Table of Content

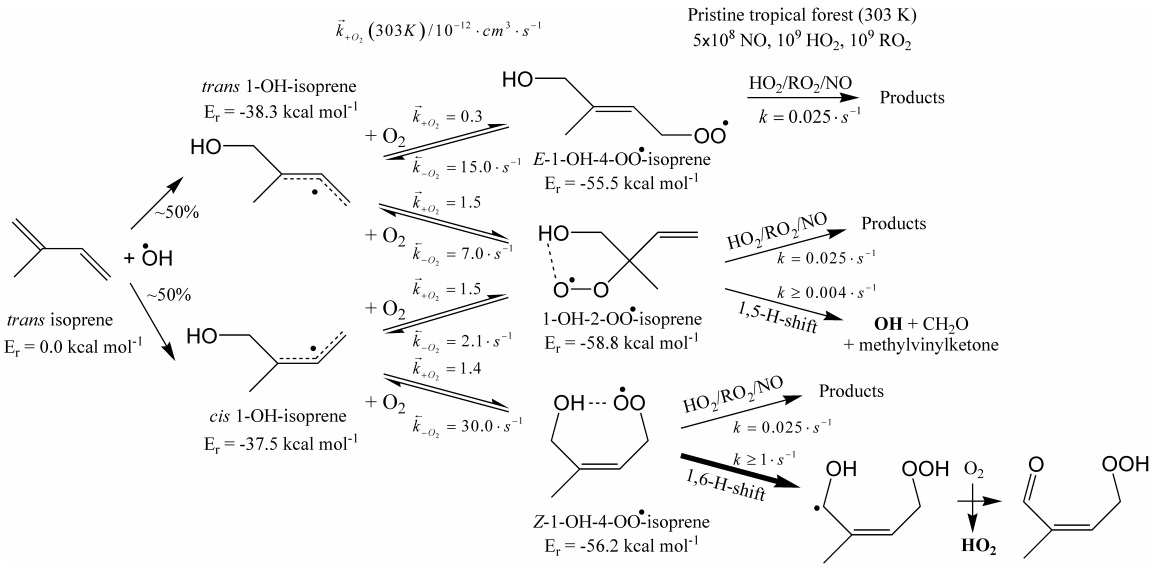

Fig. S1 Reaction scheme for OH and HO_2 radical formation following 1-OH addition to isoprene (60%), in pristine forest BL conditions, at 303 K. Note: to obtain the pseudo-first-order k'_{+O2}, in these conditions, multiply the k_{+O2} values listed by 5×10^{18} cm^{-3}.

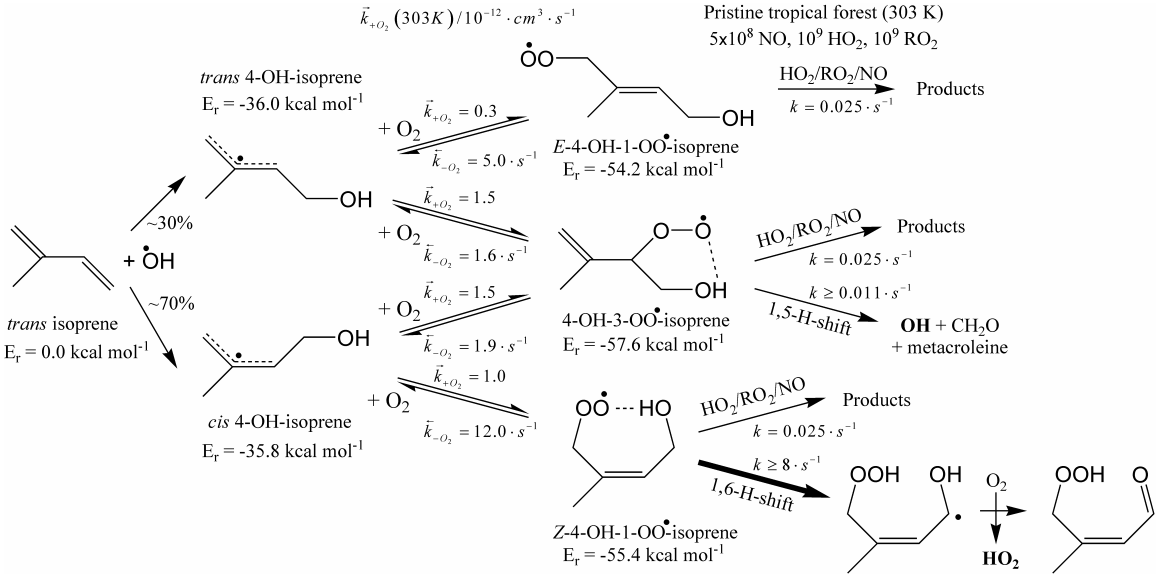

Fig. S2 Reaction scheme for OH and HO_2 radical formation following 4-OH addition to isoprene (30%), in pristine forest BL conditions, at 303 K. Note: to obtain the pseudo-first-order k'_{+O2}, in these conditions, multiply the k_{+O2} values listed by 5×10^{18} cm^{-3}.

Rate coefficient expressions for 1,6-H-migration and 1,6-D-migration

Over the temperature range 200-400K, the Arrhenius plots for the 1,6-H-migration in Z-1-OH-4-OO-isoprene and Z-4-OH-1-OO-isoprene shows significant curvature, which is not captured by the Arrhenius expressions given in the main paper. The modified Arrhenius expressions below reproduce the MC-TST predictions within 2 %:

1,6-H-migration in Z-1-OH-4-OO-isoprene:

$$k(T) = 5.93\times10^{-13} T^{7.36} \exp\left(\frac{-8.376\ \text{kcal mol}^{-1}}{RT}\right) s^{-1}$$

1,6-H-migration in Z-4-OH-1-OO-isoprene:

$$k(T) = 5.72\times10^{-21} T^{10.0} \exp\left(\frac{-5.076\ \text{kcal mol}^{-1}}{RT}\right) s^{-1}$$

For D-migration in perdeuterated Z-δ-hydroxy-peroxy isoprene radicals, we predicted the rate coefficients using the same theoretical kinetic methodology as described in the main text. The results are summarized in the Arrhenius expressions below. The predicted rate coefficients are slower than the non-deuterated case by a factor of ~30 at room temperature, owing to the primary kinetic isotope effect (i.e. a higher reaction barrier for the deuterated radical due to a lower ZPE for the C-D stretch) and to the substantial reduction in tunneling of the heavier deuterium atom compared to the hydrogen atom. The difference in reaction rate is governed by the migration of a deuterium atom rather than a hydrogen atom; deuteration in other positions in the hydroxy-peroxy radicals does not affect the rate coefficient significantly.

1,6-D-migration in perdeuterated Z-1-OD-4-OO-isoprene for T-range 250 - 350 K:

$$k(T) = 5.2\times10^{9} \exp\left(\frac{-15.57\ \text{kcal mol}^{-1}}{RT}\right) s^{-1}$$

1,6-D-migration in perdeuterated Z-4-OD-1-OO-isoprene:

$$k(T) = 6.50\times10^{9} \exp\left(\frac{-14.34\ \text{kcal mol}^{-1}}{RT}\right) s^{-1}$$

Conformers of Z-1-OH-4-OO$^{\bullet}$-isoprene: $HOCH_2C(CH_3)=CHCH_2OO^{\bullet}$

$HOCH_2$-(CH_3)C=CH-CH_2OO
(1)

```
----------
E(B3LYP/6-31+G(d,p)) (Hartree): -421.49197304
Electronic state : 2-A
Cartesian coordinates (Angs):
     C      -1.182733      0.817580       0.802748
     H      -2.197802      0.951988       1.188368
     H      -0.497017      0.898687       1.655710
     C      -1.066023     -0.529739       0.111573
     O      -0.974645      1.886899      -0.118966
     H      -0.061772      1.809966      -0.441786
     C      -2.298423     -0.977741      -0.628501
     H      -3.128728     -1.147547       0.069179
     H      -2.622206     -0.192962      -1.322286
     H      -2.129394     -1.897793      -1.194499
     C       0.070826     -1.251461       0.082631
     C       1.366792     -0.868426       0.713402
     H       1.279134     -0.140906       1.521223
     H       1.938439     -1.734948       1.053997
     H       0.087324     -2.177389      -0.489988
     O       2.304550     -0.261786      -0.278811
     O       1.918769      0.936090      -0.668602
Rotational constants (GHz):    2.8229500    1.4631700    1.1292000
Vibrational harmonic frequencies (cm-1):
      71.0628                88.7597               117.7750
     151.3890               195.3612               233.2759
     304.2908               375.5797               386.2984
     494.4540               545.5108               546.5944
     631.2260               762.7325               813.1760
     888.2704               954.2428               979.6459
    1041.5238              1060.7143              1064.5346
    1112.7912              1167.0631              1192.3417
    1248.0896              1280.1873              1345.3628
    1366.5595              1392.6233              1415.0301
    1427.6374              1480.2932              1483.8280
    1494.4073              1523.5375              1714.5260
    3029.6935              3033.3554              3086.9641
    3093.6513              3097.2069              3125.4807
    3150.1188              3165.7500              3743.4101
Zero-point correction (Hartree): 0.138686
```

$HOCH_2$-(CH_3)C=CH-CH_2OO
(2)

```
-------------
E(B3LYP/6-31+G(d,p)) (Hartree): -421.48955476
Electronic state : 2-A
Cartesian coordinates (Angs):
     C      -1.065861      0.940050       0.724013
     H      -1.980218      1.222164       1.254444
     H      -0.237798      0.983649       1.442607
     C      -1.214890     -0.449549       0.131387
     O      -0.900652      1.929616      -0.295837
```

H	-0.057551	1.757935	-0.740920
C	-2.580484	-0.786847	-0.402821
H	-3.321150	-0.791933	0.407328
H	-2.902351	-0.024078	-1.121627
H	-2.601047	-1.762547	-0.895682
C	-0.174325	-1.296056	0.015884
C	1.224870	-0.993104	0.451908
H	1.307725	-0.605194	1.470565
H	1.896086	-1.845307	0.334700
H	-0.325163	-2.251024	-0.482838
O	1.757775	0.083291	-0.429119
O	3.028578	0.340764	-0.173894

Rotational constants (GHz): 3.2228800 1.2675400 0.9981800

Vibrational harmonic frequencies (cm-1):

42.9755	65.2890	91.5388
120.1206	195.2972	231.3832
282.0703	364.5626	383.8969
410.7628	452.8485	576.4618
629.1496	788.7672	817.6892
919.8823	951.9022	961.5995
1030.5870	1050.0512	1064.7503
1111.6682	1173.1784	1186.1979
1215.4109	1264.1242	1348.7811
1367.6839	1387.4906	1414.1582
1418.9071	1481.5651	1491.1382
1496.5481	1519.7446	1712.8539
3030.0697	3036.2255	3083.1200
3086.8607	3099.7562	3125.5205
3146.0314	3171.4411	3792.1777

Zero-point correction (Hartree): 0.138039

$HOCH_2$-(CH_3)C=CH-CH_2OO
(3)

E(B3LYP/6-31+G(d,p)) (Hartree): -421.48870430
Electronic state : 2-A
Cartesian coordinates (Angs):

C	-1.337177	-0.923961	-0.476945
H	-1.656602	-0.922380	-1.524697
H	-0.464188	-1.581485	-0.406053
C	-1.020373	0.494980	-0.051407
O	-2.446798	-1.473467	0.244060
H	-2.196809	-1.564799	1.173372
C	-2.144258	1.481285	-0.243160
H	-2.388008	1.576871	-1.309274
H	-3.054591	1.133311	0.255822
H	-1.885646	2.471453	0.140660
C	0.166673	0.878482	0.456976
C	1.360724	0.013291	0.695159
H	1.935336	0.332646	1.567753
H	1.137834	-1.051829	0.780751
H	0.301974	1.929945	0.704870
O	2.273999	0.153869	-0.466255
O	3.437446	-0.428926	-0.236172

Rotational constants (GHz): 3.7779400 0.9414600 0.8178100

Vibrational harmonic frequencies (cm-1):

31.6699	58.6897	76.6486
112.4784	175.5894	256.3122
297.9020	317.3949	364.3090
391.0144	453.6404	573.1143
587.9521	793.5813	838.6466
916.8604	942.9964	972.6192

1027.7044	1056.3225	1066.6942
1113.8042	1179.4830	1187.7997
1208.2538	1263.0287	1350.0869
1361.6919	1389.3824	1411.0684
1421.0223	1478.1186	1490.2034
1498.7276	1517.7225	1717.6259
3034.4194	3054.4551	3086.3601
3095.5083	3097.4081	3131.5446
3142.1440	3163.9460	3817.5871

Zero-point correction (Hartree): 0.137883

$HOCH_2$-(CH_3)C=CH-CH_2OO
(4)

E(B3LYP/6-31+G(d,p)) (Hartree): -421.48880821
Electronic state : 2-A
Cartesian coordinates (Angs):

C	-1.370681	1.209047	0.031799
H	-1.861564	1.544878	-0.896668
H	-2.015706	1.544898	0.854158
C	-1.350727	-0.307716	0.026654
O	-0.135940	1.877794	0.220364
H	0.452338	1.680082	-0.522690
C	-2.685587	-0.906088	-0.350231
H	-3.482466	-0.531255	0.304970
H	-2.964842	-0.631164	-1.375342
H	-2.673129	-1.996328	-0.280335
C	-0.301005	-1.101378	0.309215
C	1.083831	-0.684144	0.697363
H	1.115024	0.148996	1.399080
H	1.673769	-1.521846	1.072135
H	-0.453453	-2.175356	0.223685
O	1.789664	-0.207650	-0.526469
O	3.090656	-0.085297	-0.327368

Rotational constants (GHz): 3.4218100 1.2253100 0.9804200
Vibrational harmonic frequencies (cm-1):

58.9354	67.9523	116.7354
123.2661	167.2004	251.2385
313.7761	342.2088	385.5391
422.9748	477.7646	490.9702
626.0091	799.6840	802.1403
913.4610	950.3161	960.8615
1034.2638	1070.2566	1090.1045
1115.6391	1173.0674	1193.7049
1222.8206	1247.4943	1364.0413
1383.7635	1394.1753	1418.3435
1424.7883	1483.3774	1485.0609
1491.5369	1496.3932	1717.9109
2981.5150	3028.0368	3055.8330
3077.2833	3104.1730	3130.2288
3157.5698	3175.2026	3796.4603

Zero-point correction (Hartree): 0.138021

$HOCH_2$-(CH_3)C=CH-CH_2OO
(5)

E(B3LYP/6-31+G(d,p)) (Hartree): -421.48874885
Electronic state : 2-A
Cartesian coordinates (Angs):

C	1.709931	-0.773927	0.520549
H	2.515232	-0.584004	1.238400

H	1.046796	-1.523921	0.965561
C	0.986327	0.521059	0.211659
O	2.367879	-1.308547	-0.633917
H	1.697223	-1.529726	-1.294622
C	1.879427	1.648891	-0.243293
H	2.567789	1.941096	0.560634
H	2.499710	1.331470	-1.088010
H	1.303216	2.529349	-0.538876
C	-0.345013	0.689128	0.317358
C	-1.363408	-0.313659	0.756083
H	-0.950210	-1.285998	1.026521
H	-1.996354	0.061955	1.564529
H	-0.768223	1.658506	0.057568
O	-2.280347	-0.629168	-0.360434
O	-3.227378	0.284254	-0.488880

Rotational constants (GHz): 3.5931600 0.9781100 0.8580900

Vibrational harmonic frequencies (cm-1):

26.6107	64.5928	85.6764
135.1993	181.6301	255.9324
256.3931	328.4872	364.8492
423.6920	504.0178	526.3042
615.0737	781.1880	836.7206
893.0570	946.2218	979.5922
1031.6301	1063.0305	1065.7685
1109.4141	1158.1301	1191.7266
1241.4702	1280.8162	1337.2974
1362.3635	1386.4089	1408.1385
1420.9996	1475.3271	1480.8029
1497.0180	1512.9519	1722.5562
3032.2809	3048.3132	3085.3649
3091.7806	3094.2346	3131.1611
3152.4829	3166.9055	3813.5483

Zero-point correction (Hartree): 0.137982

$HOCH_2$-(CH_3)C=CH-CH_2OO
(6)

E(B3LYP/6-31+G(d,p)) (Hartree): -421.48830261

Electronic state : 2-A

Cartesian coordinates (Angs):

C	1.201998	-0.967758	-0.304793
H	0.343054	-1.562148	0.026079
H	1.301062	-1.107103	-1.393385
C	0.997925	0.504154	-0.040074
O	2.397709	-1.392181	0.359844
H	2.601862	-2.296060	0.088971
C	2.184685	1.381673	-0.340126
H	3.036538	1.096479	0.285218
H	2.504250	1.258053	-1.382930
H	1.955563	2.436730	-0.170099
C	-0.167740	1.020384	0.391459
C	-1.401010	0.251258	0.735897
H	-1.207497	-0.740125	1.151355
H	-2.057351	0.802836	1.412012
H	-0.245599	2.101731	0.482757
O	-2.185353	0.030933	-0.507291
O	-3.353235	-0.529834	-0.246822

Rotational constants (GHz): 3.7491000 0.9763900 0.8401500

Vibrational harmonic frequencies (cm-1):

30.5614	61.3482	82.3299
113.7161	179.2536	249.5451
270.0738	296.5940	356.3681
392.8544	446.7925	573.4402

588.9502 780.5626 824.7277
919.5635 958.4622 975.4952
1033.1864 1062.4029 1072.6152
1126.7384 1178.9404 1188.4452
1222.3673 1242.6220 1293.0507
1355.2608 1386.4717 1418.3411
1448.7683 1477.3402 1493.8885
1496.9169 1520.2683 1721.4990
2989.8147 3035.6510 3064.6297
3088.2568 3098.7895 3132.8423
3143.5194 3169.9169 3837.3814
Zero-point correction (Hartree): 0.137603

$HOCH_2$-(CH_3)C=CH-CH_2OO
(7)

E(B3LYP/6-31+G(d,p)) (Hartree): -421.48836711
Electronic state : 2-A
Cartesian coordinates (Angs):

C	1.103225	-0.953908	-0.118450
H	0.323964	-1.542947	0.374237
H	1.114619	-1.250701	-1.179111
C	0.816127	0.526271	-0.054281
O	2.383118	-1.197466	0.480612
H	2.630664	-2.116751	0.320975
C	1.915673	1.412352	-0.580818
H	2.828426	1.278849	0.008220
H	2.166635	1.142324	-1.614735
H	1.627164	2.466382	-0.557304
C	-0.341203	1.046551	0.394731
C	-1.504341	0.293248	0.948775
H	-1.250333	-0.684086	1.361067
H	-2.047897	0.878422	1.694660
H	-0.472906	2.125449	0.336690
O	-2.554228	0.047552	-0.076706
O	-2.186042	-0.880589	-0.939461

Rotational constants (GHz): 3.2588500 1.1473300 0.9955600
Vibrational harmonic frequencies (cm-1):
38.5562 66.0409 74.5528
142.5428 188.1873 248.9380
267.3713 282.6842 360.2254
420.8599 502.1884 565.5846
574.2789 784.0825 799.8647
882.0183 960.9231 985.4469
1033.2263 1063.3217 1073.4441
1118.6749 1160.8629 1197.9982
1232.7293 1265.0860 1291.0220
1349.9272 1384.9351 1418.0690
1444.2915 1476.7849 1485.3617
1495.6845 1514.0800 1720.3570
2996.3421 3034.9548 3083.6769
3093.1321 3098.5868 3131.7998
3149.9586 3167.2206 3838.7885
Zero-point correction (Hartree): 0.137749

$HOCH_2$-(CH_3)C=CH-CH_2OO
(8)

E(B3LYP/6-31+G(d,p)) (Hartree): -421.48858878
Electronic state : 2-A
Cartesian coordinates (Angs):

C	-1.177744	-0.943396	-0.298555
H	-1.367320	-1.092847	-1.366816

H	-0.359569	-1.614816	-0.022380
C	-0.833435	0.511201	-0.054512
O	-2.397707	-1.328069	0.350213
H	-2.263164	-1.290377	1.306631
C	-1.882644	1.494854	-0.508464
H	-2.012955	1.433132	-1.596853
H	-2.854677	1.259081	-0.063357
H	-1.614259	2.522985	-0.252078
C	0.313337	0.932681	0.512596
C	1.446988	0.083942	0.986113
H	1.920509	0.500381	1.879137
H	1.188411	-0.961240	1.159041
H	0.469815	2.005300	0.617586
O	2.570798	0.076054	0.014002
O	2.288684	-0.652646	-1.049712

Rotational constants (GHz): 3.2206600 1.1169500 0.9916800

Vibrational harmonic frequencies (cm-1):

40.1968	71.3373	79.3801
137.1080	180.9080	258.5719
279.5690	310.6780	368.4635
420.8458	503.6081	562.7102
579.2083	797.5521	810.0236
884.3672	941.3135	981.4672
1026.6011	1058.0003	1068.3751
1105.0134	1158.9740	1189.4150
1236.5343	1280.0434	1347.8554
1361.4602	1385.9030	1409.3824
1420.1981	1476.7932	1483.8764
1496.8528	1513.0578	1715.4256
3033.8929	3062.9600	3089.3393
3095.5709	3105.2211	3130.3094
3147.9336	3163.5005	3818.0614

Zero-point correction (Hartree): 0.138029

$HOCH_2$-(CH_3)C=CH-CH_2OO
(9)

E(B3LYP/6-31+G(d,p)) (Hartree): -421.48829823

Electronic state : 2-A

Cartesian coordinates (Angs):

C	1.626450	-0.760041	0.555502
H	2.042755	-0.564748	1.549466
H	0.946037	-1.613204	0.650220
C	0.921756	0.483409	0.053727
O	2.759323	-1.106382	-0.251777
H	2.449306	-1.323000	-1.141483
C	1.762312	1.736107	0.076977
H	2.039448	1.988489	1.108903
H	2.698205	1.585682	-0.471448
H	1.232933	2.589143	-0.355019
C	-0.347454	0.507650	-0.395190
C	-1.307829	-0.634564	-0.485630
H	-1.790990	-0.691335	-1.464518
H	-0.879451	-1.602253	-0.221929
H	-0.761510	1.459098	-0.725918
O	-2.403843	-0.466028	0.493032
O	-3.343998	0.344505	0.038672

Rotational constants (GHz): 4.0854200 0.9280300 0.8092200

Vibrational harmonic frequencies (cm-1):

34.7822	60.0267	71.5488
134.7880	181.1459	248.7142
271.0297	313.4444	351.5270
444.1727	505.1809	542.7003

```
     585.0185                797.9292                835.4118
     886.9688                944.8137                979.1658
    1028.3277               1060.0212               1069.6366
    1107.0379               1159.1425               1191.0858
    1241.5281               1283.6229               1340.1100
    1357.3566               1386.8658               1408.7407
    1420.6272               1476.9250               1480.5453
    1496.8937               1514.3092               1720.0962
    3032.8837               3050.1654               3085.8967
    3093.3261               3095.3428               3130.8903
    3151.5724               3166.3977               3816.4479
Zero-point correction (Hartree): 0.137953
```

$HOCH_2$-(CH_3)C=CH-CH_2OO
(10)

```
-------------
E(B3LYP/6-31+G(d,p)) (Hartree): -421.48761246
Electronic state : 2-A
Cartesian coordinates (Angs):
     C      -1.559332     -0.797750       0.489641
     H      -0.879730     -1.654123       0.423377
     H      -1.838306     -0.676268       1.548368
     C      -0.904847      0.481939       0.027588
     O      -2.730775     -1.022612      -0.306137
     H      -3.239287     -1.745705       0.082387
     C      -1.780439      1.706028       0.119740
     H      -2.670905      1.584185      -0.505634
     H      -2.133062      1.853470       1.148919
     H      -1.247673      2.606647      -0.195587
     C       0.361142      0.564048      -0.419801
     C       1.333951     -0.554449      -0.607657
     H       0.893349     -1.547683      -0.515081
     H       1.874367     -0.471823      -1.553638
     H       0.752303      1.546293      -0.678804
     O       2.369577     -0.537927       0.450581
     O       3.334460      0.323803       0.179135
Rotational constants (GHz):    4.1380700    0.9331200    0.8158000
Vibrational harmonic frequencies (cm-1):
      26.6814                 55.2197                 62.5187
     133.9364                184.8224                244.2107
     263.7621                278.3976                347.3020
     440.5274                510.5760                541.8676
     579.9106                787.4468                824.8564
     888.1941                963.8099                980.1949
    1033.7514               1062.7388               1074.8850
    1123.1280               1158.6380               1205.4462
    1233.3039               1274.3495               1290.5166
    1343.2291               1384.2378               1417.0555
    1445.1944               1477.8365               1481.4186
    1496.8055               1521.1156               1726.7219
    2991.5214               3032.7901               3068.4621
    3092.4485               3095.5867               3132.0655
    3155.2245               3170.9061               3834.3430
Zero-point correction (Hartree): 0.137688
```

$HOCH_2$-(CH_3)C=CH-CH_2OO
(11)

```
-------------
E(B3LYP/6-31+G(d,p)) (Hartree): -421.48728177
Electronic state : 2-A
Cartesian coordinates (Angs):
     C       1.537739     -0.889094       0.509818
     H       2.094548     -0.828710       1.459653
```

```
     H       0.704496     -1.585625       0.654211
     C       1.053454      0.496599       0.151259
     O       2.400038     -1.350875      -0.535466
     H       2.777291     -2.201134      -0.277283
     C       2.139478      1.463856      -0.246424
     H       2.894068      1.550407       0.546229
     H       2.661284      1.102784      -1.137954
     H       1.734046      2.458208      -0.449545
     C      -0.232618      0.884344       0.216506
     C      -1.417767      0.063693       0.602320
     H      -1.196910     -0.980586       0.828154
     H      -1.977180      0.501295       1.434958
     H      -0.465731      1.920367      -0.024947
     O      -2.348399      0.060889      -0.547895
     O      -3.515091     -0.466689      -0.220934
Rotational constants (GHz):    3.9051600    0.8995700    0.7911400
Vibrational harmonic frequencies (cm-1):
      37.5699                  65.3354                  78.8695
     119.8126                 183.0027                 236.7770
     255.2068                 282.0595                 366.0134
     375.0668                 435.0416                 559.8040
     595.6153                 776.1500                 849.2431
     907.2732                 964.3967                 984.3943
    1037.0602                1064.0960                1075.8246
    1124.9480                1182.8153                1188.2976
    1220.5651                1253.5410                1285.8107
    1347.3854                1392.3837                1417.1680
    1448.0099                1477.0565                1490.0226
    1497.1481                1514.3067                1733.8251
    2978.5971                3034.0332                3062.7894
    3074.9033                3099.2277                3133.9013
    3139.8852                3161.4924                3838.6676
Zero-point correction (Hartree): 0.137477
```

$HOCH_2$-(CH_3)C=CH-CH_2OO
(12)

```
-------------
E(B3LYP/6-31+G(d,p)) (Hartree): -421.48712791
Electronic state : 2-A
Cartesian coordinates (Angs):
     C       1.721486     -0.794900       0.442266
     H       2.304001     -0.673694       1.370390
     H       1.060171     -1.658651       0.576030
     C       0.942865      0.476090       0.198531
     O       2.603414     -1.007254      -0.665766
     H       3.186699     -1.749776      -0.464567
     C       1.786931      1.685863      -0.116475
     H       2.511712      1.876592       0.685899
     H       2.365322      1.517508      -1.030263
     H       1.171383      2.579556      -0.246144
     C      -0.394891      0.568138       0.292111
     C      -1.374545     -0.521098       0.590057
     H      -0.943435     -1.523201       0.589728
     H      -1.925059     -0.349900       1.519961
     H      -0.859193      1.542401       0.147215
     O      -2.395986     -0.585952      -0.473488
     O      -3.327763      0.337532      -0.309143
Rotational constants (GHz):    4.0162200    0.9218700    0.8148400
Vibrational harmonic frequencies (cm-1):
      36.1154                  63.7960                  71.1153
     148.1427                 194.6224                 231.8883
     247.8468                 275.0557                 353.4266
     414.9202                 501.3716                 522.8269
```

```
     608.7582                773.8262                849.6360
     880.9143                961.5039                993.3888
    1039.3136               1065.8128               1074.4873
    1117.9784               1161.1159               1199.9271
    1234.0786               1279.5497               1284.9790
    1338.9832               1386.0330               1418.8519
    1445.0894               1473.2854               1480.3204
    1497.0839               1515.0096               1732.7159
    2980.8899               3032.9353               3057.1084
    3076.8581               3097.7532               3133.4198
    3147.7103               3166.0968               3837.0885
Zero-point correction (Hartree): 0.137610
```

$HOCH_2$-(CH_3)C=CH-CH_2OO
(13)

```
----------
E(B3LYP/6-31+G(d,p)) (Hartree): -421.48706600
Electronic state : 2-A
Cartesian coordinates (Angs):
     C       1.238212     -0.971337      -0.314174
     H       0.402041     -1.589530       0.014748
     H       1.331944     -1.111700      -1.402096
     C       0.995146      0.497472      -0.033367
     O       2.390848     -1.490148       0.357620
     H       3.186120     -1.262249      -0.139255
     C       2.160355      1.411822      -0.314322
     H       2.997737      1.192302       0.358526
     H       2.524495      1.279464      -1.342262
     H       1.889702      2.462384      -0.182774
     C      -0.180730      0.985414       0.403071
     C      -1.401901      0.189603       0.730493
     H      -1.195596     -0.823186       1.082671
     H      -2.044852      0.697471       1.452266
     H      -0.280888      2.063582       0.513288
     O      -2.211513      0.041966      -0.506273
     O      -3.388983     -0.500116      -0.249511
Rotational constants (GHz):    3.7429200    0.9618300    0.8285000
Vibrational harmonic frequencies (cm-1):
      26.5049                 59.4075                 77.9303
     115.2368                180.8561                221.9726
     268.7307                295.6006                353.8372
     392.8179                440.8554                573.9647
     584.0389                784.0995                827.7794
     918.5374                938.9280                966.7828
    1031.9959               1052.0233               1067.2439
    1106.6440               1178.1747               1187.6291
    1210.4822               1262.9886               1353.2999
    1365.4335               1384.4852               1413.9842
    1419.8361               1481.3390               1489.8356
    1499.6150               1510.5677               1718.6835
    3004.2098               3025.5218               3081.6166
    3088.9752               3127.9665               3133.5151
    3145.0772               3165.4706               3841.5991
Zero-point correction (Hartree): 0.137547
```

$HOCH_2$-(CH_3)C=CH-CH_2OO
(14)

```
----------
E(B3LYP/6-31+G(d,p)) (Hartree): -421.48715665
Electronic state : 2-A
Cartesian coordinates (Angs):
     C       1.125506     -0.962826      -0.123402
```

H	0.366818	-1.566091	0.373823
H	1.127627	-1.266679	-1.180958
C	0.812885	0.517673	-0.044916
O	2.368892	-1.305848	0.500252
H	3.097271	-1.110273	-0.101727
C	1.895820	1.431969	-0.561614
H	2.795073	1.362579	0.061784
H	2.185810	1.155619	-1.584583
H	1.572455	2.475867	-0.571202
C	-0.347518	1.020048	0.415589
C	-1.502528	0.245213	0.957689
H	-1.244990	-0.749457	1.322959
H	-2.031785	0.798617	1.737471
H	-0.492694	2.098494	0.376966
O	-2.567568	0.049869	-0.061497
O	-2.211396	-0.832914	-0.975580

Rotational constants (GHz): 3.2353400 1.1337900 0.9886000

Vibrational harmonic frequencies (cm-1):

38.6732	67.3282	74.1898
147.3133	179.8677	220.2447
264.0732	282.5106	356.2004
416.6256	499.4279	567.1280
568.8983	790.4178	802.5360
881.6145	938.6525	976.3295
1033.7692	1057.2410	1066.6857
1097.7083	1160.1766	1187.5644
1239.1854	1277.0808	1348.9016
1359.8846	1382.3318	1411.3167
1417.8300	1477.3427	1486.6947
1499.3633	1502.8012	1717.8368
3011.4793	3024.7983	3081.2873
3092.1357	3126.9522	3145.9841
3152.8494	3165.5450	3842.0849

Zero-point correction (Hartree): 0.137690

$HOCH_2$-(CH_3)C=CH-CH_2OO
(15)

E(B3LYP/6-31+G(d,p)) (Hartree): -421.48666382

Electronic state : 2-A

Cartesian coordinates (Angs):

C	-1.603055	-0.791128	0.507008
H	-0.936710	-1.653444	0.490207
H	-1.929416	-0.654041	1.549499
C	-0.909926	0.473587	0.041837
O	-2.716717	-1.159386	-0.316014
H	-3.460569	-0.571619	-0.134147
C	-1.757338	1.722232	0.092509
H	-2.596872	1.658566	-0.611317
H	-2.183050	1.866518	1.094463
H	-1.179753	2.613671	-0.164348
C	0.364669	0.528035	-0.383563
C	1.324693	-0.607603	-0.532695
H	0.891023	-1.589183	-0.340576
H	1.816486	-0.601399	-1.508775
H	0.778328	1.496401	-0.661212
O	2.410056	-0.506796	0.466973
O	3.342446	0.351656	0.090996

Rotational constants (GHz): 4.0942900 0.9276000 0.8060500

Vibrational harmonic frequencies (cm-1):

26.5513	50.2943	66.1000
134.4265	180.6390	221.9228
262.0610	274.5350	343.2961

433.4553	505.5875	544.8933
578.4499	794.0387	833.1665
884.7114	943.8872	975.8588
1033.9150	1053.0200	1068.9346
1098.9358	1158.3840	1187.8095
1245.9348	1281.9622	1341.2134
1362.2398	1383.0935	1411.8392
1418.9709	1478.7711	1484.7204
1498.4238	1507.0330	1725.2354
3001.8798	3024.3770	3075.1194
3089.3213	3126.6836	3139.7325
3155.6489	3169.9101	3838.2491

Zero-point correction (Hartree): 0.137636

$HOCH_2$-(CH_3)C=CH-CH_2OO
(16)

E(B3LYP/6-31+G(d,p)) (Hartree): -421.48644201
Electronic state : 2-A
Cartesian coordinates (Angs):

C	1.373068	-0.743627	0.687447
H	1.970584	-0.526173	1.589042
H	0.528642	-1.374555	0.983503
C	0.904814	0.565018	0.093818
O	2.182963	-1.415730	-0.282590
H	2.481487	-2.255302	0.088383
C	1.979436	1.374589	-0.586494
H	2.811989	1.571769	0.101216
H	2.396923	0.817865	-1.430977
H	1.591198	2.330653	-0.946718
C	-0.354818	1.026173	0.190081
C	-1.525835	0.360381	0.835334
H	-1.303273	-0.593829	1.312607
H	-2.025880	1.022601	1.549582
H	-0.575845	2.001782	-0.240503
O	-2.597449	0.097277	-0.151129
O	-2.352491	-0.992799	-0.857187

Rotational constants (GHz): 3.1723500 1.1074700 0.9517400
Vibrational harmonic frequencies (cm-1):

27.8162	63.1084	73.7964
149.5393	200.1326	212.9065
260.4149	283.6328	367.0525
402.9740	501.2428	516.8250
603.9648	766.0387	833.8873
884.3504	963.6300	991.9059
1038.7427	1068.8023	1076.6912
1115.9046	1155.9074	1193.3795
1241.0113	1276.4876	1286.9191
1341.8543	1388.1607	1418.5506
1448.5734	1478.4522	1482.1751
1497.0072	1509.3381	1729.7748
2971.3767	3035.2649	3070.1114
3077.5563	3100.0933	3134.2117
3150.5883	3165.0396	3840.2315

Zero-point correction (Hartree): 0.137591

$HOCH_2$-(CH_3)C=CH-CH_2OO
(17)

E(B3LYP/6-31+G(d,p)) (Hartree): -421.48619238
Electronic state : 2-A

Cartesian coordinates (Angs):

C	-1.547290	-0.904054	0.493151
H	-0.725250	-1.613012	0.598018
H	-2.074083	-0.870470	1.460315
C	-1.049528	0.487636	0.153118
O	-2.397208	-1.460207	-0.513266
H	-3.276371	-1.067211	-0.448158
C	-2.122713	1.477682	-0.228410
H	-2.608130	1.181919	-1.165889
H	-2.904390	1.531354	0.542020
H	-1.713792	2.481696	-0.365364
C	0.239677	0.863938	0.218130
C	1.417375	0.024705	0.588981
H	1.960832	0.423136	1.451432
H	1.192231	-1.028729	0.761997
H	0.485655	1.900664	-0.008607
O	2.366740	0.076871	-0.542984
O	3.535240	-0.446512	-0.215699

Rotational constants (GHz): 3.8920400 0.8924300 0.7826800

Vibrational harmonic frequencies (cm-1):

39.1740	64.8899	81.3610
121.2226	184.0379	231.6489
247.5805	283.6363	362.6664
372.8449	429.7447	555.9811
598.7526	776.1218	848.5862
904.9127	947.8817	980.3157
1034.1151	1051.1334	1067.9726
1110.5877	1180.6120	1188.8277
1214.3333	1258.4045	1346.1363
1363.9996	1392.4917	1412.6269
1420.0651	1481.0690	1488.1933
1498.4675	1502.7952	1730.6065
2990.8678	3022.5608	3072.8537
3080.4874	3127.9989	3130.1917
3143.5043	3158.0575	3839.1277

Zero-point correction (Hartree): 0.137463

$HOCH_2$-(CH_3)C=CH-CH_2OO
(18)

E(B3LYP/6-31+G(d,p)) (Hartree): -421.48622549

Electronic state : 2-A

Cartesian coordinates (Angs):

C	-1.722124	-0.808736	0.436387
H	-1.066369	-1.673884	0.542062
H	-2.285660	-0.712139	1.378319
C	-0.939563	0.467205	0.197727
O	-2.608523	-1.139338	-0.636701
H	-3.383936	-0.565379	-0.604388
C	-1.776814	1.686014	-0.107335
H	-2.300161	1.569820	-1.064123
H	-2.540628	1.846189	0.666118
H	-1.164835	2.589058	-0.170792
C	0.398360	0.558562	0.285951
C	1.375389	-0.536707	0.573507
H	1.913386	-0.384451	1.514007
H	0.945812	-1.538998	0.546365
H	0.867207	1.531628	0.145884
O	2.409087	-0.576890	-0.478266
O	3.324897	0.358744	-0.293893

Rotational constants (GHz): 3.9771700 0.9204900 0.8095600

Vibrational harmonic frequencies (cm-1):

34.8441	64.9674	72.9088

```
     149.0109                190.2508                219.3206
     242.7790                274.4618                351.3093
     408.1060                497.3222                523.2412
     611.1232                773.5985                851.8818
     875.9534                949.6720                982.0560
    1039.2282               1052.7076               1068.5541
    1099.9414               1160.8066               1187.8125
    1241.3281               1281.2406               1338.7752
    1360.7865               1387.4659               1411.2153
    1419.8821               1472.0785               1485.5783
    1497.8259               1501.6506               1729.2978
    2990.9358               3022.5396               3076.1711
    3077.5172               3128.0376               3130.9170
    3150.0539               3163.9797               3837.7760
Zero-point correction (Hartree): 0.137572
```

$HOCH_2$-(CH_3)C=CH-CH_2OO
(19)

```
-----------
E(B3LYP/6-31+G(d,p)) (Hartree): -421.48526572
Electronic state : 2-A
Cartesian coordinates (Angs):
     C      -1.441538     -0.770266       0.648058
     H      -0.636232     -1.454966       0.916152
     H      -2.022180     -0.571655       1.563680
     C      -0.904078      0.542505       0.110442
     O      -2.241879     -1.485359      -0.295940
     H      -3.112646     -1.073719      -0.358399
     C      -1.926704      1.433012      -0.552101
     H      -2.312241      0.966671      -1.466164
     H      -2.784557      1.613096       0.110840
     H      -1.500858      2.402076      -0.823397
     C       0.372521      0.943472       0.239001
     C       1.504579      0.199839       0.870293
     H       1.938866      0.752983       1.710076
     H       1.263639     -0.815889       1.184373
     H       0.646266      1.926637      -0.142449
     O       2.647115      0.099112      -0.059989
     O       2.456172     -0.843329      -0.967679
Rotational constants (GHz):    3.2253500    1.0585900    0.9295600
Vibrational harmonic frequencies (cm-1):
      30.7344                 58.6620                 74.8225
     155.1668                201.6490                240.8877
     250.6221                294.0326                357.1855
     397.8098                501.7079                508.6955
     609.5894                769.7173                841.4046
     881.0688                947.1999                986.3990
    1038.7781               1056.7768               1069.6045
    1101.3252               1154.1553               1189.5226
    1237.6368               1279.6855               1340.8468
    1364.0365               1388.6092               1413.2148
    1420.6630               1475.3836               1485.9681
    1494.2402               1503.3910               1728.1311
    2985.7392               3021.9775               3070.3551
    3081.9434               3128.4200               3133.7864
    3147.5543               3160.4283               3838.5520
Zero-point correction (Hartree): 0.137643
```

B3LYP/6-311G(d,p)-Optimization

Cartesian coordinates (Angs):

C	-1.166461	0.801008	0.818856
H	-2.173179	0.920173	1.226473
H	-0.464819	0.884215	1.656913
C	-1.050144	-0.540583	0.121047
O	-0.989436	1.863039	-0.111674
H	-0.085341	1.774222	-0.445459
C	-2.278095	-0.966517	-0.634088
H	-3.113482	-1.147928	0.051615
H	-2.586569	-0.159202	-1.305447
H	-2.110072	-1.869619	-1.223184
C	0.081985	-1.257453	0.078780
C	1.377635	-0.873624	0.703405
H	1.287082	-0.169268	1.528532
H	1.965028	-1.736941	1.016778
H	0.101493	-2.171045	-0.509632
O	2.294323	-0.226362	-0.282491
O	1.868905	0.950625	-0.671408

Rotational constants (GHz): 2.8446700 1.4841000 1.1472200

Vibrational harmonic frequencies (cm-1):

74.6059	95.3237	128.9140
156.7120	204.5797	234.9977
306.2059	375.8209	386.6512
496.4577	552.3463	572.2930
636.3668	759.5280	809.2990
887.5306	957.8626	980.7034
1042.5565	1060.7414	1063.1147
1113.6468	1163.4631	1194.8235
1250.2741	1278.3968	1347.8379
1372.8583	1393.3765	1408.3237
1446.7877	1476.9734	1480.8382
1492.2546	1522.1144	1713.0846
3012.7725	3018.5534	3070.8002
3075.5722	3083.8221	3109.3815
3131.9007	3148.0440	3740.9832

Zero-point correction (Hartree): 0.138580

QCISD/6-311G(d,p)-Optimization

C,0,-0.0723848559,0.6950659459,1.4754569281
H,0,-0.3993385504,0.7312803542,2.5201730534
H,0,1.0242168852,0.6626162397,1.4715697668
C,0,-0.6754460613,-0.5250580673,0.8023149622
O,0,-0.5557591916,1.8831090629,0.8678786083
H,0,-0.2427715644,1.842931307,-0.0402304765
C,0,-2.1098880261,-0.8013396932,1.1818955972
H,0,-2.1789267834,-1.0850325422,2.240421681
H,0,-2.6988777002,0.1133846391,1.0466157846
H,0,-2.5465606182,-1.6004807556,0.5748372321
C,0,-0.0447201413,-1.2535451184,-0.1353042686
C,0,1.342226278,-1.0028527936,-0.6463417722
H,0,1.9685164109,-0.4336910858,0.0419923985
H,0,1.8492565699,-1.9304891477,-0.9243435557
H,0,-0.5821074672,-2.0693593152,-0.6179696303
O,0,1.3164824199,-0.2586575431,-1.9103466059
O,0,0.884124332,0.9748991147,-1.7238430496

MPW1B95/6-31+(d,p)-Optimization

E(MPW1B95/6-31+G(d,p)) (Hartree): -421.29588712
E(MPW1B95/6-311++G(3df,3pd)) (Hartree): -421.41991028
Electronic state : 2-A
Cartesian coordinates (Angs):

C	-1.124940	0.754735	0.822807
H	-2.071456	0.786142	1.365912
H	-0.324301	0.917656	1.548870
C	-0.986937	-0.569390	0.118234
O	-1.180140	1.810455	-0.112172
H	-0.318152	1.845658	-0.541250
C	-2.219919	-1.026248	-0.591834
H	-3.018225	-1.237833	0.125099
H	-2.583705	-0.230474	-1.245471
H	-2.044082	-1.921024	-1.187782
C	0.158029	-1.260935	0.050938
C	1.449795	-0.852824	0.656988
H	1.348340	-0.200234	1.521775
H	2.074317	-1.705960	0.916586
H	0.179546	-2.174503	-0.535150
O	2.290740	-0.126167	-0.302232
O	1.777094	1.021781	-0.624519

Rotational constants (GHz): 2.8899200 1.5073100 1.1555800
Vibrational harmonic frequencies (cm-1):

92.2049	127.5254	138.7734
150.8477	190.8301	232.8615
315.7012	382.9592	388.2022
485.1060	523.4542	565.5550
643.2480	787.8560	862.0473
900.9733	958.5212	992.8386
1053.9430	1063.7430	1105.4611
1131.8733	1200.2756	1231.5201
1265.0243	1291.5035	1356.2889
1383.9069	1399.4725	1414.6524
1427.8920	1479.5648	1492.6322
1500.8021	1531.8794	1759.8733
3070.7338	3083.4213	3133.1851
3138.0163	3140.7362	3176.5874
3193.0057	3208.3572	3875.2704

Zero-point correction (Hartree): 0.140903

Transition state for 1,6-H-migration in Z-1-OH-4-OO•-isoprene

TS(1,6 H-shift)
(1)

```
------------
E(B3LYP/6-31+G(d,p)) (Hartree): -421.45985263
Electronic state : 2-A
Cartesian coordinates (Angs):
     C       0.709959     -0.821144      -0.322955
     H      -0.270279     -1.217281       0.418421
     H       0.244276     -1.105403      -1.276907
     C       0.763818      0.636984      -0.061569
     O       1.920758     -1.462865      -0.078248
     H       1.854498     -2.385934      -0.354892
     C       2.115133      1.249021       0.222069
     H       2.565336      0.807443       1.117555
     H       2.813639      1.062541      -0.601195
     H       2.026887      2.327914       0.373675
     C      -0.367500      1.377089      -0.014791
     C      -1.797359      0.936320      -0.166135
     H      -2.372138      1.277594       0.708271
     H      -2.253984      1.383003      -1.059764
     H      -0.272269      2.438078       0.214169
     O      -2.024778     -0.464297      -0.351125
     O      -1.506014     -1.180034       0.744491
Rotational constants (GHz):    2.9984700    1.5815600    1.1202700
Vibrational harmonic frequencies (cm-1):
    i1633.5348                  79.4575                 179.0332
     204.9852                  263.1206                272.0694
     300.4160                  322.5524                371.3652
     432.6382                  447.3890                533.1072
     617.8248                  730.7778                778.3982
     802.2085                  900.2189                944.8392
     963.8580                 1016.2838               1033.0225
    1074.2164                 1100.3979               1156.6430
    1189.8649                 1248.2146               1263.0975
    1271.8699                 1340.2082               1376.8497
    1421.1280                 1428.1923               1452.8751
    1478.8619                 1496.7698               1639.9603
    1674.6778                 3006.3887               3033.8474
    3043.6766                 3058.0849               3100.5717
    3129.3702                 3153.5321               3836.4146
Zero-point correction (Hartree): 0.132519
```

TS(1,6 H-shift)
(2)

```
------------
E(B3LYP/6-31+G(d,p)) (Hartree): -421.45784866
Electronic state : 2-A
Cartesian coordinates (Angs):
     C       0.765183      0.798687       0.418705
     H      -0.361515      1.237814      -0.136370
     H       0.470469      1.040433       1.449589
     C       0.781739     -0.643868       0.112465
     O       1.919804      1.460850       0.005303
     H       1.884152      2.381195       0.295558
     C       2.071931     -1.244752      -0.384817
     H       2.367790     -0.789214      -1.335992
     H       2.891134     -1.055489       0.317490
     H       1.966144     -2.322352      -0.532663
```

```
     C      -0.354087     -1.383339       0.215655
     C      -1.725196     -0.818120       0.471605
     H      -2.485508     -1.602142       0.416988
     H      -1.832555     -0.281749       1.422290
     H      -0.299087     -2.439881      -0.035922
     O      -2.060321      0.102302      -0.598414
     O      -1.589288      1.384314      -0.264720
Rotational constants (GHz):    2.9408400    1.5675000    1.1151500
Vibrational harmonic frequencies (cm-1):
    i1733.2041                81.1254               166.6928
     196.4479                 227.3132              289.3887
     297.5529                 341.6203              376.2027
     408.2169                 462.6412              512.5232
     580.8601                 630.9046              789.8598
     810.0919                 891.4915              975.1614
     980.0198                1005.0298             1052.1605
    1072.1140                1085.0519             1159.3458
    1195.8803                1251.9197             1272.3578
    1314.8496                1338.7087             1360.9082
    1416.9950                1421.9710             1476.3552
    1479.7760                1491.5613             1535.6672
    1638.9534                3028.2953             3043.9567
    3044.9194                3102.9473             3115.3824
    3133.0756                3175.0767             3838.7542
Zero-point correction (Hartree): 0.132293
```

TS(1,6 H-shift)
(3)

```
------------
E(B3LYP/6-31+G(d,p)) (Hartree): -421.45924472
Electronic state : 2-A
Cartesian coordinates (Angs):
     C      -0.605769      1.092425       0.295901
     H       0.513827      0.922172       0.947326
     C      -1.086466     -0.317259       0.075410
     C      -2.577477     -0.520257       0.218779
     H      -2.916179     -0.234265       1.222767
     H      -3.127346      0.105698      -0.494656
     H      -2.859518     -1.564038       0.051230
     C      -0.256347     -1.337427      -0.209240
     C       1.242658     -1.326058      -0.338420
     H       1.693081     -1.974812       0.426343
     H       1.547951     -1.704666      -1.322883
     H      -0.689318     -2.329502      -0.342072
     O       1.857450     -0.035362      -0.266073
     O       1.680432      0.477051       1.042462
     O      -0.241195      1.832949      -0.819605
     H       0.431781      1.329025      -1.309179
     H      -1.267364      1.704740       0.912265
Rotational constants (GHz):    2.8218000    1.7241100    1.2884300
Vibrational harmonic frequencies (cm-1):
    i1615.3931                74.7324               164.6726
     188.8451                 230.0680              264.9487
     306.1197                 368.2162              417.2528
     441.4652                 493.6809              590.2189
     646.8093                 707.5466              817.1822
     826.0749                 909.9465              950.2362
     987.4043                1027.9910             1048.2344
    1068.6135                1105.7829             1137.4470
    1166.1497                1193.9109             1275.0843
    1284.3791                1359.7159             1380.7674
    1416.2558                1431.2375             1456.2223
    1482.0451                1495.3053             1574.1131
```

```
    1716.0591                3020.8441                3026.2817
    3067.4024                3080.9918                3115.3738
    3124.0868                3143.9297                3728.7023
Zero-point correction (Hartree): 0.132845
```

TS(1,6 H-shift)
(4)

```
--------------
E(B3LYP/6-31+G(d,p)) (Hartree): -421.45748508
Electronic state : 2-A
Cartesian coordinates (Angs):
     C       0.715303     -0.841831      -0.353485
     H      -0.296778     -1.250487       0.336876
     H       0.313430     -1.115536      -1.333292
     C       0.765616      0.622062      -0.067295
     O       1.867559     -1.586694      -0.133602
     H       2.300165     -1.303183       0.683311
     C       2.124529      1.245561       0.173912
     H       2.584399      0.890948       1.106666
     H       2.820988      1.009714      -0.638411
     H       2.040171      2.331972       0.256502
     C      -0.357838      1.368498       0.016840
     C      -1.797485      0.952021      -0.107709
     H      -2.338093      1.254510       0.802432
     H      -2.272760      1.456273      -0.959842
     H      -0.246781      2.428573       0.245520
     O      -2.050063     -0.430264      -0.361764
     O      -1.518183     -1.205623       0.686198
Rotational constants (GHz):    2.9640500    1.5781100    1.1096400
Vibrational harmonic frequencies (cm-1):
    i1635.4525                 65.1676                182.3679
     206.4674                 265.1849                268.2191
     293.8778                 322.3831                363.4223
     434.4868                 443.6634                526.3412
     617.5798                 730.3525                778.9453
     802.6881                 899.5970                942.4045
     960.2863                1019.3223               1034.2403
    1069.9556                1106.6739               1137.0020
    1206.8087                1235.4132               1258.1579
    1273.8703                1352.5926               1378.7498
    1414.0685                1425.2758               1452.9750
    1488.4836                1500.0240               1616.0090
    1679.2864                3004.1114               3021.5135
    3059.9955                3081.3177               3105.5199
    3129.7768                3146.3448               3817.1497
Zero-point correction (Hartree): 0.132403
```

TS(1,6 H-shift)
(5)

```
--------------
E(B3LYP/6-31+G(d,p)) (Hartree): -421.45618655
Electronic state : 2-A
Cartesian coordinates (Angs):
     C      -0.756717     -0.817866       0.449561
     H       0.402470     -1.251595      -0.037876
     H      -0.532051     -1.040790       1.496814
     C      -0.793080      0.629484       0.119185
     O      -1.837776     -1.606045       0.068060
     H      -2.063009     -1.436987      -0.856968
     C      -2.109517      1.220164      -0.332310
     H      -2.397968      0.858531      -1.328223
     H      -2.920693      0.951886       0.353083
     H      -2.041156      2.309094      -0.395329
```

```
     C       0.328085      1.391524       0.183775
     C       1.723148      0.868860       0.410136
     H       2.457831      1.668839       0.280812
     H       1.881315      0.395736       1.386714
     H       0.238944      2.449243      -0.055240
     O       2.043130     -0.102055      -0.614034
     O       1.622496     -1.374018      -0.182260
Rotational constants (GHz):    2.8875600    1.5766900    1.1087300
Vibrational harmonic frequencies (cm-1):
    i1710.7156                58.3588               165.6572
     196.7282                 218.0918               285.6788
     293.7073                 353.7101               375.5115
     407.4358                 465.5828               510.5396
     580.7209                 632.7037               787.8781
     814.8418                 894.5842               973.7193
     976.0639                1012.3106              1048.4196
    1065.3106                1087.6217              1140.7988
    1226.8123                1233.3295              1269.1120
    1294.8439                1346.0247              1369.9452
    1418.0904                1418.9021              1476.0578
    1483.1933                1495.1878              1519.7375
    1643.7882                3028.5115              3045.9838
    3087.0661                3100.9888              3112.4960
    3131.8216                3168.1525              3816.2331
Zero-point correction (Hartree): 0.132207
```

TS(1,6 H-shift)
B3LYP/6-311G(d,p)-Optimization

Cartesian coordinates (Angs):

C	0.711480	-0.820561	-0.321767
H	-0.268607	-1.215383	0.423190
H	0.243865	-1.102519	-1.273321
C	0.756279	0.637120	-0.061014
O	1.922730	-1.453534	-0.076822
H	1.856382	-2.367161	-0.370750
C	2.106842	1.246372	0.221838
H	2.553144	0.805992	1.117621
H	2.804460	1.053620	-0.598338
H	2.022851	2.324171	0.369242
C	-0.369233	1.374405	-0.014833
C	-1.796069	0.930817	-0.168105
H	-2.370389	1.271775	0.704559
H	-2.251158	1.377001	-1.060398
H	-0.274836	2.433939	0.212515
O	-2.018183	-0.468889	-0.350031
O	-1.500986	-1.176371	0.744223

Rotational constants (GHz): 3.0168500 1.5879900 1.1259000
Vibrational harmonic frequencies (cm-1):

i1667.6162	79.8816	174.2486
204.5688	263.3319	275.3777
301.6335	324.2110	371.2783
433.5384	447.7690	532.7467
620.4529	731.9525	780.4930
803.0356	899.2767	944.5754
961.1077	1017.3261	1030.8223
1071.9686	1096.8408	1159.3635
1191.0513	1252.4771	1260.9630
1276.4766	1342.0190	1376.4971
1416.3002	1430.9491	1450.7271
1474.0979	1494.3189	1649.6859
1677.4699	2991.9807	3017.8945
3031.8561	3043.2862	3082.0694
3113.4183	3135.0547	3843.4663

Zero-point correction (Hartree): 0.132311

QCISD/6-311G(d,p)-Optimization

C,0,0.5496392858,0.9051955529,-0.4069702958
H,0,0.0089855208,1.0908070158,0.7403951008
H,0,1.5787497838,0.7258093971,-0.0673148912
C,0,-0.1470362156,-0.3142322867,-0.9232341759
O,0,0.4145673069,1.9871376445,-1.2669450792
H,0,1.0118533864,2.6723220751,-0.9623646243
C,0,-0.5450050908,-0.3051109383,-2.3832295987
H,0,-1.2366763174,0.5182080693,-2.589682392
H,0,0.3324995073,-0.1560825355,-3.0236536076
H,0,-1.0256293258,-1.2504801441,-2.6537729833
C,0,-0.4375287257,-1.3558682776,-0.1214424658
C,0,-0.1621356112,-1.5154753022,1.3539798112
H,0,-1.1102279678,-1.6899960428,1.8821369454
H,0,0.4971951971,-2.3752101547,1.5279159833
H,0,-0.9645949595,-2.2059337836,-0.5567108819
O,0,0.5239033135,-0.4334139581,1.9769278789
O,0,-0.2781006363,0.7064854906,1.8956738694

MPW1B95/6-31+G(d,p)-Optimization

E(MPW1B95/6-31+G(d,p)) (Hartree): -421.26230812
E(MPW1B95/6-311++G(3df,3pd)) (Hartree): -421.38635724
Electronic state : 2-A
Cartesian coordinates (Angs):

C	0.699289	-0.815799	-0.310080
H	-0.242951	-1.203414	0.462137
H	0.196692	-1.108224	-1.239387
C	0.744304	0.635057	-0.057688
O	1.916268	-1.428479	-0.106104
H	1.857736	-2.350782	-0.365241
C	2.083713	1.238810	0.233877
H	2.524256	0.793372	1.127644
H	2.783468	1.050492	-0.582583
H	1.996490	2.313734	0.386345
C	-0.382813	1.366933	-0.021215
C	-1.790800	0.906144	-0.198823
H	-2.394878	1.257917	0.646252
H	-2.228375	1.317400	-1.113680
H	-0.295222	2.424310	0.211114
O	-1.973251	-0.491087	-0.342621
O	-1.482939	-1.140643	0.772598

Rotational constants (GHz): 3.0698100 1.6152800 1.1512100
Vibrational harmonic frequencies (cm-1):

i1730.0848	86.1218	200.9457
233.8688	272.2891	282.3996
309.3769	322.3723	374.9683
437.8252	455.7985	535.3874
630.8628	743.8060	786.1126
819.1927	931.0407	967.3060
980.7382	1034.0810	1058.7539
1079.6679	1141.5141	1178.9916
1225.0433	1260.3579	1270.8705
1286.1382	1338.4343	1390.2852
1426.5976	1445.7447	1459.1693
1487.9737	1501.1618	1676.9937
1721.6533	3050.5710	3070.0375
3082.5174	3108.9270	3151.9015
3179.9291	3198.8250	3919.9267

Zero-point correction (Hartree): 0.134677

Conformers of Z-4-OH-1-OO•-isoprene: •$OOCH_2C(CH_3)=CHCH_2OH$

$HOCH_2$-CH=C(CH_3)-CH_2OO
(1)

E(B3LYP/6-31+G(d,p)) (Hartree): -421.49046004
Electronic state : 2-A
Cartesian coordinates (Angs):

C	-1.875056	-0.557161	0.509497
H	-2.651505	-1.294341	0.731562
H	-1.668366	-0.014208	1.441753
C	-0.645439	-1.251179	-0.022158
O	-2.444530	0.316755	-0.466941
H	-1.767322	0.975368	-0.689678
C	0.635356	-0.868932	0.131343
C	1.016959	0.348736	0.925812
H	0.245054	0.696084	1.611822
H	1.961841	0.218540	1.460450
O	1.324475	1.496417	0.031396
O	0.242827	1.984161	-0.544564
H	-0.840754	-2.113115	-0.659548
C	1.781210	-1.591795	-0.534178
H	1.428190	-2.439646	-1.126584
H	2.335679	-0.918327	-1.199659
H	2.496837	-1.967032	0.208858

Rotational constants (GHz): 2.3220500 1.7111500 1.1468600
Vibrational harmonic frequencies (cm-1):

78.2724	84.1587	120.9894
145.8319	194.9072	222.9084
302.6496	382.0278	426.2060
459.5154	506.9456	537.1679
632.4794	782.4005	823.6196
902.8052	955.5045	980.7498
1039.8346	1053.7227	1070.0851
1116.9158	1163.9940	1182.9153
1249.6036	1280.6638	1342.4369
1364.0690	1383.8690	1422.6475
1427.9134	1480.7849	1488.5739
1498.2117	1523.3856	1721.8837
3023.3569	3026.9259	3078.5147
3091.0857	3101.2854	3128.2383
3155.4366	3164.5849	3757.2903

Zero-point correction (Hartree): 0.138689

$HOCH_2$-CH=C(CH_3)-CH_2OO
(2)

E(B3LYP/6-31+G(d,p)) (Hartree): -421.48785730
Electronic state : 2-A
Cartesian coordinates (Angs):

C	1.866970	-0.460928	0.552823
H	2.825575	-0.267806	1.042581
H	1.233710	-1.002005	1.267826
C	1.235721	0.837081	0.120439
O	2.183344	-1.295520	-0.567756
H	1.356621	-1.502437	-1.027072
C	-0.076012	1.133482	0.144521
C	-1.097729	0.146932	0.651330
H	-0.819534	-0.343192	1.586956
H	-2.093586	0.582703	0.752822
O	-1.213051	-0.932048	-0.360301

O	-2.211087	-1.754259	-0.086129
H	1.919217	1.564272	-0.316287
C	-0.623532	2.430342	-0.398167
H	0.173641	3.073441	-0.779767
H	-1.332680	2.242420	-1.214692
H	-1.169115	2.985769	0.375445

Rotational constants (GHz): 2.0745400 1.6345600 1.0153800
Vibrational harmonic frequencies (cm-1):

17.8519	57.7902	80.8981
143.0274	183.2709	204.8187
284.0175	350.8302	395.0521
459.5545	462.2298	502.6597
582.0119	811.7306	869.6620
927.7079	943.5324	979.2400
1030.8528	1052.0992	1070.2901
1108.3633	1163.4147	1182.4353
1213.6109	1264.5813	1339.8659
1364.8917	1389.4701	1416.8797
1422.9280	1484.7945	1490.3293
1501.5085	1520.3112	1721.4831
3025.3583	3032.3136	3075.6044
3088.5846	3101.1835	3126.9902
3148.2785	3159.5722	3801.4785

Zero-point correction (Hartree): 0.137951

$HOCH_2$-CH=C(CH_3)-CH_2OO
(3)

E(B3LYP/6-31+G(d,p)) (Hartree): -421.48725657
Electronic state : 2-A
Cartesian coordinates (Angs):

C	1.985168	-0.378559	-0.629686
H	1.475154	-1.287057	-0.962400
H	2.786930	-0.173287	-1.350642
C	1.032308	0.795771	-0.586073
O	2.542906	-0.719419	0.650621
H	2.985027	0.060748	1.011737
C	-0.154673	0.823623	0.043999
C	-0.662867	-0.364285	0.818900
H	-0.005345	-1.231114	0.773993
H	-0.858852	-0.105237	1.865017
O	-1.990425	-0.787155	0.338500
O	-1.905943	-1.435909	-0.811686
C	-1.043596	2.041639	0.049096
H	-0.598858	2.861052	-0.521410
H	-2.023772	1.812661	-0.384375
H	-1.224565	2.392870	1.073458
H	1.353939	1.700098	-1.102277

Rotational constants (GHz): 2.6622700 1.3361500 1.0648400
Vibrational harmonic frequencies (cm-1):

38.7493	57.5260	82.6997
142.3444	187.6077	231.4592
248.1597	307.4965	370.5144
425.9318	444.7898	577.1773
633.4247	787.3396	848.1619
873.5427	958.3952	982.0976
991.0442	1050.2027	1074.6213
1110.9058	1157.4368	1178.9495
1233.7860	1284.3614	1345.3659
1357.9448	1384.7665	1408.1711
1424.1979	1475.1899	1486.0056
1496.9045	1523.4568	1721.5255
3030.3327	3034.1608	3075.2709

```
    3087.5282                3102.6238                3127.7111
    3149.7894                3172.6447                3816.5235
Zero-point correction (Hartree): 0.137826
```

$HOCH_2$-CH=C(CH_3)-CH_2OO
(4)

```
-----------------
E(B3LYP/6-31+G(d,p)) (Hartree): -421.48824812
Electronic state : 2-A
Cartesian coordinates (Angs):
     C       2.218164     -0.314392       0.477327
     H       2.914124      0.067488       1.232037
     H       1.748286     -1.214226       0.892755
     C       1.217543      0.748651       0.116186
     O       3.046602     -0.652078      -0.641304
     H       2.478015     -0.956287      -1.362024
     C      -0.125095      0.718572       0.212350
     C      -0.882234     -0.454831       0.777333
     H      -0.238837     -1.239440       1.175209
     H      -1.618532     -0.154643       1.527379
     O      -1.642159     -1.127152      -0.295456
     O      -2.906078     -0.739934      -0.341100
     H       1.673975      1.648016      -0.297829
     C      -0.979928      1.879700      -0.234113
     H      -1.713754      1.564799      -0.984621
     H      -1.550970      2.291990       0.607328
     H      -0.369925      2.679416      -0.661838
Rotational constants (GHz):    3.4336900    1.0434400    0.8867800
Vibrational harmonic frequencies (cm-1):
      30.9558                  65.1779                  88.5366
     148.0020                 196.1521                 240.6169
     250.5823                 344.7590                 366.5283
     442.7407                 486.6273                 514.1147
     606.2003                 780.1079                 859.5802
     890.9168                 959.5655                 983.7847
    1033.2858                1052.8598                1075.0505
    1113.3492                1159.2891                1183.8990
    1240.9226                1285.2505                1331.6889
    1356.3624                1381.7366                1412.7684
    1428.2165                1474.2228                1486.9097
    1497.5696                1510.8373                1722.1736
    3034.7702                3038.0164                3084.1057
    3090.3057                3091.1978                3128.9862
    3150.5181                3163.4744                3812.8652
Zero-point correction (Hartree): 0.138047
```

$HOCH_2$-CH=C(CH_3)-CH_2OO
(5)

```
-----------------
E(B3LYP/6-31+G(d,p)) (Hartree): -421.48720480
Electronic state : 2-A
Cartesian coordinates (Angs):
     C       2.237136     -0.198657      -0.599768
     H       1.857292     -0.973217      -1.273263
     H       3.129814      0.229658      -1.073368
     C       1.210526      0.892428      -0.381847
     O       2.599355     -0.905767       0.597259
     H       2.919169     -0.266525       1.248254
     C      -0.050588      0.717981       0.053115
     C      -0.580798     -0.652804       0.393335
     H       0.156770     -1.441618       0.247969
     H      -0.984218     -0.700136       1.408558
     O      -1.690954     -1.005813      -0.508455
```

```
     O      -2.874574     -0.715637       0.007208
     C      -1.002233      1.869103       0.255283
     H      -1.911200      1.739274      -0.342503
     H      -1.325240      1.931813       1.302004
     H      -0.538372      2.819257      -0.022570
     H       1.541113      1.910921      -0.583882
Rotational constants (GHz):    3.3764900    1.1540800    0.9474900
Vibrational harmonic frequencies (cm-1):
      42.7893                62.5604                81.5989
     145.3482               193.7845               229.0963
     242.2387               316.7622               370.8747
     399.2830               491.2112               571.2997
     630.5460               785.7527               852.8436
     867.9740               958.2954               982.0922
     990.0904              1051.2617              1074.1598
    1110.8706              1159.0885              1185.8748
    1237.8112              1286.1108              1341.6231
    1358.6064              1383.2680              1408.5163
    1426.8549              1476.4028              1487.6358
    1494.3784              1521.6566              1716.5748
    3034.1866              3035.6095              3087.8091
    3092.5730              3093.1947              3126.9486
    3151.4288              3171.5631              3815.3814
Zero-point correction (Hartree): 0.137929
```

$HOCH_2$-CH=C(CH_3)-CH_2OO
(6)

```
-----------------
E(B3LYP/6-31+G(d,p)) (Hartree): -421.48712415
Electronic state : 2-A
Cartesian coordinates (Angs):
     C       2.123680     -0.476486      -0.614391
     H       1.570713     -1.193872      -1.228248
     H       3.049844     -0.237559      -1.152972
     C       1.326268      0.790754      -0.396058
     O       2.421202     -1.188804       0.596866
     H       2.884633     -0.592553       1.200445
     C       0.059286      0.858356       0.048988
     C      -0.719259     -0.378855       0.406178
     H      -0.173315     -1.307286       0.238460
     H      -1.077538     -0.354020       1.440367
     O      -1.922299     -0.410708      -0.447375
     O      -2.789546     -1.317026      -0.030553
     C      -0.658455      2.168505       0.256373
     H      -0.023560      3.017543      -0.009905
     H      -1.570200      2.214825      -0.349740
     H      -0.968115      2.283548       1.303317
     H       1.843556      1.728050      -0.599758
Rotational constants (GHz):    2.7670700    1.2062300    0.9218100
Vibrational harmonic frequencies (cm-1):
      40.7357                42.8648                65.3076
     139.1065               179.0215               196.7895
     236.0005               301.7418               356.2861
     426.4439               460.9831               531.6924
     615.9106               812.9054               851.7595
     909.9037               955.0661               977.0065
     992.3410              1047.6487              1074.1329
    1104.2441              1174.9325              1191.8571
    1210.8382              1262.7228              1343.0180
    1357.9743              1395.2189              1408.6305
    1423.7206              1478.7699              1491.7691
    1497.4875              1522.7725              1722.5591
    3030.9526              3033.3797              3075.4884
```

3088.7772 3095.2290 3127.2097
3150.5873 3159.7158 3816.6707
Zero-point correction (Hartree): 0.137552

$HOCH_2$-CH=C(CH_3)-CH_2OO
(7)

E(B3LYP/6-31+G(d,p)) (Hartree): -421.48599548
Electronic state : 2-A
Cartesian coordinates (Angs):

C	-2.114369	-0.544329	0.489260
H	-1.497897	-1.406586	0.747486
H	-2.749106	-0.323801	1.362005
C	-1.293462	0.668806	0.143807
O	-2.923871	-0.982498	-0.608017
H	-3.547764	-0.282749	-0.842726
C	0.040897	0.826727	0.174334
C	0.986272	-0.253243	0.621524
H	1.624118	0.074415	1.448928
H	0.502385	-1.193152	0.887305
O	1.897163	-0.549178	-0.501786
O	2.902888	-1.314881	-0.116975
C	0.698800	2.130506	-0.211473
H	1.397446	1.984610	-1.042828
H	-0.041121	2.877054	-0.511287
H	1.280403	2.539459	0.625025
H	-1.886741	1.532404	-0.164394

Rotational constants (GHz): 2.9507300 1.0541200 0.8453900
Vibrational harmonic frequencies (cm-1):
36.1343 53.3404 77.2853
144.6270 192.4567 201.8215
219.9536 269.0252 371.5183
430.3932 456.7262 512.7462
575.4045 804.0424 875.4130
910.2467 975.6033 978.5842
1012.9593 1050.9141 1074.6687
1103.9676 1156.1549 1192.0263
1225.7939 1264.7697 1340.9624
1355.8347 1401.6329 1414.7628
1423.7049 1479.7084 1489.3998
1500.1459 1509.0999 1734.4337
2992.8176 3031.4853 3072.0978
3089.8343 3117.8152 3128.5944
3134.4373 3155.2156 3821.7014
Zero-point correction (Hartree): 0.137511

$HOCH_2$-CH=C(CH_3)-CH_2OO
(8)

E(B3LYP/6-31+G(d,p)) (Hartree): -421.48826367
Electronic state : 2-A
Cartesian coordinates (Angs):

C	-1.935299	-0.775040	-0.396348
H	-2.194788	-1.013634	-1.433378
H	-1.317319	-1.599867	-0.020909
C	-1.224057	0.548018	-0.347308
O	-3.191727	-0.728061	0.290482
H	-3.030844	-0.477488	1.210228
C	0.024665	0.817381	0.076152
C	0.957859	-0.236196	0.604878
H	1.530937	0.115923	1.467398
H	0.473668	-1.182220	0.849885
O	1.950712	-0.532349	-0.451206

O	2.936049	-1.283123	0.009019
C	0.599124	2.212941	0.027352
H	1.497271	2.241954	-0.601361
H	-0.121207	2.930161	-0.374201
H	0.900123	2.549381	1.027943
H	-1.831876	1.381430	-0.700317

Rotational constants (GHz): 3.0528400 1.0402700 0.8290100

Vibrational harmonic frequencies (cm-1):

37.7823	56.4359	71.5870
142.3817	187.1603	197.9605
269.4445	333.4505	367.9517
421.7684	493.3698	527.6455
544.0142	814.6322	877.7115
913.9042	949.2732	987.8880
1032.4466	1047.6871	1072.9935
1113.5511	1173.5257	1184.6797
1210.7404	1257.1603	1331.9990
1359.8193	1389.5079	1412.3109
1422.5802	1481.6607	1492.2365
1498.9920	1514.2874	1726.3584
3029.1284	3040.1942	3079.8331
3082.9733	3087.4296	3127.6979
3149.2029	3151.1908	3815.8217

Zero-point correction (Hartree): 0.137784

$HOCH_2$-CH=C(CH_3)-CH_2OO

(9)

E(B3LYP/6-31+G(d,p)) (Hartree): -421.48571721

Electronic state : 2-A

Cartesian coordinates (Angs):

C	-2.236291	-0.324574	0.476437
H	-1.776571	-1.241081	0.848966
H	-2.902541	0.050869	1.268880
C	-1.223913	0.733734	0.130601
O	-3.008296	-0.733993	-0.659250
H	-3.474036	0.032377	-1.019690
C	0.118182	0.684110	0.203911
C	0.867330	-0.523479	0.704299
H	1.547143	-0.280255	1.525490
H	0.217722	-1.352670	0.983879
O	1.711456	-1.077651	-0.370259
O	2.969763	-0.680469	-0.278454
H	-1.663662	1.668986	-0.222785
C	0.979777	1.859192	-0.190349
H	1.579262	2.209372	0.659237
H	1.687617	1.582607	-0.979365
H	0.371181	2.692808	-0.550299

Rotational constants (GHz): 3.5578300 1.0224700 0.8720000

Vibrational harmonic frequencies (cm-1):

27.6022	53.5223	69.1753
144.4536	194.5152	216.7534
247.4926	262.3697	368.2748
437.8693	481.6150	519.3720
603.3028	778.8838	865.7371
883.4729	970.0641	984.6205
1011.0954	1053.6819	1074.9195
1108.9989	1146.5695	1180.0883
1254.1839	1286.0397	1341.0079
1348.9695	1392.9271	1412.7058
1428.5739	1470.7501	1485.8873
1497.9407	1509.6030	1727.6983
2994.5832	3036.3131	3084.7936
3094.2047	3116.3694	3128.0525

3134.3149 3164.5199 3820.2310
Zero-point correction (Hartree): 0.137633

$HOCH_2$-CH=C(CH_3)-CH_2OO
(10)

E(B3LYP/6-31+G(d,p)) (Hartree): -421.48800647
Electronic state : 2-A
Cartesian coordinates (Angs):

C	-2.070525	-0.623012	-0.396002
H	-2.328746	-0.859681	-1.433859
H	-1.614858	-1.523338	0.034641
C	-1.150461	0.564797	-0.362754
O	-3.325494	-0.339418	0.234513
H	-3.156195	-0.060832	1.144648
C	0.112449	0.644708	0.097747
C	0.846295	-0.531166	0.687535
H	1.444530	-0.252565	1.558464
H	0.196986	-1.373775	0.926526
O	1.795748	-1.088423	-0.297519
O	3.009883	-0.580386	-0.168842
C	0.904874	1.927025	0.029712
H	1.215530	2.249009	1.031809
H	1.823715	1.788867	-0.552130
H	0.323728	2.731410	-0.428533
H	-1.601573	1.472621	-0.764218

Rotational constants (GHz): 3.8526500 0.9948900 0.8457600
Vibrational harmonic frequencies (cm-1):

35.0800	67.1413	75.0293
146.7686	195.3975	221.6325
273.7114	333.3866	344.6338
480.3891	488.4288	507.8441
586.4553	810.5219	833.0708
896.7673	959.7158	981.8626
1031.1014	1052.3911	1071.3990
1116.0063	1159.0236	1180.5080
1237.3264	1285.6959	1332.4206
1354.7033	1379.6212	1411.8897
1425.8052	1475.6528	1484.9003
1495.4915	1510.1975	1720.5923
3032.0551	3037.3521	3084.6195
3087.1818	3091.0720	3127.9065
3149.8109	3162.2264	3815.7934

Zero-point correction (Hartree): 0.137944

$HOCH_2$-CH=C(CH_3)-CH_2OO
(11)

E(B3LYP/6-31+G(d,p)) (Hartree): -421.48818359
Electronic state : 2-A
Cartesian coordinates (Angs):

C	-1.797252	-0.661479	-0.223119
H	-1.943430	-1.156096	-1.189147
H	-1.322772	-1.393327	0.440650
C	-0.964091	0.574707	-0.411996
O	-3.119657	-0.342280	0.229310
H	-3.050879	0.133899	1.067707
C	0.261535	0.849327	0.070057
C	1.038768	-0.111832	0.926263
H	1.596736	0.407059	1.711528
H	0.437710	-0.910150	1.360521
O	2.118357	-0.770885	0.155815
O	1.643541	-1.711382	-0.640936

H	-1.449491	1.334412	-1.025570
C	0.975026	2.141330	-0.249759
H	1.924586	1.945778	-0.763077
H	0.369235	2.786428	-0.891158
H	1.216455	2.696052	0.666363

Rotational constants (GHz): 2.6938500 1.2531900 0.9588900

Vibrational harmonic frequencies (cm-1):

41.0565	74.2360	83.1674
151.6865	192.4945	227.7005
270.0505	333.2234	355.4052
453.9208	485.5068	505.9864
610.2695	813.2527	828.1336
890.3507	959.3284	984.3805
1029.5849	1052.5013	1071.1032
1120.6210	1158.9734	1174.4334
1231.4885	1279.9408	1332.7980
1357.7443	1379.9562	1410.1427
1424.1168	1478.8349	1487.6130
1498.7966	1509.0567	1726.2462
3027.3632	3048.6162	3079.4527
3082.4808	3092.3676	3127.4468
3147.8877	3160.4196	3816.6323

Zero-point correction (Hartree): 0.137981

$HOCH_2$-CH=C(CH_3)-CH_2OO
(12)

E(B3LYP/6-31+G(d,p)) (Hartree): -421.48513682
Electronic state : 2-A
Cartesian coordinates (Angs):

C	-2.031221	-0.271025	0.525374
H	-1.519301	-1.163090	0.889796
H	-2.611804	0.141731	1.366297
C	-1.071430	0.768568	0.010731
O	-2.916051	-0.742760	-0.495230
H	-3.467586	-0.010655	-0.801147
C	0.263766	0.832257	0.144700
C	1.058361	-0.187246	0.915578
H	1.602045	0.275588	1.746816
H	0.470313	-1.028256	1.281183
O	2.148727	-0.752231	0.100530
O	1.700051	-1.661182	-0.749773
C	1.071839	1.968129	-0.436495
H	1.827794	1.593904	-1.135762
H	0.433619	2.677418	-0.969556
H	1.608902	2.513937	0.350429
H	-1.553683	1.584712	-0.531608

Rotational constants (GHz): 2.7243200 1.2044000 0.9599800

Vibrational harmonic frequencies (cm-1):

32.5961	48.7724	76.0499
152.3274	191.7972	217.6350
240.4903	271.9432	377.6132
419.6555	467.9179	500.7505
622.5472	777.0575	864.4111
873.6215	972.7837	986.0197
1017.8924	1054.3751	1076.0585
1109.7705	1150.7299	1163.9525
1250.0972	1285.0674	1342.0537
1354.7096	1392.5472	1414.6960
1424.5853	1472.5773	1485.7731
1498.6677	1500.7934	1733.4751
2984.2324	3029.8780	3068.7516
3088.5195	3117.0830	3128.3775

3133.0819 3162.1697 3822.0839
Zero-point correction (Hartree): 0.137501

$HOCH_2$-CH=C(CH_3)-CH_2OO
(13)

E(B3LYP/6-31+G(d,p)) (Hartree): -421.48650927
Electronic state : 2-A
Cartesian coordinates (Angs):

C	2.078971	-0.595707	0.429354
H	2.563319	-0.471702	1.411816
H	1.454881	-1.497073	0.476695
C	1.276410	0.632942	0.115719
O	3.073409	-0.724621	-0.592902
H	3.680943	-1.435616	-0.351973
C	-0.054215	0.807414	0.171565
C	-1.005809	-0.271877	0.604507
H	-0.528993	-1.225233	0.834331
H	-1.623010	0.037965	1.454343
O	-1.943698	-0.525705	-0.507611
O	-2.931702	-1.318768	-0.132094
C	-0.696710	2.133169	-0.162156
H	0.050755	2.872422	-0.460740
H	-1.418312	2.023989	-0.979449
H	-1.248900	2.530774	0.699588
H	1.893371	1.481587	-0.177686

Rotational constants (GHz): 3.0821500 1.0203400 0.8272300
Vibrational harmonic frequencies (cm-1):

38.3007	54.5199	76.6810
155.9760	193.0554	203.8023
233.6878	265.8383	365.5888
410.6829	464.1978	513.6913
573.8246	807.5990	872.1462
910.3340	978.0614	982.1858
1039.7361	1056.1951	1076.6735
1103.5139	1189.5218	1194.9569
1230.3922	1248.2190	1279.7809
1343.1787	1389.9906	1424.0570
1442.9814	1481.7223	1493.3026
1500.7412	1512.7132	1741.7308
2979.0471	3030.2739	3044.0321
3070.4638	3088.4836	3130.3246
3147.0667	3160.5033	3832.7338

Zero-point correction (Hartree): 0.137448

$HOCH_2$-CH=C(CH_3)-CH_2OO
(14)

E(B3LYP/6-31+G(d,p)) (Hartree): -421.48729031
Electronic state : 2-A
Cartesian coordinates (Angs):

C	2.100286	-0.769547	-0.071866
H	2.685432	-0.947310	-0.988518
H	2.819380	-0.795381	0.757205
C	1.498248	0.611268	-0.167053
O	1.206376	-1.847086	0.169412
H	0.584588	-1.913980	-0.569491
C	0.264941	1.052968	0.134157
C	-0.823922	0.164831	0.680084
H	-0.458119	-0.616395	1.344891
H	-1.623059	0.735582	1.157342
O	-1.454095	-0.534859	-0.469718
O	-2.611463	-1.081868	-0.139060

```
     C      -0.136621      2.491287      -0.100403
     H       0.683249      3.078528      -0.522440
     H      -0.987574      2.549117      -0.791217
     H      -0.453821      2.970408       0.834747
     H       2.205788      1.345095      -0.557115
Rotational constants (GHz):    2.2234900    1.6957600    1.0306600
Vibrational harmonic frequencies (cm-1):
      35.4008                58.4785                99.7369
     180.7003               185.5766               238.3759
     248.8412               324.3000               374.1464
     434.2171               471.7465               545.9108
     679.4624               813.3028               823.2753
     903.1334               929.5371               982.7370
     999.6718              1064.4725              1072.0877
    1129.3201              1170.6095              1193.4240
    1211.8552              1257.9039              1355.2898
    1377.6258              1396.3384              1410.2302
    1424.1282              1484.3480              1487.4260
    1492.9994              1501.8141              1731.8742
    2987.4818              3025.2556              3053.6644
    3075.7865              3098.9661              3122.7969
    3133.4605              3173.2669              3799.3592
Zero-point correction (Hartree): 0.137967
```

$HOCH_2$-CH=C(CH_3)-CH_2OO
(15)

```
------------------
E(B3LYP/6-31+G(d,p)) (Hartree): -421.48736686
Electronic state : 2-A
Cartesian coordinates (Angs):
     C       1.779302     -0.606564      -0.183567
     H       1.323074     -1.324406       0.507647
     H       1.876032     -1.109663      -1.158120
     C       0.943003      0.623164      -0.365315
     O       3.068334     -0.190041       0.289120
     H       3.681201     -0.933097       0.218628
     C      -0.300555      0.865827       0.081393
     C      -1.072962     -0.114430       0.918528
     H      -0.455509     -0.873353       1.398092
     H      -1.690532      0.392100       1.666004
     O      -2.084393     -0.841395       0.115135
     O      -1.530291     -1.774299      -0.637879
     H       1.434865      1.396766      -0.954591
     C      -1.032574      2.143883      -0.251790
     H      -0.423571      2.804208      -0.874441
     H      -1.965007      1.932522      -0.790087
     H      -1.307036      2.689526       0.660362
Rotational constants (GHz):    2.6543700    1.2800000    0.9624400
Vibrational harmonic frequencies (cm-1):
      39.4333                60.8129                81.8444
     155.6705               194.1870               228.8233
     249.1868               286.2112               352.8474
     454.8763               480.9925               506.0814
     611.5527               814.9819               824.9681
     885.5052               971.3748               984.0742
    1031.8091              1060.4278              1072.9087
    1115.7389              1160.7589              1205.9744
    1223.8949              1269.3704              1284.4279
    1349.1526              1377.5307              1423.8216
    1437.6936              1480.6662              1488.7206
    1499.4691              1515.2940              1737.4801
    2997.9962              3026.8361              3061.5245
    3077.9282              3085.6901              3126.6431
```

3155.9512 3161.0914 3831.2272
Zero-point correction (Hartree): 0.137700

$HOCH_2$-CH=C(CH_3)-CH_2OO
(16)

E(B3LYP/6-31+G(d,p)) (Hartree): -421.48587142
Electronic state : 2-A
Cartesian coordinates (Angs):

C	1.967547	-0.345293	0.479411
H	2.400368	-0.060101	1.452870
H	1.439681	-1.298466	0.608519
C	1.045540	0.737782	-0.004305
O	3.007135	-0.473192	-0.496270
H	3.630773	-1.149782	-0.203851
C	-0.284390	0.837681	0.148173
C	-1.095621	-0.179126	0.903657
H	-0.511764	-1.008336	1.302561
H	-1.674228	0.287633	1.708511
O	-2.149440	-0.771960	0.057515
O	-1.660187	-1.703039	-0.744663
C	-1.066219	2.007227	-0.400815
H	-0.414875	2.703738	-0.934607
H	-1.844454	1.667313	-1.093733
H	-1.572933	2.558025	0.402740
H	1.566232	1.535864	-0.532388

Rotational constants (GHz): 2.7411100 1.1988300 0.9501000
Vibrational harmonic frequencies (cm-1):

35.8917	46.8187	74.1481
165.5036	194.9784	224.8401
238.4170	265.1813	366.5925
417.0246	467.1853	502.4363
624.8017	784.4315	858.6589
871.5757	976.1718	999.3279
1040.1324	1056.4862	1076.1195
1106.3431	1157.4430	1198.7429
1241.2629	1273.7912	1286.7546
1343.7328	1374.0756	1424.9019
1442.3652	1477.6935	1487.9290
1500.0748	1509.0742	1741.2132
2971.3902	3027.9160	3046.5193
3069.9590	3084.5891	3129.3482
3156.7270	3161.2002	3836.1106

Zero-point correction (Hartree): 0.137455

$HOCH_2$-CH=C(CH_3)-CH_2OO
(17)

E(B3LYP/6-31+G(d,p)) (Hartree): -421.48603637
Electronic state : 2-A
Cartesian coordinates (Angs):

C	2.205146	-0.420581	0.419551
H	2.713391	-0.196571	1.371650
H	1.723312	-1.401031	0.522198
C	1.219345	0.670090	0.119762
O	3.157839	-0.438768	-0.649931
H	3.882211	-1.032889	-0.415224
C	-0.122030	0.645127	0.200162
C	-0.893896	-0.567809	0.648203
H	-0.261736	-1.431528	0.856989
H	-1.539667	-0.357848	1.505505
O	-1.789765	-1.029726	-0.428632

O	-3.039725	-0.635118	-0.250614
H	1.695479	1.600518	-0.187777
C	-0.957274	1.860840	-0.122311
H	-1.679719	1.644377	-0.916768
H	-1.538208	2.183115	0.751094
H	-0.329600	2.694750	-0.446451

Rotational constants (GHz): 3.8175400 0.9768900 0.8440200
Vibrational harmonic frequencies (cm-1):

33.1118	52.3653	68.0157
152.5648	192.0694	226.5222
247.5253	262.9700	356.7427
430.0611	490.0677	510.0645
599.4973	781.5945	864.7873
879.1455	970.7813	989.8170
1038.0074	1057.2938	1076.8977
1104.9149	1162.0264	1210.8292
1229.4381	1277.0840	1285.2622
1341.6674	1376.3198	1426.7089
1439.6381	1472.8479	1485.7832
1497.2403	1512.6619	1735.4475
2979.7800	3035.1921	3043.8793
3082.4977	3093.1644	3129.8743
3155.9525	3159.7052	3830.8762

Zero-point correction (Hartree): 0.137484

$HOCH_2$-CH=C(CH_3)-CH_2OO
(18)

E(B3LYP/6-31+G(d,p)) (Hartree): -421.48690747
Electronic state : 2-A
Cartesian coordinates (Angs):

C	2.045507	-0.601489	-0.377511
H	1.586085	-1.493839	0.065292
H	2.266509	-0.835159	-1.430740
C	1.137487	0.590022	-0.335808
O	3.253702	-0.257740	0.314440
H	3.929349	-0.917824	0.112308
C	-0.128236	0.665901	0.111790
C	-0.854157	-0.506187	0.716768
H	-0.192541	-1.322236	1.008091
H	-1.485440	-0.211738	1.558403
O	-1.758612	-1.123882	-0.275695
O	-2.983191	-0.627641	-0.218557
C	-0.927158	1.942766	0.024306
H	-0.348500	2.744521	-0.441732
H	-1.843535	1.792295	-0.558685
H	-1.241317	2.275798	1.021614
H	1.593538	1.496197	-0.733325

Rotational constants (GHz): 3.7795300 1.0104600 0.8524100
Vibrational harmonic frequencies (cm-1):

32.0868	55.7193	69.5751
151.0892	195.4449	222.3102
249.7578	287.2336	345.1862
477.8662	486.3373	508.3359
587.9031	811.9135	831.1167
894.2571	969.8787	980.5673
1032.6576	1060.4401	1073.4033
1112.5797	1157.7464	1217.0020
1222.6020	1274.7398	1287.7623
1343.7551	1376.7794	1425.4927
1438.0212	1477.3379	1485.5848
1496.3527	1519.2886	1731.8463
2993.7205	3031.6690	3049.2717

```
    3086.0529                3093.4118                3127.0796
    3157.8435                3164.1351                3828.2617
Zero-point correction (Hartree): 0.137650
```

$HOCH_2$-CH=C(CH_3)-CH_2OO
(19)

```
------------------
E(B3LYP/6-31+G(d,p)) (Hartree): -421.48721952
Electronic state : 2-A
Cartesian coordinates (Angs):
     C       1.908488     -0.755950      -0.369869
     H       1.285857     -1.567865       0.025182
     H       2.130864     -0.993471      -1.421959
     C       1.213157      0.570723      -0.319646
     O       3.126893     -0.640977       0.377366
     H       3.682188     -1.409117       0.191097
     C      -0.039779      0.841902       0.083648
     C      -0.972053     -0.206922       0.621080
     H      -0.477675     -1.129881       0.926141
     H      -1.582860      0.169141       1.446488
     O      -1.919976     -0.570274      -0.456506
     O      -2.897417     -1.335812      -0.003383
     C      -0.614046      2.236380       0.012717
     H       0.108039      2.947991      -0.395721
     H      -1.510364      2.257805      -0.619216
     H      -0.916792      2.586452       1.007960
     H       1.830140      1.398651      -0.667367
Rotational constants (GHz):    2.9888600    1.0603800    0.8348500
Vibrational harmonic frequencies (cm-1):
      33.0820                  46.5396                  65.3080
     146.5304                 184.6027                 201.7079
     250.7457                 287.0626                 367.7170
     420.6310                 494.5257                 523.9121
     545.1850                 816.4137                 875.4152
     912.6684                 956.2168                 988.4946
    1034.2222                1057.5131                1074.8979
    1108.9847                1181.7867                1195.6443
    1224.3961                1240.8269                1280.9153
    1346.6459                1389.6256                1422.3138
    1438.9838                1482.5508                1493.1143
    1500.5561                1521.5109                1737.4681
    2993.8059                3029.0035                3052.6096
    3081.5828                3083.2957                3126.9558
    3150.4832                3158.7939                3828.4555
Zero-point correction (Hartree): 0.137496
```

$HOCH_2$-CH=C(CH_3)-CH_2OO(B3LYP/6-311G(d,p)-Optimization)

Cartesian coordinates (Angs):

C	-1.861833	-0.582187	0.504553
H	-2.634127	-1.326397	0.709141
H	-1.665176	-0.056025	1.447781
C	-0.623005	-1.263270	-0.019048
O	-2.413367	0.297268	-0.470313
H	-1.722821	0.945238	-0.666829
C	0.645493	-0.862730	0.135933
C	1.003745	0.358906	0.930161
H	0.226930	0.686252	1.617263
H	1.950569	0.249030	1.461246
O	1.280685	1.513559	0.035923
O	0.196185	1.967003	-0.547576
H	-0.805528	-2.118986	-0.665219
C	1.803424	-1.554080	-0.537350
H	1.467208	-2.395732	-1.144372
H	2.343991	-0.858042	-1.187841
H	2.523974	-1.927813	0.199076

Rotational constants (GHz): 2.3371500 1.7385200 1.1638200

Vibrational harmonic frequencies (cm-1):

80.0601	93.7585	129.5904
149.5972	196.6672	223.0322
304.4785	382.5665	427.7352
459.1664	532.2206	548.1093
636.3685	783.1204	819.2354
902.1927	958.8076	980.5135
1043.3336	1056.4900	1069.3574
1114.2343	1160.1006	1187.2408
1254.0934	1279.2948	1345.1299
1371.0103	1387.4520	1416.7051
1449.9793	1477.7866	1485.0578
1495.5408	1523.1222	1719.7559
2996.0826	3014.4690	3060.6533
3080.3443	3081.4164	3111.9078
3136.3012	3148.6388	3751.4202

Zero-point correction (Hartree): 0.138568

$HOCH_2$-CH=C(CH_3)-CH_2OO(QCISD/6-311G(d,p)-Optimization)

C,0,0.0778628391,-0.0088136625,0.0189806929
H,0,0.1358567427,-0.0585517621,1.1105285981
H,0,1.1081788222,0.0280040468,-0.3605877011
C,0,-0.6579821997,-1.2227155881,-0.5033973564
O,0,-0.6276490854,1.1838115519,-0.2867050663
H,0,-0.7046841428,1.1927047899,-1.2445945018
C,0,-0.4500903212,-1.8431157848,-1.676008874
C,0,0.6183101087,-1.4089877466,-2.6460022504
H,0,1.3867175905,-0.7738936817,-2.2047614289
H,0,1.0818020168,-2.2643974276,-3.1466497377
O,0,0.0275541864,-0.6603424031,-3.7570626771
O,0,-0.4118755585,0.5172987361,-3.34826205
H,0,-1.4927001777,-1.5631672245,0.1102096179
C,0,-1.3196443381,-2.9806634669,-2.1607079875
H,0,-2.1227810589,-3.196284051,-1.4498065447
H,0,-1.7702520547,-2.7276106075,-3.1288238336
H,0,-0.7250481121,-3.8929549762,-2.3029555846

Transition state for 1,6-H-migration in Z-4-OH-1-OO•-isoprene

TS(1)

```
-------------------
E(B3LYP/6-31+G(d,p)) (Hartree): -421.46138553
Electronic state : 2-A
Cartesian coordinates (Angs):
     C      -1.465734     -0.304484      -0.273704
     H      -1.261043      0.751473       0.431862
     H      -1.566722      0.212802      -1.238402
     C      -0.230243     -1.084871      -0.085778
     O      -2.588810     -1.042395       0.090199
     H      -3.388084     -0.559186      -0.156856
     C       1.024918     -0.589226      -0.053247
     C       1.386140      0.870477      -0.212299
     H       1.966454      1.195901       0.664150
     H       2.014906      1.013957      -1.101454
     O       0.308396      1.785133      -0.418986
     O      -0.540744      1.779686       0.705122
     H      -0.381568     -2.145815       0.109255
     C       2.215527     -1.479332       0.202998
     H       2.735376     -1.189813       1.125677
     H       1.915878     -2.526033       0.297099
     H       2.950417     -1.408063      -0.609840
Rotational constants (GHz):    2.4170100    1.7041300    1.0764200
Vibrational harmonic frequencies (cm-1):
    i1616.4095                96.0812               138.8602
     189.4848                 248.5391               261.8509
     330.4293                 350.0829               383.8563
     420.1966                 458.1545               471.5027
     578.7260                 626.0366               808.9036
     871.1115                 919.4940               985.6916
     992.6179                 998.9034              1052.5393
    1076.6142                1085.6100              1134.9786
    1180.7295                1243.5124              1267.0230
    1283.2699                1332.4224              1391.8193
    1416.5422                1420.9905              1451.0506
    1483.3421                1494.0842              1639.9913
    1688.3168                3009.2368              3023.1387
    3029.7434                3062.1028              3069.2601
    3127.6548                3160.6194              3832.9102
Zero-point correction (Hartree): 0.132334
```

TS(2)

```
--------------------
E(B3LYP/6-31+G(d,p)) (Hartree): -421.46048812
Electronic state : 2-A
Cartesian coordinates (Angs):
     C      -1.491695     -0.287197      -0.332757
     H      -1.272620      0.800269       0.319905
     H      -1.646340      0.160592      -1.319015
     C      -0.248275     -1.073225      -0.144120
     O      -2.666530     -0.923742       0.051505
     H      -2.511660     -1.429898       0.861917
     C       1.010499     -0.596588      -0.044879
     C       1.406842      0.860951      -0.124651
     H       1.907263      1.151628       0.811467
     H       2.121350      1.009284      -0.945446
     O       0.372556      1.798936      -0.410730
     O      -0.560838      1.802964       0.645567
```

```
     H      -0.393363     -2.150681      -0.041043
     C       2.180958     -1.519913       0.190468
     H       2.706971     -1.264662       1.119591
     H       1.859842     -2.562394       0.258047
     H       2.917078     -1.443571      -0.620525
Rotational constants (GHz):    2.4050700    1.6984700    1.0691100
Vibrational harmonic frequencies (cm-1):
    i1608.2861                 80.9997                135.8343
     185.7846                 237.7818                259.0092
     320.9812                 351.5910                407.1247
     424.0621                 458.5438                481.7294
     583.6806                 630.3575                796.6429
     868.6178                 918.9732                973.4727
     995.0847                1007.7800               1057.8812
    1071.9262                1087.3974               1154.3630
    1164.0620                1241.4170               1261.8613
    1287.2751                1350.3220               1397.1239
    1405.4757                1422.1807               1449.3520
    1483.2471                1493.7464               1605.2476
    1689.3962                3008.4653               3024.8246
    3064.0031                3072.1992               3100.9256
    3121.0039                3127.0566               3801.6944
Zero-point correction (Hartree): 0.132272
```

TS(3)

```
-------------------
E(B3LYP/6-31+G(d,p)) (Hartree): -421.45834194
Electronic state : 2-A
Cartesian coordinates (Angs):
     C       1.477555     -0.379763       0.334400
     H       1.238135      0.853582      -0.081775
     H       1.622617     -0.119445       1.393147
     C       0.242759     -1.114215       0.032784
     O       2.588869     -0.991981      -0.242784
     H       3.395812     -0.559103       0.064584
     C      -1.014633     -0.621258       0.136949
     C      -1.275993      0.834495       0.473907
     H      -2.343326      1.064043       0.392530
     H      -0.923233      1.134318       1.467941
     O      -0.639734      1.679922      -0.507739
     O       0.675114      1.964364      -0.093186
     H       0.387144     -2.120454      -0.361064
     C      -2.219538     -1.461412      -0.193245
     H      -2.774991     -1.029767      -1.036263
     H      -1.941095     -2.486216      -0.453119
     H      -2.915947     -1.502479       0.654933
Rotational constants (GHz):    2.3978500    1.6971500    1.0602900
Vibrational harmonic frequencies (cm-1):
    i1693.9540                 70.7007                158.8619
     200.7194                 210.2849                297.4779
     304.1354                 336.5642                368.3167
     397.7057                 476.8105                493.0228
     525.7740                 629.4094                828.2257
     860.4611                 899.7241                991.1336
    1009.2511                1014.1338               1041.3768
    1065.2116                1103.2078               1132.8229
    1188.8778                1247.8255               1272.6036
    1315.2801                1336.2497               1373.0991
    1407.5805                1419.7443               1473.0814
    1484.9570                1492.0945               1523.1700
    1668.0530                3017.1997               3020.4851
    3044.3247                3068.9319               3105.8177
```

```
    3123.1186                3151.4190                3835.5239
Zero-point correction (Hartree): 0.132099
```

TS(4)

```
-------------------
E(B3LYP/6-31+G(d,p)) (Hartree): -421.45988658
Electronic state : 2-A
Cartesian coordinates (Angs):
     C       1.194038     -1.103548      -0.408058
     H       1.362986      0.083836      -0.904183
     C      -0.295244     -1.218973      -0.322660
     C      -1.162864     -0.237830      -0.008599
     C      -0.784157      1.190046       0.315265
     H      -1.218219      1.869221      -0.432277
     H      -1.182799      1.473060       1.298703
     O       0.615201      1.459714       0.423554
     O       1.201949      1.336087      -0.859431
     O       1.917743     -1.084112       0.777633
     H       1.539861     -0.394261       1.349040
     H       1.664509     -1.820794      -1.082589
     H      -0.705838     -2.198147      -0.572274
     C      -2.652502     -0.479752       0.014523
     H      -3.072244     -0.277163       1.008403
     H      -3.171016      0.183236      -0.690045
     H      -2.892001     -1.512154      -0.251652
Rotational constants (GHz):    2.7003400    1.7515000    1.2537100
Vibrational harmonic frequencies (cm-1):
    i1589.6330                 86.9106                135.6838
     175.2783                 189.2052                322.9701
     345.4423                 368.9175                405.2263
     445.8386                 484.8439                537.6124
     619.9433                 662.5347                820.3165
     846.5403                 904.0623                948.6427
     991.4864                1037.0858               1061.0236
    1071.5874                1090.8337               1153.1156
    1168.2799                1199.0308               1284.7735
    1288.0193                1346.8459               1398.8405
    1420.5432                1428.2736               1451.7014
    1484.2213                1492.8719               1576.1286
    1705.1389                3019.4670               3027.5903
    3067.8660                3075.3546               3125.8693
    3129.4620                3139.5185               3741.1597
Zero-point correction (Hartree): 0.132763
```

TS(5)

```
-------------------
E(B3LYP/6-31+G(d,p)) (Hartree): -421.45315186
Electronic state : 2-A
Cartesian coordinates (Angs):
     C       1.269696     -0.981678      -0.471962
     H       1.379220      0.338247      -0.660836
     C      -0.191038     -1.185894      -0.530883
     C      -1.087329     -0.366429       0.063141
     C      -0.650334      0.932047       0.721775
     H      -1.514303      1.488070       1.098681
     H       0.077160      0.793701       1.526774
     O      -0.073019      1.791526      -0.286696
     O       1.310468      1.532788      -0.390112
     O       1.796765     -1.180613       0.813122
     H       2.735752     -0.945698       0.812710
     H       1.848467     -1.480174      -1.257344
     H      -0.557922     -2.010099      -1.142720
```

```
     C      -2.568280     -0.617343      -0.013914
     H      -3.002551     -0.693375       0.991843
     H      -3.077899      0.215790      -0.515199
     H      -2.797936     -1.540290      -0.553360
Rotational constants (GHz):    2.4648300    1.8390400    1.2363900
Vibrational harmonic frequencies (cm-1):
    i1722.8900                80.3441               136.3768
     178.6702                 209.0623               278.0769
     322.7294                 341.7762               374.8819
     407.8019                 463.2211               581.0407
     620.7297                 647.4139               808.7495
     845.2471                 896.1417               963.0333
     990.5094                1004.8938              1041.1118
    1057.3466                1087.6244              1147.2175
    1197.3939                1238.2183              1267.0591
    1278.4432                1344.3194              1381.0614
    1410.7921                1420.1669              1473.0987
    1483.3307                1491.5014              1518.6287
    1679.5678                3022.4903              3066.5324
    3068.1558                3072.5217              3122.2208
    3126.1414                3144.1744              3802.7026
Zero-point correction (Hartree): 0.132345
```

B3LYP/6-311G(d,p)-Optimization

Cartesian coordinates (Angs):

C	-1.465521	-0.300973	-0.271741
H	-1.256582	0.751901	0.438280
H	-1.558894	0.219963	-1.233384
C	-0.230002	-1.079107	-0.084002
O	-2.585524	-1.038792	0.088470
H	-3.373962	-0.551744	-0.170294
C	1.020702	-0.589219	-0.054259
C	1.383578	0.867541	-0.219306
H	1.970924	1.189822	0.651458
H	2.005666	1.006044	-1.111487
O	0.307147	1.782447	-0.416090
O	-0.531055	1.773919	0.708865
H	-0.384635	-2.137764	0.110710
C	2.207627	-1.480284	0.203950
H	2.725377	-1.192256	1.126207
H	1.905916	-2.524373	0.296591
H	2.943332	-1.409923	-0.605900

Rotational constants (GHz): 2.4264200 1.7115100 1.0815400

Vibrational harmonic frequencies (cm-1):

i1643.7299	96.9551	138.8667
190.1201	248.7926	263.5684
330.9016	352.7037	388.3496
421.7414	459.0333	472.5939
580.5976	628.7209	801.2548
871.2566	921.8392	982.2422
993.5144	997.4092	1048.7641
1076.2482	1085.5990	1134.5415
1181.7403	1249.8551	1264.0049
1286.3340	1334.2739	1390.0422
1415.8586	1421.4176	1449.1541
1479.8039	1491.6830	1650.5538
1688.8335	2994.6440	3010.5180
3010.9010	3046.8839	3051.4961
3111.1576	3139.5875	3839.4672

Zero-point correction (Hartree): 0.132120

QCISD/6-311G(d,p)-Optimization

C,0,0.0616835165,0.0222572229,0.004828512
H,0,0.0453732367,0.0280522598,1.2825004844
H,0,1.1490970019,0.0777433414,-0.1423630168
C,0,-0.5577741884,-1.2856846436,-0.3372747644
O,0,-0.648711137,1.0648860123,-0.5753192712
H,0,-0.1330432856,1.8651488065,-0.4621663014
C,0,-0.3726455921,-2.4407576713,0.325729282
C,0,0.5332800479,-2.6215844819,1.525416792
H,0,-0.060945037,-3.0022110942,2.3686227223
H,0,1.3171987669,-3.3542636265,1.2933346232
O,0,1.2547332806,-1.4692642504,1.9441593836
O,0,0.3420022455,-0.5074538325,2.3831581894
H,0,-1.2630032349,-1.2564680699,-1.1677274133
C,0,-1.0979648084,-3.705749304,-0.0728947684
H,0,-1.7356663229,-4.0633090134,0.7465023655
H,0,-1.7271243043,-3.5368616798,-0.9517772981
H,0,-0.385728401,-4.5085444911,-0.3064445112