Electronic Supplementary Information

Trans-to-*cis* photoisomerization of cyclocurcumin in different environments rationalized by computational photochemistry

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Content

1. Multistate (MS)-CASPT2 benchmark with different active spaces

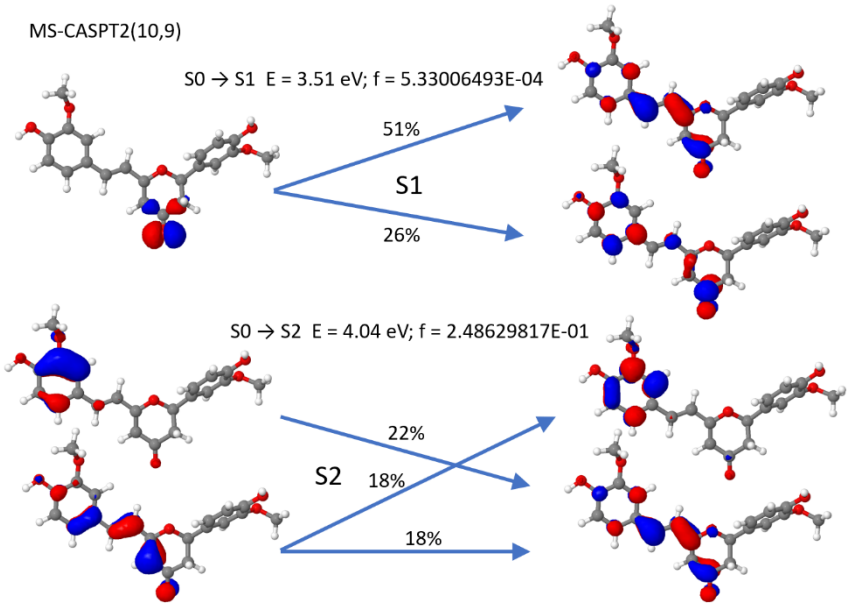

Figure S1. Franck-Condon transition energies, oscillator strengths and main orbital contributions at the MS-CASPT2(10,9)/6-31G* level of theory, calculated for the ground state structure optimized at B3LYP level.

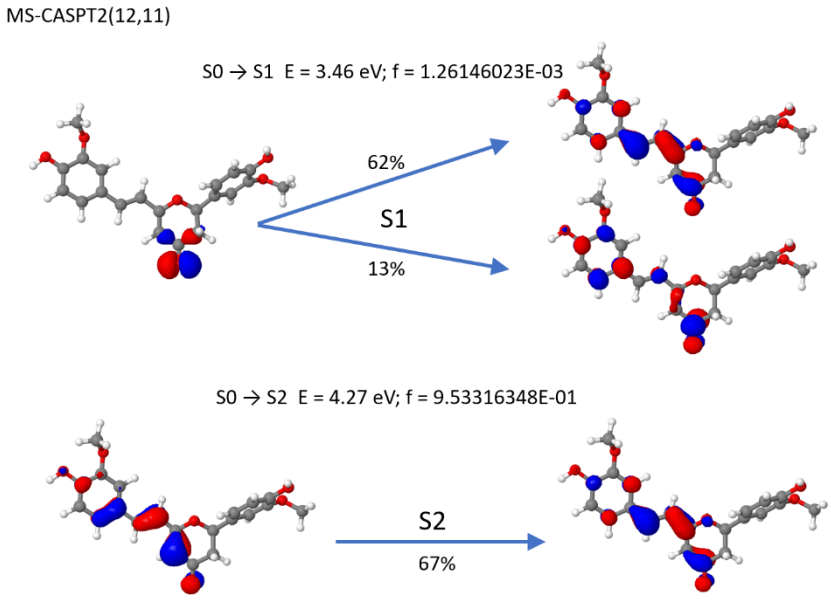

Figure S2. Franck-Condon transition energies, oscillator strengths and main orbital contributions at the MS-CASPT2(12,11)/6-31G* level of theory, calculated for the ground state structure optimized at B3LYP level.

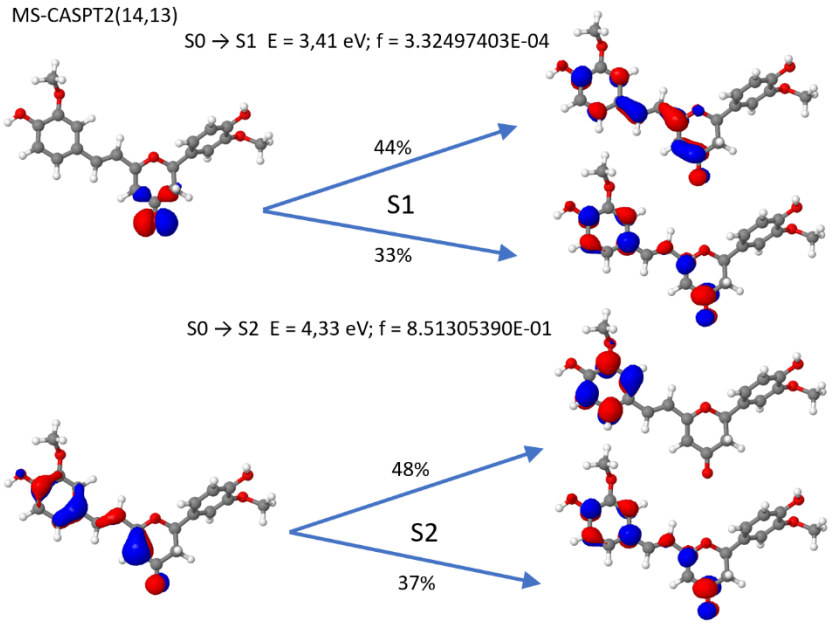

Figure S3. Franck-Condon transition energies, oscillator strengths and main orbital contributions at the MS-CASPT2(14,13)/6-31G* level of theory, calculated for the ground state structure optimized at B3LYP level.

2. Extended multistate (XMS)-CASPT2 energy pathways

The XMS-CASPT2 energy pathways are shown in Figure S4. As it can be seen, while the photoisomerization process by irradiating S_1 is described almost identically at XMS- and MS-CASPT2 levels, some differences are noted when irradiating to S_2 (compare Figure S4 and 4 in the main text). Indeed, the S_2/S_1 crossing is delayed at XMS-CASPT2 level, suggesting a longer S_2 lifetime before reaching the S_2/S_1 crossing. On the other hand, S_1 has a short lifetime as described by XMS-CASPT2, since the S_1/S_0 crossing is expected at ca. 140 degrees, against the 110 degrees of the MS-CASPT2 description. In any case, the same qualitative description is offered by both XMS- and MS-CASPT2 levels: a first S_2/S_1 crossing followed by population of the ground state through an early S_1/S_0 crossing, i.e. corresponding to a low-twisted structure around the θ dihedral angle, that should most probably result in an aborted photoisomerization process.

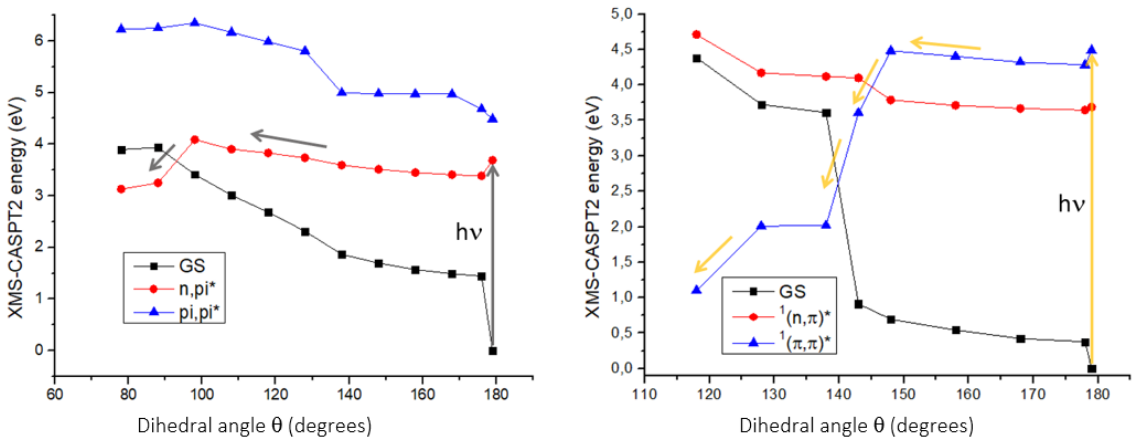

Figure S4. Photoisomerization pathway by irradiating to the S_1 state (left) and to the S_2 state (right) at XMS-CASPT2//CASSCF(10,9) level.

3. Simulated absorption spectrum of *cis*-cyclocurcumin

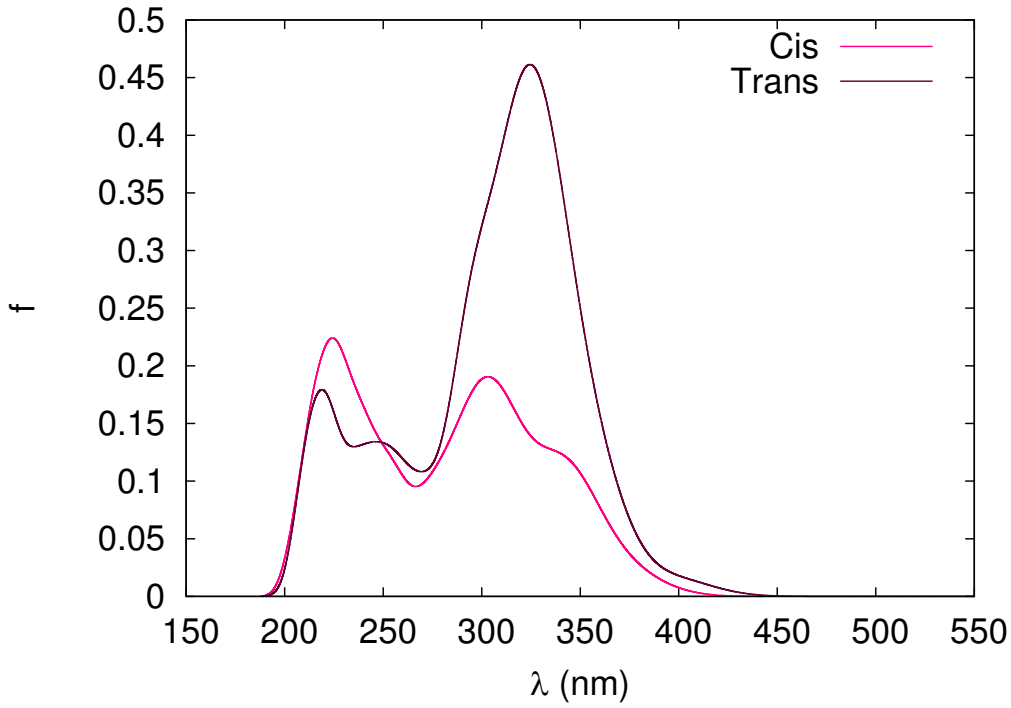

Figure S5. Simulated absorption spectrum of *cis* cyclocurcumin calculated in gas phase at TD-DFT level from 100 snapshots extracted from a Wigner distribution using the CAM-B3LYP functional. The spectrum of the *trans* isomer is also given for comparison.

4. Spin-flip TD-DFT energy pathways

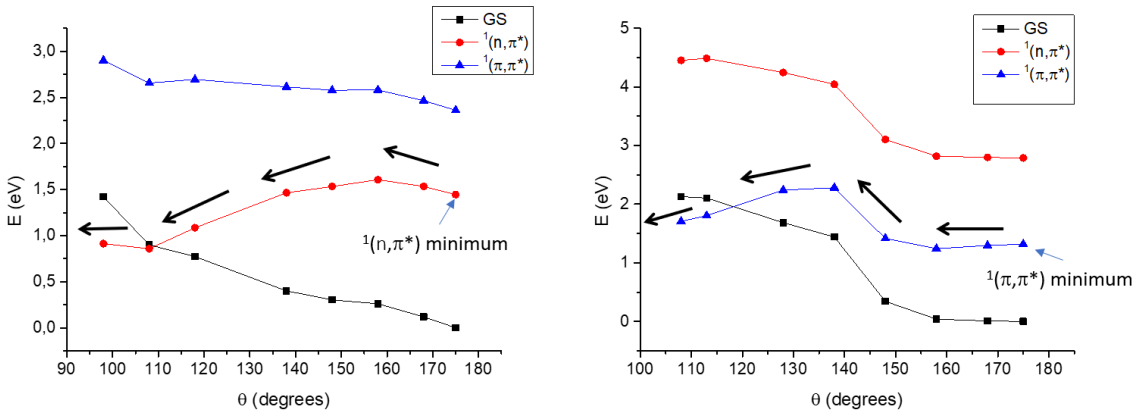

Figure S6. Photoisomerization pathway by irradiating to the S_1 state (left) and to the S_2 state (right) at spin-flip TD-DFT//CASSCF(10,9) level.

5. 3D structures and Cartesian coordinates (in Ångström) of the most relevant structures along the photoreaction

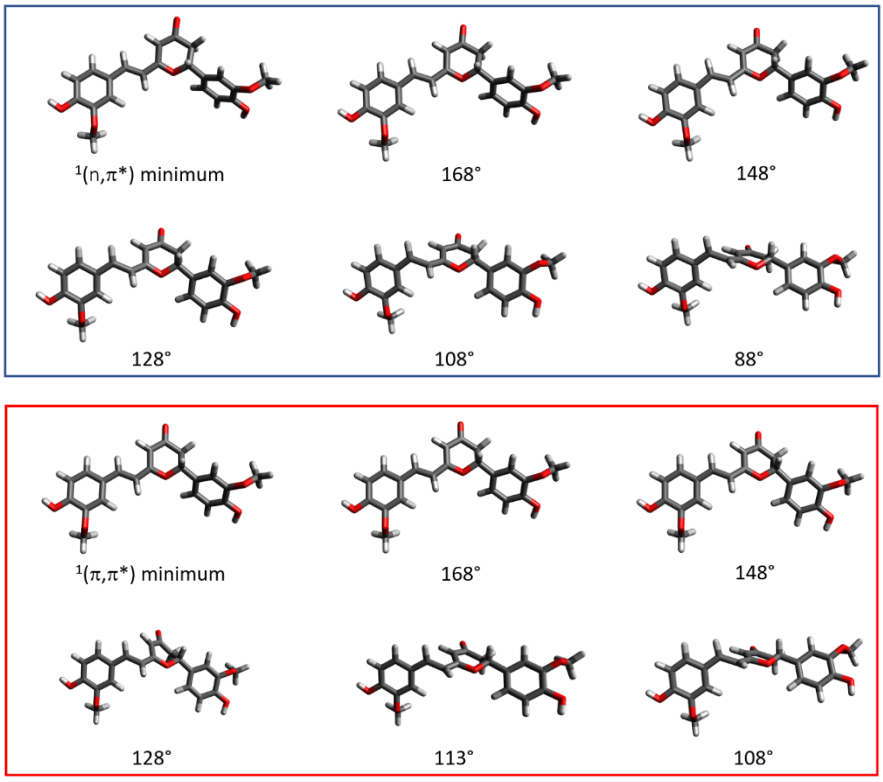

Figure S7. 3D structures of the ^{1}(n,π*) (top) and ^{1}(π,π*) (bottom) excited-state pathways.

S_0 optimized *trans*-cyclocurcumin
Level of theory: B3LYP/6-311+G*

C	4.105110	-1.665355	-1.510197
C	5.189334	-1.876053	-0.655334
C	3.132043	-0.713231	-1.209254
C	3.224484	0.043086	-0.037599
C	4.314839	-0.167915	0.813533
C	5.300566	-1.108418	0.520316
O	6.154697	-2.815893	-0.899044
O	6.307240	-1.313299	1.430354
C	7.629672	-0.995582	0.986982
C	2.215377	1.117975	0.287462
C	2.449708	2.436288	-0.453301
C	1.337985	3.438122	-0.137492
C	0.044007	2.831622	0.128427
C	-0.140068	1.478323	0.080853
O	0.894648	0.601537	-0.019634
O	1.533488	4.648701	-0.158322
C	-1.415480	0.774757	0.138924
C	-2.620410	1.344123	-0.081244
C	-3.928249	0.700500	-0.018207
C	-4.109573	-0.656021	0.321876
C	-5.073727	1.456858	-0.317592
C	-6.343937	0.889251	-0.270055
C	-6.508162	-0.451882	0.080504
C	-5.368622	-1.236446	0.371398
O	-7.730526	-1.052501	0.169776
O	-5.480017	-2.541241	0.778645
C	-5.971353	-3.465657	-0.197195
H	4.017817	-2.263992	-2.415844
H	2.287531	-0.576007	-1.876776
H	4.418154	0.393162	1.738548
H	5.937782	-3.275315	-1.725262
H	8.282024	-1.166539	1.846250
H	7.696468	0.058274	0.685166
H	7.941019	-1.635944	0.156406
H	2.226973	1.319819	1.368727
H	2.467861	2.254370	-1.537112
H	3.417128	2.865574	-0.177389
H	-0.797475	3.492404	0.299834
H	-1.329391	-0.286958	0.354600
H	-2.646374	2.400066	-0.346517

H	-3.265465	-1.291110	0.569671
H	-4.968547	2.504326	-0.587221
H	-7.220597	1.494025	-0.495941
H	-8.417035	-0.397175	-0.031935
H	-5.945505	-4.446717	0.281893
H	-5.322577	-3.476986	-1.083091
H	-6.997294	-3.229787	-0.495042

S_0 optimized *cis*-cyclocurcumin
Level of theory: B3LYP/6-311+G*

C	-4.571999	-0.726594	1.370156
C	-5.526055	-1.105376	0.423238
C	-3.602800	0.228362	1.066114
C	-3.567634	0.818522	-0.200274
C	-4.529676	0.441261	-1.143605
C	-5.511023	-0.503946	-0.850438
O	-6.478694	-2.057425	0.670550
O	-6.381274	-0.877477	-1.843588
C	-7.763934	-0.594003	-1.610014
C	-2.560534	1.890839	-0.541298
C	-2.948621	3.286930	-0.050195
C	-1.833566	4.293875	-0.331691
C	-0.489645	3.729666	-0.316249
C	-0.269139	2.405449	-0.078897
O	-1.282816	1.499772	0.019347
O	-2.066100	5.486747	-0.486702
C	1.007407	1.755443	0.227121
C	2.280736	2.047461	-0.120685
C	2.866572	3.020452	-1.050161
C	2.204397	3.527376	-2.184934
C	4.203257	3.405581	-0.850138
C	4.831916	4.300083	-1.711534
C	4.152330	4.818074	-2.815682
C	2.824237	4.407484	-3.063637
O	4.715451	5.712386	-3.680565
O	2.099182	4.904847	-4.115370
C	2.561099	4.559404	-5.424483
H	-4.582731	-1.196480	2.352675
H	-2.858764	0.496130	1.809228
H	-4.532014	0.870088	-2.142243
H	-6.355373	-2.391303	1.572807
H	-8.288898	-0.900954	-2.517388
H	-7.918921	0.481044	-1.447726
H	-8.151160	-1.154259	-0.753957

H	-2.422543	1.932200	-1.631991
H	-3.131530	3.261885	1.033413
H	-3.873792	3.620413	-0.529115
H	0.345707	4.414031	-0.393320
H	0.869244	0.886673	0.868418
H	3.031046	1.425124	0.367435
H	1.184256	3.239456	-2.409592
H	4.753868	3.009996	-0.000684
H	5.861166	4.603643	-1.526956
H	5.611885	5.921211	-3.373890
H	1.832478	4.983828	-6.118530
H	2.590462	3.468981	-5.551692
H	3.550240	4.980232	-5.628158

^{1}(n,π*) minimum
Level of theory: MS-CASPT2//SA(4)-CASSCF(10,9)/6-31G*

C	4.14054195	-1.72265988	-1.55391031
C	5.15129410	-1.93829038	-0.63506994
C	3.14941831	-0.78297625	-1.31310924
C	3.15575720	-0.04534388	-0.14259270
C	4.17802235	-0.26482022	0.77432228
C	5.17151438	-1.19405903	0.54312659
O	6.13282968	-2.84956980	-0.82362268
O	6.11884285	-1.40975475	1.49105554
C	7.39514821	-0.87759549	1.22442796
C	2.11425475	1.01430052	0.13890129
C	2.52995775	2.39540293	-0.37437609
C	1.34459202	3.31526665	-0.31779271
C	0.09081782	2.87572640	-0.26689448
C	-0.17225918	1.45212402	-0.30233934
O	0.89979456	0.62315202	-0.46324581
O	1.67535340	4.61802363	-0.31419947
C	-1.40848692	0.82217497	-0.22337090
C	-2.66542702	1.43673851	-0.15639040
C	-3.93303723	0.75159382	0.01314504
C	-4.05463429	-0.63094595	0.24587631
C	-5.13194309	1.49731764	-0.03801227
C	-6.35331591	0.90391755	0.12763208
C	-6.45974070	-0.46929602	0.36237507
C	-5.29305627	-1.23615233	0.42060185
O	-7.64996342	-1.09287988	0.53792010
O	-5.34718004	-2.56653156	0.70027768
C	-5.73487639	-3.40356399	-0.36117516
H	4.12077573	-2.29984435	-2.46353131
H	2.36477837	-0.64324172	-2.03206809
H	4.21062566	0.27370860	1.70521986

H	5.98474258	-3.33330125	-1.62409497
H	8.00898831	-1.10556253	2.08375129
H	7.34300953	0.19940062	1.09652678
H	7.83081212	-1.32601111	0.34151613
H	1.95745212	1.08226681	1.21181839
H	2.90182367	2.32892231	-1.39233557
H	3.33477370	2.78763318	0.23762489
H	-0.72921484	3.56500608	-0.19511334
H	-1.35325834	-0.25109010	-0.22211625
H	-2.72535849	2.50810374	-0.22781236
H	-3.19017188	-1.26147238	0.32628952
H	-5.08347324	2.55766462	-0.21228597
H	-7.24994862	1.50007656	0.08244206
H	-8.35579299	-0.46222112	0.53857000
H	-5.69706528	-4.41589901	0.01468392
H	-5.05055551	-3.30771429	-1.19883390
H	-6.74159044	-3.18058490	-0.69026633

$^{1}(\pi,\pi^*)$ minimum
Level of theory: MS-CASPT2//SA(4)-CASSCF(10,9)/6-31G*

C	4.04477932	-1.95101646	-1.19995327
C	5.19976440	-1.97168927	-0.44059903
C	3.05843055	-1.00392750	-0.96848378
C	3.21385773	-0.06143856	0.03252922
C	4.37807024	-0.08950327	0.79314949
C	5.36853328	-1.02405857	0.56723349
O	6.18478029	-2.87944572	-0.62787975
O	6.46484631	-1.04416634	1.36741799
C	7.65413428	-0.54203645	0.80501181
C	2.17878789	1.01238001	0.28750761
C	2.39219701	2.26586981	-0.55399504
C	1.23810836	3.23284595	-0.35130052
C	-0.00819068	2.67236134	-0.02615160
C	-0.18921150	1.22793477	0.05757723
O	0.90074320	0.45422511	0.01978748
O	1.42683207	4.46717683	-0.47594682
C	-1.37131441	0.56978774	0.14802842
C	-2.61782738	1.25262175	0.08674471
C	-3.88312542	0.70295589	0.13417551
C	-4.11362593	-0.73077543	0.24428883
C	-5.05294712	1.55788428	0.06432859
C	-6.29671117	1.04315222	0.11057678
C	-6.49643675	-0.35861022	0.22597647
C	-5.37668982	-1.24314394	0.28687348
O	-7.72126660	-0.90294786	0.27902970

O	-5.58292320	-2.57544448	0.42759841
C	-5.93633064	-3.26794398	-0.74752387
H	3.90805913	-2.68605246	-1.97557069
H	2.16414124	-1.01843638	-1.56143782
H	4.53111411	0.61034127	1.59599380
H	5.93622473	-3.50136351	-1.29717750
H	8.40893233	-0.60655439	1.57535834
H	7.53136388	0.49513117	0.50873568
H	7.96202247	-1.12888448	-0.05021470
H	2.20794213	1.28520704	1.33784315
H	2.47059019	1.99184206	-1.60335246
H	3.32180465	2.74841317	-0.27296929
H	-0.83679584	3.33053334	0.14792300
H	-1.33418765	-0.49442013	0.24079091
H	-2.58369572	2.31575710	-0.00575264
H	-3.28715829	-1.41012971	0.30352213
H	-4.91099777	2.62067322	-0.02270427
H	-7.15869107	1.68699093	0.06186530
H	-8.38874145	-0.23107513	0.26493460
H	-6.04146338	-4.30710415	-0.47304708
H	-5.15814444	-3.17093176	-1.49816702
H	-6.87401253	-2.90584585	-1.14903000