

Supporting Information

A Theoretical Stereoselectivity Model of Photochemical Denitrogenations of Diazoalkanes Towards Strained 1,3-Dihalogenated Bicyclobutanes

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Active spaces

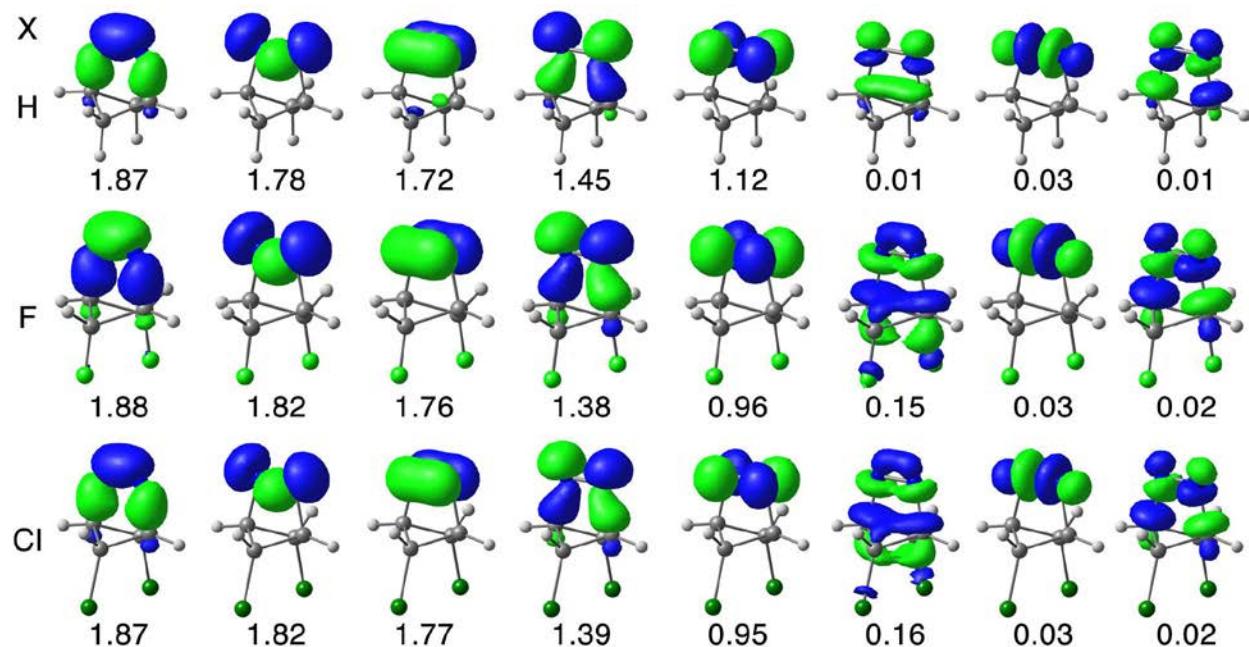


Figure S1. The (8,8) active space of **1**, **1-F**, and **1-Cl** with CASSCF(8,8)/ANO-S-VDZP. The occupation numbers are averaged over 6 states in **1** and 7 states in **1-F** and **1-Cl**. Isosurface value = 0.08.

Optimized geometries

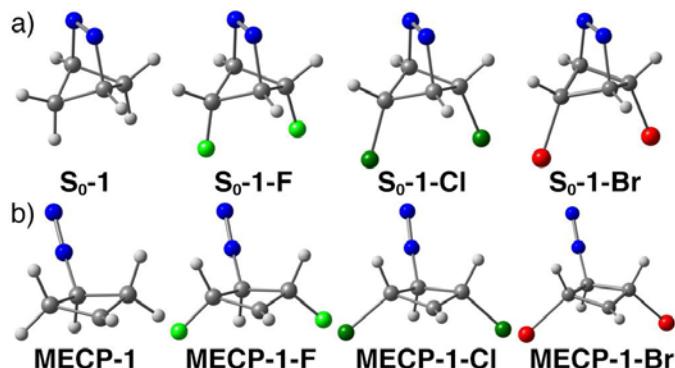


Figure S2. (a) Optimized geometries of the ground-state minimum of **1**, **1-F**, **1-Cl**, and **1-Br**, with CASSCF(8,8)/ANO-S-VDZP. (b) Optimized geometries of the minimum energy crossing points, **MECP-1**, **MECP-1-F**, **MECP-1-Cl**, and **MECP-1-Br**, with CASSCF(8,8)/ANO-S-VDZP.

Table S2. Selected geometrical parameters in **S₀-1**, **S₀-1-F**, **S₀-1-Cl**, **S₀-1-Br**, **MECP-1**, **MECP-1-F**, **MECP-1-Cl**, and **MECP-1-Br**.

Compounds	N=N (Å)	C–N (Å) ^a	C–X (Å)	α(°)	β(°)	γ(°)
1	1.30	1.50	1.09	175	53	129
MECP-1	1.20	1.43	1.09	145	164	-160
1-F	1.29	1.54	1.35	178	51	135
MECP-1-F	1.20	1.42	1.36	143	165	-160
1-Cl	1.29	1.55	1.77	176	48	138
MECP-1-Cl	1.20	1.41	1.78	142	165	-161
1-Br	1.29	1.56	1.92	174	47	139
MECP-1-Br	1.20	1.41	1.95	142	164	-163

^aThe two C–N bonds have the same lengths in **1**, **1-F**, **1-Cl**, **1-Br**. The distance of the broken C–N bond is not included in **MECP-1**, **MECP-1-F**, **MECP-1-Cl**, and **MECP-1-Br**.

CASSCF excitation energies

Table S1. Vertical excitation energies, electronic transition, and oscillator strength of **1** and **1-X** (X = F, Cl, Br) with CASSCF(8,8)/ANO-S-VDZP.

Compounds	S ₁ Energy (eV)	Transition	Oscillator strength
1	4.43	nπ [*]	1.13 × 10 ⁻²
1-F	4.28	nπ [*]	8.53 × 10 ⁻³
1-Cl	4.28	nπ [*]	6.80 × 10 ⁻³
1-Br	4.28	nπ [*]	6.26 × 10 ⁻³

CASSCF minimum energy path of 1, 1-F, 1-Cl, and 1-Br

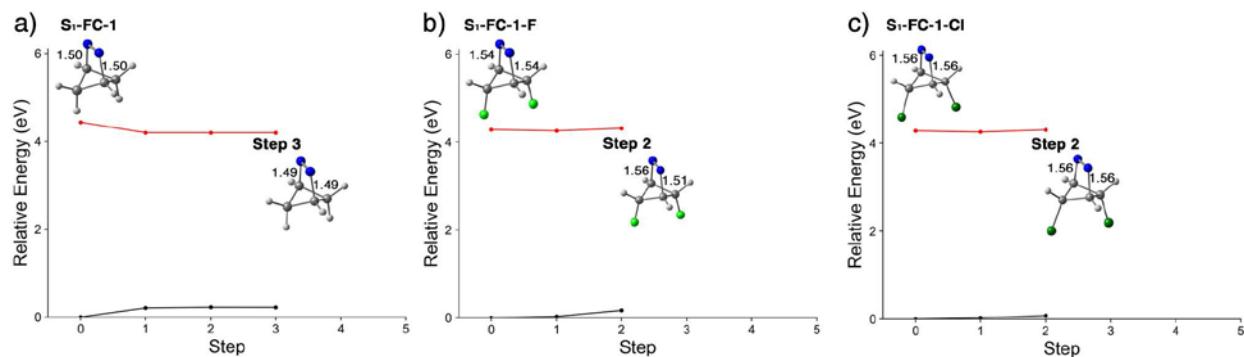


Figure S3. The minimum energy path from (a) **S₁-FC-1**, (b) **S₁-FC-1-F**, and (c) **S₁-FC-1-Cl** with CASSCF(8,8)/ANO-S-VDZP. The C–N distances are in Angstrom.

Table S3. Absolute electronic energies (Hartree) in the minimum energy path of 1, 1-F, 1-Cl with CASSCF(8,8)/ANO-S-VDZP.

Step	S₀, 1	S₁, 1	S₀, 1-F	S₁, 1-F	S₀, 1-Cl	S₁, 1-Cl
0	-263.89942956	-263.73660235	-461.63604287	-461.47865484	-1181.73082382	-1181.57336973
1	-263.89190520	-263.74518435	-461.63497943	-461.47959110	-1181.72979985	-1181.57428441
2	-263.89134053	-263.74518622	-461.62992694	-461.47760381	-1181.72802667	-1181.57258095
3	-263.89140528	-263.74518535				

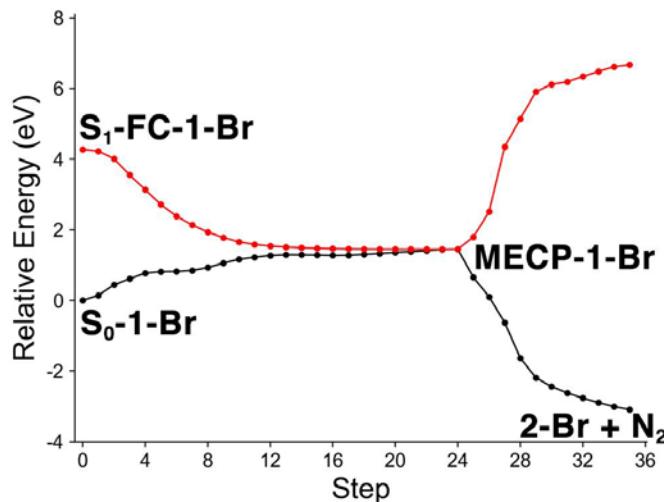


Figure S4. The minimum energy path from the **S₁-FC-1-Br** to **MECP-1-Br** and to **2-Br** with CASSCF(8,8)/ANO-S-VDZP.

Table S4. Absolute electronic energies (Hartree) in the minimum energy path of **1-Br** with CASSCF(8,8)/ANO-S-VDZP and CASPT2(8,8)/ANO-S-VDZP//CASSCF(8,8)/ANO-S-VDZP

Step	S₀, CASSCF	S₁, CASSCF	S₀, CASPT2	S₁, CASPT2
0	-5407.59819879	-5407.44107577	-5408.58905479	-5408.45033455
1	-5407.59299358	-5407.44301472	-5408.58201942	-5408.44884435
2	-5407.58199341	-5407.45074851	-5408.55936506	-5408.44032806
3	-5407.57571167	-5407.46773023	-5408.54129065	-5408.43910980
4	-5407.56982096	-5407.48306210	-5408.53158754	-5408.44942727

5	-5407.56833634	-5407.49845359	-5408.52481601	-5408.46050611
6	-5407.56812621	-5407.51051129	-5408.52156871	-5408.47013701
7	-5407.56705334	-5407.51973545	-5408.51869069	-5408.47750075
8	-5407.56401665	-5407.52706802	-5408.51587107	-5408.48348670
9	-5407.55935764	-5407.53291678	-5408.51205044	-5408.48779362
10	-5407.55545740	-5407.53731728	-5408.50927781	-5408.49110132
11	-5407.55326365	-5407.54004925	-5408.50767286	-5408.49345004
12	-5407.55142521	-5407.54167037	-5408.50628737	-5408.49499773
13	-5407.55063641	-5407.54272593	-5408.50556025	-5408.49592317
14	-5407.55071878	-5407.54348358	-5408.50549949	-5408.49653746
15	-5407.55092974	-5407.54402730	-5408.50563201	-5408.49696285
16	-5407.55137988	-5407.54441334	-5408.50595014	-5408.49728540
17	-5407.55113360	-5407.54467844	-5408.50576443	-5408.49761298
18	-5407.55027393	-5407.54484434	-5408.50514036	-5408.49795559
19	-5407.54935258	-5407.54494301	-5408.50446049	-5408.49835029
20	-5407.54833705	-5407.54500087	-5408.50355424	-5408.49859748
21	-5407.54740613	-5407.54502164	-5408.50267666	-5408.49890541
22	-5407.54638515	-5407.54501989	-5408.50147062	-5408.49911529
23	-5407.54523459	-5407.54500232	-5408.49993519	-5408.49917975
24 (MECP)	-5407.54496652	-5407.54496559	-5408.49930190	-5408.49914917
25	-5407.57425954	-5407.53222025	-5408.52207200	-5408.48554616
26	-5407.59445003	-5407.50599055	-5408.54132507	-5408.46185056
27	-5407.62129102	-5407.43838743	-5408.56396120	-5408.43455024
28	-5407.65828292	-5407.40921876	-5408.59337764	-5408.40446660
29	-5407.67876093	-5407.38103179	-5408.61320111	-5408.38849877
30	-5407.68794868	-5407.37338822	-5408.62021133	-5408.38590236
31	-5407.69458698	-5407.37077551	-5408.62233824	-5408.38834333
32	-5407.69997081	-5407.36518068	-5408.62399891	-5408.39003738
33	-5407.70468905	-5407.35994482	-5408.62458075	-5408.39583826
34	-5407.70880592	-5407.35507326	-5408.62562534	-5408.40504804
35	-5407.71192899	-5407.35313576	-5408.62734430	-5408.41193175

NAMD trajectories of 1-F and 1-Cl

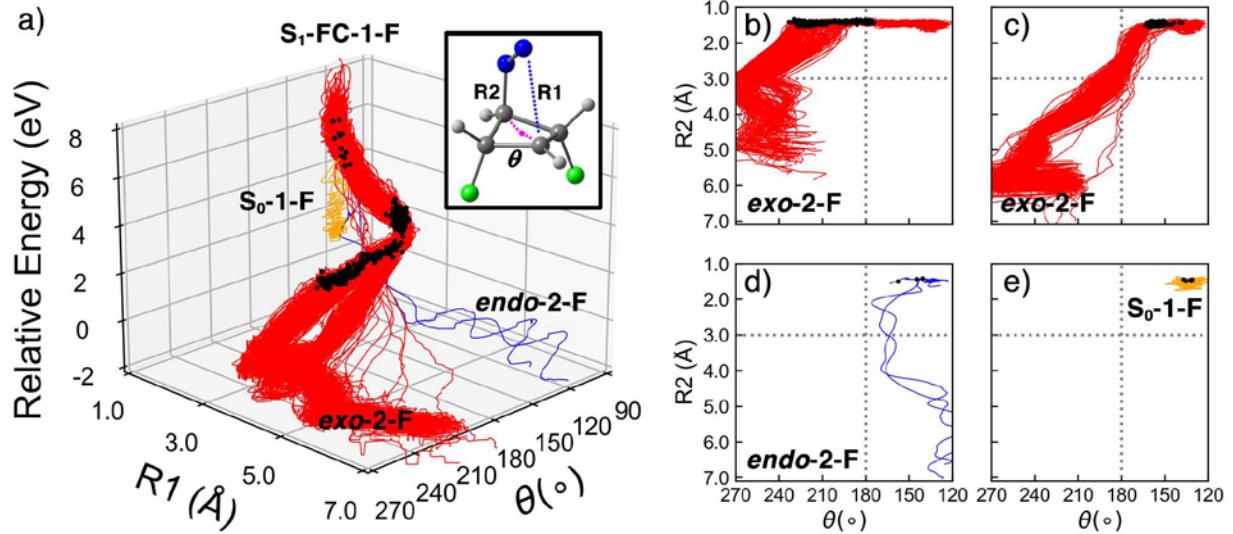


Figure S5. (a) The trajectories of **1-F** in 300 fs NAMD simulation with CASSCF(8,8)/ ANO-S-VDZP. The plot monitors the N–C bond breaking and bicyclobutane inversion with R1 and θ . (b) The subplot of trajectories undergoing concerted N–C bond breaking and bicyclobutane inversion to **exo-2-F** (44%). (c) The subplot of trajectories undergoing stepwise N–C bond breaking and bicyclobutane inversion to **exo-2-F** (54%). (d) The subplot of trajectories undergoing stepwise N–C bond breaking and bicyclobutane retention to **endo-2-F** (1%). (e) The subplot of trajectories reverted to **S₀-1-F** (1%). The subplots (b)–(e) track the second C–N bond breaking and the inversion of bicyclobutane with R2 and θ . The black dots represent the latest surface hopping points.

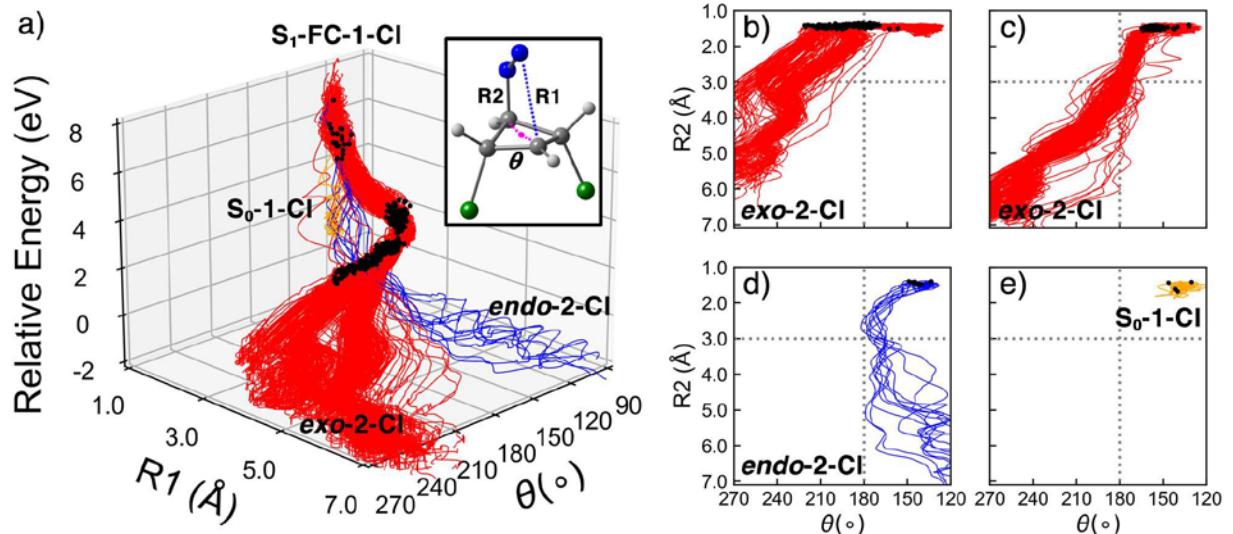


Figure S6. (a) The trajectories of **1-Cl** in 300 fs NAMD simulation with CASSCF(8,8)/ ANO-S-VDZP. The plot monitors the N–C bond breaking and bicyclobutane inversion with R1 and θ . (b) The subplot of trajectories undergoing concerted N–C bond breaking and bicyclobutane inversion to **exo-2-Cl** (47%). (c) The subplot of trajectories undergoing stepwise N–C bond breaking and

bicyclobutane inversion to **exo-2-Cl** (49%). (d) The subplot of trajectories undergoing stepwise N–C bond breaking and bicyclobutane retention to **endo-2-Cl** (2%). (e) The subplot of trajectories reverted to **S₀-1-Cl** (1%). The subplots (b)–(e) track the second C–N bond breaking and the inversion of bicyclobutane with R2 and □. The black dots represent the latest surface hopping points.

2D PESs for 1-F, 2-F, 1-Cl, and 2-Cl

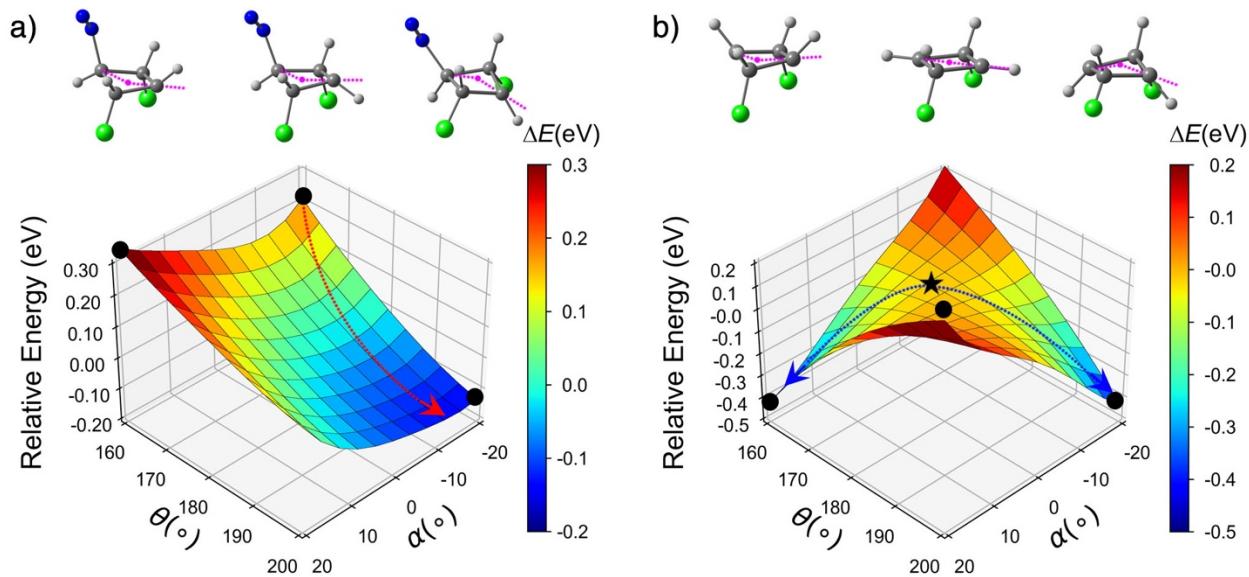


Figure S7. (a) The 2D PES of **1-F** with CASSCF(8,8)/ANO-S-VDZP, where the N–C distance was constrained at 1.48 Å. The red dotted arrow shows a path favoring the inversion of bicyclobutane. (b) The 2D PES of **2-F** with CASSCF(2,2)/ANO-S-VDZP. The blue dotted arrows represent the asymmetrically bifurcated relaxation paths, which is more inclined toward inversion structure. The star in (b) was confirmed as a transition state with CASSCF(2,2)/ANO-S-VDZP. The geometries at black dots are shown above the 2D PES.

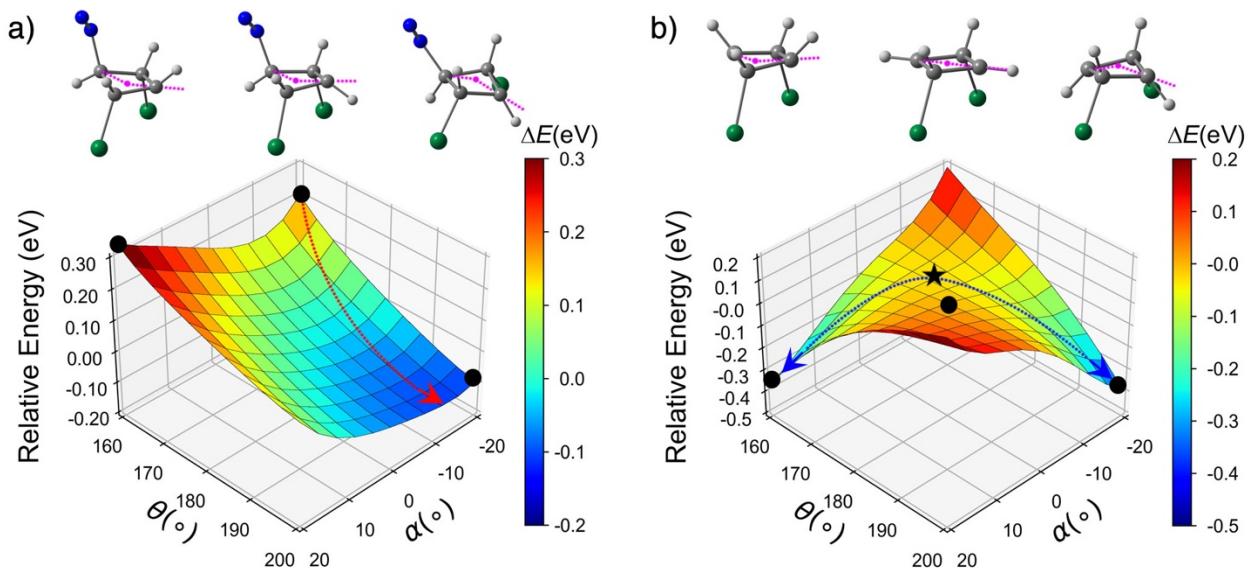


Figure S8. (a) The 2D PES of **1-Cl** with CASSCF(8,8)/ANO-S-VDZP, where the N–C distance was constrained at 1.48 Å. The red dotted arrow shows a path favoring the inversion of bicyclobutane. (b) The 2D PES of **2-Cl** with CASSCF(2,2)/ANO-S-VDZP. The blue dotted arrows represent the asymmetrically bifurcated relaxation paths, which is more inclined toward inversion structure. The star in (b) was confirmed as a transition state with CASSCF(2,2)/ANO-S-VDZP. The geometries at black dots are shown above the 2D PES.

Hyperconjugation in **2-F** and **2-Cl**

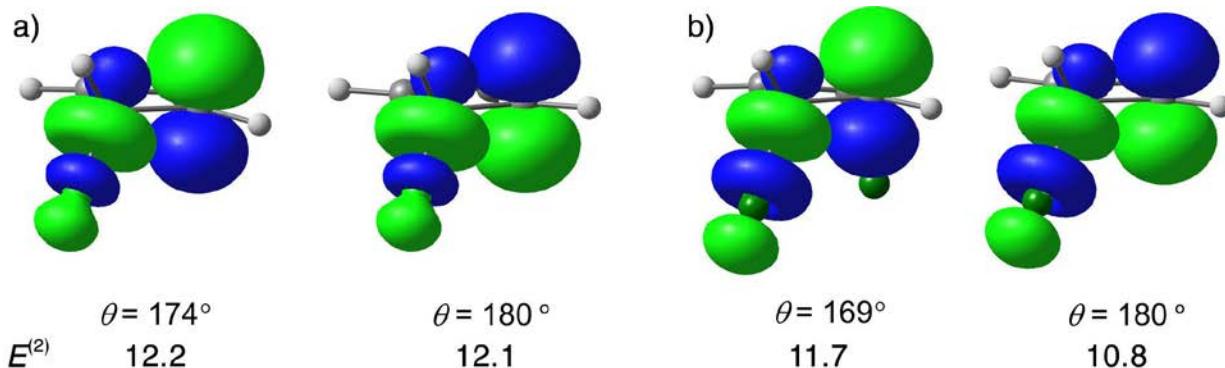


Figure S9. Hyperconjugation of $n_{\text{C}} \rightarrow \sigma^*_{\text{C}-\text{Br}}$ in terms of natural bond orbital interactions in (a) **TS-2-F** (*left*) and the planar **2-F** (*right*) and (b) **TS-2-Cl** (*left*) and the planar **2-Cl** (*right*). The $E^{(2)}$ energies are in kcal mol⁻¹.

Cartesian coordinates for optimized geometries

S₀-1

C 0.00008182 -1.21117346 0.99122121
 C -1.06614236 -0.70092450 0.00000769
 C -0.00006533 -1.21117751 -0.99121913
 C 1.06615035 -0.70090671 -0.00000747
 H 0.00014498 -1.01774745 2.05776216
 H -2.03461786 -1.19714779 0.00011938
 H -0.00013173 -1.01775546 -2.05776069
 H 2.03463416 -1.19711377 -0.00011659
 N -0.00013358 -2.67553809 0.64851470
 N 0.00017443 -2.67554085 -0.64850617
 H -1.17622381 0.38062100 0.00008177
 H 1.17621391 0.38064059 -0.00008585

S ₀ , CASSCF (Hartree)	-263.89942722
S ₁ , CASSCF (Hartree)	-263.73659797
S ₀ , CASPT2 (Hartree)	-264.65290927
S ₁ , CASPT2 (Hartree)	-264.50934306
Number of imaginary frequencies	0
The first 10 vibrational frequencies (cm ⁻¹)	
1	509.95
2	549.45
3	700.70
4	784.69
5	794.67
6	876.72
7	927.27
8	962.14
9	1002.07
10	1004.52

MECP-1

C 0.00317395 0.42621762 1.36397291
 C -1.08952110 -0.34923847 0.65994711
 C 0.00769921 -0.85608815 -0.31357125
 C 1.09793386 -0.35644583 0.67124758
 H -0.00030595 0.88483765 2.34244140
 H -1.49263104 -1.16188967 1.26748866
 H 0.01416068 -0.30541789 -1.24819682
 H 1.48887623 -1.17190580 1.28296605
 N 0.00310906 -3.43941991 -0.76400142
 N 0.00554396 -2.24024192 -0.65712032
 H -1.91487418 0.20646812 0.21709699
 H 1.93180435 0.19352747 0.23729673

S ₀ , CASSCF (Hartree)	-263.80793641
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S ₁ , CASSCF (Hartree)	-263.80793624
S ₀ , CASPT2 (Hartree)	-264.54257043
S ₁ , CASPT2 (Hartree)	-264.54258811

S₀-1-F

C 0.00006272 -1.20954321 1.00334830
C -1.07650509 -0.76006316 0.00005713
C -0.00004410 -1.20954745 -1.00334600
C 1.07650933 -0.76002870 -0.00005680
H 0.00011737 -1.00058126 2.06556302
H -2.01647855 -1.30589305 0.00009911
H -0.00010577 -1.00059036 -2.06556166
H 2.01650027 -1.30582853 -0.00009642
N -0.00000634 -2.70976142 0.64372281
N 0.00007389 -2.70976454 -0.64371316
F -1.33835006 0.56389747 0.00006991
F 1.33831132 0.56394023 -0.00007523

S ₀ , CASSCF (Hartree)	-461.63604128
S ₁ , CASSCF (Hartree)	-461.47865338
S ₀ , CASPT2 (Hartree)	-462.77092213
S ₁ , CASPT2 (Hartree)	-462.63165981
Number of imaginary frequencies	0
The first 10 vibrational frequencies (cm ⁻¹)	
1	220.57
2	297.19
3	329.65
4	336.42
5	479.24
6	484.29
7	615.90
8	651.76
9	823.72
10	875.65

MECP-1-F

C -0.00016073 0.38510598 1.39435214
C -1.08307616 -0.37813294 0.68656734
C 0.00331905 -0.88324245 -0.29209718
C 1.08511637 -0.38067164 0.69293237
H -0.00204761 1.00237980 2.27811547
H -1.55008229 -1.17194723 1.26849981
H 0.00657943 -0.28645221 -1.19935663
H 1.54677542 -1.17560026 1.27760071
N 0.00191408 -3.43892568 -0.83200317
N 0.00282450 -2.24720368 -0.66974198
F -2.07161146 0.35851712 0.11697730

F 2.07872313 0.35361502 0.12919040

S ₀ , CASSCF (Hartree)	-461.57199396
S ₁ , CASSCF (Hartree)	-461.57199306
S ₀ , CASPT2 (Hartree)	-462.67196612
S ₁ , CASPT2 (Hartree)	-462.67260766

S₀-1-CI

C 0.00005408 -1.23848746 1.00115817
 C -1.09587502 -0.81925954 0.00005082
 C -0.00003802 -1.23849158 -1.00115559
 C 1.09588600 -0.81924646 -0.00004999
 H 0.00010166 -1.03241149 2.06322200
 H -1.98439419 -1.43828944 0.00009288
 H -0.00008794 -1.03241990 -2.06322025
 H 1.98441252 -1.43826576 -0.00008955
 N 0.00004664 -2.75171953 0.64355222
 N -0.00001192 -2.75172214 -0.64354344
 Cl -1.65010798 0.85826483 0.00007278
 Cl 1.65009917 0.85828446 -0.00007907

S ₀ , CASSCF (Hartree)	-1181.73082174
S ₁ , CASSCF (Hartree)	-1181.57336720
S ₀ , CASPT2 (Hartree)	-1182.76782284
S ₁ , CASPT2 (Hartree)	-1182.62898547
Number of imaginary frequencies	0
The first 10 vibrational frequencies (cm ⁻¹)	
1	172.60
2	224.95
3	262.09
4	284.76
5	336.72
6	390.71
7	475.68
8	618.37
9	782.42
10	808.40

MECP-1-CI

C 0.00150817 0.36109945 1.40634903
 C -1.08329189 -0.37423003 0.68117352
 C 0.00298866 -0.87344665 -0.31111698
 C 1.08659398 -0.37892990 0.68642635
 H 0.00065077 0.95936013 2.30237236
 H -1.54830169 -1.17985922 1.24290537
 H 0.00645546 -0.30122077 -1.23164634
 H 1.54543381 -1.18653841 1.25039078
 N -0.00154463 -3.43900191 -0.77060768

N 0.00082007 -2.24235271 -0.65656634
 Cl -2.40878219 0.59678309 -0.01370936
 Cl 2.41942780 0.58642144 -0.00204908

S ₀ , CASSCF (Hartree)	-1181.67331177
S ₁ , CASSCF (Hartree)	-1181.67331051
S ₀ , CASPT2 (Hartree)	-1182.67400185
S ₁ , CASPT2 (Hartree)	-1182.67448586

S₀-1-Br

C -0.00019234 -1.25052528 1.00123326
 C -1.09830583 -0.84194023 -0.00077274
 C 0.00022039 -1.25093146 -1.00150427
 C 1.09831950 -0.84190129 0.00061984
 H 0.00058263 -1.04785556 2.06379562
 H -1.97876613 -1.47138411 -0.00105439
 H -0.00053971 -1.04827176 -2.06406297
 H 1.97878819 -1.47132694 0.00146635
 N 0.00613546 -2.77225770 0.64432657
 N -0.00615727 -2.77223219 -0.64440548
 Br -1.76855619 0.96240354 -0.00040311
 Br 1.76855631 0.96245897 0.00077232

S ₀ , CASSCF (Hartree)	-5407.59820241
S ₁ , CASSCF (Hartree)	-5407.44107774
S ₀ , CASPT2 (Hartree)	-5408.59499493
S ₁ , CASPT2 (Hartree)	-5408.45672362
Number of imaginary frequencies	0
The first 10 vibrational frequencies (cm ⁻¹)	
1	112.9395
2	180.0575
3	241.7021
4	259.0961
5	327.0357
6	382.7025
7	410.7488
8	699.1024
9	773.5998
10	820.9811

MECP-1-Br

C -0.00057184 0.35131181 1.41021676
 C -1.08419823 -0.35937123 0.66857636
 C 0.00022465 -0.86047008 -0.32712389
 C 1.08381864 -0.35897163 0.66929716
 H -0.00101201 0.96493584 2.29555758
 H -1.57741902 -1.16056270 1.20997770
 H 0.00046980 -0.30547276 -1.25775403

H	1.57690512	-1.15996295	1.21109083
N	0.00068656	-3.43252613	-0.74342325
N	0.00052432	-2.23446905	-0.64901666
Br	-2.51839775	0.72902431	-0.08034732
Br	2.51836450	0.72959470	-0.07859764

S ₀ , CASSCF (Hartree)	-5407.54496481
S ₁ , CASSCF (Hartree)	-5407.54496348
S ₀ , CASPT2 (Hartree)	-5408.50525428
S ₁ , CASPT2 (Hartree)	-5408.50510003

TS-2

C	-0.02655638	0.89425652	1.14586662
C	-1.12342066	0.56860772	0.14240931
C	0.01035510	0.28830584	-0.83335007
C	1.10720449	0.61395993	0.17012278
H	-0.04578938	1.20987280	2.17759260
H	-1.78024288	1.40247198	-0.12513355
H	0.02959496	-0.02731065	-1.86507517
H	1.73603230	1.47397588	-0.08144957
H	-1.75223964	-0.29141974	0.39394257
H	1.76403738	-0.21991588	0.43762655

S ₀ , CASSCF (Hartree)	-154.85163664
S ₀ , CASPT2 (Hartree)	-155.34784488
Number of imaginary frequencies	2
The first 10 vibrational frequencies (cm ⁻¹)	
1	-414.42
2	-322.59
3	206.31
4	810.26
5	895.18
6	950.68
7	987.72
8	1008.72
9	1028.53
10	1122.20

TS-2-F

C	-0.00573170	-0.06640988	1.67541489
C	-1.13859727	-0.56964614	0.83655979
C	-0.05062163	-1.19039728	0.01735834
C	1.08267536	-0.60571576	0.80087282
H	0.01891985	0.64486703	2.49084152
H	-1.89440733	-1.20828232	1.29001155
H	-0.07411195	-1.68462848	-0.94525567
H	1.83153379	-1.26878196	1.23014838
F	-1.84944853	0.42345817	0.18259636

F 1.80401790 0.36413593 0.12389720

S ₀ , CASSCF (Hartree)	-352.62835774
S ₀ , CASPT2 (Hartree)	-353.50302519
Number of imaginary frequencies	1
The first 10 vibrational frequencies (cm ⁻¹)	
1	-226.73
2	206.93
3	400.50
4	427.93
5	509.96
6	606.37
7	758.53
8	879.09
9	1002.46
10	1043.20

TS-2-CI

C -0.00308382 -0.21496932 1.75535247
 C -1.10921982 -0.68681255 0.86208345
 C -0.00409982 -1.32465964 0.07725005
 C 1.10257333 -0.69258788 0.86456340
 H -0.00223373 0.46980225 2.59189935
 H -1.89159296 -1.31322802 1.27679091
 H -0.00433603 -1.82633313 -0.88037575
 H 1.88073267 -1.32307802 1.28102056
 CI -2.02505599 0.63731421 -0.01297579
 CI 2.02727187 0.62673307 -0.00843231

S ₀ , CASSCF (Hartree)	-1072.72458749
S ₀ , CASPT2 (Hartree)	-1073.49511959
Number of imaginary frequencies	1
The first 10 vibrational frequencies (cm ⁻¹)	
1	-180.18
2	112.57
3	282.02
4	346.82
5	347.00
6	480.01
7	633.67
8	713.52
9	758.26
10	887.07

TS-2-Br

C 0.00260145 -0.18227172 1.72817813
 C -1.09903921 -0.66850542 0.84172862
 C 0.00308727 -1.29200490 0.04649673
 C 1.10472148 -0.66782837 0.84191794

H	0.00227448	0.50642008	2.56089680
H	-1.88158862	-1.29380206	1.25412643
H	0.00328771	-1.78674746	-0.91420467
H	1.88723372	-1.29288647	1.25461978
Br	-2.13703240	0.76499719	-0.10452444
Br	2.14360404	0.76548645	-0.10364887

S _{0,CASSCF} (Hartree)	-5298.59681662
S _{0,CASPT2} (Hartree)	-5299.31858588
Number of imaginary frequencies	1
The first 10 vibrational frequencies (cm ⁻¹)	
1	-122.057
2	417.8325
3	676.9243
4	959.9181
5	1281.389
6	1288.643
7	1415.587
8	1442.564
9	1585.535
10	1757.88