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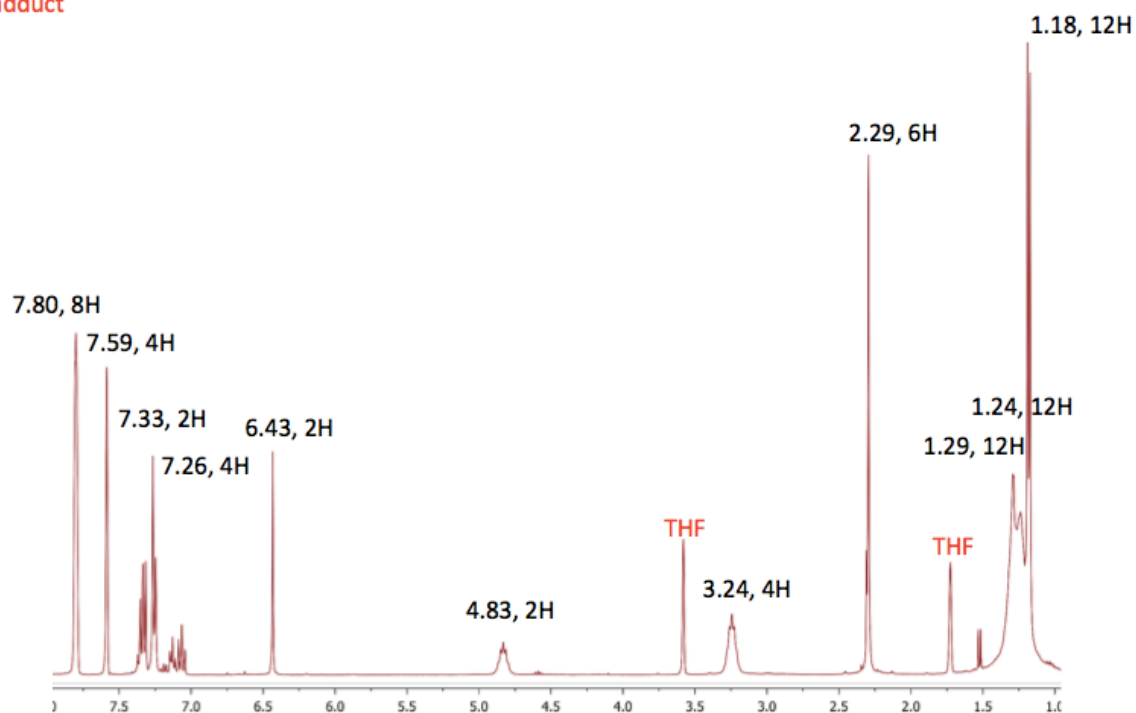
## 1. Additional synthetic details

**[2(H)<sub>2</sub>][BAR<sup>f</sup><sub>4</sub>]:** A J. Young's NMR tube containing a solution of [2-thf][BAR<sup>f</sup><sub>4</sub>] (50 mg, 0.03 mmol) in d<sub>8</sub>-thf (0.5 mL) was degassed via three freeze-pump-thaw cycles, and back-filled with H<sub>2</sub> (ca. 1 atm. pressure). Monitoring via <sup>1</sup>H NMR spectroscopy confirmed complete conversion to product after 7 d at room temperature. <sup>1</sup>H NMR (400 MHz, thf-d<sub>8</sub>, 298 K): δ<sub>H</sub> 1.17 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>, boryl), 1.20 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>, boryl), 1.28 (d, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>, NHC), 2.28 (s, 6H, backbone CH<sub>3</sub>, NHC), 2.94 (sept, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 4H, CH(CH<sub>3</sub>)<sub>2</sub>, boryl), 4.17 (s, 2H, GeH<sub>2</sub>), 4.19 (sept, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>, NHC), 6.68 (s, 2H, backbone CH, boryl), 7.31-7.42 (m, 6H, *m*- and *p*-CH, boryl), 7.58 (s, 4H, *p*-CH, [BAR<sup>f</sup><sub>4</sub>]<sup>-</sup>), 7.80 (s, 8H, *o*-CH, [BAR<sup>f</sup><sub>4</sub>]<sup>-</sup>). <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, thf-d<sub>8</sub>, 298 K): δ<sub>B</sub> -6 ([BAR<sup>f</sup><sub>4</sub>]<sup>-</sup>), 23 (boryl). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, thf-d<sub>8</sub>, 298 K): δ<sub>C</sub> 10.6 (backbone CH<sub>3</sub>, NHC), 21.2 (CH(CH<sub>3</sub>)<sub>2</sub>, NHC), 23.9, 25.8 (CH(CH<sub>3</sub>)<sub>2</sub>, boryl), 29.7 (CH(CH<sub>3</sub>)<sub>2</sub>, boryl), 56.2 (CH(CH<sub>3</sub>)<sub>2</sub>, NHC), 118.4 (br m, *p*-CH, [BAR<sup>f</sup><sub>4</sub>]<sup>-</sup>), 125.0 (2 overlapping signals backbone CH and *m*-CH, boryl), 125.7 (q, <sup>1</sup>J<sub>C-F</sub> = 273.0 Hz, CF<sub>3</sub>, [BAR<sup>f</sup><sub>4</sub>]<sup>-</sup>), 129.9 (*p*-CH, boryl), 130.2 (qq, <sup>3</sup>J<sub>C-B</sub> = 3.6 Hz, <sup>2</sup>J<sub>C-F</sub> = 32.2 Hz, *m*-C, [BAR<sup>f</sup><sub>4</sub>]<sup>-</sup>), 131.8 (backbone C, NHC), 135.8 (*o*-CH, [BAR<sup>f</sup><sub>4</sub>]<sup>-</sup>), 138.7 (*i*-C, boryl), 145.5 (imidazolylidene C), 146.7 (*o*-C, boryl), 163.0 (q, <sup>1</sup>J<sub>C-B</sub> = 50.1 Hz, *i*-C, [BAR<sup>f</sup><sub>4</sub>]<sup>-</sup>). <sup>19</sup>F{<sup>1</sup>H} NMR (377 MHz, thf-d<sub>8</sub>, 298 K): δ<sub>F</sub> -63.4 ([BAR<sup>f</sup><sub>4</sub>]<sup>-</sup>). Crystallographic data: C<sub>69</sub>H<sub>70</sub>B<sub>2</sub>F<sub>24</sub>GeN<sub>4</sub>, M<sub>r</sub> = 1505.50, triclinic, P-1, a = 13.1107(5), b = 13.1292(5), c = 21.3354(7) Å, α = 82.898(3), β = 76.234(3), γ = 84.452(3)°, V = 3531.0(2) Å<sup>3</sup>, Z = 2, R<sub>1</sub> = 0.0509 (11890, I > 2σ(I)), wR<sub>2</sub> = 0.1436 (all 14561 unique reflections).

**Generation of [2(H)(Bpin)][BAR<sup>f</sup><sub>4</sub>]:** HBpin (4.8 μL, 0.03 mmol) was added to a solution of [2-thf][BAR<sup>f</sup><sub>4</sub>] (50 mg, 0.03 mmol) in thf-d<sub>8</sub> (0.5 mL) in a J. Young's NMR tube at room temperature. The solution immediately changed colour from yellow to colourless, and <sup>1</sup>H NMR spectroscopy revealed complete conversion to the product (within ca. 5 min at room temperature). Attempts at recrystallization from fluorobenzene/hexane led instead to the formation of single crystals of [2(H)<sub>2</sub>][BAR<sup>f</sup><sub>4</sub>] (together with pinBOBpin) over a period of several days via adventitious hydrolysis. Spectroscopic data for [2(H)(Bpin)][BAR<sup>f</sup><sub>4</sub>]: <sup>1</sup>H NMR (400 MHz, thf-d<sub>8</sub>, 298 K): δ<sub>H</sub> 0.96 (s, 12H, CH<sub>3</sub>, Bpin), 0.96 (overlapping m, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, boryl), 1.14 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, boryl), 1.17 (overlapping m, 3H, CH(CH<sub>3</sub>)<sub>2</sub>, NHC), 1.19 (d, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, boryl), 1.28 (br d, 3H, CH(CH<sub>3</sub>)<sub>2</sub>, NHC), 1.41 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, boryl), 1.57 (br m, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, NHC), 2.28 (br s, 6H, backbone CH<sub>3</sub>, NHC), 2.78 (sept, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>, boryl), 3.10 (br m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>, boryl), 4.14 (s, 1H, GeH), 4.46 (br m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>, NHC), 6.57 (s, 2H, backbone CH, boryl), 7.21-7.40 (overlapping m, 6H, *m*- and *p*-CH, boryl), 7.58 (s, 4H, *p*-CH, [BAR<sup>f</sup><sub>4</sub>]<sup>-</sup>), 7.80 (s, 8H, *p*-CH, [BAR<sup>f</sup><sub>4</sub>]<sup>-</sup>). <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, thf-d<sub>8</sub>, 298 K): δ<sub>B</sub> -6 ([BAR<sup>f</sup><sub>4</sub>]<sup>-</sup>), 21 (Bpin), 24 (boryl). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, thf-d<sub>8</sub>, 298 K): δ<sub>C</sub> 10.8 (backbone CH<sub>3</sub>, NHC), 21.2, 22.7 (CH(CH<sub>3</sub>)<sub>2</sub>, NHC), 23.8, 23.9 (CH(CH<sub>3</sub>)<sub>2</sub>, boryl), 25.4 (CH<sub>3</sub>, Bpin), 26.1, 26.6 (CH(CH<sub>3</sub>)<sub>2</sub>, boryl), 29.6, 29.7 (CH(CH<sub>3</sub>)<sub>2</sub>, boryl), 56.2 (CH(CH<sub>3</sub>)<sub>2</sub>, NHC), 86.8 (quaternary-C, Bpin), 118.4 (m, *p*-CH, [BAR<sup>f</sup><sub>4</sub>]<sup>-</sup>), 125.0 (backbone CH, boryl), 125.1 (*m*-CH, boryl), 125.7 (q, <sup>1</sup>J<sub>C-F</sub> = 271.8 Hz, CF<sub>3</sub>, [BAR<sup>f</sup><sub>4</sub>]<sup>-</sup>), 129.7 (*p*-CH, boryl), 130.2 (qq, <sup>3</sup>J<sub>C-B</sub> = 3.6 Hz, <sup>2</sup>J<sub>C-F</sub> = 31.0 Hz, *m*-C, [BAR<sup>f</sup><sub>4</sub>]<sup>-</sup>), 135.8 (*o*-CH, [BAR<sup>f</sup><sub>4</sub>]<sup>-</sup>), 139.3 (*i*-C, boryl), 146.7 (imidazolylidene C), 147.0 (*o*-C, boryl), 163.0 (q, <sup>1</sup>J<sub>C-B</sub> = 48.9 Hz, *i*-C, [BAR<sup>f</sup><sub>4</sub>]<sup>-</sup>) (signal for NHC backbone C not observed/obscured by those for [BAR<sup>f</sup><sub>4</sub>]<sup>-</sup>). <sup>19</sup>F{<sup>1</sup>H} NMR (377 MHz, thf-d<sub>8</sub>, 298 K): δ<sub>F</sub> -63.4 ([BAR<sup>f</sup><sub>4</sub>]<sup>-</sup>).

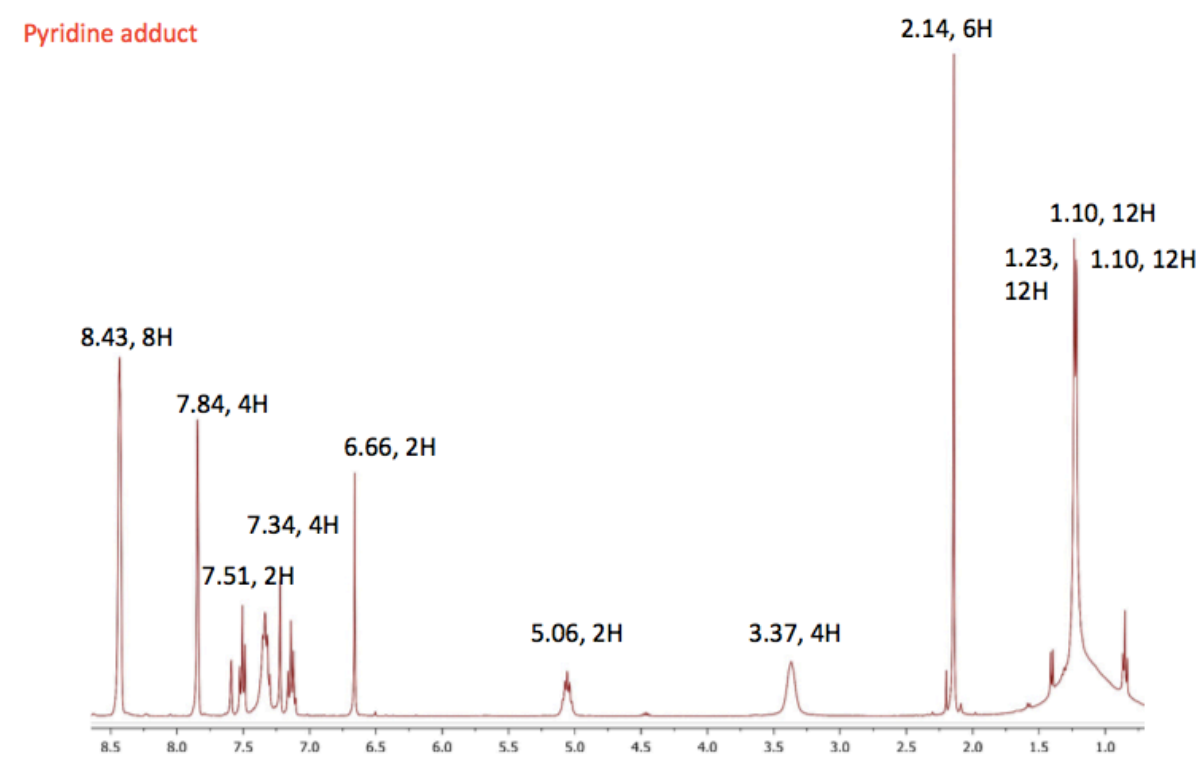
## 2. $^1\text{H}$ NMR spectra of novel compounds

THF adduct



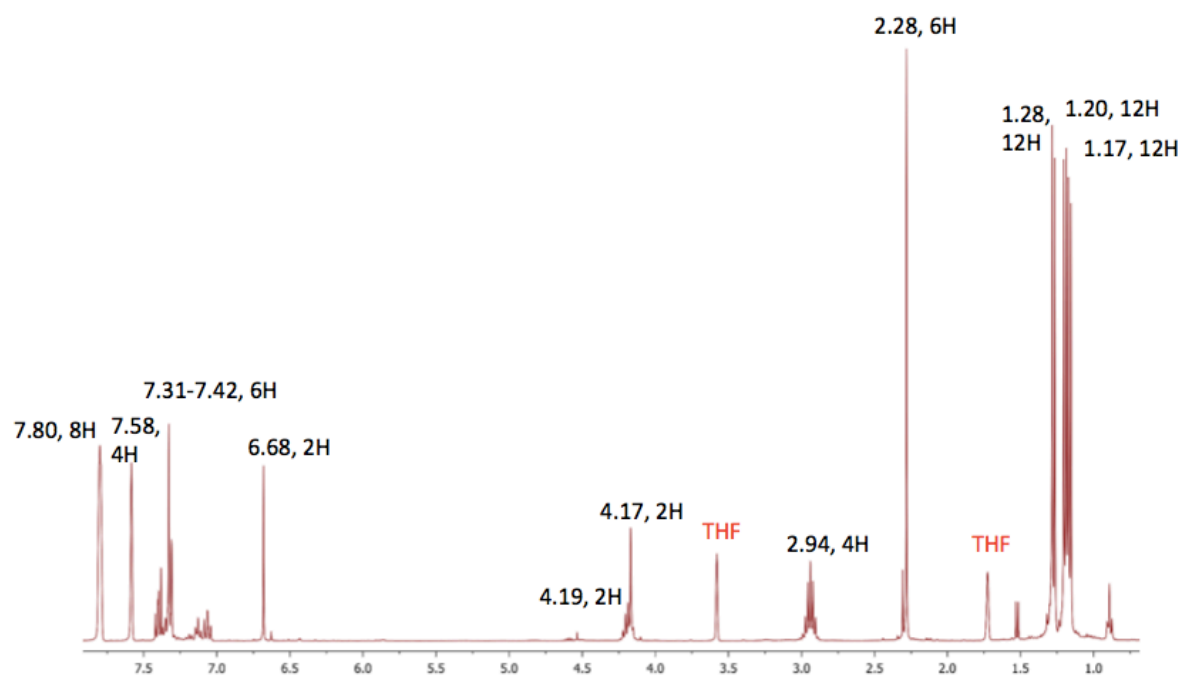
**Figure s1:**  $^1\text{H}$  NMR spectrum of  $[\mathbf{2}-(\text{thf-d}_8)][\text{BAR}_4^f]$  in  $\text{thf-d}_8$  at 298 K.

Pyridine adduct



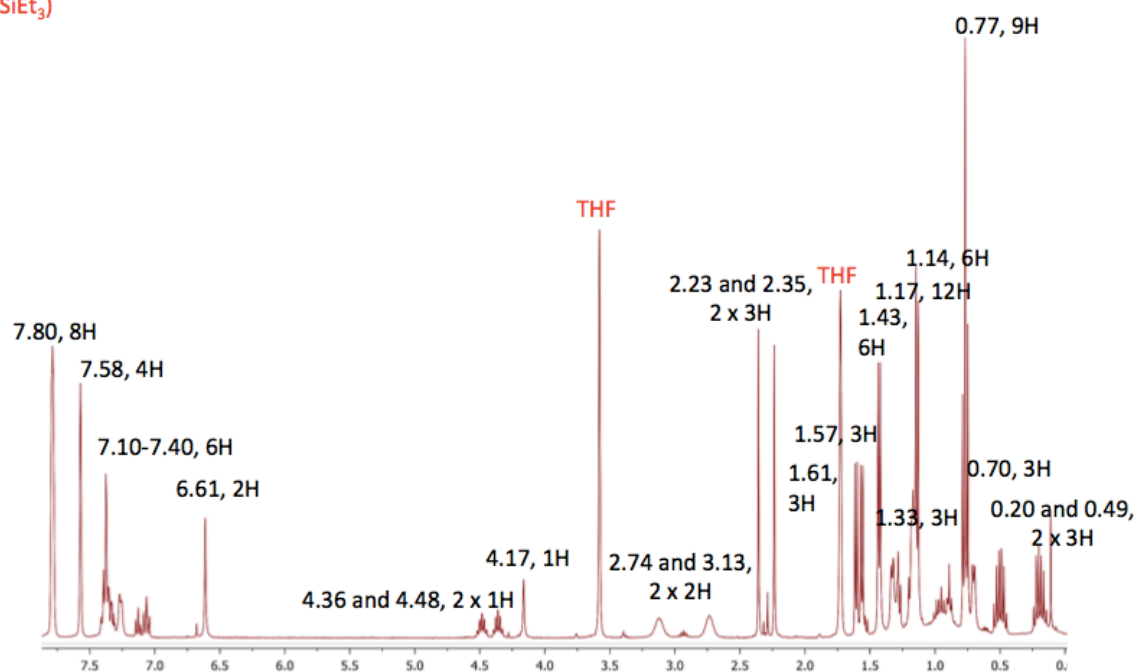
**Figure s2:**  $^1\text{H}$  NMR spectrum of  $[\mathbf{2}(\text{py-d}_5)][\text{BArf}_4]$  in  $\text{thf-d}_8$  at 298 K.

GeH<sub>2</sub>



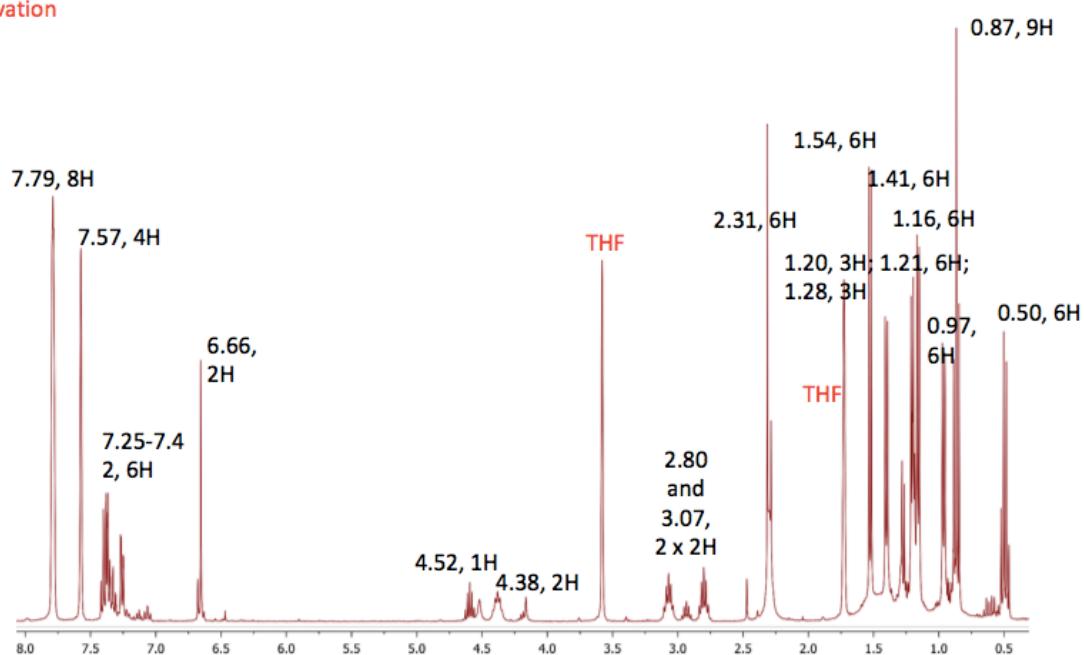
**Figure s3:** <sup>1</sup>H NMR spectrum of [2(H)<sub>2</sub>][BAR<sup>f</sup><sub>4</sub>] in thf-d<sub>8</sub> at 298 K.

GeH(SiEt<sub>3</sub>)



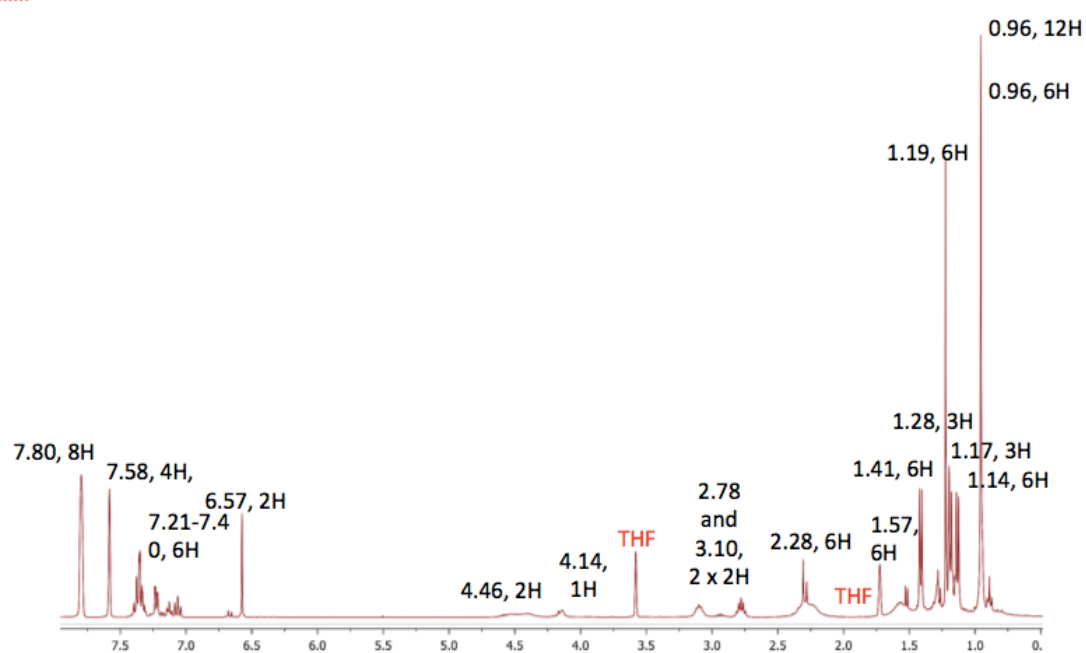
**Figure s4:** <sup>1</sup>H NMR spectrum of [2(H)(SiEt<sub>3</sub>)]<sup>+</sup>[BAR<sup>f</sup><sub>4</sub>]<sup>-</sup> in thf-d<sub>8</sub> at 298 K.

THF activation



**Figure s5:** <sup>1</sup>H NMR spectrum of [2(H)(C<sub>4</sub>D<sub>8</sub>OSiEt<sub>3</sub>)] [BArf<sub>4</sub>] in thf-d<sub>8</sub> at 298 K.

GeH(Bpin)



**Figure s6:**  $^1\text{H}$  NMR spectrum of  $[\text{2(H)(Bpin)}][\text{BAR}_4^f]$  in  $\text{thf-d}_8$  at 298 K.



### 3. xyz Coordinates for DFT optimized structure of monomeric [(IPrMe){(HCNDipp)<sub>2</sub>B}Ge]<sup>+</sup>

99

Ge	14.437464	8.327997	6.796690
C	14.263805	8.901105	4.756645
N	14.165481	8.093976	3.676912
C	13.940393	6.631878	3.838366
H	13.586791	6.545698	4.879041
C	12.822115	6.099622	2.947810
H	11.954683	6.768033	2.968266
H	12.503152	5.121430	3.329160
H	13.151513	5.959060	1.911747
C	15.258961	5.869309	3.701127
H	15.654035	5.937784	2.678995
H	15.094064	4.807752	3.927333
H	16.014404	6.259720	4.395424
C	14.442276	8.814180	2.506952
C	14.717252	10.104184	2.896496
N	14.590411	10.133316	4.292521
C	14.923012	11.239870	5.230169
H	14.578431	10.860900	6.211287
C	14.139510	12.521126	4.954245
H	14.469638	13.016397	4.034192
H	14.307252	13.218437	5.783998
H	13.064301	12.322089	4.886553
H	12.302192	6.617934	12.498584
H	11.157300	5.848358	11.378636
C	16.437038	11.449603	5.298223
H	16.950572	10.513509	5.552773
H	16.670182	12.196370	6.067422
H	16.833967	11.816175	4.343093
C	15.010702	11.290466	2.043174
H	15.249183	10.965813	1.024212
H	15.867416	11.866355	2.414068
H	14.144580	11.965203	1.983541
C	14.365335	8.253408	1.127909
H	14.787428	8.967301	0.411815
H	13.325550	8.056324	0.830696
H	14.928425	7.316249	1.033028
B	12.503878	8.923855	7.371286
N	12.293636	9.390168	8.727797
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H	10.569326	10.026188	9.869299
C	10.269598	9.344260	7.774168
H	9.200240	9.369370	7.590199
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C	10.249461	6.938603	5.691660
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H	12.660125	5.989376	6.720151
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H	8.363694	5.722144	7.321380
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H	9.211049	4.359659	6.555376
C	9.632893	6.372210	4.567329
H	9.300066	5.334862	4.601908
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H	8.924439	6.666899	2.552426

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H	8.945756	11.373575	4.345212
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H	10.489145	11.032198	2.298008
H	12.072703	10.245765	2.515748
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C	15.049677	12.611594	8.699486
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H	15.525382	13.084721	9.569266
H	14.840916	13.413935	7.978024
C	12.760388	12.848379	9.766214
H	12.550571	13.715881	9.124258
H	13.176735	13.215564	10.715251
H	11.808722	12.346705	9.986591
C	14.925671	10.713081	11.008384
H	15.501563	11.622187	11.181884
C	15.122099	9.611869	11.841302
H	15.846493	9.668936	12.654858
C	14.401285	8.437701	11.634215
H	14.572889	7.579800	12.285780
C	13.459273	8.340026	10.601059
C	12.688553	7.044681	10.384863
H	12.068009	7.166744	9.485652
C	13.637240	5.862017	10.125382
H	13.061082	4.946878	9.929404
H	14.285431	5.665791	10.990745
H	14.285387	6.055900	9.258704
C	11.741098	6.761126	11.564065
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