Supporting Information

for

Tipping the Balance: Theoretical Interrogation of Extended Divergent Heterolytic Fragmentations

Croix J. Laconsay, Ka Yi Tsui, and Dean J. Tantillo*

Department of Chemistry, University of California—Davis, CA 95616

Corresponding Author
Dean J. Tantillo: djtantillo@ucdavis.edu

Contents

S1. Benchmark Studies and References

Full gas-phase optimizations were carried out using Becke's hybrid, three-parameter functional[1] and Lee, Yang, and Parr's non-local correlation functional[2] (B3LYP) with Grimme's D3 correction and Becke and Johnson damping (BJ-damping or just "BJ").[3] See **Table S1** for a comparison of different DFT functionals. Adding D3 dispersion corrections (entry's **1** vs. **2**) provides a negligible change in the free energy barrier. Additionally, changing the basis set from 6-31G(d) to 6-31+G(d,p) does not alter the reaction barrier. An increase of ~2 kcal mol^{-1} (**2** vs. **4**) is observed with the inclusion of Becke and Johnson damping. Therefore, B3LYP-D3(BJ) and M06-2X are both justified at the 6-31G(d) basis set level; the two functionals together cover the range of different free energy barriers, which is reasonable since this study is concerned with qualitative (not quantitative) trends.

A wavefunction stability test on system 1 suggests that both the starting substrate and transition state structure towards fragmentation is stable and thus no optimizations need the "*guess=(mix,always)*" keyword.

DFT Functional Test.

Table S1. DFT functional test for entry 1 in Table 1 in the main manuscript (i.e. electrofuge substituent = $N(CH_3)_2$ and nucleofuge = O(CO)Cl. Fragmentation activation free energy barriers are reported in kcal mol^{-1}. The basis set is 6-31G(d) unless specified otherwise.

Entry	Density Functional	$\Delta G^{\ddagger}$
1	B3LYP	33.7
2	B3LYP-D3	33.5
3	B3LYP-D3/6-31+G(d,p)	34.8
4	B3LYP-D3(BJ)	35.4
5	M06-2X	46.9
6	ωB97X-D	45.3
7	B2PLYP-D3(BJ)	35.7
8	BB1K	48.1

[1] A. D. Becke, *J. Chem. Phys.* **1993,** *98*, 5648.
[2] Lee, Y.; Yang, W.; Parr, R, G. *Phys. Rev. B*, **1988**, *37*, 785.
[3] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456.

Basis Set Test.

Table S1-A. Basis set test at the B3LYP-D3(BJ) DFT level with 6-31+G(d).

Entries	X	Y_1	Y_2	Electronic Energy (Hartree)	Sum of Electronic and Free Energy (Hartree)	Relative Free Energy (kcal/mol)
Reactant 1	$N(CH_3)_2$	O(CO)Cl	H	-1373.534	-1373.323	[0]
TSS 1	$N(CH_3)_2$	O(CO)Cl	H	-1373.472	-1373.266	35.760
Product 1	$N(CH_3)_2$	O(CO)Cl	H	-1373.641	-1373.445	-76.461
Reactant 2	$N(CH_3)_2$	Cl	Cl	-1644.555	-1644.364	[0]
TSS 2	$N(CH_3)_2$	Cl	Cl	-1644.491	-1644.308	35.082
Product 2	$N(CH_3)_2$	Cl	Cl	-1644.605	-1644.427	-39.562
Reactant 3	NH_2	O(CO)Cl	H	-1294.912	-1294.754	[0]
TSSA 3	NH_2	O(CO)Cl	H	-1294.859	-1294.706	30.152
Enamine 3	NH_2	O(CO)Cl	H	-1295.026	-1294.887	-83.528
Reactant 4	NH_2	Cl	Cl	-1565.933	-1565.795	[0]
TSS 4	NH_2	Cl	Cl	-1565.876	-1565.746	30.418
Product 4	NH_2	Cl	Cl	-1566.008	-1565.882	-54.861
Reactant 5	OCH_3	O(CO)Cl	H	-1354.096	-1353.925	[0]
TSS 5	OCH_3	O(CO)Cl	H	-1354.034	-1353.868	35.583
Product 5	OCH_3	O(CO)Cl	H	-1354.194	-1354.038	-71.390
Reactant 6	OCH_3	Cl	Cl	-1625.116	-1624.965	[0]
TSS-B 6	OCH_3	Cl	Cl	-1625.052	-1624.908	35.987
Product 6	OCH_3	Cl	Cl	-1625.152	-1625.010	-28.242
Reactant 7	$OCH(CH_3)_2$	O(CO)Cl	H	-1432.742	-1432.517	[0]
TSS 7	$OCH(CH_3)_2$	O(CO)Cl	H	-1432.678	-1432.458	36.944
Product 7	$OCH(CH_3)_2$	O(CO)Cl	H	-1432.847	-1432.640	-77.045
Reactant 8	$OCH(CH_3)_2$	Cl	Cl	-1703.766	-1703.562	[0]
TSS-B 8	$OCH(CH_3)_2$	Cl	Cl	-1703.699	-1703.504	36.477

Product 8	$OCH(CH_3)_2$	Cl	Cl	-1703.801	-1703.609	-29.398
Reactant 9	H	O(CO)Cl	H	-1239.541	-1239.398	[0]
TSS 9	H	O(CO)Cl	H	-1239.476	-1239.340	36.319
Product 9	H	O(CO)Cl	H	-1239.633	-1239.510	-70.471
Reactant 10	H	Cl	Cl	-1510.565	-1510.443	[0]
TSS-A 10	H	Cl	Cl	-1510.497	-1510.382	38.155
Product 10	H	Cl	Cl	-1510.627	-1510.519	-47.729
Reactant 11	F	O(CO)Cl	H	-1338.819	-1338.685	[0]
TSS 11	F	O(CO)Cl	H	-1338.748	-1338.620	40.991
Product 11	F	O(CO)Cl	H	-1338.899	-1338.784	-62.058
Reactant 12	F	Cl	Cl	-1609.843	-1609.729	[0]
TSS-A 12	F	Cl	Cl	-1609.768	-1609.662	42.430
Product 12	F	Cl	Cl	-1609.890	-1609.791	-38.435

Table S1-B. Basis set test at the M06-2X DFT level with 6-31+G(d).

Entries	X	Y_1	Y_2	Electronic Energy (Hartree)	Sum of Electronic and Free Energy (Hartree)	Relative Free Energy (kcal/mol)
Reactant 1	$N(CH_3)_2$	O(CO)Cl	H	-1373.076	-1372.861	[0]
TSS 1	$N(CH_3)_2$	O(CO)Cl	H	-1372.994	-1372.784	48.673
Product 1	$N(CH_3)_2$	O(CO)Cl	H	-1373.166	-1372.964	-64.773
Reactant 2	$N(CH_3)_2$	Cl	Cl	-1644.139	-1643.945	[0]
TSS 2	$N(CH_3)_2$	Cl	Cl	-1644.058	-1643.871	46.779
Product 2	$N(CH_3)_2$	Cl	Cl	-1644.187	-1644.004	-36.991

Reactant 3	NH_2	O(CO)Cl	H	-1294.504	-1294.341	[0]
TSS-to-int 3	NH_2	O(CO)Cl	H	-1294.435	-1294.278	39.577
Carbanion-int 3	NH_2	O(CO)Cl	H	-1294.442	-1294.285	35.246
TSSA 3	NH_2	O(CO)Cl	H	-1294.432	-1294.276	40.977
TSS-to-A 3	NH_2	O(CO)Cl	H	-1294.441	-1294.286	34.665
TSS-to-B 3	NH_2	O(CO)Cl	H	-1294.434	-1294.281	37.510
Enamine 3	NH_2	O(CO)Cl	H	-1294.594	-1294.446	-65.910
Imine 3	NH_2	O(CO)Cl	H	-1294.541	-1294.395	-34.100
Reactant 4	NH_2	Cl	Cl	-1565.566	-1565.425	[0]
TSS 4	NH_2	Cl	Cl	-1565.496	-1565.361	40.299
Product 4	NH_2	Cl	Cl	-1565.606	-1565.478	-33.394
Reactant 5	OCH_3	O(CO)Cl	H	-1353.662	-1353.486	[0]
TSS 5	OCH_3	O(CO)Cl	H	-1353.580	-1353.409	48.325
Product 5	OCH_3	O(CO)Cl	H	-1353.742	-1353.582	-60.270
Reactant 6	OCH_3	Cl	Cl	-1624.723	-1624.569	[0]
TSS-B 6	OCH_3	Cl	Cl	-1624.644	-1624.496	46.094
Product 6	OCH_3	Cl	Cl	-1624.750	-1624.606	-23.211
Reactant 7	$OCH(CH_3)_2$	O(CO)Cl	H	-1432.254	-1432.024	[0]
TSS 7	$OCH(CH_3)_2$	O(CO)Cl	H	-1432.171	-1431.947	48.682
Product 7	$OCH(CH_3)_2$	O(CO)Cl	H	-1432.340	-1432.128	-64.681
Reactant 8	$OCH(CH_3)_2$	Cl	Cl	-1703.322	-1703.114	[0]
TSS-B 8	$OCH(CH_3)_2$	Cl	Cl	-1703.239	-1703.038	48.035
Product 8	$OCH(CH_3)_2$	Cl	Cl	-1703.348	-1703.151	-23.319
Reactant 9	H	O(CO)Cl	H	-1239.155	-1239.008	[0]
TSS 9	H	O(CO)Cl	H	-1239.070	-1238.931	48.793
Product 9	H	O(CO)Cl	H	-1239.230	-1239.101	-58.213
Reactant 10	H	Cl	Cl	-1510.222	-1510.097	[0]
TSS-A 10	H	Cl	Cl	-1510.133	-1510.016	51.103
Product 10	H	Cl	Cl	-1510.265	-1510.154	-35.979
Reactant 11	F	O(CO)Cl	H	-1338.405	-1338.267	[0]
TSS 11	F	O(CO)Cl	H	-1338.313	-1338.182	53.299

Product 11	F	O(CO)Cl	H	-1338.467	-1338.346	-49.599
Reactant 12	F	Cl	Cl	-1609.471	-1609.355	[0]
TSS-A 12	F	Cl	Cl	-1609.376	-1609.266	55.691
Product 12	F	Cl	Cl	-1609.504	-1609.401	-28.882

Other references

Full Gaussian 09 Reference:

Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

Natural Bond Orbital program:

NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, and F. Weinhold.

S2. Further Details for Structure **1**

Energetic Profile for [3,3]-sigmatropic shift. This example of the [3,3]-sigmatropic shift that interconverts products **A** and **B** corresponds to entry 3 in **Table 1** of the main manuscript.

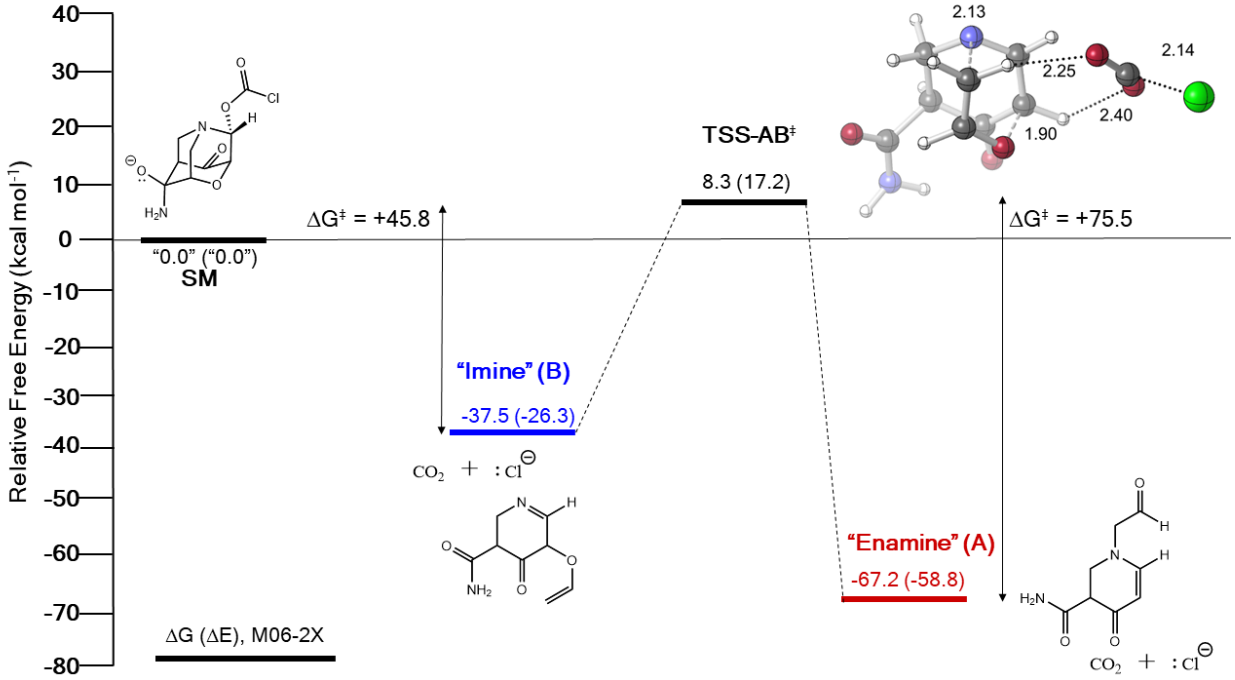


Figure S1. Representative example of [3,3]-sigmatropic shift barrier at the M06-2X/6-31G(d) level of theory for entry 3, Table 1 of main manuscript.

Entry 3. Other pathways identified for Entry 3.

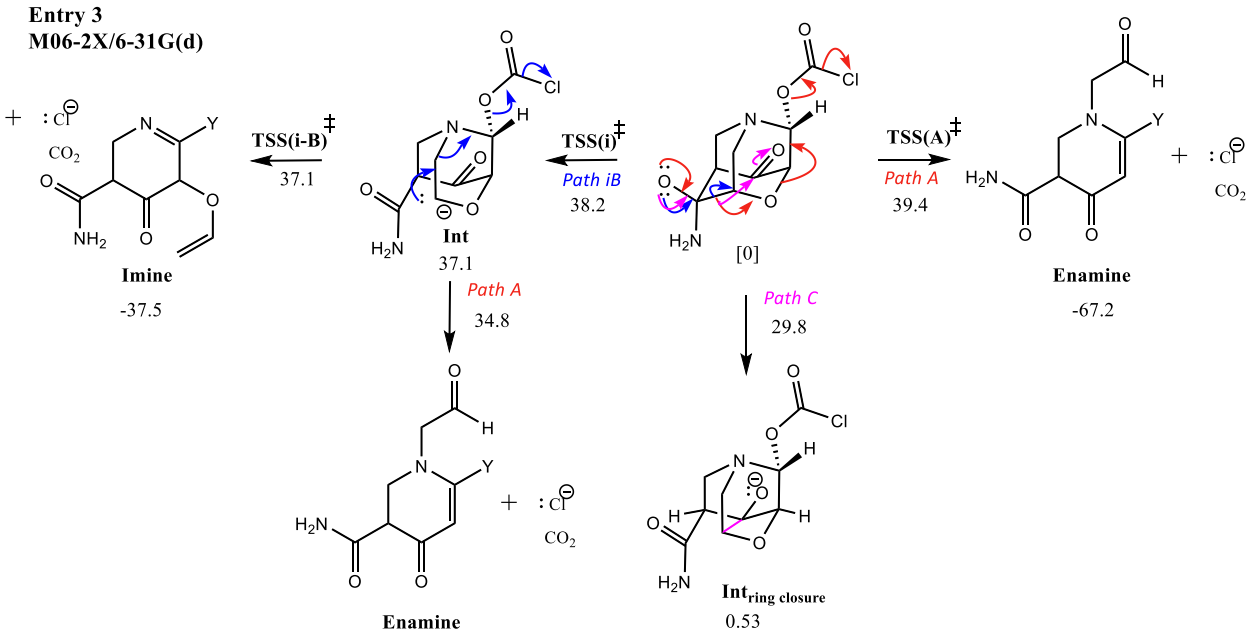


Figure S2. Another pathway (Path C, in pink) leading to ring closure of the carbanion intermediate. All numbers are free energies in kcal mol^{-1} the M06-2X/6-31G(d) level of theory for entry 3. Despite being kinetically favored, the first step towards Path C is not thermodynamically favored. We did not pursue this pathway further.

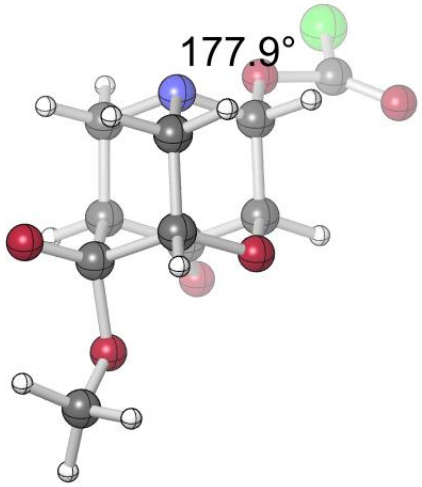


Figure S3. Under the influence of an EEF of F_y = +0.005 au, the reactant structure optimized to a conformer in which the C-O-C-Cl of the chloroformate moiety is ~178°.

S3. Natural Bond Orbital Calculations

Natural Bond Orbital (NBO) Calculations. Second-order perturbation energies were obtained using the "pop=nbo" keyword in Gaussian09**.** Wiberg Bond Orders were obtained using the "pop=nboread" keyword in Gaussian09. Natural Bond Orbital (NBO) analysis "transforms the canonical delocalized molecular orbitals from DFT calculations into localized orbitals that are closely tied to the chemical bonding concepts [and the Lewis structure depiction of molecules]." (Alabugin and coworkers, *Chem. Sci.*, **2015**, *6*, 6783). The extent of deviation from the Lewis structure, i.e. the amount of delocalization or interaction between filled orbitals and unfilled orbitals, is approximated via a second-order perturbative energy approach as $E(2) = n_i^2|F_{ij}|/\Delta E$. In this analysis, n_i represents the population of the donor orbitals, F_{ij} is the Fock matrix element for the interaction orbitals i and j, and ΔE is the energy difference between the orbitals. For literature examples of NBO analyses see: Alabugin *et al*., *WIREs Comput. Mol. Sci.*, **2018**, e1389; Alabugin and coworkers, *Chem. Sci.*, **2015**, *6*, 6783.

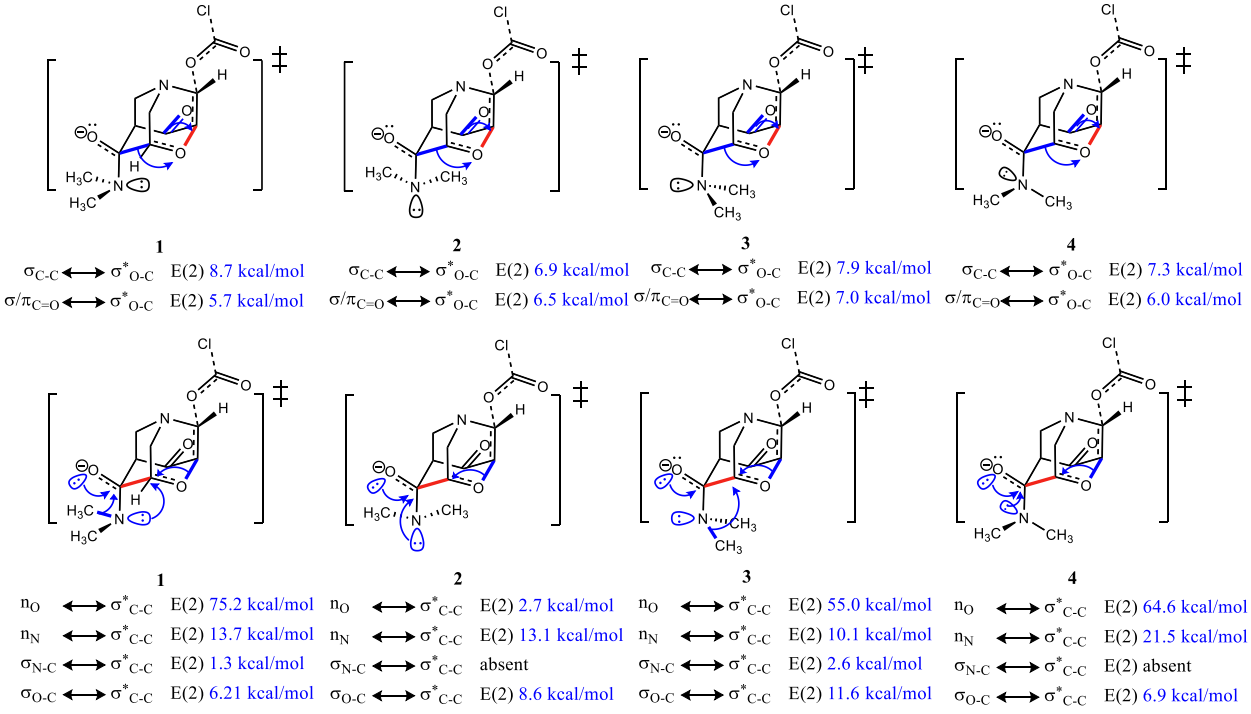
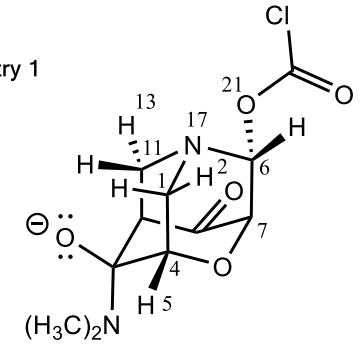


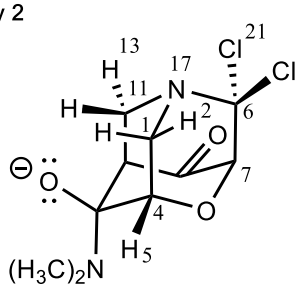
Figure S4. Natural Bond Orbital (NBO) second-order perturbative analysis of the four rotamers.

Second-order perturbation energies

Entry 1



Entry 2



Entry 4

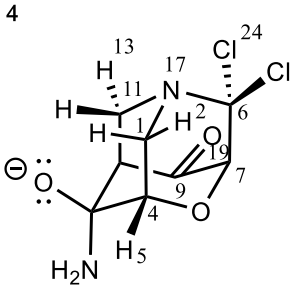


Table S2-A. Entry 1 NBO E2 values at M06-2X level of theory.

Donor	C7 - O18 σ* (E2, kcal/mol)	Donor	C1-N17 σ* (E2, kcal/mol)
C4-H5	3.14	C4-H5	1.64
C6-H20	1.11	C6-N17	0.62
C6-O21	1.51	C6-O21	1.66
C7-O18	1.11	C11-H13	4.09
C9-O19	5.66	C11-N17	0.51
C4 (CR)	0.52	C6 (CR)	0.52
C7 (CR)	1.68	C11 (CR)	0.52
C4 (LP)	60.89	C4 (LP)	6.39
O18 (LP)	1.66	O21 (LP)	0.51
O18 (LP2)	3.58		

Table S2-B. Entry 2 NBO E2 values at M06-2X level of theory.

Donor	C7 - O18 σ* (E2, kcal/mol)	Donor	C1-N17 σ* (E2, kcal/mol)
C1-C4	0.89	C1-H2	181.23
C1-C4	2.34	C1-C4 (SB)	3.03
C4-C5	2.55	C1-C4 (DB)	175.08
C6-Cl21	4.64	C1-N17	64.76
C9-O19	3.31	C4-H5	1.13
C4 (CR)	0.99	C6-Cl21	0.99
C7 (CR)	1.07	C1 (CR)	3.34
Cl21	0.98	N17 (LP)	0.75

Table S2-C. Entry 4 NBO E2 values at M06-2X level of theory.

Donor	C7 - O18 σ* (E2, kcal/mol)	Donor	C1-N17 σ* (E2, kcal/mol)
C1-C4	0.53	C4-H5	1.65
C4-H5	2.57	C6-Cl24	2.86
C6-Cl24	3.33	C1 (CR)	0.73
C9-O19	3.53	C4 (LP)	24.51
C4 (CR)	0.95		
C7 (CR)	1.13		
C4 (LP)	7.56		
O18 (LP)	0.77		
Cl24 (LP)	1.21		

Table S2-D. Entry 1 NBO E2 values at B3LYP-D3(BJ) level of theory.

Donor	C7 - O18 σ* (E2, kcal/mol)	Donor	C1-N17 σ* (E2, kcal/mol)
C4-H5	4.23	C4-H5	2.22
C4-C10	8.3	C4-C10	2.01
C6-H20	1.03	C6-O21	1.58
C6-O21	1.68	C11-H13	3.56
C7-O18	0.71	C6 (CR)	0.51
C9-O19	5.82		
C7-O18	1.69		
O18 (LP)	1.46		
C7-O18	3.49		

Table S2-E. Entry 2 NBO E2 values at B3LYP-D3(BJ) level of theory.

Donor	C7 - O18 σ* (E2, kcal/mol)	Donor	C1-N17 σ* (E2, kcal/mol)
C1-C4	0.54	C4-H5	1.64
C4-H5	2.67	C6-Cl21	3.42
C6-Cl21	5.02	C11-H13	3.83
C9-O19	3.23	C1 (CR)	0.89
C4 (CR)	0.87	C4 (LP)	14.78
C7 (CR)	1.52	N17 (LP)	1.29
C4 (LP)	5.12		
O18 (LP)	0.62		
O18 (LP2)	1.86		
Cl21 (LP)	0.56		

Table S2-F. Entry 4 NBO E2 values at B3LYP-D3(BJ) level of theory.

Donor	C7 - O18 σ* (E2, kcal/mol)	Donor	C1-N17 σ* (E2, kcal/mol)
C4-H5	2.64	C4-H5	1.52
C6-Cl24	5.11	C6-Cl24	3.36
C9-O19	3.40	C11-H13	3.68
C4 (CR)	0.82	C1 (CR)	0.73
C7 (CR)	1.60	C4 (LP)	13.46
C4 (LP)	5.52	N17 (LP)	1.25
O18 (LP)	0.65		
O18 (LP2)	2.09		

Wiberg Bond Orders

Table S3. B3LYP-D3(BJ)/6-31G(d) computed Wiberg Bond Orders for each entry in **Table 1** of main text.

Entry	X	Y^1	Y^2	C-O bond (Reactant)	C-O bond (TSS)	C-N bond (Reactant)	C-N bond (TSS)	P
1	$-N(CH_3)_2$	-O(CO)Cl	H	0.909	0.521	0.944	0.921	A
2	$-N(CH_3)_2$	-Cl	-Cl	0.918	0.809	0.923	0.703	B
3	$-NH_2$	-O(CO)Cl	H	0.901	0.539	0.944	0.922	A
4	$-NH_2$	-Cl	-Cl	0.909	0.797	0.924	0.737	A/B
5	$-OCH_3$	-O(CO)Cl	H	0.909	0.483	0.944	0.925	A
6	$-OCH_3$	-Cl	-Cl	0.918	0.866	0.923	0.484	B
7	$-OCH(CH_3)_2$	-O(CO)Cl	H	0.908	0.474	0.945	0.928	A
8	$-OCH(CH_3)_2$	-Cl	-Cl	0.915	0.863	0.925	0.493	B
9	-H	-O(CO)Cl	H	0.903	0.453	0.943	0.930	A
10	-H	-Cl	-Cl	0.911	0.471	0.922	0.888	A
11	-F	-O(CO)Cl	H	0.910	0.426	0.944	0.931	A
12	-F	-Cl	-Cl	0.917	0.443	0.924	0.893	A
13	-CH3	-O(CO)Cl	-Cl	0.921	0.506	0.929	0.910	A
14	-CH3	-Cl	-Cl	0.912	0.864	0.922	0.458	B

Table S4. M06-2X/6-31G(d) computed Wiberg Bond Orders for each entry in **Table 1** of main text.

Entry	X	Y^1	Y^2	C-O bond (Reactant)	C-O bond (TSS)	C-N bond (Reactant)	C-N bond (TSS)	P
1	$-N(CH_3)_2$	-O(CO)Cl	H	0.916	0.525	0.917	0.943	A
2	$-N(CH_3)_2$	-Cl	-Cl	0.921	0.893	0.922	0.482	B
3	$-NH_2$	-O(CO)Cl	H	0.908	0.554	0.944	0.917	A
4	$-NH_2$	-Cl	-Cl	0.915	0.872	0.925	0.768	A/B
5	$-OCH_3$	-O(CO)Cl	H	0.916	0.486	0.943	0.923	A
6	$-OCH_3$	-Cl	-Cl	0.924	0.887	0.927	0.442	B
6	$-OCH_3$	-Cl	-Cl	0.923	0.513	0.925	0.886	A
7	$-OCH(CH_3)_2$	-O(CO)Cl	H	0.915	0.480	0.943	0.924	A
8	$-OCH(CH_3)_2$	-Cl	-Cl	0.921	0.887	0.926	0.457	B
8	$-OCH(CH_3)_2$	-Cl	-Cl	0.921	0.505	0.926	0.890	A
9	-H	-O(CO)Cl	H	0.911	0.452	0.942	0.929	A
10	-H	-Cl	-Cl	0.918	0.466	0.923	0.897	A
10	-H	-Cl	-Cl	0.918	0.881	0.923	0.399	B
11	-F	-O(CO)Cl	H	0.916	0.429	0.944	0.930	A
12	-F	-Cl	-Cl	0.922	0.441	0.926	0.901	A
12	-F	-Cl	-Cl	0.922	0.880	0.926	0.370	B
13	-CH3	-O(CO)Cl	-H	0.926	0.512	0.929	0.908	A
14	-CH3	-Cl	-Cl	0.919	0.881	0.924	0.425	B

S4. External Electric Field Calculations

External Electric Field Calculations. External electric field (EEF) calculations were done using full optimization calculations along the *–x* or *+x* directions with geometric coordinates in *z*-matrix form. All EEF calculations were carried out using the Gaussian 09 suite of programs with "field=x+100" (0.01 au) and "field=x-100" (-0.01 au) keywords for the *–x* and *+x* electric fields, respectively. One atom unit (a.u. or au) is the field generated by an electric charge at a distance 1 Bohr and 1 au = 51.4 V Å^{-1}.

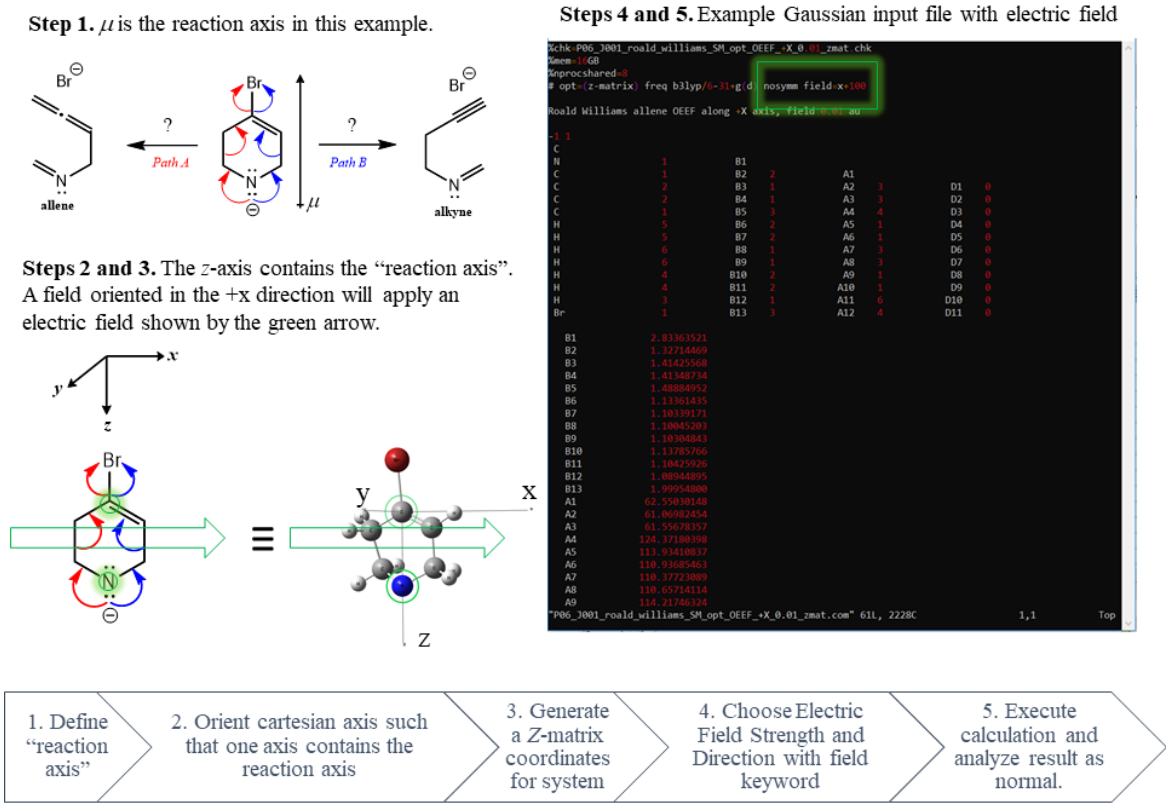


Figure S5. General protocol (or workflow) for executing EEF calculations of complex organic molecules (see ref. 44 in main manuscript for more details on EEF calculations).

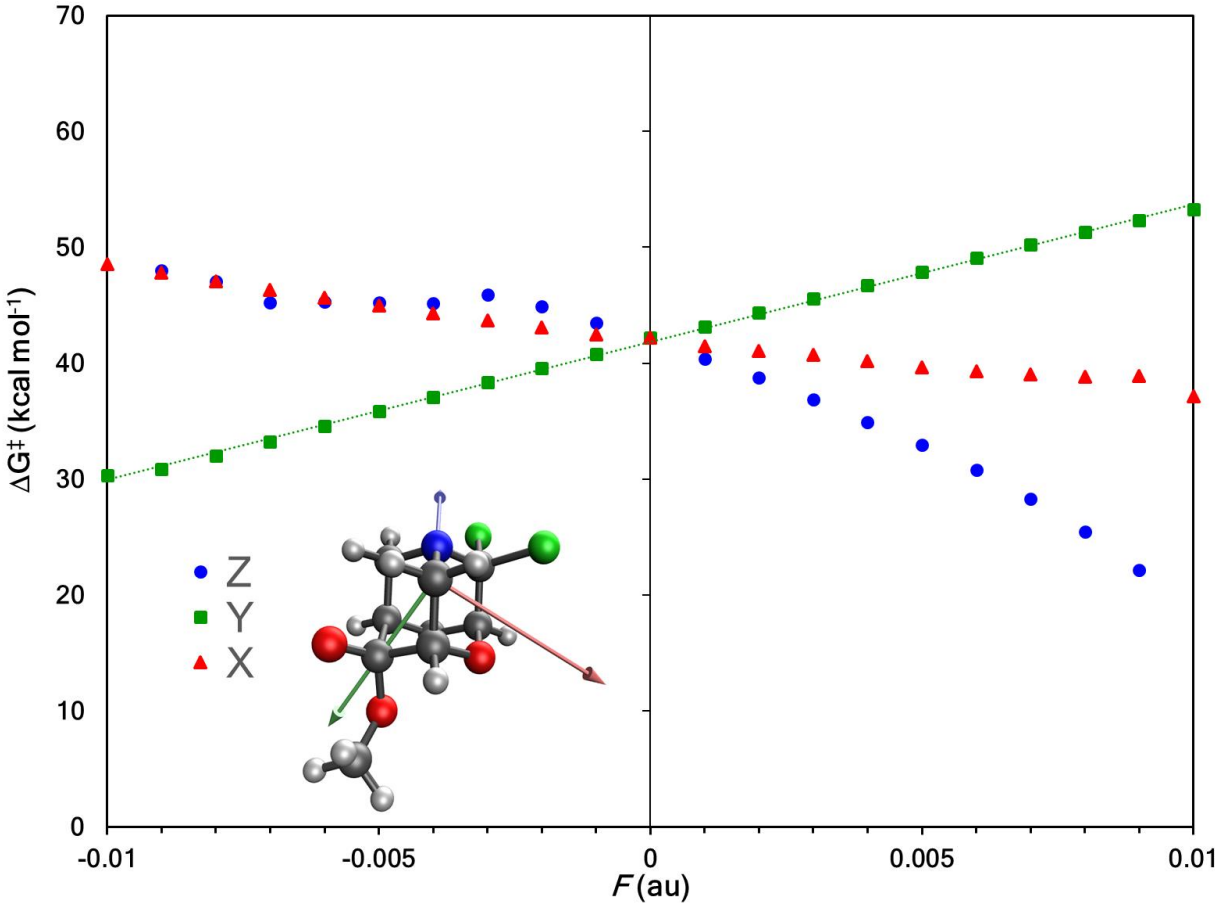


Figure S6. External electric field effects on divergent fragmentation of **1** (entry 6 in **Table 1**).

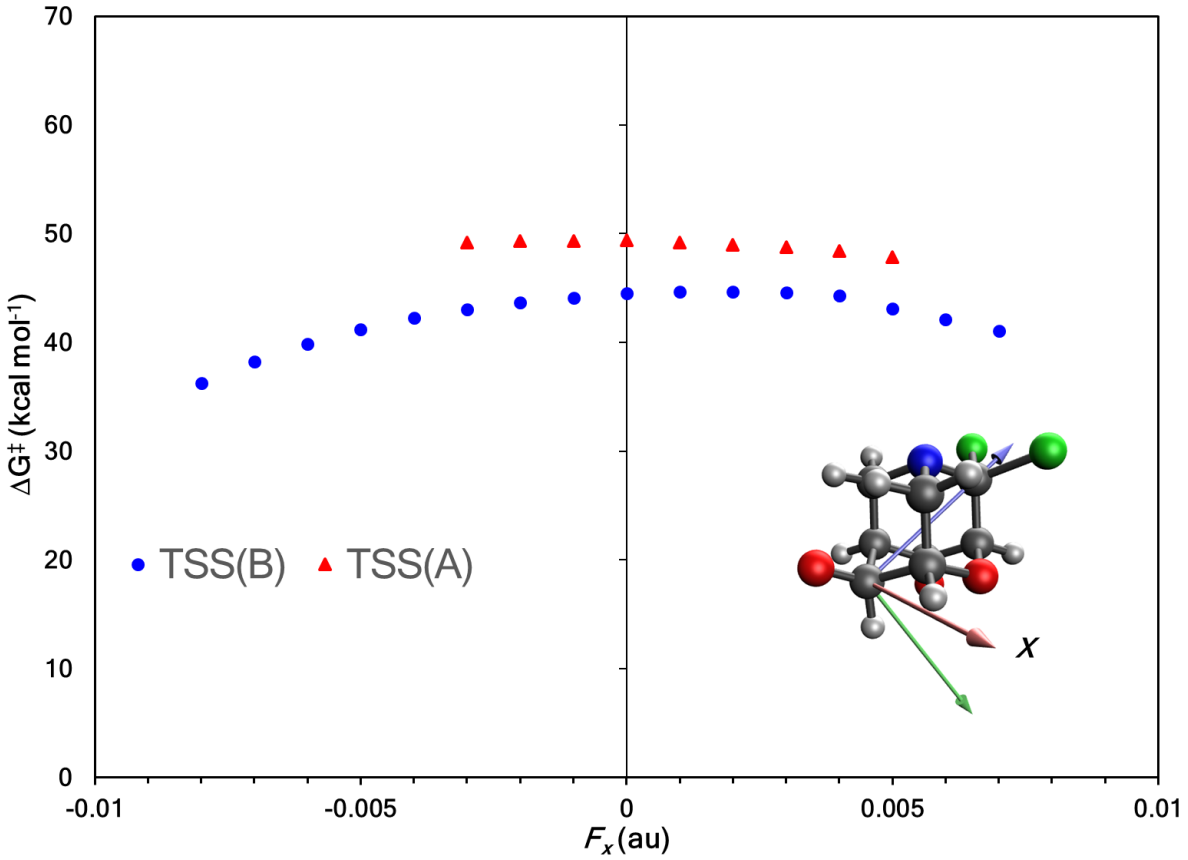


Figure S7. External electric field (F_x) effects on divergent fragmentation of **1** (entry 10 in **Table 1**).

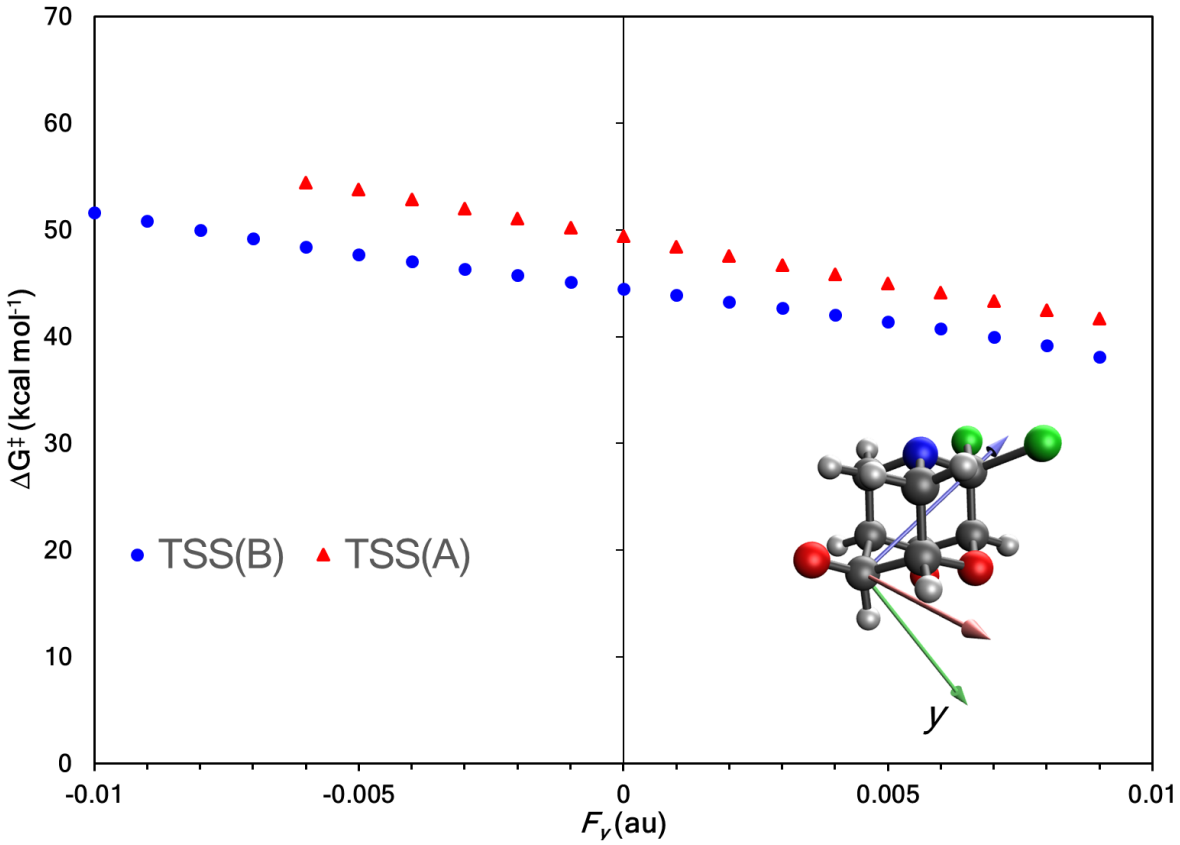


Figure S8. External electric field (F_y) effects on divergent fragmentation of **1** (entry 10 in **Table 1**).

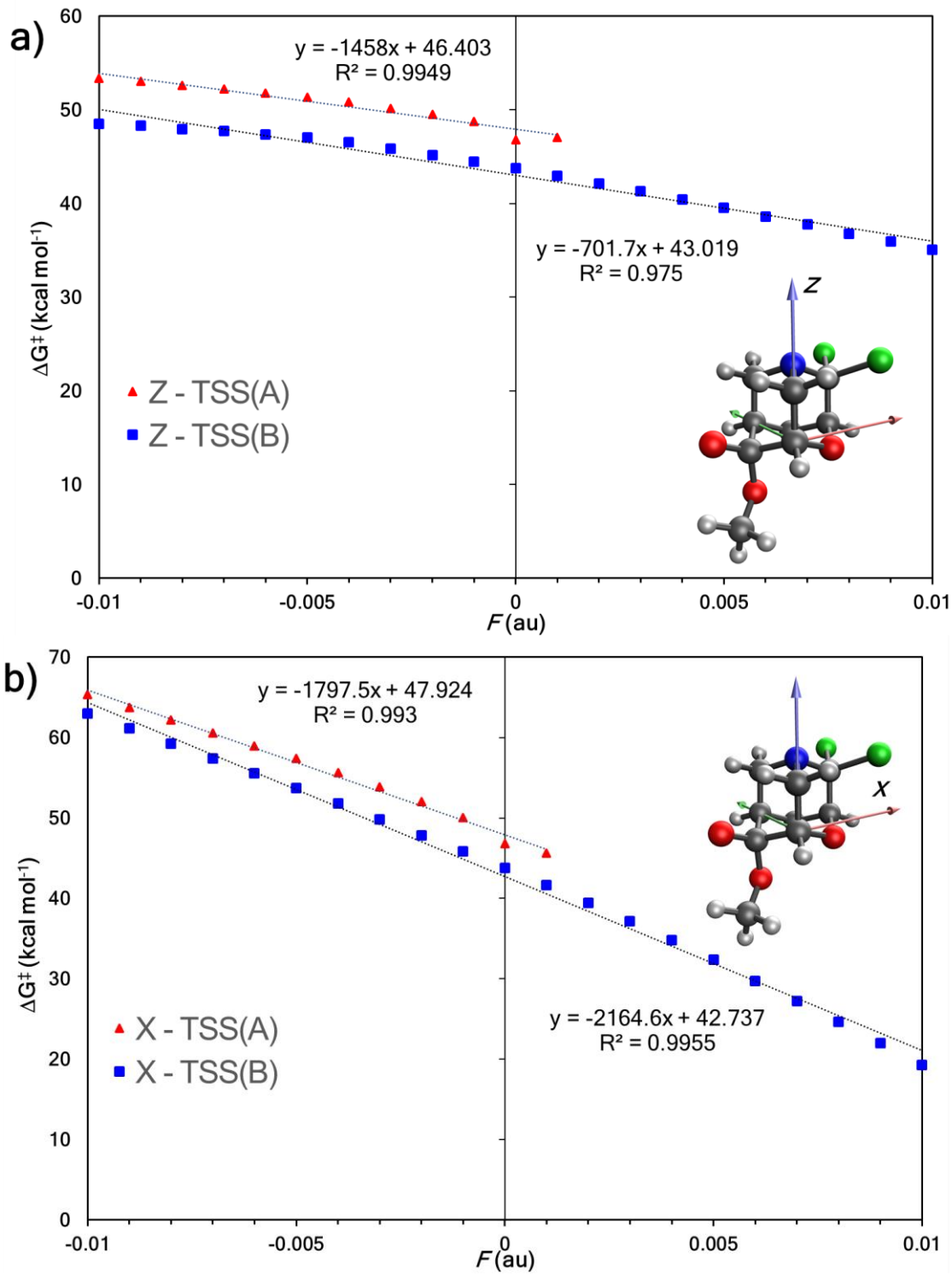


Figure S9. External electric field (a) F_z and (b) F_x effects on divergent fragmentation of **1** (entry 6 in **Table 1**). For F_z and F_x > 0.001 au, transition state structures leading to A [i.e. TSS(A)'s] optimize to TSS(B).

S5. Molecular Dynamics Simulations

Molecular Dynamics Trajectory Configuration File (used for all TSSs).

---

method b3lyp/6-31G(d)

method2 restricted

charge -1

multiplicity 1

processors 8

memory 16GB

killcheck 1

diagnostics 1

title System 4 B3LYPD3BJ n1

initialdis 2

timestep 1E-15

scaling 1.0

temperature 298

method 3 Empirical Dispersion=(GD3BJ)*

numimag 1

searchdir negative

classical 0

keepevery 1

highlevel 999

boxon 0

boxsize 7.5

etolerance 1.0

damping 1

reversetraj true

---

*used for B3LYP-D3(BJ) only. For M06-2X, this line is not present.

S6. Further Details for Figure 7

Final allene and alkyne energies are not reported in Williams's work. We find that the allene product is thermodynamically competitive (in stability) compared to the alkyne even after validating that the final allene and alkyne structures are in their lowest-energy conformational state. We note that the allene being thermodynamically lower in energy is counterintuitive to what is known about the thermodynamic stability of alkynes over allenes (Krause, N.; Hashmi, S. A. *Modern Allene Chemistry*; Weinheim: Wiley-VCH, 2004). After validating our computational method against already published data, we used this system as a simple and synthetically relevant model to probe how divergent fragmentations might be influenced by an EEF.

Table S5. Gas-phase relative enthalpies and enthalpic barriers, ΔH and $\Delta H^{\ddagger}$ (normal text), and relative free energies and free energy barriers, ΔG and $\Delta G^{\ddagger}$ (underlined), of vinylbromopiperidine fragmentation in the absence of an external electric field.

Level of theory	**Allene**	**TS-I**	**TS-II**	**alkyne**
B3LYP/ 6-31+G(d)[a]	-	8.3	10.5	-
B3LYP-D3(BJ)/ 6-31G(d)	- 23.3 - 28.1	4.2 3.5	6.9 6.1	- 19.7 - 24.4
M06-2X/ 6-31G(d)	- 22.7 - 27.1	8.7 7.7	10.5 9.6	- 22.0 - 26.4

[a]enthalpic barriers reproduced from Supporting Information, Williams and co-workers, *J. Am. Chem. Soc.* **2009**, *131*, 12910.

S7. Energies and Frequencies of Computed Structures

Table S6. Order of computed structures for mol2 file that comes with SI.

Structure number in .mol2 file	Entry number, Table 1 of main text	Level of Theory	Structure
1	1	B3LYP-D3(BJ)	P
2	1	B3LYP-D3(BJ)	R
3	1	B3LYP-D3(BJ)	TSS
4	1	M06-2X	P
5	1	M06-2X	R
6	1	M06-2X	TSS
7	2	B3LYP-D3(BJ)	P
8	2	B3LYP-D3(BJ)	R
9	2	B3LYP-D3(BJ)	TSS
10	2	M06-2X	P
11	2	M06-2X	R
12	2	M06-2X	TSS
13	3	B3LYP-D3(BJ)	P (Enamine)
14	3	B3LYP-D3(BJ)	Reactant
15	3	B3LYP-D3(BJ)	TSS(A)
16	3	M06-2X	Intermediate
17	3	M06-2X	P (Enamine)
18	3	M06-2X	P (Imine)
19	3	M06-2X	R
20	3	M06-2X	TSS(A)
21	3	M06-2X	TSS(i-A)
22	3	M06-2X	TSS(i-B)
23	3	M06-2X	TSS(i)
24	4	B3LYP-D3(BJ)	P
25	4	B3LYP-D3(BJ)	R
26	4	B3LYP-D3(BJ)	TSS-A
27	4	M06-2X	P
28	4	M06-2X	R
29	4	M06-2X	TSS-A
30	4	M06-2X	TSS-B
31	5	B3LYP-D3(BJ)	P
32	5	B3LYP-D3(BJ)	R
33	5	B3LYP-D3(BJ)	TSS
34	5	M06-2X	P
35	5	M06-2X	R
36	5	M06-2X	TSS
37	6	B3LYP-D3(BJ)	P
38	6	B3LYP-D3(BJ)	R
39	6	B3LYP-D3(BJ)	TSS-B
40	6	M06-2X	P
41	6	M06-2X	R

42	6	M06-2X	TSS-A
43	6	M06-2X	TSS-B
44	7	B3LYP-D3(BJ)	P
45	7	B3LYP-D3(BJ)	R
46	7	B3LYP-D3(BJ)	TSS
47	7	M06-2X	P
48	7	M06-2X	R
49	7	M06-2X	TSS
50	8	B3LYP-D3(BJ)	P
51	8	B3LYP-D3(BJ)	R
52	8	B3LYP-D3(BJ)	TSS-A
53	8	B3LYP-D3(BJ)	TSS-B
54	8	M06-2X	P
55	8	M06-2X	R
56	8	M06-2X	TSS-A
57	8	M06-2X	TSS-B
58	9	B3LYP-D3(BJ)	P
59	9	B3LYP-D3(BJ)	R
60	9	B3LYP-D3(BJ)	TSS
61	9	M06-2X	P
62	9	M06-2X	R
63	9	M06-2X	TSS
64	10	B3LYP-D3(BJ)	P
65	10	B3LYP-D3(BJ)	R
66	10	B3LYP-D3(BJ)	TSS-A
67	10	B3LYP-D3(BJ)	TSS-B
68	10	M06-2X	P
69	10	M06-2X	R
70	10	M06-2X	TSS-A
71	10	M06-2X	TSS-B
72	11	B3LYP-D3(BJ)	P
73	11	B3LYP-D3(BJ)	R
74	11	B3LYP-D3(BJ)	TSS
75	11	M06-2X	P
76	11	M06-2X	R
77	11	M06-2X	TSS
78	12	B3LYP-D3(BJ)	P
79	12	B3LYP-D3(BJ)	R
80	12	B3LYP-D3(BJ)	TSS-A
81	12	B3LYP-D3(BJ)	TSS-B
82	12	M06-2X	P
83	12	M06-2X	R
84	12	M06-2X	TSS-A
85	12	M06-2X	TSS-B

Table S7. All B3LYP-D3(BJ)/6-31G(d) Electronic, Free Energies, and Frequencies of computed structures for Table 1.

Entry	Structure	X	Y_1	Y_2	EE + Thermal Free Energy Corr. (a.u)	Electronic Energy (EE) (a.u)	Lowest frequency (cm^{-1})
1	Reactant 1	$N(CH_3)_2$	O(CO)Cl	H	-1373.269795	-1373.482457	38.5655
	TSS 1	$N(CH_3)_2$	O(CO)Cl	H	-1373.215991	-1373.42315	-747.7492
	Product 1	N(CH3)2	O(CO)Cl	H	-1373.395004	-1373.59012	8.9995
2	Reactant 2	$N(CH_3)_2$	Cl	Cl	-1644.319283	-1644.511048	49.8891
	TSS 2	$N(CH_3)_2$	Cl	Cl	-1644.266895	-1644.451259	-491.2602
	Product 2	N(CH3)2	Cl	Cl	-1644.383965	-1644.56353	27.6968
3	Reactant 3	NH_2	O(CO)Cl	H	-1294.696457	-1294.85567	43.9652
	TSSA 3	NH_2	O(CO)Cl	H	-1294.650978	-1294.804822	-756.9172
	Enamine Product 3	NH2	O(CO)Cl	H	-1294.829907	-1294.971958	11.9924
4	Reactant 4	NH_2	Cl	Cl	-1565.74643	-1565.88451	115.335
	TSS 4	NH_2	Cl	Cl	-1565.701455	-1565.832455	-506.4546
	Product 4	NH2	Cl	Cl	-1565.835008	-1565.962565	23.8321
5	Reactant 5	OCH_3	O(CO)Cl	H	-1353.870239	-1354.04243	39.1926
	TSS 5	OCH_3	O(CO)Cl	H	-1353.81537	-1353.982558	-685.2259
	Product 5	OCH_3	O(CO)Cl	H	-1353.98736	-1354.144007	10.2524
6	Reactant 6	OCH_3	Cl	Cl	-1624.919133	-1625.070584	69.0745
	TSS-B 6	OCH_3	Cl	Cl	-1624.865589	-1625.010496	-627.6178
	Product 6	OCH_3	Cl	Cl	-1624.968666	-1625.108912	20.6839
	Reactant 7	$OCH(CH_3)_2$	O(CO)Cl	H	-1432.463365	-1432.68927	36.0168
7	TSS 7	$OCH(CH_3)_2$	O(CO)Cl	H	-1432.405111	-1432.625363	-670.9647
	Product 7	$OCH(CH_3)_2$	O(CO)Cl	H	-1432.584807	-1432.79205	5.6254
	Reactant 8	$OCH(CH_3)_2$	Cl	Cl	-1703.516612	-1703.721695	43.3807
8	TSS-B 8	$OCH(CH_3)_2$	Cl	Cl	-1703.459376	-1703.657331	-634.2226
	TSS-A 8	$OCH(CH_3)_2$	Cl	Cl	-1703.516612	-1703.721695	-735.7903
	Product 8	$OCH(CH_3)_2$	Cl	Cl	-1703.56443	-1703.75844	26.4369
	Reactant 9	H	O(CO)Cl	H	-1239.345182	-1239.48865	38.9835
9	TSS 9	H	O(CO)Cl	H	-1239.289162	-1239.426415	-650.3903
	Product 9	H	O(CO)Cl	H	-1239.454858	-1239.579928	16.7736
	Reactant 10	H	Cl	Cl	-1510.39932	-1510.521813	113.6142
10	TSS-B 10	H	Cl	Cl	-1510.344152	-1510.459622	-572.9399
	TSS-A 10	H	Cl	Cl	-1510.341309	-1510.456728	-704.9218
	Product 10	H	Cl	Cl	-1510.475493	-1510.584319	25.146
	Reactant 11	F	O(CO)Cl	H	-1338.622195	-1338.757095	38.1675
11	TSS 11	F	O(CO)Cl	H	-1338.561404	-1338.690222	-633.2892
	Product 11	F	O(CO)Cl	H	-1338.725919	-1338.841733	3.688
	Reactant 12	F	Cl	Cl	-1609.675364	-1609.789427	120.0446
12	TSS-B 12	F	Cl	Cl	-1609.61549	-1609.722475	-582.1129
	TSS-A 12	F	Cl	Cl	-1609.6129	-1609.720007	-684.7478
	Product 12	F	Cl	Cl	-1609.739738	-1609.840808	22.5649

Table S8. All M06-2X/6-31G(d) Electronic, Free Energies, and Frequencies of computed structures for Table 1.

Entry	Structure	X	Y_1	Y_2	EE + Thermal Free Energy Corr. (a.u)	Electronic Energy (a.u)	Lowest frequency (cm^{-1})
1	Reactant 1	$N(CH_3)_2$	O(CO)Cl	H	-1372.817042	-1373.033744	35.9671
	TSS 1	$N(CH_3)_2$	O(CO)Cl	H	-1372.742257	-1372.953926	-836.8673
	Product 1	N(CH3)2	O(CO)Cl	H	-1372.917106	-1373.120713	31.2334
2	Reactant 2	$N(CH_3)_2$	Cl	Cl	-1643.907916	-1644.103095	43.4229
	TSS 2	$N(CH_3)_2$	Cl	Cl	-1643.837653	-1644.025606	-700.6995
	Product 2	N(CH3)2	Cl	Cl	-1643.962181	-1644.145735	19.5719
3	Reactant 3	NH_2	O(CO)Cl	H	-1294.293944	-1294.457097	47.1917
	TSSA 3	NH_2	O(CO)Cl	H	-1294.231188	-1294.388481	-856.7606
	Enamine Product 3	NH2	O(CO)Cl	H	-1294.401017	-1294.550737	25.9946
	TSSi 3	NH_2	O(CO)Cl	H	-1294.233116	-1294.389811	-542.4581
	Carbanion Int 3	NH_2	O(CO)Cl	H	-1294.238657	-1294.396718	36.7106
	TSS-int-to-B	NH_2	O(CO)Cl	H	-1294.234846	-1294.389876	-424.1904
	TSS-int-to-A	NH_2	O(CO)Cl	H	-1294.238549	-1294.395941	-380.0193
	Imine Product 3	NH2	O(CO)Cl	H	-1294.353673	-1294.498993	25.2286
4	Reactant 4	NH_2	Cl	Cl	-1565.385197	-1565.526399	108.7459
	TSS-B 4	NH_2	Cl	Cl	-1565.323424	-1565.457975	-513.7688
	TSS-A 4	NH_2	Cl	Cl	-1565.45414	-1565.319062	-853.9383
	Product 4	NH2	Cl	Cl	-1565.441655	-1565.571749	26.6844
5	Reactant 5	OCH_3	O(CO)Cl	H	-1353.441544	-1353.617593	37.6505
	TSS 5	OCH_3	O(CO)Cl	H	-1353.366984	-1353.538272	-801.0666
	Product 5	OCH_3	O(CO)Cl	H	-1353.537775	-1353.700499	19.0107
6	Reactant 6	OCH_3	Cl	Cl	-1624.531894	-1624.686347	48.9481
	TSS-B 6	OCH_3	Cl	Cl	-1624.46213	-1624.61083	-693.845
	TSS-A 6	OCH_3	Cl	Cl	-1624.455053	-1624.603906	-804.9737
	Product 6	OCH_3	Cl	Cl	-1624.571441	-1624.715773	23.4109
7	Reactant 7	$OCH(CH_3)_2$	O(CO)Cl	H	-1703.114486	-1432.210512	29.7043
	TSS 7	$OCH(CH_3)_2$	O(CO)Cl	H	-1431.903928	-1432.128767	-798.7771
	Product 7	$OCH(CH_3)_2$	O(CO)Cl	H	-1703.114486	-1703.313427	32.3372
8	Reactant 8	$OCH(CH_3)_2$	Cl	Cl	-1703.078107	-1703.285641	22.744
	TSS-B 8	$OCH(CH_3)_2$	Cl	Cl	-1703.003183	-1703.20548	-702.5273
	TSS-A 8	$OCH(CH_3)_2$	Cl	Cl	-1702.99663	-1703.199084	-814.1151
	Product 8	$OCH(CH_3)_2$	Cl	Cl	-1703.114491	-1703.313427	32.3
9	Reactant 9	H	O(CO)Cl	H	-1238.965774	-1239.112542	32.51
	TSS 9	H	O(CO)Cl	H	-1238.890153	-1239.030321	-776.92
	Product 9	H	O(CO)Cl	H	-1239.055829	-1239.186589	31.98
10	Reactant 10	H	Cl	Cl	-1510.061281	-1510.186693	112.5
	TSS-B 10	H	Cl	Cl	-1509.990276	-1510.10823	-654.3815
	TSS-A 10	H	Cl	Cl	-1509.982587	-1510.100822	-788.38
	Product 10	H	Cl	Cl	-1510.118694	-1510.230325	22.86
11	Reactant 11	F	O(CO)Cl	H	-1338.216536	-1338.354736	37.17
	TSS 11	F	O(CO)Cl	H	-1338.135945	-1338.267744	-774.98
	Product 11	F	O(CO)Cl	H	-1338.299644	-1338.422389	22.73
12	Reactant	F	Cl	Cl	-1609.311349	-1609.428219	120.35

	12						
	TSS-B 12	F	Cl	Cl	-1609.235356	-1609.34494	-673.3424
	TSS-A 12	F	Cl	Cl	-1609.227388	-1609.337643	-787.32
	Product 12	F	Cl	Cl	-1609.361115	-1609.464989	19.82

Table S9. All B3LYP-D3(BJ)/6-31G(d) Electronic, Free Energies, and Frequencies of computed structures in intrinsic solvent (cpcm, water).

Entry	Structure	X	Y_1	Y_2	EE + Thermal Free Energy Corr. (a.u)	Electronic Energy (a.u)	Lowest frequency (cm^{-1})
1	Reactant 1	$N(CH_3)_2$	O(CO)Cl	H	-1373.343032	-1373.555408	42.88
	TSS 1	$N(CH_3)_2$	O(CO)Cl	H	-1373.287953	-1373.495586	-786.14
	Product 1	N(CH3)2	O(CO)Cl	H	-1373.487715	-1373.683201	17.22
2*	Reactant 2	$N(CH_3)_2$	Cl	Cl	-1644.396437	-1644.588048	42.12
	TSS-B 2	$N(CH_3)_2$	Cl	Cl	-1644.344122	-1644.528672	-604.60
	TSS-A 2	$N(CH_3)_2$	Cl	Cl	-1644.346035	-1644.53087	-540.99
	Product 2A	N(CH3)2	Cl	Cl	-1644.510196	-1644.68754	11.49
3	Reactant 3	NH_2	O(CO)Cl	H	-1294.778706	-1294.938171	43.68
	TSS-A 3	NH_2	O(CO)Cl	H	-1294.726598	-1294.880931	-787.76
	Product 3	NH2	O(CO)Cl	H	-1294.922005	-1295.063991	14.23
4	Reactant 4	NH_2	Cl	Cl	-1565.826738	-1565.965468	116.55
	TSS-A 4	NH_2	Cl	Cl	-1565.781759	-1565.913247	-550.27
	Product 4A	NH2	Cl	Cl	-1565.940829	-1566.066405	18.97
5	Reactant 5	OCH_3	O(CO)Cl	H	-1353.949929	-1354.122542	39.48
	TSS-A 5	OCH_3	O(CO)Cl	H	-1353.890702	-1354.058608	-755.3
	Product 5A	OCH_3	O(CO)Cl	H	-1354.073777	-1354.229315	15.05
6*	Reactant 6	OCH_3	Cl	Cl	-1624.99686	-1625.149269	-83.76
	TSS-B 6	OCH_3	Cl	Cl	-1624.946489	-1625.091186	-601.75
	TSS-A 6	OCH_3	Cl	Cl	-1624.947268	-1625.0922	-554.7
	Product 6A	OCH_3	Cl	Cl	-1625.094979	-1625.234708	20.49
7	Reactant 7	$OCH(CH_3)_2$	O(CO)Cl	H	-1432.53838	-1432.763973	34.6
	TSS-A 7	$OCH(CH_3)_2$	O(CO)Cl	H	-1432.479596	-1432.700307	-747.66
	Product 7A	$OCH(CH_3)_2$	O(CO)Cl	H	-1432.673912	-1432.882877	6.87
8*	Reactant 8	$OCH(CH_3)_2$	Cl	Cl	-1703.591376	-1703.795308	27.72
	TSS-A 8	$OCH(CH_3)_2$	Cl	Cl	-1703.540725	-1703.738763	-552.72
	Product 8A	$OCH(CH_3)_2$	Cl	Cl	-1703.690807	-1703.882741	16.5
9	Reactant 9	H	O(CO)Cl	H	-1239.424297	-1239.56791	40.28
	TSS-A 9	H	O(CO)Cl	H	-1239.362323	-1239.49959	-719.89
	Product 9A	H	O(CO)Cl	H	-1239.544233	-1239.670122	26.02
10	Reactant 10	H	Cl	Cl	-1510.477204	-1510.599905	110
	TSS-B 10	H	Cl	Cl	-1510.426098	-1510.540431	-520.35
	Product 10B	H	Cl	Cl	-1510.529307	-1510.638275	20.85
11	Reactant 11	F	O(CO)Cl	H	-1338.704305	-1338.839189	39.95
	TSS-A 11	F	O(CO)Cl	H	-1338.635694	-1338.764652	-694.32
	Product 11A	F	O(CO)Cl	H	-1338.813084	-1338.929671	17.87
12	Reactant 12	F	Cl	Cl	-1609.755747	-1609.86987	115.13
	TSS-B 12	F	Cl	Cl	-1609.69784	-1609.803533	-530.86
	Product 12B	F	Cl	Cl	-1609.794666	-1609.896309	35.21

*Note: Entries that switch their kinetic product selectivity in implicit solvent are highlighted in red. IRC calculations that confirm this switch will be provided at the end of S8. Entries 2 and 6 switched their kinetic product from B to A due to a change in activation barriers when implicit solvent is included at B3LYP-D3(BJ). For entries 2 and 6, we fail to identify TSS-A as a viable TSS at M06-2X, hence these entries agree with our original gas phase results at M06-2X. Entry 8 also changed from B to A, but in this case, there is no viable TSS leading to product B at B3LYP-D3(BJ).

Table S10. All M06-2X/6-31G(d) Electronic, Free Energies, and Frequencies of computed structures intrinsic solvent (cpcm, water).

Entry	Structure	X	Y_1	Y_2	EE + Thermal Free Energy Corr. (a.u)	Electronic Energy (a.u)	Lowest frequency (cm^{-1})
1	Reactant 1	$N(CH_3)_2$	O(CO)Cl	H	-1372.89712	-1373.114057	37.05
	TSS 1	$N(CH_3)_2$	O(CO)Cl	H	-1372.815972	-1373.027842	-925.22
	Product 1	N(CH3)2	O(CO)Cl	H	-1373.013321	-1373.212297	14.44
2	Reactant 2	$N(CH_3)_2$	Cl	Cl	-1643.986073	-1644.181289	39.99
	TSS-B 2	$N(CH_3)_2$	Cl	Cl	-1643.915716	-1644.103804	-743.1
	Product 2B	N(CH3)2	Cl	Cl	-1644.05669	-1644.238625	8.26
3	Reactant 3	NH_2	O(CO)Cl	H	-1294.378861	-1294.541823	42.14
	TSSA 3	NH_2	O(CO)Cl	H	-1294.307312	-1294.465476	-948.36
	Product 3A	NH2	O(CO)Cl	H	-1294.497261	-1294.643241	20.34
4	Reactant 4	NH_2	Cl	Cl	-1565.467556	-1565.60947	115.3
	TSS-B 4	NH_2	Cl	Cl	-1565.403303	-1565.535722	-766.26
	Product 4B	NH2	Cl	Cl	-1565.537434	-1565.667722	36.55
5	Reactant 5	OCH_3	O(CO)Cl	H	-1353.522658	-1353.699891	45.44
	TSS-A 5	OCH_3	O(CO)Cl	H	-1353.443945	-1353.615958	-916.43
	Product 5A	OCH_3	O(CO)Cl	H	-1353.629581	-1353.791828	21.49
6	Reactant 6	OCH_3	Cl	Cl	-1624.611382	-1624.766952	89.95
	TSS-B 6	OCH_3	Cl	Cl	-1624.543389	-1624.69056	-749.68
	Product 6	OCH_3	Cl	Cl	-1624.665336	-1624.810237	32.16
7	Reactant 7	$OCH(CH_3)_2$	O(CO)Cl	H	-1431.980281	-1432.210511	29.66
	TSS-A 7	$OCH(CH_3)_2$	O(CO)Cl	H	-1431.903928	-1432.128767	-798.7771
	Product 7A	$OCH(CH_3)_2$	O(CO)Cl	H	-1432.079331	-1432.296171	19.91
8	Reactant 8	$OCH(CH_3)_2$	Cl	Cl	-1703.152197	-1703.360979	51.8
	TSS-B 8	$OCH(CH_3)_2$	Cl	Cl	-1703.083619	-1703.284375	-763.44
	Product 8B	$OCH(CH_3)_2$	Cl	Cl	-1703.210141	-1703.405103	19.32
9	Reactant 9	H	O(CO)Cl	H	-1239.046936	-1239.194029	38.97
	TSS 9	H	O(CO)Cl	H	-1238.963594	-1239.104256	-903.94
	Product 9	H	O(CO)Cl	H	-1239.146539	-1239.275734	-2.14
10	Reactant 10	H	Cl	Cl	-1510.141352	-1510.266885	108.88
	TSS-B 10	H	Cl	Cl	-1510.072105	-1510.188576	-644.43
	TSS-A 10	H	Cl	Cl	-1510.057159	-1510.175341	-919.75
	Product 10	H	Cl	Cl	-1510.183873	-1510.297222	34.80
11	Reactant 11	F	O(CO)Cl	H	-1338.300378	-1338.438416	36.26
	TSS-A 11	F	O(CO)Cl	H	-1338.210441	-1338.342822	-892
	Product 11A	F	O(CO)Cl	H	-1338.388648	-1338.512077	37.92
12	Reactant 12	F	Cl	Cl	-1609.361115	-1609.464989	19.82

TSS-B 12	F	Cl	Cl	-1609.317198	-1609.425225	-639.99
TSS-A 12	F	Cl	Cl	-1609.302987	-1609.412962	-917.65
Product 12B	F	Cl	Cl	-1609.423909	-1609.528481	34.23

Table S11. All B3LYP-D3(BJ)/6-31G(d) Electronic, Free Energies, and Frequencies of computed structures for Table S5.

Structure	EE + Thermal Enthalpies (a.u)	EE + Thermal Free Energy Corr. (a.u)	Electronic Energy (a.u)	Lowest frequency (cm^{-1})
Allene	-2821.087821	-2821.135968	-2821.204282	19.7912
TS-I	-2821.044107	-2821.085566	-2821.158695	-321.0759
Reactant	-2821.050769	-2821.091152	-2821.166432	92.0399
TS-II	-2821.039701	-2821.081389	-2821.154758	-311.7494
Alkyne	-2821.082196	-2821.129999	-2821.19902	25.5604

Table S12. All M06-2X/6-31G(d) Electronic, Free Energies, and Frequencies of computed structures for Table S5.

Structure	EE + Thermal Enthalpies (a.u)	EE + Thermal Free Energy Corr. (a.u)	Electronic Energy (a.u)	Lowest frequency (cm^{-1})
Allene	-2821.01671	-2821.063445	-2821.134715	53.5215
TS-I	-2820.966692	-2821.007943	-2821.082686	-296.6608
Reactant	-2820.980616	-2821.020229	-2821.097829	112.3043
TS-II	-2820.96394	-2821.004969	-2821.080337	-294.5554
Alkyne	-2821.01562	-2821.06227	-2821.134059	46.7943

Table S13. All M06-2X/6-31G(d) Electronic, Free Energies, and Frequencies of computed structures for Figure 7, "Path A" (i.e. computed structures corresponding to red circles).

Structure	Electric Field, F_x (a.u.)	Electronic Energy (a.u)	EE + Thermal Free Energy Corr. (a.u)	Lowest frequency (cm^{-1})
TSS	-0.013	-2821.089777	-2821.01687	-279.3364
Reactant		-2821.10647	112.5578	112.5578
TSS	-0.012	-2821.088457	-2821.014915	-274.5964
Reactant		-2821.105254	112.402	112.402
TSS	-0.011	-2821.087261	-2821.013496	-271.0758
Reactant		-2821.10413	112.2267	112.2267
TSS	-0.01	-2821.086194	-2821.012315	-269.1069
Reactant		-2821.103098	112.0283	112.0283
TSS	-0.009	-2821.085264	-2821.011173	-267.8724
Reactant		-2821.102157	111.9116	111.9116

TSS	-0.008	-2821.084456	-2821.01024	-267.1136
Reactant		-2821.101307	111.5928	111.5928
TSS	-0.007	-2821.083767	-2821.009463	-267.1037
Reactant		-2821.100551	-2821.023071	111.3269
TSS	-0.006	-2821.083199	-2821.008892	-268.1234
Reactant		-2821.099885	-2821.02239	111.0864
TSS	-0.005	-2821.082775	-2821.008415	-268.0966
Reactant		-2821.099311	-2821.021801	110.911
TSS	-0.004	-2821.08253	-2821.007962	-271.8453
Reactant		-2821.098828	-2821.021309	110.6961
TSS	-0.003	-2821.082405	-2821.007699	-276.4384
Reactant		-2821.098437	-2821.020912	110.4956
TSS	-0.002	-2821.082398	-2821.007578	-281.4872
Reactant		-2821.098136	-2821.020609	110.3111
TSS	-0.001	-2821.082507	-2821.0076	-286.3528
Reactant		-2821.097927	-2821.020401	110.1429
TSS	0	-2821.08273	-2821.007943	-291.0887
Reactant		-2821.097829	-2821.020231	112.3043
TSS	0.001	-2821.083068	-2821.008039	-295.4792
Reactant		-2821.097784	-2821.020275	109.716
TSS	0.002	-2821.083519	-2821.00845	-299.399
Reactant		-2821.097849	-2821.020355	109.6048
TSS	0.003	-2821.084086	-2821.008987	-302.2601
Reactant		-2821.098006	-2821.020529	109.4987
TSS	0.004	-2821.084766	-2821.009651	-303.9776
Reactant		-2821.098254	-2821.0208	109.4028
TSS	0.005	-2821.085561	-2821.010439	-304.1189
Reactant		-2821.098596	-2821.021178	109.1714
TSS	0.006	-2821.086472	-2821.011336	-302.0619
Reactant		-2821.099029	-2821.021632	109.2452
TSS	0.007	-2821.087496	-2821.012311	-294.783

Reactant		-2821.099552	-2821.022193	109.1837
TSS	0.008	-2821.088633	-2821.01339	-285.5938
Reactant		-2821.10017	-2821.022855	109.0863
TSS	0.009	-2821.089878	-2821.01457	-272.5679
Reactant		-2821.100881	-2821.023612	109.0486
TSS	0.01	-2821.091227	-2821.015842	-256.8915
Reactant		-2821.101686	-2821.024479	108.8424
TSS	0.011	-2821.092676	-2821.017202	-238.9821
Reactant		-2821.102581	-2821.025419	109.0563
TSS	0.012	-2821.094219	-2821.018652	-219.8945
Reactant		-2821.103574	-2821.026482	108.9642
TSS	0.013	-2821.095851	-2821.020194	-200.8479
Reactant		-2821.104659	-2821.027629	109.0659
TSS	0.014	-2821.097568	-2821.021827	-183.4867
Reactant		-2821.105844	-2821.028901	108.914
TSS	0.015	-2821.099365	-2821.023556	-168.8583
Reactant		-2821.107117	-2821.030245	109.1469
TSS	0.016	-2821.101239	-2821.025385	-158.5769
Reactant		-2821.108495	-2821.031722	108.942
TSS	0.017	-2821.103187	-2821.027315	-152.0324
Reactant		-2821.109966	-2821.03329	108.8616
TSS	0.018	-2821.10521	-2821.029335	-148.3664
Reactant		-2821.111536	-2821.034965	109.0456
TSS	0.019	-2821.107307	-2821.031447	-145.5935
Reactant		-2821.113205	-2821.036746	109.0525
TSS	0.02	-2821.109481	-2821.033642	-142.7807
Reactant		-2821.114973	-2821.038633	109.1803
TSS	0.021	-2821.111731	-2821.035932	-139.1938
Reactant		-2821.116844	-2821.040637	109.4014
TSS	0.022	-2821.114059	-2821.038288	-132.6079
Reactant		-2821.118817	-2821.042742	109.674

TSS	0.023	-2821.116466	-2821.040741	-124.8629
Reactant		-2821.120895	-2821.044957	110.0535
TSS	0.024	-2821.118952	-2821.043289	-116.3223
Reactant		-2821.12308	-2821.047284	110.5546
TSS	0.025	-2821.121518	-2821.045934	-109.9413
Reactant		-2821.125373	-2821.049727	111.1831
TSS	0.026	-2821.124166	-2821.048677	-106.2372
Reactant		-2821.127777	-2821.052291	111.9428
TSS	0.027	-2821.126898	-2821.051525	-105.7098
Reactant		-2821.130297	-2821.054978	112.8261
TSS	0.028	-2821.129716	-2821.05447	-107.2314
Reactant		-2821.132935	-2821.057808	113.7877
TSS	0.029	-2821.132626	-2821.057518	-110.4882
Reactant		-2821.135697	-2821.060812	114.7841
TSS	0.03	-2821.13563	-2821.060677	-114.2721
Reactant		-2821.138591	-2821.064034	115.7713
TSS	0.031	-2821.138733	-2821.063952	-117.9826
Reactant		-2821.141634	-2821.067577	116.9822

Table S14. All M06-2X/6-31G(d) Electronic, Free Energies, and Frequencies of computed structures for Figure 7, "Path B" (i.e. computed structures corresponding to blue squares).

Structure	Electric Field, F_x (a.u.)	Electronic Energy (a.u)	EE + Thermal Free Energy Corr. (a.u)	Lowest frequency (cm^{-1})
TSS	-0.036	-2821.160323	-2821.085022	-46.0698
Reactant		-2821.160658	-2821.085461	119.9547
TSS	-0.035	-2821.156743	-2821.0813	-65.8516
Reactant		-2821.157214	-2821.081855	119.8376
TSS	-0.034	-2821.153248	-2821.077677	-77.8992
Reactant		-2821.153874	-2821.078363	119.6616
TSS	-0.033	-2821.149838	-2821.074148	-88.7619
Reactant		-2821.150638	-2821.074984	119.4433
TSS	-0.032	-2821.146512	-2821.070708	-94.7644
Reactant		-2821.147503	-2821.071715	119.1926
TSS	-0.031	-2821.143268	-2821.067364	-100.2788
Reactant		-2821.14447	-2821.068558	118.7734
TSS	-0.03	-2821.140105	-2821.064107	-103.3795
Reactant		-2821.141538	-2821.065502	118.4925
TSS	-0.029	-2821.137022	-2821.060939	-104.4314
Reactant		-2821.138705	-2821.062551	118.1926

TSS	-0.028	-2821.134017	-2821.057864	-102.99
Reactant		-2821.135971	-2821.059709	117.7567
TSS	-0.027	-2821.131089	-2821.054859	-99.2838
Reactant		-2821.133336	-2821.056964	117.4665
TSS	-0.026	-2821.128233	-2821.051946	-98.3259
Reactant		-2821.130797	-2821.054326	117.0343
TSS	-0.025	-2821.125449	-2821.049119	-102.7782
Reactant		-2821.128354	-2821.051804	116.0789
TSS	-0.024	-2821.122733	-2821.046385	-112.192
Reactant		-2821.126012	-2821.049358	116.1173
TSS	-0.023	-2821.120086	-2821.043729	-122.1342
Reactant		-2821.123761	-2821.047037	115.1904
TSS	-0.022	-2821.117509	-2821.041154	-130.6959
Reactant		-2821.12161	-2821.044794	115.1914
TSS	-0.021	-2821.115003	-2821.038648	-135.9378
Reactant		-2821.119551	-2821.042669	114.5528
TSS	-0.02	-2821.112566	-2821.036214	-137.747
Reactant		-2821.117588	-2821.040637	114.1897
TSS	-0.019	-2821.110199	-2821.033853	-137.1124
Reactant		-2821.115719	-2821.038703	113.8698
TSS	-0.018	-2821.107899	-2821.031566	-135.374
Reactant		-2821.113944	-2821.036868	113.482
TSS	-0.017	-2821.105665	-2821.029361	-135.126
Reactant		-2821.112263	-2821.035131	113.2759
TSS	-0.016	-2821.103496	-2821.027243	-138.6753
Reactant		-2821.110675	-2821.033491	113.1705
TSS	-0.015	-2821.101389	-2821.025207	-147.1586
Reactant		-2821.109181	-2821.031948	112.9719
TSS	-0.014	-2821.099346	-2821.023256	-159.9379
Reactant		-2821.107779	-2821.030499	112.7013
TSS	-0.013	-2821.097371	-2821.021381	-177.3588
Reactant		-2821.10647	-2821.02915	112.5578
TSS	-0.012	-2821.095469	-2821.019581	-198.3589
Reactant		-2821.105254	-2821.027898	112.402
TSS	-0.011	-2821.093646	-2821.017851	-221.7764
Reactant		-2821.10413	-2821.026742	112.2267
TSS	-0.01	-2821.091909	-2821.016187	-245.1477
Reactant		-2821.103098	-2821.025682	112.0283
TSS	-0.009	-2821.090266	-2821.014594	-266.0546
Reactant		-2821.102157	-2821.024714	111.9116
TSS	-0.008	-2821.088724	-2821.013078	-282.4528
Reactant		-2821.101307	-2821.023846	111.5928
TSS	-0.007	-2821.087288	-2821.011652	-294.2756
Reactant		-2821.100551	-2821.023071	111.3269
TSS	-0.006	-2821.085962	-2821.010331	-301.7698
Reactant		-2821.099885	-2821.02239	111.0864
TSS	-0.005	-2821.084749	-2821.009128	-305.684
Reactant		-2821.099311	-2821.021801	110.911
TSS	-0.004	-2821.08365	-2821.008051	-306.8716
Reactant		-2821.098828	-2821.021309	110.6961
TSS	-0.003	-2821.082667	-2821.007102	-305.9138
Reactant		-2821.098437	-2821.020912	110.4956
TSS	-0.002	-2821.0818	-2821.006286	-303.0472
Reactant		-2821.098136	-2821.020609	110.3111
TSS	-0.001	-2821.081052	-2821.005597	-298.3393
Reactant		-2821.097927	-2821.020401	110.1429
TSS	0	-2821.080422	-2821.004969	-292.3049

Reactant		-2821.097829	-2821.020231	112.3043
TSS	0.001	-2821.079912	-2821.004579	-285.2719
Reactant		-2821.097784	-2821.020275	109.716
TSS	0.002	-2821.079522	-2821.004254	-277.8535
Reactant		-2821.097849	-2821.020355	109.6048
TSS	0.003	-2821.079251	-2821.00405	-269.8659
Reactant		-2821.098006	-2821.020529	109.4987
TSS	0.004	-2821.0791	-2821.003987	-263.2727
Reactant		-2821.098254	-2821.0208	109.4028
TSS	0.005	-2821.07907	-2821.004053	-256.6789
Reactant		-2821.098596	-2821.021178	109.1714
TSS	0.006	-2821.079162	-2821.004256	-250.7652
Reactant		-2821.099029	-2821.021632	109.2452
TSS	0.007	-2821.079376	-2821.004595	-246.4147
Reactant		-2821.099552	-2821.022193	109.1837
TSS	0.008	-2821.079715	-2821.005078	-241.8906
Reactant		-2821.10017	-2821.022855	109.0863
TSS	0.009	-2821.080179	-2821.00569	-237.6434
Reactant		-2821.100881	-2821.023612	109.0486
TSS	0.01	-2821.080772	-2821.00639	-234.5714
Reactant		-2821.101686	-2821.024479	108.8424

Energies and Frequencies for selected structures from Figure 5. These electric field magnitudes were selected as representative of the other data reported in Figure 5 of the main text.

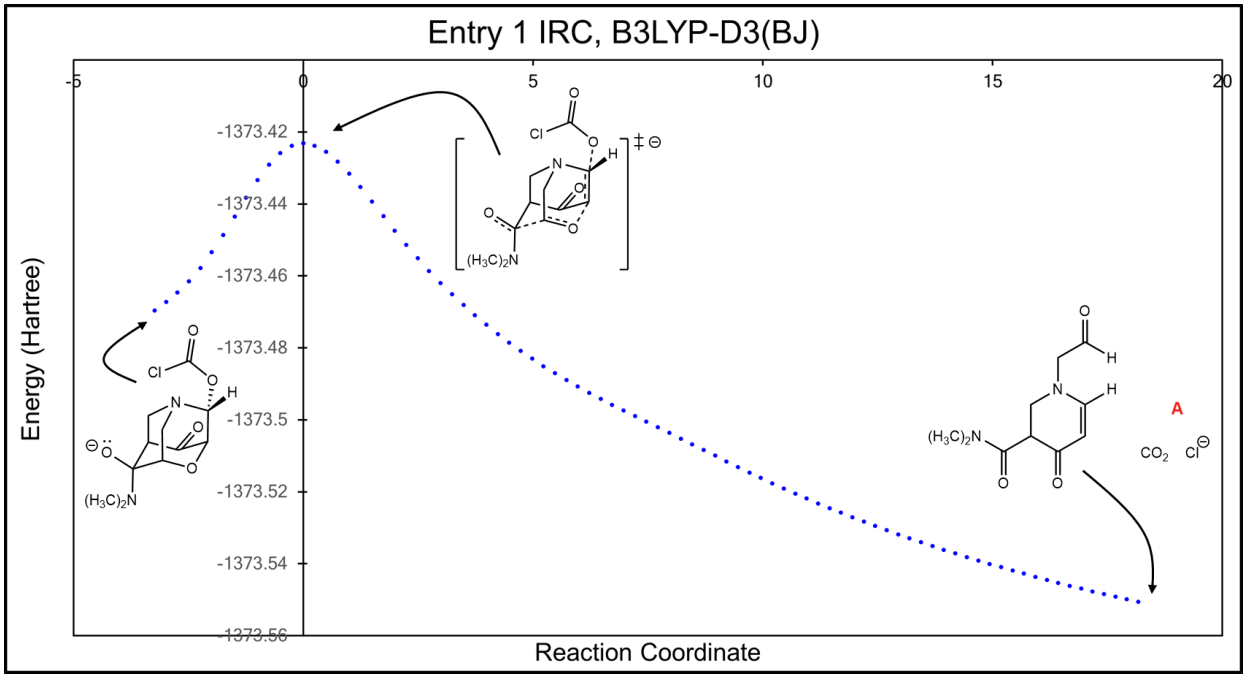
Table S15. Selected M06-2X/6-31G(d) Electronic, Free Energies, and Frequencies of computed structures for Figure 5a.

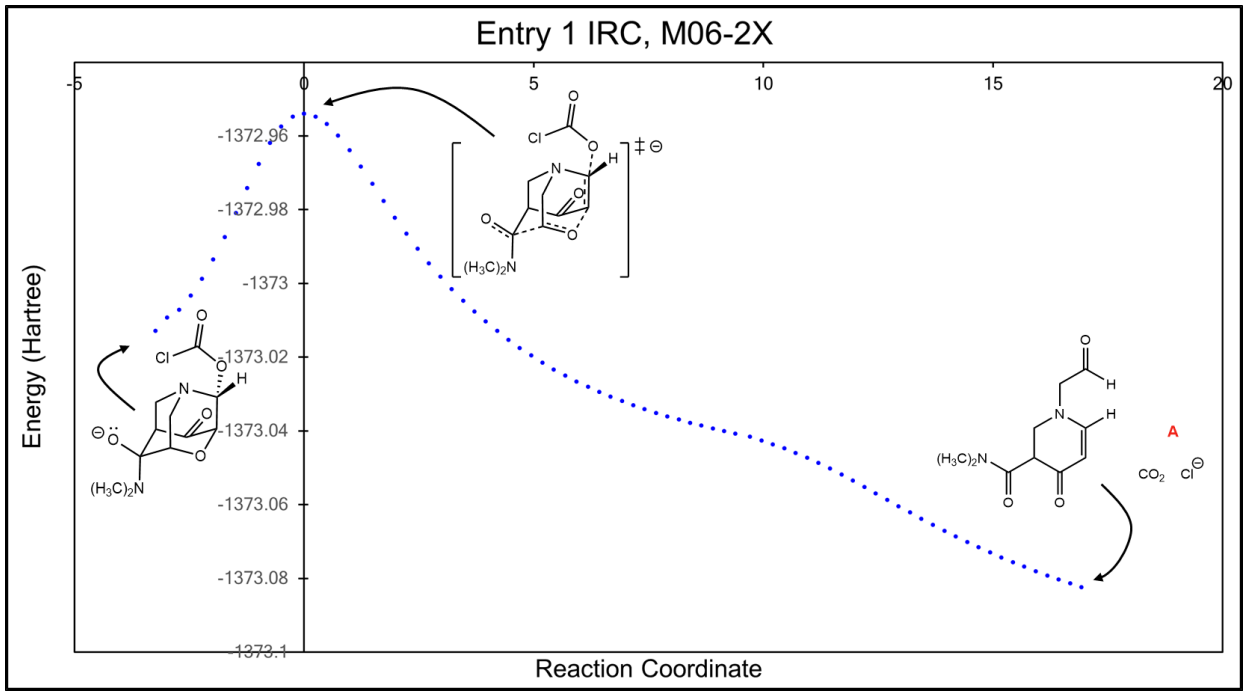
Structure	Electric Field Orientation	Electric Field Magnitude (a.u.)	Electronic Energy (a.u)	EE + Thermal Free Energy Corr. (a.u)	Lowest frequency (cm^{-1})
TSS	*-z*	0.009	-1353.50695202	-1353.335235	-723.4406
Reactant	*-z*	0.009	-1353.60611140	-1353.429378	37.4440
TSS	*+z*	0.005	-1353.56420139	-1353.395154	-824.3495
Reactant	*+z*	0.005	-1353.63165352	-1353.45573	35.8897
TSS	*-y*	0.01	-1353.54183977	-1353.371754	-808.8271
Reactant	*-y*	0.01	-1353.62393201	-1353.447870	37.4316
TSS	*+y*	0.01	-1353.55922012	-1353.390339	-869.5986
Reactant	*+y*	0.01	-1353.63642099	-1353.460093	42.1180
TSS	*-x*	0.01	-1353.55288018	-1353.382571	-849.0915
Reactant	*-x*	0.01	-1353.63970206	-1353.464397	34.6943
TSS	*+x*	0.008	-1353.54919698	-1353.379089	-507.3482
Reactant	*+x*	0.008	-1353.61313922	-1353.436501	41.2199

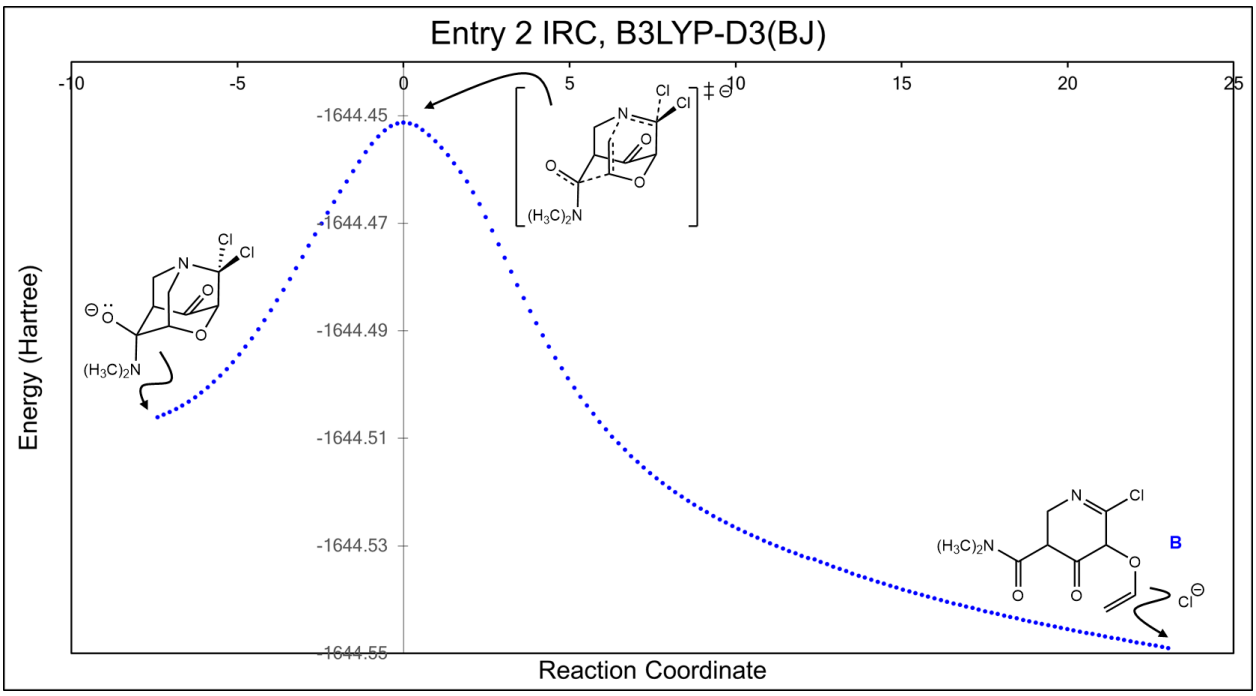
Table S16. Selected M06-2X/6-31G(d) Electronic, Free Energies, and Frequencies of computed structures for Figure 5b.

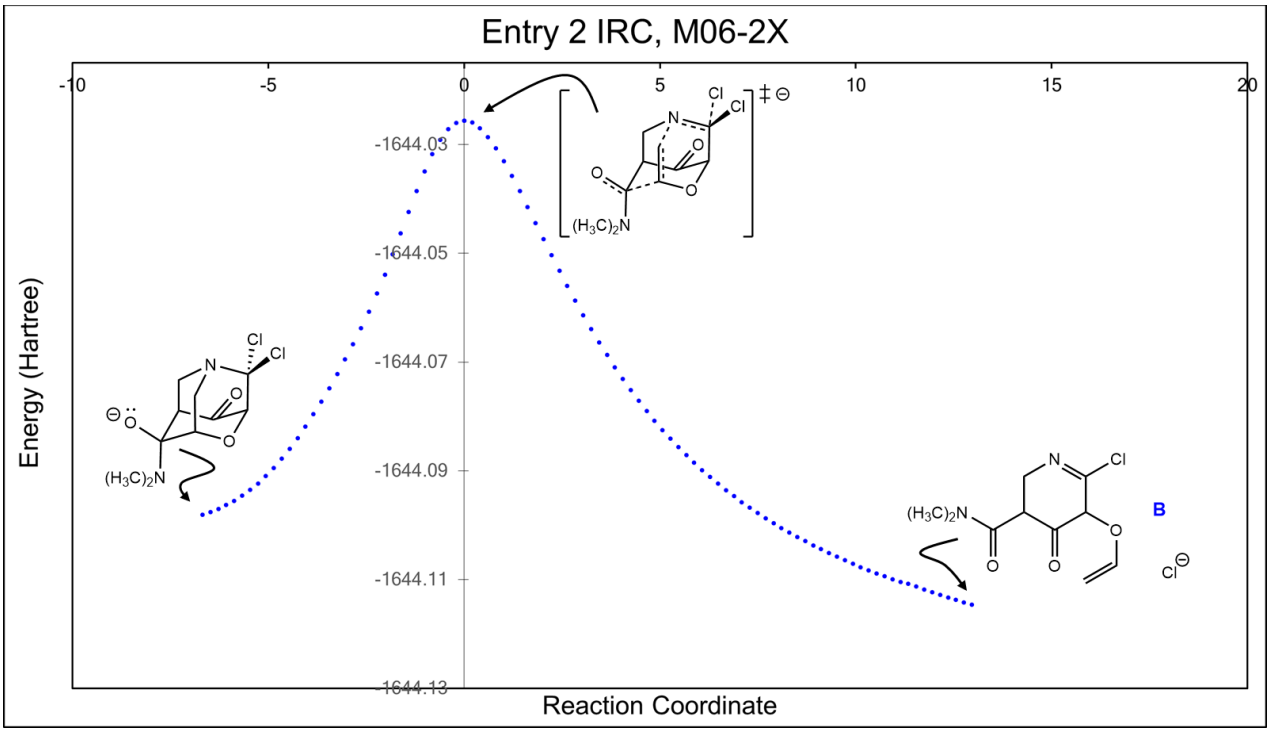
Structure	Electric Field Orientation	Electric Field Magnitude (a.u.)	Electronic Energy (a.u)	EE + Thermal Free Energy Corr. (a.u)	Lowest frequency (cm^{-1})
TSS	*-z*	0.01	-1624.564579	-1624.416272	-602.7448
Reactant	*-z*	0.01	-1624.673996	-1624.518702	63.4948
TSS	*+z*	0.01	-1624.676175	-1624.528013	-608.1987
Reactant	*+z*	0.01	-1624.738477	-1624.587123	50.1178
TSS	*-y*	0.01	-1624.611779	-1624.463329	-696.7201
Reactant	*-y*	0.01	-1624.686136	-1624.531186	62.73
TSS	*+y*	0.01	-1624.625538	-1624.477033	-713.56
Reactant	*+y*	0.01	-1624.700686	-1624.546627	61.4060
TSS	*-x*	0.008	-1624.631917	-1624.484716	-668.17
Reactant	*-x*	0.008	-1624.696963	-1624.542353	59.7804
TSS	*+x*	0.009	-1624.620813	-1624.470985	-562.40
Reactant	*+x*	0.009	-1624.686898	-1624.532075	78.6549

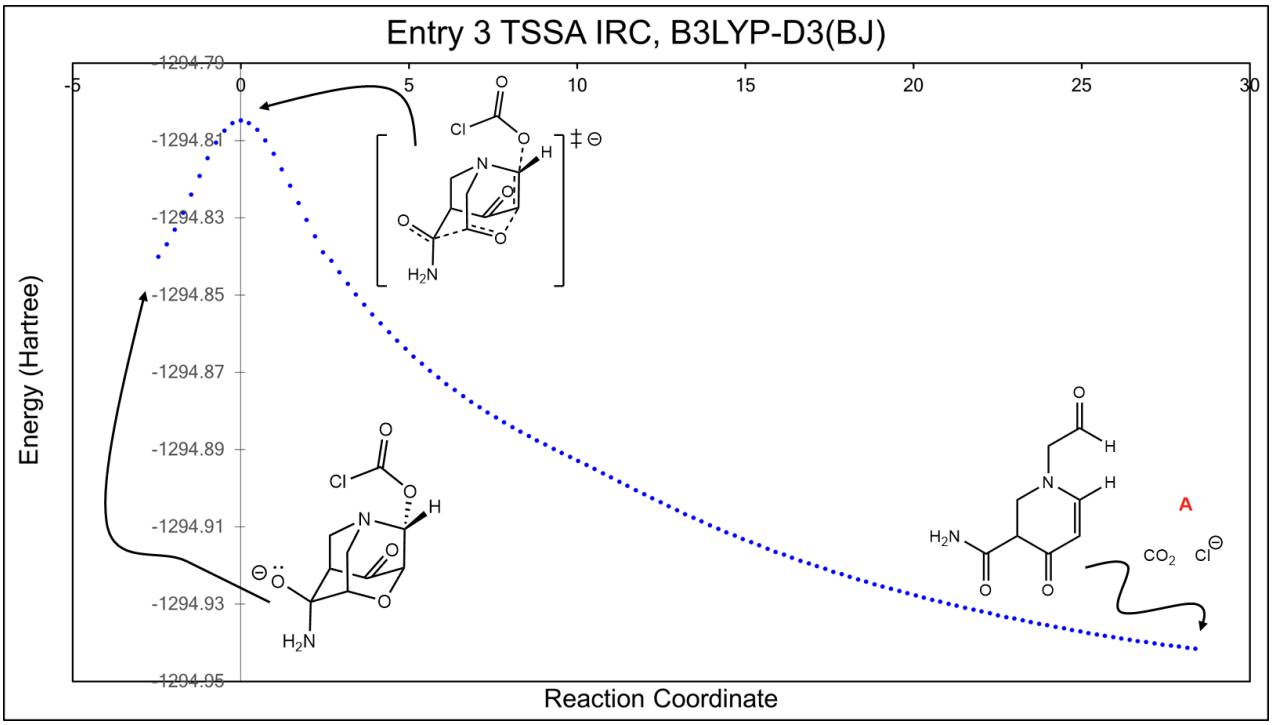
S8. Intrinsic Reaction Coordinates (IRCs) of Computed Transition State Structures in Table 1

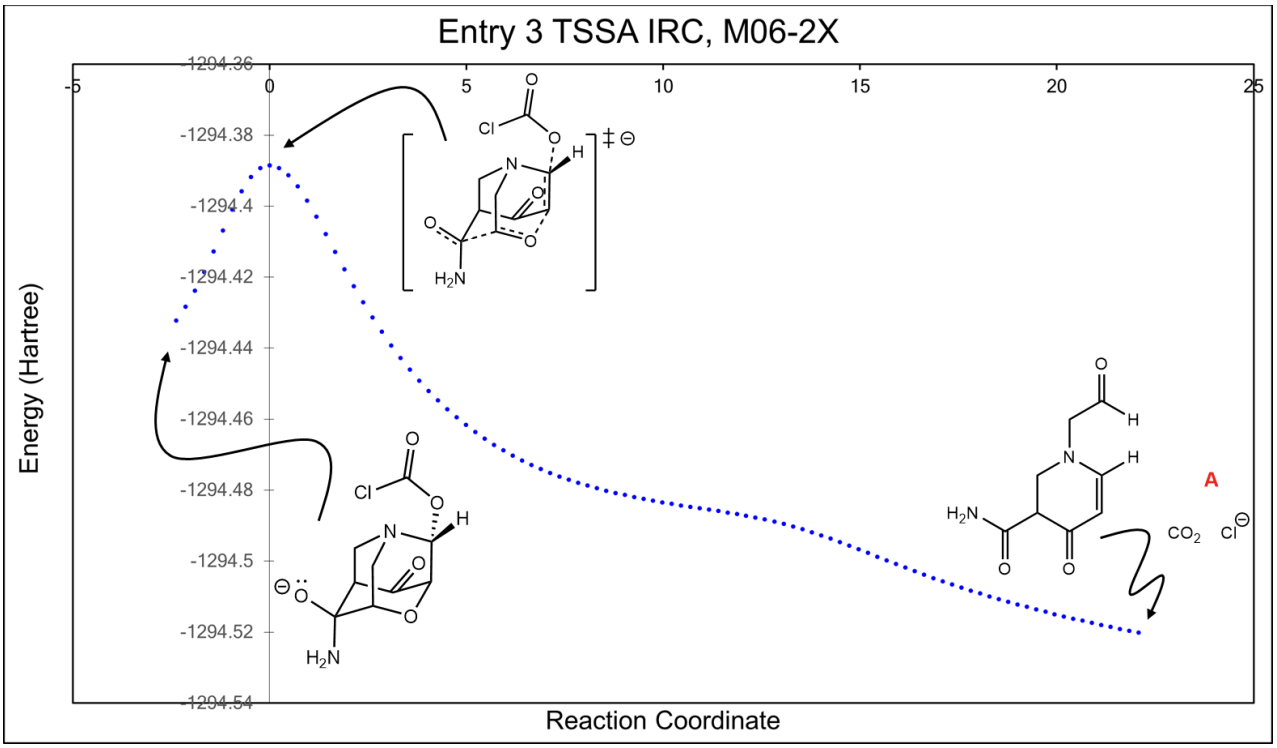


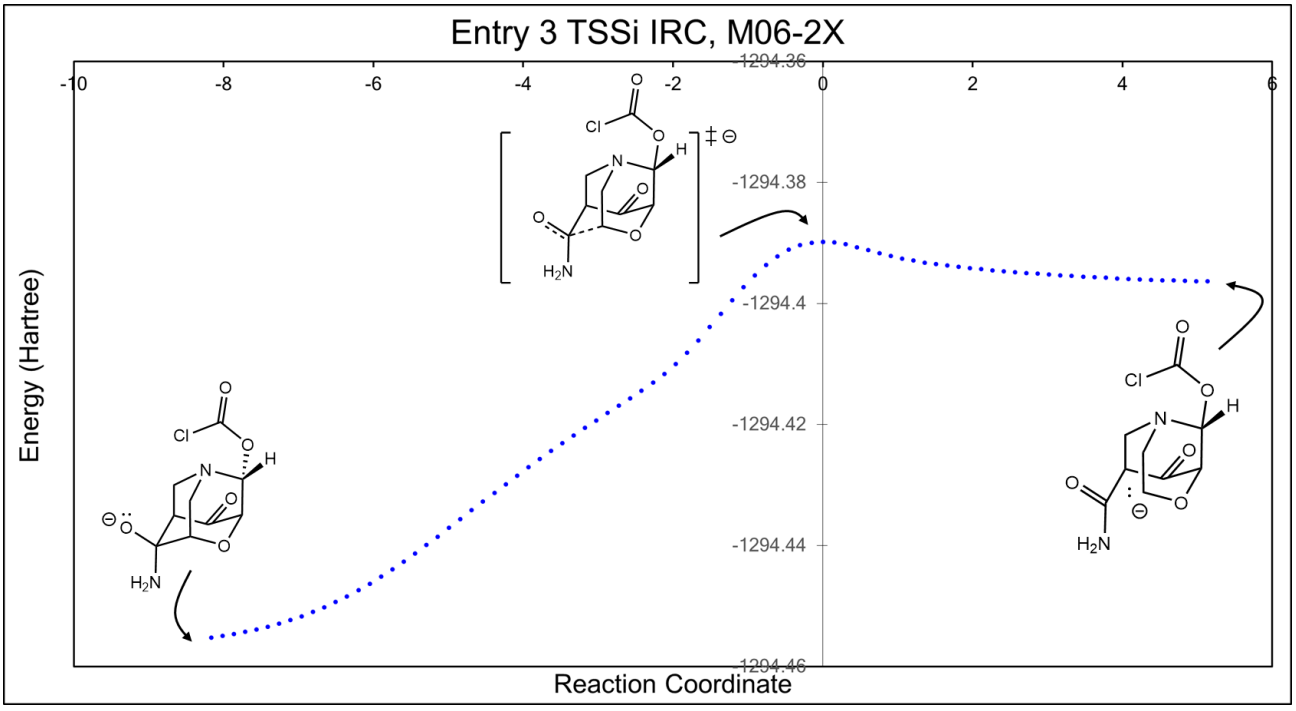


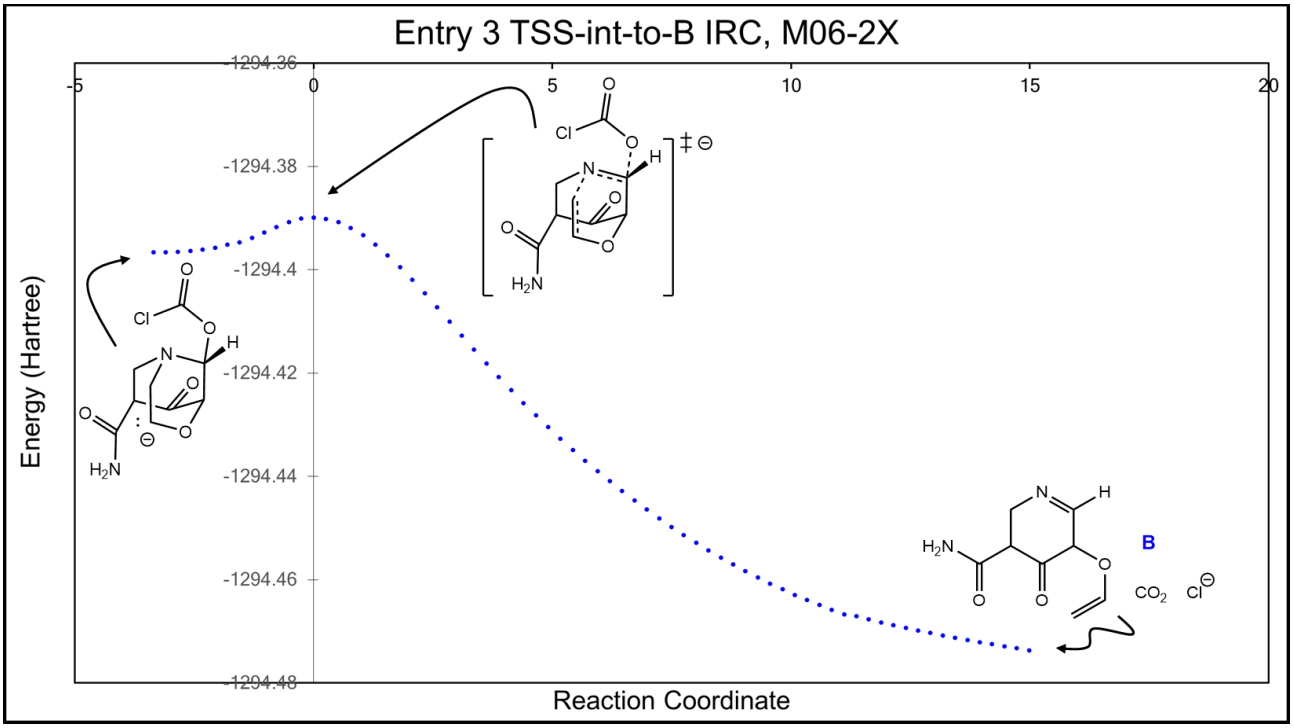

Entry 2 IRC, B3LYP-D3(BJ)
Energy (Hartree)
Reaction Coordinate
-10
-5
0
5
10
15
20
25
-1644.45
-1644.47
-1644.49
-1644.51
-1644.53
-1644.55
B

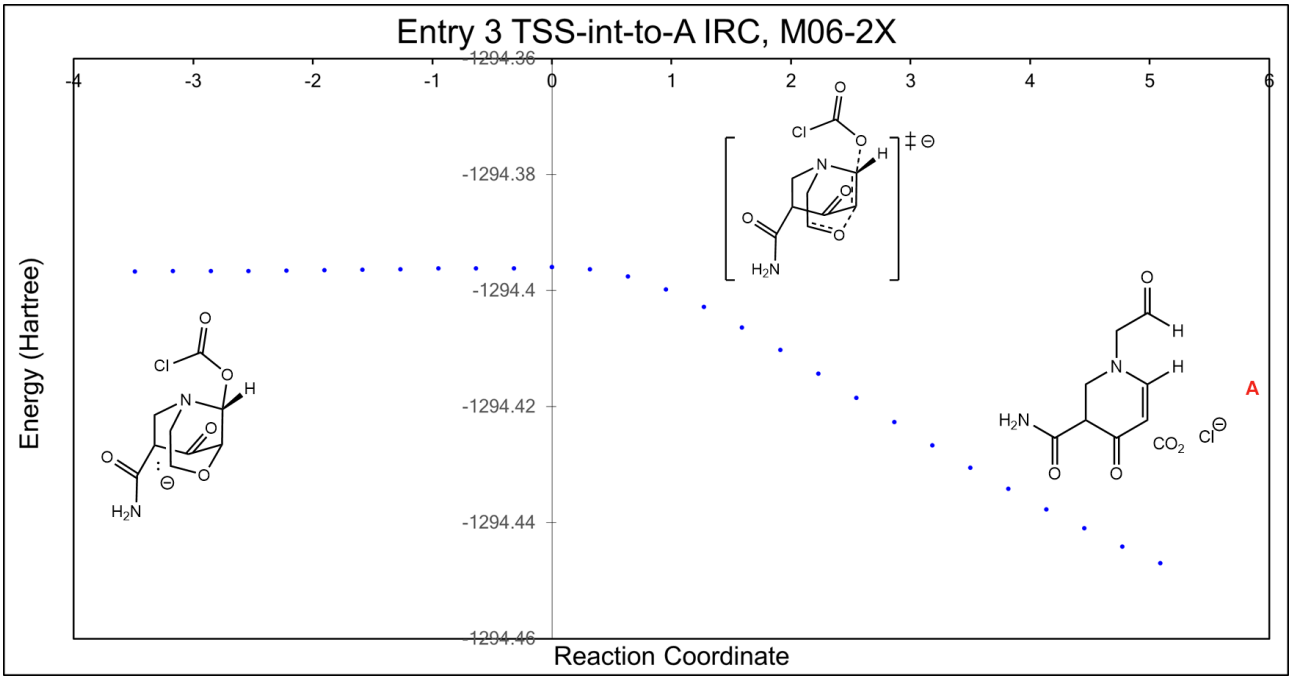

Entry 2 IRC, M06-2X
Energy (Hartree)
Reaction Coordinate
-10
-5
0
5
10
15
20
-1644.03
-1644.05
-1644.07
-1644.09
-1644.11
-1644.13
B

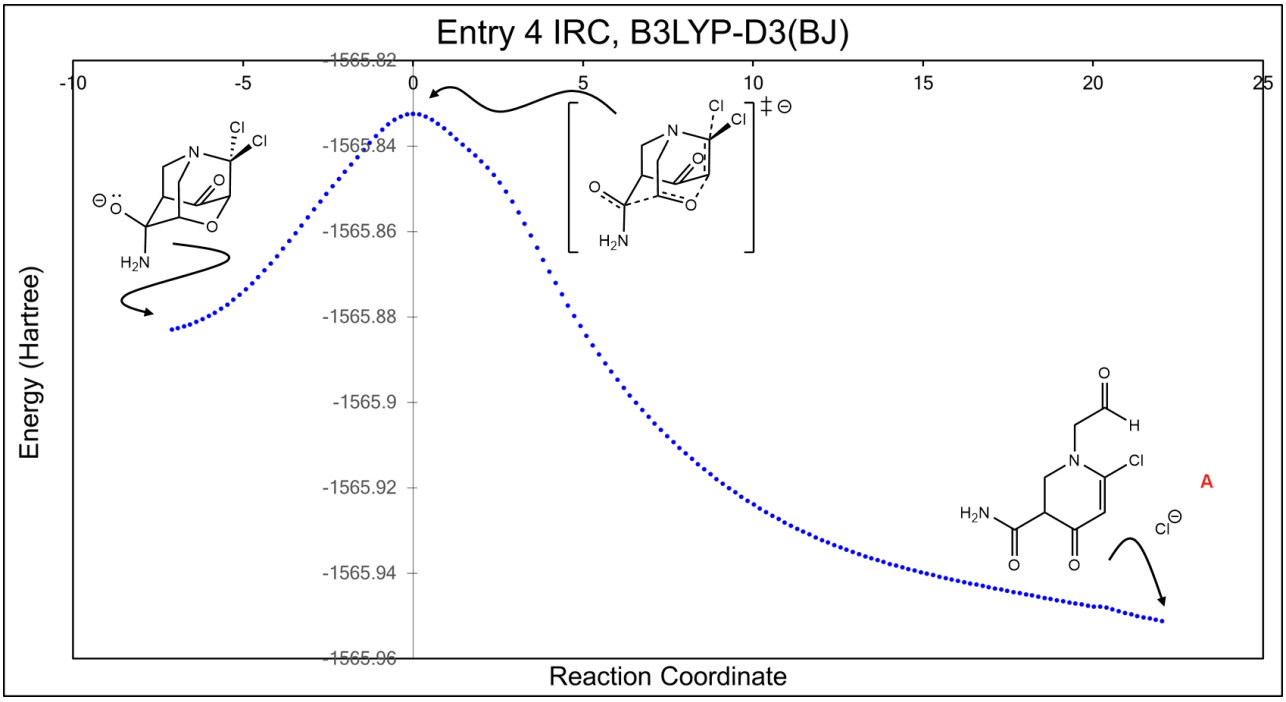

Entry 3 TSSA IRC, B3LYP-D3(BJ)
Energy (Hartree)
Reaction Coordinate
-1294.70
-1294.81
-1294.83
-1294.85
-1294.87
-1294.89
-1294.91
-1294.93
-1294.95
-5
0
5
10
15
20
25
30
A

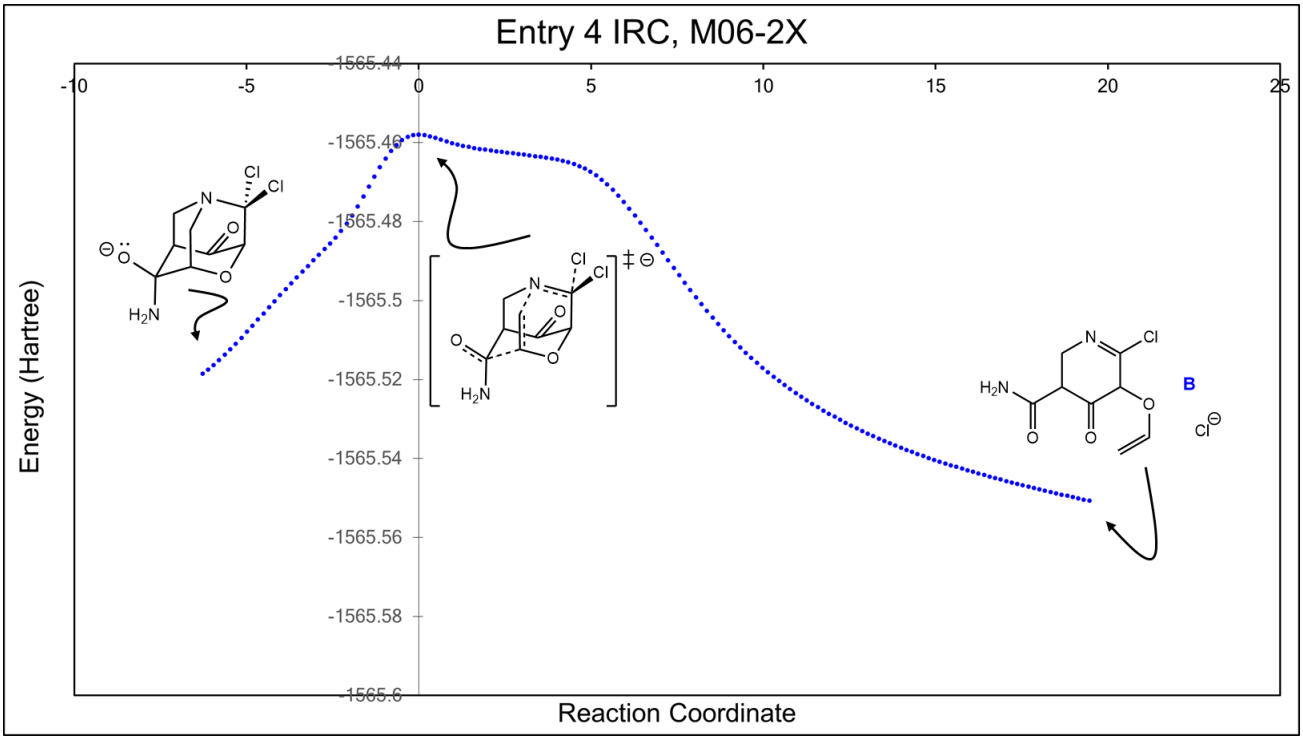

Entry 3 TSSA IRC, M06-2X
Energy (Hartree)
Reaction Coordinate
-1294.36
-1294.38
-1294.4
-1294.42
-1294.44
-1294.46
-1294.48
-1294.5
-1294.52
-1294.54
-5
0
5
10
15
20
25
A

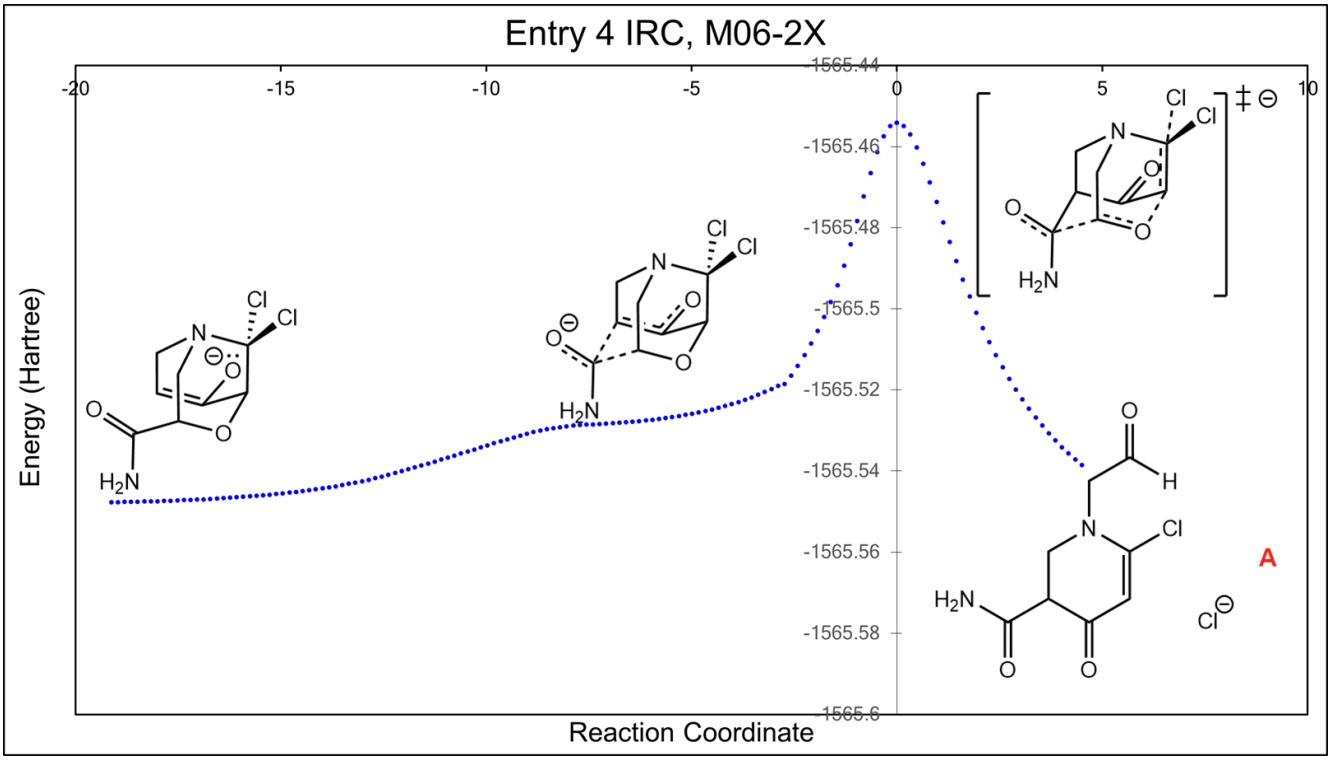

Entry 3 TSSi IRC, M06-2X
Energy (Hartree)
Reaction Coordinate
-1294.36
-1294.38
-1294.4
-1294.42
-1294.44
-1294.46
-10
-8
-6
-4
-2
0
2
4
6

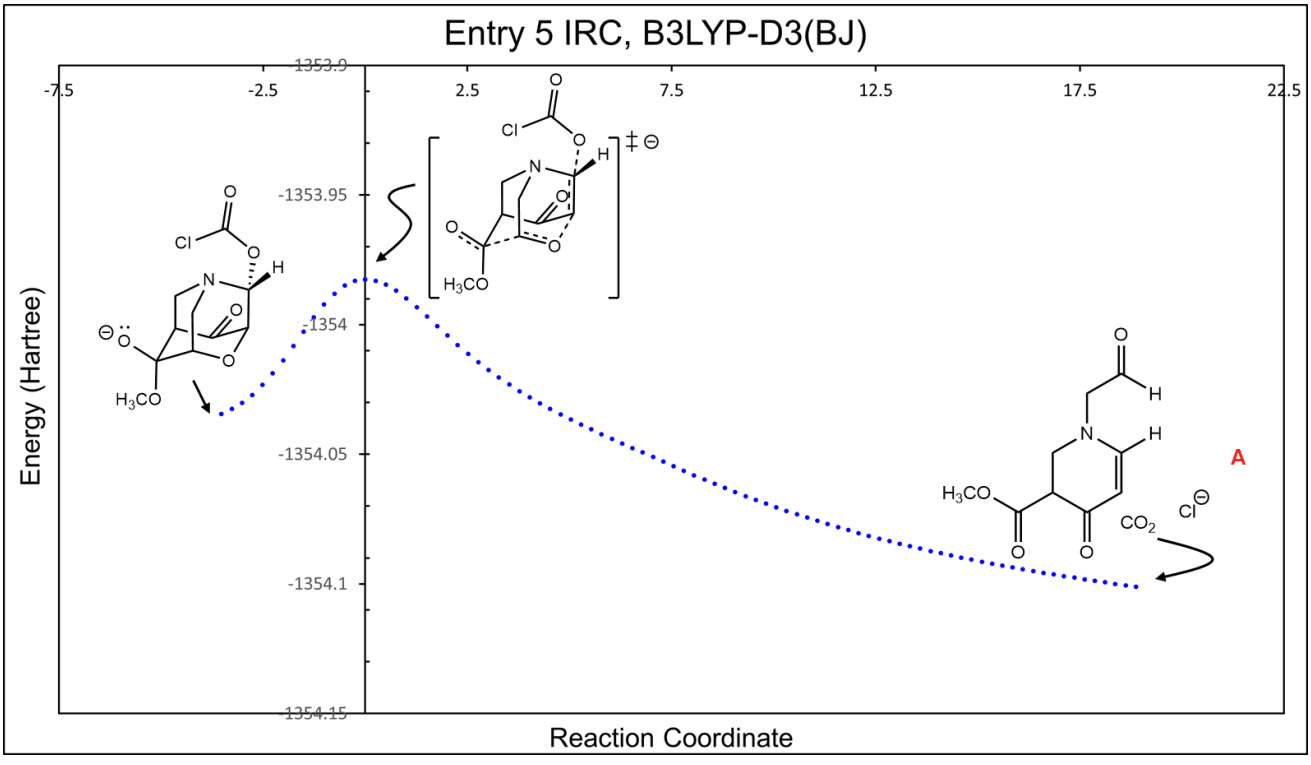

Entry 3 TSS-int-to-B IRC, M06-2X
Energy (Hartree)
Reaction Coordinate
-1294.36
-1294.38
-1294.4
-1294.42
-1294.44
-1294.46
-1294.48
-5
0
5
10
15
20
B

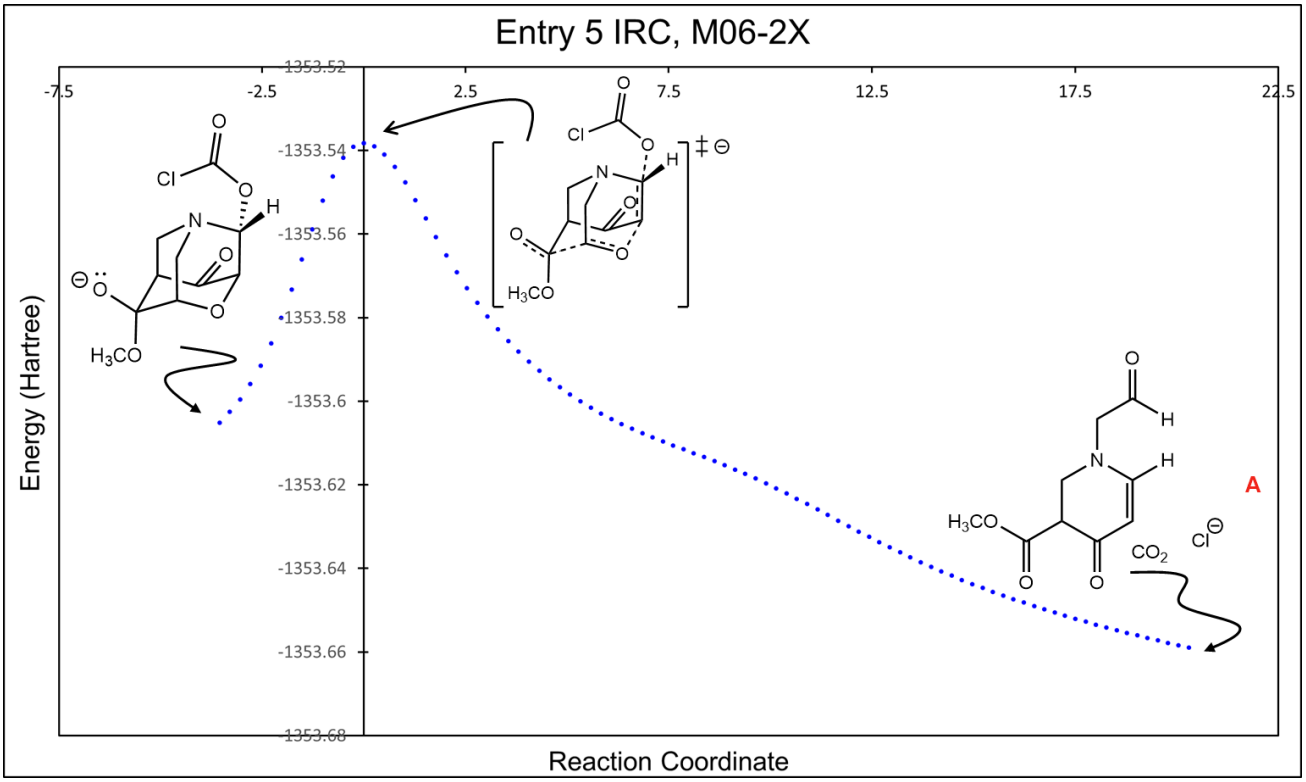

Entry 3 TSS-int-to-A IRC, M06-2X
Energy (Hartree)
-1294.36
-1294.38
-1294.4
-1294.42
-1294.44
-1294.46
-4
-3
-2
-1
0
1
2
3
4
5
6
Reaction Coordinate
A

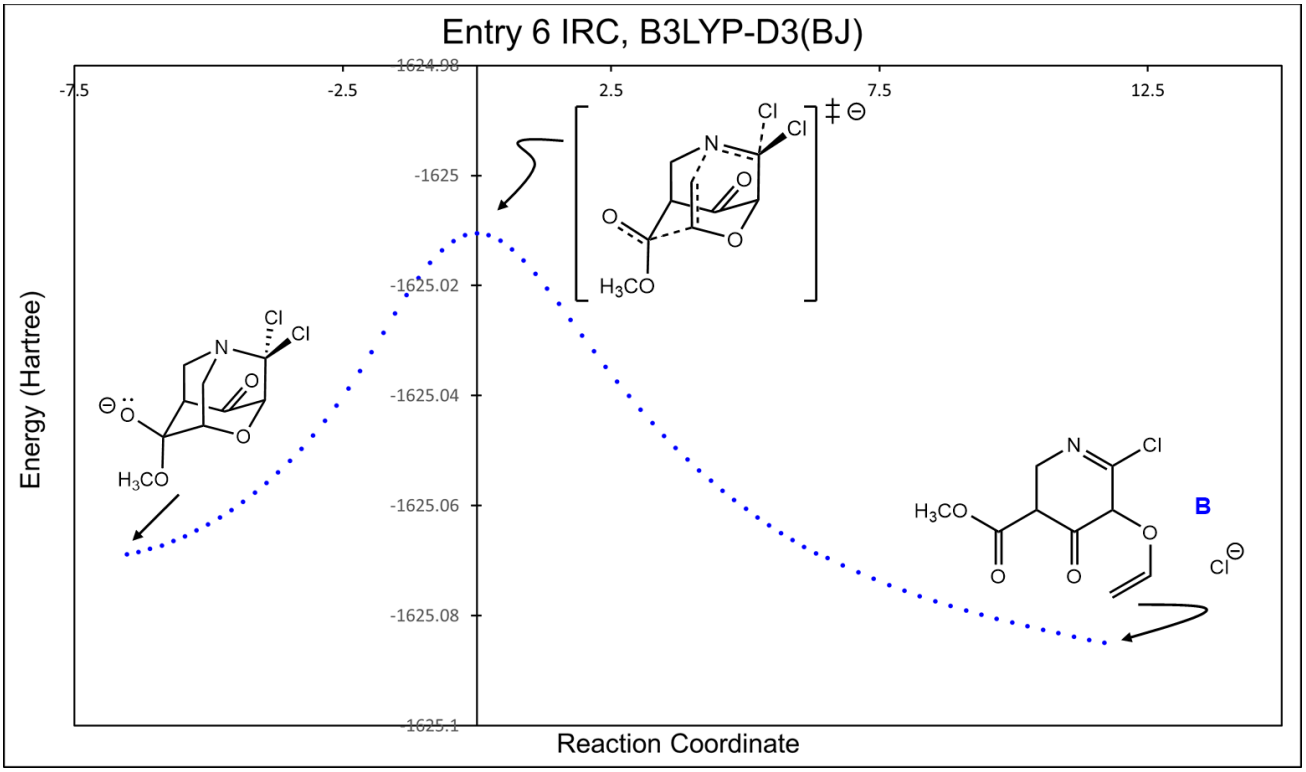

Entry 4 IRC, B3LYP-D3(BJ)
Energy (Hartree)
Reaction Coordinate
-1565.82
-1565.84
-1565.86
-1565.88
-1565.9
-1565.92
-1565.94
-1565.96
-10
-5
0
5
10
15
20
25
A

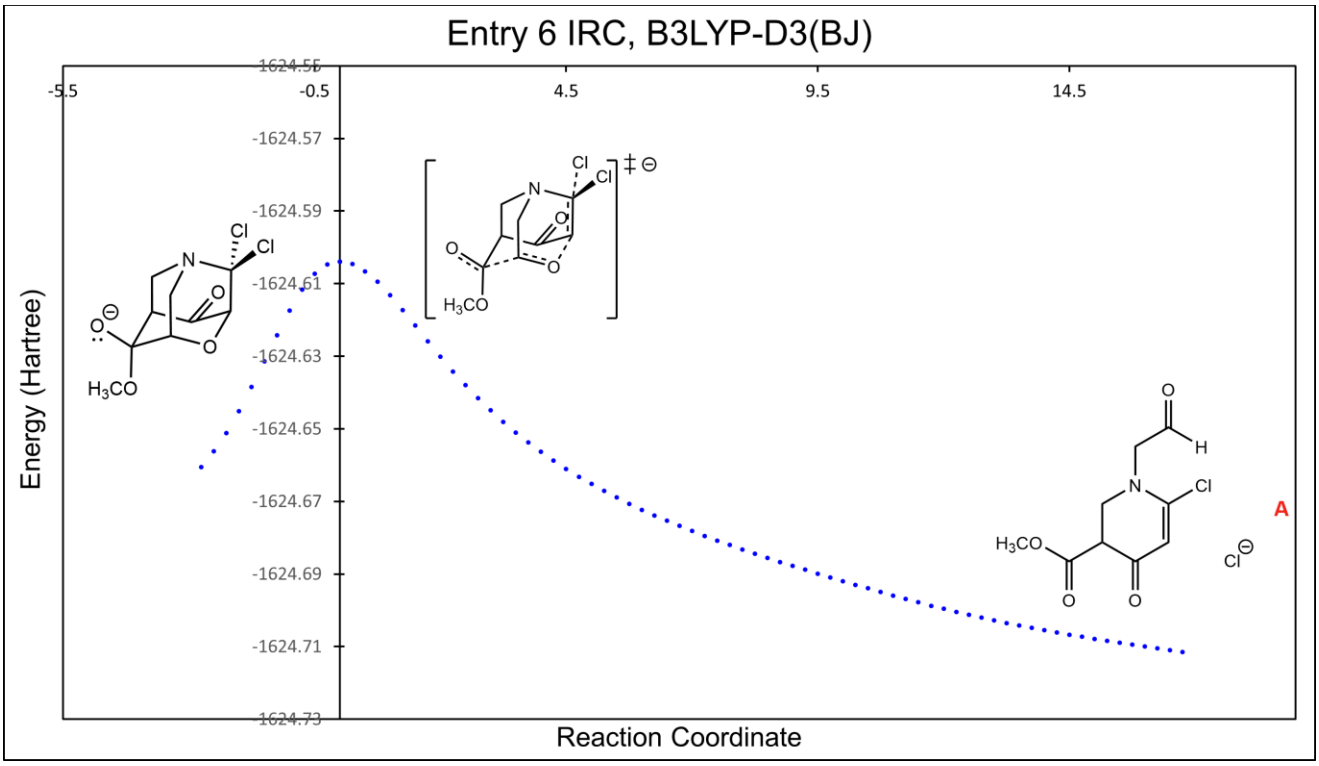

Entry 4 IRC, M06-2X
Energy (Hartree)
Reaction Coordinate
-1565.44
-1565.46
-1565.48
-1565.5
-1565.52
-1565.54
-1565.56
-1565.58
-1565.6
-10
-5
0
5
10
15
20
25
B

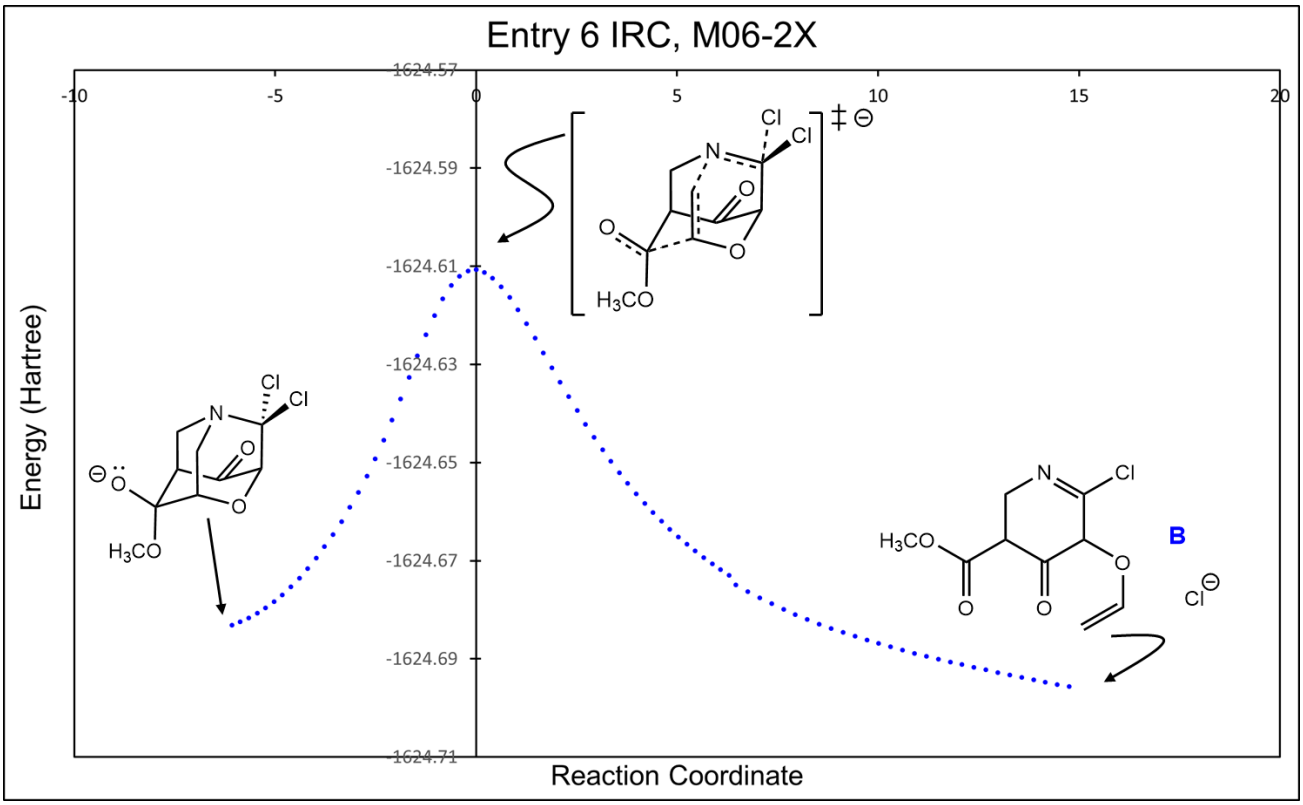

Entry 4 IRC, M06-2X
Energy (Hartree)
Reaction Coordinate
-20
-15
-10
-5
0
5
10
-1565.44
-1565.46
-1565.48
-1565.5
-1565.52
-1565.54
-1565.56
-1565.58
-1565.6
A

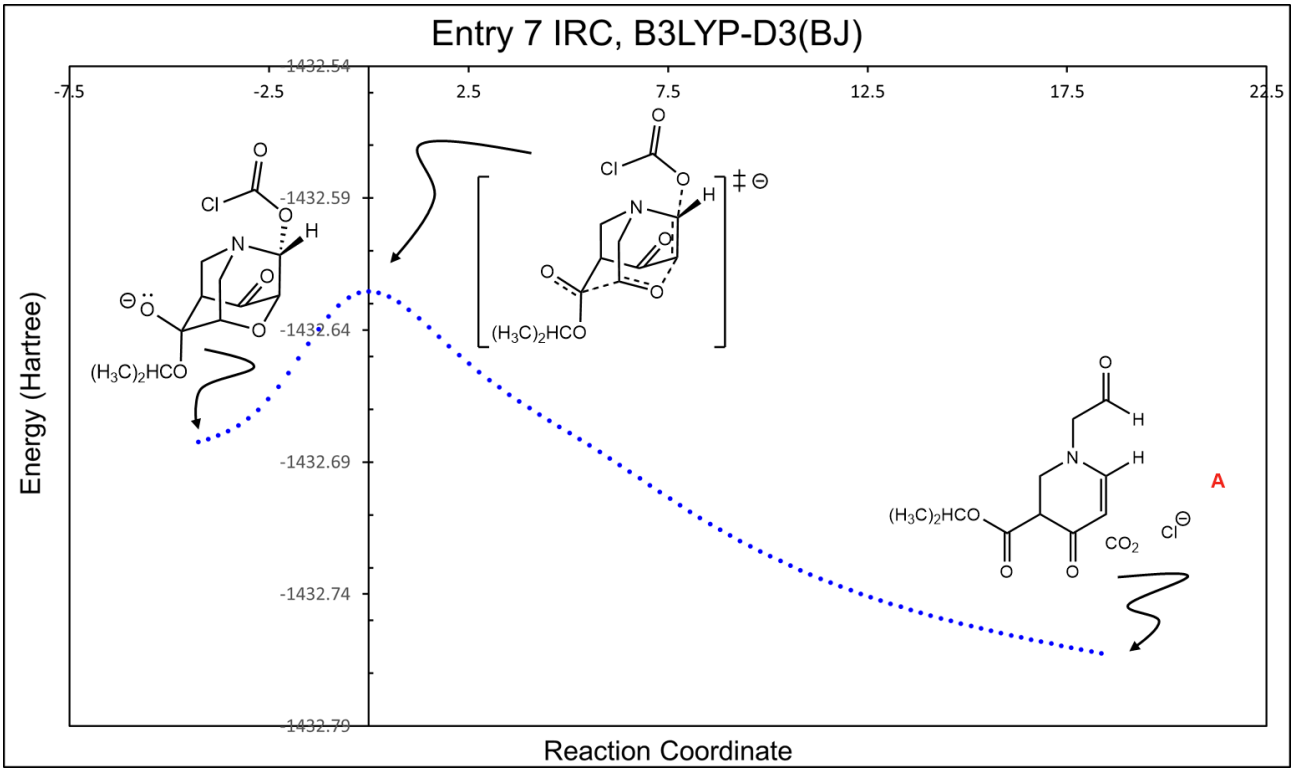

Entry 5 IRC, B3LYP-D3(BJ)
Energy (Hartree)
Reaction Coordinate
-7.5
-2.5
2.5
7.5
12.5
17.5
22.5
-1353.9
-1353.95
-1354
-1354.05
-1354.1
-1354.15
A

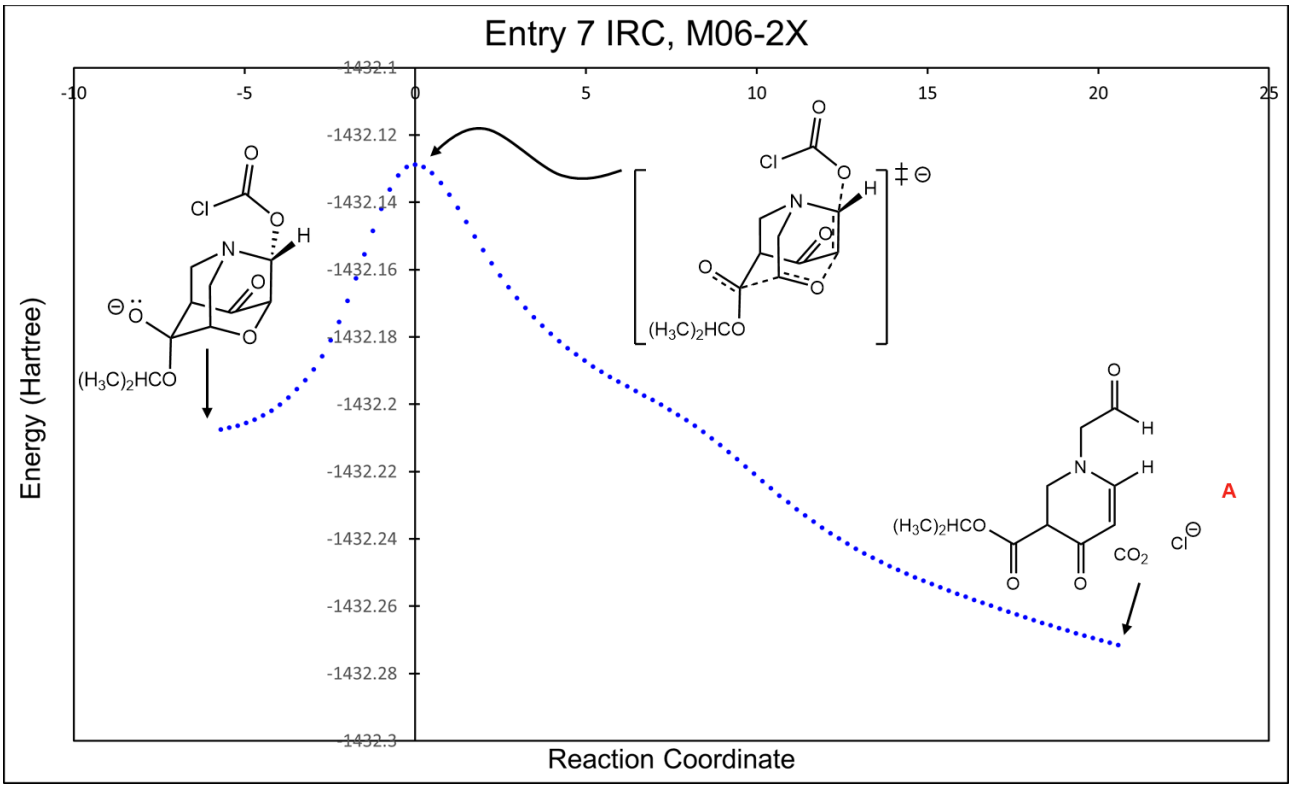

Entry 5 IRC, M06-2X
Energy (Hartree)
Reaction Coordinate
-7.5
-2.5
2.5
7.5
12.5
17.5
22.5
-1353.52
-1353.54
-1353.56
-1353.58
-1353.6
-1353.62
-1353.64
-1353.66
-1353.68
A
CO2

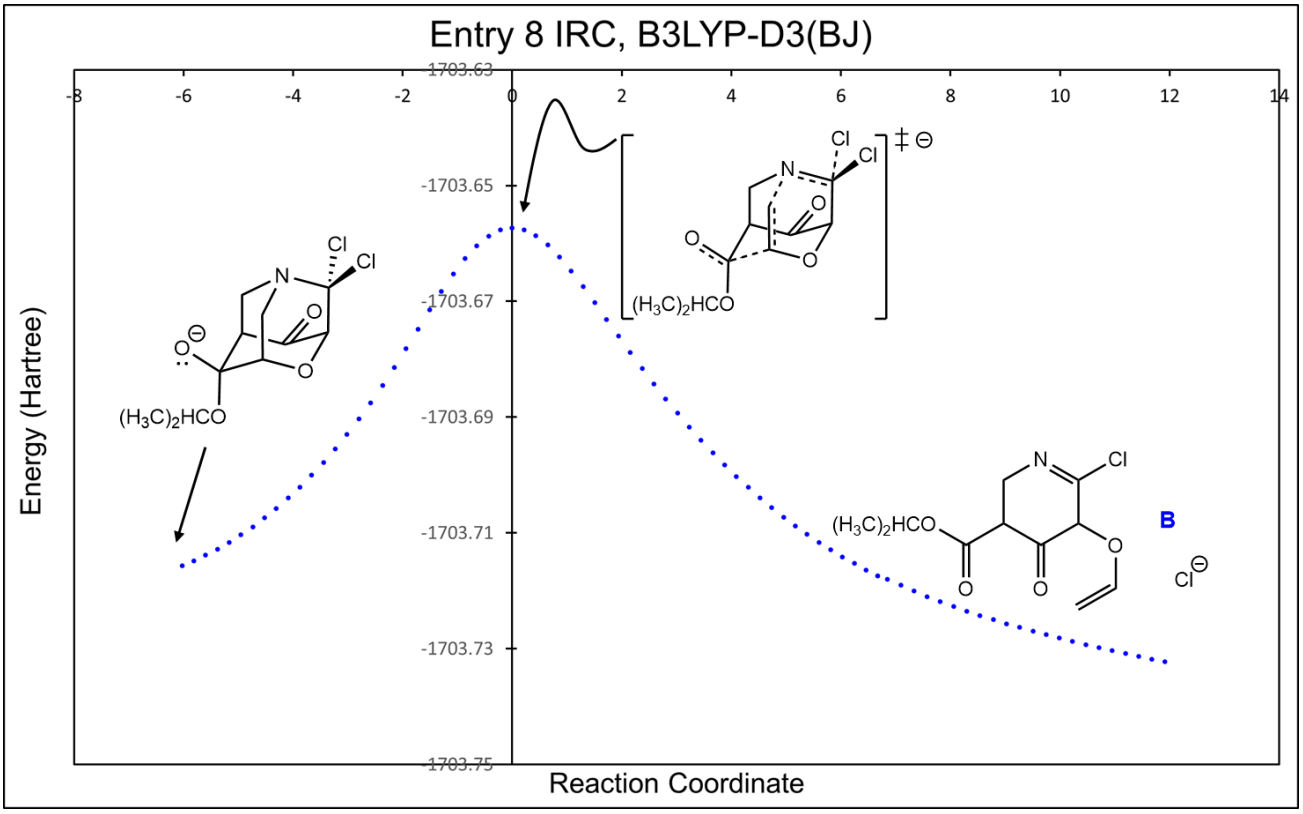

Entry 6 IRC, B3LYP-D3(BJ)
Energy (Hartree)
Reaction Coordinate
-7.5
-2.5
2.5
7.5
12.5
1624.98
-1625
-1625.02
-1625.04
-1625.06
-1625.08
-1625.1
B

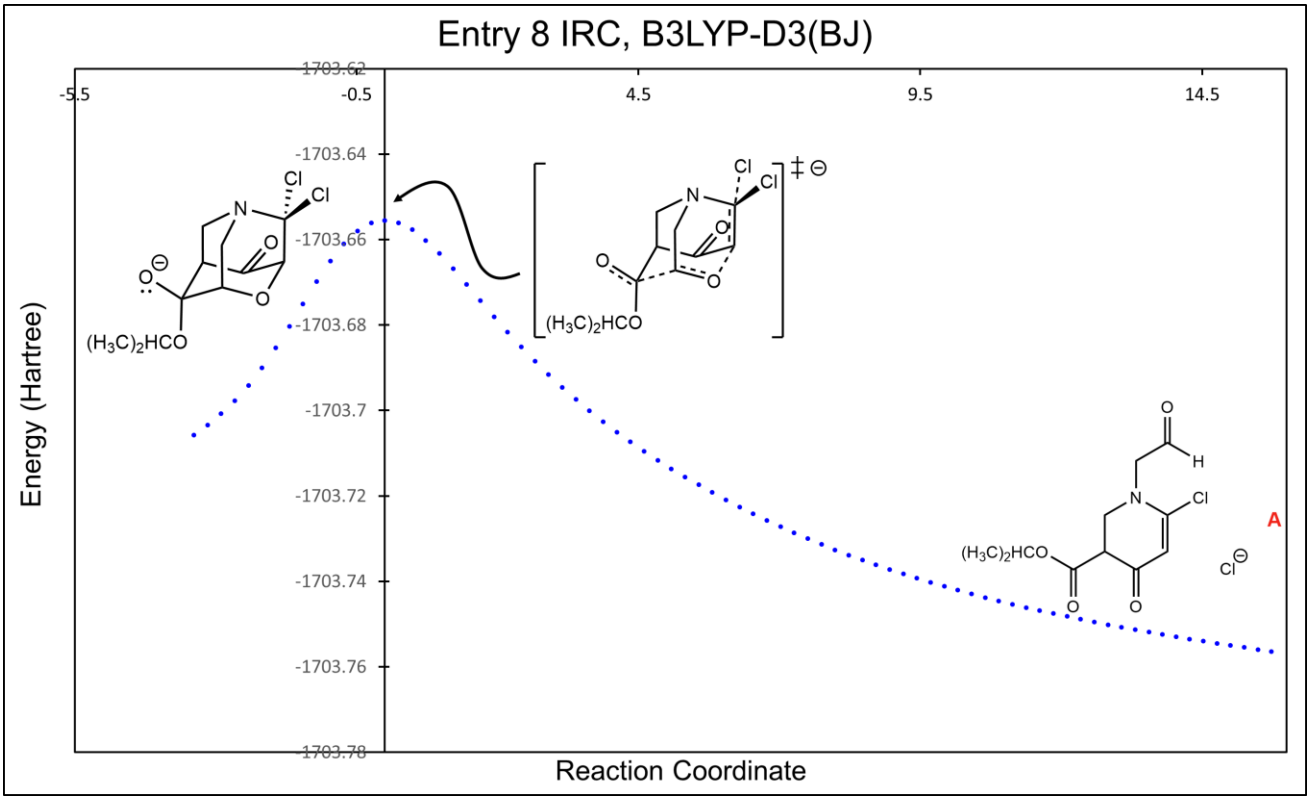

Entry 6 IRC, B3LYP-D3(BJ)
Energy (Hartree)
Reaction Coordinate
-5.5
-0.5
4.5
9.5
14.5
-1624.55
-1624.57
-1624.59
-1624.61
-1624.63
-1624.65
-1624.67
-1624.69
-1624.71
-1624.73
A

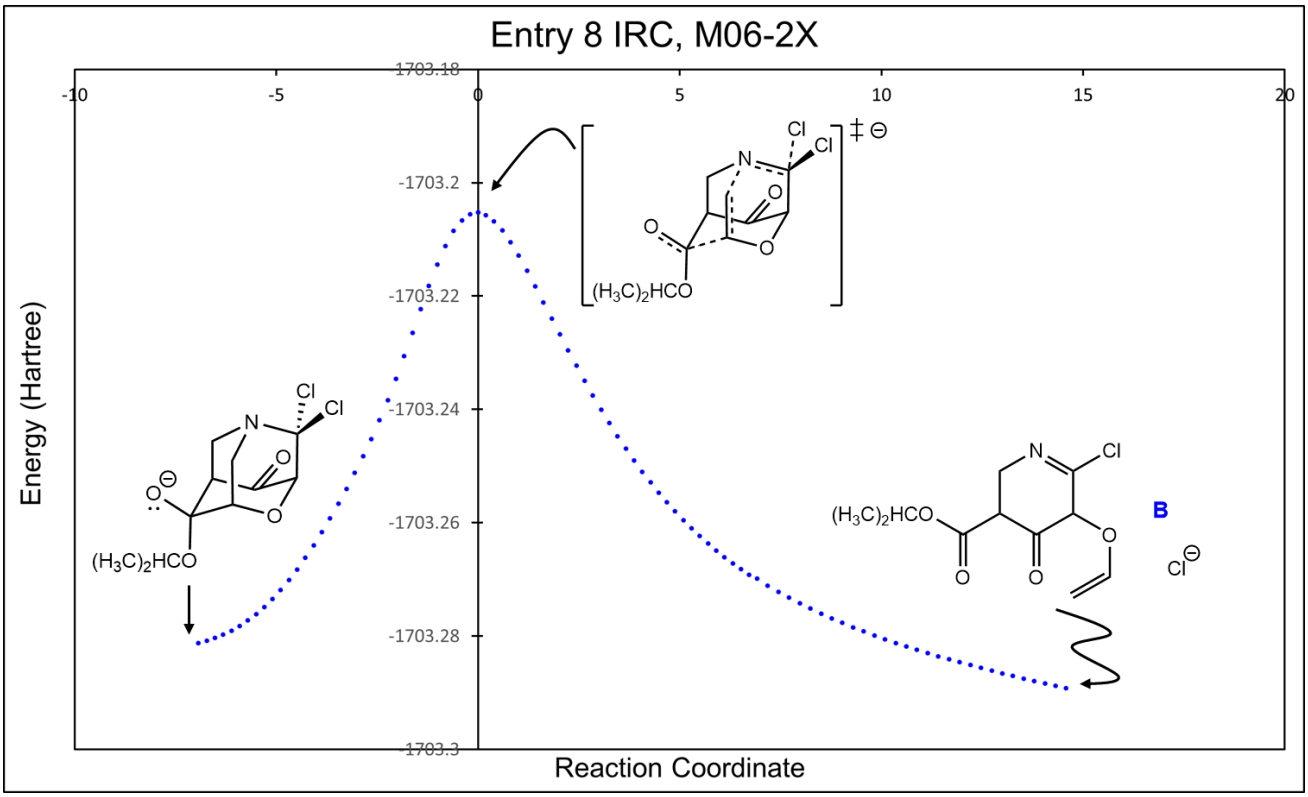

Entry 6 IRC, M06-2X
Energy (Hartree)
Reaction Coordinate
-10
-5
0
5
10
15
20
1624.57
-1624.59
-1624.61
-1624.63
-1624.65
-1624.67
-1624.69
-1624.71
B

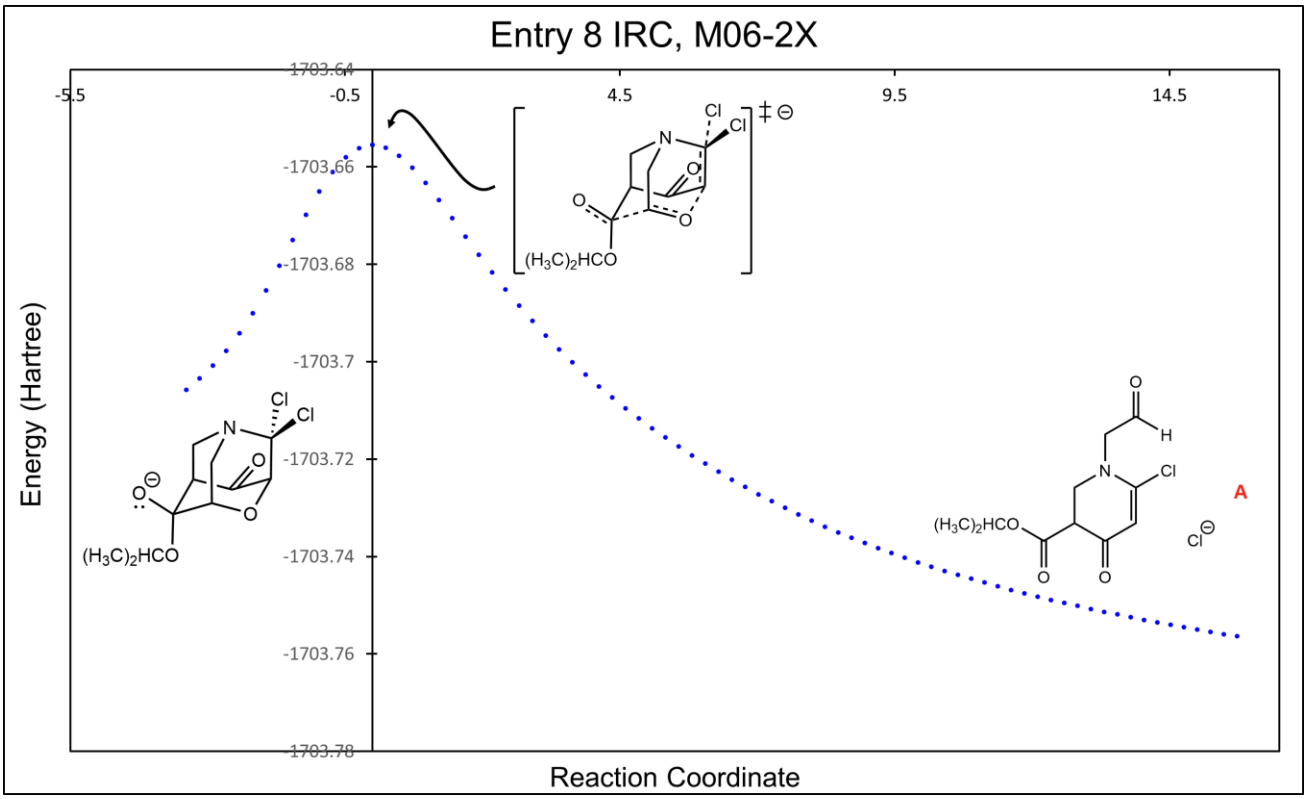

Entry 7 IRC, B3LYP-D3(BJ)
Energy (Hartree)
Reaction Coordinate
-1432.54
-1432.59
-1432.64
-1432.69
-1432.74
-1432.79
-7.5
-2.5
2.5
7.5
12.5
17.5
22.5
A

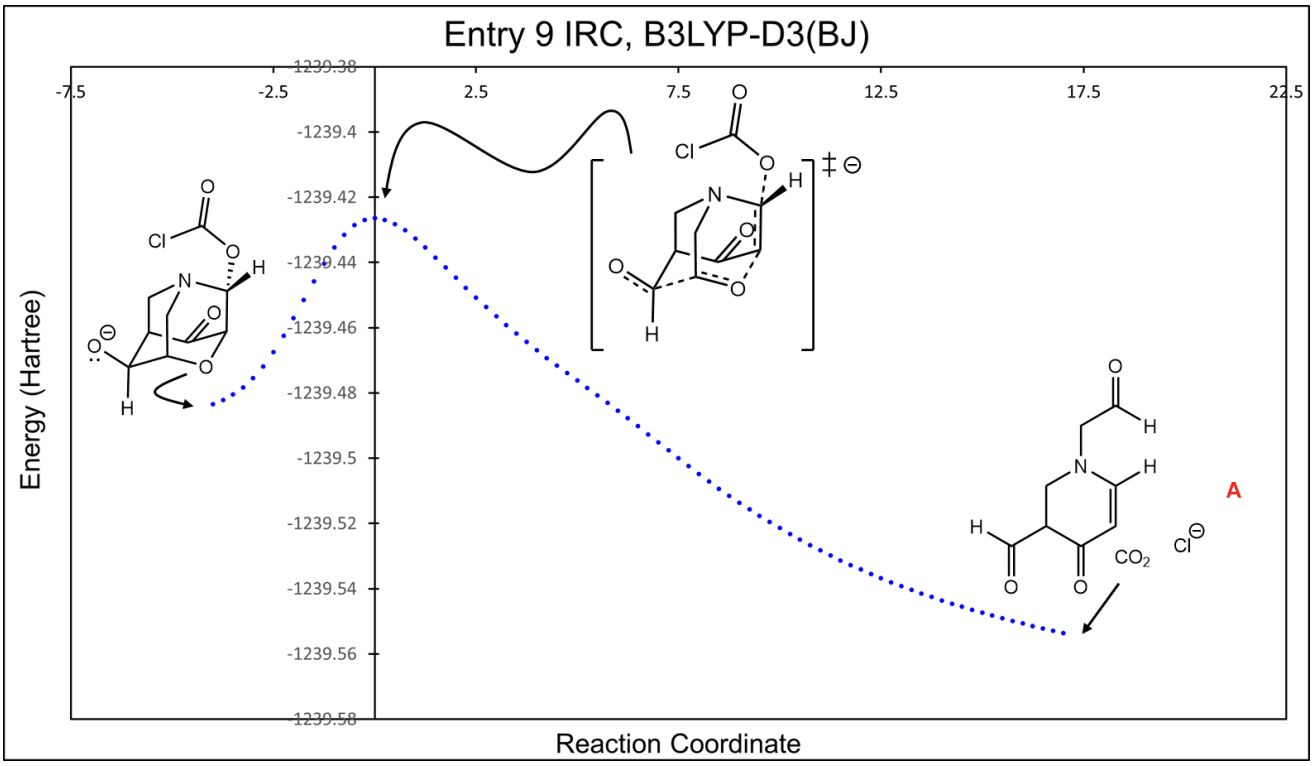

Entry 7 IRC, M06-2X
Energy (Hartree)
Reaction Coordinate
-1432.1
-1432.12
-1432.14
-1432.16
-1432.18
-1432.2
-1432.22
-1432.24
-1432.26
-1432.28
-1432.3
-10
-5
0
5
10
15
20
25
A

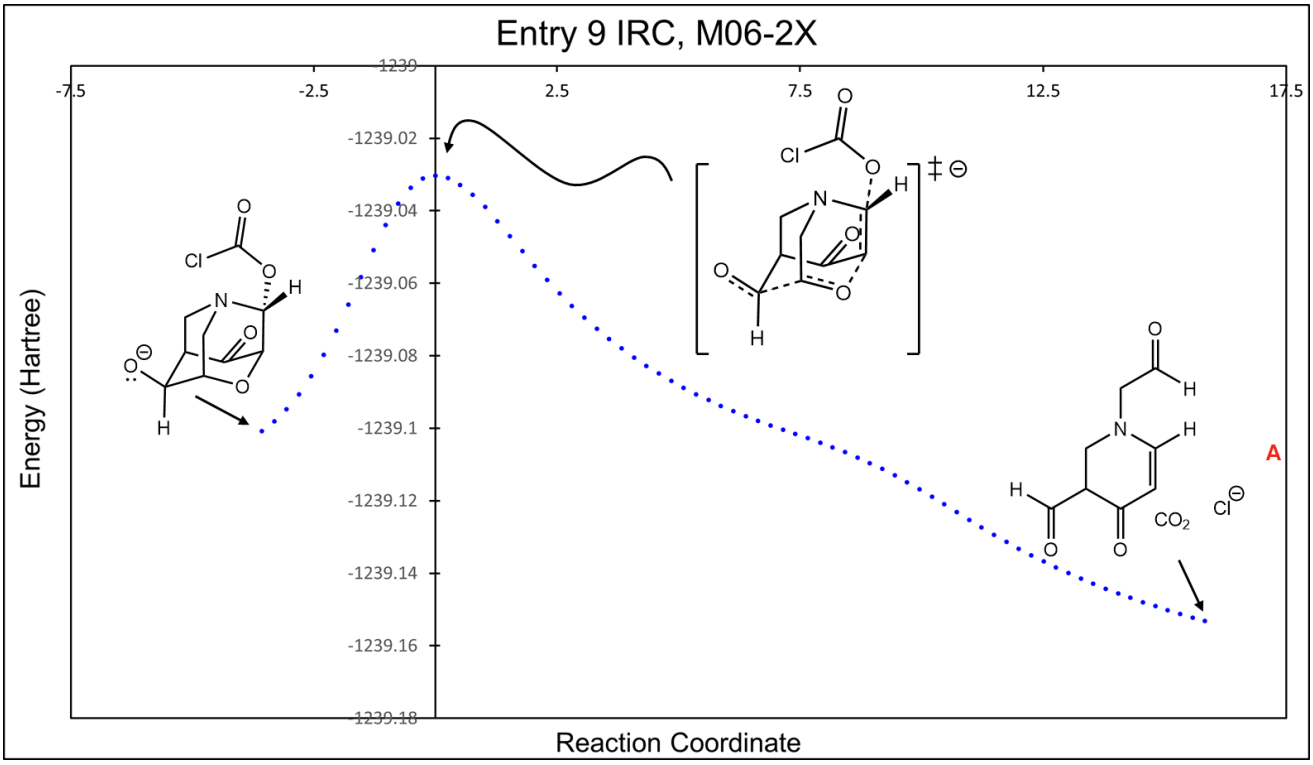

Entry 8 IRC, B3LYP-D3(BJ)
Energy (Hartree)
Reaction Coordinate
-1703.63
-1703.65
-1703.67
-1703.69
-1703.71
-1703.73
-1703.75
-8
-6
-4
-2
0
2
4
6
8
10
12
14
B

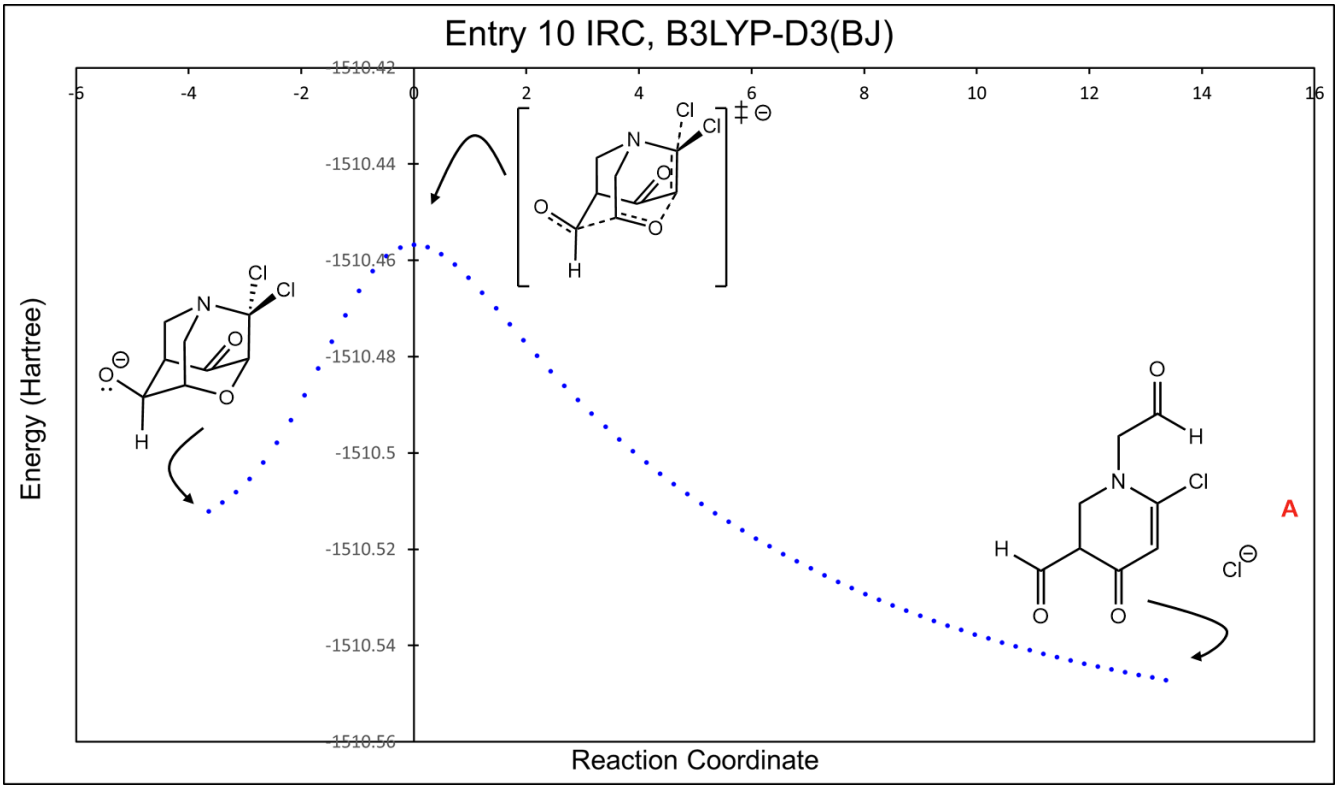

Entry 8 IRC, B3LYP-D3(BJ)
Energy (Hartree)
Reaction Coordinate
1703.62
-1703.64
-1703.66
-1703.68
-1703.7
-1703.72
-1703.74
-1703.76
-1703.78
-5.5
-0.5
4.5
9.5
14.5
A

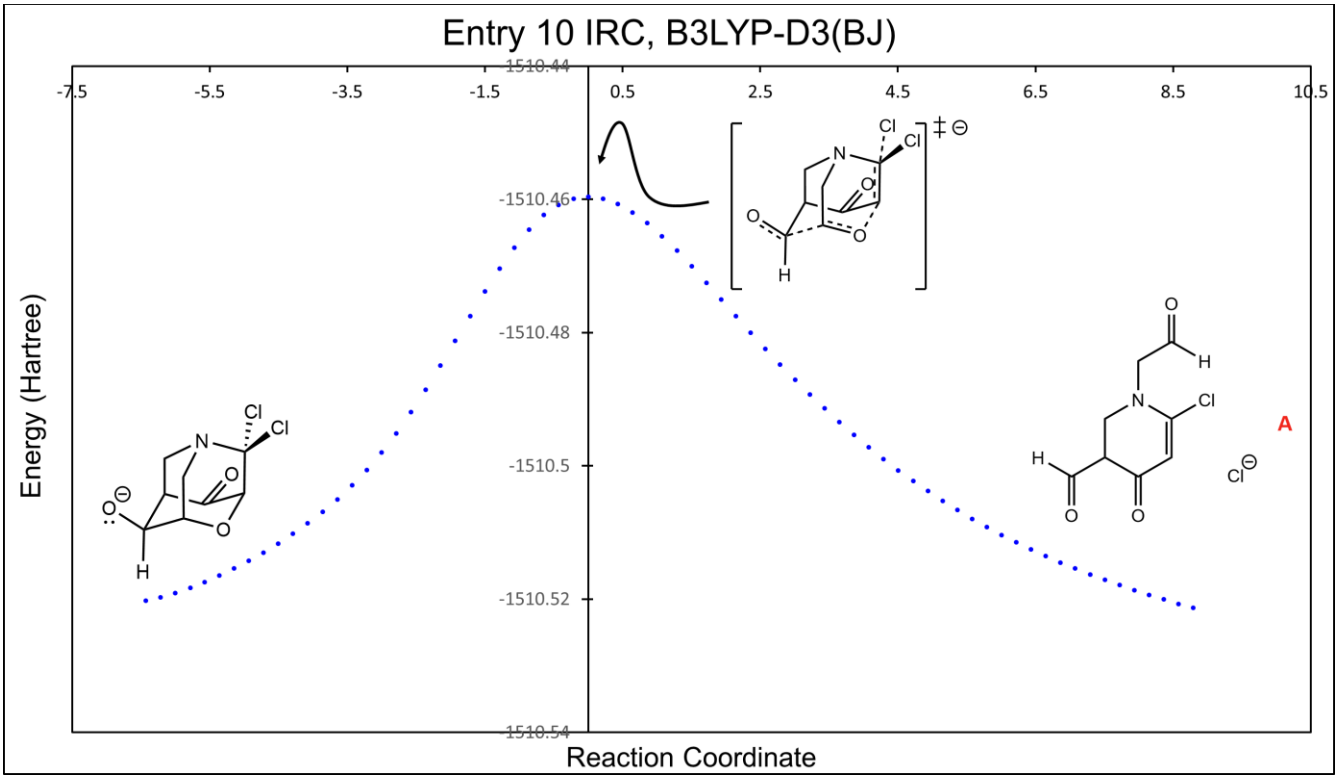

Entry 8 IRC, M06-2X
Energy (Hartree)
Reaction Coordinate
1703.18
-1703.2
-1703.22
-1703.24
-1703.26
-1703.28
-1703.3
-10
-5
0
5
10
15
20
B

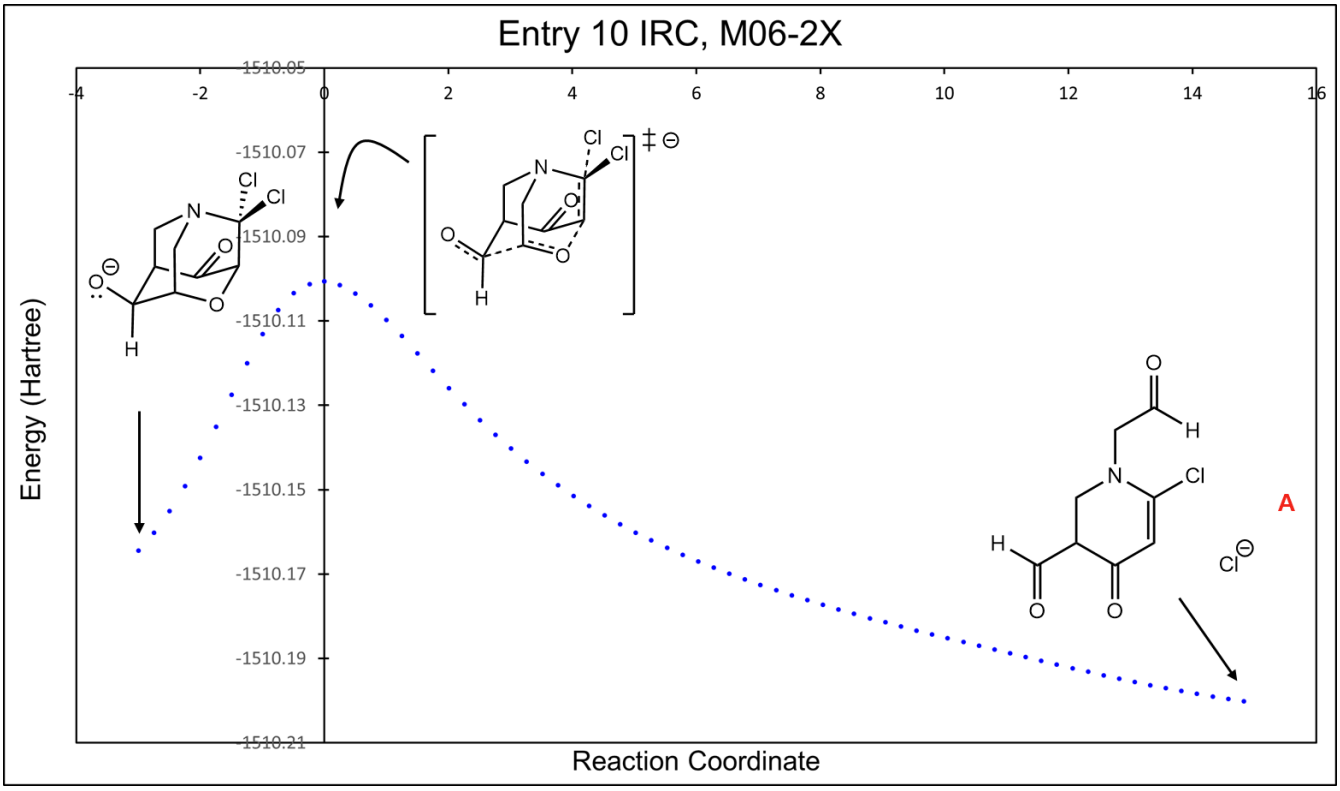

Entry 8 IRC, M06-2X
Energy (Hartree)
Reaction Coordinate
1703.64
-1703.66
-1703.68
-1703.7
-1703.72
-1703.74
-1703.76
-1703.78
-5.5
-0.5
4.5
9.5
14.5
A

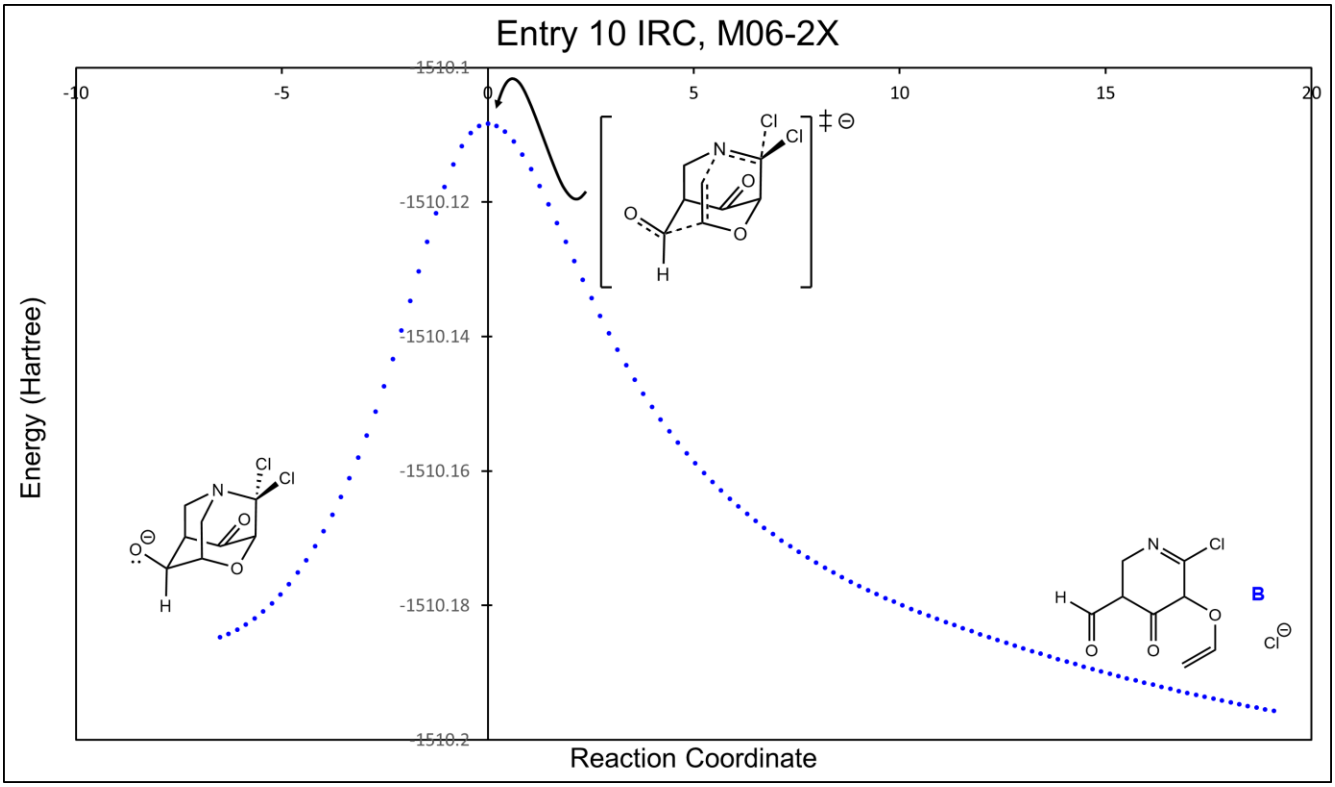

Entry 9 IRC, B3LYP-D3(BJ)
Energy (Hartree)
Reaction Coordinate
-7.5
-2.5
2.5
7.5
12.5
17.5
22.5
-1239.38
-1239.4
-1239.42
-1239.44
-1239.46
-1239.48
-1239.5
-1239.52
-1239.54
-1239.56
-1239.58
A

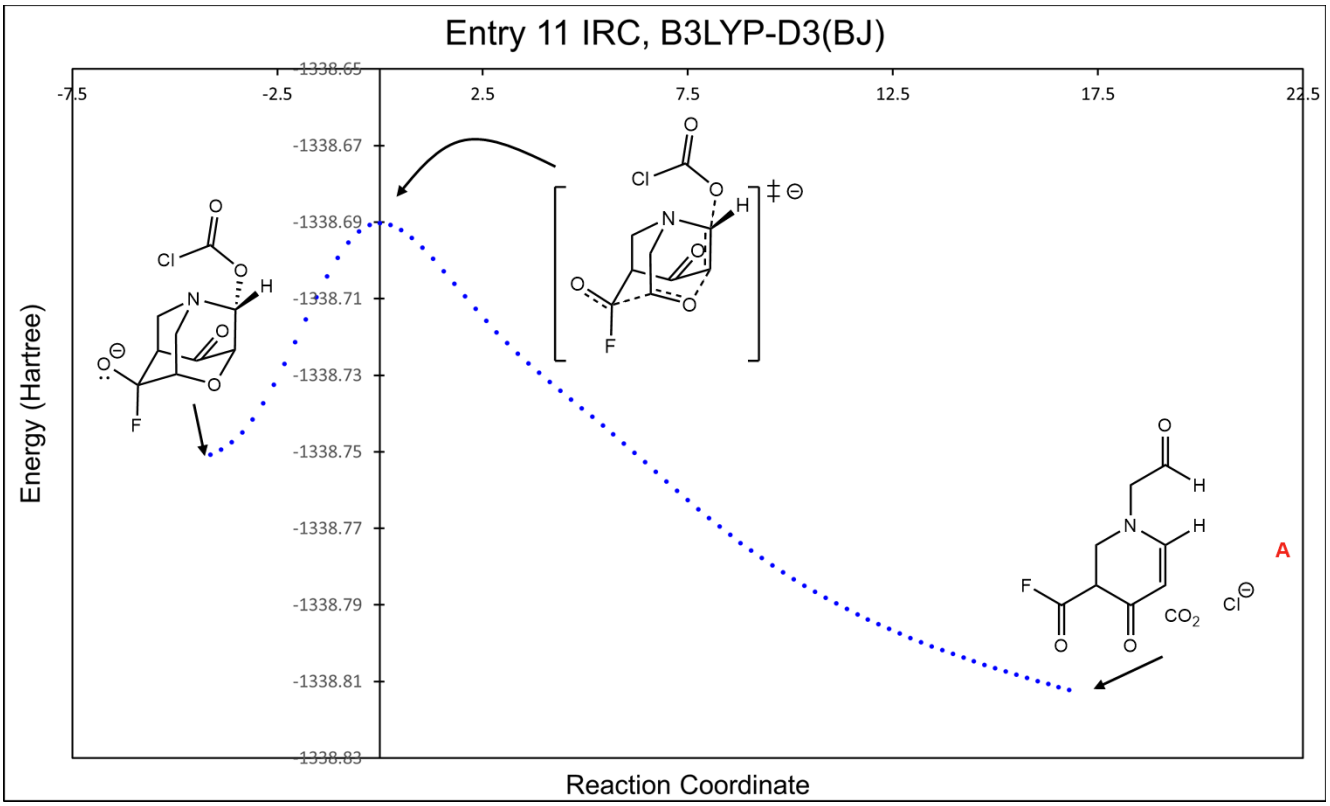

Entry 9 IRC, M06-2X
Energy (Hartree)
Reaction Coordinate
-7.5
-2.5
2.5
7.5
12.5
17.5
1239
-1239.02
-1239.04
-1239.06
-1239.08
-1239.1
-1239.12
-1239.14
-1239.16
-1239.18
A

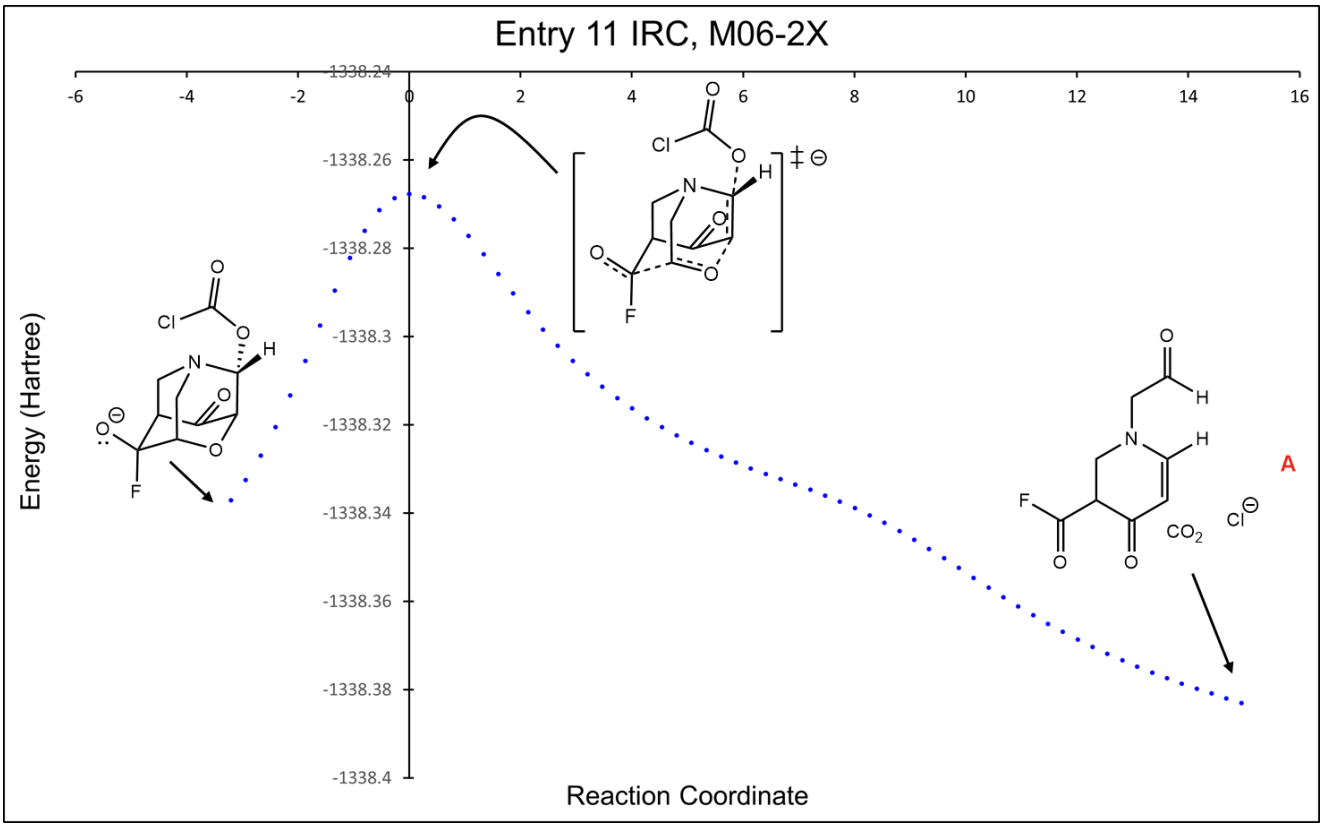

Entry 10 IRC, B3LYP-D3(BJ)
Energy (Hartree)
Reaction Coordinate
-1510.42
-1510.44
-1510.46
-1510.48
-1510.5
-1510.52
-1510.54
-1510.56
-6
-4
-2
0
2
4
6
8
10
12
14
16
A

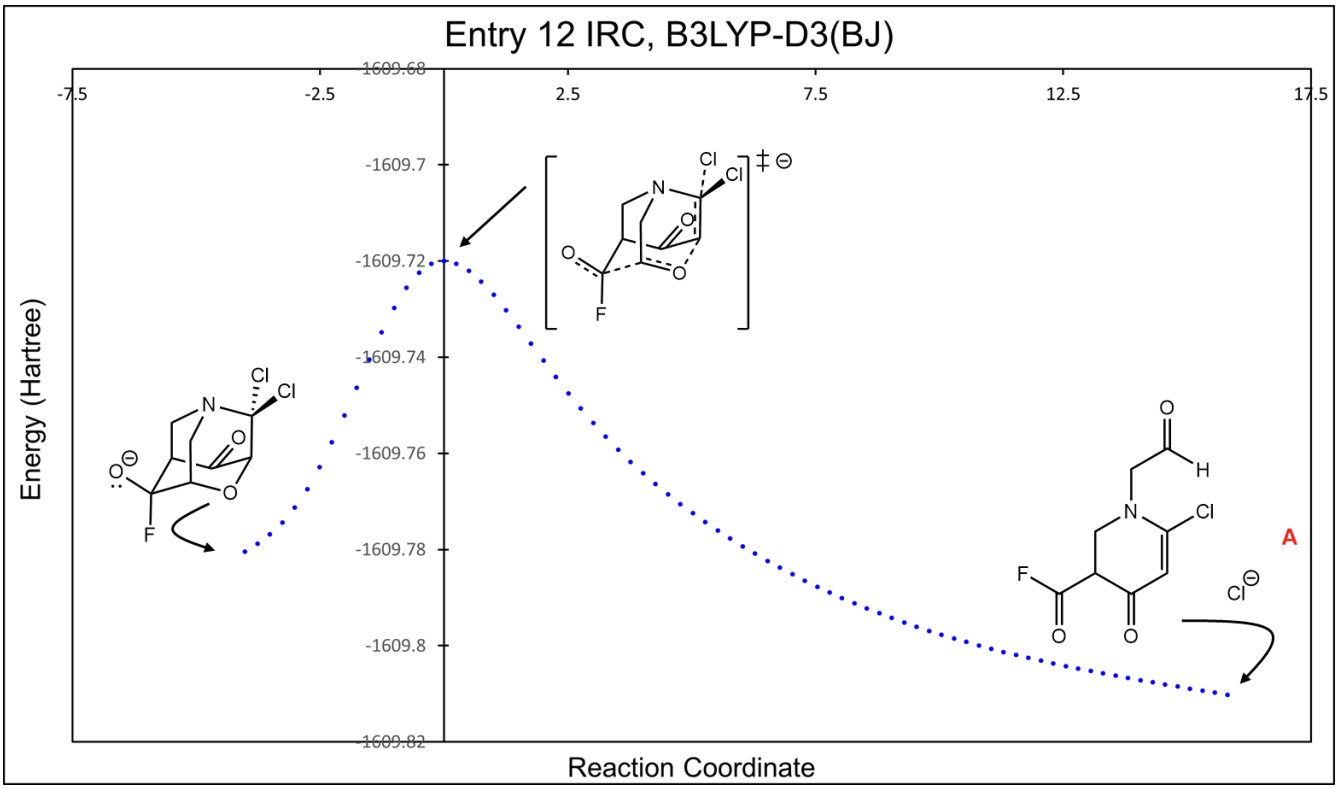

Entry 10 IRC, B3LYP-D3(BJ)
Energy (Hartree)
Reaction Coordinate
-1510.44
-1510.46
-1510.48
-1510.5
-1510.52
-1510.54
-7.5
-5.5
-3.5
-1.5
0.5
2.5
4.5
6.5
8.5
10.5
A

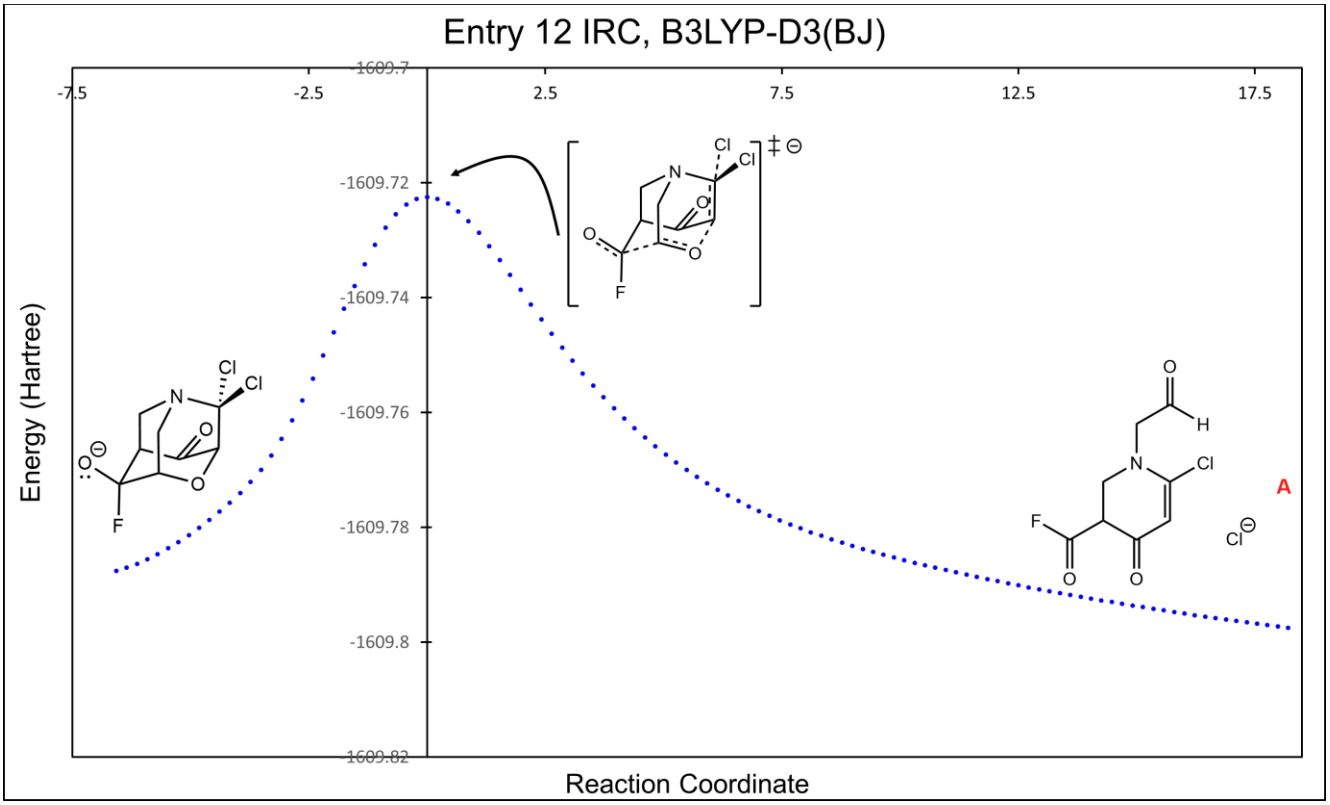

Entry 10 IRC, M06-2X
Energy (Hartree)
Reaction Coordinate
1510.05
-1510.07
-1510.09
-1510.11
-1510.13
-1510.15
-1510.17
-1510.19
-1510.21
-4
-2
0
2
4
6
8
10
12
14
16
A
Cl
Cl
N
O
H
‡ ⊖

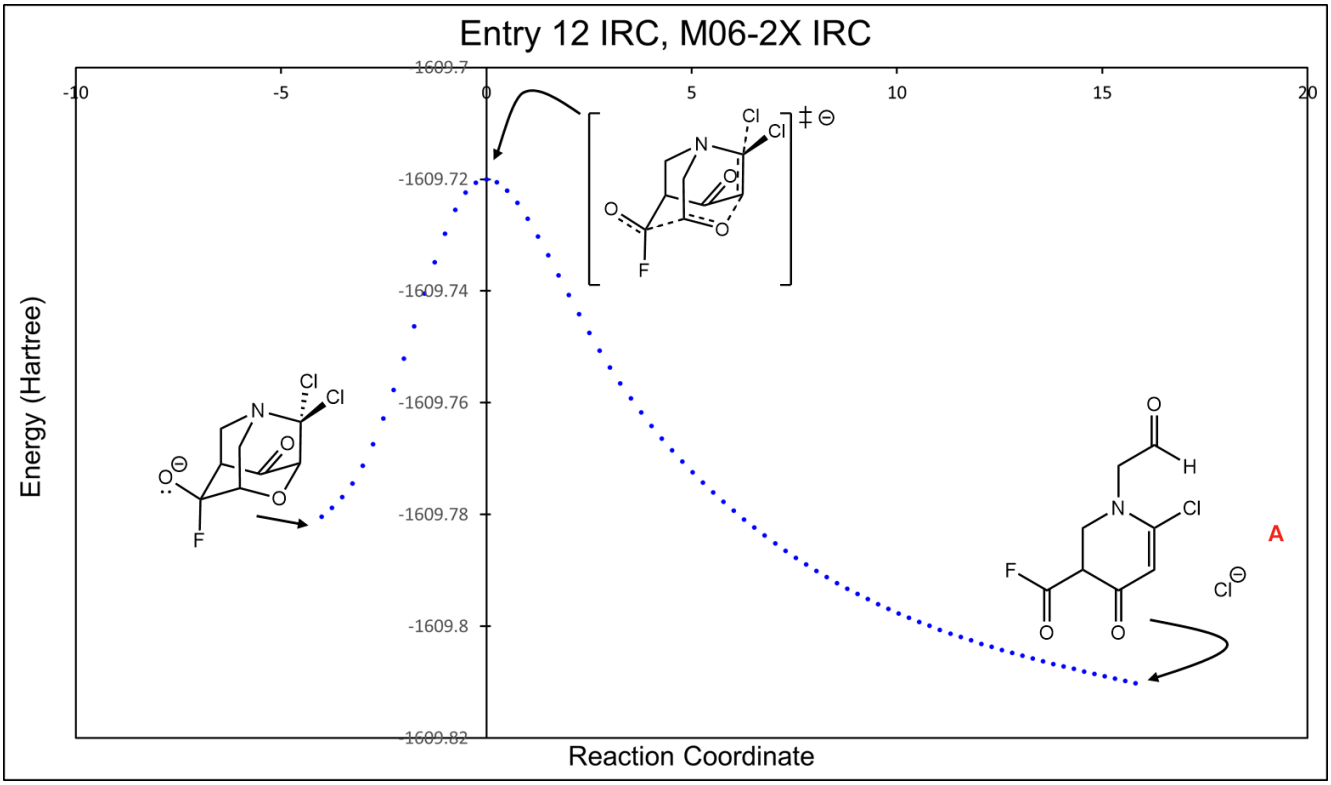

Entry 10 IRC, M06-2X
Energy (Hartree)
Reaction Coordinate
1510.1
-1510.12
-1510.14
-1510.16
-1510.18
-1510.2
-10
-5
0
5
10
15
20
B
Cl
Cl
N
O
H
‡ ⊖

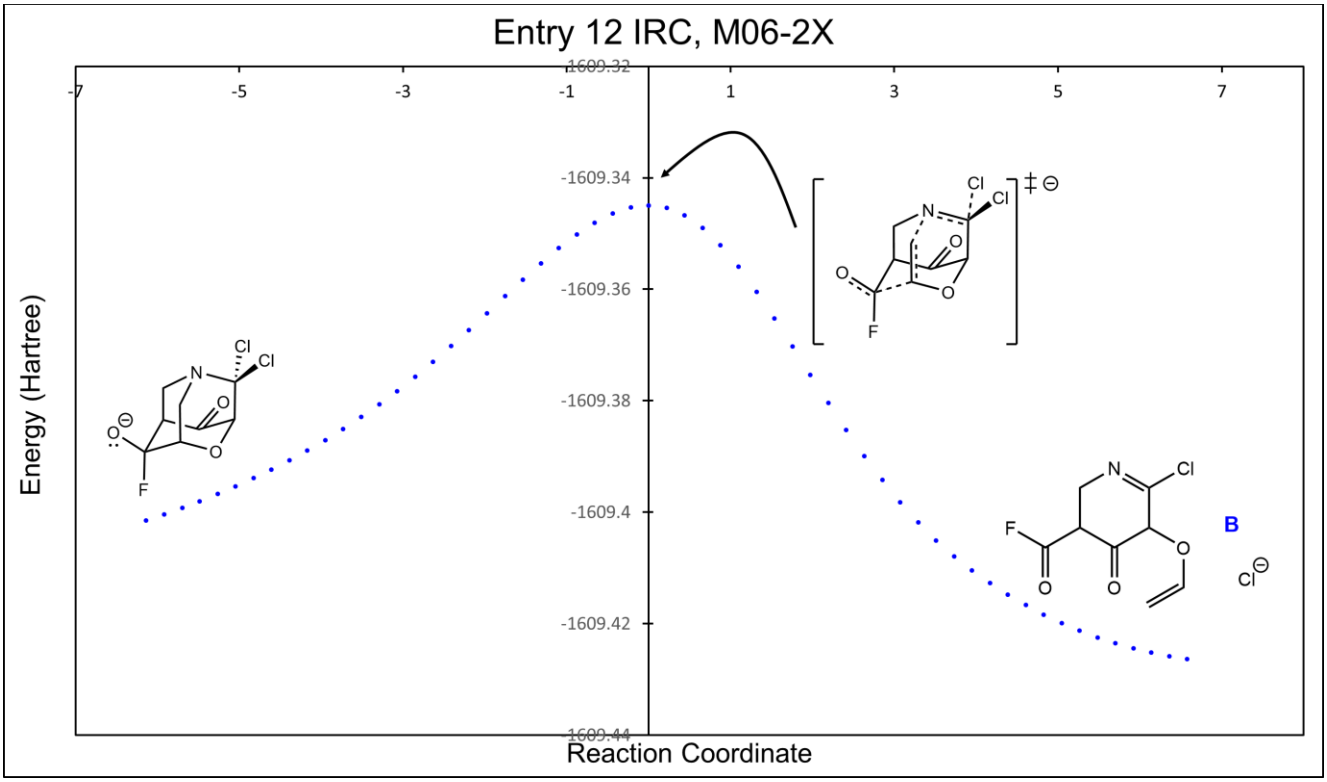

Entry 11 IRC, B3LYP-D3(BJ)
Energy (Hartree)
Reaction Coordinate
-1338.65
-1338.67
-1338.69
-1338.71
-1338.73
-1338.75
-1338.77
-1338.79
-1338.81
-1338.83
-7.5
-2.5
2.5
7.5
12.5
17.5
22.5
A

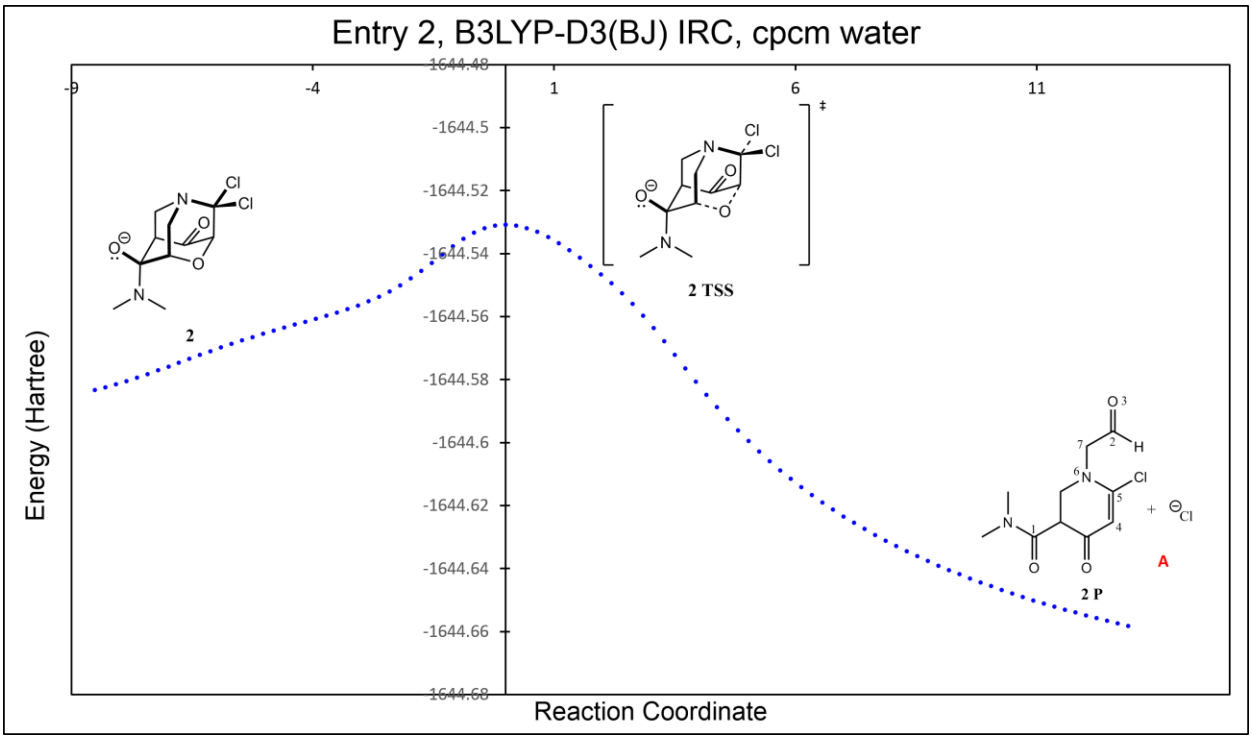

Entry 11 IRC, M06-2X
Energy (Hartree)
Reaction Coordinate
-1338.24
-1338.26
-1338.28
-1338.3
-1338.32
-1338.34
-1338.36
-1338.38
-1338.4
-6
-4
-2
0
2
4
6
8
10
12
14
16
A

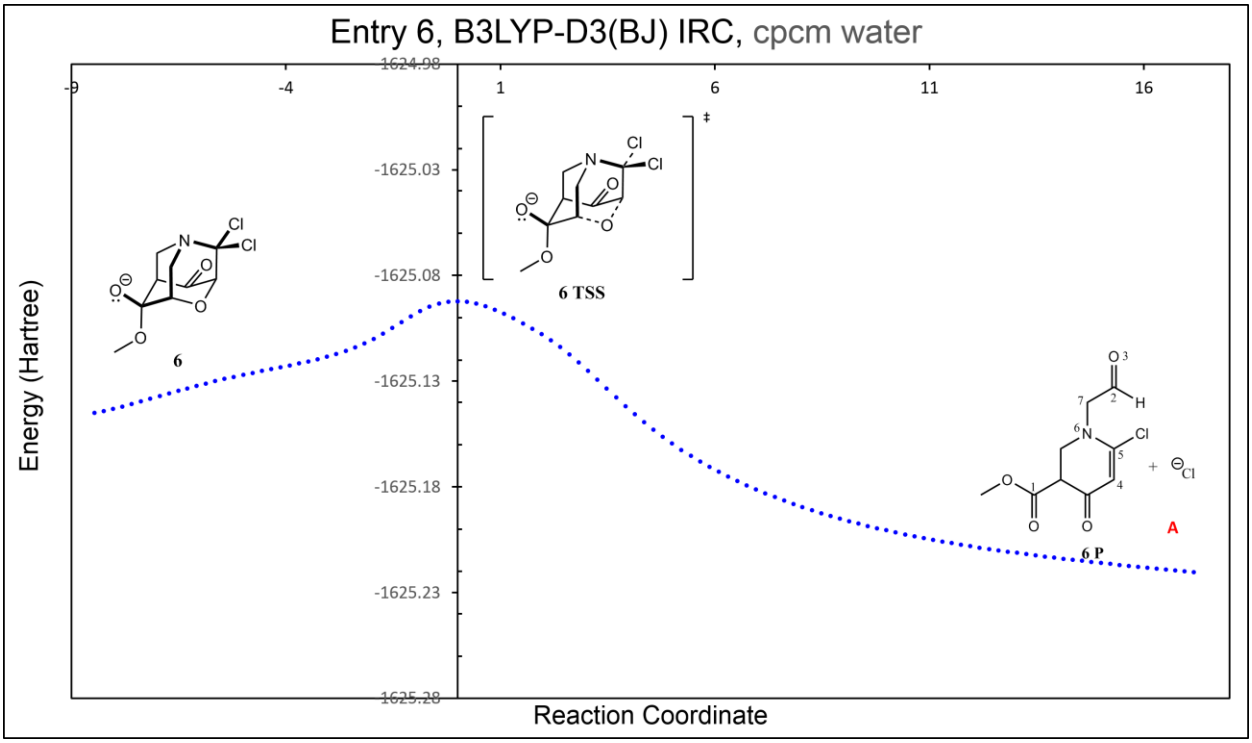

Entry 12 IRC, B3LYP-D3(BJ)
Energy (Hartree)
Reaction Coordinate
1609.68
-1609.7
-1609.72
-1609.74
-1609.76
-1609.78
-1609.8
-1609.82
-7.5
-2.5
2.5
7.5
12.5
17.5
A

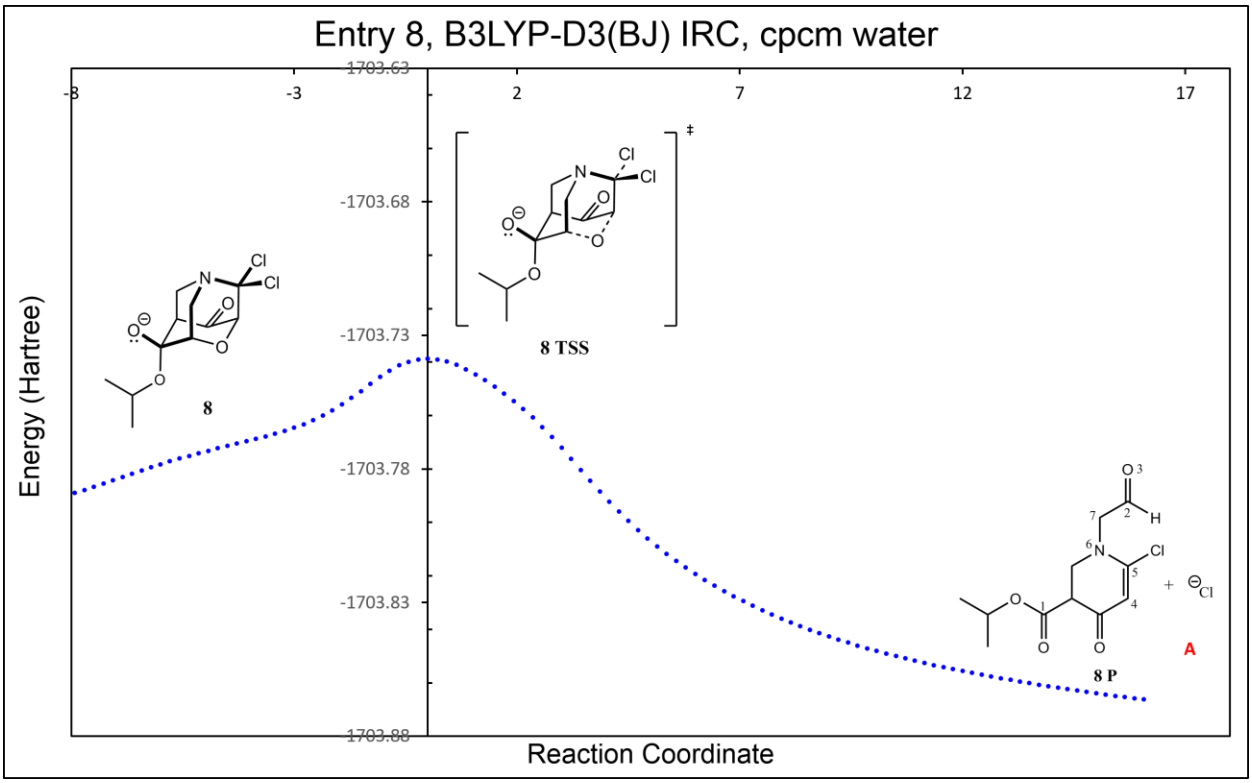

Entry 12 IRC, B3LYP-D3(BJ)
Energy (Hartree)
Reaction Coordinate
-1609.7
-1609.72
-1609.74
-1609.76
-1609.78
-1609.8
-1609.82
-7.5
-2.5
2.5
7.5
12.5
17.5
A


Entry 12 IRC, M06-2X IRC
Energy (Hartree)
Reaction Coordinate
1609.7
-1609.72
-1609.74
-1609.76
-1609.78
-1609.8
-1609.82
-10
-5
0
5
10
15
20
A


Entry 12 IRC, M06-2X
Energy (Hartree)
Reaction Coordinate
1609.32
-1609.34
-1609.36
-1609.38
-1609.4
-1609.42
-1609.44
-7
-5
-3
-1
1
3
5
7
B


Entry 2, B3LYP-D3(BJ) IRC, cpcm water
Energy (Hartree)
Reaction Coordinate
2
2 TSS
2 P
A


Entry 6, B3LYP-D3(BJ) IRC, cpcm water
Energy (Hartree)
Reaction Coordinate
6
6 TSS
6 P
A


Entry 8, B3LYP-D3(BJ) IRC, cpcm water
Energy (Hartree)
Reaction Coordinate
-1703.63
-1703.68
-1703.73
-1703.78
-1703.83
-1703.88
-8
-3
2
7
12
17
8
8 TSS
8 P
A