

Single methyl substitute effect on photoisomerization of trans, trans-1,4-diphenyl-1,3-butadiene revealed by on-the-fly trajectory surface hopping dynamic simulations

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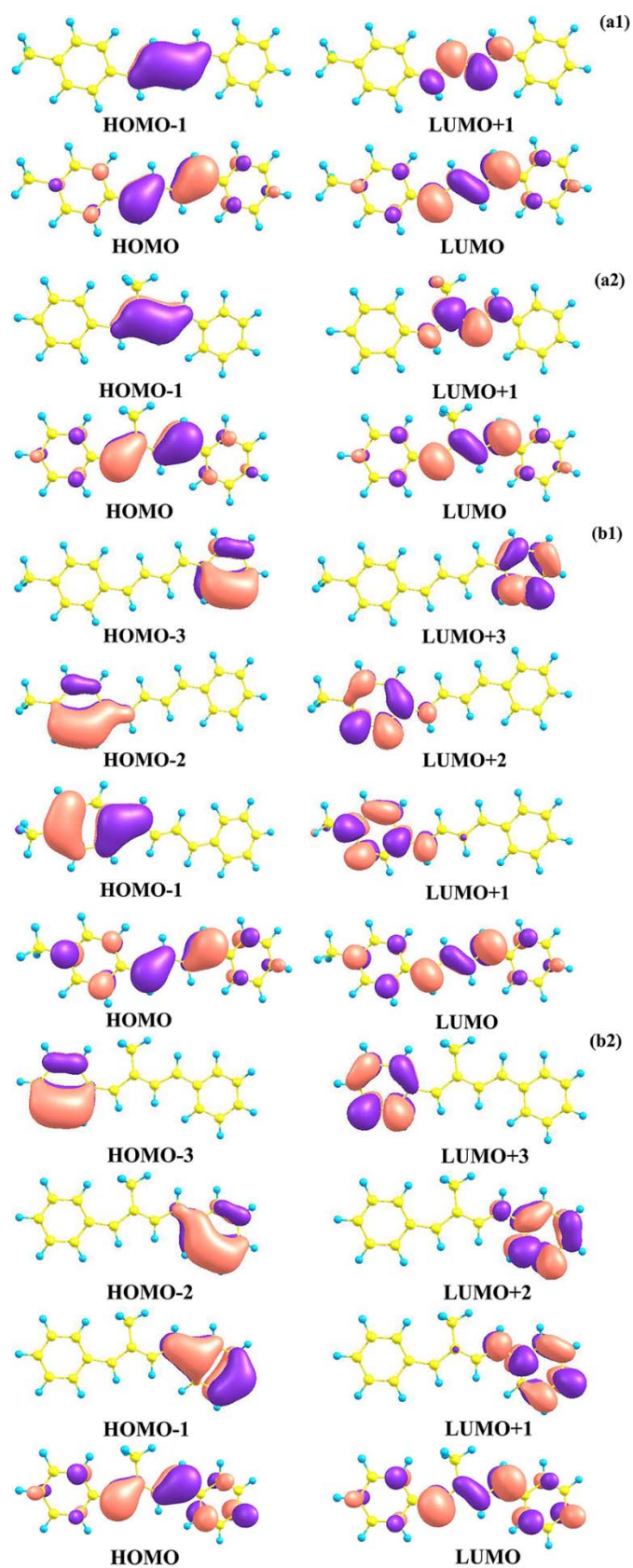


Figure S1. (a1) and (a2) are SA2-CASSCF(4,4)/6-31G and SA2-CASSCF(8,8)/6-31G computed HOMO and LUMO for tt-DPB-me1, (b1) and (b2) are the corresponding molecular orbitals for tt-DPB-me2.

S2. Cartesian coordinates of reactants tt-DPB-me1/tt-DPB-me2 optimized at SA2-CASSCF(4,4)/6-31G level.

tt-DPB-me1 (S₀)

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.38437309
C	1.19606276	0.00000000	2.11071635
C	2.39663919	0.00002978	1.39105617
C	2.39647191	0.00003319	0.00697141
C	1.19948024	0.00008625	-0.69694248
C	1.13321235	-0.00002396	3.57342814
C	2.16160220	0.00025288	4.43662380
C	1.99493424	0.00022017	5.88585482
C	3.02768632	0.00043339	6.75823619
C	2.95339267	-0.00027511	8.23817923
C	4.13511841	-0.00515345	8.97004402
C	1.75442925	0.00697873	8.94837304
C	4.12560085	-0.00395633	10.35836935
C	1.74520360	0.00812651	10.33253133
C	2.93077827	0.00004166	11.06396763
C	2.91041723	-0.02445207	12.57374102
H	-0.93171858	-0.00005274	-0.53266759
H	-0.93452161	-0.00001235	1.91375818
H	3.33498941	0.00001156	1.90950426
H	3.32975225	0.00001927	-0.52309658
H	1.20285250	0.00019686	-1.76982017
H	0.13627778	-0.00015981	3.98084784
H	3.17468819	0.00039384	4.07677628
H	0.98103295	-0.00024409	6.24455611
H	4.02782280	0.00036165	6.35859423
H	5.07657600	-0.00742357	8.45248425
H	0.81720236	0.01476793	8.42707537
H	5.05836827	-0.00483781	10.89111229
H	0.80410666	0.01707689	10.85092487
H	3.83574980	0.35870684	12.98579089
H	2.09801971	0.57551128	12.96640023
H	2.77928477	-1.03604233	12.94577143

tt-DPB-me1 (S₁)

C	-0.03214188	-0.11622713	-0.08536850
C	-0.07494482	-0.05257634	1.29412203
C	1.09876889	0.07842508	2.05553446
C	2.31709900	0.14240454	1.36484310
C	2.35542023	0.07818881	-0.01904196
C	1.18558604	-0.05114503	-0.75236605

C	1.00234465	0.14073492	3.49513947
C	2.15468586	0.27866657	4.43463234
C	1.97837943	0.33219171	5.84644342
C	3.13120994	0.47065968	6.78539243
C	3.03398481	0.53124479	8.22450042
C	4.20035937	0.66292043	8.99159380
C	1.81730615	0.46531135	8.91920543
C	4.15319429	0.72495532	10.37207600
C	1.77905137	0.52812528	10.30045822
C	2.94217617	0.65873683	11.05559003
C	2.88257988	0.72405302	12.56234425
H	-0.94443107	-0.21633866	-0.64188066
H	-1.02139673	-0.10379998	1.79923621
H	3.23811547	0.24232609	1.90291997
H	3.30122035	0.12937718	-0.52407767
H	1.21991200	-0.10047368	-1.82348195
H	0.02310547	0.08373798	3.93200447
H	3.14815951	0.33991712	4.03749643
H	0.98495402	0.27112865	6.24392636
H	4.11029631	0.52972897	6.34833447
H	5.15062237	0.71680247	8.49360136
H	0.89452828	0.36478631	8.38375914
H	5.06841395	0.82614959	10.92508510
H	0.82890308	0.47480201	10.80000362
H	2.45192335	-0.18084118	12.97888596
H	3.87009693	0.84544373	12.98928032
H	2.27344572	1.55752942	12.89664338

tt-DPB-me2 (S₀)

C	-0.25843133	0.00031783	0.26426297
C	0.02632522	0.00054602	1.61974866
C	1.34072881	0.00027258	2.09518054
C	2.36626793	-0.00027441	1.14898874
C	2.08380675	-0.00050234	-0.21062460
C	0.77403969	-0.00019387	-0.66036720
C	1.51001576	0.00054848	3.56893258
C	2.60967166	0.00086605	4.37198647
C	2.36056095	0.00106203	5.82650754
C	3.26314077	0.00073541	6.81920114
C	2.98013320	0.00106633	8.25904166
C	4.05729832	-0.00441134	9.15282345
C	1.68892416	0.00699639	8.79903658
C	3.85705783	-0.00408551	10.52266734
C	1.48856311	0.00723764	10.16868920
C	2.57005512	0.00125134	11.03940368

H	-1.27960372	0.00053550	-0.06569105
H	-0.78412781	0.00093826	2.32418435
H	3.38957533	-0.00055458	1.45018542
H	2.89325026	-0.00092880	-0.91551120
H	0.56141773	-0.00036072	-1.71206747
H	0.56351827	0.00051695	4.08095045
H	1.31758183	0.00124547	6.08559678
H	4.31023367	-0.00018923	6.58450470
H	5.05897783	-0.00886015	8.76530196
H	0.83397487	0.01195571	8.15256970
H	4.70234407	-0.00781498	11.18409746
H	0.48798998	0.01238571	10.55719854
H	2.41124040	0.00095475	12.10045924
C	4.03427806	0.00101335	3.86208599
H	4.23485905	-0.87661617	3.25904695
H	4.23419547	0.87793809	3.25781217
H	4.75174631	0.00188238	4.66665782
tt-DPB-me2 (S₁)			
C	-0.29464826	0.00150893	0.20128553
C	-0.03403878	0.00149791	1.55771909
C	1.28106369	0.00072985	2.06051511
C	2.32132512	-0.00003908	1.11950812
C	2.05565655	-0.00002996	-0.24121069
C	0.75203718	0.00074603	-0.71184283
C	1.43359723	0.00080654	3.50297663
C	2.65229116	0.00023827	4.39501974
C	2.37831612	-0.00055655	5.80275295
C	3.38510950	-0.00226358	6.90647173
C	3.05755299	-0.00009761	8.31519089
C	4.10217337	-0.00300859	9.25558971
C	1.74458918	0.00468438	8.80679240
C	3.84787125	-0.00124899	10.61344347
C	1.49372574	0.00643962	10.17001182
C	2.53895255	0.00348719	11.08095762
H	-1.31083371	0.00210698	-0.14425827
H	-0.85454972	0.00209073	2.25048958
H	3.34058824	-0.00067085	1.43520311
H	2.87500785	-0.00063893	-0.93484630
H	0.55421170	0.00074909	-1.76620476
H	0.50621760	0.00128332	4.04529011
H	1.34601943	-0.00046366	6.08923413
H	4.42544889	-0.00586422	6.65420916
H	5.11782289	-0.00671006	8.90623976
H	0.91314610	0.00716904	8.13161798

H	4.66623373	-0.00356304	11.30791630
H	0.47879751	0.01013764	10.51953614
H	2.33976396	0.00485962	12.13508969
C	4.05242645	0.00046698	3.84852756
H	4.24239888	-0.87592063	3.23672320
H	4.24176866	0.87645658	3.23598610
H	4.78956648	0.00109127	4.63692579

S3. Cartesian coordinates of photoproducts of tt-DPB-me1/tt-DPB-me2 optimized at SA2-CASSCF(4,4)/6-31G level.

cc-DPB-me1 (S₀)

C	0.12146604	0.12868765	-0.03501916
C	0.07611067	0.05699556	1.33781724
C	1.25114481	0.07971313	2.11411795
C	2.47608509	0.20085884	1.43057257
C	2.51992248	0.26079521	0.05500163
C	1.34648241	0.22505315	-0.69525674
C	1.14666638	0.01973327	3.58518123
C	2.01747286	-0.56324921	4.46329390
C	3.22233583	-1.35269146	4.13443759
C	4.26546106	-1.58041506	4.92948176
C	4.52381016	-1.03875240	6.28199131
C	5.13104098	-1.85477637	7.24028458
C	4.22409263	0.27159246	6.64550541
C	5.39932875	-1.38800900	8.51373528
C	4.49678024	0.73834829	7.92463488
C	5.08305178	-0.08055098	8.88117516
C	5.38082641	0.42156037	10.27342598
H	-0.79000170	0.10597657	-0.60125446
H	-0.87170861	-0.02468415	1.83570252
H	3.38662939	0.26698088	1.99119691
H	3.46714374	0.35101591	-0.44174270
H	1.38397701	0.27886284	-1.76581179
H	0.25153407	0.45386987	3.99236697
H	1.76525868	-0.51045809	5.50682475
H	3.22069206	-1.83771957	3.17522190
H	5.02111569	-2.25719327	4.56889707
H	5.38802658	-2.86571711	6.98294740
H	3.79429054	0.93831102	5.92430844
H	5.86087837	-2.04291245	9.23000565
H	4.25621197	1.75522580	8.17337867
H	4.84361796	-0.15295847	11.02105434
H	6.43871599	0.34364035	10.50174657
H	5.09421527	1.45944820	10.38630039

cc-DPB-me1 (S₁)

C	-5.22287949	-0.63431470	0.56644360
C	-4.36692740	-0.91143171	-0.48466393
C	-3.02399581	-0.51034187	-0.45297196
C	-2.57331630	0.17490281	0.68215494
C	-3.43216167	0.44862690	1.73451985
C	-4.75991776	0.04879075	1.68333904
C	-2.16013187	-0.83578499	-1.57943746
C	-0.76183916	-0.41576243	-1.75812726
C	-0.29412391	0.95255213	-1.62366921
C	1.12327379	1.34548725	-1.61087761
C	2.17373283	0.76142817	-0.78961017
C	3.49876052	1.18622153	-0.96395752
C	1.93378356	-0.20183524	0.19442995
C	4.52625704	0.66836735	-0.20009468
C	2.96979755	-0.71565721	0.95929903
C	4.28250839	-0.29630679	0.77722402
C	5.41317023	-0.86699695	1.59819508
H	-6.24729043	-0.95071560	0.51628026
H	-4.73454455	-1.44201465	-1.34313705
H	-1.55148722	0.49193280	0.74271164
H	-3.06320502	0.97326948	2.59521998
H	-5.42218779	0.26401849	2.49954328
H	-2.56514477	-1.50268647	-2.31926421
H	-0.05606421	-1.16127787	-2.07909769
H	-1.02901596	1.73772732	-1.60357699
H	1.39845662	2.19031753	-2.21650339
H	3.71659162	1.93003325	-1.70784044
H	0.93546544	-0.55083443	0.36857792
H	5.52992814	1.01706836	-0.36115015
H	2.74940470	-1.45211678	1.70962348
H	6.05553722	-1.50089565	0.99453959
H	6.03255437	-0.08086211	2.01601049
H	5.03927525	-1.46566976	2.41922164

cc-DPB-me2 (S₀)

C	-1.64769346	0.24557319	0.21494035
C	-1.36203583	0.09477914	1.56225106
C	-0.09833528	-0.31490770	1.99218517
C	0.88134409	-0.53963796	1.02642258
C	0.59691126	-0.38982766	-0.32480355
C	-0.66725974	-0.00075599	-0.73563062
C	0.15167890	-0.44948424	3.44415657
C	0.88757357	-1.37231758	4.08544780
C	1.47101868	-2.52605548	3.37525071

C	2.55900478	-3.25316573	3.65267991
C	3.62937906	-3.00796779	4.64431273
C	4.10557607	-4.08157940	5.43420191
C	4.24540838	-1.76937077	4.77900425
C	5.12432445	-3.89591467	6.33154720
C	5.29194527	-1.58536347	5.69637605
C	5.72567514	-2.63381327	6.46852568
H	-2.62875137	0.55532016	-0.09100735
H	-2.12645169	0.28932616	2.29143325
H	1.87257921	-0.81222284	1.32938573
H	1.36734516	-0.56659893	-1.05107718
H	-0.88416934	0.11878577	-1.77979919
H	-0.34402866	0.29204366	4.04587972
H	0.89206601	-2.85545037	2.53051623
H	2.71227331	-4.13404252	3.05195706
H	3.65159923	-5.04924600	5.32878836
H	3.92363752	-0.94805876	4.16807964
H	5.46900979	-4.71684738	6.93081730
H	5.75342023	-0.62042365	5.78436354
H	6.52635419	-2.49736711	7.16982146
C	1.00176259	-1.30800600	5.59585701
H	0.82860114	-2.28273664	6.03753344
H	1.97867673	-0.97846861	5.92269275
H	0.26972812	-0.61986136	5.99968254
cc-DPB-me2 (S₁)			
C	-0.94129591	0.73906607	0.14672389
C	-1.15379326	0.27756677	1.43365499
C	-0.18403647	-0.48072449	2.10554894
C	1.01170739	-0.75356158	1.42862804
C	1.22350134	-0.28651330	0.14147376
C	0.25063038	0.45971379	-0.50822511
C	-0.45696171	-0.92056795	3.46698785
C	0.39468827	-1.76359118	4.32941792
C	0.97293253	-3.00608794	3.83624558
C	2.09588046	-3.73745614	4.44274674
C	3.40745023	-3.19933660	4.77869352
C	4.34889617	-4.03292238	5.39858795
C	3.78684913	-1.88118662	4.49834202
C	5.60985472	-3.56900790	5.72854396
C	5.05163059	-1.41982798	4.82699205
C	5.96891505	-2.25783542	5.44448332
H	-1.70206217	1.31585647	-0.34385938
H	-2.07871012	0.50222532	1.93129160
H	1.77621733	-1.33245178	1.90578644

H	2.14957614	-0.50736850	-0.35437830
H	0.41772246	0.81682158	-1.50603437
H	-1.35528731	-0.53627287	3.91822788
H	0.52265458	-3.44216467	2.96103165
H	1.96870593	-4.79835397	4.56603267
H	4.08216437	-5.04943107	5.62047619
H	3.09436629	-1.21714662	4.02101224
H	6.31147275	-4.22723930	6.20448190
H	5.32029516	-0.40583198	4.59938343
H	6.94656796	-1.89676938	5.69917450
C	0.55290336	-1.33949385	5.76676257
H	0.95559904	-2.13549948	6.37789854
H	1.21561209	-0.48307686	5.86222780
H	-0.40647928	-1.04519401	6.18343133
ct-DPB-me1 (S₀)			
C	-0.00000000	-0.00000000	0.00000000
C	-0.00000000	-0.00000000	1.38642006
C	1.19411967	-0.00000000	2.10978313
C	2.39414642	0.01361601	1.39423499
C	2.39571774	0.01317067	0.00965606
C	1.19891016	0.00371491	-0.69480038
C	1.13298410	-0.00738375	3.57867649
C	2.14678389	-0.21415001	4.43031792
C	1.98345710	-0.16850969	5.87514535
C	2.90462483	-0.44067640	6.80673374
C	4.28695800	-0.92923474	6.60804689
C	5.33497730	-0.34781809	7.35905423
C	4.60128342	-1.96154119	5.75392662
C	6.62688874	-0.77536730	7.22312076
C	5.92896644	-2.40455988	5.61266720
C	6.95700932	-1.82319223	6.33362191
C	8.38866893	-2.28215542	6.19656405
H	-0.93160366	-0.00201546	-0.53280887
H	-0.93469239	-0.00437792	1.91554522
H	3.33060100	0.03688107	1.91600305
H	3.32930315	0.02643582	-0.51961980
H	1.20334283	0.00434388	-1.76774945
H	0.15177592	0.16138702	3.98957829
H	3.13342485	-0.40809620	4.05727297
H	1.01567149	0.15428716	6.21911534
H	2.62829532	-0.27760819	7.83417479
H	5.10568698	0.44902432	8.04202808
H	3.82452745	-2.45549323	5.20297935
H	7.40517297	-0.31219773	7.80157282

H	6.13970570	-3.21456306	4.93934960	
H	8.47030458	-3.11624278	5.51113101	
H	9.02169121	-1.48373687	5.82322390	
H	8.79290843	-2.59813821	7.15244903	ct-
DPB-me1 (S₁)				
C	-5.27882926	-1.25682399	0.39796188	
C	-3.99248500	-0.78107436	0.23242808	
C	-3.70452661	0.59138728	0.32434172	
C	-4.77021104	1.46252567	0.59052146	
C	-6.05920969	0.98097061	0.75595448	
C	-6.32254210	-0.37718622	0.66128158	
C	-2.34496580	1.04127920	0.14383368	
C	-1.88422575	2.46116451	0.20819012	
C	-0.50935467	2.75709091	-0.00774896	
C	0.24912218	4.05012690	-0.01786179	
C	-0.18682168	5.41240584	-0.23077150	
C	0.78257970	6.42761320	-0.16654407	
C	-1.50208933	5.81682830	-0.49917147	
C	0.45900613	7.75708070	-0.35712703	
C	-1.81851426	7.15113012	-0.68904710	
C	-0.85055951	8.14848424	-0.62270516	
C	-1.21465000	9.59815645	-0.83145920	
H	-5.47057497	-2.31014045	0.32245411	
H	-3.19340331	-1.46937495	0.02919506	
H	-4.59841719	2.51696933	0.66970550	
H	-6.85806578	1.66853256	0.95904810	
H	-7.32182743	-0.74565520	0.78997212	
H	-1.59804759	0.29573948	-0.05556762	
H	-2.59956286	3.22208809	0.41441627	
H	0.12234769	1.90817398	-0.20106273	
H	1.29841272	3.92676680	0.17101121	
H	1.80296360	6.16078189	0.03657591	
H	-2.28902880	5.09899542	-0.56350994	
H	1.23295230	8.49961221	-0.29889345	
H	-2.83922956	7.41937103	-0.89294267	
H	-1.65664212	9.75629095	-1.80981541	
H	-1.93414820	9.93390646	-0.09165796	
H	-0.34317494	10.23624661	-0.75655881	
ct-DPB-me2 (S₀)				
C	-2.90306122	-0.70291358	1.86703762	
C	-1.58258612	-0.34024192	1.83023311	
C	-0.57025778	-1.28822615	1.55551650	
C	-0.94471245	-2.58970103	1.29806361	
C	-2.29766404	-2.97062358	1.33421504	

C	-3.27536507	-2.03753148	1.61990678
C	0.83847812	-0.83096572	1.49864760
C	1.91812000	-1.37831209	2.07620577
C	1.83078932	-2.53171635	2.97747832
C	2.87631156	-3.20594504	3.47461776
C	2.82202186	-4.34373964	4.40634301
C	3.98547288	-5.08218568	4.63215832
C	1.66253987	-4.72344939	5.08764459
C	3.99165083	-6.16844605	5.49341184
C	1.66708972	-5.80855213	5.94776529
C	2.83082706	-6.53773129	6.15415776
H	-3.65655076	0.03033048	2.08318207
H	-1.30158732	0.67914256	2.01891358
H	-0.19900839	-3.31907749	1.04772309
H	-2.56488983	-3.98977299	1.12894680
H	-4.30995911	-2.32123438	1.64481762
H	0.98716495	0.06329206	0.91797274
H	0.83838740	-2.82810504	3.25334032
H	3.86982393	-2.92849135	3.17382730
H	4.89048591	-4.80466775	4.12451636
H	0.75541396	-4.16699292	4.95740743
H	4.89836755	-6.72177345	5.64680649
H	0.76512920	-6.08156440	6.46141638
H	2.83146897	-7.37682033	6.82286481
C	3.28122615	-0.76853624	1.83818725
H	3.75361665	-0.48497611	2.77267766
H	3.94342942	-1.46849118	1.33808817
H	3.20764401	0.11320241	1.21593358
ct-DPB-mel (S₁)			
C	-2.68353574	-1.70972710	1.87995533
C	-1.56073741	-0.90518049	1.98812873
C	-0.27371174	-1.45505954	1.99846931
C	-0.15545006	-2.84520358	1.88600503
C	-1.27875832	-3.64811452	1.78488562
C	-2.54925494	-3.08691077	1.78102515
C	0.88590320	-0.56613236	2.06619919
C	2.25678333	-0.93468997	2.40457216
C	2.52194098	-1.38768578	3.76242664
C	3.15725278	-2.71120652	3.75364789
C	2.61201168	-3.94207847	4.31366294
C	3.33616480	-5.13381909	4.17760164
C	1.40804424	-3.98278645	5.02632159
C	2.88189240	-6.31537124	4.73697648
C	0.95289247	-5.16725068	5.58160428

C	1.68636912	-6.33759431	5.44268114
H	-3.65940187	-1.26251169	1.87576324
H	-1.67712160	0.15958561	2.06857188
H	0.81680836	-3.29612785	1.87883756
H	-1.16182037	-4.71205356	1.70525453
H	-3.41740483	-3.71205487	1.69864272
H	0.68696977	0.48825316	1.95346553
H	1.82852763	-1.12278314	4.53788715
H	4.07682136	-2.80687147	3.20586660
H	4.26202873	-5.12565556	3.63298199
H	0.82087196	-3.09319770	5.13433394
H	3.45573007	-7.21498978	4.62211113
H	0.02498643	-5.17677623	6.12060904
H	1.33103478	-7.25273791	5.87559966
C	3.35648972	-0.72052321	1.40107790
H	4.33624491	-0.89074207	1.82851428
H	3.23877022	-1.35459270	0.52817900
H	3.32247516	0.30777260	1.04816530
tc-DPB-me1 (S₀)			
C	0.00000000	0.00000000	-0.00000000
C	0.00000000	-0.00000000	1.36965878
C	1.21008094	0.00000000	2.10072014
C	2.39874731	0.02796417	1.40252558
C	2.40731197	0.02961521	-0.00313827
C	1.21787860	0.01147896	-0.70559383
C	1.15139362	0.01701324	3.57950489
C	1.87077847	-0.71096758	4.44100102
C	2.94278950	-1.64568468	4.13496902
C	3.66013790	-2.25844621	5.08731452
C	4.77755604	-3.19305012	4.90052054
C	5.51747133	-3.59530361	6.01029317
C	5.14540001	-3.71519581	3.65686339
C	6.58591050	-4.47195687	5.88739452
C	6.20988387	-4.58820777	3.53753588
C	6.95275869	-4.98305452	4.65038398
C	8.11288119	-5.93779759	4.50235334
H	-0.92859840	-0.00702658	-0.53811063
H	-0.93073077	-0.00780384	1.90560485
H	3.32907516	0.07158240	1.93448526
H	3.34465794	0.05354759	-0.52546679
H	1.21790577	0.01628211	-1.77860458
H	0.42613528	0.69626819	3.99288177
H	1.61688879	-0.62879283	5.48413731
H	3.13423973	-1.84799911	3.09944651

H	3.41601807	-2.05063281	6.11584508	
H	5.25815191	-3.21703109	6.98183930	
H	4.59365127	-3.44847513	2.77668421	
H	7.13514416	-4.75817237	6.76488183	
H	6.46626284	-4.97370356	2.56768903	
H	7.79382004	-6.87915744	4.06750404	
H	8.88116324	-5.52471174	3.85704857	
H	8.56804637	-6.15413266	5.46054408	tc-
DPB-me1 (S₁)				
C	-0.03214188	-0.11622713	-0.08536850	
C	-0.07494482	-0.05257634	1.29412203	
C	1.09876889	0.07842508	2.05553446	
C	2.31709900	0.14240454	1.36484310	
C	2.35542023	0.07818881	-0.01904196	
C	1.18558604	-0.05114503	-0.75236605	
C	1.00234465	0.14073492	3.49513947	
C	2.15468586	0.27866657	4.43463234	
C	1.97837943	0.33219171	5.84644342	
C	3.13120994	0.47065968	6.78539243	
C	3.03398481	0.53124479	8.22450042	
C	4.20035937	0.66292043	8.99159380	
C	1.81730615	0.46531135	8.91920543	
C	4.15319429	0.72495532	10.37207600	
C	1.77905137	0.52812528	10.30045822	
C	2.94217617	0.65873683	11.05559003	
C	2.88257988	0.72405302	12.56234425	
H	-0.94443107	-0.21633866	-0.64188066	
H	-1.02139673	-0.10379998	1.79923621	
H	3.23811547	0.24232609	1.90291997	
H	3.30122035	0.12937718	-0.52407767	
H	1.21991200	-0.10047368	-1.82348195	
H	0.02310547	0.08373798	3.93200447	
H	3.14815951	0.33991712	4.03749643	
H	0.98495402	0.27112865	6.24392636	
H	4.11029631	0.52972897	6.34833447	
H	5.15062237	0.71680247	8.49360136	
H	0.89452828	0.36478631	8.38375914	
H	5.06841395	0.82614959	10.92508510	
H	0.82890308	0.47480201	10.80000362	
H	2.45192335	-0.18084118	12.97888596	
H	3.87009693	0.84544373	12.98928032	
H	2.27344572	1.55752942	12.89664338	
tc-DPB-me2 (S₀)				
C	-2.18281723	0.84474905	0.62239519	

C	-1.37745504	0.57028803	1.71633940
C	-0.30471846	-0.31792599	1.62040831
C	-0.08387095	-0.94609609	0.39659134
C	-0.89022058	-0.67498462	-0.70088130
C	-1.93870075	0.22390519	-0.59338695
C	0.50691938	-0.58251155	2.82744285
C	1.83463745	-0.77638637	2.93406300
C	2.36357397	-1.00228144	4.29058126
C	3.52119169	-1.52765627	4.70853622
C	4.59346793	-2.19908587	3.93823479
C	5.94038469	-1.80620659	4.12392250
C	4.33245074	-3.26911027	3.09069041
C	6.95620125	-2.44305575	3.45994932
C	5.37705548	-3.92125101	2.41624823
C	6.67494481	-3.51216440	2.59328976
H	-2.99695566	1.53731698	0.71964633
H	-1.57600953	1.05283520	2.65514165
H	0.70481406	-1.66510118	0.30299362
H	-0.70241009	-1.17305264	-1.63292594
H	-2.56222300	0.43177246	-1.44166568
H	-0.06590742	-0.59341776	3.73898747
H	1.70270246	-0.66271315	5.06968836
H	3.70143393	-1.49670657	5.77010486
H	6.15997679	-0.99192667	4.78891689
H	3.32249913	-3.60814927	2.96290801
H	7.97212160	-2.12767159	3.60290425
H	5.15301326	-4.74579749	1.76662462
H	7.47613612	-4.00873482	2.08037258
C	2.79206903	-0.65583402	1.76822341
H	3.73291234	-0.23663358	2.09853972
H	3.01562772	-1.60887831	1.30552851
H	2.38383859	-0.00572627	1.00684989

tc-DPB-me2 (S₁)

C	-1.85492090	-2.02243901	0.58885884
C	-1.21111293	-1.32860734	1.59817148
C	0.14647959	-0.99324511	1.50025694
C	0.83473115	-1.38864534	0.34695505
C	0.18948774	-2.08764118	-0.66059363
C	-1.15627460	-2.40675160	-0.54756529
C	0.75388606	-0.22874521	2.58615450
C	2.14227219	0.21828396	2.76794277
C	2.66274707	-0.47232591	3.94128136
C	3.98341077	-1.09533490	3.98298804
C	4.49561384	-2.11936807	3.07855701

C	5.87174534	-2.37383723	3.03217569
C	3.65802937	-2.90366672	2.27677412
C	6.38993622	-3.36497150	2.21509395
C	4.17834441	-3.89279118	1.45884670
C	5.54621940	-4.12909595	1.42132422
H	-2.89560468	-2.26467543	0.68862882
H	-1.76036367	-1.03706654	2.47383919
H	1.87322136	-1.15766467	0.23731697
H	0.73857902	-2.38157847	-1.53467147
H	-1.65216738	-2.94622239	-1.33121703
H	0.10414871	-0.03921457	3.42523945
H	2.05433624	-0.47005444	4.82995588
H	4.68885432	-0.67127343	4.67817527
H	6.53450760	-1.78726997	3.64068909
H	2.59830078	-2.74613023	2.30446453
H	7.44898119	-3.53918476	2.19700207
H	3.51455409	-4.48246018	0.85551337
H	5.94635734	-4.89653887	0.78716639
C	3.02389133	0.79639119	1.70062987
H	3.82169179	1.37126908	2.16139000
H	3.50209289	0.05531624	1.06564852
H	2.45314518	1.45972303	1.06067686

S4. Cartesian coordinates of conical intersections and global minimal of S₁ of tt-DPB-me1/tt-DPB-me2 optimized at SA2-CASSCF(4,4)/6-31G.

CI1-me1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.38364859
C	1.20049059	0.00000000	2.10505887
C	2.40079205	0.01087774	1.38609641
C	2.39788747	0.01295822	0.00011691
C	1.20002528	0.00605702	-0.69985522
C	1.17455352	-0.03083716	3.56228976
C	2.36760779	-0.10991467	4.39615357
C	2.72064494	1.06348614	5.15949188
C	2.51477428	0.55891639	6.51996373
C	1.33722325	0.80307507	7.35067652
C	1.19958997	0.13332940	8.57224867
C	0.33510761	1.70791981	6.99422059
C	0.11483764	0.36234536	9.39697673
C	-0.75454713	1.92838662	7.82277930
C	-0.88482092	1.26571589	9.03802877
C	-2.05746722	1.52512688	9.95214510
H	-0.93195808	-0.00317698	-0.53249156

H	-0.93257347	-0.00397082	1.91651773
H	3.33498928	0.02464155	1.91367210
H	3.32994511	0.02199607	-0.53219056
H	1.20023963	0.00806064	-1.77278276
H	0.24021901	0.17260445	4.05384713
H	2.93339874	-1.01568294	4.51394532
H	2.40616702	2.04024374	4.84658879
H	3.22675474	-0.15991305	6.88550719
H	1.95204145	-0.57222396	8.87227598
H	0.40316910	2.24409757	6.06815354
H	0.03912094	-0.16864711	10.32798225
H	-1.51049891	2.62823779	7.51843502
H	-1.77549204	2.17457008	10.77553679
H	-2.87138372	2.00341113	9.42180373
H	-2.43524212	0.60338778	10.37958556

CI2-me1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.38627124
C	1.20250392	0.00000000	2.09886622
C	2.40156259	-0.00870720	1.37924051
C	2.39964081	-0.01674124	-0.00490902
C	1.19749324	-0.00892723	-0.70077066
C	1.22261957	-0.01903281	3.56188261
C	0.05351753	0.25909325	4.39774642
C	0.09300945	1.70405647	4.33739278
C	0.33316341	2.46116574	5.56021784
C	-0.61995764	3.40742144	6.12530413
C	-0.32252470	4.07596042	7.32025803
C	-1.83629831	3.70325518	5.50614713
C	-1.19517829	5.00098100	7.85896621
C	-2.70865037	4.63226967	6.05325252
C	-2.40754569	5.29775269	7.23554861
C	-3.35993483	6.30084568	7.83993517
H	-0.93250095	-0.00041796	-0.53130042
H	-0.92830190	-0.01283009	1.92320006
H	3.33478061	-0.00805577	1.91097745
H	3.32999534	-0.02559348	-0.53975651
H	1.19532755	-0.01292400	-1.77373241
H	2.17775783	-0.15402449	4.03908640
H	-0.08697984	-0.23684540	5.33973183
H	-0.01135373	2.19094666	3.38629643
H	1.17852925	2.18514220	6.16293064
H	-2.10746587	3.20177518	4.59717378
H	0.60426255	3.86739706	7.82198765

H	-3.63628467	4.83794044	5.55218664
H	-0.93548723	5.49953247	8.77493226
H	-2.86018991	7.23972086	8.05289472
H	-4.18597528	6.51000494	7.17196437
H	-3.77582738	5.93480847	8.77357820

CI1-me2

C	-0.06807743	0.09145349	0.13612173
C	-0.00639709	-0.06335142	1.50988624
C	1.22302337	-0.08095798	2.18001071
C	2.38733201	0.07951543	1.42121979
C	2.32280190	0.23840094	0.04566991
C	1.09734956	0.24247227	-0.60450686
C	1.25721658	-0.26547875	3.62965975
C	2.47913616	-0.34309939	4.42056749
C	2.74298117	0.87812873	5.16016745
C	2.52210332	0.50934668	6.56074040
C	1.31948218	0.81062681	7.33452872
C	1.17685704	0.27475774	8.62082762
C	0.30399391	1.64380773	6.85345277
C	0.06848515	0.56370266	9.39656748
C	-0.80906349	1.92711760	7.63027926
C	-0.93252090	1.39127222	8.90355800
H	-1.02170739	0.09703113	-0.35653344
H	-0.91310428	-0.17731938	2.07427692
H	3.34264922	0.09166146	1.90954200
H	3.22869702	0.36210472	-0.51672991
H	1.04976929	0.36483112	-1.66934762
H	0.33028206	-0.15380997	4.16437334
H	2.42958258	1.82494062	4.76324365
H	3.21986916	-0.17601819	7.00586018
H	1.94406837	-0.36907562	9.00883287
H	0.38421456	2.07201535	5.87420619
H	-0.01776511	0.14353102	10.38036279
H	-1.57688756	2.56854819	7.24165720
H	-1.79366022	1.61446753	9.50331665
C	3.32427155	-1.58296152	4.50484171
H	2.77808597	-2.41887627	4.92909218
H	3.63238711	-1.88448240	3.50776117
H	4.21788015	-1.41509549	5.09323070

CI2-me2

C	-0.00000000	-0.00000000	0.00000000
C	-0.00000000	-0.00000000	1.38419636
C	1.19993942	-0.00000000	2.10243459
C	2.40123755	-0.00052815	1.38793438

C	2.39947022	-0.00829450	0.00163659
C	1.20111185	-0.00735650	-0.69762667
C	1.18187636	0.02538698	3.56527830
C	2.35140404	-0.21498997	4.41590815
C	2.35242627	1.08098364	5.06627737
C	2.14739418	1.19347190	6.50859586
C	3.20166372	0.99532163	7.49446910
C	2.91864774	1.14252873	8.85874440
C	4.50451444	0.63772932	7.12868505
C	3.89389907	0.93077994	9.81696109
C	5.47989582	0.42807468	8.09067908
C	5.18115609	0.57153018	9.43790778
C	3.58163551	-0.90061831	3.89539677
H	-0.93116395	0.00233363	-0.53353069
H	-0.93248478	-0.00107078	1.91719079
H	3.33040932	0.01634957	1.92329587
H	3.33130147	-0.00828717	-0.53087644
H	1.20179615	-0.00964287	-1.77059235
H	0.22585944	0.15635835	4.04528840
H	2.52537654	1.95474696	4.46657990
H	1.21661452	1.60347087	6.85502820
H	1.92622248	1.42019218	9.16164330
H	4.75506294	0.53143105	6.09110448
H	3.65302989	1.04681507	10.85649913
H	6.47289849	0.15515014	7.78792332
H	5.93822953	0.40889774	10.18056133
H	3.37460173	-1.95345575	3.73556549
H	3.92427393	-0.49615208	2.94454726
H	4.39780937	-0.81616141	4.60331651

S₁-me1 (min)

C	-6.39289431	1.84533215	2.37077165
C	-5.13289574	2.38464925	2.18467220
C	-4.34471756	2.02207697	1.08305313
C	-4.87186119	1.09135453	0.17878451
C	-6.13436613	0.55264271	0.36838392
C	-6.90205576	0.92607896	1.46209117
C	-3.02605542	2.60623869	0.91836096
C	-2.18116536	2.42339751	-0.27124646
C	-0.73785781	2.31104771	-0.24338783
C	0.06323578	2.17373050	0.98207513
C	1.37480626	2.76477518	1.17148847
C	2.12662473	2.44903632	2.31262839
C	1.94041842	3.65776288	0.25650139
C	3.37750610	2.99528975	2.52111274

C	3.19684604	4.20257044	0.47275165
C	3.93871898	3.88471454	1.60440602
C	5.30013470	4.48882733	1.84896115
H	-6.97778765	2.14016352	3.22107935
H	-4.74873776	3.09597431	2.89180731
H	-4.28925631	0.78145729	-0.66639991
H	-6.51716441	-0.16068229	-0.33650039
H	-7.87947818	0.50762248	1.60573745
H	-2.66429563	3.25010721	1.69952316
H	-2.65132623	2.45067302	-1.23711024
H	-0.23325090	2.25354329	-1.19029824
H	-0.32572238	1.55690167	1.77214618
H	1.72083560	1.76476472	3.03452943
H	1.39524724	3.93631344	-0.62407495
H	3.92817365	2.72881346	3.40463498
H	3.60222591	4.88602405	-0.25013117
H	6.02332178	3.73067692	2.12861252
H	5.67186782	4.99097353	0.96461110
H	5.26706097	5.21873919	2.65220214

S₁-me2 (min)

C	-6.27919030	1.95780240	2.40646276
C	-5.12928630	2.63001747	2.03185093
C	-4.29368526	2.13021287	1.02382185
C	-4.65342895	0.92136377	0.41544496
C	-5.80595769	0.25023725	0.79241378
C	-6.62595540	0.76408939	1.78662587
C	-3.08718538	2.85987407	0.65871168
C	-2.25610870	2.57486927	-0.52134609
C	-0.80749913	2.44642679	-0.42490558
C	-0.08030431	2.20518880	0.82880415
C	1.24589529	2.71316051	1.12728292
C	1.90307089	2.29411159	2.29316176
C	1.90843119	3.62343809	0.29388582
C	3.16652162	2.75990489	2.60877689
C	3.17387548	4.08883011	0.61344019
C	3.81053847	3.66017157	1.76924586
H	-6.90426338	2.36270235	3.17944551
H	-4.87057925	3.55281797	2.51670521
H	-4.02207658	0.50095471	-0.34296730
H	-6.06028283	-0.67613418	0.31338125
H	-7.51760425	0.24255026	2.07661794
H	-2.76840279	3.64705056	1.31901442
H	-0.24739237	2.49709241	-1.34105200
H	-0.55102041	1.57909010	1.56552020

H	1.41392434	1.59717121	2.94780639
H	1.42929105	3.97515705	-0.59844263
H	3.64917853	2.42302412	3.50631542
H	3.66143666	4.78803124	-0.03898212
H	4.79092639	4.02138345	2.01309900
C	-2.85605233	2.68080094	-1.90209550
H	-2.41179389	1.95782722	-2.57896375
H	-3.92549165	2.52337237	-1.88761078
H	-2.67867126	3.66919050	-2.32281286

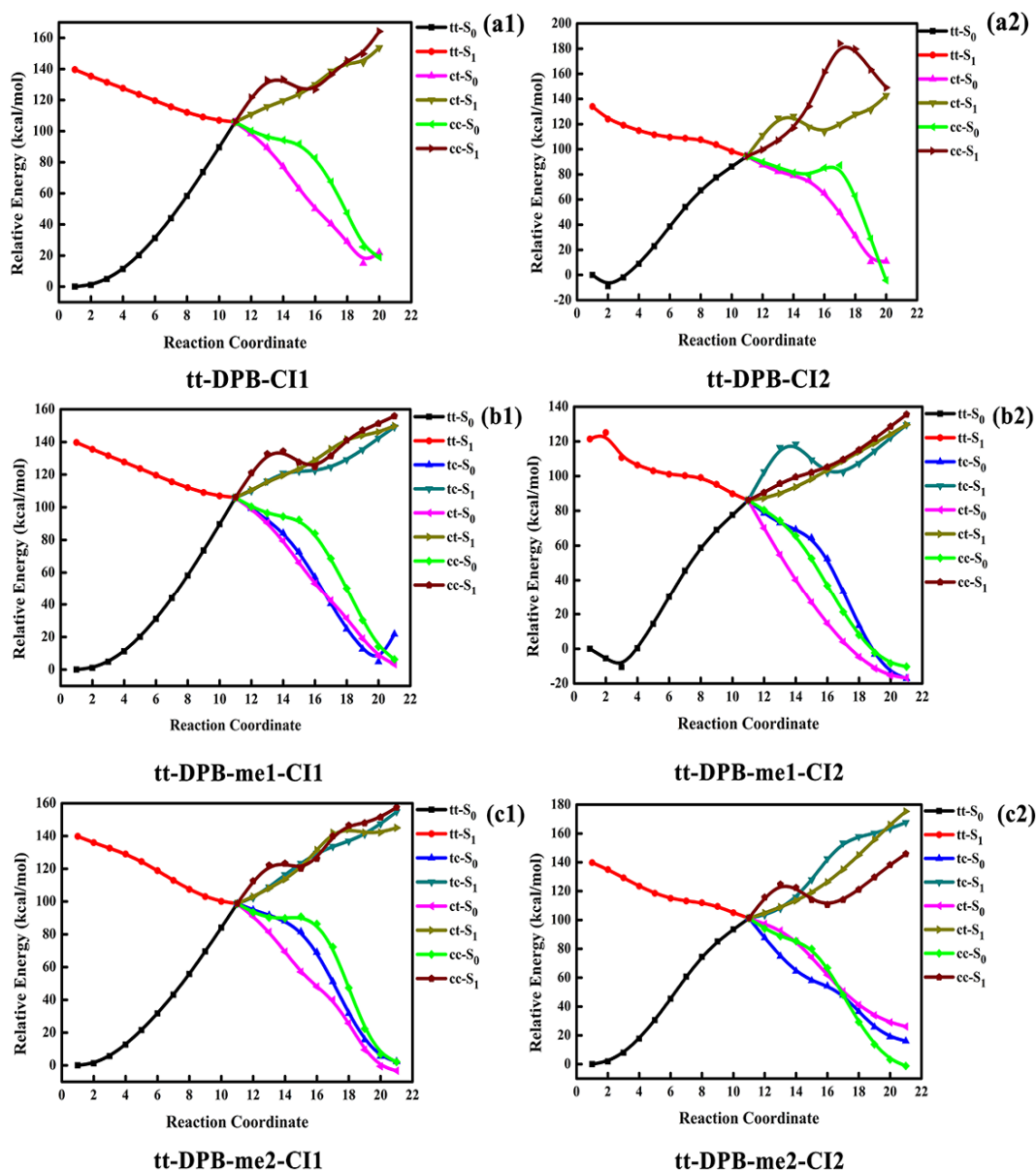


Figure S5. Relative energies with respect to the linear interpolation of internal coordinates (LIICs) from reactants to photoproducts at SA2-CASSCF(4,4)/6-31G level. (a1) and (a2) are the energy curves of photoisomerization of tt-DPB, (b1) and (b2) are curves for tt-DPB-me1, (c1) and (c2) are curves for tt-DPB-me2, respectively.

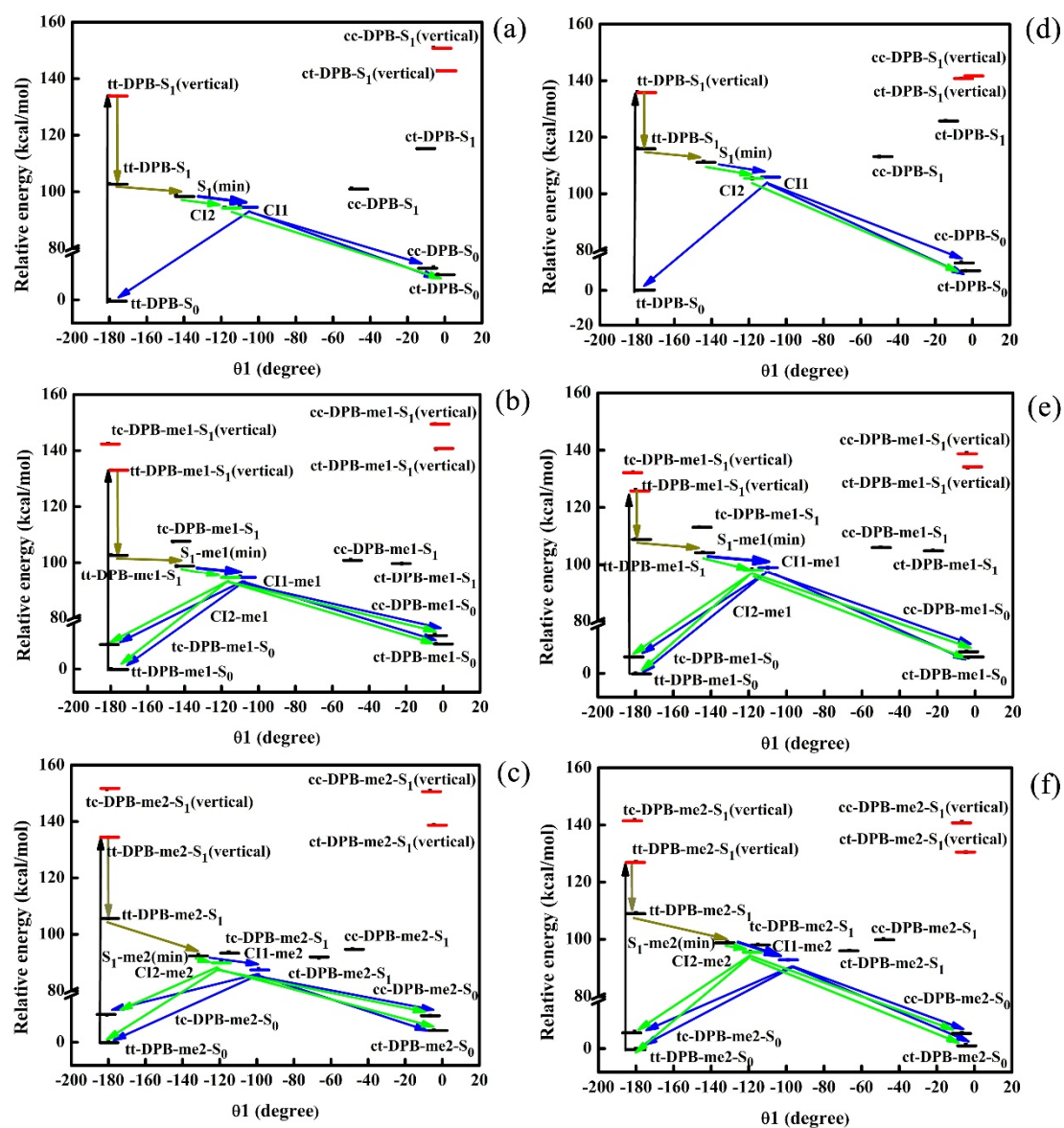


Figure S6. (a)-(c), (d)-(f) show the energies from SA2-CASSCF(4,4) and ICMRCI with 6-31G basis set calculations relative to the energy minima with respect to θ_1 .