	-0.102334	-0.459278
H	0.831045	-2.143514	-0.381549
H	-0.898707	-0.688210	1.563597

S_0 geometry with relative electronic energy 3.45 eV labeled **I2** in Fig. 7 of the main text
$E(S_0)$ = -235.496951236 a.u.

N	0.965752	0.014262	0.742758
B	0.083647	1.242124	-0.064398
C	-1.375277	0.595502	0.007053
C	-1.199494	-0.733740	-0.021709
C	0.273756	-1.012464	-0.096941
C	0.999068	0.133715	-0.731113
H	1.842454	-0.168881	1.230423
H	0.435837	2.375455	0.116088
H	-2.351392	1.071023	0.111869
H	-1.946298	-1.525435	0.053623
H	0.697885	-2.018268	-0.083561

H	1.954699	0.057570	-1.249495

S_0 geometry with relative electronic energy 6.52 eV labeled **I3** in Fig. 7 of the main text

$E(S_0)$ = -235.384370051 a.u.

N	-1.641728	-0.107651	0.596060
B	-0.820386	0.811017	-0.452616
C	0.667033	1.138556	-0.017680
C	1.630240	0.168885	0.192419
C	1.356705	-1.174017	-0.052649
C	-1.227573	-0.714760	-0.444475
H	-1.998673	-0.470973	1.479280
H	-1.472831	1.631783	-1.049688
H	0.988864	2.181158	0.097892
H	2.632476	0.465157	0.543082
H	2.183451	-1.851305	-0.326303
H	-1.297693	-1.769335	-0.719299

S_0 geometry with relative electronic energy 6.04 eV labeled **I4** in Fig. 7 of the main text

$E(S_0)$ = -235.402144184 a.u.

N	-2.465600	0.597172	0.000422
B	-0.379918	-0.730422	-0.000461
C	0.481988	0.524912	-0.000124
C	1.908113	0.550826	-0.000407
C	2.717272	-0.516231	0.000589
C	-1.949615	-0.576735	-0.000088
H	-3.494286	0.543025	0.000655
H	0.117938	-1.829297	-0.001129
H	-0.019944	1.497512	0.000192
H	2.406817	1.535845	-0.001467
H	3.793246	-0.691768	0.001574
H	-2.591532	-1.480045	-0.000296

S_0 geometry with relative electronic energy 4.08 eV labeled **I5** in Fig. 7 of the main text

$E(S_0)$ = -235.474140560 a.u.

N	-2.945911	-0.148588	-0.102278
B	-0.525600	-0.209036	0.004277
C	0.687666	-0.888779	-0.058919
C	2.057798	-0.400752	0.103311
C	2.484220	0.851985	-0.095329
C	-1.868656	0.505700	0.121876
H	-3.766910	0.456323	0.027410
H	1.815738	1.638349	-0.456952
H	0.570405	-1.970881	-0.216790
H	2.791599	-1.149471	0.420295
H	3.524818	1.126037	0.085033
H	-1.852445	1.576015	0.409933

S_0 geometry with relative electronic energy 2.80 eV labeled **P1** in Fig. 7 of the main text

$E(S_0)$ = -235.521086390 a.u.

N	-1.322575	-0.596780	-0.204670
B	-1.291098	0.792739	-0.330142
C	0.091388	0.875851	0.500544

C	1.364043	0.582279	-0.280676
C	1.223044	-0.749837	-0.261143
C	-0.062803	-0.685215	0.551518
H	-1.851444	-1.371590	-0.584897
H	-2.053486	1.544536	-0.873206
H	0.170749	1.459203	1.427131
H	2.101352	1.246879	-0.737139
H	1.772532	-1.576040	-0.715875
H	-0.120222	-1.227689	1.505927

S_0 geometry with relative electronic energy 3.96 eV labeled **P2** in Fig. 7 of the main text
$E(S_0)$ = -235.478277909 a.u.

N	1.468699	0.081573	0.066347
B	0.594197	1.226238	0.137478
C	-0.970109	1.008872	-0.109438
C	-1.487060	-0.247127	-0.101226
C	-0.409490	-1.145936	0.444039
C	0.684579	-1.016486	-0.348651
H	2.451415	0.173062	-0.181724
H	1.095079	2.315665	0.268100
H	-1.635072	1.860407	-0.301068
H	-2.530774	-0.495891	-0.318199
H	-0.203784	-0.922214	1.500361
H	0.663741	-1.229171	-1.427639

S_0 geometry with relative electronic energy 3.26 eV labeled **P3** in Fig. 7 of the main text
$E(S_0)$ = -235.504347546 a.u.

N	1.277400	-0.068432	0.754005
B	-0.617603	1.309225	-0.030118
C	-1.565589	0.093072	0.113992
C	-0.838134	-1.034503	-0.050572
C	0.596039	-0.765779	-0.363188
C	0.781169	0.703330	-0.433568
H	2.290330	-0.190142	0.650787
H	-0.864716	2.466295	0.184673
H	-2.614073	0.062828	0.416730
H	-1.211469	-2.053964	0.088932
H	1.176722	-1.465530	-0.967549
H	1.528512	1.136690	-1.101010

S_0 geometry with relative electronic energy 3.25 eV labeled **P4** in Fig. 7 of the main text
$E(S_0)$ = -235.504558743 a.u.

N	2.385028	0.339416	-0.107228
B	-0.025668	-0.130616	-0.206646
C	-0.809546	1.164331	-0.179204
C	-1.781894	0.342218	0.303226
C	-1.361286	-1.016966	-0.215476
C	1.450906	-0.475905	0.204900
H	3.301632	-0.040183	0.170559
H	-1.473047	-1.878448	0.459690
H	-0.693053	2.240695	-0.069124
H	-2.573201	0.554405	1.035843

H	-1.782898	-1.240363	-1.202313
H	1.664638	-1.441003	0.708494

S_0 geometry with relative electronic energy 3.81 eV labeled **TS1** in Fig. 7 of the main text
$E(S_0)$ = -235.483653817 a.u.
Imaginary frequency = 575.7054i cm^{-1}

N	1.455493	-0.141275	-0.449489
B	0.625274	1.208913	-0.028613
C	-0.819443	1.163845	0.117892
C	-1.471050	-0.112828	-0.112058
C	-0.661170	-1.183965	-0.029664
C	0.706881	-0.806220	0.404245
H	2.419084	-0.024403	-0.130228
H	1.423310	2.070307	0.221890
H	-1.418574	2.046966	0.348047
H	-2.518119	-0.196278	-0.419239
H	-0.851986	-2.192552	-0.399225
H	1.100159	-1.124683	1.385758

S_0 geometry with relative electronic energy 3.75 eV labeled **TS2** in Fig. 7 of the main text
$E(S_0)$ = -235.486101678 a.u.
Imaginary frequency = 292.2099i cm^{-1}

N	1.368164	-0.530521	-0.459074
B	1.014712	0.904523	-0.188618
C	-0.441620	1.161853	0.097686
C	-1.503240	0.192769	-0.216359
C	-0.952318	-1.000875	0.022216
C	0.387918	-0.613652	0.550052
H	2.316872	-0.705180	-0.131636
H	1.861781	1.675492	0.183603
H	-0.688194	2.071781	0.661404
H	-2.487094	0.436377	-0.623598
H	-1.247854	-2.011011	-0.264350
H	0.649340	-0.717004	1.609616

S_0 geometry with relative electronic energy 4.01 eV labeled **TS3** in Fig. 7 of the main text
$E(S_0)$ = -235.476667788 a.u.
Imaginary frequency = 206.8320i cm^{-1}

N	-1.472891	-0.123656	-0.277579
B	-0.747832	1.137825	-0.107171
C	0.815984	1.103357	0.090068
C	1.504516	-0.085927	-0.000953
C	0.583232	-1.197286	-0.194906
C	-0.573389	-0.901428	0.482439
H	-2.469987	-0.122699	-0.069772
H	-1.387754	2.160089	-0.066682
H	1.389254	2.036613	0.164021
H	2.590727	-0.126926	-0.147472
H	0.491717	-1.552409	-1.231421
H	-0.546608	-0.730489	1.570341

S_0 geometry with relative electronic energy 4.12 eV labeled **TS4** in Fig. 7 of the main text

$E(S_0)$ = -235.472637056 a.u.
Imaginary frequency = 386.8801i cm^{-1}

N	1.199417	0.033367	0.721541
B	0.410859	1.131541	-0.200322
C	-1.120388	0.919680	-0.012770
C	-1.395903	-0.434142	0.080876
C	-0.212623	-1.166313	-0.103789
C	0.897941	-0.333157	-0.623225
H	2.201325	0.097693	0.931433
H	0.988490	2.155059	-0.451305
H	-1.916302	1.662317	0.102005
H	-2.330843	-0.875110	0.431502
H	-0.058313	-2.194275	0.234472
H	1.651260	-0.653367	-1.343830

S_0 geometry with relative electronic energy 3.46 eV labeled **TS5** in Fig. 7 of the main text
$E(S_0)$ = -235.496643653 a.u.
Imaginary frequency = 194.8184i cm^{-1}

N	1.004129	-0.016263	0.761693
B	-0.012030	1.277414	-0.071385
C	-1.409686	0.534692	0.031260
C	-1.156258	-0.782354	-0.030926
C	0.322268	-0.991497	-0.146756
C	0.978401	0.232229	-0.697367
H	1.921595	-0.237249	1.153480
H	0.277387	2.416696	0.169554
H	-2.407159	0.944073	0.197098
H	-1.860902	-1.610122	0.067102
H	0.780227	-1.977674	-0.240020
H	1.911752	0.232628	-1.259408

S_0 geometry with relative electronic energy 6.53 eV labeled **TS6** in Fig. 7 of the main text
$E(S_0)$ = -235.384109021 a.u.
Imaginary frequency = 126.1113i cm^{-1}

N	-1.606039	-0.086218	0.596559
B	-0.812072	0.820989	-0.448273
C	0.685519	1.138433	-0.022345
C	1.618318	0.145872	0.196137
C	1.259934	-1.179909	-0.064989
C	-1.186756	-0.713461	-0.436785
H	-1.947107	-0.419038	1.496545
H	-1.454716	1.639135	-1.060118
H	1.031277	2.175612	0.078558
H	2.633068	0.407051	0.535326
H	2.075490	-1.890813	-0.291487
H	-1.297465	-1.758974	-0.725478

S_0 geometry with relative electronic energy 6.67 eV labeled **TS7** in Fig. 7 of the main text
$E(S_0)$ = -235.378889579 a.u.
Imaginary frequency = 71.6223i cm^{-1}

N	-2.177463	-0.271987	0.006486
B	-0.630724	0.001431	0.620556

C	0.515723	-0.863477	-0.019831
C	1.818326	-0.404932	-0.214989
C	2.258727	0.865462	0.046837
C	-1.606234	0.811628	-0.317170
H	-3.093927	-0.621692	-0.276886
H	-0.628960	0.273674	1.797005
H	0.322734	-1.908843	-0.289143
H	2.557325	-1.101589	-0.649095
H	3.282113	1.186872	0.271880
H	-1.962680	1.616252	-0.971023

S_0 geometry with relative electronic energy 6.48 eV labeled **TS8** in Fig. 7 of the main text
$E(S_0)$ = -235.385726198 a.u.
Imaginary frequency = 581.6152i cm^{-1}

N	2.527650	0.398580	-0.056793
B	0.228073	-0.345991	0.272437
C	-0.592530	0.901810	0.144195
C	-1.902970	0.512954	-0.102407
C	-2.272428	-0.814616	0.056067
C	1.733421	-0.604927	-0.080049
H	3.497354	0.097722	-0.231854
H	-0.520905	-1.281610	0.650203
H	-0.265739	1.936042	0.032347
H	-2.676343	1.207391	-0.469109
H	-2.757514	-1.358986	-0.771505
H	2.096273	-1.632001	-0.281549

S_0 geometry with relative electronic energy 4.21 eV labeled **TS9** in Fig. 7 of the main text
$E(S_0)$ = -235.469381730 a.u.
Imaginary frequency = 227.0296i cm^{-1}

N	-2.588298	0.062151	-0.230340
B	-0.193066	0.438251	-0.056512
C	0.948887	1.236224	-0.153858
C	1.790176	0.120574	0.256671
C	1.598190	-1.111601	-0.290385
C	-1.489975	-0.296547	0.317964
H	-3.371098	-0.490350	0.143946
H	1.116327	-1.218000	-1.262444
H	1.237164	2.281645	-0.157605
H	2.446581	0.225399	1.132173
H	1.995338	-2.012857	0.183580
H	-1.424561	-1.104051	1.072935

5.2. 1-silyl-2-chloroazaborine

S_0 geometry with relative electronic energy 0 eV in Fig. 6 of the main text
$E(S_0)$ = -986.031147901 a.u.
$E(S_1)$ = -985.851212998 a.u.

N	-0.041349	0.658470	0.000300
B	0.071150	-0.772152	0.000079
C	1.441516	-1.394726	-0.000296

C	2.518532	-0.551526	-0.000203
C	2.353702	0.864913	0.000116
C	1.110439	1.417296	0.000344
H	1.605811	-2.474046	-0.000631
H	3.539228	-0.946761	-0.000538
H	3.222323	1.522848	0.000204
H	0.979969	2.501057	0.000685
Si	-1.647861	1.483474	-0.000270
H	-2.407457	1.128735	1.225667
H	-1.321094	2.938013	-0.000279
H	-2.406612	1.128215	-1.226535
Cl	-1.456092	-1.725350	0.000173

S_1 geometry with relative electronic energy 4.57 eV in Fig. 6 of the main text

$E(S_0)$ = -985.960666250 a.u.

$E(S_1)$ = -985.863100540 a.u.

N	-0.236492	-0.700218	-0.177351
B	0.218744	0.734405	-0.162899
C	1.664793	1.050041	-0.446556
C	2.604150	-0.000135	-0.306301
C	2.128795	-1.149768	0.310674
C	0.728639	-1.280459	0.598051
H	2.016238	2.058742	-0.677694
H	3.653404	0.097416	-0.589078
H	2.793460	-1.949710	0.647980
H	0.421441	-1.982981	1.385445
Si	-1.915954	-1.276479	-0.249305
H	-1.830048	-2.748089	-0.479558
H	-2.653899	-1.033944	1.026743
H	-2.580036	-0.582455	-1.381863
Cl	-1.011397	1.971950	0.275237

S_1 geometry with relative electronic energy 4.59 eV in Fig. 6 of the main text

$E(S_0)$ = -985.920071453 a.u.

$E(S_1)$ = -985.862360761 a.u.

Imaginary frequency = 288.2017i cm^{-1}

N	0.243341	-0.718582	-0.248990
B	-0.252939	0.706456	-0.158627
C	-1.700709	1.018712	-0.422949
C	-2.619634	-0.056887	-0.292871
C	-2.109221	-1.187731	0.299790
C	-0.691956	-1.179183	0.631731
H	-2.065579	2.026154	-0.634205
H	-3.665407	0.010701	-0.599481
H	-2.708786	-2.059614	0.573010
H	-0.356922	-1.724822	1.527840
Si	1.946166	-1.239378	-0.233557
H	1.916692	-2.709907	-0.481622
H	2.646002	-0.519428	-1.325810
H	2.595663	-0.988373	1.087689
Cl	0.981320	1.955583	0.256720

S_1/S_0 CI geometry with relative electronic energy 4.18 eV in Fig. 6 of the main text

$E(S_0)$ = -985.879160627 a.u.

$E(S_1)$ = -985.876176215 a.u.

N	-0.194626	-0.724072	-0.257598
B	0.223278	0.719654	-0.124200
C	1.662910	1.119463	-0.159266
C	2.640113	0.064905	-0.242779
C	2.186159	-1.152912	0.111492
C	0.775276	-1.142479	0.612945
H	1.981198	2.164602	-0.145250
H	3.658504	0.231912	-0.604764
H	2.724167	-2.093799	-0.023949
H	0.508313	-1.568646	1.588823
Si	-1.879021	-1.309156	-0.163125
H	-2.639946	-0.700910	-1.281657
H	-1.787806	-2.789256	-0.317892
H	-2.504520	-0.997240	1.155794
Cl	-1.116140	1.895170	0.141322

S_0 geometry with relative electronic energy 2.50 eV in Fig. 6 of the main text

$E(S_0)$ = -985.939169363 a.u.

N	0.238970	0.605409	0.254618
B	0.178513	-0.800342	0.209271
C	-1.362541	-0.883319	0.602386
C	-2.350770	-0.612502	-0.523515
C	-2.201356	0.718780	-0.505635
C	-1.204826	0.676921	0.640598
H	-1.698788	-1.441791	1.484732
H	-2.933475	-1.291888	-1.149106
H	-2.580015	1.531566	-1.127183
H	-1.401784	1.247389	1.558344
Si	1.356318	1.917261	-0.115181
H	2.662071	1.311534	-0.488336
H	0.818135	2.741050	-1.238921
H	1.506740	2.795702	1.082699
Cl	1.458251	-1.962979	-0.154199

S_0 geometry with relative electronic energy 3.97 eV in Fig. 6 of the main text

$E(S_0)$ = -985.885400615 a.u.

Imaginary frequency = 675.2052i cm^{-1}

N	0.174037	-0.761530	-0.305119
B	-0.282500	0.755542	-0.144703
C	-1.686224	1.131963	-0.039132
C	-2.659792	0.070887	-0.185189
C	-2.184286	-1.164394	0.053347
C	-0.778941	-1.129442	0.540342
H	-2.004333	2.166932	0.097318
H	-3.672282	0.247870	-0.559475
H	-2.600381	-2.115083	-0.287620
H	-0.523783	-1.493834	1.554739
Si	1.897397	-1.260680	-0.105277
H	1.865406	-2.735570	-0.321521

H	2.705748	-0.592454	-1.149252
H	2.382910	-0.978998	1.275325
Cl	1.137227	1.838211	0.088677

5.3. Benzene

S_0 geometry with relative electronic energy 0 eV in Fig. 6 of the main text
$E(S_0)$ = -232.189104862 a.u.
$E(S_1)$ = -231.985712633 a.u.

C	0.000000	1.393025	-0.000000
C	1.206395	0.696512	-0.000000
C	1.206395	-0.696512	-0.000000
C	-0.000000	-1.393025	-0.000000
C	-1.206395	-0.696512	-0.000000
C	-1.206395	0.696512	-0.000000
H	0.000000	2.484890	-0.000000
H	2.151978	1.242445	-0.000000
H	2.151978	-1.242445	-0.000000
H	-0.000000	-2.484890	-0.000000
H	-2.151978	-1.242445	-0.000000
H	-2.151978	1.242445	-0.000000

S_1 geometry with relative electronic energy 5.47 eV in Fig. 6 of the main text
$E(S_0)$ = -232.182004010 a.u.
$E(S_1)$ = -231.988104390 a.u.

C	-1.301000	0.575854	0.000012
C	-1.149207	-0.838764	0.000018
C	0.151792	-1.414611	0.000006
C	1.301000	-0.575855	-0.000012
C	1.149205	0.838766	-0.000018
C	-0.151790	1.414610	-0.000006
H	-2.297584	1.016977	0.000022
H	-2.029519	-1.481276	0.000032
H	0.268071	-2.498240	0.000010
H	2.297584	-1.016979	-0.000022
H	2.029510	1.481286	-0.000032
H	-0.268063	2.498239	-0.000010

S_1 geometry with relative electronic energy 5.69 eV in Fig. 6 of the main text
$E(S_0)$ = -232.106070922 a.u.
$E(S_1)$ = -231.980182592 a.u.
Imaginary frequency = 77.2944i cm^{-1}

C	-1.457168	-0.000000	-0.389333
C	-0.703065	1.111596	0.135655
C	0.708569	1.177542	0.036921
C	1.454202	0.000000	-0.135533
C	0.708569	-1.177542	0.036921
C	-0.703065	-1.111596	0.135655
H	-2.542966	-0.000000	-0.293762
H	-1.220206	1.900227	0.698035
H	1.203104	2.147649	0.140895

H	2.528911	0.000000	-0.305818
H	1.203104	-2.147649	0.140895
H	-1.220205	-1.900227	0.698035

S_1/S_0 CI geometry with relative electronic energy 5.64 eV in Fig. 6 of the main text

$E(S_0)$ = -231.981422886 a.u.

$E(S_1)$ = -231.982165646 a.u.

C	1.465195	-0.003750	-0.579512
C	0.695731	-0.893595	0.254463
C	-0.725021	-1.141168	0.051772
C	-1.470559	0.000715	-0.169495
C	-0.722241	1.142849	0.040525
C	0.700822	0.893524	0.249868
H	2.554948	-0.021448	-0.537393
H	1.268300	-1.573450	0.892431
H	-1.130728	-2.147525	0.037937
H	-2.521833	0.000173	-0.441779
H	-1.093265	2.167780	0.066141
H	1.259016	1.583022	0.896934

S_0 geometry with relative electronic energy 3.63 eV in Fig. 6 of the main text

$E(S_0)$ = -232.055816672 a.u.

C	1.302244	0.669065	-0.265009
C	1.302342	-0.668733	-0.265153
C	0.000038	-0.784198	0.523120
C	-1.302346	-0.668746	-0.265362
C	-1.302212	0.669094	-0.264932
C	0.000018	0.783614	0.523689
H	1.955469	1.421215	-0.711245
H	1.956045	-1.420695	-0.711019
H	-0.000180	-1.353137	1.462346
H	-1.956271	-1.420810	-0.710926
H	-1.955408	1.421518	-0.710929
H	-0.000155	1.351327	1.463663

S_0 geometry with relative electronic energy 4.93 eV in Fig. 6 of the main text

$E(S_0)$ = -232.007624167 a.u.

Imaginary frequency = 477.9972i cm^{-1}

C	-1.245835	-0.778016	-0.167949
C	-1.289963	0.581844	-0.205045
C	-0.000187	1.135413	0.221708
C	1.289779	0.582107	-0.205093
C	1.246099	-0.777726	-0.167874
C	0.000086	-0.907311	0.572299
H	-1.798576	-1.520287	-0.742824
H	-2.116173	1.219181	-0.539037
H	-0.000265	2.140336	0.665192
H	2.115752	1.219642	-0.539282
H	1.799351	-1.519890	-0.742387
H	0.000038	-0.556845	1.610063

5.4. 1-silyl-2-chlorobenzene

S_0 geometry with relative electronic energy 0 eV in Fig. 6 of the main text

$E(S_0)$ = -982.530470826 a.u.

$E(S_1)$ = -982.337812977 a.u.

C	0.116575	0.669386	-0.000089
C	-0.165937	-0.700025	0.000051
C	-1.463569	-1.197912	0.000040
C	-2.530363	-0.304453	-0.000105
C	-2.291594	1.066292	-0.000251
C	-0.983004	1.539878	-0.000241
H	-1.629547	-2.274921	0.000150
H	-3.552360	-0.686977	-0.000112
H	-3.126148	1.769193	-0.000371
H	-0.806105	2.617490	-0.000352
Si	1.878760	1.353868	-0.000017
H	2.625750	0.919718	-1.215220
H	1.760715	2.842891	-0.000089
H	2.625564	0.919809	1.215333
Cl	1.159226	-1.852962	0.000263

S_1 geometry with relative electronic energy 5.15 eV in Fig. 6 of the main text

$E(S_0)$ = -982.522806498 a.u.

$E(S_1)$ = -982.341310439 a.u.

C	-0.200221	-0.680410	-0.000059
C	0.192838	0.697928	0.000062
C	1.536785	1.149461	0.000038
C	2.589373	0.199276	-0.000118
C	2.245656	-1.173395	-0.000250
C	0.895842	-1.604591	-0.000224
H	1.735226	2.219850	0.000136
H	3.628497	0.521429	-0.000138
H	3.036353	-1.925428	-0.000374
H	0.686992	-2.674697	-0.000332
Si	-1.972958	-1.266445	-0.000012
H	-2.733147	-0.805935	-1.204680
H	-1.925100	-2.759762	-0.000130
H	-2.733019	-0.806116	1.204805
Cl	-1.037413	1.907722	0.000246

S_1 geometry with relative electronic energy 5.37 eV in Fig. 6 of the main text

$E(S_0)$ = -982.395451189 a.u.

$E(S_1)$ = -982.333227980 a.u.

Imaginary frequency = 244.8654i cm^{-1}

C	0.426394	-0.695014	-0.211136
C	-0.324461	0.527489	-0.195661
C	-1.687902	0.653523	-0.616739
C	-2.522772	-0.442809	-0.394644
C	-1.926899	-1.416612	0.393305
C	-0.527609	-1.255476	0.703603
H	-2.036377	1.600152	-1.032116
H	-3.548570	-0.496110	-0.755032
H	-2.479618	-2.253269	0.825965

H	-0.189628	-1.617181	1.687759
Si	2.261895	-0.935431	-0.256665
H	2.530495	-2.389371	-0.473686
H	2.836831	-0.134160	-1.375496
H	2.952684	-0.537263	1.015330
Cl	0.449832	2.040979	0.331071

S_1/S_0 CI geometry with relative electronic energy 5.49 eV in Fig. 6 of the main text

$E(S_0)$ = -982.330651172 a.u.

$E(S_1)$ = -982.326710373 a.u.

C	0.424303	-0.696071	-0.278234
C	-0.398481	0.474865	-0.072823
C	-1.740577	0.662421	-0.591219
C	-2.564893	-0.441503	-0.364999
C	-1.931038	-1.399947	0.372411
C	-0.544743	-1.079828	0.711666
H	-2.037456	1.575176	-1.105417
H	-3.587993	-0.520315	-0.730057
H	-2.361871	-2.332233	0.718824
H	-0.189218	-1.412996	1.702139
Si	2.281160	-0.932278	-0.246322
H	2.798092	-0.657392	1.126476
H	2.659105	-2.328884	-0.627248
H	2.914362	0.018352	-1.204731
Cl	0.494195	1.975915	0.288689

S_0 geometry with relative electronic energy 3.34 eV in Fig. 6 of the main text

$E(S_0)$ = -982.407816686 a.u.

C	0.467847	0.499095	0.259489
C	-0.140656	-0.698166	0.244568
C	-1.531560	-0.227043	0.602493
C	-2.375609	0.329550	-0.540356
C	-1.807475	1.540247	-0.502122
C	-0.861195	1.187846	0.641415
H	-2.023555	-0.665626	1.479485
H	-3.130608	-0.133281	-1.177326
H	-1.921686	2.443944	-1.103000
H	-0.879151	1.787794	1.560026
Si	2.183000	1.127392	-0.129503
H	3.066130	-0.007016	-0.521656
H	2.108358	2.119290	-1.244812
H	2.752567	1.816245	1.067424
Cl	0.409285	-2.290236	-0.145884

S_0 geometry with relative electronic energy 4.57 eV in Fig. 6 of the main text

$E(S_0)$ = -982.362506697 a.u.

Imaginary frequency = 398.0661i cm^{-1}

C	-0.306429	-0.573781	0.386645
C	0.078951	0.724665	0.183656
C	1.513712	0.916865	0.131994
C	2.404449	-0.056358	-0.511196
C	1.993844	-1.321221	-0.236366

C	1.021261	-1.002935	0.802807
H	1.898338	1.915179	0.369840
H	3.228412	0.254984	-1.160886
H	2.140915	-2.246229	-0.791908
H	1.412877	-0.615987	1.749680
Si	-1.809953	-1.536217	-0.162711
H	-2.512044	-0.826659	-1.268438
H	-1.356228	-2.883950	-0.622412
H	-2.754801	-1.728202	0.977335
Cl	-0.997227	2.089087	-0.089442