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

Substitution pattern dependent behavior of the singlet excited states in symmetrically fluorinated biphenyls

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Supporting Information

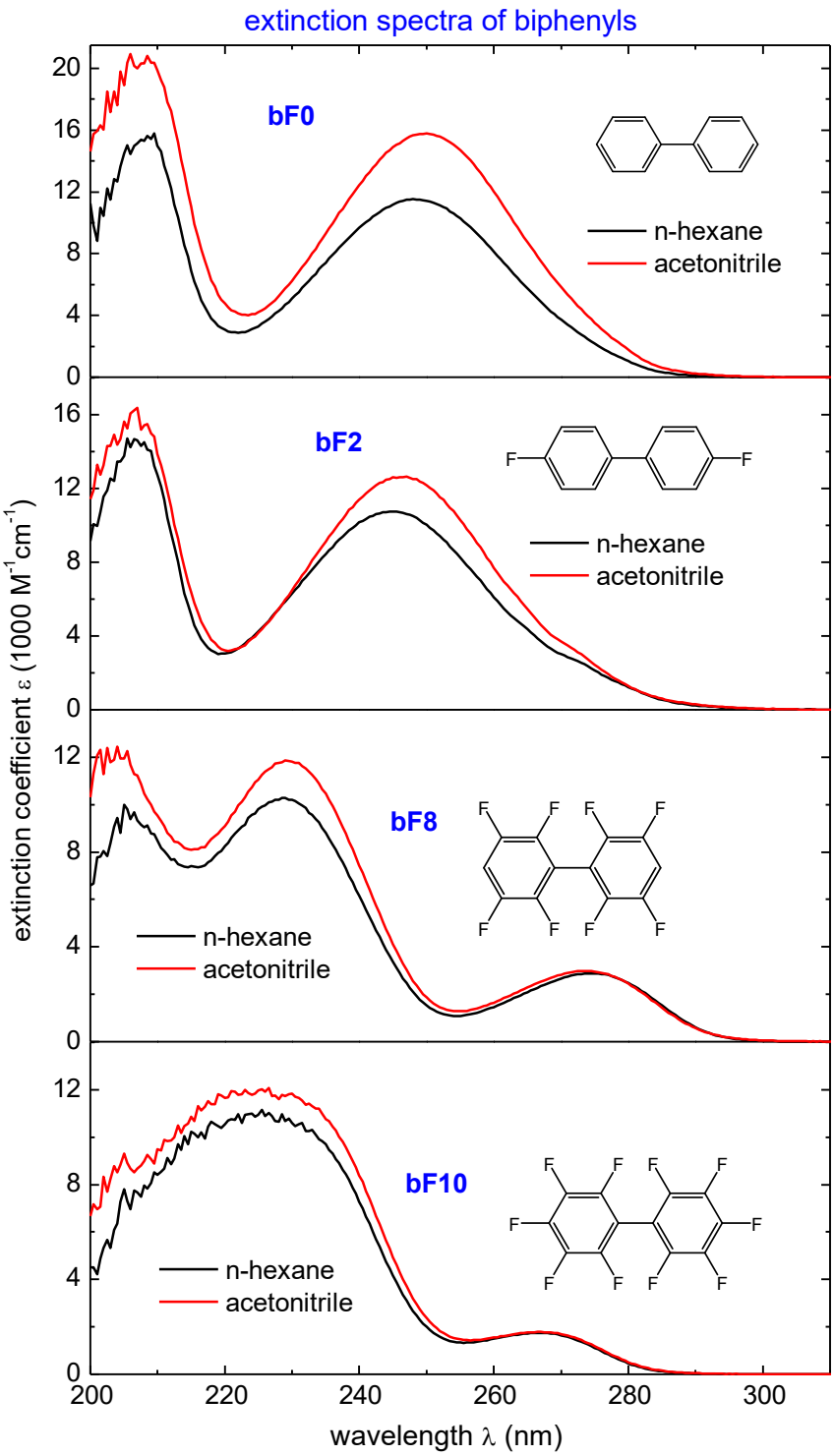

Fig. S1. Extinction spectra of biphenyls in n-hexane and acetonitrile. The $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ bands in **bP0** and **bP2** are partly hidden in the slope of the $S_3 \leftarrow S_0$ band.

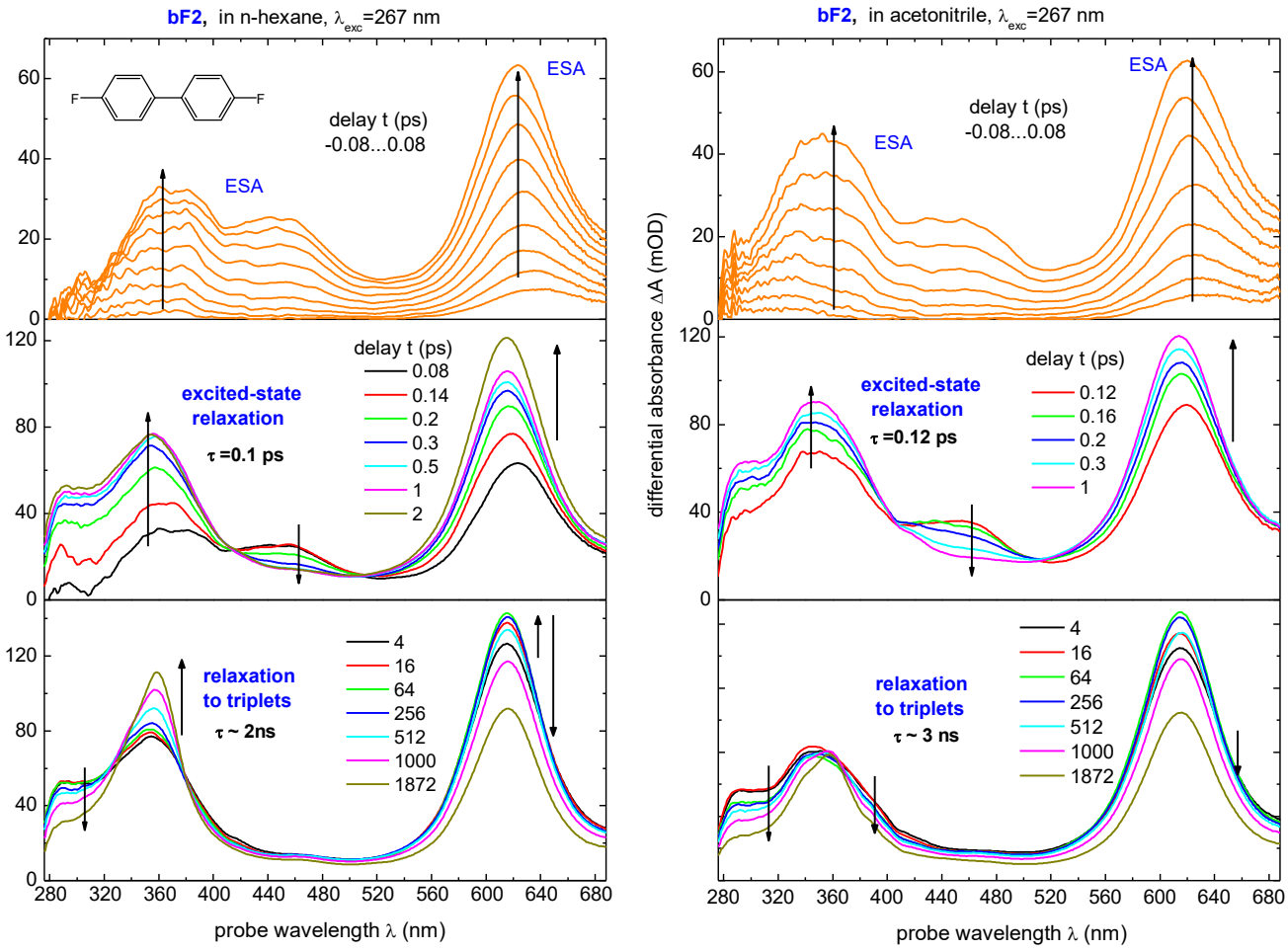

Fig. S2. Transient absorption spectra of **bP2** upon optical excitation at 267 nm. The excitation populates the S_3 state that undergoes fast $S_3 \rightarrow S_1$ relaxation with τ=0.1 ps. At late time S_1 decays to triplets with τ~1 ns.

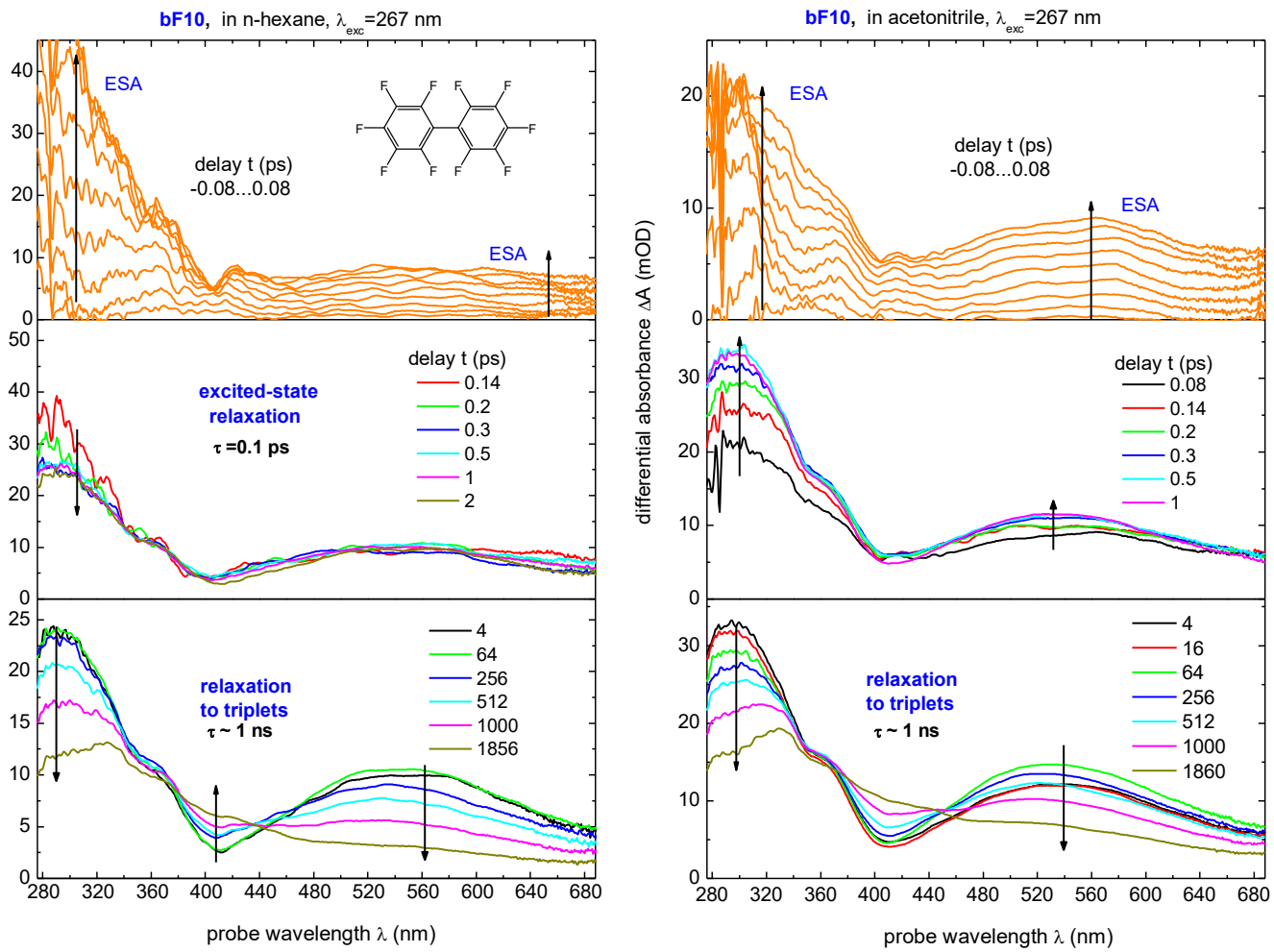

Fig. S3. Transient absorption spectra of **bP10** upon optical excitation at 267 nm. Evolution with τ=0.1 ps is related to sudden polarization

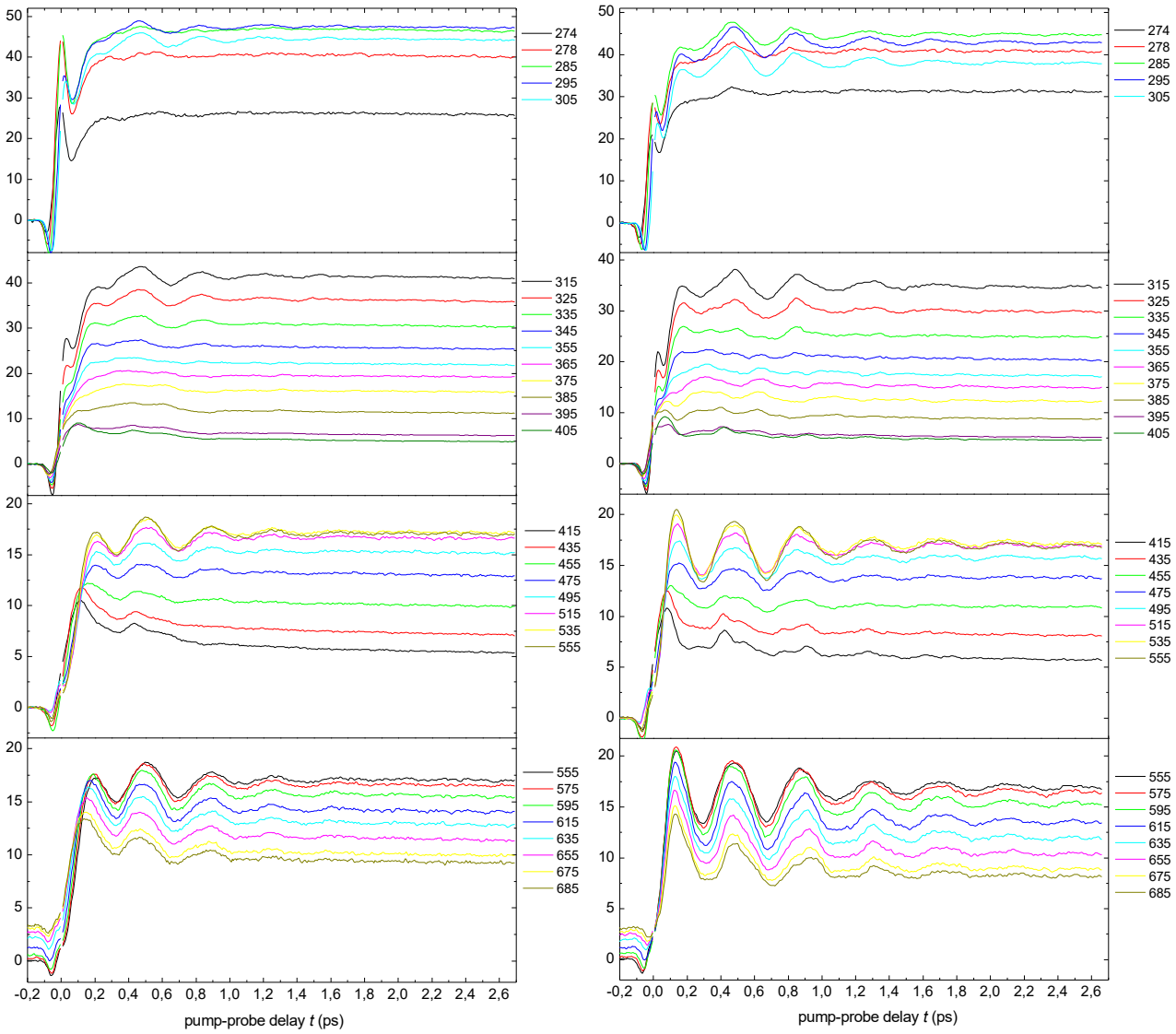

Fig. S4. Oscillations of the transient absorption signal in **bP10** at different wavelengths in acetonitrile (ν_{osc}=85 cm^{-1}) and perfluorohexane (ν_{osc}=81.9 cm^{-1})

Optimized ground state geometry:

bP0

C	-7.510725658	3.317114438	-0.082870661
C	-8.042557045	2.040871890	0.031643904
C	-6.140820225	3.511795421	-0.009548070
C	-5.272750723	2.435349538	0.178659123
C	-5.821622754	1.157090878	0.291078673
C	-7.191484304	0.961422898	0.219096430
H	-5.166940912	0.310402212	0.462075234
H	-8.165929668	4.166258534	-0.238611840
H	-5.733917952	4.509842156	-0.123987429
H	-7.596701130	-0.038819769	0.318475026
H	-9.113734280	1.888513768	-0.024941987
C	-3.813260779	2.643782883	0.257251602
C	-3.282151794	3.753236611	0.916582767
C	-1.912425731	3.948858585	0.991255702
C	-1.043584944	3.038852681	0.406609905
C	-1.557578394	1.931697033	-0.252607057
C	-2.927417611	1.736441100	-0.325684562
H	-3.951508874	4.457261088	1.397278489
H	-0.888224197	1.219090171	-0.720301765
H	-3.319308805	0.880946869	-0.863578598
H	-1.521510897	4.812605458	1.516327810
H	0.027469437	3.191529607	0.464527649

bP2

C	-1.726655055	0.463098142	0.703230278
C	-0.458451631	0.595390998	0.140023073
C	-2.677320306	1.440159900	0.438298370
C	-2.398367091	2.535771434	-0.368200101
C	-1.124897515	2.648970044	-0.923618469
C	-0.136912534	1.685502573	-0.679875543
C	1.211306340	1.816155357	-1.271736406
C	1.830941657	3.068695265	-1.376485807
C	3.102324343	3.202329816	-1.932213743
C	3.753835629	2.062189433	-2.384184241
C	3.174511880	0.802966121	-2.297804562
C	1.901780700	0.690411335	-1.740582841
H	1.430152397	-0.285927203	-1.693018020
H	1.325431860	3.950450898	-0.995829372
H	3.590938321	4.166801005	-2.006970542
F	4.982279695	2.180861683	-2.921365210
H	3.709764602	-0.062423267	-2.670792987
H	0.299036636	-0.149034754	0.363557557
H	-3.169450482	3.272570706	-0.560743249
H	-0.906186962	3.487765916	-1.576727510
H	-1.978312136	-0.372477875	1.345889455
F	-3.904360010	1.321930150	0.978708888

bP8

C	-5.370584314	0.632705747	-1.482366639
C	-6.481090596	1.282645811	-2.020660497
C	-7.120968300	0.696553907	-3.112660972
C	-6.661652615	-0.502631489	-3.647447925
C	-5.557213208	-1.143836444	-3.107732729
C	-4.916844620	-0.566475049	-2.022021747
C	-6.965171689	2.555064224	-1.451770971
H	-5.201725901	-2.077269376	-3.525947387
C	-7.005589269	3.715541594	-2.224525445
C	-7.462072528	4.913944277	-1.685556646
C	-7.887134729	4.983292469	-0.367672377
C	-7.849224504	3.833171340	0.405651421
C	-7.394323046	2.631244396	-0.126841658
H	-8.241789082	5.917533772	0.049504114
F	-8.258510898	3.868294819	1.675750112
F	-7.390971987	1.537495756	0.634881184
F	-6.581973154	3.685467525	-3.487982555
F	-7.480922947	6.006544147	-2.452157016
F	-4.720114271	1.174569921	-0.452973105
F	-3.846828364	-1.157381452	-1.485666454
F	-7.302579576	-1.037988434	-4.688728161
F	-8.198794096	1.277502658	-3.639190230

bP10

C	3.536008538	0.000000003	0.000000004
C	-3.536004646	0.000000001	0.000000003
C	2.843421589	-0.593778317	1.043074810
C	-2.843421481	-0.593762019	-1.043086269
C	2.843421594	0.593778320	-1.043074807
C	-2.843421474	0.593762018	1.043086270
C	1.459554294	-0.589209229	1.031636650
C	-1.459553740	-0.589194058	-1.031650026
C	1.459554298	0.589209228	-1.031636657
C	-1.459553734	0.589194054	1.031650020
C	0.737174595	-0.000000001	-0.000000005
C	-0.737180836	-0.000000003	-0.000000005
F	3.506150768	-1.166723749	2.034021196
F	-3.506157087	-1.166689295	-2.034039177
F	3.506150777	1.166723754	-2.034021189
F	-3.506157074	1.166689295	2.034039183
F	4.855729839	0.000000004	0.000000010
F	-4.855726743	0.000000000	0.000000007
F	0.822171702	-1.183366017	2.029946438
F	-0.822166636	-1.183332084	-2.029965964
F	0.822171710	1.183366015	-2.029946448
F	-0.822166622	1.183332078	2.029965953

D_{2h} stationary point in the excited **bP0**, XMCQDPT2/Def2-TZVP

C	3.551310566	-0.000004324	-0.000078108
C	-3.551320292	-0.000010662	-0.000040082
C	2.857209349	-0.000301036	1.223587222
C	-2.857112908	0.000260799	-1.223640840
C	2.857105974	0.000290239	-1.223680043
C	-2.857206251	-0.000266716	1.223622785
C	1.442959188	-0.000290463	1.228449239
C	-1.442867924	0.000277035	-1.228386042
C	1.442870827	0.000296050	-1.228437956
C	-1.442955120	-0.000264661	1.228509257
C	0.718451006	0.000008015	0.000036139
C	-0.718434344	0.000008851	0.000079045
H	-0.923238313	-0.000460687	2.172558268
H	-3.401065625	-0.000471470	2.158282869
H	-4.634158519	-0.000021413	-0.000106564
H	-3.400873236	0.000459823	-2.158357129
H	-0.923076806	0.000483522	-2.172386746
H	0.923056856	0.000534229	-2.172426208
H	3.400864000	0.000502018	-2.158395657
H	4.634134747	-0.000002132	-0.000153351
H	3.401034029	-0.000534653	2.158266584
H	0.923195780	-0.000526481	2.172472349

False alternative D_{2h} stationary point in the excited **bP0**, XMCQDPT2/Def2-TZVP, rejected by the XMCQDPT2/Def2-TZVPP recalculation

C	3.557847173	-0.000004232	-0.000042980
C	-3.557853760	-0.000002273	-0.000055247
C	2.847402913	-0.000314559	1.220230146
C	-2.847336198	0.000244360	-1.220276235
C	2.847336340	0.000312488	-1.220262568
C	-2.847407604	-0.000247776	1.220220306
C	1.471044436	-0.000309097	1.237586569
C	-1.470975804	0.000255799	-1.237538650
C	1.470978198	0.000314247	-1.237570621
C	-1.471040559	-0.000252924	1.237631509
C	0.703060446	0.000002008	0.000032117
C	-0.703046140	0.000002346	0.000062446
H	-0.954605887	-0.000426262	2.189516296
H	-3.394098456	-0.000435350	2.157864225
H	-4.643486585	-0.000004778	-0.000097046
H	-3.393920761	0.000432513	-2.157980521
H	-0.954454608	0.000433736	-2.189369955
H	0.954452253	0.000577195	-2.189397163
H	3.393926411	0.000560039	-2.157962350
H	4.643465451	-0.000012093	-0.000113345
H	3.394046346	-0.000558227	2.157900625
H	0.954556302	-0.000571401	2.189439175

Slightly distorted C_{2v} stationary point in the excited **bP2**, XMCQDPT2/Def2-TZVP

C	-1.869318865	0.194952620	0.169145834
C	-0.574218932	0.352344428	-0.344267871
C	-2.698028759	1.321376745	0.223009346
C	-2.302502244	2.594957141	-0.201337695
C	-1.006743529	2.746890477	-0.714603744
C	-0.124779657	1.629807989	-0.788558520
C	1.201053543	1.788268115	-1.313650029
C	1.645508557	3.069309610	-1.756079601
C	2.952975432	3.230039543	-2.272348233
C	3.777123069	2.098495817	-2.321817535
C	3.388592266	0.820249806	-1.900809094
C	2.080001528	0.667240715	-1.384992567
H	1.762343987	-0.310586155	-1.056611420
H	0.995124315	3.929499015	-1.712324481
H	3.327953799	4.185647365	-2.616701408
F	5.014552630	2.247536187	-2.805817475
H	4.085377354	-0.005519503	-1.971109738
H	0.075032732	-0.508854474	-0.390383862
H	-2.997135852	3.423461315	-0.131869556
H	-0.689189141	3.724804224	-1.043465323
H	-2.241589892	-0.762106440	0.514419663
F	-3.936018157	1.173157215	0.709866959

Polar stationary point in the excited **bP8**, XMCQDPT2/Def2-TZVP

C	-5.515446496	0.521239496	-1.367140344
C	-6.554951481	1.319624513	-1.941850329
C	-7.107780347	0.713758030	-3.114651033
C	-6.658789658	-0.536527740	-3.650879160
C	-5.641204413	-1.317420336	-3.064935969
C	-5.094746244	-0.740260586	-1.900095569
C	-6.993418653	2.584844759	-1.403281657
H	-5.313409250	-2.263737247	-3.467881310
C	-7.218104623	3.707526018	-2.230399662
C	-7.645405955	4.922371181	-1.704912378
C	-7.861285132	5.085469043	-0.338756722
C	-7.640188152	3.989249122	0.491322339
C	-7.221254013	2.765935777	-0.021103398
H	-8.190656606	6.034762999	0.065166200
F	-7.871044925	4.095208875	1.807301371
F	-7.119667462	1.715552902	0.805340820
F	-6.928759225	3.630177838	-3.536901900
F	-7.812688206	5.963077053	-2.532721762
F	-4.828380547	0.986173354	-0.339335807
F	-4.104377849	-1.351073774	-1.267744018
F	-7.285175822	-0.978182295	-4.730820733
F	-8.149309837	1.269786410	-3.706885692

Non-polar stationary point in the excited **bP10**, XMCQDPT2/Def2-TZVP

C	3.609329886	-0.037566142	0.053707254
C	-3.592394913	-0.217239921	0.135064711
C	2.862157052	-0.522936435	1.116846500
C	-2.885515540	-0.533642913	-1.024319151
C	2.964058706	0.470786240	-1.063261599
C	-2.816753454	0.422085013	1.102730724
C	1.483326304	-0.504110221	1.045469468
C	-1.474251625	-0.432987663	-1.125126326
C	1.582534613	0.493115987	-1.110176440
C	-1.412991296	0.550525211	0.984832805
C	0.797529531	-0.003310410	-0.065636932
C	-0.659282310	0.034603468	-0.084984280
F	3.474110265	-1.025285900	2.177550185
F	-3.530610304	-0.895081495	-2.122883196
F	3.674596417	0.960690746	-2.066801311
F	-3.391278868	1.033568565	2.125219388
F	4.929117279	-0.053573015	0.108073568
F	-4.672183734	-0.962329393	0.504671444
F	0.795281706	-1.013710612	2.061951411
F	-0.945925560	-0.750700767	-2.286238013
F	1.007378107	1.056566259	-2.164864563
F	-0.814257788	1.325021565	1.866548215

Non-polar stationary point in the excited **bP10**, TD-PBE0/Def2-TZVPP

C	3.609394462	-0.037833197	0.054402220
C	-3.591483538	-0.214091197	0.135068220
C	2.861730462	-0.523735197	1.116865220
C	-2.884402538	-0.531153197	-1.024037780
C	2.965135462	0.472871803	-1.062012780
C	-2.816483538	0.429567803	1.100259220
C	1.482924462	-0.503128197	1.045359220
C	-1.473312538	-0.430789197	-1.124663780
C	1.583635462	0.496748803	-1.109088780
C	-1.412744538	0.557241803	0.983021220
C	0.798307462	-0.000213197	-0.065229780
C	-0.658816538	0.039087803	-0.085347780
F	3.473100462	-1.027957197	2.176869220
F	-3.529651538	-0.892170197	-2.122885780
F	3.676514462	0.963026803	-2.064658780
F	-3.391796538	1.046740803	2.119231220
F	4.929136462	-0.055562197	0.108946220
F	-4.670857538	-0.958516197	0.505888220
F	0.793982462	-1.012461197	2.061169220
F	-0.944425538	-0.749857197	-2.285257780
F	1.009053462	1.061548803	-2.163175780
F	-0.813899538	1.332927803	1.863608220

Polar stationary point in the excited **bP10**, TD-PBE0/Def2-TZVPP

C	3.626206462	0.131349803	0.086656220
C	-3.579836538	-0.025949197	0.102436220
C	2.891780462	-0.456832197	1.124129220
C	-2.913880538	-0.475569197	-1.025518780
C	2.941853462	0.518418803	-1.079722780
C	-2.781898538	0.408785803	1.139863220
C	1.540687462	-0.593345197	1.022189220
C	-1.478671538	-0.515448197	-1.092245780
C	1.589423462	0.374593803	-1.177621780
C	-1.349540538	0.417828803	1.019463220
C	0.812664462	-0.149307197	-0.114982780
C	-0.635231538	-0.066694197	-0.079890780
F	3.540153462	-0.956734197	2.185031220
F	-3.583033538	-0.917698197	-2.046664780
F	3.640772462	0.986413803	-2.121290780
F	-3.309141538	0.873951803	2.233061220
F	4.833415462	0.675168803	0.348615220
F	-4.892401538	-0.024736197	0.178333220
F	0.872018462	-1.334856197	1.937041220
F	-1.011744538	-1.056375197	-2.175270780
F	0.973240462	0.704117803	-2.329398780
F	-0.731792538	0.945211803	2.030113220