Supporting Information

Multiconfigurational Dynamics Explain Photochemical Reactivity and Torquoselectivity Towards Fluorinated Polyacetylenes

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Excited-state configurations and oscillator strengths

Table S1. Computed electronic configurations and transition oscillator strengths for first excited state of **2**. All methods use the aug-cc-PVDZ basis set unless otherwise noted, and the CAS(4,4)/ANO-S-VDZP optimized geometry.

Method	**Energy S_0 (hartree)**	**Energy S_1 (hartree)**	**Configurations (Weights)**	**Oscillator Strength**
TD-CAM-B3LYP	-1060.72931146	-1060.56465761	67 → 68 (0.70052)	0.0696
CAS(4,4)	-1055.70973255	-1055.44777369	67 → 68 (0.42562) 66 → 68 (0.23235) 67 → 69 (0.13007)	0.0047
CAS(4,4)*	-1055.81262213	-1055.55089635	67 → 68 (0.41974) 66 → 68 (0.23111) 67 → 69 (0.13119)	0.0043
XMS-CASPT2(4,4)	-1058.50946994	-1058.31753590	67 → 68 (0.96195)	0.2291
XMS-CASPT2(4,4)*	-1058.50710175	-1058.30952911	67 → 68 (0.96116)	0.2377

*computed with the ANO-S-VDZP basis set

Orbital transformation

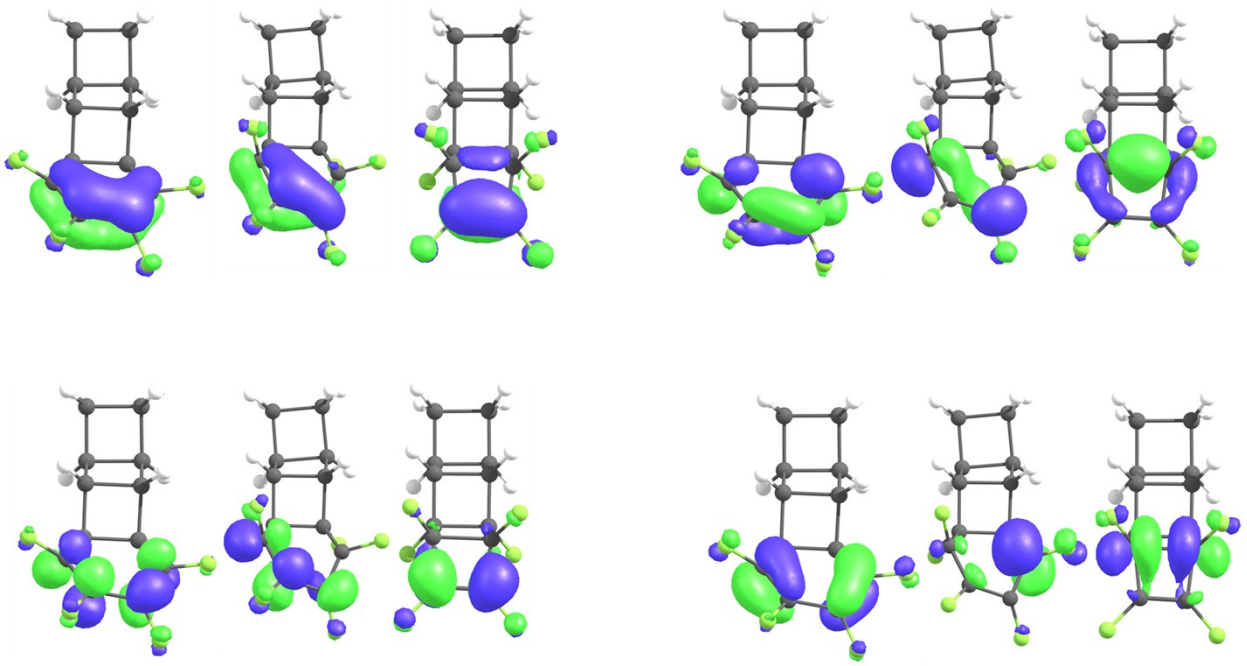

Figure S1. Snapshots of active space orbitals as the ring-closing reaction proceeds along the reaction coordinate. Geometries shown are points 5, 12, and 19 from the reaction coordinate diagram. Orbitals are computed at the SA-3-CASSCF(4,4)/ANO-L-VTZP level. Isovalue = 0.075.

Reaction coordinate diagram energies

Table S2. Absolute and relative electronic energies for reaction coordinate diagram towards **3**, computed at the CASSCF(4,4)/ANO-L-VTZP level

	Energy S_0 (hartree)	Energy S_1 (hartree)	Energy S_2 (hartree)	Relative S_0 Energy (eV)	Relative S_1 Energy (eV)	Relative S_2 Energy (eV)
0 (2)	-1056.031814	-1055.769871	-1055.753543	0.00	7.13	7.57
1	-1056.028624	-1055.782301	-1055.762151	0.09	6.79	7.34
2	-1056.020137	-1055.797391	-1055.767175	0.32	6.38	7.20
3	-1056.007197	-1055.813633	-1055.766847	0.67	5.94	7.21
4	-1055.990465	-1055.829027	-1055.760858	1.13	5.52	7.37
5	-1055.970612	-1055.842409	-1055.749087	1.67	5.15	7.69
6	-1055.948537	-1055.853760	-1055.731525	2.27	4.85	8.17
7	-1055.922424	-1055.862931	-1055.718102	2.98	4.60	8.54
8	-1055.894750	-1055.867321	-1055.714190	3.73	4.48	8.64
9 (MECP-anti)	-1055.868247	-1055.866566	-1055.711402	4.45	4.50	8.72
10	-1055.881545	-1055.852746	-1055.704702	4.09	4.87	8.90
11	-1055.894832	-1055.831310	-1055.694001	3.73	5.46	9.19

12	-1055.909510	-1055.802601	-1055.682989	3.33	6.24	9.49
13	-1055.925580	-1055.766409	-1055.679584	2.89	7.22	9.58
14	-1055.940443	-1055.728160	-1055.672560	2.49	8.26	9.78
15	-1055.955110	-1055.694846	-1055.646815	2.09	9.17	10.48
16	-1055.959842	-1055.679491	-1055.608989	1.96	9.59	11.51
17	-1055.970544	-1055.661635	-1055.597756	1.67	10.07	11.81
18 (3)	-1055.965786	-1055.669525	-1055.632148	1.80	9.86	10.88

Table S3. Absolute and relative electronic energies for reaction coordinate diagram towards **3a**, computed at the CASSCF(4,4)/ANO-L-VTZP level

	Energy S_0 (hartree)	**Energy S_1 (hartree)**	**Energy S_2 (hartree)**	**Relative S_0 Energy (eV)**	**Relative S_1 Energy (eV)**	**Relative S_2 Energy (eV)**
0 (2)	-1056.031814	-1055.769871	-1055.753543	0.00	7.13	7.57
1	-1056.028460	-1055.779689	-1055.754868	0.09	6.86	7.54
2	-1056.019397	-1055.792563	-1055.754421	0.34	6.51	7.55
3	-1056.005684	-1055.807387	-1055.750780	0.71	6.11	7.65
4	-1055.988366	-1055.822382	-1055.743008	1.18	5.70	7.86
5	-1055.968268	-1055.836506	-1055.730824	1.73	5.31	8.19
6	-1055.944102	-1055.848400	-1055.722524	2.39	4.99	8.42
7	-1055.917794	-1055.856726	-1055.722157	3.10	4.76	8.43
8	-1055.890286	-1055.861611	-1055.722945	3.85	4.63	8.40
9 (MECP-syn)	-1055.862740	-1055.861104	-1055.721715	4.60	4.65	8.44
10	-1055.870955	-1055.846630	-1055.713895	4.38	5.04	8.65
11	-1055.878843	-1055.824725	-1055.700196	4.16	5.64	9.02
12	-1055.888204	-1055.796270	-1055.682803	3.91	6.41	9.50
13	-1055.901303	-1055.759658	-1055.672149	3.55	7.41	9.79
14	-1055.914469	-1055.720507	-1055.665573	3.19	8.47	9.97
15	-1055.928112	-1055.689429	-1055.638584	2.82	9.32	10.70
16	-1055.932718	-1055.672037	-1055.611757	2.70	9.79	11.43
17	-1055.937557	-1055.651806	-1055.612968	2.56	10.34	11.40
18 (3a)	-1055.955210	-1055.631437	-1055.603728	2.08	10.89	11.65

Table S4. Absolute and relative electronic energies for reaction coordinate diagram towards **3**, computed at the XMS-CASPT2(4,4)/ANO-L-VTZP level

	Energy S_0 (hartree)	**Energy S_1 (hartree)**	**Energy S_2 (hartree)**	**Relative S_0 Energy (eV)**	**Relative S_1 Energy (eV)**	**Relative S_2 Energy (eV)**
0 (2)	-1059.371465	-1059.181887	-1059.121894	0.00	5.16	6.79
1	-1059.369750	-1059.190593	-1059.133358	0.05	4.92	6.48

2	-1059.363546	-1059.198078	-1059.145627	0.22	4.72	6.15
3	-1059.353055	-1059.204004	-1059.155546	0.50	4.56	5.88
4	-1059.338632	-1059.209365	-1059.159735	0.89	4.41	5.76
5	-1059.320785	-1059.215045	-1059.155790	1.38	4.26	5.87
6	-1059.299927	-1059.220528	-1059.141753	1.95	4.11	6.25
7	-1059.276619	-1059.224428	-1059.116478	2.58	4.00	6.94
8	-1059.253237	-1059.226974	-1059.107531	3.22	3.93	7.18
9 (MECP-anti)	-1059.235934	-1059.219827	-1059.106077	3.69	4.13	7.22
10	-1059.241537	-1059.217040	-1059.102109	3.54	4.20	7.33
11	-1059.255109	-1059.200102	-1059.095352	3.17	4.66	7.51
12	-1059.270072	-1059.178485	-1059.089760	2.76	5.25	7.67
13	-1059.285588	-1059.158638	-1059.083665	2.34	5.79	7.83
14	-1059.301929	-1059.140814	-1059.064146	1.89	6.28	8.36
15	-1059.319080	-1059.125091	-1059.032755	1.43	6.70	9.22
16	-1059.334103	-1059.114125	-1059.063981	1.02	7.00	8.37
17	-1059.346173	-1059.099562	-1059.053292	0.69	7.40	8.66
18 (3)	-1059.350527	-1059.090978	-1059.069573	0.57	7.63	8.21

Table S5. Absolute and relative electronic energies for reaction coordinate diagram towards **3a**, computed at the XMS-CASPT2(4,4)/ANO-L-VTZP level

	Energy S_0 (hartree)	**Energy S_1 (hartree)**	**Energy S_2 (hartree)**	**Relative S_0 Energy (eV)**	**Relative S_1 Energy (eV)**	**Relative S_2 Energy (eV)**
0 (2)	-1059.371465	-1059.181887	-1059.121894	0.00	5.16	6.79
1	-1059.368711	-1059.184089	-1059.129349	0.07	5.10	6.59
2	-1059.361794	-1059.187665	-1059.137976	0.26	5.00	6.35
3	-1059.350985	-1059.192600	-1059.144692	0.56	4.87	6.17
4	-1059.336555	-1059.198749	-1059.146307	0.95	4.70	6.13
5	-1059.318783	-1059.204946	-1059.140574	1.43	4.53	6.28
6	-1059.298230	-1059.210007	-1059.125667	1.99	4.39	6.69
7	-1059.276052	-1059.217188	-1059.118899	2.60	4.20	6.87
8	-1059.252631	-1059.221542	-1059.118576	3.23	4.08	6.88
9 (MECP-syn)	-1059.232382	-1059.217119	-1059.119488	3.78	4.20	6.86
10	-1059.232521	-1059.214888	-1059.113891	3.78	4.26	7.01
11	-1059.241805	-1059.196958	-1059.103049	3.53	4.75	7.30
12	-1059.252812	-1059.173611	-1059.089630	3.23	5.38	7.67
13	-1059.266148	-1059.149269	-1059.079136	2.87	6.05	7.95
14	-1059.282369	-1059.131618	-1059.061581	2.42	6.53	8.43
15	-1059.299692	-1059.118317	-1059.031100	1.95	6.89	9.26
16	-1059.314972	-1059.107597	-1059.073479	1.54	7.18	8.11
17	-1059.327827	-1059.093883	-1059.077837	1.19	7.55	7.99

18 (3a)	-1059.323931	-1059.065719	-1059.047127	1.29	8.32	8.83

Branching plane vectors

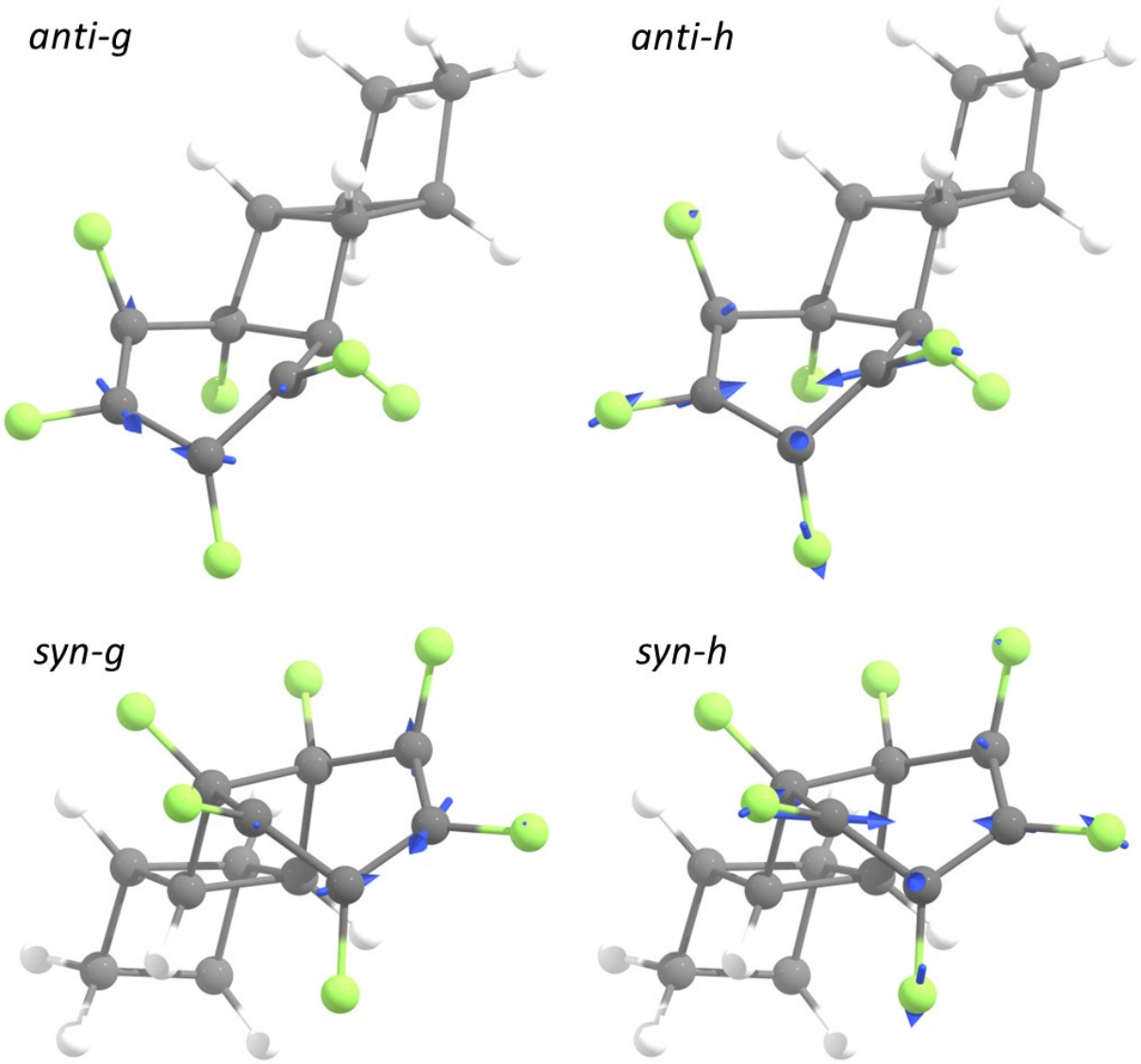

Figure S2. Branching plane vectors *g* (left) and *h* (right) for **MECP-*anti*** (top) and **MECP-*syn*** (bottom). **MECP-*syn*** geometry is rotated upside-down to better illustrate the equivalency between the *syn* and *anti* vectors.

Coordinates of optimized geometries

2

E(CASSCF) = −1055.8126224143039

C	-1.19616696	-0.76479943	-0.58527735
C	-2.60224890	-0.83585764	0.02827159
C	-2.63097196	0.72658123	0.15360359
C	-1.22428931	0.80557585	-0.45770553
C	-3.72335589	-0.76383329	-1.03193713
C	-3.75099972	0.78335389	-0.90882105
H	-4.64670199	-1.23589435	-0.70311642
H	-3.46396631	-1.16233679	-2.01169283
H	-4.68990795	1.16464922	-0.51310986
H	-3.50774535	1.34049862	-1.81237748
H	-1.01525571	-1.30308291	-1.51059419
H	-1.06364347	1.49217699	-1.28324144
H	-2.74127551	-1.51619474	0.86088634
H	-2.79355873	1.25985354	1.08341677
C	-0.05595431	-0.82217439	0.44649344
C	1.23259407	-1.40725393	-0.04669913
C	2.30327692	-0.66374247	-0.34450113
C	2.27691791	0.80036746	-0.21639578
C	1.18002485	1.44299914	0.19713129
C	-0.08603696	0.73584660	0.57578439
F	1.23850628	-2.71868677	-0.17915725
F	3.41351810	-1.18199457	-0.81758432
F	3.36950396	1.43156830	-0.58126232
F	1.14073959	2.75685790	0.29617968
F	-0.42294702	1.14452657	1.81973233
F	-0.36812068	-1.44465200	1.60548082

3

E(CASSCF) = −1055.7531246562328

C	1.40780878	-0.79376312	0.43714828
C	2.60006482	-0.78357578	-0.53105354
C	2.59808408	0.78163081	-0.53347308
C	1.40611366	0.79182225	0.43469704
C	3.96441331	-0.77417288	0.19278491
C	3.96273634	0.77778598	0.18980069
H	4.76528670	-1.20258159	-0.40618254
H	3.97290372	-1.25176537	1.17134234
H	4.76204543	1.20522350	-0.41196349
H	3.97148892	1.25954124	1.16631133
H	1.47374269	-1.40755176	1.32883197
H	1.46977541	1.40835558	1.32444240

H	2.51055951	-1.39584936	-1.42220090
H	2.50712604	1.39103360	-1.42644970
C	0.07088603	-0.78814380	-0.29044113
C	-1.14528552	-0.77403121	0.63224587
C	-2.47184741	-0.66964239	-0.06727865
C	-2.48276081	0.67829055	-0.03213000
C	-1.14551013	0.77472445	0.63423477
C	0.06885622	0.78180656	-0.29365116
F	-1.07977624	-1.47409947	1.76738113
F	-3.16749991	-1.57806759	-0.68894622
F	-3.15363317	1.58540603	-0.68362446
F	-1.05926682	1.46977972	1.77317763
F	-0.05129309	1.52823366	-1.40193574
F	-0.04776362	-1.54027762	-1.39552673

3a

E(CASSCF) = −1055.7407926394415

C	1.08058233	0.31224694	0.79482066
C	2.50160266	-0.27141943	0.78260858
C	2.50207984	-0.27218047	-0.78240170
C	1.08079955	0.31052070	-0.79651047
C	3.60286123	0.81133070	0.77602441
C	3.60206087	0.81209375	-0.77588331
H	4.54125468	0.46357587	1.20288768
H	3.33374954	1.75072947	1.25684481
H	4.54054121	0.46691683	-1.20461381
H	3.33037838	1.75163651	-1.25496374
H	0.89767511	1.18360867	1.41663660
H	0.89784337	1.18040127	-1.42037552
H	2.67017535	-1.15252456	1.39280078
H	2.67229892	-1.15369366	-1.39157486
C	0.01412927	-0.77785164	0.76900871
C	-1.47618911	-0.30141890	0.76066628
C	-1.78708713	1.16429751	0.69782963
C	-1.78672996	1.16374661	-0.69934411
C	-1.47593143	-0.30211420	-0.76081470
C	0.01422697	-0.77925560	-0.76844659
F	-2.33792015	-1.07902094	1.41797557
F	-1.80236352	2.12114686	1.57153516
F	-1.80051293	2.12007335	-1.57370836
F	-2.33788404	-1.07996023	-1.41755823
F	0.20504500	-1.87770737	-1.51151779
F	0.20562297	-1.87475302	1.51419833

MECP-*anti*

E(CASSCF) = −1055.6510797252110

C	-1.28238495	0.46629979	0.75656221
C	-2.59145807	0.90993764	0.10126802
C	-2.62181376	-0.40451313	-0.74819493
C	-1.40388937	-0.93338732	0.04131371
C	-3.84549996	0.41693257	0.86615322
C	-3.96124459	-0.79490063	-0.09614339
H	-4.68711489	1.10441156	0.82483002
H	-3.66174305	0.16198122	1.90871378
H	-4.79398735	-0.69028208	-0.78919309
H	-4.00793345	-1.78423970	0.35673250
H	-1.14093225	0.60456821	1.82367233
H	-1.52451253	-1.87468180	0.56061974
H	-2.63379392	1.90683134	-0.32243032
H	-2.54675280	-0.43461826	-1.83006459
C	-0.06040745	0.77281355	-0.13634596
C	1.25551450	1.08978753	0.51055886
C	2.53237030	0.62551337	0.07182257
C	2.38377336	-0.75967936	0.14521980
C	1.08838800	-1.41360978	0.04500558
C	-0.05502926	-0.68623026	-0.62959095
F	1.21683751	2.06650569	1.37514605
F	3.31238015	1.28730810	-0.78848002
F	3.39679191	-1.53501282	0.41665525
F	0.74916579	-2.08872530	1.15505439
F	0.02303445	-0.85822259	-1.96678468
F	-0.29456733	1.71553048	-1.08437407

MECP-*syn*

E(CASSCF) = −1055.6454206497895

C	-1.21339573	-0.79532201	0.19610068
C	-2.58910712	-0.19023810	0.54769454
C	-2.41259407	0.86031992	-0.59825482
C	-0.98751742	0.36075320	-0.85400425
C	-3.74417261	-0.84714491	-0.23213233
C	-3.47534743	0.10102477	-1.43071362
H	-4.70854795	-0.65830739	0.23554439
H	-3.65220761	-1.91618676	-0.41805298
H	-4.32900449	0.71193939	-1.71475317
H	-3.08552699	-0.38135272	-2.32559723
H	-1.17758209	-1.85476894	-0.03660111
H	-0.65757963	0.20761239	-1.87674542
H	-2.75119636	0.06252187	1.59034710
H	-2.55504057	1.92706871	-0.46913945
C	-0.04731323	-0.22999694	1.01544893
C	1.23510408	-1.00617252	0.77361458
C	1.82779371	-1.20190021	-0.51579466

C	2.18054786	0.08598902	-0.90787186
C	1.43912646	1.24449147	-0.41711105
C	0.04121653	1.01077264	0.10469455
F	1.58474623	-1.80430592	1.74181628
F	1.47467225	-2.19587947	-1.34923183
F	3.19320584	0.32088126	-1.70026978
F	2.14733967	2.10001392	0.31603089
F	-0.38773598	2.14446894	0.69169474
F	-0.23610336	-0.03347359	2.32638189

Anti S_1 minimum
E(CASSCF) = −1055.6538537074716

C	-1.33283783	-0.91860902	-0.34513644
C	-2.61268407	-0.73022966	0.49561674
C	-2.62804523	0.79071526	0.12430172
C	-1.29090473	0.63337757	-0.60560499
C	-3.89898175	-0.94278491	-0.32629853
C	-3.84601377	0.53501996	-0.79693274
H	-4.76021913	-1.14512596	0.30757556
H	-3.85140042	-1.70724580	-1.10047954
H	-4.72545086	1.11669566	-0.53015744
H	-3.64831674	0.67976253	-1.85802461
H	-1.35567913	-1.66812319	-1.12488919
H	-1.16672100	1.09365618	-1.58068305
H	-2.58542595	-1.11086503	1.51062534
H	-2.71424960	1.59297424	0.84820745
C	-0.03396624	-0.80995946	0.45913317
C	1.17643825	-1.36025220	-0.24430506
C	2.44097493	-0.66623784	-0.19302276
C	2.51498535	0.73247100	-0.06988615
C	1.18815029	1.26884503	-0.23217020
C	-0.08085343	0.73157502	0.34640469
F	0.95502916	-2.03998908	-1.37601551
F	3.52202620	-1.36609164	-0.38232787
F	3.36489606	1.32219409	0.78270862
F	1.08943421	2.46970140	-0.73389276
F	-0.33875634	1.38943213	1.50551156
F	-0.07526690	-1.27873894	1.72991582

Syn S_1 minimum
E(CASSCF) = −1055.6464885191979

C	-1.15779641	-0.83587928	-0.40386890
C	-2.60192575	-0.73250804	0.13006645
C	-2.55478397	0.82030412	-0.05860680
C	-1.07791867	0.73768798	-0.45729044

C	-3.65721226	-0.83589284	-0.98842135
C	-3.51451852	0.68417297	-1.26612927
H	-4.63980648	-1.09549922	-0.59925945
H	-3.42046862	-1.51073639	-1.80966268
H	-4.44024712	1.24376016	-1.15369712
H	-3.07183277	0.94278145	-2.22672463
H	-0.98437118	-1.49143492	-1.25149154
H	-0.73095456	1.30774297	-1.31367486
H	-2.80377088	-1.22852532	1.07366350
H	-2.82630248	1.53303902	0.71157823
C	-0.07396084	-0.82022048	0.68176508
C	1.28984355	-1.18513165	0.13768748
C	2.00552358	-0.42718503	-0.85879925
C	2.10011191	0.89588970	-0.40711062
C	1.20451967	1.39797186	0.62483034
C	-0.13551135	0.72024752	0.77415247
F	1.61881291	-2.43938458	0.28525330
F	1.88262843	-0.72930233	-2.16476050
F	2.99980201	1.71113653	-0.88517984
F	1.78195711	1.75153663	1.76875931
F	-0.70752164	1.15825631	1.91235706
F	-0.31236068	-1.50847514	1.80807103