Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information for "Theoretical studies on isomerization mechanism of the *ortho*-Green Fluorescent Protein chromophore"

Yue-jie Ai,' Rong-zhen liao, Wei-hai Fang, and Yi Luo

SI-1: Geometrical structures of (1-5) and (1-7) tautomer, and corresponding transition states of structure D. The geometricl parameters are given in Å.

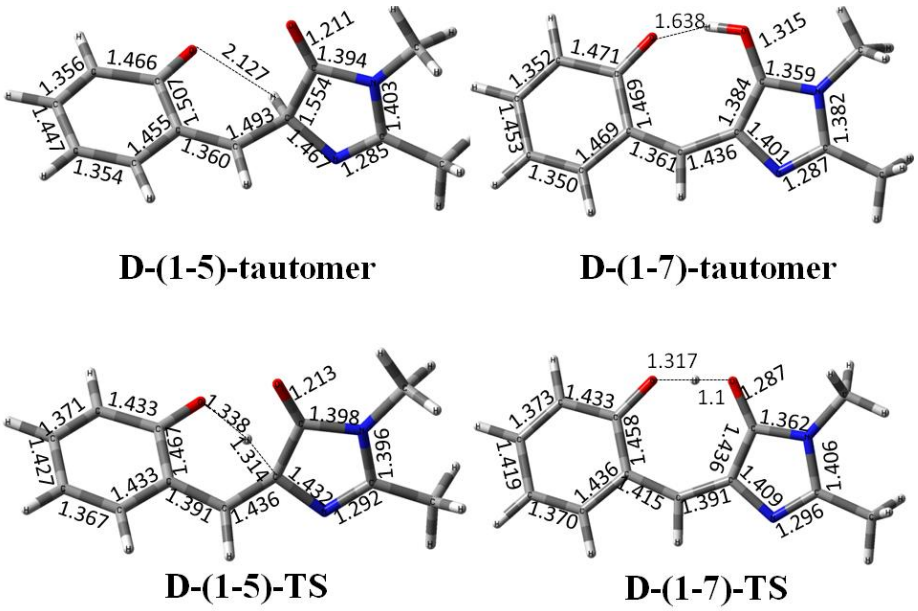

Figure S1

SI-2: Energy profile for the ground-state hydrogen transfer from A to E along the O-H bond coordinate.

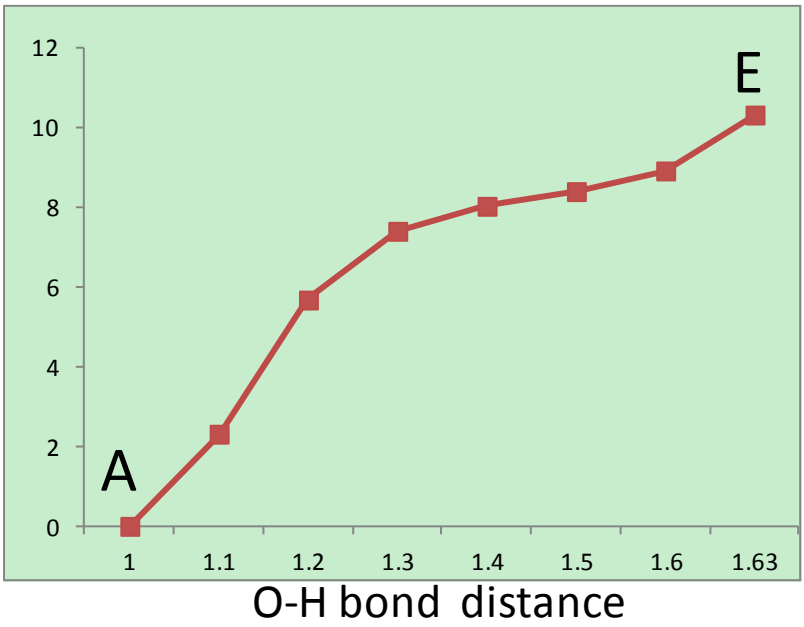

Figure S2

SI-3: Transition orbitals for first singlet excited-state of o-HBDI and its ESIPT tautomer.

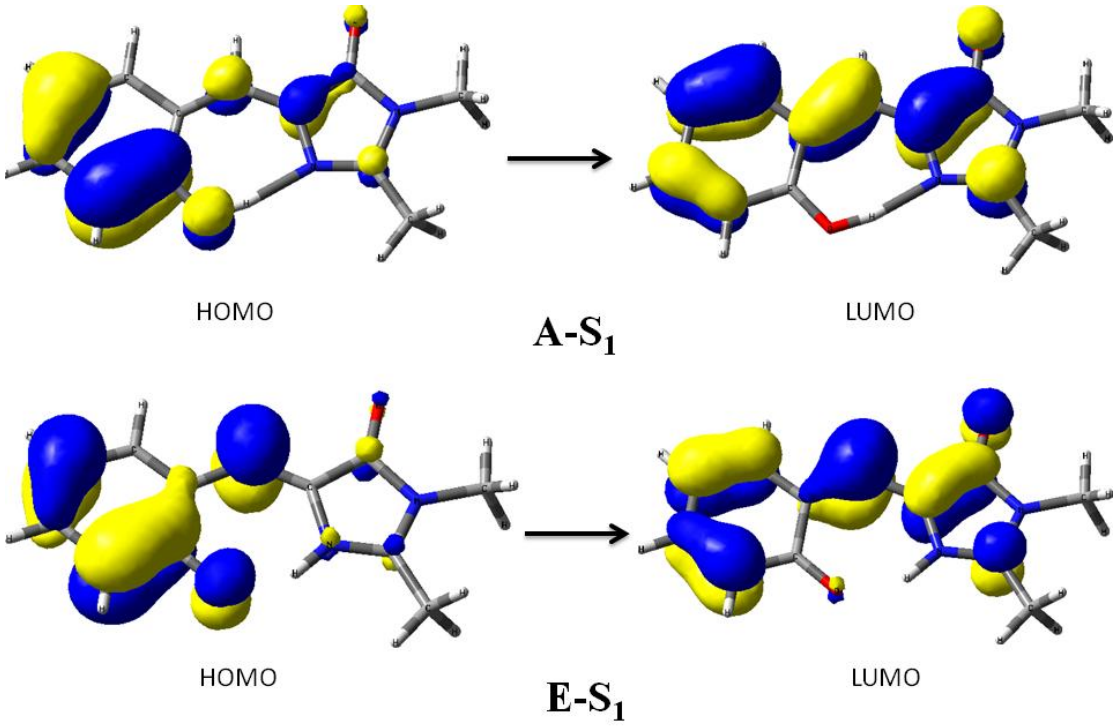

Figure S3

SI-4: Table S1. Calculated vertical excitation energies and oscillator strengths for all the isomers and their anion form at PCM//TDDFT/B3LYP/6-31G(d) level.

absorption	PCM//TDDFT/B3LYP/6-31G(d) (eV)	f
o-HBDI (A)	3.3919eV 365.53 nm	f=0.3851
B	3.3084 eV 374.76 nm	f=0.5949
C	3.2501 eV 381.48 nm	f=0.5020
D	3.2335 eV 383.44 nm	f=0.3130
E	2.8742eV 431.42nm	f=0.4843
F	2.6359 eV 470.36 nm	f=0.5763
G	2.6741 eV 463.64 nm	f=0.5411
H	2.5608 eV 484.15 nm	f=0.2540
D-(1-5)	2.7621 eV 448.87 nm	f=0.0234
D-(1-7)	2.0144 eV 615.48 nm	f=0.1205
A-anion	2.6314 eV 471.23 nm	f=0.2607
B-anion	2.8226 eV 439.26 nm	f=0.5742
C-anion	2.7217 eV 455.54 nm	f=0.5380
D-anion	2.7003 eV 459.15 nm	f=0.3305
E-anion	2.9939 eV 414.12 nm	f=0.6024
F-anion	2.7264 eV 454.75 nm	f=0.5790
G-anion	2.8613 eV 433.31 nm	f=0.5862
H-anion	2.8127 eV 440.81 nm	f=0.3521

SI-5: Cartesian coordinates (Å) of geometry of A-S_1 calculated at CAS(12,11)/6-31G(d) level.

C	-1.419327	-0.500399	0.00384
H	-1.761042	-1.042339	-0.872851
H	-1.761051	-1.042173	0.880616
H	-0.338264	-0.487921	0.003822
C	-1.926483	0.902718	0.003653
N	-1.181299	1.964308	0.003352
C	-2.013063	3.069058	0.003109
C	-1.652685	4.416822	0.001398
H	-2.502999	5.074427	0.001032
C	-0.415061	5.064424	-0.000999
C	-0.404202	6.4898	-0.004374
H	-1.352194	6.993301	-0.004271
C	0.913688	4.487459	-0.000866

C	0.787834	7.300559	-0.008616
H	0.673831	8.3684	-0.011762
C	2.094645	5.300189	-0.004563
H	3.026507	4.769038	-0.004208
C	2.045002	6.714199	-0.008812
C	-3.393014	2.601319	0.003387
O	-4.43982	3.209389	0.003141
N	-3.267278	1.213397	0.003795
C	-4.383306	0.299918	0.003011
H	-5.285319	0.892134	0.003937
H	-4.378455	-0.33147	0.884556
H	-4.378959	-0.329459	-0.88
H	2.945295	7.296405	-0.012077
O	1.161813	3.204024	0.002584
H	0.372636	2.629988	0.003375

SI-6: Cartesian coordinates (Å) of geometry of E-S_1 calculated at CAS(12,11)/6-31G(d) level.

C	-1.403145	-0.489848	0.005202
H	-1.73485	-1.03545	-0.871603
H	-1.734279	-1.032777	0.883884
H	-0.322635	-0.453188	0.004797
C	-1.960243	0.891736	0.00329
N	-1.25169	1.981446	0.001337
C	-2.058466	3.119907	0.000069
C	-1.673297	4.453288	-0.001784
H	-2.516041	5.119082	-0.002127
C	-0.367242	5.125017	-0.003216
C	-0.387768	6.498832	-0.003888
H	-1.338988	7.00115	-0.003314
C	0.94602	4.464848	-0.004078
C	0.809577	7.326722	-0.005316
H	0.705438	8.395618	-0.005705
C	2.10103	5.292341	-0.00546
H	3.050643	4.790946	-0.006096
C	2.031724	6.718764	-0.00609
C	-3.406082	2.626711	0.00117
O	-4.48815	3.170946	0.000558
N	-3.253742	1.20327	0.003203
C	-4.374808	0.286305	0.004834
H	-5.270006	0.886795	0.004173
H	-4.365245	-0.337806	0.88985

H	-4.365691	-0.340413	-0.878342
H	2.939813	7.293949	-0.007157
O	1.063827	3.213505	-0.003273
H	-0.246321	2.080235	0.00062

SI-7: Cartesian coordinates (Å) of geometry of conical intersection (CI) calculated at CAS(8,7)/6-31G(d) level.

C	2.509696	2.423854	-0.528336
H	1.822595	3.033523	-1.102004
H	3.499571	2.543236	-0.950547
H	2.527857	2.800972	0.494787
C	2.0686	1.00203	-0.568091
N	0.755846	0.647274	-0.424683
C	0.688182	-0.662132	0.067384
C	-0.4214	-1.297241	0.393733
H	-0.33989	-2.234507	0.913271
C	-1.762103	-0.702913	0.114258
C	-2.625428	-1.253141	-0.810136
H	-2.345484	-2.149248	-1.335207
C	-2.109716	0.533526	0.774171
C	-3.891989	-0.678303	-1.044977
H	-4.570703	-1.147157	-1.733179
C	-3.403128	1.078367	0.520559
H	-3.679213	1.971346	1.050668
C	-4.265645	0.470346	-0.359814
C	2.089523	-1.134034	0.237713
O	2.477922	-2.205121	0.594504
N	2.859974	-0.061861	-0.127116
C	4.299808	-0.128252	-0.242158
H	4.609184	-1.104628	0.095169
H	4.770522	0.625968	0.376439
H	4.610993	0.00955	-1.271498
H	-5.239472	0.895498	-0.528517
O	-1.246183	1.135595	1.471695
H	0.110989	1.301126	-0.002214

SI-8: Cartesian coordinates (Å) of geometry of A-E-S_1-TS calculated at CAS(12,11)/6-31G(d) level.

C	-1.29962	-0.38923	-0.00028
H	-1.61051	-0.95019	-0.87628
H	-1.6067	-0.94994	0.87723

H	-0.22049	-0.31614	-0.00277
C	-1.89125	0.979626	0.000576
N	-1.22226	2.090646	-0.00161
C	-2.1131	3.157864	-0.00096
C	-1.76734	4.501	-0.00235
H	-2.59552	5.18341	-0.0026
C	-0.45925	5.110538	-0.00332
C	-0.37801	6.491588	-0.00721
H	-1.29706	7.047941	-0.00995
C	0.826149	4.422814	-0.00013
C	0.864279	7.255926	-0.00768
H	0.805374	8.327755	-0.01089
C	2.045219	5.180366	-0.00012
H	2.950234	4.604401	0.003157
C	2.068419	6.599785	-0.0039
C	-3.44478	2.616857	0.001738
O	-4.535	3.142722	0.003509
N	-3.23542	1.231199	0.002182
C	-4.30806	0.266147	0.008331
H	-5.23193	0.822762	-0.00637
H	-4.28061	-0.35013	0.900191
H	-4.26708	-0.3753	-0.86491
H	3.003722	7.125554	-0.00384
O	0.955236	3.161117	0.002921
H	0.012767	2.540423	0.000542

SI-9: Cartesian coordinates (Å) of geometry of A-S0 calculated at B3LYP/6-31G(d) level .

C	-1.42736	-0.50942	0.004899
H	-1.78566	-1.05321	-0.87785
H	-1.78467	-1.0506	0.889656
H	-0.336	-0.51515	0.004304
C	-1.91194	0.900484	0.003107
N	-1.13916	1.95103	0.00134
C	-1.97209	3.077692	0.000169
C	-1.61563	4.390887	-0.00172
H	-2.47907	5.054844	-0.00221
C	-0.34086	5.074623	-0.00309
C	-0.4067	6.494027	-0.00452
H	-1.39299	6.951785	-0.00448
C	0.959504	4.475746	-0.00317
C	0.717543	7.297363	-0.00591

H	0.621668	8.378665	-0.00697
C	2.09531	5.308573	-0.00457
H	3.065028	4.821085	-0.00457
C	1.982354	6.688957	-0.00592
C	-3.38205	2.627132	0.00137
O	-4.43637	3.242466	0.000989
N	-3.25772	1.219551	0.00324
C	-4.39583	0.321188	0.004869
H	-5.28834	0.950826	0.005546
H	-4.40272	-0.31311	0.897767
H	-4.40473	-0.31392	-0.88745
H	2.881524	7.299731	-0.007
O	1.214628	3.162732	-0.00205
H	0.389761	2.593536	-0.00059

PCM

C	-3.149519	2.257782	0.000129
H	-3.795042	2.32467	0.883644
H	-3.795328	2.324835	-0.883165
H	-2.458313	3.102071	0.00009
C	-2.378248	0.984619	-0.000123
N	-1.074703	0.898394	-0.000324
C	-0.750963	-0.463949	-0.000251
C	0.482355	-1.036294	-0.000125
H	0.44367	-2.124421	-0.000124
C	1.825858	-0.492584	-0.000032
C	2.874284	-1.451281	0.000075
H	2.596393	-2.502275	0.000072
C	2.197837	0.889337	-0.000025
C	4.212635	-1.100585	0.000199
H	4.981782	-1.866409	0.000287
C	3.563746	1.230254	0.000095
H	3.814171	2.286728	0.000092
C	4.55498	0.260009	0.000207
C	-2.008527	-1.246702	-0.000494
O	-2.208777	-2.456381	-0.000066
N	-2.997956	-0.252858	0.000009
C	-4.425816	-0.529041	0.000532
H	-4.53862	-1.61433	-0.000222
H	-4.904995	-0.115968	-0.891609
H	-4.904149	-0.117305	0.893753
H	5.59904	0.56132	0.000299
O	1.346377	1.92669	-0.000148

H	0.377474	1.65047	-0.000338

SI-10: Cartesian coordinates (Å) of geometry of B-S0 calculated at B3LYP/6-31G(d) level.

C	-4.53308	4.792044	-3.82118
H	-5.53694	5.150496	-3.56131
H	-4.65049	4.032654	-4.60443
H	-3.9501	5.624414	-4.21846
C	-3.82991	4.236598	-2.62866
N	-2.70048	4.691724	-2.16589
C	-2.39344	3.899933	-1.05227
C	-1.32255	3.965094	-0.21844
H	-1.3826	3.212024	0.56771
C	-0.19279	4.870909	-0.21156
C	-0.11379	5.986056	-1.08109
H	-0.91871	6.129653	-1.79248
C	0.873812	4.676192	0.707637
C	0.949769	6.873065	-1.02559
H	0.98235	7.723353	-1.70039
C	1.939832	5.579795	0.765103
H	2.730323	5.394723	1.485286
C	1.976619	6.671483	-0.09307
C	-3.46302	2.881454	-0.85979
O	-3.59789	1.998216	-0.02673
N	-4.34922	3.162906	-1.91196
C	-5.57214	2.422446	-2.14967
H	-5.62888	1.653613	-1.3757
H	-5.56302	1.940683	-3.13347
H	-6.45263	3.070154	-2.07648
H	2.812255	7.364405	-0.04118
O	0.941487	3.629991	1.580145
H	0.254554	2.977572	1.378949

PCM

C	3.39635	2.268031	0.188688
H	4.042961	2.360887	-0.692032
H	4.049487	2.21102	1.067652
H	2.770602	3.158414	0.266792
C	2.526427	1.062739	0.089631
N	1.221114	1.087039	0.097379
C	0.810988	-0.247988	-0.012188
C	-0.446539	-0.762587	-0.047045
H	-0.442849	-1.847791	-0.139825

C	-1.73195	-0.091868	-0.01656
C	-1.853187	1.314991	-0.128701
H	-0.941257	1.896472	-0.196205
C	-2.932108	-0.847086	0.0872
C	-3.091516	1.938844	-0.162204
H	-3.153102	3.018887	-0.256032
C	-4.1793	-0.213551	0.044048
H	-5.071356	-0.827068	0.122763
C	-4.260104	1.168333	-0.082704
C	2.014176	-1.124134	-0.090134
O	2.116625	-2.342268	-0.192286
N	3.068948	-0.213644	-0.018713
C	4.47339	-0.585743	-0.056406
H	4.513739	-1.67332	-0.137204
H	4.986833	-0.273594	0.857641
H	4.974215	-0.142175	-0.92203
H	-5.234954	1.647038	-0.111662
O	-2.966412	-2.203852	0.226523
H	-2.086222	-2.553468	0.433833

SI-11: Cartesian coordinates (Å) of geometry of C-S0 calculated at B3LYP/6-31G(d) level.

C	-4.35718	4.891074	-3.83878
H	-5.3022	5.399897	-3.61077
H	-4.5548	4.186868	-4.65672
H	-3.62905	5.630424	-4.1765
C	-3.81169	4.191991	-2.63896
N	-2.65713	4.438535	-2.10188
C	-2.53134	3.568851	-0.99954
C	-1.41425	3.641672	-0.22003
H	-0.73573	4.398518	-0.61489
C	-0.9449	2.926429	0.949375
C	-1.51234	1.716982	1.418164
H	-2.39785	1.339537	0.921747
C	0.195184	3.426344	1.64182
C	-0.95779	1.023427	2.483645
H	-1.41103	0.093967	2.815194
C	0.75466	2.717227	2.707412
H	1.625837	3.135828	3.200932
C	0.184971	1.519643	3.123096
C	-3.76017	2.724437	-0.91548
O	-4.1085	1.828982	-0.1548
N	-4.52951	3.18976	-1.98753
C	-5.83603	2.656649	-2.3187

H	-6.06012	1.887209	-1.57689
H	-5.84153	2.20535	-3.317
H	-6.60593	3.434573	-2.27382
H	0.624877	0.978679	3.956786
O	0.814873	4.602109	1.326582
H	0.246651	5.133611	0.749744

PCM

C	-4.376296	1.423596	-0.226425
H	-4.937788	1.285793	0.705365
H	-4.964629	0.968345	-1.032081
H	-4.270918	2.491738	-0.423272
C	-3.023113	0.805811	-0.135011
N	-1.899658	1.446437	-0.267293
C	-0.872639	0.492548	-0.113873
C	0.429873	0.894128	-0.153077
H	0.497522	1.970436	-0.311269
C	1.701078	0.197058	-0.072147
C	1.853711	-1.194198	-0.281828
H	0.961986	-1.790987	-0.42504
C	2.884508	0.957973	0.14622
C	3.105771	-1.792736	-0.309122
H	3.190203	-2.861398	-0.482392
C	4.143762	0.351751	0.10928
H	5.019089	0.970838	0.278989
C	4.25576	-1.014943	-0.121821
C	-1.500147	-0.842667	0.125724
O	-1.024226	-1.961292	0.309599
N	-2.862202	-0.556915	0.10667
C	-3.902468	-1.553416	0.30041
H	-3.404613	-2.512627	0.450328
H	-4.551274	-1.617197	-0.578045
H	-4.508271	-1.320166	1.181125
H	5.239315	-1.475926	-0.143377
O	2.88224	2.300965	0.394129
H	1.999491	2.597687	0.664235

SI-12: Cartesian coordinates (Å) of geometry of D-S0 calculated at B3LYP/6-31G(d) level.

C	-4.40077	-1.32027	0.219748
H	-4.96037	-1.19543	-0.71584
H	-4.96099	-0.80204	1.008184
H	-4.35149	-2.38297	0.462724

C	-3.01046	-0.79348	0.099949
N	-1.93213	-1.49106	0.262615
C	-0.84728	-0.60868	0.066344
C	0.427907	-1.10124	0.08859
H	0.412599	-2.18444	0.204201
C	1.773482	-0.57616	-0.02568
C	2.760855	-1.54512	-0.35859
H	2.425694	-2.5607	-0.55466
C	2.228535	0.749667	0.255824
C	4.106671	-1.24597	-0.44625
H	4.823527	-2.0156	-0.71556
C	3.606348	1.031199	0.187971
H	3.911975	2.045953	0.421671
C	4.531059	0.060718	-0.16039
C	-1.38708	0.727845	-0.25023
O	-0.83284	1.800106	-0.53828
N	-2.75833	0.549697	-0.21279
C	-3.71559	1.60677	-0.48076
H	-3.14363	2.517203	-0.66952
H	-4.37526	1.766503	0.378422
H	-4.32349	1.375802	-1.36194
H	5.586721	0.315199	-0.20765
O	1.448923	1.754031	0.678849
H	0.563734	1.774464	0.213498

PCM

C	-4.393608	-1.365489	0.255968
H	-4.939479	-1.246294	-0.687554
H	-4.957634	-0.832461	1.030552
H	-4.35606	-2.425594	0.511905
C	-3.002832	-0.842763	0.144325
N	-1.921768	-1.53793	0.324125
C	-0.838298	-0.654454	0.125741
C	0.44034	-1.134102	0.148363
H	0.44805	-2.217019	0.266325
C	1.777888	-0.582553	0.021484
C	2.776287	-1.520063	-0.360295
H	2.460725	-2.537173	-0.57786
C	2.210822	0.741401	0.333543
C	4.1145	-1.185457	-0.468781
H	4.841757	-1.930479	-0.77599
C	3.577033	1.060617	0.242768
H	3.870124	2.074039	0.498973

C	4.517276	0.121077	-0.155638
C	-1.385769	0.677784	-0.205288
O	-0.82052	1.748908	-0.493735
N	-2.749342	0.49646	-0.18034
C	-3.72105	1.542433	-0.463175
H	-3.164996	2.462834	-0.645329
H	-4.390449	1.687482	0.389056
H	-4.310325	1.295632	-1.350821
H	5.565148	0.40123	-0.219188
O	1.403624	1.71049	0.809011
H	0.53055	1.732325	0.317132

SI-13: Cartesian coordinates (Å) of geometry of E-S0 calculated at B3LYP/6-31G(d) level.

C	-1.36868	-0.48409	0.004359
H	-1.69895	-1.04322	-0.8794
H	-1.69809	-1.04111	0.889772
H	-0.27694	-0.44715	0.00378
C	-1.92472	0.895871	0.002992
N	-1.21096	2.005654	0.00123
C	-2.03499	3.136096	0.000316
C	-1.64419	4.464056	-0.00152
H	-2.50819	5.128321	-0.00182
C	-0.38789	5.104549	-0.00298
C	-0.40769	6.539678	-0.00466
H	-1.37951	7.029753	-0.0047
C	0.914228	4.415719	-0.0029
C	0.734886	7.292701	-0.00617
H	0.685761	8.377245	-0.00741
C	2.083122	5.265527	-0.00454
H	3.041577	4.755145	-0.00446
C	1.996776	6.63178	-0.00609
C	-3.40151	2.651121	0.001699
O	-4.48823	3.211779	0.001581
N	-3.24322	1.216216	0.00333
C	-4.37607	0.309087	0.005043
H	-5.268	0.939202	0.004869
H	-4.37799	-0.3222	0.899465
H	-4.37908	-0.32423	-0.88794
H	2.907416	7.227626	-0.00728
O	1.063434	3.15679	-0.00153
H	-0.22294	2.160001	0.000488

PCM

C	3.072228	2.293944	0.000226
H	3.712443	2.385699	-0.884219
H	3.712431	2.385546	0.884696
H	2.35004	3.112066	0.000291
C	2.363703	0.988718	0.000104
N	1.056553	0.825291	0.000045
C	0.730964	-0.535266	0.000021
C	-0.527969	-1.085764	0.00003
H	-0.499058	-2.174776	0.000064
C	-1.832424	-0.515968	-0.000037
C	-2.918174	-1.447594	0.000097
H	-2.671932	-2.507489	0.000194
C	-2.135082	0.91706	-0.000255
C	-4.235121	-1.055743	0.000145
H	-5.033958	-1.79073	0.00027
C	-3.529462	1.270856	-0.000071
H	-3.756283	2.333488	-0.000106
C	-4.532907	0.330649	0.00009
C	1.992632	-1.262663	-0.000057
O	2.249321	-2.462685	-0.000088
N	2.974033	-0.227753	-0.000022
C	4.407488	-0.484789	-0.000073
H	4.529379	-1.568547	-0.000109
H	4.87723	-0.065915	0.89364
H	4.877187	-0.065864	-0.893786
H	-5.571413	0.654984	0.000171
O	-1.261269	1.855018	-0.000247
H	0.220164	1.499469	0.000091

SI-14: Cartesian coordinates (Å) of geometry of F-S0 calculated at B3LYP/6-31G(d) level.

C	-1.46258	-0.55079	-0.23208
H	-1.88279	-1.03211	-1.12364
H	-1.73261	-1.16772	0.633651
H	-0.37314	-0.55175	-0.32387
C	-1.97101	0.838736	-0.08058
N	-1.21978	1.940868	-0.07163
C	-1.99898	3.106008	0.046262
C	-1.56254	4.433295	0.034998
H	-2.37468	5.15684	-0.0283
C	-0.2905	4.99613	0.051944
C	0.935391	4.287521	0.296634
H	0.904775	3.241684	0.598219
C	-0.23321	6.470065	-0.18967

C	2.150538	4.91044	0.26736
H	3.059717	4.357392	0.485489
C	1.106949	7.059274	-0.22398
H	1.153585	8.127068	-0.41702
C	2.227856	6.316351	-0.01603
C	-3.36623	2.659078	0.129576
O	-4.43893	3.232945	0.245733
N	-3.25659	1.206641	0.057361
C	-4.42386	0.345954	0.122197
H	-5.28112	1.014611	0.226941
H	-4.37492	-0.32311	0.987146
H	-4.53229	-0.24499	-0.79284
H	3.207225	6.79025	-0.04392
O	-1.24878	7.156983	-0.37083
H	-0.22744	1.943916	-0.25729

PCM

C	-3.511777	2.239401	0.112698
H	-4.163839	2.193881	0.991839
H	-4.151924	2.293973	-0.774856
H	-2.911221	3.149206	0.167744
C	-2.639941	1.039528	0.049944
N	-1.30936	1.049572	0.051505
C	-0.787113	-0.257046	-0.001672
C	0.525714	-0.699796	-0.009129
H	0.591925	-1.787255	-0.001305
C	1.778142	-0.068494	-0.016335
C	1.997861	1.343315	-0.103706
H	1.153293	2.019821	-0.196843
C	2.949089	-0.978023	0.057392
C	3.256934	1.884677	-0.108849
H	3.395434	2.958812	-0.184875
C	4.253705	-0.334359	0.051802
H	5.118907	-0.989864	0.109414
C	4.394211	1.02376	-0.024486
C	-1.939817	-1.130448	-0.044701
O	-2.046413	-2.352835	-0.099918
N	-3.063789	-0.236001	-0.015362
C	-4.44673	-0.694637	-0.049267
H	-4.409972	-1.783998	-0.07737
H	-4.955237	-0.322681	-0.942122
H	-4.983185	-0.369019	0.845202
H	5.38922	1.464592	-0.027079

O	2.837307	-2.225683	0.126296
H	-0.770176	1.898413	0.144085

SI-15: Cartesian coordinates (Å) of geometry of G-S0 calculated at B3LYP/6-31G(d) level.

C	-4.36844	-1.35016	0.368233
H	-4.95778	-1.34021	-0.55684
H	-4.94092	-0.80648	1.129799
H	-4.26746	-2.38847	0.695846
C	-3.02858	-0.7385	0.161302
N	-1.85739	-1.34092	0.345453
C	-0.765	-0.49439	0.066997
C	0.542567	-0.99058	0.217834
H	0.598907	-2.03125	0.549207
C	1.80043	-0.44521	0.038579
C	2.08605	0.899158	-0.38988
H	1.253819	1.563543	-0.5982
C	2.931649	-1.38461	0.33336
C	3.372962	1.328325	-0.53042
H	3.578726	2.344753	-0.85418
C	4.273852	-0.83959	0.155665
H	5.099897	-1.5123	0.366914
C	4.472301	0.443624	-0.25274
C	-1.34663	0.760235	-0.33086
O	-0.89621	1.848185	-0.68268
N	-2.77591	0.521488	-0.24405
C	-3.74418	1.553863	-0.56709
H	-3.16052	2.432715	-0.84867
H	-4.37077	1.793327	0.297943
H	-4.3786	1.252769	-1.40683
H	5.486876	0.819282	-0.37551
O	2.744998	-2.55512	0.706399
H	-1.75311	-2.29822	0.652846

PCM

C	-4.365612	-1.474231	0.000203
H	-4.949845	-1.195055	-0.883638
H	-4.947392	-1.198753	0.886853
H	-4.22198	-2.556368	-0.002219
C	-3.054832	-0.777016	-0.000149
N	-1.86439	-1.358053	-0.000334
C	-0.813695	-0.41178	-0.000219
C	0.511401	-0.844579	-0.000096

H	0.62514	-1.930408	-0.000062
C	1.750596	-0.195286	-0.000018
C	1.945502	1.225371	-0.00007
H	1.067257	1.862256	-0.000155
C	2.932844	-1.097359	0.000097
C	3.201494	1.773228	-0.000032
H	3.332248	2.851649	-0.000086
C	4.229497	-0.440184	0.000141
H	5.103501	-1.086613	0.000219
C	4.350449	0.922222	0.000071
C	-1.471946	0.875681	-0.000415
O	-1.06065	2.037876	0.000006
N	-2.87095	0.55865	0.000018
C	-3.913256	1.576765	0.000308
H	-3.40481	2.541064	0.002798
H	-4.537346	1.489698	0.893172
H	-4.534676	1.493005	-0.894756
H	5.340745	1.374407	0.000092
O	2.83426	-2.348486	0.000156
H	-1.729009	-2.361182	-0.000234

SI-16: Cartesian coordinates (Å) of geometry of H-S0 calculated at B3LYP/6-31G(d) level.

C	-4.36359	-1.21763	0.504278
H	-5.05569	-1.07556	-0.33465
H	-4.77965	-0.68418	1.368016
H	-4.33512	-2.28428	0.743993
C	-3.00145	-0.72186	0.169628
N	-1.88043	-1.44518	0.210315
C	-0.73806	-0.67606	-0.08615
C	0.535032	-1.2608	-0.14789
H	0.530266	-2.34766	-0.2746
C	1.792218	-0.66939	-0.0812
C	2.938033	-1.44944	-0.46744
H	2.768016	-2.46715	-0.81752
C	2.008137	0.692922	0.483285
C	4.202264	-0.93823	-0.44457
H	5.048363	-1.53947	-0.76505
C	3.386241	1.184242	0.437894
H	3.539888	2.198037	0.796182
C	4.417019	0.411103	-0.00033
C	-1.23161	0.633496	-0.43896
O	-0.73043	1.641152	-0.90464
N	-2.67287	0.524025	-0.20587

C	-3.56403	1.647256	-0.42608
H	-2.92717	2.4675	-0.76498
H	-4.07289	1.936724	0.498993
H	-4.30684	1.420631	-1.19793
H	5.43056	0.808134	-0.00483
O	1.103982	1.34913	1.02064
H	-1.84466	-2.39957	0.539222

PCM

C	-4.38313	-1.220592	0.425344
H	-5.013816	-1.095989	-0.461779
H	-4.847322	-0.663405	1.246529
H	-4.357541	-2.279258	0.690283
C	-3.010146	-0.717876	0.164683
N	-1.894792	-1.434218	0.250441
C	-0.747045	-0.650992	-0.002021
C	0.520434	-1.222031	-0.04099
H	0.511343	-2.312241	-0.108092
C	1.799632	-0.639039	-0.020738
C	2.901536	-1.454162	-0.446033
H	2.684877	-2.469438	-0.775049
C	2.073341	0.711527	0.517689
C	4.187692	-0.984499	-0.489304
H	4.998152	-1.615202	-0.842461
C	3.457125	1.15786	0.411929
H	3.664033	2.166959	0.760071
C	4.455062	0.353858	-0.066017
C	-1.252858	0.657285	-0.36268
O	-0.726949	1.670554	-0.806677
N	-2.682284	0.536745	-0.190682
C	-3.601326	1.638539	-0.439287
H	-2.988261	2.489121	-0.738933
H	-4.159392	1.888927	0.466585
H	-4.297275	1.390611	-1.244882
H	5.476101	0.728457	-0.111899
O	1.207195	1.413964	1.086524
H	-1.875243	-2.401647	0.547103

SI-17: Cartesian coordinates (Å) of geometry of AB-TS calculated at B3LYP/6-31G(d) level.

C	-3.43569	3.387243	-4.23811
H	-4.38752	3.846808	-4.53175
H	-3.45413	2.346803	-4.58533

H	-2.61758	3.914008	-4.73144
C	-3.23401	3.459973	-2.76203
N	-2.23374	4.060437	-2.19077
C	-2.426	3.89196	-0.80998
C	-1.64803	4.352622	0.188745
H	-1.97733	4.105612	1.199595
C	-0.40858	5.154182	0.021226
C	-0.44577	6.55345	-0.03382
H	-1.41028	7.052265	0.005478
C	0.84069	4.508927	-0.03604
C	0.726555	7.300894	-0.13293
H	0.677595	8.384963	-0.17506
C	2.019376	5.254171	-0.13083
H	2.96588	4.724352	-0.17379
C	1.958998	6.644226	-0.1766
C	-3.68214	3.099215	-0.5766
O	-4.21398	2.724446	0.452651
N	-4.13926	2.865231	-1.87829
C	-5.34802	2.124163	-2.18259
H	-5.78107	1.822508	-1.22622
H	-5.12953	1.229177	-2.77506
H	-6.07073	2.744485	-2.72335
H	2.879745	7.216676	-0.25186
O	0.956263	3.147752	0.004337
H	0.064783	2.763583	-0.04926

SI-18: Cartesian coordinates (Å) of geometry of BC-TS calculated at B3LYP/6-31G(d) level.

C	3.828352	1.573242	-1.16737
H	4.703246	1.011661	-1.52009
H	4.176374	2.254284	-0.37959
H	3.431757	2.164714	-1.99435
C	2.758631	0.663812	-0.67152
N	1.51643	0.626431	-1.17815
C	0.834046	-0.29514	-0.46263
C	-0.54634	-0.70423	-0.73799
H	-0.66963	-1.46338	-1.51065
C	-1.69165	-0.07834	-0.19362
C	-1.61045	1.111611	0.588149
H	-0.62743	1.526658	0.787429
C	-3.00336	-0.60805	-0.42906
C	-2.74426	1.758	1.046398
H	-2.64958	2.672895	1.624255
C	-4.1386	0.056571	0.022588

H	-5.1095	-0.38077	-0.18815
C	-4.01573	1.239146	0.753179
C	1.703868	-0.90129	0.550842
O	1.518648	-1.78232	1.38771
N	2.935538	-0.21899	0.352371
C	4.124612	-0.47444	1.142422
H	3.864045	-1.25792	1.857365
H	4.439118	0.421995	1.687289
H	4.951198	-0.82061	0.512944
H	-4.90854	1.746827	1.106887
O	-3.19234	-1.7779	-1.10854
H	-2.37002	-2.292	-1.08465

SI-19: Cartesian coordinates (Å) of geometry of CD-TS calculated at B3LYP/6-31G(d) level.

C	-4.81612	5.149351	-3.35125
H	-5.8872	4.941129	-3.23817
H	-4.52422	4.822791	-4.357
H	-4.65066	6.224114	-3.26276
C	-4.01728	4.450117	-2.30312
N	-3.26121	5.05327	-1.43697
C	-2.69666	4.039097	-0.64037
C	-1.85699	4.273704	0.388525
H	-1.62066	5.322882	0.577144
C	-1.24276	3.250551	1.27541
C	-1.8699	2.842078	2.459696
H	-2.84847	3.248987	2.699894
C	0.023499	2.721228	0.964519
C	-1.25879	1.932542	3.320543
H	-1.76195	1.62513	4.232479
C	0.642569	1.812371	1.826831
H	1.618317	1.421856	1.555243
C	0.001539	1.422307	2.999264
C	-3.19295	2.700978	-1.1243
O	-2.96801	1.566139	-0.75057
N	-4.03526	3.060087	-2.18716
C	-4.76333	2.094816	-2.98746
H	-4.50589	1.107077	-2.59852
H	-4.47388	2.151503	-4.04232
H	-5.8456	2.241972	-2.90416
H	0.488341	0.713104	3.663483
O	0.698203	3.072821	-0.17113
H	0.113315	3.626572	-0.71557

SI-20: Cartesian coordinates (Å) of geometry of AD-TS calculated at B3LYP/6-31G(d) level.

C	-3.75135	-1.80738	-0.66858
H	-4.63419	-1.38215	-1.16297
H	-4.08389	-2.21567	0.294858
H	-3.36148	-2.62218	-1.28098
C	-2.68234	-0.78618	-0.48979
N	-1.4423	-0.91055	-0.98551
C	-0.73874	0.173449	-0.56367
C	0.587974	0.529007	-1.0779
H	0.593049	0.957523	-2.08059
C	1.853177	0.212707	-0.52851
C	3.030312	0.686483	-1.18447
H	2.901463	1.264156	-2.09648
C	2.051945	-0.56219	0.663851
C	4.297541	0.451031	-0.68796
H	5.167519	0.836377	-1.21172
C	3.335576	-0.79102	1.158023
H	3.433135	-1.3833	2.06253
C	4.453663	-0.28541	0.498229
C	-1.61604	1.071131	0.203926
O	-1.43568	2.168167	0.722623
N	-2.85353	0.368239	0.211848
C	-4.04031	0.856059	0.88968
H	-3.78178	1.82828	1.314595
H	-4.34468	0.178728	1.694545
H	-4.87148	0.977783	0.187604
H	5.445486	-0.47457	0.898856
O	1.024109	-1.11497	1.363595
H	0.211771	-1.08054	0.828684

SI-21: Cartesian coordinates (Å) of geometry of EF-TS calculated at B3LYP/6-31G(d) level.

C	-2.39798	2.454935	0.568846
H	-1.55127	3.139704	0.490921
H	-2.81308	2.522139	1.581334
H	-3.1784	2.771877	-0.1323
C	-1.9588	1.064972	0.2729
N	-0.72548	0.710499	-0.03027
C	-0.67342	-0.66248	-0.35448
C	0.471205	-1.2135	-0.84059
H	0.320615	-2.26165	-1.12523
C	1.842321	-0.83754	-0.47703
C	2.382329	-1.34359	0.734455

H	1.94721	-2.24457	1.167031
C	2.195826	0.542249	-0.80847
C	3.497507	-0.7791	1.327651
H	3.907921	-1.21069	2.23566
C	3.44795	1.022725	-0.29583
H	3.79438	1.988557	-0.65412
C	4.063644	0.38356	0.759681
C	-2.0377	-1.17092	-0.24427
O	-2.53805	-2.2648	-0.40742
N	-2.77206	-0.017	0.24318
C	-4.19049	-0.07228	0.55648
H	-4.49805	-1.10783	0.398454
H	-4.76904	0.58101	-0.10415
H	-4.37196	0.205669	1.598999
H	4.961151	0.813052	1.201883
O	1.392945	1.307512	-1.4573
H	0.039778	1.272268	-0.42715

SI-22: Cartesian coordinates (Å) of geometry of FG-TS calculated at B3LYP/6-31G(d) level.

C	-1.8728	-0.62981	-1.04097
H	-2.79003	-1.0743	-1.44787
H	-1.5409	-1.26749	-0.21104
H	-1.10678	-0.66948	-1.82147
C	-2.09225	0.775418	-0.60422
N	-1.43156	1.84835	-1.04967
C	-1.85388	3.023261	-0.41943
C	-1.36014	4.346062	-0.82521
H	-1.87755	4.883101	-1.62355
C	-0.29101	4.987304	-0.28492
C	0.48288	4.451733	0.822698
H	0.176945	3.494125	1.233575
C	0.097722	6.330248	-0.86495
C	1.527279	5.139781	1.341039
H	2.091236	4.739405	2.178721
C	1.236852	7.003885	-0.22959
H	1.513161	7.971912	-0.636
C	1.904604	6.433154	0.801894
C	-2.88562	2.669183	0.483911
O	-3.61029	3.283225	1.270471
N	-2.96848	1.215284	0.320551
C	-3.91669	0.429144	1.082782
H	-4.45182	1.146421	1.710398
H	-3.40913	-0.30596	1.716859

H	-4.62772	-0.08638	0.428071
H	2.749082	6.950602	1.252385
O	-0.49536	6.822874	-1.82397
H	-0.7037	1.810529	-1.74866

SI-23: Cartesian coordinates (Å) of geometry of GH-TS calculated at B3LYP/6-31G(d) level.

C	-4.27854	-0.88404	0.793379
H	-5.01348	-0.83547	-0.01795
H	-4.51399	-0.08322	1.504279
H	-4.38675	-1.84426	1.303374
C	-2.89794	-0.71962	0.265081
N	-1.90104	-1.58077	0.453899
C	-0.68068	-1.08953	-0.0799
C	0.542386	-1.58384	0.21831
H	0.554438	-2.45704	0.884421
C	1.767356	-0.82254	0.014039
C	2.709541	-1.04622	-0.98514
H	2.529751	-1.83057	-1.71924
C	1.901395	0.280747	0.991781
C	3.888774	-0.29876	-1.04517
H	4.630652	-0.50191	-1.81177
C	3.167836	0.955549	0.914785
H	3.35487	1.711454	1.673772
C	4.106198	0.684525	-0.06954
C	-1.03766	0.165052	-0.75859
O	-0.43646	0.942138	-1.45734
N	-2.45956	0.320277	-0.45497
C	-3.22131	1.474669	-0.90568
H	-2.51679	2.10386	-1.45302
H	-3.6223	2.033092	-0.05503
H	-4.03534	1.1745	-1.57246
H	5.035088	1.253697	-0.08355
O	0.966884	0.589673	1.783408
H	-1.9578	-2.37354	1.078574

SI-24: Cartesian coordinates (Å) of geometry of EH-TS calculated at B3LYP/6-31G(d) level.

C	-1.80197	-0.62962	-0.93291
H	-2.71594	-1.14459	-1.25718
H	-1.41329	-1.17033	-0.06028
H	-1.06512	-0.71823	-1.73718
C	-2.05367	0.802526	-0.62121
N	-1.47561	1.849103	-1.21837

C	-1.89289	3.056274	-0.66431
C	-1.36393	4.359651	-1.06639
H	-1.85777	4.872852	-1.89998
C	-0.36743	5.055795	-0.45292
C	-0.09949	6.427761	-0.86201
H	-0.65723	6.818252	-1.71059
C	0.469503	4.469797	0.662927
C	0.772558	7.21226	-0.18717
H	0.939666	8.241874	-0.49003
C	1.33009	5.417452	1.385222
H	1.874433	5.01567	2.234244
C	1.481402	6.697165	0.968246
C	-2.82275	2.758287	0.360359
O	-3.50092	3.424509	1.148155
N	-2.89027	1.299991	0.311071
C	-3.75208	0.559271	1.208158
H	-4.27208	1.314896	1.802548
H	-3.1737	-0.09255	1.872196
H	-4.48282	-0.04207	0.656133
H	2.156851	7.365089	1.498514
O	0.482174	3.268833	0.928244
H	-0.71834	1.762005	-1.87997

SI-25:CASPT2//CASSCF single point energies for the ground state and the first excited-state.

CI-CAS(8,7)	S_0	-722.1362331
	S_1	-722.1342248
CI-CAS(12,11)	S_0	-722.14356
	S_0	-722.1346386

SI-26: The energy profile for the N2-H transfer process in the first excited state calculated at the CASSCF/6-31G(d) level in vacuum.

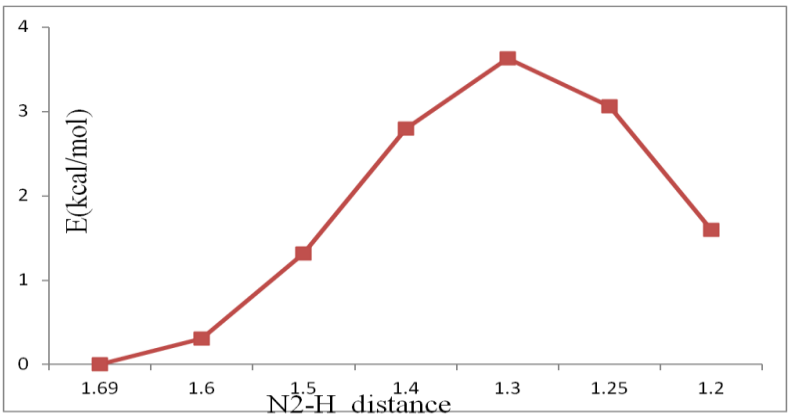

Figure S4

SI-27: Energy profiles along the rotation around C3-C4 double bond (angle τ) in A-S_1 and E-S_1 potential energy surfaces at CASSCF/6-31G(d) level in vacuum.

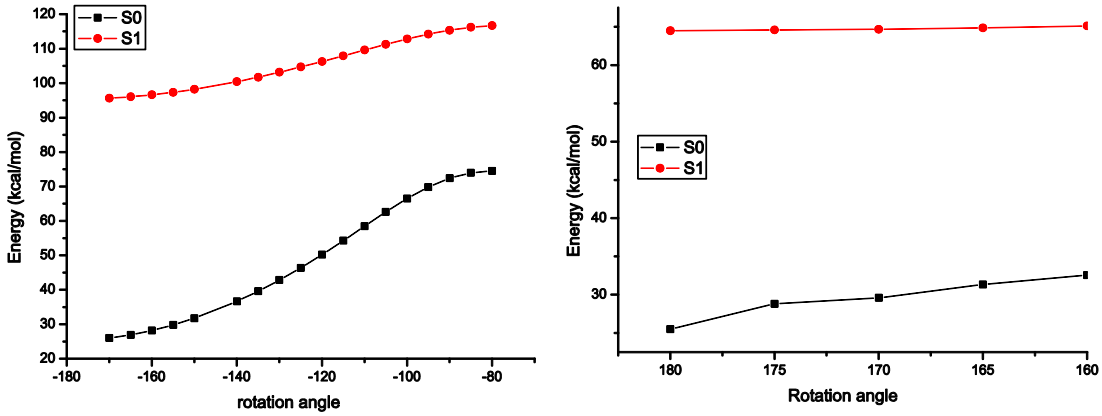

Figure S5

SI-28:Calculated relative energies with different methods for important geometries.

	TDDFT/vacuum kcal/mol	CASSCF/vacuum kcal/mol	CASPT2/PCM//CASSCF kcal/mol
A-S_1	Turn to structure E-S_1	96.71	75.68
E-S_1	49.48	83.89	63.50
A-E-TS-S_1	------	100.34	69.91
CI	40	71.40	57.25