

## **Supporting Information: Nonadiabatic Dynamics Simulation of Photoinduced Ring-Opening Reaction of 2(5H)-Thiophenone with Internal Conversion and Intersystem Crossing**

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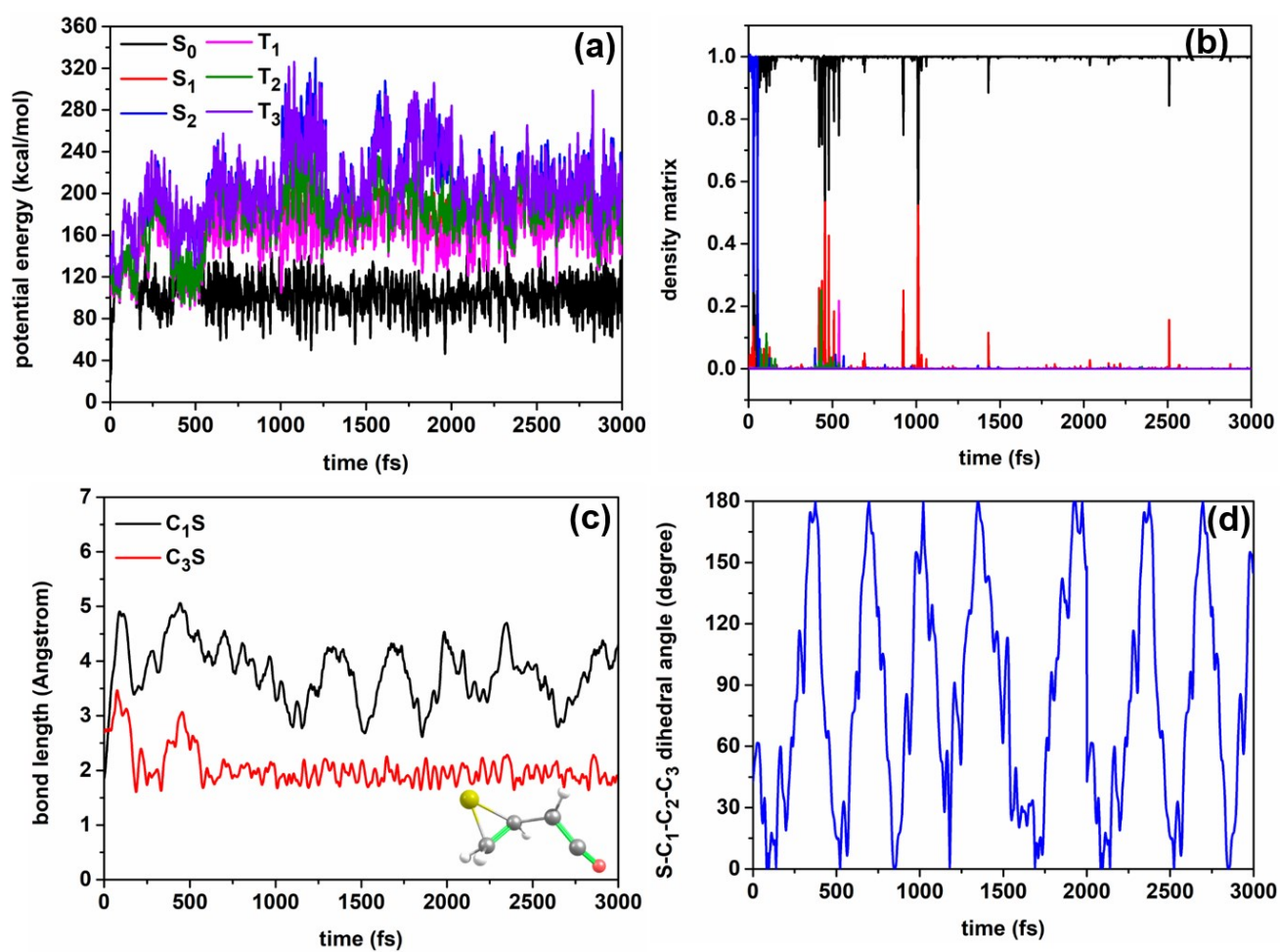
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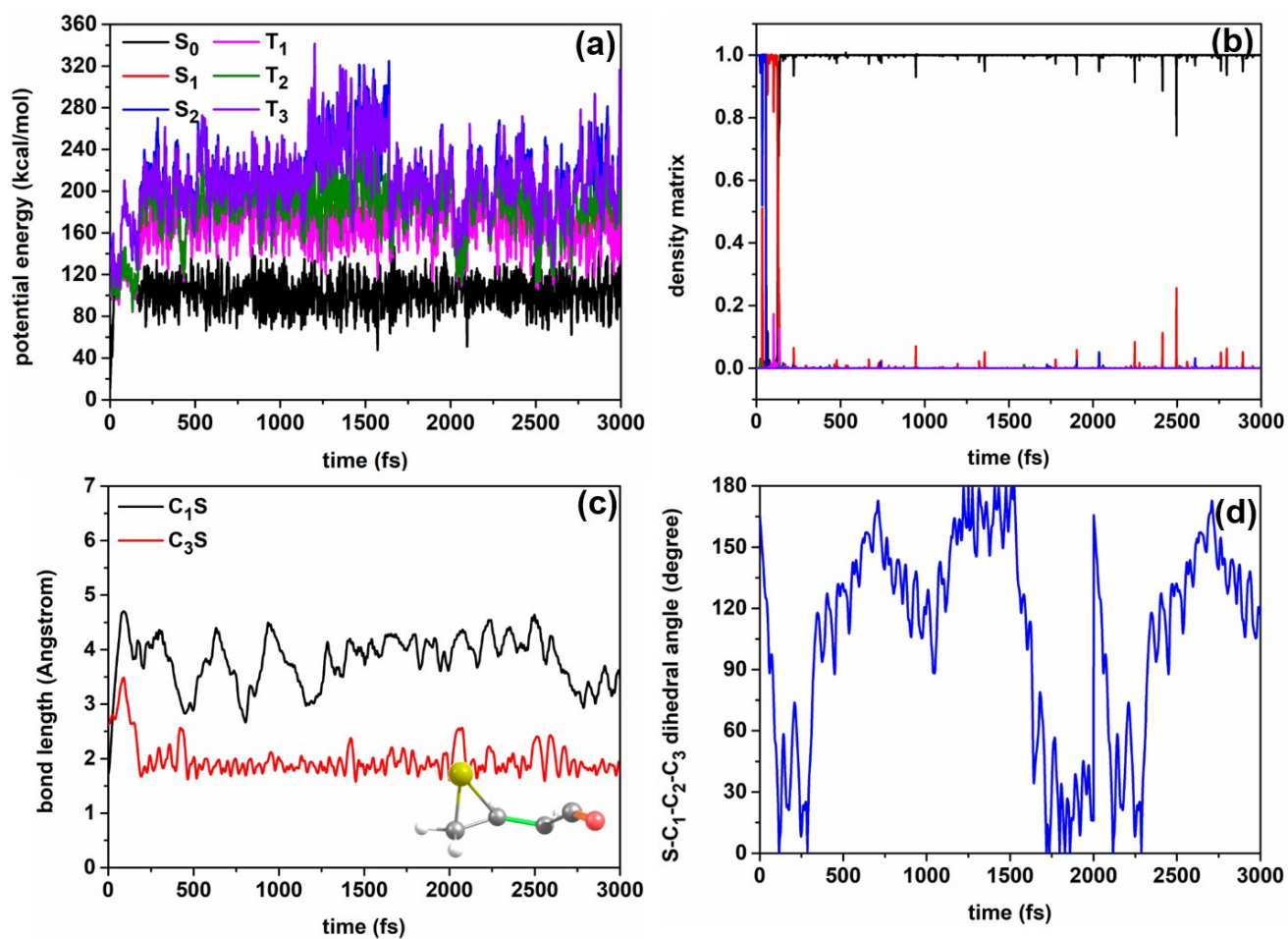
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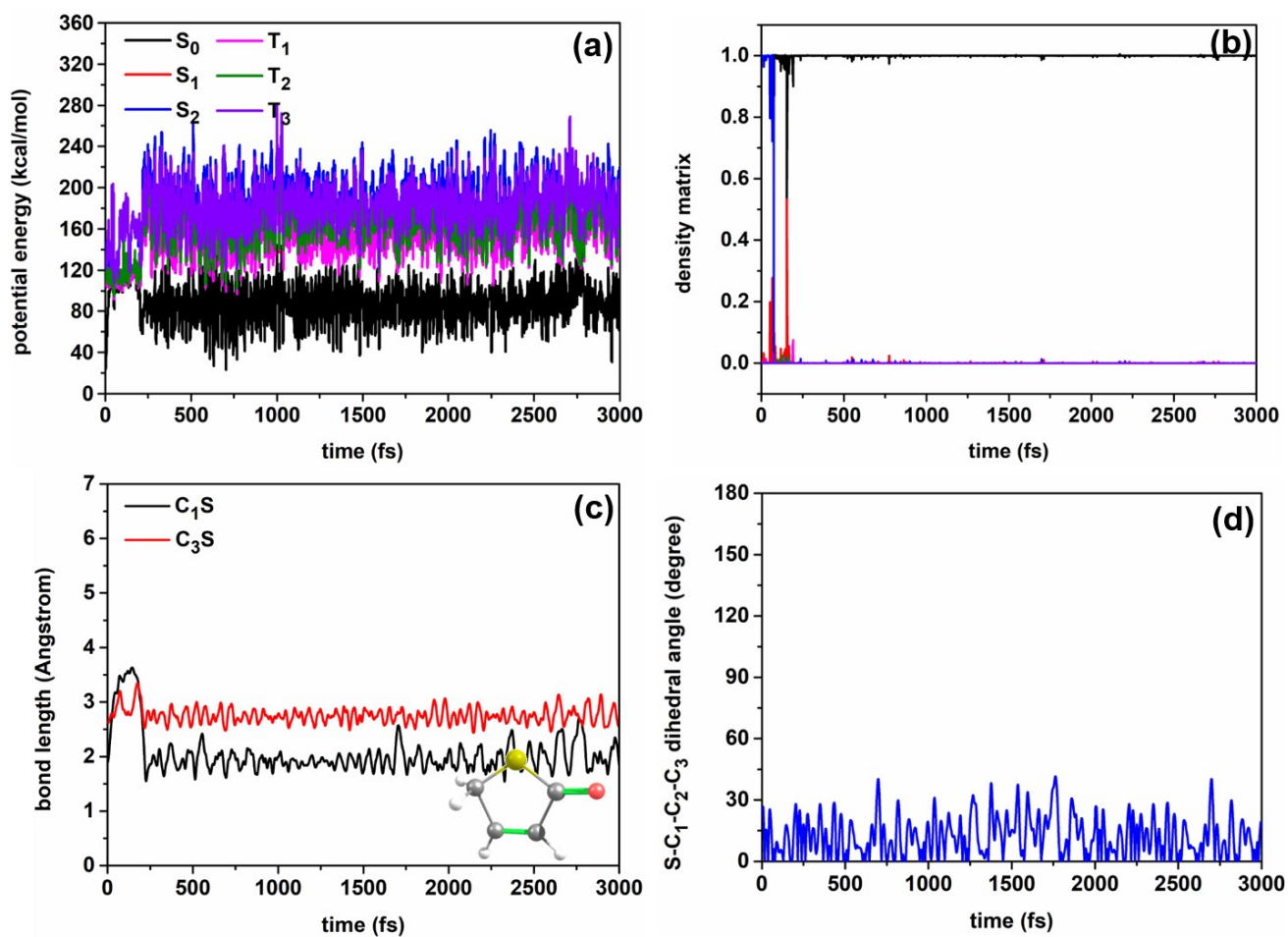
## 1. Additional representative trajectories from nonadiabatic dynamics simulations



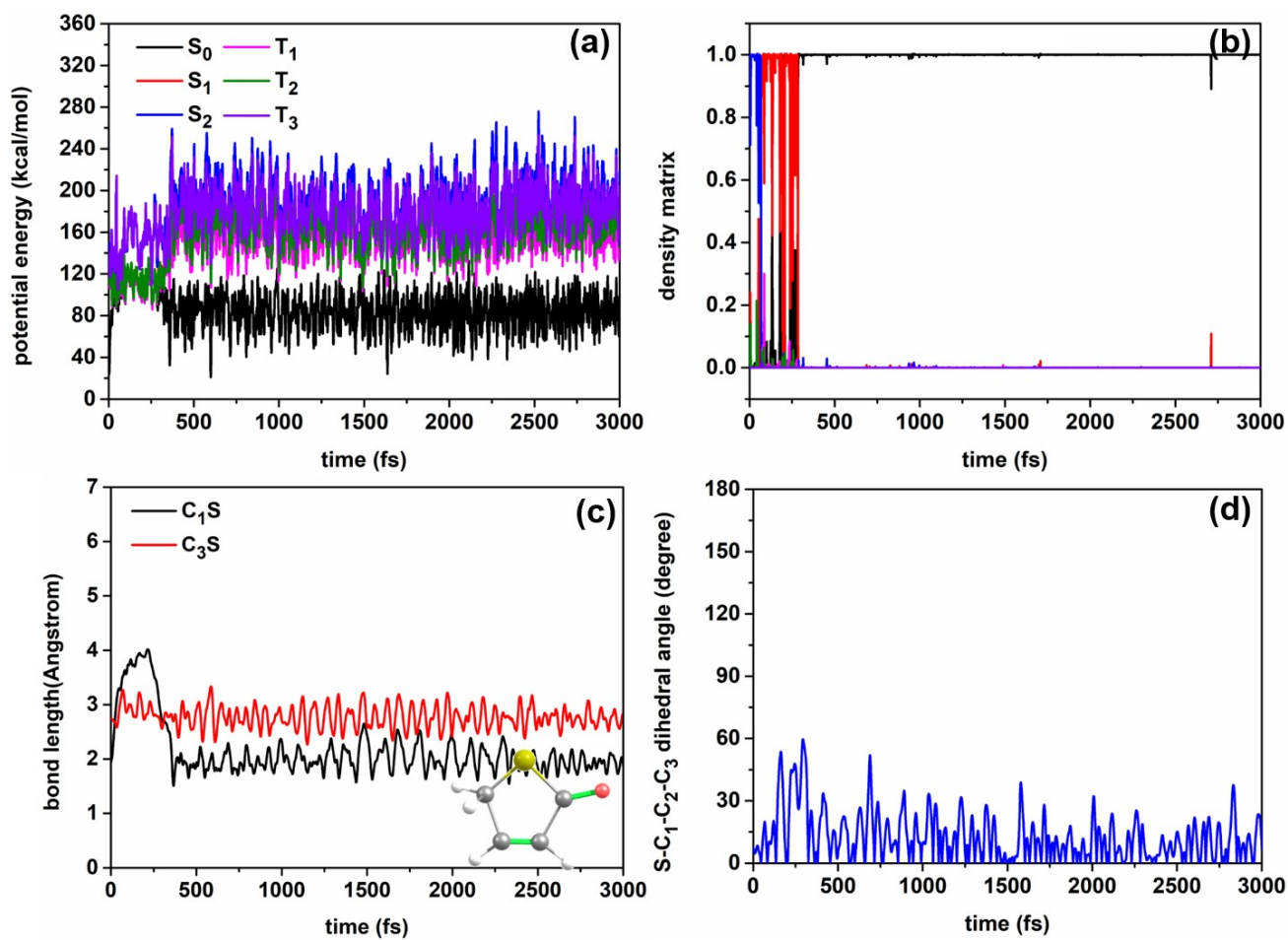
**Figure S1.** Potential energies (a), diagonal elements of density matrix (b),  $C_1$ -S and  $C_3$ -S distances (c) and S-C<sub>1</sub>-C<sub>2</sub>-C<sub>3</sub> dihedral angle (d) plotted as a function of time for a representative of type-I trajectories.



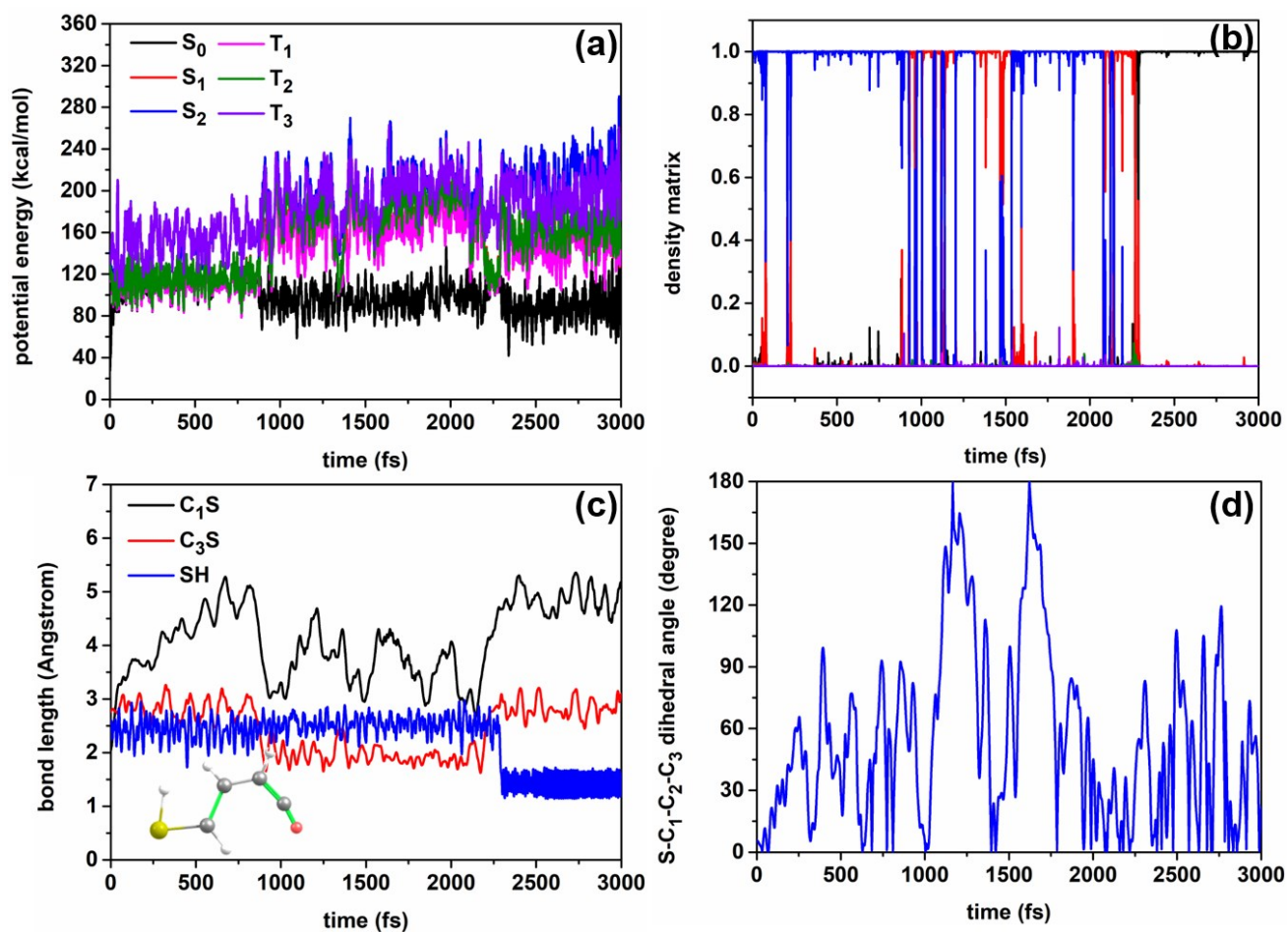
**Figure S2.** Potential energies (a), diagonal elements of density matrix (b),  $C_1-S$  and  $C_3-S$  distances (c) and  $S-C_1-C_2-C_3$  dihedral angle (d) plotted as a function of time for a representative of type-I trajectories.



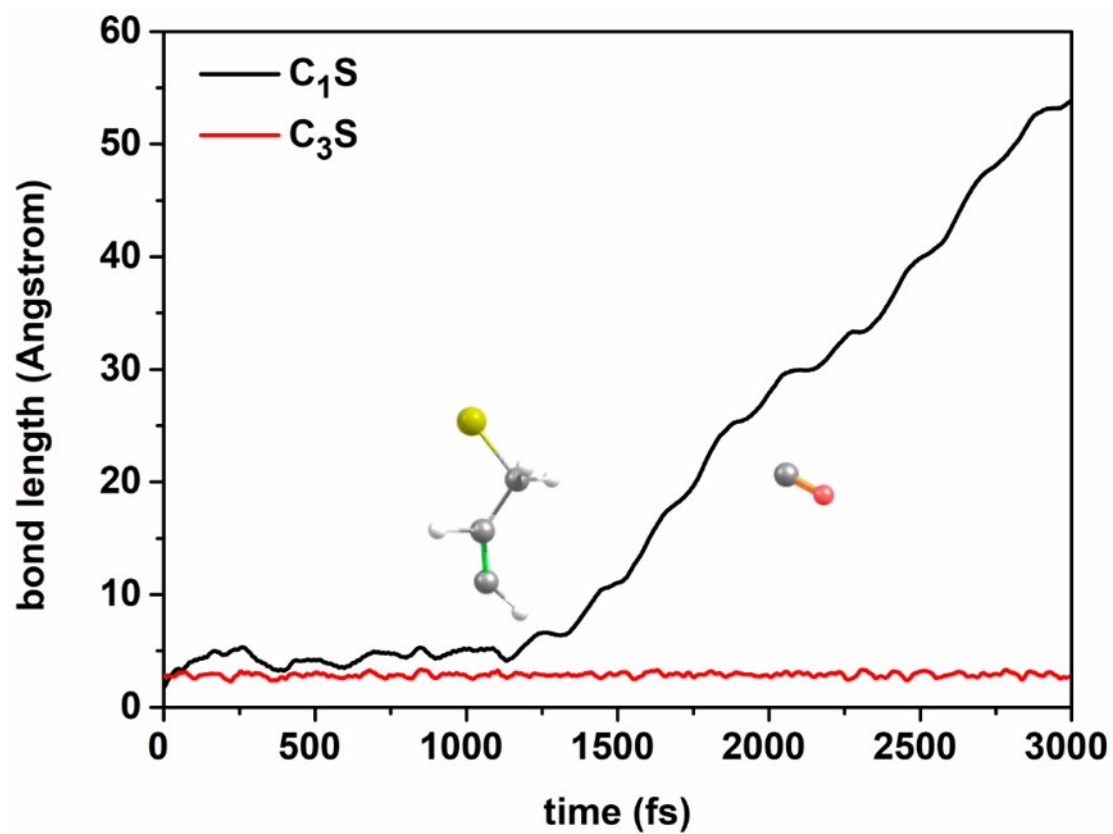
**Figure S3.** Potential energies (a), diagonal elements of density matrix (b), C<sub>1</sub>-S and C<sub>3</sub>-S distances (c) and S-C<sub>1</sub>-C<sub>2</sub>-C<sub>3</sub> dihedral angle (d) plotted as a function of time for a representative of type-II trajectories.



**Figure S4.** Potential energies (a), diagonal elements of density matrix (b),  $C_1-S$  and  $C_3-S$  distances (c) and S- $C_1-C_2-C_3$  dihedral angle (d) plotted as a function of time for a representative of type-II trajectories.



**Figure S5.** Potential energies (a), diagonal elements of density matrix (b),  $C_1-S$ ,  $C_3-S$  and  $S-H$  distances (c) and  $S-C_1-C_2-C_3$  dihedral angle (d) plotted as a function of time for one of minor trajectories leading to P3 product.



**Figure S6.** C<sub>1</sub>-S and C<sub>3</sub>-S distances plotted as a function of time for one of minor trajectories leading to CO fragment.



## 2. Cartesian coordinates for critical structures optimized at the CASPT2 level (Unit: Angstrom)

2TP-S<sub>0</sub>

C	-1.594052670	-0.221340360	0.000359410
C	-1.143316950	1.214774370	-0.000318150
C	0.191465370	1.418445160	0.000128340
C	1.016936960	0.179689910	-0.002278880
S	-0.102655030	-1.260805830	0.000070230
H	-2.206714590	-0.440544280	0.893142340
H	-1.884602640	2.020447600	-0.000585320
H	0.692543980	2.389656740	0.001391540
O	2.229211880	0.114756210	0.000816990
H	-2.206590160	-0.441111640	-0.892353760

2TP-S<sub>1</sub>

C	-1.616526120	-0.195104230	0.000056610
C	-1.176305770	1.243748060	-0.000100520
C	0.214386710	1.429621230	0.000076610
C	0.943311580	0.238465820	-0.000063130
S	-0.088344860	-1.238317580	-0.000605160
H	-2.208908700	-0.462395850	0.895339670
H	-1.905076610	2.057461470	-0.000319430
H	0.715044280	2.400048440	0.000290440
O	2.244275420	0.022862470	0.000428670
H	-2.209629380	-0.462422100	-0.894730240

2TP-T<sub>1</sub>

C	-1.638925260	-0.182291550	0.015888210
C	-1.182883020	1.248125230	0.117207390
C	0.215257740	1.416947970	-0.021555290
C	0.942088780	0.204254240	-0.103272500
S	-0.129327870	-1.235669230	0.093772080
H	-2.292054030	-0.486369080	0.856455560
H	-1.892363120	2.071182530	-0.013487550
H	0.735062380	2.377988480	-0.025653230
O	2.214462950	0.058606190	0.007074240
H	-2.185175560	-0.387347780	-0.926043920

2TP-T<sub>2</sub>

C	-1.641831190	-0.185563860	0.002625690
C	-1.197125210	1.248952230	-0.003382490
C	0.231048850	1.419431780	0.025311090
C	0.950337580	0.214083180	-0.001419580
S	-0.129725920	-1.240255400	-0.027338650
H	-2.228602290	-0.443527560	0.905696530
H	-1.906356840	2.075121320	-0.033641410
H	0.744326560	2.380152630	0.003176170
O	2.228022530	0.052198100	0.008250040
H	-2.263951070	-0.435166430	-0.878892390

2TP-T<sub>3</sub>

C	-1.638939000	-0.163080000	0.010864000
C	-1.189237000	1.257032000	0.032895000
C	0.225901000	1.432764000	-0.025483000
C	1.018583000	0.272754000	-0.029758000
S	-0.184532000	-1.260241000	0.050173000
H	-2.288348000	-0.469766000	0.860916000
H	-1.904179000	2.072598000	0.029998000
H	0.710811000	2.395989000	-0.019364000
O	2.243264000	-0.002108000	-0.001391000
H	-2.207181000	-0.450516000	-0.908465000

## PI

C	28.093744550	28.486091730	25.142131600
C	28.032476120	27.278928830	25.715766370
C	26.818845770	26.825565420	26.463409150
C	26.668938780	27.149674730	27.918314280
S	25.514738340	28.068957800	26.828772490
H	28.912195450	26.634432380	25.625183920
H	26.417053660	25.854212070	26.146982450
H	26.195828150	26.406964680	28.570823960
O	28.172652140	29.538132850	24.626174320
H	27.457490570	27.758082210	28.374033430

## P2

C	28.089774940	28.295146410	25.641774390
C	27.181278990	27.350420520	25.886272160
C	27.000994100	26.757978730	27.259683810
C	25.617581850	26.906088800	27.853455400
S	24.310618420	27.587260890	27.143282050
H	26.532316250	27.064631010	25.055469470
H	27.227301080	25.671835060	27.253724880
H	25.526343050	26.478755460	28.867124750
O	28.905305110	29.118115480	25.430640480
H	27.722272420	27.196607220	27.975405050

## P3

C	28.313533950	28.003758520	25.499228330
C	28.150700870	26.683751880	25.715631890
C	27.223230370	26.025605730	26.632780760
C	26.330034690	26.588898570	27.490548000
S	26.039030690	28.340103390	27.518546750
H	28.833052280	26.072510210	25.115919810
H	27.274471230	24.931282030	26.612353430
H	25.705505000	25.954783290	28.126410910
O	28.551973120	29.111058800	25.194733460
H	26.261540340	28.522463370	28.837958820

Br-S<sub>0</sub>

C	-1.573437390	-0.698364840	0.387324470
C	-0.140174680	-0.400979840	0.710390350
C	0.464686350	0.786189810	0.447047950
C	1.897733240	0.968774400	0.801569890
S	-1.749734270	-2.090839870	-0.769164780
H	-2.112830040	-1.031273570	1.297878520
H	0.447840830	-1.206084400	1.166377670
H	-0.071716440	1.622050530	-0.024379870
O	2.559281530	1.962291850	0.658146330
H	-2.103946910	0.189863190	0.003110620

2TP-T<sub>3</sub>/T<sub>2</sub>

C	-1.612768879	-0.187719789	0.001602547
C	-1.190641709	1.242845683	0.002766739
C	0.245287812	1.429519975	-0.002303829
C	1.061894809	0.269231247	-0.005476788
S	-0.193887135	-1.290475925	-0.000281712
H	-2.242115841	-0.479131770	0.876755217
H	-1.922564312	2.050405361	-0.002945626
H	0.732882211	2.407779033	0.003256544
O	2.274531572	0.070155904	0.002482160
H	-2.240411134	-0.478654574	-0.875465189

Br-S<sub>2</sub>/S<sub>1</sub>/S<sub>0</sub>

C	-1.646777974	-0.254680605	-0.049012106
C	-1.116816163	1.135985874	0.162728917
C	0.249353260	1.471703669	0.011398386
C	1.283039260	0.602461380	-0.212497905
S	-0.604122247	-1.523598015	0.767808380
H	-2.640338415	-0.327207041	0.431169209
H	-1.813655454	1.952319201	0.361249641
H	0.588757054	2.507541177	0.148205652
O	2.242921293	-0.023729534	-0.489433050
H	-1.756228448	-0.455371268	-1.131233009

Br- S<sub>2</sub>/S<sub>1</sub>/S<sub>0</sub>/T<sub>1</sub>/T<sub>2</sub>

C	-1.628532880	-0.246960118	-0.044149822
C	-1.113855382	1.149393521	0.157795621
C	0.253223010	1.488724433	0.018630277
C	1.275671364	0.602837073	-0.213371916
S	-0.657394647	-1.527079547	0.839325260
H	-2.653271687	-0.311721305	0.360721608
H	-1.814711292	1.955555153	0.393113166
H	0.590012398	2.520609437	0.190135693
O	2.200210181	-0.027034565	-0.583655822
H	-1.665236494	-0.518857798	-1.118153001

Br-S<sub>2</sub>/T<sub>3</sub>

C	-1.660085614	-0.238418294	-0.027493372
C	-1.094234228	1.140049129	0.159213621
C	0.255120458	1.445259224	0.020412415
C	1.254397372	0.485507383	-0.260399627
S	-0.772461654	-1.613241263	0.805436370
H	-2.666253102	-0.303276367	0.420017629
H	-1.807849151	1.941263875	0.363573213
H	0.635060229	2.472068874	0.128271798
O	2.395725552	0.232759717	-0.506222848
H	-1.753257911	-0.476539849	-1.102417697

2TP-S<sub>1</sub>/T<sub>1</sub>/T<sub>2</sub>

C	-1.618997158	-0.198249669	0.000076331
C	-1.183310162	1.240788266	-0.000424224
C	0.224265698	1.425249773	0.000208126
C	0.953800865	0.233247874	0.000228086
S	-0.095392411	-1.241075289	-0.000717533
H	-2.216624021	-0.460875928	0.893743153
H	-1.909152805	2.056119898	-0.000199081
H	0.727672145	2.394067554	0.000277748
O	2.247263686	0.045773587	0.000274940
H	-2.217297404	-0.461074134	-0.893084622

2TP-S<sub>2</sub>/T<sub>2</sub>/T<sub>3</sub>

C	-1.648283535	-0.207920175	-0.000118016
C	-1.179038376	1.217814511	-0.000308749
C	0.248751474	1.424357958	0.000875230
C	1.098244973	0.305468910	0.000693098
S	-0.190870079	-1.294684167	-0.001064635
H	-2.263569715	-0.468252346	0.887189284
H	-1.896329855	2.040101658	-0.000226976
H	0.709244316	2.416751443	-0.000614380
O	2.298980409	0.068269166	0.000427305
H	-2.264912314	-0.467942119	-0.886479174