Electronic Supplementary Information

THEORETICAL STUDY ON THE PHOTOOXYGENATION AND PHOTOREARRANGEMENT REACTIONS OF 3-HYDROXYFLAVONE

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Table S1 – The calculated excitation energies on the S_1 optimized structures of the normal (N*) and phototautomeric (PT*) forms of 3HF in hexane.[a]

State	Excitation energies (eV)			
	N* form multiplicity		PT* form multiplicity	
	triplet	singlet	singlet	triplet
1	1.60	3.41	2.47	1.76
2	2.00			2.39
3	2.08			2.66
4	2.54			3.06
5	2.66			3.12
6	2.89			3.34
7	2.95			3.47
8	3.04			3.61
9	3.07			3.68
10	3.49			4.02
11	3.68			4.03
12	3.68			4.19
13	3.89			4.38
14	4.04			4.44
15	4.13			4.55
16	4.14			4.63
17	4.23			4.67
18	4.32			4.68
19	4.45			4.79
20	4.46			4.88

[a] The excitation energies were calculated on the optimized S_1 structures employing the M062X functional with the 6-311++G** basis set.

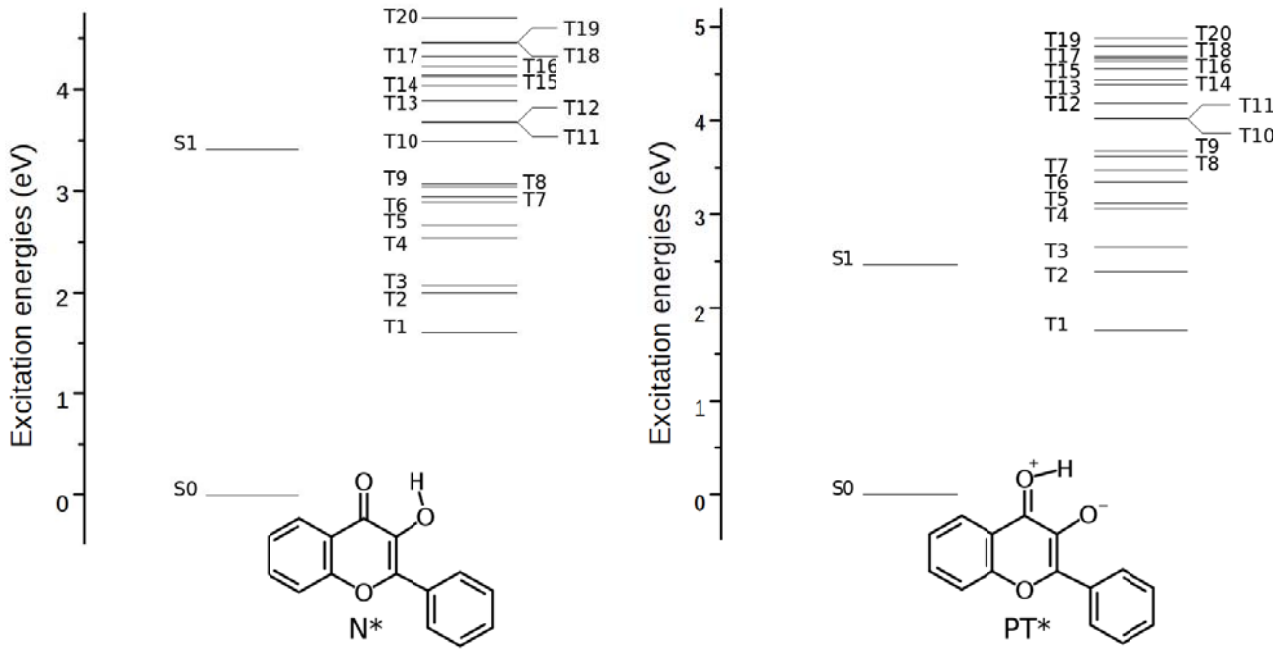

Table S2. Descartes coordinates of the stationary points in the photooxygenation reaction of 3HF with $^3O_2$ in *n*-hexane (see Fig. 3 in the main text)

^{1}N

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.401366
C	1.223740	0.000000	2.082939
C	2.416651	-0.004765	1.370612
C	2.409772	-0.015043	-0.020238
C	1.196638	-0.012502	-0.702590
C	-1.283280	0.012587	2.119764
C	-1.509589	-0.354319	3.407300
C	-2.846734	-0.323208	3.992115
C	-3.908736	0.131088	3.102721
C	-3.581821	0.486440	1.795014
O	-2.313523	0.424817	1.329209
C	-4.562144	0.929689	0.902038
C	-5.869265	1.009379	1.336463
C	-6.218003	0.653832	2.650653
C	-5.245169	0.219279	3.523802
O	-3.002959	-0.677720	5.155841
O	-0.533189	-0.791322	4.231100
H	-5.476336	-0.062762	4.543947
H	-7.249366	0.723505	2.972071
H	-6.635695	1.352295	0.651883
H	-4.273220	1.200790	-0.105429
H	-0.980844	-1.007836	5.066755
H	1.241596	0.009610	3.162835
H	3.356882	0.000788	1.908748
H	1.181488	-0.020119	-1.785842
H	-0.940638	0.004465	-0.534471
H	3.343525	-0.022685	-0.569748

^{1}N*

C	-3.671874	0.339735	0.027178
C	-2.268629	0.356271	0.006687
C	-1.589121	-0.874487	-0.007605
C	-2.262810	-2.075990	-0.001772
C	-3.666101	-2.071094	0.019245
C	-4.362077	-0.868512	0.033431
O	-0.208254	-0.949250	-0.029462
C	0.597193	0.139160	-0.017151
C	-0.053347	1.404037	-0.022356
C	-1.502390	1.573100	-0.004981
C	1.987078	-0.140046	-0.003171
C	2.421561	-1.499736	-0.039839
C	3.764489	-1.807693	-0.029033
C	4.728932	-0.794491	0.020975
C	4.321972	0.543346	0.061719
C	2.984328	0.879474	0.051591
O	0.612815	2.535341	-0.047870
O	-1.934825	2.748841	-0.011129
H	-4.190352	1.290499	0.037260
H	-5.444902	-0.869760	0.049093
H	-4.199860	-3.013059	0.023589
H	-1.697975	-2.999556	-0.013638
H	-0.099032	3.222360	-0.041128
H	2.695104	1.918614	0.088356
H	5.064414	1.331226	0.104569
H	4.073770	-2.845660	-0.059988
H	1.682884	-2.288055	-0.080013
H	5.782836	-1.044501	0.030069

^{3}N*

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.425649
C	1.260017	0.000000	2.091133
C	2.433352	0.006757	1.363646
C	2.414629	0.016830	-0.033670
C	1.186417	0.012200	-0.702756
C	-1.221364	-0.005515	2.118965
C	-1.446687	0.037624	3.575396
C	-2.661446	-0.406126	4.172740
C	-3.695007	-0.867001	3.234543
C	-3.502895	-0.652054	1.867374
O	-2.365625	-0.042159	1.374009
C	-4.469022	-1.009308	0.941560
C	-5.645800	-1.602589	1.389961
C	-5.852424	-1.833716	2.747894
C	-4.878732	-1.462363	3.666174
O	-2.791703	-0.327872	5.411855
O	-0.532939	0.547633	4.370953
H	-5.014744	-1.614698	4.730302
H	-6.770824	-2.295871	3.086922
H	-6.404382	-1.884619	0.669979
H	-4.290525	-0.818646	-0.109087
H	-0.912339	0.488477	5.273344
H	1.301168	-0.010658	3.170393
H	3.380781	0.001493	1.889509
H	1.162716	0.015837	-1.786186
H	-0.945576	-0.005805	-0.524669
H	3.341879	0.023263	-0.592742

^{1}PT

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.405991
C	1.227907	0.000000	2.088509
C	2.418468	-0.000021	1.371422
C	2.410023	-0.000021	-0.018897
C	1.194542	0.000000	-0.701383
C	-1.259739	-0.000022	2.138412
C	-1.403875	0.000592	3.541081
C	-2.760400	0.000466	4.012439
C	-3.876109	-0.000134	3.155613
C	-3.601563	-0.000728	1.779769
O	-2.343477	-0.000713	1.331439
C	-4.634695	-0.001376	0.831585
C	-5.935027	-0.001379	1.275825
C	-6.234347	-0.000765	2.658831
C	-5.226679	-0.000173	3.586566
O	-2.881949	0.001074	5.317244
O	-0.499046	0.001235	4.428889
H	-5.432034	0.000304	4.649595
H	-7.268129	-0.000799	2.980126
H	-6.743766	-0.001843	0.555519
H	-4.382859	-0.001823	-0.221190
H	-1.941392	0.001415	5.628067
H	1.228378	0.000049	3.169125
H	3.359862	-0.000037	1.907752
H	1.179755	0.000016	-1.784731
H	-0.938893	0.000016	-0.537404
H	3.342748	-0.000021	-0.570377

^{1}PT*

C	0.000081	-0.000015	-0.000061
C	0.000002	-0.000002	1.413285
C	1.243700	0.000019	2.086292
C	2.435920	0.000028	1.390341
C	2.411187	0.000010	-0.007866
C	1.197009	-0.000011	-0.695985
O	1.321781	0.000010	3.449887
C	0.223087	0.000080	4.261694
C	-1.075596	0.000091	3.650308
C	-1.156352	0.000010	2.207558
C	0.529807	0.000140	5.652798
C	1.889620	0.000303	6.066407
C	2.219199	0.000358	7.408659
C	1.221988	0.000247	8.384613
C	-0.119884	0.000077	7.994636
C	-0.473502	0.000021	6.658978
O	-2.162100	0.000154	4.282548
O	-2.367072	0.000011	1.659848
H	-0.951536	-0.000030	-0.516235
H	1.190393	-0.000023	-1.778708
H	3.345888	0.000012	-0.554549
H	3.366935	0.000042	1.942893
H	-3.000269	0.000061	2.401088
H	-1.513635	-0.000121	6.370177
H	-0.899829	-0.000023	8.747027
H	3.262757	0.000488	7.701016
H	2.671153	0.000396	5.319225
H	1.485714	0.000288	9.435419

^{3}PT*

C	0.018096	-0.000282	-0.003160
C	0.026891	-0.000029	1.411670
C	1.278701	0.000235	2.071441
C	2.453428	0.000255	1.338903
C	2.429500	0.000014	-0.055590
C	1.203504	-0.000254	-0.718042
C	-1.221117	-0.000080	2.116643
C	-1.424768	0.000465	3.559967
C	-2.784813	0.000375	4.056333
C	-3.891651	-0.000151	3.168517
C	-3.611801	-0.000646	1.789495
O	-2.322198	-0.000656	1.306382
C	-4.623740	-0.001166	0.853256
C	-5.953630	-0.001205	1.282970
C	-6.255219	-0.000722	2.641895
C	-5.233578	-0.000197	3.581523
O	-2.969753	0.000873	5.377096
O	-0.500292	0.001010	4.389207
H	-5.446936	0.000187	4.643072
H	-7.287649	-0.000755	2.967870
H	-6.749336	-0.001616	0.548706
H	-4.365594	-0.001539	-0.198218
H	-2.086941	0.001217	5.784303
H	1.314481	0.000421	3.149820
H	3.401935	0.000454	1.862795
H	1.172420	-0.000440	-1.801196
H	-0.927245	-0.000486	-0.527369
H	3.355009	0.000032	-0.618471

TS0

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.422300
C	1.249500	0.000000	2.100500
C	2.430700	-0.000100	1.386200
C	2.415800	-0.000100	-0.011400
C	1.193900	-0.000100	-0.692100
C	-1.208000	0.000100	2.167900
C	-2.529900	-0.000200	1.679300
C	-3.696100	-0.000100	2.572400
C	-3.476100	-0.000300	3.965000
C	-2.128900	-0.000000	4.402800
O	-1.061900	0.000600	3.523200
C	-1.811800	-0.000300	5.741800
C	-2.843600	-0.000800	6.694300
C	-4.175300	-0.001000	6.289000
C	-4.496500	-0.000800	4.939000
O	-2.941400	-0.000600	0.461000
O	-4.777800	-0.000400	1.891000
H	-4.072300	-0.000600	0.779800
H	-5.525700	-0.001100	4.602100
H	-4.965500	-0.001400	7.029600
H	-2.592800	-0.000900	7.747400
H	-0.769800	-0.000100	6.036000
H	1.263700	0.000000	3.181900
H	3.375900	-0.000100	1.915800
H	3.346800	-0.000200	-0.565200
H	1.179800	-0.000100	-1.775400
H	-0.939000	0.000100	-0.535500

TS1

C	-3.641928	0.401431	-0.298625
C	-2.224772	0.402160	-0.309357
C	-1.545595	-0.822182	-0.395030
C	-2.240703	-2.037334	-0.473123
C	-3.614628	-2.009960	-0.461071
C	-4.319886	-0.786521	-0.373819
O	-0.209072	-0.866688	-0.406056
C	0.578714	0.228627	-0.329707
C	0.014379	1.517076	-0.228951
C	-1.422042	1.553483	-0.222671
C	2.001099	-0.088210	-0.340465
C	2.964218	0.929622	-0.244132
C	4.315638	0.605559	-0.245566
C	4.728523	-0.718716	-0.341798
C	3.776960	-1.732723	-0.438138
C	2.426219	-1.424866	-0.437876
O	0.606561	2.633372	-0.140280
O	-1.933981	2.755876	-0.126426
O	-0.654955	-0.571676	2.386680
O	0.505031	-0.388460	2.571751
H	-1.132809	3.336473	-0.082451
H	-4.160940	1.349080	-0.229455
H	-5.402392	-0.795263	-0.365894
H	-4.166206	-2.940120	-0.519764
H	-1.680812	-2.961473	-0.538773
H	2.637467	1.956739	-0.167182
H	5.050579	1.398032	-0.169948
H	5.784262	-0.962622	-0.341817
H	4.090747	-2.766970	-0.513827
H	1.694250	-2.217956	-0.514280

NP

C	0.033271	0.134902	0.029928
C	0.027501	-0.030558	1.412666
C	1.223649	-0.192693	2.108677
C	2.428053	-0.197368	1.415566
C	2.438574	-0.037713	0.033140
C	1.242217	0.128529	-0.656995
C	-1.259270	0.043118	2.176073
O	-2.345281	-0.311050	1.338157
C	-3.596528	-0.227311	1.913759
C	-3.810656	0.396962	3.145118
C	-2.605450	0.947500	3.871759
C	-1.607718	1.396058	2.816562
C	-4.658434	-0.770395	1.204424
C	-5.941238	-0.678832	1.729752
C	-6.167194	-0.053546	2.953777
C	-5.098848	0.485359	3.659199
O	-1.827531	-0.129556	4.443351
O	-1.231288	-0.812935	3.304627
O	-1.179615	2.485515	2.606135
O	-2.925597	1.837609	4.847542
H	-5.249318	0.986195	4.607565
H	-7.170627	0.016170	3.353625
H	-6.771379	-1.100025	1.175696
H	-4.463838	-1.251599	0.254410
H	1.205981	-0.327433	3.183349
H	-0.901355	0.261543	-0.500621
H	1.248106	0.253459	-1.732974
H	3.357793	-0.329995	1.955240
H	-2.170115	2.412805	5.022888
H	3.378613	-0.043549	-0.505577

TS2a

C	2.362700	1.394900	0.400800
C	2.074900	0.206100	-0.260700
C	3.082300	-0.703800	-0.567600
C	4.393200	-0.416000	-0.208200
C	4.694100	0.774000	0.448800
C	3.680400	1.676500	0.749700
C	0.634000	-0.138700	-0.610800
C	0.062500	-1.002000	0.656500
C	-1.401000	-1.505200	-0.012800
C	-2.181500	-0.202600	0.058600
C	-1.517200	0.969600	-0.321100
O	-0.172200	1.037200	-0.625000
C	-2.207900	2.174800	-0.363800
C	-3.553600	2.209300	-0.021500
C	-4.217300	1.050100	0.372200
C	-3.525200	-0.153800	0.411100
O	0.490500	-0.934000	-1.612000
O	0.479400	-1.290500	1.694200
O	-1.827200	-2.551300	0.786000
O	-1.074100	-1.864700	-1.217500
H	-1.627600	-2.359200	1.712100
H	-4.019000	-1.073500	0.702600
H	-5.265400	1.083700	0.640700
H	-4.085300	3.152400	-0.059100
H	-1.674600	3.068800	-0.662100
H	2.837900	-1.620600	-1.089500
H	5.180900	-1.119500	-0.448700
H	5.718000	0.997400	0.723400
H	3.911200	2.604600	1.258500
H	1.569100	2.093800	0.629000

TS2b

O	0.803787	-1.564878	1.440490
C	1.418812	-1.436757	-0.159308
C	0.051450	-1.063829	-0.745218
C	-0.601378	-0.191278	0.342752
O	-0.553511	-1.090207	1.454071
C	2.229042	-0.198002	-0.151246
C	1.530349	0.962576	0.207384
O	0.204057	0.943382	0.590102
C	3.575152	-0.140755	-0.486690
C	4.231595	1.083254	-0.467081
C	3.533681	2.233072	-0.103070
C	2.185008	2.183323	0.237488
C	-2.031986	0.193888	0.128284
C	-2.979701	-0.818375	-0.027460
C	-4.309916	-0.488664	-0.248590
C	-4.694478	0.847694	-0.317233
C	-3.746795	1.853683	-0.165323
C	-2.412314	1.530581	0.057398
O	1.846338	-2.652685	-0.151808
O	-0.404672	-1.411063	-1.787246
H	-2.677502	-1.857487	0.026742
H	-5.045494	-1.274314	-0.369156
H	-5.732868	1.103390	-0.491224
H	-4.044516	2.893726	-0.219199
H	-1.669630	2.307610	0.177164
H	1.640040	3.070619	0.533351
H	4.045604	3.187559	-0.080879
H	5.279578	1.142994	-0.730322
H	4.082592	-1.058686	-0.758678
H	1.083072	-2.614273	0.934817

XP

C	0.457815	0.391119	-0.004424
C	0.194940	0.121478	1.461061
C	1.267687	-0.145805	2.311709
C	1.031529	-0.429165	3.650872
C	-0.270498	-0.453597	4.142574
C	-1.337839	-0.191610	3.291296
C	-1.108640	0.096965	1.949742
H	2.277881	-0.131729	1.924992
H	1.866161	-0.632506	4.310694
H	-0.451544	-0.676180	5.187425
H	-2.352810	-0.208548	3.669466
H	-1.936916	0.308973	1.286912
O	-0.676260	1.024272	-0.547657
C	-0.973108	0.959679	-1.877925
C	-1.773088	1.983379	-2.378965
H	-2.061294	2.790336	-1.717728
C	-2.175277	1.944140	-3.703973
H	-2.794243	2.744575	-4.091785
C	-1.791634	0.893071	-4.544118
H	-2.110922	0.877591	-5.578062
C	-1.000444	-0.120536	-4.040588
H	-0.681043	-0.951615	-4.658288
C	-0.585247	-0.098918	-2.702899
C	0.261080	-1.169622	-2.167435
O	0.549763	-2.184528	-2.746082
C	0.856135	-0.910295	-0.763461
O	1.665056	-1.652840	-0.296601
H	2.907443	1.117823	-1.352819
O	1.562585	1.258812	-0.050775
O	1.968979	1.343135	-1.419083

SA

C	0.000100	0.000900	-0.001700
C	-0.001100	0.001600	1.396900
C	1.188900	0.000800	2.108800
C	2.401600	0.001700	1.431700
C	2.424300	-0.011000	0.040600
C	1.230000	-0.016800	-0.663400
O	-1.165900	0.044800	2.140800
C	-1.999700	-1.030800	2.082600
O	-1.710400	-2.048500	1.520600
C	-1.215100	0.017100	-0.867900
O	-2.347200	0.346800	-0.225500
C	-3.272200	-0.780600	2.806600
C	-4.157400	-1.849500	2.948900
C	-5.364900	-1.662200	3.607600
C	-5.689500	-0.407800	4.118900
C	-4.807400	0.659400	3.972600
C	-3.595600	0.476500	3.317200
O	-1.191800	-0.212400	-2.048200
H	1.220700	-0.030800	-1.746100
H	3.366800	-0.017700	-0.491900
H	3.327800	0.004700	1.993500
H	1.142700	-0.003200	3.190500
H	-3.884300	-2.814600	2.539800
H	-2.903800	1.299400	3.194200
H	-5.064500	1.634300	4.368600
H	-6.053100	-2.490800	3.722200
H	-3.065900	0.313100	-0.872500
H	-6.632900	-0.261400	4.631800

Table S3. Descartes coordinates of the stationary points in the photosensitized oxygenation of 3HF in acetonitrile (see Fig. 5.in the main article)

^{1}N

C	-0.000981	-0.005020	0.000597
C	-0.001034	-0.005367	1.405807
C	1.217611	0.018637	2.084043
C	2.431621	0.043788	1.391022
C	2.407696	0.044036	0.011413
C	1.189884	0.019622	-0.691292
O	1.285682	0.023720	3.435482
C	0.164142	0.001495	4.202142
C	-1.066019	-0.029273	3.627249
C	-1.234246	-0.035537	2.180380
C	0.470098	-0.019352	5.640839
C	1.716725	-0.496249	6.067681
C	2.029475	-0.526734	7.420108
C	1.109753	-0.072952	8.362314
C	-0.125357	0.412734	7.943097
C	-0.449971	0.439535	6.591815
O	-2.207807	-0.083327	4.349539
O	-2.367695	-0.077113	1.703764
H	-0.954828	-0.024542	-0.512472
H	1.192890	0.020444	-1.773782
H	3.342517	0.063680	-0.535454
H	3.358696	0.063066	1.949766
H	-2.927554	-0.125162	3.697702
H	-1.409048	0.824206	6.275567
H	-0.841197	0.776485	8.670330
H	2.993280	-0.905129	7.738668
H	2.434804	-0.847365	5.337880
H	1.356135	-0.095078	9.417151

TS1

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.404363
C	1.219805	0.000000	2.080763
C	2.432878	0.007814	1.388208
C	2.408260	0.010647	0.009084
C	1.190534	0.005548	-0.692417
O	1.293781	-0.010785	3.440041
C	0.165567	0.005123	4.189731
C	-1.065421	-0.009207	3.625036
C	-1.242382	-0.010012	2.171027
C	0.423708	0.014871	5.647220
C	0.539332	1.229872	6.321130
C	0.791421	1.241527	7.688256
C	0.927109	0.042142	8.380775
C	0.808574	-1.170182	7.707983
C	0.555984	-1.187449	6.340764
O	-2.182042	-0.017146	4.371310
O	-2.370439	-0.017842	1.698841
O	-0.166751	-2.564877	3.359334
O	0.978971	-2.728043	3.052101
H	-2.923271	-0.037261	3.743961
H	-0.957020	-0.004021	-0.507683
H	1.192574	0.005364	-1.774946
H	3.343142	0.015462	-0.538212
H	3.358394	0.006415	1.949616
H	0.453799	-2.126119	5.809033
H	0.909795	-2.103827	8.247937
H	1.121790	0.052374	9.446634
H	0.879671	2.185679	8.211952
H	0.427497	2.159092	5.774265

NP

O	-0.042471	0.011170	-0.008678
C	-0.012487	-0.001080	1.409931
C	1.498603	0.002649	1.692661
C	1.985609	-0.926515	0.591151
O	1.272563	-0.342207	-0.524680
C	1.427525	-2.296771	0.904150
C	0.175404	-2.361583	1.521296
O	-0.526460	-1.229234	1.886212
C	2.102990	-3.470935	0.589962
C	1.528995	-4.702223	0.881899
C	0.277551	-4.754200	1.492341
C	-0.405437	-3.587327	1.814258
C	-0.805260	1.144563	1.961748
C	-1.596326	0.980487	3.096214
C	-2.279847	2.074045	3.619699
C	-2.168846	3.323343	3.017583
C	-1.370559	3.483909	1.887468
C	-0.687115	2.396205	1.357829
O	3.314291	-0.945915	0.311663
O	2.121494	0.589268	2.518838
H	3.078672	-3.406941	0.124383
H	2.055480	-5.616047	0.638431
H	-0.172935	-5.711775	1.723341
H	-1.376638	-3.610347	2.292237
H	-0.070946	2.513831	0.474133
H	-1.679046	0.007097	3.561401
H	-2.899386	1.947139	4.499106
H	-1.282485	4.455202	1.416389
H	3.674058	-0.049511	0.345174
H	-2.703153	4.171913	3.427773

TS2a

C	-0.004578	0.018944	0.006377
C	-0.003629	-0.012856	1.396232
C	1.209932	-0.009470	2.093607
C	2.412060	0.001524	1.397229
C	2.399655	0.016445	0.007498
C	1.196114	0.030957	-0.693476
O	1.311061	0.016463	3.472708
C	0.144199	0.081595	4.283381
C	-0.918218	0.981930	3.437496
C	-1.276379	-0.113708	2.220096
C	0.419752	0.846916	5.570815
C	1.515678	1.700091	5.644721
C	1.734678	2.423598	6.814534
C	0.861669	2.300998	7.890011
C	-0.237168	1.449533	7.800812
C	-0.461686	0.717395	6.640973
O	-0.478011	-1.040594	4.446203
O	-1.393923	2.022508	3.595501
O	-2.455396	0.323010	1.648215
O	-1.404150	-1.244778	2.860046
H	-2.420298	1.279354	1.505127
H	-0.953987	0.025357	-0.516096
H	1.193298	0.049748	-1.775733
H	3.340335	0.025025	-0.529504
H	3.340023	0.006453	1.955485
H	-1.309487	0.047746	6.566751
H	-0.918381	1.349726	8.636965
H	1.036060	2.867044	8.797050
H	2.590195	3.084841	6.879648
H	2.190802	1.793016	4.804544

TS2b

C	-0.002275	0.044675	0.002694
C	0.000293	-0.001880	1.394252
C	1.204902	-0.047093	2.098812
C	2.407955	-0.053234	1.404650
C	2.409750	-0.010909	0.012253
C	1.207245	0.039340	-0.685405
C	-1.282581	0.034116	2.164874
C	-1.489625	1.229590	3.112327
C	-2.766540	0.876939	3.882812
O	-2.397661	-0.779727	3.947773
O	-1.251398	-1.036834	3.117034
O	-2.399067	-0.101930	1.314708
C	-3.603282	0.500235	1.632605
C	-3.883961	0.985681	2.917046
C	-4.565865	0.563371	0.638952
C	-5.804677	1.124326	0.938560
C	-6.088202	1.616185	2.211581
C	-5.122420	1.543673	3.207784
O	-2.826970	0.978831	5.171284
O	-0.802889	2.190986	3.255848
H	1.201174	-0.080986	3.182028
H	3.342863	-0.090153	1.950043
H	3.349166	-0.015142	-0.527463
H	1.207359	0.073854	-1.767958
H	-0.940459	0.084920	-0.534364
H	-4.342541	0.171938	-0.345354
H	-6.558463	1.175841	0.162384
H	-7.056030	2.051307	2.423703
H	-5.308574	1.914916	4.208481
H	-2.279196	-0.230109	5.000968

SA

C	0.002766	-0.052650	-0.002533
C	0.001973	0.016508	1.391719
C	1.205748	0.060054	2.097090
C	2.410888	0.030249	1.408265
C	2.413441	-0.038365	0.016370
C	1.212093	-0.078574	-0.687173
C	-1.259037	0.062010	2.172354
O	-1.334196	0.220481	3.361069
O	-2.350996	-0.110712	1.383464
C	-3.603749	0.012081	1.959406
C	-4.065994	1.213733	2.505949
C	-5.353872	1.245020	3.045756
C	-6.169127	0.122890	3.020296
C	-5.693777	-1.059986	2.462168
C	-4.407205	-1.117599	1.939343
C	-3.283580	2.482140	2.566608
O	-3.537844	3.382308	3.326598
O	-2.288286	2.553557	1.674487
H	-5.704391	2.174206	3.477474
H	-7.168517	0.170587	3.433367
H	-6.320044	-1.943323	2.437985
H	-4.009105	-2.029969	1.513401
H	1.183391	0.115608	3.178570
H	-0.934788	-0.081889	-0.542147
H	1.217625	-0.129557	-1.769006
H	3.346323	0.061345	1.953157
H	-1.839842	3.404596	1.790153
H	3.354129	-0.059764	-0.521083

XP

C	0.027754	0.054916	-0.020819
C	0.003365	0.020064	1.535259
O	1.292096	0.008909	2.102035
C	2.350515	-0.592999	1.483944
C	2.429485	-0.791201	0.102036
C	1.309542	-0.403362	-0.754431
C	3.584674	-1.364285	-0.448601
C	4.641745	-1.725934	0.362578
C	4.549590	-1.514002	1.743215
C	3.414902	-0.952273	2.306513
C	-0.757708	1.194234	2.110378
C	-2.152420	1.197240	2.067040
C	-2.855347	2.289476	2.562135
C	-2.171227	3.380452	3.092275
C	-0.780555	3.377163	3.127302
C	-0.070342	2.285234	2.637324
O	-0.703262	-1.132016	1.922170
O	-0.146033	-2.231090	1.197550
O	1.304258	-0.438014	-1.959979
O	-0.945741	0.370490	-0.636264
H	-2.682208	0.349945	1.651478
H	-3.938176	2.287728	2.533094
H	-2.721648	4.230782	3.476927
H	-0.244181	4.223776	3.538310
H	1.011272	2.279611	2.667633
H	3.332936	-0.784030	3.372645
H	5.374573	-1.794626	2.387049
H	5.532766	-2.169222	-0.062319
H	3.620507	-1.513347	-1.521203
H	-0.939614	-2.630955	0.811629

Table S4. Descartes coordinates of the stationary points in the photorearrangement reaction of 3HF in *n*-hexane (see Fig. 7 in the main article)

^{1}N

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.401366
C	1.223740	0.000000	2.082939
C	2.416651	-0.004765	1.370612
C	2.409772	-0.015043	-0.020238
C	1.196638	-0.012502	-0.702590
C	-1.283280	0.012587	2.119764
C	-1.509589	-0.354319	3.407300
C	-2.846734	-0.323208	3.992115
C	-3.908736	0.131088	3.102721
C	-3.581821	0.486440	1.795014
O	-2.313523	0.424817	1.329209
C	-4.562144	0.929689	0.902038
C	-5.869265	1.009379	1.336463
C	-6.218003	0.653832	2.650653
C	-5.245169	0.219279	3.523802
O	-3.002959	-0.677720	5.155841
O	-0.533189	-0.791322	4.231100
H	-5.476336	-0.062762	4.543947
H	-7.249366	0.723505	2.972071
H	-6.635695	1.352295	0.651883
H	-4.273220	1.200790	-0.105429
H	-0.980844	-1.007836	5.066755
H	1.241596	0.009610	3.162835
H	3.356882	0.000788	1.908748
H	1.181488	-0.020119	-1.785842
H	-0.940638	0.004465	-0.534471
H	3.343525	-0.022685	-0.569748

^{3}N*

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.425649
C	1.260017	0.000000	2.091133
C	2.433352	0.006757	1.363646
C	2.414629	0.016830	-0.033670
C	1.186417	0.012200	-0.702756
C	-1.221364	-0.005515	2.118965
C	-1.446687	0.037624	3.575396
C	-2.661446	-0.406126	4.172740
C	-3.695007	-0.867001	3.234543
C	-3.502895	-0.652054	1.867374
O	-2.365625	-0.042159	1.374009
C	-4.469022	-1.009308	0.941560
C	-5.645800	-1.602589	1.389961
C	-5.852424	-1.833716	2.747894
C	-4.878732	-1.462363	3.666174
O	-2.791703	-0.327872	5.411855
O	-0.532939	0.547633	4.370953
H	-5.014744	-1.614698	4.730302
H	-6.770824	-2.295871	3.086922
H	-6.404382	-1.884619	0.669979
H	-4.290525	-0.818646	-0.109087
H	-0.912339	0.488477	5.273344
H	1.301168	-0.010658	3.170393
H	3.380781	0.001493	1.889509
H	1.162716	0.015837	-1.786186
H	-0.945576	-0.005805	-0.524669
H	3.341879	0.023263	-0.592742

^{1}N*

C	-3.671874	0.339735	0.027178
C	-2.268629	0.356271	0.006687
C	-1.589121	-0.874487	-0.007605
C	-2.262810	-2.075990	-0.001772
C	-3.666101	-2.071094	0.019245
C	-4.362077	-0.868512	0.033431
O	-0.208254	-0.949250	-0.029462
C	0.597193	0.139160	-0.017151
C	-0.053347	1.404037	-0.022356
C	-1.502390	1.573100	-0.004981
C	1.987078	-0.140046	-0.003171
C	2.421561	-1.499736	-0.039839
C	3.764489	-1.807693	-0.029033
C	4.728932	-0.794491	0.020975
C	4.321972	0.543346	0.061719
C	2.984328	0.879474	0.051591
O	0.612815	2.535341	-0.047870
O	-1.934825	2.748841	-0.011129
H	-4.190352	1.290499	0.037260
H	-5.444902	-0.869760	0.049093
H	-4.199860	-3.013059	0.023589
H	-1.697975	-2.999556	-0.013638
H	-0.099032	3.222360	-0.041128
H	2.695104	1.918614	0.088356
H	5.064414	1.331226	0.104569
H	4.073770	-2.845660	-0.059988
H	1.682884	-2.288055	-0.080013
H	5.782836	-1.044501	0.030069

TS1

C	-0.084663	0.110321	0.060867
C	-0.029839	0.025182	1.456038
C	1.234694	-0.075640	2.047351
C	2.394766	-0.058981	1.279794
C	2.320536	0.050554	-0.101743
C	1.071644	0.126987	-0.707621
C	-1.282240	0.037716	2.281833
C	-1.387215	-0.650794	3.606834
C	-2.725250	-1.142614	3.857278
C	-3.514623	-0.825695	2.654449
C	-2.730406	0.026162	1.746226
O	-2.099538	1.209308	2.311334
C	-3.282986	0.209866	0.406768
C	-4.472381	-0.371965	0.075056
C	-5.199725	-1.174794	0.988547
C	-4.700926	-1.396397	2.279409
O	-0.474863	-0.715838	4.573776
O	-3.113487	-1.711220	4.871573
H	1.360254	-0.192993	3.112857
H	3.356783	-0.136933	1.771399
H	3.223303	0.063141	-0.700130
H	0.991961	0.189468	-1.786199
H	-1.036474	0.135482	-0.444121
H	-5.216857	-2.046030	2.977826
H	-6.139357	-1.616527	0.683809
H	-4.892470	-0.183533	-0.905922
H	-2.816876	0.922337	-0.259138
H	0.179606	-0.015237	4.492476

IM1

C	-0.262160	-0.441536	0.491628
C	-0.010882	-0.367601	1.863020
C	1.131305	0.281224	2.324515
C	2.017067	0.856680	1.416061
C	1.765426	0.784541	0.051068
C	0.623249	0.133888	-0.410513
C	-1.000843	-0.987762	2.841334
C	-2.328890	-0.210587	2.961891
C	-3.414519	-1.045316	2.710858
C	-2.950206	-2.422550	2.364465
C	-1.513197	-2.349356	2.415067
C	-4.708404	-0.550131	2.762325
C	-4.885717	0.793168	3.089443
C	-3.791105	1.619132	3.350989
C	-2.488432	1.122606	3.292497
O	-0.539068	-0.995934	4.139484
O	-0.728482	-3.372994	2.127605
O	-3.641889	-3.389022	2.079224
H	-5.548457	-1.201322	2.551053
H	-5.886260	1.205472	3.140965
H	-3.955318	2.659900	3.602526
H	-1.632174	1.756888	3.490456
H	-1.154427	-0.944272	0.130551
H	1.322106	0.335298	3.389155
H	2.905654	1.359464	1.778780
H	0.421973	0.075458	-1.473346
H	2.456477	1.231650	-0.653394
H	0.202566	-3.114135	2.157439

^{3}IN*

C	-0.076879	0.142945	0.015415
C	-0.059079	-0.006390	1.404149
C	1.158386	-0.154861	2.064326
C	2.348489	-0.164300	1.339847
C	2.326753	-0.024891	-0.041550
C	1.109539	0.132042	-0.702607
C	-1.353863	0.053747	2.197534
C	-2.451727	-0.869047	1.474855
C	-3.581255	0.039432	1.038880
C	-3.225735	1.395818	1.495941
C	-2.003665	1.410059	2.155937
C	-1.495445	2.585171	2.677980
C	-2.243546	3.754175	2.528997
C	-3.467518	3.736911	1.859325
C	-3.977453	2.554549	1.330655
O	-4.570239	-0.342323	0.441512
O	-2.340401	-2.060429	1.360347
O	-1.221108	-0.365033	3.516246
H	1.184834	-0.242404	3.143652
H	3.291234	-0.278676	1.861275
H	3.252423	-0.036014	-0.604196
H	1.086067	0.242215	-1.779935
H	-1.021806	0.262561	-0.504754
H	-4.927901	2.525735	0.812961
H	-4.030695	4.656027	1.750902
H	-1.867772	4.685558	2.934466
H	-0.539069	2.591444	3.188212
H	-0.828915	-1.247551	3.526932

TS2

C	-0.002955	-0.000296	-0.022716
C	-0.064358	-0.011155	1.466966
C	1.320357	-0.022718	1.903190
C	2.296922	0.023275	0.743115
C	1.320530	0.014768	-0.453910
C	-1.046010	-0.027170	-0.937454
C	-0.729732	-0.020418	-2.293302
C	0.601006	0.005995	-2.717930
C	1.648781	0.024785	-1.798335
C	3.290399	-1.128261	0.697249
C	4.601630	-0.914271	0.283166
C	5.489971	-1.984607	0.211176
C	5.072174	-3.265773	0.552439
C	3.760187	-3.478247	0.968687
C	2.871504	-2.413104	1.041224
O	2.898927	1.260534	0.647282
O	1.716420	-0.095566	3.177601
O	-1.057549	-0.009089	2.172635
H	4.924277	0.086539	0.024170
H	6.511085	-1.813411	-0.108476
H	5.765542	-4.096521	0.498549
H	3.429495	-4.473829	1.239127
H	1.849751	-2.583294	1.366656
H	-2.072593	-0.053098	-0.591165
H	-1.522817	-0.037715	-3.031031
H	0.821882	0.010024	-3.778536
H	2.683343	0.037139	-2.120937
H	1.871811	0.773858	3.568691

^{1}IN

C	-0.085327	0.406407	0.093420
C	-0.026738	0.054683	1.444862
C	1.187442	-0.346763	1.994268
C	2.330955	-0.398077	1.200706
C	2.267723	-0.056770	-0.144805
C	1.054843	0.346002	-0.697408
C	-1.291371	0.084260	2.301608
C	-2.340843	-0.869001	1.691452
C	-3.419600	-0.011662	0.976422
C	-3.151905	1.368078	1.417761
C	-2.000153	1.419597	2.205944
C	-1.591201	2.618017	2.776320
C	-2.357282	3.752948	2.539599
C	-3.508440	3.703503	1.740064
C	-3.917617	2.508705	1.172013
O	-4.278441	-0.441325	0.257096
O	-2.364074	-2.052741	1.843395
O	-1.052677	-0.252543	3.644298
H	1.243253	-0.603549	3.044224
H	3.272605	-0.706186	1.639390
H	3.157966	-0.100322	-0.760567
H	0.996750	0.617716	-1.744501
H	-1.019254	0.740361	-0.347913
H	-4.809188	2.443047	0.559503
H	-4.080001	4.608082	1.572457
H	-2.058832	4.698299	2.977434
H	-0.698188	2.660520	3.388446
H	-0.986750	-1.214817	3.701816