

**Photoisomerization mechanisms from trans,
trans-1,4-diphenyl-1,3-butadiene: CASSCF on-the-fly
trajectory surface hopping dynamic simulations**

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S1. Molecular orbital informations of CAS(4,4) and CAS(10,10)

We have adopted SA2-CASSCF(4,4) method with 4 active electrons and 4 active orbitals for all geometry optimizations. This is because that corresponding to the $\pi\pi^*$ excitations displayed in Figure 1a clearly show excitations from HOMO-1 to central delocalized C8-C9 π orbital and from HOMO to C7-C8 and C9-C10 two π orbitals, relatively. LUMO+1 and LUMO are assigned to π^* orbitals with respect to HOMO-1 and HOMO, respectively. We have checked the other active spaces, for instance, CAS(10,10) with larger basis set 6-31G* shown in Figure 1b, HOMO is π orbital while LUMO is not classified as π^* orbital. In addition, electrons are partially localized in phenyl groups in HOMO-1 and LUMO+1 orbitals, which seem to have little effect on the photoisomerization of tt-DPB.

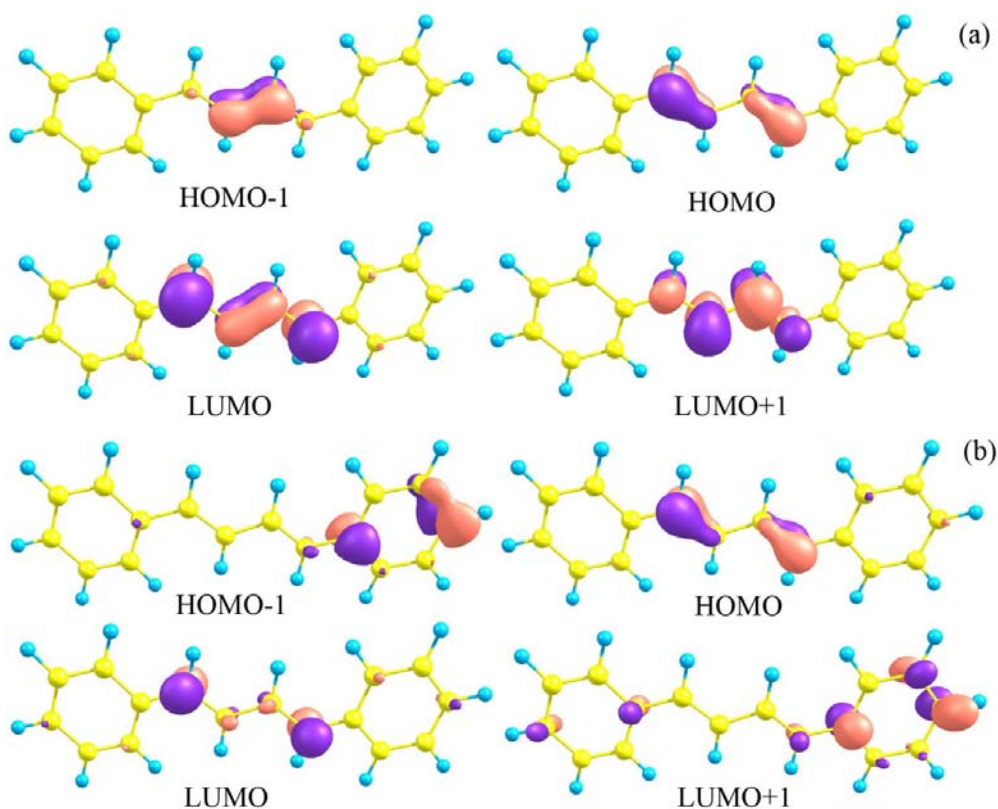


Figure S1. (a) SA2-CASSCF(4,4)/6-31G computed HOMO-1, HOMO, LUMO and LUMO+1 of tt-DPB, (b) SA2-CASSCF(10,10)/6-31G* computed HOMO-1, HOMO, LUMO and LUMO+1 of tt-DPB.

S2. Cartesian coordinates of saddle points optimized by CASSCF(4,4)

/6-31G

tt-DPB (S_0)

C	-3.32170517	-1.38530688	0.00007559
C	-1.93472396	-1.32609065	0.00072303
C	-1.26486752	-0.10564123	0.00019386
C	-2.02675350	1.06199531	-0.00105675
C	-3.41117247	1.00707292	-0.00171436
C	-4.06508157	-0.21745248	-0.00117624
C	0.21700255	-0.10990215	0.00098027
C	1.03903666	0.96359885	0.00101296
C	2.49438783	0.86651844	0.00181693
C	3.30704522	1.93523756	0.00184549
C	4.77129884	1.94272194	0.00261436
C	5.43937198	3.17228631	0.00231992
C	5.54805359	0.77860702	0.00364228
C	6.82219110	3.23880975	0.00299157
C	6.93059092	0.84522122	0.00432534
C	7.57620705	2.07456866	0.00401052
H	-3.81430789	-2.33873024	0.00054986
H	-1.36747044	-2.23815213	0.00167917
H	-1.54617558	2.02039476	-0.00152621
H	-3.97833930	1.91821272	-0.00264256
H	-5.13731942	-0.25736874	-0.00172982
H	0.66361019	-1.08976644	0.00160421
H	0.63239075	1.95914726	0.00043176
H	2.90239773	-0.12816695	0.00239169
H	2.85239671	2.91154969	0.00122629
H	4.86572540	4.08029689	0.00152780
H	5.07543958	-0.18367262	0.00392147
H	7.30931114	4.19515612	0.00272657
H	7.50477624	-0.06159131	0.00509982
H	8.64799831	2.12290938	0.00454317

tt-DPB (S₁)

C	-3.3859972520	-1.4086255889	-0.0001557682
C	-2.0044798248	-1.3916577752	0.0007442927
C	-1.2894820750	-0.1820385769	0.0004241576
C	-2.0285018474	1.0092678621	-0.0008726734
C	-3.4142384859	0.9876348805	-0.0017856180
C	-4.1013427057	-0.2168848050	-0.0014829182
C	0.1543342315	-0.2163127670	0.0014477000
C	1.0482187214	0.9796690566	0.0013758161
C	2.4672695141	0.8635318987	0.0017266909
C	3.3610946097	2.0595568847	0.0017118727
C	4.8048883308	2.0254453647	0.0025159490
C	5.5197544297	3.2351574607	0.0022744385
C	5.5440578404	0.8342185329	0.0035064437
C	6.9012695569	3.2522848024	0.0030085731
C	6.9297910113	0.8560188948	0.0042426138
C	7.6167535355	2.0606238942	0.0039615807
H	-3.9065191192	-2.3472554637	0.0001749484
H	-1.4617623868	-2.3184690986	0.0017209036
H	-1.5268369793	1.9559109358	-0.0011975464
H	-3.9568703414	1.9137787578	-0.0027326268
H	-5.1740650309	-0.2289739715	-0.0022666523
H	0.6301237215	-1.1789170221	0.0024421481
H	0.6118419702	1.9584442951	0.0010726731
H	2.9036878414	-0.1152253248	0.0020553204
H	2.8851977965	3.0221083011	0.0009293687
H	4.9769284658	4.1619088432	0.0014919869
H	5.0425058473	-0.1124876988	0.0037361186
H	7.4216856150	4.1909757126	0.0028342955
H	7.4725324332	-0.0700642505	0.0050299824
H	8.6894755463	2.0728389449	0.0044739188

ct-DPB (S₀)

C	0.1761719289	-0.6005293038	-4.2470358929
C	1.1591863595	-0.0888413774	-3.4371090186
C	1.4480102856	1.2957084713	-3.4365940220
C	0.7251542474	2.1146866229	-4.3000121479
C	-0.2775747062	1.5884188451	-5.1220213091
C	-0.5560091498	0.2421628826	-5.0949777024
C	2.5154694541	1.8751372294	-2.5892424390
C	2.7408229200	1.6514179716	-1.2888027520
C	1.9424936123	0.8435095565	-0.3828226559
C	2.2874580842	0.6321605850	0.8962133680
C	1.5468629899	-0.1400743051	1.9044682897
C	2.1428472030	-0.3675819789	3.1456132887
C	0.2681033242	-0.6569169040	1.6880073836
C	1.4923910772	-1.0918011441	4.1335457949
C	-0.3828927081	-1.3804531383	2.6728609577
C	0.2264891809	-1.6024709740	3.9007252572
H	-0.0272935202	-1.6544407770	-4.2396915858
H	1.7338569773	-0.7447319162	-2.8125174173
H	0.9356645396	3.1675138887	-4.3302967835
H	-0.8256690606	2.2418395782	-5.7735468449
H	-1.3221588459	-0.1671276309	-5.7249872077
H	3.1685841530	2.5662721348	-3.0926299428
H	3.5863027092	2.1465926841	-0.8426043089
H	1.0346931108	0.4257723569	-0.7720999729
H	3.2118452739	1.0590251010	1.2474739024
H	3.1246549973	0.0237308688	3.3369095795
H	-0.2285987227	-0.4902280989	0.7524439684
H	1.9737838019	-1.2543907559	5.0788749310
H	-1.3662875715	-1.7668026956	2.4843318544
H	-0.2810663351	-2.1618717367	4.6627960878

ct-DPB (S_I)

C	-0.0566515021	0.8345228547	0.0576532290
C	0.0058419608	0.6417783521	1.4108868761
C	1.0714748558	-0.0971579079	2.0194784084
C	2.0772087648	-0.5921798796	1.1376072736
C	2.0003334978	-0.3768450286	-0.2253030019
C	0.9399774586	0.3218070636	-0.7847992630
C	1.0781086682	-0.2418650043	3.4271499458
C	1.9240267385	-1.0177352097	4.2409119903
C	2.8100432679	-2.0507507684	3.9523415727
C	3.5859663086	-2.6090108672	4.9901632388
C	4.5933333624	-3.5756264523	4.8779411137
C	5.2542539506	-4.0592033243	6.0467105975
C	5.0047945068	-4.1167696112	3.6240520203
C	6.2381751413	-5.0094300465	5.9658520079
C	5.9984154143	-5.0698983150	3.5620571655
C	6.6216004735	-5.5271563309	4.7204655852
H	-0.8769536209	1.3842168744	-0.3635628192
H	-0.7642002613	1.0415046910	2.0435270271
H	2.9288362853	-1.0999390538	1.5334919868
H	2.7799406557	-0.7562057279	-0.8587042605
H	0.8840145861	0.4724790884	-1.8450239207
H	0.3341696132	0.3242448631	3.9562758837
H	1.8406147477	-0.7790629796	5.2910569935
H	2.8804747914	-2.4475465817	2.9655405879
H	3.3883286847	-2.2478227136	5.9865040311
H	4.9652454168	-3.6665946464	7.0040766478
H	4.5443602699	-3.7758933614	2.7197117588
H	6.7195972837	-5.3592390367	6.8586522327
H	6.2954227303	-5.4636368615	2.6088717090
H	7.3919075395	-6.2708995790	4.6614100024

cc-DPB (S_0)

C	3.9713349374	0.8856393185	-0.6362021646
C	2.6237202973	0.5228448821	-0.5033908241
C	2.2578887425	-0.2333345354	0.6170833634
C	3.2019616669	-0.6113593853	1.5582871894
C	4.5325750532	-0.2479003752	1.4075085763
C	4.9123042045	0.5043409109	0.3036994691
C	1.6696912837	0.9577692887	-1.5142074798
C	0.2469024651	0.5920656380	-1.5877797928
C	-0.2533272623	-0.7690303379	-1.5090047394
C	-1.6757269292	-1.1236182693	-1.3884526524
C	-2.6256670063	-0.5762239664	-0.4297810835
C	-3.9737662153	-0.9513195053	-0.5149487302
C	-2.2553230631	0.3023036211	0.5959567229
C	-4.9109048595	-0.4653385719	0.3793787991
C	-3.1955589266	0.7851808847	1.4919623200
C	-4.5267363789	0.4073951922	1.3889358575
H	4.2750850405	1.4690059921	-1.4853415092
H	1.2354339996	-0.5235227846	0.7538569755
H	2.8973256524	-1.1889075552	2.4102206996
H	5.2608732083	-0.5438574017	2.1376315845
H	5.9382167698	0.7934203223	0.1774149390
H	2.0263119959	1.6678389132	-2.2385692480
H	-0.4594231724	1.3792878415	-1.7834186339
H	0.4523324497	-1.5735738666	-1.6169034185
H	-2.0351990266	-1.9113667789	-2.0258758934
H	-4.2809294116	-1.6273480701	-1.2909993834
H	-1.2323472064	0.6057968863	0.6946656609
H	-5.9372897737	-0.7665578111	0.2909922611
H	-2.8874974499	1.4557446863	2.2714479906
H	-5.2520730850	0.7847338370	2.0836231445

cc-DPB (S_I)

C	4.0750569233	1.0022495575	-0.4258830817
C	2.7930653800	0.4720913368	-0.1612598559
C	2.6693221118	-0.6566038833	0.6725075263
C	3.7951864254	-1.2361364787	1.2219934877
C	5.0481980832	-0.6966854394	0.9466577226
C	5.1947521311	0.4221226615	0.1235854286
C	1.6388953060	1.0647373872	-0.7386372877
C	0.2858097808	0.6659861791	-0.5455413543
C	-0.3920782425	-0.2394002981	-1.4125859399
C	-1.6806239569	-0.6977053837	-1.4295279020
C	-2.8012338438	-0.3237350661	-0.5549195716
C	-3.8239986620	-1.2523316002	-0.3151538799
C	-2.9363404289	0.9387044027	0.0355255677
C	-4.9100084237	-0.9466657220	0.4870209855
C	-4.0235364210	1.2443295743	0.8414253854
C	-5.0159416909	0.3052934609	1.0790994917
H	4.1652100941	1.8629984499	-1.0617832786
H	1.6820961810	-1.0319446899	0.8525628232
H	3.7084310878	-2.0951364837	1.8560745985
H	5.9218784002	-1.1491105322	1.3753091738
H	6.1699309262	0.8192874763	-0.0738698662
H	1.9019853373	1.9269834215	-1.3663566421
H	-0.2073271725	1.1929941903	0.2544748824
H	0.2355257296	-0.6803965209	-2.1751556173
H	-1.9074607885	-1.4628781987	-2.1511703998
H	-3.7549285705	-2.2260126577	-0.7642652815
H	-2.2033704404	1.6933121255	-0.1641413369
H	-5.6731526708	-1.6846708672	0.6521548926
H	-4.0995221581	2.2242909681	1.2758384191
H	-5.8556324271	0.5441416303	1.7038109102

S_1 (min)

C	-3.0015384632	-0.3125468595	-2.1897949844
C	-1.6337414733	-0.3626578472	-1.9906453529
C	-1.0419678319	0.2388129345	-0.8709178225
C	-1.8795137915	0.8972327589	0.0381526284
C	-3.2493471983	0.9464313290	-0.1647826294
C	-3.8182382161	0.3422356641	-1.2765148294
C	0.3969032843	0.1676151959	-0.6922154103
C	1.1059690720	0.6173156145	0.5149580331
C	2.4114214156	1.2442723718	0.5131428587
C	3.1204373776	1.6874667036	-0.6963005979
C	4.5582696184	1.6051606197	-0.8788067506
C	5.1518690562	2.2025870309	-1.9997306999
C	5.3929387607	0.9400741052	0.0280282818
C	6.5187327000	2.1420140975	-2.2022188109
C	6.7618341628	0.8803982534	-0.1782637983
C	7.3326027503	1.4806964283	-1.2911353344
H	-3.4311464988	-0.7823905132	-3.0538041096
H	-1.0109257289	-0.8736413855	-2.7009678781
H	-1.4573514171	1.3807068428	0.8970585204
H	-3.8716432803	1.4594049381	0.5435638637
H	-4.8792267173	0.3816434499	-1.4304930985
H	0.9754221461	-0.2847493165	-1.4771903060
H	0.6665001779	0.4041532629	1.4719853623
H	2.8538805116	1.4572959461	1.4689140638
H	2.5435660406	2.1458168407	-1.4791516223
H	4.5312549348	2.7185563056	-2.7083438573
H	4.9691279856	0.4598625375	0.8879208018
H	6.9498600880	2.6089825566	-3.0670163098
H	7.3819755711	0.3629393722	0.5286726478
H	8.3929618533	1.4336804222	-1.4474552192

CII-1

C	-1.2110347326	0.2070588257	-3.9952550724
C	-1.0738885283	0.1524646222	-2.6195090235
C	0.0731779796	0.6503113755	-1.9887056282
C	1.0725392596	1.2147799944	-2.7888976189
C	0.9315808117	1.2702215246	-4.1665794324
C	-0.2080097283	0.7664735336	-4.7768558816
C	0.2074820614	0.5538068072	-0.5402946298
C	1.3451778244	1.0750197830	0.2076893846
C	1.1168580390	2.2280172598	1.0462366951
C	1.3378046193	1.6303340068	2.3658161035
C	0.2932271088	1.1892171494	3.2893551612
C	0.6516670877	0.5058186574	4.4573767132
C	-1.0633104259	1.4488924388	3.0691942105
C	-0.3059806595	0.1012235683	5.3706736733
C	-2.0218049363	1.0367691655	3.9819557779
C	-1.6495533405	0.3631709779	5.1361121032
H	-2.0973853797	-0.1832717837	-4.4579506034
H	-1.8546533754	-0.2813352186	-2.0229568201
H	1.9558071021	1.6160750483	-2.3305614128
H	1.7097842984	1.7081633976	-4.7621797801
H	-0.3150832013	0.8107699077	-5.8435004577
H	-0.6455215311	0.2219173654	0.0237049511
H	2.3062251161	0.5945875034	0.2085174936
H	0.3139112387	2.9092963401	0.8416357189
H	2.3508740856	1.3739291063	2.6206623741
H	1.6879314265	0.2950855667	4.6452870496
H	-1.3699064290	1.9753009261	2.1870768322
H	-0.0072855298	-0.4193017196	6.2603908863
H	-3.0575798724	1.2454321768	3.7932517840
H	-2.3932471529	0.0482207330	5.8423286184

CI1-2

C	-3.4069541238	-0.3819598456	-2.9941262465
C	-2.7336079772	0.1116963143	-1.8907746937
C	-1.3391729401	0.0211447173	-1.7967668426
C	-0.6467000787	-0.5929244544	-2.8460748717
C	-1.3239011349	-1.0885768893	-3.9490987789
C	-2.7050455458	-0.9850262164	-4.0302251964
C	-0.6500326122	0.5758165981	-0.6380483740
C	0.7913302056	0.4971099475	-0.4340887423
C	1.2664477949	-0.3648686406	0.6222991458
C	1.8357237525	0.6351516399	1.5295314521
C	1.1903107686	1.1650666676	2.7300327775
C	1.7913105232	2.2215849678	3.4245487811
C	-0.0010498665	0.6372000281	3.2380810999
C	1.2270580149	2.7281147844	4.5821048565
C	-0.5683922981	1.1505044027	4.3940689829
C	0.0416222446	2.1957354725	5.0721276211
H	-4.4757981463	-0.2991135410	-3.0466700807
H	-3.2844444581	0.5759625552	-1.0941079420
H	0.4207697925	-0.6879221979	-2.7936088726
H	-0.7737083819	-1.5567628719	-4.7429595115
H	-3.2271783528	-1.3697165171	-4.8849413345
H	-1.2480626213	0.9240075980	0.1847378322
H	1.4877608691	1.1014524867	-0.9856174202
H	0.6790638582	-1.1949717024	0.9637956853
H	2.7454552662	1.1154883798	1.2153967660
H	2.7059899140	2.6425814361	3.0508098869
H	-0.4831066121	-0.1760336332	2.7326021260
H	1.7070308655	3.5369843454	5.0989385603
H	-1.4835846380	0.7313269817	4.7664698289
H	-0.3979781879	2.5888135318	5.9683720082

CII-3

C	-0.2669425757	-0.3241451758	-5.6651337739
C	-0.6487136634	-1.0451937804	-4.5474556446
C	0.2285851591	-1.2299199494	-3.4722906835
C	1.5032840529	-0.6608724192	-3.5581461522
C	1.8815488444	0.0668658825	-4.6757290017
C	1.0011342650	0.2380426495	-5.7339864661
C	-0.2002282018	-2.0273139697	-2.3238609346
C	0.5424519416	-2.1927575186	-1.0715417356
C	-0.1594683267	-1.2463601852	-0.2370780848
C	0.5811043066	-0.0761291425	0.2185589985
C	0.9897905135	0.1404012393	1.6010641089
C	1.7336825534	1.2774279324	1.9406001443
C	0.6454443188	-0.7508898832	2.6231506590
C	2.1085174032	1.5187547181	3.2504544851
C	1.0240982880	-0.5078357380	3.9340551814
C	1.7551933112	0.6267472785	4.2551142257
H	-0.9557592932	-0.1975863141	-6.4783063465
H	-1.6329152424	-1.4727017093	-4.5013738775
H	2.2005166015	-0.7890956987	-2.7540093330
H	2.8643030986	0.4959390549	-4.7209714168
H	1.2977031150	0.7990531324	-6.5990405743
H	-1.2027273866	-2.4162978438	-2.3502490880
H	1.6112803688	-2.2756888334	-1.0337713771
H	-1.2056055547	-1.3842533890	-0.0346068797
H	0.9801479187	0.5805674969	-0.5333582893
H	2.0117408367	1.9722086117	1.1701540974
H	0.0874768214	-1.6369354987	2.3889357690
H	2.6759538067	2.3981787801	3.4885359863
H	0.7503654863	-1.2047854946	4.7031056514
H	2.0474939099	0.8126584650	5.2705609350

CII-4

C	-2.1532346909	-0.7844832304	-5.0336083886
C	-2.5706853213	-0.2994372293	-3.8066742208
C	-1.7743633559	0.5860557559	-3.0707774676
C	-0.5406843235	0.9646871767	-3.6100043140
C	-0.1212081367	0.4723955143	-4.8361225466
C	-0.9237418634	-0.4021151101	-5.5541441490
C	-2.2659577790	1.1031454254	-1.7942305550
C	-1.4990618404	1.9187133991	-0.8487565343
C	-1.1166365501	0.9040254983	0.1046017697
C	0.3017670939	0.5840673013	0.2104080647
C	1.1279655960	0.9211894644	1.3632129373
C	2.4927302673	0.6066736116	1.3615691585
C	0.5962696643	1.5413771034	2.4991329870
C	3.2907944650	0.8909322412	2.4555296078
C	1.3984366425	1.8269970197	3.5927022385
C	2.7473633789	1.5029051246	3.5780530151
H	-2.7817118896	-1.4606439546	-5.5809483727
H	-3.5212440003	-0.6040762026	-3.4101972960
H	0.0898861078	1.6459602644	-3.0738290296
H	0.8296145535	0.7750804136	-5.2314594234
H	-0.5979254284	-0.7790729912	-6.5042827992
H	-3.2244128089	0.7450844157	-1.4623093910
H	-0.8038202942	2.6739869034	-1.1600474960
H	-1.8727555125	0.3695059123	0.6495680998
H	0.7944153148	0.2207399897	-0.6734171511
H	2.9214668690	0.1338739568	0.4976923885
H	-0.4434090921	1.8056076537	2.5218570287
H	4.3337723749	0.6383865510	2.4337803050
H	0.9708308012	2.3038589594	4.4540285528
H	3.3664804422	1.7253019513	4.4256283286

CI2-1

C	-2.6627595195	-0.4124016118	-3.7025238505
C	-2.1209021649	-0.9203567158	-2.5352002886
C	-2.0174247801	-0.1300165449	-1.3833745038
C	-2.4891530453	1.1859864978	-1.4440969298
C	-3.0327009486	1.6918904781	-2.6143300723
C	-3.1213655151	0.8980500755	-3.7486772426
C	-1.4122319292	-0.6800742507	-0.1768660807
C	-1.2798563310	0.0595539761	1.0725583650
C	-1.9492298655	-0.4325278911	2.2571172623
C	-0.7641983586	-0.7210092915	3.0663515797
C	-0.0184864733	0.2938350447	3.8112969451
C	1.2434605258	-0.0045557372	4.3348875618
C	-0.5498096209	1.5659558545	4.0419317242
C	1.9508379962	0.9358281710	5.0636950720
C	0.1634963855	2.5091713079	4.7653196245
C	1.4144765877	2.1989314157	5.2790488754
H	-2.7295387087	-1.0355936925	-4.5738728847
H	-1.7691251514	-1.9348933615	-2.5089351388
H	-2.4378033223	1.8097980193	-0.5728548294
H	-3.3891618510	2.7040480109	-2.6390829744
H	-3.5433028881	1.2918144107	-4.6531446280
H	-1.2022150046	-1.7334174038	-0.1608619980
H	-0.6620675138	0.9343905624	1.1458747429
H	-2.7485548213	-1.1439093498	2.1679596462
H	-0.3534664716	-1.7154823295	3.0433060587
H	1.6669407752	-0.9771403415	4.1664433955
H	-1.5247155766	1.8042319274	3.6637851862
H	2.9169777690	0.6877375765	5.4595288718
H	-0.2595745037	3.4810362476	4.9335091555
H	1.9632765171	2.9290668751	5.8420420566

CI2-2

C	-0.3085831544	0.3772881135	-3.4165578513
C	0.2762407970	-0.6003848916	-2.6304195354
C	0.8220531559	-0.2862376163	-1.3817870876
C	0.7634789892	1.0404831938	-0.9456933433
C	0.1702794557	2.0168705523	-1.7308839098
C	-0.3669961666	1.6905643602	-2.9678116593
C	1.4605554770	-1.3269997788	-0.5755106214
C	1.8113576912	-1.1650918401	0.8362573264
C	0.5050750074	-1.4126480804	1.4070102066
C	0.3136016247	-2.5764734602	2.2640296862
C	-0.0809383824	-2.4945984041	3.6647932368
C	-0.2223905192	-3.6658834117	4.4198551248
C	-0.3485223936	-1.2720938623	4.2908622249
C	-0.6258460609	-3.6176263253	5.7424194827
C	-0.7512394773	-1.2265167272	5.6162172246
C	-0.8934251975	-2.3964822960	6.3481711088
H	-0.7201868548	0.1175004592	-4.3729846684
H	0.3120667635	-1.6151494748	-2.9805604271
H	1.1947155981	1.3015251530	0.0009346318
H	0.1342900528	3.0307971259	-1.3809472892
H	-0.8222030696	2.4484748940	-3.5757591117
H	1.5879231229	-2.2936756690	-1.0310640659
H	2.6797344709	-1.6407366120	1.2517280336
H	-0.3091925386	-0.7610000470	1.1526530912
H	0.6362187309	-3.5313814341	1.8925893352
H	-0.0175093720	-4.6147215893	3.9600162414
H	-0.2331144841	-0.3574570890	3.7422626265
H	-0.7301209579	-4.5282754248	6.3009192500
H	-0.9508356013	-0.2780151534	6.0773526671
H	-1.2045288706	-2.3584485239	7.3742855410

CI2-3

C	0.9205203653	0.1030030638	-6.3140891605
C	1.7039898472	-0.0452271926	-5.1833364293
C	1.1453796041	0.0390800695	-3.9017027567
C	-0.2273748614	0.2888807192	-3.7976007222
C	-1.0095978547	0.4388140515	-4.9318335200
C	-0.4419768915	0.3453686168	-6.1942678792
C	1.9880699865	-0.1535126222	-2.7280274246
C	1.5011529715	-0.0590968145	-1.3569023714
C	2.0467106011	0.9569492498	-0.4834450367
C	2.6779165239	0.0748092466	0.4993314857
C	1.9547087314	-0.5848938229	1.5868406725
C	2.5639535222	-1.6122319443	2.3140331475
C	0.6610773480	-0.1944639255	1.9442769696
C	1.9034297958	-2.2290823404	3.3624146010
C	-0.0018307704	-0.8185137877	2.9896432573
C	0.6152251295	-1.8363877376	3.7025030528
H	1.3696295551	0.0312448927	-7.2862393167
H	2.7567886228	-0.2317732833	-5.2857165089
H	-0.6800348219	0.3740047430	-2.8288192812
H	-2.0608154714	0.6299648956	-4.8295035342
H	-1.0498883260	0.4611072738	-7.0707740650
H	3.0503905434	-0.2000404909	-2.8803412629
H	0.7790753293	-0.7512784078	-0.9672562247
H	2.5736231428	1.7963882729	-0.8965865840
H	3.7142632385	-0.1842746752	0.3691676439
H	3.5575022454	-1.9251561700	2.0522226713
H	0.1871609587	0.6051095588	1.4092199220
H	2.3879582916	-3.0143562896	3.9101443618
H	-0.9946483792	-0.5059974675	3.2511145845
H	0.1016994254	-2.3158030493	4.5134703494

CI2-4

C	-2.70057563	-3.55263511	3.00169487
C	-1.95447768	-3.88847978	1.88526161
C	-0.74046355	-3.24939909	1.61428524
C	-0.29760156	-2.26157168	2.49851771
C	-1.04224728	-1.93209545	3.62043142
C	-2.24513522	-2.57446268	3.87647054
C	0.02227482	-3.59772921	0.41518177
C	1.41053812	-3.19474076	0.18563780
C	1.16469833	-1.84253798	-0.26660975
C	1.51962186	-1.47491612	-1.63208308
C	2.50143934	-0.45063437	-1.96582727
C	2.76588249	-0.14786758	-3.30763122
C	3.21778894	0.24020913	-0.98213044
C	3.71531729	0.79787573	-3.65176018
C	4.16736416	1.18805025	-1.32959027
C	4.42243433	1.47112530	-2.66360691
H	-3.63093798	-4.05253926	3.19190848
H	-2.30921782	-4.65046753	1.21655884
H	0.62178817	-1.74836024	2.29468208
H	-0.68770360	-1.17085884	4.28872445
H	-2.82193329	-2.31524653	4.74327661
H	-0.44311188	-4.26775083	-0.28674414
H	2.17387270	-3.38827604	0.91556691
H	0.76794311	-1.12349991	0.42472511
H	0.91209637	-1.86094802	-2.42944819
H	2.22391689	-0.66320205	-4.07862126
H	3.02510174	0.04100150	0.05422321
H	3.90324644	1.01168288	-4.68667378
H	4.70519250	1.70690192	-0.55908825
H	5.15746424	2.20592523	-2.92995817

S3. Cartesian coordinates of saddle points optimized by CASSCF(4,4)

/6-31G*

tt-DPB (S_0)

C	-3.3158123231	-1.3851332125	0.0001327762
C	-1.9304584338	-1.3206534333	0.0007429052
C	-1.2658759642	-0.1001332556	0.0001874621
C	-2.0317154784	1.0635237577	-0.0010879977
C	-3.4131719815	1.0031879499	-0.0017171887
C	-4.0624085524	-0.2222968106	-0.0012046522
C	0.2178696847	-0.1002958086	0.0009668084
C	1.0365542931	0.9708401097	0.0010119386
C	2.4940826759	0.8696807235	0.0018126498
C	3.3047705498	1.9333095215	0.0018526530
C	4.7728600648	1.9392057458	0.0026191056
C	5.4394326803	3.1664460779	0.0023414548
C	5.5493830223	0.7768453295	0.0036260634
C	6.8208865693	3.2337247701	0.0030050108
C	6.9291750966	0.8440901328	0.0042988112
C	7.5742752631	2.0721765415	0.0040154563
H	-3.8052978671	-2.3427735628	0.0007045737
H	-1.3597096716	-2.2330039504	0.0016836953
H	-1.5543792033	2.0258690310	-0.0016059613
H	-3.9844787339	1.9144766732	-0.0026115122
H	-5.1368708724	-0.2660601487	-0.0018477331
H	0.6682109644	-1.0795711539	0.0015791398
H	0.6305723480	1.9678078415	0.0004484809
H	2.9003532470	-0.1272220609	0.0023760146
H	2.8500108489	2.9109103888	0.0012474851
H	4.8654166162	4.0766305030	0.0015769601
H	5.0769604903	-0.1878001829	0.0038973780
H	7.3078754356	4.1927526347	0.0027367909
H	7.5043938108	-0.0648135188	0.0050470875
H	8.6484103908	2.1207423469	0.0045723340

tt-DPB (S_1)

C	-3.3799722675	-1.4062596236	-0.0002418544
C	-2.0011376322	-1.3864121233	0.0008836121
C	-1.2886715919	-0.1764571780	0.0006024808
C	-2.0305823723	1.0115257306	-0.0008713463
C	-3.4141694351	0.9859161678	-0.0019981174
C	-4.0981316828	-0.2179209094	-0.0017063726
C	0.1524206782	-0.2100628832	0.0018555612
C	1.0496808798	0.9809630296	0.0017689406
C	2.4657390421	0.8625349939	0.0016040386
C	3.3629996250	2.0535606190	0.0016125506
C	4.8040926523	2.0199545937	0.0024356439
C	5.5165583435	3.2299096533	0.0022866218
C	5.5460038580	0.8319715223	0.0033618220
C	6.8953933068	3.2497571890	0.0030294015
C	6.9295912596	0.8575810286	0.0041052311
C	7.6135532590	2.0614182617	0.0039349294
H	-3.8986540675	-2.3485938845	0.0000201716
H	-1.4563702564	-2.3143945061	0.0020049345
H	-1.5314529231	1.9619089779	-0.0011610753
H	-3.9594925390	1.9131738610	-0.0031087450
H	-5.1731387138	-0.2325551617	-0.0026042377
H	0.6271705375	-1.1736985548	0.0030402756
H	0.6165086363	1.9617927209	0.0018952254
H	2.8989110969	-0.1182947644	0.0014893356
H	2.8882497945	3.0171966939	0.0008551503
H	4.9717905946	4.1578922275	0.0015739545
H	5.0468747803	-0.1184119586	0.0035232693
H	7.4140748518	4.1920916252	0.0029020580
H	7.4749147292	-0.0696768563	0.0048173387
H	8.6885605259	2.0760524879	0.0044971914

ct-DPB (S₀)

C	0.1937695817	-0.6058616603	-4.2546536547
C	1.1717386866	-0.0937125658	-3.4460240485
C	1.4490850964	1.2924841847	-3.4365093118
C	0.7222289794	2.1100242113	-4.2911707014
C	-0.2803661741	1.5812196872	-5.1143867178
C	-0.5474684225	0.2375167952	-5.0956255365
C	2.5161459304	1.8748696064	-2.5853823340
C	2.7367255970	1.6551638718	-1.2890114688
C	1.9351880009	0.8426494048	-0.3826736675
C	2.2776571449	0.6402514417	0.8930552829
C	1.5388809261	-0.1353954076	1.9049933578
C	2.1465944122	-0.3817502719	3.1337727270
C	0.2523506855	-0.6339917192	1.6998877759
C	1.5016384004	-1.1089659494	4.1211883977
C	-0.3925103099	-1.3593617820	2.6836206982
C	0.2293291461	-1.6020397374	3.8998018610
H	-0.0016938861	-1.6636480434	-4.2538825610
H	1.7531399087	-0.7505224975	-2.8251822167
H	0.9249181263	3.1665884338	-4.3154948696
H	-0.8365000056	2.2367662477	-5.7607489057
H	-1.3139410571	-0.1743869645	-5.7275575542
H	3.1719640456	2.5675033000	-3.0865266554
H	3.5798613622	2.1548726117	-0.8404000163
H	1.0304361165	0.4174131379	-0.7746966131
H	3.2001938106	1.0747510954	1.2433845601
H	3.1369588670	-0.0030829850	3.3179485596
H	-0.2564222729	-0.4493682839	0.7718600448
H	1.9947368325	-1.2871001916	5.0603108558
H	-1.3851480564	-1.7322842085	2.5033964458
H	-0.2761958623	-2.1649157219	4.6639789263

ct-DPB (S_I)

C	-0.0714684500	0.8604633602	0.0736026516
C	0.0025560112	0.6556595260	1.4206322688
C	1.0700422142	-0.0933292930	2.0125847037
C	2.0643149885	-0.5839225904	1.1156866017
C	1.9755632025	-0.3546052465	-0.2407253680
C	0.9141653214	0.3523819025	-0.7839816972
C	1.0871421917	-0.2525005213	3.4164535768
C	1.9355282631	-1.0398173117	4.2159295981
C	2.8259861314	-2.0637457479	3.9210505453
C	3.5914997309	-2.6206765887	4.9647280481
C	4.6005267336	-3.5861856262	4.8704896109
C	5.2447156916	-4.0592049995	6.0513714954
C	5.0293437939	-4.1367417412	3.6275673506
C	6.2283937819	-5.0072014121	5.9921732685
C	6.0225084278	-5.0872903275	3.5877451660
C	6.6290191888	-5.5337838217	4.7574191742
H	-0.8956821097	1.4187119335	-0.3345191331
H	-0.7621441614	1.0535064009	2.0641552467
H	2.9211481534	-1.0965815870	1.4988474924
H	2.7496172509	-0.7319933772	-0.8859067026
H	0.8485991078	0.5135239634	-1.8442711482
H	0.3477096815	0.3077408326	3.9602846445
H	1.8483699020	-0.8149266603	5.2689991396
H	2.9106875784	-2.4512960330	2.9294098163
H	3.3830765334	-2.2574563119	5.9583652639
H	4.9422005069	-3.6590456880	7.0033593681
H	4.5811080915	-3.8034669696	2.7120782108
H	6.6981710117	-5.3498121247	6.8967238331
H	6.3337555235	-5.4895196791	2.6400383465
H	7.4022072974	-6.2787997604	4.7147052474

cc-DPB (S_0)

C	3.8175697184	1.0296325301	-0.7482858557
C	2.6576588802	0.5445463777	-0.1405284110
C	2.7855865826	-0.5063975034	0.7670581163
C	4.0224749925	-1.0721336989	1.0294782218
C	5.1590222719	-0.5937697883	0.4007379170
C	5.0519603358	0.4643107732	-0.4881301891
C	1.3672362570	1.1932064972	-0.4467794960
C	0.1528109135	0.6407251024	-0.5408007912
C	-0.1779358125	-0.7879494006	-0.4711875508
C	-1.4091987217	-1.3173888155	-0.3098546028
C	-2.6837629024	-0.5888033541	-0.0667539699
C	-3.8241573977	-0.9484857338	-0.7798670395
C	-2.7883334459	0.4214807559	0.8831819973
C	-5.0294200212	-0.3021103281	-0.5681355999
C	-3.9952399319	1.0693877229	1.0985290539
C	-5.1177414385	0.7121691991	0.3723900660
H	3.7447242605	1.8523244640	-1.4381267098
H	1.9197250286	-0.8667305770	1.2897637429
H	4.0975450082	-1.8799209112	1.7357358397
H	6.1188029706	-1.0318692380	0.6088472141
H	5.9296837769	0.8499940982	-0.9756289759
H	1.4343369048	2.2519330463	-0.6338875960
H	-0.6691055774	1.3035870242	-0.7459544707
H	0.6344289764	-1.4756899604	-0.6246967173
H	-1.4986941198	-2.3892859306	-0.3709369627
H	-3.7643876404	-1.7376381660	-1.5092908461
H	-1.9268668048	0.6947162010	1.4646485315
H	-5.8976563814	-0.5908636760	-1.1334150554
H	-4.0567662057	1.8477621215	1.8382703323
H	-6.0541124766	1.2133701681	0.5414098071

cc-DPB (S_I)

C	3.9600713953	0.9298454646	-0.5536131953
C	2.6167039962	0.5439746731	-0.4681157493
C	2.2448596107	-0.2907112507	0.5910392080
C	3.1781606033	-0.7195391934	1.5178991111
C	4.5044440543	-0.3322069902	1.4142683482
C	4.8899059685	0.4969308005	0.3715676792
C	1.6761492836	1.0367891191	-1.4630339872
C	0.2556374130	0.6829157032	-1.5827748190
C	-0.2552413591	-0.6720686892	-1.5871355969
C	-1.6757309493	-1.0268688867	-1.4699467736
C	-2.6164845629	-0.5409550351	-0.4718629764
C	-3.9597118325	-0.9267329919	-0.5599725793
C	-2.2451147916	0.2872976707	0.5925088801
C	-4.8897947353	-0.5001107907	0.3678785652
C	-3.1786426889	0.7097466432	1.5220560668
C	-4.5047546574	0.3224807412	1.4158998065
H	4.2710307858	1.5746011587	-1.3571271387
H	1.2229382363	-0.6037883553	0.6928686446
H	2.8666825312	-1.3588184896	2.3250250150
H	5.2268572415	-0.6697650168	2.1355446830
H	5.9158174105	0.8073107925	0.2808328226
H	2.0404249193	1.7976825986	-2.1307513583
H	-0.4448919224	1.4862352960	-1.7335026233
H	0.4451550506	-1.4742267470	-1.7445532056
H	-2.0401711701	-1.7824021376	-2.1436379904
H	-4.2702712367	-1.5668329967	-1.3673536170
H	-1.2234313026	0.6005449488	0.6961591513
H	-5.9154581942	-0.8107711477	0.2753883146
H	-2.8675654522	1.3443353104	2.3330299492
H	-5.2273856451	0.6552167981	2.1392053648

S_1 (min)

C	-3.0103250896	-0.3092556142	-2.1851217857
C	-1.6442332146	-0.3578336983	-1.9904557913
C	-1.0499750927	0.2426929828	-0.8731553087
C	-1.8854383209	0.8983633709	0.0375398637
C	-3.2537935476	0.9454821845	-0.1615225572
C	-3.8249198086	0.3425122477	-1.2703342632
C	0.3879420338	0.1734215992	-0.7009330079
C	1.1033741616	0.6188976869	0.5025891449
C	2.4156603686	1.2227409185	0.5015685200
C	3.1287127005	1.6693309783	-0.7028541419
C	4.5660978846	1.5978642698	-0.8789204158
C	5.1584445021	2.1985029418	-1.9971727053
C	5.4027816243	0.9396264498	0.0288031842
C	6.5239417937	2.1477734409	-2.1954686391
C	6.7705111102	0.8902705808	-0.1739396956
C	7.3397706385	1.4934165860	-1.2836388217
H	-3.4420672378	-0.7798598356	-3.0506716557
H	-1.0224078140	-0.8677598065	-2.7055286199
H	-1.4620244880	1.3827932934	0.8979793256
H	-3.8756313615	1.4577828440	0.5512573466
H	-4.8887772430	0.3804345483	-1.4214235179
H	0.9624451132	-0.2855784853	-1.4860533742
H	0.6652232639	0.4091540517	1.4616469828
H	2.8552327930	1.4324593016	1.4600142861
H	2.5530800816	2.1311735362	-1.4855073853
H	4.5356317812	2.7103207875	-2.7100320970
H	4.9808086429	0.4554665546	0.8901105226
H	6.9542271272	2.6184928485	-3.0616855846
H	7.3933819426	0.3764850248	0.5368756695
H	8.4032125447	1.4541980711	-1.4373178379

CII-1

C	-1.1691836081	0.2125482220	-4.0585119303
C	-1.0763935160	0.1727448990	-2.6808788433
C	0.0599404236	0.6521330647	-2.0209125915
C	1.0947834540	1.1826148276	-2.7955219684
C	0.9979904289	1.2232208157	-4.1755122445
C	-0.1314648805	0.7384814213	-4.8144985008
C	0.1473891851	0.5668089312	-0.5683578179
C	1.2583436824	1.0951837450	0.2120049139
C	1.0251409775	2.2419103199	1.0317991706
C	1.2837365477	1.6550056136	2.3458094342
C	0.2722290828	1.2033060457	3.3004685462
C	0.6751068039	0.5237914281	4.4540726533
C	-1.0919512743	1.4516792995	3.1288600630
C	-0.2456164665	0.1109551640	5.3980568948
C	-2.0129435973	1.0303877219	4.0719996582
C	-1.5968609414	0.3602657716	5.2109113584
H	-2.0519161644	-0.1639419058	-4.5444300839
H	-1.8870030338	-0.2367196900	-2.1035007689
H	1.9747222219	1.5717375298	-2.3157238900
H	1.8060345647	1.6371559344	-4.7524099877
H	-0.2047939126	0.7722564170	-5.8867091312
H	-0.7399559729	0.2871126121	-0.0287232535
H	2.2225864314	0.6173202859	0.2276529974
H	0.1668136709	2.8624970120	0.8505865578
H	2.3021473070	1.3832656387	2.5631562970
H	1.7207809689	0.3213553500	4.6077877373
H	-1.4362070410	1.9759928298	2.2570361799
H	0.0896889369	-0.4086045718	6.2781020940
H	-3.0585524329	1.2304645452	3.9180658755
H	-2.3147886099	0.0375197615	5.9433397503

CII-2

C	4.32322156	-2.06727634	3.58613936
C	3.58739527	-1.81852266	2.44388347
C	3.84883892	-0.69845299	1.64782165
C	4.88367341	0.15639236	2.03600680
C	5.62067124	-0.09667347	3.17976498
C	5.34506295	-1.20688999	3.96104878
C	3.03498431	-0.44006771	0.46641546
C	3.26973764	0.66117269	-0.45799045
C	2.32939842	1.73661286	-0.48286083
C	1.84274097	1.59913420	-1.85479958
C	0.59199631	0.96146906	-2.26415865
C	0.18904968	1.04046452	-3.60066407
C	-0.21207814	0.23915223	-1.37880592
C	-0.96774298	0.42244387	-4.03558083
C	-1.37427274	-0.37247307	-1.81520477
C	-1.75814705	-0.28651504	-3.14357212
H	4.10274159	-2.93383143	4.18409329
H	2.79719850	-2.49225785	2.16142206
H	5.11736602	1.01768626	1.43644405
H	6.41387481	0.57394110	3.45939472
H	5.91988332	-1.40199401	4.84855624
H	2.35865114	-1.21230990	0.14542890
H	4.15010468	0.70997050	-1.07518983
H	2.60033979	2.69268379	-0.07394671
H	2.36739824	2.15432166	-2.61291855
H	0.79260093	1.59133941	-4.30088254
H	0.07010070	0.15325535	-0.34609569
H	-1.25535021	0.49651951	-5.06933440
H	-1.97923204	-0.92150718	-1.11548342
H	-2.65984877	-0.76592727	-3.47992667

CII-3

C	4.64157285	4.67099305	-1.18037998
C	3.40154352	4.36166581	-0.65510574
C	2.32969254	4.02026032	-1.48543041
C	2.54920847	4.00266372	-2.86514676
C	3.79001167	4.32038033	-3.38924775
C	4.84235618	4.65439528	-2.55240437
C	1.04460799	3.66394278	-0.88529828
C	-0.20584147	3.42924369	-1.60606573
C	-0.20435718	2.00056937	-1.61968817
C	-0.13649666	1.32219051	-2.90716067
C	-1.24190700	0.57352212	-3.49203366
C	-1.06485812	-0.09776986	-4.70639578
C	-2.50041915	0.51721996	-2.88760341
C	-2.10588599	-0.78761084	-5.29665004
C	-3.54098804	-0.17646624	-3.48039972
C	-3.35128168	-0.83064937	-4.68662515
H	5.45074350	4.92888265	-0.52038967
H	3.25609859	4.38187368	0.41095108
H	1.74970516	3.73939559	-3.53221493
H	3.93564890	4.30246832	-4.45484566
H	5.80604033	4.89708889	-2.96282937
H	0.97936157	3.73975196	0.18625862
H	-1.10690176	3.96017774	-1.35925092
H	-0.30662558	1.45966707	-0.69482349
H	0.83797531	1.20219874	-3.34627081
H	-0.10254922	-0.07078451	-5.18739602
H	-2.66288423	1.01133516	-1.94666633
H	-1.94700638	-1.29438402	-6.23206317
H	-4.50148099	-0.20779019	-2.99709976
H	-4.16114441	-1.36941922	-5.14487872

CI1-4

C	-2.2151052709	-0.7931127478	-5.0252788979
C	-2.5888024286	-0.2972358012	-3.7908861007
C	-1.7669297614	0.5902399006	-3.0896204624
C	-0.5531077365	0.9605209845	-3.6741220510
C	-0.1775278453	0.4564798659	-4.9070456427
C	-1.0046172328	-0.4203846916	-5.5899317845
C	-2.2182755908	1.1193722199	-1.8032033493
C	-1.4254452049	1.9314210767	-0.8811351010
C	-1.0466146168	0.9210079467	0.0552680086
C	0.3690807280	0.6090558238	0.1997703829
C	1.1579571975	0.9349563340	1.3812844840
C	2.5275234654	0.6515173399	1.4058845570
C	0.5853930521	1.5094857886	2.5190212241
C	3.2902420565	0.9216960081	2.5253860214
C	1.3525704127	1.7809192483	3.6384650177
C	2.7064905439	1.4881647357	3.6493702081
H	-2.8657622447	-1.4733516247	-5.5456364372
H	-3.5285237129	-0.5966538205	-3.3604067276
H	0.1003150471	1.6448343522	-3.1659395294
H	0.7625863229	0.7536275060	-5.3370672318
H	-0.7113351644	-0.8071555436	-6.5493221821
H	-3.1567388656	0.7437126661	-1.4338730087
H	-0.6928320502	2.6332616498	-1.2352762210
H	-1.8074418914	0.3788212908	0.5896688773
H	0.8966870907	0.3072143983	-0.6875484065
H	2.9898921297	0.2124422903	0.5389611622
H	-0.4620445816	1.7518701053	2.5246404528
H	4.3412881518	0.6928908462	2.5222527159
H	0.8915073655	2.2245536289	4.5031708295
H	3.3005113192	1.7005511119	4.5201045395

CI2-1

C	-2.6719223328	-0.3772136889	-3.6833101962
C	-2.1524286974	-0.9150135124	-2.5219185419
C	-2.0198471088	-0.1407577646	-1.3643034698
C	-2.4392376072	1.1913466135	-1.4145106922
C	-2.9604795395	1.7270894077	-2.5791659502
C	-3.0786680945	0.9486660791	-3.7189321306
C	-1.4340547657	-0.7249470978	-0.1645484232
C	-1.2949071886	-0.0137767742	1.0997036525
C	-1.9529294003	-0.5038580579	2.2723087362
C	-0.7666265226	-0.7522618543	3.0880555685
C	-0.0285157907	0.2868845237	3.8049036378
C	1.2417522890	0.0172914489	4.3200875724
C	-0.5749400517	1.5539533896	4.0174322258
C	1.9417681424	0.9797858460	5.0221116078
C	0.1316527160	2.5193585488	4.7139040819
C	1.3905345886	2.2376344474	5.2189282170
H	-2.7621715958	-0.9917176050	-4.5615413862
H	-1.8398713279	-1.9446658403	-2.5050290390
H	-2.3657228644	1.8080496210	-0.5371991707
H	-3.2780413273	2.7546977773	-2.5948452203
H	-3.4849684957	1.3672417173	-4.6221792106
H	-1.2867624784	-1.7895984969	-0.1535105666
H	-0.6759076478	0.8618473724	1.1757480584
H	-2.6974885938	-1.2736285227	2.1675437401
H	-0.3274944987	-1.7356181861	3.0665530775
H	1.6788853228	-0.9538921738	4.1658814061
H	-1.5585637432	1.7727872941	3.6445518104
H	2.9176958119	0.7522907610	5.4126367795
H	-0.3048867575	3.4901037674	4.8685819406
H	1.9359697509	2.9878688891	5.7628965865

CI2-2

C	0.8874798169	0.1060956654	-6.2901370727
C	1.6948714678	-0.0149929082	-5.1759590855
C	1.1585581111	0.0499122525	-3.8855024874
C	-0.2181521864	0.2523968153	-3.7567073129
C	-1.0244253130	0.3745588693	-4.8748151553
C	-0.4785016293	0.3010365503	-6.1458571268
C	2.0295752443	-0.1178526241	-2.7291484449
C	1.5729219902	-0.0227352766	-1.3485798669
C	2.1177909252	0.9775294992	-0.4820511691
C	2.7117565019	0.0887086077	0.5136569598
C	1.9589903531	-0.5755531325	1.5769799457
C	2.5399981361	-1.6186126418	2.3023439026
C	0.6646698613	-0.1745870461	1.9134144568
C	1.8519230023	-2.2397870911	3.3270151779
C	-0.0258829274	-0.8038451176	2.9349572690
C	0.5631215913	-1.8369243477	3.6456000716
H	1.3225248490	0.0506293867	-7.2723395465
H	2.7533146970	-0.1658169342	-5.2990001171
H	-0.6585494973	0.3233595954	-2.7787368798
H	-2.0816025530	0.5308601947	-4.7521626782
H	-1.1071450884	0.3973978931	-7.0128412128
H	3.0902830110	-0.1057332057	-2.9025568435
H	0.8522874480	-0.7172248616	-0.9561547838
H	2.7083996360	1.7694342202	-0.9085546815
H	3.7424285959	-0.1998494528	0.3923356720
H	3.5368556224	-1.9412464354	2.0568889670
H	0.2092851346	0.6385113481	1.3786820642
H	2.3171229931	-3.0397965642	3.8749898131
H	-1.0221722926	-0.4816626063	3.1808261506
H	0.0263309019	-2.3215760195	4.4413546555

CI2-3

C	-0.3419821493	0.3992667007	-3.3703964233
C	0.2604962123	-0.5874842170	-2.6136941662
C	0.8292916052	-0.2928417091	-1.3721897524
C	0.7749968012	1.0248568096	-0.9140038549
C	0.1635660581	2.0101907692	-1.6700613772
C	-0.3963800278	1.7031137056	-2.8994375784
C	1.4870197671	-1.3440375055	-0.5970225395
C	1.8535718532	-1.2195560265	0.8117377282
C	0.5626249253	-1.4611824188	1.3802862806
C	0.3562726558	-2.6052387498	2.2589274077
C	-0.0647566303	-2.4950315372	3.6497651437
C	-0.1948391743	-3.6482521467	4.4309716713
C	-0.3730844140	-1.2657021949	4.2384872326
C	-0.6254021707	-3.5764113924	5.7414630655
C	-0.8030471873	-1.1966915797	5.5520721981
C	-0.9331168778	-2.3489131406	6.3099945390
H	-0.7724918058	0.1528818862	-4.3246785796
H	0.2928081823	-1.5977880293	-2.9828885815
H	1.2238708132	1.2732609239	0.0300570529
H	0.1312470285	3.0201886182	-1.3016893752
H	-0.8674499380	2.4708716957	-3.4867137715
H	1.5891848034	-2.3067600492	-1.0692681595
H	2.6996302459	-1.7651616142	1.1917235399
H	-0.2515844556	-0.8078788185	1.1235403554
H	0.7280559249	-3.5579778359	1.9282245500
H	0.0412408068	-4.6055089216	3.9995941489
H	-0.2678086630	-0.3596285046	3.6698483406
H	-0.7196636959	-4.4771866492	6.3217809546
H	-1.0338875440	-0.2395394316	5.9852493467
H	-1.2664251131	-2.2922524961	7.3306980725

CI2-4

C	4.51908579	0.22787501	5.32321455
C	3.31375257	0.67347189	4.81540445
C	2.72772965	0.05283520	3.70948273
C	3.39064724	-1.02970208	3.12822122
C	4.59402409	-1.47964743	3.64376644
C	5.16318327	-0.85429209	4.74112249
C	1.46531643	0.55478765	3.16831754
C	0.63045257	-0.17515820	2.21719034
C	1.37588664	0.11179265	1.02968792
C	0.75226733	0.84958427	-0.06128360
C	0.57240630	0.31421467	-1.40473821
C	0.00189858	1.11293733	-2.40157618
C	0.92984664	-0.99506630	-1.73779989
C	-0.21220970	0.62006595	-3.67404179
C	0.71526596	-1.48574503	-3.01385844
C	0.14289320	-0.68385101	-3.98768303
H	4.95517926	0.72023654	6.17415584
H	2.81700660	1.50931896	5.27656115
H	2.96388904	-1.50723352	2.26550189
H	5.09109608	-2.31482019	3.18306695
H	6.09989043	-1.20312953	5.13753726
H	1.07666820	1.46239430	3.59900425
H	0.35422742	-1.19431427	2.42433776
H	2.38402761	-0.25180915	0.94538797
H	0.60480511	1.90555062	0.07469033
H	-0.27724596	2.12587077	-2.16875642
H	1.38532862	-1.62896783	-0.99880887
H	-0.65436570	1.25259598	-4.42334412
H	0.99915581	-2.49641492	-3.24842798
H	-0.02174212	-1.06737404	-4.97861482

S4. Cartesian coordinates of some saddle points at SA2-CASSCF

(10,10)/6-31G*

tt-DPB(S_0)

C	-3.2990121440	-1.3882187779	0.0001275063
C	-1.9213304119	-1.3216602807	0.0007153632
C	-1.2480073960	-0.0902312908	0.0001979461
C	-2.0243556660	1.0780294896	-0.0010558195
C	-3.4133127410	1.0092277903	-0.0016760490
C	-4.0563652524	-0.2272008996	-0.0012259871
C	0.2236437815	-0.0891854477	0.0009792884
C	1.0412669937	0.9749116037	0.0010083819
C	2.4741247652	0.8686625013	0.0018060449
C	3.2917721205	1.9327152716	0.0018351704
C	4.7634189450	1.9336939413	0.0026110898
C	5.4367423023	3.1651426722	0.0023137936
C	5.5397851343	0.7654481850	0.0036453003
C	6.8144389321	3.2316850839	0.0029747645
C	6.9287452286	0.8342522292	0.0043219661
C	7.5717819186	2.0706835779	0.0040228096
H	-3.7857720495	-2.3474634625	0.0007261339
H	-1.3477191311	-2.2322228037	0.0016085498
H	-1.5516274600	2.0425435993	-0.0015639955
H	-3.9910297703	1.9163071212	-0.0025122261
H	-5.1302711911	-0.2789615024	-0.0019287131
H	0.6764347916	-1.0675742794	0.0016156911
H	0.6352367863	1.9721717424	0.0004271957
H	2.8801447574	-0.1285971218	0.0023893310
H	2.8390369737	2.9111266154	0.0012135768
H	4.8631306415	4.0757004145	0.0015390002
H	5.0670858807	-0.1990783312	0.0039353437
H	7.3011883715	4.1909358492	0.0026767018
H	7.5064510982	-0.0728322702	0.0050805827
H	8.6456887608	2.1224517598	0.0045992484

ct-DPB(S₀)

C	0.2623442077	-0.6479351451	-4.3012622130
C	1.2712253107	-0.1166167503	-3.5033603020
C	1.4753504604	1.2703473716	-3.4387733634
C	0.6539969436	2.0977706278	-4.2096369671
C	-0.3554972043	1.5610946097	-5.0034846851
C	-0.5546906682	0.1984155217	-5.0504378152
C	2.5596857278	1.8652422074	-2.6093965640
C	2.7809203551	1.6623625856	-1.2951679423
C	1.9631447349	0.8561111375	-0.3819457888
C	2.2898132937	0.6607937354	0.8906767089
C	1.5351407795	-0.1115435951	1.8986704780
C	2.1421984288	-0.4054584007	3.1093761490
C	0.2198630776	-0.5599113262	1.6896736992
C	1.4845446875	-1.1359703289	4.0937815362
C	-0.4434955483	-1.2892467594	2.6664784087
C	0.1875368802	-1.5841001658	3.8772168108
H	0.1192007956	-1.7128587344	-4.3439100170
H	1.9089443844	-0.7730861214	-2.9393377212
H	0.8008524041	3.1634328470	-4.1827508064
H	-0.9808460421	2.2173385581	-5.5827253312
H	-1.3335848631	-0.2136456629	-5.6671305163
H	3.2247638768	2.5353723891	-3.1280099067
H	3.6257259197	2.1607122352	-0.8490565085
H	1.0629766742	0.4286765959	-0.7833398627
H	3.2099030703	1.0927931866	1.2514647877
H	3.1470411887	-0.0651464861	3.2912569941
H	-0.2893781568	-0.3290754509	0.7726616974
H	1.9839593360	-1.3507093526	5.0216065093
H	-1.4507868472	-1.6221924052	2.4895470303
H	-0.3275575975	-2.1472808833	4.6345881614

cc-DPB(S_0)

C	3.8076317117	0.9826276462	-0.7908223665
C	2.6576940683	0.5637566391	-0.1048905386
C	2.7834130203	-0.4424232705	0.8407558719
C	4.0126035051	-1.0458279533	1.0868041211
C	5.1446174599	-0.6405824020	0.3889164429
C	5.0378786801	0.3829407719	-0.5535994238
C	1.3680977710	1.2404183904	-0.3862091911
C	0.1628041044	0.6943054963	-0.5129639834
C	-0.1560777061	-0.7422906226	-0.4985961148
C	-1.3826924018	-1.2854449720	-0.3607418816
C	-2.6648873709	-0.5826244461	-0.0936140340
C	-3.8180614478	-0.9647349047	-0.8005585833
C	-2.7819093757	0.4257939776	0.8658350841
C	-5.0357363296	-0.3364256171	-0.5695668916
C	-4.0065359956	1.0497254228	1.0959685291
C	-5.1252732145	0.6790708546	0.3851336142
H	3.7298104381	1.7721425517	-1.5177647797
H	1.9230810754	-0.7487892245	1.4068174415
H	4.0843773142	-1.8227141379	1.8269942568
H	6.0953127288	-1.1054001618	0.5796149504
H	5.9068075802	0.7102185243	-1.0962974739
H	1.4391446842	2.3084466904	-0.5136511990
H	-0.6621181599	1.3594288824	-0.6984118799
H	0.6657137097	-1.4140904543	-0.6709392321
H	-1.4614446009	-2.3551452595	-0.4623551891
H	-3.7523311348	-1.7488121389	-1.5347129749
H	-1.9224855249	0.7139357585	1.4427841966
H	-5.9072111702	-0.6335144574	-1.1249189615
H	-4.0740478118	1.8225339927	1.8412657113
H	-6.0679876072	1.1635834236	0.5675144789

S5. Geometries and energies of saddle points at CASSCF(4,4)/6-31G*

Table S1. Key dihedral angles (degree) for optimized structures from SA2-CAS(4,4) and relative energies (kcal·mol⁻¹) from ICMRCI//CASSCF with 6-31G.

Species		θ1	θ2	θ3	CASSCF: S ₀ /S ₁ (kcal·mol ⁻¹)	ICMRCI: S ₀ /S ₁ (kcal·mol ⁻¹)
tt-DPB(S ₀)		-180.0	-180.0	180.0	0/133.9	0/125.0
tt-DPB(S ₁)		-180.0	180.0	-180.0	8.2/103.5	13.1/109.9
ct-DPB(S ₀)		-3.6	178.7	177.0	10.2/141.5	7.5/133.0
ct-DPB(S ₁)		-13.7	-175.3	177.0	8.5/115.5	10.4/118.0
cc-DPB(S ₀)		-5.7	-4.9	166.4	13.2/149.4	9.7/139.9
cc-DPB(S ₁)		-49.7	-49.7	168.8	34.9/101.9	39.0/107.6
S ₁ (min)		-145.5	-145.4	10.1	26.0/99.7	30.5/105.8
CI1	-1	110.0	-100.3	116.9	92.5	95.6/
	-2	-110.0	100.3	-116.9	92.5	97.0
	-3	100.3	-110.0	-116.9	92.5	94.1
	-4	-100.3	110.0	116.9	92.5	98.6
CI2	-1	119.0	79.16	118.4	91.8	94.6
	-2	-119.0	-79.20	-118.4	91.8	96.1
	-3	79.16	119.0	118.4	91.8	94.6
	-4	-79.20	-119.0	-118.4	91.8	96.1