

## Supporting information

### **Probing $\pi \rightarrow \pi^*$ photoisomerization mechanism of *cis*-azobenzene by multi-state ab initio on-the-fly trajectory dynamics simulation**

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## Supporting information

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## S1. Potential energy surfaces for the intersecting states

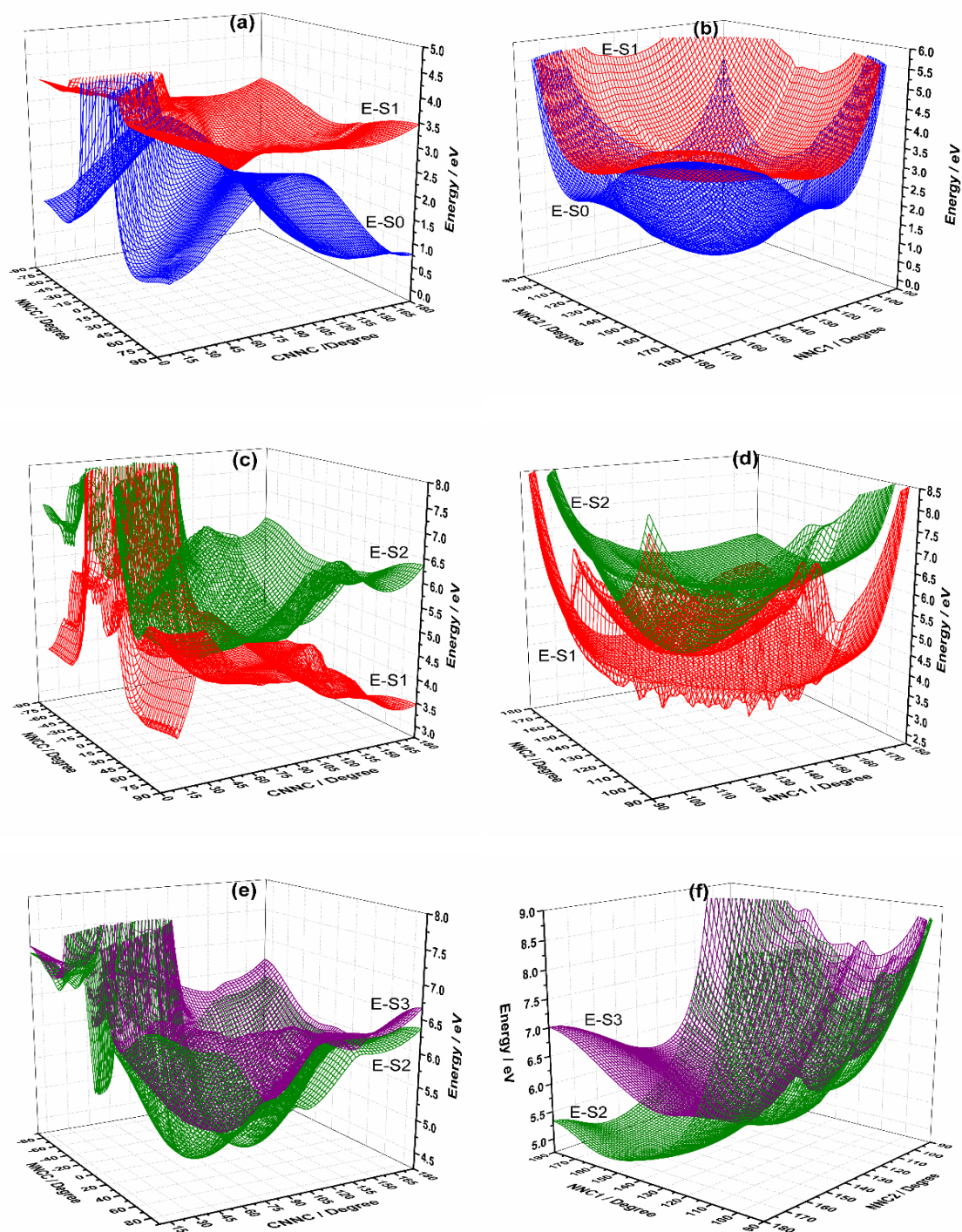


Fig.S1. Potential energy surfaces for two adjacent adiabatic states show distribution of conical intersections along rotation (left panel) and inversion (right panel) isomerization pathways; (a) and (b) for  $S_0$  and  $S_1$ , (c) and (d) for  $S_1$  and  $S_2$ , and (e) and (f) for  $S_2$  and  $S_3$ .

## S2.A typical resonance trajectory for S<sub>2</sub> state photoisomerization

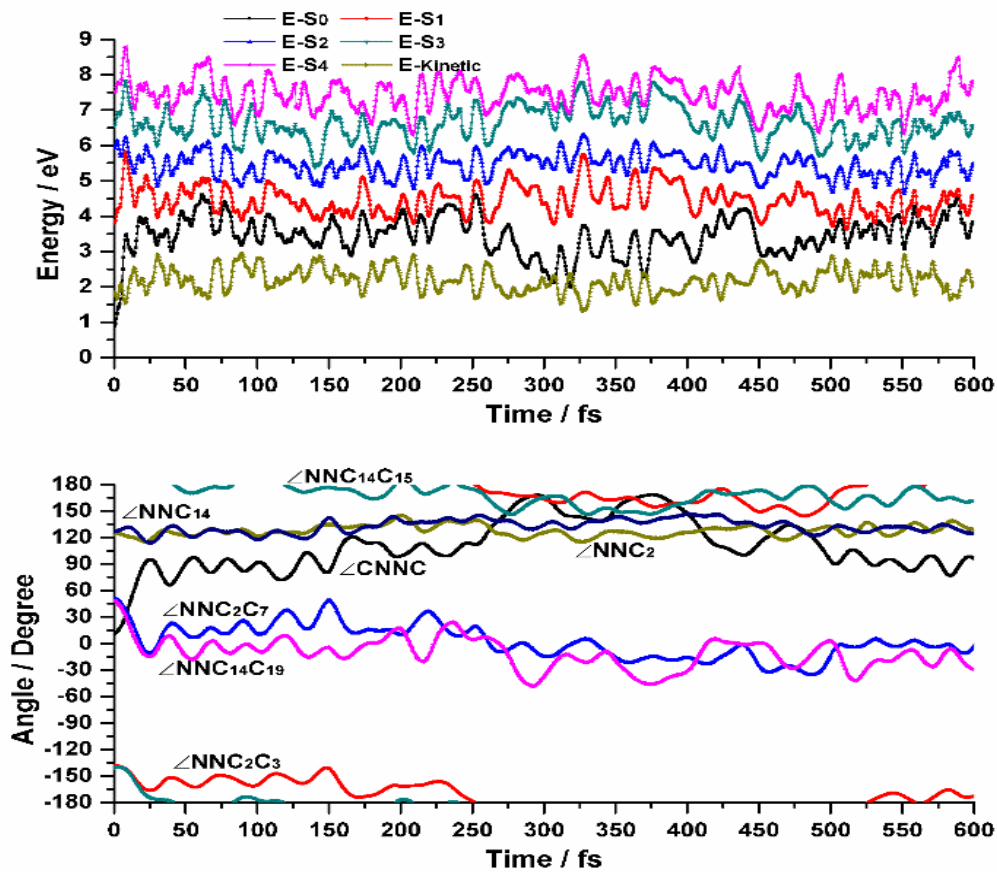


Fig. S2. Potential energies and two NNC bond angles, CNNC and four NNCC dihedral angles evolve along resonance trajectory started from Franck-Condon region of S<sub>2</sub> state of cis-azobenzene.

### S3. Typical trajectories for S<sub>3</sub> state photoisomerization

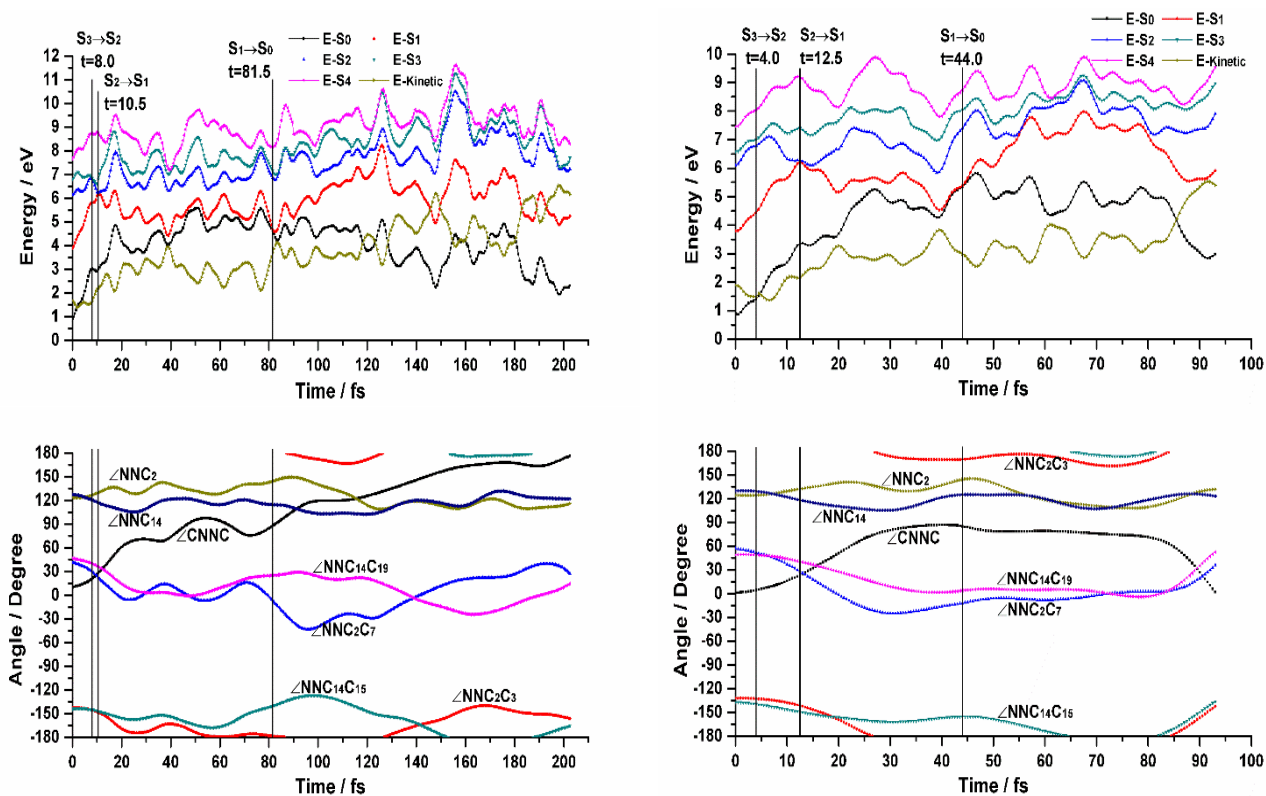


Fig. S3. Potential energies and two NNC bond angles, CnNC and four NNCC dihedral angles evolve along reactive (nonreactive) trajectory in left (right) panel, started from Franck-Condon region of S<sub>3</sub> state of cis-azobenzene. It results in cis-1 case.

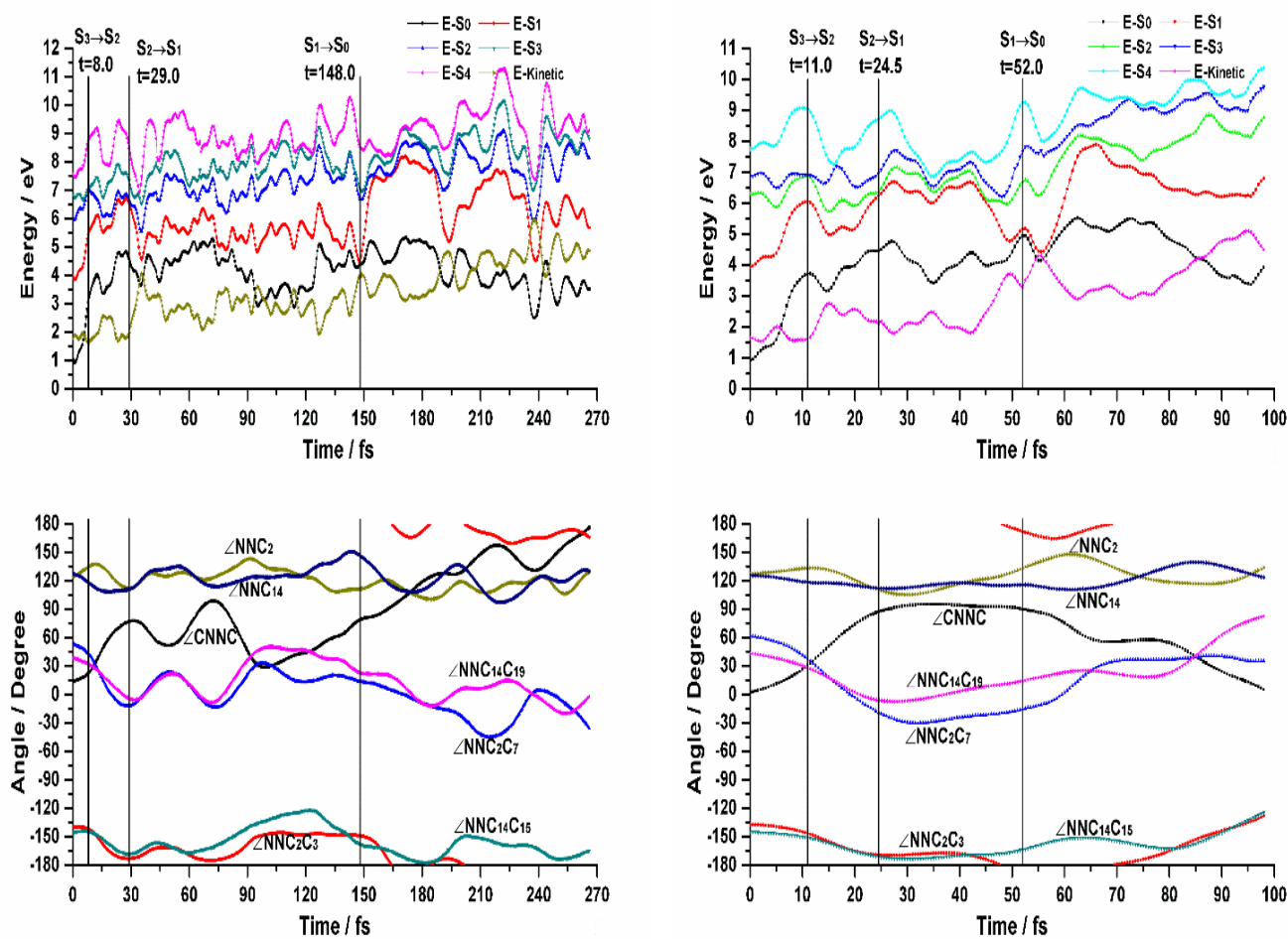


Fig. S4. Potential energies and two NNC bond angles, CNNC and four NNCC dihedral angles evolve along reactive (nonreactive) trajectory in left (right) panel, started from Franck-Condon region of  $S_3$  state of cis-azobenzene. It results in cis-2 case.

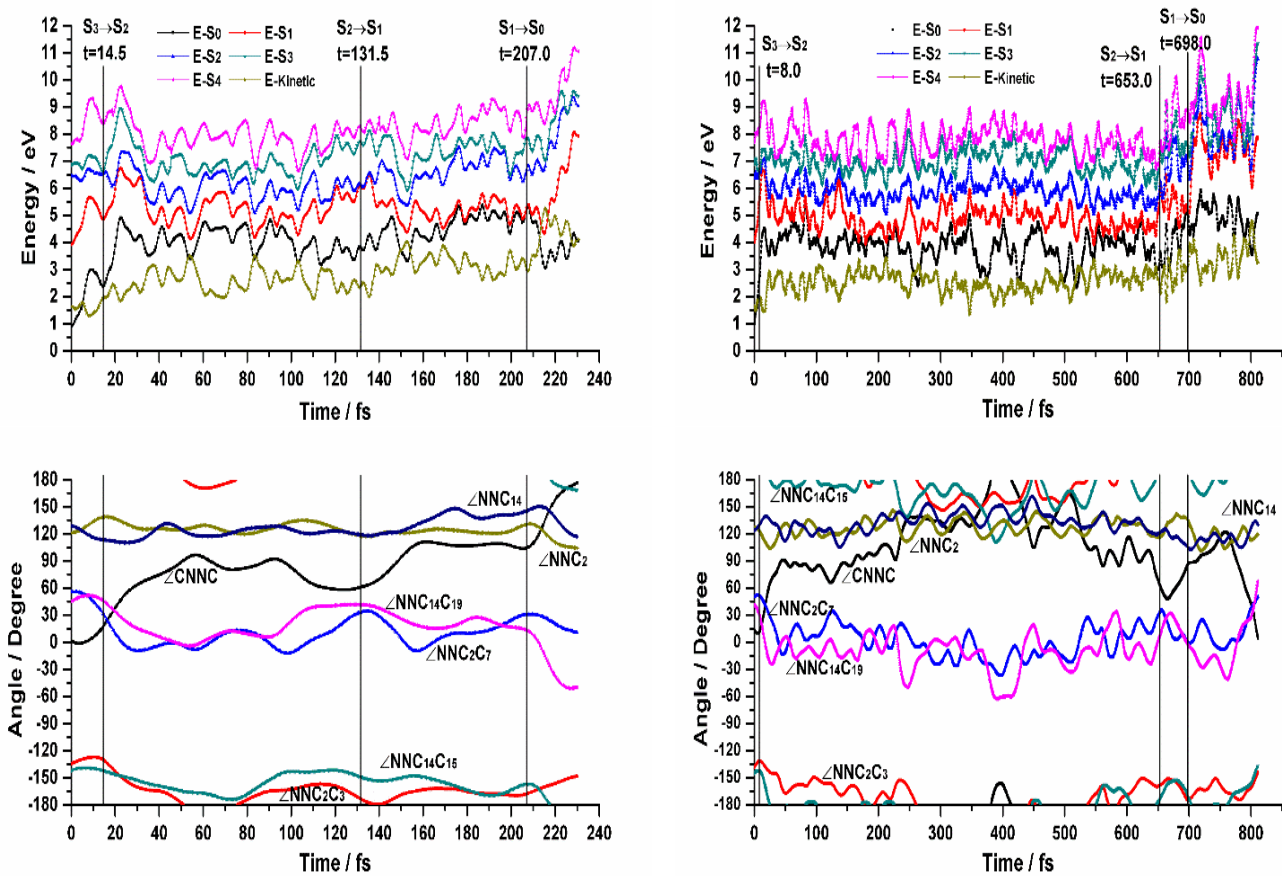


Fig. S5. Potential energies and two NNC bond angles, CNC and four NNCC dihedral angles evolve along reactive (nonreactive) trajectory in left (right) panel, started from Franck-Condon region of  $S_3$  state of cis-azobenzene. It results in cis-3 case.

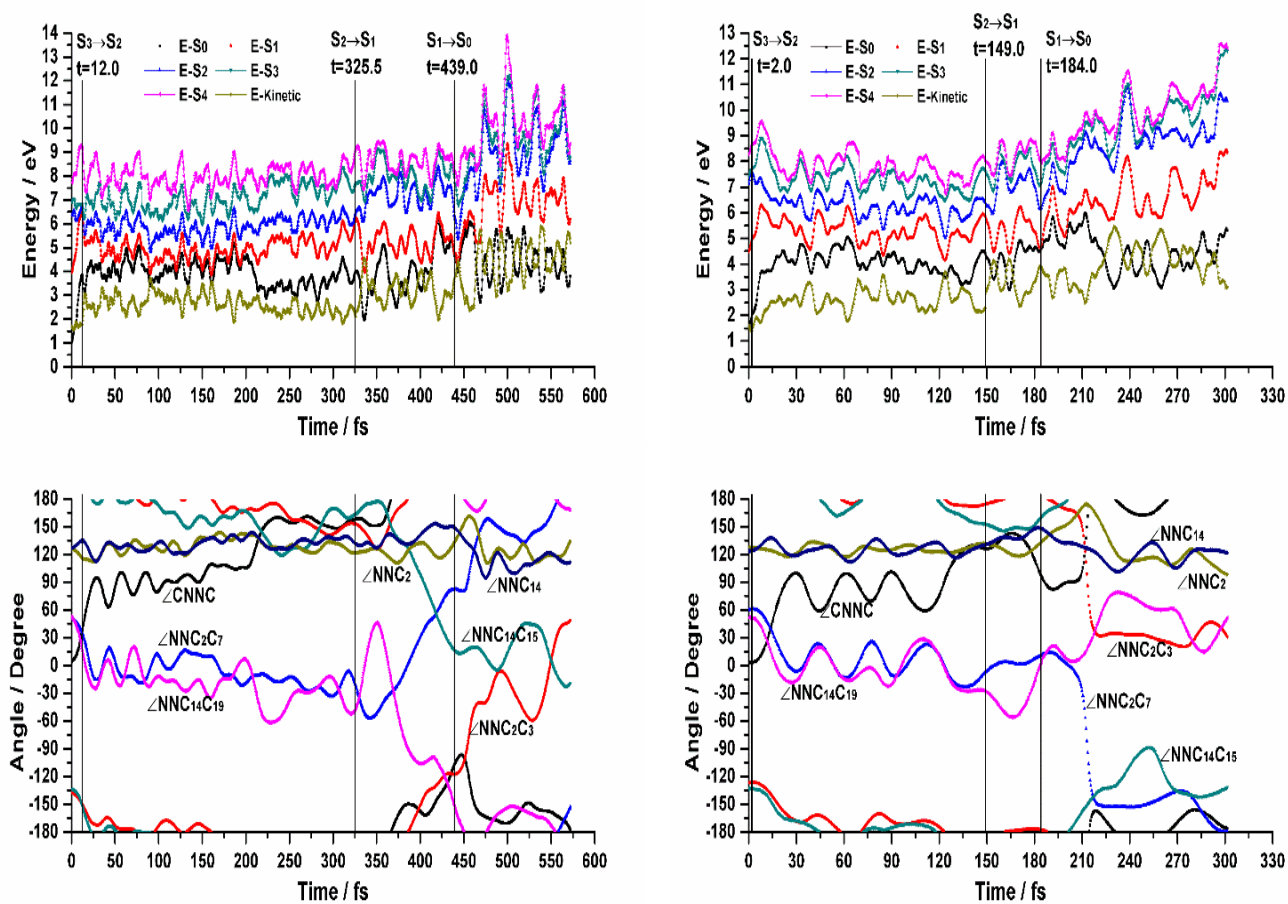


Fig. S6. Potential energies and two NNC bond angles, CNC and four NNCC dihedral angles evolve along fast (slow) reactive trajectory in left (right) panel, started from Franck-Condon region of  $S_3$  state of cis-azobenzene. It results in cis-4 case.



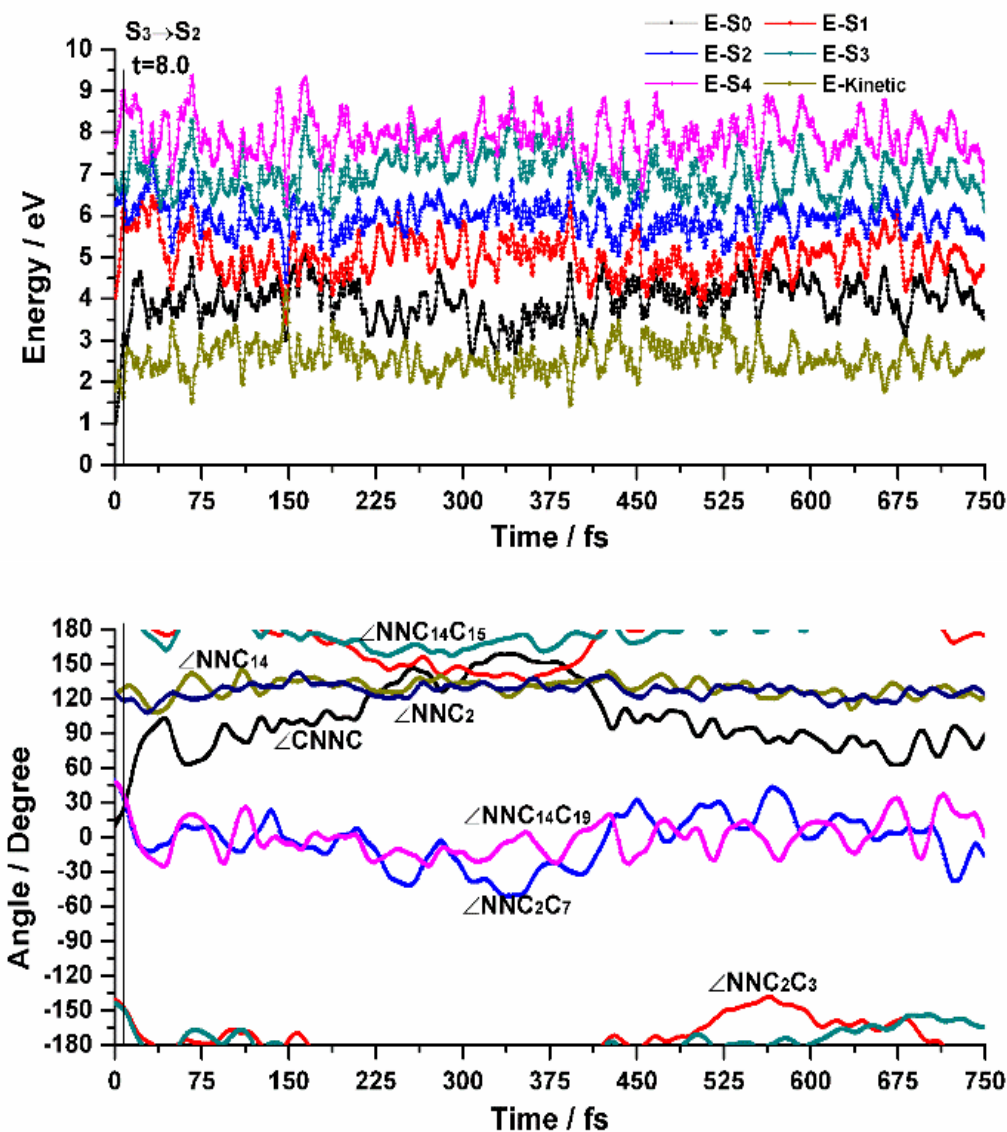


Fig. S7. Potential energies and two NNC bond angles, CNNC and four NNCC dihedral angles evolve along resonance trajectory started from Franck-Condon region of  $S_3$  state of cis-azobenzene.

#### S4. Cartesian coordinates for optimized geometries in the low-lying singlet states of azobenzene

##### *trans* S<sub>0</sub>

N	-0.0000002584	0.4761975572	0.3945359199
C	0.0000016133	0.1781634530	1.7872213143
C	-0.0000431852	1.2736724775	2.6359314022
C	-0.0000459828	1.0857647860	4.0105215159
C	-0.0000031946	-0.1994280957	4.5308021010
C	0.0000444789	-1.2966614591	3.6757901950
C	0.0000461540	-1.1131758542	2.3040861473
H	-0.0000780341	2.2563270882	2.2081506323
H	-0.0000848108	1.9339678566	4.6668892042
H	-0.0000049920	-0.3487777136	5.5933147807
H	0.0000807982	-2.2904250056	4.0798421488
H	0.0000847961	-1.9490322236	1.6355311542
N	-0.0000000374	-0.4656960273	-0.3944957528
C	0.0000019782	-0.1760860514	-1.7813608900
C	-0.0000420565	-1.2837563061	-2.6299801717
C	-0.0000464841	-1.0967054273	-4.0160958567
C	-0.0000044138	0.1944791495	-4.5374022346
C	0.0000443856	1.3008046888	-3.6702647186
C	0.0000467476	1.1213388907	-2.3088032039
H	-0.0000755853	-2.2647344005	-2.1983986760
H	-0.0000806686	-1.9453266485	-4.6721799098
H	-0.0000042003	0.3481135168	-5.5992106109
H	0.0000820252	2.2933219614	-4.0778541290
H	0.0000842983	1.9587403887	-1.6419527136

##### *cis* S<sub>0</sub>

N	0.6152646078	-0.0165051799	1.8431040148
C	1.4641108918	0.0565926111	0.6942658635
C	2.6067454658	-0.7492187805	0.7224828593
C	3.5340110882	-0.6703419747	-0.2956629494
C	3.3636205644	0.2456740191	-1.3291105825
C	2.2537521348	1.0827814533	-1.3320752053
C	1.3046042102	0.9946570468	-0.3326630719
H	2.7432703521	-1.4204329765	1.5472055432
H	4.3985082771	-1.3053265294	-0.2787481239
H	4.0935611154	0.3172287682	-2.1117482568
H	2.1314001500	1.8069365619	-2.1141487218
H	0.4572830135	1.6505062830	-0.3384386862
N	-0.6152646098	0.0165051778	1.8431040160
C	-1.4641108893	-0.0565926132	0.6942658622

C	-2.6067454639	0.7492187701	0.7224828653
C	-3.5340110902	0.6703419643	-0.2956629414
C	-3.3636205670	-0.2456740177	-1.3291105832
C	-2.2537521350	-1.0827814394	-1.3320752188
C	-1.3046042073	-0.9946570374	-0.3326630803
H	-2.7432703482	1.4204329618	1.5472055523
H	-4.3985082841	1.3053265115	-0.2787481085
H	-4.0935611223	-0.3172287654	-2.1117482537
H	-2.1314001456	-1.8069365347	-2.1141487478
H	-0.4572830078	-1.6505062708	-0.3384386978

***TS-inv-rot S<sub>0</sub>***

N	-0.3580494788	1.3552840414	0.6694632624
C	-0.1148525761	0.4991921025	1.8037905724
C	-0.3593878875	1.0677859052	3.0496300408
C	-0.1465670703	0.3328348158	4.1974041040
C	0.3203707844	-0.9789220294	4.1119222994
C	0.5709939482	-1.5417110073	2.8577019844
C	0.3565513049	-0.8093670662	1.7096140236
H	-0.7139811000	2.0786557630	3.0901033798
H	-0.3396392429	0.7711955799	5.1572917774
H	0.4885430115	-1.5520115503	5.0027993148
H	0.9339309727	-2.5490661813	2.7876422001
H	0.5532240683	-1.2386698287	0.7469719244
N	-0.2334521901	0.9108296705	-0.4560203061
C	-0.1171543556	0.3856838788	-1.6977063455
C	-0.8409477647	-0.7698606710	-2.0634001360
C	-0.7434454119	-1.2621247835	-3.3449264353
C	0.1095385497	-0.6733599956	-4.2757430145
C	0.8455538276	0.4519786667	-3.9074360801
C	0.7185921798	1.0018105471	-2.6531738815
H	-1.4748074586	-1.2413933718	-1.3386640027
H	-1.3181969420	-2.1259367597	-3.6192974966
H	0.1968595739	-1.0790196482	-5.2642054008
H	1.5025996992	0.9152334545	-4.6182941368
H	1.2503494775	1.8910021972	-2.3803075211

***TS-rot S<sub>0</sub>***

N	0.4199987058	-1.5839917730	0.5897548848
C	0.1017403426	-0.6478466899	1.5260494207
C	0.9503574432	-0.6048680386	2.6733712977
C	0.7212461800	0.2914194953	3.6795658481
C	-0.3634485792	1.1770432753	3.6052956579
C	-1.2171201186	1.1384580123	2.5064868945

C	-1.0047729312	0.2481842218	1.4779743005
H	1.7678020725	-1.2970023179	2.7112599635
H	1.3707393301	0.3168910208	4.5328899404
H	-0.5402005722	1.8762845548	4.3989665593
H	-2.0557466774	1.8061217283	2.4618150926
H	-1.6841349294	0.2147272913	0.6516788032
N	-0.4199981527	-1.5839918836	-0.5897549907
C	-0.1017400900	-0.6478466405	-1.5260494435
C	-0.9503569040	-0.6048685751	-2.6733715014
C	-0.7212460117	0.2914190803	-3.6795660799
C	0.3634481488	1.1770435255	-3.6052955998
C	1.2171194141	1.1384588150	-2.5064866292
C	1.0047725429	0.2481848826	-1.4779740590
H	-1.7678010769	-1.2970033855	-2.7112603278
H	-1.3707389675	0.3168901460	-4.5328903286
H	0.5401999253	1.8762849106	-4.3989664580
H	2.0557455386	1.8061230604	-2.4618146266
H	1.6841343811	0.2147283906	-0.6516784166

**TS-planar-inv S<sub>0</sub>**

N	0.0000000000	1.3680729567	0.6562104691
C	0.0000000000	0.5061082048	1.8182638792
C	0.0000000000	1.1849650039	3.0358547871
C	0.0000000000	0.4708036466	4.2360267044
C	0.0000000000	-0.9231479913	4.2140206805
C	0.0000000000	-1.5939366205	2.9855131358
C	0.0000000000	-0.8854701601	1.8014166930
H	0.0000000000	2.2567058726	3.0219578249
H	0.0000000000	0.9959570381	5.1717231524
H	0.0000000000	-1.4801022104	5.1309587100
H	0.0000000000	-2.6671403897	2.9648010275
H	0.0000000000	-1.4064911623	0.8685273932
N	0.0000000000	0.9150996620	-0.4835817774
C	0.0000000000	0.3383505517	-1.7455654938
C	0.0000000000	1.1919938645	-2.8502971288
C	0.0000000000	0.6805671813	-4.1368820566
C	0.0000000000	-0.6936925682	-4.3332126081
C	0.0000000000	-1.5524843417	-3.2431727464
C	0.0000000000	-1.0406776050	-1.9552158909
H	0.0000000000	2.2475761305	-2.6712235872
H	0.0000000000	1.3459258811	-4.9778132991
H	0.0000000000	-1.0932595465	-5.3290061160
H	0.0000000000	-2.6142664088	-3.3946329833
H	0.0000000000	-1.7069571939	-1.1196890226

**Cl-rot  $S_0/S_1$** 

N	0.1702732367	-1.3162993400	0.6194980406
C	0.0266343105	-0.5034143936	1.7631082386
C	-0.6413834443	0.7280260103	1.7669295308
C	-0.7196699742	1.4575364837	2.9317002270
C	-0.1443394171	0.9761839604	4.1102590595
C	0.5107153063	-0.2571778115	4.1045159930
C	0.5915601408	-0.9936314644	2.9448531121
H	-1.0930959044	1.0903894645	0.8648982195
H	-1.2298007855	2.4014418995	2.9342874177
H	-0.2108657958	1.5481578946	5.0149570852
H	0.9505369491	-0.6332264749	5.0077206768
H	1.0850888684	-1.9446300865	2.9186276165
N	-0.2903728551	-0.9822678462	-0.4762776462
C	-0.0998166353	-0.4246670112	-1.6980292126
C	-1.0680971655	-0.5974541898	-2.7085333517
C	-0.8825221160	-0.0183643711	-3.9402075463
C	0.2628970376	0.7298319934	-4.2188097225
C	1.2257831459	0.8914920735	-3.2234427556
C	1.0574070091	0.3380175978	-1.9758512588
H	-1.9389168122	-1.1841545281	-2.4955306331
H	-1.6280672061	-0.1531883616	-4.7002232619
H	0.4021124571	1.1705585816	-5.1859557412
H	2.1139471007	1.4584860240	-3.4276539183
H	1.7979550113	0.4658654786	-1.2112773486

**Cl-inv  $S_0/S_1$** 

N	0.0000000000	-0.2417509647	0.5531958788
C	0.0000000000	-0.1112497348	1.8792376905
C	0.0000000000	1.1733152102	2.4961231455
C	0.0000000000	1.2658483196	3.8610546313
C	0.0000000000	0.1247179818	4.6717492593
C	0.0000000000	-1.1376055696	4.0623843350
C	0.0000000000	-1.2720049947	2.7022732067
H	0.0000000000	2.0504626613	1.8800099710
H	0.0000000000	2.2384522828	4.3152066836
H	0.0000000000	0.2146307983	5.7393655725
H	0.0000000000	-2.0202282435	4.6730629088
H	0.0000000000	-2.2391573609	2.2405030718
N	0.0000000000	0.2421659015	-0.5532148671
C	0.0000000000	0.1114372816	-1.8792710556
C	0.0000000000	1.2720234396	-2.7024928578
C	0.0000000000	1.1373824763	-4.0625942648
C	0.0000000000	-0.1250222568	-4.6717232935

C	0.0000000000	-1.2660242179	-3.8608148164
C	0.0000000000	-1.1732359173	-2.4959098977
H	0.0000000000	2.2392589580	-2.2409012277
H	0.0000000000	2.0199060771	-4.6734167997
H	0.0000000000	-0.2151475143	-5.7393214575
H	0.0000000000	-2.2386999975	-4.3148118719
H	0.0000000000	-2.0502629386	-1.8796246280

***trans S<sub>1</sub>***

N	-0.0000004397	0.3795817526	0.4834405461
C	0.0000000025	0.1712663192	1.8310104285
C	-0.0000004599	1.2919047293	2.6866383373
C	-0.0000009150	1.1046859112	4.0677117910
C	0.0000007452	-0.1832909368	4.6076597073
C	0.0000003094	-1.2947839992	3.7442112627
C	0.0000006518	-1.1334463814	2.3871461390
H	-0.0000002112	2.2744847111	2.2590664400
H	-0.0000028575	1.9593780743	4.7161745611
H	0.0000026481	-0.3270082363	5.6701245306
H	-0.0000003736	-2.2852189410	4.1574189584
H	0.0000016947	-1.9778292975	1.7277903878
N	-0.0000002031	-0.4126669768	-0.4774199670
C	-0.0000000913	-0.1769188414	-1.8455056030
C	-0.0000006086	-1.2769631959	-2.7011653532
C	-0.0000006026	-1.0811190603	-4.0704884439
C	0.0000003354	0.2028264491	-4.6012951952
C	0.0000005889	1.2940440449	-3.7438479533
C	0.0000006089	1.1166854547	-2.3699980816
H	-0.0000006793	-2.2637672582	-2.2836134861
H	-0.0000016009	-1.9321056900	-4.7239178430
H	0.0000013465	0.3492713465	-5.6635989233
H	0.0000007002	2.2901741833	-4.1430335202
H	0.0000015366	1.9566168771	-1.7056621707

***cis S<sub>1</sub>***

N	0.0000000000	1.1295158505	0.6055838093
C	0.0000000000	0.4405980397	1.7815786050
C	0.0000000000	1.2014485221	2.9747759332
C	0.0000000000	0.5782853310	4.1943193106
C	0.0000000000	-0.8180827543	4.2858088165
C	0.0000000000	-1.5734809963	3.1132149336
C	0.0000000000	-0.9715377200	1.8783620379
H	0.0000000000	2.2697495867	2.8952488348
H	0.0000000000	1.1706363553	5.0889724980

H	0.0000000000	-1.3007107366	5.2428674850
H	0.0000000000	-2.6453162673	3.1712271628
H	0.0000000000	-1.5728657635	0.9952925759
N	0.0000000000	1.1295219283	-0.6055862358
C	0.0000000000	0.4406004317	-1.7815798004
C	0.0000000000	1.2014481897	-2.9747785291
C	0.0000000000	0.5782823459	-4.1943206194
C	0.0000000000	-0.8180859335	-4.2858069702
C	0.0000000000	-1.5734815300	-3.1132114250
C	0.0000000000	-0.9715352964	-1.8783598803
H	0.0000000000	2.2697494184	-2.8952536611
H	0.0000000000	1.1706313701	-5.0889751311
H	0.0000000000	-1.3007160783	-5.2428645547
H	0.0000000000	-2.6453169351	-3.1712212274
H	0.0000000000	-1.5728612671	-0.9952890086

***TS-rot S<sub>1</sub>***

N	0.9379440359	0.3256435793	0.5396234524
C	0.3713916520	0.1179725949	1.7905970438
C	0.6767450654	1.0421113541	2.8014738933
C	0.1605015271	0.8748414368	4.0638684041
C	-0.6584111566	-0.2199760678	4.3561055007
C	-0.9486626550	-1.1470960082	3.3525175742
C	-0.4393351563	-0.9916874892	2.0841289461
H	1.3108036169	1.8730152282	2.5640688900
H	0.3890191211	1.5898539392	4.8303409726
H	-1.0558736525	-0.3499292145	5.3434462433
H	-1.5756022938	-1.9901629115	3.5709382827
H	-0.6506866963	-1.7055109531	1.3133214269
N	0.7428217858	-0.3379651593	-0.4849789289
C	0.3065710757	-0.1242238312	-1.7796096895
C	0.6587526554	-1.0401922561	-2.7766310305
C	0.2036662227	-0.8608742103	-4.0639019546
C	-0.5945516373	0.2361930946	-4.3915766491
C	-0.9351416332	1.1505636359	-3.3954405828
C	-0.5036216956	0.9744868582	-2.0982010330
H	1.2834866982	-1.8723044707	-2.5204014939
H	0.4756804405	-1.5691360061	-4.8226099425
H	-0.9388184811	0.3759731866	-5.3972564589
H	-1.5433612729	2.0014155930	-3.6358380528
H	-0.7683530132	1.6735947694	-1.3300735515

***TS-planar-inv S<sub>1</sub>***

N	0.0000567191	1.1986685690	0.6535867104
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C	0.0000077745	0.4808927290	1.8178146604
C	0.0001961274	1.2126426704	3.0277182299
C	0.0001453936	0.5421788453	4.2475357087
C	-0.0000832706	-0.8551187305	4.2889155361
C	-0.0002756478	-1.5777742101	3.0817216081
C	-0.0002403025	-0.9370958823	1.8745679571
H	0.0003731800	2.2826963382	2.9783872093
H	0.0002889016	1.1062440931	5.1602710249
H	-0.0001160612	-1.3730115012	5.2275949945
H	-0.0004579580	-2.6508665576	3.1087496754
H	-0.0004236601	-1.5045630706	0.9675094278
N	0.0001056298	0.9391529805	-0.5409053236
C	0.0000489382	0.3650376715	-1.7854190325
C	-0.0002665239	1.2087148367	-2.9029639391
C	-0.0002630605	0.6694771028	-4.1748616246
C	0.0000093234	-0.7075772890	-4.3630876119
C	0.0002645695	-1.5415576057	-3.2554191963
C	0.0002973841	-1.0213562583	-1.9712777389
H	-0.0004721779	2.2688999096	-2.7514663593
H	-0.0005036370	1.3271271959	-5.0225348504
H	0.0000031326	-1.1201350557	-5.3526344688
H	0.0004482201	-2.6067583328	-3.3854312074
H	0.0005022178	-1.6798827945	-1.1288369716

***Cl-cis S<sub>1</sub>/S<sub>2</sub>***

N	-1.9801121243	-0.0596441587	0.6515393997
C	-0.8674143348	0.1504795983	1.3656811627
C	-0.8500264505	-0.2981570171	2.7135703089
C	0.3022868892	-0.3187112600	3.4301093229
C	1.5274960600	0.1503133494	2.8536802089
C	1.5397616727	0.6707336175	1.5807409428
C	0.3508013131	0.6794511057	0.7698117587
H	-1.7747116666	-0.6585634850	3.1176642318
H	0.3049533045	-0.6873490305	4.4370211230
H	2.4246180248	0.1396376301	3.4414514442
H	2.4376276239	1.0954371978	1.1750174564
H	0.2562223219	1.4962639370	0.0774301133
N	-1.9801106612	0.0596519808	-0.6515570595
C	-0.8674104954	-0.1504783684	-1.3656919874
C	-0.8500157525	0.2981491867	-2.7135841873
C	0.3023035490	0.3187042409	-3.4301126266
C	1.5275047435	-0.1503190528	-2.8536649981
C	1.5397643156	-0.6707280606	-1.5807203174
C	0.3507970599	-0.6794452765	-0.7698023144
H	-1.7746987817	0.6585489670	-3.1176891241



H	0.3049784594	0.6873403307	-4.4370252887
H	2.4246299945	-0.1396518809	-3.4414307117
H	2.4376282648	-1.0954232147	-1.1749829948
H	0.2562159125	-1.4962545687	-0.0774166829

***Cl-rot-a S<sub>1</sub>/S<sub>2</sub>***

N	-1.8061814152	-0.2302994854	0.6130922638
C	-0.8106064523	0.0755528892	1.4701626471
C	-0.8235921117	-0.5599608901	2.7599186194
C	0.2484144893	-0.4721252701	3.5728563012
C	1.4163201124	0.2671604557	3.1724121093
C	1.4477257691	0.9121718451	1.9769724194
C	0.3419631901	0.8564783235	1.0945718429
H	-1.7007885786	-1.1138566553	3.0282937404
H	0.2429210134	-0.9560880426	4.5299458118
H	2.2553791934	0.3162006839	3.8386550132
H	2.3055396436	1.4909532047	1.6944086760
H	0.3063061192	1.4978486570	0.2408408165
N	-1.8061807858	0.2303050444	-0.6130951476
C	-0.8106437544	-0.0755801045	-1.4701921026
C	-0.8235706538	0.5600236788	-2.7599090803
C	0.2484545435	0.4722019971	-3.5728190634
C	1.4163241920	-0.2671540877	-3.1723863500
C	1.4476764051	-0.9122384880	-1.9769865570
C	0.3419011874	-0.8565420092	-1.0946020992
H	-1.7007378135	1.1139727288	-3.0282682657
H	0.2430131675	0.9562339648	-4.5298730610
H	2.2554029171	-0.3161765274	-3.8386062536
H	2.3054558017	-1.4910762174	-1.6944380259
H	0.3061947723	-1.4979500981	-0.2409027295

***Cl-rot-b S<sub>1</sub>/S<sub>2</sub>***

N	0.8736555515	0.5073629842	0.4593048264
C	0.3779702357	0.1846696223	1.6711962948
C	0.4419237084	1.1989159813	2.7033346606
C	-0.0809580338	0.9649445659	3.9285160673
C	-0.6854327151	-0.2879423426	4.2312190044
C	-0.7291660831	-1.2987613601	3.2579779682
C	-0.2110861025	-1.0994916129	2.0117872857
H	0.9055798852	2.1312003096	2.4499693165
H	-0.0406755516	1.7225639193	4.6868220803
H	-1.0837523910	-0.4653667931	5.2103568348
H	-1.1615754237	-2.2485367150	3.5078929592

H	-0.1954250730	-1.8833110033	1.2845425763
N	0.8741842124	-0.5059111306	-0.4593236032
C	0.3776613666	-0.1842297663	-1.6710361596
C	0.4424079770	-1.1987236145	-2.7027360013
C	-0.0804670463	-0.9654423955	-3.9281466283
C	-0.6852657223	0.2870093351	-4.2312730840
C	-0.7296444740	1.2980872941	-3.2586752538
C	-0.2116864059	1.0994893795	-2.0121296477
H	0.9063989280	-2.1307258795	-2.4489467766
H	-0.0397672069	-1.7233009410	-4.6861801964
H	-1.0837087931	0.4638064864	-5.2104830778
H	-1.1624563268	2.2475562777	-3.5090196580
H	-0.1966275919	1.8835144944	-1.2851043187

***Cl-trans S<sub>1</sub>/S<sub>2</sub>***

N	-0.0001163568	0.5512588296	0.3805899657
C	-0.0000592469	0.2262902582	1.7218724623
C	-0.0004834446	1.2990298063	2.6469601109
C	-0.0003978822	1.0597826041	4.0037463623
C	0.0001162644	-0.2457968322	4.4864095090
C	0.0005392840	-1.3124543078	3.6020021616
C	0.0004603339	-1.0946493265	2.2328674632
H	-0.0009443620	2.2934593780	2.2501104811
H	-0.0007432399	1.8829909601	4.6913140664
H	0.0001228281	-0.4247983439	5.5442446606
H	0.0008994828	-2.3172901287	3.9770009077
H	0.0006987460	-1.9015067993	1.5342194131
N	-0.0001416924	-0.5512620569	-0.3805903027
C	-0.0000963545	-0.2262914719	-1.7218726557
C	-0.0005150124	-1.2990297261	-2.6469615820
C	-0.0003800506	-1.0597808520	-4.0037477029
C	0.0001369140	0.2457989765	-4.4864092423
C	0.0005405014	1.3124554171	-3.6020004353
C	0.0004166673	1.0946487435	-2.2328661164
H	-0.0009346278	-2.2934598731	-2.2501132846
H	-0.0006575413	-1.8829884590	-4.6913163377
H	0.0002025260	0.4248018301	-5.5442441700
H	0.0009535109	2.3172916986	-3.9769979444
H	0.0006761805	1.9015053899	-1.5342170973

***trans S<sub>2</sub>***

N	0.0000000000	0.1951561910	0.5700957550
C	0.0000000000	0.0951955865	1.9248272038
C	0.0000000000	1.2558481414	2.7170890209

C	0.0000000000	1.1422068845	4.0883834008
C	0.0000000000	-0.1056384275	4.7128943040
C	0.0000000000	-1.2507775097	3.9187027481
C	0.0000000000	-1.1694087988	2.5436493307
H	0.0000000000	2.2162934848	2.2423772235
H	0.0000000000	2.0360073817	4.6825351421
H	0.0000000000	-0.1818131295	5.7817790303
H	0.0000000000	-2.2204654414	4.3791062539
H	0.0000000000	-2.0537067537	1.9383297293
N	0.0000000000	-0.1951519481	-0.5700960883
C	0.0000000000	-0.0951938565	-1.9248263234
C	0.0000000000	-1.2558478087	-2.7170868802
C	0.0000000000	-1.1422088735	-4.0883813104
C	0.0000000000	0.1056353493	-4.7128946609
C	0.0000000000	1.2507756316	-3.9187049833
C	0.0000000000	1.1694093970	-2.5436514127
H	0.0000000000	-2.2162925157	-2.2423736682
H	0.0000000000	-2.0360105390	-4.6825313363
H	0.0000000000	0.1818080430	-5.7817795194
H	0.0000000000	2.2204629375	-4.3791098677
H	0.0000000000	2.0537086231	-1.9383335682

**rot S<sub>2</sub>**

N	1.1910193638	0.3102261277	0.5349439958
C	0.4882622380	0.0916546660	1.7059139732
C	0.7317886526	0.9425358868	2.7929597963
C	0.0412614101	0.7670762119	3.9694076920
C	-0.8948135058	-0.2622834759	4.0981843633
C	-1.1248016661	-1.1161420792	3.0197238125
C	-0.4468728794	-0.9494953482	1.8318475122
H	1.4584324761	1.7221787100	2.6824445692
H	0.2281287352	1.4248444888	4.7960840285
H	-1.4263071978	-0.3984884269	5.0193370756
H	-1.8355680288	-1.9146864032	3.1129848127
H	-0.6138936533	-1.6106044272	1.0049806255
N	1.1910433934	-0.3101272545	-0.5349445544
C	0.4882636128	-0.0916182608	-1.7059130613
C	0.7318806750	-0.9424595036	-2.7929698527
C	0.0413412874	-0.7670531929	-3.9694185833
C	-0.8948394150	0.2622116580	-4.0981844803
C	-1.1249158219	1.1160338311	-3.0197139587
C	-0.4469764030	0.9494387532	-1.8318364205
H	1.4586016555	-1.7220313841	-2.6824617703
H	0.2282814117	-1.4247889076	-4.7961043924
H	-1.4263451596	0.3983736707	-5.0193365866

H	-1.8357586691	1.9145108042	-3.1129686578
H	-0.6140683037	1.6105197104	-1.0049613878

**TS-rot-a S<sub>2</sub>**

N	-0.4937988766	1.0564463984	0.5281716165
C	-0.1889606606	0.4467297895	1.7402855379
C	0.4701690064	1.2014881857	2.7161974329
C	0.7878554645	0.6288719069	3.9261658410
C	0.4452195499	-0.6984755593	4.1989657744
C	-0.2276653557	-1.4404791645	3.2277187911
C	-0.5456491941	-0.8821469903	2.0083628042
H	0.7208839416	2.2200534531	2.4982483515
H	1.3004576710	1.2108814187	4.6675318710
H	0.6897030364	-1.1386721149	5.1454606814
H	-0.5065049204	-2.4570226056	3.4297218668
H	-1.0801250405	-1.4432488975	1.2683539035
N	-0.9917917567	0.6520906694	-0.5289330107
C	-0.4003646493	0.2365471136	-1.7461522729
C	-0.0811066225	1.1902236668	-2.7195082013
C	0.4563095231	0.7866383839	-3.9236842577
C	0.6641604083	-0.5644074281	-4.1879257613
C	0.3288186034	-1.5116874782	-3.2272740299
C	-0.2004229230	-1.1223627535	-2.0128701508
H	-0.2595166483	2.2260306587	-2.5114087466
H	0.7094551739	1.5217977464	-4.6630219148
H	1.0762183131	-0.8727571671	-5.1288314301
H	0.4826024602	-2.5547272855	-3.4265452462
H	-0.4631018377	-1.8506396250	-1.2722832814

**TS-rot-a S<sub>2</sub>**

N	0.1582644003	0.2088669294	0.5700898397
C	0.0547131659	0.0985290631	1.9163956383
C	-0.5521907892	1.1282404291	2.6643354583
C	-0.6093153914	1.0350636859	4.0352355437
C	-0.1113598513	-0.0845466525	4.7023911497
C	0.4730631808	-1.1111337927	3.9591348543
C	0.5844870310	-1.0239314734	2.5913197298
H	-0.9569016420	1.9760414477	2.1491115606
H	-1.0625339710	1.8309217821	4.5947181274
H	-0.1781295238	-0.1563633029	5.7697490232
H	0.8570273050	-1.9795351072	4.4596691425
H	1.0550053691	-1.8018972592	2.0237316771
N	0.1582453157	-0.2089652979	-0.5700947186
C	0.0547062357	-0.0985709560	-1.9163983818

C	0.5844939557	1.0239124061	-2.5912712566
C	0.4730835586	1.1111706285	-3.9590847608
C	-0.1113447455	0.0846217018	-4.7023881950
C	-0.6093167738	-1.0350101066	-4.0352807956
C	-0.5521999959	-1.1282457352	-2.6643842068
H	1.0550137442	1.8018519003	-2.0236482663
H	0.8570610192	1.9795890389	-4.4595793904
H	-0.1781061552	0.1564828171	-5.7697435628
H	-1.0625403110	-1.8308408117	-4.5947984851
H	-0.9569205197	-1.9760656242	-2.1491989569

***Cl-rot S<sub>2</sub>/S<sub>3</sub>***

N	0.7635010872	-1.2676450119	0.5332495632
C	0.2472275114	-0.5243846781	1.6025662903
C	1.1171446705	-0.3108727231	2.6720963685
C	0.7012430950	0.4126587001	3.7744826184
C	-0.5910095375	0.9220754214	3.8251474266
C	-1.4637346415	0.7019585157	2.7681328785
C	-1.0513792468	-0.0170150869	1.6582688559
H	2.1048320046	-0.7227918763	2.6148733515
H	1.3759600173	0.5753460622	4.5922258655
H	-0.9155005770	1.4803256068	4.6818436641
H	-2.4641032736	1.0870645062	2.8089596806
H	-1.7323703794	-0.1977084697	0.8508733427
N	-0.0135253098	-1.4976047674	-0.5215518532
C	0.0477983878	-0.6089202483	-1.6106422643
C	-0.7865458185	-0.9012967459	-2.7303883650
C	-0.8096804186	-0.0596209935	-3.8257855881
C	0.0254949636	1.1547067485	-3.8386111075
C	0.8938128528	1.4200857285	-2.6792969754
C	0.9108135343	0.6099716296	-1.6313715017
H	-1.3828693211	-1.7912767236	-2.6948541703
H	-1.4260306209	-0.2805354793	-4.6741928099
H	-0.0080159516	1.8344958668	-4.6641277868
H	1.5223442982	2.2895222081	-2.7051463362
H	1.5461449075	0.7943878504	-0.7894818594

***rot S<sub>3</sub>***

N	-1.4405062692	-0.2912143035	0.5388806103
C	-0.5934284940	-0.0442668693	1.6123828490
C	-0.7652160331	-0.8909267901	2.7753060969
C	0.0358112006	-0.7596061285	3.8449246524
C	1.0937787175	0.2308827161	3.8586102015
C	1.2546640826	1.0855683744	2.7049195111

C	0.4591089530	0.9571776079	1.6284956387
H	-1.5550120291	-1.6143927659	2.7413431347
H	-0.0991395438	-1.3850281126	4.7058040501
H	1.7385846672	0.3310794327	4.7070036187
H	2.0201754525	1.8372157948	2.7225593400
H	0.5755755965	1.6016135561	0.7811030838
N	-1.3311284199	0.5046845266	-0.5289677362
C	-0.5583858256	0.1489105916	-1.5963167814
C	-0.5819506820	1.0157048553	-2.7300658738
C	0.1812090975	0.7367008544	-3.8276381913
C	0.9917674981	-0.4078451640	-3.8593267956
C	1.0195285648	-1.2714429541	-2.7698735509
C	0.2658616794	-1.0148967603	-1.6485596113
H	-1.2129184032	1.8806632061	-2.6855623712
H	0.1595293934	1.3940294313	-4.6750625650
H	1.5846739153	-0.6190776094	-4.7275526225
H	1.6314647325	-2.1520308915	-2.8052554262
H	0.2740774086	-1.6899528874	-0.8170280564

***trans S<sub>3</sub>***

N	0.0000000000	0.6238910940	0.4100651433
C	0.0000000000	0.2294959509	1.7115456013
C	0.0000000000	1.3043117099	2.6998292526
C	0.0000000000	1.0202628968	4.0604775555
C	0.0000000000	-0.3092143638	4.5062035757
C	0.0000000000	-1.3316017315	3.5615847306
C	0.0000000000	-1.0861638115	2.2014171651
H	0.0000000000	2.3082624113	2.3285230030
H	0.0000000000	1.8266428625	4.7686018733
H	0.0000000000	-0.5342358988	5.5542600765
H	0.0000000000	-2.3516621901	3.8988781014
H	0.0000000000	-1.8991903278	1.5099468199
N	0.0000000000	-0.4585159413	-0.4320750919
C	0.0000000000	-0.2153196496	-1.7261848386
C	0.0000000000	-1.3373702340	-2.6459005967
C	0.0000000000	-1.1193246917	-3.9816392206
C	0.0000000000	0.2153515712	-4.4735445524
C	0.0000000000	1.3198538002	-3.6251592434
C	0.0000000000	1.1405048181	-2.2646985437
H	0.0000000000	-2.3221885951	-2.2236782743
H	0.0000000000	-1.9350076751	-4.6758475977
H	0.0000000000	0.3722519731	-5.5349558735
H	0.0000000000	2.3073196184	-4.0416958160
H	0.0000000000	1.9461105173	-1.5633436952