

Supporting Information

Catalytic Metal-Free Ketone Hydrogenation: A Computational Experiment

Haixia Li, Lili Zhao, Gang Lu, Fang Huang, and Zhi-Xiang Wang*

ESI1: Optimized structures of the products of the hydrogen activations via ketone (3-6) + H₂ + B(C₆F₅)₃ tri-molecular reactions.

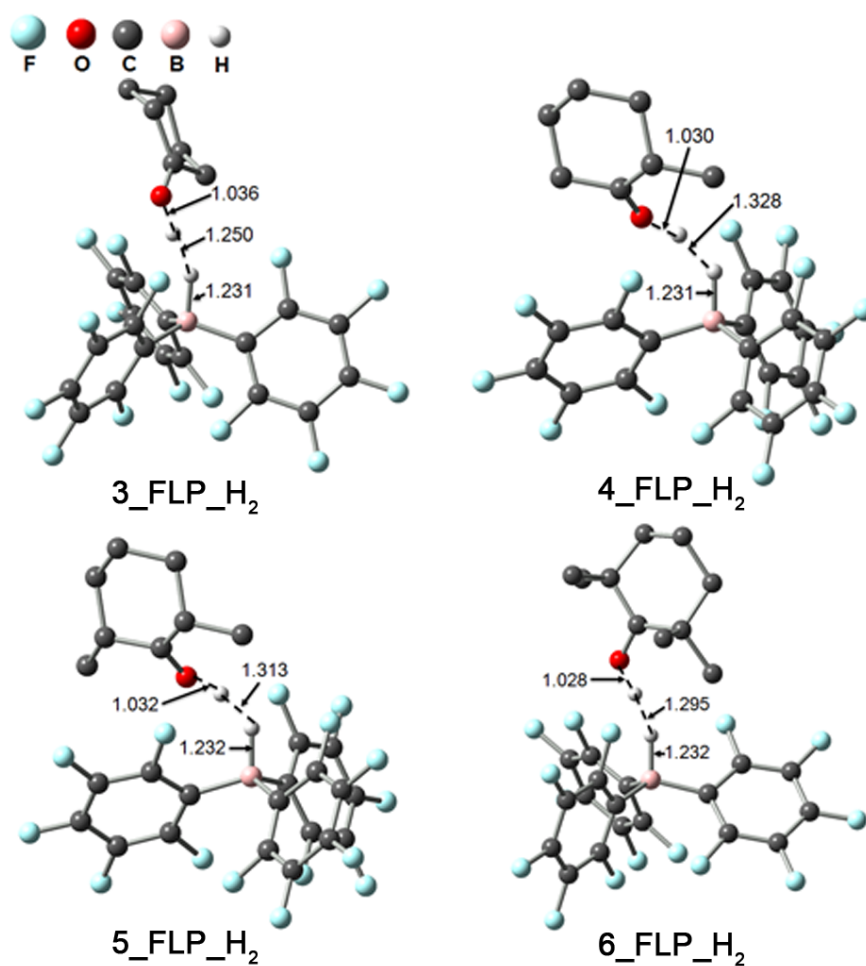


Fig. S1 M05-2X/6-31G(d,p) optimized structures of the zwitterionic products in the hydrogen activation via the FLP of ketones (3-6) with B(C₆F₅)₃. All distances are in Å. Trivial hydrogen atoms are omitted for clarity.

ESI2: Optimized structures of the H-bond and alkoxide complexes involved in the hydrogenations of ketones (4-6).

In the Fig. S2, we use 1_XOH_Y and $1_XO_H_Y$ ($X=3-6$; $Y=ax$ or eq) to denote the H-bond alcohol complexes between **1** and alcohols XOH_Y and the alkoxide complexes with broken O-H bonds.

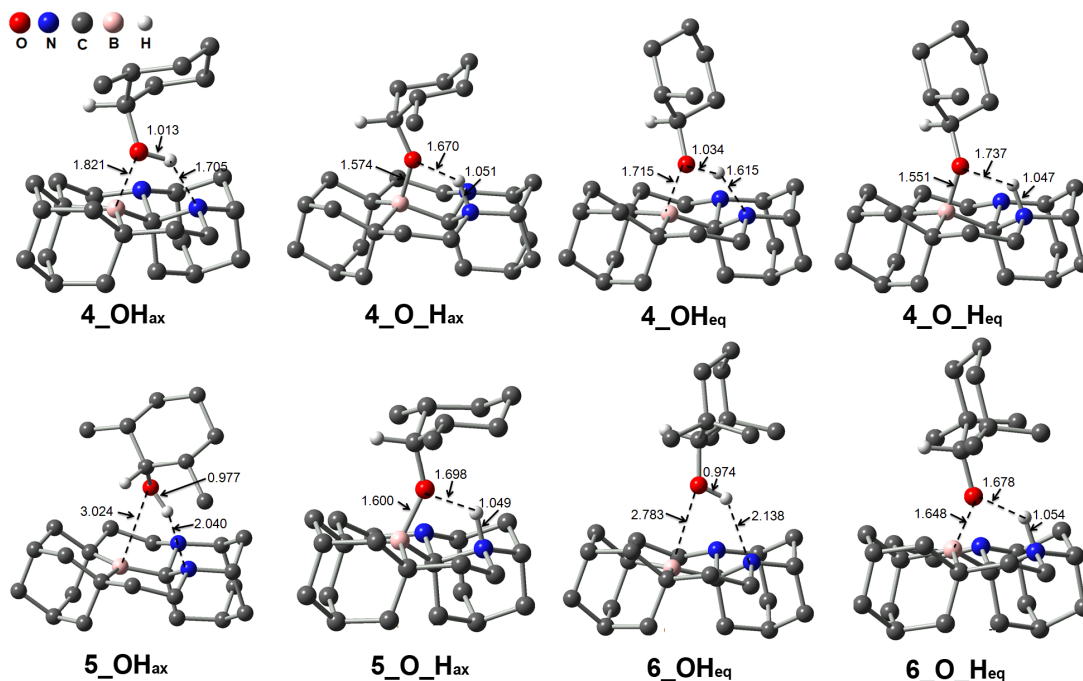


Fig. S2 Optimized structures of the H-bond and alkoxide complexes involved in the hydrogenations of ketones (4-6). All distances are in Å. Trivial hydrogen atoms are omitted for clarity.

ESI3. Optimized structures of alkoxide complexes involved in benzophenone (**8**) hydrogenations catalyzed by **2** and **7**.

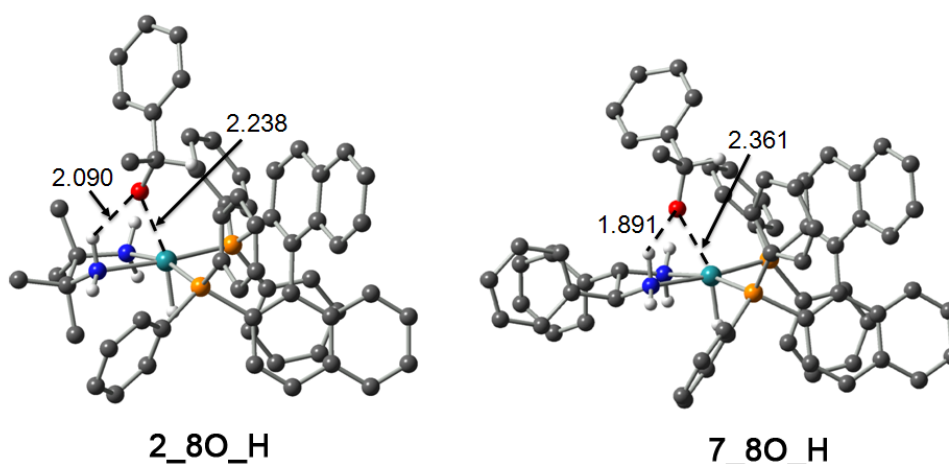


Fig. S3 The optimized structures of the alkoxide complexes involved in **8** (benzophenone) hydrogenations catalyzed by **2** and **7**. All distances are in Å. Trivial hydrogen atoms are omitted for clarity.

ESI4. Vibration modes of the optimized transition states, corresponding to the imaginary frequencies.

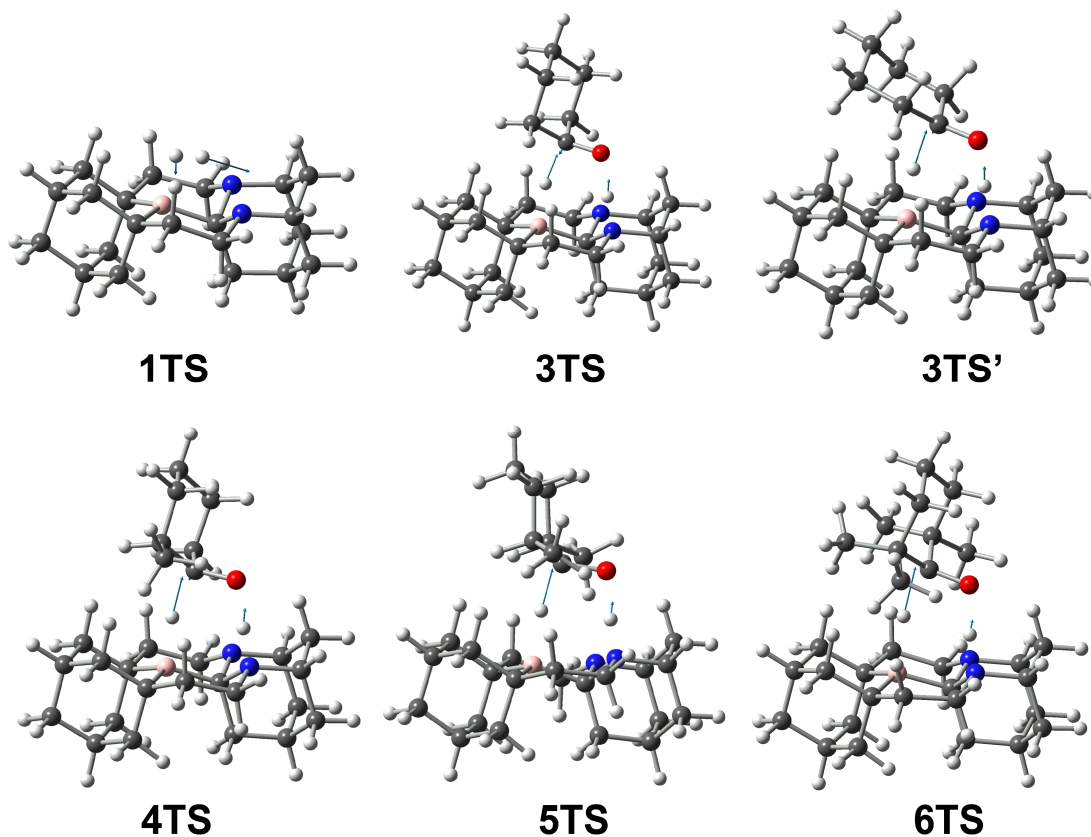


Fig. S4 The vibration modes of the optimized transition states at the level of M05-2X/6-31G(d,p).

ESI5. The energetic information of some important stationary points.

1

M05-2X/6-31G(d,p):

$E(\text{RM052X+HF-M052X}) = -953.251823$

Zero-point correction= 0.508044

Thermal correction to Energy= 0.524436

Thermal correction to Enthalpy= 0.525381

Thermal correction to Gibbs Free Energy= 0.467204

M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)

Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -953.446583

H₂

M05-2X/6-31G(d,p):

$E(\text{RM052X+HF-M052X}) = -1.167737697$
Zero-point correction= 0.010293
Thermal correction to Energy= 0.012653
Thermal correction to Enthalpy= 0.013597
Thermal correction to Gibbs Free Energy= -0.00119

M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)

Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -1.165804

3

M05-2X/6-31G(d,p):

$E(\text{RM052X+HF-M052X}) = -309.857203$
Zero-point correction= 0.153573
Thermal correction to Energy= 0.160005
Thermal correction to Enthalpy= 0.16095
Thermal correction to Gibbs Free Energy= 0.123214

M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)

Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -309.936848

4

M05-2X/6-31G(d,p):

$E(\text{RM052X+HF-M052X}) = -349.1706483$
Zero-point correction= 0.182246
Thermal correction to Energy= 0.190056
Thermal correction to Enthalpy= 0.191001
Thermal correction to Gibbs Free Energy= 0.150253

M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)

Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -349.255907

5

M05-2X/6-31G(d,p):

$E(\text{RM052X+HF-M052X}) = -388.4837451$
Zero-point correction= 0.21048
Thermal correction to Energy= 0.219718
Thermal correction to Enthalpy= 0.220662
Thermal correction to Gibbs Free Energy= 0.176807

M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)

Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -388.57465

6

M05-2X/6-31G(d,p):

E(RM052X+HF-M052X) = -467.102036

Zero-point correction= 0.266852

Thermal correction to Energy= 0.278917

Thermal correction to Enthalpy= 0.279861

Thermal correction to Gibbs Free Energy= 0.230264

M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)

Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -467.207255

5RCP

M05-2X/6-31G(d,p):

E(RM052X+HF-M052X) = -1263.12734

Zero-point correction= 0.668214

Thermal correction to Energy= 0.690132

Thermal correction to Enthalpy= 0.691076

Thermal correction to Gibbs Free Energy= 0.622537

M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)

Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -1263.393902

DCP_1

M05-2X/6-31G(d,p):

E(RM052X+HF-M052X) = -1263.122585

Zero-point correction= 0.663216

Thermal correction to Energy= 0.68713

Thermal correction to Enthalpy= 0.688074

Thermal correction to Gibbs Free Energy= 0.613163

M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)

Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -1263.383102

DCP_2

M05-2X/6-31G(d,p):

E(RM052X+HF-M052X) = -1263.11522

Zero-point correction= 0.66244

Thermal correction to Energy= 0.687286

Thermal correction to Enthalpy= 0.68823

Thermal correction to Gibbs Free Energy= 0.607775

M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)

Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -1263.3751

3IMA

M05-2X/6-31G(d,p):

E(RM052X+HF-M052X) = -1264.3151

Zero-point correction= 0.686058

Thermal correction to Energy= 0.710673

Thermal correction to Enthalpy= 0.711617

Thermal correction to Gibbs Free Energy= 0.634137

M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)

Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -1264.5806

3TS

M05-2X/6-31G(d,p):

E(RM052X+HF-M052X) = -1264.298617

Zero-point correction= 0.682885

Thermal correction to Energy= 0.706043

Thermal correction to Enthalpy= 0.706987

Thermal correction to Gibbs Free Energy= 0.635175

Vibration Harmonic Frequencies: -532.8914 cm⁻¹

M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)

Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -1264.567073

3IMB

M05-2X/6-31G(d,p):

E(RM052X+HF-M052X) = -1264.3406

Zero-point correction= 0.687886

Thermal correction to Energy= 0.712449

Thermal correction to Enthalpy= 0.713393

Thermal correction to Gibbs Free Energy= 0.635505

M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)

Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -1264.6043

4IMA

M05-2X/6-31G(d,p):

E(RM052X+HF-M052X) = -1303.63
Zero-point correction= 0.714476
Thermal correction to Energy= 0.740677
Thermal correction to Enthalpy= 0.741621
Thermal correction to Gibbs Free Energy= 0.659958

M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)

Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -1303.89991

4TS

M05-2X/6-31G(d,p):

E(RM052X+HF-M052X) = -1303.6033
Zero-point correction= 0.711521
Thermal correction to Energy= 0.736132
Thermal correction to Enthalpy= 0.737076
Thermal correction to Gibbs Free Energy= 0.662445
Vibration Harmonic Frequencies: -801.4511cm⁻¹

M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)

Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -1303.8773

4IMB

M05-2X/6-31G(d,p):

E(RM052X+HF-M052X) = -1303.65276
Zero-point correction= 0.716423
Thermal correction to Energy= 0.742419
Thermal correction to Enthalpy= 0.743363
Thermal correction to Gibbs Free Energy= 0.662936

M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)

Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -1303.921183

5IMA

M05-2X/6-31G(d,p):

E(RM052X+HF-M052X) = -1342.94231
Zero-point correction= 0.742951
Thermal correction to Energy= 0.77035
Thermal correction to Enthalpy= 0.771294
Thermal correction to Gibbs Free Energy= 0.68734

M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)

Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -1343.21967

5TS

M05-2X/6-31G(d,p):

E(RM052X+HF-M052X) = -1342.8987

Zero-point correction= 0.739875

Thermal correction to Energy= 0.7659

Thermal correction to Enthalpy= 0.766845

Thermal correction to Gibbs Free Energy= 0.68931

Vibration Harmonic Frequencies: -1081.2198cm⁻¹

M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)

Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -1343.1826

5IMB

M05-2X/6-31G(d,p):

E(RM052X+HF-M052X) = -1342.963966

Zero-point correction= 0.743977

Thermal correction to Energy= 0.771668

Thermal correction to Enthalpy= 0.772613

Thermal correction to Gibbs Free Energy= 0.687732

M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)

Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -1343.237649

6IMA

M05-2X/6-31G(d,p):

E(RM052X+HF-M052X) = -1421.55946

Zero-point correction= 0.800354

Thermal correction to Energy= 0.830388

Thermal correction to Enthalpy= 0.831332

Thermal correction to Gibbs Free Energy= 0.742422

M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)

Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -1421.85015

6TS

M05-2X/6-31G(d,p):

E(RM052X+HF-M052X) = -1421.5003

Zero-point correction= 0.796591

Thermal correction to Energy= 0.825247

Thermal correction to Enthalpy= 0.826191

Thermal correction to Gibbs Free Energy= 0.74424

Vibration Harmonic Frequencies: -1252.9938cm⁻¹

M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)

Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -1421.7997

6IMB

M05-2X/6-31G(d,p):

E(RM052X+HF-M052X) = -1421.578903

Zero-point correction= 0.801248

Thermal correction to Energy= 0.831273

Thermal correction to Enthalpy= 0.832217

Thermal correction to Gibbs Free Energy= 0.744117

M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)

Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -1421.867217

3TS'

M05-2X/6-31G(d,p):

E(RM052X+HF-M052X) = -1264.29222

Zero-point correction= 0.682477

Thermal correction to Energy= 0.705617

Thermal correction to Enthalpy= 0.706561

Thermal correction to Gibbs Free Energy= 0.635056

Vibration Harmonic Frequencies: -796.6519cm⁻¹

M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)

Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -1264.56157

3OH_{ax}

M05-2X/6-31G(d,p):

E(RM052X+HF-M052X) = -311.06379

Zero-point correction= 0.177852

Thermal correction to Energy= 0.184546

Thermal correction to Enthalpy= 0.185491

Thermal correction to Gibbs Free Energy= 0.147738

M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)

Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -311.14098

3OH_{eq}

M05-2X/6-31G(d,p):

E(RM052X+HF-M052X) = -311.0635916

Zero-point correction= 0.177344
Thermal correction to Energy= 0.184184
Thermal correction to Enthalpy= 0.185128
Thermal correction to Gibbs Free Energy= 0.147
M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)
Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -311.142108

4OH_{ax}

M05-2X/6-31G(d,p):
E(RM052X+HF-M052X) = -350.37614
Zero-point correction= 0.206022
Thermal correction to Energy= 0.214214
Thermal correction to Enthalpy= 0.215158
Thermal correction to Gibbs Free Energy= 0.174147
M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)
Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -350.45952

3OH_{eq}

M05-2X/6-31G(d,p):
E(RM052X+HF-M052X) = -350.3735649
Zero-point correction= 0.206213
Thermal correction to Energy= 0.214324
Thermal correction to Enthalpy= 0.215268
Thermal correction to Gibbs Free Energy= 0.174355
M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)
Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -350.458675

5OH_{ax}

M05-2X/6-31G(d,p):
E(RM052X+HF-M052X) = -389.68819
Zero-point correction= 0.234608
Thermal correction to Energy= 0.2442
Thermal correction to Enthalpy= 0.245144
Thermal correction to Gibbs Free Energy= 0.20111
M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)
Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -389.77835

6OH_{eq}

M05-2X/6-31G(d,p):
E(RM052X+HF-M052X) = -468.3063187

Zero-point correction= 0.291104
Thermal correction to Energy= 0.30322
Thermal correction to Enthalpy= 0.304164
Thermal correction to Gibbs Free Energy= 0.255327
M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)
Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -468.412206

1_3OH_{ax}

M05-2X/6-31G(d,p):
E(RM052X+HF-M052X) = -1264.3479
Zero-point correction= 0.688245
Thermal correction to Energy= 0.711628
Thermal correction to Enthalpy= 0.712572
Thermal correction to Gibbs Free Energy= 0.640072
M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)
Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -1264.608185

1_3O_H_{ax}

M05-2X/6-31G(d,p):
E(RM052X+HF-M052X) = -1264.35
Zero-point correction= 0.690154
Thermal correction to Energy= 0.713267
Thermal correction to Enthalpy= 0.714211
Thermal correction to Gibbs Free Energy= 0.642358
M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)
Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -1264.61

1_3OH_{eq}

M05-2X/6-31G(d,p):
E(RM052X+HF-M052X) = -1264.3511
Zero-point correction= 0.688112
Thermal correction to Energy= 0.711529
Thermal correction to Enthalpy= 0.712473
Thermal correction to Gibbs Free Energy= 0.6392
M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)
Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -1264.6095

1_3O_H_{eq}

M05-2X/6-31G(d,p):
E(RM052X+HF-M052X) = -1264.36

Zero-point correction= 0.690196
Thermal correction to Energy= 0.713414
Thermal correction to Enthalpy= 0.714358
Thermal correction to Gibbs Free Energy= 0.641927
M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)
Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -1264.62

1_4OH_{ax}

M05-2X/6-31G(d,p):
E(RM052X+HF-M052X) = -1303.6561
Zero-point correction= 0.717687
Thermal correction to Energy= 0.742464
Thermal correction to Enthalpy= 0.743408
Thermal correction to Gibbs Free Energy= 0.668254
M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)
Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -1303.923

1_4O_H_{ax}

M05-2X/6-31G(d,p):
E(RM052X+HF-M052X) = -1303.659473
Zero-point correction= 0.71887
Thermal correction to Energy= 0.743288
Thermal correction to Enthalpy= 0.744232
Thermal correction to Gibbs Free Energy= 0.670388
M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)
Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -1303.93

1_4OH_{eq}

M05-2X/6-31G(d,p):
E(RM052X+HF-M052X) = -1303.6585
Zero-point correction= 0.716559
Thermal correction to Energy= 0.741435
Thermal correction to Enthalpy= 0.742379
Thermal correction to Gibbs Free Energy= 0.666437
M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)
Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -1303.9247

1_4O_H_{eq}

M05-2X/6-31G(d,p):
E(RM052X+HF-M052X) = -1303.661621

Zero-point correction= 0.718502
Thermal correction to Energy= 0.7431
Thermal correction to Enthalpy= 0.744044
Thermal correction to Gibbs Free Energy= 0.669253
M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)
Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -1303.93

1_5OH_{ax}

M05-2X/6-31G(d,p):
E(RM052X+HF-M052X) = -1342.9635
Zero-point correction= 0.744428
Thermal correction to Energy= 0.771907
Thermal correction to Enthalpy= 0.772852
Thermal correction to Gibbs Free Energy= 0.689163
M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)
Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -1343.2388

1_5O_H_{ax}

M05-2X/6-31G(d,p):
E(RM052X+HF-M052X) = -1342.96
Zero-point correction= 0.747752
Thermal correction to Energy= 0.773546
Thermal correction to Enthalpy= 0.77449
Thermal correction to Gibbs Free Energy= 0.697522
M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)
Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -1343.23

1_6OH_{eq}

M05-2X/6-31G(d,p):
E(RM052X+HF-M052X) = -1421.579776
Zero-point correction= 0.801487
Thermal correction to Energy= 0.831259
Thermal correction to Enthalpy= 0.832203
Thermal correction to Gibbs Free Energy= 0.745819
M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)
Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -1421.869494

1_6O_H_{eq}

M05-2X/6-31G(d,p):
E(RM052X+HF-M052X) = -1421.561

Zero-point correction=	0.804882
Thermal correction to Energy=	0.833175
Thermal correction to Enthalpy=	0.834119
Thermal correction to Gibbs Free Energy=	0.753009

M05-2X/6-311++G(2d,p)//M05-2X/6-31G(d,p)

Total free energy in solution (THF): with all non electrostatic terms (a.u.) = -1421.856876