Electronic supporting information

On the decarboxylation of 2-methyl-1-tetralone-2-carboxylic acid – oxidation of the enol intermediate by triplet oxygen

Abdelkhalek Riahi, [a] Jacques Muzart,*[a] Manabu Abe*[b,c] and Norbert Hoffmann*[a]

[a] CNRS-Université de Reims Champagne-Ardenne,
Institut de Chimie Moléculaire de Reims, UMR 7312,
UFR des Sciences Exactes et Naturelles, BP 1039,
51687 Reims Cedex 2, France.
Fax: +33 3 26 91 31 66; Tel: +33 3 26 91 33 10;
E-mail: norbert.hoffmann@univ-reims.fr ; jacques.muzart@univ-reims.fr

[b] Hiroshima University, Department of Chemistry,
Graduate School of Science,
1-3-1 Kagamiyama, Higashi-Hiroshima,
Hiroshima 739-8526, Japan.
Fax and Tel: +81-82-424-7432;
E-mail: mabe@hiroshima-u.ac.jp

[c] Institute for Molecular Science (IMS), Okazaki,
Aichi 444-8787, Japan

Experimental Section

Spectroscopic data

2-Hydroperoxy-2-methyl-1-tetralone (7)[1]

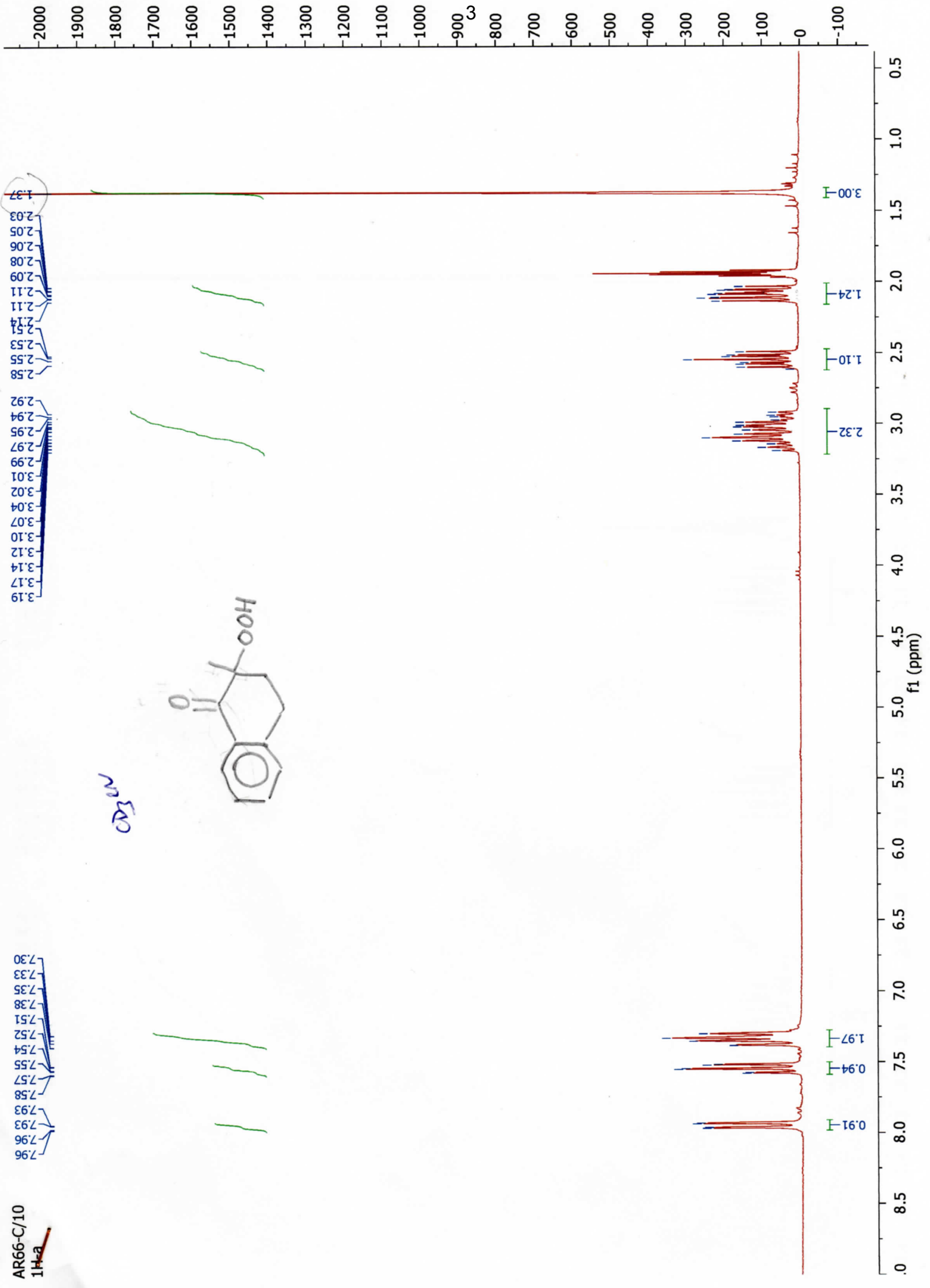
^{1}H NMR (250 MHz, $CDCl_3$): 1.48 (s, Me-C(2), 3 H), 2.05-2.14 (m, H-C(3), 1 H), 2.62-2.72 (m, H-C(3), 1 H), 3.11-3.17 (m, H-C(4), 2 H), 7.26 (d, J = 7.5 Hz, H-C(5), 1 H), 7.35 (dd, J = 7.5, 7.5 Hz, H-C(7), 1 H), 7.53 (ddd, J = 2.5, 7.5, 7.5 Hz, H-C(6), 1 H), 8.04 (dd, J = 2 ,5, 7.5 Hz, H-C(8), 1 H). ^{1}H NMR (250 MHz, CD_3CN): 1.37 (s, Me-C(2), 3 H), 2.03-2.14 (m, H-C(3), 1 H), 2.49-2.62 (m, H-C(3), 1 H), 2.92-3.19 (m, H-C(4), 2 H), 7.30-7.38 (m, H-C(5), H-C(7), 2 H), 7.54 (ddd, J = 2.5, 7.5, 7.5 Hz, H-C(6), 1 H), 7.95 (dd, J = 2 ,5, 7.5 Hz, H-C(8), 1 H). MS: 215 (M + Na).

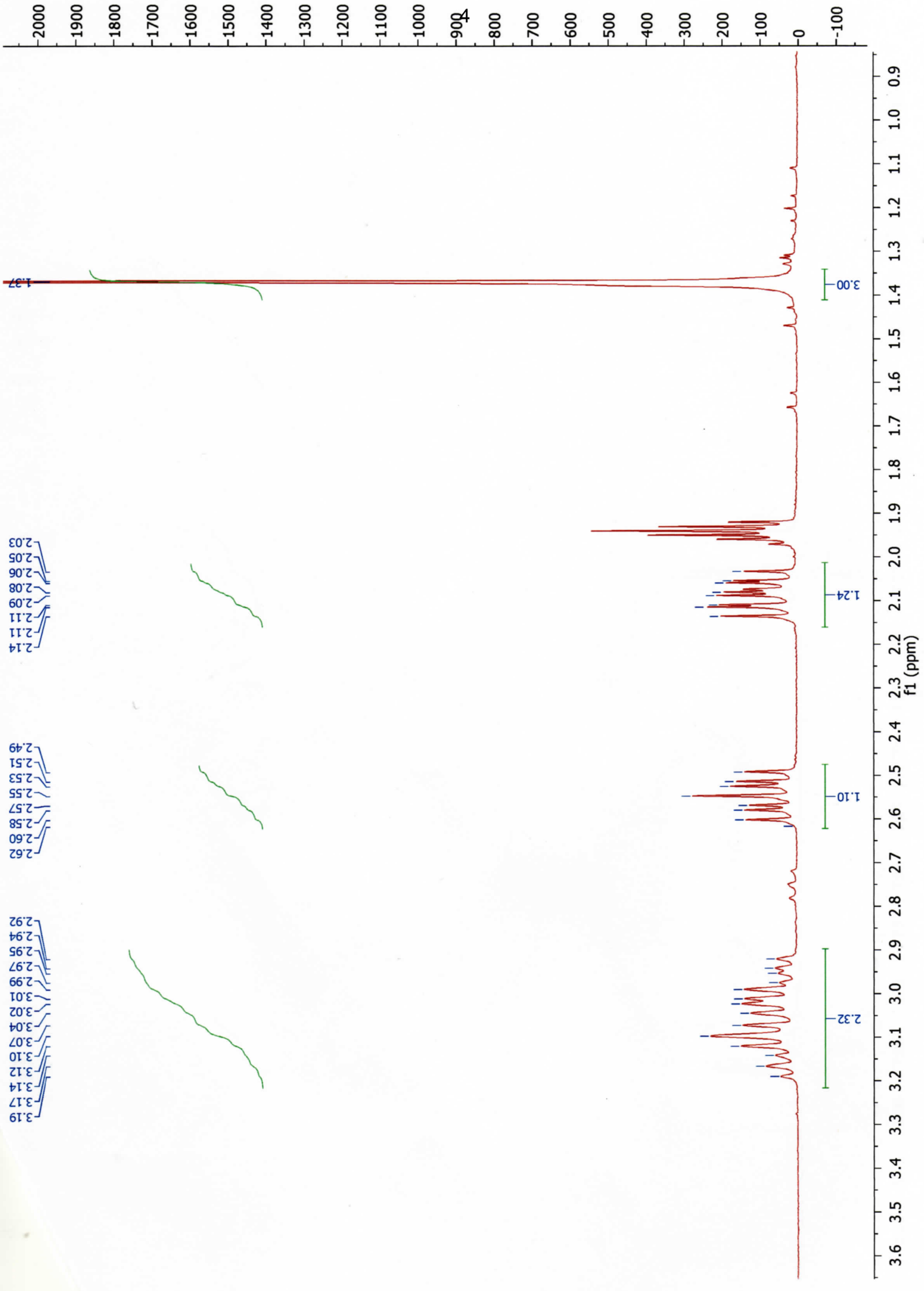
2-Hydroxy-2-methyl-1-tetralone (5)

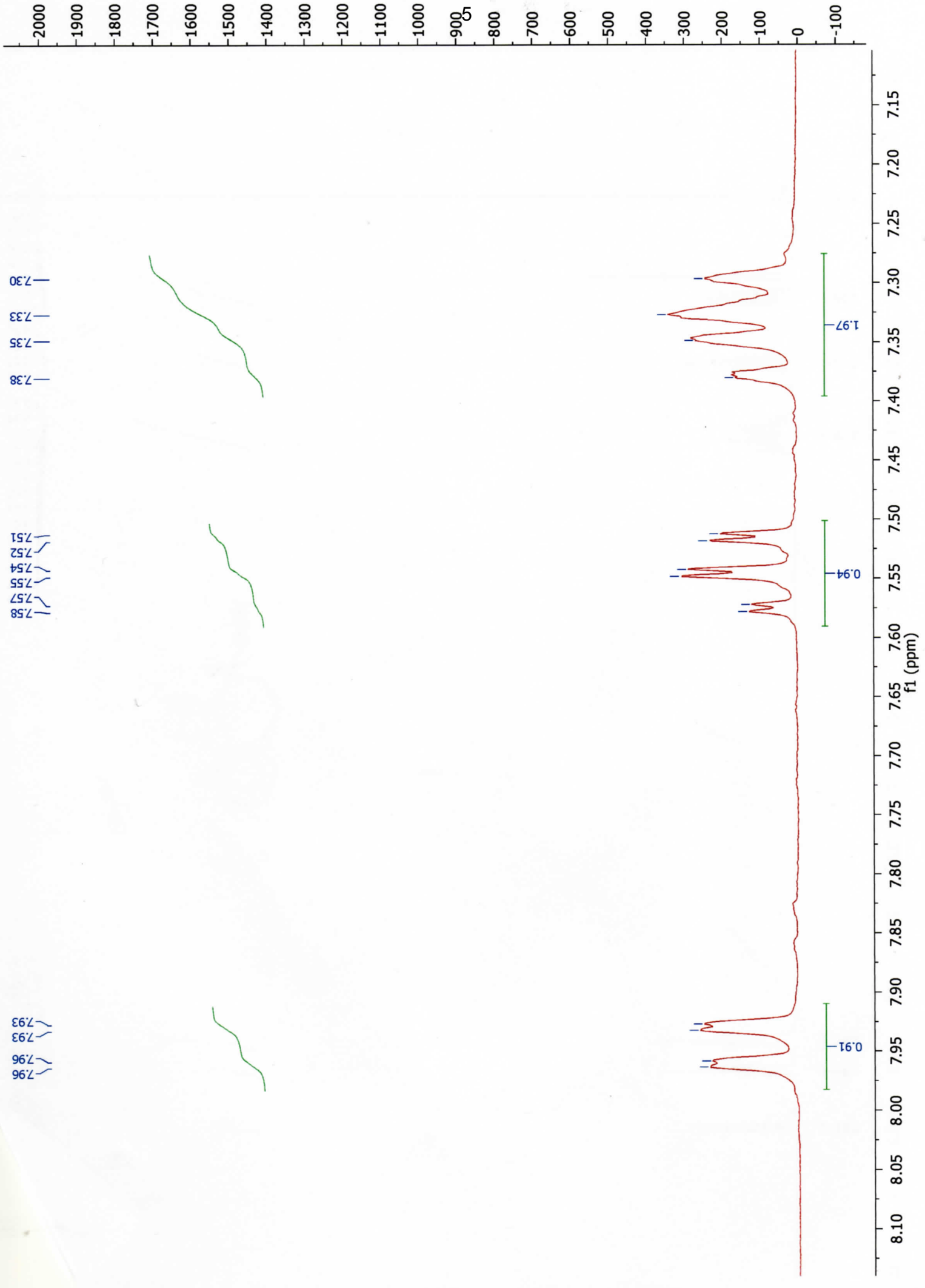
^{1}H NMR (250 MHz, $CDCl_3$): 1.40 (s, Me-C(2), 3 H), 2.21-2.27 (m, H-C(3), 2 H), 3.04-3.12 (m, H-C(4), 2 H), 7.26 (d, J = 7.5 Hz, H-C(5), 1 H), 7.35 (dd, J = 7.5, 7.5 Hz, H-C(7), 1 H), 7.53 (ddd, J = 2.5, 7.5, 7.5 Hz, H-C(6), 1 H), 8.01 (dd, J = 2.5, 7.5 Hz, H-C(8), 1 H). ^{1}H NMR (250 MHz, CD_3CN): 1.32 (s, Me-C(2), 3 H), 2.11-2.17 (m, H-C(3), 2 H), 3.03-3.08 (m, H-C(4), 2 H), 3.78 (m, OH, 1H), 7.31-7.39 (m, H-C(5), H-C(7), 2 H), 7.55 (ddd, J = 2.5, 7.5,7.5 Hz, H-C(6), 1 H), 7.95 (dd, J = 2.5, 7.5 Hz, H-C(8), 1 H). ESHRMS for ($C_{11}H_{12}O_2$ + Na): calcd: 199.0735. Found: 199.0733.

On pages 3 to 5: ^{1}H NMR spectra of compound **7**.

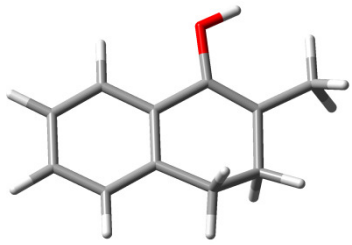
[1] T. Arai, H. Takasugi, T. Sato, H. Noguchi, H. Kanoh, K. Kaneko and A. Yanagisawa, *Chem. Lett.* 2005, **34**, 1590.







3
At B3LYP / 6-31 G (d)



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(Hartree/Particle)
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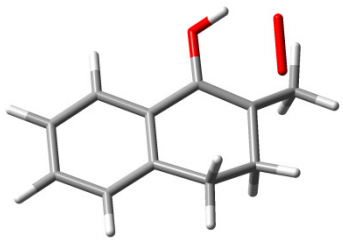
Thermal correction to Enthalpy= 0.214064
Thermal correction to Gibbs Free Energy= 0.166837
Sum of electronic and zero-point Energies= -501.413431
Sum of electronic and thermal Energies= -501.402985
Sum of electronic and thermal Enthalpies= -501.402040
Sum of electronic and thermal Free Energies= -501.449268

H,0,-2.0948866128,-0.3833781369,-2.0838685468
C,0,-2.0606815592,-0.1722075796,-1.020890635
C,0,-1.9473549604,0.3656051153,1.7097302237
C,0,-0.8178633233,0.0303233016,-0.4046699463
C,0,-3.2374701909,-0.1109769425,-0.2749213767
C,0,-3.1835329527,0.1541609935,1.0934724891
C,0,-0.7624660488,0.3108864171,0.9768148477
H,0,-4.1947167442,-0.273719988,-0.7632142391
H,0,-4.0971846914,0.1981336033,1.6804844179
H,0,-1.9027203376,0.5805347023,2.7754404845
C,0,0.4408127432,-0.0607085151,-1.1672984214
C,0,1.6451233105,-0.1778831741,-0.5654712718
C,0,1.7029319438,-0.2195300023,0.9496665444
H,0,2.6758498527,0.1555643721,1.2928252367
H,0,1.6442722092,-1.2654295396,1.2959773375
C,0,0.5851583729,0.6080466004,1.5942856299
H,0,0.8112677021,1.6755656964,1.4440696631
H,0,0.557308042,0.4430699345,2.6776404519
O,0,0.2342647293,-0.0593675524,-2.5268225639
H,0,1.0839334101,-0.1887371064,-2.9736981411
C,0,2.9526746615,-0.3622094002,-1.2890578683
H,0,3.647394692,0.4624278071,-1.0757882956
H,0,2.864395831,-0.4258950873,-2.380977469
H,0,3.4524899208,-1.2852755192,-0.9617285514

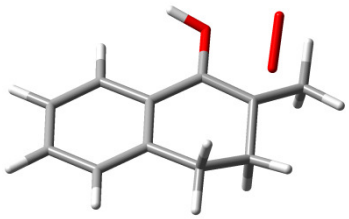
TS1
At UB3LYP / 6-31 G (d)



Zero-point correction= 0.207752
(Hartree/Particle)
Thermal correction to Energy= 0.219943Thermal correction to Enthalpy= 0.220887
Thermal correction to Gibbs Free Energy= 0.168880
Sum of electronic and zero-point Energies= -651.703000
Sum of electronic and thermal Energies= -651.690809
Sum of electronic and thermal Enthalpies= -651.689865
Sum of electronic and thermal Free Energies= -651.741872
S**2 before annihilation 2.0318,after 2.0006
Imaginary frequency; -381.2198

H,0,-1.4827591105,-2.509801326,0.2829864013
C,0,-1.8309397863,-1.4915915555,0.1473617535
C,0,-2.6893171171,1.1422701522,-0.2127740596
C,0,-0.8813767135,-0.4469061492,0.0919055395
C,0,-3.18797501,-1.2129108216,0.0417276052
C,0,-3.624593675,0.1050553384,-0.1305918033
C,0,-1.3249263064,0.8878862306,-0.1114958997
H,0,-3.9103992814,-2.0229769886,0.0946492457
H,0,-4.6857747359,0.3244082377,-0.2090867202
H,0,-3.0276119328,2.1638663729,-0.3723592267
C,0,0.9503618985,1.7343625075,0.5739290742
H,0,1.7480291035,2.4398611129,0.3130806624
H,0,0.6993686845,1.9216139232,1.6285805914
C,0,-0.2835344014,1.9647145123,-0.3069132112
H,0,0.0352026094,1.9650507586,-1.3596104089
H,0,-0.7085640396,2.9549623193,-0.1087145404
C,0,0.5237698913,-0.7084957989,0.2503537912
C,0,1.4937957143,0.323475888,0.4762902299
C,0,2.6488353574,0.0205798891,1.4116464793
H,0,3.3924354222,0.8222641845,1.3719640235
H,0,3.1433609953,-0.9206958821,1.1626175422
H,0,2.2761340284,-0.0571128361,2.4402351722
O,0,2.4307264208,0.3954082835,-1.0761571317
O,0,2.8620341987,-0.7742460885,-1.4133012192
O,0,0.9422667298,-2.002892791,0.1946207077
H,0,1.8189040558,-1.9855114733,-0.2489395984

TS1'
At UB3LYP / 6-31 G (d)



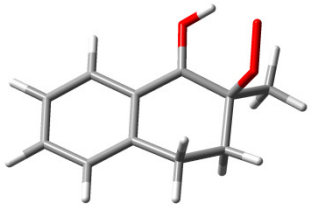
Zero-point correction= 0.207174 (Hartree/Particle)
Thermal correction to Energy= 0.219721
Thermal correction to Enthalpy= 0.220666
Thermal correction to Gibbs Free Energy= 0.167497
Sum of electronic and zero-point Energies= -651.697518
Sum of electronic and thermal Energies= -651.684970
Sum of electronic and thermal Enthalpies= -651.684026
Sum of electronic and thermal Free Energies= -651.737194

S**2 before annihilation 2.0340, after 2.0006

Imaginary frequency; -426.3916

H,0,1.6169667367,-2.49739386,-0.282500351
C,0,1.8764621381,-1.4559285897,-0.1069080364
C,0,2.6039680249,1.2145432956,0.1907761953
C,0,0.8693789483,-0.4603427889,-0.1130443247
C,0,3.21419515,-1.1200283732,0.0626114167
C,0,3.5863600298,0.2180919669,0.2159696
C,0,1.2577709385,0.902710236,0.0328326356
H,0,3.9696547755,-1.9010181727,0.0596731432
H,0,4.6312702501,0.4864409031,0.3420898901
H,0,2.8926215626,2.257787162,0.2998347249
C,0,-1.015432335,1.5878665417,-0.8285651435
H,0,-1.8238974217,2.315772992,-0.7000081423
H,0,-0.7327934546,1.6059497407,-1.8908315069
C,0,0.1857904579,1.9680700479,0.0481653305
H,0,-0.1680071784,2.1107015483,1.0784102776
H,0,0.6022444123,2.9283320183,-0.2764805889
C,0,-0.5187126263,-0.7865021936,-0.2926269263
C,0,-1.5430169184,0.2031056427,-0.49671369
C,0,-2.7893942063,-0.2421304977,-1.2286129577
H,0,-3.5200744144,0.5716236778,-1.2648144282
H,0,-3.2355406466,-1.1007258708,-0.7219589722
H,0,-2.544368144,-0.5385910487,-2.2553422032
O,0,-2.2203023961,0.5606356113,1.1007011198
O,0,-2.7490120689,-0.4583717783,1.6738597062
O,0,-0.9436504115,-2.0833901245,-0.2823683502
H,0,-0.3151472023,-2.6235720861,0.2230415816

T-DR
At UB3LYP / 6-31 G (d)



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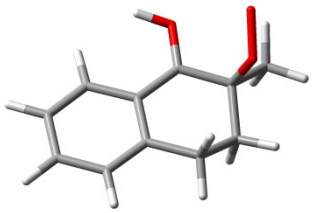
Thermal correction to Energy= 0.221421
Thermal correction to Enthalpy= 0.222365
Thermal correction to Gibbs Free Energy= 0.170453
Sum of electronic and zero-point Energies= -651.704286
Sum of electronic and thermal Energies= -651.692052
Sum of electronic and thermal Enthalpies= -651.691108
Sum of electronic and thermal Free Energies= -651.743020
S**2 before annihilation 2.0279, after 2.0004

H,0,1.5028147302,-2.5038517717,-0.1190226101
C,0,1.8207020417,-1.4677868801,-0.0772006136
C,0,2.6054027557,1.2123514127,0.0408122908
C,0,0.8321862669,-0.4495884659,-0.0529411432
C,0,3.168719713,-1.1401163861,-0.0593927332
C,0,3.571861405,0.2003107366,-0.0094008507
C,0,1.2482643699,0.9129323011,0.0300661593
H,0,3.9142765171,-1.9305406,-0.0871443162
H,0,4.6276187526,0.4559935108,-0.000822887
H,0,2.9165976815,2.2530610574,0.104851262
C,0,-1.0560658948,1.6403997416,-0.6551578254
H,0,-1.8529692708,2.3744766196,-0.4887900098
H,0,-0.8009019426,1.6791240858,-1.7214547935
C,0,0.1838617481,1.9727173686,0.1826423537
H,0,-0.1126657232,2.0452181024,1.2396345893
H,0,0.5742493226,2.9566927072,-0.1003672939
C,0,-0.554905115,-0.7629102708,-0.0962090254
C,0,-1.6151865016,0.2463695702,-0.3671919101
C,0,-2.6362924715,-0.1922278615,-1.4202548297
H,0,-3.3927613267,0.5871229143,-1.5580830447
H,0,-3.1399404143,-1.1166462101,-1.1296054671
H,0,-2.1288375783,-0.3641070934,-2.3744250006
O,0,-2.4490777867,0.4531871908,0.9269761137
O,0,-2.9107237522,-0.681590826,1.4069708277
O,0,-0.9332400222,-2.0696039236,0.0104033681
H,0,-1.8140457246,-2.0642450702,0.4368825295

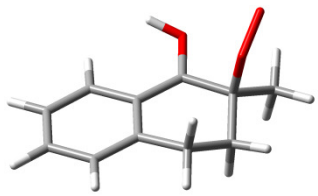
T-DR'
At UB3LYP / 6-31 G (d)



Zero-point correction= 0.208441 (Hartree/Particle)
Thermal correction to Energy= 0.221068
Thermal correction to Enthalpy 0.222012
Thermal correction to Gibbs Free Energy= 0.169031
Sum of electronic and zero-point Energies= -651.698315
Sum of electronic and thermal Energies= -651.685688
Sum of electronic and thermal Enthalpies= -651.684744
Sum of electronic and thermal Free Energies= -651.737725
S**2 before annihilation 2.0274, after 2.0004

H,0,-2.1733839862,-0.9965703342,-1.8625033143
C,0,-2.1315319798,-0.545645879,-0.8734467668
C,0,-2.0611273134,0.4615887303,1.7220363244
C,0,-0.8853899061,-0.1335027681,-0.3261530014
C,0,-3.3069712916,-0.4358902843,-0.1442365913
C,0,-3.2827877562,0.072426679,1.1587466792
C,0,-0.870631058,0.3738331942,1.0109653228
H,0,-4.2450125761,-0.7616777135,-0.5857534998
H,0,-4.1999622862,0.1535395823,1.7346391696
H,0,-2.0367644876,0.845222719,2.7399226465
C,0,1.6203113392,0.0021819055,1.0580888312
H,0,2.5703024721,0.3852100339,1.4465405042
H,0,1.5338452247,-1.0438574115,1.3776476743
C,0,0.4443068862,0.8216599315,1.6049313792
H,0,0.6158941699,1.8808114592,1.3672947092
H,0,0.4092039321,0.7481469189,2.6978445584
C,0,0.3304053005,-0.228082006,-1.0623870976
C,0,1.6695656571,0.0304368,-0.470772992
C,0,2.7865043579,-0.8189073385,-1.0657468831
H,0,3.7385694749,-0.5712111549,-0.5855309093
H,0,2.8670408762,-0.6344568277,-2.138304568
H,0,2.5786381436,-1.8822189662,-0.908653624
O,0,2.0741930598,1.5029401403,-0.7369111972
O,0,2.1230476082,1.8061449705,-2.012456426
O,0,0.3519008294,-0.6020306939,-2.3735622451
H,0,-0.5171666904,-0.4330916868,-2.7712386827

S-DR'
At BS-UB3LYP / 6-31 G (d)



Zero-point correction 0.208985 (Hartree/Particle)
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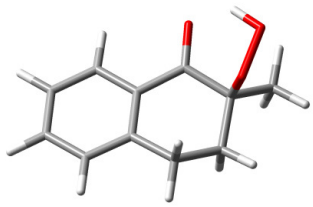
Thermal correction to Enthalpy= 0.222352
Thermal correction to Gibbs Free Energy= 0.171066
Sum of electronic and zero-point Energies= -651.700006
Sum of electronic and thermal Energies= -651.687584
Sum of electronic and thermal Enthalpies= -651.686640
Sum of electronic and thermal Free Energies= -651.737925

S**2 before annihilation 0.8601, after 0.1276

H,0,-1.5859267358,-2.5087478146,0.2932819195
C,0,-1.8621481338,-1.4714022489,0.1222163835
C,0,-2.6315490181,1.1927561479,-0.1834820385
C,0,-0.8687365076,-0.4586779569,0.0861330736
C,0,-3.2078003247,-1.1516407831,-0.0016186609
C,0,-3.6003285091,0.1827521032,-0.156011675
C,0,-1.2758761365,0.8996548729,-0.0699798941
H,0,-3.9535417589,-1.9403660018,0.036734123
H,0,-4.6523877254,0.4367158216,-0.2458842249
H,0,-2.9374389699,2.2294863551,-0.3022525746
C,0,1.0107274858,1.6350478723,0.6933037141
H,0,1.7966619017,2.3846227868,0.5543082105
H,0,0.7384413327,1.6419923675,1.7556396476
C,0,-0.21869895,1.97338822,-0.1594094155
H,0,0.0927352254,2.085827988,-1.2071145554
H,0,-0.6346474115,2.938806851,0.1473233881
C,0,0.52139906,-0.7680538165,0.2281854182
C,0,1.5928959116,0.2579272912,0.3711344525
C,0,2.7459324896,-0.1256559475,1.2866538551
H,0,3.5074727998,0.6605331564,1.2692649809
H,0,3.1999328473,-1.0645486539,0.9727667582
H,0,2.3770377031,-0.2294454062,2.3118584548
O,0,2.0683972058,0.3785964802,-1.0545926359
O,0,2.9695174285,-0.5412004995,-1.4188031742
O,0,0.9928533325,-2.0243999749,0.1124402093
H,0,0.3275304576,-2.6042612103,-0.2991047398

7 At B3LYP / 6-31 G (d) 	Zero-point correction= 0.211286 (Hartree/Particle) Thermal correction to Energy= 0.223354 Thermal correction to Enthalpy= 0.224298 Thermal correction to Gibbs Free Energy= 0.173542 Sum of electronic and zero-point Energies= -651.768913 Sum of electronic and thermal Energies= -651.756845 Sum of electronic and thermal Enthalpies= -651.755900 Sum of electronic and thermal Free Energies= -651.806657

H,0,-1.5691089679,-2.4975763607,0.4181289607
C,0,-1.9036595323,-1.4816985736,0.2336529472
C,0,-2.6811289733,1.1502250394,-0.2627978179
C,0,-0.9345737268,-0.4698204016,0.1283559441
C,0,-3.2526514739,-1.1769460052,0.1062780913
C,0,-3.6398535169,0.1447885759,-0.1425459817
C,0,-1.3189962147,0.8623928866,-0.1294238021
H,0,-4.0016449471,-1.9583424257,0.1975563371
H,0,-4.6936159701,0.3918781823,-0.2419470798
H,0,-2.9914342347,2.1729738238,-0.4632208068
C,0,0.9463931814,1.6613509401,0.6090038589
H,0,1.7285830456,2.4106605955,0.4461985397
H,0,0.6362848047,1.7345132351,1.6589686868
C,0,-0.2616064538,1.9281547533,-0.2962451647
H,0,0.0704081322,1.9518800323,-1.34280047
H,0,-0.6855326933,2.9153159163,-0.0797217124
C,0,0.4955738829,-0.837838981,0.2624716968
C,0,1.5621013467,0.2728219221,0.3969305193
C,0,2.5991501568,-0.0566334091,1.4672851811
H,0,3.3922769758,0.697513346,1.450045083
H,0,3.041054424,-1.0372436244,1.2931812363
H,0,2.130788519,-0.053460595,2.457754761
O,0,2.1505236249,0.3505687259,-0.9308826376
O,0,3.0037505574,-0.7925856205,-1.1851363852
O,0,0.869739665,-2.0073844453,0.1770218075
H,0,2.3711283886,-1.5392825325,-1.0958147928