Supplementary Information
Synthesis of Bismuthanyl-substituted monomeric Triel Hydrides

Robert Szlosek[a], Christian Marquardt,[a] Oliver Hegen,[a] Gábor Balázs,[a] Christoph Riesinger[a], Alexey Y. Timoshkin[b], and Manfred Scheer[a]*

[a] Department of Inorganic Chemistry, Universität Regensburg, 93053 Regensburg, Germany

[b] Institute of Chemistry, Universitetskaya nab. 7/9, 199034 St. Petersburg, Russia

*Manfred.Scheer@ur.de

Table of Contents

Author contributions

R. Szlosek – performing experimental work (incl. reproductions and analytical data of **1b** and **1c**), writing of the original draft, acquisition (**1a**, **2**) and refinement of (**2**) of X-ray data.

Ch. Marquardt – original preparation of **1c** & acquisition/refinement of X-ray data for **1c**.

O. Hegen – original preparation of **1b** & acquisition/refinement of X-ray data for **1b**.

G. Balázs – conceptualization, project management.

Ch. Riesinger – refinement of X-ray data for **1a**.

A. Y. Timoshkin – conceptualization, quantum chemical calculations, funding, project management.

M. Scheer – writing of the original draft, conceptualization, funding, project management.

1. General Information

a. Working Techniques

All working steps were carried out under argon inert gas atmosphere using standard Schlenk and glove-box techniques under exclusion of light due to the sensitivity of the reagents and products. All glassware was dried in an oven at 150 °C and pre-conditioned in high vacuum (< 10^{-3} mbar, 650 °C) shortly before use. Traces of H_2O and O_2 were removed from argon gas by by passing it through a BASF R 3-11 ($CuO/MgSiO_3$) catalyst, concentrated H_2SO_4, Orange Gel and Sicapent® supported on pumice stone. Prior to use, solvents were purified using an MBraun SPS-800 solvent purification system, degassed at room temperature, and stored over molecular sieves for at least 48 hours. C_6D_6 was dried over Na/K, distilled, degassed at room temperature, and stored over molecular sieves (4 Å). CD_3CN was dried repeatedly over molecular sieves (3 Å). Elemental Analysis (CHNS) was performed by the in-house facility. Mass spectra were recorded on a Jeol AccuTOF GCX mass spectrometer (LIFDI-MS) mass spectrometer by the in-house facility.

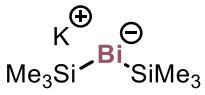
IDipp·GaH_2(OTf),[1] IDipp·BH_2I,[1] IMe_4·BH_3,[2] and $Bi(SiMe_3)_3$[3] were prepared according to literature procedures. BH_3·SMe_2/ BH_3·THF was purchased from ABCR and used as received. 1,4-benzoquinone was freshly sublimed prior to use. Preparation involving $KBi(SiMe_3)_2(THF)_{0.3}$ or the bismuth containing products were conducted under exclusion of light.

b. Spectroscopic Analysis

All NMR spectra were recorded on a BRUKER Avance 400 (frequencies: ^{1}H: 400.13 MHz, ^{11}B: 128.43 MHz, ^{13}C: 100.66 MHz, ^{29}Si: 79.50) or Avance 300 (^{1}H: 300.13 MHz, ^{13}C: 75.47 MHz) spectrometers. Substances of reference are $Si(CH_3)_4$ (^{1}H, ^{13}C, ^{29}Si) and BF_3·Et_2O (^{11}B). Chemical shifts δ are presented in ppm referring to the external standards and coupling constants J are given in Hz without consideration of absolute signs.

2. Experimental Details

a. Synthesis of $KBi(SiMe_3)_2(THF)_{0.3}$

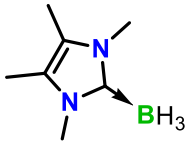


A round-bottom flask was charged with $Bi(SiMe_3)_3$ (18.0 g, 42.0 mmol) and the compound dissolved in tetrahydrofuran (10 mL). The solution was cooled to -65 °C and solid KO^tBu was added (4.8 g, 42.0 mmol). After stirring at room temperature for 1.5 hours, all volatiles were removed *in vacuo*, yielding a brown-greenish crude product. The solid product was transferred onto a glass frit and washed three times with 30 mL of *n*-pentane each. The product was then dried *in vacuo* (16.8 g, 96%). According to ^{1}H NMR spectroscopy (*vide infra*), the content of tetrahydrofuran in the final product was determined.

^{1}H NMR (300.13 MHz, CD_3CN, 298 K): 0.63 (s, $Si(CH_3)_3$).

$^{13}C\{^1H\}$ NMR (75.47 MHz, CD_3CN, 298 K): 12.1 (s).

b. Synthesis of $IMe_4{\cdot}BH_3$



A Schlenk tube was charged with IMe_4 (1.27 g, 10.3 mmol) and the compound dissolved in toluene (10 mL). After cooling the solution to -40 °C, neat $BH_3{\cdot}SMe_2$ (1.45 mL, excess) was added *via* syringe. The mixture was stirred overnight at room temperature and then all volatiles were removed *in vacuo*, yielding $IMe_4{\cdot}BH_3$ as a white powder (1.24 g, 87%).

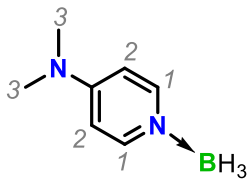
^{1}H NMR (400.30 MHz, C_6D_6, 298 K): 1.20 (s, 6 H, 2 × CH_3), 2.03 (q, broad, 3 H, BH_3, $^1J_{HB}$ = 87 Hz), 3.13 (s, 6 H, 2 × NCH_3).

$^{11}B\{^1H\}$ NMR (128.43 MHz, C_6D_6, 298 K): -35.8 (s, broad).

^{11}B NMR (128.43 MHz, C_6D_6, 298 K): -35.8 (q, broad, $^1J_{HB}$ = 87 Hz).

The NMR data are consistent with the literature values.[2]

c. Synthesis of $DMAP{\cdot}BH_3$



$BH_3{\cdot}THF$ (5 mL, 1.0 M in THF, 5.0 mmol) was added to a solution of DMAP (610 mg, 5.0 mmol) in toluene (8 mL), resulting in an immediate precipitation of a white solid. All volatiles are then removed *in vacuo* and the product dried under reduced pressure. The residue is washed twice with *n*-hexane (10 mL each) and dried under reduced pressure (355 mg, 52%).

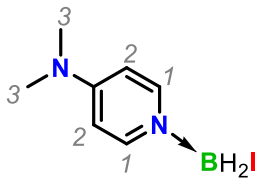
^{1}H NMR (400.30 MHz, C_6D_6, 298 K): 1.89 (s, 6 H, C3*H*), 3.63 (q, 3 H, BH_3, $^1J_{HB}$ = 95 Hz), 5.49 (m, 2 H, C2*H*), 8.04 (m, 2 H, C1*H*).

$^{11}B\{^1H\}$ NMR (128.43 MHz, C_6D_6, 298 K): -12.2 (s, broad).

^{11}B NMR (128.43 MHz, C_6D_6, 298 K): -12.2 (q, broad, $^1J_{HB}$ = 95 Hz).

The NMR data are consistent with the literature values.[4]

d. Synthesis of DMAP·BH_2I



Solid I_2 (250 mg, 0.98 mmol) was slowly added to a solution of BH_3·DMAP (272 mg, 2.0 mmol) in benzene (5 mL, gas evolution and precipitation of the product could be observed). After stirring for two hours at room temperature, all volatiles are removed *in vacuo* in the residue is washed with *n*-hexane (10 mL each). After drying under reduced pressure, the product is obtained as a white solid (425 mg, 81%).

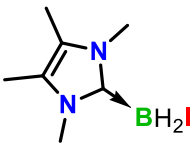
^1H NMR (400.30 MHz, CD_2Cl_2, 298 K): 3.04 (s, 6 H, C3*H*), 3.54 (q, 2 H, BH_2, $^1J_{HB}$ ≈ 130 Hz), 6.52 (m, 2 H, C2*H*), 8.06 (m, 2 H, C1*H*).

$^{11}B\{^1H\}$ NMR (128.43 MHz, CD_2Cl_2, 298 K): -11.7 (s, broad).

^{11}B NMR (128.43 MHz, CD_2Cl_2, 298 K): -11.7 (t, broad, $^1J_{HB}$ = 130 Hz).

Elemental Analysis ($C_7H_{12}BIN_2$) [%]: calc. C 32.10, H 4.62, N 10.70; found C 32.82, H 4.55, N 10.83.

e. Synthesis of IMe_4·BH_2I



A Schlenk tube was charged with IMe_4·BH_3 (272 mg, 1.97 mmol) and the solid dissolved in benzene (5 mL). Then, a solution of I_2 (243 mg, 0.94 mmol) in benzene was added under cooling with a water bath (room temperature) and the reaction mixture stirred overnight at room temperature. Subsequently, all volatiles were removed *in vacuo*, yielding a slightly yellowish powder (511 mg, 97%).

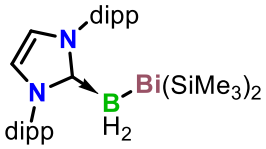
^1H NMR (400.30 MHz, CD_2Cl_2, 298 K): 1.11 (s, 6 H, 2 × CH_3), 3.02 (s, 6 H, 2 × NCH_3), 3.10 (m, broad, 2 H, BH_2).

$^{11}B\{^1H\}$ NMR (128.43 MHz, CD_2Cl_2, 298 K): -30.5 (s, broad).

^{11}B NMR (128.43 MHz, CD_2Cl_2, 298 K): -30.5 (t, broad, $^1J_{HB}$ = 102 Hz).

Elemental Analysis ($C_7H_{14}BIN_2$) [%]: calc. C 31.86, H 5.35, N 10.61; found C 32.76, H 5.21, N 10.41.

f. Synthesis of IDipp·$BH_2Bi(SiMe_3)_2$ (1a)



IDipp·BH_2I (212 mg, 0.4 mmol) was dissolved in tetrahydrofuran (5 mL) and cooled to -80 °C. Then, solid $KBi(SiMe_3)_2(THF)_{0.3}$ (250 mg, 0.6 mmol) was added. The solution was allowed to reach room temperature over 18 hours and the formation of a black suspension was observed. All volatiles were subsequently removed *in vacuo* and the residue suspended in toluene (8 mL). The solution was filtered through a P4 glass frit covered with Celite and all volatiles removed *in vacuo*, yielding IDipp·$BH_2Bi(SiMe_3)_2$ as a black powder (169 mg, 56%).

^{1}H NMR (400.30 MHz, C_6D_6, 298 K): 0.53 (s, 18 H, 2 × Si(C*H*$_3$)$_3$, $^2J_{HSi}$ = 6.78 Hz), 1.02 (d, 12 H, 4 × ^{i}Pr-C*H*$_3$, $^3J_{HH}$ = 6.92 Hz), 1.47 (d, 12 H, 4 × ^{i}Pr-CH$_3$, $^3J_{HH}$ = 6.92 Hz), 2.24 (q, broad, 2 H, B*H*$_2$, $^1J_{HB}$ ≈ 100 Hz), 2.28 (sep, 4 H, 4 × ^{i}Pr-C*H*, $^3J_{HH}$ = 6.92 Hz), 6.34 (s, 2 H, NC*H*C*H*N), 7.14 (d, 4 H, 4 × aryl-C$_{meta}$*H*, $^3J_{HH}$ = 7.66 Hz), 7.25 (t, 2 H, 2 × aryl-C$_{para}$H, $^3J_{HH}$ = 7.66 Hz).

^{13}C{^{1}H} NMR (100.66 MHz, C_6D_6, 298 K): 5.1 (s, ^{29}Si satellite peaks with $^1J_{SiC}$ = 41 Hz, Si(*C*H$_3$)$_3$), 23.3 (s, ^{i}Pr-*C*H$_3$), 25.4 (s, ^{i}Pr-*C*H$_3$), 28.7 (s, *C*H(CH$_3$)$_2$), 121.7 (s, *Ar*), 124.5 (s, *Ar*), 130.1 (s, N*C*H), 134.3 (s, *Ar*), 145.4 (s, *Ar*).

^{11}B{^{1}H} NMR (128.43 MHz, C_6D_6, 298 K): -42.1 (s, broad).

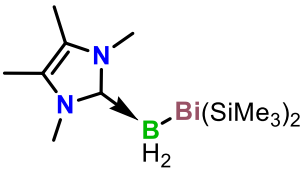
^{11}B NMR (128.43 MHz, C_6D_6, 298 K): -42.1 (t, very broad, $^1J_{HB}$ ≈ 100 Hz).

^{1}H, ^{29}Si HMBC (F2: 400.13 MHz F1: 79.50 MHz, C_6D_6, 298 K): 0.52 ppm/-32.2 ppm (s, *Si*(C*H*$_3$)$_3$).

LIFDI-MS (*m/z*): 756.44 ([M]$^+$ 89%), 389.31 ([IDipp-H]$^+$, 100%).

Elemental Analysis ($C_{33}H_{56}BBiN_2Si_2$+ 0.1 Bi**) [%]:** calc. C 50.97, H 7.26, N 3.60; found C 50.37, H 7.07, N 3.55. Elemental bismuth results from sample decomposition at room temperature.

g. Synthesis of $IMe_4·BH_2Bi(SiMe_3)_2$ (1b)



$IMe_4·BH_2I$ (40 mg, 0.15 mmol) was dissolved in tetrahydrofuran (5 mL) and cooled to -80 °C. Then, solid $KBi(SiMe_3)_2(THF)_{0.3}$ (94 mg, 0.23 mmol) was added. The solution was allowed to reach room temperature over 18 hours and the formation of a black precipitate was observed. All volatiles were subsequently removed *in vacuo* and the residue suspended in *n*-hexane (10 mL). The solution was filtered through a P4 glass frit covered with Celite. The black-brown solution was collected, and all volatiles were removed *in vacuo*, yielding the product as a black-brown powder (61 mg, 83%). Single crystals suitable for X-ray structure determination were obtained by storing a saturated solution of $IMe_4·BH_2Bi(SiMe_3)_2$ in *n*-hexane at -30 °C overnight.

^{1}H NMR (400.30 MHz, C_6D_6, 298 K): 0.81 (s, 18 H, 2 × Si(C*H*$_3$)$_3$, $^2J_{HSi}$ = 6.73 Hz), 1.09 (s, 6 H, 2 × C(C*H*$_3$)), 2.43 (q, very broad, 2 H, B*H*$_2$, $^1J_{HB}$ ≈ 107 Hz), 2.90 (s, 6 H, 2 × N(C*H*$_3$)).

$^{13}C\{^1H\}$ NMR (100.66 MHz, C_6D_6, 298 K): 6.5 (s, Si(CH_3)$_3$), 7.8 (s, C(CH_3)), 32.0 (s, C(CH_3), 122.6 (s, N(CH_3)).

$^{11}B\{^1H\}$ NMR (128.43 MHz, C_6D_6, 298 K): -39.5 (s, broad).

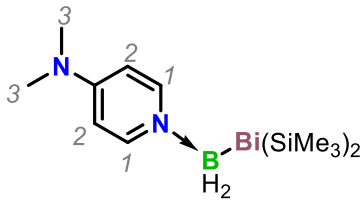
^{11}B NMR (128.43 MHz, C_6D_6, 298 K): -39.5 (t, broad, $^1J_{HB}$ = 107 Hz).

^1H, ^{29}Si HMBC (F2: 400.13 MHz F1: 79.50 MHz, C_6D_6, 298 K): 0.92 ppm/-33.7 ppm (s, Si(CH_3)$_3$).

LIFDI-MS (*m*/*z*): 492.20 ([M]$^+$, 10%), 261.20 ([(IMe$_4$)$_2$BH$_2$]$^+$, 40%), 247.20 ([(IMe$_4$)$_2$-H]$^+$, 100%).

Elemental Analysis ($C_{13}H_{32}BBiN_2Si_2$**) [%]:** calc. C 31.69, H 6.55, N 5.69; found C 31.61, H 6.24, N 5.66.

h. Synthesis of DMAP·BH$_2$Bi(SiMe$_3$)$_2$ (1c)



DMAP·BH_2I (39 mg, 0.15 mmol) was dissolved in toluene (5 mL) and cooled to -80 °C. Then, solid KBi(SiMe$_3$)$_2$(THF)$_{0.3}$ (75 mg, 0.18 mmol) was added to the solution. The mixture was stirred overnight in the cooling bath. Afterwards, the suspension was filtered through a P3 glass frit covered with Celite and the volatiles removed *in vacuo*, yielding DMAP·BH$_2$Bi(SiMe$_3$)$_2$ as a brown, extremely electrostatic solid (10 mg, 13%).

^1H NMR (400.30 MHz, C_6D_6, 298 K): 0.95 (s, 18 H, 2 × Si(CH_3)$_3$, $^2J_{HSi}$ = 6.98 Hz), 1.97 (s, 6 H, C3H), 4.74 (q, 2 H, $^1J_{BH}$ ≈ 120 Hz, BH_2), 5.50 (m, 2 H, C2H), 8.00 (m, 2 H, C1H).

$^{13}C\{^1H\}$ NMR (100.66 MHz, C_6D_6, 298 K): 6.2 (s, ^{29}Si satellite peaks with $^1J_{SiC}$ = 41 Hz, Si(CH_3)$_3$), 38.5 (s, C3), 106.7 (s, C2), 145.8 (s, C1), 153.6 (s, C(NMe$_2$)).

$^{11}B\{^1H\}$ NMR (128.43 MHz, C_6D_6, 298 K): -15.2 (s, broad).

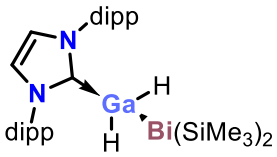
^{11}B NMR (128.43 MHz, C_6D_6, 298 K): -15.2 (t, very broad, $^1J_{HB}$ ≈ 120 Hz).

^1H, ^{29}Si HMBC (F2: 400.13 MHz F1: 79.50 MHz, C_6D_6, 298 K): 0.96 ppm/-29.8 ppm (s, Si(CH_3)$_3$).

LIFDI-MS (*m*/*z*): could not be performed due to the too fast decomposition of the sample.

Elemental Analysis ($C_{13}H_{30}BBiN_2Si_2$**) [%]:** could not be performed, as it was not possible to prepare an analytically clean sample of **1c** due to its extreme sensitivity and electrostatic nature.

i. Synthesis of IDipp·GaH$_2$Bi(SiMe$_3$)$_2$ (2)



IDipp·GaH$_2$(OTf) (91 mg, 0.15 mmol) was dissolved in tetrahydrofuran (5 mL) and cooled to -80 °C. Then, solid KBi(SiMe$_3$)$_2$(THF)$_{0.3}$ (112 mg, 0.27 mmol) was added in one portion. The solution was allowed to reach room temperature over 18 hours and the formation of a black precipitate was observed. All volatiles were subsequently removed *in vacuo* and the residue suspended in *n*-hexane (10 mL). The solution was filtered through a P4 glass frit covered with Celite. After removing the solvent *in vacuo*, IDipp·GaH$_2$Bi(SiMe$_3$)$_2$ could be obtained as a black powder (19 mg, 16%). Single crystals of **2** suitable for X-ray structure determination could be grown by slow evaporation of a solution of **2** in *n*-pentane at -80 °C under reduced pressure.

^{1}H NMR (300.13 MHz, C$_6$D$_6$, 298 K): 0.70 (s, 18 H, 2 × Si(C*H*$_3$)$_3$, $^2J_{HSi}$ = 7.15 Hz), 0.98 (d, 12 H, 4 × ^{i}Pr-C*H*$_3$, $^3J_{HH}$ = 6.89 Hz), 1.44 (d, 12 H, 4 × ^{i}Pr-CH$_3$, $^3J_{HH}$ = 6.89 Hz), 2.69 (sep, 4 H, 4 × ^{i}Pr-C*H*, $^3J_{HH}$ = 6.89 Hz), 4.97 (s, broad, 2 H, Ga*H*$_2$), 6.43 (s, 2 H, NC*H*C*H*N), 7.10 (d, superimposed, 4 H, 4 × aryl-C$_{meta}$*H*, $^3J_{HH}$ = 7.13 Hz), 7.25 (dd, 2 H, 2 × aryl-C$_{para}$H, $^3J_{HH}$ = 7.18 Hz, $^3J_{HH}$ = 8.56 Hz).

^{13}C{^{1}H} NMR (100.66 MHz, C$_6$D$_6$, 298 K): 6.0 (s, ^{29}Si satellite peaks with $^1J_{SiC}$ = 42 Hz, Si(*C*H$_3$)$_3$), 23.8 (s, ^{i}Pr-*C*H$_3$), 25.4 (s, ^{i}Pr-*C*H$_3$), 29.1 (s, *C*H(CH$_3$)$_2$), 124.1 (s, *Ar*), 124.4 (s, *Ar*), 130.7 (s, N*C*H), 135.2 (s, *Ar*), 145.5 (s, *Ar*).

^{1}H, ^{29}Si HMBC (F2: 400.13 MHz F1: 79.50 MHz, C$_6$D$_6$, 298 K): 0.70 ppm/-37.7 ppm (s, *Si*(C*H*$_3$)$_3$).

LIFDI-MS (*m*/*z*): 814.34 ([(M]$^+$, 46%), 459.24 ([IDipp-GaH$_2$]$^+$, 100%), 389.31 ([IDipp-H]$^+$, 31%).

Elemental Analysis (C$_{33}$H$_{56}$GaBiN$_2$Si$_2$**) [%]:** calc. C 48.59, H 6.92, N 3.43; found C 48.56, H 6.89, N 3.27.

j. Desilylation attempts of IDipp·BH$_2$Bi(SiMe$_3$)$_2$ with 1,4-benzoquinone/MeOH-*d*$_4$

Note: this experiment was conducted under exclusion of light to avoid decomposition of any forming Bi-D/Bi-H containing species.

A J.-Young tube was charged with IDipp·BH$_2$Bi(SiMe$_3$)$_2$ (83 mg, 0.12 mmol) and cooled to -80 °C. Then, a cold (-80 °C) solution of 1,4-benzoquinone (12 mg, 0.12 mmol) in 0.6 mL THF and 0.1 mL MeOH-*d*$_4$ was added to the tube. After vigorous shaking, the sample was submitted to variable-temperature NMR experiments. At T < 0 °C, no reaction was observed. Thus, the sample was warmed to room temperature and the NMR spectra were recorded subsequently (see below).

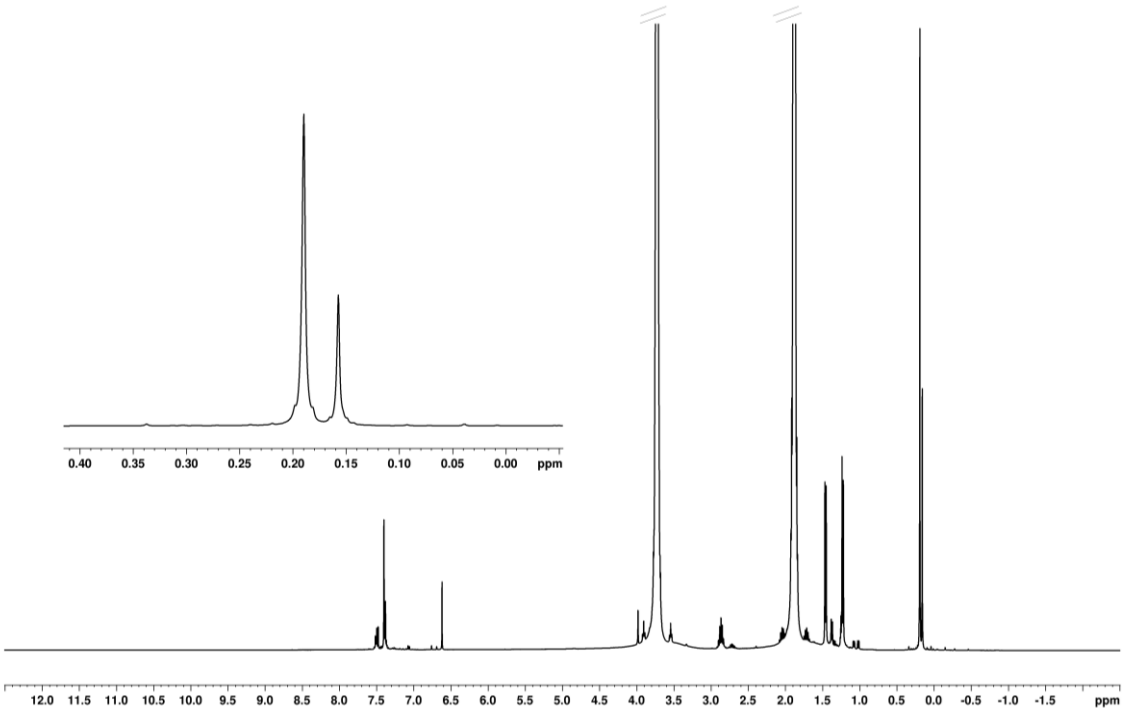


Figure S1: ^{1}H NMR spectrum of the reaction mixture of IDipp·$BH_2Bi(SiMe_3)_2$ with 1,4-benzoquinone and MeOH-d_4 (298 K; truncated signals correspond to tetrahydrofuran). The zoomed region shows a second resonance of {$SiMe_3$} groups.

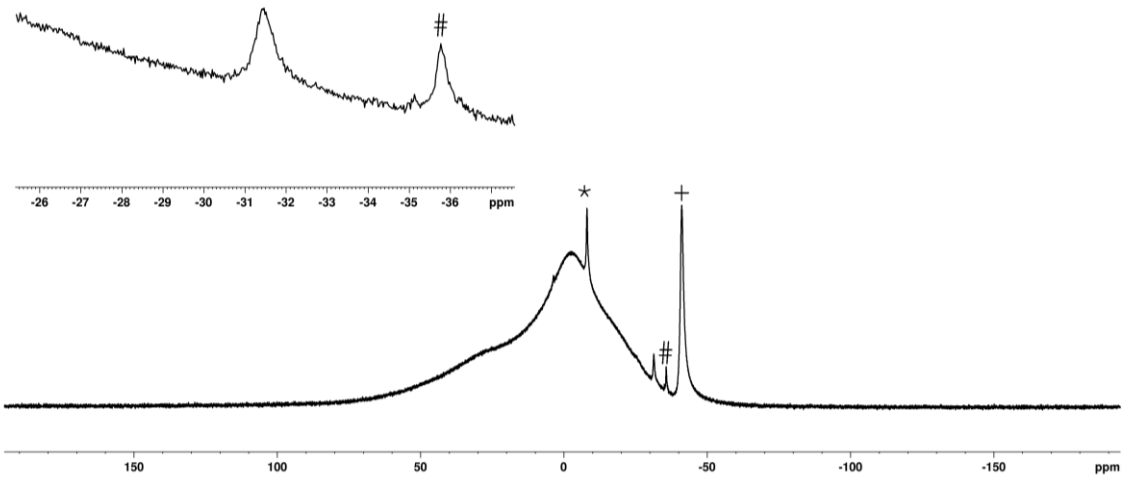


Figure S2: ^{11}B{^{1}H} NMR spectrum of the reaction mixture of IDipp·$BH_2Bi(SiMe_3)_2$ with 1,4-benzoquinone and MeOH-d_4 (298 K, * = IDipp·BH_2OMe, # = IDipp·BH_3, + = starting material).

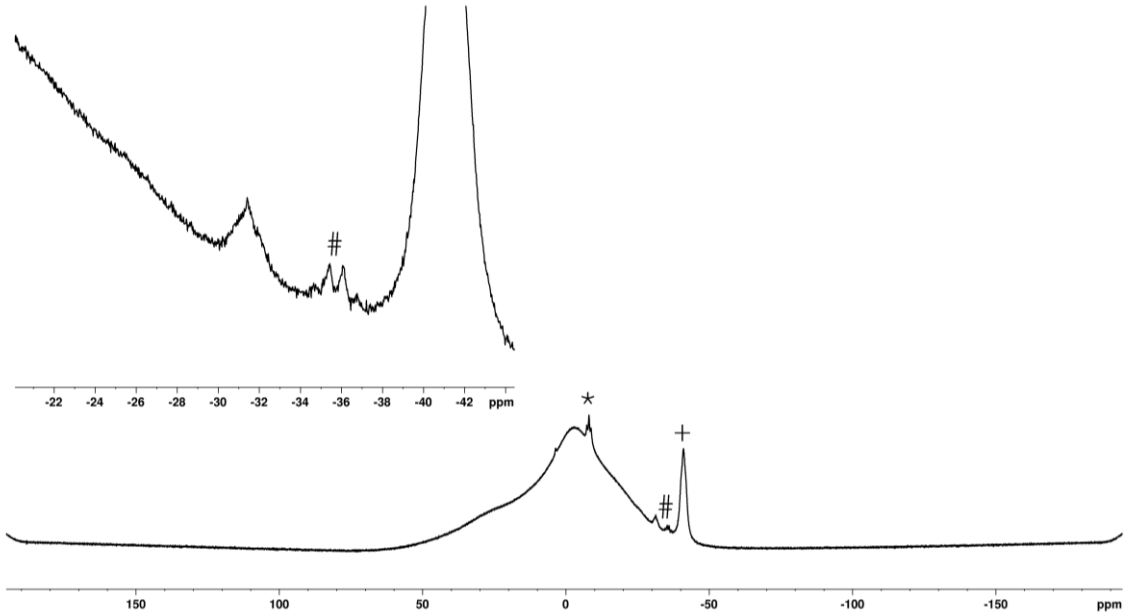


Figure S3: ^{11}B NMR spectrum of the reaction mixture of IDipp·$BH_2Bi(SiMe_3)_2$ with 1,4-benzoquinone and MeOH-d_4 (298 K, * = IDipp·BH_2OMe, # = IDipp·BH_3, + = starting material).

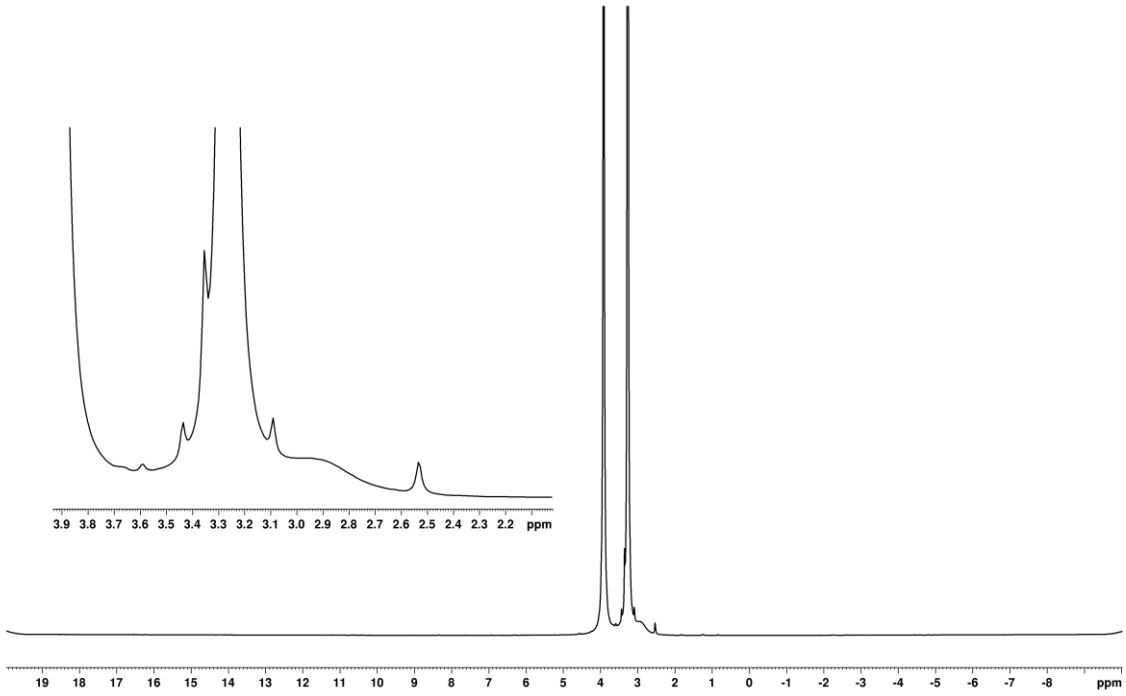


Figure S4: ^{2}H NMR spectrum of the reaction mixture of IDipp·$BH_2Bi(SiMe_3)_2$ with 1,4-benzoquinone and MeOH-d_4 (298 K).

3. NMR Data

a. $KBi(SiMe_3)_2(THF)_{0.3}$

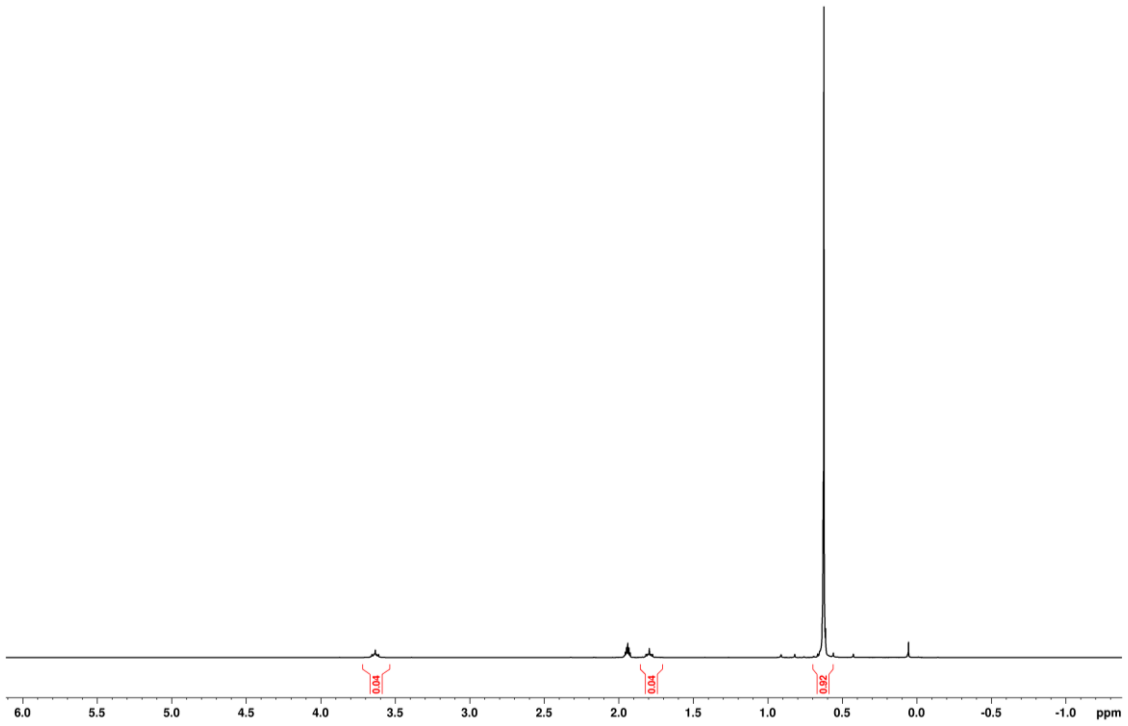


Figure S5: ^{1}H NMR spectrum of $KBi(SiMe_3)_2(THF)_{0.3}$ (CD_3CN, 298 K).

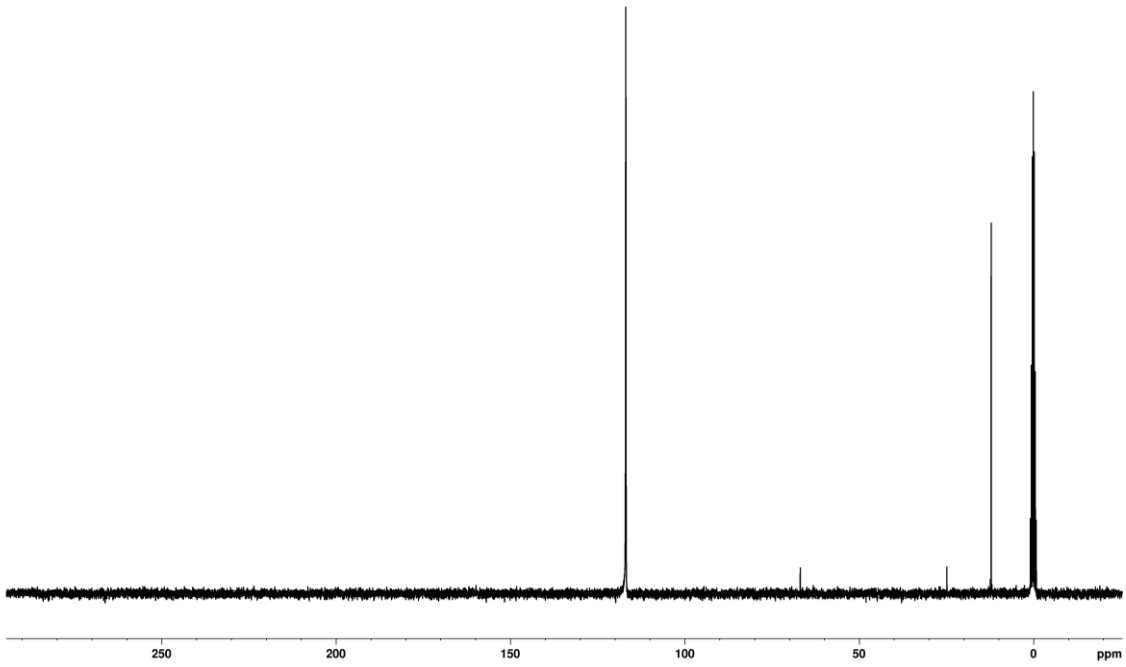


Figure S6: $^{13}C\{^{1}H\}$ NMR spectrum of $KBi(SiMe_3)_2(THF)_{0.3}$ (CD_3CN, 298 K).

b. DMAP·BH_3

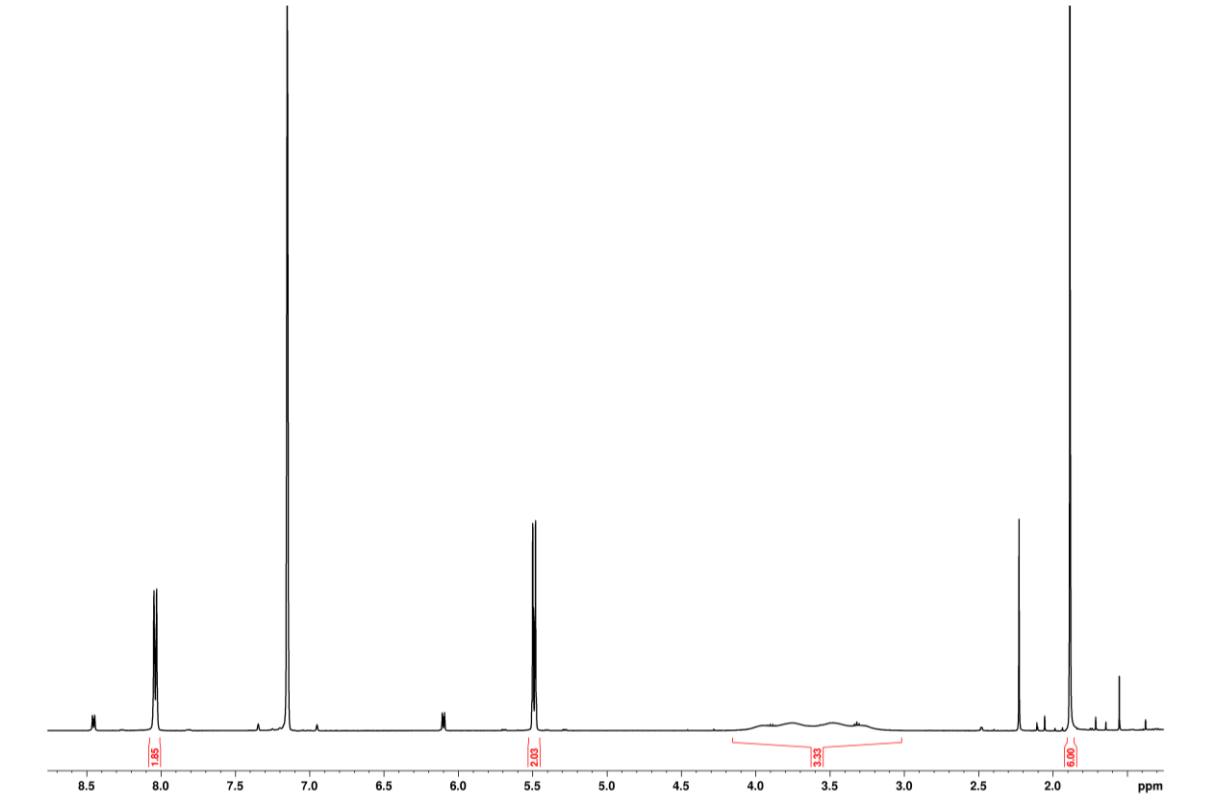


Figure S7: ^{1}H NMR spectrum of DMAP·BH_3 (C_6D_6, 298 K).

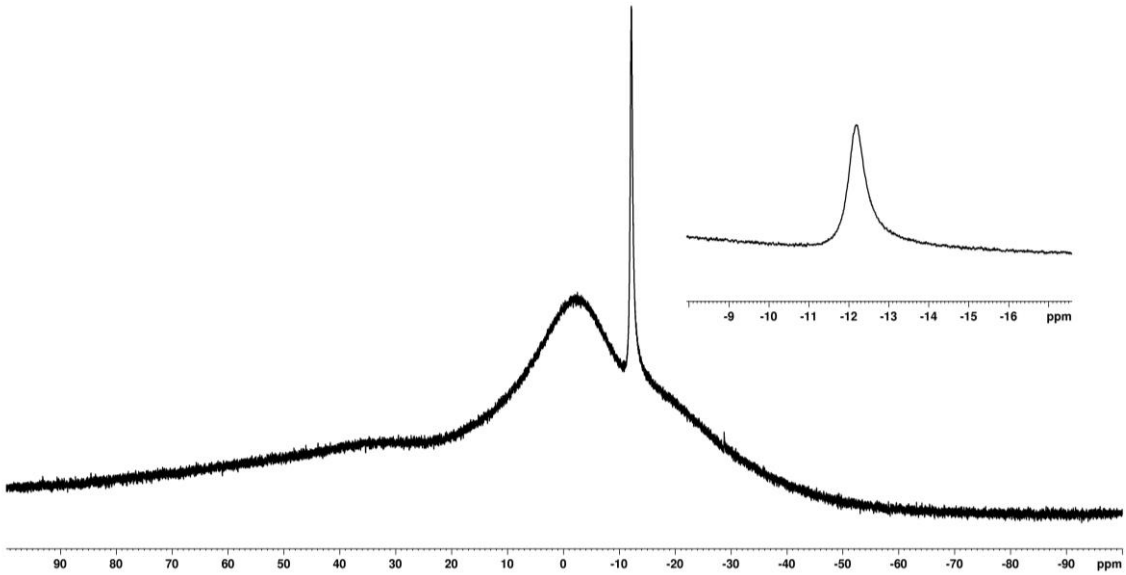


Figure S8: $^{11}B\{^{1}H\}$ NMR spectrum of DMAP·BH_3 (C_6D_6, 298 K).

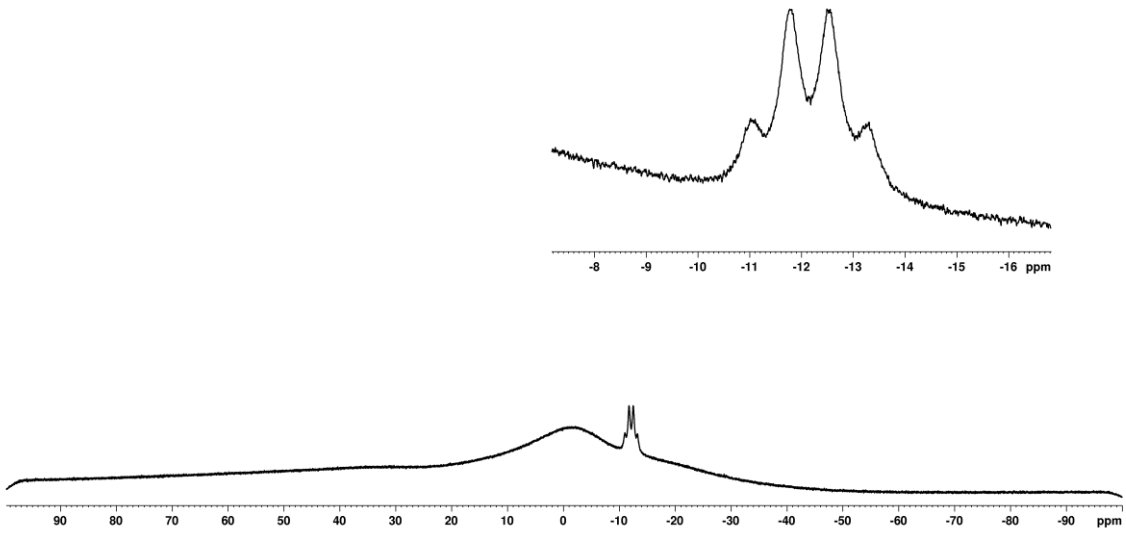


Figure S9: ^{11}B NMR spectrum of DMAP·BH_3 (C_6D_6, 298 K).

c. $IMe_4 \cdot BH_2I$

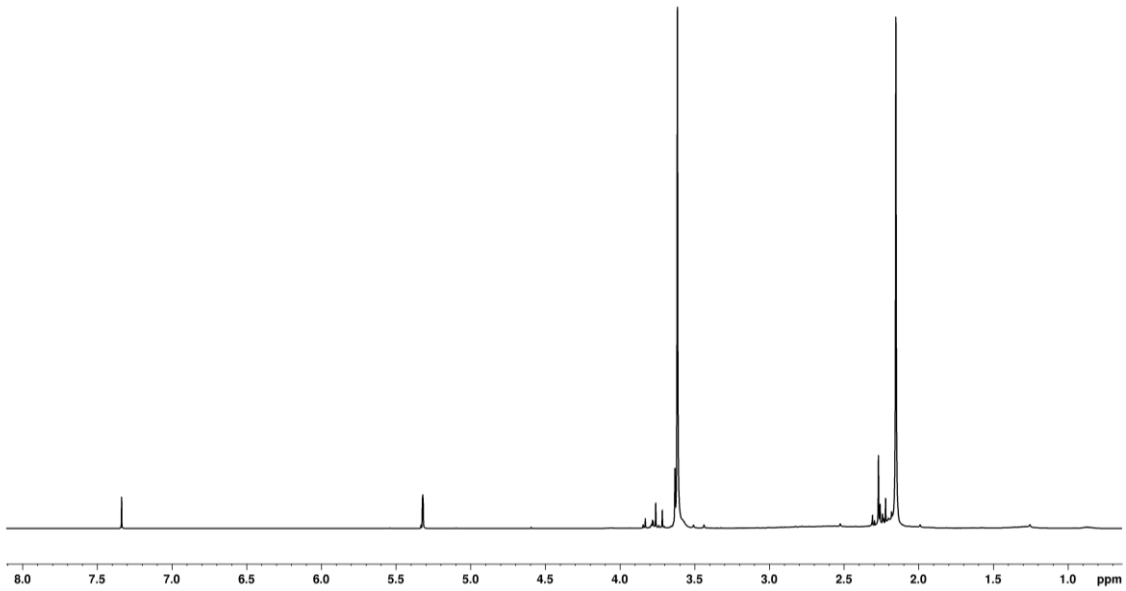


Figure S10: ^1H NMR spectrum of $IMe_4 \cdot BH_2I$ (CD_2Cl_2, 298 K).

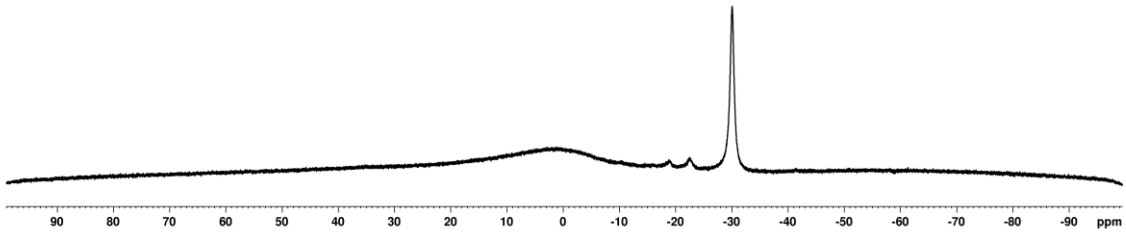


Figure S11: $^{11}B\{^{1}H\}$ NMR spectrum of $IMe_4 \cdot BH_2I$ (CD_2Cl_2, 298 K).

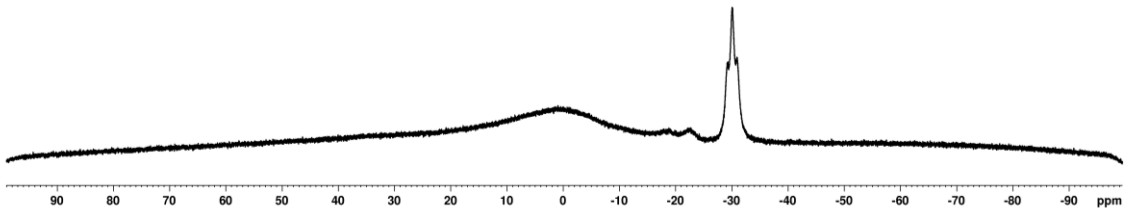


Figure S12: ^{11}B NMR spectrum of $IMe_4 \cdot BH_2I$ (CD_2Cl_2, 298 K).

d. DMAP·BH_2I

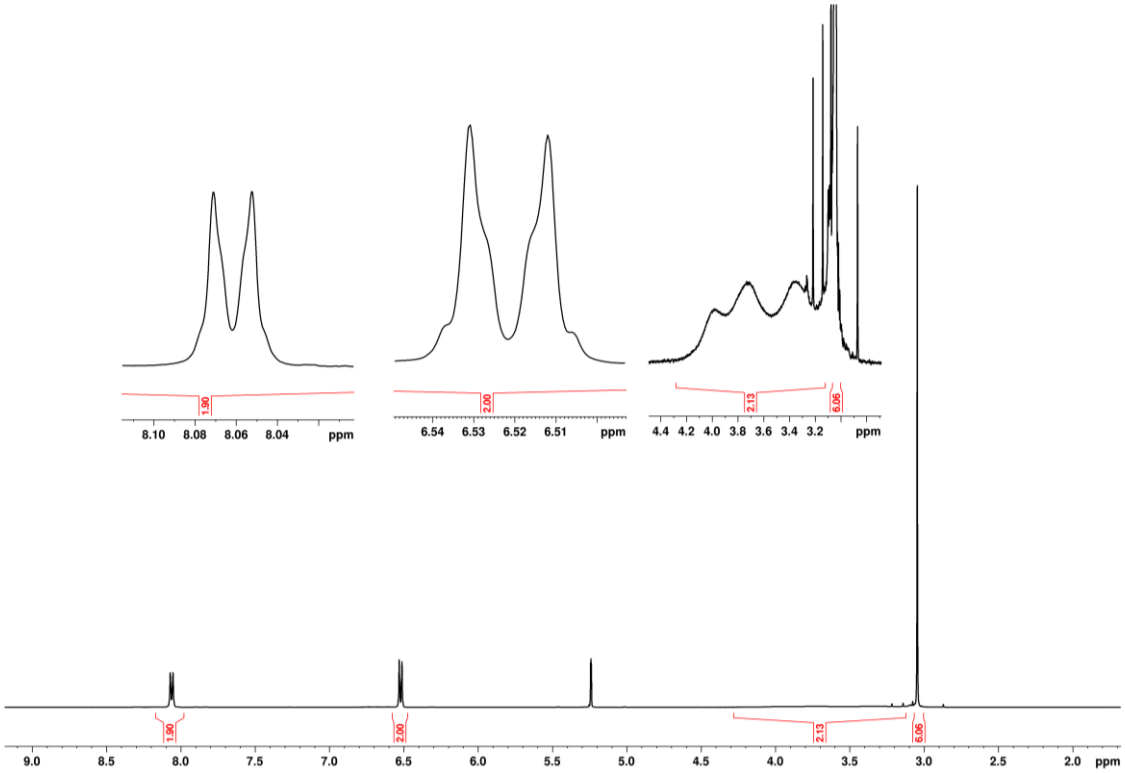


Figure S13: ^{1}H NMR spectrum of DMAP·BH_2I (C_6D_6, 298 K).

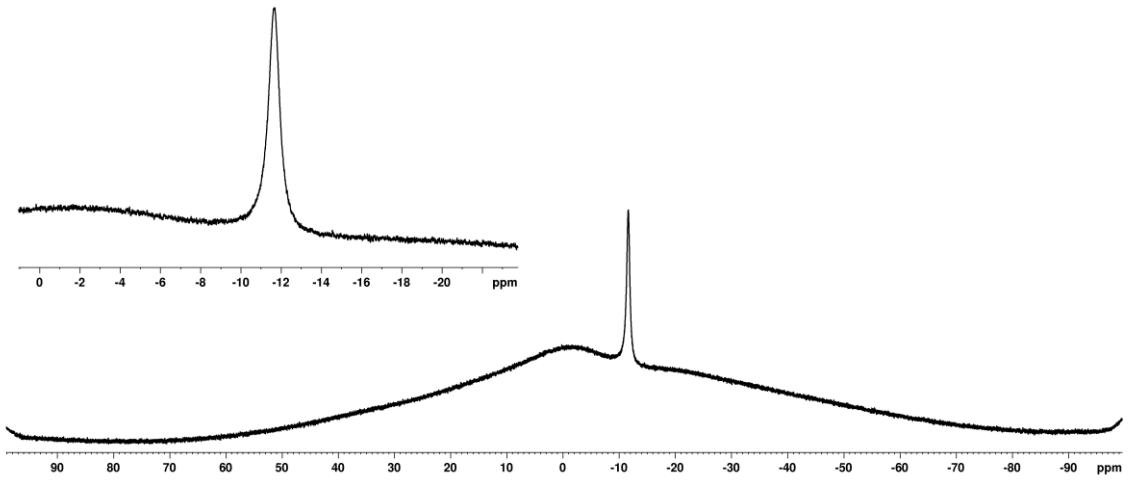


Figure S14: $^{11}B\{^{1}H\}$ NMR spectrum of DMAP·BH_2I (CD_2Cl_2, 298 K).

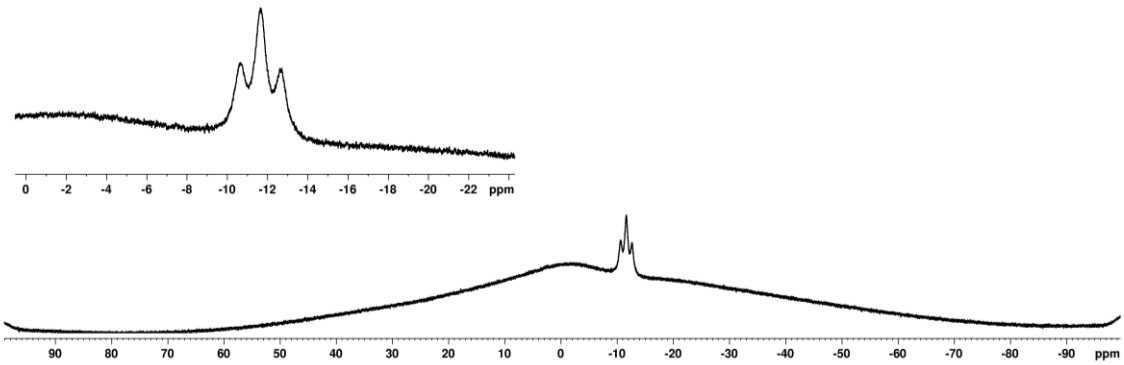


Figure S15: ^{11}B NMR spectrum of DMAP·BH_2I (CD_2Cl_2, 298 K).

e. DMAP·$BH_2Bi(SiMe_3)_2$

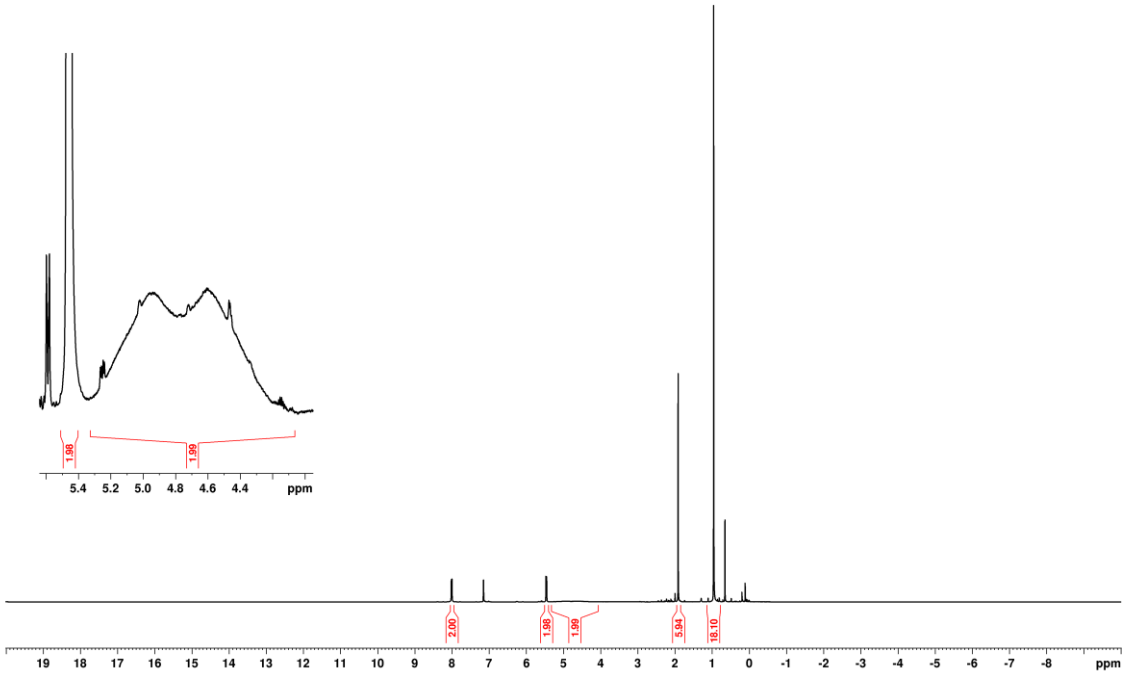


Figure S16: ^1H NMR spectrum of DMAP·$BH_2Bi(SiMe_3)_2$ (C_6D_6, 298 K).

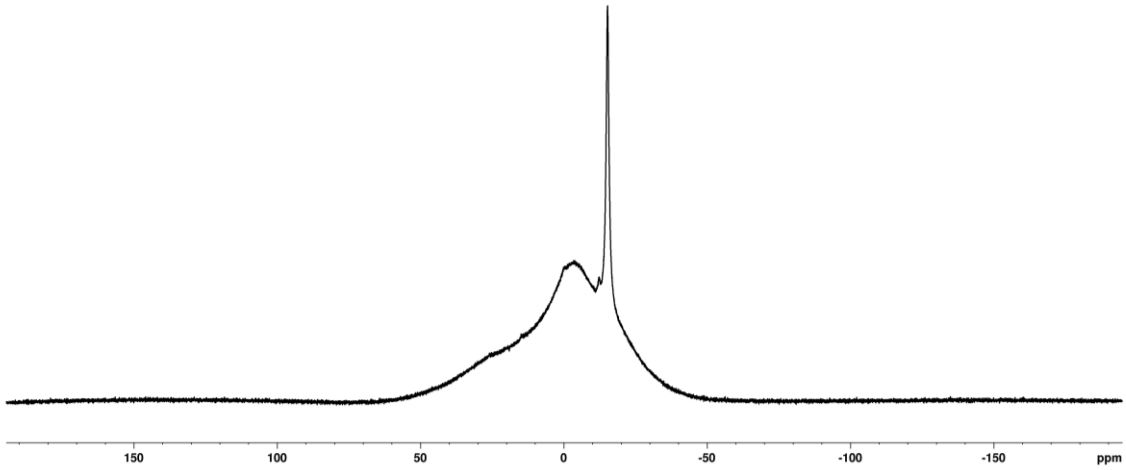


Figure S17: $^{11}B\{^{1}H\}$ NMR spectrum of DMAP·$BH_2Bi(SiMe_3)_2$ (C_6D_6, 298 K).

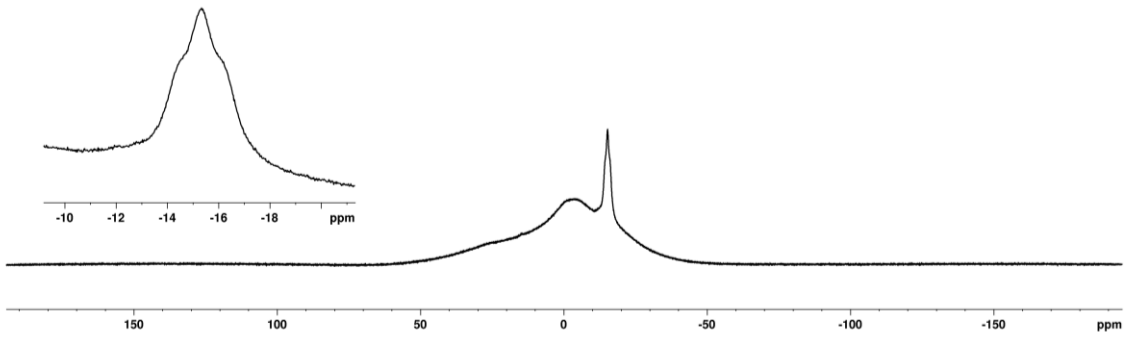


Figure S18: ^{11}B NMR spectrum of DMAP·$BH_2Bi(SiMe_3)_2$ (C_6D_6, 298 K).

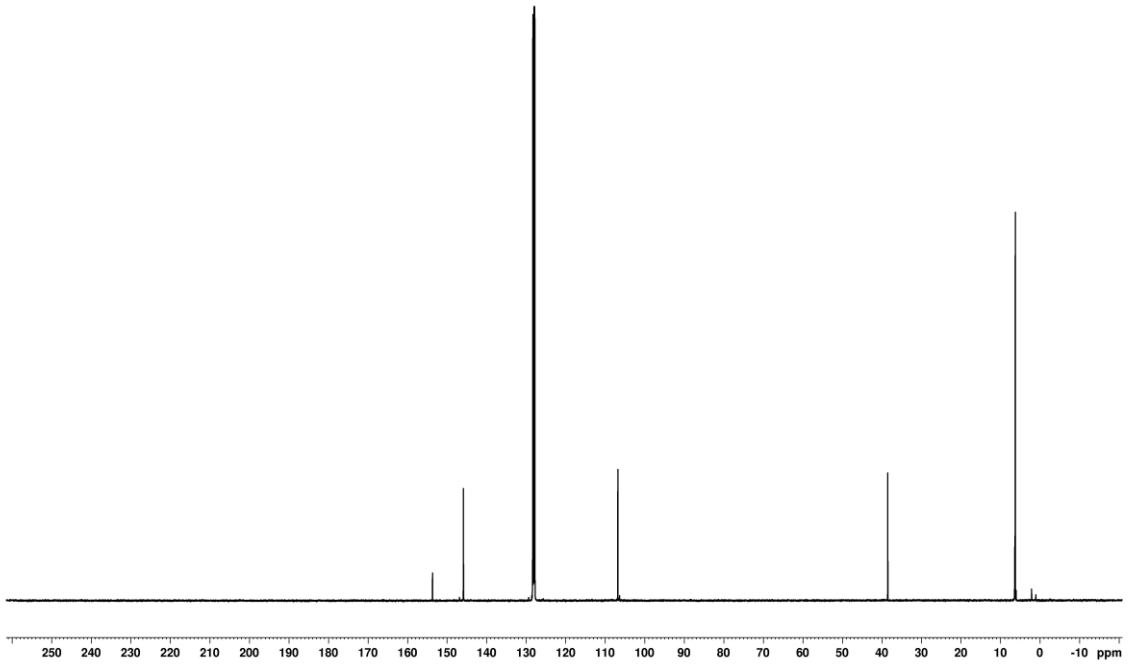


Figure S 19: $^{13}C\{^{1}H\}$ NMR spectrum of DMAP·$BH_2Bi(SiMe_3)_2$ (C_6D_6, 298 K).

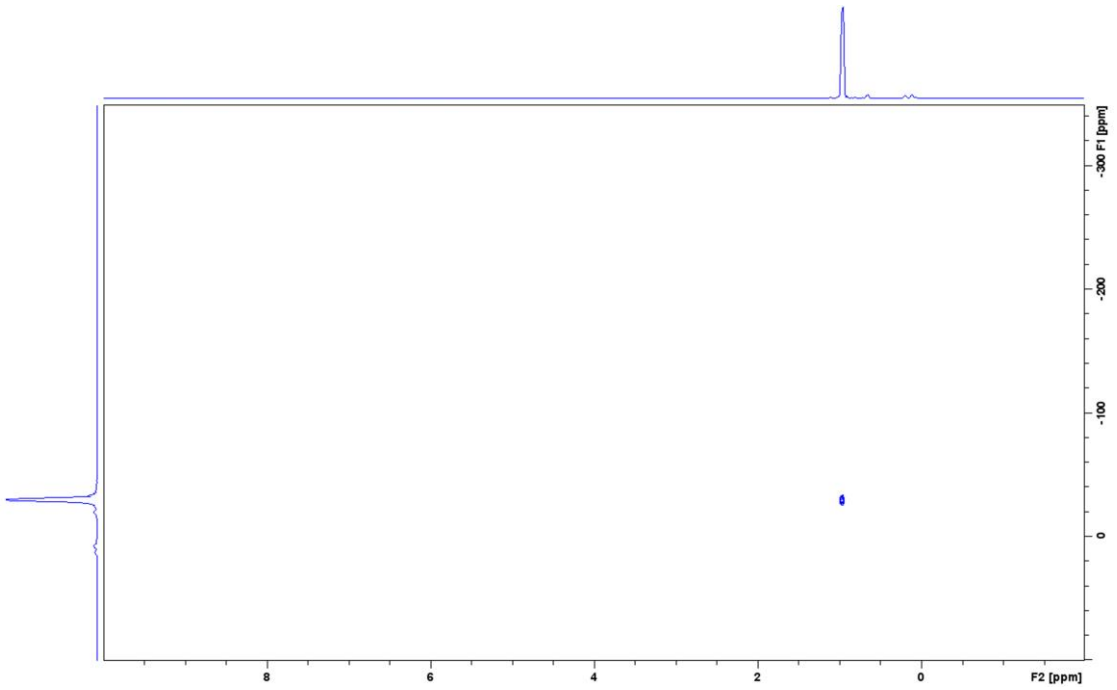


Figure S 20: ^{1}H, ^{29}Si HMBC spectrum of DMAP·$BH_2Bi(SiMe_3)_2$ (C_6D_6, 298 K).

f. IDipp·$BH_2Bi(SiMe_3)_2$

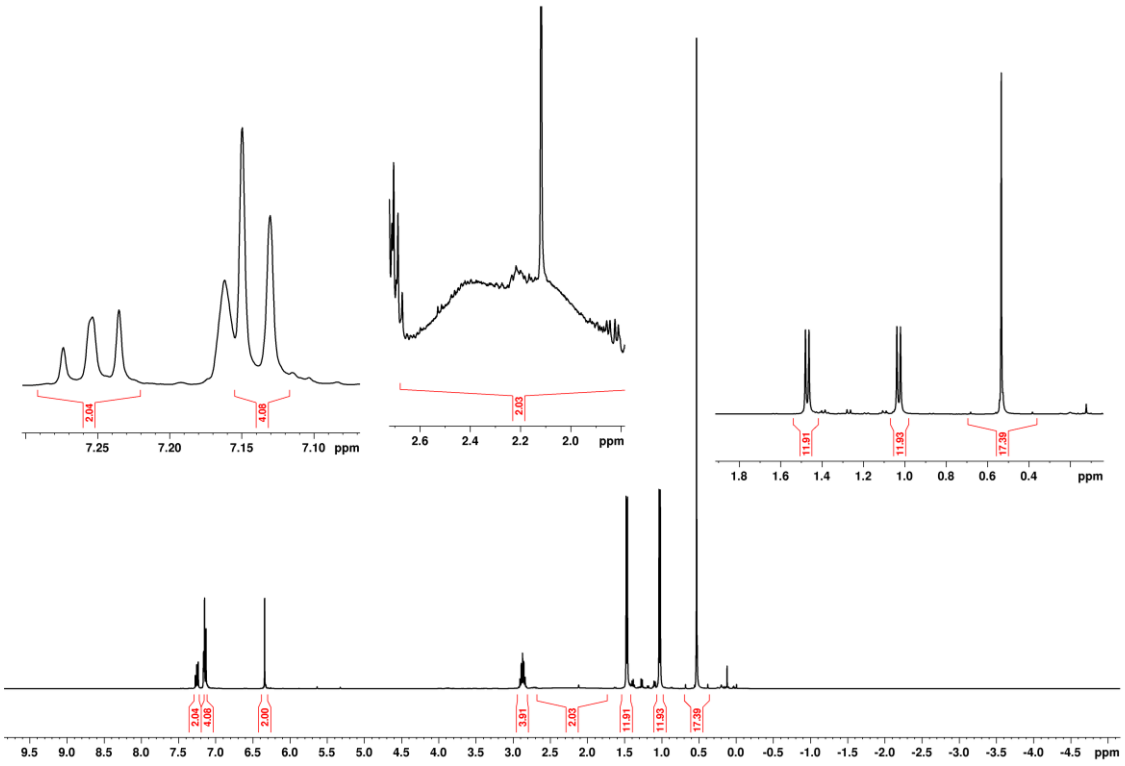


Figure S21: ^{1}H NMR spectrum of IDipp·$BH_2Bi(SiMe_3)_2$ (C_6D_6, 298 K).

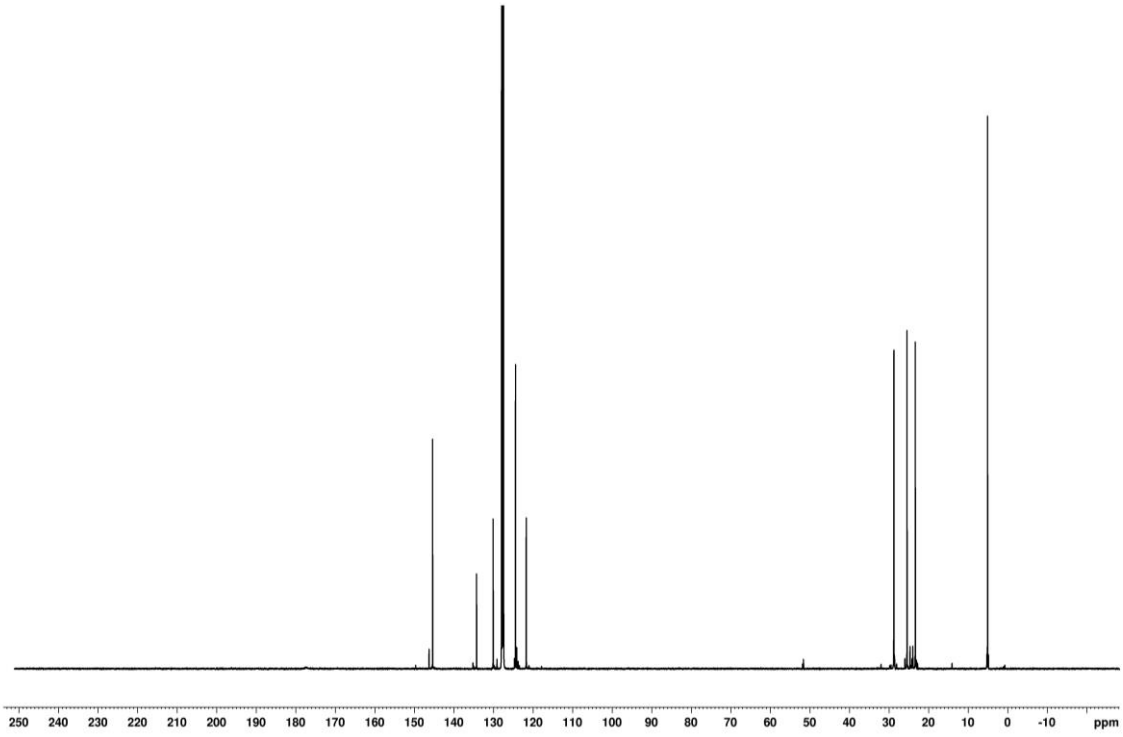


Figure S 22: $^{13}C\{^{1}H\}$ NMR spectrum of IDipp·$BH_2Bi(SiMe_3)_2$ (C_6D_6, 298 K).

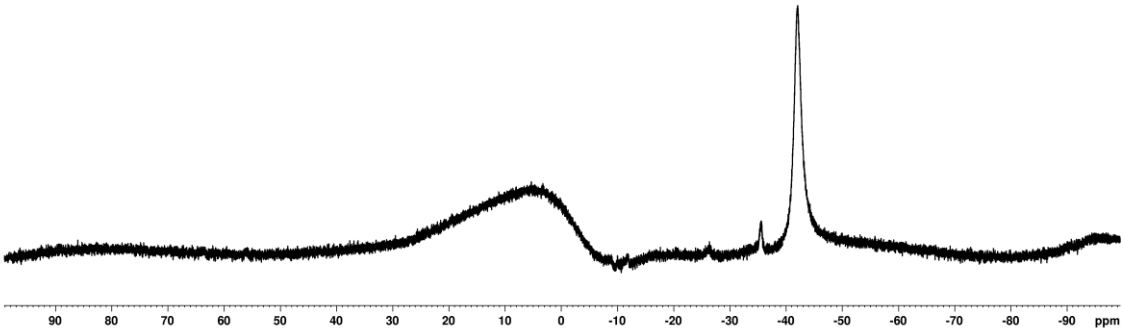


Figure S23: $^{11}B\{^{1}H\}$ NMR spectrum of IDipp·$BH_2Bi(SiMe_3)_2$ (C_6D_6, 298 K).

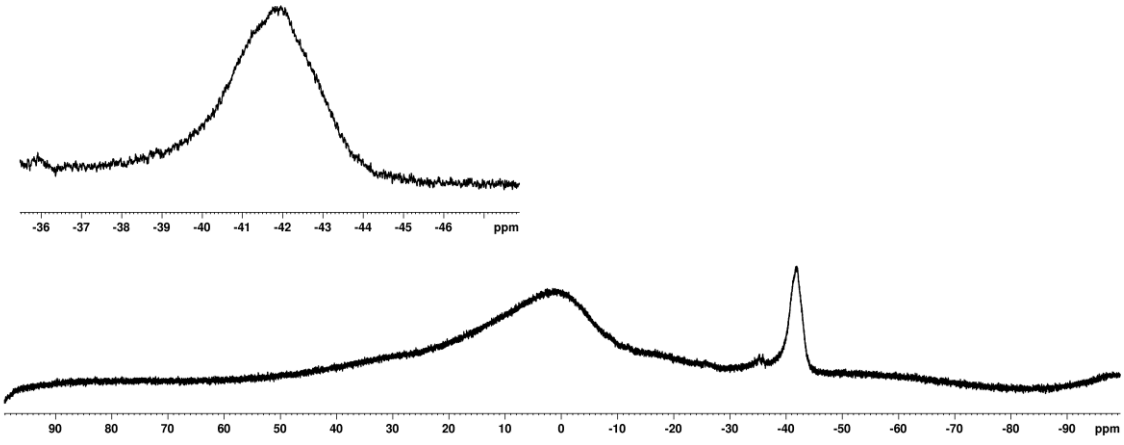


Figure S24: ^{11}B NMR spectrum of IDipp·$BH_2Bi(SiMe_3)_2$ (C_6D_6, 298 K).

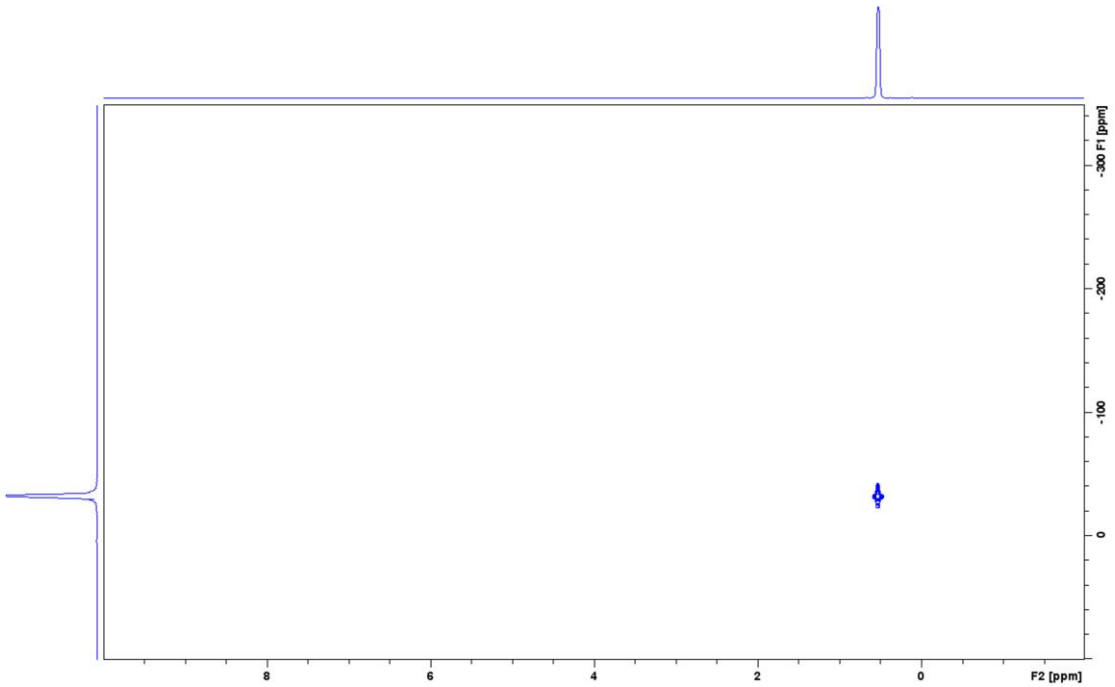


Figure S 25: ^{1}H, ^{29}Si HMBC spectrum of IDipp·$BH_2Bi(SiMe_3)_2$ (C_6D_6, 298 K).

g. $IMe_4 \cdot BH_2Bi(SiMe_3)_2$

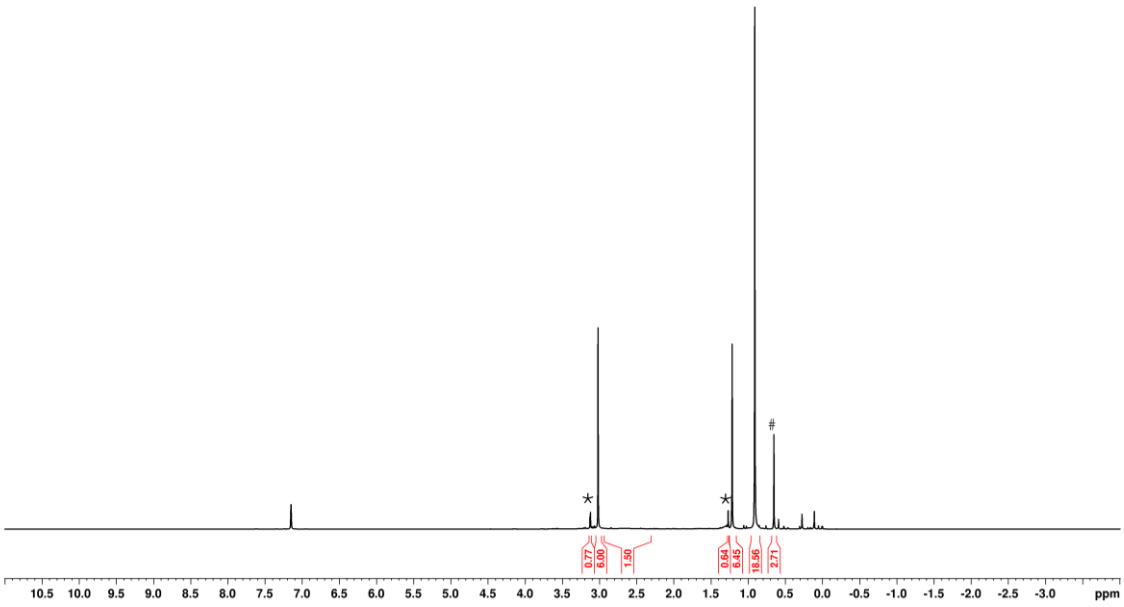


Figure S26: ^{1}H NMR spectrum of $IMe_4 \cdot BH_2Bi(SiMe_3)_2$ (C_6D_6, 298 K; side products from sample decomposition * = $IMe_4 \cdot BH_3$, # = $Me_3Si\text{-}SiMe_3$; ratios */**1b** = 0.09, #/**1b** = 0.14).

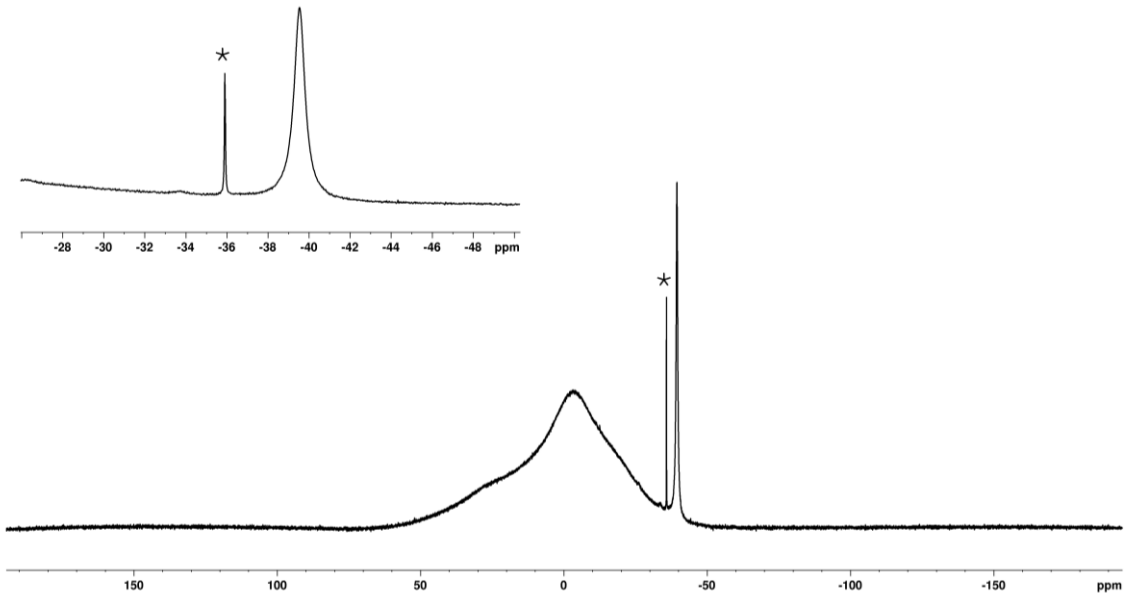


Figure S27: $^{11}B\{^{1}H\}$ NMR spectrum of $IMe_4 \cdot BH_2Bi(SiMe_3)_2$ (C_6D_6, 298 K, * = $IMe_4 \cdot BH_3$).

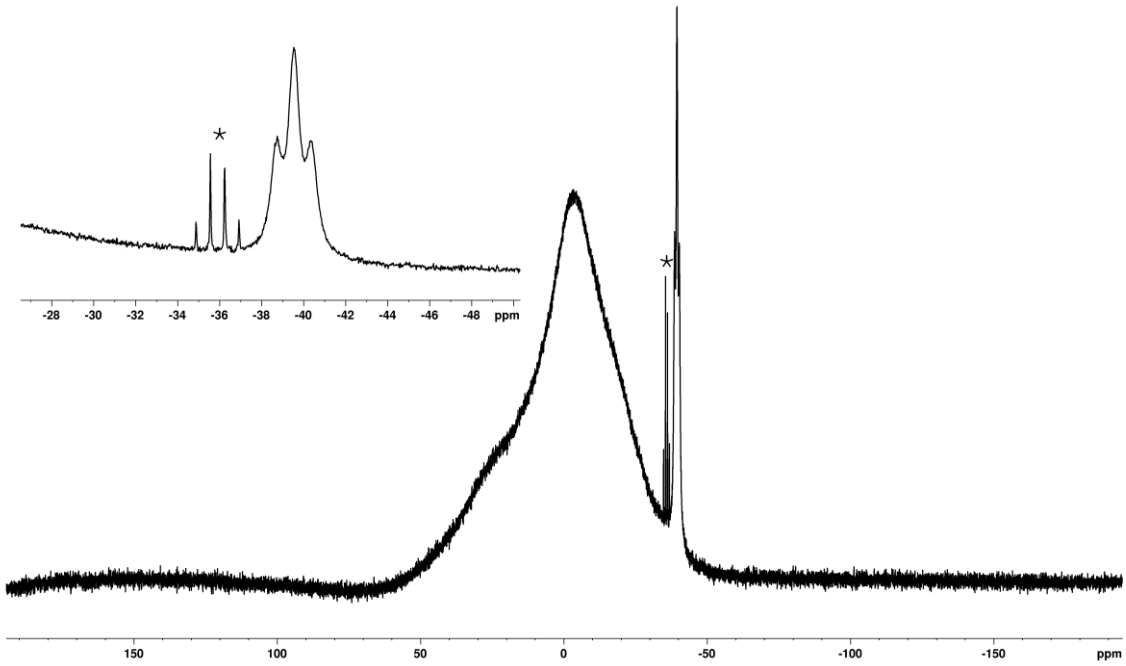


Figure S28: ^{11}B NMR spectrum of $IMe_4 \cdot BH_2Bi(SiMe_3)_2$ (C_6D_6, 298 K, * = $IMe_4 \cdot BH_3$).

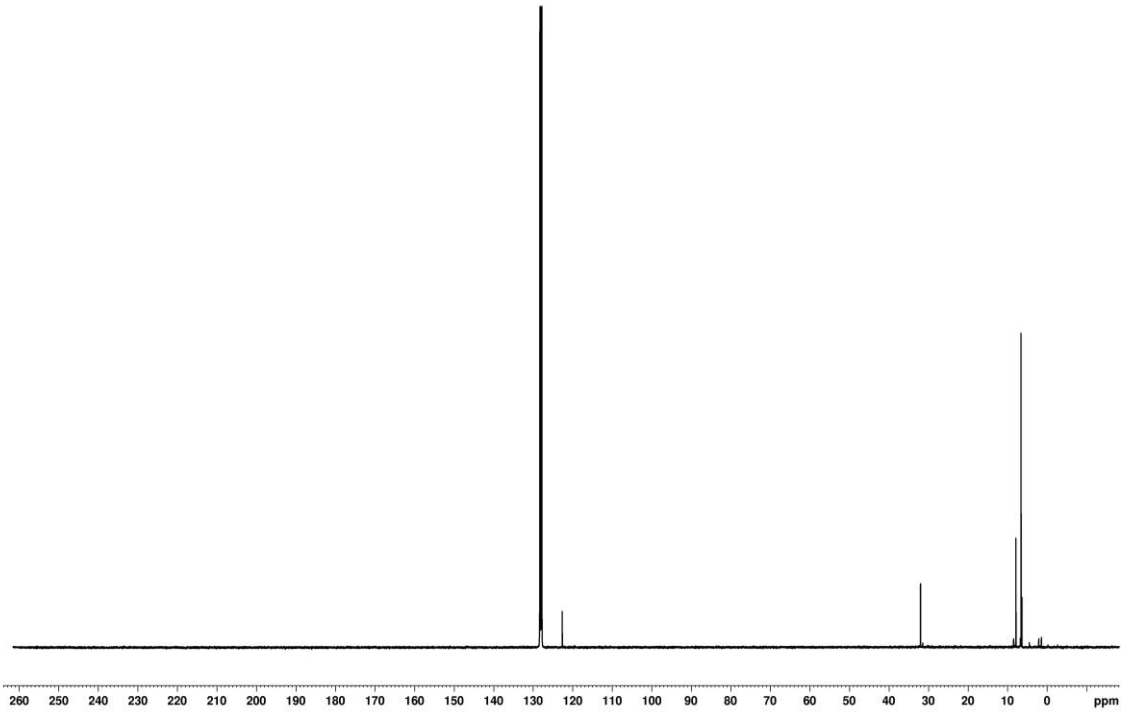


Figure S 29: $^{13}C\{^{1}H\}$ NMR spectrum of $IMe_4{\cdot}BH_2Bi(SiMe_3)_2$ (C_6D_6, 298 K).

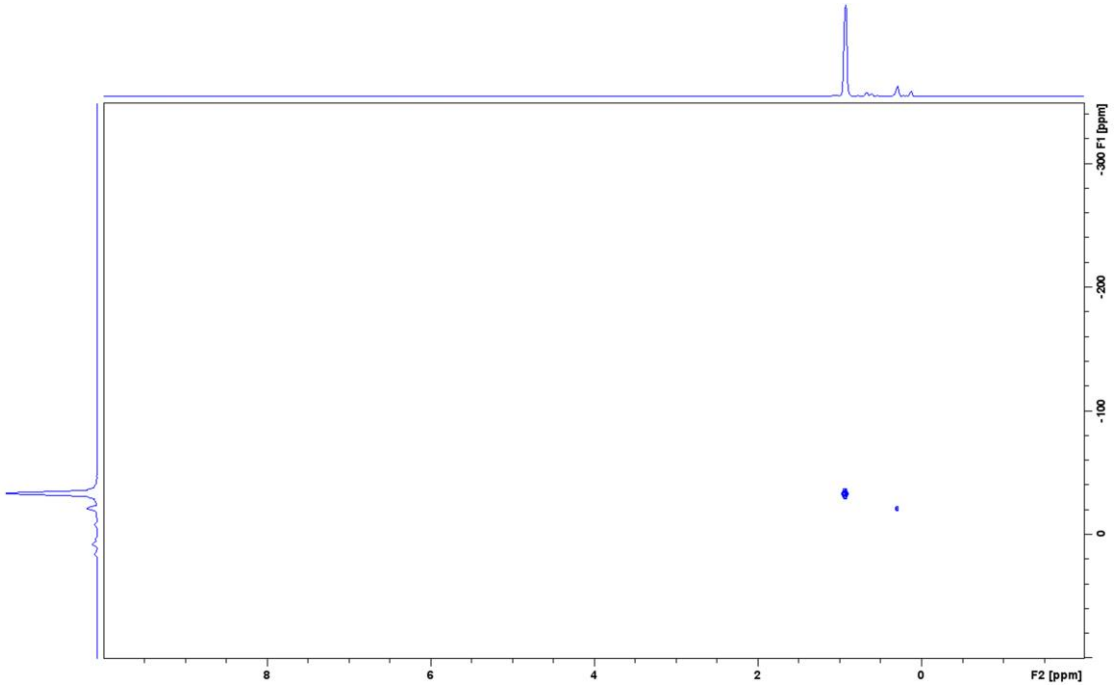


Figure S 30: ^{1}H, ^{29}Si HMBC spectrum of $IMe_4{\cdot}BH_2Bi(SiMe_3)_2$ (C_6D_6, 298 K).

h. Crude NMR spectra of desilylation attempt

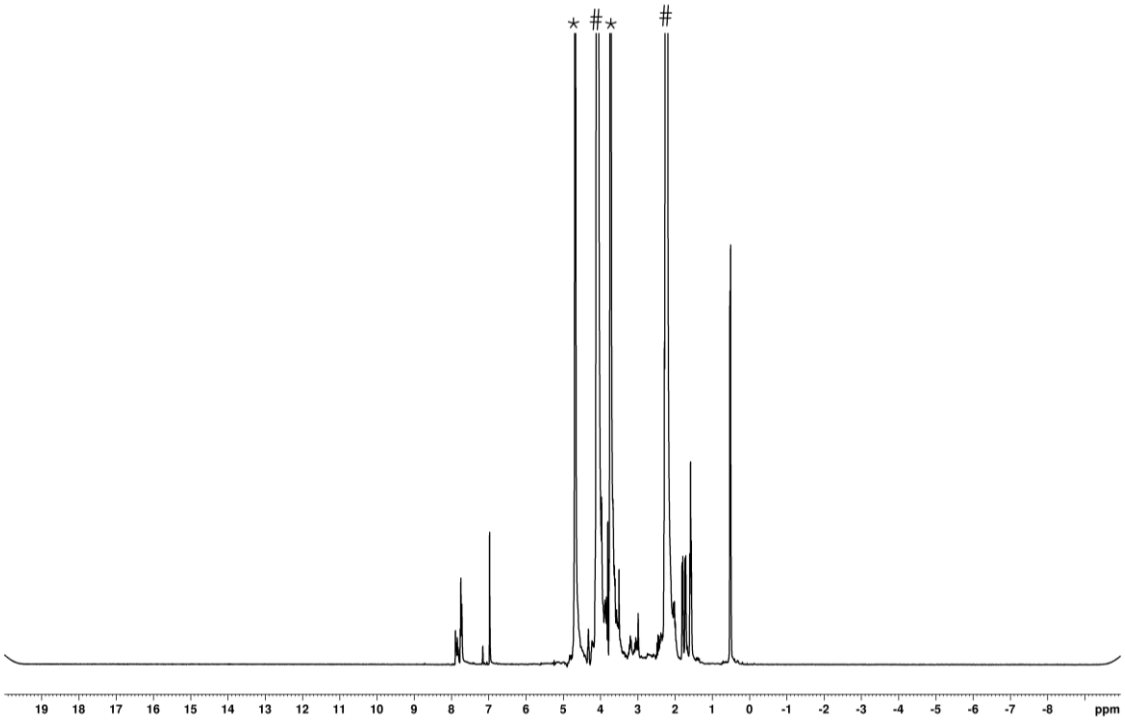


Figure S 31: ^{1}H NMR spectrum of the reaction mixture of IDipp·$BH_2Bi(SiMe_3)_2$ with benzoquinone in THF/MeOH (C_6D_6-cap., 298 K; * = MeOH, # = THF).

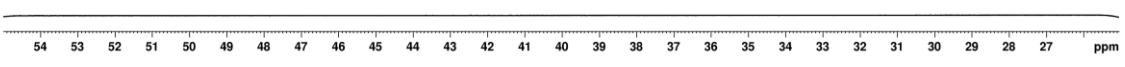


Figure S 32: Expanded ^{1}H NMR spectrum (> 20 ppm) of the reaction mixture of IDipp·$BH_2Bi(SiMe_3)_2$ with benzoquinone in THF/MeOH, showing no signs of Bi-H moieties (C_6D_6-cap., 298 K).

i. IDipp·GaH$_2$Bi(SiMe$_3$)$_2$

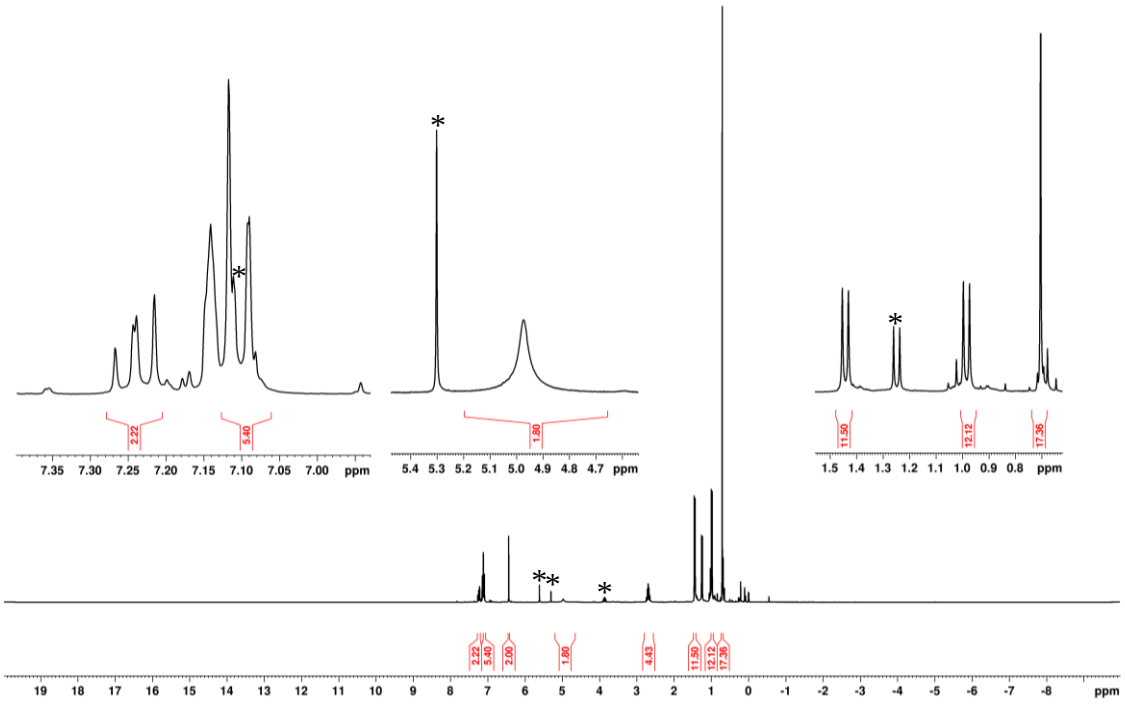


Figure S33: ^{1}H NMR spectrum of IDipp·GaH$_2$Bi(SiMe$_3$)$_2$ (C$_6$D$_6$, 298 K, * = IDipp-H$_2$).

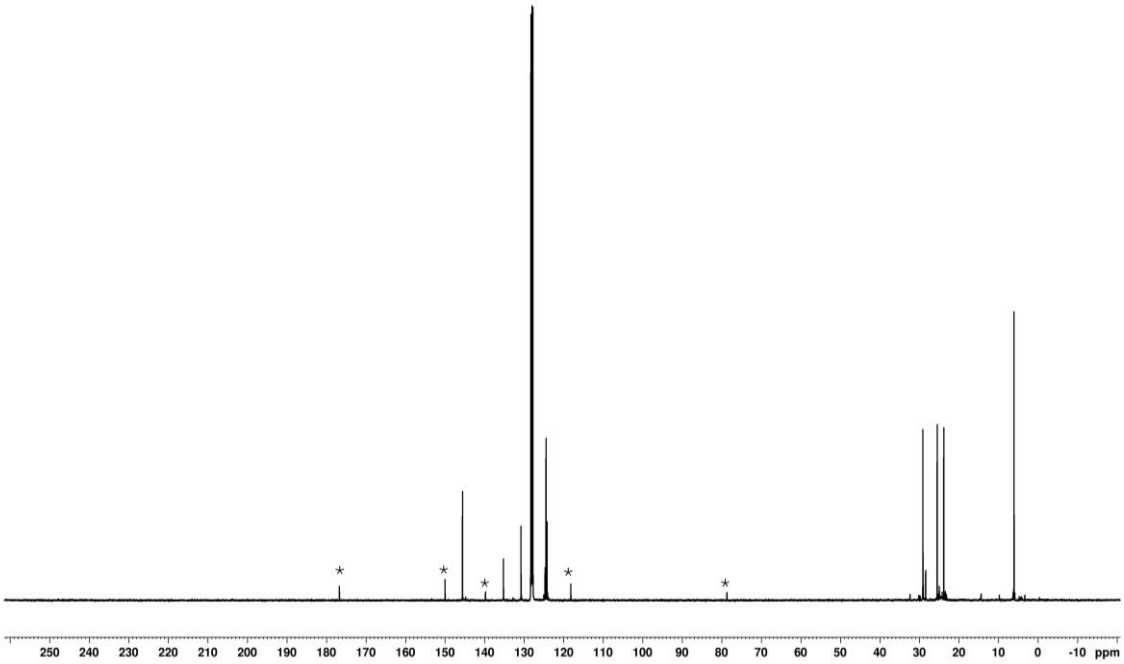


Figure S 34: ^{13}C{^{1}H} NMR spectrum of IDipp·GaH$_2$Bi(SiMe$_3$)$_2$ (C$_6$D$_6$, 298 K, * = IDipp-H$_2$).

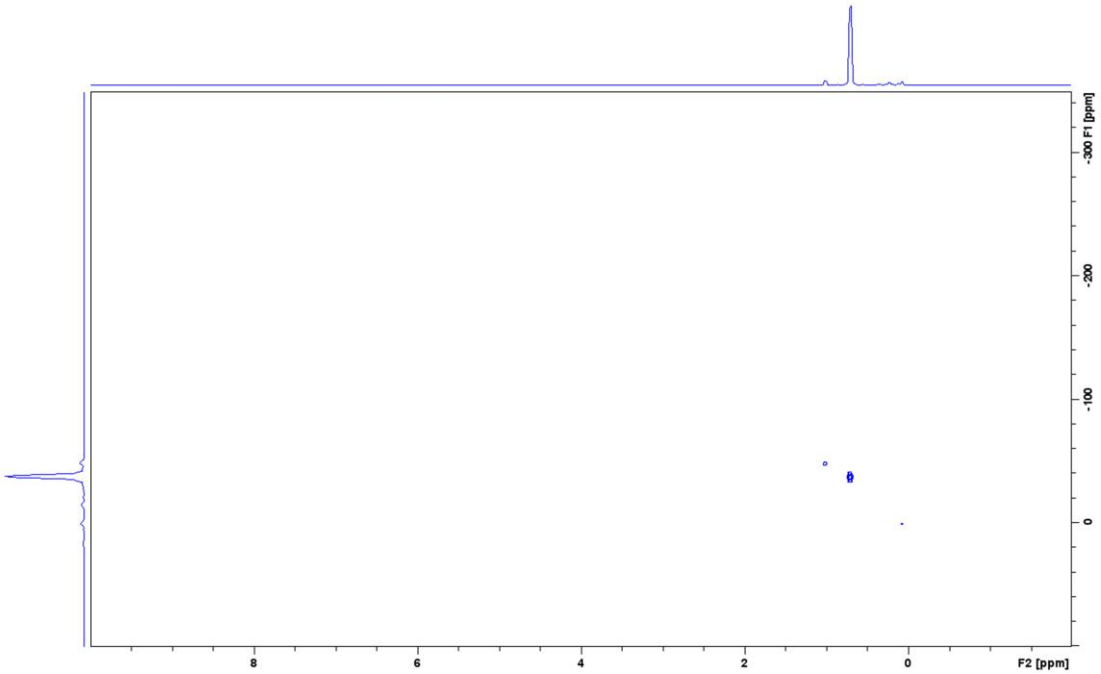


Figure S 35: ^{1}H, ^{29}Si HMBC spectrum of IIDipp·$GaH_2Bi(SiMe_3)_2$ (C_6D_6, 298 K).

4. Mass spectra

a. IDipp·$BH_2Bi(SiMe_3)_2$

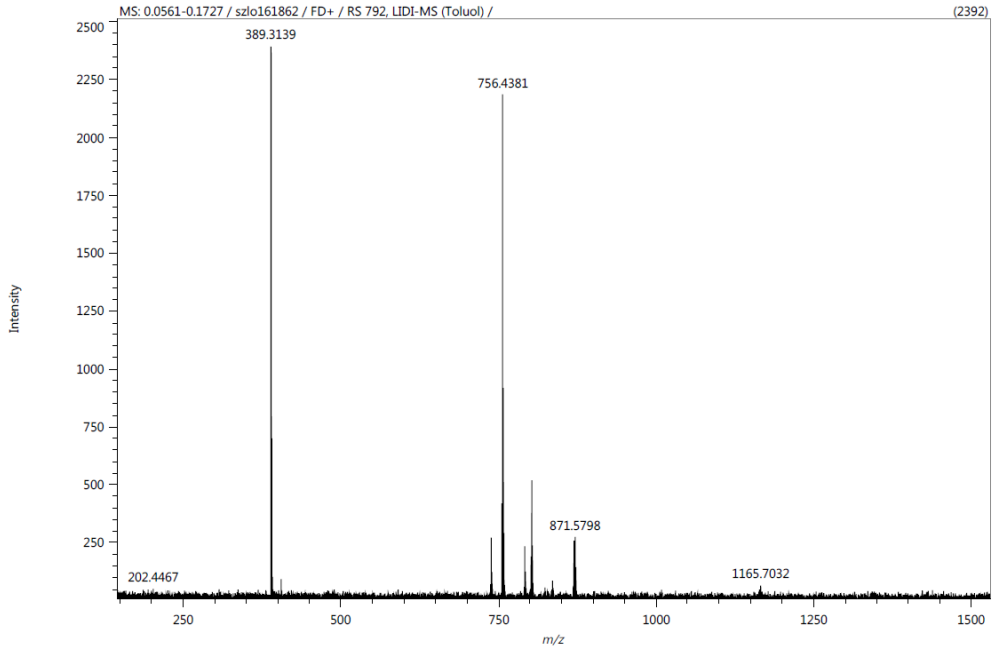


Figure S 36: LIFDI-MS spectrum of a solution of IDipp·$BH_2Bi(SiMe_3)_2$ in toluene.

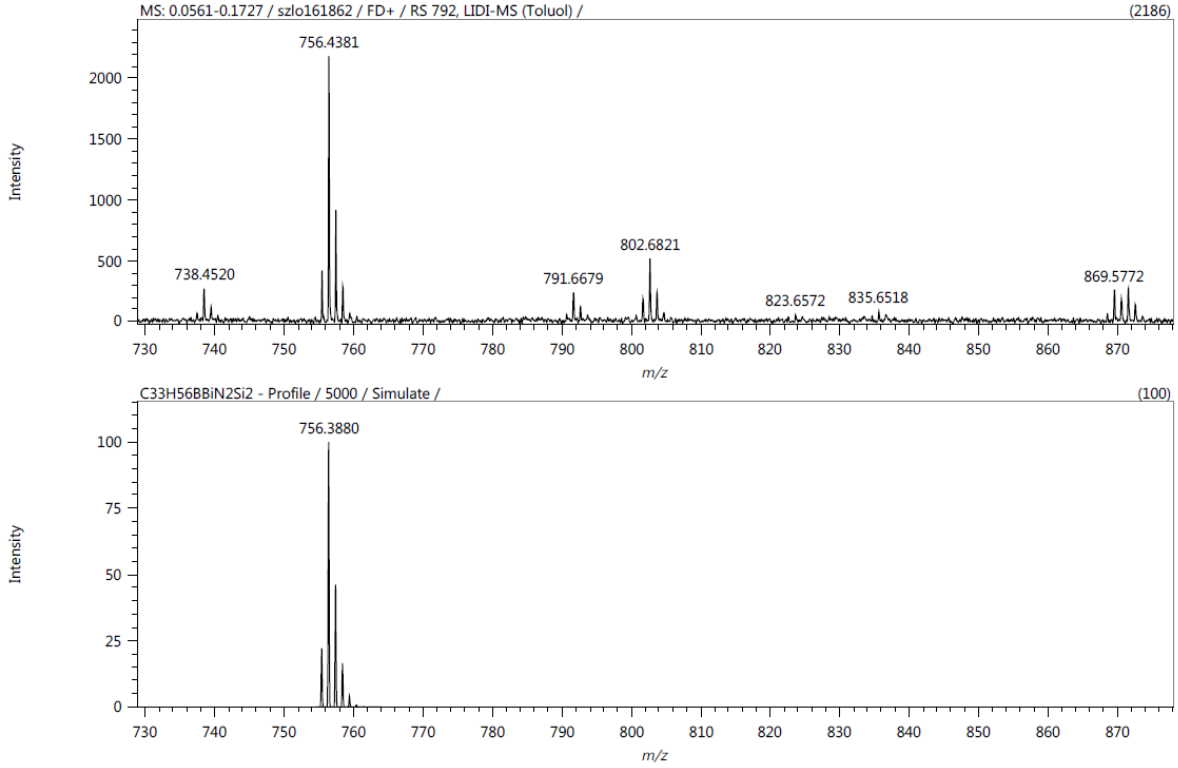


Figure S 37: Zoomed region within the LIFDI-MS spectrum of a solution of IDipp·$BH_2Bi(SiMe_3)_2$ in toluene (top: experiment, bottom: simulated product signal).

b. $IMe_4 \cdot BH_2Bi(SiMe_3)_2$

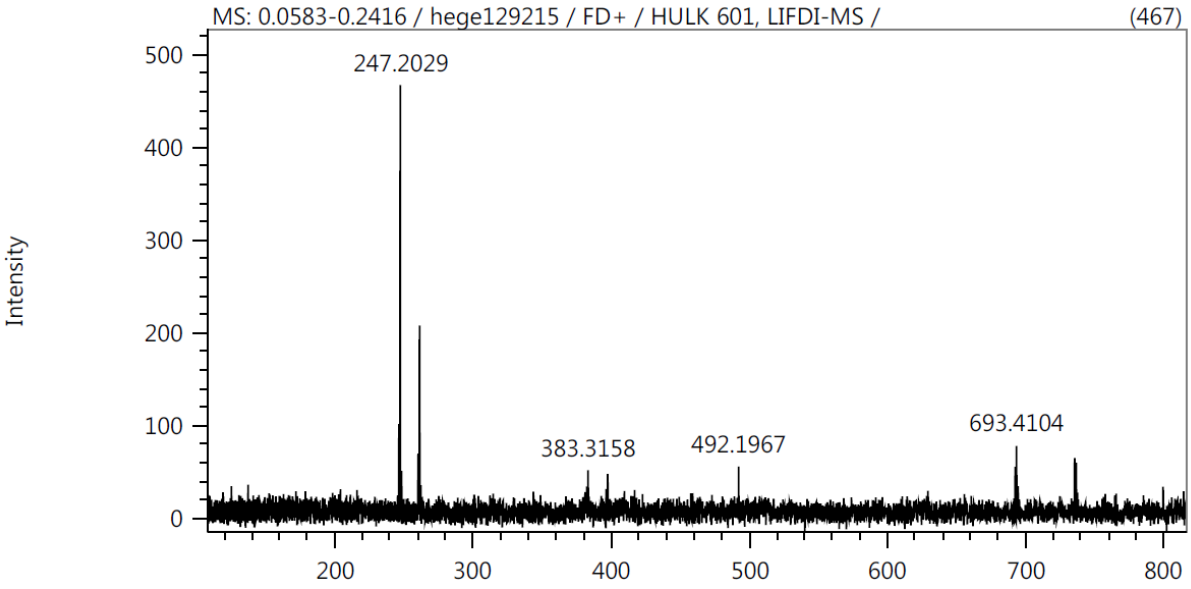


Figure S 38: LIFDI-MS spectrum of a solution of $IMe_4 \cdot BH_2Bi(SiMe_3)_2$ in toluene.

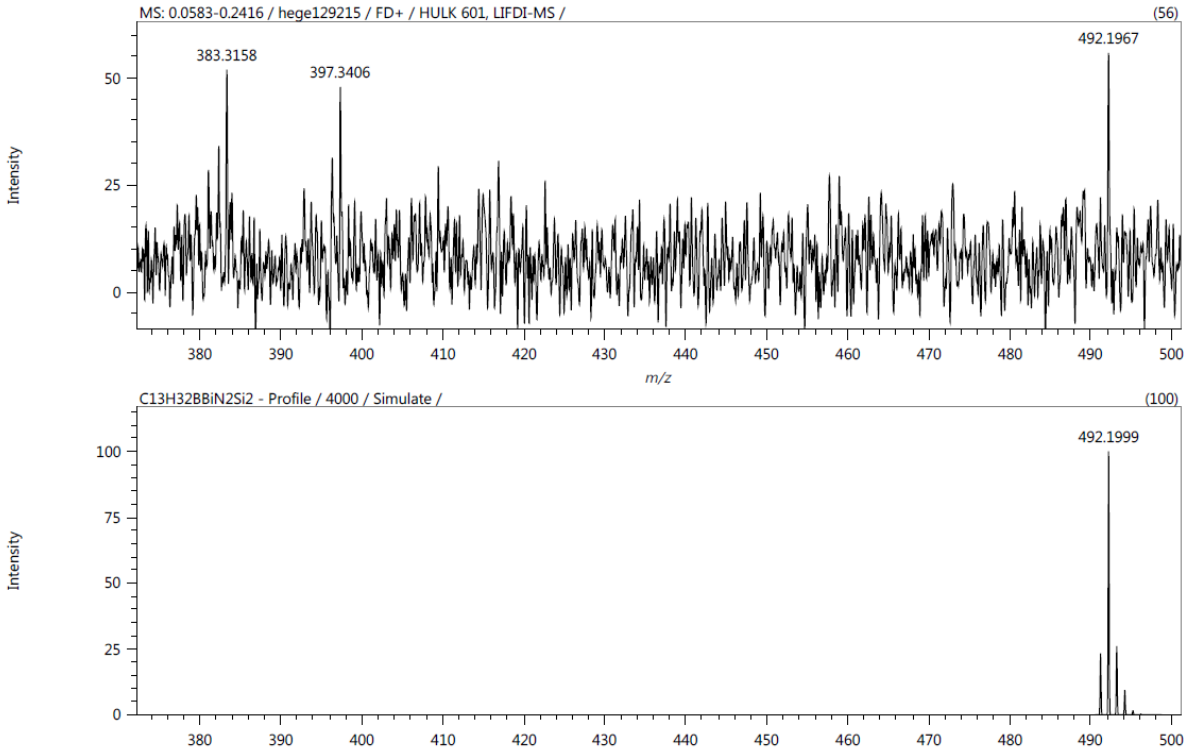


Figure S 39: Zoomed region within the LIFDI-MS spectrum of a solution of $IMe_4 \cdot BH_2Bi(SiMe_3)_2$ in toluene (top: experiment, bottom: simulated product signal).

c. IDipp·GaH$_2$Bi(SiMe$_3$)$_2$

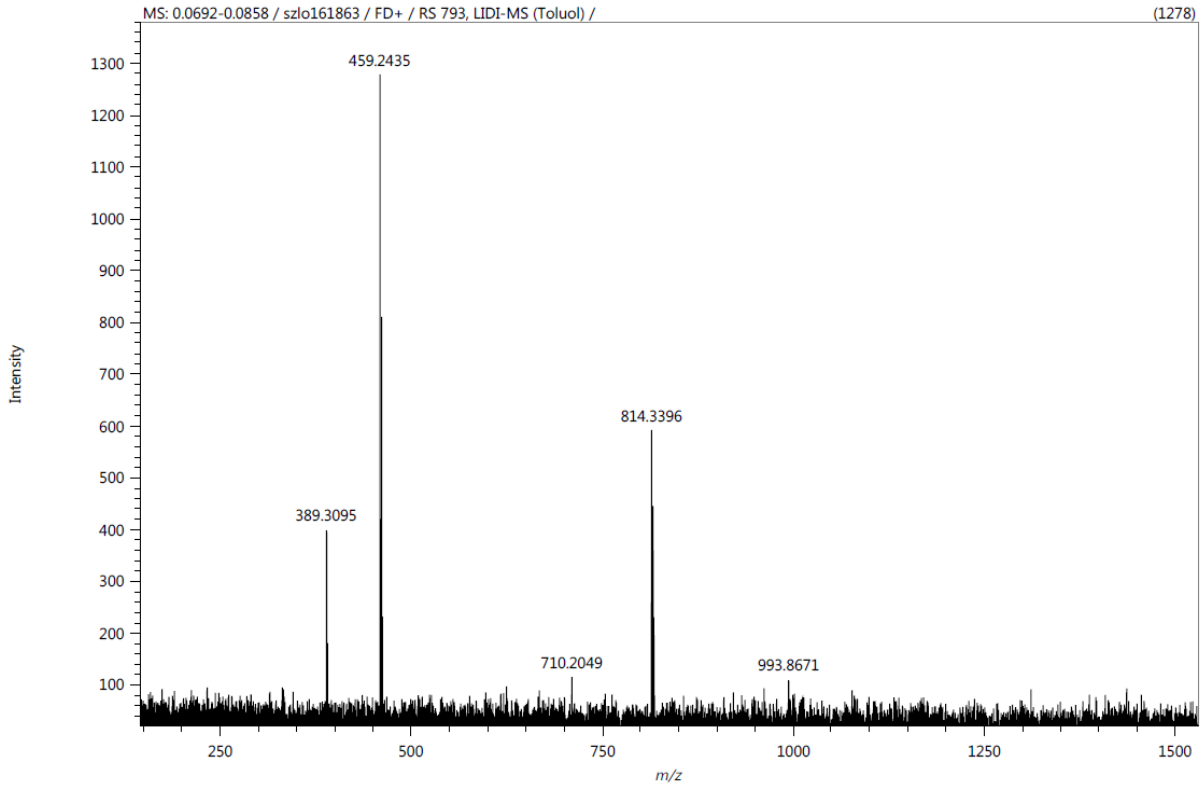


Figure S 40: LIFDI-MS spectrum of a solution of IDipp·GaH$_2$Bi(SiMe$_3$)$_2$ in toluene.

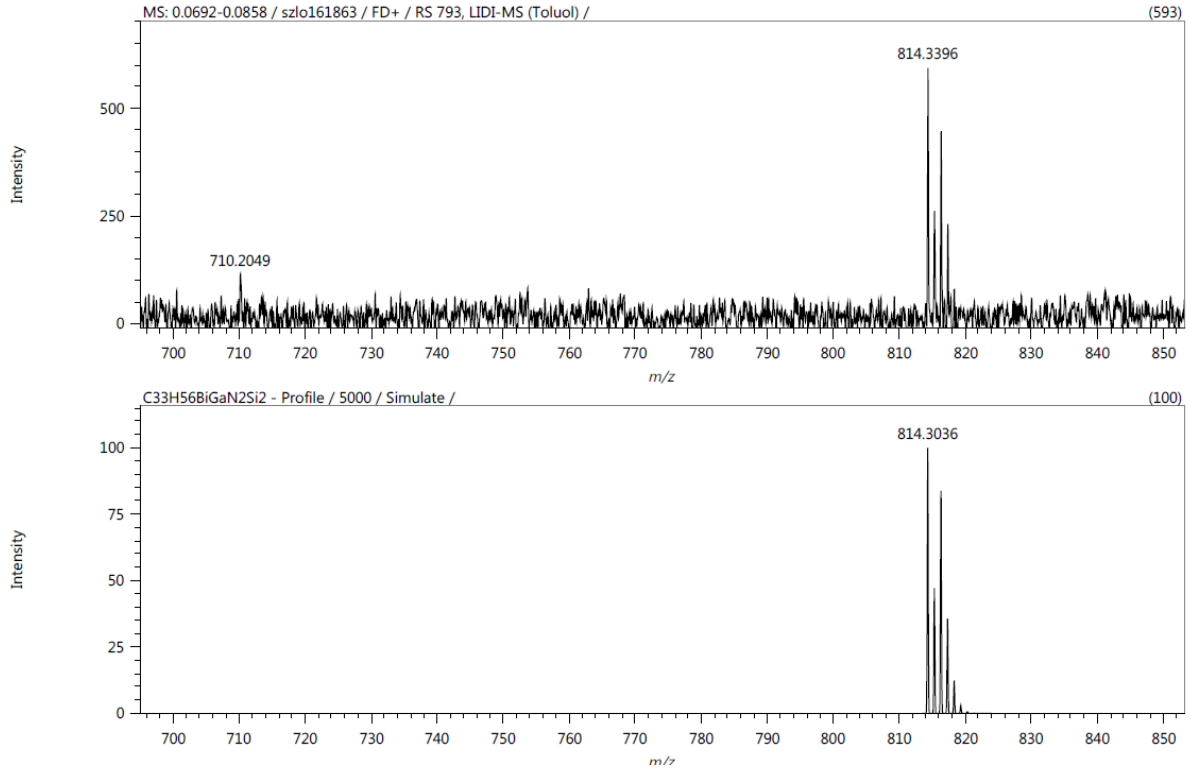


Figure S 41: Zoomed region within the LIFDI-MS spectrum of a solution of IDipp·GaH$_2$Bi(SiMe$_3$)$_2$ in toluene (top: experiment, bottom: simulated product signal).

5. Crystallographic Data

Single Crystal X-ray structure determination: Single-crystal X-ray diffraction data sets were collected using an Oxford Diffraction GV50 diffractometer (**1b**, **1c**) or a Rigaku XtaLAB Synergy R, DW system diffractometer (**1a**, **2**) equipped with a HyPix-Arc 150 detector operating at T = 123.01(10) K. Crystals were selected under mineral oil. Data reduction, scaling and absorption corrections were performed using CrysAlisPro (Rigaku, V1.171.41.90a, 2020). A gaussian absorption correction was performed using CrysAlisPro 1.171.41.90a (Rigaku Oxford Diffraction, 2020). Numerical absorption correction based on gaussian integration over a multifaceted crystal model. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. Using Olex2,[5] the structures were solved with ShelXT[6] and a least-squares refinement on $F2$ was carried out with ShelXL.[7] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms at the carbon atoms have been located in idealized positions and refined isotropically according to the riding model. Figures were created with Olex2.

CCDC-2347535 (**1a**), CCDC-2340840 (**1b**), CCDC-2340841 (**1c**), and CCDC-2340842 (**2**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table S1: Crystallographic data for compounds **1a** and **1b**.

Compound	1a	1b
CCDC	2347535	2340840
Formula	$C_{33}H_{56}BBiN_2Si_2$	$C_{13}H_{32}BBiN_2Si_2$
Dcalc	1.342	1.568
μ/mm^{-1}	4.793	17.605
Formula Weight	756.76	492.37
Colour	clear light yellow	clear light yellow
Shape	plate-shaped	block
Size/mm^3	0.31×0.29×0.07	0.19×0.13×0.12
T/K	123.01(10)	123.00(10)
Crystal System	monoclinic	triclinic
Space Group	$P2_1/c$	P-1
a/Å	18.0837(3)	9.5403(4)
b/Å	10.2928(2)	9.8557(6)
c/Å	40.2707(12)	12.1971(4)
α/°	90	97.044(4)
β/°	91.900(2)	108.604(4)
γ/°	90	101.577(4)
V/Å^3	7491.5(3)	1043.07(9)
Z	8	2
Z'	2	1
Wavelength/Å	0.71073	1.54184
Radiation type	MoK_a	CuK_α
Θ_{min}/°	2.222	3.904
Θ_{max}/°	25.123	74.073
Measured Refl's.	92561	6314
Indep't Refl's	13330	3974
Refl's I≥2 σ(I)	11815	3703
R_{int}	0.0581	0.0365
Parameters	855	190
Restraints	241	0
Largest Peak	0.778	1.572
Deepest Hole	-1.762	-2.289
GooF	1.168	1.050
wR_2 (all data)	0.0696	0.0919
wR_2	0.0679	0.0891
R_1 (all data)	0.0436	0.0377
R_1	0.0362	0.0350

Table S2: Crystallographic data for compounds **1c** and **2**.

Compound	**1c**	**2**
CCDC	2340841	2340842
Formula	$C_{13}H_{30}BBiN_2Si_2$	$C_{33}H_{56}BiGaN_2Si_2$
Dcalc	1.563	1.432
μ/mm^{-1}	17.621	10.653
Formula Weight	490.36	815.67
Colour	brown	clear colourless
Shape	block-shaped	plate-shaped
Size/mm^3	0.22×0.12×0.10	0.50×0.31×0.14
T/K	123(1)	122.99(10)
Crystal System	triclinic	orthorhombic
Space Group	*P*-1	*Pbca*
a/Å	7.3161(2)	19.3792(3)
b/Å	9.8444(2)	19.2881(2)
c/Å	15.3209(3)	20.2475(2)
α/°	90.6300(10)	90
β/°	103.624(2)	90
γ/°	103.085(2)	90
V/Å^3	1042.14(4)	7568.27(16)
Z	2	8
Z'	1	1
Wavelength/Å	1.54178	1.54184
Radiation type	CuK_a	CuK_a
Θ_{min}/°	4.622	3.902
Θ_{max}/°	66.582	73.674
Measured Refl's.	10095	26333
Indep't Refl's	3613	7278
Refl's I≥2 σ(I)	3417	6764
R_{int}	0.0278	0.0513
Parameters	188	375
Restraints	0	1
Largest Peak	0.718	1.405
Deepest Hole	-0.543	-1.568
GooF	1.090	1.071
wR_2 (all data)	0.0532	0.0929
wR_2	0.0526	0.0916
R_1 (all data)	0.0221	0.0343
R_1	0.0202	0.0323

a. Crystal structures

IDipp·$BH_2Bi(SiMe_3)_2$ (1a)

1a crystallized by slow evaporation of a *n*-pentane solution at -30 °C as clear light-yellow plate shaped crystals in the monoclinic space group $P2_1/c$. The structure of **1a** is shown in Figure S42.

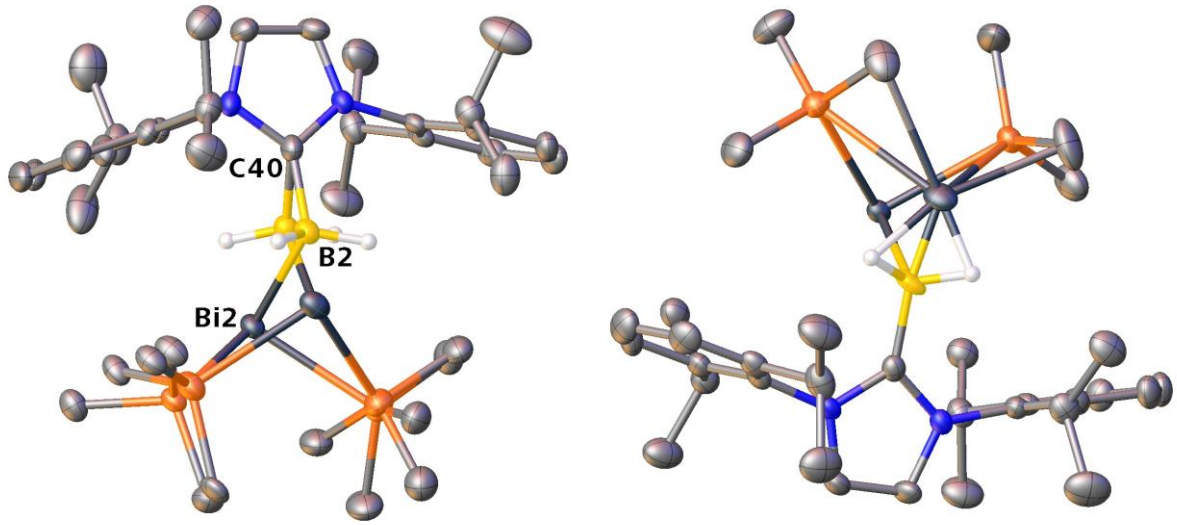


Figure S42: Molecular structure of **1a** in the solid state (asymmetric unit). Anisotropic displacement ellipsoids are shown at 50% probability level. Hydrogen atoms bound to carbon are omitted for clarity. Selected bond lengths [Å] and angles [°]: C40-B2 1.587(7), B2-Bi2 2.424(5), C40-B2-Bi2 110.9(3).

The asymmetric unit contains two molecules of **1a** and had to be refined with further DANG, SADI and SIMU restraints due to disorder (right molecule: only the bismuth atom of the minor component could be located due to a small occupancy of 0.0377(7); left molecule: the chain structure is disordered by rotation of roughly 180° with an occupancy of the minor component of 0.1079(7)). Hydrogen atoms bound to B were fixed in idealized position using DFIX and DANG restraints.

IMe_4·$BH_2Bi(SiMe_3)_2$ (1b)

1b crystallized from a saturated *n*-hexane solution at -28 °C as clear light-yellow block-shaped crystals in the triclinic space group *P*-1. The structure of **1b** in the solid state is shown in Figure S43.

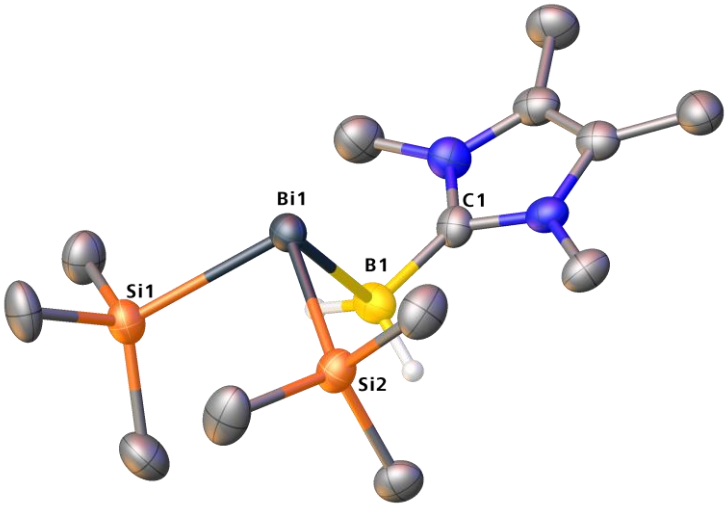


Figure S43: Molecular structure of **1b** in the solid state. Anisotropic displacement ellipsoids are shown at 50% probability level. Hydrogen atoms bound to carbon are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-B1 1.569(9), B1-Bi1 2.442(7), Bi1-Si1 2.6278(17), Bi1-Si2 2.6452(18), C1-B1-Bi1 107.2(4), B1-Bi1-Si1 89.12(18), B1-Bi1-Si2 97.05(19).

The asymmetric unit contains one molecule of **1b** and was refined without further restrains/constraints. H-atoms bound to B were refined freely.

DMAP·$BH_2Bi(SiMe_3)_2$ (1c)

1c crystallized by storing a saturated solution of **1c** in toluene at-28 °C as brown block-shaped crystals in the triclinic space group *P*-1. The structure of **1c** in the solid state is shown in Figure S44.

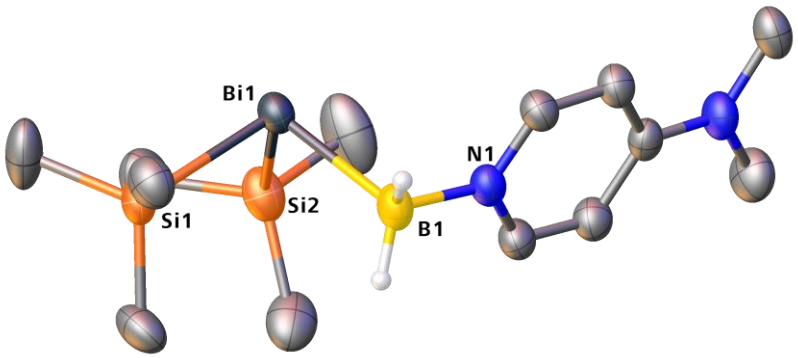


Figure S44: Molecular structure of **1c** in the solid state. Anisotropic displacement ellipsoids are shown at 50% probability level. Hydrogen atoms bound to carbon are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1-B1 1.578(5), B1-Bi1 2.424(5), Bi1-Si1 2.6331(9), Bi1-Si2 2.6322(11), N1-B1-Bi1 106.9(2), B1-Bi1-Si1 94.53(10), B1-Bi1-Si2 100.10(12).

The asymmetric unit contains one molecule of **1c** and was refined without further restrains/constraints. H-atoms bound to B were refined freely.

IDipp·$GaH_2Bi(SiMe_3)_2$ (2)

2 crystallized by slow evaporation of a *n*-pentane solution under reduced pressure at -80 °C over the course of two days as clear colourless plate-shaped crystals in the orthorhombic space group *Pbca*. The structure of **2** in the solid state is shown in Figure S44.

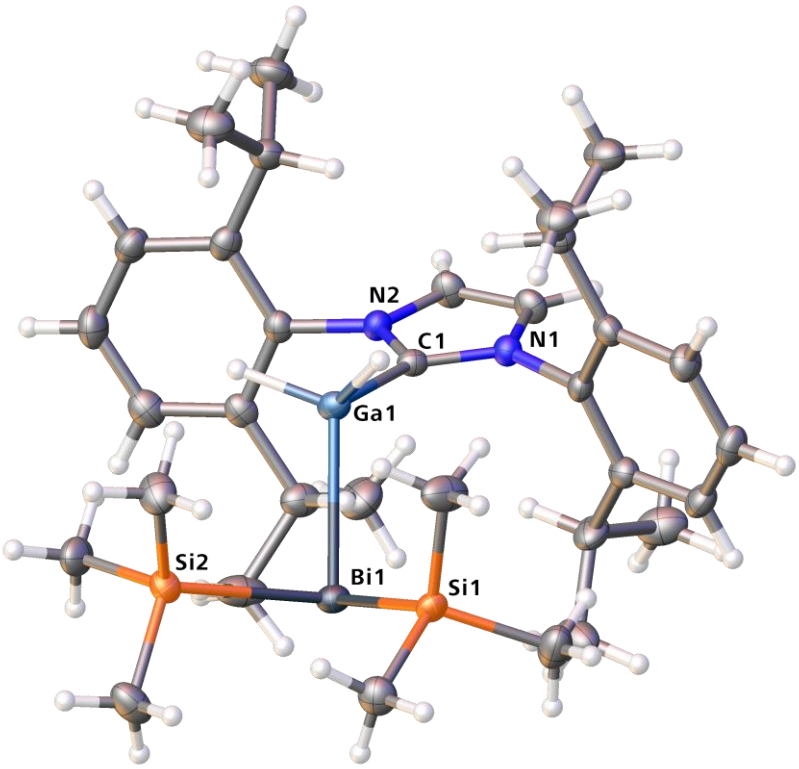


Figure S45: Molecular structure of **2** in the solid state. Anisotropic displacement ellipsoids are shown at 50% probability level. Selected bond lengths [Å] and angles [°]: N1-C1 1.352(4), N2-C1 1.357(4), C1-Ga1 2.061(3), Ga1-Bi1 2.7234(4), Bi1-Si1 2.6487(9), Bi1-Si2 2.6403(9), N1-B1-Bi1 106.9(2), N1-C1-N2 104.2(3), N1-C1-Ga1 129.2(2), C1-Ga1-Bi1 110.10(8), Ga1-Bi1-Si1 95.26(2), B1-Bi1-Si2 87.85(2).

The asymmetric unit contains one molecule of **2**. H atoms bound to Ga were refined by applying a SADI restraint.

6. Computational Details

a. General Information

The geometries of the compounds have been fully optimized with gradient-corrected density functional theory (DFT) in form of Becke's three-parameter hybrid method B3LYP with def2-TZVP all electron basis set (ECP on Bi).[8] The Gaussian 09 programme package was used throughout.[9] All structures correspond to minima on their respective potential energy surfaces as verified by computation of second derivatives. Natural bond orbital analysis (NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, and F. Weinhold) was performed as implemented in Gaussian 09.[10]

b. Molecular Properties and Thermodynamics

Table S3: Reaction energies ΔE, standard reaction enthalpies $\Delta H°_{298}$, Gibbs energies $\Delta G°_{298}$ (kJ mol^{-1}) and standard reaction entropies $\Delta S°_{298}$ (J mol^{-1} K^{-1}) for the considered gas phase processes). B3LYP/def2-TZVP(ECP on Bi) level of theory.

Process	ΔE	$\Delta H°_{298}$	$\Delta S°_{298}$	$\Delta G°_{298}$
1a = $BH_2Bi(SiMe_3)_2$ + IDipp	203.8	190.3	253.8	114.6
1b = $BH_2Bi(SiMe_3)_2$ + IMe_4	233.1	219.8	186.9	164.1
1c = $BH_2Bi(SiMe_3)_2$ + DMAP	139.7	130.2	176.0	77.8
2 = $GaH_2Bi(SiMe_3)_2$ + IDipp	109.9	99.5	242.1	27.4
1a + 2 MeOH = IDipp·BH_2BiH_2 + 2$MeOSiMe_3$	-170.6	-194.3	34.4	-204.6
1b + 2 MeOH = IMe_4·BH_2BiH_2 + 2$MeOSiMe_3$	-178.1	-201.8	13.6	-205.8
1c + 2 MeOH = DMAP·BH_2BiH_2 + 2$MeOSiMe_3$	-163.9	-184.4	8.0	-186.8
1a + 2 MeOH = IDipp·$BH_2Bi(OMe)_2$ + 2 $HSiMe_3$	-4.2	-24.0	5.5	-25.7
1b + 2 MeOH = IMe_4·$BH_2Bi(OMe)_2$ + 2 $HSiMe_3$	-25.5	-44.7	-14.1	-40.5
1c + 2 MeOH = DMAP·$BH_2Bi(OMe)_2$ + 2 $HSiMe_3$	-15.3	-31.8	-5.8	-30.1
IDipp·BH_2BiH_2 = 2 H_2 + $Bi_{(solid)}$ + $B_{(solid)}$ +IDipp		-8.9	239.5	-80.3
IMe_4·BH_2BiH_2 = 2 H_2 + $Bi_{(solid)}$ + $B_{(solid)}$ +IMe_4		28.1	193.3	-29.6
DMAP·BH_2BiH_2 = 2 H_2 + $Bi_{(solid)}$ + $B_{(solid)}$ + DMAP		-78.9	188.0	-135.0
IDipp·BH_2BiH_2 = ½ H_2 + $Bi_{(solid)}$ + IDipp·BH_3		-131.4	64.6	-150.7
IMe_4·BH_2BiH_2 = ½ H_2 + $Bi_{(solid)}$ + IMe·BH_3		-105.2	46.7	-119.1
DMAP·BH_2BiH_2 = ½ H_2 + $Bi_{(solid)}$ + DMAP·BH_3		-128.7	51.7	-144.1
$B_{(solid)}$ = $B_{(gas)}$[11]		561.6	147.5	517.6
$Bi_{(solid)}$ = $Bi_{(gas)}$[11]		208.4	130.0	169.6

Table S4: Total energies E^o_0, sum of electronic and thermal enthalpies H^o_{298} (Hartree) and standard entropies S^o_{298} (cal $mol^{-1}K^{-1}$). B3LYP/def2-TZVP (ECP on Bi) level of theory.

Compound	E^o_0	H^o_{298}	S^o_{298}
DMAP	-382.4014129	-382.230446	91.131
IMe_4	-383.5797905	-383.386841	96.208
IDipp	-1160.4538534	-1159.854780	201.957
$BH_2Bi(SiMe_3)_2$	-1059.4617525	-1059.198250	152.893
$GaH_2Bi(SiMe_3)_2$	-2959.5435301	-2959.285449	157.331
1a	-2219.9932453	-2219.125522	294.179
1b	-1443.1303448	-1442.668822	204.426
1c	-1441.9163855	-1441.478291	201.97
2	-4120.0392468	-4119.178145	301.431
Bi ($^4S_{3/2}$)	-214.6848603	-214.6825	44.67
B ($^2P_{1/2}$)	-24.6639213	-24.661561	34.519
H_2	-1.1794826	-1.166608	31.223
$HSi(CH_3)_3$	-409.9478771	-409.821002	79.024
CH_3OH	-115.7756771	-115.72035	56.963
$CH_3OSi(CH_3)_3$	-524.5731799	-524.409144	98.141
$DMAP{\cdot}BH_2BiH_2$	-624.3838154	-624.170929	121.523
$DMAP{\cdot}BH_2Bi(OMe)_2$	-853.577813	-853.289115	156.463
$IDipp{\cdot}BH_2BiH_2$	-1402.46322	-1401.821945	220.033
$IDipp{\cdot}BH_2Bi(OMe)_2$	-1631.650437	-1630.933371	251.378
$IMe_4{\cdot}BH_2BiH_2$	-625.60319	-625.368077	125.327
$IMe_4{\cdot}BH_2Bi(OMe)_2$	-854.7956626	-854.484536	156.93
$DMAP{\cdot}BH_3$	-409.0805685	-408.874761	104.676
$IDipp{\cdot}BH_3$	-1187.160529	-1186.526817	206.272
$IMe_4{\cdot}BH_3$	-410.2905744	-410.062966	107.271

Table S5: Dipole moments μ in Debye, the E-Bi and E-LB bond distances in Å, the E-Bi and E-LB Wiberg bond indices (WBI) and their changes upon complex formation. B3LYP/def2-TZVP(ECP on Bi) level of theory.

Compound	μ	***R*(E-Bi)**	**Δ*R*(E-Bi)**	**WBI(E-Bi)**	**ΔWBI(E-Bi)**
$BH_2Bi(SiMe_3)_2$	1.51	2.291	-	1.208	-
$GaH_2Bi(SiMe_3)_2$	1.64	2.688	-	0.979	-
1a	6.61	2.484	0.193	0.845	-0.364
1b	7.62	2.501	0.210	0.841	-0.367
1c	10.9	2.463	0.172	0.890	-0.318
2	7.69	2.785	0.097	0.880	-0.099

Table S6: Selected results from NBO analysis. B3LYP/def2-TZVP(ECP on Bi) level of theory.

Compound	**Orbital**	**Occupation**	**Contribution**	**Bi configuration**	**B/Ga**
$BH_2Bi(SiMe_3)_2$	Bi-B bonding	1.9712	51.67% Bi, 48.33% B	$sp^{8.48}d^{0.01}$ (s – 10.54% p – 89.35%)	$sp^{2.20}$ (s 31.25%, p 68.69%)
	Bi LP	1.9098		$sp^{0.32}d^{0.0}$ (s – 75.49% p – 24.49%)	
	B LP* vacant	0.1687			$sp^{99.99}$ (s 0.29 %, p 99.38 %)
IDipp·$BH_2Bi(SiMe_3)_2$ (**1a**)	Bi-B bonding	1.8367	53.82% Bi, 46.18% B	$sp^{9.68}d^{0.01}$ (s – 9.36% p – 90.57%)	$sp^{5.16}$ (s 16.23%, p 83.74%)
	Bi LP	1.9646		$sp^{0.32}d^{0.0}$ (s – 75.93% p – 24.06%)	
$GaH_2Bi(SiMe_3)_2$	Bi-Ga bonding	1.9193	60.3% Bi, 39.68% Ga	$sp^{12.91}d^{0.01}$ (s – 7.18% p – 92.72%)	$sp^{2.13}$ (s 31.92%, p 67.94%)
	Bi LP	1.9415		$sp^{0.28}d^{0.0}$ (s – 78.11% p – 21.87%)	
	Ga LP* vacant	0.0829			$sp^{99.99}d^{6.78}$ (s 0.19 %, p 98.49 % d 1.27 %)
IDipp·$GaH_2Bi(SiMe_3)_2$ (**2**)	Bi-Ga bonding	1.9206	62.49% Bi, 37.51% Ga	$sp^{9.19}d^{0.01}$ (s – 9.80% p – 90.11%)	$sp^{2.75}$ (s 26.65%, p 73.29%)
	Bi LP	1.9599		$sp^{0.33}d^{0.0}$ (s – 74.9% p – 25.1%)	
	Ga LP* vacant	0.3509			$sp^{13.84}d^{0.03}$ (s 6.72 %, p 93.07 % d 0.20 %)

Discussion of the results of the NBO analysis

In $BH_2Bi(SiMe_3)_2$, the Bi lone pair has predominantly *s*-character (75.5 %), occupation 1.91 ē and donates electron density to a vacant orbital of boron (99.4% *p* character), the E(2) value 3.75 kcal mol^{-1}. The same Bi lone pair also donates to each of two antibonding orbitals of neighbouring Si-C bonds (E(2) values 2.82 and 2.91 kcal mol^{-1}). Overall, these data indicate weak involvement of Bi lone pair into the interaction with boron centre (occupation of the vacant B orbital 0.17 ē).

In analogous gallium compound $GaH_2Bi(SiMe_3)_2$, the Bi lone pair also has predominantly *s*-character (78 %), occupation 1.94 ē and donates electron density to a vacant orbital of gallium (98.5% p character), the E(2) value is 1.59 kcal mol^{-1}. The same Bi lone pair also donates to each of two antibonding orbitals of neighbouring Si-C bonds (both E(2) values 1.37 kcal mol^{-1}).

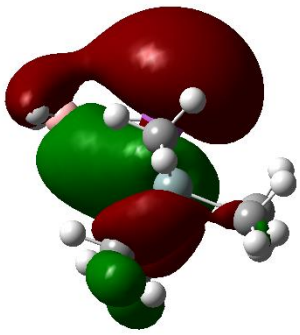
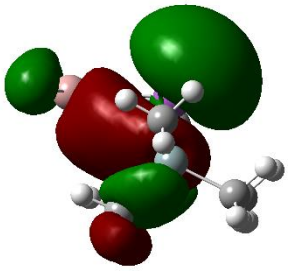
Overall, these data indicate much weaker involvement of Bi lone pair into the interaction with gallium centre than with the boron centre (E(2) values are 1.59 and 3.75 kcal mol^{-1}, for Ga and B, respectively). It should be noted that the total occupation of the vacant Ga orbital (0.08 ē) is smaller compared to 0.17 ē for vacant boron orbital.

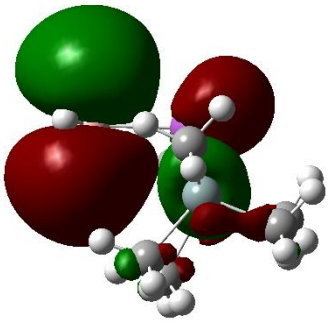
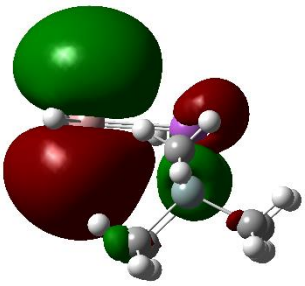
In comparison, for IDipp·$GaH_2Bi(SiMe_3)_2$, the strong donation from the carbon lone pair to the Ga vacant orbital with E(2) value of 160.96 kcal mol^{-1} is the evidence of strong C-Ga donor-acceptor bond, occupation of vacant Ga orbital is 0.35 ē. According to NBO analysis, the Bi lone pair (occupation 1.96) does not interact with vacant orbital on Ga after it complexed with NHC.

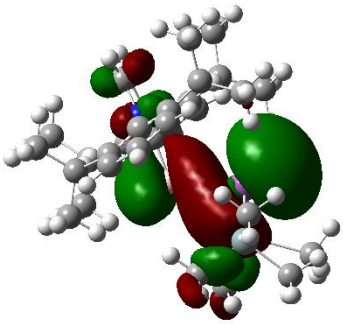
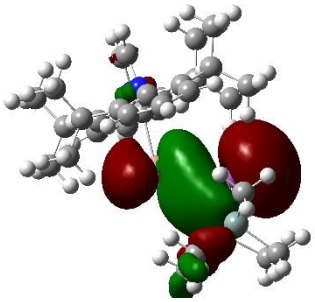
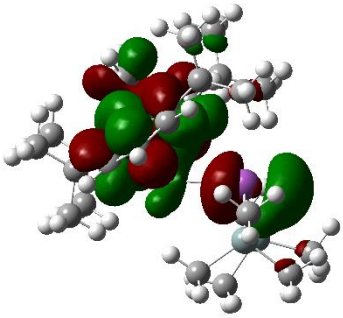
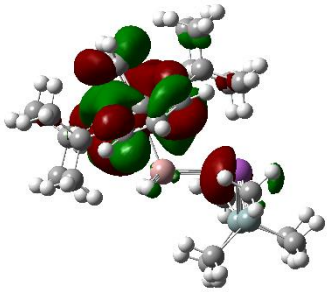
For IDipp·$BH_2Bi(SiMe_3)_2$, the NBO analysis does not identify the boron vacant orbital, due the strong covalent C-B bond (occupation 1.9665 ē).

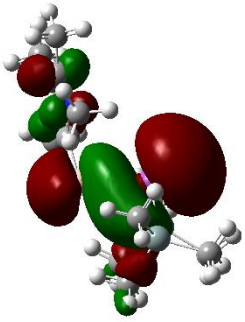
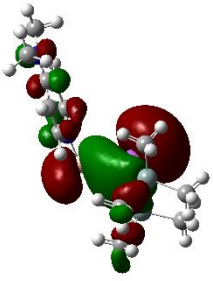
Thus, a weak π interaction between Bi-B exist in $BH_2Bi(SiMe_3)_2$ and a much weaker π interaction Bi-Ga can be identified in $GaH_2Bi(SiMe_3)_2$, while after complexation with IDipp π-interactions are absent both in IDipp·$BH_2Bi(SiMe_3)_2$ and IDipp·$BH_2Bi(SiMe_3)_2$. Note that after the coordination of the NHC, both boron and gallium atoms change initial sp^2 hybridization ($sp^{2.2}$ for B, $sp^{2.13}$ for Ga) to $sp^{5.2}$ for B, and $sp^{2.75}$ for Ga.

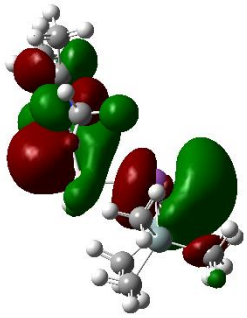
c. Frontier Molecular Orbitals

$BH_2Bi(SiMe_3)_2$	$GaH_2Bi(SiMe_3)_2$
	
HOMO	HOMO

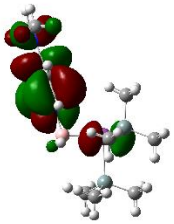
	
LUMO	LUMO

1a	**2**
	
HOMO	HOMO
	
LUMO	LUMO

1b	**1c**
	
HOMO	HOMO



LUMO



LUMO

Figure S46: Canonical frontier molecular orbitals of the studied compounds. B3LYP/def2-TZVP (ECP on Bi) level of theory.

d. Cartesian Coordinates of optimized Structures

Table S7: Optimized geometries of the computationally studied compounds. Cartesian coordinates in Ångströms. B3LYP/def2-TZVP (ECP on Bi) level of theory.

DMAP			
7	-2.664387000	0.000007000	0.020859000
7	1.550059000	-0.000004000	-0.087102000
6	0.178850000	-0.000008000	-0.039012000
6	-0.570648000	-1.193118000	-0.015110000
1	-0.092052000	-2.160779000	-0.014376000
6	-0.570626000	1.193101000	-0.015123000
1	-0.092027000	2.160762000	-0.014397000
6	-1.953416000	-1.129170000	0.010031000
1	-2.524007000	-2.053033000	0.025352000
6	2.278814000	1.248571000	0.032671000
1	1.981164000	1.955653000	-0.745288000
1	3.341646000	1.053004000	-0.088174000
1	2.127967000	1.731534000	1.006166000
6	2.278866000	-1.248554000	0.032638000
1	2.128115000	-1.731511000	1.006152000
1	3.341679000	-1.052948000	-0.088300000
1	1.981188000	-1.955655000	-0.745289000
6	-1.953407000	1.129163000	0.009993000
1	-2.523974000	2.053042000	0.025331000
IMe_4			
7	1.058721000	-0.707717000	-0.000052000
7	-1.058756000	-0.707680000	0.000000000
6	0.679300000	0.636539000	0.000006000
6	-0.000044000	-1.561853000	-0.000050000
6	-0.679261000	0.636577000	0.000033000
6	-1.655840000	1.760614000	0.000062000
1	-2.304963000	1.737906000	-0.880115000
1	-1.135980000	2.718010000	-0.000517000
1	-2.304203000	1.738583000	0.880824000
6	2.431331000	-1.171720000	0.000087000
1	2.966486000	-0.825041000	-0.886935000
1	2.406417000	-2.257832000	0.000161000
1	2.966353000	-0.824873000	0.887114000
6	-2.431373000	-1.171667000	-0.000026000
1	-2.406491000	-2.257785000	0.000021000
1	-2.966428000	-0.824940000	-0.887085000
1	-2.966487000	-0.824864000	0.886967000
6	1.655912000	1.760560000	-0.000070000
1	2.304175000	1.738714000	0.880772000
1	1.136071000	2.717965000	-0.000936000
1	2.305141000	1.737636000	-0.880162000
IDipp			
7	-1.062433000	-0.000212000	0.517841000
7	1.062454000	-0.000280000	0.517849000
6	0.000014000	0.000056000	-0.342234000
6	2.435803000	-0.000119000	0.090083000
6	-2.435780000	0.000031000	0.090065000
6	0.674932000	-0.000753000	1.853545000
1	1.379330000	-0.001039000	2.666612000
6	-0.674922000	-0.000632000	1.853539000
1	-1.379327000	-0.000814000	2.666601000
6	3.085112000	-1.228217000	-0.111543000
6	-3.085203000	-1.228019000	-0.111480000
6	-3.084628000	1.228314000	-0.111866000
6	-2.381093000	-2.563361000	0.075298000
1	-1.394840000	-2.364457000	0.492766000
6	3.084766000	1.228118000	-0.111753000
6	-4.415996000	-1.199657000	-0.527711000
1	-4.940552000	-2.131324000	-0.697703000
6	-5.077330000	0.000517000	-0.734708000
1	-6.110261000	0.000711000	-1.060472000
6	-4.415425000	1.200441000	-0.528121000
1	-4.939541000	2.132307000	-0.698421000
6	-2.380115000	2.563426000	0.074960000
1	-1.393617000	2.364152000	0.491658000
6	2.380838000	-2.563492000	0.075097000
1	1.394747000	-2.364530000	0.492922000
6	4.415910000	-1.199950000	-0.527761000
1	4.940385000	-2.131651000	-0.697814000
6	2.380387000	2.563287000	0.075167000
1	1.393834000	2.364081000	0.491766000
6	5.077357000	0.000178000	-0.734668000
1	6.110292000	0.000298000	-1.060423000
6	4.415565000	1.200150000	-0.528000000
1	4.939772000	2.131978000	-0.698225000
6	-3.118372000	-3.476164000	1.065973000
1	-3.245495000	-2.990985000	2.035635000
1	-2.553854000	-4.398309000	1.220872000
1	-4.109001000	-3.755087000	0.701175000
6	-2.166931000	-3.265346000	-1.274824000
1	-3.119796000	-3.508481000	-1.750746000
1	-1.615644000	-4.198288000	-1.135832000
1	-1.599191000	-2.631234000	-1.956427000
6	2.166153000	-3.265043000	-1.275172000
1	1.598303000	-2.630639000	-1.956411000
1	1.614771000	-4.197947000	-1.136293000
1	3.118847000	-3.508169000	-1.751443000
6	3.118233000	-3.476719000	1.065286000
1	4.108667000	-3.755811000	0.700088000
1	2.553539000	-4.398763000	1.220140000
1	3.245805000	-2.991821000	2.035030000
6	2.167166000	3.266116000	-1.274636000
1	3.120312000	3.509567000	-1.749827000
1	1.615798000	4.198973000	-1.135410000
1	1.599859000	2.632440000	-1.957010000

6	-2.166707000	3.266069000	-1.274911000
1	-1.599409000	2.632249000	-1.957158000
1	-1.615255000	4.198886000	-1.135752000
1	-3.119789000	3.509558000	-1.750211000
6	-3.116700000	3.475804000	1.066580000
1	-4.107629000	3.754729000	0.702587000
1	-2.552150000	4.397934000	1.221440000
1	-3.243080000	2.990214000	2.036131000
6	3.117003000	3.475466000	1.066950000
1	3.243232000	2.989758000	2.036461000
1	2.552561000	4.397655000	1.221855000
1	4.108002000	3.754295000	0.703073000

$BH_2Bi(SiMe_3)_2$

83	-0.002005000	-0.842442000	-0.281012000
14	2.143182000	0.756132000	0.081801000
14	-2.139361000	0.765344000	0.079266000
5	-0.025012000	-1.730894000	1.831002000
6	3.612625000	-0.383956000	0.394127000
1	3.755399000	-1.085611000	-0.430029000
1	3.480492000	-0.964611000	1.308907000
1	4.531038000	0.202042000	0.498447000
6	1.985881000	1.975008000	1.514032000
1	1.803127000	1.462275000	2.459817000
1	1.172525000	2.684840000	1.354118000
1	2.911961000	2.549962000	1.615895000
6	-3.658627000	-0.343099000	-0.063274000
1	-3.658370000	-1.120841000	0.702982000
1	-3.703860000	-0.833371000	-1.037642000
1	-4.572432000	0.246530000	0.059385000
6	2.423557000	1.720616000	-1.516209000
1	3.317501000	2.346296000	-1.431855000
1	1.579890000	2.375194000	-1.744258000
1	2.563005000	1.049505000	-2.365968000
6	-2.162591000	1.638769000	1.750685000
1	-1.282613000	2.268360000	1.890707000
1	-2.191510000	0.918529000	2.570375000
1	-3.048797000	2.276361000	1.831340000
6	-2.168970000	2.051884000	-1.301857000
1	-3.069313000	2.669292000	-1.224620000
1	-2.170353000	1.580055000	-2.286390000
1	-1.305521000	2.718163000	-1.252324000
1	0.994368000	-2.007128000	2.381649000
1	-1.059843000	-2.014723000	2.348495000

$GaH_2Bi(SiMe_3)_2$

83	-0.000031000	-0.152184000	-0.862241000
14	2.111107000	0.943210000	0.427436000
14	-2.111313000	0.942877000	0.427520000
31	0.000364000	-2.384629000	0.635269000
6	3.648165000	0.157680000	-0.334777000
1	3.692132000	0.330294000	-1.411975000
1	3.672621000	-0.920744000	-0.166450000
1	4.551555000	0.586041000	0.110483000
6	2.151060000	0.670141000	2.295281000
1	2.224543000	-0.390811000	2.541672000
1	1.263340000	1.070947000	2.787042000
1	3.024481000	1.170970000	2.725340000
6	-3.648033000	0.157709000	-0.335771000
1	-3.671608000	-0.921048000	-0.169451000
1	-3.692422000	0.332275000	-1.412638000
1	-4.551622000	0.584541000	0.110543000
6	2.134421000	2.799735000	0.083026000
1	3.040776000	3.246149000	0.504122000
1	1.277273000	3.306564000	0.529977000
1	2.125199000	3.009689000	-0.988250000
6	-2.151714000	0.668590000	2.295171000
1	-1.264375000	1.069777000	2.787307000
1	-2.224581000	-0.392523000	2.541004000
1	-3.025588000	1.168636000	2.725233000
6	-2.134668000	2.799665000	0.084535000
1	-3.043439000	3.244816000	0.501727000
1	-2.120456000	3.010700000	-0.986466000
1	-1.280153000	3.306834000	0.536153000
1	1.352042000	-3.091638000	1.057199000
1	-1.350950000	-3.093061000	1.055878000

1a

83	0.607590000	1.771163000	0.507854000
7	0.275022000	-2.464525000	0.376229000
7	-1.772611000	-1.771262000	0.403114000
6	-0.516980000	-1.416110000	-0.012502000
6	-3.000654000	-1.034298000	0.221971000
6	1.700731000	-2.593511000	0.194580000
6	-1.754421000	-3.014606000	1.014408000
1	-2.648893000	-3.472206000	1.393868000
6	-0.479389000	-3.446336000	0.997049000
1	-0.038093000	-4.354238000	1.363648000
6	-3.502398000	-0.287901000	1.301301000
6	2.537993000	-2.353550000	1.296900000
6	2.193255000	-3.027728000	-1.047395000
6	2.008684000	-1.960726000	2.670209000
1	0.953989000	-1.705192000	2.566245000
6	-3.694129000	-1.164589000	-0.992112000
6	3.908896000	-2.538520000	1.115623000
1	4.583101000	-2.359674000	1.942653000
6	4.423126000	-2.944147000	-0.104475000
1	5.491439000	-3.074660000	-0.224221000
6	3.572201000	-3.188688000	-1.170914000
1	3.986672000	-3.516260000	-2.115032000
6	1.282356000	-3.385032000	-2.212939000
1	0.293182000	-2.982600000	-2.000653000
6	-2.780657000	-0.183562000	2.638735000
1	-1.755730000	-0.527158000	2.494954000
6	-4.735932000	0.340110000	1.130098000
1	-5.151500000	0.924258000	1.940096000
6	-3.187069000	-2.018380000	-2.144786000
1	-2.161224000	-2.308769000	-1.922784000
6	-5.437209000	0.234451000	-0.059464000
1	-6.390797000	0.735290000	-0.170995000
6	-4.919073000	-0.509107000	-1.107450000
1	-5.477923000	-0.587097000	-2.030714000
6	2.104666000	-3.143638000	3.649882000
1	1.573338000	-4.022588000	3.280733000
1	1.675819000	-2.872106000	4.616913000
1	3.145185000	-3.432108000	3.813882000
6	2.710427000	-0.726031000	3.251388000
1	3.771299000	-0.907793000	3.433453000
1	2.255137000	-0.458265000	4.207094000
1	2.618866000	0.132280000	2.586664000
6	-2.696691000	1.256731000	3.161378000
1	-2.230407000	1.918100000	2.432151000
1	-2.092252000	1.285714000	4.070050000
1	-3.680989000	1.658111000	3.410178000
6	-3.437218000	-1.094395000	3.691107000
1	-4.465178000	-0.782656000	3.889388000
1	-2.885136000	-1.046998000	4.632288000
1	-3.463642000	-2.136640000	3.369487000
6	-3.153220000	-1.250164000	-3.473166000
1	-4.155091000	-0.974236000	-3.808128000
1	-2.708022000	-1.872242000	-4.252529000
1	-2.557757000	-0.341956000	-3.383932000
6	1.735770000	-2.761956000	-3.539343000
1	1.823625000	-1.679297000	-3.454134000
1	1.004960000	-2.980708000	-4.320697000
1	2.696006000	-3.160912000	-3.872389000
5	-0.106740000	-0.168621000	-0.868691000
6	1.147110000	-4.912186000	-2.344413000
1	2.110506000	-5.373352000	-2.573337000
1	0.454658000	-5.164518000	-3.150612000
1	0.772143000	-5.364417000	-1.424266000
6	-4.015411000	-3.307692000	-2.277522000
1	-4.005862000	-3.888255000	-1.353052000
1	-3.614845000	-3.937038000	-3.075354000
1	-5.056902000	-3.084095000	-2.519083000
1	-1.047810000	0.255177000	-1.476282000
1	0.858738000	-0.408060000	-1.532092000
14	-0.811864000	3.594221000	-0.885163000
6	-2.660301000	3.281756000	-0.628534000
1	-2.939162000	3.358104000	0.424162000
1	-3.244510000	4.024805000	-1.181283000
1	-2.956596000	2.292958000	-0.981632000
6	-0.439364000	5.326590000	-0.214147000

1	-1.038499000	6.078691000	-0.737583000
1	-0.676509000	5.392115000	0.850166000
1	0.611748000	5.593716000	-0.333525000
6	-0.497837000	3.588049000	-2.750884000
1	-1.179705000	4.283714000	-3.250788000
1	0.522041000	3.889602000	-2.995391000
1	-0.662374000	2.593914000	-3.170139000
14	2.940573000	2.271932000	-0.770189000
6	3.313039000	4.130461000	-0.804461000
1	2.609231000	4.676862000	-1.434604000
1	3.274877000	4.568166000	0.195313000
1	4.317662000	4.300489000	-1.205064000
6	3.013164000	1.626226000	-2.545835000
1	2.245759000	2.080670000	-3.173822000
1	3.990041000	1.847202000	-2.988107000
1	2.864313000	0.546021000	-2.572795000
6	4.355976000	1.452250000	0.186608000
1	5.313280000	1.680053000	-0.293819000
1	4.407413000	1.811880000	1.216618000
1	4.248711000	0.366495000	0.214600000

1b

83	-0.662870000	-0.132254000	-0.615296000
14	-1.835879000	2.218612000	-0.028059000
14	-2.540410000	-1.758527000	0.414778000
7	3.083066000	0.855697000	0.754279000
7	2.989220000	-1.241553000	0.280171000
6	4.284492000	0.535800000	0.125449000
6	2.270684000	-0.230825000	0.837542000
6	4.223814000	-0.786765000	-0.176255000
6	5.213364000	-1.673454000	-0.845661000
1	5.564028000	-2.469930000	-0.183457000
1	6.084127000	-1.098067000	-1.154478000
1	4.795433000	-2.147043000	-1.737545000
6	-1.776243000	-3.487479000	0.550758000
1	-1.407952000	-3.839440000	-0.415636000
1	-2.520641000	-4.207238000	0.905810000
1	-0.942452000	-3.495489000	1.255387000
6	-1.968882000	2.612826000	1.816723000
1	-2.604668000	1.893550000	2.335138000
1	-2.397660000	3.609808000	1.961266000
1	-0.991792000	2.589208000	2.301597000
6	2.737786000	2.184800000	1.224478000
1	3.562983000	2.604579000	1.799040000
1	1.861634000	2.106719000	1.859137000
1	2.515358000	2.846565000	0.385649000
6	2.486298000	-2.593437000	0.107144000
1	1.824756000	-2.832344000	0.934292000
1	3.318051000	-3.293924000	0.095046000
1	1.924942000	-2.681430000	-0.825141000
6	5.359438000	1.538455000	-0.103952000
1	5.000878000	2.391546000	-0.685584000
1	6.184612000	1.088192000	-0.652523000
1	5.762300000	1.928360000	0.834994000
6	-0.804414000	3.590574000	-0.837473000
1	0.206997000	3.631370000	-0.427190000
1	-1.267424000	4.568783000	-0.672887000
1	-0.719105000	3.437234000	-1.915443000
6	-3.161714000	-1.264615000	2.130858000
1	-2.329643000	-1.134997000	2.825276000
1	-3.825469000	-2.036302000	2.534148000
1	-3.721453000	-0.327851000	2.100456000
6	-3.571925000	2.319209000	-0.779657000
1	-3.554475000	2.114071000	-1.852094000
1	-3.989284000	3.321113000	-0.636467000
1	-4.256238000	1.606185000	-0.315906000
6	-4.026610000	-1.882859000	-0.752534000
1	-4.523391000	-0.919036000	-0.878425000
1	-4.764517000	-2.591074000	-0.361976000
1	-3.722345000	-2.228564000	-1.742929000
5	0.809468000	-0.312187000	1.398733000
1	0.520480000	0.590008000	2.132081000
1	0.548312000	-1.400157000	1.834526000

1c

83	1.030644000	-0.303616000	-0.638716000
14	3.352036000	-1.145643000	0.417390000
14	1.195975000	2.312327000	-0.028633000
7	-1.821691000	-0.850789000	0.915255000
7	-5.817442000	-0.135276000	-0.122851000
6	-4.523098000	-0.371685000	0.220456000
5	-0.314191000	-1.096968000	1.265699000
6	-3.807627000	0.477927000	1.093757000
1	-4.265544000	1.349278000	1.534160000
6	3.289443000	-3.037766000	0.409398000
1	3.148360000	-3.426050000	-0.601794000
1	2.467495000	-3.406388000	1.026219000
1	4.221197000	-3.456863000	0.802481000
6	-3.804671000	-1.485717000	-0.270641000
1	-4.261091000	-2.202850000	-0.934266000
6	-2.499133000	0.207147000	1.406480000
1	-1.938328000	0.843420000	2.074901000
6	-6.511975000	-1.039368000	-1.025280000
1	-6.005130000	-1.108897000	-1.992010000
1	-7.516931000	-0.665425000	-1.199381000
1	-6.592826000	-2.047248000	-0.606520000
6	3.683033000	-0.581448000	2.193150000
1	2.841657000	-0.817337000	2.847193000
1	3.858266000	0.494850000	2.248176000
1	4.572126000	-1.083069000	2.589298000
6	-6.519151000	1.018188000	0.416878000
1	-6.580532000	0.979458000	1.508678000
1	-7.531711000	1.033900000	0.023788000
1	-6.031344000	1.955360000	0.133159000
6	-2.495749000	-1.679997000	0.089558000
1	-1.930238000	-2.522218000	-0.281360000
6	-0.337992000	3.155008000	-0.765237000
1	-1.259431000	2.748506000	-0.341087000
1	-0.385054000	3.014064000	-1.847327000
1	-0.324989000	4.231539000	-0.566390000
6	4.811032000	-0.603763000	-0.660826000
1	5.749154000	-1.015144000	-0.274534000
1	4.909459000	0.483279000	-0.688584000
1	4.690581000	-0.950991000	-1.689217000
6	1.222032000	2.712943000	1.822348000
1	2.126924000	2.334421000	2.300169000
1	0.372382000	2.266481000	2.342326000
1	1.185770000	3.795858000	1.980102000
6	2.718636000	3.117856000	-0.816327000
1	2.705951000	4.201565000	-0.661456000
1	2.756429000	2.932401000	-1.891788000
1	3.642618000	2.731112000	-0.381736000
1	-0.107024000	-2.279499000	1.295785000
1	-0.037570000	-0.495583000	2.264264000

2

83	2.247926000	0.100666000	0.512241000
7	-2.482864000	-1.178908000	0.485786000
7	-2.593426000	0.965284000	0.497739000
6	-1.804496000	-0.066574000	0.094613000
6	-2.332626000	2.377759000	0.325891000
6	-2.071898000	-2.554450000	0.307209000
6	-3.741193000	0.502898000	1.118125000
1	-4.491891000	1.170240000	1.499225000
6	-3.671664000	-0.844050000	1.110476000
1	-4.348530000	-1.589194000	1.485920000
6	-1.697893000	3.072956000	1.367287000
6	-1.399179000	-3.192528000	1.361161000
6	-2.424237000	-3.215515000	-0.880441000
6	-1.086042000	-2.501061000	2.681396000
1	-1.228865000	-1.428631000	2.544903000
6	-2.788011000	3.008335000	-0.842341000
6	-1.059302000	-4.533841000	1.185229000
1	-0.534578000	-5.057220000	1.973136000
6	-1.380808000	-5.207708000	0.018723000
1	-1.103090000	-6.247860000	-0.097794000
6	-2.058728000	-4.555219000	-0.998579000
1	-2.307394000	-5.096110000	-1.901662000
6	-3.219702000	-2.545942000	-1.991908000
1	-3.183328000	-1.468900000	-1.828604000
6	-1.262569000	2.399552000	2.662147000
1	-1.242503000	1.322468000	2.491272000
6	-1.512900000	4.445202000	1.200516000
1	-1.021354000	5.014069000	1.977968000

6	-3.524544000	2.265782000	-1.947876000
1	-3.397372000	1.196561000	-1.778192000
6	-1.944899000	5.093355000	0.054954000
1	-1.786850000	6.159047000	-0.054148000
6	-2.576831000	4.381703000	-0.951883000
1	-2.909952000	4.901408000	-1.840317000
6	-2.058796000	-2.963629000	3.780381000
1	-3.099485000	-2.789528000	3.501443000
1	-1.864656000	-2.426881000	4.711491000
1	-1.943379000	-4.031529000	3.978308000
6	0.366835000	-2.701479000	3.130609000
1	0.581570000	-3.746711000	3.360837000
1	0.559158000	-2.120951000	4.035053000
1	1.068234000	-2.368852000	2.366394000
6	0.149703000	2.805629000	3.101757000
1	0.878278000	2.626642000	2.311949000
1	0.449558000	2.219265000	3.972288000
1	0.201622000	3.858769000	3.384651000
6	-2.274917000	2.674926000	3.788046000
1	-2.328638000	3.743098000	4.009600000
1	-1.977233000	2.156872000	4.702277000
1	-3.279302000	2.340020000	3.523737000
6	-2.954931000	2.564179000	-3.341499000
1	-3.117237000	3.603790000	-3.632894000
1	-3.449760000	1.937039000	-4.086170000
1	-1.885600000	2.357948000	-3.377271000
6	-2.630629000	-2.802676000	-3.385370000
1	-1.583531000	-2.504221000	-3.426020000
1	-3.179830000	-2.224272000	-4.131276000
1	-2.704064000	-3.853614000	-3.671897000
31	-0.034602000	0.032382000	-1.081419000
6	-4.696097000	-2.975778000	-1.936960000
1	-4.796509000	-4.050118000	-2.106742000
1	-5.271958000	-2.459128000	-2.707950000
1	-5.148420000	-2.748762000	-0.969743000
6	-5.032560000	2.566334000	-1.897604000
1	-5.464859000	2.304903000	-0.929861000
1	-5.559777000	1.997740000	-2.666813000
1	-5.226819000	3.626742000	-2.072583000
1	-0.242456000	1.392522000	-1.872428000
1	-0.140280000	-1.299816000	-1.935273000
14	3.369809000	2.153857000	-0.825960000
6	2.448221000	3.734882000	-0.342936000
1	2.507028000	3.916104000	0.732488000
1	2.891412000	4.598158000	-0.850071000
1	1.393935000	3.687937000	-0.620687000
6	5.169915000	2.364314000	-0.273943000
1	5.612881000	3.241456000	-0.756823000
1	5.238069000	2.507179000	0.806684000
1	5.781287000	1.497730000	-0.531551000
6	3.341249000	2.022453000	-2.711149000
1	3.748668000	2.937024000	-3.154638000
1	3.941556000	1.184377000	-3.068937000
1	2.323441000	1.891579000	-3.082095000
14	3.517351000	-1.904117000	-0.770471000
6	5.383549000	-1.761237000	-0.479786000
1	5.801249000	-0.879089000	-0.968715000
1	5.618407000	-1.693223000	0.584417000
1	5.898144000	-2.639494000	-0.882876000
6	3.224001000	-2.028533000	-2.632745000
1	3.574845000	-1.140235000	-3.159648000
1	3.763283000	-2.892299000	-3.035766000
1	2.164395000	-2.154269000	-2.859985000
6	2.944796000	-3.532737000	0.007668000
1	3.459649000	-4.376122000	-0.463851000
1	3.163198000	-3.564813000	1.077271000
1	1.871324000	-3.682784000	-0.121749000

H_2

1	0.000000000	0.000000000	0.380000000
1	0.000000000	0.000000000	-0.380000000

$HSi(CH_3)_3$

6	1.545938000	-0.892548000	-0.221316000
14	0.000000000	0.000000000	0.374025000
6	0.000000000	1.785095000	-0.221316000
1	0.000000000	0.000000000	1.863245000
6	-1.545938000	-0.892548000	-0.221316000
1	0.000000000	1.838333000	-1.313166000
1	0.881763000	2.321263000	0.137266000
1	-0.881763000	2.321263000	0.137266000
1	-1.592043000	-0.919166000	-1.313166000
1	-2.451155000	-0.397002000	0.137266000
1	-1.569391000	-1.924261000	0.137266000
1	2.451155000	-0.397002000	0.137266000
1	1.592043000	-0.919166000	-1.313166000
1	1.569391000	-1.924261000	0.137266000

CH_3OH

8	-0.046596000	-0.756501000	0.000000000
6	-0.046596000	0.663615000	0.000000000
1	0.438484000	1.078506000	0.890984000
1	0.438484000	1.078506000	-0.890984000
1	-1.089053000	0.979408000	0.000000000
1	0.864424000	-1.066100000	0.000000000

$CH_3OSi(CH_3)_3$

6	-0.522153000	-1.535462000	1.078412000
14	-0.377723000	0.000016000	0.004045000
6	-1.680089000	0.003234000	-1.337530000
6	-0.520612000	1.531445000	1.084431000
1	-2.687101000	0.002876000	-0.912943000
1	-1.584433000	-0.877842000	-1.975698000
1	-1.583569000	0.886740000	-1.972211000
1	-1.491588000	1.563635000	1.585876000
1	-0.422622000	2.444218000	0.492065000
1	0.246563000	1.554117000	1.862466000
1	-0.427691000	-2.445955000	0.481953000
1	-1.492133000	-1.567424000	1.581804000
1	0.246622000	-1.563419000	1.854688000
8	1.069807000	0.000839000	-0.807514000
6	2.354798000	0.000152000	-0.220531000
1	3.096790000	0.000393000	-1.020411000
1	2.518811000	0.888706000	0.399095000
1	2.518353000	-0.889188000	0.398103000

DMAP·BH_2BiH_2

5	-0.833281000	0.302899000	1.625804000
1	-1.027624000	-0.578699000	2.411963000
1	-1.036667000	1.417374000	2.024942000
83	-2.333790000	-0.020341000	-0.281074000
7	0.637553000	0.208497000	1.093192000
6	3.279437000	0.014750000	0.096905000
6	1.323987000	1.300574000	0.697880000
6	1.271102000	-0.980676000	1.000577000
6	2.549510000	-1.118205000	0.525134000
6	2.605047000	1.250965000	0.206446000
1	0.796293000	2.238040000	0.796004000
1	0.695611000	-1.835260000	1.324772000
1	2.974082000	-2.108958000	0.489293000
1	3.074308000	2.177523000	-0.084215000
7	4.547591000	-0.080506000	-0.384959000
6	5.261558000	1.113738000	-0.805987000
6	5.200525000	-1.376418000	-0.476553000
1	6.250330000	0.831981000	-1.156800000
1	5.384122000	1.822203000	0.018795000
1	4.744906000	1.624846000	-1.623860000
1	5.302267000	-1.847964000	0.505530000
1	6.196078000	-1.244317000	-0.890782000
1	4.649738000	-2.059237000	-1.130066000
1	-1.716330000	-1.686417000	-0.637186000
1	-3.659149000	-0.701582000	0.727722000

DMAP·$BH_2Bi(OMe)_2$

5	0.536924000	-0.000206000	2.031996000
1	0.737618000	1.014161000	2.643269000
1	0.737668000	-1.014755000	2.642959000
83	2.066302000	-0.000026000	0.188652000
7	-0.888752000	-0.000155000	1.412075000
6	-3.447191000	-0.000017000	0.218352000
6	-1.518852000	-1.153723000	1.102154000
6	-1.518752000	1.153518000	1.102180000
6	-2.762762000	1.195812000	0.527201000
6	-2.762879000	-1.195903000	0.527144000
1	-0.973335000	-2.056174000	1.329077000

1	-0.973099000	2.055888000	1.329081000
1	-3.190084000	2.162687000	0.314352000
1	-3.190280000	-2.162748000	0.314320000
7	-4.686906000	0.000070000	-0.343978000
6	-5.345175000	-1.255485000	-0.663734000
6	-5.345221000	1.255698000	-0.663336000
1	-6.322930000	-1.046202000	-1.088643000
1	-5.489386000	-1.871932000	0.228450000
1	-4.775439000	-1.838149000	-1.394224000
1	-5.488858000	1.872112000	0.228956000
1	-6.323252000	1.046524000	-1.087664000
1	-4.775863000	1.838350000	-1.394138000
8	1.012355000	1.600883000	-0.729081000
6	1.353242000	2.039042000	-2.021971000
1	2.438824000	2.082988000	-2.190082000
1	0.923316000	1.397127000	-2.803337000
1	0.958124000	3.051454000	-2.169414000
8	1.012257000	-1.600687000	-0.729375000
6	1.353015000	-2.038716000	-2.022336000
1	0.922937000	-1.396783000	-2.803606000
1	2.438580000	-2.082551000	-2.190585000
1	0.957968000	-3.051153000	-2.169802000

IDipp·BH_2BiH_2

83	0.055659000	-2.315795000	-1.455897000
7	1.066288000	0.997391000	0.945083000
7	-1.097203000	0.990058000	0.933110000
6	2.572225000	-1.316990000	1.905430000
1	1.488348000	-1.255132000	1.796762000
6	2.278515000	3.147025000	-0.622724000
1	1.220193000	2.972948000	-0.433218000
6	-4.441879000	1.716391000	-0.505127000
1	-4.933937000	2.470482000	-1.105000000
6	-4.558671000	-0.336534000	0.733099000
1	-5.140686000	-1.175792000	1.088834000
6	-2.332685000	3.083332000	-0.694456000
1	-1.270558000	2.917400000	-0.520130000
6	4.406921000	1.808342000	-0.454724000
1	4.890551000	2.585790000	-1.031285000
6	3.190477000	-0.222867000	1.045197000
6	2.990931000	-2.728569000	1.472707000
1	2.787433000	-2.902341000	0.416333000
1	2.434209000	-3.472201000	2.046198000
1	4.052441000	-2.909572000	1.651974000
6	-3.086132000	1.852981000	-0.211194000
6	-0.697116000	1.538441000	2.140969000
1	-1.406389000	1.878350000	2.872205000
6	0.649872000	1.542624000	2.149105000
1	1.348856000	1.887361000	2.888066000
6	-2.913076000	-1.063799000	3.427690000
1	-2.585838000	-0.078042000	3.760656000
1	-2.429661000	-1.810044000	4.062082000
1	-3.990707000	-1.129243000	3.593397000
6	-5.171901000	0.634523000	-0.041285000
1	-6.223629000	0.547519000	-0.284249000
6	-2.745653000	4.327136000	0.110791000
1	-3.803366000	4.557066000	-0.034952000
1	-2.166947000	5.196994000	-0.207947000
1	-2.581096000	4.185569000	1.180741000
6	-0.010342000	0.659407000	0.169450000
6	-2.502055000	3.322849000	-2.200924000
1	-2.202834000	2.444251000	-2.772010000
1	-1.878925000	4.162294000	-2.516856000
1	-3.534090000	3.567764000	-2.459954000
6	3.048181000	1.917629000	-0.163004000
6	2.693855000	4.387309000	0.186426000
1	2.548098000	4.234730000	1.257573000
1	2.101704000	5.254146000	-0.115099000
1	3.746658000	4.629197000	0.025459000
6	2.459488000	0.884745000	0.584057000
6	4.547027000	-0.277077000	0.725220000
1	5.139802000	-1.116859000	1.061505000
6	5.150152000	0.723844000	-0.018743000
1	6.204132000	0.658516000	-0.258738000
6	-2.574903000	-1.317432000	1.947389000
1	-1.491415000	-1.245705000	1.838360000
6	-3.204439000	-0.255070000	1.055848000
6	2.905166000	-1.099232000	3.392482000
1	3.983079000	-1.155694000	3.559765000
1	2.428970000	-1.867342000	4.005788000
1	2.564555000	-0.126270000	3.749147000
6	-2.976925000	-2.745776000	1.554503000
1	-2.402598000	-3.466197000	2.140545000
1	-2.787915000	-2.937586000	0.498879000
1	-4.033085000	-2.937565000	1.753334000
5	0.005663000	0.128609000	-1.301052000
6	2.423787000	3.398832000	-2.129983000
1	3.451624000	3.646684000	-2.402711000
1	1.794861000	4.239879000	-2.429702000
1	2.116748000	2.524328000	-2.703223000
6	-2.486923000	0.849325000	0.566419000
1	1.039891000	0.399181000	-1.846337000
1	-0.984856000	0.437121000	-1.896518000
1	-1.733342000	-2.546452000	-1.531113000
1	0.124711000	-2.198061000	-3.248954000

IDipp·$BH_2Bi(OMe)_2$

83	-0.445418000	-2.277011000	-0.631940000
7	1.136728000	1.557046000	0.829378000
7	-1.027501000	1.553283000	0.866092000
6	2.674048000	-0.311826000	2.465480000
1	1.587457000	-0.243756000	2.391053000
6	2.301707000	3.061958000	-1.393432000
1	1.246967000	2.946968000	-1.146826000
6	-4.405477000	1.737601000	-0.663478000
1	-4.921855000	2.259473000	-1.458143000
6	-4.458294000	0.161787000	1.146631000
1	-5.016378000	-0.537660000	1.754098000
6	-2.335949000	3.035370000	-1.289093000
1	-1.267028000	2.942245000	-1.102485000
6	4.447876000	1.872423000	-0.818337000
1	4.916288000	2.416388000	-1.628011000
6	3.270669000	0.446558000	1.288026000
6	3.032731000	-1.804001000	2.448064000
1	2.750126000	-2.261591000	1.499655000
1	2.503297000	-2.319523000	3.253142000
1	4.100551000	-1.962830000	2.612725000
6	-3.052111000	1.991310000	-0.445375000
6	-0.604370000	2.448303000	1.835807000
1	-1.298705000	2.999377000	2.442072000
6	0.742394000	2.449096000	1.813335000
1	1.455976000	3.001115000	2.396158000
6	-2.798297000	0.389309000	3.914814000
1	-2.504245000	1.439247000	3.901006000
1	-2.290867000	-0.091048000	4.754120000
1	-3.873335000	0.348144000	4.102883000
6	-5.101806000	0.830120000	0.117783000
1	-6.151464000	0.645115000	-0.073361000
6	-2.758885000	4.454122000	-0.870760000
1	-3.825038000	4.614234000	-1.045922000
1	-2.208651000	5.200636000	-1.447610000
1	-2.564913000	4.635839000	0.188062000
6	0.046601000	0.998704000	0.219965000
6	-2.544683000	2.824444000	-2.794756000
1	-2.248683000	1.819841000	-3.095782000
1	-1.939858000	3.538856000	-3.357017000
1	-3.585377000	2.978462000	-3.087304000
6	3.091836000	2.063894000	-0.560058000
6	2.702624000	4.506054000	-1.047714000
1	2.556645000	4.720245000	0.012860000
1	2.102653000	5.215964000	-1.621568000
1	3.753361000	4.689881000	-1.281863000
6	2.525150000	1.334971000	0.497619000
6	4.623530000	0.296957000	0.984270000
1	5.226724000	-0.384241000	1.569071000
6	5.207310000	0.998510000	-0.057171000
1	6.258706000	0.862583000	-0.278171000
6	-2.448741000	-0.324471000	2.596201000
1	-1.366780000	-0.261189000	2.466487000
6	-3.105954000	0.375831000	1.412751000
6	3.087605000	0.332001000	3.800379000
1	4.170474000	0.285147000	3.935289000
1	2.623339000	-0.195332000	4.636757000
1	2.792466000	1.381273000	3.858037000

6	-2.809640000	-1.813138000	2.698177000
1	-2.222678000	-2.282559000	3.490050000
1	-2.607890000	-2.347782000	1.769417000
1	-3.862263000	-1.959100000	2.947346000
5	0.031928000	0.056369000	-1.024171000
6	2.436180000	2.800249000	-2.900079000
1	3.458083000	2.962185000	-3.248850000
1	1.789132000	3.481560000	-3.456846000
1	2.146971000	1.778928000	-3.146553000
6	-2.419152000	1.288688000	0.593119000
1	1.083071000	0.035285000	-1.593825000
1	-0.923104000	0.282241000	-1.721998000
8	1.577629000	-2.892427000	-0.446277000
6	1.864897000	-4.263506000	-0.611803000
1	1.308671000	-4.906300000	0.086859000
1	1.648062000	-4.612994000	-1.628617000
1	2.933350000	-4.419112000	-0.424470000
8	-0.648300000	-2.804142000	-2.656356000
6	0.110900000	-2.193761000	-3.676872000
1	-0.130913000	-1.131185000	-3.798446000
1	1.190480000	-2.275212000	-3.501078000
1	-0.118178000	-2.704828000	-4.618736000

$IMe_4{\cdot}BH_2BiH_2$

5	-0.267447000	0.000060000	1.566794000
6	1.132136000	0.000025000	0.871093000
1	-0.507731000	-1.007863000	2.175224000
1	-0.507717000	1.008034000	2.175144000
7	1.861052000	1.077238000	0.477567000
6	3.011883000	0.679147000	-0.198479000
6	3.011845000	-0.679187000	-0.198487000
7	1.861022000	-1.077223000	0.477605000
6	1.427481000	2.453277000	0.641654000
6	3.993581000	1.647263000	-0.758061000
6	3.993487000	-1.647351000	-0.758083000
6	1.427412000	-2.453244000	0.641735000
1	2.294984000	3.108117000	0.677046000
1	0.870978000	2.540872000	1.570104000
1	0.777697000	2.752198000	-0.183526000
1	2.294895000	-3.108109000	0.677145000
1	0.777620000	-2.752168000	-0.183438000
1	0.870906000	-2.540797000	1.570186000
1	3.528340000	-2.328648000	-1.474835000
1	4.458356000	-2.256630000	0.022188000
1	4.790077000	-1.116868000	-1.276380000
1	4.790132000	1.116743000	-1.276380000
1	4.458497000	2.256499000	0.022218000
1	3.528466000	2.328602000	-1.474793000
83	-1.961076000	0.000002000	-0.199406000
1	-1.180222000	-1.280894000	-1.218762000
1	-1.180195000	1.280792000	-1.218874000

$IMe_4{\cdot}BH_2Bi(OMe)_2$

5	0.153965000	0.000106000	1.868816000
6	1.472965000	-0.000074000	1.024796000
1	-0.025244000	-1.008299000	2.500962000
1	-0.025137000	1.008721000	2.500684000
7	2.149301000	1.077120000	0.559437000
6	3.228751000	0.679890000	-0.221654000
6	3.228517000	-0.680730000	-0.221607000
7	2.148919000	-1.077538000	0.559483000
6	1.735205000	2.454101000	0.796829000
6	4.144259000	1.642780000	-0.892057000
6	4.143783000	-1.643922000	-0.891910000
6	1.734232000	-2.454334000	0.796934000
1	2.532069000	3.124396000	0.486564000
1	1.542009000	2.596016000	1.858229000
1	0.826401000	2.663923000	0.232599000
1	2.530040000	-3.125038000	0.484857000
1	0.824335000	-2.663221000	0.234122000
1	1.542835000	-2.596743000	1.858606000
1	3.606724000	-2.299769000	-1.581771000
1	4.671007000	-2.278304000	-0.174200000
1	4.895694000	-1.106666000	-1.466954000
1	4.895701000	1.105303000	-1.467508000
1	4.672051000	2.276756000	-0.174401000
1	3.607248000	2.299031000	-1.581567000
83	-1.685931000	0.000423000	0.336615000
8	-0.923960000	1.604164000	-0.841355000
6	-1.621805000	2.032295000	-1.987639000
1	-1.381731000	1.420305000	-2.867635000
1	-2.713547000	2.015349000	-1.858965000
1	-1.336140000	3.066456000	-2.214211000
8	-0.925806000	-1.604803000	-0.840484000
6	-1.624438000	-2.033361000	-1.986126000
1	-2.716156000	-2.014014000	-1.857583000
1	-1.383066000	-1.423190000	-2.867028000
1	-1.340850000	-3.068449000	-2.211073000

$DMAP{\cdot}BH_3$

7	-2.169417000	-0.000014000	-0.019902000
7	2.014287000	0.000006000	0.012820000
6	0.653412000	0.000006000	0.001103000
5	-3.782020000	0.000010000	0.034661000
6	-0.097883000	1.195933000	-0.007748000
1	0.379730000	2.162897000	-0.010841000
6	-0.097864000	-1.195930000	-0.007775000
1	0.379769000	-2.162884000	-0.010895000
6	-1.471837000	1.146592000	-0.018489000
1	-2.067533000	2.048204000	-0.028727000
6	2.746236000	-1.255778000	0.006196000
1	2.502836000	-1.868198000	0.879344000
1	3.811996000	-1.046219000	0.030180000
1	2.536434000	-1.842649000	-0.893412000
6	2.746253000	1.255781000	0.006152000
1	2.536359000	1.842676000	-0.893418000
1	3.812012000	1.046204000	0.030004000
1	2.502965000	1.868185000	0.879344000
6	-1.471821000	-1.146611000	-0.018512000
1	-2.067508000	-2.048227000	-0.028769000
1	-4.143517000	-1.010098000	-0.525992000
1	-4.143516000	1.009642000	-0.526855000
1	-4.083011000	0.000520000	1.210741000

$IDipp{\cdot}BH_3$

5	0.000000000	-0.072951000	-1.921517000
1	1.008018000	0.449696000	-2.341361000
1	-1.008021000	0.449690000	-2.341361000
7	-1.075771000	0.004809000	0.501640000
7	1.075770000	0.004810000	0.501639000
6	0.000000000	-0.007258000	-0.329580000
6	-0.674309000	0.019790000	1.828965000
1	-1.381367000	0.031222000	2.638122000
6	0.674309000	0.019791000	1.828964000
1	1.381367000	0.031224000	2.638122000
6	-2.461291000	0.002435000	0.097868000
6	-3.114874000	1.232378000	-0.070557000
6	-4.466070000	1.202037000	-0.411664000
1	-4.999139000	2.133294000	-0.553155000
6	-5.136402000	0.001164000	-0.581757000
1	-6.185585000	0.000569000	-0.850151000
6	-4.463688000	-1.198573000	-0.416165000
1	-4.995224000	-2.130387000	-0.559461000
6	-3.111951000	-1.227863000	-0.074700000
6	-2.409230000	2.570081000	0.090350000
1	-1.362947000	2.373518000	0.322965000
6	-2.991932000	3.381738000	1.257845000
1	-2.439312000	4.315360000	1.383734000
1	-4.039072000	3.637152000	1.082447000
1	-2.938307000	2.827782000	2.197207000
6	-2.431792000	3.379974000	-1.215211000
1	-1.860882000	4.303443000	-1.094379000
1	-1.992784000	2.809932000	-2.033932000
1	-3.450319000	3.655737000	-1.497053000
6	-2.407372000	-2.565243000	0.093918000
1	-1.355511000	-2.369269000	0.299806000
6	-2.969951000	-3.350722000	1.289250000
1	-2.419401000	-4.284523000	1.422739000
1	-2.894437000	-2.778434000	2.216063000
1	-4.021824000	-3.603561000	1.140013000
6	-2.460062000	-3.400543000	-1.194138000
1	-1.893660000	-4.325471000	-1.064107000
1	-3.484982000	-3.674822000	-1.453204000
1	-2.028110000	-2.851447000	-2.030605000

6	2.461291000	0.002436000	0.097868000
6	3.114872000	1.232381000	-0.070560000
6	4.466068000	1.202040000	-0.411667000
1	4.999135000	2.133298000	-0.553160000
6	5.136402000	0.001168000	-0.581757000
1	6.185584000	0.000575000	-0.850152000
6	4.463689000	-1.198569000	-0.416164000
1	4.995227000	-2.130383000	-0.559458000
6	3.111952000	-1.227860000	-0.074698000
6	2.409226000	2.570083000	0.090345000
1	1.362943000	2.373518000	0.322957000
6	2.991925000	3.381741000	1.257842000
1	2.938297000	2.827784000	2.197203000
1	4.039064000	3.637155000	1.082446000
1	2.439303000	4.315362000	1.383729000
6	2.431790000	3.379976000	-1.215217000
1	1.860879000	4.303444000	-1.094385000
1	3.450318000	3.655741000	-1.497056000
1	1.992785000	2.809933000	-2.033939000
6	2.407376000	-2.565241000	0.093924000
1	1.355514000	-2.369268000	0.299810000
6	2.969955000	-3.350715000	1.289258000
1	2.419406000	-4.284517000	1.422750000
1	4.021828000	-3.603552000	1.140024000
1	2.894438000	-2.778424000	2.216070000
6	2.460069000	-3.400546000	-1.194129000
1	1.893668000	-4.325474000	-1.064096000
1	2.028117000	-2.851453000	-2.030599000
1	3.484990000	-3.674824000	-1.453193000
1	0.000003000	-1.258676000	-2.217371000

$IMe_4 \cdot BH_3$

7	-0.858916000	0.750008000	-0.006097000
7	1.122481000	-0.067284000	-0.015043000
6	-1.003430000	-0.638215000	0.001148000
6	0.447016000	1.105663000	-0.012688000
6	0.252366000	-1.154236000	-0.002608000
6	0.729297000	-2.563581000	-0.000406000
1	1.294041000	-2.804198000	-0.905246000
1	-0.114851000	-3.248819000	0.052499000
1	1.378443000	-2.770363000	0.854402000
6	-1.974853000	1.681433000	0.001832000
1	-2.610956000	1.519265000	-0.869266000
1	-1.570593000	2.687607000	-0.025835000
1	-2.571047000	1.553355000	0.906416000
6	2.572041000	-0.162375000	0.008684000
1	2.977576000	0.820785000	-0.207142000
1	2.913971000	-0.871863000	-0.744681000
1	2.921433000	-0.486529000	0.990659000
6	-2.332559000	-1.306724000	0.005923000
1	-2.926962000	-1.026738000	0.879692000
1	-2.210066000	-2.388277000	0.023738000
1	-2.919162000	-1.055663000	-0.881969000
5	1.111675000	2.560699000	0.004661000
1	0.271353000	3.427622000	-0.079793000
1	1.891653000	2.626989000	-0.929720000
1	1.732565000	2.662470000	1.049603000

7. References

[1] R. Szlosek, M. Seidl, G. Balázs, M. Scheer, *Chem. Eur. J.* **2023**, *29*, e202301752.

[2] N. Kuhn, G. Henkel, T. Kratz, J. Kreutzberg, R. Boese, A. H. Maulitz, *Chem. Ber.* **1993**, *126*, 2041–2045.

[3] G. Becker, M. Rößler, *Z. Naturforsch. B* **1982**, *37*, 91–96.

[4] F. Barth, F. Achrainer, A. M. Pütz, H. Zipse, *Chem. Eur. J.* **2017**, *23*, 13455–13464.

[5] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341.

[6] G. M. Sheldrick, *Acta Cryst. A* **2015**, *71*, 3–8.

[7] G. M. Sheldrick, *Acta Cryst. C* **2015**, *71*, 3–8.

[8] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789; c) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-305.

[9] Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[10] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899–926.

[11] Thermal Constants of Substances database, Eds. V.S. Iorish and V.S. Yungman, https://www.chem.msu.ru/cgi-bin/tkv.pl?show=welcome.html/welcome.html