Supporting online information for

Analysis of the primary photo-cycle reactions occurring in the LOV blue-light receptor by multi-configurational quantum-chemical methods

Tatiana Domratcheva, Roman Fedorov, Ilme Schlichting*

Max-Plank Institute for Medical Research, Department of Biomolecular Mechanisms, Jahnstrasse 29, 69120 Heidelberg, Germany

*corresponding author e-mail: Tatjana.Domratcheva@mpimf-heidelberg.mpg.de

This PDF file includes:

Figures S1 to S5

Tables S1 and S2

Cartesian coordinates of the model complexes

(A) (B)

Figure S1. Minimum-energy structures (CASSCF(2,2)/6-31G(d)) of the complexes A) between lumiflavin and thiomethanol (S_0 electronic state) and B) lumiflavine semiquinone and thiomethyl radical SCH_3 (T_1 electronic state). The arrangement of the molecules in the equilibrium complexes is unfavorable for the LOV photoreaction. In the ground electronic state the energy of the equilibrium structure (A) is 2.9 kcal/mol lower than that of the complex **R.**

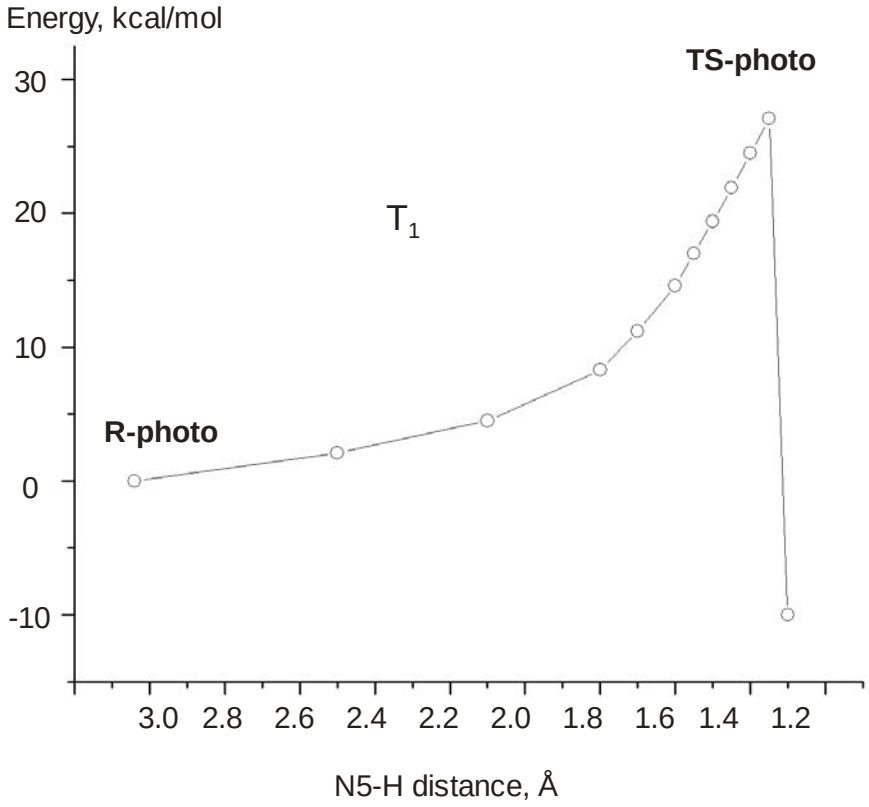

Figure S2. Energy profile of the photo-reaction calculated by the CASSCF(2,2)/6-31G(d) method in the triplet electronic state. Geometry optimization was performed with the N5-H distance fixed. To keep the thiomethanol fragment above the isoalloxazine ring, dihedral angles S-N5-C5a-C9a and S-N5-C4a-C10a were fixed during the optimization at 90 and -90 degrees, respectively.

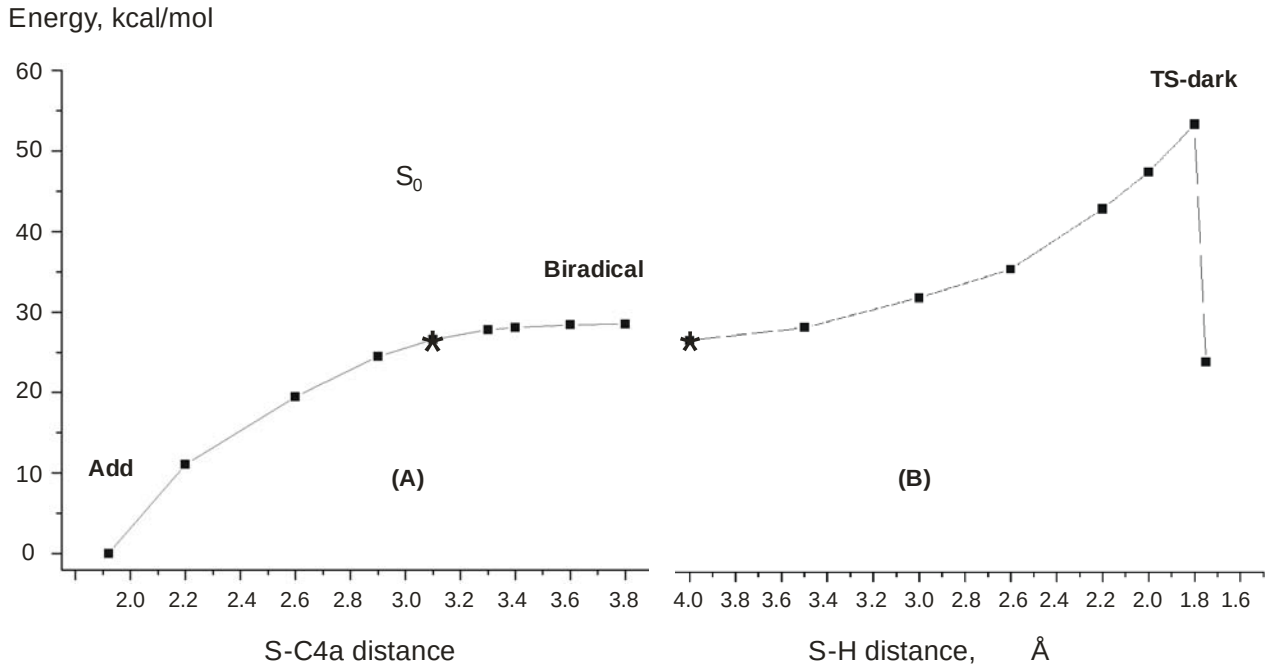

Figure S3. Energy profile of the dark-reaction (S-C4a covalent adduct dissociation) calculated by the CASSCF(2,2)/6-31G(d) method in the ground electronic state. Geometry optimization was performed with the S-C4a (A) and S-H (B) distances fixed, respectively. To keep the thiomethanol fragment above the isoalloxazine ring, dihedral angles S-N5-C5a-C9a and S-N5-C4a-C10a were fixed during the optimization at 90 and -90 degrees, respectively. The energy indicated by the asterisk corresponds to the same structure with the S-C4a and S-H distances of 3.10 and 3.98 Å, respectively.

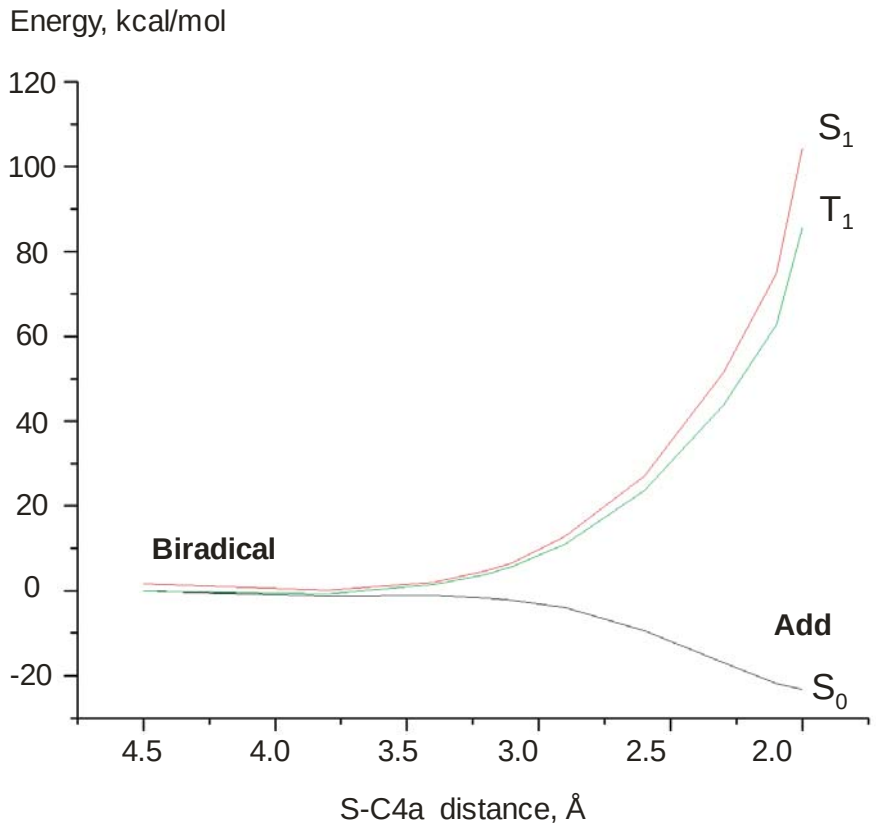

Figure S4. Adiabatic energy profiles along the S-C4a-bond internal coordinate calculated by the state-averaged CASSCF(4,3)/6-31G(d) method for the S_0, T_1, and S_1 electronic states. Biradical structure is a minimum in the T_1 and S_1 electronic sates. In the S_0 electronic state, **Biradical** lies on the energy surface slope connecting **TS-dark** and **Add** (see also Figure S3).

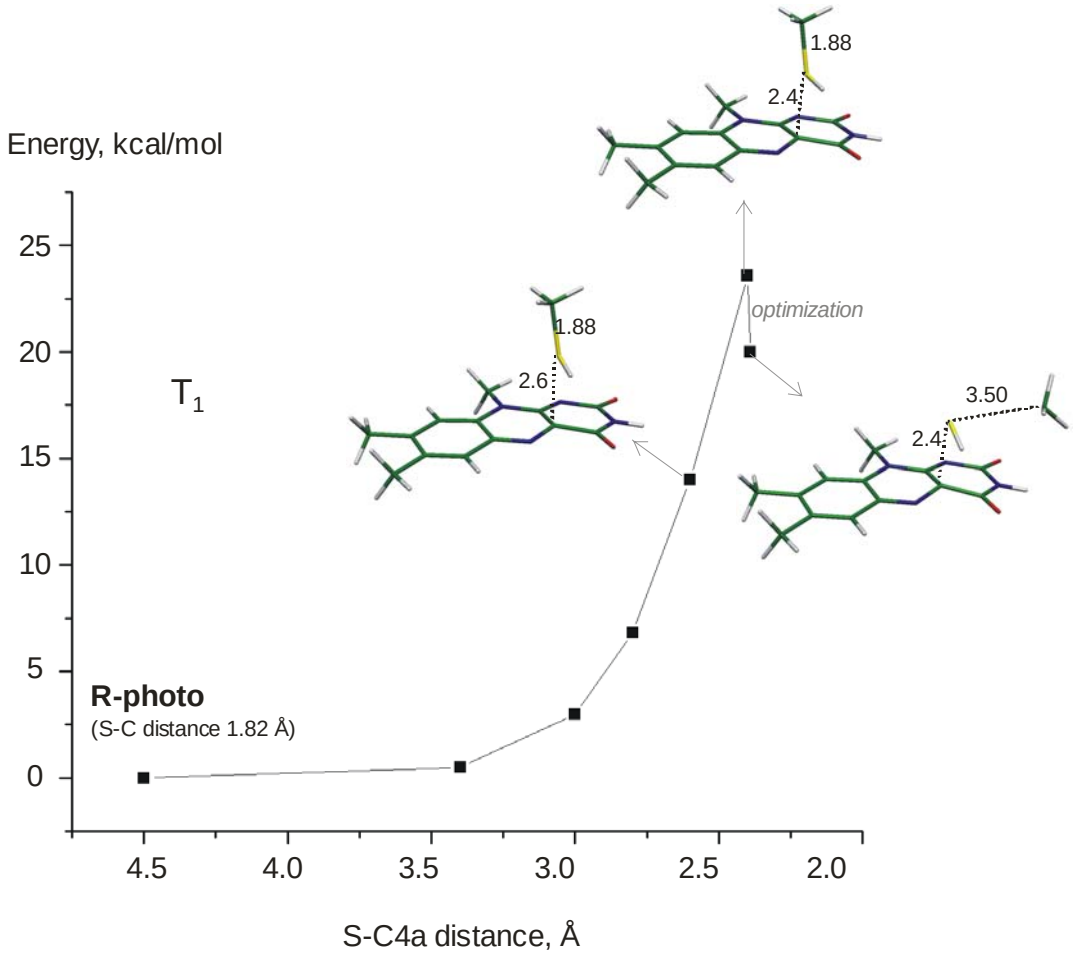

Figure S5. Energy profile for the zwitterionic covalent adduct formation (suggested by Schleicher, E.; Kowalczyk, R. M.; Kay, C. W. M.; Hegemann, P.; Bacher, A.; Fischer, M.; Bittl, R.; Richter, G.; Weber, S. *J. Am. Chem. Soc.* **2004**, *126*, 11067-11076) calculated by the CASSCF(2,2)/6-31G(d) method in the triplet electronic state. Geometry optimization was performed with the S-C4a distance fixed. To keep the thiomethanol fragment above the isoalloxazine ring, dihedral angles S-N5-C5a-C9a and S-N5-C4a-C10a were fixed during the optimization at 90 and -90 degrees, respectively.

Table S1. Total energies [Hartree] of the model complexes evaluated by different methods with the 6-31G(d) basis set. The CASSCF equations were solved for the S_0, S_1 and T_1 electronic states, respectively.

Electronic state	Method	**R**	**R-photo**	**TS-photo**	**Biradical**	**Add**	**TS-dark**
S_0	RHF	-1304.549556			-1304.454579	-1304.4518615	
	CASSCF(2,2)	-1304.576423			-1304.520331	-1304.565059	-1304.480149
	MCQDPT2	-1307.440091			-1307.411408	-1307.460488	-1307.393553
S_1	CASSCF(2,2)	-1304.398787					
	MCQDPT2	-1307.319341					
T_1	ROHF	-1304.443636	-1304.467340	-1304.428341	-1304.515333		
	UHF	-1304.449436*					
	CASSCF(4,4)	-1304.465046	-1304.489505	-1304.436685	-1304.532676	-1304.396474	
	MCQDPT2	-1307.349787	-1307.366718	-1307.346167	-1307.402157	-1307.331776	

*S^2=2.5

Table S2. Total energies [Hartree] of the model complexes calculated with averaging for the S_0-S_1, and T_1-T_2 electronic states, respectively, with the 6-31G(d) basis set

Electronic state	Method	**R**	**R-photo**	**Add**
S_0	CASSCF(2,2)	-1304.545306		-1304.539754
	MCQDPT2	-1307.438864		-1307.462566
S_1	CASSCF(2,2)	-1304.378703		-1304.351097
	MCQDPT2	-1307.333678		-1307.338455
T_1	CASSCF(4,4)	-1304.453892	-1304.480753	
	MCQDPT2	-1307.349698	-1307.368241	
T_2	CASSCF(4,4)	-1304.411000	-1304.407687	
	MCQDPT2	-1307.307689	-1307.307975	

Cartesian coordinates of the model complexes, [Å]

R

C	16.9862480667	54.5875113266	17.8327483868
S	16.9209222432	55.0167113193	16.0675785887
H	16.0251331683	54.2455567914	18.1919579296
H	17.7366479007	53.8334564885	18.0267924123
H	16.6459346219	53.8085619679	15.5962260134
H	17.2542058302	55.4898159369	18.3651698866
C	18.4800430934	48.2698527471	17.9553434924
C	16.6780473682	47.8873726720	20.2708158064
C	16.2513286632	48.7404222363	19.1002223222
C	17.1169190400	48.9206795667	17.9968995841
C	15.0089386577	49.3399592209	19.1205530116
C	14.5725507750	50.1351072926	18.0561534921
C	15.4268048651	50.3166137339	16.9711712573
C	16.6845410808	49.7048961441	16.9587538672
N	13.3288799023	50.7493800999	18.0403296333
N	15.0596021550	51.0888019434	15.8980837937
C	12.9420748300	51.5142791968	16.9864090022
C	13.9215122458	51.6409269947	15.8976119422
N	11.7901386727	52.0767530015	16.9862247916
C	11.3913369426	52.8568962682	15.9250162017
N	12.2767011979	53.0140594539	14.8545772424
C	13.5253818486	52.4835494833	14.7245279696
O	14.2240396286	52.6699553927	13.7799555028
C	12.4141233261	50.5663101603	19.1679092253
O	10.3336401484	53.3992260462	15.8793425240
H	18.4073729377	47.1879873347	18.0100590527
H	19.1033324778	48.5951847335	18.7826966943
H	18.9945730854	48.5199866260	17.0361305661
H	17.5824192282	48.2760951036	20.7281586376
H	16.8896893881	46.8704931015	19.9558111582
H	15.9078587751	47.8496340579	21.0304116209
H	14.3766406977	49.1844317802	19.9708441129
H	17.3020096554	49.8732275085	16.0957327603
H	11.9517464807	53.5939703098	14.1093922284
H	12.8716514749	50.9411974961	20.0738421153
H	12.1837424932	49.5155638119	19.2836602021
H	11.5134545535	51.1141341871	18.9648246570

R-photo

C	17.2034484480	54.5301528117	17.7802198534
S	16.9913237369	54.9454830260	16.0242539739
H	16.2752177510	54.1936238643	18.2218204579
H	17.9683050896	53.7780864894	17.9177957965
H	16.6717819552	53.7380387790	15.5898889211
H	17.5152288485	55.4360323825	18.2824583204
C	18.5033515704	48.3598031795	18.0126790432
C	16.6445217312	47.8825569282	20.2691157598
C	16.2233272398	48.7527555589	19.1148677803
C	17.1335350800	48.9898307823	18.0068447418
C	14.9760335544	49.3263852299	19.1020183114
C	14.5424035657	50.1371325679	18.0562014878
C	15.4399968160	50.3938852098	16.9340268330
C	16.7413848600	49.7707604667	16.9843556393
N	13.2856646064	50.7131691826	18.0362843428
N	15.1422196759	51.1324121511	15.9179601389
C	12.9099289105	51.5033770492	16.9715624362
C	13.8855391070	51.6909900999	15.9129991911
N	11.7453787521	52.0208951518	16.9672624175
C	11.3284455050	52.8230794749	15.9111010396
N	12.2207161791	53.0335940324	14.8755828675
C	13.4972664935	52.5352748885	14.7748526716
O	14.2045588942	52.7770755460	13.8467443647
C	12.3547091437	50.4774828387	19.1341287961
O	10.2471249990	53.3159783227	15.8849229779
H	18.4372466898	47.2770301662	18.0511629798
H	19.0789618195	48.6791342951	18.8758484830
H	19.0532568774	48.6319299764	17.1217452333
H	17.5259212494	48.2792834473	20.7644985004
H	16.8866069241	46.8763279769	19.9397042207
H	15.8550460054	47.8089187267	21.0060940135
H	14.3203063403	49.1376394939	19.9276071109
H	17.3787090740	49.9722129605	16.1447429302
H	11.9058566549	53.6207316526	14.1323066717
H	12.7769219892	50.8397878833	20.0633864792
H	12.1455278423	49.4185038298	19.2227037684
H	11.4426791154	51.0050573854	18.9274856533

TS-photo

C	15.7030430673	54.8132080050	17.1296051488
S	17.1165897087	53.6875899063	16.9007397265
C	16.6514100022	47.4018578023	19.6948791970
C	16.3844953513	48.4669186794	18.6641605661
C	18.6317887041	47.9280018374	17.5599713827
C	17.3468358947	48.7151358084	17.6192026658
C	15.2267756204	49.1950534802	18.7237590653
C	14.9399339474	50.1966942518	17.7842837736
C	15.8725964514	50.4316829706	16.7211383178
C	17.0737825952	49.6681419658	16.6981956983
N	15.7461173793	51.4468683056	15.8646806576
N	13.8011723845	50.9564338449	17.8538606248
C	14.4253363159	51.8594704506	15.7111442346
C	14.0248550589	52.5633622356	14.4834580587
C	13.4368015164	51.7183192405	16.7588103563
N	12.2748680796	52.2340431795	16.7228075697
C	11.8695336271	52.9782701456	15.6152118633
N	12.7471855040	53.0685217919	14.5488741808
O	14.7194935197	52.6942491252	13.5265225915
O	10.8053340650	53.5023647287	15.5692543132
C	12.8996528863	50.8574759085	18.9995731854
H	14.9241981514	54.3776702456	17.7455062594
H	15.2798311682	55.1215959875	16.1814498235
H	16.0654359355	55.6991092162	17.6354152954
H	17.5640506477	47.6131553644	20.2430653355
H	16.7735287087	46.4296137087	19.2279777855
H	15.8392554180	47.3343806876	20.4064892913
H	18.4408246559	46.8646220212	17.4543187530
H	19.2200699540	48.0659009826	18.4615381610
H	19.2328486740	48.2451939211	16.7183612720
H	14.5282288576	48.9925875071	19.5096811875
H	17.7588526627	49.8920328558	15.9026867519
H	16.4430761193	52.4852015548	16.2198039877
H	12.4242809134	53.5826775312	13.7561723359
H	12.3823427370	49.9055563232	19.0011310498
H	12.1750683404	51.6474015490	18.9303874664
H	13.4699243171	50.9663856725	19.9112331680

Biradical

C	14.7408132157	55.3865966268	17.4702635797
S	16.0956911986	54.2465090109	17.0940344596
C	16.9678471129	47.6477954480	20.0057002760
C	16.6089915604	48.4591736574	18.7822303517
C	18.6463895252	47.5576634713	17.5655409256
C	17.4046005825	48.4152455597	17.6315313929
C	15.4775650012	49.2595837514	18.8005703634
C	15.0981711083	50.0286071823	17.7062388792
C	15.9021016562	49.9811386291	16.5721516759
C	17.0340234530	49.1833732649	16.5439424225
N	15.5357254689	50.7490862395	15.4761474821
N	13.9350125591	50.8258424024	17.7171404341
C	14.5382553042	51.6427223338	15.5595350706
C	14.2158758507	52.4322569393	14.3787614379
C	13.6481315654	51.6647804879	16.6884804672
N	12.6115507850	52.4344787904	16.7421461448
C	12.2903423710	53.2458218405	15.6833587051
N	13.1078087641	53.2030799722	14.5454025635
O	14.8679962941	52.3848622198	13.3712542549
O	11.3553422418	53.9860843739	15.6815990315
C	13.0639643699	50.7990452241	18.8859003858
H	13.8873374406	54.8366866022	17.8436444440
H	14.4565568880	55.9655374867	16.6037696428
H	15.0825350121	56.0561321553	18.2515635303
H	17.9457924985	47.9213876525	20.3901137860
H	16.9946409533	46.5851947942	19.7836405217
H	16.2472284289	47.8006169290	20.7996246360
H	18.4132161977	46.5084754274	17.7197697208
H	19.3669302141	47.8434255212	18.3258160140
H	19.1305762879	47.6498049143	16.6010599101
H	14.8859666389	49.2807310589	19.6933239980
H	17.6318578832	49.1713803736	15.6491337696
H	16.0941280361	50.7718357167	14.6488006886
H	12.8281112095	53.7841026551	13.7837566619
H	12.7570924318	49.7810859887	19.0886629962
H	12.1992057805	51.4014129684	18.6794923742
H	13.5809943312	51.1985459272	19.7503914106

Add

C	15.0108494178	54.8333038156	17.0485074279
S	15.9925492283	53.3374210297	16.7429129429
C	17.0045727217	47.7869797525	20.0377325273
C	16.6317446873	48.6068373458	18.8234690845
C	18.7216527219	47.8212666641	17.6244474702
C	17.4436045711	48.6247670092	17.6863406729
C	15.4657301716	49.3590741732	18.8329984337
C	15.0823409731	50.1210433977	17.7408162339
C	15.9022251487	50.1522417837	16.6226276250
C	17.0675849353	49.4074175531	16.6057144483
N	15.4807761816	50.9278461838	15.5410612431
N	13.8629928378	50.8457709331	17.7111779290
C	14.7921740014	52.1264150657	15.8699907221
C	14.3132853575	52.7722552637	14.5801654188
C	13.6423381307	51.8105894939	16.8044491828
N	12.5236453297	52.4380008560	16.7754762122
C	12.2223881701	53.3104810114	15.7592931484
N	13.1189796992	53.4021670030	14.6834850665
O	14.9721344497	52.7476757481	13.5873524877
O	11.2294431878	53.9631659634	15.7249025870
C	12.8229891079	50.5155830153	18.6808629005
H	14.1391889171	54.6258729915	17.6526165292
H	14.7218454730	55.3235052363	16.1303384376
H	15.6653758837	55.4938539909	17.6023594212
H	17.9624685048	48.0933561105	20.4476639664
H	17.0804506648	46.7302630308	19.7984827758
H	16.2636109738	47.8936603878	20.8209308589
H	18.5298384807	46.7602600068	17.7537358470
H	19.4168048344	48.1201526731	18.4033241410
H	19.2177563603	47.9532451458	16.6707056971
H	14.8517965242	49.3426955694	19.7123428719
H	17.6899149414	49.4422673710	15.7283311486
H	16.1282234474	51.0429098823	14.7898665244
H	12.7956602286	53.9146841987	13.8895760246
H	12.7167575448	49.4408702426	18.7332557990
H	11.8976093714	50.9587245988	18.3625271102
H	13.0810448998	50.9001266479	19.6605600541

TS-dark

C	17.4908902302	53.3283170102	18.2195738000
S	16.5919492014	53.9303120270	16.7666596629
C	16.9745131583	47.8144739365	19.8087180743
C	16.6111195308	48.7968474258	18.7196824746
C	18.8555696336	48.3954309595	17.5964577635
C	17.5049995700	49.0684166064	17.6729613762
C	15.3754000916	49.4215324667	18.7518207165
C	14.9957386025	50.3357716891	17.7716821063
C	15.8830257945	50.5951678288	16.7380848895
C	17.1189808867	49.9694196699	16.6997788969
N	15.5650153813	51.5701555745	15.7688189249
N	13.7309684919	50.9428227985	17.7559956552
C	14.2609893058	51.7960850113	15.5814494220
C	13.8641730192	52.6886784571	14.4799242372
C	13.2735936446	51.5413807435	16.6237971568
N	12.0402397801	51.8804745552	16.5275604337
C	11.5870058707	52.5606796485	15.4190098234
N	12.5261096233	52.9433694789	14.4560408428
O	14.6439944919	53.1372174857	13.6933352324
O	10.4445337842	52.8488819668	15.2535871591
C	12.8260441518	50.7681637324	18.8860334523
H	17.6923575142	54.1930039681	18.8418579172
H	18.4301125135	52.8709969059	17.9436200153
H	16.8917292123	52.6310346592	18.7884712394
H	17.8724521171	48.1233947133	20.3350030369
H	17.1643825341	46.8265067675	19.4007981795
H	16.1777679734	47.7251391120	20.5365306406
H	18.7594798932	47.3159736431	17.5291547022
H	19.4599234468	48.6113731402	18.4724662317
H	19.4046967954	48.7316608817	16.7256595927
H	14.6999545803	49.1817765844	19.5485439685
H	17.7767703550	50.2047297966	15.8822826534
H	16.1795250955	52.4613718890	15.8116092828
H	12.1794064830	53.5098303672	13.7107698692
H	12.4428499270	49.7548231351	18.9221682949
H	12.0018070429	51.4479911095	18.7723934155
H	13.3565458954	50.9875036133	19.8023352582