

Supporting information for

Catalyst and solvent-free for ipso-hydroxylation of aryl boronic acids to phenols

1. Scheme and Figure

Scheme S1

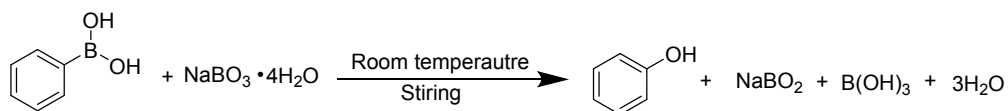


Figure S1

H_2O_2 oxidative pathway

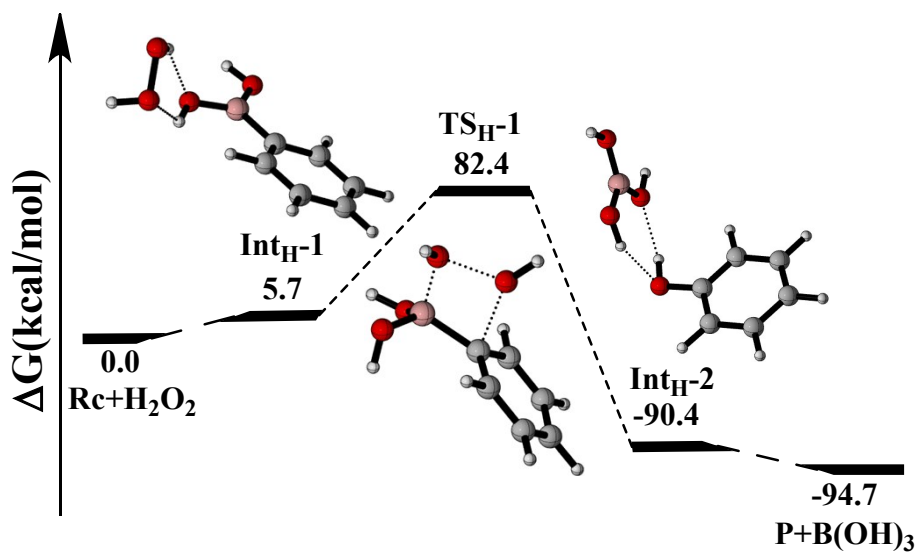
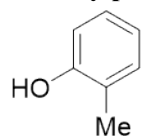


Fig. S1 Computed free energy profiles of the oxidative pathway with H_2O_2 .

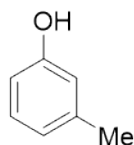
2. NMR data

2-methylphenol (Table 2, 2a)



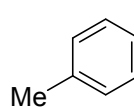
Yellow liquid (94.08 mg 87% yield) ¹H NMR (400 MHz, Chloroform-*d*)
δ (ppm) 7.15–7.03 (m, 2H), 6.84 (t, *J* = 7.4 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 4.62 (s, 1H), 2.24 (s, 3H).

3-methylphenol (Table 2, 2b)



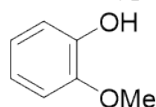
Yellow liquid (88.67 mg 82% yield) ¹H NMR (400 MHz, Chloroform-*d*)
δ (ppm) 7.11 (t, *J* = 7.7 Hz, 1H), 6.74 (d, *J* = 7.5 Hz, 1H), 6.64 (d, *J* = 8.3 Hz, 2H), 5.04 (s, 1H), 2.28 (s, 3H).

4-methylphenol (Table 2, 2c)



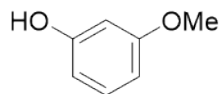
Yellow liquid (88.67 mg 82% yield) ¹H NMR (400 MHz, Chloroform-*d*)
δ (ppm) 7.03 (d, *J* = 8.4 Hz, 2H), 6.73 (d, *J* = 8.4 Hz, 2H), 4.72 (s, 1H), 2.27 (s, 3H).

2-methoxyphenol (Table 2, 2d)



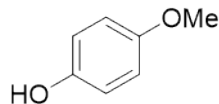
Yellow liquid (100.55 mg 81% yield) ¹H NMR (400 MHz, Chloroform-*d*)
δ (ppm) 6.96–6.80 (m, 4H), 5.46 (s, 1H), 3.86 (s, 3H).

3-methoxyphenol (Table 2, 2e)



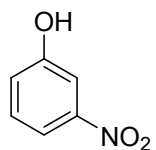
Yellow liquid (101.77 mg 82% yield) ¹H NMR (400 MHz, Chloroform-*d*)
δ (ppm) 7.12 (t, *J* = 8.1 Hz, 1H), 6.49 (dd, *J* = 8.6, 1.7 Hz, 1H), 6.47–6.37 (m, 2H), 5.24 (s, 1H), 3.75 (s, 3H).

4-methoxyphenol (Table 2, 2f)



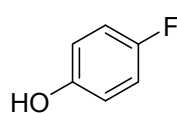
White solid (106.76 mg 86% yield) ¹H NMR (400 MHz, Chloroform-*d*)
δ (ppm) 6.77 (m, *J* = 7.8, 4.6 Hz, 4H), 4.71 (s, 1H), 3.76 (s, 3H).

3-nitrophenol (Table 2, 2g)



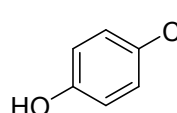
Pale yellow solid (123.80 mg 89% yield) ¹H NMR (400 MHz, DMSO-*d*)
δ (ppm) 10.45 (s, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.56 (t, *J* = 2.2 Hz, 1H), 7.47 (t, *J* = 8.2 Hz, 1H), 7.23 (dd, *J* = 8.2, 2.3 Hz, 1H).

4-fluorophenol (Table 2, 2h)



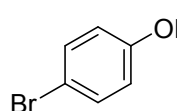
Yellow solid (89.66 mg 80% yield) ¹H NMR (400 MHz, Chloroform-*d*)
δ (ppm) 6.92 (t, *J* = 8.6 Hz, 2H), 6.81–6.73 (m, 2H), 4.80 (s, 1H).
¹³C NMR (101 MHz, Chloroform-*d*) δ (ppm) 158.59, 156.22, 151.12, 116.41.

4-chlorophenol (Table 2, 2i)



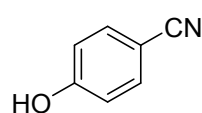
White solid (102.83 mg 80% yield) ¹H NMR (400 MHz, Chloroform-*d*)
δ (ppm) 7.18 (d, *J* = 8.7 Hz, 2H), 6.76 (d, *J* = 8.7 Hz, 2H), 4.89 (s, 1H).
¹³C NMR (101 MHz, Chloroform-*d*) δ (ppm) 153.91, 129.61, 125.75, 116.76.

4-bromophenol (Table 2, 2j)



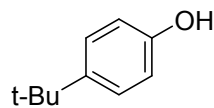
White solid (143.55 mg 83% yield) ¹H NMR (400 MHz, Chloroform-*d*)
δ (ppm) 7.32 (d, *J* = 8.7 Hz, 2H), 6.71 (d, *J* = 8.7 Hz, 2H), 4.95 (s, 1H).
¹³C NMR (101 MHz, Chloroform-*d*) δ (ppm) 154.32, 132.61, 117.34, 113.13.

4-cyanophenol (Table 2, 2k)



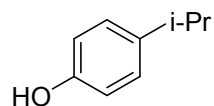
Grey white solid (95.30 mg 80% yield) ¹H NMR (400 MHz, Chloroform-*d*)
δ (ppm) 7.57–7.55 (d, *J* = 8.7 Hz, 2H), 6.93–6.91 (d, *J* = 8.4 Hz, 2H), 5.65 (s, 1H).

4-tert-butylphenol (Table 2, 2l)



White solid (120.18 mg 80% yield) ¹H NMR (400 MHz, Chloroform-*d*)
δ (ppm) 7.29–7.23 (m, 2H), 6.76 (dd, *J* = 8.8, 2.8 Hz, 2H), 4.55 (s, 1H), 1.29 (d, *J* = 2.4 Hz, 9H).

4-isopropylphenol (Table 3, 2m)

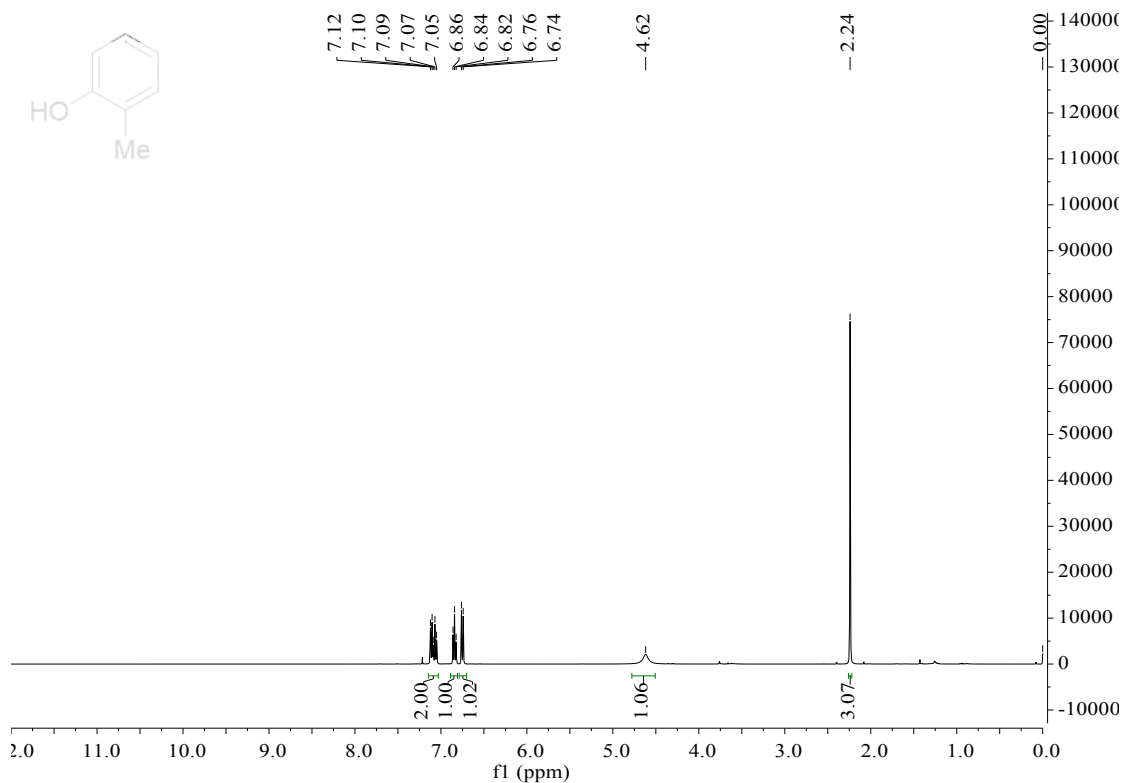


White solid (119.88 mg 88% yield) ¹H NMR (400 MHz, Chloroform-*d*)
δ (ppm) 7.09 (d, *J* = 8.4 Hz, 2H), 6.76 (d, *J* = 8.5 Hz, 2H), 4.56 (s, 1H), 2.85 (p, *J* = 6.9 Hz, 1H), 1.21 (d, *J* = 6.9 Hz, 6H).

3. NMR Spectra of synthesized products

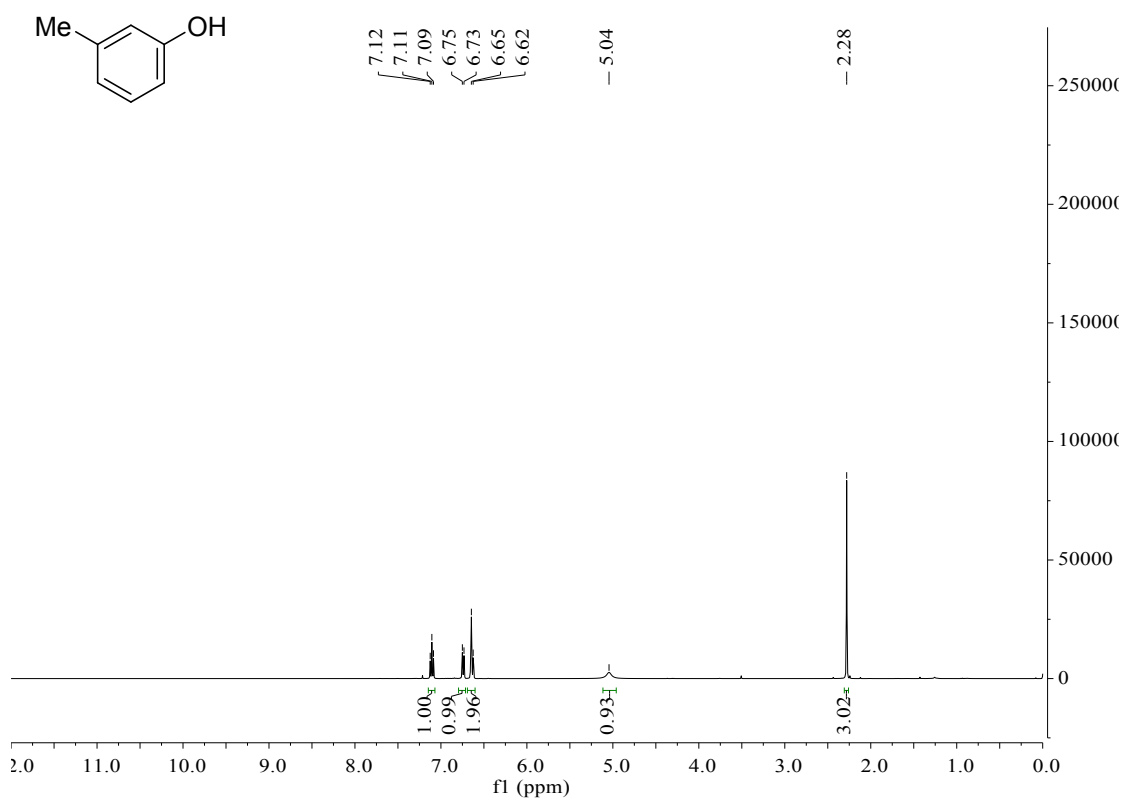
2-methylphenol (2a)

¹H NMR



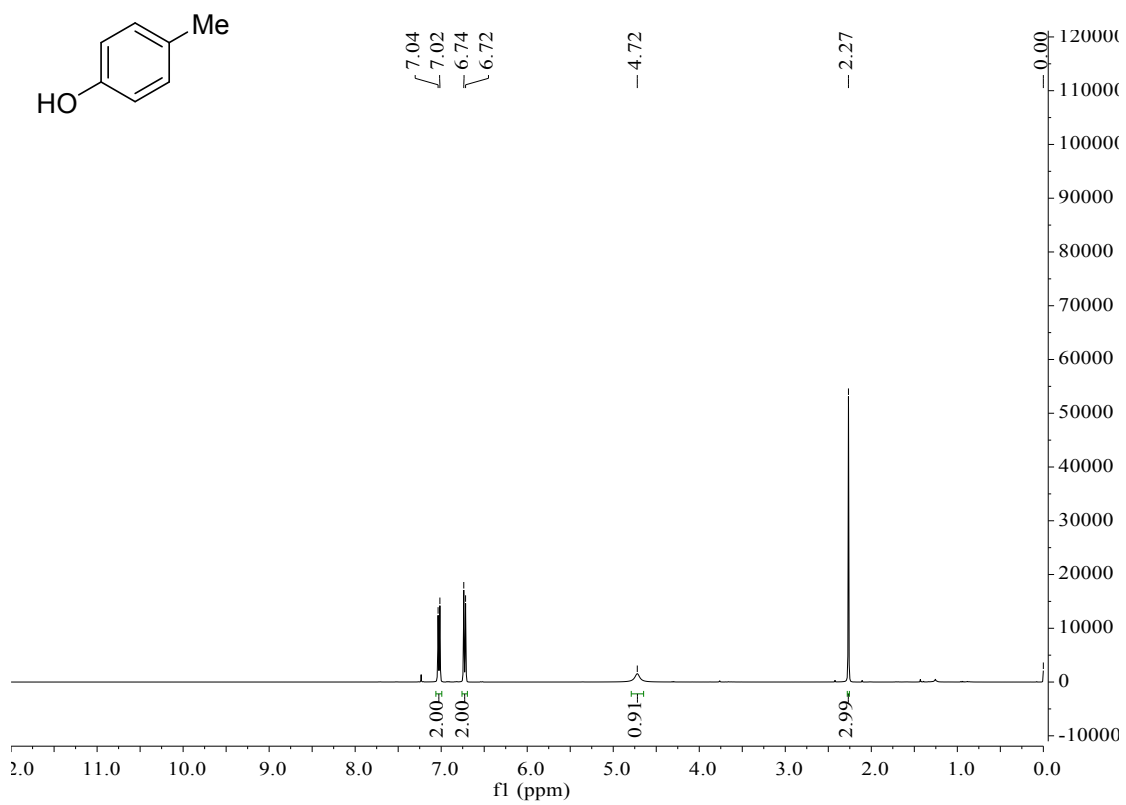
3-methylphenol (2b)

¹H NMR



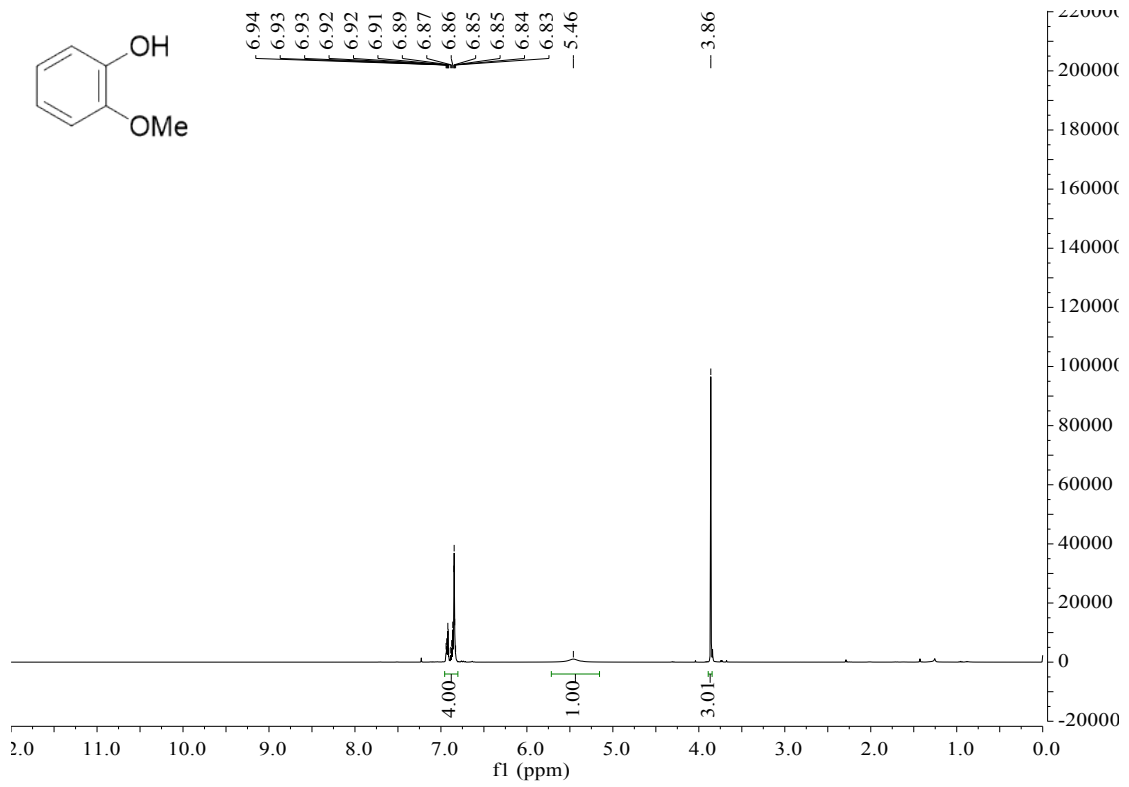
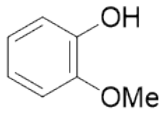
4-methylphenol (2c)

¹H NMR



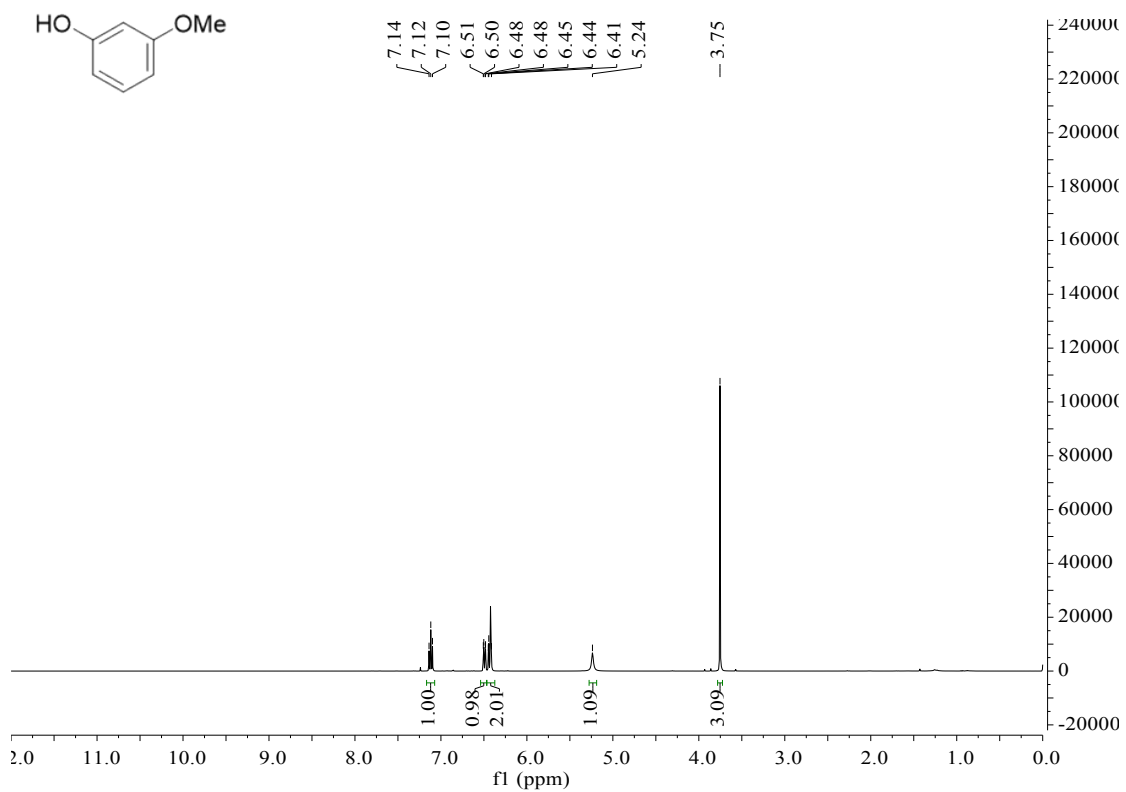
2-methoxyphenol (2d)

¹H NMR



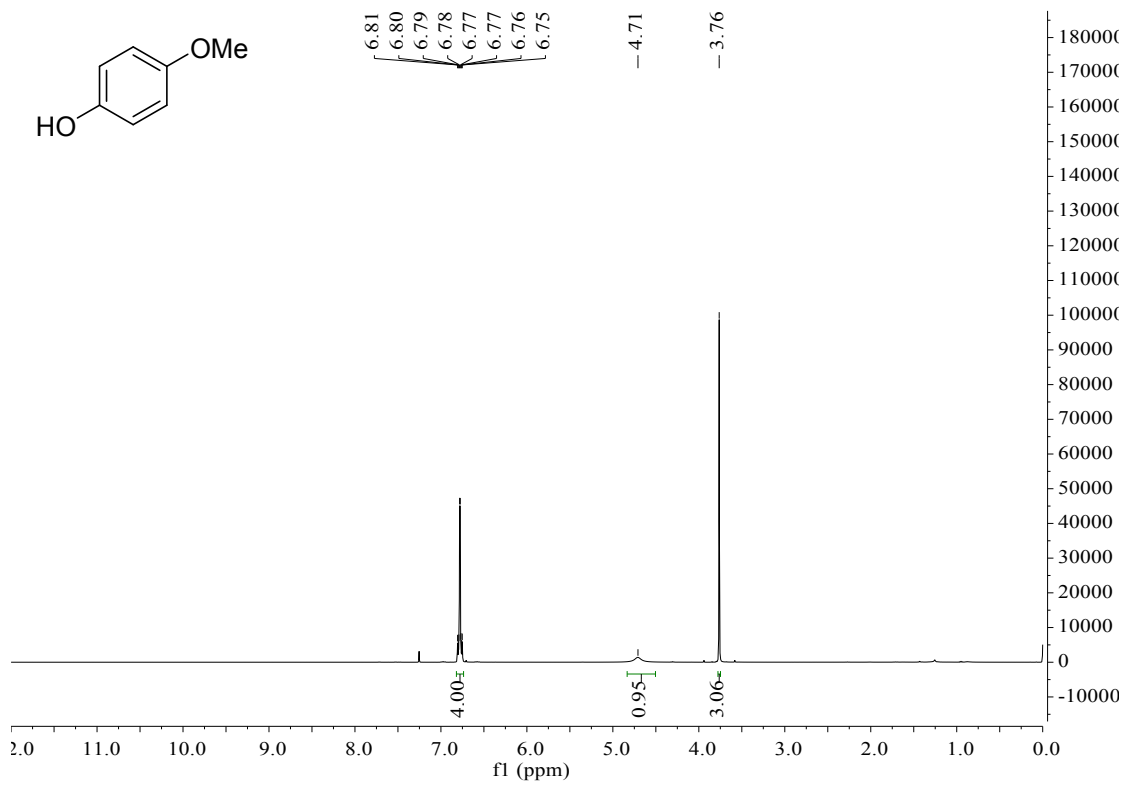
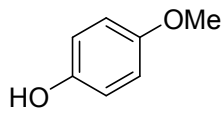
3-methoxyphenol (2e)

¹H NMR



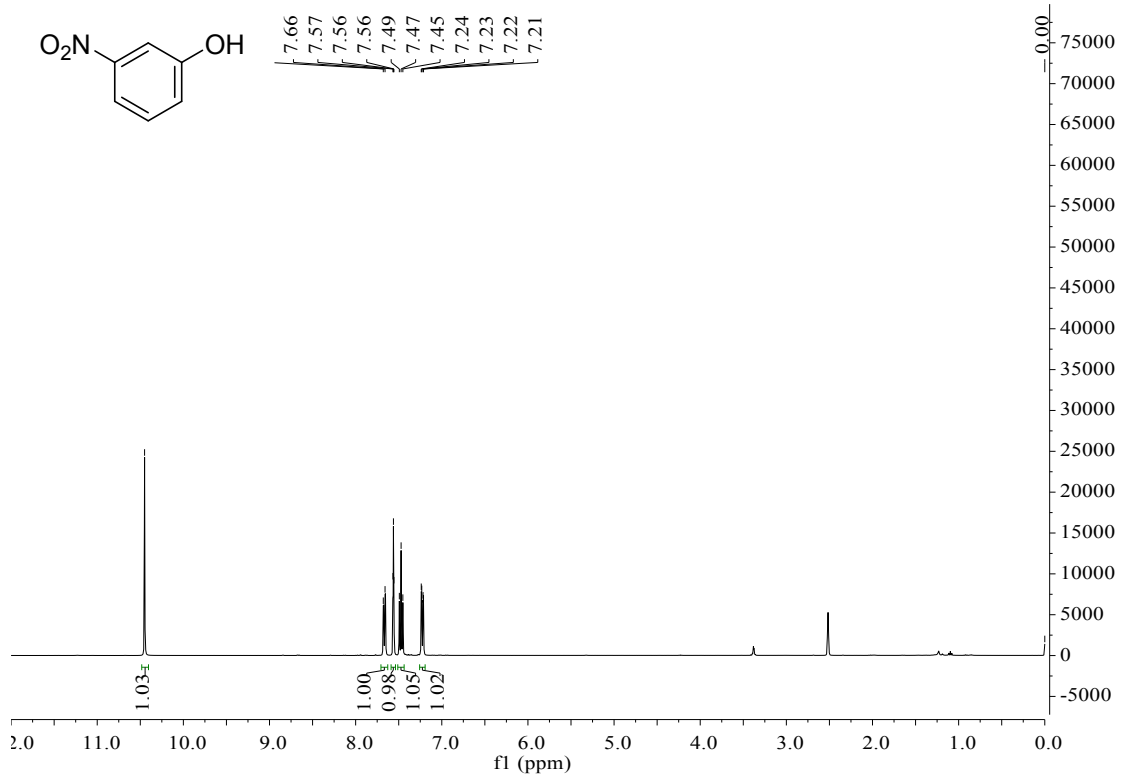
4-methoxyphenol (2f)

¹H NMR



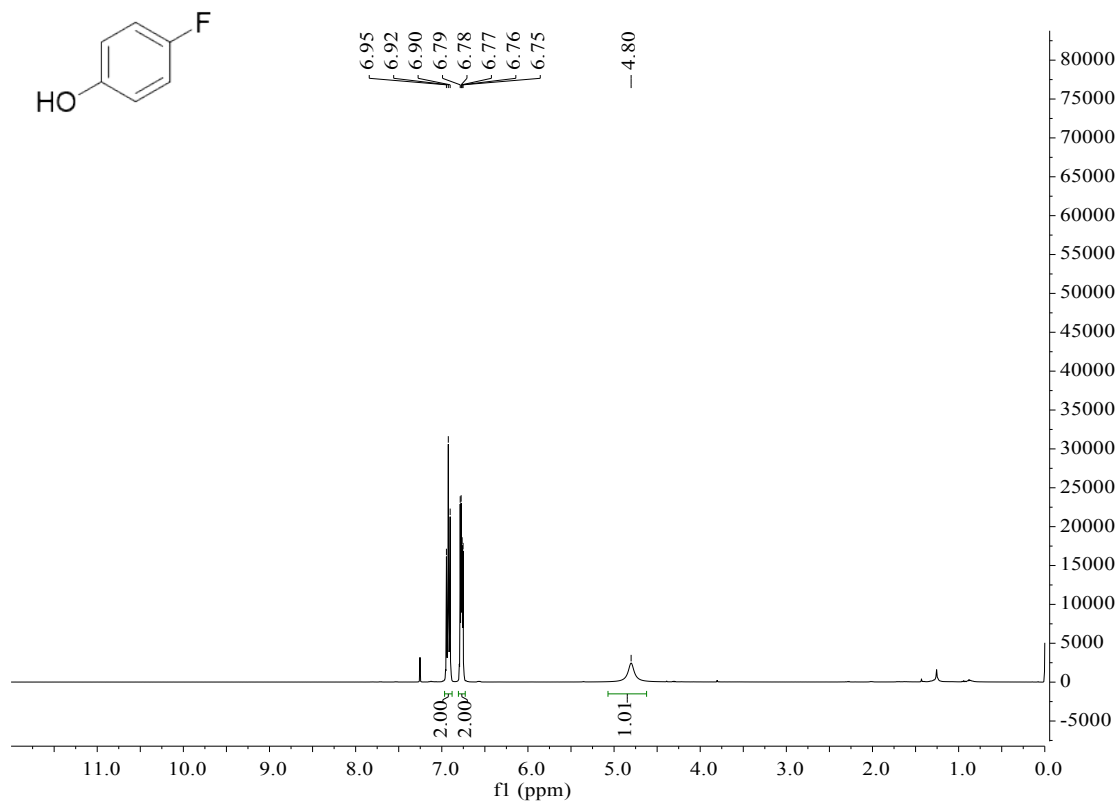
3-nitrophenol (2g)

¹H NMR

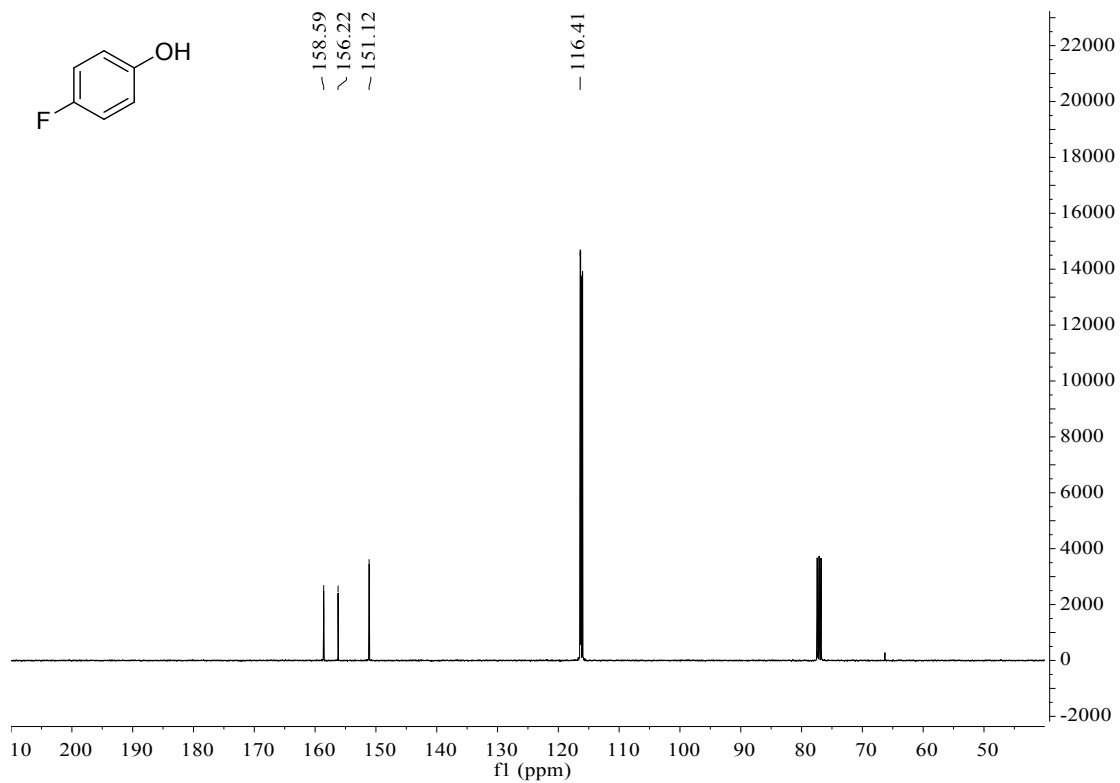


4-fluorophenol (2h)

^1H NMR

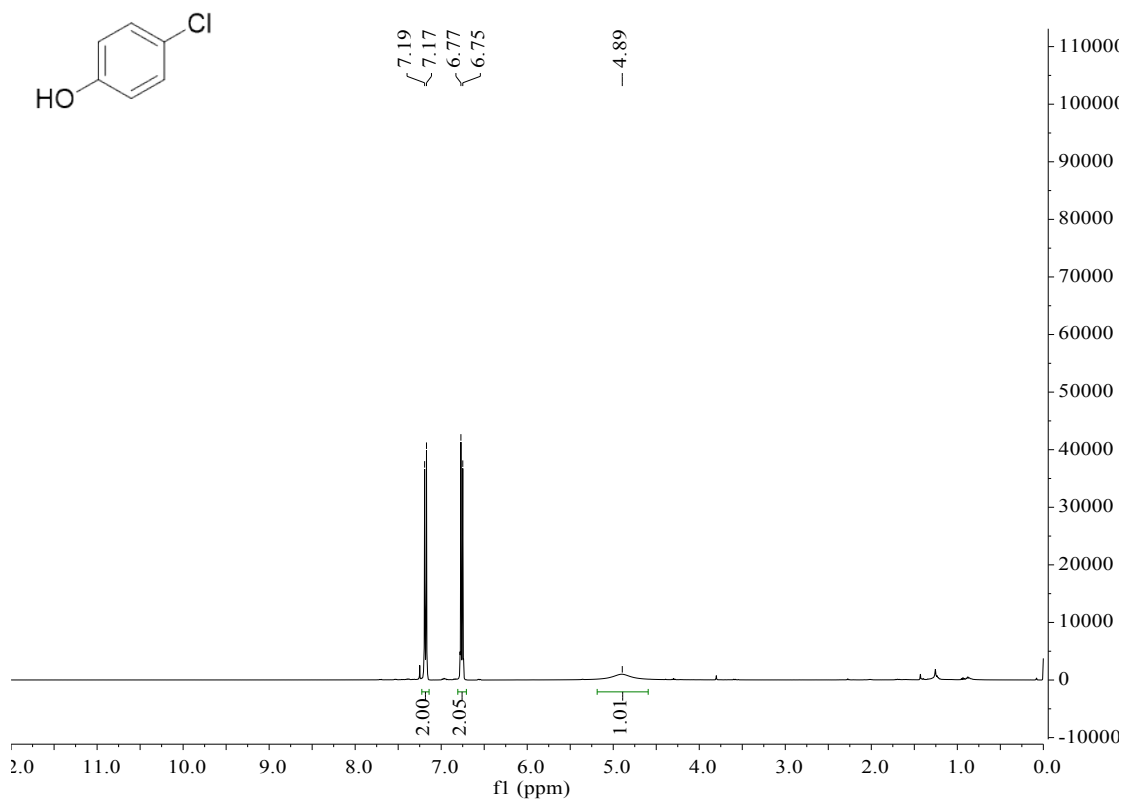


^{13}C NMR

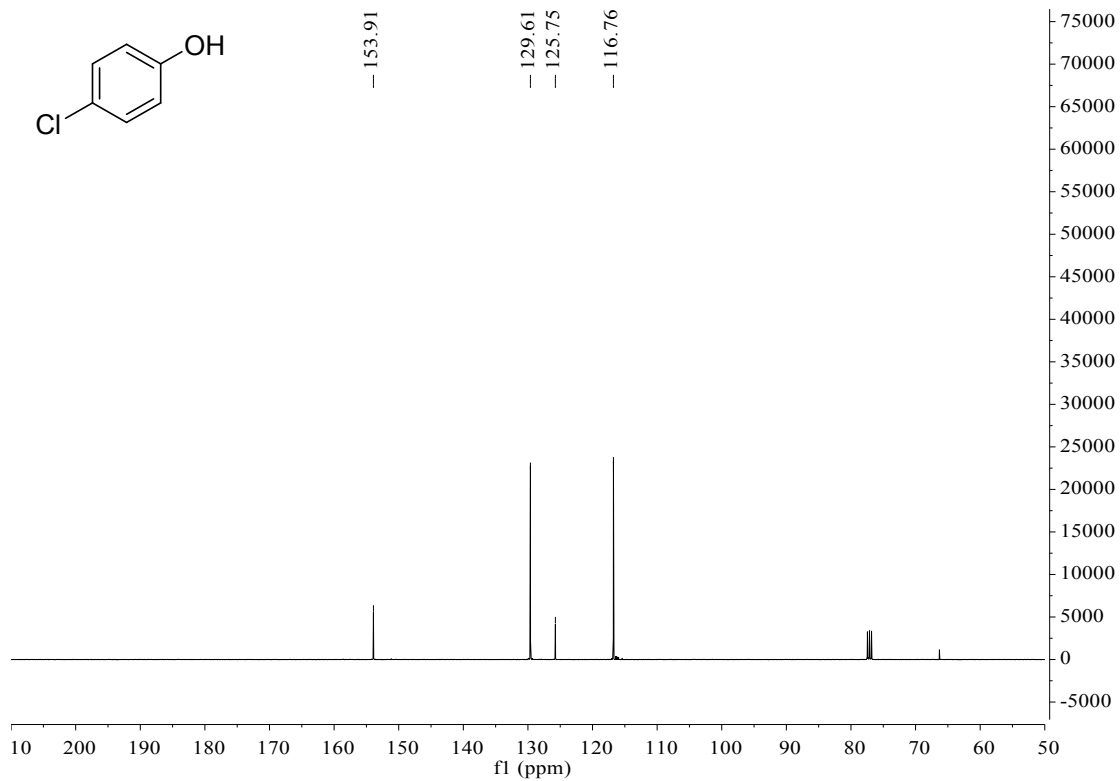


4-chlorophenol (2i)

^1H NMR

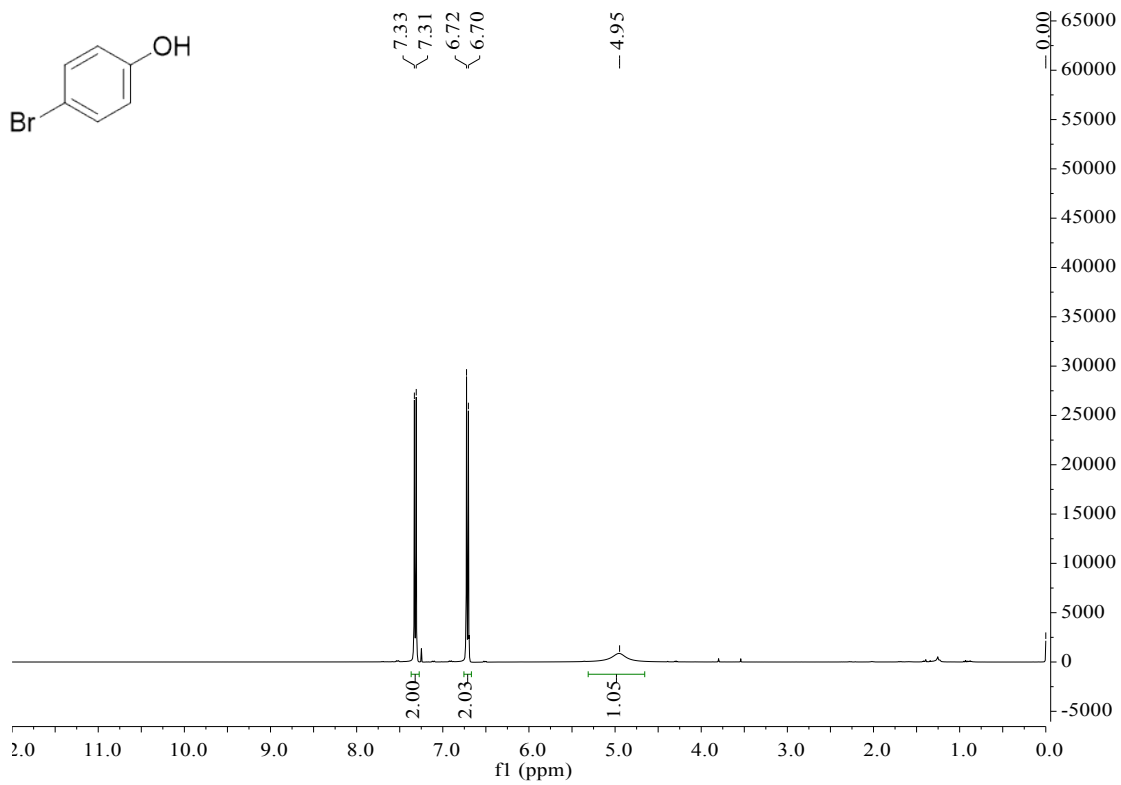


^{13}C NMR

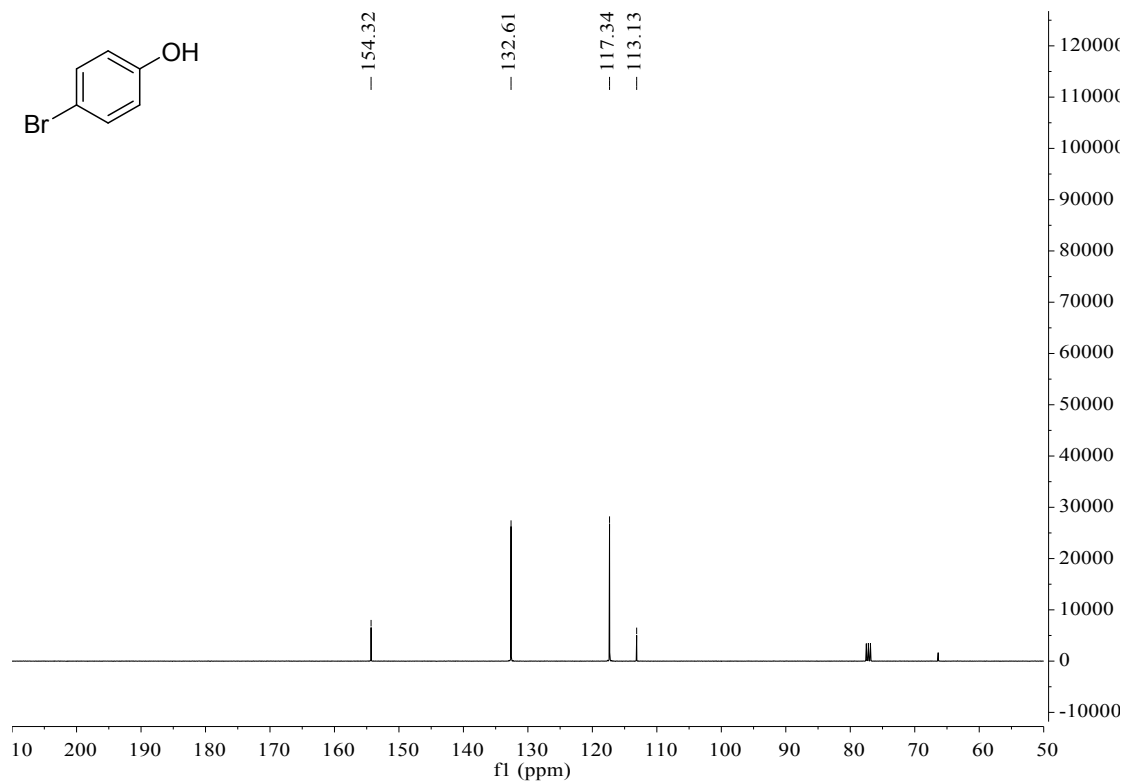


4-bromophenol (2j)

^1H NMR

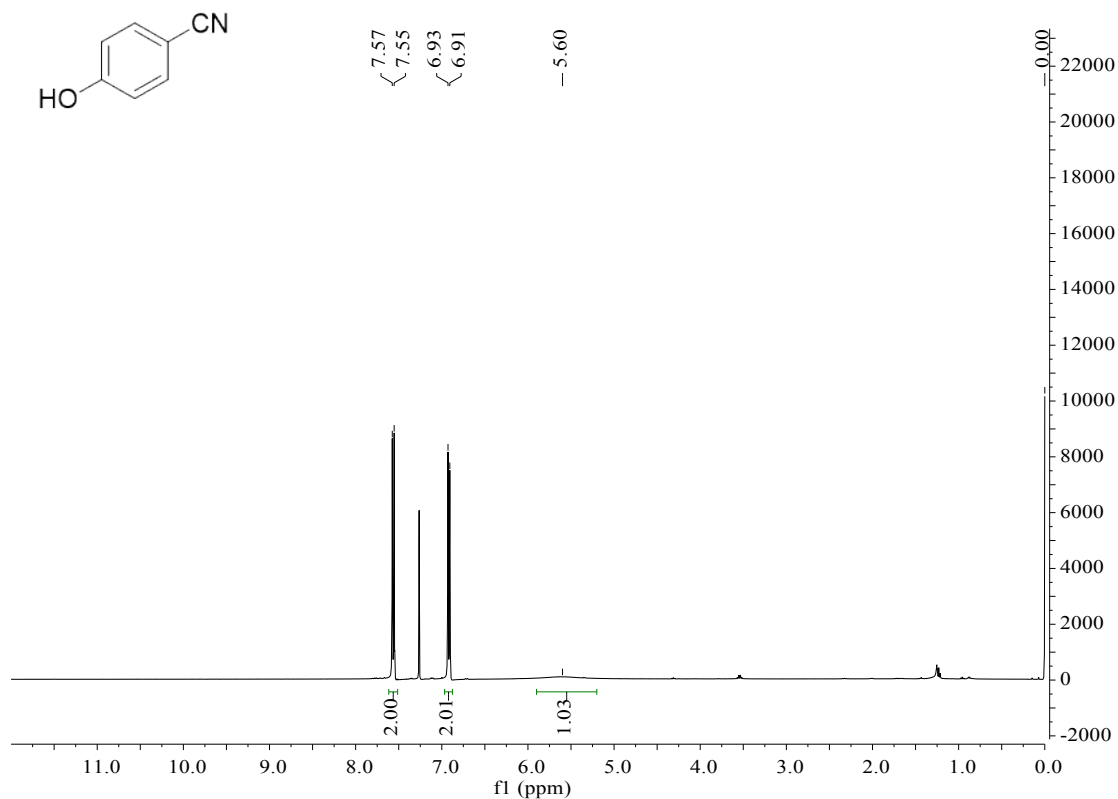


^{13}C NMR



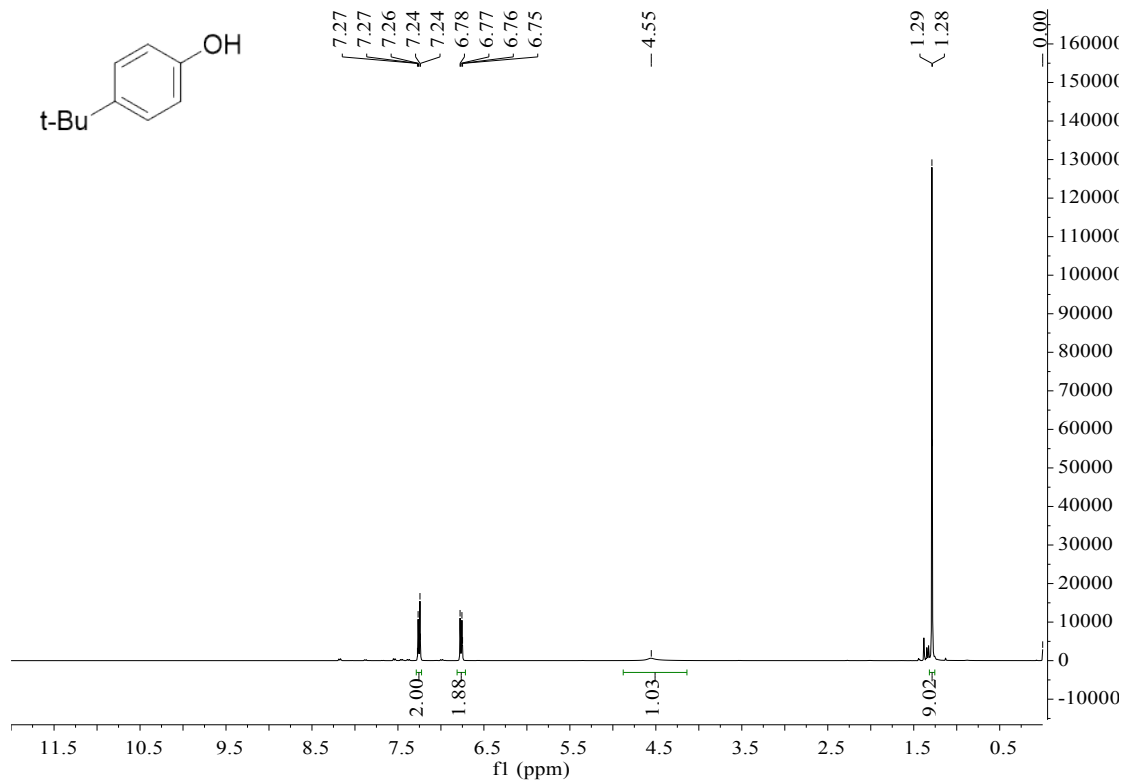
4-cyanophenol (2k)

¹H NMR



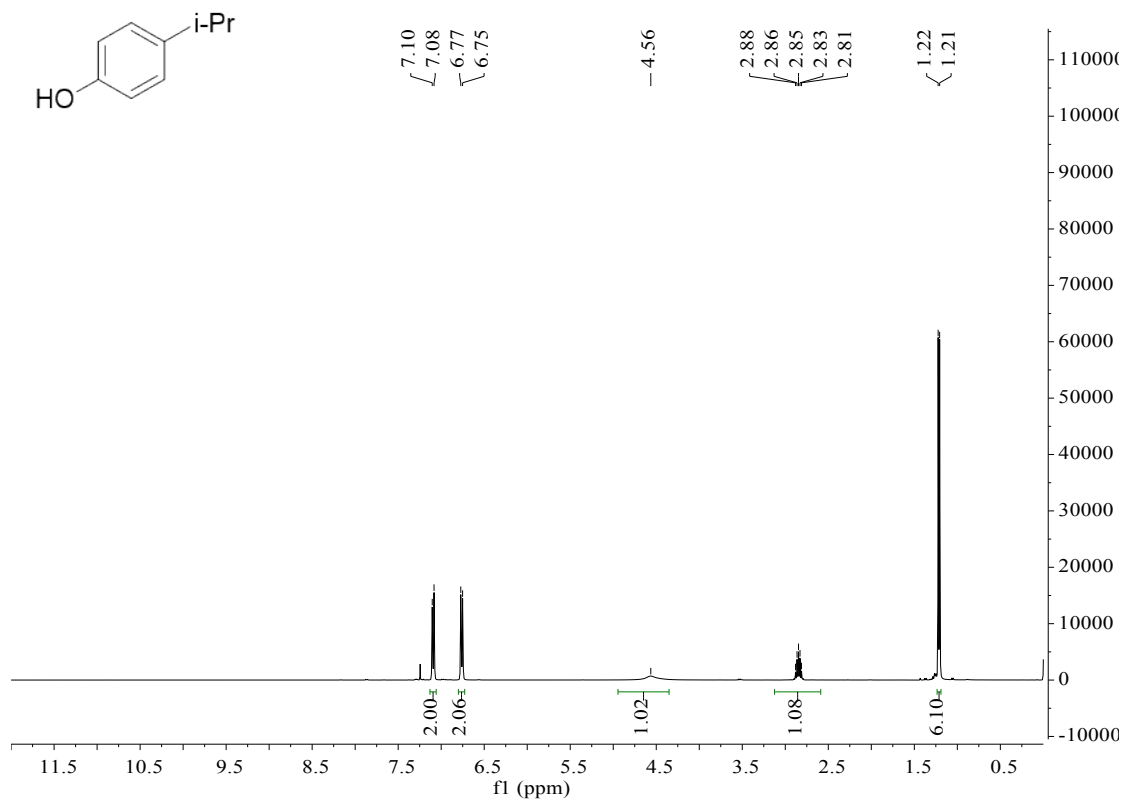
4-tert-butylphenol (2l)

¹H NMR



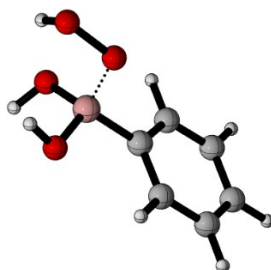
4-isopropylphenol (2m)

¹H NMR



4. Optimized structure informations:

Int-1.log



Sum of electronic and zero-point Energies = -559.208813

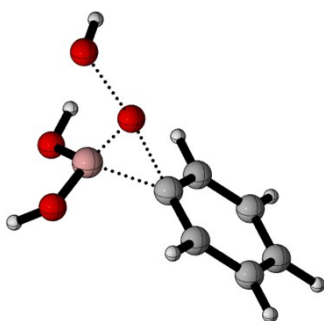
Sum of electronic and thermal Energies = -559.198213

Sum of electronic and thermal Enthalpies = -559.197268

Sum of electronic and thermal Free Energies = -559.245192

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C	2.47318600	-1.28483900	0.01078800
C	1.09426400	-1.17001200	0.15037000
C	0.44532200	0.06929000	0.10435600
C	1.24958600	1.19663000	-0.08460600
C	2.63251300	1.09936200	-0.22047200
H	4.32494100	-0.22738100	-0.28187900
H	2.94577500	-2.25994000	0.05036000
H	0.50254300	-2.06734900	0.30445100
H	0.77873900	2.17323300	-0.12184400
H	3.22915300	1.99363800	-0.36230200
B	-1.16870300	0.16524400	0.24319100
O	-1.73418800	-0.75513900	1.26438900
H	-1.85865100	-0.27577900	2.08643800
O	-1.57361800	1.54622800	0.50175000
H	-2.52181200	1.61215300	0.35033500
H	-3.23254900	-0.83306500	-0.08346400
O	-3.13815800	-0.38655700	-0.94253200
O	-1.70295600	-0.34618800	-1.05711600

TS-1.log



Sum of electronic and zero-point Energies = -559.162532

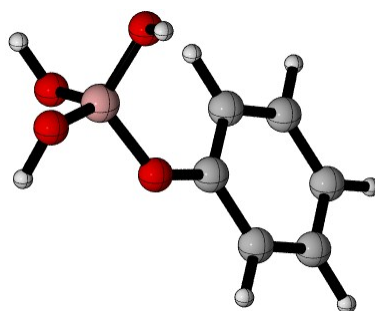
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Sum of electronic and thermal Enthalpies = -559.150518

Sum of electronic and thermal Free Energies = -559.199042

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C	-2.46293600	-1.22961300	-0.04645200
C	-1.07365300	-1.20162900	-0.10342800
C	-0.38612300	0.00239700	0.01447000
C	-1.10212200	1.17583200	0.23331900
C	-2.49103600	1.15372000	0.29334200
H	-4.25610900	-0.07000200	0.19824800
H	-2.99087200	-2.16992300	-0.15365400
H	-0.52728200	-2.12757100	-0.25067000
H	-0.56620300	2.11251000	0.33784500
H	-3.04132300	2.07384900	0.45184800
B	1.33512200	0.12864800	-0.49704300
O	1.74670900	-0.88136800	-1.41226500
H	1.71309300	-1.74722100	-0.99810300
O	1.65365900	1.43296000	-0.95861100
H	1.94915200	1.39641600	-1.87184000
H	3.03636500	-1.14656600	1.63661400
O	3.05483700	-0.19678000	1.48376300
O	1.31328100	-0.11320400	0.87226200

Int-2.log



Sum of electronic and zero-point Energies = -559.349793

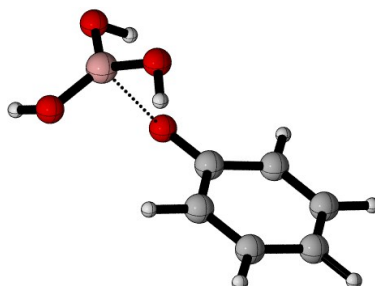
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Sum of electronic and thermal Enthalpies = -559.338286

Sum of electronic and thermal Free Energies = -559.385946

C	3.22724600	-0.39202500	-0.00371300
C	2.20389600	-1.33325100	-0.00646800
C	0.86812300	-0.94994000	-0.00884900
C	0.52518000	0.41110000	-0.00863100
C	1.56370500	1.35519900	-0.00655600
C	2.89190200	0.95890700	-0.00368100
H	4.26391600	-0.70394700	-0.00135400
H	2.44592600	-2.39033300	-0.00637800
H	0.08083500	-1.68887600	-0.00853600
H	1.29949100	2.40642800	-0.00713700
H	3.67200700	1.71163800	-0.00125300
B	-1.94640600	-0.00890900	0.00748600
O	-2.00407500	-0.92589600	-1.12448700
H	-2.33248800	-0.45359000	-1.89354700
O	-1.89265400	-0.75981100	1.25790500
H	-2.62301800	-1.38327400	1.27452100
H	-3.04327600	1.55011300	0.61664100
O	-3.09094100	0.89925900	-0.08818000
O	-0.72628900	0.87350500	-0.01811200

TS-2.log



Sum of electronic and zero-point Energies = -559.308743

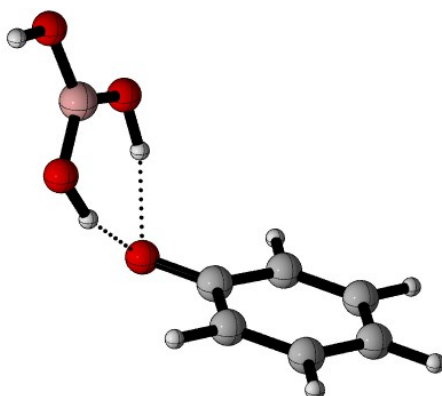
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Sum of electronic and thermal Free Energies = -559.346044

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C	1.74681100	1.33798200	-0.00821900
C	0.63897700	0.55239600	-0.44160100
C	0.87896200	-0.85319700	-0.50790900
C	2.10422700	-1.40526000	-0.17439900
H	4.12343900	-1.04527900	0.50533900
H	3.77897700	1.41255400	0.64461600
H	1.60459000	2.41203000	0.05649300
H	0.06089600	-1.48488400	-0.84119600
H	2.23684700	-2.48085500	-0.24325600
B	-2.37110500	-0.16904700	0.28064400
O	-1.65219300	-0.52363500	1.39365800
H	-1.19933100	-1.36209400	1.26290700
O	-2.94711600	1.08237400	0.20305700
H	-2.18950100	1.68311200	0.13299700
H	-3.17695300	-0.78739200	-1.36413800
O	-2.70542500	-1.15838900	-0.61320100
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Int-3.log



Sum of electronic and zero-point Energies = -559.350127

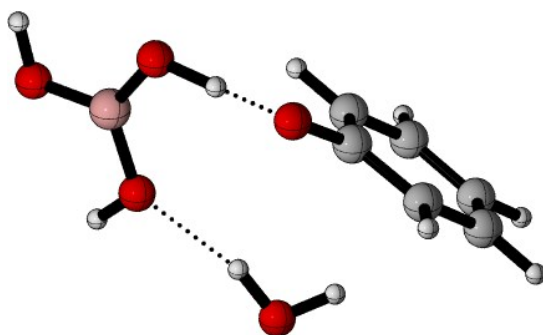
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Sum of electronic and thermal Enthalpies = -559.338576

Sum of electronic and thermal Free Energies = -559.388868

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C	2.60839800	1.31862400	-0.35042000
C	1.41675100	1.15748100	0.34100600
C	0.91164800	-0.12702000	0.65096200
C	1.68393600	-1.23157000	0.22108900
C	2.87445700	-1.05747800	-0.46858400
H	4.28392100	0.34790500	-1.30106400
H	2.96272000	2.32022800	-0.56960700
H	0.84597500	2.02349300	0.65993400
H	1.31847900	-2.22796700	0.44604900
H	3.43849600	-1.93013200	-0.78054800
B	-2.78456400	-0.00598600	-0.22722500
O	-3.95331100	0.13051200	-0.94115700
H	-4.27385600	1.03681200	-0.91918300
O	-2.22747300	-1.25427300	-0.17908100
H	-1.40526700	-1.19232900	0.36093800
H	-1.38277000	0.74667900	0.84437100
O	-2.22330000	1.06706500	0.39860900
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Int-4.log



Sum of electronic and zero-point Energies = -635.764159

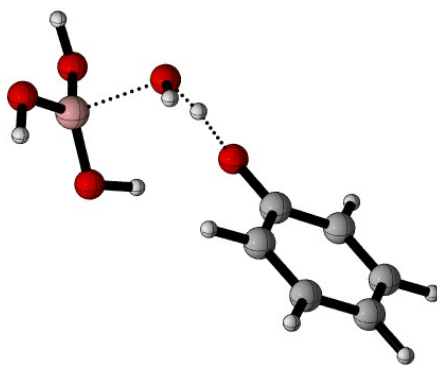
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Sum of electronic and thermal Enthalpies = -635.749590

Sum of electronic and thermal Free Energies = -635.805351

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C	-0.76641600	0.39176200	1.01925600
C	-0.91236700	0.99800300	-0.25340600
C	-2.16796800	0.84291800	-0.88746000
C	-3.18873200	0.10757800	-0.30323900
H	-3.81370500	-1.07744600	1.38952500
H	-1.64190900	-0.79763600	2.56337900
H	0.18214000	0.49527100	1.53395400
H	-2.30658900	1.29829800	-1.86187000
H	-4.13181200	0.00003000	-0.82813300
B	2.74593200	-0.02311200	0.06575700
O	2.29106600	1.23066200	0.08474700
H	1.30291600	1.39359500	-0.30479000
O	3.99292000	-0.36429600	0.55658300
H	4.45449400	0.40725600	0.89771900
H	2.47633000	-1.90612900	-0.39212200
O	1.99697800	-1.07278000	-0.45011700
O	0.05817400	1.65502700	-0.83008600
O	-0.59154100	-2.13266000	-1.14616100
H	-1.33448700	-1.60901800	-0.82061100
H	0.18956400	-1.62639900	-0.87261100

TS-3.log



Sum of electronic and zero-point Energies = -635.750103

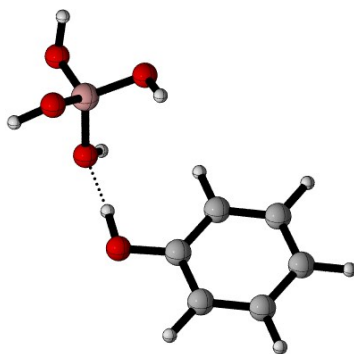
Sum of electronic and thermal Energies = -635.737690

Sum of electronic and thermal Enthalpies = -635.736745

Sum of electronic and thermal Free Energies = -635.789908

C	-3.01640200	-0.50012000	0.94003400
C	-1.79601200	-0.33845500	1.59265700
C	-0.76641600	0.39176200	1.01925600
C	-0.91236700	0.99800300	-0.25340600
C	-2.16796800	0.84291800	-0.88746000
C	-3.18873200	0.10757800	-0.30323900
H	-3.81370500	-1.07744600	1.38952500
H	-1.64190900	-0.79763600	2.56337900
H	0.18214000	0.49527100	1.53395400
H	-2.30658900	1.29829800	-1.86187000
H	-4.13181200	0.00003000	-0.82813300
B	2.74593200	-0.02311200	0.06575700
O	2.29106600	1.23066200	0.08474700
H	1.30291600	1.39359500	-0.30479000
O	3.99292000	-0.36429600	0.55658300
H	4.45449400	0.40725600	0.89771900
H	2.47633000	-1.90612900	-0.39212200
O	1.99697800	-1.07278000	-0.45011700
O	0.05817400	1.65502700	-0.83008600
O	-0.59154100	-2.13266000	-1.14616100
H	-1.33448700	-1.60901800	-0.82061100
H	0.18956400	-1.62639900	-0.87261100

Int-5.log



Sum of electronic and zero-point Energies = -635.764832

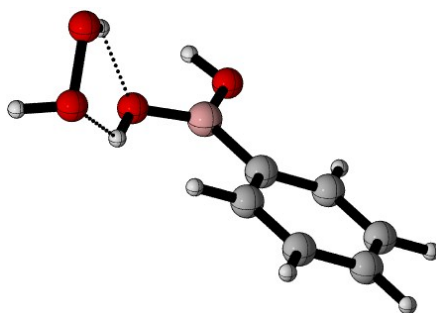
Sum of electronic and thermal Energies = -635.751747

Sum of electronic and thermal Enthalpies = -635.750803

Sum of electronic and thermal Free Energies = -635.805770

C	-3.01640200	-0.50012000	0.94003400
C	-1.79601200	-0.33845500	1.59265700
C	-0.76641600	0.39176200	1.01925600
C	-0.91236700	0.99800300	-0.25340600
C	-2.16796800	0.84291800	-0.88746000
C	-3.18873200	0.10757800	-0.30323900
H	-3.81370500	-1.07744600	1.38952500
H	-1.64190900	-0.79763600	2.56337900
H	0.18214000	0.49527100	1.53395400
H	-2.30658900	1.29829800	-1.86187000
H	-4.13181200	0.00003000	-0.82813300
B	2.74593200	-0.02311200	0.06575700
O	2.29106600	1.23066200	0.08474700
H	1.30291600	1.39359500	-0.30479000
O	3.99292000	-0.36429600	0.55658300
H	4.45449400	0.40725600	0.89771900
H	2.47633000	-1.90612900	-0.39212200
O	1.99697800	-1.07278000	-0.45011700
O	0.05817400	1.65502700	-0.83008600
O	-0.59154100	-2.13266000	-1.14616100
H	-1.33448700	-1.60901800	-0.82061100
H	0.18956400	-1.62639900	-0.87261100

Int_H-1.log



Sum of electronic and zero-point Energies = -559.647785

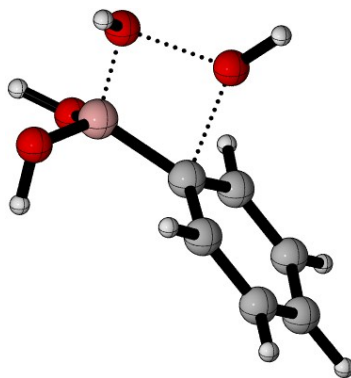
Sum of electronic and thermal Energies = -559.635874

Sum of electronic and thermal Enthalpies = -559.634930

Sum of electronic and thermal Free Energies = -559.687391

C	3.01059900	-1.27137400	0.09720400
C	3.16213500	0.10740800	0.19524500
C	2.04904700	0.93283700	0.11003600
C	0.76902900	0.40284700	-0.08321600
C	0.63777200	-0.98627200	-0.17650300
C	1.74609900	-1.81901400	-0.08576900
H	3.87657600	-1.91872600	0.16360700
H	4.14659500	0.53581500	0.33860000
H	2.16953500	2.00724400	0.19003900
H	-0.34109100	-1.43751900	-0.31024800
H	1.62471700	-2.89291100	-0.15624800
B	-0.46703100	1.35876200	-0.18198800
O	-0.30786400	2.66759400	0.15860800
H	-1.11477100	3.18225600	0.04401000
O	-1.70603200	0.94500100	-0.59216500
H	-1.74996500	0.02451300	-0.88566800
O	-2.96130400	-1.50078100	-0.24060600
H	-3.72965700	-1.59030600	-0.82228400
H	-3.12159900	0.14067200	0.65591600
O	-3.48395900	-0.74224300	0.84294100

TS_H-1.log



Sum of electronic and zero-point Energies = -559.528297

Sum of electronic and thermal Energies = -559.517019

Sum of electronic and thermal Enthalpies = -559.516075

Sum of electronic and thermal Free Energies = -559.565093

C	2.96337300	0.03306400	-0.20461200
C	2.28423000	1.20398700	0.14774900
C	0.91156700	1.19124500	0.27496300
C	0.16120800	0.02150700	-0.00941200
C	0.88519400	-1.16404300	-0.28839400
C	2.26373200	-1.15087400	-0.41555300
H	4.04299900	0.04390800	-0.29176600
H	2.84003300	2.11553200	0.32845100
H	0.37872900	2.09421500	0.54736400
H	0.33152400	-2.08374400	-0.43886000
H	2.79737800	-2.06004600	-0.66166800
B	-1.47500800	0.14197900	-0.38539800
O	-1.70741400	1.48059600	-0.83685400
H	-2.60296100	1.56555500	-1.17906200
O	-1.93740000	-0.93064000	-1.23244400
H	-1.42157600	-0.98806000	-2.04136900
O	-0.67471200	-0.52999200	1.77810100
H	-0.52918600	-0.79529200	2.72214700
H	-2.61465700	-0.97803200	0.91422900
O	-2.26335600	-0.07412000	0.91608300

Int_H-2.log



Sum of electronic and zero-point Energies = -559.800449

Sum of electronic and thermal Energies = -559.789080

Sum of electronic and thermal Enthalpies = -559.788136

Sum of electronic and thermal Free Energies = -559.840573

C	3.21124500	0.80032200	0.62482500
C	3.11265300	-0.58704600	0.64830200
C	2.02545200	-1.22756300	0.07160400
C	1.02899800	-0.47206500	-0.53623800
C	1.11483700	0.91599800	-0.56620200
C	2.20852500	1.54474000	0.01635600
H	4.06083400	1.29492400	1.07709900
H	3.88815700	-1.17760500	1.12033000
H	1.93557300	-2.30663000	0.08372800
H	0.32993900	1.49275900	-1.04174700
H	2.27317900	2.62553700	-0.00856100
B	-2.74660900	0.05332600	0.24055300
O	-3.82330900	0.69620100	0.77291100
H	-4.07740200	0.35034800	1.63445500
O	-2.27222100	0.44680700	-0.98886900
H	-2.76324900	1.17778600	-1.37812400
O	-0.02567700	-1.14365200	-1.09016300
H	-0.67115800	-0.50572400	-1.43902200
H	-1.38454100	-1.33094500	0.41671100
O	-2.13736200	-0.96603100	0.90368300