Supplementary Information

Theoretical Exploration of 4π-Photocyclization Mechanism of α-Tropone Derivatives

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This file includes:

Figure S1. *Wavelengths, energy, and the oscillator strengths (focs) associated with the $S_0 \rightarrow S_n$ excitations for substituted α-tropone systems calculated at NEVPT2(12,10)/cc-PVDZ.*

System	Excitation	Wavelength (nm)	Energy (eV)	focs
1a	$S_0 \rightarrow S_1$	323	3.8436	0.00012
	$S_0 \rightarrow S_2$	316	3.9233	0.00198
	$S_0 \rightarrow S_3$	286	4.3295	0.06572
	$S_0 \rightarrow S_4$	249	4.9891	0.05579
	$S_0 \rightarrow S_5$	191	6.4812	0.09936
1b	$S_0 \rightarrow S_1$	315	3.9344	0.00002
	$S_0 \rightarrow S_2$	303	4.0938	0.00237
	$S_0 \rightarrow S_3$	274	4.0938	0.07167
	$S_0 \rightarrow S_4$	260	4.7658	0.07093
	$S_0 \rightarrow S_5$	191	6.4929	0.10748
1c	$S_0 \rightarrow S_1$	324	3.8306	0.00135
	$S_0 \rightarrow S_2$	323	3.8355	0.00057
	$S_0 \rightarrow S_3$	298	4.1602	0.10001
	$S_0 \rightarrow S_4$	253	4.8946	0.03199
	$S_0 \rightarrow S_5$	194	6.3826	0.12683
1d	$S_0 \rightarrow S_1$	311	3.9862	0.00019
	$S_0 \rightarrow S_2$	286	4.3379	0.09284
	$S_0 \rightarrow S_3$	285	4.3442	0.00131
	$S_0 \rightarrow S_4$	247	5.0234	0.03248
	$S_0 \rightarrow S_5$	200	6.1958	0.26902
1e	$S_0 \rightarrow S_1$	310	3.9964	0.000003
	$S_0 \rightarrow S_2$	304	4.0732	0.00080
	$S_0 \rightarrow S_3$	281	4.4192	0.00992
	$S_0 \rightarrow S_4$	254	4.8806	0.04776
	$S_0 \rightarrow S_5$	190	6.5246	0.11100
1f	$S_0 \rightarrow S_1$	316	3.9230	0.00205
	$S_0 \rightarrow S_2$	313	3.9626	0.00003
	$S_0 \rightarrow S_3$	285	4.3578	0.08900
	$S_0 \rightarrow S_4$	261	4.7535	0.04146
	$S_0 \rightarrow S_5$	193	6.4167	0.13907
1g	$S_0 \rightarrow S_1$	304	4.0767	0.03672
	$S_0 \rightarrow S_2$	293	4.2282	0.00009
	$S_0 \rightarrow S_3$	274	4.5319	0.00452
	$S_0 \rightarrow S_4$	264	4.6891	0.05689
	$S_0 \rightarrow S_5$	209	5.9456	0.08514
1h	$S_0 \rightarrow S_1$	270	4.5881	0.11852
	$S_0 \rightarrow S_2$	256	4.8443	0.00505
	$S_0 \rightarrow S_3$	214	5.7924	0.09836
	$S_0 \rightarrow S_4$	185	6.7023	0.53653
	$S_0 \rightarrow S_5$	164	7.5749	0.17250
1i	$S_0 \rightarrow S_1$	267	4.6460	0.02365
	$S_0 \rightarrow S_2$	250	4.9572	0.01671
	$S_0 \rightarrow S_3$	200	6.2023	0.05531
	$S_0 \rightarrow S_4$	180	6.8810	0.10230
	$S_0 \rightarrow S_5$	179	6.9462	0.06532

Figure S2. *Wavelengths, energy, and the oscillator strengths (focs) associated with the $S_0 \rightarrow S_n$ excitations for substituted α-tropone systems calculated at NEVPT2(12,10)/cc-PVTZ.*

System	Excitation	Wavelength (nm)	Energy (eV)	focs
1a	$S_0 \rightarrow S_1$	324	3.8303	0.00011
	$S_0 \rightarrow S_2$	319	3.8844	0.00202
	$S_0 \rightarrow S_3$	292	4.2415	0.06674
	$S_0 \rightarrow S_4$	254	4.8914	0.05736
	$S_0 \rightarrow S_5$	194	6.3905	0.09303
1b	$S_0 \rightarrow S_1$	318	3.9051	0.00002
	$S_0 \rightarrow S_2$	306	4.0571	0.00227
	$S_0 \rightarrow S_3$	285	4.3575	0.07708
	$S_0 \rightarrow S_4$	263	4.7224	0.06713
	$S_0 \rightarrow S_5$	194	6.3925	0.10632
1c	$S_0 \rightarrow S_1$	333	3.7242	0.00092
	$S_0 \rightarrow S_2$	323	3.8366	0.00076
	$S_0 \rightarrow S_3$	306	4.0516	0.10083
	$S_0 \rightarrow S_4$	258	4.8028	0.03257
	$S_0 \rightarrow S_5$	198	6.2750	0.12074
1d	$S_0 \rightarrow S_1$	313	3.9649	0.00018
	$S_0 \rightarrow S_2$	291	4.2657	0.08795
	$S_0 \rightarrow S_3$	290	4.2804	0.00123
	$S_0 \rightarrow S_4$	254	4.8750	0.03990
	$S_0 \rightarrow S_5$	204	6.0819	0.27366
1e	$S_0 \rightarrow S_1$	314	3.9517	0.000006
	$S_0 \rightarrow S_2$	308	4.0279	0.00068
	$S_0 \rightarrow S_3$	287	4.3190	0.09983
	$S_0 \rightarrow S_4$	260	4.7625	0.04852
	$S_0 \rightarrow S_5$	193	6.4215	0.10456
1f	$S_0 \rightarrow S_1$	319	3.8870	0.00182
	$S_0 \rightarrow S_2$	317	3.9173	0.00005
	$S_0 \rightarrow S_3$	290	4.2748	0.08955
	$S_0 \rightarrow S_4$	268	4.6286	0.04375
	$S_0 \rightarrow S_5$	196	6.3139	0.13339
1g	$S_0 \rightarrow S_1$	310	4.0022	0.03330
	$S_0 \rightarrow S_2$	294	4.2132	0.00008
	$S_0 \rightarrow S_3$	272	4.5518	0.00074
	$S_0 \rightarrow S_4$	271	4.5732	0.06166
	$S_0 \rightarrow S_5$	211	5.8884	0.08237
1h	$S_0 \rightarrow S_1$	285	4.3475	0.12064
	$S_0 \rightarrow S_2$	260	4.7733	0.00544
	$S_0 \rightarrow S_3$	213	5.8206	0.08413
	$S_0 \rightarrow S_4$	186	6.6668	0.49759
	$S_0 \rightarrow S_5$	169	7.3285	0.21000
1i	$S_0 \rightarrow S_1$	269	4.6032	0.02266
	$S_0 \rightarrow S_2$	255	4.8615	0.01837
	$S_0 \rightarrow S_3$	207	6.1207	0.05609
	$S_0 \rightarrow S_4$	184	6.7576	0.11202
	$S_0 \rightarrow S_5$	182	6.8141	0.06550

Optimized S_0/T_1 crossing geometries for the substituted α-tropone systems at CASSCF(12,10)/cc-PVDZ level.

1a			
C	-1.70245200	0.86111800	1.11183000
C	-2.36444000	1.64636700	0.10247600
C	-1.83467900	2.77414300	-0.63416200
C	-1.52543900	1.57082800	2.22966800
C	-1.29200100	3.86155300	-0.07400100
C	-2.13809700	2.86443100	2.06071400
C	-1.51620500	4.02048900	1.35640400
H	-1.53049800	-0.19941700	0.98896900
H	-3.07224200	1.07502800	-0.49603700
H	-1.93029500	2.71413000	-1.71181400
H	-1.15168600	1.20385500	3.17514400
H	-0.85271100	4.66820300	-0.63978700
O	-1.31514700	5.07609200	1.97524100
H	-2.70349000	3.22308600	2.91805500
1b			
C	-1.24269921	-1.89185769	0.92696219
C	-1.56855116	-1.32462948	-0.39032873
C	-1.82736944	0.01641707	-0.72196341
C	-0.08198816	-1.50022461	1.40643229
C	-1.15805800	1.11080468	-0.13547200
C	0.54879014	-0.58844653	0.44442975
C	0.12080233	0.85124118	0.44764970
H	-1.92127670	-2.59098398	1.39570815
H	-2.03304543	-2.03499219	-1.06931005
H	-2.49757714	0.20350910	-1.55004064
H	0.38538717	-1.79031325	2.33599557
H	-1.48254345	2.13044331	-0.27369414
O	0.88100614	1.72706576	0.87245747
O	1.85091982	-0.87603541	0.24398251
C	2.55894800	-0.13606006	-0.77917503
H	3.43712792	-0.72919637	-1.01142030
H	1.94009256	-0.03265229	-1.66888408
H	2.85039062	0.84036975	-0.40631226
1c			
C	-2.39265084	1.01270946	1.18570814
C	-1.48174016	1.55993553	0.17738156
C	-1.48793118	2.72036415	-0.49593907
C	-2.45496150	1.72348654	2.28736280
C	-2.11402563	3.92636578	-0.01122795
C	-1.58184105	2.89775940	2.14699808
C	-2.04849553	4.08244433	1.38887212
H	-2.89039341	0.07231388	0.99887798
H	-0.85053344	0.79882691	-0.27571122
H	-0.87086742	2.79534305	-1.38112409
H	-3.01589511	1.51324125	3.18539382
H	-2.38373764	4.75153613	-0.65057867

O	-2.27967666	5.17049128	1.99642492
C	-0.62138939	3.14249540	3.18678000
N	0.20533452	3.27317262	3.99674042
1d			
C	-2.19590620	0.91841746	1.11225423
C	-1.19279942	1.57127130	0.28339810
C	-1.35058254	2.74510913	-0.51502416
C	-2.58922038	1.66042069	2.14373716
C	-1.95564463	3.89731159	-0.09744822
C	-1.82140742	2.89894734	2.15991356
C	-2.21109678	4.05467954	1.30047788
H	-2.51798799	-0.09045673	0.89550125
H	-0.47955418	0.87498354	-0.15250955
H	-0.89919818	2.72085499	-1.49817443
H	-3.29068720	1.39329467	2.92242640
O	-2.66124087	5.08487332	1.80379654
O	-1.32637242	3.30424481	3.35731645
H	-1.21015350	2.56858195	3.93616481
H	-2.13761850	4.72985382	-0.75948142
1e			
C	-1.51391534	0.90423781	1.17636293
C	-2.43729849	1.69448675	0.36085730
C	-2.19138871	2.84850529	-0.40999784
C	-0.98305185	1.58473161	2.19890778
C	-1.27707610	3.86314423	-0.06261853
C	-1.57086305	2.92925097	2.20580423
C	-0.93741927	3.95403102	1.32174147
H	-1.36825471	-0.14532347	0.96216108
H	-3.27653972	1.11634635	-0.01881540
H	-2.80997599	2.98939658	-1.28575810
H	-0.29626568	1.21337353	2.94662501
H	-0.98688033	4.64364887	-0.74881991
O	-0.23772490	4.84331663	1.81667581
C	-2.21952483	3.42145633	3.47582362
H	-1.47783105	3.57327690	4.26479689
H	-2.73460205	4.36771028	3.31838020
H	-2.94016393	2.68583174	3.83491512
1f			
C	-2.27345481	0.96045189	1.15180592
C	-1.50100088	1.51509909	0.05130519
C	-1.71655816	2.74462049	-0.64020951
C	-2.18568848	1.67309361	2.27130071
C	-1.96929003	3.93539398	-0.03693806
C	-1.29574260	2.79330727	2.05211379
C	-1.72201175	4.04194067	1.36879966
H	-2.78363994	0.01404074	1.04282019
H	-1.06208376	0.75429890	-0.58980158
H	-1.61257114	2.71467191	-1.71679813
H	-2.60668248	1.43885052	3.23686790
H	-2.21346720	4.82889669	-0.59060218

O	-1.78282037	5.10577550	1.99231123
Cl	-0.14066195	3.06723206	3.40868890
1g			
C	-2.22629615	0.96488852	1.18566925
C	-1.46570268	1.53929630	0.08608949
C	-1.65870788	2.74920656	-0.59358705
C	-2.21190918	1.71631510	2.29525393
C	-2.09424507	3.95592212	0.00668329
C	-1.34456540	2.87349334	2.07103500
C	-1.87343678	4.07688930	1.38345742
H	-2.70437163	-0.00022771	1.07742787
H	-1.00100277	0.78523033	-0.54906543
H	-1.34732776	2.78316786	-1.63092380
H	-2.68226752	1.51171771	3.24852009
H	-2.38239111	4.81753218	-0.57727473
O	-1.98613578	5.16278093	2.02839467
N	-0.43349880	3.14423687	3.08016473
H	0.03286807	2.34185923	3.45546472
H	0.19430979	3.90516118	2.90964316
1h			
C	-2.31882103	0.98013782	1.20580594
C	-1.67089109	1.49110721	0.04931499
C	-1.60229655	2.69737937	-0.60252471
C	-2.21494627	1.75362955	2.33441405
C	-1.86468484	3.96925060	-0.05395268
C	-1.27073803	2.80674688	2.00985936
C	-1.71964811	4.05167065	1.32696886
H	-2.73378509	-0.01767589	1.17657937
H	-1.41382018	0.68343836	-0.63613038
H	-1.31122892	2.64930087	-1.64415710
H	-2.51837758	1.49036127	3.33521315
H	-2.04744164	4.84110286	-0.66403106
O	-1.85210458	5.08673525	2.03510503
C	-0.01976441	2.88664652	2.76843315
O	0.32648039	2.02557558	3.55107463
H	0.62271851	3.75414461	2.57671190
1i			
C	-2.35166451	0.99619814	1.20630281
C	-1.47224827	1.50371485	0.15596455
C	-1.53054438	2.72323223	-0.55384043
C	-2.38538980	1.75095511	2.31189417
C	-1.96831655	3.95933651	-0.00163515
C	-1.44900911	2.86557599	2.12562407
C	-1.91180382	4.07623511	1.38594850
H	-2.86130327	0.05045508	1.07509885
H	-0.97928845	0.71687617	-0.41061894
H	-1.12553979	2.72655695	-1.55731242
H	-2.94208755	1.57089749	3.22087805
H	-2.20424885	4.81485886	-0.61705418
O	-2.18757752	5.12283151	2.04374507

C	-0.40468467	3.06948819	3.18411399
F	0.26823964	1.94988737	3.39516551
F	-0.93389113	3.42046274	4.34858425
F	0.46734583	4.00080815	2.85010751
3a			
C	-1.71599073	0.84484084	1.07818460
C	-2.41261516	1.67549014	0.10550760
C	-1.76510903	2.70656566	-0.67927439
C	-1.48714834	1.55536086	2.19777033
C	-1.18840462	3.82500425	-0.07022267
C	-1.99848229	2.90499538	2.10450578
C	-1.56878048	3.98406390	1.29273697
H	-1.57587589	-0.21632845	0.94362168
H	-3.25455276	1.20635170	-0.39380080
H	-1.81023830	2.64179455	-1.75780441
H	-1.15356168	1.17506147	3.15122967
H	-0.71828142	4.62044508	-0.62746992
O	-1.65062050	5.15366925	1.85069125
H	-2.49741812	3.26997886	2.99697705
H	-1.44843605	5.87716723	1.27015264
3b			
C	-1.61085656	0.92084022	0.72303685
C	-2.52402826	1.83381803	0.08663141
C	-2.40195075	3.16608158	-0.31176581
C	-1.03284875	1.39416867	1.85479712
C	-1.57651975	4.13594551	0.23646053
C	-1.67603412	2.66402232	2.16246501
C	-1.15229898	3.90949353	1.56689106
H	-1.50206434	-0.07836232	0.32853178
H	-3.31453258	1.32698654	-0.45928858
H	-3.03386461	3.45533563	-1.14106256
H	-0.33791580	0.89787021	2.51224813
H	-1.40367072	5.08732713	-0.23988849
O	-0.47318597	4.73808317	2.20413353
H	-2.19399487	2.78166520	3.10531679
B	-0.03908173	4.52663294	3.78956816
F	0.82414668	5.54315820	3.99323565
F	0.52436546	3.27692368	3.83467212
F	-1.21106435	4.61140975	4.48631735

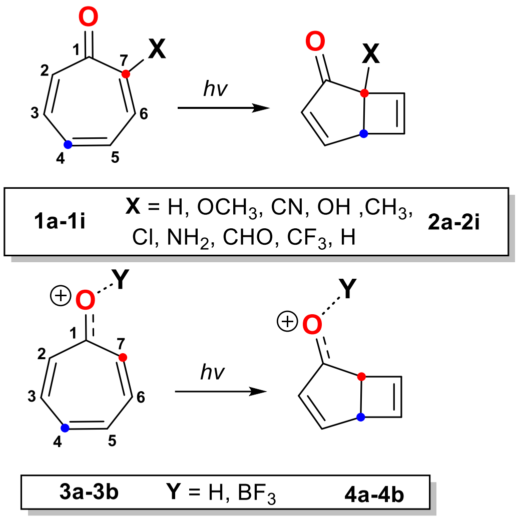

Table S3. *Energy gaps at the T_1/S_0 crossing for the substituted α-tropone systems. ($\Delta E_1 = E(T_1)- E(S_0)$ and $\Delta E_2 = E(S_1)- E(S_0)$ in kcal mol^{-1}.*

Reaction	ΔE_1	ΔE_2
1a	0.19	29.28
1b	1.15	1.78
1c	2.92	26.61
1d	1.14	5.05
1e	0.61	15.41
1f	0.74	21.06
1g	6.19	9.39
1h	0.79	22.32
1i	0.50	24.47
3a	1.04	7.28
3b	0.95	17.41

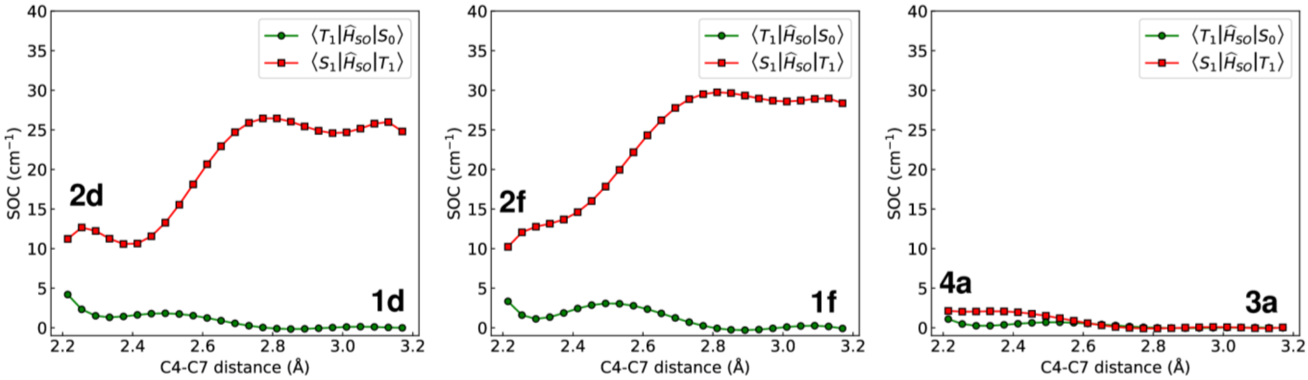

Figure S1. *Spin-orbit couplings associated with* $T_1 \rightarrow S_0$ and $S_1 \rightarrow T_1$ transitions calculated *for 4π-photocyclization of 2-hydroxy tropone, 2-chloro tropone, and hydroxytropenium ion.*

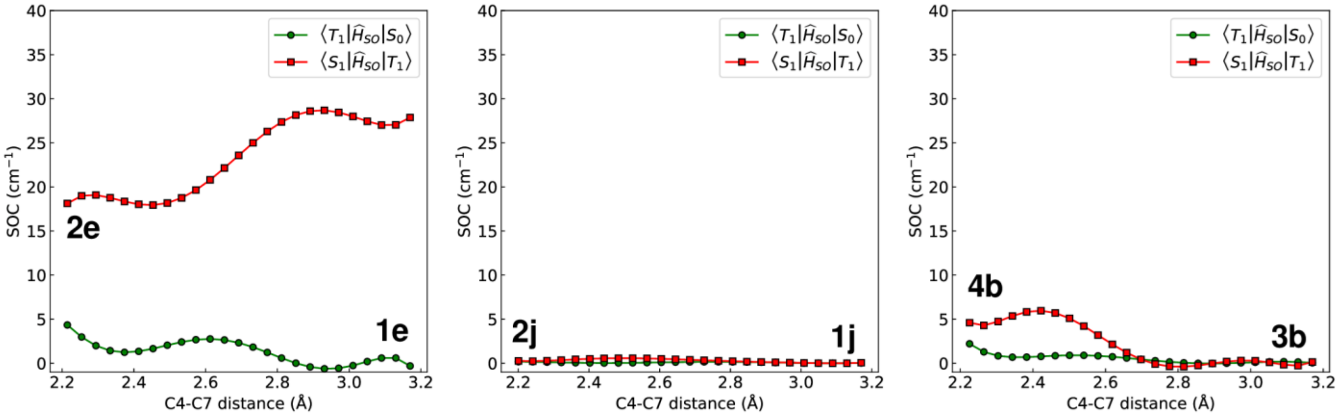

Figure S2. *Spin-orbit couplings associated with* $T_1 \rightarrow S_0$ and $S_1 \rightarrow T_1$ *transitions calcul*ated *for 4π-photocyclization of 2-methyl tropone, cycloheptatriene, and BF*$_3$ *tropone.*

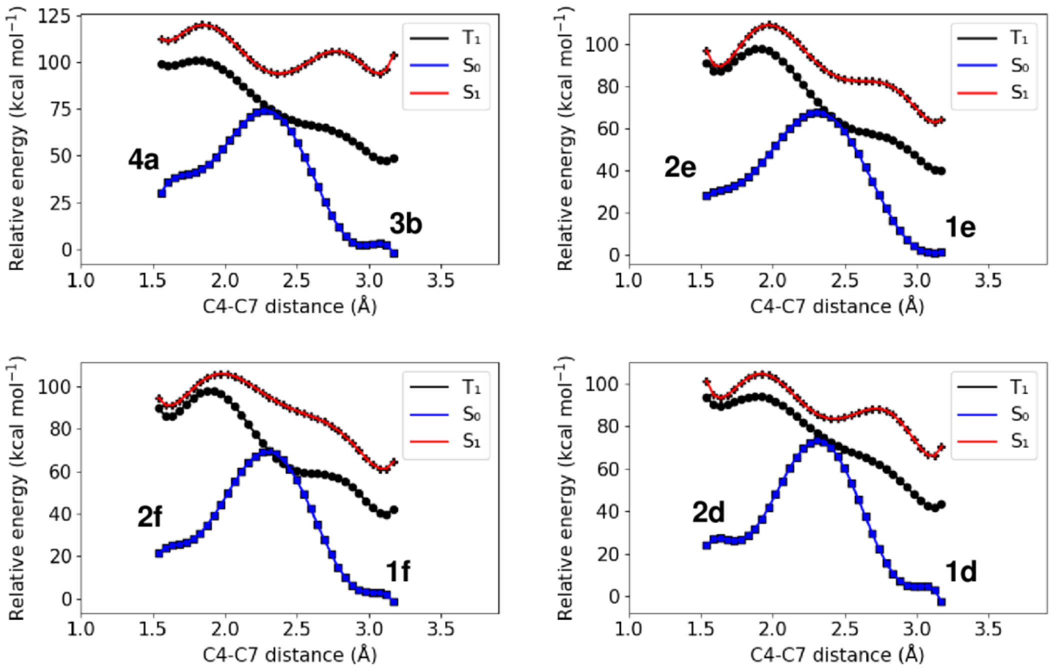

Figure S3. *Relative energies for 4π-photocyclization of BF_3-tropone, 2-methyl tropone, 2-chloro tropone, and 2-hydroxy tropone in the T_1, S_1, and S_0 excited states.*