Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

- Supporting Information -

The Activated Reaction of Dichlorocarbene with Triplet Molecular Oxygen

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Table of Contents

1. Optimized CCSD(T) Geometries and Energies

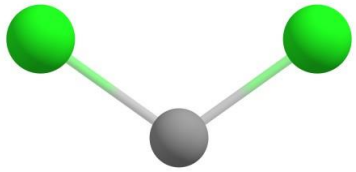

Figure S1. Optimized geometry of the ^{1}**1** (in Å) at the CCSD(T)/cc-pVTZ level of theory. The energies are given in units of E_h.

17	0.000000000	-1.409685000	0.146935000
6	0.000000000	0.000000000	-0.856360000
17	0.000000000	1.409685000	0.146935000

	HF	MP2	CCSD	CCSD(T)	BD(TQ)
cc-pVDZ	-956.7634533	-957.1506236	-957.1836938	-957.1986123	-957.1988455
cc-pVTZ	-956.8060378	-957.3213668	-957.3581745	-957.3868493	-957.3867113
cc-pVQZ	-956.8168706	-957.3797264	-957.4122815	-957.4455353	
cc-pV5Z	-956.8198944	-957.4030743	-957.4304256	-957.4653784	
CBS limit	[-956.8210653]	[-957.4255688]	[-957.4474603]	[-957.4841958]	
ZPVE = 0.00415363 E_h					

FC-CCSD(T)/cc-pCVTZ: -957.39723700489
AE-CCSD(T)/cc-pCVTZ: -958.121026146216

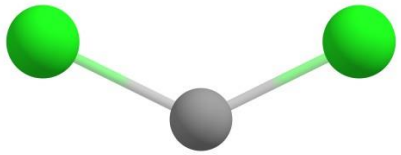

Figure S2. Optimized geometry of the ^{3}**1** (in Å) at the CCSD(T)/cc-pVTZ level of theory. The energies are given in units of E_h.

17	0.000000000	-1.512917000	0.108913000
6	0.000000000	0.000000000	-0.633020000
17	0.000000000	1.512917000	0.108913000

	QRO-HF	MP2	CCSD	CCSD(T)	(U)BD(TQ)
cc-pVDZ	-956.7633594	-957.1268160	-957.1573655	-957.1683226	-957.1690504
cc-pVTZ	-956.8060062	-957.2951752	-957.3313959	-957.3554542	-957.3559647
cc-pVQZ	-956.8169120	-957.3523901	-957.3851872	-957.4136639	
cc-pV5Z	-956.8201773	-957.3755544	-957.4035411	-957.4336640	
CBS limit	[-956.8215728]	[-957.3978274]	[-957.4207673]	[-957.4526173]	
ZPVE = 0.00449644 E_h					

(U)CCSD(T)/cc-pVTZ:	-957.3553544
FC-CCSD(T)/cc-pCVTZ:	-957.36644600532
AE-CCSD(T)/cc-pCVTZ:	-958.090719019151

Figure S3. Optimized geometry of $^{3}O_{2}$ (in Å) at the CCSD(T)/cc-pVTZ level of theory. The energies are given in units of E_h.

8	0.000000000	0.000000000	0.606070000
8	0.000000000	0.000000000	-0.606070000

	QRO-HF	MP2	CCSD	CCSD(T)	(U)BD(TQ)
cc-pVDZ	-149.6066634	-149.9873024	-149.9748027	-149.9857423	-149.9870783
cc-pVTZ	-149.6510115	-150.1275076	-150.1095890	-150.1290357	-150.1290981
cc-pVQZ	-149.6623319	-150.1739260	-150.1520146	-150.1738628	
cc-pV5Z	-149.6652394	-150.1914237	-150.1661837	-150.1889739	
CBS limit	[-149.6662442]	[-150.2077362]	[-150.1790039]	[-150.2027824]	
ZPVE = 0.00361060 E_h					

(U)CCSD(T)/cc-pVTZ: -150.1290363
FC-CCSD(T)/cc-pCVTZ: -150.136597664944
AE-CCSD(T)/cc-pCVTZ: -150.244052466017

Figure S4. Electronic energies of **^{3}O** atom given in units of E_h.

	QRO-HF	MP2	CCSD	CCSD(T)	(U)BD(TQ)
cc-pVDZ	-74.7874720	-74.8940703	-74.9091433	-74.9099097	-74.9101209
cc-pVTZ	-74.8055722	-74.9550515	-74.9708938	-74.9738680	-74.9742207
cc-pVQZ	-74.8107535	-74.9751410	-74.9896980	-74.9934644	
cc-pV5Z	-74.8121344	-74.9827489	-74.9959292	-74.9999990	
CBS limit	[-74.8126361]	[-74.9897839]	[-75.0015198]	[-75.0059079]	
ZPVE = –					

(U)CCSD(T)/cc-pVTZ: -74.9739618
FC-CCSD(T)/cc-pCVTZ: -74.977371733738
AE-CCSD(T)/cc-pCVTZ: -75.030882682384

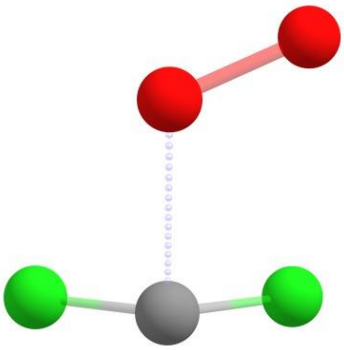

Figure S5. Optimized geometry of ^{3}**TS$_{add}$** (in Å) at the CCSD(T)/cc-pVTZ level of theory. The energies are given in units of E_h.

8	-2.155398000	-0.840258000	-0.221280000
8	-1.095315000	-1.346841000	0.136647000
6	0.278278000	0.043568000	0.617283000
17	-0.313760000	1.515892000	-0.045089000
17	1.732339000	-0.505920000	-0.127309000

	QRO-HF	MP2	CCSD	CCSD(T)	(U)BD(TQ)
cc-pVDZ	-1106.3176580	-1107.1070599	-1107.1373730	-1107.1668855	-1107.1678087
cc-pVTZ	-1106.4022872	-1107.4209598	-1107.4470752	-1107.5001238	-1107.4988467
cc-pVQZ	-1106.4241215	-1107.5269459	-1107.5443529	-1107.6048948	
cc-pV5Z	-1106.4299386	-1107.5683908	-1107.5771428	-1107.6405569	
CBS limit	[-1106.4320513]	[-1107.6078834]	[-1107.6075549]	[-1107.6739824]	
ZPVE = 0.00919654 E_h					

(U)CCSD(T)/cc-pVTZ: -1107.4985498
FC-CCSD(T)/cc-pCVTZ: -1107.51810452866
AE-CCSD(T)/cc-pCVTZ: -1108.34943569184

Optimized geometry of ^{3}**TS$_{add}$** (in Å) at the CCSD(T)/cc-pVDZ level of theory. The energies are given in units of E_h.

8	-2.150708000	-0.828153000	-0.210301000
8	-1.081913000	-1.341570000	0.132189000
6	0.264845000	0.030239000	0.606336000
17	-0.333281000	1.524326000	-0.047197000
17	1.747200000	-0.518404000	-0.120776000

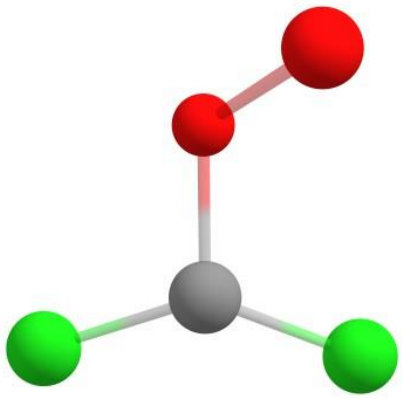

Figure S6. Optimized geometry of ^{3}**CI$_a$** (in Å) at the CCSD(T)/cc-pVTZ level of theory. The energies are given in units of E_h.

8	0.272646000	-2.228158000	0.369362000
8	-0.481461000	-1.283192000	-0.217199000
6	0.179306000	-0.051958000	-0.093292000
17	-0.047090000	0.915714000	-1.485378000
17	0.056875000	0.691778000	1.450463000

	QRO-HF	MP2	CCSD	CCSD(T)	(U)BD(TQ)
cc-pVDZ	-1106.4071094	-1107.1317415	-1107.1717452	-1107.1947818	-1107.1958744
cc-pVTZ	-1106.4969876	-1107.4481895	-1107.4888252	-1107.5339338	-1107.5334273
cc-pVQZ	-1106.5188651	-1107.5535344	-1107.5868363	-1107.6389755	
cc-pV5Z	-1106.5248767	-1107.5949177	-1107.6200182	-1107.6748212	
CBS limit	[-1106.5271544]	[-1107.6343068]	[-1107.6508025]	[-1107.7084003]	
ZPVE = 0.01179035 E_h					

(U)CCSD(T)/cc-pVTZ:	-1107.5337776
FC-CCSD(T)/cc-pCVTZ:	-1107.55185915468
AE-CCSD(T)/cc-pCVTZ:	-1108.38380361765

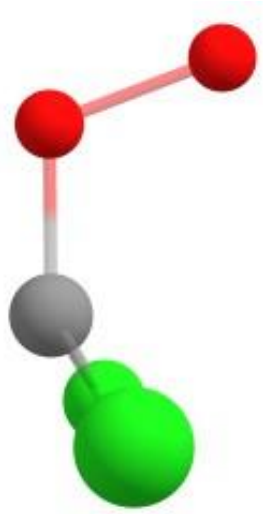

Figure S7. Optimized geometry of ^{3}**CI$_b$** (in Å) at the CCSD(T)/cc-pVTZ level of theory. The energies are given in units of E_h.

8	-1.959684000	0.566385000	-0.000001000
8	-1.314765000	-0.629541000	0.000000000
6	0.054463000	-0.455883000	0.000000000
17	0.740225000	0.092360000	1.470328000
17	0.740224000	0.092361000	-1.470328000

	QRO-HF	MP2	CCSD	CCSD(T)	(U)BD(TQ)
cc-pVDZ	-1106.4080136	-1107.1338691	-1107.1741548	-1107.1974610	-1107.1985250
cc-pVTZ	-1106.4977612	-1107.4502124	-1107.4911335	-1107.5365633	-1107.5360251
cc-pVQZ	-1106.5195875	-1107.5555590	-1107.5891354	-1107.6416264	
cc-pV5Z	-1106.5255746	-1107.5969318	-1107.6223119	-1107.6774788	
CBS limit	[-1106.5278376]	[-1107.6363209]	[-1107.6531017]	[-1107.7110760]	
ZPVE = 0.01172053 E_h					

(U)CCSD(T)/cc-pVTZ:	-1107.5363584
FC-CCSD(T)/cc-pCVTZ:	-1107.55452795885
AE-CCSD(T)/cc-pCVTZ:	-1108.38650843678

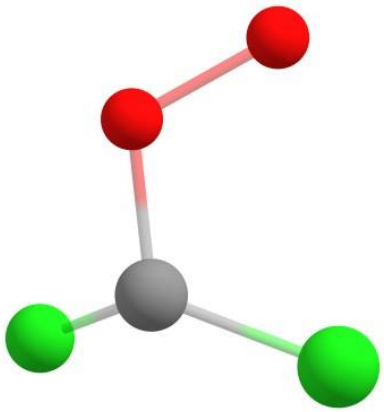

Figure S8. Optimized geometry of $^{3}\mathbf{TS}_{\mathbf{rot}}$ (in Å) at the CCSD(T)/cc-pVTZ level of theory. The energies are given in units of E_h.

8	1.785490000	1.223925000	-0.219241000
8	0.520216000	1.331577000	0.176083000
6	-0.119316000	0.054381000	0.383373000
17	0.750152000	-1.355847000	-0.017837000
17	-1.763813000	0.168548000	-0.093735000

	QRO-HF	MP2	CCSD	CCSD(T)	(U)BD(TQ)
cc-pVDZ	-1106.3996717	-1107.1267362	-1107.1653604	-1107.1888087	-1107.1898228
cc-pVTZ	-1106.4893936	-1107.4432689	-1107.4823376	-1107.5279108	-1107.5273121
cc-pVQZ	-1106.5112762	-1107.5488333	-1107.5805174	-1107.6331691	
cc-pV5Z	-1106.5173150	-1107.5903518	-1107.6138175	-1107.6691529	
CBS limit	[-1106.5196167]	[-1107.6298780]	[-1107.6447212]	[-1107.7028722]	
ZPVE = 0.01158300 E_h					

(U)CCSD(T)/cc-pVTZ: -1107.527757
FC-CCSD(T)/cc-pCVTZ: -1107.54590567806
AE-CCSD(T)/cc-pCVTZ: -1108.37779440201

Optimized geometry of $^{3}\mathbf{TS}_{\mathbf{rot}}$ (in Å) at the CCSD(T)/cc-pVDZ level of theory. The energies are given in units of E_h.

8	1.793304000	1.228605000	-0.223915000
8	0.521256000	1.338143000	0.178307000
6	-0.119836000	0.055571000	0.394927000
17	0.756056000	-1.369039000	-0.021099000
17	-1.778050000	0.169304000	-0.099576000

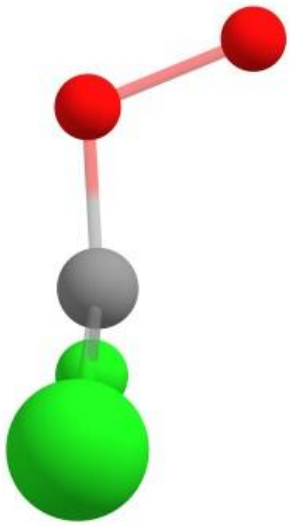

Figure S9. Optimized geometry of ^{3}**TS$_{inv}$** (in Å) at the CCSD(T)/cc-pVTZ level of theory. The energies are given in units of E_h.

8	-2.177064000	0.445951000	-0.001193000
8	-1.287325000	-0.595516000	0.002244000
6	-0.008376000	-0.116603000	0.000214000
17	0.794680000	0.058088000	1.483737000
17	0.793899000	0.047253000	-1.485002000

	QRO-HF	MP2	CCSD	CCSD(T)	(U)BD(TQ)
cc-pVDZ	-1106.3986910	-1107.1267530	-1107.1680308	-1107.1911819	-1107.1923707
cc-pVTZ	-1106.4891237	-1107.4441753	-1107.4858745	-1107.5311142	-1107.5307118
cc-pVQZ	-1106.5111599	-1107.5497275	-1107.5839615	-1107.6362296	
cc-pV5Z	-1106.5173507	-1107.5912723	-1107.6172659	-1107.6721959	
CBS limit	[-1106.5197695]	[-1107.6307836]	[-1107.6481316]	[-1107.7058545]	
ZPVE = 0.01078400 E_h					

(U)CCSD(T)/cc-pVTZ: -1107.5308758
FC-CCSD(T)/cc-pCVTZ: -1107.54931809346
AE-CCSD(T)/cc-pCVTZ: -1108.38149474799

Optimized geometry of ^{3}**TS$_{inv}$** (in Å) at the CCSD(T)/cc-pVDZ level of theory. The energies are given in units of E_h.

8	0.347126000	-2.215570000	0.004111000
8	-0.667637000	-1.264025000	-0.002232000
6	-0.119502000	-0.012114000	-0.001267000
17	0.092824000	0.800061000	-1.495762000
17	0.094837000	0.795539000	1.495149000

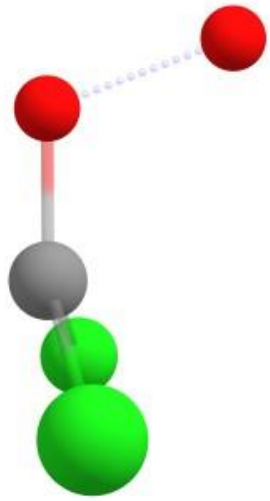

Figure S10. Optimized geometry of ^{3}**TSo–o** (in Å) at the CCSD(T)/cc-pVTZ level of theory. The energies are given in units of E_h.

8	-2.110133000	0.555790000	0.000097000
8	-1.252937000	-0.689709000	-0.000059000
6	0.012159000	-0.374178000	-0.000021000
17	0.765571000	0.096581000	-1.466231000
17	0.765471000	0.096649000	1.466213000

	QRO-HF	MP2	CCSD	CCSD(T)	(U)BD(TQ)
cc-pVDZ	-1106.3851442	-1107.1369080	-1107.1697445	-1107.1951934	-1107.1963680
cc-pVTZ	-1106.4734087	-1107.4523916	-1107.4846546	-1107.5325152	-1107.5319850
cc-pVQZ	-1106.4950317	-1107.5575048	-1107.5820144	-1107.6370521	
cc-pV5Z	-1106.5009550	-1107.5986897	-1107.6149032	-1107.6726485	
CBS limit	[-1106.5031898]	[-1107.6379203]	[-1107.6454297]	[-1107.7060156]	
ZPVE = 0.00990299 E_h					

(U)CCSD(T)/cc-pVTZ: -1107.5318482
FC-CCSD(T)/cc-pCVTZ: -1107.55040856666
AE-CCSD(T)/cc-pCVTZ: -1108.38236716715

Optimized geometry of ^{3}**TSo–o** (in Å) at the CCSD(T)/cc-pVDZ level of theory. The energies are given in units of E_h.

8	-2.092306000	0.561395000	-0.000003000
8	-1.269230000	-0.696314000	0.000001000
6	0.019064000	-0.401255000	0.000001000
17	0.761300000	0.110655000	-1.477893000
17	0.761302000	0.110653000	1.477893000

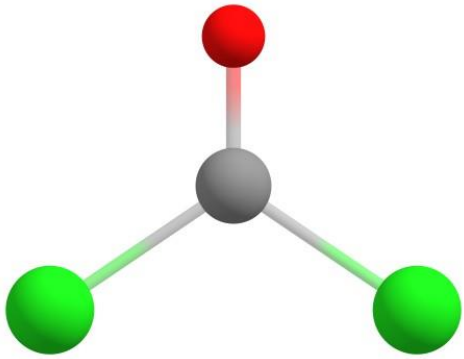

Figure S11. Optimized geometry of **phosgene** (in Å) at the CCSD(T)/cc-pVTZ level of theory. The energies are given in units of E_h.

8	0.000000000	0.000000000	1.689510000
6	0.000000000	0.000000000	0.507944000
17	0.000000000	1.451070000	-0.473549000
17	0.000000000	-1.451070000	-0.473549000

	HF	MP2	CCSD	CCSD(T)	BD(TQ)
cc-pVDZ	-1031.7327041	-1032.3190120	-1032.3391733	-1032.3593130	-1032.3592427
cc-pVTZ	-1031.7995498	-1032.5630524	-1032.5853890	-1032.6236121	-1032.6223007
cc-pVQZ	-1031.8163299	-1032.6460544	-1032.6626258	-1032.7065873	
cc-pV5Z	-1031.8206228	-1032.6782871	-1032.6881112	-1032.7341845	
CBS limit	[-1031.8220986]	[-1032.7090768]	[-1032.7118218]	[-1032.7601108]	
ZPVE = 0.01050856 E_h					

FC-CCSD(T)/cc-pCVTZ: -1032.63756233569
AE-CCSD(T)/cc-pCVTZ: -1033.41618003596

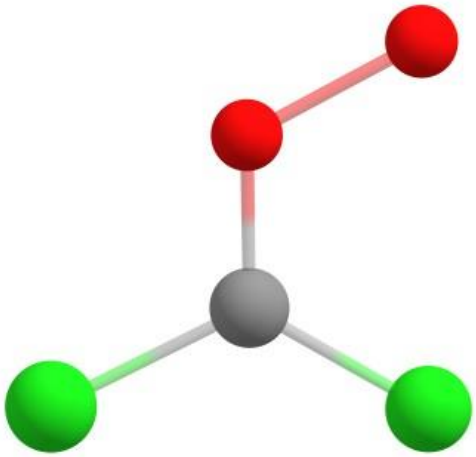

Figure S12. Optimized geometry of **^{1}CI** (in Å) at the CCSD(T)/cc-pVTZ level of theory. The energies are given in units of E_h.

8	-1.903816000	-1.186421000	0.000000000
8	-0.544640000	-1.230144000	0.000000000
6	0.091135000	-0.125765000	0.000000000
17	-0.701501000	1.361212000	0.000000000
17	1.790167000	-0.212700000	0.000000000

	HF	MP2	CCSD	CCSD(T)	BD(TQ)
cc-pVDZ	-1106.3933196	-1107.1698829	-1107.1974039	-1107.2294146	-1107.2280490
cc-pVTZ	-1106.4888510	-1107.4957581	-1107.5203741	-1107.5752619	-1107.5717546
cc-pVQZ	-1106.5123486	-1107.6051248	-1107.6209921	-1107.6831353	
cc-pV5Z	-1106.5190241	-1107.6483023	-1107.6552644	-1107.7201789	
CBS limit	[-1106.5216731]	[-1107.6892485]	[-1107.6868674]	[-1107.7546895]	
ZPVE = 0.01296280 E_h					

FC-CCSD(T)/cc-pCVTZ: -1107.59350500271
AE-CCSD(T)/cc-pCVTZ: -1108.42574896807

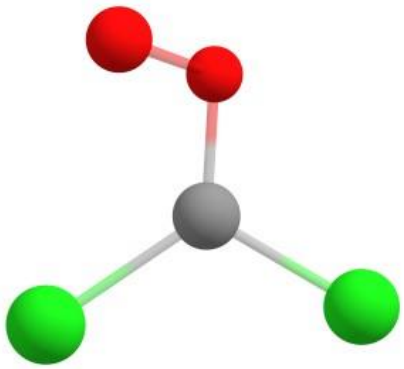

Figure S13. Optimized geometry of ^{1}**TS**$_{\mathbf{diox}}$ (in Å) at the CCSD(T)/cc-pVTZ level of theory. The energies are given in units of E_h.

8	-1.574528000	1.293728000	0.444253000
8	-0.431674000	1.281861000	-0.519794000
6	0.026624000	0.176701000	-0.133968000
17	-0.809030000	-1.310381000	-0.031558000
17	1.717618000	0.071717000	0.112210000

	HF	MP2	CCSD	CCSD(T)	BD(TQ)
cc-pVDZ	-1106.3769364	-1107.1371980	-1107.1700988	-1107.2009706	-1107.1996914
cc-pVTZ	-1106.4708371	-1107.4626869	-1107.4929520	-1107.5465984	-1107.5432968
cc-pVQZ	-1106.4937176	-1107.5714677	-1107.5931573	-1107.6541080	
cc-pV5Z	-1106.5000720	-1107.6142816	-1107.6272104	-1107.6909615	
CBS limit	[-1106.5025153]	[-1107.6549774]	[-1107.6587146]	[-1107.7254040]	
ZPVE = 0.01147640 E_h					

FC-CCSD(T)/cc-pCVTZ: -1107.56470226333
AE-CCSD(T)/cc-pCVTZ: -1108.39665985948

Optimized geometry of ^{1}**TS**$_{\mathbf{diox}}$ (in Å) at the CCSD(T)/cc-pVDZ level of theory. The energies are given in units of E_h.

8	-1.600401000	1.309452000	0.448996000
8	-0.428978000	1.285885000	-0.522357000
6	0.030597000	0.178047000	-0.134342000
17	-0.809887000	-1.325321000	-0.031147000
17	1.737678000	0.065564000	0.109992000

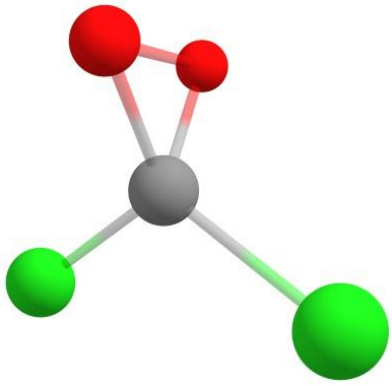

Figure S14. Optimized geometry of ^{1}**3** (in Å) at the CCSD(T)/cc-pVTZ level of theory. The energies are given in units of E_h.

8	-0.774141000	0.000000000	-1.405911000
6	-0.000003000	0.000000000	-0.284130000
8	0.774141000	0.000000000	-1.405905000
17	0.000002000	1.453896000	0.691821000
17	0.000002000	-1.453896000	0.691821000

	HF	MP2	CCSD	CCSD(T)	BD(TQ)
cc-pVDZ	-1106.4476276	-1107.2325683	-1107.2536471	-1107.2815662	-1107.2824438
cc-pVTZ	-1106.5405867	-1107.5549393	-1107.5740867	-1107.6250517	-1107.6237613
cc-pVQZ	-1106.5621220	-1107.6615673	-1107.6725947	-1107.7307512	
cc-pV5Z	-1106.5679368	-1107.7032019	-1107.7057238	-1107.7665592	
CBS limit	[-1106.5700876]	[-1107.7429342]	[-1107.7365322]	[-1107.8001783]	
ZPVE = 0.01345403 E_h					

FC-CCSD(T)/cc-pCVTZ: -1107.64255295999
AE-CCSD(T)/cc-pCVTZ: -1108.47459382731

2. Optimized CASSCF Geometries and Energies

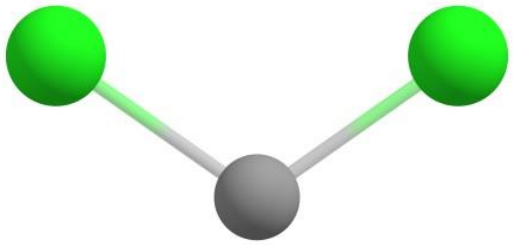

Figure S15. Optimized geometry of ^{1}**1** (in Å) at the CASSCF/cc-pVTZ level of theory. The electronic energies are given in units of E_h.

17	0.000000000	-1.405109000	0.140662000
6	0.000000000	0.000000000	-0.843814000
17	0.000000000	1.405109000	0.140662000

CASSCF: -956.827423451077
ZPVE: 2.81 kcal mol^{-1}
NEVPT2: -957.313301720415

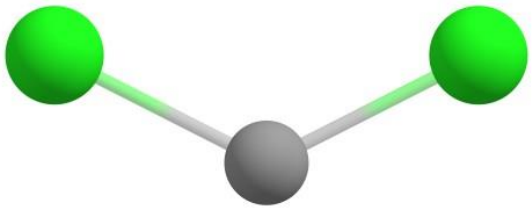

Figure S16. Optimized geometry of ^{3}**1** (in Å) at the CASSCF/cc-pVTZ level of theory. The electronic energies are given in units of E_h.

17	0.000000000	-1.506335000	0.115982000
6	0.000000000	0.000000000	-0.647158000
17	0.000000000	1.506335000	0.115982000

CASSCF: -956.806399483346
ZPVE: 2.98 kcal mol^{-1}
NEVPT2: -957.289330172388

Figure S17. Optimized geometry of $^{3}\mathbf{O_2}$ (in Å) at the CASSCF/cc-pVTZ level of theory. The electronic energies are given in units of E_h.

8	0.000000000	0.000000000	0.608010000
8	0.000000000	0.000000000	-0.608010000

CASSCF: -149.752032245556
ZPVE: 2.20 kcal mol^{-1}
NEVPT2: -150.088923907962

Figure S18. Optimized geometry of $^1\mathbf{O_2}$ (in Å) at the CASSCF/cc-pVTZ level of theory. The electronic energies are given in units of E_h.

8	0.000000000	0.000000000	0.614507000
8	0.000000000	0.000000000	-0.614507000

CASSCF: -149.719366610829
ZPVE: 2.08 kcal mol^{-1}
NEVPT2: -150.053439044401

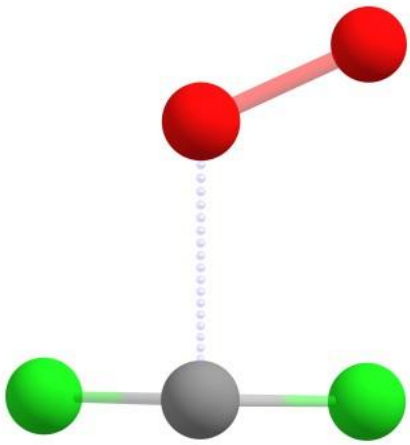

Figure S19. Optimized geometry of ^{3}**TS$_{add}$** (in Å) at the CASSCF/cc-pVTZ level of theory. The electronic energies are given in units of E_h.

8	-2.245280000	-0.882491000	-0.194286000
8	-1.187897000	-1.386653000	0.165150000
6	0.310889000	0.051433000	0.531121000
17	-0.285754000	1.535986000	-0.043106000
17	1.764547000	-0.542582000	-0.130028000

CASSCF: -1106.55147855008
ZPVE: 5.83 kcal mol^{-1}
NEVPT2: -1107.39137907818

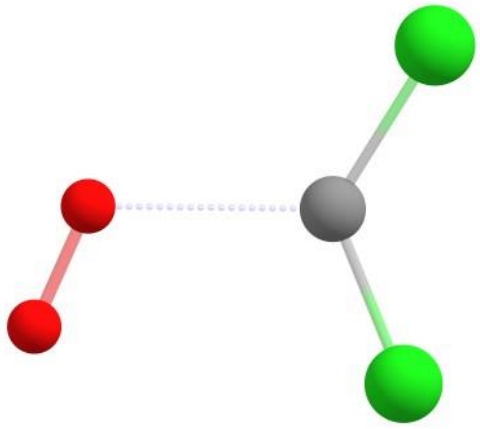

Figure S20. Optimized geometry of ^{1}**TS**$_{\mathbf{add}}$ (in Å) at the CASSCF/cc-pVTZ level of theory. The electronic energies are given in units of E_h.

8	-2.419085000	-0.957324000	-0.039134000
8	-1.313948000	-1.457734000	0.059120000
6	0.341264000	0.032660000	0.208648000
17	-0.203814000	1.623917000	0.029565000
17	1.952089000	-0.465824000	0.070651000

CASSCF: -1106.55553268667
ZPVE: 5.82 kcal mol^{-1}
NEVPT2: -1107.38358149462

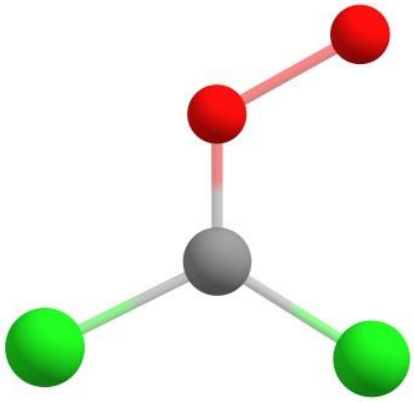

Figure S21. Optimized geometry of **^{1}CI** (in Å) at the CASSCF/cc-pVTZ level of theory. The electronic energies are given in units of E_h.

8	-2.143463000	-0.790068000	0.026299000
8	-0.810004000	-1.105773000	0.058595000
6	0.038715000	-0.164780000	0.065752000
17	-0.387997000	1.461088000	0.037549000
17	1.673395000	-0.622465000	0.105932000

CASSCF: -1106.62425642351
ZPVE: 8.31 kcal mol^{-1}
NEVPT2: -1107.46828569791

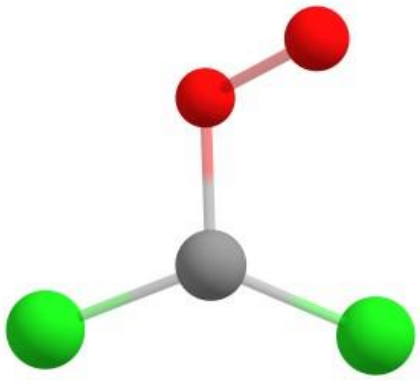

Figure S22. Optimized geometry of $^{3}\mathbf{CI_a}$ (in Å) at the CASSCF/cc-pVTZ level of theory. The electronic energies are given in units of E_h.

8	-2.089180000	-0.906571000	0.265432000
8	-0.862400000	-1.062000000	-0.308479000
6	0.004892000	-0.114777000	0.273149000
17	-0.313335000	1.523088000	-0.122650000
17	1.622693000	-0.659273000	0.173646000

CASSCF: -1106.58661829021
ZPVE: 7.79 kcal mol^{-1}
NEVPT2: -1107.42541960065

3. Energies at Other Levels

Table S1. Energies ΔH_0 at various levels of theory given in units of E_h.

method	**$^1CCl_2$**	**$^3CCl_2$**	**$^3O_2$**	**$^3TS_{add}$**
PBE/6-311+G(d)	-958.004339	-957.973026	-150.225984	–
PBE/def2-TZVPP	-958.018886	-957.989466	-150.245317	-1108.264247
BLYP/def2-TZVPP	-958.427761	-958.394271	-150.383820	-1108.808198
PBE0/def2-TZVPP	-958.083275	-958.061778	-150.231673	-1108.307507
B3LYP/6-31G(d)	-958.379084	-958.352233	-150.316261	-1108.689995
B3LYP/def2-TZVPP	-958.462562	-958.435020	-150.386034	-1108.838951
B3LYP(SMD:*n*-pentane)/def2-TZVPP	-958.463214	-958.435495	-150.387606	-1108.841662
B3LYP-D3/def2-TZVPP	-958.462946	-958.435619	-150.386035	-1108.842144
M06-2X/def2-TZVPP	-958.384447	-958.356818	-150.323160	-1108.692055
B2PLYP/def2-TZVPP	-958.140478	-958.112029	-150.295295	-1108.419910
DSD-PBEP86/def2-TZVPP	-957.711185	-957.683408	-150.155414	-1107.848115
CBS-QB3	-957.431235	-957.397941	-150.164554	-1107.585144
G4	-958.140112	-958.107322	-150.278657	-1108.402671

4. Correlation of the Oxygen Addition Barrier Heights With the Singlet-Triplet Gaps

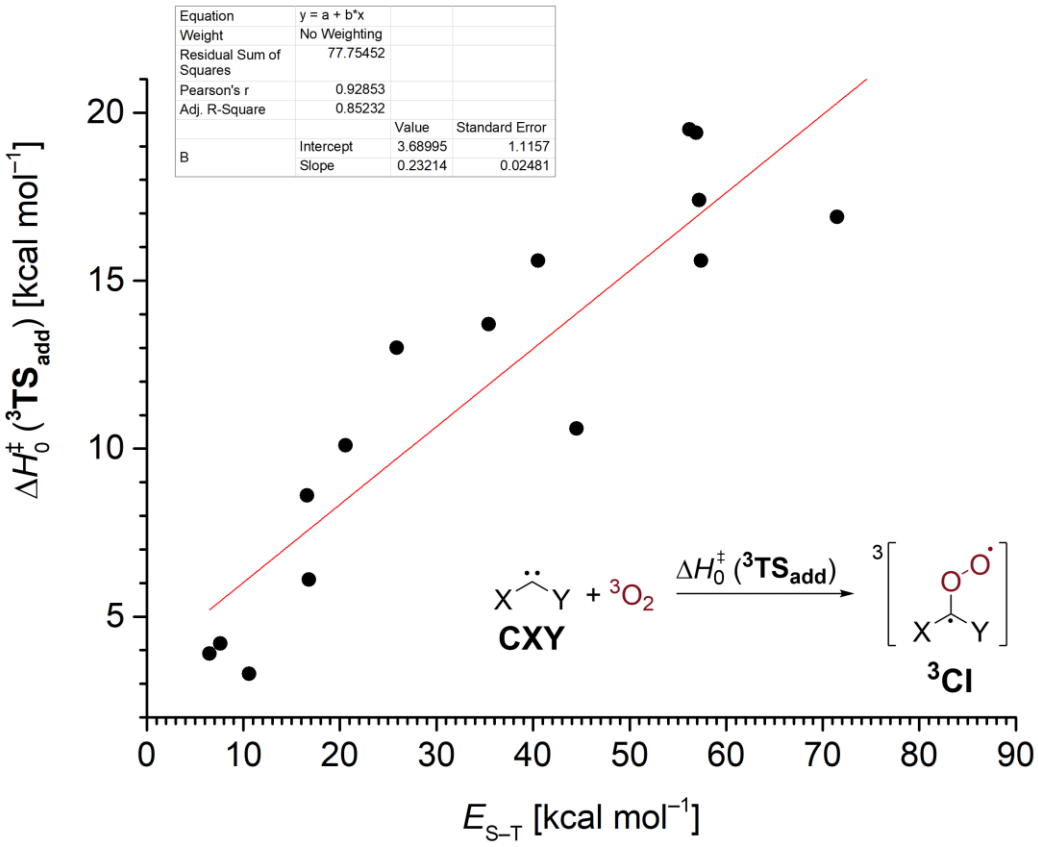

Figure S23. $^3O_2$ addition barriers to various carbenes CXY at the G4 level as a function of the carbene's singlet-triplet gap.