

Supporting Information

O,N-HETEROCYCLIC GERMYLENES AS EFFICIENT CATALYSTS FOR  
HYDROBORATION AND CYANOSILYLATION OF BENZALDEHYDE.

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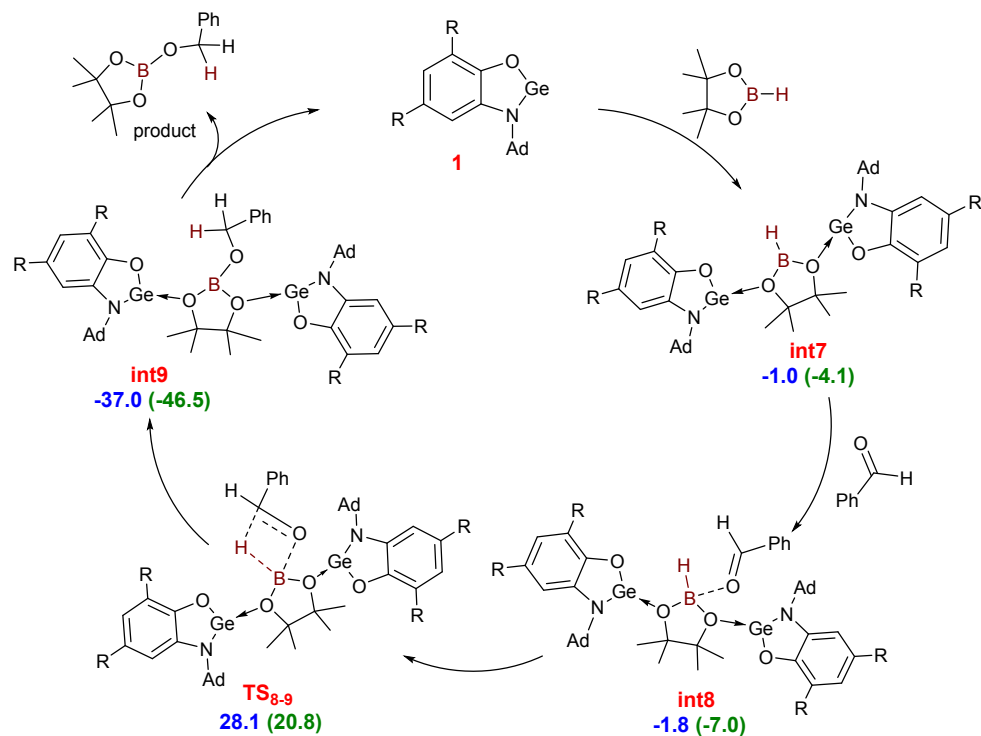
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**Scheme S1. Catalytic cycle and proposed mechanism for hydroboration of benzaldehyde using two molecules of **1** as catalysts.** The DFT B3LYP/def2svp and CAM-B3LYP/def2svp (SMD, solvent – benzene) calculated relative enthalpies ( $\Delta H^{298}$ , kcal/mol) of the intermediates and TS are shown in blue and green, respectively.



**Table S1.** Total energies without ( $E_{\text{total}}$ ), with ( $E_{\text{total}}^{\text{ZPE}}$ ) taking into account for the energies of zero-point harmonic vibrations and total enthalpies ( $H_{\text{total}}^{298}$ ), all values are given in a.u.; relative energies without ( $\Delta E$ ), with ( $\Delta E^{\text{ZPE}}$ ) taking into account for the energies of zero-point harmonic vibrations and relative enthalpies ( $\Delta H^{298}$ ), all values are given in kcal/mol, of reactants, intermediates and transition states for cyanosilylation of benzaldehyde with **1** as catalyst calculated by the DFT B3LYP/def2svp method with inclusion of nonspecific solvation (SMD, solvent – benzene). The DFT CAM-B3LYP/def2svp (SMD, solvent – benzene) data are shown in brackets.

Structure	$E_{\text{total}}$	$\Delta E$	$E_{\text{total}}^{\text{ZPE}}$	$\Delta E^{\text{ZPE}}$	$H_{\text{total}}^{298}$	$\Delta H^{298}$
<b>1</b>	-2906.037040 (-2905.659206)		-2905.659724 (-2905.277274)		-2905.640698 (-2905.258513)	
TMSCN	-501.895293 (-501.752940)		-501.776491 (-501.632991)		-501.766081 (-501.622669)	
PhCHO	-345.334643 (-345.148149)		-345.224558 (-345.036780)		-345.217366 (-345.029637)	
PhCH(CN)OSiMe <sub>3</sub>	-847.254612 (-846.934685)		-847.022382 (-846.699862)		-847.005016 (-846.682670)	
<b>1</b> +TMSCN+PhCHO	-3753.266977 (-3752.560295)	0.0 (0.0)	-3752.660773 (-3751.947045)	0.0 (0.0)	-3752.624145 (-3751.910819)	0.0 (0.0)
<b>int1</b>	-3407.936990 (-3407.419266)		-3407.440458 (-3406.916932)		-3407.409639 (-3406.886523)	
<b>int1</b> +PhCHO	-3753.271633 (-3752.567415)	-2.9 (-4.5)	-3752.665016 (-3751.953712)	-2.7 (-4.2)	-3752.627005 (-3751.916160)	-1.8 (-3.4)
<b>int2</b>	-3753.278444 (-3752.577135)	-7.2 (-10.6)	-3752.670697 (-3751.962214)	-6.2 (-9.5)	-3752.631502 (-3751.923571)	-4.6 (-8.0)
<b>TS<sub>2-3</sub></b>	-3753.227816 (-3752.530357)	24.6 (18.8)	-3752.619827 (-3751.914952)	25.7 (20.1)	-3752.582289 (-3751.878099)	26.3 (20.5)
<b>int3</b>	-3753.296855 (-3752.601766)	-18.7 (-26.0)	-3752.686765 (-3751.984465)	-16.3 (-23.5)	-3752.649011 (-3751.947172)	-15.6 (-22.8)
<b>1</b> +PhCH(CN)OSiMe <sub>3</sub>	-3753.291652 (-3752.593891)	-15.5 (-21.1)	-3752.682106 (-3751.977136)	-13.4 (-18.9)	-3752.645714 (-3751.941183)	-13.5 (-19.1)

**Figure S1. Optimized geometries of reaction intermediates and transition state for cyanosilylation of benzaldehyde with 1 as catalyst calculated by the DFT B3LYP/def2svp (SMD, solvent – benzene) method.** Hereinafter bond lengths are given in Å, the DFT CAM-B3LYP/def2svp (SMD, solvent – benzene) data are shown in brackets.

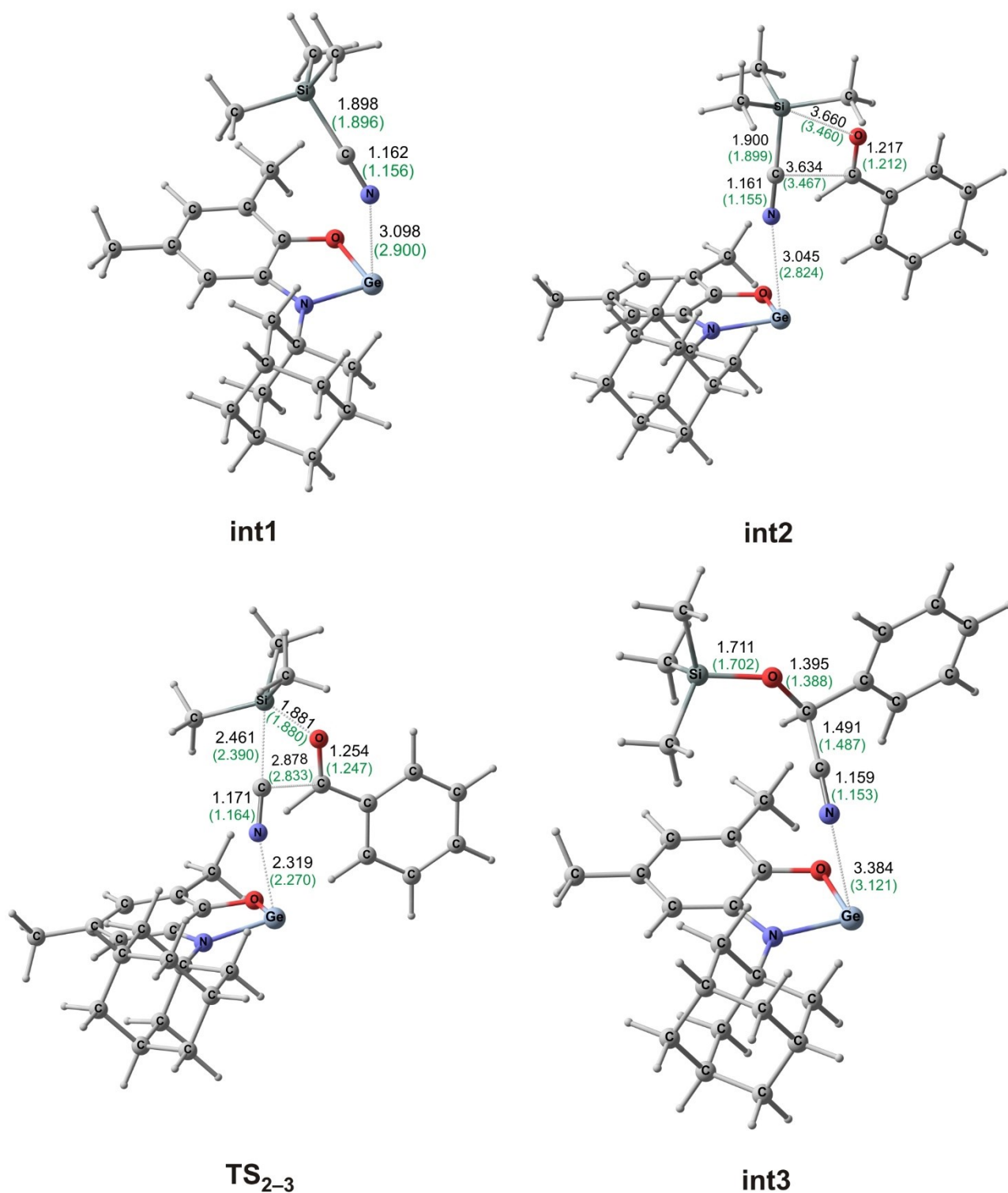
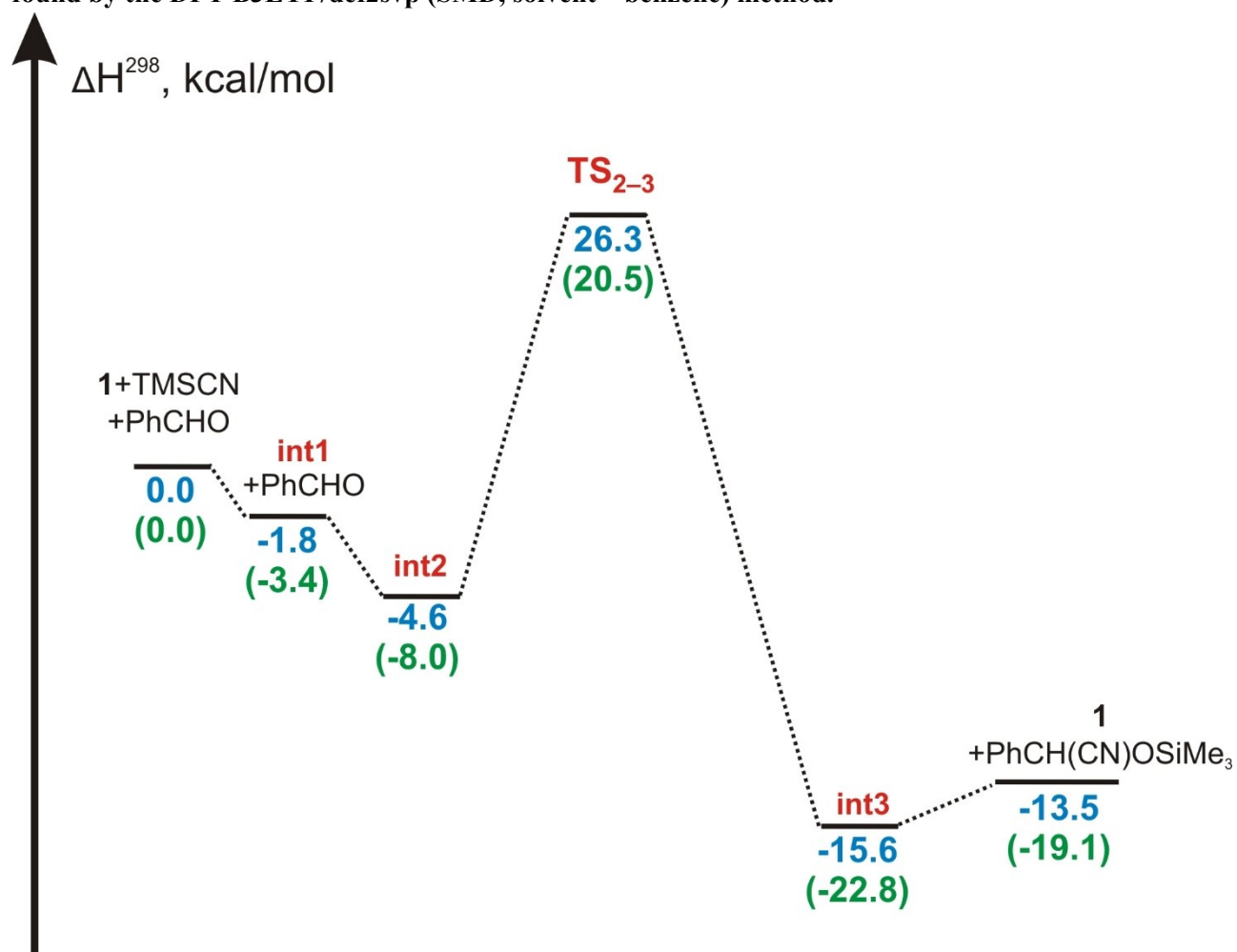


Figure S2. Energy profile of cyanosilylation of benzaldehyde catalyzed by 1, in accordance with path found by the DFT B3LYP/def2svp (SMD, solvent – benzene) method.

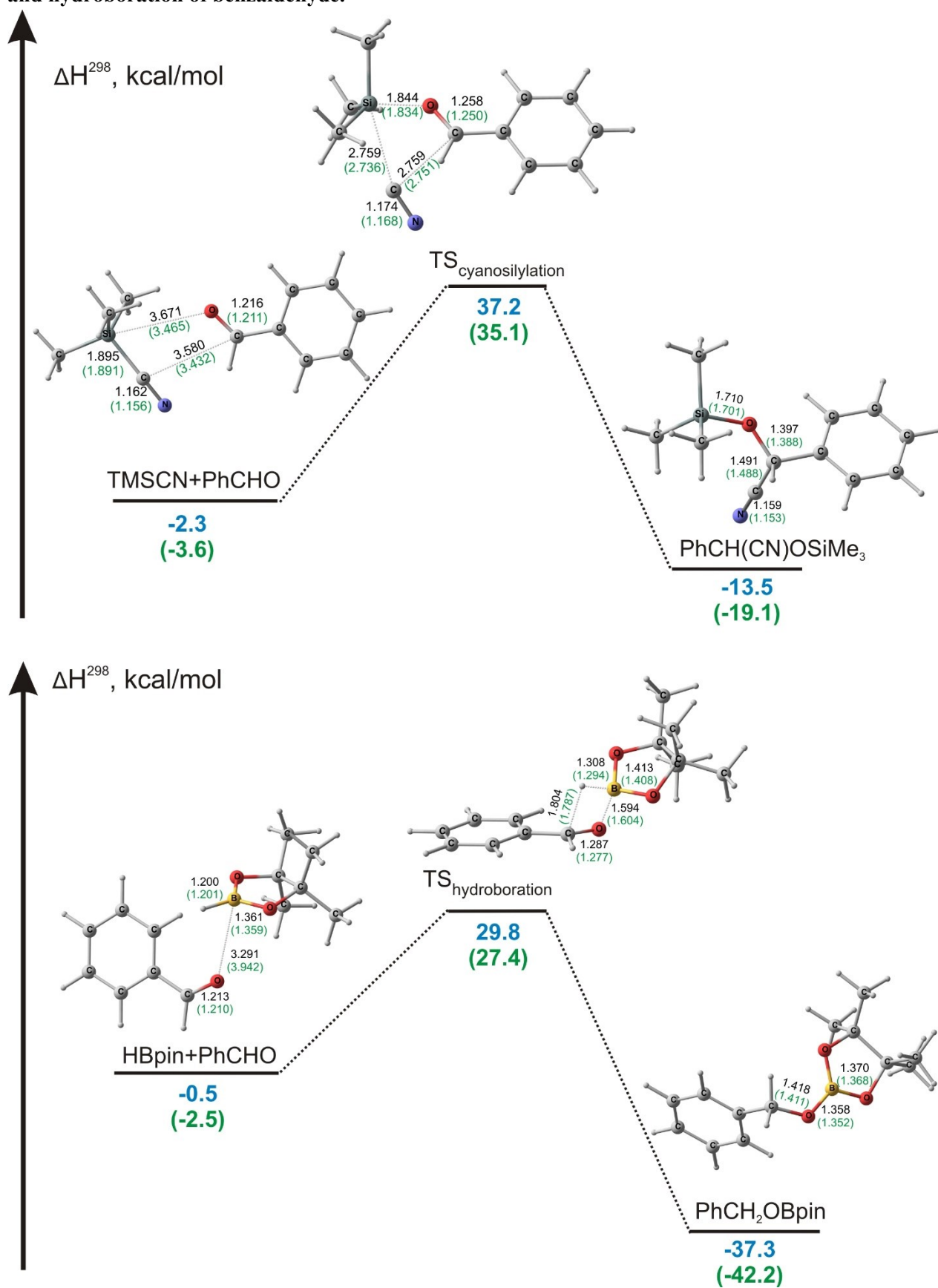




**Table S2.** Total energies without ( $E_{\text{total}}$ ), with ( $E_{\text{total}}^{\text{ZPE}}$ ) taking into account for the energies of zero-point harmonic vibrations and total enthalpies ( $H_{\text{total}}^{298}$ ), all values are given in a.u.; relative energies without ( $\Delta E$ ), with ( $\Delta E^{\text{ZPE}}$ ) taking into account for the energies of zero-point harmonic vibrations and relative enthalpies ( $\Delta H^{298}$ ), all values are given in kcal/mol, of reactants, transition states and products for cyanosilylation and hydroboration of benzaldehyde calculated by the DFT B3LYP/def2svp method with inclusion of nonspecific solvation (SMD, solvent – benzene). The DFT CAM-B3LYP/def2svp (SMD, solvent – benzene) data are shown in brackets.

Structure	$E_{\text{total}}$	$\Delta E$	$E_{\text{total}}^{\text{ZPE}}$	$\Delta E^{\text{ZPE}}$	$H_{\text{total}}^{298}$	$\Delta H^{298}$
Cyanosilylation of benzaldehyde						
TMSCN	-501.895293 (-501.752940)		-501.776491 (-501.632991)		-501.766081 (-501.622669)	
PhCHO	-345.334643 (-345.148149)		-345.224558 (-345.036780)		-345.217366 (-345.029637)	
(TMSCN+PhCHO)	-847.235781 (-846.908995)	-3.7 (-5.0)	-847.006082 (-846.676687)	-3.2 (-4.3)	-846.987174 (-846.658061)	-2.3 (-3.6)
TS <sub>cyanosilylation</sub>	-847.171811 (-846.846317)	36.5 (34.4)	-846.942114 (-846.614188)	37.0 (34.9)	-846.924244 (-846.596441)	37.2 (35.1)
PhCH(CN)OSiMe <sub>3</sub>	-847.254612 (-846.934685)	-15.5 (-21.1)	-847.022382 (-846.699862)	-13.4 (-18.9)	-847.005016 (-846.682670)	-13.5 (-19.1)
Hydroboration of benzaldehyde						
HBpin	-411.575518 (-411.365462)		-411.386133 (-411.174067)		-411.375683 (-411.163733)	
PhCHO	-345.334643 (-345.148149)		-345.224558 (-345.036780)		-345.217366 (-345.029637)	
(HBpin+PhCHO)	-756.913088 (-756.519813)	-1.8 (-3.9)	-756.612828 (-756.216074)	-1.3 (-3.3)	-756.593830 (-756.197330)	-0.5 (-2.5)
TS <sub>hydroboration</sub>	-756.861894 (-756.469329)	30.3 (27.8)	-756.562821 (-756.166856)	30.0 (27.6)	-756.545563 (-756.149714)	29.8 (27.4)
PhCH <sub>2</sub> OBpin	-756.973881 (-756.586327)	-40.0 (-45.6)	-756.669073 (-756.277878)	-36.6 (-42.1)	-756.652415 (-756.260596)	-37.3 (-42.2)

Figure S3. DFT B3LYP/def2svp (SMD, solvent – benzene) computational results on cyanosilylation and hydroboration of benzaldehyde.



**Table S3.** Total energies without ( $E_{\text{total}}$ ), with ( $E_{\text{total}}^{\text{ZPE}}$ ) taking into account for the energies of zero-point harmonic vibrations and total enthalpies ( $H_{\text{total}}^{298}$ ), all values are given in a.u.; relative energies without ( $\Delta E$ ), with ( $\Delta E^{\text{ZPE}}$ ) taking into account for the energies of zero-point harmonic vibrations and relative enthalpies ( $\Delta H^{298}$ ), all values are given in kcal/mol, of reactants, intermediates and transition states for hydroboration of benzaldehyde with **1** as catalyst, calculated by the DFT B3LYP/def2svp method with inclusion of nonspecific solvation (SMD, solvent – benzene). The DFT CAM-B3LYP/def2svp (SMD, solvent – benzene) data are shown in brackets.

Structure	$E_{\text{total}}$	$\Delta E$	$E_{\text{total}}^{\text{ZPE}}$	$\Delta E^{\text{ZPE}}$	$H_{\text{total}}^{298}$	$\Delta H^{298}$
<b>1</b>	-2906.037040 (-2905.659206)		-2905.659724 (-2905.277274)		-2905.640698 (-2905.258513)	
HBpin	-411.575518 (-411.365462)		-411.386133 (-411.174067)		-411.375683 (-411.163733)	
PhCHO	-345.334643 (-345.148149)		-345.224558 (-345.036780)		-345.217366 (-345.029637)	
PhCH <sub>2</sub> OBpin	-756.973881 (-756.586327)		-756.669073 (-756.277878)		-756.652415 (-756.260596)	
Path 1						
<b>1</b> + HBpin +PhCHO	-3662.947202 (-3662.172818)	0.0 (0.0)	-3662.270415 (-3661.488121)	0.0 (0.0)	-3662.233747 (-3661.451883)	0.0 (0.0)
<b>int4</b>	-3317.615541 (-3317.030072)		-3317.048189 (-3316.456423)		-3317.017299 (-3316.425939)	
<b>int4</b> +PhCHO	-3662.950184 (-3662.178221)	-1.9 (-3.4)	-3662.272747 (-3661.493203)	-1.5 (-3.2)	-3662.234665 (-3661.455576)	-0.6 (-2.3)
<b>int5</b>	-3662.953462 (-3662.183385)	-3.9 (-6.6)	-3662.275612 (-3661.497204)	-3.3 (-5.7)	-3662.237101 (-3661.458469)	-2.1 (-4.1)
<b>TS<sub>5-6</sub></b>	-3662.902698 (-3662.136438)	27.9 (22.8)	-3662.226063 (-3661.451349)	27.8 (23.1)	-3662.188351 (-3661.414255)	28.5 (23.6)
<b>int6</b>	-3663.012506 (-3662.252742)	-41.0 (-50.2)	-3662.330072 (-3661.561984)	-37.4 (-46.3)	-3662.291853 (-3661.524514)	-36.5 (-45.6)
<b>1</b> + PhCH <sub>2</sub> OBpin	-3663.010922 (-3662.245525)	-40.0 (-45.6)	-3662.328797 (-3661.555272)	-36.6 (-42.1)	-3662.293113 (-3661.519109)	-37.3 (-42.2)
Path 2						
<b>1+1</b> +HBpin+PhCHO	-6568.984243 (-6567.832024)	0.0 (0.0)	-6567.930139 (-6566.765395)	0.0 (0.0)	-6567.874445 (-6566.710396)	0.0 (0.0)
<b>int7</b>	-6223.655414 (-6222.694252)		-6222.709985 (-6221.738137)		-6222.658719 (-6221.687357)	
<b>int7</b> +PhCHO	-6568.990057 (-6567.842402)	-3.6 (-6.5)	-6567.934543 (-6566.774917)	-2.8 (-6.0)	-6567.876085 (-6566.716994)	-1.0 (-4.1)
<b>int8</b>	-6568.993149 (-6567.848999)	-5.6 (-10.7)	-6567.937329 (-6566.780557)	-4.5 (-9.5)	-6567.877314 (-6566.721475)	-1.8 (-7.0)
<b>TS<sub>8-9</sub></b>	-6568.942902 (-6567.802359)	25.9 (18.6)	-6567.887510 (-6566.734313)	26.8 (19.5)	-6567.829617 (-6566.677303)	28.1 (20.8)
<b>int9</b>	-6569.052726 (-6567.915497)	-43.0 (-52.4)	-6567.992081 (-6566.842214)	-38.9 (-48.2)	-6567.933421 (-6566.784533)	-37.0 (-46.5)
<b>1+1</b> +PhCH <sub>2</sub> OBpin	-6569.047962 (-6567.904731)	-40.0 (-45.6)	-6567.988521 (-6566.832546)	-36.6 (-42.1)	-6567.933811 (-6566.777622)	-37.3 (-42.2)
Path 3						

<b>1</b> + HBpin+PhCHO	-3662.947202 (-3662.172818)	0.0 (0.0)	-3662.270415 (-3661.488121)	0.0 (0.0)	-3662.233747 (-3661.451883)	0.0 (0.0)
<b>int10</b>	-3251.376556 (-3250.817220)		-3250.888390 (-3250.323213)		-3250.860891 (-3250.296131)	
<b>int10</b> +HBpin	-3662.952074 (-3662.182682)	-3.1 (-6.2)	-3662.274523 (-3661.497280)	-2.6 (-5.7)	-3662.236574 (-3661.459864)	-1.8 (-5.0)
<b>int11</b>	-3662.954200 (-3662.184986)	-4.4 (-7.6)	-3662.276269 (-3661.498777)	-3.7 (-6.7)	-3662.237679 (-3661.459950)	-2.5 (-5.1)
<b>TS<sub>11-12</sub></b>	-3662.904431 (-3662.138437)	26.8 (21.6)	-3662.227335 (-3661.453417)	27.0 (21.8)	-3662.189742 (-3661.416240)	27.6 (22.4)
<b>int12</b>	-3663.012044 (-3662.252971)	-40.7 (-50.3)	-3662.328940 (-3661.561826)	-36.7 (-46.3)	-3662.291086 (-3661.524464)	-36.0 (-45.5)
<b>1</b> +PhCH <sub>2</sub> OBpin	-3663.010922 (-3662.245525)	-40.0 (-45.6)	-3662.328797 (-3661.555272)	-36.6 (-42.1)	-3662.293113 (-3661.519109)	-37.3 (-42.2)

**Figure S4. Optimized geometries of reaction intermediates and transition state for hydroboration of benzaldehyde with 1 as catalyst calculated by the DFT B3LYP/def2svp (SMD, solvent – benzene) method.**

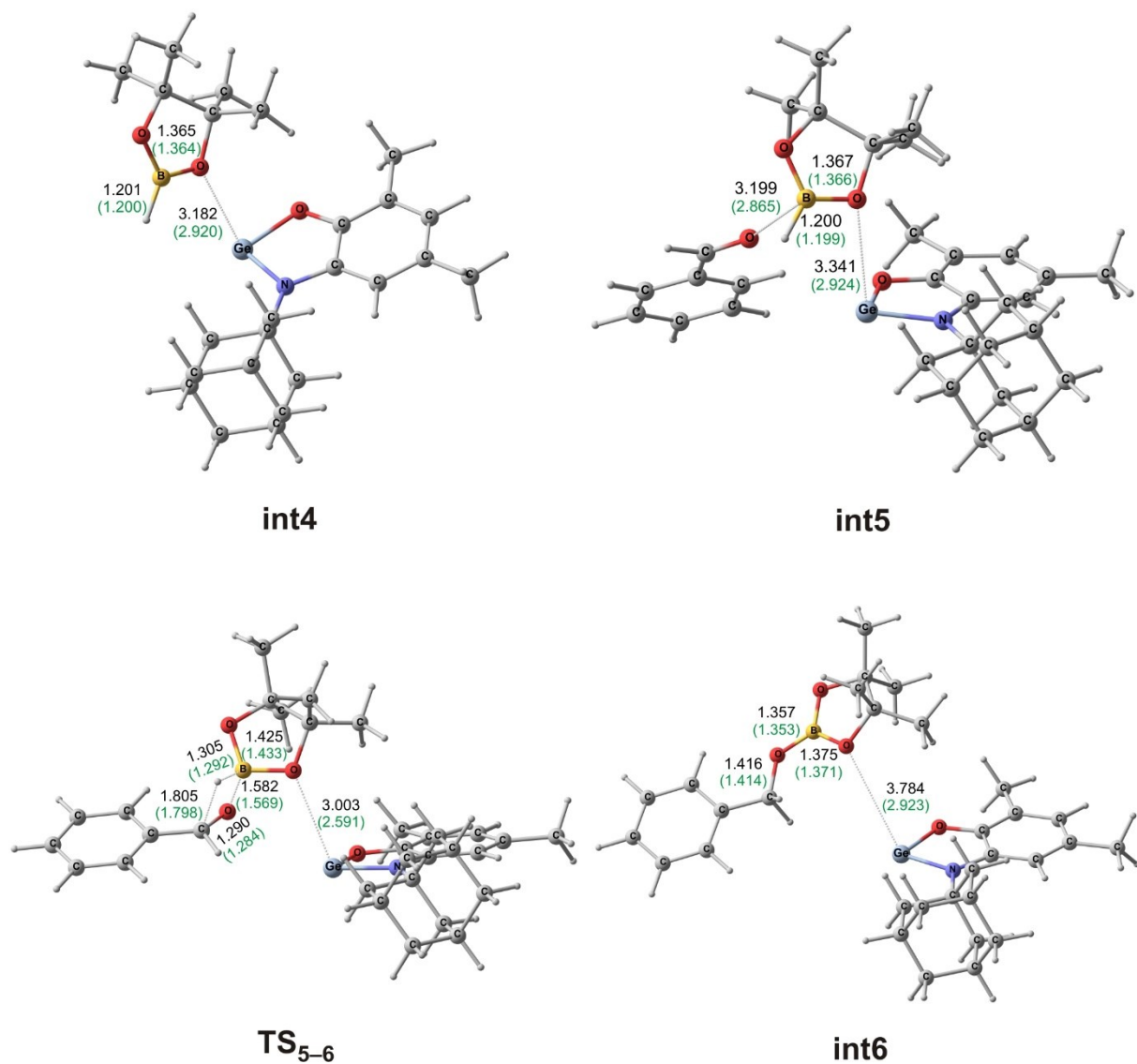
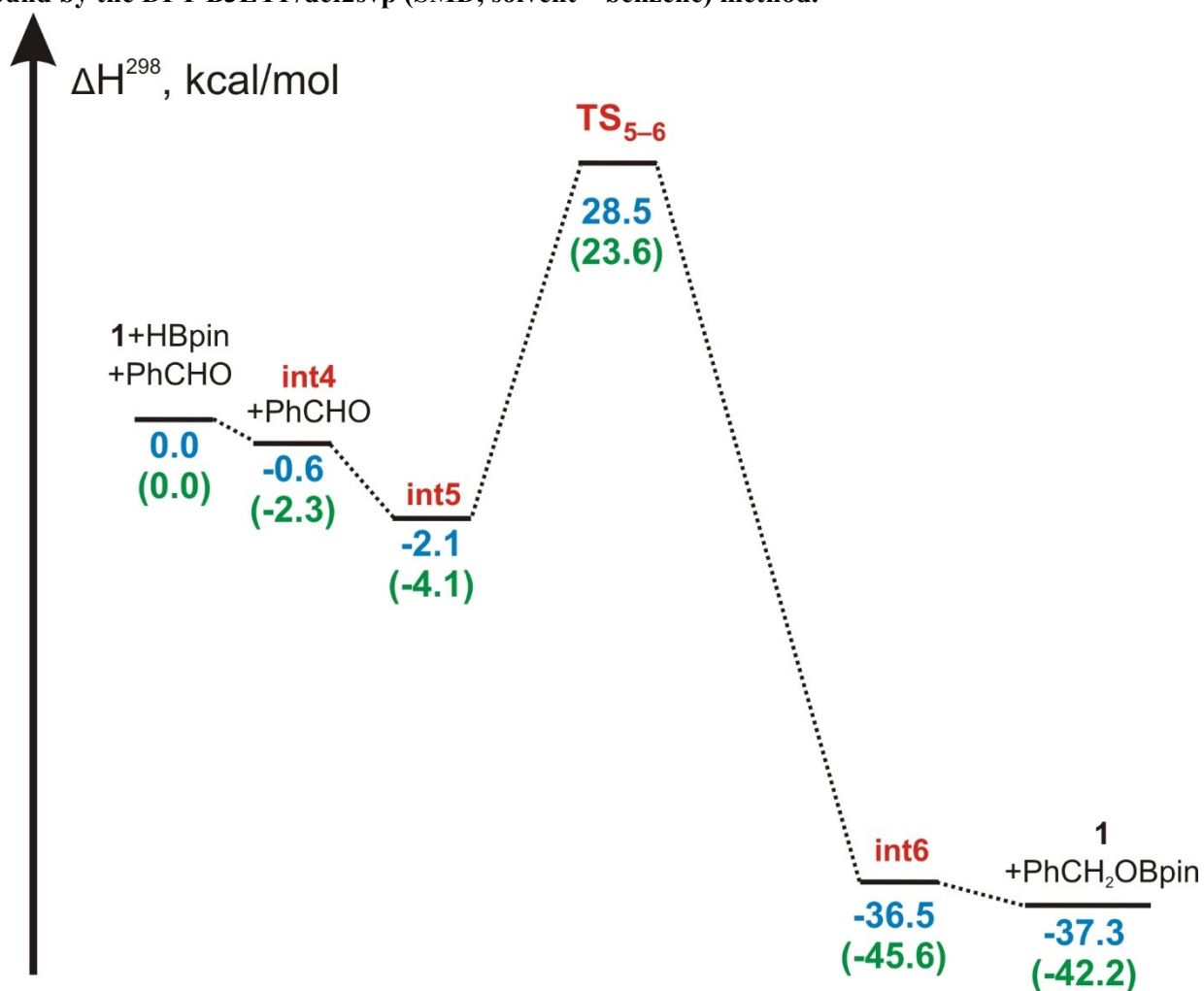
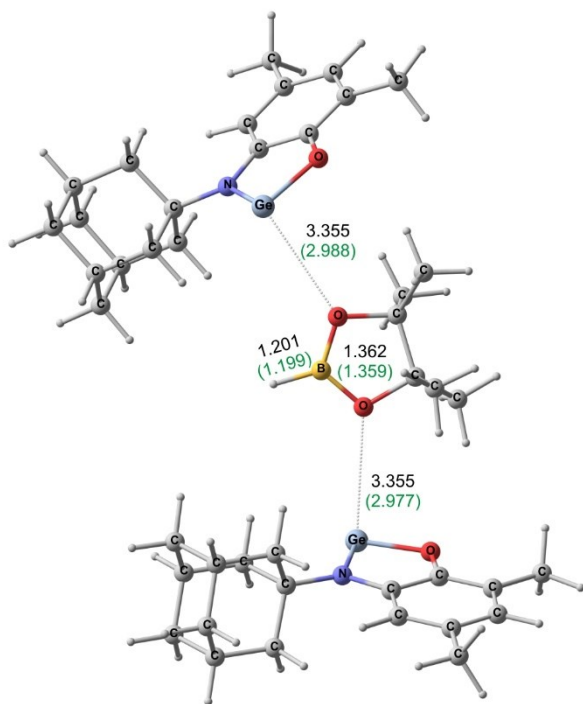


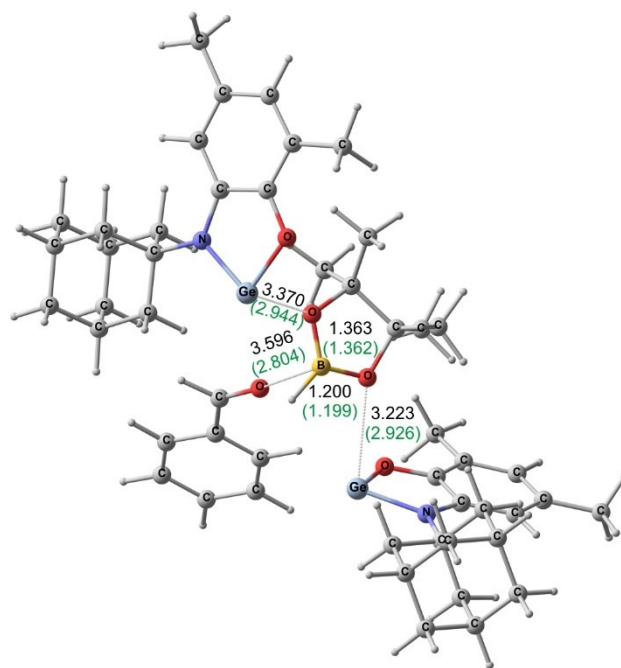
Figure S5. Energy profile of hydroboration of benzaldehyde catalyzed by 1, in accordance with path 1 found by the DFT B3LYP/def2svp (SMD, solvent – benzene) method.



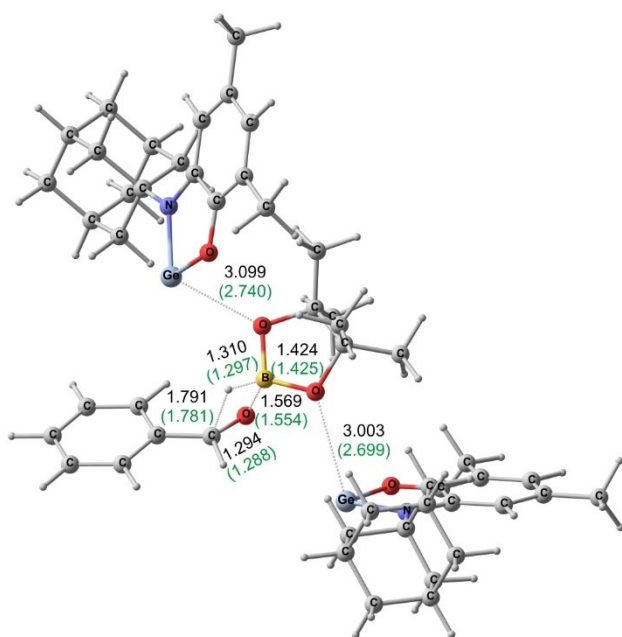
**Figure S6. Optimized geometries of reaction intermediates and transition state for hydroboration of benzaldehyde with 1 as catalyst calculated by the DFT B3LYP/def2svp (SMD, solvent – benzene) method.**



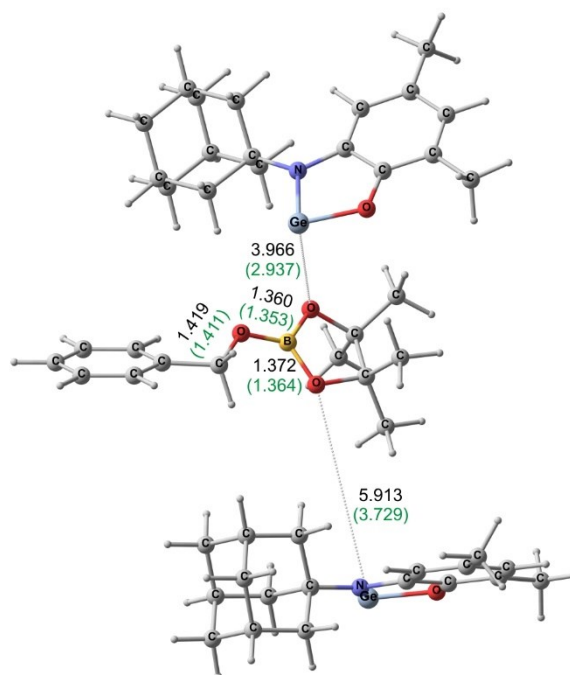
**int7**



**int8**

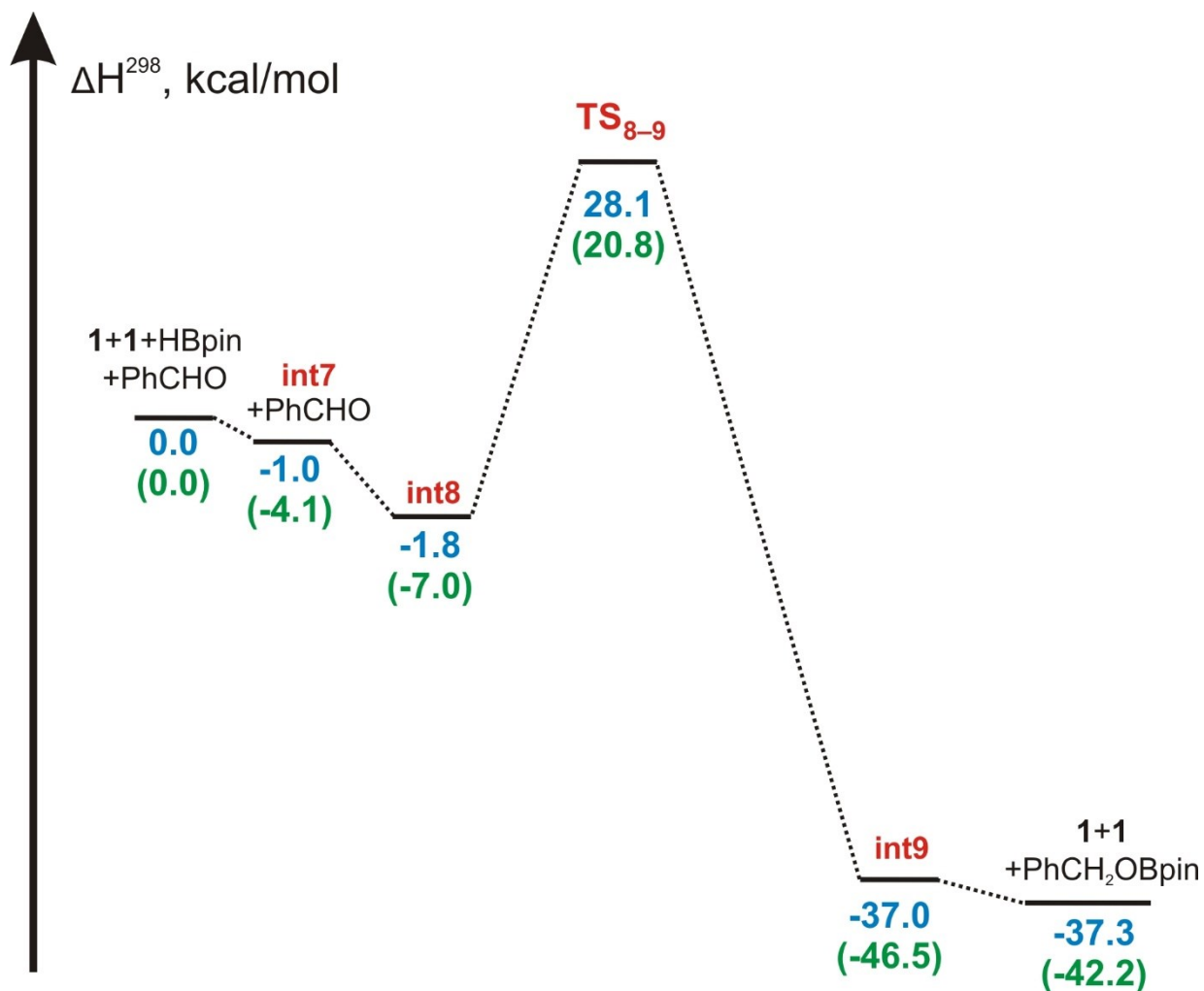


**TS<sub>8-9</sub>**

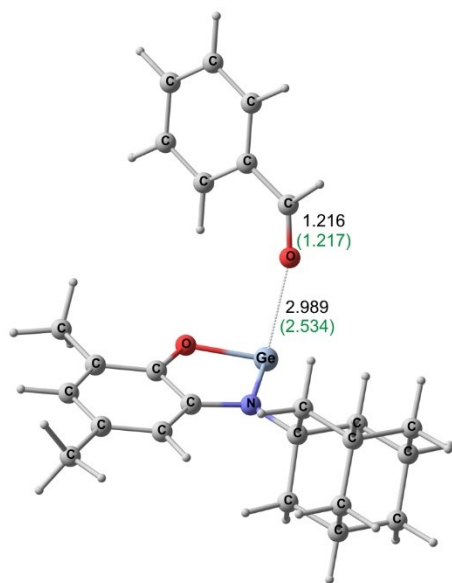


**int9**

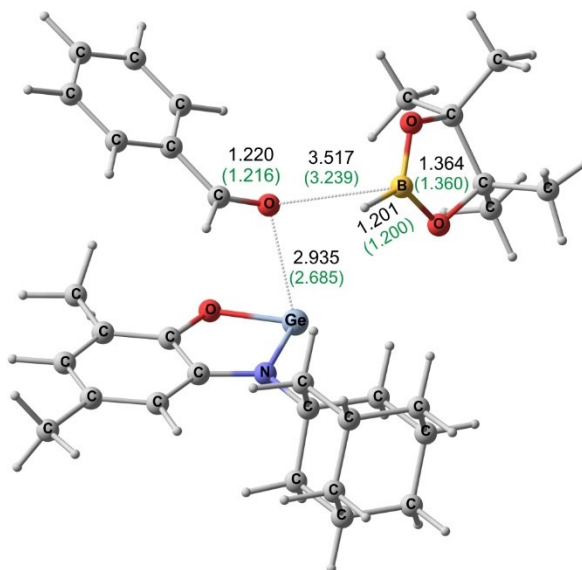
Figure S7. Energy profile of hydroboration of benzaldehyde catalyzed by 1, in accordance with path 2 found by the DFT B3LYP/def2svp (SMD, solvent – benzene) method.



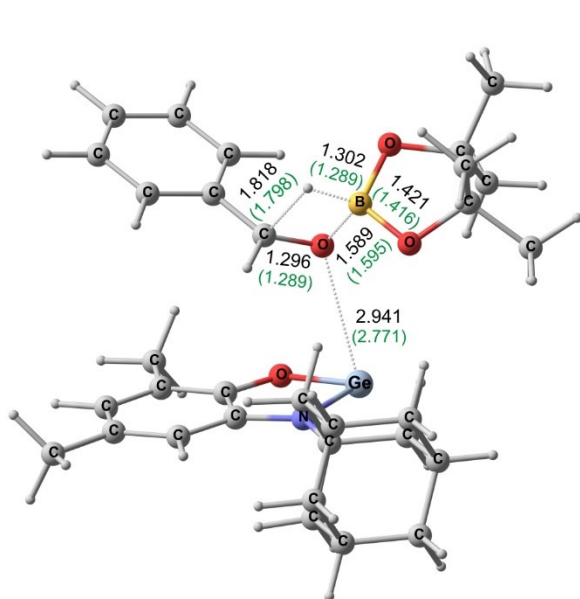
**Figure S8. Optimized geometries of reaction intermediates and transition state for hydroboration of benzaldehyde with 1 as catalyst calculated by the DFT B3LYP/def2svp (SMD, solvent – benzene) method.**



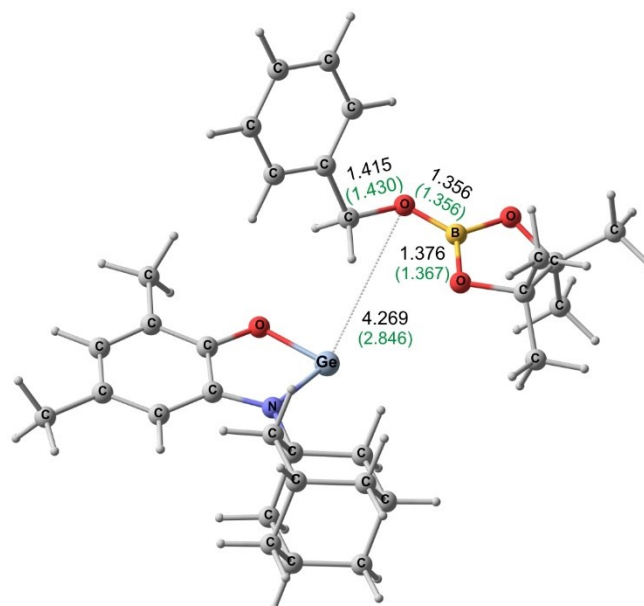
**int10**



**int11**



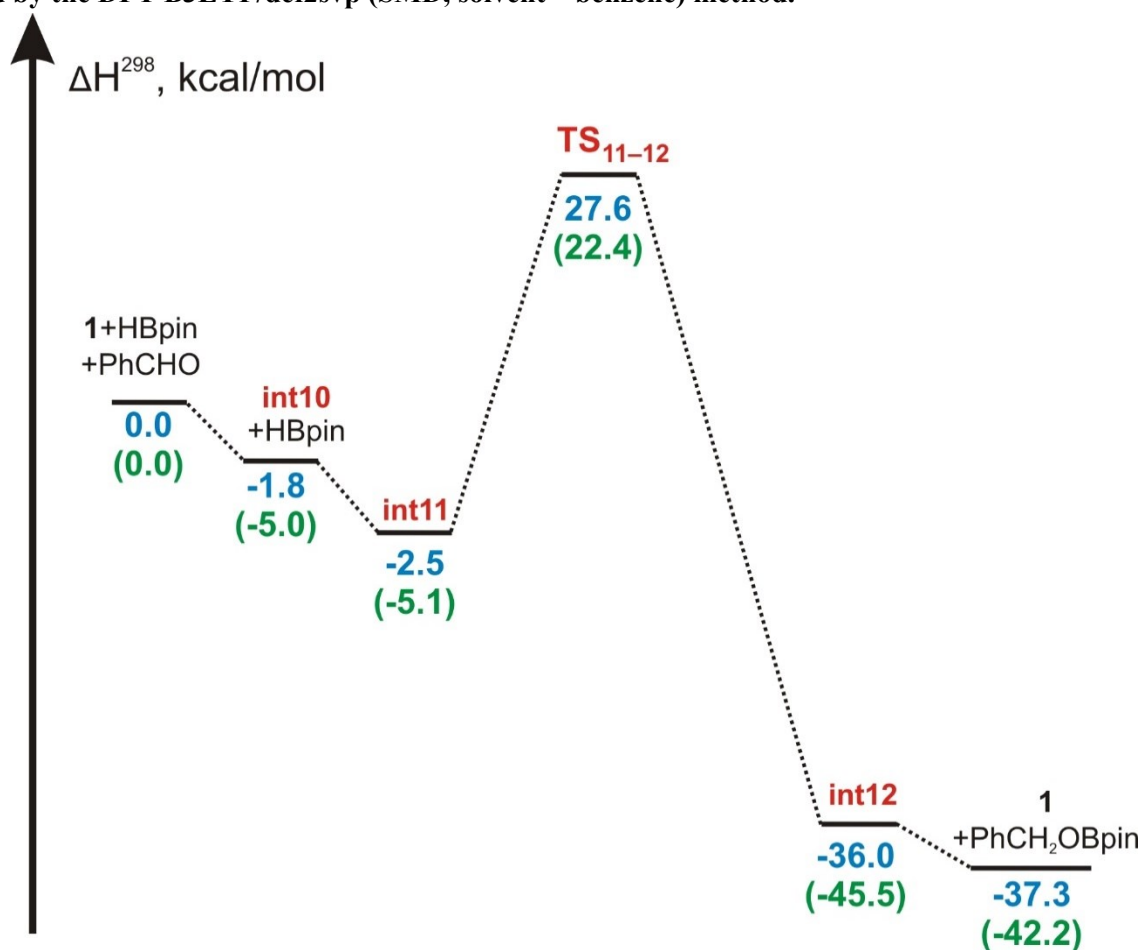
**TS<sub>11-12</sub>**



**int12**



**Figure S9.** Energy profile of hydroboration of benzaldehyde catalyzed by **1**, in accordance with path 3 found by the DFT B3LYP/def2svp (SMD, solvent – benzene) method.



**Table S4.** Total energies without ( $E_{\text{total}}$ ), with ( $E_{\text{total}}^{\text{ZPE}}$ ) taking into account for the energies of zero-point harmonic vibrations and total enthalpies ( $H_{\text{total}}^{298}$ ), all values are given in a.u.; relative energies without ( $\Delta E$ ), with ( $\Delta E^{\text{ZPE}}$ ) taking into account for the energies of zero-point harmonic vibrations and relative enthalpies ( $\Delta H^{298}$ ), all values are given in kcal/mol, of reactant, transition state and product for oxidative addition of HBpin to **1** calculated by the DFT B3LYP/def2svp method with inclusion of nonspecific solvation (SMD, solvent – benzene). The DFT CAM-B3LYP/def2svp (SMD, solvent – benzene) data are shown in brackets.

Structure	$E_{\text{total}}$	$\Delta E$	$E_{\text{total}}^{\text{ZPE}}$	$\Delta E^{\text{ZPE}}$	$H_{\text{total}}^{298}$	$\Delta H^{298}$
<b>1</b> + HBpin	-3317.612559 (-3317.024668)	0.0 (0.0)	-3317.045857 (-3316.451341)	0.0 (0.0)	-3317.016381 (-3316.422246)	0.0 (0.0)
<b>int13</b>	-3317.614419 (-3317.027876)	-1.2 (-2.0)	-3317.047125 (-3316.453982)	-0.8 (-1.7)	-3317.016189 (-3316.424339)	0.0 (-1.3)
<b>TS<sub>13-14</sub></b>	-3317.539644 (-3316.957748)	45.8 (42.0)	-3316.976370 (-3316.387494)	43.6 (40.1)	-3316.946473 (-3316.358043)	43.9 (40.3)
<b>int14</b>	-3317.594082 (-3317.014944)	11.6 (6.1)	-3317.027850 (-3316.442096)	11.3 (5.8)	-3316.997666 (-3316.412221)	11.7 (6.3)

Figure S10. Optimized geometries of reaction intermediates and transition state for oxidative addition of HBpin to 1 calculated by the DFT B3LYP/def2svp (SMD, solvent – benzene) method.

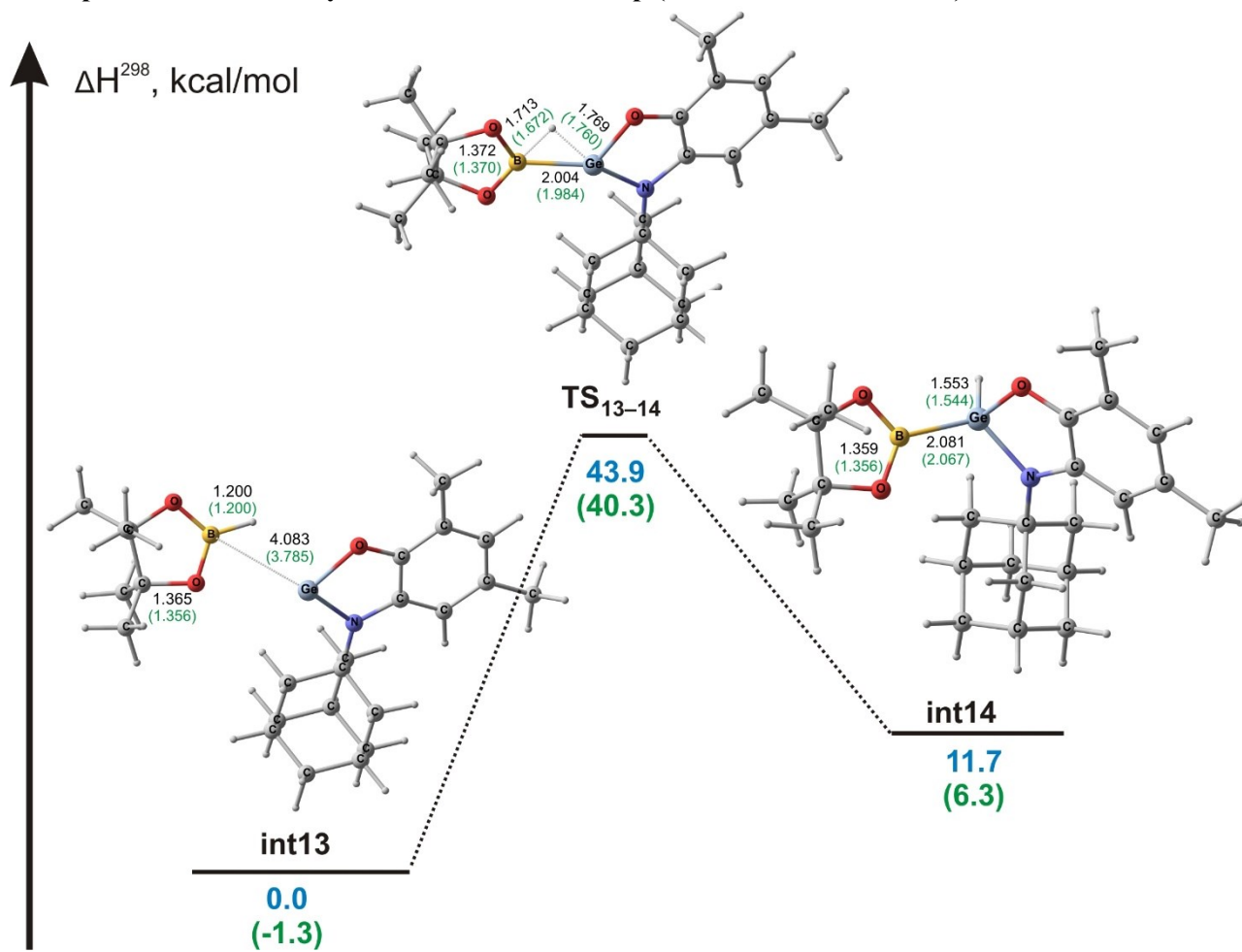


Figure S11.  $^1\text{H}$  NMR spectra of  $^{\text{Ad}}\text{APGe}$  (1) in benzene- $\text{d}_6$ . (\*) indicates signals of Hexane.

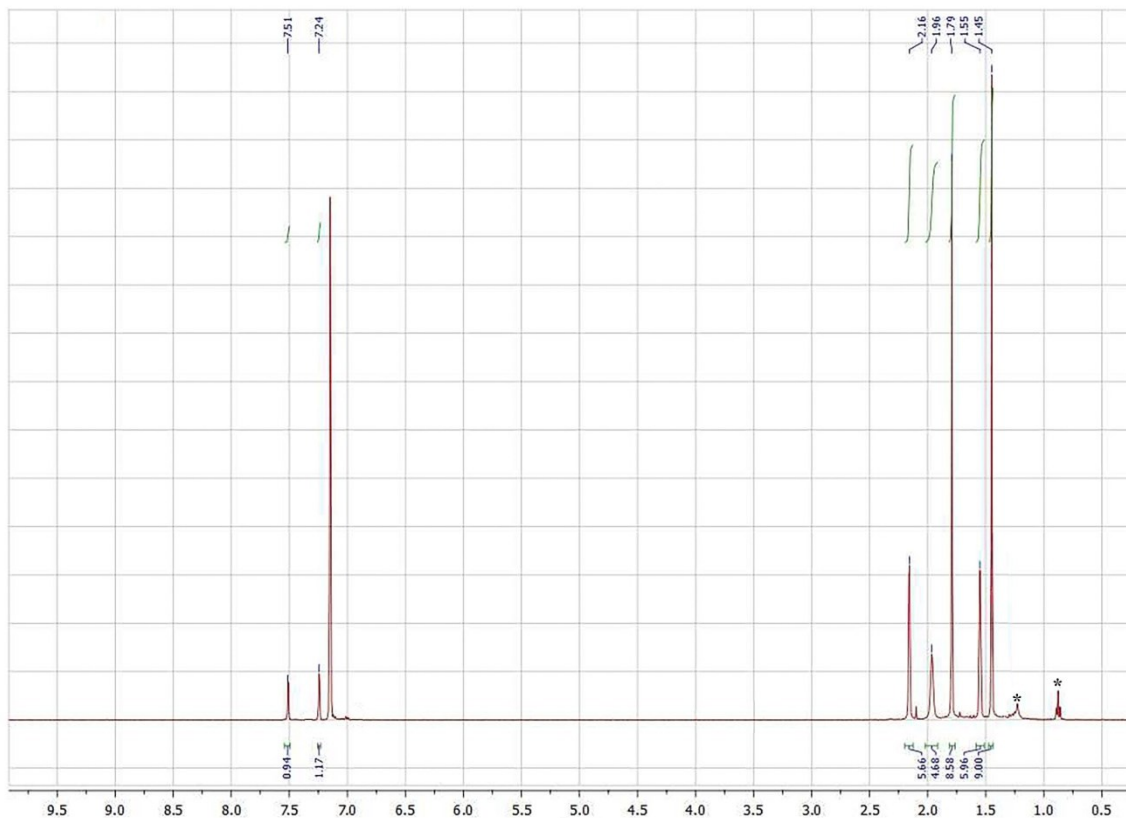
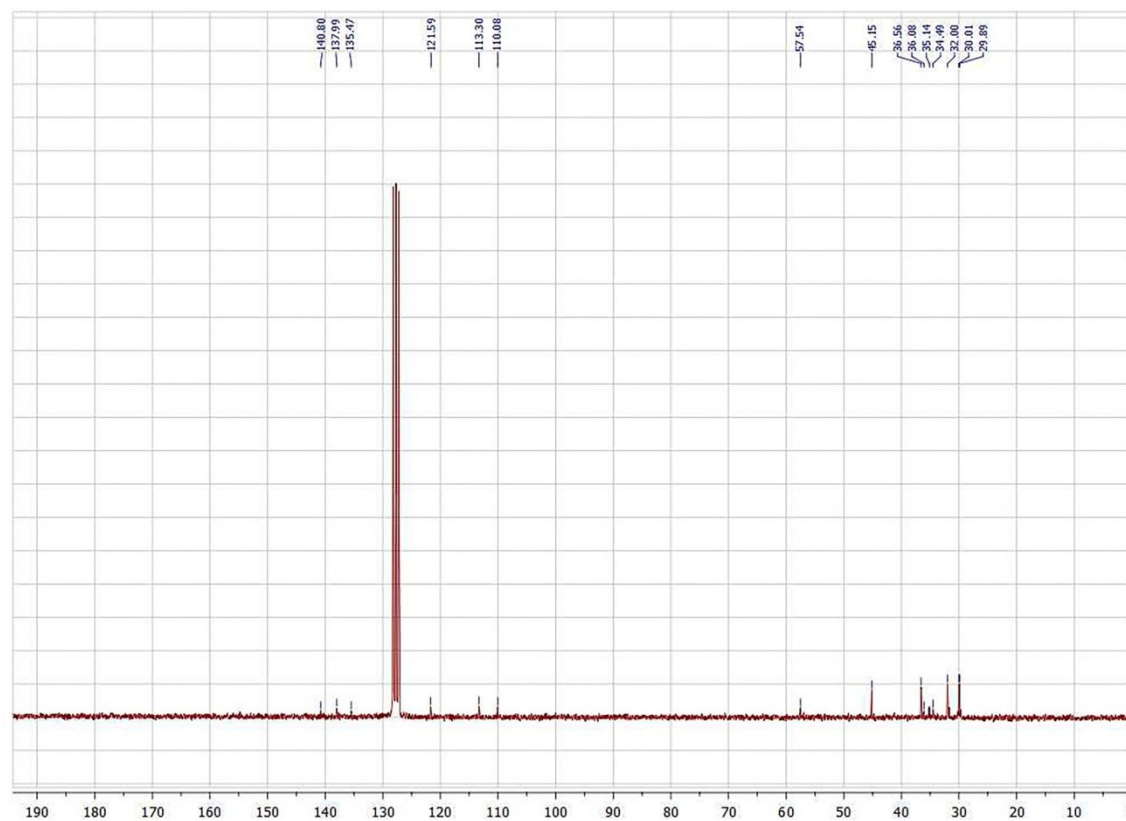
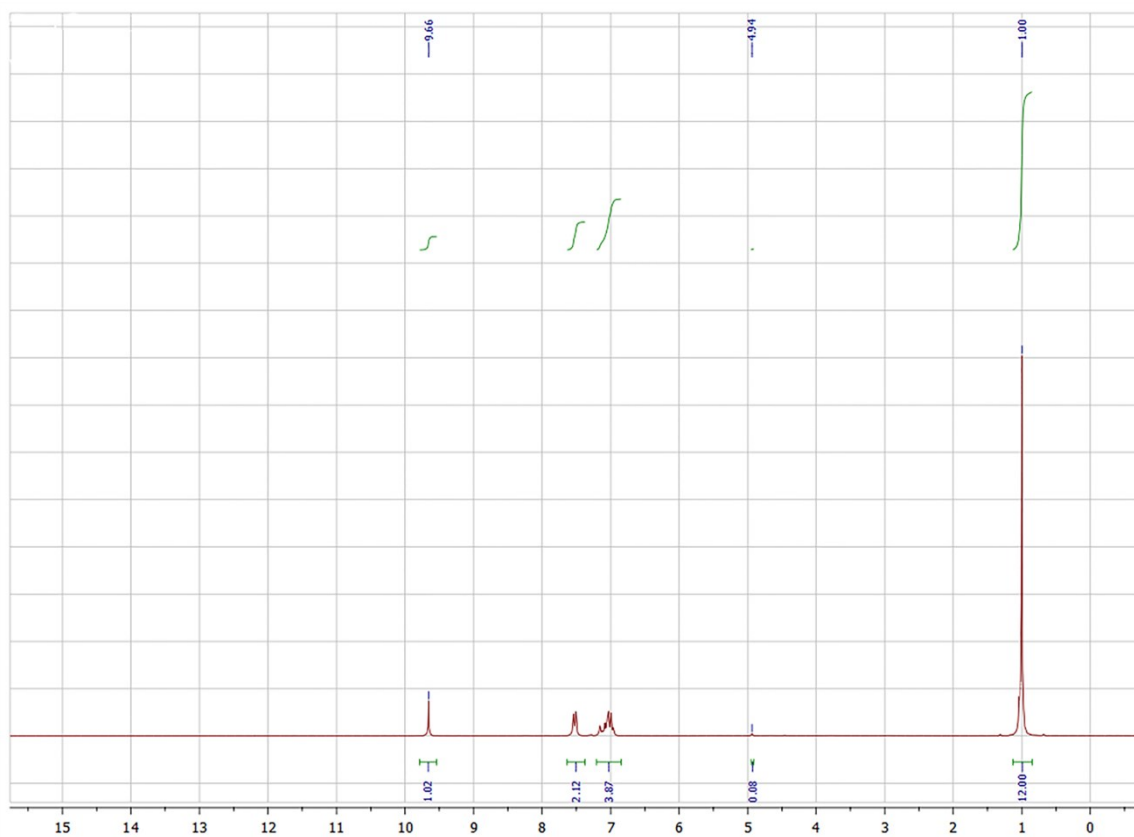


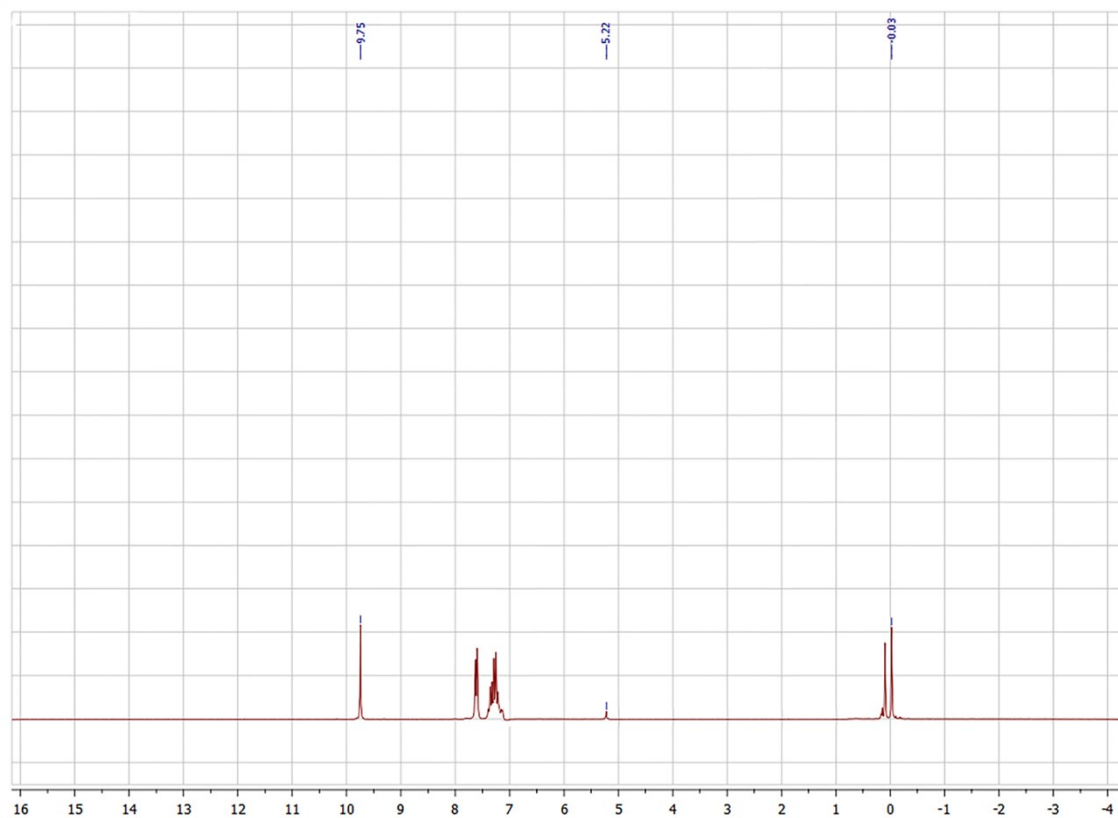
Figure S12.  $^{13}\text{C}$  NMR spectra of  $^{\text{Ad}}\text{APGe}$  (1) in benzene- $\text{d}_6$ .



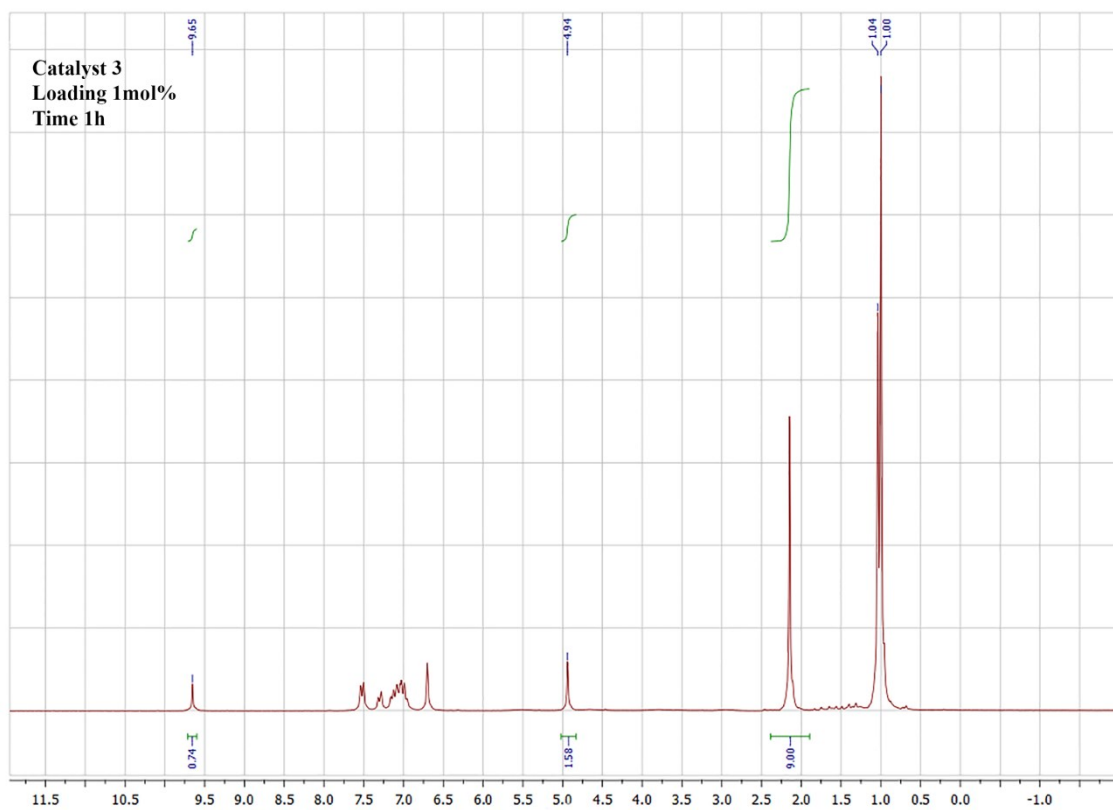
**Figure S13.**  $^1\text{H}$  NMR spectra for Hydroboration of  $\text{C}_6\text{H}_5\text{CHO}$  with HBpin in absence of catalyst in benzene- $\text{d}_6$ .



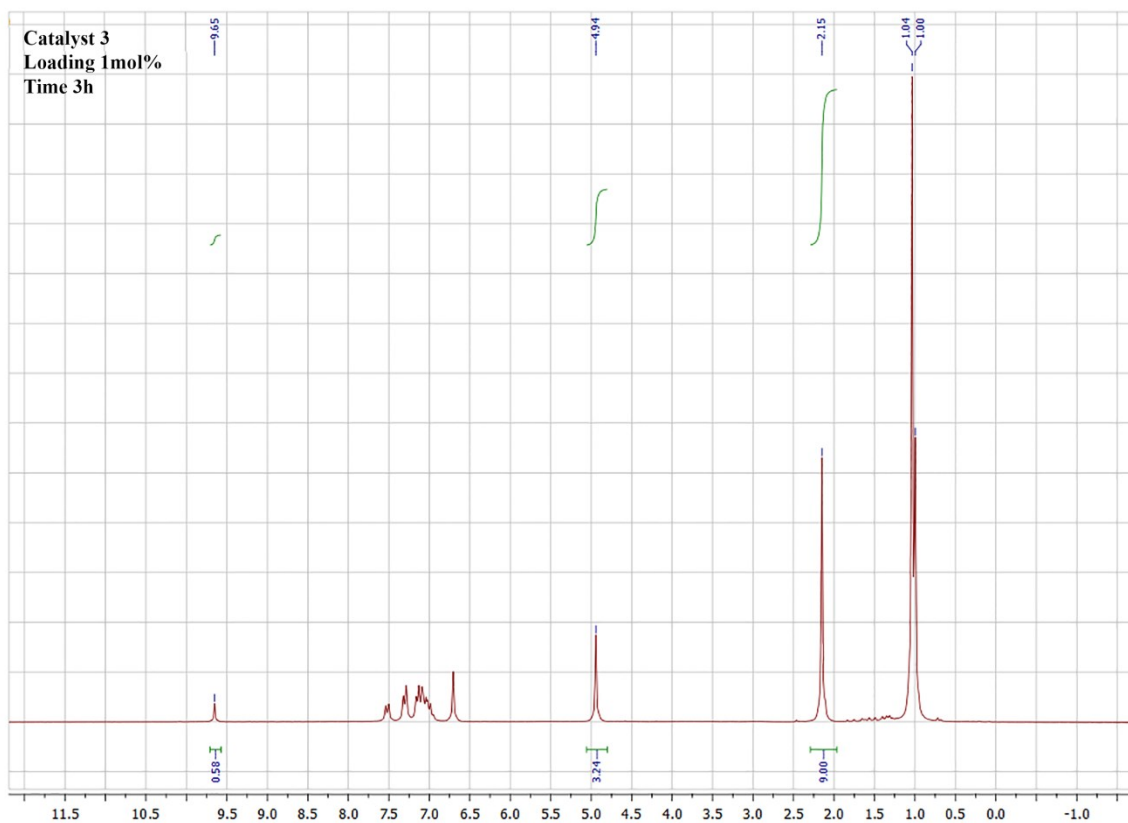
**Figure S14.**  $^1\text{H}$  NMR spectra for Cyanosilylation of  $\text{C}_6\text{H}_5\text{CHO}$  with HBpin in absence of catalyst in benzene- $\text{d}_6$ .



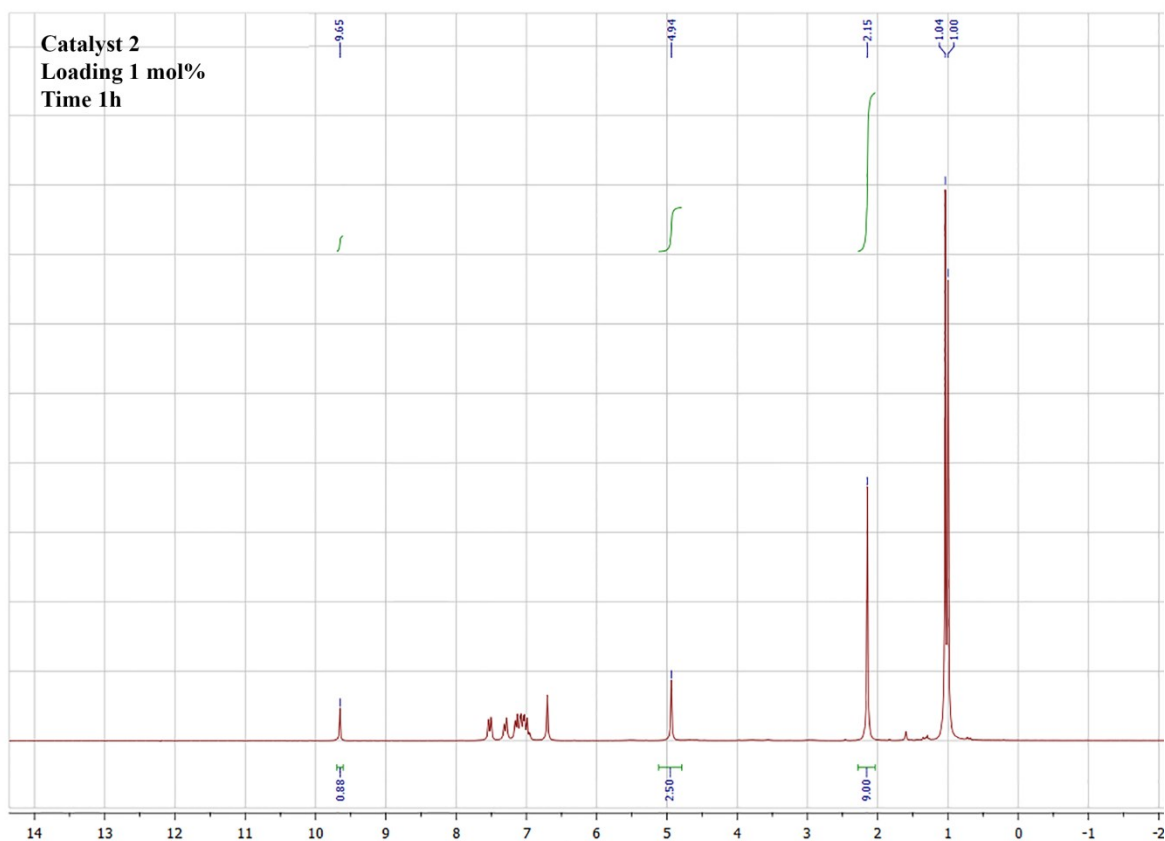
**Figure S15.**  $^1\text{H}$  NMR spectra for Hydroboration of  $\text{C}_6\text{H}_5\text{CHO}$  with HBpin in benzene- $\text{d}_6$  using catalyst (3) loading of 1 mol% for 1 hrs at room temperature.



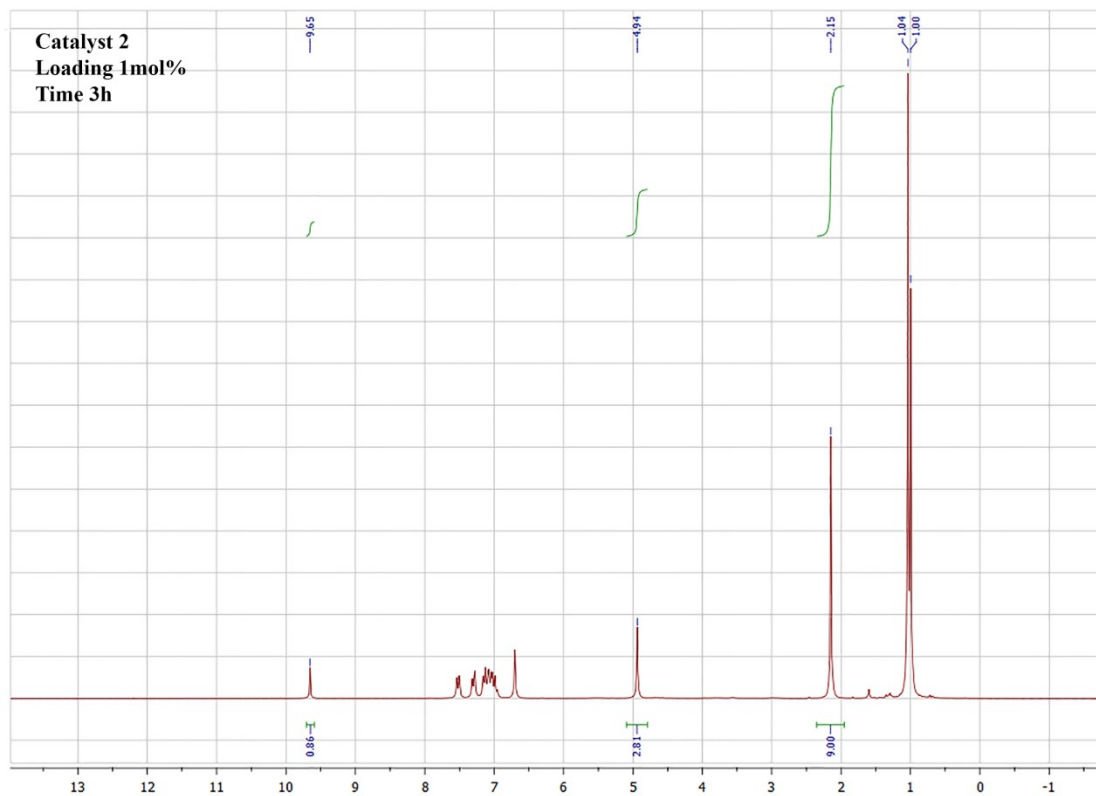
**Figure S16.**  $^1\text{H}$  NMR spectra for Hydroboration of  $\text{C}_6\text{H}_5\text{CHO}$  with HBpin in benzene- $\text{d}_6$  using catalyst (3) loading of 1 mol% for 3 hrs at room temperature.



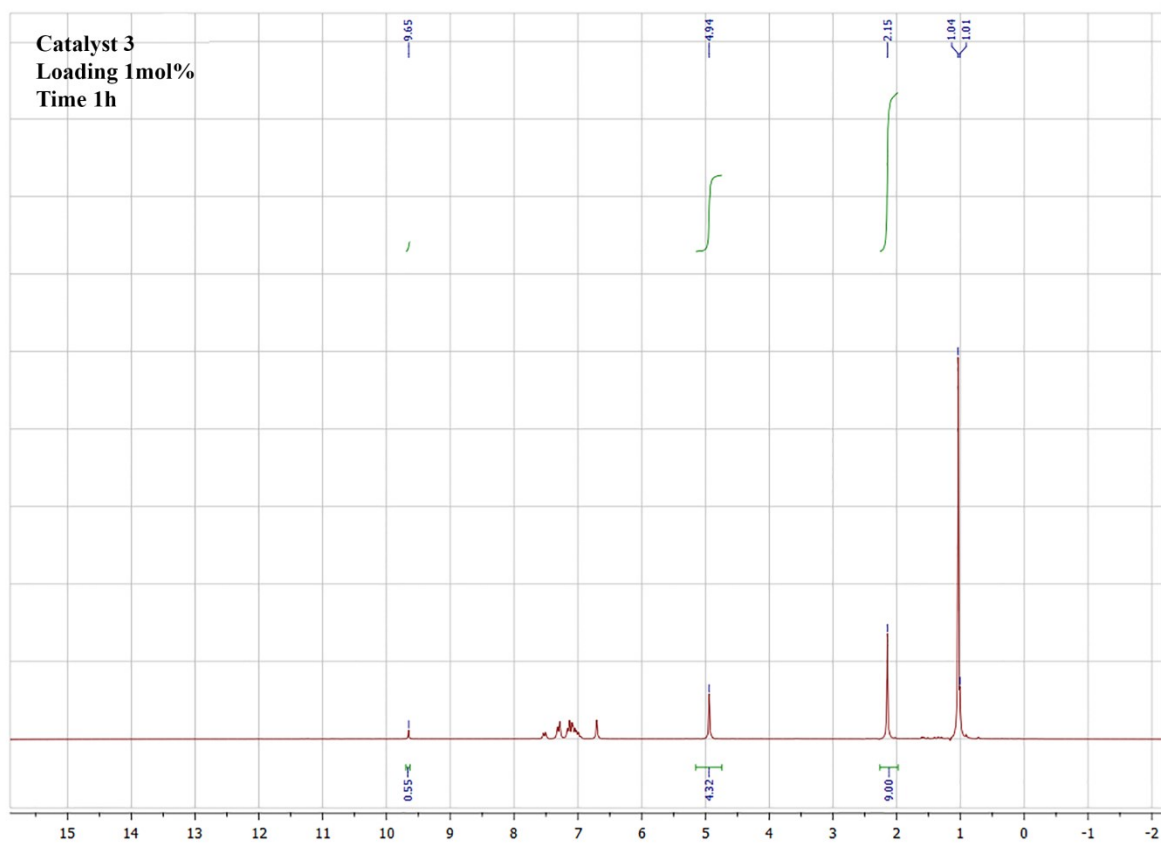
**Figure S17.**  $^1\text{H}$  NMR spectra for Hydroboration of  $\text{C}_6\text{H}_5\text{CHO}$  with HBpin in benzene- $\text{d}_6$  using catalyst (2) loading of 1 mol% for 1 hrs at room temperature.



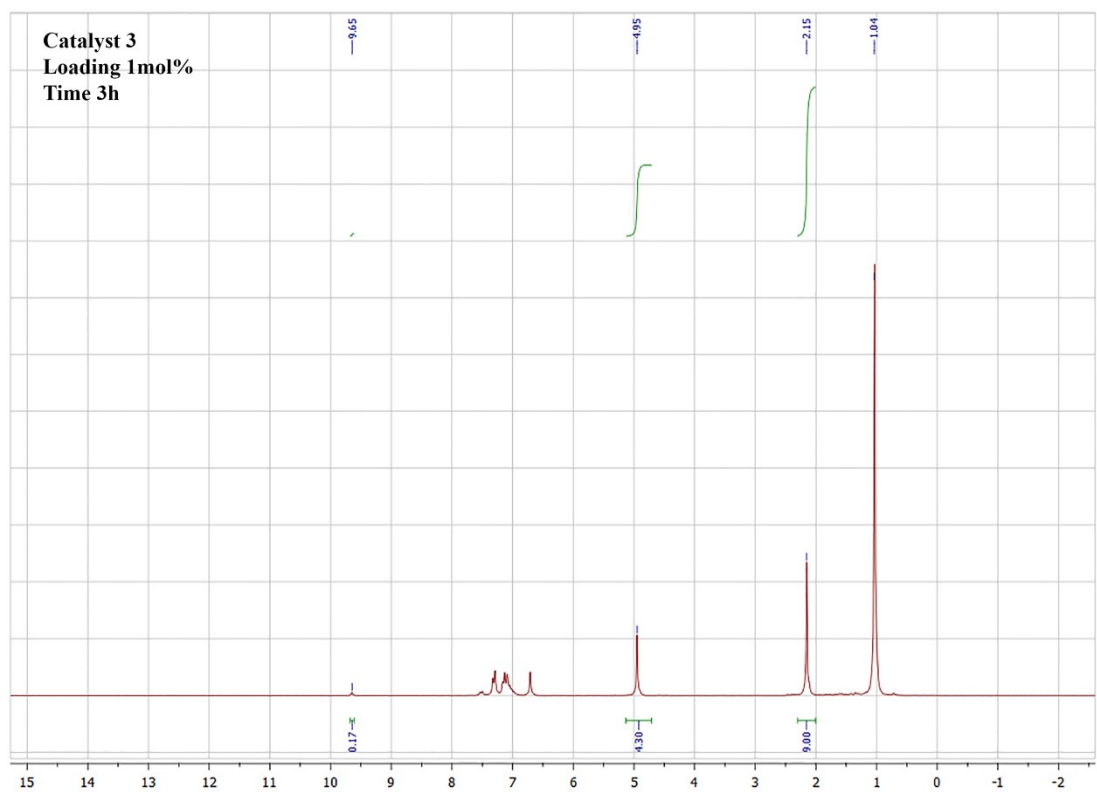
**Figure S18.**  $^1\text{H}$  NMR spectra for Hydroboration of  $\text{C}_6\text{H}_5\text{CHO}$  with HBpin in benzene- $\text{d}_6$  using catalyst (2) loading of 1 mol% for 3 hrs at room temperature.



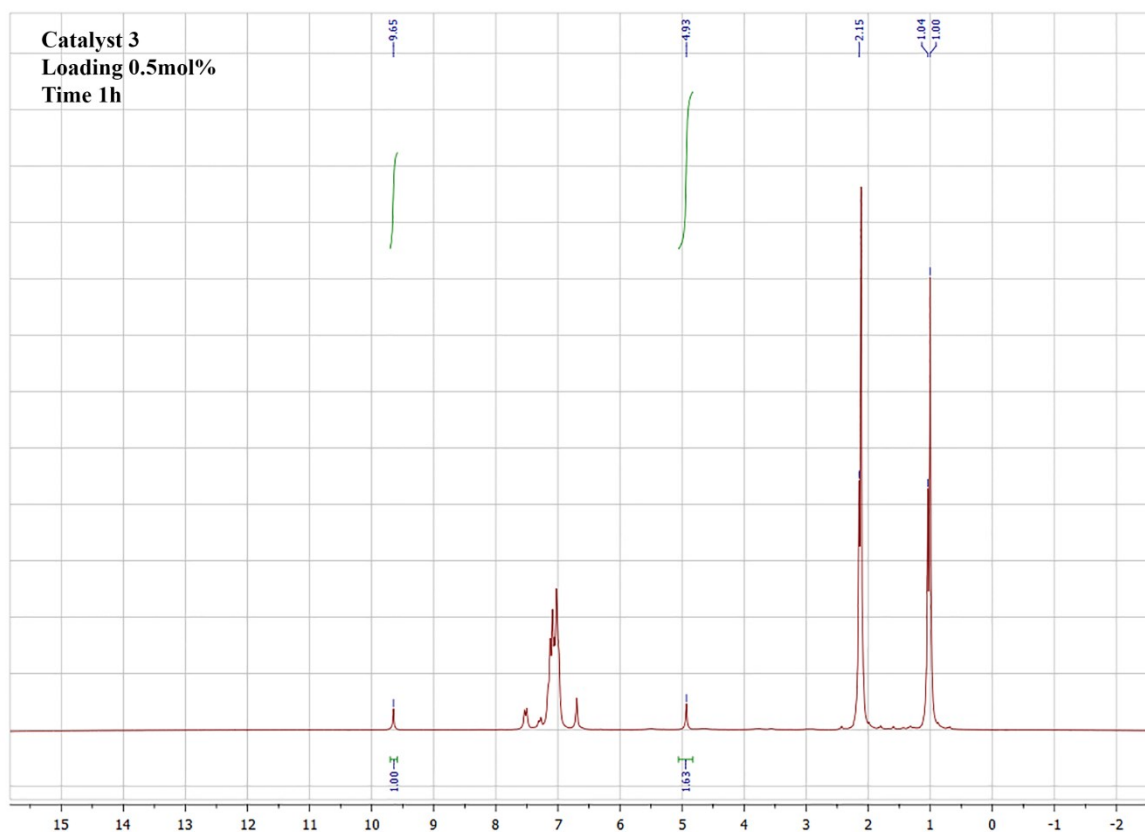
**Figure S19.**  $^1\text{H}$  NMR spectra for Hydroboration of  $\text{C}_6\text{H}_5\text{CHO}$  with HBpin in benzene- $\text{d}_6$  using catalyst (1) loading of 1 mol% for 1 hrs at room temperature.



**Figure S20.**  $^1\text{H}$  NMR spectra for Hydroboration of  $\text{C}_6\text{H}_5\text{CHO}$  with HBpin in benzene- $\text{d}_6$  using catalyst (1) loading of 1 mol% for 3 hrs at room temperature.



**Figure S21.**  $^1\text{H}$  NMR spectra for Hydroboration of  $\text{C}_6\text{H}_5\text{CHO}$  with HBpin in benzene- $\text{d}_6$  using catalyst (1) loading of 0.5 mol% for 1 hrs at room temperature.



**Figure S22.**  $^1\text{H}$  NMR spectra for Hydroboration of  $\text{C}_6\text{H}_5\text{CHO}$  with HBpin in benzene- $\text{d}_6$  using catalyst (1) loading of 0.5 mol% for 3 hrs at room temperature.

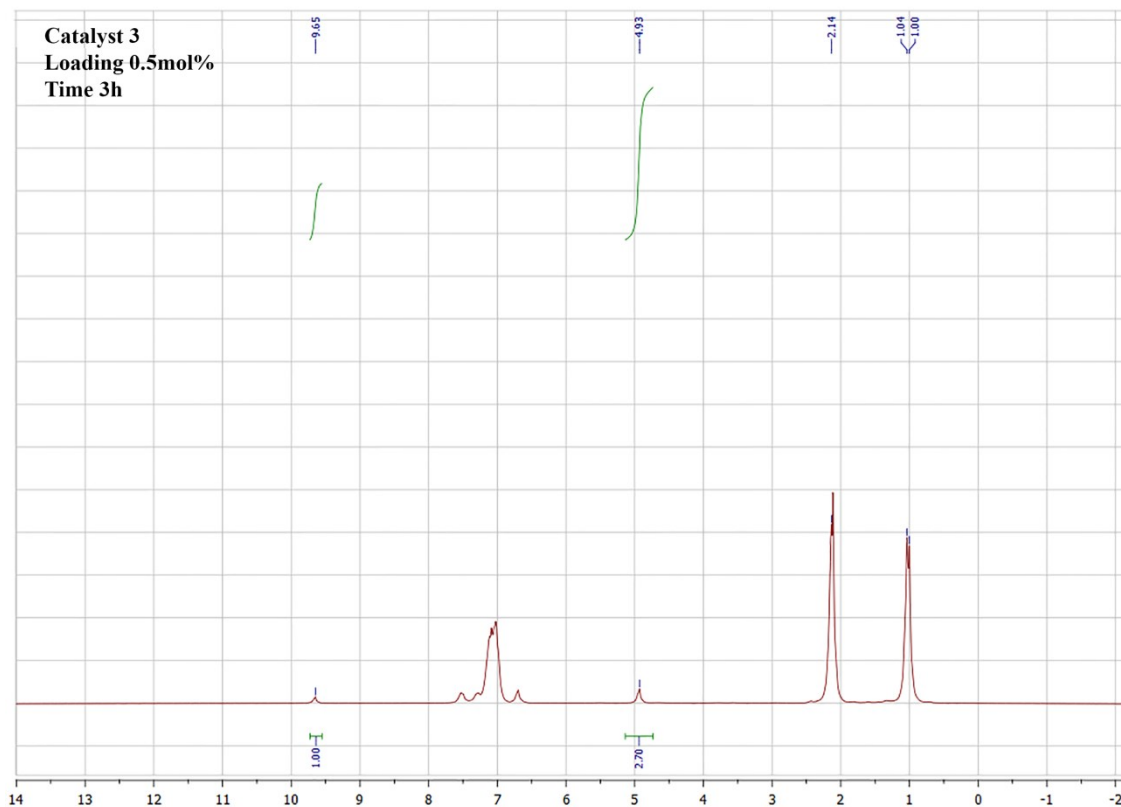




Figure S23.  $^1\text{H}$  NMR spectra for Cyanosilylation of  $\text{C}_6\text{H}_5\text{CHO}$  with  $\text{TMSCN}$  in benzene- $\text{d}_6$  using catalyst (1) loading of 1 mol% for 1 hrs at room temperature.

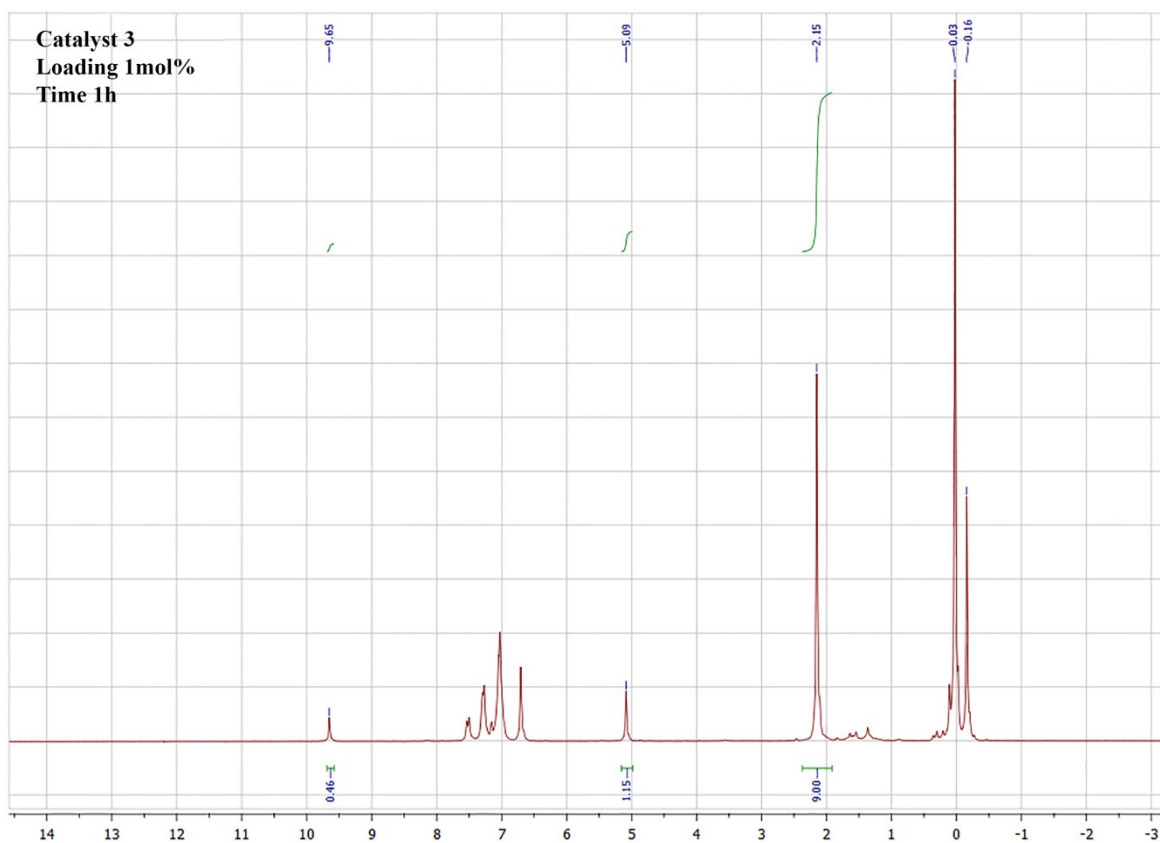


Figure S24.  $^1\text{H}$  NMR spectra for Cyanosilylation of  $\text{C}_6\text{H}_5\text{CHO}$  with  $\text{TMSCN}$  in benzene- $\text{d}_6$  using catalyst (1) loading of 1 mol% for 3 hrs at room temperature.

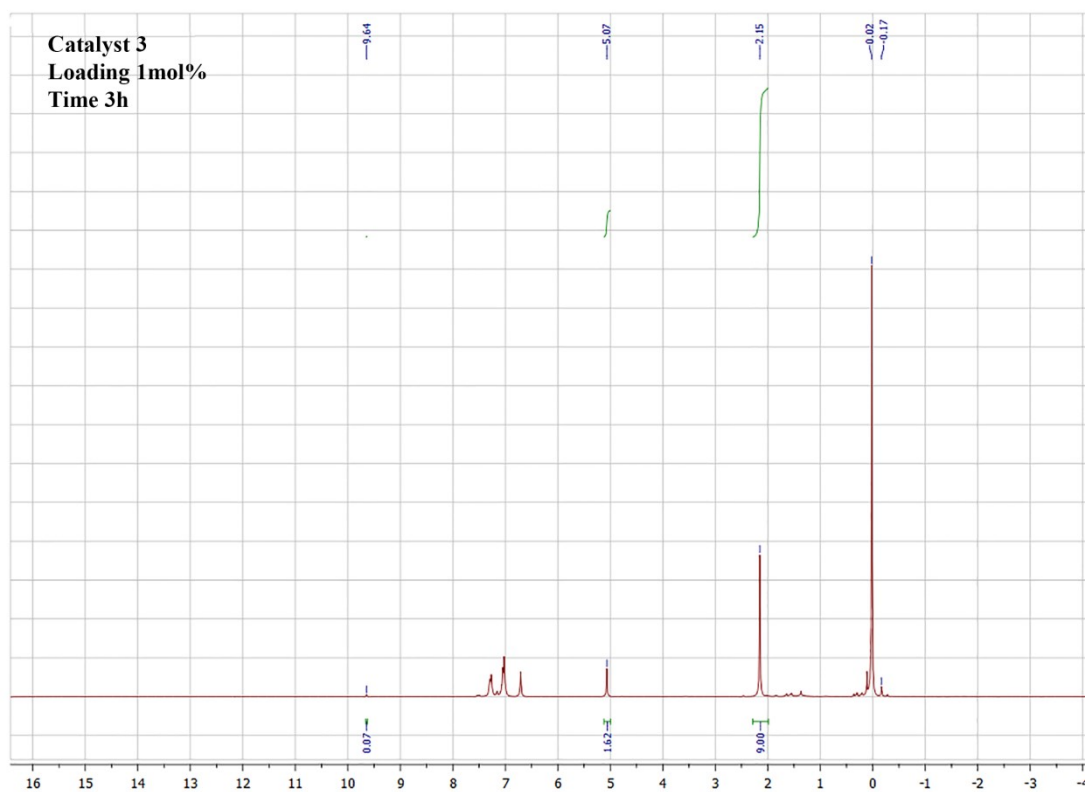


Figure S25.  $^1\text{H}$  NMR spectra for Cyanosilylation of  $\text{C}_6\text{H}_5\text{CHO}$  with  $\text{TMSCN}$  in benzene- $\text{d}_6$  using catalyst (1) loading of 0.25 mol% for 1 hrs at room temperature.

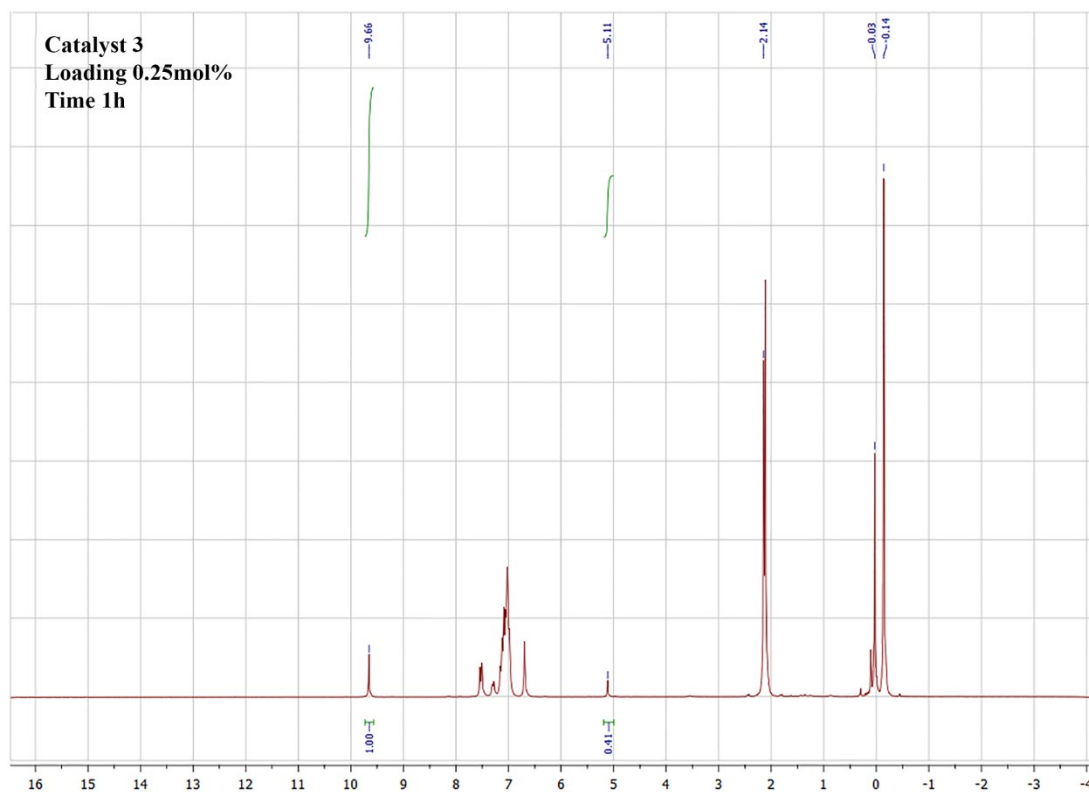
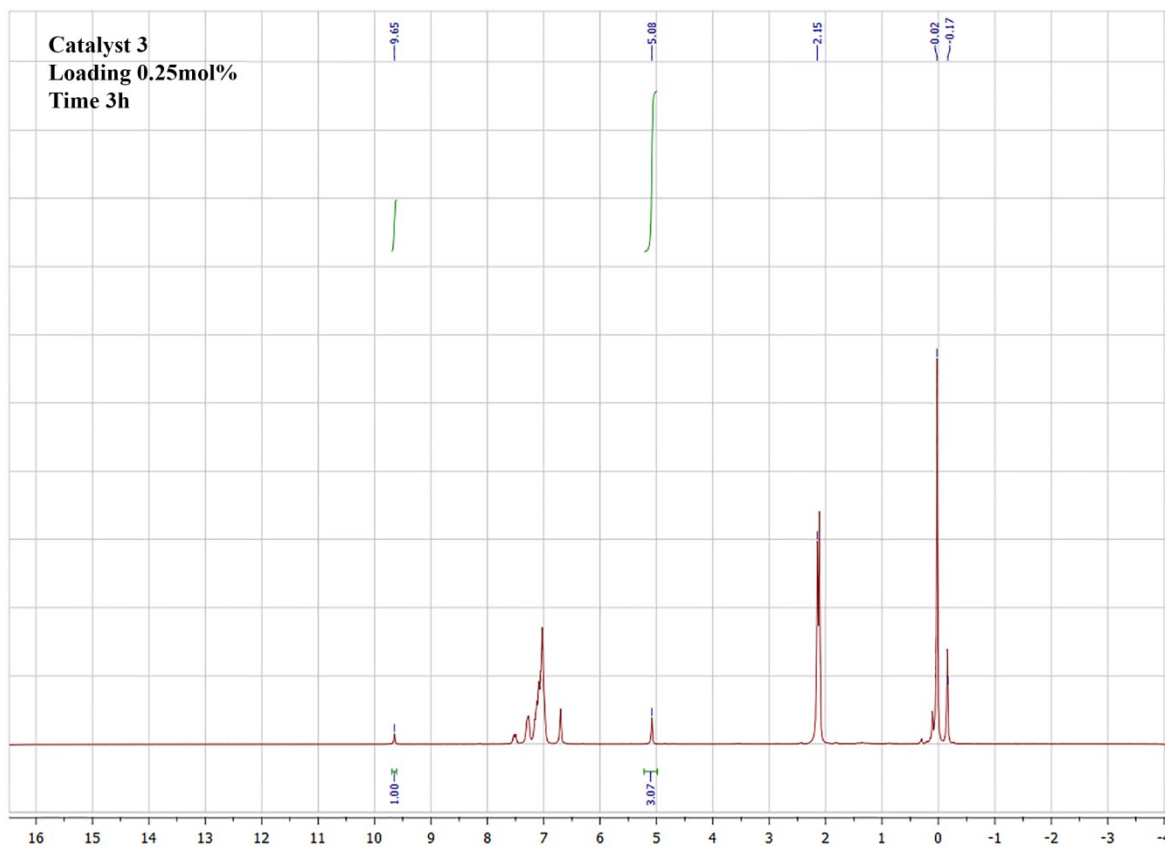
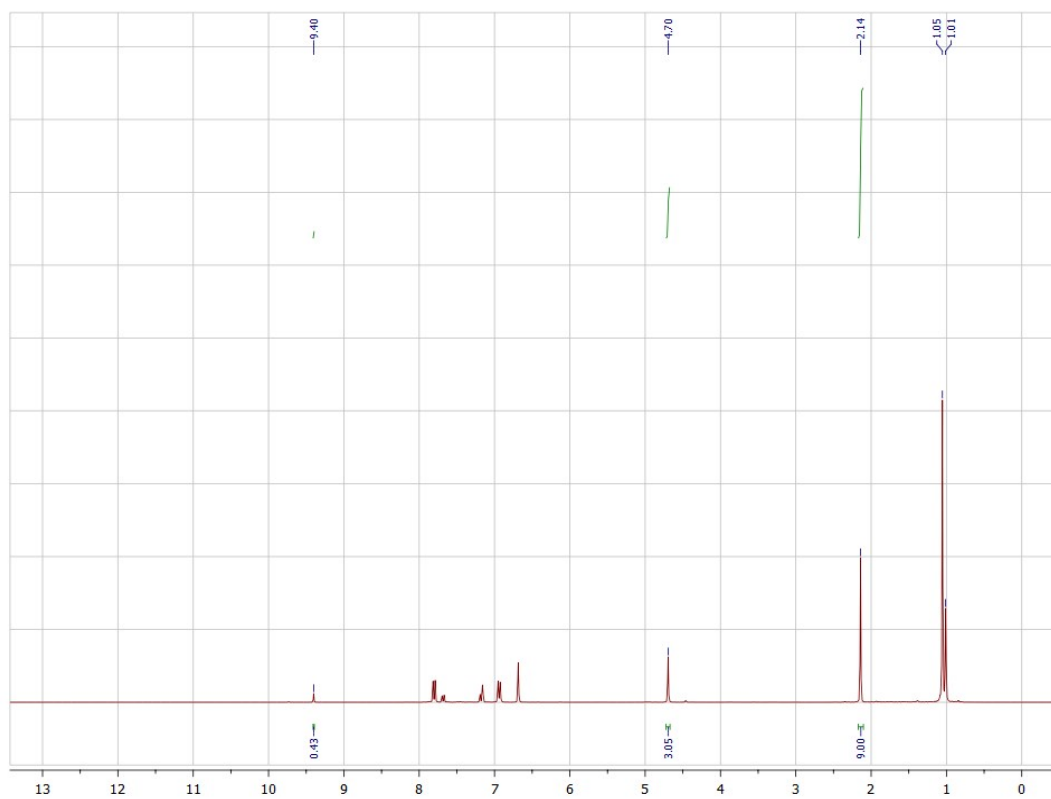


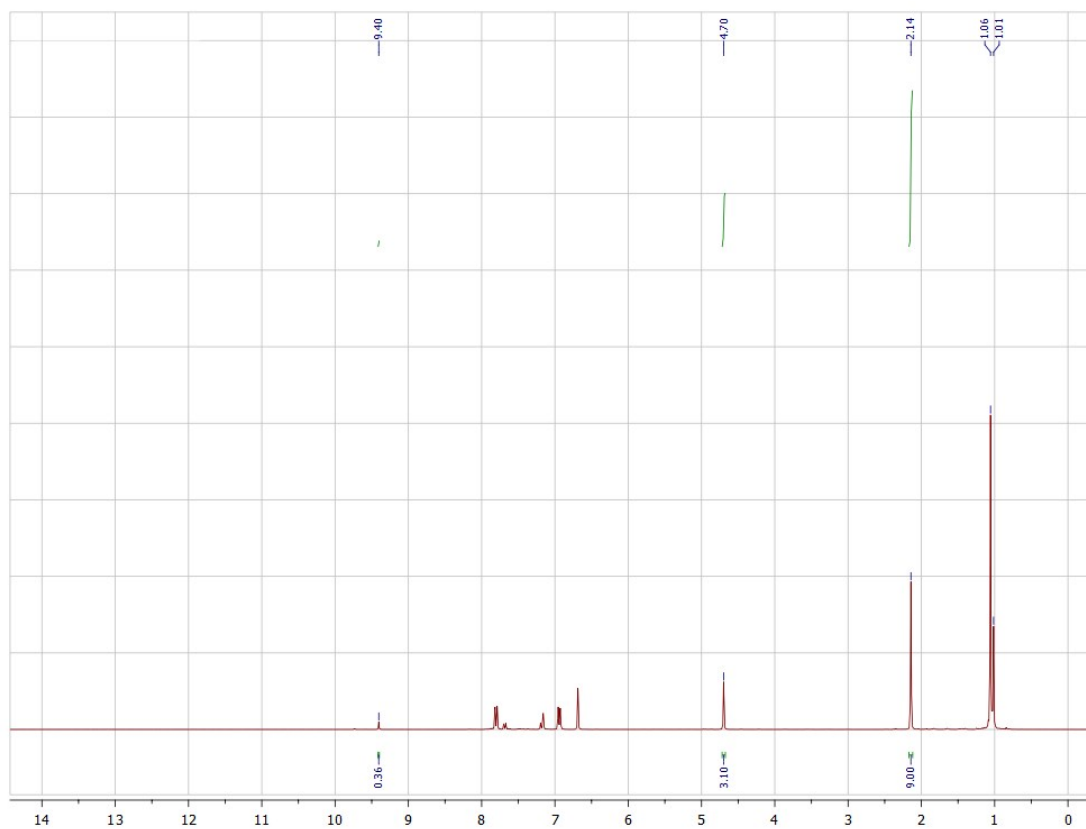
Figure S26.  $^1\text{H}$  NMR spectra for Cyanosilylation of  $\text{C}_6\text{H}_5\text{CHO}$  with  $\text{TMSCN}$  in benzene- $\text{d}_6$  using catalyst (1) loading of 0.25 mol% for 3 hrs at room temperature.



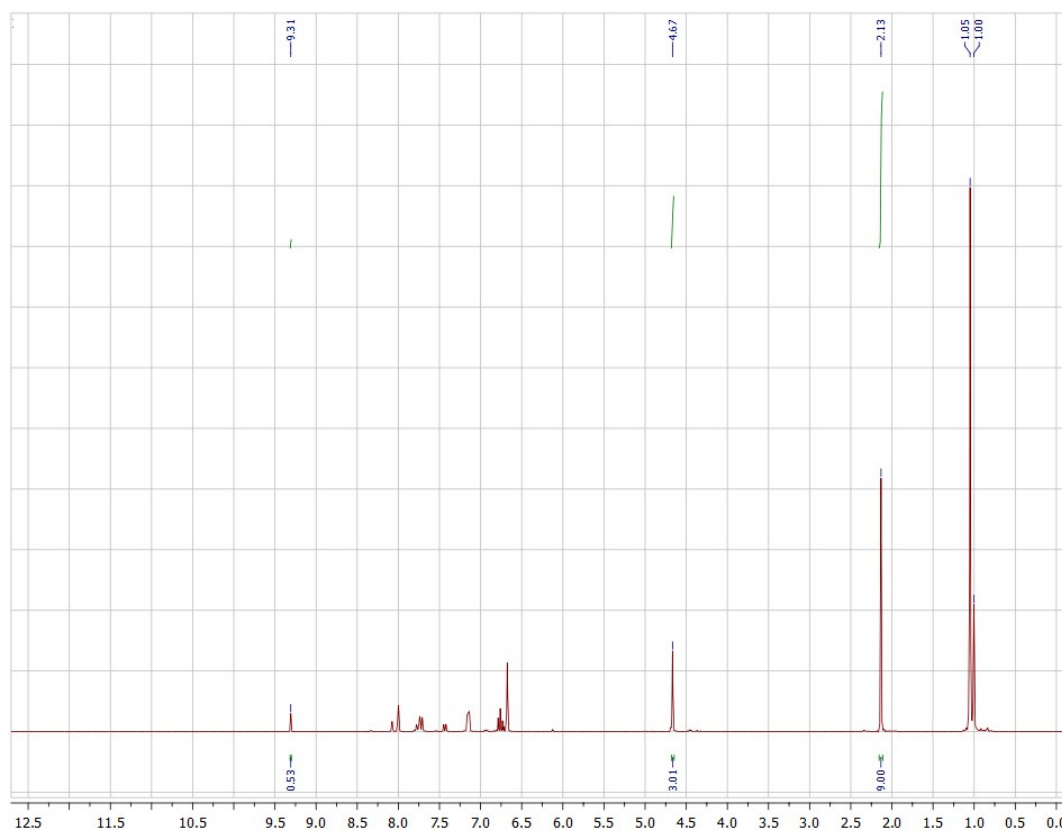
**Figure S27.**  $^1\text{H}$  NMR spectra for Hydroboration of 4-Nitrobenzaldehyde with HBPin in benzene- $\text{d}_6$  using catalyst (1) loading of 1 mol% for 1 hrs at room temperature.



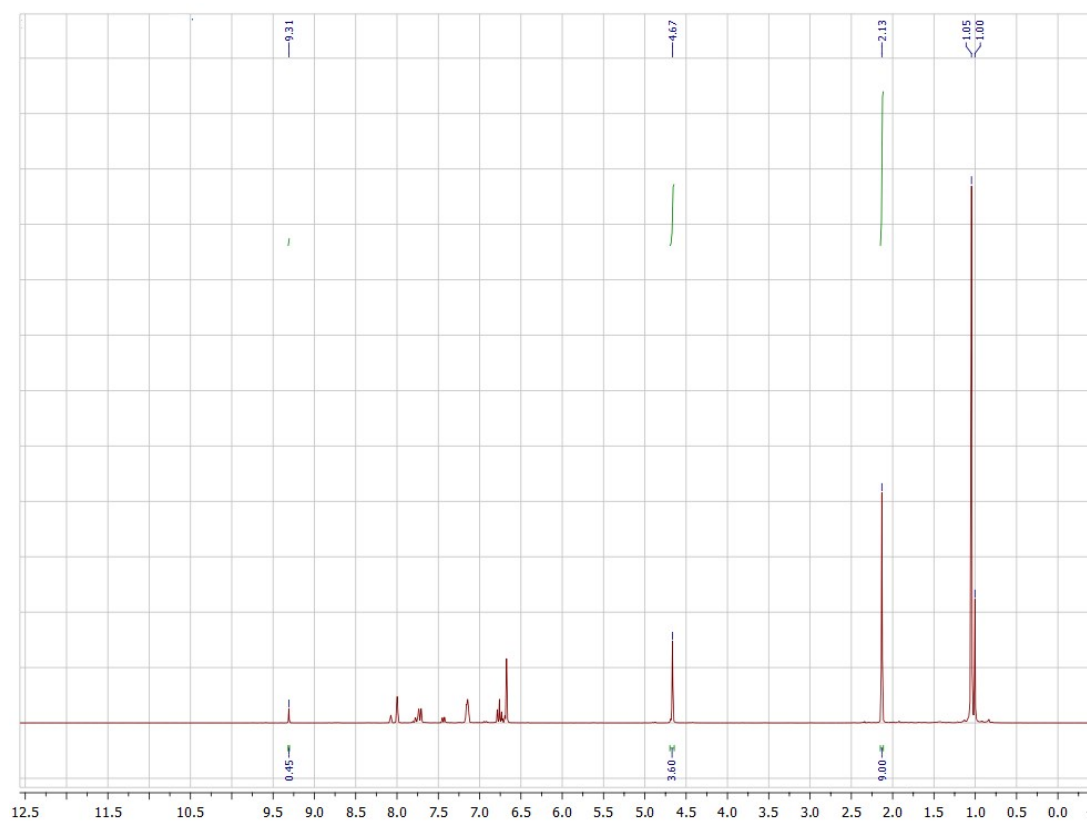
**Figure S28.**  $^1\text{H}$  NMR spectra for Hydroboration of 4-Nitrobenzaldehyde with HBPin in benzene- $\text{d}_6$  using catalyst (1) loading of 1 mol% for 3 hrs at room temperature.



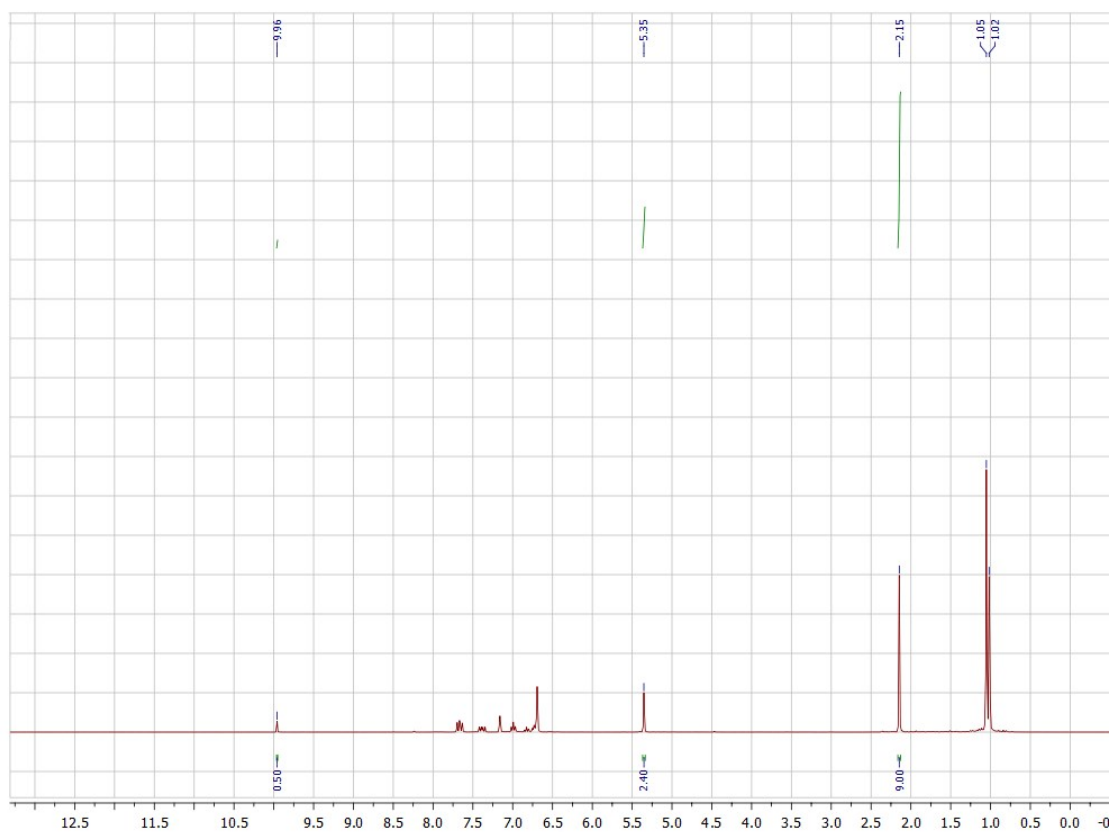
**Figure S29.**  $^1\text{H}$  NMR spectra for Hydroboration of 3-Nitrobenzaldehyde with HBPIn in benzene- $\text{d}_6$  using catalyst (1) loading of 1 mol% for 1 hrs at room temperature.



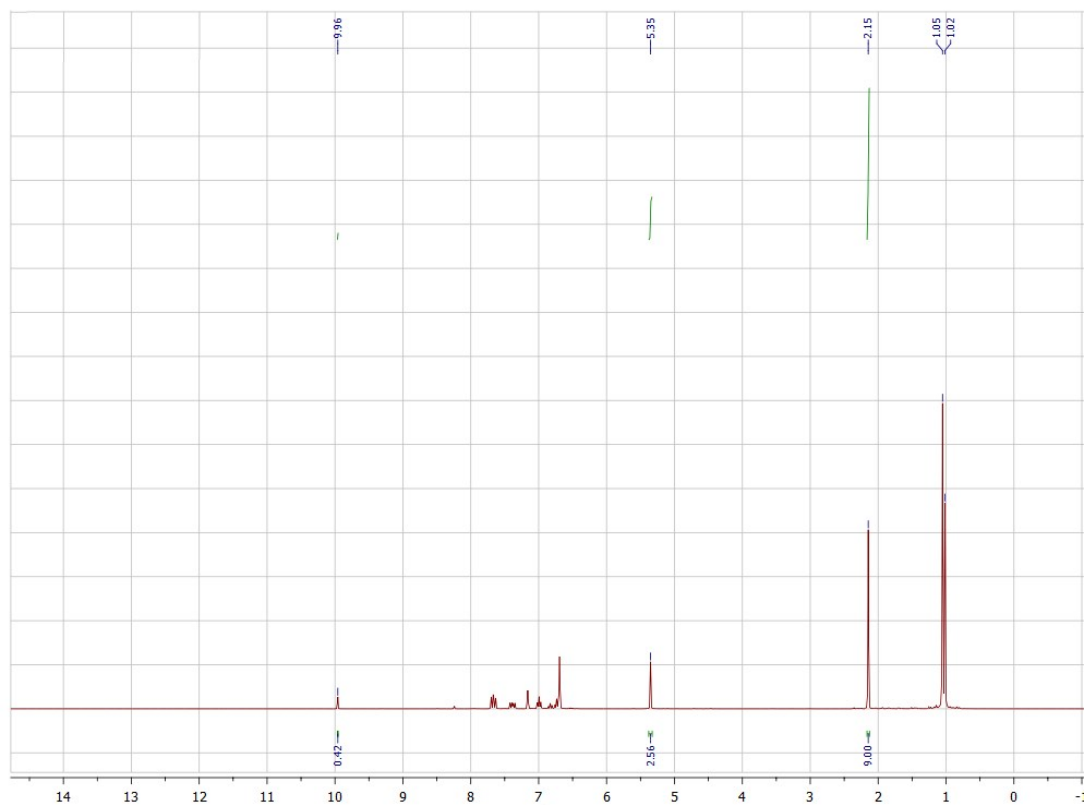
**Figure S30.**  $^1\text{H}$  NMR spectra for Hydroboration of 3-Nitrobenzaldehyde with HBPIn in benzene- $\text{d}_6$  using catalyst (1) loading of 1 mol% for 3 hrs at room temperature.



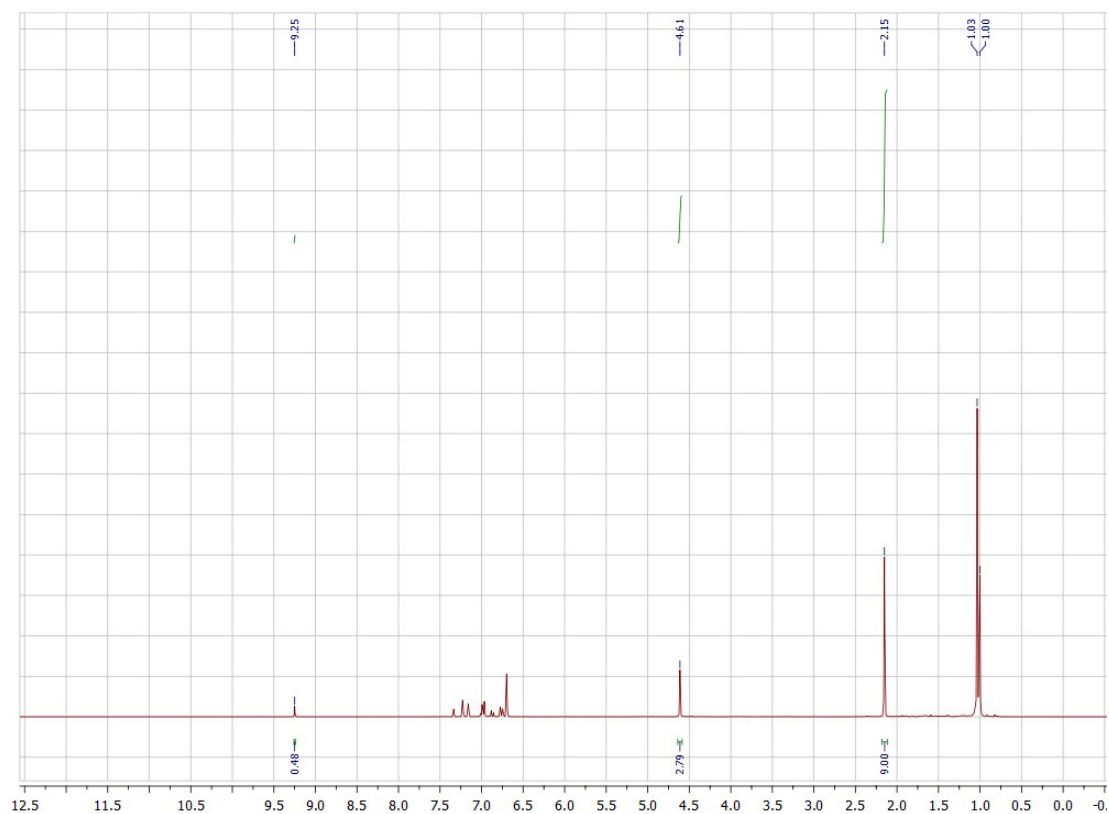
**Figure S31.  $^1\text{H}$  NMR spectra for Hydroboration of 2-Nitrobenzaldehyde with HBPIn in benzene- $\text{d}_6$  using catalyst (1) loading of 1 mol% for 1 hrs at room temperature.**



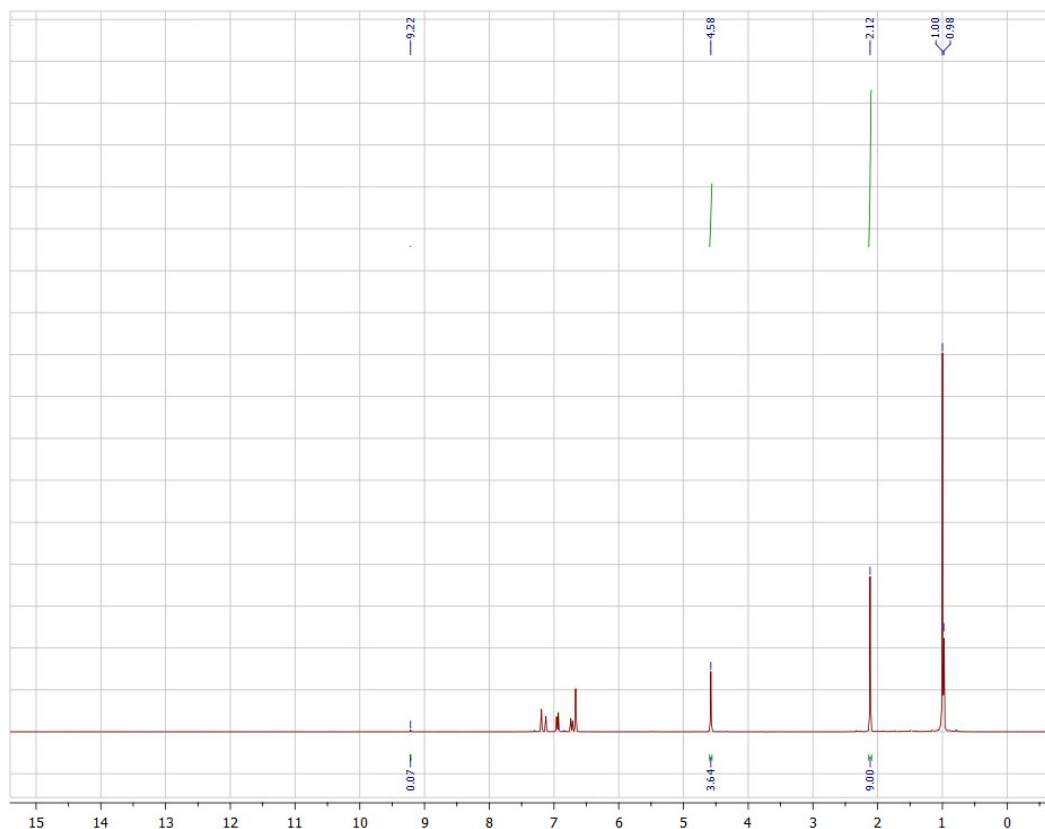
**Figure S32.  $^1\text{H}$  NMR spectra for Hydroboration of 2-Nitrobenzaldehyde with HBPIn in benzene- $\text{d}_6$  using catalyst (1) loading of 1 mol% for 3 hrs at room temperature.**



**Figure S33.**  $^1\text{H}$  NMR spectra for Hydroboration of 3,4-Dichlorobenzaldehyde with HBPIn in benzene- $\text{d}_6$  using catalyst (1) loading of 1 mol% for 1 hrs at room temperature.



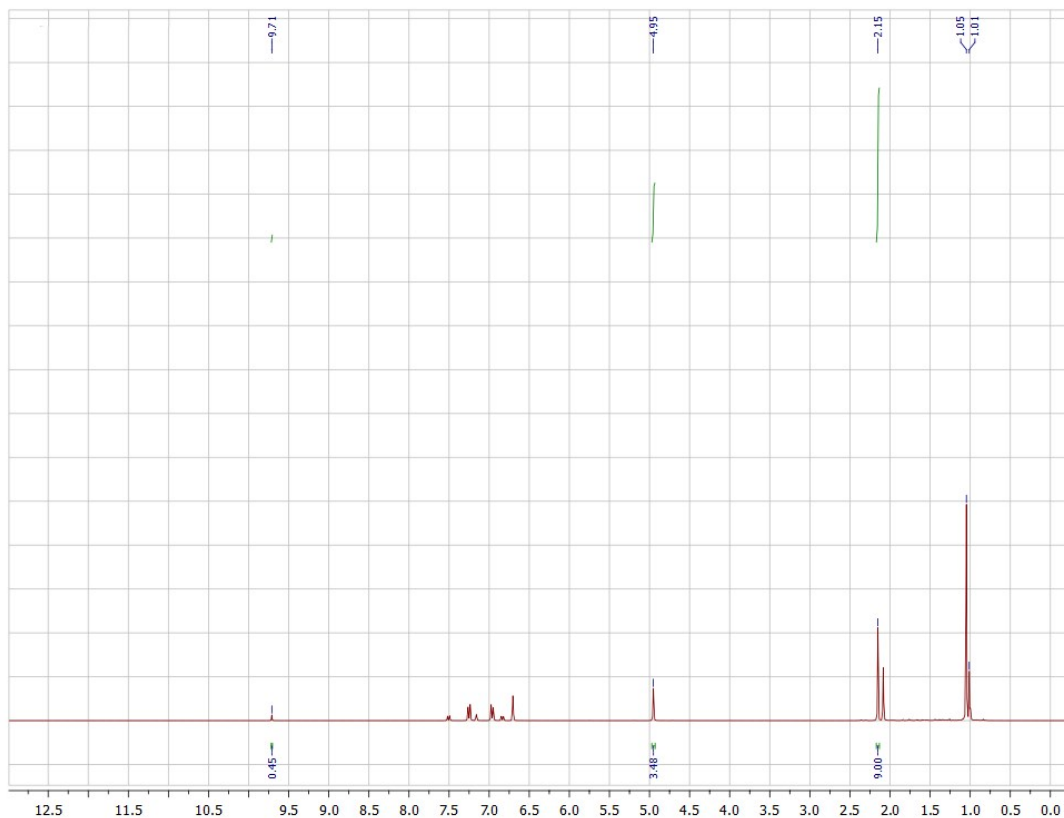
**Figure S34.**  $^1\text{H}$  NMR spectra for Hydroboration of 3,4-Dichlorobenzaldehyde with HBPIn in benzene- $\text{d}_6$  using catalyst (1) loading of 1 mol% for 3 hrs at room temperature.



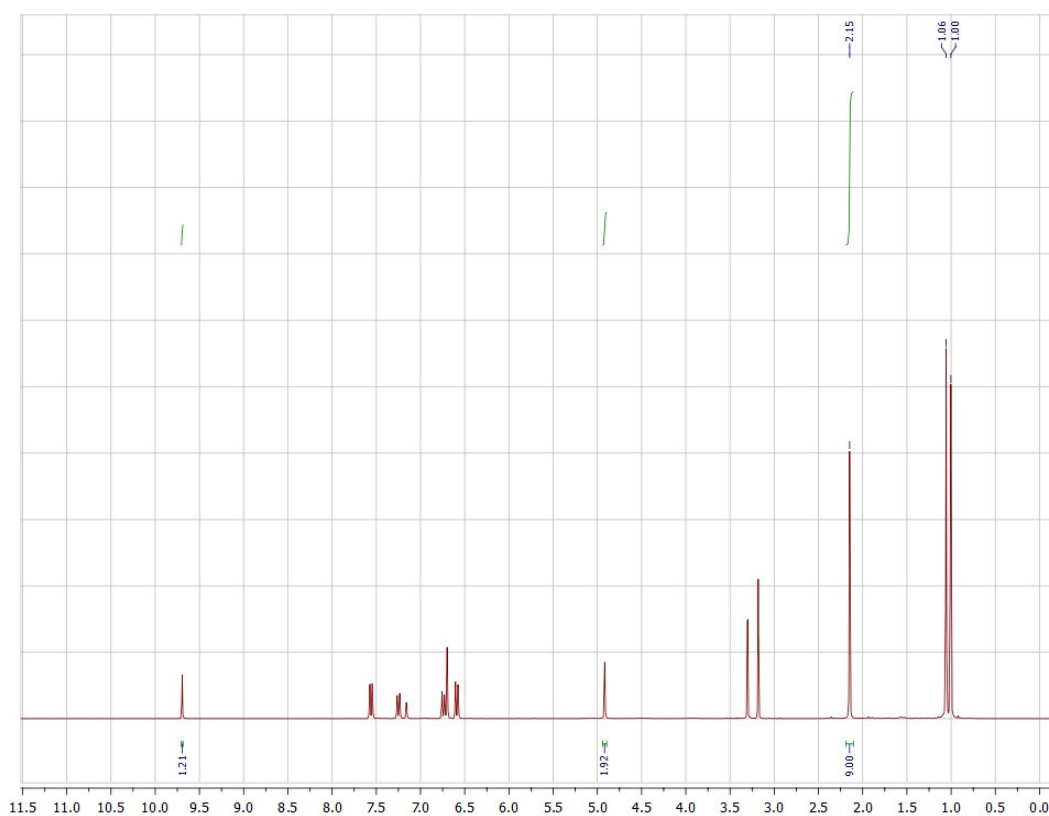
**Figure S35.**  $^1\text{H}$  NMR spectra for Hydroboration of 4-Methylbenzaldehyde with HBPin in benzene- $\text{d}_6$  using catalyst (1) loading of 1 mol% for 1 hrs at room temperature.



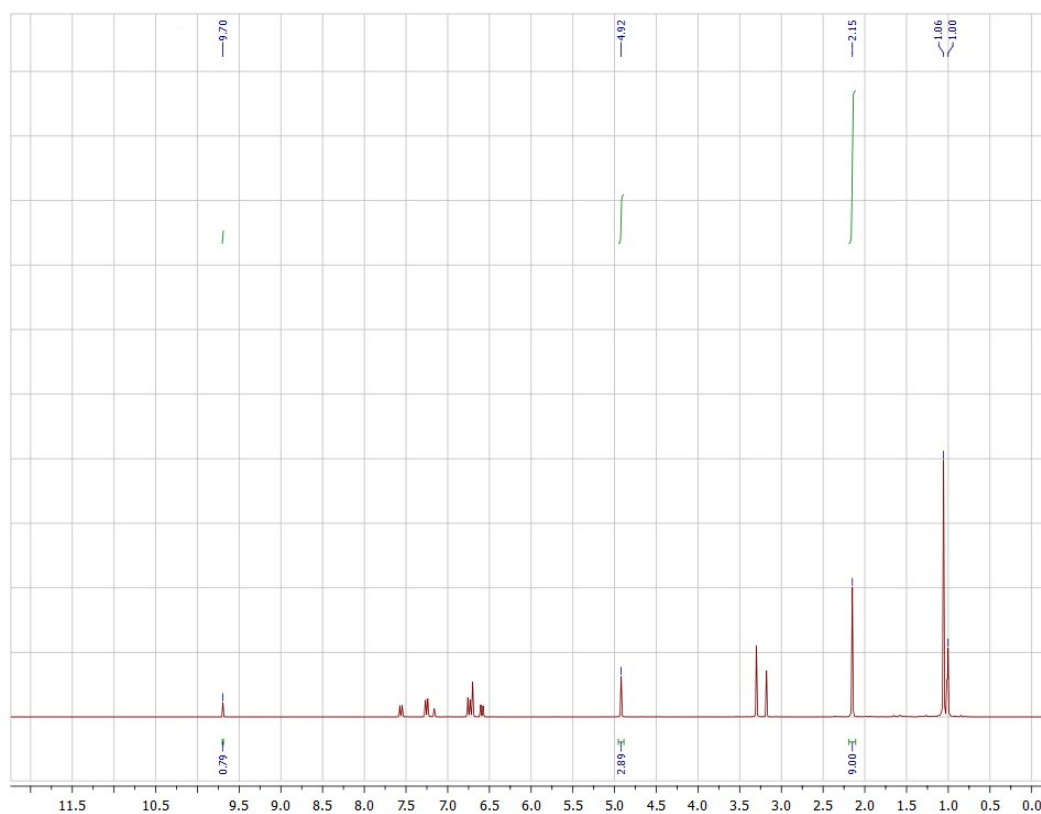
**Figure S36.**  $^1\text{H}$  NMR spectra for Hydroboration of 4-Methylbenzaldehyde with HBPin in benzene- $\text{d}_6$  using catalyst (1) loading of 1 mol% for 3 hrs at room temperature.



**Figure S37.**  $^1\text{H}$  NMR spectra for Hydroboration of 4-Methoxybenzaldehyde with HBPin in benzene- $\text{d}_6$  using catalyst (1) loading of 1 mol% for 1 hrs at room temperature.

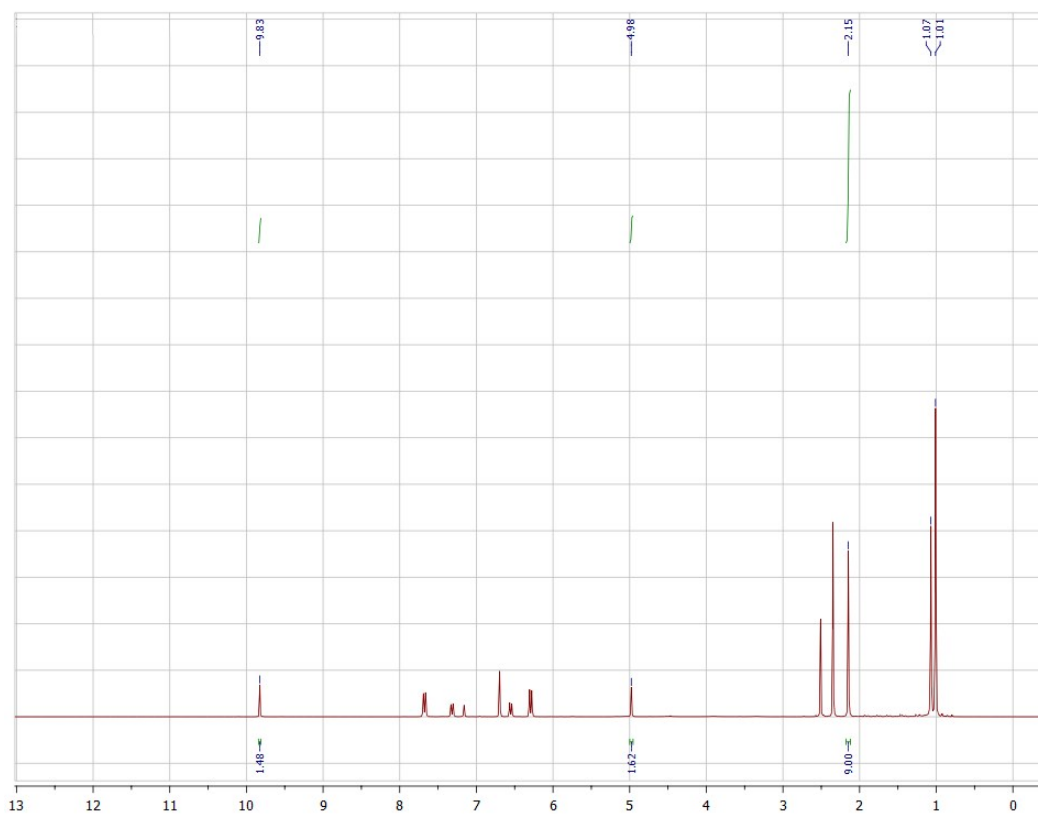


**Figure S38.**  $^1\text{H}$  NMR spectra for Hydroboration of 4-Methoxybenzaldehyde with HBPin in benzene- $\text{d}_6$  using catalyst (1) loading of 1 mol% for 3 hrs at room temperature.

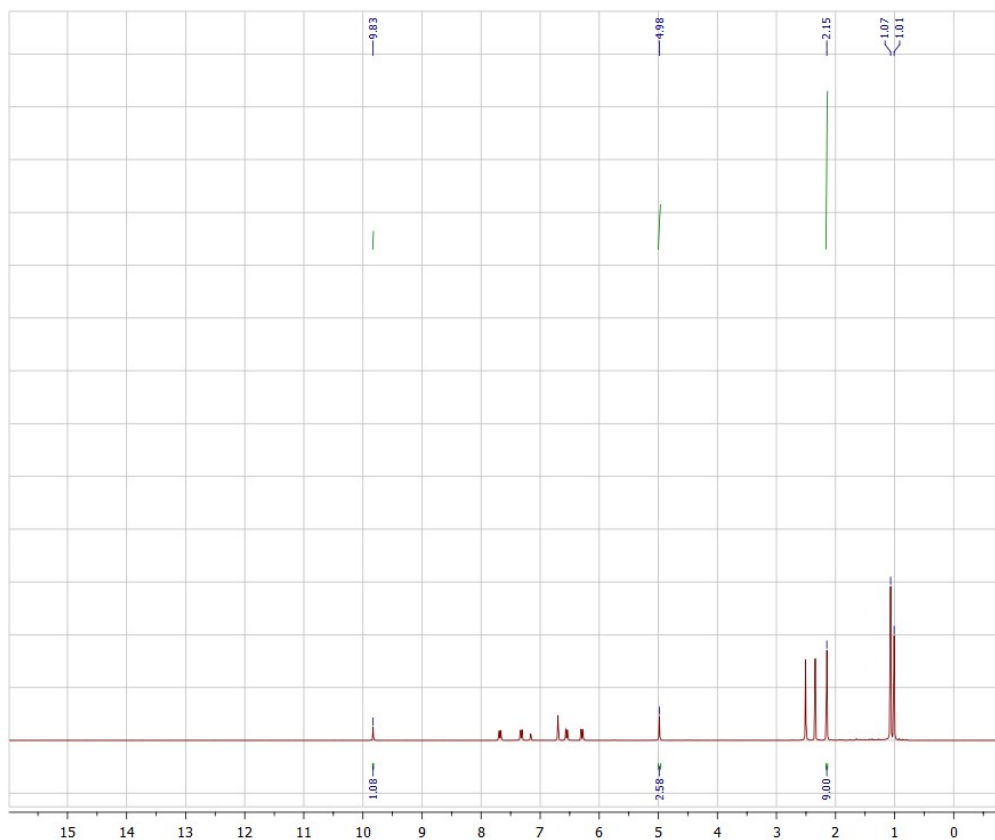




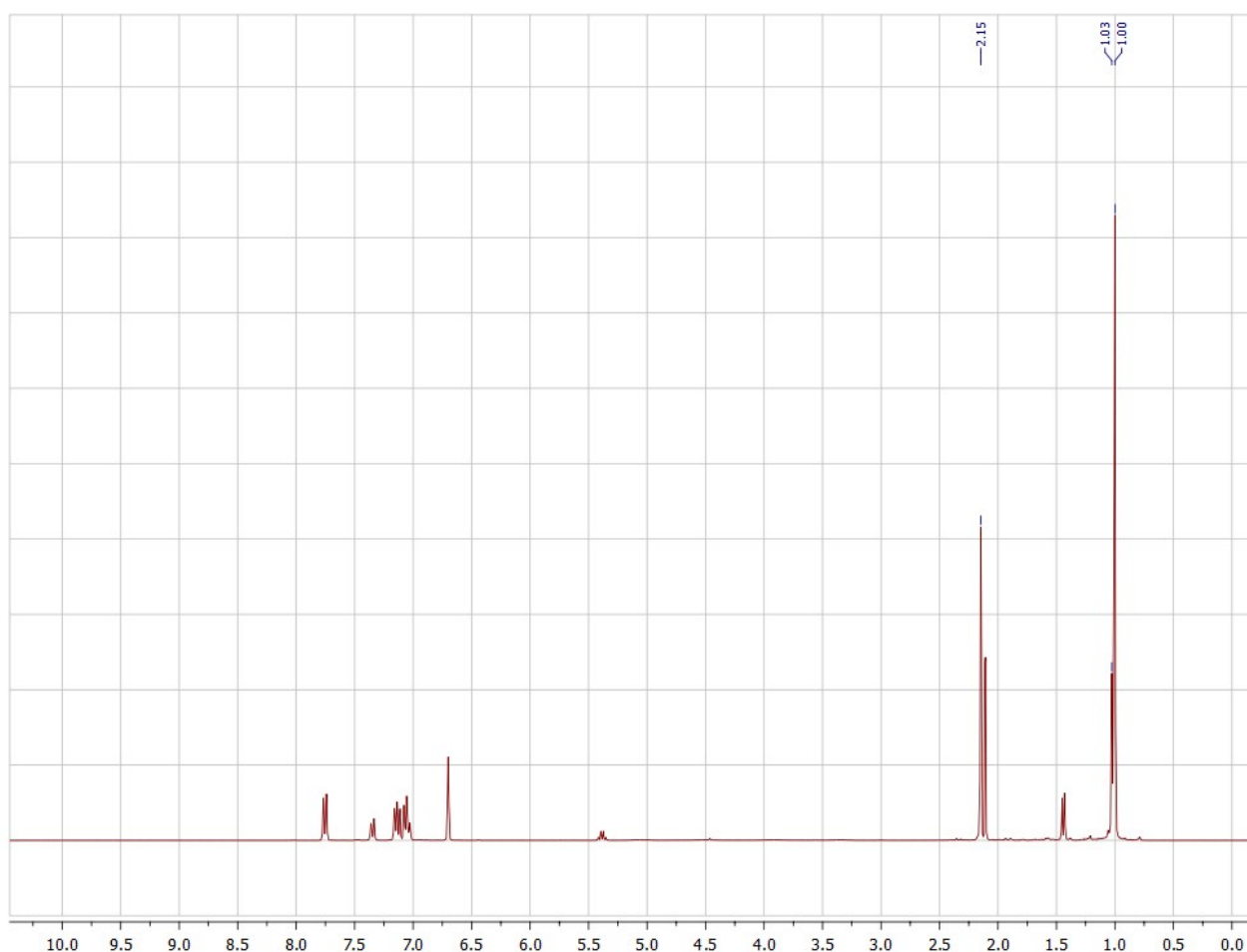
**Figure S39.**  $^1\text{H}$  NMR spectra for Hydroboration of 4-(dimethylamino)benzaldehyde with HBPin in benzene- $\text{d}_6$  using catalyst (1) loading of 1 mol% for 1 hrs at room temperature.



**Figure S40.**  $^1\text{H}$  NMR spectra for Hydroboration of 4-(dimethylamino)benzaldehyde with HBPin in benzene- $\text{d}_6$  using catalyst (1) loading of 1 mol% for 3 hrs at room temperature.



**Figure S41.  $^1\text{H}$  NMR spectra for Hydroboration of PhCHO with HBPin in benzene- $d_6$  using catalyst (1) loading of 1 mol% for 1-3 hrs at room temperature.**



## **NMR spectra of pure products.**

### **4,4,5,5-tetramethyl-2-(benzyloxy)-1,3,2-dioxaborolane**

$^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  (ppm) = 1.04 (s, 12H), 4.94 (s, 2H), 7.15-7.19 (m, 1H), 7.26-7.35 (m, 4H).

$^{13}\text{C}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  (ppm) = 24.5, 66.6, 82.9, 126.6, 127.3, 128.2, 139.1.

$^{11}\text{B}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  (ppm) = 22.5.

### **2-phenyl-2-((trimethylsilyl)oxy)propanenitrile**

$^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  (ppm) = 0.03 (s, 9H), 5.11 (s, 1H), 7.33-7.42 (m, 3H), 7.54-7.55 (m, 2H).

$^{13}\text{C}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  (ppm) = 1.0, 33.6, 71.6, 121.6, 124.6, 128.6, 142.0.

$^{29}\text{Si}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  (ppm) = 24.3.

**4,4,5,5-tetramethyl-2-((4-methoxybenzyl)oxy)-1,3,2-dioxaborolane (a)**

$^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  (ppm) = 1.06 (s, 12H), 3.21 (s, 3H), 4.87 (s, 2H), 6.53 (d, 2H), 7.51 (d, 2H).

$^{13}\text{C}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  (ppm) = 24.6, 55.4, 66.6, 83.0, 113.8, 113.9, 128.6, 129.5, 131.6, 159.1.

$^{11}\text{B}$  NMR (400 MHz  $\text{C}_6\text{D}_6$ )  $\delta$  (ppm) = 22.3.

**2-((2,4-dichlorobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (b).**

$^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = 1.03 (s, 12H), 4.61 (s, 2H), 6.99 (d, 1H), 6.75 (d, 1H), 7.21 (dd, 1H).

$^{13}\text{C}$ -{1H} NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = 24.5, 63.5, 83.0, 127.0, 128.6, 128.8, 131.9, 133.4, 135.4,.

$^{11}\text{B}$ {1H} NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = B 22.3

**4,4,5,5-tetramethyl-2-((4-methylbenzyl)oxy)-1,3,2-dioxaborolane (c)**

$^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  (ppm) = 1.02 (s, 12H), 1.96 (s, 3H), 4.91 (s, 2H), 7.20 (d, 2H), 7.48-7.5 (m, 2H).

$^{13}\text{C}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  (ppm) = 21.3, 24.7, 66.7, 83.0, 127.0, 127.2, 129.1, 129.3, 136.4, 137.1.

$^{11}\text{B}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  (ppm) = 22.5.

**N,N-dimethyl-4-(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)aniline (d)**

$^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  (ppm) = 1.07 (s, 12H), 2.20 (s, 6H), 4.98 (s, 2H), 6.30 (d, 2H), 7.86 (d, 2H).

$^{13}\text{C}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  (ppm) = 24.7, 40.3, 61.6, 83.2, 112.1, 127.2, 129.1, 149.7.

$^{11}\text{B}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  (ppm) = 22.3.

**4,4,5,5-tetramethyl-2-((4-nitrobenzyl)oxy)-1,3,2-dioxaborolane (e)**

$^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  (ppm) = 1.05 (s, 12H), 4.70 (s, 2H), 6.98 (d, 2H), 7.81 (d, 2H).

$^{13}\text{C}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  (ppm) = 24.6, 65.5, 83.4, 123.5, 126.8, 146.5, 147.2.

$^{11}\text{B}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  (ppm) = 22.5.

**2-((3-nitrobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (f)**

$^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = 1.05 (s, 12H), 4.67 (s, 2H), 6.7-7.81 (m, 1H), 7.25(m, 2H), 7.5(m, 1H), 8.1 (m, 2H).

$^{13}\text{C}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = 24.4, 65.6, 83.3, 121.3, 122.0, 126.7, 129.6, 132.4, 141.2.

$^{11}\text{B}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = 22.4

**2-((2-nitrobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (g)**

$^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = 1.05 (s, 12H), 5.35 (s, 2H), 6.99 (m, 1H), 7.44 (m, 1H), 7.55 – 7.63 (m, 2H).

$^{13}\text{C}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = 24.5, 63.6, 83.1, 127.0, 128.6, 128.8, 132.4, 133.4, 135.4.

$^{11}\text{B}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = 22.4

**4,4,5,5-tetramethyl-2-(1-phenylethoxy)-1,3,2-dioxaborolane (h)**

$^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  (ppm) = 1.03 (s, 12H), 1.47-1.49 (m, 3H), 5.79 (s, 1H), 7.00-7.07 (m, 1H), 7.10-7.17 (m, 2H), 7.31-7.34 (m, 2H).

$^{13}\text{C}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  (ppm) = 24.3, 25.4, 72.6, 82.2, 125.3, 127.0, 128.2, 145.0.

$^{11}\text{B}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  (ppm) = 22.6.

**Figure S42. Spin density distribution calculated by the DFT B3LYP/def2tzvp method for paramagnetic germylene 1a.**

