Supplementary Material

Unexpected dual orbital effects in radical addition reactions involving acyl, silyl and related radicals

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Ab Initio and DFT Calculations. Ab initio molecular orbital and DFT calculations were carried out on Dell PowerEdge 400SC and DACS XJ-3000 computers with the Gaussian 98[1] and the Gaussian 03[2] programs using standard computational methods[3] and basis sets. NBO[4] calculations were performed on Dell PowerEdge 400SC computers using the Gaussian 03 program. Geometries were optimised to saddle points or minima using standard gradient mimimization techniques. Further single-point calculations were carried out using ROMP2, QCISD and CCSD(T) methods.

References

1 Gaussian 98, Revision A.9, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.

2 Gaussian 03, Revision B.04, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2003.

3 W. J. Hehre, L. Radom, P. v. R. Schleyer and P. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986.

4 NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, and F. Weinhold.

Table S1 Calculated energy barriers[a] ($\Delta E_1^{\ddagger}$, $\Delta E_2^{\ddagger}$, Scheme 1) and transition state (imaginary) frequencies[b] for the reaction of acetyl radical with methanimine at various levels of theory.

Method	$\Delta E_1^{\ddagger}$	$\Delta E_1^{\ddagger}$ + ZPE	ν_1	$\Delta E_2^{\ddagger}$	$\Delta E_1^{\ddagger}$ + ZPE	ν_2
UHF/6-311G**	56.8	58.8	594i	37.7	41.0	449i
MP2/6-311G**	47.3	60.9	686i	54.0	61.9	516i
MP2/cc-pVDZ	48.0	61.8	731i	54.3	62.4	534i
MP2/aug-cc-pVDZ	33.0	47.7	574i	48.0	55.8	496i
BHLYP/6-311G**	22.6	29.0	550i	19.5	24.4	350i
BHLYP/cc-pVDZ	20.4	27.0	547i	17.1	22.4	361i
B3LYP/6-311G**	7.6	13.3	344i	11.8	17.0	274i
B3LYP/cc-pVDZ	4.9	10.5	342i	8.3	14.1	289i
ROMP2/cc-pVDZ // BHLYP/cc-pVDZ	28.8			18.3		
QCISD/6-311G**// MP2/6-311G**	40.1			30.6		
QCISD/cc-pVDZ// MP2/cc-pVDZ	39.8			30.4		
QCISD/cc-pVDZ// BHLYP/cc-pVDZ	33.0			26.1		
QCISD/aug-cc-pVDZ// MP2/aug-cc-pVDZ	28.8			23.9		
QCISD/cc-pVDZ// B3LYP/cc-pVDZ	26.1			26.0		
CCSD(T)/6-311G**// MP2/6-311G**	35.1			27.3		
CCSD(T)/cc-pVDZ// MP2/cc-pVDZ	35.3			27.0		
CCSD(T)/aug-cc-pVDZ// MP2/aug-cc-pVDZ	23.0			19.2		
CCSD(T)/cc-pVDZ// BHLYP/cc-pVDZ	27.2			21.9		
CCSD(T)/cc-pVDZ// B3LYP/cc-pVDZ	22.0			22.1		

[a]Energies in kJ mol^{-1}. [b]Frequencies in cm^{-1}.

Gaussian Archive entries for optimised transition states.

Reaction of acetyl radical with methanimine: Transition state 3

UHF/6-311G**

1\1\GINC-G98\FTS\UHF\6-311G(d,p)\C3H6N1O1(2)\MATSU\16-May-2005\1\\#HF/6-311G** SCF=DIRECT OPT=(TS,EF,READFC,MAXCYCLE=100) NOSYMM FREQ=NORAMAN GEOM=CHECK GUESS=READ\\TS for addition to nitrogen of imine\\0,2\C\O,1,r2\C,1,r3,2,a3\N,1,r4,2,a4,3,d4,0\C,4,r5,1,a5,2,d5,0\H,3,r6,1,a6,2,d6,0\H,3,r7,1,a7,2,d7,0\H,3,r8,1,a8,2,d8,0\H,4,r9,1,a9,2,d9,0\H,5,r10,4,a10,1,d10,0\H,5,r11,4,a11,1,d11,0\\r2=1.16272448\r3=1.50432095\a3=129.35241614\r4=1.99107933\a4=117.48896019\d4=153.86937645\r5=1.31934244\a5=112.69565994\d5=14.42361853\r6=1.08413671\a6=110.19837904\d6=226.44436699\r7=1.08325131\a7=107.91942949\d7=108.53710982\r8=1.08381492\a8=110.01783225\d8=348.17875565\r9=1.00418539\a9=100.15008563\d9=132.3898663\r10=1.07922969\a10=123.0037858\d10=104.24523152\r11=1.07556706\a11=118.44416796\d11=-69.30563997\\Version=x86-Linux-G98RevA.9\HF=-246.3744199\S2=1.005119\S2-1=0.\S2A=0.760217\RMSD=8.240e-09\RMSF=2.739e-06\Dipole=-0.1029741,0.3512542,-0.9306971\PG=C01 [X(C3H6N1O1)]\\@

MP2/6-311G**

1\1\ CHEMISTRY CLUSTER KIRKLAND-KNET5\FTS\UMP2-FC\6-311G(d,p)\C3H6N1O1(2)\HIROSHI\16-May-2005\1\\#MP2/6-311G** SCF=DIRECT OPT=(TS,EF,CALCHFFC,MAXCYCLE=100) NOSYMM FREQ=NORAMAN\\TS for addition to nitorgen of imine\\0,2\C\O,1,r2\C,1,r3,2,a3\N,1,r4,2,a4,3,d4,0\C,4,r5,1,a5,2,d5,0\H,3,r6,1,a6,2,d6,0\H,3,r7,1,a7,2,d7,0\H,3,r8,1,a8,2,d8,0\H,4,r9,1,a9,2,d9,0\H,5,r10,4,a10,1,d10,0\H,5,r11,4,a11,1,d11,0\\r2=1.2223954\r3=1.51801246\a3=124.65042078\r4=1.76588121\a4=109.24841904\d4=124.33673948\r5=1.25097908\a5=116.47411713\d5=7.63510449\r6=1.0927799\a6=111.71725127\d6=173.79797951\r7=1.09886014\a7=110.64005704\d7=51.47921365\r8=1.09269408\a8=107.9458183\d8=293.3479316\r9=1.0179727\a9=124.02108618\d9=173.41276736\r10=1.0881745\a10=123.70838963\d10=167.50178173\r11=1.09199551\a11=115.54893759\d11=-10.92919791\\Version=x86-Linux-G03RevB.04\HF=-246.3672269\MP2=-247.1570942\PUHF=-246.3750591\PMP2-0=-247.1635975\S2=0.831467\S2-1=0.803382\S2A=0.752174\RMSD=3.031e-09\RMSF=9.917e-05\Dipole=-0.8269389,-1.3467298,-1.0521902\PG=C01 [X(C3H6N1O1)]\\@

MP2/cc-pVDZ

1\1\ CHEMISTRY CLUSTER KIRKLAND-KNET9\FTS\UMP2-FC\CC-pVDZ\C3H6N1O1(2)\HIROSHI\16-May-2005\1\\#MP2/CC-PVDZ SCF=DIRECT OPT=(TS,EF,CALCHFFC,MAXCYCLE=100) NOSYMM FREQ=NORAMAN\\TS for addition to nitorogen of imine\\0,2\C\O,1,r2\C,1,r3,2,a3\N,1,r4,2,a4,3,d4,0\C,4,r5,1,a5,2,d5,0\H,3,r6,1,a6,2,d6,0\H,3,r7,1,a7,2,d7,0\H,3,r8,1,a8,2,d8,0\H,4,r9,1,a9,2,d9,0\H,5,r10,4,a10,1,d10,0\H,5,r11,4,a11,1,d11,0\\r2=1.22971492\r3=1.52184069\a3=124.9559357\r4=1.76251887\a4=109.43277767\d4=124.75672785\r5=1.25699425\a5=116.26457421\d5=8.17009989\r6=1.10188821\a6=111.79419295\d6=174.18269192\r7=1.10794769\a7=111.14775309\d7=51.67010068\r8=1.10177322\a8=108.05235965\d8=293.54129655\r9=1.02473851\a9=124.54114912\d9=173.960543\r10=1.09728868\a10=123.6325648\d10=167.6826281\r11=1.10153407\a11=115.29463436\d11=-10.83965775\\Version=x86-Linux-G03RevB.04\HF=-246.3225359\MP2=-247.0681638\PUHF=-246.3309082\PMP2-0=-247.0751458\S2=0.838922\S2-1=0.808896\S2A=0.752494\RMSD=4.402e-09\RMSF=6.043e-06\Dipole=-0.8266819,-1.3138347,-1.0366035\PG=C01 [X(C3H6N1O1)]\\@

MP2/aug-cc-pVDZ

1\1\ CHEMISTRY CLUSTER KIRKLAND-KNET7\FTS\UMP2-FC\Aug-CC-pVDZ\C3H6N1O1(2)\HIROSHI\16-May-2005\1\\#MP2/AUG-CC-PVDZ SCF=DIRECT OPT=(TS,EF,READFC,MAXCYCLE=100) NOSYMM FREQ=NORAMAN GEOM=CHECK GUESS=READ\\TS for addition to nitrogen of imine\\0,2\C\O,1,r2\C,1,r3,2,a3\N,1,r4,2,a4,3,d4,0\C,4,r5,1,a5,2,d5,0\H,3,r6,1,a6,2,d6,0\H,3,r7,1,a7,2,d7,0\H,3,r8,1,a8,2,d8,0\H,4,r9,1,a9,2,d9,0\H,5,r10,4,a10,1,d10,0\H,5,r11,4,a11,1,d11,0\\r2=1.23679937\r3=1.51894309\a3=124.89704457\r4=1.77683678\a4=108.42803376\d4=123.31952185\r5=1.25834625\a5=116.04294613\d5=5.75600067\r6=1.10068733\a6=111.45382641\d6=173.63806259\r7=1.10705157\a7=110.77987548\d7=51.35716318\r8=1.10021673\a8=107.9569032\d8=292.86390341\r9=1.02269959\a9=124.9339869\d9=176.0706696\r10=1.09520218\a10=123.1823142\d10=171.5444368\r11=1.10039664\a11=115.57928113\d11=-7.43791851\\Version=x86-Linux-G03RevB.04\HF=-246.3397303\MP2=-247.1254475\PUHF=-246.3465024\PMP2-0=-247.1310173\S2=0.8

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.1019471\PG=C01 [X(C3H6N1O1)]\\@

QCISD/6-311G//MP2/6-311G****
QCISD=-247.2056287

QCISD/cc-pVDZ//MP2/cc-pVDZ
QCISD=-247.1227516

QCISD/aug-cc-pVDZ//MP2/aug-cc-pVDZ
QCISD=-247.1761025

CCSD(T)/6-311G//MP2/6-311G****
CCSD(T)=-247.235539

CCSD(T)/cc-pVDZ//MP2/cc-pVDZ
CCSD(T)=-247.1475336

CCSD(T)/aug-cc-pVDZ//MP2/aug-cc-pVDZ
CCSD(T)=-247.2058905

BHLYP/6-311G**
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311G** SCF=DIRECT OPT=(TS,EF,READFC,MAXCYCLE=100) NOSYMM FREQ=NORAMAN GEOM=
CHECK GUESS=READ\\TS for addition to nitrogen of imine\\0,2\C\O,1,r2\C,1,r3,2,a3\N,1,r4,2,a4,3,d4,0\C,4,
r5,1,a5,2,d5,0\H,3,r6,1,a6,2,d6,0\H,3,r7,1,a7,2,d7,0\H,3,r8,1,a8,2,d8,0\H,4,r9,1,a9,2,d9,0\H,5,r10,4,a10,1,d10,0
\H,5,r11,4,a11,1,d11,0\\r2=1.1844393\r3=1.50279658\a3=127.07902466\r4=1.93996518\a4=110.16492649\d4
=128.7314157\r5=1.26866426\a5=117.11005553\d5=14.98049108\r6=1.08223045\a6=111.7176096\d6=171.0
3646425\r7=1.0877186\a7=110.38991611\d7=48.69630087\r8=1.08543862\a8=107.48414852\d8=290.744272
44\r9=1.00990387\a9=117.25080126\d9=157.155385\r10=1.08149978\a10=123.55255094\d10=144.16868789
\r11=1.08015449\a11=117.77956861\d11=-33.0204734\\Version=x86-Linux-G98RevA.9\HF=-247.7194693\S
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641071\PG=C01 [X(C3H6N1O1)]\\@

BHLYP/cc-pVDZ
1\1\GINC-G98\FTS\UBHandHLYP\CC-pVDZ\C3H6N1O1(2)\MATSU\16-May-2005\1\\#BHANDHLYP/C
C-PVDZ SCF=DIRECT OPT=(TS,EF,READFC,MAXCYCLE=100) NOSYMM FREQ=NORAMAN GEOM
=CHECK GUESS=READ\\TS for addition to imine\\0,2\C\O,1,r2\C,1,r3,2,a3\N,1,r4,2,a4,3,d4,0\C,4,r5,1,a5,2,
d5,0\H,3,r6,1,a6,2,d6,0\H,3,r7,1,a7,2,d7,0\H,3,r8,1,a8,2,d8,0\H,4,r9,1,a9,2,d9,0\H,5,r10,4,a10,1,d10,0\H,5,r11,
4,a11,1,d11,0\\r2=1.19127853\r3=1.50416665\a3=126.97283901\r4=1.93519003\a4=109.75647156\d4=127.70
590358\r5=1.27203886\a5=116.70844848\d5=15.36874282\r6=1.09345373\a6=107.4686894\d6=289.3863730
1\r7=1.09037183\a7=111.74687048\d7=169.86581515\r8=1.09603528\a8=110.68748987\d8=407.2242523\r9=
1.01615576\a9=118.91610565\d9=158.93726369\r10=1.08991785\a10=123.63343936\d10=146.47460454\r11
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6173\PG=C01 [X(C3H6N1O1)]\\@

QCISD/cc-pVDZ//BHLYP/cc-pVDZ
QCISD=-247.1230743

CCSD(T)/cc-pVDZ//BHLYP/cc-pVDZ
CCSD(T)=-247.1476174

B3LYP/6-311G**
1\1\GINC-G98\FTS\UB3LYP\6-311G(d,p)\C3H6N1O1(2)\MATSU\16-May-2005\1\\#B3LYP/6-311G** SCF
=DIRECT OPT=(TS,EF,READFC,MAXCYCLE=100) NOSYMM FREQ=NORAMAN GEOM=CHECK GU

ESS=READ\\TS for addition to nitrogen of imine\\0,2\C\O,1,r2\C,1,r3,2,a3\N,1,r4,2,a4,3,d4,0\C,4,r5,1,a5,2,d5,0\H,3,r6,1,a6,2,d6,0\H,3,r7,1,a7,2,d7,0\H,3,r8,1,a8,2,d8,0\H,4,r9,1,a9,2,d9,0\H,5,r10,4,a10,1,d10,0\H,5,r11,4,a11,1,d11,0\\r2=1.18973994\r3=1.5116179\a3=127.67460073\r4=2.0803567\a4=110.43615511\d4=128.70045169\r5=1.2798418\a5=117.91678051\d5=13.75418639\r6=1.09364249\a6=107.53092293\d6=287.40162858\r7=1.08869372\a7=111.50597494\d7=167.63532352\r8=1.09557007\a8=110.29972834\d8=405.36471708\r9=1.02069864\a9=113.7761805\d9=150.19934603\r10=1.09112958\a10=124.07147074\d10=137.10635428\r11=1.08849519\a11=118.15506106\d11=-40.10550414\\Version=x86-Linux-G98RevA.9\HF=-247.8820617\S2=0.758692\S2-1=0.\S2A=0.750032\RMSD=5.279e-09\RMSF=1.214e-05\Dipole=-0.4109617,-0.4071988,-0.9226147\PG=C01 [X(C3H6N1O1)]\\@

B3LYP/cc-pVDZ

1\1\GINC-G98\FTS\UB3LYP\CC-pVDZ\C3H6N1O1(2)\MATSU\16-May-2005\1\\#B3LYP/CC-PVDZ SCF=DIRECT OPT=(TS,EF,READFC,MAXCYCLE=100) NOSYMM FREQ=NORAMAN GEOM=CHECK GUESS=READ\\TS for addition to imine\\0,2\C\O,1,r2\C,1,r3,2,a3\N,1,r4,2,a4,3,d4,0\C,4,r5,1,a5,2,d5,0\H,3,r6,1,a6,2,d6,0\H,3,r7,1,a7,2,d7,0\H,3,r8,1,a8,2,d8,0\H,4,r9,1,a9,2,d9,0\H,5,r10,4,a10,1,d10,0\H,5,r11,4,a11,1,d11,0\\r2=1.19668012\r3=1.51356917\a3=127.55944593\r4=2.08453949\a4=109.87730008\d4=127.15983772\r5=1.2833721\a5=117.48123346\d5=14.41259712\r6=1.10249035\a6=107.50731768\d6=285.14526269\r7=1.09762508\a7=111.51758936\d7=165.62066784\r8=1.10471357\a8=110.62583126\d8=403.00702596\r9=1.02780598\a9=115.73652791\d9=152.06678391\r10=1.100473\a10=124.27504587\d10=139.46790952\r11=1.0984021\a11=117.82488834\d11=-37.64533789\\Version=x86-Linux-G98RevA.9\HF=-247.8215383\S2=0.758256\S2-1=0.\S2A=0.75003\RMSD=7.682e-09\RMSF=1.108e-05\Dipole=-0.3851384,-0.4517884,-0.9030972\PG=C01 [X(C3H6N1O1)]\\@

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

QCISD=-247.127663

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

CCSD(T)=-247.1519945

Reaction of aetyl radical with methanimine: Transition state 4

UHF/6-311G**

1\1\GINC-G98\FTS\UHF\6-311G(d,p)\C3H6N1O1(2)\MATSU\21-Apr-2005\1\\#HF/6-311G** SCF=DIRECT GEOM=CHECK GUESS=READ FREQ=NORAMAN OPT=(TS,EF,READFC,MAXCYCLE=100) NOSYMM\\TS for addition to cabon of imine\\0,2\C\O,1,r2\C,1,r3,2,a3\C,1,r4,2,a4,3,d4,0\N,4,r5,1,a5,2,d5,0\H,3,r6,1,a6,2,d6,0\H,3,r7,1,a7,2,d7,0\H,3,r8,1,a8,2,d8,0\H,4,r9,1,a9,2,d9,0\H,4,r10,1,a10,2,d10,0\H,5,r11,4,a11,1,d11,0\\r2=1.16086706\r3=1.50202992\a3=129.976605\r4=2.14857906\a4=116.537753\d4=182.54516533\r5=1.31771026\a5=108.18126326\d5=-158.2737564\r6=1.08359169\a6=108.73195823\d6=120.50444169\r7=1.08377009\a7=110.20395608\d7=-1.01687656\r8=1.08350992\a8=108.86013393\d8=237.15810943\r9=1.0810922\a9=91.87496212\d9=-32.65546159\r10=1.0793839\a10=90.69020189\d10=-277.14307782\r11=1.00680931\a11=109.88209891\d11=91.23378278\\Version=x86-Linux-G98RevA.9\HF=-246.3816669\S2=0.973617\S2-1=0.\S2A=0.758323\RMSD=8.024e-09\RMSF=3.228e-06\Dipole=0.283181,-0.2944516,-0.2479698\PG=C01 [X(C3H6N1O1)]\\@

MP2/6-311G**

1\1\GINC-G98\FTS\UMP2-FC\6-311G(d,p)\C3H6N1O1(2)\MATSU\22-Apr-2005\1\\#MP2/6-311G** SCF=DIRECT GEOM=CHECK GUESS=READ FREQ=NUMER OPT=(TS,EF,READFC,MAXCYCLE=100) NOSYMM\\TS for addition to cabon of imine\\0,2\C\O,1,r2\C,1,r3,2,a3\C,1,r4,2,a4,3,d4,0\N,4,r5,1,a5,2,d5,0\H,3,r6,1,a6,2,d6,0\H,3,r7,1,a7,2,d7,0\H,3,r8,1,a8,2,d8,0\H,4,r9,1,a9,2,d9,0\H,4,r10,1,a10,2,d10,0\H,5,r11,4,a11,1,d11,0\\r2=1.18111003\r3=1.50309489\a3=131.45982414\r4=2.13166497\a4=119.75682218\d4=183.24013393\r5=1.28615354\a5=108.72405836\d5=-164.7029938\r6=1.09134511\a6=107.80016669\d6=124.91375618\r7=1.09237913\a7=110.84180913\d7=2.08803791\r8=1.0920527\a8=107.72389969\d8=239.59038066\r9=1.09572494\a9=90.26567782\d9=-37.360563\r10=1.09293047\a10=86.602305\d10=-282.98980874\r11=1.02114453\a11=108.69865576\d11=93.09572409\\Version=x86-Linux-G98RevA.9\HF=-246.3781894\MP2=-247.1545547\PUHF=-246.3956153\PMP2-0=-247.169159\S2=0.942448\S2-1=0.878735\S2A=0.757242\RMSD=7.280e-09\RMSF=3.902e-06\Dipole=0.4975461,-0.2865186,0.234316\PG=C01 [X(C3H6N1O1)]\\@

MP2/cc-pVDZ
1\1\GINC-G98\FTS\UMP2-FC\CC-pVDZ\C3H6N1O1(2)\MATSU\22-Apr-2005\1\\#MP2/CC-PVDZ SCF=DIRECT GEOM=CHECK GUESS=READ FREQ=NUMER OPT=(TS,EF,READFC,MAXCYCLE=100) NOSYMM\\TS for addition to cabon of imine\\0,2\C\O,1,r2\C,1,r3,2,a3\C,1,r4,2,a4,3,d4,0\N,4,r5,1,a5,2,d5,0\H,3,r6,1,a6,2,d6,0\H,3,r7,1,a7,2,d7,0\H,3,r8,1,a8,2,d8,0\H,4,r9,1,a9,2,d9,0\H,4,r10,1,a10,2,d10,0\H,5,r11,4,a11,1,d11,0\\r2=1.18796031\r3=1.50889422\a3=131.17762424\r4=2.13375184\a4=120.28137948\d4=177.4863356\r5=1.29396884\a5=107.3134783\d5=-143.77745646\r6=1.09905647\a6=108.12726708\d6=140.62887079\r7=1.10111587\a7=110.96968319\d7=16.0442122\r8=1.10313367\a8=106.93560766\d8=256.00967193\r9=1.10458184\a9=89.95923733\d9=-16.63015596\r10=1.10247197\a10=88.58573889\d10=-262.40964056\r11=1.02997278\a11=108.22471889\d11=91.21777926\\Version=x86-Linux-G98RevA.9\HF=-246.3335915\MP2=-247.0657758\PUHF=-246.3513684\PMP2-0=-247.0807275\S2=0.949974\S2-1=0.884926\S2A=0.757877\RMSD=5.994e-09\RMSF=5.729e-06\Dipole=0.4588585,0.0458281,0.2505477\PG=C01 [X(C3H6N1O1)]\\@

MP2/aug-cc-pVDZ
1\1\GINC-G98\FTS\UMP2-FC\Aug-CC-pVDZ\C3H6N1O1(2)\MATSU\23-Apr-2005\1\\#MP2/AUG-CC-PVDZ SCF=DIRECT GEOM=CHECK GUESS=READ FREQ=NUMER OPT=(TS,EF,READFC,MAXCYCLE=100) NOSYMM\\TS for addition to cabon of imine\\0,2\C\O,1,r2\C,1,r3,2,a3\C,1,r4,2,a4,3,d4,0\N,4,r5,1,a5,2,d5,0\H,3,r6,1,a6,2,d6,0\H,3,r7,1,a7,2,d7,0\H,3,r8,1,a8,2,d8,0\H,4,r9,1,a9,2,d9,0\H,4,r10,1,a10,2,d10,0\H,5,r11,4,a11,1,d11,0\\r2=1.19183019\r3=1.50489801\a3=131.67387934\r4=2.134144\a4=119.05566832\d4=182.94596047\r5=1.29363532\a5=108.96860819\d5=-174.55922877\r6=1.10057515\a6=107.23755289\d6=116.77443322\r7=1.09967308\a7=110.91031136\d7=-5.05206995\r8=1.099176\a8=107.80443064\d8=231.28541428\r9=1.10258593\a9=89.85371916\d9=-47.75246704\r10=1.09961704\a10=86.36123532\d10=-292.8044455\r11=1.02649239\a11=109.74458103\d11=93.09654793\\Version=x86-Linux-G98RevA.9\HF=-246.3506427\MP2=-247.1197374\PUHF=-246.3679952\PMP2-0=-247.1342893\S2=0.943345\S2-1=0.879465\S2A=0.757678\RMSD=5.877e-09\RMSF=1.575e-06\Dipole=0.5743364,-0.4223146,0.1463729\PG=C01 [X(C3H6N1O1)]\\@

QCISD/6-311G//MP2/6-311G****
QCISD=-247.209226

QCISD/cc-pVDZ//MP2/cc-pVDZ
QCISD=-247.1263378

QCISD/aug-cc-pVDZ//MP2/aug-cc-pVDZ
QCISD=-247.1779781

CCSD(T)/6-311G//MP2/6-311G****
CCSD(T)=-247.23850

CCSD(T)/cc-pVDZ//MP2/cc-pVDZ
CCSD(T)=-247.1506932

CCSD(T)/aug-cc-pVDZ//MP2/aug-cc-pVDZ
CCSD(T)=-247.2073063

BHLYP/6-311G**
1\1\GINC-G98\FTS\UBHandHLYP\6-311G(d,p)\C3H6N1O1(2)\MATSU\21-Apr-2005\1\\#BHANDHLYP/6-311G** SCF=DIRECT GEOM=CHECK GUESS=READ FREQ=NORAMAN OPT=(TS,EF,READFC,MAXCYCLE=100) NOSYMM\\TS for addition to cabon of imine\\0,2\C\O,1,r2\C,1,r3,2,a3\C,1,r4,2,a4,3,d4,0\N,4,r5,1,a5,2,d5,0\H,3,r6,1,a6,2,d6,0\H,3,r7,1,a7,2,d7,0\H,3,r8,1,a8,2,d8,0\H,4,r9,1,a9,2,d9,0\H,4,r10,1,a10,2,d10,0\H,5,r11,4,a11,1,d11,0\\r2=1.16570981\r3=1.49058539\a3=131.17169585\r4=2.1800781\a4=118.16678356\d4=183.77220328\r5=1.2939813\a5=108.51084118\d5=-174.24055356\r6=1.08571215\a6=107.84729545\d6=113.23532703\r7=1.0846204\a7=110.84490113\d7=-7.75792777\r8=1.08331455\a8=108.82569282\d8=228.72363381\r9=1.08567909\a9=91.02361607\d9=-47.47867371\r10=1.08256335\a10=86.9906222\d10=-292.59509488\r11=1.0123742\a11=110.06381241\d11=93.29174639\\Version=x86-Linux-G98RevA.9\HF=-247.7206422\S2

=0.804131\S2-1=0.\S2A=0.750461\RMSD=3.925e-09\RMSF=7.974e-06\Dipole=0.462098,-0.4630837,-0.0975713\PG=C01 [X(C3H6N1O1)]\\@

BHLYP/cc-pVDZ

1\1\GINC-G98\FTS\UBHandHLYP\CC-pVDZ\C3H6N1O1(2)\MATSU\21-Apr-2005\1\\#BHANDHLYP/CC-PVDZ SCF=DIRECT GEOM=CHECK GUESS=READ FREQ=NORAMAN OPT=(TS,EF,READFC,MAXCYCLE=100) NOSYMM\\TS for addition to cabon of imine\\0,2\C\O,1,r2\C,1,r3,2,a3\C,1,r4,2,a4,3,d4,0\N,4,r5,1,a5,2,d5,0\H,3,r6,1,a6,2,d6,0\H,3,r7,1,a7,2,d7,0\H,3,r8,1,a8,2,d8,0\H,4,r9,1,a9,2,d9,0\H,4,r10,1,a10,2,d10,0\H,5,r11,4,a11,1,d11,0\\r2=1.17158271\r3=1.49315637\a3=130.8299989\r4=2.18738489\a4=119.15398514\d4=174.29940843\r5=1.29750226\a5=106.24786847\d5=-137.82066987\r6=1.09069828\a6=108.77224258\d6=139.86368632\r7=1.092665\a7=110.88346651\d7=15.75031607\r8=1.09467112\a8=107.48022484\d8=255.8305536\9\r9=1.09352969\a9=90.06983068\d9=-11.5860006\r10=1.09186353\a10=89.90263229\d10=-256.62488074\r11=1.01964757\a11=109.45610198\d11=90.62494756\\Version=x86-Linux-G98RevA.9\HF=-247.6674124\S2=0.805596\S2-1=0.\S2A=0.75048\RMSD=7.735e-09\RMSF=1.683e-05\Dipole=0.3836943,0.0530261,-0.0032674\PG=C01 [X(C3H6N1O1)]\\@

QCISD/cc-pVDZ//BHLYP/cc-pVDZ

QCISD=-247.125692

CCSD(T)/cc-pVDZ//BHLYP/cc-pVDZ

CCSD(T)-247.1496267

B3LYP/6-311G**

1\1\GINC-G98\FTS\UB3LYP\6-311G(d,p)\C3H6N1O1(2)\MATSU\22-Apr-2005\1\\#B3LYP/6-311G** SCF=DIRECT GEOM=CHECK GUESS=READ FREQ=NORAMAN OPT=(TS,EF,READFC,MAXCYCLE=100) NOSYMM\\TS for addition to cabon of imine\\0,2\C\O,1,r2\C,1,r3,2,a3\C,1,r4,2,a4,3,d4,0\N,4,r5,1,a5,2,d5,0\H,3,r6,1,a6,2,d6,0\H,3,r7,1,a7,2,d7,0\H,3,r8,1,a8,2,d8,0\H,4,r9,1,a9,2,d9,0\H,4,r10,1,a10,2,d10,0\H,5,r11,4,a11,1,d11,0\\r2=1.17820024\r3=1.49786992\a3=131.2341849\r4=2.21032552\a4=118.92590494\d4=184.84783179\r5=1.30308591\a5=108.78987117\d5=-179.77002595\r6=1.09471765\a6=107.42283609\d6=104.2043824\r7=1.0924779\a7=111.08159203\d7=-15.84991132\r8=1.09074479\a8=108.96020812\d8=219.67780031\r9=1.09516455\a9=91.24335966\d9=-52.34558962\r10=1.09120544\a10=86.24036358\d10=-297.75464875\r11=1.02315539\a11=109.76072909\d11=93.97160611\\Version=x86-Linux-G98RevA.9\HF=-247.8804593\S2=0.768963\S2-1=0.\S2A=0.750077\RMSD=8.210e-09\RMSF=9.244e-06\Dipole=0.527476,-0.5270567,-0.0477872\PG=C01 [X(C3H6N1O1)]\\@

B3LYP/cc-pVDZ

1\1\GINC-G98\FTS\UB3LYP\CC-pVDZ\C3H6N1O1(2)\MATSU\22-Apr-2005\1\\#B3LYP/CC-PVDZ SCF=DIRECT GEOM=CHECK GUESS=READ FREQ=NORAMAN OPT=(TS,EF,READFC,MAXCYCLE=100) NOSYMM\\TS for addition to cabon of imine\\0,2\C\O,1,r2\C,1,r3,2,a3\C,1,r4,2,a4,3,d4,0\N,4,r5,1,a5,2,d5,0\H,3,r6,1,a6,2,d6,0\H,3,r7,1,a7,2,d7,0\H,3,r8,1,a8,2,d8,0\H,4,r9,1,a9,2,d9,0\H,4,r10,1,a10,2,d10,0\H,5,r11,4,a11,1,d11,0\\r2=1.18479732\r3=1.50135765\a3=130.85739089\r4=2.2214376\a4=119.75075915\d4=169.45946175\r5=1.30652748\a5=105.58347571\d5=-133.09686503\r6=1.09966078\a6=108.44117548\d6=140.65928421\r7=1.10144641\a7=111.22067272\d7=16.37253661\r8=1.10348959\a8=107.48744057\d8=256.47614076\r9=1.10359478\a9=90.23711895\d9=-6.3759065\r10=1.10114657\a10=89.96206115\d10=-251.66784345\r11=1.03108807\a11=109.15349827\d11=90.58972576\\Version=x86-Linux-G98RevA.9\HF=-247.8202464\S2=0.769184\S2-1=0.\S2A=0.750077\RMSD=2.437e-09\RMSF=3.724e-05\Dipole=0.4137521,0.1267083,0.0556882\PG=C01 [X(C3H6N1O1)]\\@

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

QCISD=-247.1277132

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

CCSD(T)=-247.1519435

Reaction of silyl radical with formaldehyde: Transition state 6

BHandHLYP/6-311G**

1\1\CHEMISTRY CLUSTER KIRKLAND-KNET13\FTS\UBHandHLYP\6-311G(d,p)\C1H5O1Si1(2)\UWIL
LE\16-Mar-2005\1\\#BHANDHLYP/6-311G** SCF=(QC,DIRECT) OPT=(TS,EF,Z-MATRIX,READFC,
MAXCYCLE=100) GEOM=CHECKPOINT GUESS=CHECK\\Formaldehyde – SiH3 Transition state\\0,2\C\
O,1,r1\Si,2,r2,1,a1\H,1,r3,2,a2,3,d1,0\H,1,r4,2,a3,3,d2,0\H,3,r5,2,a4,1,d3,0\H,3,r6,2,a5,1,d4,0\H,3,r7,2,a6,1,d5,
0\\r1=1.22449131\r2=2.19687836\r3=1.08959798\r4=1.08829226\r5=1.49133414\r6=1.47041939\r7=1.477371
3\a1=131.45196005\a2=121.35540054\a3=120.59892903\a4=143.92115007\a5=89.8356462\a6=92.45872785\
d1=311.93725674\d2=128.93374265\d3=78.0393882\d4=158.46425313\d5=47.17342113\\Version=x86-Linu
x-G03RevB.04\State=2-A\HF=-405.6922289\S2=0.775453\S2-1=0.\S2A=0.750105\RMSD=2.222e-09\RMSF
=2.916e-05\Dipole=-0.1792275,-0.0932345,-1.06404\PG=C01 [X(C1H5O1Si1)]\\@

BHandHLYP/cc-pVDZ

1\1\ CHEMISTRY CLUSTER KIRKLAND-KNET13\FTS\UBHandHLYP\CC-pVDZ\C1H5O1Si1(2)\UWIL
LE\08-Mar-2005\1\\#BHANDHLYP/CC-PVDZ SCF=TIGHT OPT=(TS,EF,Z-MATRIX,CALCFC,MAX
CYCLE=100)\\Formaldehyde – SiH3 Transition state\\0,2\C\O,1,r1\Si,2,r2,1,a1\H,1,r3,2,a2,3,d1,0\H,1,r4,2,a3,
3,d2,0\H,3,r5,2,a4,1,d3,0\H,3,r6,2,a5,1,d4,0\H,3,r7,2,a6,1,d5,0\\r1=1.22811791\r2=2.19489244\r3=1.0983957\r
4=1.0972914\r5=1.50356368\r6=1.48127531\r7=1.48818521\a1=131.06075366\a2=121.4590529\a3=120.5479
2987\a4=144.5535309\a5=89.60361276\a6=92.4062282\d1=312.64859203\d2=129.47099304\d3=-77.7715630
9\d4=158.84216521\d5=47.83616056\\Version=x86-Linux-G03RevB.04\State=2-A\HF=-405.6576697\S2=0.7
76468\S2-1=0.\S2A=0.750116\RMSD=3.694e-09\RMSF=3.628e-05\Dipole=-0.2093609,-0.0598939,-1.02811
25\PG=C01 [X(C1H5O1Si1)]\\@

BHandHLYP/aug-cc-pVDZ

1\1\ CHEMISTRY CLUSTER KIRKLAND-KNET18\FTS\UBHandHLYP\Aug-CC-pVDZ\C1H5O1Si1(2)\U
WILLE\08-Mar-2005\1\\#BHANDHLYP/AUG-CC-PVDZ SCF=(QC,DIRECT) OPT=(TS,EF,Z-MATRIX,
READFC,MAXCYCLE=100) GEOM=CHECKPOINT GUESS=CHECK\\Formaldehyde – SiH3 Transition
state\\0,2\C\O,1,r1\Si,2,r2,1,a1\H,1,r3,2,a2,3,d1,0\H,1,r4,2,a3,3,d2,0\H,3,r5,2,a4,1,d3,0\H,3,r6,2,a5,1,d4,0\H,3,r
7,2,a6,1,d5,0\\r1=1.22778762\r2=2.23246792\r3=1.09526315\r4=1.09403069\r5=1.4999964\r6=1.47983749\r7
=1.48644197\a1=129.67280131\a2=121.11706839\a3=120.65579935\a4=143.44128023\a5=89.94649093\a6=9
1.9929288\d1=310.52833578\d2=127.62308413\d3=-80.24634185\d4=155.89286304\d5=44.49605746\\ Versi
on=x86-Linux-G03RevB.04\State=2-A\HF=-405.6677824\S2=0.775678\S2-1=0.\S2A=0.750121\RMSD=0.00
e+00\RMSF=1.866e-05\Dipole=-0.1795944,-0.0514929,-0.9962081\PG=C01 [X(C1H5O1Si1)]\\@

BHandHLYP/cc-pVTZ

1\1\ CHEMISTRY CLUSTER KIRKLAND-KNET13\FTS\UBHandHLYP\CC-pVTZ\C1H5O1Si1(2)\UWIL
LE\09-Mar-2005\1\\#BHANDHLYP/CC-PVTZ SCF=VERYTIGHT OPT=(TS,EF,Z-MATRIX,READFC,
MAXCYCLE=100) GEOM=CHECKPOINT GUESS=CHECK\\Formaldehyde – SiH3 Transition state\\
0,2\C\O,1,r1\Si,2,r2,1,a1\H,1,r3,2,a2,3,d1,0\H,1,r4,2,a3,3,d2,0\H,3,r5,2,a4,1,d3,0\H,3,r6,2,a5,1,d4,0\H,3,r7,2,a
6,1,d5,0\\r1=1.21929696\r2=2.19118659\r3=1.08750037\r4=1.08630006\r5=1.49299888\r6=1.47045682\r7=1.
47750415\a1=130.14255819\a2=121.25575014\a3=120.65064199\a4=147.68038049\a5=88.67529329\a6=90.5
0738652\d1=316.99150399\d2=134.18208636\d3=-81.65949726\d4=154.35954432\d5=42.96690953\\Versio
n=x86-Linux-G03RevB.04\State=2-A\HF=-405.7111652\S2=0.772914\S2-1=0.\S2A=0.750109\RMSD=9.26
8e-09\RMSF=1.725e-05\Dipole=-0.2736079,-0.0516992,-1.1020217\PG=C01 [X(C1H5O1Si1)]\\@

Reaction of silyl radical with methanimine: Transition state 9

BHandHLYP/6-311G**

1\1\ CHEMISTRY CLUSTER KIRKLAND-KNET13\FTS\UBHandHLYP\6-311G(d,p)\C1H6N1Si1(2)\UWIL
LE\30-Mar-2005\1\\#BHANDHLYP/6-311G** SCF=(QC,DIRECT) OPT=(TS,EF,Z-MATRIX,READFC,
MAXCYCLE=100) GEOM=CHECKPOINT GUESS=CHECK\\Imin – SiH3 transition state\\0,2\C\N,1,r1\
Si,2,r2,1,a1\H,1,r3,2,a2,3,d1,0\H,1,r4,2,a3,3,d2,0\H,3,r5,2,a4,1,d3,0\H,3,r6,2,a5,1,d4,0\H,3,r7,2,a6,1,d5,0\H,3,r
8,2,a7,1,d6,0\\r1=1.26420036\r2=2.31491671\r3=1.08281317\r4=1.08085071\r5=1.01075777\r6=1.47996299\r

7=1.47718983\r8=1.50149415\a1=127.05860528\a2=123.59416914\a3=118.69360091\a4=113.4930=95117\a5=85.86827529\a6=88.35409727\a7=155.87771384\d1=210.32482049\d2=29.16656039\d3=-210.2295263\d4=--35.95389342\d5=213.09102175\d6=84.04169687\\Version=x86-Linux-G03RevB.04\State=2-A\HF=-385.8286304\S2=0.763192\S21=0.\S2A=0.750054\RMSD=0.000e+00\RMSF=1.190e-05\Dipole=-1.1665428,0.3499591,-1.166931\PG=C01 [X(C1H6N1Si1)]\\@

Reaction of silyl radical with ethylene: Transition state 10

BHandHLYP/6-311G**

1\1\ CHEMISTRY CLUSTER KIRKLAND-KNET14\FTS\UBHandHLYP\6-311G(d,p)\C2H7Si1(2)\UWILLE\20-Apr-2005\1\\#BHANDHLYP/6-311G** SCF=TIGHT OPT=(TS,EF,CALCFC,Z-MATRIX,MAXCYCLE=100)\\ Transition state silyl radical addition to ethene\\0,2\C\Si,1,r1\C,1,r2,2,a1\H,2,r3,1,a2,3,d1,0\H,2,r4,1,a3,4,d2,0\H,2,r5,1,a4,4,d3,0\H,1,r6,3,a5,2,d4,0\H,1,r7,3,a6,2,d5,0\H,3,r8,1,a7,2,d6,0\H,3,r9,1,a8,2,d7,0\\r1=2.6796\r2=1.3445\r3=1.4848\r4=1.4766\r5=1.4768\r6=1.0763\r7=1.0763\r8=1.0764\r9=1.0764\a1=99.9583\a2=132.5892\a3=97.0166\a4=97.1001\a5=121.0537\a6=121.0505\a7=121.4685\a8=121.469\d1=180.0198\d2=124.431\d3=-124.5786\d4=97.8212\d5=-97.8023\d6=88.329\d7=-88.411\\Version=x86-Linux-G03RevB.04\State=2-A\HF=-369.7833004\S2=0.794042\S2-1=0.\S2A=0.750218\RMSD=2.706e-09\RMSF=4.726e-05\Dipole=-0.0168435,0.000352,-0.452439\Polar=55.2235785,0.0050864,45.4724266,-15.4099149,0.0095759,69.7543347\PG=C01 [X(C2H7Si1)]\\@

5-*endo* Cyclization of silyl radical to alkyne: Transition state 11

BHandHLYP/6-311G**

1\1\ CHEMISTRY CLUSTER KIRKLAND-KNET14\FTS\UBHandHLYP\6-311G(d,p)\C3H5O1Si1(2)\UWILLE\17-May-2005\1\\#BHANDHLY/6-311G** SCF=VERYTIGHT OPT=(TS,NOEIGENTEST,Z-MATRIX,READFC,MAXCYCLE=100) GEOM=CHECKPOINT GUESS=CHECK\\ Transition state 5-endo cyclization with SiH2\\0,2\C,1.0860338507,-0.4918368019,-0.8710930127\C,1.4314972805,0.2839539002,0.3246477978\C,0.9836100405,0.8342662648,1.3101681808\Si,-1.3004870352,0.1108764691,0.1834738318\O,-0.3043897582,-0.7357369863,-0.841749883\H,-1.7784592776,1.3693254969,-0.4334353753\H,-2.4395988917,-0.7864081768,0.4614885786\H,1.6086834452,-1.4419770291,-0.8889442459\H,1.3490799396,0.0574639035,-1.7712418704\H,0.8953843125,1.3769209499,2.2151605362\\Version=x86-Linux-G03RevB.04\State=2-A\HF=-481.8616307\S2=0.786532\S2-1=0.\S2A=0.750274\RMSD=9.747e-09\RMSF=2.718e-05\Dipole=0.3479653,0.2787703,0.3141821\PG=C01 [X(C3H5O1Si1)]\\@