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

Impact of hydroxylation on the photophysics of chalcones: insights on the relation between chemical composition and electronic structure

SUPPORTING INFORMATION

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Conformational analysis

The conformational analysis (CA) was carried fior compound 2,4’-**C** (**Figure S1**).

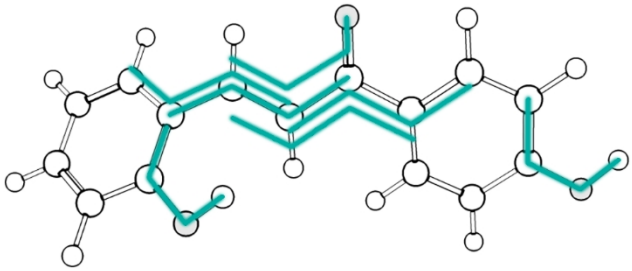

Figure S1: dihedrals scanned during the conformational analysis of 2,4’-**Ct**.

Employed was the default Amber 99 suite as implemented in Hyperchem 8.0.7. Simultaneously varied without constraints were all dihedrals involving the hydroxy groups, as well as dihedrals involving atoms from the central enon fragment (**Figure S1**), with the *range for acyclic torsion variation* set to +/-180. No *ring torsion flexing* was explored. The *initial conformations to vary* at each step were selected by means of uniform sampling of the low energy region of the PES applying the *usage directed* method. As a pre-optimisation check, geometries containing atoms closer than 0.5 Å were discarded. Structures with energy less than 36 kcal/mol above the most stable conformation passed the *acceptance energy criterion*. Only conformers different by more than 0.02 kcal/mol were chosen to satisfy the *duplication test*. Geometry optimisation was terminated for an *RMS gradient* of 0.001 or after 1000 iterations. The CA was terminated manually at 27347 iterated initial structures to 440 *unconverged*, 577 *close contact* and 26770 successful *optimisations*. 77 independent conformations were obtained at an *accept rate* of 1.

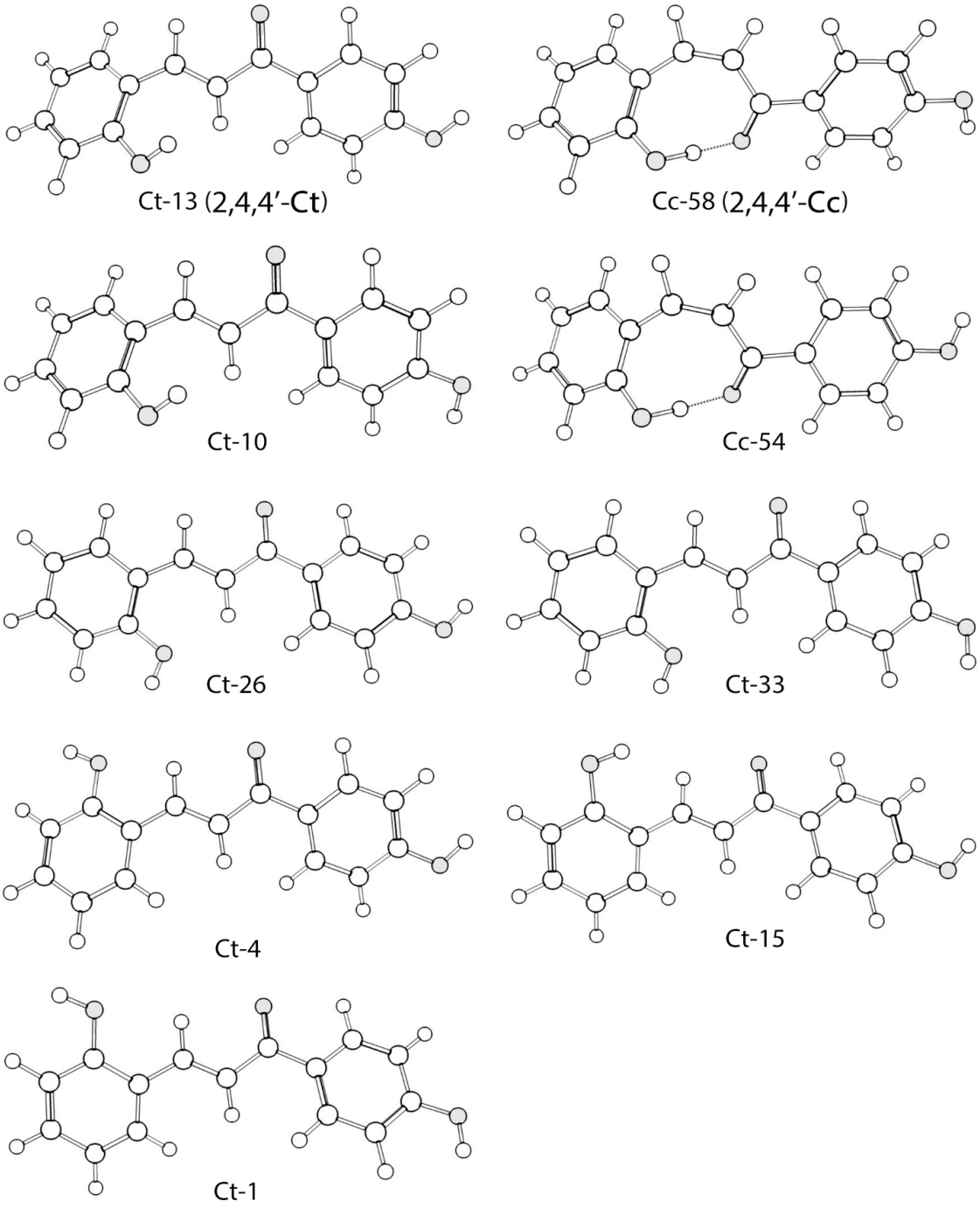

Figure S2: 2,4’-**C** isomers within 1 kcal/mol of the most stable conformer at the mpw1mp91/6-31G* level in vacuo. The most stable *Ct* and *Cc* forms *Ct*-13 and *Cc*-58 were functionalised at C_4 to obtain 2,4,4'-*Ct* and 2,4,4'-*Cc*.

Table S1: CA conformer stability. Colour code of column 1: white denotes *trans*-conformations (*Ct*), blue and yellow denote *cis*-conformations with (*Cc*) and w/o (*Ccs*) π-π stacking. Color gradient applied to column 2 with green denoting the lowest, red the highest relative energy with respect to the most stable *Ct* conformer *Ct*-13 (Figure S2).

Conformer	ΔE [kcal/mol]
2,4'-*Ct*	0.00
2,4'-*Cc*	0.07
Ct-10	0.14
Cc-54	0.16
Ct-26	0.23
Ct-33	0.44
Ct-4	0.79
Ct-15	0.84
Ct-1	0.99
Ct-12	1.02
Ct-31	2.59
Ct-32	2.96
Ct-28	3.23
Ct-17	3.79
Cc-42	5.22
Ccs-45	6.22
Ccs-22	6.69
Cc-72	6.82
Cc-51	7.14
Cc-46	7.32
Ccs-68	7.38
Cc-55	8.18
Cc-49	8.28
Ccs-57	8.55

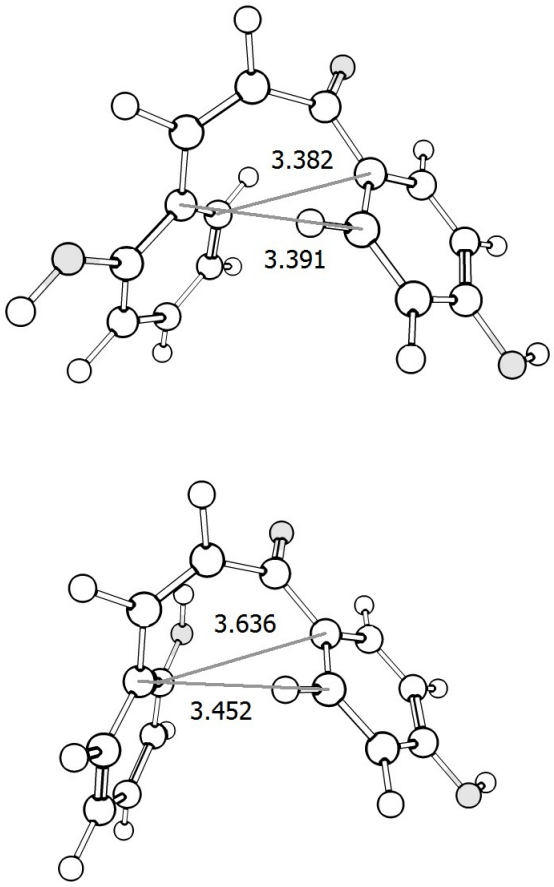

Figure S3: Two examples of π-π stacked *Cc* configurations: *Ccs*-22 (top) and *Ccs*-45 (bottom).

Molecular dynamics

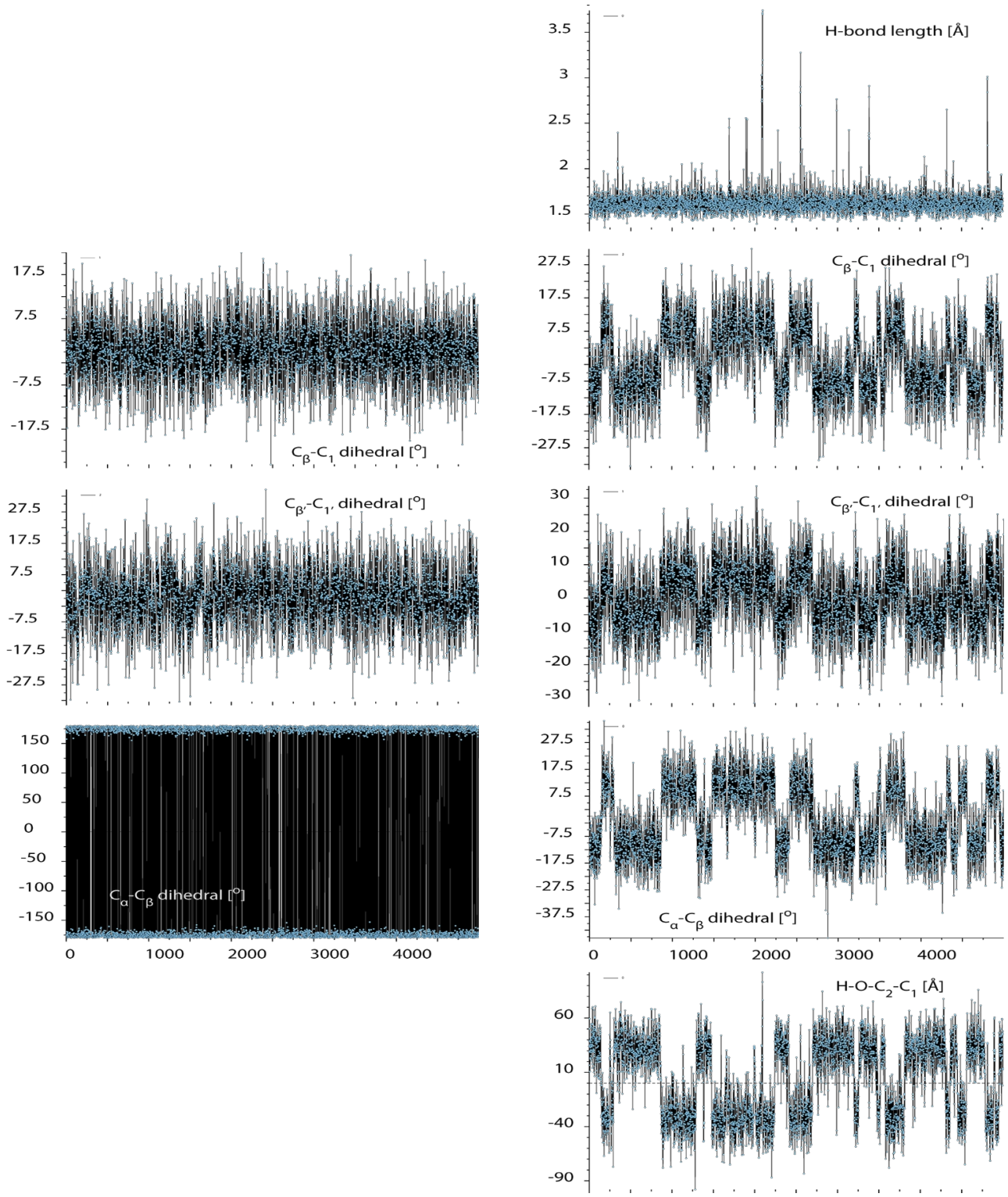

Figure S4: Evolution of several major internal coordinates during the 1 ns classical MD performed for *2,4,4'-Ct* (left) and *2,4,4'-Cc* (right). The *Cc* results document a clear anti-correlation in the plots of the H-O-C_2-C_1 (+40°/-40°) and C_{β}-C_{α}-$C_{\beta'}$-O (-10°/+10°) dihedrals, rationalized through the intramolecular H-bond present in the *Cc* form. The x-asis runs over 5000 snapshots obtained in steps of 200 fs along the MD trajectory.

Active space benchmarking

Table S2: Benchmarking of the transition energies of the $^1\pi_1\pi^*$ and $^1n_O\pi^*$ states as a function of the active space in *2,4,4'-Ct* (left) and *2,4,4'-Cc* (right) at the SS-CASPT2//SA-CASSCF/ANO-L[321,21] level of theory.

		2,4,4'-Ct					*2,4,4'-Cc*				
		vacuo			PCM		vacuo			PCM	
AS	state	ΔE [eV]	μ [D]	f	ΔE [eV]	μ [D]	ΔE [eV]	μ [D]	f	ΔE [eV]	μ [D]
[16,16] SA5	GS	-	1.78	-	-	2.69	-	3.79	-	-	4.72
	$^1\pi_1\pi^*$	3.89	7.94	0.43	3.59	12.01	3.62	6.74	0.34	3.70	7.27
[18,17] SA5	GS	-	1.77	-	-	2.67	-	3.68	-	-	4.58
	$^1n_O\pi^*$	3.19	2.73	0.00	3.42	2.13	3.52	2.94	0.00	3.69	2.58
	$^1\pi_1\pi^*$	3.93	7.00	0.39	3.53	12.32	3.57	6.45	0.32	3.68	5.98
[12,12] SA5	GS	-	1.93	-	-	2.92	-	3.85	-	-	4.85
	$^1\pi_1\pi^*$	3.70	6.52	0.42	3.35	12.28	3.37	5.87	0.42	3.27	8.76
[14,13] SA5	GS	-	1.89	-	-	2.86	-	3.70	-	-	4.66
	$^1n_O\pi^*$	3.22	2.82	0.00	3.47	2.53	3.56	2.95	0.00	3.65	3.33
	$^1\pi_1\pi^*$	3.72	6.61	0.4	3.33	12.15	3.34	5.42	0.37	3.24	8.46
[8,8] SA2	GS	-	1.82	-	-	2.78	-	3.98	-	-	5.08
	$^1\pi_1\pi^*$	3.61	8.91	0.58	3.34	13.55	3.32	7.87	0.40	3.30	10.50
[10,9] SA3	GS	-	1.91	-	-	2.91	-	3.78	-	-	4.78
	$^1n_O\pi^*$	3.25	2.90	0.00	3.55	2.25	3.60	3.29	0.00	3.84	2.82
	$^1\pi_1\pi^*$	3.56	8.99	0.54	3.33	13.72	3.32	7.73	0.33	3.26	9.59

Table S2 shows that the reduction of the active space (AS) results in a considerable red-shift of the $^1\pi_1\pi^*$ transition energy (from 3.69 eV at RAS(4,8|0,0|4,8) to 3.34 eV at CAS(8,8) in *2,4,4'-Ct* and from 3.70 eV at RAS(4,8|0,0|4,8) to 3.30 eV at CAS(8,8) in *2,4,4'-Cc* in PCM water) associated with the overestimation of the dynamic correlation by the non-variational CASPT2 method typical for states with pronounced ionic (in terms of valence bond theory) character. Simultaneously, the transition energy of the $^1n_O\pi^*$ state exhibits a slight blue-shift (from 3.42 eV at RAS(4,9|0,0|4,8) to 3.55 eV at CAS(10,9) in *2,4,4'-Ct* and from 3.69 eV at RAS(4,9|0,0|4,8) to 3.84 eV at CAS(10,9) in *2,4,4'-Cc* in PCM water), characteristic for covalent states. As a consequence, with the decrease of the AS size a state order inversion is observed for the $^1\pi_1\pi^*$ and $^1n_O\pi^*$ states in *2,4,4'-Ct* at PCM level, while in 2,4,4'-Cc the $^1\pi_1\pi^*$ / $^1n_O\pi^*$ degeneracy, observed at RAS(4,9|0,0|4,8), is lifted. Oscillator strengths and permanent dipole moments of $^1\pi_1\pi^*$ and $^1n_O\pi^*$ are less affected, overall exhibiting a slight increase with AS reduction (see also **Figure S5**). The blue-shift of the transition energy of the $^1\pi_1\pi^*$ state from gas-phase to aqueous solution at the RAS(4,9|0,0|4,8) level in *2,4,4'-Cc* with five states included in the state-averaging (SA-5), opposite to the red-shift observed with seven states (SA-7, Table 2 in the main text), can be traced back to WF mixing between the $^1\pi_1\pi^*$ state and the close lying aromatic transitions Ar^*_1, and Ar^*_2 in the SA-5 computation. The exculsion of the phenyl-localized MOs from the AS purifies the $^1\pi_1\pi^*$ and $^1n_O\pi^*$ WF, being described by coefficients of ca. 0.9 for the leading CSF HOMO→LUMO ($^1\pi_1\pi^*$) and n_O→LUMO ($^1n_O\pi^*$).

In summary, the benchmarking demonstrates the suitability of the reduced CAS(8,8) and CAS(10,9) to describe the $^1\pi_1\pi^*$ and the $^1n_O\pi^*$ states with qualitative agreement.

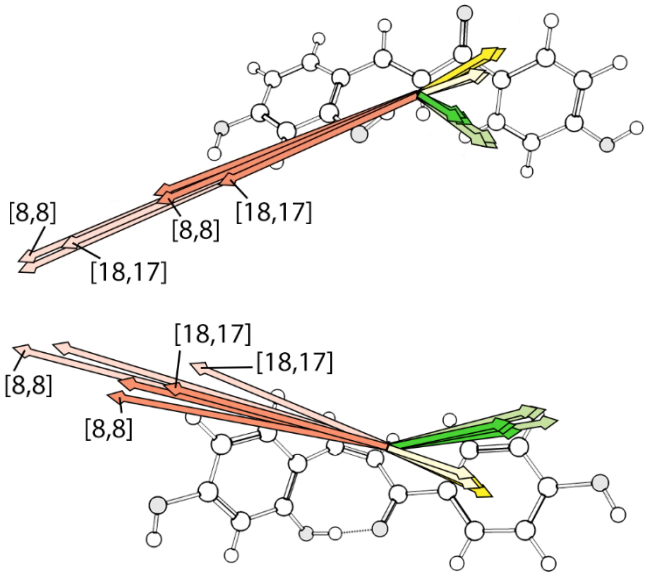

Figure S5: Permanent dipole moments for GS, $^1n_o\pi^*$ and $^1\pi_1\pi^*$ states at the SS-CASPT2//SA-CASSCF/ANO-L[321,21] level of theory with various active space sizes (according to **Table S2**). Color legend: dark green – GS in vacuo, light green – GS in PCM, dark yellow - $^1n_o\pi^*$ in vacuo, light yellow - $^1n_o\pi^*$ in PCM, dark pink - $^1\pi_1\pi^*$ in vacuo, light pink - $^1\pi_1\pi^*$ in PCM.

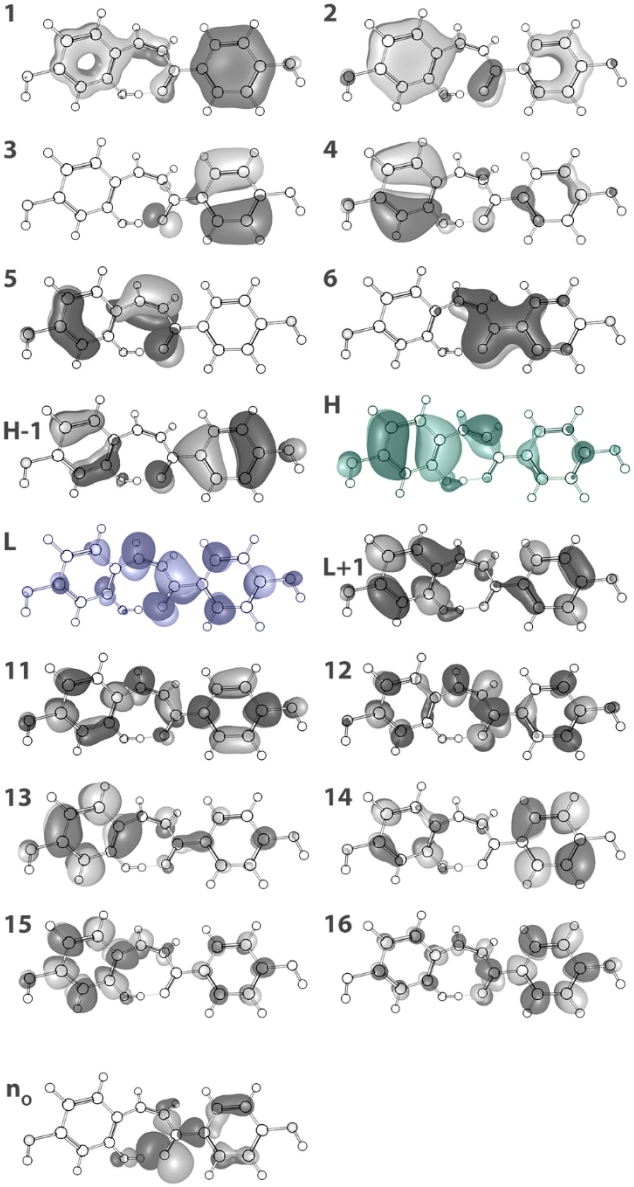

Figure S6: Molecular orbitals of *2,4,4'-Cc* comprising the various active spaces (AS) used. RAS(4,8|0,0|4,8) comprises orbitals 1 through 16, CAS(12,12) comprises orbitals 3 through 14, CAS(8,8) comprises orbitals 5 through 12. RAS(4,9|0,0|4,8), CAS(14,13) and CAS(10,9) are obtained by adding orbtial n_o. HOMO and LUMO are highlighted.

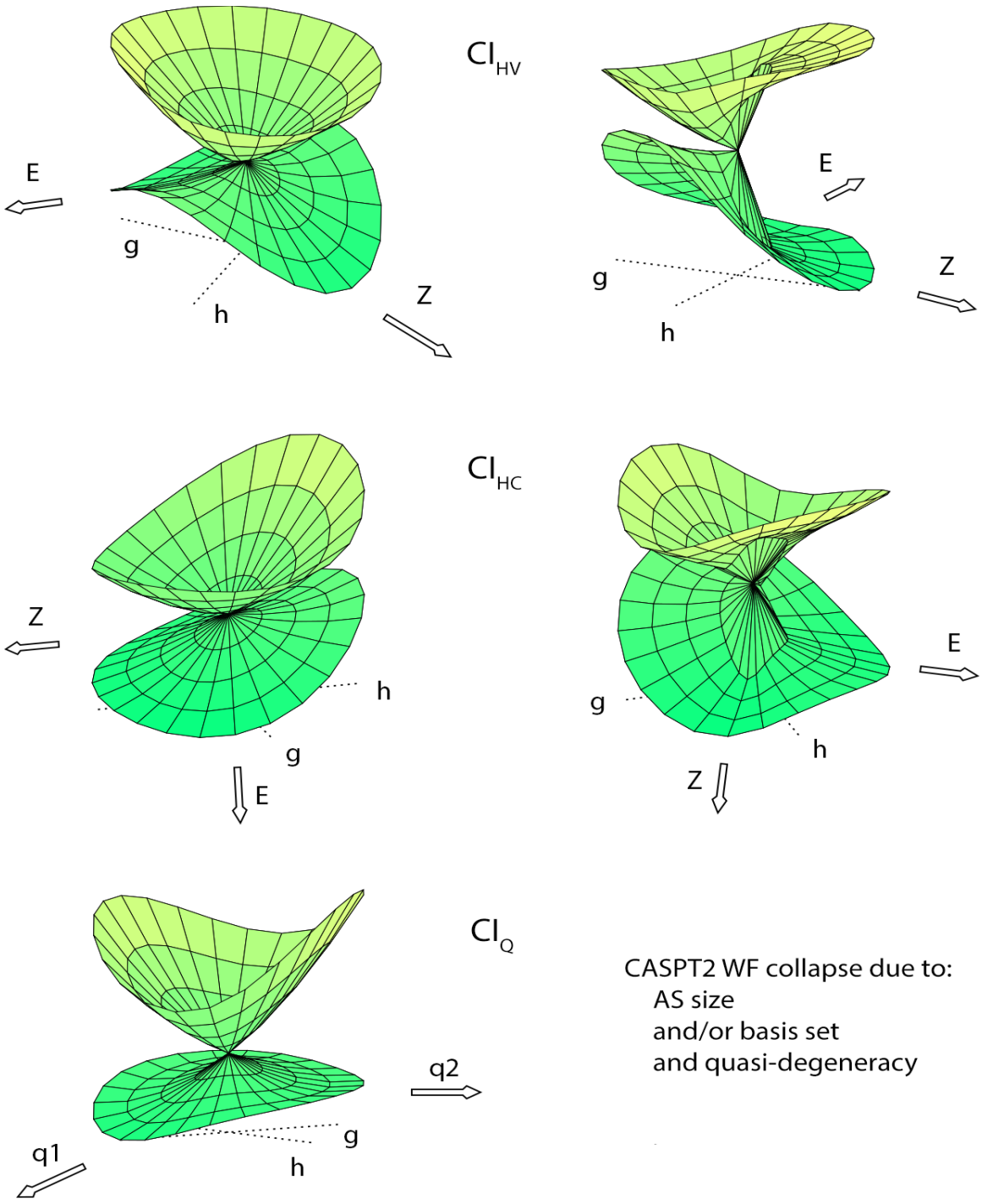

Figure S7: Topology of the PES of the ground state and the $^1\pi_1\pi^*$ state in the vicinity of the conical intersections $\mathbf{CI_{HV}}$, $\mathbf{CI_{HC}}$ and $\mathbf{CI_{Q}}$ in the branching space determined by the gradient difference (***g***) and derivative coupling (***h***) vectors at the SA(2)-CASSCF(8,8) (left) and at the SS-CASPT2/SA(2)-CASSCF(8,8) (right) levels of theory. Arrows denote the steepest gradient towards each product accessible from a conical intersection.

Cartesian geometries

MP2/ANO-L optimized 2,4,4'-**Ct** geometry of the most stable confomer from the conformational analysis

C	-4.73127429	0.65992890	-0.96789959
C	-3.44806949	1.19706769	-0.83153906
C	-2.44853035	0.56842993	-0.05002935
C	-2.81048512	-0.60130127	0.66082104
C	-4.09846683	-1.14693687	0.54743524
C	-5.04610917	-0.52757426	-0.27946232
H	-5.49113066	1.13931510	-1.58886953
H	-3.18806180	2.11995860	-1.36011086
H	-4.34107562	-2.04555805	1.12346943
O	-1.95257697	-1.25099378	1.51384018
H	-1.20657467	-0.65149921	1.70692424
C	-1.11487183	1.15704921	0.00299713
H	-1.04395410	2.24320615	-0.13880460
C	0.06635200	0.49475828	0.16994519
H	0.10182359	-0.59353860	0.22323602
C	1.34245413	1.26058912	0.20909850
O	1.35388655	2.48625139	0.38736448
C	2.61332158	0.49773492	0.04157289
C	3.81770019	1.11402977	0.43900520
C	2.65781579	-0.79547518	-0.52272543
C	5.04089173	0.44737004	0.29178318
H	3.77630478	2.11974093	0.86583971
C	3.88007288	-1.46301629	-0.68755169
H	1.74512588	-1.28114408	-0.87414300
C	5.07126154	-0.84254775	-0.27224124
H	5.97206142	0.92591417	0.61438844
H	3.92727876	-2.45862324	-1.13775330
O	6.23566051	-1.54900302	-0.44740218
H	6.98474436	-1.00906902	-0.13817673
O	-6.31798124	-1.02108675	-0.44234064
H	-6.41197857	-1.83641886	0.08141365

MP2/ANO-L optimized 2,4,4'-**Cc** geometry of the most stable confomer from the conformational analysis

C	-3.18119490	3.42914404	-1.05508262
C	-2.15971955	2.85419857	-0.29645040
C	-0.87278113	2.58014834	-0.83227359
C	-0.62199799	2.96430940	-2.17649230
C	-1.64229965	3.56868152	-2.93751389
C	-2.90860957	3.79354677	-2.38788367
H	-4.17207777	3.61587725	-0.63396364
H	-2.35444179	2.59417301	0.74962484
H	-1.40762371	3.85702792	-3.96670300
O	0.59883580	2.86024767	-2.76709174
H	0.91149970	1.93014455	-2.58734876
C	0.13114681	2.08399702	0.11279932
H	0.06068949	2.56009674	1.10079610
C	1.08718104	1.10576583	0.03378080
H	1.68548748	0.94311882	0.93289032
C	1.29161803	0.13602333	-1.05569050
O	0.98057368	0.36339060	-2.24299780
C	1.88035439	-1.18109815	-0.69750115
C	2.43676822	-1.96450230	-1.73014980
C	1.87284758	-1.68563077	0.62118231
C	2.99549649	-3.21785112	-1.44976094
H	2.43076368	-1.57426185	-2.75145760
C	2.41591804	-2.94544332	0.90589218
H	1.41057770	-1.11479398	1.42839502
C	2.98415540	-3.70845414	-0.13002282
H	3.43726846	-3.81508043	-2.25421805
H	2.40342344	-3.35330013	1.92052801
O	3.50932988	-4.92772190	0.21458454
H	3.86404552	-5.36030878	-0.58244863
O	-3.93554243	4.37089613	-3.09828776
H	-3.61962138	4.57447505	-3.99662523

MP2/ANO-L refined geometry of the most stable 2,4,4'-**Ct** form from the MD simulation

C	-3.18119490	3.42914404	-1.05508262
C	-2.15971955	2.85419857	-0.29645040
C	-0.87278113	2.58014834	-0.83227359
C	-0.62199799	2.96430940	-2.17649230
C	-1.64229965	3.56868152	-2.93751389
C	-2.90860957	3.79354677	-2.38788367
H	-4.17207777	3.61587725	-0.63396364
H	-2.35444179	2.59417301	0.74962484
H	-1.40762371	3.85702792	-3.96670300
O	0.59883580	2.86024767	-2.76709174
H	0.91149970	1.93014455	-2.58734876
C	0.13114681	2.08399702	0.11279932
H	0.06068949	2.56009674	1.10079610
C	1.08718104	1.10576583	0.03378080
H	1.68548748	0.94311882	0.93289032
C	1.29161803	0.13602333	-1.05569050
O	0.98057368	0.36339060	-2.24299780
C	1.88035439	-1.18109815	-0.69750115
C	2.43676822	-1.96450230	-1.73014980
C	1.87284758	-1.68563077	0.62118231
C	2.99549649	-3.21785112	-1.44976094
H	2.43076368	-1.57426185	-2.75145760
C	2.41591804	-2.94544332	0.90589218
H	1.41057770	-1.11479398	1.42839502
C	2.98415540	-3.70845414	-0.13002282
H	3.43726846	-3.81508043	-2.25421805
H	2.40342344	-3.35330013	1.92052801
O	3.50932988	-4.92772190	0.21458454
H	3.86404552	-5.36030878	-0.58244863
O	-3.93554243	4.37089613	-3.09828776
H	-3.61962138	4.57447505	-3.99662523

MP2/ANO-L refined geometry of the most stable 2,4,4'-**Cc** form from the MD simulation

C	1.079846180	4.518475850	1.920586260
C	0.802866450	3.153916580	1.864884110
C	0.763634140	2.424173110	0.641953910
C	1.075777310	3.134083860	-0.551228220
C	1.382141610	4.508715840	-0.495965870
C	1.378306320	5.196155120	0.721178700
H	1.090522510	5.062892350	2.867989870
H	0.595267100	2.615631290	2.794890730
H	1.625086730	5.013249920	-1.435861620
O	1.181364140	2.541218580	-1.765489020
H	0.360522660	1.981840530	-1.877025490
C	0.557940950	0.987584010	0.777473240
H	0.902528290	0.617216230	1.753856620
C	0.000000000	0.000000000	0.000000000
H	0.015906260	-0.995610060	0.447123150
C	-0.809859140	0.128460780	-1.215722770
O	-1.007042870	1.217052510	-1.800430700
C	-1.501321830	-1.090620370	-1.713856540
C	-2.658633710	-0.920313620	-2.505503620
C	-1.022602120	-2.394009470	-1.468674000
C	-3.340979960	-2.027483140	-3.019911230
H	-3.015593760	0.094518120	-2.702965260
C	-1.688229940	-3.507969790	-2.003767730
H	-0.105339080	-2.554833400	-0.898554910
C	-2.853329870	-3.324428070	-2.768698990
H	-4.248031340	-1.909299120	-3.620459220
H	-1.299127310	-4.516983600	-1.827312080
O	-3.562390970	-4.366887330	-3.309986170
H	-3.136217800	-5.207806120	-3.066902710
O	1.663313070	6.536434480	0.820905760
H	1.852114060	6.886027020	-0.068194980

MP2/ANO-L optimized geometry of 2,4’-**Ct**

C	-4.8433654	0.5899817	-1.0103986
C	-3.5654095	1.1460903	-0.8622858
C	-2.5798162	0.5249148	-0.0576174
C	-2.9389171	-0.6424800	0.6612670
C	-4.2226132	-1.1976917	0.5279116
C	-5.1681271	-0.5939769	-0.3170137
H	-5.5829089	1.0761165	-1.6535974
H	-3.2975706	2.0650881	-1.3942509
H	-4.4627698	-2.0971338	1.1026279
O	-2.0827535	-1.2747053	1.5303706
H	-1.3477189	-0.6652380	1.7321243
C	-1.2461237	1.1223798	0.0059752
H	-1.1758146	2.2102253	-0.1266984
C	-0.0673260	0.4566184	0.1663695
H	-0.0381582	-0.6319900	0.2193450
C	1.2136013	1.2186093	0.2056198
O	1.2283836	2.4429218	0.3902111
C	2.4800318	0.4516072	0.0290450
C	3.6882406	1.0592959	0.4283016
C	2.5161429	-0.8364631	-0.5451089
C	4.9079834	0.3879233	0.2736274
H	3.6525843	2.0621520	0.8626385
C	3.7346272	-1.5081798	-0.7186923
H	1.5997027	-1.3152099	-0.8970268
C	4.9298916	-0.8975014	-0.3011270
H	5.8424385	0.8606686	0.5959128
H	3.7759394	-2.5010058	-1.1755057
O	6.0891070	-1.6087481	-0.4878445
H	6.8434924	-1.0793623	-0.1734920
H	-6.1633101	-1.0387185	-0.4166416

MP2/ANO-L optimized geometry of 2,4’-**Cc**

C	-3.2880623	3.2355990	-1.1318610
C	-2.2202662	2.7595511	-0.3599889
C	-0.9101363	2.6485185	-0.8923191
C	-0.6813527	3.0768809	-2.2259206
C	-1.7540828	3.5804612	-2.9902596
C	-3.0484506	3.6584046	-2.4559417
H	-4.2926220	3.2925652	-0.7021252
H	-2.3893422	2.4566802	0.6790035
H	-1.5402960	3.9094211	-4.0116228
O	0.5614263	3.0984967	-2.7906235
H	0.9402141	2.1935409	-2.6385548
C	0.1464256	2.2388784	0.0479451
H	0.1032388	2.7622935	1.0138756
C	1.1058884	1.2706896	-0.0334442
H	1.7419338	1.1289904	0.8449151
C	1.2854529	0.2990905	-1.1329158
O	1.0224400	0.5707513	-2.3202567
C	1.7926942	-1.0514136	-0.7798547
C	2.3097633	-1.8625318	-1.8108989
C	1.7421280	-1.5566236	0.5373301
C	2.7879356	-3.1484532	-1.5300143
H	2.3342871	-1.4689530	-2.8309227
C	2.2043899	-2.8482751	0.8224744
H	1.3100387	-0.9582285	1.3419888
C	2.7334815	-3.6413479	-0.2117754
H	3.2005524	-3.7703087	-2.3317725
H	2.1576422	-3.2587049	1.8353723
O	3.1790262	-4.8920384	0.1326414
H	3.5072057	-5.3456795	-0.6642038
H	-3.8675572	4.0469245	-3.0691886

SA-3-CASSCF(10,9)/ANO-L optimized geometry of **ISC_t**

C	-4.7433195	0.7586005	-0.8802584
C	-3.4890396	1.2638547	-0.7139165
C	-2.4817533	0.5826647	0.0184532
C	-2.8436316	-0.6203128	0.6044155
C	-4.1345578	-1.1576519	0.4422664
C	-5.0651960	-0.4811631	-0.2937352
H	-5.4951421	1.2842709	-1.4490232
H	-3.2390148	2.2140209	-1.1648985
H	-4.3648899	-2.0992584	0.9192241
O	-2.0048406	-1.3589490	1.3711151
H	-1.2751880	-0.8377109	1.6749244
C	-1.1406753	1.1877325	0.1346343
H	-1.1108901	2.2582835	0.2813918
C	0.0549724	0.4949145	0.0057512
H	0.0238386	-0.5595830	-0.2054148
C	1.3253250	1.0732193	0.1306286
O	1.3692024	2.3943471	0.4584014
C	2.6207556	0.4342372	0.0016576
C	3.7932450	1.1489814	0.2210122
C	2.7464066	-0.9497878	-0.3301633
C	5.0612648	0.5322625	0.1056206
H	3.7534947	2.1948169	0.4829599
C	3.9640655	-1.5375282	-0.4379743
H	1.8682585	-1.5433332	-0.5221655
C	5.1453394	-0.7870920	-0.2146175
H	5.9548988	1.1147032	0.2815917
H	4.0571672	-2.5803074	-0.7032946
O	6.3083816	-1.4623024	-0.3408954
H	7.0526976	-0.8984730	-0.1838886
O	-6.3203100	-0.9362505	-0.4911341
H	-6.4552497	-1.7696482	-0.0625828

SA-3-CASSCF(10,9)/ANO-L optimized geometry of **ISC_c**

C	-3.15557145	3.17904785	-1.54315323
C	-2.35541766	2.69430919	-0.55151199
C	-0.94613864	2.62212742	-0.68241148
C	-0.39706165	3.09677104	-1.86097996
C	-1.20697142	3.60264057	-2.89463427
C	-2.56339681	3.63704943	-2.73627112
H	-4.22893083	3.21934144	-1.43738535
H	-2.80500846	2.34237640	0.36665813
H	-0.73265786	3.95767561	-3.79796378
O	0.93169527	3.12644045	-2.10027980
H	1.41905119	2.77319914	-1.36947257
C	-0.11320045	2.12068421	0.44024869
H	-0.11287118	2.70763360	1.34950083
C	0.65434371	0.95675877	0.45554021
H	1.23467930	0.77713676	1.34509356
C	0.74308858	-0.03131648	-0.53227398
O	-0.03616801	0.07326056	-1.64137125
C	1.57029907	-1.23500856	-0.50306296
C	1.43449927	-2.20948961	-1.47932937
C	2.54350633	-1.45591666	0.51422834
C	2.22806531	-3.37962090	-1.46550582
H	0.71167533	-2.08976370	-2.27087325
C	3.30337690	-2.58247949	0.52835869
H	2.69951474	-0.72177622	1.28678650
C	3.14534799	-3.56400763	-0.47628505
H	2.09803468	-4.12084592	-2.24167043
H	4.04253986	-2.74478272	1.29897551
O	3.94502761	-4.64835653	-0.38072734
H	3.78669676	-5.25623616	-1.08920901
O	-3.40098909	4.10525859	-3.68564540
H	-2.92498742	4.38470527	-4.45486349

SA-2-CASSCF(8,8)/ANO-L optimized geometry of 2,4,4'-**Qc**

C	-3.1137935	4.0495025	-1.2295611
C	-2.6353801	3.0556802	-0.4731005
C	-1.4116838	2.3242799	-0.8262203
C	-0.7170820	2.7395717	-2.1085802
C	-1.2791077	3.8483972	-2.8693096
C	-2.3985372	4.4490536	-2.4616353
H	-4.0119504	4.5948253	-0.9839067
H	-3.1484727	2.7676365	0.4312085
H	-0.7593555	4.1381445	-3.7702316
O	0.2839464	2.1955084	-2.4914238
H	0.1918502	0.4336660	-2.4763602
C	-0.9262402	1.3972399	0.0605335
H	-1.4858591	1.3706685	0.9881518
C	0.2040054	0.4696331	0.0973032
H	0.6293223	0.3777748	1.0817490
C	0.6603831	-0.4208112	-0.8555582
O	0.1355821	-0.4422187	-2.1024075
C	1.7070476	-1.4237941	-0.6123144
C	2.2499240	-2.1340707	-1.6755801
C	2.1992988	-1.7332358	0.6909774
C	3.2566773	-3.1101523	-1.4761303
H	1.8979974	-1.9403273	-2.6742945
C	3.1646011	-2.6696501	0.8817968
H	1.7987131	-1.2352979	1.5578518
C	3.7086396	-3.3710070	-0.2213353
H	3.6591449	-3.6436189	-2.3267544
H	3.5267574	-2.9025059	1.8725293
O	4.6651297	-4.2863880	0.0652025
H	4.9718429	-4.7135952	-0.7217595
O	-2.9909434	5.4537391	-3.0962728
H	-2.5203865	5.6981673	-3.8840581

SA-2-CASSCF(8,8)/ANO-L optimized geometry of 2,4,4'-**Qt**

C	-2.70361814	2.27633386	-2.11129407
C	-1.55288573	1.86516024	-1.53717182
C	-0.49507243	2.81640224	-1.20971830
C	-0.73744352	4.28725135	-1.50486933
C	-2.00642660	4.64494149	-2.14246102
C	-2.90984592	3.70623480	-2.42564326
H	-3.51095406	1.59931748	-2.34334735
H	-1.41227570	0.82590373	-1.29678076
H	-2.16769630	5.68921444	-2.36692568
O	0.08234281	5.11804218	-1.23802386
H	0.74629905	0.93157630	-2.64414326
C	0.67968090	2.49450848	-0.59408411
H	1.29683840	3.33192186	-0.29988700
C	1.18779811	1.17322907	-0.22830203
H	1.69158535	1.12090255	0.72292510
C	1.23253152	0.05607258	-1.01121188
O	0.82289685	0.05027208	-2.30668334
C	1.76467057	-1.24909251	-0.57633743
C	2.17715285	-2.18913341	-1.50523971
C	1.86467119	-1.59219921	0.79884565
C	2.69722193	-3.43646559	-1.10077927
H	2.10342571	-1.96816735	-2.55727985
C	2.36819069	-2.79442586	1.19205778
H	1.51955953	-0.90298206	1.55265950
C	2.79516634	-3.73260210	0.22778059
H	3.01494185	-4.15130496	-1.84734301
H	2.43766634	-3.05591852	2.23766911
O	3.28075407	-4.90080263	0.70285292
H	3.54263746	-5.47552580	-0.00249323
O	-4.08905515	3.93781169	-3.00327621
H	-4.20868779	4.86033855	-3.19133223

SA-2-CASSCF(6,6)/ANO-L optimized geometry of the $^1\pi_2\pi^*$ state in 2,4'-Ct obtained by removing the HOMO (and thus the $^1\pi_1\pi^*$ state from the state-averaging)

C	-4.84573563	0.62782952	-0.97330459
C	-3.58140035	1.15549942	-0.83838056
C	-2.59050545	0.53580617	-0.05122226
C	-2.96987206	-0.62073817	0.65434466
C	-4.24141953	-1.15404351	0.52497730
C	-5.17689855	-0.54590245	-0.29727200
H	-5.57321004	1.11874511	-1.60396217
H	-3.31866819	2.06292627	-1.36345080
H	-4.48756824	-2.04165495	1.08985275
O	-2.12839636	-1.24674786	1.51116163
H	-1.39658295	-0.68018757	1.72044477
C	-1.26006597	1.10802359	-0.00019629
H	-1.18564635	2.17192483	-0.17262100
C	-0.04414013	0.40338874	0.16838545
H	-0.02895264	-0.67285934	0.20359067
C	1.16716829	1.08991134	0.21460622
O	1.35324811	2.33014107	0.34470056
C	2.46122576	0.36032407	0.04313304
C	3.66790649	1.03507389	0.43227715
C	2.57805346	-0.92425835	-0.58944268
C	4.88700362	0.43297889	0.28847264
H	3.56163588	2.02766051	0.83669630
C	3.78045512	-1.52831120	-0.71519092
H	1.68468879	-1.39798255	-0.95863641
C	4.95246059	-0.84832532	-0.27540443
H	5.79636607	0.93132456	0.59073815
H	3.89372475	-2.50175403	-1.16721977
O	6.08670102	-1.48397602	-0.45596163
H	6.84160814	-0.98343904	-0.16945095
H	-6.16371975	-0.97518919	-0.39761852

SA-2-CASSCF(8,8)/ANO-L optimized **CI_{Hv}** geometry

C	-4.79655707	1.01233312	-0.24681576
C	-3.57761528	1.36343699	-0.71296958
C	-2.41377778	0.53664654	-0.54275271
C	-2.59820555	-0.69929872	0.16472398
C	-3.85645098	-1.05792674	0.64186649
C	-4.93109162	-0.22120041	0.44180661
H	-5.66702741	1.63619398	-0.37498132
H	-3.45261228	2.30046505	-1.23531025
H	-3.96359436	-1.99299306	1.17056118
O	-1.61593758	-1.53536584	0.38614029
H	-0.78738277	-1.17432969	0.03543568
C	-1.18409088	0.95971297	-1.04137623
H	-1.20288736	1.92938246	-1.53632395
C	0.09492049	0.25919637	-0.94126390
H	0.46214483	-0.20840242	-1.84387192
C	1.02715012	0.74168086	0.04559652
O	0.68958851	1.56013090	0.89530572
C	2.43716206	0.22181761	0.04960444
C	3.39426502	0.89002839	0.79107465
C	2.84056118	-0.93183450	-0.66247318
C	4.72837435	0.45026050	0.82694052
H	3.10513043	1.76595257	1.34993845
C	4.13439375	-1.37093231	-0.62691319
H	2.12082132	-1.49518631	-1.23359900
C	5.09269485	-0.66796061	0.12454250
H	5.46076955	0.99329985	1.40874978
H	4.44054724	-2.25660273	-1.16400440
O	6.35290216	-1.15789816	0.10826030
H	6.92963921	-0.63315316	0.64503153
O	-6.15256519	-0.51501605	0.87936084
H	-6.17565396	-1.34487946	1.33780086

SA-2-CASSCF(8,8)/ANO-L optimized **CI_{HC}** geometry

C	0.23552377	-0.12551575	-0.07837768
C	-0.08769257	0.23422226	1.17919073
C	0.88466399	0.26394556	2.24384788
C	2.17745151	-0.32268098	1.97042394
C	2.51648239	-0.65740618	0.65595243
C	1.57322925	-0.55013159	-0.33849249
H	-0.47030110	-0.10463302	-0.89326075
H	-1.08724668	0.57521106	1.40600219
H	3.49258678	-1.07437933	0.46093115
O	3.01365610	-0.64920716	2.89622868
H	2.65290003	-0.61520892	3.80918440
C	0.57187211	0.88134500	3.44381543
H	-0.49705825	0.99384344	3.62481510
C	1.49885025	1.49627955	4.39172825
H	1.80981652	2.50385742	4.16323623
C	2.07482446	0.74836336	5.41037184
O	2.04100207	-0.50887922	5.37601196
C	2.83615373	1.41043169	6.51527396
C	3.71587594	0.66417898	7.27717729
C	2.68466638	2.78096595	6.83246698
C	4.45188675	1.24878514	8.32372577
H	3.83453314	-0.38519628	7.05960761
C	3.39655470	3.35717441	7.84617635
H	1.98097961	3.38163311	6.27851480
C	4.29501731	2.58031163	8.60057935
H	5.13699202	0.64663561	8.90526467
H	3.27728627	4.40206088	8.09281222
O	4.96468044	3.21821610	9.58914631
H	5.53415500	2.62104562	10.05278607
O	1.83057998	-0.88072777	-1.59427936
H	2.72985879	-1.15908757	-1.71474914

SA-2-CASSCF(8,8)/ANO-L optimized **CI_{Q}** geometry

C	-3.01340550	2.58906634	-1.18558242
C	-1.90621770	2.30039313	-0.40978026
C	-0.61650493	2.68783926	-0.80449699
C	-0.41967672	3.28864385	-2.10406439
C	-1.59510673	3.64017152	-2.86265786
C	-2.82604626	3.29286493	-2.41930599
H	-4.01401820	2.32928056	-0.87908500
H	-2.04209021	1.79971804	0.53857186
H	-1.45130405	4.13331408	-3.81338815
O	0.72422059	3.39989462	-2.56250387
H	1.24095799	1.72723135	-2.28946026
C	0.53844809	2.51747601	0.10347515
H	0.73524265	3.31336602	0.81496078
C	1.32042236	1.40618001	0.17191060
H	1.99051468	1.27930452	1.01059060
C	1.43482986	0.43087937	-0.88096513
O	1.33043477	0.77119216	-2.14056245
C	1.81782398	-0.93942403	-0.64169511
C	2.20116752	-1.77048608	-1.71120446
C	1.80054669	-1.50107160	0.65294056
C	2.56195379	-3.08237897	-1.49772961
H	2.21788523	-1.36683887	-2.71036440
C	2.16213406	-2.80737840	0.86903562
H	1.48085214	-0.90596690	1.49293374
C	2.54665098	-3.60602525	-0.20845782
H	2.85877172	-3.70544681	-2.32986352
H	2.14457985	-3.23620511	1.85960851
O	2.88721085	-4.87625192	0.05790433
H	3.12530011	-5.34802746	-0.72819078
O	-3.95571597	3.55648466	-3.09830960
H	-3.76779073	4.01901666	-3.90375409

SA-2-CASSCF(8,8)/ANO-L optimized $^{3}\pi_{1}\pi^{*}$ geometry of 2,4,4'-trihydroxylated chalcone

C	-4.88046892	0.44529147	-0.83648660
C	-3.64471106	0.82566122	-1.25138411
C	-2.45831124	0.52737630	-0.51340686
C	-2.63933257	-0.12240016	0.70893640
C	-3.91547569	-0.53059558	1.14131730
C	-5.01469099	-0.26024763	0.38051322
H	-5.76402362	0.66455985	-1.41674762
H	-3.54336988	1.35670469	-2.18710868
H	-3.99503012	-1.04025949	2.09051933
O	-1.61543544	-0.40384345	1.54797105
H	-0.97657687	0.29786615	1.55027585
C	-1.17887381	0.92447020	-1.05824162
H	-1.21532183	1.57425744	-1.92357337
C	0.11597945	0.24398670	-0.85225305
H	0.35370914	-0.59095388	-1.49610336
C	1.10805672	0.66535766	0.11646534
O	0.75054890	1.39403439	1.05922696
C	2.52516358	0.18169949	0.02474981
C	3.30984004	0.14395943	1.15039573
C	3.09047560	-0.24139010	-1.20003832
C	4.65116244	-0.30303349	1.09050580
H	2.90653478	0.46676630	2.09799600
C	4.38724108	-0.66611334	-1.26746441
H	2.50825415	-0.21332791	-2.10774305
C	5.17611796	-0.70170327	-0.10390430
H	5.25047848	-0.32497595	1.99005457
H	4.82607001	-0.97522891	-2.20459581
O	6.44620908	-1.14217685	-0.25284268
H	6.91041889	-1.13627036	0.57214677
O	-6.26703080	-0.61893894	0.73275878
H	-6.27199207	-1.08297401	1.55814623