

Electronic Supplementary Information

Femtosecond electronic relaxation and real-time vibrational dynamics in 2'-hydroxychalcone†

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† Electronic supplementary information (ESI) available: Calculated geometries, energies and normal modes at crucial points, recorded Raman spectra of 2'HC and formalisms for obtaining two-photon absorption cross-sections and molar absorption coefficients of transient species are supplied.

Table S1 Cartesian coordinates (in Å) of the optimized structures for 2'HC along the decay path from S_{3FC} to S_1/S_0 in methanol. S_1/S_0 and $S_{0MIN(SFTDDFT)}$ geometries were computed at the SF-TDDFT/BHLYP/6-31G(d) level, whereas the other geometries were computed at ω B97XD/6-31G(d). The solvent effect of methanol was taken into account by CPCM. Energies in the atomic units (Hartree) for each geometry are also shown.

S_{0MIN} 0.00 eV (ω B97XD/MeOH) E: -729.028818973835			
C	-1.157045510308	0.005377209848	2.284494470222
C	-1.064994586424	0.006829660082	3.701103326884
O	0.105787330303	0.001839974485	4.350927357140
H	0.809172345324	-0.003321427208	3.655411335038
C	-2.230241732984	0.013794779580	4.479868137734
H	-2.125634854930	0.014891010412	5.559791887805
C	-3.473502329903	0.018881789649	3.875161408652
H	-4.367166404479	0.024156573048	4.491974710539
C	-3.587282958028	0.017112384585	2.479965911621
H	-4.563573362325	0.020882691628	2.007787594023
C	-2.442003026994	0.010464824034	1.706477557572
H	-2.552284178811	0.008895170132	0.628791661761
C	0.083100150111	-0.001460574526	1.479303796475
O	1.191714177420	-0.007879676041	2.043314755108
C	0.018374235285	-0.000521576833	0.005379334500
H	-0.948833005154	0.007958402875	-0.479909317070
C	1.151997134672	-0.009291948466	-0.715887049857
H	2.089109070585	-0.016346432555	-0.161665570997
C	1.276936972927	-0.009844119090	-2.175354516923
C	0.170974642473	-0.009450469076	-3.039990886294
H	-0.837893850314	-0.009711291392	-2.639401964140
C	0.351924636830	-0.009495749078	-4.416458019305
H	-0.512887388845	-0.009330403437	-5.072561193448
C	1.638703500414	-0.009990767394	-4.956688473670
H	1.775778454608	-0.010041126073	-6.033652509586
C	2.744944574446	-0.010728033432	-4.111387455026
H	3.748632942134	-0.011310308500	-4.524683295934
C	2.563516339205	-0.010863039505	-2.732379971668
H	3.428288940263	-0.011497527791	-2.074192446584
S_{3MIN} 4.03 eV (ω B97XD/MeOH) E: -728.880554845702			
C	-1.161365165925	0.006598910383	2.254405744925
C	-1.081321996389	0.010643080271	3.683044983488
O	0.090903519835	0.011273211145	4.309663076688
H	0.782396857765	0.007984629963	3.561436646699
C	-2.245532513278	0.014119136252	4.475391367261
H	-2.121207642802	0.017142868463	5.553334564590
C	-3.515100946414	0.013629017606	3.890295736287
H	-4.403171220708	0.016305243852	4.511531143047
C	-3.610897725426	0.009532197922	2.504941816100
H	-4.580257050989	0.008835354552	2.018433910354
C	-2.444797753560	0.006075190772	1.705455401709
H	-2.578849740322	0.002806671730	0.629907976850
C	0.074841612605	0.003032077035	1.464332167982
O	1.206296464348	0.002693465230	2.067435025677
C	0.045602562518	-0.000190561383	0.021943388235
H	-0.912341454043	0.000781988065	-0.485015561699
C	1.212241168637	-0.004247937943	-0.715522498224
H	2.145178771495	-0.005046175283	-0.157883357984
C	1.310137585847	-0.007430450471	-2.145971953947
C	0.179731231721	-0.006978041146	-3.010633062649
H	-0.821879860351	-0.004220319746	-2.593827416905
C	0.338966838157	-0.010041311423	-4.384222684346
H	-0.536374629127	-0.009668534975	-5.026367332658
C	1.618051806627	-0.013627060847	-4.951757137250
H	1.735190020528	-0.015998692520	-6.030876577036

C	2.746658496131	-0.014183970570	-4.121531675799
H	3.740468127146	-0.016942831758	-4.558167993294
C	2.597780062900	-0.011198526688	-2.748206139738
H	3.474264830599	-0.011678628511	-2.106028983767
S ₃ /S ₂ 4.04 eV (ωB97XD/MeOH) E: -728.880411102224 E: -728.880411153302			
C	-1.159851689694	0.008751343743	2.253566549817
C	-1.080156283692	0.009099948559	3.683254204112
O	0.092928919273	0.007998711098	4.302427185182
H	0.776960808215	0.006724861545	3.534470499358
C	-2.244895252403	0.010592196382	4.477502108350
H	-2.118807006595	0.010548111504	5.555340932828
C	-3.517827381539	0.012417983489	3.894796343946
H	-4.405023743381	0.013533357950	4.517052296377
C	-3.613095171073	0.012798122745	2.510901126778
H	-4.581997678684	0.014164865279	2.023487838254
C	-2.443586610595	0.010959744207	1.708747872297
H	-2.580834830202	0.011090799946	0.633462112107
C	0.076441662146	0.005648925821	1.464979927417
O	1.206171635246	0.004868961216	2.066494970819
C	0.042391220713	0.002322610761	0.020536636278
H	-0.913281323618	0.003994074744	-0.490795037527
C	1.211627343576	-0.003671396117	-0.717284804203
H	2.141841972894	-0.005145707212	-0.155092397513
C	1.310940149718	-0.007959490037	-2.144000723330
C	0.179003039592	-0.007381228168	-3.011059319720
H	-0.822410412759	-0.004243798221	-2.594144623135
C	0.339215120402	-0.010737012677	-4.383605402020
H	-0.535269663209	-0.009868070133	-5.026806510268
C	1.619332160193	-0.015229418119	-4.950382791049
H	1.736913520609	-0.017823674408	-6.029430577328
C	2.749119590701	-0.016525405196	-4.119608133319
H	3.742504962962	-0.020334618844	-4.557014466028
C	2.600696392491	-0.012904472726	-2.747576612599
H	3.476560806013	-0.013690327328	-2.104678631271
S ₂ /S ₁ 3.73 eV (ωB97XD/MeOH) E: -728.891756440863 E: -728.891762573608			
C	-1.157173328796	0.147267167513	2.265693559550
C	-1.088595444731	-0.178599350292	3.650177254332
O	0.069482949113	-0.415394511711	4.286956937224
H	0.816698803815	-0.287588347806	3.662925348668
C	-2.262110642080	-0.290964477218	4.404464747850
H	-2.173026198019	-0.555275728935	5.452822437819
C	-3.495601881326	-0.067787233972	3.816704228404
H	-4.398102588358	-0.152613890407	4.413303247404
C	-3.577802057595	0.278209817973	2.461236069035
H	-4.541969128140	0.471026569489	2.002942976343
C	-2.424876108040	0.392323580302	1.704369795026
H	-2.501699350995	0.696311904766	0.666220394811
C	0.074397009536	0.198179220194	1.468058646624
O	1.202789669266	0.320302449435	2.101921054427
C	0.076067829276	0.089852865016	0.052097618021
H	-0.887772390395	-0.076428168522	-0.415965654558
C	1.227787747374	0.160647528045	-0.700248826447
H	2.166841236261	0.329860861571	-0.179347518414
C	1.308788336978	0.034951688794	-2.137195416234
C	0.185084398754	-0.188500996307	-2.965226747803
H	-0.805100146075	-0.277842972974	-2.529855045964
C	0.326045232386	-0.296897893677	-4.339835590357
H	-0.551430118426	-0.467799061037	-4.956187542461
C	1.585327257495	-0.188878475802	-4.934582960325
H	1.689376126584	-0.275294368247	-6.011705569859
C	2.708162791888	0.030659087905	-4.134815720327
H	3.691095413545	0.115765354855	-4.588189374300
C	2.572552999974	0.141272508339	-2.759299633697

H	3.450373838281	0.313234872607	-2.141898140239
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S₁MIN-trans 3.66 eV (ωB97XD/MeOH) E: -728.894293124907

C	-1.174890202321	0.258830471177	2.275717048215
C	-1.063473020754	-0.268955428041	3.592046361220
O	0.107504825687	-0.585510406541	4.166724938839
H	0.840066447846	-0.244282518264	3.618392450816
C	-2.225409861357	-0.536101947169	4.326058758045
H	-2.120006012860	-0.966741207072	5.315975351808
C	-3.468380164549	-0.227179554593	3.802169459570
H	-4.358792302167	-0.422745445130	4.391012649665
C	-3.585251420954	0.351107148844	2.528639824200
H	-4.562665161925	0.590607504395	2.124141627607
C	-2.448508421786	0.614631946274	1.788812344710
H	-2.527332386904	1.073195299775	0.808696404355
C	0.025924704045	0.386463172678	1.431688921913
O	1.059266524922	0.800429496458	2.108470867211
C	0.055734037319	0.168589108748	0.042060295970
H	-0.887814903912	-0.136128179375	-0.401636588857
C	1.192105333994	0.319885140633	-0.714439692635
H	2.112028612355	0.600788918267	-0.206877654813
C	1.298653224477	0.092705932723	-2.145542225304
C	0.182800903910	-0.109658982472	-2.981632555559
H	-0.820525338336	-0.081220986513	-2.567555969284
C	0.343583462259	-0.333322992277	-4.342360038937
H	-0.531889184489	-0.486872729885	-4.966467743506
C	1.617492101547	-0.352667978312	-4.911764393726
H	1.737938047164	-0.524054970279	-5.976992733764
C	2.732856720052	-0.143058573854	-4.101909922492
H	3.729204638986	-0.151417608376	-4.533876244774
C	2.575203116788	0.076410029850	-2.739502587810
H	3.450187938486	0.236275338302	-2.114508378118

S₁TS-taut 3.66 eV (ωB97XD/MeOH) E: -728.894192004780

C	-1.169897858375	0.247143513031	2.266484564905
C	-1.058786928995	-0.199210821880	3.618744430687
O	0.116459838219	-0.402154574483	4.224012536198
H	0.829948971200	-0.052007400512	3.647251795689
C	-2.216765272181	-0.495702206525	4.349887894749
H	-2.103191914236	-0.867421204323	5.362478986979
C	-3.464303152985	-0.272397139194	3.796710852201
H	-4.354276300002	-0.481811531617	4.381256996652
C	-3.586294795732	0.242331119932	2.494528246669
H	-4.567969989120	0.413586548096	2.066236387141
C	-2.453863559872	0.523289488238	1.754412696244
H	-2.547804632648	0.928658089836	0.752693697722
C	0.041704054147	0.367533012335	1.441064346755
O	1.092547470906	0.755125302505	2.098287007289
C	0.056743024419	0.173530546262	0.042787222903
H	-0.895271932980	-0.074199298773	-0.417156771057
C	1.204837649123	0.285143026899	-0.708727149038
H	2.134730973415	0.496999333055	-0.185759785790
C	1.302452216791	0.086584924661	-2.138393728294
C	0.176416012114	-0.009689498476	-2.985113041764
H	-0.823241290127	0.090797524366	-2.573716656209
C	0.327137518954	-0.216664337909	-4.348406013531
H	-0.553448615709	-0.288276853833	-4.979892015498
C	1.599827804550	-0.321155183496	-4.913103049256
H	1.712292679431	-0.477823131618	-5.981440387926
C	2.725681051725	-0.214123932043	-4.095262764171
H	3.719876722373	-0.288758984497	-4.525605156710
C	2.579609981556	-0.013872887516	-2.730371651596
H	3.460462531541	0.064546557435	-2.098348917356

S₁MIN-taut 3.16 eV (ωB97XD/MeOH) E: -728.912557911594

C	-1.175278760460	0.103802514199	2.266535239799
C	-1.084266675861	-0.195240416546	3.703702530092
O	0.044788870302	-0.357285895400	4.260083496727
H	1.042434059351	0.076520623968	3.068572457594
C	-2.301583322690	-0.288297319652	4.450818868819
H	-2.214234458329	-0.540371775800	5.502887681844
C	-3.532132232760	-0.078791280783	3.855184063089
H	-4.443334218653	-0.159224463745	4.438809259905
C	-3.597885791604	0.250511416394	2.495298554443
H	-4.558037457175	0.432830824228	2.024543912686
C	-2.426781871342	0.355929689604	1.724264100536
H	-2.523086160489	0.650335721821	0.684657104298
C	0.053111609089	0.142665555920	1.472628544145
O	1.226318960930	0.254010944535	2.099800958558
C	0.059395570382	0.050798333371	0.071852043409
H	-0.899018812980	-0.079197473518	-0.416970050471
C	1.214043265844	0.099619523199	-0.681236899234
H	2.153565008590	0.226430127176	-0.148748756647
C	1.303014370908	0.008710525109	-2.114749635767
C	0.181453644022	-0.163898878880	-2.958755932814
H	-0.814975818948	-0.237334332928	-2.535059733069
C	0.334415806581	-0.242273635873	-4.333629962626
H	-0.539810974904	-0.374786614865	-4.963722428806
C	1.603067938629	-0.152604384751	-4.912080978653
H	1.715897867088	-0.214815994547	-5.989979141702
C	2.723627721335	0.017202332123	-4.097427072968
H	3.712660062859	0.087571199828	-4.539627112590
C	2.576616814173	0.096993993957	-2.721400101462
H	3.451627243638	0.230189141834	-2.090710434560

S₁TS-twist 3.29 eV (ωB97XD/MeOH) E: -728.907894862094

C	-1.255618668828	0.311854019056	2.242639884274
C	-1.137646852144	-0.649660285618	3.323067756697
O	0.010648426722	-1.114472855574	3.590293946568
H	1.022340451974	0.665381128940	2.977863908882
C	-2.318759857587	-0.961854810400	4.069971776342
H	-2.253589570387	-1.734729545707	4.828874080647
C	-3.498479136122	-0.297368513248	3.812687673599
H	-4.391448476864	-0.538157206272	4.380621732527
C	-3.561316214634	0.694138184015	2.816894109522
H	-4.500672654338	1.199519541686	2.620029019350
C	-2.431371710049	1.013605274856	2.053366575072
H	-2.495154330974	1.770754207709	1.278107442449
C	-0.034770168326	0.499828845106	1.436253388987
O	1.038896388274	1.009554237793	2.064961833439
C	0.033380139121	0.195813137998	0.072876763852
H	-0.897200914322	-0.139111944666	-0.375751099343
C	1.176487913678	0.306606189330	-0.677949889763
H	2.079927177049	0.638202815550	-0.171903055271
C	1.304127934424	0.036419269045	-2.098803953382
C	0.227538486982	-0.369275565213	-2.911039100731
H	-0.764278735626	-0.486310148336	-2.485684774827
C	0.413213695936	-0.621623117915	-4.263325247311
H	-0.431240361121	-0.933242593620	-4.870742790064
C	1.673613130745	-0.475367923730	-4.844169314878
H	1.813527276518	-0.672841882435	-5.902404966787
C	2.750333576082	-0.071703771571	-4.056155158233
H	3.735190203345	0.046464369518	-4.497889351032
C	2.567041447806	0.181612889412	-2.702954423370
H	3.410893660224	0.495966054279	-2.094196192670

S₁MIN-twist 3.17 eV (ωB97XD/MeOH) E: -728.912483130990

C	-1.460915431061	0.386894985550	2.132267052393
C	-1.364162615586	-0.840186057884	2.909052421275
O	-0.328436960074	-1.546475778586	2.855436053575

H	0.481848542909	1.689569406751	2.755014244104
C	-2.497031874034	-1.205854134363	3.731071194517
H	-2.424369572430	-2.124007991666	4.304148082468
C	-3.609160224439	-0.417095214316	3.770795243177
H	-4.457244420803	-0.695465833391	4.387264911942
C	-3.673953908434	0.777716695942	3.004829537486
H	-4.569227018890	1.387884613071	3.049841332765
C	-2.614920453418	1.169848133620	2.204357783610
H	-2.679433136660	2.083210866163	1.622251638493
C	-0.314371887084	0.744646436116	1.294015811189
O	0.686058989076	1.480214325303	1.834268343733
C	-0.187509494408	0.308432109263	-0.037452216184
H	-1.035344835517	-0.260631578115	-0.408954954480
C	0.898436006063	0.526934020819	-0.830724140553
H	1.736249487606	1.078611273935	-0.412005178456
C	1.060314992711	0.076294945804	-2.215496247512
C	0.039661261499	-0.548016985160	-2.950981136529
H	-0.937250814426	-0.706377211171	-2.504089030866
C	0.253834746669	-0.964837513826	-4.260213203279
H	-0.553087808816	-1.444544734272	-4.806704988443
C	1.490015249748	-0.767462747594	-4.873411890855
H	1.653397629039	-1.092832862994	-5.896146337118
C	2.511384498370	-0.144022005875	-4.159761394715
H	3.479763988052	0.019228111175	-4.623834535054
C	2.296962838767	0.272125605998	-2.850207949200
H	3.101243417870	0.756661684306	-2.301966169872

S ₀ MIN (SF-TDDFT/BHHLYP/MeOH) 0.00 eV -728.839532798200			
C	-1.151300816812	0.019880341529	2.274216888993
C	-1.067674866878	-0.021228687264	3.682420557015
O	0.100669442797	-0.055928932699	4.335869577828
H	0.808990471941	-0.028948539688	3.660444549254
C	-2.226590679333	-0.029110130314	4.454650647341
H	-2.127271686411	-0.062696609898	5.526983404471
C	-3.463022796103	0.009186263618	3.848987781719
H	-4.352016118017	0.003705019147	4.459244821583
C	-3.571767155448	0.057198445085	2.460762056828
H	-4.540506850396	0.089794434573	1.990868638533
C	-2.428797054624	0.061648367903	1.694578533030
H	-2.534288812643	0.105319711533	0.625731914083
C	0.086656135712	0.016505067749	1.473023296114
O	1.185490280387	0.017474061892	2.040148003153
C	0.023984727791	0.004765503859	0.015143123280
H	-0.934726677330	-0.017130484004	-0.463823819860
C	1.157684035944	0.013294627061	-0.712835526030
H	2.088394738068	0.032591622708	-0.165631933282
C	1.275499540201	-0.001962437387	-2.160536671091
C	0.169917676292	-0.028802869856	-3.019157993899
H	-0.830453411075	-0.038074691627	-2.618653064869
C	0.342668591208	-0.043694423998	-4.389554392407
H	-0.519546227268	-0.064750944300	-5.036840711771
C	1.621706451569	-0.032333689412	-4.935251276850
H	1.750744152157	-0.043863689364	-6.005872521646
C	2.726735659403	-0.005862421352	-4.099706463224
H	3.721696308704	0.003319316534	-4.515479255253
C	2.554444810137	0.009306632096	-2.725273893082
H	3.418292387565	0.030399135833	-2.078915695413

S ₁ /S ₀ (SF-TDDFT/BHHLYP/MeOH) 2.63 eV -728.742858622200 -728.742857868100			
C	-1.461961470519	0.326354471051	2.125525307428
C	-1.387322255310	-0.868618021975	2.941765388485
O	-0.375830840474	-1.602264077300	2.924148257486
H	0.489695814491	1.655746512434	2.696869526959
C	-2.526358250594	-1.157817895184	3.770132146148
H	-2.481335735873	-2.050981166158	4.371769806552

C	-3.615290515451	-0.334210476931	3.789729168495
H	-4.457925151475	-0.570483392021	4.420016580847
C	-3.651670920245	0.821941684845	2.993884331989
H	-4.517944947275	1.462174560440	3.014630041135
C	-2.575972535802	1.140839749503	2.172165486998
H	-2.615657670244	2.026918415933	1.558760158509
C	-0.308884279471	0.641924007568	1.271621379363
O	0.676065707437	1.390668869532	1.788129108759
C	-0.192574098456	0.201260088911	-0.033041909560
H	-1.017882247454	-0.385814528401	-0.398010043348
C	0.892533452703	0.467270395727	-0.843287135542
H	1.707056351440	1.028660347029	-0.413047929720
C	1.056664027361	0.061871655938	-2.206159163207
C	0.058386764837	-0.602952912435	-2.944321741393
H	-0.895017377407	-0.819956853507	-2.491658139648
C	0.277670070720	-0.976318611400	-4.254005207452
H	-0.502297363265	-1.481057376688	-4.801240661264
C	1.493932091177	-0.701497777006	-4.872194785515
H	1.659997820625	-0.994966167228	-5.896237593429
C	2.490831951846	-0.042229593177	-4.163436311040
H	3.435013260727	0.176403465768	-4.636538807559
C	2.275271173441	0.337885481778	-2.853824795378
H	3.053558364803	0.849711707558	-2.309478187490

Table S2 Cartesian coordinates (in Å) of the optimized structures for 2'HC along the decay path from S_{3FC} to S₁/S₀ in a vacuum. S₁/S₀ and S_{0MIN}(SF-TDDFT) geometries were computed at the SF-TDDFT/BHHLYP/6-31G(d) level, whereas the other geometries were computed at ωB97XD/6-31G(d). Energies in the atomic units (Hartree) for each geometry are also shown.

S _{0MIN} 0.00 eV (ωB97XD/vacuum) E: -729.019813395901			
C	-1.162162430585	0.006235049579	2.284055715937
C	-1.060399701138	0.008929661398	3.700220530481
O	0.106604555780	0.006488685884	4.345260320256
H	0.812982902845	0.001768610977	3.654797070507
C	-2.224151205433	0.014481562942	4.484003965579
H	-2.108571924452	0.016600885664	5.562474031540
C	-3.468395701518	0.016834265641	3.886507657655
H	-4.359264572838	0.020982437141	4.507961490226
C	-3.590932503447	0.013720303766	2.491631886380
H	-4.570265120808	0.015292634638	2.025254927898
C	-2.450185682653	0.008556606196	1.714054189854
H	-2.563624320517	0.005829274035	0.636141244187
C	0.073995984775	0.000924999024	1.474903657964
O	1.184200439449	-0.003512544408	2.027735391525
C	0.005814211287	0.001021590180	-0.003022332027
H	-0.961753699510	0.008138407195	-0.488860934605
C	1.139754310258	-0.007409242645	-0.720279036940
H	2.070097624343	-0.014263787381	-0.154326184406
C	1.273381874391	-0.008720640450	-2.179393146783
C	0.174798547244	0.001135430062	-3.051394732202
H	-0.835833435279	0.010570064575	-2.654797653724
C	0.362445520285	-0.000858946167	-4.426139307542
H	-0.498886182292	0.006871597220	-5.087160527022
C	1.650935553433	-0.012712412944	-4.959312545097
H	1.794225563078	-0.014260555789	-6.035608011293
C	2.750845543398	-0.022474995006	-4.107619142063
H	3.757192415743	-0.031684512007	-4.514776768365
C	2.561203126914	-0.020434277897	-2.730447908001
H	3.421560564789	-0.028050151449	-2.066323275347
S _{3MIN} 4.27 eV (ωB97XD/vacuum) E: -728.863016281400			
C	-1.165199368091	0.006106900147	2.258174727016
C	-1.072570054511	0.008415751308	3.677372143836
O	0.095797071794	0.007321015997	4.316709682801
H	0.795600524062	0.004739719888	3.598089683411
C	-2.237771831727	0.012006055975	4.462727401373
H	-2.114498384384	0.013729314875	5.540769729166
C	-3.502890838113	0.013266878039	3.875800416458
H	-4.389557845494	0.016003074234	4.501259894416
C	-3.611591749107	0.010968233530	2.491345329378
H	-4.584545074973	0.011819064580	2.011097652244
C	-2.451144981804	0.007482554928	1.703474328388
H	-2.573650825514	0.005826264345	0.625621745238
C	0.069020648603	0.002400643784	1.455410656582
O	1.202352962561	0.001276139686	2.030720944486
C	0.029041990161	-0.000106143418	0.013754824932
H	-0.924124757045	0.000780375469	-0.501995177936
C	1.217357264987	-0.003811698375	-0.715803122543
H	2.134898911463	-0.004514506853	-0.133502528897
C	1.316845390934	-0.006789692982	-2.134307187072
C	0.178140274364	-0.005994244042	-3.000954845913
H	-0.820804266980	-0.003018912313	-2.577359576106
C	0.333807381281	-0.008905451115	-4.373513193276
H	-0.542889386354	-0.008178366121	-5.014241991946
C	1.610117846070	-0.012790132450	-4.943860267397
H	1.724283869981	-0.015061433473	-6.023454623577
C	2.745495017161	-0.013764432994	-4.116487258915

H	3.736466264925	-0.016865042067	-4.559871656701
C	2.605414027414	-0.010812517459	-2.746502385112
H	3.482212175846	-0.011529413140	-2.104934769745
S ₃ /S ₂ 4.46 eV (ωB97XD/vacuum) E: -728.855744771478 E: -728.855744860718			
C	-1.151106405491	0.045998929899	2.254918097765
C	-1.069196504171	-0.118417268647	3.667594123319
O	0.096227216956	-0.226455980685	4.263760554175
H	0.763618909475	-0.158917230641	3.448235779428
C	-2.245824220605	-0.163962308035	4.453585123169
H	-2.126447906805	-0.297061529355	5.524539054409
C	-3.522846778669	-0.040308596524	3.877155707692
H	-4.409923701032	-0.078142056293	4.500495152093
C	-3.620268734615	0.126134111895	2.509888400189
H	-4.586813842311	0.221871357953	2.026182749949
C	-2.431978974341	0.169772177379	1.721516731370
H	-2.556848845092	0.310983526582	0.651918617112
C	0.082514525276	0.072097967661	1.461260194679
O	1.199467451059	-0.023378444302	2.010721964382
C	0.015561725030	0.201890148844	-0.000614698661
H	-0.906210289776	0.333668423844	-0.558610311413
C	1.235540383478	0.196206422905	-0.722633687712
H	2.125842696211	0.235970439438	-0.098745866848
C	1.341267122817	0.075123974646	-2.109999659456
C	0.175542249625	-0.071912906859	-2.970354765333
H	-0.812093200142	-0.092607282617	-2.522499850473
C	0.321168413062	-0.191067805480	-4.334269646931
H	-0.556320953762	-0.297929064826	-4.964694812898
C	1.593904344658	-0.170186984239	-4.917682227670
H	1.697751723985	-0.253567555001	-5.995207006871
C	2.750981840113	-0.036065450724	-4.109473526656
H	3.730329821698	-0.025834219820	-4.577259061943
C	2.636109155251	0.078303012680	-2.751702880150
H	3.515665035358	0.177794190624	-2.122483672256
S ₂ /S ₁ 3.74 eV (ωB97XD/vacuum) E: -728.882420752806 E: -728.882420846868			
C	-1.174413563850	0.156028627644	2.250690726067
C	-1.093435952804	-0.199523154797	3.637210199603
O	0.071205775161	-0.428664790991	4.222643972424
H	0.791309070526	-0.209260658069	3.551378250817
C	-2.258902832570	-0.330136956901	4.414114428078
H	-2.145869717485	-0.619643713387	5.452932991959
C	-3.499873742724	-0.094151041234	3.847596562892
H	-4.398265784511	-0.193767589204	4.447106816873
C	-3.587665808855	0.288194947032	2.504077151390
H	-4.556223710569	0.490176990411	2.058692508022
C	-2.434237941249	0.425168379222	1.725720134071
H	-2.526865186361	0.755234132384	0.697083220376
C	0.081688220548	0.217004743237	1.461744440715
O	1.174765373545	0.367562017124	2.134623178279
C	0.074753262371	0.096858131812	0.052043311222
H	-0.886689843099	-0.090648390503	-0.415054662483
C	1.216550469391	0.176906975705	-0.704070011808
H	2.150698566790	0.358963955132	-0.179031586685
C	1.307268629809	0.040875496829	-2.143789429283
C	0.193071816905	-0.170710192901	-2.980055030802
H	-0.802608610256	-0.238089801065	-2.552008968227
C	0.343297190036	-0.294156161171	-4.353177328307
H	-0.532496990832	-0.456643889993	-4.975055416628
C	1.606426277247	-0.211213233014	-4.938517984124
H	1.719154746074	-0.308782705153	-6.013904855859
C	2.721163534312	-0.001522088757	-4.129219731111
H	3.710852180277	0.064990479632	-4.571720672386
C	2.573039544736	0.123093826851	-2.755473266832
H	3.447917284848	0.285855664108	-2.131038373731

S₁MIN-trans 3.55 eV (ωB97XD/vacuum) E: -728.889170055549

C	-1.182640715122	0.287030508379	2.283158706616
C	-1.109933500873	-0.431066342107	3.503579304218
O	0.025997642793	-0.953567554929	3.980991590185
H	0.776606058000	-0.572221386638	3.487735523469
C	-2.284038013074	-0.655546496615	4.234922173255
H	-2.215641566262	-1.233290430666	5.149969952028
C	-3.481827617473	-0.119047544076	3.801750031581
H	-4.381174208800	-0.285567526143	4.386664145850
C	-3.546918146189	0.652753396894	2.631324043450
H	-4.493437230259	1.067140980183	2.301241981132
C	-2.397906017823	0.875705403886	1.896330076306
H	-2.423097011262	1.470041597755	0.988960076006
C	0.024333560906	0.385575298463	1.420246547076
O	1.015786736550	0.783791492377	2.160062357135
C	0.057805074977	0.144444039390	0.050374197083
H	-0.878551163726	-0.201574047190	-0.377401094467
C	1.186175129793	0.325341609622	-0.722207367643
H	2.081547106568	0.697826308349	-0.231372220406
C	1.303907822627	0.066807695542	-2.143148329147
C	0.251573152909	-0.435928413862	-2.932311799561
H	-0.709785306277	-0.658421946980	-2.479293746908
C	0.420995552486	-0.659982284972	-4.290730973088
H	-0.407410266208	-1.048993359845	-4.875934440763
C	1.642842149169	-0.392479668327	-4.906919312403
H	1.770895840306	-0.569896883217	-5.970285255982
C	2.696874784637	0.102901679008	-4.143065234562
H	3.654808736579	0.314911482825	-4.609125578364
C	2.529602836004	0.327955565439	-2.783804687739
H	3.358220836560	0.715356827447	-2.196170089794

S₁TS-taut 3.66 eV (ωB97XD/vacuum) E: -728.885175233444

C	-1.187227924640	0.272276408969	2.225031790848
C	-1.086166813648	-0.253861946313	3.564460252060
O	0.087745964112	-0.479797433382	4.094766816474
H	0.762265659723	-0.052692205037	3.440993862359
C	-2.249534589007	-0.519255863754	4.325565344713
H	-2.129232166471	-0.956479566665	5.310272489180
C	-3.480456231639	-0.165610081510	3.819444973801
H	-4.379248204868	-0.345105047283	4.399477629749
C	-3.574546217850	0.449449094568	2.554766446633
H	-4.550935295508	0.699201502081	2.152641161965
C	-2.431481682924	0.702234845652	1.790165791107
H	-2.522509910876	1.161875286541	0.812104044015
C	0.072940837666	0.362882868629	1.421348230862
O	1.083084999738	0.709165041838	2.140497883310
C	0.073073944106	0.156325408966	0.033093347148
H	-0.871100323196	-0.145344873425	-0.412975874876
C	1.201753759946	0.303927348005	-0.741084353371
H	2.109793158667	0.614702071167	-0.230146584214
C	1.306492721098	0.084474115389	-2.165977315915
C	0.222692944777	-0.310673492655	-2.977172074629
H	-0.756652240467	-0.466210568082	-2.534400264608
C	0.382626866279	-0.507748490029	-4.340538410603
H	-0.470310119040	-0.812959523407	-4.940546420922
C	1.625080767208	-0.317600622646	-4.944875835113
H	1.745497220965	-0.472584263933	-6.012688912040
C	2.709612101428	0.073972204582	-4.161632965460
H	3.683671040164	0.226139090994	-4.618057152376
C	2.552671649253	0.270789012423	-2.797761590107
H	3.404629696980	0.575903189007	-2.195181859925

S₀MIN 0.00 eV (SF-TDDFT/BHHLYP/vacuum) E: -728.826896402300

C	-1.342414066283	0.029506825365	2.187058394901
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C	-1.235885449647	0.131035745529	3.592006486271
O	-0.073400558713	0.260276338244	4.222568360307
H	0.630005888755	0.253727582552	3.544437270304
C	-2.387035357742	0.098754228344	4.380878962388
H	-2.267285543717	0.182163417111	5.447475437413
C	-3.625754723234	-0.038605008050	3.800123387748
H	-4.504497402549	-0.063447544873	4.424466028181
C	-3.753474114743	-0.147995472074	2.416172461651
H	-4.724328546439	-0.258922081716	1.963805237837
C	-2.623681050234	-0.112446510393	1.633594279460
H	-2.737491548571	-0.202783435546	0.568398846465
C	-0.118541626825	0.074792293301	1.368348885169
O	0.986631684514	0.161811687972	1.906160670308
C	-0.201030902882	0.022282555246	-0.097064911929
H	-1.165346329812	-0.021976327828	-0.566004717837
C	0.918576799874	0.038304218832	-0.832391243878
H	1.849747717149	0.087146477742	-0.288591046300
C	1.025654148265	-0.002224937623	-2.284227220202
C	-0.083599062261	-0.062968062060	-3.134482043437
H	-1.078437179500	-0.081845765817	-2.721782719385
C	0.078709921271	-0.098953732060	-4.504581325568
H	-0.787366314231	-0.145496941632	-5.144444478094
C	1.352397961952	-0.075312156609	-5.060565085038
H	1.474889287529	-0.103584476802	-6.130951549857
C	2.461812183793	-0.015223004015	-4.233776636527
H	3.452769748070	0.003482044017	-4.657024857014
C	2.298075921702	0.020971838857	-2.859674762652
H	3.163049706799	0.067992768607	-2.217267833082

S₁/S₀ 2.87 eV (SF-TDDFT/BHLYP/vacuum) E: -728.721463279200 E: -728.721463009000

C	-1.253637960472	0.293383672244	2.224709188598
C	-1.258847282898	-0.876958655292	3.084328020413
O	-0.256168713790	-1.605288925651	3.174476984689
H	0.968205900156	1.077446202175	2.905602818908
C	-2.442333558108	-1.135954235483	3.860726276007
H	-2.442034250247	-2.027410448509	4.465119035690
C	-3.502846632844	-0.273845892845	3.834531331564
H	-4.381894957622	-0.471152460563	4.425837606588
C	-3.447441029498	0.874344592626	3.038025337672
H	-4.285867433294	1.550880593844	3.019889963151
C	-2.325929109598	1.150876251941	2.249576299318
H	-2.312218815083	2.034721634219	1.633325577260
C	-0.059945680953	0.553801010525	1.389301951067
O	0.937547910957	1.271150959496	1.966948977057
C	0.046152624765	0.170224130167	0.084269202654
H	-0.808417326165	-0.343565062098	-0.324270892043
C	1.158473160576	0.414156924210	-0.719794573362
H	1.993093840313	0.915015321851	-0.257129933703
C	1.304888493185	0.061488637338	-2.092088348921
C	0.304230993177	-0.582865874285	-2.848701153127
H	-0.638532575480	-0.829952391856	-2.389926926444
C	0.509427692762	-0.904826382626	-4.172906035293
H	-0.273443630961	-1.398770817338	-4.726378808525
C	1.712749770875	-0.599598523020	-4.800238009040
H	1.866932759283	-0.854858637775	-5.835724982326
C	2.712670459898	0.038001954082	-4.076133519581
H	3.650359409851	0.280610368763	-4.550288489101
C	2.513955292459	0.362644403049	-2.751100866117
H	3.296482906279	0.856301650771	-2.196445458485

The cross-section of two-photon absorption

The wavelength and pulse energy is $\lambda = 270$ nm and $P = 90$ nJ for the pump, and $\lambda = 540$ nm and $P = 10$ nJ for the probe, respectively. Therefore, the photon energies and the number of photons are $h\nu = 7.37 \times 10^{-19}$ J and $N = 1.22 \times 10^{11}$ pulse⁻¹, and $h\nu = 3.68 \times 10^{-19}$ J and $N = 2.72 \times 10^{10}$ pulse⁻¹, respectively. Using the pump focused area $s = 0.25$ mm² and the pulse duration $\tau = 10$ fs on assumption of a rectangular temporal pulse shape, the photon fluxes (intensities) of the pump and probe pulses are calculated to be $I_0 = 4.88 \times 10^{27}$ photon cm⁻² s⁻¹ and $I_0 = 1.09 \times 10^{27}$ photon cm⁻² s⁻¹, respectively.

The attenuation by multi-photon absorption over path length l is given by Eq. (S1), where C and $\sigma^{(k)}$ is the number density (concentration) of an absorbing sample and the cross-section of the k th order absorption.

$$-\frac{dl}{dl} = C\sigma^{(1)}I + C\sigma^{(2)}I^2 + \dots \quad (\text{S1})$$

In the present study, the concentrations of the sample are $C_{\text{Vis}} = 6.02 \times 10^{19}$ molecule cm⁻³ (0.1 mol/L) for the Vis probe experiments, and $C_{\text{DUV}} = 6.02 \times 10^{18}$ molecule cm⁻³ (0.01 mol/L) for the DUV probe experiments. Using the two-photon cross-sections of typical organic molecules $\sigma^{(2)} = \sigma_{\text{TPA}} = 6000$ GM (Göppert-Mayer unit, 10^{-50} cm⁴ s photon⁻¹) and the penetration depth $\delta_p = l = 5.8$ μ m, the attenuation of the pump pulse by two-photon absorbance ΔI_{Vis} in the Vis probe experiments is estimated as,

$$\Delta I_{\text{Vis}} = C_{\text{Vis}} \sigma^{(2)} I^2 \delta_p = 4.99 \times 10^{23} \text{ photon cm}^{-2} \text{ s}^{-1}. \quad (\text{S2})$$

The attenuation of the pump pulse ΔI_{DUV} in the DUV probe experiments becomes the same value since the effects of C and δ_p cancel each other. The attenuated photon flux by two-photon absorption is negligible compared to the incident photon flux, $I_0 = 4.88 \times 10^{27}$ photon cm⁻² s⁻¹.

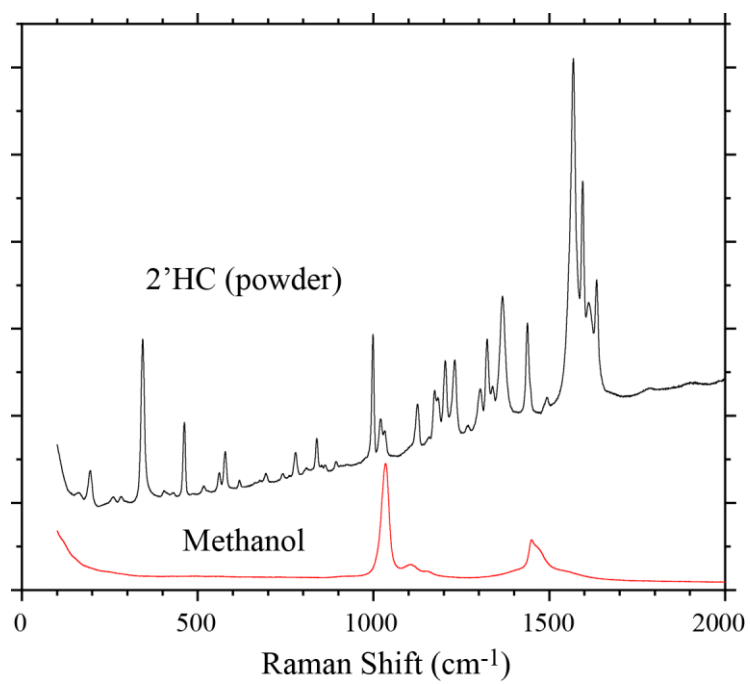


Fig. S1 Raman spectra of *trans*-2'-hydroxychalcone (2'HC) and methanol.

Formalism for obtaining the molar absorption coefficients

The rate equations for sequential process $A \rightarrow B \rightarrow C \rightarrow D$ are given as Eqs. (S3.1) – (S3.4),

$$\frac{d[A]}{dt} = -k_1[A], \quad (\text{S3.1})$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B], \quad (\text{S3.2})$$

$$\frac{d[C]}{dt} = k_2[B] - k_3[C], \quad (\text{S3.3})$$

$$\frac{d[D]}{dt} = k_3[C] - k_4[D]. \quad (\text{S3.4})$$

where k_4 can be regarded to be zero in the present case (see text). The difference absorbance ΔA corresponds to the total absorbance of transient components A – D subtracted by that of the ground state G,

$$\Delta A = (\varepsilon_A[A] + \varepsilon_B[B] + \varepsilon_C[C] + \varepsilon_D[D] - \varepsilon_G[G])l. \quad (\text{S4})$$

where ε_j ($j = A - D$ and G) and l are the molar absorption coefficients of the j th component and the optical path length, respectively. On the other hand, the temporal absorbance change should be expressed in terms of the decay functions with the rate constants k_i as Eq. (S5),

$$\Delta A = \Delta A_1 e^{-k_1 t} + \Delta A_2 e^{-k_2 t} + \Delta A_3 e^{-k_3 t} + \Delta A_\infty. \quad (\text{S5})$$

where ΔA_∞ is due to the long-lived components D and G.

Solving the differential equations in Eqs. (S3.1) – (S3.4) gives the following expressions for $[A] - [D]$ with respect to the exponential functions with the rate constants $k_1 - k_3$ as in Eqs. (S6) – (S9).

$$[A] = [A]_0 e^{-k_1 t}, \quad (\text{S6})$$

$$[B] = \frac{k_1}{-k_1 + k_2} [A]_0 (e^{-k_1 t} - e^{-k_2 t}), \quad (\text{S7})$$

$$[C] = \frac{-k_1 k_2 [A]_0}{(-k_1 + k_2)(-k_2 + k_3)(-k_3 + k_1)} [(-k_2 + k_3)e^{-k_1 t} + (-k_3 + k_1)e^{-k_2 t} + (-k_1 + k_2)e^{-k_3 t}], \quad (\text{S8})$$

$$[D] = \frac{-k_1 k_2 k_3 [A]_0}{(-k_1 + k_2)(-k_2 + k_3)(-k_3 + k_1)} \left[\frac{-k_2 + k_3}{-k_1} e^{-k_1 t} + \frac{-k_3 + k_1}{-k_2} e^{-k_2 t} + \frac{-k_1 + k_2}{-k_3} e^{-k_3 t} \right] + [A]_0. \quad (S9)$$

Therefore, comparisons of the coefficients for the exponential functions in Eq. (S5) and those in the expressions in Eqs. (S6) – (S9) for $[A] - [D]$ give the following explicit expressions for $\Delta A_1 - \Delta A_\infty$ in terms of $\varepsilon_A - \varepsilon_G$,

$$\Delta A_1 = [A]_0 l \left[\varepsilon_A - \frac{-k_1}{-k_1 + k_2} \varepsilon_B + \frac{-k_1 k_2 (-k_2 + k_3)}{(-k_1 + k_2)(-k_2 + k_3)(-k_3 + k_1)} \varepsilon_C - \frac{-k_2 k_3 (-k_2 + k_3)}{(-k_1 + k_2)(-k_2 + k_3)(-k_3 + k_1)} \varepsilon_D \right], \quad (S10)$$

$$\Delta A_2 = [A]_0 l \left[\frac{-k_1}{-k_1 + k_2} \varepsilon_B - \frac{k_3 k_1 (-k_3 + k_1)}{(-k_1 + k_2)(-k_2 + k_3)(-k_3 + k_1)} \varepsilon_C + \frac{k_1 k_3 (-k_3 + k_1)}{(-k_1 + k_2)(-k_2 + k_3)(-k_3 + k_1)} \varepsilon_D \right], \quad (S11)$$

$$\Delta A_3 = [A]_0 l \left[\frac{-k_1 k_2 (-k_1 + k_2)}{(-k_1 + k_2)(-k_2 + k_3)(-k_3 + k_1)} \varepsilon_C - \frac{-k_1 k_2 (-k_1 + k_2)}{(-k_1 + k_2)(-k_2 + k_3)(-k_3 + k_1)} \varepsilon_D \right], \quad (S12)$$

$$\Delta A_\infty = [A]_0 l \varepsilon_D - [G] l \varepsilon_G. \quad (S13)$$

Finally, the inversed expressions of Eqs. (S10) – (S13) are obtained as below. Note that if $k_1 > k_2 > k_3$ and ε_j are non-negative, ΔA_l ($l = 1-3$) in Eqs. (S10) – (S13) are all positive.

$$\varepsilon_A = \frac{1}{[A]_0} \left(\Delta A_1 + \Delta A_2 + \Delta A_3 + \Delta A_\infty + \varepsilon_G [G] l \right), \quad (S10)$$

$$\varepsilon_B = \frac{1}{[A]_0} \left(\frac{-k_1 + k_2}{-k_1} \Delta A_2 + \frac{-k_3 + k_1}{k_1} \Delta A_3 + \Delta A_\infty + \varepsilon_G [G] l \right), \quad (S11)$$

$$\varepsilon_C = \frac{1}{[A]_0} \left(\frac{(-k_2 + k_3)(-k_3 + k_1)}{-k_1 k_2} \Delta A_3 + \Delta A_\infty + \varepsilon_G [G] l \right), \quad (S12)$$

$$\varepsilon_D = \frac{1}{[A]_0} \left(\Delta A_\infty + \varepsilon_G [G] l \right). \quad (S13)$$

Convolution of the apparatus Gaussian function

The exponential function and the Gaussian function are given as Eqs. (S14) and (S15), respectively.

$$f(t) = \begin{cases} \exp\left(-\frac{t}{\tau_1}\right) & \text{for } t \geq 0, \\ 0 & \text{for } t < 0 \end{cases}, \quad (\text{S14})$$

$$g(t) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left[-\frac{(t-\mu)^2}{2\sigma^2}\right]. \quad (\text{S15})$$

The convolution $f(t)*g(t)$ is represented by Eq. (S16) for the region $t \geq 0$.

$$f(t) * g(t) = \frac{1}{2} \exp\left(\frac{\mu}{\tau_1} + \frac{\sigma^2}{2\tau_1^2} - \frac{t}{\tau_1}\right) \text{erfc}\left[-\frac{\mu + \frac{\sigma^2}{\tau_1}t}{\sqrt{2}\sigma}\right], \quad (\text{S16})$$

$$\text{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-s^2} ds. \quad (\text{S17})$$

where $\text{erfc}(x)$ is the complementary error function defined by Eq. (S17). In the present case, the FWHM of the Gaussian function is set to be 10 fs. The time constant τ_1 for the fastest component was determined by single-parameter fitting after subtracting the k_2 and k_3 components.

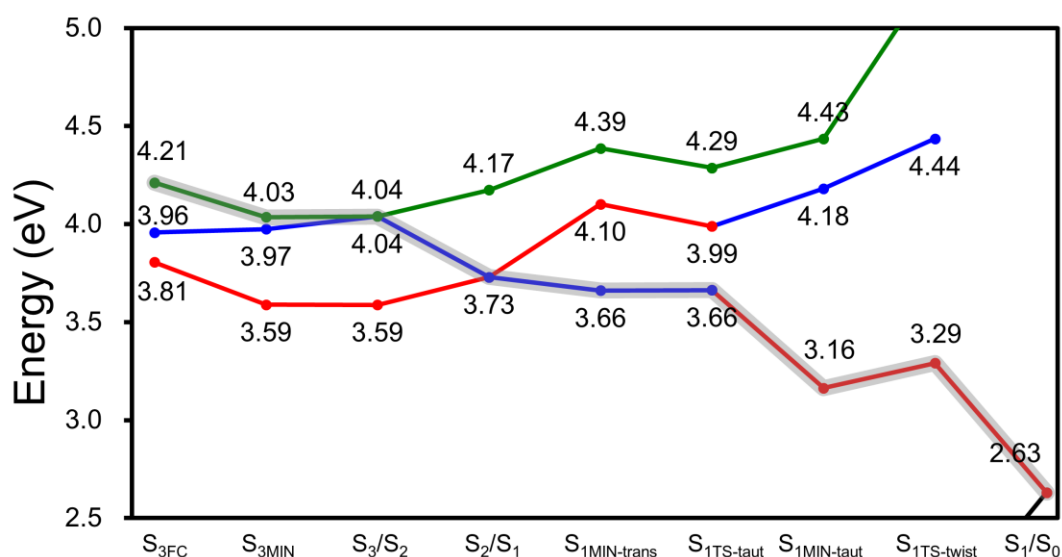


Fig. S2 Variations of electronic potential energy at the crucial geometries for 2'-hydroxychalcone (2'HC) in methanol. The red, blue, and green lines indicate the energies of the $\pi_1\pi^*$, $n\pi^*$, and $\pi_2\pi^*$ configurations on each geometry, respectively. S_1/S_0 were computed at the SF-TDDFT/BHHLYP/6-31G(d) level, whereas the other geometries were at the ω B97XD/6-31G(d) level. The solvent effect of methanol was treated with the conductor-like polarizable continuum model (CPCM). All of the optimized geometries are given in Table S1.

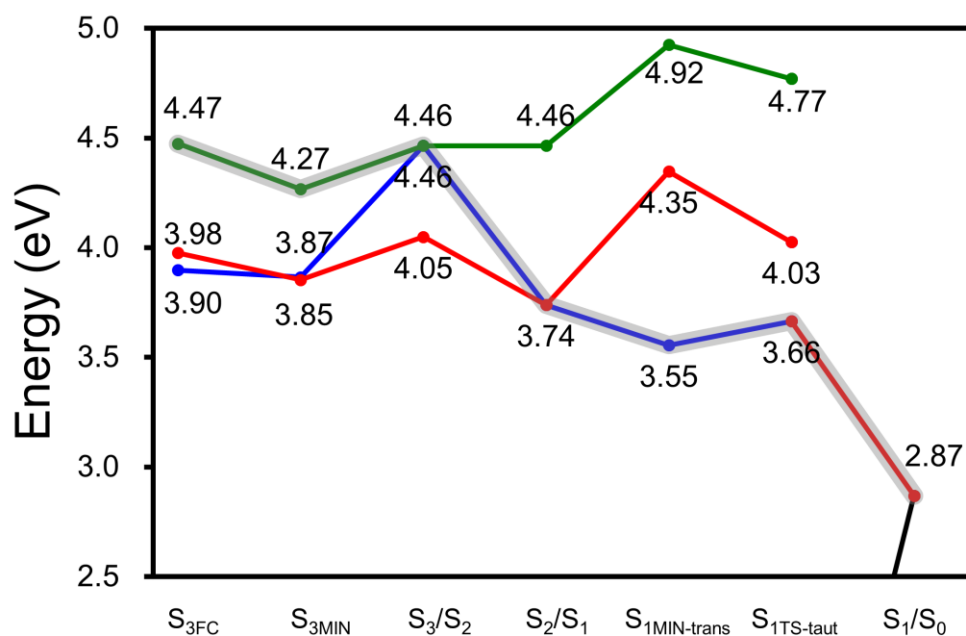


Fig. S3 Variations of electronic potential energy at the crucial geometries for 2'HC in the vacuum. The red, blue, green lines indicated the energies for $\pi_1\pi^*$, $n\pi^*$, and $\pi_2\pi^*$ on each geometry, respectively. S_1/S_0 were computed at the SF-TDDFT/BHHLYP/6-31G(d) level, whereas the other geometries were at the ω B97XD/6-31G(d) level. All of the optimized geometries are given in Table S2.

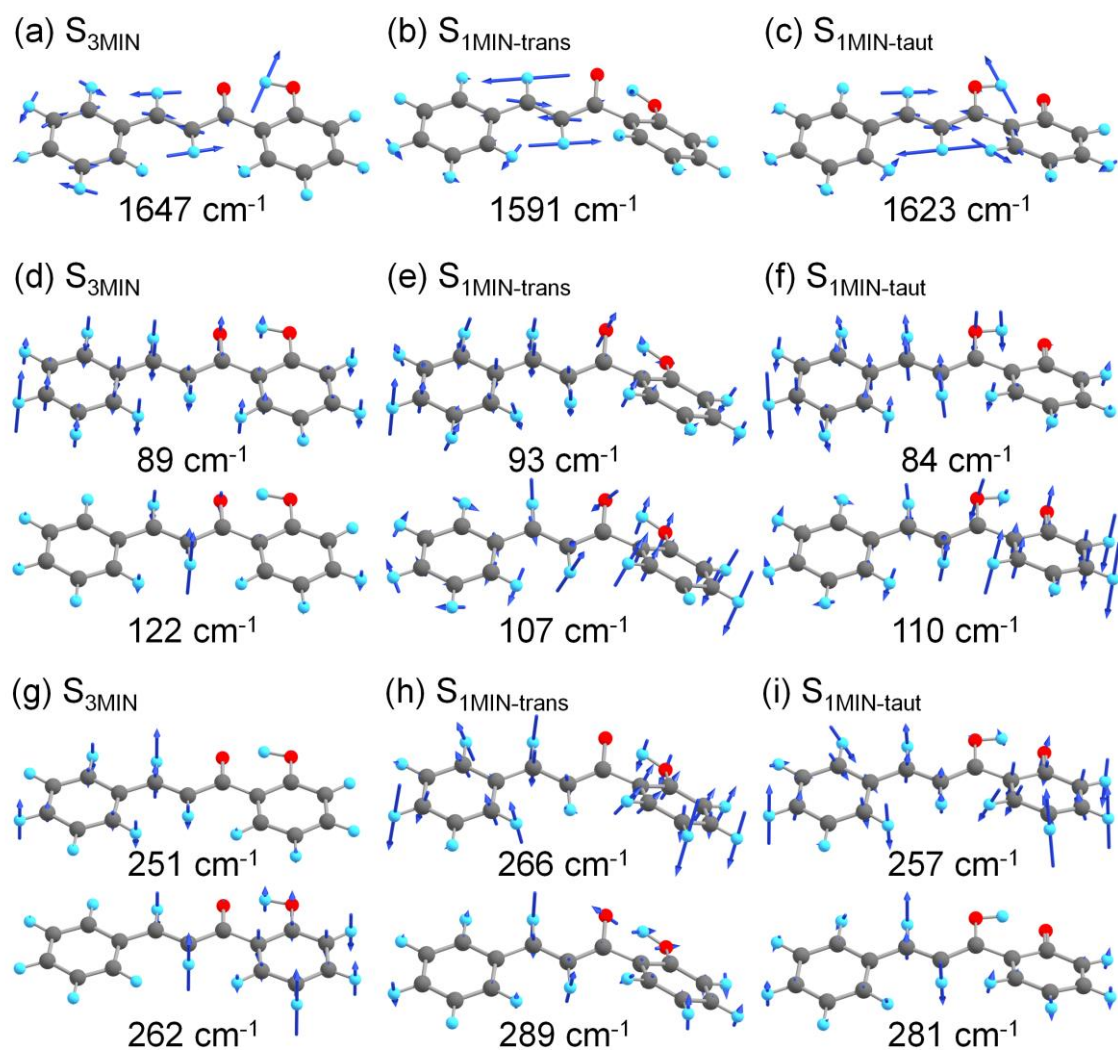


Fig. S4 Normal mode vectors on the crucial points along the decay path after the S_3 excitation of 2'HC. The normal mode vectors and frequencies were computed at the TDDFT/ ω B97XD/6-31G(d) level with CPCM (methanol). (a) – (c) show the normal modes that have the largest contribution of the C7-C8 bond stretching motion at $S_{3\text{MIN}}$, $S_{1\text{MIN-trans}}$ and $S_{1\text{MIN-taut}}$ in the vibrational frequency range from 1500 cm^{-1} to 1700 cm^{-1} , respectively. (d) – (f) show all of the normal modes at $S_{3\text{MIN}}$, $S_{1\text{MIN-trans}}$, and $S_{1\text{MIN-taut}}$ in the frequency range from 70 cm^{-1} to 150 cm^{-1} . (g) – (i) show all of the normal modes at $S_{3\text{MIN}}$, $S_{1\text{MIN-trans}}$, and $S_{1\text{MIN-taut}}$ in the vibrational frequency range from 220 cm^{-1} to 290 cm^{-1} .