

SUPPORTING INFORMATION.

TROPOSPHERIC DEGRADATION OF 2-FLUOROPROPENE BY CHLORINE ATOMS: PRODUCT QUANTIFICATION AND THEORETICAL STUDIES

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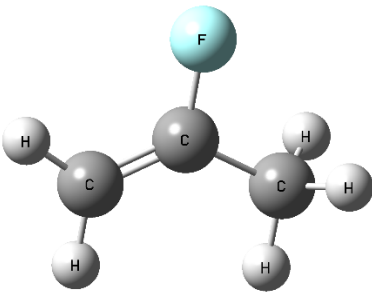
†Deceased 1 January 2018

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I. Energies, geometries, and vibrations of the species reported in this paper.

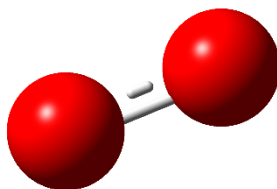
A. Reactants.

2-FP						
						
Method	Ee		E+ZPE	ΔH	ΔG	
BMK/6-31G(d,p)	-217.0254		-216.9525	-216.947	-216.9792	
BMK/6-311++G(2df.2dp)	-217.0982		-217.0256	-217.0201	-217.0522	
M06/6-31G(d,p)	-217.0224		-216.9503	-216.9448	-216.9769	
M06/6-311++G(2df.2dp)	-217.0947		-217.0229	-217.0175	-217.0496	
M06-2X/DG3/aug-cc-pVTZ	-217.1432		-217.0705	-217.065	-217.0972	
G4	-217.105619		-217.034553	-217.02902	-217.06127	
SVECV-f12	-217.1201		-217.0474	-217.0419	-217.0741	
Coordinates (xyz)				Vibrations (cm ⁻¹)		
C	0.925363	-1.043001	0.000000	212.2233	1055.0877	3137.5893
C	0.000000	0.107922	0.000000	397.5942	1288.7123	3160.2626
C	0.284665	1.394784	0.000000	475.9973	1376.5772	3260.3371
H	1.960293	-0.706449	0.000000	489.7479	1414.8473	49.008808
H	0.755378	-1.668198	0.879424	747.9489	1444.9335	74.375051
H	0.755378	-1.668198	-0.879424	870.1089	1459.5183	
F	-1.283044	-0.285669	0.000000	872.7437	1756.2147	
H	-0.499082	2.138840	0.000000	953.44	3026.5843	
H	1.315261	1.716797	0.000000	1014.9953	3093.0402	

Cl					
Method	Ee		E+ZPE	ΔH	ΔG
BMK/6-31G(d,p)	-459.990592		-459.990592	-459.988231	-460.006269
BMK/6-311++G(2df.2dp)	-460.023364		-460.023364	-460.021003	-460.039041
M06/6-31G(d,p)	-460.100069		-460.100069	-460.097708	-460.115746
M06/6-311++G(2df.2dp)	-460.127832		-460.127832	-460.125472	-460.143509
M06-2X/DG3/aug-cc-pVTZ	-460.141208		-460.141208	-460.138847	-460.156885
G4	-460.015052		-460.015052	-460.012692	-460.030729

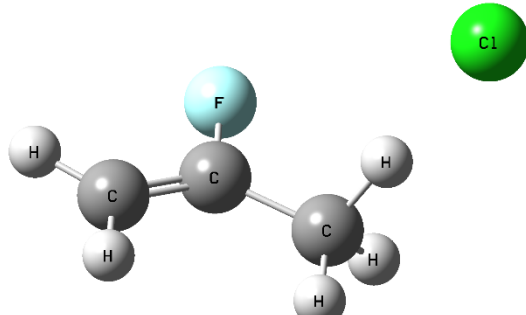
SVECV-f12	-460.043466	-460.043466	-460.041106	-460.059143
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O₂

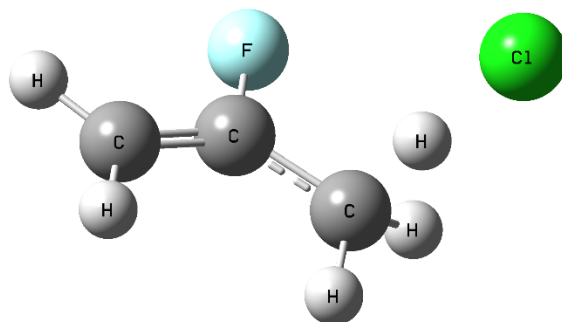


Method	Ee	E+ZPE	ΔH	ΔG
BMK/6-31G(d,p)	-150.252676	-150.248648	-150.245341	-150.268619
BMK/6-311++G(2df.2dp)	-150.304078	-150.300076	-150.296769	-150.32003
M06/6-31G(d,p)	-150.248288	-150.24436	-150.241054	-150.264326
M06/6-311++G(2df.2dp)	-150.299304	-150.295421	-150.292115	-150.31537
M06-2X/DG3/aug-cc-pVTZ	-150.324795	-150.320798	-150.317492	-150.340738
G4	-150.282393	-150.278657	-150.27535	-150.298623
SVECV-f12	-150.303471	-150.303471	-150.301111	-150.319148
Coordinates (xyz)			Vibrations (cm ⁻¹)	
O	0.000000	0.000000	0.595652	1714.0895
O	0.000000	0.000000	-0.595652	

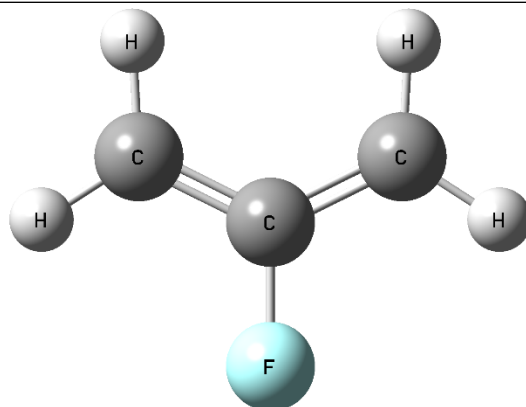
B. Pathway I.

PCR-E1						
						
Method	Ee			E+ZPE	ΔH	ΔG
BMK/6-31G(d,p)	-677.029483			-676.962345	-676.954026	-676.996323
BMK/6-311++G(2df.2dp)	-677.140196			-677.073417	-677.064937	-677.108098
M06/6-31G(d,p)	-677.129371			-677.058357	-677.05058	-677.091597
M06/6-311++G(2df.2dp)	-677.228917			-677.158337	-677.150579	-677.192158
M06-2X/DG3/aug-cc-pVTZ	-677.286922			-677.214417	-677.208215	-677.245149
G4	-677.118674			-677.050507	-677.042886	-677.083191
SVECV-f12	-677.16463			-677.092125	-677.085923	-677.122857
Coordinates (xyz)				Vibrations (cm ⁻¹)		
C	-0.432960	1.008813	0.688149	21.2388	960.1392	3081.3522
C	-1.326910	0.024774	0.075665	47.7569	992.7272	3161.9648
C	-2.306423	0.254159	-0.804754	168.2112	1017.6305	3165.1764
H	-0.711423	2.035729	0.444628	258.7179	1287.7709	3266.9521
H	-0.354996	0.868488	1.770779	404.8833	1329.8893	
H	0.614019	0.838814	0.305041	476.0385	1355.5728	
F	-1.075020	-1.223676	0.467960	493.9472	1383.7401	
H	-2.912194	-0.560777	-1.185009	716.1847	1442.0111	
H	-2.508068	1.264142	-1.141398	883.0243	1659.415	
Cl	2.349741	-0.068223	-0.244708	888.0066	2518.6603	

TSE1

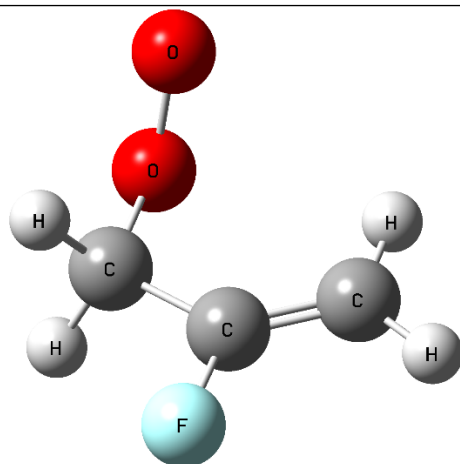


Method	Ee	E+ZPE	ΔH	ΔG		
BMK/6-31G(d,p)	-677.015807	-676.94263	-676.935567	-676.975165		
BMK/6-311++G(2df.2dp)	-677.121545	-677.048685	-677.041654	-677.081113		
M06/6-31G(d,p)	-677.127715	-677.062157	-677.055035	-677.094018		
M06/6-311++G(2df.2dp)	-677.228042	-677.162311	-677.155255	-677.194257		
M06-2X/DG3/aug-cc-pVTZ	-677.284297	-677.214124	-677.206907	-677.247439		
G4	-677.119078	-677.050567	-677.042945	-677.083237		
SVECV-f12	-677.168772	-677.098599	-677.091382	-677.131914		
Coordinates (xyz)				Vibrations (cm ⁻¹)		
C	-0.242297	0.151803	1.076289	<i>i</i> 633.1684	902.4778	3092.2116
C	-1.293184	0.023082	0.107773	54.38	962.1886	3157.2222
C	-1.975568	1.020405	-0.467466	70.9674	965.2004	3186.8297
H	-0.188457	1.126392	1.551674	373.5677	1005.624	3265.626
H	-0.154082	-0.682859	1.767922	416.8261	1192.4098	
H	0.822592	0.077898	0.468009	471.776	1247.2428	
F	-1.557862	-1.228230	-0.253421	508.8619	1370.879	
H	-2.745476	0.817267	-1.197982	601.0094	1381.7013	
H	-1.758031	2.042752	-0.197036	684.3191	1456.0498	
Cl	2.300618	0.029464	-0.259493	870.9699	1614.3766	

E1

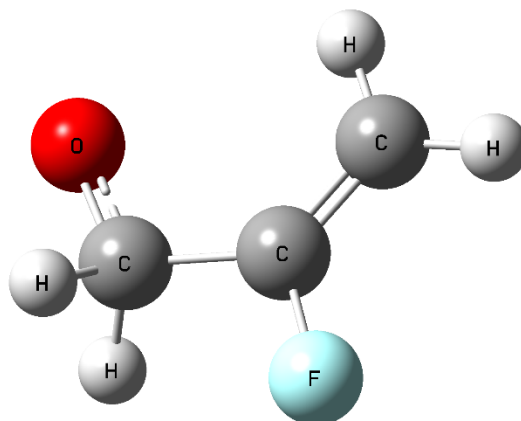
Method	Ee	E+ZPE	ΔH	ΔG		
BMK/6-31G(d,p)	-216.373248	-216.31458	-216.309385	-216.341447		
BMK/6-311++G(2df.2dp)	-216.446624	-216.388016	-216.38286	-216.414854		
M06/6-31G(d,p)	-216.372037	-216.313916	-216.308678	-216.340792		
M06/6-311++G(2df.2dp)	-216.444445	-216.38656	-216.381349	-216.41341		
M06-2X/DG3/aug-cc-pVTZ	-216.490534	-216.432122	-216.426933	-216.458972		
G4	-216.451032	-216.393681	-216.388405	-216.420581		
SVECV-f12	-216.46573	-216.407318	-216.402129	-216.434168		
Coordinates (xyz)				Vibrations (cm ⁻¹)		
C	1.226949	0.652768	0.000000	413.1732	935.3222	3268.434
C	0.000000	0.043256	-0.000002	482.7068	1005.9078	3270.2172
C	-1.226949	0.652768	0.000000	499.4644	1292.8992	
H	2.134807	0.067442	0.000001	562.1007	1350.5345	
H	1.287643	1.730872	0.000002	627.9122	1453.9961	
F	0.000000	-1.298820	0.000001	735.4493	1491.2517	
H	-2.134807	0.067442	0.000001	774.0538	3155.6415	
H	-1.287643	1.730871	0.000003	929.6553	3160.0545	

E1O2



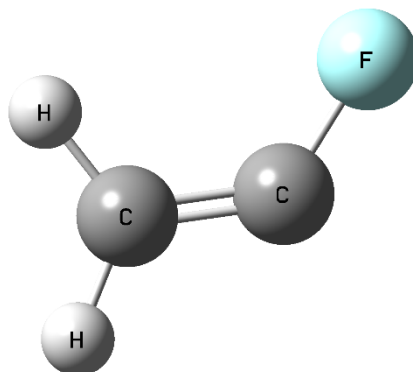
Method	Ee	E+ZPE	ΔH	ΔG		
BMK/6-31G(d,p)	-366.662667	-366.592771	-366.585661	-366.623856		
BMK/6-311++G(2df.2dp)	-366.78486	-366.708993	-366.708049	-366.74611		
M06/6-31G(d,p)	-366.654471	-366.585516	-366.578408	-366.616458		
M06/6-311++G(2df.2dp)	-366.775862	-366.707183	-366.700098	-366.738086		
M06-2X/DG3/aug-cc-pVTZ	-366.850257	-366.780359	-366.77325	-366.811592		
G4	-366.768168	-366.700415	-366.693129	-366.731954		
SVECV-f12	-366.802486	-366.732588	-366.725479	-366.763821		
Coordinates (xyz)				Vibrations (cm ⁻¹)		
C	0.875846	1.393163	-0.150169	82.3312	946.7268	3032.7844
C	0.877650	0.085606	-0.028785	117.7006	976.3219	3091.9511
H	1.792695	1.953066	-0.035550	262.2168	1050.9583	3166.4422
H	-0.043044	1.918279	-0.359576	396.6908	1208.6836	3270.5464
F	2.000298	-0.591946	0.234197	460.6003	1247.1123	
C	-0.257413	-0.868102	-0.148150	472.5447	1278.628	
H	-0.067042	-1.584296	-0.951593	585.9016	1379.7013	
H	-0.410646	-1.412845	0.786910	751.6509	1389.846	
O	-1.472294	-0.199365	-0.499068	889.1344	1429.1191	
O	-2.059099	0.29803	0.5509	894.9373	1764.0664	

E1O



Method	Ee	E+ZPE	ΔH	ΔG		
BMK/6-31G(d,p)	-291.535039	-291.471533	-291.465339	-291.500507		
BMK/6-311++G(2df.2dp)	-291.632437	-291.569299	-291.563096	-291.59828		
M06/6-31G(d,p)	-291.529507	-291.467562	-291.461089	-291.496752		
M06/6-311++G(2df.2dp)	-291.62656	-291.564349	-291.558126	-291.593329		
M06-2X/DG3/aug-cc-pVTZ	-291.686107	-291.623166	-291.616801	-291.652269		
G4	-291.622304	-291.560823	-291.554507	-291.589918		
SVECV-f12	-291.64703	-291.584089	-291.577724	-291.613192		
Coordinates (xyz)			Vibrations (cm ⁻¹)			
C	-0.760604	1.345937	0.000000	124.5179	942.4237	2879.1718
C	-0.489752	0.060874	0.000000	256.6793	1107.345	3162.3834
H	-1.780342	1.702426	0.000000	409.9778	1127.2291	3266.8251
H	0.056891	2.051303	-0.000001	436.0779	1231.7149	
F	-1.458001	-0.864943	0.000001	538.8267	1301.779	
C	0.853743	-0.592523	0.000000	582.6683	1369.402	
H	0.931915	-1.296492	0.855443	759.228	1402.7502	
H	0.931914	-1.296494	-0.855441	887.6122	1759.0641	
O	1.920164	0.217251	-0.000001	895.0447	2866.7744	

FCCH₂

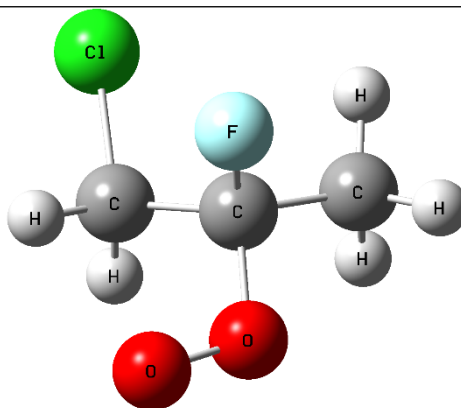


Method	Ee	E+ZPE	ΔH	ΔG	
BMK/6-31G(d,p)	-177.043089	-177.011957	-177.007633	-177.036701	
BMK/6-311++G(2df.2dp)	-177.105282	-177.074315	-177.07	-177.099036	
M06/6-31G(d,p)	-177.04264	-177.011823	-177.007474	-177.036578	
M06/6-311++G(2df.2dp)	-177.104511	-177.073879	-177.069538	-177.098606	
M06-2X/DG3/aug-cc-pVTZ	-177.140062	-177.108889	-177.104583	-177.133611	
G4	-177.099745	-177.069401	-177.065044	-177.094147	
SVECV-f12	-177.115925	-177.084752	-177.080446	-177.109474	
Coordinates (xyz)				Vibrations (cm ⁻¹)	
C	1.190173	0.117388	0.000000	438.9627	1365.9202
C	0.002882	-0.424264	0.000000	629.8457	1729.8577
H	1.308563	1.197594	0.000001	828.9906	3106.7193
H	2.070237	-0.507390	0.000000	940.7917	3236.4772
F	-1.170793	0.127895	0.000000	1168.4226	

C. Pathway II.

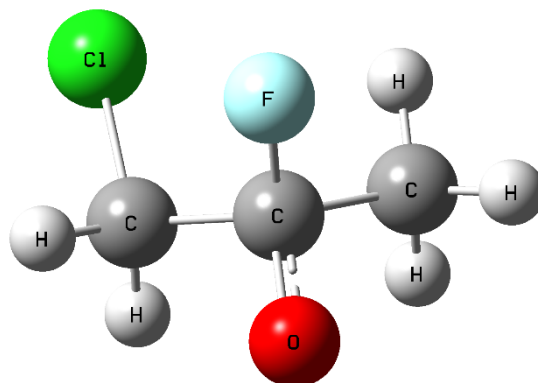
A1						
Method	Ee			E+ZPE	ΔH	ΔG
BMK/6-31G(d,p)	-677.0548953			-676.980331	-676.973217	-677.011488
BMK/6-311++G(2df,2dp)	-677.1594274			-677.085351	-677.078226	-677.116513
M06/6-31G(d,p)	-677.1619948			-677.088538	-677.081356	-677.119709
M06/6-311++G(2df,2dp)	-677.2616455			-677.1886	-677.181433	-677.219732
M06-2X/DG3/aug-cc-pVTZ	-677.319223			-677.245051	-677.237923	-677.276168
G4	-677.151909			-677.079786	-677.072432	-677.111205
SVECV-f12	-677.1964616			-677.12229	-677.115162	-677.153407
Coordinates (xyz)				Vibrations (cm ⁻¹)		
C	1.568272	1.147723	-0.108242	89.4908	1006.7392	3069.803
C	0.941821	-0.119127	0.288692	137.7101	1110.5204	3087.1751
C	-0.352738	-0.247930	0.911623	163.3881	1204.7672	3124.4628
H	1.282151	1.945019	0.577311	364.3307	1323.8181	3164.086
H	2.656435	1.062959	-0.124236	413.1823	1340.0628	
H	1.244628	1.439992	-1.116131	494.4081	1403.491	
F	1.340732	-1.183020	-0.412435	553.9706	1432.5529	
H	-0.556595	-1.261279	1.247263	813.9491	1439.4093	
H	-0.493586	0.468489	1.716372	886.9692	1467.8873	
Cl	-1.714338	0.135765	-0.302418	986.2857	2984.911	

A1O2



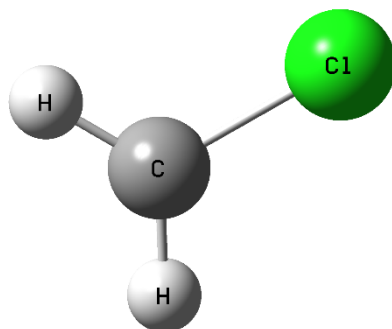
Method	Ee	E+ZPE	ΔH	ΔG		
BMK/6-31G(d,p)	-827.3678562	-827.283761	-827.275173	-827.317035		
BMK/6-311++G(2df.2dp)	-827.519983	-827.436515	-827.427902	-827.469832		
M06/6-31G(d,p)	-827.4698813	-827.386915	-827.37836	-827.420014		
M06/6-311++G(2df.2dp)	-827.6169345	-827.534454	-827.52588	-827.5676		
M06-2X/DG3/aug-cc-pVTZ	-827.701997	-827.61821	-827.609701	-827.651432		
G4	-827.496749	-827.415536	-827.406779	-827.448988		
SVECV-f12	-827.5597829	-827.475996	-827.467487	-827.509218		
Coordinates (xyz)				Vibrations (cm ⁻¹)		
C	0.244433	1.741995	-0.455130	90.8132	869.7763	1457.8132
C	0.459156	0.347823	0.039215	130.3886	902.1385	3048.8996
H	-0.706473	2.117508	-0.082538	191.5256	982.7767	3076.5906
H	1.050632	2.378752	-0.092888	209.2852	1101.6302	3137.8353
H	0.234431	1.759656	-1.544889	269.9688	1126.0189	3149.9786
F	0.503183	0.324562	1.386731	337.3588	1244.9494	3151.0633
O	1.785574	-0.015248	-0.441928	389.5958	1251.8922	
O	2.146150	-1.204000	-0.058665	409.5301	1302.8415	
C	-0.506541	-0.701854	-0.456765	506.4276	1323.8347	
Cl	-2.179021	-0.313213	0.002505	640.3173	1413.2157	
H	-0.454186	-0.763307	-1.542841	768.2531	1435.9425	
H	-0.245776	-1.662853	-0.019167	828.9503	1455.071	

A10



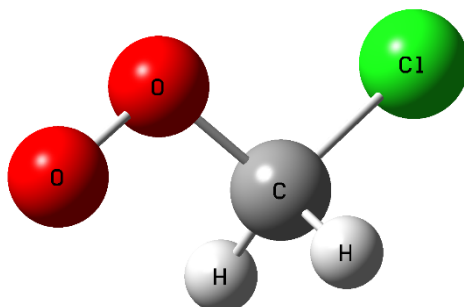
Method	Ee	E+ZPE	ΔH	ΔG		
BMK/6-31G(d,p)	-752.2456923	-752.16646	-752.158929	-752.198008		
BMK/6-311++G(2df.2dp)	-752.3735498	-752.295085	-752.287476	-752.326739		
M06/6-31G(d,p)	-752.348761	-752.270865	-752.263312	-752.302326		
M06/6-311++G(2df.2dp)	-752.4721357	-752.394918	-752.387317	-752.426434		
M06-2X/DG3/aug-cc-pVTZ	-752.541888	-752.463191	-752.455627	-752.494747		
G4	-752.356466	-752.280106	-752.272321	-752.3119		
SVECV-f12	-752.4097354	-752.331038	-752.323474	-752.362594		
Coordinates (xyz)				Vibrations (cm ⁻¹)		
C	0.995962	1.390876	-0.329702	102.891	914.2029	3045.5781
C	0.845812	-0.099812	-0.005267	205.7634	965.7773	3080.7069
H	0.187744	1.919664	0.174456	222.0046	1018.967	3147.7631
H	1.955900	1.736935	0.047373	278.5121	1088.6175	3156.0563
H	0.940526	1.546661	-1.405017	322.4081	1166.483	3158.8864
F	0.793656	-0.225774	1.366423	428.2487	1227.1951	
O	1.848156	-0.755384	-0.533362	466.4936	1263.7688	
C	-0.455669	-0.707839	-0.580253	577.2868	1357.6879	
Cl	-1.905395	0.102497	0.035112	737.1998	1421.6268	
H	-0.435274	-0.614961	-1.66311	796.738	1434.4902	
H	-0.501963	-1.755055	-0.290189	859.0831	1450.4326	

CH₂Cl



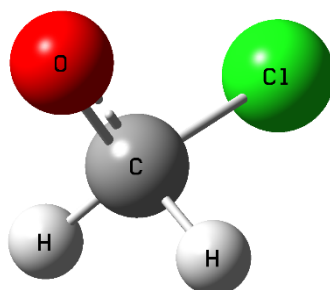
Method	Ee	E+ZPE	ΔH	ΔG	
BMK/6-31G(d,p)	-499.2635229	-499.240968	-499.23709	-499.264858	
BMK/6-311++G(2df.2dp)	-499.3115905	-499.288822	-499.284398	-499.313108	
M06/6-31G(d,p)	-499.3705547	-499.348312	-499.344426	-499.372174	
M06/6-311++G(2df.2dp)	-499.4143551	-499.391836	-499.387392	-499.416126	
M06-2X/DG3/aug-cc-pVTZ	-499.43853	-499.415799	-499.411278	-499.440256	
G4	-499.310928	-499.289052	-499.285154	-499.312918	
SVECV-f12	-499.3387019	-499.315971	-499.31145	-499.340428	
Coordinates (xyz)			Vibrations (cm ⁻¹)		
C	0.000000	0.000000	-1.110923	222.5605	3134.1263
Cl	0.000000	0.000000	0.582254	855.0293	3289.8838
H	0.000000	0.951820	-1.616391	977.2457	
H	0.000000	-0.951820	-1.616391	1375.1168	

CH₂ClO₂



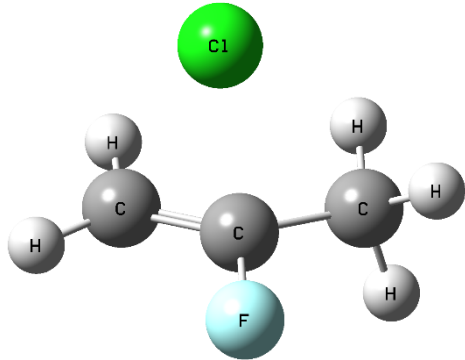
Method	Ee	E+ZPE	ΔH	ΔG	
BMK/6-31G(d,p)	-649.571217	-649.53618	-649.530704	-649.565117	
BMK/6-311++G(2df.2dp)	-649.66885	-649.633985	-649.628529	-649.662732	
M06/6-31G(d,p)	-649.672316	-649.63805	-649.632575	-649.66677	
M06/6-311++G(2df.2dp)	-649.72012	-649.72465	-649.719175	-649.753347	
M06-2X/DG3/aug-cc-pVTZ	-649.816885	-649.781617	-649.776371	-649.81003	
G4	-649.646051	-649.612114	-649.606747	-649.64072	
SVECV-f12	-649.6944036	-649.659136	-649.65389	-649.687549	
Coordinates (xyz)				Vibrations (cm ⁻¹)	
Cl	-1.549829	-0.119807	0.000055	70.5985	1184.9226
C	0.053522	0.590363	0.000036	286.2522	1248.1873
H	0.199063	1.182931	-0.900873	449.624	1316.4818
H	0.199082	1.182911	0.900955	828.8656	1437.2063
O	1.002079	-0.490400	0.000011	943.8496	3060.741
O	2.201398	0.006487	-0.000165	983.578	3145.2623

CH₂ClO

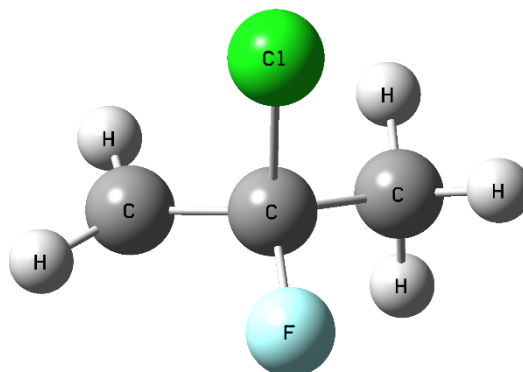


Method	Ee	E+ZPE	ΔH	ΔG	
BMK/6-31G(d,p)	-574.452432	-574.423384	-574.419019	-574.449633	
BMK/6-311++G(2df.2dp)	-574.524811	-574.496179	-574.49179	-574.522423	
M06/6-31G(d,p)	-574.556838	-574.528685	-574.524262	-574.554948	
M06/6-311++G(2df.2dp)	-574.625378	-574.597641	-574.593205	-574.62389	
M06-2X/DG3/aug-cc-pVTZ	-574.65812	-574.629371	-574.624979	-574.655611	
G4	-574.505902	-574.478264	-574.478264	-574.473792	
SVECV-f12	-574.5446651	-574.515916	-574.511524	-574.542156	
Coordinates (xyz)				Vibrations (cm ⁻¹)	
Cl	0.548480	-0.929223	0.000000	398.4346	1205.5535
C	0.000000	0.820894	0.000000	622.9231	1277.9176
H	0.478073	1.283334	0.886673	683.9125	2880.7437
H	0.478073	1.283334	-0.886673	1023.4573	2916.3703
O	-1.285039	1.038095	0.000000	1165.7086	

D. Pathway III.

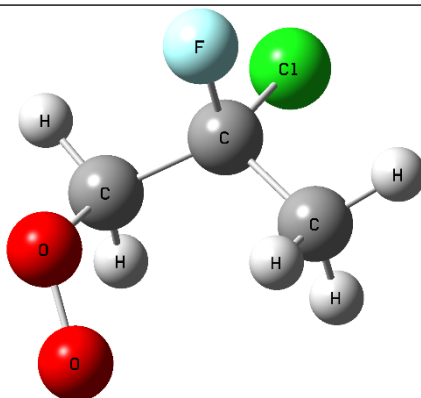
TSA2						
						
Method	Ee			E+ZPE	ΔH	ΔG
BMK/6-31G(d,p)	-677.036039			-676.963138	-676.956446	-676.993222
BMK/6-311++G(2df,2dp)	-677.140622			-677.067981	-677.061336	-677.098002
M06/6-31G(d,p)	-677.146842			-677.074914	-677.068206	-677.104952
M06/6-311++G(2df,2dp)	-677.245649			-677.173991	-677.167324	-677.203976
M06-2X/DG3/aug-cc-pVTZ	-677.302039			-677.229336	-677.222683	-677.259326
G4	-677.135838			-677.065014	-677.05824	-677.095088
SVECV-f12	-677.178835			-677.106132	-677.099479	-677.136122
Coordinates (xyz)				Vibrations (cm ⁻¹)		
C	-1.174754	1.234325	0.379118	<i>i</i> 255.3279	986.4132	3131.8753
C	-0.713010	-0.150170	0.059800	185.411	1033.002	3171.0928
C	-0.411086	-1.141597	0.965488	223.1866	1056.0032	3181.1872
H	-0.790670	1.548362	1.346906	266.585	1349.3644	3298.0123
H	-0.834187	1.923499	-0.391717	374.2842	1398.4697	
H	-2.268870	1.236779	0.398910	399.3998	1441.3926	
F	-1.000296	-0.522670	-1.172469	485.3556	1482.8926	
H	-0.256810	-2.155061	0.623817	626.799	1496.3957	
H	-0.240694	-0.884673	1.999494	834.1644	1557.0791	
Cl	1.599235	0.19881	-0.108919	860.7229	3046.651	

A2



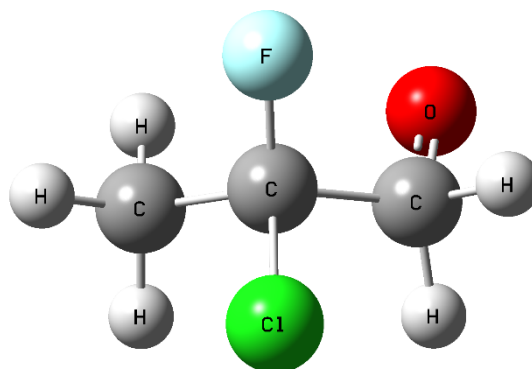
Method	Ee	E+ZPE	ΔH	ΔG		
BMK/6-31G(d,p)	-677.048253	-676.975197	-676.968329	-677.004979		
BMK/6-311++G(2df.2dp)	-677.153222	-677.080659	-677.073789	-677.110425		
M06/6-31G(d,p)	-677.156293	-677.084678	-677.077534	-677.114758		
M06/6-311++G(2df.2dp)	-677.256152	-677.184944	-677.17777	-677.215078		
M06-2X/DG3/aug-cc-pVTZ	-677.314508	-677.242295	-677.235249	-677.272232		
G4	-677.14964	-677.079176	-677.071962	-677.109268		
SVECV-f12	-677.193156	-677.120943	-677.113897	-677.15088		
Coordinates (xyz)				Vibrations (cm ⁻¹)		
C	0.990834	1.253704	-0.430433	256.9448	926.772	3145.6993
C	0.421179	-0.065980	0.012192	267.2406	994.0457	3157.9799
C	0.769716	-1.227609	-0.801357	277.2973	1064.2954	3166.6266
H	0.703651	1.470074	-1.462489	312.1792	1272.3782	3281.1294
H	0.625703	2.052774	0.219462	375.7652	1296.2597	
H	2.083284	1.206437	-0.363308	396.0372	1401.9543	
F	0.732724	-0.284322	1.313825	466.202	1422.0847	
H	0.733880	-2.211770	-0.347050	546.1041	1455.6921	
H	0.800361	-1.131211	-1.881238	600.5087	1462.684	
Cl	-1.448928	0.083054	-0.039542	861.1525	3049.6971	

A2O₂



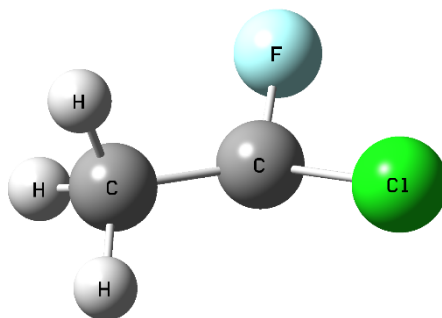
Method	Ee	E+ZPE	ΔH	ΔG		
BMK/6-31G(d,p)	-827.360959	-827.276357	-827.267909	-827.309429		
BMK/6-311++G(2df.2dp)	-827.51474	-827.430617	-827.42218	-827.463602		
M06/6-31G(d,p)	-827.463065	-827.379944	-827.371426	-827.413022		
M06/6-311++G(2df.2dp)	-827.611656	-827.529044	-827.520495	-827.562198		
M06-2X/DG3/aug-cc-pVTZ	-827.694275	-827.61021	-827.601753	-827.643306		
G4	-827.48885	-827.40749	-827.398731	-827.44103		
SVECV-f12	-827.551842	-827.467777	-827.45932	-827.500873		
Coordinates (xyz)				Vibrations (cm ⁻¹)		
C	-0.085773	1.506119	-0.514919	78.8813	923.2559	1456.5122
C	-0.384349	0.209178	0.170021	118.09	968.4135	3042.8566
H	-0.003739	1.360787	-1.591010	213.3258	1006.9859	3064.7138
H	-0.885587	2.214989	-0.305230	270.6783	1093.3472	3131.2189
H	0.855937	1.907367	-0.137853	295.0618	1179.0638	3141.5298
F	-0.485650	0.416986	1.504861	311.9353	1240.0131	3144.6467
Cl	-1.970437	-0.440352	-0.404004	384.8594	1249.5531	
O	1.918433	-0.516172	0.375283	406.5223	1307.5706	
O	2.592217	0.060842	-0.576543	486.1572	1351.6838	
C	0.60793	-0.909171	-0.064503	548.5051	1404.5078	
H	0.657156	-1.174071	-1.120163	721.1506	1417.6557	
H	0.332464	-1.770081	0.545061	856.0974	1447.7537	

A2O



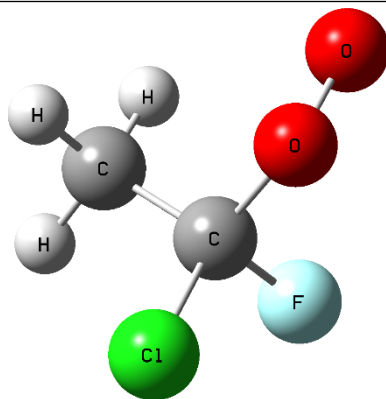
Method	Ee	E+ZPE	ΔH	ΔG		
BMK/6-31G(d,p)	-752.22676	-752.146053	-752.138619	-752.17727		
BMK/6-311++G(2df.2dp)	-752.356191	-752.27586	-752.268404	-752.307084		
M06/6-31G(d,p)	-752.337939	-752.260908	-752.253302	-752.29222		
M06/6-311++G(2df.2dp)	-752.462294	-752.385884	-752.378257	-752.417205		
M06-2X/DG3/aug-cc-pVTZ	-752.525037	-752.444993	-752.437541	-752.476263		
G4	-752.344464	-752.269256	-752.261416	-752.300909		
SVECV-f12	-752.392015	-752.311971	-752.304519	-752.343241		
Coordinates (xyz)				Vibrations (cm ⁻¹)		
C	0.151182	1.470418	-0.735026	131.9151	981.0867	2920.471
C	-0.008201	0.225477	0.087130	217.9983	1064.4421	2962.6092
H	0.003433	1.256802	-1.797218	260.6473	1098.743	3053.9309
H	-0.572300	2.223964	-0.414947	296.1121	1118.2142	3152.8235
H	1.166145	1.851101	-0.580427	344.28	1259.856	3164.7862
F	0.123839	0.534431	1.401794	370.3609	1286.0653	
Cl	-1.669298	-0.480895	-0.149461	414.6171	1304.9513	
O	2.279514	-0.481352	-0.143407	479.7996	1374.652	
C	0.991740	-0.877198	-0.237586	638.7338	1403.8117	
H	0.8057	-1.282852	-1.253916	731.7871	1454.5176	
H	0.816096	-1.745043	0.431342	862.5736	1463.0875	

H₃C-CFCl



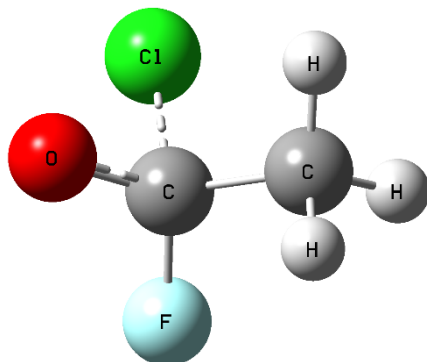
Method	Ee	E+ZPE	ΔH	ΔG		
BMK/6-31G(d,p)	-637.763518	-637.717263	-637.711693	-637.745715		
BMK/6-311++G(2df.2dp)	-637.858792	-637.812911	-637.807326	-637.841367		
M06/6-31G(d,p)	-637.871365	-637.825884	-637.820245	-637.854372		
M06/6-311++G(2df.2dp)	-637.962206	-637.917042	-637.911388	-637.945544		
M06-2X/DG3/aug-cc-pVTZ	-638.011519	-637.960983	-637.955379	-637.98944		
G4	-637.843622	-637.798934	-637.793239	-637.827489		
SVECV-f12	-637.889115	-637.838579	-637.832975	-637.867036		
Coordinates (xyz)				Vibrations (cm ⁻¹)		
C	-1.336851	-0.978619	0.044140	184.9251	1149.9123	3136.8259
H	-2.319327	-0.726660	-0.357142	316.596	1268.5264	
H	-1.003686	-1.918917	-0.390938	378.2092	1390.6079	
H	-1.435294	-1.116228	1.128791	407.5455	1435.5258	
C	-0.381506	0.096645	-0.273278	661.3182	1446.1235	
F	-0.773409	1.319531	0.062302	956.7893	2984.6496	
Cl	1.295831	-0.166008	0.025494	1023.5547	3083.2054	

H₃C-CFCIO₂



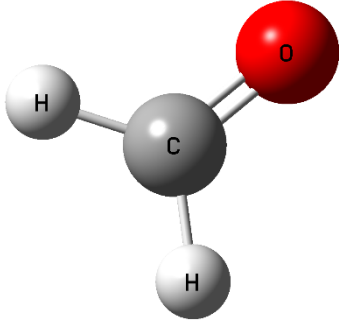
Method	Ee	E+ZPE	ΔH	ΔG		
BMK/6-31G(d,p)	-788.076214	-788.021021	-788.013871	-788.05203		
BMK/6-311++G(2df.2dp)	-788.218828	-788.164074	-788.156896	-788.195115		
M06/6-31G(d,p)	-788.181189	-788.126919	-788.119701	-788.157953		
M06/6-311++G(2df.2dp)	-788.318546	-788.264705	-788.257458	-788.295776		
M06-2X/DG3/aug-cc-pVTZ	-788.38818	-788.33346	-788.326261	-788.364517		
G4	-788.184636	-788.131723	-788.124318	-788.162999		
SVECV-f12	-788.249725	-788.195005	-788.187806	-788.226062		
Coordinates (xyz)				Vibrations (cm ⁻¹)		
C	-0.283585	1.471749	-0.629146	119.1182	818.5657	3052.3585
H	0.398506	2.24546	-0.281914	241.032	969.1685	3147.9317
H	-0.143493	1.316593	-1.696992	254.2575	1104.1852	3153.3285
H	-1.311519	1.771931	-0.429103	312.2158	1163.9411	
C	0.001814	0.208881	0.110261	377.9079	1232.9511	
F	-0.19556	0.355936	1.417818	406.467	1239.317	
Cl	1.640048	-0.397445	-0.174374	467.2879	1395.2277	
O	-0.831658	-0.891034	-0.332055	530.6361	1444.8627	
O	-2.090048	-0.592044	-0.202281	751.6904	1450.8265	

H₃C-CFCIO

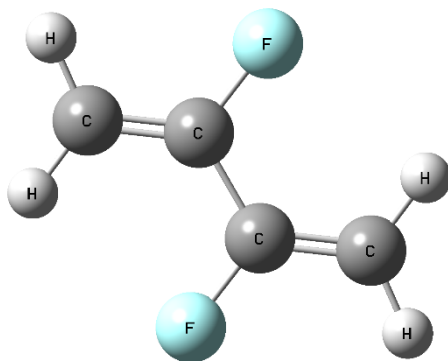


Method	Ee	E+ZPE	ΔH	ΔG		
BMK/6-31G(d,p)	-712.955546	-712.905503	-712.899043	-712.93532		
BMK/6-311++G(2df.2dp)	-713.073712	-713.023991	-713.017558	-713.053686		
M06/6-31G(d,p)	-713.062728	-713.013274	-713.00683	-713.042893		
M06/6-311++G(2df.2dp)	-713.176287	-713.127213	-713.120762	-713.156817		
M06-2X/DG3/aug-cc-pVTZ	-713.229757	-713.180083	-713.173647	-713.209783		
G4	-713.044156	-712.996029	-712.989256	-713.026062		
SVECV-f12	-713.100658	-713.050984	-713.044548	-713.080684		
Coordinates (xyz)				Vibrations (cm ⁻¹)		
C	1.20231	1.158641	-0.069957	239.7172	980.5511	3136.0079
H	1.075777	1.533231	-1.08411	247.1449	1020.496	3162.4671
H	0.854751	1.893279	0.65162	271.3807	1186.2501	
H	2.257455	0.943212	0.103329	375.9164	1282.0135	
C	0.429252	-0.117255	0.091854	422.3967	1378.3233	
F	0.777675	-0.991305	-0.872618	482.4201	1443.0966	
Cl	-1.402528	0.197339	-0.129173	570.9289	1448.1101	
O	0.358317	-0.631382	1.280911	848.7021	3045.3694	

E. Products.

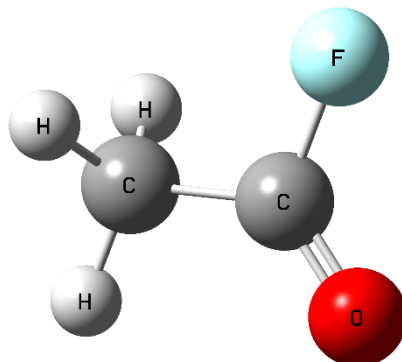
P1_H ₂ C=O					
					
Method	E _e		E+ZPE	ΔH	ΔG
BMK/6-31G(d,p)	-114.441354		-114.41422	-114.410411	-114.435224
BMK/6-311++G(2df.2dp)	-114.481024		-114.454004	-114.450195	-114.474994
M06/6-31G(d,p)	-114.437406		-114.410787	-114.406975	-114.43179
M06/6-311++G(2df.2dp)	-114.478223		-114.451814	-114.448002	-114.472803
M06-2X/DG3/aug-cc-pVTZ	-114.498971		-114.471958	-114.468148	-114.492949
G4	-114.479393		-114.453181	-114.449367	-114.474181
SVECV-f12	-114.487282		-114.460269	-114.456459	-114.48126
Coordinates (xyz)			Vibrations (cm ⁻¹)		
C	0.000000	0.519713	0.000000	1206.7935	2844.3568
H	0.935624	1.119788	0.000000	1258.3967	2896.738
O	0.000000	-0.669732	0.000000	1516.5624	
H	-0.935630	1.119789	0.000000	1882.8041	

P2_C₄H₄F₂



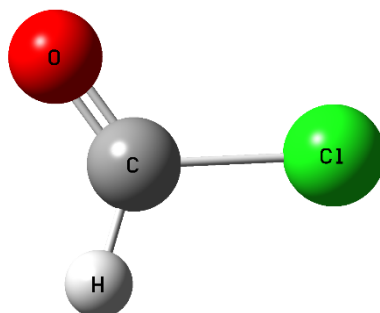
Method	Ee	E+ZPE	ΔH	ΔG		
BMK/6-31G(d,p)	-354.285654	-354.214924	-354.208289	-354.243618		
BMK/6-311++G(2df.2dp)	-354.402983	-354.33335	-354.32667	-354.362057		
M06/6-31G(d,p)	-354.284512	-354.214378	-354.207714	-354.243054		
M06/6-311++G(2df.2dp)	-354.406208	-354.335772	-354.329152	-354.364457		
M06-2X/DG3/aug-cc-pVTZ	-354.475155	-354.404636	-354.39797	-354.434015		
G4	-354.394621	-354.325749	-354.318993	-354.355185		
SVECV-f12	-354.429722	-354.359203	-354.352537	-354.388582		
Coordinates (xyz)				Vibrations (cm ⁻¹)		
C	-0.310985	1.822613	0	104.4326	895.707	3169.519
H	0.252796	2.743929	0	261.2858	898.6248	3169.8934
H	-1.388813	1.857077	0	372.955	953.7757	3275.6295
C	0.310985	0.657465	0	389.8444	958.5811	3275.8279
C	-0.310985	-0.657465	0	507.5537	1206.1969	
C	0.310985	-1.822613	0	513.8962	1364.9576	
H	-0.252796	-2.743929	0	717.1233	1378.0575	
H	1.388813	-1.857077	0	727.0667	1417.8005	
F	1.64302	0.596033	0	762.3581	1697.6076	
F	-1.64302	-0.596033	0	796.1905	1750.3238	

P3_CH₃C(=O)F



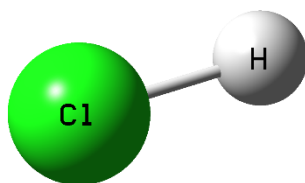
Method	Ee	E+ZPE	ΔH	ΔG		
BMK/6-31G(d,p)	-252.978607	-252.928829	-252.923601	-252.955577		
BMK/6-311++G(2df.2dp)	-253.064578	-253.015111	-253.009887	-253.041854		
M06/6-31G(d,p)	-252.976402	-252.927196	-252.921974	-252.953881		
M06/6-311++G(2df.2dp)	-253.063042	-253.014135	-253.008913	-253.040827		
M06-2X/DG3/aug-cc-pVTZ	-253.101715	-253.052503	-253.047969	-253.07851		
G4	-253.045629	-252.997631	-252.99305	-253.023673		
SVECV-f12	-253.072712	-253.0235	-253.018966	-253.049507		
Coordinates (xyz)				Vibrations (cm ⁻¹)		
C	0.128792	-0.135281	-0.000002	136.651	1213.1476	3167.7564
F	0.64598	1.107025	0.000007	419.6449	1388.0378	
O	0.836592	-1.075308	-0.000007	578.885	1441.0953	
C	-1.35329	-0.072204	0	612.5613	1448.2692	
H	-1.694198	0.479156	0.87663	868.8967	1953.0842	
H	-1.6942	0.479185	-0.87661	1004.3129	3048.9809	
H	-1.771173	-1.074198	-0.000015	1061.2759	3125.2085	

P4_CH(=O)Cl

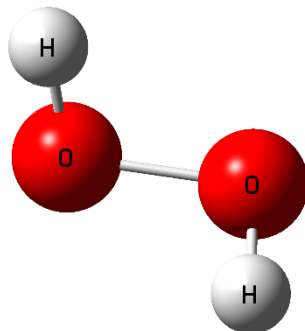


Method	Ee	E+ZPE	ΔH	ΔG	
BMK/6-31G(d,p)	-573.921007	-573.90133	-573.897173	-573.926541	
BMK/6-311++G(2df.2dp)	-573.995087	-573.975589	-573.971426	-574.000786	
M06/6-31G(d,p)	-574.026534	-574.007291	-574.003107	-574.032504	
M06/6-311++G(2df.2dp)	-574.097108	-574.078017	-574.073836	-574.10321	
M06-2X/DG3/aug-cc-pVTZ	-574.131838	-574.109206	-574.105036	-574.134393	
G4	-573.976899	-573.958066	-573.95385	-573.983302	
SVECV-f12	-574.016748	-573.994116	-573.989946	-574.019303	
Coordinates (xyz)				Vibrations (cm ⁻¹)	
C	0	0.797747	0	463.6657	1896.6745
H	-0.903955	1.422673	0	742.2709	3011.6959
Cl	-0.470786	-0.913071	0	958.6175	
O	1.113415	1.164131	0	1306.7403	

HCl



Method	Ee	E+ZPE	ΔH	ΔG
BMK/6-31G(d,p)	-460.652146	-460.645236	-460.641931	-460.663144
BMK/6-311++G(2df.2dp)	-460.691111	-460.684343	-460.681038	-460.702238
M06/6-31G(d,p)	-460.763827	-460.757068	-460.753764	-460.774953
M06/6-311++G(2df.2dp)	-460.797364	-460.790599	-460.787295	-460.808479
M06-2X/DG3/aug-cc-pVTZ	-460.807507	-460.800702	-460.797398	-460.81858
G4	-460.685342	-460.678701	-460.675396	-460.696585
SVECV-f12	-460.714454	-460.707649	-460.704344	-460.725527
Coordinates (xyz)			Vibrations (cm ⁻¹)	
H	0	0	-1.209193	2969.1491
Cl	0	0	0.071129	

H₂O₂

Method	Ee	E+ZPE	ΔH	ΔG	
BMK/6-31G(d,p)	-151.47345	-151.446056	-151.441882	-151.468345	
BMK/6-311++G(2df.2dp)	-151.532943	-151.505526	-151.501379	-151.527774	
M06/6-31G(d,p)	-151.473675	-151.446634	-151.442482	-151.468897	
M06/6-311++G(2df.2dp)	-151.533273	-151.506185	-151.502059	-151.528412	
M06-2X/DG3/aug-cc-pVTZ	-151.553652	-151.526513	-151.522355	-151.548117	
G4	-151.520696	-151.494549	-151.490368	-151.516197	
SVECV-f12	-151.539996	-151.539996	-151.537636	-151.554948	
Coordinates (xyz)			Vibrations (cm ⁻¹)		
O	-1.47058819	-2.18009994	0.00043871	410.227	3827.2693
H	-1.79082077	-1.27508595	-0.00043846	1018.5736	3829.139
O	-0.15058824	-2.17976074	0.00043865	1347.2608	
H	0.16964434	-3.08477473	0.00131582	1457.9789	

II. Summary of energies of the three reaction paths, energies (kcal/mol)

A. Energies for the final products.

ROUTE	REACTANTS	PRODUCTS	ENERGY	BMK		M06		M062X/GD3	G4	SVEVC-f12
				6-31G(d,p)	6-311++G(2df,2pd)	6-31G(d,p)	6-311++G(2df,2pd)	aug-cc-pVTZ		
I	2FP + 2Cl + O ₂	→ 2P1 + P2 + 2HCl	ΔE	-60.7	-66.8	-58.9	-62.7	-61.0	-62.9	-63.6
			Δ(E+ZPE)	-64.3	-70.1	-62.4	-66.5	-64.5	-66.4	-65.8
			ΔH	-63.7	-69.5	-61.8	-65.9	-63.9	-65.8	-64.9
			ΔG	-64.9	-70.7	-63.0	-67.1	-65.3	-67.2	-68.0
II	2FP + 2Cl + 3O ₂	→ 2P3 + 2P4 + H ₂ O ₂	ΔE	-153.6	-160.2	-151.4	-155.9	-149.8	-149.7	-151.0
			Δ(E+ZPE)	-151.2	-157.7	-148.8	-153.3	-145.6	-147.7	-151.6
			ΔH	-152.0	-158.5	-149.6	-154.2	-146.9	-148.9	-152.5
			ΔG	-145.4	-151.9	-143.0	-147.6	-139.2	-141.3	-147.1
III	FP + O ₂	→ P1 + P3	ΔE	-89.8	-92.4	-89.0	-89.9	-83.2	-86.0	-85.6
			Δ(E+ZPE)	-89.9	-92.6	-89.0	-90.0	-83.5	-86.3	-83.4
			ΔH	-89.8	-92.4	-88.8	-89.8	-83.8	-86.6	-83.1
			ΔG	-90.6	-93.3	-89.7	-90.7	-83.8	-86.6	-86.3

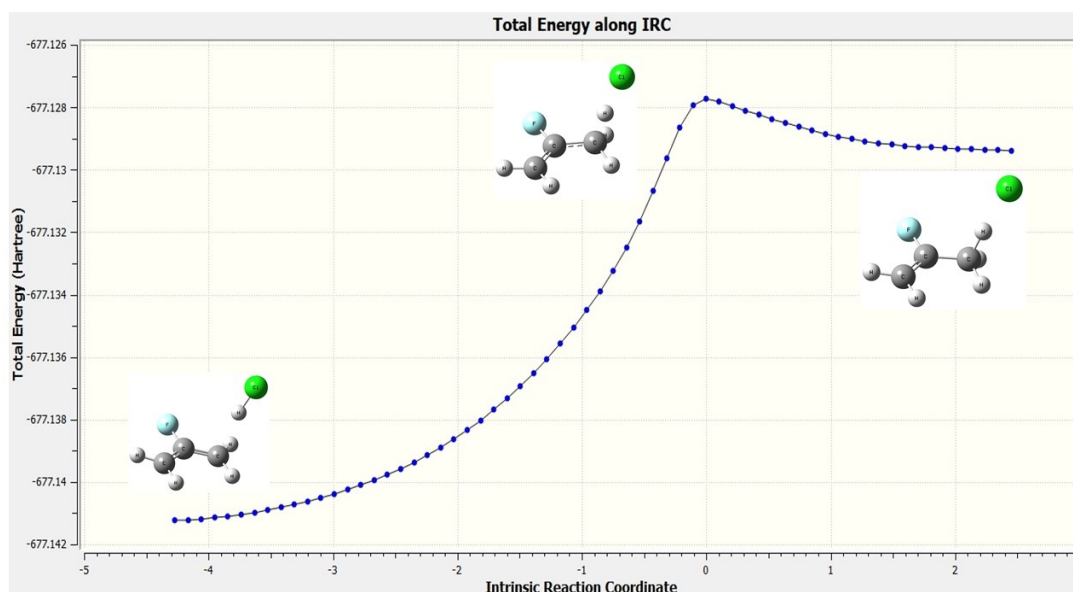
B. Energies for the products of the first dimerization.

ROUTE	REACTANTS	FIRST DIMER	ENERGY	BMK		M06		M062X/GD3
				6-31G(d,p)	6-311++G(2df,2pd)	6-31G(d,p)	6-311++G(2df,2pd)	aug-cc-pVTZ
I	2FP + 2Cl	→ P13 +2HCl	ΔE	-81.8	-87.3	-84.0	-88.5	-87.8
			$\Delta(E+ZPE)$	-84.4	-89.9	-86.6	-91.0	-90.4
			ΔH	-84.2	-89.6	-86.4	-90.7	-90.2
			ΔG	-75.3	-80.8	-77.5	-81.9	-81.2
II	2FP + 2Cl	→ P14	ΔE	-129.7	-125.2	-130.7	-126.6	-126.1
			$\Delta(E+ZPE)$	-122.0	-118.0	-124.0	-119.9	-119.6
			ΔH	-124.3	-120.2	-126.1	-122.1	-121.5
			ΔG	-91.8	-88.1	-94.1	-90.0	-90.8
III	2FP + 2Cl	→ P15	ΔE	-137.0	-133.4	-138.3	-135.0	-134.0
			$\Delta(E+ZPE)$	-130.3	-126.7	-131.9	-128.6	-127.5
			ΔH	-132.3	-128.7	-133.9	-130.6	-129.5
			ΔG	-101.5	-97.8	-103.1	-99.8	-98.5

C. Energies for the products of the dimerization processes.

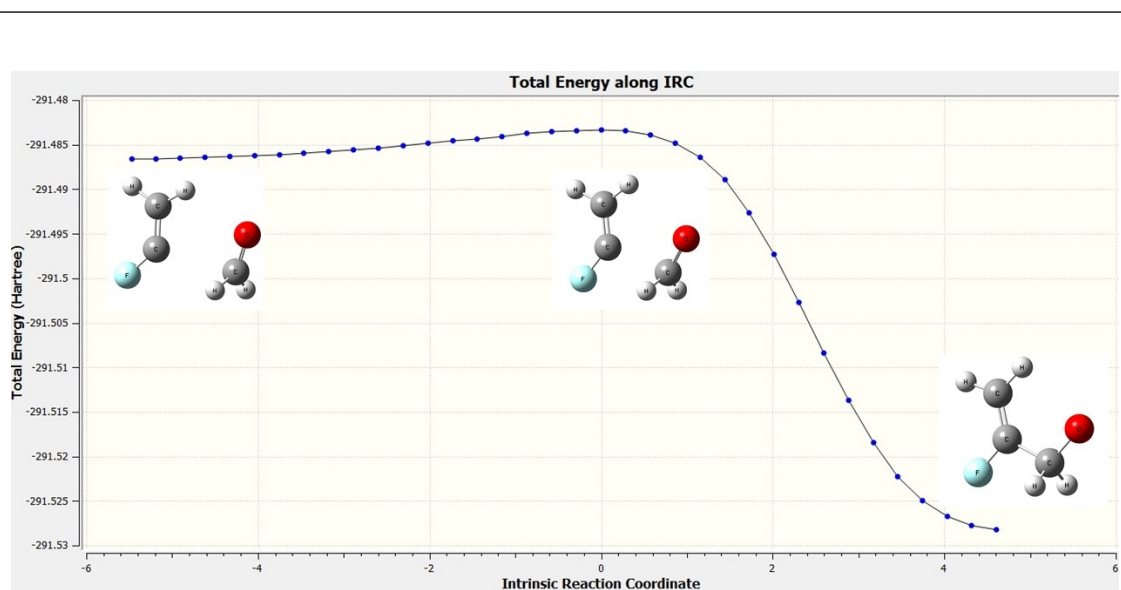
ROUTE	REACTANTS	DIMERS	ENERGY	BMK		M06		M062X/GD3
				6-31G(d,p)	6-311++G(2df,2pd)	6-31G(d,p)	6-311++G(2df,2pd)	aug-cc-pVTZ
I.a	2FP + 2Cl + O ₂	→ P9 + 2HCl	ΔE	-90.0	-95.4	-94.0	-98.6	-88.3
			Δ(E+ZPE)	-90.1	-95.4	-94.4	-98.8	-88.9
			ΔH	-90.5	-95.8	-94.8	-99.2	-90.7
			ΔG	-71.6	-76.9	-75.8	-80.0	-67.8
I.b	2FP + 2Cl + 2O ₂	→ 2P1+P10+2HCl	ΔE	-258.7	-265.6	-262.6	-271.8	-256.2
			Δ(E+ZPE)	-261.2	-268.3	-265.6	-274.6	-259.2
			ΔH	-260.7	-267.7	-265.0	-274.1	-258.7
			ΔG	-253.5	-260.5	-257.9	-266.9	-251.3
II.a	2FP + 2Cl + O ₂	→ P7	ΔE	-159.8	-153.9	-162.4	-157.2	-156.0
			Δ(E+ZPE)	-149.9	-144.5	-153.3	-148.3	-146.9
			ΔH	-152.9	-147.3	-156.1	-151.1	-149.7
			ΔG	-110.4	-105.2	-113.8	-108.8	-107.6
II.b	2FP + 2Cl + O ₂	→ 2P3 + P12	ΔE	-220.7	-221.1	-220.0	-222.6	-211.0
			Δ(E+ZPE)	-215.3	-215.9	-215.0	-217.6	-206.3
			ΔH	-217.1	-217.6	-216.8	-219.4	-208.9
			ΔG	-201.3	-202.0	-201.0	-203.7	-191.4

ROUTE	REACTANTS	DIMERS	ENERGY	BMK		M06		M062X/GD3	
				6-31G(d,p)	6-311++G(2df,2pd)	6-31G(d,p)	6-311++G(2df,2pd)	aug-cc-pVTZ	
II.c	2FP + 2Cl + 2O ₂	→	2P3 + P5	ΔE	-229.1	-229.8	-229.9	-233.0	-220.3
				Δ(E+ZPE)	-221.2	-222.1	-222.5	-225.7	-213.1
				ΔH	-223.6	-224.4	-224.9	-228.0	-216.7
				ΔG	-197.7	-198.7	-198.8	-202.0	-188.0
III.a	2FP + 2Cl + O ₂	→	P8	ΔE	-147.5	-143.7	-149.7	-146.6	-141.9
				Δ(E+ZPE)	-138.1	-134.5	-140.8	-137.7	-133.0
				ΔH	-140.8	-137.1	-143.5	-140.4	-136.3
				ΔG	-99.7	-95.9	-102.4	-99.2	-92.7
III.b	2FP + 2Cl + O ₂	→	2P1 + P11	ΔE	-166.5	-167.7	-169.0	-172.1	-163.1
				Δ(E+ZPE)	-164.3	-165.7	-167.5	-170.7	-161.5
				ΔH	-165.3	-166.7	-168.4	-171.6	-162.5
				ΔG	-146.1	-147.6	-149.4	-152.6	-143.4
III.c	2FP + 2Cl + 2O ₂	→	2P1 + P6	ΔE	-193.1	-192.7	-197.3	-197.8	-190.4
				Δ(E+ZPE)	-188.5	-188.3	-193.1	-194.1	-186.2
				ΔH	-190.4	-190.1	-195.0	-195.8	-188.0
				ΔG	-160.0	-160.1	-164.2	-165.9	-157.9



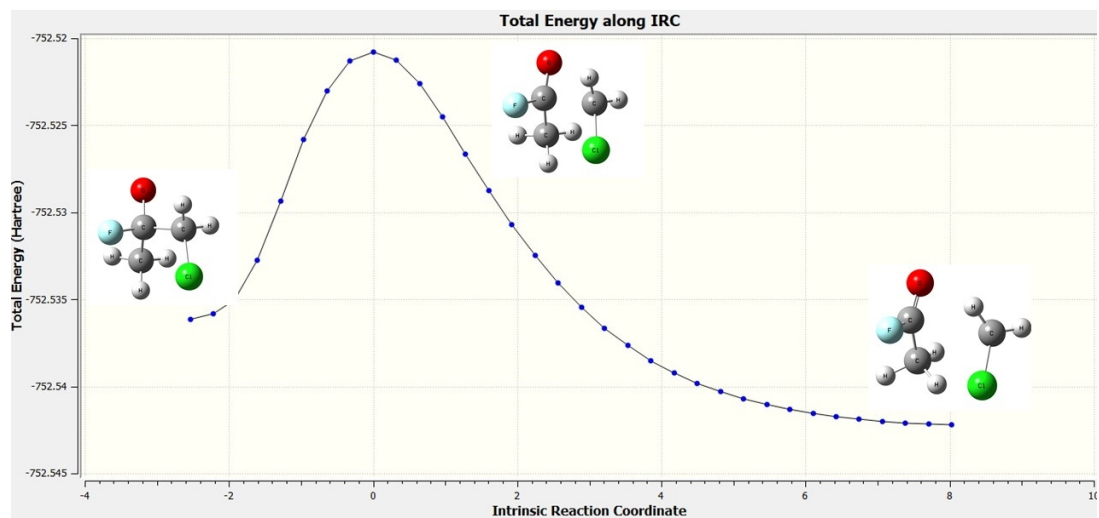
a) Figure S 1. Change in energy and the intrinsic reaction coordinate (IRC) relative to the **TS_E1**.

<i>RxCoord</i>	<i>R. Energy</i>	<i>RxCoord</i>	<i>R. Energy</i>	<i>RxCoord</i>	<i>R. Energy</i>
-4.27223	-0.01352	-1.92138	-0.01063	-0.00053	0.42185
-4.16546	-0.01350	-1.81451	-0.01031	-0.00067	0.52872
-4.05863	-0.01347	-1.70765	-0.00998	-0.00080	0.63559
-3.95178	-0.01343	-1.60079	-0.00961	-0.00092	0.74246
-3.84492	-0.01338	-1.49393	-0.00922	-0.00103	0.84933
-3.73806	-0.01332	-1.38707	-0.00880	-0.00113	0.95620
-3.63119	-0.01326	-1.28021	-0.00834	-0.00122	1.06307
-3.52433	-0.01319	-1.17336	-0.00786	-0.00130	1.16993
-3.41746	-0.01311	-1.06653	-0.00734	-0.00137	1.27678
-3.31059	-0.01301	-0.95974	-0.00678	-0.00143	1.38363
-3.20372	-0.01291	-0.85300	-0.00618	-0.00148	1.49047
-3.09686	-0.01280	-0.74634	-0.00553	-0.00152	1.59725
-2.99000	-0.01267	-0.63983	-0.00479	-0.00155	1.70385
-2.88314	-0.01254	-0.53352	-0.00394	-0.00157	1.81017
-2.77628	-0.01239	-0.42699	-0.00297	-0.00159	1.91654
-2.66943	-0.01223	-0.32029	-0.00193	-0.00161	2.02318
-2.56257	-0.01205	-0.21350	-0.00094	-0.00163	2.12998
-2.45570	-0.01186	-0.10669	-0.00022	-0.00165	2.23684
-2.34884	-0.01165	0.00000	0.00000	-0.00166	2.34371
-2.24198	-0.01143	0.10389	-0.00010	-0.00168	2.45058
-2.13511	-0.01118	0.20833	-0.00024		
-2.02824	-0.01091	0.31513	-0.00039		



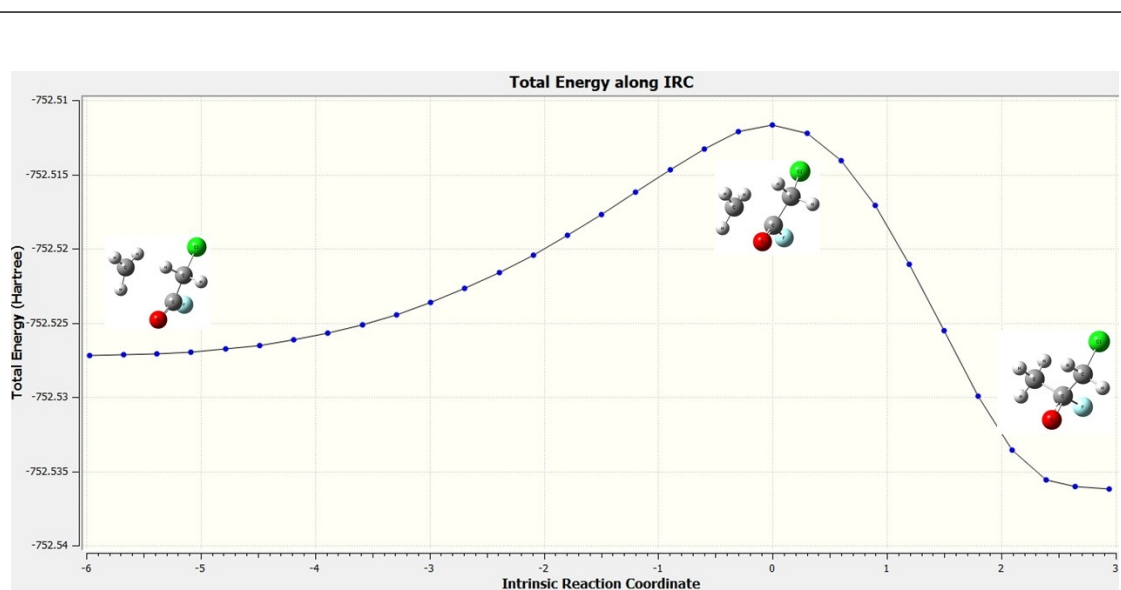
b) Figure S 2. Change in energy and the intrinsic reaction coordinate (IRC) relative to the **TS_E10**.

<i>RxCoord</i>	<i>R. Energy</i>	<i>RxCoord</i>	<i>R. Energy</i>	<i>RxCoord</i>	<i>R. Energy</i>
-5.47293	-0.00328	-2.01920	-0.00153	1.44178	-0.00562
-5.18953	-0.00324	-1.73057	-0.00125	1.73038	-0.00927
-4.90438	-0.00318	-1.44204	-0.00100	2.01903	-0.01397
-4.61587	-0.00311	-1.15358	-0.00072	2.30767	-0.01937
-4.32728	-0.00301	-0.86526	-0.00042	2.59627	-0.02501
-4.03879	-0.00290	-0.57665	-0.00018	2.88482	-0.03039
-3.75043	-0.00276	-0.28810	-0.00005	3.17323	-0.03512
-3.46184	-0.00259	0.00000	0.00000	3.46140	-0.03892
-3.17325	-0.00242	0.28789	-0.00011	3.74872	-0.04164
-2.88463	-0.00224	0.57623	-0.00055	4.03500	-0.04339
-2.59613	-0.00205	0.86479	-0.00147	4.32225	-0.04444
-2.30769	-0.00181	1.15321	-0.00307	4.60813	-0.04490



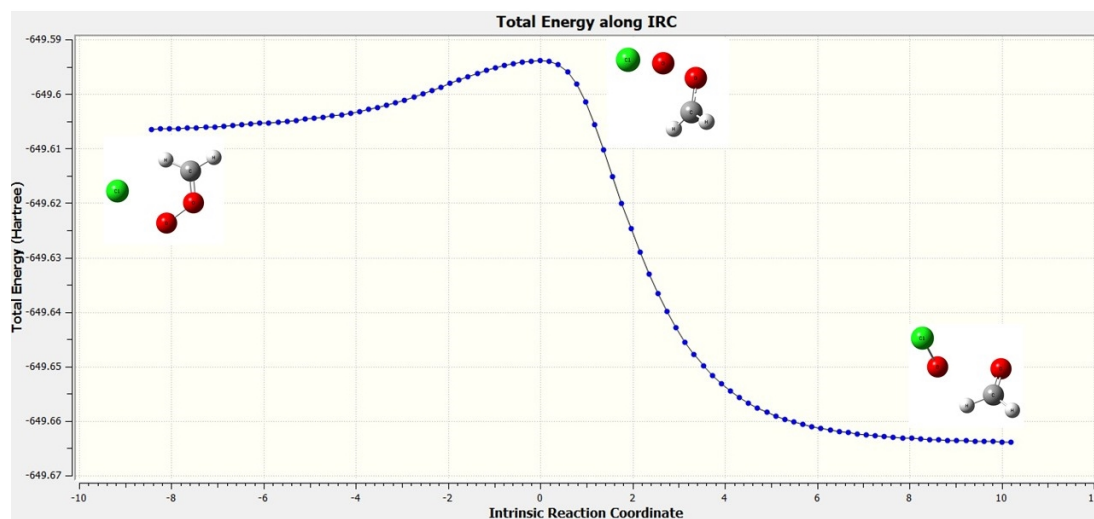
c) Figure S 3. Change in energy and the intrinsic reaction coordinate (IRC) relative to the **TS_A101**.

<i>RxCoord</i>	<i>R. Energy</i>	<i>RxCoord</i>	<i>R. Energy</i>	<i>RxCoord</i>	<i>R. Energy</i>
-2.53639	-0.01537	1.28481	-0.00588	5.13932	-0.01994
-2.22120	-0.01506	1.60601	-0.00799	5.46046	-0.02027
-1.92520	-0.01427	1.92721	-0.00995	5.78144	-0.02054
-1.60605	-0.01200	2.24843	-0.01172	6.10258	-0.02077
-1.28499	-0.00857	2.56964	-0.01331	6.42349	-0.02096
-0.96376	-0.00505	2.89087	-0.01469	6.74401	-0.02112
-0.64249	-0.00224	3.21214	-0.01588	7.06468	-0.02124
-0.32130	-0.00054	3.53343	-0.01689	7.38399	-0.02133
0.00000	0.00000	3.85470	-0.01775	7.70428	-0.02140
0.32128	-0.00048	4.17594	-0.01846	8.02420	-0.02145
0.64244	-0.00182	4.49712	-0.01905		
0.96368	-0.00375	4.81829	-0.01954		



d) Figure S 4. Change in energy and the intrinsic reaction coordinate (IRC) relative to the **TS_A102**.

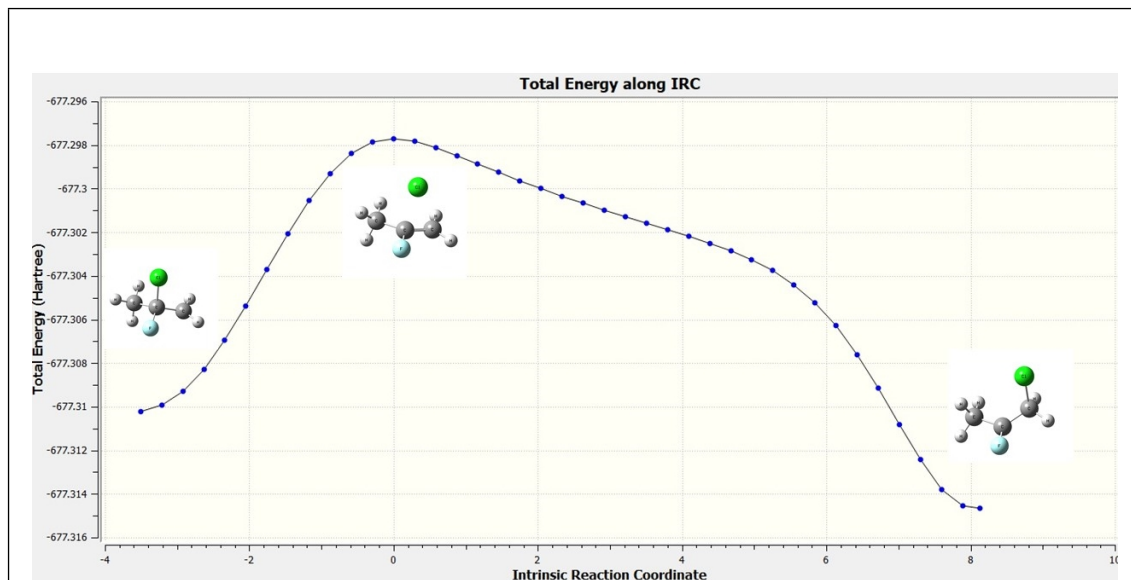
<i>RxCoord</i>	<i>R. Energy</i>	<i>RxCoord</i>	<i>R. Energy</i>	<i>RxCoord</i>	<i>R. Energy</i>
-5.96838	-0.01554	-2.39192	-0.00996	1.19615	-0.00939
-5.67584	-0.01549	-2.09291	-0.00876	1.49520	-0.01388
-5.38059	-0.01543	-1.79389	-0.00744	1.79421	-0.01829
-5.08276	-0.01531	-1.49487	-0.00603	2.09302	-0.02190
-4.78406	-0.01512	-1.19584	-0.00454	2.38979	-0.02391
-4.48518	-0.01485	-0.89685	-0.00303	2.64771	-0.02438
-4.18621	-0.01450	-0.59785	-0.00161	2.94166	-0.02454
-3.88714	-0.01404	-0.29900	-0.00048		
-3.58810	-0.01347	0.00000	0.00000		
-3.28906	-0.01279	0.29908	-0.00059		
-2.99000	-0.01198	0.59805	-0.00241		
-2.69095	-0.01104	0.89710	-0.00543		



e) Figure S 5. Change in energy and the intrinsic reaction coordinate (IRC) relative to the **TS_CIO2**.

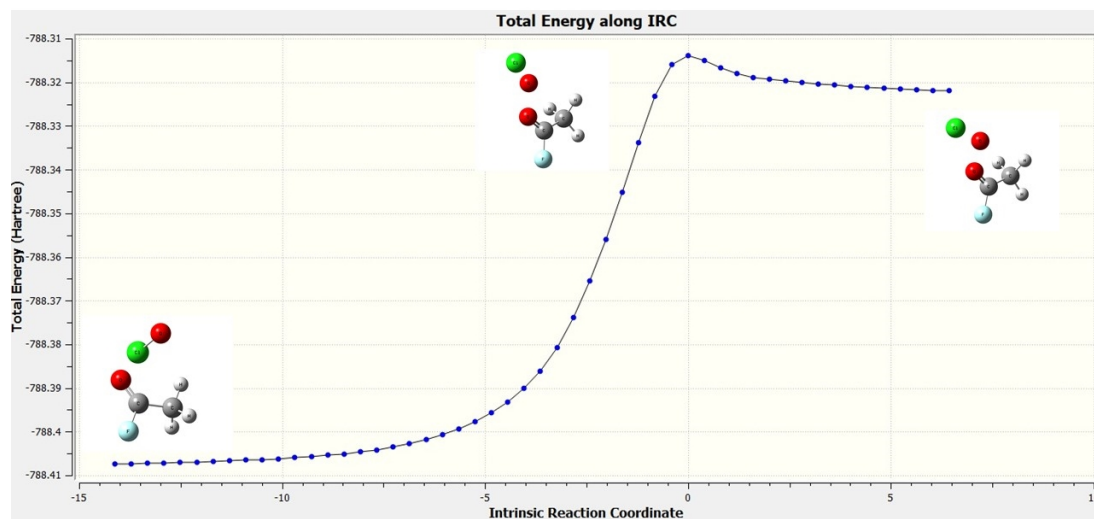
<i>RxCoord</i>	<i>Energy</i>	<i>RxCoord</i>	<i>Energy</i>	<i>RxCoord</i>	<i>Energy</i>	<i>RxCoord</i>	<i>Energy</i>
-8.435	-0.013	-3.726	-0.009	0.980	-0.008	5.691	-0.067
-8.239	-0.013	-3.530	-0.009	1.176	-0.012	5.887	-0.067
-8.043	-0.012	-3.334	-0.008	1.372	-0.016	6.084	-0.067
-7.847	-0.012	-3.138	-0.008	1.568	-0.021	6.280	-0.068
-7.651	-0.012	-2.941	-0.007	1.765	-0.026	6.476	-0.068
-7.454	-0.012	-2.745	-0.007	1.961	-0.031	6.672	-0.068
-7.258	-0.012	-2.549	-0.006	2.157	-0.035	6.869	-0.068
-7.062	-0.012	-2.352	-0.005	2.354	-0.039	7.065	-0.069
-6.865	-0.012	-2.156	-0.005	2.550	-0.043	7.261	-0.069
-6.669	-0.012	-1.960	-0.004	2.746	-0.046	7.457	-0.069
-6.473	-0.012	-1.763	-0.004	2.943	-0.049	7.654	-0.069
-6.277	-0.012	-1.567	-0.003	3.139	-0.052	7.850	-0.069
-6.080	-0.011	-1.371	-0.002	3.335	-0.054	8.046	-0.069
-5.884	-0.011	-1.175	-0.002	3.532	-0.056	8.242	-0.069
-5.688	-0.011	-0.978	-0.001	3.728	-0.058	8.439	-0.069
-5.492	-0.011	-0.782	-0.001	3.924	-0.059	8.635	-0.070
-5.296	-0.011	-0.586	-0.001	4.121	-0.061	8.831	-0.070
-5.100	-0.011	-0.390	0.000	4.317	-0.062	9.028	-0.070
-4.903	-0.011	-0.195	0.000	4.513	-0.063	9.224	-0.070
-4.707	-0.010	0.000	0.000	4.710	-0.064	9.420	-0.070
-4.511	-0.010	0.195	0.000	4.906	-0.064	9.616	-0.070
-4.315	-0.010	0.391	-0.001	5.102	-0.065	9.812	-0.070
-4.118	-0.010	0.587	-0.002	5.299	-0.066	10.008	-0.070
-3.922	-0.009	0.783	-0.004	5.495	-0.066	10.204	-0.070

-8.435	-0.013	-3.726	-0.009	0.980	-0.008	5.691	-0.067
-8.239	-0.013	-3.530	-0.009	1.176	-0.012	5.887	-0.067



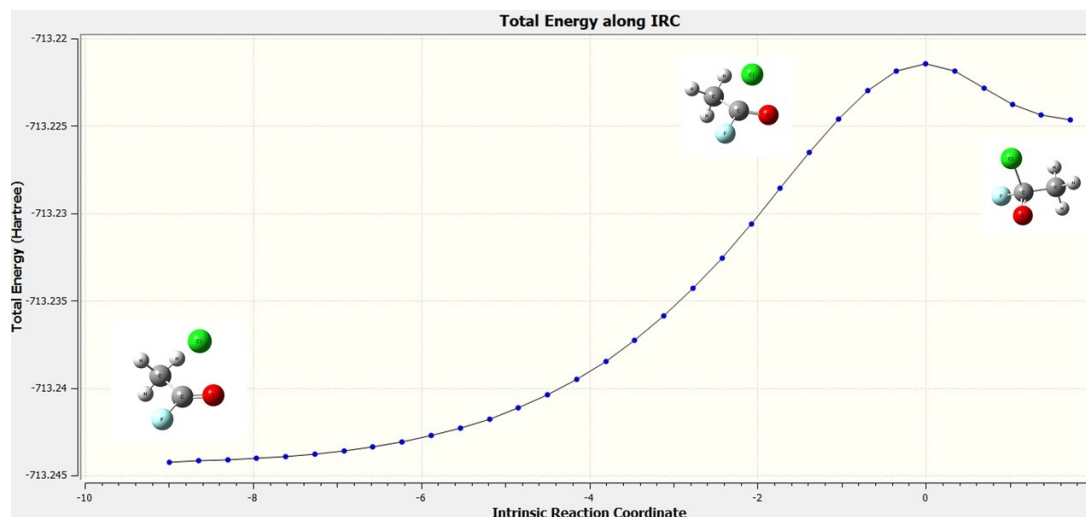
f) Figure S 6. Change in energy and the intrinsic reaction coordinate (IRC) relative to the **TS_A1A2**.

<i>RxCoord</i>	<i>R. Energy</i>	<i>RxCoord</i>	<i>R. Energy</i>	<i>RxCoord</i>	<i>R. Energy</i>
-3.501	-0.012	0.584	0.000	4.67451	-0.005
-3.212	-0.012	0.876	-0.001	4.96658	-0.006
-2.921	-0.012	1.168	-0.001	5.25858	-0.006
-2.630	-0.011	1.460	-0.002	5.55061	-0.007
-2.338	-0.009	1.752	-0.002	5.84269	-0.008
-2.045	-0.008	2.044	-0.002	6.13483	-0.009
-1.753	-0.006	2.337	-0.003	6.42702	-0.010
-1.461	-0.004	2.629	-0.003	6.71924	-0.011
-1.169	-0.003	2.921	-0.003	7.01148	-0.013
-0.877	-0.002	3.213	-0.004	7.30373	-0.015
-0.584	-0.001	3.50574	-0.004	7.59594	-0.016
-0.292	0.000	3.79799	-0.004	7.88735	-0.017
0.000	0.000	4.09020	-0.004	8.12383	-0.017
0.292	0.000	4.38239	-0.005		



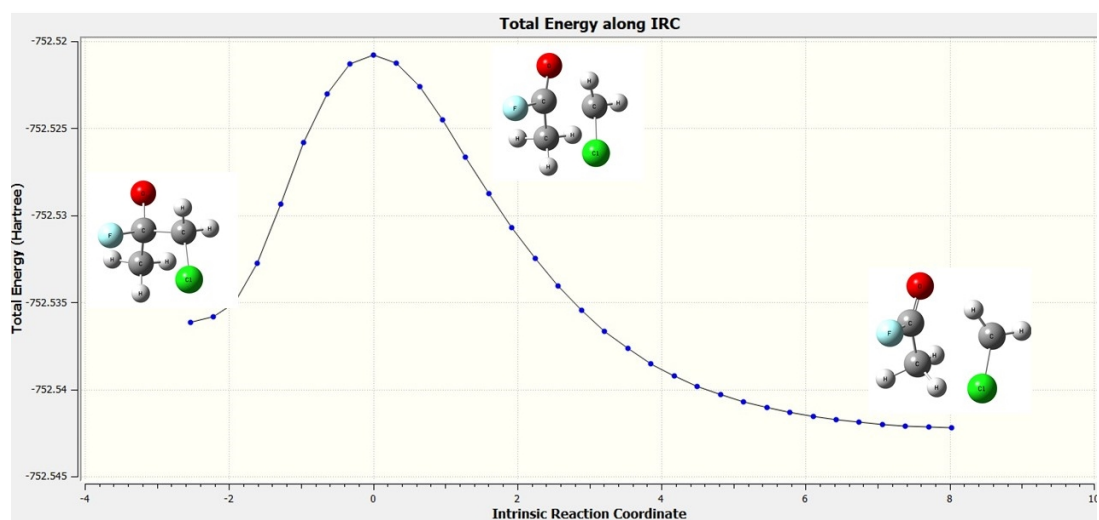
g) Figure S 7. Change in energy and the intrinsic reaction coordinate (IRC) relative to the **TS_CIFetrO2**.

<i>RxCoord</i>	<i>R. Energy</i>	<i>RxCoord</i>	<i>R. Energy</i>	<i>RxCoord</i>	<i>R. Energy</i>
-14.121	-0.094	-6.85976	-0.089	0.40319	-0.001
-13.718	-0.093	-6.45608	-0.088	0.80501	-0.003
-13.314	-0.093	-6.05239	-0.087	1.20627	-0.004
-12.911	-0.093	-5.64864	-0.086	1.60454	-0.005
-12.507	-0.093	-5.24493	-0.084	1.99778	-0.005
-12.104	-0.093	-4.84115	-0.082	2.40023	-0.006
-11.700	-0.093	-4.43744	-0.079	2.80382	-0.006
-11.296	-0.093	-4.03433	-0.076	3.20760	-0.006
-10.893	-0.093	-3.63243	-0.072	3.61144	-0.007
-10.490	-0.092	-3.22982	-0.067	4.01528	-0.007
-10.086	-0.092	-2.82629	-0.060	4.41915	-0.007
-9.683	-0.092	-2.42252	-0.052	4.82300	-0.007
-9.280	-0.092	-2.01870	-0.042	5.22688	-0.008
-8.877	-0.092	-1.61491	-0.031	5.63073	-0.008
-8.47354	-0.091	-1.21116	-0.020	6.03461	-0.008
-8.07061	-0.091	-0.80740	-0.009	6.43838	-0.008
-7.66697	-0.090	-0.40365	-0.002		



h) Figure S 8. Change in energy and the intrinsic reaction coordinate (IRC) relative to the TS_CIFetrO.

<i>RxCoord</i>	<i>R. Energy</i>	<i>RxCoord</i>	<i>R. Energy</i>	<i>RxCoord</i>	<i>R. Energy</i>
-8.993	-0.02278	-5.189	-0.02032	-1.38353	-0.00505
-8.647	-0.02273	-4.843	-0.01969	-1.03766	-0.00314
-8.302	-0.02266	-4.497	-0.01895	-0.69172	-0.00153
-7.956	-0.02258	-4.15116	-0.01806	-0.34589	-0.00041
-7.611	-0.02247	-3.80510	-0.01703	0.00000	0.00000
-7.265	-0.02234	-3.45905	-0.01583	0.34588	-0.00040
-6.919	-0.02215	-3.11303	-0.01444	0.69134	-0.00136
-6.573	-0.02192	-2.76707	-0.01286	1.03547	-0.00233
-6.227	-0.02163	-2.42117	-0.01110	1.37469	-0.00290
-5.881	-0.02128	-2.07530	-0.00916	1.71791	-0.00319
-5.535	-0.02084	-1.72944	-0.00711		



i) Figure S 9. Change in energy and the intrinsic reaction coordinate (IRC) relative to the **TS_A20**.

<i>RxCoord</i>	<i>R. Energy</i>	<i>RxCoord</i>	<i>R. Energy</i>	<i>RxCoord</i>	<i>R. Energy</i>
-2.0997	-0.0175	1.2032	-0.0019	4.5134	-0.0056
-1.8054	-0.0121	1.5040	-0.0025	4.8142	-0.0057
-1.5044	-0.0083	1.8048	-0.0030	5.1149	-0.0058
-1.2034	-0.0049	2.1058	-0.0035	5.4154	-0.0059
-0.9026	-0.0025	2.4067	-0.0039	5.7159	-0.0060
-0.6017	-0.0010	2.7077	-0.0043	6.0164	-0.0060
-0.3009	-0.0002	3.0087	-0.0046	6.3171	-0.0061
0.0000	0.0000	3.3097	-0.0048	6.6178	-0.0061
0.3009	-0.0002	3.6106	-0.0051	6.9186	-0.0062
0.6017	-0.0007	3.9116	-0.0053		
0.9025	-0.0013	4.2125	-0.0055		