The Primary Steps in Excited State Hydrogen Transfer: The Phototauto–merization of *o*-Nitrobenzyl Derivatives

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Supporting Information

Table SI.1 DFT total energies and zero-point vibrational energies (ZPVEs).

Molecule	BMK[a,b]	B2PLYP[a,c]	ZPVE[a,d]
1a	-475.8903688	-475.8578670688	0.132081 (0.131605)
1b	-664.412636	-664.3609786833	0.147589 (0.146728)
1c	-590.3765853	-590.3306527024	0.166126 (0.164856)
1d	-570.5069104	-570.4608329156	0.178092 (0.177786)
(Z)-**2a**	-475.8392832		0.130588
(Z)-**2b**	-664.3691309		0.147082
(Z)-**2c**	-590.3377337		0.164372
(Z)-**2d**	-570.4749671		0.176016
TS[2a→(Z)-2a]	-475.8135493		0.125283
³1a	-475.7985288		0.129154
³1b	-664.3202148		0.144567
³1c	-590.2834847		0.161889
³1d	-570.4153762		0.175305
³1e	-549.7995167		0.109599
TS[³1a →(Z)-3a]	-475.7766674		0.122449
TS[³1b →(Z)-3b]	-664.3030515		0.138625
TS[³1c →(Z)-3c]	-590.2735001		0.157848
TS[³1d →(Z)-3d]	-570.4136914		0.172672
TS[³1e →(Z)-3e]	-549.7976034		0.128331
(Z)-**3a**	-475.8174509		0.128331
(Z)-**3b**	-664.3486387		0.143922
(Z)-**3c**	-590.317325		0.161772
(Z)-**3d**	-570.4548241		0.173875
4a		-475.2037134402	(0.118004)
4b		-663.7147922248	(0.132965)
4c		-589.6933157134	(0.151600)
4d		-569.8324905080	(0.164174)

[a] In Hartrees.

[b] (U)BMK/6-311+G(d,p) total energies on (U)BMK/6-311+G(d,p) optimized geometries.

[c] (U)B2PLYP/6-311+G(3df,2p) total energies UB3LYP/6-31G(d) geometries.

[d] Unscaled ZPVEs for (U)BMK/6-311+G(d,p) optimized geometries; numbers in parentheses are for (U)B3LYP/6-31G(d) optimized geometries.

Table SI.2 TD-DFT total, electronic transition and zero-point vibrational (ZPVEs) energies.

| Molecule | M06-2X | | | Relative Energy[d] |
	Total Energy[a]	Transition Energy[b]	ZPVE[c]	M06-2X
[1]1a	-475.987524	0.074568	0.129744	–
[1]1b	-664.542808	0.0762915	0.145911	–
[1]1c	-590.500396	0.0767399	0.164218	–
[1]1d	-570.624486	0.0693863	0.177205	–
[1]1e	-549.994194	0.0737816	0.110912	–
TS[[1]1a →(Z)-2a]	-475.953442	0.0619924	0.124994	10.52
TS[[1]1b →(Z)-2b]	-664.514485	0.0647486	0.141501	7.76
TS[[1]1c →(Z)-2c]	-590.480037	0.0684419	0.160172	5.03
TS[[1]1d →(Z)-2d]	-570.629369	0.0772985	0.174374	0.12
TS[[1]1e →(Z)-2e]	-550.000090	0.0802862	0.109155	-0.72

[a] Total electronic energy in Hartrees of S_0 state calculated with respective functional and 6-311+G(3df,2p) basis set on optimized geometries (6-31G(d) basis set) in the S_1 state.

[b] Energy in Hartrees that correspond to the $S_0 \rightarrow S_1$ electronic transition obtained from TD-DFT calculation with 6-31G(d) basis set on the S_1 state optimized geometry.

[c] Unscaled ZPVEs for geometries from TD-DFT calculation with 6-31G(d) basis set.

[d] Relative energy of the activation barrier of hydrogen atom transfer in S_1 state relative to the corresponding energy minimum calculated as sum of total electronic energy, transition energy and ZPVE according to the specific reaction; In kcal mol^{-1}.

Table SI.3 CASPT2/CASSCF total and zero-point vibrational (ZPVEs) energies.

Molecule	Electronic State	MS-CASPT2 Total Energy[a]	Relative Energy[b]
1a	S_0	-475.1712926 [c]	89.9
	S_1 (nπ*)	-475.0279723 [c]	
1b	S_0	-663.4424209 [d]	89.7
	S_1(nπ*)	-663.2994593 [d]	
1c	S_0	-589.4986371 [c]	89.8
	S_1(nπ*)	-589.3555267 [c]	
1d	S_0	-569.6405185 [c]	90.0
	S_1(nπ*)	-569.4970521 [c]	
^{1}1a	S_1(nπ*)	-475.0598398 [c]	–
^{1}1b	S_1(nπ*)	-663.3242709 [d]	–
^{1}1c	S_1(nπ*)	-589.3811744 [c]	–
^{1}1d	S_1(nπ*)	-569.5219719 [c]	–
^{1}1e	S_1(nπ*)	-548.9633673 [d]	–
TS[^{1}1a →(Z)-2a]	S_1(nπ*)	-475.0392471 [c]	12.9
TS[^{1}1b →(Z)-2b]	S_1(nπ*)	-663.3094658 [d]	9.3
TS[^{1}1c →(Z)-2c]	S_1(nπ*)	-589.3706268 [c]	6.6
TS[^{1}1d →(Z)-2d]	S_1(nπ*)	-569.5202425 [c]	1.1
TS[^{1}1e →(Z)-2e]	S_1(nπ*)	-548.9598113 [d]	2.2

[a] Total energy in Hartrees from MS-CASPT2/ANO-L-VTZP calculation with SA-CASSCF reference wavefunction on geometries optimized with SA-CASSCF(10,9)/6-31G(d) level of theory (see Experimental Section for details); two states were averaged in the CASSCF reference wavefunction.

[b] Relative energy in kcal mol^{-1} for specific vertical electronic transition of hydrogen atom transfer reaction.

[c] SA-CASSCF(14,11)/ANO-L-VTZP reference wavefunction.

[d] SA-CASSCF(16,13)/ANO-L-VTZP reference wavefunction.

Table SI4. Isotope substitution effect on ESHT/ESDT energy barriers.[a]

Molecule	S_1 (nπ*) barrier [b]		T_1 (nπ*) barrier [c]	
	H	D	H	D
1a	9.9	10.9	9.6	10.8
1b	6.5	7.4	7.1	8.2
1c	4.1	4.9	3.8	4.6
1d	−0.7	−0.4	−0.6	−0.2
1e	1.1	1.3	0.0	0.3

[a] In kcal mol^{-1}.

[b] Calculated by MS-CASPT2/ANO-L-VTZP with TD-M06-2X ZPVEs.

[c] Calculated at UBMK/6-311+(d,p) level of theory (0K); with ZPVEs.

Table SI.5 Spin-orbit coupling values at S_1 minimum energy geometry of ^{1}**1a**.[a]

	S_0	$S_1(n\pi^*)$	$T_1(n\pi^*)$	$T_2(\pi\pi^*)$
S_0	–	–	66.1	0.02
$S_1(n\pi^*)$	–	–	0.25	65.75
$T_1(n\pi^*)$	66.1	0.25	–	–
$T_2(\pi\pi^*)$	0.02	65.75	–	–

[a] Calculated with CASSCF(10,9)/6-31G(d) wavefunction. For every triplet state, the modulus of all the three sublevels is shown for clarity. In cm^{-1}.

Table SI.6 Spin-orbit coupling values at the geometry of **TS[^{1}1a →(Z)-2a]**.[a]

	S_0	$S_1(n\pi^*)$	$T_1(n\pi^*)$	$T_2(\pi\pi^*)$
S_0	–	–	62.0	6.7
$S_1(n\pi^*)$	–	–	6.0	61.4
$T_1(n\pi^*)$	62.0	6.0	–	–
$T_2(\pi\pi^*)$	6.7	61.4	–	–

[a] Calculated with CASSCF(10,9)/6-31G(d) wavefunction. For every triplet state, the modulus of all the three sublevels is shown for clarity. In cm^{-1}.

Table SI.7 Spin-orbit coupling values at T_1 minimum energy geometry of ^{3}**1a**.[a]

	S_0	$S_1(n\pi^*)$	$T_1(n\pi^*)$	$T_2(\pi\pi^*)$
S_0	–	–	59.7	29.7
$S_1(n\pi^*)$	–	–	26.1	57.4
$T_1(n\pi^*)$	59.7	26.1	–	–
$T_2(\pi\pi^*)$	29.7	57.4	–	–

[a] Calculated with CASSCF(10,9)/6-31G(d) wavefunction. For every triplet state, the modulus of all the three sublevels is shown for clarity. In cm^{-1}.

Table SI.8 Spin-orbit coupling values at the geometry of **TS[^{3}1a →(Z)-3a]**.[a]

	S_0	$S_1(n\pi^*)$	$T_1(n\pi^*)$	$T_2(\pi\pi^*)$
S_0	–	–	55.8	11.8
$S_1(n\pi^*)$	–	–	11.1	56.6
$T_1(n\pi^*)$	55.8	11.1	–	–
$T_2(\pi\pi^*)$	11.8	56.6	–	–

[a] Calculated with CASSCF(10,9)/6-31G(d) wavefunction. For every triplet state, the modulus of all the three sublevels is shown for clarity. In cm^{-1}.
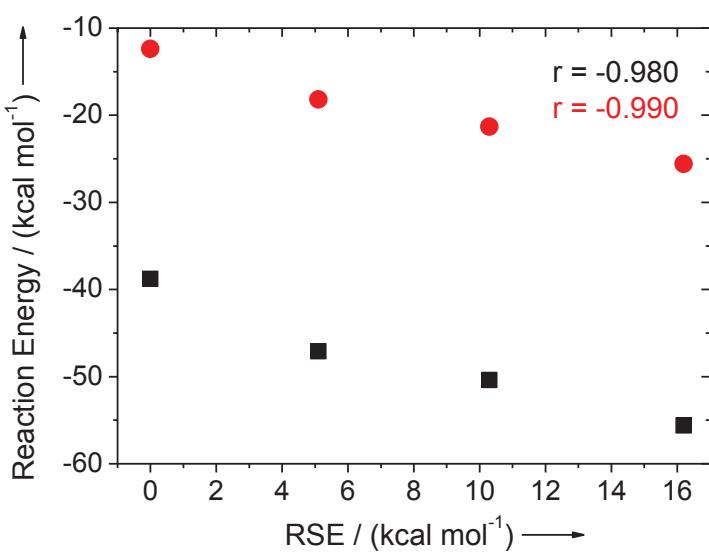
Figure SI1. Correlation of radical stabilization (RSE) and reaction energies for hydrogen atom transfer on S_1 (black squares) and T_1 (red circles) surfaces; Pearson correlation coefficients are shown.
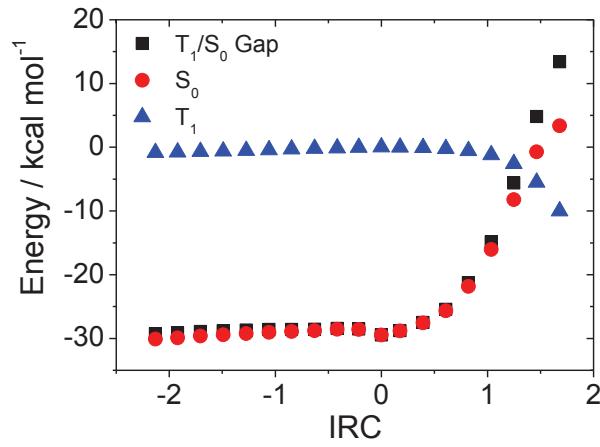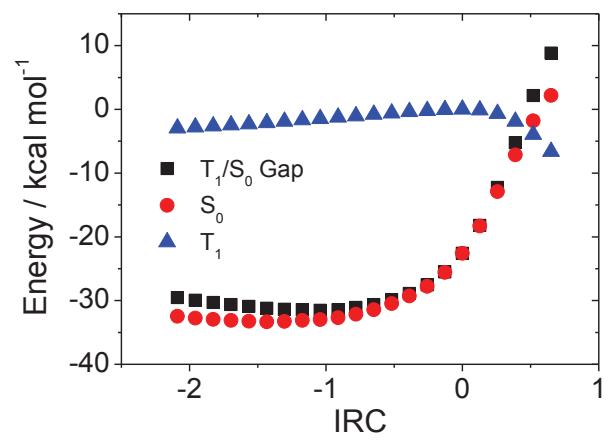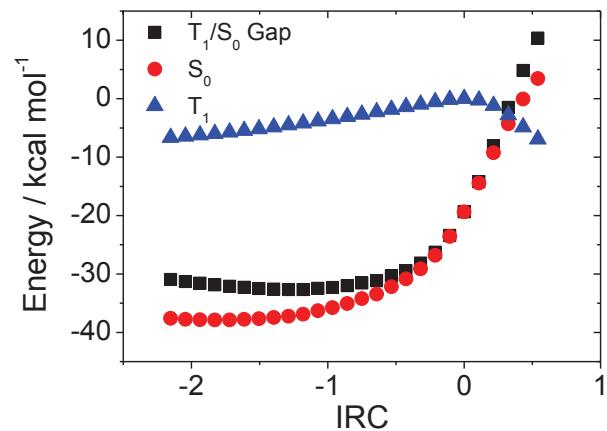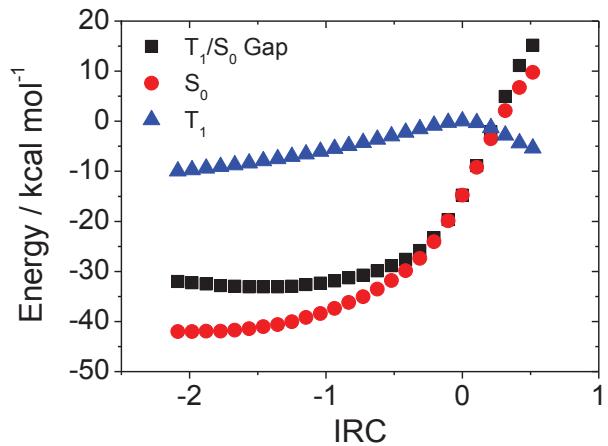
Figure SI2. The T_1 (blue triangles) and S_0 (red circles) energy surfaces ((U)BMK/6-311+G(d,p)) along the part of the IRC coordinate (local minima are not shown) of ESHT on the T_1 energy surface of **1a** (top left), **1b** (top right), **1c** (bottom left) and **1d** (bottom right). The energies are in kcal mol^{-1} relative to the corresponding triplet ESHT transition state (0 kcal mol^{-1} by definition). The T_1/S_0 energy gap is plotted as black squares.

S$_1$(nπ*) SOMO 1   S$_1$(nπ*) SOMO 2
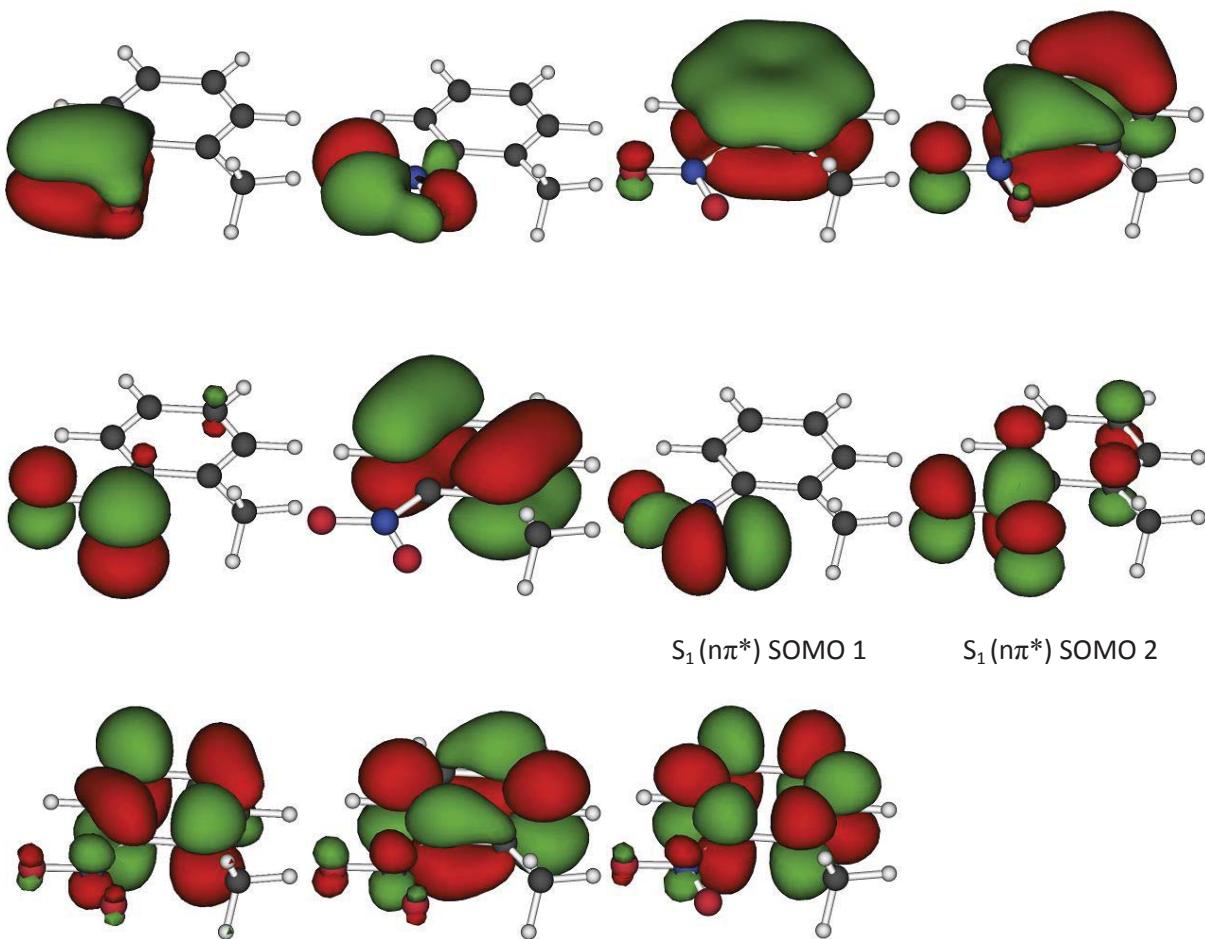
Figure SI3. Orbitals involved in the active space of size (14,11) used for MS-CASPT2 energy calculations of S$_1$ minima of **1a** and **1c-d**. The (10,9) active space used for geometry optimizations can be obtained by omitting the first two orbitals.

S$_1$ (nπ*) SOMO 1   S$_1$ (nπ*) SOMO 2
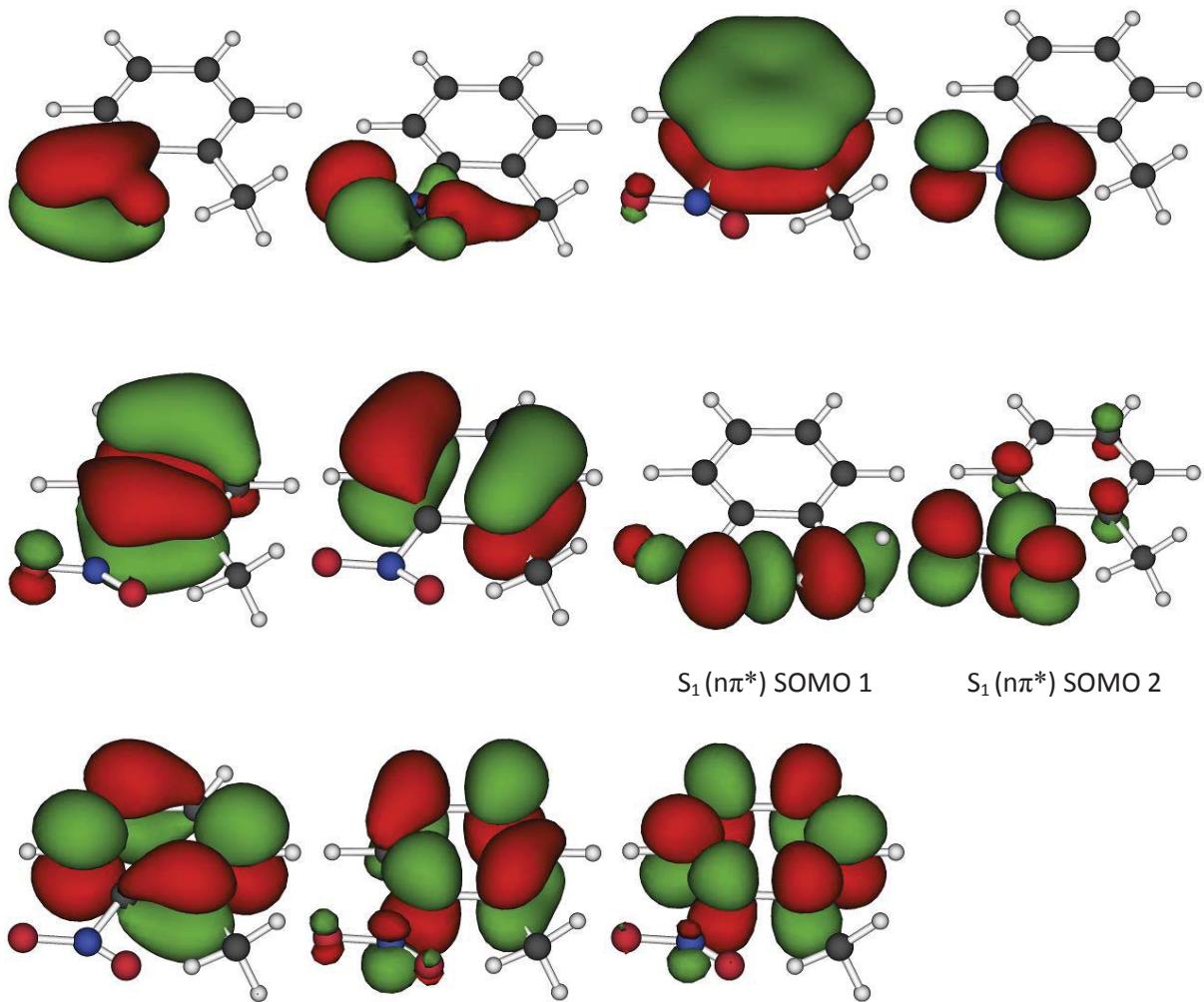
Figure SI4. Orbitals involved in the active space of size (14,11) used for MS-CASPT2 energy calculations of S$_1$ transition states of **1a** and **1c-d**. The (10,9) active space used for geometry optimizations can be obtained by omitting the first two orbitals.

$S_1 (n\pi^*)$ SOMO 1

$S_1 (n\pi^*)$ SOMO 2

Figure SI5. Orbitals involved in the active space of size (16,13) used for MS-CASPT2 energy calculations of S_1 minimum of **1b**. The (10,9) active space used for geometry optimizations can be obtained by omitting the first three and the very last orbitals.

S$_1$(nπ*) SOMO 1
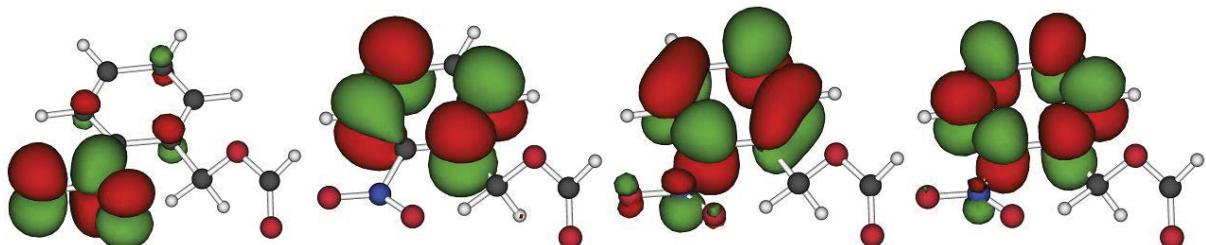
S$_1$(nπ*) SOMO 2
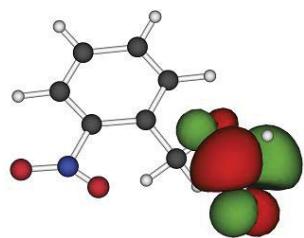
Figure SI6. Orbitals involved in the active space of size (16,13) used for MS-CASPT2 energy calculations of S$_1$ minimum of **1b**. The (10,9) active space used for geometry optimizations can be obtained by omitting the first three and the very last orbitals.

Cartesian Coordinates

1a (S$_0$ minimum geometry BMK/6-311+G(d,p))

```
6       0.415189     0.985874    -0.058397
6      -0.196162    -0.278804     0.013822
6       0.528591    -1.471118     0.080787
6       1.917460    -1.427005     0.103093
6       2.562161    -0.190012     0.032556
6       1.818765     0.985630    -0.056739
6      -0.322680     2.304054    -0.159758
1      -1.139540     2.258478    -0.883601
1       0.376304     3.088362    -0.459395
1      -0.769118     2.572318     0.801565
7      -1.657451    -0.412548     0.020597
8      -2.321258     0.508935     0.482492
8      -2.136495    -1.449628    -0.424250
1      -0.012295    -2.409134     0.116050
1       2.488472    -2.346648     0.170140
1       3.646558    -0.140566     0.040632
1       2.333867     1.938849    -0.127691
```

1b (S$_0$ minimum geometry BMK/6-311+G(d,p))

```
6       0.160706     1.846740     0.059724
6       1.395113     2.496291     0.046814
6       2.582558     1.764220     0.013009
6       2.523484     0.376010    -0.009996
6       1.281363    -0.260716     0.016934
6       0.065231     0.448587     0.052093
7       1.308807    -1.727445     0.006934
8       2.340249    -2.280889    -0.350884
6      -1.299706    -0.219873     0.064854
8      -2.291201     0.792530    -0.114256
6      -3.558450     0.381082    -0.128767
1      -4.220537     1.246587    -0.274271
8       0.298234    -2.323403     0.367497
8      -3.922276    -0.748117    -0.004868
1       1.424429     3.581349     0.059434
1       3.543937     2.266221     0.001871
1       3.415730    -0.236947    -0.049889
1      -0.755286     2.423104     0.070679
1      -1.394488    -0.961298    -0.732448
1      -1.477268    -0.741912     1.008194
```

1c (S$_0$ minimum geometry BMK/6-311+G(d,p))

```
6        0.778328     2.575023      0.038041
6        2.056753     2.012932      0.017163
6        2.191499     0.630071     -0.000421
6        1.048095    -0.172934      0.022129
6       -0.253529     0.363250      0.049574
6       -0.353766     1.761316      0.047607
7        1.274263    -1.620843      0.009877
6       -1.529801    -0.464821      0.059176
8        0.359429    -2.350979      0.381635
8        2.366216    -2.031504     -0.363788
8       -2.628645     0.384128     -0.115374
6       -3.848454    -0.308753     -0.114143
1        0.660105     3.654239      0.044068
1        2.939803     2.642560      0.010398
1        3.162851     0.151818     -0.030031
1       -1.347546     2.191504      0.047347
1       -1.609694    -1.010685      1.009819
1       -1.495032    -1.222401     -0.737723
1       -4.643679     0.428949     -0.236711
1       -4.000198    -0.849118      0.831876
1       -3.897198    -1.030639     -0.942726
```

1d (S$_0$ minimum geometry BMK/6-311+G(d,p))

```
6        2.164181     1.936070      0.014150
6        2.231643     0.548198     -0.028605
6        1.051834    -0.196885      0.019567
6       -0.224322     0.392900      0.082080
6       -0.253717     1.794644      0.112316
6        0.915032     2.555638      0.087456
7        1.211699    -1.653725      0.015171
8        0.359537    -2.327654      0.585500
8        2.196854    -2.121141     -0.544727
6       -1.531635    -0.393590      0.089353
7       -2.676191     0.445195     -0.235814
6       -3.939505    -0.267077     -0.079948
1        3.075297     2.524038     -0.008792
1        3.177499     0.023914     -0.093430
1       -1.223659     2.275615      0.164509
1        0.848206     3.638702      0.123069
1       -1.441485    -1.266181     -0.575493
1       -1.683478    -0.804639      1.094193
1       -2.590977     0.777022     -1.192968
1       -4.082723    -0.518953      0.975899
1       -4.763843     0.383168     -0.384479
1       -3.995596    -1.201998     -0.662415
```

(*Z*)-**2a** (S$_0$ minimum geometry BMK/6-311+G(d,p))

```
6        -1.947047     0.935619    -0.000064
6        -2.594299    -0.246475    -0.000067
6        -1.847556    -1.492917     0.000007
6        -0.497844    -1.489430     0.000050
6         0.245247    -0.236629     0.000024
6        -0.480032     1.058594     0.000015
6         0.044902     2.309729     0.000078
7         1.555733    -0.372189    -0.000001
8         2.225015    -1.437929    -0.000018
8         2.322324     0.780507    -0.000015
1        -2.504386     1.867317    -0.000110
1        -3.678968    -0.276622    -0.000118
1        -2.384184    -2.435998     0.000027
1         0.082548    -2.403007     0.000098
1         1.100425     2.523368     0.000141
1        -0.640917     3.151392     0.000055
1         3.216407     0.407299    -0.000083
```

(*Z*)-**2b** (S$_0$ minimum geometry BMK/6-311+G(d,p))

```
6         0.162177    -1.951817    -0.000269
6         1.376093    -2.541263    -0.000207
6         2.587092    -1.743347     0.000107
6         2.524030    -0.394725     0.000244
6         1.241956     0.293549     0.000088
6        -0.011445    -0.494596    -0.000041
6        -1.272267     0.018827     0.000087
7         1.319505     1.609242     0.000044
8        -2.327235    -0.850188    -0.000028
8         0.127177     2.314263    -0.000082
8         2.352007     2.330257     0.000112
6        -3.579859    -0.349626    -0.000009
1        -4.290594    -1.186071    -0.000186
8        -3.864569     0.805299    -0.000004
1        -0.738531    -2.551892    -0.000472
1         1.452606    -3.623651    -0.000370
1         3.553030    -2.237521     0.000223
1         3.411411     0.224564     0.000453
1        -1.537034     1.061912     0.000279
1         0.446870     3.228910    -0.000212
```

(*Z*)-**2c** (S_0 minimum geometry BMK/6-311+G(d,p))

```
6      -0.386389    1.865478    0.000007
6       0.723232    2.635432    0.000002
6       2.037795    2.022988   -0.000008
6       2.177796    0.679349   -0.000008
6       1.014763   -0.196955    0.000003
6      -0.336282    0.402433    0.000001
6      -1.521072   -0.282395   -0.000012
7       1.295605   -1.481217    0.000014
8       0.224542   -2.372779    0.000023
8       2.431896   -2.042291    0.000014
8      -2.682744    0.377027   -0.000021
6      -3.848878   -0.423602   -0.000016
1      -1.371323    2.316129    0.000013
1       0.639023    3.717043    0.000006
1       2.920955    2.653690   -0.000016
1       3.146479    0.196227   -0.000014
1      -1.583527   -1.361961   -0.000020
1       0.697459   -3.217873    0.000037
1      -4.697902    0.260268   -0.000121
1      -3.887917   -1.053434    0.896509
1      -3.887822   -1.053588   -0.896437
```

(*Z*)-**2d** (S_0 minimum geometry BMK/6-311+G(d,p))

```
6      -0.265794    1.899499    0.070619
6       0.879090    2.622539    0.055506
6       2.153352    1.944088   -0.026078
6       2.218717    0.594073   -0.055158
6       1.014232   -0.225304   -0.008275
6      -0.303286    0.444963    0.010931
6      -1.523829   -0.206819   -0.052785
7       1.243747   -1.519513    0.011787
8       2.363552   -2.129714   -0.020646
8       0.143234   -2.379473    0.072447
6      -3.971566   -0.371886    0.031947
7      -2.739844    0.376120   -0.121286
1      -1.204669    2.439468    0.137673
1       0.846593    3.705450    0.105019
1       3.068705    2.526407   -0.057722
1       3.159739    0.061362   -0.104833
1      -1.559193   -1.285573   -0.076611
1       0.598885   -3.233714    0.082412
1      -4.295804   -0.430796    1.079251
1      -3.824956   -1.388124   -0.342665
1      -4.765278    0.095662   -0.556626
1      -2.811124    1.380187   -0.074056
```

(*E*)-2a (S$_0$ minimum geometry BMK/6-311+G(d,p))

```
6        1.947079     0.935614    -0.000068
6        2.594316    -0.246586    -0.000042
6        1.847685    -1.492864     0.000030
6        0.497832    -1.489479     0.000015
6       -0.245050    -0.236730     0.000015
6        0.480197     1.058401     0.000030
6       -0.044702     2.309616     0.000129
7       -1.555813    -0.372034    -0.000083
8       -2.225508    -1.437691     0.000079
8       -2.322442     0.780577    -0.000079
1        2.504479     1.867260    -0.000114
1        3.678984    -0.276780    -0.000092
1        2.384373    -2.435924     0.000102
1       -0.082342    -2.403129     0.000021
1       -1.100110     2.523750     0.000137
1        0.641074     3.151341     0.000054
1       -3.216311     0.406790    -0.000179
```


(*E*)-2b (S$_0$ minimum geometry BMK/6-311+G(d,p))

```
6        0.011532    -0.494420    -0.000008
6       -0.161707    -1.951673    -0.000115
6       -1.375476    -2.541429    -0.000266
6       -2.586649    -1.743776    -0.000327
6       -2.523932    -0.395125    -0.000223
6       -1.242031     0.293484    -0.000052
7       -1.319795     1.609122     0.000060
8       -2.352488     2.329961     0.000038
6        1.272290     0.019090     0.000110
8        2.327188    -0.849901     0.000146
6        3.579819    -0.349333     0.000166
8        3.864455     0.805567     0.000126
8       -0.127663     2.314320     0.000226
1        4.290439    -1.185801     0.000221
1        0.739205    -2.551460    -0.000070
1       -1.451730    -3.623831    -0.000342
1       -3.552482    -2.238154    -0.000452
1       -3.411508     0.223871    -0.000258
1        1.537173     1.062156     0.000179
1       -0.447550     3.228877     0.000301
```

(*E*)-**2c** (S$_0$ minimum geometry BMK/6-311+G(d,p))

```
6       -0.386040    1.865718   -0.000172
6        0.723925    2.635359   -0.000214
6        2.038170    2.022603   -0.000161
6        2.178028    0.678810   -0.000050
6        1.014834   -0.196712    0.000020
6       -0.336021    0.402885   -0.000070
6       -1.520914   -0.282108   -0.000064
7        1.294924   -1.481300    0.000182
8        0.224009   -2.372629    0.000260
8        2.431292   -2.043221    0.000290
8       -2.682750    0.377525   -0.000109
6       -3.848986   -0.423362   -0.000033
1       -1.370893    2.316520   -0.000217
1        0.640145    3.716986   -0.000290
1        2.921462    2.653131   -0.000208
1        3.146654    0.195587    0.000001
1       -1.583841   -1.361565   -0.000014
1        0.697315   -3.217587    0.000426
1       -4.698279    0.260172    0.000227
1       -3.887544   -1.053493    0.896287
1       -3.887865   -1.053207   -0.896540
```

(*E*)-**2d** (S$_0$ minimum geometry BMK/6-311+G(d,p))

```
6       -0.265733    1.899511    0.070974
6        0.879183    2.622522    0.055668
6        2.153387    1.944028   -0.026263
6        2.218701    0.593992   -0.055407
6        1.014211   -0.225324   -0.008272
6       -0.303282    0.445000    0.011116
6       -1.523827   -0.206759   -0.052798
7        1.243685   -1.519543    0.011808
8        2.363476   -2.129743   -0.020972
8        0.143161   -2.379457    0.072991
6       -3.971535   -0.371837    0.031721
7       -2.739826    0.376178   -0.121516
1       -1.204584    2.439487    0.138373
1        0.846750    3.705430    0.105296
1        3.068762    2.526310   -0.058031
1        3.159712    0.061273   -0.105240
1       -1.559188   -1.285507   -0.076719
1        0.598800   -3.233711    0.082732
1       -4.295909   -0.430567    1.078994
1       -3.824794   -1.388145   -0.342656
1       -4.765186    0.095535   -0.557065
1       -2.811101    1.380245   -0.074311
```

TS[1a→(*Z*)-2a] (geometry BMK/6-311+G(d,p))

```
6        0.363081     1.032521     0.094876
6        1.773600     1.070217    -0.181538
6        2.542789    -0.061456    -0.169599
6        1.969083    -1.349238     0.070475
6        0.617735    -1.466721     0.224214
6       -0.196843    -0.293534     0.198561
7       -1.545992    -0.473981    -0.009487
8       -2.314184     0.586677    -0.114133
6       -0.420840     2.211765     0.144106
1        0.062489     3.127861    -0.182132
8       -2.058522    -1.574389    -0.196885
1        2.227576     2.043770    -0.336909
1        3.614421     0.018759    -0.327160
1        2.603165    -2.228041     0.102093
1        0.129509    -2.426305     0.343221
1       -1.104536     2.348050     0.983441
1       -1.620653     1.474142    -0.314574
```

¹1a (S1 planar minimum geometry CAS(10,9)/6-31G(d))

```
C        2.5877522115    -0.1935282558     0.0007451993
C        1.8334208191     0.9810419220    -0.0000639221
C        0.4354906195     0.9783119388    -0.0008470121
C       -0.1977055577    -0.2881354283    -0.0002683696
C        0.5499328789    -1.4816656426     0.0002232542
C        1.9364482519    -1.4288176981     0.0007733474
C       -0.3073173626     2.2987703224    -0.0028455852
H       -0.9359073559     2.4105378470    -0.8792147709
H        0.4040382376     3.1148681221    -0.0054508807
H       -0.9339229664     2.4145389396     0.8743951496
H        0.0311040066    -2.4187461399     0.0004520402
H        2.5003153170    -2.3433464674     0.0014974474
H        3.6607944138    -0.1421482549     0.0012509699
H        2.3400078903     1.9291643560    -0.0004510175
O       -2.4299854237     0.5967893428     0.0083692570
O       -2.2187046937    -1.5010071220    -0.0014285165
N       -1.5733382862    -0.4445287816    -0.0024925904
```

¹1b (S1 planar minimum geometry CAS(10,9)/6-31G(d))

C	0.3779409150	1.0155928886	0.0717294571
C	1.7668575600	1.2483391951	-0.0681782064
C	2.5846420011	0.1283266150	-0.2521569716
C	2.0679862228	-1.1664972730	-0.2974324638
C	0.6956081810	-1.3720717561	-0.1563497033
C	-0.1490398566	-0.2872369275	0.0280000233
C	2.3723395551	2.6406622180	-0.0263392712
O	3.7774117593	2.5351608873	-0.1827924130
C	4.4632783226	3.6641580636	-0.1759075028
O	4.0055057124	4.7461168593	-0.0479237447
N	-0.5720257865	2.0245323803	0.2623589651
O	-1.7828116145	1.8894674153	0.3941043129
O	-0.1656246990	3.3432675182	0.3161391031
H	2.1689836472	3.1323590561	0.9137707169
H	2.7321143646	-1.9987197479	-0.4398411192
H	0.2838974335	-2.3637339929	-0.1887198887
H	-1.2057207903	-0.4176862866	0.1388294108
H	3.6389355126	0.2767512054	-0.3603242611
H	1.9851465552	3.2631333835	-0.8199540292
H	5.5189650049	3.4561272983	-0.3058254140

¹1c (S1 planar minimum geometry CAS(10,9)/6-31G(d))

C	2.5321624203	-0.0256427333	-0.2918098218
C	1.9911526409	-1.3035472624	-0.1451596950
C	0.6313763904	-1.4550654123	0.0837775755
C	-0.1968454841	-0.3215899370	0.1675402020
C	0.3287647776	0.9833905848	0.0224515028
C	1.7041761465	1.0935533111	-0.2071461221
N	-1.5481799515	-0.6010939331	0.4014964842
O	-2.4531333236	0.4379512772	0.4959868806
C	-0.5190734610	2.2436013663	0.1045057108
O	0.2836406749	3.3639703976	-0.0778011426
C	-0.4131658995	4.5708436013	-0.0167871383
O	-2.0693558246	-1.7017093289	0.5420998762
H	-1.0115959463	2.3007923331	1.0724838512
H	3.5839542808	0.1028406670	-0.4695169434
H	2.6172994268	-2.1743735376	-0.2077746891
H	0.1911308936	-2.4239539351	0.2000292045
H	2.1195815105	2.0733603431	-0.3197289496
H	-1.2952351561	2.2229175349	-0.6570236140
H	0.3035599569	5.3645036412	-0.1710457433
H	-1.1763414703	4.6264924753	-0.7895397340
H	-0.8881536022	4.7047645469	0.9522993054

¹1d (S1 minimum geometry CAS(10,9)/6-31G(d))

C	−0.0942100126	−2.6607510642	0.6568478118
C	0.0250834559	−2.1230676037	1.9391019536
C	0.0596278493	−0.7459846088	2.1062440692
C	−0.0076657400	0.0978468238	0.9853094289
C	−0.0863467459	−0.4199314105	−0.3257637366
C	−0.1496153468	−1.8142995474	−0.4494900235
C	−0.0871083534	0.4532378782	−1.5761255468
C	0.0995752147	0.4789339852	−3.9850236591
N	0.0012253632	1.4710985953	1.2839747731
N	0.2300264498	−0.3017033961	−2.7706102600
O	−0.4458443774	2.3746180682	0.3383697057
O	0.3811425576	2.0025179989	2.3221618554
H	0.5991157442	1.2867647660	−1.4388344608
H	−0.1386684645	−3.7251114300	0.5157825078
H	0.0750051425	−2.7637440332	2.8001606023
H	0.1324282478	−0.3048959710	3.0796140316
H	−0.2330468361	−2.2283468037	−1.4340759192
H	−1.0739128637	0.8841753888	−1.7157203062
H	0.4070117098	−0.1228195787	−4.8317117266
H	−0.9400102523	0.7504102097	−4.1309130184
H	0.6897665988	1.3974663004	−3.9837594760
H	1.1635806232	−0.6590048956	−2.7007678984

TS[¹1a →(*Z*)-2a] (S1 geometry CASPT2/ANO-L-VTZP//CAS(10,9)/6-31G(d))

C	0.0361024431	−0.0660035748	−2.6443153463
C	1.3080534714	−0.0407002585	−2.0630070504
C	1.4476992222	0.0209741606	−0.6798517125
C	0.2930736709	0.0531021805	0.1054423312
C	−0.9886976080	0.0444150787	−0.4467521046
C	−1.1009664812	−0.0240551575	−1.8388412285
C	−2.1585865644	0.1105675273	0.4976299891
N	0.4268537617	0.1753983674	1.5161590594
O	−0.6811307670	−0.2481750340	2.2736285285
O	1.4821122350	0.0108881010	2.1191823216
H	−2.6535912754	1.0751220606	0.4843975513
H	−0.0658599167	−0.1182475602	−3.7127748731
H	2.1853617220	−0.0758964307	−2.6822579006
H	2.4114801077	0.0371260746	−0.2118846809
H	−2.0788322312	−0.0437037028	−2.2860222162
H	−1.6979328327	−0.0410435969	1.5284486658
H	−2.8840221939	−0.6755940128	0.3275060953

TS[^{1}1b →(*Z*)-2b] (S1 geometry CASPT2/ANO-L-VTZP//CAS(10,9)/6-31G(d))

```
C        −2.2949776180          0.0158271807         −1.9876208525
C        −1.2861385702         −0.1158139358         −2.9483169692
C         0.0478266938         −0.0880237731         −2.5731997582
C         0.3499208006          0.0674691341         −1.2183073769
C        −0.6384305995          0.2189599818         −0.2538349572
C        −1.9744448748          0.1818862026         −0.6623550615
C        −0.2015431996          0.4286493416          1.1651403515
C        −0.6128697407         −0.4165941118          3.3005041589
N         1.7364350378          0.1572491003         −0.8226829251
O         1.9927906566         −0.1126738179          0.5291804618
O        −0.8485813107         −0.5082100666          2.0024509559
O         0.0913634544          0.3807212527          3.8151679303
O         2.6738016343         −0.1369201911         −1.5520231115
H        −0.3796152160          1.4330063622          1.5226096772
H        −3.3257482151         −0.0121233230         −2.2900801336
H        −1.5432475227         −0.2457355432         −3.9832130277
H         0.8388502072         −0.1929166897         −3.2883198609
H        −2.7490997322          0.2792365480          0.0758906740
H         0.9135398277          0.2384872821          1.1577489898
H        −1.1646119310         −1.1834459733          3.8313508303
```

TS[^{1}1c →(*Z*)-2c] (S1 geometry CASPT2/ANO-L-VTZP//CAS(10,9)/6-31G(d))

```
C        −1.4727941826         −0.1718761946         −2.5212999353
C        −0.1093931264         −0.1119577401         −2.2535038078
C         0.3043696958          0.0728514618         −0.9310715868
C        −0.6057141852          0.2257682335          0.1148941964
C        −1.9713168678          0.1526737776         −0.1766017973
C        −2.4050448331         −0.0458939212         −1.4850084517
C        −0.0732721927          0.4719758954          1.4996004491
C        −0.3038060359         −0.1519704964          3.7384830806
N         1.6967228313          0.1809030153         −0.6630131944
O         2.5728839220         −0.1003805077         −1.4744898832
O        −0.7209038328         −0.3371681706          2.4187892343
O         2.0904899750         −0.1165163379          0.6541599125
H        −0.1638334254          1.5228479603          1.7732154777
H        −3.4566194029         −0.1025681585         −1.6985099128
H        −1.8060711885         −0.3261153755         −3.5310602124
H         0.6210226003         −0.2164920063         −3.0302986604
H        −2.6790591896          0.2416417193          0.6258165803
H         1.0215350658          0.2360923091          1.4289485703
H        −0.8816404150         −0.8249427592          4.3552252667
H         0.7521341382         −0.3816324941          3.8551281125
H        −0.4773094447          0.8702216076          4.0677275928
```

TS[¹1d →(Z)-2d] (S1 geometry CASPT2/ANO-L-VTZP//CAS(10,9)/6-31G(d))

```
C        -0.0381314627       -2.4356660791        1.4342803206
C        -0.1656355049       -1.5258811892        2.4898336933
C        -0.1088436738       -0.1582808482        2.2477804571
C         0.0742293686        0.2860974125        0.9336771950
C         0.2235413984       -0.6007726524       -0.1347098773
C         0.1544647740       -1.9729842711        0.1352545566
C         0.4668173885       -0.0605877744       -1.5242701699
C        -0.1188247210       -0.2431977957       -3.8679789959
N         0.1806414630        1.6880110688        0.7151966219
N        -0.3526019675       -0.7108881534       -2.5163489037
O        -0.0937597992        2.1325273193       -0.5870832731
O        -0.1191512134        2.5322514029        1.5541675240
H         1.5099365935       -0.1919423052       -1.7971454137
H        -0.0878414837       -3.4919933238        1.6254817311
H        -0.3163494692       -1.8790627734        3.4933951778
H        -0.2114645115        0.5558553070        3.0396800458
H         0.2465355860       -2.6617714945       -0.6829701498
H         0.2903228477        1.0357215986       -1.4450499808
H        -0.7876879814       -0.7591222448       -4.5461447457
H        -0.2631812459        0.8313012265       -3.9931287314
H         0.8982241425       -0.4799716705       -4.1610264858
H        -1.3198927207       -0.6090985025       -2.2776067855
```

¹1a (S1 planar minimum geometry TD-M06-2X/6-31G(d))

```
6         1.844486        0.981877        0.000480
6         0.451374        0.987747       -0.000871
6        -0.177114       -0.273654       -0.000710
6         0.547812       -1.472775       -0.000186
6         1.932406       -1.427016        0.000946
6         2.586243       -0.197088        0.001498
6        -0.308082        2.289134       -0.002787
1        -0.956794        2.375827       -0.879256
1         0.395745        3.124605       -0.011365
1        -0.945487        2.384874        0.881075
1         0.011835       -2.415085       -0.000324
1         2.498627       -2.352349        0.001598
1         3.670202       -0.153216        0.002518
1         2.358983        1.938873        0.000483
8        -2.226588       -1.485012       -0.002795
8        -2.445750        0.543499        0.007337
7        -1.559593       -0.385825       -0.003041
```

¹1b (S1 planar minimum geometry TD-M06-2X/6-31G(d))

```
6        0.204190    -1.881988    -0.000052
6        1.453054    -2.500052     0.000119
6        2.614516    -1.731880     0.000113
6        2.527615    -0.349474     0.000040
6        1.265298     0.256401    -0.000004
6        0.073439    -0.496323    -0.000128
7        1.240217     1.642085     0.000197
8        2.267374     2.414901     0.000025
6       -1.282747     0.168169    -0.000450
8       -2.280492    -0.854734    -0.000232
6       -3.544394    -0.410358     0.000170
8       -3.873330     0.742038     0.000344
8        0.224555     2.426835    -0.000075
1       -1.421043     0.805454    -0.880015
1        1.514710    -3.583056     0.000293
1        3.590066    -2.206456     0.000126
1        3.413832     0.274293    -0.000017
1       -0.696624    -2.482908    -0.000147
1       -1.421236     0.805973     0.878719
1       -4.231909    -1.267184     0.000309
```


¹1c (S1 planar minimum geometry TD-M06-2X/6-31G(d))

```
6       -2.195092     0.629962    -0.000054
6       -1.036602    -0.157435    -0.000023
6        0.253140     0.408383     0.000058
6        0.333142     1.797385     0.000126
6       -0.809239     2.595551     0.000096
6       -2.073060     2.009883     0.000006
7       -1.217073    -1.531836    -0.000233
8       -0.328635    -2.459753     0.000590
6        1.510043    -0.432787     0.000022
8        2.628316     0.413760    -0.000124
6        3.832845    -0.311850    -0.000147
8       -2.346971    -2.146476    -0.000311
1        1.525377    -1.090738    -0.883661
1       -0.708870     3.675841     0.000135
1       -2.966328     2.625476     0.000000
1       -3.164570     0.144937    -0.000093
1        1.318974     2.246101     0.000185
1        1.525504    -1.090631     0.883781
1        4.647279     0.414109    -0.000201
1        3.914741    -0.948501     0.892332
1        3.914669    -0.948555    -0.892593
```

¹1d (S1 planar minimum geometry TD-M06-2X/6-31G(d))

```
6        -0.272453     1.815219      0.147709
6         0.888151     2.584119      0.092805
6         2.130955     1.968183     -0.030551
6         2.212544     0.585116     -0.083438
6         1.036994    -0.169778     -0.019730
6        -0.234895     0.424098      0.078655
7         1.175957    -1.558409     -0.099573
8         2.300701    -2.177605     -0.193776
6        -1.514746    -0.387551      0.101319
7        -2.677348     0.438548     -0.180765
6        -3.917773    -0.312658     -0.053207
8         0.347920    -2.448781      0.322737
1        -1.649440    -0.825129      1.099120
1         0.818979     3.665741      0.147033
1         3.038984     2.560439     -0.072929
1         3.166028     0.075337     -0.160989
1        -1.244004     2.286738      0.246253
1        -1.423419    -1.242803     -0.589909
1        -4.757984     0.322293     -0.343755
1        -3.946181    -1.233197     -0.659090
1        -4.056958    -0.596466      0.994706
1        -2.597902     0.796666     -1.131131
```


TS[¹1a →(Z)-2a] (S1 geometry TD-M06-2X/6-31G(d))

```
6         2.006078    -1.327558     -0.000133
6         0.629310    -1.459387     -0.000005
6        -0.161623    -0.302243      0.000022
6         0.408924     0.980050     -0.000073
6         1.799141     1.077814     -0.000202
6         2.597794    -0.060960     -0.000232
7        -1.544994    -0.465178      0.000147
8        -2.143014    -1.567139      0.000268
6        -0.483422     2.176798     -0.000027
8        -2.375677     0.574783      0.000179
1        -0.455952     2.783395      0.906656
1         3.678014     0.037492     -0.000334
1         2.626664    -2.217649     -0.000155
1         0.135989    -2.424325      0.000075
1         2.254668     2.064205     -0.000279
1        -1.596052     1.661506      0.000049
1        -0.456060     2.783387     -0.906717
```

TS[¹1b →(Z)-2b] (S1 geometry TD-M06-2X/6-31G(d))

6	-0.542415	-1.938266	0.221940
6	-1.868284	-2.324629	0.072454
6	-2.860882	-1.352212	-0.093791
6	-2.537326	-0.007844	-0.120297
6	-1.194618	0.369061	0.023547
6	-0.187044	-0.590700	0.204094
7	-0.896154	1.727913	-0.012619
8	-1.744133	2.646993	-0.115904
6	1.224813	-0.148550	0.385034
8	2.040923	-0.648514	-0.637922
6	3.373744	-0.485241	-0.465459
8	3.879500	0.065602	0.467219
8	0.346278	2.176338	0.086689
1	1.668039	-0.316177	1.371150
1	-2.130945	-3.376803	0.084242
1	-3.897697	-1.651198	-0.209070
1	-3.282848	0.766241	-0.256544
1	0.237396	-2.683047	0.351369
1	1.147039	1.050209	0.293819
1	3.903612	-0.937692	-1.312429

TS[¹1c →(Z)-2c] (S1 geometry TD-M06-2X/6-31G(d))

6	-2.466365	-1.553012	-0.135652
6	-2.268574	-0.183310	-0.135014
6	-0.967692	0.316530	0.020392
6	0.124108	-0.548042	0.195610
6	-0.104730	-1.921745	0.181900
6	-1.387668	-2.429906	0.013961
6	1.496468	0.003447	0.421435
6	3.750468	-0.193042	-0.161260
7	-0.801884	1.699270	-0.006184
8	-1.744757	2.531810	-0.059459
8	2.413479	-0.568906	-0.428148
8	0.383812	2.270483	0.047362
1	1.825195	-0.040798	1.473459
1	-1.549301	-3.502296	-0.001019
1	-3.470334	-1.944937	-0.263135
1	-3.081923	0.520258	-0.265528
1	0.743779	-2.589208	0.298328
1	1.373202	1.158625	0.219665
1	4.381166	-0.764736	-0.841460
1	3.894404	0.879308	-0.340499
1	4.020645	-0.423722	0.877210

TS[¹1d →(Z)-2d] (S1 geometry TD-M06-2X/6-31G(d))

```
6      -1.213735    -2.502417     0.031538
6      -2.355401    -1.713670    -0.133119
6      -2.257552    -0.334026    -0.140555
6      -0.999620     0.268241     0.021336
6       0.161457    -0.505751     0.201145
6       0.025100    -1.893523     0.199495
6       1.513810     0.121644     0.422102
6       3.876954     0.010447    -0.156907
7      -0.963435     1.658420    -0.007283
7       2.539822    -0.523454    -0.335370
8       0.122360     2.368483     0.079247
8      -1.987106     2.403032    -0.097561
1       1.794119     0.099204     1.484566
1      -1.291322    -3.584413     0.031304
1      -3.327247    -2.179104    -0.262323
1      -3.123473     0.302952    -0.276829
1       0.921463    -2.492059     0.332588
1       1.418842     1.222310     0.178095
1       4.583673    -0.573436    -0.749975
1       3.961909     1.069728    -0.444995
1       4.157384    -0.078096     0.896929
1       2.281839    -0.609639    -1.314486
```

³1a (T1 minimum geometry UBMK/6-311+G(d,p))

```
6      -0.458399     0.983778    -0.061208
6       0.184880    -0.268863    -0.048618
6      -0.521938    -1.475019     0.001089
6      -1.911924    -1.445848     0.071627
6      -2.580200    -0.220048     0.082108
6      -1.855362     0.971663     0.013122
6       0.297572     2.292006    -0.164468
1       0.760797     2.556337     0.790882
1      -0.385766     3.094265    -0.453419
1       1.098351     2.234876    -0.908905
7       1.600498    -0.321108    -0.171158
8       2.377225     0.508944     0.486582
8       2.232873    -1.460207    -0.217648
1       0.028942    -2.408071    -0.005314
1      -2.467509    -2.376370     0.121122
1      -3.663761    -0.190188     0.133993
1      -2.383100     1.920996     0.006369
```

³1b (T1 minimum geometry UBMK/6-311+G(d,p))

```
6       0.201199    -1.883597     0.171773
6       1.452587    -2.501574     0.122840
6       2.609397    -1.734475    -0.021359
6       2.516390    -0.348475    -0.107808
6       1.257748     0.257697    -0.040719
6       0.073582    -0.494532     0.082923
7       1.179626     1.671183    -0.177760
8       2.264128     2.391591    -0.307696
6      -1.289200     0.172036     0.121081
8      -2.275556    -0.804792    -0.212991
6      -3.540766    -0.389159    -0.213472
1      -4.200064    -1.226937    -0.481907
8       0.331230     2.379164     0.525998
8      -3.905494     0.719048     0.037122
1       1.518754    -3.582609     0.188889
1       3.583996    -2.209372    -0.062391
1       3.396469     0.273307    -0.217082
1      -0.696723    -2.482318     0.263058
1      -1.508147     0.579404     1.112919
1      -1.351749     1.002625    -0.590183
```

³1c (T1 minimum geometry UBMK/6-311+G(d,p))

```
6       0.844038     2.592200     0.094962
6       2.098188     1.988078    -0.016896
6       2.196039     0.601671    -0.087327
6       1.028922    -0.169432    -0.032670
6      -0.248151     0.415850     0.068688
6      -0.312219     1.810257     0.135078
7       1.145757    -1.576582    -0.171668
6      -1.520133    -0.414147     0.106120
8       0.356766    -2.405047     0.466148
8       2.313925    -2.158729    -0.247888
8      -2.615541     0.398821    -0.200175
6      -3.836272    -0.289202    -0.134510
1       0.763675     3.673315     0.144343
1       2.999437     2.591116    -0.048885
1       3.155742     0.107521    -0.174353
1      -1.290088     2.272118     0.199993
1      -1.640752    -0.861191     1.105396
1      -1.446206    -1.250572    -0.608978
1      -4.624600     0.419290    -0.395567
1      -4.021457    -0.677619     0.877989
1      -3.859722    -1.129917    -0.843617
```

³1d (T1 minimum geometry UBMK/6-311+G(d,p))

6	2.174394	1.929349	-0.041903
6	2.220921	0.541180	-0.125003
6	1.030706	-0.189254	-0.032051
6	-0.223325	0.434571	0.115048
6	-0.232582	1.831099	0.203445
6	0.947032	2.574088	0.128245
7	1.099747	-1.602306	-0.167060
8	0.341462	-2.395347	0.561138
8	2.238509	-2.208252	-0.336953
6	-1.525247	-0.353833	0.171299
7	-2.660854	0.443415	-0.263728
6	-3.927158	-0.265847	-0.129806
1	3.093586	2.502389	-0.104590
1	3.154355	0.005547	-0.251186
1	-1.191149	2.323628	0.324311
1	0.906552	3.656459	0.197384
1	-1.418523	-1.285685	-0.413425
1	-1.709951	-0.670331	1.205474
1	-2.524215	0.730360	-1.229045
1	-4.131117	-0.443250	0.931372
1	-4.735181	0.353910	-0.527235
1	-3.944824	-1.240120	-0.646661

TS[³1a →(Z)-3a] (T1 geometry UBMK/6-311+G(d,p))

6	2.607600	-0.027144	-0.030396
6	2.037250	-1.305926	-0.023788
6	0.656478	-1.463490	-0.002177
6	-0.158840	-0.320401	0.009753
6	0.394108	0.975217	0.018476
6	1.785483	1.101940	-0.009028
7	-1.545998	-0.488365	0.069850
6	-0.522014	2.163024	0.085693
8	-2.371488	0.590734	-0.188251
8	-2.137340	-1.592536	0.070363
1	-0.560639	2.674270	1.051239
1	3.685917	0.089877	-0.050898
1	2.672822	-2.185170	-0.041241
1	0.186592	-2.439818	-0.001733
1	2.224107	2.095638	-0.008404
1	-1.642700	1.609854	-0.023030
1	-0.473870	2.849006	-0.762986

TS[³1b →(Z)-3b] (T1 geometry UBMK/6-311+G(d,p))

```
6      -0.478151    -1.932474    -0.226836
6      -1.794347    -2.371114    -0.091707
6      -2.825504    -1.436244     0.075400
6      -2.552435    -0.075335     0.112505
6      -1.222588     0.357783    -0.029956
6      -0.175660    -0.568017    -0.202745
7      -0.955089     1.723562     0.069999
8      -1.824487     2.615226     0.218411
6       1.231368    -0.070143    -0.351251
8       2.053562    -0.551832     0.663758
6       3.388160    -0.450303     0.492569
1       3.894389    -0.875048     1.369192
8       0.283045     2.203825    -0.284417
8       3.920244     0.022237    -0.459819
1      -2.017474    -3.432286    -0.115578
1      -3.851515    -1.774100     0.179658
1      -3.330596     0.665296     0.252083
1       0.329313    -2.647547    -0.352039
1       1.688302    -0.181523    -1.340036
1       1.089240     1.139705    -0.254609
```

TS[³1c →(Z)-3c] (T1 geometry UBMK/6-311+G(d,p))

```
6       1.438179    -2.413979     0.047225
6       2.500975    -1.518979    -0.133795
6       2.278740    -0.148082    -0.150290
6       0.970570     0.335835     0.028046
6      -0.107800    -0.549922     0.219956
6       0.144198    -1.924373     0.219767
7       0.758059     1.712981    -0.067203
6      -1.503516    -0.017626     0.407111
8      -0.430716     2.250464     0.337168
8       1.670212     2.564733    -0.229727
8      -2.386912    -0.582663    -0.468695
6      -3.741590    -0.258079    -0.236582
1       1.618786    -3.483626     0.050803
1       3.510634    -1.893727    -0.268127
1       3.080773     0.563779    -0.303771
1      -0.690517    -2.606229     0.348796
1      -1.383212     1.148420     0.234278
1      -1.856708    -0.066232     1.451163
1      -4.330012    -0.805386    -0.973509
1      -3.909013     0.819094    -0.363212
1      -4.046360    -0.556000     0.775409
```

TS[³1d →(*Z*)-3d] (T1 geometry UBMK/6-311+G(d,p))

```
6       0.007907    -1.894066     0.250157
6       1.259127    -2.489411     0.087189
6       2.388618    -1.689655    -0.120518
6       2.269957    -0.305535    -0.163645
6       1.006828     0.282322     0.013046
6      -0.145233    -0.503513     0.216932
7       0.904140     1.678153    -0.108621
8       1.899663     2.440320    -0.315816
6      -1.517690     0.121866     0.380081
7      -2.523472    -0.552326    -0.379832
6      -3.875173    -0.040258    -0.231567
8      -0.123046     2.331047     0.470322
1       1.352146    -3.569945     0.119429
1       3.365295    -2.144977    -0.249081
1       3.124920     0.338593    -0.330107
1      -0.876805    -2.504622     0.399818
1      -1.427390     1.220164     0.115508
1      -1.815834     0.136302     1.437291
1      -4.563645    -0.649059    -0.822678
1      -3.975074     1.011068    -0.545303
1      -4.174198    -0.111776     0.819054
1      -2.253077    -0.667978    -1.350866
```

(Z)-3a (T1 geometry UBMK/6-311+G(d,p))

```
6       1.932347     0.949226    -0.017577
6       2.596235    -0.263138     0.112717
6       1.875883    -1.462715     0.146399
6       0.477213    -1.434963     0.060708
6      -0.181347    -0.223194    -0.060724
6       0.514087     1.022854    -0.118573
6      -0.132789     2.266844    -0.299061
7      -1.611209    -0.243314    -0.193427
8      -2.225481    -1.269664    -0.571733
8      -2.243678     0.516556     0.818086
1       2.496270     1.876426    -0.057382
1       3.679484    -0.278443     0.178923
1       2.391499    -2.412873     0.235269
1      -0.109254    -2.346715     0.074397
1      -1.209878     2.344452    -0.349686
1       0.461151     3.171102    -0.371086
1      -3.167308     0.244628     0.729399
```


(Z)-3b (T1 geometry UBMK/6-311+G(d,p))

```
6      -0.055882    -0.566116     0.008746
6      -0.290544    -1.965077     0.091128
6      -1.581237    -2.479069     0.101493
6      -2.687940    -1.627456     0.028062
6      -2.491971    -0.241870    -0.043721
6      -1.206949     0.274005    -0.046763
7      -1.047503     1.693393    -0.176055
8      -1.961080     2.425007    -0.625326
6       1.254708    -0.034961    -0.051929
8       2.287004    -0.917924    -0.056049
6       3.552241    -0.447802    -0.099686
8       3.856413     0.701558    -0.137065
8      -0.282284     2.233981     0.883252
1       4.243910    -1.299426    -0.096211
1       0.563746    -2.629978     0.136087
1      -1.726615    -3.553204     0.158191
1      -3.695564    -2.028529     0.025288
1      -3.327583     0.445432    -0.110679
1       1.505757     1.014911    -0.072534
1      -0.386122     3.186135     0.749772
```

(Z)-3c (T1 geometry UBMK/6-311+G(d,p))

```
6      -0.263563    1.901908    0.084708
6       0.935733    2.601625    0.117693
6       2.161321    1.927597    0.059771
6       2.173408    0.529603   -0.021822
6       0.979097   -0.172188   -0.048309
6      -0.287282    0.482892   -0.007075
6      -1.511330   -0.225912   -0.086683
7       1.039221   -1.599181   -0.190097
8       0.353688   -2.269838    0.855200
8       2.060822   -2.182046   -0.625331
8      -2.654945    0.465901   -0.102774
6      -3.840819   -0.302104   -0.133237
1      -1.209572    2.429562    0.116235
1       0.917907    3.685330    0.180490
1       3.096382    2.476536    0.074442
1       3.100778   -0.028969   -0.080035
1      -1.568612   -1.307417   -0.112140
1       0.692076   -3.171358    0.769498
1      -4.673431    0.401461   -0.156448
1      -3.916612   -0.930989    0.761699
1      -3.869362   -0.932554   -1.030110
```

(Z)-3d (T1 geometry UBMK/6-311+G(d,p))

```
6      -0.138595    1.935899    0.063087
6       1.098294    2.565774    0.123572
6       2.285949    1.826234    0.088791
6       2.213192    0.429425    0.002660
6       0.981741   -0.200632   -0.051317
6      -0.255546    0.517872   -0.036037
6      -1.502927   -0.147999   -0.145854
7       0.966109   -1.629425   -0.189261
8       1.944986   -2.265315   -0.649202
8       0.281247   -2.261516    0.882135
6      -3.944329   -0.242443   -0.038362
7      -2.705441    0.488939   -0.212675
1      -1.031088    2.552577    0.071390
1       1.137446    3.649012    0.187888
1       3.250225    2.320394    0.123240
1       3.106895   -0.183121   -0.037078
1      -1.542870   -1.226528   -0.216094
1       0.570204   -3.179176    0.787872
1      -4.113367   -0.541160    1.005659
1      -3.921657   -1.144027   -0.657635
1      -4.782448    0.374519   -0.370284
1      -2.734547    1.470774    0.015889
```

4a (radical geometry UB3LYP/6-31G(d))

```
6        1.894445     0.922647     0.000128
6        2.552661    -0.290087     0.000148
6        1.818525    -1.487402     0.000083
6        0.427623    -1.439093    -0.000003
6       -0.244998    -0.218582    -0.000018
6        0.464759     1.033801     0.000046
6       -0.084362     2.324844     0.000025
7       -1.709613    -0.299037    -0.000104
8       -2.366437     0.745893    -0.000005
8       -2.223545    -1.421477    -0.000269
1        2.464867     1.847195     0.000176
1        3.638649    -0.315956     0.000214
1        2.325013    -2.447351     0.000099
1       -0.162901    -2.346105    -0.000057
1       -1.145166     2.511340    -0.000035
1        0.594773     3.172040     0.000068
```


4b (radical geometry UB3LYP/6-31G(d))

```
6        0.030993    -0.480135    -0.000015
6        0.206688    -1.901184     0.000013
6        1.455439    -2.488654     0.000064
6        2.614990    -1.696016     0.000089
6        2.494703    -0.311376     0.000063
6        1.240190     0.297576     0.000010
7        1.239653     1.759583    -0.000013
8        0.155015     2.353183     0.000078
6       -1.273378     0.046708    -0.000065
8       -2.308406    -0.851517    -0.000084
6       -3.589560    -0.362515    -0.000132
8       -3.896764     0.796571    -0.000161
8        2.329195     2.339291     0.000151
1       -4.277302    -1.217038    -0.000141
1       -0.682310    -2.519760    -0.000005
1        1.537108    -3.571907     0.000084
1        3.599085    -2.153500     0.000129
1        3.367770     0.328279     0.000081
1       -1.534634     1.090205    -0.000090
```

4c (radical geometry UB3LYP/6-31G(d))

```
6       -0.324064    1.819868   -0.000029
6        0.826603    2.577421   -0.000058
6        2.090497    1.956620   -0.000063
6        2.168553    0.572380   -0.000039
6        1.011279   -0.213319   -0.000010
6       -0.296044    0.387276   -0.000003
6       -1.520694   -0.307013    0.000025
7        1.216509   -1.650608    0.000013
8        2.377314   -2.078954    0.000007
8        0.224118   -2.397019    0.000039
8       -2.663454    0.404410    0.000028
6       -3.867623   -0.365119    0.000060
1       -1.294160    2.302212   -0.000024
1        0.754332    3.661618   -0.000076
1        2.998807    2.550764   -0.000086
1        3.123461    0.062844   -0.000043
1       -1.592542   -1.383700    0.000045
1       -4.689392    0.352083    0.000058
1       -3.925457   -0.993860    0.896049
1       -3.925482   -0.993895   -0.895903
```

4d (radical geometry UB3LYP/6-31G(d))

```
6       -0.201451    1.860474   -0.048348
6        0.985248    2.555273   -0.007480
6        2.213464    1.864478    0.037430
6        2.209095    0.481288    0.030871
6        1.010053   -0.245043   -0.012841
6       -0.267965    0.427135   -0.047181
6       -1.521679   -0.223751   -0.076246
7        1.150589   -1.683640   -0.004197
8        0.129959   -2.394726   -0.076556
8        2.291300   -2.166460    0.077958
6       -3.974698   -0.314245    0.091652
7       -2.720998    0.411321   -0.026402
1       -1.122746    2.430993   -0.121410
1        0.971479    3.641806   -0.020290
1        3.153007    2.406744    0.069316
1        3.132046   -0.083062    0.060815
1       -1.564300   -1.296708   -0.173502
1       -4.222570   -0.557780    1.134737
1       -3.904662   -1.246699   -0.474179
1       -4.787001    0.283993   -0.331484
1       -2.744858    1.382777    0.251840
```

¹1a CI (S1 conical intersection geometry CAS(10,9)/6-31G(d))

C	1.7703773842	1.1048271175	−0.1059420319
C	2.5913054920	−0.0247940972	−0.1199313487
C	2.0439551616	−1.3064274352	−0.0069060244
C	0.6613796351	−1.4589761807	0.0759261079
C	−0.1453619147	−0.3235726198	0.0512797280
C	0.3763025070	0.9968992554	0.0113576852
C	−0.5272784307	2.1518693948	0.1058871249
N	−1.5498907269	−0.4684165653	0.0575111217
O	−2.1300106350	−1.2979117352	0.7288311330
O	−2.2409967888	0.4053101748	−0.6242512405
H	−1.0198170304	2.2833808849	1.0603033901
H	3.6559663059	0.0967956608	−0.2020403316
H	2.6793477063	−2.1721588949	−0.0036521628
H	0.2069970673	−2.4297090500	0.1253807225
H	2.2108548834	2.0840350977	−0.1472076910
H	−1.7381437594	1.3426608255	−0.4959934254
H	−0.1804863558	3.0715804708	−0.3343027428

¹1b CI (S1 conical intersection geometry CAS(12,11)/6-31G(d))

C	2.0570909141	−1.2596412983	−0.2070692132
C	0.6775451865	−1.4401275268	−0.0758651908
C	−0.1576259330	−0.3288781810	0.0279972172
C	0.4068522385	0.9437722815	0.0024177608
C	1.8069967564	1.1576851871	−0.0588249088
C	2.6145073251	0.0210271435	−0.1921989919
N	−0.4341875478	2.0791265160	0.0383770466
O	−0.0472915024	3.1323857321	−0.6282190683
C	2.3283648985	2.5307936510	0.0451983501
O	3.5890215089	2.6590751970	−0.5223274259
C	4.2601469580	3.7922143170	−0.3263226734
O	3.8859234887	4.7135385478	0.3282373988
O	−1.4399884865	2.1350965995	0.7163418861
H	2.2553919459	2.9891341382	1.0205645184
H	2.7013349948	−2.1140590345	−0.3049721965
H	0.2552272029	−2.4273955315	−0.0743049505
H	−1.2231156992	−0.4332386458	0.0955645968
H	3.6778529649	0.1468574482	−0.2538795658
H	1.0231934457	3.1779293354	−0.5214131840
H	5.2071353399	3.7588051235	−0.8469054055

¹1c CI (S1 conical intersection geometry CAS(10,9)/6-31G(d))

```
C         0.6458419917      -1.4737494261       0.0560082669
C        -0.1246321294      -0.3095314239       0.0785488234
C         0.4535130772       0.9826505682       0.0403673912
C         1.8426864724       1.0566259077      -0.1311044729
C         2.6180514310      -0.1009943870      -0.1958322313
C         2.0263820099      -1.3649574352      -0.0807384036
C        -0.6420801262       4.4578888333      -0.1406554456
C        -0.4097925243       2.1670621867       0.2092256095
N        -1.5287201519      -0.4064331325       0.1382630418
O        -2.2278955645       0.5308160243      -0.4442374608
O         0.1309488357       3.3063448321      -0.3121068535
O        -2.1044265986      -1.2945032392       0.7352050125
H        -0.7893955637       2.2905724134       1.2227217289
H         3.6824554866      -0.0188899410      -0.3193765057
H         2.6301071908      -2.2524306811      -0.1184692661
H         0.1617108059      -2.4292903036       0.1096102734
H         2.3024930503       2.0241681542      -0.1821437242
H        -1.6437291532       1.4602138750      -0.3236175237
H        -0.0968503587       5.2777833118      -0.5848017023
H        -1.6049949427       4.3568343269      -0.6316528400
H        -0.8044822386       4.6669755359       0.9137172821
```


¹1d CI (S1 conical intersection geometry CAS(10,9)/6-31G(d))

```
C         0.6466732403      -1.4959205369       0.0413231130
C        -0.1187967489      -0.3198265115       0.0549474931
C         0.4816467212       0.9612228666       0.0525228652
C         1.8797100945       1.0165193852      -0.0636377977
C         2.6444704210      -0.1456828525      -0.1189263524
C         2.0279843825      -1.4035972881      -0.0487037727
C        -0.3631015419       2.1742980873       0.2141843035
C        -0.6451893975       4.5496637482      -0.1826432911
N        -1.5162701175      -0.4216016253       0.0808051013
N         0.1127871339       3.3394123075      -0.4208895768
O        -2.2282681023       0.5746042118      -0.3827039078
O        -2.0934708339      -1.3985913899       0.5200534994
H        -0.6374354615       2.3627562606       1.2465078996
H         3.7141526110      -0.0764222833      -0.1967458340
H         2.6202038074      -2.2993091326      -0.0804671488
H         0.1514600672      -2.4461612084       0.0678714228
H         2.3521431100       1.9801488862      -0.0733686335
H        -1.5979785969       1.4962883415      -0.2091523411
H        -0.1779104797       5.3730248839      -0.7083423073
H        -1.6847201322       4.4774202260      -0.5017009829
H        -0.6323320719       4.7798519313       0.8764824900
H         0.2674548949       3.1892876928      -1.3976362422
```