

## Supplementary Material

### **Radicals Masquerading as Electrophiles: A Computational Study of the Intramolecular Addition Reactions of Acyl Radicals to Imines**

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HF/6-311G<sup>\*\*</sup>, MP2/6-311G<sup>\*\*</sup>, MP2/cc-pVDZ, BHandHLYP/6-311G<sup>\*\*</sup>, BHandHLYP/cc-pVDZ, B3LYP/6-311G<sup>\*\*</sup> and B3LYP/cc-pVDZ Gaussian Archive entries for the optimized structures in this study and higher-level calculated single-point energies (48 pages).

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## 5-Aza-5-hexenoyl radical (4)

### UHF/6-311G\*\*

021\1\ MAR CCENTRE-ANET03\FOpt\UHF\6311G(d,p)\C5H8N1O1(2)\CHANTAL\12-Nov-2004\1\#\UHF/6-311G\*\* OPT=GRAD OPTCYC=100\ground state for 5exo/6endo\0,2\O\C,1,r1\C,2,r2,1,a1\C,3,r3,2,a2,1,d1,O\C,4,r4,3,a3,2,d2,0\N,5,r5,4,a4,3,d3,O\C,6,r6,5,a5,4,d4,0\H,3,r7,2,a6,1,d5,0\H,3,r8,2,a7,1,d6,0\H,4,r9,3,a8,2,d7,0\H,4,r10,3,a9,2,d8,0\H,5,r11,4,a10,3,d9,0\H,5,r12,4,a11,3,d10,0\H,7,r13,6,a12,5,d11,0\H,7,r14,6,a13,5,d12,0\|r1=1.15767788|r2=1.52088863|r3=1.52822621|r4=1.52787225|r5=1.44543214|r6=1.24428529|r7=1.08759773|r8=1.08676639|r9=1.08657217|r10=1.08647568|r11=1.09098455|r12=1.08722753|r13=1.08799729|r14=1.08000793|a1=128.84338349|a2=114.55983816|a3=113.79631494|a4=110.79152258|a5=119.25665069|a6=104.29301265|a7=108.14718243|a8=109.33690559|a9=108.76830144|a10=109.75129271|a11=108.88763041|a12=123.41141008|a13=119.58212645|d1=206.60215414|d2=75.59462478|d3=-56.96827674|d4=-126.67201456|d5=86.7483272|d6=-27.60559654|d7=-47.25996069|d8=163.79983667|d9=178.58748557|d10=60.96156256|d11=-0.27077118|d12=179.80945112\Version=DEC-AXP-OSF/1-G98RevA.7\HF=-323.3186964\S2=0.762318\S2-1=0.\S2A=0.750116\RMSD=9.912e-09\RMSF=1.331e-05\Dipole=0.3658312,-0.4016069,1.6100546\PG=C01 [X(C5H8N1O1)]\@\

### MP2/6-311G\*\*

1\1\ MARCCENTRE-ANET06\FOpt\UMP2-FC\6-311G(d,p)\C5H8N1O1(2)\HIROSHI\12-Sep-2004\1\#\MP2/6-311G\*\* SCF=QC OPT=(Z-MATRIX,CALCHFFC,MAXCYCLE=100) NOSYMM FREQ=NORAMAN\substrate for 5-exo and 6-endo terminal imine\0,2\O\C,1,r1\C,2,r2,1,a1\C,3,r3,2,a2,1,d1,O\C,4,r4,3,a3,2,d2,0\N,5,r5,4,a4,3,d3,O\C,6,r6,5,a5,4,d4,0\H,3,r7,2,a6,1,d5,0\H,3,r8,2,a7,1,d6,0\H,4,r9,3,a8,2,d7,0\H,4,r10,3,a9,2,d8,0\H,5,r11,4,a10,3,d9,0\H,5,r12,4,a11,3,d10,0\H,7,r13,6,a12,5,d11,0\H,7,r14,6,a13,5,d12,0\|r1=1.18702451|r2=1.52705313|r3=1.52908692|r4=1.52889836|r5=1.45486289|r6=1.25441415|r7=1.09721415|r8=1.09735245|r9=1.09562961|r10=1.09569743|r11=1.10305975|r12=1.09661005|r13=1.10108204|r14=1.09029264|a1=127.30248002|a2=113.66132011|a3=112.39048062|a4=109.46721208|a5=117.26550076|a6=104.37142755|a7=108.76417596|a8=109.13932553|a9=109.58872048|a10=110.15033265|a11=109.01191549|a12=123.43352159|a13=119.30803162|d1=212.55473475|d2=77.24157914|d3=-54.27362669|d4=-121.35397897|d5=93.01270886|d6=-22.27025874|d7=-44.26193895|d8=198.18094314|d9=181.88758279|d10=63.19538195|d11=-1.39796839|d12=178.64869004\Version=DEC-AXP-OSF/1-G98RevA.7\HF=-323.3152987\MP2=-324.3821232\PUHF=-323.3188781\PMP2-0=-324.3845449\S2=0.765807\S2-1=0.755503\S2A=0.750205\RMSD=0.000e+00\RMSF=5.750e-05\Dipole=0.3374892,-0.4261074,1.2090623\PG=C01 [X(C5H8N1O1)]\@\

### MP2/cc-pVDZ

1\1\ CHEMISTRY CLUSTER KIRKLAND-KNET18\FOpt\UMP2-FC\CC-pVDZ\C5H8N1O1(2)\HIROSHI\13-Sep-2004\1\#\MP2/CC-PVDZ SCF=QC OPT=(Z-MATRIX,CALCHFFC,MAXCYCLE=100) NOSYMM FREQ=NUMER\substrate for 5-exo and 6-endo chantal's\0,2\O\C,1,r1\C,2,r2,1,a1\C,3,r3,2,a2,1,d1,O\C,4,r4,3,a3,2,d2,0\N,5,r5,4,a4,3,d3,O\C,6,r6,5,a5,4,d4,0\H,3,r7,2,a6,1,d5,0\H,3,r8,2,a7,1,d6,0\H,4,r9,3,a8,2,d7,0\H,4,r10,3,a9,2,d8,0\H,5,r11,4,a10,3,d9,0\H,5,r12,4,a11,3,d10,0\H,7,r13,6,a12,5,d11,0\H,7,r14,6,a13,5,d12,0\|r1=1.19471096|r2=1.53123998|r3=1.53174066|r4=1.53158596|r5=1.45742149|r6=1.25763392|r7=1.1059224|r8=1.10634926|r9=1.1048|r10=1.10424416|r11=1.11177735|r12=1.10556758|r13=1.1108755|r14=1.09994011|a1=127.417

31771a2=113.58445748a3=112.42497533a4=109.5116194a5=117.17469814a6=104.3324449  
 7a7=108.95629645a8=109.16367534a9=109.5771897a10=110.43727302a11=108.82718619\  
 a12=123.62795107a13=119.32681505d1=213.2643192d2=75.82065745d3=-54.46290006d4  
 =-122.18079784d5=93.77763092d6=-21.24170597d7=-45.83549439d8=196.86013302d9=18  
 1.30668524d10=62.91229349d11=-1.40470843d12=178.74750035\\Version=x86-Linux-G03R  
 evB.04\\HF=-323.2608484\\MP2=-324.2698557\\PUHF=-323.2645137\\PMP2-0=-324.2723548\\S2  
 =0.76644\\S2-1=0.755893\\S2A=0.750223\\RMSD=0.000e+00\\RMSF=5.920e-05\\Dipole=0.32427  
 37,-0.4320306,1.1535771\\PG=C01 [X(C5H8N1O1)]\\@

### **MP2/aug-cc-pVDZ//MP2/cc-pVDZ**

MP2=-324.3315862

### **QCISD/cc-pVDZ//MP2/cc-pVDZ**

QCISD=-324.3356391

### **CCSD(T)/cc-pVDZ//MP2/cc-pVDZ**

CCSD(T)=-324.3704033

### **BHandHLYP/6-311G\*\***

021\1\MARCCENTRE-BNET2\FOpt\UBHandHLYP\6-311G(d,p)\C5H8N1O1(2)\CHANTAL\0  
 1-Sep-2001\1\#\BHANDHLYP/6-311G\*\* OPT=GRAD GEOM=CHECKPOINT GUESS=REA  
 D\\ground state for 5exo/6endo at BHandH\0,2\O\C,1,r1\N,2,r2,1,a1\C,3,r3,2,a2,1,d1,O\C,3,r4,2,  
 a3,1d2,O\C,5,r5,3,a4,2,d3,O\C,6,r6,5,a5,3,d4,O\H,4,r7,3,a6,2,d5,O\H,4,r8,3,a7,2,d6,O\H,5,r9,3,a8,  
 2,d7,O\H,5,r10,3,a9,2,d8,O\H,6,r11,5,a10,3,d9,O\H,6,r12,5,a11,3,d10,O\H,7,r13,6,a12,5,d11,O\H,7,  
 r14,6,a13,5,d12,0\\r1=1.1667666\\r2=2.85737761\\r3=1.25015736\\r4=1.44179349\\r5=1.52285114  
 \\r6=1.52124639\\r7=1.0814187\\r8=1.09064975\\r9=1.09299131\\r10=1.08877029\\r11=1.08656284  
 \\r12=1.08701811\\r13=1.08854561\\r14=1.08886126\\a1=115.56235108\\a2=136.99345706\\a3=90.  
 21707342\\a4=110.40155987\\a5=113.14440894\\a6=119.48401789\\a7=123.25722925\\a8=112.361  
 59579\\a9=107.32477349\\a10=108.46053735\\a11=109.48415738\\a12=109.76799155\\a13=112.09  
 760135\\d1=86.45534595\\d2=-137.84543609\\d3=-20.37749231\\d4=55.42355571\\d5=-52.54998  
 19\\d6=-232.51747416\\d7=-143.77412719\\d8=97.98058609\\d9=-183.22976962\\d10=-66.620630  
 89\\d11=-190.19377661\\d12=50.27124582\\Version=DEC-AXP-OSF/1-G98RevA.7\\HF=-325.1  
 244076\\S2=0.754843\\S2-1=0.750014\\S2A=0.750014\\RMSD=1.460e-09\\RMSF=2.769e-05\\Dipole=0.  
 3808829,-0.4148176,1.42846\\PG=C01 [X(C5H8N1O1)]\\@

### **BHandHLYP/cc-pVDZ**

021\1\MARCCENTRE-BNET4\FOpt\UBHandHLYP\CC-pVDZ\C5H8N1O1(2)\CANTAL\03-S  
 ep-2001\1\#\BHANDHLYP/CC-PVDZ OPT=GRAD GEOM=CHECKPOINT GUESS=READ\\  
 ground state for 5exo/6endo at BHandH\0,2\O\C,1,r1\N,2,r2,1,a1\C,3,r3,2,a2,1,d1,O\C,3,r4,2,a3,  
 1,d2,O\C,5,r5,3,a4,2,d3,O\C,6,r6,5,a5,3,d4,O\H,4,r7,3,a6,2,d5,O\H,4,r8,3,a7,2,d6,O\H,5,r9,3,a8,2,d  
 7,O\H,5,r10,3,a9,2,d8,O\H,6,r11,5,a10,3,d9,O\H,6,r12,5,a11,3,d10,O\H,7,r13,6,a12,5,d11,O\H,7,r1  
 4,6,a13,5,d12,0\\r1=1.17261371\\r2=2.83660539\\r3=1.255182\\r4=1.44211144\\r5=1.52280974\\r6  
 =1.52094834\\r7=1.08989699\\r8=1.09898251\\r9=1.10081026\\r10=1.0968056\\r11=1.09421774\\r1  
 2=1.09522868\\r13=1.09633462\\r14=1.09690214\\a1=115.45176774\\a2=137.15644549\\a3=90.33  
 791058\\a4=110.44671813\\a5=113.16390071\\a6=119.40282649\\a7=123.3127351\\a8=112.464502  
 \\a9=107.29643156\\a10=108.49096824\\a11=109.47503721\\a12=109.79778432\\a13=112.1988849

9\d1=87.54929108\d2=-137.07400738\d3=-20.9506 6523\d4=55.55302837\d5=-52.70220723\d6  
 =-232.57641746\d7=-144.55306453\d8=97.32261318\d9=-183.00760 311\d10=-66.46766983\d1  
 1=-188.65319688\d12=51. 87649813\\Version=DEC-AXP-OSF/1-G98RevA.7\HF=-325.060213  
 4\S2=0.754782\S2-1=0.\S2A=0.750014\RMS D=8.935e-09\RMSF=1.364e-05\Dipole=0 .355135  
 5,-0.4087608,1.3544509\PG=C01 [X(C5H8N1O1)]\@

**BHandHLYP/aug-cc-pVDZ//BHandHLYP/cc-pVDZ**  
 HF=-325.0814497

**QCISD/cc-pVDZ//BHandHLYP/cc-pVDZ**  
 QCISD=-324.333087

**CCSD(T)/cc-pVDZ//BHandHLYP/cc-pVDZ**  
 CCSD(T)=-324.3669938

**B3LYP/6-311G\*\***

021\1\MARCCENTRE-BNET1\FOpt\UB3LYP\6-311G(d,p)\C5H8N1O1(2)\CHANTAL\01-Sep-  
 p-2001\1\#B3LYP/6-311G\*\* OPT=GRAD GEOM=CHECKPOINT GUESS=READ OPTCYC=  
 100\ground state for 5exo/6endo\0,2\O\C,1,r1 \N,2,r2,1,a \C,3,r3,2,a2,1,d1,\O\C,3,r4 ,2,a3,1,d2,  
 \O\C,5,r5,3,a4,2,d3,\O\C,6,r6,5,a5,3,d4 ,\O\H,4,r7,3,a 6,2,d5,\O\H,4,r8,3,a7,2,d6,\O\H,5,r9,3,a8,2,d7,\O  
 H,5,r10,3,a9,2,d8,\O\H,6,r11,5,a10,3,d9,\O\H,6,r12,5,a11,3,d10,\O\H,7,r13,6,a12,5,d11,\O\H,7,r14,6,a  
 13,5,d12,0\r1=1.18052996\r2=2.85444856\r3=1.2622047\r4=1.45256307\r5=1.53388645\r6=1.5  
 3105051\r7=1.08947083\r8=1.09996236\r9=1.09695289\r10=1.10173112\r11=1.0946193\r12=1.  
 09413655\r13=1.09751933\r14=1.09655499\A1=115.32407585\A2=137.58473282\A3=90.268214  
 19\A4=110.4393418\A5=113.23025215\A6=119.33141045\A7=123.45032599\A8=107.18330012\A  
 9=112.52034869\A10=109.38199107\A11=108.43617268\A12=112.1314212\A13=109.64067419\  
 d1=-86.9484 8536\d2=136.74621703\d3= 21.07155631\d4=-55.67856832\d5=51. 64865702\d6=  
 231.62745442\d7=-97.17282527\d8=144.6059573\d9=66.28205192\d10=182.85157231\d11=-52  
 .16724765\d12=188.4599932\\Version=DEC-AXP-OSF/1-G98RevA.7\HF=-325.3270799\S2=0.  
 752626\S2-1=0.\S2A=0.750004\RMSD=5.318e-09\RMSF=1.344e-05\Dipole=0.3604 196,0.4339  
 267,1.3 299806\PG=C01 [X(C5H8N 1O1)]\@

**B3LYP/cc-pVDZ**

021\1\MARCCENTRE-BNET1\FOpt\UB3LYP\CC-pVDZ\C5H8N1O1(2)\CHANTAL\03-Sep-2  
 001\1\#B3LYP/CC-PVDZ OPT=GRAD GEOM=CHECKPOINT GUESS=READ\ground state  
 for 5exo/6endo\0,2\O\C,1,r1\N,2,r2,1,a\C,3,r3,2,a2 ,1,d1,\O\C,3,r4,2,a3,1,d2,\O\C,5,r5,3,a4,2,d3,0  
 \C,6,r6,5,a5,3,d4,\O\H,4,r7,3,a6,2,d5,\O\H,4,r8,3,a7,2,d6,\O\H,5,r9,3,a8,2,d7,\O\H,5,r10,3,a9,2,d8,\O\H  
 ,6,r11,5,a10,3,d9,\O\H,6,r12,5,a11,3,d10,\O\H,7,r13,6,a12,5,d11,\O\H,7,r14,6,a13,5,d12,0\r1=1.187  
 07561\r2=2.82163544\r3=1.26762282\r4=1.45263257\r5=1.53408514\r6=1.53100811\r7=1.0986  
 0754\r8=1.10907691\r9=1.10577482\r10=1.11033005\r11=1.10354022\r12=1.10243646\r13=1.1  
 0633701\r14=1.10503659\A1=115.17009487\A2=137.67025198\A3=90.59726886\A4=110.383186  
 1\A5=113.0867179\A6=119.22691119\A7=123.52483169\A8=107.12699277\A9=112.6791092\A10  
 =109.38707317\A11=108.50470643\A12=112.23332338\A13=109.72425462\d1=-87.58184699\d2  
 =136.09 806 653\d3=21.6359897\d4=-55.68 296192\d5=51.3498438 5\d6=231.21679626\d7=-9  
 6.42475661\d8 =145.44617836\ d9=66.18175227\d10=182.76782164\d11=-53.82440813\d12=1  
 86.78937807 \\V ersion=DEC-AXP-OSF/1-G98RevA.7\HF=-325.2544578\S2=0.752559\S2-1=0

\S2 A=0.750004\RMSD=6.214e-09\RMSF=2.256e-05\Dipole=0.3335547,0.426128 6,1.2431702  
 \PG=C01 [X(C5 H8N1O1)]\@

**B3LYP/aug-cc-pVDZ//B3LYP/cc-pVDZ**  
 HF=-325.2736382

**QCISD/cc-pVDZ//B3LYP/cc-pVDZ**  
 QCISD=-324.2979571

**CCSD(T)/cc-pVDZ//B3LYP/cc-pVDZ**  
 CCSD(T)=-324.3329481

## Transition state 10 for 5-exo cyclization of 5-aza-5-hexenoyl radical (4)

### UHF/6-311G\*\*

1\ \ CHEMISTRY CLUSTER KIRKLAND-KNET2\FTS\UHF\6-311G(d,p)\C5H8N1O1(2)\HI  
 ROSHI\09-Sep-2004\1\#\HF/6-311G\*\* SCF=QC OPT=(TS,EF,CALCFC,MAXCYCLE=100) N  
 OSYMM FREQ=NORAMAN\TS for 5-exo\0,2\O\C,1,r1\N,2,r2,1,a1\C,3,r3,2,a2,1,d1,0\C,3,r4,  
 2,a3,1,d2,0\C,5,r5,3,a4,2,d3,0\C,6,r6,5,a5,3,d4,0\H,4,r7,3,a6,2,d5,0\H,4,r8,3,a7,2,d6,0\H,5,r9,3,a  
 8,2,d7,0\H,5,r10,3,a9,2,d8,0\H,6,r11,5,a10,3,d9,0\H,6,r12,5,a11,3,d10,0\H,7,r13,6,a12,5,d11,0\H,  
 7,r14,6,a13,5,d12,0\ r1=1.18427273 r2=1.82020714 r3=1.27779472 r4=1.44952397 r5=1.535199  
 22 r6=1.52660631 r7=1.08046913 r8=1.07673288 r9=1.0864315 r10=1.08621251 r11=1.085237  
 2 r12=1.08383677 r13=1.08376805 r14=1.08928916 a1=117.3906066 a2=124.64147211 a3=107  
 .12048843 a4=106.13961384 a5=106.80430286 a6=122.32841783 a7=118.07533886 a8=112.50  
 015777 a9=106.86907023 a10=109.57642285 a11=110.80237237 a12=112.02854935 a13=112.2  
 668229 d1=39.7047167 d2=-163.53762515 d3=-3.75411765 d4=28.37934215 d5=149.99210127  
 d6=-27.97619241 d7=-127.54684721 d8=113.79081575 d9=-89.62497834 d10=151.53426232  
 d11=-163.00917512 d12=75.43617949 \Version=x86-Linux-G03RevB.04\HF=-323.2903361\S2  
 =0.951903\S2-1=0.\S2A=0.75745\RMSD=0.000e+00\RMSF=4.026e-06\Dipole=0.8957156,-0.0  
 570767,1.752193\PG=C01 [X(C5H8N1O1)]\@

### MP2/6-311G\*\*

021\ \MAR CCENTRE-ANET05\FTS\UMP2-FC\6-311G(d,p)\C5H8N1O1( 2)\CHANTAL\12-J  
 un-2001\1\#\MP2/6-311G\*\* OPT=(EF,TS,READFC,NOFRE EZE) GEOM=CHECKPOINT GU  
 ESS=READ\ trans state for 5exo\0,2\O\C,1,r 1\N,2,r2,1,a1\C,3,r3 ,2,a2,1,d1,0\C,3,r4,2,a3,1,d2,  
 0\C,5,r5,3,a4,2, d3,0\C,6,r6,5,a5,3, d4,0\H,4,r7,3,a6,2,d5, 0\H,4,r8,3,a7,2,d6,0\H,5,r9,3,a8,2,d7,0\  
 H,5,r10,3,a9,2,d8,0\H,6,r11,5,a10,3,d9,0\H,6,r12,5,a11,3,d10,0\H,7,r13,6,a12,5,d11,0\H,7,r14,6,a  
 13,5,d12,0\ r1=1.2205989 r3=1.2360814 r4=1.45542982 r5=1.53870195 r6=1.52957438 r7=1.09  
 256867 r8=1.09369726 r9=1.09509104 r10=1.09534339 r11=1.09386907 r12=1.09295383 r13=  
 1.09313149 r14=1.10277281 a1=112.93257406 a2=121.102788 a3=109.43395996 a4=103.9299  
 0432 a5=105.37519182 a6=123.72846328 a7=116.11625571 a8=111.82910548 a9=108.1785838  
 5 a10=109.62296366 a11=110.81215011 a12=112.01546727 a13=111.25651214 d1=24.101953  
 74 d2=-156.25879988 d3=-7.47159764 d4=32.87653079 d5=176.11089177 d6=-3.83707569 d7  
 =-130.36687786 d8=109.48 849271 d9=-84.32595662 d10=155.740791 74 d11=-167.68280934

\d12=71.03884145\r2=1.78116144\\Version=DEC-AXP-OSF/1-G98RevA.7\HF=-323.28665\MP2=-324.35826\PUHF=-323.2943149\PMP2-0=-324.3646197\S2=0.828053\S2-1=0.801011\S2A=0.75226\RMS D=8.611e-09\RMSF=5.420e-05\Dipole=1.474 5765,-0.1889647,1.3840493\PG=C01 [X(C5H8N 1O1)]\@

### MP2/cc-pVDZ

021\1\MARCCENTRE-BNET4\FTS\UMP2-FC\CC-pVDZ\C5H8N1O1(2)\CHANTAL\05-Jul-2001\1\#\MP 2/CC-PVDZ OPT=(EF,TS,READFC,NOFREEZE) GEOM=CHECKPOINT GUESS=READ\trans state for 5exo\0,2\O\C,1,r1\N,2,r 2,1,a1\C ,3,r3,2,a 2,1,d1,0\C,3,r4,2,a3,1,d2,0\C,5,r5,3,a4, 2,d3 ,0\C,6,r6,5,a5,3,d4,0\H,4,r7,3,a 6,2,d5,0\H,4 ,r8,3,a7,2,d6,0\H,5,r9,3,a8,2,d7,0\H,5,r10,3,a9,2,d8,0\H,6,r11,5,a10,3,d9,0\H,6,r12,5,a11,3,d10,0\H,7,r13,6,a12,5,d11,0\H,7,r14,6,a13,5,d12,0\r1=1.22640685\r3=1.24195986\r4=1.45713902\r5=1.54100032\r6=1.53269594\r7=1.10169477\r8=1.10275358\r9=1.10376759\r10=1.10396194\r11=1.10306623\r12=1.1014335\r13=1.10179704\r14=1.11171387\A1=113.30660935\A2=121.20021009\A3=109.27833976\A4=104.01860439\A5=105.36815269\A6=123.74547065\A7=115.97351701\A8=112.10241708\A9=107.96914952\A10=109.58529806\A11=110.8415392\A12=112.00189369\A13=111.34609238\d1=24.80609027\d2=-157.04114272\d3=-7.77631741\d4=33.28767577\d5=174.48119714\d6=-5.37034862\d7=-131.21760761\d8=109.043885 93\d9=-83.95841206\d10=156.45448918\d11=-167.659899 38\d12=71.42053419\r2=1.78486594\\Version=DEC-AXP-OSF/1-G98RevA.7\HF=-323.231837\MP2=-324.24532\PUHF=-323.2401767\PMP2-0=-324.2522828\S2=0.837838\S2-1=0.8083 04\S2A=0.752681\RMSD=9.962e-09\RMSF=6.263e-06\Dipole=1.4218814,-0.1578874,1.3521748\PG=C01 [X(C5H8N1O1)]\@

### MP2/aug-cc-pVDZ//MP2/cc-pVDZ

MP2=-324.3127272

### QCISD/cc-pVDZ//MP2/aug-cc-pVDZ

QCISD=-324.3138232

### CCSD(T)/cc-pVDZ//MP2/aug-cc-pVDZ

CCSD(T)=-324.3497803

### BHandHLYP/6-311G\*\*

021\1\MARCCENTRE-BNET1\FTS\UBHandHLYP\6-311G(d,p)\C5H8N1O1(2)\CHANTAL\04-Sep-2001\ 1\#\BHANDHLYP/6-311G\*\* OPT=(EF,TS,CALCFC,NOFREEZE) GEOM=CHECKPOINT GUESS=READ\trans state for 5exo\0,2\O\C,1, r1\N,2,r2,1,a1\C,3,r3,2,a2,1,d1,0\C,3,r4,2,a3, 1,d2 ,0\C,5,r5,3,a4,2,d3,0\C,6,r6,5,a5,3 ,d4,0\H,4,r7,3,a6,2,d5,0\H,4,r8,3,a7,2,d6,0\H,5,r9,3,a8,2,d7,0\H,5,r10,3,a9,2,d8,0\H,6,r11,5,a10,3,d9,0\H,6,r12,5,a11,3,d10,0\H,7,r13,6,a12,5,d11,0\H,7,r14,6,a13,5,d12,0\r1=1.18502635\r3=1.26091495\r4=1.44299365\r5=1.52869867\r6=1.52038318\r7=1.08433831\r8=1.07993269\r9=1.08877526\r10=1.08818895\r11=1.08589404\r12=1.08426995\r13=1.08485272\r14=1.09138247\A1=116.69952154\A2=126.39023956\A3=105.56575541\A4=106.65766982\A5=107.09958036\A6=122.68107673\A7=118.3231426\A8=112.6488866\A9=106.95331284\A10=109.60479711\A11=110.74613862\A12=111.89610431\A13=112.20355809\d1=43.62422806\d2=-158.66308675\d3=-7.92920876\d4=32.71910252\d5=150.93927239\d6=-27.38280098\d7=-132.1632999\d8=109.21401548\d9=-85.42595354\d10=155.64437581\d11=-166.02868878\d12=72.75513528\r2=1.91279673\\Version=DEC-AXP-OSF/1-G98RevA.7\HF

=-325.1091645\S2=0.773225\S2-1=0.\S2A=0.750209\RMSD=6.628e-09\RMSF= 3.168e-05\Dipole=0.775 22 04,-0.1262243,1.5421562\PG=C01 [X(C5H8N1O1)]\@

### BHandHLYP/cc-pVDZ

021\1\MARCCENTRE-ANET03\FTS\SUBHandHLYP\CC-pVDZ\C5H8N1O1(2)\CHANTAL\06-Sep-2001\1\#BHANDHLYP/CC-PVDZ OPT=(EF,TS,CALCFC,NOFREEZE) GEOM=CHECKPOINT GUESS=READ\trans state for 5exo\0,2\O\C,1,r 1\N,2,r2,1,a1\C,3,r3, 2,a2,1,d1,0\C,3,r4,2,a3,1,d2,0\C,5,r5,3,a4,2,d3,0\C,6,r6,5,a5,3,d4,0\H,4,r7,3,a6,2,d5,0\H,4,r8,3,a7,2,d6,0\H,5,r9,3,a8,2,d7,0\H,5,r10,3,a9,2,d8,0\H,6,r11,5,a10,3,d9,0\H,6,r12,5,a11,3,d10,0\H,7,r13,6,a12,5,d11,0\H,7,r14,6,a13,5,d12,0\r1=1.189424\r3=1.26696719\r4=1.44341104\r5=1.52815061\r6=1.52007104\r7=1.09266865\r8=1.08805818\r9=1.09675671\r10=1.0961706\r11=1.09415521\r12=1.09198608\r13=1.09268771\r14=1.09930261\ a1=117.04745206\ a2=126.57700834\ a3=105.26502007\ a4=106.83917232\ a5=107.06565882\ a6=122.61299006\ a7=118.2383207\ a8=112.75451463\ a9=106.82142092\ a10=109.57801906\ a11=110.74506417\ a12=112.00018571\ a13=112.31158847\ d1=45.16928815\ d2=-158.95375998\ d3=-8.10835818 \ d4=33.08443763\ d5=148.9286995\ d6=-29.30635196\ d7=-132.65622172\ d8=108.97972421\ d9=-85.02660143\ d10=156.18751116\ d11=-166.16572418\ d12=72.63347 1\r2=1.91620477\ \Version=DEC-AXP-OSF/1-G98RevA.7\HF=-325.0450628\S2=0.775609\S2-1=0.\S2A=0.750237\RMSD=9.119e-09\RMSF=8.570e-06\Dipole=0.7053041,-0.1203202,1.4784545\PG=C01 [X(C5H8N1O1)]\@

### BHandHLYP/aug-cc-pVDZ//BHandHLYP/cc-pVDZ

HF=-325.0674218

### QCISD/cc-pVDZ//BHandHLYP/cc-pVDZ

QCISD=-324.3192637

### CCSD(T)/cc-pVDZ//BHandHLYP/cc-pVDZ

CCSD(T)=-324.3532409

### B3LYP/6-311G\*\*

021\1\MARCCENTRE-ANET06\FTS\SUB3LYP\6-311G(d,p)\C5H8N1O1(2)\CHANTAL\07-Jun-2001\1\# B3LYP/6-311G\*\* OPT=(EF,TS,READFC,NOFREEZE) GEOM=CHECKPOINT GUESS=READ\trans state for 5exo\0,2\O\C,1,r 1\N,2,r2, 1,a1\C,3,r3,2,a2,1,d1,0\C,3,r4,2,a3,1,d2,0\C, 5,r5,3,a4,2,d3,0\C,6,r6,5,a5,3,d4,0\H,4,r7,3,a6,2,d5,0\H,4,r8,3,a7,2,d6,0\H,5,r9,3,a8,2,d7,0\H,5,r10,3,a9,d8,0\H,6,r11,5,a10,3,d9,0\H,6,r12,5,a11,3,d10,0\H,7,r13,6,a12,5,d11,0\H,7,r14,6,a13,5,d12,0\r1=1.19026558\r3=1.27534565\r4=1.45259335\r5=1.53787557\r6=1.52910562\r7=1.09369988\r8=1.0873478\r9=1.09818485\r10=1.09698529\r11=1.09374016\r12=1.09212846\r13=1.09315966\r14=1.09948004\ a1=118.02075511\ a2=128.26792041\ a3=103.42322609\ a4=107.67190075\ a5=107.89592065\ a6=122.74079814\ a7=118.71213947\ a8=112.74322199\ a9=106.90819269\ a10=109.47854008\ a11=110.60550232\ a12=111.75705673\ a13=112.3308638\ d1=50.19908532\ d2=-156.97545021\ d3=-10.10738448\ d4=35.1477454\ d5=144.78861015\ d6=-33.24678081\ d7=-134.4471803\ d8=107.18644499\ d9=-83.30356209\ d10=157.99300299\ d11=-167.61760632\ d12=71.35373587\r2=2.02619045\ \Version=DEC-AXP-OSF/1-G98RevA.7\HF=-325.3185986\S2=0.758604\S2-1=0.\S2A=0.750032\RMSD= 5.247e-09\RMSF=3.878e-05\Dipole=0.4785391,-0.1611161,1.390388\PG=C01 [X(C5H8N1O1)]\@

**B3LYP/cc-pVDZ**

021\1\ MAR CCENTRE-ANET06FTSUB3LYPCC-pVDZ\C5H8N1O1(2)\CHANTAL\11-Jun-2001\1\# B3LYP/CC-PVDZ OPT=(EF,TS,READFC,NOFREEZE) GEOM=CHECKPOINT GUESS=READ\trans state for 5exo\0,2\O\C,1,r1\N,2,r2,1,a1\C,3,r3,2,a2,1,d1,0\C,3,r4,2,a3,1,d2,0\C,5,r5,3,a4,2,d3,0\C,6,r6,5,a5,3,d4,0\H,4,r7,3,a6,2,d5,0\H,4,r8,3,a7,2,d6,0\H,5,r9,3,a8,2,d7,0\H,5,r10,3,a9,2,d8,0\H,6,r11,5,a10,3,d9,0\H,6,r12,5,a11,3,d10,0\H,7,r13,6,a12,5,d11,0\H,7,r14,6,a13,5,d12,0\|r1=1.1957796|r3=1.28100627|r4=1.45305514|r5=1.5373889|r6=1.52889905|r7=1.10281945|r8=1.09624623|r9=1.10688994|r10=1.10584267|r11=1.10272712|r12=1.10048562|r13=1.10169144|r14=1.10822009|a1=118.20583632|a2=128.50178541|a3=103.13267561|a4=107.80440378|a5=107.79529899|a6=122.70820325|a7=118.58965597|a8=112.85565846|a9=106.79890469|a10=109.47848783|a11=110.59477812|a12=111.87928192|a13=112.41712635|d1=51.90341856|d2=-156.69283535|d3=-10.63521286|d4=35.88413806|d5=143.44384467|d6=-34.63066156|d7=-135.31534572|d8=106.54684434|d9=-82.53324417|d10=158.84028158|d11=-167.90832237|d12=71.03465687|r2=2.03064735\Version=DEC-AXP-OSF/1-G98RevA.7\HF=-325.2463694\S2=0.758942\S2-1=0.\S2A=0.750034\RMSD=9.517e-09\RMSF=1.794e-05\Dipole=0.4285768,-0.1683706,1.3158724|PG=C01 [X(C5H8N1O1)]\|@

**B3LYP/aug-cc-pVDZ//B3LYP/cc-pVDZ**

HF=-325.2658278

**QCISD/cc-pVDZ//B3LYP/cc-pVDZ**

QCISD=-324.2902914

**CCSD(T)/cc-pVDZ//B3LYP/cc-pVDZ**

CCSD(T)=-324.3253738

**2-Pyrrolidon-1-ly-methyl radical (6)****UHF/6-311G\*\***

021\1\GINC-SATORINFOpt\UHF\6-311G(d,p)\C5H8N1O1(2)\CHANTALF\30-Jul-2002\1\#UHF/6-311G\*\* OPT=GRAD GEOM=CHECKPOINT GUESS=READ OPTCYC=100\cyc state for 5exo\0,2\O\C,1,r1\N,2,r2,1,a1\C,3,r3,2,a2,1,d1,0\C,3,r4,2,a3,1,d2,0\C,5,r5,3,a4,2,d3,0\C,6,r6,5,a5,3,d4,0\H,4,r7,3,a6,2,d5,0\H,4,r8,3,a7,2,d6,0\H,5,r9,3,a8,2,d7,0\H,5,r10,3,a9,2,d8,0\H,6,r11,5,a10,3,d9,0\H,6,r12,5,a11,3,d10,0\H,7,r13,6,a12,5,d11,0\H,7,r14,6,a13,5,d12,0\|r1=1.1904805|r2=1.36573294|r3=1.38889049|r4=1.45224841|r5=1.53342768|r6=1.53032146|r7=1.07038826|r8=1.07286701|r9=1.08382859|r10=1.088187|r11=1.08483174|r12=1.08264812|r13=1.08151746|r14=1.08701142|a1=125.40697629|a2=122.83456567|a3=113.27425029|a4=103.19700765|a5=103.37714076|a6=116.36419434|a7=117.05805179|a8=110.5337335|a9=110.55165845|a10=109.56155847|a11=112.29785065|a12=114.73181196|a13=111.99563697|d1=-6.5658733|d2=-175.79640088|d3=-20.18468657|d4=27.98883826|d5=11.75945247|d6=166.68363687|d7=-140.96505018|d8=99.51804429|d9=-89.14877388|d10=150.82115625|d11=-147.34211379|d12=89.37701297\Version=NEC-SX-4-SUPER-UX-G98RevA.7\HF=-323.3663933\S2=0.765223\S2-1=0.\S2A=0.75017\RMSD=7.815e-09\RMSF=3.627e-05\Dipole=0.0291434,0.0658084,1.663422\PG=C01 [X(C5H8N1O1)]\|@



**MP2/6-311G\*\***

021\1\MARCCENTRE-ANET06\FOpt\UMP2-FC\6-311G(d,p)\C5H8N1O1(2)\CHANTAL\20-Jun-2001\1\#\MP2/6-311G\*\* OPT=GRAD GEOM=CHECKPOINT GUESS=READ OPTCYC=100\cyc state for 5exo\0,2\OC,1,r1\N,2,r2,1,a1\C,3,r3,2,a2,1,d1,0\C,3,r4,2,a3,1,d2,0\C,5,r5,3,a4,2,d3,0\C,6,r6,5,a5,3,d4,0\H,4,r7,3,a6,2,d5,0\H,4,r8,3,a7,2,d6,0\H,5,r9,3,a8,2,d7,0\H,5,r10,3,a9,2,d8,0\H,6,r11,5,a10,3,d9,0\H,6,r12,5,a11,3,d10,0\H,7,r13,6,a12,5,d11,0\H,7,r14,6,a13,5,d12,0\vr1=1.21580697vr2=1.39146763vr3=1.37840457vr4=1.4576841vr5=1.53526505vr6=1.53054882vr7=1.07929714vr8=1.07985036vr9=1.09399145vr10=1.09840056vr11=1.09383869vr12=1.09211837vr13=1.09131005vr14=1.09699117\va1=124.91974464va2=122.64865398va3=112.7937321va4=102.69933434va5=103.04194441va6=115.98854205va7=117.61108623va8=110.34774919va9=110.31320798va10=109.27412489va11=112.14525444va12=114.83046543va13=111.49958756vd1=-6.50308352vd2=-175.90486565vd3=-22.13682567vd4=31.67455564vd5=11.0427666vd6=170.07192233vd7=-142.96653932vd8=96.9748821vd9=-85.00661426vd10=154.41941946vd11=-151.12715381vd12=85.39275884\Version=DEC-AXP-OSF/1-G98RevA.7\HF=-323.3636722\MP2=-324.4283208\PUHF=-323.3671581\PMP2-0=-324.4307268\S2=0.767534\S2-1=0.756588\S2A=0.750222\RMSD=3.485e-09\RMSF=1.620e-05\Dipole=0.0310242,0.064151,1.4979482\PG=C01[X(C5H8N1O1)]\@

**MP2/cc-pVDZ**

021\1\MARCCENTRE-ANET05\FOpt\UMP2-FC\CC-pVDZ\C5H8N1O1(2)\CHANTAL\04-Jul-2001\1\#\MP2/CC-PVDZ OPT=GRAD GEOM=CHECKPOINT GUESS=READ OPTCYC=100\cyc state for 5exo\0,2\OC,1,r1\N,2,r2,1,a1\C,3,r3,2,a2,1,d1,0\C,3,r4,2,a3,1,d2,0\C,5,r5,3,a4,2,d3,0\C,6,r6,5,a5,3,d4,0\H,4,r7,3,a6,2,d5,0\H,4,r8,3,a7,2,d6,0\H,5,r9,3,a8,2,d7,0\H,5,r10,3,a9,2,d8,0\H,6,r11,5,a10,3,d9,0\H,6,r12,5,a11,3,d10,0\H,7,r13,6,a12,5,d11,0\H,7,r14,6,a13,5,d12,0\vr1=1.22149381vr2=1.39641697vr3=1.38305813vr4=1.45935403vr5=1.53815412vr6=1.53329475vr7=1.08887995vr8=1.08940781vr9=1.10247178vr10=1.10741858vr11=1.10299309vr12=1.10060416vr13=1.09975611vr14=1.10588014va1=124.80670422va2=122.4679687va3=112.7914239va4=102.67101494va5=103.00876216va6=115.89842687va7=117.70906028va8=110.50075918va9=110.50295635va10=109.24041034va11=112.26831479va12=114.987476va13=111.55323364vd1=-6.57185176vd2=-176.27358292vd3=-22.1362389vd4=32.02943124vd5=10.58402028vd6=170.04954514vd7=-143.10308623vd8=97.13101363vd9=-84.61271601vd10=155.1497574vd11=-151.93919535vd12=84.85192276\Version=DEC-AXP-OSF/1-G98RevA.7\HF=-323.3089247\MP2=-324.3160422\PUHF=-323.3124217\PMP2-0=-324.3184756\S2=0.767901\S2-1=0.756929\S2A=0.750231\RMSD=7.038e-09\RMSF=2.422e-05\Dipole=0.0270807,0.0627106,1.4487752\PG=C01[X(C5H8N1O1)]\@

**MP2/aug-cc-pVDZ//MP2/cc-pVDZ**

MP2=-324.3795581

**QCISD/cc-pVDZ//MP2/aug-cc-pVDZ**

QCISD=-324.3775825

**CCSD(T)/cc-pVDZ//MP2/aug-cc-pVDZ**

CCSD(T)=-324.4118215

**BHandHLYP/6-311G\*\***

021\1\MAR CCENTRE-BNET1\FOpt\UBHandHLYP\6-311G(d,p)\C5H8N1 O1(2)\C HANTA  
 L\30-Aug-2001\1\#BHANDHLYP/6-311G\*\* OPT=GRAD GEOM=CHECKPOINT GUESS=R  
 EAD\cyc state for 5exo\0,2\O\C,1,r1\N,2,r2,1,a1\C,3,r3,2,a2,1,d1,0\C,3,r4,2,a3,1,d2,0\C,5,r5,3,  
 a4,2,d3,0\C,6,r6,5,a5,3,d4,0\H,4,r7,3,a6,2,d5,0\H,4,r8,3,a7,2,d6,0\H,5,r9,3,a8,2,d7,0\H,5,r10,3,a9  
 ,2,d8,0\H,6,r11,5,a10,3,d9,0\H,6,r12,5,a11,3,d10,0\H,7,r13,6,a12,5,d11,0\H,7,r14,6,a13,5,d12,0\  
 r1=1.19990178\r2=1.37398825\r3=1.36756386\r4=1.45145568\r5=1.52966748\r6=1.52544682\r  
 7=1.06990379\r8=1.07047166\r9=1.08482283\r10=1.0890404\r11=1.08511701\r12=1.08301075  
 \r13=1.08243518\r14=1.08802198\A1=124.74291366\A2=123.02559829\A3=113.07068112\A4=1  
 03.4333197\A5=103.69214716\A6=117.24489794\A7=118.55240149\A8=110.40373397\A9=110.1  
 3751881\A10=109.56467942\A11=112.07569295\A12=114.55987308\A13=112.09663239\A14=-3.6  
 6361 084\A15=-17 7.05488977\A16=-18.62654 62\A17=27.17575702\A18=4.77858524\A19=176.47785  
 32\A20=-139.63879 098\A21=101.1 1646586\A22=-90.11280685\A23=150.1114228 3\A24=-147.102  
 88448\A25=90.01956575\Version=DEC-AXP-OSF/1-G98RevA.7\HF=-325.1767436\S2=0.7588  
 65\S2-1=0.\S2A=0.7 50049\RMSD=5.202e-09\RMSF=1.950e-05\Dipole=0.0274194,0.0165 424,  
 1.637287\PG=C01 [X (C5H8N1O1)]\@

### **BHandHLYP/cc-pVDZ**

021\1\MARCCENTRE-ANET04\FOpt\UBHandHLYP\CC-pVDZ\C5H8N1O1(2)\CHA NTAL\  
 31-Aug-2001\ 1\#BHANDHLYP/CC-PVDZ OPT=GRAD GEOM=CHECKPOINT GUESS=RE  
 AD\cyc state for 5exo\0,2\O\C,1,r1\N,2,r2,1,a1\C,3,r3, 2,a2,1,d1,0\C,3,r4,2,a3,1,d2,0\C,5,r5,3,a  
 4,2,d3,0\C,6,r 6,5,a5,3,d4,0\H,4,r7,3,a6,2 ,d5,0\H,4,r8,3, a7,2,d6,0\H,5,r9,3,a8,2,d7,0\H,5,r10,3,a  
 9,2,d8,0\H,6,r11,5,a10,3,d9,0\H,6,r12,5,a11,3,d10,0\H,7,r13,6,a12,5,d11,0\H,7,r14,6,a13,5,d12,0\  
 \r1=1.20434868\r2=1.37669959\r3=1.36983901\r4=1.45033686\r5=1.52942728\r6=1.52506516\r  
 7=1.07856446\r8=1.07902321\r9=1.09276672\r10=1.09736832\r11=1.09343839\r12=1.0908409  
 7\r13=1.09020823\r14=1.09618547\A1=124.56568627\A2=122.93501601\A3=112.92539844\A4=  
 103.38322517\A5=103.58087286\A6=116.97318015\A7=118.41024821\A8=110.53935993\A9=110  
 .28637083\A10=109.50193151\A11=112.16384662\A12=114.79532873\A13=112.06580752\A14=-4  
 .00113666\A15=-177.22527272\A16=-19.0894 6547\A17=28.08082017\A18=5.12062855\A19=175.879  
 52194\A20=-140.20580125\A21=100.71463819\A22=-89.0807451\A23=151.25577096\A24=-148.29  
 837296\A25=88.84994825\Version=DEC-AXP-OSF/1-G98RevA.7\HF=-325.1131208\S2 =0.75  
 904 9\S2-1=0.\S2A= 0.750051\RMSD=6.712e-09\RMSF=5.945e-05\Dipole=0.0190248,0.02209  
 17,1.5702298\PG=C0 1 [X(C5H8N1O1)]\@

### **BHandHLYP/aug-cc-pVDZ//BHandHLYP/cc-pVDZ**

HF=-325.134848

### **QCISD/cc-pVDZ//BHandHLYP/cc-pVDZ**

QCISD=-324.3865143

### **CCSD(T)/cc-pVDZ//BHandHLYP/cc-pVDZ**

CCSD(T)=-324.4204976

### **B3LYP/6-311G\*\***

021\1\MARCCENTRE-ANET05\FOpt\UB3LYP\6-311G(d,p)\C5H8N1O1(2)\CHANTAL\07-Ju  
 n-2001\1\# B3LYP/6-311G\*\* OPT=GRAD GEOM=CHECKPOINT GUESS=READ OPTCYC  
 =100\cyc st ate for 5exo\0,2\O\C,1,r1\N,2,r2,1,a1\C,3, r3,2,a2,1,d1,0\C,3,r4,2,a3,1,d2,0\C,5 ,r5,

3,a4,2,d3,0\C ,6,r6,5,a5,3,d4,0\H,4,r7,3,a6,2,d5,0\H,4,r8,3,a7,2,d6,0\H,5,r9,3,a8,2,d7,0\H,5,r10,3,a9,2,d8,0\H,6,r11,5,a10,3,d9,0\H,6,r12,5,a11,3,d10,0\H,7,r13,6,a12,5,d11,0\H,7,r14,6,a13,5,d12,0\|r1=1.21366451|r2=1.3938503|r3=1.36783274|r4=1.46414713|r5=1.54016242|r6=1.53526495|r7=1.0774533|r8=1.07752297|r9=1.09267206|r10=1.09692231|r11=1.09260222|r12=1.09072653|r13=1.09034715|r14=1.09613287|a1=124.38451611|a2=123.31282906|a3=112.83850496|a4=103.64354163|a5=103.89143002|a6=117.20113805|a7=118.86683625|a8=110.28944668|a9=109.89766865|a10=109.61575218|a11=111.87318549|a12=114.33918599|a13=112.10857496|d1=-2.69594618|d2=-177.47739637|d3=-17.96685599|d4=26.70219614|d5=2.93091554|d6=178.49009631|d7=139.15567068|d8=101.83140242|d9=-90.78666208|d10=149.63945634|d11=-146.77011078|d12=90.81681224\\Version=DEC-AXP-OSF/1-G98RevA.7\HF=-325.3754062\S2=0.755347\S2-1=0.\S2 A=0.750018\RMSD=6.105e-09\RMSF=3.013e-05\Dipole=0.0472262,0.0051886,1.599497\PG=C01[X(C5H8N1O1)]\|@

### **B3LYP/cc-pVDZ**

021\1\MARCCENTRE-ANET04FOpt\UB3LYP\CC-pVDZ\C5H8N1O1(2)\CHANTAL\12-Jun2001\1\#\B3LYP/CC-PVDZ OPT=GRAD GEOM=CHECKPOINT GUESS=READ OPTCYC=100\|cyc state for 5exo\0,2\O\C,1,r1\N,2,r2,1,a1\C,3,r3,2,a2,1,d1,0\C,3,r4,2,a3,1,d2,0\C,5,r5,3,a4,2,d3,0\C,6,r6,5,a5,3,d4,0\H,4,r7,3,a6,2,d5,0\H,4,r8,3,a7,2,d6,0\H,5,r9,3,a8,2,d7,0\H,5,r10,3,a9,2,d8,0\H,6,r11,5,a10,3,d9,0\H,6,r12,5,a11,3,d10,0\H,7,r13,6,a12,5,d11,0\H,7,r14,6,a13,5,d12,0\|r1=1.21867797|r2=1.39635956|r3=1.37020018|r4=1.46255411|r5=1.54040076|r6=1.53510067|r7=1.08660578|r8=1.08651478|r9=1.1013473|r10=1.10603398|r11=1.10159698|r12=1.09923878|r13=1.09893698|r14=1.10500924|a1=124.19204664|a2=123.25323306|a3=112.70707018|a4=103.5834585|a5=103.76297683|a6=116.96293614|a7=118.73688622|a8=110.39886466|a9=110.01201199|a10=109.582014|a11=111.9036168|a12=114.52898349|a13=112.11909564|d1=-2.98848101|d2=-177.6252805|d3=-18.49878053|d4=27.70587177|d5=2.97710681|d6=178.53618189|d7=-139.77676232|d8=101.3998332|d9=-89.69169165|d10=150.80955652|d11=-147.9782031|d12=89.61020227\\Version=DEC-AXP-OSF/1-G98RevA.7\HF=-325.3037786\S2=0.755464\S2-1=0.\S2A=0.750019\RMSD=3.727e-09\RMSF=6.875e-05\Dipole=0.0363788,0.0075974,1.5234603\PG=C01[X(C5H8N1O1)]\|@

### **B3LYP/aug-cc-pVDZ//B3LYP/cc-pVDZ**

HF=-325.3229337

### **QCISD/cc-pVDZ//B3LYP/cc-pVDZ**

QCISD=-324.3472107

### **CCSD(T)/cc-pVDZ//B3LYP/cc-pVDZ**

CCSD(T)=-324.3823198

## **Transition state 11 for 6-endo cyclization of 5-aza-5-hexenoyl radical (4)**

### **UHF/6-311G\*\***

021\1\MARCCENTRE-ANET03\FTSUHF\6-311G(d,p)\C5H8N1O1(2)\CHANTAL\10-Nov2001\1\#\UHF/6-311G\*\* OPT=(EF,TS,READFC,NOFREEZE) OPTCYC=100 GEOM=CHECKP

OINT GUE SS=READ\trans state for 6endo\0,2\O\C,1,r1\C,2,r2,1,a1\N,3,r3,2,a2,1,d1,O\C,4,r4,3,a3,2,d2,0\C,5,r5,4,a4,3,d3,O\C,6,r6,5,a5,4,d4,0\H,3,r7,2,a6,1,d5,0\H,3,r8,2,a7,1,d6,0\H,5,r9,4,a8,3,d7,0\H,5,r10,4,a9,3,d8,0\H,6,r11,5,a10,4,d9,0\H,6,r12,5,a11,4,d10,0\H,7,r13,6,a12,5,d11,0\H,7,r14,6,a13,5,d12,0\|r1=1.16022408\r3=1.31383134\r4=1.45404405\r5=1.54244484\r6=1.53132069\r7=1.08397022\r8=1.07689693\r9=1.08912943\r10=1.08360973\r11=1.08624057\r12=1.08481445\r13=1.08544175\r14=1.08715365\|a1=125.59249345\|a2=96.44216065\|a3=115.36866073\|a4=112.97291147\|a5=113.04596397\|a6=92.29982468\|a7=100.19247438\|a8=110.2328272\|a9=107.16440348\|a10=110.50779711\|a11=108.83934289\|a12=111.82631088\|a13=111.27775679\|d1=-138.295758\|d2=-74.12383231\|d3=49.0863088\|d4=33.58339878\|d5=98.58960449\|d6=-18.34285637\|d7=-73.98219096\|d8=169.864263\|d9=-88.2962612\|d10=155.348713\|d11=173.01032138\|d12=52.42137135\r2=2.187871\|Version=DEC-AXP-OSF/1-G98RevA.7\HF=-323.2941444\|S2=0.84263\|S2-1=0.\|S2A=0.760893\|RMSD=9.193e-09\|RMSF=7.748e-06\|Dipole=-0.6111796,0.6131908,0.9160947\|PG=C01 [X(C5H8N1O1)]\|@

### MP2/6-311G\*\*

021\1\MARCCENTRE-ANET04\FTS\UMP2-FC\6-311G(d,p)\C5H8N1O1(2)\CHANTAL\20-Jun-2001\1\#\ MP2/6-311G\*\* OPT=(EF,TS,READFC,NOFREEZE) GEOM=CHECKPOINT GUESS=READ\trans state for 6endo\0,2\O\C,1,r1\C,2,r2,1,a1\N,3,r3,2,a2,1,d1,O\C,4,r4,3,a3,2,d2,0\C,5,r5,4,a4,3,d3,O\C,6,r6,5,a5,4,d4,0\H,3,r7,2,a6,1,d5,0\H,3,r8,2,a7,1,d6,0\H,5,r9,4,a8,3,d7,0\H,5,r10,4,a9,3,d8,0\H,6,r11,5,a10,4,d9,0\H,6,r12,5,a11,4,d10,0\H,7,r13,6,a12,5,d11,0\H,7,r14,6,a13,5,d12,0\|r1=1.1844264\r3=1.2790504\r4=1.46156811\r5=1.542869\r6=1.52608913\r7=1.09911753\r8=1.08987872\r9=1.10001676\r10=1.09411244\r11=1.09456989\r12=1.09432984\r13=1.09626\r14=1.09652299\|a1=119.9881617\|a2=91.97497226\|a3=114.2513454\|a4=111.25905436\|a5=111.31444806\|a6=95.77110123\|a7=96.05419152\|a8=111.27717186\|a9=107.56991163\|a10=110.30202784\|a11=109.92888582\|a12=111.28686281\|a13=112.21761695\|d1=-109.5798972\|d2=-81.50608971\|d3=49.49763574\|d4=36.51729444\|d5=125.67176791\|d6=9.38329012\|d7=72.9971399\|d8=169.65741882\|d9=-83.65987905\|d10=158.63720737\|d11=81.14547826\|d12=60.02375894\r2=2.106175\|05\|Version=DEC-AXP-OSF/1-G98RevA.7\HF=-323.2890169\|MP2=-324.349388\|PUHF=-323.3063297\|PMP2-0=-324.3641578\|S2=0.859463\|S2-1=0.826337\|S2A=0.759145\|RMSD=7.820e-09\|RMSF=2.964e-05\|Dipole=-0.6758012,0.4661289,0.8364448\|PG=C01 [X(C5H8N1O1)]\|@

### MP2/cc-pVDZ

021\1\MARCCENTRE-ANET08\FTS\UMP2-FC\CC-pVDZ\C5H8N1O1(2)\CHAN TAL\27-Jul-2001\1\#\MP2/CC-PVDZ OPT=(EF,TS,READFC,NOFREEZE) GEOM=CHECKPOINT GUESS=READ\trans state for 6endo\0,2\O\C,1,r1\C,2,r2,1,a1\N,3,r3,2,a2,1,d1,O\C,4,r4,3,a3,2,d2,0\C,5,r5,4,a4,3,d3,O\C,6,r6,5,a5,4,d4,0\H,3,r7,2,a6,1,d5,0\H,3,r8,2,a7,1,d6,0\H,5,r9,4,a8,3,d7,0\H,5,r10,4,a9,3,d8,0\H,6,r11,5,a10,4,d9,0\H,6,r12,5,a11,4,d10,0\H,7,r13,6,a12,5,d11,0\H,7,r14,6,a13,5,d12,0\|r1=1.19116818\r3=1.28622175\r4=1.4646456\r5=1.54499617\r6=1.52864052\r7=1.10782163\r8=1.09858137\r9=1.10887903\r10=1.10322901\r11=1.10399343\r12=1.10310195\r13=1.10484333\r14=1.10558116\|a1=120.54088357\|a2=92.33538571\|a3=114.02125037\|a4=111.66779776\|a5=111.14132427\|a6=95.01900823\|a7=96.37254494\|a8=111.46199622\|a9=107.57975771\|a10=110.65686246\|a11=109.89371372\|a12=111.51886609\|a13=112.29225708\|d1=-110.31212788\|d2=-80.90212971\|d3=48.72856994\|d4=37.00039055\|d5=124.65098175\|d6=8.62991318\|d7=-74.30444255\|d8=168.8174893\|d9=-83.61356676\|d10=159.05633595\|d11=180.46866126\|d12=59.60350983\r2=2.11460713\|Version=DEC-AXP-OSF/1-G98RevA.7\HF=-323.2349463\|MP

2=-324.236819\PUHF=-323.2524591\PMP2-0=-324.2517872\S2=0.864549\S2-1=0.800557\S2A=0.759532\RMSD=4.743e-09\RMSF=4.671e-06\Dipole=-0.6621665,0.4472104,0.7778915\PG=C01 [X(C5H8N1O 1)]\@

**MP2/aug-cc-pVDZ//MP2/cc-pVDZ**

MP2=-324.3018932

**QCISD/cc-pVDZ//MP2/aug-cc-pVDZ**

QCISD=-324.3125244

**CCSD(T)/cc-pVDZ//MP2/aug-cc-pVDZ**

CCSD(T)=-324.3487017

**BHandHLYP/6-311G\*\***

021\1\MARCCENTRE-BNET1\FTS\UBHandHLYP\6-311G(d,p)\C5H8N1O1(2)\CHANTAL\01-Sep-2001\1 \#BHANDHLYP/6-311G\*\* OPT=(EF,TS,CALCFC,NOFREEZE) GEOM=CHECKPOINT GUESS=READ\trans state for 6endo\0,2\O\C,1,r1\C,2,r2,1,a1\N,3,r3,2,a2,1,d1,0\C,4,r4,3,a3,2,d2,0\C,5,r5,4,a4,3,d3,0\C,6,r6,5,a5,4,d4,0\H,3,r7,2,a6,1,d5,0\H,3,r8,2,a7,1,d6,0\H,5,r9,4,a8,3,d7,0\H,5,r10,4,a9,3,d8,0\H,6,r11,5,a10,4,d9,0\H,6,r12,5,a11,4,d10,0\H,7,r13,6,a12,5,d11,0\H,7,r14,6,a13,5,d12,0\vr1=1.16707801\vr3=1.29013742\vr4=1.45095466\vr5=1.53563931\vr6=1.52160207\vr7=1.08759747\vr8=1.07984295\vr9=1.09093781\vr10=1.08524582\vr11=1.08627402\vr12=1.08539445\vr13=1.08732172\vr14=1.08816348\va1=121.75703135\va2=93.54277471\va3=115.61720364\va4=112.42617821\va5=112.37692863\va6=93.70023287\va7=98.21478142\va8=110.69190485\va9=107.3921815\va10=110.44840199\va11=109.30282659\va12=111.24003262\va13=112.11273428\vd1=-116.01240709\vd2=-77.46871248\vd3=47.55602514\vd4=36.97320607\vd5=119.92398667\vd6=3.24373204\vd7=-75.42065825\vd8=168.31789547\vd9=-84.375836\vd10=158.91742193\vd11=178.49227182\vd12=58.37883666\vr2=2.17193919\Version=D EC-AXP-OSF/1-G98RevA.7\HF=-325.1042483\S2=0.808347\S2-1=0\S2A=0.750597\RMSD=2.893e-09\RMSF=1.914e-05\Dipole=-0.7129359,0.4379257,0.9720748\PG=C01 [X(C5H8N1O1)]\@

**BHandHLYP/cc-pVDZ**

021\1\MARCCENTRE-BNET4\FTS\UBHandHLYP\CC-pVDZ\C5H8N1O1(2)\CHANTAL\04-Sep-2001\1 \#BHANDHLYP/CC-PVDZ OPT=(EF,TS,CALCFC,NOFREEZE) GEOM=CHECKPOINT GUESS=READ\trans state for 6endo\0,2\O\C,1,r1\C,2,r2,1,a1\N,3,r3,2,a2,1,d1,0\C,4,r4,3,a3,2,d2,0\C,5,r5,4,a4,3,d3,0\C,6,r6,5,a5,4,d4,0\H,3,r7,2,a6,1,d5,0\H,3,r8,2,a7,1,d6,0\H,5,r9,4,a8,3,d7,0\H,5,r10,4,a9,3,d8,0\H,6,r11,5,a10,4,d9,0\H,6,r12,5,a11,4,d10,0\H,7,r13,6,a12,5,d11,0\H,7,r14,6,a13,5,d12,0\vr1=1.17246768\vr3=1.29337633\vr4=1.45129544\vr5=1.53466259\vr6=1.52117645\vr7=1.09547904\vr8=1.08798795\vr9=1.09878206\vr10=1.09348176\vr11=1.09426384\vr12=1.09317949\vr13=1.09496239\vr14=1.09607817\va1=121.90067318\va2=93.39359167\va3=115.46910549\va4=112.6720923\va5=112.30283921\va6=93.21613966\va7=98.40692458\va8=110.79069622\va9=107.37755712\va10=110.58813448\va11=109.33224162\va12=111.28894567\va13=112.23113647\vd1=-114.90612128\vd2=-77.3179696\vd3=46.9691371\vd4=37.61248798\vd5=120.81921031\vd6=4.28879196\vd7=-76.31412892\vd8=167.73455089\vd9=83.8296531\vd10=159.61442208\vd11=178.59871594\vd12=58.63389014\vr2=2.17938933\Version=DEC-AXP-OSF/1-G98RevA.7\HF=-325.0

403456 \S2=0.808892\ S2-1=0.\S2A=0.75060 1\RMSD =7.732e-09\RMSF=8.939e-05\Dipole=-0.6824444,0.3922382,0.933495\PG=C01 [X(C5H8N1O1)]\@

**BHandHLYP/aug-cc-pVDZ//BHandHLYP/cc-pVDZ**

HF=-325.0633157

**QCISD/cc-pVDZ//BHandHLYP/cc-pVDZ**

QCISD=-324.3129220

**CCSD(T)/cc-pVDZ//BHandHLYP/cc-pVDZ**

CCSD(T)=-324.3490819

**B3LYP/6-311G\*\***

021\1\MARCCENTRE-BNET1\FTS\SUB3LYP\6-311G(d,p)\C5H8N1O1(2)\CHA NTAL\08-Jun-2001\1\#\B3 LYP/6-311G\*\* OPT=(EF,TS,READFC,NOFREEZE) GEOM=CHECKPOINT GUESS=READ\trans state for 6endo\0,2\O\C,1,r1\C,2,r2, 1,a1\N,3,r3,2,a2,1,d1,0\C,4,r4,3,a3,2,d2,0\C, 5,r5,4,a4 ,3,d3,0\C,6,r6,5,a5,4,d4,0\H,3,r7,2,a6,1,d5,0\H,3,r8,2,a7,1,d6,0\H,5,r9,4,a8,3,d7,0\H,5,r10,4,a9,3,d8,0\H,6,r11,5,a10,4,d9,0\H,6,r12,5,a11,4,d10,0\H,7,r13,6,a12,5,d11,0\H,7,r14,6,a13,5,d12,0\r1=1.18020821\r3=1.29858707\r4=1.46266508\r5=1.54594025\r6=1.53095791\r7=1.09684697\r8=1.08815962\r9=1.0994559\r10=1.09345051\r11=1.09357539\r12=1.09318003\r13=1.09567076\r14=1.09637856\A1=120.53001599\A2=93.00191203\A3=115.65059165\A4=112.59420114\A5=112.27267221\A6=93.6133094\A7=98.46342848\A8=110.71354112\A9=107.31896115\A10=110.4573154\A11=109.3988214\A12=110.82370623\A13=112.29833383\d1=-110.76026095\d2=-77.57982073\d3=46.53058642\d4 =38.10247654\d5=124.70213736\d6=8.21433317\d7=-76.47621978\d8=167.42859513\d9=-83.23561424\d10=159.99726672\d11=179.88423611\d12=60.1599928\r2= 2.19896073\Version=DEC-AXP-OSF/1-G98RevA.7\HF=-325.310949\S2=0.768181\S2-1=0.\S2A=0.750079\RMSD=9.022e-09\RMSF=2.657e-05\Dipole=-0.7349772,0.3540328,0.9502747\PG =C01[X(C5H8N1O1)]\@

**B3LYP/cc-pVDZ**

021\1\MARCCENTRE-ANET06FTS\SUB3LYP\CC-pVDZ\C5H8N1O1(2)\CHAN TAL\13-Jun-2001\1\#\B3LYP/CC-PVDZ OPT=(EF,TS,READFC,NOFREEZE) GEOM=CHECKPOINT GUESS=READ\trans state for 6endo\0,2\O\C,1,r1\C,2, r2,1,a1\ N,3,r3,2,a2,1,d1,0\C,4,r4,3,a3,2,d2,0\C,5,r5,4,a4,3,d3,0\C,6,r6,5,a5,4,d4,0\H,3,r7,2,a6,1,d5,0\H,3,r8,2,a7,1,d6,0\H,5,r9,4,a8,3,d7,0\H,5,r10,4,a9,3,d8,0\H,6,r11,5,a10,4,d9,0\H,6,r12,5,a11,4,d10,0\H,7,r13,6,a12,5,d11,0\H,7,r14,6,a13,5,d12,0\r1=1.18641223\r3=1.30141409\r4=1.46272229\r5=1.54470727\r6=1.53083887\r7=1.10557469\r8=1.0971657\r9=1.10827336\r10=1.10277354\r11=1.10249455\r12=1.10181883\r13=1.1042602\r14=1.10532266\A1=120.54757887\A2=92.79474361\A3=115.56056559\A4=112.91931838\A5=112.14173288\A6=92.80948827\A7=98.76747495\A8=110.79553215\A9=107.29114839\A10=110.61847874\A11=109.43124331\A12=110.84628335\A13=112.4371573\d1=-109.11814393\d2=-77.25511375\d3=45.56495266\d4= 39.22898523\d5=126.07220804\d6=9.78026495\d7=-77.81840635\d8=166.47368513\d9=-82.20884056\d10=161.15496239\d11=180.01035526\d12=60.413591\r2=2.21317101\Version=DEC-AXP-OSF/1-G98RevA.7\HF=-325.2387474\S2=0.767865\S2-1=0.\S2A=0.750077\RMSD=9.506e-09\RMSF=1.378e-05\Dipole=-0.6961464,0.2976405,0.9079103\PG=C01 [X(C5H8N1O1)]\@

**B3LYP/aug-cc-pVDZ//B3LYP/cc-pVDZ**  
 HF=-325.25954452

**QCISD/cc-pVDZ//B3LYP/cc-pVDZ**  
 QCISD=-324.2838977

**CCSD(T)/cc-pVDZ//B3LYP/cc-pVDZ**  
 CCSD(T)=-324.3190448

### 3-Piperidon-1-yl radical (7)

#### UHF/6-311G\*\*

021\1\GINC-GIUNDA\FOpt\UHF\6-311G(d,p)\C5H8N1O1(2)\HERB\02-Nov-2001\1\#UHF/  
 6-311G\*\* OPT=GRAD OPTCYC=100\cyc state for 6endo\0,2\0\C,1,r1\C,2,r2,1,a1\N,3,r3,2,a  
 2,1,d1,0\C,4,r4,3,a3,2,d2,0\C,5,r5,4,a4,3,d3,0\C,6,r6,5,a5,4,d4,0\H,3,r7,2,a6,1,d5,0\H,3,r8,2,a7,  
 1,d6,0\H,5,r9,4,a8,3,d7,0\H,5,r10,4,a9,3,d8,0\H,6,r11,5,a10,4,d9,0\H,6,r12,5,a11,4,d10,0\H,7,r13  
 ,6,a12,5,d11,0\H,7,r14,6,a13,5,d12,0\|r1=1.18461793\r2=1.52823011\r3=1.4438697\r4=1.44646  
 221\r5=1.53082799\r6=1.53053876\r7=1.09426677\r8=1.08072384\r9=1.08279933\r10=1.09268  
 565\r11=1.08693137\r12=1.08484352\r13=1.08258565\r14=1.08991918\|a1=120.94919789\|a2=1  
 14.61357218\|a3=112.65195066\|a4=110.88884306\|a5=110.73660096\|a6=106.4858072\|a7=108.4  
 0549712\|a8=108.50742983\|a9=109.53270027\|a10=108.85538167\|a11=109.87535615\|a12=112.6  
 8908065\|a13=109.51959887\|d1=142.34982144\|d2=49.91419727\|d3=-60.49099553\|d4=59.9762  
 0022\|d5=-97.21371515\|d6=18.63544907\|d7=177.82563047\|d8=60.6000318\|d9=-60.85167049\|d  
 10=182.16704555\|d11=-170.99573852\|d12=69.21240154\|Version=DEC-AXP-OSF/1-G94Re  
 vE.2\HF=-323.3479805\|S2=0.763\|S2-1=0.\|S2A=0.75\|RM SD=7.201e-09\|RMSF=3.832e-05\|Dip  
 ole=-0.6086215,-0.4409821,1.094299\|PG=C01 [X(C5H8N1O1)]\|@

#### MP2/6-311G\*\*

021\1\MARCCENTRE-BNET1\FOpt\UMP2-FC\6-311G(d,p)\C5H8N1O1(2)\CHANTAL\22-Jun-2001\1\#MP2/6-311G\*\*  
 OPT=GRAD GEOM=CHECKPOINT GUESS=READ OPTCYC=100\cyc state for 6endo\0,2\0\C,1,r1\C,2,r2,1,a1\N,3,r3,2,a2,1,d1,0\C,4,r4,3,a3,2,d2,0\C,5,r5,4,a  
 4,3,d3,0\C,6,r6,5,a5,4,d4,0\H,3,r7,2,a6,1,d5,0\H,3,r8,2,a7,1,d6,0\H,5,r9,4,a8,3,d7,0\H,5,r10,4,a9  
 ,3,d8,0\H,6,r11,5,a10,4,d9,0\H,6,r12,5,a11,4,d10,0\H,7,r13,6,a12,5,d11,0\H,7,r14,6,a13,5,d12,0\|  
 r1=1.212425\r2=1.54120105\r3=1.4453956\r4=1.44754426\r5=1.53834767\r6=1.5322292\r7=1.  
 09141793\r8=1.10523148\r9=1.09299821\r10=1.10341569\r11=1.09539657\r12=1.09447078\r1  
 3=1.09279027\r14=1.09890173\|a1=121.61301886\|a2=112.07282201\|a3=110.1688137\|a4=109.4  
 5806704\|a5=110.22220417\|a6=108.23009316\|a7=106.16650731\|a8=108.92645372\|a9=110.8128  
 721\|a10=108.53958828\|a11=109.75508087\|a12=112.83797951\|a13=109.20104421\|d1=133.082  
 60541\|d2=58.33230937\|d3=-66.16579418\|d4=61.81456544\|d5=10.52030748\|d6=-106.5156733  
 3\|d7=173.02380212\|d8=53.68836587\|d9=-58.43887881\|d10=184.06763898\|d11=171.4008648  
 3\|d12=68.08600676\|Version=DEC-AXP-OSF/1-G98RevA.7\HF=-323.3451303\|MP2=-324.39  
 78361\|PUHF=-323.349043\|PMP2-0=-324.4003756\|S2=0.763727\|S2-1=0.754025\|S2A=0.7501  
 57\|RMSD=6.038e-09\|RMSF=2.058e-05\|Dipole=-0.5969257,-0.452753,0.9362087\|PG=C01 [X(C  
 5H8N1O1)]\|@

**MP2/cc-pVDZ**

021\1\MARCCENTRE-ANET08\FOpt\UMP2-FC\CC-pVDZ\C5H8N1O1(2)\CHANTAL\12-Ju  
 1-2001\1\#MP2/CC-PVDZ OPT=GRAD GEOM=CHECKPOINT GUESS= READ OPTCYC=1  
 00\cyc state for 6endo\0,2\O\C,1,r1\C,2,r2,1,a1\N,3,r3,2,a2,1,d1,0\C,4,r4,3,a3,2,d2,0\C,5,r5,4,a  
 4,3,d3,0\C,6,r6,5,a5,4,d4,0\H,3,r7,2,a6,1,d5,0\H,3,r8,2,a7,1,d6,0\H,5,r9,4,a8,3,d7,0\H,5,r10,4,a9  
 ,3,d8,0\H,6,r11,5,a10,4,d9,0\H,6,r12,5,a11,4,d10,0\H,7,r13,6,a12,5,d11,0\H,7,r14,6,a13,5,d12,0\  
 r1=1.21820822\r2=1.54376253\r3=1.44900707\r4=1.45121404\r5=1.540556\r6=1.53458872\r7=  
 1.10009061\r8=1.11365902\r9=1.10175721\r10=1.11217469\r11=1.10458613\r12=1.10316487\r  
 13=1.10141936\r14=1.10764412\ a1=121.70149944\ a2=112.26779755\ a3=110.07620589\ a4=109  
 .53886985\ a5=110.19667481\ a6=108.29703223\ a7=106.03802577\ a8=109.00980668\ a9=110.95  
 919108\ a10=108.59325636\ a11=109.84293339\ a12=113.01390482\ a13=109.2057518\ d1=132.9  
 6256332\ d2=58.17679027\ d3=-65.9706969\ d4=61.88593154\ d5=10.03437854\ d6=-106.538218  
 57\ d7=173.16205549\ d8=54.12712335\ d9=-58.47957331\ d10=184.27474301\ d11=-171.9120288  
 3\ d12=67.83015225 \Version=DEC-AXP-OSF/1-G98RevA.7\HF=-323.2911461\MP2=-324.286  
 102\UHF=-323.2950073\PMP2-0=-324.2886117\S2=0.763569\S2-1=0.754006\S2A=0.7501  
 54\RMSD=5.095e-09\RMSF=4.193e-05\Dipole=-0.5703335,-0.424568,0.9063738\PG=C01 [X(  
 C5H8N1O1)]\@

**MP2/aug-cc-pVDZ//MP2/cc-pVDZ**

MP2=-324.3499991

**QCISD/cc-pVDZ//MP2/aug-cc-pVDZ**

QCISD=-324.355741

**CCSD(T)/cc-pVDZ//MP2/aug-cc-pVDZ**

CCSD(T)=-324.3891381

**BHandHLYP/6-311G\*\***

021\1\MARCCENTRE-BNET2\FOpt\UBHandHLYP\6-311G(d,p)\C5H8N1O1(2)\CHANTAL\3  
 1-Aug-2001\1\#BHANDHLYP/6-311G\*\* OPT=GRAD GEOM=CHECKPOINT GUESS=READ  
 OPTCYC=100\cyc state for 6endo\0,2\O\C,1,r1\C,2,r2,1,a1\N,3,r3,2,a2,1,d1,0\C,4,r4,3,a3,2,  
 d2,0\C,5,r5,4,a4,3,d3,0\C,6,r6,5,a5,4,d4,0\H,3,r7,2,a6,1,d5,0\H,3,r8,2,a7,1,d6,0\H,5,r9,4,a8,3,  
 d7,0\H,5,r10,4,a9,3,d8,0\H,6,r11,5,a10,4,d9,0\H,6,r12,5,a11,4,d10,0\H,7,r13,6,a12,5,d11,0\H,7,  
 ,r14,6,a13,5,d12,0\r1=1.19239949\r2=1.5298357\r3=1.43354937\r4=1.43780764\r5=1.52988254  
 \r6=1.52456487\r7=1.08248204\r8=1.09764983\r9=1.08413517\r10=1.09533715\r11=1.0869310  
 9\r12=1.08540652\r13=1.08355938\r14=1.0907601\ a1=121.04410272\ a2=114.25175024\ a3=112  
 .0703018\ a4=110.47300089\ a5=110.69510564\ a6=108.27500619\ a7=105.67400705\ a8=108.831  
 7854\ a9=110.1928826\ a10=108.70490293\ a11=109.76696175\ a12=112.88334628\ a13=109.4465  
 006\ d1=140.68820762\ d2=52.28700938\ d3=-62.34299635\ d4=60.24055995\ d5=16.63612966\ d  
 6=-98.8224546\ d7=176.16501929\ d8=58.20409187\ d9=-60.50866501\ d10=182.59220751\ d11  
 =-170.41830631\ d12=69.84878558 \Version=DEC-AXP-OSF/1-G98RevA.7\HF=-325.150360  
 6\S2=0.75625\S2-1=0.\S2A=0.75003\RMSD=5.566e-09\RMSF=1.221e-05\Dipole=-0.6213595  
 ,-0.4593413,1.0111595\PG=C01 [X(C5H8N1O1)]\@

**BHandHLYP/cc-pVDZ**



021\1\MARCCENTRE-BNET4\FOpt\UBHandHLYP\CC-pVDZ\C5H8N1O1(2)\CHANTAL\3  
 1-Aug-2001\1\#\BHANDHLYP/CC-PVDZ OPT=GRAD GEOM=CHECKPOINT GUESS=RE  
 AD OPTCYC= 100\cyc state for 6endo\0,2\O\C,1,r1\C,2,r2,1,a1\N,3,r3,2,a2,1,d1,0\C,4,r4,3,a3,  
 2,d2,0\C,5,r5,4,a4,3,d3,0\C,6,r6,5,a5,4,d4,0\H,3,r7,2,a6,1,d5,0\H,3,r8,2,a7,1,d6,0\H,5,r9,4,a8,3,  
 d7,0\H,5,r10,4,a9,3,d8,0\H,6,r11,5,a10,4,d9,0\H,6,r12,5,a11,4,d10,0\H,7,r13,6,a12,5,d11,0\H,7,r  
 14,6,a13,5,d12,0\|r1=1.19704618|r2=1.52917356|r3=1.43429831|r4=1.43873295|r5=1.52940186  
 |r6=1.52420688|r7=1.09055589|r8=1.10533047|r9=1.09230846|r10=1.10323139|r11=1.0952428  
 2|r12=1.09332873|r13=1.09137353|r14=1.09862401|a1=121.14337545|a2=114.32509195|a3=11  
 1.82301696|a4=110.6517671|a5=110.69130917|a6=108.34848559|a7=105.51914998|a8=108.88  
 664709|a9=110.18137567|a10=108.69348054|a11=109.84454466|a12=113.02506881|a13=109.4  
 508018|d1=139.79656893|d2=52.46241702|d3=-62.15643083|d4=60.20881356|d5=15.4124318  
 3|d6=-99.79884599|d7=176.2491409|d8=58.49625179|d9=-60.49813136|d10=182.7145268|d1  
 1=-170.80144008|d12=69.47132364\Version=DEC-AXP-OSF/1-G98RevA.7\HF=-325.088098  
 S2=0.756136\S2-1=0.\S2A=0.750029\RMSD=7.300e-09\RMSF=2.039e-05\Dipole=-0.5862849  
 ,-0.4257582,0.9785423\PG=C01[X(C5H8N1O1)]\@\

### **BHandHLYP/aug-cc-pVDZ//BHandHLYP/cc-pVDZ**

HF=-325.1108967

### **QCISD/cc-pVDZ//BHandHLYP/cc-pVDZ**

QCISD=-324.3602945

### **CCSD(T)/cc-pVDZ//BHandHLYP/cc-pVDZ**

CCSD(T)=-324.39630201

### **B3LYP/6-311G\*\***

021\1\MARCCENTRE-ANET04\FOpt\UB3LYP\6-311G(d,p)\C5H8N1O1(2)\CHANTAL\09-Ju  
 n-2001\1\#\B3LYP/6-311G\*\* OPT=GRAD GEOM=CHECKPOINT GUESS=READ OPTCYC  
 =100\cyc state for 6endo\0,2\O\C,1,r1\C,2,r2,1,a1\N,3,r3,2,a2,1,d1,0\C,4,r4,3,a3,2,d2,0\C,5,r5,  
 4,a4,3,d3,0\C,6,r6,5,a5,4,d4,0\H,3,r7,2,a6,1,d5,0\H,3,r8,2,a7,1,d6,0\H,5,r9,4,a8,3,d7,0\H,5,r10,  
 4,a9,3,d8,0\H,6,r11,5,a10,4,d9,0\H,6,r12,5,a11,4,d10,0\H,7,r13,6,a12,5,d11,0\H,7,r14,6,a13,5,d1  
 2,0\|r1=1.20318709|r2=1.55174055|r3=1.43660024|r4=1.44498946|r5=1.54492272|r6=1.534577  
 43|r7=1.09048116|r8=1.10722509|r9=1.09232752|r10=1.10446451|r11=1.09403812|r12=1.0932  
 8267|r13=1.09133803|r14=1.09856333|a1=121.25565375|a2=113.16567104|a3=111.5701484|a4  
 =109.94511706|a5=110.83437173|a6=108.13744772|a7=104.88370159|a8=108.99995715|a9=1  
 11.07659048|a10=108.58826123|a11=109.62930026|a12=112.81745252|a13=109.45447648|d1  
 =137.54014396|d2=55.9799349|d3=-64.54995009|d4=59.75222286|d5=13.91977685|d6=-101.  
 54776217|d7=174.55995176|d8=55.76481525|d9=-60.94264874|d10=182.13684745|d11=-169.  
 48635614|d12=70.87942245\Version=DEC-AXP-OSF/1-G98RevA.7\HF=-325.3488445\S2=0.  
 754365\S2-1=0.\S2A=0.750015\RMSD=7.116e-09\RMSF=2.298e-05\Dipole=-0.6462603,-0.47  
 45604,0.927838\PG=C01[X(C5H8N1O1)]\@\

### **B3LYP/cc-pVDZ**

021\1\MARCCENTRE-BNET1\FOpt\UB3LYP\CC-pVDZ\C5H8N1O1(2)\CHANTAL\19-Jun-2  
 001\1\#\B3LYP/CC-PVDZ OPT=GRAD OPTCYC=100\cyc state for 6endo\0,2\O\C,1,r1\C,2,r  
 2,1,a1\N,3,r3,2,a2,1,d1,0\C,4,r4,3,a3,2,d2,0\C,5,r5,4,a4,3,d3,0\C,6,r6,5,a5,4,d4,0\H,3,r7,2,a6,1,d

5,0\H,3,r8,2,a7,1,d6,0\H,5,r9,4,a8,3,d7,0\H,5,r10,4,a9,3,d8,0\H,6,r11,5,a10,4,d9,0\H,6,r12,5,a11,4,d10,0\H,7,r13,6,a12,5,d11,0\H,7,r14,6,a13,5,d12,0\|r1=1.2084061\r2=1.55098826\r3=1.43785512\r4=1.44606212\r5=1.54434322\r6=1.53447804\r7=1.09926013\r8=1.1158126\r9=1.1012138\r10=1.11328022\r11=1.10313658\r12=1.10189351\r13=1.09982293\r14=1.10720318\|a1=121.38256863\|a2=113.20444973\|a3=111.26646194\|a4=110.12229283\|a5=110.7544706\|a6=108.25671579\|a7=104.6775069\|a8=109.04851322\|a9=111.1177975\|a10=108.61164981\|a11=109.73234864\|a12=112.97020977\|a13=109.42969129\|d1=136.37325058\|d2=56.1718683\|d3=-64.38092859\|d4=59.91529098\|d5=12.43560098\|d6=-102.78928178\|d7=174.62899126\|d8=56.02708866\|d9=-60.71239028\|d10=182.40491616\|d11=-170.17250805\|d12=70.1366062\|Version=DEC-AXP-OSF/1-G98RevA.7\HF=-325.2757639\|S2=0.754341\|S2-1=0.\|S2A=0.750014\|RMSD=5.283e-09\|RMSF=2.869e-05\|Dipole =-0.6060593,-0.4312019,0.8887932\|PG=C01 [X(C5H8N1O1)]\|@

### **B3LYP/aug-cc-pVDZ//B3LYP/cc-pVDZ**

HF=-325.2946968

### **QCISD/cc-pVDZ//B3LYP/cc-pVDZ**

QCISD=-324.3189624

### **CCSD(T)/cc-pVDZ//B3LYP/cc-pVDZ**

CCSD(T)=-324.3539646

## **6-Aza-5-hexenyl radical (5)**

### **UHF/6-311G\*\***

1\| MARCCENTRE-ANET07\POpt\UHF\6-311G(d,p)\C5H8N1O1(2)\HIROSHI\12-Aug-2004\1\|#HF/6-311G\*\* SCF=QC OPT=(Z-MATRIX,READFC,MAXCYCLE=100) NOSYMM FREQ=NORAMAN GEOM=CHECK GUESS=READ\|substrate for 5-exo and 6-endo terminal imine\|0,2\|X\C,1,1,0,2,r1,1,90.\|C,2,r2,1,a1,3,d1,0\C,4,r3,2,a2,3,d2,0\C,5,r4,4,a3,2,d3,0\C,6,r5,5,a4,4,d4,0\N,7,r6,6,a5,5,d5,0\H,4,r7,2,a6,3,d6,0\H,4,r8,2,a7,3,d7,0\H,5,r9,4,a8,2,d8,0\H,5,r10,4,a9,2,d9,0\H,6,r11,5,a10,4,d10,0\H,6,r12,5,a11,4,d11,0\H,7,r13,6,a12,5,d12,0\H,8,r14,7,a13,6,d13,0\|r1=1.15708144\r2=1.5201443\r3=1.52658403\r4=1.53186153\r5=1.50282823\r6=1.24968016\r7=1.08766399\r8=1.08688245\r9=1.08800026\r10=1.08609336\r11=1.08417341\r12=1.08940711\r13=1.08939814\r14=1.00447382\|a1=140.84735308\|a2=112.98335205\|a3=112.10267508\|a4=112.03471367\|a5=121.90331254\|a6=105.48390496\|a7=107.77424843\|a8=109.28044613\|a9=109.26501741\|a10=110.76884978\|a11=109.41069936\|a12=115.62841058\|a13=111.42388952\|d1=182.733038\|d2=208.54213249\|d3=181.38618751\|d4=181.03650368\|d5=241.26326841\|d6=87.80323379\|d7=-27.03147322\|d8=59.38418813\|d9=-57.04359405\|d10=60.30205641\|d11=-58.51072525\|d12=60.85292117\|d13=179.76241501\|Version=DEC-AXP-OSF/1-G98RevA.7\HF=-323.330295\|S2=0.761781\|S2-1=0.\|S2A=0.750101\|RMSD=0.000e+00\|RMSF=4.392e-06\|Dipole=-0.6392038,-0.7396328,0.3594431\|PG=C01 [X(C5H8N1O1)]\|@

### **MP2/6-311G\*\***

1\| MARCCENTRE-ANET05\POpt\UMP2-FC\6-311G(d,p)\C5H8N1O1(2)\HIROSHI\14-Aug-2004\1\|#MP2/6-311G\*\* SCF=DIRECT OPT=(Z-MATRIX,READFC,MAXCYCLE=100) NOSYMM FREQ=NORAMAN GEOM=CHECK GUESS=READ\|substrate for 5-exo and 6-endo ter

minal imine\0,2\X\C,1,1.\O,2,r1,1,90.\C,2,r2,1,a1,3,d1,0\C,4,r3,2,a2,3,d2,0\C,5,r4,4,a3,2,d3,0\C,6,r5,5,a4,4,d4,0\N,7,r6,6,a5,5,d5,0\H,4,r7,2,a6,3,d6,0\H,4,r8,2,a7,3,d7,0\H,5,r9,4,a8,2,d8,0\H,5,r10,4,a9,2,d9,0\H,6,r11,5,a10,4,d10,0\H,6,r12,5,a11,4,d11,0\H,7,r13,6,a12,5,d12,0\H,8,r14,7,a13,6,d13,0\|r1=1.18699624\r2=1.52495691\r3=1.52860897\r4=1.53327346\r5=1.50121611\r6=1.27665602\r7=1.09708676\r8=1.09748681\r9=1.09689432\r10=1.09519422\r11=1.09452108\r12=1.09813458\r13=1.10035324\r14=1.02277282\|a1=142.35612918\|a2=112.18261622\|a3=111.77189613\|a4=111.28593571\|a5=120.75384094\|a6=105.73408344\|a7=108.87154963\|a8=109.40414921\|a9=109.24013298\|a10=110.46935599\|a11=109.39612967\|a12=115.75472899\|a13=109.20981564\|d1=185.85336729\|d2=218.08382188\|d3=182.61465992\|d4=181.11786278\|d5=245.17343557\|d6=98.52049242\|d7=-17.58209756\|d8=60.73809772\|d9=-56.20217583\|d10=61.36498619\|d11=-57.95627505\|d12=63.85649459\|d13=178.68802419\|Version=DEC-AXP-OSF/1-G98RevA.7\HF=-323.3263664\MP2=-324.3927888\PUHF=-323.3298156\PMP2-0=-324.3950176\S2=0.763739\S2-1=0.753956\S2A=0.750142\RMSD=3.601e-09\RMSF=5.081e-05\Dipole=-0.3284429,-0.6821077,0.4494504\PG=C01 [X(C5H8N1O1)]\|@

### MP2/cc-pVDZ

1\ MARCCENTRE-ANET08\POpt\UMP2-FC\CC-pVDZ\C5H8N1O1(2)\HIROSHI\24-Aug-2004\1\#\MP2/CC-PVDZ SCF=QC OPT=(Z-MATRIX,CALCHFFC,MAXCYCLE=100) NOSY MM FREQ=NORAMAN\substrate for 5-exo and 6-endo terminal imine\0,2\X\C,1,1.\O,2,r1,1,90.\C,2,r2,1,a1,3,d1,0\C,4,r3,2,a2,3,d2,0\C,5,r4,4,a3,2,d3,0\C,6,r5,5,a4,4,d4,0\N,7,r6,6,a5,5,d5,0\H,4,r7,2,a6,3,d6,0\H,4,r8,2,a7,3,d7,0\H,5,r9,4,a8,2,d8,0\H,5,r10,4,a9,2,d9,0\H,6,r11,5,a10,4,d10,0\H,6,r12,5,a11,4,d11,0\H,7,r13,6,a12,5,d12,0\H,8,r14,7,a13,6,d13,0\|r1=1.19453748\r2=1.52891929\r3=1.53087448\r4=1.53503018\r5=1.50545665\r6=1.2788313\r7=1.10605284\r8=1.10623587\r9=1.10605818\r10=1.10425582\r11=1.10321329\r12=1.10684398\r13=1.1101802\r14=1.03098786\|a1=141.64597632\|a2=112.16490384\|a3=112.01271645\|a4=111.5735627\|a5=120.76943107\|a6=105.57852011\|a7=108.95483181\|a8=109.32093934\|a9=109.22725409\|a10=110.70912533\|a11=109.31546659\|a12=115.43436966\|a13=108.81020321\|d1=190.69026969\|d2=216.36133086\|d3=182.99940992\|d4=181.44803065\|d5=243.75020028\|d6=96.68260498\|d7=-18.95965602\|d8=61.01776575\|d9=-55.42200755\|d10=61.32943952\|d11=-57.78984031\|d12=62.63332593\|d13=179.01721501\|Version=DEC-AXP-OSF/1-G98RevA.7\HF=-323.2712395\MP2=-324.2792284\PUHF=-323.2747455\PMP2-0=-324.281496\S2=0.76394\S2-1=0.75403\S2A=0.750149\RMSD=0.000e+00\RMSF=8.677e-05\Dipole=-0.3253737,-0.6780411,0.3733075\PG=C01 [X(C5H8N1O1)]\|@

### MP2/aug-cc-pVDZ//MP2/cc-pVDZ

MP2=-324.3439748

### QCISD/cc-pVDZ//MP2/cc-pVDZ

QCISD=-324.3446595

### CCSD(T)/ cc-pVDZ//MP2/cc-pVDZ

CCSD(T)=-324.3787341

### BHandHLYP/6-311G\*\*

1\ MARCCENTRE-ANET08\POpt\UBHandHLYP\6-311G(d,p)\C5H8N1O1(2)\HIROSHI\14-Aug-2004\1\#\BHANDHLYP/6-311G\*\* SCF=DIRECT OPT=(Z-MATRIX,READFC,MAXCY

CLE=100) NOSYMM FREQ=NORAMAN GEOM=CHECK GUESS=READ\\substrate for 5-exo and 6-endo terminal imine\\0,2\\XC,1,1.\\O,2,r1,1,90.\\C,2,r2,1,a1,3,d1,0\\C,4,r3,2,a2,3,d2,0\\C,5,r4,4,a3,2,d3,0\\C,6,r5,5,a4,4,d4,0\\N,7,r6,6,a5,5,d5,0\\H,4,r7,2,a6,3,d6,0\\H,4,r8,2,a7,3,d7,0\\H,5,r9,4,a8,2,d8,0\\H,5,r10,4,a9,2,d9,0\\H,6,r11,5,a10,4,d10,0\\H,6,r12,5,a11,4,d11,0\\H,7,r13,6,a12,5,d12,0\\H,8,r14,7,a13,6,d13,0\\r1=1.16628457\\r2=1.5127436\\r3=1.52016813\\r4=1.52616644\\r5=1.49508816\\r6=1.25577707\\r7=1.08931511\\r8=1.08883318\\r9=1.08828771\\r10=1.08654601\\r11=1.08537436\\r12=1.09032631\\r13=1.09172914\\r14=1.01119093\\a1=140.94321362\\a2=113.25084881\\a3=112.12227756\\a4=112.11888221\\a5=121.64157546\\a6=105.226819\\a7=107.998737\\a8=109.28842197\\a9=109.23332942\\a10=110.85144838\\a11=109.28988951\\a12=115.48757189\\a13=111.13643233\\d1=169.74506393\\d2=205.87897147\\d3=181.93137839\\d4=181.53252502\\d5=241.09856467\\d6=85.21867961\\d7=-29.25477693\\d8=59.86223242\\d9=-56.36698139\\d10=60.83702362\\d11=-57.87202113\\d12=60.4889129\\d13=179.6026973\\Version=DEC-AXP-OSF/1-G98RevA.7\\HF=-325.1347798\\S2=0.754829\\S2-1=0.\\S2A=0.750014\\RMSD=6.564e-09\\RMSF=4.541e-06\\Dipole=-0.5632934,-0.6234412,0.4897908\\PG=C01 [X(C5H8N1O1)]\\@

### **BHandHLYP/cc-pVDZ**

1\\ MARCCENTRE-ANET08\\POpt\\UBHandHLYP\\CC-pVDZ\\C5H8N1O1(2)\\HIROSHI\\14-Aug-2004\\1\\#BHANDHLYP/CC-PVDZ SCF=DIRECT OPT=(Z-MATRIX,READFC,MAXCYCLE=100) NOSYMM FREQ=NORAMAN GEOM=CHECK GUESS=READ\\substrate for 5-exo and 6-endo terminal imine\\0,2\\XC,1,1.\\O,2,r1,1,90.\\C,2,r2,1,a1,3,d1,0\\C,4,r3,2,a2,3,d2,0\\C,5,r4,4,a3,2,d3,0\\C,6,r5,5,a4,4,d4,0\\N,7,r6,6,a5,5,d5,0\\H,4,r7,2,a6,3,d6,0\\H,4,r8,2,a7,3,d7,0\\H,5,r9,4,a8,2,d8,0\\H,5,r10,4,a9,2,d9,0\\H,6,r11,5,a10,4,d10,0\\H,6,r12,5,a11,4,d11,0\\H,7,r13,6,a12,5,d12,0\\H,8,r14,7,a13,6,d13,0\\r1=1.17208327\\r2=1.513668\\r3=1.51992051\\r4=1.52534126\\r5=1.49646679\\r6=1.26064636\\r7=1.0973115\\r8=1.09678261\\r9=1.09654566\\r10=1.09478571\\r11=1.09346082\\r12=1.09819316\\r13=1.10017091\\r14=1.01816088\\a1=141.00693139\\a2=113.21080684\\a3=112.34459541\\a4=112.34591566\\a5=121.53211604\\a6=105.1497724\\a7=108.09747273\\a8=109.2402127\\a9=109.19639126\\a10=110.91186169\\a11=109.22321285\\a12=115.32408094\\a13=110.53150568\\d1=169.4768242\\d2=205.69983225\\d3=182.17858055\\d4=181.58835782\\d5=240.25278741\\d6=85.02753712\\d7=-29.22897317\\d8=60.02863232\\d9=-55.89112821\\d10=60.70770074\\d11=-57.83783852\\d12=59.68921785\\d13=179.69939825\\Version=DEC-AXP-OSF/1-G98RevA.7\\HF=-325.0692202\\S2=0.754751\\S2-1=0.\\S2A=0.750014\\RMSD=4.272e-09\\RMSF=4.332e-06\\Dipole=-0.5520906,-0.576524,0.469096\\PG=C01 [X(C5H8N1O1)]\\@

### **BHandHLYP/aug-cc-pVDZ//BHandHLYP/cc-pVDZ**

HF=-325.0942615

### **QCISD/cc-pVDZ//BHandHLYP/cc-pVDZ**

QCISD=-324.3419981

### **CCSD(T)/cc-pVDZ//BHandHLYP/cc-pVDZ**

CCSD(T)=-324.3753074

### **B3LYP/6-311G\*\***

1\\ MARCCENTRE-ANET07\\POpt\\UB3LYP\\6-311G(d,p)\\C5H8N1O1(2)\\HIROSHI\\13-Aug-2004\\1\\#B3LYP/6-311G\*\* SCF=DIRECT OPT=(Z-MATRIX,READFC,MAXCYCLE=100) NOSYMM FREQ=NORAMAN GEOM=CHECK GUESS=READ\\substrate for 5-exo and 6-endo t

erminal imine\0,2\X\C,1,1.\O,2,r1,1,90.\C,2,r2,1,a1,3,d1,0\C,4,r3,2,a2,3,d2,0\C,5,r4,4,a3,2,d3,0\C,6,r5,5,a4,4,d4,0\N,7,r6,6,a5,5,d5,0\H,4,r7,2,a6,3,d6,0\H,4,r8,2,a7,3,d7,0\H,5,r9,4,a8,2,d8,0\H,5,r10,4,a9,2,d9,0\H,6,r11,5,a10,4,d10,0\H,6,r12,5,a11,4,d11,0\H,7,r13,6,a12,5,d12,0\H,8,r14,7,a13,6,d13,0\r1=1.18004129\r2=1.5229315\r3=1.53087221\r4=1.53755393\r5=1.50360678\r6=1.26809175\r7=1.09754935\r8=1.09726129\r9=1.09575459\r10=1.09402352\r11=1.09313839\r12=1.09826138\r13=1.10090577\r14=1.02212378\A1=141.5928637\A2=113.28626841\A3=112.26976642\A4=112.29943953\A5=121.46439191\A6=105.09495884\A7=108.21951923\A8=109.23525758\A9=109.17128229\A10=110.82787728\A11=109.1817482\A12=115.29033712\A13=110.79299194\A14=171.87535978\A15=206.8590774\A16=182.45539099\A17=181.84430222\A18=241.43648838\A19=86.39335414\A20=-28.0114343\A21=60.33220858\A22=-55.77482218\A23=61.03193649\A24=-57.54192849\A25=60.81510898\A26=179.60126515\Version=DEC-AXP-OSF/1-G98RevA.7\HF=-325.3367074\S2=0.752593\S2-1=0.\S2A=0.750004\RMSD=4.164e-09\RMSF=1.102e-05\Dipole=-0.5002616,-0.6030576,0.4840293\PG=C01 [X(C5H8N1O1)]\@

### **B3LYP/cc-pVDZ**

1\ MARCCENTRE-ANET07\POpt\UB3LYP\CC-pVDZ\C5H8N1O1(2)\HIROSHI\14-Aug-2004\1\#B3LYP/CC-PVDZ SCF=DIRECT OPT=(Z-MATRIX,READFC,MAXCYCLE=100) NO SYMM FREQ=NORAMAN GEOM=CHECK GUESS=READ\substrate for 5-exo and 6-endo terminal imine\0,2\X\C,1,1.\O,2,r1,1,90.\C,2,r2,1,a1,3,d1,0\C,4,r3,2,a2,3,d2,0\C,5,r4,4,a3,2,d3,0\C,6,r5,5,a4,4,d4,0\N,7,r6,6,a5,5,d5,0\H,4,r7,2,a6,3,d6,0\H,4,r8,2,a7,3,d7,0\H,5,r9,4,a8,2,d8,0\H,5,r10,4,a9,2,d9,0\H,6,r11,5,a10,4,d10,0\H,6,r12,5,a11,4,d11,0\H,7,r13,6,a12,5,d12,0\H,8,r14,7,a13,6,d13,0\r1=1.18652525\r2=1.52433916\r3=1.53073621\r4=1.53673929\r5=1.50539579\r6=1.27351084\r7=1.10638164\r8=1.10603743\r9=1.10482438\r10=1.10302116\r11=1.101994\r12=1.10693903\r13=1.110186\r14=1.02977189\A1=141.59727853\A2=113.18150573\A3=112.4715409\A4=112.4842532\A5=121.32997617\A6=105.00001062\A7=108.36961901\A8=109.18780573\A9=109.13347294\A10=110.90622481\A11=109.09088859\A12=115.07422409\A13=110.13865618\A14=171.25157388\A15=206.65586712\A16=182.78454582\A17=181.95138712\A18=240.52265679\A19=86.21292475\A20=-27.98640619\A21=60.59745038\A22=-55.19158537\A23=60.8986342\A24=-57.52067184\A25=59.91246467\A26=179.67109702\Version=DEC-AXP-OSF/1-G98RevA.7\HF=-325.2622798\S2=0.752508\S2-1=0.\S2A=0.750004\RMSD=3.398e-09\RMSF=9.429e-06\Dipole=-0.4839423,-0.5452952,0.4670074\PG=C01 [X(C5H8N1O1)]\@

### **B3LYP/aug-cc-pVDZ//B3LYP/cc-pVDZ**

HF=-325.2920111

### **QCISD/cc-pVDZ//B3LYP/cc-pVDZ**

QCISD=-324.3444173

### **CCSD(T)/cc-pVDZ//B3LYP/cc-pVDZ**

CCSD(T)=-324.3782917

## **Transition state for 6-endo cyclization (E)-13 of 6-aza-5-hexenoyl radical (5)**

**UHF/6-311G\*\***

1\ CHEMCLUSTER-KNET18\FTS\UHF\6-311G(d,p)\C5H8N1O1(2)\CARLHS\14-Jul-2004\1\#\UHF/6-311G\*\* OPT=(EF,TS,READFC) GEOM=CHECKPOINT GUESS=READ\Ryu endo transition state\0,2\N\C,1,cn2\O,2,oc3,1,ocn3\C,2,cc4,1,ccn4,3,dih4,0\C,1,cn5,2,cnc5,3,dih5,0\C,5,cc6,1,ccn6,2,dih6,0\C,6,cc7,5,ccc7,1,dih7,0\H,6,hc8,5,hcc8,1,dih8,0\H,6,hc9,5,hcc9,1,dih9,0\H,7,hc10,6,hcc10,5,dih10,0\H,7,hc11,6,hcc11,5,dih11,0\H,4,hc12,2,hcc12,1,dih12,0\H,4,hc13,2,hcc13,1,dih13,0\H,5,hc14,1,hcn14,2,dih14,0\H,1,hn15,5,hnc15,6,dih15,0\cn2=1.92554667\oc3=1.16860245\ocn3=118.37995569\cc4=1.51484997\ccn4=103.94840002\dih4=148.7292707\cn5=1.31356733\cnc5=114.95349237\dih5=-191.17857929\cc6=1.50303422\ccn6=116.47199372\dih6=49.25725551\cc7=1.53956972\ccc7=110.21431716\dih7=-57.70901788\hc8=1.08762327\hcc8=109.3752602\dih8=62.70242296\hc9=1.08485159\hcc9=110.45762391\dih9=-179.21871015\hc10=1.08586364\hcc10=109.27537228\dih10=180.92588914\hc11=1.08799356\hcc11=109.20790303\dih11=-62.85718167\hc12=1.08583717\hcc12=106.70336273\dih12=167.17437954\hc13=1.08722989\hcc13=106.77242994\dih13=-78.55035934\hc14=1.0807587\hcn14=121.83561412\dih14=-117.19448335\hn15=1.00348315\hnc15=113.91571892\dih15=-188.27663228\Version=x86-Linux-G03RevB.04\State=2-A\HF=-323.2998172\S2=1.007978\S2-1=0.\S2A=0.760367\RM SD=8.602e-09\RMSF=1.579e-05\Dipole=-1.3037135,-0.1968775,-0.7197969\PG=C01 [X(C5H8N1O1)]\@

**MP2/6-311G\*\***

1\ CHEMCLUSTER-KNET5\FTS\UMP2-FC\6-311G(d,p)\C5H8N1O1(2)\CARLHS\15-Jul-2004\1\#\MP2/6-311G\*\* OPT=(EF,TS,READFC) GEOM=CHECKPOINT GUESS=READ\Ryu endo transition state\0,2\N\C,1,cn2\O,2,oc3,1,ocn3\C,2,cc4,1,ccn4,3,dih4,0\C,1,cn5,2,cnc5,3,dih5,0\C,5,cc6,1,ccn6,2,dih6,0\C,6,cc7,5,ccc7,1,dih7,0\H,6,hc8,5,hcc8,1,dih8,0\H,6,hc9,5,hcc9,1,dih9,0\H,7,hc10,6,hcc10,5,dih10,0\H,7,hc11,6,hcc11,5,dih11,0\H,4,hc12,2,hcc12,1,dih12,0\H,4,hc13,2,hcc13,1,dih13,0\H,5,hc14,1,hcn14,2,dih14,0\H,1,hn15,5,hnc15,6,dih15,0\cn2=1.69580282\oc3=1.23231389\ocn3=110.78323491\cc4=1.52051622\ccn4=102.09472094\dih4=135.88709325\cn5=1.25944285\cnc5=129.79887266\dih5=-154.93064745\cc6=1.49634221\ccn6=120.19047689\dih6=1.1491378\cc7=1.53322471\ccc7=112.379612\dih7=-13.59388412\hc8=1.09944927\hcc8=106.93339804\dih8=108.82829805\hc9=1.09663081\hcc9=108.29638062\dih9=-137.27470928\hc10=1.09463282\hcc10=108.83771928\dih10=169.06257706\hc11=1.09530839\hcc11=108.60658649\dih11=-74.08313935\hc12=1.09416886\hcc12=107.38598877\dih12=169.42479525\hc13=1.10355909\hcc13=109.85722043\dih13=-74.22463237\hc14=1.09450238\hcn14=120.74447557\dih14=-178.71884449\hn15=1.01891664\hnc15=119.32351346\dih15=-178.68663723\Version=x86-Linux-G03RevB.04\State=2-A\HF=-323.2960644\MP2=-324.3682346\PUHF=-323.3033466\PMP2-0=-324.3741046\S2=0.814017\S2-1=0.788745\S2A=0.751915\RM SD=9.102e-09\RMSF=1.884e-05\Dipole=-1.3299912,0.4515072,-2.0682047\PG=C01 [X(C5H8N1O1)]\@

**MP2/cc-pVDZ**

1\ CHEMCLUSTER-KNET19\FTS\UMP2-FC\CC-pVDZ\C5H8N1O1(2)\CARLHS\14-Jul-2004\1\#\MP2/CC-PVDZ OPT=(EF,TS,READFC) GEOM=CHECKPOINT GUESS=READ\Ryu endo transition state\0,2\N\C,1,cn2\O,2,oc3,1,ocn3\C,2,cc4,1,ccn4,3,dih4,0\C,1,cn5,2,cnc5,3,dih5,0\C,5,cc6,1,ccn6,2,dih6,0\C,6,cc7,5,ccc7,1,dih7,0\H,6,hc8,5,hcc8,1,dih8,0\H,6,hc9,5,hcc9,1,dih9,0\H,7,hc10,6,hcc10,5,dih10,0\H,7,hc11,6,hcc11,5,dih11,0\H,4,hc12,2,hcc12,1,dih12,0\H,4,hc13,2,hcc13,1,dih13,0\H,5,hc14,1,hcn14,2,dih14,0\H,1,hn15,5,hnc15,6,dih15,0\cn2=1.70686088\oc3=1.23611776\ocn3=111.47933405\cc4=1.52558592\ccn4=101.92556148\dih4=136.87327196

cn5=1.26386706\cnc5=129.710325\dih5=-158.05876896\cc6=1.50047474\ccn6=120.08666353\dih6=4.22437734\cc7=1.53606976\ccc7=112.37395825\dih7=-15.49487037\hc8=1.10822583\hcc8=106.85020617\dih8=107.10783117\hc9=1.1048931\hcc9=108.40337025\dih9=-139.33977267\hc10=1.10316116\hcc10=108.79598077\dih10=169.70369478\hc11=1.10447562\hcc11=108.59296256\dih11=-73.85112682\hc12=1.10306881\hcc12=107.27550093\dih12=169.43618507\hc13=1.11229436\hcc13=110.37417399\dih13=-74.48809876\hc14=1.10332203\hcn14=120.79802419\dih14=-175.71327735\hn15=1.02561437\hnc15=118.98254545\dih15=-178.89003907\\Version=x86-Linux-G03RevB.04\State=2-A\HF=-323.2415158\MP2=-324.2546109\PUHF=-323.2495473\PMP2-0=-324.2611595\S2=0.824558\S2-1=0.796502\S2A=0.752374\RMSD=5.280e-09\RMSF=3.710e-05\Dipole=-1.2946531,0.3964719,-2.0082828\PG=C01 [X(C5H8N1O1)]\@

**MP2/aug-cc-pVDZ//MP2/cc-pVDZ**  
MP2=-324.3239646

**QCISD/cc-pVDZ//MP2/cc-pVDZ**  
QCISD=-324.3230833

**CCSD(T)/cc-pVDZ//MP2/cc-pVDZ**  
CCSD(T)=-324.3584996

### **BHandHLYP/6-311G\*\***

1\1\ CHEMCLUSTER-KNET18\FTS\UBHandHLYP\6-311G(d,p)\C5H8N1O1(2)\HIROSHI\12-Aug-2004\1\#\BHANDHLYP/6-311G\*\* OPT=(EF,TS,READFC,MAXCYCLE=100) NOSYMM FREQ=NORAMAN GEOM=CHECK GUESS=READ\Ryu endo transition state\0,2\N\C,1,cn2\O,2,oc3,1,ocn3\C,2,cc4,1,ccn4,3,dih4,0\C,1,cn5,2,cnc5,3,dih5,0\C,5,cc6,1,ccn6,2,dih6,0\C,6,cc7,5,ccc7,1,dih7,0\H,6,hc8,5,hcc8,1,dih8,0\H,6,hc9,5,hcc9,1,dih9,0\H,7,hc10,6,hcc10,5,dih10,0\H,7,hc11,6,hcc11,5,dih11,0\H,4,hc12,2,hcc12,1,dih12,0\H,4,hc13,2,hcc13,1,dih13,0\H,5,hc14,1,hcn14,2,dih14,0\H,1,hn15,5,hnc15,6,dih15,0\cn2=1.88298011\oc3=1.18972985\ocn3=113.55215312\cc4=1.50972437\ccn4=100.88077571\dih4=139.13475818\cn5=1.26998733\cnc5=123.75788639\dih5=-173.4630211\cc6=1.49683863\ccn6=118.77666419\dih6=30.22137007\cc7=1.53109078\ccc7=112.06818761\dih7=-37.7961112\hc8=1.09013721\hcc8=108.37694583\dih8=83.90906634\hc9=1.08571333\hcc9=109.58945569\dih9=-160.36162788\hc10=1.08605011\hcc10=108.6258552\dih10=176.39703719\hc11=1.08732596\hcc11=108.83813445\dih11=-67.8180355\hc12=1.08696983\hcc12=105.84418884\dih12=167.26933665\hc13=1.09024548\hcc13=109.12575624\dih13=-78.20036906\hc14=1.08455425\hcn14=121.76259431\dih14=-147.49671483\hn15=1.00834838\hnc15=116.70845475\dih15=-182.51204388\\Version=x86-Linux-G03RevB.04\HF=-325.1180933\S2=0.773233\S2-1=0.\S2A=0.75022\RMSD=9.141e-09\RMSF=1.855e-05\Dipole=-1.3266292,0.1636849,-1.3991407\PG=C01 [X(C5H8N1O1)]\@

### **BHandHLYP/cc-pVDZ**

1\1\ CHEMCLUSTER-KNET19\FTS\UBHandHLYP\CC-pVDZ\C5H8N1O1(2)\HIROSHI\12-Aug-2004\1\#\BHANDHLYP/CC-PVDZ OPT=(EF,TS,READFC,MAXCYCLE=100) NOSYMM FREQ=NORAMAN GEOM=CHECK GUESS=READ\Ryu endo transition state\0,2\N\C,1,cn2\O,2,oc3,1,ocn3\C,2,cc4,1,ccn4,3,dih4,0\C,1,cn5,2,cnc5,3,dih5,0\C,5,cc6,1,ccn6,2,dih6,0\C,6,cc7,5,ccc7,1,dih7,0\H,6,hc8,5,hcc8,1,dih8,0\H,6,hc9,5,hcc9,1,dih9,0\H,7,hc10,6,hcc10,5,dih10,0\H,7,hc11,6,hcc11,5,dih11,0\H,4,hc12,2,hcc12,1,dih12,0\H,4,hc13,2,hcc13,1,dih13,0\H,5,hc14,1,hcn

14,2,dih14,0\H,1,hn15,5,hnc15,6,dih15,0\cn2=1.88802093\oc3=1.19453796\ocn3=113.57373374\cc4=1.51145434\ccn4=100.64067969\dih4=138.90613679\cn5=1.27444402\cnc5=123.55222573\dih5=-173.88648927\cc6=1.49816761\ccn6=118.72336763\dih6=30.56244712\cc7=1.53059004\ccc7=112.11340947\dih7=-37.74813746\hc8=1.09823823\hcc8=108.33297403\dih8=84.01950088\hc9=1.09340623\hcc9=109.56664162\dih9=-160.47154629\hc10=1.09383131\hcc10=108.61164206\dih10=176.45935954\hc11=1.09547222\hcc11=108.81208101\dih11=-67.89327446\hc12=1.09477264\hcc12=105.77560598\dih12=167.79931128\hc13=1.09826748\hcc13=109.32958639\dih13=-77.81928898\hc14=1.09276139\hcn14=121.8183516\dih14=-147.22683769\hn15=1.01430837\hnc15=116.22614127\dih15=-182.66579257\Version=x86-Linux-G03RevB.04\HF=-325.0539307\S2=0.773889\S2-1=0.\S2A=0.75023\RMSD=9.884e-09\RMSF=2.475e-05\Dipole=-1.2649411,0.162998,-1.3574669\PG=C01 [X(C5H8N1O1)]\@

### QCISD/cc-pVDZ//BHandHLYP/cc-pVDZ

QCISD=-324.3225235

### CCSD(T)/cc-pVDZ//BHandHLYP/cc-pVDZ

CCSD(T)=-324.3580242

### B3LYP/6-311G\*\*

1\ CHEMCLUSTER-KNET18\FTS\SUB3LYP\6-311G(d,p)\C5H8N1O1(2)\HIROSHI\12-Aug-2004\1\#B3LYP/6-311G\*\* OPT=(EF,TS,READFC,MAXCYCLE=100) NOSYMM FREQ=NO RAMAN GEOM=CHECK GUESS=READ\Ryu endo transition state\0,2\N\C,1,cn2\O,2,oc3,1,ocn3\C,2,cc4,1,ccn4,3,dih4,0\C,1,cn5,2,cnc5,3,dih5,0\C,5,cc6,1,ccn6,2,dih6,0\C,6,cc7,5,ccc7,1,dih7,0\H,6,hc8,5,hcc8,1,dih8,0\H,6,hc9,5,hcc9,1,dih9,0\H,7,hc10,6,hcc10,5,dih10,0\H,7,hc11,6,hc11,5,dih11,0\H,4,hc12,2,hcc12,1,dih12,0\H,4,hc13,2,hcc13,1,dih13,0\H,5,hc14,1,hcn14,2,dih14,0\H,1,hn15,5,hnc15,6,dih15,0\cn2=2.01246671\oc3=1.19398198\ocn3=114.30227003\cc4=1.52150158\ccn4=99.6712289\dih4=138.78518048\cn5=1.28223736\cnc5=120.88232056\dih5=-174.55319718\cc6=1.50623501\ccn6=118.40114631\dih6=35.1894727\cc7=1.54320419\ccc7=111.9398317\dih7=-44.22479386\hc8=1.09767995\hcc8=108.89172492\dih8=77.27592002\hc9=1.0932462\hcc9=109.76472582\dih9=-166.48403394\hc10=1.09397927\hcc10=108.56996661\dih10=179.65807399\hc11=1.09502677\hcc11=108.92495685\dih11=-64.67663884\hc12=1.09567263\hcc12=105.56565853\dih12=166.72340027\hc13=1.09766995\hcc13=108.59127002\dih13=-79.27564591\hc14=1.09388538\hcn14=122.41170641\dih14=-140.91570342\hn15=1.01859557\hnc15=115.52601008\dih15=-183.9793437\Version=x86-Linux-G03RevB.04\HF=-325.3262503\S2=0.758465\S2-1=0.\S2A=0.750033\RMSD=5.382e-09\RMSF=1.360e-05\Dipole=-1.2069205,0.1349515,-1.0776516\PG=C01 [X(C5H8N1O1)]\@

### B3LYP/cc-pVDZ

1\ CHEMCLUSTER-KNET18\FTS\SUB3LYP\CC-pVDZ\C5H8N1O1(2)\HIROSHI\12-Aug-2004\1\#B3LYP/CC-pVDZ OPT=(EF,TS,READFC,MAXCYCLE=100) NOSYMM FREQ=NOR AMAN GEOM=CHECK GUESS=READ\Ryu endo transition state\0,2\N\C,1,cn2\O,2,oc3,1,ocn3\C,2,cc4,1,ccn4,3,dih4,0\C,1,cn5,2,cnc5,3,dih5,0\C,5,cc6,1,ccn6,2,dih6,0\C,6,cc7,5,ccc7,1,dih7,0\H,6,hc8,5,hcc8,1,dih8,0\H,6,hc9,5,hcc9,1,dih9,0\H,7,hc10,6,hcc10,5,dih10,0\H,7,hc11,6,hcc11,5,dih11,0\H,4,hc12,2,hcc12,1,dih12,0\H,4,hc13,2,hcc13,1,dih13,0\H,5,hc14,1,hcn14,2,dih14,0\H,1,hn15,5,hnc15,6,dih15,0\cn2=2.02101665\oc3=1.19991534\ocn3=114.09967479\cc4=1.52382206\ccn4=99.20849397\dih4=138.08572558\cn5=1.28631341\cnc5=120.90149892\dih5=-174.2



8554211\cc6=1.50815321\ccn6=118.40755014\dih6=34.71227155\cc7=1.54237302\ccc7=112.09423321\dih7=-43.36160554\hc8=1.10668413\hcc8=108.79106108\dih8=78.24221264\hc9=1.10164651\hcc9=109.68306506\dih9=-165.83914699\hc10=1.10242681\hcc10=108.52487416\dih10=179.57259575\hc11=1.10387081\hcc11=108.91830432\dih11=-64.86289556\hc12=1.10421031\hcc12=105.45999839\dih12=167.49383758\hc13=1.10653884\hcc13=108.87092825\dih13=-78.62352169\hc14=1.10302982\hcn14=122.51784533\dih14=-141.85977502\hn15=1.02523729\hnc15=114.99253785\dih15=-183.8323894\\Version=x86-Linux-G03RevB.04\HF=-325.2535139\S2=0.758131\S2-1=0.\S2A=0.750031\RMSD=8.324e-09\RMSF=1.316e-05\Dipole=-1.134607,0.1558484,-1.0585868\PG=C01 [X(C5H8N1O1)]\@

#### QCISD/cc-pVDZ//B3LYP/cc-pVDZ

QCISD=-324.3271747

#### CCSD(T)/cc-pVDZ//B3LYP/cc-pVDZ

CCSD(T)=-324.3628204

### Transition state for 6-endo cyclization (Z)-13 of 6-aza-5-hexenoyl radical (5)

#### UHF/6-311G\*\*

1\ CHEMISTRY CLUSTER KIRKLAND-KNET12\FTS\UHF\6-311G(d,p)\C5H8N1O1(2)\HIROSHI\13-May-2005\1\#\HF/6-311G\*\* SCF=DIRECT OPT=(EF,TS,CALCF,MAXCYCLE=100) NOSYMM GEOM=MODIFY GUESS=READ FREQ=NORAMAN\6-Endo TS another conformation of imine\0,2\N\C,1,cn2\O,2,oc3,1,ocn3\C,2,cc4,1,ccn4,3,dih4,0\C,1,cn5,2,cnc5,3,dih5,0\C,5,cc6,1,ccn6,2,dih6,0\C,6,cc7,5,ccc7,1,dih7,0\H,6,hc8,5,hcc8,1,dih8,0\H,6,hc9,5,hcc9,1,dih9,0\H,7,hc10,6,hcc10,5,dih10,0\H,7,hc11,6,hcc11,5,dih11,0\H,4,hc12,2,hcc12,1,dih12,0\H,4,hc13,2,hcc13,1,dih13,0\H,5,hc14,1,hcn14,2,dih14,0\H,1,hn15,5,hnc15,6,dih15,0\cn2=2.02137769\oc3=1.15851196\ocn3=121.98729017\cc4=1.51879053\ccn4=108.02558021\dih4=189.31010244\cn5=1.34036028\cnc5=101.08602187\dih5=-236.50626701\cc6=1.50351763\ccn6=120.76188201\dih6=60.60258644\cc7=1.54042059\ccc7=108.64843641\dih7=-70.83138483\hc8=1.08923763\hcc8=110.26805666\dih8=49.50753441\hc9=1.08507153\hcc9=111.26595853\dih9=-191.45440679\hc10=1.08603818\hcc10=110.09644093\dih10=178.57927782\hc11=1.08710011\hcc11=109.03861034\dih11=-64.65562877\hc12=1.08574122\hcc12=107.84879095\dih12=169.23097329\hc13=1.08808513\hcc13=106.37464211\dih13=-75.19721843\hc14=1.07969123\hcn14=116.01319927\dih14=-93.63331638\hn15=1.00496685\hnc15=110.06437063\dih15=-34.05693542\\Version=x86-Linux-G03RevB.04\HF=-323.2880465\S2=1.034083\S2-1=0.\S2A=0.763219\RMSD=8.285e-09\RMSF=1.680e-05\Dipole=-1.7505402,-0.2265867,0.0331551\PG=C01 [X(C5H8N1O1)]\@

#### MP2/6-311G\*\*

1\ CHEMISTRY CLUSTER KIRKLAND-KNET2\FTS\UMP2-FC\6-311G(d,p)\C5H8N1O1(2)\HIROSHI\13-May-2005\1\#\MP2/6-311G\*\* SCF=DIRECT OPT=(EF,TS,READFC,MAXCYCLE=100) NOSYMM GEOM=CHECK GUESS=READ FREQ=NUMER\6-Endo TS another conformation of imine\0,2\N\C,1,cn2\O,2,oc3,1,ocn3\C,2,cc4,1,ccn4,3,dih4,0\C,1,cn5,2,cnc5,3,dih5,0\C,5,cc6,1,ccn6,2,dih6,0\C,6,cc7,5,ccc7,1,dih7,0\H,6,hc8,5,hcc8,1,dih8,0\H,6,hc9,5,hcc9,1,di

h9,0\H,7,hc10,6,hcc10,5,dih10,0\H,7,hc11,6,hcc11,5,dih11,0\H,4,hc12,2,hcc12,1,dih12,0\H,4,hc13,2,hcc13,1,dih13,0\H,5,hc14,1,hcn14,2,dih14,0\H,1,hn15,5,hnc15,6,dih15,0\cn2=1.94449283\oc3=1.19188981\ocn3=119.3036488\cc4=1.53795914\ccn4=104.33718951\dih4=211.12342676\cn5=1.29432149\enc5=94.80213788\dih5=-268.57709254\cc6=1.49665446\ccn6=123.41356357\dih6=73.55710347\cc7=1.54721268\ccc7=104.87451848\dih7=-77.30892905\hc8=1.09722863\hcc8=110.54174401\dih8=40.58513567\hc9=1.09415257\hcc9=112.53001481\dih9=-197.49972566\hc10=1.0978845\hcc10=110.41821964\dih10=174.80688304\hc11=1.09623263\hcc11=109.363569\dih11=-66.90538853\hc12=1.09548498\hcc12=106.36291608\dih12=178.07254145\hc13=1.09581614\hcc13=108.6206471\dih13=-65.21549124\hc14=1.0917746\hcn14=116.70593429\dih14=-88.98849708\hn15=1.0222362\hnc15=109.68422122\dih15=-21.26699695\Version=x86-Linux-G03RevB.04\HF=-323.2797154\MP2=-324.3474069\PUHF=-323.2969722\PMP2-0=-324.3622281\S2=0.965464\S2-1=0.903111\S2A=0.759128\RMSD=4.407e-09\RMSF=1.638e-05\Dipole=-1.3273473,-0.9468741,-0.0720323\PG=C01 [X(C5H8N1O1)]\@

### MP2/cc-pVDZ

1\ CHEMISTRY CLUSTER KIRKLAND-KNET2\FTS\UMP2-FC\CC-pVDZ\C5H8N1O1(2)\HIROSHI\13-May-2005\1\#MP2/CC-PVDZ SCF=DIRECT OPT=(EF,TS,READFC,MAXCYCLE=100) NOSYMM GEOM=CHECK GUESS=READ FREQ=NUMER\6-Endo TS another conformation of imine\0,2\N\C,1,cn2\O,2,oc3,1,ocn3\C,2,cc4,1,ccn4,3,dih4,0\C,1,cn5,2,cnc5,3,dih5,0\C,5,cc6,1,ccn6,2,dih6,0\C,6,cc7,5,ccc7,1,dih7,0\H,6,hc8,5,hcc8,1,dih8,0\H,6,hc9,5,hcc9,1,dih9,0\H,7,hc10,6,hcc10,5,dih10,0\H,7,hc11,6,hcc11,5,dih11,0\H,4,hc12,2,hcc12,1,dih12,0\H,4,hc13,2,hcc13,1,dih13,0\H,5,hc14,1,hcn14,2,dih14,0\H,1,hn15,5,hnc15,6,dih15,0\cn2=1.95920072\oc3=1.19758048\ocn3=119.72204646\cc4=1.54301207\ccn4=104.61503342\dih4=209.79931852\cn5=1.30060855\enc5=95.30197177\dih5=-265.9622889\cc6=1.50113609\ccn6=123.35440381\dih6=72.63506489\cc7=1.54880006\ccc7=105.12508753\dih7=-77.14615028\hc8=1.10607521\hcc8=110.42971076\dih8=40.78831686\hc9=1.10267899\hcc9=112.705802\dih9=-197.60085359\hc10=1.10669333\hcc10=110.4845895\dih10=175.20074062\hc11=1.10536973\hcc11=109.4071711\dih11=-66.87224179\hc12=1.1043842\hcc12=106.36372435\dih12=176.85931801\hc13=1.10520619\hcc13=108.44844827\dih13=-66.94190799\hc14=1.10111821\hcn14=116.64116716\dih14=-89.95915583\hn15=1.02956613\hnc15=109.25260311\dih15=-21.0595511\Version=x86-Linux-G03RevB.04\HF=-323.2267141\MP2=-324.2349872\PUHF=-323.2443446\PMP2-0=-324.2501678\S2=0.973413\S2-1=0.909706\S2A=0.759797\RMSD=5.580e-09\RMSF=3.166e-05\Dipole=-1.3121116,-0.8623299,-0.0522211\PG=C01 [X(C5H8N1O1)]\@

### MP2/aug-cc-pVDZ//MP2/cc-pVDZ

MP2=-324.3008119

### QCISD/cc-pVDZ//MP2/cc-pVDZ

QCISD=-324.3092654

### CCSD(T)/cc-pVDZ//MP2/cc-pVDZ

CCSD(T)=-324.3465306

### BHandHLYP/6-311G\*\*

1\ CHEMISTRY CLUSTER KIRKLAND-KNET8\FTS\UBHandHLYP\6-311G(d,p)\C5H8N1O1(2)\HIROSHI\13-May-2005\1\#BHANDHLYP/6-311G\*\* SCF=DIRECT OPT=(EF,TS,REA

DFC,MAXCYCLE=100) NOSYMM GEOM=CHECK GUESS=READ FREQ=NORAMAN\6-Endo TS another conformation of imine\0,2\N\C,1,cn2\O,2,oc3,1,ocn3\C,2,cc4,1,ccn4,3,dih4,0\C,1,cn5,2,cnc5,3,dih5,0\C,5,cc6,1,ccn6,2,dih6,0\C,6,cc7,5,ccc7,1,dih7,0\H,6,hc8,5,hcc8,1,dih8,0\H,6,hc9,5,hcc9,1,dih9,0\H,7,hc10,6,hcc10,5,dih10,0\H,7,hc11,6,hcc11,5,dih11,0\H,4,hc12,2,hcc12,1,dih12,0\H,4,hc13,2,hcc13,1,dih13,0\H,5,hc14,1,hcn14,2,dih14,0\H,1,hn15,5,hnc15,6,dih15,0\cn2=2.01239789\oc3=1.16704848\ocn3=120.40507399\cc4=1.51842089\ccn4=105.83880069\di h4=202.93461607\cn5=1.30977474\cnc5=97.77767167\dih5=-255.78645065\cc6=1.49358101\cc n6=121.86469593\dih6=67.32283693\cc7=1.53684813\ccc7=107.22523274\dih7=-74.05211323\ hc8=1.0896825\hcc8=110.39754249\dih8=45.34293515\hc9=1.08558174\hcc9=112.09231607\di h9=-194.56739463\hc10=1.08783005\hcc10=110.2333401\dih10=175.94160707\hc11=1.087173 74\hcc11=109.20761306\dih11=-66.89948532\hc12=1.08695986\hcc12=107.07372011\dih12=1 72.64227366\hc13=1.08782032\hcc13=107.68342186\dih13=-71.27591189\hc14=1.0817352\hc n14=116.73261494\dih14=-92.30340118\hn15=1.01090137\hnc15=110.4140751\dih15=-26.495 86048\Version=x86-Linux-G03RevB.04\HF=-325.1006124\S2=0.813835\S2-1=0.\S2A=0.7506 74\RMSD=5.438e-09\RMSF=2.024e-05\Dipole=-1.5772327,-0.6384903,0.0496038\PG=C01 [X(C5H8N1O1)]\@

### **BHandHLYP/cc-pVDZ**

1\ CHEMISTRY CLUSTER KIRKLAND-KNET8\FTS\UBHandHLYP\CC-pVDZ\C5H8N1O 1(2)\HIROSHI\13-May-2005\1\#\BHANDHLYP/CC-PVDZ SCF=DIRECT OPT=(EF,TS,READ FC,MAXCYCLE=100) NOSYMM GEOM=CHECK GUESS=READ FREQ=NORAMAN\6-En do TS another conformation of imine\0,2\N\C,1,cn2\O,2,oc3,1,ocn3\C,2,cc4,1,ccn4,3,dih4,0\C,1 ,cn5,2,cnc5,3,dih5,0\C,5,cc6,1,ccn6,2,dih6,0\C,6,cc7,5,ccc7,1,dih7,0\H,6,hc8,5,hcc8,1,dih8,0\H,6 ,hc9,5,hcc9,1,dih9,0\H,7,hc10,6,hcc10,5,dih10,0\H,7,hc11,6,hcc11,5,dih11,0\H,4,hc12,2,hcc12,1, di h12,0\H,4,hc13,2,hcc13,1,dih13,0\H,5,hc14,1,hcn14,2,dih14,0\H,1,hn15,5,hnc15,6,dih15,0\cn 2=2.01967648\oc3=1.17277965\ocn3=120.68391516\cc4=1.51976863\ccn4=105.88001208\dih4 =202.72151679\cn5=1.31226725\cnc5=97.75608252\dih5=-254.85241185\cc6=1.49478176\ccn6 =121.997934\dih6=67.05318263\cc7=1.53602034\ccc7=107.24014262\dih7=-74.26466496\hc8= 1.097624\hcc8=110.27300635\dih8=45.02096004\hc9=1.09340399\hcc9=112.20592939\dih9=-1 94.94043654\hc10=1.09586446\hcc10=110.28313359\dih10=176.21648552\hc11=1.09547596\h cc11=109.22045872\dih11=-66.75948835\hc12=1.09483805\hcc12=106.99349688\dih12=172.2 8110642\hc13=1.09604711\hcc13=107.49820988\dih13=-71.8963235\hc14=1.0907417\hcn14=1 16.61603302\dih14=-92.41093191\hn15=1.01739704\hnc15=109.93718823\dih15=-25.9003153\ \Version=x86-Linux-G03RevB.04\HF=-325.0372067\S2=0.814849\S2-1=0.\S2A=0.75069\RMS D=5.301e-09\RMSF=1.801e-05\Dipole=-1.5171071,-0.5886757,0.0385967\PG=C01 [X(C5H8N 1O1)]\@

### **QCISD/cc-pVDZ//BHandHLYP/cc-pVDZ**

QCISD=-324.3091481

### **CCSD(T)/cc-pVDZ//BHandHLYP/cc-pVDZ**

CCSD(T)=-324.3456051

### **B3LYP/6-311G\*\***

1\ CHEMISTRY CLUSTER KIRKLAND-KNET8\FTS\UB3LYP\6-311G(d,p)\C5H8N1O1(2)\ HIROSHI\13-May-2005\1\#\B3LYP/6-311G\*\* SCF=DIRECT OPT=(EF,TS,READFC,MAXCY

CLE=100) NOSYMM GEOM=CHECK GUESS=READ FREQ=NORAMAN\6-Endo TS another conformation of imine\0,2\N\C,1,cn2\O,2,oc3,1,ocn3\C,2,cc4,1,ccn4,3,dih4,0\C,1,cn5,2,cnc5,3,dih5,0\C,5,cc6,1,ccn6,2,dih6,0\C,6,cc7,5,ccc7,1,dih7,0\H,6,hc8,5,hcc8,1,dih8,0\H,6,hc9,5,hcc9,1,dih9,0\H,7,hc10,6,hcc10,5,dih10,0\H,7,hc11,6,hcc11,5,dih11,0\H,4,hc12,2,hcc12,1,dih12,0\H,4,hc13,2,hcc13,1,dih13,0\H,5,hc14,1,hcn14,2,dih14,0\H,1,hn15,5,hnc15,6,dih15,0\cn2=2.03284295\oc3=1.18003313\ocn3=119.90980965\cc4=1.52974113\ccn4=104.89108898\dih4=205.67434537\cn5=1.31858455\cnc5=97.09211759\dih5=-259.6292818\cc6=1.50082676\ccn6=122.36611159\dih6=68.53403245\cc7=1.54936463\ccc7=107.05315278\dih7=-74.17176059\hc8=1.09750893\hcc8=110.53761781\dih8=45.0319617\hc9=1.09355577\hcc9=112.30646598\dih9=-194.5848927\hc10=1.0964616\hcc10=110.18671742\dih10=174.94231883\hc11=1.09460634\hcc11=109.28709059\dih11=-67.82585183\hc12=1.09495993\hcc12=106.79095922\dih12=173.8542596\hc13=1.09531535\hcc13=107.93161289\dih13=-70.17534603\hc14=1.09020356\hcn14=116.58530996\dih14=-91.38575191\hn15=1.02184725\hnc15=110.04993252\dih15=-25.16115051\Version=x86-Linux-G03RevB.04\HF=-325.309441\S2=0.770007\S2-1=0.\S2A=0.750094\RMSD=3.072e-09\RMSF=3.059e-05\Dipole=-1.4708347,-0.7056775,0.0938366\PG=C01 [X(C5H8N1O1)]\@

### B3LYP/cc-pVDZ

1\ CHEMISTRY CLUSTER KIRKLAND-KNET8\FTS\SUB3LYP\CC-pVDZ\C5H8N1O1(2)\H IROSHI\13-May-2005\1\#\B3LYP/CC-PVDZ SCF=DIRECT OPT=(EF,TS,READFC,MAXCYCLE=100) NOSYMM GEOM=CHECK GUESS=READ FREQ=NORAMAN\6-Endo TS another conformation of imine\0,2\N\C,1,cn2\O,2,oc3,1,ocn3\C,2,cc4,1,ccn4,3,dih4,0\C,1,cn5,2,cnc5,3,dih5,0\C,5,cc6,1,ccn6,2,dih6,0\C,6,cc7,5,ccc7,1,dih7,0\H,6,hc8,5,hcc8,1,dih8,0\H,6,hc9,5,hcc9,1,dih9,0\H,7,hc10,6,hcc10,5,dih10,0\H,7,hc11,6,hcc11,5,dih11,0\H,4,hc12,2,hcc12,1,dih12,0\H,4,hc13,2,hcc13,1,dih13,0\H,5,hc14,1,hcn14,2,dih14,0\H,1,hn15,5,hnc15,6,dih15,0\cn2=2.04543698\oc3=1.18647784\ocn3=120.10357835\cc4=1.53183015\ccn4=104.89351201\dih4=205.83844538\cn5=1.32058809\cnc5=96.99053334\dih5=-258.90308609\cc6=1.5023422\ccn6=122.59331987\dih6=68.19818676\cc7=1.54843365\ccc7=107.00006754\dih7=-74.62389094\hc8=1.10613813\hcc8=110.40532769\dih8=44.40169239\hc9=1.10204906\hcc9=112.44296509\dih9=-195.18061132\hc10=1.10524178\hcc10=110.22700477\dih10=175.51724969\hc11=1.10366245\hcc11=109.33706914\dih11=-67.34456137\hc12=1.10356156\hcc12=106.71913693\dih12=173.52287802\hc13=1.10429805\hcc13=107.77208974\dih13=-70.71732144\hc14=1.10004784\hcn14=116.438873\dih14=-91.64356551\hn15=1.02894573\hnc15=109.52101449\dih15=-24.38622094\Version=x86-Linux-G03RevB.04\HF=-325.2375621\S2=0.77014\S2-1=0.\S2A=0.750095\RMSD=4.216e-09\RMSF=3.612e-05\Dipole=-1.402543,-0.6577614,0.0789167\PG=C01 [X(C5H8N1O1)]\@

### QCISD/cc-pVDZ//B3LYP/cc-pVDZ

QCISD=-324.3116551

### CCSD(T)/cc-pVDZ//B3LYP/cc-pVDZ

CCSD(T)=-324.34850

## 2-Piperidon-6-yl radical (9)

**UHF/6-311G\*\***

1\1\ CHEMCLUSTER-KNET1\FOpt\UHF\6-311G(d,p)\C5H8N1O1(2)\HIROSHI\12-Aug-2004\1\#\UHF/6-311G\*\* OPT=(Z-MATRIX,READFC,MAXCYCLE=100) GEOM=CHECKGUES S=READ FREQ=NORAMAN\Ryu endo product\0,2\N\C,1,cn2\O,2,oc3,1,ocn3\C,2,cc4,1,ccn4,3,dih4,0\C,1,cn5,2,cnc5,3,dih5,0\C,5,cc6,1,ccn6,2,dih6,0\C,6,cc7,5,ccc7,1,dih7,0\H,6,hc8,5,hcc8,1,dih8,0\H,6,hc9,5,hcc9,1,dih9,0\H,7,hc10,6,hcc10,5,dih10,0\H,7,hc11,6,hcc11,5,dih11,0\H,4,hc12,2,hcc12,1,dih12,0\H,4,hc13,2,hcc13,1,dih13,0\H,5,hc14,1,hcn14,2,dih14,0\H,1,hn15,5,hnc15,6,dih15,0\cn2=1.36427872\oc3=1.19439201\ocn3=121.31716172\cc4=1.51501143\ccn4=116.15570488\dih4=178.10288337\cn5=1.401957\cnc5=126.7186184\dih5=-186.78811235\cc6=1.49711619\ccn6=117.19964153\dih6=14.96110603\cc7=1.52831094\ccc7=109.9045356\dih7=-38.09507477\hc8=1.09312991\hcc8=110.45028741\dih8=82.54154457\hc9=1.0851069\hcc9=109.36324541\dih9=-160.28598738\hc10=1.08488011\hcc10=110.68782463\dih10=177.29864741\hc11=1.08714356\hcc11=109.32305007\dih11=-64.93022466\hc12=1.08213686\hcc12=106.96640568\dih12=151.75673398\hc13=1.08830202\hcc13=106.32344794\dih13=-94.17018869\hc14=1.07490312\hcn14=114.63256941\dih14=-194.81957314\hn15=0.99543974\hnc15=118.58765798\dih15=-174.915228\Version=x86-Linux-G03RevB.04\State=2-A\HF=-323.3767551\S2=0.766986\S2-1=0.\S2A=0.750222\RMSD=6.434e-09\RMSF=7.513e-05\Dipole=-1.1772457,0.0740455,-0.8988129\PG=C01 [X(C5H8N1O1)]\@\

**MP2/6-311G\*\***

1\1\ CHEMCLUSTER-KNET1\FOpt\UMP2-FC\6-311G(d,p)\C5H8N1O1(2)\HIROSHI\13-Aug-2004\1\#\MP2/6-311G\*\* OPT=(Z-MATRIX,READFC,MAXCYCLE=100) GEOM=CHECKGUESS=READ FREQ=NORAMAN\Ryu endo product\0,2\N\C,1,cn2\O,2,oc3,1,ocn3\C,2,cc4,1,ccn4,3,dih4,0\C,1,cn5,2,cnc5,3,dih5,0\C,5,cc6,1,ccn6,2,dih6,0\C,6,cc7,5,ccc7,1,dih7,0\H,6,hc8,5,hcc8,1,dih8,0\H,6,hc9,5,hcc9,1,dih9,0\H,7,hc10,6,hcc10,5,dih10,0\H,7,hc11,6,hcc11,5,dih11,0\H,4,hc12,2,hcc12,1,dih12,0\H,4,hc13,2,hcc13,1,dih13,0\H,5,hc14,1,hcn14,2,dih14,0\H,1,hn15,5,hnc15,6,dih15,0\cn2=1.38360532\oc3=1.21953792\ocn3=121.29047455\cc4=1.51836817\ccn4=115.04450981\dih4=178.58162389\cn5=1.3963252\cnc5=127.25862108\dih5=-186.2453567\cc6=1.49254228\ccn6=117.11511168\dih6=12.80192191\cc7=1.5307795\ccc7=109.56600901\dih7=-37.59261479\hc8=1.10373376\hcc8=111.09891654\dih8=82.34962539\hc9=1.09468139\hcc9=109.4539723\dih9=-159.81867924\hc10=1.09430755\hcc10=110.82677708\dih10=179.58097447\hc11=1.09601837\hcc11=109.09675937\dih11=-62.0144814\hc12=1.09254355\hcc12=106.77927977\dih12=153.1232163\hc13=1.09773848\hcc13=107.03804289\dih13=-92.16848732\hc14=1.08336203\hcn14=115.26177551\dih14=-193.43920047\hn15=1.01202454\hnc15=118.86362602\dih15=-176.33899195\Version=x86-Linux-G03RevB.04\State=2-A\HF=-323.3741923\MP2=-324.4377101\PUHF=-323.3779872\PMP2-0=-324.4403844\S2=0.770143\S2-1=0.758141\S2A=0.7503\RMSD=8.225e-09\RMSF=6.169e-06\Dipole=-0.9179602,0.0804484,-0.8164436\PG=C01 [X(C5H8N1O1)]\@\

**MP2/cc-pVDZ**

1\1\ CHEMCLUSTER-KNET10\FOpt\UMP2-FC\CC-pVDZ\C5H8N1O1(2)\HIROSHI\13-Aug-2004\1\#\MP2/CC-PVDZ OPT=(Z-MATRIX,READFC,MAXCYCLE=100) GEOM=CHECKGUESS=READ FREQ=NORAMAN\Ryu endo product\0,2\N\C,1,cn2\O,2,oc3,1,ocn3\C,2,cc4,1,ccn4,3,dih4,0\C,1,cn5,2,cnc5,3,dih5,0\C,5,cc6,1,ccn6,2,dih6,0\C,6,cc7,5,ccc7,1,dih7,0\H,6,hc8,5,hcc8,1,dih8,0\H,6,hc9,5,hcc9,1,dih9,0\H,7,hc10,6,hcc10,5,dih10,0\H,7,hc11,6,hcc11,5,dih11,0\H,4,hc12,2,hcc12,1,dih12,0\H,4,hc13,2,hcc13,1,dih13,0\H,5,hc14,1,hcn14,2,dih14,0\H,1,hn15,5,hnc15,6,dih15,0\cn2=1.38360532\oc3=1.21953792\ocn3=121.29047455\cc4=1.51836817\ccn4=115.04450981\dih4=178.58162389\cn5=1.3963252\cnc5=127.25862108\dih5=-186.2453567\cc6=1.49254228\ccn6=117.11511168\dih6=12.80192191\cc7=1.5307795\ccc7=109.56600901\dih7=-37.59261479\hc8=1.10373376\hcc8=111.09891654\dih8=82.34962539\hc9=1.09468139\hcc9=109.4539723\dih9=-159.81867924\hc10=1.09430755\hcc10=110.82677708\dih10=179.58097447\hc11=1.09601837\hcc11=109.09675937\dih11=-62.0144814\hc12=1.09254355\hcc12=106.77927977\dih12=153.1232163\hc13=1.09773848\hcc13=107.03804289\dih13=-92.16848732\hc14=1.08336203\hcn14=115.26177551\dih14=-193.43920047\hn15=1.01202454\hnc15=118.86362602\dih15=-176.33899195\Version=x86-Linux-G03RevB.04\State=2-A\HF=-323.3741923\MP2=-324.4377101\PUHF=-323.3779872\PMP2-0=-324.4403844\S2=0.770143\S2-1=0.758141\S2A=0.7503\RMSD=8.225e-09\RMSF=6.169e-06\Dipole=-0.9179602,0.0804484,-0.8164436\PG=C01 [X(C5H8N1O1)]\@\

c15,6,dih15,0\cn2=1.38736189\oc3=1.22477637\ocn3=121.25060374\cc4=1.52212402\ccn4=114.94116529\dih4=178.48649472\cn5=1.39969869\cnc5=127.08186492\dih5=-187.28552309\cc6=1.49678945\ccn6=117.25685682\dih6=13.50253041\cc7=1.53355651\ccc7=109.66559388\dih7=-37.5366236\hc8=1.11258214\hcc8=111.13512358\dih8=82.5417906\hc9=1.103185\hcc9=109.43829663\dih9=-160.01724953\hc10=1.1027348\hcc10=110.83833453\dih10=179.18022487\hc11=1.10518957\hcc11=109.28382035\dih11=-62.64261322\hc12=1.10101236\hcc12=106.85227818\dih12=154.37114559\hc13=1.10672334\hcc13=106.9785533\dih13=-91.30634501\hc14=1.09272554\hcn14=115.18705427\dih14=-192.89304932\hn15=1.01838889\hnc15=118.90625119\dih15=-176.85438364\Version=x86-Linux-G03RevB.04\State=2-AHF=-323.3198023\MP2=-324.325058\PUHF=-323.3236295\PMP2-0=-324.3277808\S2=0.770909\S2-1=0.758733\S2A=0.750317\RMSD=3.749e-09\RMSF=6.444e-06\Dipole=-0.8769125,0.075817,-0.7973193\PG=C01 [X(C5H8N1O1)]\@

### **MP2/aug-cc-pVDZ//MP2/cc-pVDZ**

MP2=-324.3895209

### **QCISD/cc-pVDZ//MP2/cc-pVDZ**

QCISD=-324.3874007

### **CCSD(T)/cc-pVDZ//MP2/cc-pVDZ**

CCSD(T)=-324.4211575

### **BHandHLYP/6-311G\*\***

1\ \ CHEMCLUSTER-KNET1\FOpt\UBHandHLYP\6-311G(d,p)\C5H8N1O1(2)\HIROSHI\13-Aug-2004\1\#\BHANDHLYP/6-311G\*\* OPT=(Z-MATRIX,READFC,MAXCYCLE=100) GEOM=CHECK GUESS=READ FREQ=NORAMAN\Ryu endo product\0,2\N\C,1,cn2\O,2,oc3,1,ocn3\C,2,cc4,1,ccn4,3,dih4,0\C,1,cn5,2,cnc5,3,dih5,0\C,5,cc6,1,ccn6,2,dih6,0\C,6,cc7,5,ccc7,1,dih7,0\H,6,hc8,5,hcc8,1,dih8,0\H,6,hc9,5,hcc9,1,dih9,0\H,7,hc10,6,hcc10,5,dih10,0\H,7,hc11,6,hcc11,5,dih11,0\H,4,hc12,2,hcc12,1,dih12,0\H,4,hc13,2,hcc13,1,dih13,0\H,5,hc14,1,hcn14,2,dih14,0\H,1,hn15,5,hnc15,6,dih15,0\cn2=1.36745381\oc3=1.204662\ocn3=121.14964358\cc4=1.51004785\ccn4=115.68337686\dih4=178.93786023\cn5=1.38627306\cnc5=127.06679649\dih5=-184.18198875\cc6=1.48466914\ccn6=118.06873494\dih6=9.75524975\cc7=1.52494336\ccc7=110.15256837\dih7=-34.51560226\hc8=1.0957391\hcc8=110.86816677\dih8=85.9965554\hc9=1.0860591\hcc9=109.61625291\dih9=-156.97562945\hc10=1.08525425\hcc10=110.62657101\dih10=176.59137463\hc11=1.08744858\hcc11=109.2753849\dih11=-65.72559607\hc12=1.08323962\hcc12=106.84394743\dih12=151.39919424\hc13=1.08919002\hcc13=106.73776664\dih13=-94.62180656\hc14=1.0734587\hcn14=115.84662516\dih14=-190.8692849\hn15=1.00198635\hnc15=118.97566925\dih15=-176.1650755\Version=x86-Linux-G03RevB.04\State=2-AHF=-325.1874116\S2=0.759293\S2-1=0.\S2A=0.750057\RMSD=7.269e-09\RMSF=2.258e-05\Dipole=-1.0549122,0.0674546,-0.8804355\PG=C01 [X(C5H8N1O1)]\@

### **BHandHLYP/cc-pVDZ**

1\ \ CHEMCLUSTER-KNET10\FOpt\UBHandHLYP\CC-pVDZ\C5H8N1O1(2)\HIROSHI\13-Aug-2004\1\#\BHANDHLYP/CC-PVDZ OPT=(Z-MATRIX,READFC,MAXCYCLE=100) GEOM=CHECK GUESS=READ FREQ=NORAMAN\Ryu endo product\0,2\N\C,1,cn2\O,2,oc3,1,ocn3\C,2,cc4,1,ccn4,3,dih4,0\C,1,cn5,2,cnc5,3,dih5,0\C,5,cc6,1,ccn6,2,dih6,0\C,6,cc7,5,ccc7,1,d

ih7,0\H,6,hc8,5,hcc8,1,dih8,0\H,6,hc9,5,hcc9,1,dih9,0\H,7,hc10,6,hcc10,5,dih10,0\H,7,hc11,6,hc11,5,dih11,0\H,4,hc12,2,hcc12,1,dih12,0\H,4,hc13,2,hcc13,1,dih13,0\H,5,hc14,1,hcn14,2,dih14,0\H,1,hn15,5,hnc15,6,dih15,0\cn2=1.36900923\oc3=1.20887204\ocn3=121.01927844\cc4=1.51080184\ccn4=115.62702247\dih4=178.961229\cn5=1.38701614\cnc5=126.98427525\dih5=-184.64636866\cc6=1.48642043\ccn6=118.14527175\dih6=9.49387276\cc7=1.52471753\ccc7=110.2148785\dih7=-33.9997477\hc8=1.10374507\hcc8=110.88746777\dih8=86.56760707\hc9=1.09396452\hcc9=109.59895334\dih9=-156.61695714\hc10=1.09299706\hcc10=110.655797\dih10=176.54156315\hc11=1.09569117\hcc11=109.3404937\dih11=-65.84637199\hc12=1.09098764\hcc12=106.92515314\dih12=152.43470174\hc13=1.09724898\hcc13=106.73422604\dih13=-93.69462328\hc14=1.08195985\hcn14=115.82002226\dih14=-191.33372086\hn15=1.00680167\hnc15=19.07336673\dih15=-176.87662872\Version=x86-Linux-G03RevB.04\State=2-A\HF=-325.1241732\S2=0.759572\S2-1=0.\S2A=0.75006\RMSD=9.267e-09\RMSF=1.646e-05\Dipole=-0.9996037,0.0640393,-0.8498498\PG=C01 [X(C5H8N1O1)]\@

### **BHandHLYP/aug-cc-pVDZ//BHandHLYP/cc-pVDZ**

HF=-325.1465853

### **QCISD/cc-pVDZ//BHandHLYP/cc-pVDZ**

QCISD=-324.385348

### **CCSD(T)/cc-pVDZ//BHandHLYP/cc-pVDZ**

CCSD(T)=-324.4185092

### **B3LYP/6-311G\*\***

1\1\ CHEMCLUSTER-KNET1\FOpt\UB3LYP\6-311G(d,p)\C5H8N1O1(2)\HIROSHI\13-Aug-2004\1\#\B3LYP/6-311G\*\* OPT=(Z-MATRIX,READFC,MAXCYCLE=100) GEOM=CHECK GUESS=READ FREQ=NORAMAN\Ryu endo product\0,2\N\C,1,cn2\O,2,oc3,1,ocn3\C,2,cc4,1,ccn4,3,dih4,0\C,1,cn5,2,cnc5,3,dih5,0\C,5,cc6,1,ccn6,2,dih6,0\C,6,cc7,5,ccc7,1,dih7,0\H,6,hc8,5,hcc8,1,dih8,0\H,6,hc9,5,hcc9,1,dih9,0\H,7,hc10,6,hcc10,5,dih10,0\H,7,hc11,6,hcc11,5,dih11,0\H,4,hc12,2,hcc12,1,dih12,0\H,4,hc13,2,hcc13,1,dih13,0\H,5,hc14,1,hcn14,2,dih14,0\H,1,hn15,5,hnc15,6,dih15,0\cn2=1.38243777\oc3=1.21955576\ocn3=121.03294333\cc4=1.52124524\ccn4=115.26219594\dih4=179.45543817\cn5=1.38804723\cnc5=127.42633099\dih5=-182.89764815\cc6=1.48996948\ccn6=118.49140209\dih6=6.89271486\cc7=1.53682034\ccc7=110.39747006\dih7=-32.25889966\hc8=1.1045219\hcc8=111.06136395\dih8=88.31363318\hc9=1.09414582\hcc9=109.71372318\dih9=-154.85636523\hc10=1.09294963\hcc10=110.52412694\dih10=175.79490572\hc11=1.09495528\hcc11=109.23460788\dih11=-66.66640085\hc12=1.09115678\hcc12=106.84762276\dih12=150.86010493\hc13=1.09700778\hcc13=107.09147666\dih13=-95.18729246\hc14=1.08013395\hcn14=116.37752785\dih14=-187.77143585\hn15=1.01186156\hnc15=119.02160146\dih15=-177.1503749\Version=x86-Linux-G03RevB.04\State=2-A\HF=-325.385203\S2=0.755623\S2-1=0.\S2A=0.750021\RMSD=6.703e-09\RMSF=2.588e-05\Dipole=-0.9930404,0.0456982,-0.8921055\PG=C01 [X(C5H8N1O1)]\@

### **B3LYP/cc-pVDZ**

1\1\ CHEMCLUSTER-KNET10\FOpt\UB3LYP\CC-pVDZ\C5H8N1O1(2)\HIROSHI\13-Aug-2004\1\#\B3LYP/CC-PVDZ OPT=(Z-MATRIX,READFC,MAXCYCLE=100) GEOM=CHECK GUESS=READ FREQ=NORAMAN\Ryu endo product\0,2\N\C,1,cn2\O,2,oc3,1,ocn3\C,2,cc4,1,

ccn4,3,dih4,0\C,1,cn5,2,cnc5,3,dih5,0\C,5,cc6,1,ccn6,2,dih6,0\C,6,cc7,5,ccc7,1,dih7,0\H,6,hc8,5,hcc8,1,dih8,0\H,6,hc9,5,hcc9,1,dih9,0\H,7,hc10,6,hcc10,5,dih10,0\H,7,hc11,6,hcc11,5,dih11,0\H,4,hc12,2,hcc12,1,dih12,0\H,4,hc13,2,hcc13,1,dih13,0\H,5,hc14,1,hcn14,2,dih14,0\H,1,hn15,5,hnc15,6,dih15,0\ncn2=1.38414122\oc3=1.22416614\ocn3=120.89157077\cc4=1.52247638\ccn4=115.1678005\dih4=179.4370687\cn5=1.38917671\cnc5=127.3353446\dih5=-183.47640989\cc6=1.49209762\ccn6=118.54783483\dih6=6.74470057\cc7=1.53656551\ccc7=110.40342002\dih7=-31.85448784\hc8=1.11340387\hcc8=111.08666785\dih8=88.76798016\hc9=1.10275238\hcc9=109.69044281\dih9=-154.62501934\hc10=1.10135214\hcc10=110.55606725\dih10=175.86644738\hc11=1.10393914\hcc11=109.32352036\dih11=-66.61234781\hc12=1.09957826\hcc12=106.96437541\dih12=152.120589\hc13=1.10593205\hcc13=107.08493546\dih13=-94.01135113\hc14=1.08921659\hcn14=116.32354652\dih14=-188.27259718\hn15=1.01680987\hnc15=119.1192008\dih15=-177.79216022\Version=x86-Linux-G03RevB.04\State=2-A\HF=-325.3138077\S2=0.755738\S2-1=0.\S2A=0.750022\RMSD=6.481e-09\RMSF=2.477e-05\Dipole=-0.9272688,0.0446581,-0.8540774\PG=C01 [X(C5H8N1O1)]\@

**B3LYP/aug-cc-pVDZ//B3LYP/cc-pVDZ**  
HF=-325.3405322

**QCISD//cc-pVDZ//B3LYP/cc-pVDZ**  
QCISD=-324.3869501

**CCSD(T)/cc-pVDZ//B3LYP/cc-pVDZ**  
CCSD(T)=-324.4206715

## Transition state for 5-exo cyclization (E)-12 of 6-aza-5-hexenoyl radical (5)

**UHF/6-311G\*\***

1\ \ CHEMCLUSTER-KNET10\FTS\UHF\6-311G(d,p)\C5H8N1O1(2)\HIROSHI\12-Aug-2004  
\ \ #UHF/6-311G\*\* OPT=(TS,EF,READFC,MAXCYCLE=100) NOSYMM FREQ=NORAMA  
N GEOM=CHECK GUESS=READ\ \ Ryu exo transition state\ \ 0,2\C\O,1,r1\C,1,r2,2,a1\C,3,r3,1,a  
2,2,d1,0\C,4,r4,3,a3,1,d2,0\C,1,r5,2,a4,3,d3,0\N,6,r6,1,a5,2,d4,0\H,3,r7,1,a6,2,d5,0\H,3,r8,1,a7,2,  
d6,0\H,4,r9,3,a8,1,d7,0\H,4,r10,3,a9,1,d8,0\H,5,r11,4,a10,3,d9,0\H,5,r12,4,a11,3,d10,0\H,6,r13,1  
,a12,2,d11,0\H,7,r14,6,a13,1,d12,0\ \ r1=1.15924735\ r2=1.50989367\ r3=1.52670584\ r4=1.533710  
66\ r5=2.12615852\ r6=1.32120413\ r7=1.08450162\ r8=1.08786575\ r9=1.08389266\ r10=1.087872  
78\ r11=1.08533061\ r12=1.08666249\ r13=1.0859251\ r14=1.00592172\ a1=132.23060813\ a2=107  
.20605619\ a3=108.22228269\ a4=127.6626973\ a5=105.72827394\ a6=109.62509154\ a7=106.211  
1664\ a8=111.23426435\ a9=109.36557899\ a10=110.47039779\ a11=110.30303102\ a12=92.86984  
926\ a13=110.00576745\ d1=200.63303263\ d2=-43.7416462\ d3=178.04630166\ d4=-53.8078792\  
d5=-34.7527398\ d6=81.97619049\ d7=-166.02302722\ d8=75.95155051\ d9=-70.247691\ d10=171  
.02911258\ d11=68.8116406\ d12=86.21302035\ \ Version=x86-Linux-G03RevB.04\HF=-323.309  
8331\S2=0.968152\S2-1=0.\S2A=0.758214\RMSD=7.691e-09\RMSF=2.401e-06\Dipole=0.4959  
901,0.7353737,-0.869923\PG=C01 [X(C5H8N1O1)]\@

**MP2/6-311G\*\***



1\ \ CHEMCLUSTER-KNET16\FTS\UMP2-FC\6-311G(d,p)\C5H8N1O1(2)\HIROSHI\12-Aug-2004\1\#\MP2/6-311G\*\* OPT=(EF,TS,READFC,MAXCYCLE=200) NOSYMM GEOM=CHECK GUESS=READ FREQ=NORAMAN\Ryu exo transition state\0,2\C\O,1,r1\C,1,r2,2,a1\C,3,r3,1,a2,2,d1,0\C,4,r4,3,a3,1,d2,0\C,1,r5,2,a4,3,d3,0\N,6,r6,1,a5,2,d4,0\H,3,r7,1,a6,2,d5,0\H,3,r8,1,a7,2,d6,0\H,4,r9,3,a8,1,d7,0\H,4,r10,3,a9,1,d8,0\H,5,r11,4,a10,3,d9,0\H,5,r12,4,a11,3,d10,0\H,6,r13,1,a12,2,d11,0\H,7,r14,6,a13,1,d12,0\r1=1.1794515\r2=1.51603831\r3=1.52617225\r4=1.53345366\r5=2.1188636\r6=1.2905172\r7=1.09460157\r8=1.09747911\r9=1.09316288\r10=1.09637839\r11=1.09482135\r12=1.09586743\r13=1.10083842\r14=1.02122399\A1=133.04733291\A2=106.02029732\A3=107.0330103\A4=126.68866749\A5=104.47602796\A6=109.44057445\A7=105.99918014\A8=111.53061023\A9=109.26663626\A10=110.55328709\A11=110.75830435\A12=90.44409888\A13=109.22520243\A14=200.37257903\A15=-47.88556937\A16=170.75707099\A17=-54.61392691\A18=-34.850045\A19=82.56996747\A20=-169.79639287\A21=71.33155893\A22=-69.58019994\A23=170.50193448\A24=69.74022525\A25=86.90713715\Version=x86-Linux-G03RevB.04\HF=-323.3067726\MP2=-324.3659979\PUHF=-323.3242446\PMP2-0=-324.3806676\S2=0.945275\S2-1=0.88115\S2A=0.757801\RMSD=7.695e-09\RMSF=1.662e-05\Dipole=0.6881955,0.8771364,-0.5606652\PG=C01 [X(C5H8N1O1)]\ \@

### MP2/cc-pVDZ

1\ \ CHEMCLUSTER-KNET16\FTS\UMP2-FC\CC-pVDZ\C5H8N1O1(2)\HIROSHI\12-Aug-2004\1\#\MP2/CC-PVDZ OPT=(EF,TS,READFC,MAXCYCLE=200) NOSYMM GEOM=CHECK GUESS=READ FREQ=NORAMAN\Ryu exo transition state\0,2\C\O,1,r1\C,1,r2,2,a1\C,3,r3,1,a2,2,d1,0\C,4,r4,3,a3,1,d2,0\C,1,r5,2,a4,3,d3,0\N,6,r6,1,a5,2,d4,0\H,3,r7,1,a6,2,d5,0\H,3,r8,1,a7,2,d6,0\H,4,r9,3,a8,1,d7,0\H,4,r10,3,a9,1,d8,0\H,5,r11,4,a10,3,d9,0\H,5,r12,4,a11,3,d10,0\H,6,r13,1,a12,2,d11,0\H,7,r14,6,a13,1,d12,0\r1=1.18654029\r2=1.52217389\r3=1.5284149\r4=1.53593732\r5=2.12383847\r6=1.29846653\r7=1.10300189\r8=1.10619654\r9=1.10180819\r10=1.10563327\r11=1.10354135\r12=1.10432564\r13=1.10958461\r14=1.0297996\A1=132.71104251\A2=105.89661227\A3=107.02115609\A4=127.25780164\A5=104.13557474\A6=109.62502394\A7=105.96615685\A8=111.64278122\A9=109.27953923\A10=110.58828734\A11=110.70550598\A12=90.61498371\A13=108.60948313\A14=201.12691568\A15=-48.46856191\A16=170.58979553\A17=-55.6265808\A18=-33.8918705\A19=83.32970262\A20=-170.54811751\A21=70.9083411\A22=-69.87228489\A23=170.47837942\A24=68.92714136\A25=86.86286539\Version=x86-Linux-G03RevB.04\HF=-323.2519908\MP2=-324.2522342\PUHF=-323.2698335\PMP2-0=-324.2672688\S2=0.953366\S2-1=0.887794\S2A=0.758347\RMSD=8.553e-09\RMSF=2.659e-06\Dipole=0.6388232,0.8259779,-0.5328663\PG=C01 [X(C5H8N1O1)]\ \@

### MP2/aug-cc-pVDZ//MP2/cc-pVDZ

MP2=-324.318663

### QCISD/cc-pVDZ//MP2/cc-pVDZ

QCISD=-324.3269134

### CCSD(T)/cc-pVDZ//MP2/cc-pVDZ

CCSD(T)=-324.3623263

### BHandHLYP/6-311G\*\*

1\ \ MARCCENTRE-ANET08\FTS\UBHandHLYP\6-311G(d,p)\C5H8N1O1(2)\HIROSHI\13-Aug-2004\1\ \#BHANDHLYP/6-311G\*\* OPT=(EF,TS,READFC,MAXCYCLE=100) NOSYMM  
 M FREQ=NORAMAN GEOM=CHECK GUESS=READ\Ryu exo transition state\0,2\C\O,1,r1\C,1,r2,2,a1\C,3,r3,1,a2,2,d1,0\C,4,r4,3,a3,1,d2,0\C,1,r5,2,a4,3,d3,0\N,6,r6,1,a5,2,d4,0\H,3,r7,1,a6,2,d5,0\H,3,r8,1,a7,2,d6,0\H,4,r9,3,a8,1,d7,0\H,4,r10,3,a9,1,d8,0\H,5,r11,4,a10,3,d9,0\H,5,r12,4,a11,3,d10,0\H,6,r13,1,a12,2,d11,0\H,7,r14,6,a13,1,d12,0\r1=1.16431136\r2=1.50171585\r3=1.52083082\r4=1.52707093\r5=2.14531466\r6=1.30012979\r7=1.08607304\r8=1.08946079\r9=1.08446645\r10=1.08822437\r11=1.08631065\r12=1.08748805\r13=1.09013514\r14=1.01142177\ a1=132.97808825\ a2=107.39162012\ a3=108.11581012\ a4=127.18197166\ a5=105.63981747\ a6=109.49179832\ a7=105.94486299\ a8=111.21661946\ a9=109.30262517\ a10=110.73702099\ a11=110.29237774\ a12=91.0309349\ a13=110.17085845\ d1=198.01886214\ d2=-44.84169401\ d3=173.00184807\ d4=-51.79837348\ d5=-36.95935236\ d6=79.36755585\ d7=-167.15055576\ d8=74.91725817\ d9=-70.38235836\ d10=170.74431174\ d11=71.52188753\ d12=86.72221163\ \Version=DEC-AXP-OSF/1-G98RevA.7\HF=-325.119639\S2=0.807853\S2-1=0.\S2A=0.750522\RMSD=7.475e-09\RMSF=1.094e-04\Dipole=0.6434254,0.8017116,-0.7453473\PG=C01 [X(C5H8N1O1)]\@

### **BHandHLYP/cc-pVDZ**

1\ \ MARCCENTRE-ANET08\FTS\UBHandHLYP\CC-pVDZ\C5H8N1O1(2)\HIROSHI\13-Aug-2004\1\ \#BHANDHLYP/CC-PVDZ OPT=(EF,TS,CALCFC,MAXCYCLE=100) NOSYMM  
 FREQ=NORAMAN\Ryu exo transition state\0,2\C\O,1,r1\C,1,r2,2,a1\C,3,r3,1,a2,2,d1,0\C,4,r4,3,a3,1,d2,0\C,1,r5,2,a4,3,d3,0\N,6,r6,1,a5,2,d4,0\H,3,r7,1,a6,2,d5,0\H,3,r8,1,a7,2,d6,0\H,4,r9,3,a8,1,d7,0\H,4,r10,3,a9,1,d8,0\H,5,r11,4,a10,3,d9,0\H,5,r12,4,a11,3,d10,0\H,6,r13,1,a12,2,d11,0\H,7,r14,6,a13,1,d12,0\r1=1.16987511\r2=1.50392559\r3=1.52036891\r4=1.52666135\r5=2.15135083\r6=1.30406498\r7=1.09358784\r8=1.09716389\r9=1.09218705\r10=1.09628321\r11=1.09406189\r12=1.09512788\r13=1.0981991\r14=1.01850249\ a1=132.57091427\ a2=107.36850129\ a3=108.109549\ a4=127.80560302\ a5=105.64087351\ a6=109.60738588\ a7=105.79305396\ a8=111.30309587\ a9=109.26974635\ a10=110.76220667\ a11=110.27155862\ a12=90.85188497\ a13=109.61517987\ d1=198.54508856\ d2=-45.32558529\ d3=172.9874982\ d4=-52.31370976\ d5=-36.22887849\ d6=79.95710442\ d7=-167.80169502\ d8=74.42854245\ d9=-70.26982878\ d10=170.9240716\ d11=71.28108124\ d12=86.73219177\ \Version=DEC-AXP-OSF/1-G98RevA.7\HF=-325.054825\S2=0.810532\S2-1=0.\S2A=0.75055\RMSD=7.083e-09\RMSF=5.643e-05\Dipole=0.6100894,0.748571,-0.7076534\PG=C01 [X(C5H8N1O1)]\@

### **QCISD/cc-pVDZ// BHandHLYP/cc-pVDZ**

QCISD=-324.3255825

### **CCSD(T)/cc-pVDZ//BHandHLYP/cc-pVDZ**

CCSD(T)=-324.3604867

### **B3LYP/6-311G\*\***

1\ \ MARCCENTRE-ANET08\FTS\UB3LYP\6-311G(d,p)\C5H8N1O1(2)\HIROSHI\13-Aug-2004\1\ \#B3LYP/6-311G\*\* OPT=(EF,TS,READFC,MAXCYCLE=100) NOSYMM  
 FREQ=NORAMAN GEOM=CHECK GUESS=READ\Ryu exo transition state\0,2\C\O,1,r1\C,1,r2,2,a1\C,3,r3,1,a2,2,d1,0\C,4,r4,3,a3,1,d2,0\C,1,r5,2,a4,3,d3,0\N,6,r6,1,a5,2,d4,0\H,3,r7,1,a6,2,d5,0\H,3,r8,1,a7,2,d6,0\H,4,r9,3,a8,1,d7,0\H,4,r10,3,a9,1,d8,0\H,5,r11,4,a10,3,d9,0\H,5,r12,4,a11,3,d10,0\H,6,r13,1,a12,2,d11,0\H,7,r14,6,a13,1,d12,0\r1=1.1766747\r2=1.50983956\r3=1.53103803\r4=1.5

3790418\r5=2.16207559\r6=1.31019436\r7=1.0939822\r8=1.0974588\r9=1.09184673\r10=1.09534511\r11=1.09380756\r12=1.09508384\r13=1.09940865\r14=1.02209936\|a1=133.0253312\|a2=107.57464918\|a3=108.16206075\|a4=127.02527559\|a5=105.98512044\|a6=109.48394003\|a7=105.95209727\|a8=111.16157416\|a9=109.23393155\|a10=110.76501895\|a11=110.18514821\|a12=90.93291839\|a13=109.84690065\|d1=196.29947599\|d2=-44.78919718\|d3=170.35069526\|d4=-50.78476577\|d5=-38.53968449\|d6=77.52905446\|d7=-167.12670518\|d8=75.04115133\|d9=-71.2357283\|d10=170.00757504\|d11=72.97944343\|d12=86.76699366\|Version=DEC-AXP-OSF/1-G98Rev A.7\HF=-325.3252706\|S2=0.771\|S2-1=0.\|S2A=0.750088\|RMSD=4.328e-09\|RMSF=6.100e-05\|Dipole=0.6722976,0.8008273,-0.6674247\|PG=C01 [X(C5H8N1O1)]\|@

### B3LYP/cc-pVDZ

1\| MARCCENTRE-ANET08\|FTS\|UB3LYP\|CC-pVDZ\|C5H8N1O1(2)\|HIROSHI\|12-Aug-2004\|1\|#B3LYP/CC-PVDZ OPT=(EF,TS,CALCFC,MAXCYCLE=100) NOSYMM FREQ=NORAMAN\|Ryu exo transition state\|0,2\|C\|O,1,r1\|C,1,r2,2,a1\|C,3,r3,1,a2,2,d1,0\|C,4,r4,3,a3,1,d2,0\|C,1,r5,2,a4,3,d3,0\|N,6,r6,1,a5,2,d4,0\|H,3,r7,1,a6,2,d5,0\|H,3,r8,1,a7,2,d6,0\|H,4,r9,3,a8,1,d7,0\|H,4,r10,3,a9,1,d8,0\|H,5,r11,4,a10,3,d9,0\|H,5,r12,4,a11,3,d10,0\|H,6,r13,1,a12,2,d11,0\|H,7,r14,6,a13,1,d12,0\|r1=1.1830083\r2=1.51298343\r3=1.53046844\r4=1.53729877\r5=2.17225972\r6=1.31379308\r7=1.10239774\r8=1.10615321\r9=1.10049652\r10=1.10444388\r11=1.10255063\r12=1.10370757\r13=1.10847924\r14=1.02988505\|a1=132.5534732\|a2=107.49966545\|a3=108.11499638\|a4=127.73309899\|a5=105.94057105\|a6=109.60353491\|a7=105.78635348\|a8=111.24641822\|a9=109.21021645\|a10=110.79841049\|a11=110.12459928\|a12=90.63210012\|a13=109.24774653\|d1=196.46189488\|d2=-45.56213239\|d3=169.76074889\|d4=-50.76461178\|d5=-38.18951015\|d6=77.75395872\|d7=-168.04782225\|d8=74.25638219\|d9=-70.74052914\|d10=170.55410754\|d11=73.35496211\|d12=86.80459727\|Version=DEC-AXP-OSF/1-G98Rev A.7\HF=-325.2519149\|S2=0.771983\|S2-1=0.\|S2A=0.750093\|RMSD=5.784e-09\|RMSF=7.426e-05\|Dipole=0.6352267,0.7402305,-0.6303845\|PG=C01 [X(C5H8N1O1)]\|@

### QCISD/cc-pVDZ//B3LYP/cc-pVDZ

QCISD=-324.3278202

### CCSD(T)/cc-pVDZ//B3LYP/cc-pVDZ

CCSD(T)=-324.3631334

## Transition state for 5-exo cyclization (Z)-12 of 6-aza-5-hexenoyl radical (5)

### UHF/6-311G\*\*

1\| CHEMISTRY CLUSTER KIRKLAND-KNET18\|FTS\|UHF\|6-311G(d,p)\|C5H8N1O1(2)\|HIROSHI\|12-May-2005\|1\|#UHF/6-311G\*\* OPT=(TS,EF,CALCFC,MAXCYCLE=100)NOSYMM FREQ=NORAMAN GEOM=MODIFY GUESS=READ\|5-exo chantal another isomer of imine\|0,2\|C\|O,1,r1\|C,1,r2,2,a1\|C,3,r3,1,a2,2,d1,0\|C,4,r4,3,a3,1,d2,0\|C,1,r5,2,a4,3,d3,0\|N,6,r6,1,a5,2,d4,0\|H,3,r7,1,a6,2,d5,0\|H,3,r8,1,a7,2,d6,0\|H,4,r9,3,a8,1,d7,0\|H,4,r10,3,a9,1,d8,0\|H,5,r11,4,a10,3,d9,0\|H,5,r12,4,a11,3,d10,0\|H,6,r13,1,a12,2,d11,0\|H,7,r14,6,a13,1,d12,0\|r1=1.15775251\r2=1.51354051\r3=1.52630289\r4=1.53269399\r5=2.1216753\r6=1.32220422\r7=1.08432749\r8=1.08814585\r9=1.08383489\r10=1.08730059\r11=1.08865896\r12=1.08644108\r13=1.08292914\r14

=1.00786489\A1=131.34599619\A2=107.68147346\A3=108.15821763\A4=128.22316454\A5=107.93525293\A6=109.45717811\A7=106.19861968\A8=111.29509661\A9=109.54164956\A10=109.92733548\A11=110.39558951\A12=92.46612289\A13=110.06745175\D1=198.35012048\D2=-41.23392949\D3=180.51639622\D4=-44.10389597\D5=-36.94524245\D6=79.39373685\D7=-163.70489381\D8=78.07526976\D9=-69.50772623\D10=172.45771803\D11=72.85381456\D12=-88.96517711  
 \Version=x86-Linux-G03RevB.04\HF=-323.3058643\S2=0.970715\S2-1=0.\S2A=0.758546\RM  
 SD=5.617e-09\RMSF=2.943e-06\Dipole=1.1049886,0.0134126,-1.5596852\PG=C01 [X(C5H8N  
 1O1)]\@

### MP2/6-311G\*\*

1\ CHEMISTRY CLUSTER KIRKLAND-KNET7\FTS\UMP2-FC\6-311G(d,p)\C5H8N1O1(2)\HIROSHI\12-May-2005\1\#MP2/6-311G\*\* OPT=(TS,EF,READFC,MAXCYCLE=100) NOS  
 YMM FREQ=NUMER GEOM=CHECK GUESS=READ\5-exo chantal another isomer of imine  
 \0,2\C\O,1,r1\C,1,r2,2,a1\C,3,r3,1,a2,2,d1,0\C,4,r4,3,a3,1,d2,0\C,1,r5,2,a4,3,d3,0\N,6,r6,1,a5,2,d  
 4,0\H,3,r7,1,a6,2,d5,0\H,3,r8,1,a7,2,d6,0\H,4,r9,3,a8,1,d7,0\H,4,r10,3,a9,1,d8,0\H,5,r11,4,a10,3,d  
 9,0\H,5,r12,4,a11,3,d10,0\H,6,r13,1,a12,2,d11,0\H,7,r14,6,a13,1,d12,0\vr1=1.17690439vr2=1.521  
 15961vr3=1.52594971vr4=1.53172228vr5=2.11753509vr6=1.29019807vr7=1.09455319vr8=1.0977  
 6543vr9=1.0930674vr10=1.09607867vr11=1.09775002vr12=1.09580937vr13=1.09781375vr14=1.0  
 2348543\A1=132.0933589\A2=106.68563048\A3=107.06979083\A4=127.06384349\A5=108.16657  
 949\A6=109.34118595\A7=105.79557511\A8=111.45974802\A9=109.48998583\A10=110.1237077  
 8\A11=110.84332066\A12=88.98952721\A13=108.38927251\D1=198.97897213\D2=-44.03160598  
 \D3=177.41537172\D4=-42.97336443\D5=-35.95430634\D6=80.90568606\D7=-166.3536483\D8=  
 74.68947641\D9=-67.77421151\D10=173.11964262\D11=74.10604287\D12=-90.51021157\Ver  
 sion=x86-Linux-G03RevB.04\HF=-323.3029617\MP2=-324.3620511\PUHF=-323.3208195\PMP  
 2-0=-324.377035\S2=0.948226\S2-1=0.882847\S2A=0.758261\RMSD=3.999e-09\RMSF=6.096  
 e-06\Dipole=1.4056047,0.1921539,-1.218439\PG=C01 [X(C5H8N1O1)]\@

### MP2/cc-pVDZ

1\ CHEMISTRY CLUSTER KIRKLAND-KNET7\FTS\UMP2-FC\CC-pVDZ\C5H8N1O1(2)\HIROSHI\14-May-2005\1\#MP2/CC-PVDZ OPT=(TS,EF,READFC,MAXCYCLE=100) NOS  
 YMM FREQ=NUMER GEOM=CHECK GUESS=READ\5-exo chantal another isomer of imine  
 \0,2\C\O,1,r1\C,1,r2,2,a1\C,3,r3,1,a2,2,d1,0\C,4,r4,3,a3,1,d2,0\C,1,r5,2,a4,3,d3,0\N,6,r6,1,a5,2,d  
 4,0\H,3,r7,1,a6,2,d5,0\H,3,r8,1,a7,2,d6,0\H,4,r9,3,a8,1,d7,0\H,4,r10,3,a9,1,d8,0\H,5,r11,4,a10,3,d  
 9,0\H,5,r12,4,a11,3,d10,0\H,6,r13,1,a12,2,d11,0\H,7,r14,6,a13,1,d12,0\vr1=1.18384118vr2=1.526  
 87255vr3=1.52814232vr4=1.53416531vr5=2.12248186vr6=1.29724176vr7=1.10297687vr8=1.1065  
 3493vr9=1.10164554vr10=1.10532062vr11=1.1065454vr12=1.10449456vr13=1.10677597vr14=1.0  
 3206031\A1=131.86535077\A2=106.61649394\A3=107.08653593\A4=127.43072447\A5=107.9255  
 3165\A6=109.515082\A7=105.70870611\A8=111.5790311\A9=109.50890029\A10=110.17764647\  
 A11=110.70737235\A12=89.01553259\A13=108.04155932\D1=199.4219903\D2=-44.33227978\D3=  
 177.57881188\D4=-43.14790201\D5=-35.2225122\D6=81.37284871\D7=-166.83483449\D8=74.  
 51446412\D9=-67.95751845\D10=173.3123518\D11=73.70167949\D12=-90.61334777\Ver  
 sion=x86-Linux-G03RevB.04\HF=-323.2487603\MP2=-324.2491222\PUHF=-323.2669476\PMP2-0  
 =-324.264432\S2=0.955457\S2-1=0.888789\S2A=0.758807\RMSD=4.753e-09\RMSF=7.875e-0  
 6\Dipole=1.3416348,0.1733236,-1.1718938\PG=C01 [X(C5H8N1O1)]\@

**MP2/aug-cc-pVDZ//MP2/cc-pVDZ**

MP2=-324.3148613

**QCISD/cc-pVDZ//MP2/cc-pVDZ**

QCISD=-324.3242623

**CCSD(T)/cc-pVDZ//MP2/cc-pVDZ**

CCSD(T)=-324.3597089

**BHandHLYP/6-311G\*\***

1\1\ CHEMISTRY CLUSTER KIRKLAND-KNET18\FTS\UBHandHLYP\6-311G(d,p)\C5H8N1O1(2)HIROSHI\12-May-2005\1\#\BHANDHLYP/6-311G\*\* OPT=(TS,EF,READFC,MAXCYCLE=100) NOSYMM FREQ=NORAMAN GEOM=CHECK GUESS=READ\5-exo chantalanoter isomer of imine\0,2\C\O,1,r1\C,1,r2,2,a1\C,3,r3,1,a2,2,d1,0\C,4,r4,3,a3,1,d2,0\C,1,r5,2,a4,3,d3,0\N,6,r6,1,a5,2,d4,0\H,3,r7,1,a6,2,d5,0\H,3,r8,1,a7,2,d6,0\H,4,r9,3,a8,1,d7,0\H,4,r10,3,a9,1,d8,0\H,5,r11,4,a10,3,d9,0\H,5,r12,4,a11,3,d10,0\H,6,r13,1,a12,2,d11,0\H,7,r14,6,a13,1,d12,0\vr1=1.16267689vr2=1.50542865vr3=1.52076854vr4=1.52607811vr5=2.13818813vr6=1.30024659vr7=1.08573654vr8=1.08945055vr9=1.08415864vr10=1.08753413vr11=1.08914901vr12=1.08711859vr13=1.08697326vr14=1.01404349va1=132.08794333va2=107.8416984va3=108.10965852va4=127.70121156va5=108.41774935va6=109.40782641va7=105.88510376va8=111.2489933va9=109.4578374va10=110.19254122va11=110.35491717va12=90.02782867va13=109.90366991vd1=197.37161517vd2=-41.8524342vd3=178.33290104vd4=-42.47898652vd5=-37.47488083vd6=78.49019165vd7=-164.4654179vd8=77.45884109vd9=-69.55125514vd10=172.31844936vd11=74.31848193vd12=-90.2841274\Version=x86-Linux-G03RevB.04\HF=-325.115921\S2=0.808811\S2-1=0.\S2A=0.750521\RMSD=7.170e-09\RMSF=2.549e-05\Dipole=1.2947856,0.0943015,-1.3935639\PG=C01 [X(C5H8N1O1)]\@

**BHandHLYP/cc-pVDZ**

1\1\ CHEMISTRY CLUSTER KIRKLAND-KNET18\FTS\UBHandHLYP\CC-pVDZ\C5H8N1O1(2)HIROSHI\12-May-2005\1\#\BHANDHLYP/CC-PVDZ OPT=(TS,EF,READFC,MAXCYCLE=100) NOSYMM FREQ=NORAMAN GEOM=CHECK GUESS=READ\5-exo chantalanother isomer of imine\0,2\C\O,1,r1\C,1,r2,2,a1\C,3,r3,1,a2,2,d1,0\C,4,r4,3,a3,1,d2,0\C,1,r5,2,a4,3,d3,0\N,6,r6,1,a5,2,d4,0\H,3,r7,1,a6,2,d5,0\H,3,r8,1,a7,2,d6,0\H,4,r9,3,a8,1,d7,0\H,4,r10,3,a9,1,d8,0\H,5,r11,4,a10,3,d9,0\H,5,r12,4,a11,3,d10,0\H,6,r13,1,a12,2,d11,0\H,7,r14,6,a13,1,d12,0\vr1=1.16843053vr2=1.50709431vr3=1.52025428vr4=1.52553966vr5=2.1452411vr6=1.30333953vr7=1.09350071vr8=1.09739008vr9=1.0920383vr10=1.09583503vr11=1.09704563vr12=1.09514066vr13=1.09548811vr14=1.02122222va1=131.77963035va2=107.81208227va3=108.10148214va4=128.20027274va5=108.41209652va6=109.55862137va7=105.70508523va8=111.33436791va9=109.43725424va10=110.22711436va11=110.31112846va12=89.79699142va13=109.35258285vd1=198.03966191vd2=-42.33179777vd3=178.6091175vd4=-42.84930366vd5=-36.53665585vd6=79.27884858vd7=-165.07952949vd8=76.98483779vd9=-69.36850916vd10=172.63605779vd11=73.79700486vd12=-90.40583545\Version=x86-Linux-G03RevB.04\HF=-325.051829\S2=0.811152\S2-1=0.\S2A=0.750544\RMSD=9.713e-09\RMSF=2.851e-05\Dipole=1.2372046,0.0850938,-1.3243816\PG=C01 [X(C5H8N1O1)]\@

**QCISD/cc-pVDZ//BHandHLYP/cc-pVDZ**

QCISD=-324.3228176

**CCSD(T)/cc-pVDZ//BHandHLYP/cc-pVDZ**

CCSD(T)=-324.35780

**B3LYP/6-311G\*\***

1\ CHEMISTRY CLUSTER KIRKLAND-KNET18\FTS\UB3LYP\6-311G(d,p)\C5H8N1O1(2)\HIROSHI\13-May-2005\1\#B3LYP/6-311G\*\* OPT=(TS,EF,READFC,MAXCYCLE=100) NOSYMM FREQ=NORAMAN GEOM=CHECK GUESS=READ\5-exo chantal another isomer of imine\0,2\C\O,1,r1\C,1,r2,2,a1\C,3,r3,1,a2,2,d1,0\C,4,r4,3,a3,1,d2,0\C,1,r5,2,a4,3,d3,0\N,6,r6,1,a5,2,d4,0\H,3,r7,1,a6,2,d5,0\H,3,r8,1,a7,2,d6,0\H,4,r9,3,a8,1,d7,0\H,4,r10,3,a9,1,d8,0\H,5,r11,4,a10,3,d9,0\H,5,r12,4,a11,3,d10,0\H,6,r13,1,a12,2,d11,0\H,7,r14,6,a13,1,d12,0\vr1=1.17521972vr2=1.51356742vr3=1.53119775vr4=1.53657586vr5=2.15404972vr6=1.30994389vr7=1.09391011vr8=1.09768276vr9=1.0917951vr10=1.09498886vr11=1.09686166vr12=1.09501318vr13=1.09610466vr14=1.02517142va1=132.17894828va2=107.97163904va3=108.16462549va4=127.53443227va5=109.04148286va6=109.4886763va7=105.84774369va8=111.18107505va9=109.38022374va10=110.24067983va11=110.25735117va12=89.79481395va13=109.51160346vd1=196.56995433vd2=-41.60778083vd3=177.23617159vd4=-41.46075884vd5=-38.07635819vd6=77.66009126vd7=-164.30820041vd8=77.76197826vd9=-70.21374353vd10=171.79122032vd11=75.11517851vd12=-90.41448433\Version=x86-Linux-G03RevB.04\HF=-325.3218267\S2=0.771322\S2-1=0.\S2A=0.750088\RMSD=6.761e-09\RMSF=2.790e-05\Dipole=1.3346548,0.1121686,-1.281008\PG=C01 [X(C5H8N1O1)]\@

**B3LYP/cc-pVDZ**

1\ CHEMISTRY CLUSTER KIRKLAND-KNET18\FTS\UB3LYP\CC-pVDZ\C5H8N1O1(2)\HIROSHI\13-May-2005\1\#B3LYP/CC-PVDZ OPT=(TS,EF,READFC,MAXCYCLE=100) NOSYMM FREQ=NORAMAN GEOM=CHECK GUESS=READ\5-exo chantal another isomer of imine\0,2\C\O,1,r1\C,1,r2,2,a1\C,3,r3,1,a2,2,d1,0\C,4,r4,3,a3,1,d2,0\C,1,r5,2,a4,3,d3,0\N,6,r6,1,a5,2,d4,0\H,3,r7,1,a6,2,d5,0\H,3,r8,1,a7,2,d6,0\H,4,r9,3,a8,1,d7,0\H,4,r10,3,a9,1,d8,0\H,5,r11,4,a10,3,d9,0\H,5,r12,4,a11,3,d10,0\H,6,r13,1,a12,2,d11,0\H,7,r14,6,a13,1,d12,0\vr1=1.1816389vr2=1.51589974vr3=1.53072362vr4=1.53594984vr5=2.16610827vr6=1.31269546vr7=1.10239048vr8=1.10642196vr9=1.10036184vr10=1.10407185vr11=1.10552048vr12=1.10381106vr13=1.10541186vr14=1.03312646va1=131.83557617va2=107.91521184va3=108.13246702va4=128.15040788va5=109.09493347va6=109.68212437va7=105.61206022va8=111.2553001va9=109.36461493va10=110.29994605va11=110.17139075va12=89.4034204va13=108.90579268vd1=197.2383901vd2=-42.30455191vd3=177.48534697vd4=-41.60283565vd5=-37.11502318vd6=78.49075141vd7=-165.1243633vd8=77.06133413vd9=-69.67266233vd10=172.45289182vd11=74.78392567vd12=-90.55341771\Version=x86-Linux-G03RevB.04\HF=-325.2492606\S2=0.772227\S2-1=0.\S2A=0.750092\RMSD=4.724e-09\RMSF=3.417e-05\Dipole=1.2716591,0.097143,-1.2003418\PG=C01 [X(C5H8N1O1)]\@

**QCISD/cc-pVDZ//B3LYP/cc-pVDZ**

QCISD=-324.3250534

CCSD(T)/cc-pVDZ//B3LYP/cc-pVDZ  
 CCSD(T)=-324.3604392

## Cyclopentanon-2-yl-aminyl radical (8)

### UHF/6-311G\*\*

1\ \ CHEMCLUSTER-KNET23\FOpt\UHF\6-311G(d,p)\C5H8N1O1(2)\HIROSHI\12-Aug-2004\1\ \#UHF/6-311G\*\* OPT=(Z-MATRIX,READFC,MAXCYCLE=100) NOSYMM FREQ=NO RAMAN GEOM=CHECK GUESS=READ\Ryu exo product\0,2\C\O,1,r1\C,1,r2,2,a1\C,3,r3,1,a2,2,d1,0\C,4,r4,3,a3,1,d2,0\C,1,r5,2,a4,3,d3,0\N,6,r6,1,a5,2,d4,0\H,3,r7,1,a6,2,d5,0\H,3,r8,1,a7,2,d6,0\H,4,r9,3,a8,1,d7,0\H,4,r10,3,a9,1,d8,0\H,5,r11,4,a10,3,d9,0\H,5,r12,4,a11,3,d10,0\H,6,r13,1,a12,2,d11,0\H,7,r14,6,a13,1,d12,0\ r1=1.18344142\ r2=1.51770117\ r3=1.53602421\ r4=1.53751994\ r5=1.53250242\ r6=1.43521384\ r7=1.08318991\ r8=1.08758032\ r9=1.08287434\ r10=1.08710149\ r11=1.08705872\ r12=1.08281452\ r13=1.09561449\ r14=1.01066218\ a1=126.85327911\ a2=104.78276724\ a3=104.22524123\ a4=124.34842397\ a5=114.35448212\ a6=111.01904285\ a7=107.00116111\ a8=112.7591111\ a9=109.97990496\ a10=110.48399117\ a11=113.29633373\ a12=105.14190135\ a13=106.81912912\ d1=185.76472877\ d2=-28.04852129\ d3=178.4559951\ d4=-35.16228263\ d5=-49.4404136\ d6=67.47172828\ d7=-150.66048968\ d8=89.59074254\ d9=-77.73960594\ d10=161.32793072\ d11=83.23070548\ d12=40.71055291\ \Version=x86-Linux-G03RevB.04\HF=-323.3499773\ S2=0.760578\ S2-1=0.\ S2A=0.750083\ RMSD=6.053e-09\ RMSF=7.947e-05\ Dipole=0.5177586,0.4424111,-0.959214\ PG=C01 [X(C5H8N1O1)]\ \@

### MP2/6-311G\*\*

1\ \ CHEMCLUSTER-KNET16\FOpt\UMP2-FC\6-311G(d,p)\C5H8N1O1(2)\HIROSHI\13-Aug-2004\1\ \#MP2/6-311G\*\* OPT=(Z-MATRIX,READFC,MAXCYCLE=100) NOSYMM FREQ=NORAMAN GEOM=CHECK GUESS=READ\Ryu exo product\0,2\C\O,1,r1\C,1,r2,2,a1\C,3,r3,1,a2,2,d1,0\C,4,r4,3,a3,1,d2,0\C,1,r5,2,a4,3,d3,0\N,6,r6,1,a5,2,d4,0\H,3,r7,1,a6,2,d5,0\H,3,r8,1,a7,2,d6,0\H,4,r9,3,a8,1,d7,0\H,4,r10,3,a9,1,d8,0\H,5,r11,4,a10,3,d9,0\H,5,r12,4,a11,3,d10,0\H,6,r13,1,a12,2,d11,0\H,7,r14,6,a13,1,d12,0\ r1=1.21098102\ r2=1.52290376\ r3=1.53563524\ r4=1.53938917\ r5=1.54574746\ r6=1.43621876\ r7=1.09273105\ r8=1.09785927\ r9=1.09228102\ r10=1.09620666\ r11=1.09634927\ r12=1.09228376\ r13=1.10793179\ r14=1.02786573\ a1=127.56558976\ a2=104.40327421\ a3=103.81446716\ a4=124.11206657\ a5=113.55463825\ a6=111.09751647\ a7=106.76223301\ a8=112.94134903\ a9=109.79761654\ a10=110.31611093\ a11=113.41033235\ a12=104.34425929\ a13=104.58486176\ d1=189.28554616\ d2=-31.56660909\ d3=178.42636875\ d4=-37.25944069\ d5=-45.29922286\ d6=71.97922196\ d7=-154.17510577\ d8=85.44527695\ d9=-74.66514485\ d10=163.6957633\ d11=81.07836675\ d12=43.08289159\ \Version=x86-Linux-G03RevB.04\HF=-323.3474422\ MP2=-324.4015559\ PUHF=-323.3509418\ PMP2-0=-324.4037857\ S2=0.761288\ S2-1=0.753054\ S2A=0.750098\ RMSD=5.146e-09\ RMSF=1.153e-05\ Dipole=0.5095838,0.4631839,-0.7509419\ PG=C01 [X(C5H8N1O1)]\ \@

### MP2/cc-pVDZ

1\ \ CHEMCLUSTER-KNET18\FOpt\UMP2-FC\CC-pVDZ\C5H8N1O1(2)\HIROSHI\13-Aug-2004\1\ \#MP2/CC-PVDZ OPT=(Z-MATRIX,READFC,MAXCYCLE=100) NOSYMM FREQ=NORAMAN GEOM=CHECK GUESS=READ\Ryu exo product\0,2\C\O,1,r1\C,1,r2,2,a1\C,3,r3,1,a2,2,d1,0\C,4,r4,3,a3,1,d2,0\C,1,r5,2,a4,3,d3,0\N,6,r6,1,a5,2,d4,0\H,3,r7,1,a6,2,d5,0\H,3,r8,1,

a7,2,d6,0\H,4,r9,3,a8,1,d7,0\H,4,r10,3,a9,1,d8,0\H,5,r11,4,a10,3,d9,0\H,5,r12,4,a11,3,d10,0\H,6,r13,1,a12,2,d11,0\H,7,r14,6,a13,1,d12,0\|r1=1.21724471|r2=1.52787735|r3=1.53859638|r4=1.54185363|r5=1.54806578|r6=1.44056473|r7=1.10123249|r8=1.1065801|r9=1.10089348|r10=1.10535668|r11=1.10534963|r12=1.10072753|r13=1.11679524|r14=1.0370782|a1=127.65849635|a2=104.35095028|a3=103.8226925|a4=124.06555857|a5=113.96529146|a6=111.43180517|a7=106.72083021|a8=113.1192536|a9=109.79865596|a10=110.37719629|a11=113.5321542|a12=104.52062115|a13=104.03951027|d1=188.36430318|d2=-31.54354211|d3=177.89239083|d4=-35.68471059|d5=-45.9498375|d6=71.0316418|d7=-154.48028039|d8=85.41057819|d9=-74.30453726|d10=164.27876396|d11=82.51479327|d12=40.18780577\\Version=x86-Linux-G03RevB.04\HF=-323.2927363\MP2=-324.2884601\PUHF=-323.2961869\PMP2-0=-324.2906578\S2=0.761017\S2-1=0.752976\S2A=0.750094\RMSD=8.092e-09\RMSF=8.793e-06\Dipole=0.5057118,0.423137,-0.7247183\PG=C01 [X(C5H8N1O1)]\@

### **MP2/aug-cc-pVDZ//MP2/cc-pVDZ**

MP2=-324.3528176

### **QCISD/cc-pVDZ//MP2/cc-pVDZ**

QCISD=-324.3556962

### **CCSD(T)/cc-pVDZ//MP2/cc-pVDZ**

CCSD(T)=-324.3889473

### **BHandHLYP/6-311G\*\***

1\ \ CHEMCLUSTER-KNET16\FOpt\UBHandHLYP\6-311G(d,p)\C5H8N1O1(2)\HIROSHI\13-Aug-2004\1\#\BHANDHLYP/6-311G\*\* OPT=(Z-MATRIX,READFC,MAXCYCLE=100) NO SYMM FREQ=NORAMAN GEOM=CHECK GUESS=READ\Ryu exo product\0,2\C\O,1,r1\C,1,r2,2,a1\C,3,r3,1,a2,2,d1,0\C,4,r4,3,a3,1,d2,0\C,1,r5,2,a4,3,d3,0\N,6,r6,1,a5,2,d4,0\H,3,r7,1,a6,2,d5,0\H,3,r8,1,a7,2,d6,0\H,4,r9,3,a8,1,d7,0\H,4,r10,3,a9,1,d8,0\H,5,r11,4,a10,3,d9,0\H,5,r12,4,a11,3,d10,0\H,6,r13,1,a12,2,d11,0\H,7,r14,6,a13,1,d12,0\|r1=1.1910651|r2=1.51207609|r3=1.52969532|r4=1.53279697|r5=1.53594065|r6=1.42347977|r7=1.0838031|r8=1.0889483|r9=1.08319183|r10=1.08739252|r11=1.08733408|r12=1.08315412|r13=1.09981227|r14=1.01837758|a1=127.32119286|a2=104.91876194|a3=104.32243277|a4=124.13630089|a5=114.13173129|a6=111.0831368|a7=106.75628412|a8=112.8384577|a9=109.88508753|a10=110.62730247|a11=113.26671506|a12=104.06974349|a13=106.02225725|d1=187.94951928|d2=-29.1421149|d3=178.55853385|d4=-36.73032029|d5=-46.67288172|d6=69.88571184|d7=-151.84271607|d8=88.50241029|d9=-77.89401198|d10=161.12512022|d11=81.06077992|d12=41.3942276\\Version=x86-Linux-G03RevB.04\HF=-325.1504128\S2=0.755167\S2-1=0.\S2A=0.75002\RMSD=3.554e-09\RMSF=5.882e-05\Dipole=0.5406099,0.4606348,-0.8906925\PG=C01 [X(C5H8N1O1)]\@

### **BHandHLYP/cc-pVDZ**

1\ \ CHEMCLUSTER-KNET18\FOpt\UBHandHLYP\CC-pVDZ\C5H8N1O1(2)\HIROSHI\13-Aug-2004\1\#\BHANDHLYP/CC-PVDZ OPT=(Z-MATRIX,READFC,MAXCYCLE=100) NO SYMM FREQ=NORAMAN GEOM=CHECK GUESS=READ\Ryu exo product\0,2\C\O,1,r1\C,1,r2,2,a1\C,3,r3,1,a2,2,d1,0\C,4,r4,3,a3,1,d2,0\C,1,r5,2,a4,3,d3,0\N,6,r6,1,a5,2,d4,0\H,3,r7,1,a6,2,d5,0\H,3,r8,1,a7,2,d6,0\H,4,r9,3,a8,1,d7,0\H,4,r10,3,a9,1,d8,0\H,5,r11,4,a10,3,d9,0\H,5,r12,4,a11,3,d10,0\H,6,r13,1,a12,2,d11,0\H,7,r14,6,a13,1,d12,0\|r1=1.19597534|r2=1.51368005|r3=1.52



984376\r4=1.53242818\r5=1.53466138\r6=1.42491103\r7=1.09162244\r8=1.09686452\r9=1.09122463\r10=1.09567564\r11=1.0955448\r12=1.09100968\r13=1.10772384\r14=1.02614072\|a1=127.3805532\|a2=104.81659678\|a3=104.30581253\|a4=124.07289572\|a5=114.48853326\|a6=111.31981203\|a7=106.63909521\|a8=112.97440234\|a9=109.83443394\|a10=110.61994107\|a11=113.35993247\|a12=104.01399882\|a13=105.43773011\|d1=187.35140034\|d2=-29.23704332\|d3=178.23521137\|d4=-35.38559878\|d5=-47.04440293\|d6=69.32858542\|d7=-152.19953915\|d8=88.259306\|d9=-77.36380014\|d10=161.71441031\|d11=82.2530997\|d12=38.76423162\|Version=x86-Linux-G03RevB.04\HF=-325.0870677\|S2=0.755021\|S2-1=0.\|S2A=0.750019\|RMSD=2.744e-09\|RMSF=5.093e-05\|Dipole=0.5276762,0.4155639,-0.8555422\|PG=C01 [X(C5H8N1O1)]\|@

### **BHandHLYP/aug-cc-pVDZ//BHandHLYP/cc-pVDZ**

HF=-325.1109304

### **QCISD/cc-pVDZ//BHandHLYP/cc-pVDZ**

QCISD=-324.3536345

### **CCSD(T)/cc-pVDZ//BHandHLYP/cc-pVDZ**

CCSD(T)=-324.3862521

### **B3LYP/6-311G\*\***

1\| CHEMCLUSTER-KNET16\FOpt\UB3LYP\6-311G(d,p)\C5H8N1O1(2)\HIROSHI\13-Aug-2004\1\|#B3LYP/6-311G\*\* OPT=(Z-MATRIX,READFC,MAXCYCLE=100) NOSYMM FREQ=NORAMAN GEOM=CHECK GUESS=READ\|Ryu exo product\|0,2\|C\O,1,r1\|C,1,r2,2,a1\|C,3,r3,1,a2,2,d1,0\|C,4,r4,3,a3,1,d2,0\|C,1,r5,2,a4,3,d3,0\|N,6,r6,1,a5,2,d4,0\|H,3,r7,1,a6,2,d5,0\|H,3,r8,1,a7,2,d6,0\|H,4,r9,3,a8,1,d7,0\|H,4,r10,3,a9,1,d8,0\|H,5,r11,4,a10,3,d9,0\|H,5,r12,4,a11,3,d10,0\|H,6,r13,1,a12,2,d11,0\|H,7,r14,6,a13,1,d12,0\|r1=1.20147298\r2=1.52293462\r3=1.53808032\r4=1.54307099\r5=1.56377761\r6=1.42558951\r7=1.09141586\r8=1.09725586\r9=1.09078326\r10=1.09489809\r11=1.09459868\r12=1.0908373\r13=1.10935209\r14=1.02919937\|a1=127.65819703\|a2=105.18598068\|a3=104.38979884\|a4=124.27721008\|a5=113.75760709\|a6=110.94982793\|a7=106.58323243\|a8=112.81877697\|a9=109.81715468\|a10=110.74073718\|a11=113.05440775\|a12=102.61137506\|a13=105.80827464\|d1=191.4167226\|d2=-30.46190678\|d3=179.27993845\|d4=-41.0423885\|d5=-42.81777869\|d6=73.49122563\|d7=-153.11708242\|d8=87.35630832\|d9=-78.55765185\|d10=160.59960659\|d11=77.03419138\|d12=48.2533047\|Version=x86-Linux-G03RevB.04\HF=-325.3447509\|S2=0.753719\|S2-1=0.\|S2A=0.750011\|RMSD=7.869e-09\|RMSF=5.308e-05\|Dipole=0.5391165,0.5098617,-0.8100616\|PG=C01 [X(C5H8N1O1)]\|@

### **B3LYP/cc-pVDZ**

1\| CHEMCLUSTER-KNET18\FOpt\UB3LYP\CC-pVDZ\C5H8N1O1(2)\HIROSHI\13-Aug-2004\1\|#B3LYP/CC-pVDZ OPT=(Z-MATRIX,READFC,MAXCYCLE=100) NOSYMM FREQ=NORAMAN GEOM=CHECK GUESS=READ\|Ryu exo product\|0,2\|C\O,1,r1\|C,1,r2,2,a1\|C,3,r3,1,a2,2,d1,0\|C,4,r4,3,a3,1,d2,0\|C,1,r5,2,a4,3,d3,0\|N,6,r6,1,a5,2,d4,0\|H,3,r7,1,a6,2,d5,0\|H,3,r8,1,a7,2,d6,0\|H,4,r9,3,a8,1,d7,0\|H,4,r10,3,a9,1,d8,0\|H,5,r11,4,a10,3,d9,0\|H,5,r12,4,a11,3,d10,0\|H,6,r13,1,a12,2,d11,0\|H,7,r14,6,a13,1,d12,0\|r1=1.20732222\r2=1.5249415\r3=1.53836247\r4=1.54270451\r5=1.56024666\r6=1.42833127\r7=1.09992323\r8=1.10598426\r9=1.09949397\r10=1.10398851\r11=1.1036164\r12=1.09935833\r13=1.11834988\r14=1.03793561\|a1=127.67797019\|a2=105.01594311\|a3=104.30701508\|a4=124.22910643\|a5=114.28681561\|a6=111.26786474\|a7=106

.44492275\A8=112.97036199\A9=109.76518163\A10=110.73165188\A11=113.15686648\A12=102.60220427\A13=105.09737598\D1=190.82091644\D2=-30.78429462\D3=178.90950907\D4=-39.30875262\D5=-43.15607215\D6=73.01645397\D7=-153.68862913\D8=86.84504884\D9=-77.71045284\D10=161.4666773\D11=78.53636884\D12=44.76235733\\Version=x86-Linux-G03RevB.04\HF=-325.2730075\S2=0.75363\S2-1=0.\S2A=0.75001\RMSD=4.123e-09\RMSF=5.415e-05\Dipole=0.5198238,0.4517465,-0.7747745\PG=C01 [X(C5H8N1O1)]\@

**B3LYP/aug-cc-pVDZ//B3LYP/cc-pVDZ**  
HF=-325.3014067

**QCISD/cc-pVDZ//B3LYP/cc-pVDZ**  
QCISD=-324.3554417

**CCSD(T)/cc-pVDZ//B3LYP/cc-pVDZ**  
CCSD(T)=-324.3885733