Electronic Supporting Information for

Vanadate-dependent Bromoperoxidases from *Ascophyllum nodosum* in Synthesis of Brominated Phenols and Pyrroles †

Diana Wischang[a], Madlen Radlow[a], and Jens Hartung*[a]

[a] *Fachbereich Chemie, Organische Chemie, Technische Universität Kaiserslautern, Erwin-Schrödinger-Straße, D-67663 Kaiserslautern, Germany*

Contents

1 General Remarks

In the graphics for presenting final geometries from B3LYP/6-311++G**-calculations, oxygen atoms were depicted in red, carbons in grey, bromines in dark blue, nitrogens in light blue, and hydrogens in white.

2 Computational Chemistry

All calculations were carried out with Gaussian03[1], using the density functional/Hartree-Fock hybrid model B3LYP and split valence triple-ζ basis set 6-311++G(d,p). No symmetry or internal coordinate constraints were applied during energy function minimization. The ultrafine grid in combination with the tight option for energy function minimization was used. The absence of imaginary modes of vibration characterized computed structures as minima. Approximate Gibbs free energies ($G_{298.15}$) were obtained through thermochemical analysis for 298.15 K by unscaled frequency calculation from the thermal correction reported by Gaussian03. Likewise obtained Gibbs free energies took into account zero-point correction, thermal correction, and entropy.

Natural bond orbital-analysis were performed by B3LYP/6-31G**-single point calculations, using the NBO 5.9-software[2] implemented in Gaussian 03

3 Bromine compounds

3.1 Bromohydroxonium (H_2OBr^+)

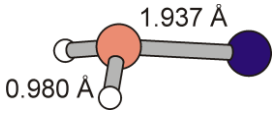

Figure S1 Equilibrium geometry of the bromohydroxonium ion

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.018697	1.490173	0.000000
2	35	0	-0.018697	-0.446820	0.000000
3	1	0	0.401989	1.858662	0.805248
4	1	0	0.401989	1.858662	-0.805248

Zero-point correction=	0.025202 (Hartree/Particle)
Thermal correction to Energy=	0.028393
Thermal correction to Enthalpy=	0.029338
Thermal correction to Gibbs Free Energy=	0.000457
Sum of electronic and zero-point Energies=	-2650.186059
Sum of electronic and thermal Energies=	-2650.182868
Sum of electronic and thermal Enthalpies=	-2650.181923
Sum of electronic and thermal Free Energies=	-2650.210804

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NATURAL BOND ORBITALS (Summary):

NBO	Occupancy	Energy
1. BD (1) O 1-Br 2	1.99799	-0.94247
53. BD*(1) O 1-Br 2	0.00203	-0.37492

3.2 Hypobromous acid (HOBr)

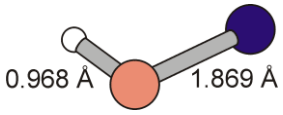

Figure S2 Equilibrium geometry of hypobromous acid

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.021407	1.481732	0.000000
2	35	0	0.021407	-0.387367	0.000000
3	1	0	-0.920510	1.703991	0.000000

Zero-point correction= 0.012634 (Hartree/Particle)
Thermal correction to Energy= 0.015642
Thermal correction to Enthalpy= 0.016587
Thermal correction to Gibbs Free Energy= -0.011573
Sum of electronic and zero-point Energies= -2649.931076
Sum of electronic and thermal Energies= -2649.928067
Sum of electronic and thermal Enthalpies= -2649.927123
Sum of electronic and thermal Free Energies= -2649.955283

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NATURAL BOND ORBITALS (Summary):

NBO	Occupancy	Energy
1. BD (1) O 1-Br 2	1.99897	-0.60174
49. BD*(1) O 1-Br 2	0.00071	-0.05133

3.3 *tert*-Butyl hypobromite (*t*BuOBr)

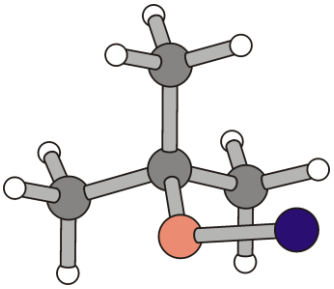

Figure S3 Equilibrium geometry of *tert*-butyl hypobromite

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.281312	0.000002	0.036688
2	6	0	-2.413636	-0.000077	-1.002326
3	6	0	-1.320321	1.268587	0.889247
4	6	0	-1.320284	-1.268483	0.889398
5	8	0	-0.122277	-0.000032	-0.847550
6	35	0	1.573791	-0.000001	-0.027764
7	1	0	-2.355177	-0.887239	-1.635252
8	1	0	-3.377655	0.000011	-0.486826
9	1	0	-2.355120	0.886946	-1.635443
10	1	0	-0.488622	1.293258	1.596691
11	1	0	-1.262769	2.156882	0.256345
12	1	0	-2.250271	1.309522	1.462498
13	1	0	-0.488661	-1.292988	1.596936
14	1	0	-2.250294	-1.309442	1.462550
15	1	0	-1.262575	-2.156846	0.256606

Zero-point correction= 0.124496 (Hartree/Particle)
Thermal correction to Energy= 0.132442
Thermal correction to Enthalpy= 0.133386
Thermal correction to Gibbs Free Energy= 0.091849
Sum of electronic and zero-point Energies= -2807.118862
Sum of electronic and thermal Energies= -2807.110916
Sum of electronic and thermal Enthalpies= -2807.109971
Sum of electronic and thermal Free Energies= -2807.151509

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```
NATURAL BOND ORBITALS (Summary):
============================================================================
           NBO                 Occupancy    Energy
============================================================================
   8. BD ( 1) O  3-Br  4        1.98966    -0.56882
 144. BD*( 1) O  3-Br  4        0.04402    -0.04198
============================================================================
```

3.4 Bromine

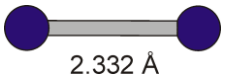

Figure S4 Equilibrium geometry of bromine

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 Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic     Atomic              Coordinates (Angstroms)
 Number     Number      Type              X           Y           Z
 ---------------------------------------------------------------------
    1         35             0        0.000000    0.000000    1.165844
    2         35             0        0.000000    0.000000   -1.165844
 ---------------------------------------------------------------------

 Zero-point correction=                           0.000709 (Hartree/Particle)
 Thermal correction to Energy=                    0.003476
 Thermal correction to Enthalpy=                  0.004420
 Thermal correction to Gibbs Free Energy=        -0.023470
 Sum of electronic and zero-point Energies=          -5148.284218
 Sum of electronic and thermal Energies=             -5148.281451
 Sum of electronic and thermal Enthalpies=           -5148.280506
 Sum of electronic and thermal Free Energies=        -5148.308396


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NATURAL BOND ORBITALS (Summary):
============================================================================
           NBO                 Occupancy    Energy
============================================================================
   1. BD ( 1)Br  1-Br  2        2.00000    -0.54013
  60. BD*( 1)Br  1-Br  2        0.00011    -0.10725
============================================================================
```

3.5 *N*-Bromosuccinimide

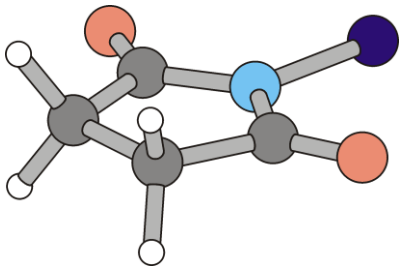

Figure S5 Equilibrium geometry of *N*-bromosuccinimide

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.914709	-1.188802	0.000000
2	6	0	2.379101	-0.768529	0.000017
3	6	0	2.379101	0.768529	-0.000017
4	6	0	0.914709	1.188802	0.000000
5	7	0	0.163248	0.000000	0.000000
6	8	0	0.464609	-2.301314	-0.000007
7	8	0	0.464609	2.301314	0.000007
8	35	0	-1.701023	0.000000	0.000000
9	1	0	2.858421	-1.203574	-0.878965
10	1	0	2.858380	-1.203527	0.879045
11	1	0	2.858380	1.203527	-0.879045
12	1	0	2.858421	1.203574	0.878965

```
Zero-point correction=                           0.080637 (Hartree/Particle)
Thermal correction to Energy=                    0.088079
Thermal correction to Enthalpy=                  0.089023
Thermal correction to Gibbs Free Energy=         0.046807
Sum of electronic and zero-point Energies=          -2934.198890
Sum of electronic and thermal Energies=             -2934.191447
Sum of electronic and thermal Enthalpies=           -2934.190503
Sum of electronic and thermal Free Energies=        -2934.232719
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```

NATURAL BOND ORBITALS (Summary):

NBO	Occupancy	Energy
3. BD (1) N 1-Br 8	1.98487	-0.69085
144. BD*(1) N 1-Br 8	0.06092	-0.01520

3.6 Hydrogen tribromide

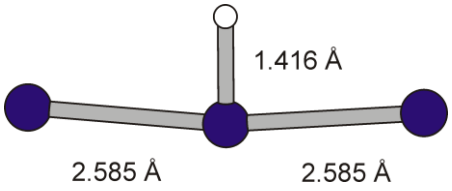

Figure S6 Equilibrium geometry of hydrogentribromide

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	0.000000	-0.114065	0.000013
2	35	0	2.607212	0.038206	-0.000008
3	35	0	-2.607212	0.038206	-0.000008
4	1	0	-0.000001	1.317850	0.000056

Zero-point correction= 0.008630 (Hartree/Particle)
Thermal correction to Energy= 0.014264
Thermal correction to Enthalpy= 0.015208
Thermal correction to Gibbs Free Energy= -0.023326
Sum of electronic and zero-point Energies= -7722.984594
Sum of electronic and thermal Energies= -7722.978960
Sum of electronic and thermal Enthalpies= -7722.978016
Sum of electronic and thermal Free Energies= -7723.016550

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NATURAL BOND ORBITALS (Summary):

NBO	Occupancy	Energy
1. BD (1)Br 1-Br 3	1.99786	-0.45775
94. BD*(1)Br 1-Br 3	0.65211	-0.21676

SECOND ORDER PERTURBATION THEORY ANALYSIS OF FOCK MATRIX IN NBO BASIS

Donor NBO (i)	Acceptor NBO (j)	kcal/mol	a.u.	a.u.
50. LP (4)Br 2	94. BD*(1)Br 1-Br 3	143.52	0.08	0.095

3.7 Tribromide

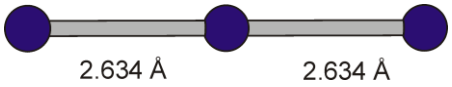

Figure S7 Equilibrium geometry of the tribromide anion

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	0.000000	2.638697	-0.000337
2	35	0	0.000000	0.000000	0.000675
3	35	0	0.000000	-2.638697	-0.000337

Zero-point correction= 0.000926 (Hartree/Particle)
Thermal correction to Energy= 0.005773
Thermal correction to Enthalpy= 0.006718
Thermal correction to Gibbs Free Energy= -0.024428
Sum of electronic and zero-point Energies= -7722.574577
Sum of electronic and thermal Energies= -7722.569730
Sum of electronic and thermal Enthalpies= -7722.568786
Sum of electronic and thermal Free Energies= -7722.599931

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NATURAL BOND ORBITALS (Summary):

NBO	Occupancy	Energy
1. BD (1)Br 1-Br 2	1.99878	-0.22301
90. BD*(1)Br 1-Br 2	0.51981	0.00474

SECOND ORDER PERTURBATION THEORY ANALYSIS OF FOCK MATRIX IN NBO BASIS

Donor NBO (i)	Acceptor NBO (j)	kcal/mol	a.u.	a.u.
53. LP (4)Br 3	90. BD*(1)Br 1-Br 2	110.30	0.12	0.103

3.8 Hydrogen bromide

Figure S8 Equilibrium geometry of the hydrogen bromide

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	0.000000	0.000000	0.039645
2	1	0	0.000000	0.000000	-1.387561

```
 Zero-point correction=                           0.005936 (Hartree/Particle)
 Thermal correction to Energy=                    0.008296
 Thermal correction to Enthalpy=                  0.009240
 Thermal correction to Gibbs Free Energy=        -0.013294
 Sum of electronic and zero-point Energies=          -2574.747238
 Sum of electronic and thermal Energies=             -2574.744878
 Sum of electronic and thermal Enthalpies=           -2574.743933
 Sum of electronic and thermal Free Energies=        -2574.766468

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```

3.9 Bromide (Br^-)

```
 Zero-point correction=                           0.000000 (Hartree/Particle)
 Thermal correction to Energy=                    0.001416
 Thermal correction to Enthalpy=                  0.002360
 Thermal correction to Gibbs Free Energy=        -0.016176
 Sum of electronic and zero-point Energies=          -2574.237838
 Sum of electronic and thermal Energies=             -2574.236422
 Sum of electronic and thermal Enthalpies=           -2574.235477
 Sum of electronic and thermal Free Energies=        -2574.254013

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4 Hydrogen peroxide and Water

4.1 Hydrogen peroxide

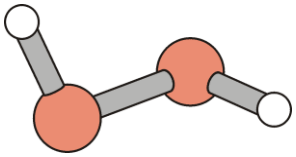

Figure S9 Equilibrium geometry of hydrogen peroxide

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.727018	-0.051877
2	8	0	0.000000	-0.727018	-0.051877
3	1	0	0.828619	0.902776	0.415013
4	1	0	-0.828619	-0.902776	0.415013

Zero-point correction= 0.026433 (Hartree/Particle)
Thermal correction to Energy= 0.029676
Thermal correction to Enthalpy= 0.030620
Thermal correction to Gibbs Free Energy= 0.004772
Sum of electronic and zero-point Energies= -151.575737
Sum of electronic and thermal Energies= -151.572494
Sum of electronic and thermal Enthalpies= -151.571550
Sum of electronic and thermal Free Energies= -151.597397

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NATURAL BOND ORBITALS (Summary):

NBO	Occupancy	Energy
1. BD (1) O 1- O 2	1.99703	-0.71864
38. BD*(1) O 1- O 2	0.00270	0.08347

4.2 Water

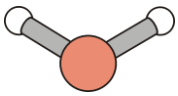

Figure S10 Equilibrium geometry of water

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.000000	0.117057
2	1	0	0.000000	0.763568	-0.468229
3	1	0	0.000000	-0.763568	-0.468229

Zero-point correction= 0.021283 (Hartree/Particle)
Thermal correction to Energy= 0.024119
Thermal correction to Enthalpy= 0.025063
Thermal correction to Gibbs Free Energy= 0.003640
Sum of electronic and zero-point Energies= -76.437249
Sum of electronic and thermal Energies= -76.434413
Sum of electronic and thermal Enthalpies= -76.433469
Sum of electronic and thermal Free Energies= -76.454892

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5 Alkenes

5.1 Ethene

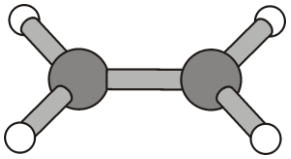

Figure S11 Equilibrium geometry of ethene

```
 Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic     Atomic              Coordinates (Angstroms)
 Number     Number      Type              X           Y           Z
 ---------------------------------------------------------------------
    1          6             0        0.000000    0.664435    0.000000
    2          6             0        0.000000   -0.664435    0.000000
    3          1             0        0.000000    1.235179    0.922763
    4          1             0        0.000000    1.235179   -0.922763
    5          1             0        0.000000   -1.235179   -0.922763
    6          1             0        0.000000   -1.235179    0.922763
 ---------------------------------------------------------------------

 Zero-point correction=                           0.050776 (Hartree/Particle)
 Thermal correction to Energy=                    0.053818
 Thermal correction to Enthalpy=                  0.054762
 Thermal correction to Gibbs Free Energy=         0.028597
 Sum of electronic and zero-point Energies=            -78.564763
 Sum of electronic and thermal Energies=               -78.561720
 Sum of electronic and thermal Enthalpies=             -78.560776
 Sum of electronic and thermal Free Energies=          -78.586942

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RMSF=3.477e-08\ Dipole=0.,0.,0.\PG=CS [SG(C2),X(H4)]\NImag=0\\\@

NATURAL BOND ORBITALS (Summary):
=======================================================================
           NBO                  Occupancy    Energy
=======================================================================
   1. BD ( 1) C  1- C  2        1.99641    -0.73768
   2. BD ( 2) C  1- C  2        1.99946    -0.26693
  45. BD*( 1) C  1- C  2        0.00412     0.68082
  46. BD*( 2) C  1- C  2        0.00000     0.04837
=======================================================================
```

5.2 Propene

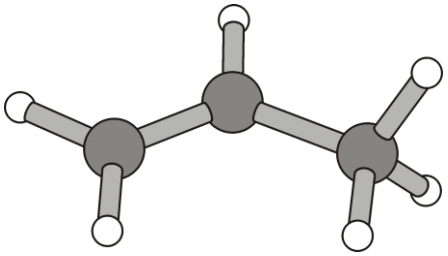

Figure S12 Equilibrium geometry of propene

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.281672	0.220382	0.000000
2	6	0	0.133711	-0.453652	-0.000001
3	6	0	-1.234078	0.162696	0.000000
4	1	0	2.239277	-0.287969	0.000002
5	1	0	1.303980	1.306357	-0.000002
6	1	0	0.166104	-1.542065	0.000000
7	1	0	-1.807191	-0.153488	0.878664
8	1	0	-1.182810	1.254104	-0.000001
9	1	0	-1.807190	-0.153492	-0.878662

Zero-point correction= 0.079249 (Hartree/Particle)
Thermal correction to Energy= 0.083343
Thermal correction to Enthalpy= 0.084287
Thermal correction to Gibbs Free Energy= 0.054233
Sum of electronic and zero-point Energies= -117.866374
Sum of electronic and thermal Energies= -117.862280
Sum of electronic and thermal Enthalpies= -117.861336
Sum of electronic and thermal Free Energies= -117.891390

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NATURAL BOND ORBITALS (Summary):

NBO	Occupancy	Energy
1. BD (1) C 1- C 2	1.99161	-0.72947
2. BD (2) C 1- C 2	1.98260	-0.25801
67. BD*(1) C 1- C 2	0.00884	0.68842
68. BD*(2) C 1- C 2	0.03182	0.06086

5.3 2-Methylpropene

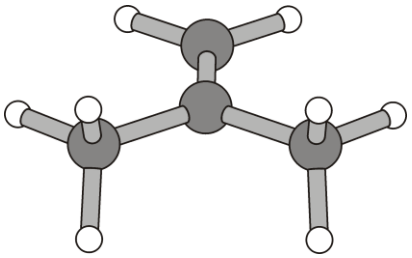

Figure S13 Equilibrium geometry of 2-methylprpene

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.000010	1.458481	0.000001
2	6	0	-0.000001	0.123683	-0.000014
3	6	0	1.275838	-0.678686	0.000001
4	6	0	-1.275829	-0.678702	0.000000
5	1	0	-0.924126	2.026779	0.000022
6	1	0	0.924095	2.026795	-0.000011
7	1	0	1.325646	-1.331991	0.878871
8	1	0	1.325679	-1.332045	-0.878827
9	1	0	2.158837	-0.037043	0.000000
10	1	0	-1.325656	-1.332028	-0.878853
11	1	0	-1.325627	-1.332048	0.878841
12	1	0	-2.158834	-0.037069	0.000024

```
 Zero-point correction=                           0.107271 (Hartree/Particle)
 Thermal correction to Energy=                    0.112594
 Thermal correction to Enthalpy=                  0.113538
 Thermal correction to Gibbs Free Energy=         0.079952
 Sum of electronic and zero-point Energies=           -157.167850
 Sum of electronic and thermal Energies=              -157.162528
 Sum of electronic and thermal Enthalpies=            -157.161583
 Sum of electronic and thermal Free Energies=         -157.195170

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RMSF=7.008e-07\Dipole=-0.0001647,-0.0000392,0.2257258\PG=C01 [X(C4H8)]\
NImag=0\\\@
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NATURAL BOND ORBITALS (Summary):

NBO	Occupancy	Energy
1. BD (1) C 1- C 2	1.98707	-0.72389
2. BD (2) C 1- C 2	1.96303	-0.25131
89. BD*(1) C 1- C 2	0.01417	0.68669
90. BD*(2) C 1- C 2	0.05915	0.06978

5.4 (2*E*)-But-2-ene

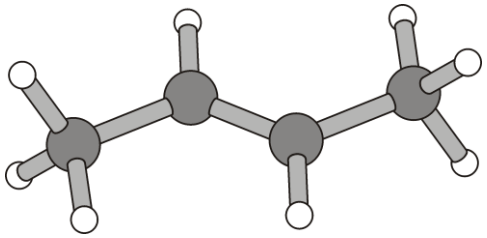

Figure S14 Equilibrium geometry of (2*E*)-but-2-ene

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.961715	0.079276	0.000001
2	6	0	0.537257	-0.394370	-0.000003
3	6	0	-0.537257	0.394371	-0.000001
4	6	0	-1.961714	-0.079276	0.000001
5	1	0	2.502313	-0.290013	0.878840
6	1	0	2.502321	-0.290021	-0.878829
7	1	0	2.021052	1.170557	-0.000003
8	1	0	0.390739	-1.474547	0.000000
9	1	0	-0.390741	1.474548	-0.000004
10	1	0	-2.502320	0.290020	0.878833
11	1	0	-2.502316	0.290010	-0.878837
12	1	0	-2.021047	-1.170558	0.000006

```
 Zero-point correction=                           0.107305 (Hartree/Particle)
 Thermal correction to Energy=                    0.112803
 Thermal correction to Enthalpy=                  0.113747
 Thermal correction to Gibbs Free Energy=         0.079884
 Sum of electronic and zero-point Energies=           -157.167295
 Sum of electronic and thermal Energies=              -157.161798
 Sum of electronic and thermal Enthalpies=            -157.160854
 Sum of electronic and thermal Free Energies=         -157.194716

Version=AM64L-G03RevE.01\State=1-A\HF=-157.2746005\RMSD=6.093e-09\
RMSF=2.424e-07\Dipole=-0.000002,-0.0000015,-0.0000016\PG=C01[X(C4H8)]\
NImag=0\\\@

NATURAL BOND ORBITALS (Summary):
```

NBO	Occupancy	Energy
5. BD (1) C 2- C 3	1.98684	-0.72294
6. BD (2) C 2- C 3	1.96379	-0.25029
93. BD*(1) C 2- C 3	0.01350	0.70082
94. BD*(2) C 2- C 3	0.05812	0.07270

5.5 (2*Z*)-But-2-ene

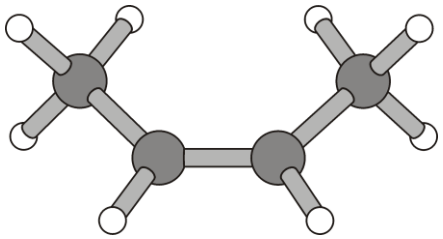

Figure S15 Equilibrium geometry of (2*Z*)-but-2-ene

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.590789	-0.521875	0.000001
2	6	0	-0.668030	0.663340	-0.000003
3	6	0	0.668030	0.663340	0.000002
4	6	0	1.590789	-0.521875	-0.000001
5	1	0	-1.164883	1.631677	-0.000004
6	1	0	1.164883	1.631677	0.000005
7	1	0	-2.245928	-0.502610	0.878255
8	1	0	-1.060760	-1.475253	-0.000007
9	1	0	-2.245948	-0.502605	-0.878239
10	1	0	2.245957	-0.502587	-0.878233
11	1	0	1.060763	-1.475254	-0.000034
12	1	0	2.245919	-0.502625	0.878261

Zero-point correction= 0.107483 (Hartree/Particle)
Thermal correction to Energy= 0.113005
Thermal correction to Enthalpy= 0.113950
Thermal correction to Gibbs Free Energy= 0.079633
Sum of electronic and zero-point Energies= -157.165161
Sum of electronic and thermal Energies= -157.159638
Sum of electronic and thermal Enthalpies= -157.158694
Sum of electronic and thermal Free Energies= -157.193010

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NImag=0\\\@

NATURAL BOND ORBITALS (Summary):

NBO	Occupancy	Energy
5. BD (1) C 2- C 3	1.98717	-0.72168
6. BD (2) C 2- C 3	1.96603	-0.24991
93. BD*(1) C 2- C 3	0.01452	0.69838
94. BD*(2) C 2- C 3	0.05991	0.07370

5.6 2-Methylbut-2-ene

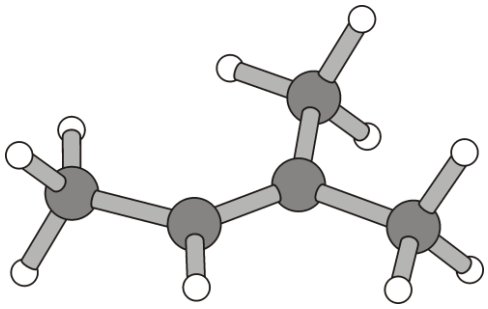

Figure S16 Equilibrium geometry of 2-methylbut-2-ene

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.111828	-0.078490	0.000001
2	6	0	0.732344	-0.672982	-0.000003
3	6	0	-0.448631	-0.041348	-0.000004
4	6	0	-1.741985	-0.819947	0.000001
5	6	0	-0.625120	1.456281	0.000000
6	1	0	2.677639	-0.410406	0.878209
7	1	0	2.677715	-0.410578	-0.878093
8	1	0	2.110800	1.012117	-0.000104
9	1	0	0.709742	-1.761985	0.000001
10	1	0	-2.349592	-0.572823	0.878891
11	1	0	-2.349595	-0.572830	-0.878888
12	1	0	-1.567004	-1.897738	0.000005
13	1	0	-1.198959	1.775157	-0.878224
14	1	0	-1.198833	1.775166	0.878303
15	1	0	0.317478	2.002840	-0.000069

Zero-point correction= 0.135208 (Hartree/Particle)
Thermal correction to Energy= 0.142141
Thermal correction to Enthalpy= 0.143085
Thermal correction to Gibbs Free Energy= 0.105312
Sum of electronic and zero-point Energies= -196.465780
Sum of electronic and thermal Energies= -196.458848
Sum of electronic and thermal Enthalpies= -196.457903
Sum of electronic and thermal Free Energies= -196.495677

Version=AM64L-G03RevE.01\State=1-A\HF=-196.6009887\RMS D=9.491e-09\
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\NImag=0\\\@

NATURAL BOND ORBITALS (Summary):

NBO	Occupancy	Energy
5. BD (1) C 2- C 3	1.98265	-0.71779
6. BD (2) C 2- C 3	1.94439	-0.24422
115. BD*(1) C 2- C 3	0.01992	0.70082
116. BD*(2) C 2- C 3	0.08316	0.08173

5.7 2,3-Dimethylbut-2-ene

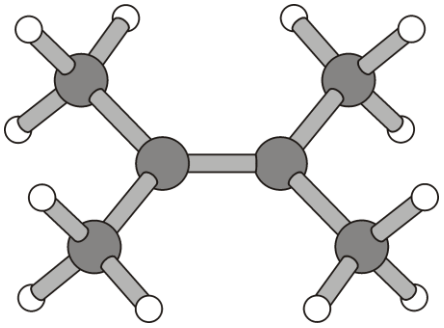

Figure S17 Equilibrium geometry of 2,3-dimethylbut-2-ene

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.526105	1.249401	0.000000
2	6	0	-0.673411	0.000000	0.000000
3	6	0	0.673411	0.000000	0.000000
4	6	0	1.526105	-1.249401	0.000000
5	6	0	1.526105	1.249401	0.000000
6	6	0	-1.526105	-1.249401	0.000000
7	1	0	-2.183980	1.260919	-0.877524
8	1	0	-2.183988	1.260913	0.877519
9	1	0	-0.959870	2.178254	0.000007
10	1	0	2.183977	-1.260921	-0.877526
11	1	0	2.183991	-1.260910	0.877517
12	1	0	0.959870	-2.178254	0.000010
13	1	0	2.183975	1.260922	0.877527
14	1	0	2.183992	1.260910	-0.877516
15	1	0	0.959870	2.178254	-0.000012
16	1	0	-0.959870	-2.178254	-0.000005
17	1	0	-2.183981	-1.260919	0.877523
18	1	0	-2.183986	-1.260914	-0.877520

```
 Zero-point correction=                           0.162718 (Hartree/Particle)
 Thermal correction to Energy=                    0.171467
 Thermal correction to Enthalpy=                  0.172411
 Thermal correction to Gibbs Free Energy=         0.129195
 Sum of electronic and zero-point Energies=           -235.761075
 Sum of electronic and thermal Energies=              -235.752327
 Sum of electronic and thermal Enthalpies=            -235.751383
 Sum of electronic and thermal Free Energies=         -235.794599

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NImag=0\\\@

NATURAL BOND ORBITALS (Summary):
=======================================================================
           NBO                 Occupancy    Energy
=======================================================================
   6. BD ( 1) C  2- C  4        1.97917    -0.71517
   7. BD ( 2) C  2- C  4        1.92402    -0.23913
 138. BD*( 1) C  2- C  4        0.02632     0.70270
 139. BD*( 2) C  2- C  4        0.10420     0.08909
=======================================================================
```

5.8 Prop-1-en-2-ol

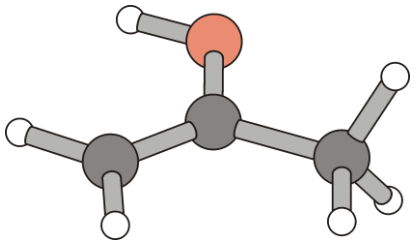

Figure S18 Equilibrium geometry of prop-1-en-2-ol

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.983577	-1.038209	0.000000
2	6	0	0.082430	-0.052002	-0.000001
3	6	0	-1.403162	-0.229550	0.000000
4	8	0	0.410927	1.280491	-0.000001
5	1	0	2.050437	-0.840906	0.000001
6	1	0	0.667112	-2.071482	0.000000
7	1	0	-1.841023	0.248672	0.881249
8	1	0	-1.841025	0.248685	-0.881241
9	1	0	-1.670167	-1.285877	-0.000007
10	1	0	1.370177	1.375546	0.000004

Zero-point correction= 0.084249 (Hartree/Particle)
Thermal correction to Energy= 0.089111
Thermal correction to Enthalpy= 0.090055
Thermal correction to Gibbs Free Energy= 0.057433
Sum of electronic and zero-point Energies= -193.114443
Sum of electronic and thermal Energies= -193.109581
Sum of electronic and thermal Enthalpies= -193.108636
Sum of electronic and thermal Free Energies= -193.141258

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NImag=0\\\@

NATURAL BOND ORBITALS (Summary):

NBO	Occupancy	Energy
1. BD (1) C 1- C 2	1.99166	-0.74018
2. BD (2) C 1- C 2	1.98062	-0.26273
5. BD (1) C 2- O 3	1.99404	-0.88648
7. BD (1) O 3- H 10	1.98881	-0.72527
15. LP (1) O 3	1.98033	-0.58083
16. LP (2) O 3	1.87417	-0.30556
81. BD*(1) C 1- C 2	0.01719	0.66768
82. BD*(2) C 1- C 2	0.15262	0.05678

6 Phenol

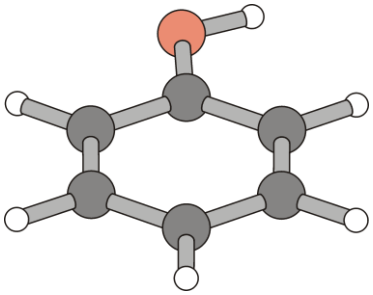

Figure S19 Equilibrium geometry of phenol

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.938000	-0.024022	0.000000
2	6	0	-0.220884	-1.221618	0.000001
3	6	0	1.169783	-1.188854	0.000000
4	6	0	1.855137	0.027220	0.000000
5	6	0	1.131328	1.217258	0.000000
6	6	0	-0.262789	1.197727	-0.000001
7	8	0	-2.305386	-0.110368	-0.000003
8	1	0	-0.763921	-2.158944	0.000003
9	1	0	1.722189	-2.121926	-0.000001
10	1	0	2.938339	0.045626	0.000001
11	1	0	1.649027	2.169958	-0.000001
12	1	0	-0.822906	2.128462	-0.000001
13	1	0	-2.687090	0.773507	0.000022

Zero-point correction= 0.103929 (Hartree/Particle)
Thermal correction to Energy= 0.109541
Thermal correction to Enthalpy= 0.110485
Thermal correction to Gibbs Free Energy= 0.074872
Sum of electronic and zero-point Energies= -307.454797
Sum of electronic and thermal Energies= -307.449185
Sum of electronic and thermal Enthalpies= -307.448240
Sum of electronic and thermal Free Energies= -307.483854

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NImag=0\\\@

NATURAL BOND ORBITALS (Summary):

NBO	Occupancy	Energy
1. BD (1) C 1- C 2	1.98109	-0.70222
2. BD (2) C 1- C 2	1.65930	-0.24949
3. BD (1) C 1- C 6	1.97651	-0.68592
4. BD (1) C 1- H 12	1.97966	-0.52252
5. BD (1) C 2- C 3	1.97468	-0.69251
6. BD (1) C 2- O 7	1.99491	-0.89705
7. BD (1) C 3- C 4	1.97705	-0.68414
8. BD (2) C 3- C 4	1.69764	-0.23908
10. BD (1) C 4- C 5	1.98069	-0.67950
12. BD (1) C 5- C 6	1.98041	-0.68219
13. BD (2) C 5- C 6	1.68168	-0.23748
121. BD*(2) C 1- C 2	0.39337	0.03571
125. BD*(1) C 2- O 7	0.02411	0.35741
127. BD*(2) C 3- C 4	0.33501	0.04471
132. BD*(2) C 5- C 6	0.34586	0.04420

7 *O*-Methyl pyrrole-2-carboxylate

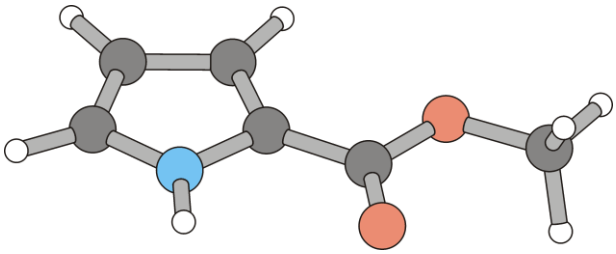

Figure S20 Equilibrium geometry of *O*-methyl pyrrole-2-carboxylate

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	1.413380	0.997704	0.000000
2	6	0	0.476513	-0.011602	0.000000
3	6	0	1.161922	-1.217983	-0.000001
4	6	0	2.542943	-0.916892	0.000000
5	6	0	2.665162	0.463673	0.000001
6	6	0	-0.936553	0.340879	0.000000
7	8	0	-1.348277	1.486026	-0.000002
8	8	0	-1.739908	-0.743285	0.000000
9	6	0	-3.152885	-0.475568	0.000001
10	1	0	1.165027	1.975633	0.000008
11	1	0	0.703691	-2.193673	-0.000002
12	1	0	3.360253	-1.620754	-0.000001
13	1	0	3.542509	1.090311	0.000002
14	1	0	-3.631357	-1.452484	-0.000054
15	1	0	-3.435463	0.089988	0.889112
16	1	0	-3.435447	0.090083	-0.889054

Zero-point correction= 0.125314 (Hartree/Particle)
Thermal correction to Energy= 0.133576
Thermal correction to Enthalpy= 0.134520
Thermal correction to Gibbs Free Energy= 0.091907
Sum of electronic and zero-point Energies= -438.060068
Sum of electronic and thermal Energies= -438.051806
Sum of electronic and thermal Enthalpies= -438.050862
Sum of electronic and thermal Free Energies= -438.093474

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e-06\Dipole=0.2879537,-0.0000389,-0.0559288\PG=C01 [X(C6H7N1O2)]\
NImag=0\\\@

NATURAL BOND ORBITALS (Summary):

	NBO	Occupancy	Energy
1.	BD (1) C 1- N 2	1.98695	-0.80582
2.	BD (1) C 1- C 5	1.98058	-0.68497
3.	BD (2) C 1- C 5	1.78969	-0.24982
5.	BD (1) N 2- C 3	1.98265	-0.79137
7.	BD (1) C 3- C 4	1.97544	-0.68553
8.	BD (2) C 3- C 4	1.77181	-0.24739
10.	BD (1) C 4- C 5	1.97502	-0.65294
13.	BD (1) C 6- O 7	1.99267	-0.91125
14.	BD (1) C 6- O 9	1.99677	-1.06648
15.	BD (2) C 6- O 9	1.98371	-0.36859
16.	BD (1) O 7- C 8	1.99134	-0.80200
29.	LP (1) N 2	1.56168	-0.25437
152.	BD*(1) C 1- N 2	0.01316	0.48258
154.	BD*(2) C 1- C 5	0.35339	0.03114
159.	BD*(2) C 3- C 4	0.39398	0.03937
166.	BD*(2) C 6- O 9	0.30684	0.01742

8 References

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