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Supplementary information

Catalytic and Non-Catalytic Hydroboration of Carbonyls: The Quantum-Chemical Studies

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Thermodynamic calculations

Calculating molar concentrations of substrates:

$$n_{HBPin} : n_{PhCHO} : n_{KF} = 1.2 : 1.0 : 0.01$$

$$n_{HBPin} = \frac{0.26\ g}{127.98\ g\ \cdot mol^{-3}} = 2.03 \cdot 10^{-3}\ mol$$

$$n_{PhCHO} = n_{PhCMeO} = 2.03 \cdot 10^{-3} mol \cdot \frac{1.0}{1.2} = 1.69 \cdot 10^{-3}\ mol$$

$$n_{KF} = 2.03 \cdot 10^{-3} mol \cdot \frac{0.01}{1.2} = 1.69 \cdot 10^{-5}\ mol$$

Acetophenone + pinacolborane activation energy

Calculating the volume V of reaction mixture:

$$V_{DMF} = 1\ cm^3$$

$$V_{HBPin} = \frac{0.26\ g}{0.882\ g\ \cdot cm^{-3}} = 0.29\ cm^3$$

$$V_{PhCMeO} = \frac{1.69 \cdot 10^{-3}\ mol \cdot 120.15\ g\ \cdot mol^{-3}}{1.028\ g\ \cdot cm^{-3}} = 0.20\ cm^3$$

Assuming that no volume contraction takes place, the total volume of reaction mixture can be taken as $V = 1.5\ cm^3$.

Calculating the concentration $[\mathbf{I3}]$ in the reaction mixture:

$$[\mathbf{I3}] = \frac{1.69 \cdot 10^{-5}\ mol}{1.5\ cm^3} = 1.13 \cdot 10^{-5}\ mol\ \cdot cm^{-3} = 1.13 \cdot 10^{-2}\ mol\ \cdot dm^{-3}$$

For a pseudo-first order reaction, half-time is given as:

$$t_{1/2} = \frac{\ln(2)}{k'} = \frac{\ln(2)}{k \cdot [\mathbf{I3}]}$$

$$k = \frac{\ln(2)}{t_{1/2} \cdot [\mathbf{I3}]} = \frac{0.693}{540\ s \cdot 1.13 \cdot 10^{-2}\ mol\ \cdot dm^{-3}} = 0.113\ dm^3 \cdot mol^{-1} \cdot s^{-1}$$

Substituting into Eyring equation:

$$k = \frac{\kappa \cdot k_B \cdot T}{h} e^{\frac{-\Delta G^{\ddagger}}{RT}}$$

$$e^{\frac{-\Delta G^{\ddagger}}{RT}} = \frac{\mathrm{k} \cdot \mathrm{h}}{\kappa \cdot k_B \cdot T} = \frac{0.113\ \mathrm{dm^3 \cdot mol^{-1} \cdot s^{-1}} \cdot 6.626\ \cdot 10^{-34}\ \mathrm{J \cdot s}}{1 \cdot 1.381\ \mathrm{J \cdot K^{-1}} \cdot 333.15\ K} = 1.632 \cdot 10^{-13}\ \mathrm{dm^3 \cdot mol^{-1}}$$

$$\frac{-\Delta G^{\ddagger}}{RT} = \ln\left(\frac{\mathrm{k} \cdot \mathrm{h}}{\kappa \cdot k_B \cdot T}\right)$$

$$\Delta G^{\ddagger} = -RT \ln\left(\frac{\mathrm{k} \cdot \mathrm{h}}{\kappa \cdot k_B \cdot T}\right)$$

$$\Delta G^{\ddagger} = -8.314\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}} \cdot 333.15\ K \cdot \ln\left(\frac{0.113\ \mathrm{dm^3 \cdot mol^{-1} \cdot s^{-1}} \cdot 6.626\ \cdot 10^{-34}\ \mathrm{J \cdot s}}{1 \cdot 1.381\ \mathrm{J \cdot K^{-1}} \cdot 333.15\ K}\right)$$

$$\Delta G^{\ddagger} = 87.9\ \cdot 10^{3}\ \mathrm{J \cdot mol^{-1}} = \ \boldsymbol{21.0\ kcal/mol}$$

Benzaldehyde + pinacolborane activation energy

Calculating the volume V of reaction mixture:

$$\mathrm{V_{DMF}} = 1\ \mathrm{cm^3}$$

$$\mathrm{V_{HBPin}} = \frac{0.26\ \mathrm{g}}{0.882\ \mathrm{g}\ \cdot \mathrm{cm^{-3}}} = 0.29\ \mathrm{cm^3}$$

$$\mathrm{V_{PhCMeO}} = \frac{1.69 \cdot 10^{-3}\ \mathrm{mol} \cdot 106.12\ \mathrm{g}\ \cdot \mathrm{mol^{-3}}}{1.044\ \mathrm{g}\ \cdot \mathrm{cm^{-3}}} = 0.17\ \mathrm{cm^3}$$

Assuming that no volume contraction takes place, the total volume of reaction mixture can be taken as $\mathrm{V} = 1.5\ \mathrm{cm^3}$.

Calculating the concentration [**I3**] in the reaction mixture:

$$[\mathbf{I3}] = \frac{1.69 \cdot 10^{-5}\ \mathrm{mol}}{1.5\ \mathrm{cm^3}} = 1.13 \cdot 10^{-5}\ \mathrm{mol}\ \cdot \mathrm{cm^{-3}} = 1.13 \cdot 10^{-2}\ \mathrm{mol}\ \cdot \mathrm{dm^{-3}}$$

For a pseudo-first order reaction, half-time is given as:

$$\mathrm{t_{1/2}} = \frac{\ln(2)}{\mathrm{k'}} = \frac{\ln(2)}{\mathrm{k} \cdot [\mathbf{I3}]}$$

$$\mathrm{k} = \frac{\ln(2)}{\mathrm{t_{1/2}} \cdot [\mathbf{I3}]} = \frac{0.693}{135\ \mathrm{s} \cdot 1.13 \cdot 10^{-2}\ \mathrm{mol}\ \cdot \mathrm{dm^{-3}}} = 0.453\ \mathrm{dm^3 \cdot mol^{-1} \cdot s^{-1}}$$

Substituting into Eyring equation:

$$\mathrm{k} = \frac{\kappa \cdot k_B \cdot T}{\mathrm{h}}\, e^{\frac{-\Delta G^{\ddagger}}{RT}}$$

$$\frac{-\Delta G^{\ddagger}}{RT} = \ln\left(\frac{\mathrm{k}\cdot\mathrm{h}}{\kappa\cdot k_B\cdot T}\right)$$

$$\Delta G^{\ddagger} = -RT\ln\left(\frac{\mathrm{k}\cdot\mathrm{h}}{\kappa\cdot k_B\cdot T}\right)$$

$$\Delta G^{\ddagger} = -8.314\ \mathrm{J}\cdot\mathrm{mol}^{-1}\cdot\mathrm{K}^{-1}\cdot 333.15\ K\cdot\ln\left(\frac{0.453\ \mathrm{dm}^3\cdot\mathrm{mol}^{-1}\cdot\mathrm{s}^{-1}\cdot 6.626\ \cdot 10^{-34}\ \mathrm{J}\cdot\mathrm{s}}{1\cdot 1.381\ \mathrm{J}\cdot\mathrm{K}^{-1}\cdot 333.15\ K}\right)$$

$$\Delta G^{\ddagger} = 84.1\cdot 10^{3}\ \ \mathrm{J}\cdot\mathrm{mol}^{-1} = \ \boldsymbol{20.1\ kcal/mol}$$

Possible transformations of I7

Assuming that **I7** is in equilibrium with **I9** and **TS4**, and with **I8** and **TS3**:

$$\mathrm{K}_1 = \frac{[\mathbf{I9}]}{[\mathbf{I7}][\mathbf{FBPin}]} \Longrightarrow [\mathbf{I7}] = \frac{[\mathbf{I9}]}{\mathrm{K}_1[\mathbf{FBPin}]}$$

$$\mathrm{K}_2 = \frac{[\mathbf{TS4}]}{[\mathbf{I9}]} \Longrightarrow [\mathbf{I9}] = \frac{[\mathbf{TS4}]}{\mathrm{K}_2}$$

$$\mathrm{K}_3 = \frac{[\mathbf{I8}]}{[\mathbf{I7}][\mathbf{PhCHO}]} \Longrightarrow [\mathbf{I7}] = \frac{[\mathbf{I8}]}{\mathrm{K}_3[\mathbf{PhCHO}]}$$

$$\mathrm{K}_4 = \frac{[\mathbf{TS3}]}{[\mathbf{I8}]} \Longrightarrow [\mathbf{I8}] = \frac{[\mathbf{TS3}]}{\mathrm{K}_4}$$

$$\frac{[\mathbf{TS4}]}{\mathrm{K}_1\mathrm{K}_2[\mathbf{FBPin}]} = \frac{[\mathbf{TS3}]}{\mathrm{K}_3\mathrm{K}_4[\mathbf{PhCHO}]} \Longrightarrow \frac{[\mathbf{TS4}]}{[\mathbf{TS3}]} = \frac{\mathrm{K}_1\mathrm{K}_2[\mathbf{FBPin}]}{\mathrm{K}_3\mathrm{K}_4[\mathbf{PhCHO}]}$$

$$\mathrm{K}_n = \mathrm{e}^{-\frac{\Delta G}{RT}}$$

$$\frac{[\mathbf{TS4}]}{[\mathbf{TS3}]} = \frac{\exp\left(-\frac{\Delta G_1}{RT}\right)\cdot\exp\left(-\frac{\Delta G_2}{RT}\right)\cdot[\mathbf{FBPin}]}{\exp\left(-\frac{\Delta G_3}{RT}\right)\cdot\exp\left(-\frac{\Delta G_4}{RT}\right)\cdot[\mathbf{PhCHO}]}$$

$$\frac{[\mathbf{TS4}]}{[\mathbf{TS3}]} = \exp\left(\frac{\Delta G_3 + \Delta G_4 - \Delta G_1 - \Delta G_2}{RT}\right)\cdot\frac{[\mathbf{FBPin}]}{[\mathbf{PhCHO}]}$$

$$\frac{[\mathbf{TS4}]}{[\mathbf{TS3}]} = \exp\left(\frac{(3.4 + 12.1 - 7.8 - 6.4)\ \mathrm{kcal}\cdot\mathrm{mol}^{-1}}{1.987\cdot 10^{-3}\ \mathrm{kcal}\cdot\mathrm{mol}^{-1}\cdot\mathrm{K}^{-1}\cdot 298\ \mathrm{K}}\right)\cdot\frac{[\mathbf{FBPin}]}{[\mathbf{PhCHO}]}$$

$$\frac{[\mathbf{TS4}]}{[\mathbf{TS3}]} = 9.0\cdot\frac{[\mathbf{FBPin}]}{[\mathbf{PhCHO}]}$$

The [**FBPin**]:[**PhCHO**] ratio of 1:9 would result in equal concentrations of **TS4** and **TS3**; the actual ratio must be lower, at least through most of the reaction time (due to initial **KF**:**PhCHO** ratio of 1:100), which means that the **TS3** pathway is preferred over **TS4** pathway.

Energy profiles

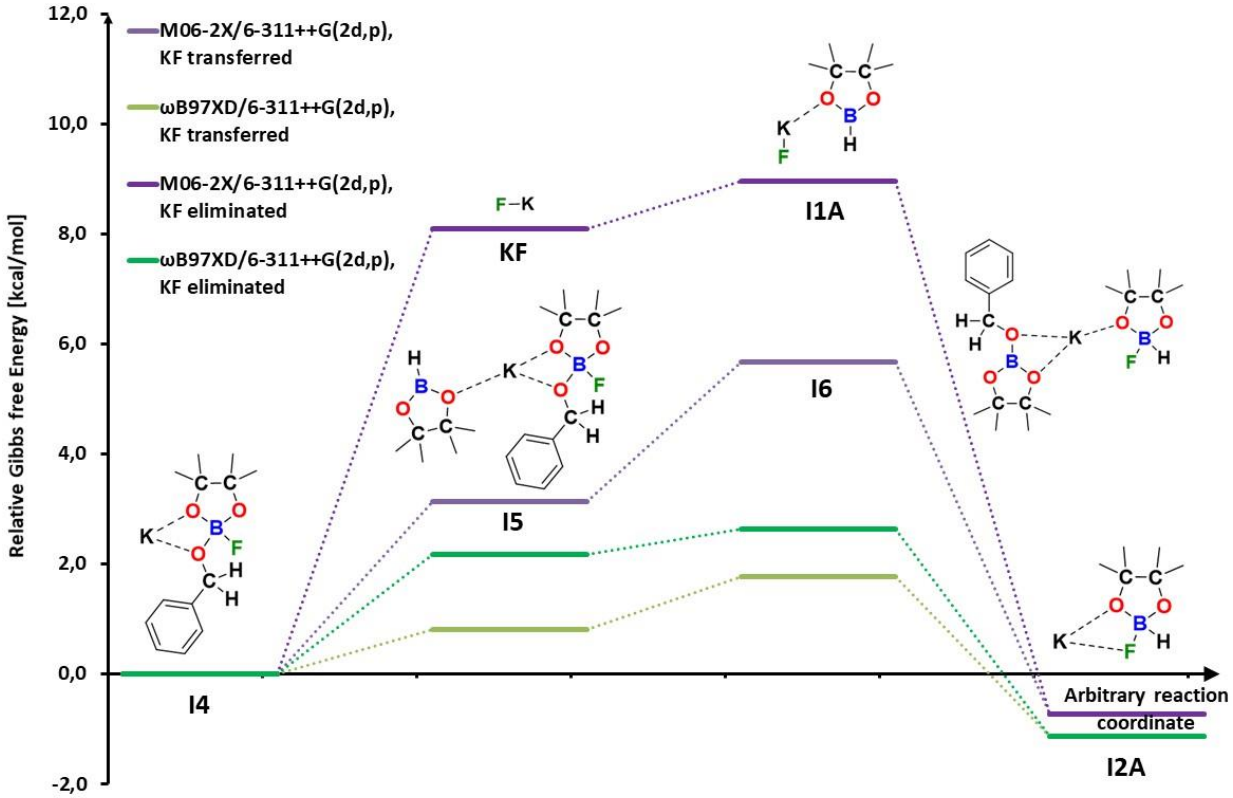

Figure S01. Gibbs free energy profiles for the two competing pathways from **I4** to **I2A** in KF-mediated reaction between benzaldehyde and pinacolborane.

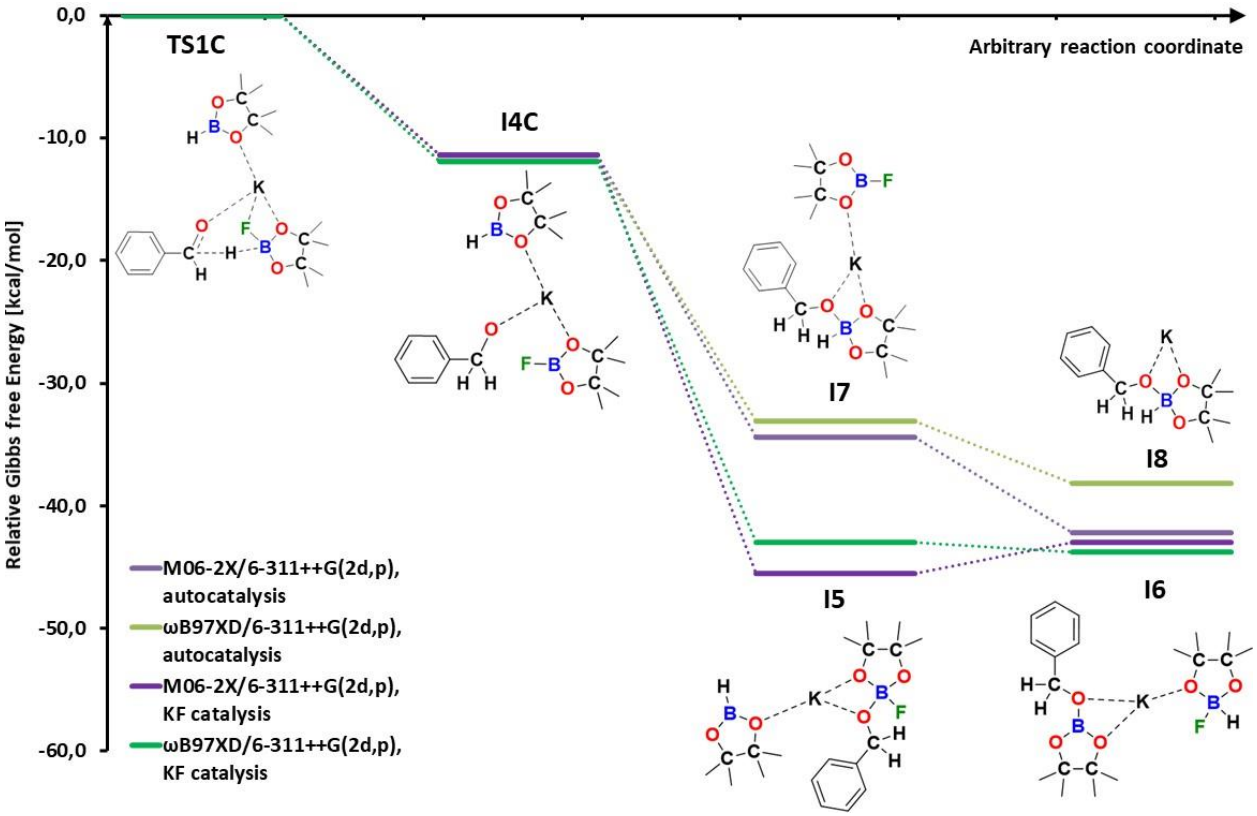

Figure S02. Gibbs free energy profiles for **TS1C** decay to **I6** (KF-mediated) vs to **I8** (autocatalytic pathway) in the reaction between benzaldehyde and pinacolborane.

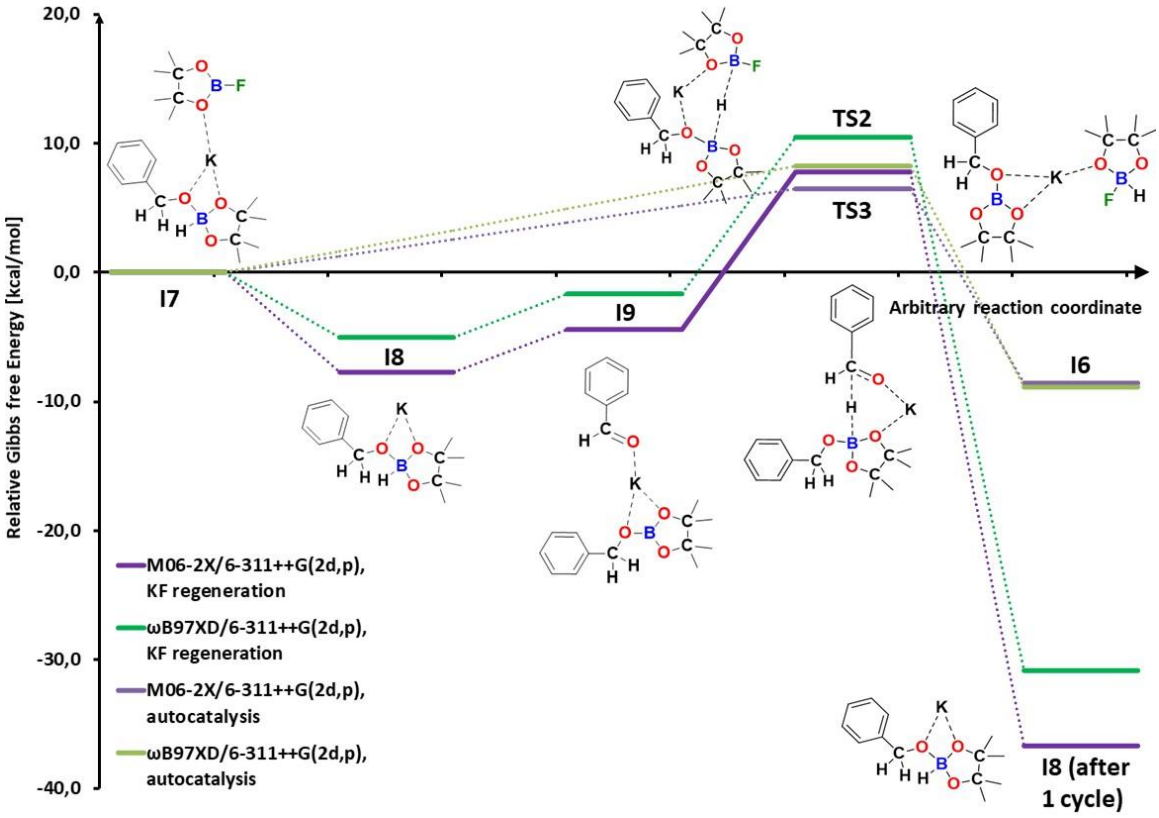

Figure S03. Gibbs free energy profiles from **I7** through **TS3** to **I6** (back to [HBPinF]K) vs. autocatalytic pathway (through **I8, I9**, **TS2** and **I8** again) in the reaction between benzaldehyde and pinacolborane.

Cartesian coordinates, Mulliken and APT charges of all atoms, and absolute energies at all stationary points

All coordinates are given in ångströms.

All energies are given in hartrees.

Benzaldehyde + pinacolborane

Pinacolborane

HF/6-31G(d), N,N-dimethylformamide solution

Electronic energy: -409.292909

Electronic energy + zero-point energy: -409.088358

Electronic energy + thermal energy correction: -409.079504

Electronic energy + thermal enthalpy correction: -409.078560

Electronic energy + thermal free energy correction: -409.120903

Table S01. Cartesian coordinates, Mulliken and APT charges of all atoms at **pinacolborane** in the reaction of benzaldehyde with pinacolborane (HF/6-31G(d), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	1.060470	1.180592	-0.384086	-0.605802	-0.956945
C	0.782551	-0.182778	-0.050923	0.268621	0.498197
C	-0.782551	-0.182778	0.050923	0.268621	0.498197
O	-1.060470	1.180593	0.384085	-0.605802	-0.956945
C	-1.480701	-0.461800	-1.281577	-0.487780	0.039312
H	-1.371659	-1.497245	-1.584475	0.162371	-0.025235
H	-2.537105	-0.246641	-1.172785	0.183836	-0.019869
H	-1.092902	0.170282	-2.072233	0.172366	-0.022540
C	1.368288	-1.079204	-1.134483	-0.484075	0.060229
H	2.448085	-0.986304	-1.133494	0.180925	-0.020167
H	1.119392	-2.120303	-0.953364	0.158236	-0.025650
H	1.013252	-0.803583	-2.117841	0.181216	-0.018595
C	-1.368288	-1.079203	1.134484	-0.484075	0.060229
H	-2.448085	-0.986303	1.133494	0.180925	-0.020167
H	-1.119393	-2.120302	0.953366	0.158236	-0.025650
H	-1.013252	-0.803581	2.117841	0.181216	-0.018595
C	1.480701	-0.461799	1.281577	-0.487780	0.039312
H	2.537105	-0.246641	1.172785	0.183836	-0.019869

H	1.092902	0.170284	2.072232	0.172366	-0.022540
H	1.371659	-1.497244	1.584477	0.162371	-0.025235
B	0.000000	1.930007	-0.000001	0.596945	1.197327
H	0.000001	3.113437	-0.000000	-0.056777	-0.214804

HF/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -409.413872

Electronic energy + zero-point energy: -409.211908

Electronic energy + thermal energy correction: -409.203030

Electronic energy + thermal enthalpy correction: -409.202086

Electronic energy + thermal free energy correction: -409.244460

Table S02. Cartesian coordinates, Mulliken and APT charges of all atoms at **pinacolborane** in the reaction of benzaldehyde with pinacolborane (HF/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	1.059381	1.181627	-0.377682	-0.715416	-0.948089
C	0.782094	-0.182158	-0.051217	0.532767	0.496465
C	-0.782094	-0.182158	0.051217	0.532767	0.496465
O	-1.059381	1.181627	0.377682	-0.715416	-0.948089
C	-1.479664	-0.467719	-1.276944	-0.495092	0.026031
H	-1.364762	-1.503348	-1.575143	0.143880	-0.017933
H	-2.536676	-0.259121	-1.165948	0.174744	-0.017377
H	-1.097192	0.163521	-2.070014	0.132172	-0.019009
C	1.364044	-1.073578	-1.136324	-0.821733	0.045149
H	2.443746	-0.984613	-1.133734	0.148055	-0.018239
H	1.111437	-2.113783	-0.957429	0.153802	-0.018257
H	1.010008	-0.794069	-2.118148	0.159062	-0.014122
C	-1.364044	-1.073578	1.136324	-0.821733	0.045149
H	-2.443746	-0.984613	1.133734	0.148055	-0.018239
H	-1.111437	-2.113783	0.957429	0.153802	-0.018257
H	-1.010008	-0.794069	2.118148	0.159062	-0.014122
C	1.479664	-0.467719	1.276944	-0.495092	0.026031
H	2.536676	-0.259121	1.165948	0.174744	-0.017377
H	1.097192	0.163521	2.070014	0.132172	-0.019009
H	1.364762	-1.503348	1.575143	0.143880	-0.017933
B	0.000000	1.929230	-0.000000	1.119715	1.169322
H	0.000000	3.112104	-0.000000	0.055799	-0.198561

B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -412.000110

Electronic energy + zero-point energy: -411.810684

Electronic energy + thermal energy correction: -411.801094

Electronic energy + thermal enthalpy correction: -411.800150

Electronic energy + thermal free energy correction: -411.843215

Table S03. Cartesian coordinates, Mulliken and APT charges of all atoms at **pinacolborane** in the reaction of benzaldehyde with pinacolborane (B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	-0.984520	-0.579323	-1.202930	-0.521128	-0.812001
C	-0.551619	-0.564839	0.192864	0.194180	0.435869
C	0.551619	0.564839	0.192864	0.194180	0.435869
O	0.984520	0.579323	-1.202930	-0.521128	-0.812001
C	0.000000	1.960874	0.489492	-0.381483	-0.018085
H	-0.296299	2.061170	1.535328	0.138184	-0.003823
H	0.777328	2.697386	0.281050	0.161344	-0.001841
H	-0.860716	2.193047	-0.139232	0.131275	-0.003494
C	-1.765516	-0.285269	1.069071	-0.637388	0.001627
H	-2.477612	-1.106913	0.976348	0.139819	-0.004149
H	-1.475594	-0.206554	2.119660	0.148053	-0.003496
H	-2.272114	0.633103	0.777354	0.148437	0.000336
C	1.765516	0.285269	1.069071	-0.637388	0.001627
H	2.477612	1.106913	0.976348	0.139819	-0.004149
H	1.475594	0.206554	2.119660	0.148053	-0.003496
H	2.272114	-0.633103	0.777354	0.148437	0.000336
C	-0.000000	-1.960874	0.489492	-0.381483	-0.018085
H	-0.777328	-2.697386	0.281050	0.161344	-0.001841
H	0.860716	-2.193047	-0.139232	0.131275	-0.003494
H	0.296299	-2.061170	1.535328	0.138184	-0.003823
B	-0.000000	-0.000000	-1.947716	0.905586	0.982017
H	-0.000000	-0.000000	-3.132682	0.051828	-0.163903

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -411.819249

Electronic energy + zero-point energy: -411.627362

Electronic energy + thermal energy correction: -411.618050

Electronic energy + thermal enthalpy correction: -411.617106

Electronic energy + thermal free energy correction: -411.659489

Table S04. Cartesian coordinates, Mulliken and APT charges of all atoms at **pinacolborane** in the reaction of benzaldehyde with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	-0.337899	-1.087785	-1.186879	-0.381547	-0.835186
C	0.000000	-0.780864	0.186095	-0.019522	0.436288
C	-0.000000	0.780864	0.186095	-0.019522	0.436288
O	0.337899	1.087785	-1.186879	-0.381547	-0.835186
C	-1.380647	1.374530	0.441850	-0.422414	-0.045006
H	-1.687089	1.233661	1.479452	0.164125	0.006079
H	-1.345633	2.443162	0.229393	0.189480	0.007426
H	-2.128162	0.919816	-0.210074	0.154772	0.005046
C	-1.026734	-1.416559	1.103807	-0.619310	-0.023734
H	-0.948261	-2.502233	1.039899	0.170433	0.005374
H	-0.845168	-1.119551	2.139302	0.181065	0.006340
H	-2.039499	-1.129874	0.827052	0.164682	0.009009
C	1.026734	1.416559	1.103807	-0.619310	-0.023734
H	0.948261	2.502233	1.039899	0.170433	0.005374
H	0.845168	1.119551	2.139302	0.181065	0.006340
H	2.039499	1.129874	0.827052	0.164682	0.009009
C	1.380647	-1.374530	0.441850	-0.422414	-0.045006
H	1.345633	-2.443162	0.229393	0.189480	0.007426
H	2.128162	-0.919816	-0.210074	0.154772	0.005046
H	1.687089	-1.233661	1.479452	0.164125	0.006079
B	0.000000	-0.000000	-1.936329	0.751477	1.018482
H	0.000000	-0.000000	-3.119368	0.084995	-0.161751

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -411.870683

Electronic energy + zero-point energy: -411.679335

Electronic energy + thermal energy correction: -411.669999

Electronic energy + thermal enthalpy correction: -411.669055

Electronic energy + thermal free energy correction: -411.711535

Table S05. Cartesian coordinates, Mulliken and APT charges of all atoms at **pinacolborane** in the reaction of benzaldehyde with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	-0.996900	-0.551316	-1.191897	-0.498378	-0.830634
C	-0.551844	-0.556890	0.184431	0.193557	0.440071
C	0.551844	0.556890	0.184431	0.193557	0.440071
O	0.996900	0.551316	-1.191897	-0.498378	-0.830634
C	-0.000000	1.952031	0.462625	-0.470483	-0.028348
H	-0.306888	2.057573	1.504987	0.161055	0.000252
H	0.779731	2.686296	0.255350	0.187016	0.001434
H	-0.855410	2.176073	-0.177301	0.153283	-0.000217
C	-1.739295	-0.276399	1.087636	-0.685369	-0.008403
H	-2.451450	-1.100552	1.022725	0.163693	-0.000699
H	-1.414095	-0.187913	2.127347	0.177782	0.000577
H	-2.253944	0.639936	0.802425	0.165481	0.004157
C	1.739295	0.276399	1.087636	-0.685369	-0.008403
H	2.451450	1.100552	1.022725	0.163693	-0.000699
H	1.414095	0.187913	2.127347	0.177782	0.000577
H	2.253944	-0.639936	0.802425	0.165481	0.004157
C	0.000000	-1.952031	0.462625	-0.470483	-0.028348
H	-0.779731	-2.686296	0.255350	0.187016	0.001434
H	0.855410	-2.176073	-0.177301	0.153283	-0.000217
H	0.306888	-2.057573	1.504987	0.161055	0.000252
B	0.000000	0.000000	-1.938234	0.852038	1.010001
H	0.000000	0.000000	-3.125836	0.052689	-0.166381

Benzaldehyde

HF/6-31G(d), N,N-dimethylformamide solution

Electronic energy: -343.446899

Electronic energy + zero-point energy: -343.328662

Electronic energy + thermal energy correction: -343.322705

Electronic energy + thermal enthalpy correction: -343.321761

Electronic energy + thermal free energy correction: -343.359009

Table S06. Cartesian coordinates, Mulliken and APT charges of all atoms at **benzaldehyde** in the reaction of benzaldehyde with pinacolborane (HF/6-31G(d), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	2.204664	-0.236911	0.000000	-0.202670	0.117268
C	1.717763	1.060540	0.000000	-0.238783	-0.153257
C	0.348401	1.279624	-0.000000	-0.214636	0.056063
C	-0.530547	0.203632	-0.000000	-0.125327	-0.401558
C	-0.035210	-1.099246	-0.000000	-0.198191	0.038907
C	1.328976	-1.317967	-0.000000	-0.237409	-0.164467
H	3.266104	-0.410201	0.000000	0.243087	0.044990
H	2.397262	1.893561	0.000000	0.240630	0.048447
H	-0.037024	2.284354	-0.000000	0.253455	0.059111
H	-0.720460	-1.926607	-0.000001	0.250707	0.076617
H	1.714216	-2.321702	-0.000000	0.239970	0.044928
C	-1.988745	0.460742	-0.000000	0.341751	1.383621
O	-2.827552	-0.392081	0.000001	-0.547016	-1.082184
H	-2.271489	1.514760	-0.000002	0.194432	-0.068486

HF/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -343.542690

Electronic energy + zero-point energy: -343.425894

Electronic energy + thermal energy correction: -343.419896

Electronic energy + thermal enthalpy correction: -343.418952

Electronic energy + thermal free energy correction: -343.456271

Table S07. Cartesian coordinates, Mulliken and APT charges of all atoms at **benzaldehyde** in the reaction of benzaldehyde with pinacolborane (HF/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	0.548586	-2.144767	0.000000	-0.285954	0.103329
C	1.589057	-1.235633	0.000000	-0.166608	-0.172477
C	1.312318	0.121038	0.000000	-0.924962	0.035034
C	0.000000	0.564162	-0.000000	1.014672	-0.423379
C	-1.043888	-0.355139	-0.000000	-0.258479	0.034816
C	-0.769267	-1.705349	0.000000	-0.179017	-0.195222
H	0.758743	-3.198841	0.000000	0.217828	0.065697
H	2.607216	-1.578066	0.000000	0.223018	0.066783
H	2.116152	0.835296	0.000000	0.206076	0.080244
H	-2.059337	-0.006633	-0.000000	0.228462	0.090593
H	-1.572817	-2.418440	0.000000	0.219648	0.065861
C	-0.260078	2.020383	-0.000000	0.028686	1.444073
O	-1.343136	2.516496	-0.000000	-0.528303	-1.149799

H	0.634761	2.646548	-0.000000	0.204933	-0.045554

B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -345.690520

Electronic energy + zero-point energy: -345.581184

Electronic energy + thermal energy correction: -345.574844

Electronic energy + thermal enthalpy correction: -345.573900

Electronic energy + thermal free energy correction: -345.611792

Table S08. Cartesian coordinates, Mulliken and APT charges of all atoms at **benzaldehyde** in the reaction of benzaldehyde with pinacolborane (B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	0.545652	-2.159140	0.000000	-0.263156	0.056314
C	1.596066	-1.245444	0.000000	-0.094907	-0.137492
C	1.322960	0.117734	0.000000	-0.809087	0.043493
C	-0.000000	0.569521	-0.000000	0.947375	-0.458540
C	-1.052562	-0.354681	0.000000	-0.305123	0.036634
C	-0.778237	-1.713451	0.000000	-0.113633	-0.153039
H	0.755450	-3.222674	0.000000	0.184015	0.065027
H	2.621591	-1.595072	0.000000	0.191173	0.063869
H	2.132674	0.839961	-0.000000	0.170048	0.078321
H	-2.074933	0.003709	-0.000000	0.188595	0.089204
H	-1.590220	-2.431217	0.000000	0.187465	0.063370
C	-0.251026	2.021679	-0.000000	-0.006056	1.337098
O	-1.350454	2.542630	-0.000000	-0.444880	-1.023601
H	0.661943	2.646952	-0.000000	0.168172	-0.060657

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -345.539599

Electronic energy + zero-point energy: -345.429053

Electronic energy + thermal energy correction: -345.422736

Electronic energy + thermal enthalpy correction: -345.421792

Electronic energy + thermal free energy correction: -345.459659

Table S09. Cartesian coordinates, Mulliken and APT charges of all atoms at **benzaldehyde** in the reaction of benzaldehyde with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	0.563207	-2.147020	0.000000	-0.349683	0.032254
C	1.605471	-1.228093	0.000000	-0.083426	-0.137793
C	1.322566	0.131774	0.000000	-1.015393	0.003325
C	-0.000000	0.566772	-0.000000	0.955137	-0.412489
C	-1.045403	-0.357783	-0.000000	-0.227855	0.002760
C	-0.761879	-1.713013	0.000000	-0.123525	-0.156115
H	0.780888	-3.208391	0.000000	0.225777	0.078551
H	2.632707	-1.570498	0.000000	0.238128	0.076925
H	2.124636	0.862409	0.000000	0.204517	0.091192
H	-2.068775	-0.002039	-0.000000	0.226207	0.102079
H	-1.567776	-2.436588	0.000000	0.232323	0.077044
C	-0.270434	2.019598	-0.000000	-0.084139	1.289843
O	-1.376334	2.507420	-0.000000	-0.404622	-1.007847
H	0.627829	2.662340	-0.000000	0.206555	-0.039729

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -345.561749

Electronic energy + zero-point energy: -345.451341

Electronic energy + thermal energy correction: -345.445037

Electronic energy + thermal enthalpy correction: -345.444093

Electronic energy + thermal free energy correction: -345.481932

Table S10. Cartesian coordinates, Mulliken and APT charges of all atoms at **benzaldehyde** in the reaction of benzaldehyde with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	0.553414	-2.150363	-0.000000	-0.313592	0.050585
C	1.597927	-1.235506	-0.000000	-0.172966	-0.137596
C	1.320379	0.123922	-0.000000	-0.833902	0.022375
C	-0.000000	0.566570	-0.000000	0.972693	-0.441669
C	-1.046745	-0.356140	0.000000	-0.314508	0.020734
C	-0.768499	-1.711413	0.000000	-0.179737	-0.155158
H	0.767304	-3.213146	-0.000000	0.232306	0.068640
H	2.624751	-1.581257	-0.000000	0.239808	0.068231

H	2.127997	0.849097	-0.000000	0.216315	0.081870
H	-2.070633	-0.000676	0.000000	0.226379	0.093719
H	-1.578080	-2.431837	0.000000	0.236253	0.067702
C	-0.260948	2.019464	0.000000	-0.071731	1.332820
O	-1.361251	2.523116	0.000000	-0.434588	-1.017012
H	0.645497	2.653685	-0.000000	0.197272	-0.055242

KF

HF/6-31G(d), N,N-dimethylformamide solution

Electronic energy: -698.609250

Electronic energy + zero-point energy: -698.608471

Electronic energy + thermal energy correction: -698.605740

Electronic energy + thermal enthalpy correction: -698.604796

Electronic energy + thermal free energy correction: -698.630763

Table S11. Cartesian coordinates, Mulliken and APT charges of all atoms at **KF** in the reaction of benzaldehyde with pinacolborane (HF/6-31G(d), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
F	0.000000	0.000000	-1.565290	-0.864290	-0.981443
K	0.000000	0.000000	0.741453	0.864290	0.981443

HF/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -698.707381

Electronic energy + zero-point energy: -698.706774

Electronic energy + thermal energy correction: -698.703949

Electronic energy + thermal enthalpy correction: -698.703005

Electronic energy + thermal free energy correction: -698.729241

Table S12. Cartesian coordinates, Mulliken and APT charges of all atoms at **KF** in the reaction of benzaldehyde with pinacolborane (HF/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
F	0.000000	0.000000	-1.625556	-0.947677	-1.014530
K	0.000000	0.000000	0.770000	0.947677	1.014530

B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -699.910213

Electronic energy + zero-point energy: -699.909569

Electronic energy + thermal energy correction: -699.906766

Electronic energy + thermal enthalpy correction: -699.905822

Electronic energy + thermal free energy correction: -699.931975

Table S13. Cartesian coordinates, Mulliken and APT charges of all atoms at **KF** in the reaction of benzaldehyde with pinacolborane (B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
F	0.000000	0.000000	-1.595511	-0.912297	-1.011445
K	0.000000	0.000000	0.755768	0.912297	1.011445

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -699.849787

Electronic energy + zero-point energy: -699.849093

Electronic energy + thermal energy correction: -699.846318

Electronic energy + thermal enthalpy correction: -699.845374

Electronic energy + thermal free energy correction: -699.871455

Table S14. Cartesian coordinates, Mulliken and APT charges of all atoms at **KF** in the reaction of benzaldehyde with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
F	0.000000	0.000000	-1.585305	-0.922403	-1.011979
K	0.000000	0.000000	0.750934	0.922403	1.011979

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -699.869640

Electronic energy + zero-point energy: -699.868980

Electronic energy + thermal energy correction: -699.866186

Electronic energy + thermal enthalpy correction: -699.865242

Electronic energy + thermal free energy correction: -699.891376

Table S15. Cartesian coordinates, Mulliken and APT charges of all atoms at **KF** in the reaction of benzaldehyde with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
F	0.000000	0.000000	-1.596236	-0.922586	-1.014469
K	0.000000	0.000000	0.756112	0.922586	1.014469

Fluoropinacolborane

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -511.151085

Electronic energy + zero-point energy: -510.965974

Electronic energy + thermal energy correction: -510.955886

Electronic energy + thermal enthalpy correction: -510.954942

Electronic energy + thermal free energy correction: -510.999418

Table S16. Cartesian coordinates, Mulliken and APT charges of all atoms at **fluoropinacolborane** in the reaction of benzaldehyde with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	0.350330	1.092764	0.858371	-0.629183	-1.141084
C	0.458375	0.634663	-0.522283	0.003731	0.633273
C	-0.458375	-0.634663	-0.522283	0.003731	0.633273
O	-0.350330	-1.092764	0.858371	-0.629183	-1.141084
C	-1.924167	-0.305361	-0.761165	-0.427737	-0.065462
H	-2.090548	-0.001758	-1.795659	0.193180	0.022870
H	-2.522352	-1.195478	-0.561074	0.203066	0.006585
H	-2.264611	0.496151	-0.102086	0.173272	0.003055
C	0.000000	1.740280	-1.448708	-0.692380	-0.044016
H	0.703630	2.573024	-1.399590	0.187002	0.006441
H	-0.026790	1.375357	-2.477732	0.211651	0.024193
H	-0.990037	2.105456	-1.178927	0.185059	0.010683
C	-0.000000	-1.740280	-1.448708	-0.692380	-0.044016
H	-0.703630	-2.573024	-1.399590	0.187002	0.006441
H	0.026790	-1.375357	-2.477732	0.211651	0.024193

H	0.990037	-2.105456	-1.178927	0.185059	0.010683
C	1.924167	0.305361	-0.761165	-0.427737	-0.065462
H	2.522352	1.195478	-0.561074	0.203066	0.006585
H	2.264611	-0.496151	-0.102086	0.173272	0.003055
H	2.090548	0.001758	-1.795659	0.193180	0.022870
B	0.000000	0.000000	1.579866	1.599176	1.894395
F	0.000000	0.000000	2.909193	-0.414498	-0.807470

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -511.200545

Electronic energy + zero-point energy: -510.015919

Electronic energy + thermal energy correction: -511.005778

Electronic energy + thermal enthalpy correction: -511.004834

Electronic energy + thermal free energy correction: -511.049473

Table S17. Cartesian coordinates, Mulliken and APT charges of all atoms at **fluoropinacolborane** in the reaction of benzaldehyde with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	0.369580	1.086868	0.862381	-0.744752	-1.138549
C	0.462876	0.634872	-0.521551	0.218001	0.640915
C	-0.462876	-0.634872	-0.521551	0.218001	0.640915
O	-0.369580	-1.086868	0.862381	-0.744752	-1.138549
C	-1.927678	-0.309169	-0.778852	-0.484231	-0.040565
H	-2.084288	-0.014053	-1.817877	0.193913	0.014835
H	-2.528823	-1.198751	-0.580965	0.201328	-0.002910
H	-2.282512	0.495999	-0.131348	0.171211	-0.004947
C	-0.000000	1.750080	-1.435968	-0.764864	-0.021280
H	0.704258	2.583221	-1.386364	0.180192	-0.003268
H	-0.034345	1.395190	-2.468626	0.212735	0.015849
H	-0.988180	2.116997	-1.159274	0.187596	0.002762
C	0.000000	-1.750080	-1.435968	-0.764864	-0.021280
H	-0.704258	-2.583221	-1.386364	0.180192	-0.003268
H	0.034345	-1.395190	-2.468626	0.212735	0.015849
H	0.988180	-2.116997	-1.159274	0.187596	0.002762
C	1.927678	0.309169	-0.778852	-0.484231	-0.040564
H	2.528823	1.198751	-0.580965	0.201328	-0.002910
H	2.282512	-0.495999	-0.131348	0.171211	-0.004947
H	2.084288	0.014053	-1.817877	0.193913	0.014835
B	-0.000000	-0.000000	1.581000	1.695981	1.877712

F	-0.000000	-0.000000	2.913586	-0.438240	-0.803396

HF

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -600.503292

Electronic energy + zero-point energy: -600.501929

Electronic energy + thermal energy correction: -600.499407

Electronic energy + thermal enthalpy correction: -600.498463

Electronic energy + thermal free energy correction: -600.521259

Table S18. Cartesian coordinates, Mulliken and APT charges of all atoms at **HF** in the reaction of benzaldehyde with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
K	0.000000	0.000000	0.123772	0.871683	0.941936
H	0.000000	0.000000	-2.351670	-0.871683	-0.941936

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -600.521460

Electronic energy + zero-point energy: -600.519751

Electronic energy + thermal energy correction: -600.517297

Electronic energy + thermal enthalpy correction: -600.516353

Electronic energy + thermal free energy correction: -600.539094

Table SXX. Cartesian coordinates, Mulliken and APT charges of all atoms at **HF** in the reaction of benzaldehyde with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
K	0.000000	0.000000	0.126470	0.901816	0.953680
H	0.000000	0.000000	-2.402921	-0.901816	-0.953680

I1A

HF/6-31G(d), N,N-dimethylformamide solution

Electronic energy: -1107.925473

Electronic energy + zero-point energy: -1107.718856

Electronic energy + thermal energy correction: -1107.706181

Electronic energy + thermal enthalpy correction: -1107.705237

Electronic energy + thermal free energy correction: -1107.757729

Table S19. Cartesian coordinates, Mulliken and APT charges of all atoms at **I1A** in the reaction of benzaldehyde with pinacolborane (HF/6-31G(d), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	0.179996	-0.956098	0.546230	-0.669436	-1.294854
C	-0.776844	-0.633347	-0.493608	0.281588	0.657254
C	-1.576299	0.542271	0.163156	0.278431	0.672738
O	-1.422838	0.264712	1.569190	-0.616041	-1.249378
C	-0.952856	1.914434	-0.090619	-0.538735	0.036305
H	-1.149651	2.247047	-1.104474	0.177025	-0.028717
H	-1.402270	2.630169	0.589825	0.178963	-0.041309
H	0.119405	1.912620	0.061269	0.201253	0.041345
C	-0.018233	-0.270722	-1.762852	-0.560805	0.042676
H	0.470247	-1.156764	-2.159150	0.185017	-0.042427
H	-0.704920	0.088980	-2.522218	0.187903	-0.013942
H	0.731604	0.486147	-1.578463	0.211501	0.045048
C	-3.061869	0.577371	-0.162052	-0.503398	0.093061
H	-3.520984	1.419897	0.344099	0.182823	-0.037201
H	-3.217208	0.701482	-1.228526	0.182365	-0.025486
H	-3.568083	-0.323107	0.160249	0.185530	-0.033812
C	-1.610721	-1.892102	-0.720164	-0.505768	0.069195
H	-0.949387	-2.708869	-0.988058	0.187904	-0.037734
H	-2.155404	-2.180867	0.172074	0.182459	-0.036840
H	-2.320549	-1.752955	-1.527402	0.185548	-0.021671
B	-0.331278	-0.507958	1.725040	0.623588	1.525548
H	0.153225	-0.768594	2.774899	-0.056389	-0.273069
F	2.422048	1.698920	-0.497852	-0.809202	-1.059315
K	2.910295	-0.486422	0.228149	0.827875	1.012585

HF/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1108.139234

Electronic energy + zero-point energy: -1107.936538

Electronic energy + thermal energy correction: -1107.923145

Electronic energy + thermal enthalpy correction: -1107.922201

Electronic energy + thermal free energy correction: -1107.978608

Table S20. Cartesian coordinates, Mulliken and APT charges of all atoms at **I1A** in the reaction of benzaldehyde with pinacolborane (HF/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	0.216711	-0.078341	0.459015	-0.830121	-1.317208
C	-0.930748	-0.651782	-0.211469	0.550707	0.673127
C	-1.996559	0.482495	-0.044896	0.691560	0.680356
O	-1.540840	1.153222	1.144116	-0.764282	-1.253415
C	-1.969592	1.513366	-1.168153	-0.560373	0.043600
H	-2.349693	1.097708	-2.093498	0.173749	-0.015178
H	-2.599183	2.350075	-0.888178	0.188651	-0.029072
H	-0.968551	1.890493	-1.343696	0.148370	-0.031817
C	-0.549204	-0.976263	-1.644408	-0.992179	0.053556
H	0.181486	-1.778490	-1.656855	0.171794	-0.036021
H	-1.418460	-1.316653	-2.195890	0.193033	-0.005518
H	-0.128293	-0.121586	-2.156055	0.200983	-0.019584
C	-3.418397	0.001072	0.179596	-0.937274	0.066934
H	-4.073964	0.857494	0.290679	0.166688	-0.028736
H	-3.761952	-0.577205	-0.671142	0.183835	-0.014665
H	-3.503692	-0.605946	1.070339	0.178736	-0.024852
C	-1.275617	-1.932999	0.538399	-0.551738	0.041621
H	-0.414118	-2.591372	0.525321	0.194782	-0.032260
H	-1.533856	-1.736385	1.572436	0.152364	-0.029118
H	-2.102483	-2.450650	0.067662	0.181547	-0.010782
B	-0.235933	0.878587	1.308757	1.229021	1.510368
H	0.459906	1.408467	2.106838	0.042280	-0.251738
F	4.387745	1.215557	-0.452702	-0.939863	-1.019510
K	2.912450	-0.577541	0.220163	0.927729	1.049914

<u>B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution</u>

Electronic energy: -1111.929160

Electronic energy + zero-point energy: -1111.738828

Electronic energy + thermal energy correction: -1111.724751

Electronic energy + thermal enthalpy correction: -1111.723807

Electronic energy + thermal free energy correction: -1111.781450

Table S21. Cartesian coordinates, Mulliken and APT charges of all atoms at **I1A** in the reaction of benzaldehyde with pinacolborane (B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	0.259095	-0.042203	0.423776	-0.665311	-1.174729
C	-0.933571	-0.670062	-0.194371	0.240829	0.622797
C	-2.011828	0.471248	-0.056380	0.323771	0.626082
O	-1.506435	1.250175	1.088756	-0.566794	-1.105288
C	-2.047530	1.428935	-1.245224	-0.446804	-0.029856
H	-2.466584	0.943766	-2.128343	0.168854	0.007895
H	-2.681627	2.281151	-0.993441	0.177223	-0.005509
H	-1.053934	1.806011	-1.494236	0.143611	-0.009001
C	-0.586820	-1.057088	-1.622786	-0.786977	-0.018328
H	0.158826	-1.855987	-1.622359	0.160945	-0.014492
H	-1.473530	-1.438166	-2.133914	0.187337	0.016493
H	-0.194752	-0.215453	-2.192738	0.183447	0.003699
C	-3.414277	-0.012064	0.275554	-0.743922	-0.003709
H	-4.083404	0.846287	0.364120	0.158276	-0.007966
H	-3.794300	-0.653907	-0.522219	0.178812	0.008142
H	-3.444101	-0.566574	1.212814	0.169188	-0.001130
C	-1.238734	-1.913131	0.636476	-0.439968	-0.032337
H	-0.368200	-2.572534	0.627471	0.184255	-0.009906
H	-1.467369	-1.663838	1.674015	0.148014	-0.007537
H	-2.082428	-2.463988	0.217628	0.176647	0.012349
B	-0.185527	0.977881	1.223196	1.016074	1.301140
H	0.535085	1.562496	1.962738	0.051763	-0.211895
F	4.386905	1.175628	-0.466343	-0.907110	-1.019202
K	2.907215	-0.559481	0.223668	0.887837	1.052289

<u>M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution</u>

Electronic energy: -1111.689986

Electronic energy + zero-point energy: -1111.497139

Electronic energy + thermal energy correction: -1111.483435

Electronic energy + thermal enthalpy correction: -1111.482490

Electronic energy + thermal free energy correction: -1111.539361

BSSE correction: 0.000821067965

Table S22. Cartesian coordinates, Mulliken and APT charges of all atoms at **I1A** in the reaction of benzaldehyde with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	0.191854	-0.203267	0.683952	-0.600160	-1.195723
C	-0.860958	-0.635108	-0.237210	0.160769	0.605474
C	-1.913839	0.503720	-0.077234	0.133993	0.619334
O	-1.672551	0.960438	1.285409	-0.429681	-1.125065
C	-1.647874	1.691620	-0.990642	-0.485503	-0.064602
H	-1.861890	1.439460	-2.030311	0.192160	0.020991
H	-2.298995	2.515021	-0.693870	0.205216	0.007920
H	-0.611201	2.026901	-0.916455	0.166640	0.002222
C	-0.276681	-0.764420	-1.629081	-0.847448	-0.058022
H	0.405355	-1.617360	-1.671405	0.188129	-0.005453
H	-1.075692	-0.952209	-2.349329	0.227080	0.036487
H	0.253548	0.138661	-1.932657	0.194448	0.010950
C	-3.352089	0.046760	-0.201337	-0.748649	-0.040539
H	-4.017052	0.905195	-0.093523	0.190785	0.007498
H	-3.518824	-0.393531	-1.186897	0.209529	0.021063
H	-3.607789	-0.688684	0.560259	0.183679	0.009795
C	-1.350778	-1.983434	0.267514	-0.483861	-0.066526
H	-0.507329	-2.675171	0.304075	0.211848	0.005588
H	-1.776633	-1.902371	1.269329	0.170632	0.006967
H	-2.105547	-2.396322	-0.403192	0.200266	0.025361
B	-0.399182	0.622805	1.605595	0.878431	1.347749
H	0.161753	0.997311	2.578157	0.091269	-0.204607
F	4.220744	1.202029	-0.447115	-0.913762	-1.021202
K	2.780442	-0.554810	0.211313	0.904193	1.054340

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1111.761722

Electronic energy + zero-point energy: -1111.569548

Electronic energy + thermal energy correction: -1111.555720

Electronic energy + thermal enthalpy correction: -1111.554776

Electronic energy + thermal free energy correction: -1111.612072

BSSE correction: 0.000745966073

Table S23. Cartesian coordinates, Mulliken and APT charges of all atoms at **I1A** in the reaction of benzaldehyde with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	0.205637	-0.157857	0.639349	-0.683184	-1.192847
C	-0.878747	-0.646651	-0.214144	0.317190	0.617099
C	-1.938644	0.496781	-0.077429	0.365653	0.627249
O	-1.628277	1.057317	1.231878	-0.551401	-1.123473
C	-1.747368	1.618747	-1.089459	-0.548074	-0.041194
H	-2.018831	1.289001	-2.093889	0.194586	0.013430
H	-2.394397	2.454689	-0.816962	0.203974	-0.000512
H	-0.715165	1.975679	-1.106163	0.170208	-0.006589
C	-0.344558	-0.850068	-1.618152	-0.918362	-0.033192
H	0.349834	-1.694224	-1.637447	0.190063	-0.014034
H	-1.166494	-1.090765	-2.295896	0.226802	0.026580
H	0.162698	0.038082	-1.996154	0.209646	0.003392
C	-3.377175	0.020903	-0.081907	-0.821959	-0.017646
H	-4.047167	0.878586	0.006252	0.186009	-0.002357
H	-3.599077	-0.488444	-1.022661	0.210379	0.013117
H	-3.581208	-0.662560	0.742104	0.186787	0.003270
C	-1.330796	-1.973213	0.379079	-0.541553	-0.043117
H	-0.479024	-2.655888	0.415366	0.212700	-0.003157
H	-1.717392	-1.851810	1.393068	0.172155	-0.002385
H	-2.106566	-2.429211	-0.238403	0.203315	0.016838
B	-0.344662	0.735121	1.518410	0.973525	1.339130
H	0.261501	1.178177	2.439408	0.054721	-0.213024
F	4.254739	1.220928	-0.443499	-0.916889	-1.018326
K	2.819305	-0.568419	0.202794	0.903709	1.051748

I2A

HF/6-31G(d), N,N-dimethylformamide solution

Electronic energy: -1107.960496

Electronic energy + zero-point energy: -1107.754501

Electronic energy + thermal energy correction: -1107.742503

Electronic energy + thermal enthalpy correction: -1107.741559

Electronic energy + thermal free energy correction: -1107.792520

Table S24. Cartesian coordinates, Mulliken and APT charges of all atoms at **I2A** in the reaction of benzaldehyde with pinacolborane (HF/6-31G(d), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	0.467773	0.190085	-0.706956	-0.791740	-1.345993
C	-0.592122	0.807944	-0.000593	0.318350	0.674124
C	-1.661993	-0.330570	0.046804	0.331923	0.705882
O	-0.874051	-1.492183	0.127014	-0.724979	-1.291641
C	-2.600816	-0.281746	1.249244	-0.505254	0.108185
H	-3.166470	0.645238	1.275684	0.162728	-0.051928
H	-3.309851	-1.102139	1.189325	0.165757	-0.058526
H	-2.059852	-0.382664	2.181891	0.172565	-0.050467
C	-0.092352	1.203749	1.395124	-0.533682	0.059379
H	0.755388	1.878746	1.295647	0.159800	-0.083214
H	-0.849393	1.730116	1.966432	0.175506	-0.037081
H	0.225055	0.338326	1.965768	0.183301	-0.035422
C	-2.501816	-0.401101	-1.235130	-0.508954	0.077836
H	-3.070661	-1.325748	-1.226523	0.164324	-0.061598
H	-3.202917	0.423577	-1.315632	0.159561	-0.054071
H	-1.875701	-0.405446	-2.120665	0.170076	-0.047366
C	-1.017628	2.068438	-0.747180	-0.505413	0.110046
H	-0.214775	2.799977	-0.720673	0.169028	-0.060175
H	-1.239705	1.860599	-1.786140	0.176272	-0.045787
H	-1.892893	2.521121	-0.290390	0.166813	-0.045692
B	0.391311	-1.257447	-0.504256	0.883373	2.011618
H	0.579726	-1.874020	-1.558550	-0.322109	-0.529857
F	1.479742	-1.658970	0.379350	-0.532633	-0.973232
K	3.057811	0.322462	-0.071532	0.865385	1.024979

HF/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1108.147067

Electronic energy + zero-point energy: -1107.944035

Electronic energy + thermal energy correction: -1107.931921

Electronic energy + thermal enthalpy correction: -1107.930977

Electronic energy + thermal free energy correction: -1107.982302

Table S25. Cartesian coordinates, Mulliken and APT charges of all atoms at **I2A** in the reaction of benzaldehyde with pinacolborane (HF/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	0.472190	0.176374	-0.697916	-0.925774	-1.372367

C	-0.589107	0.807228	-0.005801	0.470013	0.688974
C	-1.662689	-0.325834	0.052225	0.943896	0.709940
O	-0.877216	-1.488337	0.135638	-0.972712	-1.312569
C	-2.594471	-0.264202	1.255148	-0.943207	0.081128
H	-3.154108	0.666169	1.273367	0.162283	-0.038752
H	-3.308272	-1.080402	1.202066	0.147829	-0.049633
H	-2.051900	-0.359445	2.186629	0.166349	-0.040930
C	-0.093918	1.222054	1.382749	-0.626519	0.033069
H	0.752401	1.896272	1.274960	0.150118	-0.072239
H	-0.853876	1.757657	1.940299	0.180948	-0.027540
H	0.219556	0.366457	1.969130	0.183752	-0.031463
C	-2.506969	-0.401444	-1.223295	-0.553476	0.050860
H	-3.087137	-1.318248	-1.200478	0.167275	-0.051517
H	-3.197833	0.430814	-1.306667	0.157060	-0.040832
H	-1.886283	-0.422149	-2.111744	0.139806	-0.041075
C	-1.007016	2.055745	-0.770238	-0.905443	0.080862
H	-0.200792	2.782921	-0.751952	0.147757	-0.052059
H	-1.230503	1.834777	-1.805412	0.169366	-0.036464
H	-1.879697	2.517403	-0.318398	0.170423	-0.033995
B	0.380213	-1.263754	-0.505425	1.561283	2.017576
H	0.559891	-1.883583	-1.557901	-0.231778	-0.483398
F	1.470063	-1.683427	0.369910	-0.707002	-1.017915
K	3.060639	0.327126	-0.065393	0.947752	1.040340

B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1111.934495

Electronic energy + zero-point energy: -1111.743952

Electronic energy + thermal energy correction: -1111.731080

Electronic energy + thermal enthalpy correction: -1111.730136

Electronic energy + thermal free energy correction: -1111.782682

Table S26. Cartesian coordinates, Mulliken and APT charges of all atoms at **I2A** in the reaction of benzaldehyde with pinacolborane (B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	0.484890	0.185130	-0.738357	-0.775470	-1.265604
C	-0.588573	0.813969	-0.002129	0.107820	0.633348
C	-1.665086	-0.332617	0.054650	0.624564	0.666322
O	-0.863448	-1.520815	0.102795	-0.793563	-1.215486
C	-2.569686	-0.294075	1.283208	-0.719582	0.016005

H	-3.139025	0.638337	1.325715	0.160908	-0.017546
H	-3.284812	-1.119611	1.236870	0.141001	-0.028770
H	-1.999558	-0.395907	2.206749	0.160720	-0.018691
C	-0.073119	1.212103	1.388556	-0.491780	-0.032849
H	0.767084	1.906034	1.279953	0.140869	-0.050307
H	-0.836229	1.735078	1.969061	0.173455	-0.009362
H	0.257606	0.344669	1.961979	0.174240	-0.009109
C	-2.534627	-0.386768	-1.210043	-0.446090	-0.014328
H	-3.118603	-1.310152	-1.192503	0.157890	-0.028272
H	-3.232169	0.452375	-1.265895	0.151723	-0.022859
H	-1.924569	-0.390277	-2.115278	0.142249	-0.018085
C	-1.024805	2.069172	-0.751027	-0.750051	0.016884
H	-0.217056	2.806188	-0.741978	0.137128	-0.031573
H	-1.270604	1.852411	-1.790356	0.162512	-0.014136
H	-1.896463	2.526348	-0.275269	0.167966	-0.012060
B	0.401063	-1.268056	-0.537871	1.321440	1.845757
H	0.616926	-1.889115	-1.575846	-0.225849	-0.439575
F	1.518366	-1.681749	0.374702	-0.629980	-0.989505
K	3.019511	0.342865	-0.063209	0.907879	1.039803

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1111.711379

Electronic energy + zero-point energy: -1111.518145

Electronic energy + thermal energy correction: -1111.505620

Electronic energy + thermal enthalpy correction: -1111.504675

Electronic energy + thermal free energy correction: -1111.556667

BSSE correction: 0.002685831003

Table S27. Cartesian coordinates, Mulliken and APT charges of all atoms at **I2A** in the reaction of benzaldehyde with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	0.466319	0.147624	-0.793051	-0.675561	-1.262944
C	-0.554596	0.792205	-0.023281	-0.190165	0.622635
C	-1.639815	-0.321425	0.072507	0.422610	0.657642
O	-0.862878	-1.508059	0.165348	-0.648849	-1.217754
C	-2.543452	-0.209500	1.289218	-0.716228	-0.023734
H	-3.059643	0.754077	1.302765	0.192557	-0.001587
H	-3.298681	-0.998105	1.257612	0.172790	-0.013799

H	-1.976528	-0.317899	2.213792	0.174401	-0.006449
C	0.010974	1.159245	1.349976	-0.468387	-0.077416
H	0.848976	1.852926	1.226550	0.157695	-0.042943
H	-0.728578	1.674016	1.966102	0.205737	0.012716
H	0.350271	0.269912	1.885589	0.189568	0.007354
C	-2.492506	-0.392687	-1.194978	-0.463127	-0.055688
H	-3.088030	-1.307191	-1.161299	0.186737	-0.013605
H	-3.172938	0.457694	-1.277167	0.176119	-0.006874
H	-1.862304	-0.425241	-2.086194	0.159792	-0.003345
C	-1.003758	2.052519	-0.741934	-0.718099	-0.025693
H	-0.196181	2.788663	-0.738945	0.170138	-0.015800
H	-1.270214	1.841979	-1.777215	0.173564	-0.000998
H	-1.867196	2.496017	-0.239285	0.200924	0.002935
B	0.382938	-1.299177	-0.531477	1.112953	1.834503
H	0.544940	-1.954742	-1.553695	-0.145855	-0.424767
F	1.503093	-1.670731	0.356593	-0.588034	-0.978591
K	2.939208	0.357985	-0.055684	0.918721	1.034201

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1111.773658

Electronic energy + zero-point energy: -1111.581200

Electronic energy + thermal energy correction: -1111.568572

Electronic energy + thermal enthalpy correction: -1111.567628

Electronic energy + thermal free energy correction: -1111.619728

BSSE correction: 0.002336229611

Table S28. Cartesian coordinates, Mulliken and APT charges of all atoms at **I2A** in the reaction of benzaldehyde with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	0.471742	0.163392	-0.760869	-0.769149	-1.276737
C	-0.568888	0.798455	-0.012099	0.106568	0.631499
C	-1.652919	-0.325961	0.061338	0.623595	0.662915
O	-0.874073	-1.512582	0.126664	-0.770329	-1.225827
C	-2.554552	-0.245844	1.283664	-0.781617	0.002317
H	-3.082226	0.711612	1.316210	0.190157	-0.011158
H	-3.303029	-1.041552	1.242048	0.164978	-0.023828
H	-1.987074	-0.363643	2.207520	0.177627	-0.012626
C	-0.032898	1.182202	1.369971	-0.573058	-0.050676

H	0.804699	1.878711	1.256896	0.156463	-0.046674
H	-0.788405	1.699329	1.965449	0.202078	0.000820
H	0.303821	0.305268	1.926765	0.198441	-0.003040
C	-2.517200	-0.378108	-1.201216	-0.531412	-0.026247
H	-3.113060	-1.293820	-1.178953	0.183371	-0.023681
H	-3.201463	0.471803	-1.263239	0.174304	-0.016535
H	-1.900666	-0.395218	-2.102822	0.161966	-0.013620
C	-1.010234	2.056525	-0.742431	-0.772904	0.002632
H	-0.204518	2.795791	-0.730761	0.164028	-0.026075
H	-1.263229	1.846885	-1.781954	0.178068	-0.009374
H	-1.881356	2.501488	-0.253450	0.198720	-0.006162
B	0.381422	-1.282716	-0.534386	1.211912	1.867411
H	0.576034	-1.921991	-1.570292	-0.192503	-0.438706
F	1.499532	-1.685234	0.371505	-0.616210	-0.995861
K	2.993493	0.350311	-0.062460	0.914906	1.039234

I3A

HF/6-31G(d), N,N-dimethylformamide solution

Electronic energy: -1451.420375

Electronic energy + zero-point energy: -1451.095331

Electronic energy + thermal energy correction: -1451.075092

Electronic energy + thermal enthalpy correction: -1451.074148

Electronic energy + thermal free energy correction: -1451.149823

Table S29. Cartesian coordinates, Mulliken and APT charges of all atoms at **I3A** in the reaction of benzaldehyde with pinacolborane (HF/6-31G(d), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	1.272985	-0.145908	0.070486	-0.787501	-1.359113
C	2.220688	0.436462	-0.803384	0.319177	0.679145
C	3.188150	1.153601	0.192822	0.330959	0.703143
O	3.167420	0.300769	1.309740	-0.726339	-1.294840
C	4.626284	1.298355	-0.297660	-0.505371	0.109325
H	4.677945	1.877583	-1.215209	0.162255	-0.052466
H	5.216109	1.814066	0.454411	0.165258	-0.060313
H	5.087140	0.334056	-0.472025	0.172366	-0.050706
C	2.914395	-0.679825	-1.595480	-0.531751	0.061792
H	2.166827	-1.247430	-2.145586	0.161435	-0.081205
H	3.616227	-0.288967	-2.324571	0.173662	-0.040672
H	3.446316	-1.361253	-0.941237	0.182050	-0.036427

C	2.670679	2.532340	0.623697	-0.509368	0.078393
H	3.266962	2.880462	1.461514	0.163922	-0.062006
H	2.745303	3.268529	-0.170453	0.159093	-0.054521
H	1.637420	2.484561	0.949627	0.169639	-0.048180
C	1.495242	1.356388	-1.780701	-0.506616	0.106542
H	0.853132	0.768320	-2.430569	0.169513	-0.060096
H	0.871202	2.074497	-1.263969	0.175498	-0.046722
H	2.196580	1.897237	-2.409500	0.166138	-0.046841
B	1.902152	-0.374522	1.371632	0.888906	2.021196
H	1.163227	-0.024675	2.300157	-0.326878	-0.534108
F	2.101939	-1.804191	1.551733	-0.529227	-0.972638
K	0.278148	-2.650274	-0.105471	0.821785	1.081772
C	-4.334728	2.400365	0.292476	-0.194517	0.159747
C	-5.355008	1.476858	0.128852	-0.241061	-0.182413
C	-5.043725	0.138912	-0.055436	-0.204124	0.089626
C	-3.715520	-0.271965	-0.075592	-0.133052	-0.477238
C	-2.692154	0.661950	0.089613	-0.202793	0.067161
C	-3.003780	1.994735	0.273141	-0.242950	-0.201958
H	-4.572554	3.439292	0.435716	0.246848	0.048284
H	-6.381370	1.795236	0.144753	0.243519	0.050543
H	-5.828461	-0.586072	-0.183167	0.258852	0.064979
H	-1.665775	0.345158	0.073111	0.269173	0.086805
H	-2.219442	2.718603	0.401210	0.245586	0.051063
C	-3.420768	-1.701434	-0.273469	0.373860	1.508242
O	-2.315306	-2.174615	-0.305252	-0.598231	-1.260245
H	-4.289143	-2.346088	-0.397105	0.220286	-0.045050

HF/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1451.699938

Electronic energy + zero-point energy: -1451.379409

Electronic energy + thermal energy correction: -1451.358956

Electronic energy + thermal enthalpy correction: -1451.358011

Electronic energy + thermal free energy correction: -1451.435009

Table S30. Cartesian coordinates, Mulliken and APT charges of all atoms at **I3A** in the reaction of benzaldehyde with pinacolborane (HF/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	1.849842	0.123732	0.247120	-0.902258	-1.370334
C	2.772817	0.553567	-0.734212	0.493728	0.693316
C	4.061581	0.801112	0.112794	0.914804	0.708668

O	3.955812	-0.172034	1.120688	-0.975997	-1.317442
C	5.370995	0.603744	-0.639356	-0.957697	0.081522
H	5.446201	1.281074	-1.484805	0.162331	-0.039193
H	6.204717	0.808225	0.025279	0.150001	-0.050824
H	5.476538	-0.411273	-0.999561	0.165515	-0.041235
C	2.951947	-0.563402	-1.766653	-0.611661	0.035603
H	1.988436	-0.796325	-2.212982	0.162084	-0.071846
H	3.611332	-0.266146	-2.574444	0.181137	-0.030640
H	3.349059	-1.465449	-1.316510	0.184045	-0.032307
C	4.074831	2.183804	0.771784	-0.538260	0.051759
H	4.884082	2.215376	1.494174	0.167641	-0.052000
H	4.236585	2.979007	0.051724	0.157169	-0.041946
H	3.149221	2.382679	1.299619	0.136411	-0.040721
C	2.214016	1.784096	-1.435772	-0.957666	0.078480
H	1.326928	1.512164	-1.999973	0.146613	-0.052878
H	1.933954	2.554048	-0.729200	0.170934	-0.037414
H	2.935453	2.199489	-2.132882	0.169580	-0.035499
B	2.574470	-0.453258	1.368891	1.614708	2.031466
H	2.139354	-0.052734	2.454790	-0.248756	-0.489439
F	2.353066	-1.892368	1.382977	-0.699606	-1.023830
K	0.095409	-1.912355	0.012456	0.881683	1.105514
C	-5.801088	2.001245	0.424991	-0.145194	0.140737
C	-6.468942	0.930373	-0.137734	-0.458551	-0.201098
C	-5.774494	-0.230595	-0.429282	-0.577846	0.069228
C	-4.418007	-0.315945	-0.158278	0.722406	-0.491069
C	-3.750045	0.765661	0.408268	0.047774	0.062251
C	-4.441218	1.920636	0.698826	-0.335629	-0.227118
H	-6.336833	2.904540	0.653502	0.225906	0.068069
H	-7.520090	0.997361	-0.347640	0.223507	0.070335
H	-6.283900	-1.070113	-0.867172	0.226024	0.081567
H	-2.699292	0.695447	0.617181	0.233103	0.087903
H	-3.931175	2.758300	1.136891	0.231983	0.068324
C	-3.713219	-1.566724	-0.482907	0.021277	1.545124
O	-2.545195	-1.757609	-0.301931	-0.636265	-1.309086
H	-4.332013	-2.351460	-0.917745	0.255022	-0.023950

B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1457.635434

Electronic energy + zero-point energy: -1457.334791

Electronic energy + thermal energy correction: -1457.313234

Electronic energy + thermal enthalpy correction: -1457.312290

Electronic energy + thermal free energy correction: -1457.390785

Table S31. Cartesian coordinates, Mulliken and APT charges of all atoms at **I3A** in the reaction of benzaldehyde with pinacolborane (B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	1.813676	0.166707	0.274361	-0.756002	-1.265684
C	2.765288	0.552064	-0.740589	0.135177	0.639120
C	4.072293	0.785948	0.104125	0.587859	0.665526
O	3.942884	-0.173834	1.160794	-0.798475	-1.222547
C	5.372818	0.523119	-0.650124	-0.722097	0.017470
H	5.468096	1.184085	-1.515861	0.161215	-0.018301
H	6.223482	0.713330	0.009746	0.141529	-0.030586
H	5.438514	-0.509790	-0.992474	0.160081	-0.018422
C	2.911514	-0.595564	-1.750852	-0.490495	-0.029957
H	1.937043	-0.808491	-2.202392	0.156307	-0.049969
H	3.585646	-0.331946	-2.568930	0.173443	-0.012818
H	3.285973	-1.505114	-1.278567	0.176091	-0.008699
C	4.126522	2.189026	0.727088	-0.427768	-0.012949
H	4.946218	2.218791	1.449093	0.157963	-0.028829
H	4.307336	2.964895	-0.020769	0.151561	-0.024357
H	3.201979	2.427711	1.256061	0.138753	-0.018243
C	2.236730	1.787658	-1.462992	-0.787768	0.014577
H	1.330247	1.532462	-2.018844	0.136812	-0.032956
H	1.988832	2.586658	-0.764504	0.163884	-0.014639
H	2.969881	2.167202	-2.179763	0.166907	-0.013856
B	2.542905	-0.426059	1.402693	1.368691	1.863481
H	2.105741	-0.039325	2.485989	-0.239092	-0.446496
F	2.295269	-1.900655	1.413479	-0.625222	-0.996947
K	0.102168	-1.852498	0.014213	0.833253	1.115972
C	-5.807879	1.992982	0.437151	-0.096985	0.086094
C	-6.475623	0.910529	-0.129368	-0.374351	-0.160320
C	-5.772914	-0.248899	-0.431966	-0.389660	0.079464
C	-4.400513	-0.326905	-0.168539	0.550852	-0.522682
C	-3.734045	0.766803	0.401535	-0.093745	0.061782
C	-4.438035	1.921119	0.702365	-0.229947	-0.178173
H	-6.353984	2.898594	0.674780	0.193577	0.068462
H	-7.537769	0.972051	-0.333027	0.190222	0.068335
H	-6.279676	-1.100083	-0.873618	0.191735	0.080043
H	-2.671838	0.700739	0.603425	0.179627	0.085163
H	-3.927889	2.768799	1.143838	0.197746	0.066404
C	-3.696382	-1.566990	-0.502486	0.049602	1.431932
O	-2.502207	-1.766937	-0.328645	-0.536211	-1.202546

H	-4.324432	-2.359745	-0.943191	0.204932	-0.033848

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1457.262377

Electronic energy + zero-point energy: -1456.957642

Electronic energy + thermal energy correction: -1456.936658

Electronic energy + thermal enthalpy correction: -1456.935713

Electronic energy + thermal free energy correction: -1457.012677

BSSE correction: 0.003183255429

Table S32. Cartesian coordinates, Mulliken and APT charges of all atoms at **I3A** in the reaction of benzaldehyde with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	1.657287	0.168691	0.297986	-0.643490	-1.265037
C	2.587152	0.525958	-0.728540	-0.235844	0.627615
C	3.875884	0.835500	0.091603	0.421293	0.656669
O	3.807473	-0.109844	1.149638	-0.650723	-1.222983
C	5.169951	0.640585	-0.681156	-0.733455	-0.024080
H	5.187625	1.269836	-1.574972	0.191969	-0.002405
H	6.017982	0.921066	-0.052220	0.174700	-0.015201
H	5.297893	-0.399496	-0.980988	0.173844	-0.005456
C	2.779992	-0.665866	-1.668415	-0.431578	-0.076061
H	1.824122	-0.918054	-2.138439	0.166091	-0.041130
H	3.472837	-0.432130	-2.478988	0.207948	0.009781
H	3.160199	-1.535270	-1.127312	0.190104	0.005828
C	3.842893	2.243161	0.688841	-0.446434	-0.055326
H	4.656264	2.332726	1.411735	0.186583	-0.014370
H	3.974907	3.013471	-0.074141	0.176552	-0.007974
H	2.899413	2.422580	1.208555	0.149076	-0.003899
C	2.039851	1.705979	-1.513425	-0.755848	-0.026028
H	1.156163	1.397894	-2.077668	0.169452	-0.017330
H	1.753992	2.522245	-0.850718	0.172137	0.000126
H	2.783633	2.074453	-2.224837	0.200542	0.001701
B	2.417459	-0.390105	1.427424	1.191824	1.848721
H	1.993956	0.017522	2.504280	-0.170826	-0.430416
F	2.217113	-1.849650	1.453550	-0.577930	-0.983905
K	0.156773	-1.951334	-0.043078	0.840849	1.110390
C	-5.449024	2.086823	0.406480	-0.140200	0.062611

C	-6.195270	1.045108	-0.130992	-0.429079	-0.160172
C	-5.580653	-0.169090	-0.404412	-0.492064	0.039217
C	-4.222581	-0.334474	-0.139501	0.541608	-0.480643
C	-3.474347	0.713715	0.401020	-0.025246	0.030189
C	-4.089869	1.922703	0.672910	-0.187960	-0.182805
H	-5.926646	3.035317	0.621250	0.233913	0.082163
H	-7.250006	1.179687	-0.335028	0.232996	0.081765
H	-6.146496	-0.993865	-0.823971	0.225150	0.092521
H	-2.419469	0.571357	0.604247	0.126666	0.092768
H	-3.518301	2.741107	1.092437	0.243949	0.080399
C	-3.604841	-1.632091	-0.443811	-0.071353	1.392923
O	-2.431216	-1.891341	-0.266058	-0.464321	-1.186797
H	-4.281246	-2.395838	-0.859950	0.239106	-0.013368

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1457.350835

Electronic energy + zero-point energy: -1457.046605

Electronic energy + thermal energy correction: -1457.025704

Electronic energy + thermal enthalpy correction: -1457.024760

Electronic energy + thermal free energy correction: -1457.098851

BSSE correction: 0.003299791987

Table S33. Cartesian coordinates, Mulliken and APT charges of all atoms at **I3A** in the reaction of benzaldehyde with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	0.998091	-0.288982	0.103638	-0.781276	-1.339440
C	1.842483	0.386228	-0.829532	0.079193	0.641969
C	2.700470	1.295433	0.109082	0.494124	0.659326
O	2.841444	0.498004	1.276664	-0.777557	-1.233911
C	4.076650	1.637132	-0.439971	-0.832010	0.005323
H	3.994420	2.153337	-1.400702	0.186840	-0.011502
H	4.597787	2.300452	0.255444	0.169455	-0.024967
H	4.685619	0.742477	-0.575191	0.179467	-0.012211
C	2.688445	-0.647728	-1.576006	-0.522541	-0.047464
H	2.029160	-1.344647	-2.103456	0.170219	-0.042187
H	3.324074	-0.179333	-2.330937	0.203372	-0.005316
H	3.323113	-1.212626	-0.890288	0.192639	-0.002158
C	1.968327	2.586959	0.483717	-0.480537	-0.027314

H	2.518676	3.080668	1.288333	0.184028	-0.024203
H	1.902969	3.279114	-0.359503	0.196180	-0.014996
H	0.957275	2.378001	0.841151	0.053998	-0.012139
C	0.975610	1.140023	-1.825858	-0.850416	-0.004318
H	0.412508	0.431056	-2.439404	0.184112	-0.024023
H	0.261702	1.792573	-1.323077	0.130880	-0.011653
H	1.593602	1.746845	-2.493511	0.203309	-0.008479
B	1.682359	-0.347756	1.398918	1.583026	1.880976
H	0.913303	-0.084654	2.328834	-0.251061	-0.442531
F	2.107546	-1.749128	1.641829	-0.614221	-0.992133
K	0.374738	-2.837407	0.000673	0.867470	1.093088
C	-3.539980	2.450916	0.417688	-0.046990	0.086845
C	-4.677693	1.695072	0.165364	-0.538931	-0.169564
C	-4.555116	0.339217	-0.096590	-0.365539	0.056528
C	-3.295530	-0.259152	-0.103936	0.686954	-0.499192
C	-2.152505	0.503549	0.147374	-0.321192	-0.002613
C	-2.280678	1.856370	0.407039	-0.099599	-0.177363
H	-3.632779	3.511348	0.623336	0.246221	0.068948
H	-5.655284	2.161919	0.173166	0.239095	0.069776
H	-5.435341	-0.263192	-0.296123	0.239636	0.079412
H	-1.166588	0.049007	0.132276	-0.034238	0.197794
H	-1.397346	2.453700	0.601984	0.241171	0.069996
C	-3.213152	-1.698218	-0.379849	0.055863	1.412608
O	-2.186209	-2.349564	-0.392930	-0.508413	-1.163128
H	-4.177201	-2.194851	-0.586266	0.237268	-0.029783

TS1A

HF/6-31G(d), N,N-dimethylformamide solution

Electronic energy: -1451.374652

Electronic energy + zero-point energy: -1451.050509

Electronic energy + thermal energy correction: -1451.031537

Electronic energy + thermal enthalpy correction: -1451.030593

Electronic energy + thermal free energy correction: -1451.099739

Table S34. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS1A** in the reaction of benzaldehyde with pinacolborane (HF/6-31G(d), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	1.661187	0.667960	0.188461	-0.760006	-1.499099
C	2.821850	-0.160633	0.118024	0.310049	0.736434

C	2.198557	-1.576536	-0.128842	0.287599	0.724814
O	1.023920	-1.263873	-0.868463	-0.703303	-1.495347
C	3.058744	-2.522062	-0.957884	-0.502772	0.100100
H	4.009222	-2.712846	-0.469493	0.172841	-0.044405
H	2.545634	-3.471439	-1.073260	0.174938	-0.048325
H	3.250454	-2.126098	-1.946738	0.180214	-0.039245
C	3.668884	0.333751	-1.056659	-0.512569	0.058865
H	3.900570	1.383689	-0.906097	0.177962	-0.052365
H	4.605609	-0.207251	-1.134243	0.175281	-0.044765
H	3.138763	0.239241	-1.997918	0.180056	-0.038266
C	1.777484	-2.280315	1.163883	-0.512190	0.065344
H	1.173504	-3.144890	0.908733	0.175305	-0.048081
H	2.635147	-2.623866	1.731952	0.172323	-0.038669
H	1.183037	-1.634562	1.799891	0.179408	-0.041575
C	3.611378	-0.015412	1.412016	-0.506706	0.090917
H	3.999741	0.995335	1.491097	0.177874	-0.049082
H	2.994538	-0.203656	2.281217	0.183350	-0.038012
H	4.454775	-0.698479	1.430580	0.175654	-0.035586
B	0.622054	0.019265	-0.512007	1.137795	2.643118
H	-0.448045	-0.065845	0.402854	-0.366003	-1.169932
F	0.017775	0.782809	-1.496552	-0.452483	-0.937989
K	0.541990	3.134056	-0.047998	0.845349	1.030014
C	-4.888303	-1.228175	-0.586259	-0.233104	-0.055098
C	-4.065820	-1.985028	0.237692	-0.230567	-0.023439
C	-2.935662	-1.414724	0.800635	-0.241480	-0.066824
C	-2.613185	-0.085720	0.547629	-0.028564	-0.212933
C	-3.442034	0.667294	-0.272544	-0.239100	-0.075223
C	-4.573842	0.098554	-0.839167	-0.229696	-0.017693
H	-5.767228	-1.668593	-1.023116	0.229079	0.031526
H	-4.306797	-3.013507	0.441829	0.229680	0.031565
H	-2.299793	-2.005090	1.439031	0.232225	0.036959
H	-3.198733	1.696993	-0.456519	0.239148	0.072886
H	-5.210535	0.690398	-1.473495	0.228532	0.027116
C	-1.381131	0.542359	1.168265	0.267649	2.132052
O	-1.257011	1.800515	1.153022	-0.782033	-1.456259
H	-1.074206	0.004864	2.069780	0.168266	-0.253499

HF/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1451.655746

Electronic energy + zero-point energy: -1451.336186

Electronic energy + thermal energy correction: -1451.317037

Electronic energy + thermal enthalpy correction: -1451.316092

Electronic energy + thermal free energy correction: -1451.386302

Table S35. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS1A** in the reaction of benzaldehyde with pinacolborane (HF/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	1.653096	0.639763	0.207737	-1.080898	-1.518155
C	2.806173	-0.197587	0.156338	0.628669	0.753497
C	2.180108	-1.598119	-0.154497	0.658777	0.729913
O	1.034465	-1.251248	-0.920135	-1.057366	-1.522314
C	3.059180	-2.523661	-0.980470	-1.029424	0.074205
H	3.990032	-2.735520	-0.464327	0.175628	-0.034862
H	2.543879	-3.465174	-1.139556	0.156143	-0.041858
H	3.288372	-2.100843	-1.949339	0.173999	-0.031613
C	3.702478	0.319793	-0.967666	-0.473885	0.032069
H	3.942581	1.360279	-0.774428	0.178217	-0.045584
H	4.633584	-0.232640	-1.023780	0.178268	-0.036042
H	3.209469	0.261303	-1.931100	0.130932	-0.032136
C	1.713905	-2.336280	1.100005	-0.592029	0.043065
H	1.118205	-3.191385	0.799250	0.197134	-0.040939
H	2.552039	-2.698578	1.684465	0.179205	-0.029467
H	1.100872	-1.707480	1.734295	0.131289	-0.037368
C	3.547708	-0.100211	1.479557	-0.922329	0.063406
H	3.943402	0.902851	1.602163	0.164158	-0.042594
H	2.899155	-0.308873	2.319697	0.168849	-0.031124
H	4.382830	-0.792719	1.505128	0.181835	-0.026651
B	0.628733	0.023928	-0.537983	2.118510	2.667277
H	-0.470526	-0.086107	0.314530	-0.032944	-1.130902
F	0.088524	0.815663	-1.533666	-0.688654	-0.974702
K	0.639509	3.147508	-0.012243	0.936148	1.044474
C	-4.936836	-1.210234	-0.534148	-0.388824	-0.070451
C	-4.108718	-1.944802	0.298739	-0.221529	-0.045426
C	-2.965494	-1.367826	0.819989	-0.181949	-0.085885
C	-2.636161	-0.055203	0.515847	0.615262	-0.210185
C	-3.470449	0.676845	-0.311956	0.044690	-0.087100
C	-4.615276	0.101234	-0.837130	-0.334683	-0.049119
H	-5.827033	-1.655902	-0.939731	0.207800	0.055623
H	-4.355372	-2.962265	0.542917	0.220441	0.053884
H	-2.324653	-1.941543	1.466793	0.235810	0.056890
H	-3.222467	1.696190	-0.538202	0.276016	0.086857
H	-5.257100	0.677045	-1.479446	0.216913	0.050000
C	-1.391361	0.571657	1.103800	-0.639316	2.122646
O	-1.248880	1.819891	1.071205	-0.744225	-1.489090

H	-1.059301	0.037213	1.995303	0.213362	-0.220240

B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1457.611974

Electronic energy + zero-point energy: -1457.312454

Electronic energy + thermal energy correction: -1457.292226

Electronic energy + thermal enthalpy correction: -1457.291281

Electronic energy + thermal free energy correction: -1457.362939

Table S36. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS1A** in the reaction of benzaldehyde with pinacolborane (B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	1.678995	0.704324	0.146217	-0.865812	-1.427363
C	2.845612	-0.167573	0.133340	0.216585	0.711728
C	2.199554	-1.584806	-0.120348	0.357415	0.686327
O	1.030684	-1.256894	-0.917060	-0.819361	-1.409634
C	3.070870	-2.545938	-0.918221	-0.801597	0.003493
H	4.005775	-2.749514	-0.390475	0.172528	-0.013577
H	2.545624	-3.495327	-1.047369	0.147316	-0.020135
H	3.307471	-2.152450	-1.906459	0.165635	-0.007701
C	3.748391	0.295110	-1.012984	-0.371838	-0.045328
H	4.003160	1.346763	-0.861417	0.163547	-0.019974
H	4.679737	-0.274308	-1.043989	0.170104	-0.020689
H	3.252247	0.199949	-1.980471	0.133930	-0.008427
C	1.726197	-2.267495	1.166288	-0.464472	-0.027138
H	1.121968	-3.137811	0.900871	0.177614	-0.017953
H	2.568834	-2.612403	1.768960	0.171469	-0.007839
H	1.113768	-1.603368	1.778258	0.129215	-0.013041
C	3.579340	-0.025725	1.459805	-0.700136	-0.006938
H	3.986262	0.984545	1.550024	0.149378	-0.021526
H	2.919514	-0.202952	2.308740	0.162391	-0.008220
H	4.414996	-0.727638	1.515640	0.176863	-0.004500
B	0.636505	0.042127	-0.563717	1.833680	2.454592
H	-0.443236	0.007197	0.323093	-0.144204	-0.889996
F	0.050086	0.819074	-1.583811	-0.585689	-0.932997
K	0.541022	3.114143	-0.032350	0.871453	1.037967
C	-4.897490	-1.276982	-0.555337	-0.314615	-0.081953
C	-4.045903	-2.005701	0.273278	-0.211012	-0.035715
C	-2.915240	-1.400838	0.812913	-0.177900	-0.080726

C	-2.621892	-0.064843	0.532413	0.519743	-0.181946
C	-3.481350	0.660653	-0.292166	0.006355	-0.083513
C	-4.612303	0.057773	-0.835683	-0.243600	-0.042786
H	-5.779961	-1.745539	-0.975970	0.172485	0.051231
H	-4.265810	-3.042818	0.500573	0.183088	0.048126
H	-2.253443	-1.968794	1.459621	0.195663	0.054038
H	-3.257282	1.701069	-0.495456	0.215758	0.084675
H	-5.274871	0.629886	-1.475795	0.180571	0.044680
C	-1.396559	0.589254	1.136009	-0.511396	1.809485
O	-1.299003	1.863443	1.153788	-0.629351	-1.364253
H	-1.038238	0.028180	2.019740	0.168197	-0.212475

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1457.247559

Electronic energy + zero-point energy: -1456.943795

Electronic energy + thermal energy correction: -1456.924296

Electronic energy + thermal enthalpy correction: -1456.923352

Electronic energy + thermal free energy correction: -1456.991403

BSSE correction: 0.004669957205

Table S37. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS1A** in the reaction of benzaldehyde with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	1.087457	0.253538	0.402937	-0.697150	-1.296448
C	1.558974	-1.063542	0.752153	0.104802	0.672627
C	1.156709	-1.902280	-0.502846	-0.213126	0.632281
O	1.297548	-0.946891	-1.568517	-0.538900	-1.370721
C	2.064662	-3.085852	-0.779231	-0.783368	-0.026615
H	2.073529	-3.765728	0.076114	0.205271	0.002851
H	1.694560	-3.635877	-1.646953	0.183013	-0.006930
H	3.085538	-2.765320	-0.984650	0.180441	0.001963
C	3.070805	-0.977649	0.934973	-0.464329	-0.073640
H	3.293002	-0.232733	1.702566	0.185752	-0.011872
H	3.487530	-1.932964	1.259739	0.196630	0.000066
H	3.562236	-0.679186	0.006518	0.162187	0.005754
C	-0.297388	-2.360737	-0.446615	-0.293687	-0.071925
H	-0.589305	-2.726328	-1.433237	0.196578	-0.006755
H	-0.427697	-3.170690	0.274066	0.206684	0.007222

H	-0.959131	-1.538228	-0.170382	0.133360	0.022277
C	0.897000	-1.505078	2.042955	-0.713260	-0.044154
H	1.250077	-0.883834	2.869077	0.187500	-0.005629
H	-0.187416	-1.415152	1.982732	0.124573	0.009308
H	1.153923	-2.543625	2.265540	0.212016	0.011226
B	1.048731	0.320059	-1.017305	1.276015	2.380916
H	-0.233440	0.732456	-1.338679	0.396139	-0.878686
F	1.782008	1.383098	-1.560119	-0.529874	-1.004447
K	1.622496	2.797239	0.705160	0.908466	1.042735
C	-3.920490	-0.991629	0.784458	-0.402177	-0.081407
C	-3.889799	-0.845207	-0.599103	-0.307839	-0.053404
C	-3.000363	0.049338	-1.181159	-0.226523	-0.085975
C	-2.140287	0.802397	-0.387085	0.293693	-0.196585
C	-2.181212	0.663723	0.995899	0.064657	-0.091673
C	-3.067356	-0.233423	1.580691	-0.196505	-0.054645
H	-4.610536	-1.691260	1.240935	0.221813	0.068223
H	-4.557550	-1.429105	-1.221497	0.232348	0.065073
H	-2.962425	0.158540	-2.260878	0.217123	0.066437
H	-1.504016	1.256605	1.599169	0.223387	0.093399
H	-3.091706	-0.346381	2.658472	0.239426	0.060400
C	-1.133541	1.727658	-1.024605	-0.592967	1.756174
O	-0.626498	2.673191	-0.344637	-0.598725	-1.350025
H	-1.360663	1.908082	-2.090273	0.206557	-0.187393

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1457.332426

Electronic energy + zero-point energy: -1457.029140

Electronic energy + thermal energy correction: -1457.009536

Electronic energy + thermal enthalpy correction: -1457.008592

Electronic energy + thermal free energy correction: -1457.077324

BSSE correction: 0.004316895237

Table S38. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS1A** in the reaction of benzaldehyde with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	1.178092	0.305947	0.373691	-0.821216	-1.320745
C	1.647600	-0.999603	0.752322	0.268249	0.676470
C	1.206000	-1.882579	-0.466545	0.117286	0.639577

O	1.273491	-0.957654	-1.563813	-0.735385	-1.374347
C	2.130321	-3.052553	-0.755176	-0.822369	-0.000502
H	2.188640	-3.715247	0.112226	0.206935	-0.007755
H	1.740209	-3.630766	-1.596400	0.176221	-0.017101
H	3.136787	-2.718371	-1.007969	0.184293	-0.008254
C	3.164129	-0.915821	0.906038	-0.495145	-0.045393
H	3.403570	-0.145509	1.643549	0.190400	-0.020414
H	3.583208	-1.861303	1.257372	0.194445	-0.011249
H	3.646793	-0.650176	-0.037003	0.164665	-0.003849
C	-0.230011	-2.384072	-0.338086	-0.577091	-0.051225
H	-0.548110	-2.794266	-1.299289	0.189399	-0.015894
H	-0.308063	-3.173304	0.413079	0.198045	-0.000554
H	-0.911989	-1.578223	-0.066573	0.339674	0.015168
C	1.013245	-1.389416	2.075082	-0.787415	-0.021233
H	1.387011	-0.739631	2.870585	0.180574	-0.016206
H	-0.072464	-1.297505	2.040014	0.151288	0.002694
H	1.270596	-2.420015	2.333000	0.211899	0.002404
B	1.062374	0.327564	-1.043029	1.438458	2.427019
H	-0.223362	0.752110	-1.296878	0.428704	-0.890307
F	1.780043	1.368852	-1.663080	-0.560646	-1.026971
K	1.448841	2.889962	0.732257	0.899072	1.044717
C	-3.872196	-1.118890	0.795007	-0.371332	-0.069202
C	-3.822898	-1.012793	-0.589840	-0.346852	-0.041819
C	-2.971850	-0.090975	-1.183947	-0.249630	-0.075581
C	-2.168754	0.731812	-0.401685	0.561538	-0.211299
C	-2.229734	0.631363	0.983131	-0.106624	-0.080930
C	-3.075677	-0.292893	1.580283	-0.307450	-0.049911
H	-4.532113	-1.841622	1.261641	0.225484	0.057495
H	-4.445939	-1.651170	-1.206249	0.233803	0.054904
H	-2.920242	-0.016146	-2.266270	0.217430	0.056696
H	-1.600720	1.277324	1.584391	0.240598	0.080209
H	-3.112497	-0.373787	2.661138	0.238416	0.052392
C	-1.206390	1.694057	-1.054589	-0.637066	1.820944
O	-0.780457	2.700995	-0.410821	-0.625350	-1.362631
H	-1.413272	1.810716	-2.134804	0.186697	-0.207314

I4

HF/6-31G(d), N,N-dimethylformamide solution

Electronic energy: -1451.466834

Electronic energy + zero-point energy: -1451.137105

Electronic energy + thermal energy correction: -1451.118279

Electronic energy + thermal enthalpy correction: -1451.117335

Electronic energy + thermal free energy correction: -1451.186481

Table S39. Cartesian coordinates, Mulliken and APT charges of all atoms at **I4** in the reaction of benzaldehyde with pinacolborane (HF/6-31G(d), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	1.655284	0.830527	0.331591	-0.818290	-1.376792
C	2.917822	0.212502	0.454637	0.325176	0.709267
C	2.591654	-1.271074	0.076521	0.319248	0.714605
O	1.576152	-1.126316	-0.890064	-0.763664	-1.306347
C	3.753030	-2.047943	-0.536495	-0.504603	0.106636
H	4.595901	-2.106754	0.146207	0.162093	-0.051316
H	3.435152	-3.062148	-0.759967	0.164810	-0.059269
H	4.089824	-1.597580	-1.461879	0.171496	-0.049900
C	3.884705	0.877349	-0.532245	-0.513161	0.073829
H	3.902170	1.946076	-0.338930	0.166405	-0.064620
H	4.897961	0.502956	-0.426743	0.162187	-0.053855
H	3.569546	0.729658	-1.558417	0.173374	-0.037788
C	2.027165	-2.068722	1.258246	-0.511239	0.072503
H	1.634849	-3.010320	0.886076	0.162679	-0.062068
H	2.784351	-2.292536	2.003195	0.158676	-0.054872
H	1.214781	-1.537499	1.740045	0.173682	-0.036151
C	3.436882	0.420064	1.873980	-0.507823	0.105937
H	3.637887	1.474841	2.039349	0.168194	-0.060459
H	2.712853	0.102223	2.613684	0.174959	-0.047929
H	4.362304	-0.123491	2.040535	0.165295	-0.047811
B	0.869851	0.092419	-0.644371	1.161969	2.300331
H	-1.157606	-1.805695	-0.816577	0.162701	-0.137768
F	0.766653	0.871515	-1.859492	-0.532761	-0.950368
K	-0.195627	2.705541	0.000128	0.843994	1.048656
C	-5.405136	-0.326823	0.749666	-0.242459	-0.108592
C	-5.206559	-0.739760	-0.560974	-0.223512	0.009828
C	-3.922033	-0.859692	-1.066073	-0.258099	-0.097634
C	-2.812431	-0.574844	-0.273897	-0.035789	0.020593
C	-3.020383	-0.165485	1.038480	-0.250422	-0.129861
C	-4.307744	-0.040049	1.545319	-0.225076	0.025763
H	-6.401810	-0.229631	1.142579	0.227721	0.034252
H	-6.050884	-0.963112	-1.189460	0.229598	0.031448
H	-3.779645	-1.173915	-2.086445	0.228546	0.035015
H	-2.175838	0.053156	1.664931	0.240028	0.067476
H	-4.449758	0.279583	2.563112	0.229212	0.029138
C	-1.417484	-0.748870	-0.842083	0.032727	0.901082
O	-0.486581	-0.009131	-0.124951	-0.775203	-1.432021

H	-1.430017	-0.457396	-1.889532	0.157331	-0.120939

HF/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1451.745638

Electronic energy + zero-point energy: -1451.420061

Electronic energy + thermal energy correction: -1451.401123

Electronic energy + thermal enthalpy correction: -1451.400179

Electronic energy + thermal free energy correction: -1451.470834

Table S40. Cartesian coordinates, Mulliken and APT charges of all atoms at **I4** in the reaction of benzaldehyde with pinacolborane (HF/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	-1.614862	0.887084	0.483329	-1.282634	-1.382178
C	-2.637937	0.623791	-0.454951	0.762128	0.701369
C	-2.915308	-0.898637	-0.230914	0.662851	0.732376
O	-1.648833	-1.387162	0.130594	-1.223845	-1.339047
C	-3.895128	-1.155010	0.918716	-0.546300	0.044669
H	-4.911509	-0.882721	0.653803	0.158952	-0.045134
H	-3.882637	-2.214290	1.154776	0.167833	-0.053070
H	-3.616776	-0.610929	1.812622	0.136286	-0.032570
C	-3.819656	1.543368	-0.177629	-0.898044	0.077642
H	-3.532510	2.573984	-0.363999	0.147928	-0.052855
H	-4.658150	1.310859	-0.827101	0.173221	-0.037163
H	-4.149407	1.472187	0.850334	0.174894	-0.037616
C	-3.404957	-1.648006	-1.463270	-0.874061	0.079307
H	-3.584164	-2.687786	-1.207233	0.156514	-0.049865
H	-4.336906	-1.232297	-1.834477	0.171431	-0.038239
H	-2.674399	-1.625182	-2.261355	0.165773	-0.041787
C	-2.098245	0.922412	-1.856530	-0.739484	0.038832
H	-1.783199	1.961936	-1.904251	0.156052	-0.072333
H	-1.248693	0.294511	-2.097345	0.166090	-0.032738
H	-2.854311	0.785387	-2.621413	0.178181	-0.028174
B	-0.915516	-0.349262	0.795590	3.430447	2.377532
H	1.349350	-1.623073	1.566077	0.166444	-0.103256
F	-0.904359	-0.550550	2.208871	-0.827424	-0.981706
K	0.599385	2.357311	0.073153	0.944230	1.058094
C	5.288807	0.021489	-0.580876	-0.293751	-0.089173
C	4.534275	-0.732164	-1.460639	-0.309827	-0.030640
C	3.268998	-1.166127	-1.097020	-0.252297	-0.102101
C	2.742594	-0.855935	0.146972	0.502938	-0.034909

C	3.511545	-0.101746	1.025632	-0.004416	-0.103326
C	4.773107	0.336341	0.666187	-0.328183	-0.040459
H	6.270788	0.357800	-0.860373	0.214440	0.058198
H	4.927857	-0.984025	-2.428950	0.220835	0.054459
H	2.688898	-1.751442	-1.788366	0.223428	0.056589
H	3.122513	0.139113	1.999812	0.228604	0.057292
H	5.356125	0.916347	1.358778	0.220808	0.053293
C	1.347592	-1.288182	0.532789	-0.835685	0.925520
O	0.466765	-0.220990	0.364184	-1.252209	-1.491539
H	1.046934	-2.129062	-0.084679	0.137854	-0.095291

B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1457.677962

Electronic energy + zero-point energy: -1457.372933

Electronic energy + thermal energy correction: -1457.352818

Electronic energy + thermal enthalpy correction: -1457.351874

Electronic energy + thermal free energy correction: -1457.424187

Table S41. Cartesian coordinates, Mulliken and APT charges of all atoms at **I4** in the reaction of benzaldehyde with pinacolborane (B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	-1.623237	0.901233	0.504033	-1.048459	-1.300023
C	-2.652694	0.630299	-0.468150	0.390244	0.653966
C	-2.923890	-0.907724	-0.255459	0.331585	0.691525
O	-1.632780	-1.402642	0.118280	-0.998673	-1.258618
C	-3.916161	-1.176626	0.886752	-0.402293	-0.023347
H	-4.938135	-0.904656	0.611264	0.154341	-0.027830
H	-3.902238	-2.244788	1.117291	0.156280	-0.029879
H	-3.646332	-0.632208	1.792449	0.136988	-0.009531
C	-3.847510	1.537641	-0.190204	-0.738506	0.011060
H	-3.568003	2.581052	-0.361093	0.137151	-0.032713
H	-4.681484	1.304065	-0.857388	0.169061	-0.015737
H	-4.191189	1.446227	0.839980	0.166948	-0.014657
C	-3.393330	-1.649180	-1.504379	-0.695902	0.014511
H	-3.566029	-2.701255	-1.261971	0.144416	-0.029472
H	-4.332637	-1.235956	-1.881466	0.167550	-0.016566
H	-2.649905	-1.606396	-2.300617	0.158665	-0.019654
C	-2.097112	0.941512	-1.865172	-0.554710	-0.027514
H	-1.798268	1.993901	-1.910312	0.141715	-0.048908
H	-1.231245	0.319696	-2.098887	0.152262	-0.009927

H	-2.847403	0.793435	-2.644869	0.171626	-0.009013
B	-0.919993	-0.352906	0.814750	2.863017	2.259944
H	1.410634	-1.519045	1.706634	0.153324	-0.088815
F	-0.929429	-0.573278	2.252339	-0.745487	-0.958431
K	0.557924	2.333026	0.069076	0.903170	1.058188
C	5.302353	0.026712	-0.656456	-0.231604	-0.071311
C	4.529508	-0.790817	-1.476422	-0.242775	-0.048313
C	3.273774	-1.219032	-1.050963	-0.183134	-0.074165
C	2.775057	-0.842068	0.197198	0.381607	-0.024907
C	3.562024	-0.024421	1.014351	-0.024673	-0.086053
C	4.815458	0.409578	0.591897	-0.264777	-0.051428
H	6.280121	0.360063	-0.985138	0.177517	0.055075
H	4.903814	-1.096150	-2.447121	0.182824	0.051227
H	2.674329	-1.855282	-1.693739	0.183736	0.054146
H	3.192654	0.267273	1.992541	0.185920	0.054976
H	5.415661	1.039776	1.238607	0.184139	0.050277
C	1.395141	-1.262868	0.640848	-0.712021	0.813477
O	0.483497	-0.198087	0.404917	-1.082316	-1.412144
H	1.084400	-2.155301	0.085706	0.131242	-0.079417

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1457.326115

Electronic energy + zero-point energy: -1457.016683

Electronic energy + thermal energy correction: -1456.997368

Electronic energy + thermal enthalpy correction: -1456.996424

Electronic energy + thermal free energy correction: -1457.064124

BSSE correction: 0.005217745459

Table S42. Cartesian coordinates, Mulliken and APT charges of all atoms at **I4** in the reaction of benzaldehyde with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	1.276197	0.799380	0.398781	-0.817455	-1.306157
C	2.673470	0.829871	0.114799	0.054085	0.677458
C	3.005327	-0.689003	-0.025867	0.064058	0.679696
O	1.836171	-1.202877	-0.657089	-0.709353	-1.262933
C	4.219748	-0.983682	-0.889692	-0.693142	-0.026675
H	5.109775	-0.492615	-0.487417	0.196504	-0.003138
H	4.405966	-2.060063	-0.907656	0.174390	-0.016808

H	4.066261	-0.646956	-1.914888	0.171264	-0.005353
C	2.896111	1.586985	-1.193686	-0.448303	-0.065097
H	2.449321	2.579905	-1.105916	0.182630	-0.017381
H	3.959396	1.708978	-1.411458	0.188143	-0.005732
H	2.423699	1.066707	-2.028528	0.157368	0.006477
C	3.164745	-1.362057	1.337202	-0.466682	-0.061177
H	3.188335	-2.444066	1.191309	0.184598	-0.016332
H	4.090675	-1.061987	1.832900	0.183591	-0.009231
H	2.320356	-1.120800	1.985452	0.139422	0.008278
C	3.403661	1.532485	1.246195	-0.691734	-0.029782
H	3.141989	2.593336	1.252188	0.170337	-0.016518
H	3.134339	1.108274	2.213272	0.180142	-0.002928
H	4.485915	1.451974	1.115810	0.196917	-0.000870
B	0.722053	-0.385902	-0.250833	2.153143	2.169277
H	-0.924490	-2.257334	-0.809222	0.166303	-0.045415
F	-0.032907	0.023726	-1.434726	-0.686999	-0.954190
K	-1.241622	1.589619	0.328229	0.837790	1.026890
C	-4.767490	0.573836	-0.109350	-0.413752	-0.091681
C	-4.323685	0.105619	1.125088	-0.172836	-0.065481
C	-3.218703	-0.734863	1.192120	0.186097	-0.107400
C	-2.536556	-1.111849	0.032731	0.142208	-0.052726
C	-3.002617	-0.656926	-1.198762	-0.168267	-0.095465
C	-4.112312	0.181546	-1.271261	-0.144539	-0.052308
H	-5.623005	1.235967	-0.163722	0.228499	0.076721
H	-4.837655	0.397904	2.033021	0.241095	0.072570
H	-2.862864	-1.086292	2.155350	0.235969	0.077779
H	-2.475878	-0.938553	-2.103228	0.224553	0.081773
H	-4.458198	0.536299	-2.234799	0.241882	0.070745
C	-1.221572	-1.847838	0.160621	-1.022197	0.756081
O	-0.245671	-0.961697	0.675311	-0.648191	-1.321234
H	-1.331572	-2.680681	0.861034	0.182463	-0.071730

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1457.403786

Electronic energy + zero-point energy: -1457.095222

Electronic energy + thermal energy correction: -1457.075605

Electronic energy + thermal enthalpy correction: -1457.074660

Electronic energy + thermal free energy correction: -1457.144391

BSSE correction: 0.005855443950

Table S43. Cartesian coordinates, Mulliken and APT charges of all atoms at **I4** in the reaction of benzaldehyde with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	1.659917	0.196479	-1.088491	-1.013009	-1.304774
C	2.767265	0.485158	-0.238135	0.249360	0.656346
C	2.321159	-0.154636	1.119992	0.345700	0.661326
O	1.596960	-1.299209	0.698445	-0.925894	-1.243706
C	3.475584	-0.586096	2.011811	-0.778832	0.003296
H	4.118626	0.264509	2.255090	0.203407	-0.010777
H	3.087390	-0.993892	2.948986	0.163991	-0.024970
H	4.081369	-1.355959	1.532816	0.179467	-0.011517
C	4.014328	-0.184932	-0.815893	-0.505032	-0.030506
H	4.153420	0.156344	-1.844761	0.186328	-0.024221
H	4.911967	0.071312	-0.247962	0.180755	-0.016223
H	3.907563	-1.271171	-0.827587	0.162340	-0.003255
C	1.387558	0.757366	1.921470	-0.663160	-0.029106
H	0.963424	0.182750	2.748357	0.215216	-0.018163
H	1.913494	1.619707	2.338212	0.193293	-0.014706
H	0.555907	1.117894	1.312981	0.166484	-0.040642
C	2.985295	1.989683	-0.186865	-0.675519	-0.008049
H	3.276017	2.358035	-1.174321	0.181853	-0.020915
H	2.089015	2.526868	0.130411	0.155477	-0.032581
H	3.786468	2.239270	0.513915	0.210127	0.001014
B	1.005415	-1.018807	-0.590455	2.601900	2.277621
H	-0.898983	-1.804963	1.090586	0.162321	-0.057691
F	1.216208	-2.151024	-1.458918	-0.736940	-0.967476
K	-0.503639	1.670484	-1.455340	0.919465	1.069798
C	-4.950513	0.722696	0.552792	-0.385849	-0.085411
C	-4.927093	-0.387911	-0.278632	-0.353721	-0.043915
C	-3.762205	-1.137392	-0.409073	-0.238442	-0.085168
C	-2.614122	-0.790812	0.293757	0.596603	-0.016726
C	-2.649216	0.324164	1.132457	-0.040653	-0.108786
C	-3.806382	1.078483	1.260243	-0.312628	-0.048366
H	-5.856427	1.309812	0.652491	0.227775	0.060188
H	-5.815364	-0.670440	-0.832625	0.234106	0.057194
H	-3.744824	-1.999707	-1.067942	0.227599	0.060041
H	-1.758840	0.597765	1.690989	0.216342	0.066872
H	-3.820089	1.941718	1.916384	0.236616	0.057159
C	-1.320520	-1.543162	0.112092	-0.736159	0.788032
O	-0.428671	-0.714155	-0.587895	-1.015909	-1.419390
H	-1.506418	-2.476365	-0.434599	0.165222	-0.091846

P

HF/6-31G(d), N,N-dimethylformamide solution

Electronic energy: -752.807734

Electronic energy + zero-point energy: -752.479538

Electronic energy + thermal energy correction: -752.464063

Electronic energy + thermal enthalpy correction: -752.463119

Electronic energy + thermal free energy correction: -752.523971

Table S44. Cartesian coordinates, Mulliken and APT charges of all atoms at **P** in the reaction of benzaldehyde with pinacolborane (HF/6-31G(d), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	-1.743665	1.152308	0.757377	-0.649939	-1.287195
C	-2.762991	0.197889	0.431806	0.278291	0.684230
C	-1.943273	-0.918183	-0.303428	0.284110	0.695776
O	-0.852379	-0.168009	-0.858242	-0.660571	-1.277491
C	-1.335483	-1.948903	0.647342	-0.505771	0.064110
H	-2.093515	-2.599941	1.067584	0.179967	-0.026435
H	-0.629925	-2.560877	0.096056	0.182158	-0.039030
H	-0.799379	-1.474024	1.462041	0.178539	-0.038232
C	-3.451353	-0.242618	1.715322	-0.503848	0.093470
H	-3.977770	0.599942	2.151222	0.180137	-0.041081
H	-4.176854	-1.023908	1.513687	0.179391	-0.028492
H	-2.742741	-0.608097	2.446917	0.184462	-0.034515
C	-2.675341	-1.627160	-1.433055	-0.503870	0.090526
H	-2.020190	-2.366712	-1.881264	0.180478	-0.038592
H	-3.554169	-2.140941	-1.057503	0.180219	-0.027099
H	-2.981891	-0.938322	-2.209254	0.184599	-0.034022
C	-3.767624	0.907584	-0.475680	-0.505680	0.069245
H	-4.148956	1.781825	0.040706	0.181452	-0.041405
H	-3.306958	1.240653	-1.399670	0.177192	-0.039702
H	-4.606465	0.266513	-0.721733	0.179712	-0.029856
B	-0.715422	0.961648	-0.112415	0.878372	2.007458
H	1.088084	1.182008	-1.991116	0.193986	-0.063873
C	4.363977	-1.014319	0.720591	-0.235384	-0.064682
C	4.061260	-1.112663	-0.627901	-0.225452	-0.009097
C	3.097041	-0.285473	-1.187275	-0.251814	-0.081661
C	2.430474	0.652975	-0.409641	-0.032858	-0.034598
C	2.742409	0.747977	0.943662	-0.237219	-0.089493
C	3.699722	-0.081527	1.505275	-0.226445	-0.010053
H	5.106914	-1.657914	1.157445	0.230719	0.036850

H	4.566714	-1.835749	-1.243508	0.231877	0.035107
H	2.861137	-0.375438	-2.233686	0.232538	0.039948
H	2.235022	1.468998	1.558973	0.233914	0.056916
H	3.928928	0.001111	2.553159	0.231466	0.033677
C	1.416381	1.582292	-1.041395	-0.009784	0.928488
O	0.309250	1.833103	-0.202942	-0.617422	-1.399693
H	1.872279	2.546190	-1.231276	0.202478	-0.099505

HF/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -753.021740

Electronic energy + zero-point energy: -752.697547

Electronic energy + thermal energy correction: -752.682027

Electronic energy + thermal enthalpy correction: -752.681083

Electronic energy + thermal free energy correction: -752.741949

Table S45. Cartesian coordinates, Mulliken and APT charges of all atoms at **P** in the reaction of benzaldehyde with pinacolborane (HF/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	-1.720472	1.159166	0.707929	-0.946988	-1.302914
C	-2.816889	0.276721	0.437363	0.613993	0.697594
C	-2.104189	-0.920025	-0.282166	0.237687	0.713084
O	-0.962108	-0.277591	-0.867793	-0.889269	-1.293590
C	-1.573567	-1.976750	0.681316	-0.385948	0.039886
H	-2.380234	-2.545838	1.127907	0.189716	-0.017716
H	-0.938173	-2.662677	0.132475	0.191043	-0.033203
H	-0.982501	-1.534823	1.475521	0.160500	-0.032741
C	-3.501497	-0.073487	1.746590	-1.001139	0.067238
H	-3.953066	0.818300	2.167378	0.164663	-0.034840
H	-4.287943	-0.802513	1.583050	0.178071	-0.019119
H	-2.804895	-0.471218	2.471879	0.172202	-0.027512
C	-2.910050	-1.586865	-1.382540	-1.067897	0.065284
H	-2.327606	-2.389841	-1.820964	0.162242	-0.033073
H	-3.822118	-2.014769	-0.980469	0.184605	-0.018396
H	-3.170260	-0.892361	-2.169636	0.180244	-0.026199
C	-3.787335	1.033782	-0.464182	-0.384941	0.045026
H	-4.093987	1.943459	0.039814	0.182191	-0.034785
H	-3.327105	1.311247	-1.405982	0.133525	-0.034369
H	-4.674069	0.447464	-0.674021	0.176244	-0.020437
B	-0.728769	0.861032	-0.168482	2.676256	2.033082
H	1.075579	0.745649	-2.001565	0.210990	-0.041797

C	4.601489	-0.827781	0.801067	-0.374871	-0.104201
C	4.396235	-0.954460	-0.562128	-0.285156	-0.017390
C	3.357969	-0.275749	-1.173822	-0.479620	-0.114708
C	2.513646	0.542731	-0.436896	0.708860	-0.004390
C	2.725078	0.666083	0.927435	0.055445	-0.129121
C	3.761303	-0.017043	1.542443	-0.342588	-0.012414
H	5.404452	-1.358144	1.279819	0.205600	0.058956
H	5.039067	-1.586372	-1.147960	0.220926	0.055368
H	3.200850	-0.387088	-2.232365	0.214823	0.057718
H	2.081202	1.292987	1.514785	0.227572	0.077962
H	3.911180	0.086790	2.602012	0.217394	0.054211
C	1.424038	1.312399	-1.149004	-0.554430	0.859182
O	0.351120	1.649759	-0.304209	-1.117928	-1.393984
H	1.827781	2.246579	-1.519550	0.165983	-0.077691

B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -757.753329

Electronic energy + zero-point energy: -757.449510

Electronic energy + thermal energy correction: -757.432851

Electronic energy + thermal enthalpy correction: -757.431907

Electronic energy + thermal free energy correction: -757.495527

Table S46. Cartesian coordinates, Mulliken and APT charges of all atoms at **P** in the reaction of benzaldehyde with pinacolborane (B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	-1.722412	1.221022	0.643819	-0.735085	-1.196230
C	-2.854170	0.318221	0.423327	0.246999	0.661972
C	-2.158293	-0.943362	-0.224351	0.055843	0.674481
O	-0.975907	-0.353469	-0.861096	-0.684574	-1.180366
C	-1.647889	-1.950817	0.804905	-0.321709	-0.031456
H	-2.473750	-2.478408	1.285595	0.179412	0.002561
H	-1.022814	-2.689286	0.298507	0.171837	-0.010682
H	-1.046699	-1.470316	1.579315	0.156470	-0.010540
C	-3.533942	0.058530	1.758902	-0.767470	-0.005138
H	-3.970678	0.987066	2.133678	0.154966	-0.014196
H	-4.340637	-0.669026	1.643349	0.174403	0.002714
H	-2.833735	-0.314210	2.505902	0.163545	-0.006010
C	-2.977863	-1.652589	-1.291100	-0.819446	-0.006664
H	-2.410296	-2.497674	-1.687421	0.152745	-0.012394
H	-3.905385	-2.041725	-0.864848	0.178797	0.003304

H	-3.227012	-0.990989	-2.120292	0.171356	-0.005008
C	-3.814709	1.035499	-0.524967	-0.317751	-0.027729
H	-4.110512	1.986021	-0.075934	0.169216	-0.012688
H	-3.349942	1.245947	-1.490427	0.138240	-0.011870
H	-4.717476	0.446417	-0.696838	0.170254	-0.000165
B	-0.731364	0.837675	-0.224948	2.120446	1.870437
H	1.070207	0.511365	-2.033400	0.180571	-0.022761
C	4.677303	-0.741536	0.868947	-0.295075	-0.090658
C	4.488608	-0.963786	-0.493553	-0.221957	-0.029586
C	3.429828	-0.355211	-1.159963	-0.313911	-0.098745
C	2.548611	0.488441	-0.478854	0.545819	0.014488
C	2.743452	0.706753	0.885072	0.011873	-0.116205
C	3.800185	0.093327	1.555064	-0.294644	-0.021279
H	5.498307	-1.219164	1.391326	0.172087	0.055550
H	5.161513	-1.618235	-1.036251	0.183022	0.052839
H	3.282528	-0.539925	-2.219314	0.181449	0.056245
H	2.065328	1.354748	1.426607	0.187698	0.081172
H	3.937357	0.270090	2.616077	0.181856	0.051248
C	1.442179	1.173611	-1.249044	-0.500631	0.728356
O	0.367735	1.615645	-0.412951	-0.941408	-1.283889
H	1.835404	2.070871	-1.735368	0.164757	-0.061108

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -757.438890

Electronic energy + zero-point energy: -757.131387

Electronic energy + thermal energy correction: -757.115130

Electronic energy + thermal enthalpy correction: -757.114186

Electronic energy + thermal free energy correction: -757.176430

BSSE correction: 0.002188574290

Table S47. Cartesian coordinates, Mulliken and APT charges of all atoms at **P** in the reaction of benzaldehyde with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	-1.758516	0.797943	1.137643	-0.562704	-1.201219
C	-2.716192	-0.002022	0.396935	0.245844	0.645516
C	-1.810608	-0.697233	-0.670922	-0.401266	0.658246
O	-0.761476	0.286471	-0.867198	-0.509738	-1.188967
C	-1.139855	-1.958525	-0.143100	-0.320308	-0.071671

H	-1.861093	-2.769955	-0.032443	0.211665	0.017080
H	-0.371715	-2.271259	-0.852555	0.206444	0.004582
H	-0.663962	-1.779295	0.823646	0.173235	0.002766
C	-3.410099	-0.955863	1.347366	-0.783958	-0.040523
H	-4.034458	-0.390610	2.041723	0.191873	0.000919
H	-4.053423	-1.639407	0.788660	0.204748	0.017309
H	-2.693057	-1.539650	1.923323	0.179908	0.007410
C	-2.493396	-0.971196	-1.994574	-0.858577	-0.043464
H	-1.797148	-1.473888	-2.668349	0.185935	0.002818
H	-3.354510	-1.625905	-1.842829	0.211541	0.018039
H	-2.831295	-0.050639	-2.469040	0.186261	0.008493
C	-3.721291	0.960331	-0.221216	-0.366439	-0.064590
H	-4.180811	1.547934	0.575152	0.199221	0.001740
H	-3.235775	1.645010	-0.919961	0.163664	0.001492
H	-4.508321	0.420581	-0.750252	0.193061	0.013857
B	-0.707175	1.019650	0.289168	1.750953	1.893172
H	1.123274	1.980549	-1.294233	0.207247	-0.022962
C	4.150123	-1.350540	0.289463	-0.481735	-0.113857
C	4.320506	-0.445144	-0.754337	-0.229559	-0.035973
C	3.430449	0.606895	-0.914812	-0.252588	-0.111282
C	2.361085	0.773040	-0.035095	0.334566	0.025681
C	2.196919	-0.131497	1.007815	-0.001043	-0.138972
C	3.087198	-1.190282	1.167613	-0.258390	-0.025788
H	4.841877	-2.174758	0.414164	0.216452	0.070642
H	5.145548	-0.563332	-1.446711	0.228972	0.067398
H	3.560631	1.307462	-1.733522	0.228761	0.069331
H	1.375799	-0.012591	1.705022	0.228029	0.089618
H	2.946795	-1.889714	1.983304	0.231776	0.065964
C	1.425234	1.940332	-0.244586	-0.580161	0.673798
O	0.282682	1.895522	0.597023	-0.590567	-1.268951
H	1.945553	2.871967	-0.013976	0.216877	-0.027651

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -757.507371

Electronic energy + zero-point energy: -757.200497

Electronic energy + thermal energy correction: -757.184162

Electronic energy + thermal enthalpy correction: -757.183218

Electronic energy + thermal free energy correction: -757.245885

BSSE correction: 0.002181436939

Table S48. Cartesian coordinates, Mulliken and APT charges of all atoms at **P** in the reaction of benzaldehyde with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	-1.752621	0.876523	1.075532	-0.704050	-1.196284
C	-2.689743	-0.004596	0.406451	0.434097	0.652658
C	-1.773697	-0.738449	-0.634290	-0.190909	0.661684
O	-0.749280	0.254254	-0.893272	-0.676980	-1.187161
C	-1.068367	-1.959205	-0.054602	-0.394788	-0.045214
H	-1.770119	-2.779547	0.108179	0.212044	0.007586
H	-0.305484	-2.294680	-0.760260	0.208938	-0.005161
H	-0.577191	-1.727709	0.893469	0.195401	-0.006340
C	-3.329476	-0.918278	1.433205	-0.863278	-0.016554
H	-3.958623	-0.332366	2.107034	0.184503	-0.009327
H	-3.961665	-1.658174	0.936195	0.205023	0.008358
H	-2.582071	-1.441871	2.029313	0.180101	-0.000315
C	-2.459834	-1.096770	-1.937170	-0.944408	-0.017707
H	-1.757119	-1.614630	-2.593769	0.177331	-0.007783
H	-3.302263	-1.766039	-1.746376	0.212922	0.009003
H	-2.827646	-0.211863	-2.456610	0.191204	0.000638
C	-3.747943	0.876230	-0.246729	-0.396444	-0.037808
H	-4.218420	1.492987	0.521884	0.197289	-0.008163
H	-3.311915	1.538988	-0.997786	0.159354	-0.008793
H	-4.523298	0.273243	-0.723215	0.192847	0.004906
B	-0.707942	1.060894	0.211996	2.017483	1.868700
H	1.164544	2.000922	-1.399870	0.200863	-0.032141
C	4.078780	-1.348816	0.360868	-0.457540	-0.100560
C	4.167709	-0.605302	-0.810365	-0.243017	-0.027652
C	3.302505	0.457125	-1.027964	-0.246701	-0.101144
C	2.342257	0.796321	-0.077906	0.474009	0.020837
C	2.260568	0.051744	1.093346	-0.138491	-0.129807
C	3.121897	-1.017417	1.309886	-0.322461	-0.020308
H	4.749407	-2.183638	0.529452	0.219855	0.060666
H	4.907839	-0.859431	-1.560863	0.234131	0.057605
H	3.367241	1.026607	-1.949968	0.229415	0.059257
H	1.518123	0.302172	1.842284	0.240895	0.082324
H	3.043228	-1.592519	2.225743	0.231596	0.056386
C	1.432397	1.973648	-0.340144	-0.500792	0.715477
O	0.264773	1.972084	0.467579	-0.725203	-1.265057
H	1.959862	2.902787	-0.111048	0.205760	-0.042806

I5

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1869.165276

Electronic energy + zero-point energy: -1868.663968

Electronic energy + thermal energy correction: -1868.633053

Electronic energy + thermal enthalpy correction: -1868.632109

Electronic energy + thermal free energy correction: -1868.728542

BSSE correction: 0.007223970855

Table S49. Cartesian coordinates, Mulliken and APT charges of all atoms at **I5** in the reaction of benzaldehyde with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	0.117329	1.279076	0.389254	-0.849342	-1.350546
C	-0.076303	2.690629	0.501837	0.007269	0.676847
C	1.285567	3.251496	-0.016638	0.041368	0.666970
O	1.620126	2.331679	-1.052860	-0.560681	-1.249754
C	1.205026	4.653452	-0.595071	-0.840173	-0.026280
H	0.823078	5.358159	0.148168	0.197846	-0.001269
H	2.202091	4.984292	-0.894860	0.179945	-0.014910
H	0.557926	4.682236	-1.471590	0.175529	-0.004693
C	-1.240529	3.104420	-0.395860	-0.264658	-0.065717
H	-2.135004	2.556262	-0.095068	0.169604	-0.008067
H	-1.451443	4.172420	-0.308125	0.211682	-0.006598
H	-1.026168	2.872554	-1.441109	0.168938	0.002784
C	2.369944	3.198246	1.060007	-0.468441	-0.066353
H	3.335336	3.401524	0.591354	0.201109	-0.015070
H	2.202905	3.944638	1.839800	0.193149	-0.006017
H	2.411261	2.208019	1.516826	0.119651	0.014914
C	-0.393040	3.042919	1.945604	-0.790782	-0.032323
H	-1.375950	2.648591	2.215777	0.153447	-0.014211
H	0.345157	2.619697	2.626597	0.180268	-0.002721
H	-0.415789	4.127364	2.081480	0.209452	-0.000274
B	1.114991	1.046424	-0.654629	2.610487	2.227862
H	3.780008	0.708514	-1.108127	0.168208	-0.061867
F	0.485844	0.376932	-1.779673	-0.612856	-0.971939
K	-0.105602	-1.331214	0.338215	0.739644	1.110460
C	5.746425	-3.225824	0.725746	-0.394767	-0.130498
C	5.934691	-2.773553	-0.578114	-0.388749	-0.031996
C	5.096738	-1.801852	-1.105101	0.084952	-0.123778
C	4.059992	-1.262668	-0.341698	0.964462	0.076793

C	3.878298	-1.717274	0.960137	-0.690648	-0.150050
C	4.717295	-2.694884	1.490892	-0.439255	-0.020636
H	6.398199	-3.986443	1.138335	0.212951	0.068533
H	6.734258	-3.182978	-1.184289	0.222816	0.064654
H	5.243005	-1.454397	-2.123174	0.235056	0.065698
H	3.083508	-1.296013	1.563162	0.149585	0.091819
H	4.564305	-3.039549	2.507014	0.243220	0.061043
C	3.178620	-0.195999	-0.944770	-0.612805	0.659036
O	2.087899	0.094506	-0.115929	-1.019973	-1.365980
H	2.845583	-0.536251	-1.934341	0.144091	-0.062894
O	-2.683732	-1.890576	0.086704	-0.525992	-1.203207
C	-3.516694	-0.687129	0.022989	0.321006	0.600764
C	-4.953729	-1.291978	-0.026847	-0.154704	0.618737
O	-4.724865	-2.592898	-0.641521	-0.396635	-1.130127
C	-5.537492	-1.556730	1.353418	-0.422708	-0.064849
H	-5.780600	-0.621385	1.859705	0.192743	0.020676
H	-6.454269	-2.137260	1.240825	0.211684	0.008002
H	-4.844164	-2.124316	1.977374	0.163670	0.001789
C	-3.227617	0.170829	1.238657	-0.600417	-0.068616
H	-2.213578	0.574052	1.176010	-0.063899	0.031336
H	-3.916819	1.018238	1.265589	0.280212	0.031381
H	-3.330877	-0.393471	2.164931	0.200340	0.014185
C	-5.931607	-0.507928	-0.876857	-0.693171	-0.041052
H	-6.909931	-0.990121	-0.843705	0.199655	0.006068
H	-6.036091	0.506212	-0.485020	0.204981	0.020705
H	-5.606510	-0.452201	-1.914918	0.179583	0.010533
C	-3.123017	0.040324	-1.254866	-0.545432	-0.081516
H	-2.061849	0.299751	-1.214809	-0.020647	0.028896
H	-3.299072	-0.582344	-2.134380	0.194982	0.006168
H	-3.687931	0.967465	-1.362404	0.237308	0.028885
B	-3.425398	-2.919130	-0.433199	0.910626	1.365291
H	-2.964155	-3.982324	-0.672893	0.075217	-0.207019

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1869.300431

Electronic energy + zero-point energy: -1868.800110

Electronic energy + thermal energy correction: -1868.769056

Electronic energy + thermal enthalpy correction: -1868.768111

Electronic energy + thermal free energy correction: -1868.865165

BSSE correction: 0.007223970855

Table S50. Cartesian coordinates, Mulliken and APT charges of all atoms at **I5** in the reaction of benzaldehyde with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	0.327211	-1.626702	0.062938	-1.144918	-1.357054
C	0.810386	-2.877769	-0.416125	0.252233	0.672126
C	2.350427	-2.759462	-0.156364	0.301769	0.664234
O	2.404362	-2.006763	1.045028	-0.899606	-1.260434
C	3.048791	-4.094971	0.049887	-0.848930	0.001666
H	2.922799	-4.739335	-0.824895	0.201274	-0.011327
H	4.119916	-3.934124	0.198689	0.168154	-0.026028
H	2.659710	-4.615610	0.925536	0.180723	-0.012768
C	0.162358	-3.995955	0.401366	-0.521194	-0.033984
H	-0.924022	-3.891647	0.340558	0.197661	-0.023356
H	0.431772	-4.984550	0.021723	0.195540	-0.016281
H	0.452978	-3.934493	1.451666	0.161063	-0.002526
C	3.073489	-1.983742	-1.261166	-0.607292	-0.030657
H	4.093141	-1.772510	-0.930169	0.217908	-0.019371
H	3.126629	-2.549758	-2.194319	0.202193	-0.015671
H	2.589238	-1.025903	-1.461063	0.150741	-0.036237
C	0.421336	-3.037848	-1.878152	-0.716388	-0.013334
H	-0.667158	-3.086946	-1.969180	0.195121	-0.018738
H	0.780035	-2.210448	-2.493755	0.166420	-0.030429
H	0.835822	-3.962084	-2.289533	0.225281	-0.001346
B	1.241990	-1.146222	1.100841	2.934649	2.291488
H	3.377792	0.362129	1.542810	0.153350	-0.067859
F	0.668660	-1.228661	2.423252	-0.691624	-0.969908
K	0.083357	0.627343	-1.340420	0.843131	1.111548
C	3.232300	4.551236	-0.793262	-0.389671	-0.089410
C	2.752080	4.646458	0.504743	-0.375112	-0.040213
C	2.514984	3.494012	1.247760	-0.272188	-0.091427
C	2.763604	2.238440	0.706699	0.769048	-0.007732
C	3.252819	2.152872	-0.597688	0.034146	-0.112128
C	3.482625	3.298353	-1.344978	-0.350882	-0.044510
H	3.413211	5.448053	-1.374933	0.229198	0.060280
H	2.553693	5.619326	0.940599	0.237240	0.057329
H	2.128245	3.572705	2.258797	0.228781	0.059562
H	3.458388	1.175652	-1.024952	0.217610	0.067987
H	3.863476	3.217072	-2.357032	0.241048	0.056280
C	2.468701	0.973924	1.473158	-0.917480	0.790863
O	1.465114	0.266979	0.794140	-1.122458	-1.425541
H	2.156867	1.225286	2.494896	0.185648	-0.091188
O	-2.515424	0.956974	-0.816279	-0.681491	-1.198288

C	-3.204016	0.072544	0.128355	0.764128	0.620000
C	-4.658443	0.651768	0.111891	0.287109	0.624923
O	-4.442899	2.042473	-0.269379	-0.519028	-1.126134
C	-5.540988	0.034884	-0.965178	-0.534165	-0.038211
H	-5.789918	-0.999108	-0.719850	0.193553	0.012321
H	-6.469994	0.604578	-1.031233	0.210048	-0.003838
H	-5.056889	0.053951	-1.944100	0.167578	-0.006719
C	-3.078217	-1.356437	-0.361238	-1.055701	-0.058202
H	-2.035896	-1.673972	-0.288562	0.105379	0.063475
H	-3.677676	-2.016360	0.270625	0.250974	0.015267
H	-3.414222	-1.463770	-1.392701	0.211680	-0.000358
C	-5.361656	0.614268	1.453810	-0.797658	-0.016877
H	-6.368815	1.023832	1.351983	0.190593	-0.004903
H	-5.447714	-0.417720	1.802059	0.209281	0.012694
H	-4.828385	1.193476	2.207376	0.183638	0.002022
C	-2.494716	0.235208	1.465656	-0.755736	-0.060220
H	-1.445641	-0.046074	1.355892	-0.004953	0.033420
H	-2.545269	1.264538	1.827516	0.197383	-0.004116
H	-2.935735	-0.420906	2.218260	0.245369	0.016902
B	-3.241687	2.112438	-0.890728	1.050186	1.350076
H	-2.841719	3.081681	-1.451207	0.049647	-0.217140

I6

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1869.164549

Electronic energy + zero-point energy: -1868.662640

Electronic energy + thermal energy correction: -1868.631932

Electronic energy + thermal enthalpy correction: -1868.630988

Electronic energy + thermal free energy correction: -1868.725808

BSSE correction: 0.007732800238

Table S51. Cartesian coordinates, Mulliken and APT charges of all atoms at **I6** in the reaction of benzaldehyde with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	2.148283	0.087000	0.975881	-0.612075	-1.298096
C	3.328181	0.808905	0.523183	-0.209081	0.678510
C	3.880003	-0.134393	-0.601477	0.076509	0.683057

O	2.683026	-0.814585	-1.071168	-0.536496	-1.220861
C	4.521980	0.593017	-1.764414	-0.746592	-0.047877
H	5.369005	1.186516	-1.413237	0.211043	0.017549
H	4.891501	-0.134341	-2.489395	0.196619	0.003815
H	3.812762	1.251989	-2.263611	0.191603	0.012169
C	2.859037	2.156548	-0.002934	-0.401467	-0.091020
H	2.343400	2.685223	0.800886	0.198458	0.003098
H	3.708106	2.762999	-0.322503	0.230004	0.015069
H	2.167371	2.032830	-0.836297	0.193971	0.047539
C	4.812659	-1.211889	-0.065897	-0.361711	-0.068927
H	5.013832	-1.928705	-0.863448	0.204991	0.003391
H	5.761213	-0.783791	0.261706	0.199140	0.015825
H	4.360964	-1.746321	0.772556	0.154965	-0.000950
C	4.267108	0.996978	1.697476	-0.786225	-0.047226
H	3.812383	1.674179	2.422825	0.180317	0.002181
H	4.487455	0.052725	2.193780	0.191289	0.009590
H	5.204249	1.442774	1.356889	0.217682	0.018004
B	1.779128	-0.745981	-0.056976	2.339970	2.021850
H	1.063560	-3.064142	-1.192442	0.161993	-0.026909
F	0.202083	0.903804	-1.416341	-0.528478	-1.014890
K	-0.243698	-0.118249	2.176445	0.802692	1.097198
C	-3.197508	-4.604354	0.348286	-0.132979	-0.088680
C	-2.140245	-5.255180	-0.273984	-0.432038	-0.053008
C	-1.021874	-4.535424	-0.682559	-0.328404	-0.101741
C	-0.955017	-3.160420	-0.483642	0.515897	0.011141
C	-2.023939	-2.510266	0.135416	-0.147671	-0.121842
C	-3.136035	-3.229207	0.553500	-0.432997	-0.054849
H	-4.066401	-5.164203	0.672544	0.230571	0.070315
H	-2.179757	-6.325863	-0.434893	0.227677	0.067031
H	-0.191327	-5.046891	-1.156817	0.224369	0.071034
H	-1.995160	-1.432590	0.262462	-0.118260	0.113732
H	-3.960401	-2.715047	1.033422	0.229381	0.065722
C	0.247001	-2.383228	-0.945475	-0.237840	0.733732
O	0.655566	-1.495753	0.096821	-1.146427	-1.393219
H	0.004907	-1.789743	-1.830831	0.192267	-0.026972
O	-1.812059	2.096217	-1.771805	-0.678801	-1.247546
C	-2.677453	2.695759	-0.823891	0.584292	0.658564
C	-1.984390	2.349570	0.525377	-0.570610	0.639257
O	-1.498099	1.027894	0.275469	-0.685714	-1.320852
C	-0.798368	3.272758	0.804530	-0.477983	-0.066867
H	-1.127420	4.276637	1.082450	0.223538	-0.004686
H	-0.211676	2.877310	1.638984	0.213038	-0.040222
H	-0.148692	3.341113	-0.069140	0.152343	0.017971
C	-2.789585	4.185802	-1.102445	-0.723308	-0.021615
H	-3.322245	4.343526	-2.043202	0.182730	-0.016808

H	-3.346935	4.690573	-0.308800	0.192422	-0.005383
H	-1.805106	4.645614	-1.188131	0.167018	-0.005779
C	-2.917879	2.327787	1.725626	-0.717886	-0.035586
H	-2.355398	2.169348	2.651311	0.145470	-0.033535
H	-3.435949	3.284912	1.827076	0.219339	0.008270
H	-3.661751	1.536391	1.633087	0.176983	0.000374
C	-4.060376	2.048587	-0.927853	-0.396492	-0.053763
H	-4.410389	2.138949	-1.958251	0.195307	-0.016156
H	-4.012186	0.987582	-0.672787	0.138197	-0.005178
H	-4.788767	2.533675	-0.274065	0.177596	-0.009797
B	-1.220050	0.907122	-1.173404	1.274071	1.898287
H	-1.658557	-0.150729	-1.620109	-0.004213	-0.443433

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1869.298138

Electronic energy + zero-point energy: -1868.797555

Electronic energy + thermal energy correction: -1868.767388

Electronic energy + thermal enthalpy correction: -1868.766444

Electronic energy + thermal free energy correction: -1868.859445

BSSE correction: 0.007233779251

Table S52. Cartesian coordinates, Mulliken and APT charges of all atoms at **I6** in the reaction of benzaldehyde with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	2.234973	0.257080	1.040984	-0.773753	-1.288892
C	3.164541	1.297077	0.631771	0.211610	0.679768
C	3.855078	0.650672	-0.627544	0.213723	0.687794
O	2.851406	-0.287488	-1.105829	-0.657629	-1.212859
C	4.169879	1.633788	-1.737174	-0.850895	-0.024470
H	4.855104	2.403480	-1.374090	0.215014	0.008877
H	4.653927	1.110927	-2.564896	0.193881	-0.006106
H	3.268461	2.116599	-2.114069	0.194580	0.002407
C	2.335084	2.531467	0.305557	-0.758197	-0.075937
H	1.771364	2.820806	1.195402	0.216483	-0.006367
H	2.976034	3.368981	0.023550	0.220066	0.009737
H	1.626542	2.332889	-0.499104	0.224044	0.049771
C	5.090468	-0.170279	-0.281013	-0.385425	-0.043992
H	5.409524	-0.719645	-1.169041	0.204495	-0.005138

H	5.913184	0.472450	0.037716	0.201810	0.008479
H	4.884797	-0.892436	0.512491	0.159985	-0.006847
C	4.107240	1.588193	1.782836	-0.808199	-0.021568
H	3.549392	2.034571	2.609053	0.176973	-0.007907
H	4.597216	0.685133	2.146295	0.195268	-0.000699
H	4.873781	2.300278	1.468231	0.222873	0.009309
B	2.021323	-0.535584	-0.061520	2.516714	1.977815
H	1.583466	-2.827479	-1.462476	0.185358	-0.036589
F	-0.057266	1.069805	-1.478021	-0.570655	-1.019261
K	-0.291641	-0.325057	2.035723	0.784633	1.094460
C	-2.183533	-5.159329	0.370526	-0.219187	-0.064156
C	-0.953738	-5.597436	-0.099398	-0.402151	-0.054080
C	-0.021769	-4.680464	-0.573009	-0.398384	-0.079554
C	-0.314494	-3.322044	-0.590952	0.629175	-0.022637
C	-1.556991	-2.889475	-0.126292	0.091575	-0.117922
C	-2.483667	-3.801270	0.356767	-0.302514	-0.058959
H	-2.908904	-5.872791	0.744732	0.237797	0.061110
H	-0.714272	-6.654756	-0.092520	0.234904	0.059021
H	0.943248	-5.024959	-0.930009	0.227316	0.062066
H	-1.806483	-1.833050	-0.162147	0.076277	0.114722
H	-3.445859	-3.453364	0.715492	0.237178	0.057952
C	0.698239	-2.320982	-1.072704	-0.820070	0.801443
O	1.063144	-1.491533	0.034531	-1.135506	-1.407520
H	0.276877	-1.688653	-1.857626	0.220615	-0.028914
O	-2.256238	1.925396	-1.738154	-0.824067	-1.250626
C	-3.192734	2.310347	-0.748508	0.719605	0.665440
C	-2.442013	1.969237	0.576131	-0.245772	0.642199
O	-1.740297	0.777420	0.218745	-0.763409	-1.320880
C	-1.430936	3.052293	0.960052	-0.646624	-0.040043
H	-1.928717	3.957608	1.316225	0.215816	-0.013399
H	-0.792324	2.692884	1.772724	0.216656	-0.048005
H	-0.790725	3.311687	0.115901	0.178697	0.008968
C	-3.531588	3.784372	-0.911570	-0.792050	0.005259
H	-4.085541	3.935579	-1.841988	0.174633	-0.026921
H	-4.158154	4.134460	-0.086068	0.192715	-0.014221
H	-2.630891	4.398158	-0.951051	0.169282	-0.012933
C	-3.351015	1.680337	1.761924	-0.788222	-0.008251
H	-2.762615	1.529936	2.673408	0.140499	-0.043307
H	-4.019547	2.524794	1.950307	0.218540	-0.000804
H	-3.955760	0.788706	1.593275	0.191692	-0.006555
C	-4.467422	1.476551	-0.913887	-0.453385	-0.027000
H	-4.836529	1.600172	-1.935055	0.192407	-0.025574
H	-4.268466	0.414962	-0.749943	0.149338	-0.014239
H	-5.256168	1.793333	-0.226548	0.173477	-0.019769
B	-1.464807	0.818186	-1.230389	1.435367	1.915411

H	-1.715645	-0.271762	-1.758455	-0.064977	-0.459104

TS1C

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1869.087847

Electronic energy + zero-point energy: -1868.591983

Electronic energy + thermal energy correction: -1868.561044

Electronic energy + thermal enthalpy correction: -1868.560100

Electronic energy + thermal free energy correction: -1868.655617

BSSE correction: 0.006078498706

Table S53. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS1C** in the reaction of benzaldehyde with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	1.000745	0.583999	0.670660	-0.544360	-1.299133
C	1.417817	1.958551	0.785398	-0.322659	0.670170
C	1.930369	2.272686	-0.656599	0.100644	0.635151
O	1.068402	1.462343	-1.472630	-0.488660	-1.380389
C	1.778720	3.724785	-1.070173	-0.798546	-0.023866
H	2.324612	4.375232	-0.382523	0.205131	0.002048
H	2.192497	3.864848	-2.071017	0.188150	-0.007432
H	0.732164	4.027557	-1.085105	0.179518	0.000756
C	0.190873	2.783689	1.159015	-0.400402	-0.075529
H	-0.235746	2.383748	2.081790	0.230125	-0.010898
H	0.452170	3.829858	1.330326	0.220302	-0.002402
H	-0.567897	2.735418	0.375263	0.106060	0.008659
C	3.372242	1.819237	-0.866295	-0.304557	-0.072878
H	3.595217	1.839572	-1.935044	0.200959	-0.008484
H	4.072374	2.483177	-0.354911	0.207720	0.006871
H	3.523229	0.803254	-0.498478	0.119643	0.021780
C	2.475012	2.071965	1.867119	-0.787694	-0.041187
H	2.028174	1.864591	2.842032	0.176518	-0.006936
H	3.287960	1.364875	1.702803	0.124061	0.008106
H	2.886544	3.084038	1.891357	0.219260	0.009632
B	0.703442	0.346170	-0.699849	0.897161	2.434708
H	1.467121	-0.748507	-1.063465	0.701775	-0.893228
F	-0.576098	-0.170879	-0.934541	-0.528848	-1.066264

K	-0.692169	-1.199204	1.601871	0.762979	1.081368
C	5.881942	-1.207545	0.081393	-0.343194	-0.084285
C	5.445862	-1.431137	-1.221170	-0.321867	-0.050591
C	4.109536	-1.723088	-1.463610	-0.239790	-0.091770
C	3.203313	-1.795601	-0.409603	0.414477	-0.190115
C	3.643687	-1.585349	0.892496	0.270134	-0.099165
C	4.979475	-1.288587	1.137610	-0.286393	-0.055409
H	6.922905	-0.975778	0.272974	0.225472	0.067126
H	6.147382	-1.375862	-2.045257	0.232278	0.064664
H	3.760323	-1.883477	-2.479266	0.216476	0.067658
H	2.925209	-1.646063	1.701368	0.222448	0.094952
H	5.319018	-1.116862	2.152590	0.240203	0.061549
C	1.740428	-2.048553	-0.680960	-0.891711	1.763665
O	0.990432	-2.472052	0.250275	-0.545548	-1.352868
H	1.572549	-2.422769	-1.706860	0.212388	-0.190435
O	-3.177414	-1.184575	0.561118	-0.450092	-1.180364
C	-4.070188	-0.027141	0.553173	0.105561	0.613810
C	-4.840105	-0.218453	-0.792156	0.195864	0.622389
O	-3.889431	-0.973749	-1.595489	-0.401383	-1.125353
C	-6.079961	-1.090139	-0.650271	-0.423799	-0.061498
H	-6.862704	-0.569352	-0.096720	0.188596	0.018140
H	-6.458594	-1.325268	-1.646077	0.208349	0.005674
H	-5.851095	-2.026939	-0.138243	0.166544	0.001768
C	-4.939391	-0.069252	1.792577	-0.780574	-0.042774
H	-4.320145	0.079575	2.679221	0.163638	0.002662
H	-5.677910	0.734600	1.754887	0.224467	0.022397
H	-5.460174	-1.020914	1.888165	0.189672	0.012032
C	-5.177873	1.072318	-1.509138	-0.738669	-0.039380
H	-5.724177	0.846260	-2.426353	0.198882	0.004905
H	-5.813687	1.695868	-0.876710	0.210017	0.019114
H	-4.280973	1.633415	-1.768438	0.187190	0.010474
C	-3.183867	1.210282	0.564226	-0.878377	-0.082571
H	-2.570613	1.204956	1.468646	0.242279	-0.009602
H	-2.526264	1.236304	-0.305609	0.267944	0.030024
H	-3.786485	2.119667	0.583120	0.228897	0.027309
B	-3.039669	-1.594658	-0.739301	0.976268	1.365892
H	-2.264973	-2.429512	-1.063081	0.049074	-0.210650

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1869.226358

Electronic energy + zero-point energy: -1868.731232

Electronic energy + thermal energy correction: -1868.700255

Electronic energy + thermal enthalpy correction: -1868.699311

Electronic energy + thermal free energy correction: -1868.795185

BSSE correction: 0.005666841408

Table S54. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS1C** in the reaction of benzaldehyde with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	0.844195	0.606472	0.561532	-0.682803	-1.327666
C	1.300429	1.949064	0.791276	-0.120501	0.676171
C	1.997931	2.309165	-0.567602	0.474712	0.640172
O	1.252330	1.536863	-1.518306	-0.655547	-1.379828
C	1.901647	3.777217	-0.947023	-0.853380	0.000411
H	2.364675	4.402372	-0.178961	0.207006	-0.009353
H	2.431791	3.949129	-1.887085	0.180473	-0.018766
H	0.866072	4.092426	-1.076844	0.179929	-0.007918
C	0.075267	2.813867	1.076110	-0.578108	-0.047562
H	-0.464689	2.393534	1.927934	0.227222	-0.016428
H	0.359949	3.838200	1.327093	0.218325	-0.015215
H	-0.602792	2.839553	0.220860	0.149830	-0.002199
C	3.458562	1.866520	-0.613350	-0.563712	-0.049158
H	3.818609	1.942788	-1.641954	0.192845	-0.017266
H	4.085581	2.501819	0.016485	0.196266	-0.004100
H	3.572811	0.833379	-0.285945	0.335439	0.018795
C	2.225983	1.956027	1.995280	-0.887176	-0.017471
H	1.659684	1.712835	2.898194	0.166758	-0.018400
H	3.027798	1.225223	1.886957	0.143563	-0.001332
H	2.669249	2.945840	2.132439	0.224287	0.000104
B	0.740346	0.411394	-0.845790	1.202310	2.462919
H	1.492766	-0.698357	-1.114699	0.593203	-0.903968
F	-0.517979	-0.033770	-1.285901	-0.517733	-1.075596
K	-0.640149	-1.341816	1.494854	0.778668	1.081158
C	5.859733	-1.202036	0.244546	-0.353445	-0.071290
C	5.507726	-1.333067	-1.093677	-0.351977	-0.040553
C	4.194524	-1.620037	-1.439645	-0.258954	-0.078000
C	3.226586	-1.781268	-0.454309	0.716510	-0.211173
C	3.584613	-1.661459	0.883218	0.026959	-0.081562
C	4.895773	-1.369227	1.232460	-0.354065	-0.049761
H	6.883745	-0.972728	0.517216	0.227425	0.056704
H	6.257216	-1.208089	-1.867194	0.233998	0.054799
H	3.913029	-1.708130	-2.484916	0.218338	0.057409
H	2.824040	-1.791729	1.644324	0.240176	0.077897

H	5.168062	-1.267983	2.277309	0.240695	0.052835
C	1.791216	-2.043639	-0.837453	-0.913951	1.833055
O	0.995670	-2.561999	-0.002656	-0.569505	-1.358029
H	1.690054	-2.315424	-1.904539	0.201211	-0.205668
O	-3.149678	-1.248710	0.451602	-0.585823	-1.181187
C	-4.022516	-0.084895	0.595836	0.690582	0.617526
C	-4.890921	-0.158950	-0.708210	0.269543	0.629818
O	-4.032846	-0.900477	-1.621460	-0.521956	-1.119243
C	-6.163122	-0.979660	-0.541139	-0.435421	-0.037301
H	-6.881524	-0.461799	0.097036	0.189464	0.010769
H	-6.620088	-1.126837	-1.521695	0.209254	-0.003207
H	-5.956268	-1.961314	-0.109347	0.171364	-0.006880
C	-4.801073	-0.221509	1.888740	-0.839006	-0.019185
H	-4.116193	-0.165202	2.738161	0.156103	-0.005173
H	-5.519649	0.596388	1.979574	0.230640	0.014463
H	-5.339361	-1.167358	1.942366	0.197011	0.002815
C	-5.212104	1.187845	-1.325464	-0.824150	-0.014812
H	-5.821663	1.043906	-2.220012	0.193551	-0.003911
H	-5.781741	1.798057	-0.620616	0.212489	0.011017
H	-4.309308	1.729485	-1.607465	0.192677	0.001354
C	-3.116909	1.138015	0.652249	-1.300098	-0.062721
H	-2.465658	1.069099	1.526617	0.277747	-0.019163
H	-2.492073	1.218226	-0.237943	0.319315	0.025605
H	-3.702630	2.052544	0.758319	0.220219	0.020535
B	-3.130499	-1.580866	-0.874962	1.029918	1.352233
H	-2.393536	-2.403081	-1.313778	0.031286	-0.217517

I4C

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1869.107042

Electronic energy + zero-point energy: -1868.607552

Electronic energy + thermal energy correction: -1868.575592

Electronic energy + thermal enthalpy correction: -1868.574648

Electronic energy + thermal free energy correction: -1868.673806

BSSE correction: 0.006171195728

Table S55. Cartesian coordinates, Mulliken and APT charges of all atoms at **I4C** in the reaction of benzaldehyde with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	0.499814	0.859133	0.583542	-0.601842	-1.204835
C	1.151186	2.156808	0.771649	-0.801267	0.650298
C	1.802890	2.403358	-0.633006	0.471633	0.641275
O	0.915226	1.660817	-1.526635	-0.409318	-1.135846
C	1.829752	3.854360	-1.061467	-0.802916	-0.046556
H	2.405456	4.441276	-0.342584	0.218269	0.026073
H	2.313833	3.936812	-2.035859	0.199962	0.008378
H	0.826468	4.271910	-1.134038	0.190602	0.009925
C	0.049766	3.151764	1.101003	-0.362640	-0.075814
H	-0.472276	2.818189	1.999166	0.214401	0.008444
H	0.470646	4.139565	1.293588	0.243557	0.025511
H	-0.674449	3.231363	0.287209	0.163559	0.006015
C	3.180089	1.772776	-0.765803	-0.342626	-0.081945
H	3.488909	1.818448	-1.811477	0.215887	0.006700
H	3.913549	2.311890	-0.163904	0.216021	0.023476
H	3.167717	0.726979	-0.452037	0.201400	0.039350
C	2.139295	2.046642	1.911979	-0.773819	-0.055458
H	1.601524	1.890613	2.848881	0.190542	0.007758
H	2.832619	1.219430	1.762336	0.126609	0.023649
H	2.709431	2.974351	1.996419	0.235401	0.027345
B	0.309900	0.731576	-0.757465	1.512417	1.882704
H	1.590305	-2.234276	-1.628780	0.140035	-0.201860
F	-0.444512	-0.247533	-1.248015	-0.337368	-0.826879
K	-0.493930	-1.496193	1.485931	0.758007	1.104997
C	5.693314	-0.714128	0.207120	-0.539802	-0.159203
C	5.428034	-1.122243	-1.099753	-0.181239	-0.017233
C	4.244707	-1.784723	-1.394360	-0.149346	-0.122034
C	3.300162	-2.050411	-0.399513	0.173703	-0.010262
C	3.575187	-1.639576	0.900064	0.008804	-0.155703
C	4.764030	-0.978028	1.205022	-0.209219	-0.013123
H	6.615433	-0.194668	0.440091	0.206378	0.062031
H	6.145776	-0.918482	-1.886539	0.228415	0.053004
H	4.040193	-2.095660	-2.415690	0.213169	0.051443
H	2.833399	-1.844656	1.663614	0.187808	0.098391
H	4.962095	-0.663115	2.223959	0.240528	0.048812
C	1.988514	-2.764732	-0.732766	-0.499607	0.900960
O	1.101213	-2.843650	0.286913	-0.770132	-1.384708
H	2.293524	-3.760101	-1.132183	0.106015	-0.210935
O	-2.940660	-1.187459	0.392101	-0.465001	-1.179354
C	-3.830892	-0.037978	0.538618	0.035288	0.614903
C	-4.809799	-0.230406	-0.660814	0.237935	0.617367
O	-3.990188	-0.959887	-1.618692	-0.369135	-1.121079
C	-5.992799	-1.127623	-0.325515	-0.390371	-0.062797
H	-6.682581	-0.625931	0.354812	0.190373	0.019914

H	-6.526464	-1.363658	-1.247335	0.207728	0.006426
H	-5.665182	-2.062933	0.132810	0.165564	0.001968
C	-4.481991	-0.092905	1.904781	-0.820853	-0.044801
H	-3.728596	0.068486	2.678566	0.159686	0.000595
H	-5.230892	0.697384	1.991187	0.225265	0.023587
H	-4.962698	-1.053936	2.082384	0.191936	0.013191
C	-5.285637	1.060681	-1.293845	-0.799512	-0.041181
H	-5.974604	0.834012	-2.109151	0.203270	0.004942
H	-5.817054	1.663916	-0.554392	0.209374	0.020718
H	-4.456358	1.643295	-1.692815	0.183180	0.008969
C	-2.963459	1.206383	0.409767	-0.775932	-0.078024
H	-2.177393	1.173461	1.166369	0.247237	0.008942
H	-2.499235	1.269552	-0.576719	0.250015	0.004986
H	-3.553045	2.109654	0.575414	0.243458	0.026458
B	-3.009220	-1.583371	-0.917514	0.935416	1.358362
H	-2.285497	-2.400480	-1.375762	0.053102	-0.208236

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1869.248340

Electronic energy + zero-point energy: -1868.749520

Electronic energy + thermal energy correction: -1868.717644

Electronic energy + thermal enthalpy correction: -1868.716700

Electronic energy + thermal free energy correction: -1868.814988

BSSE correction: 0.006453300909

Table S56. Cartesian coordinates, Mulliken and APT charges of all atoms at **I4C** in the reaction of benzaldehyde with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	0.474580	0.929348	0.324176	-0.837753	-1.192875
C	1.238882	2.073080	0.826317	-0.343754	0.643704
C	2.074511	2.487337	-0.436008	0.464584	0.644099
O	1.222297	2.042764	-1.534682	-0.580317	-1.134422
C	2.310618	3.976573	-0.569118	-0.824640	-0.022541
H	2.864316	4.343865	0.298037	0.224782	0.017713
H	2.907082	4.174526	-1.462003	0.195069	-0.001188
H	1.375381	4.530591	-0.647810	0.189561	0.002094
C	0.224800	3.122958	1.253959	-0.536815	-0.051319
H	-0.429184	2.698669	2.018582	0.255885	-0.005068

H	0.727962	3.991591	1.681956	0.244738	0.018484
H	-0.393974	3.454286	0.417190	0.198955	-0.000039
C	3.381054	1.718933	-0.558899	-0.635902	-0.050582
H	3.814664	1.908850	-1.542569	0.213617	-0.000555
H	4.096152	2.041215	0.199895	0.220340	0.015194
H	3.223607	0.644125	-0.454525	0.444038	0.011294
C	2.070794	1.621048	2.008766	-0.921918	-0.044685
H	1.424521	1.408640	2.864378	0.187824	-0.013573
H	2.657565	0.732220	1.775645	0.160691	0.019405
H	2.752836	2.419897	2.307808	0.248313	0.027520
B	0.431415	1.072132	-1.027662	1.843794	1.883062
H	0.681081	-1.981866	-0.756432	0.044634	-0.227481
F	-0.343941	0.311774	-1.793988	-0.296889	-0.822308
K	-0.434083	-1.071339	1.918996	0.802561	1.098452
C	5.366336	-1.277714	-0.513330	-0.443498	-0.148090
C	4.629759	-1.550259	-1.663452	-0.301163	-0.009631
C	3.326829	-2.014404	-1.560936	-0.096739	-0.110557
C	2.732928	-2.222545	-0.314752	0.344419	-0.008658
C	3.475180	-1.942947	0.825394	-0.067953	-0.150307
C	4.782687	-1.473128	0.730492	-0.318808	-0.000514
H	6.384399	-0.912131	-0.590559	0.212698	0.050304
H	5.074874	-1.396399	-2.640943	0.222468	0.044419
H	2.757087	-2.224068	-2.463224	0.227020	0.042175
H	3.002475	-2.108011	1.787756	0.241414	0.100965
H	5.346882	-1.257773	1.632335	0.224468	0.039334
C	1.295165	-2.737976	-0.202466	-0.561193	0.909354
O	0.855109	-2.976774	1.054334	-0.787793	-1.347223
H	1.250269	-3.633695	-0.867560	0.088328	-0.219938
O	-2.673069	-0.928547	0.417128	-0.608136	-1.183119
C	-3.714498	0.095384	0.422286	0.343421	0.626389
C	-4.616025	-0.347970	-0.780076	0.387884	0.627374
O	-3.684589	-1.091231	-1.617602	-0.504549	-1.124306
C	-5.717264	-1.321883	-0.381499	-0.423879	-0.038509
H	-6.485293	-0.822385	0.211893	0.190404	0.010248
H	-6.185414	-1.715802	-1.285711	0.209359	-0.003836
H	-5.323045	-2.162667	0.193490	0.167797	-0.006348
C	-4.402212	0.079978	1.773121	-0.945210	-0.021307
H	-3.708872	0.420971	2.545861	0.152416	-0.010822
H	-5.255273	0.762348	1.765134	0.231361	0.015934
H	-4.754305	-0.916393	2.039144	0.201966	0.004418
C	-5.194175	0.798398	-1.585627	-0.867826	-0.016937
H	-5.811273	0.402991	-2.395132	0.197853	-0.004513
H	-5.826927	1.421752	-0.949377	0.210826	0.010856
H	-4.413773	1.422467	-2.020782	0.187875	0.001872
C	-3.019215	1.431961	0.203000	-0.881226	-0.060699

H	-2.277067	1.581286	0.988658	0.216259	0.005201
H	-2.511656	1.472608	-0.761977	0.230493	0.004530
H	-3.735854	2.253600	0.254750	0.233460	0.016837
B	-2.652894	-1.484728	-0.831039	0.992235	1.350710
H	-1.810367	-2.248278	-1.175298	0.132149	-0.209992

I7

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1869.150934

Electronic energy + zero-point energy: -1868.649456

Electronic energy + thermal energy correction: -1868.618910

Electronic energy + thermal enthalpy correction: -1868.617966

Electronic energy + thermal free energy correction: -1868.712050

BSSE correction: 0.007761330594

Table S63. Cartesian coordinates, Mulliken and APT charges of all atoms at **I7** in the reaction of benzaldehyde with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	-0.094310	1.781686	0.417388	-0.798643	-1.344234
C	0.118796	3.186905	0.374549	-0.087430	0.672366
C	1.420486	3.303637	-0.475857	0.243954	0.659825
O	1.257058	2.260924	-1.425852	-0.597254	-1.276211
C	1.570674	4.630329	-1.203266	-0.769035	-0.019559
H	1.564710	5.465745	-0.497727	0.194341	-0.008748
H	2.521373	4.649119	-1.741632	0.173579	-0.019352
H	0.767811	4.776067	-1.925960	0.175142	-0.007905
C	-1.078878	3.838088	-0.317097	-0.423208	-0.059066
H	-1.989185	3.560221	0.218727	0.206024	-0.016273
H	-1.002926	4.927794	-0.321038	0.201539	-0.013477
H	-1.163826	3.487943	-1.347941	0.150160	0.000099
C	2.674634	3.038212	0.361188	-0.553623	-0.069548
H	3.525199	2.924456	-0.314878	0.190222	-0.017316
H	2.889494	3.862640	1.045628	0.187477	-0.016795
H	2.569912	2.115225	0.934070	0.162907	0.008882
C	0.240366	3.719966	1.793624	-0.740487	-0.031203
H	-0.716863	3.614778	2.310923	0.166820	-0.018586
H	0.998806	3.176570	2.359126	0.161742	-0.013018

H	0.506336	4.780427	1.789978	0.205197	-0.003173
B	0.529057	1.171927	-0.776921	1.152293	1.940290
H	2.938412	0.179861	-1.607451	0.146347	-0.063689
K	0.202176	-0.199559	1.991036	0.904574	1.107078
C	4.381733	-3.810962	0.597900	-0.218014	-0.116156
C	5.042189	-2.897728	-0.213688	-0.416816	-0.036385
C	4.343723	-1.837995	-0.784712	-0.261402	-0.119536
C	2.978736	-1.679536	-0.560994	0.680634	0.033882
C	2.323908	-2.606231	0.251690	-0.267953	-0.122193
C	3.017435	-3.661723	0.829365	-0.497418	-0.039892
H	4.924042	-4.633527	1.048341	0.218473	0.067921
H	6.104956	-3.003644	-0.397250	0.225319	0.063719
H	4.867142	-1.120337	-1.407629	0.217323	0.067972
H	1.255763	-2.511022	0.409125	-0.024096	0.070366
H	2.493107	-4.373358	1.456429	0.232290	0.063395
C	2.220641	-0.535625	-1.189400	-0.188717	0.740129
O	1.396999	0.087756	-0.245318	-0.836630	-1.448085
H	1.619293	-0.915653	-2.029171	0.184597	-0.081000
O	-2.700538	-1.551764	-1.595879	-0.392854	-1.166271
C	-3.833890	-1.395430	-0.694237	0.358819	0.646370
C	-3.175615	-0.739136	0.566357	-0.512051	0.651547
O	-1.799144	-1.244156	0.491893	-0.845303	-1.223157
C	-3.106087	0.775308	0.474809	-0.339726	-0.082965
H	-4.107453	1.204248	0.538927	0.241708	0.023165
H	-2.510244	1.165390	1.300648	0.238446	0.010666
H	-2.629954	1.097735	-0.452166	0.140285	0.025876
C	-4.886340	-0.540568	-1.367144	-0.776651	-0.045851
H	-5.299619	-1.079897	-2.221032	0.203454	0.007931
H	-5.699037	-0.331295	-0.668320	0.213146	0.023774
H	-4.471638	0.403143	-1.718745	0.194250	0.012526
C	-3.779239	-1.171725	1.885847	-0.909395	-0.049976
H	-3.285407	-0.650385	2.708616	0.157611	-0.002173
H	-4.838607	-0.907328	1.909830	0.230620	0.028187
H	-3.681323	-2.244938	2.043012	0.194090	0.013154
C	-4.371475	-2.792921	-0.422603	-0.344608	-0.067880
H	-4.645759	-3.254111	-1.372374	0.210385	0.008108
H	-3.622079	-3.421646	0.063150	0.169131	0.002624
H	-5.258014	-2.752573	0.211682	0.195969	0.020634
B	-1.599179	-1.601582	-0.809770	1.863887	1.974733
H	-0.286954	0.667624	-1.569173	0.167582	-0.495958
F	-0.435498	-2.059125	-1.247533	-0.359022	-0.849583

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1869.284954

Electronic energy + zero-point energy: -1868.784874

Electronic energy + thermal energy correction: -1868.753890

Electronic energy + thermal enthalpy correction: -1868.752945

Electronic energy + thermal free energy correction: -1868.849269

BSSE correction: 0.006978828094

Table S64. Cartesian coordinates, Mulliken and APT charges of all atoms at **I7** in the reaction of benzaldehyde with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	0.624181	1.643327	-0.019256	-0.877863	-1.352306
C	1.033497	2.975123	0.243737	0.210436	0.674478
C	2.544739	2.949040	-0.160396	0.552448	0.664691
O	2.551128	2.062589	-1.265375	-0.742541	-1.299676
C	3.096165	4.300097	-0.593324	-0.811302	0.007411
H	2.988437	5.041444	0.204162	0.190165	-0.019187
H	4.160866	4.209179	-0.826157	0.166932	-0.031516
H	2.586391	4.670118	-1.483855	0.179806	-0.016064
C	0.210236	3.920869	-0.633592	-0.591593	-0.032931
H	-0.850945	3.747938	-0.437286	0.193477	-0.020740
H	0.429103	4.970746	-0.422354	0.185420	-0.022321
H	0.396648	3.731908	-1.693021	0.153245	-0.010663
C	3.430962	2.382254	0.954524	-0.638620	-0.032652
H	4.428761	2.198253	0.547747	0.186649	-0.028826
H	3.528337	3.076230	1.793973	0.182408	-0.027016
H	3.041594	1.431913	1.324666	0.163710	-0.015934
C	0.775413	3.299877	1.708651	-0.761694	-0.006902
H	-0.300363	3.300305	1.906080	0.183194	-0.027625
H	1.244949	2.572029	2.373247	0.172809	-0.026968
H	1.162838	4.290568	1.963012	0.209549	-0.012121
B	1.489264	1.073786	-1.075221	1.663205	2.000236
H	3.501522	-0.902612	-1.686852	0.148803	-0.104224
K	0.298007	-0.487766	1.447625	0.809944	1.101462
C	2.540249	-4.882213	0.826254	-0.356357	-0.089179
C	3.718337	-4.174694	0.630336	-0.322746	-0.039454
C	3.709055	-2.993472	-0.103642	-0.112779	-0.090542
C	2.527957	-2.509437	-0.655822	0.708754	-0.007896
C	1.351232	-3.233375	-0.461499	-0.098815	-0.118436
C	1.353512	-4.408313	0.277175	-0.313236	-0.045022
H	2.545444	-5.801306	1.401230	0.229972	0.058665

H	4.647606	-4.540146	1.053162	0.235013	0.054954
H	4.630941	-2.438516	-0.246471	0.230038	0.059006
H	0.425988	-2.873121	-0.900346	0.210096	0.076005
H	0.430637	-4.959876	0.418872	0.238418	0.055521
C	2.485600	-1.186557	-1.379381	-0.926680	0.843931
O	1.931234	-0.230945	-0.520967	-0.954733	-1.495378
H	1.881273	-1.280841	-2.294151	0.171238	-0.093387
O	-3.615826	-0.734333	-1.515552	-0.560962	-1.143594
C	-4.369078	-0.332221	-0.330744	0.332484	0.650770
C	-3.235382	0.173103	0.627633	0.246284	0.650120
O	-2.094010	-0.640925	0.196961	-0.979412	-1.202961
C	-2.849356	1.625403	0.390262	-0.846228	-0.063927
H	-3.629400	2.294740	0.757261	0.235806	0.018491
H	-1.922747	1.845372	0.922078	0.246204	0.017462
H	-2.679913	1.830453	-0.668514	0.205353	0.002798
C	-5.373389	0.730557	-0.723405	-0.808522	-0.026029
H	-6.134056	0.294427	-1.374057	0.198921	-0.000552
H	-5.870487	1.119391	0.168309	0.216171	0.018277
H	-4.901325	1.559176	-1.250513	0.188403	0.004415
C	-3.489100	-0.081996	2.098283	-0.990223	-0.034388
H	-2.684017	0.347602	2.700074	0.158883	-0.012438
H	-4.418587	0.404902	2.401453	0.239134	0.026849
H	-3.564180	-1.146337	2.320086	0.214724	0.009245
C	-5.079105	-1.576273	0.183904	-0.396890	-0.046105
H	-5.715620	-1.974091	-0.608635	0.212824	0.000326
H	-4.371546	-2.354343	0.479546	0.164579	-0.004033
H	-5.709811	-1.335765	1.041450	0.199490	0.016847
B	-2.359445	-0.991401	-1.090812	1.996356	1.891850
H	0.908463	0.859533	-2.156631	-0.190704	-0.487510
F	-1.440108	-1.555333	-1.866941	-0.349441	-0.815304

I8

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1357.986981

Electronic energy + zero-point energy: -1357.671969

Electronic energy + thermal energy correction: -1357.653198

Electronic energy + thermal enthalpy correction: -1357.652254

Electronic energy + thermal free energy correction: -1357.720507

BSSE correction: 0.003201778782

Table S57. Cartesian coordinates, Mulliken and APT charges of all atoms at **I8** in the reaction of benzaldehyde with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	1.745008	0.685103	-0.895282	-0.769652	-1.325849
C	2.931032	0.353821	-0.179710	0.333898	0.653181
C	2.495199	-0.909352	0.624730	-0.081859	0.656486
O	1.634571	-1.571535	-0.288388	-0.523626	-1.271933
C	3.645046	-1.832564	0.996627	-0.763684	-0.021099
H	4.394716	-1.303650	1.591472	0.196771	-0.007494
H	3.268542	-2.668098	1.591602	0.172746	-0.017608
H	4.125729	-2.238295	0.106516	0.169809	-0.006722
C	4.032756	0.037110	-1.189778	-0.513484	-0.054314
H	4.151395	0.891787	-1.859221	0.188197	-0.017452
H	4.991116	-0.151838	-0.701435	0.174029	-0.010030
H	3.765020	-0.835701	-1.788220	0.168099	0.002353
C	1.713476	-0.543956	1.889160	-0.496594	-0.060268
H	1.255593	-1.451829	2.287936	0.194444	-0.013457
H	2.358564	-0.116350	2.660281	0.189137	-0.014450
H	0.911123	0.161943	1.666549	0.163641	-0.018562
C	3.352225	1.535812	0.679402	-0.636306	-0.033349
H	3.637086	2.375417	0.040595	0.184524	-0.014326
H	2.549517	1.862905	1.342996	0.153485	-0.021033
H	4.214838	1.275785	1.298414	0.203527	0.002797
B	0.963337	-0.560151	-1.103297	1.317525	1.934838
H	-1.116174	-2.118354	-0.330589	0.151025	-0.079890
K	-0.178969	2.277264	-0.301830	0.934179	1.070694
C	-5.159851	0.187057	0.746148	-0.378006	-0.115660
C	-5.121817	-0.502179	-0.459565	-0.378774	-0.035506
C	-3.906370	-0.939644	-0.976366	-0.320897	-0.118747
C	-2.716538	-0.700875	-0.294233	0.844020	0.035619
C	-2.764770	-0.012765	0.918921	-0.160834	-0.139400
C	-3.975900	0.431185	1.435151	-0.371152	-0.035564
H	-6.104779	0.534172	1.146380	0.214718	0.067799
H	-6.038754	-0.692847	-1.004726	0.225970	0.065596
H	-3.880441	-1.466488	-1.924354	0.216326	0.067949
H	-1.844632	0.160603	1.467359	0.154798	0.074593
H	-3.997545	0.964466	2.378317	0.239487	0.063420
C	-1.395561	-1.185336	-0.840607	-0.584763	0.728106
O	-0.407506	-0.214035	-0.645179	-0.880779	-1.444274
H	-1.509857	-1.424404	-1.906253	0.163024	-0.075921
H	0.902518	-0.932629	-2.280844	-0.092968	-0.470522

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1358.068764

Electronic energy + zero-point energy: -1357.754582

Electronic energy + thermal energy correction: -1357.735679

Electronic energy + thermal enthalpy correction: -1357.734735

Electronic energy + thermal free energy correction: -1357.804113

BSSE correction: 0.003157133326

Table S58. Cartesian coordinates, Mulliken and APT charges of all atoms at **I8** in the reaction of benzaldehyde with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	1.736103	0.751641	-0.877774	-0.859993	-1.328440
C	2.896854	0.408496	-0.130847	0.431221	0.656149
C	2.474882	-0.931408	0.558576	0.264846	0.661607
O	1.664063	-1.541725	-0.430039	-0.674549	-1.282434
C	3.641536	-1.850500	0.892216	-0.786410	0.007848
H	4.352472	-1.354550	1.559656	0.197017	-0.016864
H	3.273689	-2.747109	1.398729	0.163124	-0.028608
H	4.170054	-2.164661	-0.008565	0.175575	-0.014748
C	4.060848	0.218751	-1.105295	-0.542416	-0.026681
H	4.176270	1.129871	-1.698027	0.186521	-0.027451
H	5.003411	0.029327	-0.585709	0.172887	-0.020046
H	3.866152	-0.610740	-1.788380	0.170111	-0.007729
C	1.646911	-0.702798	1.828390	-0.679364	-0.035178
H	1.220205	-1.658923	2.141961	0.195716	-0.023007
H	2.253736	-0.314418	2.650608	0.185208	-0.023996
H	0.816820	-0.017306	1.648096	0.180638	-0.023405
C	3.230846	1.537318	0.833954	-0.696873	-0.005621
H	3.495753	2.439461	0.275540	0.181115	-0.025096
H	2.394896	1.775115	1.495184	0.155786	-0.031735
H	4.084799	1.269243	1.462222	0.202724	-0.006243
B	0.993295	-0.492035	-1.191309	1.543713	1.975428
H	-1.054250	-2.126888	-0.469038	0.147026	-0.090935
K	-0.272631	2.266257	-0.173556	0.922618	1.067770
C	-5.065671	0.150876	0.803321	-0.406401	-0.097723
C	-5.044062	-0.295283	-0.510279	-0.361905	-0.034924
C	-3.851937	-0.730183	-1.080722	-0.354557	-0.099961
C	-2.672101	-0.731915	-0.345419	0.748557	0.017475
C	-2.704922	-0.286418	0.976846	-0.064230	-0.120084

C	-3.889893	0.154670	1.547212	-0.352757	-0.034262
H	-5.992644	0.495396	1.247588	0.222069	0.058679
H	-5.955278	-0.298345	-1.098127	0.232929	0.054888
H	-3.838962	-1.066964	-2.112444	0.221056	0.057866
H	-1.790542	-0.292651	1.562362	0.220566	0.065099
H	-3.899779	0.497864	2.575865	0.236580	0.054101
C	-1.366236	-1.187222	-0.948077	-0.614595	0.786822
O	-0.396823	-0.199475	-0.755230	-0.967550	-1.466845
H	-1.508574	-1.402626	-2.017124	0.141070	-0.095934
H	0.976221	-0.789631	-2.401204	-0.137075	-0.495779

I9

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1703.544257

Electronic energy + zero-point energy: -1703.117531

Electronic energy + thermal energy correction: -1703.090782

Electronic energy + thermal enthalpy correction: -1703.089838

Electronic energy + thermal free energy correction: -1703.176406

BSSE correction: 0.004797194489

Table S59. Cartesian coordinates, Mulliken and APT charges of all atoms at **I9** in the reaction of benzaldehyde with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	-2.714010	-1.019500	0.122919	-0.761680	-1.338202
C	-4.054961	-0.575495	-0.059889	0.469668	0.666462
C	-3.857483	0.815282	-0.736555	-0.173974	0.663762
O	-2.730586	0.591118	-1.569990	-0.503200	-1.283245
C	-5.035571	1.261965	-1.587985	-0.792060	-0.019763
H	-5.951060	1.312993	-0.992254	0.196640	-0.008967
H	-4.839699	2.257458	-1.993538	0.173758	-0.018695
H	-5.197919	0.580472	-2.422956	0.171812	-0.006428
C	-4.770031	-1.563924	-0.979489	-0.511164	-0.056346
H	-4.695260	-2.563580	-0.546062	0.187201	-0.017879
H	-5.827874	-1.318910	-1.096439	0.176637	-0.010356
H	-4.301382	-1.579162	-1.965275	0.166148	0.001502
C	-3.528383	1.908107	0.283823	-0.516542	-0.065920
H	-3.199118	2.798404	-0.256575	0.192534	-0.015148

H	-4.397335	2.175793	0.889707	0.188945	-0.016264
H	-2.715710	1.597824	0.943350	0.162944	-0.006070
C	-4.760031	-0.529923	1.286704	-0.688397	-0.035573
H	-4.859719	-1.541989	1.686953	0.184452	-0.015541
H	-4.211007	0.075633	2.009875	0.158359	-0.016641
H	-5.763346	-0.108232	1.184496	0.203061	0.001099
B	-1.863936	-0.382681	-0.907761	1.377310	1.938897
H	-0.246693	1.600277	-1.620829	0.159154	-0.064342
K	-1.136038	-0.982671	2.112288	0.858218	1.114902
C	3.540233	2.599652	1.102767	-0.367739	-0.123140
C	3.594403	2.395182	-0.274685	-0.275924	-0.021200
C	2.518632	1.821803	-0.935213	-0.171402	-0.127266
C	1.366907	1.447658	-0.238932	0.748041	0.071947
C	1.316112	1.668609	1.131934	0.041052	-0.137502
C	2.397544	2.237698	1.801943	-0.481590	-0.026856
H	4.383170	3.038951	1.622547	0.223866	0.068131
H	4.482945	2.672800	-0.830051	0.234166	0.063834
H	2.570310	1.648582	-2.005903	0.223574	0.065592
H	0.416879	1.417891	1.679453	0.167869	0.058088
H	2.341214	2.400323	2.871957	0.233386	0.061675
C	0.224784	0.823514	-1.001720	-0.931406	0.656689
O	-0.722912	0.228096	-0.166214	-0.959076	-1.425971
H	0.644262	0.085477	-1.704245	0.216113	-0.072127
H	-1.399150	-1.177755	-1.736244	-0.012514	-0.471316
C	5.343254	-0.855387	-1.170285	-0.243615	0.047083
C	4.353578	-1.236330	-2.068951	-0.358384	-0.149871
C	3.099243	-1.597802	-1.595950	-0.327081	0.020343
C	2.843821	-1.581160	-0.226805	0.545692	-0.447679
C	3.839034	-1.200301	0.675151	0.217059	0.010654
C	5.088281	-0.838599	0.200737	-0.313575	-0.159054
H	6.320972	-0.566649	-1.537494	0.237021	0.078009
H	4.558688	-1.246392	-3.132143	0.243554	0.078782
H	2.310901	-1.889341	-2.282126	0.229651	0.089312
H	3.618315	-1.185214	1.735938	0.252821	0.100984
H	5.865485	-0.535182	0.891411	0.241596	0.075479
C	1.495856	-1.935598	0.245288	-0.508673	1.332786
O	1.186362	-2.000604	1.418740	-0.360920	-1.107099
H	0.754379	-2.148905	-0.543180	0.176613	-0.001551

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1703.648639

Electronic energy + zero-point energy: -1703.223142

Electronic energy + thermal energy correction: -1703.196975

Electronic energy + thermal enthalpy correction: -1703.196031

Electronic energy + thermal free energy correction: -1703.281973

BSSE correction: 0.004520750419

Table S60. Cartesian coordinates, Mulliken and APT charges of all atoms at **I9** in the reaction of benzaldehyde with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	-2.648348	-1.007946	0.215509	-0.879157	-1.340122
C	-4.006001	-0.631490	0.020407	0.590108	0.669754
C	-3.877600	0.671746	-0.834872	0.127487	0.667697
O	-2.752362	0.392458	-1.649234	-0.679073	-1.290600
C	-5.083253	0.953782	-1.720055	-0.827398	0.008049
H	-5.994215	1.050260	-1.121985	0.196279	-0.018096
H	-4.934423	1.892716	-2.260458	0.165760	-0.029285
H	-5.231178	0.161104	-2.454475	0.177939	-0.015124
C	-4.716046	-1.755605	-0.735488	-0.536191	-0.027149
H	-4.599685	-2.686820	-0.175010	0.189054	-0.027271
H	-5.784977	-1.559504	-0.850431	0.175042	-0.019989
H	-4.278181	-1.895930	-1.726039	0.166425	-0.008202
C	-3.591761	1.907815	0.025263	-0.641395	-0.038047
H	-3.314979	2.734024	-0.634641	0.188788	-0.024165
H	-4.465800	2.214087	0.606251	0.185650	-0.025894
H	-2.756437	1.734759	0.706356	0.175038	-0.014223
C	-4.673378	-0.435636	1.374347	-0.736748	-0.010463
H	-4.711475	-1.386772	1.912952	0.185371	-0.025449
H	-4.138297	0.288855	1.991959	0.166164	-0.025338
H	-5.699676	-0.078041	1.253359	0.201620	-0.007092
B	-1.838806	-0.459714	-0.892859	1.496592	1.967998
H	-0.248176	1.513182	-1.807135	0.169615	-0.087675
K	-1.088865	-0.633478	2.220197	0.856739	1.110571
C	3.492654	2.788226	0.864590	-0.354560	-0.114829
C	3.621373	2.345065	-0.447596	-0.379002	-0.007114
C	2.563070	1.704273	-1.072554	-0.087086	-0.115583
C	1.356010	1.497917	-0.405761	0.924234	0.064515
C	1.230091	1.962878	0.897657	-0.078402	-0.129277
C	2.291861	2.598430	1.532995	-0.456226	-0.016501
H	4.322981	3.278685	1.359804	0.223923	0.057173
H	4.555654	2.486614	-0.979564	0.237514	0.053848
H	2.677642	1.341636	-2.089236	0.235444	0.054854
H	0.285477	1.849435	1.415203	0.225792	0.055610

H	2.175950	2.948981	2.552683	0.234460	0.052531
C	0.227199	0.796680	-1.119752	-0.980652	0.696403
O	-0.715452	0.269369	-0.238524	-1.027893	-1.441295
H	0.657254	0.004508	-1.753312	0.229462	-0.079790
H	-1.348500	-1.328899	-1.640613	-0.077128	-0.486918
C	5.302342	-1.068651	-1.151415	-0.182668	0.068601
C	4.271109	-1.520221	-1.964457	-0.459798	-0.150585
C	3.034497	-1.808232	-1.407208	-0.458709	0.045648
C	2.835062	-1.648696	-0.038216	0.897112	-0.482365
C	3.873625	-1.195721	0.776343	0.094018	0.035920
C	5.104942	-0.906323	0.217847	-0.433215	-0.165641
H	6.268126	-0.836709	-1.585850	0.243292	0.068779
H	4.430381	-1.641650	-3.029166	0.243251	0.069979
H	2.215545	-2.152321	-2.030371	0.238234	0.082132
H	3.701217	-1.065307	1.838225	0.271125	0.094599
H	5.914186	-0.547209	0.842550	0.241634	0.066657
C	1.504894	-1.931703	0.514870	-0.534000	1.359756
O	1.226735	-1.868799	1.697605	-0.389035	-1.110578
H	0.735332	-2.212885	-0.225018	0.245169	-0.016418

TS2

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1703.526008

Electronic energy + zero-point energy: -1703.100463

Electronic energy + thermal energy correction: -1703.074694

Electronic energy + thermal enthalpy correction: -1703.073749

Electronic energy + thermal free energy correction: -1703.157275

BSSE correction: 0.005073508446

Table S61. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS2** in the reaction of benzaldehyde with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	2.217909	-0.342541	0.753150	-0.671058	-1.449009
C	3.501317	-0.225500	0.132773	0.184865	0.710212
C	3.173230	-0.578626	-1.350767	-0.094642	0.711426
O	1.870092	-0.010654	-1.526750	-0.484711	-1.484828
C	4.131282	0.026626	-2.360889	-0.769440	-0.036323

H	5.154174	-0.307684	-2.169139	0.201747	-0.003427
H	3.853613	-0.291907	-3.368127	0.181288	-0.012019
H	4.105964	1.115618	-2.327495	0.178014	-0.002189
C	3.986344	1.214089	0.290364	-0.405467	-0.068261
H	3.975133	1.473305	1.351012	0.203030	-0.007634
H	5.004970	1.335159	-0.083880	0.206893	-0.002286
H	3.333757	1.908297	-0.242535	0.124331	0.001390
C	3.067221	-2.086371	-1.569413	-0.437343	-0.082676
H	2.640487	-2.266871	-2.558073	0.203451	-0.009076
H	4.044240	-2.572399	-1.522773	0.192105	-0.016051
H	2.411589	-2.539372	-0.822769	0.121045	0.005178
C	4.471365	-1.177810	0.807696	-0.812142	-0.033725
H	4.673581	-0.838956	1.826307	0.177595	-0.012902
H	4.066260	-2.188512	0.854315	0.177584	0.000651
H	5.419795	-1.204814	0.265345	0.203505	-0.002372
B	1.243434	0.035717	-0.238923	1.471171	2.463495
H	-0.506501	-1.085224	-1.969751	0.186412	-0.062448
K	0.458338	-0.781421	2.586290	0.847725	1.065058
C	-4.500788	-2.836479	-0.048953	-0.356272	-0.117744
C	-4.541642	-1.809497	-0.987148	-0.439949	-0.031005
C	-3.387685	-1.101482	-1.295481	-0.017779	-0.120283
C	-2.175744	-1.409740	-0.678615	0.761138	0.059756
C	-2.141419	-2.443163	0.253433	-0.083848	-0.135876
C	-3.297352	-3.150985	0.569415	-0.390130	-0.031784
H	-5.401315	-3.385583	0.198247	0.221911	0.069489
H	-5.476286	-1.554872	-1.472928	0.234130	0.065608
H	-3.425187	-0.291642	-2.017271	0.217290	0.068231
H	-1.201042	-2.709173	0.721088	0.199930	0.075760
H	-3.254723	-3.952201	1.297906	0.236031	0.064085
C	-0.931357	-0.647614	-1.057673	-0.825436	0.662790
O	0.021055	-0.695530	-0.023012	-0.906604	-1.420618
H	-1.204663	0.387766	-1.296278	0.172313	-0.039553
H	0.904092	1.321669	-0.014837	0.158224	-0.942188
C	-3.423199	2.778273	-0.833466	-0.355271	-0.083398
C	-2.284468	3.378554	-1.366317	-0.250983	-0.050287
C	-1.058425	3.216686	-0.737235	-0.342305	-0.100547
C	-0.960081	2.452960	0.423056	0.102576	-0.187733
C	-2.100402	1.870181	0.963396	0.458642	-0.103413
C	-3.330009	2.029513	0.334419	-0.261338	-0.054167
H	-4.380706	2.899476	-1.325990	0.227692	0.069649
H	-2.356169	3.969587	-2.271584	0.237485	0.066545
H	-0.163542	3.668785	-1.154480	0.230274	0.070764
H	-2.017046	1.293815	1.877479	0.250795	0.085248
H	-4.215959	1.566231	0.753077	0.220056	0.060682
C	0.376670	2.251849	1.082059	-0.602485	1.773408

O	0.454585	1.725656	2.213028	-0.506135	-1.270829
H	1.131609	2.993673	0.772986	0.224088	-0.174775

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1703.630627

Electronic energy + zero-point energy: -1703.205457

Electronic energy + thermal energy correction: -1703.179624

Electronic energy + thermal enthalpy correction: -1703.178680

Electronic energy + thermal free energy correction: -1703.262843

BSSE correction: 0.004691203360

Table S62. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS2** in the reaction of benzaldehyde with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	2.215328	-0.495786	0.723781	-0.815631	-1.455489
C	3.512192	-0.227529	0.192908	0.271585	0.711179
C	3.269445	-0.383163	-1.345471	0.173858	0.714973
O	1.938125	0.112483	-1.506261	-0.699356	-1.485246
C	4.218520	0.428167	-2.211687	-0.812851	-0.008318
H	5.256562	0.141355	-2.021183	0.201669	-0.013632
H	4.006111	0.243162	-3.267946	0.176522	-0.023811
H	4.112911	1.497679	-2.026675	0.176114	-0.010461
C	3.915543	1.195293	0.581382	-0.455102	-0.040254
H	3.852481	1.295360	1.667538	0.204299	-0.018886
H	4.940737	1.418286	0.276569	0.206107	-0.012128
H	3.250669	1.935032	0.131133	0.136180	-0.006781
C	3.291514	-1.846088	-1.789680	-0.476047	-0.054745
H	2.919207	-1.907844	-2.815126	0.200101	-0.019174
H	4.302242	-2.261544	-1.768750	0.188427	-0.027951
H	2.647677	-2.459034	-1.155293	0.138994	-0.003135
C	4.503668	-1.217539	0.779747	-0.851941	-0.004808
H	4.635731	-1.022674	1.847361	0.173560	-0.024031
H	4.160613	-2.245704	0.659973	0.187276	-0.008293
H	5.479160	-1.116474	0.296369	0.203484	-0.012601
B	1.258473	-0.048679	-0.255374	2.121429	2.498480
H	-0.557339	-1.043943	-2.126244	0.198482	-0.087344
K	0.367657	-1.046394	2.496105	0.819418	1.061978
C	-4.548058	-2.763077	-0.159566	-0.325832	-0.109037

C	-4.573529	-1.651611	-0.994214	-0.513497	-0.019971
C	-3.396753	-0.983530	-1.300356	-0.023163	-0.106158
C	-2.176757	-1.415549	-0.785255	0.758294	0.053317
C	-2.158427	-2.534348	0.041475	-0.280248	-0.129888
C	-3.336242	-3.203032	0.355334	-0.357760	-0.022288
H	-5.467366	-3.281933	0.087376	0.226797	0.059506
H	-5.515156	-1.297558	-1.399035	0.230496	0.055064
H	-3.424254	-0.106115	-1.938835	0.234722	0.055230
H	-1.213371	-2.896125	0.429943	0.230892	0.070551
H	-3.304964	-4.072160	1.003189	0.237959	0.053020
C	-0.910617	-0.683312	-1.150278	-0.651723	0.685099
O	0.083626	-0.882238	-0.180522	-1.115187	-1.450627
H	-1.138992	0.382611	-1.270517	0.229673	-0.033211
H	0.820485	1.164271	0.115100	-0.148941	-0.934984
C	-3.390923	2.939481	-0.765963	-0.296966	-0.072476
C	-2.201439	3.489102	-1.234229	-0.298661	-0.042235
C	-1.010178	3.221058	-0.577937	-0.334726	-0.091509
C	-0.996211	2.399698	0.545403	0.337370	-0.208429
C	-2.187124	1.863023	1.018044	0.215647	-0.096855
C	-3.381758	2.130416	0.362988	-0.426486	-0.048445
H	-4.323098	3.144596	-1.280240	0.228928	0.058738
H	-2.205951	4.125345	-2.112131	0.237930	0.057060
H	-0.076812	3.636348	-0.946894	0.236169	0.062208
H	-2.170811	1.233834	1.900764	0.266854	0.081771
H	-4.307468	1.702078	0.730560	0.232978	0.051753
C	0.303371	2.093225	1.236925	-0.476368	1.820664
O	0.319605	1.517282	2.345198	-0.540840	-1.279381
H	1.112239	2.797986	0.978881	0.219112	-0.188008

TS3

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1869.144970

Electronic energy + zero-point energy: -1868.643789

Electronic energy + thermal energy correction: -1868.614442

Electronic energy + thermal enthalpy correction: -1868.613498

Electronic energy + thermal free energy correction: -1868.702435

BSSE correction: 0.008337969786

Table S65. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS3** in the reaction of benzaldehyde with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	-0.704106	1.615936	0.652422	-0.796651	-1.367781
C	-1.045797	2.988079	0.456140	-0.098330	0.688407
C	0.010765	3.451929	-0.594089	0.113440	0.666467
O	0.166395	2.289014	-1.404820	-0.530666	-1.337227
C	-0.440827	4.613119	-1.463191	-0.821870	-0.025078
H	-0.691422	5.482457	-0.849457	0.199308	-0.005695
H	0.365946	4.898771	-2.142117	0.175332	-0.015924
H	-1.310966	4.343427	-2.061409	0.174078	-0.004417
C	-2.470215	3.063697	-0.089748	-0.374057	-0.066106
H	-3.145803	2.573111	0.613682	0.200596	-0.013008
H	-2.798245	4.098107	-0.212553	0.214542	-0.009236
H	-2.543409	2.554860	-1.053438	0.167796	-0.000449
C	1.354166	3.789460	0.055393	-0.467557	-0.074983
H	2.099741	3.916187	-0.732508	0.208709	-0.013113
H	1.303257	4.717355	0.629704	0.194339	-0.012677
H	1.681396	2.981383	0.712699	0.124582	0.012656
C	-0.970237	3.716619	1.788071	-0.817455	-0.032644
H	-1.754996	3.349238	2.453911	0.170780	-0.015645
H	-0.006188	3.558931	2.272443	0.170113	-0.006412
H	-1.120100	4.790707	1.650352	0.204971	-0.002781
B	0.006160	1.144346	-0.537196	1.447895	2.116872
H	2.769720	1.334233	-1.178283	0.105541	-0.068189
K	0.305126	-0.169675	2.208519	0.873197	1.094445
C	5.235087	-2.434961	0.427552	-0.209402	-0.118329
C	5.624610	-1.308902	-0.287659	-0.452483	-0.036986
C	4.669856	-0.402808	-0.736533	-0.360223	-0.118357
C	3.315430	-0.610958	-0.486396	0.638899	0.039455
C	2.933519	-1.747118	0.226835	-0.179546	-0.127738
C	3.885036	-2.651219	0.683638	-0.596464	-0.035928
H	5.977456	-3.138554	0.784585	0.219131	0.068073
H	6.674271	-1.129395	-0.488517	0.224542	0.064004
H	4.979887	0.482442	-1.282034	0.227540	0.066562
H	1.879806	-1.932716	0.399779	-0.012059	0.085993
H	3.572437	-3.529422	1.236490	0.229581	0.062233
C	2.285421	0.368457	-0.994437	-0.126479	0.733051
O	1.244211	0.510322	-0.066747	-0.851478	-1.442811
H	1.898232	0.017019	-1.959884	0.189422	-0.065356
O	-2.015961	-1.679010	-1.694434	-0.492994	-1.305031
C	-2.958460	-2.308700	-0.796673	0.433793	0.664975

C	-2.497791	-1.780525	0.599625	-0.411747	0.659102
O	-1.063319	-1.619300	0.403467	-0.787555	-1.310067
C	-3.096895	-0.420773	0.922041	-0.322235	-0.079946
H	-4.168530	-0.512239	1.107835	0.238752	0.016447
H	-2.634497	-0.010268	1.821794	0.207745	-0.015085
H	-2.926164	0.284993	0.110602	0.065185	0.035522
C	-4.366625	-1.908416	-1.187989	-0.753468	-0.039977
H	-4.608916	-2.340104	-2.160899	0.194642	0.000764
H	-5.084742	-2.288324	-0.457694	0.207431	0.014550
H	-4.470262	-0.826160	-1.254717	0.195453	0.005808
C	-2.724264	-2.748109	1.744367	-0.855975	-0.044847
H	-2.416115	-2.290643	2.687928	0.160238	-0.008841
H	-3.786846	-2.988858	1.823772	0.228173	0.019647
H	-2.163938	-3.672004	1.606690	0.191202	0.009861
C	-2.779367	-3.815816	-0.938198	-0.390293	-0.072712
H	-2.932802	-4.090116	-1.983064	0.200680	0.001549
H	-1.773520	-4.124327	-0.644781	0.173097	0.001600
H	-3.503756	-4.358481	-0.328417	0.194225	0.006997
B	-0.866609	-1.451816	-0.963441	1.707657	2.379379
H	-0.679480	0.261720	-1.166053	0.393182	-0.680927
F	0.336128	-1.745130	-1.500749	-0.556801	-0.940117

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1869.276172

Electronic energy + zero-point energy: -1868.776541

Electronic energy + thermal energy correction: -1868.746724

Electronic energy + thermal enthalpy correction: -1868.745780

Electronic energy + thermal free energy correction: -1868.837009

BSSE correction: 0.007793767757

Table S66. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS3** in the reaction of benzaldehyde with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	-0.454813	1.626644	0.738451	-0.896140	-1.379924
C	-0.764172	3.007256	0.569938	0.131163	0.693817
C	0.197348	3.433071	-0.590297	0.389201	0.670921
O	0.249142	2.257296	-1.392464	-0.748256	-1.342858
C	-0.313154	4.590432	-1.433729	-0.828885	0.001614

H	-0.480962	5.477560	-0.816333	0.200166	-0.014204
H	0.426834	4.846154	-2.196874	0.167633	-0.026576
H	-1.245680	4.335209	-1.938307	0.172660	-0.012294
C	-2.236975	3.137378	0.179441	-0.535157	-0.043372
H	-2.855037	2.685936	0.958890	0.209511	-0.021828
H	-2.535538	4.183574	0.078019	0.214869	-0.017843
H	-2.441246	2.623095	-0.762450	0.194027	-0.010339
C	1.607857	3.756343	-0.088286	-0.547551	-0.049122
H	2.272523	3.851736	-0.950578	0.203007	-0.024521
H	1.635264	4.697742	0.466686	0.189422	-0.022941
H	1.991102	2.958096	0.550121	0.142945	0.009071
C	-0.525050	3.733862	1.884576	-0.876626	-0.005552
H	-1.244984	3.391618	2.633098	0.166986	-0.026668
H	0.479153	3.547474	2.267280	0.177759	-0.012216
H	-0.656031	4.812683	1.761255	0.203077	-0.012862
B	0.135893	1.130251	-0.500580	1.735772	2.167243
H	2.835369	1.081800	-1.444073	0.154790	-0.080428
K	0.464675	-0.417453	2.115009	0.878263	1.089594
C	5.196665	-2.644272	0.421037	-0.312739	-0.096288
C	5.624065	-1.439958	-0.119145	-0.418387	-0.036385
C	4.697008	-0.531470	-0.620083	-0.485101	-0.098063
C	3.336444	-0.816509	-0.594951	0.721421	0.014945
C	2.917402	-2.033206	-0.055175	0.100420	-0.122248
C	3.837291	-2.939004	0.451829	-0.468752	-0.033823
H	5.916876	-3.351533	0.816601	0.223703	0.058779
H	6.681466	-1.200932	-0.145255	0.231759	0.054950
H	5.036632	0.414183	-1.030667	0.222709	0.057292
H	1.859993	-2.275662	-0.050982	0.182731	0.081621
H	3.495359	-3.880946	0.866425	0.232322	0.053308
C	2.322483	0.166815	-1.124099	-0.579090	0.786492
O	1.382727	0.453896	-0.124223	-0.907566	-1.481817
H	1.830292	-0.255464	-2.009948	0.177943	-0.072026
O	-2.299407	-1.349185	-1.654331	-0.671895	-1.308989
C	-3.295929	-1.892957	-0.762821	0.493312	0.671894
C	-2.643206	-1.705462	0.656152	-0.063450	0.660668
O	-1.221911	-1.709551	0.350582	-0.831823	-1.311831
C	-2.992874	-0.369011	1.293936	-0.558342	-0.068974
H	-4.059528	-0.314039	1.517984	0.230247	0.014297
H	-2.463669	-0.258013	2.244005	0.212623	-0.032503
H	-2.711824	0.462430	0.651317	0.102503	0.046256
C	-4.596760	-1.137429	-0.960369	-0.819266	-0.016887
H	-4.981233	-1.330885	-1.964333	0.187053	-0.009387
H	-5.346466	-1.473168	-0.239758	0.209117	0.005677
H	-4.458026	-0.062035	-0.847673	0.199307	-0.003661
C	-2.924190	-2.834428	1.630696	-0.923828	-0.019711

H	-2.444225	-2.624609	2.589931	0.166994	-0.017255
H	-3.999275	-2.919504	1.806817	0.229643	0.007659
H	-2.552769	-3.790938	1.263997	0.198395	0.001346
C	-3.483190	-3.358478	-1.143592	-0.416101	-0.044946
H	-3.777006	-3.413786	-2.193820	0.203525	-0.008175
H	-2.559248	-3.927604	-1.018411	0.157805	-0.008307
H	-4.265706	-3.828214	-0.544260	0.194498	-0.004385
B	-1.089927	-1.401526	-0.997141	1.869510	2.410009
H	-0.632140	0.256884	-1.050042	0.158670	-0.705517
F	0.019866	-1.822389	-1.653299	-0.548508	-0.952726

I1B

HF/6-31G(d), N,N-dimethylformamide solution

Electronic energy: -1042.060740

Electronic energy + zero-point energy: -1041.939655

Electronic energy + thermal energy correction: -1041.930445

Electronic energy + thermal enthalpy correction: -1041.929501

Electronic energy + thermal free energy correction: -1041.976773

Table S67. Cartesian coordinates, Mulliken and APT charges of all atoms at **I1B** in the reaction of benzaldehyde with pinacolborane (HF/6-31G(d), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	-3.360370	-0.398425	-0.500711	-0.233974	-0.045281
C	-2.950639	0.920772	-0.348642	-0.233818	-0.041107
C	-1.670244	1.200745	0.097798	-0.241816	-0.032767
C	-0.781522	0.172277	0.397668	-0.077133	-0.200638
C	-1.199956	-1.141436	0.249001	-0.245994	-0.071620
C	-2.483189	-1.427792	-0.199974	-0.229982	-0.022725
H	-4.355624	-0.618162	-0.845394	0.227612	0.033313
H	-3.628313	1.724764	-0.577088	0.227640	0.030456
H	-1.357570	2.224378	0.214512	0.228646	0.037173
H	-0.517905	-1.933755	0.494239	0.236107	0.075569
H	-2.796660	-2.451410	-0.310234	0.226437	0.027796
C	0.618515	0.477233	0.903603	0.573880	1.924906
O	1.372431	-0.492661	1.201755	-0.834338	-1.378660
H	0.600383	1.327383	1.588831	0.112791	-0.236590
F	1.224769	1.251737	-0.336585	-0.594480	-1.108933
K	3.211461	-0.337778	-0.565374	0.858423	1.009108

HF/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1042.259846

Electronic energy + zero-point energy: -1042.141633

Electronic energy + thermal energy correction: -1042.131103

Electronic energy + thermal enthalpy correction: -1042.130159

Electronic energy + thermal free energy correction: -1042.182192

Table S68. Cartesian coordinates, Mulliken and APT charges of all atoms at **I1B** in the reaction of benzaldehyde with pinacolborane (HF/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	-4.159969	-0.249862	-0.291409	-0.141837	0.137503
C	-3.745952	1.036885	-0.004588	-0.400382	-0.201597
C	-2.402079	1.290653	0.207592	-0.682819	0.066048
C	-1.479778	0.259105	0.133051	0.773240	-0.486815
C	-1.901743	-1.035092	-0.156385	0.105040	0.059848
C	-3.238852	-1.287385	-0.368020	-0.363948	-0.223693
H	-5.202653	-0.451024	-0.457281	0.222209	0.067613
H	-4.461363	1.835869	0.053351	0.222046	0.071009
H	-2.069346	2.288472	0.430440	0.222654	0.081509
H	-1.182254	-1.829711	-0.213713	0.243939	0.092575
H	-3.570452	-2.284203	-0.592181	0.223261	0.067608
C	-0.058582	0.565511	0.364865	-0.022114	1.526490
O	0.824004	-0.243020	0.330140	-0.625881	-1.282477
H	0.163711	1.610787	0.579947	0.239882	-0.022012
F	5.011588	0.913977	-0.866047	-0.947591	-1.020422
K	3.502514	-0.575301	0.318005	0.932300	1.066814

B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1045.610913

Electronic energy + zero-point energy: -1045.500154

Electronic energy + thermal energy correction: -1045.489236

Electronic energy + thermal enthalpy correction: -1045.488292

Electronic energy + thermal free energy correction: -1045.541306

Table S69. Cartesian coordinates, Mulliken and APT charges of all atoms at **I1B** in the reaction of benzaldehyde with pinacolborane (B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	-4.176710	-0.224921	-0.270091	-0.106882	0.082766
C	-3.735301	1.064610	0.014078	-0.332677	-0.160871
C	-2.380329	1.299982	0.210607	-0.514795	0.073486
C	-1.464924	0.245076	0.123540	0.641213	-0.518682
C	-1.915675	-1.051092	-0.162897	-0.033146	0.059795
C	-3.267415	-1.281964	-0.358579	-0.264668	-0.175858
H	-5.233319	-0.411030	-0.424312	0.189387	0.068269
H	-4.444694	1.880540	0.081289	0.189272	0.068895
H	-2.022655	2.299754	0.431716	0.188707	0.080266
H	-1.200602	-1.861870	-0.229257	0.200317	0.091416
H	-3.621033	-2.281736	-0.580541	0.190533	0.065912
C	-0.044137	0.532564	0.335839	0.019496	1.411853
O	0.851806	-0.299420	0.287440	-0.534924	-1.173196
H	0.193634	1.588090	0.552671	0.191397	-0.029693
F	4.985308	0.907300	-0.854132	-0.916451	-1.020567
K	3.502811	-0.552085	0.326375	0.893222	1.076208

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1045.400361

Electronic energy + zero-point energy: -1045.288380

Electronic energy + thermal energy correction: -1045.277512

Electronic energy + thermal enthalpy correction: -1045.276568

Electronic energy + thermal free energy correction: -1045.329513

Table S70. Cartesian coordinates, Mulliken and APT charges of all atoms at **I1B** in the reaction of benzaldehyde with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	-4.138411	-0.278233	-0.276889	-0.169684	0.059130
C	-3.737709	1.025243	-0.009936	-0.380328	-0.162499
C	-2.392363	1.301929	0.191543	-0.605081	0.034580
C	-1.455241	0.272896	0.125923	0.583397	-0.477608
C	-1.859784	-1.036536	-0.142609	0.027873	0.024476
C	-3.201355	-1.309072	-0.343875	-0.290189	-0.177925

H	-5.187792	-0.496512	-0.435106	0.227866	0.081554
H	-4.470493	1.820713	0.040434	0.230673	0.082590
H	-2.061214	2.313656	0.399604	0.222085	0.092076
H	-1.117621	-1.824216	-0.191306	0.228299	0.104294
H	-3.525005	-2.320998	-0.553275	0.233079	0.078320
C	-0.038802	0.597351	0.344499	-0.030060	1.380195
O	0.858400	-0.222042	0.318057	-0.482572	-1.161559
H	0.182107	1.658769	0.541987	0.225466	-0.010836
F	4.936577	0.881252	-0.849090	-0.923258	-1.021683
K	3.464506	-0.565674	0.313846	0.902434	1.074895

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1045.441814

Electronic energy + zero-point energy: -1045.330022

Electronic energy + thermal energy correction: -1045.319117

Electronic energy + thermal enthalpy correction: -1045.318173

Electronic energy + thermal free energy correction: -1045.371336

Table S71. Cartesian coordinates, Mulliken and APT charges of all atoms at **I1B** in the reaction of benzaldehyde with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	-4.181724	-0.127620	-0.240224	-0.174982	0.076266
C	-3.674628	1.129062	0.062959	-0.383473	-0.159126
C	-2.308845	1.293852	0.237746	-0.609217	0.052449
C	-1.454054	0.200557	0.109168	0.730136	-0.500683
C	-1.967876	-1.061514	-0.195811	0.010701	0.043353
C	-3.330045	-1.222532	-0.369874	-0.339553	-0.176737
H	-5.248982	-0.258665	-0.377994	0.237617	0.071388
H	-4.342400	1.976340	0.161915	0.238773	0.071869
H	-1.898077	2.269916	0.474616	0.232634	0.084494
H	-1.292932	-1.903648	-0.293838	0.240629	0.094867
H	-3.735906	-2.198726	-0.607184	0.239230	0.070014
C	-0.013957	0.409439	0.299950	-0.111162	1.399512
O	0.825059	-0.467568	0.215923	-0.512715	-1.149207
H	0.285834	1.445697	0.533506	0.228296	-0.026625
F	4.962890	0.957713	-0.839124	-0.925814	-1.019506
K	3.502776	-0.523013	0.342644	0.898901	1.067673

I3B

HF/6-31G(d), N,N-dimethylformamide solution

Electronic energy: -1451.393981

Electronic energy + zero-point energy: -1451.065422

Electronic energy + thermal energy correction: -1451.046995

Electronic energy + thermal enthalpy correction: -1451.046050

Electronic energy + thermal free energy correction: -1451.113815

Table S72. Cartesian coordinates, Mulliken and APT charges of all atoms at **I3B** in the reaction of benzaldehyde with pinacolborane (HF/6-31G(d), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	-5.404099	-0.516986	-0.285832	-0.226867	-0.019674
C	-4.828206	-0.766918	0.953818	-0.231880	-0.055528
C	-3.455770	-0.685534	1.108930	-0.232124	-0.047067
C	-2.640936	-0.350743	0.029817	-0.112113	-0.129617
C	-3.220140	-0.106997	-1.206244	-0.229264	-0.068506
C	-4.598533	-0.189561	-1.362922	-0.230404	-0.039069
H	-6.470840	-0.581467	-0.407967	0.233089	0.038260
H	-5.447827	-1.025113	1.794273	0.233230	0.036484
H	-3.015418	-0.882212	2.070490	0.240563	0.051863
H	-2.597611	0.143748	-2.043536	0.248844	0.080784
H	-5.037447	0.001658	-2.326245	0.232474	0.035512
C	-1.141040	-0.293472	0.221178	0.602288	1.629309
O	-0.498575	0.232574	-0.822321	-0.765487	-1.502335
H	-0.744104	-1.247166	0.524459	0.198649	-0.078966
F	-0.921100	0.539573	1.361294	-0.483599	-0.932550
K	0.210363	2.713612	0.272875	0.834183	1.042183
O	1.361062	-1.405196	-0.701705	-0.748099	-1.339398
C	2.469152	-1.279020	0.160228	0.325081	0.715796
C	3.010129	0.154844	-0.165596	0.327530	0.698851
O	1.833474	0.841287	-0.528136	-0.810298	-1.405338
C	3.669461	0.880268	1.004714	-0.516825	0.100852
H	4.533721	0.334919	1.372008	0.170184	-0.043959
H	4.010574	1.859906	0.681589	0.172843	-0.058019
H	2.981590	1.022615	1.829604	0.176402	-0.052710
C	1.989119	-1.415265	1.610222	-0.523644	0.058721
H	1.455510	-2.355191	1.714926	0.165099	-0.059641
H	2.815905	-1.422680	2.313722	0.161264	-0.056059
H	1.312903	-0.616265	1.886476	0.174510	-0.029145
C	3.973500	0.173849	-1.359295	-0.511836	0.073845

H	4.141508	1.205069	-1.655223	0.167515	-0.062556
H	4.935027	-0.265402	-1.114052	0.163234	-0.053037
H	3.566394	-0.353750	-2.213884	0.174415	-0.042501
C	3.450876	-2.412656	-0.131213	-0.502727	0.105693
H	2.995017	-3.363377	0.129460	0.163883	-0.060374
H	3.715353	-2.452617	-1.180422	0.170509	-0.050453
H	4.362229	-2.310831	0.451269	0.160444	-0.054969
B	0.925326	-0.115674	-1.179900	0.946823	2.126730
H	0.945134	-0.028419	-2.413258	-0.317886	-0.553412

HF/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1451.668336

Electronic energy + zero-point energy: -1451.344156

Electronic energy + thermal energy correction: -1451.325575

Electronic energy + thermal enthalpy correction: -1451.324631

Electronic energy + thermal free energy correction: -1451.392737

Table S73. Cartesian coordinates, Mulliken and APT charges of all atoms at **I3B** in the reaction of benzaldehyde with pinacolborane (HF/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	-5.393998	-0.538800	-0.303744	-0.239949	-0.034974
C	-4.756198	-1.251564	0.697976	-0.324853	-0.077005
C	-3.386386	-1.149723	0.852210	-0.169235	-0.064859
C	-2.641542	-0.334807	0.012589	0.608988	-0.137811
C	-3.281813	0.369895	-0.991794	0.014312	-0.082907
C	-4.654685	0.269508	-1.147805	-0.432913	-0.061919
H	-6.458648	-0.618716	-0.428428	0.213563	0.060458
H	-5.323632	-1.887360	1.352951	0.214950	0.057703
H	-2.893665	-1.708310	1.628335	0.239129	0.063351
H	-2.710527	0.989406	-1.655424	0.246737	0.091370
H	-5.143910	0.819814	-1.930923	0.216865	0.055225
C	-1.150157	-0.236061	0.226091	-0.668198	1.662540
O	-0.502411	0.332509	-0.784757	-0.883267	-1.517209
H	-0.735734	-1.184216	0.522997	0.193846	-0.045740
F	-0.977213	0.584366	1.387330	-0.348584	-0.971304
K	0.305472	2.751075	0.445057	1.009765	1.057470
O	1.312781	-1.349596	-0.798823	-0.920044	-1.361276
C	2.433306	-1.325470	0.054368	0.554136	0.722319
C	3.002663	0.117678	-0.153753	0.983750	0.711767
O	1.838344	0.855538	-0.443600	-1.048431	-1.437744

C	3.688640	0.723915	1.063797	-1.013348	0.072406
H	4.542811	0.127862	1.369610	0.175132	-0.033656
H	4.050694	1.718312	0.820066	0.165686	-0.051213
H	3.014163	0.810308	1.906211	0.154932	-0.043146
C	1.969622	-1.576593	1.491483	-0.663475	0.037457
H	1.409883	-2.505994	1.521112	0.171480	-0.051208
H	2.807721	-1.671427	2.174158	0.178387	-0.044227
H	1.325030	-0.785364	1.852402	0.201161	-0.033156
C	3.953994	0.217021	-1.349957	-0.523823	0.047141
H	4.148828	1.265211	-1.553526	0.173853	-0.054420
H	4.903697	-0.268123	-1.152193	0.159747	-0.040720
H	3.526256	-0.221622	-2.243054	0.144810	-0.035649
C	3.384865	-2.447606	-0.345642	-0.955748	0.080047
H	2.912761	-3.407066	-0.157301	0.148754	-0.052382
H	3.635986	-2.404060	-1.397280	0.168630	-0.041770
H	4.304113	-2.411290	0.231529	0.169781	-0.042239
B	0.908810	-0.018080	-1.166339	1.866210	2.117222
H	0.931486	0.171357	-2.389066	-0.182735	-0.519942

B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1457.609239

Electronic energy + zero-point energy: -1457.306037

Electronic energy + thermal energy correction: -1457.286046

Electronic energy + thermal enthalpy correction: -1457.285102

Electronic energy + thermal free energy correction: -1457.355878

Table S74. Cartesian coordinates, Mulliken and APT charges of all atoms at **I3B** in the reaction of benzaldehyde with pinacolborane (B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	-5.433669	-0.497015	-0.267686	-0.223020	-0.041377
C	-4.760175	-1.379048	0.573565	-0.227290	-0.070910
C	-3.376041	-1.304041	0.694268	-0.357415	-0.052536
C	-2.655148	-0.348653	-0.023152	0.302884	-0.162405
C	-3.333100	0.527315	-0.871372	-0.001762	-0.069126
C	-4.717346	0.454659	-0.990463	-0.236947	-0.059597
H	-6.511661	-0.555243	-0.365465	0.175735	0.058098
H	-5.311574	-2.127046	1.131516	0.182043	0.055626
H	-2.850556	-1.993192	1.346730	0.187619	0.063925
H	-2.774588	1.256925	-1.444474	0.199939	0.087808

H	-5.237837	1.137971	-1.651751	0.183154	0.053534
C	-1.163257	-0.281893	0.143708	-0.435577	1.613683
O	-0.513565	0.325733	-0.843415	-0.744680	-1.456165
H	-0.727276	-1.230487	0.452558	0.202223	-0.016987
F	-0.972533	0.552941	1.423567	-0.301708	-1.001821
K	0.293296	2.651379	0.498538	0.965125	1.058988
O	1.341068	-1.366615	-0.819181	-0.740737	-1.255103
C	2.459441	-1.297795	0.082734	0.246823	0.670986
C	3.031485	0.149187	-0.174504	0.556370	0.666837
O	1.847308	0.885732	-0.523179	-0.875797	-1.337314
C	3.685250	0.807215	1.037252	-0.718834	0.005495
H	4.552133	0.233085	1.374246	0.170921	-0.009843
H	4.035609	1.807957	0.769648	0.152924	-0.029333
H	2.993129	0.899957	1.875186	0.153227	-0.022492
C	1.958539	-1.491438	1.520334	-0.499051	-0.034370
H	1.401813	-2.430196	1.576484	0.150832	-0.027471
H	2.786261	-1.551663	2.231543	0.169858	-0.026137
H	1.294535	-0.684765	1.832312	0.191185	-0.003611
C	4.004724	0.203821	-1.360617	-0.450159	-0.019477
H	4.208042	1.250397	-1.600766	0.158340	-0.030227
H	4.956118	-0.279645	-1.127865	0.155225	-0.021486
H	3.585425	-0.271155	-2.248862	0.147613	-0.012857
C	3.428944	-2.428874	-0.256336	-0.744165	0.015782
H	2.955550	-3.391997	-0.047325	0.140553	-0.031132
H	3.710742	-2.415627	-1.309218	0.162609	-0.019043
H	4.337764	-2.366451	0.348410	0.165426	-0.020421
B	0.934027	-0.038953	-1.227799	1.592572	1.958083
H	0.930030	0.113841	-2.448398	-0.156056	-0.477601

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1457.251558

Electronic energy + zero-point energy: -1456.943636

Electronic energy + thermal energy correction: -1456.924396

Electronic energy + thermal enthalpy correction: -1456.923452

Electronic energy + thermal free energy correction: -1456.992760

Table S75. Cartesian coordinates, Mulliken and APT charges of all atoms at **I3B** in the reaction of benzaldehyde with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT

C	-5.366802	-0.510537	-0.249427	-0.345936	-0.059006
C	-4.712204	-1.176995	0.782392	-0.256892	-0.081694
C	-3.331366	-1.095304	0.892900	-0.103060	-0.074089
C	-2.597187	-0.344481	-0.022470	0.346880	-0.131597
C	-3.251068	0.314398	-1.056138	-0.137812	-0.097061
C	-4.635359	0.231991	-1.167788	-0.324864	-0.063497
H	-6.444446	-0.576162	-0.339451	0.217525	0.071225
H	-5.278514	-1.762578	1.496487	0.230231	0.069743
H	-2.816205	-1.616075	1.693225	0.240059	0.077512
H	-2.673052	0.882168	-1.774082	0.218453	0.110779
H	-5.142021	0.746135	-1.975679	0.231343	0.066349
C	-1.100913	-0.261987	0.137497	-0.611594	1.504342
O	-0.490363	0.386678	-0.862257	-0.641199	-1.430066
H	-0.654848	-1.231877	0.361531	0.133655	-0.011424
F	-0.894895	0.490567	1.377574	-0.216599	-0.926138
K	0.241396	2.642980	0.481508	0.985909	1.056996
O	1.341446	-1.297572	-0.925903	-0.568529	-1.258257
C	2.395179	-1.294315	0.034258	-0.098982	0.662081
C	2.995255	0.138987	-0.113398	0.485247	0.656965
O	1.840073	0.914125	-0.415910	-0.757548	-1.341808
C	3.652704	0.682180	1.144089	-0.746914	-0.032596
H	4.469091	0.030050	1.464924	0.203820	0.003888
H	4.070868	1.671669	0.944076	0.177926	-0.014174
H	2.936856	0.768707	1.962423	0.162967	-0.008575
C	1.815272	-1.529845	1.428775	-0.453730	-0.079813
H	1.219930	-2.445786	1.412443	0.195357	-0.012553
H	2.605125	-1.651005	2.173851	0.200241	-0.009364
H	1.171703	-0.704124	1.735905	0.186519	0.016230
C	3.971686	0.235811	-1.285676	-0.503124	-0.059211
H	4.192049	1.289033	-1.471933	0.187552	-0.016306
H	4.910228	-0.279077	-1.070523	0.178723	-0.005591
H	3.539479	-0.191094	-2.192480	0.169248	0.000846
C	3.374024	-2.411493	-0.294007	-0.762052	-0.022831
H	2.894936	-3.379318	-0.128135	0.173346	-0.016814
H	3.693708	-2.363792	-1.334757	0.173556	-0.005496
H	4.256843	-2.356376	0.348543	0.197237	-0.004979
B	0.945952	0.063684	-1.234784	1.297947	1.922647
H	1.001466	0.323049	-2.432740	-0.064906	-0.456663

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1457.332746

Electronic energy + zero-point energy: -1457.025727

Electronic energy + thermal energy correction: -1457.006304

Electronic energy + thermal enthalpy correction: -1457.005360

Electronic energy + thermal free energy correction: -1457.074332

Table S76. Cartesian coordinates, Mulliken and APT charges of all atoms at **I3B** in the reaction of benzaldehyde with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	-5.399794	-0.461443	-0.247888	-0.315156	-0.046015
C	-4.724936	-1.408614	0.511144	-0.296279	-0.071059
C	-3.341825	-1.351244	0.620395	-0.400157	-0.064386
C	-2.627963	-0.350000	-0.028015	0.250883	-0.148428
C	-3.305616	0.593256	-0.793167	-0.102039	-0.078694
C	-4.688000	0.538999	-0.899953	-0.259031	-0.063201
H	-6.479416	-0.505138	-0.336336	0.221780	0.061986
H	-5.275114	-2.194751	1.015450	0.232851	0.060092
H	-2.811119	-2.091266	1.210773	0.232590	0.067847
H	-2.747321	1.363920	-1.311630	0.238461	0.089737
H	-5.212451	1.276261	-1.497224	0.235948	0.058100
C	-1.134677	-0.293064	0.130054	-0.183640	1.592712
O	-0.505196	0.322329	-0.865137	-0.761935	-1.460634
H	-0.703484	-1.258560	0.398202	0.229684	-0.019411
F	-0.928556	0.500371	1.382753	-0.280174	-0.979969
K	0.330963	2.631372	0.508744	0.959440	1.056259
O	1.333224	-1.366279	-0.843026	-0.720908	-1.264665
C	2.405527	-1.282807	0.090738	0.235283	0.667564
C	2.996213	0.141900	-0.181097	0.556777	0.659138
O	1.839807	0.880821	-0.554354	-0.864830	-1.345007
C	3.641175	0.801691	1.028105	-0.802540	-0.007488
H	4.477496	0.201754	1.396845	0.204738	-0.002888
H	4.031274	1.784731	0.750047	0.180163	-0.023487
H	2.930127	0.932354	1.845965	0.168115	-0.021369
C	1.854975	-1.423382	1.511146	-0.570490	-0.054704
H	1.270527	-2.344993	1.573526	0.190870	-0.022852
H	2.659332	-1.483010	2.248963	0.192934	-0.016957
H	1.203727	-0.589251	1.775731	0.179160	0.015153
C	3.983753	0.154796	-1.349846	-0.531915	-0.031281
H	4.203538	1.192459	-1.613190	0.186283	-0.025297
H	4.924041	-0.337233	-1.090203	0.179035	-0.014121
H	3.565921	-0.338522	-2.229845	0.168177	-0.007111
C	3.382865	-2.419894	-0.172954	-0.807037	0.003721
H	2.911160	-3.375882	0.070077	0.167321	-0.025955

H	3.687894	-2.449687	-1.219485	0.178294	-0.014820
H	4.276684	-2.317908	0.449235	0.195869	-0.014151
B	0.926053	-0.041397	-1.255638	1.425290	1.966394
H	0.932786	0.106173	-2.481468	-0.113814	-0.474754

TS1B

HF/6-31G(d), N,N-dimethylformamide solution

Electronic energy: -1451.322469

Electronic energy + zero-point energy: -1450.998123

Electronic energy + thermal energy correction: -1450.978979

Electronic energy + thermal enthalpy correction: -1450.978035

Electronic energy + thermal free energy correction: -1451.047019

Table S77. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS1B** in the reaction of benzaldehyde with pinacolborane (HF/6-31G(d), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	5.073005	-1.219046	0.035904	-0.183574	0.224396
C	4.890254	-0.092484	0.825143	-0.245723	-0.242273
C	3.669548	0.558064	0.812820	-0.183700	0.141399
C	2.633758	0.078320	0.013437	-0.045883	-0.651355
C	2.823662	-1.054478	-0.779362	-0.183572	0.123943
C	4.043936	-1.700389	-0.766331	-0.242913	-0.264221
H	6.021576	-1.725318	0.043085	0.251631	0.048568
H	5.691791	0.274137	1.439628	0.247458	0.054539
H	3.515823	1.434286	1.416990	0.269900	0.072072
H	2.019627	-1.418416	-1.389666	0.268245	0.100432
H	4.198861	-2.572938	-1.374120	0.246394	0.053228
C	1.375311	0.813202	-0.006247	0.177241	1.987850
O	0.446227	0.535199	-0.881119	-0.682958	-1.317862
H	-1.336308	2.925909	-0.795631	0.797256	1.031461
F	-0.616017	-1.514684	0.035058	-0.707770	-1.376273
K	-2.004377	-1.731530	-0.169926	0.302319	0.767686
O	-2.644720	-0.500594	0.551704	0.310610	0.723918
C	-1.668474	0.509863	0.322993	-0.755565	-1.451974
C	-3.976966	-0.029746	-0.019053	-0.516027	0.091027
O	-4.730030	-0.807623	0.058455	0.177606	-0.039703
C	-4.330116	0.831324	0.540580	0.180253	-0.049824
H	-3.889782	0.259771	-1.058992	0.182795	-0.042766
H	-2.269820	-1.739479	-1.678367	-0.511960	0.053963

H	-1.631945	-2.485989	-2.140315	0.173378	-0.050223
C	-3.300539	-1.988578	-1.907904	0.170671	-0.046734
H	-2.040432	-0.780608	-2.130395	0.174740	-0.041636
H	-2.778888	-0.695514	2.063689	-0.511389	0.067950
H	-3.021652	0.258984	2.519729	0.177347	-0.051756
C	-3.567685	-1.397584	2.311184	0.172588	-0.041418
H	-1.854058	-1.050234	2.504729	0.178121	-0.040683
H	-2.379724	-3.087380	0.415300	-0.504490	0.092617
H	-1.890352	-3.875002	-0.149110	0.171913	-0.049872
C	-2.067267	-3.176966	1.447812	0.177867	-0.041550
H	-3.451200	-3.254349	0.361349	0.169982	-0.044096
H	-0.405092	-0.129702	0.192267	0.923364	1.868146
H	0.405849	0.093961	1.188920	-0.160779	-0.744848
B	0.444613	3.424974	0.708976	-0.796002	-1.062651
H	1.311549	1.775900	0.485185	0.330630	0.148524

HF/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1451.623769

Electronic energy + zero-point energy: -1451.303828

Electronic energy + thermal energy correction: -1451.284318

Electronic energy + thermal enthalpy correction: -1451.283374

Electronic energy + thermal free energy correction: -1451.354030

Table S78. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS1B** in the reaction of benzaldehyde with pinacolborane (HF/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	5.224312	-0.964842	-0.121844	-0.216294	0.241347
C	4.984477	-0.075464	0.911691	-0.338408	-0.285517
C	3.729203	0.479383	1.052032	-0.537133	0.158174
C	2.719503	0.139785	0.159150	0.648979	-0.736424
C	2.965108	-0.755031	-0.879244	0.309280	0.148806
C	4.219597	-1.304531	-1.017924	-0.531118	-0.318155
H	6.202009	-1.396661	-0.234054	0.233940	0.070776
H	5.769593	0.183155	1.596669	0.233318	0.074127
H	3.527357	1.174193	1.846573	0.238884	0.086812
H	2.179003	-1.009551	-1.562828	0.271400	0.109301
H	4.421314	-1.993621	-1.816187	0.229439	0.073065
C	1.420807	0.766271	0.317208	-0.217991	2.184296
O	0.487219	0.658099	-0.569382	-0.787014	-1.360387

H	-1.643795	2.714025	-0.626729	0.940440	1.079536
F	-0.473172	-1.596191	-0.122814	-0.884502	-1.390148
K	-1.854247	-1.847505	-0.337216	0.575608	0.774022
O	-2.534562	-0.815475	0.620840	0.598350	0.734778
C	-1.605344	0.265436	0.592813	-1.058756	-1.470409
C	-3.893747	-0.307821	0.166468	-1.022180	0.057218
O	-4.607590	-1.122807	0.109506	0.187082	-0.024794
C	-4.271642	0.415163	0.882138	0.178876	-0.039959
H	-3.848166	0.167721	-0.805086	0.165359	-0.040558
H	-2.162284	-1.590025	-1.812012	-0.544568	0.029908
H	-1.511234	-2.212205	-2.416437	0.182805	-0.039815
C	-3.188778	-1.837361	-2.058384	0.181999	-0.033496
H	-1.983405	-0.557369	-2.089167	0.129849	-0.048344
H	-2.636145	-1.310953	2.062051	-0.439640	0.041829
H	-2.928466	-0.481333	2.696795	0.180331	-0.042547
C	-3.380209	-2.092330	2.164630	0.176524	-0.028339
H	-1.687605	-1.691292	2.422931	0.154093	-0.035087
H	-2.144242	-3.305002	-0.014281	-0.969346	0.065522
H	-1.635356	-3.942810	-0.729561	0.159593	-0.040958
C	-1.798857	-3.572490	0.975303	0.173980	-0.032114
H	-3.207584	-3.512658	-0.079222	0.180936	-0.031034
H	-0.324712	-0.281232	0.342418	1.881328	1.828887
H	0.492475	-0.246847	1.354799	-0.048782	-0.708309
B	-0.503917	4.749386	0.115454	-0.932952	-1.025489
H	1.351732	1.552829	1.051819	0.316290	-0.026521

B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1457.571310

Electronic energy + zero-point energy: -1457.272013

Electronic energy + thermal energy correction: -1457.251123

Electronic energy + thermal enthalpy correction: -1457.250178

Electronic energy + thermal free energy correction: -1457.324482

Table S79. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS1B** in the reaction of benzaldehyde with pinacolborane (B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	5.302018	-1.047600	-0.126400	-0.159682	0.165927
C	5.043161	-0.196641	0.947592	-0.259096	-0.229820
C	3.777884	0.344651	1.102477	-0.441792	0.170678

C	2.766114	0.032135	0.178940	0.596940	-0.777106
C	3.033002	-0.828715	-0.899621	0.240788	0.144719
C	4.300935	-1.361231	-1.049089	-0.394874	-0.266099
H	6.292587	-1.470270	-0.247893	0.199645	0.072915
H	5.828219	0.041329	1.654355	0.200963	0.072473
H	3.558384	1.010848	1.928814	0.207359	0.087576
H	2.245292	-1.063253	-1.603308	0.220481	0.109541
H	4.518636	-2.022144	-1.878913	0.199704	0.072302
C	1.471799	0.635420	0.353244	-0.280403	2.123250
O	0.526831	0.556544	-0.555161	-0.663460	-1.271777
H	-1.411141	2.704080	-0.663880	0.880144	1.080489
F	-0.613424	-1.642244	-0.099082	-0.707458	-1.328786
K	-2.035876	-1.774134	-0.344726	0.243460	0.756896
O	-2.650777	-0.690281	0.619367	0.242132	0.709573
C	-1.622021	0.338133	0.606703	-0.851125	-1.399928
C	-3.958873	-0.072373	0.142941	-0.723907	-0.017498
O	-4.740655	-0.832846	0.077441	0.182406	-0.007969
C	-4.292152	0.685885	0.855918	0.159892	-0.019323
H	-3.860872	0.395233	-0.837553	0.159844	-0.015508
H	-2.296417	-1.477099	-1.825078	-0.420032	-0.052311
H	-1.681293	-2.145953	-2.430999	0.167896	-0.016808
C	-3.342031	-1.644078	-2.093034	0.170352	-0.016594
H	-2.033776	-0.450685	-2.088390	0.146124	-0.025925
H	-2.807011	-1.185338	2.059306	-0.392327	-0.026300
H	-3.046231	-0.334735	2.701587	0.165886	-0.019490
C	-3.615753	-1.913371	2.147562	0.168419	-0.010718
H	-1.888282	-1.643609	2.429825	0.151294	-0.012453
H	-2.449611	-3.206976	-0.032333	-0.754712	-0.007785
H	-1.977084	-3.888870	-0.743610	0.148114	-0.021159
C	-2.147958	-3.504168	0.971804	0.167060	-0.009333
H	-3.532142	-3.327894	-0.121895	0.172990	-0.010973
H	-0.374179	-0.327546	0.379775	1.537333	1.671560
H	0.415743	-0.372287	1.397404	-0.036280	-0.618077
B	-0.301717	4.700316	0.119706	-0.901119	-1.025314
H	1.388223	1.387854	1.138987	0.257042	-0.030846

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1457.198740

Electronic energy + zero-point energy: -1456.895145

Electronic energy + thermal energy correction: -1456.874892

Electronic energy + thermal enthalpy correction: -1456.873948

Electronic energy + thermal free energy correction: -1456.945506

Table S80. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS1B** in the reaction of benzaldehyde with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	4.994983	-1.233137	-0.000829	-0.284645	0.119369
C	4.880712	-0.074547	0.760899	-0.263023	-0.213724
C	3.680456	0.617226	0.777088	-0.733080	0.108106
C	2.602396	0.143919	0.025834	0.619098	-0.678481
C	2.717459	-1.021000	-0.739159	0.381600	0.078478
C	3.918114	-1.707114	-0.749661	-0.330898	-0.236989
H	5.933096	-1.775115	-0.012762	0.237793	0.083230
H	5.724571	0.283976	1.336256	0.244090	0.084162
H	3.566989	1.522971	1.362225	0.243029	0.098219
H	1.862249	-1.370638	-1.304263	0.235867	0.124520
H	4.023709	-2.611115	-1.335856	0.243347	0.082547
C	1.365395	0.902525	0.042473	-0.379159	1.983828
O	0.397318	0.641171	-0.776830	-0.588658	-1.349182
H	-1.407146	2.734677	-0.802969	0.941179	1.069021
F	-0.509309	-1.475165	0.241548	-0.538785	-1.263270
K	-1.859589	-1.690189	-0.202832	-0.031062	0.703626
O	-2.633952	-0.562995	0.547349	0.217139	0.683450
C	-1.676962	0.515972	0.543711	-0.750322	-1.348002
C	-3.901690	-0.098069	-0.144581	-0.744510	-0.054542
O	-4.607864	-0.926537	-0.238624	0.210178	0.009321
C	-4.378440	0.686773	0.446848	0.188887	-0.003948
H	-3.697042	0.291764	-1.142457	0.168419	-0.005619
H	-1.911079	-1.518116	-1.718917	-0.467042	-0.082300
H	-1.180357	-2.190788	-2.171887	0.201585	-0.003066
C	-2.898774	-1.765396	-2.112978	0.200121	0.005010
H	-1.663211	-0.496847	-2.015250	0.148374	-0.000164
H	-2.927152	-0.925471	1.998228	-0.470092	-0.065755
H	-3.278660	-0.033372	2.519729	0.196330	-0.005794
C	-3.700531	-1.692501	2.068452	0.187642	0.004450
H	-2.027026	-1.287415	2.499013	0.173104	0.003324
H	-2.285350	-3.095762	0.175326	-0.753414	-0.038755
H	-1.723309	-3.821647	-0.415963	0.183707	-0.005627
C	-2.100025	-3.294411	1.230464	0.182050	0.003782
H	-3.348983	-3.240010	-0.029604	0.204675	0.004571
H	-0.381726	-0.083337	0.448947	1.105773	1.565380
H	0.413580	0.181150	1.389092	0.146641	-0.513153
B	0.317538	3.584496	0.629349	-0.846059	-1.079059

H	1.333993	1.857069	0.580358	0.320123	0.133039

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1457.287338

Electronic energy + zero-point energy: -1456.984643

Electronic energy + thermal energy correction: -1456.964209

Electronic energy + thermal enthalpy correction: -1456.963265

Electronic energy + thermal free energy correction: -1457.035401

Table S81. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS1B** in the reaction of benzaldehyde with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	5.070140	-1.241106	0.021005	-0.250453	0.134575
C	4.908736	-0.101919	0.801096	-0.309761	-0.209907
C	3.691632	0.557118	0.805230	-0.652215	0.122084
C	2.640276	0.071474	0.024952	0.557910	-0.712176
C	2.804764	-1.075314	-0.757127	0.392977	0.093789
C	4.022566	-1.727864	-0.757594	-0.456462	-0.234986
H	6.023093	-1.757782	0.018219	0.248771	0.071816
H	5.730875	0.267976	1.401289	0.249724	0.074266
H	3.545506	1.448040	1.406108	0.256014	0.090126
H	1.974173	-1.439666	-1.348972	0.289197	0.114966
H	4.163333	-2.617318	-1.359547	0.244752	0.073117
C	1.383115	0.792477	0.034414	-0.320891	2.033217
O	0.429853	0.519573	-0.802100	-0.654326	-1.334396
H	-1.345355	2.791377	-0.780120	0.930200	1.069586
F	-0.614636	-1.538152	0.197000	-0.704469	-1.284068
K	-1.987718	-1.682578	-0.197203	0.284324	0.717029
O	-2.673975	-0.492515	0.551703	0.353495	0.696542
C	-1.651029	0.518924	0.512503	-0.894408	-1.372856
C	-3.921013	0.047650	-0.125605	-0.821230	-0.029851
O	-4.685214	-0.730729	-0.193686	0.211105	-0.000259
C	-4.333963	0.873338	0.459657	0.187517	-0.015677
H	-3.711420	0.407917	-1.134000	0.176358	-0.013670
H	-2.079951	-1.551497	-1.717220	-0.575658	-0.058324
H	-1.409427	-2.282791	-2.173977	0.197278	-0.013041
C	-3.093830	-1.748489	-2.072986	0.198506	-0.005792
H	-1.780132	-0.558587	-2.059115	0.159433	-0.006709
H	-2.970822	-0.808043	2.014482	-0.504592	-0.038479

H	-3.255455	0.114819	2.525006	0.195847	-0.015348
C	-3.794339	-1.518938	2.110620	0.189968	-0.006106
H	-2.093372	-1.221156	2.516676	0.173419	-0.005914
H	-2.479224	-3.054236	0.228331	-0.815277	-0.012890
H	-1.972543	-3.826305	-0.355950	0.176535	-0.016303
C	-2.281086	-3.240110	1.284141	0.188220	-0.004922
H	-3.554103	-3.147031	0.051658	0.203772	-0.005373
H	-0.398085	-0.157062	0.395854	1.356687	1.614621
H	0.418134	0.054060	1.347561	0.071454	-0.547393
B	0.507128	3.613008	0.559054	-0.862606	-1.079037
H	1.333119	1.750187	0.570824	0.328882	0.117741

Acetophenone + pinacolborane

Pinacolborane

HF/6-31G(d), N,N-dimethylformamide solution

Electronic energy: -409.292909

Electronic energy + zero-point energy: -409.088358

Electronic energy + thermal energy correction: -409.079504

Electronic energy + thermal enthalpy correction: -409.078560

Electronic energy + thermal free energy correction: -409.120903

Table S82. Cartesian coordinates, Mulliken and APT charges of all atoms at **pinacolborane** in the reaction of acetophenone with pinacolborane (HF/6-31G(d), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	1.060470	1.180592	-0.384086	-0.605802	-0.956945
C	0.782551	-0.182778	-0.050923	0.268621	0.498197
C	-0.782551	-0.182778	0.050923	0.268621	0.498197
O	-1.060470	1.180593	0.384085	-0.605802	-0.956945
C	-1.480701	-0.461800	-1.281577	-0.487780	0.039312
H	-1.371659	-1.497245	-1.584475	0.162371	-0.025235
H	-2.537105	-0.246641	-1.172785	0.183836	-0.019869
H	-1.092902	0.170282	-2.072233	0.172366	-0.022540
C	1.368288	-1.079204	-1.134483	-0.484075	0.060229
H	2.448085	-0.986304	-1.133494	0.180925	-0.020167
H	1.119392	-2.120303	-0.953364	0.158236	-0.025650

H	1.013252	-0.803583	-2.117841	0.181216	-0.018595
C	-1.368288	-1.079203	1.134484	-0.484075	0.060229
H	-2.448085	-0.986303	1.133494	0.180925	-0.020167
H	-1.119393	-2.120302	0.953366	0.158236	-0.025650
H	-1.013252	-0.803581	2.117841	0.181216	-0.018595
C	1.480701	-0.461799	1.281577	-0.487780	0.039312
H	2.537105	-0.246641	1.172785	0.183836	-0.019869
H	1.092902	0.170284	2.072232	0.172366	-0.022540
H	1.371659	-1.497244	1.584477	0.162371	-0.025235
B	0.000000	1.930007	-0.000001	0.596945	1.197327
H	0.000001	3.113437	-0.000000	-0.056777	-0.214804

HF/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -409.413872

Electronic energy + zero-point energy: -409.211908

Electronic energy + thermal energy correction: -409.203030

Electronic energy + thermal enthalpy correction: -409.202086

Electronic energy + thermal free energy correction: -409.244460

Table S83. Cartesian coordinates, Mulliken and APT charges of all atoms at **pinacolborane** in the reaction of benzaldehyde with pinacolborane (HF/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	1.059381	1.181627	-0.377682	-0.715416	-0.948089
C	0.782094	-0.182158	-0.051217	0.532767	0.496465
C	-0.782094	-0.182158	0.051217	0.532767	0.496465
O	-1.059381	1.181627	0.377682	-0.715416	-0.948089
C	-1.479664	-0.467719	-1.276944	-0.495092	0.026031
H	-1.364762	-1.503348	-1.575143	0.143880	-0.017933
H	-2.536676	-0.259121	-1.165948	0.174744	-0.017377
H	-1.097192	0.163521	-2.070014	0.132172	-0.019009
C	1.364044	-1.073578	-1.136324	-0.821733	0.045149
H	2.443746	-0.984613	-1.133734	0.148055	-0.018239
H	1.111437	-2.113783	-0.957429	0.153802	-0.018257
H	1.010008	-0.794069	-2.118148	0.159062	-0.014122
C	-1.364044	-1.073578	1.136324	-0.821733	0.045149
H	-2.443746	-0.984613	1.133734	0.148055	-0.018239
H	-1.111437	-2.113783	0.957429	0.153802	-0.018257
H	-1.010008	-0.794069	2.118148	0.159062	-0.014122
C	1.479664	-0.467719	1.276944	-0.495092	0.026031

H	2.536676	-0.259121	1.165948	0.174744	-0.017377
H	1.097192	0.163521	2.070014	0.132172	-0.019009
H	1.364762	-1.503348	1.575143	0.143880	-0.017933
B	0.000000	1.929230	-0.000000	1.119715	1.169322
H	0.000000	3.112104	-0.000000	0.055799	-0.198561

B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -412.000110

Electronic energy + zero-point energy: -411.810684

Electronic energy + thermal energy correction: -411.801094

Electronic energy + thermal enthalpy correction: -411.800150

Electronic energy + thermal free energy correction: -411.843215

Table S84. Cartesian coordinates, Mulliken and APT charges of all atoms at **pinacolborane** in the reaction of acetophenone with pinacolborane (B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	-0.984520	-0.579323	-1.202930	-0.521128	-0.812001
C	-0.551619	-0.564839	0.192864	0.194180	0.435869
C	0.551619	0.564839	0.192864	0.194180	0.435869
O	0.984520	0.579323	-1.202930	-0.521128	-0.812001
C	0.000000	1.960874	0.489492	-0.381483	-0.018085
H	-0.296299	2.061170	1.535328	0.138184	-0.003823
H	0.777328	2.697386	0.281050	0.161344	-0.001841
H	-0.860716	2.193047	-0.139232	0.131275	-0.003494
C	-1.765516	-0.285269	1.069071	-0.637388	0.001627
H	-2.477612	-1.106913	0.976348	0.139819	-0.004149
H	-1.475594	-0.206554	2.119660	0.148053	-0.003496
H	-2.272114	0.633103	0.777354	0.148437	0.000336
C	1.765516	0.285269	1.069071	-0.637388	0.001627
H	2.477612	1.106913	0.976348	0.139819	-0.004149
H	1.475594	0.206554	2.119660	0.148053	-0.003496
H	2.272114	-0.633103	0.777354	0.148437	0.000336
C	-0.000000	-1.960874	0.489492	-0.381483	-0.018085
H	-0.777328	-2.697386	0.281050	0.161344	-0.001841
H	0.860716	-2.193047	-0.139232	0.131275	-0.003494
H	0.296299	-2.061170	1.535328	0.138184	-0.003823
B	-0.000000	-0.000000	-1.947716	0.905586	0.982017
H	-0.000000	-0.000000	-3.132682	0.051828	-0.163903

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -411.819249

Electronic energy + zero-point energy: -411.627362

Electronic energy + thermal energy correction: -411.618050

Electronic energy + thermal enthalpy correction: -411.617106

Electronic energy + thermal free energy correction: -411.659489

Table S85. Cartesian coordinates, Mulliken and APT charges of all atoms at **pinacolborane** in the reaction of acetophenone with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	-0.337899	-1.087785	-1.186879	-0.381547	-0.835186
C	0.000000	-0.780864	0.186095	-0.019522	0.436288
C	-0.000000	0.780864	0.186095	-0.019522	0.436288
O	0.337899	1.087785	-1.186879	-0.381547	-0.835186
C	-1.380647	1.374530	0.441850	-0.422414	-0.045006
H	-1.687089	1.233661	1.479452	0.164125	0.006079
H	-1.345633	2.443162	0.229393	0.189480	0.007426
H	-2.128162	0.919816	-0.210074	0.154772	0.005046
C	-1.026734	-1.416559	1.103807	-0.619310	-0.023734
H	-0.948261	-2.502233	1.039899	0.170433	0.005374
H	-0.845168	-1.119551	2.139302	0.181065	0.006340
H	-2.039499	-1.129874	0.827052	0.164682	0.009009
C	1.026734	1.416559	1.103807	-0.619310	-0.023734
H	0.948261	2.502233	1.039899	0.170433	0.005374
H	0.845168	1.119551	2.139302	0.181065	0.006340
H	2.039499	1.129874	0.827052	0.164682	0.009009
C	1.380647	-1.374530	0.441850	-0.422414	-0.045006
H	1.345633	-2.443162	0.229393	0.189480	0.007426
H	2.128162	-0.919816	-0.210074	0.154772	0.005046
H	1.687089	-1.233661	1.479452	0.164125	0.006079
B	0.000000	-0.000000	-1.936329	0.751477	1.018482
H	0.000000	-0.000000	-3.119368	0.084995	-0.161751

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -411.870683

Electronic energy + zero-point energy: -411.679335

Electronic energy + thermal energy correction: -411.669999

Electronic energy + thermal enthalpy correction: -411.669055

Electronic energy + thermal free energy correction: -411.711535

Table S86. Cartesian coordinates, Mulliken and APT charges of all atoms at **S pinacolborane** in the reaction of acetophenone with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	-0.996900	-0.551316	-1.191897	-0.498378	-0.830634
C	-0.551844	-0.556890	0.184431	0.193557	0.440071
C	0.551844	0.556890	0.184431	0.193557	0.440071
O	0.996900	0.551316	-1.191897	-0.498378	-0.830634
C	-0.000000	1.952031	0.462625	-0.470483	-0.028348
H	-0.306888	2.057573	1.504987	0.161055	0.000252
H	0.779731	2.686296	0.255350	0.187016	0.001434
H	-0.855410	2.176073	-0.177301	0.153283	-0.000217
C	-1.739295	-0.276399	1.087636	-0.685369	-0.008403
H	-2.451450	-1.100552	1.022725	0.163693	-0.000699
H	-1.414095	-0.187913	2.127347	0.177782	0.000577
H	-2.253944	0.639936	0.802425	0.165481	0.004157
C	1.739295	0.276399	1.087636	-0.685369	-0.008403
H	2.451450	1.100552	1.022725	0.163693	-0.000699
H	1.414095	0.187913	2.127347	0.177782	0.000577
H	2.253944	-0.639936	0.802425	0.165481	0.004157
C	0.000000	-1.952031	0.462625	-0.470483	-0.028348
H	-0.779731	-2.686296	0.255350	0.187016	0.001434
H	0.855410	-2.176073	-0.177301	0.153283	-0.000217
H	0.306888	-2.057573	1.504987	0.161055	0.000252
B	0.000000	0.000000	-1.938234	0.852038	1.010001
H	0.000000	0.000000	-3.125836	0.052689	-0.166381

Acetophenone

HF/6-31G(d), N,N-dimethylformamide solution

Electronic energy: -382.490566

Electronic energy + zero-point energy: -382.342545

Electronic energy + thermal energy correction: -382.3335168

Electronic energy + thermal enthalpy correction: -382.334223

Electronic energy + thermal free energy correction: -382.375307

Table S87. Cartesian coordinates, Mulliken and APT charges of all atoms at **acetophenone** in the reaction of acetophenone with pinacolborane (HF/6-31G(d), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	2.577005	0.119938	-0.000001	-0.206733	0.094668
C	1.808036	1.272520	0.000010	-0.239188	-0.144750
C	0.424050	1.183536	0.000010	-0.219106	0.033291
C	-0.201231	-0.060101	0.000001	-0.129489	-0.356614
C	0.582461	-1.213340	-0.000009	-0.201114	0.010681
C	1.962245	-1.125625	-0.000011	-0.236960	-0.136277
H	3.650254	0.189759	-0.000002	0.241108	0.043754
H	2.281193	2.237940	0.000018	0.238286	0.043623
H	-0.154524	2.087915	0.000019	0.253485	0.066793
H	0.102349	-2.173208	-0.000017	0.249008	0.081220
H	2.557625	-2.021028	-0.000020	0.237690	0.041088
C	-1.694547	-0.206475	0.000003	0.562397	1.395469
O	-2.196756	-1.296926	0.000023	-0.582056	-1.114104
C	-2.552830	1.034713	-0.000020	-0.596646	-0.082608
H	-2.350112	1.640798	0.876892	0.212020	0.019960
H	-2.350086	1.640788	-0.876934	0.212019	0.019959
H	-3.593790	0.741446	-0.000034	0.205279	-0.016152

HF/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -382.596939

Electronic energy + zero-point energy: -382.450770

Electronic energy + thermal energy correction: -382.443322

Electronic energy + thermal enthalpy correction: -382.442378

Electronic energy + thermal free energy correction: -382.483818

Table S88. Cartesian coordinates, Mulliken and APT charges of all atoms at **acetophenone** in the reaction of acetophenone with pinacolborane (HF/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	2.572176	0.123088	-0.000001	-0.237475	0.080657
C	1.802336	1.270717	0.000006	-0.452738	-0.166538
C	0.420961	1.177854	0.000006	-0.906392	0.014878
C	-0.199952	-0.063468	0.000001	0.802248	-0.371584
C	0.584549	-1.212408	-0.000005	0.316050	0.001756

C	1.960946	-1.121463	-0.000007	-0.425179	-0.165712
H	3.644626	0.195035	-0.000002	0.215035	0.064143
H	2.272222	2.236892	0.000011	0.222435	0.063341
H	-0.158853	2.080251	0.000011	0.229398	0.085041
H	0.108846	-2.173667	-0.000010	0.231664	0.096537
H	2.557773	-2.014989	-0.000012	0.220051	0.061218
C	-1.693493	-0.206448	0.000002	0.526145	1.477308
O	-2.194320	-1.292868	0.000013	-0.606433	-1.182626
C	-2.547924	1.032787	-0.000012	-0.710188	-0.091339
H	-2.339313	1.636003	0.876844	0.191201	0.020717
H	-2.339301	1.635993	-0.876872	0.191201	0.020716
H	-3.589035	0.743468	-0.000017	0.192978	-0.008514

B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -385.025334

Electronic energy + zero-point energy: -384.888341

Electronic energy + thermal energy correction: -384.880441

Electronic energy + thermal enthalpy correction: -384.879496

Electronic energy + thermal free energy correction: -384.921563

Table S89. Cartesian coordinates, Mulliken and APT charges of all atoms at **acetophenone** in the reaction of acetophenone with pinacolborane (B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	2.585831	0.117942	0.000002	-0.181258	0.029337
C	1.813002	1.275328	-0.000014	-0.391274	-0.128985
C	0.424681	1.186993	-0.000015	-0.756014	0.009589
C	-0.205831	-0.062684	-0.000002	0.802035	-0.403028
C	0.582630	-1.220518	0.000013	0.166713	0.004106
C	1.967191	-1.131954	0.000016	-0.354416	-0.123635
H	3.667592	0.187954	0.000003	0.182589	0.062583
H	2.290619	2.248117	-0.000025	0.187282	0.059579
H	-0.160735	2.097192	-0.000027	0.194832	0.084555
H	0.094248	-2.186744	0.000023	0.190910	0.096410
H	2.567311	-2.034515	0.000029	0.184903	0.057150
C	-1.697709	-0.200948	-0.000004	0.358152	1.402589
O	-2.216828	-1.306865	-0.000032	-0.511670	-1.041817
C	-2.546432	1.045898	0.000028	-0.601775	-0.193288
H	-2.333025	1.658377	0.880281	0.179130	0.037062
H	-2.333056	1.658398	-0.880218	0.179131	0.037063

H	-3.598507	0.765801	0.000042	0.170729	0.010730

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -384.855152

Electronic energy + zero-point energy: -384.716629

Electronic energy + thermal energy correction: -384.708846

Electronic energy + thermal enthalpy correction: -384.707902

Electronic energy + thermal free energy correction: -384.749651

Table S90. Cartesian coordinates, Mulliken and APT charges of all atoms at **acetophenone** in the reaction of acetophenone with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	2.576543	0.119836	-0.000000	-0.250056	0.011431
C	1.804168	1.274471	0.000002	-0.429212	-0.132815
C	0.417706	1.183490	0.000002	-0.789383	-0.023379
C	-0.203176	-0.065274	0.000000	0.722665	-0.363700
C	0.579833	-1.220848	-0.000002	0.276975	-0.025685
C	1.962487	-1.129708	-0.000002	-0.391987	-0.130045
H	3.657582	0.191769	-0.000000	0.221746	0.075377
H	2.280325	2.247183	0.000004	0.232420	0.073998
H	-0.173623	2.090450	0.000003	0.218978	0.096884
H	0.090066	-2.186521	-0.000003	0.224366	0.107873
H	2.564807	-2.029941	-0.000004	0.228717	0.072002
C	-1.696210	-0.203114	0.000001	0.247206	1.375298
O	-2.209238	-1.302874	0.000005	-0.462647	-1.039714
C	-2.532387	1.046458	-0.000004	-0.663636	-0.229071
H	-2.306895	1.651815	0.880731	0.202450	0.052861
H	-2.306888	1.651815	-0.880737	0.202450	0.052861
H	-3.585250	0.774553	-0.000008	0.208946	0.025823

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -384.885860

Electronic energy + zero-point energy: -384.747514

Electronic energy + thermal energy correction: -384.739727

Electronic energy + thermal enthalpy correction: -384.738783

Electronic energy + thermal free energy correction: -384.780606

Table S91. Cartesian coordinates, Mulliken and APT charges of all atoms at **acetophenone** in the reaction of acetophenone with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	2.577656	0.118069	-0.000000	-0.270521	0.026086
C	1.806597	1.272371	0.000000	-0.425910	-0.131039
C	0.421548	1.183240	0.000001	-0.775147	-0.006434
C	-0.203602	-0.063424	0.000000	0.723170	-0.386458
C	0.580247	-1.217895	-0.000000	0.196308	-0.012118
C	1.962017	-1.128975	-0.000001	-0.394664	-0.125633
H	3.659427	0.188790	-0.000000	0.227985	0.066728
H	2.283642	2.245418	0.000001	0.237736	0.064585
H	-0.164930	2.093631	0.000001	0.227113	0.088952
H	0.091791	-2.184714	-0.000001	0.223564	0.101108
H	2.562568	-2.031198	-0.000001	0.235598	0.062084
C	-1.696157	-0.202146	0.000000	0.391139	1.400002
O	-2.210280	-1.303206	0.000001	-0.496420	-1.042508
C	-2.536421	1.044692	-0.000001	-0.715036	-0.208471
H	-2.315662	1.653056	0.880948	0.204726	0.043639
H	-2.315660	1.653056	-0.880950	0.204726	0.043638
H	-3.590236	0.772023	-0.000002	0.205634	0.015839

KF

HF/6-31G(d), N,N-dimethylformamide solution

Electronic energy: -698.609250

Electronic energy + zero-point energy: -698.608471

Electronic energy + thermal energy correction: -698.605740

Electronic energy + thermal enthalpy correction: -698.604796

Electronic energy + thermal free energy correction: -698.630763

Table S92. Cartesian coordinates, Mulliken and APT charges of all atoms at **KF** in the reaction of acetophenone with pinacolborane (HF/6-31G(d), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
F	0.000000	0.000000	-1.565290	-0.864290	-0.981443
K	0.000000	0.000000	0.741453	0.864290	0.981443

HF/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -698.707381

Electronic energy + zero-point energy: -698.706774

Electronic energy + thermal energy correction: -698.703949

Electronic energy + thermal enthalpy correction: -698.703005

Electronic energy + thermal free energy correction: -698.729241

Table S93. Cartesian coordinates, Mulliken and APT charges of all atoms at **KF** in the reaction of acetophenone with pinacolborane (HF/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
F	0.000000	0.000000	-1.625556	-0.947677	-1.014530
K	0.000000	0.000000	0.770000	0.947677	1.014530

B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -699.910213

Electronic energy + zero-point energy: -699.909569

Electronic energy + thermal energy correction: -699.906766

Electronic energy + thermal enthalpy correction: -699.905822

Electronic energy + thermal free energy correction: -699.931975

Table S94. Cartesian coordinates, Mulliken and APT charges of all atoms at **KF** in the reaction of acetophenone with pinacolborane (B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
F	0.000000	0.000000	-1.595511	-0.912297	-1.011445
K	0.000000	0.000000	0.755768	0.912297	1.011445

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -699.849787

Electronic energy + zero-point energy: -699.849093

Electronic energy + thermal energy correction: -699.846318

Electronic energy + thermal enthalpy correction: -699.845374

Electronic energy + thermal free energy correction: -699.871455

Table S95. Cartesian coordinates, Mulliken and APT charges of all atoms at **KF** in the reaction of acetophenone with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
F	0.000000	0.000000	-1.585305	-0.922403	-1.011979
K	0.000000	0.000000	0.750934	0.922403	1.011979

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -699.869640

Electronic energy + zero-point energy: -699.868980

Electronic energy + thermal energy correction: -699.866186

Electronic energy + thermal enthalpy correction: -699.865242

Electronic energy + thermal free energy correction: -699.891376

Table S96. Cartesian coordinates, Mulliken and APT charges of all atoms at **KF** in the reaction of acetophenone with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
F	0.000000	0.000000	-1.596236	-0.922586	-1.014469
K	0.000000	0.000000	0.756112	0.922586	1.014469

I1A

HF/6-31G(d), N,N-dimethylformamide solution

Electronic energy: -1107.925473

Electronic energy + zero-point energy: -1107.718856

Electronic energy + thermal energy correction: -1107.706181

Electronic energy + thermal enthalpy correction: -1107.705237

Electronic energy + thermal free energy correction: -1107.757729

Table S97. Cartesian coordinates, Mulliken and APT charges of all atoms at **I1A** in the reaction of acetophenone with pinacolborane (HF/6-31G(d), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	0.179996	-0.956098	0.546230	-0.669436	-1.294854
C	-0.776844	-0.633347	-0.493608	0.281588	0.657254
C	-1.576299	0.542271	0.163156	0.278431	0.672738
O	-1.422838	0.264712	1.569190	-0.616041	-1.249378
C	-0.952856	1.914434	-0.090619	-0.538735	0.036305
H	-1.149651	2.247047	-1.104474	0.177025	-0.028717
H	-1.402270	2.630169	0.589825	0.178963	-0.041309
H	0.119405	1.912620	0.061269	0.201253	0.041345
C	-0.018233	-0.270722	-1.762852	-0.560805	0.042676
H	0.470247	-1.156764	-2.159150	0.185017	-0.042427
H	-0.704920	0.088980	-2.522218	0.187903	-0.013942
H	0.731604	0.486147	-1.578463	0.211501	0.045048
C	-3.061869	0.577371	-0.162052	-0.503398	0.093061
H	-3.520984	1.419897	0.344099	0.182823	-0.037201
H	-3.217208	0.701482	-1.228526	0.182365	-0.025486
H	-3.568083	-0.323107	0.160249	0.185530	-0.033812
C	-1.610721	-1.892102	-0.720164	-0.505768	0.069195
H	-0.949387	-2.708869	-0.988058	0.187904	-0.037734
H	-2.155404	-2.180867	0.172074	0.182459	-0.036840
H	-2.320549	-1.752955	-1.527402	0.185548	-0.021671
B	-0.331278	-0.507958	1.725040	0.623588	1.525548
H	0.153225	-0.768594	2.774899	-0.056389	-0.273069
F	2.422048	1.698920	-0.497852	-0.809202	-1.059315
K	2.910295	-0.486422	0.228149	0.827875	1.012585

HF/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1108.139234

Electronic energy + zero-point energy: -1107.936538

Electronic energy + thermal energy correction: -1107.923145

Electronic energy + thermal enthalpy correction: -1107.922201

Electronic energy + thermal free energy correction: -1107.978608

Table S98. Cartesian coordinates, Mulliken and APT charges of all atoms at **I1A** in the reaction of acetophenone with pinacolborane (HF/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	0.216711	-0.078341	0.459015	-0.830121	-1.317208
C	-0.930748	-0.651782	-0.211469	0.550707	0.673127
C	-1.996559	0.482495	-0.044896	0.691560	0.680356
O	-1.540840	1.153222	1.144116	-0.764282	-1.253415

C	-1.969592	1.513366	-1.168153	-0.560373	0.043600
H	-2.349693	1.097708	-2.093498	0.173749	-0.015178
H	-2.599183	2.350075	-0.888178	0.188651	-0.029072
H	-0.968551	1.890493	-1.343696	0.148370	-0.031817
C	-0.549204	-0.976263	-1.644408	-0.992179	0.053556
H	0.181486	-1.778490	-1.656855	0.171794	-0.036021
H	-1.418460	-1.316653	-2.195890	0.193033	-0.005518
H	-0.128293	-0.121586	-2.156055	0.200983	-0.019584
C	-3.418397	0.001072	0.179596	-0.937274	0.066934
H	-4.073964	0.857494	0.290679	0.166688	-0.028736
H	-3.761952	-0.577205	-0.671142	0.183835	-0.014665
H	-3.503692	-0.605946	1.070339	0.178736	-0.024852
C	-1.275617	-1.932999	0.538399	-0.551738	0.041621
H	-0.414118	-2.591372	0.525321	0.194782	-0.032260
H	-1.533856	-1.736385	1.572436	0.152364	-0.029118
H	-2.102483	-2.450650	0.067662	0.181547	-0.010782
B	-0.235933	0.878587	1.308757	1.229021	1.510368
H	0.459906	1.408467	2.106838	0.042280	-0.251738
F	4.387745	1.215557	-0.452702	-0.939863	-1.019510
K	2.912450	-0.577541	0.220163	0.927729	1.049914

B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1111.929160

Electronic energy + zero-point energy: -1111.738828

Electronic energy + thermal energy correction: -1111.724751

Electronic energy + thermal enthalpy correction: -1111.723807

Electronic energy + thermal free energy correction: -1111.781450

Table S99. Cartesian coordinates, Mulliken and APT charges of all atoms at **I1A** in the reaction of acetophenone with pinacolborane (B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	0.259095	-0.042203	0.423776	-0.665311	-1.174729
C	-0.933571	-0.670062	-0.194371	0.240829	0.622797
C	-2.011828	0.471248	-0.056380	0.323771	0.626082
O	-1.506435	1.250175	1.088756	-0.566794	-1.105288
C	-2.047530	1.428935	-1.245224	-0.446804	-0.029856
H	-2.466584	0.943766	-2.128343	0.168854	0.007895
H	-2.681627	2.281151	-0.993441	0.177223	-0.005509
H	-1.053934	1.806011	-1.494236	0.143611	-0.009001

C	-0.586820	-1.057088	-1.622786	-0.786977	-0.018328
H	0.158826	-1.855987	-1.622359	0.160945	-0.014492
H	-1.473530	-1.438166	-2.133914	0.187337	0.016493
H	-0.194752	-0.215453	-2.192738	0.183447	0.003699
C	-3.414277	-0.012064	0.275554	-0.743922	-0.003709
H	-4.083404	0.846287	0.364120	0.158276	-0.007966
H	-3.794300	-0.653907	-0.522219	0.178812	0.008142
H	-3.444101	-0.566574	1.212814	0.169188	-0.001130
C	-1.238734	-1.913131	0.636476	-0.439968	-0.032337
H	-0.368200	-2.572534	0.627471	0.184255	-0.009906
H	-1.467369	-1.663838	1.674015	0.148014	-0.007537
H	-2.082428	-2.463988	0.217628	0.176647	0.012349
B	-0.185527	0.977881	1.223196	1.016074	1.301140
H	0.535085	1.562496	1.962738	0.051763	-0.211895
F	4.386905	1.175628	-0.466343	-0.907110	-1.019202
K	2.907215	-0.559481	0.223668	0.887837	1.052289

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1111.689986

Electronic energy + zero-point energy: -1111.497139

Electronic energy + thermal energy correction: -1111.483435

Electronic energy + thermal enthalpy correction: -1111.482490

Electronic energy + thermal free energy correction: -1111.539361

Table S100. Cartesian coordinates, Mulliken and APT charges of all atoms at **I1A** in the reaction of acetophenone with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	0.191854	-0.203267	0.683952	-0.600160	-1.195723
C	-0.860958	-0.635108	-0.237210	0.160769	0.605474
C	-1.913839	0.503720	-0.077234	0.133993	0.619334
O	-1.672551	0.960438	1.285409	-0.429681	-1.125065
C	-1.647874	1.691620	-0.990642	-0.485503	-0.064602
H	-1.861890	1.439460	-2.030311	0.192160	0.020991
H	-2.298995	2.515021	-0.693870	0.205216	0.007920
H	-0.611201	2.026901	-0.916455	0.166640	0.002222
C	-0.276681	-0.764420	-1.629081	-0.847448	-0.058022
H	0.405355	-1.617360	-1.671405	0.188129	-0.005453
H	-1.075692	-0.952209	-2.349329	0.227080	0.036487
H	0.253548	0.138661	-1.932657	0.194448	0.010950

C	-3.352089	0.046760	-0.201337	-0.748649	-0.040539
H	-4.017052	0.905195	-0.093523	0.190785	0.007498
H	-3.518824	-0.393531	-1.186897	0.209529	0.021063
H	-3.607789	-0.688684	0.560259	0.183679	0.009795
C	-1.350778	-1.983434	0.267514	-0.483861	-0.066526
H	-0.507329	-2.675171	0.304075	0.211848	0.005588
H	-1.776633	-1.902371	1.269329	0.170632	0.006967
H	-2.105547	-2.396322	-0.403192	0.200266	0.025361
B	-0.399182	0.622805	1.605595	0.878431	1.347749
H	0.161753	0.997311	2.578157	0.091269	-0.204607
F	4.220744	1.202029	-0.447115	-0.913762	-1.021202
K	2.780442	-0.554810	0.211313	0.904193	1.054340

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1111.761722

Electronic energy + zero-point energy: -1111.569548

Electronic energy + thermal energy correction: -1111.555720

Electronic energy + thermal enthalpy correction: -1111.554776

Electronic energy + thermal free energy correction: -1111.612072

Table S101. Cartesian coordinates, Mulliken and APT charges of all atoms at **I1A** in the reaction of acetophenone with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	0.205637	-0.157857	0.639349	-0.683184	-1.192847
C	-0.878747	-0.646651	-0.214144	0.317190	0.617099
C	-1.938644	0.496781	-0.077429	0.365653	0.627249
O	-1.628277	1.057317	1.231878	-0.551401	-1.123473
C	-1.747368	1.618747	-1.089459	-0.548074	-0.041194
H	-2.018831	1.289001	-2.093889	0.194586	0.013430
H	-2.394397	2.454689	-0.816962	0.203974	-0.000512
H	-0.715165	1.975679	-1.106163	0.170208	-0.006589
C	-0.344558	-0.850068	-1.618152	-0.918362	-0.033192
H	0.349834	-1.694224	-1.637447	0.190063	-0.014034
H	-1.166494	-1.090765	-2.295896	0.226802	0.026580
H	0.162698	0.038082	-1.996154	0.209646	0.003392
C	-3.377175	0.020903	-0.081907	-0.821959	-0.017646
H	-4.047167	0.878586	0.006252	0.186009	-0.002357
H	-3.599077	-0.488444	-1.022661	0.210379	0.013117
H	-3.581208	-0.662560	0.742104	0.186787	0.003270

C	-1.330796	-1.973213	0.379079	-0.541553	-0.043117
H	-0.479024	-2.655888	0.415366	0.212700	-0.003157
H	-1.717392	-1.851810	1.393068	0.172155	-0.002385
H	-2.106566	-2.429211	-0.238403	0.203315	0.016838
B	-0.344662	0.735121	1.518410	0.973525	1.339130
H	0.261501	1.178177	2.439408	0.054721	-0.213024
F	4.254739	1.220928	-0.443499	-0.916889	-1.018326
K	2.819305	-0.568419	0.202794	0.903709	1.051748

I2A

HF/6-31G(d), N,N-dimethylformamide solution

Electronic energy: -1107.960496

Electronic energy + zero-point energy: -1107.754501

Electronic energy + thermal energy correction: -1107.742503

Electronic energy + thermal enthalpy correction: -1107.741559

Electronic energy + thermal free energy correction: -1107.792520

Table S102. Cartesian coordinates, Mulliken and APT charges of all atoms at **I2A** in the reaction of acetophenone with pinacolborane (HF/6-31G(d), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	0.467773	0.190085	-0.706956	-0.791740	-1.345993
C	-0.592122	0.807944	-0.000593	0.318350	0.674124
C	-1.661993	-0.330570	0.046804	0.331923	0.705882
O	-0.874051	-1.492183	0.127014	-0.724979	-1.291641
C	-2.600816	-0.281746	1.249244	-0.505254	0.108185
H	-3.166470	0.645238	1.275684	0.162728	-0.051928
H	-3.309851	-1.102139	1.189325	0.165757	-0.058526
H	-2.059852	-0.382664	2.181891	0.172565	-0.050467
C	-0.092352	1.203749	1.395124	-0.533682	0.059379
H	0.755388	1.878746	1.295647	0.159800	-0.083214
H	-0.849393	1.730116	1.966432	0.175506	-0.037081
H	0.225055	0.338326	1.965768	0.183301	-0.035422
C	-2.501816	-0.401101	-1.235130	-0.508954	0.077836
H	-3.070661	-1.325748	-1.226523	0.164324	-0.061598
H	-3.202917	0.423577	-1.315632	0.159561	-0.054071
H	-1.875701	-0.405446	-2.120665	0.170076	-0.047366
C	-1.017628	2.068438	-0.747180	-0.505413	0.110046
H	-0.214775	2.799977	-0.720673	0.169028	-0.060175
H	-1.239705	1.860599	-1.786140	0.176272	-0.045787

H	-1.892893	2.521121	-0.290390	0.166813	-0.045692
B	0.391311	-1.257447	-0.504256	0.883373	2.011618
H	0.579726	-1.874020	-1.558550	-0.322109	-0.529857
F	1.479742	-1.658970	0.379350	-0.532633	-0.973232
K	3.057811	0.322462	-0.071532	0.865385	1.024979

HF/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1108.147067

Electronic energy + zero-point energy: -1107.944035

Electronic energy + thermal energy correction: -1107.931921

Electronic energy + thermal enthalpy correction: -1107.930977

Electronic energy + thermal free energy correction: -1107.982302

Table S103. Cartesian coordinates, Mulliken and APT charges of all atoms at **I2A** in the reaction of acetophenone with pinacolborane (HF/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	0.472190	0.176374	-0.697916	-0.925774	-1.372367
C	-0.589107	0.807228	-0.005801	0.470013	0.688974
C	-1.662689	-0.325834	0.052225	0.943896	0.709940
O	-0.877216	-1.488337	0.135638	-0.972712	-1.312569
C	-2.594471	-0.264202	1.255148	-0.943207	0.081128
H	-3.154108	0.666169	1.273367	0.162283	-0.038752
H	-3.308272	-1.080402	1.202066	0.147829	-0.049633
H	-2.051900	-0.359445	2.186629	0.166349	-0.040930
C	-0.093918	1.222054	1.382749	-0.626519	0.033069
H	0.752401	1.896272	1.274960	0.150118	-0.072239
H	-0.853876	1.757657	1.940299	0.180948	-0.027540
H	0.219556	0.366457	1.969130	0.183752	-0.031463
C	-2.506969	-0.401444	-1.223295	-0.553476	0.050860
H	-3.087137	-1.318248	-1.200478	0.167275	-0.051517
H	-3.197833	0.430814	-1.306667	0.157060	-0.040832
H	-1.886283	-0.422149	-2.111744	0.139806	-0.041075
C	-1.007016	2.055745	-0.770238	-0.905443	0.080862
H	-0.200792	2.782921	-0.751952	0.147757	-0.052059
H	-1.230503	1.834777	-1.805412	0.169366	-0.036464
H	-1.879697	2.517403	-0.318398	0.170423	-0.033995
B	0.380213	-1.263754	-0.505425	1.561283	2.017576
H	0.559891	-1.883583	-1.557901	-0.231778	-0.483398
F	1.470063	-1.683427	0.369910	-0.707002	-1.017915
K	3.060639	0.327126	-0.065393	0.947752	1.040340

B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1111.934495

Electronic energy + zero-point energy: -1111.743952

Electronic energy + thermal energy correction: -1111.731080

Electronic energy + thermal enthalpy correction: -1111.730136

Electronic energy + thermal free energy correction: -1111.782682

Table S104. Cartesian coordinates, Mulliken and APT charges of all atoms at **I2A** in the reaction of acetophenone with pinacolborane (B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	0.484890	0.185130	-0.738357	-0.775470	-1.265604
C	-0.588573	0.813969	-0.002129	0.107820	0.633348
C	-1.665086	-0.332617	0.054650	0.624564	0.666322
O	-0.863448	-1.520815	0.102795	-0.793563	-1.215486
C	-2.569686	-0.294075	1.283208	-0.719582	0.016005
H	-3.139025	0.638337	1.325715	0.160908	-0.017546
H	-3.284812	-1.119611	1.236870	0.141001	-0.028770
H	-1.999558	-0.395907	2.206749	0.160720	-0.018691
C	-0.073119	1.212103	1.388556	-0.491780	-0.032849
H	0.767084	1.906034	1.279953	0.140869	-0.050307
H	-0.836229	1.735078	1.969061	0.173455	-0.009362
H	0.257606	0.344669	1.961979	0.174240	-0.009109
C	-2.534627	-0.386768	-1.210043	-0.446090	-0.014328
H	-3.118603	-1.310152	-1.192503	0.157890	-0.028272
H	-3.232169	0.452375	-1.265895	0.151723	-0.022859
H	-1.924569	-0.390277	-2.115278	0.142249	-0.018085
C	-1.024805	2.069172	-0.751027	-0.750051	0.016884
H	-0.217056	2.806188	-0.741978	0.137128	-0.031573
H	-1.270604	1.852411	-1.790356	0.162512	-0.014136
H	-1.896463	2.526348	-0.275269	0.167966	-0.012060
B	0.401063	-1.268056	-0.537871	1.321440	1.845757
H	0.616926	-1.889115	-1.575846	-0.225849	-0.439575
F	1.518366	-1.681749	0.374702	-0.629980	-0.989505
K	3.019511	0.342865	-0.063209	0.907879	1.039803

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1111.711379

Electronic energy + zero-point energy: -1111.518145

Electronic energy + thermal energy correction: -1111.505620

Electronic energy + thermal enthalpy correction: -1111.504675

Electronic energy + thermal free energy correction: -1111.556667

Table S105. Cartesian coordinates, Mulliken and APT charges of all atoms at **I2A** in the reaction of acetophenone with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	0.466319	0.147624	-0.793051	-0.675561	-1.262944
C	-0.554596	0.792205	-0.023281	-0.190165	0.622635
C	-1.639815	-0.321425	0.072507	0.422610	0.657642
O	-0.862878	-1.508059	0.165348	-0.648849	-1.217754
C	-2.543452	-0.209500	1.289218	-0.716228	-0.023734
H	-3.059643	0.754077	1.302765	0.192557	-0.001587
H	-3.298681	-0.998105	1.257612	0.172790	-0.013799
H	-1.976528	-0.317899	2.213792	0.174401	-0.006449
C	0.010974	1.159245	1.349976	-0.468387	-0.077416
H	0.848976	1.852926	1.226550	0.157695	-0.042943
H	-0.728578	1.674016	1.966102	0.205737	0.012716
H	0.350271	0.269912	1.885589	0.189568	0.007354
C	-2.492506	-0.392687	-1.194978	-0.463127	-0.055688
H	-3.088030	-1.307191	-1.161299	0.186737	-0.013605
H	-3.172938	0.457694	-1.277167	0.176119	-0.006874
H	-1.862304	-0.425241	-2.086194	0.159792	-0.003345
C	-1.003758	2.052519	-0.741934	-0.718099	-0.025693
H	-0.196181	2.788663	-0.738945	0.170138	-0.015800
H	-1.270214	1.841979	-1.777215	0.173564	-0.000998
H	-1.867196	2.496017	-0.239285	0.200924	0.002935
B	0.382938	-1.299177	-0.531477	1.112953	1.834503
H	0.544940	-1.954742	-1.553695	-0.145855	-0.424767
F	1.503093	-1.670731	0.356593	-0.588034	-0.978591
K	2.939208	0.357985	-0.055684	0.918721	1.034201

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1111.773658

Electronic energy + zero-point energy: -1111.581200

Electronic energy + thermal energy correction: -1111.568572

Electronic energy + thermal enthalpy correction: -1111.567628

Electronic energy + thermal free energy correction: -1111.619728

Table S106. Cartesian coordinates, Mulliken and APT charges of all atoms at **I2A** in the reaction of acetophenone with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	0.471742	0.163392	-0.760869	-0.769149	-1.276737
C	-0.568888	0.798455	-0.012099	0.106568	0.631499
C	-1.652919	-0.325961	0.061338	0.623595	0.662915
O	-0.874073	-1.512582	0.126664	-0.770329	-1.225827
C	-2.554552	-0.245844	1.283664	-0.781617	0.002317
H	-3.082226	0.711612	1.316210	0.190157	-0.011158
H	-3.303029	-1.041552	1.242048	0.164978	-0.023828
H	-1.987074	-0.363643	2.207520	0.177627	-0.012626
C	-0.032898	1.182202	1.369971	-0.573058	-0.050676
H	0.804699	1.878711	1.256896	0.156463	-0.046674
H	-0.788405	1.699329	1.965449	0.202078	0.000820
H	0.303821	0.305268	1.926765	0.198441	-0.003040
C	-2.517200	-0.378108	-1.201216	-0.531412	-0.026247
H	-3.113060	-1.293820	-1.178953	0.183371	-0.023681
H	-3.201463	0.471803	-1.263239	0.174304	-0.016535
H	-1.900666	-0.395218	-2.102822	0.161966	-0.013620
C	-1.010234	2.056525	-0.742431	-0.772904	0.002632
H	-0.204518	2.795791	-0.730761	0.164028	-0.026075
H	-1.263229	1.846885	-1.781954	0.178068	-0.009374
H	-1.881356	2.501488	-0.253450	0.198720	-0.006162
B	0.381422	-1.282716	-0.534386	1.211912	1.867411
H	0.576034	-1.921991	-1.570292	-0.192503	-0.438706
F	1.499532	-1.685234	0.371505	-0.616210	-0.995861
K	2.993493	0.350311	-0.062460	0.914906	1.039234

I3A

<u>HF/6-31G(d), N,N-dimethylformamide solution</u>

Electronic energy: -1490.464782

Electronic energy + zero-point energy: -1490.110305

Electronic energy + thermal energy correction: -1490.089432

Electronic energy + thermal enthalpy correction: -1490.088488

Electronic energy + thermal free energy correction: -1490.165782

Table S107. Cartesian coordinates, Mulliken and APT charges of all atoms at **I3A** in the reaction of acetophenone with pinacolborane (HF/6-31G(d), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	2.540956	0.180259	-0.514212	-0.785809	-1.346084
C	3.704983	-0.619326	-0.439349	0.318237	0.679463
C	4.816418	0.444996	-0.165997	0.332537	0.705182
O	4.142018	1.401419	0.612471	-0.726999	-1.298317
C	6.024376	-0.069729	0.612235	-0.505365	0.108949
H	6.525236	-0.875698	0.083435	0.162091	-0.052864
H	6.740604	0.735840	0.745113	0.165184	-0.059146
H	5.743507	-0.424444	1.596089	0.172234	-0.050707
C	3.548522	-1.615642	0.717275	-0.531561	0.062219
H	2.663031	-2.225073	0.549271	0.160949	-0.083140
H	4.391856	-2.294304	0.789474	0.173097	-0.040574
H	3.436540	-1.107377	1.668216	0.182739	-0.034819
C	5.308120	1.123200	-1.451450	-0.509308	0.078499
H	5.912337	1.983681	-1.180855	0.163610	-0.062306
H	5.918092	0.463042	-2.060007	0.158913	-0.055643
H	4.479844	1.476821	-2.055648	0.169933	-0.046902
C	3.856620	-1.397307	-1.743055	-0.505888	0.107618
H	3.043731	-2.111560	-1.841010	0.168594	-0.060485
H	3.824499	-0.742310	-2.604460	0.175611	-0.046636
H	4.789633	-1.952996	-1.765801	0.165722	-0.047347
B	2.745840	1.391927	0.278499	0.889822	2.025315
H	2.339849	2.397329	-0.318071	-0.328158	-0.535838
F	1.939515	1.306971	1.487066	-0.529064	-0.978287
K	0.155339	-0.384879	0.614759	0.808304	1.090042
C	-6.715878	1.655436	-0.407027	-0.199401	0.131777
C	-7.014771	0.303434	-0.349771	-0.240554	-0.172412
C	-5.998825	-0.624006	-0.181189	-0.210077	0.061034
C	-4.675920	-0.203993	-0.067593	-0.134622	-0.424354
C	-4.386273	1.159283	-0.126128	-0.195148	0.036334
C	-5.399405	2.084099	-0.295114	-0.239511	-0.170271
H	-7.504837	2.374330	-0.538236	0.244882	0.046672
H	-8.033215	-0.029409	-0.436039	0.241319	0.047355
H	-6.247838	-1.667200	-0.138965	0.258883	0.070751
H	-3.367980	1.487296	-0.039468	0.260020	0.082376
H	-5.167583	3.132928	-0.339761	0.242069	0.046482
C	-3.553857	-1.171630	0.116703	0.605140	1.528819
O	-2.420003	-0.771332	0.229769	-0.641470	-1.300491
C	-3.843493	-2.648484	0.161470	-0.600686	-0.094415
H	-4.505159	-2.878254	0.989937	0.223804	0.030084

H	-4.331276	-2.968293	-0.752935	0.222974	0.030456
H	-2.914629	-3.188766	0.282924	0.216952	-0.008390

HF/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1490.754996

Electronic energy + zero-point energy: -1490.405177

Electronic energy + thermal energy correction: -1490.383238

Electronic energy + thermal enthalpy correction: -1490.382293

Electronic energy + thermal free energy correction: -1490.464668

Table S108. Cartesian coordinates, Mulliken and APT charges of all atoms at **I3A** in the reaction of acetophenone with pinacolborane (HF/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	2.561218	0.153747	-0.506217	-0.886682	-1.374555
C	3.751588	-0.606097	-0.437724	0.383957	0.695332
C	4.822179	0.488515	-0.129774	0.971090	0.708685
O	4.101947	1.408814	0.650311	-0.959255	-1.318799
C	6.030308	0.000135	0.658395	-0.971215	0.081843
H	6.560711	-0.781850	0.123212	0.160810	-0.039454
H	6.720092	0.824350	0.811853	0.150120	-0.050729
H	5.746543	-0.378743	1.631569	0.167137	-0.041409
C	3.617486	-1.632885	0.690759	-0.645383	0.036540
H	2.757141	-2.268119	0.495889	0.155199	-0.072341
H	4.483795	-2.282086	0.752660	0.179849	-0.031785
H	3.479468	-1.154479	1.653009	0.197518	-0.030887
C	5.312791	1.201952	-1.393256	-0.508918	0.051735
H	5.892424	2.070562	-1.097816	0.166352	-0.052385
H	5.947185	0.566523	-2.002187	0.157097	-0.042431
H	4.485443	1.545583	-2.003432	0.141768	-0.040293
C	3.944052	-1.346582	-1.754233	-0.916410	0.077895
H	3.158262	-2.086132	-1.876224	0.145418	-0.052337
H	3.900381	-0.674482	-2.600925	0.167179	-0.037814
H	4.895924	-1.868592	-1.775077	0.170880	-0.035550
B	2.718009	1.362806	0.287226	1.587805	2.030575
H	2.292608	2.361518	-0.304957	-0.236188	-0.489031
F	1.892086	1.252707	1.481457	-0.697249	-1.023172
K	0.157588	-0.503460	0.535467	0.916366	1.112565
C	-6.698465	1.707278	-0.366958	-0.212970	0.112673
C	-7.021950	0.364707	-0.310774	-0.492630	-0.190545
C	-6.023338	-0.581104	-0.161162	-0.167515	0.041321

C	-4.694992	-0.189080	-0.065857	0.658236	-0.429294
C	-4.379951	1.165042	-0.123147	-0.315580	0.025152
C	-5.374586	2.108145	-0.273165	-0.378898	-0.193334
H	-7.474292	2.441881	-0.483735	0.220260	0.066135
H	-8.047060	0.051979	-0.383126	0.221482	0.065989
H	-6.292065	-1.618482	-0.119798	0.249221	0.087788
H	-3.355203	1.473153	-0.050319	0.232091	0.096372
H	-5.122657	3.151559	-0.317080	0.232648	0.064680
C	-3.592007	-1.182511	0.097729	0.740147	1.582931
O	-2.453046	-0.808630	0.191686	-0.680545	-1.344101
C	-3.914577	-2.648691	0.144131	-0.890713	-0.102825
H	-4.573702	-2.859643	0.978908	0.201848	0.028740
H	-4.421354	-2.950197	-0.765653	0.200612	0.028747
H	-2.998816	-3.211347	0.254093	0.185061	-0.002629

B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1496.971160

Electronic energy + zero-point energy: -1496.642973

Electronic energy + thermal energy correction: -1496.619800

Electronic energy + thermal enthalpy correction: -1496.618855

Electronic energy + thermal free energy correction: -1496.702364

Table S109. Cartesian coordinates, Mulliken and APT charges of all atoms at **I3A** in the reaction of acetophenone with pinacolborane (B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	2.532428	0.180777	-0.557904	-0.748212	-1.270187
C	3.722572	-0.625609	-0.428288	0.048595	0.641606
C	4.822643	0.457047	-0.120127	0.636909	0.665147
O	4.096322	1.444733	0.622384	-0.784528	-1.225093
C	5.988858	-0.044033	0.727349	-0.733422	0.018127
H	6.518952	-0.859598	0.227995	0.159609	-0.018773
H	6.702099	0.769175	0.886355	0.141897	-0.030687
H	5.655548	-0.393000	1.704847	0.160597	-0.018545
C	3.530166	-1.618948	0.727160	-0.505665	-0.029208
H	2.659436	-2.249938	0.521600	0.143006	-0.050570
H	4.386674	-2.288684	0.832835	0.174026	-0.014023
H	3.375598	-1.107550	1.678526	0.183231	-0.008775
C	5.372378	1.115350	-1.394534	-0.407179	-0.013446
H	5.975018	1.980926	-1.108709	0.156953	-0.029231

H	6.008397	0.436258	-1.967485	0.151343	-0.024576
H	4.566878	1.464344	-2.043315	0.144065	-0.018380
C	3.930757	-1.402753	-1.724679	-0.752464	0.015382
H	3.122338	-2.127378	-1.856236	0.135096	-0.032734
H	3.935260	-0.743558	-2.592561	0.160846	-0.015367
H	4.872925	-1.957020	-1.703467	0.167553	-0.014316
B	2.708559	1.407935	0.228651	1.341364	1.864445
H	2.292741	2.399707	-0.369441	-0.227598	-0.445184
F	1.845425	1.326201	1.447168	-0.620367	-0.998558
K	0.166078	-0.425663	0.514157	0.866161	1.127475
C	-6.696912	1.686163	-0.377123	-0.159929	0.055315
C	-7.013832	0.332904	-0.300886	-0.416533	-0.148750
C	-6.005475	-0.610776	-0.143634	-0.132925	0.037391
C	-4.666784	-0.207889	-0.060102	0.626435	-0.467842
C	-4.359618	1.157443	-0.137662	-0.334579	0.028485
C	-5.366876	2.097346	-0.295367	-0.299811	-0.147978
H	-7.484340	2.420749	-0.500223	0.187342	0.065177
H	-8.046691	0.011873	-0.364134	0.186828	0.062887
H	-6.267291	-1.658991	-0.086128	0.211553	0.087777
H	-3.325238	1.470058	-0.073354	0.185722	0.095326
H	-5.119574	3.150643	-0.354938	0.196824	0.061912
C	-3.561624	-1.191341	0.109797	0.563555	1.524575
O	-2.397593	-0.806080	0.190075	-0.588866	-1.228453
C	-3.878122	-2.659118	0.183018	-0.759749	-0.208657
H	-4.536096	-2.865821	1.031351	0.190600	0.045621
H	-4.402530	-2.984444	-0.719171	0.188365	0.045589
H	-2.955251	-3.225801	0.292935	0.163351	0.017096

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1496.578794

Electronic energy + zero-point energy: -1496.246263

Electronic energy + thermal energy correction: -1496.223687

Electronic energy + thermal enthalpy correction: -1496.222743

Electronic energy + thermal free energy correction: -1496.304229

Table S110. Cartesian coordinates, Mulliken and APT charges of all atoms at **I3A** in the reaction of acetophenone with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	2.269714	0.265133	-0.434828	-0.633429	-1.269531

C	3.478905	-0.480320	-0.601281	-0.283308	0.631535
C	4.565042	0.570538	-0.220141	0.446468	0.657433
O	3.934331	1.308896	0.816625	-0.633774	-1.224877
C	5.860636	-0.030066	0.299823	-0.727595	-0.022659
H	6.299726	-0.706644	-0.438122	0.191227	-0.003009
H	6.580159	0.767518	0.498781	0.174268	-0.015321
H	5.696834	-0.579339	1.226907	0.174596	-0.006653
C	3.471440	-1.669916	0.360795	-0.442714	-0.076768
H	2.623856	-2.321986	0.126914	0.155239	-0.040679
H	4.371280	-2.279099	0.256322	0.209473	0.008892
H	3.397762	-1.335012	1.397906	0.192293	0.007429
C	4.869195	1.517685	-1.381866	-0.441381	-0.055646
H	5.469201	2.348259	-1.004566	0.186177	-0.014672
H	5.430285	1.021408	-2.176736	0.176408	-0.007810
H	3.947368	1.923325	-1.803899	0.158146	-0.004417
C	3.564125	-0.986213	-2.031321	-0.734746	-0.025563
H	2.787223	-1.734559	-2.206091	0.165047	-0.016990
H	3.423575	-0.175593	-2.745682	0.171521	-0.000730
H	4.533692	-1.455620	-2.217627	0.201096	0.001402
B	2.507659	1.297038	0.586736	1.118814	1.850145
H	2.008365	2.371553	0.268542	-0.144358	-0.430064
F	1.824563	0.896377	1.828814	-0.576248	-0.985808
K	0.260981	-0.849083	0.833428	0.889683	1.118512
C	-6.269288	1.914878	-0.380433	-0.220694	0.034989
C	-6.683731	0.596995	-0.528910	-0.495900	-0.151770
C	-5.769478	-0.438340	-0.387055	-0.101635	0.004343
C	-4.434472	-0.157011	-0.095383	0.667675	-0.426351
C	-4.024752	1.169809	0.052191	-0.359177	-0.003642
C	-4.938173	2.201316	-0.089748	-0.322208	-0.151784
H	-6.983847	2.721658	-0.491365	0.226867	0.079453
H	-7.719124	0.374812	-0.755115	0.231984	0.077089
H	-6.101307	-1.462105	-0.504762	0.236581	0.100688
H	-2.986910	1.380730	0.278110	0.170627	0.106989
H	-4.616601	3.229010	0.025334	0.246618	0.075868
C	-3.429210	-1.246145	0.064456	0.472551	1.501910
O	-2.267766	-0.973614	0.321051	-0.515348	-1.229715
C	-3.864519	-2.671450	-0.092498	-0.849502	-0.246887
H	-4.640646	-2.907437	0.638847	0.212554	0.061276
H	-4.292814	-2.825219	-1.085285	0.209133	0.061821
H	-3.010622	-3.329562	0.048904	0.196973	0.031569

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1496.671724

Electronic energy + zero-point energy: -1496.339949

Electronic energy + thermal energy correction: -1496.317280

Electronic energy + thermal enthalpy correction: -1496.316336

Electronic energy + thermal free energy correction: -1496.397519

Table S111. Cartesian coordinates, Mulliken and APT charges of all atoms at **I3A** in the reaction of acetophenone with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	2.409907	0.248561	-0.525253	-0.739909	-1.280956
C	3.519123	-0.643929	-0.403291	0.028173	0.636941
C	4.719013	0.343875	-0.230411	0.654398	0.662618
O	4.140878	1.417766	0.497082	-0.756818	-1.234335
C	5.890131	-0.226233	0.555181	-0.802933	0.003565
H	6.281841	-1.126141	0.072439	0.188768	-0.011537
H	6.697171	0.509887	0.600989	0.167030	-0.024538
H	5.601555	-0.475486	1.576994	0.178416	-0.014097
C	3.317794	-1.535406	0.825570	-0.583574	-0.046789
H	2.399416	-2.119732	0.706684	0.154004	-0.047807
H	4.132471	-2.253998	0.939812	0.204108	-0.003409
H	3.248538	-0.944442	1.741296	0.210126	-0.003297
C	5.224445	0.878243	-1.573380	-0.498523	-0.026464
H	5.916582	1.702281	-1.383415	0.182953	-0.024121
H	5.755405	0.112394	-2.144395	0.174384	-0.017047
H	4.401611	1.258718	-2.182850	0.161068	-0.013178
C	3.593070	-1.517897	-1.645399	-0.781015	0.002105
H	2.730220	-2.188861	-1.679937	0.160526	-0.026856
H	3.592467	-0.918129	-2.555892	0.177086	-0.012032
H	4.497085	-2.133314	-1.632631	0.198230	-0.008182
B	2.737954	1.491023	0.179664	1.225344	1.886175
H	2.379593	2.486650	-0.456590	-0.200097	-0.444793
F	1.950835	1.547637	1.442067	-0.602097	-0.998109
K	0.136522	-0.192137	0.773613	0.892829	1.117560
C	-6.472398	1.710997	-0.458213	-0.257591	0.051928
C	-6.839792	0.373871	-0.390800	-0.450578	-0.148805
C	-5.873006	-0.603127	-0.204897	-0.154022	0.018156
C	-4.529454	-0.247408	-0.082977	0.650175	-0.447679
C	-4.169586	1.099698	-0.152495	-0.355643	0.012340
C	-5.135046	2.073543	-0.339488	-0.325468	-0.148902
H	-7.228988	2.473532	-0.603744	0.234154	0.068772
H	-7.881440	0.090327	-0.483407	0.239823	0.067729
H	-6.174029	-1.642020	-0.154695	0.243951	0.091435

H	-3.126532	1.376507	-0.059973	0.202142	0.092177
H	-4.847809	3.116987	-0.393244	0.251784	0.066504
C	-3.466303	-1.271437	0.123016	0.556692	1.520762
O	-2.300864	-0.928864	0.250084	-0.562752	-1.218706
C	-3.841800	-2.721136	0.174197	-0.901017	-0.225703
H	-4.535705	-2.900227	0.999618	0.218374	0.053118
H	-4.349971	-3.014055	-0.747892	0.214599	0.052504
H	-2.947194	-3.325737	0.310283	0.202901	0.022955

TS1A

HF/6-31G(d), N,N-dimethylformamide solution

Electronic energy: -1490.413115

Electronic energy + zero-point energy: -1490.059222

Electronic energy + thermal energy correction: -1490.038977

Electronic energy + thermal enthalpy correction: -1490.038033

Electronic energy + thermal free energy correction: -1490.109033

Table S112. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS1A** in the reaction of acetophenone with pinacolborane (HF/6-31G(d), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	1.669698	0.728125	0.085551	-0.762001	-1.497681
C	2.897442	0.006254	-0.017734	0.305928	0.740217
C	2.400628	-1.477233	-0.114363	0.290323	0.728328
O	1.141146	-1.334807	-0.761431	-0.705019	-1.499197
C	3.277849	-2.394350	-0.958027	-0.502826	0.098147
H	4.281025	-2.458991	-0.548382	0.172713	-0.045315
H	2.854678	-3.393755	-0.964958	0.174756	-0.048170
H	3.343562	-2.054796	-1.983534	0.180220	-0.040527
C	3.606528	0.485097	-1.286821	-0.513917	0.057739
H	3.749015	1.559694	-1.225870	0.178432	-0.053263
H	4.581888	0.025211	-1.401708	0.176036	-0.044379
H	3.021450	0.274455	-2.175270	0.180546	-0.037938
C	2.167706	-2.123731	1.252658	-0.514064	0.063333
H	1.634209	-3.057817	1.109808	0.174438	-0.047919
H	3.102487	-2.343439	1.757009	0.171689	-0.039441
H	1.570299	-1.493510	1.899825	0.183179	-0.037950
C	3.759933	0.324227	1.196250	-0.506546	0.092314
H	4.050370	1.370063	1.173154	0.178148	-0.048521
H	3.229373	0.146771	2.122732	0.183284	-0.037635

H	4.666244	-0.273114	1.195416	0.175791	-0.036295
B	0.657095	-0.057369	-0.501821	1.154263	2.651702
H	-0.375326	-0.122339	0.471295	-0.367405	-1.167608
F	-0.041369	0.560549	-1.525769	-0.454198	-0.950589
K	0.347031	3.073039	-0.382180	0.835838	1.031895
C	-4.761949	-1.293179	-0.899430	-0.234219	-0.059554
C	-3.738167	-2.105900	-0.428161	-0.233863	-0.028329
C	-2.646174	-1.547759	0.214028	-0.235574	-0.068522
C	-2.553738	-0.168898	0.394555	-0.030308	-0.218669
C	-3.578668	0.635180	-0.084668	-0.241661	-0.090892
C	-4.678293	0.077906	-0.725651	-0.230284	-0.012319
H	-5.611244	-1.727104	-1.397262	0.228058	0.032180
H	-3.791075	-3.171945	-0.564144	0.228247	0.030039
H	-1.854576	-2.188631	0.559970	0.234332	0.048804
H	-3.509004	1.697681	0.049244	0.237809	0.082960
H	-5.465328	0.716120	-1.088290	0.226848	0.024316
C	-1.382534	0.488520	1.127320	0.449400	2.104836
O	-1.286705	1.750745	1.031123	-0.808201	-1.469335
C	-1.108288	-0.097541	2.510768	-0.506848	-0.072361
H	-1.054152	-1.179020	2.521593	0.169824	-0.032226
H	-0.181324	0.311560	2.895428	0.178586	-0.048335
H	-1.916078	0.213011	3.170111	0.178247	-0.053839

HF/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1490.704122

Electronic energy + zero-point energy: -1490.355123

Electronic energy + thermal energy correction: -1490.334739

Electronic energy + thermal enthalpy correction: -1490.333795

Electronic energy + thermal free energy correction: -1490.405232

Table S113. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS1A** in the reaction of acetophenone with pinacolborane (HF/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	1.663831	0.704615	0.089397	-1.103047	-1.515930
C	2.886000	-0.024145	-0.007027	0.650070	0.758512
C	2.380647	-1.501097	-0.133290	0.464834	0.733726
O	1.130193	-1.337935	-0.788311	-1.022746	-1.520520
C	3.260023	-2.407357	-0.980820	-0.984579	0.072817
H	4.257541	-2.482616	-0.560014	0.178141	-0.035555

H	2.832479	-3.404278	-1.006467	0.160632	-0.041778
H	3.339287	-2.052178	-1.999395	0.172393	-0.032899
C	3.618029	0.467183	-1.255104	-0.459739	0.029950
H	3.771849	1.538240	-1.172733	0.180518	-0.047056
H	4.589634	-0.001939	-1.360200	0.179631	-0.035896
H	3.045935	0.277204	-2.155863	0.131807	-0.031740
C	2.132650	-2.167977	1.218569	-0.570664	0.039764
H	1.601054	-3.099225	1.054640	0.184112	-0.040863
H	3.062859	-2.396435	1.726568	0.188131	-0.029910
H	1.530280	-1.548011	1.869989	0.153913	-0.033127
C	3.732959	0.266599	1.221100	-0.919324	0.064722
H	4.033100	1.309474	1.217421	0.166580	-0.042089
H	3.190109	0.078158	2.137435	0.174936	-0.030753
H	4.633621	-0.338740	1.220183	0.181068	-0.027338
B	0.647169	-0.064434	-0.507041	2.277333	2.659754
H	-0.383185	-0.154487	0.448353	-0.223357	-1.139532
F	-0.024178	0.566996	-1.535104	-0.688957	-0.979982
K	0.429769	3.092314	-0.342915	0.955597	1.048526
C	-4.784382	-1.272569	-0.882802	-0.428127	-0.072850
C	-3.800449	-2.086727	-0.342832	-0.254789	-0.055720
C	-2.706056	-1.528960	0.288693	-0.568253	-0.082614
C	-2.570518	-0.148932	0.390029	0.460187	-0.211052
C	-3.555239	0.656094	-0.156229	0.453432	-0.108627
C	-4.657852	0.099414	-0.787239	-0.303310	-0.039353
H	-5.636628	-1.706897	-1.373438	0.208029	0.055869
H	-3.886353	-3.155912	-0.416554	0.217363	0.051899
H	-1.948640	-2.176143	0.690864	0.262308	0.064628
H	-3.454846	1.721207	-0.083708	0.258103	0.098350
H	-5.414188	0.740654	-1.203329	0.219047	0.047204
C	-1.392743	0.508761	1.107626	0.033352	2.131699
O	-1.273850	1.759122	0.981670	-0.810400	-1.507819
C	-1.105100	-0.056312	2.492739	-0.748108	-0.107487
H	-1.052418	-1.136511	2.517542	0.201350	-0.012187
H	-0.175516	0.358281	2.861845	0.170528	-0.033656
H	-1.909021	0.265136	3.150859	0.202005	-0.041087

B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1496.940156

Electronic energy + zero-point energy: -1496.612902

Electronic energy + thermal energy correction: -1496.591259

Electronic energy + thermal enthalpy correction: -1496.590315

Electronic energy + thermal free energy correction: -1496.664082

Table S114. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS1A** in the reaction of acetophenone with pinacolborane (B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	1.672210	0.763611	0.018846	-0.883018	-1.419571
C	2.921131	0.013904	-0.032875	0.236939	0.718021
C	2.414106	-1.479402	-0.113134	0.160579	0.689311
O	1.140663	-1.342944	-0.799263	-0.781288	-1.410873
C	3.301099	-2.406758	-0.934366	-0.759241	0.001627
H	4.302179	-2.469088	-0.500853	0.174240	-0.014427
H	2.874357	-3.412623	-0.937213	0.150617	-0.019639
H	3.389219	-2.073310	-1.967970	0.164821	-0.008518
C	3.668403	0.464015	-1.290833	-0.365002	-0.047928
H	3.824193	1.544458	-1.243484	0.165452	-0.019663
H	4.647908	-0.012771	-1.366312	0.172357	-0.019223
H	3.104395	0.239461	-2.197903	0.131815	-0.008446
C	2.156460	-2.102913	1.260695	-0.416415	-0.030661
H	1.626579	-3.048308	1.124384	0.167758	-0.017019
H	3.091731	-2.312875	1.783750	0.175497	-0.007839
H	1.545097	-1.458677	1.892840	0.161484	-0.006842
C	3.744086	0.346164	1.203951	-0.695230	-0.006793
H	4.044839	1.396413	1.175200	0.151190	-0.020263
H	3.181870	0.178798	2.122195	0.165962	-0.007208
H	4.652858	-0.259715	1.236389	0.176523	-0.004605
B	0.658035	-0.052424	-0.550767	1.998396	2.460395
H	-0.376626	-0.071800	0.426244	-0.353878	-0.911123
F	-0.062070	0.557231	-1.593831	-0.583497	-0.939770
K	0.323905	3.049856	-0.333283	0.891499	1.039581
C	-4.770907	-1.298304	-0.901984	-0.348490	-0.085795
C	-3.788060	-2.115268	-0.345114	-0.216519	-0.043949
C	-2.695364	-1.551903	0.305824	-0.402839	-0.084182
C	-2.562689	-0.163495	0.410327	0.446754	-0.181447
C	-3.549306	0.644574	-0.154544	0.256740	-0.099447
C	-4.647157	0.084321	-0.804438	-0.232778	-0.034625
H	-5.623018	-1.737634	-1.408195	0.171148	0.051413
H	-3.872705	-3.193776	-0.419983	0.182065	0.045691
H	-1.935899	-2.203072	0.722841	0.199740	0.061140
H	-3.442801	1.719136	-0.073767	0.199317	0.101803
H	-5.405952	0.728906	-1.234732	0.180262	0.041067
C	-1.385858	0.500847	1.135310	-0.032960	1.835231
O	-1.316545	1.783575	1.072376	-0.687360	-1.393569

C	-1.059153	-0.122847	2.497997	-0.621818	-0.160749
H	-0.961133	-1.208512	2.470155	0.172916	0.001102
H	-0.134574	0.310907	2.881559	0.157309	-0.017298
H	-1.869633	0.132303	3.188984	0.168955	-0.024911

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1496.558101

Electronic energy + zero-point energy: -1496.226397

Electronic energy + thermal energy correction: -1496.205339

Electronic energy + thermal enthalpy correction: -1496.204395

Electronic energy + thermal free energy correction: -1496.275768

Table S115. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS1A** in the reaction of acetophenone with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	1.212708	0.257483	0.502853	-0.720127	-1.326284
C	1.878081	-1.017914	0.619368	0.251802	0.681094
C	1.491397	-1.717578	-0.723368	-0.277030	0.641958
O	1.413793	-0.607714	-1.636997	-0.537391	-1.389587
C	2.526004	-2.702881	-1.233288	-0.802446	-0.025692
H	2.694842	-3.491061	-0.495657	0.208008	0.002952
H	2.164744	-3.168944	-2.152319	0.183587	-0.006255
H	3.474520	-2.210915	-1.446263	0.180195	0.002768
C	3.374457	-0.744737	0.725118	-0.448435	-0.074943
H	3.555142	-0.092038	1.581988	0.192474	-0.009731
H	3.937142	-1.667878	0.875931	0.194072	-0.001130
H	3.747561	-0.250268	-0.174238	0.162108	0.005640
C	0.122399	-2.387075	-0.652598	-0.381535	-0.075271
H	-0.194987	-2.645260	-1.664969	0.204125	-0.005800
H	0.162764	-3.303073	-0.059667	0.204811	0.008022
H	-0.621523	-1.720128	-0.214012	0.141938	0.024068
C	1.382340	-1.728163	1.863742	-0.655692	-0.044235
H	1.714635	-1.188155	2.753026	0.188252	-0.005520
H	0.294099	-1.784961	1.880622	0.144839	0.009384
H	1.789777	-2.741050	1.909543	0.211356	0.011272
B	1.041804	0.511414	-0.882198	1.156335	2.431244
H	-0.334612	0.738295	-1.032577	0.515422	-0.917844
F	1.524638	1.746447	-1.313662	-0.508241	-0.989747
K	1.277801	2.790628	1.164116	0.961650	1.046002

C	-3.579840	-1.779940	0.996845	-0.334265	-0.088822
C	-3.697265	-1.483409	-0.355780	-0.407446	-0.054192
C	-3.002658	-0.408048	-0.900276	0.118044	-0.112314
C	-2.185768	0.386570	-0.097144	0.189388	-0.188457
C	-2.086292	0.091876	1.261372	-0.177992	-0.108783
C	-2.773529	-0.985149	1.805973	-0.217787	-0.048800
H	-4.116195	-2.621365	1.419140	0.223642	0.066775
H	-4.329510	-2.092121	-0.991580	0.225844	0.061525
H	-3.098289	-0.202418	-1.959220	0.221096	0.080166
H	-1.451550	0.715867	1.877988	0.213595	0.099204
H	-2.679229	-1.208688	2.862542	0.237100	0.059039
C	-1.343147	1.531805	-0.647658	-0.043460	1.808300
O	-0.968653	2.420655	0.196028	-0.622792	-1.390182
C	-1.725944	2.033847	-2.036126	-0.953117	-0.178574
H	-1.764966	1.244287	-2.786661	0.155053	0.010584
H	-2.706339	2.516046	-1.977583	0.197224	-0.016754
H	-0.991193	2.778174	-2.342432	0.205796	0.008922

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1496.651938

Electronic energy + zero-point energy: -1496.320732

Electronic energy + thermal energy correction: -1496.299590

Electronic energy + thermal enthalpy correction: -1496.298645

Electronic energy + thermal free energy correction: -1496.370447

Table S116. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS1A** in the reaction of acetophenone with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	1.284629	0.325820	0.471990	-0.852224	-1.352917
C	1.934196	-0.949784	0.625746	0.393429	0.687036
C	1.517679	-1.702504	-0.687129	-0.019682	0.648577
O	1.377864	-0.628620	-1.634102	-0.717539	-1.391711
C	2.562976	-2.675230	-1.204100	-0.843336	-0.002435
H	2.772765	-3.442280	-0.454136	0.210919	-0.007020
H	2.189126	-3.173654	-2.101775	0.177467	-0.016429
H	3.494885	-2.169124	-1.456831	0.185056	-0.005414
C	3.435246	-0.687844	0.711170	-0.475777	-0.046799
H	3.628362	-0.005796	1.543005	0.195869	-0.016244
H	3.991864	-1.609818	0.892699	0.193008	-0.012035

H	3.812662	-0.227692	-0.204664	0.162853	-0.003994
C	0.174484	-2.415073	-0.557654	-0.611197	-0.052746
H	-0.156577	-2.727227	-1.550781	0.198309	-0.014819
H	0.258760	-3.305096	0.069863	0.197032	-0.000409
H	-0.586796	-1.761406	-0.132202	0.331899	0.019496
C	1.446792	-1.602516	1.906212	-0.750663	-0.018080
H	1.792665	-1.028013	2.769250	0.182082	-0.016416
H	0.358281	-1.650902	1.940727	0.163581	-0.000044
H	1.846681	-2.616041	1.993586	0.212553	0.002232
B	1.054854	0.523433	-0.911347	1.498686	2.488645
H	-0.322346	0.775715	-0.993910	0.423173	-0.935365
F	1.533008	1.737470	-1.419860	-0.549170	-1.009399
K	1.132155	2.850548	1.192787	0.931616	1.046279
C	-3.506676	-1.864918	1.011864	-0.321522	-0.077109
C	-3.612334	-1.604995	-0.347538	-0.410605	-0.046207
C	-2.955091	-0.514633	-0.905146	0.024679	-0.102679
C	-2.188962	0.334286	-0.110130	0.288756	-0.199499
C	-2.101881	0.073552	1.254934	-0.204432	-0.099338
C	-2.749405	-1.018364	1.813499	-0.358146	-0.039654
H	-4.013241	-2.719869	1.445528	0.225836	0.056266
H	-4.205704	-2.255620	-0.980489	0.226347	0.051433
H	-3.039722	-0.340605	-1.970989	0.218273	0.073998
H	-1.508302	0.737536	1.870896	0.226923	0.085667
H	-2.661694	-1.213075	2.876918	0.235831	0.049797
C	-1.393425	1.509603	-0.673339	0.015938	1.845138
O	-1.099807	2.444737	0.152373	-0.687308	-1.402931
C	-1.760068	1.945324	-2.089439	-0.882867	-0.155047
H	-1.718059	1.132564	-2.816658	0.163002	-0.000748
H	-2.772714	2.361210	-2.084874	0.198543	-0.028446
H	-1.065859	2.727466	-2.398439	0.202808	-0.000630

I4

HF/6-31G(d), N,N-dimethylformamide solution

Electronic energy: -1451.466834

Electronic energy + zero-point energy: -1451.137105

Electronic energy + thermal energy correction: -1451.118279

Electronic energy + thermal enthalpy correction: -1451.117335

Electronic energy + thermal free energy correction: -1451.186481

Table S117. Cartesian coordinates, Mulliken and APT charges of all atoms at **I4** in the reaction of acetophenone with pinacolborane (HF/6-31G(d), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	1.655284	0.830527	0.331591	-0.818290	-1.376792
C	2.917822	0.212502	0.454637	0.325176	0.709267
C	2.591654	-1.271074	0.076521	0.319248	0.714605
O	1.576152	-1.126316	-0.890064	-0.763664	-1.306347
C	3.753030	-2.047943	-0.536495	-0.504603	0.106636
H	4.595901	-2.106754	0.146207	0.162093	-0.051316
H	3.435152	-3.062148	-0.759967	0.164810	-0.059269
H	4.089824	-1.597580	-1.461879	0.171496	-0.049900
C	3.884705	0.877349	-0.532245	-0.513161	0.073829
H	3.902170	1.946076	-0.338930	0.166405	-0.064620
H	4.897961	0.502956	-0.426743	0.162187	-0.053855
H	3.569546	0.729658	-1.558417	0.173374	-0.037788
C	2.027165	-2.068722	1.258246	-0.511239	0.072503
H	1.634849	-3.010320	0.886076	0.162679	-0.062068
H	2.784351	-2.292536	2.003195	0.158676	-0.054872
H	1.214781	-1.537499	1.740045	0.173682	-0.036151
C	3.436882	0.420064	1.873980	-0.507823	0.105937
H	3.637887	1.474841	2.039349	0.168194	-0.060459
H	2.712853	0.102223	2.613684	0.174959	-0.047929
H	4.362304	-0.123491	2.040535	0.165295	-0.047811
B	0.869851	0.092419	-0.644371	1.161969	2.300331
H	-1.157606	-1.805695	-0.816577	0.162701	-0.137768
F	0.766653	0.871515	-1.859492	-0.532761	-0.950368
K	-0.195627	2.705541	0.000128	0.843994	1.048656
C	-5.405136	-0.326823	0.749666	-0.242459	-0.108592
C	-5.206559	-0.739760	-0.560974	-0.223512	0.009828
C	-3.922033	-0.859692	-1.066073	-0.258099	-0.097634
C	-2.812431	-0.574844	-0.273897	-0.035789	0.020593
C	-3.020383	-0.165485	1.038480	-0.250422	-0.129861
C	-4.307744	-0.040049	1.545319	-0.225076	0.025763
H	-6.401810	-0.229631	1.142579	0.227721	0.034252
H	-6.050884	-0.963112	-1.189460	0.229598	0.031448
H	-3.779645	-1.173915	-2.086445	0.228546	0.035015
H	-2.175838	0.053156	1.664931	0.240028	0.067476
H	-4.449758	0.279583	2.563112	0.229212	0.029138
C	-1.417484	-0.748870	-0.842083	0.032727	0.901082
O	-0.486581	-0.009131	-0.124951	-0.775203	-1.432021
H	-1.430017	-0.457396	-1.889532	0.157331	-0.120939

HF/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1451.745638

Electronic energy + zero-point energy: -1451.420061

Electronic energy + thermal energy correction: -1451.401123

Electronic energy + thermal enthalpy correction: -1451.400179

Electronic energy + thermal free energy correction: -1451.470834

Table S118. Cartesian coordinates, Mulliken and APT charges of all atoms at **I4** in the reaction of acetophenone with pinacolborane (HF/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	-1.614862	0.887084	0.483329	-1.282634	-1.382178
C	-2.637937	0.623791	-0.454951	0.762128	0.701369
C	-2.915308	-0.898637	-0.230914	0.662851	0.732376
O	-1.648833	-1.387162	0.130594	-1.223845	-1.339047
C	-3.895128	-1.155010	0.918716	-0.546300	0.044669
H	-4.911509	-0.882721	0.653803	0.158952	-0.045134
H	-3.882637	-2.214290	1.154776	0.167833	-0.053070
H	-3.616776	-0.610929	1.812622	0.136286	-0.032570
C	-3.819656	1.543368	-0.177629	-0.898044	0.077642
H	-3.532510	2.573984	-0.363999	0.147928	-0.052855
H	-4.658150	1.310859	-0.827101	0.173221	-0.037163
H	-4.149407	1.472187	0.850334	0.174894	-0.037616
C	-3.404957	-1.648006	-1.463270	-0.874061	0.079307
H	-3.584164	-2.687786	-1.207233	0.156514	-0.049865
H	-4.336906	-1.232297	-1.834477	0.171431	-0.038239
H	-2.674399	-1.625182	-2.261355	0.165773	-0.041787
C	-2.098245	0.922412	-1.856530	-0.739484	0.038832
H	-1.783199	1.961936	-1.904251	0.156052	-0.072333
H	-1.248693	0.294511	-2.097345	0.166090	-0.032738
H	-2.854311	0.785387	-2.621413	0.178181	-0.028174
B	-0.915516	-0.349262	0.795590	3.430447	2.377532
H	1.349350	-1.623073	1.566077	0.166444	-0.103256
F	-0.904359	-0.550550	2.208871	-0.827424	-0.981706
K	0.599385	2.357311	0.073153	0.944230	1.058094
C	5.288807	0.021489	-0.580876	-0.293751	-0.089173
C	4.534275	-0.732164	-1.460639	-0.309827	-0.030640

C	3.268998	-1.166127	-1.097020	-0.252297	-0.102101
C	2.742594	-0.855935	0.146972	0.502938	-0.034909
C	3.511545	-0.101746	1.025632	-0.004416	-0.103326
C	4.773107	0.336341	0.666187	-0.328183	-0.040459
H	6.270788	0.357800	-0.860373	0.214440	0.058198
H	4.927857	-0.984025	-2.428950	0.220835	0.054459
H	2.688898	-1.751442	-1.788366	0.223428	0.056589
H	3.122513	0.139113	1.999812	0.228604	0.057292
H	5.356125	0.916347	1.358778	0.220808	0.053293
C	1.347592	-1.288182	0.532789	-0.835685	0.925520
O	0.466765	-0.220990	0.364184	-1.252209	-1.491539
H	1.046934	-2.129062	-0.084679	0.137854	-0.095291

B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1457.677962

Electronic energy + zero-point energy: -1457.372933

Electronic energy + thermal energy correction: -1457.352818

Electronic energy + thermal enthalpy correction: -1457.351874

Electronic energy + thermal free energy correction: -1457.424187

Table S119. Cartesian coordinates, Mulliken and APT charges of all atoms at **I4** in the reaction of acetophenone with pinacolborane (B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	-1.623237	0.901233	0.504033	-1.048459	-1.300023
C	-2.652694	0.630299	-0.468150	0.390244	0.653966
C	-2.923890	-0.907724	-0.255459	0.331585	0.691525
O	-1.632780	-1.402642	0.118280	-0.998673	-1.258618
C	-3.916161	-1.176626	0.886752	-0.402293	-0.023347
H	-4.938135	-0.904656	0.611264	0.154341	-0.027830
H	-3.902238	-2.244788	1.117291	0.156280	-0.029879
H	-3.646332	-0.632208	1.792449	0.136988	-0.009531
C	-3.847510	1.537641	-0.190204	-0.738506	0.011060
H	-3.568003	2.581052	-0.361093	0.137151	-0.032713
H	-4.681484	1.304065	-0.857388	0.169061	-0.015737
H	-4.191189	1.446227	0.839980	0.166948	-0.014657
C	-3.393330	-1.649180	-1.504379	-0.695902	0.014511

H	-3.566029	-2.701255	-1.261971	0.144416	-0.029472
H	-4.332637	-1.235956	-1.881466	0.167550	-0.016566
H	-2.649905	-1.606396	-2.300617	0.158665	-0.019654
C	-2.097112	0.941512	-1.865172	-0.554710	-0.027514
H	-1.798268	1.993901	-1.910312	0.141715	-0.048908
H	-1.231245	0.319696	-2.098887	0.152262	-0.009927
H	-2.847403	0.793435	-2.644869	0.171626	-0.009013
B	-0.919993	-0.352906	0.814750	2.863017	2.259944
H	1.410634	-1.519045	1.706634	0.153324	-0.088815
F	-0.929429	-0.573278	2.252339	-0.745487	-0.958431
K	0.557924	2.333026	0.069076	0.903170	1.058188
C	5.302353	0.026712	-0.656456	-0.231604	-0.071311
C	4.529508	-0.790817	-1.476422	-0.242775	-0.048313
C	3.273774	-1.219032	-1.050963	-0.183134	-0.074165
C	2.775057	-0.842068	0.197198	0.381607	-0.024907
C	3.562024	-0.024421	1.014351	-0.024673	-0.086053
C	4.815458	0.409578	0.591897	-0.264777	-0.051428
H	6.280121	0.360063	-0.985138	0.177517	0.055075
H	4.903814	-1.096150	-2.447121	0.182824	0.051227
H	2.674329	-1.855282	-1.693739	0.183736	0.054146
H	3.192654	0.267273	1.992541	0.185920	0.054976
H	5.415661	1.039776	1.238607	0.184139	0.050277
C	1.395141	-1.262868	0.640848	-0.712021	0.813477
O	0.483497	-0.198087	0.404917	-1.082316	-1.412144
H	1.084400	-2.155301	0.085706	0.131242	-0.079417

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1457.326115

Electronic energy + zero-point energy: -1457.016683

Electronic energy + thermal energy correction: -1456.997368

Electronic energy + thermal enthalpy correction: -1456.996424

Electronic energy + thermal free energy correction: -1457.064124

Table S120. Cartesian coordinates, Mulliken and APT charges of all atoms at **I4** in the reaction of acetophenone with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	1.276197	0.799380	0.398781	-0.817455	-1.306157

C	2.673470	0.829871	0.114799	0.054085	0.677458
C	3.005327	-0.689003	-0.025867	0.064058	0.679696
O	1.836171	-1.202877	-0.657089	-0.709353	-1.262933
C	4.219748	-0.983682	-0.889692	-0.693142	-0.026675
H	5.109775	-0.492615	-0.487417	0.196504	-0.003138
H	4.405966	-2.060063	-0.907656	0.174390	-0.016808
H	4.066261	-0.646956	-1.914888	0.171264	-0.005353
C	2.896111	1.586985	-1.193686	-0.448303	-0.065097
H	2.449321	2.579905	-1.105916	0.182630	-0.017381
H	3.959396	1.708978	-1.411458	0.188143	-0.005732
H	2.423699	1.066707	-2.028528	0.157368	0.006477
C	3.164745	-1.362057	1.337202	-0.466682	-0.061177
H	3.188335	-2.444066	1.191309	0.184598	-0.016332
H	4.090675	-1.061987	1.832900	0.183591	-0.009231
H	2.320356	-1.120800	1.985452	0.139422	0.008278
C	3.403661	1.532485	1.246195	-0.691734	-0.029782
H	3.141989	2.593336	1.252188	0.170337	-0.016518
H	3.134339	1.108274	2.213272	0.180142	-0.002928
H	4.485915	1.451974	1.115810	0.196917	-0.000870
B	0.722053	-0.385902	-0.250833	2.153143	2.169277
H	-0.924490	-2.257334	-0.809222	0.166303	-0.045415
F	-0.032907	0.023726	-1.434726	-0.686999	-0.954190
K	-1.241622	1.589619	0.328229	0.837790	1.026890
C	-4.767490	0.573836	-0.109350	-0.413752	-0.091681
C	-4.323685	0.105619	1.125088	-0.172836	-0.065481
C	-3.218703	-0.734863	1.192120	0.186097	-0.107400
C	-2.536556	-1.111849	0.032731	0.142208	-0.052726
C	-3.002617	-0.656926	-1.198762	-0.168267	-0.095465
C	-4.112312	0.181546	-1.271261	-0.144539	-0.052308
H	-5.623005	1.235967	-0.163722	0.228499	0.076721
H	-4.837655	0.397904	2.033021	0.241095	0.072570
H	-2.862864	-1.086292	2.155350	0.235969	0.077779
H	-2.475878	-0.938553	-2.103228	0.224553	0.081773
H	-4.458198	0.536299	-2.234799	0.241882	0.070745
C	-1.221572	-1.847838	0.160621	-1.022197	0.756081
O	-0.245671	-0.961697	0.675311	-0.648191	-1.321234
H	-1.331572	-2.680681	0.861034	0.182463	-0.071730

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1457.403786

Electronic energy + zero-point energy: -1457.095222

Electronic energy + thermal energy correction: -1457.075605

Electronic energy + thermal enthalpy correction: -1457.074660

Electronic energy + thermal free energy correction: -1457.144391

Table S121. Cartesian coordinates, Mulliken and APT charges of all atoms at **I4** in the reaction of acetophenone with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	1.659917	0.196479	-1.088491	-1.013009	-1.304774
C	2.767265	0.485158	-0.238135	0.249360	0.656346
C	2.321159	-0.154636	1.119992	0.345700	0.661326
O	1.596960	-1.299209	0.698445	-0.925894	-1.243706
C	3.475584	-0.586096	2.011811	-0.778832	0.003296
H	4.118626	0.264509	2.255090	0.203407	-0.010777
H	3.087390	-0.993892	2.948986	0.163991	-0.024970
H	4.081369	-1.355959	1.532816	0.179467	-0.011517
C	4.014328	-0.184932	-0.815893	-0.505032	-0.030506
H	4.153420	0.156344	-1.844761	0.186328	-0.024221
H	4.911967	0.071312	-0.247962	0.180755	-0.016223
H	3.907563	-1.271171	-0.827587	0.162340	-0.003255
C	1.387558	0.757366	1.921470	-0.663160	-0.029106
H	0.963424	0.182750	2.748357	0.215216	-0.018163
H	1.913494	1.619707	2.338212	0.193293	-0.014706
H	0.555907	1.117894	1.312981	0.166484	-0.040642
C	2.985295	1.989683	-0.186865	-0.675519	-0.008049
H	3.276017	2.358035	-1.174321	0.181853	-0.020915
H	2.089015	2.526868	0.130411	0.155477	-0.032581
H	3.786468	2.239270	0.513915	0.210127	0.001014
B	1.005415	-1.018807	-0.590455	2.601900	2.277621
H	-0.898983	-1.804963	1.090586	0.162321	-0.057691
F	1.216208	-2.151024	-1.458918	-0.736940	-0.967476
K	-0.503639	1.670484	-1.455340	0.919465	1.069798
C	-4.950513	0.722696	0.552792	-0.385849	-0.085411
C	-4.927093	-0.387911	-0.278632	-0.353721	-0.043915
C	-3.762205	-1.137392	-0.409073	-0.238442	-0.085168
C	-2.614122	-0.790812	0.293757	0.596603	-0.016726
C	-2.649216	0.324164	1.132457	-0.040653	-0.108786
C	-3.806382	1.078483	1.260243	-0.312628	-0.048366
H	-5.856427	1.309812	0.652491	0.227775	0.060188

H	-5.815364	-0.670440	-0.832625	0.234106	0.057194
H	-3.744824	-1.999707	-1.067942	0.227599	0.060041
H	-1.758840	0.597765	1.690989	0.216342	0.066872
H	-3.820089	1.941718	1.916384	0.236616	0.057159
C	-1.320520	-1.543162	0.112092	-0.736159	0.788032
O	-0.428671	-0.714155	-0.587895	-1.015909	-1.419390
H	-1.506418	-2.476365	-0.434599	0.165222	-0.091846

P

HF/6-31G(d), N,N-dimethylformamide solution

Electronic energy: -791.847060

Electronic energy + zero-point energy: -791.489214

Electronic energy + thermal energy correction: -791.472376

Electronic energy + thermal enthalpy correction: -791.471432

Electronic energy + thermal free energy correction: -791.534928

Table S122. Cartesian coordinates, Mulliken and APT charges of all atoms at **P** in the reaction of acetophenone with pinacolborane (HF/6-31G(d), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	1.803023	0.755499	-1.104937	-0.650858	-1.296987
C	2.887878	0.048715	-0.489683	0.277968	0.687496
C	2.147526	-0.809846	0.593483	0.284725	0.703401
O	0.994120	-0.003158	0.874174	-0.661673	-1.286793
C	1.634968	-2.147498	0.060740	-0.505674	0.063182
H	2.447138	-2.841335	-0.123739	0.179762	-0.027286
H	0.973206	-2.587859	0.798594	0.182033	-0.039225
H	1.072997	-2.022839	-0.858628	0.178337	-0.039100
C	3.622887	-0.748104	-1.557542	-0.503763	0.091384
H	4.088760	-0.066264	-2.261191	0.180004	-0.040998
H	4.403356	-1.357358	-1.113565	0.179244	-0.029028
H	2.952843	-1.392584	-2.111294	0.184257	-0.035029
C	2.917391	-1.031542	1.886966	-0.503897	0.088991
H	2.316365	-1.623606	2.569063	0.180417	-0.039222
H	3.839237	-1.571429	1.696931	0.180024	-0.027666
H	3.157485	-0.097765	2.378254	0.184490	-0.033447
C	3.824642	1.098770	0.107213	-0.505568	0.068661
H	4.144315	1.771172	-0.681472	0.181434	-0.041747
H	3.328458	1.690428	0.869220	0.176977	-0.039872
H	4.706972	0.645465	0.544494	0.179437	-0.030267

B	0.780442	0.793885	-0.208074	0.880600	2.038845
H	-1.064928	1.409454	1.487783	0.197347	-0.085317
C	-4.124235	-1.698560	-0.438044	-0.236068	-0.070642
C	-3.910270	-1.309911	0.875250	-0.226400	-0.007405
C	-3.024968	-0.280703	1.160925	-0.248071	-0.083394
C	-2.346864	0.377261	0.141396	-0.028204	-0.043366
C	-2.567885	-0.018301	-1.174350	-0.239223	-0.096639
C	-3.448831	-1.049687	-1.461585	-0.226983	-0.002918
H	-4.806320	-2.499598	-0.661872	0.230405	0.035735
H	-4.424624	-1.809864	1.677001	0.231663	0.033588
H	-2.858805	0.008597	2.184525	0.232200	0.039140
H	-2.048698	0.475671	-1.975324	0.234465	0.060120
H	-3.607143	-1.346089	-2.483638	0.231069	0.032346
C	-1.418900	1.534071	0.472867	0.160865	0.946391
O	-0.307408	1.564097	-0.405786	-0.627932	-1.457933
C	-2.120333	2.880258	0.357139	-0.494467	0.095835
H	-2.972994	2.921573	1.026418	0.177763	-0.033058
H	-1.436128	3.680744	0.619925	0.177652	-0.060370
H	-2.469632	3.043029	-0.657377	0.175645	-0.037407

HF/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -792.071707

Electronic energy + zero-point energy: -791.718304

Electronic energy + thermal energy correction: -791.701426

Electronic energy + thermal enthalpy correction: -791.700482

Electronic energy + thermal free energy correction: -791.763936

Table S123. Cartesian coordinates, Mulliken and APT charges of all atoms at **P** in the reaction of acetophenone with pinacolborane (HF/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	1.790778	0.701207	-1.131824	-0.945327	-1.309831
C	2.906437	0.042338	-0.520545	0.704445	0.699284
C	2.214098	-0.791271	0.611992	0.196705	0.718109
O	1.041234	-0.009936	0.881504	-0.861818	-1.303233
C	1.736958	-2.163729	0.147954	-0.392693	0.040196
H	2.569937	-2.834274	-0.026908	0.193317	-0.019162
H	1.110342	-2.595625	0.920149	0.195550	-0.032768
H	1.150627	-2.097534	-0.761541	0.166032	-0.033448
C	3.631640	-0.777148	-1.573135	-0.973629	0.066602
H	4.066731	-0.112430	-2.311497	0.166461	-0.035493

H	4.435034	-1.350918	-1.123574	0.177737	-0.019674
H	2.964313	-1.456759	-2.085324	0.172893	-0.027404
C	3.015010	-0.932477	1.894000	-1.072266	0.063378
H	2.448185	-1.515590	2.611640	0.163888	-0.033094
H	3.949248	-1.450095	1.704397	0.185552	-0.018840
H	3.234701	0.027785	2.340350	0.181329	-0.026050
C	3.832415	1.132060	0.011272	-0.382302	0.045442
H	4.122666	1.775556	-0.811663	0.182076	-0.035344
H	3.341762	1.745118	0.759064	0.137609	-0.034770
H	4.731543	0.712060	0.446361	0.177621	-0.021635
B	0.787951	0.744728	-0.217687	2.804350	2.054034
H	-1.045680	1.314044	1.482344	0.183343	-0.071063
C	-4.247444	-1.629389	-0.437319	-0.322460	-0.092885
C	-3.994728	-1.271954	0.874603	-0.301515	-0.024311
C	-3.067373	-0.283923	1.158936	-0.526456	-0.108187
C	-2.384590	0.363064	0.140538	0.804797	-0.031167
C	-2.643592	-0.001210	-1.173323	0.245543	-0.115856
C	-3.567135	-0.990830	-1.460130	-0.417442	-0.022801
H	-4.962999	-2.399651	-0.660941	0.210078	0.058215
H	-4.512468	-1.764856	1.677563	0.219477	0.054479
H	-2.872134	-0.018814	2.183123	0.218806	0.056407
H	-2.120846	0.484041	-1.976197	0.234084	0.075199
H	-3.754817	-1.263430	-2.483074	0.213397	0.053014
C	-1.410565	1.476846	0.477332	-0.475876	0.919881
O	-0.315599	1.483473	-0.419449	-1.064854	-1.451770
C	-2.063543	2.847127	0.410283	-0.896084	0.069779
H	-2.902277	2.898141	1.095672	0.182373	-0.021677
H	-1.346289	3.613575	0.684489	0.132546	-0.053350
H	-2.424161	3.051033	-0.592591	0.182710	-0.030205

B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -797.083381

Electronic energy + zero-point energy: -796.752138

Electronic energy + thermal energy correction: -796.733965

Electronic energy + thermal enthalpy correction: -796.733021

Electronic energy + thermal free energy correction: -796.799531

Table S124. Cartesian coordinates, Mulliken and APT charges of all atoms at **P** in the reaction of acetophenone with pinacolborane (B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	1.788432	0.688506	-1.170562	-0.735818	-1.205316
C	2.937830	0.034930	-0.544076	0.314105	0.662089
C	2.263612	-0.785812	0.624610	0.029967	0.677711
O	1.057669	0.000339	0.900595	-0.666638	-1.188730
C	1.795142	-2.176414	0.198246	-0.333954	-0.030962
H	2.641177	-2.844472	0.027264	0.181699	0.001574
H	1.181510	-2.603203	0.994262	0.174842	-0.010705
H	1.193410	-2.139366	-0.711899	0.159858	-0.011211
C	3.646467	-0.809085	-1.592366	-0.741165	-0.004959
H	4.068069	-0.158562	-2.362037	0.155870	-0.015066
H	4.467533	-1.370840	-1.141155	0.174279	0.001834
H	2.967999	-1.511833	-2.075127	0.163428	-0.005480
C	3.084072	-0.877311	1.901734	-0.819042	-0.008409
H	2.532181	-1.448745	2.651542	0.153174	-0.012786
H	4.027794	-1.394347	1.713711	0.179518	0.002623
H	3.302965	0.106257	2.316371	0.172244	-0.004528
C	3.864153	1.145541	-0.048948	-0.311904	-0.025611
H	4.142344	1.777182	-0.895178	0.168187	-0.013356
H	3.377912	1.774972	0.699139	0.141636	-0.012506
H	4.778948	0.737206	0.384469	0.171399	-0.001601
B	0.791211	0.737191	-0.227068	2.216813	1.888247
H	-1.031993	1.257827	1.499180	0.145886	-0.051994
C	-4.315553	-1.612995	-0.455325	-0.280351	-0.081452
C	-4.024415	-1.304679	0.870669	-0.220990	-0.035015
C	-3.076974	-0.328611	1.168345	-0.395867	-0.090236
C	-2.412519	0.355538	0.149133	0.579900	-0.022189
C	-2.710079	0.040108	-1.178382	0.198600	-0.100725
C	-3.653335	-0.938684	-1.478578	-0.339224	-0.029296
H	-5.048514	-2.376379	-0.689808	0.173722	0.055008
H	-4.528798	-1.828797	1.674604	0.183521	0.051386
H	-2.848002	-0.099189	2.203941	0.180847	0.053846
H	-2.196325	0.555878	-1.980698	0.194724	0.076077
H	-3.871184	-1.175410	-2.514017	0.179638	0.049591
C	-1.424926	1.453664	0.499228	-0.380884	0.836155
O	-0.327805	1.477798	-0.437282	-0.879455	-1.346465
C	-2.068578	2.834741	0.479987	-0.756077	-0.008298
H	-2.900671	2.873377	1.186185	0.169395	0.000704
H	-1.337796	3.595632	0.763894	0.131441	-0.031200
H	-2.450361	3.068125	-0.516971	0.166677	-0.008749

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -796.749538

Electronic energy + zero-point energy: -796.414387

Electronic energy + thermal energy correction: -796.396675

Electronic energy + thermal enthalpy correction: -796.395731

Electronic energy + thermal free energy correction: -796.460222

Table S125. Cartesian coordinates, Mulliken and APT charges of all atoms at **P** in the reaction of acetophenone with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	1.802955	0.871924	-1.057658	-0.538244	-1.211801
C	2.794206	0.052158	-0.387329	0.344112	0.647259
C	1.917893	-0.782136	0.601551	-0.502827	0.656860
O	0.827005	0.131591	0.884425	-0.450894	-1.199370
C	1.302678	-2.012988	-0.051504	-0.299969	-0.071444
H	2.056593	-2.780886	-0.232774	0.212194	0.016024
H	0.543366	-2.422814	0.617201	0.206188	0.003834
H	0.824772	-1.759846	-1.000712	0.181236	0.003111
C	3.537102	-0.774365	-1.416809	-0.783397	-0.041107
H	4.137872	-0.118032	-2.049152	0.192921	0.000205
H	4.209035	-1.477273	-0.919059	0.204099	0.016443
H	2.851010	-1.333837	-2.051624	0.180745	0.008259
C	2.609163	-1.154590	1.896392	-0.887783	-0.040990
H	1.935307	-1.752676	2.512589	0.184621	0.001795
H	3.499946	-1.751073	1.686773	0.212002	0.017244
H	2.903130	-0.270915	2.461606	0.187883	0.008000
C	3.749573	0.996890	0.329057	-0.377716	-0.063122
H	4.184459	1.679407	-0.402866	0.200174	0.001535
H	3.228394	1.587409	1.085618	0.160485	0.001344
H	4.558538	0.446130	0.811605	0.192872	0.013114
B	0.736325	0.961909	-0.202779	1.963734	1.915168
H	-1.180089	1.709817	1.419781	0.193129	-0.055726
C	-3.633572	-1.957572	-0.383047	-0.485580	-0.107384
C	-3.753441	-1.301619	0.837974	-0.207647	-0.037255
C	-3.041431	-0.132620	1.072722	-0.442637	-0.105946
C	-2.204749	0.397131	0.092792	0.397247	-0.002163
C	-2.090708	-0.261099	-1.128392	0.230382	-0.138594
C	-2.800299	-1.434356	-1.363903	-0.245654	-0.032323
H	-4.183424	-2.872818	-0.566130	0.218886	0.071129
H	-4.396598	-1.705607	1.610794	0.234098	0.067391
H	-3.128050	0.372156	2.029624	0.229370	0.069281
H	-1.441106	0.139829	-1.898167	0.228565	0.092242
H	-2.699656	-1.940652	-2.316723	0.231717	0.065434

C	-1.470527	1.694206	0.365504	-0.397065	0.783081
O	-0.297079	1.807463	-0.442184	-0.744332	-1.324014
C	-2.343811	2.898985	0.063863	-0.791108	-0.033290
H	-3.249200	2.868746	0.671546	0.198914	0.015865
H	-1.802345	3.820206	0.284459	0.173168	-0.014400
H	-2.629101	2.897187	-0.990384	0.196109	0.004313

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -796.827205

Electronic energy + zero-point energy: -796.492402

Electronic energy + thermal energy correction: -796.474672

Electronic energy + thermal enthalpy correction: -796.473728

Electronic energy + thermal free energy correction: -796.538233

Table S126. Cartesian coordinates, Mulliken and APT charges of all atoms at **P** in the reaction of acetophenone with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
O	1.769905	0.916200	-1.031456	-0.680640	-1.204166
C	2.764516	0.056569	-0.420660	0.503341	0.653222
C	1.904828	-0.785464	0.584779	-0.277349	0.660824
O	0.833221	0.132808	0.911930	-0.624535	-1.194687
C	1.257090	-2.006901	-0.058295	-0.397152	-0.045574
H	1.997691	-2.779536	-0.273907	0.213159	0.007689
H	0.520178	-2.420510	0.633503	0.213095	-0.006296
H	0.743351	-1.747492	-0.987050	0.198435	-0.006330
C	3.443934	-0.760996	-1.501558	-0.860839	-0.016065
H	4.031849	-0.104320	-2.146823	0.186266	-0.009893
H	4.122298	-1.490060	-1.051562	0.203937	0.007333
H	2.720672	-1.292697	-2.119917	0.182013	-0.001710
C	2.627732	-1.181906	1.856416	-0.946843	-0.015245
H	1.963857	-1.776588	2.487923	0.176679	-0.008621
H	3.503365	-1.790220	1.617104	0.213210	0.008193
H	2.952788	-0.310355	2.424662	0.193050	-0.000870
C	3.777268	0.960374	0.272107	-0.402683	-0.036714
H	4.200670	1.646885	-0.464070	0.198375	-0.008822
H	3.311962	1.551877	1.064016	0.157825	-0.008195
H	4.592910	0.378846	0.706165	0.193393	0.004358
B	0.724673	0.990562	-0.150392	2.314337	1.890100
H	-1.224593	1.705916	1.490460	0.168268	-0.063320

C	-3.547181	-1.984426	-0.430279	-0.378474	-0.089821
C	-3.553464	-1.459382	0.855809	-0.270898	-0.033427
C	-2.881211	-0.275223	1.127342	-0.312600	-0.093939
C	-2.200795	0.400316	0.119819	0.428731	-0.014119
C	-2.202861	-0.127451	-1.167952	0.028327	-0.118980
C	-2.869256	-1.314746	-1.441017	-0.378447	-0.030066
H	-4.064778	-2.912967	-0.642893	0.224465	0.060820
H	-4.074946	-1.978092	1.652472	0.232376	0.056720
H	-2.875546	0.124332	2.136672	0.228543	0.059279
H	-1.671181	0.386631	-1.960880	0.233481	0.079127
H	-2.857711	-1.718781	-2.447192	0.229264	0.055993
C	-1.494594	1.704725	0.430452	-0.162520	0.825959
O	-0.305798	1.848581	-0.351656	-0.933096	-1.325842
C	-2.376343	2.905208	0.139362	-0.856652	-0.012446
H	-3.290562	2.851542	0.734197	0.199710	0.006033
H	-1.851591	3.829980	0.389069	0.166741	-0.025274
H	-2.650658	2.927905	-0.918484	0.195704	-0.005226

I1B

HF/6-31G(d), N,N-dimethylformamide solution

Electronic energy: -1081.101492

Electronic energy + zero-point energy: -1080.951486

Electronic energy + thermal energy correction: -1080.940799

Electronic energy + thermal enthalpy correction: -1080.939855

Electronic energy + thermal free energy correction: -1080.990386

Table S127. Cartesian coordinates, Mulliken and APT charges of all atoms at **I1B** in the reaction of acetophenone with pinacolborane (HF/6-31G(d), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	-3.391857	-0.707065	-0.295871	-0.234460	-0.047841
C	-2.836446	0.274202	-1.107689	-0.235716	-0.038044
C	-1.549851	0.728545	-0.871400	-0.236191	-0.047193
C	-0.792443	0.209837	0.177539	-0.085985	-0.180084
C	-1.355722	-0.772655	0.980450	-0.242865	-0.075535
C	-2.647700	-1.228653	0.748827	-0.231220	-0.023785
H	-4.392311	-1.058227	-0.478678	0.227104	0.033161
H	-3.405719	0.682093	-1.924776	0.226360	0.028807
H	-1.129610	1.481422	-1.512234	0.229952	0.049182
H	-0.774662	-1.178112	1.786823	0.234961	0.074824

H	-3.068190	-1.989352	1.383484	0.225668	0.026748
C	0.617058	0.706079	0.504145	0.756160	1.851841
O	1.330219	-0.057249	1.217809	-0.847059	-1.384452
F	1.253758	0.740188	-0.979606	-0.609353	-1.147545
K	2.968669	-1.063553	-0.462960	0.852466	1.012998
C	0.679366	2.190993	0.832648	-0.527502	0.017616
H	0.214754	2.350740	1.801827	0.164133	-0.044141
H	1.718205	2.495976	0.898841	0.169186	-0.063291
H	0.172822	2.811576	0.103043	0.164362	-0.043266

HF/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1081.314783

Electronic energy + zero-point energy: -1081.167129

Electronic energy + thermal energy correction: -1081.155172

Electronic energy + thermal enthalpy correction: -1081.1154228

Electronic energy + thermal free energy correction: -1081.210029

Table S128. Cartesian coordinates, Mulliken and APT charges of all atoms at **I1B** in the reaction of acetophenone with pinacolborane (HF/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	-3.820457	-1.233761	-0.107665	-0.290123	0.111735
C	-3.855668	0.127847	-0.342232	-0.451597	-0.189924
C	-2.690202	0.870687	-0.277182	-1.246858	0.038437
C	-1.482678	0.255530	0.023498	1.129788	-0.423145
C	-1.457874	-1.115745	0.257962	0.602836	0.023472
C	-2.618882	-1.856768	0.192907	-0.424182	-0.191629
H	-4.725714	-1.810883	-0.158370	0.217933	0.065446
H	-4.785480	0.612596	-0.575545	0.228210	0.066753
H	-2.735220	1.926072	-0.462450	0.230048	0.088153
H	-0.527005	-1.595342	0.490061	0.251148	0.097622
H	-2.591048	-2.915190	0.374918	0.228440	0.064130
C	-0.205831	1.026410	0.102025	0.334579	1.568998
O	0.821828	0.463886	0.371612	-0.692572	-1.325304
F	4.765688	-1.014116	-1.238802	-0.947901	-1.022322
K	3.402518	-0.151763	0.580903	0.939554	1.074677
C	-0.215546	2.505541	-0.158916	-0.705091	-0.101380
H	-0.872545	3.005915	0.543657	0.202250	0.028773
H	0.788162	2.891992	-0.055886	0.190531	-0.003590
H	-0.581993	2.705843	-1.159596	0.203007	0.029098

B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1084.946499

Electronic energy + zero-point energy: -1084.808032

Electronic energy + thermal energy correction: -1084.795576

Electronic energy + thermal enthalpy correction: -1084.794632

Electronic energy + thermal free energy correction: -1084.851521

Table S129. Cartesian coordinates, Mulliken and APT charges of all atoms at **I1B** in the reaction of acetophenone with pinacolborane (B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	-3.856278	-1.203817	-0.109972	-0.216694	0.054698
C	-3.868943	0.170167	-0.332532	-0.384953	-0.148740
C	-2.686060	0.897255	-0.266660	-0.904877	0.034388
C	-1.476277	0.254429	0.023576	0.924878	-0.461579
C	-1.475441	-1.129386	0.245605	0.339061	0.026321
C	-2.656455	-1.853106	0.179387	-0.320305	-0.146026
H	-4.779319	-1.769570	-0.161665	0.185479	0.064481
H	-4.800177	0.676107	-0.557906	0.191670	0.063928
H	-2.711250	1.964517	-0.442757	0.198715	0.087729
H	-0.540251	-1.626658	0.469102	0.204798	0.097155
H	-2.646078	-2.922734	0.352434	0.192680	0.061029
C	-0.190548	1.001951	0.101591	0.285347	1.508673
O	0.853982	0.409326	0.360591	-0.599200	-1.204842
F	4.760315	-0.987693	-1.221920	-0.916499	-1.022164
K	3.404619	-0.158959	0.571127	0.896904	1.083440
C	-0.179205	2.485869	-0.139718	-0.626535	-0.205922
H	-0.833177	2.995700	0.572614	0.189812	0.045728
H	0.836268	2.864423	-0.036727	0.169043	0.015552
H	-0.553235	2.712895	-1.141618	0.190677	0.046152

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1084.716871

Electronic energy + zero-point energy: -1084.576780

Electronic energy + thermal energy correction: -1084.564559

Electronic energy + thermal enthalpy correction: -1084.563615

Electronic energy + thermal free energy correction: -1084.619398

Table S130. Cartesian coordinates, Mulliken and APT charges of all atoms at **I1B** in the reaction of acetophenone with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	-3.886459	-1.148754	-0.118582	-0.301668	0.035020
C	-3.870527	0.228761	-0.299447	-0.443603	-0.151328
C	-2.670382	0.924027	-0.232905	-0.891644	0.000932
C	-1.479661	0.241076	0.015936	0.959389	-0.419873
C	-1.503006	-1.143419	0.196269	0.308256	-0.007110
C	-2.701035	-1.835356	0.129637	-0.358222	-0.150084
H	-4.823542	-1.689905	-0.171120	0.224268	0.079330
H	-4.792591	0.762533	-0.493183	0.237907	0.077753
H	-2.668459	1.997078	-0.376327	0.222989	0.098234
H	-0.574474	-1.666271	0.388053	0.221894	0.108139
H	-2.714943	-2.909062	0.270347	0.238964	0.073861
C	-0.173878	0.956968	0.095093	0.251478	1.485188
O	0.851643	0.333376	0.314910	-0.543645	-1.204285
F	4.840676	-0.865050	-1.175958	-0.923331	-1.023059
K	3.378408	-0.200236	0.566302	0.909382	1.084481
C	-0.142133	2.442923	-0.097935	-0.737271	-0.241648
H	-0.773849	2.930586	0.647800	0.211879	0.062356
H	0.880847	2.800404	-0.007082	0.200389	0.029833
H	-0.539467	2.700209	-1.082280	0.212590	0.062260

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1084.767075

Electronic energy + zero-point energy: -1084.627189

Electronic energy + thermal energy correction: -1084.614917

Electronic energy + thermal enthalpy correction: -1084.613973

Electronic energy + thermal free energy correction: -1084.669716

Table S131. Cartesian coordinates, Mulliken and APT charges of all atoms at **I1B** in the reaction of acetophenone with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	-4.013092	-0.967154	-0.180645	-0.330185	0.049265
C	-3.866902	0.399190	-0.378956	-0.409829	-0.149621
C	-2.615356	0.986774	-0.268197	-0.999349	0.015428

C	-1.499837	0.208672	0.042533	1.048388	-0.440758
C	-1.656230	-1.164438	0.239954	0.372610	0.007881
C	-2.905707	-1.749364	0.129186	-0.346543	-0.145390
H	-4.991798	-1.424965	-0.268157	0.230659	0.069061
H	-4.729102	1.009143	-0.621114	0.244620	0.067690
H	-2.516319	2.053412	-0.426542	0.230942	0.092294
H	-0.787826	-1.765550	0.479898	0.237962	0.101430
H	-3.019790	-2.815897	0.283513	0.244823	0.066023
C	-0.139333	0.804820	0.167546	0.198418	1.492188
O	0.815978	0.094739	0.441619	-0.573575	-1.183521
F	4.874823	-0.809116	-1.254496	-0.925558	-1.020023
K	3.440367	-0.170975	0.548414	0.904848	1.074604
C	0.038715	2.277534	-0.049647	-0.759060	-0.218826
H	-0.587570	2.842174	0.645530	0.214886	0.053221
H	1.082557	2.550425	0.096129	0.198165	0.015083
H	-0.271905	2.547729	-1.062255	0.217776	0.053972

I3B

HF/6-31G(d), N,N-dimethylformamide solution

Electronic energy: -1490.426378

Electronic energy + zero-point energy: -1490.069188

Electronic energy + thermal energy correction: -1490.049313

Electronic energy + thermal enthalpy correction: -1490.048368

Electronic energy + thermal free energy correction: -1490.118833

Table S132. Cartesian coordinates, Mulliken and APT charges of all atoms at **I3B** in the reaction of acetophenone with pinacolborane (HF/6-31G(d), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	5.310486	0.271454	0.297286	-0.226598	-0.022257
C	4.807431	-0.198025	-0.908006	-0.231199	-0.047760
C	3.470921	-0.546345	-1.016777	-0.225223	-0.063263
C	2.617044	-0.426702	0.077420	-0.131130	-0.137335
C	3.127537	0.044590	1.281021	-0.221678	-0.077469
C	4.467945	0.390256	1.390352	-0.229758	-0.036403
H	6.348527	0.540252	0.381783	0.234254	0.040913
H	5.454090	-0.292671	-1.762317	0.234371	0.036878
H	3.093984	-0.908767	-1.955300	0.243285	0.061893
H	2.479056	0.141547	2.130556	0.249867	0.080475
H	4.848990	0.752063	2.328966	0.234334	0.036027

C	1.149716	-0.837456	-0.032720	0.795776	1.676711
O	0.422602	-0.152515	0.860025	-0.786451	-1.592447
F	0.751540	-0.424235	-1.340765	-0.485807	-0.946185
K	0.362887	2.208535	-0.614108	0.821376	1.050434
O	-1.834332	-1.279350	0.721416	-0.741882	-1.370154
C	-2.898829	-0.869889	-0.104858	0.332178	0.725532
C	-2.995712	0.670579	0.171322	0.323571	0.701831
O	-1.664399	1.002123	0.490440	-0.799087	-1.406253
C	-3.447812	1.514173	-1.018694	-0.518438	0.099649
H	-4.444822	1.234897	-1.346066	0.170941	-0.043307
H	-3.475692	2.562157	-0.733356	0.173769	-0.057985
H	-2.775715	1.416255	-1.863136	0.174137	-0.056191
C	-2.547215	-1.192709	-1.561759	-0.521282	0.061887
H	-2.327191	-2.253040	-1.641989	0.163672	-0.061411
H	-3.368109	-0.973127	-2.237516	0.157684	-0.059524
H	-1.672851	-0.647815	-1.891335	0.177282	-0.023473
C	-3.886098	1.011383	1.373686	-0.511875	0.072919
H	-3.745569	2.058505	1.624867	0.167007	-0.063303
H	-4.938416	0.856487	1.158619	0.162582	-0.054745
H	-3.627599	0.424475	2.246988	0.174412	-0.042011
C	-4.149133	-1.663294	0.273739	-0.502951	0.105408
H	-3.993499	-2.714159	0.047642	0.162874	-0.061808
H	-4.368582	-1.584904	1.331143	0.169696	-0.051173
H	-5.018791	-1.329150	-0.285244	0.159505	-0.057542
B	-1.054979	-0.151172	1.173867	0.946245	2.196002
H	-1.075413	-0.036603	2.406978	-0.332189	-0.563913
C	0.975822	-2.345456	-0.003863	-0.542185	-0.031615
H	1.287551	-2.716630	0.966317	0.181531	-0.014743
H	-0.059040	-2.604714	-0.161267	0.218516	0.021880
H	1.591685	-2.810690	-0.764653	0.178865	-0.026169

HF/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1490.714383

Electronic energy + zero-point energy: -1490.361652

Electronic energy + thermal energy correction: -1490.341753

Electronic energy + thermal enthalpy correction: -1490.340809

Electronic energy + thermal free energy correction: -1490.411222

Table S133. Cartesian coordinates, Mulliken and APT charges of all atoms at **I3B** in the reaction of acetophenone with pinacolborane (HF/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	5.137565	0.718153	-0.080898	-0.368991	-0.076398
C	4.797990	-0.309666	-0.939143	-0.396986	-0.025287
C	3.554148	-0.915721	-0.851080	0.342799	-0.113534
C	2.632906	-0.494364	0.092863	0.148600	-0.088587
C	2.984371	0.533761	0.958972	-0.411816	-0.117981
C	4.225229	1.137114	0.873307	-0.404092	-0.036431
H	6.101673	1.187847	-0.151538	0.216484	0.060967
H	5.498719	-0.644335	-1.682504	0.222881	0.054978
H	3.309132	-1.712999	-1.524991	0.236910	0.085302
H	2.289749	0.860122	1.711648	0.266292	0.071101
H	4.479529	1.931597	1.551230	0.226137	0.057061
C	1.258357	-1.142036	0.233817	0.785208	1.691051
O	0.321421	-0.181496	0.301586	-1.231043	-1.599867
F	1.041293	-1.871339	-0.942377	-0.447675	-0.906212
K	0.270149	2.338755	-0.501860	0.981984	1.071987
O	-1.888176	-1.321363	0.469431	-0.934154	-1.379217
C	-2.887500	-0.775539	-0.352210	0.703690	0.726765
C	-3.019791	0.678971	0.200491	0.759911	0.715059
O	-1.694938	0.970993	0.585149	-1.067525	-1.420086
C	-3.491284	1.716204	-0.810833	-0.918131	0.068597
H	-4.485920	1.480859	-1.176554	0.177305	-0.032143
H	-3.535470	2.693740	-0.339883	0.172549	-0.049230
H	-2.829065	1.784076	-1.665441	0.157001	-0.051676
C	-2.415525	-0.814692	-1.809129	-0.730596	0.045048
H	-2.152454	-1.836806	-2.061182	0.178010	-0.050303
H	-3.189394	-0.488760	-2.496688	0.165717	-0.047621
H	-1.536621	-0.201182	-1.965050	0.162096	-0.047874
C	-3.911589	0.761369	1.441870	-0.598427	0.049019
H	-3.797184	1.743663	1.889411	0.173536	-0.054428
H	-4.959946	0.623584	1.199935	0.157920	-0.042401
H	-3.630649	0.022025	2.182364	0.139568	-0.036077
C	-4.149888	-1.620427	-0.229580	-0.929596	0.082080
H	-3.968952	-2.606533	-0.646540	0.149160	-0.052729
H	-4.446357	-1.747937	0.803341	0.166918	-0.041300
H	-4.977708	-1.176427	-0.774806	0.173450	-0.043669
B	-1.027590	-0.276602	0.965024	2.001233	2.113158
H	-0.844805	-0.383835	2.181850	-0.170352	-0.505371
C	1.235085	-2.173697	1.347750	-0.847597	-0.049646
H	1.419877	-1.700648	2.303545	0.205498	0.002981
H	0.274018	-2.669422	1.376404	0.181050	-0.013957
H	2.008396	-2.911569	1.170547	0.205074	-0.013130

B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1496.933102

Electronic energy + zero-point energy: -1496.602802

Electronic energy + thermal energy correction: -1496.581422

Electronic energy + thermal enthalpy correction: -1496.580477

Electronic energy + thermal free energy correction: -1496.653829

Table S134. Cartesian coordinates, Mulliken and APT charges of all atoms at **I3B** in the reaction of acetophenone with pinacolborane (B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	5.169103	0.766940	-0.051429	-0.294232	-0.070347
C	4.878945	-0.331719	-0.854605	-0.325017	-0.035939
C	3.634456	-0.953009	-0.776169	0.237859	-0.091248
C	2.660132	-0.476505	0.100860	0.071784	-0.092530
C	2.962481	0.620451	0.912692	-0.291484	-0.115180
C	4.207038	1.239649	0.837308	-0.335684	-0.037089
H	6.137419	1.249720	-0.115144	0.178835	0.058086
H	5.622235	-0.708585	-1.548046	0.184046	0.052133
H	3.420562	-1.806097	-1.406175	0.198650	0.085816
H	2.226441	0.983035	1.621783	0.221143	0.070390
H	4.424579	2.089034	1.474790	0.189716	0.054555
C	1.288005	-1.136379	0.233918	0.625459	1.628423
O	0.323769	-0.187600	0.263957	-1.086471	-1.527592
F	1.101817	-1.916009	-0.994894	-0.367468	-0.888553
K	0.230062	2.287800	-0.547794	0.928486	1.077253
O	-1.913402	-1.340085	0.518288	-0.744225	-1.278588
C	-2.919190	-0.782580	-0.336929	0.276661	0.675917
C	-3.042913	0.690584	0.202684	0.401343	0.670181
O	-1.692030	0.983893	0.600372	-0.912099	-1.318712
C	-3.493467	1.719772	-0.830621	-0.642663	0.004108
H	-4.500903	1.495994	-1.191062	0.173730	-0.009788
H	-3.518287	2.714996	-0.377938	0.155235	-0.029225
H	-2.829731	1.753487	-1.696296	0.154550	-0.029290
C	-2.436094	-0.843691	-1.794001	-0.541419	-0.021207
H	-2.179435	-1.878324	-2.033951	0.163093	-0.027238
H	-3.208090	-0.516536	-2.495287	0.155234	-0.030982
H	-1.543694	-0.236527	-1.952081	0.170174	-0.026169
C	-3.942717	0.793857	1.441540	-0.503758	-0.018038
H	-3.827564	1.788624	1.879448	0.160205	-0.030876
H	-4.997552	0.654895	1.193720	0.153021	-0.023900
H	-3.664986	0.056897	2.196892	0.140016	-0.012018
C	-4.193446	-1.613631	-0.204283	-0.747217	0.019390

H	-4.020907	-2.617029	-0.602967	0.139244	-0.032050
H	-4.500269	-1.714992	0.836842	0.160928	-0.018720
H	-5.017572	-1.168221	-0.768404	0.167332	-0.022056
B	-1.031210	-0.285148	0.981886	1.714629	1.942484
H	-0.799005	-0.387374	2.183299	-0.157852	-0.460219
C	1.252924	-2.177690	1.343255	-0.713651	-0.130757
H	1.414144	-1.700527	2.311001	0.189846	0.023646
H	0.288749	-2.685514	1.354019	0.167751	0.008721
H	2.044128	-2.911289	1.182006	0.184266	0.007212

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1496.559626

Electronic energy + zero-point energy: -1496.224676

Electronic energy + thermal energy correction: -1496.203905

Electronic energy + thermal enthalpy correction: -1496.202961

Electronic energy + thermal free energy correction: -1496.274881

Table S135. Cartesian coordinates, Mulliken and APT charges of all atoms at **I3B** in the reaction of acetophenone with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	5.121724	0.757235	-0.068152	-0.387447	-0.086378
C	4.834108	-0.351904	-0.853581	-0.352260	-0.046162
C	3.589770	-0.968522	-0.769978	0.420855	-0.108011
C	2.620858	-0.473003	0.095665	-0.072281	-0.092087
C	2.917472	0.632566	0.891421	-0.216698	-0.126790
C	4.160781	1.247080	0.809804	-0.349521	-0.047884
H	6.090464	1.236960	-0.137227	0.220853	0.073063
H	5.579505	-0.739611	-1.537682	0.230341	0.067422
H	3.371359	-1.831584	-1.385818	0.237987	0.097350
H	2.173518	1.001900	1.590204	0.249073	0.082222
H	4.379817	2.106113	1.432583	0.240181	0.069591
C	1.251058	-1.122727	0.232541	0.262880	1.596750
O	0.302991	-0.156488	0.273593	-1.019761	-1.520875
F	1.048277	-1.884930	-0.957097	-0.290635	-0.858509
K	0.195685	2.265877	-0.527019	0.944642	1.074834
O	-1.884978	-1.333586	0.550516	-0.560405	-1.278572
C	-2.832092	-0.778303	-0.352213	-0.020717	0.664336
C	-3.013665	0.668434	0.201540	0.283270	0.656872
O	-1.698751	0.992000	0.647916	-0.788678	-1.316191

C	-3.461890	1.689511	-0.831705	-0.647486	-0.036730
H	-4.434738	1.415893	-1.248060	0.204780	0.005672
H	-3.560343	2.671910	-0.363352	0.185910	-0.012624
H	-2.753685	1.768447	-1.658632	0.158588	-0.020104
C	-2.250565	-0.786581	-1.767208	-0.504464	-0.060824
H	-1.961717	-1.809431	-2.017522	0.193723	-0.011351
H	-2.977138	-0.442826	-2.507060	0.188298	-0.012034
H	-1.356308	-0.164136	-1.831269	0.165770	-0.016708
C	-3.954294	0.708298	1.404491	-0.543113	-0.056708
H	-3.883162	1.692054	1.873245	0.188159	-0.016268
H	-4.993424	0.540725	1.113741	0.176633	-0.007505
H	-3.669198	-0.046057	2.140352	0.162039	0.001521
C	-4.101812	-1.614286	-0.326927	-0.751399	-0.021393
H	-3.903686	-2.596558	-0.762212	0.174185	-0.016501
H	-4.457293	-1.759228	0.693072	0.172219	-0.005318
H	-4.893513	-1.137768	-0.911341	0.199092	-0.006243
B	-1.015532	-0.268484	1.016308	1.391296	1.915867
H	-0.776300	-0.374293	2.213516	-0.041582	-0.441918
C	1.213800	-2.134050	1.362303	-0.710217	-0.164420
H	1.400593	-1.634999	2.313515	0.209608	0.036265
H	0.236597	-2.616121	1.393619	0.180973	0.025670
H	1.988191	-2.884158	1.197819	0.215308	0.020672

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1496.649545

Electronic energy + zero-point energy: -1496.315334

Electronic energy + thermal energy correction: -1496.294499

Electronic energy + thermal enthalpy correction: -1496.293554

Electronic energy + thermal free energy correction: -1496.365721

Table S136. Cartesian coordinates, Mulliken and APT charges of all atoms at **I3B** in the reaction of acetophenone with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	5.089307	0.799687	-0.050836	-0.380410	-0.075145
C	4.812710	-0.283655	-0.873087	-0.374446	-0.037852
C	3.583431	-0.928092	-0.796643	0.318330	-0.097893
C	2.616077	-0.487896	0.098392	0.048585	-0.097381
C	2.903733	0.591325	0.931516	-0.359518	-0.120146
C	4.131380	1.234301	0.857150	-0.376681	-0.041184

H	6.047561	1.302345	-0.114586	0.229459	0.062795
H	5.556072	-0.630586	-1.581975	0.236563	0.057384
H	3.376089	-1.771356	-1.443081	0.240670	0.088815
H	2.163009	0.922349	1.652461	0.276511	0.075355
H	4.340558	2.073797	1.510407	0.241723	0.059929
C	1.253843	-1.159636	0.227018	0.529302	1.628542
O	0.297266	-0.212147	0.273554	-1.102413	-1.536422
F	1.062892	-1.917022	-0.985982	-0.346044	-0.879024
K	0.241134	2.244500	-0.536386	0.937606	1.072576
O	-1.924875	-1.340149	0.555103	-0.729889	-1.284223
C	-2.857809	-0.761724	-0.345110	0.265128	0.667785
C	-2.994021	0.696664	0.204294	0.424743	0.662863
O	-1.676632	0.974437	0.667933	-0.903096	-1.320596
C	-3.389800	1.731738	-0.838589	-0.719565	-0.009928
H	-4.373607	1.502403	-1.256911	0.204170	-0.002931
H	-3.444179	2.722551	-0.378936	0.186704	-0.022674
H	-2.679214	1.774056	-1.666898	0.164705	-0.026605
C	-2.288038	-0.801833	-1.766357	-0.628920	-0.034747
H	-2.033518	-1.835727	-2.011364	0.192387	-0.021506
H	-3.010838	-0.444324	-2.504386	0.184740	-0.022753
H	-1.375567	-0.209157	-1.851139	0.180947	-0.024115
C	-3.952743	0.784781	1.392525	-0.582256	-0.028022
H	-3.853241	1.770633	1.853835	0.187042	-0.026262
H	-4.993914	0.655496	1.087132	0.175122	-0.017221
H	-3.713478	0.030013	2.144627	0.162599	-0.007448
C	-4.151255	-1.562262	-0.308800	-0.772541	0.006986
H	-3.983935	-2.555184	-0.734952	0.166236	-0.027081
H	-4.512479	-1.688984	0.712389	0.178074	-0.014604
H	-4.931280	-1.070201	-0.897032	0.198771	-0.015803
B	-1.027274	-0.303923	1.020876	1.592582	1.952790
H	-0.778871	-0.427275	2.221397	-0.086110	-0.455190
C	1.231765	-2.193083	1.337865	-0.790718	-0.143436
H	1.400256	-1.706951	2.300063	0.219285	0.028314
H	0.267325	-2.701324	1.359469	0.192086	0.013448
H	2.024485	-2.924269	1.171529	0.218538	0.012610

TS1B

HF/6-31G(d), N,N-dimethylformamide solution

Electronic energy: -1490.358291

Electronic energy + zero-point energy: -1490.004115

Electronic energy + thermal energy correction: -1489.983654

Electronic energy + thermal enthalpy correction: -1489.982710

Electronic energy + thermal free energy correction: -1490.053901

Table S137. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS1B** in the reaction of acetophenone with pinacolborane (HF/6-31G(d), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	4.918635	-1.498496	-0.371344	-0.186688	0.192725
C	4.747351	-0.900323	0.870021	-0.244844	-0.225603
C	3.590622	-0.195391	1.143018	-0.187396	0.107352
C	2.588884	-0.095008	0.176280	-0.062589	-0.605981
C	2.762705	-0.710077	-1.063476	-0.184855	0.087650
C	3.929034	-1.401299	-1.338034	-0.240864	-0.225949
H	5.822715	-2.040633	-0.583134	0.250795	0.050664
H	5.512750	-0.982418	1.619772	0.246650	0.053317
H	3.467712	0.254316	2.109219	0.271010	0.077761
H	1.992234	-0.639062	-1.805335	0.270658	0.103265
H	4.063424	-1.864290	-2.298461	0.246133	0.051945
C	1.348541	0.667689	0.422500	0.408984	2.160491
O	0.420643	0.637313	-0.505977	-0.686192	-1.333757
K	-1.486641	2.759135	-0.619640	0.779962	1.038451
O	-0.662461	-1.593755	-0.267627	-0.702712	-1.384698
C	-2.065295	-1.747374	-0.436262	0.303739	0.765420
C	-2.643984	-0.765688	0.637190	0.303188	0.728554
O	-1.661115	0.265831	0.647637	-0.749371	-1.448408
C	-3.995753	-0.150922	0.295703	-0.515464	0.089756
H	-4.758071	-0.917829	0.202910	0.180676	-0.036303
H	-4.299468	0.526498	1.087814	0.183511	-0.045760
H	-3.965351	0.408832	-0.631380	0.179390	-0.048772
C	-2.416793	-1.341456	-1.870498	-0.507946	0.055037
H	-1.824763	-1.938540	-2.556136	0.178122	-0.046198
H	-3.464672	-1.508760	-2.095319	0.174390	-0.043847
H	-2.189030	-0.298103	-2.063093	0.166522	-0.058064
C	-2.704583	-1.377063	2.038761	-0.511569	0.064909
H	-2.908869	-0.588391	2.755704	0.177777	-0.050444
H	-3.491289	-2.118955	2.120502	0.174507	-0.039304
H	-1.765192	-1.843420	2.313978	0.178528	-0.040423
C	-2.427087	-3.212797	-0.227232	-0.505016	0.093961
H	-1.983523	-3.812756	-1.015548	0.173408	-0.048516
H	-2.057026	-3.584313	0.719671	0.178871	-0.040538
H	-3.502336	-3.359012	-0.261057	0.171271	-0.043067
B	-0.418841	-0.330160	0.297606	0.934779	1.870305
H	0.420108	-0.431398	1.300978	-0.158592	-0.780502
F	0.339950	4.272527	-0.464834	-0.826038	-1.045473

C	1.304250	1.832563	1.364582	-0.579907	-0.215978
H	2.113973	1.841867	2.075519	0.224127	0.040690
H	1.339775	2.720603	0.736875	0.261611	0.148173
H	0.362025	1.849008	1.895640	0.231434	0.027161

HF/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1490.676740

Electronic energy + zero-point energy: -1490.327341

Electronic energy + thermal energy correction: -1490.306510

Electronic energy + thermal enthalpy correction: -1490.305565

Electronic energy + thermal free energy correction: -1490.378439

Table S138. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS1B** in the reaction of acetophenone with pinacolborane (HF/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	5.186986	-0.599830	-0.407943	-0.280781	0.189431
C	4.960845	0.087254	0.773345	-0.422456	-0.254341
C	3.712386	0.609060	1.037967	-0.262815	0.101845
C	2.676122	0.436912	0.124574	0.403899	-0.626873
C	2.909779	-0.260617	-1.056035	-0.042575	0.089545
C	4.163585	-0.770883	-1.323628	-0.408160	-0.255380
H	6.162195	-1.001716	-0.613824	0.234385	0.069776
H	5.755476	0.217005	1.483849	0.222155	0.070647
H	3.553000	1.135600	1.957389	0.269151	0.090398
H	2.114601	-0.396140	-1.760395	0.214799	0.113273
H	4.341123	-1.301638	-2.240179	0.230689	0.070059
C	1.337713	1.010360	0.358587	0.657677	2.211012
O	0.409696	0.785448	-0.527521	-0.838039	-1.356281
K	-2.106404	2.249969	-0.898496	0.925076	1.088037
O	-0.134625	-1.621677	-0.163746	-0.889216	-1.394941
C	-1.446100	-2.142252	-0.315640	0.564376	0.773362
C	-2.278744	-1.249209	0.662628	0.472011	0.733133
O	-1.577948	-0.010463	0.593275	-1.065626	-1.457406
C	-3.726765	-1.020134	0.259727	-0.975867	0.058579
H	-4.272606	-1.957549	0.244125	0.192910	-0.024592
H	-4.207064	-0.367119	0.980946	0.182117	-0.037718
H	-3.814061	-0.566732	-0.719588	0.163756	-0.045484
C	-1.855851	-1.976013	-1.778712	-0.462014	0.032293
H	-1.120466	-2.470929	-2.403539	0.186016	-0.038412

H	-2.823831	-2.420856	-1.980264	0.185727	-0.033349
H	-1.890703	-0.933684	-2.075403	0.137040	-0.055582
C	-2.231664	-1.738271	2.109326	-0.428541	0.041462
H	-2.656382	-0.973189	2.750336	0.180576	-0.041290
H	-2.806892	-2.647111	2.242326	0.179853	-0.027827
H	-1.215964	-1.925200	2.437784	0.169092	-0.035182
C	-1.432248	-3.623451	0.030483	-0.942678	0.066489
H	-0.835181	-4.160570	-0.699177	0.161040	-0.041490
H	-1.004170	-3.802152	1.007663	0.171671	-0.033026
H	-2.435838	-4.036344	0.009940	0.182717	-0.031777
B	-0.218922	-0.310517	0.332293	2.318401	1.812161
H	0.576854	-0.165277	1.355113	-0.288978	-0.716742
F	-2.664888	4.476247	-0.076433	-0.929963	-1.028046
C	1.151876	2.174754	1.273021	-0.984769	-0.191938
H	1.710628	2.081240	2.190097	0.224446	0.061552
H	1.519077	3.042365	0.728157	0.267610	0.037979
H	0.105986	2.314393	1.500231	0.125287	0.016642

B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1496.904892

Electronic energy + zero-point energy: -1496.577878

Electronic energy + thermal energy correction: -1496.555615

Electronic energy + thermal enthalpy correction: -1496.554671

Electronic energy + thermal free energy correction: -1496.630954

Table S139. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS1B** in the reaction of acetophenone with pinacolborane (B3LYP/6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	5.202358	-0.727840	-0.408614	-0.257208	0.125526
C	5.014040	0.027766	0.747469	-0.265325	-0.210238
C	3.775933	0.588813	1.016428	-0.332167	0.120740
C	2.704452	0.391796	0.128677	0.339376	-0.724818
C	2.903827	-0.378371	-1.029658	-0.092288	0.100507
C	4.147284	-0.927189	-1.297289	-0.290229	-0.219628
H	6.173031	-1.162865	-0.616363	0.196856	0.070766
H	5.834497	0.177990	1.438315	0.193193	0.068720
H	3.643772	1.166586	1.920429	0.216647	0.089099
H	2.079232	-0.530687	-1.711232	0.169672	0.119389
H	4.297304	-1.512303	-2.196393	0.200930	0.068960

C	1.393512	0.998590	0.360317	0.564700	2.292079
O	0.432661	0.780082	-0.525900	-0.729170	-1.254729
K	-1.976443	2.280855	-0.909877	0.848245	1.091123
O	-0.191021	-1.636330	-0.149603	-0.693265	-1.325190
C	-1.547420	-2.116528	-0.309104	0.187267	0.755596
C	-2.362092	-1.183416	0.666374	0.179598	0.700215
O	-1.610879	0.057859	0.588505	-0.870446	-1.374793
C	-3.799550	-0.907400	0.244717	-0.683757	-0.012950
H	-4.381145	-1.832326	0.237616	0.185839	-0.008953
H	-4.269345	-0.224261	0.956539	0.161527	-0.018598
H	-3.861716	-0.464886	-0.750269	0.162221	-0.020078
C	-1.944434	-1.943225	-1.778956	-0.370270	-0.049307
H	-1.217277	-2.467212	-2.403133	0.169313	-0.016391
H	-2.931439	-2.363482	-1.984546	0.174157	-0.018222
H	-1.947927	-0.894235	-2.081814	0.155069	-0.032848
C	-2.336803	-1.665059	2.119727	-0.374220	-0.026128
H	-2.746570	-0.879947	2.759253	0.165837	-0.019567
H	-2.943615	-2.562400	2.255119	0.170141	-0.009771
H	-1.321510	-1.882249	2.456320	0.163467	-0.013485
C	-1.586894	-3.596595	0.053816	-0.735347	-0.003164
H	-0.996921	-4.167258	-0.667676	0.148513	-0.021532
H	-1.175241	-3.779194	1.046157	0.164654	-0.010961
H	-2.610745	-3.978050	0.025122	0.174580	-0.012461
B	-0.241415	-0.308439	0.358058	1.951523	1.606827
H	0.520810	-0.205868	1.391009	-0.252480	-0.626697
F	-2.534929	4.487240	-0.120647	-0.897748	-1.029951
C	1.232932	2.161579	1.278472	-0.760357	-0.320476
H	1.821187	2.076305	2.189029	0.204576	0.074220
H	1.591832	3.041021	0.727185	0.239663	0.056840
H	0.186685	2.315702	1.534252	0.116715	0.040331

M06-2X/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1496.513671

Electronic energy + zero-point energy: -1496.182369

Electronic energy + thermal energy correction: -1496.160655

Electronic energy + thermal enthalpy correction: -1496.159711

Electronic energy + thermal free energy correction: -1496.233839

Table S140. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS1B** in the reaction of acetophenone with pinacolborane (M06-2X//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	4.980222	-1.133873	-0.211812	-0.332049	0.098517
C	4.898677	-0.071017	0.681818	-0.295450	-0.207815
C	3.711816	0.630662	0.816223	-0.226503	0.072148
C	2.599241	0.266997	0.051621	0.295917	-0.650743
C	2.686020	-0.802641	-0.845372	-0.108851	0.057512
C	3.875737	-1.498473	-0.975732	-0.263627	-0.207817
H	5.910193	-1.680175	-0.314266	0.232334	0.083092
H	5.761249	0.210443	1.272246	0.241631	0.081733
H	3.657116	1.457772	1.511436	0.240186	0.105463
H	1.815381	-1.078785	-1.424881	0.177403	0.133387
H	3.945308	-2.325398	-1.671106	0.247016	0.080977
C	1.335318	1.013689	0.145260	0.565138	2.251500
O	0.376145	0.711636	-0.688195	-0.618303	-1.341781
K	-1.881653	2.287075	-1.036276	0.905536	1.082208
O	-0.254948	-1.585717	0.147199	-0.528761	-1.289880
C	-1.593623	-1.971995	-0.200333	-0.098245	0.711824
C	-2.452305	-0.970704	0.632409	0.164201	0.683724
O	-1.651462	0.226651	0.578607	-0.739335	-1.345262
C	-3.822045	-0.674949	0.050826	-0.684879	-0.053040
H	-4.420293	-1.588256	0.010369	0.213966	0.011405
H	-4.345099	0.044562	0.684437	0.196371	-0.001241
H	-3.758005	-0.270452	-0.960333	0.163235	-0.010497
C	-1.775547	-1.787121	-1.704596	-0.403121	-0.080530
H	-1.005155	-2.361159	-2.222620	0.207560	0.000137
H	-2.752919	-2.141125	-2.037907	0.205332	0.004649
H	-1.666780	-0.740064	-1.996622	0.135071	-0.016550
C	-2.580180	-1.388844	2.092406	-0.460147	-0.066739
H	-3.007700	-0.560015	2.659470	0.197252	-0.004778
H	-3.234520	-2.255393	2.202139	0.190194	0.005627
H	-1.603385	-1.631448	2.515824	0.179539	0.003650
C	-1.802953	-3.427692	0.171209	-0.754880	-0.040803
H	-1.191936	-4.063070	-0.473211	0.183758	-0.005580
H	-1.520533	-3.615408	1.206596	0.182538	0.004009
H	-2.849856	-3.709507	0.034206	0.206875	0.004922
B	-0.291471	-0.200144	0.436450	1.390755	1.553845
H	0.470837	0.080928	1.406647	-0.001533	-0.551343
F	-1.394135	4.217561	0.270648	-0.880878	-1.058251
C	1.269815	2.318677	0.855586	-0.947634	-0.364812
H	1.729206	2.275967	1.840782	0.221059	0.082508

H	1.841760	3.027814	0.244436	0.271856	0.070886
H	0.242090	2.674151	0.925549	0.129475	0.113742

ωB97XD/6-311++G(2d,p), N,N-dimethylformamide solution

Electronic energy: -1496.611869

Electronic energy + zero-point energy: -1496.281256

Electronic energy + thermal energy correction: -1496.259348

Electronic energy + thermal enthalpy correction: -1496.258403

Electronic energy + thermal free energy correction: -1496.333622

Table S141. Cartesian coordinates, Mulliken and APT charges of all atoms at **TS1B** in the reaction of acetophenone with pinacolborane (ωB97XD//6-311++G(2d,p), N,N-dimethylformamide solution).

Symbol	X	Y	Z	Mulliken	APT
C	5.040280	-1.036716	-0.265368	-0.339945	0.112152
C	4.915980	-0.069845	0.725331	-0.303317	-0.202326
C	3.715457	0.596903	0.894830	-0.270373	0.086786
C	2.627721	0.295213	0.070630	0.327713	-0.678604
C	2.758450	-0.681802	-0.920538	-0.134861	0.068901
C	3.962509	-1.341241	-1.088531	-0.314388	-0.202660
H	5.982782	-1.555862	-0.396271	0.238600	0.071810
H	5.757474	0.164496	1.365766	0.245115	0.071575
H	3.630404	1.345878	1.671004	0.246443	0.093687
H	1.909755	-0.915225	-1.549135	0.230292	0.125281
H	4.063152	-2.094863	-1.860155	0.249613	0.071424
C	1.346412	1.004038	0.200752	0.652807	2.297319
O	0.392289	0.718209	-0.646360	-0.708239	-1.326023
K	-1.960787	2.287123	-0.998880	0.897744	1.081936
O	-0.238170	-1.614269	0.080565	-0.693514	-1.302879
C	-1.580543	-2.014409	-0.223979	0.171788	0.724342
C	-2.427912	-1.026182	0.643927	0.281019	0.692594
O	-1.635342	0.173533	0.588433	-0.891762	-1.360329
C	-3.812325	-0.727899	0.096380	-0.756483	-0.027971
H	-4.412121	-1.640951	0.067095	0.215986	0.001694
H	-4.322432	-0.010660	0.744192	0.196533	-0.012088
H	-3.777280	-0.319928	-0.915271	0.173520	-0.018258
C	-1.812407	-1.832961	-1.723386	-0.493432	-0.055711
H	-1.052151	-2.398175	-2.266866	0.203302	-0.009975
H	-2.794886	-2.201098	-2.027048	0.205931	-0.006150
H	-1.727248	-0.786364	-2.024923	0.153122	-0.024939

C	-2.530806	-1.461026	2.102955	-0.478647	-0.039580
H	-2.953076	-0.640442	2.687349	0.196850	-0.014660
H	-3.181650	-2.330591	2.215583	0.191695	-0.003748
H	-1.549205	-1.705844	2.514602	0.183788	-0.005806
C	-1.757623	-3.476274	0.145877	-0.804793	-0.014051
H	-1.154297	-4.101554	-0.516830	0.176835	-0.016026
H	-1.446337	-3.668598	1.172822	0.187646	-0.005193
H	-2.803254	-3.775427	0.034613	0.207563	-0.004667
B	-0.276784	-0.240880	0.417871	1.718524	1.578591
H	0.491058	-0.000446	1.408105	-0.130361	-0.581487
F	-1.567522	4.361688	0.147414	-0.897141	-1.042160
C	1.254652	2.281461	0.957593	-0.988721	-0.337850
H	1.747531	2.232545	1.926326	0.225401	0.080062
H	1.771721	3.034151	0.350184	0.292233	0.064880
H	0.217337	2.587475	1.081560	0.135916	0.070110

Benzaldehyde + pinacolborane, catalyst-free, bimolecular

Substrates

M06-2X/6-311++G(2d,p), gas phase

Electronic energy: -757.353019

Electronic energy + zero-point energy: -757.049453

Electronic energy + thermal energy correction: -757.027917

Electronic energy + thermal enthalpy correction: -757.026862

Electronic energy + thermal free energy correction: -757.104666

Table S142. Cartesian coordinates, Mulliken and APT charges of all atoms at **Substrates** in the catalyst-free reaction of benzaldehyde with pinacolborane (M06-2X//6-311++G(2d,p), bimolecular, gas phase).

Symbol	X	Y	Z	Mulliken	APT
C	-4.542590	1.409939	0.285938	-0.044227	0.026185
C	-5.028498	0.109385	0.323997	-0.397500	-0.089972
C	-4.160521	-0.951571	0.109249	-0.248288	0.022799
C	-2.813002	-0.709476	-0.140738	0.442964	-0.299609
C	-2.325687	0.597175	-0.180097	-0.071081	-0.000204
C	-3.194593	1.653478	0.034069	-0.089211	-0.099950
H	-5.217001	2.240634	0.453801	0.179669	0.044809

H	-6.076818	-0.074681	0.520396	0.176322	0.043911
H	-4.524761	-1.973035	0.136394	0.173094	0.050159
H	-1.272234	0.764723	-0.371686	0.020770	0.122257
H	-2.824552	2.670453	0.008496	0.200365	0.048256
C	-1.906624	-1.855120	-0.363616	-0.077258	1.003330
O	-0.721285	-1.760769	-0.560488	-0.350599	-0.821294
H	-2.391398	-2.850170	-0.339171	0.150410	-0.055035
O	1.016056	0.928593	0.301106	-0.364241	-0.877138
C	2.205815	0.704481	-0.492573	-0.358775	0.460795
C	3.006200	-0.308039	0.389745	0.115388	0.458607
O	1.960548	-0.971977	1.132915	-0.428061	-0.867595
C	3.790461	-1.345180	-0.391769	-0.681089	-0.027063
H	4.528066	-0.859708	-1.035116	0.174246	0.002461
H	4.318372	-1.999307	0.302953	0.171570	0.002264
H	3.131715	-1.956668	-1.005299	0.178942	0.016463
C	1.750317	0.108124	-1.818990	-0.337405	-0.062908
H	1.045669	0.797685	-2.286423	0.182870	0.004426
H	2.594353	-0.036445	-2.495566	0.178325	-0.003986
H	1.242805	-0.843455	-1.664479	0.164751	0.050354
C	3.904718	0.375985	1.414641	-0.378478	-0.046344
H	4.273372	-0.377094	2.111413	0.189738	0.005468
H	4.758729	0.858901	0.937040	0.162038	0.000325
H	3.349283	1.124205	1.982358	0.149437	0.004589
C	2.901821	2.033289	-0.721525	-0.607559	-0.025111
H	2.273462	2.668588	-1.346802	0.166463	0.003942
H	3.090115	2.553367	0.215928	0.164838	0.006353
H	3.852289	1.879012	-1.237607	0.183078	0.002585
B	0.871901	-0.153834	1.125364	0.766846	1.071422
H	-0.080421	-0.319426	1.808300	0.141645	-0.175551

ωB97XD/6-311++G(2d,p), gas phase

Electronic energy: -757.427291

Electronic energy + zero-point energy: -757.124386

Electronic energy + thermal energy correction: -757.102762

Electronic energy + thermal enthalpy correction: -757.101707

Electronic energy + thermal free energy correction: -757.180781

Table S143. Cartesian coordinates, Mulliken and APT charges of all atoms at **Substrates** in the catalyst-free reaction of benzaldehyde with pinacolborane (ωB97XD//6-311++G(2d,p), bimolecular, gas phase).

Symbol	X	Y	Z	Mulliken	APT
C	4.321205	1.535492	-0.114338	-0.140999	0.040232
C	4.909816	0.343686	0.284826	-0.426774	-0.085964
C	4.144123	-0.810201	0.347126	-0.136150	0.029115
C	2.793216	-0.771906	0.014209	0.701852	-0.306935
C	2.204696	0.426568	-0.387963	-0.356778	-0.007330
C	2.971739	1.576091	-0.450690	-0.124422	-0.097952
H	4.917164	2.439401	-0.165612	0.182531	0.037373
H	5.960976	0.315275	0.544744	0.176169	0.036850
H	4.594004	-1.748359	0.656828	0.177449	0.043405
H	1.152027	0.446277	-0.644123	0.076582	0.133425
H	2.518958	2.508871	-0.764867	0.196542	0.042982
C	1.999055	-2.015198	0.098038	-0.050890	1.001814
O	0.818828	-2.100691	-0.131597	-0.375759	-0.790182
H	2.574694	-2.913760	0.403544	0.130570	-0.069434
O	-1.129963	0.718931	-0.879212	-0.423133	-0.867593
C	-1.916227	0.767742	0.334462	-0.142809	0.447634
C	-3.076665	-0.242887	0.022773	0.472423	0.450157
O	-2.483516	-1.111462	-0.965994	-0.492148	-0.842225
C	-3.519649	-1.083192	1.207535	-0.766642	-0.009622
H	-3.896380	-0.444396	2.010567	0.172512	-0.001465
H	-4.323874	-1.753137	0.899079	0.166040	-0.004694
H	-2.701632	-1.689634	1.593221	0.191571	0.009093
C	-1.008838	0.313542	1.473815	-0.484522	-0.048464
H	-0.142708	0.976234	1.522073	0.182189	-0.000685
H	-1.527869	0.358565	2.433272	0.161883	-0.010698
H	-0.647650	-0.701948	1.308620	0.156236	0.038890
C	-4.286832	0.411793	-0.637594	-0.425716	-0.026400
H	-4.961500	-0.370980	-0.987298	0.189379	-0.001258
H	-4.829034	1.048525	0.064366	0.156776	-0.003367
H	-3.991428	1.013174	-1.499295	0.153601	-0.000305
C	-2.365838	2.199601	0.566740	-0.718256	-0.006700
H	-1.495950	2.827210	0.768166	0.157441	-0.003072
H	-2.884992	2.605577	-0.300330	0.165040	0.000098
H	-3.031361	2.253979	1.432022	0.184198	-0.001342
B	-1.422650	-0.458115	-1.509901	0.899709	1.046755
H	-0.831792	-0.841305	-2.464695	0.014306	-0.172137

Transition state

M06-2X/6-311++G(2d,p), gas phase

Electronic energy: -757.304641

Electronic energy + zero-point energy: -757.002037

Electronic energy + thermal energy correction: -756.982111

Electronic energy + thermal enthalpy correction: -756.981056

Electronic energy + thermal free energy correction: -757.052821

Table S144. Cartesian coordinates, Mulliken and APT charges of all atoms at **Transition state** in the catalyst-free reaction of benzaldehyde with pinacolborane (M06-2X//6-311++G(2d,p), bimolecular, gas phase).

Symbol	X	Y	Z	Mulliken	APT
C	-4.705449	0.888615	0.428789	-0.208619	0.042384
C	-4.688990	-0.486141	0.633048	-0.237292	-0.104491
C	-3.553682	-1.211578	0.307986	-0.697308	0.052698
C	-2.447299	-0.556815	-0.226723	0.609210	-0.396517
C	-2.460866	0.822505	-0.429844	0.517641	0.017328
C	-3.595091	1.542806	-0.098496	-0.299966	-0.109289
H	-5.590920	1.457132	0.685130	0.179983	0.049376
H	-5.556500	-0.985745	1.043784	0.189624	0.047081
H	-3.521702	-2.284435	0.463105	0.171659	0.055816
H	-1.572099	1.297993	-0.826035	0.235329	0.101492
H	-3.619131	2.614723	-0.245413	0.193678	0.048890
C	-1.256361	-1.331873	-0.594311	-0.430788	1.442868
O	-0.338553	-0.856290	-1.328699	-0.386595	-0.960787
H	-1.321136	-2.417212	-0.439885	0.235790	-0.049399
O	0.744497	0.634340	0.401891	-0.516042	-0.948608
C	2.097626	0.896372	-0.008783	-0.245876	0.522358
C	2.790212	-0.476417	0.267528	0.242235	0.508697
O	1.748635	-1.418359	-0.035557	-0.581769	-0.999980
C	3.988969	-0.765698	-0.617866	-0.632755	-0.034929
H	4.755999	0.001872	-0.487742	0.170327	-0.007463
H	4.419549	-1.729949	-0.344279	0.166702	-0.003199
H	3.700469	-0.805692	-1.666669	0.170635	0.009998
C	2.094036	1.253261	-1.493741	-0.396345	-0.073232
H	1.414998	2.093347	-1.647387	0.166606	-0.001710
H	3.089674	1.545107	-1.833152	0.171589	-0.005796
H	1.745048	0.414678	-2.097002	0.159220	0.027900
C	3.161171	-0.649775	1.737631	-0.389517	-0.053730
H	3.437112	-1.691367	1.905149	0.183357	-0.000697
H	4.004420	-0.015560	2.017608	0.159207	-0.008510
H	2.310938	-0.409695	2.378283	0.153337	0.006800
C	2.638508	2.052943	0.811096	-0.659228	-0.033025
H	2.117439	2.971200	0.536114	0.163490	-0.001093
H	2.491035	1.881202	1.875950	0.168733	0.007346
H	3.704771	2.193359	0.617630	0.177105	-0.004062

B	0.538506	-0.725909	0.116068	1.008534	1.250163
H	-0.315825	-1.248182	0.885514	0.088110	-0.394677

ωB97XD/6-311++G(2d,p), gas phase

Electronic energy: -757.374728

Electronic energy + zero-point energy: -757.072901

Electronic energy + thermal energy correction: -757.052871

Electronic energy + thermal enthalpy correction: -757.051816

Electronic energy + thermal free energy correction: -757.124054

Table S145. Cartesian coordinates, Mulliken and APT charges of all atoms at **Transition state** in the catalyst-free reaction of benzaldehyde with pinacolborane (ωB97XD//6-311++G(2d,p), bimolecular, gas phase).

Symbol	X	Y	Z	Mulliken	APT
C	-4.760227	0.853605	0.438531	-0.215329	0.049201
C	-4.712931	-0.520526	0.634145	-0.231337	-0.099573
C	-3.564421	-1.218958	0.301499	-0.629777	0.061108
C	-2.472724	-0.540405	-0.232576	0.612149	-0.414170
C	-2.519323	0.838784	-0.425670	0.466895	0.022626
C	-3.666393	1.532874	-0.087743	-0.363821	-0.104028
H	-5.657347	1.402029	0.701206	0.182672	0.041365
H	-5.568421	-1.042009	1.045093	0.190064	0.039773
H	-3.511835	-2.292266	0.451911	0.171192	0.050434
H	-1.644512	1.339531	-0.821593	0.287923	0.096216
H	-3.712312	2.605652	-0.228753	0.189654	0.042607
C	-1.266017	-1.289536	-0.603831	-0.386977	1.477074
O	-0.359279	-0.799510	-1.345110	-0.459368	-0.967694
H	-1.319472	-2.378439	-0.459655	0.236381	-0.062413
O	0.776863	0.655012	0.393448	-0.679098	-0.963155
C	2.140244	0.901489	0.016256	0.002601	0.532079
C	2.801683	-0.500167	0.250765	0.399479	0.517405
O	1.739272	-1.406917	-0.077742	-0.731009	-1.012027
C	3.991887	-0.792867	-0.647188	-0.691683	-0.018759
H	4.780890	-0.051514	-0.493357	0.166353	-0.014019
H	4.398783	-1.777434	-0.408771	0.159586	-0.009927
H	3.704908	-0.789922	-1.697839	0.174310	0.004720
C	2.169550	1.328248	-1.451540	-0.461770	-0.055555
H	1.518026	2.195316	-1.575897	0.163007	-0.006915
H	3.178013	1.607977	-1.764486	0.167390	-0.012732
H	1.806143	0.533805	-2.104372	0.168450	0.020384

C	3.178643	-0.732957	1.712978	-0.425237	-0.035489
H	3.432171	-1.786279	1.844414	0.178550	-0.007054
H	4.040274	-0.130226	2.008959	0.157172	-0.015290
H	2.342453	-0.496946	2.373917	0.150735	0.001273
C	2.690665	2.014413	0.891058	-0.707995	-0.016092
H	2.188040	2.953597	0.651598	0.156243	-0.007469
H	2.531415	1.803649	1.947798	0.171568	0.002448
H	3.761504	2.147081	0.714692	0.174480	-0.010967
B	0.546333	-0.693072	0.082673	1.181194	1.283495
H	-0.319052	-1.210894	0.856906	0.075355	-0.408882

Products

M06-2X/6-311++G(2d,p), gas phase

Electronic energy: -757.421051

Electronic energy + zero-point energy: -757.112805

Electronic energy + thermal energy correction: -757.092742

Electronic energy + thermal enthalpy correction: -757.091687

Electronic energy + thermal free energy correction: -757.165144

Table S146. Cartesian coordinates, Mulliken and APT charges of all atoms at **Products** in the catalyst-free reaction of benzaldehyde with pinacolborane (M06-2X//6-311++G(2d,p), bimolecular, gas phase).

Symbol	X	Y	Z	Mulliken	APT
C	-1.689141	1.008928	0.967876	-0.475414	-0.895403
C	-2.546775	-0.029256	0.447531	0.153315	0.467823
C	-1.587490	-0.798306	-0.518851	-0.602462	0.462325
C	-0.703739	0.253239	-0.960870	-0.484930	-0.869857
C	-0.718043	-1.823197	0.202634	-0.140097	-0.057630
C	-1.298812	-2.694143	0.510741	0.197011	0.002697
H	0.073582	-2.145842	-0.474924	0.175205	0.012288
H	-0.245862	-1.382692	1.083148	0.160865	0.015260
H	-3.074498	-0.858879	1.602034	-0.696817	-0.029502
H	-3.739652	-0.249608	2.214863	0.178953	0.004839
H	-3.640383	-1.714841	1.227104	0.175378	0.005430
C	-2.263308	-1.220024	2.231522	0.166949	0.009940
O	-2.265110	-1.422400	-1.722712	-0.747501	-0.026507
H	-1.522935	-1.943371	-2.328576	0.169494	0.006439
O	-3.015644	-2.148129	-1.401280	0.182849	0.005692
C	-2.746530	-0.667794	-2.342227	0.171200	0.008978

C	-3.692578	0.657350	-0.286639	-0.304083	-0.048065
O	-4.192672	1.336045	0.404538	0.189204	0.007164
C	-3.320370	1.239715	-1.131219	0.146900	0.007939
H	-4.420530	-0.067822	-0.653700	0.168128	0.001592
H	-0.691095	1.185166	0.048660	1.796088	1.433531
H	1.128536	1.948139	-1.711213	0.175866	-0.020351
C	3.714023	-1.383389	0.545453	-0.358929	-0.052649
H	3.578414	-1.073773	-0.801224	-0.264265	-0.024747
H	2.829450	0.029823	-1.189344	-0.340024	-0.067570
H	2.218733	0.838509	-0.238313	0.528077	-0.028141
C	2.359679	0.524999	1.111232	0.005948	-0.095629
H	3.101444	-0.581578	1.500957	-0.218244	-0.023829
H	4.290678	-2.247916	0.849389	0.172427	0.041559
H	4.045446	-1.699506	-1.551647	0.182586	0.038891
C	2.702422	0.254917	-2.242380	0.163232	0.044965
H	1.871320	1.146500	1.852948	0.204428	0.069622
H	3.202295	-0.818963	2.552836	0.184688	0.039432
H	1.398015	2.035809	-0.656087	-0.588370	0.567393
B	0.229051	2.175129	0.143954	-0.628472	-0.980147
H	1.966940	2.956877	-0.520937	0.200818	-0.033771

ωB97XD/6-311++G(2d,p), gas phase

Electronic energy: -757.490243

Electronic energy + zero-point energy: -757.182414

Electronic energy + thermal energy correction: -757.162367

Electronic energy + thermal enthalpy correction: -757.161312

Electronic energy + thermal free energy correction: -757.234093

Table S147. Cartesian coordinates, Mulliken and APT charges of all atoms at **Products** in the catalyst-free reaction of benzaldehyde with pinacolborane (ωB97XD//6-311++G(2d,p), bimolecular, gas phase).

Symbol	X	Y	Z	Mulliken	APT
C	-1.666650	1.063912	0.922584	-0.617904	-0.887022
C	-2.514472	-0.013801	0.475224	0.321162	0.470133
C	-1.565024	-0.807791	-0.488991	-0.326851	0.463968
C	-0.705752	0.235826	-0.987382	-0.665261	-0.865144
C	-0.665958	-1.804468	0.239480	-0.276161	-0.043080
C	-1.230632	-2.669813	0.592249	0.198968	-0.003820
H	0.107490	-2.146873	-0.449871	0.192609	0.006968
H	-0.166097	-1.339604	1.091912	0.172803	0.009650

H	-2.985751	-0.801774	1.683805	-0.749083	-0.012066
H	-3.642566	-0.180543	2.294975	0.171389	-0.002732
H	-3.547357	-1.684638	1.367687	0.171956	-0.000548
C	-2.147884	-1.121592	2.301761	0.170537	0.004660
O	-2.261858	-1.480301	-1.656726	-0.803454	-0.008907
H	-1.527819	-2.009853	-2.266480	0.158898	-0.000809
O	-2.992924	-2.208034	-1.295540	0.181755	-0.000451
C	-2.772195	-0.755479	-2.289662	0.174720	0.002456
C	-3.704294	0.614098	-0.244367	-0.327397	-0.029716
O	-4.198855	1.309193	0.435692	0.186889	0.000281
C	-3.384171	1.171432	-1.126842	0.145923	0.003025
H	-4.428194	-0.142646	-0.553242	0.166392	-0.004908
H	-0.684256	1.207339	-0.017729	2.041792	1.410229
H	1.184599	1.959583	-1.792114	0.156471	-0.028036
C	3.623087	-1.409678	0.576125	-0.269689	-0.039718
H	3.390533	-1.205111	-0.775721	-0.339430	-0.024676
H	2.685086	-0.086776	-1.198115	-0.393552	-0.055628
H	2.216330	0.842151	-0.278811	0.705796	-0.043665
C	2.458194	0.633829	1.076235	-0.019332	-0.074743
H	3.153813	-0.486916	1.502078	-0.272491	-0.024288
H	4.165710	-2.286757	0.908720	0.170853	0.034706
H	3.747125	-1.924763	-1.503484	0.176528	0.032992
C	2.477381	0.054420	-2.253274	0.165893	0.040253
H	2.079257	1.347492	1.799337	0.202144	0.058372
H	3.331500	-0.641480	2.560008	0.179640	0.032946
H	1.421781	2.045044	-0.728121	-0.603594	0.602000
B	0.230291	2.205258	0.034031	-0.743129	-0.981552
H	1.995003	2.962262	-0.579622	0.194209	-0.041130

Benzaldehyde + pinacolborane, catalyst-free, tetramolecular

Substrates

M06-2X/6-311++G(2d,p), gas phase

Electronic energy: -1514.722868

Electronic energy + zero-point energy: -1514.114365

Electronic energy + thermal energy correction: -1514.069232

Electronic energy + thermal enthalpy correction: -1514.068177

Electronic energy + thermal free energy correction: -1514.201305

Table S148. Cartesian coordinates, Mulliken and APT charges of all atoms at **Substrates** in the catalyst-free reaction of benzaldehyde with pinacolborane (M06-2X//6-311++G(2d,p), tetramolecular, gas phase).

Symbol	X	Y	Z	Mulliken	APT
C	0.515627	-4.158290	0.928017	-0.283341	0.034952
C	-0.269134	-4.592961	-0.134762	-0.381892	-0.078831
C	-0.677522	-3.686812	-1.101903	-0.310164	0.013085
C	-0.302800	-2.350027	-1.000917	0.661125	-0.279876
C	0.491789	-1.916990	0.059073	-0.076091	-0.025578
C	0.902040	-2.823736	1.022611	-0.144287	-0.102343
H	0.833718	-4.865358	1.684427	0.193705	0.046603
H	-0.562901	-5.632613	-0.203211	0.195646	0.044449
H	-1.306170	-4.003895	-1.926849	0.192133	0.059187
H	0.791633	-0.877789	0.120418	0.199815	0.111959
H	1.532716	-2.486865	1.835443	0.213225	0.065389
C	-0.792977	-1.385901	-2.005430	-0.406775	0.950902
O	-0.597078	-0.194802	-1.948779	-0.241104	-0.811909
H	-1.382258	-1.819397	-2.833427	0.165138	-0.033102
O	-3.512813	-1.603585	-1.004401	-0.274482	-0.828490
C	-3.965069	-1.605588	0.375536	0.414926	0.412792
C	-3.779137	-0.110922	0.782830	-0.631286	0.399017
O	-3.947866	0.573069	-0.486090	-0.359458	-0.800989
C	-4.809975	0.416577	1.762179	-0.729463	-0.016676
H	-4.760961	-0.140954	2.700291	0.190037	0.009082
H	-4.598905	1.465127	1.975729	0.172540	0.008336
H	-5.818776	0.343187	1.359928	0.168235	0.004609
C	-5.427584	-2.036006	0.351577	-0.390963	-0.040610
H	-5.497667	-3.012244	-0.128598	0.192386	0.007506
H	-5.832341	-2.113540	1.361667	0.173871	0.006300
H	-6.034922	-1.329203	-0.216274	0.146913	0.005768
C	-2.370259	0.197734	1.273412	-0.353734	-0.037750
H	-2.265781	1.275985	1.394468	0.177427	0.005120
H	-2.173683	-0.283304	2.232844	0.238336	0.004103
H	-1.623126	-0.137855	0.550192	-0.232832	0.013997
C	-3.139518	-2.591210	1.179730	-0.475109	-0.027856
H	-3.316664	-3.601746	0.808895	0.177142	0.010942
H	-2.073182	-2.383409	1.109656	0.050379	0.009532
H	-3.437423	-2.554415	2.230386	0.208687	0.004092
B	-3.661554	-0.325970	-1.467575	1.120056	0.986608
H	-3.561593	-0.032879	-2.609945	-0.010532	-0.153936
C	-2.706263	4.829841	0.129534	-0.432568	0.027238
C	-2.758981	3.595537	-0.503292	-0.180486	-0.111899
C	-1.583274	2.890085	-0.729817	0.333322	0.005143

C	-0.365811	3.420203	-0.315156	0.465515	-0.303606
C	-0.315503	4.660360	0.322401	-0.284809	-0.006682
C	-1.485776	5.363674	0.542690	-0.309575	-0.092598
H	-3.620531	5.383220	0.307107	0.180383	0.039940
H	-3.705297	3.168262	-0.807932	0.179267	0.070840
H	-1.607201	1.921008	-1.217458	0.024348	0.097771
H	0.646813	5.046505	0.635389	0.209712	0.075801
H	-1.456988	6.326447	1.037201	0.185237	0.035427
C	0.872432	2.645259	-0.547832	-0.077659	0.971592
O	1.976914	3.035041	-0.251929	-0.334200	-0.811767
H	0.726356	1.656438	-1.021144	0.070222	0.011227
O	3.096371	-0.372083	0.904030	-0.450204	-0.857125
C	3.980437	-0.507560	-0.240035	-0.195538	0.409719
C	5.258872	0.256722	0.235854	0.231089	0.436026
O	5.181463	0.123858	1.677594	-0.405286	-0.845829
C	6.568744	-0.343250	-0.239447	-0.650315	-0.026211
H	6.611237	-0.341476	-1.331007	0.176200	0.008648
H	7.397846	0.257172	0.136137	0.175126	0.002189
H	6.694925	-1.363926	0.117334	0.161404	0.006335
C	4.216229	-2.000792	-0.436541	-0.562377	-0.029523
H	3.256173	-2.491021	-0.601243	0.126237	-0.000572
H	4.855545	-2.187440	-1.300672	0.187747	-0.001274
H	4.682230	-2.443162	0.446115	0.160052	0.001979
C	5.211382	1.747578	-0.073770	-0.440112	-0.049713
H	6.023962	2.238106	0.463030	0.188812	-0.004581
H	5.339860	1.929308	-1.142215	0.162164	0.011129
H	4.264563	2.190396	0.237066	0.163127	0.050213
C	3.305077	0.090891	-1.459354	-0.646217	-0.025463
H	2.414191	-0.490202	-1.707742	0.160747	-0.000567
H	3.014087	1.124419	-1.277870	0.218087	0.059656
H	3.981731	0.057417	-2.316794	0.213949	-0.008544
B	3.879751	-0.113068	1.990153	1.000503	1.039531
H	3.463593	-0.113599	3.099237	0.045889	-0.160833

ωB97XD/6-311++G(2d,p), gas phase

Electronic energy: -1514.875573

Electronic energy + zero-point energy: -1514.268073

Electronic energy + thermal energy correction: -1514.222665

Electronic energy + thermal enthalpy correction: -1514.221610

Electronic energy + thermal free energy correction: -1514.357345

Table S149. Cartesian coordinates, Mulliken and APT charges of all atoms at **Substrates** in the catalyst-free reaction of benzaldehyde with pinacolborane (ωB97XD//6-311++G(2d,p), tetramolecular, gas phase).

Symbol	X	Y	Z	Mulliken	APT
C	0.273496	-4.202663	0.784786	-0.207290	0.046767
C	-0.555474	-4.592130	-0.259601	-0.357584	-0.076987
C	-0.918266	-3.669982	-1.227623	-0.356878	0.023086
C	-0.451441	-2.361333	-1.151360	0.581792	-0.296186
C	0.387262	-1.976077	-0.108332	-0.155696	-0.022028
C	0.747599	-2.897287	0.858801	-0.372706	-0.102597
H	0.555158	-4.922145	1.544971	0.191464	0.039437
H	-0.921507	-5.610276	-0.312845	0.189687	0.037151
H	-1.582099	-3.954897	-2.036966	0.187271	0.052771
H	0.761347	-0.961153	-0.059154	0.356372	0.110747
H	1.408014	-2.593222	1.661211	0.207578	0.058678
C	-0.885558	-1.381395	-2.164152	-0.153355	0.964413
O	-0.590113	-0.209773	-2.151957	-0.297551	-0.800424
H	-1.534666	-1.786230	-2.964300	0.181477	-0.045650
O	-3.726071	-1.496010	-0.901642	-0.408546	-0.810102
C	-4.048467	-1.444904	0.512273	0.441590	0.413382
C	-3.751721	0.051659	0.866355	-0.214373	0.401266
O	-3.967311	0.714520	-0.405444	-0.483100	-0.791163
C	-4.685298	0.661733	1.895642	-0.754670	-0.002214
H	-4.605424	0.126680	2.845219	0.189129	0.003539
H	-4.405314	1.702401	2.067280	0.175727	0.002647
H	-5.722845	0.636796	1.565161	0.170880	-0.001268
C	-5.524696	-1.811426	0.633796	-0.334479	-0.023826
H	-5.681060	-2.795730	0.189970	0.195149	0.001061
H	-5.837958	-1.849658	1.678794	0.176215	0.002031
H	-6.158177	-1.095880	0.106125	0.144094	-0.000008
C	-2.300281	0.298420	1.262554	-0.624865	-0.025940
H	-2.129678	1.372329	1.340967	0.203308	0.001914
H	-2.072046	-0.160240	2.226359	0.235639	0.000724
H	-1.610535	-0.098055	0.515556	-0.215165	0.007173
C	-3.198665	-2.454656	1.260205	-0.681417	-0.009967
H	-3.454585	-3.463795	0.933370	0.170764	0.005759
H	-2.135143	-2.302507	1.088404	0.256709	0.003302
H	-3.392949	-2.384412	2.333542	0.192361	-0.001014
B	-3.823980	-0.222849	-1.379698	1.124545	0.967696
H	-3.790760	0.040999	-2.537261	-0.000379	-0.158979
C	-2.426088	4.867632	0.111751	-0.383252	0.035734
C	-2.535044	3.655125	-0.552328	-0.217022	-0.108379
C	-1.391900	2.917305	-0.825836	0.151972	0.010686

C	-0.145966	3.393398	-0.431528	0.529740	-0.318935
C	-0.040547	4.613431	0.236658	-0.387298	0.004700
C	-1.179585	5.347856	0.507180	-0.289168	-0.086820
H	-3.317546	5.445424	0.328343	0.175366	0.032897
H	-3.503160	3.266945	-0.841193	0.188448	0.066947
H	-1.464356	1.963034	-1.336369	0.170044	0.092924
H	0.940682	4.962859	0.535243	0.210800	0.070920
H	-1.104736	6.295220	1.027785	0.184142	0.028377
C	1.058176	2.587418	-0.721094	-0.068950	0.988690
O	2.186567	2.939081	-0.466467	-0.376492	-0.814982
H	0.863574	1.608983	-1.200199	0.152042	0.005798
O	2.985660	-0.391871	0.838607	-0.551602	-0.853085
C	3.987386	-0.647231	-0.179409	0.084331	0.418920
C	5.245049	0.106056	0.385713	0.441375	0.439907
O	4.974899	0.145528	1.809346	-0.534183	-0.841841
C	6.565312	-0.611262	0.164941	-0.724745	-0.009252
H	6.758781	-0.730655	-0.904047	0.176157	0.002889
H	7.375999	-0.019331	0.592675	0.170941	-0.004766
H	6.576663	-1.593696	0.635284	0.158699	-0.000549
C	4.168431	-2.160471	-0.247443	-0.605212	-0.015197
H	3.212529	-2.622481	-0.497149	0.143630	-0.003541
H	4.894685	-2.435963	-1.014361	0.184920	-0.006966
H	4.503249	-2.564981	0.710055	0.165305	-0.001550
C	5.347827	1.552155	-0.085266	-0.488571	-0.034821
H	6.123490	2.053533	0.496029	0.179715	-0.011666
H	5.622853	1.601167	-1.141007	0.156177	0.002801
H	4.408389	2.089012	0.049132	0.189370	0.053349
C	3.476030	-0.119334	-1.507620	-0.874705	-0.012828
H	2.591022	-0.683017	-1.810554	0.184430	-0.006034
H	3.211513	0.934794	-1.438367	0.235597	0.052414
H	4.237314	-0.243732	-2.282056	0.197207	-0.014571
B	3.639218	-0.031066	1.977172	1.115904	1.028043
H	3.088616	0.097434	3.023073	0.001191	-0.165405

Transition state

M06-2X/6-311++G(2d,p), gas phase

Electronic energy: -1514.692998

Electronic energy + zero-point energy: -1514.083796

Electronic energy + thermal energy correction: -1514.042078

Electronic energy + thermal enthalpy correction: -1514.041023

Electronic energy + thermal free energy correction: -1514.162342

Table S150. Cartesian coordinates, Mulliken and APT charges of all atoms at **Transition state** in the catalyst-free reaction of benzaldehyde with pinacolborane (M06-2X//6-311++G(2d,p), tetramolecular, gas phase).

Symbol	X	Y	Z	Mulliken	APT
C	-2.417456	3.103146	-3.191927	-0.337205	0.080946
C	-2.700139	1.748052	-3.309358	-0.297925	-0.123209
C	-1.869661	0.817517	-2.704524	-0.261943	0.076647
C	-0.747382	1.256741	-2.001195	0.498890	-0.417719
C	-0.457826	2.620656	-1.889476	-0.196435	0.055698
C	-1.300843	3.541735	-2.480941	-0.198226	-0.148426
H	-3.073652	3.829367	-3.655922	0.191509	0.051723
H	-3.573588	1.420410	-3.857950	0.200224	0.055364
H	-2.092881	-0.241715	-2.735202	0.204568	0.103315
H	0.420621	2.931782	-1.336951	0.206258	0.078390
H	-1.094336	4.600704	-2.397578	0.195995	0.049581
C	0.121874	0.267458	-1.403378	-0.337471	1.136448
O	1.198827	0.597245	-0.873568	-0.493501	-1.018891
H	-0.147765	-0.790699	-1.459393	0.155008	0.094306
O	2.133419	-1.642859	-0.967979	-0.514309	-1.104696
C	3.491346	-2.097726	-0.877781	0.166379	0.548834
C	4.263444	-0.765526	-0.619138	-0.245690	0.535662
O	3.330933	-0.025715	0.185546	-0.477766	-1.063271
C	5.561248	-0.926966	0.150543	-0.583549	-0.032197
H	6.246601	-1.586570	-0.387294	0.181917	-0.004745
H	6.041436	0.045747	0.265690	0.170249	0.001704
H	5.380115	-1.338556	1.142066	0.164687	0.008116
C	3.587623	-3.061612	0.302030	-0.392496	-0.057704
H	2.855403	-3.857148	0.161727	0.192615	0.010965
H	4.581303	-3.506949	0.375977	0.177809	-0.011166
H	3.362315	-2.548622	1.238929	0.158116	0.003832
C	4.503678	0.021922	-1.904825	-0.333530	-0.068784
H	4.839747	1.024975	-1.640298	0.181173	0.005380
H	5.266023	-0.450073	-2.527465	0.176858	-0.013360
H	3.582697	0.108553	-2.484147	0.137849	0.001540
C	3.862943	-2.804842	-2.168148	-0.555339	-0.036921
H	3.289422	-3.728439	-2.256474	0.176082	0.005031
H	3.645601	-2.182164	-3.034380	0.170387	0.008080
H	4.925641	-3.059091	-2.171823	0.182475	-0.008734
B	2.053655	-0.492592	-0.155492	1.498350	1.808546
H	1.330023	-0.653186	0.899174	-0.116817	-0.648622
C	1.838271	3.575784	3.009638	-0.297377	0.000581

C	2.403263	2.372832	3.418263	-0.299328	-0.057351
C	1.846172	1.173838	3.005470	-0.165074	0.002318
C	0.723340	1.178204	2.184220	0.626617	-0.238549
C	0.156941	2.381002	1.773488	-0.124874	-0.028583
C	0.716379	3.579991	2.189069	-0.165853	-0.071582
H	2.274045	4.512866	3.333008	0.180504	0.041154
H	3.280489	2.372637	4.052030	0.187789	0.043785
H	2.293127	0.229781	3.296618	0.176071	0.056916
H	-0.723706	2.358418	1.142234	0.101756	0.070582
H	0.275142	4.519059	1.879321	0.187983	0.041187
C	0.123694	-0.099093	1.740612	-0.463674	1.418294
O	-0.872491	-0.067560	0.967522	-0.516243	-1.182363
H	0.270411	-0.982590	2.369958	0.270125	-0.054333
O	-2.447997	-1.805315	1.737593	-0.551405	-0.967161
C	-3.797395	-1.844371	1.278314	0.476540	0.509383
C	-3.751093	-0.936119	0.011047	-0.455425	0.451992
O	-2.448094	-1.220345	-0.504738	-0.505488	-0.938669
C	-4.781664	-1.274090	-1.053622	-0.652481	-0.013576
H	-5.794611	-1.207012	-0.649036	0.183571	-0.008360
H	-4.701127	-0.562782	-1.879448	0.117724	-0.018470
H	-4.622658	-2.277355	-1.446019	0.179422	0.005960
C	-4.135712	-3.293426	0.929563	-0.390567	-0.056214
H	-3.946130	-3.912777	1.806914	0.183250	-0.002455
H	-5.182507	-3.408297	0.639829	0.155118	-0.016608
H	-3.499971	-3.646604	0.116114	0.156600	0.010469
C	-3.846050	0.549774	0.367878	-0.449530	-0.042802
H	-3.567951	1.142670	-0.505992	0.180902	-0.016830
H	-4.863082	0.819928	0.660318	0.191905	-0.020380
H	-3.167154	0.800293	1.182865	0.173345	0.016526
C	-4.720780	-1.345701	2.377832	-0.624813	-0.030125
H	-4.706148	-2.050449	3.210659	0.176778	-0.006144
H	-4.400172	-0.373802	2.749515	0.159503	0.002976
H	-5.748895	-1.266395	2.014720	0.164489	-0.009102
B	-1.612512	-1.503908	0.620914	1.496751	1.412003
H	-0.661636	-2.222094	0.403660	-0.109807	-0.266132

ωB97XD/6-311++G(2d,p), gas phase

Electronic energy: -1514.836571

Electronic energy + zero-point energy: -1514.228730

Electronic energy + thermal energy correction: -1514.186674

Electronic energy + thermal enthalpy correction: -1514.185619

Electronic energy + thermal free energy correction: -1514.309062

Table S151. Cartesian coordinates, Mulliken and APT charges of all atoms at **Transition state** in the catalyst-free reaction of benzaldehyde with pinacolborane (ωB97XD//6-311++G(2d,p), tetramolecular, gas phase).

Symbol	X	Y	Z	Mulliken	APT
C	-2.265930	3.557045	-2.865148	-0.243581	0.092127
C	-2.620937	2.227883	-3.046554	-0.408150	-0.118670
C	-1.797092	1.224167	-2.565286	-0.267157	0.075527
C	-0.613089	1.563690	-1.911144	0.542669	-0.426741
C	-0.256702	2.903368	-1.727406	-0.294102	0.057883
C	-1.087304	3.896864	-2.204291	-0.280255	-0.144115
H	-2.914756	4.341338	-3.237647	0.192711	0.042288
H	-3.545105	1.975136	-3.551122	0.195815	0.048129
H	-2.077763	0.180413	-2.643019	0.225686	0.111441
H	0.664073	3.141688	-1.208986	0.239860	0.074143
H	-0.824157	4.938314	-2.067007	0.193001	0.042794
C	0.230975	0.498853	-1.423879	-0.143267	1.123604
O	1.313099	0.742562	-0.858370	-0.588239	-0.985940
H	-0.059524	-0.539126	-1.601078	0.201207	0.086768
O	2.184342	-1.525298	-1.067245	-0.691479	-1.112357
C	3.516366	-2.040983	-0.956634	0.191022	0.558156
C	4.332464	-0.759827	-0.575052	-0.016906	0.543757
O	3.390999	-0.024207	0.219086	-0.660787	-1.074396
C	5.575712	-1.026075	0.255715	-0.638903	-0.015134
H	6.267661	-1.677221	-0.285244	0.176580	-0.012480
H	6.087230	-0.084725	0.465417	0.167875	-0.005127
H	5.323769	-1.494581	1.206363	0.169657	0.003300
C	3.522718	-3.094834	0.150222	-0.423636	-0.042339
H	2.766213	-3.846746	-0.079241	0.197416	0.006130
H	4.493332	-3.589161	0.229859	0.179347	-0.018456
H	3.277710	-2.650605	1.117054	0.154870	-0.000582
C	4.689284	0.092659	-1.792359	-0.406998	-0.052331
H	5.056234	1.060270	-1.446037	0.180464	-0.000242
H	5.467601	-0.376791	-2.398167	0.171552	-0.022268
H	3.814683	0.265034	-2.422530	0.137362	-0.002031
C	3.910550	-2.674200	-2.279693	-0.621661	-0.020423
H	3.299031	-3.560202	-2.459819	0.173698	-0.001115
H	3.762786	-1.984333	-3.109824	0.173366	0.002885
H	4.959517	-2.981736	-2.259919	0.182460	-0.016117
B	2.115423	-0.425019	-0.193411	1.906629	1.812099
H	1.341816	-0.616959	0.825432	-0.150209	-0.651820
C	1.505597	3.351805	3.403753	-0.196396	0.004602

C	2.067795	2.128951	3.747676	-0.352786	-0.048553
C	1.592192	0.964623	3.170154	-0.235235	0.003238
C	0.553818	1.020481	2.247481	0.688570	-0.245064
C	-0.010184	2.244060	1.904555	-0.193406	-0.027751
C	0.466638	3.408512	2.484142	-0.257465	-0.063117
H	1.878591	4.263487	3.855528	0.180360	0.032805
H	2.881417	2.086279	4.461304	0.181006	0.034993
H	2.041367	0.008343	3.415147	0.191516	0.050677
H	-0.824882	2.266945	1.190713	0.163120	0.067236
H	0.024908	4.362737	2.222365	0.181961	0.034676
C	0.047155	-0.222391	1.623900	-0.309477	1.415041
O	-0.891511	-0.149646	0.786774	-0.590928	-1.184642
H	0.187356	-1.159101	2.173652	0.304145	-0.060159
O	-2.364989	-2.062646	1.404800	-0.716042	-0.967331
C	-3.743754	-2.064830	1.044249	0.465174	0.512000
C	-3.793428	-1.051855	-0.149621	-0.113970	0.457649
O	-2.509660	-1.235745	-0.748359	-0.693014	-0.936814
C	-4.861356	-1.348362	-1.191380	-0.634221	0.003505
H	-5.857599	-1.338252	-0.740882	0.180639	-0.014171
H	-4.837390	-0.582491	-1.971062	0.124073	-0.021315
H	-4.697537	-2.317321	-1.661375	0.182295	0.000260
C	-4.110419	-3.487111	0.616509	-0.422152	-0.035906
H	-3.862568	-4.169382	1.431535	0.178967	-0.008137
H	-5.176015	-3.585143	0.394288	0.153017	-0.023607
H	-3.536577	-3.786286	-0.262410	0.157394	0.004773
C	-3.933008	0.400676	0.317373	-0.586018	-0.029768
H	-3.749547	1.064992	-0.529693	0.188262	-0.016165
H	-4.937864	0.599521	0.697588	0.180872	-0.026489
H	-3.208887	0.640085	1.095912	0.181865	0.011125
C	-4.579571	-1.660209	2.249237	-0.665552	-0.011229
H	-4.497689	-2.425280	3.023933	0.167289	-0.011899
H	-4.237283	-0.715390	2.670301	0.163598	-0.003583
H	-5.634494	-1.563749	1.976540	0.164556	-0.015248
B	-1.613934	-1.612667	0.288201	1.508610	1.423937
H	-0.632281	-2.239500	-0.044447	-0.038543	-0.263916

Products

M06-2X/6-311++G(2d,p), gas phase

Electronic energy: -1514.860359

Electronic energy + zero-point energy: -1514.241653

Electronic energy + thermal energy correction: -1514.200025

Electronic energy + thermal enthalpy correction: -1514.198969

Electronic energy + thermal free energy correction: -1514.317112

Table S152. Cartesian coordinates, Mulliken and APT charges of all atoms at **Products** in the catalyst-free reaction of benzaldehyde with pinacolborane (M06-2X//6-311++G(2d,p), tetramolecular, gas phase).

Symbol	X	Y	Z	Mulliken	APT
C	1.842239	-3.699537	1.560797	-0.374408	-0.118200
C	1.676405	-4.479893	0.419225	-0.264204	-0.037977
C	0.780400	-4.090584	-0.565945	-0.296259	-0.110730
C	0.031203	-2.922706	-0.422247	0.887024	0.023146
C	0.195964	-2.150594	0.721232	0.083734	-0.138586
C	1.101380	-2.534647	1.707378	-0.401138	-0.028233
H	2.548589	-3.997274	2.326402	0.227356	0.069402
H	2.253990	-5.388135	0.293863	0.232662	0.067627
H	0.663103	-4.692498	-1.461541	0.243563	0.070678
H	-0.377363	-1.240816	0.848120	-0.074744	0.099248
H	1.228236	-1.915867	2.587639	0.225313	0.072929
C	-0.935900	-2.542506	-1.517227	-1.114365	0.675527
O	-1.370403	-1.195423	-1.416714	-0.491406	-1.310599
H	-1.794540	-3.219631	-1.503789	0.252036	-0.022665
O	-3.366492	-1.819262	-0.203857	-0.461435	-1.211465
C	-4.601103	-1.114859	0.098058	0.295960	0.681500
C	-4.118021	0.368663	0.204398	-0.570410	0.651168
O	-2.984932	0.389661	-0.702317	-0.635702	-1.255218
C	-5.133466	1.396764	-0.250601	-0.875621	-0.040608
H	-6.039428	1.323587	0.355177	0.216726	0.015528
H	-4.719196	2.399134	-0.124034	0.171475	0.000208
H	-5.398936	1.261539	-1.298375	0.188865	0.008869
C	-5.542681	-1.345116	-1.075868	-0.367318	-0.070079
H	-5.686869	-2.418811	-1.205968	0.207833	0.002487
H	-6.515203	-0.885228	-0.893688	0.200282	0.014682
H	-5.130392	-0.936837	-2.001117	0.162114	0.000903
C	-3.594473	0.718933	1.590556	-0.349570	-0.073926
H	-3.106616	1.694953	1.547759	0.184681	0.001363
H	-4.410115	0.773294	2.313439	0.238259	0.015842
H	-2.867886	-0.019006	1.939018	0.217399	-0.000450
C	-5.195433	-1.676050	1.373016	-0.772868	-0.047889
H	-5.522647	-2.703276	1.202559	0.201621	0.003202
H	-4.472294	-1.673492	2.187634	0.183932	0.010347
H	-6.064849	-1.086025	1.671483	0.207858	0.018533
B	-2.534617	-0.901597	-0.789215	2.070058	1.944394
H	-0.870714	1.047977	1.118770	0.180725	-0.009977

C	-0.304964	5.578701	-0.237442	-0.453985	-0.119426
C	-1.333099	4.709783	-0.594889	-0.318343	-0.032154
C	-1.218405	3.351798	-0.336623	-0.051047	-0.134146
C	-0.075450	2.842320	0.282788	0.268007	0.049695
C	0.947929	3.712456	0.638330	-0.041213	-0.140448
C	0.832857	5.076231	0.377994	-0.308645	-0.025047
H	-0.393322	6.639472	-0.438675	0.219137	0.068536
H	-2.224951	5.093730	-1.076182	0.236738	0.063036
H	-2.014677	2.669102	-0.616563	0.107253	0.115569
H	1.837082	3.330825	1.125702	0.186727	0.089552
H	1.637488	5.745111	0.659846	0.229882	0.063014
C	-0.001005	1.356188	0.535281	-0.761417	0.627178
O	1.150025	0.980398	1.275463	-0.521756	-1.303002
H	-0.038129	0.817264	-0.415278	0.131083	0.016260
O	2.401680	0.591293	-0.753001	-0.304264	-1.189637
C	3.647237	-0.094731	-1.042370	-0.579636	0.663562
C	4.443084	0.086289	0.292595	0.255763	0.639922
O	3.383973	0.166532	1.278756	-0.439401	-1.211371
C	5.355826	-1.072720	0.638695	-0.727536	-0.034330
H	6.097587	-1.216736	-0.150184	0.210969	0.014226
H	5.884331	-0.856257	1.568976	0.196349	-0.001533
H	4.793494	-1.997470	0.766942	0.175995	0.007697
C	3.298268	-1.548998	-1.325490	-0.331326	-0.071259
H	2.577834	-1.584519	-2.145131	0.202105	0.002080
H	4.184357	-2.115606	-1.617526	0.237404	0.009872
H	2.851415	-2.020947	-0.448452	0.174630	0.026802
C	5.206817	1.402597	0.349303	-0.281990	-0.060165
H	5.578838	1.549798	1.364526	0.197008	0.001129
H	6.058360	1.394173	-0.332987	0.196811	0.013341
H	4.561244	2.245589	0.092616	0.176598	-0.001312
C	4.295643	0.542896	-2.253954	-0.837441	-0.043096
H	3.685397	0.349908	-3.138211	0.190165	0.002344
H	4.399249	1.620614	-2.133315	0.186968	0.005971
H	5.284712	0.110247	-2.420727	0.220153	0.016778
B	2.264177	0.586028	0.610807	1.720039	1.922336
H	-0.443303	-2.649723	-2.485266	0.208188	-0.022954

ωB97XD/6-311++G(2d,p), gas phase

Electronic energy: -1496.611869

Electronic energy + zero-point energy: -1514.386124

Electronic energy + thermal energy correction: -1514.344152

Electronic energy + thermal enthalpy correction: -1514.343097

Electronic energy + thermal free energy correction: -1514.463347

Table S153. Cartesian coordinates, Mulliken and APT charges of all atoms at **Products** in the catalyst-free reaction of benzaldehyde with pinacolborane (ωB97XD//6-311++G(2d,p), tetramolecular, gas phase).

Symbol	X	Y	Z	Mulliken	APT
C	3.010798	-2.626642	-1.470731	-0.359155	-0.047018
C	2.252164	-2.663925	-2.633022	-0.057952	-0.042187
C	0.892396	-2.923712	-2.561643	-0.195485	-0.039483
C	0.273740	-3.131727	-1.333616	0.648780	-0.064053
C	1.040534	-3.095957	-0.175466	0.162597	-0.052901
C	2.403243	-2.849523	-0.243311	-0.469310	-0.044748
H	4.074828	-2.426386	-1.524462	0.178352	0.038265
H	2.722662	-2.495817	-3.594809	0.181107	0.032266
H	0.298921	-2.953921	-3.469962	0.181952	0.041664
H	0.556503	-3.223980	0.785478	0.228067	0.063791
H	2.987849	-2.816338	0.668843	0.192759	0.034414
C	-1.215730	-3.338813	-1.260077	-1.078708	0.636802
O	-1.928742	-2.104278	-1.285374	-0.637945	-0.991287
H	-1.473700	-3.898673	-0.357565	0.181188	-0.025977
O	-1.713837	-1.845455	1.107203	-0.748393	-0.860115
C	-2.387942	-1.037635	2.092352	-0.049192	0.487567
C	-2.889676	0.199123	1.251558	0.070520	0.440327
O	-2.959667	-0.335375	-0.083124	-0.820431	-0.872619
C	-4.269079	0.707978	1.636565	-0.732843	-0.009380
H	-4.276713	1.046662	2.675765	0.183052	-0.003390
H	-4.528190	1.556168	1.000367	0.167060	-0.000156
H	-5.033090	-0.058186	1.510648	0.159847	-0.002878
C	-3.526050	-1.885167	2.652888	-0.279393	-0.032070
H	-3.108859	-2.804387	3.067640	0.186075	-0.002614
H	-4.062218	-1.360338	3.446064	0.179255	-0.005938
H	-4.238367	-2.157769	1.871754	0.151558	-0.000916
C	-1.902347	1.361483	1.237822	-0.490610	-0.043039
H	-2.218350	2.087266	0.486553	0.260425	0.001962
H	-1.865923	1.856742	2.210789	0.225740	-0.009132
H	-0.903121	1.020744	0.979088	0.118890	0.024012
C	-1.395100	-0.692195	3.188995	-0.752819	-0.020130
H	-1.126832	-1.597525	3.737471	0.167075	-0.007716
H	-0.485116	-0.268005	2.766770	0.124482	0.026378
H	-1.835061	0.015963	3.896100	0.189975	-0.003709
B	-2.161340	-1.444298	-0.124472	2.456346	1.397473
H	-0.241916	-0.354999	-2.713735	0.184685	-0.004461
C	-2.356111	3.883021	-1.977977	-0.330737	-0.029812

C	-2.867944	2.643693	-2.332832	-0.201345	-0.039371
C	-2.027857	1.541879	-2.413905	-0.253424	-0.045105
C	-0.671216	1.669369	-2.146625	0.669325	-0.048233
C	-0.161334	2.918336	-1.799289	0.053627	-0.062790
C	-0.999173	4.019140	-1.711062	-0.221025	-0.040125
H	-3.011895	4.743420	-1.909912	0.166933	0.028956
H	-3.926467	2.529165	-2.534680	0.178054	0.033012
H	-2.434130	0.566298	-2.652728	0.192909	0.062454
H	0.897778	3.017517	-1.586371	0.249737	0.060522
H	-0.594402	4.986943	-1.437879	0.170308	0.027210
C	0.222613	0.457921	-2.156347	-0.858048	0.560418
O	0.405628	-0.032160	-0.829668	-0.961524	-0.967760
H	1.193580	0.685192	-2.603758	0.220954	-0.020178
O	2.409840	1.267657	-0.467509	-0.531517	-0.877693
C	3.346070	1.378282	0.622731	0.029274	0.485833
C	2.472666	0.949770	1.854246	-0.130892	0.471582
O	1.521619	0.048972	1.260092	-0.673180	-0.887745
C	3.229486	0.215300	2.945635	-0.562982	-0.005902
H	4.019574	0.847916	3.358008	0.197347	-0.004945
H	2.543833	-0.044795	3.754018	0.177545	0.002675
H	3.676177	-0.704476	2.570247	0.171774	0.004359
C	4.490768	0.411742	0.338132	-0.254595	-0.030709
H	4.919076	0.650924	-0.636575	0.201915	0.004483
H	5.276317	0.492165	1.092071	0.179000	-0.010881
H	4.134136	-0.618446	0.308344	0.149975	0.005639
C	1.676493	2.108912	2.450581	-0.346251	-0.029679
H	0.951823	1.707975	3.161290	0.196537	0.004440
H	2.324291	2.812960	2.976497	0.197213	-0.011067
H	1.124591	2.649147	1.678117	0.234397	0.006263
C	3.864455	2.804187	0.679003	-0.687710	-0.011062
H	4.462471	3.013083	-0.209755	0.174984	0.000564
H	3.048385	3.524709	0.717647	0.173123	0.004483
H	4.499289	2.945510	1.557347	0.192930	-0.001645
B	1.421484	0.401780	-0.063112	1.553341	1.365386
H	-1.562387	-3.903777	-2.127379	0.174476	-0.042580