Supplementary material

Diels-Alder Reaction of Vinylene Carbonate and 2,5-Dimethylfuran: Kinetic *vs* Thermodynamic Control

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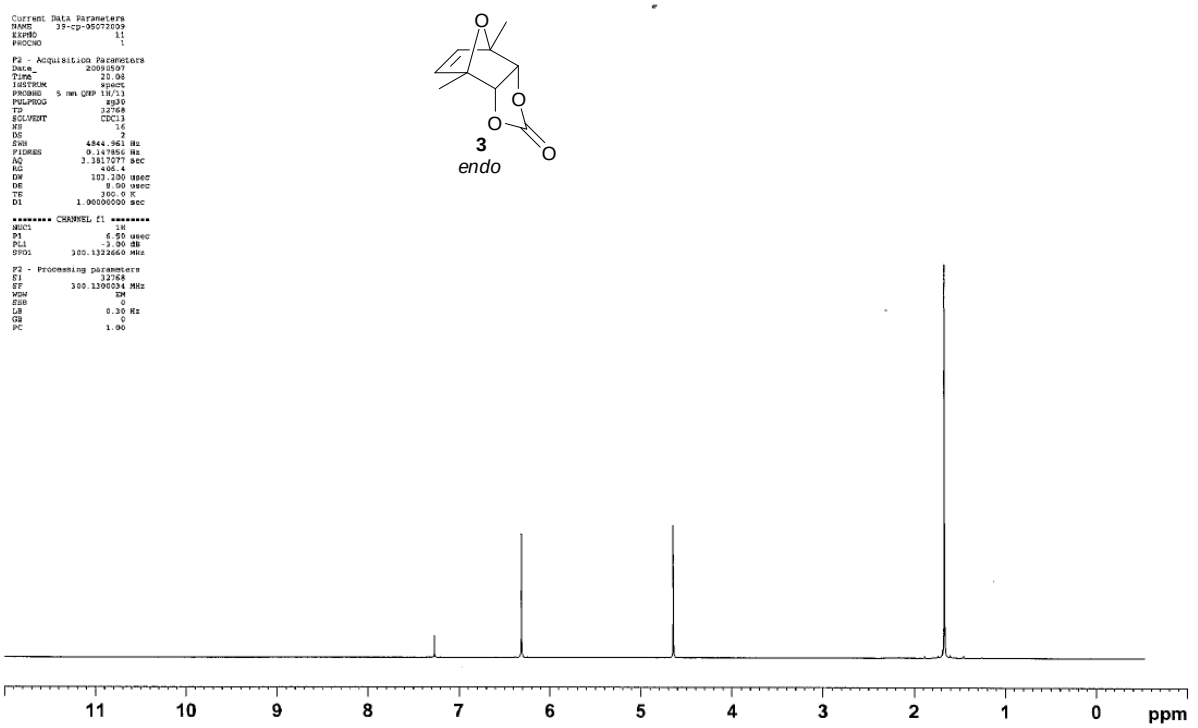
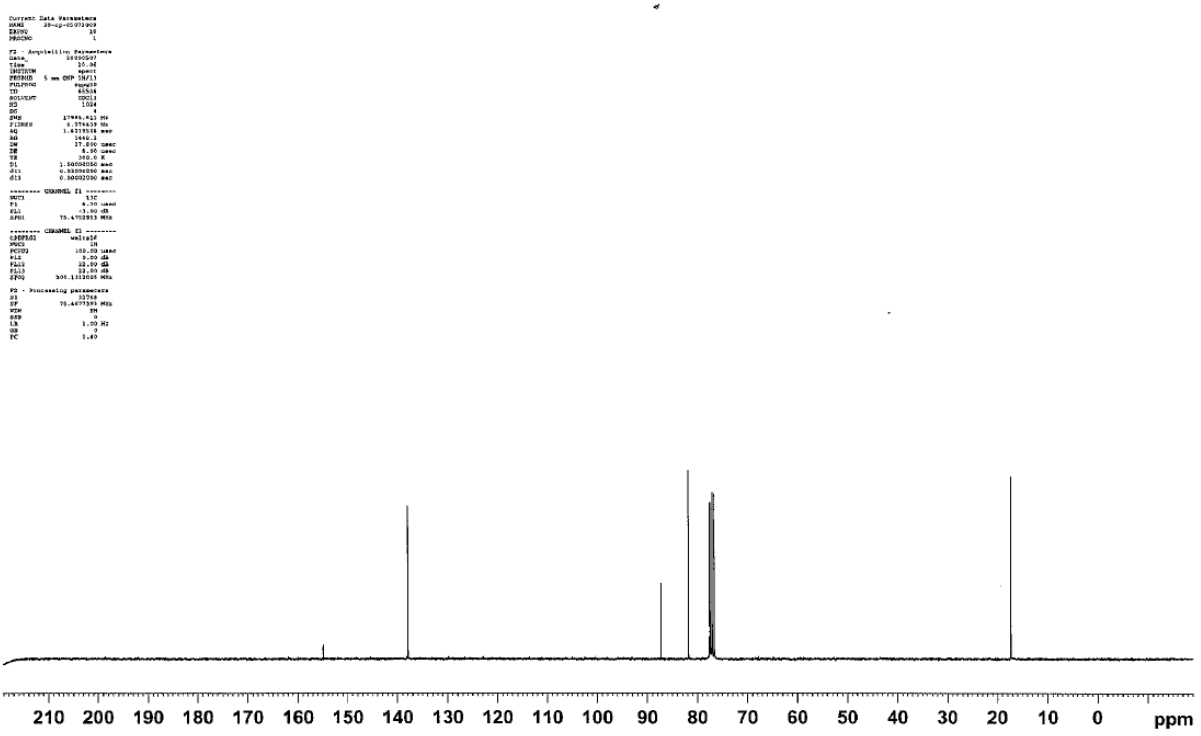
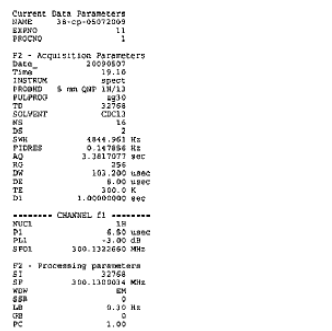
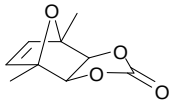
^{1}H and ^{13}C NMR Spectral Data









4
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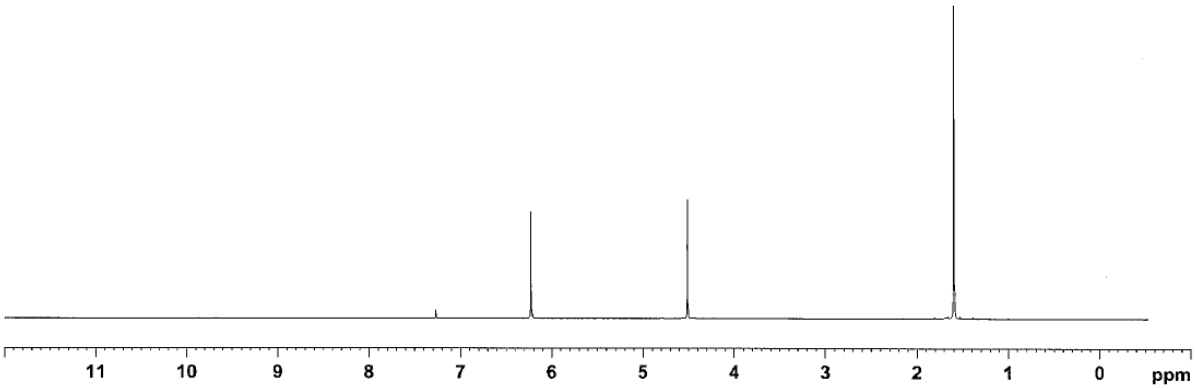
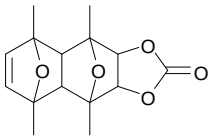
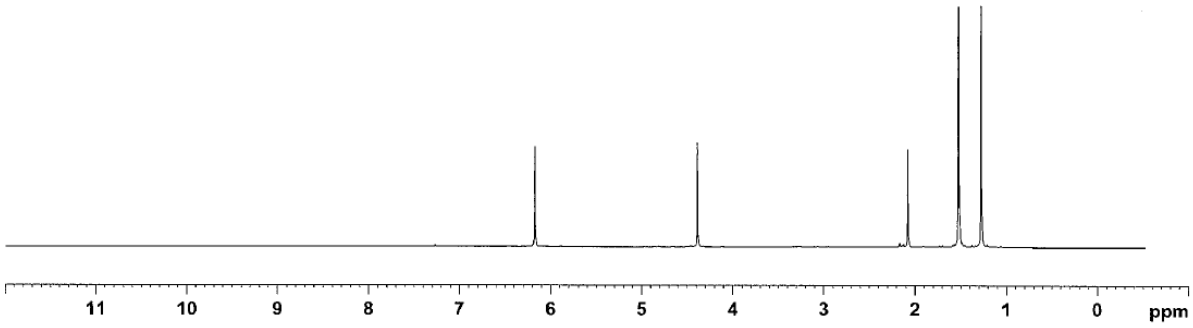
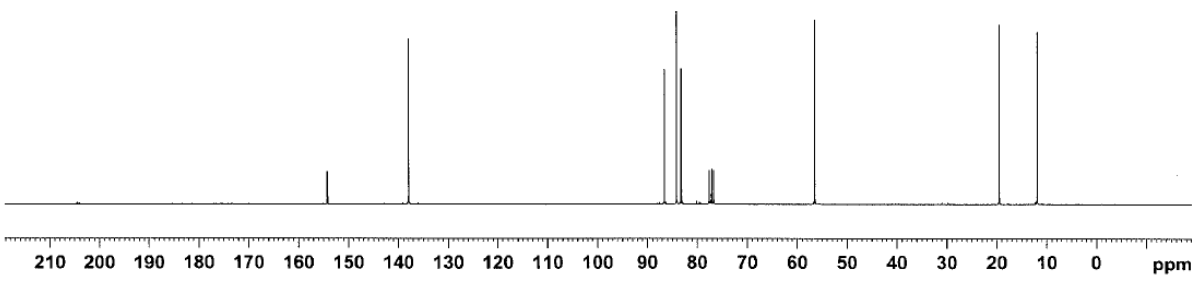
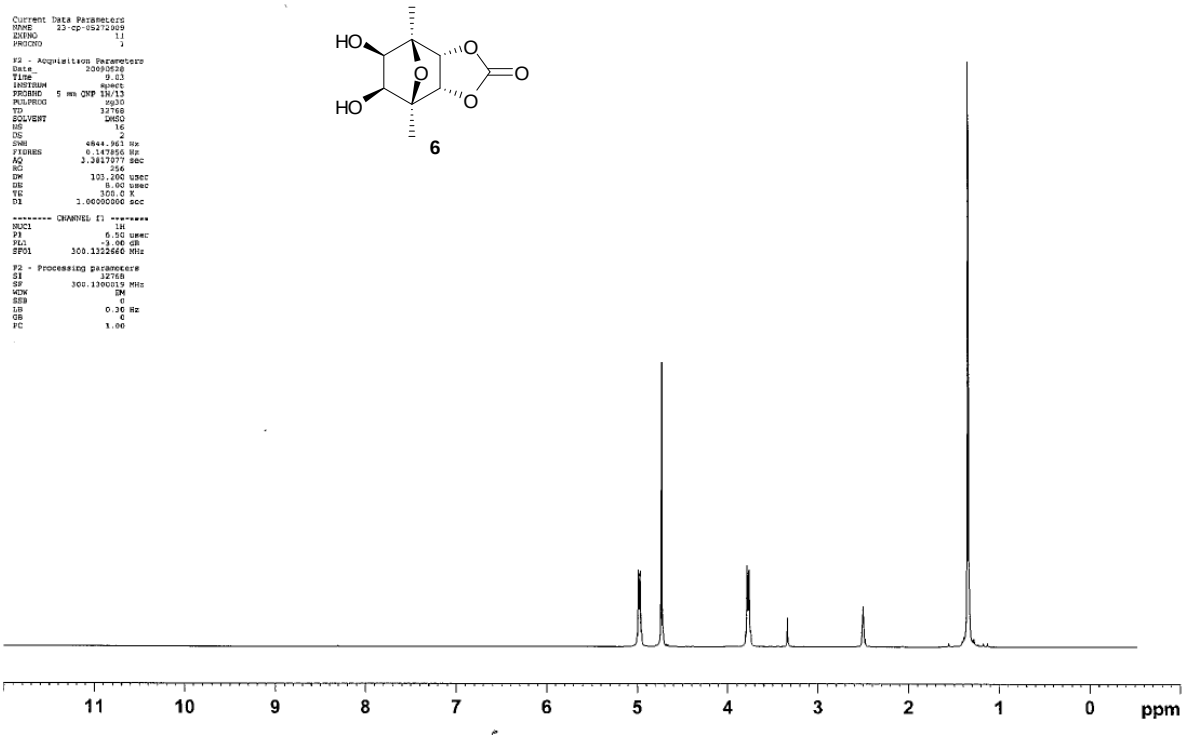


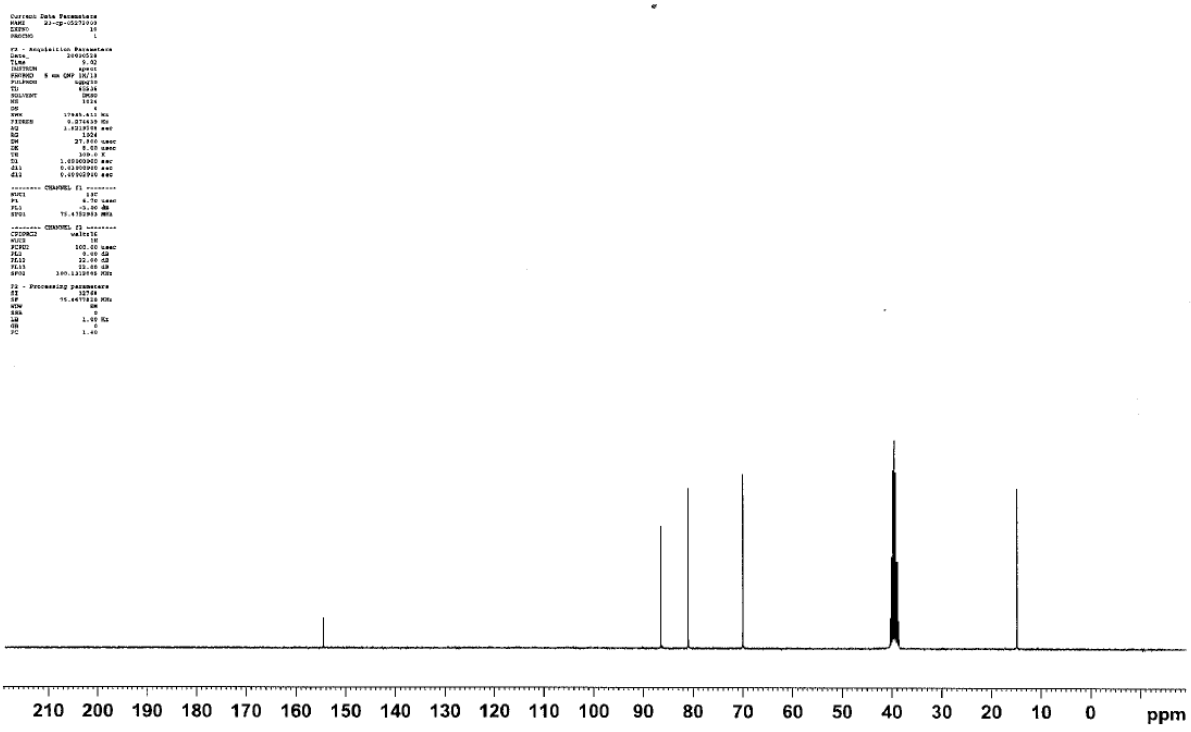


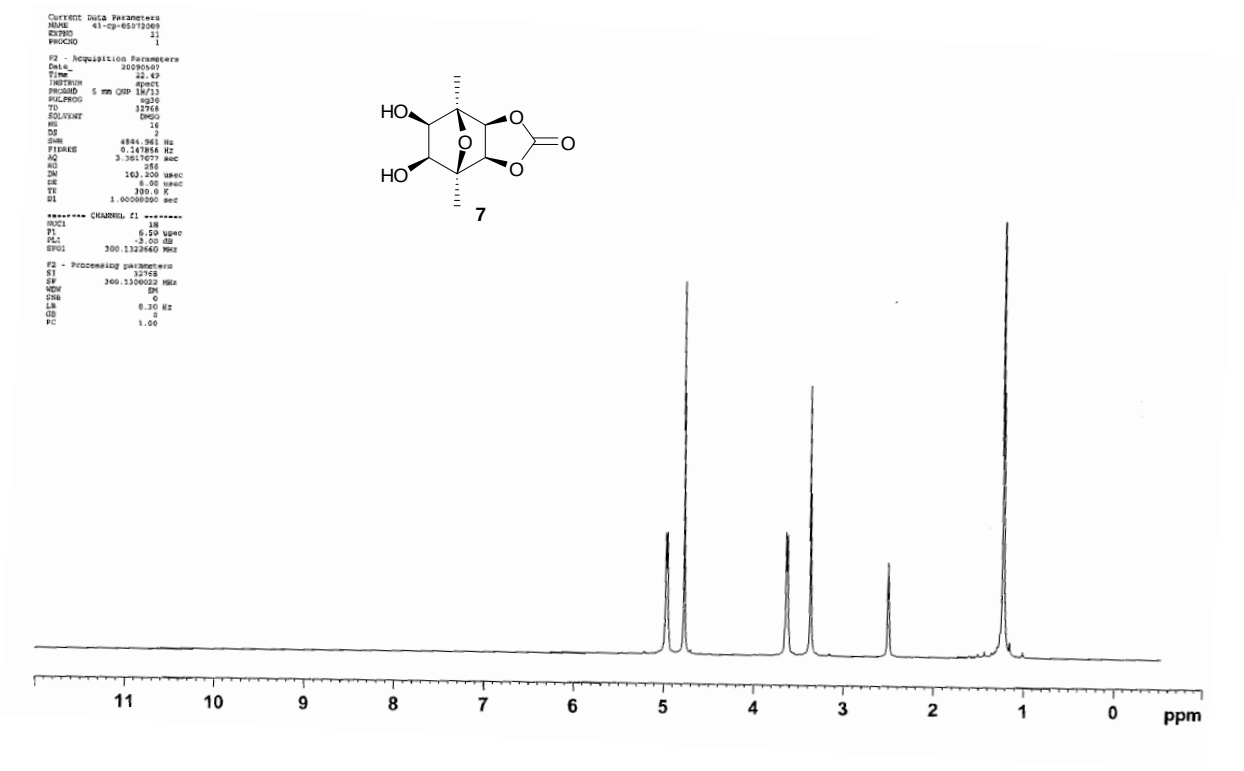
Bisadduct **5**







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O
O
O
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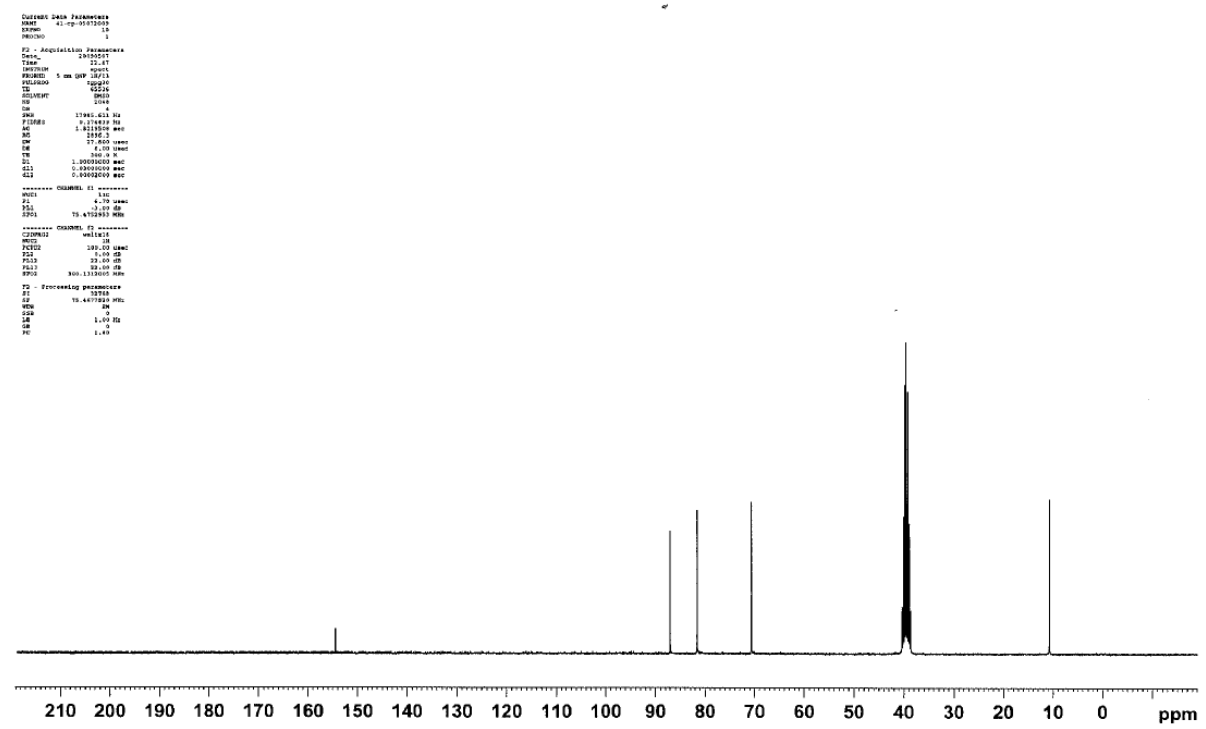
10
9
8
7
6
5
4
3
2
1
0
ppm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120
110
100
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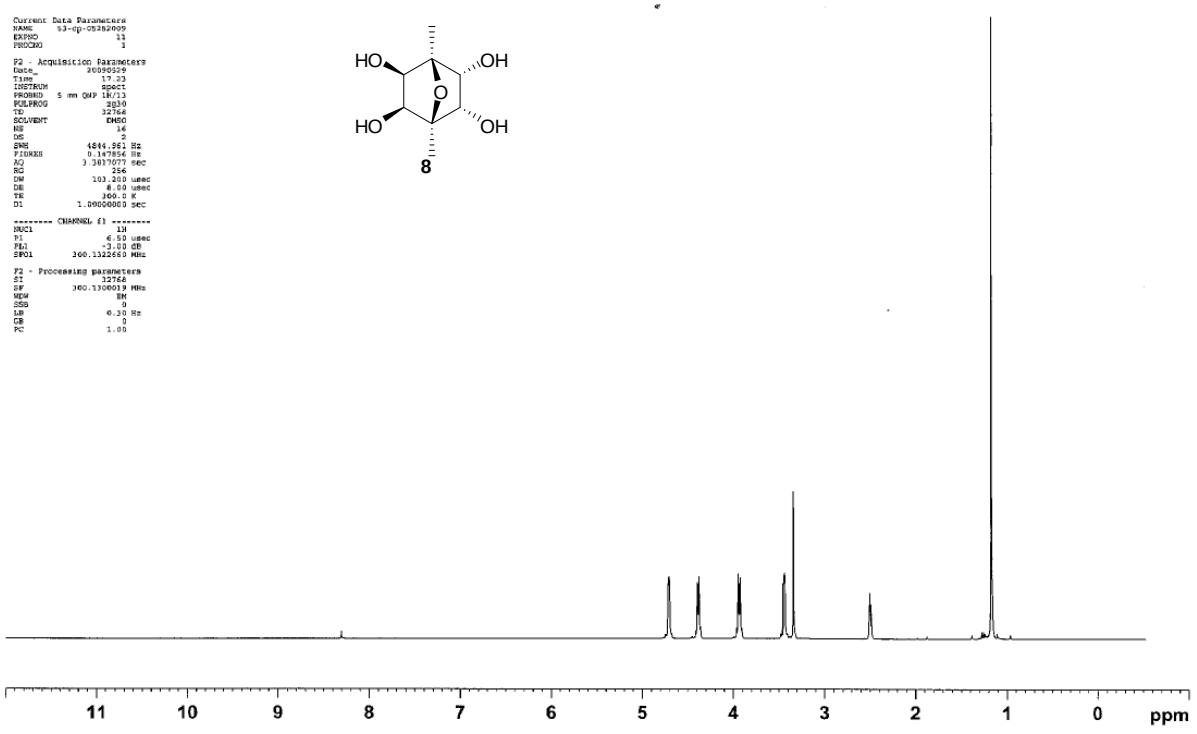
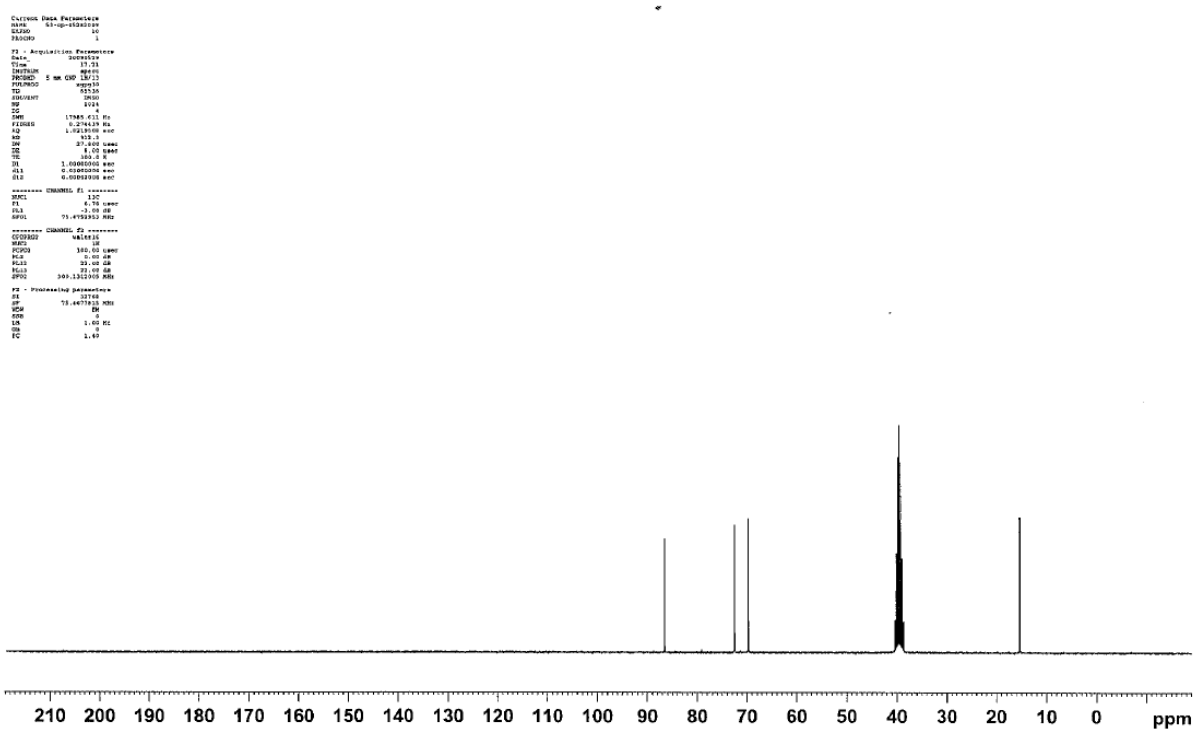
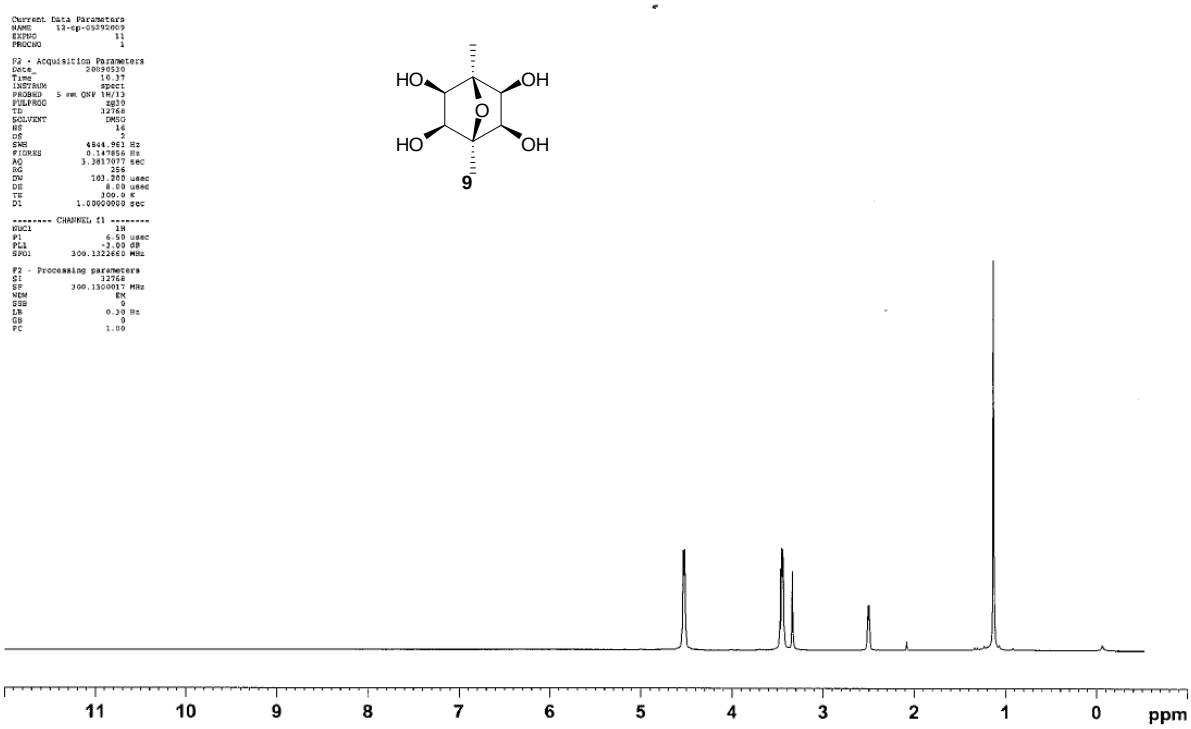
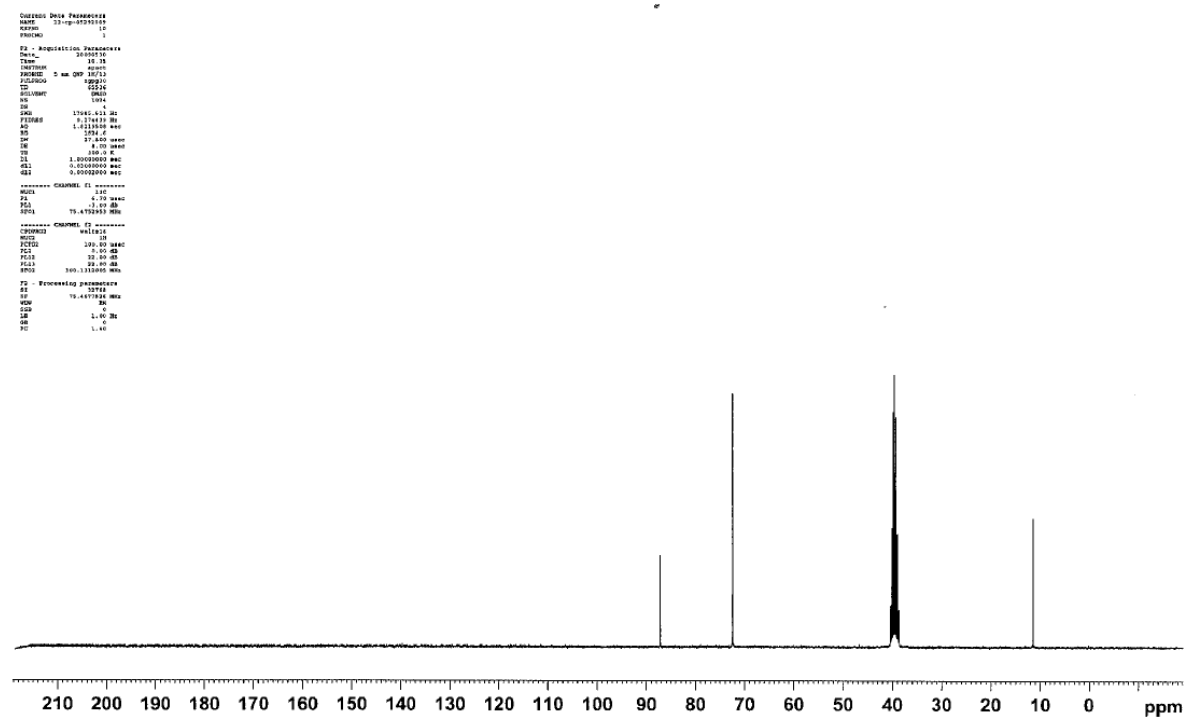
60
50
40
30
20
10
0
ppm









Cartesian coordinates (Å), MO5-2X/cc-pVTZ electronic energies (a.u.), B3PW91/6-31G thermal enthalpies and Gibbs free energies corrections at 400 K (a.u.)**

1

C,-1.1084044674,-0.0044072636,0.0000742272
O,0.0000010155,-0.8131829234,0.0000342446
C,-0.7180585613,1.3010952811,-0.000037889
C,1.1084047515,-0.0044048886,-0.0001054438
C,0.718056032,1.3010968197,-0.0001541319
C,2.4324948824,-0.6844999162,-0.0001703881
C,-2.4324931362,-0.6845051436,0.000222641
H,-1.3727868753,2.1612456197,-0.0000372649
H,1.3727824965,2.1612485598,-0.0002601356
H,3.2314264065,0.0608507022,-0.0002811392
H,2.559364677,-1.3216909954,-0.8834392343
H,2.5595070882,-1.32158122,0.883157187
H,-2.5593616902,-1.3215876599,0.8835699759
H,-3.2314262843,0.0608437426,0.0002412828
H,-2.5595038038,-1.321695556,-0.8830264453

E(MO5-2x) = -308.741939
H(B3PW91) = 0.133984
G(B3PW91) = 0.07542

2

O,0.022535502,1.1099313721,-0.000001185
C,-0.7876945621,0.0000000028,-0.0000085611
C,1.3329296981,0.6659805534,0.0000142582
O,0.0225354997,-1.109931368,0.0000019904
C,1.3329296969,-0.6659805517,0.0000161627
O,-1.9813757918,0.000000004,-0.0000215111
H,2.1101860758,1.4114891925,0.0000217856
H,2.1101860732,-1.4114891923,0.0000258035

E(MO5-2x) = -341.266981
H(B3PW91) = 0.057428
G(B3PW91) = 0.009342

3

C,-0.6211003705,0.6674915416,1.4513253795
C,-0.6211270665,-0.6674609298,1.4513258619
C,-1.0104986007,1.0915247822,0.0392270772
O,-1.8617587045,0.0000394081,-0.3775912686
C,-1.0105421731,-1.0914795834,0.0392278618
C,0.2213826574,0.7716956963,-0.8860779798
C,0.2213521161,-0.7717003148,-0.8860772976
H,0.1078100142,1.2327892051,-1.8696695145
H,0.1077613715,-1.2327902658,-1.8696684063
O,1.4996514735,-1.1227285546,-0.3570748049
H,-0.3189587566,1.3429805935,2.2420953424
H,-0.3190125568,-1.3429615006,2.2420963411
O,1.4996958804,1.1226739406,-0.357075879
C,2.1962819429,-0.0000409357,-0.0131666662
O,3.2745535147,-0.0000620428,0.5011285821
C,-1.6738553781,-2.4335407803,-0.1602944389
C,-1.6737582857,2.4336122802,-0.1602962184
H,-0.983986688,-3.239019826,0.1096309269
H,-2.5674529378,-2.5147506485,0.4640240117
H,-1.9677018044,-2.5648244526,-1.2059657984
H,-0.9838570914,3.2390640623,0.1096274121
H,-1.967600414,2.5649063719,-1.2059674827
H,-2.567352071,2.5148588077,0.4640228781

E(MO5-2x) = -650.038269
H(B3PW91) = 0.194946
G(B3PW91) = 0.121415

TS formation 3

C,-1.0668386418,-1.1698933138,-0.6910150021
C,-1.0641597024,-1.1739490232,0.6883636489
C,0.2911764878,-1.2385378379,-1.0976792455
O,1.0378728971,-1.6348658123,-0.0067707228
C,0.2954233506,-1.2449706889,1.08933873
H,-1.9069544546,-0.9985731859,-1.3501342957
H,-1.9017069443,-1.0065173268,1.3517375359
C,0.7934017339,0.8241146905,-0.7004805558
C,0.7961221164,0.8200077174,0.7023077675
H,1.659739487,0.836837138,-1.3476128137
H,1.6649589601,0.8289383631,1.3461441286
C,0.8457166534,-1.5981307925,-2.4397089556
H,0.2944606368,-1.0718296883,-3.2234031085
H,1.902135549,-1.3243737737,-2.5149776976
H,0.7643900201,-2.6748277239,-2.6284766293
C,0.8551741652,-1.6124142236,2.4270712817
H,0.3069689385,-1.0907246193,3.215971422
H,0.7745804142,-2.6902006048,2.6098421192
H,1.9118781432,-1.3390803147,2.4998368428
O,-0.2458399833,1.6715666854,-1.1056014013
O,-0.2415297431,1.6650613569,1.1164138739

C,-0.8955020296,2.125194817,0.0080080698
O,-1.8743581534,2.8137862648,0.011922225

E(MO5-2x) = -649.980133
H(B3PW91) = 0.192052
G(B3PW91) = 0.11525

4

C,-2.2344100538,-0.5327709577,-0.6673639867
C,-2.2344119091,-0.5327608444,0.6673665863
C,-0.7630171269,-0.5587212946,-1.0895392974
O,-0.1577321567,-1.2813255244,0.0000098588
C,-0.7630201657,-0.5587048163,1.0895464058
C,-0.244855899,0.8868872122,-0.7781139932
C,-0.2448580128,0.886898972,0.7781006882
O,1.1327308118,1.0411301761,-1.1184539693
C,1.9106878617,1.0495595173,-0.0000049656
O,1.1327277817,1.0411470155,1.1184420621
H,-0.8142939898,1.6816820684,1.262895218
H,-3.0753947019,-0.443218488,-1.3450178893
H,-3.075398441,-0.4431981083,1.3450167946
H,-0.8142906042,1.6816629481,-1.2629220824
O,3.1043074071,1.0926931625,-0.0000036758
C,-0.3907557138,-1.1441853145,2.4311187079
C,-0.3907489309,-1.144222061,-2.4311017082
H,-0.8733361778,-0.5863549088,3.239804511
H,-0.713534812,-2.1869964906,2.4863294654
H,0.6906577057,-1.0979357486,2.575458235
H,-0.8733272213,-0.5864039369,-3.2397972789
H,0.6906648809,-1.0979745786,-2.5754389546
H,-0.7135277816,-2.1870341038,-2.4862975687

E(MO5-2x) = -650.041291
H(B3PW91) = 0.195024
G(B3PW91) = 0.121467

TS formation 4

C,-1.3816722011,1.759421804,-0.9414170909
C,-0.0827872655,2.2140573316,-0.9909255719
C,-1.4255474264,0.7659067912,0.0756490637
O,-0.2833274254,0.9003953259,0.8351694065
C,0.63918193,1.4886034843,-0.0030502042
H,-2.1919943888,1.9888256211,-1.6209458229
H,0.3598195279,2.8820112827,-1.7182110731
C,-0.4920794589,-0.83727876,-1.0315789424
C,0.8350399157,-0.3727608117,-1.0821639556
H,-1.1703892758,-0.9638836092,-1.8620113718
H,1.3862522945,-0.0690088907,-1.9594613521

C,-2.612438439,0.1857382009,0.775397367
H,-2.9514128381,0.8457437761,1.5819004951
H,-3.4375303343,0.0601593814,0.0691244214
H,-2.3688324861,-0.7886636345,1.2058604819
C,1.9730653126,1.7907556768,0.6006157261
H,2.6464640338,2.1896767702,-0.162774253
H,1.8808961692,2.5371487548,1.3977108159
H,2.4192770851,0.8872702387,1.0233572381
O,1.5744159976,-1.1583016039,-0.1857937548
O,-0.5183042232,-1.8907951518,-0.106026874
C,0.7254358554,-2.0242168033,0.4440237358
O,1.0218198729,-2.77484045,1.3268682244

E(MO5-2x) = -649.980238
H(B3PW91) = 0.192129
G(B3PW91) = 0.115869

10
C,-0.9263089209,0.0004636289,-0.6795262063
O,-0.9377867255,-0.0000883033,0.6846597837
C,0.3519454684,-0.0002833317,-1.1454914771
C,0.365062819,-0.000303653,1.0892811487
C,1.1982605261,0.0002189876,0.0137162506
H,0.6584684772,-0.0004942921,-2.18144766
H,2.2783549567,0.0003683058,0.0373299959
H,0.5252523585,-0.0005432688,2.1560058976
H,-1.8935412689,0.0008018908,-1.1570446968

E(MO5-2x) = -230.083326
H(B3PW91) = 0.075213
G(B3PW91) = 0.030013

10+2 *endo*
C,-1.1126826023,-1.317290762,-0.6685400097
C,-1.1126793922,-1.3173207219,0.6684857646
C,0.3516067568,-1.3094167903,-1.0755881828
O,0.9838474804,-2.0280442848,-0.0000479435
C,0.3516118675,-1.3094647982,1.0755273267
C,0.9273366805,0.1187929582,-0.7744360033
C,0.9273396502,0.1187587126,0.7744360926
H,1.9059069134,0.2661756333,-1.2336622206
H,1.9059114668,0.266122008,1.2336652109
O,0.0804433799,1.2112166959,1.1229128408
H,-1.9541579502,-1.2385988225,-1.3444538323
H,-1.9541514804,-1.238658933,1.3444071645
O,0.0804399687,1.2112669649,-1.1228613775
C,-0.4340145933,1.7939261522,0.0000395565
O,-1.2126984026,2.6991694219,0.000061005

H,0.6229703138,-1.7334803838,2.0412034899
H,0.6229604887,-1.7333894573,-2.0412845123

E(MO5-2x) = -571.376912
H(B3PW91) = 0.136838
G(B3PW91) = 0.075017

TS formation 10+2 *endo*
C,-1.0921486182,0.6913963701,1.3727843331
C,-1.0926109191,-0.690835832,1.3728469944
C,-1.62641299,1.0788260509,0.1210212619
O,-2.2673836127,0.0005556736,-0.4403421985
C,-1.6272955476,-1.0780712627,0.1212502693
H,-0.6506589791,1.3553369455,2.1025810335
H,-0.6516016588,-1.3550188854,2.1027167843
C,0.1096033188,0.701833067,-1.0997518431
C,0.1095419972,-0.7016988729,-1.0999055614
H,-0.1917129255,1.3456243768,-1.9133533946
H,-0.1920706831,-1.3454098348,-1.9134471972
O,1.2657559023,1.1110957787,-0.4274066494
O,1.2656541726,-1.1112414877,-0.4276749221
C,1.9261776833,-0.000154104,0.0189263766
O,2.9177321816,-0.0002800649,0.687704964
H,-2.0081091228,2.0472938111,-0.1739069248
H,-2.0094937359,-2.0463270153,-0.1737005032

E(MO5-2x) = -571.319413
H(B3PW91) = 0.133574
G(B3PW91) = 0.069081

10+2 *exo*
C,-2.295172792,-0.818892317,-0.6683509255
C,-2.295172998,-0.8188959384,0.6683456736
C,-0.8237357136,-0.7989990444,-1.0722339337
O,-0.1979769994,-1.5187604003,-0.0000041987
C,-0.8237360442,-0.7990048542,1.0722292432
C,-0.3219052783,0.6478603887,-0.7802248008
C,-0.3219055189,0.6478561611,0.7802281047
O,1.0528596298,0.8057709912,-1.1194315511
C,1.8310319068,0.8221140198,0.000002456
O,1.0528592846,0.8057649257,1.1194361345
H,-0.8996999622,1.4361796013,1.2646850918
H,-3.1374562846,-0.7539315031,-1.3458291358
H,-3.1374566996,-0.7539387953,1.3458239762
H,-0.8996995723,1.4361864538,-1.2646776946
O,3.0235021677,0.8767915584,0.0000027879
H,-0.5347482589,-1.203194033,-2.0412220967
H,-0.5347488883,-1.2032050931,2.0412153053

E(MO5-2x) = -571.379238
H(B3PW91) = 0.136724
G(B3PW91) = 0.074766

TS formation 10+2 *exo*

C,-1.4582870568,1.9690821382,-0.7740719353
C,-0.1571148353,2.4278023615,-0.8271254711
C,-1.4712409578,0.9526901601,0.2132155584
O,-0.3383471453,1.072760701,0.9775605517
C,0.5609268741,1.6691168043,0.1303558368
H,-2.2788595325,2.2172322083,-1.4333800359
H,0.2767317127,3.118190094,-1.5375807728
C,-0.5502731964,-0.656653448,-0.8817855199
C,0.7744943914,-0.1896124355,-0.93579776
H,-1.2329603837,-0.7821893105,-1.7083350194
H,1.3232020191,0.1189725301,-1.8125534408
O,1.51379743,-0.9562415279,-0.0277150659
O,-0.5783359158,-1.6938138772,0.0575833156
C,0.6666712871,-1.820680193,0.6085029076
O,0.9652749915,-2.5651835183,1.4947303488
H,1.5385745029,1.855485425,0.5548050723
H,-2.3161334192,0.4965316971,0.7119752627

E(MO5-2x) = -571.317422
H(B3PW91) = 0.133552
G(B3PW91) = 0.069136

11

C,-1.0192613939,-0.0004349365,-0.5171773275
C,-1.039574243,-0.0003779994,0.9738404819
C,0.2237253544,-0.0001526822,1.4067775257
C,1.1222277119,-0.0000226989,0.2167169514
O,0.315077457,0.0002715525,-0.9193801826
O,-1.9299353773,-0.0001190108,-1.2954772123
O,2.3188614914,0.0006547851,0.1606063713
H,0.6090647819,-0.0000334832,2.4173965938
H,-1.9637979268,-0.0004952283,1.5356658058

E(MO5-2x) = -379.395368
H(B3PW91) = 0.063818
G(B3PW91) = 0.011796

1 + 11 *endo*

C,-0.6955054563,-0.8923790462,1.3797457622
C,0.6391289548,-0.9255231689,1.3811448208
C,-1.1175973264,-1.0568717195,-0.0798361862
O,-0.050243264,-1.8709539672,-0.5989998418
C,1.0564983337,-1.1136342593,-0.076812772
C,-0.7579279277,0.312286792,-0.8141181666
C,0.7715260258,0.2694934574,-0.8171728983
H,-1.220852454,0.32952985,-1.8032977402
H,1.230660388,0.2531026221,-1.8081145927
C,1.1954951405,1.5114649486,-0.0638485839
H,-1.3707524907,-0.6929914321,2.2031518877
H,1.3215657992,-0.7603669429,2.206216165
C,-1.1073676325,1.5725026504,-0.0517898945
O,0.0638280811,2.2080578455,0.355668378
O,-2.1869435092,2.0170669656,0.2195195902
O,2.29992164,1.9000104255,0.1932128665
C,2.3916821222,-1.7530709476,-0.3724620441
C,-2.4827284086,-1.6266460741,-0.3813958331
H,3.2001171153,-1.0877141926,-0.0554160304
H,2.4872334461,-2.7041678196,0.1579880948
H,2.495791426,-1.9397086296,-1.4451546123
H,-3.2572978655,-0.9156310799,-0.0793406599
H,-2.5864371472,-1.8199115205,-1.4529824682
H,-2.634488809,-2.5652686686,0.1581788225

E(MO5-2x) = -688.161156
H(B3PW91) = 0.200937
G(B3PW91) = 0.12326

TS formation 1+11 *endo*

C,-1.3435831733,0.6841420497,1.2027331003
C,-1.3435827019,-0.6841362898,1.202733908
C,-1.6303814551,1.0915765123,-0.1425195734
O,-2.1709572521,0.0000016805,-0.7888862088
C,-1.6303794475,-1.0915723077,-0.1425190019
H,-1.041010265,1.3498123005,1.9997282512
H,-1.0410087308,-1.3498053641,1.9997296201
C,0.2356019501,0.707605397,-1.0315041582
C,0.2355972292,-0.7076104882,-1.0315012668
H,0.0536203765,1.3268875879,-1.9005796682
H,0.0536155591,-1.326894359,-1.9005757488
C,1.2581183808,-1.1419666317,-0.0528970122
C,1.2581258717,1.1419591093,-0.0529028394
O,1.7604592652,-0.0000044615,0.5823112838
O,1.637289527,2.2447363829,0.2427711613
O,1.637272017,-2.2447459331,0.2427827468
C,-2.0832124886,2.4403066601,-0.605655916
H,-3.0662154261,2.6893009046,-0.1906478062
H,-1.3663558904,3.1979282355,-0.2782870149
H,-2.1533141659,2.4718226415,-1.6955117014

C,-2.0832087169,-2.4403032913,-0.6056531205
H,-1.3663260371,-3.1979166185,-0.2783220167
H,-3.0661915814,-2.6893196311,-0.1906105948
H,-2.1533517242,-2.4718049015,-1.6955067534

E(MO5-2x) = -688.125319
H(B3PW91) = 0.198678
G(B3PW91) = 0.11833

1+11 *exo*
C,-2.239799192,0.6374815704,0.7392968111
C,-2.2225567732,-0.6955498871,0.7389624053
C,-1.0374201541,1.0757667122,-0.0986259404
O,-0.9199161594,-0.0116285298,-1.0336535806
C,-1.0092492251,-1.1021682469,-0.0991723497
C,0.2237855585,0.7733352589,0.824193685
C,0.2437178348,-0.7676803838,0.8238070524
C,1.5353875039,1.166041148,0.1685112239
O,2.236255318,0.0289880599,-0.2098535532
C,1.5650338941,-1.1260017984,0.1679360832
O,1.9738557686,2.2636283631,-0.0310311938
O,2.0317423216,-2.2117809304,-0.0321544043
H,0.1803980355,-1.2552761648,1.798408009
H,-2.8953538477,1.3112537055,1.2782848593
H,-2.860461424,-1.386322927,1.2776080856
H,0.1478818261,1.258640914,1.7990388866
C,-1.0455527963,-2.4450925851,-0.7919507144
C,-1.1084501508,2.4176505403,-0.7907299386
H,-1.082839939,-3.2527101625,-0.0550321094
H,-1.9361840134,-2.5058737484,-1.4230094833
H,-0.1604258082,-2.5953331876,-1.4122703864
H,-1.1666109623,3.2236630886,-0.053405972
H,-0.2275080331,2.5910467955,-1.4109663574
H,-2.0003583273,2.4556918359,-1.4217657002

E(MO5-2x) = -688.16234
H(B3PW91) = 0.20107
G(B3PW91) = 0.123554

TS formation 1+11 *exo*
C,-0.6831510906,-2.1152446789,-0.9811188794
C,0.6833681423,-2.1152161897,-0.9807880162
C,-1.094147918,-0.7386692509,-0.9813120284
O,0.0001251989,0.0071472314,-1.3586576559
C,1.0943277838,-0.7385972067,-0.9806465124
H,-1.3516050511,-2.9584972324,-0.8682681382
H,1.3517856993,-2.9584535797,-0.8676070324

C,-0.7105793741,-0.4075618153,1.0787803181
C,0.7105851159,-0.4073511034,1.0785835416
H,-1.3369535916,-1.1695958775,1.522493182
H,1.3372310373,-1.1690167435,1.5225715759
C,-2.4350324438,-0.2022211668,-1.3719333214
H,-2.5380242821,-0.2090651854,-2.4627650576
H,-3.2210925501,-0.8326552779,-0.9490951539
H,-2.5859775027,0.8161003732,-1.0104850224
C,2.4352863687,-0.202224499,-1.3712223923
H,3.2213025388,-0.8322561577,-0.9476991542
H,2.5386214159,-0.2098031506,-2.46201271
H,2.5859570672,0.8163586882,-1.0104071723
C,1.1354363301,1.0050398428,1.2225933371
C,-1.1359276251,1.0045902627,1.2227207504
O,-2.2382661075,1.4768068069,1.3322348109
O,2.2376395742,1.4775604126,1.3320987065
O,-0.0003619493,1.8143628608,1.185250339

E(MO5-2x) = -688.12381
H(B3PW91) = 0.198811
G(B3PW91) = 0.118122