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Experimental and computational kinetic investigations for the reactions of Cl atoms with unsaturated ketones in gas phase

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Table S-1-1: Optimized temperature and pressure conditions during GC analysis.

Inlet	temperature	160°C
	pressure	24.05 PSI
Column (HP Plot Q)	flow	1.96 ml min^{-1}
	pressure	24.05 PSI
Oven	temperature	220 °C
	total run time	6 minutes
Detector (FID)	temperature	240 °C

Table S-2: Optimized geometries of the reactant, pre-reactive complexes, transition states and products for the reaction of Cl atoms with 4-hexen-3-one obtained at MP2/6-311++G(d,p) level of theory.

Table S-2-1: Optimized parameters of 4-hexen-3-one.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.581029	0.539883	-0.00019
2	8	0	1.246095	1.57039	-0.000073
3	6	0	-0.90185	0.626268	0.000025
4	1	0	-1.29409	1.642654	-0.000005
5	6	0	-1.73961	-0.42907	0.00025
6	1	0	-1.32682	-1.43732	0.000282
7	6	0	-3.23424	-0.31767	0.000233
8	1	0	-3.55312	0.72749	0.000015
9	1	0	-3.65687	-0.81227	0.881509
10	1	0	-3.65682	-0.81257	-0.880893
11	6	0	1.244458	-0.83059	-0.001184
12	1	0	0.884886	-1.38052	-0.879659
13	1	0	0.882679	-1.38303	0.874794
14	6	0	2.766844	-0.74598	0.000895
15	1	0	3.203408	-1.74846	0.000005
16	1	0	3.125246	-0.20675	-0.878495
17	1	0	3.122919	-0.20939	0.882859

Table S-2-2: Optimized parameters of pre-reactive complex RC1a.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.151513	-0.435593	0.482926
2	8	0	-1.843712	-0.562184	1.457935
3	6	0	0.286611	-0.932888	0.538826
4	1	0	0.671791	-1.079985	1.548027
5	6	0	0.901311	-1.389257	-0.458597
6	1	0	0.449148	-1.278402	-1.445679
7	6	0	2.206456	-2.117312	-0.41517
8	1	0	2.609694	-2.150202	0.597069
9	1	0	2.93417	-1.648704	-1.086297
10	1	0	2.055625	-3.140793	-0.774312
11	6	0	-1.683483	0.135362	-0.81953
12	1	0	-1.741112	-0.704271	-1.524646
13	1	0	-0.943822	0.833338	-1.222557
14	6	0	-3.051455	0.792235	-0.659661
15	1	0	-3.408991	1.165913	-1.623107
16	1	0	-3.777251	0.079996	-0.264159
17	1	0	-2.993374	1.629875	0.038907
18	17	0	1.990956	2.027966	0.122383

Table S-2-3: Optimized parameters of transition state TS1a.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.93723	-0.44786	0.493372
2	8	0	-1.55542	-0.69642	1.500794
3	6	0	0.578175	-0.48671	0.554144
4	1	0	0.978948	-0.50671	1.564367
5	6	0	1.345527	-0.88498	-0.48859
6	1	0	0.887938	-0.94875	-1.4734
7	6	0	2.790555	-1.22289	-0.38796
8	1	0	3.168139	-1.06271	0.622522
9	1	0	3.364803	-0.61234	-1.09149
10	1	0	2.936413	-2.27193	-0.67053
11	6	0	-1.59927	-0.15293	-0.83704
12	1	0	-1.43237	-1.03061	-1.47711
13	1	0	-1.076	0.68569	-1.30572
14	6	0	-3.09165	0.124459	-0.68903
15	1	0	-3.53763	0.321558	-1.66717
16	1	0	-3.60209	-0.72517	-0.23198
17	1	0	-3.25433	0.995137	-0.04978
18	17	0	1.146641	1.714861	0.112032

Table S-2-4: Optimized parameters of transition state TS2a.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.075995	-0.516091	0.449314
2	8	0	-1.742701	-0.756891	1.413188
3	6	0	0.405412	-0.845798	0.474759
4	1	0	0.760081	-1.253835	1.418376
5	6	0	1.269218	-0.638371	-0.555575
6	1	0	0.871634	-0.290224	-1.505447
7	6	0	2.67002	-1.162353	-0.570894
8	1	0	3.037011	-1.33706	0.441788
9	1	0	3.338894	-0.469944	-1.084496
10	1	0	2.671631	-2.110724	-1.121387
11	6	0	-1.639453	0.078703	-0.827187
12	1	0	-1.470734	-0.65479	-1.626962
13	1	0	-1.038449	0.960137	-1.077023
14	6	0	-3.117899	0.425771	-0.704134
15	1	0	-3.48836	0.839218	-1.645623
16	1	0	-3.703663	-0.460253	-0.452142
17	1	0	-3.272561	1.161988	0.08711
18	17	0	1.480489	1.507026	0.333094

Table S-2-5: Optimized parameters of transition state TS1.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.213756	-1.280299	-0.22397
2	8	0	-0.208594	-1.999491	-1.10767
3	6	0	1.571279	-0.672258	-0.3108
4	1	0	2.234135	-1.151681	-1.02934
5	6	0	1.939464	0.425545	0.330613
6	1	0	1.239737	0.91371	1.007251
7	6	0	3.269997	1.093316	0.176117
8	1	0	3.914083	0.544352	-0.51406
9	1	0	3.769682	1.169059	1.147594
10	1	0	3.135357	2.113487	-0.19837
11	6	0	-0.641906	-1.052011	1.026222
12	1	0	-0.255167	-0.269497	1.681294
13	1	0	-0.568866	-1.998752	1.583689
14	6	0	-2.083889	-0.809669	0.680574
15	1	0	-2.767543	-0.658249	1.514874
16	1	0	-2.057116	0.426249	0.128945
17	1	0	-2.477249	-1.399049	-0.14631
18	17	0	-1.771206	1.769326	-0.37569

Table S-2-6: Optimized parameters of transition state TS2.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.2142	-1.28056	-0.22369
2	8	0	0.207869	-2.00003	-1.1073
3	6	0	-1.57165	-0.67235	-0.31039
4	1	0	-2.23474	-1.15183	-1.02868
5	6	0	-1.93935	0.425923	0.330526
6	1	0	-1.23934	0.914188	1.006794
7	6	0	-3.26966	1.094108	0.175874
8	1	0	-3.91401	0.545094	-0.51402
9	1	0	-3.13468	2.114074	-0.19905
10	1	0	-3.76924	1.17044	1.147362
11	6	0	0.641822	-1.05193	1.026193
12	1	0	0.568819	-1.99846	1.584012
13	1	0	0.255385	-0.26913	1.681096
14	6	0	2.083748	-0.80991	0.679998
15	1	0	2.767716	-0.65866	1.514077
16	1	0	2.476651	-1.39958	-0.1469
17	1	0	2.057232	0.425603	0.128554
18	17	0	1.771706	1.769225	-0.37564

Table S-2-7: Optimized parameters of transition state TS3.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.897202	1.08465	-0.042735
2	8	0	-0.819893	2.292432	-0.054908
3	6	0	-2.232197	0.401567	-0.033306
4	1	0	-3.077987	1.085266	-0.084428
5	6	0	-2.407657	-0.903528	0.032148
6	1	0	-1.539713	-1.560763	0.084479
7	6	0	-3.74048	-1.585335	0.029637
8	1	0	-4.556678	-0.862118	-0.024655
9	1	0	-3.858037	-2.189001	0.935503
10	1	0	-3.811051	-2.267243	-0.824149
11	6	0	0.361741	0.212976	-0.060375
12	1	0	0.412286	-0.286945	-1.034886
13	1	0	0.274948	-0.57054	0.698305
14	6	0	1.592343	1.043885	0.179794
15	1	0	2.612767	0.116277	0.093307
16	1	0	1.870401	1.746115	-0.602776
17	1	0	1.734992	1.421973	1.190429
18	17	0	3.555172	-0.970457	-0.036638

Table S-2-8: Optimized parameters of transition state TS4.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.125275	-1.274754	-0.28786
2	8	0	-0.616331	-2.058069	-1.02651
3	6	0	1.355265	-1.052035	-0.16643
4	1	0	1.977072	-1.850265	-0.56348
5	6	0	1.852937	0.074492	0.269619
6	1	0	1.17993	0.85267	0.628486
7	6	0	3.307878	0.412341	0.32217
8	1	0	3.922718	-0.413017	-0.0395
9	1	0	3.593923	0.653518	1.350414
10	1	0	3.505398	1.300742	-0.28503
11	6	0	-1.022223	-0.426223	0.652253
12	1	0	-0.997653	0.88894	0.167771
13	1	0	-0.55406	-0.275835	1.627132
14	6	0	-2.431819	-0.900872	0.784536
15	1	0	-3.014744	-0.227644	1.416104
16	1	0	-2.906047	-0.993545	-0.19415
17	1	0	-2.416689	-1.898271	1.238787
18	17	0	-0.99881	2.201739	-0.38707

Table S-2-9: Optimized parameters of Transition state TS5.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.303671	-1.39152	-0.06322
2	8	0	0.794456	-2.4597	-0.29174
3	6	0	-1.132259	-1.0892	-0.34564
4	1	0	-1.613869	-1.76455	-1.04954
5	6	0	-1.799292	-0.1554	0.298758
6	1	0	-1.277243	0.476454	1.015265
7	6	0	-3.257166	0.128202	0.130938
8	1	0	-3.709314	-0.53061	-0.61283
9	1	0	-3.392959	1.169818	-0.17785
10	1	0	-3.777761	0.002145	1.085759
11	6	0	1.187184	-0.30256	0.564076
12	1	0	1.038387	-0.20755	1.64423
13	1	0	0.753202	0.928287	0.124144
14	6	0	2.626922	-0.31961	0.125296
15	1	0	3.17388	0.520944	0.556577
16	1	0	3.084135	-1.25677	0.461662
17	1	0	2.704286	-0.28268	-0.96385
18	17	0	0.534544	2.317805	-0.23594

Table S-2-10: Optimized parameters of Transition State TS6.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.122955	-0.85452	-0.20024
2	8	0	1.756456	-1.20466	-1.16975
3	6	0	-0.22434	-1.50104	0.080487
4	1	0	-0.2072	-2.59507	0.123714
5	6	0	-1.3524	-0.89161	0.180965
6	1	0	-1.29069	0.561917	-0.02782
7	6	0	-2.78273	-1.22777	0.349552
8	1	0	-2.88495	-2.31425	0.460884
9	1	0	-3.35624	-0.90047	-0.52143
10	1	0	-3.19054	-0.73508	1.235994
11	6	0	1.618787	0.146426	0.819038
12	1	0	1.762592	-0.42264	1.748848
13	1	0	0.810181	0.853334	1.027302
14	6	0	2.895551	0.85624	0.387756
15	1	0	3.225757	1.547629	1.167168
16	1	0	3.694001	0.136979	0.193594
17	1	0	2.724502	1.422748	-0.53061
18	17	0	-1.3533	1.936222	-0.30735

Table S-2-11: Optimized parameters of Transition State TS7.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.073568	-0.288956	-0.178647
2	8	0	1.168865	-1.36879	-0.679157
3	6	0	-0.248064	0.438654	-0.057724
4	1	0	-1.361273	-0.611024	0.10387
5	6	0	-0.603489	1.674562	-0.113172
6	1	0	0.198707	2.421404	-0.146436
7	6	0	-2.00301	2.217361	-0.126094
8	1	0	-2.739098	1.416771	-0.066868
9	1	0	-2.160903	2.789865	-1.044827
10	1	0	-2.134645	2.901211	0.717747
11	6	0	2.246997	0.477494	0.418418
12	1	0	2.039771	0.567004	1.49229
13	1	0	2.233166	1.498929	0.020239
14	6	0	3.581077	-0.210906	0.15445
15	1	0	4.392488	0.348585	0.627184
16	1	0	3.572532	-1.226714	0.553348
17	1	0	3.777691	-0.275789	-0.917802
18	17	0	-2.438343	-1.454657	0.206537

Table S-2-12: Optimized parameters of Transition State TS8.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.789195	-0.482782	-0.24481
2	8	0	-2.670488	-1.196373	-0.64266
3	6	0	-0.3577	-0.987245	-0.24695
4	1	0	-0.142641	-1.719276	-1.02398
5	6	0	0.548195	-0.658794	0.649512
6	1	0	0.317295	0.065482	1.427579
7	6	0	1.906991	-1.214674	0.655448
8	1	0	2.642794	-0.278147	0.197064
9	1	0	2.085563	-2.029042	-0.04628
10	1	0	2.360601	-1.365127	1.63517
11	6	0	-2.023513	0.93746	0.233419
12	1	0	-1.40528	1.590034	-0.39636
13	1	0	-1.61216	1.0289	1.246113
14	6	0	-3.492847	1.338527	0.195908
15	1	0	-3.612409	2.372641	0.528847
16	1	0	-3.88961	1.246571	-0.81706
17	1	0	-4.086881	0.689992	0.843197
18	17	0	3.526767	0.84553	-0.34754

Table S-2-13: Optimized parameters of Transition State TS9.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.787045	-0.48282	-0.24738
2	8	0	2.663302	-1.19121	-0.66391
3	6	0	0.355424	-0.98819	-0.23877
4	1	0	0.139876	-1.73047	-1.00584
5	6	0	-0.549353	-0.6484	0.65439
6	1	0	-0.318153	0.085345	1.423393
7	6	0	-1.906864	-1.20743	0.670281
8	1	0	-2.086741	-2.02871	-0.02304
9	1	0	-2.645416	-0.27776	0.20373
10	1	0	-2.358645	-1.34692	1.652547
11	6	0	2.027974	0.930913	0.247168
12	1	0	1.632703	1.006724	1.267615
13	1	0	1.401088	1.593408	-0.36341
14	6	0	3.496934	1.331974	0.193785
15	1	0	3.621731	2.361017	0.540228
16	1	0	4.100336	0.67392	0.822531
17	1	0	3.8787	1.255136	-0.82619
18	17	0	-3.525815	0.842454	-0.35631

Table S-2-14: Optimized parameters of Transition State TS10.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.78928	-0.48287	-0.24476
2	8	0	-2.67072	-1.19637	-0.64245
3	6	0	-0.35785	-0.9875	-0.2469
4	1	0	-0.14291	-1.71978	-1.02373
5	6	0	0.548133	-0.65879	0.649368
6	1	0	0.317296	0.065729	1.427236
7	6	0	1.906919	-1.21468	0.655368
8	1	0	2.085548	-2.02901	-0.04638
9	1	0	2.360491	-1.36512	1.635108
10	1	0	2.642787	-0.27812	0.196997
11	6	0	-2.02331	0.937469	0.233338
12	1	0	-1.40498	1.589862	-0.39654
13	1	0	-1.61187	1.028935	1.245994
14	6	0	-3.49257	1.338814	0.195862
15	1	0	-3.61192	2.372996	0.528671
16	1	0	-3.88941	1.246797	-0.81707
17	1	0	-4.08669	0.69048	0.843274
18	17	0	3.526776	0.845495	-0.34751

Table S-2-15: Optimized parameters of product P1a.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.822969	-0.277692	0.524851
2	8	0	-1.356744	-0.379237	1.61537
3	6	0	0.683614	-0.024684	0.446027
4	1	0	1.072484	-0.021734	1.465922
5	6	0	1.42425	-0.95306	-0.427488
6	1	0	1.009898	-1.162621	-1.408435
7	6	0	2.85989	-1.253165	-0.157554
8	1	0	3.022273	-1.48207	0.900696
9	1	0	3.489088	-0.383724	-0.40066
10	1	0	3.211197	-2.09592	-0.756815
11	6	0	-1.583854	-0.422794	-0.778028
12	1	0	-1.362146	-1.430132	-1.156091
13	1	0	-1.176982	0.280532	-1.511965
14	6	0	-3.087974	-0.239376	-0.59976
15	1	0	-3.602935	-0.374558	-1.554291
16	1	0	-3.483167	-0.959403	0.119119
17	1	0	-3.309018	0.762888	-0.223914
18	17	0	0.890913	1.701486	-0.143812

Table S-2-16: Optimized parameters of product P2a.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.214862	0.623243	-0.280282
2	8	0	-1.977717	1.263201	-0.948326
3	6	0	0.238793	0.941454	-0.28777
4	1	0	0.542544	1.73234	-0.969566
5	6	0	1.281576	0.20715	0.466678
6	1	0	0.869656	-0.267993	1.358129
7	6	0	2.478257	1.072139	0.828206
8	1	0	2.921336	1.502201	-0.073629
9	1	0	3.237405	0.481093	1.345189
10	1	0	2.152916	1.883454	1.487251
11	6	0	-1.661332	-0.527809	0.606742
12	1	0	-1.396623	-0.266462	1.640184
13	1	0	-1.051952	-1.403316	0.349222
14	6	0	-3.150216	-0.822893	0.479224
15	1	0	-3.43118	-1.650457	1.135768
16	1	0	-3.74095	0.055884	0.744488
17	1	0	-3.400853	-1.089569	-0.549476
18	17	0	1.840361	-1.17897	-0.573985

Table S-2-17: Optimized parameters of product P1.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.646914	0.532025	0.016519
2	8	0	1.314771	1.559352	0.001344
3	6	0	-0.833397	0.622686	-0.01116
4	1	0	-1.218672	1.641362	-0.03103
5	6	0	-1.683243	-0.427788	-0.00845
6	1	0	-1.283258	-1.440708	0.012612
7	6	0	-3.17637	-0.298166	-0.02126
8	1	0	-3.482456	0.750629	-0.04207
9	1	0	-3.610466	-0.771277	0.866262
10	1	0	-3.600002	-0.803618	-0.89588
11	6	0	1.298816	-0.847616	0.091188
12	1	0	0.824361	-1.503579	-0.64983
13	1	0	1.025722	-1.274867	1.070885
14	6	0	2.777844	-0.819911	-0.093
15	1	0	3.322732	-1.748297	-0.20239
16	1	0	3.320483	0.108164	0.017679

Table S-2-18: Optimized parameters of product P2.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.64691	0.532025	0.016518
2	8	0	-1.31477	1.559352	0.001345
3	6	0	0.833396	0.622685	-0.01116
4	1	0	1.218672	1.641361	-0.03103
5	6	0	1.683243	-0.42779	-0.00845
6	1	0	1.283258	-1.44071	0.012614
7	6	0	3.17637	-0.29817	-0.02126
8	1	0	3.482455	0.750629	-0.04208
9	1	0	3.600002	-0.80362	-0.89588
10	1	0	3.610465	-0.77128	0.866264
11	6	0	-1.29882	-0.84762	0.091189
12	1	0	-1.02572	-1.27487	1.070887
13	1	0	-0.82436	-1.50358	-0.64983
14	6	0	-2.77784	-0.81991	-0.093
15	1	0	-3.32273	-1.7483	-0.20239
16	1	0	-3.32048	0.108163	0.017675

Table S-2-19: Optimized parameters of product P3.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.606183	0.552459	-0.03633
2	8	0	1.201533	1.558448	0.206862
3	6	0	-0.88386	0.548488	-0.299113
4	1	0	-1.26262	1.435647	-0.802957
5	6	0	-1.68434	-0.37736	0.166937
6	1	0	-1.2538	-1.228339	0.697602
7	6	0	-3.17871	-0.36676	0.050629
8	1	0	-3.52408	0.50668	-0.506484
9	1	0	-3.63579	-0.354689	1.045245
10	1	0	-3.52601	-1.273355	-0.455526
11	6	0	1.286894	-0.763955	-0.141903
12	1	0	0.717816	-1.639449	-0.432558
13	6	0	2.760126	-0.829955	0.03032
14	1	0	3.089303	-1.837129	0.294251
15	1	0	3.262028	-0.543244	-0.904883
16	1	0	3.08315	-0.111209	0.787175

Table S-2-20: Optimized parameters of product P4.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.606016	0.55272	-0.03581
2	8	0	1.201228	1.558917	0.206826
3	6	0	-0.88366	0.548093	-0.29932
4	1	0	-1.26252	1.4347	-0.80413
5	6	0	-1.68426	-0.37756	0.166961
6	1	0	-1.25394	-1.22821	0.698349
7	6	0	-3.17862	-0.3668	0.05035
8	1	0	-3.52321	0.502237	-0.51408
9	1	0	-3.63546	-0.3455	1.044968
10	1	0	-3.527	-1.27742	-0.44769
11	6	0	1.28686	-0.76392	-0.14096
12	1	0	0.718092	-1.63946	-0.43212
13	6	0	2.760298	-0.82991	0.029976
14	1	0	3.088	-1.83408	0.307136
15	1	0	3.26093	-0.55813	-0.91042
16	1	0	3.085487	-0.10128	0.776177

Table S-2-21: Optimized parameters of product P5.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.605949	0.55341	-0.03617
2	8	0	1.199665	1.560352	0.207301
3	6	0	-0.883833	0.547741	-0.29997
4	1	0	-1.263231	1.433579	-0.80567
5	6	0	-1.683935	-0.378014	0.166877
6	1	0	-1.253187	-1.228027	0.698907
7	6	0	-3.178353	-0.367772	0.05065
8	1	0	-3.522899	0.498149	-0.5186
9	1	0	-3.63457	-0.340296	1.045418
10	1	0	-3.527372	-1.281155	-0.44176
11	6	0	1.287621	-0.762498	-0.14121
12	1	0	0.718797	-1.637696	-0.43337
13	6	0	2.760859	-0.830476	0.030437
14	1	0	3.083079	-1.828377	0.33587
15	1	0	3.262187	-0.590615	-0.91829
16	1	0	3.090024	-0.082725	0.755367

Table S-2-22: Optimized parameters of product P6.

Center Number	Atomic Number	Atomic Number	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.589786	0.585521	-0.05047
2	8	0	1.28867	1.552997	0.104695
3	6	0	-0.916542	0.724635	-0.12853
4	1	0	-1.27405	1.747084	-0.28749
5	6	0	-1.742214	-0.25042	0.044381
6	6	0	-3.188601	-0.50929	0.095136
7	1	0	-3.469971	-1.23616	-0.67132
8	1	0	-3.748836	0.420151	-0.07291
9	1	0	-3.467293	-0.91913	1.069413
10	6	0	1.150295	-0.81628	-0.21369
11	1	0	0.970819	-1.09273	-1.26109
12	1	0	0.538885	-1.50126	0.38482
13	6	0	2.629662	-0.90957	0.138623
14	1	0	2.998518	-1.92536	-0.02756
15	1	0	3.214175	-0.2176	-0.47048
16	1	0	2.794073	-0.64658	1.186361

Table S-2-23: Optimized parameters of product P7.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.581459	0.548416	-0.07474
2	8	0	1.142664	1.588813	0.107447
3	6	0	-0.90895	0.443375	-0.23069
4	6	0	-1.81595	-0.37383	0.178764
5	1	0	-1.49426	-1.27987	0.706528
6	6	0	-3.3	-0.20821	0.000336
7	1	0	-3.5263	0.710447	-0.54168
8	1	0	-3.79184	-0.17922	0.977055
9	1	0	-3.70618	-1.06181	-0.55074
10	6	0	1.305528	-0.78623	-0.19187
11	1	0	1.11917	-1.14499	-1.21214
12	1	0	0.80719	-1.50393	0.47129
13	6	0	2.795239	-0.6761	0.107969
14	1	0	3.280361	-1.64773	-0.01772
15	1	0	3.267689	0.044226	-0.56233
16	1	0	2.958868	-0.33216	1.131537

Table S-2-24: Optimized parameters of product P8.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.51786	0.558781	0.000048
2	8	0	1.168345	1.567285	0.000003
3	6	0	-0.976887	0.624113	-0.000132
4	1	0	-1.379834	1.634383	0.000031
5	6	0	-1.832715	-0.464986	-0.000318
6	1	0	-1.407722	-1.465759	-0.000745
7	6	0	-3.201898	-0.349166	0.000113
8	1	0	-3.675156	0.626693	0.000531
9	1	0	-3.841937	-1.222563	-0.00005
10	6	0	1.165945	-0.820003	0.000449
11	1	0	0.79277	-1.363668	-0.876504
12	1	0	0.793472	-1.362655	0.878342
13	6	0	2.687945	-0.749219	-0.000228
14	1	0	3.115404	-1.755553	0.000428
15	1	0	3.047025	-0.213883	-0.881183
16	1	0	3.04772	-0.212399	0.879533

Table S-2-25: Optimized parameters of product P9.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.51786	0.558779	0.000042
2	8	0	-1.16835	1.567283	0.000008
3	6	0	0.976889	0.624112	-0.00014
4	1	0	1.379836	1.634381	0.000019
5	6	0	1.832721	-0.46499	-0.00032
6	1	0	1.40773	-1.46576	-0.00072
7	6	0	3.201899	-0.34916	0.00012
8	1	0	3.675154	0.626697	0.000552
9	1	0	3.841943	-1.22256	-3.7E-05
10	6	0	-1.16595	-0.82	0.000428
11	1	0	-0.79346	-1.36268	0.878299
12	1	0	-0.7928	-1.36365	-0.87655
13	6	0	-2.68795	-0.74922	-0.00021
14	1	0	-3.11541	-1.75555	0.000428
15	1	0	-3.0477	-0.21242	0.879572
16	1	0	-3.04705	-0.21386	-0.88114

Table S-2-26: Optimized parameters of product P10.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.513137	0.536496	-3.7E-05
2	8	0	1.174999	1.573703	-8.7E-05
3	6	0	-0.964834	0.623313	0.000071
4	1	0	-1.363819	1.635967	0.000319
5	6	0	-1.808205	-0.446386	-5.9E-05
6	1	0	-1.384251	-1.452386	-0.00033
7	6	0	-3.277903	-0.329916	0.000053
8	1	0	-3.83192	-0.378452	-0.9293
9	1	0	-3.831817	-0.378291	0.929469
10	6	0	1.182477	-0.830318	-8.3E-05
11	1	0	0.825653	-1.384039	-0.87738
12	1	0	0.82547	-1.384221	0.877024
13	6	0	2.704671	-0.738379	0.000115
14	1	0	3.145559	-1.738878	0.000075
15	1	0	3.059637	-0.198972	-0.8806
16	1	0	3.059435	-0.199206	0.881059

Table S-3: Vibrational frequencies for the reactant, pre-reactive complexes, transition states and products for the reaction of Cl atom with 4-hexen-3-one obtained at MP2/6-311++G(d, p) level of theory.

Table S-3-1: Normal mode frequencies of R1, RC1a, TS1a, TS2a, TS1 and TS2 (cm^{-1}).

R1	RC1a	TS1a	TS2a	TS1	TS2
41.7	43.5	-396.1	-451.6	-1043.4	-1043.5
76.0	65.4	39.8	35.0	26.2	26.2
157.3	112.9	67.3	58.3	50.6	50.6
158.8	145.6	141.8	119.6	92.8	92.8
191.7	158.8	146.4	155.9	124.5	124.5
230.0	168.4	164.9	189.2	165.2	165.2
278.0	217.5	171.7	213.3	221.2	221.2
359.9	251.4	227.0	237.7	228.4	228.4
498.1	274.1	257.0	265.5	289.9	289.9
524.7	357.8	275.4	277.3	357.3	357.3
638.8	476.5	357.3	363.0	399.6	399.6
754.1	525.6	481.5	493.4	506.1	506.1
782.8	612.2	540.1	528.3	517.8	517.8
837.7	641.0	657.8	642.9	564.9	564.9
958.9	784.0	778.2	761.7	654.3	654.3
994.9	817.5	795.1	781.7	771.2	771.2
1021.3	953.0	848.8	850.2	796.5	796.5
1061.8	975.5	954.8	953.2	863.8	863.8
1089.4	1007.0	1022.7	1016.5	972.5	972.5
1100.7	1022.6	1058.2	1024.9	985.5	985.5
1139.7	1090.3	1093.2	1082.4	997.4	997.4
1232.4	1099.4	1105.8	1101.1	1036.6	1036.6
1288.1	1144.3	1108.3	1107.9	1059.2	1059.2
1301.1	1209.1	1153.6	1148.0	1092.7	1092.7
1331.7	1286.2	1225.9	1215.8	1108.2	1108.2
1393.9	1289.5	1287.2	1292.2	1147.5	1147.5
1423.7	1321.5	1296.4	1300.7	1173.7	1173.7
1429.8	1391.7	1351.1	1317.0	1237.3	1237.3
1478.9	1414.6	1393.9	1393.8	1265.7	1265.7
1492.1	1430.0	1415.9	1418.8	1308.3	1308.3
1506.9	1477.2	1429.5	1430.8	1377.5	1377.5
1511.3	1482.3	1473.8	1472.6	1398.6	1398.6
1517.5	1488.7	1482.8	1483.2	1422.4	1422.4
1692.0	1512.9	1494.6	1498.5	1460.0	1460.0
1723.3	1517.6	1514.5	1511.6	1468.7	1468.7
3066.3	1631.2	1517.7	1517.4	1493.3	1493.3

3071.7	1688.9	1693.3	1606.0	1506.1	1506.1
3086.8	3066.2	2234.0	2316.0	1907.0	1907.0
3118.6	3068.4	3066.1	3070.9	3056.7	3056.7
3140.1	3087.7	3073.1	3076.5	3070.8	3070.8
3168.5	3127.7	3089.2	3090.7	3144.9	3144.9
3175.0	3142.9	3141.4	3131.4	3148.2	3148.2
3183.6	3176.8	3151.2	3165.8	3161.8	3161.8
3188.3	3180.6	3178.7	3180.9	3172.5	3172.5
3193.9	3185.2	3188.3	3189.2	3179.0	3179.0
	3199.4	3196.8	3199.0	3203.3	3203.3
	3203.3	3221.1	3221.0	3252.4	3252.4
	6294.3	3230.6	3230.5	5369.4	5369.0

Table S-3-2: Normal mode frequencies of TS3, TS4, TS5, TS6 and TS7 (cm^{-1}).

TS3	TS4	TS5	TS6	TS7
-999.1	-1191.3	-1073.6	-603.5	-371.1
31.3	38.5	26.8	31.9	26.3
45.3	70.0	69.6	44.9	60.4
51.0	91.0	92.8	99.2	72.7
66.6	133.3	142.8	126.0	126.7
161.5	165.6	166.0	165.6	145.3
189.7	186.4	191.3	175.1	156.4
217.7	206.1	216.2	221.5	221.0
224.8	238.6	229.2	252.6	233.4
354.6	276.6	270.1	266.3	261.6
385.5	363.0	351.8	297.1	335.1
504.2	449.8	421.4	462.9	462.7
543.5	514.7	519.2	516.0	518.1
556.7	608.5	553.2	600.0	578.2
652.5	659.9	685.0	657.4	587.9
777.6	759.1	766.5	762.4	733.6
784.4	790.0	811.7	794.1	795.3
869.2	848.5	884.0	849.4	818.4
905.6	929.4	943.1	869.3	865.6
973.0	966.9	966.8	906.7	955.4
975.4	1004.9	1013.6	990.0	1021.8
1068.7	1038.3	1044.1	1024.7	1067.0
1089.1	1091.5	1081.4	1084.5	1104.6
1100.2	1118.9	1119.7	1094.0	1128.8
1130.3	1145.3	1142.2	1105.7	1134.5
1132.5	1156.8	1156.1	1154.5	1137.0
1173.8	1167.7	1166.2	1183.3	1284.8
1246.2	1219.7	1232.4	1252.0	1297.9
1296.1	1308.2	1308.0	1294.8	1362.1
1306.6	1374.0	1357.6	1389.3	1388.7
1361.1	1390.9	1386.8	1408.2	1427.6
1382.9	1416.8	1413.0	1429.0	1429.3
1424.1	1422.9	1421.4	1459.7	1457.9
1472.5	1486.6	1489.4	1471.2	1503.9
1493.8	1491.4	1493.6	1498.1	1507.4
1494.4	1495.4	1498.2	1512.4	1511.3
1506.9	1505.0	1504.5	1517.3	1517.1
1969.8	2246.1	2191.1	2006.4	2032.4
3072.8	2997.9	3070.8	2153.7	2425.3
3089.8	3060.7	3073.6	3062.3	3077.9

3148.6	3078.9	3138.3	3067.2	3085.6
3150.3	3151.6	3146.3	3087.3	3090.0
3157.4	3154.8	3154.3	3134.8	3115.2
3166.5	3169.9	3159.2	3143.4	3128.0
3182.1	3185.6	3185.6	3157.6	3164.2
3202.9	3198.7	3192.8	3176.6	3179.9
3262.2	3214.6	3214.5	3177.4	3191.2
5305.1	3271.5	3438.0	3183.8	3215.0

Table S-3-3: Normal mode frequencies of Transition States TS8, TS9, TS10 and products P1a and P2a (cm^{-1}).

TS8	TS9	TS10	P1a	P2a
-1545.1	-1545.1	-1545.2	39.7	45.4
27.2	27.2	27.2	63.0	62.7
41.0	41.0	41.0	82.7	93.3
66.9	66.9	66.9	106.1	149.3
107.4	107.4	107.4	167.3	215.3
176.9	176.9	176.9	179.4	258.0
186.0	186.0	186.0	233.5	269.7
228.6	228.6	228.6	262.0	292.6
272.1	272.1	272.1	299.8	314.2
344.1	344.1	344.1	329.0	389.4
420.5	420.5	420.5	459.7	467.5
466.2	466.2	466.2	543.3	496.2
501.8	501.8	501.8	550.3	626.2
540.8	540.8	540.8	645.5	630.2
648.4	648.4	648.4	712.0	694.1
782.0	782.0	782.0	782.8	782.6
793.7	793.7	793.7	826.5	832.7
869.8	869.8	869.8	949.9	964.4
947.9	947.9	947.9	1009.4	1023.5
1013.7	1013.7	1013.7	1023.1	1042.2
1028.0	1028.0	1028.0	1085.7	1092.4
1100.5	1100.5	1100.5	1100.7	1096.5
1102.4	1102.4	1102.4	1131.1	1129.4
1112.4	1112.4	1112.4	1190.8	1196.9
1135.6	1135.6	1135.6	1208.7	1211.2
1162.1	1162.1	1162.1	1282.8	1280.5
1218.2	1218.2	1218.2	1292.6	1296.7
1263.8	1263.8	1263.8	1293.8	1320.0
1298.4	1298.4	1298.4	1393.9	1394.8
1313.1	1313.1	1313.1	1412.1	1423.6
1365.3	1365.3	1365.3	1428.2	1429.5
1393.5	1393.5	1393.5	1450.3	1435.7
1430.6	1430.6	1430.6	1474.2	1469.8
1459.1	1459.1	1459.1	1495.7	1503.8
1489.1	1489.1	1489.1	1502.1	1509.5
1512.4	1512.4	1512.4	1515.1	1510.9
1517.1	1517.1	1517.1	1519.1	1516.8
1763.7	1763.7	1763.7	1758.0	2116.4
2335.7	2335.8	2335.8	3034.7	3065.7

3074.9	3074.9	3074.9	3069.5	3076.3
3090.1	3090.1	3090.1	3086.3	3090.1
3120.5	3120.5	3120.5	3119.1	3116.0
3138.5	3138.5	3138.5	3132.3	3151.6
3180.3	3180.3	3180.3	3153.7	3170.3
3187.2	3187.2	3187.2	3172.9	3179.6
3206.2	3206.2	3206.2	3173.8	3185.0
3215.3	3215.3	3215.3	3186.6	3189.2
3240.5	3240.5	3240.5	3234.9	3223.1

Table S-3-4: Normal mode frequencies of products P1, P2, P3, P4 and P5 (cm^{-1}).

P1	P2	P3	P4	P5
57.8	57.8	43.3	57.8	43.3
82.2	82.2	76.0	82.2	76.0
144.9	144.9	111.4	144.9	111.4
162.1	162.1	152.2	162.1	152.2
170.8	170.8	222.6	170.8	222.6
192.0	192.0	235.8	192.0	235.8
293.3	293.3	277.6	293.3	277.6
360.2	360.2	364.0	360.2	364.0
383.9	383.9	492.3	383.9	492.3
499.7	499.7	504.8	499.7	504.8
512.9	512.9	630.4	512.9	630.4
639.9	639.9	742.3	639.9	742.3
758.4	758.4	792.2	758.4	792.2
771.3	771.3	893.4	771.3	893.4
913.1	913.1	964.2	913.1	964.2
965.2	965.2	991.7	965.2	991.7
983.9	983.9	1058.9	983.9	1058.9
1018.9	1018.9	1093.7	1018.9	1093.7
1060.3	1060.3	1117.2	1060.3	1117.2
1121.8	1121.8	1145.6	1121.8	1145.6
1139.6	1139.6	1154.6	1139.6	1154.6
1181.4	1181.4	1215.9	1181.4	1215.9
1229.0	1229.0	1299.2	1229.0	1299.2
1303.2	1303.2	1377.7	1303.2	1377.7
1348.6	1348.6	1401.0	1348.6	1401.0
1394.5	1394.5	1423.5	1394.5	1423.5
1423.9	1423.9	1436.7	1423.9	1436.7
1458.5	1458.5	1488.2	1458.5	1488.2
1475.5	1475.5	1496.7	1475.5	1496.7
1492.6	1492.6	1499.2	1492.6	1499.2
1507.8	1507.8	1508.8	1507.8	1508.8
1698.4	1698.4	2082.9	1698.4	2082.9
1902.0	1902.0	2759.4	1902.0	2759.4
3018.9	3018.9	3045.5	3018.9	3045.5
3066.1	3066.1	3074.3	3066.1	3074.3
3090.5	3090.5	3132.0	3090.5	3132.0
3139.8	3139.8	3151.2	3139.8	3151.2
3168.5	3168.5	3174.6	3168.5	3174.6
3192.7	3192.7	3189.1	3192.7	3189.1
3195.8	3195.8	3194.4	3195.8	3194.4
3215.9	3215.9	3235.7	3215.9	3235.7
3339.0	3339.0	3252.8	3339.0	3252.8

Table S-3-5: Normal mode frequencies of products P6, P7, P8, P9 and P10 (cm^{-1}).

P6	P7	P8	P9	P10
59.7	66.4	42.4	42.4	56.8
80.5	71.3	58.3	58.3	96.2
129.3	130.0	142.6	142.6	157.5
169.0	163.3	162.2	162.1	165.6
218.4	217.5	218.7	218.7	232.3
253.2	231.4	279.1	279.1	273.4
277.0	265.4	365.1	365.1	326.1
337.6	332.9	497.5	497.5	329.2
484.8	507.2	525.9	525.9	424.6
542.9	553.3	573.1	573.1	502.3
620.0	624.7	647.5	647.5	519.0
776.3	774.7	757.5	757.5	648.0
787.5	814.7	781.2	781.2	731.7
884.8	865.2	818.5	818.5	790.5
966.6	955.4	841.0	841.0	828.7
1019.8	1022.4	994.2	994.2	962.3
1078.8	1083.5	1021.3	1021.3	1018.6
1089.7	1101.8	1044.4	1044.4	1025.3
1108.3	1125.7	1094.3	1094.3	1087.9
1115.9	1132.5	1110.1	1110.1	1102.5
1207.4	1157.7	1144.2	1144.2	1117.3
1249.8	1292.7	1221.2	1221.2	1225.4
1289.6	1301.3	1288.7	1288.7	1265.2
1389.7	1374.5	1312.6	1312.6	1289.9
1407.7	1418.9	1340.0	1340.0	1344.3
1428.5	1427.5	1393.4	1393.4	1394.2
1462.3	1456.1	1430.0	1430.0	1430.1
1477.9	1501.3	1465.3	1465.3	1476.7
1490.4	1506.9	1478.8	1478.8	1478.9
1512.7	1511.0	1509.9	1509.9	1511.7
1518.1	1516.6	1517.2	1517.2	1517.6
1978.7	1983.2	1538.6	1538.6	1624.9
2265.6	2359.1	2195.3	2195.3	2163.6
3051.7	3075.2	3072.1	3072.1	3070.8
3073.5	3081.0	3089.6	3089.6	3087.0
3086.2	3088.7	3120.8	3120.8	3117.3
3122.3	3105.4	3178.6	3178.6	3169.8
3127.4	3122.7	3189.8	3189.8	3175.7
3148.0	3160.5	3200.1	3200.1	3183.3
3173.1	3177.9	3214.1	3214.1	3202.9
3174.4	3188.7	3220.5	3220.5	3209.8
3185.8	3198.7	3313.2	3313.2	3316.3

Table S-4: Optimized geometries of the reactant, transition states and products for the reaction of Cl atoms with 5-hexen-2-one obtained at MP2/6-311++G (d,p) level of theory.

Table S-4-1: Optimized parameters of 5-hexen-2-one.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.564782	0.226346	0.135764
2	8	0	1.889818	1.396796	-0.0469
3	6	0	0.191428	-0.12299	0.673844
4	1	0	0.208262	-1.09047	1.180293
5	1	0	-0.09937	0.642888	1.392507
6	6	0	-0.83044	-0.14789	-0.47662
7	1	0	-0.84339	0.835539	-0.95016
8	1	0	-0.50497	-0.86777	-1.23413
9	6	0	-2.2034	-0.50452	0.005556
10	1	0	-2.32364	-1.49452	0.435447
11	6	0	-3.25433	0.321523	-0.04531
12	1	0	-3.16769	1.315253	-0.46465
13	1	0	-4.22508	0.027006	0.32668
14	6	0	2.484631	-0.92343	-0.20584
15	1	0	3.355013	-0.55216	-0.73883
16	1	0	1.963062	-1.66651	-0.80932
17	1	0	2.803206	-1.41788	0.713002

Table S-4-2: Optimized parameters of Transition State TS1a.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.5918	-0.03007	-0.07954
2	8	0	-3.36352	-0.60903	-0.83434
3	6	0	-1.37007	-0.73148	0.485643
4	1	0	-1.44209	-0.73901	1.577213
5	1	0	-1.38708	-1.7615	0.131819
6	6	0	-0.06453	-0.03475	0.065059
7	1	0	0.005777	0.005136	-1.02292
8	1	0	-0.05652	0.994197	0.43058
9	6	0	1.120838	-0.74535	0.619634
10	1	0	1.202634	-0.79692	1.699597
11	6	0	2.087338	-1.30568	-0.13382
12	1	0	2.001599	-1.32769	-1.21039
13	1	0	2.89644	-1.8622	0.313036
14	6	0	-2.79268	1.423553	0.294297
15	1	0	-2.40181	1.650457	1.284685
16	1	0	-3.85205	1.659919	0.243885
17	1	0	-2.2689	2.052916	-0.42667
18	17	0	3.169148	0.796445	-0.22669

Table S-4-3: Optimized parameters of Transition State TS2a.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.37631	-0.0793	-0.01453
2	8	0	-3.21842	-0.68871	-0.6472
3	6	0	-1.14996	-0.77459	0.54449
4	1	0	-1.14805	-0.65799	1.630244
5	1	0	-1.23237	-1.83601	0.313161
6	6	0	0.145865	-0.18422	-0.03143
7	1	0	0.148211	-0.2668	-1.11804
8	1	0	0.205947	0.875806	0.202742
9	6	0	1.378605	-0.83935	0.505399
10	1	0	1.543184	-0.77101	1.577234
11	6	0	2.238016	-1.56429	-0.24451
12	1	0	2.095975	-1.67082	-1.31375
13	1	0	3.101668	-2.04771	0.196167
14	6	0	-2.48794	1.415205	0.20777
15	1	0	-2.0006	1.732796	1.12804
16	1	0	-3.53844	1.697131	0.216931
17	1	0	-2.00685	1.930116	-0.6239
18	17	0	2.475827	1.099023	-0.16673

Table S-4-4: Optimized parameters of Transition State TS1.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.64331	1.531136	-0.12727
2	8	0	-0.7221	2.734601	-0.26311
3	6	0	0.485403	0.694934	-0.66659
4	1	0	0.067519	-0.05103	-1.34809
5	1	0	1.146825	1.352695	-1.22839
6	6	0	1.257216	-0.02054	0.455085
7	1	0	1.654025	0.718623	1.155131
8	1	0	0.575538	-0.67013	1.009648
9	6	0	2.379869	-0.84209	-0.10318
10	1	0	2.093329	-1.64691	-0.77333
11	6	0	3.663611	-0.63178	0.162182
12	1	0	3.979454	0.163896	0.824392
13	1	0	4.438896	-1.24773	-0.27017
14	6	0	-1.72636	0.851996	0.689817
15	1	0	-1.86907	-0.51063	0.251559
16	1	0	-2.71046	1.279281	0.529584
17	1	0	-1.47872	0.747949	1.743017
18	17	0	-2.03642	-1.85381	-0.13228

Table S-4-5: Optimized parameters of Transition State TS2.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.337603	0.536032	0.06876
2	8	0	0.824621	1.603546	-0.20887
3	6	0	-1.06424	0.425108	0.633976
4	1	0	-1.00561	-0.0543	1.618433
5	1	0	-1.46076	1.43289	0.763682
6	6	0	-1.9867	-0.40324	-0.27804
7	1	0	-2.02446	0.051479	-1.27237
8	1	0	-1.57341	-1.41115	-0.39577
9	6	0	-3.37313	-0.49913	0.288006
10	1	0	-3.45947	-0.98147	1.26048
11	6	0	-4.46288	-0.02509	-0.30342
12	1	0	-4.40975	0.465726	-1.27032
13	1	0	-5.44064	-0.11054	0.155097
14	6	0	1.088364	-0.75698	-0.18115
15	1	0	0.787603	-1.5501	0.505103
16	1	0	2.425106	-0.52489	-0.08703
17	1	0	0.875054	-1.08963	-1.2015
18	17	0	3.850308	-0.27745	0.013313

Table S-4-6: Optimized parameters of Transition State TS3.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.495907	1.430109	-0.03731
2	8	0	0.760854	2.031646	-1.03711
3	6	0	-0.90658	1.123899	0.425684
4	1	0	-0.97146	1.197805	1.513251
5	1	0	-1.58415	1.84119	-0.03226
6	6	0	-1.27256	-0.31236	-0.01005
7	1	0	-1.19569	-0.37928	-1.09727
8	1	0	-0.54233	-1.01555	0.399399
9	6	0	-2.65707	-0.67735	0.427177
10	1	0	-2.83408	-0.70932	1.498278
11	6	0	-3.64994	-0.92579	-0.40118
12	1	0	-3.50688	-0.90009	-1.47353
13	1	0	-4.63883	-1.17036	-0.04106
14	6	0	1.607709	0.905212	0.871736
15	1	0	1.343747	0.639422	1.890356
16	1	0	2.542365	1.442938	0.756527
17	1	0	1.910766	-0.26126	0.320551
18	17	0	2.452053	-1.54124	-0.18199

Table S-4-7: Optimized parameters of Transition State TS4.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.498196	-0.9303	-0.21006
2	8	0	2.020414	-1.63196	-1.03359
3	6	0	0.103887	-0.36963	-0.47531
4	1	0	0.247224	0.961917	-0.36403
5	1	0	-0.17758	-0.52713	-1.51584
6	6	0	-0.9588	-0.79462	0.511953
7	1	0	-1.0478	-1.88655	0.461776
8	1	0	-0.64103	-0.54463	1.528332
9	6	0	-2.29232	-0.16435	0.21973
10	1	0	-2.32627	0.918897	0.273932
11	6	0	-3.37601	-0.84623	-0.10016
12	1	0	-3.36751	-1.92742	-0.16374
13	1	0	-4.31351	-0.35027	-0.30878
14	6	0	2.118703	-0.62799	1.132457
15	1	0	1.80692	0.340461	1.516669
16	1	0	3.200109	-0.67547	1.037556
17	1	0	1.802407	-1.39942	1.835449
18	17	0	0.358338	2.38494	-0.14731

Table S-4-8: Optimized parameters of Transition State TS5.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.829752	-0.03814	0.007916
2	8	0	2.199368	1.038744	-0.43504
3	6	0	0.414105	-0.28601	0.475219
4	1	0	0.319597	-0.36694	1.558451
5	1	0	-0.24583	0.98266	0.271716
6	6	0	-0.41828	-1.26547	-0.3188
7	1	0	-0.52535	-0.90444	-1.34467
8	1	0	0.135957	-2.21127	-0.3765
9	6	0	-1.76625	-1.52819	0.2879
10	1	0	-1.76314	-1.94607	1.290003
11	6	0	-2.90706	-1.28577	-0.31768
12	1	0	-2.94034	-0.86021	-1.31176
13	1	0	-3.85438	-1.49419	0.158043
14	6	0	2.756728	-1.23467	0.099544
15	1	0	2.623736	-1.77281	1.037344
16	1	0	3.782224	-0.89035	-0.00032
17	1	0	2.5341	-1.92573	-0.71487
18	17	0	-1.0068	2.171107	0.088726

Table S-4-9: Optimized parameters of Transition State TS6.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.90003	-0.25261	-0.29318
2	8	0	-2.3636	0.460308	-1.14799
3	6	0	-0.65921	-1.08681	-0.54102
4	1	0	-0.91405	-2.13599	-0.3989
5	1	0	-0.35331	-0.94345	-1.57629
6	6	0	0.485912	-0.71017	0.415907
7	1	0	0.766444	0.531544	0.282291
8	1	0	0.160508	-0.86151	1.451161
9	6	0	1.71081	-1.537	0.155551
10	1	0	1.598068	-2.61203	0.287514
11	6	0	2.881471	-1.04744	-0.23421
12	1	0	3.024831	0.018773	-0.37998
13	1	0	3.732736	-1.69116	-0.42002
14	6	0	-2.50959	-0.31225	1.093494
15	1	0	-2.3338	-1.26965	1.581768
16	1	0	-3.57701	-0.10746	1.025721
17	1	0	-2.05636	0.468071	1.70308
18	17	0	1.10615	2.035179	0.120489

Table S-4-10: Optimized parameters of Transition State TS7.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.66516	-0.94246	0.05707
2	8	0	-2.32688	-1.85371	-0.37375
3	6	0	-0.26664	-1.16244	0.598088
4	1	0	-0.24534	-0.84593	1.639862
5	1	0	-0.04915	-2.22871	0.557147
6	6	0	0.78658	-0.36726	-0.19393
7	1	0	0.748995	-0.6555	-1.24341
8	1	0	0.512792	0.881571	-0.13171
9	6	0	2.167341	-0.59938	0.345914
10	1	0	2.332155	-0.30046	1.379987
11	6	0	3.161582	-1.15036	-0.3396
12	1	0	3.028021	-1.46403	-1.37033
13	1	0	4.138221	-1.30621	0.102482
14	6	0	-2.18285	0.48211	0.033213
15	1	0	-1.75358	1.091547	0.82709
16	1	0	-3.26945	0.47063	0.104537
17	1	0	-1.91411	0.930531	-0.9221
18	17	0	0.181252	2.393823	-0.05636

Table S-4-11: Optimized parameters of Transition State TS8.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.36252	-0.22637	-0.26285
2	8	0	-3.24381	0.218689	-0.95502
3	6	0	-0.90153	0.028987	-0.5747
4	1	0	-0.40916	-0.92946	-0.73242
5	1	0	-0.84541	0.601731	-1.49922
6	6	0	-0.19374	0.779516	0.567494
7	1	0	-0.70076	1.725344	0.752583
8	1	0	-0.25918	0.192162	1.482182
9	6	0	1.249364	1.033339	0.243719
10	1	0	2.092723	-0.17578	0.027187
11	6	0	1.793956	2.237893	0.123296
12	1	0	1.205448	3.138401	0.269449
13	1	0	2.840911	2.365653	-0.12391
14	6	0	-2.67497	-1.02552	0.986833
15	1	0	-1.88548	-1.73412	1.232839
16	1	0	-3.62492	-1.54143	0.855088
17	1	0	-2.78197	-0.3334	1.820764
18	17	0	2.87382	-1.29563	-0.17336

Table S-4-12: Optimized parameters of Transition State TS9.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.94424	0.274408	-0.19383
2	8	0	-3.58309	1.296261	0.038667
3	6	0	-1.46324	0.331422	-0.52355
4	1	0	-1.30609	-0.08667	-1.52243
5	1	0	-1.16837	1.3796	-0.54012
6	6	0	-0.61231	-0.4441	0.491863
7	1	0	-0.77605	-0.04713	1.494736
8	1	0	-0.90074	-1.49791	0.501347
9	6	0	0.85238	-0.35962	0.139786
10	1	0	1.144156	-0.7754	-0.82023
11	6	0	1.748338	0.180984	0.902034
12	1	0	1.785842	0.663147	1.866023
13	1	0	3.13359	0.142629	0.313286
14	6	0	-3.58574	-1.09484	-0.13
15	1	0	-3.22269	-1.74418	-0.92585
16	1	0	-4.66444	-0.98611	-0.19378
17	1	0	-3.34051	-1.56892	0.82188
18	17	0	4.35346	0.048314	-0.31895

Table S-4-13: Optimized parameters of Transition State TS10.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.357388	-0.3787	-0.24012
2	8	0	2.601157	-1.37236	-0.9134
3	6	0	1.289184	0.615615	-0.65618
4	1	0	1.760666	1.591904	-0.80507
5	1	0	0.875761	0.283447	-1.60726
6	6	0	0.17714	0.742847	0.395454
7	1	0	-0.28468	-0.22859	0.569208
8	1	0	0.598984	1.08298	1.343657
9	6	0	-0.8665	1.727733	-0.04588
10	1	0	-0.5253	2.751229	-0.20792
11	6	0	-2.10397	1.487203	-0.26651
12	1	0	-2.58704	0.054107	-0.0412
13	1	0	-2.93389	2.097846	-0.58953
14	6	0	3.083396	-0.11326	1.063093
15	1	0	3.159137	0.950401	1.282727
16	1	0	4.073031	-0.55967	1.015837
17	1	0	2.535446	-0.58854	1.878032
18	17	0	-3.00595	-1.23205	0.174679

Table S-4-14: Optimized parameters of Product P1a.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.49914	-0.17048	-0.03196
2	8	0	-3.22216	-1.00105	-0.57241
3	6	0	-1.17271	-0.57504	0.588358
4	1	0	-1.22683	-0.40351	1.667823
5	1	0	-1.04795	-1.64391	0.41916
6	6	0	0.015114	0.210111	0.008038
7	1	0	0.05153	0.093526	-1.07628
8	1	0	-0.10307	1.275468	0.218646
9	6	0	1.299717	-0.24654	0.60701
10	1	0	1.408514	-0.13808	1.68016
11	6	0	2.339812	-0.73059	-0.10573
12	1	0	2.239807	-0.9269	-1.16334
13	1	0	3.218355	-1.11918	0.385635
14	6	0	-2.8774	1.29268	0.032892
15	1	0	-2.66692	1.712636	1.016169
16	1	0	-3.9325	1.397516	-0.20235
17	1	0	-2.29681	1.857314	-0.69778
18	17	0	2.794161	0.424862	-0.2506

Table S-4-15: Optimized parameters of Product P2a.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.321178	0.189807	0.031005
2	8	0	3.06886	1.065798	-0.39198
3	6	0	0.948789	0.534316	0.584602
4	1	0	0.926027	0.269531	1.6464
5	1	0	0.825499	1.613432	0.499991
6	6	0	-0.18231	-0.20357	-0.1504
7	1	0	-0.14794	0.023509	-1.21709
8	1	0	-0.06933	-1.28048	-0.03809
9	6	0	-1.50817	0.212887	0.405124
10	1	0	-1.7419	-0.12648	1.407305
11	6	0	-2.25878	1.205126	-0.13352
12	1	0	-2.01636	1.617316	-1.10219
13	1	0	-3.14854	1.565653	0.357845
14	6	0	2.713723	-1.27072	0.008845
15	1	0	2.434536	-1.76983	0.936367
16	1	0	3.784972	-1.34845	-0.1525
17	1	0	2.197755	-1.77884	-0.80683
18	17	0	-2.3413	-0.66582	-0.16879

Table S-4-16: Optimized parameters of Product P1.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.65311	-0.22147	0.084115
2	8	0	-2.26885	-1.23089	-0.17722
3	6	0	-0.24797	-0.23442	0.651119
4	1	0	-0.24422	0.310182	1.599693
5	1	0	0.010873	-1.27429	0.8454
6	6	0	0.7734	0.399641	-0.3116
7	1	0	0.743014	-0.12748	-1.2678
8	1	0	0.50057	1.440662	-0.50474
9	6	0	2.160408	0.338344	0.253041
10	1	0	2.330937	0.895555	1.169424
11	6	0	3.153277	-0.36034	-0.28256
12	1	0	3.015143	-0.92921	-1.19274
13	1	0	4.135002	-0.38526	0.167838
14	6	0	-2.2172	1.158607	-0.18777
15	1	0	-2.06026	1.920696	0.568429
16	1	0	-2.09308	1.514098	-1.20583

Table S-4-17: Optimized parameters of Product P2.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.64598	-0.2196	0.07491
2	8	0	-2.2516	-1.24298	-0.16114
3	6	0	-0.24031	-0.22322	0.647338
4	1	0	-0.24059	0.335844	1.587406
5	1	0	0.026297	-1.25819	0.859282
6	6	0	0.781908	0.400172	-0.31958
7	1	0	0.755412	-0.13962	-1.26888
8	1	0	0.503704	1.436447	-0.52683
9	6	0	2.168481	0.351177	0.248023
10	1	0	2.334366	0.920125	1.158169
11	6	0	3.170004	-0.35199	-0.27754
12	1	0	3.036838	-0.933	-1.18076
13	1	0	4.150851	-0.36765	0.17558
14	6	0	-2.23541	1.139608	-0.18647
15	1	0	-2.20961	1.905795	0.577975
16	1	0	-2.3367	1.467267	-1.21295

Table S-4-18: Optimized parameters of Product P3.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.602108	0.05343	-0.00562
2	8	0	1.813112	1.244423	0.070707
3	6	0	0.232636	-0.54861	-0.18379
4	1	0	0.241543	-1.11556	-1.11988
5	1	0	0.08425	-1.29668	0.601406
6	6	0	-0.88277	0.491773	-0.16994
7	1	0	-0.88215	1.014378	0.787584
8	1	0	-0.66929	1.24181	-0.93416
9	6	0	-2.22009	-0.13934	-0.41266
10	1	0	-2.35468	-0.63231	-1.37117
11	6	0	-3.21843	-0.14025	0.464596
12	1	0	-3.12052	0.341547	1.428798
13	1	0	-4.16429	-0.61512	0.247028
14	6	0	2.7807	-0.88881	0.136059
15	1	0	2.890126	-1.34127	1.11786
16	1	0	3.705219	-0.52144	-0.29505

Table S-4-19: Optimized parameters of Product P4.

Center Number	Atomic Number	Atomic Type	Coordinates	(Angstroms)	
			X	Y	Z
1	6	0	1.621244	0.084057	0.048731
2	8	0	1.798616	1.27601	0.063847
3	6	0	0.249033	-0.5316	-0.13817
4	1	0	0.283103	-1.1051	-1.07103
5	1	0	0.087502	-1.27182	0.651471
6	6	0	-0.87523	0.498372	-0.15724
7	1	0	-0.89522	1.029101	0.795154
8	1	0	-0.65017	1.242664	-0.92268
9	6	0	-2.2018	-0.14436	-0.41908
10	1	0	-2.31716	-0.64085	-1.37881
11	6	0	-3.20744	-0.15415	0.429876
12	1	0	-3.13221	0.330438	1.39472
13	1	0	-4.14475	-0.63727	0.193986
14	6	0	2.746653	-0.88545	0.129613
15	1	0	2.702874	-1.72695	0.801095
16	1	0	3.682288	-0.62958	-0.33704

Table S-4-20: Optimized parameters of Product P5.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.634589	0.101213	0.046216
2	8	0	1.809343	1.274902	0.032824
3	6	0	0.251321	-0.53217	-0.10828
4	1	0	0.287601	-1.14053	-1.01882
5	1	0	0.077659	-1.24111	0.707545
6	6	0	-0.86505	0.500529	-0.17371
7	1	0	-0.88646	1.068692	0.757059
8	1	0	-0.6305	1.212289	-0.96601
9	6	0	-2.19	-0.15161	-0.41592
10	1	0	-2.3005	-0.67451	-1.36271
11	6	0	-3.20251	-0.13656	0.433038
12	1	0	-3.13361	0.375328	1.384757
13	1	0	-4.14049	-0.6237	0.208674
14	6	0	2.711388	-0.89249	0.189587
15	1	0	2.502506	-1.94161	0.226702
16	1	0	3.710587	-0.56757	-0.02537

Table S-4-21: Optimized parameters of Product P6.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.6022	-0.23413	-0.00434
2	8	0	-2.32546	-1.19758	-0.22535
3	6	0	-0.17635	-0.45513	0.493191
4	1	0	-0.20708	-0.36197	1.588889
5	1	0	0.100583	-1.48516	0.270566
6	6	0	0.867795	0.501112	-0.01915
7	1	0	0.60655	1.555385	0.066028
8	6	0	2.278052	0.186929	0.329943
9	1	0	2.510931	0.314179	1.385167
10	6	0	3.209027	-0.2277	-0.49498
11	1	0	3.017978	-0.36636	-1.54916
12	1	0	4.206242	-0.4418	-0.13936
13	6	0	-2.08257	1.18827	-0.16686
14	1	0	-1.83504	1.789094	0.708891
15	1	0	-3.15752	1.1803	-0.32078
16	1	0	-1.60152	1.640883	-1.03425

Table S-4-22: Optimized parameters of Product P7.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.59335	-0.21345	0.010991
2	8	0	-2.16279	-1.20289	-0.43972
3	6	0	-0.23389	-0.3573	0.680623
4	1	0	-0.29787	-0.03526	1.724271
5	1	0	0.00901	-1.42226	0.671343
6	6	0	0.877315	0.407985	-0.01957
7	1	0	0.749375	0.508412	-1.0985
8	6	0	2.250623	0.056997	0.367453
9	1	0	2.422242	-0.14665	1.418555
10	6	0	3.241187	-0.01558	-0.4937
11	1	0	3.091592	0.189559	-1.54515
12	1	0	4.240462	-0.28705	-0.18657
13	6	0	-2.19371	1.167494	-0.07523
14	1	0	-2.21477	1.63835	0.906839
15	1	0	-3.1982	1.091693	-0.48117
16	1	0	-1.58863	1.80941	-0.71522

Table S-4-23: Optimized parameters of Product P8.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.56965	-0.25056	0.066665
2	8	0	-2.19753	-1.25149	-0.26415
3	6	0	-0.1474	-0.35429	0.587811
4	1	0	-0.10986	0.044673	1.604501
5	1	0	0.120584	-1.40902	0.61891
6	6	0	0.850358	0.419326	-0.28806
7	1	0	0.836518	0.027839	-1.31252
8	1	0	0.579598	1.475658	-0.33825
9	6	0	2.234146	0.300013	0.216774
10	6	0	3.363829	-0.20145	-0.14082
11	1	0	3.458779	-0.71563	-1.09356
12	1	0	4.250092	-0.13483	0.474713
13	6	0	-2.16776	1.135238	-0.04184
14	1	0	-1.91499	1.745141	0.824849
15	1	0	-3.24599	1.050123	-0.14166
16	1	0	-1.77563	1.638342	-0.92701

Table S-4-24: Optimized parameters of Product P9.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.488834	0.128389	0.020328
2	8	0	1.59415	1.351034	0.001481
3	6	0	0.134191	-0.54896	-0.09951
4	1	0	0.156658	-1.20795	-0.97338
5	1	0	-0.00649	-1.20689	0.76281
6	6	0	-1.01031	0.453528	-0.20101
7	1	0	-1.02918	1.085303	0.685792
8	1	0	-0.83991	1.112283	-1.05405
9	6	0	-2.33115	-0.25227	-0.37498
10	1	0	-2.4384	-0.86824	-1.26391
11	6	0	-3.30669	-0.17214	0.461566
12	1	0	-3.50422	0.335167	1.393582
13	6	0	2.687937	-0.77978	0.165368
14	1	0	2.593572	-1.38175	1.069581
15	1	0	3.592666	-0.18127	0.21578
16	1	0	2.745192	-1.4675	-0.67862

Table S-4-25: Optimized parameters of Product P10.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.55188	-0.2471	0.047114
2	8	0	-2.24306	-1.21596	-0.25332
3	6	0	-0.12186	-0.41908	0.528008
4	1	0	-0.08903	-0.15533	1.590338
5	1	0	0.127782	-1.47543	0.438701
6	6	0	0.895785	0.437397	-0.23643
7	1	0	0.849524	0.208487	-1.30176
8	1	0	0.655607	1.496367	-0.11647
9	6	0	2.291773	0.194175	0.263444
10	1	0	2.464634	0.424872	1.317511
11	6	0	3.278195	-0.26626	-0.42931
12	1	0	4.311753	-0.50364	-0.24523
13	6	0	-2.08322	1.165511	-0.06481
14	1	0	-1.8284	1.752209	0.817647
15	1	0	-3.16128	1.130968	-0.19371
16	1	0	-1.63889	1.661347	-0.92855

Table S-5: Vibrational frequencies for the reactant, pre-reactive complexes, transition states and products for the reaction of Cl atoms with 5-hexen-2-one obtained at MP2/6-311++G (d,p) level of theory.

Table S-5-1: Normal mode frequencies of R1, TS1a, TS2a, TS1, TS2 and TS3 (cm^{-1}).

R1	TS1a	TS2a	TS1	TS2	TS3
30.6	-349.6	-351.9	-965.2	-1238.2	-1059.3
73.5	31.1	33.2	37.5	20.1	27.9
93.2	58.0	64.1	57.3	37.4	60.1
116.5	74.0	87.0	72.0	68.1	67.6
174.5	85.0	96.3	102.9	96.0	74.8
315.0	141.8	141.9	123.8	105.8	119.7
365.0	162.0	231.3	169.4	146.2	172.7
446.0	226.5	250.2	284.4	273.9	309.7
480.3	349.1	301.3	374.6	348.4	341.8
601.5	410.2	409.4	401.0	406.8	385.5
652.9	427.1	429.4	432.8	428.4	442.9
765.3	533.3	527.0	483.5	495.1	491.5
859.9	575.7	577.2	560.7	527.3	518.4
932.1	747.4	623.4	602.5	617.5	609.4
939.9	784.7	788.9	671.6	677.8	672.5
957.3	835.1	823.9	790.2	788.2	763.7
1000.7	948.2	949.6	837.7	836.6	862.9
1040.8	969.7	964.0	906.9	915.4	900.8
1060.0	1019.3	983.2	943.8	922.2	923.9
1108.7	1035.9	1030.3	974.0	965.4	975.1
1172.8	1052.1	1050.3	979.9	989.6	976.8
1211.9	1068.0	1068.2	1027.3	992.5	985.9
1253.0	1090.7	1089.3	1031.4	1037.1	1063.0
1323.3	1166.3	1163.6	1079.4	1070.6	1081.5
1342.6	1249.2	1249.8	1086.7	1083.9	1099.4
1355.1	1283.0	1288.1	1141.4	1133.8	1154.9
1425.4	1305.9	1301.3	1196.7	1174.8	1190.4
1441.3	1340.5	1331.8	1235.1	1243.8	1204.1
1500.6	1361.5	1350.8	1289.7	1286.4	1257.5
1509.0	1397.4	1393.9	1307.7	1295.0	1328.4
1526.5	1439.0	1439.0	1348.9	1345.8	1345.8
1534.7	1501.3	1501.0	1393.2	1385.5	1404.6
1535.7	1520.3	1521.3	1410.9	1416.5	1441.9
1737.8	1525.7	1525.7	1470.4	1486.3	1475.4
1784.6	1537.9	1538.1	1513.9	1512.9	1496.6
3106.9	1541.3	1550.1	1523.7	1522.8	1515.5
3129.7	1698.8	1658.3	1540.4	1543.3	1536.3
3135.7	1788.0	1784.9	2246.9	2427.8	2354.1
3156.0	3119.5	3117.9	3119.6	3094.0	3113.0

3194.3	3130.1	3130.6	3133.2	3126.8	3121.2
3217.5	3133.1	3150.2	3139.1	3142.5	3140.5
3223.2	3192.4	3202.8	3181.6	3178.9	3165.1
3239.0	3212.3	3219.0	3203.9	3205.4	3197.1
3261.6	3218.9	3223.6	3222.3	3217.7	3202.4
3337.3	3262.1	3261.8	3233.8	3230.6	3227.9
	3262.4	3263.2	3312.6	3311.7	3316.5
	3268.2	3271.8	3339.3	3340.8	3338.0
	3372.0	3381.3	4149.6	4097.7	4014.1

Table S-5-2: Normal mode frequencies of transition states TS4, TS5, TS6, TS7, TS8 and TS9 (cm^{-1}).

TS4	TS5	TS6	TS7	TS8	TS9
-776.8	-1173.7	-896.5	-1229.0	-400.7	-427.7
28.6	26.9	47.9	21.1	27.4	26.4
64.8	51.9	64.2	59.8	39.3	42.8
88.8	60.8	85.6	88.4	76.3	51.0
99.3	96.3	124.6	125.5	101.3	96.5
128.6	118.4	173.4	138.4	126.3	99.4
158.4	161.4	183.1	154.0	134.3	128.1
183.3	170.1	200.2	171.7	226.5	184.6
300.0	315.9	288.2	289.8	286.8	316.8
371.2	360.3	405.1	378.0	359.2	363.9
418.3	449.3	446.0	412.0	412.8	435.1
500.7	464.6	493.9	482.9	517.3	477.3
573.2	532.6	543.7	541.8	574.5	556.2
600.0	610.2	564.9	578.7	612.1	601.4
696.6	675.8	707.7	698.2	699.7	760.8
776.0	785.7	772.4	805.8	775.8	789.9
866.1	839.2	825.0	833.1	832.6	824.8
908.1	879.8	921.2	946.1	866.4	866.9
941.8	950.7	949.6	972.4	919.7	938.6
980.3	962.9	989.0	1020.7	964.7	971.0
1024.3	1009.7	1048.5	1051.9	999.5	995.2
1045.3	1035.4	1054.7	1086.1	1042.6	1007.5
1053.6	1068.0	1078.7	1096.6	1047.5	1072.3
1100.5	1079.9	1086.5	1123.5	1094.4	1116.4
1130.7	1118.4	1138.4	1143.2	1101.6	1135.1
1148.3	1155.0	1157.0	1194.3	1199.2	1205.6
1208.7	1186.7	1188.3	1221.0	1269.6	1214.1
1253.1	1225.5	1257.1	1268.9	1295.6	1289.3
1282.9	1271.5	1285.2	1302.2	1309.9	1327.5
1298.8	1314.1	1293.9	1310.2	1349.8	1343.6
1392.8	1400.9	1379.4	1379.3	1404.0	1357.3
1413.3	1431.2	1421.8	1418.9	1439.3	1426.2
1441.6	1446.3	1436.8	1445.7	1471.0	1442.5
1502.4	1490.5	1489.8	1504.2	1507.6	1510.2
1514.5	1521.1	1523.0	1512.6	1526.6	1525.8
1524.5	1523.9	1525.9	1515.9	1527.3	1529.4
1528.4	1530.3	1538.4	1534.3	1539.2	1534.8
2110.0	2475.8	1794.2	1796.3	1785.6	1785.2
2922.3	2990.9	2887.0	1823.2	2088.2	1992.9
3090.6	3113.8	3067.7	3115.5	3092.0	3113.6
3134.7	3136.1	3128.7	3137.6	3129.2	3130.9
3151.9	3179.1	3195.9	3176.9	3137.8	3150.8

3218.3	3195.5	3207.4	3183.7	3176.6	3165.2
3224.7	3228.7	3216.6	3226.7	3208.2	3214.6
3247.9	3232.6	3219.7	3249.1	3218.3	3218.8
3267.7	3275.6	3262.7	3264.1	3222.3	3233.9
3338.4	3343.4	3359.3	3264.9	3261.5	3263.8
3433.2	3509.8	3382.7	3355.3	3320.3	3336.5

Table S-5-3: Normal mode frequencies of TS10, P1a, P2a, P1, P2 and P3 (cm^{-1}).

TS10	P1a	P2a	P1	P2	P3
-464.5	24.3	33.9	48.8	48.8	48.8
28.2	48.0	61.1	72.1	72.1	73.4
39.1	66.4	111.0	108.5	108.5	111.0
75.8	92.4	133.2	175.5	175.5	177.0
112.8	133.9	140.4	262.9	262.9	261.6
132.9	166.2	234.9	317.3	317.3	318.2
161.6	253.0	237.8	367.4	367.4	368.5
215.0	298.4	299.7	447.9	447.9	450.4
323.2	411.1	342.3	506.8	506.8	506.4
410.0	418.3	410.8	603.8	603.8	603.9
434.2	531.5	431.3	629.8	629.8	629.6
525.9	574.5	535.6	647.9	647.9	668.8
566.0	581.8	579.4	807.0	807.0	808.5
575.2	689.2	621.9	866.9	866.9	868.6
759.2	778.4	735.5	920.4	920.4	962.0
775.2	823.3	792.7	960.6	960.6	968.2
801.3	898.0	837.0	990.9	990.9	992.7
835.4	948.3	931.8	1028.6	1028.6	1039.9
943.9	1030.0	945.6	1039.6	1039.6	1075.7
952.4	1053.8	1026.9	1109.6	1109.6	1110.9
971.4	1089.4	1039.2	1142.5	1142.5	1144.2
1026.1	1121.2	1093.9	1202.5	1202.5	1203.4
1066.6	1187.2	1153.7	1246.5	1246.5	1249.2
1100.8	1206.1	1183.3	1328.3	1328.3	1329.3
1139.2	1241.2	1228.6	1343.2	1343.2	1343.3
1197.3	1278.4	1282.5	1393.9	1393.9	1404.0
1257.0	1317.8	1293.2	1439.3	1439.3	1438.1
1286.3	1333.3	1327.9	1504.2	1504.2	1504.4
1300.9	1342.6	1348.9	1507.7	1507.7	1507.7
1337.5	1398.0	1406.2	1509.6	1509.6	1515.0
1361.1	1438.2	1433.3	1534.7	1534.7	1535.2
1417.2	1473.3	1439.0	2112.0	2112.0	2111.4
1438.1	1519.7	1520.6	2492.5	2492.5	3108.3
1518.7	1525.6	1526.0	3110.4	3110.4	3120.8
1525.7	1534.0	1529.8	3141.7	3141.7	3145.0
1537.4	1539.4	1538.8	3161.8	3161.8	3163.2
1545.3	1541.2	1552.4	3200.5	3200.5	3201.9
1785.4	1786.0	1782.5	3223.7	3223.7	3224.0
2008.2	3080.1	3114.5	3260.6	3260.6	3260.7
3112.8	3118.4	3130.3	3283.9	3283.9	3336.7
3128.6	3130.1	3135.8	3338.9	3338.9	3396.4
3140.1	3139.5	3180.0	3396.3	3396.3	4031.9
3166.1	3178.0	3198.7			

3203.9	3208.9	3214.8
3216.9	3218.7	3219.2
3218.8	3252.6	3258.5
3261.4	3260.6	3260.9
3344.1	3275.7	3381.9

Table S-5-4: Normal mode frequencies of products P4, P5, P6, P7, P8, P9 and P10 (cm^{-1}).

P4	P5	P6	P7	P8	P9	P10
31.3	31.3	45.2	45.2	52.7	28.5	51.0
46.5	46.5	70.2	70.2	70.9	76.4	74.5
140.6	140.6	135.2	135.2	108.4	97.2	114.2
167.9	167.9	151.2	151.2	140.0	121.7	139.5
196.9	196.9	265.6	265.6	194.1	177.5	190.3
298.8	298.8	290.6	290.6	298.2	321.3	308.3
403.0	403.0	384.8	384.8	355.2	362.0	409.8
414.0	414.0	469.1	469.1	411.4	434.9	419.1
516.4	516.4	546.6	546.6	514.5	477.4	528.0
561.2	561.2	568.1	568.1	571.8	601.4	575.0
597.8	597.8	608.7	608.7	633.2	753.7	731.6
729.6	729.6	776.9	776.9	780.6	789.3	785.3
826.0	826.0	802.1	802.1	829.2	864.1	834.4
872.7	872.7	837.4	837.4	924.5	910.9	867.2
985.6	985.6	909.5	909.5	965.4	955.7	956.7
1049.1	1049.1	954.6	954.6	1025.9	986.2	990.5
1065.8	1065.8	1029.4	1029.4	1028.8	1015.6	1023.4
1092.9	1092.9	1049.9	1049.9	1066.5	1066.7	1065.5
1129.7	1129.7	1062.5	1062.5	1093.9	1117.0	1099.7
1166.2	1166.2	1133.5	1133.5	1139.0	1142.4	1149.4
1190.0	1190.0	1178.6	1178.6	1212.0	1212.8	1211.4
1210.3	1210.3	1199.6	1199.6	1282.6	1215.6	1281.4
1281.8	1281.8	1285.9	1285.9	1297.8	1311.0	1292.4
1299.5	1299.5	1311.8	1311.8	1340.1	1338.5	1335.2
1388.2	1388.2	1340.8	1340.8	1402.2	1350.2	1351.8
1434.2	1434.2	1402.5	1402.5	1437.6	1426.2	1407.7
1442.4	1442.4	1433.1	1433.1	1480.5	1441.8	1437.2
1505.7	1505.7	1515.7	1515.7	1514.3	1509.4	1519.6
1522.9	1522.9	1527.1	1527.1	1526.5	1526.4	1526.4
1527.4	1527.4	1530.8	1530.8	1528.7	1532.6	1538.3
1537.0	1537.0	1535.6	1535.6	1539.1	1535.4	1542.5
1845.7	1845.7	1573.4	1573.4	1785.8	1784.6	1783.1
2716.5	2716.5	1791.8	1791.8	2007.2	1910.7	1924.4
3041.5	3041.5	3126.0	3126.0	3079.1	3109.7	3114.8
3131.4	3131.4	3129.4	3129.4	3129.0	3130.0	3128.2
3198.0	3198.0	3197.9	3197.9	3131.8	3145.3	3131.2
3204.7	3204.7	3218.9	3218.9	3169.1	3160.0	3163.8
3221.0	3221.0	3236.5	3236.5	3189.7	3206.6	3192.7
3261.5	3261.5	3256.9	3256.9	3218.0	3217.8	3213.9
3274.8	3274.8	3262.1	3262.1	3219.2	3222.2	3218.5
3315.9	3315.9	3263.8	3263.8	3260.6	3262.1	3260.0
3347.1	3347.1	3373.7	3373.7	3307.5	3345.6	3362.3

Table S-6: Optimized geometries of the reactant, pre-reactive complexes, transition states and products for the reaction of Cl atoms with 3-penten-2-one obtained at MP2/6-311++G (d,p) level of theory.

Table S-6-1: Optimized parameters of 3-penten-2-one.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.149964	-0.20473	-0.00013
2	8	0	1.995717	-1.09283	0.00052
3	1	0	2.63424	1.32835	0.000152
4	6	0	1.546191	1.259825	0.000098
5	1	0	1.146538	1.764158	0.885013
6	1	0	1.146346	1.764665	-0.88443
7	6	0	-0.29034	-0.56349	-0.00079
8	1	0	-0.49061	-1.63406	-0.00143
9	6	0	-1.30481	0.323217	-0.00097
10	1	0	-1.07945	1.389207	-2.4E-05
11	6	0	-2.75493	-0.05493	0.000508
12	1	0	-2.88056	-1.14028	-0.01093
13	1	0	-3.26333	0.365709	-0.8737
14	1	0	-3.25537	0.345419	0.888855

Table S-6-2: Optimized parameters of pre-reactive complex RC1a.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.59948	-0.14148	-0.18685
2	8	0	-2.43351	-0.23691	-1.05439
3	1	0	-2.69037	-1.28877	1.231626
4	6	0	-1.7907	-0.67384	1.213053
5	1	0	-1.91846	0.16377	1.907228
6	1	0	-0.91877	-1.25156	1.52528
7	6	0	-0.31587	0.600816	-0.50766
8	1	0	-0.14133	0.742016	-1.57094
9	6	0	0.313976	1.391483	0.394499
10	1	0	0.042981	1.298754	1.443858
11	6	0	1.384835	2.365415	0.052523
12	1	0	1.629333	2.331524	-1.00965
13	1	0	2.283206	2.149719	0.638843
14	1	0	1.054548	3.37598	0.319321
15	17	0	1.892372	-1.58121	-0.10846

Table S-6-3: Optimized parameters of Transition State TS1a.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.330851	-0.40964	-0.24889
2	8	0	2.145564	-0.15626	-1.12982
3	1	0	2.858397	-0.60774	1.228142
4	6	0	1.771979	-0.68211	1.176971
5	1	0	1.457146	-1.68201	1.490383
6	1	0	1.321742	0.042665	1.861906
7	6	0	-0.11596	-0.45145	-0.57787
8	1	0	-0.34942	-0.2452	-1.62152
9	6	0	-1.06653	-0.94402	0.240172
10	1	0	-0.79616	-1.2365	1.254307
11	6	0	-2.50267	-1.12373	-0.1484
12	1	0	-2.67679	-0.80433	-1.1787
13	1	0	-3.1552	-0.54364	0.513023
14	1	0	-2.79837	-2.17406	-0.05253
15	17	0	-0.5607	1.774501	0.170095

Table S-6-4: Optimized parameters of Transition State TS2a.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.67879	0.146459	-0.14202
2	8	0	-2.58372	0.35122	-0.94399
3	1	0	-2.95171	-0.9934	1.136518
4	6	0	-1.91106	-0.66923	1.116
5	1	0	-1.69545	-0.07002	2.005722
6	1	0	-1.25375	-1.54378	1.131776
7	6	0	-0.3281	0.704388	-0.40202
8	1	0	-0.24435	1.276948	-1.32474
9	6	0	0.664539	0.745029	0.508149
10	1	0	0.527471	0.246639	1.467282
11	6	0	1.975085	1.440095	0.295718
12	1	0	2.019437	1.908209	-0.69056
13	1	0	2.805034	0.730792	0.384271
14	1	0	2.128588	2.212335	1.057231
15	17	0	1.588496	-1.22223	-0.34532

Table S-6-5: Optimized parameters of Transition State TS1.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.694385	-0.05249	-0.02408
2	8	0	2.871121	0.162573	-0.17455
3	1	0	2.022445	-2.12215	0.306306
4	6	0	1.167979	-1.44974	0.239251
5	1	0	0.513148	-1.7625	-0.56802
6	1	0	0.584404	-1.48507	1.164183
7	6	0	0.745108	1.126452	-0.00041
8	1	0	1.25861	2.089298	0.009416
9	6	0	-0.54999	1.110161	0.002276
10	1	0	-1.20496	-0.07063	-0.12892
11	6	0	-1.50229	2.256082	0.074711
12	1	0	-0.94929	3.196531	0.156601
13	1	0	-2.15908	2.150625	0.943511
14	1	0	-2.13587	2.288928	-0.81685
15	17	0	-1.77821	-1.38403	-0.08355

Table S-6-6: Optimized parameters of Transition State TS2.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.776507	-0.09331	-0.06795
2	8	0	2.890922	0.097726	-0.48293
3	1	0	2.23924	-1.97986	0.795617
4	6	0	1.355431	-1.36839	0.615939
5	1	0	0.660008	-1.90542	-0.01902
6	1	0	0.831275	-1.15147	1.555579
7	6	0	0.812709	1.082116	-0.01952
8	1	0	1.317895	2.052337	-0.01546
9	6	0	-0.49318	1.082425	0.018417
10	1	0	-1.18632	-0.10725	-0.32378
11	6	0	-1.51372	2.141538	0.204008
12	1	0	-1.00973	3.094078	0.402667
13	1	0	-2.15846	1.894163	1.052037
14	1	0	-2.14349	2.23958	-0.68437
15	17	0	-1.95908	-1.29319	-0.20031

Table S-6-7: Optimized parameters of Transition State TS3.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.758066	-0.05694	-0.03612
2	8	0	2.805553	0.17071	-0.56685
3	1	0	2.289239	-2.00995	0.6231
4	6	0	1.390039	-1.39875	0.549265
5	1	0	0.679733	-1.88974	-0.12049
6	1	0	0.891558	-1.28416	1.514662
7	6	0	0.773907	1.100183	0.192661
8	1	0	1.285351	2.05866	0.329376
9	6	0	-0.48135	1.121214	0.062453
10	1	0	-1.15051	-0.12939	-0.18883
11	6	0	-1.55763	2.135984	0.090349
12	1	0	-1.11442	3.122302	0.270785
13	1	0	-2.2702	1.905055	0.886717
14	1	0	-2.09548	2.144719	-0.8607
15	17	0	-1.89753	-1.3349	-0.18068

Table S-6-8: Optimized parameters of Transition State TS4.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.771248	-0.04095	-0.01244
2	8	0	2.702313	0.245645	-0.7298
3	1	0	2.489042	-1.97466	0.508672
4	6	0	1.545899	-1.42862	0.546762
5	1	0	0.828076	-1.94612	-0.09353
6	1	0	1.120942	-1.40326	1.553975
7	6	0	0.810203	1.059012	0.377005
8	1	0	1.30622	2.002334	0.628489
9	6	0	-0.50872	1.098371	0.105212
10	1	0	-1.14522	-0.14021	-0.03644
11	6	0	-1.55598	2.140661	0.037853
12	1	0	-1.10247	3.122991	0.214946
13	1	0	-2.33964	1.961856	0.778945
14	1	0	-2.01811	2.142695	-0.95347
15	17	0	-1.94902	-1.33539	-0.18174

Table S-6-9: Optimized parameters of Transition State TS5

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.457348	-0.57485	-0.00177
2	8	0	1.379528	-1.79874	-0.00658
3	1	0	3.590016	-0.62244	0.006334
4	6	0	2.801541	0.12871	0.006279
5	1	0	2.896475	0.758356	0.889712
6	1	0	2.903441	0.76532	-0.87137
7	6	0	0.216063	0.239059	-0.00435
8	1	0	-0.87591	-0.44772	-0.0111
9	6	0	0.178185	1.585883	0.000166
10	1	0	1.113273	2.144007	0.005561
11	6	0	-1.08403	2.393708	-0.00252
12	1	0	-1.96632	1.749211	-0.00819
13	1	0	-1.12108	3.045742	-0.88187
14	1	0	-1.12839	3.040564	0.88033
15	17	0	-2.2272	-1.09872	0.003316

Table S-6-10: Optimized parameters of Transition State TS6

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.466463	-0.55632	0.021922
2	8	0	1.41418	-1.76664	0.041356
3	1	0	3.595956	-0.54126	-0.07615
4	6	0	2.787942	0.188926	-0.05596
5	1	0	2.905519	0.846977	0.805241
6	1	0	2.822823	0.801273	-0.95728
7	6	0	0.214047	0.264986	0.072943
8	1	0	-0.89582	-0.47634	0.189919
9	6	0	0.118774	1.578293	-0.00196
10	1	0	1.036867	2.162654	-0.0763
11	6	0	-1.16285	2.354775	0.012869
12	1	0	-2.02631	1.691715	0.090292
13	1	0	-1.25421	2.948584	-0.90253
14	1	0	-1.17152	3.053164	0.856074
15	17	0	-2.169	-1.13751	-0.03288

Table S-6-11: Optimized parameters of Transition State TS7

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.33286	0.005832	-0.19221
2	8	0	-3.27039	-0.47698	-0.81825
3	1	0	-3.44149	1.765232	0.28325
4	6	0	-2.4462	1.365411	0.471581
5	1	0	-1.69679	2.047512	0.072784
6	1	0	-2.28392	1.279843	1.545016
7	6	0	-1.06051	-0.75	-0.07785
8	1	0	-1.06035	-1.71553	-0.58152
9	6	0	0.033087	-0.32166	0.582425
10	1	0	0.0089	0.64739	1.078686
11	6	0	1.311089	-1.097	0.688873
12	1	0	1.240033	-2.04849	0.163953
13	1	0	1.555033	-1.29353	1.738462
14	1	0	2.292153	-0.42341	0.190989
15	17	0	3.32482	0.490669	-0.39897

Table S-6-12: Optimized parameters of Transition State TS8

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.34903	0.026419	-0.16215
2	8	0	3.334223	-0.52075	-0.54507
3	1	0	3.367236	1.8411	0.294544
4	6	0	2.349441	1.455871	0.340736
5	1	0	1.987725	1.495778	1.37175
6	1	0	1.683448	2.066148	-0.27554
7	6	0	1.012113	-0.70549	-0.19494
8	1	0	1.011598	-1.58117	-0.84229
9	6	0	-0.0204	-0.40213	0.540824
10	1	0	0.002343	0.468436	1.19358
11	6	0	-1.26151	-1.19613	0.548261
12	1	0	-1.27581	-2.026	-0.15793
13	1	0	-2.22712	-0.37037	0.126376
14	1	0	-1.62257	-1.48179	1.536739
15	17	0	-3.30428	0.510743	-0.31312

Table S-6-13: Optimized parameters of Product P1a

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.332938	-0.32658	-0.19311
2	8	0	2.07892	-0.57321	-1.10963
3	1	0	2.882879	-0.14558	1.250252
4	6	0	1.793481	-0.17609	1.23691
5	1	0	1.455023	-1.03836	1.821482
6	1	0	1.374059	0.72859	1.680914
7	6	0	-0.15105	-0.21709	-0.48873
8	1	0	-0.38349	-0.09616	-1.54338
9	6	0	-1.1001	-0.66437	0.368592
10	1	0	-0.81275	-0.87532	1.396268
11	6	0	-2.5302	-0.85883	0.009099
12	1	0	-2.72702	-0.55459	-1.01942
13	1	0	-3.16488	-0.27969	0.686704
14	1	0	-2.79528	-1.91498	0.134755
15	17	0	-0.50178	1.307028	-0.0663

Table S-6-14: Optimized parameters of Product P2a

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.5485	-0.29414	-0.04156
2	8	0	2.39888	-0.83295	-0.68486
3	1	0	2.88922	1.05413	0.91229
4	6	0	1.834001	0.790817	0.973054
5	1	0	1.607131	0.417764	1.977143
6	1	0	1.208736	1.665128	0.777472
7	6	0	0.104912	-0.72962	-0.21496
8	1	0	-0.05579	-1.4511	-1.01226
9	6	0	-0.93953	-0.28517	0.534505
10	1	0	-0.73462	0.383968	1.366576
11	6	0	-2.3004	-0.90456	0.492912
12	1	0	-2.4705	-1.41693	-0.4553
13	1	0	-3.07622	-0.15212	0.642131
14	1	0	-2.36794	-1.63269	1.309998
15	17	0	-1.03976	0.960671	-0.61781

Table S-6-15: Optimized parameters of Product P1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.15346	-0.18252	0.042028
2	8	0	-1.92532	-1.073	-0.23161
3	1	0	-2.57268	1.39885	-0.25225
4	6	0	-1.52808	1.278616	0.038299
5	1	0	-0.8714	1.822198	-0.64821
6	1	0	-1.35898	1.686588	1.039499
7	6	0	0.297931	-0.5	0.329999
8	1	0	0.455433	-1.42267	0.90213
9	6	0	1.311406	0.163691	-0.11311
10	6	0	2.783379	0.06892	-0.10854
11	1	0	3.095836	-0.80855	0.473019
12	1	0	3.224095	0.965011	0.334973
13	1	0	3.163163	-0.02967	-1.12832

Table S-6-16: Optimized parameters of Product P2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.14288	-0.17195	-0.02145
2	8	0	-2.05659	-0.95486	-0.14795
3	1	0	-2.39018	1.57884	-0.16446
4	6	0	-1.35072	1.323248	0.046308
5	1	0	-0.67556	1.796193	-0.67791
6	1	0	-1.0589	1.685128	1.036256
7	6	0	0.264581	-0.63477	0.220376
8	1	0	0.37126	-1.68574	0.521145
9	6	0	1.282921	0.121932	-0.03544
10	6	0	2.747588	0.054208	-0.08325
11	1	0	3.100897	-0.9431	0.217333
12	1	0	3.188426	0.795872	0.586639
13	1	0	3.107831	0.255694	-1.09473

Table S-6-17: Optimized parameters of Product P3

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.15262	-0.17411	0.011636
2	8	0	-2.03643	-0.97371	-0.14607
3	1	0	-2.432	1.534902	-0.19761
4	6	0	-1.39003	1.319484	0.037215
5	1	0	-0.7224	1.804417	-0.68269
6	1	0	-1.13236	1.705382	1.02767
7	6	0	0.279191	-0.6284	0.199732
8	1	0	0.404953	-1.67927	0.478015
9	6	0	1.293549	0.129527	-0.0394
10	6	0	2.761181	0.065993	-0.07523
11	1	0	3.107019	-0.93318	0.222584
12	1	0	3.194897	0.806697	0.601625
13	1	0	3.123649	0.275726	-1.0848

Table S-6-18: Optimized parameters of Product P4

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.15623	-0.17335	0.005689
2	8	0	-2.04246	-0.97534	-0.12301
3	1	0	-2.442	1.524754	-0.19364
4	6	0	-1.39597	1.321169	0.033337
5	1	0	-0.74096	1.817682	-0.68845
6	1	0	-1.14048	1.705016	1.025385
7	6	0	0.280944	-0.62991	0.167784
8	1	0	0.403386	-1.68706	0.420626
9	6	0	1.301697	0.129714	-0.04191
10	6	0	2.770842	0.066933	-0.06094
11	1	0	3.112015	-0.93931	0.216496
12	1	0	3.194322	0.790854	0.640074
13	1	0	3.145689	0.303506	-1.06024

Table S-6-19: Optimized parameters of Product P5

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.1776	-0.25147	0.024024
2	8	0	-1.92746	-1.17041	-0.09317
3	1	0	-2.68301	1.245164	-0.18362
4	6	0	-1.61634	1.202729	0.037713
5	1	0	-1.05432	1.784062	-0.69788
6	1	0	-1.41642	1.622767	1.02764
7	6	0	0.316974	-0.43658	0.195535
8	6	0	1.346411	0.275729	-0.10274
9	1	0	1.157866	1.290875	-0.47154
10	6	0	2.789604	-0.11962	0.009106
11	1	0	2.894928	-1.13214	0.39587
12	1	0	3.306969	0.582373	0.66976
13	1	0	3.259384	-0.05457	-0.97666

Table S-6-20: Optimized parameters of Product P6

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.17005	-0.25109	0.032425
2	8	0	-1.91036	-1.18011	-0.10069
3	1	0	-2.704	1.225776	-0.18083
4	6	0	-1.63803	1.194787	0.047542
5	1	0	-1.07843	1.787109	-0.68088
6	1	0	-1.45089	1.615307	1.039593
7	6	0	0.318652	-0.41904	0.200373
8	6	0	1.347913	0.280349	-0.13423
9	1	0	1.171667	1.270411	-0.57286
10	6	0	2.788563	-0.11402	0.024871
11	1	0	2.875725	-1.10131	0.47853
12	1	0	3.307795	0.619295	0.649286
13	1	0	3.278711	-0.12158	-0.95317

Table S-6-21: Optimized parameters of Product P7

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.089625	-0.21666	0.004703
2	8	0	1.859762	-1.11642	-0.17017
3	1	0	2.599524	1.289345	-0.02243
4	6	0	1.516692	1.233186	0.084211
5	1	0	1.202352	1.65983	1.041056
6	1	0	1.038125	1.810924	-0.71211
7	6	0	-0.39039	-0.51803	0.180603
8	1	0	-0.60186	-1.54246	0.482072
9	6	0	-1.35827	0.334334	-0.07912
10	1	0	-1.12878	1.352525	-0.3858
11	6	0	-2.78064	-0.00706	0.043226
12	1	0	-2.99835	-1.05786	0.232012
13	1	0	-3.45122	0.464397	-0.67518

Table S-6-22: Optimized parameters of Product P8

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.08964	-0.21666	0.004665
2	8	0	-1.85987	-1.11636	-0.16993
3	1	0	-2.59938	1.289463	-0.02299
4	6	0	-1.5166	1.233236	0.084095
5	1	0	-1.03768	1.810959	-0.71202
6	1	0	-1.20264	1.659825	1.041087
7	6	0	0.390398	-0.51813	0.180338
8	1	0	0.601817	-1.54274	0.481257
9	6	0	1.358272	0.334343	-0.07893
10	1	0	1.128771	1.352697	-0.38506
11	6	0	2.780654	-0.0071	0.04326
12	1	0	2.998325	-1.058	0.231598
13	1	0	3.451253	0.464592	-0.67497

Table S-7: Vibrational frequencies for the reactant, transition states and products for the reaction of Cl atoms with 3-penten-2-one obtained at MP2/6-311++G (d,p) level of theory.

Table S-7-1: Normal mode frequencies of R1, TS1a, TS2a, TS1, TS2 and TS3 (cm^{-1}).

R1	TS1a	TS2a	TS1	TS2	TS3
87.7	-400.1	-458.3	-630.1	-391.1	-630.1
130.4	62.2	36.8	33.4	27.8	33.4
177.9	112.1	116.2	105.5	78.6	105.5
191.0	143.2	147.4	120.0	119.7	120.0
192.4	150.6	189.5	144.2	138.8	144.2
365.1	167.8	191.2	174.0	162.7	174.0
498.5	202.8	232.4	176.6	167.7	176.6
542.4	261.6	263.5	271.2	236.2	271.2
548.7	361.2	366.8	295.5	342.0	295.5
779.6	479.4	489.6	459.1	465.6	459.1
817.3	540.3	547.8	497.1	524.1	497.1
965.1	588.1	563.0	580.8	533.6	580.8
996.9	801.5	789.7	685.5	620.5	685.5
1015.2	822.5	809.3	770.5	693.0	770.5
1037.8	961.5	958.0	832.8	803.2	832.8
1066.0	1026.8	1007.8	836.0	860.2	836.0
1142.8	1053.0	1029.0	926.4	960.7	926.4
1285.0	1062.6	1059.3	991.1	1007.5	991.1
1309.9	1096.2	1090.0	1037.3	1064.8	1037.3
1331.0	1163.2	1154.3	1051.6	1129.9	1051.6
1401.4	1273.6	1270.2	1097.2	1135.3	1097.2
1424.4	1288.4	1300.5	1152.9	1179.7	1152.9
1492.4	1350.4	1315.8	1230.8	1291.2	1230.8
1492.5	1399.9	1397.4	1271.5	1377.0	1271.5
1495.3	1417.0	1420.3	1401.2	1388.0	1401.2
1506.7	1482.1	1482.1	1409.1	1428.6	1409.1
1693.2	1487.9	1486.4	1470.5	1478.3	1470.5
1725.1	1494.0	1497.2	1478.3	1494.6	1478.3
3067.5	1497.5	1497.9	1494.5	1503.5	1494.5
3080.4	1691.4	1606.2	1497.1	1506.3	1497.1
3141.2	2278.1	2345.5	2056.4	2027.2	2056.4
3164.9	3074.2	3077.8	2219.7	2487.0	2219.7
3169.8	3084.4	3084.9	3064.3	3085.6	3064.3
3189.9	3152.2	3167.2	3084.2	3087.0	3084.2
3196.9	3175.4	3176.3	3134.6	3119.7	3134.6
3203.0	3198.1	3200.4	3160.1	3165.4	3160.1
	3214.7	3217.4	3176.3	3178.6	3176.3
	3222.4	3222.4	3177.9	3210.3	3177.9
	3232.9	3232.4	3211.0	3217.2	3211.0

Table S-7-2: Normal mode frequencies of TS4, TS5, TS6, TS7, TS8 and P1a (cm^{-1}).

TS4	TS5	TS6	TS7	TS8	P1a
-630.1	-391.1	-1576.3	-1576.3	-1576.5	64.8
33.4	27.8	29.1	29.1	28.9	74.1
105.5	78.6	48.9	48.9	48.9	105.9
120.0	119.7	102.1	102.1	102.1	107.9
144.2	138.8	138.0	138.0	137.9	184.7
174.0	162.7	197.7	197.7	197.7	205.2
176.6	167.7	208.6	208.6	208.6	287.9
271.2	236.2	350.2	350.2	350.2	333.1
295.5	342.0	409.8	409.8	409.8	457.8
459.1	465.6	461.3	461.3	461.3	538.2
497.1	524.1	501.9	501.9	501.9	548.0
580.8	533.6	550.7	550.7	550.7	572.0
685.5	620.5	589.2	589.2	589.1	728.9
770.5	693.0	808.3	808.3	808.3	812.7
832.8	803.2	832.3	832.3	832.3	952.5
836.0	860.2	946.6	946.6	946.5	1004.0
926.4	960.7	1008.9	1008.9	1008.8	1018.6
991.1	1007.5	1029.3	1029.3	1029.2	1046.2
1037.3	1064.8	1081.0	1081.0	1081.0	1130.4
1051.6	1129.9	1105.6	1105.6	1105.6	1190.9
1097.2	1135.3	1138.2	1138.2	1138.1	1262.4
1152.9	1179.7	1158.4	1158.4	1158.3	1283.2
1230.8	1291.2	1262.4	1262.4	1262.3	1293.9
1271.5	1377.0	1274.3	1274.3	1274.3	1401.5
1401.2	1388.0	1312.9	1312.9	1312.9	1412.3
1409.1	1428.6	1364.8	1364.8	1364.8	1450.1
1470.5	1478.3	1399.4	1399.4	1399.4	1485.5
1478.3	1494.6	1483.1	1483.1	1483.1	1495.6
1494.5	1503.5	1489.6	1489.6	1489.6	1497.7
1497.1	1506.3	1496.8	1496.8	1496.8	1501.9
2056.4	2027.2	1756.7	1756.7	1756.8	1758.9
2219.7	2487.0	2409.7	2409.7	2409.7	3036.1
3064.3	3085.6	3085.2	3085.2	3085.2	3082.9
3084.2	3087.0	3140.7	3140.7	3140.7	3120.1
3134.6	3119.7	3171.7	3171.7	3171.7	3156.9
3160.1	3165.4	3211.1	3211.1	3211.1	3172.1
3176.3	3178.6	3213.3	3213.3	3213.3	3174.4
3177.9	3210.3	3217.1	3217.1	3217.1	3206.0
3211.0	3217.2	3242.5	3242.5	3242.5	3233.2

Table S-7-3: Normal mode frequencies of products P2a, P1, P2, P3, P4 and P5 cm^{-1}.

P2a	P1	P2	P3	P4	P5
58.7	73.3	63.9	73.3	64.6	63.9
66.3	122.5	135.4	122.5	133.3	135.4
168.4	152.3	161.2	152.3	159.7	161.2
186.3	170.2	200.1	170.2	167.7	200.1
271.3	264.8	371.0	264.8	224.5	371.0
281.7	341.0	495.7	341.0	337.8	495.7
312.7	485.6	553.3	485.6	502.0	553.3
391.4	531.3	556.6	531.3	540.4	556.6
474.1	569.8	586.4	569.8	600.3	586.4
502.0	803.7	781.8	803.7	789.6	781.8
547.4	842.6	813.3	842.6	855.6	813.3
644.3	968.2	856.7	968.2	961.5	856.7
699.8	1024.2	985.4	1024.2	1014.4	985.4
811.8	1068.0	1041.2	1068.0	1065.7	1041.2
970.2	1088.4	1041.6	1088.4	1128.0	1041.6
999.8	1094.3	1056.4	1094.3	1133.0	1056.4
1045.2	1248.1	1140.5	1248.1	1215.4	1140.5
1054.1	1272.8	1282.8	1272.8	1303.3	1282.8
1127.1	1394.3	1313.9	1394.3	1386.0	1313.9
1197.0	1408.6	1341.1	1408.6	1419.6	1341.1
1269.3	1477.4	1397.0	1477.4	1476.9	1397.0
1284.7	1479.9	1471.1	1479.9	1494.8	1471.1
1320.4	1490.3	1489.4	1490.3	1500.8	1489.4
1399.7	1493.1	1495.8	1493.1	1506.3	1495.8
1424.4	1982.2	1538.9	1982.2	1973.1	1538.9
1435.1	2317.2	2210.0	2317.2	2415.0	2210.0
1485.8	3053.4	3083.7	3053.4	3082.3	3083.7
1499.0	3083.8	3170.5	3083.8	3084.1	3170.5
1503.3	3131.9	3201.2	3131.9	3110.4	3201.2
1509.0	3149.6	3214.3	3149.6	3161.5	3214.3
2115.6	3171.8	3216.2	3171.8	3175.2	3216.2
3077.8	3175.8	3223.3	3175.8	3200.8	3223.3
3080.6	3210.5	3314.9	3210.5	3209.6	3314.9
3150.7					
3166.7					
3171.6					
3186.5					
3214.8					
3226.9					

Table S-7-4: Normal mode frequencies of products P6, P7 and P8 cm^{-1}.

P6	P7	P8
63.9	63.9	63.9
135.4	135.4	135.4
161.2	161.2	161.2
200.1	200.1	200.1
371.0	371.0	371.0
495.7	495.7	495.7
553.3	553.3	553.3
556.6	556.6	556.6
586.4	586.4	586.4
781.8	781.8	781.8
813.3	813.3	813.3
856.7	856.7	856.7
985.4	985.4	985.4
1041.2	1041.2	1041.2
1041.6	1041.6	1041.6
1056.4	1056.4	1056.4
1140.5	1140.5	1140.5
1282.8	1282.8	1282.8
1313.9	1313.9	1313.9
1341.1	1341.1	1341.1
1397.0	1397.0	1397.0
1471.1	1471.1	1471.1
1489.4	1489.4	1489.4
1495.8	1495.8	1495.8
1538.9	1538.9	1538.9
2210.0	2210.0	2210.0
3083.7	3083.7	3083.7
3170.5	3170.5	3170.5
3201.2	3201.2	3201.2
3214.3	3214.3	3214.3
3216.2	3216.2	3216.2
3223.3	3223.3	3223.3
3314.9	3314.9	3314.9

Table S-8-1: The concentrations (integrated areas under the peaks in GC) of test and reference compounds for the reaction of Cl atoms with 4-hexen-3-one using GC at 298K and 760 Torr of N_2.

	Relative to 1,3-butadiene		**Relative to isoprene**		**Relative to 1-pentene**	
Laser pulses	reference	test	reference	test	reference	test
Before photolysis	3665.2	3172.5	3936.7	4820.3	4808.6	3463.8
	3626.2	3150.9	3994.7	4885.5	4829	3430.7
1200	3240.4	2816.2	3728.8	4455.8	4362.2	3091.8
	3247.2	2822.9	3508.8	4275	4325.9	3068.6
1400	2886.9	2580.3	3198.1	3912.5	3758.6	2675.5
	2421.6	2251.2	3006.9	3640.3	3746.9	2637.1
1600	2059.6	1957.4	2458.2	2973.0	3150.5	2263.2
	2022.2	1938.5	2470.5	2990.0	3155.1	2275.5
1800	1667.5	1598.2	2293.1	28170.2	2629.2	1893.3
	1662.5	1591.9	2273.0	2797.5	2610.9	1829

Table S-8-2: The concentrations (integrated areas under the peaks) of test and reference compounds for the reaction of Cl atoms with 5-hexen-2-one using GC at 298K and 760 Torr of N_2.

	Relative to 1,3-butadiene		**Relative to isoprene**		**Relative to 1-pentene**	
Laser pulses	reference	test	reference	test	reference	test
Before photolysis	4876.0	3204.0	4016.2	3102.2	4808.6	3463.8
	4895.2	3259.6	3997.9	2991.5	4829	3430.7
1200	4559.5	3033	3794.6	2802.7	4362.2	3091.8
	4495.4	2946.7	3764.6	2823.7	4325.9	3068.6
1400	3993.9	2658.7	3356	2462.1	3758.6	2675.5
	3911.4	2620.0	3314.5	2460.1	3746.9	2637.1
1600	3268.4	2123.0	2696.1	2037.9	3150.5	2263.2
	3240.2	2112.0	2677.2	1998.4	3155.1	2275.5
1800	2711.3	1910.5	2214.6	1792.2	2629.2	1893.3
	2759.4	1943.2	2254.6	1823.1	2610.9	1829.0

Table S-9-1: Calculated individual CVT/SCT rate coefficients (cm^3 $molecule^{-1}$ s^{-1}) for the reaction of Cl atoms with 4-hexen-3-one obtained at CCSD(T)/6-31+G(d,p)//MP2/6-311++G(d,p) level of theory.

T (K)	TS1a	TS2a	TS1	TS2	TS3	TS4
275	3.72×10^{-10}	2.09×10^{-10}	1.12×10^{-14}	1.12×10^{-14}	9.11×10^{-14}	8.66×10^{-15}
298	2.30×10^{-10}	1.35×10^{-10}	1.82×10^{-14}	1.82×10^{-14}	1.24×10^{-13}	1.44×10^{-14}
325	1.44×10^{-10}	8.85×10^{-11}	2.78×10^{-14}	2.78×10^{-14}	1.64×10^{-13}	2.24×10^{-14}
350	1.00×10^{-10}	6.38×10^{-11}	4.05×10^{-14}	4.05×10^{-14}	2.10×10^{-13}	3.31×10^{-14}
375	7.39×10^{-11}	4.83×10^{-11}	5.67×10^{-14}	5.67×10^{-14}	2.64×10^{-13}	4.69×10^{-14}
400	5.67×10^{-11}	3.81×10^{-11}	7.69×10^{-14}	7.69×10^{-14}	3.25×10^{-13}	6.44×10^{-14}

Table S-9-2: Calculated individual CVT/SCT rate coefficients (cm^3 $molecule^{-1}$ s^{-1}) for the reaction of Cl atoms with 4-hexen-3-one obtained at CCSD(T)/6-31+G(d,p)//MP2/6-311++G(d,p) level of theory.

T (K)	TS5	TS6	TS7	TS8	TS9	TS10
275	4.01×10^{-12}	3.06×10^{-29}	3.30×10^{-24}	1.42×10^{-12}	1.42×10^{-12}	1.67×10^{-12}
298	3.99×10^{-12}	2.27×10^{-27}	3.33×10^{-23}	1.49×10^{-12}	1.49×10^{-12}	1.79×10^{-12}
325	4.03×10^{-12}	7.28×10^{-26}	2.39×10^{-22}	1.57×10^{-12}	1.57×10^{-12}	1.92×10^{-12}
350	4.11×10^{-12}	1.26×10^{-24}	1.31×10^{-21}	1.67×10^{-12}	1.67×10^{-12}	2.07×10^{-12}
375	4.23×10^{-12}	1.38×10^{-23}	5.81×10^{-21}	1.79×10^{-12}	1.79×10^{-12}	2.23×10^{-12}
400	4.38×10^{-12}	1.06×10^{-22}	2.15×10^{-20}	1.92×10^{-12}	1.92×10^{-12}	2.40×10^{-12}

Table S-9-3: Calculated individual CVT/SCT rate coefficients (cm^3 $molecule^{-1}$ s^{-1}) for the reaction of Cl atoms with 5-hexen-2-one obtained at CCSD(T)/6-31+G(d,p)//MP2/6-311++G(d,p) level of theory.

T (K)	TS1a	TS2a	TS1	TS2	TS3	TS4
275	6.83×10^{-10}	3.10×10^{-10}	1.47×10^{-14}	1.92×10^{-14}	1.25×10^{-14}	1.70×10^{-14}
298	4.35×10^{-10}	1.22×10^{-10}	2.23×10^{-14}	2.86×10^{-14}	1.92×10^{-14}	2.55×10^{-14}
325	2.80×10^{-10}	1.95×10^{-10}	3.22×10^{-14}	4.05×10^{-14}	2.81×10^{-14}	3.65×10^{-14}
350	1.99×10^{-10}	1.25×10^{-10}	4.46×10^{-14}	5.52×10^{-14}	3.92×10^{-14}	5.01×10^{-14}
375	1.49×10^{-10}	8.80×10^{-11}	5.98×10^{-14}	7.29×10^{-14}	5.30×10^{-14}	6.66×10^{-14}
400	1.16×10^{-10}	6.39×10^{-11}	7.79×10^{-14}	9.38×10^{-14}	6.96×10^{-14}	8.61×10^{-14}

Table S-9-4: Calculated individual CVT/SCT rate coefficients (cm^3 $molecule^{-1}$ s^{-1}) for the reaction of Cl atoms with 5-hexen-2-one obtained at CCSD(T)/6-31+G(d,p)//MP2/6-311++G(d,p) level of theory.

T (K)	TS5	TS6	TS7	TS8	TS9	TS10
275	5.23×10^{-13}	1.08×10^{-14}	2.94×10^{-14}	4.57×10^{-21}	1.99×10^{-25}	2.06×10^{-24}
298	5.91×10^{-13}	1.68×10^{-14}	4.21×10^{-14}	2.42×10^{-20}	2.43×10^{-24}	2.07×10^{-23}
325	6.63×10^{-13}	2.48×10^{-14}	5.79×10^{-14}	1.01×10^{-19}	2.05×10^{-23}	1.48×10^{-22}
350	7.40×10^{-13}	3.50×10^{-14}	7.69×10^{-14}	3.45×10^{-19}	1.29×10^{-22}	8.09×10^{-22}
375	8.22×10^{-13}	4.76×10^{-14}	9.94×10^{-14}	1.01×10^{-18}	6.40×10^{-22}	3.56×10^{-21}
400	9.09×10^{-13}	6.29×10^{-14}	1.25×10^{-13}	2.62×10^{-18}	2.63×10^{-21}	1.31×10^{-20}

Table S-9-5: Calculated individual CVT/SCT rate coefficients (cm^3 $molecule^{-1}$ s^{-1}) for the reaction of Cl atoms with 3-penten-2-one obtained at CCSD(T)/6-31+G(d,p)//MP2/6-311++G(d,p) level of theory.

T (K)	TS1a	TS2a	TS1	TS2	TS3	TS4
275	2.18×10^{-10}	1.33×10^{-10}	5.76×10^{-13}	2.33×10^{-13}	2.33×10^{-13}	3.15×10^{-20}
298	1.47×10^{-10}	9.33×10^{-11}	6.66×10^{-13}	2.90×10^{-13}	2.90×10^{-13}	1.47×10^{-19}
325	1.00×10^{-10}	6.61×10^{-11}	7.62×10^{-13}	3.53×10^{-13}	3.53×10^{-13}	5.46×10^{-19}
350	7.48×10^{-11}	5.07×10^{-11}	8.64×10^{-13}	4.24×10^{-13}	4.24×10^{-13}	1.70×10^{-18}
375	5.83×10^{-11}	4.06×10^{-11}	9.74×10^{-13}	5.01×10^{-13}	5.01×10^{-13}	4.60×10^{-18}
400	4.71×10^{-11}	3.36×10^{-11}	1.09×10^{-12}	5.85×10^{-13}	5.85×10^{-13}	1.11×10^{-17}

Table S-9-6: Calculated individual CVT/SCT rate coefficients (cm^3 $molecule^{-1}$ s^{-1}) for the reaction of Cl atoms with 3-penten-2-one obtained at CCSD(T)/6-31+G(d,p)//MP2/6-311++G(d,p) level of theory.

T (K)	TS5	TS6	TS7	TS8
275	2.15×10^{-24}	5.00×10^{-15}	5.00×10^{-15}	1.60×10^{-15}
298	2.22×10^{-23}	8.58×10^{-15}	8.58×10^{-15}	3.01×10^{-15}
325	1.63×10^{-22}	1.37×10^{-14}	1.37×10^{-14}	5.22×10^{-15}
350	9.05×10^{-22}	2.07×10^{-14}	2.07×10^{-14}	8.46×10^{-15}
375	4.05×10^{-21}	3.00×10^{-14}	3.00×10^{-14}	1.30×10^{-14}
400	1.51×10^{-20}	4.17×10^{-14}	4.17×10^{-14}	1.90×10^{-14}

Table S-10-1: Sum of electronic and zero point energy [E, Hartree], heat of reaction [H, Hartree], Gibbs free energy [G, Hartree] and entropy of reaction [S, cal mol^{-1} K^{-1}] for the reaction of Cl atoms with 4-hexen-3-one obtained at MP2/6-311++G(d, p) level of theory.

TSs	E	H	G	S
R1	-308.881620	-308.871933	-308.915570	91.843
R2	-459.586161	-459.583800	-459.601838	37.964
TS1a	-768.471724	-768.460867	-768.508678	100.628
TS2a	-768.468602	-768.457810	-768.505614	100.612
TS1	-768.454468	-768.443454	-768.492356	102.923
TS2	-768.454469	-768.443454	-768.492356	102.922
TS3	-768.452909	-768.441524	-768.492239	106.740
TS4	-768.456773	-768.445524	-768.494400	102.868
TS5	-768.456096	-768.444808	-768.494001	103.536
TS6	-768.444802	-768.433404	-768.482986	104.355
TS7	-768.438560	-768.427049	-768.477182	105.515
TS8	-768.452991	-768.441794	-768.491701	105.039
TS9	-768.452991	-768.441794	-768.491701	105.039
TS10	-768.452991	-768.441793	-768.491701	105.038

Table S-10-2: Sum of electronic and zero point energy [E, Hartree], heat of reaction [H, Hartree], Gibbs free energy [G, Hartree] and entropy of reaction [S, cal mol^{-1} K^{-1}] for the reaction of Cl atoms with 5-hexen-2-one obtained at the MP2/6-311++G(d, p) level of theory.

TSs	E	H	G	S
R1	-308.74798	-308.738412	-308.782483	92.755
R2	-459.552	-459.550073	-459.568111	37.964
TS1a	-768.301	-768.290247	-768.339121	102.863
TS2a	-768.301	-768.290180	-768.338388	101.464
TS1	-768.275	-768.264274	-768.313173	102.917
TS2	-768.271511	-768.260377	-768.310624	105.754
TS3	-768.277303	-768.266278	-768.315931	104.505
TS4	-768.284211	-768.273097	-768.322452	103.877
TS5	-768.285159	-768.273879	-768.323979	105.445
TS6	-768.284751	-768.273866	-768.321956	101.214
TS7	-768.288771	-768.277652	-768.327205	104.295
TS8	-768.275114	-768.263912	-768.314043	105.510
TS9	-768.271624	-768.260282	-768.311192	107.149
TS10	-768.267861	-768.256823	-768.306540	104.639

Table S-10-3: Sum of electronic and zero point energy [E, Hartree], heat of reaction [H, Hartree], Gibbs free energy [G, Hartree] and entropy of reaction [S, cal mol^{-1} K^{-1}] for the reaction of Cl atoms with 3-penten-2-one obtained at MP2/6-311++G (d, p) level of theory.

TSs	E	H	G	S
R1	-269.714064	-269.705728	-269.745412	83.523
R2	-459.586161	-459.5838	-459.601838	37.964
TS1a	-729.30275	-729.293161	-729.337567	93.459
TS2a	-729.29952	-729.290036	-729.334439	93.454
TS1	-729.292	-729.274148	-729.321843	97.951
TS2	-729.292	-729.274148	-729.321843	97.951
TS3	-729.296	-729.274167	-729.321952	97.963
TS4	-729.27495	-729.264890	-729.310934	96.907
TS5	-729.26923	-729.259035	-729.305761	98.344
TS6	-729.292	-729.274092	-729.320715	97.962
TS7	-729.284	-729.274088	-729.320623	97.940
TS8	-729.284	-729.274089	-729.320628	97.949