

Electronic Supplementary Information for:

Exploring Norrish Type I and Type II Reactions: An *ab initio* Mechanistic Study Highlighting Singlet-State Mediated Chemistry.

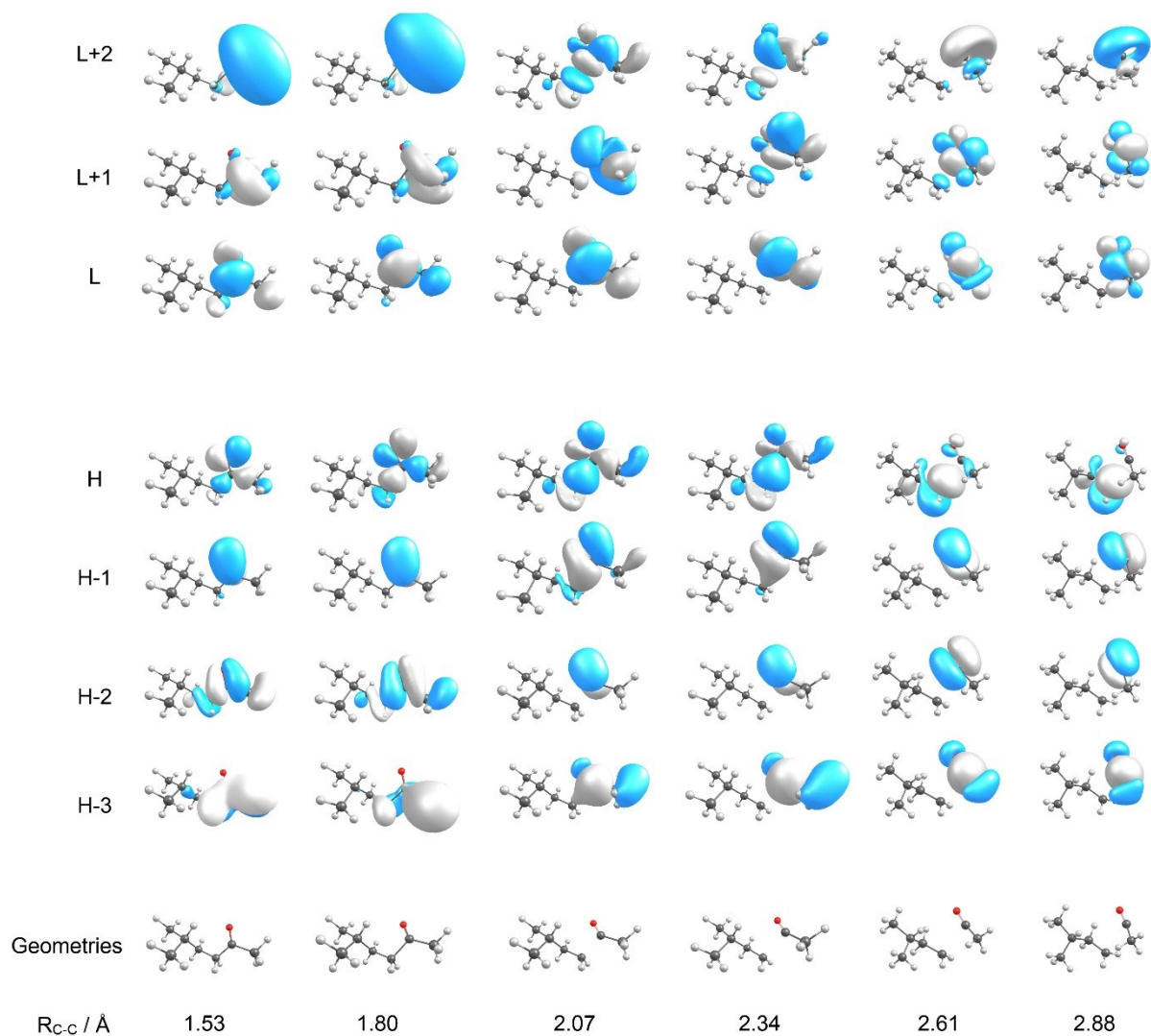
Barbara Marchetti^{†,‡}, Tolga N. V. Karsili^{‡,*} and Michael N. R. Ashfold[‡]

[†]*Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104, USA*

[‡]*School of Chemistry, University of Bristol, Bristol, BS8 1TS, UK*

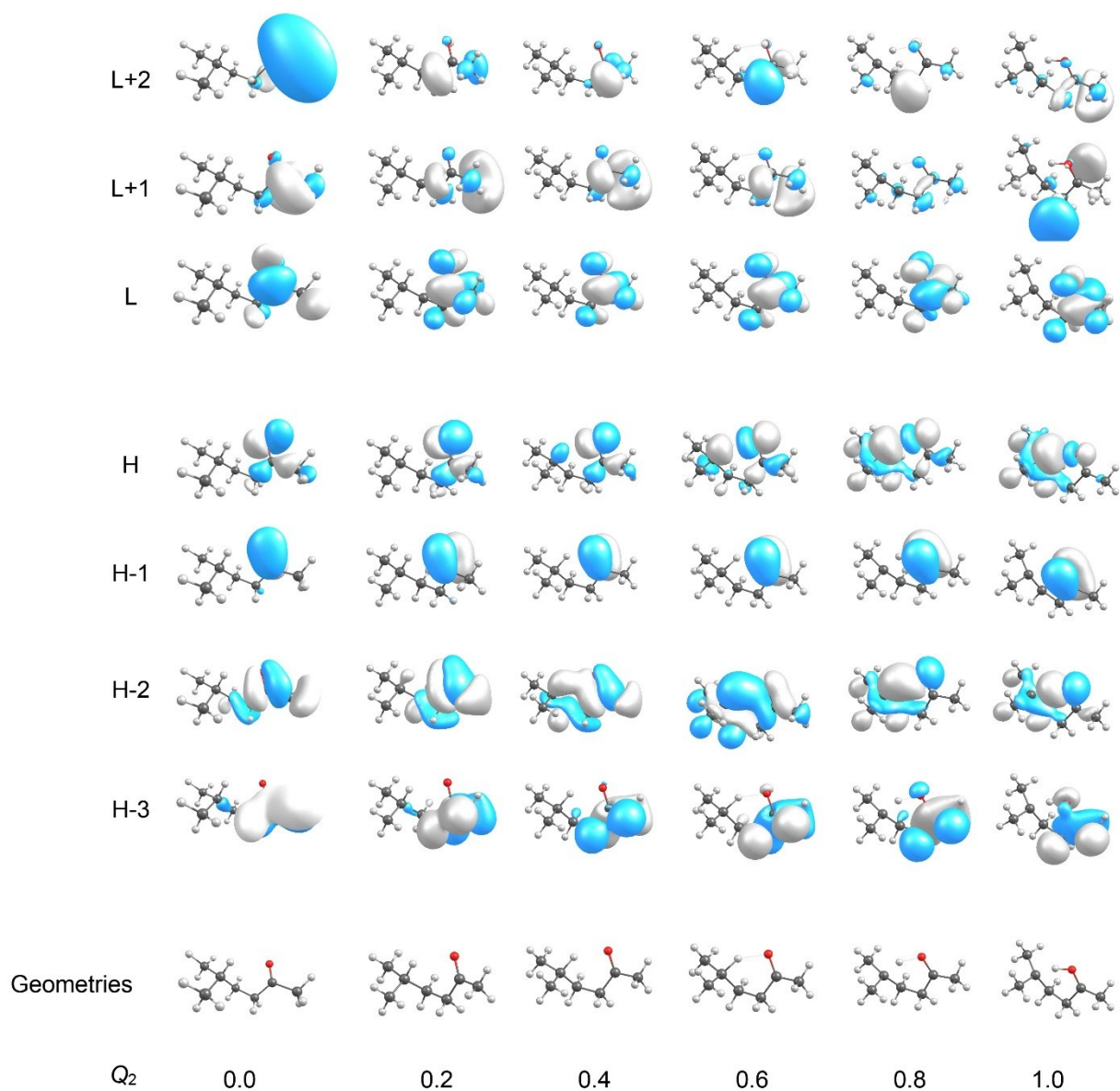
[‡]*Department of Chemistry, University of Louisiana, Lafayette, LA 70503, USA*

Figure S1: Full set of orbitals included in the CASSCF/CASPT2 active space (10 electrons in 8 orbitals) of 5-MHONE for various points of the LIIC along R_{C-C} . The corresponding geometries are also depicted. The predominant electronic excitations contributing to each excited singlet and triplet states are tabulated below.



$R_{C-C} / \text{Å}$	Excited State					
	S_1	S_2	S_3	T_1	T_2	T_3
1.53 (S_0 min)	$H \rightarrow L$	$H \rightarrow L+1$	$H \rightarrow L+2$	$H \rightarrow L$	$H \rightarrow L$	$H \rightarrow L+1$
1.80						
2.07	$H \rightarrow L$	$H \rightarrow L+1$	$H-1 \rightarrow L$	$H \rightarrow L$	$H \rightarrow L+1$	$H \rightarrow L+2$
2.34				$H \rightarrow L$	$H \rightarrow L+2$	$H \rightarrow L+1$
2.61	$H \rightarrow L$ $H \rightarrow L+1$	$H \rightarrow L+2$	H	$H \rightarrow L$ $H \rightarrow L+1$	$H \rightarrow L+1$ $H \rightarrow L$	$H \rightarrow L+2$
2.88 (Cl_{C-C})	$H \rightarrow L$ $H \rightarrow L+1$	$H \rightarrow L+2$	H	$H \rightarrow L$ $H \rightarrow L+1$	$H \rightarrow L+1$ $H \rightarrow L$	

Figure S2: Full set of orbitals included in the CASSCF/CASPT2 active space (10 electrons in 8 orbitals) of 5-MHONE for various points of the LIIC along Q_2 (PT coordinate). The corresponding geometries are also depicted. The predominant electronic excitations contributing to each excited singlet and triplet states are tabulated below.



Q_2	Excited State					
	S_1	S_2	S_3	T_1	T_2	T_3
0.0 (S_0 min)						
0.2						
0.4	$H \rightarrow L$	$H \rightarrow L+1$	$H \rightarrow L+2$	$H \rightarrow L$	$H-1 \rightarrow L$	$H \rightarrow L+1$
0.6						
0.8						
1.0 (Cl_{O-H})	H	$H \rightarrow L+2$	$H \rightarrow L+1$	$H \rightarrow L$	$H \rightarrow L+2$	$H \rightarrow L+1$

Table S1: Cartesian coordinates of the optimised critical structures of 5-MHONE.

- Ground state parent

Atom	x	y	z
C	-2.62504	-0.17205	0.195945
C	-1.94423	-1.50435	-0.12494
H	-2.70886	-2.21138	-0.48622
H	-1.58112	-1.92381	0.831562
C	-0.77227	-1.38742	-1.1247
H	-0.07688	-0.61873	-0.75391
H	-0.22261	-2.34499	-1.14492
C	-1.17947	-1.02354	-2.57921
H	-1.75762	-0.0862	-2.53888
O	-2.12107	0.934593	-0.15194
C	-3.93273	-0.23067	0.975905
H	-3.80889	-0.81941	1.896555
H	-4.24873	0.787525	1.228581
H	-4.71427	-0.71602	0.372301
C	0.086768	-0.76219	-3.4311
H	-0.18344	-0.4736	-4.45742
H	0.690727	0.045923	-2.99395
H	0.708836	-1.66982	-3.48332
C	-2.05666	-2.11719	-3.2362
H	-1.5141	-3.07554	-3.26671
H	-2.99914	-2.27385	-2.69246
H	-2.31085	-1.83647	-4.26889

- Cl_{c-c}

Atom	x	y	z
C	-2.65292	0.784557	0.752372
C	-1.8263	-1.85256	-0.0785
H	-2.72079	-2.37487	-0.37133
H	-1.46746	-2.0809	0.911383
C	-0.8134	-1.45831	-1.114
H	-0.25136	-0.61246	-0.72794
H	-0.08688	-2.26321	-1.25044
C	-1.39812	-1.08296	-2.48539
H	-2.19119	-0.35605	-2.31973
O	-1.60458	1.297616	0.422714
C	-4.00718	0.21077	0.887942
H	-3.96197	-0.60236	1.600048
H	-4.70087	0.955724	1.266638
H	-4.38949	-0.17807	-0.0479
C	-0.32903	-0.41723	-3.35653
H	-0.73185	-0.13191	-4.32407
H	0.062213	0.47709	-2.88191

H	0.504793	-1.09268	-3.53306
C	-1.99934	-2.29074	-3.21211
H	-1.2373	-3.04142	-3.40723
H	-2.78882	-2.76507	-2.63853
H	-2.42363	-1.99612	-4.16758

- TS 1

Atom	x	y	z
C	-1.83075	0.824508	0.066375
C	-2.37832	-1.84421	-0.22241
H	-3.3815	-1.95441	-0.62746
H	-2.14908	-2.48579	0.623182
C	-1.32813	-1.41688	-1.0667
H	-1.15875	-0.22778	-0.57697
H	-0.34265	-1.84777	-0.85947
C	-1.60664	-1.16386	-2.54239
H	-2.57359	-0.64242	-2.60792
O	-2.10285	1.925149	-0.23684
C	-3.24073	-0.21371	1.050926
H	-3.51337	-1.13867	1.558961
H	-3.03476	0.51133	1.843067
H	-4.08807	0.137727	0.460105
C	-0.53745	-0.26653	-3.16426
H	-0.7403	-0.08916	-4.22527
H	-0.49168	0.704548	-2.6612
H	0.448552	-0.73779	-3.08498
C	-1.72368	-2.4839	-3.30607
H	-0.78194	-3.04047	-3.24524
H	-2.51437	-3.11204	-2.8861
H	-1.94545	-2.30903	-4.36447

- TS 2

Atom	x	y	z
C	-2.33175	0.899019	2.474947
C	-2.79521	-1.46321	-0.75249
H	-3.84036	-1.40473	-1.06271
H	-2.52332	-2.37671	-0.22203
C	-1.77118	-0.77875	-1.60008
H	-2.0435	0.278292	-1.7383
H	-0.79463	-0.7831	-1.09332
C	-1.58451	-1.40369	-3.00153
H	-2.56233	-1.38213	-3.50338
O	-1.16305	0.798391	2.718534
C	-3.25935	0.331616	1.48073
H	-2.7939	-0.37634	0.74943

H	-4.0641	-0.18068	2.022252
H	-3.71972	1.163889	0.93398
C	-0.60144	-0.57338	-3.82536
H	-0.48611	-0.98354	-4.83409
H	-0.93742	0.464622	-3.91748
H	0.385759	-0.56791	-3.34966
C	-1.12513	-2.85593	-2.90692
H	-0.16421	-2.91732	-2.38238
H	-1.84851	-3.46862	-2.36234
H	-0.99153	-3.29095	-3.90292

- TS 3

Atom	x	y	z
C	1.84186	1.411355	0.045379
C	2.54339	-2.40756	-0.54303
H	-3.5845	-2.17483	-0.78226
H	2.37355	-2.91696	0.406107
C	1.48055	-1.53979	-1.11248
H	1.39513	-0.55737	-0.59951
H	0.49815	-2.01698	-0.97552
C	1.67642	-1.227	-2.60212
H	-2.6738	-0.77262	-2.71373
O	1.40355	2.495951	-0.18054
C	2.99585	0.892969	0.843895
H	2.73247	0.979713	1.903041
H	3.88159	1.502126	0.644091
H	3.18711	-0.16141	0.606865
C	0.63713	-0.21803	-3.08849
H	0.79276	0.035726	-4.14232
H	0.67654	0.709714	-2.50643
H	0.37154	-0.6348	-2.98933
C	1.63755	-2.50223	-3.43861
H	0.65368	-2.97812	-3.351
H	2.38761	-3.2172	-3.09047
H	1.81497	-2.28829	-4.49842

- Product 1

Atom	x	y	z
C	-0.76517	2.29228	-0.34617
C	-2.2151	-1.93655	0.035893
H	-2.76803	-2.7586	-0.43306
H	-1.7842	-2.35133	0.955518
C	-1.06523	-1.49236	-0.87198
H	-0.44738	-0.76857	-0.32304
H	-0.4172	-2.35623	-1.08014

C	-1.47211	-0.86439	-2.20899
H	-2.05573	0.041842	-1.99996
O	-0.00704	3.066421	-0.73443
C	-3.179	-0.80888	0.399646
H	-3.90963	-1.14292	1.142692
H	-2.6373	0.046332	0.814937
H	-3.73469	-0.45675	-0.47384
C	-0.22697	-0.44423	-2.98985
H	-0.49562	0.046399	-3.9312
H	0.38958	0.250426	-2.40998
H	0.388323	-1.31865	-3.23011
C	-2.33427	-1.80607	-3.04782
H	-1.80105	-2.7453	-3.23594
H	-3.27911	-2.04801	-2.5533
H	-2.57205	-1.35581	-4.01715

- Product 2

Atom	x	y	z
C	-2.5427	0.291878	0.750647
C	-0.96446	1.151424	-2.79686
H	-0.88539	2.242199	-2.73761
H	-0.89493	0.866808	-3.84999
C	0.120811	0.4852	-1.95359
H	-0.06944	0.698319	-0.89467
H	0.05575	-0.60643	-2.06508
C	1.549667	0.924359	-2.28727
H	1.596783	2.017442	-2.17275
O	-1.60631	0.695353	1.347317
C	-3.58946	-0.15857	0.083756
H	-1.95786	0.866447	-2.43871
H	-3.66066	-1.21125	-0.14957
H	-4.36856	0.528636	-0.21362
C	2.538991	0.302607	-1.30251
H	3.561384	0.641166	-1.49932
H	2.286738	0.564386	-0.26991
H	2.525154	-0.79002	-1.38633
C	1.940522	0.579839	-3.72367
H	1.861373	-0.50088	-3.88997
H	1.302599	1.082371	-4.45549
H	2.975156	0.874831	-3.92653

- Product 3

Atom	x	y	z
C	-1.38007	0.837178	1.004612
C	-2.8017	-2.8578	-0.6253

H	-3.61728	-3.31756	-1.17744
H	-2.72804	-3.10417	0.429723
H	-1.92529	-2.0402	-1.22434
H	-1.09131	0.486138	2.016373
H	-1.11465	-1.59974	-0.64144
C	-1.95421	-1.66081	-2.67679
H	-2.75587	-2.2325	-3.16459
O	-0.51967	1.016547	0.150539
C	-2.85181	1.028704	0.778437
H	-3.31343	1.526655	1.636094
H	-3.01633	1.602443	-0.13412
H	-3.318	0.042771	0.668141
C	-2.25322	-0.16618	-2.83379
H	-2.22399	0.127415	-3.88851
H	-3.24581	0.07253	-2.43965
H	-1.51709	0.430848	-2.28628
C	-0.62366	-2.02128	-3.34316
H	0.197481	-1.46478	-2.87864
H	-0.41083	-3.08979	-3.24473
H	-0.64154	-1.76969	-4.40856

- Cl_{O-H}

Atom	x	y	z
C	-2.61154	-0.28663	-0.05348
C	-1.96952	-1.64959	-0.10964
H	-2.71713	-2.39407	-0.39093
H	-1.64045	-1.92509	0.88809
C	-0.78253	-1.70182	-1.07989
H	0.02248	-1.09704	-0.67275
H	-0.40709	-2.72462	-1.13861
C	-1.13903	-1.18823	-2.46815
H	-2.03995	-0.09140	-1.92436
O	-2.68689	0.45193	-1.19997
C	-3.69473	0.01266	0.93579
H	-3.40121	-0.29587	1.93396
H	-3.90753	1.07509	0.95242
H	-4.61971	-0.50855	0.68760
C	-0.00536	-0.54802	-3.23680
H	-0.35849	-0.08935	-4.15490
H	0.49366	0.21613	-2.64964
H	0.74554	-1.29086	-3.51264
C	-2.03366	-2.08580	-3.29617
H	-1.49102	-2.97592	-3.61957
H	-2.90642	-2.41983	-2.74611
H	-2.38226	-1.57651	-4.18887

- TS(S₁)

Atom	x	y	z
C	-2.40900	-0.28921	0.58580
C	-1.55984	-1.52005	0.21084
H	-2.23860	-2.35864	0.09839
H	-0.92292	-1.75380	1.06004
C	-0.65977	-1.35508	-1.02653
H	0.02677	-0.53514	-0.83856
H	-0.04566	-2.24975	-1.11461
C	-1.36363	-1.10795	-2.36955
H	-2.03666	-0.23343	-2.25199
O	-1.67321	0.86254	0.66133
C	-3.81946	-0.06563	0.09661
H	-4.05050	-0.68248	-0.76477
H	-4.54099	-0.30063	0.87336
H	-3.96797	0.97080	-0.18671
C	-0.33392	-0.74655	-3.44465
H	-0.81537	-0.54409	-4.39677
H	0.23354	0.13586	-3.16556
H	0.37082	-1.56021	-3.59764
C	-2.20642	-2.30448	-2.82312
H	-1.58280	-3.18453	-2.95978
H	-2.98218	-2.56012	-2.10915
H	-2.69390	-2.09662	-3.77091

- TS 4

Atom	x	y	z
C	-1.57310	0.19790	0.37012
C	-1.23766	1.38487	-0.25396
H	-0.70740	2.12904	0.329786
H	-1.83514	1.76101	-1.08006
C	0.58320	0.67168	-1.12663
H	0.13023	0.15463	-1.97082
H	0.86178	1.70292	-1.33078
C	1.30671	-0.06967	-0.18009
H	0.27171	-0.18667	0.806427
O	-0.75844	-0.22226	1.321987
C	-2.52358	-0.80849	-0.21276
H	-3.07966	-1.29996	0.590041
H	-3.23243	-0.34091	-0.90095
H	-1.96937	-1.58795	-0.75086
C	1.53596	-1.55013	-0.42907
H	1.68882	-2.09550	0.507608
H	0.68183	-1.99937	-0.94425
H	2.42605	-1.70416	-1.05227
C	2.38199	0.63761	0.621253

H	2.09226	1.66962	0.843064
H	2.56700	0.12962	1.573317
H	3.33072	0.66322	0.070698

- TS 5

Atom	x	y	z
C	-3.26594	-0.34602	0.25725
C	-2.60459	-0.40791	-1.1288
H	-2.28423	0.61310	-1.38347
H	-3.37108	-0.69889	-1.8526
C	-1.38492	-1.34499	-1.23795
H	-0.62344	-1.04457	-0.51272
H	-1.69368	-2.36360	-0.97607
C	-0.70153	-1.42347	-2.62632
H	-4.10293	1.31917	-0.25294
O	-4.32036	0.56672	0.330475
C	-3.61575	-1.61481	0.972916
H	-2.71970	-2.21491	1.160822
H	-4.07912	-1.37776	1.934702
H	-4.32111	-2.22532	0.393943
C	0.42730	-2.40878	-2.74708
H	0.80322	-2.71631	-1.76298
H	0.11545	-3.32307	-3.27092
H	1.27187	-1.99039	-3.308
C	-0.75749	-0.25607	-3.56711
H	-0.11234	0.57077	-3.23482
H	-0.41955	-0.55077	-4.56655
H	-1.77292	0.14448	-3.66638

- Product 4

Atom	x	y	z
C	-2.37534	-0.69941	-0.31820
C	-2.37652	-2.02849	-0.06151
H	-1.54294	-2.67486	-0.33410
H	-3.22181	-2.49354	0.43838
C	1.05512	-2.167141	-2.41263
H	1.98441	-1.72656	-2.04867
H	0.82127	-3.17196	-2.05735
C	0.25354	-1.51737	-3.29646
H	-0.59417	-0.65294	-1.22209
O	-1.30914	-0.02649	-0.96505
C	-3.47016	0.27591	0.03054
H	-4.29902	-0.24106	0.52956
H	-3.08218	1.05813	0.69677
H	-3.84708	0.76548	-0.87760

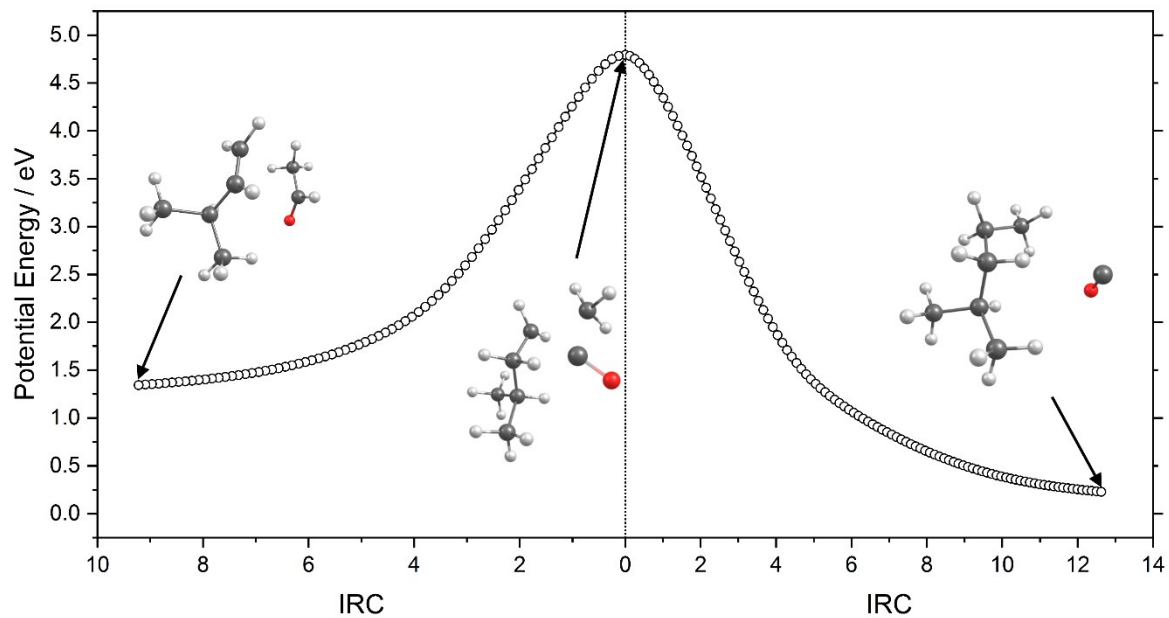
C	0.57874	-0.12178	-3.80926
H	-0.20537	0.58845	-3.50707
H	1.54008	0.23233	-3.41226
H	0.63399	-0.11571	-4.90850
C	-1.03642	-2.13104	-3.82087
H	-1.01528	-2.19666	-4.91937
H	-1.19072	-3.14033	-3.41518
H	-1.89936	-1.50871	-3.53961

- Product 5

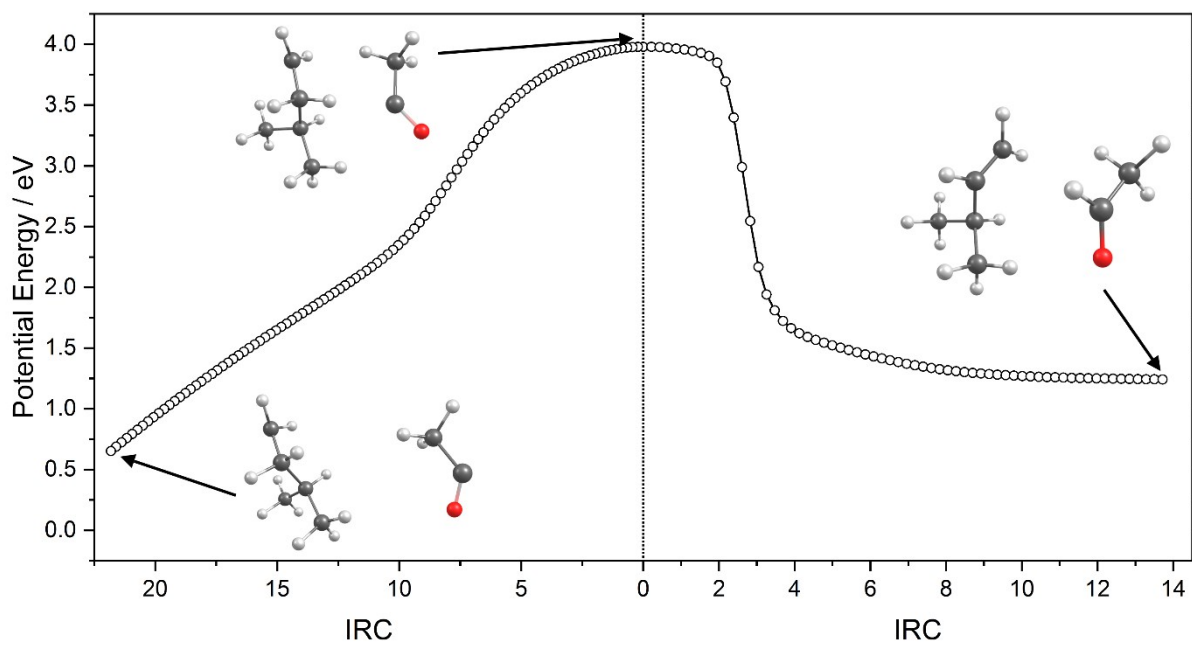
Atom	x	y	z
C	-2.75068	-0.76943	-0.71474
C	-2.60841	-2.17650	-0.06871
H	-3.28361	-2.88498	-0.56397
H	-2.74944	-2.24157	1.018184
C	-1.14517	-2.24762	-0.63299
H	-0.40288	-1.89842	0.100135
H	-0.80664	-3.20495	-1.0512
C	-1.51849	-1.11610	-1.6672
H	-4.14588	0.29409	-1.72886
O	-4.06260	-0.61303	-1.36087
C	-2.51240	0.38344	0.269321
H	-1.58998	0.23354	0.846631
H	-2.43072	1.34627	-0.25902
H	-3.35896	0.43411	0.967719
C	-0.46419	-0.02817	-1.9244
H	-0.88420	0.79757	-2.52114
H	-0.07298	0.38786	-0.9855
H	0.38285	-0.45155	-2.48594
C	-2.00300	-1.72371	-3.00072
H	-1.14686	-2.15848	-3.53931
H	-2.75359	-2.50705	-2.83779
H	-2.45932	-0.95212	-3.63768

Figure S3: Intrinsic reaction paths associated with the various transition states.

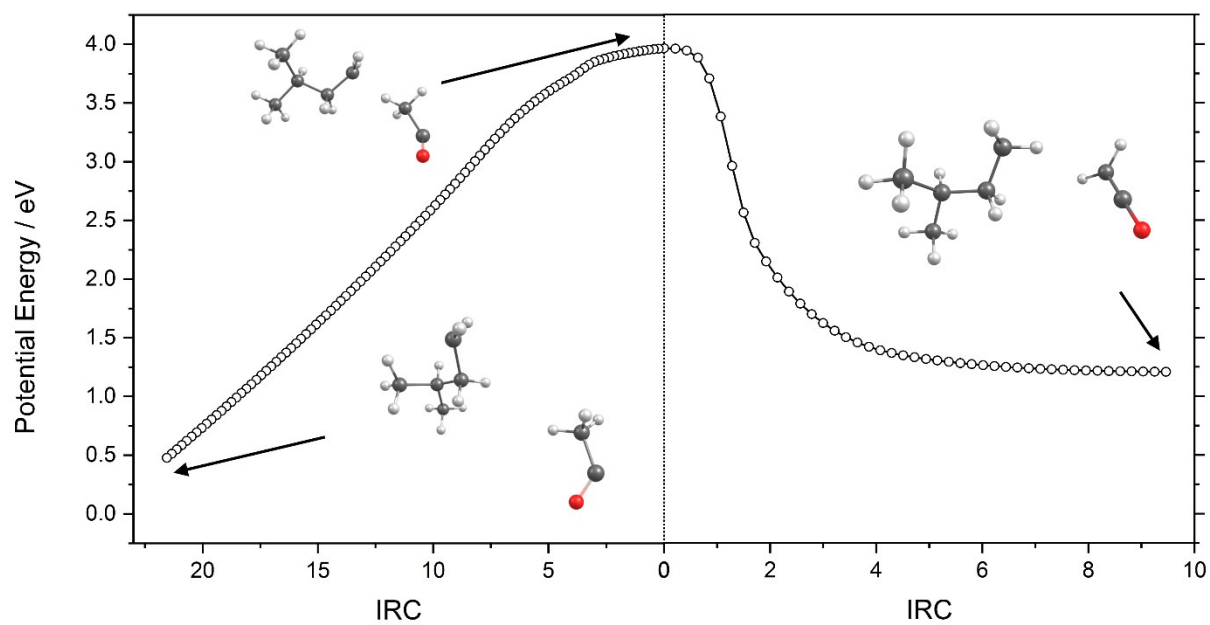
Reaction 1



Reaction 2



Reaction 3



Reaction 4

