Supporting Information

for

Mechanistic Insights and the Origin of Regio-Selective Borylation in an Iridium-Catalyzed Alkyl C(sp3)-H Bond Functionalization

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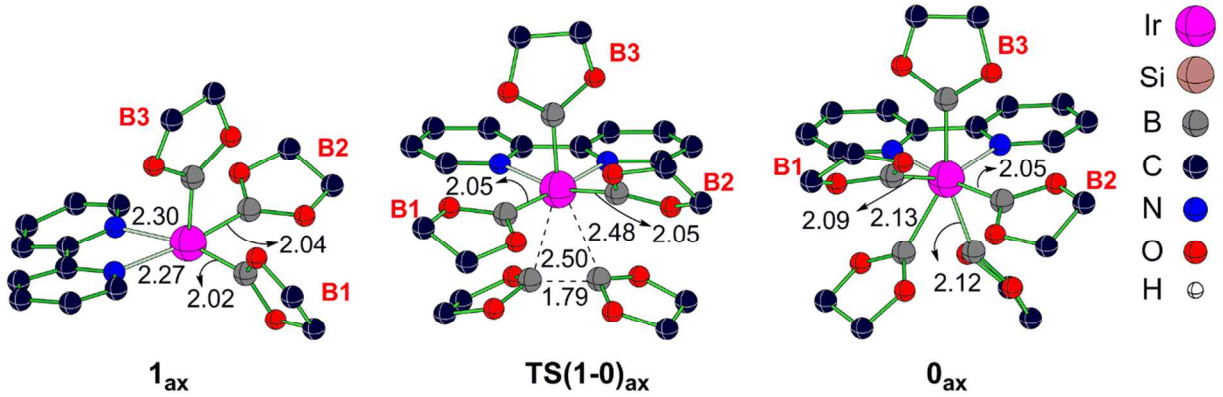


Figure S1: SMD_{THF}/B3LYP-D3/6-31G** optimized geometries of key intermediates and transition states for oxidative addition of B_2eg_2 to active catalyst **1**.

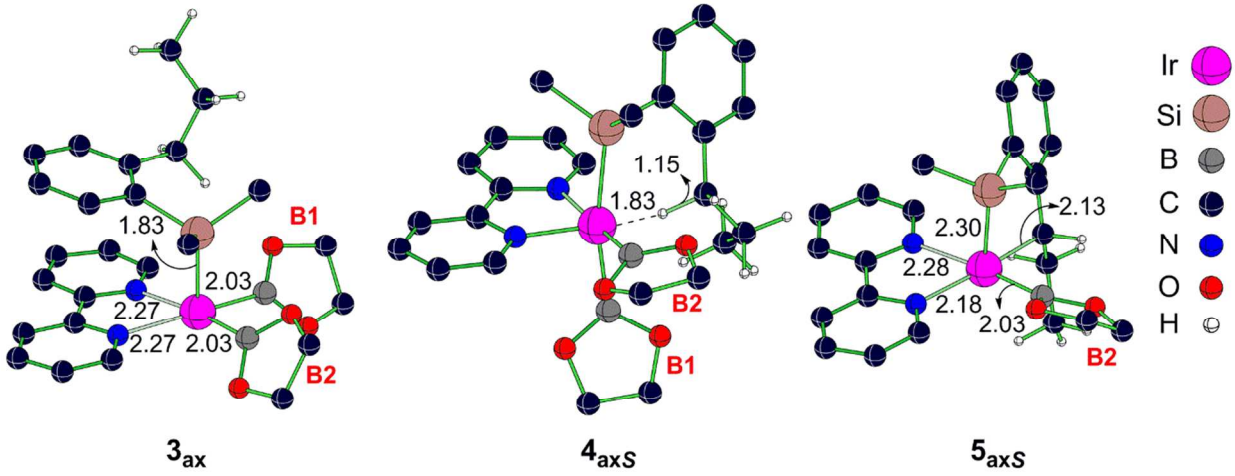


Figure S2: SMD_{THF}/B3LYP-D3/6-31G** optimized geometries of key intermediates for C–H bond activation.

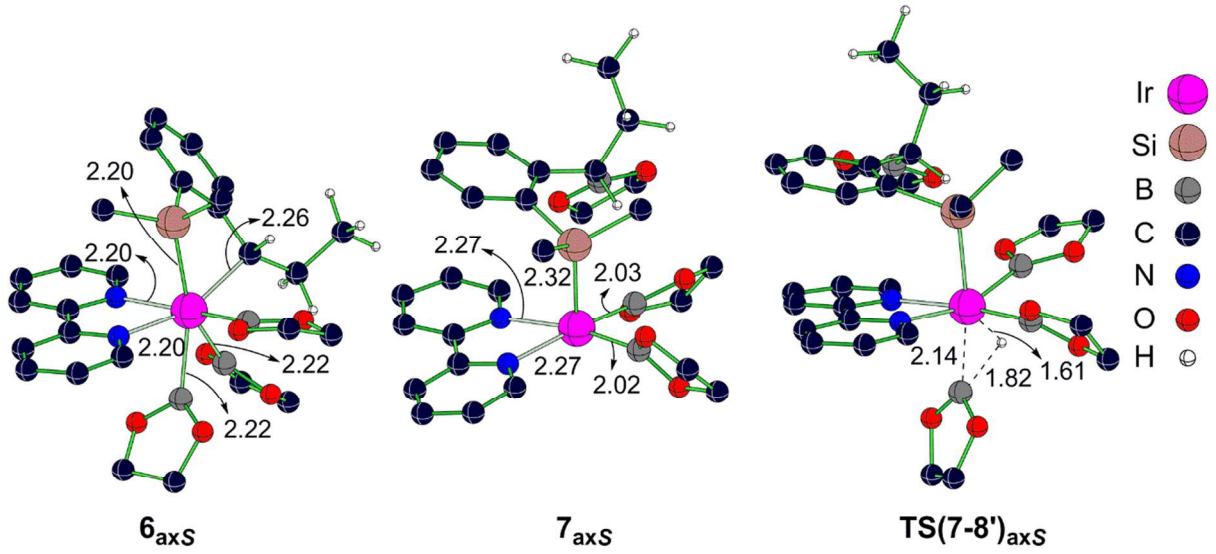


Figure S3: SMD_{THF}/B3LYP-D3/6-31G** optimized geometries of key intermediates for C–B bond formation and H–Beg addition.

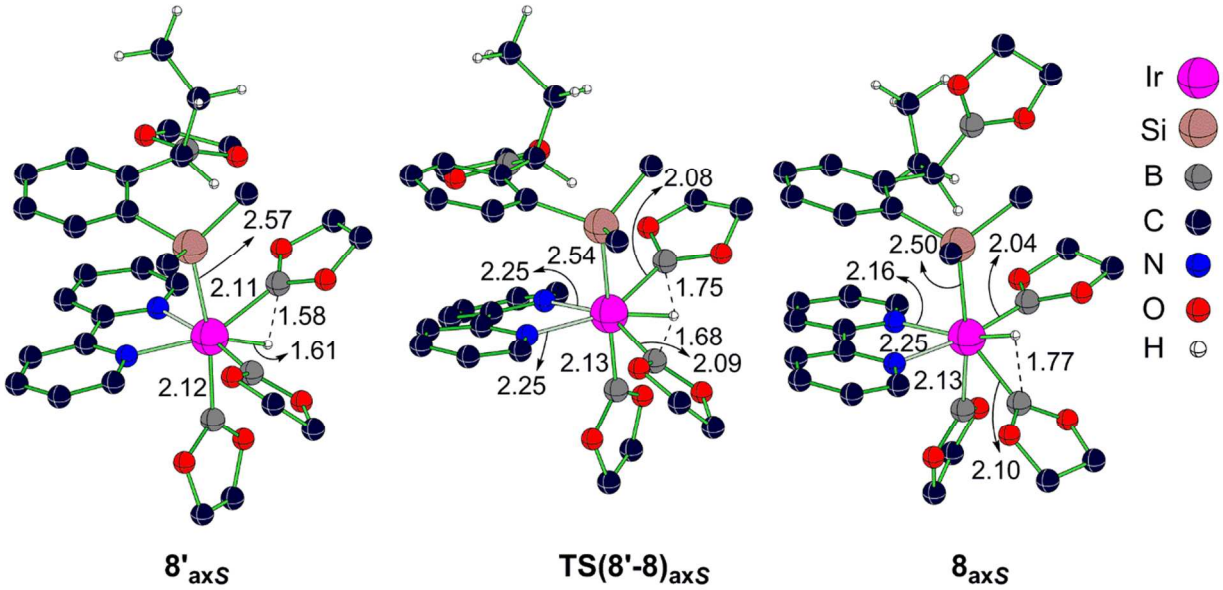
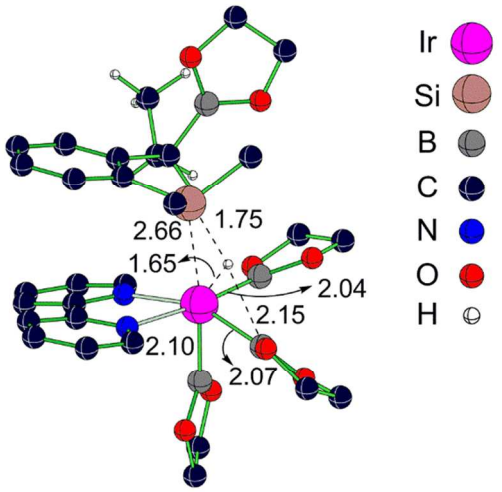
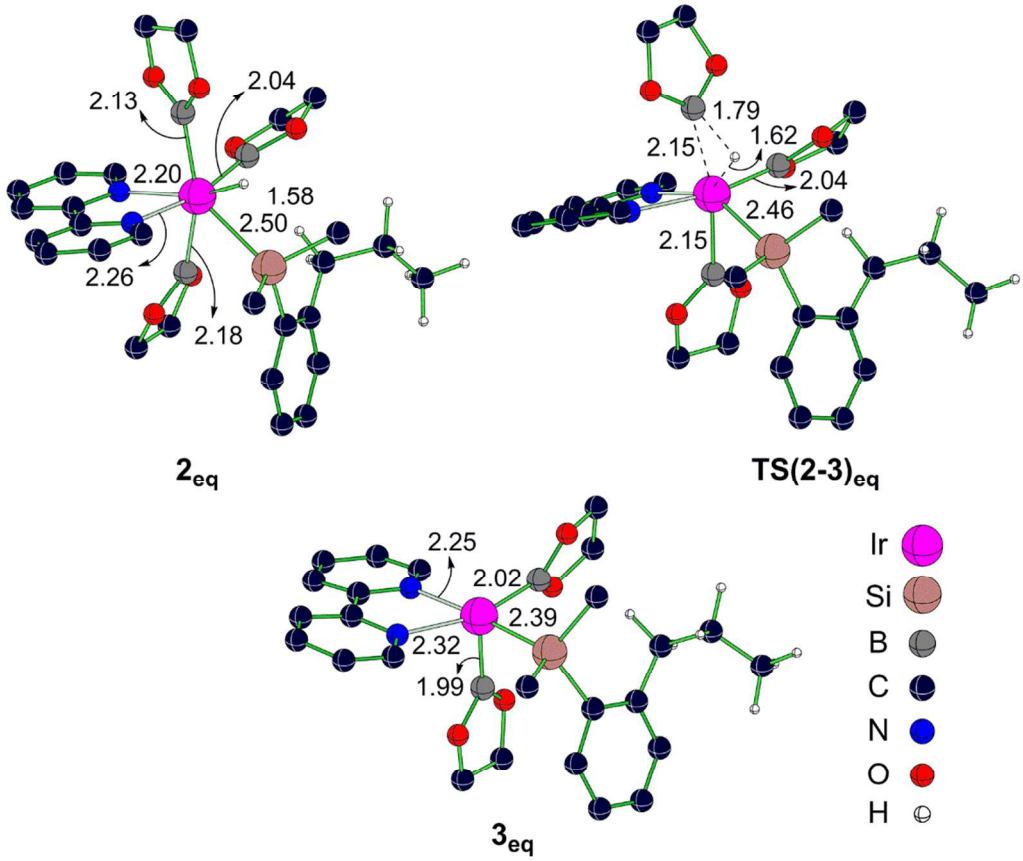


Figure S4: SMD_{THF}/B3LYP-D3/6-31G** optimized geometries of key intermediates and transition states for isomerization of **8** to **8'** prior to reductive elimination of Si–H bond.



TS(8-P)$_{axS}$

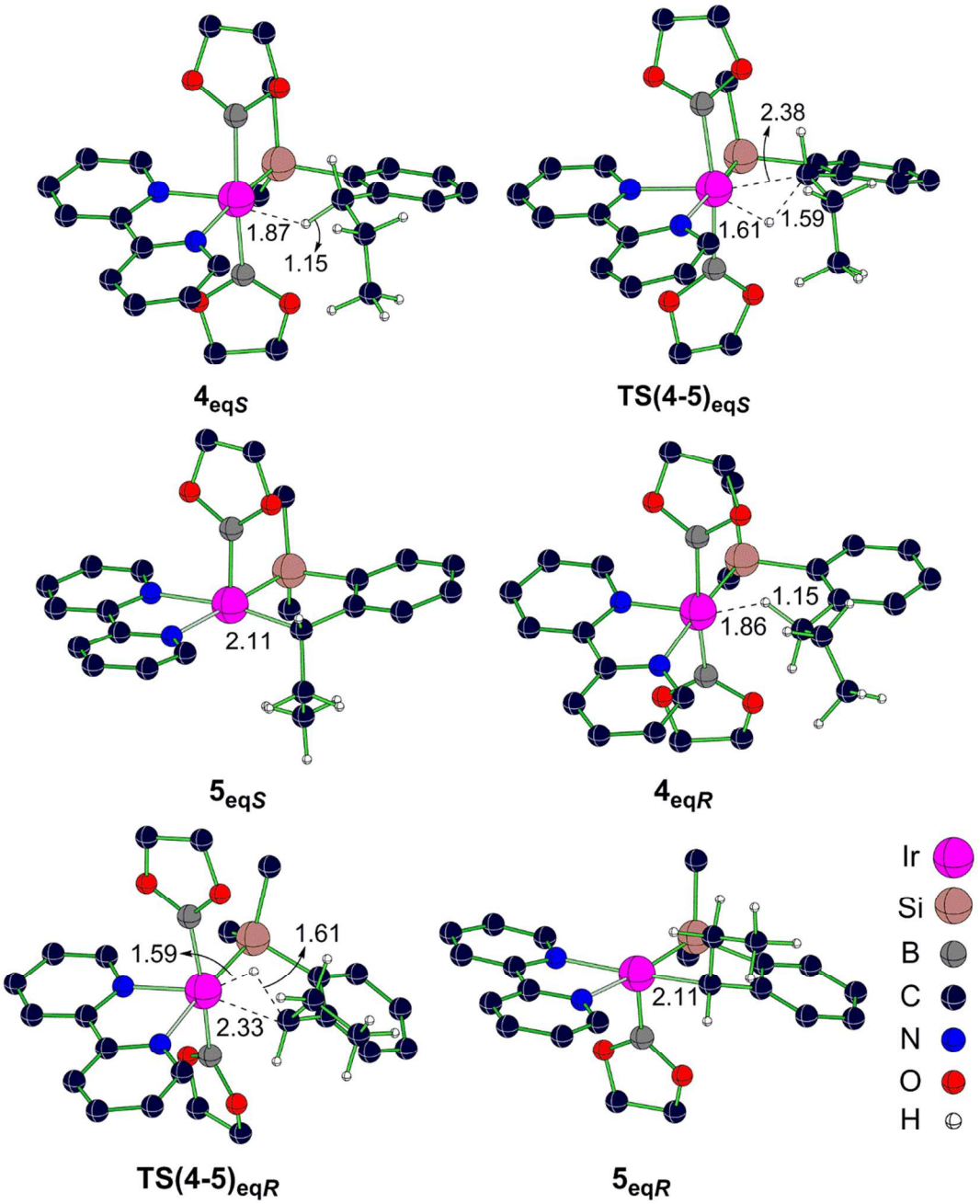
Figure S5: SMD$_{THF}$/B3LYP-D3/6-31G** optimized geometries of transition state for reductive elimination of Si–H bond.



2$_{eq}$ **TS(2-3)$_{eq}$**

3$_{eq}$

Figure S6: SMD$_{THF}$/B3LYP-D3/6-31G** optimized geometries of transition state for reductive elimination of H–Beg molecule when Si atom is at equatorial position.



4_{eqS} $TS(4\text{-}5)_{eqS}$ 5_{eqS} 4_{eqR} $TS(4\text{-}5)_{eqR}$ 5_{eqR}

Figure S7: SMD_{THF}/B3LYP-D3/6-31G** optimized geometries of transition state for C–H activation when Si atom is at equatorial position.

Table S1: Relative Free Energies[a] of Key Intermediates and Transition States when Si atom is at Axial or Equatorial position with respect to bipyridine plane

Intermediate	ΔG (Axial)	ΔG (Equatorial)
2	-3.1	9.7
TS(2-3)	1.7	10.3
3	-11.8	-0.8
4_S	22.9	27.1
TS(4-5)$_S$	29.9	36.5
5_S	-0.5	1.2
TS(6-7)	29.6	30.9
TS(7-8)	-4.6	3.5

[a]Relative Free energies are with respect to infinitely separated reactants (**1, A** and B_2eg_2) and are obtained using SMD_{THF}/B3LYP-D3/6-31G** level of theory.

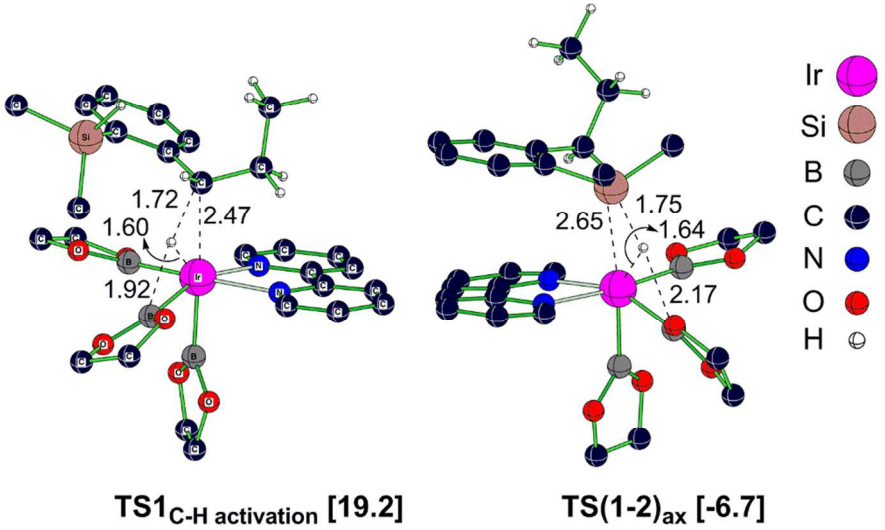
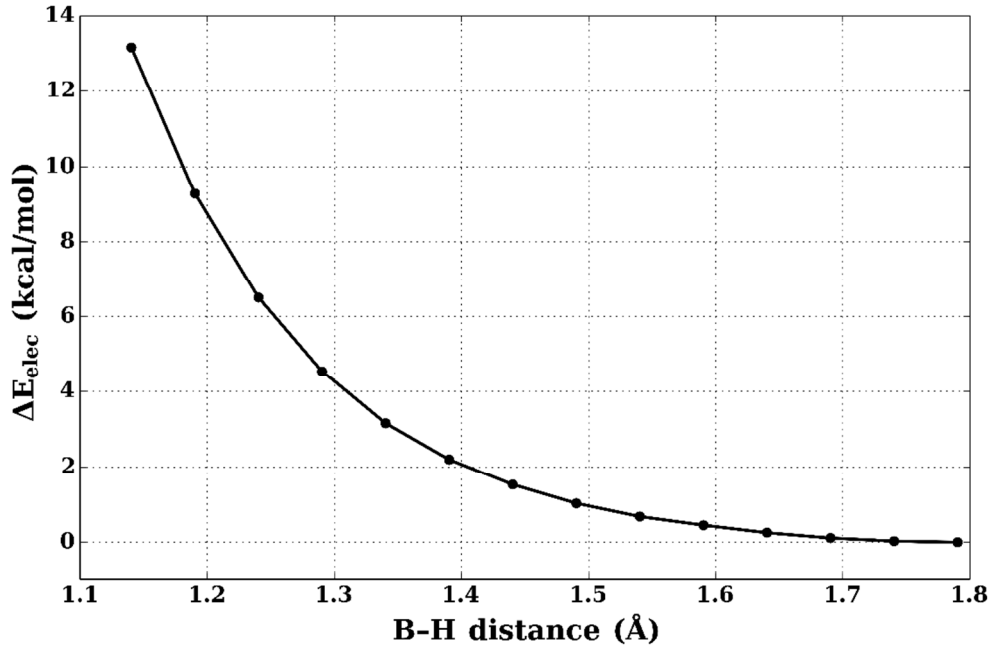
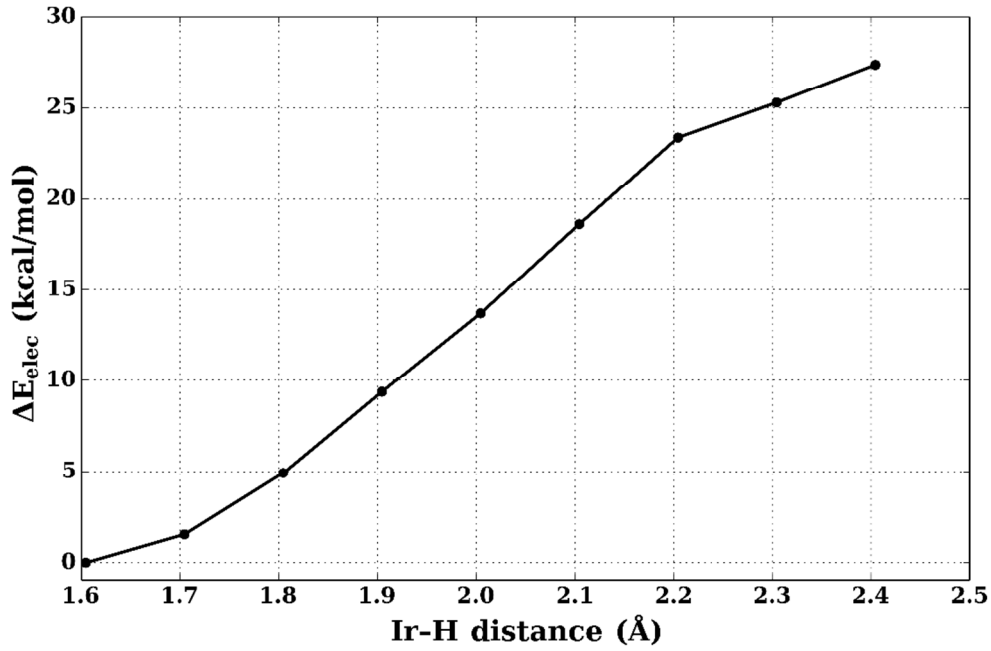


Figure S8: Comparison of C–H and Si–H activation using B3LYP-D3/6-31G** level of theory.



(a)



(b)

Figure S9: Relaxed potential energy surface scan, at B3LYP-D3/6-31G** level of theory, for transfer of hydride ligand to equatorial boryl ligand in intermediate $\mathbf{2_{ax}}$. (a) Variation of electronic energy with B–H distance. (b) Variation of electronic energy with Ir–H distance.

Table S2: Wiberg Bond Indices for C–H Bonds in **A** which can undergo C1–H Activation.

C–H bond	Wiberg Bond Index	Average
C1–H	0.9149	0.9085
C1–H	0.9021	
C2–H	0.9151	0.9156
C2–H	0.9162	
C3–H	0.9310	0.9295
C3–H	0.9263	
C3–H	0.9313	
C4–H	0.9113	0.9113

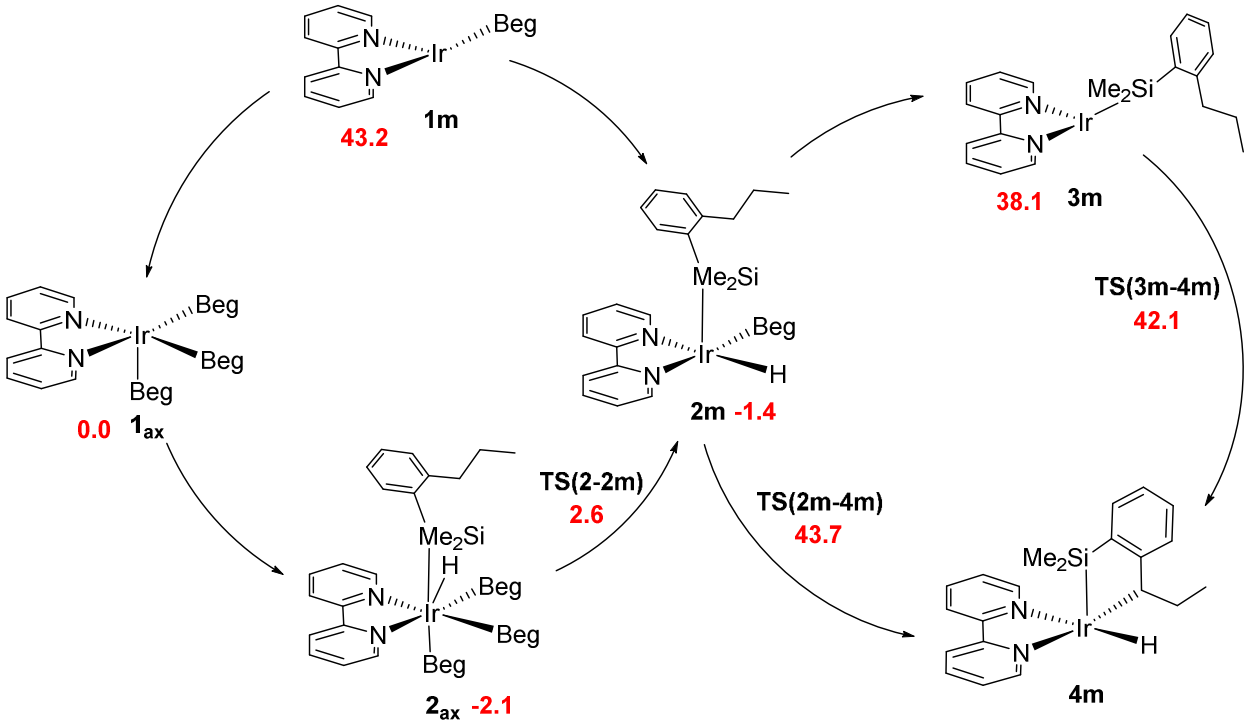


Figure S10: Possible pathways for C-H activation involving mono-borylated Ir species. Relative free energies (kcal/mol) with respect to the infinitely separated reactants obtained at the SMD_{THF}/B3LYP-D3/6-31G**,LANL2DZ(Ir) level of theory are shown in red.

Calculation of Percentage Yield

Let $\Delta G^{\ddagger}_{C1\text{-}H(R/S)}$, $\Delta G^{\ddagger}_{C2\text{-}H(R/S)}$, $\Delta G^{\ddagger}_{C3\text{-}H}$ and $\Delta G^{\ddagger}_{C4\text{-}H}$ be the relative free energy of TSs for C-H activation at C1, C2 C3 and C4 respectively, where (R/S) denotes the R/S configuration in the intermediate $\mathbf{5_{ax}}$.

Then the ratio of the regio-isomers obtained can be given as:

$$\frac{P_{C1-H(R/S)}}{P_{C1-H(S/R)}} = \frac{e^{\frac{-\Delta G^{\ddagger}_{C1-H(R/S)}}{RT}}}{e^{\frac{-\Delta G^{\ddagger}_{C1-H(S/R)}}{RT}}} = e^{\frac{-\Delta\Delta G^{\ddagger}_{1}}{RT}}$$

Similarly,

where, $\Delta\Delta G^{\ddagger}_{i} = \Delta G^{\ddagger}_{Ci\text{-}H} - \Delta G^{\ddagger}_{C1\text{-}H(S/R)}$ and $i = 2,3,4$

The % yield can be calculated as:

$$\%\ yield = \frac{1 + \frac{P_{C1-H(R/S)}}{P_{C1-H(S/R)}}}{1 + \frac{P_{C1-H(R/S)}}{P_{C1-H(S/R)}} + \frac{P_{C2-H(R)}}{P_{C1-H(S/R)}} + \frac{P_{C2-H(S)}}{P_{C1-H(S/R)}} + \frac{P_{C3-H}}{P_{C1-H(S/R)}} + \frac{P_{C4-H}}{P_{C1-H(S/R)}}}$$

Entropy Contributions for Free energy Calculation

Fundamental equations used for calculation of entropic contributions are provided below. For details please refer to Gaussian whitepapers on thermochemistry available on http ://www.aussian.com. Or "Molecular Thermodynamics" by Macquarrie and Simon (1999).

Translational Entropy:

$$S_{trans} = R(\ln q_{trans} + 1 + \tfrac{3}{2})$$

Where, $q_{trans} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \frac{k_B T}{P}$

Rotational Entropy:

For non-linear polyatomic molecules

$$S_{rot} = R(\ln q_{rot} + \frac{3}{2})$$

Where $q_{rot} = \frac{\pi^{1/2}}{\sigma_r}\left(\frac{T^{3/2}}{(\Theta_{r,x}\Theta_{r,y}\Theta_{r,z})^{1/2}}\right)$

Vibrational Entropy:

For non-linear polyatomic molecules

$$S_{vib} = R\sum_{K}\left(\frac{\Theta_{v,K}}{e^{\Theta_{v,K}/T}-1} - \ln\left(1-e^{-\Theta_{v,K}/T}\right)\right)$$

Where, $\Theta_{v,K} = {h\nu_K}/{k_B}$ is the vibrational temperature of Kth vibrational mode with frequency ν_K

The above expression is for calculation of vibrational entropy contribution if one assumes harmonic oscillator model. Alternatively, one can apply Rigid-Rotor Harmonic Oscillator (RRHO) model as prescribed by Grimme (*Chem. – Eur. J.* **2012**, *18* (32), 9955–9964) to obtain more accurate vibrational entropy.

Energies (in hartrees/particle) for stationary points at SMD_{THF}/B3LYP-D3/6-31G**,LANL2DZ(Ir) Level of Theory

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$[Ir(COD)(OMe)]_2$

Number of imaginary frequencies : 0
The smallest frequency is : 19.1892 cm(-1)

Hartree-Fock electronic energy : HF=-1063.9994874
Zero-point correction= 0.452175 (Hartree/Particle)
Thermal correction to Energy= 0.475667
Thermal correction to Enthalpy= 0.476611
Thermal correction to Gibbs Free Energy= 0.399740
Sum of electronic and zero-point Energies= -1063.547313
Sum of electronic and thermal Energies= -1063.523820
Sum of electronic and thermal Enthalpies= -1063.522876
Sum of electronic and thermal Free Energies= -1063.599748

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bpy

Number of imaginary frequencies : 0
The smallest frequency is : 66.0744 cm(-1)

Hartree-Fock electronic energy : HF=-495.4079179
Zero-point correction= 0.158229 (Hartree/Particle)
Thermal correction to Energy= 0.166852
Thermal correction to Enthalpy= 0.167797
Thermal correction to Gibbs Free Energy= 0.124392
Sum of electronic and zero-point Energies= -495.249688
Sum of electronic and thermal Energies= -495.241065
Sum of electronic and thermal Enthalpies= -495.240121
Sum of electronic and thermal Free Energies= -495.283526

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cod

Number of imaginary frequencies : 0
The smallest frequency is : 85.3328 cm(-1)

Hartree-Fock electronic energy : HF=-312.0661408
Zero-point correction= 0.180541 (Hartree/Particle)
Thermal correction to Energy= 0.187932
Thermal correction to Enthalpy= 0.188876
Thermal correction to Gibbs Free Energy= 0.149100
Sum of electronic and zero-point Energies= -311.885600
Sum of electronic and thermal Energies= -311.878209
Sum of electronic and thermal Enthalpies= -311.877265
Sum of electronic and thermal Free Energies= -311.917041

B_2eg_2

Number of imaginary frequencies : 0
The smallest frequency is : 34.2210 cm(-1)

Hartree-Fock electronic energy : HF=-508.0303777
Zero-point correction= 0.141098 (Hartree/Particle)
Thermal correction to Energy= 0.150398
Thermal correction to Enthalpy= 0.151343
Thermal correction to Gibbs Free Energy= 0.104663
Sum of electronic and zero-point Energies= -507.889280
Sum of electronic and thermal Energies= -507.879979
Sum of electronic and thermal Enthalpies= -507.879035
Sum of electronic and thermal Free Energies= -507.925715

HBeg

Number of imaginary frequencies : 0
The smallest frequency is : 33.5169 cm(-1)

Hartree-Fock electronic energy : HF=-254.6128095
Zero-point correction= 0.078997 (Hartree/Particle)
Thermal correction to Energy= 0.083617
Thermal correction to Enthalpy= 0.084561
Thermal correction to Gibbs Free Energy= 0.050585
Sum of electronic and zero-point Energies= -254.533813
Sum of electronic and thermal Energies= -254.529193
Sum of electronic and thermal Enthalpies= -254.528248
Sum of electronic and thermal Free Energies= -254.562225

A

Number of imaginary frequencies : 0
The smallest frequency is : 55.5404 cm(-1)

Hartree-Fock electronic energy : HF=-719.5879563
Zero-point correction= 0.259322 (Hartree/Particle)
Thermal correction to Energy= 0.273433
Thermal correction to Enthalpy= 0.274377
Thermal correction to Gibbs Free Energy= 0.219073
Sum of electronic and zero-point Energies= -719.328634
Sum of electronic and thermal Energies= -719.314523
Sum of electronic and thermal Enthalpies= -719.313579
Sum of electronic and thermal Free Energies= -719.368883

0

Number of imaginary frequencies : 0
The smallest frequency is : 25.6836 cm(-1)

Hartree-Fock electronic energy : HF=-1870.3406966
Zero-point correction= 0.513974 (Hartree/Particle)

Thermal correction to Energy= 0.550583
Thermal correction to Enthalpy= 0.551527
Thermal correction to Gibbs Free Energy= 0.442625
Sum of electronic and zero-point Energies= -1869.826722
Sum of electronic and thermal Energies= -1869.790114
Sum of electronic and thermal Enthalpies= -1869.789170
Sum of electronic and thermal Free Energies= -1869.898072

1

Number of imaginary frequencies : 0
The smallest frequency is : 27.1167 cm(-1)

Hartree-Fock electronic energy : HF=-1362.2893714
Zero-point correction= 0.371972 (Hartree/Particle)
Thermal correction to Energy= 0.398176
Thermal correction to Enthalpy= 0.399120
Thermal correction to Gibbs Free Energy= 0.312299
Sum of electronic and zero-point Energies= -1361.917400
Sum of electronic and thermal Energies= -1361.891196
Sum of electronic and thermal Enthalpies= -1361.890251
Sum of electronic and thermal Free Energies= -1361.977072

$TS(1\text{-}2)_{ax}$

Number of imaginary frequencies : 1
The smallest frequency is : -89.0940 cm(-1)

Hartree-Fock electronic energy : HF=-2081.9013023
Zero-point correction= 0.632825 (Hartree/Particle)
Thermal correction to Energy= 0.673636
Thermal correction to Enthalpy= 0.674580
Thermal correction to Gibbs Free Energy= 0.558138
Sum of electronic and zero-point Energies= -2081.268478
Sum of electronic and thermal Energies= -2081.227666
Sum of electronic and thermal Enthalpies= -2081.226722
Sum of electronic and thermal Free Energies= -2081.343164

2_{ax}

Number of imaginary frequencies : 0
The smallest frequency is : 15.0905 cm(-1)

Hartree-Fock electronic energy : HF=-2081.9082723
Zero-point correction= 0.633104 (Hartree/Particle)
Thermal correction to Energy= 0.674542
Thermal correction to Enthalpy= 0.675486
Thermal correction to Gibbs Free Energy= 0.557421
Sum of electronic and zero-point Energies= -2081.275168
Sum of electronic and thermal Energies= -2081.233730
Sum of electronic and thermal Enthalpies= -2081.232786

Sum of electronic and thermal Free Energies= -2081.350851

$TS(2\text{-}2')_{ax}$

Number of imaginary frequencies : 1
The smallest frequency is : -535.2956 cm(-1)

Hartree-Fock electronic energy : HF=-2081.8781524
Zero-point correction= 0.633760 (Hartree/Particle)
Thermal correction to Energy= 0.674441
Thermal correction to Enthalpy= 0.675385
Thermal correction to Gibbs Free Energy= 0.560855
Sum of electronic and zero-point Energies= -2081.244392
Sum of electronic and thermal Energies= -2081.203711
Sum of electronic and thermal Enthalpies= -2081.202767
Sum of electronic and thermal Free Energies= -2081.317297

$2'_{ax}$

Number of imaginary frequencies : 0
The smallest frequency is : 22.6859 cm(-1)

Hartree-Fock electronic energy : HF=-2081.9061918
Zero-point correction= 0.634782 (Hartree/Particle)
Thermal correction to Energy= 0.675636
Thermal correction to Enthalpy= 0.676580
Thermal correction to Gibbs Free Energy= 0.561477
Sum of electronic and zero-point Energies= -2081.271410
Sum of electronic and thermal Energies= -2081.230556
Sum of electronic and thermal Enthalpies= -2081.229612
Sum of electronic and thermal Free Energies= -2081.344715

$TS(2'\text{-}3)_{ax}$

Number of imaginary frequencies : 1
The smallest frequency is : -297.8976 cm(-1)

Hartree-Fock electronic energy : HF=-2081.9025127
Zero-point correction= 0.632530 (Hartree/Particle)
Thermal correction to Energy= 0.673338
Thermal correction to Enthalpy= 0.674282
Thermal correction to Gibbs Free Energy= 0.559189
Sum of electronic and zero-point Energies= -2081.269983
Sum of electronic and thermal Energies= -2081.229175
Sum of electronic and thermal Enthalpies= -2081.228231
Sum of electronic and thermal Free Energies= -2081.343324

3_{ax}

Number of imaginary frequencies : 0

The smallest frequency is : 28.4266 cm(-1)

Hartree-Fock electronic energy : HF=-1827.2896277
Zero-point correction= 0.554317 (Hartree/Particle)
Thermal correction to Energy= 0.589868
Thermal correction to Enthalpy= 0.590812
Thermal correction to Gibbs Free Energy= 0.487052
Sum of electronic and zero-point Energies= -1826.735311
Sum of electronic and thermal Energies= -1826.699760
Sum of electronic and thermal Enthalpies= -1826.698815
Sum of electronic and thermal Free Energies= -1826.802576

TS(3-4')$_{axS}$

Number of imaginary frequencies : 1
The smallest frequency is : -55.5678 cm(-1)

Hartree-Fock electronic energy : HF=-1827.2276328
Zero-point correction= 0.552598 (Hartree/Particle)
Thermal correction to Energy= 0.587728
Thermal correction to Enthalpy= 0.588672
Thermal correction to Gibbs Free Energy= 0.484692
Sum of electronic and zero-point Energies= -1826.675035
Sum of electronic and thermal Energies= -1826.639905
Sum of electronic and thermal Enthalpies= -1826.638961
Sum of electronic and thermal Free Energies= -1826.742941

4'$_{axS}$

Number of imaginary frequencies : 0
The smallest frequency is : 15.5725 cm(-1)

Hartree-Fock electronic energy : HF=-1827.2331902
Zero-point correction= 0.553215 (Hartree/Particle)
Thermal correction to Energy= 0.588620
Thermal correction to Enthalpy= 0.589565
Thermal correction to Gibbs Free Energy= 0.485998
Sum of electronic and zero-point Energies= -1826.679975
Sum of electronic and thermal Energies= -1826.644570
Sum of electronic and thermal Enthalpies= -1826.643626
Sum of electronic and thermal Free Energies= -1826.747193

TS(4'-5)$_{axS}$

Number of imaginary frequencies : 1
The smallest frequency is : -788.5840 cm(-1)

Hartree-Fock electronic energy : HF=-1827.216716
Zero-point correction= 0.549069 (Hartree/Particle)
Thermal correction to Energy= 0.584541
Thermal correction to Enthalpy= 0.585485

Thermal correction to Gibbs Free Energy= 0.480670
Sum of electronic and zero-point Energies= -1826.667647
Sum of electronic and thermal Energies= -1826.632175
Sum of electronic and thermal Enthalpies= -1826.631231
Sum of electronic and thermal Free Energies= -1826.736046

5_{axS}

Number of imaginary frequencies : 0
The smallest frequency is : 26.3917 cm(-1)

Hartree-Fock electronic energy : HF=-1572.6327226
Zero-point correction= 0.471047 (Hartree/Particle)
Thermal correction to Energy= 0.500807
Thermal correction to Enthalpy= 0.501751
Thermal correction to Gibbs Free Energy= 0.410565
Sum of electronic and zero-point Energies= -1572.161676
Sum of electronic and thermal Energies= -1572.131916
Sum of electronic and thermal Enthalpies= -1572.130972
Sum of electronic and thermal Free Energies= -1572.222157

$TS(5\text{-}6)_{ax}$

Number of imaginary frequencies : 1
The smallest frequency is : -74.7171 cm(-1)

Hartree-Fock electronic energy : HF=-2080.6651267
Zero-point correction= 0.613529 (Hartree/Particle)
Thermal correction to Energy= 0.653028
Thermal correction to Enthalpy= 0.653972
Thermal correction to Gibbs Free Energy= 0.542972
Sum of electronic and zero-point Energies= -2080.051598
Sum of electronic and thermal Energies= -2080.012099
Sum of electronic and thermal Enthalpies= -2080.011155
Sum of electronic and thermal Free Energies= -2080.122154

6_{ax}

Number of imaginary frequencies : 0
The smallest frequency is : 24.0769 cm(-1)

Hartree-Fock electronic energy : HF=-2080.6662796
Zero-point correction= 0.613641 (Hartree/Particle)
Thermal correction to Energy= 0.654039
Thermal correction to Enthalpy= 0.654983
Thermal correction to Gibbs Free Energy= 0.541280
Sum of electronic and zero-point Energies= -2080.052638
Sum of electronic and thermal Energies= -2080.012241
Sum of electronic and thermal Enthalpies= -2080.011297
Sum of electronic and thermal Free Energies= -2080.125000

$TS(6\text{-}7)_{ax}$

Number of imaginary frequencies : 1
The smallest frequency is : -110.9513 cm(-1)

Hartree-Fock electronic energy : HF=-2080.6427932
Zero-point correction= 0.613459 (Hartree/Particle)
Thermal correction to Energy= 0.652871
Thermal correction to Enthalpy= 0.653815
Thermal correction to Gibbs Free Energy= 0.542767
Sum of electronic and zero-point Energies= -2080.029335
Sum of electronic and thermal Energies= -2079.989922
Sum of electronic and thermal Enthalpies= -2079.988978
Sum of electronic and thermal Free Energies= -2080.100026

7_{ax}

Number of imaginary frequencies : 0
The smallest frequency is : 28.5546 cm(-1)

Hartree-Fock electronic energy : HF=-2080.7216389
Zero-point correction= 0.616140 (Hartree/Particle)
Thermal correction to Energy= 0.655921
Thermal correction to Enthalpy= 0.656865
Thermal correction to Gibbs Free Energy= 0.544245
Sum of electronic and zero-point Energies= -2080.105499
Sum of electronic and thermal Energies= -2080.065718
Sum of electronic and thermal Enthalpies= -2080.064774
Sum of electronic and thermal Free Energies= -2080.177394

$TS(7\text{-}8')_{ax}$

Number of imaginary frequencies : 1
The smallest frequency is : -371.5501 cm(-1)

Hartree-Fock electronic energy : HF=-2335.3306793
Zero-point correction= 0.693349 (Hartree/Particle)
Thermal correction to Energy= 0.738957
Thermal correction to Enthalpy= 0.739902
Thermal correction to Gibbs Free Energy= 0.613870
Sum of electronic and zero-point Energies= -2334.637331
Sum of electronic and thermal Energies= -2334.591722
Sum of electronic and thermal Enthalpies= -2334.590778
Sum of electronic and thermal Free Energies= -2334.716809

$8'_{ax}$

Number of imaginary frequencies : 0
The smallest frequency is : 19.4078 cm(-1)

Hartree-Fock electronic energy : HF=-2335.3343391
Zero-point correction= 0.695478 (Hartree/Particle)
Thermal correction to Energy= 0.741201
Thermal correction to Enthalpy= 0.742145
Thermal correction to Gibbs Free Energy= 0.615268
Sum of electronic and zero-point Energies= -2334.638861
Sum of electronic and thermal Energies= -2334.593139
Sum of electronic and thermal Enthalpies= -2334.592194
Sum of electronic and thermal Free Energies= -2334.719071

$TS(8'\text{-}8)_{ax}$

Number of imaginary frequencies : 1
The smallest frequency is : -512.2836 cm(-1)

Hartree-Fock electronic energy : HF=-2335.3073354
Zero-point correction= 0.694538 (Hartree/Particle)
Thermal correction to Energy= 0.739785
Thermal correction to Enthalpy= 0.740729
Thermal correction to Gibbs Free Energy= 0.615616
Sum of electronic and zero-point Energies= -2334.612798
Sum of electronic and thermal Energies= -2334.567551
Sum of electronic and thermal Enthalpies= -2334.566607
Sum of electronic and thermal Free Energies= -2334.691719

8_{ax}

Number of imaginary frequencies : 0
The smallest frequency is : 23.9463 cm(-1)

Hartree-Fock electronic energy : HF=-2335.336597
Zero-point correction= 0.694651 (Hartree/Particle)
Thermal correction to Energy= 0.740296
Thermal correction to Enthalpy= 0.741240
Thermal correction to Gibbs Free Energy= 0.615118
Sum of electronic and zero-point Energies= -2334.641946
Sum of electronic and thermal Energies= -2334.596301
Sum of electronic and thermal Enthalpies= -2334.595357
Sum of electronic and thermal Free Energies= -2334.721479

$TS(8\text{-}1)_{ax}$

Number of imaginary frequencies : 1
The smallest frequency is : -104.1864 cm(-1)

Hartree-Fock electronic energy : HF=-2335.3303822
Zero-point correction= 0.693495 (Hartree/Particle)
Thermal correction to Energy= 0.738684
Thermal correction to Enthalpy= 0.739628
Thermal correction to Gibbs Free Energy= 0.614062
Sum of electronic and zero-point Energies= -2334.636887

Sum of electronic and thermal Energies= -2334.591699
Sum of electronic and thermal Enthalpies= -2334.590754
Sum of electronic and thermal Free Energies= -2334.716320

P

Number of imaginary frequencies : 0
The smallest frequency is : 32.6989 cm(-1)

Hartree-Fock electronic energy : HF=-973.0120485
Zero-point correction= 0.319632 (Hartree/Particle)
Thermal correction to Energy= 0.338525
Thermal correction to Enthalpy= 0.339470
Thermal correction to Gibbs Free Energy= 0.272151
Sum of electronic and zero-point Energies= -972.692416
Sum of electronic and thermal Energies= -972.673523
Sum of electronic and thermal Enthalpies= -972.672579
Sum of electronic and thermal Free Energies= -972.739897

TS(4-5)$_{axS}$ for C2

Number of imaginary frequencies : 1
The smallest frequency is : -820.5779 cm(-1)

Hartree-Fock electronic energy : HF=-1827.2155451
Zero-point correction= 0.549926 (Hartree/Particle)
Thermal correction to Energy= 0.584907
Thermal correction to Enthalpy= 0.585851
Thermal correction to Gibbs Free Energy= 0.483852
Sum of electronic and zero-point Energies= -1826.665619
Sum of electronic and thermal Energies= -1826.630638
Sum of electronic and thermal Enthalpies= -1826.629694
Sum of electronic and thermal Free Energies= -1826.731693

TS(4-5)$_{axR}$ for C2

Number of imaginary frequencies : 1
The smallest frequency is : -878.1545 cm(-1)

Hartree-Fock electronic energy : HF=-1827.2148305
Zero-point correction= 0.550782 (Hartree/Particle)
Thermal correction to Energy= 0.585401
Thermal correction to Enthalpy= 0.586345
Thermal correction to Gibbs Free Energy= 0.485852
Sum of electronic and zero-point Energies= -1826.664049
Sum of electronic and thermal Energies= -1826.629429
Sum of electronic and thermal Enthalpies= -1826.628485
Sum of electronic and thermal Free Energies= -1826.728978

TS(4-5)$_{ax}$ for C3

Number of imaginary frequencies : 1
The smallest frequency is : -734.0848 cm(-1)

Hartree-Fock electronic energy : HF=-1827.2176096
Zero-point correction= 0.551222 (Hartree/Particle)
Thermal correction to Energy= 0.585716
Thermal correction to Enthalpy= 0.586661
Thermal correction to Gibbs Free Energy= 0.484711
Sum of electronic and zero-point Energies= -1826.666388
Sum of electronic and thermal Energies= -1826.631893
Sum of electronic and thermal Enthalpies= -1826.630949
Sum of electronic and thermal Free Energies= -1826.732898

$TS(4\text{-}5)_{axS}$ for C4

Number of imaginary frequencies : 1
The smallest frequency is : -659.3468 cm(-1)

Hartree-Fock electronic energy : HF=-1827.2116455
Zero-point correction= 0.548968 (Hartree/Particle)
Thermal correction to Energy= 0.584747
Thermal correction to Enthalpy= 0.585691
Thermal correction to Gibbs Free Energy= 0.479618
Sum of electronic and zero-point Energies= -1826.662678
Sum of electronic and thermal Energies= -1826.626899
Sum of electronic and thermal Enthalpies= -1826.625954
Sum of electronic and thermal Free Energies= -1826.732027

$TS(4\text{-}5)_{axR}$ for C1

Number of imaginary frequencies : 1
The smallest frequency is : -636.5070 cm(-1)

Hartree-Fock electronic energy : HF=-1827.2145231
Zero-point correction= 0.549299 (Hartree/Particle)
Thermal correction to Energy= 0.584592
Thermal correction to Enthalpy= 0.585536
Thermal correction to Gibbs Free Energy= 0.481903
Sum of electronic and zero-point Energies= -1826.665224
Sum of electronic and thermal Energies= -1826.629931
Sum of electronic and thermal Enthalpies= -1826.628987
Sum of electronic and thermal Free Energies= -1826.732620

$TS1_{\text{C-H activation}}$

Number of imaginary frequencies : 1
The smallest frequency is : -738.5778 cm(-1)

Hartree-Fock electronic energy : HF=-2081.824264
Zero-point correction= 0.629461 (Hartree/Particle)

Thermal correction to Energy= 0.670574
Thermal correction to Enthalpy= 0.671518
Thermal correction to Gibbs Free Energy= 0.554021
Sum of electronic and zero-point Energies= -2081.194803
Sum of electronic and thermal Energies= -2081.153690
Sum of electronic and thermal Enthalpies= -2081.152746
Sum of electronic and thermal Free Energies= -2081.270243

2_{eq}

Number of imaginary frequencies : 0
The smallest frequency is : 23.6390 cm(-1)

Hartree-Fock electronic energy : HF=-2081.8909557
Zero-point correction= 0.634945 (Hartree/Particle)
Thermal correction to Energy= 0.675906
Thermal correction to Enthalpy= 0.676850
Thermal correction to Gibbs Free Energy= 0.560446
Sum of electronic and zero-point Energies= -2081.256011
Sum of electronic and thermal Energies= -2081.215050
Sum of electronic and thermal Enthalpies= -2081.214106
Sum of electronic and thermal Free Energies= -2081.330509

$TS(2\text{-}3)_{eq}$

Number of imaginary frequencies : 1
The smallest frequency is : -298.2391 cm(-1)

Hartree-Fock electronic energy : HF=-2081.8868416
Zero-point correction= 0.632268 (Hartree/Particle)
Thermal correction to Energy= 0.673167
Thermal correction to Enthalpy= 0.674111
Thermal correction to Gibbs Free Energy= 0.557360
Sum of electronic and zero-point Energies= -2081.254574
Sum of electronic and thermal Energies= -2081.213674
Sum of electronic and thermal Enthalpies= -2081.212730
Sum of electronic and thermal Free Energies= -2081.329482

3_{eq}

Number of imaginary frequencies : 0
The smallest frequency is : 17.7039 cm(-1)

Hartree-Fock electronic energy : HF=-1827.2722256
Zero-point correction= 0.554979 (Hartree/Particle)
Thermal correction to Energy= 0.590439
Thermal correction to Enthalpy= 0.591383
Thermal correction to Gibbs Free Energy= 0.487257
Sum of electronic and zero-point Energies= -1826.717247
Sum of electronic and thermal Energies= -1826.681786
Sum of electronic and thermal Enthalpies= -1826.680842

Sum of electronic and thermal Free Energies= -1826.784969

$4'_{eqS}$

Number of imaginary frequencies : 0
The smallest frequency is : 16.5870 cm(-1)

Hartree-Fock electronic energy : HF=-1827.2235261
Zero-point correction= 0.552280 (Hartree/Particle)
Thermal correction to Energy= 0.588262
Thermal correction to Enthalpy= 0.589206
Thermal correction to Gibbs Free Energy= 0.483047
Sum of electronic and zero-point Energies= -1826.671246
Sum of electronic and thermal Energies= -1826.635264
Sum of electronic and thermal Enthalpies= -1826.634320
Sum of electronic and thermal Free Energies= -1826.740479

$TS(4'\text{-}5)_{eqS}$

Number of imaginary frequencies : 1
The smallest frequency is : -873.0586 cm(-1)

Hartree-Fock electronic energy : HF=-1827.2072595
Zero-point correction= 0.548899 (Hartree/Particle)
Thermal correction to Energy= 0.584323
Thermal correction to Enthalpy= 0.585267
Thermal correction to Gibbs Free Energy= 0.481677
Sum of electronic and zero-point Energies= -1826.658361
Sum of electronic and thermal Energies= -1826.622936
Sum of electronic and thermal Enthalpies= -1826.621992
Sum of electronic and thermal Free Energies= -1826.725583

$4'_{eqR}$

Number of imaginary frequencies : 0
The smallest frequency is : 22.5467 cm(-1)

Hartree-Fock electronic energy : HF=-1827.2214547
Zero-point correction= 0.553212 (Hartree/Particle)
Thermal correction to Energy= 0.588863
Thermal correction to Enthalpy= 0.589807
Thermal correction to Gibbs Free Energy= 0.484977
Sum of electronic and zero-point Energies= -1826.668242
Sum of electronic and thermal Energies= -1826.632592
Sum of electronic and thermal Enthalpies= -1826.631647
Sum of electronic and thermal Free Energies= -1826.736478

$TS(4'\text{-}5)_{eqR}$

Number of imaginary frequencies : 1

The smallest frequency is : -717.1842 cm(-1)

Hartree-Fock electronic energy : HF=-1827.2046684
Zero-point correction= 0.549554 (Hartree/Particle)
Thermal correction to Energy= 0.584768
Thermal correction to Enthalpy= 0.585712
Thermal correction to Gibbs Free Energy= 0.481930
Sum of electronic and zero-point Energies= -1826.655115
Sum of electronic and thermal Energies= -1826.619901
Sum of electronic and thermal Enthalpies= -1826.618957
Sum of electronic and thermal Free Energies= -1826.722738

$5_{eq}s$

Number of imaginary frequencies : 0
The smallest frequency is : 29.5021 cm(-1)

Hartree-Fock electronic energy : HF=-1572.6307915
Zero-point correction= 0.470936 (Hartree/Particle)
Thermal correction to Energy= 0.500583
Thermal correction to Enthalpy= 0.501527
Thermal correction to Gibbs Free Energy= 0.411141
Sum of electronic and zero-point Energies= -1572.159856
Sum of electronic and thermal Energies= -1572.130208
Sum of electronic and thermal Enthalpies= -1572.129264
Sum of electronic and thermal Free Energies= -1572.219651

$TS(6\text{-}7)_{eq}$

Number of imaginary frequencies : 1
The smallest frequency is : -151.3126 cm(-1)

Hartree-Fock electronic energy : HF=-2080.6403912
Zero-point correction= 0.612949 (Hartree/Particle)
Thermal correction to Energy= 0.652337
Thermal correction to Enthalpy= 0.653281
Thermal correction to Gibbs Free Energy= 0.542392
Sum of electronic and zero-point Energies= -2080.027442
Sum of electronic and thermal Energies= -2079.988054
Sum of electronic and thermal Enthalpies= -2079.987110
Sum of electronic and thermal Free Energies= -2080.097999

$TS(7\text{-}8)_{eq}$

Number of imaginary frequencies : 1
The smallest frequency is : -257.8434 cm(-1)

Hartree-Fock electronic energy : HF=-2335.3203844
Zero-point correction= 0.694401 (Hartree/Particle)
Thermal correction to Energy= 0.739299
Thermal correction to Enthalpy= 0.740243

Thermal correction to Gibbs Free Energy= 0.616470
Sum of electronic and zero-point Energies= -2334.625983
Sum of electronic and thermal Energies= -2334.581086
Sum of electronic and thermal Enthalpies= -2334.580142
Sum of electronic and thermal Free Energies= -2334.703914

1m

Number of imaginary frequencies : 0
The smallest frequency is : 30.8867 cm(-1)
Hartree-Fock electronic energy : HF=-854.1662867
Zero-point correction= 0.230819 (Hartree/Particle)
Thermal correction to Energy= 0.246053
Thermal correction to Enthalpy= 0.246997
Thermal correction to Gibbs Free Energy= 0.186233

Sum of electronic and zero-point Energies= -853.935468
Sum of electronic and thermal Energies= -853.920233
Sum of electronic and thermal Enthalpies= -853.919289
Sum of electronic and thermal Free Energies= -853.980054

TS(3m-4m)

Number of imaginary frequencies : 1
The smallest frequency is : -896.6111 cm(-1)
Hartree-Fock electronic energy : HF=-1319.140903
Zero-point correction= 0.406244 (Hartree/Particle)
Thermal correction to Energy= 0.431256
Thermal correction to Enthalpy= 0.432200
Thermal correction to Gibbs Free Energy= 0.351340

Sum of electronic and zero-point Energies= -1318.734659
Sum of electronic and thermal Energies= -1318.709647
Sum of electronic and thermal Enthalpies= -1318.708703
Sum of electronic and thermal Free Energies= -1318.789563

3m

Number of imaginary frequencies : 0
The smallest frequency is : 9.8758 cm(-1)
Hartree-Fock electronic energy : HF=-1319.1515139
Zero-point correction= 0.410888 (Hartree/Particle)
Thermal correction to Energy= 0.435982
Thermal correction to Enthalpy= 0.436926
Thermal correction to Gibbs Free Energy= 0.355170

Sum of electronic and zero-point Energies= -1318.740626
Sum of electronic and thermal Energies= -1318.715532
Sum of electronic and thermal Enthalpies= -1318.714588
Sum of electronic and thermal Free Energies= -1318.796344

TS(2m-4m)

Number of imaginary frequencies : 1
The smallest frequency is : -837.3016 cm(-1)
Hartree-Fock electronic energy : HF=-1573.7756554
Zero-point correction= 0.486932 (Hartree/Particle)
Thermal correction to Energy= 0.517250
Thermal correction to Enthalpy= 0.518194
Thermal correction to Gibbs Free Energy= 0.425452

Sum of electronic and zero-point Energies= -1573.288723
Sum of electronic and thermal Energies= -1573.258405
Sum of electronic and thermal Enthalpies= -1573.257461
Sum of electronic and thermal Free Energies= -1573.350204

TS(2-2m)

Number of imaginary frequencies : 1
The smallest frequency is : -75.0656 cm(-1)
Hartree-Fock electronic energy : HF=-2081.9014461
Zero-point correction= 0.633472 (Hartree/Particle)
Thermal correction to Energy= 0.674352
Thermal correction to Enthalpy= 0.675296
Thermal correction to Gibbs Free Energy= 0.558118

Sum of electronic and zero-point Energies= -2081.267974
Sum of electronic and thermal Energies= -2081.227094
Sum of electronic and thermal Enthalpies= -2081.226150
Sum of electronic and thermal Free Energies= -2081.343328

2m

Number of imaginary frequencies : 0
The smallest frequency is : 30.7013 cm(-1)
Hartree-Fock electronic energy : HF=-1573.8525629
Zero-point correction= 0.492001 (Hartree/Particle)
Thermal correction to Energy= 0.522534
Thermal correction to Enthalpy= 0.523478
Thermal correction to Gibbs Free Energy= 0.430865

Sum of electronic and zero-point Energies= -1573.360562
Sum of electronic and thermal Energies= -1573.330029
Sum of electronic and thermal Enthalpies= -1573.329085
Sum of electronic and thermal Free Energies= -1573.421697