

SUPPLEMENTARY INFORMATION

A Comparison of the Reactivities of Phosphonyl and Acyl Radicals towards Double Bonds

Elizabeth H. Krenske^{*a,b,‡} and Carl H. Schiesser^{a,c,d}

^aAustralian Research Council Centre of Excellence for Free Radical Chemistry and Biotechnology

^bResearch School of Chemistry, The Australian National University, Canberra ACT 0200 Australia

^cSchool of Chemistry, The University of Melbourne, Victoria, Australia 3010

^dBio21 Molecular Science and Biotechnology Institute, The University of Melbourne, Victoria, Australia 3010

[‡]*Current address:* Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095, USA.

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Table S1 BHandHLYP/6-311G** geometries of reactants, complexes, transition states, and products

H₂P(=O)•

```
1\1\GINC-AC1\FOpt\UBHandHLYP\6-311G(d,p)\H2O1P1(2)\EXK501\23-Apr-2007\
0\#\ BHANDHLYP/6-311G** OPT FREQ=NORAMAN MAXDISK=134217728\H2P=Orad_C
s_BHLYP_6-311Gss\0,2\O,0.0738240411,1.063061687,0.\P,0.0480410698,-0.
4360857518,0.\H,-0.6556041882,-0.98160361,1.094142587\H,-0.6556041882,
-0.98160361,-1.094142587\Version=IA64L-G03RevC.02\State=2-A'\HF=-417.
7110972\S2=0.761479\S2-1=0.\S2A=0.750032\RMSD=7.195e-09\RMSF=1.014e-04
\Dipole=-0.2367646,-1.2421766,0.\PG=CS [SG(O1P1),X(H2)]\@
```

HC(=O)•

```
1\1\GINC-AC1\FOpt\UBHandHLYP\6-311G(d,p)\C1H1O1(2)\EXK501\23-Apr-2007\
0\#\ BHANDHLYP/6-311G** OPT FREQ=NORAMAN MAXDISK=134217728\HCOrad_Cs_
BHLYP_6-311Gss\0,2\H,-0.8580143164,1.2116266859,0.\C,0.0590326535,0.5
767342079,0.\O,0.0629772994,-0.5840039917,0.\Version=IA64L-G03RevC.02
\State=2-A'\HF=-113.8220685\S2=0.755232\S2-1=0.\S2A=0.750017\RMSD=6.36
5e-09\RMSF=5.256e-05\Dipole=-0.3888622,0.5817856,0.\PG=CS [SG(C1H1O1)]
\@
```

CH₂=CH₂

```
1\1\GINC-AC56\FOpt\RBHandHLYP\6-311G(d,p)\C2H4\EXK501\23-Apr-2007\0\#\
BHANDHLYP/6-311G** OPT FREQ=NORAMAN MAXDISK=134217728\ethylene_D2h_B
HLYP_6-311Gss\0,1\C,0.,0.,0.6587492069\C,0.,0.,-0.6587492069\H,0.,0.9
166871426,1.2247939729\H,0.,-0.9166871426,1.2247939729\H,0.,0.91668714
26,-1.2247939729\H,0.,-0.9166871426,-1.2247939729\Version=IA64L-G03Re
vC.02\State=1-AG\HF=-78.5547476\RMSD=5.170e-09\RMSF=5.355e-05\Dipole=0
.,0.,0.\PG=D02H [C2"(C1.C1),SG(H4)]\@
```

CH₂=CH(OMe)

```
1\1\ HOUK_PENTIUM-N17\POpt\RBHandHLYP\6-311G(d,p)\C3H6O1\KRENSKE\01-Se
p-2007\1\#\ BHANDHLYP/6-311G** OPT=(Z-MATRIX) FREQ=NORAMAN\MeO-CH=CH2
_a1_BHLYP_6-311Gss_sym\0,1\C\H,1,hc2\H,1,hc3,2,hch3\C,1,cc4,3,cch4,2,
dih4,0\H,4,hc5,1,hcc5,2,dih5,0\O,4,oc6,1,occ6,2,dih6,0\C,6,co7,4,coc7,
1,dih7,0\H,7,hc8,6,hco8,4,dih8,0\H,7,hc8,6,hco8,4,-dih8,0\H,7,hc10,6,h
co10,4,dih10,0\hc2=1.07387922\hc3=1.07379904\hch3=117.54805519\cc4=1.
32304675\cch4=118.79353532\hc5=1.07669498\hcc5=121.66431491\oc6=1.3411
5636\occ6=128.27423196\co7=1.40433403\coc7=117.35110741\hc8=1.08814215
\hco8=110.85917681\hc10=1.08036796\hco10=106.89119282\dih4=-180.\dih5=
-180.\dih6=0.\dih7=0.\dih8=-60.\dih10=-180.\Version=IA32L-G03RevC.02\
State=1-A'\HF=-193.0488273\RMSD=5.337e-09\RMSF=8.923e-04\Dipole=0.0044
096,0.,0.3836855\PG=CS [SG(C3H4O1),X(H2)]\@
```

CH₂=CH(NH₂)

```
1\1\GINC-AC59\FOpt\RBHandHLYP\6-311G(d,p)\C2H5N1\EXK501\05-May-2007\0\
\# BHANDHLYP/6-311G** OPT FREQ=NORAMAN MAXDISK=134217728\enamine_BHLYP_6-311Gss_a1\0,1\H,2.1533257729,0.3748638477,-0.0053165692\C,1.24148
28769,-0.1917723899,0.0093244632\C,0.0686615134,0.4248088078,-0.003237
6079\H,1.3212406997,-1.2665592453,0.0132234212\H,0.0301084209,1.503089
2644,-0.0123145228\N,-1.1786491779,-0.1700360362,-0.0776806296\H,-1.19
76566561,-1.1483013096,0.1359249642\H,-1.9173403334,0.3289411885,0.375
7259821\Version=IA64L-G03RevC.02\State=1-A\HF=-133.8973483\RMSD=5.661
e-09\RMSF=3.457e-06\Dipole=-0.4812462,0.0047001,0.404557\PG=C01 [X(C2H
5N1)]\@
```

CH₂=CH(CN)

```
1\1\GINC-N84\FOpt\RBHandHLYP\6-311G(d,p)\C3H3N1\KRENSKE\30-Aug-2007\0\
\# BHANDHLYP/6-311G** OPT FREQ=NORAMAN\acrylonitrile_Cs_BHLYP_6-311Gs
s\0,1\C,-0.0000129205,0.7710337839,0.\H,-0.6971174448,1.5913719521,0.
\C,1.306975826,0.9733308349,0.\H,2.0055194409,0.1553385788,0.\H,1.7062
99455,1.9718049508,0.\C,-0.577125409,-0.5335616332,0.\N,-1.0562466329,
-1.5690476279,0.\Version=IA32L-G03RevC.02\State=1-A'\HF=-170.7688313\
RMSD=3.980e-09\RMSF=7.302e-05\Dipole=0.8076861,1.3698521,0.\PG=CS [SG(
C3H3N1)]\@
```

CH₂=NH

```
1\1\GINC-AC1\FOpt\RBHandHLYP\6-311G(d,p)\C1H3N1\EXK501\23-Apr-2007\0\
\# BHANDHLYP/6-311G** OPT FREQ=NORAMAN MAXDISK=134217728\CH2=NH_Cs_BHLYP_6-311Gss\0,1\N,0.053088978,-0.6763810497,0.\C,0.0578135727,0.57774
80704,0.\H,1.0075231348,1.0996835825,0.\H,-0.8322426724,1.2034337408,0.
.\H,-0.8937847444,-1.0349383979,0.\Version=IA64L-G03RevC.02\State=1-A
'\HF=-94.5934707\RMSD=8.524e-09\RMSF=3.946e-05\Dipole=-0.5659271,0.577
5777,0.\PG=CS [SG(C1H3N1)]\@
```

Complex: H₂P(=O)• + CH₂=CH₂

```
1\1\GINC-AC49\FOpt\UBHandHLYP\6-311G(d,p)\C2H6O1P1(2)\EXK501\21-May-20
07\0\# BHANDHLYP/6-311G** OPT FREQ=NORAMAN MAXDISK=134217728\Comp_Pa
dduct-ethylene_BHLYP_6-311Gss\0,2\O,-2.2376326374,-1.2826178201,0.\P,
-0.9107377242,-0.5829019235,0.\C,1.5337423839,1.7862128734,0.\C,2.4331
258193,0.8204348962,0.\H,-0.0958967679,-0.933839364,1.0950741186\H,-0.
0958967679,-0.933839364,-1.0950741186\H,1.1531979688,2.2059267745,0.91
63406147\H,1.1531979688,2.2059267745,-0.9163406147\H,2.823157671,0.410
2049874,0.9168104271\H,2.823157671,0.4102049874,-0.9168104271\Version
=IA64L-G03RevC.02\State=2-A'\HF=-496.2692321\S2=0.761566\S2-1=0.\S2A=0
.750036\RMSD=7.621e-09\RMSF=7.123e-06\Dipole=1.34429,0.5118363,0.\PG=C
S [SG(C2O1P1),X(H6)]\@
```

Complex: $\text{H}_2\text{P(=O)}\cdot + \text{CH}_2=\text{CH(OMe)}$

```
1\1\ HOUK_DUAL-N35\FOpt\UBHandHLYP\6-311G(d,p)\C3H8O2P1(2)\KRENSKE\02-
Sep-2007\0\#\ BHANDHLYP\6-311G** OPT FREQ=NORAMAN\Comp_Padduct-MeO-CH
=CH2_BHLYP_6-311Gss_start\0,2\C,1.3596945566,-1.557390229,0.418911706
\C,0.0497463045,-1.7205671123,0.444718215\P,0.6253195443,1.7915626198,
0.1814942396\O,0.5025630972,3.2656132808,-0.0748019755\H,0.0463820021,
1.3923509178,1.4040658947\H,-0.074764119,1.0021547253,-0.7495824949\H,
1.935216415,-1.6985740153,1.3140723786\H,1.8720891999,-1.3013403931,-0
.4911939756\H,-0.4750285866,-2.0019534665,1.3471630819\O,-0.7266943809
,-1.5114041141,-0.6351272246\C,-2.0353332979,-2.0281739716,-0.56237062
79\H,-2.5512702011,-1.6986892281,-1.4531068388\H,-2.0255141576,-3.1148
590183,-0.5353410437\H,-2.5584988262,-1.6494142748,0.313387245\Version=
AM64L-G03RevC.02\State=2-A\HF=-610.7616898\S2=0.761271\S2-1=0.\S2A=0
.750033\RMSD=3.503e-09\RMSF=8.021e-06\Dipole=-0.7427542,-1.8422336,0.4
714022\PG=C01 [X(C3H8O2P1)]\@
```

Complex: $\text{H}_2\text{P(=O)}\cdot + \text{CH}_2=\text{CH(NH}_2\text{)}$ (with hydrogen-bonding)

```
1\1\GINC-AC52\FOpt\UBHandHLYP\6-311G(d,p)\C2H7N1O1P1(2)\EXK501\09-Jun-
2007\0\#\ BHANDHLYP\6-311G** OPT FREQ=NORAMAN MAXDISK=134217728\Comp_
Padduct-enamine_BHLYP_6-311Gss_start\0,2\H,-0.4791561226,-1.358251233
,1.1169727454\P,-0.0246522022,-0.3173047395,1.9483887295\O,0.745773784
4,0.7344584528,1.2072137622\H,-1.2162005496,0.168698718,2.5254408519\C
,0.0451836481,-1.2387652259,-1.7445341387\C,-0.4886339165,-0.056256208
,-2.0394162756\H,-0.3498875939,-2.1357648222,-2.1832434214\H,0.9178621
214,-1.3247012602,-1.1192885958\N,-0.0407452967,1.1749890482,-1.625433
5669\H,-1.3367066447,-0.0121918814,-2.7061389295\H,-0.7181429956,1.909
0894476,-1.6359354642\H,0.5317432298,1.1822297681,-0.7996107727\Versi
on=IA64L-G03RevC.02\State=2-A\HF=-551.6172505\S2=0.760064\S2-1=0.\S2A=
0.750028\RMSD=7.473e-09\RMSF=1.088e-05\Dipole=-1.1029512,-0.3396574,0.
832406\PG=C01 [X(C2H7N1O1P1)]\@
```

Complex: $\text{H}_2\text{P(=O)}\cdot + \text{CH}_2=\text{CH(NH}_2\text{)}$ (without hydrogen-bonding)

```
1\1\GINC-AC47\FOpt\UBHandHLYP\6-311G(d,p)\C2H7N1O1P1(2)\EXK501\17-May-
2007\0\#\ BHANDHLYP\6-311G** OPT FREQ=NORAMAN MAXDISK=134217728\Comp_
Padduct-enamine_BHLYP_6-311Gss_alb2\0,2\H,-1.22361597,1.3477846423,-0
.1154604141\P,0.1393245263,1.4443850204,0.23332663\O,0.4882648551,2.74
57817001,0.895925342\H,0.3058128061,0.3299790801,1.0777866502\C,0.0823
827963,-1.3441310619,-1.5794665337\C,-0.6293541013,-1.8675759208,-0.58
80904772\H,1.1587245351,-1.3057485108,-1.552233184\H,-0.4064848956,-0.
9645873215,-2.4565868571\N,-0.1396830946,-2.329292614,0.6173156547\H,-
1.705432292,-1.8980417409,-0.6574910007\H,-0.7011702808,-3.0112658785,
1.0850349392\H,0.8357888527,-2.5548589824,0.6357801642\Version=IA64L-
G03RevC.02\State=2-A\HF=-551.6146887\S2=0.761321\S2-1=0.\S2A=0.750039\
RMSD=8.589e-09\RMSF=1.482e-05\Dipole=-0.4878406,-2.0662632,-0.19828\PG
=C01 [X(C2H7N1O1P1)]\@
```

Complex: $\text{H}_2\text{P(=O)}^\bullet + \text{CH}_2=\text{CH(CN)}$

```
1\1\ HOUK_PENTIUM-N9\FOpt\UBHandHLYP\6-311G(d,p)\C3H5N1O1P1(2)\KRENSKE
\05-Sep-2007\0\#\ BHANDHLYP/6-311G** OPT FREQ=NORAMAN\Comp_Padduct-ac
rylonitrile_BHLYP_6-311Gss_a1\0,2\C,1.0518178307,-1.7124733257,0.4366
035877\C,-0.2403666449,-2.0014081554,0.4108604532\C,-1.0001527505,-2.0
149696808,-0.7963684496\N,-1.6229697316,-2.0159921715,-1.7524164778\P,
0.3854672788,1.718634504,0.391049805\O,0.6342446817,3.1975593327,0.383
1644215\H,-0.3679984912,1.2872538362,1.5027154512\H,-0.4070480604,1.27
56033817,-0.6872057321\H,1.5944323607,-1.7103772036,1.365125201\H,1.59
92615071,-1.4823463304,-0.460497886\H,-0.7816164416,-2.2450737334,1.30
91423162\Version=IA32L-G03RevC.02\State=2-A\HF=-588.481019\S2=0.76189
4\S2-1=0.\S2A=0.750041\RMSD=3.879e-09\RMSF=1.229e-04\Dipole=0.55152,-1
.2269464,1.1897807\PG=C01 [X(C3H5N1O1P1)]\@
```

Complex: $\text{HC(=O)}^\bullet + \text{CH}_2=\text{CH}_2$

```
1\1\GINC-AC52\FOpt\UBHandHLYP\6-311G(d,p)\C3H5O1(2)\EXK501\10-Jun-2007
\0\#\ BHANDHLYP/6-311G** OPT FREQ=NORAMAN MAXDISK=134217728\Comp_HCOa
dduct-ethylene_a2_BHLYP_6-311Gss_5\0,2\O,-2.6322972636,-0.7854076741,
0.\C,-1.9330536299,0.1431257894,0.\C,2.0947521453,0.9919052949,0.\C,2.
087696551,-0.3270683716,0.\H,2.101555243,1.557974073,0.9167179764\H,2.
101555243,1.557974073,-0.9167179764\H,2.0894497863,-0.8932468234,0.916
6925666\H,2.0894497863,-0.8932468234,-0.9166925666\H,-0.8200023485,0.1
060306168,0.\Version=IA64L-G03RevC.02\State=2-A'\HF=-192.3787414\S2=0
.755138\S2-1=0.\S2A=0.750016\RMSD=5.586e-09\RMSF=2.414e-06\Dipole=0.82
26382,0.2490938,0.\PG=CS [SG(C3H1O1),X(H4)]\@
```

Complex: $\text{HC(=O)}^\bullet + \text{CH}_2=\text{CH(OMe)}$

```
1\1\ HOUK_PENTIUM-N18\FOpt\UBHandHLYP\6-311G(d,p)\C4H7O2(2)\KRENSKE\03
-Sep-2007\0\#\ BHANDHLYP/6-311G** OPT FREQ=NORAMAN\Comp_HCOadduct-MeO
-CH=CH2_BHLYP_6-311Gss_start\0,2\C,-0.2005983787,0.314617009,-2.66492
15527\O,-0.0796649602,1.3781734893,-2.2099013544\C,-1.2176405286,-1.08
71142382,0.6197582218\C,0.0122322806,-1.3046810511,1.0633386031\O,0.93
45112542,-0.4071243261,1.4259444531\C,0.5806018605,0.9550915225,1.3551
65176\H,-0.3217084405,-0.6179745038,-2.0702387014\H,-1.8394561683,-1.9
308903232,0.3850201538\H,-1.6411328287,-0.1068646065,0.5037071789\H,0.
4002258879,-2.3029120473,1.1785203047\H,0.3411823626,1.2451769297,0.33
61010855\H,-0.2679602747,1.1674404073,2.0012524159\H,1.4425077063,1.51
01513857,1.6972500841\Version=IA32L-G03RevC.02\State=2-A\HF=-306.8748
362\S2=0.755118\S2-1=0.\S2A=0.750016\RMSD=7.881e-09\RMSF=1.527e-05\Dip
ole=-0.2248662,-0.3412269,0.1437131\PG=C01 [X(C4H7O2)]\@
```

Complex: $\text{HC(=O)}^\bullet + \text{CH}_2=\text{CH(NH}_2\text{)}$

```
1\1\GINC-AC9\FOpt\UBHandHLYP\6-311G(d,p)\C3H6N1O1(2)\EXK501\18-May-200
7\0\#\ BHANDHLYP/6-311G** OPT FREQ=NORAMAN MAXDISK=134217728\Comp_HCO
adduct_enamine_BHLYP_6-311Gss_start\0,2\C,0.2203489913,0.6412004139,-
1.9050846966\O,1.2507181276,0.7892764149,-1.3832095284\H,-0.6678501281
,1.2951288017,-1.7754658965\C,-1.3179569461,-1.0329377725,0.2963522906
\H,-0.7389909468,-1.6596166291,-0.3612212295\H,-2.3876069519,-1.075440
3769,0.2110308688\C,-0.7509741886,-0.27905075,1.2328772593\H,-1.372950
0885,0.3082313984,1.8908343236\N,0.5931348678,-0.1912693474,1.51916311
71\H,1.2121284203,-0.4890814707,0.7901027613\H,0.8890734599,0.67018104
07,1.9313844602\Version=IA64L-G03RevC.02\State=2-A\HF=-247.7242771\S2
=0.755229\S2-1=0.\S2A=0.750017\RMSD=3.923e-09\RMSF=1.650e-05\Dipole=-0
.2811383,0.6959258,0.0114985\PG=C01 [X(C3H6N1O1)]\@
```

TS: $\text{H}_2\text{P(=O)}\cdot + \text{CH}_2=\text{CH}_2$

```
1\1\GINC-AC1\FTS\UBHandHLYP\6-311G(d,p)\C2H6O1P1(2)\EXK501\23-Apr-2007
\0\0\# BHANDHLYP/6-311G** OPT=(TS,CALCFC,NOEIGENTEST,MAXCYC=200) FREQ=N
ORAMAN MAXDISK=134217728\TS_Padduct-ethylene_BHLYP_6-311Gss\0,2\O,0.
9631774507,1.9639112313,0.\P,0.0054733055,0.8252143576,0.\C,0.26862165
08,-1.6418891302,0.\C,-1.0272671948,-2.0342907537,0.\H,-0.8869400977,0
.8013836414,1.0913566364\H,-0.8869400977,0.8013836414,-1.0913566364\H,
0.8413511131,-1.6446984049,0.9115718475\H,0.8413511131,-1.6446984049,-
0.9115718475\H,-1.572233977,-2.1728981919,0.9177967604\H,-1.572233977,
-2.1728981919,-0.9177967604\Version=IA64L-G03RevC.02\State=2-A'\HF=-4
96.2616543\S2=0.811969\S2-1=0.\S2A=0.750939\RMSD=4.927e-09\RMSF=5.473e
-06\Dipole=-0.9308934,-1.303159,0.\PG=CS [SG(C2O1P1),X(H6)]\@
Imaginary frequency = -304.5i cm-1
```

TS: $\text{H}_2\text{P(=O)}\cdot + \text{CH}_2=\text{CH(OMe)}$

```
1\1\GINC-N93\FTS\UBHandHLYP\6-311G(d,p)\C3H8O2P1(2)\KRENSKE\31-Aug-200
7\0\0\# BHANDHLYP/6-311G** OPT=(TS,CALCFC,NOEIGENTEST,MAXCYC=200) FREQ=
NORAMAN\TS_Padduct-MeO-CH=CH2_BHLYP_6-311Gss_a2b3\0,2\C,-0.439123884
5,-0.5837721352,1.0806440455\C,-1.2900820467,0.4621954271,0.8824959225
\O,-2.1034534401,0.6498254081,-0.1594406864\C,-2.2650965048,-0.4064751
133,-1.0794067685\P,1.591994187,0.1616615701,-0.032789261\O,2.89088273
76,-0.4527047082,-0.4263699621\H,0.8721360857,0.7402148787,-1.10296083
04\H,1.7043255584,1.2815035636,0.8215145229\H,-0.546746073,-1.50568955
25,0.5399889089\H,0.0170681389,-0.6637570527,2.0502955908\H,-1.3050609
264,1.3134269154,1.5397910803\H,-2.6595176393,-1.2920386584,-0.5883248
867\H,-2.9709502275,-0.0574292386,-1.8188136865\H,-1.3247874857,-0.649
8090778,-1.5655657926\Version=IA32L-G03RevC.02\State=2-A'\HF=-610.7554
718\S2=0.802356\S2-1=0.\S2A=0.75069\RMSD=4.785e-09\RMSF=6.471e-06\Dipo
le=-1.8269554,0.1292788,0.310617\PG=C01 [X(C3H8O2P1)]\@
Imaginary frequency = -317.7i cm-1
```

TS: $\text{H}_2\text{P(=O)}\cdot + \text{CH}_2=\text{CH(NH}_2\text{)}$ (with hydrogen-bonding)

```
1\1\GINC-AC27\FTS\UBHandHLYP\6-311G(d,p)\C2H7N1O1P1(2)\EXK501\03-May-2
007\0\0\# BHANDHLYP/6-311G** OPT=(TS,CALCFC,NOEIGENTEST,MAXCYC=200) FRE
Q=NORAMAN MAXDISK=134217728\TS_Padduct-enamine_BHLYP_6-311Gss_start\0,2\H,-1.3350814437,0.4434411004,1.5704504028\P,-1.3722996684,0.248388
2025,0.1685033546\O,-1.0943105727,-1.1543099132,-0.2736975447\H,-2.716
9568866,0.6481609533,-0.0890501947\C,0.7726244499,1.2149568662,-0.4610
46962\C,1.6064203105,0.3988016297,0.2526491769\H,0.7478320971,2.263175
3226,-0.2257330925\H,0.5198037412,0.9470219047,-1.4718397528\N,1.79023
71546,-0.9162222813,-0.0298185323\H,2.1121678876,0.7738379175,1.127517
4891\H,2.1985555231,-1.4726768521,0.6928483424\H,1.0067300444,-1.36329
90846,-0.4830467177\Version=IA64L-G03RevC.02\State=2-A'\HF=-551.609019
7\S2=0.785631\S2-1=0.\S2A=0.750303\RMSD=9.772e-09\RMSF=1.008e-05\Dipol
e=0.6206099,0.9293726,0.6639413\PG=C01 [X(C2H7N1O1P1)]\@
Imaginary frequency = -302.7i cm-1
```

TS: $\text{H}_2\text{P}(=\text{O})\cdot + \text{CH}_2=\text{CH}(\text{NH}_2)$ (without hydrogen-bonding)

```
1\1\GINC-AC23\FTS\UBHandHLYP\6-311G(d,p)\C2H7N1O1P1(2)\EXK501\04-May-2
007\0\#\ BHANDHLYP/6-311G** OPT=(TS,CALCFC,NOEIGENTEST,MAXCYC=200) FRE
Q=NORAMAN MAXDISK=134217728\TS_Padduct-enamine_BHLYP_6-311Gss_alb2\0
,2\H,1.5338864339,1.0054119724,0.0763580501\P,0.1367584898,1.224413620
8,0.1180183462\O,-0.2547963239,2.6294821825,0.4352785317\H,-0.21447298
68,0.812733241,-1.1870324315\C,-0.256465988,-1.0796426007,0.9090885407
\C,0.367214357,-1.79418743,-0.0671542918\H,-1.3302831399,-0.9983252786
,0.919999585\H,0.2354222879,-0.9640590092,1.8562321499\N,-0.1994352473
,-2.1417961371,-1.2637580404\H,1.4187692367,-2.0135056664,0.0106441189
\H,0.2725729902,-2.8220011606,-1.8208976069\H,-1.1973450612,-2.1867627
264,-1.3131065232\Version=IA64L-G03RevC.02\State=2-A\HF=-551.6088791\
S2=0.800934\S2-1=0.\S2A=0.750687\RMSD=6.195e-09\RMSF=6.458e-06\Dipole=
0.238808,-2.6419284,-0.7081688\PG=C01 [X(C2H7N1O1P1)]\@\@
Imaginary frequency = -273.7i cm-1
```

TS: $\text{H}_2\text{P}(=\text{O})\cdot + \text{CH}_2=\text{CH}(\text{CN})$

```
1\1\GINC-N85\FTS\UBHandHLYP\6-311G(d,p)\C3H5N1O1P1(2)\KRENSKE\30-Aug-2
007\0\#\ BHANDHLYP/6-311G** OPT=(TS,CALCFC,NOEIGENTEST,MAXCYC=200) FRE
Q=NORAMAN\TS_Padduct-acrylonitrile_BHLYP_6-311Gss_alb1\0,2\H,-0.7523
079024,-1.4255330128,-0.1030985834\P,-1.5015847259,-0.2665707594,0.176
1250416\O,-2.9238357068,-0.3109698073,-0.2555884726\H,-1.3035439565,-0
.1023474247,1.5613234483\C,0.4718860584,1.2921097575,-0.4539832895\H,0
.4285374672,0.9634591756,-1.4767092222\C,1.4331483893,0.8377492639,0.3
821688982\H,-0.0838826987,2.1766420575,-0.2021813601\H,1.5594615221,1.
2552261132,1.3660817302\C,2.2915507198,-0.2356837815,0.0418713487\N,2.
9838115867,-1.1065969284,-0.2232750857\Version=IA32L-G03RevC.02\State
=2-A\HF=-588.4765854\S2=0.820811\S2-1=0.\S2A=0.751929\RMSD=1.727e-09\R
MSF=4.906e-06\Dipole=0.2396422,1.1094821,0.6330895\PG=C01 [X(C3H5N1O1P
1)]\@\@
Imaginary frequency = -241.6i cm-1
```

TS: $\text{H}_2\text{P}(=\text{O})\cdot + \text{CH}_2=\text{NH}$ (via N)

```
1\1\GINC-AC35\FTS\UBHandHLYP\6-311G(d,p)\C1H5N1O1P1(2)\EXK501\24-Apr-2
007\0\#\ BHANDHLYP/6-311G** OPT=(TS,CALCFC,NOEIGENTEST,MAXCYC=200) FRE
Q=NORAMAN MAXDISK=134217728\TS_Padduct-CH2=NH_Nattack_BHLYP_6-311Gss\
\0,2\N,1.3449757057,0.4566402784,-0.1809733588\P,-0.7988682214,0.18009
62217,0.1831275943\O,-2.0325317075,-0.4828635633,-0.3273780967\H,-0.44
23017185,-0.2145462489,1.4857095452\H,-0.895518198,1.578297417,0.30386
29361\C,2.2517907678,-0.4318491778,0.0309565483\H,1.413226265,0.860911
0775,-1.1047378329\H,2.2714859137,-0.9349271684,0.985213727\H,2.970810
1714,-0.7336567795,-0.7168632943\Version=IA64L-G03RevC.02\State=2-A\H
F=-512.3026066\S2=0.799099\S2-1=0.\S2A=0.750603\RMSD=3.123e-09\RMSF=8.
467e-05\Dipole=1.9487592,0.3792212,0.1015592\PG=C01 [X(C1H5N1O1P1)]\@\@
Imaginary frequency = -359.3i cm-1
```

TS: HC(=O)• + CH₂=CH₂

1\1\GINC-AC1\FTS\UBHandHLYP\6-311G(d,p)\C3H5O1(2)\EXK501\23-Apr-2007\0
\\# BHANDHLYP/6-311G** OPT=(TS,CALCFC,NOEIGENTEST,MAXCYC=200) FREQ=NOR
AMAN MAXDISK=134217728\\TS_HCOadduct-ethylene_a2_BHLYP_6-311Gss\\0,2\H
, -1.3408373216, 0.8544364853, -0.7567691365\C, -0.7124207905, 0.8216288073
, 0.1538930233\O, -0.1366908387, 1.7217351216, 0.6243766867\C, 0.127167839,
-1.1560116894, 0.2870533326\C, 0.6976075454, -1.2583080363, -0.9373748597\
H, -0.7978588838, -1.6637472589, 0.5019899449\H, 0.710747398, -0.8607371023
, 1.1417293362\H, 0.1671224757, -1.6834125082, -1.7721912528\H, 1.680225477
9, -0.8642750783, -1.1312013628\\Version=IA64L-G03RevC.02\State=2-A\HF=-
192.3665664\S2=0.809037\S2-1=0.\S2A=0.750689\RMSD=8.371e-09\RMSF=4.760
e-06\Dipole=-0.3533737, -0.5293349, -0.4149955\PG=C01 [X(C3H5O1)]\\@
Imaginary frequency = -556.2i cm⁻¹

TS: HC(=O)• + CH₂=CH(OMe)

1\1\GINC-N91\FTS\UBHandHLYP\6-311G(d,p)\C4H7O2(2)\KRENSKE\01-Sep-2007\
0\\# BHANDHLYP/6-311G** OPT=(TS,CALCFC,NOEIGENTEST,MAXCYC=200) FREQ=NO
RAMAN\\TS_HCOadduct-MeO-CH=CH2_BHLYP_6-311Gss_a2b2\\0,2\O, -0.142351781
9, 0.911323551, -1.9256961372\C, -0.563093375, -0.1770219052, -1.7713742278
\H, -0.154135331, -1.0841007761, -2.2599662191\C, -1.1114544597, -0.7536330
373, 0.1700279002\H, -1.7594096014, -1.5732360057, -0.0819196249\H, -1.5922
57879, 0.1797604932, 0.3960924815\C, 0.1168460434, -1.0653817374, 0.6645910
876\H, 0.5214595538, -2.0594479299, 0.5870038973\O, 1.0160730307, -0.224954
4543, 1.1772352911\C, 0.6208446518, 1.1112649405, 1.4170617503\H, 0.3273610
638, 1.6020956848, 0.4966079607\H, -0.1969671534, 1.1457034389, 2.133122048
1\H, 1.4853221938, 1.6069027569, 1.834907163\\Version=IA32L-G03RevC.02\St
ate=2-A\HF=-306.8602792\S2=0.80002\S2-1=0.\S2A=0.750583\RMSD=9.794e-09
\RMSF=5.329e-06\Dipole=-0.302311, -0.4617213, 0.4966002\PG=C01 [X(C4H7O2
)\\@
Imaginary frequency = -591.5i cm⁻¹

TS: HC(=O)• + CH₂=CH(NH₂)

1\1\GINC-AC19\FTS\UBHandHLYP\6-311G(d,p)\C3H6N1O1(2)\EXK501\03-May-200
7\0\\# BHANDHLYP/6-311G** OPT=(TS,CALCFC,NOEIGENTEST,MAXCYC=200) FREQ=
NORAMAN MAXDISK=268435456\\TS_HCOadduct_enamine_BHLYP_6-311Gss_start\\
0,2\C, 1.3361337756, 0.0557686724, -0.6929070831\O, 1.3033209434, 1.1766463
397, -0.3101804552\H, 1.1846104315, -0.25007378, -1.7465066294\C, 0.1169186
059, -1.2335099063, 0.4439925385\H, 0.6034733506, -0.9245125786, 1.35211080
81\H, 0.3469272039, -2.2209778956, 0.0884395242\C, -1.0426453633, -0.643743
0244, 0.0512910917\H, -1.6410453694, -1.0813393618, -0.7305545139\N, -1.494
7703956, 0.5443472618, 0.5386131291\H, -0.8037199318, 1.1206172517, 0.98300
56192\H, -2.115862572, 1.0615903636, -0.0496023535\\Version=IA64L-G03RevC
.02\State=2-A\HF=-247.7150511\S2=0.784239\S2-1=0.\S2A=0.750358\RMSD=9.
210e-09\RMSF=6.368e-05\Dipole=-0.8232306, -0.3474399, -0.3757943\PG=C01
[X(C3H6N1O1)]\\@
Imaginary frequency = -464.7i cm⁻¹

TS: HC(=O)• + CH₂=CH(CN)

1\1\GINC-N91\FTS\UBHandHLYP\6-311G(d,p)\C4H4N1O1(2)\KRENSKE\31-Aug-2007\0\#\ BHANDHLYP/6-311G** OPT=(TS,CALCFC,NOEIGENTEST,MAXCYC=200) FREQ=NORAMAN\TS_HCOadduct-acrylonitrile_BHLYP_6-311Gss_start\0,2\C,-1.8264718159,-0.0498089488,-0.008812479\O,-2.6641743789,0.7290878066,0.1907783686\H,-1.6115886366,-0.966026539,0.5741696019\C,0.0975526794,0.5782659339,-1.0249589327\H,0.06302986,-0.2350384887,-1.7272655507\C,0.9776320899,0.5667207033,0.004692847\H,-0.3754457552,1.4975133888,-1.3182045201\H,1.1037329573,1.425825574,0.6401200249\C,1.7261451773,-0.5848452108,0.3454812191\N,2.3263596888,-1.5167101791,0.6295053669\Version=IA32L-G03RevC.02\State=2-A\HF=-284.5851627\S2=0.816029\S2-1=0.\S2A=0.751363\RMSD=9.224e-09\RMSF=2.015e-05\Dipole=-0.7158436,0.6260791,-0.435988\PG=C01 [X(C4H4N1O1)]\@\@
Imaginary frequency = -430.1i cm⁻¹

TS: HC(=O)• + CH₂=NH (via N)

1\1\GINC-AC14\FTS\UBHandHLYP\6-311G(d,p)\C2H4N1O1(2)\EXK501\25-Apr-2007\0\#\ BHANDHLYP/6-311G** OPT=(TS,CALCFC,NOEIGENTEST,MAXCYC=200) FREQ=NORAMAN MAXDISK=134217728\TS_HCOadduct-CH2=NH_Nattack_1_BHLYP_6-311Gs\0,2\C,1.0604368681,0.5191944239,-0.1361666991\H,1.3126308935,1.3746881331,0.5081177494\O,1.4409623059,-0.5989203243,-0.0033432332\N,-0.8315982665,0.5805329847,0.0563328772\C,-1.4417181368,-0.5218537584,0.0195819749\H,-0.8602598206,-1.4144518914,0.206208111\H,-2.4937910801,-0.6155055051,-0.210985663\H,-1.377402962,1.3988569726,-0.1714161277\Version=IA64L-G03RevC.02\State=2-A\HF=-208.4120206\S2=0.766272\S2-1=0.\S2A=0.750137\RMSD=5.090e-09\RMSF=2.389e-06\Dipole=-1.6160083,0.5774648,0.05841\PG=C01 [X(C2H4N1O1)]\@\@
Imaginary frequency = -513.7i cm⁻¹

Product: H₂P(=O)• + CH₂=CH₂

1\1\GINC-AC24\FOpt\UBHandHLYP\6-311G(d,p)\C2H6O1P1(2)\EXK501\04-May-2007\0\#\ BHANDHLYP/6-311G** OPT FREQ=NORAMAN MAXDISK=134217728\Padduct-ethylene_BHLYP_6-311Gss_start\0,2\O,-1.2682023967,1.4602008598,0.\P,-0.0039459479,0.7022263266,0.\C,-0.1263595515,-1.1256287348,0.\C,1.2043684707,-1.7683498744,0.\H,0.8606185182,0.9344000486,1.0853336005\H,0.8606185182,0.9344000486,-1.0853336005\H,-0.7104791603,-1.3887933604,0.8775719446\H,-0.7104791603,-1.3887933604,-0.8775719446\H,1.7182380805,-1.9711717489,0.9217697406\H,1.7182380805,-1.9711717489,-0.9217697406\Version=IA64L-G03RevC.02\State=2-A'\HF=-496.2952941\S2=0.755946\S2-1=0.\S2A=0.750025\RMSD=5.934e-09\RMSF=4.869e-05\Dipole=1.2650013,-1.1225098,0.\PG=CS [SG(C2O1P1),X(H6)]\@\@

Product: H₂P(=O)• + CH₂=CH(OMe)

1\1\GINC-N92\FOpt\UBHandHLYP\6-311G(d,p)\C3H8O2P1(2)\KRENSKE\31-Aug-2007\0\#\ BHANDHLYP/6-311G** OPT FREQ=NORAMAN\Padduct-MeO-CH2=CH2_BHLYP_6-311Gss_start\0,2\H,2.3064183607,-1.6985133929,-0.1885024794\P,1.4675990202,-0.5740878157,-0.3235538193\O,2.1256010906,0.7403828789,-0.1967063801\H,0.8496316372,-0.8387713721,-1.5569485202\C,0.1390551676,-0.9344642741,0.8779733457\H,-0.2578292179,-1.9190925466,0.6316490719\C,-0.9329512371,0.0863938643,0.8598215645\H,0.5932346546,-0.9853039694,1.8624394936\H,-0.7933264589,1.0284977525,1.3684564141\O,-1.6378555373,0.1143862201,-0.2903654445\C,-2.5693259026,1.1642031028,-0.4071724347\H,-2.071869083,2.1288895434,-0.3394394869\H,-3.0341566198,1.0677636885,-1.3784344816\H,-3.32872117,1.0928985829,0.3669270211\Version=IA32L-G03RevC.02\State=2-A\HF=-610.7896656\S2=0.755199\S2-1=0.\S2A=0.75002\RM

SD=5.888e-09\RMSF=5.769e-06\Dipole=-1.179851,-0.835189,0.1548179\PG=C0
1 [X(C3H8O2P1)]\@

Product: $\text{H}_2\text{P(=O)}\cdot + \text{CH}_2=\text{CH}(\text{NH}_2)$

1\1\GINC-AC54\FOpt\UBHandHLYP\6-311G(d,p)\C2H7N1O1P1(2)\EXK501\04-May-2007\0\#\ BHANDHLYP/6-311G** OPT FREQ=NORAMAN MAXDISK=134217728 MAXDISK=134217728\Padduct-enamine_BHLYP_6-311Gss_start\0,2\H,-2.2103004637,-0.8861599633,-0.5703037871\P,-1.1879141266,-0.2085528047,0.1224229398\O,-1.1342102803,1.2556730204,-0.0941905937\H,-1.4160506474,-0.6161098992,1.4483387895\C,0.3216089102,-1.1010361278,-0.3418946958\C,1.5177906661,-0.4702511965,0.2857138481\H,0.3748434336,-1.0911418042,-1.4350798415\H,0.2136435999,-2.1348438908,-0.0245086015\N,1.8437812197,0.8103055275,-0.1270721327\H,2.3393036956,-1.0989624632,0.5808893892\H,1.0544294596,1.4270601283,-0.2345929299\H,2.5936590662,1.2386510524,0.3790276495\Version=IA64L-G03RevC.02\State=2-A\HF=-551.6443559\S2=0.755686\S2-1=0.\S2A=0.750022\RMSD=7.155e-09\RMSF=3.635e-06\Dipole=0.2932366,-1.2746832,0.2988432\PG=C01 [X(C2H7N1O1P1)]\@

Product: $\text{H}_2\text{P(=O)}\cdot + \text{CH}_2=\text{CH}(\text{CN})$

1\1\GINC-N82\FOpt\UBHandHLYP\6-311G(d,p)\C3H5N1O1P1(2)\KRENSKE\30-Aug-2007\0\#\ BHANDHLYP/6-311G** OPT FREQ=NORAMAN\Padduct-acrylonitrile_BHLYP_6-311Gss_a3b2\0,2\H,0.4727444075,-1.8053506054,-0.5891279406\P,-0.5093407932,-1.4170329388,0.3373294008\O,-1.8979616964,-1.3851677304,-0.1501088319\H,-0.2397971254,-2.2708578133,1.4221934721\C,0.1424264,0.1777999751,0.9566803392\H,-0.4633459199,0.4333345962,1.8237433174\C,0.0447813642,1.243634311,-0.0724351045\H,1.1665534855,0.0254966392,1.2844974816\H,-0.9234141139,1.5943513771,-0.3819898009\C,1.1609550392,1.7588064342,-0.7020323172\N,2.1031554164,2.1826310583,-1.2159520558\Version=IA32L-G03RevC.02\State=2-A\HF=-588.5177591\S2=0.784284\S2-1=0.\S2A=0.750463\RMSD=3.510e-09\RMSF=7.249e-06\Dipole=0.3813915,-0.4697076,1.2893109\PG=C01 [X(C3H5N1O1P1)]\@

Product: $\text{HC(=O)}\cdot + \text{CH}_2=\text{CH}_2$

1\1\GINC-AC52\FOpt\UBHandHLYP\6-311G(d,p)\C3H5O1(2)\EXK501\08-May-2007\0\#\ BHANDHLYP/6-311G** OPT FREQ=NORAMAN MAXDISK=134217728\HCOadduct-ethylene_BHLYP_6-311Gss_start-Cs\0,2\H,-0.1536227861,1.9865925011,0.\C,-0.3328426755,0.899601846,0.\O,-1.4431416023,0.4699535145,0.\C,0.9145572612,0.0596475709,0.\C,0.6709175795,-1.3992706313,0.\H,1.5111053138,0.3778427222,0.86137\H,1.5111053138,0.3778427222,-0.86137\H,1.4954584673,-2.0877176917,0.\H,-0.3346294319,-1.7740373492,0.\Version=IA64L-G03RevC.02\State=2-A\HF=-192.4128874\S2=0.755197\S2-1=0.\S2A=0.750017\RMSD=3.417e-09\RMSF=2.360e-05\Dipole=0.5843219,0.9209515,0.\PG=CS [SG(C3H3O1),X(H2)]\@

Product: HC(=O)• + CH₂=CH(OMe)

```
1\1\GINC-N94\FOpt\UBHandHLYP\6-311G(d,p)\C4H7O2(2)\KRENSKE\31-Aug-2007
\0\#\ BHANDHLYP/6-311G** OPT FREQ=NORAMAN\HCOadduct-MeO-CH2=CH2_BHLYP
_6-311Gss_start\0,2\C,1.2079221514,-0.2677118542,-1.1712734102\O,2.33
09475032,-0.0383410957,-1.4961966958\H,0.3629437392,-0.0207413628,-1.8
320721214\C,0.809724461,-0.8666043161,0.1592304736\H,0.320857701,-1.82
18097843,-0.0274581221\C,-0.1384502954,0.0195769619,0.8818001879\H,1.7
098102462,-1.0343877148,0.7396424983\H,0.199094957,0.9422362557,1.3327
560233\O,-1.3965863742,0.0036174424,0.3963980902\C,-2.2912344502,0.912
0692003,0.9925033035\H,-1.9425913668,1.9355628892,0.869701103\H,-3.241
9686794,0.7955580369,0.491140023\H,-2.4108068295,0.6973909545,2.051116
1116\Version=IA32L-G03RevC.02\State=2-A\HF=-306.9065452\S2=0.75666\S2
-1=0.\S2A=0.750033\RMSD=9.144e-09\RMSF=2.143e-05\Dipole=-1.1507078,0.2
428108,0.6961795\PG=C01 [X(C4H7O2)]\@
```

Product: HC(=O)• + CH₂=CH(NH₂)

```
1\1\GINC-AC52\FOpt\UBHandHLYP\6-311G(d,p)\C3H6N1O1(2)\EXK501\07-May-20
07\0\#\ BHANDHLYP/6-311G** OPT FREQ=NORAMAN MAXDISK=134217728\HCOaddu
ct-enamine_BHLYP_6-311Gss_alb2c2\0,2\H,0.2385418494,0.2328942064,-2.4
068651033\C,0.3619897608,0.1057391644,-1.3191074353\O,1.4032649197,-0.
2758435907,-0.8767187397\C,-0.8697310367,0.4106678884,-0.5137189326\C,
-0.6932607333,0.4602335243,0.9617349537\H,-1.5965998913,-0.3566753227,
-0.822249235\H,-1.2791127959,1.3491661354,-0.8824023684\N,-0.100489189
1,-0.6292165276,1.5856475993\H,-1.4487671574,0.9696822356,1.535323555
\H,0.7515533456,-0.9229270926,1.1428802982\H,0.0177016711,-0.520719206
1,2.5740780601\Version=IA64L-G03RevC.02\State=2-A\HF=-247.7600619\S2=
0.755402\S2-1=0.\S2A=0.75002\RMSD=3.061e-09\RMSF=3.554e-05\Dipole=-0.6
564746,0.2910051,-0.0090831\PG=C01 [X(C3H6N1O1)]\@
```

Product: HC(=O)• + CH₂=CH(CN)

```
1\1\GINC-N86\FOpt\UBHandHLYP\6-311G(d,p)\C4H4N1O1(2)\KRENSKE\01-Sep-20
07\1\#\ BHANDHLYP/6-311G** OPT=(Z-MATRIX) FREQ=NORAMAN\HCOadduct-acry
lonitrile_BHLYP_6-311Gss_alb2_sym\0,2\O\C,1,co2\H,2,hc3,1,hco3\C,2,cc
4,3,cch4,1,dih4,0\H,4,hc5,2,hcc5,1,dih5,0\H,4,hc5,2,hcc5,1,-dih5,0\C,4
,cc7,2,ccc7,1,dih7,0\H,7,hc8,4,hcc8,2,dih8,0\C,7,cc9,4,ccc9,2,dih9,0\N
,9,nc10,7,ncc10,4,dih10,0\co2=1.189547\hc3=1.099367\hco3=121.02000014
\cc4=1.505445\cch4=114.70100004\hc5=1.09194\hcc5=107.91299992\dih5=123
.73099959\cc7=1.486577\ccc7=112.92399995\hc8=1.074917\hcc8=119.0079999
7\cc9=1.381653\ccc9=121.77800005\nc10=1.153369\ncc10=179.37665909\dih4
=-180.\dih7=0.\dih8=0.\dih9=180.\dih10=0.\Version=IA32L-G03RevC.02\St
ate=2-A\HF=-284.6385938\S2=0.783562\S2-1=0.\S2A=0.750434\RMSD=6.941e-
09\RMSF=2.042e-05\Dipole=1.3129406,0.,0.5000325\PG=CS [SG(C4H2N1O1),X(
H2)]\@
```

Table S2 Total energies (*E*) and activation barriers at various levels of theory for the additions of the H₂P(=O)• and HC(=O)• radicals to ethylene^a

Level of Theory	CH ₂ =CH ₂	H ₂ P(=O)•	TS: H ₂ P(=O)• + CH ₂ =CH ₂	$\Delta E^\ddagger$	HC(=O)•	TS: HC(=O)• + CH ₂ =CH ₂	$\Delta E^\ddagger$
HF/cc-pVDZ	-78.04017	-416.72211	-494.74424	47.4	-113.25981	-191.28339	43.6
MP2/cc-pVDZ	-78.31530	-417.01233	-495.31523	32.6	-113.55444	-191.84771	57.9
B3LYP/cc-pVDZ	-78.59120	-417.74320	-496.32892	14.4	-113.86065	-192.44651	14.0
B3LYP/6-31G*	-78.58746	-417.72503	-496.31001	6.5	-113.85017	-192.43416	9.1
B3LYP/6-311G**	-78.61398	-417.77745	-496.38910	6.1	-113.88660	-192.49440	16.2
BHandHLYP/cc-pVDZ	-78.53520	-417.68081	-496.20812	20.7	-113.79869	-192.32425	25.3
BHandHLYP/aug-cc-pVDZ	-78.54075	-417.69645	-496.23033	18.0	-113.80828	-192.33925	25.7
BHandHLYP/cc-pVTZ	-78.56409	-417.73952	-496.29688	17.7	-113.83469	-192.38785	28.7
BHandHLYP/6-31G*	-78.52994	-417.66251	-496.18805	11.6	-113.78737	-192.30990	19.5
BHandHLYP/6-311G**	-78.55475	-417.71110	-496.26165	11.0	-113.82207	-192.36657	26.9
ROBHandHLYP/6-311G**	-78.55475	-417.70746	-496.25517	18.5	-113.81955	-192.36045	36.4
QCISD/cc-pVDZ// BHandHLYP/cc-pVDZ	-78.34504	-417.03764	-495.37260	26.5	-113.56714	-191.89854	35.8
QCISD/cc-pVDZ// BHandHLYP/6-311G**	-78.34393	-417.03598	-495.37012	25.7	-113.56641	-191.89685	35.4
CCSD(T)/cc-pVDZ// BHandHLYP/cc-pVDZ	-78.35438	-417.04493	-495.39095	21.9	-113.57521	-191.91765	31.3
CCSD(T)/cc-pVDZ// BHandHLYP/6-311G**	-78.35314	-417.04336	-495.38814	21.9	-113.57440	-191.91583	30.8
CCSD(T)/aug-cc-pVDZ// BHandHLYP/cc-pVDZ	-78.36824	-417.08390	-495.44845	9.7	-113.59867	-191.95862	21.8
CCSD(T)/aug-cc-pVDZ// BHandHLYP/6-311G**	-78.36705	-417.08190	-495.44500	10.4	-113.59787	-191.95689	21.1

^a Total energies (*E*) in Hartrees; barriers ($\Delta E^\ddagger$) in kJ mol⁻¹. Barriers are calculated with respect to the separated reactants. Calculations use an unrestricted representation for open-shell species unless otherwise indicated.