Electronic Supplementary Material for PCCP

Photodissociation Dynamics of 2-Methylallyl Radical

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Supporting Material

A.) CCSD/cc-pVTZ optimized geometries and CCSD(T)/cc-pVXZ energies of all stationary points discussed in this work.

A1. 2-Methylallyl radical (Cs, Doublet)
****

6	-1.263864	0.673777	0.000000
6	0.000000	0.089370	0.000000
6	1.145052	0.863791	0.000000
6	0.108099	-1.419314	0.000000
1	1.148220	-1.740563	0.000000
1	-0.378255	-1.842086	0.879756
1	-0.378255	-1.842086	-0.879756
1	1.082265	1.943108	0.000000
1	2.127852	0.415661	0.000000
1	-1.376402	1.748604	0.000000
1	-2.161144	0.071618	0.000000

CCSD(T) energies / Hartree
cc-pVDZ: -156.11212580
cc-pVTZ: -156.27463157 (T1 diagnostics: 0.02498502)
CBS (est.): -156.36169500

A2. trans-1-Methylallyl radical (Cs, Doublet)
****

6	-1.364005	-1.407209	0.000000
6	-0.147696	-0.745328	0.000000
6	0.000000	0.631414	0.000000
6	1.319994	1.332876	0.000000
1	0.756596	-1.345415	0.000000
1	-0.895453	1.243218	0.000000
1	1.427808	1.976352	0.876942
1	1.427808	1.976352	-0.876942
1	2.144783	0.620530	0.000000
1	-1.416542	-2.485177	0.000000
1	-2.294762	-0.856382	0.000000

CCSD(T) energies / Hartree
cc-pVDZ: -156.11382330
cc-pVTZ -156.27590272 (T1 diagnostics: 0.02490608)
CBS (est.): -156.36169500

A3. cis-1-Methylallyl radical (C1, Doublet)
****

6	1.505003	-0.595446	0.000008
6	0.803296	0.593236	-0.000100
6	-0.584133	0.702688	-0.000235
6	-1.506929	-0.478665	-0.000042
1	-1.018743	1.692551	0.001003
1	1.372532	1.515137	0.000242
1	2.584463	-0.604143	0.000272
1	0.999033	-1.550426	0.000057
1	-1.359750	-1.098403	0.888361
1	-2.548699	-0.165431	-0.020070

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1       -1.332260   -1.120159   -0.867647

CCSD(T) energies / Hartree
cc-pVDZ:       -156.11257442
cc-pVTZ:       -156.27508755  (T1 diagnostics: 0.02519483)
CBS (est.):    -156.36217158

A4. structure 02 (Cs, Doublet)
********************************************************************************************

6       -0.062635   -1.602334    0.000000
6        0.405347   -0.194085    0.000000
6       -0.062635    0.971253    0.767284
6       -0.062635    0.971253   -0.767284
1        0.280996   -2.136577   -0.885762
1        0.280996   -2.136577    0.885762
1        0.662088    1.612224    1.252230
1       -1.015310    0.903040    1.280914
1        0.662088    1.612224   -1.252230
1       -1.015310    0.903040   -1.280914
1       -1.160191   -1.633898    0.000000

CCSD(T) energies / Hartree
cc-pVDZ:       -156.07141298
cc-pVTZ:       -156.23362478  (T1 diagnostics: 0.01151074)
CBS (est.):    -156.32066884

A5. structure 05 (Cs, Singlet)
********************************************************************************************

6        0.846707    1.389556    0.000000
6        0.000000    0.177007    0.000000
6       -1.155334   -0.406388    0.000000
6        0.039416   -1.330067    0.000000
1        1.492980    1.398478    0.878905
1        1.492980    1.398478   -0.878905
1        0.240243    2.294016    0.000000
1        0.308158   -1.859091   -0.911305
1        0.308158   -1.859091    0.911305
1       -2.227254   -0.353436    0.000000

CCSD(T) energies / Hartree
cc-pVDZ:       -155.48579154
cc-pVTZ:       -155.64603337  (T1 diagnostics: 0.00957194)
CBS (est.):    -155.73178759

A6. structure 06 (C2v, Singlet)
********************************************************************************************

6       -0.000002    1.638012    0.000000
6        0.000000    0.317127    0.000000
6        0.769403   -0.932684    0.000000
6       -0.769404   -0.932687    0.000000
1       -0.926424    2.196400    0.000000
1        0.926417    2.196403    0.000000
1        1.267408   -1.232846    0.912025
1        1.267408   -1.232846   -0.912025
1       -1.267395   -1.232858    0.912029
1       -1.267395   -1.232858   -0.912029

CCSD(T) energies / Hartree
cc-pVDZ:       -155.50390107
cc-pVTZ:       -155.66428860  (T1 diagnostics: 0.00992564)
CBS (est.):    -155.75011462

A7. structure 08 (Cs, Singlet)
********************************************************************************************

6        0.693518    1.822458    0.000000
6        0.000000    0.712173    0.000000
6       -0.688137   -0.400785    0.000000
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6       -0.076712   -1.777566    0.000000
1        1.009924   -1.720295    0.000000
1       -0.393890   -2.339675    0.879749
1       -0.393890   -2.339675   -0.879749
1       -1.770213   -0.330903    0.000000
1        0.988028    2.296434    0.926750
1        0.988028    2.296434   -0.926750

CCSD(T) energies / Hartree
cc-pVDZ:       -155.51547520
cc-pVTZ:       -155.67572069  (T1 diagnostics: 0.01136444)
CBS (est.):    -155.76135253

A8. structure 09 (Cs, Singlet)
*******************************************************************************************

6       -0.630000    1.872498    0.000000
6        0.000000    0.845142    0.000000
6        0.745235   -0.419631    0.000000
6       -0.178773   -1.640575    0.000000
1       -1.180807    2.779500    0.000000
1        0.406582   -2.559801    0.000000
1       -0.818540   -1.638622    0.881546
1       -0.818540   -1.638622   -0.881546
1        1.396264   -0.443530   -0.875423
1        1.396264   -0.443530    0.875423

CCSD(T) energies / Hartree
cc-pVDZ:       -155.51310830
cc-pVTZ:       -155.67450686  (T1 diagnostics: 0.01063435)
CBS (est.):    -155.76053197

A9. structure10 (C1, Doublet)
*******************************************************************************************

6       -1.924356   -0.181432    0.129325
6       -0.727896   -0.028890   -0.389663
6        0.558753    0.605368   -0.029210
6        1.704833   -0.402547    0.086638
1       -2.708901   -0.727490   -0.378095
1       -2.170621    0.246019    1.101161
1        0.426772    1.133907    0.923771
1        0.807899    1.362964   -0.775171
1        1.486144   -1.147940    0.850829
1        1.856866   -0.923599   -0.858229
1        2.633836    0.101145    0.353200

CCSD(T) energies / Hartree
cc-pVDZ:       -156.07845111
cc-pVTZ:       -156.23980687  (T1 diagnostics: 0.02857313)
CBS (est.):    -156.32620691

A10. structure14 (D3h, Singlet)
*******************************************************************************************

6        0.608178    1.742514    0.000000
6        0.608178    0.405691    0.000000
6       -0.608178   -0.405691    0.000000
6       -0.608178   -1.742514    0.000000
1       -1.549786    0.131742    0.000000
1       -0.318264    2.302204    0.000000
1        1.528753    2.307840    0.000000
1        1.549786   -0.131742    0.000000
1       -1.528753   -2.307840    0.000000
1        0.318264   -2.302204    0.000000

CCSD(T) energies / Hartree
cc-pVDZ:       -155.53649606
cc-pVTZ:       -155.69581364  (T1 diagnostics: 0.01123700)
CBS (est.):    -155.78091956
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A11. TS R1 (2-Methylallyl radical -> structure 02) (C1, Doublet)
****

6	-1.520170	-0.077175	0.016161
6	-0.073995	0.014123	-0.340325
6	0.940686	-0.971609	0.068905
6	0.778626	1.031654	0.050156
1	-1.655046	-0.277036	1.086155
1	-2.038056	0.852119	-0.220373
1	-2.002790	-0.889901	-0.527075
1	1.783356	-1.226982	-0.556616
1	0.906009	-1.377483	1.071424
1	1.756575	1.139308	-0.397861
1	0.499078	1.798013	0.774962

CCSD(T) energies / Hartree
cc-pVDZ: -156.02986964
cc-pVTZ: -156.19275972 (T1 diagnostics: 0.03869680)
CBS (est.): -156.27994963

A12. TS R2 (structure 02 -> structure05 + H) (C1, Doublet)
****

6	-1.671089	-0.017704	0.040433
6	-0.197969	0.040897	-0.054797
6	1.057907	-0.776605	0.037071
6	0.909464	0.701595	-0.251782
1	-2.119787	0.948701	-0.183629
1	-2.064184	-0.760733	-0.655226
1	1.296298	-1.465079	-0.770099
1	1.438542	-1.082744	1.007997
1	1.403090	1.572113	-0.638643
1	1.428074	1.420652	1.569459
1	-1.971906	-0.322002	1.044592

CCSD(T) energies / Hartree
cc-pVDZ: -155.98062130
cc-pVTZ: -156.14325473 (T1 diagnostics: 0.02655427)
CBS (est.): -156.23033482

A13. TS R3 (structure02 -> structure06 + H) (Cs, Doublet)
****

6	0.051629	-1.576685	0.000000
6	0.104690	-0.246256	0.000000
6	0.051629	0.999211	0.769610
6	0.051629	0.999211	-0.769610
1	0.106206	-2.133738	-0.925162
1	0.106206	-2.133738	0.925162
1	0.949319	1.341966	1.266657
1	-0.873111	1.254245	1.270586
1	0.949319	1.341966	-1.266657
1	-0.873111	1.254245	-1.270586
1	-1.922284	-1.977833	0.000000

CCSD(T) energies / Hartree
cc-pVDZ: -155.99822525
cc-pVTZ: -156.16095609 (T1 diagnostics: 0.02691079)
CBS (est.): -156.24807408

A14. TS L1 (2-Methylallyl radical -> structure10) (C1, Doublet)
****

6	-1.634387	-0.187347	0.064673
6	-0.380204	0.084446	-0.351775
6	0.596940	1.015156	0.020853
6	1.147247	-0.777511	0.083805
1	-2.275932	0.613065	0.420737
1	-2.071470	-1.170939	-0.038765
1	0.574539	-1.682609	0.280703
1	1.765414	-0.895653	-0.796832

```
1        1.759573   -0.603073    0.976548
1        0.540999    1.580015    0.952354
1        1.329300    1.350735   -0.700088

CCSD(T) energies / Hartree
cc-pVDZ:       -155.97881181
cc-pVTZ:       -156.14476935  (T1 diagnostics: 0.02809018)
CBS (est.):    -156.23331804

A15. TS L2 (structure10 -> 1-Methylallyl radical) (C1, Doublet)
*********************************************************************************

6        1.727763   -0.422673   -0.019254
6        0.794043    0.530614   -0.019201
6       -0.622116    0.639812   -0.117142
6       -1.563528   -0.521083    0.071538
1        1.593558   -1.322802   -0.613971
1        2.671875   -0.301289    0.491631
1       -1.004909    1.549403   -0.564436
1        0.113442    1.188208    0.863489
1       -1.693766   -1.053303   -0.874955
1       -1.152177   -1.227614    0.792074
1       -2.544999   -0.192629    0.410519

CCSD(T) energies / Hartree
cc-pVDZ:       -156.00466406
cc-pVTZ:       -156.16865700  (T1 diagnostics: 0.02383451)
CBS (est.):    -156.25641967

A16. TS L3 (structure10 -> structure08 + H) (C1, Doublet)
*********************************************************************************

6       -1.960204   -0.207073    0.093891
6       -0.714677    0.087948   -0.155090
6        0.548589    0.464154   -0.274868
6        1.712907   -0.416109    0.117817
1       -2.536671   -0.835534   -0.572036
1       -2.452264    0.176552    0.979944
1        0.757689    1.316641   -0.910449
1        1.401977   -1.165672    0.842642
1        2.515810    0.176743    0.552799
1        2.108996   -0.928897   -0.759993
1        0.684769    1.686643    1.176589

CCSD(T) energies / Hartree
cc-pVDZ:       -156.00675621
cc-pVTZ:       -156.16961045  (T1 diagnostics: 0.03393288)
CBS (est.):    -156.25669007

A17. TS L4 (1-Methylallyl radical -> structure08 + H) (C1, Doublet)
*********************************************************************************

6        1.912496   -0.219577   -0.131068
6        0.674121    0.169462    0.044428
6       -0.581652    0.558140   -0.115040
6       -1.761069   -0.367673   -0.021415
1        0.648209    0.103294    1.963356
1       -0.775607    1.621484   -0.197088
1       -2.419682   -0.234045   -0.880795
1       -2.346080   -0.156632    0.876366
1       -1.439554   -1.406495    0.014018
1        2.588044   -0.374214    0.696154
1        2.281294   -0.395502   -1.133439

CCSD(T) energies / Hartree
cc-pVDZ:       -156.00641031
cc-pVTZ:       -156.16928489  (T1 diagnostics: 0.03497043)
CBS (est.):    -156.25639130

A18. TS L5 (1-Methylallyl radical -> structure 13 + H) (C1, Doublet)
*********************************************************************************
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```
6       -1.917545    0.091228    0.070499
6       -0.683042   -0.398007   -0.058427
6        0.518419    0.430915   -0.065191
6        1.761666   -0.064604   -0.177756
1       -0.536065   -1.466897   -0.165744
1        0.375383    1.498975    0.051606
1        2.404346   -0.450985    1.808154
1        2.624659    0.583189   -0.222474
1        1.928821   -1.121903   -0.336023
1       -2.784126   -0.553825    0.069664
1       -2.090007    1.154253    0.180062

CCSD(T) energies / Hartree
cc-pVDZ:       -156.03018951
cc-pVTZ:       -156.19173226  (T1 diagnostics: 0.04310216)
CBS (est.):    -156.27811474

A19. TS L6 (structure10 -> structure09 + H) (Cs, Doublet)
********************************************************************************

6       -0.902631    1.651907    0.000000
6        0.000000    0.836919    0.000000
6        0.910526   -0.311878    0.000000
6        0.153756   -1.644923    0.000000
1       -2.528865    0.672534    0.000000
1       -1.452425    2.561355    0.000000
1        1.558283   -0.248072    0.875791
1        1.558283   -0.248072   -0.875791
1       -0.480854   -1.726147   -0.881280
1        0.856528   -2.477606    0.000000
1       -0.480854   -1.726147    0.881280

CCSD(T) energies / Hartree
cc-pVDZ:       -156.00521335
cc-pVTZ:       -156.16885207  (T1 diagnostics: 0.02764746)
CBS (est.):    -156.25616866

A20. trans-1-Methylallyl radical -> cis-1-Methylallyl radical (C1, Doublet)
********************************************************************************

6        0.752245   -0.400132    0.276985
6        1.772007    0.366464   -0.103978
6       -0.562851   -0.443952   -0.391096
1        1.695603    1.016096   -0.966164
1        2.709533    0.361085    0.435076
1        0.884739   -1.035699    1.152237
1       -0.764272   -1.259809   -1.073465
6       -1.710100    0.350363    0.145012
1       -2.050524   -0.038779    1.113380
1       -2.562037    0.330478   -0.533422
1       -1.420850    1.390166    0.310817

CCSD(T) energies / Hartree
cc-pVDZ:       -156.08963611
cc-pVTZ:       -156.25145133  (T1 diagnostics: 0.02056100)
CBS (est.):    -156.33804862

A21. 1,3-Deuterium shift in 2-Methylallyl radical (C2v, Doublet)
********************************************************************************

6        0.000000    0.000000    1.545571
6        0.000000    0.000000    0.219822
6        0.000000    1.112282   -0.788262
6        0.000000   -1.112282   -0.788262
1        0.000000    0.924872    2.106454
1        0.000000   -0.924872    2.106454
1       -0.918096   -1.674881   -0.923385
1        0.918096   -1.674881   -0.923385
1        0.918096    1.674881   -0.923385
1       -0.918096    1.674881   -0.923385
```

```
1        0.000000    0.000000   -1.652578

CCSD(T) energies / Hartree
cc-pVDZ:       -156.01797597
cc-pVTZ:       -156.18042649  (T1 diagnostics: 0.02201973)
CBS (est.):    -156.26752474

A22. Allene (C2v, Singlet)
*****************************************************************************************

6        0.000000    0.000000    1.307863
6        0.000000    0.000000    0.000000
6        0.000000    0.000000   -1.307863
1        0.000000    0.927660    1.863294
1        0.000000   -0.927660    1.863294
1        0.927660    0.000000   -1.863294
1       -0.927660    0.000000   -1.863294

CCSD(T) energies / Hartree
cc-pVDZ:       -116.31480057
cc-pVTZ:       -116.43353626 (T1 diagnostics: 0.01228134)
CBS (est.):    -116.49671539

A23. Methyl radical (D3h, Doublet)
*****************************************************************************************

6        0.000000    0.000000    0.000000
1        0.000000    0.000000    1.077585
1        0.933216    0.000000   -0.538793
1       -0.933216    0.000000   -0.538793

CCSD(T) energies / Hartree
cc-pVDZ:       -39.71573277
cc-pVTZ:       -39.76097335 (T1 diagnostics: 0.00786646)
CBS (est.):    -39.78473962

A24. TS 2-methylallyl radical -> allene + methyl radical (Cs, Doublet)
*****************************************************************************************

6       -0.002767   -1.760628    0.000000
6        0.000000    0.528015    0.000000
6        1.298646    0.853650    0.000000
6       -1.292178    0.759888    0.000000
1        1.037082   -2.052156    0.000000
1       -0.546796   -1.893137    0.924053
1       -0.546796   -1.893137   -0.924053
1        1.853834    0.897833    0.926843
1        1.853834    0.897833   -0.926843
1       -1.643126    1.783938    0.000000
1       -2.030237   -0.026723    0.000000

CCSD(T) energies / Hartree
cc-pVDZ:       -156.01443393
cc-pVTZ:       -156.01443393 (T1 diagnotics: 0.03858790
CBS (est.):    -156.26667535
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B.) HCTH147/TZ2P harmonic and anharmonic frequencies and zero point energies of all stationary points discussed in this work.

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B1. 2-Methylallyl radical (Cs, Doublet)
*****************************************************************************************

Vibrational Energies and Rotational Constants (cm-1)
Mode(Quanta)     E(harm)     E(anharm)    Aa(z)       Ba(x)       Ca(y)
Equilibrium Geometry                     0.332089    0.294399    0.160708
Ground State   20355.646    22383.314    0.329212    0.292648    0.159631
Fundamental Bands (DE w.r.t. Ground State)
 1(1)           3224.574     3089.688    0.328918    0.292496    0.159533
```

2(1)	3221.966	3109.782	0.328886	0.292537	0.159539
3(1)	3129.315	3044.781	0.328964	0.292490	0.159527
4(1)	3121.983	3030.467	0.328985	0.292489	0.159534
5(1)	3106.850	3001.267	0.329102	0.292524	0.159588
6(1)	3014.947	3049.794	0.328978	0.292559	0.159604
7(1)	1508.901	1467.531	0.328863	0.292768	0.159520
8(1)	1484.008	1449.849	0.330110	0.292771	0.159570
9(1)	1464.411	1459.048	0.329235	0.292739	0.159751
10(1)	1386.428	1362.151	0.329037	0.291036	0.159612
11(1)	1354.032	1325.263	0.328742	0.292255	0.159990
12(1)	1327.361	1319.969	0.328656	0.292062	0.157931
13(1)	1034.213	1018.761	0.329168	0.292734	0.159752
14(1)	1012.300	1012.833	0.328795	0.292380	0.159114
15(1)	955.780	953.662	0.329420	0.292947	0.159496
16(1)	837.470	823.392	0.329127	0.291507	0.159204
17(1)	432.474	421.613	0.328364	0.291882	0.160645
18(1)	405.272	398.207	0.329086	0.292657	0.158390
19(1)	3082.963	3100.635	0.329005	0.292629	0.159608
20(1)	1465.123	1507.798	0.328021	0.293954	0.159674
21(1)	1032.790	1039.081	0.329576	0.292055	0.159544
22(1)	791.282	776.179	0.328548	0.292197	0.159677
23(1)	756.763	759.211	0.328740	0.292193	0.159707
24(1)	547.812	528.759	0.329058	0.292527	0.159673
25(1)	522.042	518.170	0.329031	0.292751	0.159700
26(1)	474.666	468.105	0.330012	0.293734	0.159870
27(1)	15.564	8510.182	0.328545	0.293132	0.160139

ZPEharm = 20355.64581 cm-1 = 58.200 Kcal/mol = 243.508 Kj/mol
ZPEfund = 24273.08997 cm-1 = 69.400 Kcal/mol = 290.371 KJ/mol
ZPEaver = 22314.36789 cm-1 = 63.800 Kcal/mol = 266.939 KJ/mol
-1/4sumXii = -962.66681 cm-1 = -2.752 Kcal/mol = -11.516 KJ/mol
x0 = 1031.61299 cm-1 = 2.950 Kcal/mol = 12.341 KJ/mol
ZPEtot = 22383.31406 cm-1 = 63.997 Kcal/mol = 267.764 KJ/mol
ZPEtot/ZPEharm = 1.09961 ZPEfund/ZPEharm= 1.19245

B2. trans-1-Methylallyl radical (Cs, Doublet)
****

Vibrational Energies and Rotational Constants (cm-1)

Mode(Quanta)	E(harm)	E(anharm)	Aa(z)	Ba(x)	Ca(y)
Equilibrium Geometry			1.278605	0.133308	0.123455
Ground State	20444.425	20208.413	1.249056	0.132937	0.122653
Fundamental Bands (DE w.r.t. Ground State)					
1(1)	3224.417	3120.122	1.245209	0.132887	0.122584
2(1)	3126.537	3041.756	1.245516	0.132887	0.122581
3(1)	3119.704	2992.717	1.243745	0.132866	0.122549
4(1)	3099.860	3006.178	1.243258	0.132862	0.122542
5(1)	3084.642	2950.341	1.247259	0.132925	0.122640
6(1)	2979.353	2848.444	1.248976	0.132913	0.122666
7(1)	1516.324	1466.323	1.239377	0.132788	0.122400
8(1)	1488.505	1442.685	1.249083	0.132953	0.122552
9(1)	1453.222	1411.152	1.252126	0.132896	0.122780
10(1)	1380.761	1349.151	1.218665	0.132834	0.122421
11(1)	1323.782	1292.536	1.250366	0.133005	0.122534
12(1)	1265.869	1239.029	1.246825	0.132846	0.122670
13(1)	1212.858	1194.623	1.245494	0.132846	0.122271
14(1)	1126.957	1101.351	1.241151	0.132795	0.122292
15(1)	977.379	964.558	1.249926	0.132778	0.122540
16(1)	871.948	866.494	1.247906	0.132878	0.122397
17(1)	499.868	502.067	1.237086	0.133245	0.122547
18(1)	284.586	290.532	1.265926	0.133556	0.122582
19(1)	3025.782	2875.910	1.250802	0.132931	0.122676
20(1)	1448.080	1414.162	1.276175	0.132944	0.122694
21(1)	1002.815	980.335	1.236582	0.133076	0.122616
22(1)	973.824	959.533	1.245990	0.132862	0.122696
23(1)	780.800	782.750	1.241557	0.132852	0.122702
24(1)	729.834	734.762	1.245624	0.132859	0.122719
25(1)	534.387	533.117	1.265730	0.132928	0.122701
26(1)	210.179	208.015	1.242434	0.132392	0.122916
27(1)	146.578	118.728	1.242621	0.132957	0.122769

```
ZPEharm     = 20444.42479 cm-1  =  58.454 Kcal/mol  = 244.570 Kj/mol
ZPEfund     = 19843.68547 cm-1  =  56.736 Kcal/mol  = 237.383 KJ/mol
ZPEaver     = 20144.05513 cm-1  =  57.595 Kcal/mol  = 240.976 KJ/mol
-1/4sumXii =     65.45657 cm-1  =   0.187 Kcal/mol  =   0.783 KJ/mol
x0          =     -1.09820 cm-1  =  -0.003 Kcal/mol  =  -0.013 KJ/mol
ZPEtot      = 20208.41349 cm-1  =  57.779 Kcal/mol  = 241.746 KJ/mol
ZPEtot/ZPEharm = 0.98846   ZPEfund/ZPEharm= 0.97062
```

B3. cis-1-Methylallyl radical (C1, Doublet)

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Vibrational Energies and Rotational Constants (cm-1)

Mode(Quanta)	E(harm)	E(anharm)	Aa(z)	Ba(x)	Ca(y)
Equilibrium Geometry			0.610809	0.178548	0.141760
Ground State	20472.630	20392.377	0.606822	0.178424	0.141313
Fundamental Bands (DE w.r.t. Ground State)					
1(1)	3227.528	3111.023	0.605369	0.178358	0.141205
2(1)	3140.629	3031.852	0.605149	0.178254	0.141125
3(1)	3134.210	3019.271	0.605431	0.178304	0.141165
4(1)	3112.111	3006.420	0.604897	0.178277	0.141124
5(1)	3102.296	2938.409	0.605401	0.178293	0.141170
6(1)	2987.646	2883.783	0.605901	0.178371	0.141276
7(1)	1507.451	1499.170	0.605940	0.178402	0.141260
8(1)	1496.058	1457.234	0.606863	0.178412	0.141093
9(1)	1440.744	1428.309	0.602499	0.178152	0.141486
10(1)	1410.400	1403.919	0.606763	0.178387	0.141211
11(1)	1369.918	1340.791	0.607692	0.177997	0.141031
12(1)	1244.334	1239.580	0.607252	0.178504	0.141500
13(1)	1185.848	1167.077	0.606430	0.178506	0.141011
14(1)	1067.696	1056.027	0.608797	0.178465	0.141285
15(1)	1006.815	1077.303	0.612268	0.178445	0.141069
16(1)	866.359	872.923	0.605974	0.178073	0.140930
17(1)	565.412	577.433	0.612300	0.178988	0.141270
18(1)	279.332	514.663	0.606949	0.178729	0.140929
19(1)	3034.103	2909.077	0.606255	0.178411	0.141290
20(1)	1451.857	1399.831	0.609969	0.179214	0.141379
21(1)	1000.158	978.877	0.604980	0.178272	0.141297
22(1)	971.068	957.352	0.600426	0.178223	0.141346
23(1)	773.550	759.670	0.605017	0.178325	0.141400
24(1)	685.737	680.984	0.607259	0.178330	0.141419
25(1)	527.129	542.563	0.600846	0.177877	0.141425
26(1)	288.132	298.642	0.605019	0.178395	0.141500
27(1)	68.737	193.729	0.614564	0.179230	0.142351

```
ZPEharm     = 20472.62982 cm-1  =  58.534 Kcal/mol  = 244.907 Kj/mol
ZPEfund     = 20172.95635 cm-1  =  57.677 Kcal/mol  = 241.322 KJ/mol
ZPEaver     = 20322.79309 cm-1  =  58.106 Kcal/mol  = 243.115 KJ/mol
-1/4sumXii =     24.50068 cm-1  =   0.070 Kcal/mol  =   0.293 KJ/mol
x0          =     45.08370 cm-1  =   0.129 Kcal/mol  =   0.539 KJ/mol
ZPEtot      = 20392.37747 cm-1  =  58.305 Kcal/mol  = 243.947 KJ/mol
ZPEtot/ZPEharm = 0.99608   ZPEfund/ZPEharm= 0.98536
```

B4. structure 02 (Cs, Doublet)

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Vibrational Energies and Rotational Constants (cm-1)

Mode(Quanta)	E(harm)	E(anharm)	Aa(z)	Ba(x)	Ca(y)
Equilibrium Geometry			0.593458	0.210354	0.175174
Ground State	20588.732	20354.731	0.590562	0.207644	0.172372
Fundamental Bands (DE w.r.t. Ground State)					
1(1)	3131.956	2998.999	0.590528	0.207330	0.172073
2(1)	3052.750	2951.118	0.590259	0.207370	0.172149
3(1)	3034.014	2945.891	0.590270	0.207593	0.172276
4(1)	2938.625	2805.255	0.590147	0.207671	0.172396
5(1)	1484.940	1435.701	0.589335	0.207342	0.172281
6(1)	1456.091	1442.077	0.590646	0.208322	0.172278
7(1)	1398.846	1360.807	0.589888	0.207219	0.172152
8(1)	1362.060	1326.410	0.590485	0.206944	0.171981
9(1)	1113.258	1074.331	0.588603	0.206813	0.171183
10(1)	998.526	983.258	0.588358	0.207974	0.172268
11(1)	978.507	950.629	0.588079	0.207580	0.172148

```
12(1)             913.772      892.510    0.589319    0.207419    0.172249
13(1)             740.600      735.415    0.587829    0.207654    0.171386
14(1)             705.510      682.625    0.588677    0.207215    0.171634
15(1)             234.281      194.751    0.589051    0.206819    0.171723
16(1)            3120.246     2987.256    0.590665    0.207313    0.172073
17(1)            3077.214     2953.054    0.590415    0.207547    0.172299
18(1)            3054.244     2953.140    0.590200    0.207376    0.172155
19(1)            1446.995     1430.507    0.590058    0.207775    0.172904
20(1)            1433.430     1393.083    0.590240    0.207715    0.172555
21(1)            1140.542     1107.829    0.594798    0.207891    0.172876
22(1)            1108.606     1081.367    0.590741    0.207391    0.172281
23(1)            1044.180     1026.573    0.589289    0.207550    0.172245
24(1)             915.176      898.245    0.591124    0.207142    0.171896
25(1)             819.367      813.029    0.592615    0.207282    0.173048
26(1)             321.941      319.898    0.596145    0.207924    0.172223
27(1)             151.788      214.418    0.591609    0.206784    0.171702

ZPEharm    = 20588.73241 cm-1  =  58.866 Kcal/mol  = 246.296 Kj/mol
ZPEfund    = 19979.08819 cm-1  =  57.123 Kcal/mol  = 239.003 KJ/mol
ZPEaver    = 20283.91030 cm-1  =  57.995 Kcal/mol  = 242.649 KJ/mol
-1/4sumXii =    45.80429 cm-1  =   0.131 Kcal/mol  =   0.548 KJ/mol
x0         =    25.01607 cm-1  =   0.072 Kcal/mol  =   0.299 KJ/mol
ZPEtot     = 20354.73066 cm-1  =  58.197 Kcal/mol  = 243.497 KJ/mol
ZPEtot/ZPEharm = 0.98863   ZPEfund/ZPEharm= 0.97039

B5. structure 05 (Cs, Singlet)
*********************************************************************************************

Vibrational Energies and Rotational Constants (cm-1)
Mode(Quanta)     E(harm)     E(anharm)    Aa(z)        Ba(x)        Ca(y)
Equilibrium Geometry                     0.692771    0.212570    0.173486
Ground State   18262.437    18053.271    0.686796    0.211633    0.172437
Fundamental Bands (DE w.r.t. Ground State)
 1(1)            3236.272     3139.875    0.684177    0.211490    0.172183
 2(1)            3090.963     2948.331    0.686672    0.211547    0.172401
 3(1)            3006.918     2845.575    0.686019    0.211600    0.172448
 4(1)            3000.206     2911.947    0.685944    0.211618    0.172436
 5(1)            1827.293     1783.662    0.682657    0.211073    0.171817
 6(1)            1507.885     1465.539    0.687145    0.211508    0.172572
 7(1)            1456.399     1434.424    0.686002    0.211761    0.172944
 8(1)            1372.972     1339.455    0.684041    0.211012    0.171879
 9(1)            1179.538     1142.230    0.687226    0.211383    0.172189
10(1)            1065.594     1034.272    0.686066    0.212483    0.172351
11(1)            1053.893     1023.607    0.678445    0.211483    0.172010
12(1)             966.228      946.514    0.685373    0.211350    0.171962
13(1)             923.411      900.117    0.687337    0.211978    0.172337
14(1)             674.582      662.360    0.687078    0.211428    0.172063
15(1)             319.562      317.754    0.705623    0.212633    0.172449
16(1)            3070.862     2930.138    0.686296    0.211654    0.172449
17(1)            3063.657     2917.475    0.685964    0.211689    0.172457
18(1)            1450.806     1419.600    0.689767    0.212140    0.172498
19(1)            1109.346     1085.290    0.695324    0.211168    0.172868
20(1)            1028.418     1007.775    0.682159    0.211085    0.172251
21(1)             972.424      945.583    0.686082    0.211532    0.171941
22(1)             698.397      716.413    0.686280    0.211270    0.172635
23(1)             292.195      295.371    0.672719    0.211256    0.172955
24(1)             157.056      203.150    0.686764    0.211176    0.172289

ZPEharm    = 18262.43712 cm-1  =  52.215 Kcal/mol  = 218.467 Kj/mol
ZPEfund    = 17708.22842 cm-1  =  50.630 Kcal/mol  = 211.837 KJ/mol
ZPEaver    = 17985.33277 cm-1  =  51.423 Kcal/mol  = 215.152 KJ/mol
-1/4sumXii =    57.04311 cm-1  =   0.163 Kcal/mol  =   0.682 KJ/mol
x0         =    10.89552 cm-1  =   0.031 Kcal/mol  =   0.130 KJ/mol
ZPEtot     = 18053.27140 cm-1  =  51.617 Kcal/mol  = 215.965 KJ/mol
ZPEtot/ZPEharm = 0.98855   ZPEfund/ZPEharm= 0.96965

B6. structure 06 (C2v, Singlet)
*********************************************************************************************

Vibrational Energies and Rotational Constants (cm-1)
Mode(Quanta)     E(harm)     E(anharm)    Aa(z)        Ba(x)        Ca(y)
```

Equilibrium Geometry			0.653808	0.229968	0.182457
Ground State	18411.183	18193.761	0.646354	0.229140	0.181320
Fundamental Bands (DE w.r.t. Ground State)					
1(1)		3105.296	3000.412	0.645771	0.228991	0.181184
2(1)		3087.627	2975.758	0.645432	0.228995	0.181250
3(1)		1796.090	1723.980	0.645856	0.227825	0.180458
4(1)		1460.009	1401.091	0.646052	0.229232	0.181362
5(1)		1422.504	1382.821	0.646361	0.229376	0.181390
6(1)		1055.226	1031.955	0.641663	0.229124	0.181056
7(1)		1011.224	973.871	0.645464	0.229233	0.181117
8(1)		743.632	727.524	0.643627	0.229329	0.180707
9(1)		3162.158	3028.419	0.645788	0.228994	0.181221
10(1)		1150.209	1121.607	0.646156	0.229855	0.182093
11(1)		938.635	917.145	0.645205	0.228895	0.181551
12(1)		600.858	613.258	0.646438	0.228887	0.181137
13(1)		3172.615	3039.192	0.645623	0.229014	0.181222
14(1)		1075.015	1044.108	0.644560	0.229221	0.180519
15(1)		893.208	900.152	0.644411	0.228885	0.181383
16(1)		739.806	730.184	0.644051	0.229336	0.181183
17(1)		279.364	276.721	0.637013	0.229796	0.181870
18(1)		3189.172	3075.613	0.646060	0.228930	0.181186
19(1)		3088.192	2976.550	0.645391	0.228996	0.181252
20(1)		1428.088	1386.972	0.645598	0.229264	0.181539
21(1)		1125.615	1101.344	0.653599	0.228633	0.181069
22(1)		1047.917	1012.961	0.644503	0.229072	0.181092
23(1)		899.257	881.439	0.646654	0.228440	0.181206
24(1)		350.646	350.181	0.656322	0.229378	0.181352

ZPEharm = 18411.18299 cm-1 = 52.640 Kcal/mol = 220.247 Kj/mol
ZPEfund = 17836.62962 cm-1 = 50.997 Kcal/mol = 213.373 KJ/mol
ZPEaver = 18123.90630 cm-1 = 51.819 Kcal/mol = 216.810 KJ/mol
-1/4sumXii = 30.70063 cm-1 = 0.088 Kcal/mol = 0.367 KJ/mol
x0 = 39.15381 cm-1 = 0.112 Kcal/mol = 0.468 KJ/mol
ZPEtot = 18193.76075 cm-1 = 52.019 Kcal/mol = 217.646 KJ/mol
ZPEtot/ZPEharm = 0.98819 ZPEfund/ZPEharm= 0.96879

B7. structure 08 (Cs, Singlet)
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Vibrational Energies and Rotational Constants (cm-1)

Mode(Quanta)	E(harm)	E(anharm)	Aa(z)	Ba(x)	Ca(y)
Equilibrium Geometry			1.162190	0.139205	0.130659
Ground State	18129.518	17906.115	1.159348	0.138552	0.129953
Fundamental Bands (DE w.r.t. Ground State)					
1(1)		3113.885	2986.001	1.159094	0.138465	0.129886
2(1)		3098.101	3000.432	1.157787	0.138433	0.129875
3(1)		3094.202	2970.732	1.162549	0.138257	0.129749
4(1)		3004.287	2924.674	1.157001	0.138545	0.129954
5(1)		2007.900	1959.518	1.151549	0.137982	0.129357
6(1)		1479.535	1447.707	1.173525	0.138613	0.130066
7(1)		1444.992	1416.326	1.152811	0.138479	0.130058
8(1)		1377.122	1338.506	1.155802	0.138195	0.129692
9(1)		1335.435	1300.471	1.156171	0.138682	0.129876
10(1)		1133.760	1113.726	1.148434	0.138822	0.130081
11(1)		1069.219	1044.250	1.182604	0.138429	0.129627
12(1)		865.778	843.254	1.164521	0.137961	0.129570
13(1)		847.431	830.377	1.152080	0.138540	0.129880
14(1)		558.926	566.765	1.185750	0.138449	0.129832
15(1)		205.263	204.090	1.180276	0.139056	0.130143
16(1)		3171.535	3059.530	1.157451	0.138475	0.129885
17(1)		3064.478	2905.490	1.158089	0.138553	0.129955
18(1)		1460.955	1430.971	1.151515	0.138804	0.130000
19(1)		1034.382	1007.362	1.138220	0.138445	0.129924
20(1)		996.680	992.211	1.166229	0.138552	0.130086
21(1)		877.842	860.366	1.155490	0.138649	0.129926
22(1)		527.490	519.817	1.146143	0.138541	0.129961
23(1)		324.739	332.436	1.162452	0.138532	0.130103
24(1)		165.099	129.650	1.143127	0.138485	0.129971

iZPEharm = 18129.51803 cm-1 = 51.835 Kcal/mol = 216.877 Kj/mol
ZPEfund = 17592.33269 cm-1 = 50.299 Kcal/mol = 210.451 KJ/mol

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ZPEaver    = 17860.92536 cm-1  =  51.067 Kcal/mol  = 213.664 KJ/mol
-1/4sumXii =    51.90393 cm-1  =   0.148 Kcal/mol  =   0.621 KJ/mol
x0         =    -6.71415 cm-1  =  -0.019 Kcal/mol  =  -0.080 KJ/mol
ZPEtot     = 17906.11513 cm-1  =  51.196 Kcal/mol  = 214.205 KJ/mol
ZPEtot/ZPEharm = 0.98768   ZPEfund/ZPEharm= 0.97037
```

B8. structure 09 (Cs, Singlet)

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Vibrational Energies and Rotational Constants (cm-1)
Mode(Quanta)     E(harm)     E(anharm)    Aa(z)       Ba(x)       Ca(y)
Equilibrium Geometry                    0.922990    0.150280    0.135724
Ground State   18254.733    18043.843    0.915763    0.149954    0.134988
Fundamental Bands (DE w.r.t. Ground State)
 1(1)           3437.762     3332.713    0.910277    0.149872    0.134802
 2(1)           3102.825     2969.656    0.914698    0.149924    0.134972
 3(1)           3021.806     2962.405    0.914244    0.149938    0.134972
 4(1)           3006.061     2911.753    0.914838    0.149878    0.134959
 5(1)           2169.069     2137.400    0.903995    0.149711    0.134529
 6(1)           1484.730     1454.384    0.943559    0.150028    0.135278
 7(1)           1450.607     1424.904    0.914773    0.150013    0.135245
 8(1)           1383.770     1340.954    0.915830    0.149588    0.134706
 9(1)           1316.794     1286.142    0.915038    0.150014    0.134648
10(1)           1068.878     1036.761    0.894143    0.149562    0.135097
11(1)           1008.061      980.208    0.910349    0.149762    0.134551
12(1)            836.552      820.645    0.917374    0.149618    0.134485
13(1)            610.963      616.576    0.919038    0.150027    0.135054
14(1)            507.143      500.900    0.920524    0.150055    0.134793
15(1)            196.656      190.766    0.913717    0.149936    0.135150
16(1)           3111.102     2955.960    0.914784    0.149922    0.134957
17(1)           3041.704     2890.627    0.915567    0.149892    0.134945
18(1)           1474.227     1443.908    0.885888    0.150314    0.135028
19(1)           1265.249     1228.698    0.914802    0.149911    0.135146
20(1)           1083.761     1059.838    0.935645    0.150209    0.134878
21(1)            772.181      758.954    0.913478    0.149743    0.134810
22(1)            602.554      643.998    0.916855    0.149904    0.135036
23(1)            343.560      341.666    0.917945    0.149757    0.135140
24(1)            213.449      192.012    0.926507    0.150655    0.135048

ZPEharm    = 18254.73259 cm-1  =  52.193 Kcal/mol  = 218.375 Kj/mol
ZPEfund    = 17740.91346 cm-1  =  50.724 Kcal/mol  = 212.228 KJ/mol
ZPEaver    = 17997.82302 cm-1  =  51.458 Kcal/mol  = 215.302 KJ/mol
-1/4sumXii =    52.10202 cm-1  =   0.149 Kcal/mol  =   0.623 KJ/mol
x0         =    -6.08162 cm-1  =  -0.017 Kcal/mol  =  -0.073 KJ/mol
ZPEtot     = 18043.84343 cm-1  =  51.590 Kcal/mol  = 215.852 KJ/mol
ZPEtot/ZPEharm = 0.98845   ZPEfund/ZPEharm= 0.97185
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B9. structure10 (C1, Doublet)

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Vibrational Energies and Rotational Constants (cm-1)
Mode(Quanta)     E(harm)     E(anharm)    Aa(z)       Ba(x)       Ca(y)
Equilibrium Geometry                    0.882113    0.137740    0.130733
Ground State   20393.031    20128.520    0.873067    0.137098    0.129692
Fundamental Bands (DE w.r.t. Ground State)
 1(1)           3129.709     2970.119    0.872969    0.136935    0.129471
 2(1)           3104.095     2967.377    0.872136    0.137096    0.129687
 3(1)           3098.191     2984.955    0.871722    0.137107    0.129710
 4(1)           3018.288     2973.134    0.871066    0.137120    0.129713
 5(1)           3016.204     2869.541    0.868952    0.137173    0.129751
 6(1)           3014.713     2857.711    0.873537    0.137004    0.129629
 7(1)           2931.098     2765.005    0.874438    0.136984    0.129604
 8(1)           1711.268     1682.976    0.870856    0.136631    0.129359
 9(1)           1482.985     1463.032    0.872302    0.137148    0.129920
10(1)           1473.343     1451.004    0.878053    0.137206    0.129729
11(1)           1431.100     1406.324    0.875012    0.137064    0.129850
12(1)           1395.680     1350.478    0.872519    0.137150    0.129785
13(1)           1378.185     1355.862    0.866992    0.136970    0.129465
14(1)           1299.317     1272.315    0.870381    0.137145    0.129379
15(1)           1248.285     1216.477    0.869442    0.137119    0.129796
16(1)           1105.401     1073.405    0.885943    0.136880    0.129458
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17(1)           1066.136     1045.729    0.860263    0.137052    0.129765
18(1)           1004.224      976.996    0.863320    0.137059    0.129297
19(1)            938.649      921.255    0.878101    0.137121    0.129756
20(1)            862.484      835.627    0.865769    0.137163    0.129680
21(1)            823.279      810.986    0.876044    0.136632    0.129222
22(1)            762.695      760.729    0.870029    0.136953    0.129575
23(1)            542.921      527.436    0.887262    0.136475    0.129070
24(1)            353.418      336.422    0.856202    0.137859    0.130265
25(1)            280.603      270.888    0.891238    0.136331    0.128866
26(1)            206.182      224.977    0.876809    0.136974    0.129613
27(1)            107.608      102.969    0.863354    0.138025    0.130191

ZPEharm    = 20393.03095 cm-1  =  58.307 Kcal/mol  = 243.955 Kj/mol
ZPEfund    = 19736.86291 cm-1  =  56.431 Kcal/mol  = 236.105 KJ/mol
ZPEaver    = 20064.94693 cm-1  =  57.369 Kcal/mol  = 240.030 KJ/mol
-1/4sumXii =    83.58606 cm-1  =   0.239 Kcal/mol  =   1.000 KJ/mol
x0         =   -20.01258 cm-1  =  -0.057 Kcal/mol  =  -0.239 KJ/mol
ZPEtot     = 20128.52042 cm-1  =  57.550 Kcal/mol  = 240.791 KJ/mol
ZPEtot/ZPEharm = 0.98703   ZPEfund/ZPEharm= 0.96782

B10. structure14 (D3h, Singlet)
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Vibrational Energies and Rotational Constants (cm-1)
Mode(Quanta)     E(harm)     E(anharm)    Aa(z)       Ba(x)       Ca(y)
Equilibrium Geometry                    1.419197    0.147464    0.133583
Ground State   18409.178    18271.002    1.395993    0.146869    0.132785
Fundamental Bands (DE w.r.t. Ground State)
 1(1)           3211.308     3100.413    1.393167    0.146790    0.132705
 2(1)           3121.749     3010.778    1.392120    0.146807    0.132703
 3(1)           3108.228     2987.702    1.392488    0.146770    0.132678
 4(1)           1662.783     1615.817    1.389030    0.146535    0.132426
 5(1)           1454.264     1418.212    1.397270    0.146944    0.132698
 6(1)           1294.070     1267.878    1.401429    0.146844    0.132836
 7(1)           1212.820     1188.405    1.397143    0.146837    0.132389
 8(1)            890.543      880.085    1.369896    0.146705    0.132536
 9(1)            510.616      508.251    1.396886    0.146996    0.132704
10(1)           1036.690     1027.262    1.393116    0.147630    0.132820
11(1)            911.697      919.837    1.369833    0.146764    0.132827
12(1)            526.176      560.262    1.392655    0.146753    0.132789
13(1)            173.745      179.149    1.335445    0.147050    0.133177
14(1)            977.314      974.307    1.389131    0.146896    0.132846
15(1)            913.353      921.324    1.423455    0.146793    0.132834
16(1)            765.434      771.775    1.383150    0.146746    0.132816
17(1)           3211.208     3100.269    1.393110    0.146788    0.132704
18(1)           3121.370     3015.486    1.391982    0.146789    0.132690
19(1)           3118.350     3045.276    1.392378    0.146804    0.132699
20(1)           1617.317     1580.006    1.393599    0.146582    0.132465
21(1)           1394.433     1363.977    1.398225    0.146886    0.132713
22(1)           1301.338     1282.355    1.401705    0.147025    0.132753
23(1)            987.070      983.630    1.415376    0.146049    0.132709
24(1)            296.482      299.233    1.454834    0.146883    0.132736

ZPEharm    = 18409.17784 cm-1  =  52.634 Kcal/mol  = 220.223 Kj/mol
ZPEfund    = 18000.84432 cm-1  =  51.467 Kcal/mol  = 215.338 KJ/mol
ZPEaver    = 18205.01108 cm-1  =  52.051 Kcal/mol  = 217.780 KJ/mol
-1/4sumXii =    19.03991 cm-1  =   0.054 Kcal/mol  =   0.228 KJ/mol
x0         =    46.95148 cm-1  =   0.134 Kcal/mol  =   0.562 KJ/mol
ZPEtot     = 18271.00248 cm-1  =  52.239 Kcal/mol  = 218.570 KJ/mol
ZPEtot/ZPEharm = 0.99249   ZPEfund/ZPEharm= 0.97782

B11. TS R1 (2-Methylallyl radical -> structure 02) (C1, Doublet)
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Vibrational Energies and Rotational Constants (cm-1)
Mode(Quanta)     E(harm)     E(anharm)    Aa(z)       Ba(x)       Ca(y)
Equilibrium Geometry                    0.432822    0.240396    0.169821
Ground State   19366.706    19113.163    0.404265    0.236739    0.168380
Fundamental Bands (DE w.r.t. Ground State)
 1(1)           -933.077     -978.670    0.377602    0.235403    0.168754
 2(1)           3191.155     3057.426    0.404261    0.236451    0.168270
```

3(1)	3151.306	2997.876	0.404599	0.236283	0.168150
4(1)	3090.435	2976.305	0.404047	0.236536	0.168332
5(1)	3086.153	2960.141	0.404084	0.236654	0.168338
6(1)	3035.936	2905.569	0.404344	0.236615	0.168317
7(1)	3005.809	2829.186	0.404478	0.236436	0.168238
8(1)	2956.577	2818.840	0.403698	0.236944	0.168496
9(1)	1514.823	1439.285	0.403375	0.236472	0.168201
10(1)	1458.585	1437.804	0.404064	0.237000	0.168684
11(1)	1451.209	1426.849	0.404178	0.237618	0.168455
12(1)	1418.689	1389.277	0.404194	0.236678	0.168420
13(1)	1404.032	1368.984	0.403570	0.236302	0.168381
14(1)	1365.554	1334.014	0.404157	0.235859	0.167937
15(1)	1261.545	1242.631	0.404527	0.236244	0.167858
16(1)	1055.064	1028.568	0.404332	0.236152	0.168227
17(1)	999.606	978.335	0.404889	0.236496	0.168265
18(1)	945.605	927.311	0.404384	0.236721	0.168737
19(1)	929.795	915.869	0.378228	0.235595	0.168204
20(1)	879.026	848.854	0.402989	0.235912	0.168145
21(1)	830.518	812.495	0.404180	0.235837	0.167885
22(1)	683.385	657.293	0.403471	0.236753	0.168224
23(1)	629.242	604.914	0.403373	0.236967	0.168072
24(1)	584.060	594.652	0.401585	0.237358	0.168183
25(1)	352.792	347.735	0.406614	0.237196	0.168264
26(1)	261.149	256.195	0.404267	0.236216	0.168376
27(1)	124.438	254.397	0.404556	0.235941	0.167976

ZPEharm = 19366.70584 cm-1 = 55.372 Kcal/mol = 231.677 Kj/mol
ZPEfund = 18716.06728 cm-1 = 53.512 Kcal/mol = 223.894 KJ/mol
ZPEaver = 19041.38656 cm-1 = 54.442 Kcal/mol = 227.786 KJ/mol
-1/4sumXii = 76.18494 cm-1 = 0.218 Kcal/mol = 0.911 KJ/mol
x0 = -4.40890 cm-1 = -0.013 Kcal/mol = -0.053 KJ/mol
ZPEtot = 19113.16260 cm-1 = 54.647 Kcal/mol = 228.644 KJ/mol
ZPEtot/ZPEharm = 0.98691 ZPEfund/ZPEharm= 0.96640

B12. TS R2 (structure 02 -> structure05 + H) (C1, Doublet)
****

Vibrational Energies and Rotational Constants (cm-1)

Mode(Quanta)	E(harm)	E(anharm)	Aa(z)	Ba(x)	Ca(y)
Equilibrium Geometry			0.545560	0.196502	0.165615
Ground State	18168.957	17862.482	0.511562	0.196060	0.164176
Fundamental Bands (DE w.r.t. Ground State)					
1(1)	-476.591	-690.437	0.485863	0.195826	0.163928
2(1)	3242.105	3149.777	0.510901	0.195755	0.164001
3(1)	3091.806	2954.836	0.511484	0.195977	0.164138
4(1)	3074.880	2927.545	0.510885	0.196059	0.164166
5(1)	3060.089	2915.298	0.511333	0.196093	0.164196
6(1)	3009.727	2840.064	0.510877	0.196013	0.164159
7(1)	2999.455	2922.949	0.511140	0.196044	0.164173
8(1)	1795.083	1760.421	0.513334	0.195318	0.163576
9(1)	1502.521	1462.217	0.510604	0.196201	0.164282
10(1)	1457.510	1433.334	0.511179	0.196164	0.164635
11(1)	1451.906	1421.106	0.511382	0.196756	0.164217
12(1)	1372.125	1339.383	0.511812	0.195300	0.163686
13(1)	1179.122	1146.267	0.513838	0.195621	0.163935
14(1)	1102.753	1077.985	0.511553	0.196624	0.164543
15(1)	1063.811	1030.429	0.513391	0.196473	0.164147
16(1)	1053.367	1018.243	0.508578	0.195473	0.163817
17(1)	1027.059	998.652	0.507208	0.195867	0.163982
18(1)	974.431	947.537	0.513225	0.196144	0.163800
19(1)	961.025	935.823	0.509807	0.195448	0.163718
20(1)	918.438	892.765	0.512440	0.196331	0.164104
21(1)	707.938	639.390	0.509589	0.195765	0.164268
22(1)	673.915	659.709	0.510996	0.195858	0.163855
23(1)	323.557	316.670	0.511730	0.196405	0.164301
24(1)	313.800	305.057	0.509927	0.196419	0.164596
25(1)	196.334	182.233	0.497390	0.196615	0.164355
26(1)	150.438	136.979	0.511176	0.195918	0.164251
27(1)	111.311	120.793	0.492526	0.196258	0.163054

ZPEharm = 18168.95730 cm-1 = 51.948 Kcal/mol = 217.349 Kj/mol

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ZPEfund    = 17422.51142 cm-1  =  49.813 Kcal/mol  = 208.420 KJ/mol
ZPEaver    = 17795.73436 cm-1  =  50.881 Kcal/mol  = 212.884 KJ/mol
-1/4sumXii =    93.16675 cm-1  =   0.266 Kcal/mol  =   1.115 KJ/mol
x0         =   -26.41892 cm-1  =  -0.076 Kcal/mol  =  -0.316 KJ/mol
ZPEtot     = 17862.48219 cm-1  =  51.071 Kcal/mol  = 213.683 KJ/mol
ZPEtot/ZPEharm = 0.98313   ZPEfund/ZPEharm= 0.95892
```

B13. TS R3 (structure02 -> structure06 + H) (Cs, Doublet)

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Vibrational Energies and Rotational Constants (cm-1)

Mode(Quanta)	E(harm)	E(anharm)	Aa(z)	Ba(x)	Ca(y)
Equilibrium Geometry			0.557336	0.200154	0.170579
Ground State	18353.149	18118.069	0.529177	0.197878	0.170674
Fundamental Bands (DE w.r.t. Ground State)					
1(1)	-424.064	-570.372	0.508938	0.195721	0.171019
2(1)	3170.511	3041.053	0.528780	0.197809	0.170595
3(1)	3110.679	2988.113	0.528514	0.197749	0.170565
4(1)	3085.218	2976.387	0.528607	0.197793	0.170622
5(1)	1767.706	1671.601	0.530865	0.196982	0.169801
6(1)	1456.367	1405.003	0.529131	0.197949	0.170701
7(1)	1419.879	1382.383	0.529383	0.198053	0.170710
8(1)	1071.975	1044.003	0.528547	0.197942	0.169974
9(1)	1052.330	1029.753	0.525929	0.197917	0.170440
10(1)	1009.767	978.181	0.528495	0.197945	0.170510
11(1)	892.440	903.413	0.527430	0.197569	0.170682
12(1)	742.700	730.516	0.527682	0.197989	0.170148
13(1)	736.894	730.059	0.527498	0.198078	0.170630
14(1)	287.873	293.742	0.519903	0.198198	0.171276
15(1)	157.022	157.689	0.518600	0.197280	0.171918
16(1)	3195.390	3067.149	0.528595	0.197703	0.170580
17(1)	3159.845	3030.126	0.528890	0.197797	0.170597
18(1)	3085.920	2977.439	0.528565	0.197791	0.170623
19(1)	1426.210	1390.187	0.528680	0.197983	0.170868
20(1)	1148.915	1120.495	0.529086	0.198456	0.171337
21(1)	1127.028	1104.439	0.533790	0.197471	0.170477
22(1)	1047.412	1015.654	0.527680	0.197822	0.170482
23(1)	939.146	925.350	0.528205	0.197761	0.170881
24(1)	900.597	857.511	0.529299	0.197309	0.170567
25(1)	633.439	657.618	0.526872	0.197523	0.170562
26(1)	350.242	348.175	0.536837	0.198124	0.170729
27(1)	154.858	148.488	0.516655	0.197451	0.171110

```
ZPEharm    = 18353.14886 cm-1  =  52.474 Kcal/mol  = 219.552 Kj/mol
ZPEfund    = 17702.07780 cm-1  =  50.613 Kcal/mol  = 211.764 KJ/mol
ZPEaver    = 18027.61333 cm-1  =  51.544 Kcal/mol  = 215.658 KJ/mol
-1/4sumXii =    48.71499 cm-1  =   0.139 Kcal/mol  =   0.583 KJ/mol
x0         =    41.74108 cm-1  =   0.119 Kcal/mol  =   0.499 KJ/mol
ZPEtot     = 18118.06941 cm-1  =  51.802 Kcal/mol  = 216.740 KJ/mol
ZPEtot/ZPEharm = 0.98719   ZPEfund/ZPEharm= 0.96453
```

B14. TS L1 (2-Methylallyl radical -> structure10) (C1, Doublet)

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Vibrational Energies and Rotational Constants (cm-1)

Mode(Quanta)	E(harm)	E(anharm)	Aa(z)	Ba(x)	Ca(y)
Equilibrium Geometry			0.488264	0.216629	0.163529
Ground State	19172.046	18881.574	0.484776	0.215265	0.162353
Fundamental Bands (DE w.r.t. Ground State)					
1(1)	-978.571	-1001.679	0.486341	0.216177	0.163509
2(1)	3171.605	3005.894	0.484266	0.215116	0.162205
3(1)	3161.883	3030.007	0.485047	0.215278	0.162401
4(1)	3149.299	3004.582	0.484656	0.215203	0.162333
5(1)	3073.160	2945.868	0.484272	0.214972	0.162111
6(1)	3012.355	2872.484	0.486983	0.215607	0.162757
7(1)	2991.901	2827.553	0.484185	0.215196	0.162294
8(1)	2905.071	2720.919	0.489171	0.215728	0.163044
9(1)	1589.744	1561.668	0.483469	0.214942	0.162252
10(1)	1463.614	1431.606	0.485093	0.215233	0.162367
11(1)	1450.894	1452.614	0.485683	0.215400	0.162352
12(1)	1405.748	1356.959	0.484880	0.215202	0.162545

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13(1)           1404.370     1337.567    0.485347    0.215251    0.162432
14(1)           1279.211     1246.241    0.482070    0.214798    0.161668
15(1)           1111.391     1079.531    0.485495    0.215122    0.162066
16(1)           1039.744     1013.712    0.484887    0.215169    0.162264
17(1)            984.253      959.338    0.485879    0.215231    0.162469
18(1)            960.333      937.676    0.482509    0.215009    0.161704
19(1)            931.931      908.765    0.482962    0.214733    0.162078
20(1)            807.425      793.574    0.483760    0.214911    0.161751
21(1)            772.544      751.537    0.482269    0.214852    0.161661
22(1)            719.629      712.399    0.483728    0.215462    0.162696
23(1)            613.568      595.072    0.484175    0.215065    0.162280
24(1)            475.882      447.847    0.482395    0.214458    0.161560
25(1)            336.133      326.107    0.490013    0.215141    0.162269
26(1)            314.833      305.910    0.480168    0.215053    0.161944
27(1)            196.142      225.654    0.482286    0.215116    0.162168

iZPEharm    = 19172.04633 cm-1  =  54.816 Kcal/mol  = 229.349 Kj/mol
ZPEfund     = 18424.70097 cm-1  =  52.679 Kcal/mol  = 220.408 KJ/mol
ZPEaver     = 18798.37365 cm-1  =  53.747 Kcal/mol  = 224.878 KJ/mol
-1/4sumXii =   107.44558 cm-1  =   0.307 Kcal/mol  =   1.285 KJ/mol
x0          =   -24.24487 cm-1  =  -0.069 Kcal/mol  =  -0.290 KJ/mol
ZPEtot      = 18881.57436 cm-1  =  53.985 Kcal/mol  = 225.874 KJ/mol
ZPEtot/ZPEharm = 0.98485   ZPEfund/ZPEharm= 0.96102

B15. TS L2 (structure10 -> 1-Methylallyl radical) (C1, Doublet)
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Vibrational Energies and Rotational Constants (cm-1)
Mode(Quanta)     E(harm)     E(anharm)    Aa(z)       Ba(x)       Ca(y)
Equilibrium Geometry                     0.676808    0.161129    0.137356
Ground State   18486.093    18262.922    0.675410    0.159655    0.136114
Fundamental Bands (DE w.r.t. Ground State)
 1(1)          -1765.010    -1849.358    0.672202    0.160452    0.136548
 2(1)           3169.673     3050.666    0.675920    0.159382    0.135955
 3(1)           3111.506     2974.240    0.675408    0.159473    0.135992
 4(1)           3097.842     2962.067    0.675148    0.159573    0.136060
 5(1)           3065.169     2931.978    0.675030    0.159670    0.136127
 6(1)           3060.380     2926.777    0.675563    0.159449    0.135992
 7(1)           2990.397     2915.092    0.675286    0.159572    0.136095
 8(1)           2144.646     2090.766    0.673677    0.159866    0.136087
 9(1)           1617.302     1614.849    0.667243    0.160137    0.136189
10(1)           1463.133     1441.650    0.676055    0.159629    0.136292
11(1)           1457.660     1420.595    0.679384    0.159875    0.136199
12(1)           1419.555     1385.556    0.676273    0.159526    0.136055
13(1)           1367.213     1339.120    0.671464    0.159428    0.135843
14(1)           1345.651     1316.171    0.673073    0.159923    0.136112
15(1)           1152.686     1120.884    0.673010    0.159784    0.136111
16(1)           1110.460     1081.093    0.675174    0.159200    0.135935
17(1)           1052.933     1038.434    0.677744    0.159475    0.135828
18(1)           1009.101      996.309    0.677704    0.159537    0.135943
19(1)            990.617      971.772    0.670727    0.159484    0.135960
20(1)            851.827      834.793    0.677848    0.158757    0.135499
21(1)            784.907      792.162    0.672662    0.159793    0.136229
22(1)            747.785      731.392    0.675579    0.159280    0.135937
23(1)            507.076      502.851    0.686107    0.159459    0.136019
24(1)            491.674      489.349    0.673777    0.158921    0.135668
25(1)            384.778      380.792    0.672136    0.159417    0.136140
26(1)            189.593      188.603    0.684175    0.159533    0.135906
27(1)            153.632      190.989    0.674895    0.159130    0.135872

ZPEharm     = 18486.09327 cm-1  =  52.854 Kcal/mol  = 221.143 Kj/mol
ZPEfund     = 17919.79554 cm-1  =  51.235 Kcal/mol  = 214.368 KJ/mol
ZPEaver     = 18202.94440 cm-1  =  52.045 Kcal/mol  = 217.756 KJ/mol
-1/4sumXii =    77.54444 cm-1  =   0.222 Kcal/mol  =   0.928 KJ/mol
x0          =   -17.56685 cm-1  =  -0.050 Kcal/mol  =  -0.210 KJ/mol
ZPEtot      = 18262.92200 cm-1  =  52.216 Kcal/mol  = 218.473 KJ/mol
ZPEtot/ZPEharm = 0.98793   ZPEfund/ZPEharm= 0.96937

B16. TS L3 (structure10 -> structure08 + H) (C1, Doublet)
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Vibrational Energies and Rotational Constants (cm-1)

Mode(Quanta)	E(harm)	E(anharm)	Aa(z)	Ba(x)	Ca(y)
Equilibrium Geometry			0.835245	0.134828	0.127650
Ground State	18122.605	17790.232	0.794435	0.134019	0.126614
Fundamental Bands (DE w.r.t. Ground State)					
1(1)	-503.550	-811.012	0.754706	0.133662	0.126269
2(1)	3161.340	3018.489	0.794106	0.133982	0.126575
3(1)	3118.284	2974.293	0.794070	0.133938	0.126548
4(1)	3103.251	2978.451	0.796370	0.133743	0.126417
5(1)	3089.852	2962.957	0.793674	0.133974	0.126581
6(1)	3078.369	2928.210	0.793459	0.134009	0.126599
7(1)	3011.045	2924.789	0.793046	0.134003	0.126599
8(1)	1971.513	1915.179	0.794681	0.133405	0.126049
9(1)	1475.620	1441.459	0.804071	0.134285	0.126781
10(1)	1464.711	1422.531	0.789580	0.133919	0.126630
11(1)	1437.256	1407.867	0.794238	0.134004	0.126654
12(1)	1377.127	1335.887	0.789425	0.133792	0.126350
13(1)	1328.781	1292.851	0.792915	0.134060	0.126594
14(1)	1124.199	1092.054	0.789197	0.134206	0.126750
15(1)	1069.378	1041.271	0.803096	0.133860	0.126372
16(1)	1028.946	998.934	0.785082	0.133960	0.126550
17(1)	983.719	968.370	0.800992	0.134058	0.126697
18(1)	886.561	877.104	0.790992	0.134006	0.126577
19(1)	862.009	842.716	0.796756	0.133586	0.126243
20(1)	848.009	823.333	0.788217	0.134026	0.126585
21(1)	561.306	553.385	0.806906	0.133909	0.126508
22(1)	522.510	515.507	0.792527	0.134031	0.126628
23(1)	366.077	368.505	0.783518	0.134013	0.126553
24(1)	310.111	286.121	0.773472	0.134353	0.126412
25(1)	219.402	218.188	0.805552	0.133959	0.126815
26(1)	195.616	192.941	0.779453	0.134228	0.126641
27(1)	153.769	84.291	0.788018	0.133931	0.126545

ZPEharm = 18122.60545 cm-1 = 51.815 Kcal/mol = 216.795 Kj/mol
ZPEfund = 17327.33600 cm-1 = 49.541 Kcal/mol = 207.281 KJ/mol
ZPEaver = 17724.97072 cm-1 = 50.678 Kcal/mol = 212.038 KJ/mol
-1/4sumXii = 79.40158 cm-1 = 0.227 Kcal/mol = 0.950 KJ/mol
x0 = -14.14074 cm-1 = -0.040 Kcal/mol = -0.169 KJ/mol
ZPEtot = 17790.23157 cm-1 = 50.865 Kcal/mol = 212.818 KJ/mol
ZPEtot/ZPEharm = 0.98166 ZPEfund/ZPEharm= 0.95612

B17. TS L4 (1-Methylallyl radical -> structure08 + H) (C1, Doublet)
****

Vibrational Energies and Rotational Constants (cm-1)

Mode(Quanta)	E(harm)	E(anharm)	Aa(z)	Ba(x)	Ca(y)
Equilibrium Geometry			0.898440	0.132885	0.129350
Ground State	18070.745	17846.878	0.864968	0.132058	0.126283
Fundamental Bands (DE w.r.t. Ground State)					
1(1)	-587.341	-850.777	0.805840	0.131706	0.125697
2(1)	3186.578	3063.021	0.864892	0.131993	0.126129
3(1)	3115.193	3009.536	0.863663	0.131998	0.126261
4(1)	3103.292	3001.253	0.862809	0.131983	0.126239
5(1)	3096.108	2980.186	0.867921	0.131828	0.125944
6(1)	3060.739	2942.273	0.864196	0.132023	0.126313
7(1)	3003.305	2952.336	0.863185	0.132029	0.126323
8(1)	1954.851	1907.933	0.865438	0.131491	0.125689
9(1)	1477.589	1452.722	0.872200	0.132212	0.126384
10(1)	1460.359	1434.444	0.865669	0.132134	0.126241
11(1)	1438.931	1413.085	0.863271	0.132048	0.126364
12(1)	1376.998	1352.404	0.859451	0.131808	0.126063
13(1)	1334.338	1301.363	0.863819	0.132078	0.126262
14(1)	1131.429	1123.070	0.857898	0.132156	0.126540
15(1)	1071.801	1050.602	0.877051	0.131855	0.125997
16(1)	1028.964	1019.740	0.853336	0.131985	0.126313
17(1)	993.660	979.580	0.870151	0.132064	0.126386
18(1)	865.733	852.516	0.867255	0.131820	0.125966
19(1)	856.505	833.502	0.863382	0.132109	0.125987
20(1)	850.197	839.530	0.865755	0.131936	0.126118
21(1)	566.889	555.535	0.859853	0.132014	0.125799
22(1)	543.539	538.601	0.858128	0.132097	0.125875

23(1)	400.637	398.092	0.861639	0.132224	0.125865
24(1)	365.430	368.445	0.865270	0.132047	0.125402
25(1)	220.485	241.017	0.863878	0.132130	0.126893
26(1)	155.985	141.913	0.871667	0.132272	0.125627
27(1)	69.294	88.707	0.869579	0.131869	0.124824

ZPEharm = 18070.74473 cm-1 = 51.667 Kcal/mol = 216.174 Kj/mol
ZPEfund = 17495.31365 cm-1 = 50.022 Kcal/mol = 209.290 KJ/mol
ZPEaver = 17783.02919 cm-1 = 50.844 Kcal/mol = 212.732 KJ/mol
-1/4sumXii = 80.64145 cm-1 = 0.231 Kcal/mol = 0.965 KJ/mol
x0 = -16.79306 cm-1 = -0.048 Kcal/mol = -0.201 KJ/mol
ZPEtot = 17846.87759 cm-1 = 51.027 Kcal/mol = 213.496 KJ/mol
ZPEtot/ZPEharm = 0.98761 ZPEfund/ZPEharm= 0.96816

B18. TS L5 (1-Methylallyl radical -> structure 13 + H) (C1, Doublet)
****

Vibrational Energies and Rotational Constants (cm-1)

Mode(Quanta)	E(harm)	E(anharm)	Aa(z)	Ba(x)	Ca(y)
Equilibrium Geometry			0.992470	0.133307	0.125915
Ground State	18346.969	18062.717	0.922808	0.131414	0.125207
Fundamental Bands (DE w.r.t. Ground State)					
1(1)	-422.197	-739.738	0.850474	0.130182	0.124994
2(1)	3215.817	3089.328	0.920602	0.131344	0.125146
3(1)	3212.058	3077.269	0.921468	0.131345	0.125132
4(1)	3125.587	2996.227	0.920791	0.131346	0.125139
5(1)	3122.306	2999.937	0.921097	0.131332	0.125118
6(1)	3120.247	3028.506	0.921182	0.131336	0.125120
7(1)	3109.513	2968.658	0.921340	0.131303	0.125106
8(1)	1648.504	1603.668	0.925333	0.131147	0.124873
9(1)	1604.912	1569.101	0.926878	0.131190	0.124897
10(1)	1453.280	1413.825	0.924979	0.131438	0.125114
11(1)	1390.650	1358.129	0.925523	0.131414	0.125130
12(1)	1300.279	1273.652	0.923672	0.131557	0.125175
13(1)	1289.753	1260.860	0.925505	0.131458	0.125249
14(1)	1213.823	1188.639	0.924253	0.131343	0.124846
15(1)	1034.251	1015.119	0.920851	0.132091	0.125248
16(1)	987.499	976.880	0.931826	0.130730	0.125156
17(1)	972.473	955.216	0.922013	0.131416	0.125236
18(1)	911.174	891.798	0.930876	0.131429	0.125233
19(1)	908.087	883.060	0.918312	0.131297	0.125167
20(1)	892.196	876.566	0.915092	0.131026	0.124975
21(1)	769.442	746.577	0.914759	0.131339	0.125226
22(1)	546.333	530.686	0.917701	0.131285	0.125264
23(1)	509.949	505.955	0.923846	0.131346	0.125089
24(1)	297.920	296.557	0.950259	0.131490	0.125169
25(1)	207.220	210.263	0.885229	0.131160	0.125702
26(1)	142.776	137.324	0.933240	0.131379	0.126788
27(1)	130.088	138.246	0.859399	0.130661	0.123887

ZPEharm = 18346.96894 cm-1 = 52.457 Kcal/mol = 219.478 Kj/mol
ZPEfund = 17626.15353 cm-1 = 50.396 Kcal/mol = 210.856 KJ/mol
ZPEaver = 17986.56124 cm-1 = 51.426 Kcal/mol = 215.167 KJ/mol
-1/4sumXii = 67.36358 cm-1 = 0.193 Kcal/mol = 0.806 KJ/mol
x0 = 8.79170 cm-1 = 0.025 Kcal/mol = 0.105 KJ/mol
ZPEtot = 18062.71652 cm-1 = 51.644 Kcal/mol = 216.078 KJ/mol
ZPEtot/ZPEharm = 0.98451 ZPEfund/ZPEharm= 0.96071

B19. TS L6 (structure10 -> structure09 + H) (Cs, Doublet)
****

Vibrational Energies and Rotational Constants (cm-1)

Mode(Quanta)	E(harm)	E(anharm)	Aa(z)	Ba(x)	Ca(y)
Equilibrium Geometry			0.664741	0.149889	0.128105
Ground State	18185.976	17944.014	0.646651	0.148699	0.126457
Fundamental Bands (DE w.r.t. Ground State)					
1(1)	-439.063	-304.781	0.642169	0.148442	0.126009
2(1)	3434.656	3259.642	0.646141	0.148569	0.126343
3(1)	3102.993	2974.314	0.645698	0.148666	0.126443
4(1)	3022.720	2966.510	0.645784	0.148675	0.126433
5(1)	3005.447	2912.871	0.646572	0.148573	0.126408

6(1)	2135.202	2086.937	0.644015	0.148424	0.126157
7(1)	1485.731	1449.247	0.654776	0.149000	0.126762
8(1)	1450.403	1426.738	0.646028	0.148756	0.126672
9(1)	1381.112	1352.554	0.645433	0.148418	0.126224
10(1)	1312.685	1279.452	0.645469	0.148834	0.126182
11(1)	1063.751	1042.560	0.634689	0.148630	0.126593
12(1)	1002.136	975.619	0.642340	0.148646	0.126123
13(1)	839.483	829.098	0.647975	0.148157	0.125967
14(1)	665.206	635.961	0.661337	0.149082	0.126370
15(1)	515.659	512.935	0.650723	0.148541	0.126202
16(1)	259.716	277.741	0.643344	0.149010	0.125990
17(1)	147.082	150.699	0.646954	0.149600	0.126207
18(1)	3113.296	2966.758	0.646424	0.148645	0.126404
19(1)	3041.481	2887.150	0.646995	0.148581	0.126392
20(1)	1472.490	1444.776	0.639425	0.148822	0.126513
21(1)	1264.005	1227.562	0.645221	0.148711	0.126603
22(1)	1083.342	1061.120	0.658495	0.148663	0.126363
23(1)	774.637	756.675	0.646440	0.148431	0.126288
24(1)	601.697	563.647	0.633315	0.148185	0.126433
25(1)	352.742	349.309	0.644913	0.148571	0.126574
26(1)	215.965	162.088	0.645788	0.148668	0.126551
27(1)	67.380	19.203	0.626940	0.147202	0.125838

ZPEharm = 18185.97637 cm-1 = 51.996 Kcal/mol = 217.553 Kj/mol
ZPEfund = 17633.19108 cm-1 = 50.416 Kcal/mol = 210.940 KJ/mol
ZPEaver = 17909.58373 cm-1 = 51.206 Kcal/mol = 214.246 KJ/mol
-1/4sumXii = 36.01724 cm-1 = 0.103 Kcal/mol = 0.431 KJ/mol
x0 = -1.58708 cm-1 = -0.005 Kcal/mol = -0.019 KJ/mol
ZPEtot = 17944.01388 cm-1 = 51.305 Kcal/mol = 214.658 KJ/mol
ZPEtot/ZPEharm = 0.98670 ZPEfund/ZPEharm= 0.96960

B20. trans-1-Methylallyl radical -> cis-1-Methylallyl radical (C1, Doublet)
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Vibrational Energies and Rotational Constants (cm-1)

Mode(Quanta)	E(harm)	E(anharm)	Aa(z)	Ba(x)	Ca(y)
Equilibrium Geometry			0.773135	0.145606	0.138850
Ground State	19951.860	19711.689	0.778135	0.145241	0.138645
Fundamental Bands (DE w.r.t. Ground State)					
1(1)	-291.810	-270.515	0.800608	0.144369	0.138201
2(1)	3199.950	3086.376	0.776689	0.145235	0.138642
3(1)	3139.079	2982.397	0.781647	0.144696	0.138154
4(1)	3110.361	3027.872	0.776751	0.145222	0.138642
5(1)	3086.395	2943.178	0.779784	0.144992	0.138495
6(1)	3021.824	2915.967	0.779829	0.144951	0.138388
7(1)	3008.404	2850.333	0.770264	0.145996	0.139120
8(1)	2944.720	2853.155	0.783246	0.144742	0.138394
9(1)	1644.411	1600.636	0.775318	0.145015	0.138408
10(1)	1461.149	1452.166	0.791210	0.145499	0.138711
11(1)	1444.757	1399.989	0.769207	0.145303	0.138932
12(1)	1427.656	1394.129	0.778908	0.145155	0.138627
13(1)	1374.691	1338.045	0.775001	0.144849	0.138263
14(1)	1321.611	1287.180	0.775444	0.145243	0.138675
15(1)	1293.289	1269.687	0.777523	0.145355	0.138765
16(1)	1120.685	1100.572	0.779260	0.145350	0.138696
17(1)	1086.259	1060.594	0.776937	0.144811	0.138255
18(1)	1022.193	1006.876	0.781579	0.145416	0.138973
19(1)	980.285	970.230	0.774888	0.145112	0.138391
20(1)	954.249	938.239	0.775214	0.145156	0.138490
21(1)	928.011	919.505	0.774264	0.145179	0.138577
22(1)	854.488	840.424	0.780903	0.144662	0.138115
23(1)	657.877	653.225	0.777363	0.145311	0.138638
24(1)	475.112	474.169	0.774065	0.145545	0.139024
25(1)	303.606	327.514	0.794362	0.145505	0.138986
26(1)	246.465	224.749	0.766756	0.146464	0.139554
27(1)	88.000	16.449	0.772621	0.145639	0.138900

ZPEharm = 19951.85961 cm-1 = 57.045 Kcal/mol = 238.677 Kj/mol
ZPEfund = 19331.57125 cm-1 = 55.272 Kcal/mol = 231.257 KJ/mol
ZPEaver = 19641.71543 cm-1 = 56.158 Kcal/mol = 234.967 KJ/mol
-1/4sumXii = 98.18775 cm-1 = 0.281 Kcal/mol = 1.175 KJ/mol

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x0          =   -28.21449 cm-1  =  -0.081 Kcal/mol  =  -0.338 KJ/mol
ZPEtot      = 19711.68869 cm-1  =  56.359 Kcal/mol  = 235.804 KJ/mol
ZPEtot/ZPEharm = 0.98796   ZPEfund/ZPEharm= 0.96891
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B21. 1,3-Deuterium shift in 2-Methylallyl radical (C2v, Doublet)

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Vibrational Energies and Rotational Constants (cm-1)
Mode(Quanta)     E(harm)     E(anharm)     Aa(z)       Ba(x)       Ca(y)
Equilibrium Geometry                     0.320050    0.242616    0.150600
Ground State   16475.940    16398.966    0.319697    0.241076    0.149491
Fundamental Bands (DE w.r.t. Ground State)
 1(1)           3159.518     3051.286    0.319458    0.241002    0.149435
 2(1)           2352.520     2292.411    0.319121    0.241002    0.149360
 3(1)           1042.594     1030.479    0.319163    0.241105    0.149533
 4(1)            964.913      946.195    0.319352    0.240654    0.149489
 5(1)            897.584      897.527    0.318152    0.240773    0.149539
 6(1)            826.014      817.365    0.319588    0.240929    0.149474
 7(1)            626.353      643.330    0.319675    0.240705    0.149533
 8(1)            369.094      387.339    0.319707    0.241151    0.149811
 9(1)            225.212      397.975    0.321618    0.241128    0.149640
10(1)             92.614      214.154    0.320742    0.241627    0.149690
11(1)          -1493.477    -1582.915    0.321030    0.240106    0.149213
12(1)           3199.171     3088.429    0.319521    0.240906    0.149402
13(1)           3113.465     2993.653    0.319469    0.240965    0.149399
14(1)           3058.735     2968.789    0.319500    0.240922    0.149455
15(1)           2215.392     2188.922    0.319181    0.240869    0.149426
16(1)           1707.855     1658.221    0.319319    0.240027    0.149012
17(1)           1427.219     1390.269    0.319690    0.241286    0.149417
18(1)           1373.935     1348.704    0.319670    0.241097    0.149599
19(1)           1253.714     1227.299    0.318058    0.242001    0.149009
20(1)           1211.803     1190.053    0.320236    0.240358    0.148926
21(1)           1053.668     1052.127    0.319624    0.241075    0.149554
22(1)            930.198      920.587    0.320421    0.240824    0.149302
23(1)            889.700      894.399    0.319725    0.240920    0.149356
24(1)            819.652      812.551    0.319408    0.240759    0.149325
25(1)            720.387      717.893    0.319713    0.240898    0.149345
26(1)            549.231      545.398    0.319486    0.241612    0.149471
27(1)            364.814      365.782    0.320478    0.241266    0.149320

ZPEharm     = 16475.93977 cm-1  =  47.107 Kcal/mol  = 197.096 Kj/mol
ZPEfund     = 16229.11083 cm-1  =  46.401 Kcal/mol  = 194.143 KJ/mol
ZPEaver     = 16352.52530 cm-1  =  46.754 Kcal/mol  = 195.620 KJ/mol
-1/4sumXii =    36.71454 cm-1  =   0.105 Kcal/mol  =   0.439 KJ/mol
x0          =     9.72633 cm-1  =   0.028 Kcal/mol  =   0.116 KJ/mol
ZPEtot      = 16398.96617 cm-1  =  46.887 Kcal/mol  = 196.175 KJ/mol
ZPEtot/ZPEharm = 0.99533   ZPEfund/ZPEharm= 0.98502
```

B22. Allene (C2v, Singlet)

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Vibrational Energies and Rotational Constants (cm-1)
Mode(Quanta)     E(harm)     E(anharm)     Aa(z)       Ba(x)       Ca(y)
Equilibrium Geometry                     0.000000    0.000000    0.000000
Ground State   11891.155    11772.510   -0.045126   -0.001007   -0.001007
Fundamental Bands (DE w.r.t. Ground State)
 1(1)           3110.850     3009.023   -0.085510   -0.001272   -0.001272
 2(1)           1452.013     1416.464   -0.016729   -0.001105   -0.001105
 3(1)           1093.445     1081.246   -0.046633   -0.001410   -0.001410
 4(1)            866.930      868.621   -0.113751   -0.001802   -0.001802
 5(1)           3106.460     3000.248   -0.081888   -0.001278   -0.001278
 6(1)           2005.172     1998.126   -0.048548   -0.002945   -0.002945
 7(1)           1398.196     1366.524    0.007430   -0.000769   -0.000769
 8(1)           3185.865     3067.999   -0.070046   -0.001294   -0.001332
 9(1)           3185.865     3068.048   -0.070046   -0.001332   -0.001294
10(1)            992.308      990.271    0.171419   -0.001256   -0.000058
11(1)            992.308      990.227    0.171419   -0.000058   -0.001256
12(1)            838.834      841.984   -0.234511   -0.001364   -0.000748
13(1)            838.834      842.068   -0.234511   -0.000748   -0.001364
14(1)            357.614      366.315   -0.057620    0.000025   -0.000502
15(1)            357.614      366.322   -0.057621   -0.000502    0.000025
```

```
ZPEharm    = 11891.15473 cm-1  =  33.999 Kcal/mol  = 142.250 Kj/mol
ZPEfund    = 11636.74325 cm-1  =  33.271 Kcal/mol  = 139.206 KJ/mol
ZPEaver    = 11763.94899 cm-1  =  33.635 Kcal/mol  = 140.728 KJ/mol
-1/4sumXii =    19.14563 cm-1  =   0.055 Kcal/mol  =   0.229 KJ/mol
x0         =   -10.58490 cm-1  =  -0.030 Kcal/mol  =  -0.127 KJ/mol
ZPEtot     = 11772.50971 cm-1  =  33.659 Kcal/mol  = 140.830 KJ/mol
ZPEtot/ZPEharm = 0.99002   ZPEfund/ZPEharm= 0.97860

B23. Methyl radical (D3h, Doublet)
*********************************************************************************************

Vibrational Energies and Rotational Constants (cm-1)
Mode(Quanta)     E(harm)     E(anharm)    Aa(y)        Ba(x)        Ca(z)
Equilibrium Geometry                     0.000000    0.000000    0.000000
Ground State    6492.319     6529.635   -0.050154   -0.049486   -0.067723
Fundamental Bands (DE w.r.t. Ground State)
 1(1)           3099.497     2985.602   -0.141768   -0.139585   -0.113151
 2(1)            544.709      935.400   -0.357170   -0.359745    0.012204
 3(1)           3283.302     3174.412   -0.158211   -0.153810   -0.109876
 4(1)           3283.301     3107.874   -0.155819   -0.155894   -0.109799
 5(1)           1386.914     1458.710    0.360072    0.052334   -0.110590
 6(1)           1386.914     1369.629    0.051665    0.360812   -0.110572

ZPEharm    =  6492.31866 cm-1  =  18.562 Kcal/mol  =  77.665 Kj/mol
ZPEfund    =  6515.81338 cm-1  =  18.630 Kcal/mol  =  77.946 KJ/mol
ZPEaver    =  6504.06602 cm-1  =  18.596 Kcal/mol  =  77.806 KJ/mol
-1/4sumXii =   -20.70960 cm-1  =  -0.059 Kcal/mol  =  -0.248 KJ/mol
x0         =    46.27809 cm-1  =   0.132 Kcal/mol  =   0.554 KJ/mol
ZPEtot     =  6529.63451 cm-1  =  18.669 Kcal/mol  =  78.112 KJ/mol
ZPEtot/ZPEharm = 1.00575   ZPEfund/ZPEharm= 1.00362

B24. TS 2-methylallyl radical -> allene + methyl radical (Cs, Doublet)
*********************************************************************************************

Vibrational Energies and Rotational Constants (cm-1)
Mode(Quanta)     E(harm)     E(anharm)    Aa(z)        Ba(x)        Ca(y)
Equilibrium Geometry                     0.284633    0.210718    0.127421
Ground State   18754.412    18636.862    0.283705    0.215450    0.126092
Fundamental Bands (DE w.r.t. Ground State)
 1(1)           -452.577     -513.672    0.283354    0.220043    0.125220
 2(1)           3256.911     3167.794    0.283565    0.215508    0.126106
 3(1)           3254.488     3144.867    0.283551    0.215581    0.126130
 4(1)           3202.731     3110.043    0.283419    0.215412    0.126030
 5(1)           3186.381     3072.392    0.283512    0.215252    0.126005
 6(1)           3108.190     3023.504    0.283539    0.215301    0.126023
 7(1)           3104.036     3010.367    0.283514    0.215286    0.126027
 8(1)           3084.807     3011.299    0.283540    0.215504    0.126107
 9(1)           1865.063     1824.908    0.282467    0.215437    0.125832
10(1)           1449.738     1413.192    0.283682    0.215591    0.126080
11(1)           1407.350     1383.478    0.283700    0.215544    0.126143
12(1)           1404.947     1408.908    0.283881    0.215594    0.126079
13(1)           1394.561     1400.188    0.283202    0.215496    0.126155
14(1)           1046.385     1042.187    0.283275    0.215857    0.126128
15(1)            996.195      994.809    0.283313    0.215743    0.126182
16(1)            995.236      972.015    0.284199    0.215951    0.126019
17(1)            863.081      870.691    0.283238    0.215047    0.126107
18(1)            803.346      814.402    0.283831    0.214564    0.125771
19(1)            781.277      770.092    0.282976    0.215781    0.126200
20(1)            761.822      743.378    0.283782    0.215724    0.126204
21(1)            503.108      489.638    0.284104    0.213996    0.125540
22(1)            456.094      511.982    0.283719    0.221679    0.125708
23(1)            349.655      381.125    0.284082    0.217375    0.126212
24(1)            330.756      329.667    0.284163    0.213023    0.126225
25(1)            219.173      221.007    0.284859    0.215420    0.125603
26(1)             75.739      166.544    0.283145    0.215192    0.125937
27(1)             60.330       10.972    0.284573    0.215727    0.126058

ZPEharm    = 18754.41222 cm-1  =  53.622 Kcal/mol  = 224.353 Kj/mol
ZPEfund    = 18387.88882 cm-1  =  52.574 Kcal/mol  = 219.968 KJ/mol
ZPEaver    = 18571.15052 cm-1  =  53.098 Kcal/mol  = 222.160 KJ/mol
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-1/4sumXii =    58.00522 cm-1  =   0.166 Kcal/mol  =   0.694 KJ/mol
x0         =     7.70623 cm-1  =   0.022 Kcal/mol  =   0.092 KJ/mol
ZPEtot     = 18636.86197 cm-1  =  53.285 Kcal/mol  = 222.946 KJ/mol
ZPEtot/ZPEharm = 0.99373   ZPEfund/ZPEharm= 0.98046
```
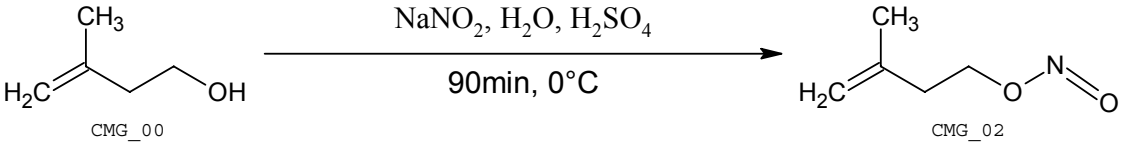

C.) Synthesis of **3-methylbut-3-en-1-yl nitrite**

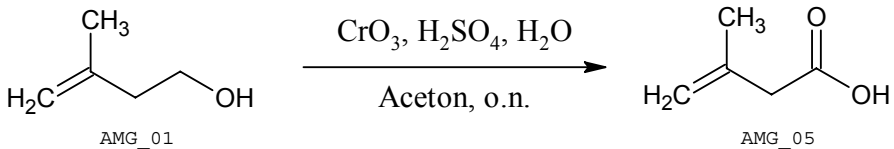


CMG_00 CMG_02

$NaNO_2$ (2.4 g) was dissolved in water (4.1 ml) and cooled to 0 °C. After the addition of CMG_00 (2 g, 2.35 ml, 23.2 mmol), H_2SO_4 (30 %, 5.3 ml) was added dropwise. The reaction mixture was stirred in the dark for 90 minutes at 0 °C under argon. To stop the reaction a solution of NaCl (0.75 g) and $NaHCO_3$ (0.1 g) in water (5 ml) was added. The product phase was washed 2 times more with the same solution. The crude product was distilled at 85 mbar (31 °C) to give pure CMG_02 (1.13 g, 9.9 mmol, 43 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.84 – 4.46 (m, =C*H*$_2$, CH_2CH_2ONO), 2.43 (t, CH_2CH_2ONO), 1.77 (s, CH_3).
^{13}C NMR (75 MHz, $CDCl_3$) δ 141.0 (CH_2=*C*), 112.9 (*C*H_2=C), 66.4 (CH_2CH_2ONO), 36.9 (CH_2CH_2ONO), 22.5 (*C*H_3).

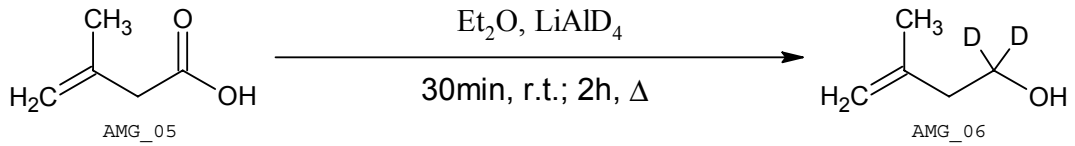
D.) Synthesis of **3-methyl(1,1-$^2H_2$)but-3-en-1-yl nitrite**



AMG_01 AMG_05

AMG_01 (12.55 ml, 18 g, 0.21 mol) was dissolved in acetone (600 ml). To this solution the Jones reagent (30 g CrO_3, 66 ml H_2O, 26 ml H_2SO_4) was added at 0 °C dropwise. The reaction mixture was stirred at room temperature over night. After the reaction was complete, it was quenched with isopropyl alcohol. The acetone was evaporated at reduced pressure. The residue was extracted with Et_2O (2x). The combined ether phases were washed 3 timed with a saturated aqueous $NaHCO_3$ solution. The combined aqueous layers were acidified with 2 M HCl to pH 3 and then extracted again with ether (3x). The extract was washed successively with brine and water, dried over $MgSO_4$ and concentrated *in vacuo* yielding pure AMG_05 (9.11 g, 91 mmol, 43 %).

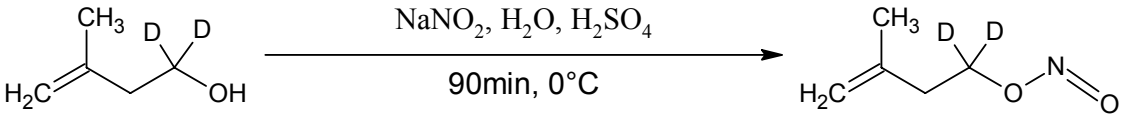
^{1}H NMR (300 MHz, $CDCl_3$) δ 4.95 (s, =C*H*$_2$), 4.89 (s, =C*H*$_2$), 3.08 (s, C*H*$_2$), 1.84 (s, C*H*$_3$).
^{13}C NMR (75 MHz, $CDCl_3$) δ 177.1 (*C*OOH), 137.8 (C_q), 115.2 (=*C*H_2), 43.1 (*C*H_2), 22.5 (CH_3).



AMG_05 AMG_06

$LiAlD_4$ (2.11 g) was suspended in dry Et_2O (60 ml). A solution of AMG_05 (5.92 g, 59.1 mmol) in dry Et_2O (20 ml) was added dropwise at 0 °C. The reaction mixture was stirred at room temperature for 4 hours before it was quenched with cold water. H_2SO_4 (10 %) was added to dissolve the precipitate and it was extracted 3 times against Et_2O. The ether phases were washed with brine, dried (over $MgSO_4$), filtrated and ether was removed under reduced pressure yielding pure AMG_06 (2.15 g, 24.4 mmol, 41 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.87 (s, =CH_2), 4.79 (s, =CH_2), 2.29 (s, CH_2CH$_2$OH), 1.76 (s, CH_3), [3.72 (t, CH$_2$CH_2OH)].
^{13}C NMR (75 MHz, $CDCl_3$) δ 142.0 (CH$_2$=*C*), 112.6 (*C*H$_2$=C), 40.7 (*C*H$_2$CH$_2$OH), 22.2 (*C*H$_3$), [60.1 (CH$_2$*C*H$_2$OH)].

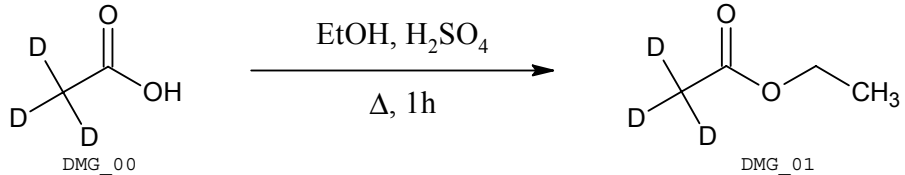


AMG_06 AMG_07

$NaNO_2$ (2.4 g) was dissolved in water (4.1 ml) and cooled to 0 °C. After the addition of AMG_06 (2 g, 2.35 ml, 22.7 mmol), H_2SO_4 (30 %, 5.3 ml) was added dropwise. The reaction mixture was stirred in the dark for 90 minutes at 0 °C under argon. To stop the reaction a solution of NaCl (0.75 g) and $NaHCO_3$ (0.1 g) in water (5 ml) was added. The product phase was washed 2 times more with the same solution. The crude product was distilled at 85 mbar (31 °C) to give pure AMG_07 (1.13 g, 9.6 mmol, 43 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.84 (s, =CH_2), 4.76 (s, =CH_2), 2.43 (s, CH_2), 1.77 (s, CH_3), [4.84-4.76 (m, CH_2)].
^{13}C NMR (75 MHz, $CDCl_3$) δ 141.0 (CH$_2$=*C*), 112.8 (*C*H$_2$=C), 36.9 (*C*H$_2$CD$_2$ONO), 22.5 (*C*H$_3$), [66.4 (CH$_2$*C*H$_2$ONO)].

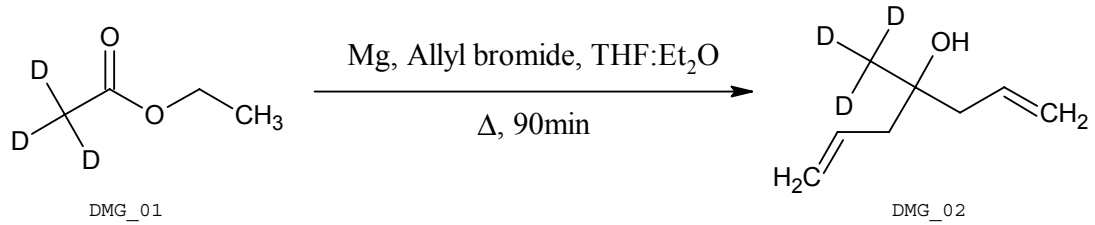
E.) Synthesis of **3-(^{2}H$_3$)methylbut-3-en-1-yl nitrite**



DMG_00 DMG_01

A solution of DMG_00 (84 ml, 95 g, 1.48 mol) in ethanol (90 ml) was added dropwise to a stirred, almost refluxing solution of ethanol (25 ml) and conc. H_2SO_4 (25 ml). The dropping funnel was rinsed with additional ethanol (10 ml). The mixture was refluxed for 60 minutes (oil bath: 95 °C). The reaction was stopped by cooling down to room temperature. The product was distilled along with some of the ethanol (oil bath: 80 – 90 °C). The combined fractions were washed with H_2O (20 ml), sat. $NaHCO_3$ (20 ml) and 40 % $CaCl_2$ (20 ml) solution. The product was then dried over $MgSO_4$ yielding DMG_01 (86.8 g, 0.95 mol, 64 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.12 (q, *J = 7.15*, OCH_2CH_3), 1.26 (t, *J = 7.15*, CH_2CH_3), [2.03 (s, CH_3)].
^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9 (C=O), 60.3 (OCH_2CH_3), 14.2 (OCH_2CH_3), [20.5 (CH_3)].



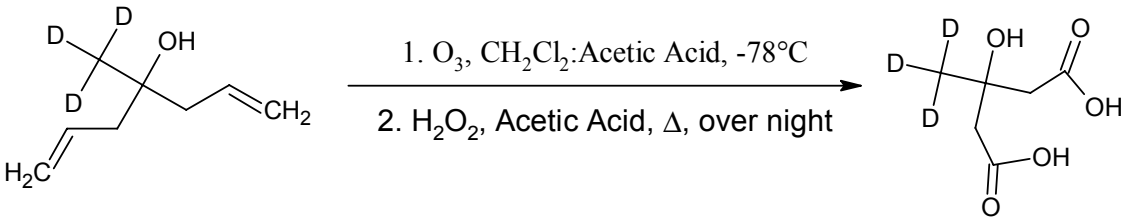
DMG_01 DMG_02

This reaction was carried out 3 times in the same way:

Dry Mg (28.1 g) was suspended in a dry 1000 ml 3-necked round-bottom flask with THF (47 ml) and Et_2O (47 ml). To this suspension was added dropwise a solution of DMG_01 (28.3 g, 0.31 mol) and allyl bromide (81.4 ml) in THF (171 ml) and Et_2O (86 ml) that the reaction was kept at mild reflux. After the addition was completed the funnel was rinsed with some THF and the reaction stirred for 90 minutes at reflux, during which time the reaction mixture solidified. The reaction was cooled to 0 °C and then quenched with H_2O (200 ml) and acidified with 6 M H_2SO_4 (150 ml). The water phase was separated and washed four times with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered and the solvents were removed *in vacuo*.

The residues from this 3 procedures were poured together and distillated under reduced pressure (85 °C at 78 mbar) yielding DMG_02 (93.3 g, 0.72 mol, 78 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.94 – 5.80 (m, 2 x CH_2=C*H*), 5.17 - 5.08 (m, 2 x CH_2=CH), 2.29 – 2.17 (m, 2 x CH_2=CHCH_2), [1.18 (s, CH_3)].
^{13}C NMR (75 MHz, $CDCl_3$) δ 133.9 (CH_2=*C*HCH_2), 118.6 (2 x *C*H_2=$CHCH_2$), 71.5 (*C*OHCD3), 46.1 (2 CH_2=CH*C*H_2), [25.8 (COH*C*H_3)].

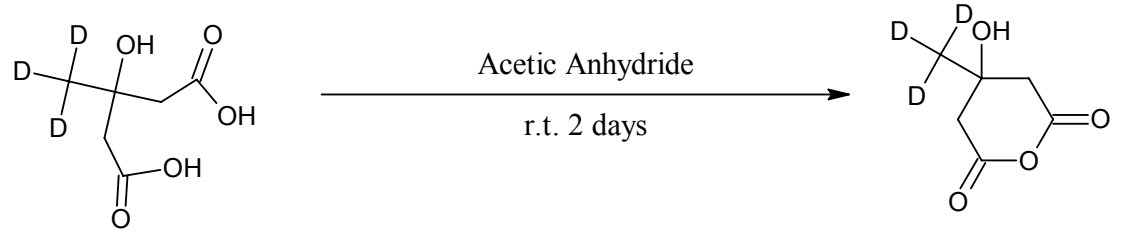


DMG_02 DMG_03

This reaction was carried out 9 times (a, b, c, d, e, f, g, h, i).

To a solution of DMG_02 (10.6 g) in CH_2Cl_2 (430 ml) acetic acid (48 ml) was added. This mixture was cooled down to about -70 °C with an *iso*-propyl alcocol dry ice solution. Ozone was bubbled through the solution until a blue color persisted (about 2 h). A stream of O_2 was bubbled into the solution to remove excess ozone (the solution turned colorless). CH_2Cl_2 was removed at room temperature *in vacuo*.
Acetic acid (28 ml) and H_2O_2 (30 %, 80 ml) were added and the mixture was refluxed over night (oil bath: 95 - 110 °C). The solvents were removed *in vacuo* yielding $DMG\_03_{a,b,c,d,e,f,g,h,i}$ (93.5 g, 0.69 mol , 94 %) which required no additional purification.

^{1}H NMR (300 MHz, d^6-Acetone) δ 2.68 (d, 2 x CH_2), [1.38 (s, C*H*$_3$)].
^{13}C NMR (75 MHz, d^6-Acetone) δ 174.1 (2 x *C*OOH), 70.9 (*C*OH), 46.1 (*C*H$_2$), [28.6 (CH$_3$)].

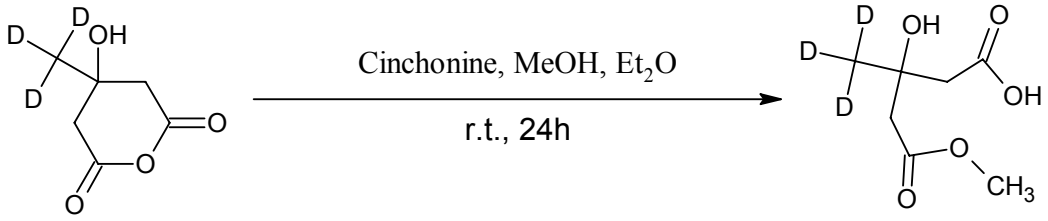


DMG_03 DMG_04

This reaction was carried out 5 times.

To DMG_03 (22.78 g, 0.14 mol) was added acetic anhydride (130 ml) and was stirred until complete solution (about 2 days). The solvent was evaporated *in vacuo*. The crude was recrystallized from chloroform to give $DMG\_04_{A,B,C,D,E}$ (63.2 g, 0.43 mol, 62 %).

^{1}H NMR (300 MHz, d^6-Acetone) δ 4.65 (bs, O*H*), 3.04 – 2.82 (m, 2 x C*H*$_2$), [1.44 (s, C*H*$_3$)].
^{13}C NMR (75 MHz, d^6-Acetone) δ 168.0 (2 x *C*=O), 68.5 (*C*OH), 45.1 (*C*H$_2$), [28.7 (*C*H$_3$)].

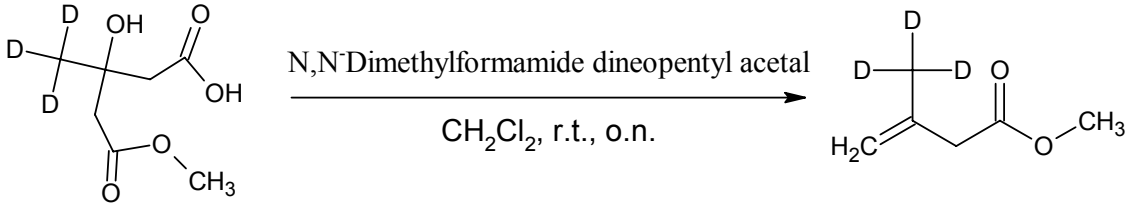


DMG_04 DMG_05

This reaction was carried out 5 times.

DMG_04 (12.64 g, 86 mmol) was dissolved in dry diethyl ether (760 ml) and methanol (70 ml). To this solution was added (+)-cinchonine (2.53 g, 8.6 mmol). This mixture was stirred for 24 hours and then filtrated. The solvents were removed *in vacuo* (5 x 10^{-1} for about 1 hour) to give DMG_05 (76.1 g, 0.42 mol, 98 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.74 (s, OC*H*$_3$), 2.70 – 2.58 (m, 2 x C*H*$_2$), [1.39 (s, C*H*$_3$)].
^{13}C NMR (75 MHz, $CDCl_3$) δ 175.4 (*C*OOH), 172.1 (*C*OOCH$_3$), 69.6 (*C*OH), 51.9 (COO*C*H$_3$), 44.9 (*C*H$_2$), 44.7 (*C*H$_2$), [27.3 (*C*H$_3$)].

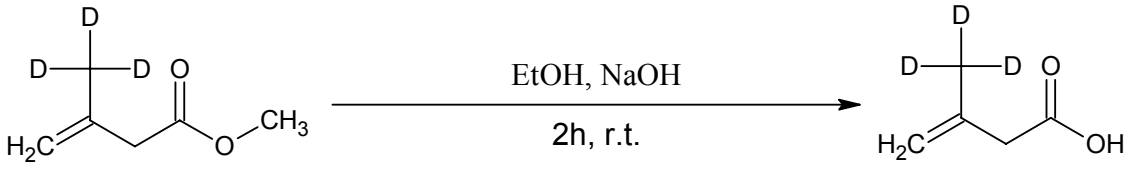


DMG_05 DMG_06

This reaction was carried out 5 times.

DMG_05 (17.1 g, 95 mmol) was dissolved in chloroform (855 ml). After addition of dimethylformamide dineopentyl acetal (44 ml) the solution was stirred over night at room temperature to give a yellow solution. After removing of the solvent at 300 mbar (40 °C) the residue was distillated at 230 mbar. All fractions containing product were combined are percolated through a short silica column with pentane. Evaporation of pentane furnished DMG_06 (49.7 g, 0.42 mol, 89 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.91 (bs, =C*H*$_2$), 4.85 (bs, =C*H*$_2$), 3.70 (s, OC*H*$_3$), 3.04 (bs, C*H*$_2$), [1.81 (s, C*H*$_3$)].
^{13}C NMR (75 MHz, $CDCl_3$) δ 171.7 (*C*OOCH$_3$), 138.3 (CH$_2$=*C*), 114.6 (*C*H$_2$=C), 51.9 (COO*C*H$_3$), 43.3 (*C*H$_2$), [25.9 (*C*H$_3$)].

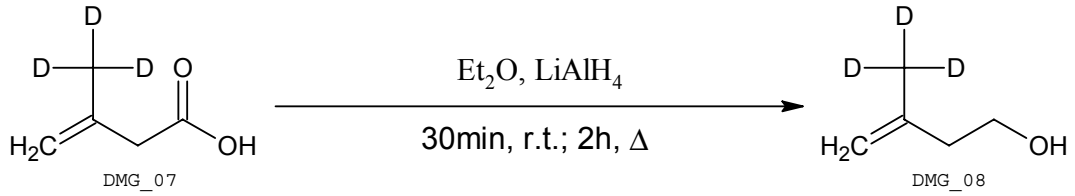


DMG_06 DMG_07

This reaction was carried out 3 times.

DMG_06 was dissolved in ethanol (72 ml). To this solution was added 1N NaOH solution (174 ml). The reaction mixture was stirred for 2 hours at room temperature. After addition of water (174 ml), the solution was saturated with NaCl following extraction with CH_2Cl_2 (4 x 72 ml). The aqueous phase was cooled in an ice bath and acidified with conc. hydrochloric acid (17 ml). After extraction with Et_2O (4 x 72 ml) the combined organic layers were dried over $MgSO_4$ and the solvent removed under reduced pressure furnishing DMG_07 (g, mol, %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.96 (s, =CH_2), 4.90(s, =CH_2), 3.09(s, CH_2), [1.85 (s, CH_3)].
^{13}C NMR (75 MHz, $CDCl_3$) δ 175.6 (*C*OOH), 138.1 (CH_2=*C*), 114.9 (*C*H_2=C), 43.2 (*C*H_2), [22.5 (*C*H_3)].

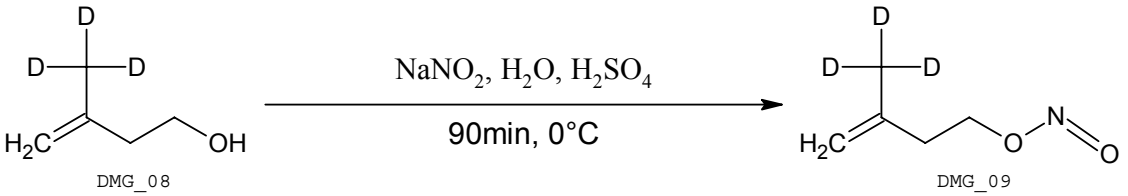


DMG_07 DMG_08

This reaction was carried out 3 times.

$LiAlH_4$ (6.5 g) was suspended in dry Et_2O (150 ml) and stirred for 30 minutes at room temperature. To this suspension was added dropwise a solution of DMG_07 (6.45 g, 63 mmol) in Et_2O (40 ml). After the addition was complete, the reaction mixture was refluxed for 2 hours. After cooling in an ice bath, cold H_2O (50 ml) was added carefully followed by cold HCl (6N, 100 ml). The ether layer was separated and the aqueous layer was saturated with NaCl and extracted with Et_2O (2 x 100 ml). The combined organic phases were washed with brine (100 ml), sodium carbonate (10 %) and again brine. The ether layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude was distilled under reduced pressure (68°C, 150 mbar) with collecting flasks cooled in a dry ice / isopropanol bath yielding DMG_08 (7.92 g, 0.09 mol, 53 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.83 (s, =CH_2), 4.76(s, =CH_2), 3.69(t, CH_2CH_2OH), 2.27 (t, CH_2CH_2OH), [1.75 (s, CH_3)].
^{13}C NMR (75 MHz, $CDCl_3$) δ 142.0 (CH_2=*C*), 112.5 (*C*H_2=C), 60.1 (CH_2CH_2OH), 40.8 (*C*H_2CH_2OH), [22.2 (*C*H_3)].



DMG_08 DMG_09

$NaNO_2$ (2.4 g) was dissolved in water (4.1 ml) and cooled to 0 °C. After the addition of DMG_08 (2 g, 2.35 ml, 22.4 mmol), H_2SO_4 (30 %, 5.3 ml) was added dropwise. The reaction mixture was stirred in the dark for 90 minutes at 0 °C under argon. To stop the reaction a solution of NaCl (0.75 g) and $NaHCO_3$ (0.1 g) in water (5 ml) was added. The product phase was washed 2 times more with the same solution. The crude product was distilled at 85 mbar (31 °C) to give pure DMG_09 (g, mmol, %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.83 – 4.75 (=C*H*$_2$, CH_2CH_2ONO), 2.43 (t, CH_2CH_2ONO), [1.77 (s, CH_3)].

^{13}C NMR (75 MHz, $CDCl_3$) δ 140.8 (CH_2=*C*), 112.8 (*C*H_2=C), 66.5 (CH_2CH_2ONO), 37.1 (CH_2CH_2ONO), [22.5 (CH_3)].