Supporting Information for:

Shape of Multireference, Equation-of-Motion Coupled-Cluster, and Density Functional Theory Potential Energy Surfaces at a Conical Intersection

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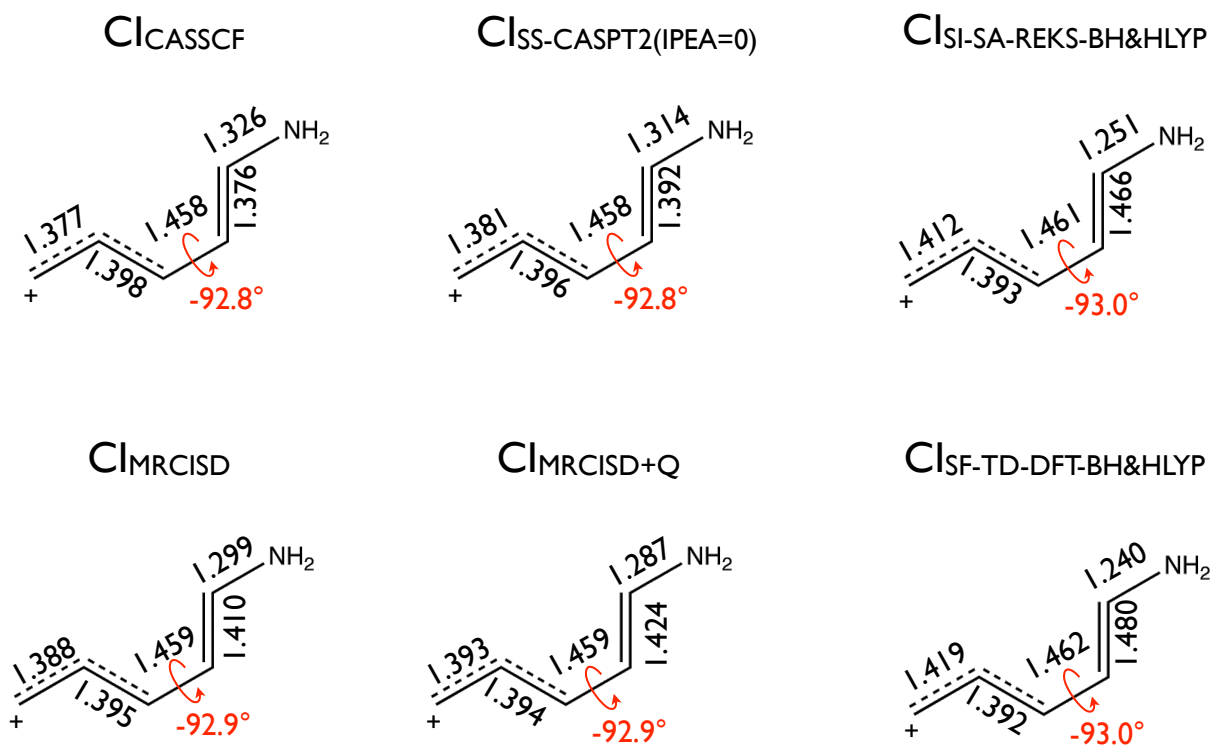

Figure S1. The structures of the crossing points used as the centers to construct the loops in Figures 3 and 4 in the main manuscript. These correspond to CASSCF, SS-CASPT2(IPEA=0), MRCISD, MRCISD+Q, SI-SA-REKS-BH&HLYP, and SF-TD-DFT-BH&HLYP crossing points. Bond lengths and dihedrals are labeled in black and red, respectively.

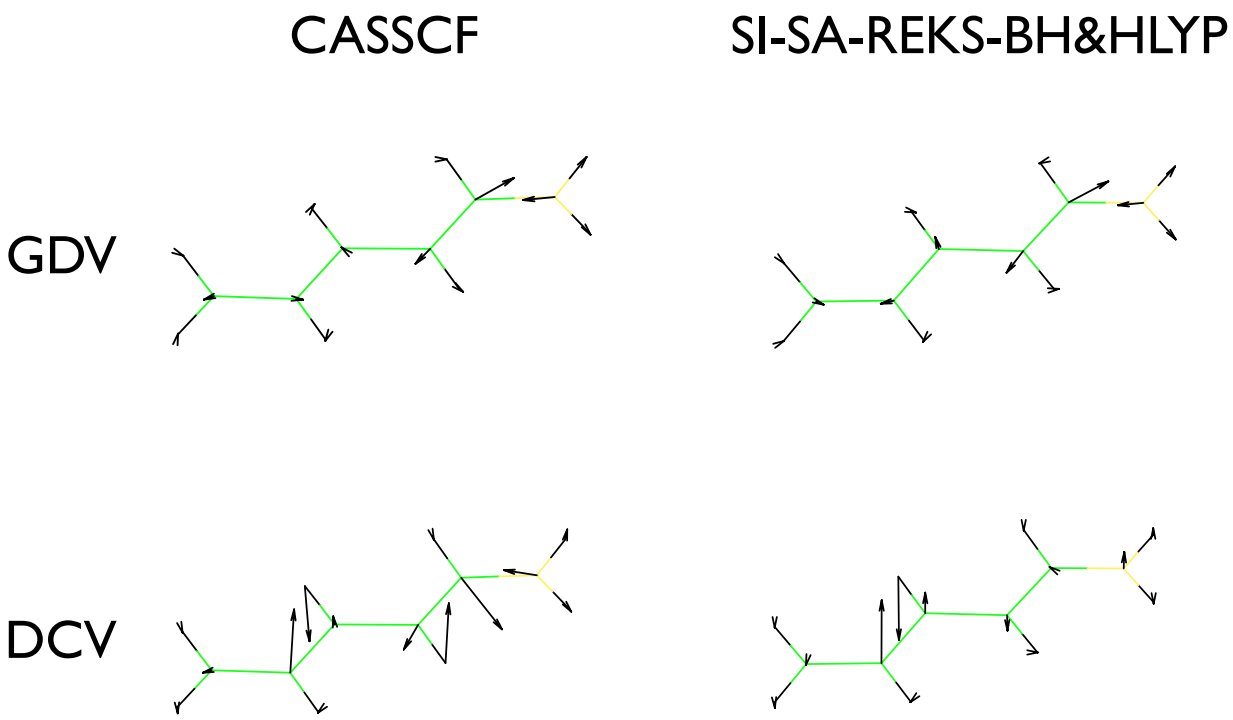

Figure S2. The PSB3 distortions corresponding to the branching plane vectors (Gradient different vector, GDV and derivative coupling vector, DCV) computed at the CASSCF and SI-SA-REKS-BH&HLYP methods.

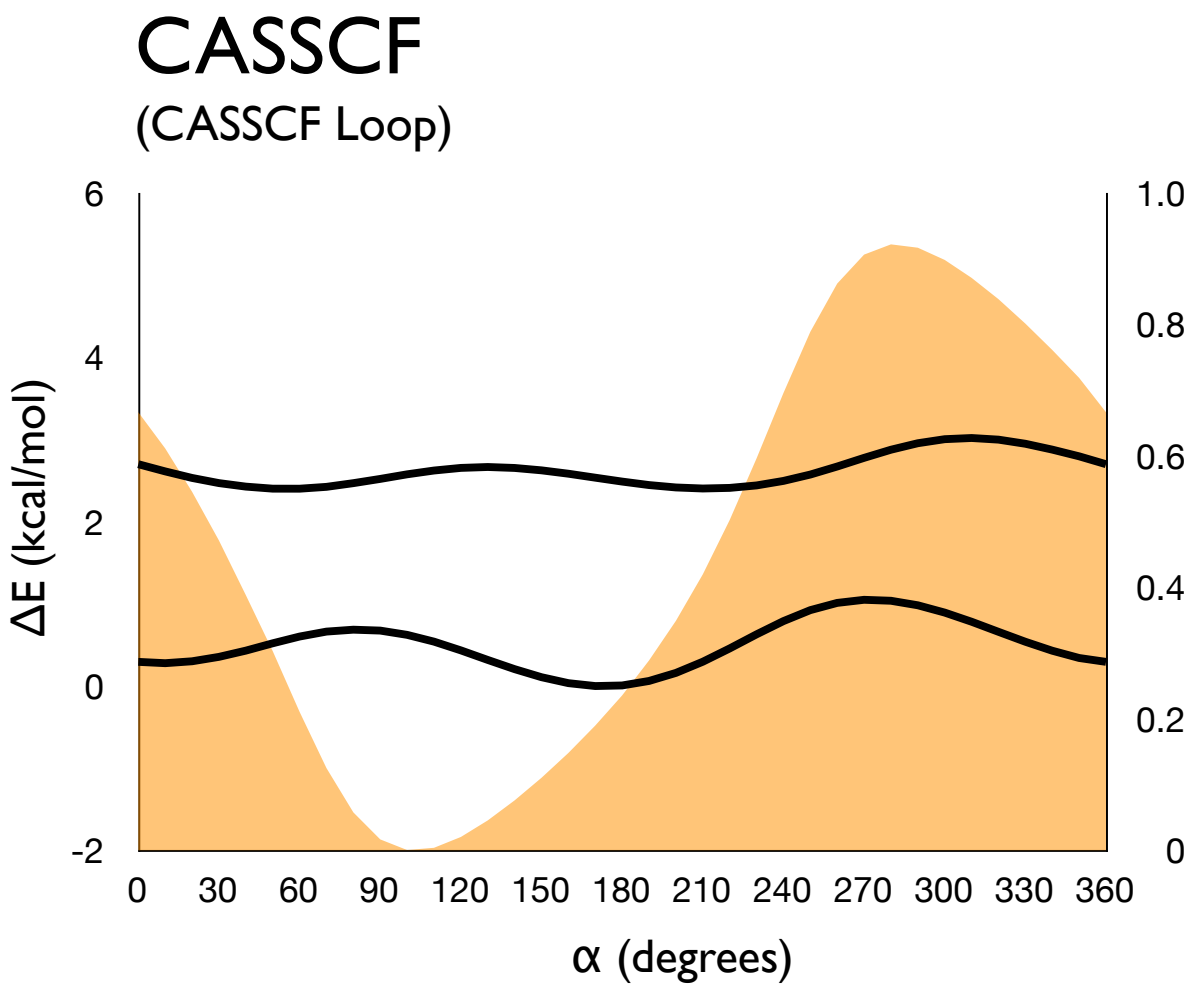

Figure S3. CASSCF S_0 and S_1 energy profiles, shown as black solid lines, along the CASSCF loop corresponding to loop A in Fig. 3 of the manuscript. The CASSCF S_0 charge transfer character along the same loop is shown in orange.

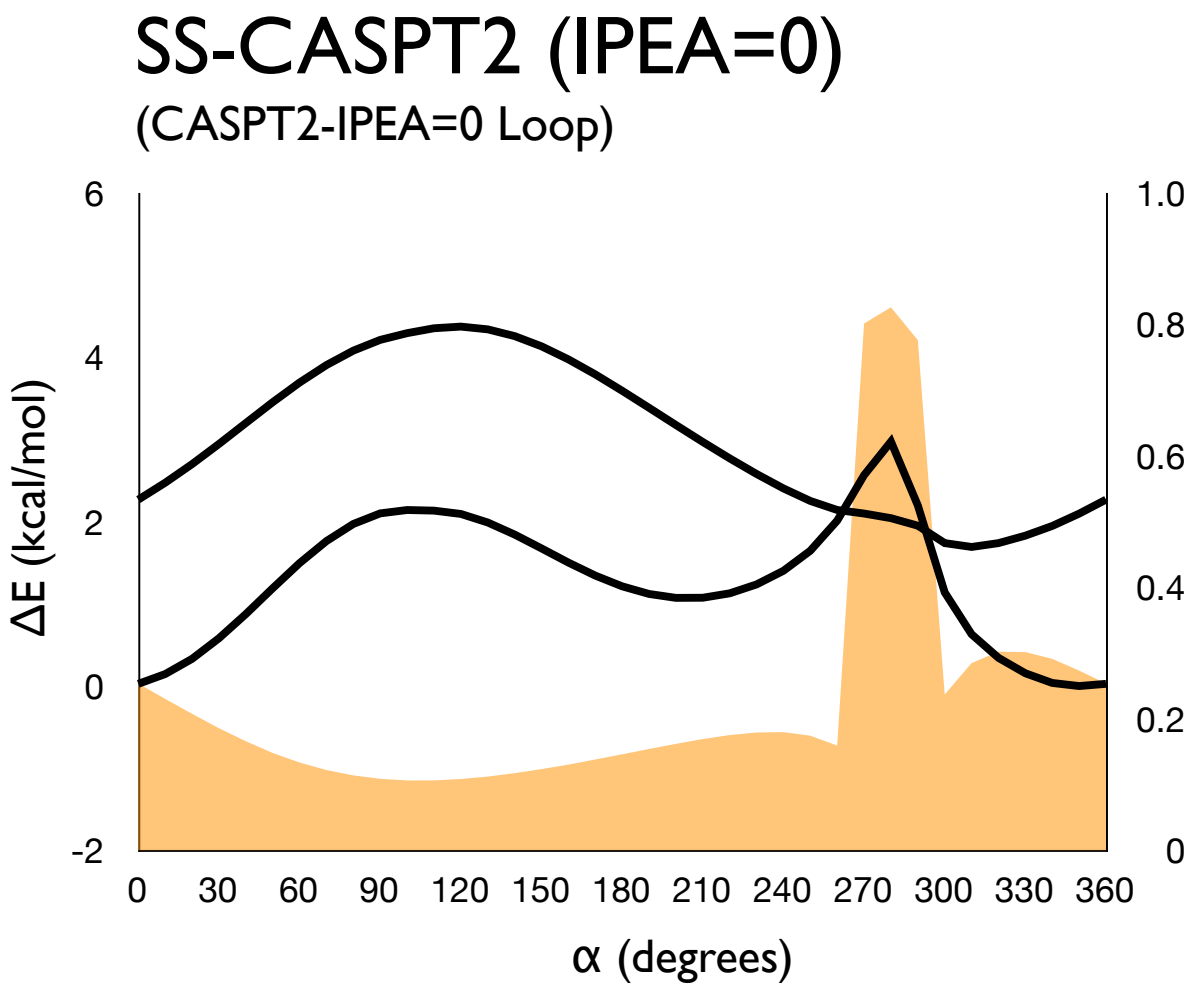

Figure S4. SS-CASPT2(IPEA=0) S_0 and S_1 energy profiles, shown as black solid lines, along the CASPT2(IPEA=0) loop corresponding to loop B in Fig. 3 of the manuscript. The SS-CASPT2(IPEA=0) S_0 charge transfer character along the same loop is shown in orange.

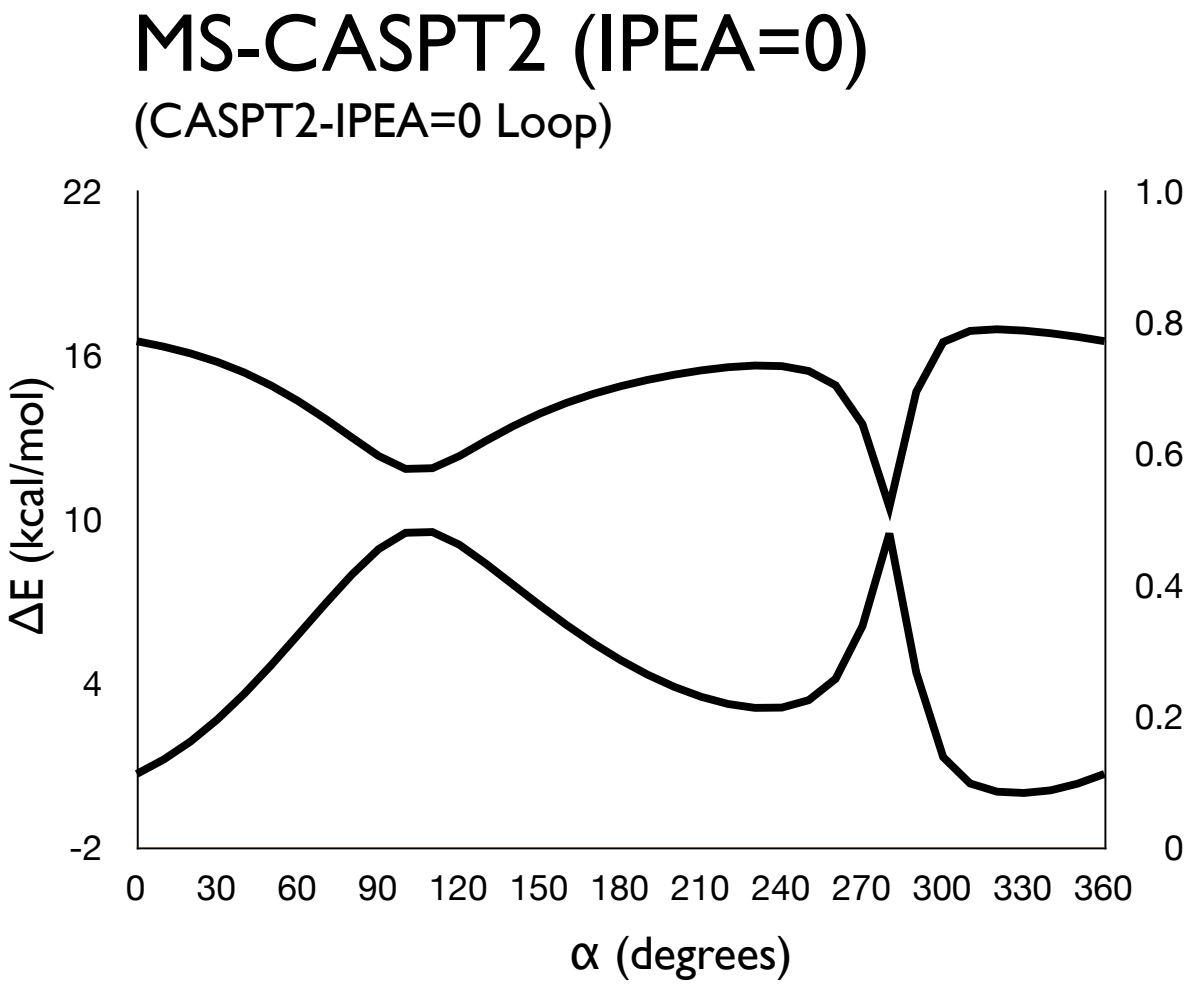

Figure S5. MS-CASPT2(IPEA=0) S_0 and S_1 energy profiles, shown as black solid lines, along the CASPT2(IPEA=0) loop corresponding to loop B in Fig. 3 of the manuscript.

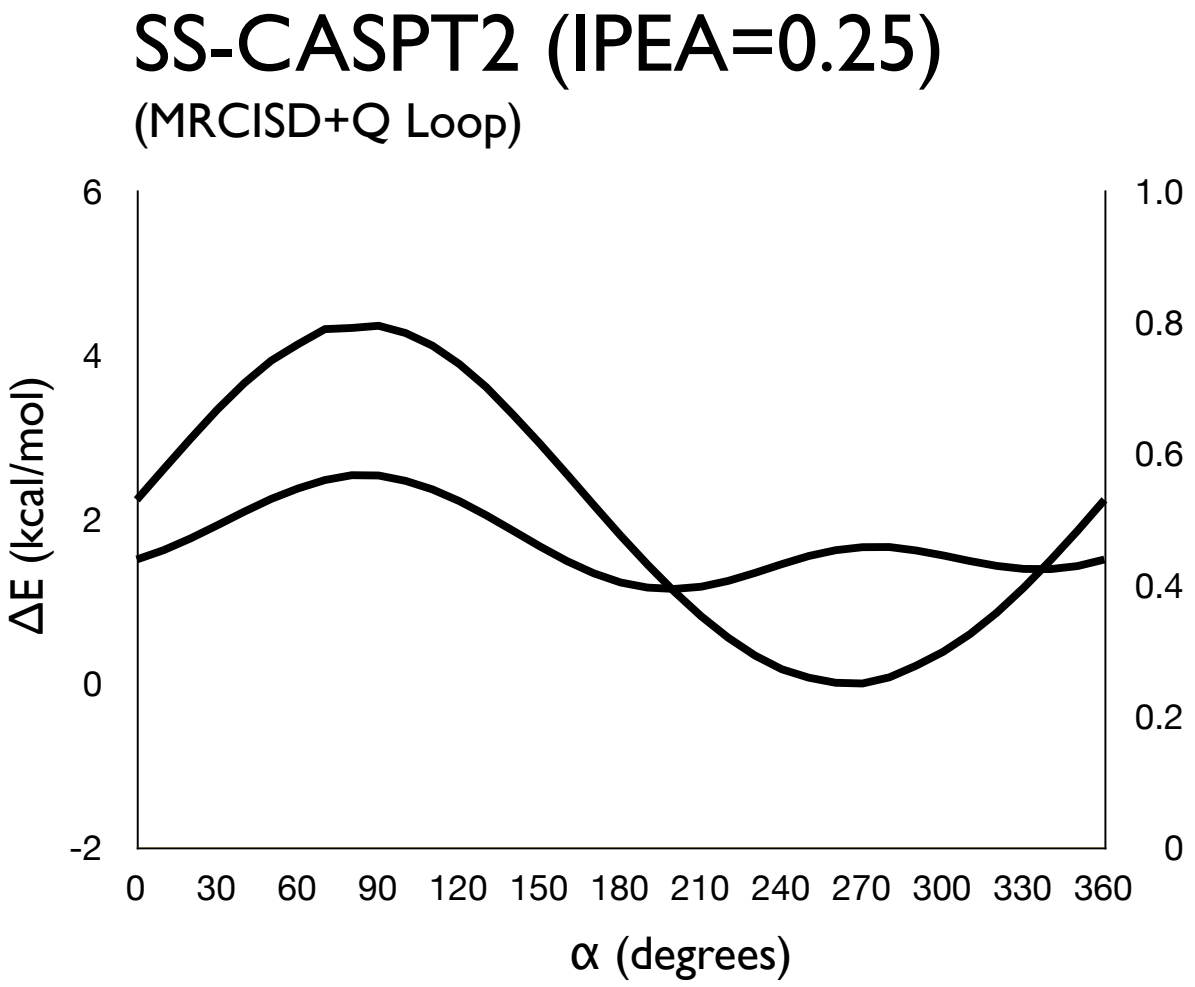

Figure S6. SS-CASPT2(IPEA=0.25) S_0 and S_1 energy profiles, shown as black solid lines, along the MRCISD+Q loop corresponding to loop D in Fig. 3 of the manuscript.

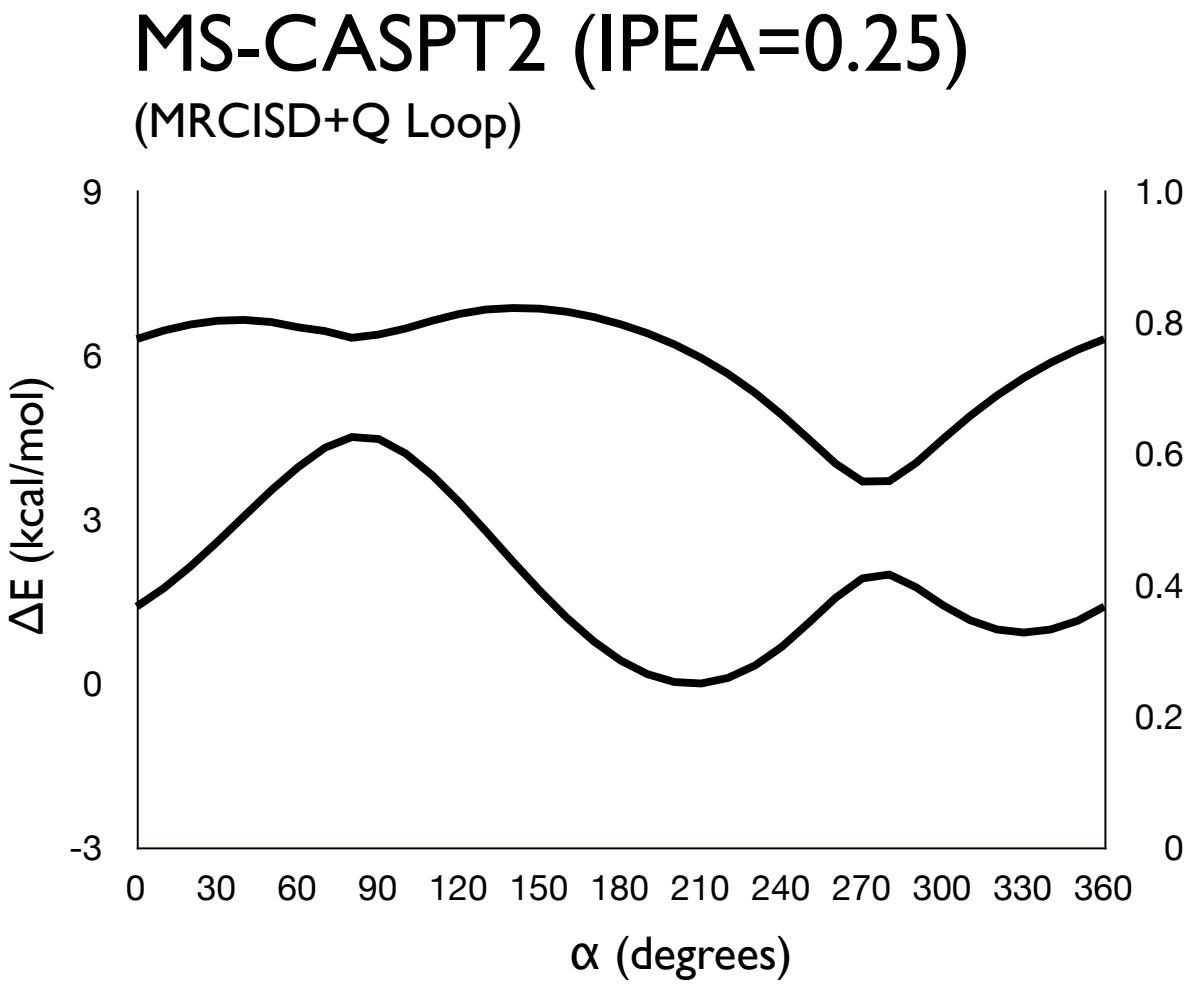

Figure S7. MS-CASPT2(IPEA=0.25) S_0 and S_1 energy profiles along the MRCISD+Q loop corresponding to loop D in Fig. 3 of the manuscript.

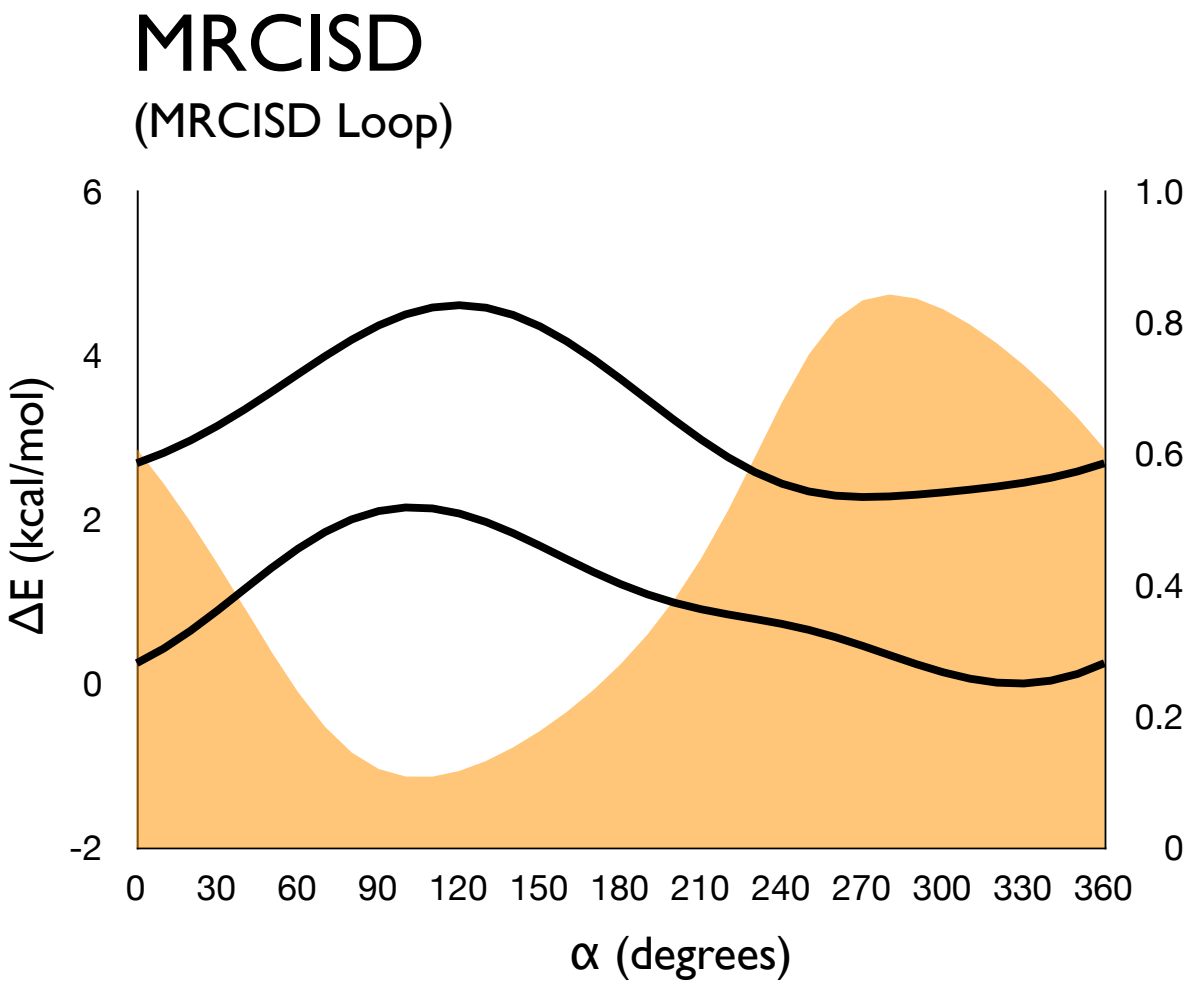

Figure S8. MRCISD S_0 and S_1 energy profiles, shown as black solid lines, along the MRCISD loop corresponding to loop C in Fig. 3 of the manuscript. The MRCISD S_0 charge transfer character along the same loop is shown in orange.

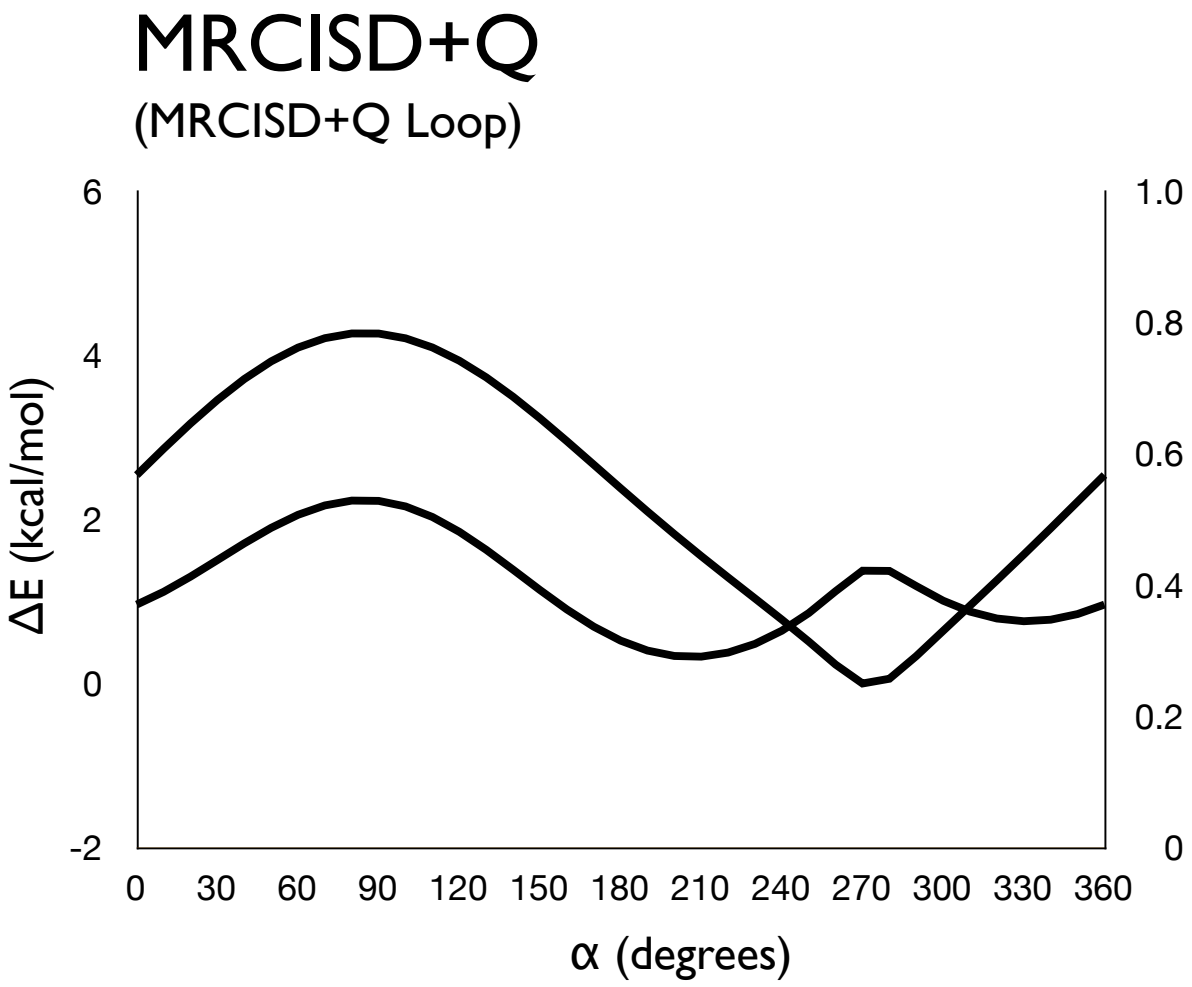

Figure S9. MRCISD+Q S_0 and S_1 energy profiles, shown as black solid lines, along the MRCISD+Q loop corresponding to loop D in Fig. 3 of the manuscript.

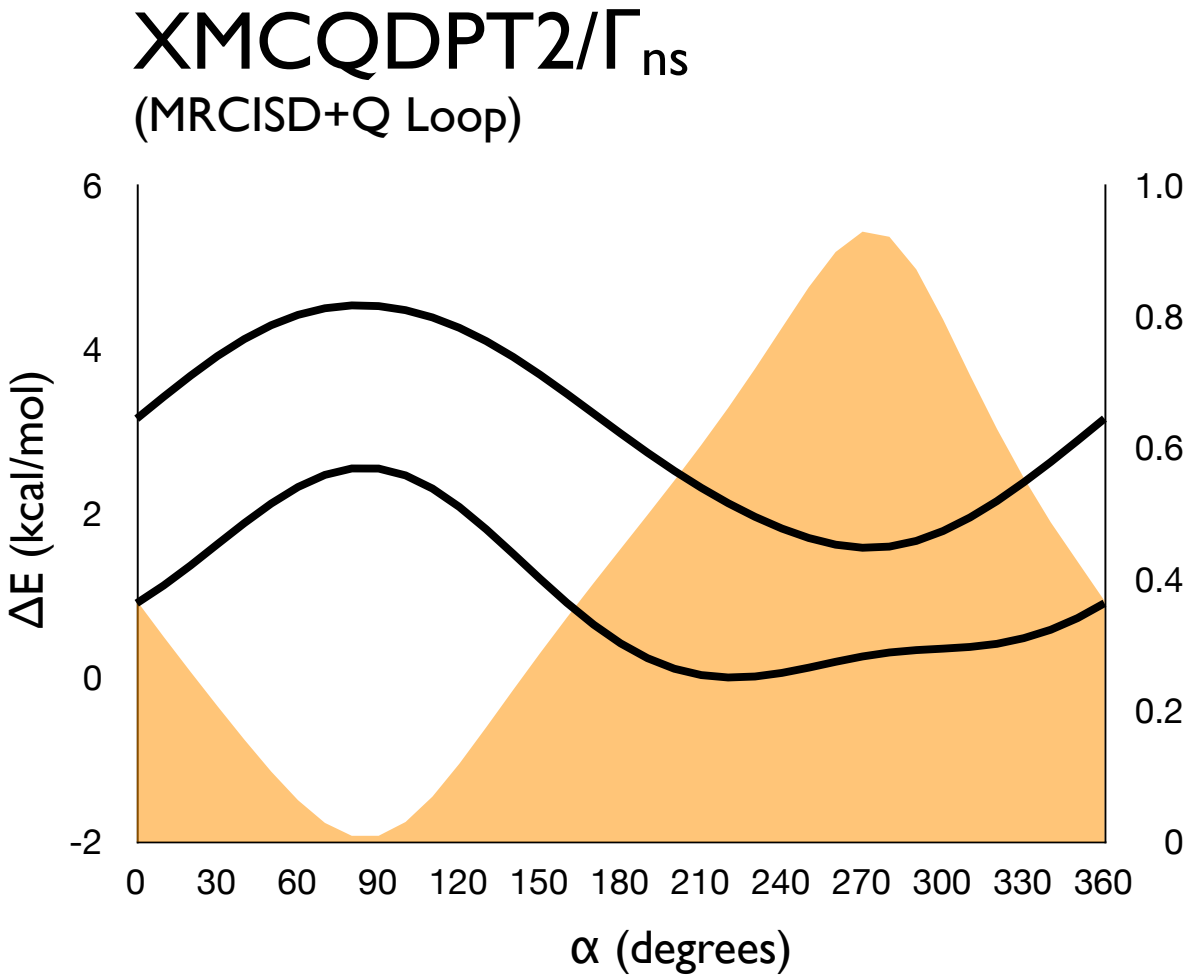

Figure S10. XMCQDPT2/Γ_{ns} S_0 and S_1 energy profiles, shown as black solid lines, along the MRCISD+Q loop corresponding to loop D in Fig. 3 of the manuscript. The XMCQDPT2/Γ_{ns} S_0 charge transfer character along the same loop is shown in orange.

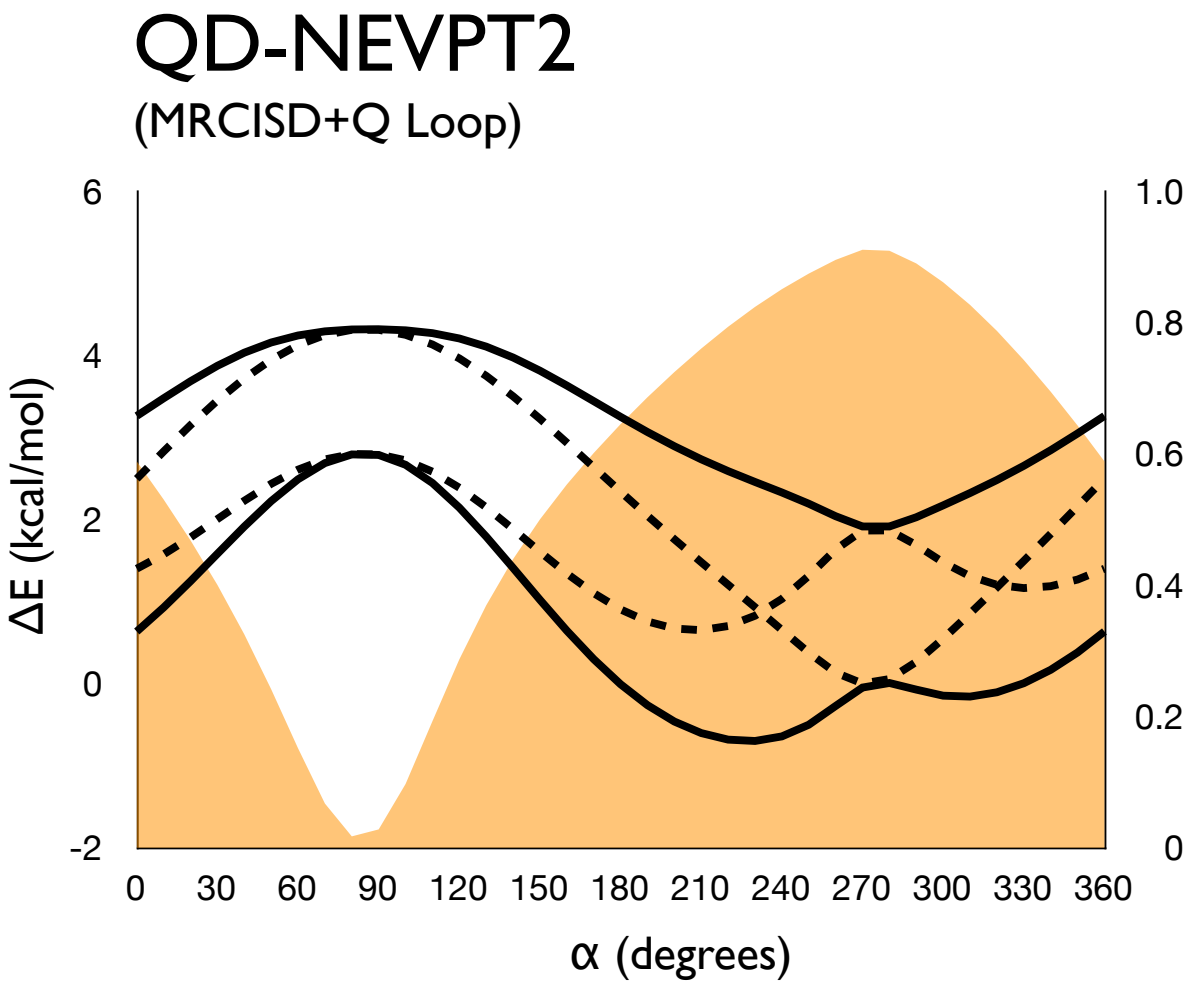

Figure S11. SS-NEVPT2 (dashed black lines) and QD-NEVPT2 (solid black lines) S_0 and S_1 energy profiles along the MRCISD+Q loop corresponding to loop D in Fig. 3 of the manuscript. NEVPT2 energies where computed with an active space of 6 electrons in 8 orbitals (unlike other multiconfigurational methods which were computed with an active space of 6 electrons in 6 orbitals). The QD-NEVPT2 S_0 charge transfer character along the same loop is shown in orange.

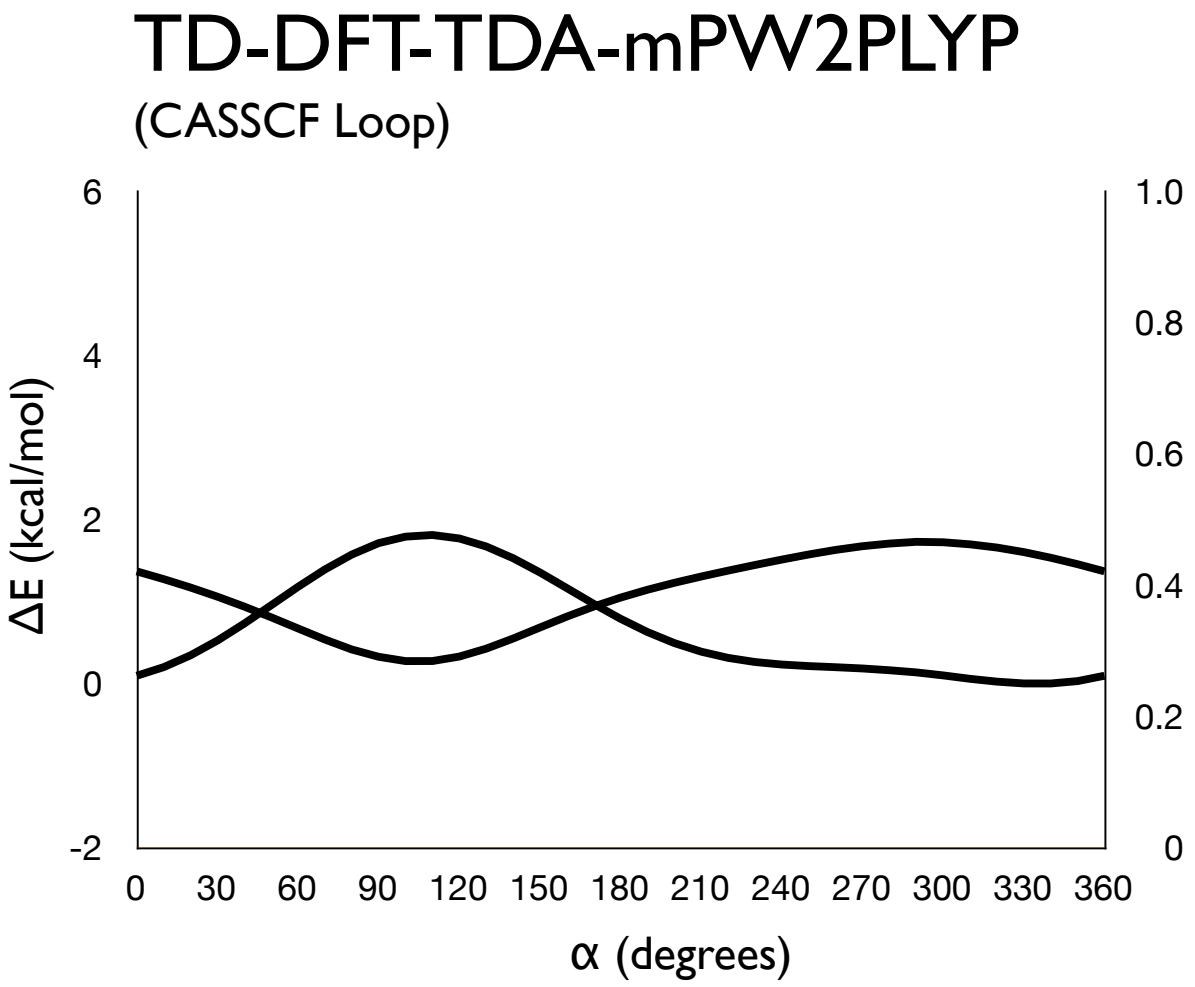

Figure S12. TD-DFT-TDA-mPW2PLYP S_0 and S_1 energy profiles, shown as black solid lines, along the CASSCF loop corresponding to loop A in Fig. 3 of the manuscript.

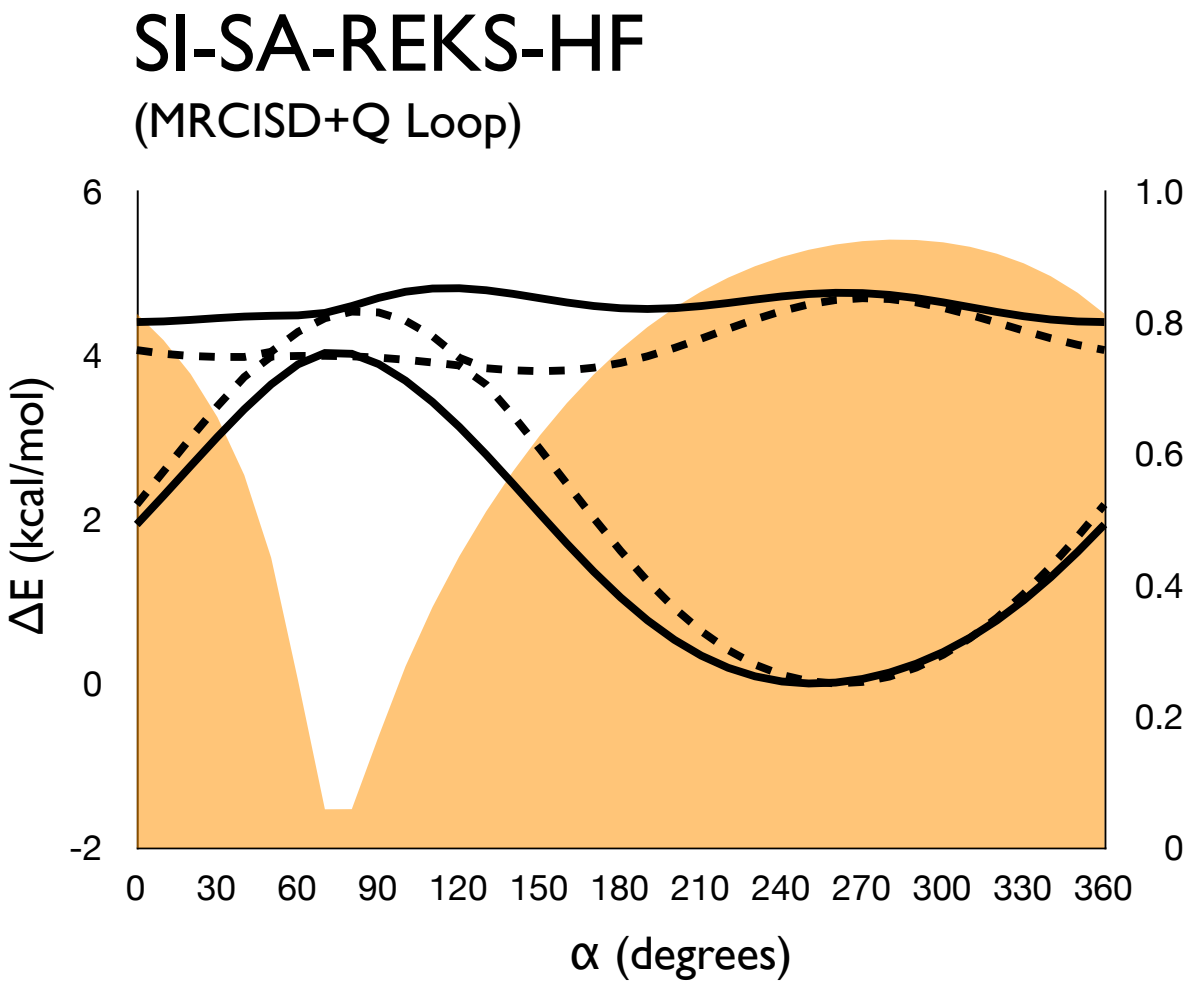

Figure S13. SA-REKS-HF (dashed black lines) and SI-SA-REKS-HF (solid black lines) S_0 and S_1 energy profiles along the MRCISD+Q loop corresponding to loop D in Fig. 3 of the manuscript. The SI-SA-REKS-HF S_0 charge transfer character along the same loop is shown in orange.

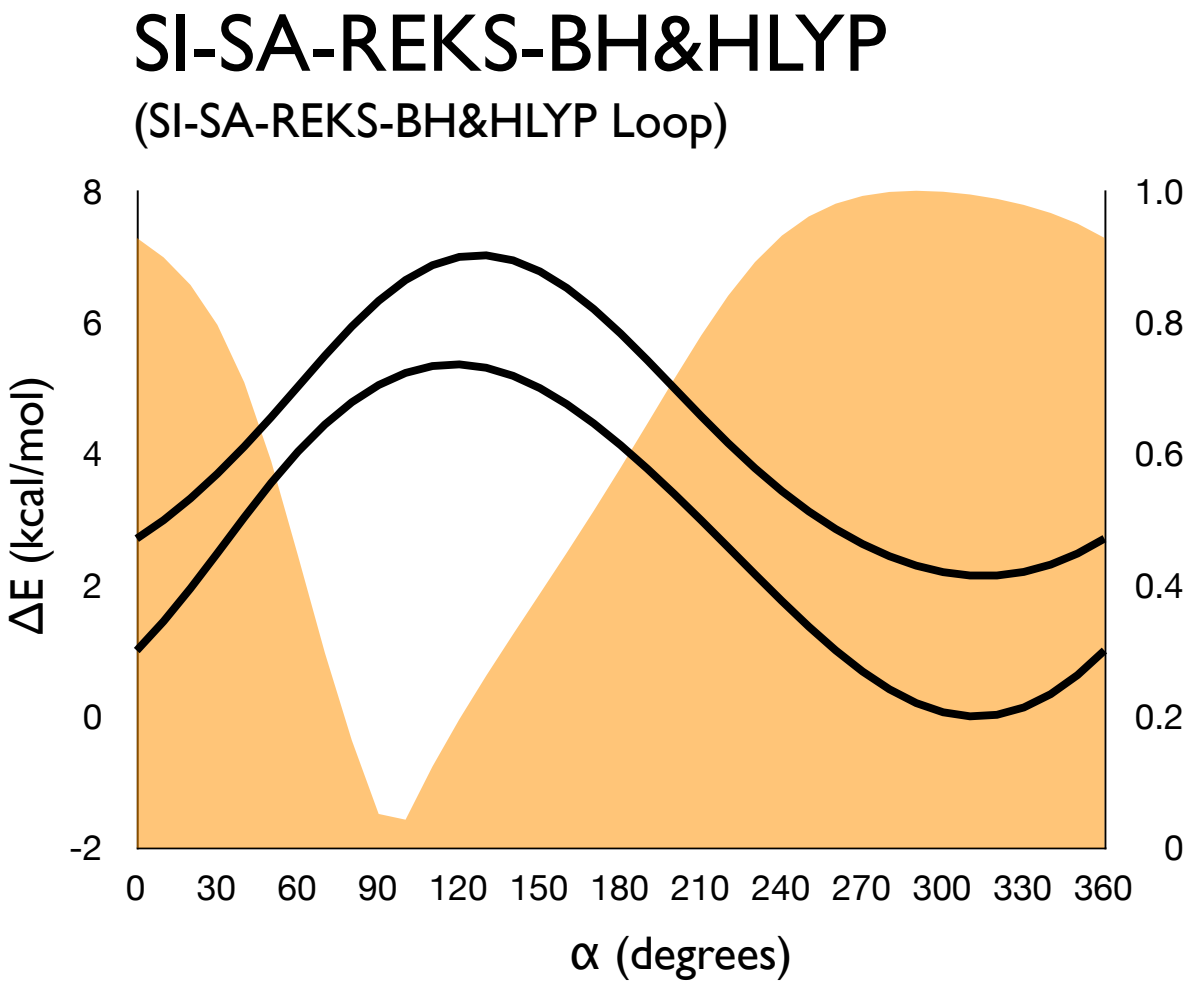

Figure S14. SI-SA-REKS-BH&HLYP S_0 and S_1 energy profiles, shown as black solid lines, along the SI-SA-REKS-BH&HLYP loop corresponding to loop E in Fig. 4 of the manuscript. The coefficient before the closed-shell configuration state function (corresponding to charge transfer character) for the S0 state in SI-SA-REKS-BH&HLYP character is shown in orange.

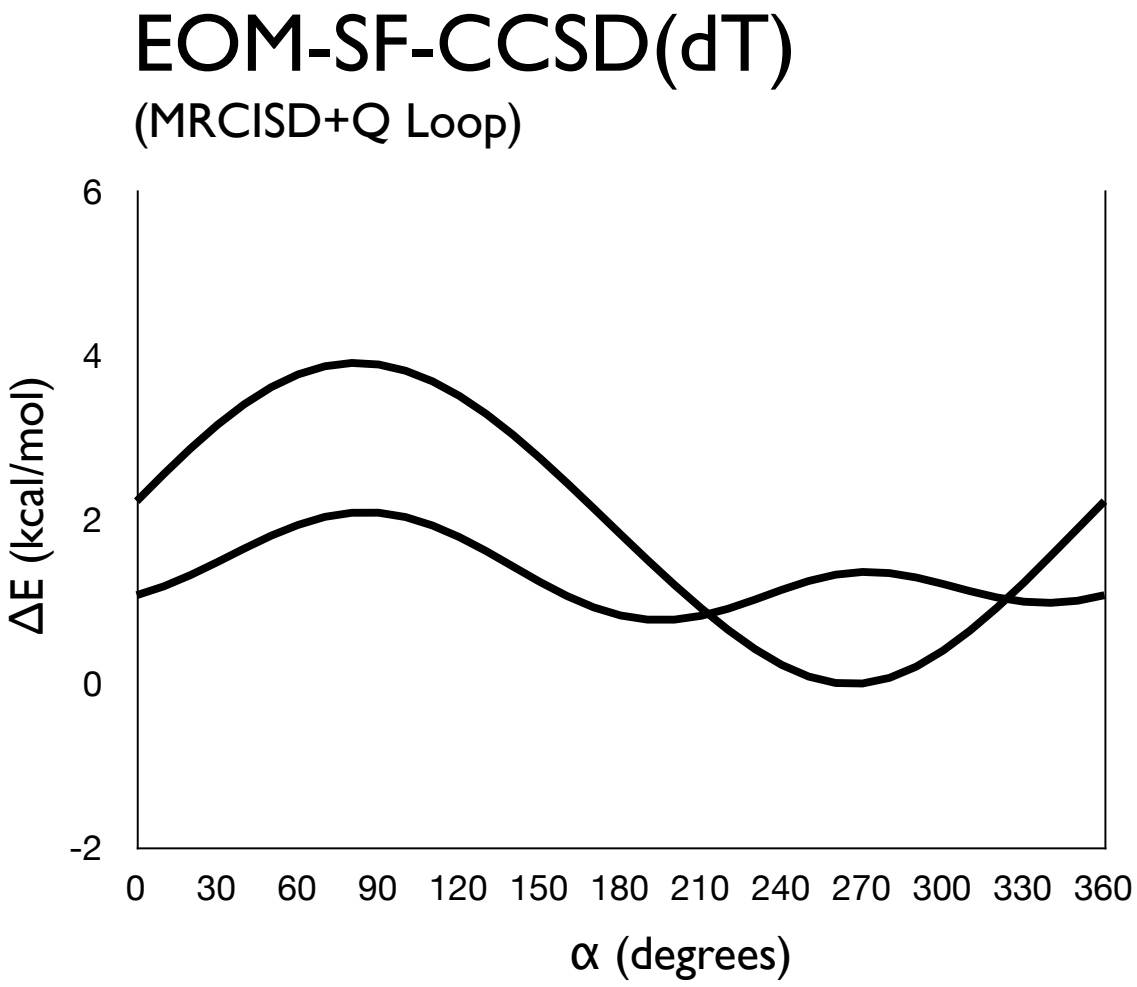

Figure S15. EOM-SF-CCSD(dT) S_0 and S_1 energy profiles, shown as black solid lines, along the MRCISD+Q loop corresponding to loop D in Fig. 3 of the manuscript.

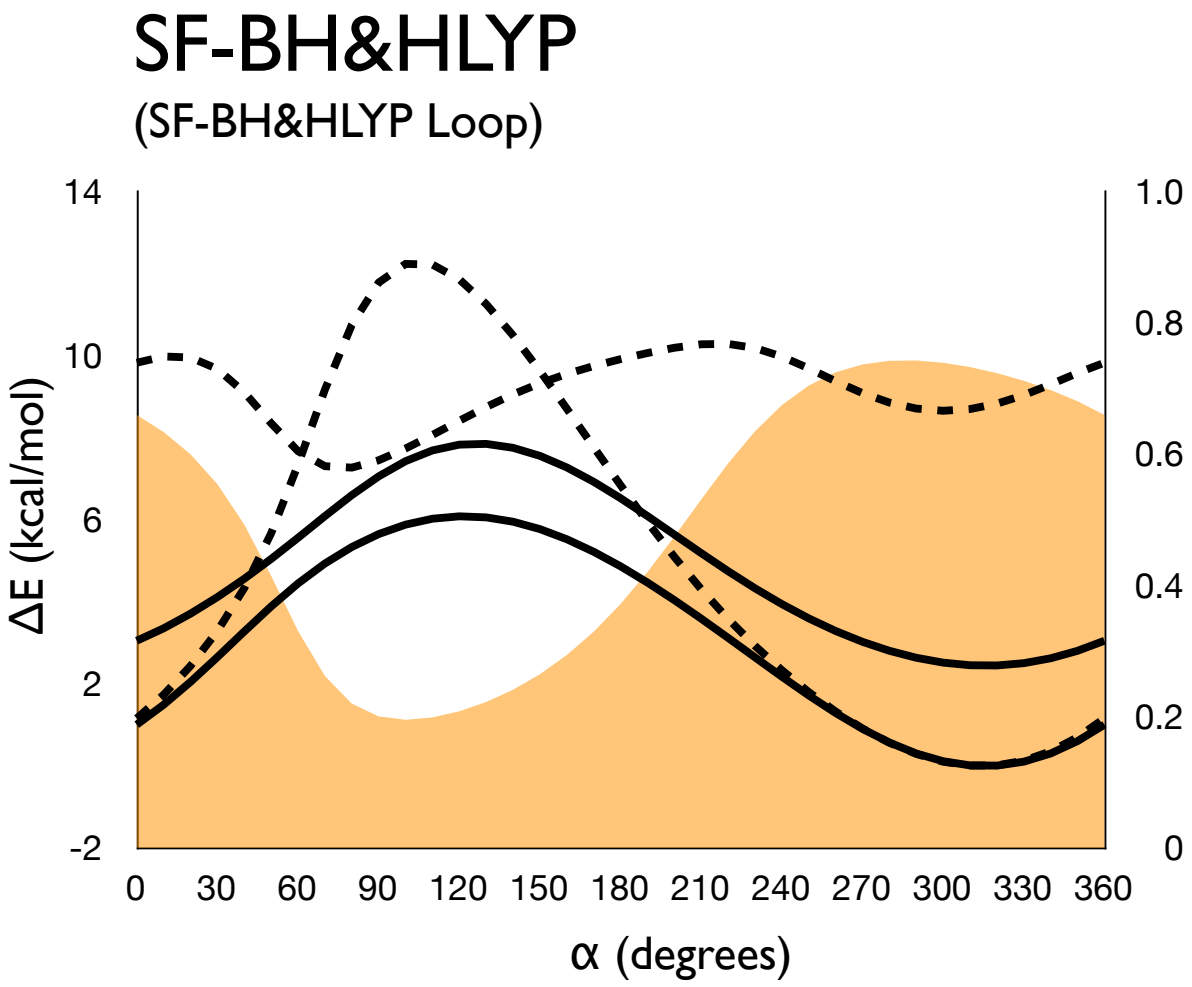

Figure S16. spin-pure SF-BH&HLYP (dashed black lines) and spin mixed SF-BH&HLYP (solid black lines) S_0 and S_1 energy profiles along the SF-BH&HLYP loop corresponding to loop F in Fig. 4 of the manuscript. The mixed-spin SF-BH&HLYP S_0 charge transfer character along the same loop is shown in orange.

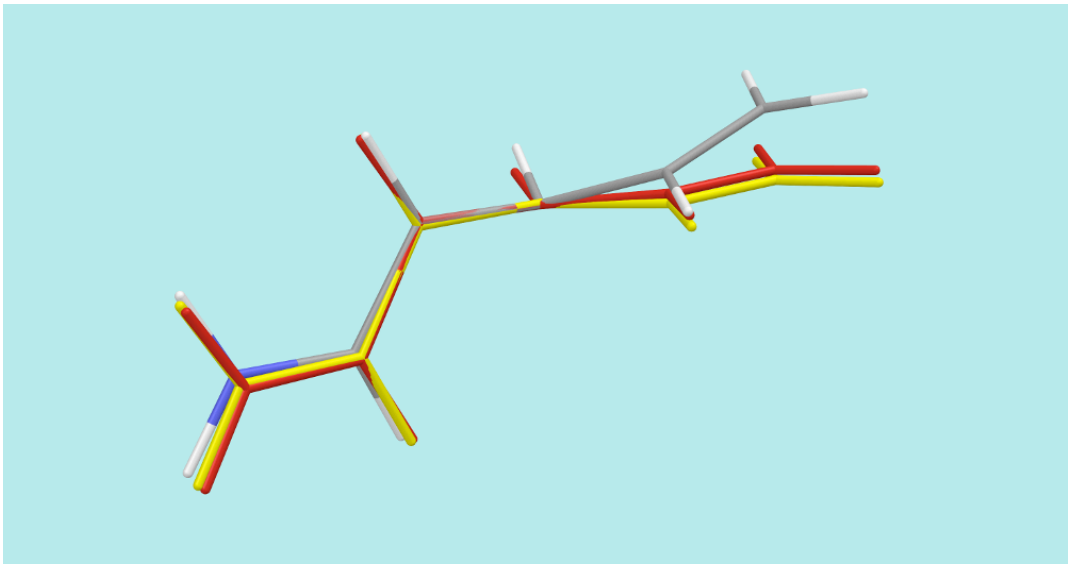

Figure S17. A figure showing the structures of three PSB3 conical intersections computed at different level of theories: mixed-spin SF-TDDFT/BH&HLYP (grey and white), SI-SA-REKS/ BH&HLYP (red), and MS-CASPT2(IPEA=0) (yellow). Notice the pyramidalization of C3 in the case of SF-BH&HLYP, which is not present with the other two methods. The MS-CASPT2 structure is from Keal et al. *Theor. Chem . Acc*., **2009**, 123:145-156.

Intersection Point Cartesian Coordinates

CI_{CASSCF} (Center of Loop A)

C	-2.849345	-0.860488	0.801696
C	-1.474218	-0.904216	0.849965
C	-0.699999	-0.062027	0.046622
C	0.758118	-0.070105	0.028753
C	1.512781	0.750770	0.834238
N	2.837650	0.793113	0.845304
H	1.237733	-0.734019	-0.673351
H	-1.219155	0.606512	-0.623496
H	1.032415	1.420752	1.523496
H	-0.981849	-1.591094	1.513974
H	3.328120	1.410074	1.455539
H	3.391765	0.220217	0.244170
H	-3.448938	-1.500680	1.419810
H	-3.365571	-0.185269	0.144608

$CI_{CASPT2(IPEA=0)}$ (Center of Loop B)

C	-2.859106	-0.868936	0.803717
C	-1.478591	-0.895284	0.841652
C	-0.702749	-0.052285	0.044173
C	0.755348	-0.068416	0.030412
C	1.521223	0.762748	0.843193
N	2.835084	0.791795	0.848182
H	1.249357	-0.729123	-0.663281
H	-1.207364	0.614607	-0.637230
H	1.042098	1.438006	1.528258
H	-0.983683	-1.581428	1.505664
H	3.338184	1.403986	1.456506
H	3.379803	0.208267	0.245476
H	-3.443119	-1.515721	1.427256
H	-3.388058	-0.201782	0.150252

CI_{MRCISD} (Center of Loop C)

C	-2.869163	-0.877955	0.810496
C	-1.481708	-0.881152	0.830931
C	-0.704478	-0.040105	0.034128
C	0.754117	-0.064243	0.024494
C	1.527601	0.775579	0.851418
N	2.826396	0.787355	0.854364
H	1.272921	-0.722503	-0.654003
H	-1.193583	0.627707	-0.657121
H	1.047743	1.455539	1.531228
H	-0.981124	-1.565812	1.493641
H	3.343439	1.395977	1.460648
H	3.363806	0.187956	0.254509
H	-3.431427	-1.535907	1.442015
H	-3.417461	-0.219889	0.163607

$CI_{MRCISD+Q}$ (Center of Loop D)

C	-2.877208	-0.885170	0.815919
C	-1.484202	-0.869847	0.822354
C	-0.705861	-0.030361	0.026092
C	0.753132	-0.060905	0.019760
C	1.532705	0.785844	0.857998
N	2.819445	0.783802	0.859310
H	1.291772	-0.717207	-0.646581
H	-1.182558	0.638188	-0.673033
H	1.052258	1.469566	1.533605
H	-0.979078	-1.553319	1.484022
H	3.347644	1.389570	1.463961
H	3.351008	0.171707	0.261736
H	-3.422074	-1.552055	1.453821
H	-3.440984	-0.234375	0.174291

$CI_{SI\text{-}SA\text{-}REKS\text{-}BH\&HLYP}$ (Center of Loop E)

C	-2.901344	-0.906817	0.832188
C	-1.491683	-0.835931	0.796622
C	-0.710010	-0.001129	0.001985
C	0.750177	-0.050891	0.005558
C	1.548014	0.816639	0.877740
N	2.798594	0.773145	0.874148
H	1.348326	-0.701318	-0.624314
H	-1.149484	0.669630	-0.720770
H	1.065806	1.511647	1.540733
H	-0.972938	-1.515841	1.455166
H	3.360257	1.370348	1.473902
H	3.312616	0.122960	0.283416
H	-3.394014	-1.600501	1.489242
H	-3.511552	-0.277833	0.206342

$CI_{SF\text{-}BH\&HLYP}$ (Center of Loop F)

C	-2.909390	-0.914032	0.837611
C	-1.494177	-0.824626	0.788045
C	-0.711393	0.008615	-0.006050
C	0.749192	-0.047553	0.000824
C	1.553117	0.826904	0.884320
N	2.791643	0.769593	0.879094
H	1.367177	-0.696022	-0.616892
H	-1.138460	0.680111	-0.736683
H	1.070322	1.525674	1.543109
H	-0.970891	-1.503349	1.445547
H	3.364462	1.363941	1.477216
H	3.299818	0.106712	0.290642
H	-3.384660	-1.616649	1.501048
H	-3.535075	-0.292319	0.217026

CASSCF Branching Plane Vectors

Derivative Coupling Vector (unscaled)

C	0.0024323242	0.0006456066	-0.0013972756
C	-0.0010566143	-0.0173473289	-0.0164343378
C	0.0004106631	-0.0022197318	0.0017297354
C	0.0039360340	0.0067622062	0.0029462521
C	-0.0112407576	0.0141765914	-0.0234341220
N	0.0091274754	-0.0013755551	0.0027783935
H	-0.0009417235	-0.0163475147	0.0149506436
H	-0.0012425043	0.0151264116	0.0153134900
H	-0.0000504582	0.0001696565	-0.0001383879
H	0.0002169387	0.0001773450	-0.0003322619
H	-0.0006375251	-0.0027951090	0.0007905030
H	-0.0007388409	0.0009355323	0.0009849002
H	-0.0000842718	0.0017225166	0.0019982334
H	-0.0001307396	0.0003693733	0.0002442341

Gradient Difference Vector (unscaled)

C	-0.0211784331	-0.0073494840	0.0066420128
C	0.0141006251	-0.0017670952	-0.0170375823
C	-0.0023799214	0.0021052101	0.0073626463
C	-0.0306415841	-0.0317599915	-0.0385554614
C	0.0805219746	0.0451810198	0.0230773243
N	-0.0669747982	-0.0065653188	-0.0034540728
H	0.0090617095	-0.0068570747	0.0117787093
H	0.0062665714	0.0087017082	0.0069717412
H	0.0003438745	-0.0001969939	-0.0000740748
H	-0.0010476031	-0.0018950154	0.0012351447
H	0.0050914046	0.0062539050	0.0082958448
H	0.0053752107	-0.0072313385	-0.0069787465
H	0.0005633183	0.0018636337	0.0001453607
H	0.0008976511	-0.0004831649	0.0005911537

SI-SA-REKS-BH&HLYP Minimum Energy Intersection Structure and Branching Plane Vectors

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MECI

C	-2.852736	-0.923422	0.839590
C	-1.505312	-0.882645	0.796538
C	-0.729179	0.012669	0.075818
C	0.705198	-0.050339	-0.002027
C	1.514748	0.809545	0.863848
N	2.796316	0.782704	0.854994
H	1.278862	-0.704156	-0.659433
H	-1.149325	0.632962	-0.723286
H	1.014788	1.498277	1.527903
H	-0.984423	-1.570022	1.451542
H	3.343352	1.375041	1.466738
H	3.318085	0.160253	0.250538
H	-3.370627	-1.601976	1.487369
H	-3.434879	-0.292692	0.195302

Derivative Coupling Vector (unscaled)

C	-0.000266	-0.000182	-0.000321
C	-0.000106	0.010250	0.011656
C	0.000226	0.003505	-0.005473
C	0.000013	-0.001576	0.004037
C	0.000340	-0.014112	0.013788
N	0.000093	0.003085	-0.002913
H	-0.000356	0.010185	-0.010159
H	0.000008	-0.010914	-0.008635
H	0.000030	-0.000063	0.000086
H	-0.000043	-0.000077	-0.000105
H	0.000040	0.001310	-0.001309
H	-0.000008	-0.000351	0.000372
H	0.000029	-0.000838	-0.000827
H	-0.000001	-0.000223	-0.000198

Gradient Difference Vector (unscaled)

C	0.002193	-0.006979	0.006510
C	-0.006870	0.001500	-0.011314
C	-0.014142	0.020647	0.022225
C	-0.026727	-0.038296	-0.041610
C	0.065087	0.035214	0.033660
N	-0.044401	-0.004628	-0.004242
H	0.008735	0.001114	-0.000199
H	0.011808	-0.005776	-0.006066
H	-0.002763	-0.000221	-0.000291
H	-0.002075	-0.002402	0.001911
H	0.003175	0.003783	0.004160
H	0.003147	-0.003937	-0.004015
H	0.001252	0.001553	-0.000899
H	0.001556	-0.001586	0.000143

SF-BH&HLYP Minimum Energy Intersection Structure and Branching Plane Vectors

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MECI

C	-2.848221	-1.057514	0.680607
C	-1.550042	-0.817836	0.908686
C	-0.797547	0.240463	0.291628
C	0.646859	0.070251	0.152148
C	1.572760	0.867980	0.899498
N	2.854326	0.725451	0.770469
H	1.091085	-0.655404	-0.528088
H	-1.206058	0.649324	-0.630428
H	1.201280	1.605330	1.594011
H	-1.048579	-1.412121	1.660506
H	3.506059	1.283134	1.307249
H	3.259378	0.045611	0.138976
H	-3.379458	-1.807119	1.239932
H	-3.410927	-0.499121	-0.049694

Derivative Coupling Vector (unscaled)

C	0.1464022	0.0127213	0.0245099
C	-0.2879974	0.0463678	0.2646564
C	0.0582477	0.3785358	-0.0162226
C	-0.1374868	-0.1947609	-0.1033964
C	0.1928887	-0.1593904	0.4176819
N	-0.1373802	0.0223361	-0.0629908
H	0.0413927	0.2682059	-0.2902238
H	0.0861506	-0.3709684	-0.2020417
H	-0.0133189	0.0070864	-0.0069319
H	-0.0057654	-0.0070288	0.0102602
H	0.0199832	0.0371549	0.0002413
H	0.0152653	-0.0207413	-0.0192662
H	0.0167748	-0.0147141	-0.0150456
H	0.0048437	-0.0048042	-0.0012306

Gradient Difference Vector (unscaled)

C	-0.0059204	0.0043829	-0.0026015
C	0.0033369	0.0248850	0.0280817
C	0.0069287	-0.0273811	-0.0313388
C	0.0178965	0.0224920	0.0302428
C	-0.0330397	-0.0331439	0.0047463
N	0.0220002	0.0033872	-0.0017810
H	-0.0061429	0.0180790	-0.0183476
H	-0.0047158	-0.0123102	-0.0032400
H	0.0016620	0.0002360	-0.0008659
H	0.0007810	0.0011330	-0.0011858
H	-0.0021434	-0.0010577	-0.0033164
H	-0.0013528	0.0024584	0.0022721
H	0.0012187	-0.0037153	-0.0030878
H	-0.0005092	0.0005548	0.0004217