Supporting Information for

# Computational Thermochemistry: Extension of Benson Group Additivity Approach to Organoboron Compounds and Reliable Predictions of their Thermochemical Properties

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**Table S1.** Standard gas phase enthalpies of formation ($\Delta_f H°$, 298 K, kJ mol$^{-1}$) and calculated total energies ($E_{tot}$, 0 K, a.u.) of gaseous atoms in their ground state with spin-orbit terms included

| Element | $\Delta_f H°$ 298 K | $E_{tot}$ 0K (CBS-QB3) | $E_{tot}$ 0K (W1X-1) |
|---|---|---|---|
| H | 217.999 | -0.499818 | –0.499973 |
| B | 570.3 | –24.601815 | –24.652107 |
| C | 716.67 | –37.785512 | –37.850225 |
| N | 472.683 | –54.520537 | –54.607186 |
| O | 249.173 | –74.987985 | –75.106205 |
| F | 79.39 | –99.643673 | –99.804797 |
| S | 276.98 | –397.658246 | –398.959687 |
| Cl | 121.302 | –459.684931 | –461.280996 |

**Table S2.** Point groups and total, internal, and external symmetry numbers ($\sigma_{tot}$, $\sigma_{int}$, and $\sigma_{ext}$ ) of monoboranes **1**–**3**, diboranes **4**, borinic **5**, boronic **6**, and boric acid derivatives **7**, catecholboranes **8**, aminoboranes **9**–**11**, thioborane **12**, and borazine **13**

| Molecule | Chemical Formula[a] | Point Group | $\sigma_{tot}$ | $\sigma_{int}$ | $\sigma_{ext}$ |
|---|---|---|---|---|---|
| **1a** | $BH_3$ | $D_{3h}$ | 6 | 1 | 6 |
| **1b** | $BH_2Me$ | $C_s$ | 3 | 3 | 1 |
| **1c** | $BH_2Et$ | $C_1$ | 3 | 3 | 1 |
| **1d** | $BH_2Vi$ | $C_s$ | 1 | 1 | 1 |
| **1e** | $BH_2Pr$ | $C_1$ | 3 | 3 | 1 |
| **1f** | $BH_2{}^iPr$ | $C_s$ | 9 | 9 | 1 |
| **1g** | $BH_2{}^sBu$ | $C_1$ | 9 | 9 | 1 |
| **1h** | $BH_2{}^tBu$ | $C_s$ | 81 | 81 | 1 |
| **1i** | $BH_2Ph$ | $C_{2v}$ | 4 | 2 | 2 |
| **2a** | $BHMe_2$ | $C_2$ | 18 | 9 | 2 |
| **2b** | BHEtMe | $C_1$ | 9 | 9 | 1 |
| **2c** | BHMeVi | $C_s$ | 3 | 3 | 1 |
| **2d** | BHMePh | $C_s$ | 6 | 6 | 1 |
| **2e** | $BHEt_2$ | $C_2$ | 18 | 9 | 2 |
| **2f** | BHEtVi | $C_1$ | 3 | 3 | 1 |
| **2g** | $BHVi_2$ | $C_{2v}$ | 2 | 1 | 2 |
| **2h** | BHPhVi | $C_s$ | 2 | 2 | 1 |
| **2i** | $BH{}^iPr_2$ | $C_2$ | 162 | 81 | 2 |
| **2j** | $BHPh_2$ | $C_2$ | 8 | 4 | 2 |
| **3a** | $BMe_3$ | $C_1$ | 27 | 27 | 1 |
| **3b** | $BEtMe_2$ | $C_1$ | 27 | 27 | 1 |
| **3c** | $BMe_2Vi$ | $C_1$ | 9 | 9 | 1 |
| **3d** | $BMe_2Ph$ | $C_2$ | 36 | 18 | 2 |
| **3e** | BEtMePh | $C_1$ | 18 | 18 | 1 |
| **3f** | $BMeVi_2$ | $C_s$ | 3 | 3 | 1 |
| **3g** | BMePhVi | $C_1$ | 6 | 6 | 1 |
| **3h** | $BMePh_2$ | $C_1$ | 12 | 12 | 1 |
| **3i** | $BF_2Me$ | $C_s$ | 3 | 3 | 1 |
| **3j** | $BEt_3$ | $C_{3h}$ | 162 | 27 | 6 |
| **3k** | $BEtVi_2$ | $C_1$ | 3 | 3 | 1 |
| **3l** | $BEtF_2$ | $C_s$ | 3 | 3 | 1 |
| **3m** | $BVi_3$ | $C_{3h}$ | 6 | 1 | 6 |
| **3n** | $BPhVi_2$ | $C_1$ | 2 | 2 | 1 |
| **3o** | $BPh_2Vi$ | $C_1$ | 4 | 4 | 1 |
| **3p** | $BF_2Vi$ | $C_s$ | 1 | 1 | 1 |
| **3q** | $B{}^iPr_3$ | $C_{3h}$ | 4374 | 729 | 6 |
| **3r** | $BBu_3$ | $C_{3h}$ | 162 | 27 | 6 |
| **3s** | $BPh_3$ | $D_3$ | 48 | 8 | 6 |
| **3t** | $BF_3$ | $D_{3h}$ | 6 | 1 | 6 |
| **3u** | $BCl_3$ | $D_{3h}$ | 6 | 1 | 6 |
| **4a** | $B_2H_6$ | $D_{2h}$ | 4 | 1 | 4 |
| **4b** | $B_2H_5Me$ | $C_s$ | 3 | 3 | 1 |
| **4c** | 1,1-$B_2H_4Me_2$ | $C_{2v}$ | 18 | 9 | 2 |
| **4d** | 1,2-*cis*-$B_2H_4Me_2$ | $C_{2v}$ | 18 | 9 | 2 |
| **4e** | 1,2-*trans*-$B_2H_4Me_2$ | $C_{2h}$ | 18 | 9 | 2 |
| **4f** | $B_2H_3Me_3$ | $C_s$ | 27 | 27 | 1 |
| **4g** | $B_2H_2Me_4$ | $D_{2h}$ | 324 | 81 | 4 |
| **5a** | $BH_2OH$ | $C_s$ | 1 | 1 | 1 |
| **5b** | $BH_2(OMe)$ | $C_s$ | 3 | 3 | 1 |
| **5c** | $BH_2(OEt)$ | $C_1$ | 3 | 3 | 1 |
| **5d** | $BH_2(OPh)$ | $C_1$ | 2 | 2 | 1 |
| **5e** | BHMe(OH) | $C_s$ | 3 | 3 | 1 |
| **5f** | BHEt(OH) | $C_s$ | 3 | 3 | 1 |
| **5g** | BHPh(OH) | $C_s$ | 2 | 2 | 1 |
| **5h** | BHMe(OMe) | $C_s$ | 9 | 9 | 1 |

**Table S2.** Continued.

| Molecule | Chemical Formula[a] | Point Group | $\sigma_{tot}$ | $\sigma_{int}$ | $\sigma_{ext}$ |
|---|---|---|---|---|---|
| **5i** | BHEt(OMe) | $C_s$ | 9 | 9 | 1 |
| **5j** | BHPh(OMe) | $C_s$ | 6 | 6 | 1 |
| **5k** | $BMe_2(OH)$ | $C_1$ | 9 | 9 | 1 |
| **5l** | $BMe_2(OMe)$ | $C_s$ | 27 | 27 | 1 |
| **5m** | BEtMe(OH) | $C_1$ | 9 | 9 | 1 |
| **5n** | BMePh(OH) | $C_s$ | 6 | 6 | 1 |
| **5o** | BMePh(OMe) | $C_s$ | 18 | 18 | 1 |
| **6a** | $BH(OH)_2$ | $C_s$ | 2 | 2 | 1 |
| **6b** | $BH(OMe)_2$ | $C_s$ | 9 | 9 | 1 |
| **6c** | $BH(^iPrO)_2$ | $C_{2v}$ | 162 | 81 | 2 |
| **6d** | $BMe(OH)_2$ | $C_s$ | 3 | 3 | 1 |
| **6e** | BMe(OH)(OMe) | $C_s$ | 9 | 9 | 1 |
| **6f** | $BMe(OMe)_2$ | $C_s$ | 27 | 27 | 1 |
| **6g** | BMe(OEt)(OMe) | $C_s$ | 27 | 27 | 1 |
| **6h** | $BMe(OEt)_2$ | $C_s$ | 27 | 27 | 1 |
| **6i** | $BEt(OH)_2$ | $C_s$ | 3 | 3 | 1 |
| **6j** | BEt(OH)(OMe) | $C_s$ | 9 | 9 | 1 |
| **6k** | $BEt(OMe)_2$ | $C_s$ | 27 | 27 | 1 |
| **6l** | $BVi(OH)_2$ | $C_s$ | 1 | 1 | 1 |
| **6m** | BVi(OH)(OMe) | $C_s$ | 3 | 3 | 1 |
| **6n** | $BVi(OMe)_2$ | $C_s$ | 9 | 9 | 1 |
| **6o** | $B(All)(OH)_2$ | $C_1$ | 1 | 1 | 1 |
| **6p** | B(All)(OH)(OMe) | $C_1$ | 3 | 3 | 1 |
| **6q** | $B(All)(OMe)_2$ | $C_1$ | 9 | 9 | 1 |
| **6r** | $BPh(OH)_2$ | $C_1$ | 2 | 2 | 1 |
| **6s** | BPh(OH)(OMe) | $C_1$ | 6 | 6 | 1 |
| **6t** | $BPh(OMe)_2$ | $C_1$ | 18 | 18 | 1 |
| **6u** | B(*p*-Tol)$(OH)_2$ | $C_1$ | 6 | 6 | 1 |
| **6v** | B(*p*-Tol)(OH)(OMe) | $C_1$ | 18 | 18 | 1 |
| **6w** | B(*p*-Tol)$(OMe)_2$ | $C_1$ | 54 | 54 | 1 |
| **7a** | $B(OH)_3$ | $C_{3h}$ | 6 | 1 | 6 |
| **7b** | $B(OH)_2(OMe)$ | $C_s$ | 3 | 3 | 1 |
| **7c** | $B(OH)_2(OPh)$ | $C_1$ | 2 | 2 | 1 |
| **7d** | $B(OH)(OMe)_2$ | $C_s$ | 9 | 9 | 1 |
| **7e** | B(OH)(OMe)(OPh) | $C_1$ | 6 | 6 | 1 |
| **7f** | $B(OMe)_3$ | $C_{3h}$ | 162 | 27 | 6 |
| **7g** | $B(OEt)(OMe)_2$ | $C_s$ | 27 | 27 | 1 |
| **7h** | $B(OMe)_2(OPh)$ | $C_1$ | 18 | 18 | 1 |
| **7i** | $B(OEt)_2(OMe)$ | $C_s$ | 27 | 27 | 1 |
| **7j** | $B(OMe)(OPh)_2$ | $C_1$ | 12 | 12 | 1 |
| **7k** | $B(OEt)_3$ | $C_{3h}$ | 162 | 27 | 6 |
| **8a** | $C_6H_4O_2BH$ | $C_{2v}$ | 2 | 1 | 2 |
| **8b** | $C_6H_4O_2BMe$ | $C_s$ | 3 | 3 | 1 |
| **8c** | 3-$C_6H_3FO_2BMe$ | $C_1$ | 3 | 3 | 1 |
| **8d** | 4-$C_6H_3FO_2BMe$ | $C_1$ | 3 | 3 | 1 |
| **8e** | 3,4-$C_6H_2F_2O_2BMe$ | $C_1$ | 3 | 3 | 1 |
| **8f** | 3,5-$C_6H_2F_2O_2BMe$ | $C_1$ | 3 | 3 | 1 |
| **8g** | 3,6-$C_6H_2F_2O_2BMe$ | $C_s$ | 3 | 3 | 1 |
| **8h** | 4,5-$C_6H_2F_2O_2BMe$ | $C_s$ | 3 | 3 | 1 |
| **8i** | 3,4,5-$C_6H_2F_2O_2BMe$ | $C_1$ | 3 | 3 | 1 |
| **8j** | 3,4,6-$C_6H_2F_2O_2BMe$ | $C_1$ | 3 | 3 | 1 |
| **8k** | $C_6F_4O_2BMe$ | $C_s$ | 3 | 3 | 1 |
| **9a** | $BH_2NH_2$ | $C_{2v}$ | 2 | 1 | 2 |
| **9b** | $BH_2NHMe$ | $C_s$ | 3 | 3 | 1 |
| **9c** | $BH_2NMe_2$ | $C_{2v}$ | 18 | 9 | 2 |

**Table S2.** Continued.

| Molecule | Chemical Formula[a] | Point Group | $\sigma_{tot}$ | $\sigma_{int}$ | $\sigma_{ext}$ |
|---|---|---|---|---|---|
| **9d** | $BHMeNH_2$ | $C_s$ | 3 | 3 | 1 |
| **9e** | $BMe_2NH_2$ | $C_{2v}$ | 18 | 9 | 2 |
| **10** | $BH(NMe_2)_2$ | $C_2$ | 162 | 81 | 2 |
| **11** | $B(NMe_2)_3$ | $D_3$ | 4372 | 729 | 6 |
| **12** | $B(SMe)_3$ | $C_{3h}$ | 162 | 27 | 6 |
| **13** | $B_3N_3H_6$ | $D_{3h}$ | 6 | 1 | 6 |

[a] Used abbreviations: Me = methyl, Et = ethyl, Pr = propyl, $^{i}$Pr = isopropyl, Bu = butyl, $^{s}$Bu = *sec*-butyl, $^{t}$Bu = *tert*-butyl, Vi = vinyl, All = allyl, Ph = phenyl, *p*-Tol = *para*-tolyl.

**Table S3.** Calculated total energies ($E_{tot}$, 0 K, a.u.), zero-point vibrational energies (ZPE, a.u.), absolute enthalpies (H, 298 K, a.u.), thermal corrections to enthalpies ($\Delta$H, 0–298 K, a.u.), and gas phase standard enthalpies of formation ($\Delta_f$H°, 298 K, kJ mol$^{-1}$) of monoboranes **1**–**3**, diboranes **4**, borinic **5**, boronic **6**, and boric acid derivatives **7**, catecholboranes **8**, aminoboranes **9**–**11**, thioborane **12**, and borazine **13**

| | | CBS-QB3 | | W1X-1 | | | |
|---|---|---|---|---|---|---|---|
| **Molecule** | **Chemical Formula**[a] | **H 298 K** | **$\Delta_f$H° 298 K** | **$E_{tot}$ 0 K** | **ZPE** | **$\Delta$H 0–298 K** | **$\Delta_f$H° 298 K** |
| **1a** | $BH_3$ | –26.518655 | 103.7 | -26.598997 | 0.025851 | 0.029682 | 103.9 |
| **1b** | $BH_2Me$ | –65.761246 | 36.7 | -65.938283 | 0.054675 | 0.059545 | 32.2 |
| **1c** | $BH_2Et$ | –104.981826 | 27.6 | -105.253988 | 0.082947 | 0.088959 | 21.3 |
| **1d** | $BH_2Vi$ | –103.777481 | 141.4 | -104.027165 | 0.061711 | 0.066868 | 135.3 |
| **1e** | $BH_2{}^iPr$ | –144.206534 | 7.6 | -144.573721 | 0.110960 | 0.118209 | –0.7 |
| **1f** | $BH_2{}^sBu$ | –144.205293 | 10.8 | -144.572057 | 0.110926 | 0.118002 | 3.2 |
| **1g** | $BH_2{}^tBu$ | –183.429488 | –7.8 | -183.891620 | 0.138665 | 0.147800 | –16.9 |
| **1h** | $BH_2Ph$ | –183.432122 | –14.7 | -183.893055 | 0.138627 | 0.147073 | –22.6 |
| **1i** | $BHMe_2$ | –257.151106 | 172.5 | -257.711858 | 0.109744 | 0.116701 | 160.9 |
| **2a** | BHEtMe | –105.004181 | –31.1 | -105.277452 | 0.082864 | 0.089190 | –39.7 |
| **2b** | BHMeVi | –144.224729 | –40.2 | -144.593118 | 0.111107 | 0.118673 | –50.4 |
| **2c** | BHMePh | –143.020269 | 74.0 | -143.365958 | 0.089510 | 0.096380 | 64.0 |
| **2d** | $BHEt_2$ | –296.393341 | 106.5 | -297.049883 | 0.137506 | 0.146252 | 91.8 |
| **2e** | BHEtVi | –183.445069 | –48.7 | -183.908629 | 0.139455 | 0.148233 | –60.4 |
| **2f** | $BHVi_2$ | -182.240707 | 65.2 | -182.681407 | 0.117687 | 0.125763 | 53.7 |
| **2g** | BHPhVi | –181.036639 | 178.3 | -181.454617 | 0.096136 | 0.103408 | 166.9 |
| **2h** | $BH{}^iPr_2$ | –334.409716 | 210.8 | -335.138434 | 0.143931 | 0.153289 | 195.0 |
| **2i** | $BHPh_2$ | –261.892520 | –83.5 | -262.545441 | 0.195543 | 0.206995 | –96.7 |
| **2j** | $BMe_3$ | –487.780504 | 249.3 | -488.819557 | 0.191540 | 0.203072 | 229.8 |
| **3a** | $BEtMe_2$ | –144.246655 | –97.8 | -144.615676 | 0.110523 | 0.118688 | –109.6 |
| **3b** | $BMe_2Vi$ | –183.467636 | –108.0 | -183.931747 | 0.138944 | 0.148181 | –121.3 |
| **3c** | $BMe_2Ph$ | –182.261487 | 10.6 | -182.702714 | 0.117199 | 0.125736 | –2.3 |
| **3d** | BEtMePh | –335.634483 | 43.3 | -336.386409 | 0.165072 | 0.175644 | 26.1 |
| **3e** | $BMeVi_2$ | –374.854927 | 34.5 | -375.701870 | 0.193251 | 0.205190 | 16.1 |
| **3f** | BMePhVi | –220.276147 | 119.5 | -220.789522 | 0.123611 | 0.132765 | 105.4 |
| **3g** | $BMePh_2$ | –373.649255 | 151.9 | -374.473261 | 0.171501 | 0.182671 | 133.7 |
| **3h** | $BF_2Me$ | –527.022255 | 184.5 | -528.156224 | 0.218896 | 0.232292 | 163.3 |
| **3i** | $BEt_3$ | –264.264391 | –806.1 | -264.754300 | 0.045190 | 0.050949 | –809.4 |
| **3j** | $BEtVi_2$ | –261.909264 | –127.5 | -262.563402 | 0.195538 | 0.207215 | –143.3 |
| **3k** | $BEtF_2$ | –259.496064 | 112.1 | -260.104453 | 0.151927 | 0.162089 | 96.3 |
| **3l** | $BVi_3$ | –303.484775 | –814.8 | -304.069684 | 0.073594 | 0.080541 | –819.0 |
| **3m** | $BPhVi_2$ | –258.290790 | 228.4 | -258.876157 | 0.129900 | 0.139746 | 213.5 |
| **3n** | $BPh_2Vi$ | –411.663842 | 260.9 | -412.559512 | 0.177674 | 0.189378 | 242.1 |
| **3o** | $BF_2Vi$ | –565.038244 | 289.9 | -566.243899 | 0.225192 | 0.239147 | 268.4 |
| **3p** | $B{}^iPr_3$ | –302.276993 | –691.9 | -302.838603 | 0.051521 | 0.057696 | –695.8 |
| **3q** | $BBu_3$ | –379.579738 | –177.9 | -380.517689 | 0.279942 | 0.295776 | –194.1 |
| **3r** | $BPh_3$ | –497.257983 | –248.7 | -498.481733 | 0.362801 | 0.382822 | –274.6 |
| **3s** | $BF_3$ | –718.413257 | 317.3 | -719.928727 | 0.272613 | 0.288855 | 293.3 |
| **3t** | $BCl_3$ | –324.263198 | –1133.9 | -324.813829 | 0.012208 | 0.016678 | –1134.6 |
| **3u** | $B_2H_6$ | –1404.159723 | –411.5 | -1409.008236 | 0.007402 | 0.012774 | –404.3 |
| **4a** | $B_2H_5Me$ | –53.098420 | 46.9 | -53.268819 | 0.061943 | 0.066508 | 40.6 |
| **4b** | 1,1-$B_2H_4Me_2$ | –92.336196 | –7.4 | -92.602500 | 0.090036 | 0.096172 | –16.8 |
| **4c** | 1,2-*cis*-$B_2H_4Me_2$ | –131.575016 | –64.5 | -131.936681 | 0.118081 | 0.125456 | –76.6 |
| **4d** | 1,2-*trans*-$B_2H_4Me_2$ | –131.572936 | –59.0 | -131.935076 | 0.118584 | 0.125869 | –71.3 |
| **4e** | $B_2H_3Me_3$ | –131.573287 | –59.9 | -131.935479 | 0.118520 | 0.125970 | –72.1 |
| **4f** | $B_2H_2Me_4$ | –170.811085 | –114.3 | -171.268753 | 0.146297 | 0.155372 | –129.2 |
| **4g** | $BH_2OH$ | –210.048178 | –166.8 | -210.600993 | 0.173958 | 0.184531 | –184.3 |
| **5a** | $BH_2(OMe)$ | –101.742245 | –271.9 | -101.950826 | 0.034827 | 0.038829 | –274.0 |
| **5b** | $BH_2(OEt)$ | –140.949456 | –246.0 | -141.251235 | 0.062610 | 0.067848 | –245.8 |
| **5c** | $BH_2(OPh)$ | –180.179013 | –278.7 | -180.575580 | 0.090611 | 0.096984 | –280.2 |
| **5d** | BHMe(OH) | –332.341437 | –115.8 | -333.023928 | 0.114665 | 0.122508 | –121.3 |
| **5e** | BHMe(OMe) | –140.985843 | –341.5 | -141.290281 | 0.062872 | 0.068231 | –347.3 |

**Table S3.** Continued.

| | | CBS-QB3 | | W1X-1 | | | |
|---|---|---|---|---|---|---|---|
| **Molecule** | **Chemical Formula**[a] | **H 298 K** | **$\Delta_f$H° 298 K** | **$E_{tot}$ 0 K** | **ZPE** | **ΔH 0–298 K** | **$\Delta_f$H° 298 K** |
| **5f** | BHEt(OH) | –180.206617 | –351.2 | -180.606024 | 0.091270 | 0.097785 | –358.0 |
| **5g** | BHPh(OH) | –332.373400 | –199.7 | -333.060286 | 0.116991 | 0.124849 | –210.6 |
| **5h** | BHMe(OMe) | –180.192712 | –314.7 | -180.590217 | 0.090288 | 0.097223 | –318.0 |
| **5i** | BHEt(OMe) | –219.413666 | –324.8 | -219.906093 | 0.118637 | 0.126784 | –329.0 |
| **5j** | BHPh(OMe) | –371.580575 | –173.7 | -372.360502 | 0.144250 | 0.153851 | –182.0 |
| **5k** | $BMe_2(OH)$ | –180.227613 | –406.3 | -180.627491 | 0.090496 | 0.097553 | –415.0 |
| **5l** | $BMe_2(OMe)$ | –219.433058 | –375.7 | -219.925849 | 0.117762 | 0.126480 | –381.7 |
| **5m** | BEtMe(OH) | –219.448802 | –417.1 | -219.943828 | 0.118873 | 0.127120 | –427.2 |
| **5n** | BMePh(OH) | –371.615272 | –264.8 | -372.397398 | 0.144431 | 0.154110 | –278.2 |
| **5o** | BMePh(OMe) | –410.820655 | –234.1 | -411.695719 | 0.171651 | 0.183110 | –244.6 |
| **6a** | $BH(OH)_2$ | –176.963929 | –642.5 | -177.298995 | 0.041865 | 0.046429 | –646.3 |
| **6b** | $BH(OMe)_2$ | –255.375035 | –581.9 | -255.896212 | 0.096884 | 0.104728 | –579.8 |
| **6c** | $BH(^iPrO)_2$ | –412.294729 | –716.7 | -413.193325 | 0.207047 | 0.220097 | –719.7 |
| **6d** | $BMe(OH)_2$ | –216.205682 | –707.3 | -216.636039 | 0.069466 | 0.075736 | –713.6 |
| **6e** | BMe(OH)(OMe) | –255.411197 | –676.9 | -255.934504 | 0.096854 | 0.104851 | –680.0 |
| **6f** | $BMe(OMe)_2$ | –294.616636 | –646.3 | -295.232753 | 0.124304 | 0.133924 | –646.1 |
| **6g** | BMe(OEt)(OMe) | –333.846250 | –679.2 | -334.557042 | 0.152193 | 0.163028 | –680.4 |
| **6h** | $BMe(OEt)_2$ | –373.075585 | –711.3 | -373.881085 | 0.180055 | 0.192232 | –713.8 |
| **6i** | $BEt(OH)_2$ | –255.426619 | –717.4 | -255.951939 | 0.097887 | 0.105249 | –724.8 |
| **6j** | BEt(OH)(OMe) | –294.632085 | –686.9 | -295.250327 | 0.125244 | 0.134407 | –690.9 |
| **6k** | $BEt(OMe)_2$ | –333.837511 | –656.2 | -334.548417 | 0.152616 | 0.163507 | –656.5 |
| **6l** | $BVi(OH)_2$ | –254.218550 | –593.7 | -254.720410 | 0.075492 | 0.082253 | –600.7 |
| **6m** | BVi(OH)(OMe) | –293.424147 | –563.6 | -294.018947 | 0.102682 | 0.111320 | –567.5 |
| **6n** | $BVi(OMe)_2$ | –332.628871 | –531.1 | -333.316686 | 0.130344 | 0.140598 | –531.7 |
| **6o** | $B(All)(OH)_2$ | –293.444941 | –618.2 | -294.041527 | 0.103148 | 0.111148 | –627.3 |
| **6p** | B(All)(OH)(OMe) | –332.650656 | –588.3 | -333.340222 | 0.130482 | 0.140307 | –594.2 |
| **6q** | $B(All)(OMe)_2$ | –371.853250 | –550.2 | -372.635372 | 0.157458 | 0.169148 | –552.7 |
| **6r** | $BPh(OH)_2$ | –407.592118 | –562.6 | -408.403978 | 0.122969 | 0.131933 | –572.6 |
| **6s** | BPh(OH)(OMe) | –446.797933 | –532.9 | -447.702788 | 0.150347 | 0.161113 | –539.8 |
| **6t** | $BPh(OMe)_2$ | –486.000215 | –494.1 | -486.998061 | 0.178027 | 0.190357 | –497.6 |
| **6u** | $B(p\text{-Tol})(OH)_2$ | –446.821508 | –594.8 | -447.727376 | 0.149677 | 0.160566 | –605.8 |
| **6v** | B(*p*-Tol)(OH)(OMe) | –486.027275 | –565.1 | -487.026126 | 0.177046 | 0.189742 | –572.9 |
| **6w** | $B(p\text{-Tol})(OMe)_2$ | –525.229467 | –526.0 | -526.321321 | 0.204758 | 0.219000 | –530.4 |
| **7a** | $B(OH)_3$ | –252.179860 | –998.0 | -252.640361 | 0.048152 | 0.053516 | –1002.1 |
| **7b** | $B(OH)_2(OMe)$ | –291.385048 | –966.8 | -291.938524 | 0.075582 | 0.082730 | –967.6 |
| **7c** | $B(OH)_2(OPh)$ | –482.776995 | –836.5 | -483.711060 | 0.127457 | 0.137301 | –842.9 |
| **7d** | $B(OH)(OMe)_2$ | –330.590349 | –935.8 | -331.236706 | 0.103002 | 0.111925 | –933.1 |
| **7e** | B(OH)(OMe)(OPh) | –521.982633 | –806.4 | -523.009563 | 0.154814 | 0.166516 | –809.2 |
| **7f** | $B(OMe)_3$ | –369.795855 | –905.4 | -370.534891 | 0.130412 | 0.141107 | –898.6 |
| **7g** | $B(OEt)(OMe)_2$ | –409.025265 | –937.7 | -409.859069 | 0.158304 | 0.170202 | –932.7 |
| **7h** | $B(OMe)_2(OPh)$ | –561.188304 | –776.5 | -562.307992 | 0.182165 | 0.195688 | –775.5 |
| **7i** | $B(OEt)_2(OMe)$ | –448.254793 | –970.4 | -449.183257 | 0.186161 | 0.199291 | –966.8 |
| **7j** | $B(OMe)(OPh)_2$ | –752.581145 | –648.5 | -754.081156 | 0.233857 | 0.250249 | –652.5 |
| **7k** | $B(OEt)_3$ | –487.484324 | –1003.0 | -488.507440 | 0.214023 | 0.228385 | –1000.8 |
| **8a** | $C_6H_4O_2BH$ | –406.371769 | –406.7 | -407.156359 | 0.100872 | 0.107878 | –409.1 |
| **8b** | $C_6H_4O_2BMe$ | –445.616339 | –478.8 | -446.495817 | 0.127999 | 0.137108 | –482.9 |
| **8c** | $3\text{-}C_6H_3FO_2BMe$ | –544.777394 | –662.6 | -545.809076 | 0.120029 | 0.130011 | –662.3 |
| **8d** | $4\text{-}C_6H_3FO_2BMe$ | –544.781329 | –672.9 | -545.813020 | 0.119864 | 0.129818 | –673.1 |
| **8e** | $3,4\text{-}C_6H_2F_2O_2BMe$ | –643.936335 | –840.8 | -645.119663 | 0.111965 | 0.122865 | –834.8 |
| **8f** | $3,5\text{-}C_6H_2F_2O_2BMe$ | –643.941285 | –853.8 | -645.125199 | 0.111846 | 0.122712 | –849.7 |
| **8g** | $3,6\text{-}C_6H_2F_2O_2BMe$ | –643.937350 | –843.5 | -645.120501 | 0.112016 | 0.122886 | –836.9 |
| **8h** | $4,5\text{-}C_6H_2F_2O_2BMe$ | –643.940103 | –850.7 | -645.123408 | 0.111797 | 0.122638 | –845.2 |
| **8i** | $3,4,5\text{-}C_6H_2F_2O_2BMe$ | –743.093405 | –1014.1 | -744.429136 | 0.103877 | 0.115725 | –1004.3 |
| **8j** | $3,4,6\text{-}C_6H_2F_2O_2BMe$ | –743.094470 | –1016.9 | -744.430099 | 0.103919 | 0.115741 | –1006.8 |

**Table S3.** Continued.

| | | CBS-QB3 | | W1X-1 | | | |
|---|---|---|---|---|---|---|---|
| **Molecule** | **Chemical Formula**[a] | **H 298 K** | **$\Delta_f$H° 298 K** | **$E_{tot}$ 0 K** | **ZPE** | **$\Delta$H 0–298 K** | **$\Delta_f$H° 298 K** |
| **8k** | $C_6F_4O_2BMe$ | –842.245787 | –1175.1 | -843.733203 | 0.095954 | 0.108799 | –1159.1 |
| **9a** | $BH_2NH_2$ | –81.867053 | –79.3 | -82.057006 | 0.047218 | 0.051405 | –81.9 |
| **9b** | $BH_2NHMe$ | –121.080686 | –70.2 | -121.364769 | 0.075325 | 0.080612 | –72.6 |
| **9c** | $BH_2NMe_2$ | –160.298671 | –72.6 | -160.676037 | 0.102939 | 0.110748 | –70.0 |
| **9d** | $BHMeNH_2$ | –121.107460 | –140.5 | -121.393293 | 0.075248 | 0.080787 | –147.0 |
| **9e** | $BMe_2NH_2$ | –160.347750 | –201.4 | -160.729100 | 0.102870 | 0.110096 | –211.0 |
| **10** | $BH(NMe_2)_2$ | –294.044512 | –159.1 | -294.716279 | 0.176298 | 0.186884 | –160.2 |
| **11** | $B(NMe_2)_3$ | –427.788792 | –241.5 | -428.752742 | 0.248621 | 0.263351 | –239.6 |
| **12** | $B(SMe)_3$ | –1337.569622 | –199.7 | -1341.851469 | 0.119859 | 0.131917 | –199.1 |
| **13** | $B_3N_3H_6$ | –242.210687 | –480.8 | -242.726208 | 0.091836 | 0.098053 | –495.7 |

[a] Used abbreviations: Me = methyl, Et = ethyl, Pr = propyl, $^{i}$Pr = isopropyl, Bu = butyl, $^{s}$Bu = *sec*-butyl, $^{t}$Bu = *tert*-butyl, Vi = vinyl, All = allyl, Ph = phenyl, *p*-Tol = *para*-tolyl.