I. Gaussian Code Changes

The following are the changes to the G98 routines needed to allow proper calculation of the structures in this paper. Most are additions to the UFF force field to allow for calculations on square planar rhodium complexes and coordinated double bonds. All routines were in the utilam.F and utilnz.F files, and changes are highlighted in bold.

```
****

*Deck AtSym

C Adding Rh4+1 (four coordinate, singly charged, square planar
C Rhodium) and C_X (alpha carbon special atom, to mimic ethylene
C coordination to Rhodium) atom types.

      Parameter (NumFF=2,MaxTyp=130,IAmbEx=(MaxTyp-49)
        .
        .
        .
      Data (AtSymm(I,1),ICh(I,1),IHy(I,1),I=1,MaxTyp)/
     $ 'H_',    1,0, 'H_b',   1,1, 'He4+4', 2,0, 'Li',    3,0,
     $ 'Be3+2', 4,4, 'B_3',   5,3, 'B_2',   5,2,
     $ 'C_X',   6,4, 'C_3',   6,3,
        .
        .
        .
     $ 'Ru6+2',44,6, 'Rh6+3',45,6, 'Rh4+1',45,4,
```

```
      .
      .
      .

End

*Deck EGHMM
      .
      .
      .
      Data Chi / 4.52800d0…
            .
            .
            .
     $  3.47000d0, 3.47500d0, 5.34300d0/
      .
      .
      .
      [line with Call GenCon commented out]

End

****

*Deck UFFP
      .
      .
      .
C     C_R, C_1, C_2, C_3, C_X
C  C_X is the alpha-carbon, similar to C_2.
      Data IDefTp(6)/0/
      Data ((Param(I,J,6),I=1,MaxPar),J=0,MaxHyb)/
     $  0.729d0,120.00d0,3.851d0,0.105d0,12.730d0,1.912d0,
     $  0.706d0,180.00d0,3.851d0,0.105d0,12.730d0,1.912d0,
     $  0.732d0,120.00d0,3.851d0,0.105d0,12.730d0,1.912d0,
     $  0.757d0, -1.00d0,3.851d0,0.105d0,12.730d0,1.912d0,
     $  0.732d0,120.00d0,3.851d0,0.105d0,12.730d0,1.912d0,
     $  MaxPar*0.0d0,MaxPar*0.0d0/
      .
      .
      .
C     Rh6+3,Rh4+1
C  Rh4+1 is a 4-coordinate square-planar Rhodium (+1)
      Data IDefTp(45)/6/
      Data ((Param(I,J,45),I=1,MaxPar),J=0,MaxHyb)/
     $  MaxPar*0.0d0,MaxPar*0.0d0,MaxPar*0.0d0,MaxPar*0.0d0,
     $  1.332d0,  90.0d0,2.929d0,0.053d0,12.0d0,3.508d0,
     $ MaxPar*0.0d0,
     $  1.332d0,  90.0d0,2.929d0,0.053d0,12.0d0,3.508d0/
      .
      .
      .
      Call UFFPB(IOut,IPrint,ToAng,NAtoms,IAtTyp,MxBond,NBond,IBond,
     $  IBType,IAn,Chi,AtParm(1,IPRad),AtParm(1,IPZeff),HaveR,RBType,
     $  NIntC(2),NDInt,MaxNC,IntCor,NDReal,RCord,IAType)
      .
      .
      .
      Call UFFPA(ToAng,NAtoms,IAtTyp,MxBond,NBond,IBond,IAType,
     $  AtParm(1,IPAng),AtParm(1,IPZeff),C,NIntC(3),NIntC(1),NIntC(2)-1,
     $  NDInt,MaxNC,IntCor,NDReal,RCord,IAn)
      .
```

```
      .
      .
End

****

*Deck UFFPB
      Subroutine UFFPB(IOut,IPrint,ToAng,NAtoms,IAtTyp,MxBond,NBond,
     $  IBond,IBType,IAn,Chi,AtRad,Z0,HaveR,RBType,IC,NDInt,MaxNC,
     $  IntCor,NDReal,RCord,IAType)
      .
      .
      .
      Data Lambda/0.1332d0/, Two/2.d0/, AmidBO/1.41d0/, OnePt5/1.5d0/,
     $ RhC/2.195d0/,RhCk/.4d0/
1000 Format(' I=',i6,' J=',i6,' Qi=',i3,' Qj=',i3,' BO=',f5.3,' Ri=',
     $ f5.3,' Rj=',f5.3,' Rbo=',f5.3,' Ren=',f5.3,' Rij=',f5.3)
C
      KPH = Hartre * Avog / (JPCal * GFloat(1000))
      Do 20 I = 1, NAtoms
        If(IAtTyp(I).ge.0) then
          Do 10 IB = 1, NBond(I)
            J = IBond(IB,I)
            If(J.gt.I.and.IAtTyp(J).ge.0) then
              IntCor(1,IC) = I
              IntCor(2,IC) = J

C If this is a Rh-C_X bond, set the bond length to the crystal structure
C bond length of 2.195 angstroms. This assumes Rh is always atom #1.
C Also using an arbitrarily fairly large force constant (.4 = 896)

              If((IAn(I).eq.45).and.((IAn(J).eq.6).and.
     $          (IAType(J).eq.4))) then
                RCord(1,IC) = RhC/ToAng
                RCord(2,IC) = RhCk
                RCord(3,IC) = 1
                IC = IC + 1
                goto 10
                endIf
      .
      .
      .
End


****


*Deck UFFPA
      Subroutine UFFPA(ToAng,NAtoms,IAtTyp,MxBond,NBond,IBond,IAType,
     $  AtAng,Z0,C,IC,NSt,NEnd,NDInt,MaxNC,IntCor,NDReal,RCord,IAn)
      .
      .
      .
                If(JT.gt.3) then
                Call ASUnit(3,C(1,I),C(1,J),VIJ)
                Call ASUnit(3,C(1,K),C(1,J),VJK)
                CosA = SProd(3,VIJ,VJK)
                endIf
```

```
C Look for C_X in the middle of the angle, and see if it's the
C Rh-C_X angle terms

                  If((IAn(J).eq.6).and.(IAType(J).eq.4)) then
                   If((IAn(I).eq.45).or.(IAn(K).eq.45)) then
                    If(((IAn(I).eq.6).and.(IAType(I).eq.2)).or.
     $                 ((IAn(K).eq.6).and.(IAType(K).eq.2))) then
                      IntCor(4,IC) = 6
                      RCord(1,IC) = 0.31867d0
                      IC = IC + 1
                      goto 10
                    else
                      IntCor(4,IC) = 7
                      RCord(1,IC) = 0.31867d0
                      IC = IC + 1
                      goto 10
                      endIf
                   else
                     IntCor(4,IC) = 2
                     RCord(1,IC) = RKijk/F9
                     IC = IC + 1
                     goto 10
                     endIf
                    endIf
C                 Linear
                  If(Abs(Sin(AtAng(J))).lt.SinLin) then
        .
        .
        .
End



****


*Deck UFFPT
        .
        .
        .
Do 201 J = 1, NAtoms
        If(NBond(J).lt.2.or.IAtTyp(J).lt.0) goto 201
        JCX = 0
        JT = IAType(J)

C If J = C_X, make the torsion like C_2.
        If((IAn(J).eq.6).and.(JT.eq.4)) then
          JCX = 1
          JT = 2
          endIf

        JOCol = IAn(J).eq.8.or.IAn(J).eq.16.or.IAn(J).eq.34.or.
     $    IAn(J).eq.52.or.IAn(J).eq.84
        JRes = JT.eq.0.and.(IAn(J).eq.6.or.IAn(J).eq.7.or.IAn(J).eq.8
     $    .or.IAn(J).eq.16)
        JRes2 = JRes.or.JT.eq.2
```

```
        Do 200 JBK = 1, NBond(J)
          K = IBond(JBK,J)
          KCX = 0
          If(NBond(K).lt.2.or.IAtTyp(K).lt.0) goto 200
          If(K.lt.J) goto 200
          KT = IAType(K)

C If K = C_X, make it look like C_2
          If((IAn(K).eq.6).and.(KT.eq.4)) then
            KCX = 1
            KT = 2
            endIf
          KOCol = IAn(K).eq.8.or.IAn(K).eq.16.or.IAn(K).eq.34.or.
     $      IAn(K).eq.52.or.IAn(J).eq.84

      .
      .
      .


If(VJK.ne.Zero) then

C Necessary to get proper number of true bonds to C_X
            If (JCX.eq.1) then
              VJK = Pt5 * VJK / (KPH*(NBond(J)-2)*(NBond(K)-1))
            else if (KCX.eq.1) then
              VJK = Pt5 * VJK / (KPH*(NBond(J)-1)*(NBond(K)-2))
            else
              VJK = Pt5 * VJK / (KPH*(NBond(J)-1)*(NBond(K)-1))
              endIf

            Call ASUnit(3,C(1,K),C(1,J),D)
            Do 110 JBI = 1, NBond(J)
              I = IBond(JBI,J)
              If(I.eq.K.or.IAtTyp(I).lt.0) goto 110

C This removes Rh-C_X-C_2-H torsions
              If((JCX.eq.1).and.(IAn(I).eq.45)) goto 110
C               goto 110
C               endIf
C             If((KCX.eq.1).and.(IAn(I).eq.45)) then
C               KCX = 0
C               VJK = 0
C               endIf
              IRes = IAType(I).eq.0.and.(IAn(I).eq.6.or.IAn(I).eq.7.or.
     $          IAn(I).eq.8.or.IAn(I).eq.16)
      .
      .
      .

End


****


*Deck UFFPI

      .
      .
```

```
Do 10 I = 1, NAtoms
      IT = IAType(I)
C Feldgus added - Gives C_X an inversion
        If((IAn(I).eq.6).and.(IT.eq.4)) then
          J = IBond(1,I)
          If (IAn(J).eq.45) J = IBond(4,I)
          K = IBond(2,I)
          If (IAn(K).eq.45) K = IBond(4,I)
          L = IBond(3,I)
          If (IAn(L).eq.45) L = IBond(4,I)
          VI = F6 / KPH
          IntCor(1,IC) = I
          IntCor(2,IC) = J
          IntCor(3,IC) = K
          IntCor(4,IC) = L
          IntCor(5,IC) = 0
          RCord(1,IC) = VI/Three
          IC = IC + 1
          goto 10
          endIf
        If(NBond(I).eq.3.and.IAtTyp(I).ge.0) then
        .
        .
        .
End

****

*Deck UFFA
        .
        .
        .
else if(IntCor(4,IC).eq.1) then

C The original expression for dE was RKijk*(One - CosT). This gave
C incorrect behavior for linear angles. One - Cos2T (with the
C corresponding change in derivative) works much better.
          dE = RKijk*(One - Cos2T)
C         Note factor of Sin(T) cancelled here and in B elements.
C          dEdT = -RKijk (The original derivative)
          dEdT = 2*RKijk

         else if(IntCor(4,IC).eq.2) then
          Cos3T = CosT*Cos2T - SinT*Sin2T
          Sin3T = SinT*Cos2T + CosT*Sin2T
          dE = RKijk*(One - Cos3T)
          dEdT = F3*RKijk*Sin3T
        else if(IntCor(4,IC).eq.3) then
          Cos4T = Cos2T*Cos2T - Sin2T*Sin2T
          Sin4T = Two*Sin2T*Cos2T
          dE = RKijk*(One - Cos4T)
          dEdT = F4*RKijk*Sin4T
        else if(IntCor(4,IC).eq.4) then
          Cos4T = Cos2T*Cos2T - Sin2T*Sin2T
          Sin4T = Two*Sin2T*Cos2T
          dE = RKijk*(One - Cos4T)
          dEdT = F4*RKijk*Sin4T
          endIf

C IntCor(4,IC) = 5 means C_2-CiR-X angle
```

```
        If(IntCor(4,IC).eq.5) then
          dE = (RKijk/2)*CosT
          dEdT = -(RKijk/2)*SinT
          endIf

C IntCor(4,IC) = 6 means a Rh-C_X-C_2 angle.
C IntCor(4,IC) = 7 means a Rh-C_X-? (any atom) angle.
C The Rh-C_X-C_2 angle from the crystal structure is about
C 73.4 degrees (73 degrees = 1.274 radians). The Rh-C_X-?
C angle is therefore 180-73 = 107 degrees = 1.867 radians.

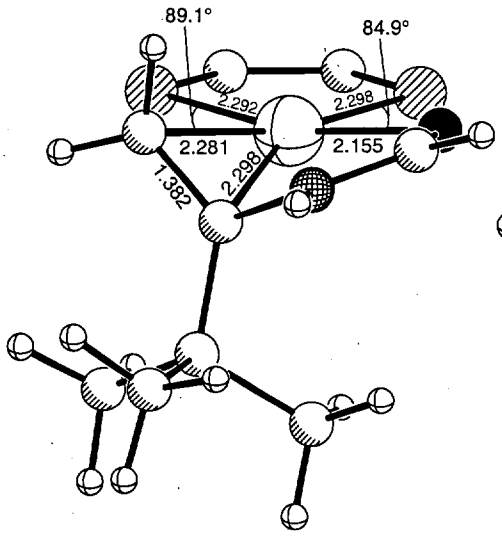
        If((IntCor(4,IC).eq.6).or.(IntCor(4,IC).eq.7)) then
           T0 = 1.274d0
           If(IntCor(4,IC).eq.7) T0 = 1.867d0
           CosT0 = Cos(T0)
           CosT02 = CosT0*CosT0
           C2 = One/(F4*One - CosT02)
           C1 = -F4*C2*CosT0
           C0 = C2*(Two*CosT02 + One)
           dE = RKijk*(C0 + C1*CosT + C2*Cos2T)
           dEdT = -RKijk*(C1*SinT + Two*C2*Sin2T)
           endIf

        If(IntCor(4,IC).eq.1) then
        .
        .
        .
End
```

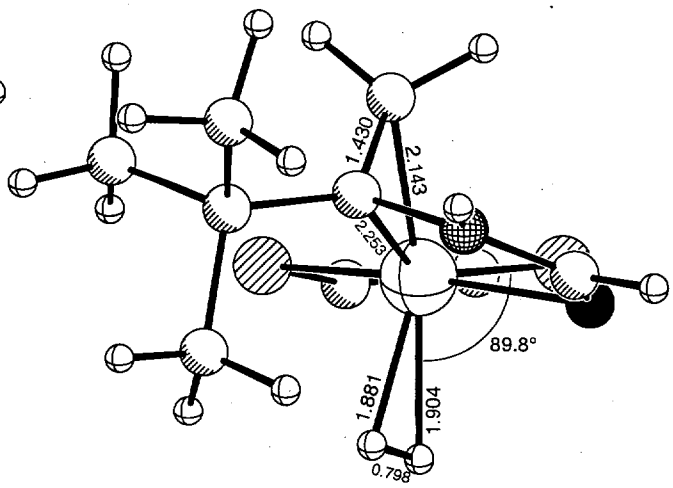
II. Figures for higher energy structures

Constrained structures have italicized labels.

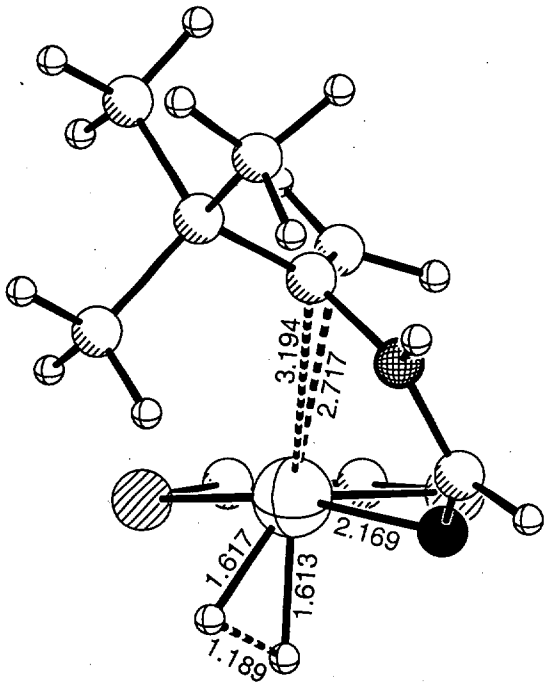
Pathway R-C



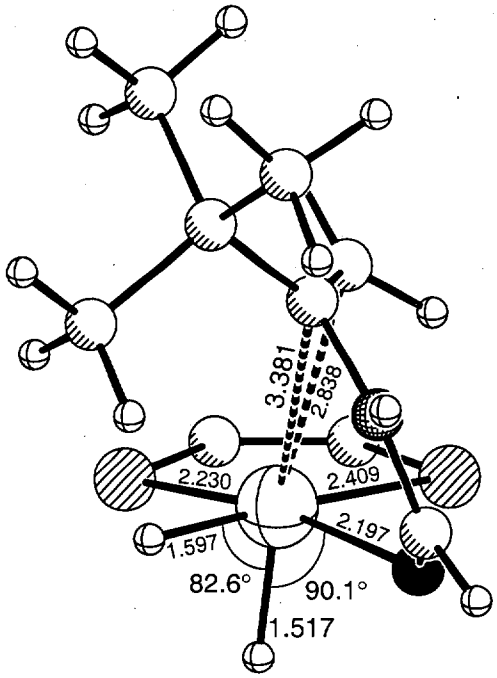
PRO-*R*



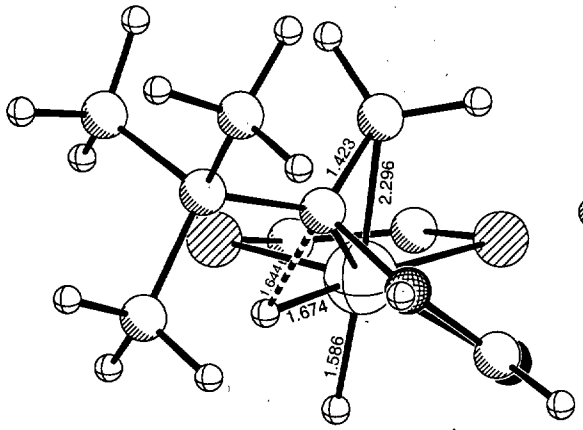
R-MOLH$_2$-C



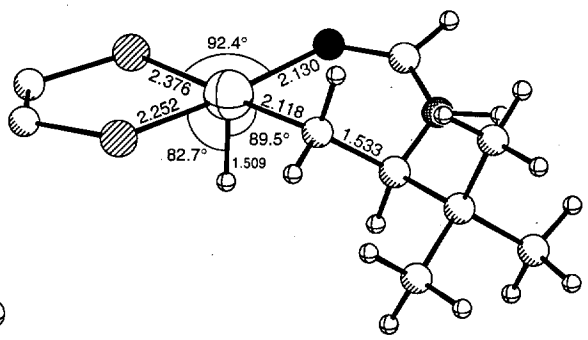
R-MOLH$_2$-C‡



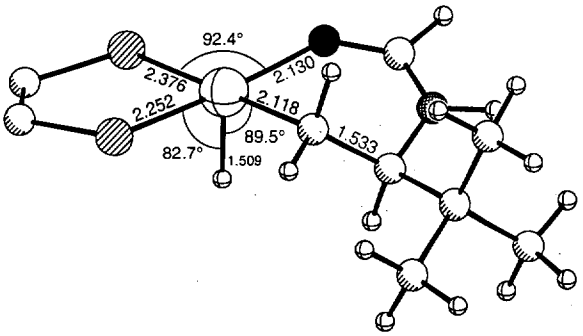
R-DIHY-C



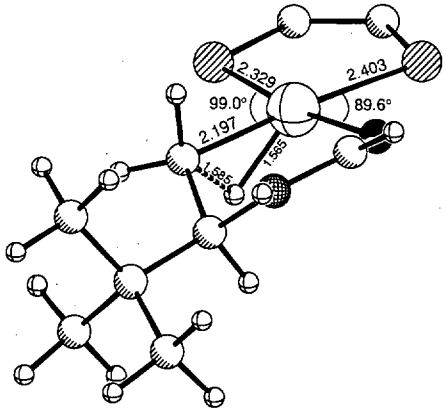
R-ALHY-Cβ‡



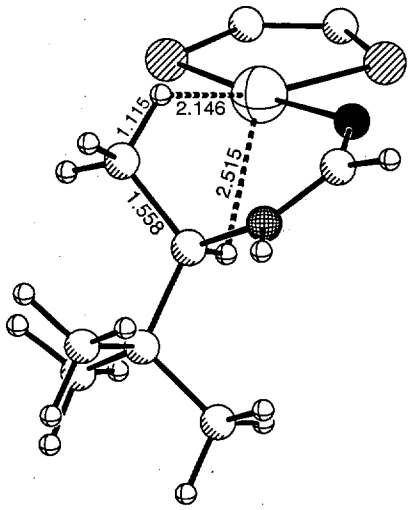
R-ALHY-C$_{trans}$β



R-ALHY-Cβ

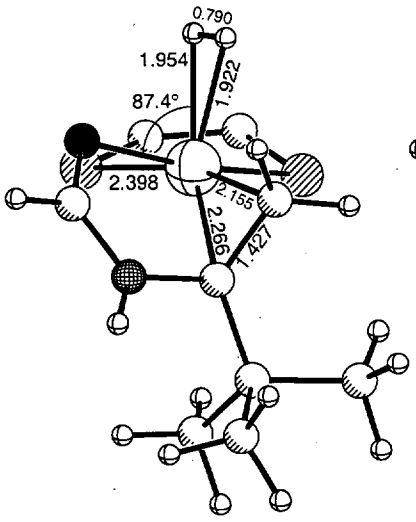


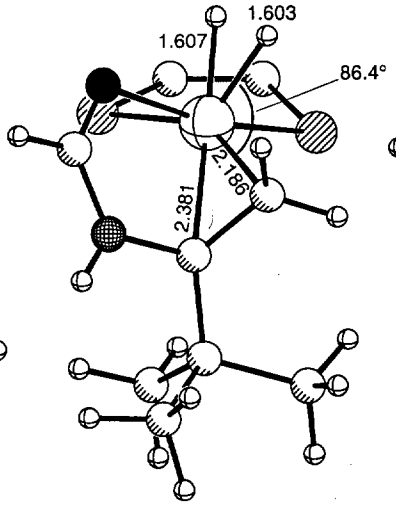
R-ALHY-Cβ‡

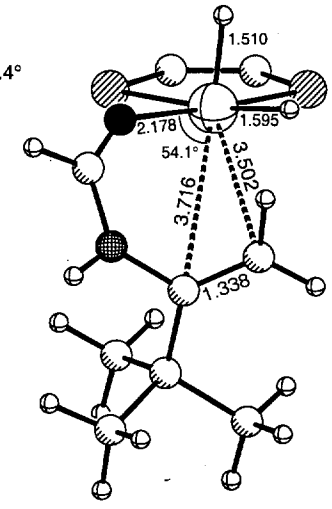


R-PROD-C

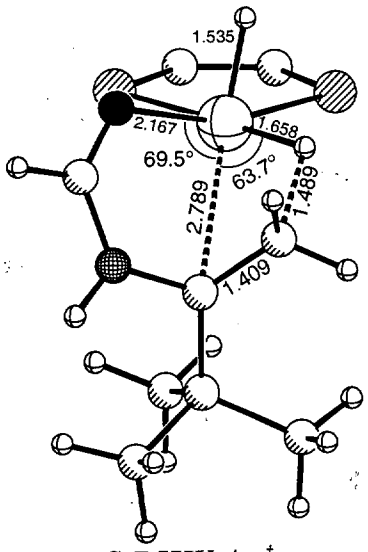
Pathway S-A

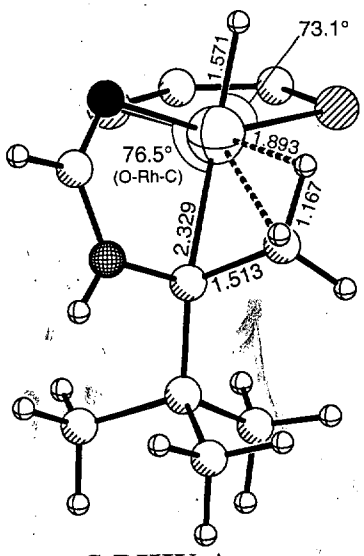




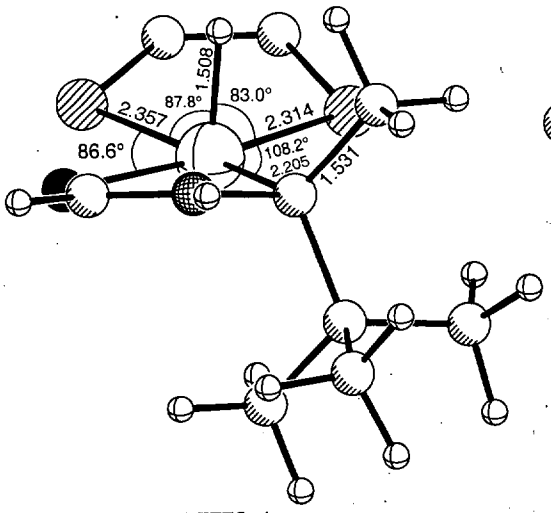


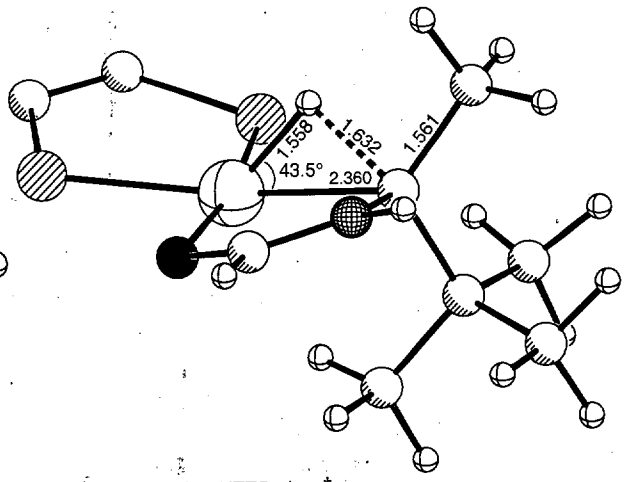
S-MOLH$_2$-A *S-MOLH$_2$-A‡* **S-DIHY-A**



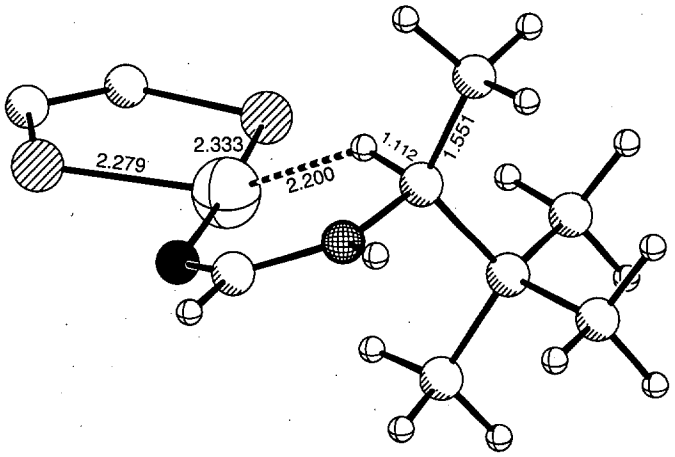


S-DIHY-Aα‡ **S-DIHY-A$_{trans}$α**





S-ALHY-Aα **S-ALHY-Aα‡**



S-PROD-A

III. NBO Results

Results of NBO analysis of selected diastereomers. The polarization for π* is exactly opposite that of π. All structures were analyzed at the B3LYP/LANL2DZ level. The results for the lower energy structure are in bold.

Structure	π occ. % α / % β	π* occ.	C=C→Rh donation			Rh→C=C backdonation		
			ΔE_{ij} (kcal/mol)	ε_j-ε_i (a.u.)	F(i,j) (a.u.)	ΔE_{ij} (kcal/mol)	ε_j-ε_i (a.u.)	F(i,j) (a.u.)
–CN Pro-R	1.686 56.1 / 43.9	0.392	71.89	0.47	0.163	73.15	0.20	0.107
–CN *Pro-S*	***1.664 61.0 / 39.0***	***0.481***	***54.81***	***0.45***	***0.144***	***140.28***	***0.11***	***0.116***
–CO_2H	1.690 56.4 / 43.6	0.353	68.74	0.45	0.158	65.20	0.20	0.103
	1.651 61.2 / 38.8	***0.471***	***51.36***	***0.44***	***0.138***	***140.09***	***0.11***	***0.114***
–CH_3	1.719 50.5 / 49.5	0.308	63.62	0.47	0.155	50.96	0.22	0.096
	1.689 56.0 / 44.0	***0.381***	***56.91***	***0.45***	***0.148***	***78.80***	***0.15***	***0.102***
–H	1.711 51.9 / 48.1	0.320	74.68	0.47	0.170	59.65	0.21	0.102
	1.688 57.5 / 42.5	***0.392***	***67.29***	***0.46***	***0.163***	***85.25***	***0.15***	***0.103***
–*t*Bu	**1.769 50.6 / 49.4**	**0.234**	**47.44**	**0.49**	**0.137**	**34.11**	**0.25**	**0.082**
	1.776 53.9 / 46.1	*0.293*	*41.38*	*0.49*	*0.129*	*41.98*	*0.23*	*0.089*
–*t*Bu (achiral)	**1.759 50.8 / 49.2**	**0.242**	**50.09**	**0.50**	**0.143**	**36.38**	**0.25**	**0.086**
	1.767 53.5 / 46.5	*0.282*	*45.65*	*0.49*	*0.135*	*41.79*	*0.24*	*0.070*
–NH_2	**1.652 44.5 / 55.5**	**0.439**	**58.93**	**0.45**	**0.146**	**32.66**	**0.21**	**0.076**
	1.647 44.3 / 55.7	*0.408*	*48.11*	*0.41*	*0.127*	*26.41*	*0.21*	*0.070*
βCN	1.680 47.8 / 52.2	0.434	64.76	0.46	0.157	80.99	0.18	0.109
	1.674 54.5 45.5	***0.469***	***64.25***	***0.46***	***0.158***	***88.76***	***0.14***	***0.103***
3	**1.694 51.9 / 48.1**	**0.273**	**73.48**	**0.45**	**0.164**	**51.88**	**0.22**	**0.097**
	1.696 51.4 / 48.6	*0.268*	*74.57*	*0.45*	*0.165*	*50.85*	*0.23*	*0.097*

IV. Full optimized geometries and energies, α-substituents

The energy preceding each geometry is direct Gaussian output. Under 'E23456', on the first line you find (left to right) the RHF energy of the core layer, the MM energy of the intermediate layer, and the B3LYP energy of the core. The second line has (left to right) the RHF layer of the intermediate layer, the MM energy of the entire molecule, and an additional number of little importance (equal to the difference in the two HF calculations minus the difference between the MM energies of the intermediate and core layer).

R-CN

```
 E23456=   -532.457513871537      0.310215898920   -541.538761310346
           -838.861767647370      0.324345071449   -306.525824371053
 ONIOM: extrapolated energy =    -847.928885913650

Rh         0.000000000000      0.000000000000      0.000000000000
 O         0.000000000000      0.000000000000      2.146990606669
 C         1.172393142473      0.000000000000      2.654478483613
 N         2.263667019732     -0.026194943647      1.869474849915
 C         2.105496093277     -0.118124178543      0.405228008648
 C         1.713733076226     -1.371833904876     -0.150401044713
 C         2.887089086379      0.860182248640     -0.311217495221
 N         3.534443601034      1.664362244421     -0.886224309860
 H         1.550339725333     -2.221144327553      0.507303200351
 H         1.987272179273     -1.614543204970     -1.169740033900
 H         3.199565172698     -0.018866634892      2.267660668862
 H         1.307896594925      0.015275840639      3.736724860593
 P        -2.102814736572      1.181896159843      0.044605488962
 P        -0.258069611959      0.096096797178     -2.352450671609
 C        -2.576520295780      1.566469502628     -1.715324560109
 C        -1.782992343518      1.124386687005     -2.732017786977
 C        -3.572106881511      0.371851274289      1.052697964530
 C        -2.248166387813      2.853714258446      1.052506618978
 C        -0.555845018462     -1.545306435622     -3.393558616992
 C         1.276159854505      0.583435386617     -3.472296992213
 C        -2.159235855478      1.398876270831     -4.099929754543
 C        -3.765617906082      2.331154181062     -2.008640567313
 C        -4.514500943418     -0.395931675225      0.161158684460
 C        -0.882430081457      3.368882100871      1.421957627332
 C        -0.861611171487     -2.707712357687     -2.486547413288
 C         1.294871598838      2.053461284286     -3.806069510916
 H        -3.091286411107     -0.316811151474      1.740113750207
 H        -2.742938661207      3.583622687316      0.418022811473
 H        -1.411965692947     -1.366112464633     -4.037347258726
 H         2.146042622409      0.354905223754     -2.867860348887
 C        -4.239876731827      1.536509224213      1.819292895687
 C        -3.125907505100      2.501190471994      2.277523499550
 C         0.728999129284     -1.734366050234     -4.234964408989
 C         1.217087641982     -0.347113105191     -4.705948700965
 H        -4.941108166519      2.067538505718      1.178543268676
 H        -4.789586510489      1.148264372777      2.674796818133
```

H	-2.526898361374	2.015415247692	3.045984566542
H	-3.548753251918	3.410804057971	2.700128766880
H	1.509200835794	-2.207157992184	-3.641112645488
H	0.518516401552	-2.379620447971	-5.085881280078
H	0.534969775181	0.044526531758	-5.457003022776
H	2.205457438203	-0.420038397771	-5.156187795573
H	-0.288222603675	3.553369932195	0.501867527434
H	-0.978161908426	4.323754615904	1.980848399539
H	-0.341721144951	2.635818409395	2.054985002607
H	-3.950570568105	-1.161866096726	-0.412335540549
H	-5.281770787751	-0.908184532624	0.779227663451
H	-5.027608358657	0.281022197384	-0.551936514238
H	2.233683357304	2.302456784803	-4.344404111540
H	0.436192369734	2.330595746374	-4.449277832234
H	1.252696673183	2.652465720012	-2.871843761907
H	-1.059334556017	-3.616860869818	-3.092870957985
H	-0.012920814486	-2.911748519901	-1.803115610028
H	-1.763871761030	-2.482457235738	-1.879134475606
C	-3.311097487300	2.137939467508	-4.376226789998
C	-4.111234294777	2.605506489366	-3.332646428572
H	-1.560820518405	1.027581047490	-4.918948652074
H	-3.586941793376	2.344313147445	-5.402232240854
H	-5.004368197546	3.176576916643	-3.550566462960
H	-4.396632185646	2.690828694255	-1.207327917001

S-CN

E23456= -532.444252847312 0.311979345467 -541.541310385767
-838.851808236593 0.324971202129 -306.527364541992
ONIOM: extrapolated energy = -847.935873918386

Rh	0.000000000000	0.000000000000	0.000000000000
O	0.000000000000	0.000000000000	2.145761000000
C	1.175669161224	0.000000000000	2.658872038194
N	2.272456854848	0.089621877087	1.887648667141
C	2.114317244885	0.269356199977	0.436136045763
C	1.472536631336	1.493538652812	-0.011490821741
C	3.084129344919	-0.427682499133	-0.359784531890
N	3.863841772879	-1.003015760941	-1.038126825620
H	1.225346035902	2.251887087824	0.729522307032
H	1.702985143556	1.891650247805	-0.993165050889
H	3.202236642381	0.079330727621	2.299835618826
H	1.300823825440	-0.070424163131	3.739889943918
P	-2.357537133239	0.356719562107	-0.192324665252
P	-0.067595959055	-0.299506728742	-2.328019720311
C	-2.786705230255	0.337281529229	-2.008233123464
C	-1.811942029565	0.051509494764	-2.917684601160
C	-3.556607120531	-0.799696621668	0.840709700623
C	-3.137639946840	1.971197344996	0.589155920429
C	0.336298579758	-2.103416755404	-2.982138464200
C	1.303446226575	0.487604174446	-3.485902581142
C	-2.146946276102	-0.032512350330	-4.320069427045
C	-4.133595093759	0.602602075660	-2.454663896184
C	-4.085798359825	-1.946766811958	0.017842332399
C	-2.047935857319	2.929490683064	0.990642861818
C	0.437599280213	-3.060015174599	-1.823421778807
C	0.861157468689	1.793525037133	-4.095931079093
H	-2.941324280545	-1.191217552784	1.644619286361

H	-3.766829509366	2.439216348726	-0.162841495351
H	-0.482252821833	-2.407571856660	-3.628479306095
H	2.149696556266	0.668261034240	-2.832940334243
C	-4.653699930452	0.136716773149	1.395921974949
C	-3.980874256627	1.469012875164	1.787342182638
C	1.657061761176	-1.964828591734	-3.779692128666
C	1.656732128672	-0.608685428718	-4.516741406887
H	-5.420402339208	0.319814794978	0.645753909090
H	-5.128789094112	-0.322601881731	2.260881766419
H	-3.344443055951	1.304136534845	2.655230670954
H	-4.725426156172	2.218214590889	2.050173070863
H	2.512881323341	-2.003845223674	-3.108230246243
H	1.742825346344	-2.788473577081	-4.485917952801
H	0.933545797516	-0.627093007351	-5.328847849885
H	2.637558093573	-0.405814893704	-4.943034601324
H	-1.463831723425	3.231441750466	0.095450677669
H	-2.492554568866	3.838276189530	1.448611772002
H	-1.359436771978	2.455545369537	1.721925972570
H	-3.239993081816	-2.522197128037	-0.414624915313
H	-4.684847777263	-2.624767740032	0.661681838580
H	-4.730534852130	-1.580540829098	-0.806831962705
H	1.706976642069	2.252190755323	-4.650268934214
H	0.019327814120	1.643216188607	-4.800507067167
H	0.539757958632	2.493993516312	-3.296561183631
H	0.688068280027	-4.077124464746	-2.192209251959
H	1.221964915717	-2.728846931199	-1.110303858676
H	-0.534374883011	-3.104634309391	-1.287516740953
C	-3.452671987589	0.221798596727	-4.744821913673
C	-4.442578005958	0.544666096658	-3.814749420496
H	-1.395814519910	-0.300535708173	-5.048542806750
H	-3.698801017773	0.164154435264	-5.797198707647
H	-5.453580190906	0.740649747836	-4.147761020040
H	-4.910200106631	0.839126196558	-1.740320189007

R-CO_2H

E23456= -627.011961594357 0.433708089254 -637.877492384337
-933.415002732857 0.448856285304 -306.546984482093
ONIOM: extrapolated energy = -944.265385326786

Rh	0.000000000000	0.000000000000	0.000000000000
O	0.000000000000	0.000000000000	2.140281000000
C	1.169912913780	0.000000000000	2.658760211922
N	2.264451892201	-0.058366194283	1.888024787149
C	2.136864295411	-0.164339686091	0.431467937625
C	1.691734581947	-1.388256304435	-0.136164600249
C	3.049252832458	0.735571479686	-0.333449789453
O	3.662947280853	1.657283156798	0.493390597349
H	4.277053949088	2.244857895941	-0.004298424543
O	3.293836862084	0.659614100887	-1.546973218800
H	1.463142132186	-2.239562495689	0.499008342680
H	1.988646362586	-1.611600408168	-1.153923597242
H	3.190821022165	0.059803172316	2.288933377347
H	1.293183980499	0.041458048252	3.741519339387
P	-2.261484441612	0.810560185434	0.103392899640
P	-0.357617038907	0.027010117941	-2.357850215339
C	-2.862459485849	1.112357745264	-1.628599027029
C	-2.043424407543	0.805791722056	-2.674171660149
C	-3.523627012239	-0.233701233810	1.171757011502

C	-2.635159718367	2.434192293470	1.129816462757
C	-0.487236203816	-1.632594121003	-3.412016539184
C	1.024476696743	0.727279403939	-3.560209074152
C	-2.509227303971	1.022751481316	-4.025672313734
C	-4.169957724594	1.673751490995	-1.871464096436
C	-4.368911157925	-1.144139454532	0.318058898590
C	-1.359528555269	3.173693275539	1.434873858206
C	-0.641908792819	-2.841503579708	-2.527458747050
C	0.805198245565	2.179264766230	-3.900744674737
H	-2.903677937481	-0.835025338996	1.828857783803
H	-3.278374759608	3.070521783867	0.528628943048
H	-1.373200565487	-1.541513830736	-4.033207872239
H	1.940706752571	0.636763720166	-2.988055790554
C	-4.336972999038	0.802795200780	1.980715631792
C	-3.377508342026	1.938746644731	2.393927320523
C	0.785468467877	-1.653193533830	-4.289277470766
C	1.051925220702	-0.215285356066	-4.785610377911
H	-5.146529360971	1.211114471267	1.378813308316
H	-4.772883120398	0.327501597143	2.857556353486
H	-2.667264269170	1.557605902951	3.125725674339
H	-3.924149346703	2.763552468767	2.847373294887
H	1.641896283713	-2.000187394511	-3.714142356523
H	0.644159767306	-2.333024090260	-5.127577395770
H	0.294783785471	0.063679471121	-5.514977436973
H	2.024124197569	-0.151487790626	-5.271030436605
H	-0.852828408844	3.456123947440	0.487717797321
H	-1.587524236085	4.098756919628	2.005490357900
H	-0.670730315241	2.544129030944	2.034512066725
H	-3.715520451139	-1.807616446305	-0.287228983378
H	-5.013986235603	-1.774631919370	0.965730734893
H	-5.016832809231	-0.558571520925	-0.365698126750
H	1.672910192883	2.561590791406	-4.478712154665
H	-0.110092251784	2.317413858385	-4.509248625682
H	0.711563637820	2.774637291276	-2.967935979080
H	-0.802858084141	-3.745053638667	-3.152728956085
H	0.259010309044	-3.001773086781	-1.904742616297
H	-1.520910783755	-2.709974388756	-1.861406459236
C	-3.775255255663	1.565585133599	-4.254610463381
C	-4.603145466836	1.892502572010	-3.179689350772
H	-1.890735909428	0.755037017685	-4.869659282683
H	-4.118304209787	1.726431464369	-5.268428899477
H	-5.584836558019	2.310531277454	-3.360969346244
H	-4.820583522761	1.924143653415	-1.044516754601

S-CO_2H

E23456= -626.995560279177 0.435762034058 -637.882936929022
-933.400710047441 0.448765192393 -306.531685246562
ONIOM: extrapolated energy = -944.275083538951

Rh	0.000000000000	0.000000000000	0.000000000000
O	0.000000000000	0.000000000000	2.140873000000
C	1.177108470123	0.000000000000	2.658747160017
N	2.271881501952	0.110280306235	1.896371632813
C	2.132202926387	0.293607576267	0.450556012544
C	1.465082399454	1.495140536639	-0.010707042073
C	3.183070896838	-0.349714067612	-0.363227755776
O	4.055448291779	-1.089518113865	0.422651345909

H	4.763951827332	-1.512012069587	-0.114481599103
O	3.327193740835	-0.245462400472	-1.593852021872
H	1.198368220380	2.259151653455	0.717511915846
H	1.705485596163	1.876370214774	-0.996751657060
H	3.202559563416	-0.013038491551	2.287254797093
H	1.295535276398	-0.092014096709	3.738558351169
P	-2.351187524135	0.354973520723	-0.106619863174
P	-0.133977941256	-0.241925523655	-2.343050256153
C	-2.865110640833	0.303218565235	-1.895609262436
C	-1.924103647130	0.036863969108	-2.845711013156
C	-3.472436738878	-0.805508755007	1.004100352908
C	-3.118534733855	1.967107061434	0.691339621269
C	0.324642299973	-1.997243788447	-3.084886670817
C	1.109588256692	0.657943204426	-3.555560431658
C	-2.323223076521	-0.062629582442	-4.231004411489
C	-4.238018384339	0.529355571672	-2.279530759290
C	-4.019828752707	-1.976709529471	0.228598606736
C	-2.027209042288	2.949354616171	1.024464408247
C	0.571832147982	-2.978507414161	-1.969603707508
C	0.563519966571	1.963374567100	-4.074496986448
H	-2.809013563210	-1.170709443678	1.781537788871
H	-3.792544002756	2.413543531504	-0.034480158554
H	-0.520491055272	-2.335621400898	-3.677519072366
H	1.988424977883	0.841442623395	-2.949569729904
C	-4.558443349596	0.118430702917	1.600270207221
C	-3.892332974679	1.469008506728	1.937176972237
C	1.569841105169	-1.755901994674	-3.974944488126
C	1.445063701239	-0.375506454862	-4.654415670861
H	-5.365124142811	0.275518288406	0.887028019063
H	-4.980914157919	-0.335325133431	2.494928112509
H	-3.210963271992	1.329269394309	2.774796603288
H	-4.636996250154	2.208638283968	2.225534351505
H	2.473989442229	-1.765049554013	-3.369920311844
H	1.647176177705	-2.548640167470	-4.716709460066
H	0.674619749022	-0.403888235366	-5.421123294041
H	2.383918326559	-0.102961809076	-5.133058862156
H	-1.491283097707	3.245189509921	0.097630132834
H	-2.464734064225	3.858593483775	1.488320303615
H	-1.297212378782	2.498893348149	1.729865557011
H	-3.185659305450	-2.543997482774	-0.236080740975
H	-4.572542219053	-2.654105373493	0.913244264155
H	-4.712013161812	-1.637439596632	-0.568698110042
H	1.343070099781	2.484174782493	-4.669492055460
H	-0.321989458829	1.798483647603	-4.720315573790
H	0.272472820407	2.614756619407	-3.223536129180
H	0.852703395141	-3.967331171933	-2.389876387897
H	1.388406604004	-2.620348520304	-1.307409880828
H	-0.351191447375	-3.098205961536	-1.363295481936
C	-3.654204957883	0.150725687699	-4.595696421663
C	-4.608539344532	0.452048733466	-3.622735876183
H	-1.600272680331	-0.307628857146	-4.994208662246
H	-3.946890205032	0.080449069297	-5.635285774498
H	-5.638898806231	0.617991742446	-3.909380749249
H	-4.986115561610	0.751715385730	-1.530969806210

R-CH_3

E23456= -480.508982826501 0.309198089529 -488.647828564585

```
          -786.909115999917      0.322655084304   -306.522692827463
 ONIOM: extrapolated energy =    -795.034504743226
Rh        0.000000000000      0.000000000000      0.000000000000
 O        0.000000000000      0.000000000000      2.138932745405
 C        1.170887364930      0.000000000000      2.652703936244
 N        2.264589766669      0.024647806689      1.877401153719
 C        2.157850954648     -0.001646847874      0.397279788781
 C        1.841427106982     -1.248882864836     -0.185083707315
 C        2.956213283564      1.111292616530     -0.247699107048
 H        4.012590113563      1.059425417116      0.060435295303
 H        2.932690070530      1.043097291207     -1.336201196504
 H        2.571519366471      2.094301454170      0.045760322247
 H        1.693885952873     -2.129397384822      0.434456873836
 H        2.103752120155     -1.441704015729     -1.218757175864
 H        3.191903467581      0.040585760066      2.294997705411
 H        1.296390104385     -0.019924730521      3.736588822141
 P       -2.107867449023      1.129415801760      0.089494322142
 P       -0.363344644375     -0.028149197491     -2.334776641483
 C       -2.676482846731      1.433328645828     -1.661228062119
 C       -1.927316980948      0.955851553969     -2.696362966434
 C       -3.521719010413      0.342083173822      1.191063621107
 C       -2.241914808693      2.839513909174      1.031989093598
 C       -0.716934025143     -1.747389318522     -3.223656007836
 C        1.075121741712      0.374415774168     -3.606688496960
 C       -2.381931839837      1.148420453116     -4.054318190554
 C       -3.895564177929      2.160334279565     -1.926162050379
 C       -4.483125349329     -0.484658815309      0.375824204069
 C       -0.869742737002      3.382810877894      1.330658051338
 C       -0.903963713524     -2.839567106171     -2.204185382726
 C        1.078725346432      1.820396805204     -4.032082693033
 H       -2.999828424369     -0.304584844411      1.889095104487
 H       -2.768113052710      3.538911250263      0.388642310085
 H       -1.634629041741     -1.633937523287     -3.793276342696
 H        1.989135291123      0.169091144915     -3.062689281956
 C       -4.182086394664      1.527332378405      1.931483763128
 C       -3.069092335476      2.529751392212      2.303155710302
 C        0.487133463415     -1.985121756823     -4.166672472585
 C        0.920602266910     -0.631577212851     -4.769901946714
 H       -4.917543009321      2.017670623008      1.296790973328
 H       -4.691034352546      1.168819648741      2.824351187949
 H       -2.434532158053      2.088236567100      3.069756159243
 H       -3.491886885219      3.450491482824      2.700933880887
 H        1.322935460438     -2.414496075834     -3.617111942085
 H        0.206513311530     -2.685896836795     -4.950793145118
 H        0.176343254520     -0.291849314962     -5.485961294532
 H        1.868199847746     -0.732640494880     -5.295987000841
 H       -0.314310314989      3.544520002099      0.382462100015
 H       -0.955386748674      4.353752049488      1.862877522298
 H       -0.294931715951      2.675431098817      1.963621873294
 H       -3.926728885799     -1.263614239021     -0.187360074514
 H       -5.211709097078     -0.984486390028      1.048471666885
 H       -5.041553592754      0.148540064836     -0.343265136430
 H        1.971524813573      2.022782302931     -4.660674404966
 H        0.172083737811      2.069096090504     -4.618328321673
 H        1.119876630045      2.476062722882     -3.136632800420
 H       -1.123655034183     -3.800542028775     -2.715618491934
 H        0.008997847151     -2.961882822833     -1.585962154132
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H	-1.756117967187	-2.588505565469	-1.537400212482
C	-3.560630683700	1.857363908301	-4.307507430592
C	-4.316845464195	2.364813938612	-3.243299074657
H	-1.829935076650	0.731196667127	-4.882824944322
H	-3.891457280119	2.011794067563	-5.329484768120
H	-5.232657180037	2.912383833575	-3.441125829173
H	-4.492780608655	2.543514327525	-1.110168407200

S-CH_3

E23456= -480.502254854709 0.319484023109 -488.648515339489
-786.903113995913 0.332841023788 -306.522827557841
ONIOM: extrapolated energy = -795.036017480016

Rh	-0.344929	-1.206712	0.024580
O	0.637028	-3.085447	0.293707
C	-0.156555	-4.092363	0.267620
N	-1.466527	-3.936960	0.030134
C	-2.026198	-2.604565	-0.290057
C	-1.580552	-2.025545	-1.519202
C	-3.400401	-2.407514	0.316431
H	-4.106738	-3.170047	-0.049983
H	-3.375847	-2.478616	1.409143
H	-3.814970	-1.434483	0.043587
H	-0.915832	-2.578324	-2.180736
H	-2.189165	-1.278967	-2.016317
H	-2.086297	-4.743512	0.035777
H	0.230875	-5.096681	0.445097
P	1.755965	-0.044374	0.019586
P	-1.280666	0.951679	-0.000621
C	1.406699	1.779569	-0.168775
C	0.111352	2.206073	-0.181373
C	3.027541	-0.382181	1.472860
C	3.088083	-0.514991	-1.334500
C	-2.240233	1.572231	1.597155
C	-2.815059	1.388547	-1.144321
C	-0.173819	3.619877	-0.266936
C	2.483432	2.733973	-0.288259
C	2.942413	0.662106	2.556849
C	2.469754	-1.399159	-2.384826
C	-2.061391	0.589723	2.723671
C	-2.399006	2.006643	-2.454927
H	2.732115	-1.343360	1.880969
H	3.434547	0.403260	-1.800228
H	-1.811097	2.527105	1.886358
H	-3.293638	0.437428	-1.344257
C	4.414557	-0.478238	0.797973
C	4.231454	-1.205059	-0.550955
C	-3.715217	1.742025	1.158397
C	-3.748000	2.276855	-0.289787
H	4.830206	0.512639	0.626453
H	5.101656	-1.026522	1.439881
H	3.984227	-2.248282	-0.361572
H	5.148383	-1.174526	-1.136661
H	-4.236002	0.787287	1.197841
H	-4.222105	2.427945	1.834609
H	-3.424190	3.314620	-0.306538
H	-4.759760	2.236657	-0.689378
H	1.638404	-0.860662	-2.887455

H	3.230456	-1.670147	-3.147215
H	2.067730	-2.328533	-1.929462
H	1.900547	0.728360	2.935849
H	3.610046	0.382987	3.399150
H	3.250376	1.657100	2.176203
H	-3.287404	2.127192	-3.110206
H	-1.937817	3.002261	-2.302114
H	-1.667854	1.346096	-2.967138
H	-2.620448	0.933689	3.619465
H	-2.431296	-0.413810	2.428400
H	-0.984671	0.509313	2.984576
C	0.871402	4.541770	-0.385193
C	2.200183	4.098483	-0.399519
H	-1.190734	3.979052	-0.220852
H	0.652889	5.601848	-0.464554
H	3.010181	4.814967	-0.490612
H	3.512397	2.401846	-0.283205

R-H

E23456= -441.924970652443 0.974760447047 -449.337087931857
-748.326879339812 0.982409606545 -306.525003765769
ONIOM: extrapolated energy = -755.731347459727

Rh	0.000000000000	0.000000000000	0.000000000000
O	0.000000000000	0.000000000000	2.147468000000
C	1.177447445415	0.000000000000	2.647361390821
N	2.263065655300	-0.053980110330	1.857005952275
C	2.099603543866	-0.218779229876	0.404640412675
C	1.657323032323	-1.467657043486	-0.091936319268
H	2.722363239100	0.457416293995	-0.172794675652
H	1.439031252144	-2.290639252949	0.583314521689
H	1.899895954313	-1.751946392247	-1.108851919807
H	3.196980645269	-0.047952499778	2.257868891026
H	1.317125585776	0.043759100505	3.728522122074
P	-2.009702398982	1.347322230409	-0.015637181174
P	-0.117464167660	0.177063033896	-2.339011499072
C	-2.328646363640	1.828366909912	-1.791940223330
C	-1.514983702633	1.350168879230	-2.772946500091
C	-3.617050482837	0.597983217500	0.817541800964
C	-2.158482267974	2.990680919027	1.039853120576
C	-0.447589156152	-1.381939880906	-3.488942769241
C	1.534628210146	0.600124149192	-3.305489826405
C	-1.789296689292	1.712462013180	-4.185407382058
C	-3.455593554165	2.724169906415	-2.149225141492
C	-4.509609005604	-0.082937449436	-0.188566860559
C	-0.809948575612	3.408149112428	1.563164671629
C	-0.904075356791	-2.560127781507	-2.669872526470
C	1.685078724049	2.078799453940	-3.556517993903
H	-3.247753001538	-0.140023527385	1.522520965516
H	-2.542490388892	3.771451646900	0.389722602987
H	-1.234908171149	-1.110375205958	-4.185941911379
H	2.334360340076	0.274034703117	-2.649583770925
C	-4.290411058819	1.775195349736	1.559141660519
C	-3.173996752325	2.655454007296	2.158796816268
C	0.884139647245	-1.626795278484	-4.238144726981
C	1.509863109085	-0.259704325495	-4.590593057516
H	-4.894316707545	2.367664083201	0.874731946923

H	-4.942763549124	1.393786794296	2.342574932342
H	-2.684475213697	2.110396699216	2.964126200020
H	-3.583552291471	3.575837019823	2.571041772633
H	1.576772386130	-2.188162708705	-3.613637866458
H	0.697624631463	-2.209472085514	-5.138355675780
H	0.920148621410	0.221991938094	-5.367233677644
H	2.522690027422	-0.386666060278	-4.968658908548
H	-0.113793984965	3.580288577867	0.715034587705
H	-0.905343537278	4.351186508004	2.141909863172
H	-0.383350417242	2.625140648482	2.222845442109
H	-3.937252842300	-0.863635400047	-0.733068969388
H	-5.362499243713	-0.566235006416	0.333098002530
H	-4.909807960451	0.646343442658	-0.922222422936
H	2.674529013090	2.281697972626	-4.018058308130
H	0.894539846310	2.451232512048	-4.238322211746
H	1.621468306850	2.632084591307	-2.595676067262
H	-1.102990302886	-3.427275674910	-3.334547732895
H	-0.133440370835	-2.847883533936	-1.926109244631
H	-1.840945733385	-2.302596976344	-2.131647440146
C	-2.851716832590	2.565310277267	-4.496726394581
C	-3.679532215558	3.068624591172	-3.484715747660
H	-1.178388469996	1.312801739862	-4.981914890844
H	-3.038191045165	2.838064223121	-5.530497498844
H	-4.502038164774	3.729002723918	-3.740062903167
H	-4.112776394200	3.108837355137	-1.381638554011

S-H

E23456=	-441.916169748003	0.899319499595	-449.337846836190
	-748.318545916402	0.905974921841	-306.524765272823
ONIOM: extrapolated energy =		-755.733567582343	
Rh	0.000000000000	0.000000000000	0.000000000000
O	0.000000000000	0.000000000000	2.143306000000
C	1.179411690980	0.000000000000	2.649147067828
N	2.269150958964	0.085411888106	1.868639012631
C	2.106668930686	0.272068670376	0.420830556855
C	1.519823401392	1.498529606756	-0.028852597289
H	2.836795268682	-0.275241420188	-0.165279328231
H	1.252844874934	2.272962181825	0.688210176799
H	1.728748947972	1.867223440547	-1.026167212210
H	3.197751506914	0.078493222871	2.281511831968
H	1.310034748020	-0.071542999447	3.729695687695
P	-2.395256846848	0.158082333932	-0.182246587624
P	-0.056638800942	-0.325608162932	-2.317038949077
C	-2.818390654313	0.085129332012	-2.000564881933
C	-1.825916571696	-0.125904073009	-2.908033249789
C	-3.519962998179	-1.070132698493	0.851794605226
C	-3.312321564449	1.718303505673	0.560593831972
C	0.485368891290	-2.096537720397	-2.961816102963
C	1.234837030112	0.554418706424	-3.501046405665
C	-2.170234034615	-0.252899574207	-4.345140411583
C	-4.217002770963	0.237453966229	-2.468856588564
C	-3.945225039434	-2.269100148900	0.042841207643
C	-2.306113680935	2.763652375845	0.962980326019
C	0.673503595086	-3.030868809979	-1.795993350335
C	0.684554753380	1.814715779842	-4.118529522048
H	-2.889659796330	-1.399783489855	1.671527012772

H	-3.963213793263	2.125011675009	-0.208281210402
H	-0.308124825271	-2.474226029905	-3.600242924269
H	2.071414024971	0.811256631889	-2.861359873126
C	-4.695350972243	-0.214756248627	1.376284260377
C	-4.134705280899	1.172376438551	1.753974542075
C	1.784400317795	-1.861600494947	-3.771531284709
C	1.667007139330	-0.519404515816	-4.524755199626
H	-5.463464834851	-0.104395363640	0.613565665131
H	-5.145800520519	-0.695895350847	2.242545578857
H	-3.502294766215	1.071731336976	2.634454681075
H	-4.939570056717	1.865336172809	1.992140244571
H	2.644607859016	-1.820111194373	-3.105398395023
H	1.937302964882	-2.684710005097	-4.467033907288
H	0.939175029096	-0.609171350785	-5.327650644034
H	2.622495844845	-0.242903318733	-4.966898091312
H	-1.734945274146	3.098654593207	0.071162491102
H	-2.826057827936	3.640871416918	1.402861008644
H	-1.592389828840	2.353702449600	1.708852216495
H	-3.050680847874	-2.783696927678	-0.367654220811
H	-4.498798159647	-2.981043984060	0.690771904367
H	-4.604363223662	-1.969203617340	-0.797001491126
H	1.484140168862	2.331021293503	-4.690556979809
H	-0.153003529950	1.590899017357	-4.808424717970
H	0.321448298757	2.497244985062	-3.321352512359
H	1.003364787352	-4.027647981783	-2.157895344616
H	1.434222446697	-2.628981446111	-1.092984791446
H	-0.287169044032	-3.149714215898	-1.251072945903
C	-3.495927371792	-0.106548250505	-4.763215987267
C	-4.512403893500	0.142405349418	-3.831350175877
H	-1.405196277363	-0.474730765509	-5.074398551276
H	-3.739878351614	-0.186355189959	-5.817735890693
H	-5.537680474353	0.254000443801	-4.169275696891
H	-5.014530787039	0.410608686752	-1.759687339752

R-*t*Bu (achiral)

E23456= -480.490229391834 0.341758834851 -489.928206444951
-902.631927202795 0.355438921422 -422.268244502599
ONIOM: extrapolated energy = -912.056224169340

Rh	0.000000000000	0.000000000000	0.000000000000
O	0.000000000000	0.000000000000	2.157423967299
C	1.155123139710	0.000000000000	2.633082406226
N	2.226829022579	0.246780998565	1.887252592128
C	2.107416172834	0.673182034780	0.487138764452
C	2.191823482855	-0.338941419592	-0.454046874358
C	2.457790945510	2.165901361951	0.288659724676
H	2.364068492694	-1.363960691696	-0.141539960119
H	2.438088555882	-0.104634317578	-1.479946572413
H	3.141849587788	0.233954586435	2.320940200434
H	1.320378485267	-0.214860880796	3.693937007512
P	-2.286857992309	-0.122996622238	0.184983696230
P	-0.378751366428	-0.425816960994	-2.208195625144
C	-3.035074200128	-0.374508226219	-1.463484798733
C	-2.201218666077	-0.495887936625	-2.517329010297
C	-3.082323319095	-1.394050541856	1.411462026158
C	-3.174036620314	1.379434562375	1.030817045401
C	0.284618738556	-2.132389311213	-2.871437811045

C	0.393298917559	0.529201885926	-3.718883801988
C	3.976478381344	2.355274163656	0.657092816090
C	2.259169219247	2.633722168576	-1.185335105148
C	1.585647842242	3.070743821646	1.218853644861
C	-2.754191501311	-0.709166649144	-3.853955856325
C	-4.480321736587	-0.456405101211	-1.655241949684
H	-3.492255058975	-2.237929597145	0.866678959683
H	-2.475038642603	2.200691453216	1.135389115598
H	0.680992621681	-2.715132738448	-2.048456801516
H	-0.348863592434	1.187401379416	-4.157903018338
H	-2.286638578795	-1.745007652723	2.058149912968
H	-4.003378847351	1.696813811413	0.406515918940
H	-0.545918781517	-2.671525713748	-3.315419129864
H	1.205355440383	1.133938314738	-3.339470316230
C	-4.150677732376	-0.609841939712	2.201823027301
C	-3.655807166807	0.837303907262	2.392167188836
C	1.359379297101	-1.783780935096	-3.920898343621
C	0.905112877054	-0.539766503017	-4.709796621745
H	-5.087484378214	-0.607963959567	1.648869934407
H	-4.328844525408	-1.088407208022	3.162573373544
H	-2.825775585009	0.849326207562	3.095902976402
H	-4.446161584337	1.472349062809	2.787328966392
H	2.302475894991	-1.577896717825	-3.419567403625
H	1.514629923593	-2.629644567725	-4.587621197713
H	0.112806596462	-0.815418476589	-5.400905353168
H	1.727204039297	-0.134894893854	-5.296409252840
H	4.158757609462	2.155583765362	1.707886056672
H	4.602150825724	1.697429368841	0.060599276956
H	4.267116229443	3.381080168290	0.456390934508
H	1.219699649934	2.535454428748	-1.481519805945
H	2.538462639882	3.678972168604	-1.265708887665
H	2.883740154552	2.065780616260	-1.866231419384
H	1.710463557979	2.796982190349	2.261146406615
H	1.886972890446	4.106474719995	1.100983293820
H	0.534742103070	2.986716372428	0.954731308379
C	-4.138181464674	-0.780581110906	-4.031518043944
C	-4.997709440576	-0.654806068089	-2.936834421009
H	-2.103495924040	-0.819782756950	-4.707927742761
H	-4.546550042660	-0.938175210399	-5.021386888746
H	-6.068556442340	-0.713209584855	-3.082611114692
H	-5.151503818725	-0.361503341509	-0.812725780237

S-*t*Bu (achiral)

E23456= -480.483871189831 0.357591526921 -489.927367302977
-902.624890620876 0.371760674019 -422.272937386441
ONIOM: extrapolated energy = -912.054217586924

Rh	0.000000000000	0.000000000000	0.000000000000
O	0.000000000000	0.000000000000	2.158811525867
C	1.144590015490	0.000000000000	2.660908692172
N	2.245729013825	-0.145434186983	1.935975487465
C	2.225053846897	-0.361084772105	0.485662175092
C	2.043188217767	0.786007251068	-0.283586074943
C	2.933496064678	-1.669996485669	0.082997766121
H	1.996319348769	1.761550864810	0.192847430215
H	2.328732259017	0.797375935665	-1.325211471003
H	3.139494139707	-0.113054493385	2.410107106705

H	1.273260423535	0.123628808454	3.741196917989
P	-2.160309783971	0.751102698622	0.201372084768
P	-0.490761316427	-0.054580767436	-2.228052611093
C	-2.823446696232	1.192818302113	-1.440540730245
C	-2.073363853342	0.873787623572	-2.515724044227
C	-3.511595700126	-0.283787968449	1.134103282022
C	-2.387934210812	2.269357126366	1.383029879857
C	-0.887682542181	-1.797602235796	-3.009975390876
C	0.707165851429	0.398472618885	-3.691900420823
C	4.398581939875	-1.667897231702	0.660669836580
C	2.159183607611	-2.900542660209	0.660585630959
C	3.048067522939	-1.809554901747	-1.464710007945
C	-2.557208186381	1.210123708892	-3.854379881551
C	-4.114593608909	1.853098870921	-1.609662894410
H	-4.190934259303	-0.741924902978	0.422874898755
H	-1.416458182093	2.660513244337	1.660843446903
H	-0.831559764393	-2.560627257509	-2.242135212147
H	0.503581735252	1.404557593275	-4.043336791972
H	-2.990434017534	-1.063854136208	1.676958275750
H	-2.943272973129	3.042119616577	0.860950661287
H	-1.900718568467	-1.764014783778	-3.397471908072
H	1.717071513277	0.368534054989	-3.305151031885
C	-4.212909632572	0.702317209289	2.090850014706
C	-3.169937549335	1.719335943569	2.593928474053
C	0.146437767932	-2.020393241373	-4.133882110142
C	0.503740725279	-0.670722956386	-4.789069988921
H	-5.008683554417	1.222319736040	1.561899926066
H	-4.659556703770	0.161534178164	2.922652135812
H	-2.476884461086	1.224989832091	3.271755402794
H	-3.647138353392	2.536736409703	3.130810965751
H	1.040950618989	-2.474835465817	-3.717088522491
H	-0.259098173622	-2.708306315286	-4.873080680842
H	-0.293829063448	-0.368305206785	-5.462035010955
H	1.411783504551	-0.763909759199	-5.381274259527
H	4.928667246696	-0.765076451308	0.370650560730
H	4.403099232974	-1.747924577847	1.742543600372
H	4.935832498216	-2.522291355659	0.263365394124
H	2.051440841578	-2.815106775176	1.737132548697
H	1.170114075218	-2.970341702182	0.214523819538
H	2.702510589123	-3.814226694481	0.441059535324
H	3.522919249634	-2.754556651994	-1.705538938235
H	2.067042312767	-1.795028943644	-1.921944592380
H	3.648992332437	-1.010685596779	-1.886195274246
C	-3.787877015101	1.853520486800	-4.009465362812
C	-4.564841760842	2.170799081308	-2.892246256641
H	-1.979244608190	0.962357637440	-4.729894472118
H	-4.144664731741	2.100964424391	-5.000905702716
H	-5.519404428132	2.664221578467	-3.021648461072
H	-4.720820119698	2.101712174040	-0.749352693336

R-NH_2

E23456=	-496.246724124251	0.334565294377	-504.692730329254
	-802.645537867644	0.348486613782	-306.521154000038
ONIOM: extrapolated energy =		-811.077622753244	
Rh	0.000000000000	0.000000000000	0.000000000000
O	0.000000000000	0.000000000000	2.148213900040

C	1.165370895169	0.000000000000	2.659764262285
N	2.268966165560	-0.004582661726	1.885568084240
C	2.192160329380	-0.206658595314	0.428499107869
C	1.665868841187	-1.435021312282	-0.056359287799
N	3.148029512681	0.571077336711	-0.223190435952
H	1.450825832325	-2.236244232213	0.644567420286
H	1.918357550271	-1.757573579085	-1.060946929260
H	3.199202612019	0.014249030280	2.296930585453
H	1.297032488507	0.013304891141	3.743148037796
H	3.521046827681	0.264534637633	-1.110249136932
H	3.197292127990	1.563463566192	-0.026341009840
P	-1.843193881069	1.535628561176	0.011260553740
P	-0.249061016230	0.036887188262	-2.335368475874
C	-2.277626170188	1.907056592446	-1.770003903433
C	-1.596158347471	1.274991812511	-2.769041901891
C	-3.438879982779	1.029735953425	1.030704042535
C	-1.736009107466	3.262650643417	0.931165976961
C	-0.799801136437	-1.600493671083	-3.272023270619
C	1.314415285043	0.228572021619	-3.503460487749
C	-1.957160820223	1.521398846988	-4.146146145675
C	-3.326712967616	2.844375765728	-2.097083742050
C	-4.475578821992	0.358411346061	0.166301592862
C	-0.312574327059	3.556951802648	1.323305400166
C	-1.209246433842	-2.656361443247	-2.279638135879
C	1.558528248522	1.660124818044	-3.907057432758
H	-3.080883597380	0.320749361036	1.770474917674
H	-2.081555428671	4.033078840776	0.247975547934
H	-1.652003196380	-1.350866242108	-3.897258207156
H	2.150020511690	-0.112138250604	-2.904195970320
C	-3.931893289533	2.327085160064	1.710514795322
C	-2.689312033769	3.132791266012	2.144216532163
C	0.415637379849	-2.011562659616	-4.138121648627
C	1.088475379261	-0.736070672139	-4.689869148870
H	-4.530671019318	2.920899515089	1.022905134090
H	-4.550611975807	2.081954305441	2.571850084411
H	-2.194724736244	2.609150583839	2.960600022903
H	-2.971785456414	4.122506536142	2.498350868832
H	1.138081029804	-2.565758010702	-3.541492767513
H	0.086641263842	-2.657101888805	-4.950331551413
H	0.452246961011	-0.281939563195	-5.445742413422
H	2.041900921900	-0.977039775496	-5.156602034778
H	0.326342612446	3.600688463983	0.415780792938
H	-0.258303209805	4.536206740581	1.844340657887
H	0.080264125027	2.767739387856	1.997662254837
H	-4.027275393389	-0.517444711353	-0.348940769172
H	-5.318800981573	0.006325188148	0.797295633374
H	-4.872698086290	1.059221080039	-0.595970801865
H	2.509909921671	1.731770568955	-4.475319304960
H	0.737241315847	2.042380028880	-4.545349897756
H	1.637776097555	2.297819016382	-3.001225913103
H	-1.521007042754	-3.578093411307	-2.814947964144
H	-0.368553143968	-2.901994057426	-1.597889042579
H	-2.064986948202	-2.290320589096	-1.673376432150
C	-2.973874790355	2.427364922071	-4.453352349363
C	-3.654446619435	3.090461582917	-3.431211840566
H	-1.452176847750	1.002454702108	-4.947270798543
H	-3.238481173942	2.611984984543	-5.486446197554

H	-4.443507546421	3.790579368624	-3.673183511379
H	-3.869658397139	3.354019656728	-1.313308407085

S-NH_2

E23456=	-496.253053090110	0.366417980100	-504.692529235742
	-802.650669223530	0.381766625135	-306.521822905897
ONIOM: extrapolated energy =		-811.074796724127	
Rh	0.000000000000	0.000000000000	0.000000000000
O	0.000000000000	0.000000000000	2.148641707767
C	1.134013038998	0.000000000000	2.718808508531
N	2.286624995999	-0.034286403179	2.016769138520
C	2.340386571515	0.056086346810	0.558018013829
C	1.868970100207	1.206541684973	-0.093876284139
N	3.283099416652	-0.826442347183	0.042984131760
H	1.608721995588	2.091354961712	0.480000554824
H	2.176607210964	1.381175422464	-1.118529360324
H	3.181114299625	-0.071185759786	2.499766938669
H	1.207660845294	0.012467721477	3.808153632906
H	3.728083149464	-0.619329035921	-0.840646383524
H	3.290269887384	-1.792359827077	0.346835959110
P	-2.296768654443	-0.601279760567	0.113412764411
P	-0.318638081497	-0.075642083478	-2.339104960530
C	-2.963263836322	-0.743687614295	-1.621535525079
C	-2.124927357646	-0.501653359887	-2.668749255557
C	-2.756984890472	-2.154118496495	1.213680477312
C	-3.560710614479	0.534686448523	1.085661712187
C	0.660791909035	-1.245441482841	-3.579335227514
C	0.190469528393	1.516695375590	-3.377277387291
C	-2.628111052518	-0.598898890894	-4.020488945051
C	-4.347664703928	-1.073439089662	-1.865089539110
C	-2.894946622146	-3.410910194978	0.392900973142
C	-2.941032702472	1.874662722325	1.381549953592
C	1.400215493034	-2.318010315199	-2.827839761928
C	-0.967771690833	2.462058797459	-3.573038230870
H	-1.922258143105	-2.267101001322	1.897517011818
H	-4.436120690858	0.678829618912	0.459096059452
H	-0.062051579779	-1.717533823841	-4.237246130361
H	0.944448092059	2.016229417585	-2.780847827392
C	-4.039663570803	-1.759343369450	1.980603365748
C	-3.922032647163	-0.267534384471	2.358746880105
C	1.586616599754	-0.300144130184	-4.380424256236
C	0.804821203080	0.993153816090	-4.696591491673
H	-4.921291764164	-1.909969242055	1.360861588078
H	-4.143920078720	-2.375779448734	2.871601045152
H	-3.145035463222	-0.151397967598	3.112408971881
H	-4.857041158719	0.102346631378	2.775464075079
H	2.471984629370	-0.049891846901	-3.798429575677
H	1.913286204493	-0.788728985426	-5.296584046774
H	0.029275605294	0.777708921602	-5.428200941175
H	1.464674001462	1.747643707047	-5.121053918317
H	-2.672206218858	2.382522235322	0.430973676337
H	-3.664397903850	2.512002830306	1.932849740130
H	-2.023778657039	1.757863671091	1.995321847426
H	-1.963543822250	-3.587257244632	-0.185792348243
H	-3.066855878793	-4.279497892240	1.063096861988
H	-3.747020743099	-3.333936362046	-0.312613096386

H	-0.611786899452	3.393980390748	-4.060956803806
H	-1.752256326715	2.009102907021	-4.211724197104
H	-1.411145537687	2.723989007781	-2.588991026733
H	1.941561233944	-2.975723185654	-3.540388664462
H	2.129945017525	-1.868235757190	-2.128631769508
H	0.681577337924	-2.934887311675	-2.247620397208
C	-3.966724431732	-0.923862034198	-4.249017996957
C	-4.824902035861	-1.159642878212	-3.173733101028
H	-1.977989449321	-0.416745639709	-4.863898504818
H	-4.340279983166	-0.991364809536	-5.262547242146
H	-5.862529646206	-1.408190053459	-3.354968750269
H	-5.021182444974	-1.253688590776	-1.038541948843

R-βCN

E23456= -532.454802728955 1.847667169293 -541.540844758844
-838.860362636293 1.861548057520 -306.526722068224
ONIOM: extrapolated energy = -847.932523777956

Rh	0.00000	0.00000	0.00000
O	2.14921	0.00000	0.00000
C	2.64201	1.17992	0.00000
N	1.83437	2.25681	-0.02237
C	0.39452	2.06159	-0.21103
C	-0.07879	1.61692	-1.49775
H	-0.21494	2.71265	0.40707
C	0.80268	1.36382	-2.60162
N	1.52917	1.15523	-3.51141
H	-1.09376	1.87372	-1.78135
H	2.22007	3.19748	-0.01726
H	3.72162	1.32886	0.02234
P	0.01846	-1.77038	1.64187
P	-2.34017	-0.11176	0.20598
C	-1.75879	-2.09772	2.11497
C	-2.75645	-1.38718	1.51476
C	0.95503	-3.41930	1.14692
C	1.03117	-1.62549	3.31241
C	-3.44999	-0.59039	-1.34092
C	-3.32640	1.56187	0.46598
C	-4.13333	-1.65736	1.85842
C	-2.08452	-3.09245	3.11014
C	0.01757	-4.45202	0.57473
C	1.47334	-0.20458	3.54027
C	-2.59041	-1.11129	-2.46231
C	-3.59723	1.84164	1.92224
H	1.66215	-3.11626	0.38112
H	0.37696	-1.92799	4.12517
H	-4.13379	-1.37284	-1.02484
H	-2.67726	2.33771	0.07515
C	1.69274	-3.87798	2.42550
C	2.20854	-2.61748	3.15080
C	-4.22135	0.70200	-1.70447
C	-4.60082	1.43794	-0.40126
H	1.02181	-4.42857	3.08191
H	2.51957	-4.53380	2.15886
H	3.00509	-2.16755	2.56056
H	2.61177	-2.86963	4.12991
H	-3.60382	1.35551	-2.31822

H	-5.11114	0.44799	-2.27752
H	-5.37225	0.87879	0.12341
H	-4.99453	2.42883	-0.62053
H	0.58630	0.46158	3.59552
H	2.03303	-0.13217	4.49673
H	2.12843	0.14068	2.71445
H	-0.53214	-4.02412	-0.29033
H	0.59737	-5.33299	0.22713
H	-0.71578	-4.78824	1.33579
H	-4.07308	2.83923	2.02975
H	-4.27422	1.07899	2.35685
H	-2.64245	1.84075	2.48956
H	-3.22681	-1.38563	-3.33008
H	-1.85494	-0.34512	-2.78351
H	-2.03988	-2.01508	-2.12489
C	-4.43943	-2.62141	2.82058
C	-3.41704	-3.33573	3.44698
H	-4.93533	-1.11999	1.37294
H	-5.47199	-2.81773	3.07875
H	-3.65806	-4.08334	4.19153
H	-1.30114	-3.65832	3.59532

S-βCN

E23456= -532.452712339220 1.858712242385 -541.542252789562
-838.857795312805 1.871902723863 -306.527513993656
ONIOM: extrapolated energy = -847.934145281669

Rh	0.000000000000	0.000000000000	0.000000000000
O	0.000000000000	0.000000000000	2.145971982959
C	1.176542890388	0.000000000000	2.653213852816
N	2.266727001485	0.052388396201	1.865767479156
C	2.098243487388	0.200432694581	0.421659314804
C	1.567221950775	1.448722385517	-0.085768434068
H	2.814790190642	-0.366613640251	-0.161888585681
C	1.291162822920	2.576563155556	0.767220146016
N	1.067572093297	3.509277167123	1.458521842822
H	1.808895707104	1.730822201442	-1.104533619318
H	3.196705853393	0.055050264365	2.276241955230
H	1.308768942038	-0.044136978873	3.734324891619
P	-2.405543214421	0.134369336386	-0.129366848370
P	-0.117418303432	-0.353219854575	-2.319170571311
C	-2.873969041105	0.047122469635	-1.935220236502
C	-1.902023494487	-0.166751177128	-2.867697891335
C	-3.438159863417	-1.160863852236	0.918603126149
C	-3.365108315320	1.640729465137	0.671038250679
C	0.410160211247	-2.137612309461	-2.940653745755
C	1.149617693860	0.501737114116	-3.548254983239
C	-2.264746101374	-0.306854062208	-4.258661750639
C	-4.250856347726	0.179908484669	-2.349548939180
C	-3.829368902008	-2.366811943022	0.102765524090
C	-2.393211839522	2.718421945120	1.071087753832
C	0.631280197963	-3.046641758369	-1.760673927609
C	0.592409682886	1.757079553314	-4.169684483990
H	-2.770173877333	-1.470867142804	1.715975644466
H	-4.051511879592	2.035696361778	-0.072720298798
H	-0.401119848110	-2.528584059286	-3.548108375164
H	2.004710559821	0.761649358072	-2.934939334244

C	-4.637725366602	-0.369229838628	1.486506750780
C	-4.131697865548	1.035850248905	1.873528553005
C	1.685876759087	-1.919451622997	-3.791480188923
C	1.550457509275	-0.590551387681	-4.565049487639
H	-5.429205172584	-0.283430024864	0.744741279570
H	-5.042618477402	-0.884648073408	2.355574528967
H	-3.474060774629	0.950824740966	2.737029622896
H	-4.961007111712	1.687574165321	2.142252828977
H	2.565193225784	-1.868890810044	-3.151405170899
H	1.816501758769	-2.755337632598	-4.476205723542
H	0.801422533197	-0.691552942543	-5.346731190343
H	2.494443799893	-0.323854282909	-5.036983637817
H	-1.853536149564	3.090445634653	0.174452590356
H	-2.938530210383	3.566951202689	1.535741260852
H	-1.651371461720	2.324266193251	1.797396724980
H	-2.923412927445	-2.833407351828	-0.338700192546
H	-4.332181961297	-3.112824721490	0.753707286888
H	-4.523671275008	-2.085330859882	-0.715111750997
H	1.380707595554	2.258892269138	-4.769601736783
H	-0.264451682627	1.530534757646	-4.834415032958
H	0.255754313478	2.453713289230	-3.373048829218
H	0.950082753860	-4.051397792156	-2.110168637286
H	1.412062572082	-2.630570740965	-1.088732131637
H	-0.313280892875	-3.152543009708	-1.185929780170
C	-3.598499221283	-0.178809847875	-4.651156397143
C	-4.588722852525	0.069986545735	-3.699381498507
H	-1.513046362964	-0.522125235190	-5.003288649017
H	-3.865974777089	-0.278560100903	-5.695124139812
H	-5.621859093639	0.166378922999	-4.007121816980
H	-5.028072343768	0.354029769535	-1.618326688257

R-butenal

E23456= -426.179007206769 0.371732860003 -433.278776713052
-732.579040326008 0.388295884772 -306.519779198047
ONIOM: extrapolated energy = -739.662246807523

Rh	0.000000000000	0.000000000000	0.000000000000
O	0.000000000000	0.000000000000	2.148647318340
C	1.133119489639	0.000000000000	2.701897861408
C	2.395259929352	-0.043290268538	1.887168969521
C	2.130513545139	-0.415420060327	0.423579851299
C	1.478592717903	-1.617493772847	0.073873605257
H	2.793063678823	0.059557780917	-0.294589793138
H	1.124247756329	-2.313973063475	0.832338036397
H	1.632894271825	-2.059386234525	-0.903998590267
H	3.114329398440	-0.728504880337	2.362423807570
H	2.856433977121	0.955248857841	1.961630377588
H	1.180054139325	0.058447637452	3.796903730940
P	-2.255878807446	0.861026617050	-0.150482903373
P	-0.007019656692	0.166809408158	-2.331190363247
C	-2.617943246698	1.142187367578	-1.960092955144
C	-1.659845570157	0.850031129016	-2.885009395454
C	-3.729652387248	-0.176034721879	0.600030721428
C	-2.789685134623	2.467041015654	0.822308838190
C	0.380212247346	-1.375917984987	-3.464449221057
C	1.374597673569	1.242959277445	-3.199072086700
C	-1.926894237861	1.068122787814	-4.287345051877

C	-3.895532985438	1.661386698232	-2.386645545311
H	-4.245993588368	-0.713928705064	-0.188326503858
H	-1.910117743665	2.951129958328	1.229869671117
H	0.353452228153	-2.281802880803	-2.871214584888
H	0.966999722408	2.206337475995	-3.487137070062
H	-3.292910725285	-0.891356118121	1.287772525500
H	-3.284721165143	3.147748742445	0.136714702186
H	-0.377410029798	-1.441185409491	-4.238774251084
H	2.161246558762	1.400685691963	-2.470511716602
C	-4.631969950734	0.841408629954	1.329544268770
C	-3.747392124201	1.957651717440	1.918812769493
C	1.774938708416	-1.085919719501	-4.055720618918
C	1.866503963567	0.413229337087	-4.404760720838
H	-5.343106925108	1.269315045578	0.626398845922
H	-5.195614701827	0.339954383872	2.113735798858
H	-3.164740671811	1.562343379658	2.748749915164
H	-4.354744337529	2.779850667608	2.292184721945
H	2.539130587890	-1.338474625276	-3.322934092813
H	1.939510197470	-1.700874981893	-4.938323077257
H	1.244101682442	0.624877758460	-5.271166910724
H	2.889260575655	0.690101689463	-4.652509348726
C	-3.163996248951	1.574066747073	-4.692615939769
C	-4.146272614839	1.869229930524	-3.744628491667
H	-1.174532673634	0.842424938224	-5.029999313029
H	-3.362122475750	1.737273475705	-5.744040202543
H	-5.103701614876	2.260758242245	-4.063080176546
H	-4.661825057435	1.893584932252	-1.660019343873

S-butenal

E23456= -426.179573180466 0.366137456815 -433.278638255990
-732.579384105680 0.382646480290 -306.520181710596
ONIOM: extrapolated energy = -739.661940157729

Rh	0.000000000000	0.000000000000	0.000000000000
O	0.000000000000	0.000000000000	2.150111611677
C	1.134988385436	0.000000000000	2.699460748370
C	2.394422266734	0.036901825736	1.880343948392
C	2.128601382342	0.417865709647	0.418710175919
C	1.482213796050	1.623510759096	0.075521030159
H	2.784678089171	-0.060175041042	-0.303662923863
H	1.129797974107	2.317439895537	0.837018930824
H	1.636535111269	2.068408740755	-0.900910613966
H	3.121267165517	0.714499622098	2.354366643650
H	2.847367424269	-0.965851142100	1.948780698073
H	1.185898552260	-0.055331828419	3.794451343603
P	-2.182544588151	-1.030717089448	-0.132120740102
P	-0.000934805679	-0.190820514802	-2.331437132715
C	-2.497987795487	-1.421334576034	-1.929273574502
C	-1.567247129879	-1.069950793805	-2.861576709675
C	-2.572647615878	-2.636178501024	0.908647592832
C	-3.752841233173	-0.105382322973	0.564560530652
C	1.498617974210	-1.083280514069	-3.205089921565
C	0.160397455756	1.376863536738	-3.490490187584
C	-1.802858759137	-1.364062935793	-4.255659644324
C	-3.712084755862	-2.085884538098	-2.338854031517
H	-2.517215897952	-3.515208206589	0.274837786256
H	-3.493287181621	0.920384752733	0.798740327361

H	2.113843030043	-1.571097938030	-2.458406635575
H	-0.808480825148	1.620217239108	-3.913931496337
H	-1.810516564645	-2.707182149800	1.676140108635
H	-4.530433940458	-0.113933211160	-0.192970372317
H	1.114531444456	-1.832034940800	-3.890513307698
H	0.487719555430	2.206045202305	-2.875325238233
C	-3.974303875292	-2.415808423751	1.516080595460
C	-4.157316875065	-0.914479493649	1.813509294239
C	2.243609118012	0.044303274432	-3.948413257122
C	1.207335253751	1.006230942095	-4.563619508624
H	-4.734049493016	-2.745041063473	0.810705915995
H	-4.081368657852	-3.005978285777	2.423980351685
H	-3.521792417618	-0.626016498188	2.648662772344
H	-5.188935898686	-0.693144611865	2.080180441953
H	2.874070740842	0.585278630374	-3.245139893338
H	2.885481803879	-0.378909404570	-4.718576890646
H	0.713263272094	0.521328775159	-5.402406569346
H	1.690633084325	1.907045994392	-4.936443547684
C	-2.978422328644	-2.010328567913	-4.644528009292
C	-3.930876413027	-2.370161534849	-3.688446987361
H	-1.073780329379	-1.088321969703	-5.004596830533
H	-3.152217294959	-2.231930551923	-5.689558592056
H	-4.840937670928	-2.869851422450	-3.994185264267
H	-4.455938607545	-2.366195115787	-1.605920692830

V. Structures used for CDA and NBO analysis

R-CN

O	0.	0.	2.14432
C	1.16686	0.	2.66294
N	2.26371	-0.05069	1.88683
C	2.10971	-0.17123	0.42592
C	1.65282	-1.41776	-0.10053
C	2.94731	0.74512	-0.30579
N	3.64275	1.50004	-0.89169
H	1.45144	-2.24225	0.57833
H	1.91907	-1.70221	-1.11046
H	3.19713	-0.04022	2.29027
H	1.29288	0.03313	3.74584
Rh	0.	0.	0.
P	-2.25718	0.89131	-0.01405
P	-0.22457	0.05302	-2.36206
H	-2.74299	1.28873	-1.2878
H	-1.39844	0.68585	-2.84985
H	-3.25239	0.05472	0.55699
H	-2.49473	1.9977	0.84378
H	-0.35279	-1.20755	-3.0031
H	0.93965	0.43449	-3.08003

S-CN

O	0.	0.	2.14628
C	1.1732	0.	2.66395
N	2.27203	0.08057	1.89557
C	2.11988	0.24142	0.4409

C	1.49717	1.46781	-0.02762
C	3.09056	-0.47695	-0.33424
N	3.87727	-1.06955	-0.98925
H	1.25739	2.24083	0.70073
H	1.73849	1.84795	-1.01399
H	3.20066	0.07068	2.31034
H	1.29432	-0.06331	3.74587
Rh	0.	0.	0.
P	-2.36077	0.35551	-0.18131
P	-0.08648	-0.32716	-2.32682
H	-2.86725	0.42409	-1.50614
H	-2.84094	1.55585	0.40608
H	-3.16873	-0.64506	0.42072
H	0.14419	-1.66337	-2.74839
H	-1.3189	0.01422	-2.94407
H	0.85762	0.42554	-3.07417

R-CO_2H

O	0.	0.	2.14028
C	1.16991	0.	2.65876
N	2.26445	-0.05837	1.88802
C	2.13686	-0.16434	0.43147
C	1.69173	-1.38826	-0.13616
C	3.04925	0.73557	-0.33345
O	3.66295	1.65728	0.49339
H	4.27705	2.24486	-0.0043
O	3.29384	0.65961	-1.54697
H	1.46314	-2.23956	0.49901
H	1.98865	-1.6116	-1.15392
H	3.19082	0.0598	2.28893
H	1.29318	0.04146	3.74152
Rh	0.	0.	0.
P	-2.26148	0.81056	0.10339
P	-0.35762	0.02701	-2.35785
H	-2.87967	1.03161	-1.15572
H	-1.70759	0.20112	-2.76241
H	-2.44481	2.05201	0.7679
H	-3.18284	-0.03917	0.77083
H	0.03053	-1.14508	-3.05923
H	0.32161	1.04937	-3.07189

S-CO_2H

O	0.	0.	2.14087
C	1.17711	0.	2.65875
N	2.27188	0.11028	1.89637
C	2.1322	0.29361	0.45056
C	1.46508	1.49514	-0.01071
C	3.18307	-0.34971	-0.36323
O	4.05545	-1.08952	0.42265
H	4.76395	-1.51201	-0.11448
O	3.32719	-0.24546	-1.59385
H	1.19837	2.25915	0.71751
H	1.70549	1.87637	-0.99675
H	3.20256	-0.01304	2.28725
H	1.29554	-0.09201	3.73856
Rh	0.	0.	0.
P	-2.35119	0.35497	-0.10662

P	-0.13398	-0.24193	-2.34305
H	-2.88873	0.43564	-1.41846
H	-0.8485	-1.38365	-2.79286
H	-2.82615	1.54603	0.50345
H	-3.1468	-0.64826	0.50732
H	1.10441	-0.35788	-3.02813
H	-0.76832	0.8225	-3.0366

R-Me

O	0.	0.	2.13893
C	1.17089	0.	2.6527
N	2.26459	0.02465	1.8774
C	2.15785	-0.00165	0.39728
C	1.84143	-1.24888	-0.18508
C	2.95621	1.11129	-0.2477
H	4.01259	1.05943	0.06044
H	2.93269	1.0431	-1.3362
H	2.57152	2.0943	0.04576
H	1.69389	-2.1294	0.43446
H	2.10375	-1.4417	-1.21876
H	3.1919	0.04059	2.295
H	1.29639	-0.01992	3.73659
Rh	0.	0.	0.
P	-2.10787	1.12942	0.08949
P	-0.36334	-0.02815	-2.33478
H	-2.68056	1.43572	-1.17328
H	-1.72565	-0.06153	-2.73404
H	-2.10974	2.38609	0.75067
H	-3.14755	0.42633	0.75367
H	0.19585	-1.12778	-3.038
H	0.14968	1.08541	-3.05114

S-Me

O	0.	0.	2.13689
C	1.17334	0.	2.65421
N	2.27008	0.05603	1.8857
C	2.15995	0.20139	0.41677
C	1.59138	1.43046	-0.04232
C	3.22793	-0.58858	-0.31158
H	4.23605	-0.25919	-0.01189
H	3.15483	-1.66079	-0.10016
H	3.15568	-0.44459	-1.39192
H	1.31867	2.21098	0.66582
H	1.81368	1.78846	-1.04098
H	3.1939	0.03182	2.31073
H	1.29158	-0.05079	3.73758
Rh	0.	0.	0.
P	-2.39311	0.18594	-0.05713
P	-0.19118	-0.2563	-2.3308
H	-2.96244	0.22969	-1.35727
H	-1.05792	-1.29797	-2.75518
H	-2.93996	1.33857	0.56641
H	-3.10117	-0.87316	0.57006
H	1.01253	-0.54846	-3.02516
H	-0.68423	0.8733	-3.03599

R-H

O	0.	0.	2.14747
C	1.17745	0.	2.64736
N	2.26307	-0.05398	1.85701
C	2.0996	-0.21878	0.40464
C	1.65732	-1.46766	-0.09194
H	2.72236	0.45742	-0.17279
H	1.43903	-2.29064	0.58331
H	1.8999	-1.75195	-1.10885
H	3.19698	-0.04795	2.25787
H	1.31713	0.04376	3.72852
Rh	0.	0.	0.
P	-2.0097	1.34732	-0.01564
P	-0.11746	0.17706	-2.33901
H	-2.5029	1.67739	-1.30568
H	-0.79407	1.3271	-2.82482
H	-1.91134	2.61389	0.61881
H	-3.13734	0.76602	0.62227
H	-0.78137	-0.88351	-3.01045
H	1.12973	0.23371	-3.01554

S-H

O	0.	0.	2.14331
C	1.17941	0.	2.64915
N	2.26915	0.08541	1.86864
C	2.10667	0.27207	0.42083
C	1.51982	1.49853	-0.02885
H	2.8368	-0.27524	-0.16528
H	1.25284	2.27296	0.68821
H	1.72875	1.86722	-1.02617
H	3.19775	0.07849	2.28151
H	1.31003	-0.07154	3.7297
Rh	0.	0.	0.
P	-2.39526	0.15808	-0.18225
P	-0.05664	-0.32561	-2.31704
H	-2.89688	0.1907	-1.51029
H	-0.3598	-1.64867	-2.73417
H	-2.98695	1.30635	0.40749
H	-3.12262	-0.90709	0.41168
H	1.1486	-0.04623	-3.01399
H	-1.00741	0.45577	-3.02548

R-tBu

O	0.	0.	2.15456
C	1.14707	0.	2.64775
N	2.23277	0.2319	1.9192
C	2.15538	0.61656	0.50379
C	2.20482	-0.43421	-0.39239
C	2.60017	2.07751	0.2677
H	2.33594	-1.44482	-0.02046
H	2.46649	-0.26417	-1.42651
H	3.13885	0.21374	2.37067
H	1.29358	-0.20297	3.71366
C	4.11774	2.18271	0.67618
C	2.47691	2.50698	-1.22508
C	1.76329	3.06955	1.13753
H	4.71399	1.45233	0.13664
H	4.48353	3.17395	0.43007

H	4.28912	1.82596	1.68627
H	1.44384	2.45606	-1.55128
H	2.81567	3.53248	-1.32745
H	3.09073	1.88435	-1.86665
H	1.79024	2.79347	2.18627
H	2.17109	4.07013	1.03734
H	0.73139	3.08585	0.8007
Rh	0.	0.	0.
P	-2.28871	0.02864	0.20267
P	-0.43284	-0.38018	-2.21832
H	-3.00154	0.03708	-1.02542
H	-1.52743	-1.24585	-2.48079
H	-2.83557	1.14238	0.89328
H	-2.85238	-1.07516	0.89572
H	0.62013	-0.972	-2.96491
H	-0.74597	0.76973	-2.99036

S-tBu

O	0.	0.	2.15931
C	1.14169	0.	2.66975
N	2.24846	-0.15246	1.95564
C	2.24235	-0.40661	0.51209
C	2.05746	0.71864	-0.29072
C	2.98688	-1.70912	0.1587
H	2.02117	1.70845	0.15699
H	2.35232	0.69955	-1.32983
H	3.13555	-0.13629	2.44316
H	1.26175	0.13053	3.75023
C	4.4811	-1.597	0.64665
C	2.31065	-2.9288	0.86829
C	3.02872	-1.95782	-1.37929
H	4.95159	-0.70236	0.24876
H	4.55158	-1.57925	1.72907
H	5.03426	-2.46076	0.29381
H	2.30553	-2.79217	1.94466
H	1.28554	-3.04881	0.52923
H	2.85924	-3.83714	0.64057
H	3.53033	-2.89904	-1.57689
H	2.0274	-2.01374	-1.78693
H	3.57566	-1.17031	-1.88662
Rh	0.	0.	0.
P	-2.03098	1.02643	0.18074
P	-0.53159	-0.12363	-2.21459
H	-2.65748	1.34251	-1.05376
H	-1.90205	-0.3685	-2.49439
H	-2.03777	2.26999	0.86624
H	-3.02828	0.28589	0.86878
H	0.12573	-1.1407	-2.95614
H	-0.25481	1.03992	-2.98006

R-tBu (achiral)

O	0.	0.	2.15742
C	1.15512	0.	2.63308
N	2.22683	0.24678	1.88725
C	2.10742	0.67318	0.48714
C	2.19182	-0.33894	-0.45405
C	2.45779	2.1659	0.28866

H	2.36407	-1.36396	-0.14154
H	2.43809	-0.10463	-1.47995
H	3.14185	0.23395	2.32094
H	1.32038	-0.21486	3.69394
C	3.97648	2.35527	0.65709
C	2.25917	2.63372	-1.18534
C	1.58565	3.07074	1.21885
H	4.15876	2.15558	1.70789
H	4.60215	1.69743	0.0606
H	4.26712	3.38108	0.45639
H	1.2197	2.53545	-1.48152
H	2.53846	3.67897	-1.26571
H	2.88374	2.06578	-1.86623
H	1.71046	2.79698	2.26115
H	1.88697	4.10647	1.10098
H	0.53474	2.98672	0.95473
Rh	0.	0.	0.
P	-2.28686	-0.123	0.18498
P	-0.37875	-0.42582	-2.2082
H	-2.98919	-0.16126	-1.04857
H	-1.35849	-1.41905	-2.47278
H	-2.91154	0.95181	0.87125
H	-2.78154	-1.26197	0.87377
H	0.73968	-0.883	-2.95418
H	-0.82995	0.67781	-2.97944

S-tBu (achiral)

O	0.	0.	2.15881
C	1.14459	0.	2.66091
N	2.24573	-0.14543	1.93598
C	2.22505	-0.36108	0.48566
C	2.04319	0.78601	-0.28359
C	2.9335	-1.67	0.083
H	1.99632	1.76155	0.19285
H	2.32873	0.79738	-1.32521
H	3.13949	-0.11305	2.41011
H	1.27326	0.12363	3.7412
C	4.39858	-1.6679	0.66067
C	2.15918	-2.90054	0.66059
C	3.04807	-1.80955	-1.46471
H	4.92867	-0.76508	0.37065
H	4.4031	-1.74792	1.74254
H	4.93583	-2.52229	0.26337
H	2.05144	-2.81511	1.73713
H	1.17011	-2.97034	0.21452
H	2.70251	-3.81423	0.44106
H	3.52292	-2.75456	-1.70554
H	2.06704	-1.79503	-1.92194
H	3.64899	-1.01069	-1.8862
Rh	0.	0.	0.
P	-2.16031	0.7511	0.20137
P	-0.49076	-0.05458	-2.22805
H	-2.83323	0.98455	-1.02707
H	-1.87357	-0.13599	-2.54049
H	-2.3268	1.98079	0.8917
H	-3.04472	-0.11739	0.89415
H	0.05977	-1.13991	-2.95975

H	-0.06145	1.07038	-2.98076

R-NH_2

O	0.	0.	2.14821
C	1.16537	0.	2.65976
N	2.26897	-0.00458	1.88557
C	2.19216	-0.20666	0.4285
C	1.66587	-1.43502	-0.05636
N	3.14803	0.57108	-0.22319
H	1.45083	-2.23624	0.64457
H	1.91836	-1.75757	-1.06095
H	3.1992	0.01425	2.29693
H	1.29703	0.0133	3.74315
H	3.52105	0.26453	-1.11025
H	3.19729	1.56346	-0.02634
Rh	0.	0.	0.
P	-1.84319	1.53563	0.01126
P	-0.24906	0.03689	-2.33537
H	-2.31048	1.92431	-1.27208
H	-1.56441	0.30442	-2.79872
H	-1.60836	2.78058	0.65262
H	-3.0196	1.06998	0.65597
H	0.08394	-1.1644	-3.01539
H	0.53179	1.00353	-3.02259

S-NH_2

O	0.	0.	2.14864
C	1.13401	0.	2.71881
N	2.28662	-0.03429	2.01677
C	2.34039	0.05609	0.55802
C	1.86897	1.20654	-0.09388
N	3.2831	-0.82644	0.04298
H	1.60872	2.09135	0.48
H	2.17661	1.38118	-1.11853
H	3.18111	-0.07119	2.49977
H	1.20766	0.01247	3.80815
H	3.72808	-0.61933	-0.84065
H	3.29027	-1.79236	0.34684
Rh	0.	0.	0.
P	-2.29677	-0.60128	0.11341
P	-0.31864	-0.07564	-2.3391
H	-2.93751	-0.76952	-1.14259
H	-1.653	-0.31847	-2.75973
H	-3.1462	0.32045	0.7807
H	-2.5741	-1.82208	0.78359
H	0.41508	-1.07267	-3.03481
H	0.02633	1.10661	-3.04598

R-βCN

O	0.	0.	2.14921
C	1.17992	0.	2.64201
N	2.25681	-0.02237	1.83437
C	2.06159	-0.21103	0.39452
C	1.61692	-1.49775	-0.07879
H	2.71265	0.40707	-0.21494
C	1.36382	-2.60162	0.80268
N	1.15523	-3.51141	1.52917

H	1.87372	-1.78135	-1.09376
H	3.19748	-0.01726	2.22007
H	1.32886	0.02234	3.72162
Rh	0.	0.	0.
P	-1.77038	1.64187	0.01846
P	-0.11176	0.20598	-2.34017
H	-2.21914	2.0574	-1.26308
H	-0.68605	1.41527	-2.81368
H	-1.46837	2.87131	0.66164
H	-2.96846	1.23807	0.66495
H	-0.86988	-0.78622	-3.01634
H	1.13257	0.15753	-3.02258

S-βCN

O	0.	0.	2.14597
C	1.17654	0.	2.65321
N	2.26673	0.05239	1.86577
C	2.09824	0.20043	0.42166
C	1.56722	1.44872	-0.08577
H	2.81479	-0.36661	-0.16189
C	1.29116	2.57656	0.76722
N	1.06757	3.50928	1.45852
H	1.8089	1.73082	-1.10453
H	3.19671	0.05505	2.27624
H	1.30877	-0.04414	3.73432
Rh	0.	0.	0.
P	-2.40554	0.13437	-0.12937
P	-0.11742	-0.35322	-2.31917
H	-2.93669	0.16355	-1.44596
H	-0.61549	-1.62348	-2.71258
H	-2.99561	1.27586	0.47496
H	-3.10882	-0.93884	0.47892
H	1.11205	-0.2671	-3.02442
H	-0.94586	0.54858	-3.0381

R-butenal

O	0.	0.	2.14865
C	1.13312	0.	2.7019
C	2.39526	-0.04329	1.88717
C	2.13051	-0.41542	0.42358
C	1.47859	-1.61749	0.07387
H	2.79306	0.05956	-0.29459
H	1.12425	-2.31397	0.83234
H	1.63289	-2.05939	-0.904
H	3.11433	-0.7285	2.36242
H	2.85643	0.95525	1.96163
H	1.18005	0.05845	3.7969
Rh	0.	0.	0.
P	-2.25588	0.86103	-0.15048
P	-0.00702	0.16681	-2.33119
H	-2.74244	1.04622	-1.4716
H	0.00924	1.49152	-2.84235
H	-2.47593	2.1297	0.44821
H	-3.25693	0.05419	0.45226
H	-1.12328	-0.41012	-2.99263
H	1.09019	-0.44267	-2.99533

S-butenal

O	0.	0.	2.15011
C	1.13499	0.	2.69946
C	2.39442	0.0369	1.88034
C	2.1286	0.41787	0.41871
C	1.48221	1.62351	0.07552
H	2.78468	-0.06018	-0.30366
H	1.1298	2.31744	0.83702
H	1.63654	2.06841	-0.90091
H	3.12127	0.7145	2.35437
H	2.84737	-0.96585	1.94878
H	1.1859	-0.05533	3.79445
Rh	0.	0.	0.
P	-2.18254	-1.03072	-0.13212
P	-0.00093	-0.19082	-2.33144
H	-2.66211	-1.25773	-1.44927
H	-0.07938	-1.51843	-2.82912
H	-3.24605	-0.30894	0.47153
H	-2.28961	-2.30967	0.4755
H	1.14115	0.32632	-2.99823
H	-1.06836	0.4627	-3.0022

VI. *t*Butyl geometries and energies

Only the Basis II/Basis II structure and energetics are given for those molecules that were optimized at that level. The **ALPR** and **PROD** geometries were found with a different ONIOM partition (placing *t*Bu largely in the MM layer, using a methyl group in the B3LYP layer), at the Basis I level. Energies for those structures are at the Basis II level, with *t*Bu included in the HF layer.

Constrained and incomplete optimizations have the forces included after the cartesian coordiates. Constrained structures have a note describing the constraint.

All transition state structures have the three lowest frequencies listed.

H_2:

E(Basis II/Basis II): -1.17853934
Sum of electronic and thermal free energies(Basis II/Basis II; 298K): -1.17985134

Pro-R:

E(Basis II/Basis II): -912.054427238268
Thermal Correction to Gibbs Free Energy (Basis II/Basis II;298K): 0.625926

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	45	0.616038	-0.086083	0.671423
2	8	0.533876	-0.033508	2.823770
3	6	1.661020	0.005189	3.359550