

Supplementary Information

A Convenient Route to Mixed Cationic Group 13/14/15 Compounds

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1 Experimental section

1.1 General procedures

All manipulations were performed under an atmosphere of dry argon in a Braun glovebox or using standard Schlenk techniques. All solvents are degassed and purified by standard procedures. The NMR spectra were recorded on a Bruker Avance 400 spectrometer (^1H : 400.13 MHz, ^{31}P : 161.976 MHz, ^{11}B : 128.378 MHz, ^{19}F : 376.498 MHz) with δ [ppm] referenced to external SiMe_4 (^1H , ^{13}C), H_3PO_4 (^{31}P), $\text{BF}_3\cdot\text{Et}_2\text{O}$ (^{11}B), CFCl_3 (^{19}F). Mass spectra were recorded on a ThermoQuest Finnigan TSQ 7000 (ESI-MS), a Waters/Micromass ESI LCT-TOF spectrometer (ESI-MS) or an Agilent 6220 Series TOF (ESI-MS). Elemental analyses were determined with a Vario micro cube apparatus or by the Analytical and Instrumentation Laboratory at the University of Alberta.

The compounds $\text{NHC}\cdot\text{BH}_2\text{I}$,¹ NaPH_2 ,² KAsH_2 ,³ $\text{IDipp}\cdot\text{GeH}_2\text{BH}_2\text{OTf}$ (**1**),⁴ $\text{Ph}_2\text{PBH}_2\cdot\text{NMe}_3$,⁵ $\text{Ph}_2\text{AsBH}_2\cdot\text{NMe}_3$,⁶ $\text{H}_2\text{PBH}_2\cdot\text{NMe}_3$,⁷ $\text{H}_2\text{AsBH}_2\cdot\text{NMe}_3$,⁷ and $\text{H}_2\text{PBH}_2\cdot\text{IDipp}$ ⁸ were prepared according to literature procedures.

1.2 Synthesis of IMes·BH₂PH₂

IMes·BH₂I (666 mg, 1.50 mmol, 1 eq) and NaPH₂ (84 mg, 1.5 mmol, 1 eq) were combined in 20 mL THF at -80 °C. The reaction mixture was stirred for 2 hours at room temperature. The solvent of the resulting solution was removed *in vacuo* and the residue was suspended in 2x 25 mL toluene. After filtration over diatomaceous earth all volatiles were removed *in vacuo* and the residue washed with 3x 5 mL *n*-hexane. IMes·BH₂PH₂ could be isolated as a pale-yellow powder (388 mg, 74%).

¹H NMR (C₆D₆, 298 K): δ = 1.40 (dm, 2H, ¹J_{H,P} = 177 Hz, PH₂), 1.93 (br, 2H, BH₂), 2.08 (s, 18H, ArCH₃), 5.93 (s, 2H, N-CH), 7.61 (s, 4H, ArH). ³¹P NMR (C₆D₆, 298 K): δ = -210.4 (t, br, ¹J_{P,H} = 177 Hz, PH₂). ³¹P{¹H} NMR (C₆D₆, 298 K): δ = -210.4 (br, PH₂). ¹¹B NMR (C₆D₆, 298 K): δ = -34.2 (t, br, ¹J_{B,H} = 94 Hz, BH₂). ¹¹B{¹H} NMR (C₆D₆, 298 K): δ = -34.2 (br, BH₂).

1.3 Synthesis of IDipp·BH₂AsH₂

IDipp·BH₂I (265 mg, 0.502 mmol, 1 eq) and KAsH₂ (87 mg, 0.75 mmol, 1.5 eq) were combined in 20 mL THF at -80 °C. The reaction mixture was stirred for 15 hours at room temperature. The solvent of the resulting solution was removed *in vacuo* and the residue was suspended in 25 mL toluene. After filtration over diatomaceous earth all volatiles were removed *in vacuo* and the residue washed with 5 mL *n*-hexane. IDipp·BH₂AsH₂ could be isolated as a beige-white powder (140 mg, 53%). Colorless crystals could be obtained from a concentrated toluene/*n*-hexane solution at -30 °C.

¹H NMR (C₆D₆, 298 K): δ = 0.47 (t, 2H, ³J_{H,H} = 7.7 Hz, AsH₂), 1.01 (d, 12H, ³J_{H,H} = 6.9 Hz, CH(CH₃)₂), 1.39 (d, 12H, ³J_{H,H} = 6.8 Hz, CH(CH₃)₂), 1.95 (br, 2H, BH₂), 2.79 (septet, 4H, ³J_{H,H} = 6.9 Hz, CH(CH₃)₂), 6.39 (s, 2H, N-CH), 7.09 (d, 4H, ³J_{H,H} = 7.7 Hz, ArH), 7.22 (t, 2H, ³J_{H,H} = 7.8 Hz, ArH). ¹H{¹¹B} NMR (C₆D₆, 298 K): δ = 0.47 (t, 2H, ³J_{H,H} = 7.7 Hz, AsH₂), 1.01 (d, 12H, ³J_{H,H} = 6.9 Hz, CH(CH₃)₂), 1.39 (d, 12H, ³J_{H,H} = 6.8 Hz, CH(CH₃)₂), 1.95 (t, 2H, ³J_{H,H} = 7.7 Hz, BH₂), 2.79 (septet, 4H, ³J_{H,H} = 6.9 Hz, CH(CH₃)₂), 6.39 (s, 2H, N-CH), 7.09 (d, 4H, ³J_{H,H} = 7.7 Hz, ArH), 7.22 (t, 2H, ³J_{H,H} = 7.8 Hz, ArH). ¹¹B NMR (C₆D₆, 298 K): δ = -35.0 (t, br, ¹J_{B,H} = 99 Hz, BH₂). ¹¹B{¹H} NMR (C₆D₆, 298 K): δ = -35.0 (s, br, BH₂). **Elemental analysis** (%) calculated for C₂₇H₄₀BA₂N₂: C: 67.79, H: 8.43, N: 5.86; found: C: 67.98, H: 8.61, N: 5.64.

1.4 Synthesis of [IDipp·GeH₂BH₂PPh₂BH₂·NMe₃][OTf] (2a)

Ph₂PBH₂·NMe₃ (26 mg, 0.10 mmol, 1 eq) and IDipp·GeH₂BH₂OTf (**1**) (63 mg, 0.10 mmol, 1 eq) were combined in 10 mL Et₂O at room temperature. The reaction mixture was stirred for 15 hours upon which the product precipitates as a white powder. The mother liquor was

decanted away and the precipitate washed with 5 mL Et₂O. All volatiles were removed *in vacuo* and the product [IDipp·GeH₂BH₂PPh₂BH₂·NMe₃][OTf] (**2a**) could be isolated as a white powder (83 mg, 94%). Colorless crystals could be obtained by layering a THF solution with a 3-fold amount of *n*-hexane at room temperature.

¹H NMR (CD₂Cl₂, 298 K): δ = 0.87 (br, 2H, BH₂), 1.17 (d, 12H, ³J_{H,H} = 6.8 Hz, CH(CH₃)₂), 1.25 (d, 12H, ³J_{H,H} = 6.8 Hz, CH(CH₃)₂), 2.37 (septet, 4H, ³J_{H,H} = 6.9 Hz, CH(CH₃)₂), 2.44 (s, 9H, NMe₃), 2.44 (br, 2H, BH₂), 3.21 (m, 2H, GeH₂), 7.20 – 7.33 (m, 10H, ArH), 7.36 (d, 4H, ³J_{H,H} = 7.9 Hz, ArH), 7.52 (s, 2H, N-CH), 7.59 (t, 2H, ³J_{H,H} = 7.8 Hz, ArH). **¹H{¹¹B}** NMR (CD₂Cl₂, 298 K): δ = 0.87 (m, 2H, BH₂), 1.17 (d, 12H, ³J_{H,H} = 6.8 Hz, CH(CH₃)₂), 1.25 (d, 12H, ³J_{H,H} = 6.8 Hz, CH(CH₃)₂), 2.37 (septet, 4H, ³J_{H,H} = 6.9 Hz, CH(CH₃)₂), 2.44 (s, 9H, NMe₃), 2.44 (br, 2H, BH₂), 3.21 (m, 2H, GeH₂), 7.20 – 7.33 (m, 10H, ArH), 7.36 (d, 4H, ³J_{H,H} = 7.9 Hz, ArH), 7.52 (s, 2H, N-CH), 7.59 (t, 2H, ³J_{H,H} = 7.9 Hz, ArH). **³¹P NMR** (CD₂Cl₂, 298 K): δ = -24.9 (br). **³¹P{¹H}** NMR (CD₂Cl₂, 298 K): δ = -24.9 (br). **¹¹B NMR** (CD₂Cl₂, 298 K): δ = -7.8 (br, BH₂), -38.2 (br, BH₂). **¹¹B{¹H}** NMR (CD₂Cl₂, 298 K): δ = -7.8 (br, BH₂), -38.2 (br, BH₂). **¹⁹F NMR** (CD₂Cl₂, 298 K): δ = -78.90 (s, 3F, OTf). **ESI-MS** (THF): *m/z* = 734.4 (100%, [IDipp·GeH₂BH₂PPh₂BH₂·NMe₃]⁺). **Elemental analysis** (%) calculated for C₄₃H₆₁B₂F₃GeN₃O₃PS: C: 58.54, H: 6.97, N: 4.76; found: C: 58.64, H: 6.99, N: 4.73.

1.5 Synthesis of [IDipp·GeH₂BH₂AsPh₂BH₂·NMe₃][OTf] (**2b**)

Ph₂AsBH₂·NMe₃ (60 mg, 0.20 mmol, 1 eq) and IDipp·GeH₂BH₂OTf (**1**) (125 mg, 0.200 mmol, 1 eq) were combined in 10 mL Et₂O at room temperature. The reaction mixture was stirred for 15 hours upon which the product precipitates as a white powder. The mother liquor was decanted away, and the precipitate washed with 5 mL Et₂O. All volatiles were removed *in vacuo* and the product [IDipp·GeH₂BH₂AsPh₂BH₂·NMe₃][OTf] (**2b**) could be isolated as a white powder (172 mg, 93%). Colorless crystals could be obtained by layering a THF solution with a 3-fold amount of *n*-hexane at room temperature.

¹H NMR (CD₂Cl₂, 298 K): δ = 1.02 (br, 2H, BH₂), 1.18 (d, 12H, ³J_{H,H} = 6.8 Hz, CH(CH₃)₂), 1.26 (d, 12H, ³J_{H,H} = 6.8 Hz, CH(CH₃)₂), 2.39 (septet, 4H, ³J_{H,H} = 6.9 Hz, CH(CH₃)₂), 2.54 (s, 9H, NMe₃), 2.56 (br, 2H, BH₂), 3.32 (m, 2H, GeH₂), 7.20 – 7.26 (m, 8H, ArH), 7.27 – 7.34 (m, 2H, ArH), 7.37 (d, 4H, ³J_{H,H} = 7.9 Hz, ArH), 7.56 (s, 2H, N-CH), 7.61 (t, 2H, ³J_{H,H} = 7.8 Hz, ArH). **¹H{¹¹B}** NMR (CD₂Cl₂, 298 K): δ = 1.02 (s, br, 2H, BH₂), 1.18 (d, 12H, ³J_{H,H} = 6.8 Hz, CH(CH₃)₂), 1.26 (d, 12H, ³J_{H,H} = 6.8 Hz, CH(CH₃)₂), 2.39 (septet, 4H, ³J_{H,H} = 6.9 Hz, CH(CH₃)₂), 2.54 (s, 9H, NMe₃), 2.56 (br, 2H, BH₂), 3.32 (m, 2H, GeH₂), 7.20 – 7.26 (m, 8H, ArH), 7.27 – 7.34 (m, 2H, ArH), 7.37 (d, 4H, ³J_{H,H} = 7.9 Hz, ArH), 7.56 (s, 2H, N-CH), 7.61 (t, 2H, ³J_{H,H} = 7.8 Hz, ArH). **¹¹B NMR** (CD₂Cl₂, 298 K): δ = -6.4 (br, BH₂), -37.2 (br, BH₂). **¹¹B{¹H}** NMR (CD₂Cl₂, 298 K): δ = -

6.4 (s, br, BH₂), -37.2 (s, br, BH₂). **¹⁹F NMR** (CD₂Cl₂, 298 K): δ = -78.80 (s, 3F, OTf). **ESI-MS** (THF): m/z = 778.3 (100%, [IDipp·GeH₂BH₂AsPh₂BH₂·NMe₃]⁺). **Elemental analysis** (%) calculated for C₄₃H₆₁B₂F₃GeN₃O₃AsS: C: 55.76, H: 6.64, N: 4.54; found: C: 55.95, H: 6.20, N: 4.51.

1.6 Synthesis of [IDipp·GeH₂BH₂PH₂BH₂·NMe₃][OTf] (3a)

H₂PBH₂·NMe₃ (21 mg, 0.20 mmol, 1 eq) was added to a slurry of IDipp·GeH₂BH₂OTf (**1**) (125 mg, 0.200 mmol, 1 eq) in 10 mL Et₂O at room temperature. The reaction mixture was stirred for 15 hours upon which the product precipitates as a white powder. The mother liquor was decanted away, and the precipitate washed with 5 mL Et₂O. All volatiles were removed *in vacuo* and the product [IDipp·GeH₂BH₂PH₂BH₂·NMe₃][OTf] (**3a**) could be isolated as a white powder (100 mg, 68%).

¹H NMR (CD₂Cl₂, 298 K): δ = 0.40 (br, 2H, BH₂), 1.19 (d, 12H, ³J_{H,H} = 6.8 Hz, CH(CH₃)₂), 1.31 (d, 12H, ³J_{H,H} = 6.8 Hz, CH(CH₃)₂), 1.95 (br, 2H, BH₂), 2.40 (septet, 4H, ³J_{H,H} = 6.8 Hz, CH(CH₃)₂), 2.64 (s, 9H, NMe₃), 3.05 (dm, 2H, ¹J_{H,P} = 340 Hz, PH₂), 3.53 (dt, 2H, ³J_{H,P} = 5.3 Hz, ³J_{H,H} = 5.1 Hz, GeH₂), 7.39 (d, 4H, ³J_{H,H} = 7.9 Hz, ArH), 7.54 (s, 2H, N-CH), 7.61 (t, 2H, ³J_{H,H} = 7.8 Hz, ArH). **¹H{³¹P} NMR** (CD₂Cl₂, 298 K): δ = 0.40 (br, 2H, BH₂), 1.19 (d, 12H, ³J_{H,H} = 6.8 Hz, CH(CH₃)₂), 1.31 (d, 12H, ³J_{H,H} = 6.8 Hz, CH(CH₃)₂), 1.95 (br, 2H, BH₂), 2.40 (septet, 4H, ³J_{H,H} = 6.8 Hz, CH(CH₃)₂), 2.64 (s, 9H, NMe₃), 3.05 (m, 2H, PH₂), 3.53 (t, 2H, ³J_{H,H} = 4.6 Hz, GeH₂), 7.39 (d, 4H, ³J_{H,H} = 7.8 Hz, ArH), 7.54 (s, 2H, N-CH), 7.61 (t, 2H, ³J_{H,H} = 7.8 Hz, ArH). **¹H{¹¹B} NMR** (CD₂Cl₂, 298 K): δ = 0.40 (s, 2H, BH₂), 1.19 (d, 12H, ³J_{H,H} = 6.8 Hz, CH(CH₃)₂), 1.31 (d, 12H, ³J_{H,H} = 6.8 Hz, CH(CH₃)₂), 1.95 (s, 2H, BH₂), 2.40 (septet, 4H, ³J_{H,H} = 6.8 Hz, CH(CH₃)₂), 2.64 (s, 9H, NMe₃), 3.05 (dm, 2H, ¹J_{H,P} = 340 Hz, PH₂), 3.53 (dt, 2H, ³J_{H,P} = 5.4 Hz, ³J_{H,H} = 5.1 Hz, GeH₂), 7.39 (d, 4H, ³J_{H,H} = 7.9 Hz, ArH), 7.54 (s, 2H, N-CH), 7.61 (t, 2H, ³J_{H,H} = 7.8 Hz, ArH). **³¹P NMR** (CD₂Cl₂, 298 K): δ = -116.6 (t, br, ¹J_{P,H} = 340 Hz, PH₂). **³¹P{¹H} NMR** (CD₂Cl₂, 298 K): δ = -116.6 (br, PH₂). **¹¹B NMR** (CD₂Cl₂, 298 K): δ = -10.8 (m, br, BH₂), -43.5 (m, br, BH₂). **¹¹B{¹H} NMR** (CD₂Cl₂, 298 K): δ = -10.8 (d, br, ¹J_{B,P} = 60 Hz, BH₂), -43.5 (d, br, ¹J_{B,P} = 55 Hz, BH₂). **¹⁹F NMR** (CD₂Cl₂, 298 K): δ = -78.86 (s, 3F, OTf). **ESI-MS** (THF): m/z = 389.3 (100%, [IDipp·H]⁺), 582.3 (23%, [IDipp·GeH₂BH₂PH₂BH₂·NMe₃]⁺).

1.7 Synthesis of [IDipp·GeH₂BH₂AsH₂BH₂·NMe₃][OTf] (3b)

H₂AsBH₂·NMe₃ (30 mg, 0.20 mmol, 1 eq) was added to a slurry of IDipp·GeH₂BH₂OTf (**1**) (125 mg, 0.200 mmol, 1 eq) in 10 mL Et₂O at room temperature. The reaction mixture was stirred for 15 hours upon which the product precipitates as a white powder. The mother liquor was decanted away, and the precipitate washed with 5 mL Et₂O. All volatiles were removed *in*

vacuo and the product [IDipp·GeH₂BH₂AsH₂BH₂·NMe₃][OTf] (**3b**) could be isolated as a white powder (115 mg, 74%).

¹H NMR (CD₂Cl₂, 298 K): δ = 0.69 (br, 2H, BH₂), 1.20 (d, 12H, ³J_{H,H} = 6.8 Hz, CH(CH₃)₂), 1.31 (d, 12H, ³J_{H,H} = 6.8 Hz, CH(CH₃)₂), 2.00 (m, 2H, AsH₂), 2.23 (br, 2H, BH₂), 2.40 (septet, 4H, ³J_{H,H} = 6.9 Hz, CH(CH₃)₂), 2.66 (s, 9H, NMe₃), 3.57 (t, 2H, ³J_{H,H} = 4.8 Hz, GeH₂), 7.39 (d, 4H, ³J_{H,H} = 7.8 Hz, ArH), 7.56 (s, 2H, N-CH), 7.61 (t, 2H, ³J_{H,H} = 7.9 Hz, ArH). **¹H{¹¹B} NMR** (CD₂Cl₂, 298 K): δ = 0.69 (s, 2H, BH₂), 1.20 (d, 12H, ³J_{H,H} = 6.8 Hz, CH(CH₃)₂), 1.31 (d, 12H, ³J_{H,H} = 6.8 Hz, CH(CH₃)₂), 2.00 (m, 2H, AsH₂), 2.23 (s, 2H, BH₂), 2.40 (septet, 4H, ³J_{H,H} = 6.9 Hz, CH(CH₃)₂), 2.66 (s, 9H, NMe₃), 3.57 (t, 2H, ³J_{H,H} = 4.8 Hz, GeH₂), 7.39 (d, 4H, ³J_{H,H} = 7.8 Hz, ArH), 7.56 (s, 2H, N-CH), 7.61 (t, 2H, ³J_{H,H} = 7.9 Hz, ArH). **¹¹B NMR** (CD₂Cl₂, 298 K): δ = -8.8 (t, br, ¹J_{B,H} = 110 Hz, BH₂), -40.0 (t, br, ¹J_{B,H} = 105 Hz, BH₂). **¹¹B{¹H} NMR** (CD₂Cl₂, 298 K): δ = -8.8 (s, br, BH₂), -40.0 (s, br, BH₂). **¹⁹F NMR** (CD₂Cl₂, 298 K): δ = -78.85 (s, 3F, OTf). **ESI-MS** (CH₂Cl₂): *m/z* = 626.3 (100%, [IDipp·GeH₂BH₂AsH₂BH₂·NMe₃]⁺).

1.8 Synthesis of [IDipp·GeH₂BH₂PH₂BH₂·IMes][OTf] (**4**)

H₂PBH₂·IMes (53 mg, 0.15 mmol, 1 eq) and IDipp·GeH₂BH₂OTf (**1**) (94 mg, 0.15 mmol, 1 eq) were combined in 10 mL Et₂O at room temperature. The reaction mixture was stirred for 1.5 hours upon which the product precipitates as a white powder. The mother liquor was decanted, and the precipitate washed with 5 mL Et₂O. All volatiles were removed *in vacuo* and the product [IDipp·GeH₂BH₂PH₂BH₂·IMes][OTf] (**4**) could be isolated as a white powder (100 mg, 68%).

¹H NMR (CD₂Cl₂, 298 K): δ = 0.11 (br, 2H, BH₂), 0.89 (br, 2H, BH₂), 1.15 (d, 12H, ³J_{H,H} = 6.9 Hz, CH(CH₃)₂), 1.21 (d, 12H, ³J_{H,H} = 6.9 Hz, CH(CH₃)₂), 1.94 (s, 12H, ArCH₃), 2.31 (septet, 4H, ³J_{H,H} = 6.8 Hz, CH(CH₃)₂), 2.35 (s, 6H, ArCH₃), 2.42 (dm, 2H, ¹J_{H,P} = 335 Hz, PH₂), 3.23 (m, 2H, GeH₂), 6.98 (s, 4H, ArH), 7.13 (s, 2H, N-CH), 7.33 (d, 4H, ³J_{H,H} = 7.8 Hz, ArH), 7.47 (s, 2H, N-CH), 7.57 (t, 2H, ³J_{H,H} = 7.8 Hz, ArH). **³¹P NMR** (CD₂Cl₂, 298 K): δ = -112.1 (t, br, ¹J_{P,H} = 335 Hz, PH₂). **³¹P{¹H} NMR** (CD₂Cl₂, 298 K): δ = -112.1 (br, PH₂). **¹¹B NMR** (CD₂Cl₂, 298 K): δ = -35.3 (br, BH₂), -42.8 (br, BH₂). **¹¹B{¹H} NMR** (CD₂Cl₂, 298 K): δ = -35.3 (br, BH₂), -42.8 (br, BH₂). **¹⁹F NMR** (CD₂Cl₂, 298 K): δ = -78.91 (s, 3F, OTf).

1.9 Synthesis of [IDipp·GeH₂BH₂PH₂BH₂·IDipp][OTf] (**5a**)

H₂PBH₂·IDipp (65 mg, 0.15 mmol, 1 eq) and IDipp·GeH₂BH₂OTf (**1**) (94 mg, 0.15 mmol, 1 eq) were combined in 10 mL Et₂O at room temperature. The reaction mixture was stirred for 1.5 hours upon which the product precipitates as a white powder. The mother liquor was decanted away, and the precipitate washed with 5 mL Et₂O. All volatiles were removed *in vacuo* and the

product [IDipp·GeH₂BH₂PH₂BH₂·IDipp][OTf] (**5a**) could be isolated as a white powder (145 mg, 91%). Colorless crystals could be obtained by layering a CH₂Cl₂ solution with a 3-fold amount of *n*-hexane at room temperature.

¹H NMR (CD₂Cl₂, 298 K): δ = 0.05 (br, 2H, BH₂), 0.99 (br, 2H, BH₂), 1.17 (d, 36H, ³J_{H,H} = 6.9 Hz, CH(CH₃)₂), 1.21 (d, 12H, ³J_{H,H} = 6.8 Hz, CH(CH₃)₂), 2.32 (m, 8H, ³J_{H,H} = 7.1 Hz, CH(CH₃)₂), 2.48 (dm, 2H, ¹J_{H,P} = 334 Hz, PH₂), 3.20 (m, 2H, GeH₂), 7.24 (s, 2H, N-CH), 7.30 (d, 4H, ³J_{H,H} = 7.8 Hz, ArH), 7.33 (d, 4H, ³J_{H,H} = 7.8 Hz, ArH), 7.50 (s, 2H, N-CH), 7.54 (t, 2H, ³J_{H,H} = 7.8 Hz, ArH), 7.58 (t, 2H, ³J_{H,H} = 7.8 Hz, ArH). **¹H{¹¹B} NMR** (CD₂Cl₂, 298 K): δ = 0.05 (s, br, 2H, BH₂), 0.99 (s, br, 2H, BH₂), 1.13 (d, 36H, ³J_{H,H} = 6.9 Hz, CH(CH₃)₂), 1.17 (d, 12H, ³J_{H,H} = 6.8 Hz, CH(CH₃)₂), 2.29 (m, 8H, ³J_{H,H} = 7.1 Hz, CH(CH₃)₂), 2.45 (dm, 2H, ¹J_{H,P} = 334 Hz, PH₂), 3.17 (m, 2H, GeH₂), 7.21 (s, 2H, N-CH), 7.27 (d, 4H, ³J_{H,H} = 7.8 Hz, ArH), 7.30 (d, 4H, ³J_{H,H} = 7.8 Hz, ArH), 7.46 (s, 2H, N-CH), 7.50 (t, 2H, ³J_{H,H} = 7.8 Hz, ArH), 7.54 (t, 2H, ³J_{H,H} = 7.8 Hz, ArH). **³¹P NMR** (CD₂Cl₂, 298 K): δ = -112.8 (t, br, ¹J_{P,H} = 334 Hz, PH₂). **³¹P{¹H} NMR** (CD₂Cl₂, 298 K): δ = -112.8 (br, PH₂). **¹¹B NMR** (CD₂Cl₂, 298 K): δ = -34.8 (m, br, BH₂), -42.5 (br, BH₂). **¹¹B{¹H} NMR** (CD₂Cl₂, 298 K): δ = -34.8 (d, br, ¹J_{B,P} = 61 Hz, BH₂), -42.5 (br, BH₂). **¹⁹F NMR** (CD₂Cl₂, 298 K): δ = -78.87 (s, 3F, OTf). **ESI-MS** (CH₃CN): *m/z* = 389.2 (100%, [IDipp·H]⁺), 911.4 (20%, [IDipp·GeH₂BH₂PH₂BH₂·IDipp]⁺). **Elemental analysis** (%) calculated for C₅₅H₈₀B₂F₃GeN₄O₃PS(CH₂Cl₂)_{0.14}: C: 61.80, H: 7.55, N: 5.23; found: C: 61.79, H: 7.39, N: 5.18.

1.10 Synthesis of [IDipp·GeH₂BH₂AsH₂BH₂·IDipp][OTf] (**5b**)

H₂AsBH₂·IDipp (72 mg, 0.15 mmol, 1 eq) and IDipp·GeH₂BH₂OTf (**1**) (94 mg, 0.15 mmol, 1 eq) were combined in 10 mL Et₂O at room temperature. The reaction mixture was stirred for 5 hours upon which the product precipitates as a white powder. The mother liquor was decanted away, and the precipitate washed with 5 mL Et₂O. All volatiles were removed *in vacuo* and the product [IDipp·GeH₂BH₂AsH₂BH₂·IDipp][OTf] (**5b**) could be isolated as a white powder (144 mg, 69%). Colorless crystals could be obtained by layering a CH₂Cl₂ solution with a 3-fold amount of *n*-hexane at room temperature.

¹H NMR (CD₂Cl₂, 298 K): δ = 0.36 (br, 2H, BH₂), 1.13 (d, 12H, ³J_{H,H} = 6.9 Hz, CH(CH₃)₂), 1.14 (d, 12H, ³J_{H,H} = 6.9 Hz, CH(CH₃)₂), 1.16 (d, 12H, ³J_{H,H} = 6.9 Hz, CH(CH₃)₂), 1.16 (br, 2H, BH₂), 1.18 (d, 12H, ³J_{H,H} = 6.9 Hz, CH(CH₃)₂), 1.39 (m, 2H, AsH₂), 2.30 (m, 8H, ³J_{H,H} = 6.9 Hz, CH(CH₃)₂), 3.24 (m, 2H, GeH₂), 7.21 (s, 2H, N-CH), 7.28 (d, 4H, ³J_{H,H} = 7.3 Hz, ArH), 7.30 (d, 4H, ³J_{H,H} = 7.3 Hz, ArH), 7.47 (s, 2H, N-CH), 7.51 (t, 2H, ³J_{H,H} = 7.8 Hz, ArH), 7.54 (t, 2H, ³J_{H,H} = 7.8 Hz, ArH). **¹H{¹¹B} NMR** (CD₂Cl₂, 298 K): δ = 0.36 (s, br, 2H, BH₂), 1.13 (d, 12H, ³J_{H,H} = 6.9 Hz, CH(CH₃)₂), 1.14 (d, 12H, ³J_{H,H} = 6.9 Hz, CH(CH₃)₂), 1.16 (d, 12H, ³J_{H,H} = 6.9 Hz, CH(CH₃)₂), 1.16 (br, 2H, BH₂), 1.18 (d, 12H, ³J_{H,H} = 6.9 Hz, CH(CH₃)₂), 1.39 (m, 2H, AsH₂),

2.30 (m, 8H, $^3J_{\text{H,H}} = 6.9$ Hz, $\text{CH}(\text{CH}_3)_2$), 3.24 (m, 2H, GeH_2), 7.21 (s, 2H, N-CH), 7.28 (d, 4H, $^3J_{\text{H,H}} = 7.3$ Hz, ArH), 7.30 (d, 4H, $^3J_{\text{H,H}} = 7.3$ Hz, ArH), 7.47 (s, 2H, N-CH), 7.51 (t, 2H, $^3J_{\text{H,H}} = 7.8$ Hz, ArH), 7.54 (t, 2H, $^3J_{\text{H,H}} = 7.8$ Hz, ArH). **^{11}B NMR** (CD_2Cl_2 , 298 K): $\delta = -33.3$ (t, br, $^1J_{\text{B,H}} = 88$ Hz, BH_2), -39.6 (br, BH_2). **$^{11}\text{B}\{^1\text{H}\}$ NMR** (CD_2Cl_2 , 298 K): $\delta = -33.3$ (s, br, BH_2), -39.6 (s, br, BH_2). **^{19}F NMR** (CD_2Cl_2 , 298 K): $\delta = -78.82$ (s, 3F, OTf). **ESI-MS** (CH_2Cl_2): $m/z = 955.5$ (100%, $[\text{IDipp}\cdot\text{GeH}_2\text{BH}_2\text{AsH}_2\text{BH}_2\cdot\text{IDipp}]^+$). **Elemental analysis** (%) calculated for $\text{C}_{55}\text{H}_{80}\text{B}_2\text{F}_3\text{GeN}_4\text{O}_3\text{AsS}(\text{CH}_2\text{Cl}_2)_{0.20}$: C: 59.17, H: 7.23, N: 5.00; found: C: 59.10, H: 7.36, N: 5.00.

2 NMR data

IMes·BH₂PH₂

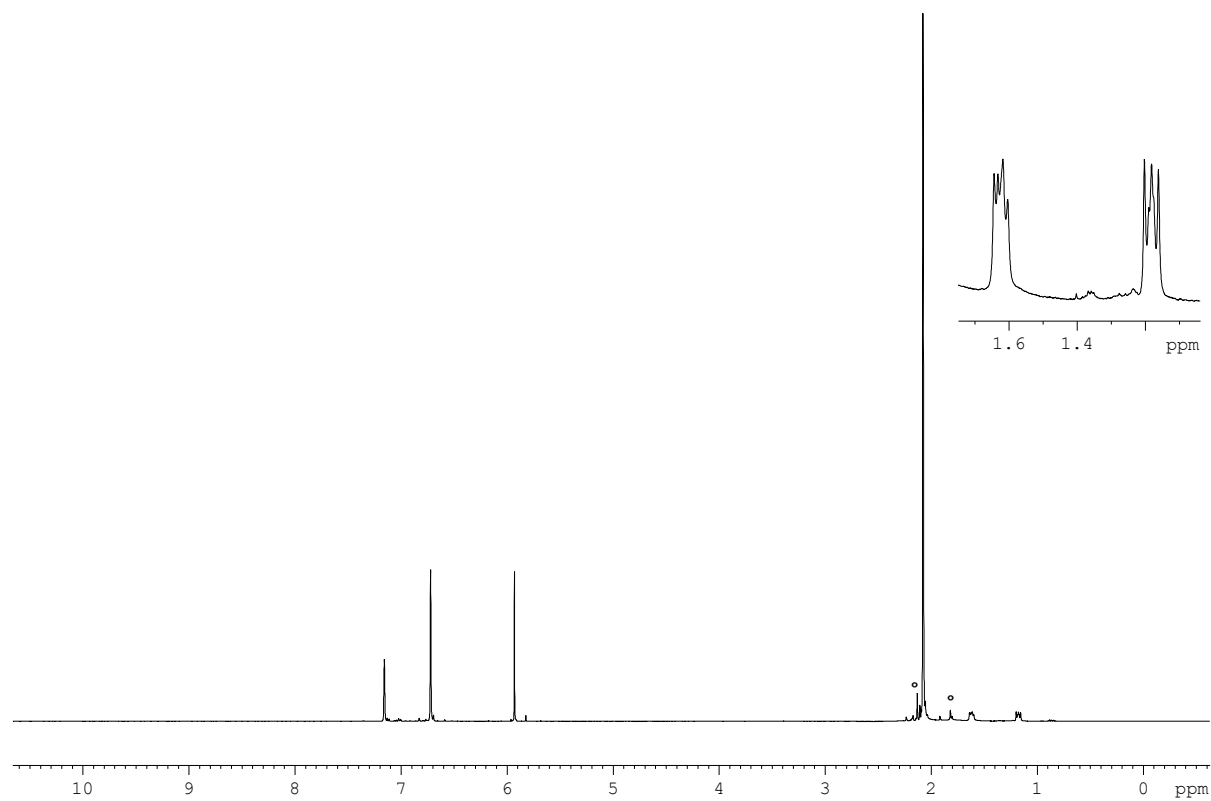


Figure S1: ¹H NMR spectrum of IMes·BH₂PH₂ in C₆D₆ at 298 K. ° = unidentified impurity.

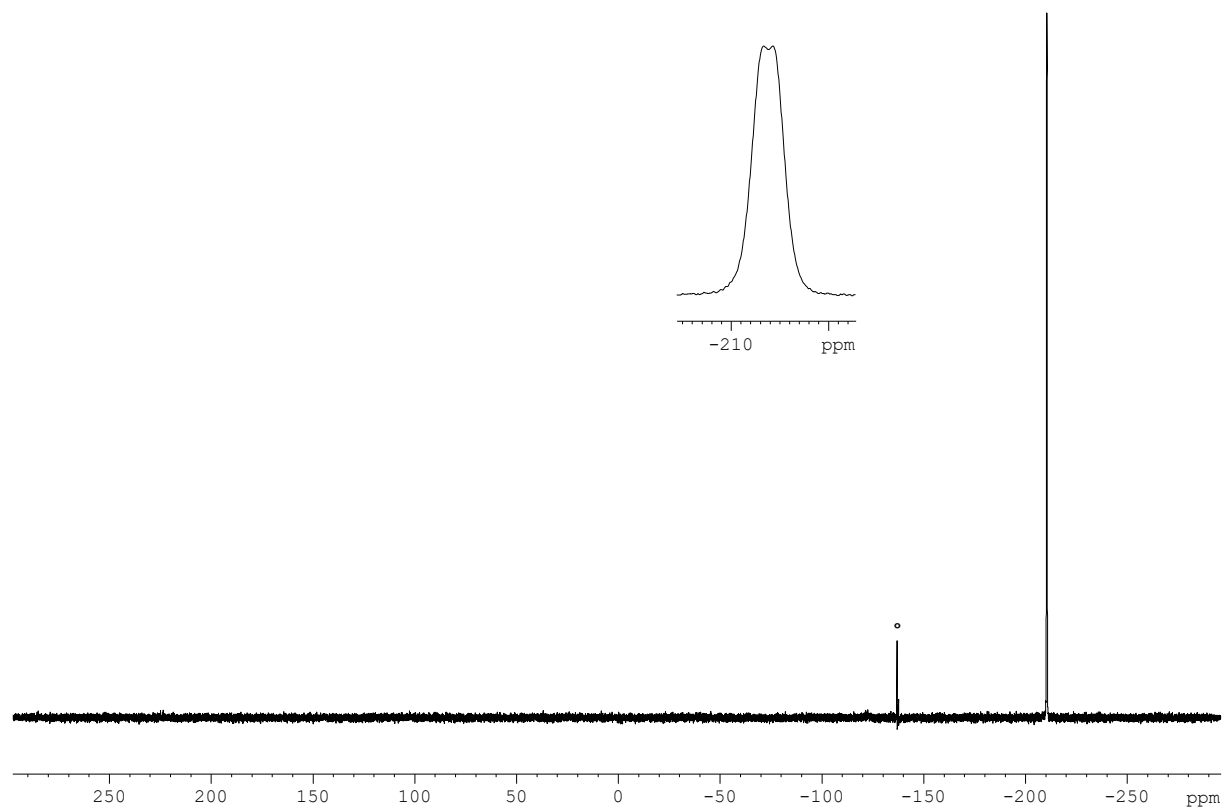


Figure S2: ³¹P{¹H} NMR spectrum of IMes·BH₂PH₂ in C₆D₆ at 298 K. ° = unidentified impurity.

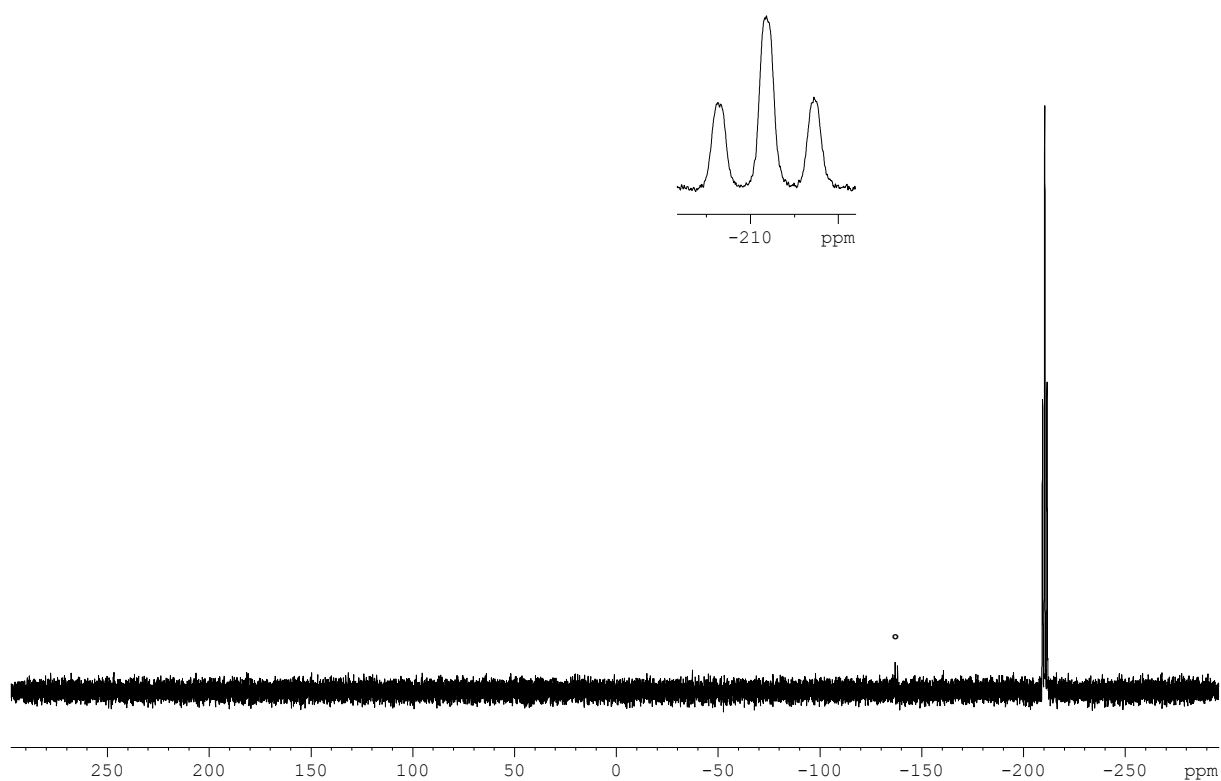


Figure S3: ^{31}P NMR spectrum of IMes·BH₂PH₂ in C₆D₆ at 298 K. ° = unidentified impurity.

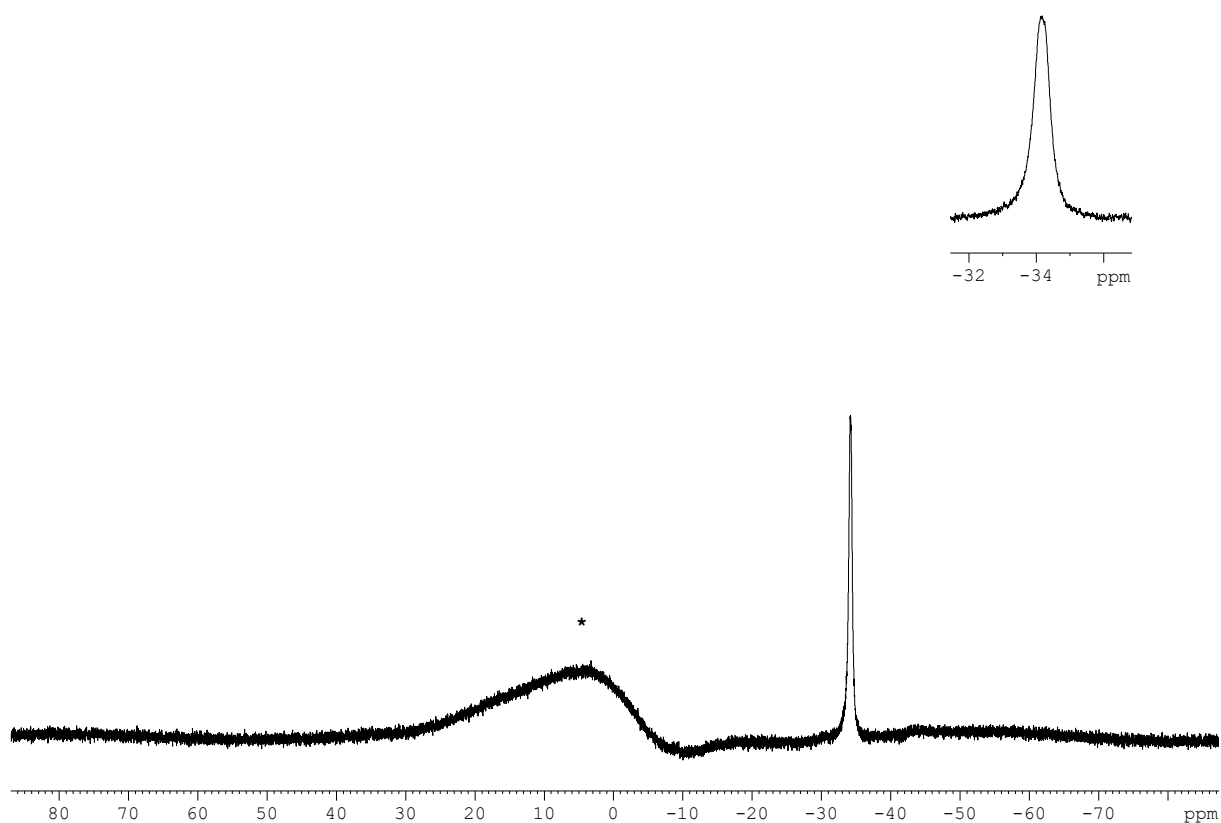


Figure S4: $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of IMes·BH₂PH₂ in C₆D₆ at 298 K. * = signal from the NMR probe.

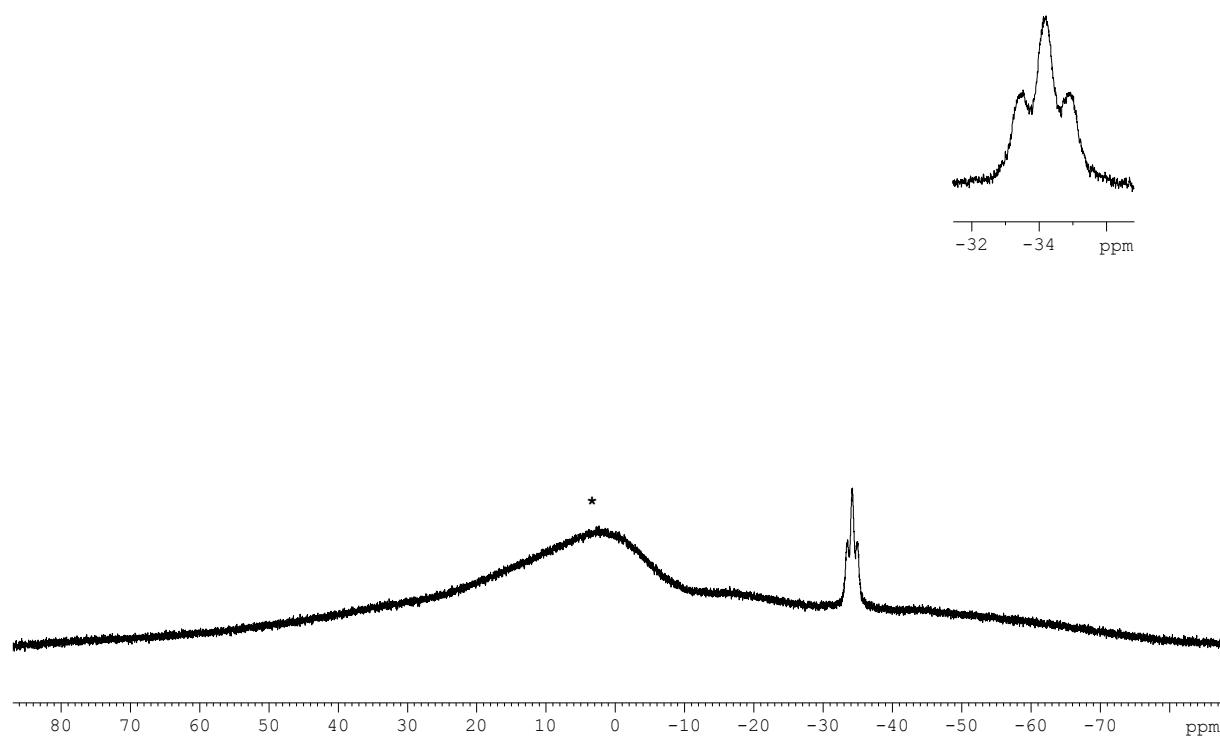


Figure S5: ^{11}B NMR spectrum of $\text{IMes}\cdot\text{BH}_2\text{PH}_2$ in C_6D_6 at 298 K. * = signal from the NMR probe.

$\text{IDipp}\cdot\text{BH}_2\text{AsH}_2$

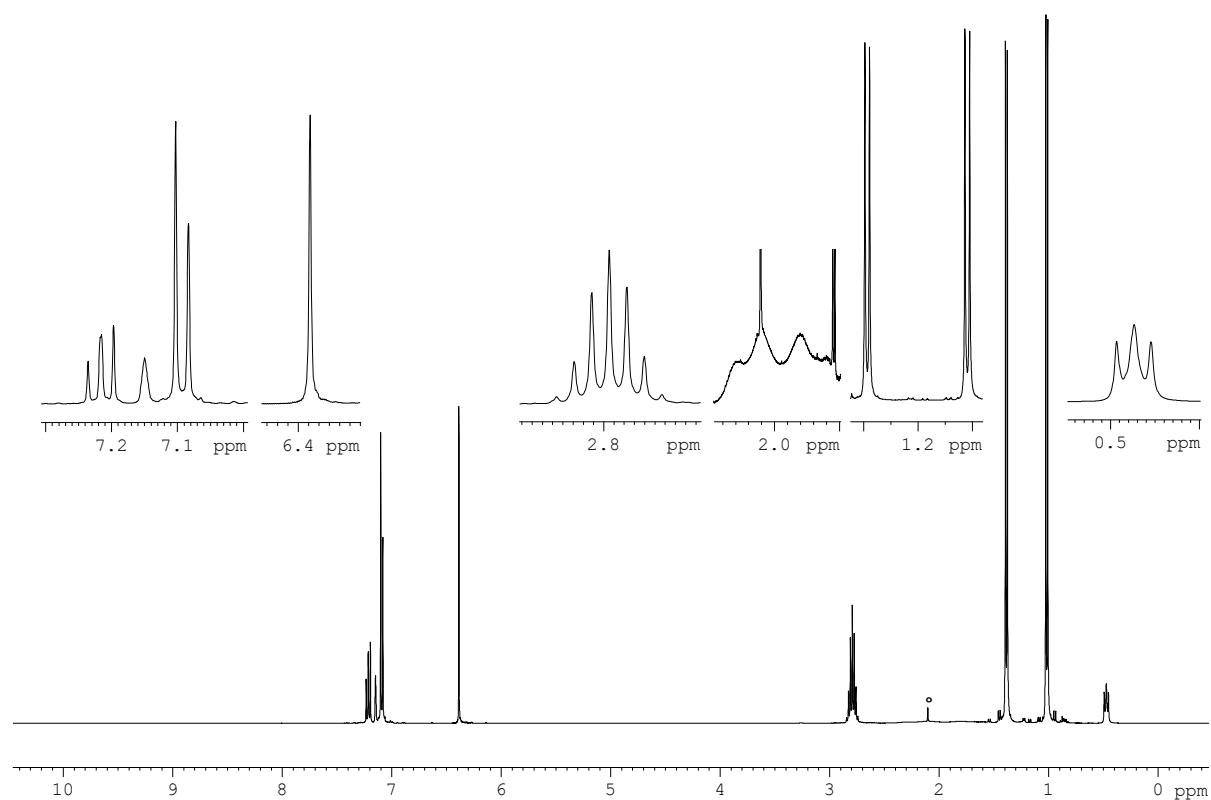


Figure S6: ^1H NMR spectrum of $\text{IDipp}\cdot\text{BH}_2\text{AsH}_2$ in C_6D_6 at 298 K. ° = unidentified impurity.

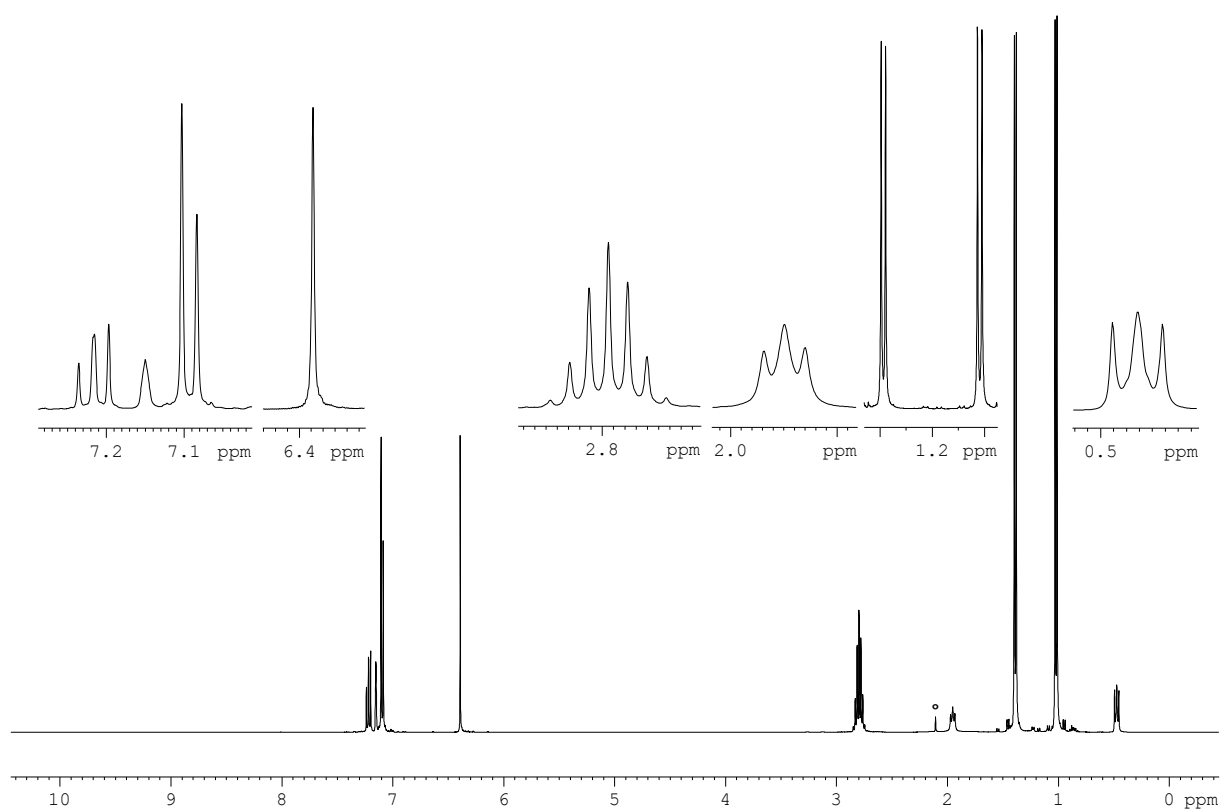


Figure S7: $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum of IDipp·BH₂AsH₂ in C₆D₆ at 298 K. ° = unidentified impurity.

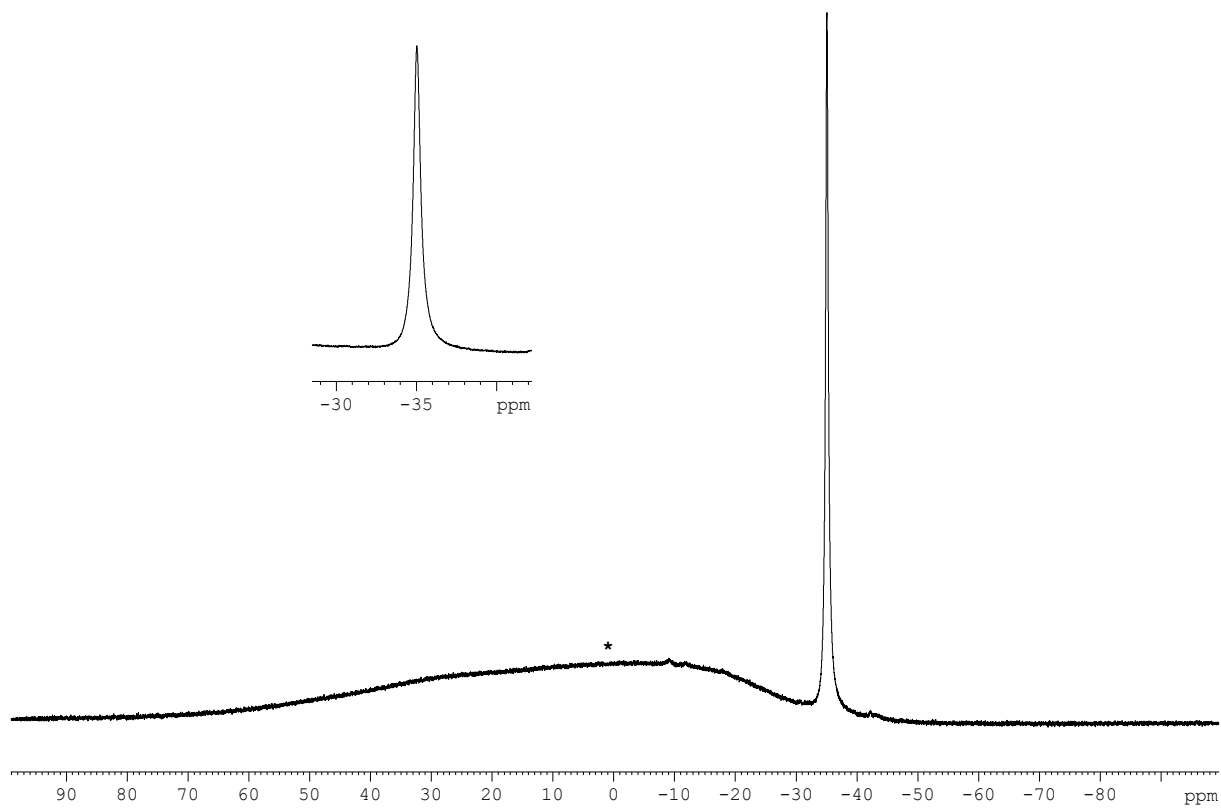


Figure S8: $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of IDipp·BH₂AsH₂ in C₆D₆ at 298 K. * = signal from the NMR probe.

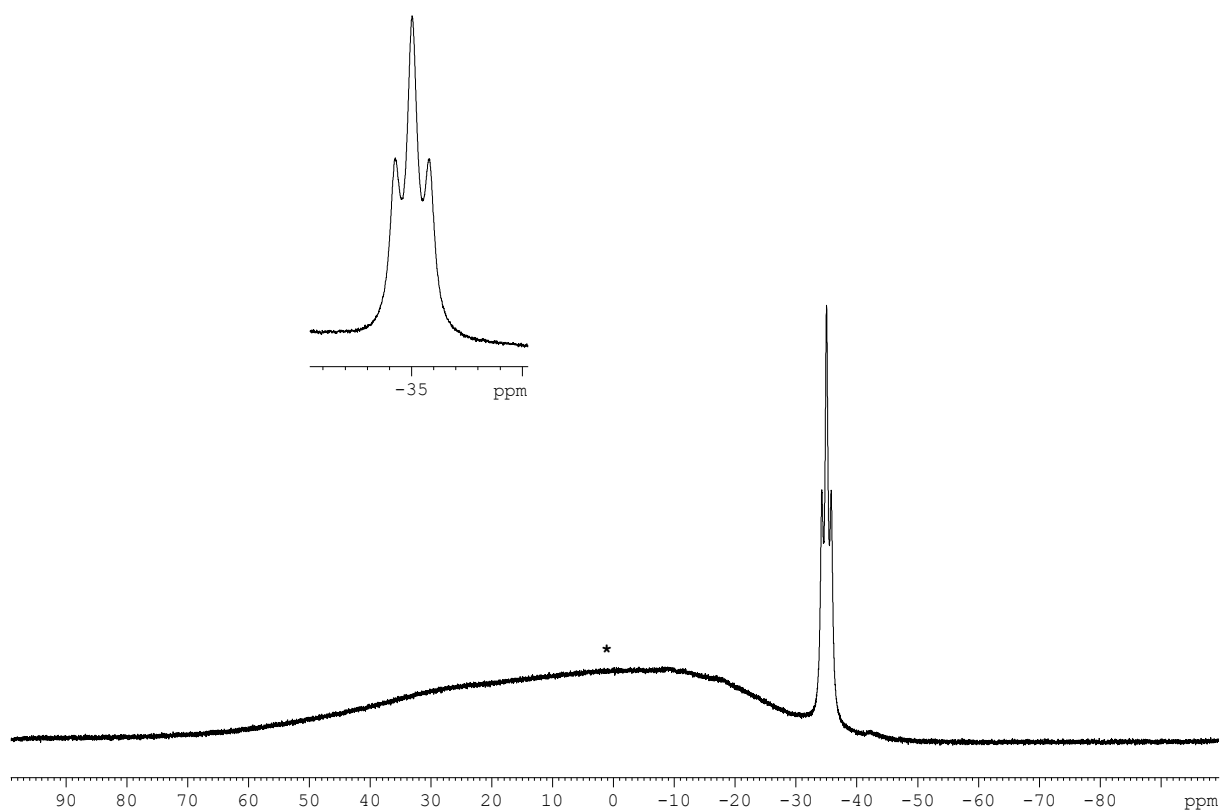


Figure S9: ^{11}B NMR spectrum of IDipp·BH₂AsH₂ in C₆D₆ at 298 K. * = signal from the NMR probe.

[IDipp·GeH₂BH₂PPh₂BH₂·NMe₃][OTf] (**2a**)

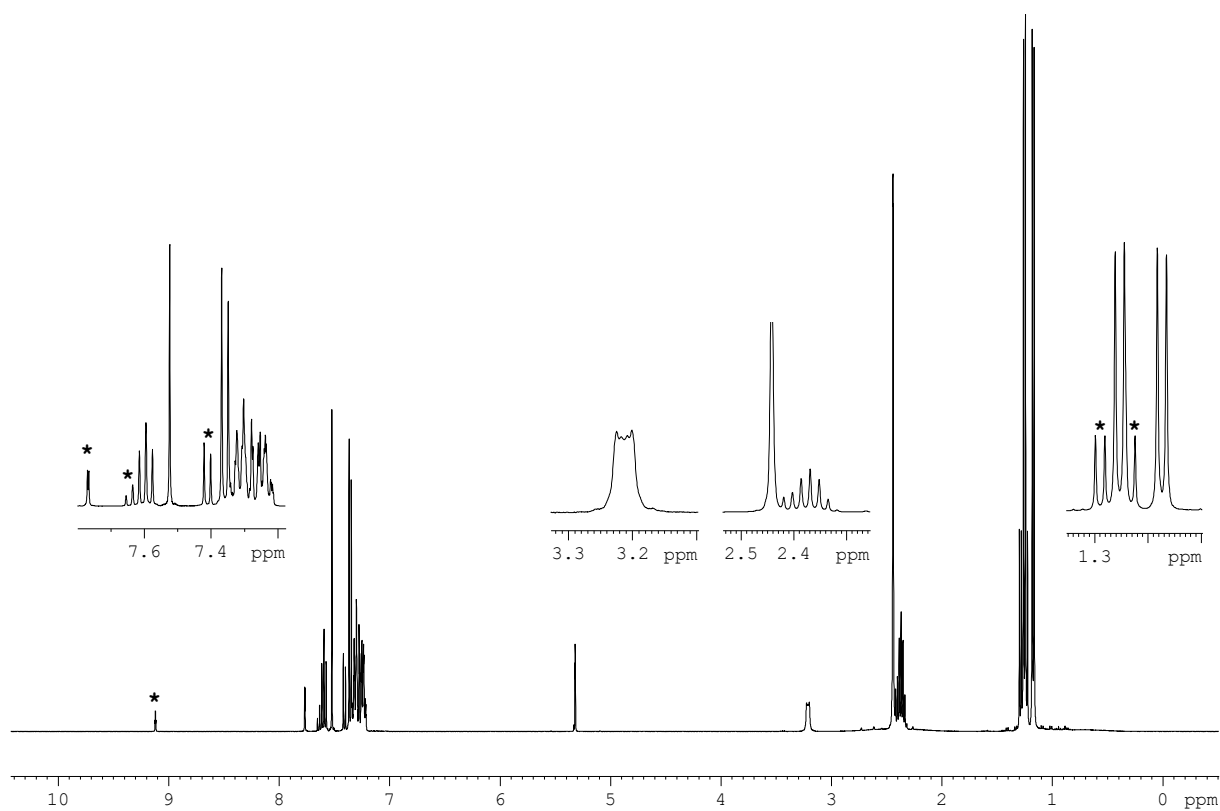


Figure S10: ^1H NMR spectrum of **2a** in CD₂Cl₂ at 298 K. * = [IDippH][OTf].

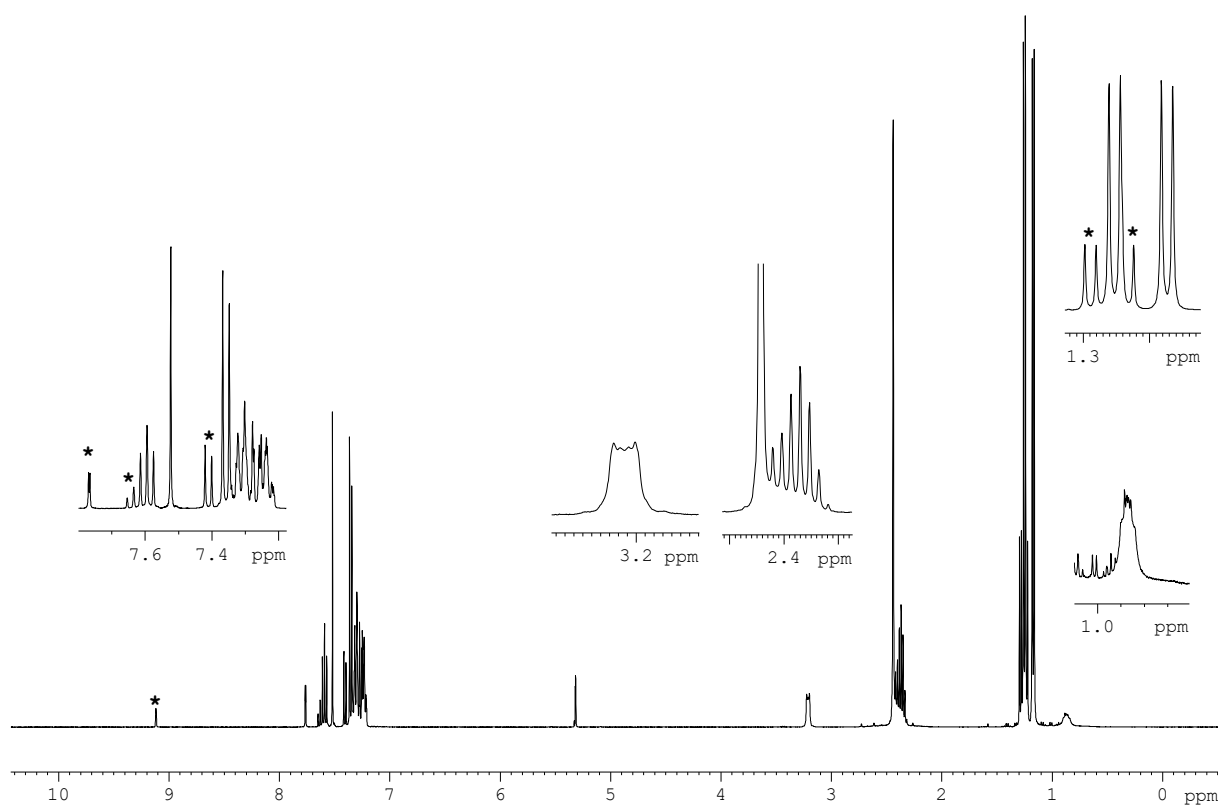


Figure S11: $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum of **2a** in CD_2Cl_2 at 298 K. * = [IDippH][OTf].

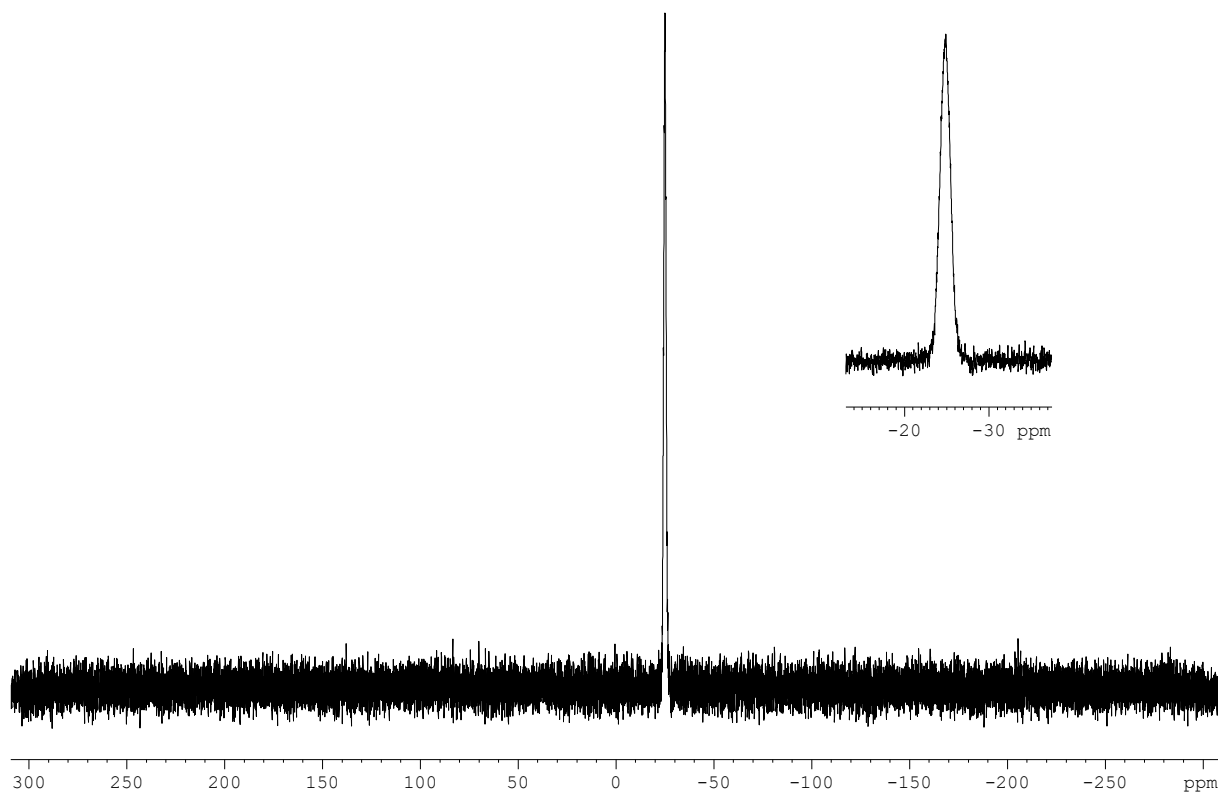


Figure S12: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2a** in CD_2Cl_2 at 298 K.

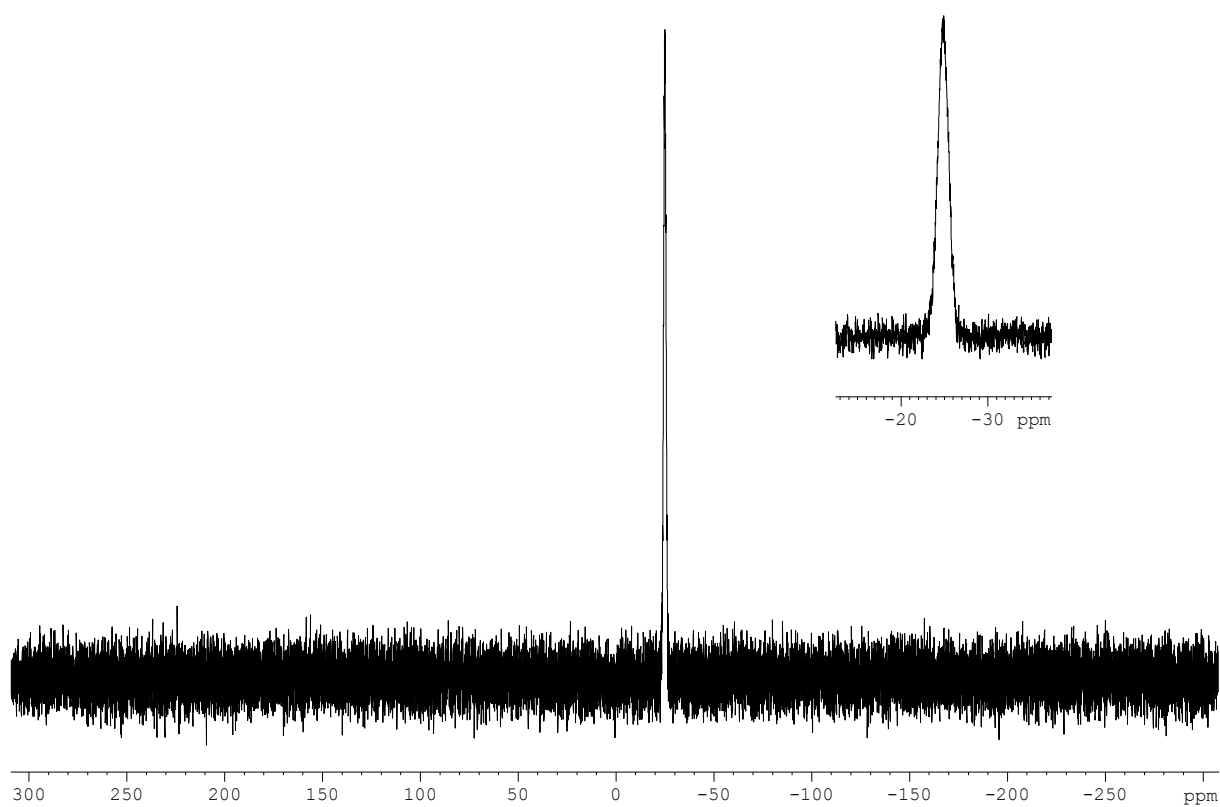


Figure S13: ^{31}P NMR spectrum of **2a** in CD_2Cl_2 at 298 K.

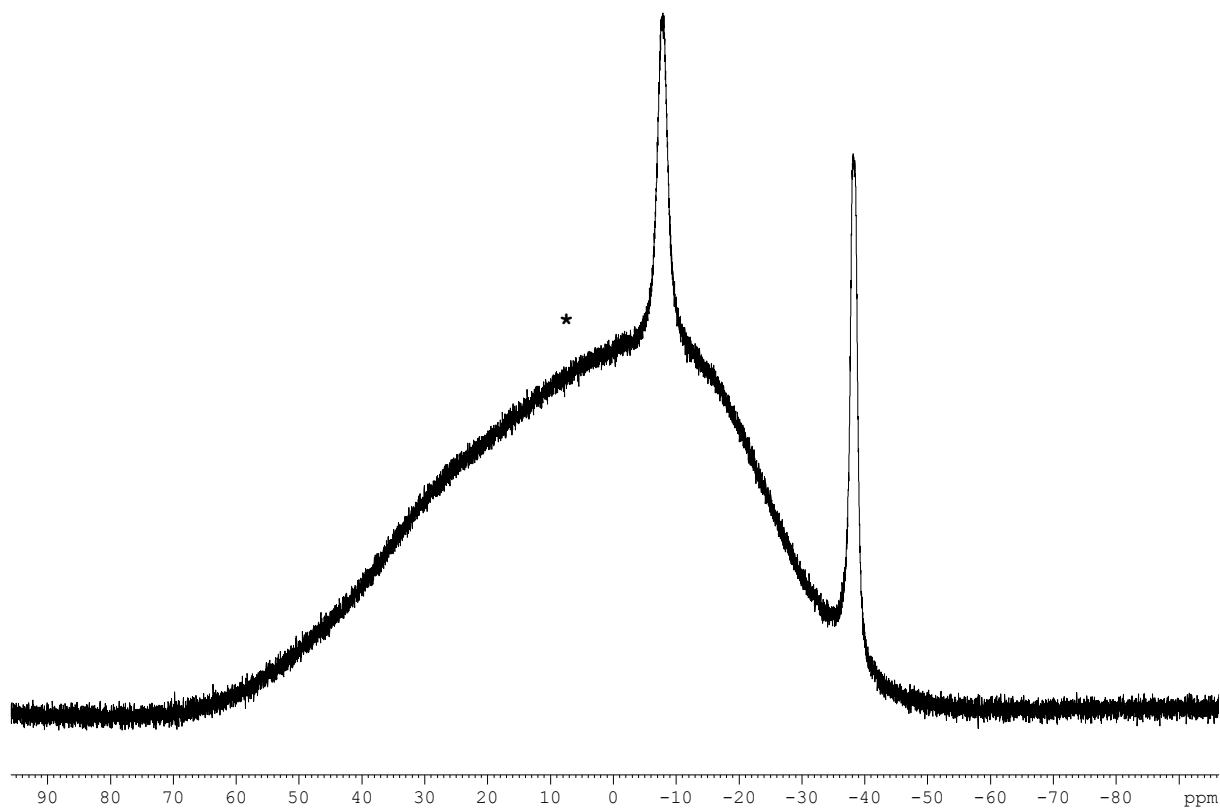


Figure S14: $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **2a** in CD_2Cl_2 at 298 K. * = signal from the NMR probe.

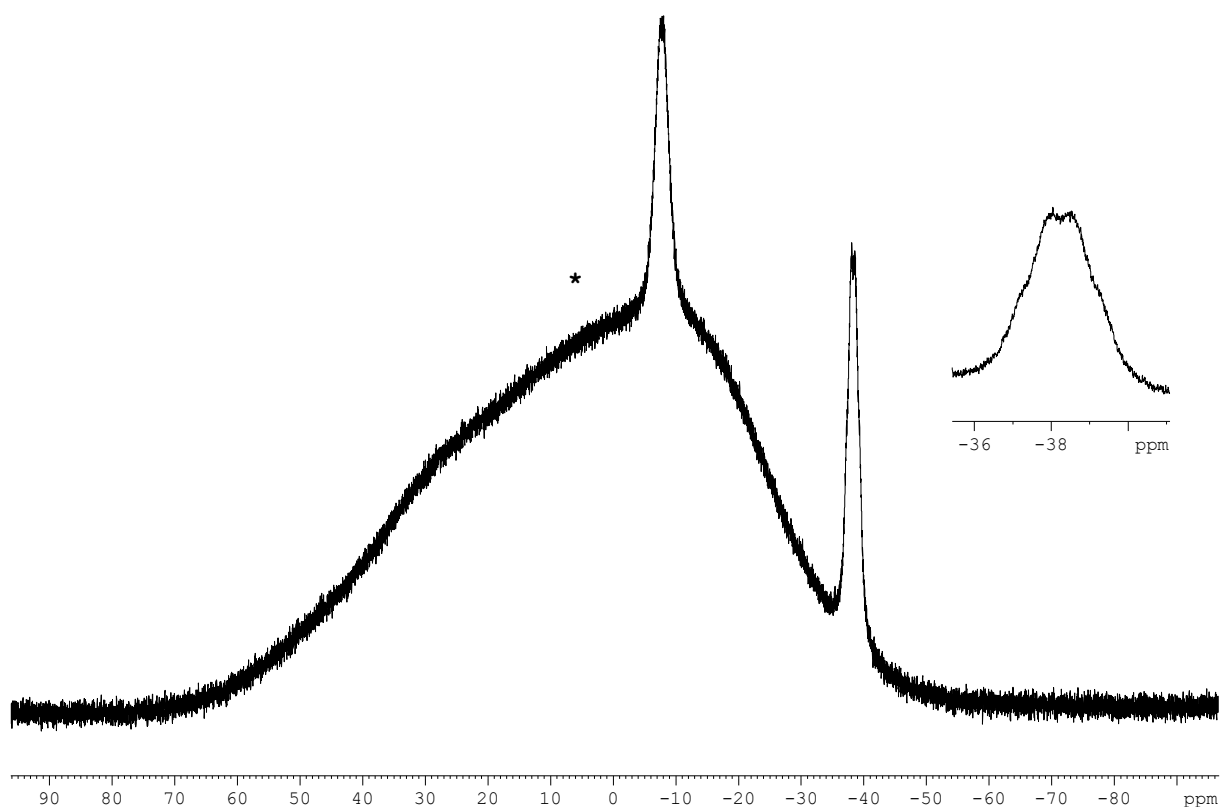


Figure S15: ^{11}B NMR spectrum of **2a** in CD_2Cl_2 at 298 K. * = signal from the NMR probe.

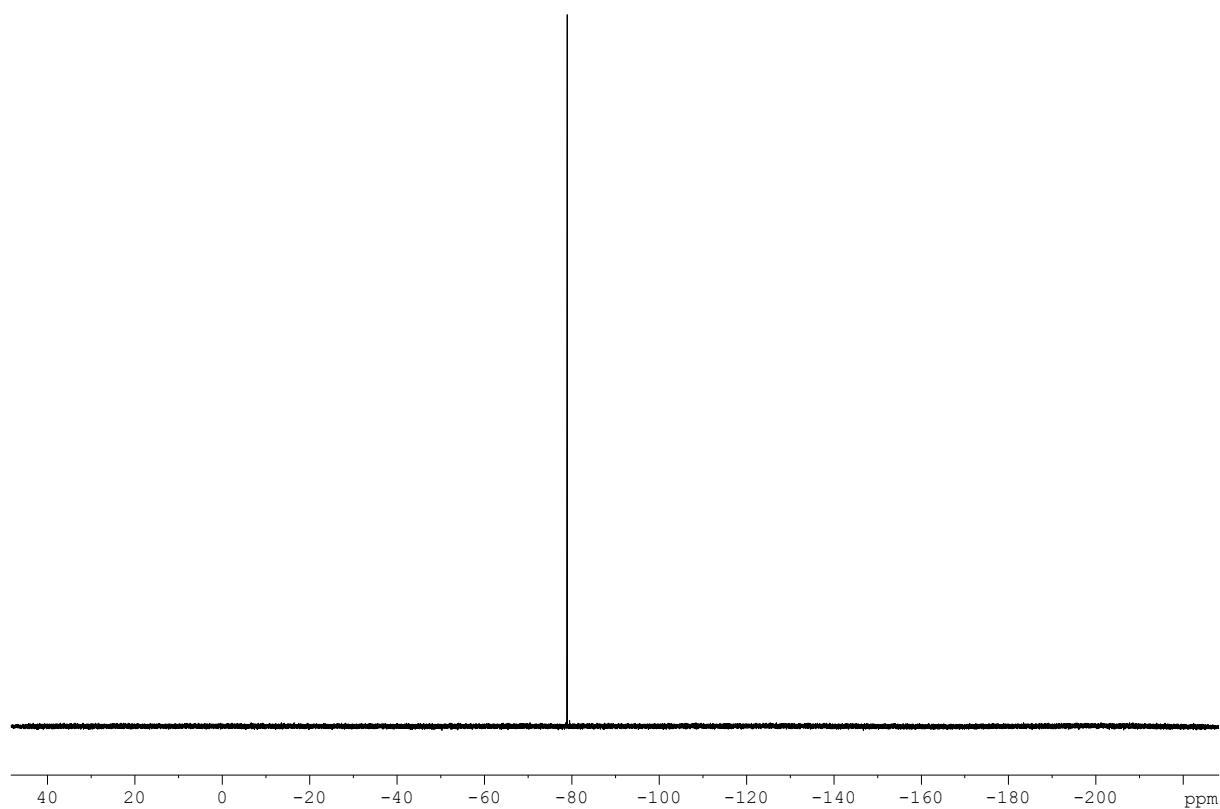


Figure S16: ^{19}F NMR spectrum of **2a** in CD_2Cl_2 at 298 K.

[IDipp·GeH₂BH₂AsPh₂BH₂·NMe₃][OTf] (**2b**)

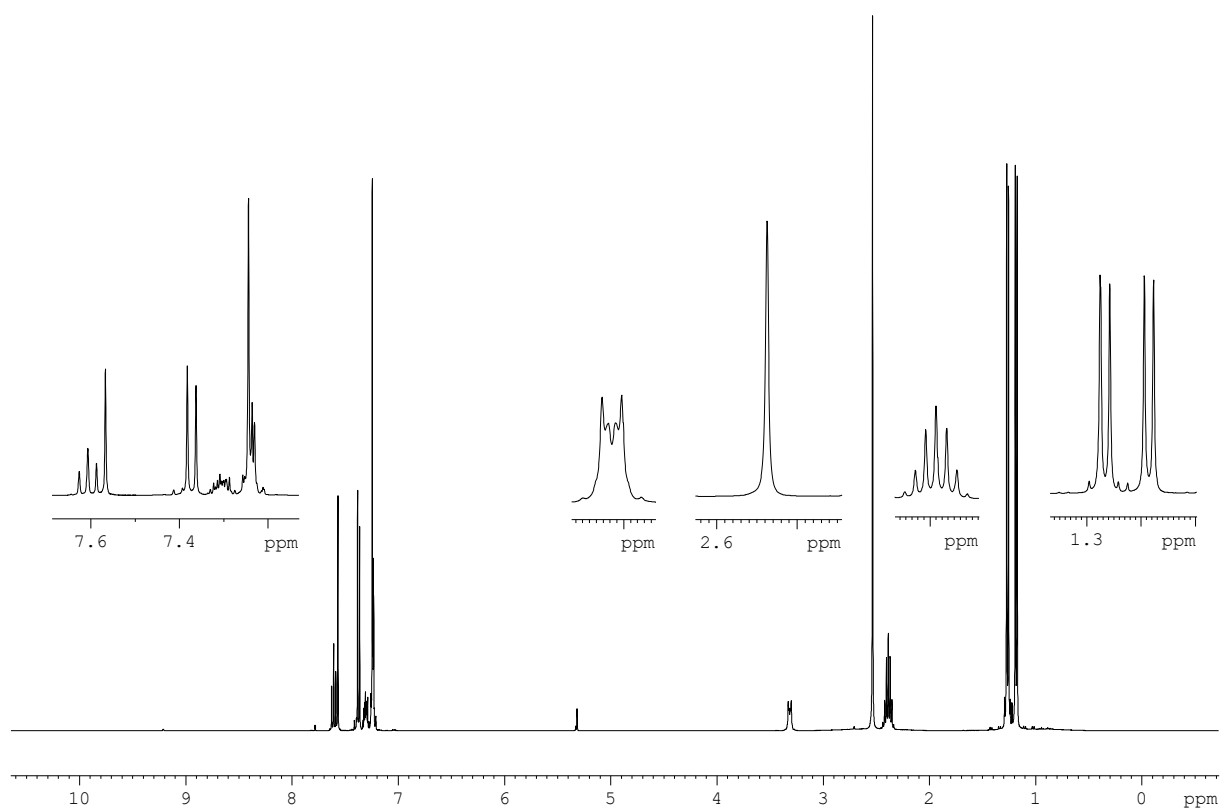


Figure S17: ¹H NMR spectrum of **2b** in CD₂Cl₂ at 298 K.

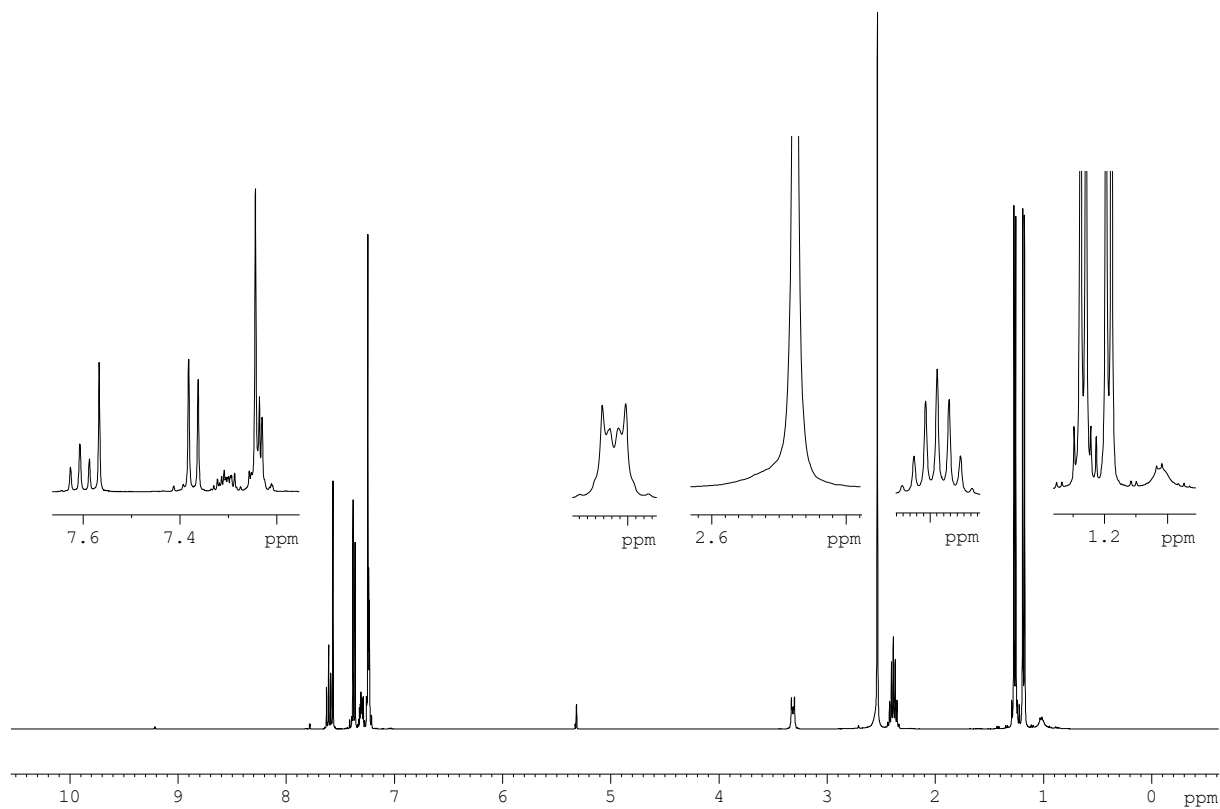


Figure S18: ¹H{¹¹B} NMR spectrum of **2b** in CD₂Cl₂ at 298 K.

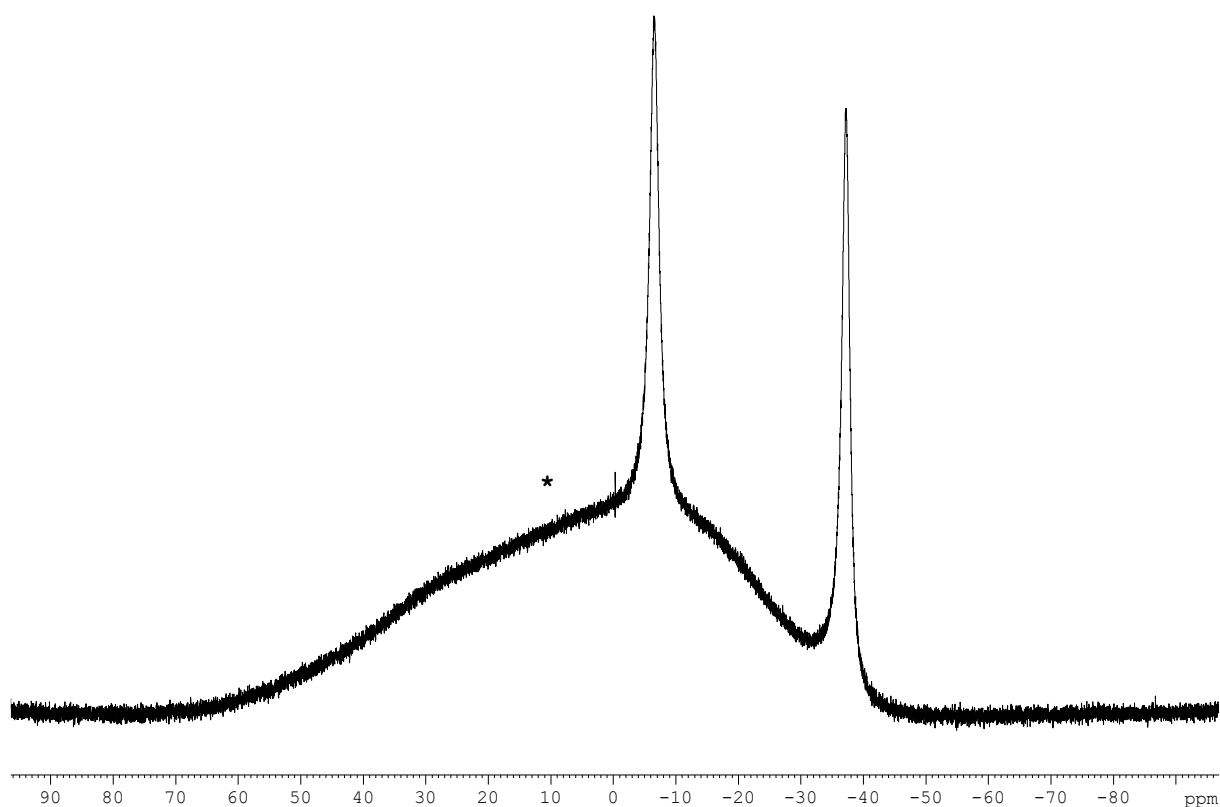


Figure S19: $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **2b** in CD_2Cl_2 at 298 K. * = signal from the NMR probe.

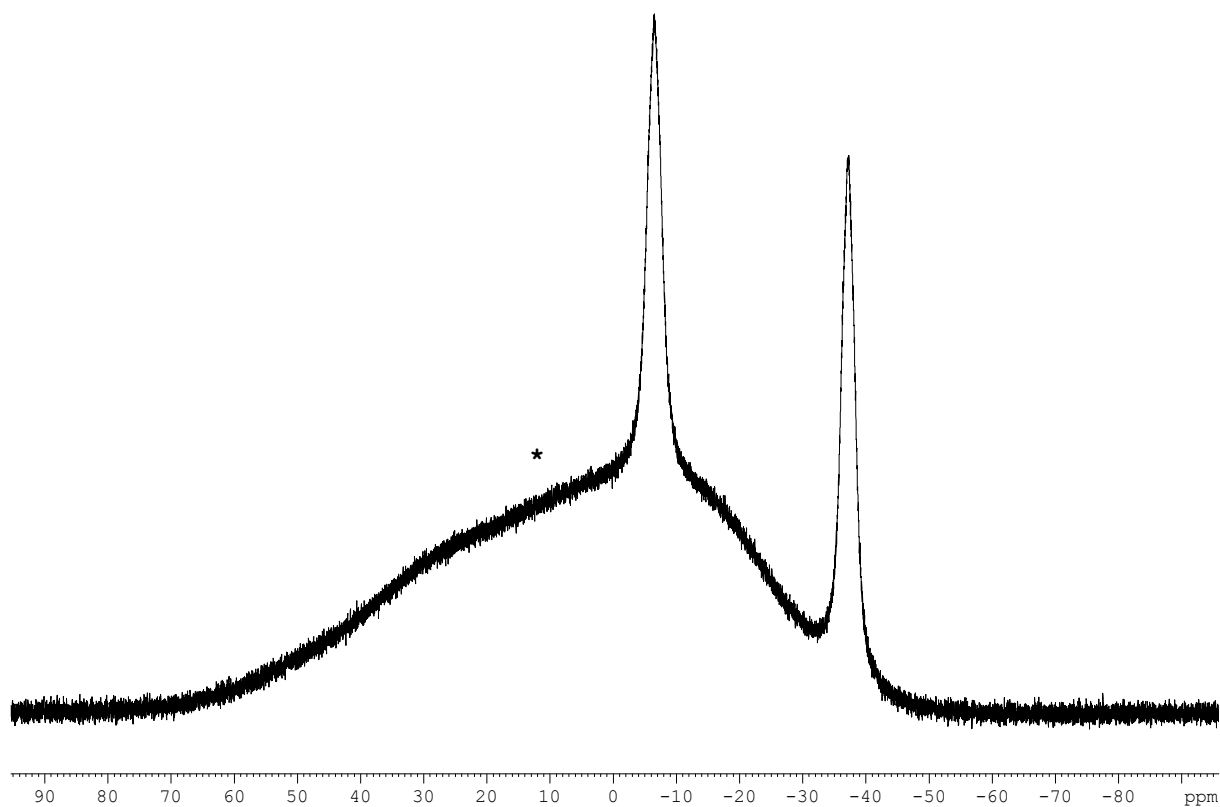


Figure S20: ^{11}B NMR spectrum of **2b** in CD_2Cl_2 at 298 K. * = signal from the NMR probe.

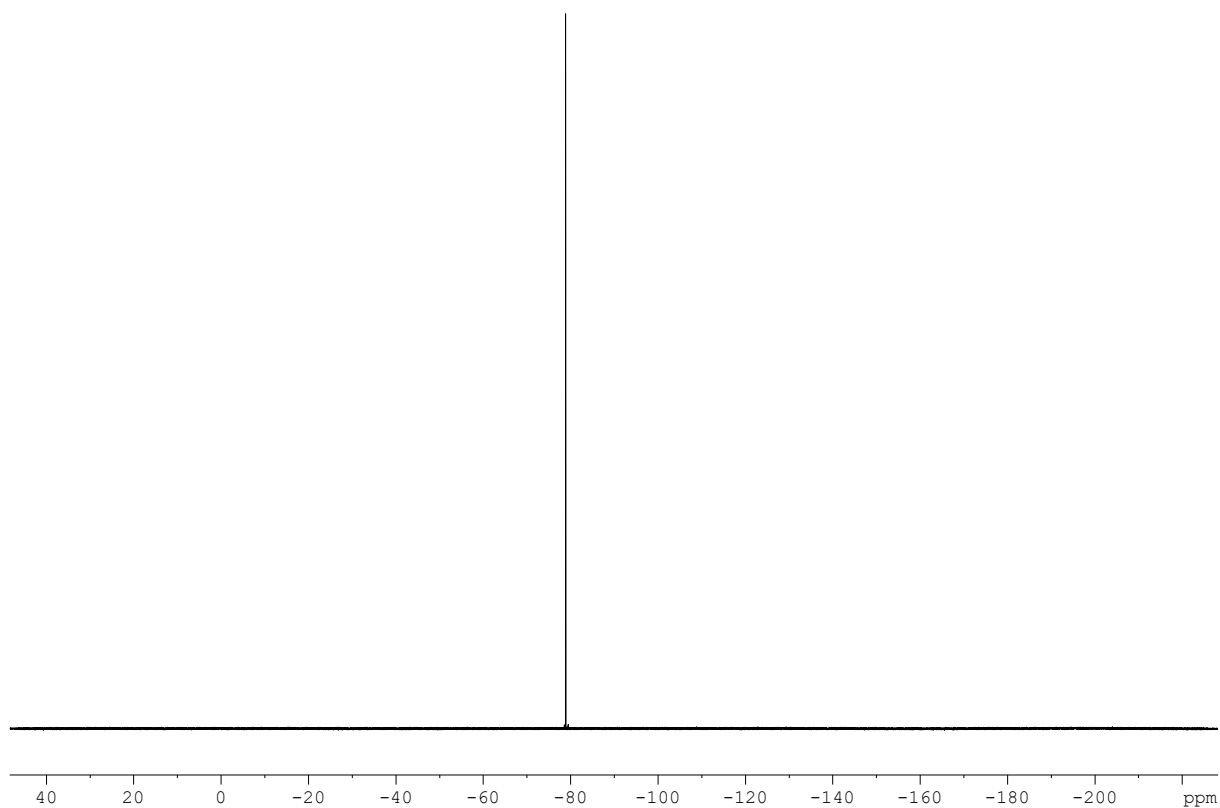


Figure S21: ^{19}F NMR spectrum of **2b** in CD_2Cl_2 at 298 K.

[IDipp·GeH₂BH₂PH₂BH₂·NMe₃][OTf] (3a)

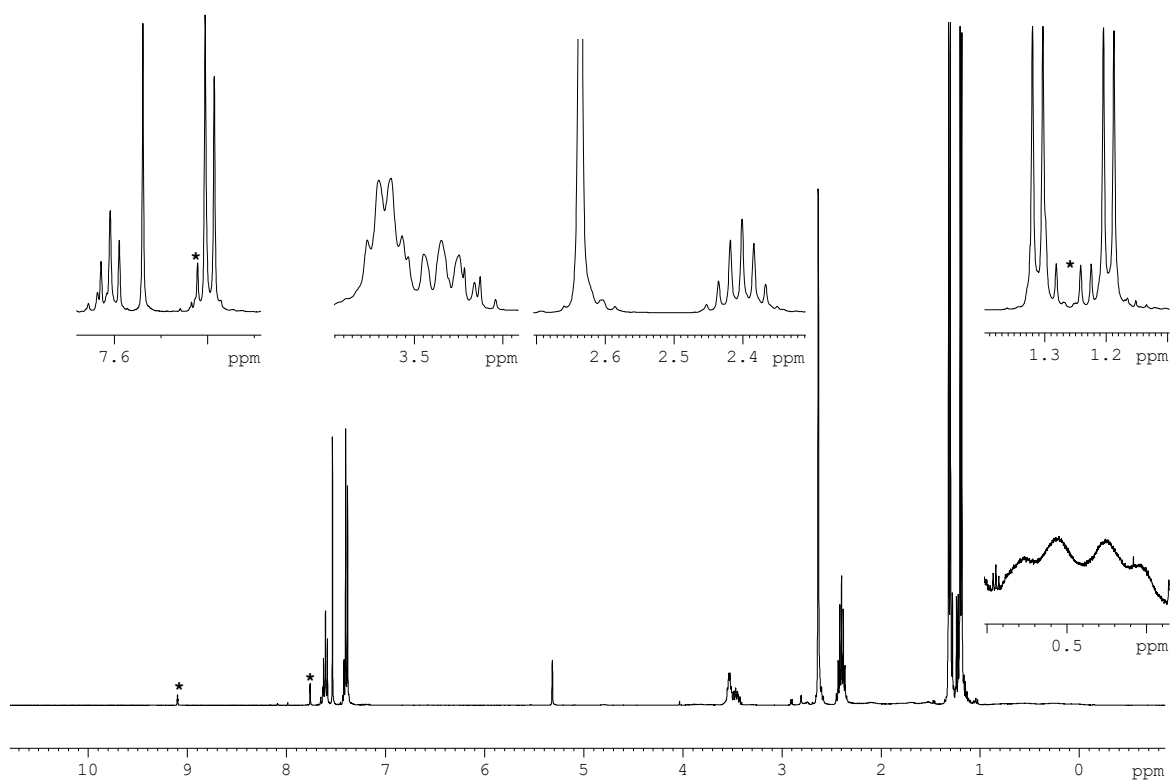


Figure S22: ^1H NMR spectrum of **3a** in CD_2Cl_2 at 298 K. * = [IDippH][OTf].

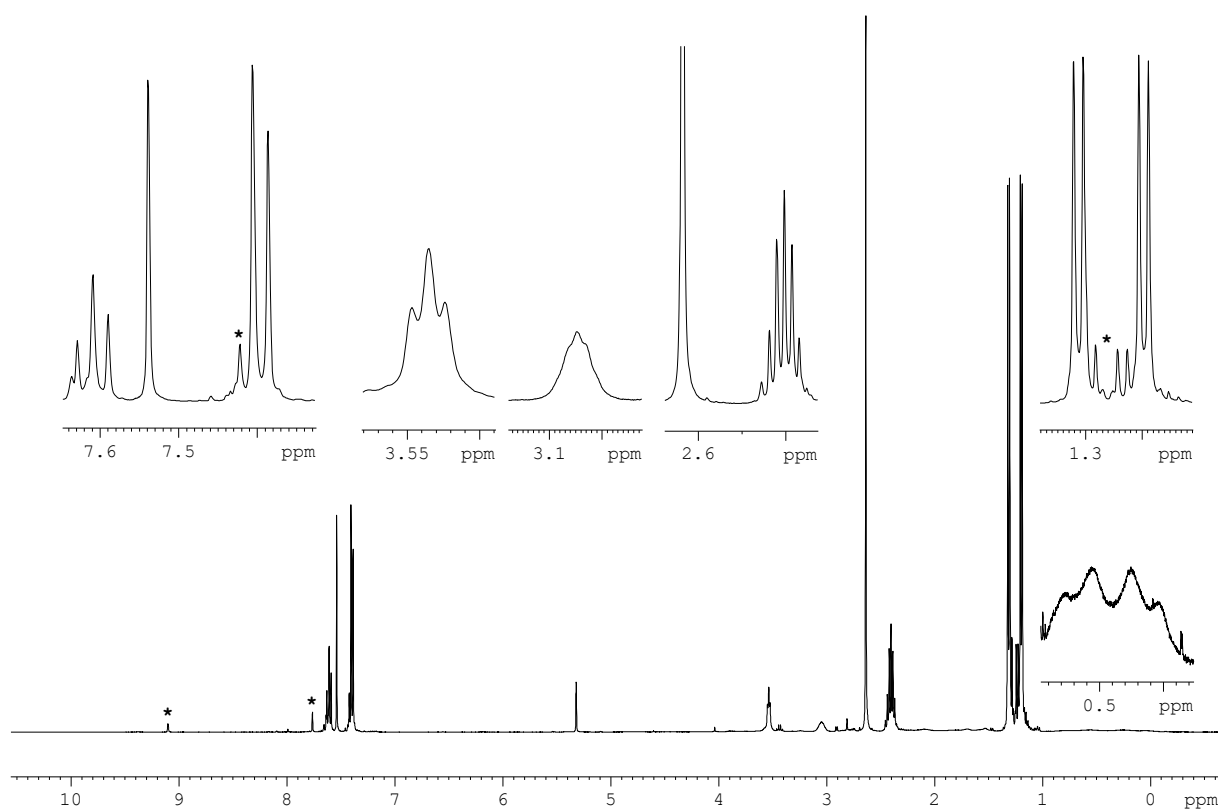


Figure S23: $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum of **3a** in CD_2Cl_2 at 298 K. * = [IDippH][OTf].

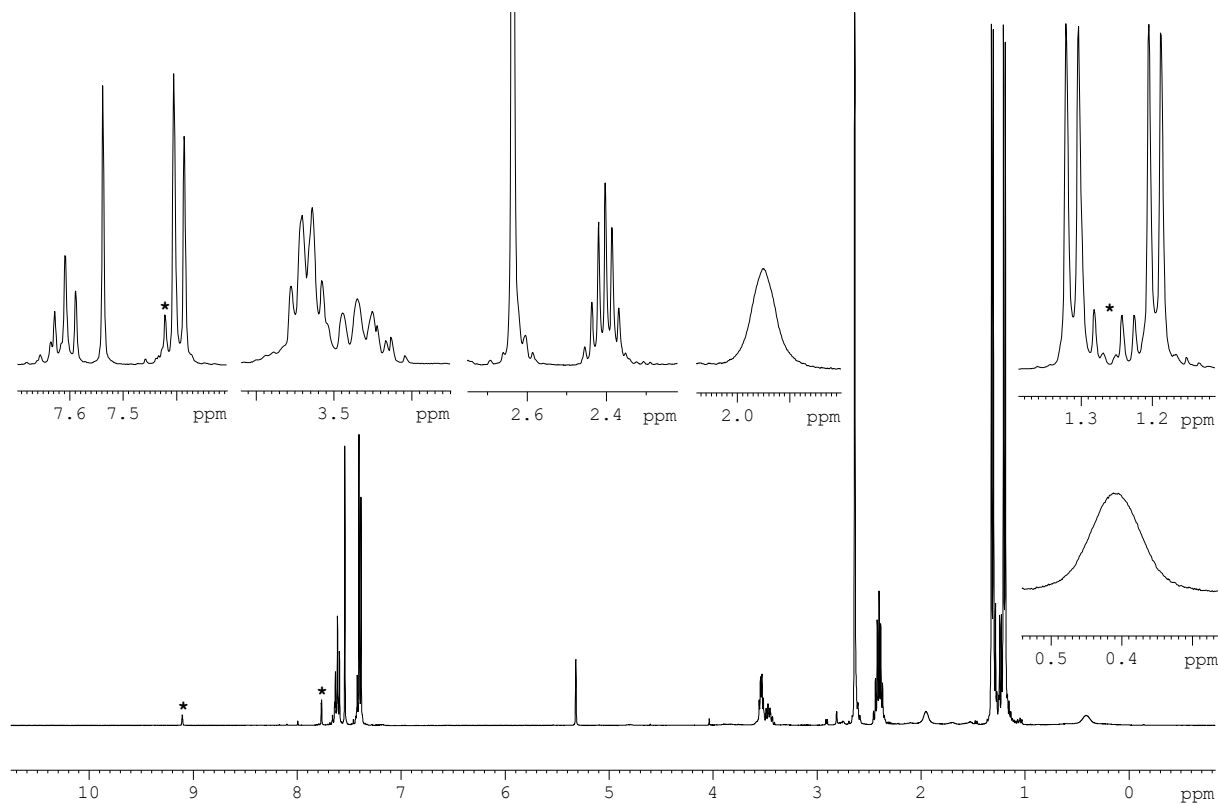


Figure S24: $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum of **3a** in CD_2Cl_2 at 298 K. * = [IDippH][OTf].

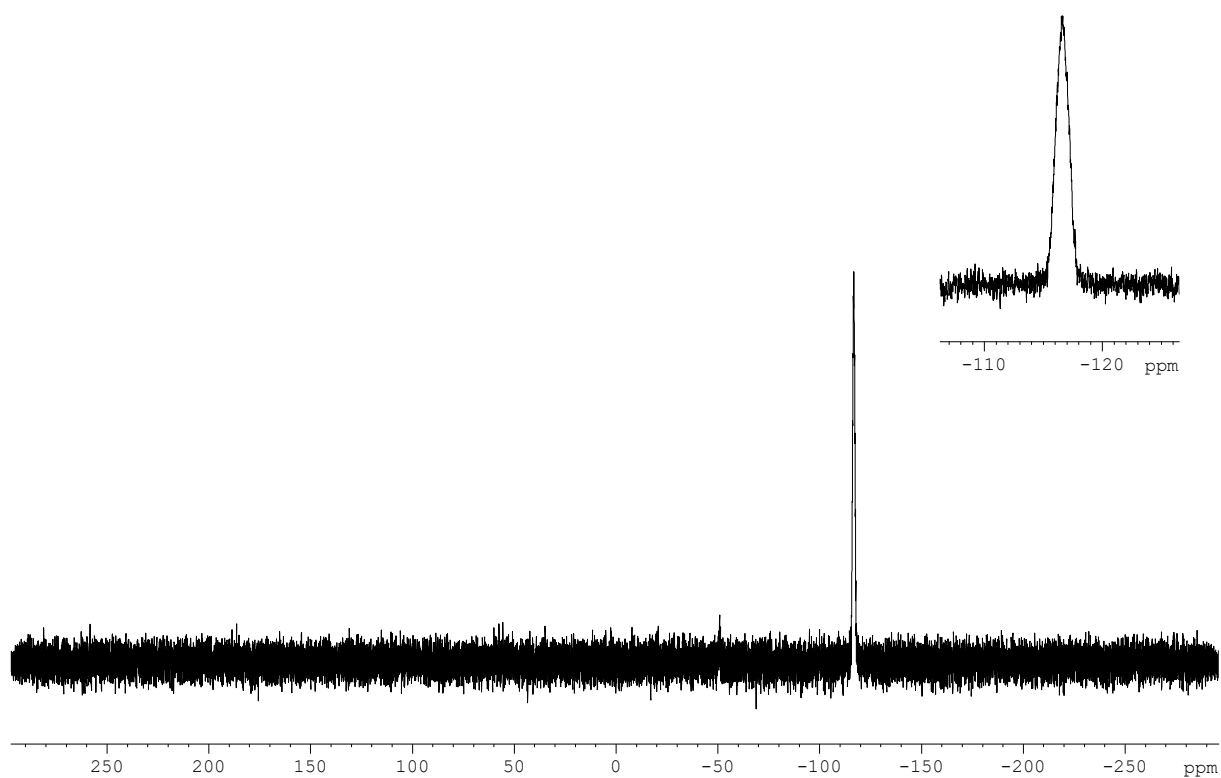


Figure S25: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3a** in CD_2Cl_2 at 298 K.

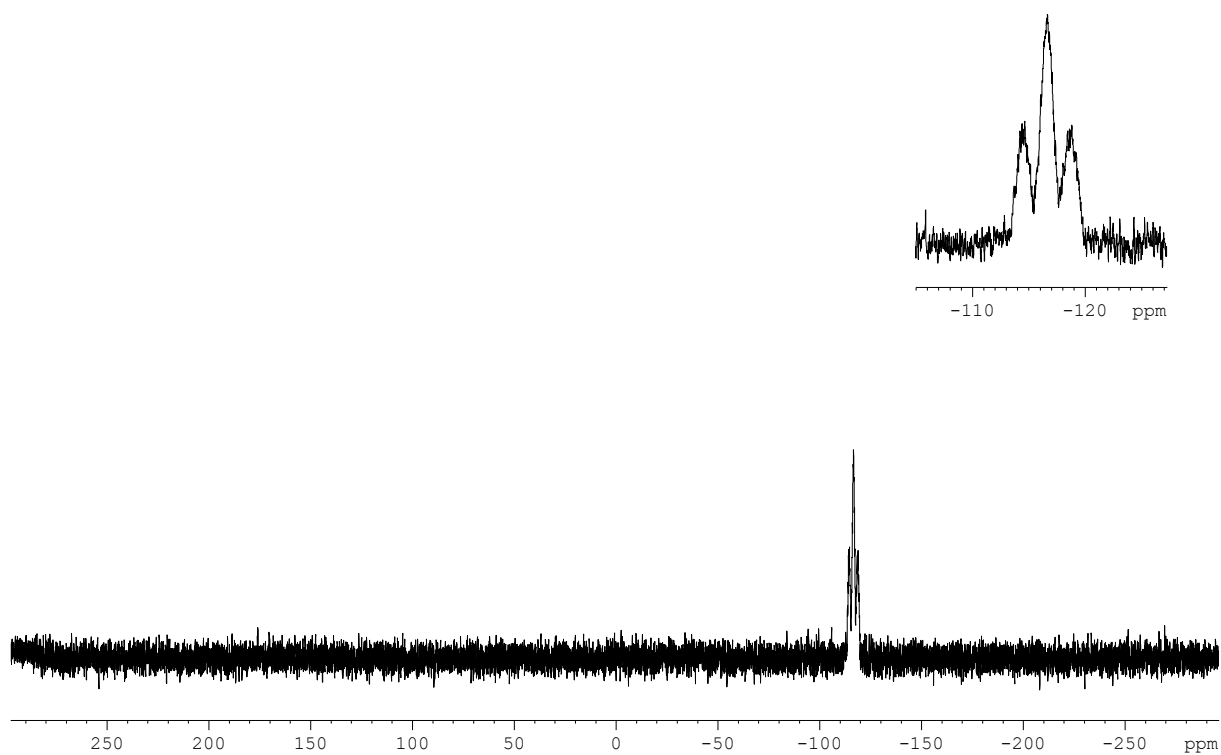


Figure S26: ^{31}P NMR spectrum of **3a** in CD_2Cl_2 at 298 K.

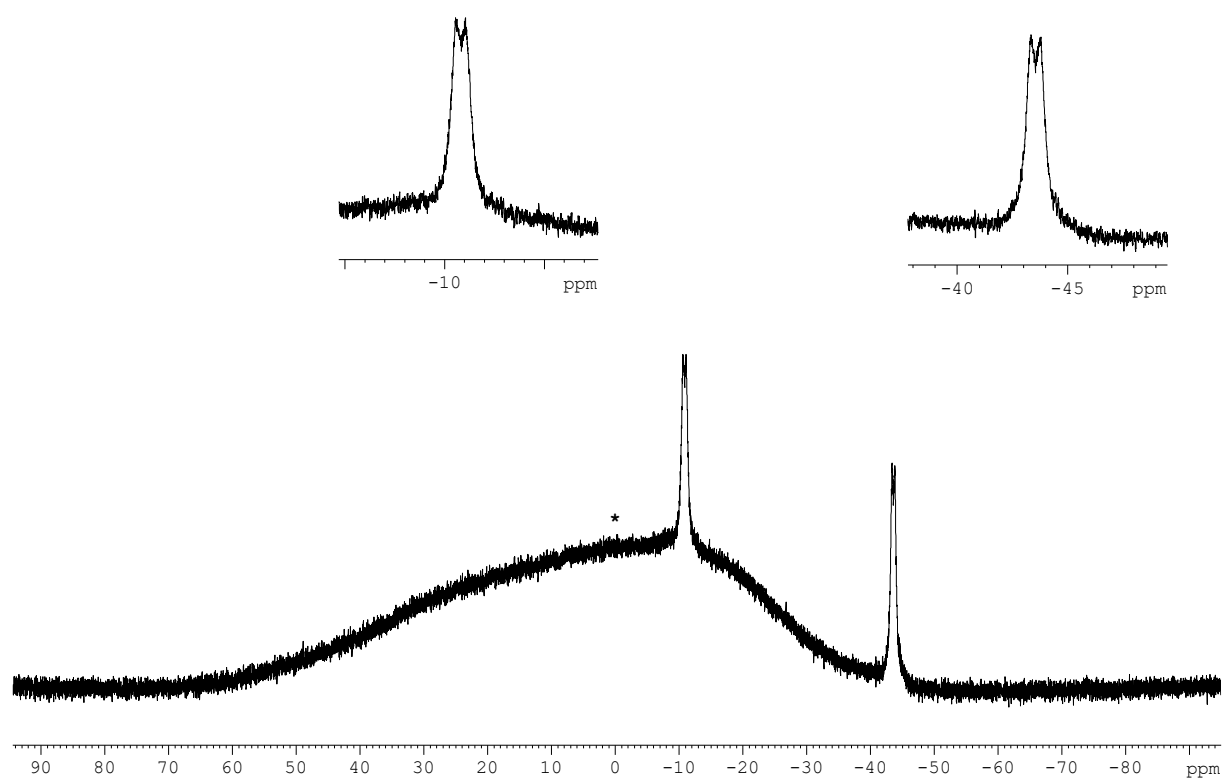


Figure S27: $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **3a** in CD_2Cl_2 at 298 K. * = signal from the NMR probe.

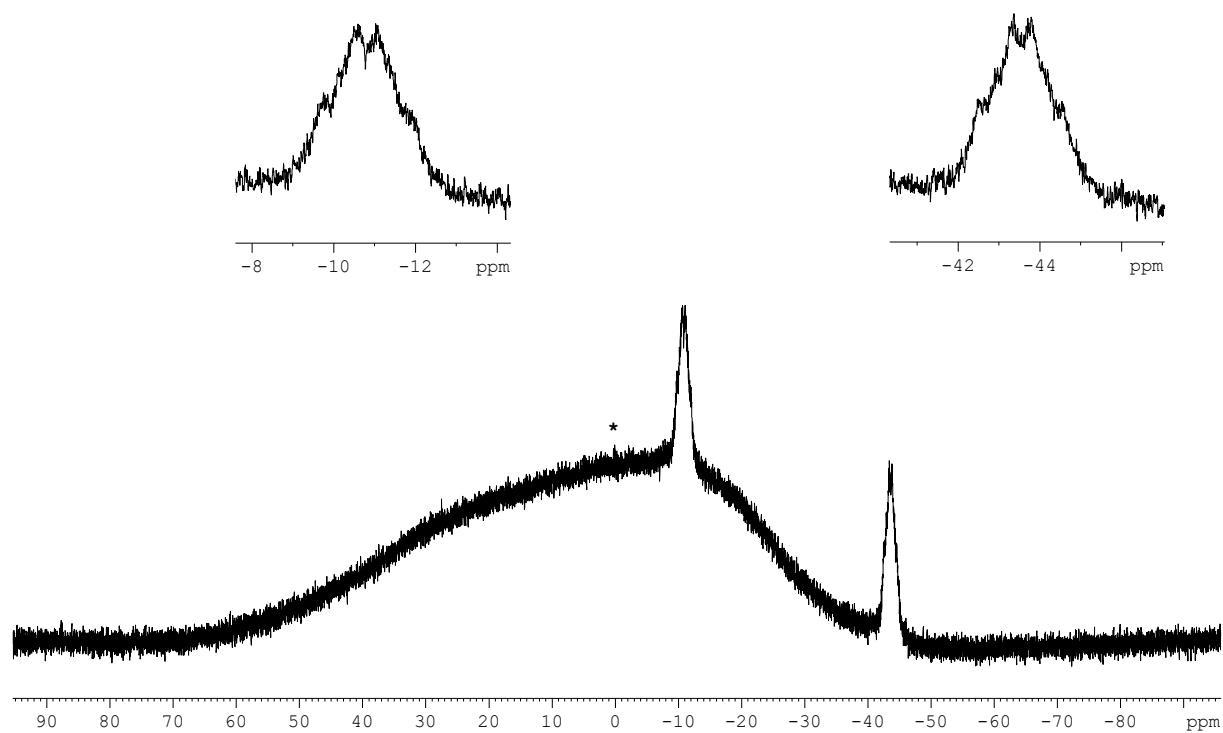


Figure S28: $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **3a** in CD_2Cl_2 at 298 K. * = signal from the NMR probe.

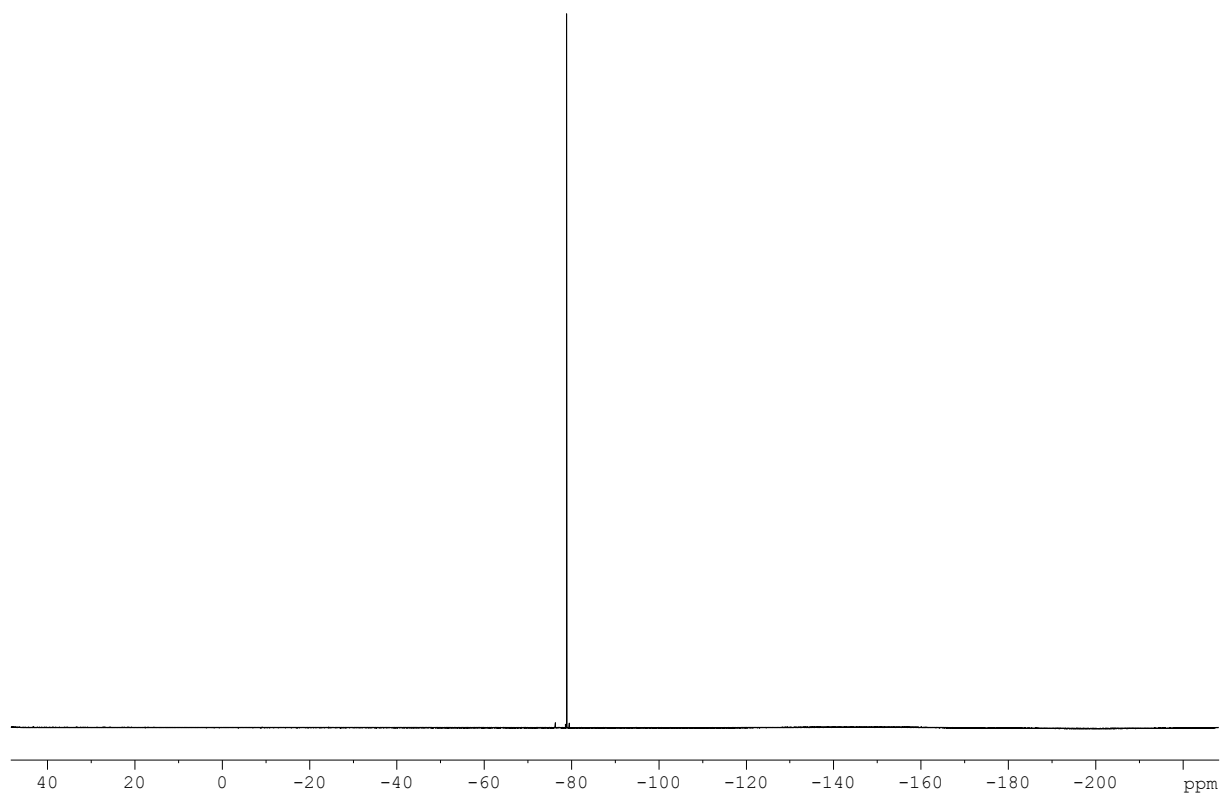


Figure S29: ^{19}F NMR spectrum of **3a** in CD_2Cl_2 at 298 K.

[IDipp· $\text{GeH}_2\text{BH}_2\text{AsH}_2\text{BH}_2\cdot\text{NMe}_3$][OTf] (**3b**)

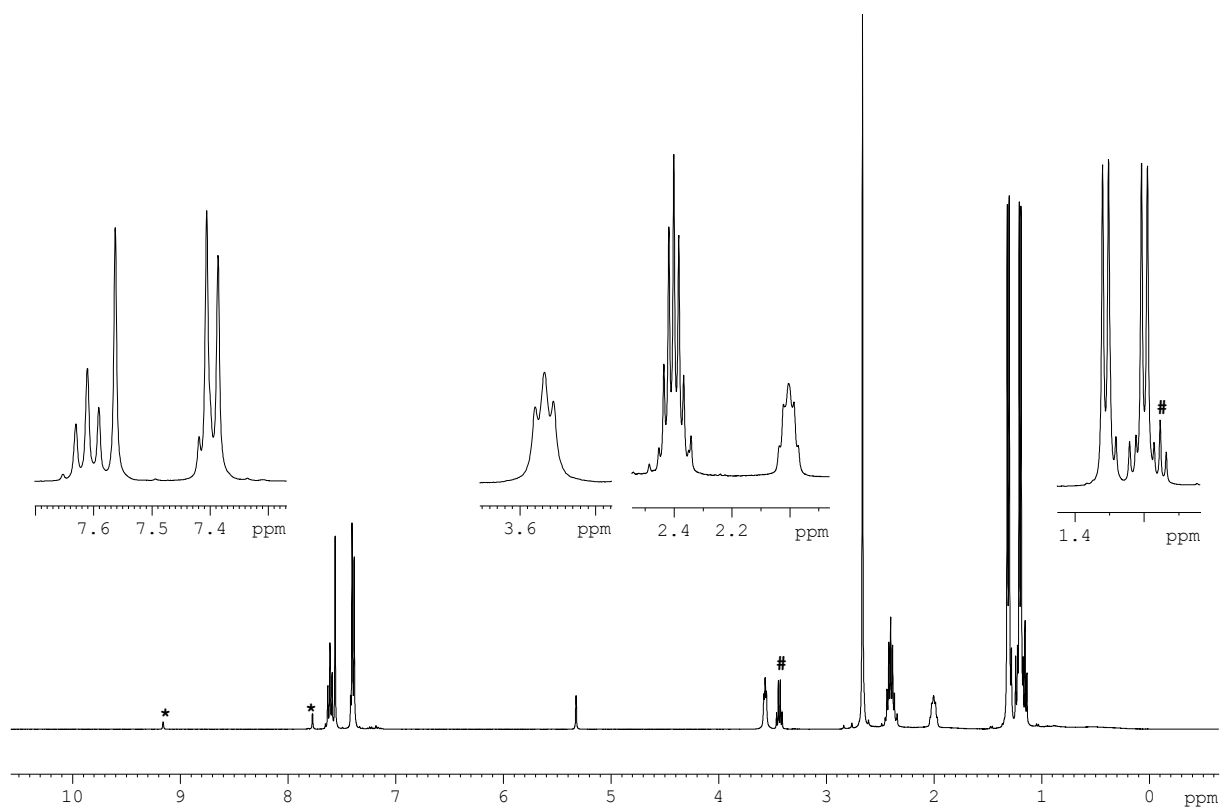


Figure S30: ^1H NMR spectrum of **3b** in CD_2Cl_2 at 298 K. * = [IDippH][OTf]. # = Et_2O .

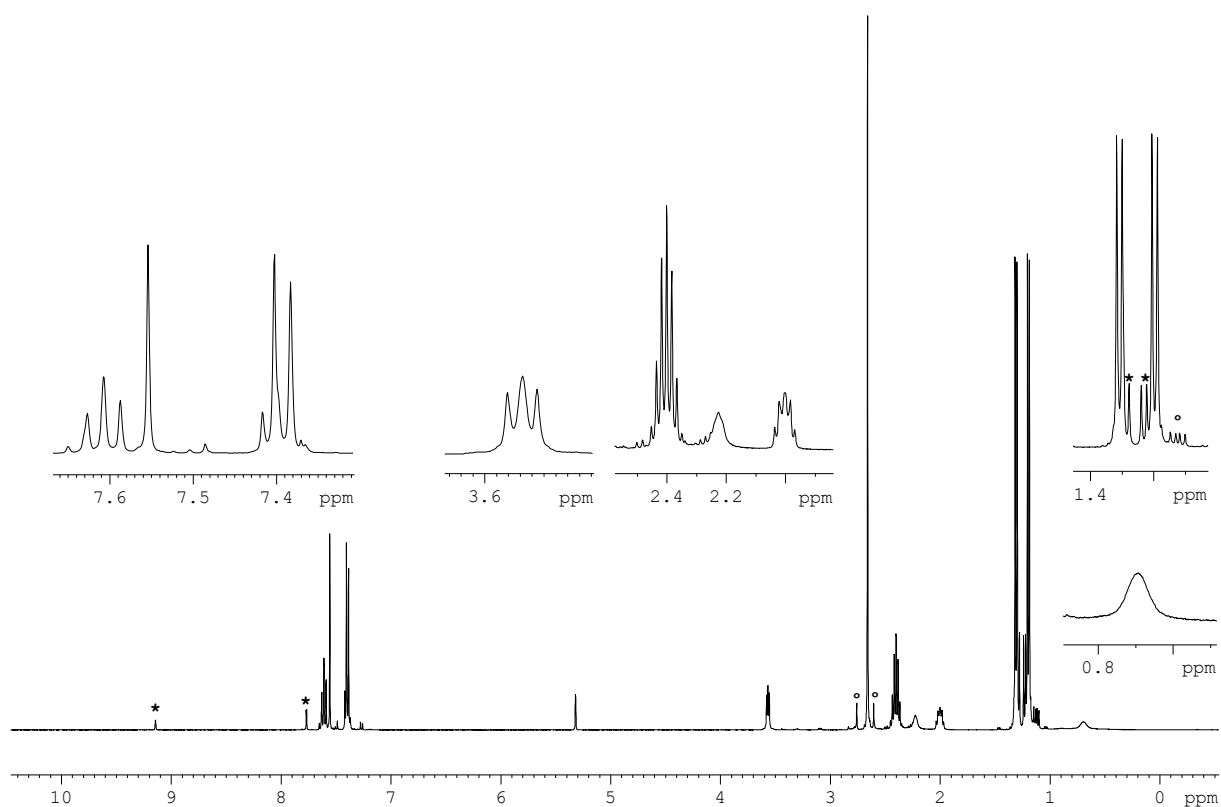


Figure S31: $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum of **3b** in CD_2Cl_2 at 298 K. ° = unidentified impurity. * = [IDippH][OTf].

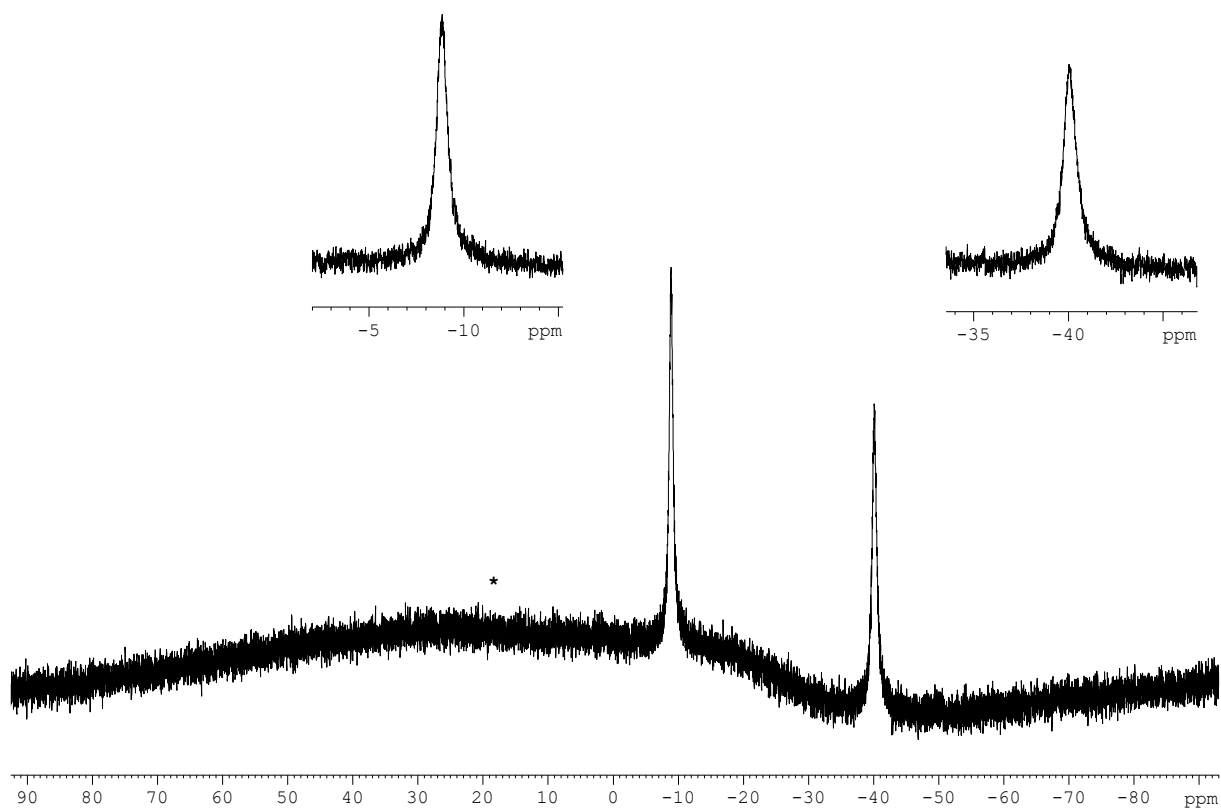


Figure S32: $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **3b** in CD_2Cl_2 at 298 K. * = signal from the NMR probe.

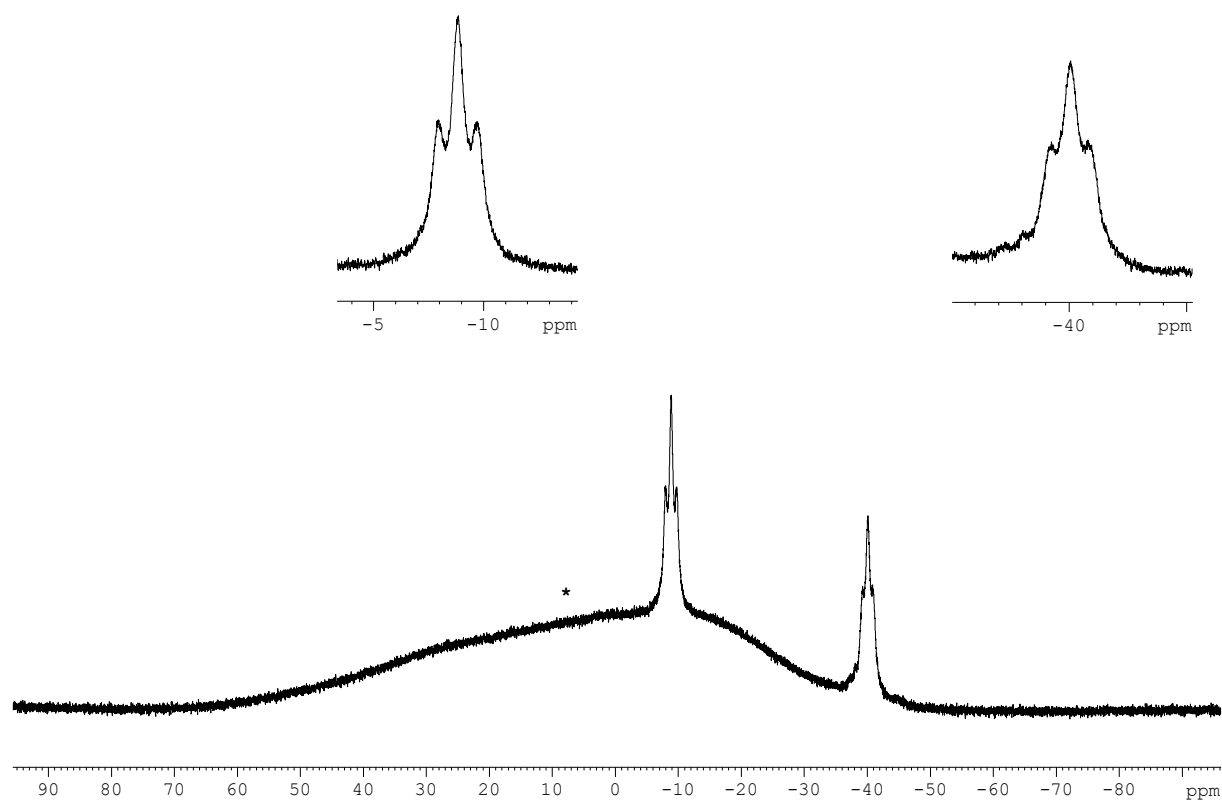


Figure S33: ^{11}B NMR spectrum of **3b** in CD_2Cl_2 at 298 K. * = signal from the NMR probe.

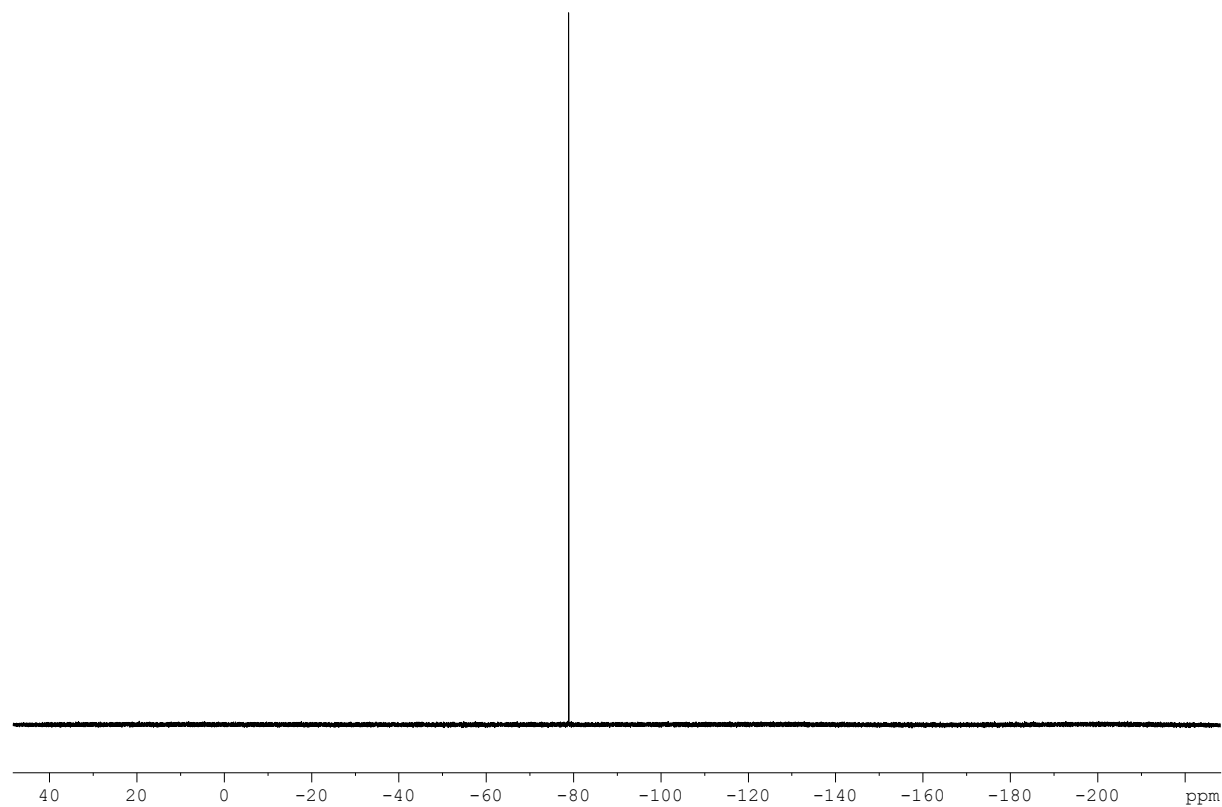


Figure S34: ^{19}F NMR spectrum of **3b** in CD_2Cl_2 at 298 K.

[IDipp·GeH₂BH₂PH₂BH₂·IMes][OTf] (**4**)

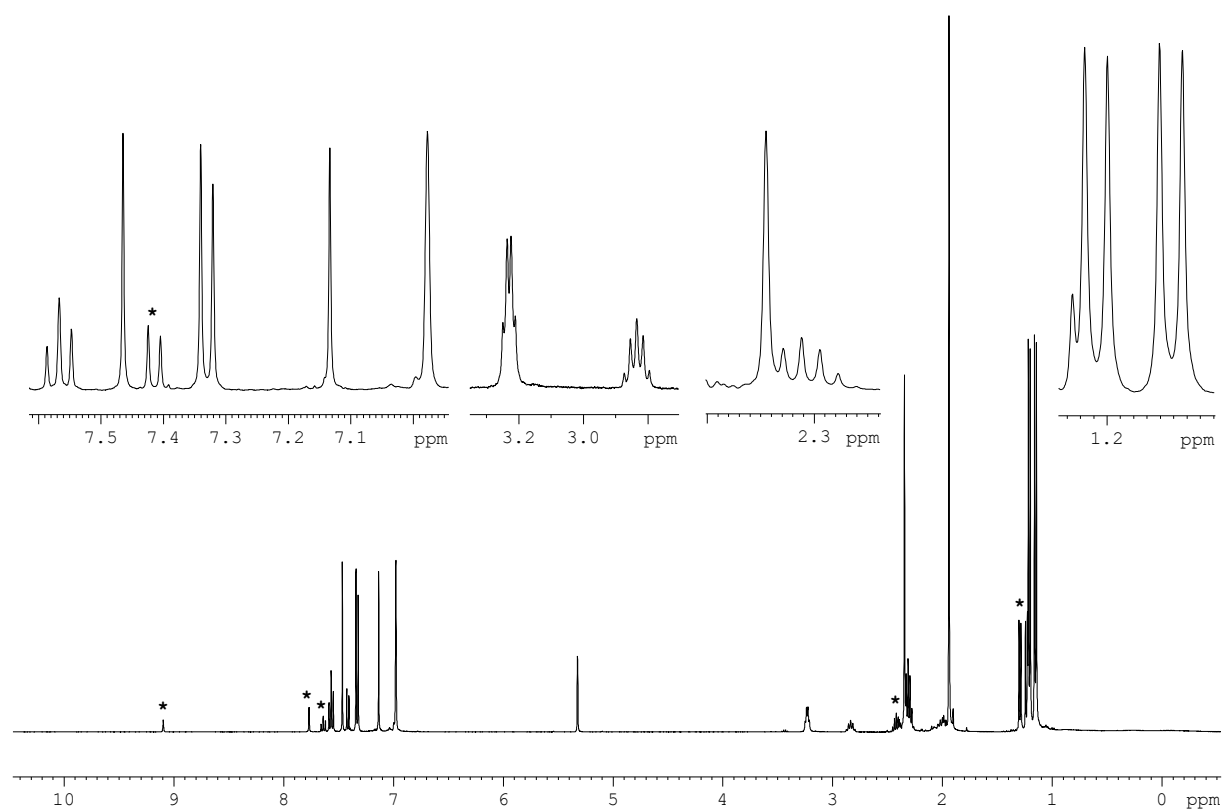


Figure S35: ¹H NMR spectrum of **4** in CD₂Cl₂ at 298 K. * = [IDippH][OTf].

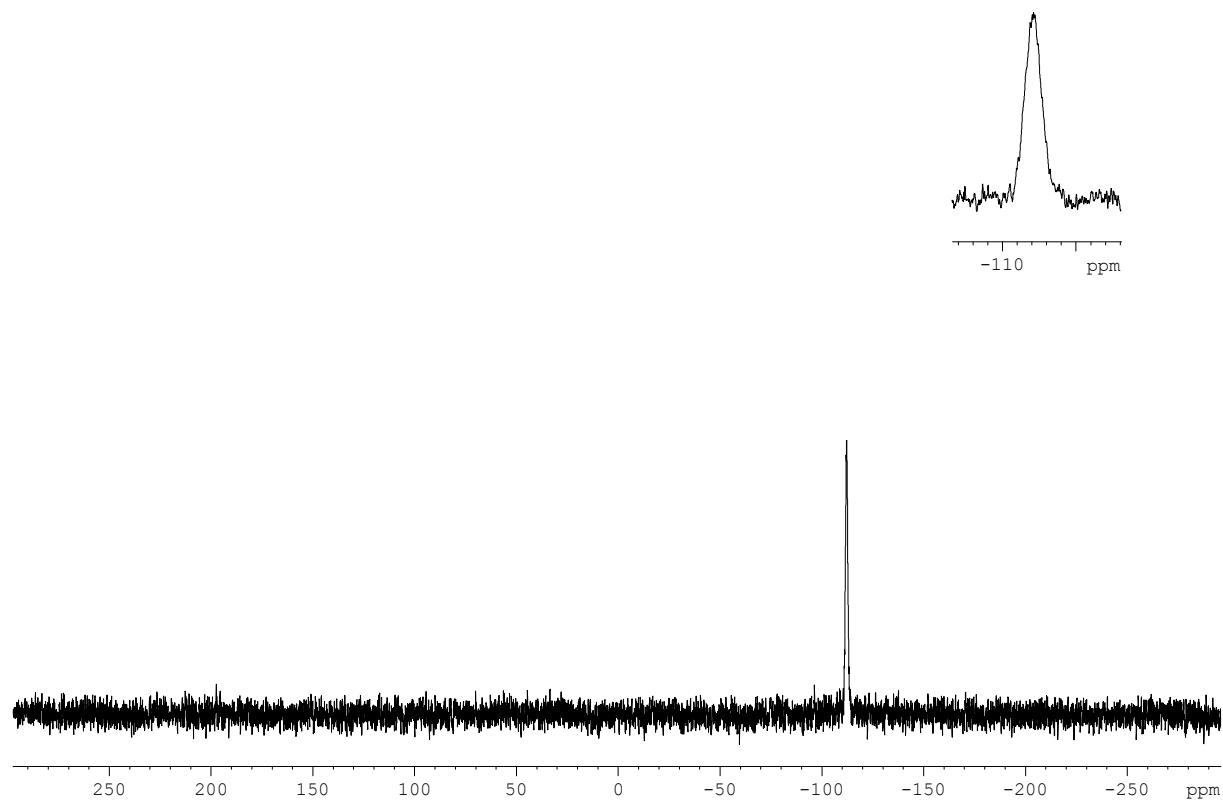


Figure S36: ³¹P{¹H} NMR spectrum of **4** in CD₂Cl₂ at 298 K.

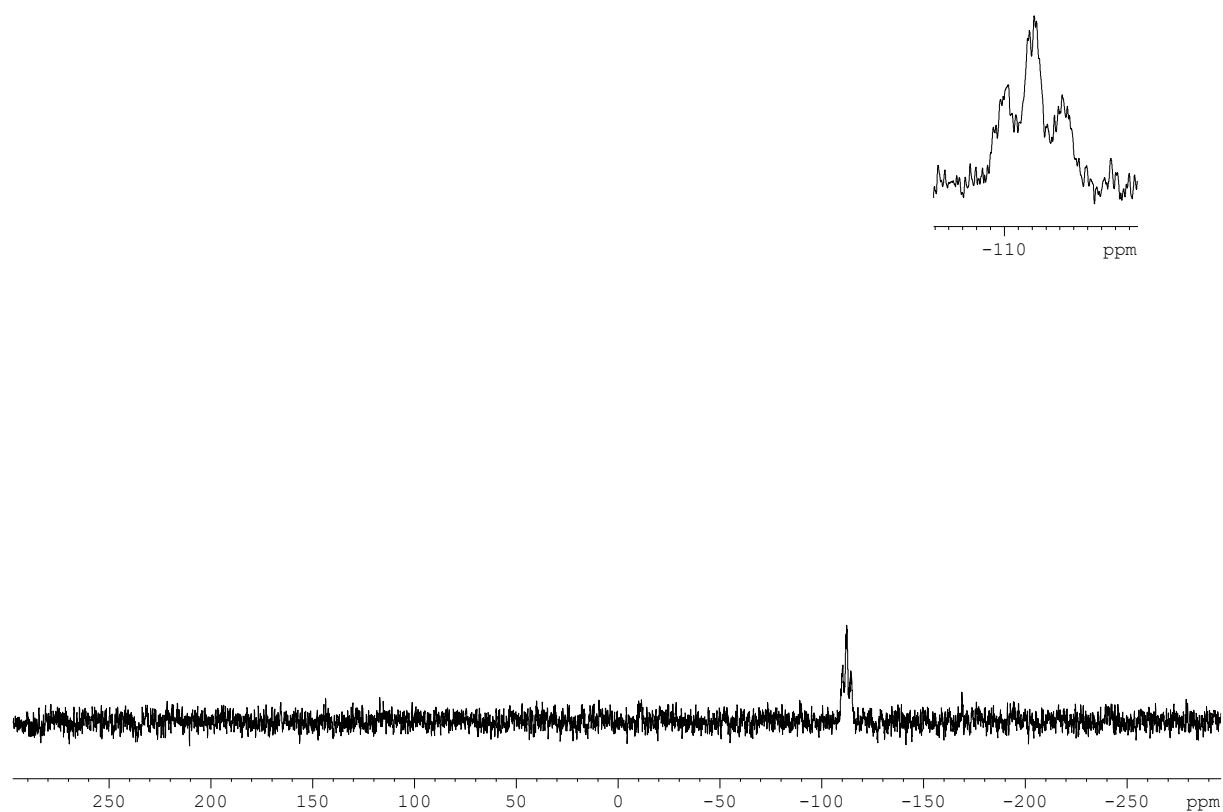


Figure S37: ^{31}P NMR spectrum of **4** in CD_2Cl_2 at 298 K.

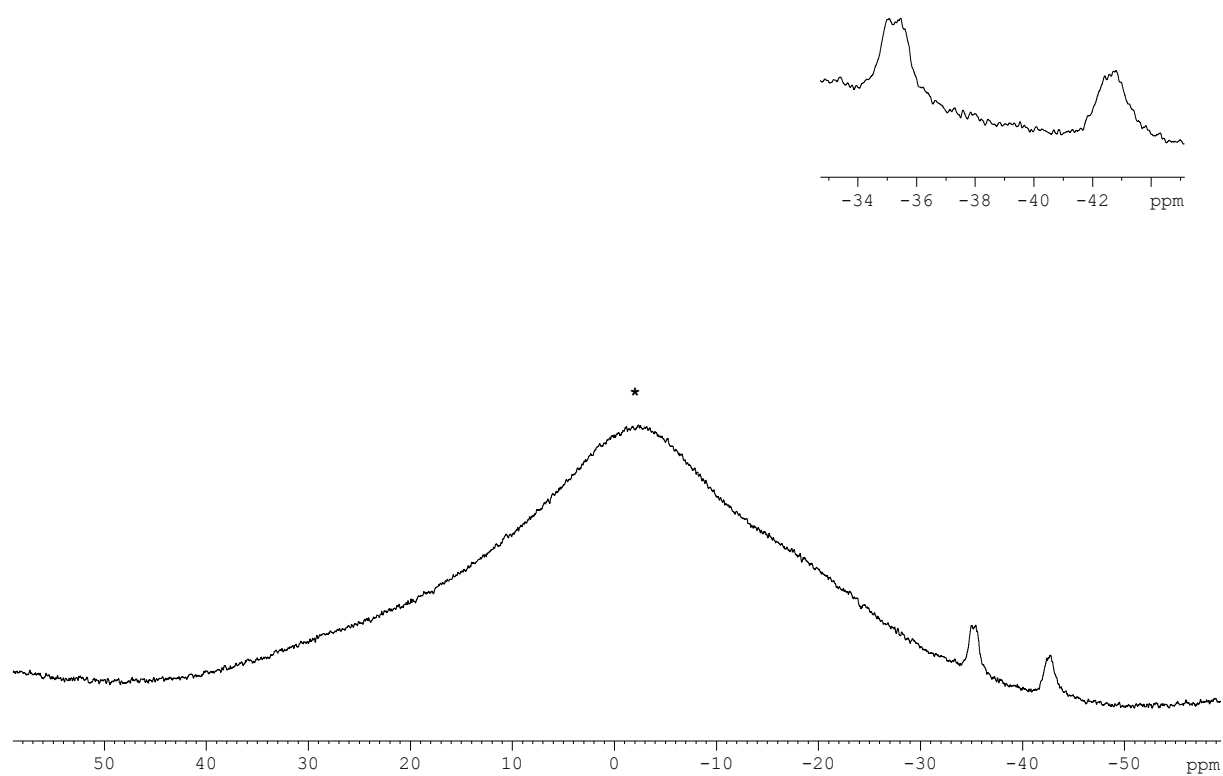


Figure S38: $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **4** in CD_2Cl_2 at 298 K. * = signal from the NMR probe.

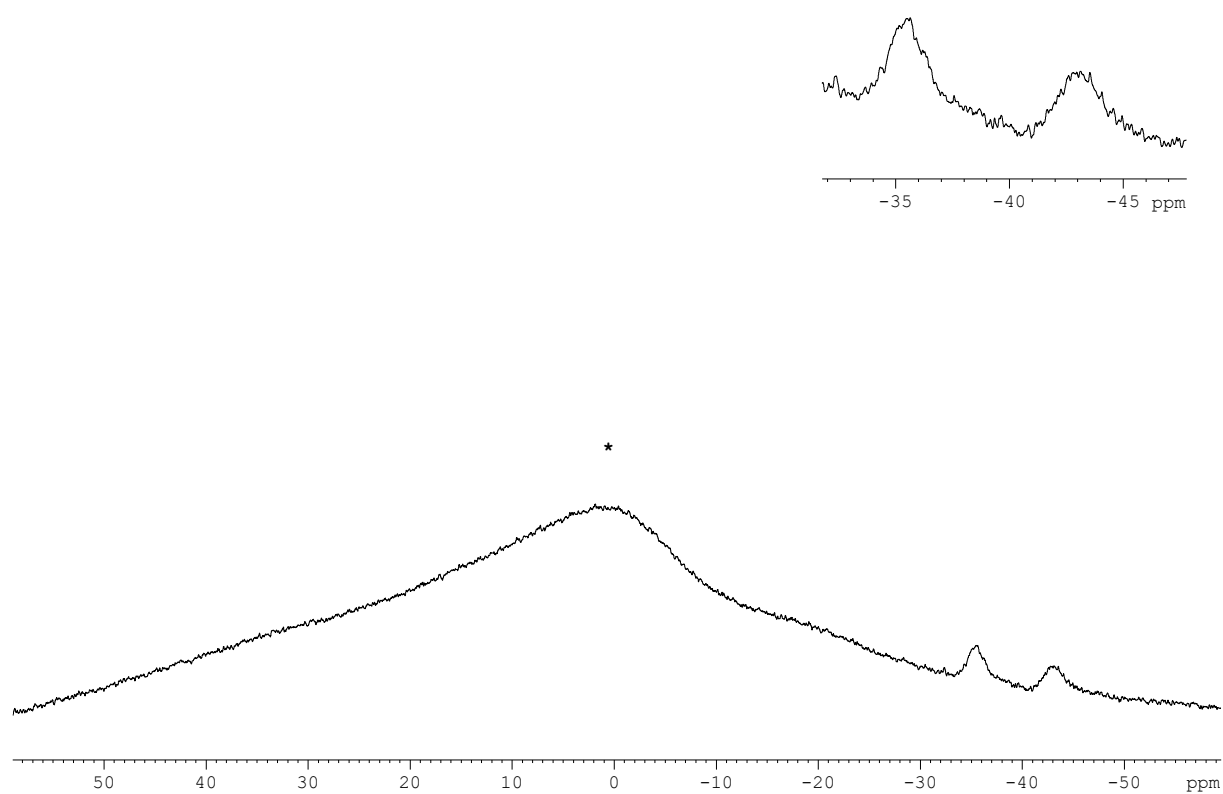


Figure S39: ^{11}B NMR spectrum of **4** in CD_2Cl_2 at 298 K. * = signal from the NMR probe.

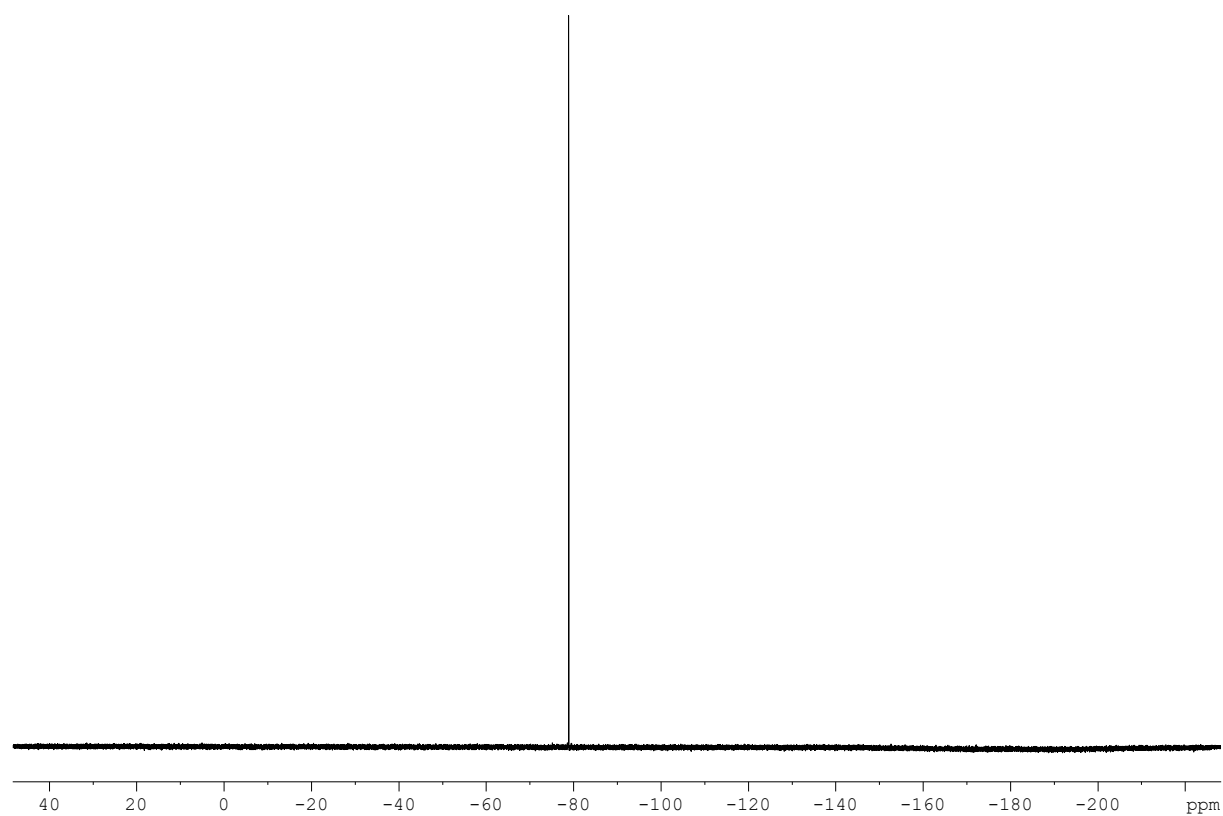


Figure S40: ^{19}F NMR spectrum of **4** in CD_2Cl_2 at 298 K.

[IDipp·GeH₂BH₂PH₂BH₂·IDipp][OTf] (**5a**)

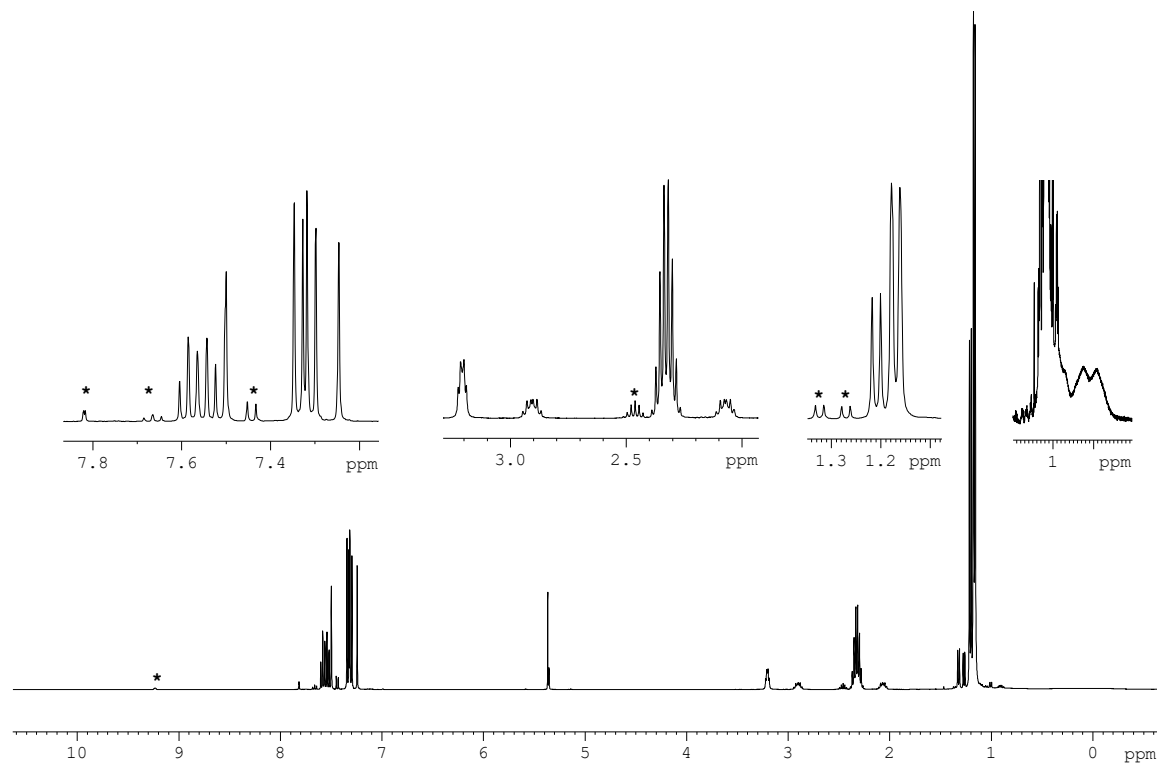


Figure S41: ¹H NMR spectrum of **5a** in CD₂Cl₂ at 298 K. * = [IDippH][OTf].

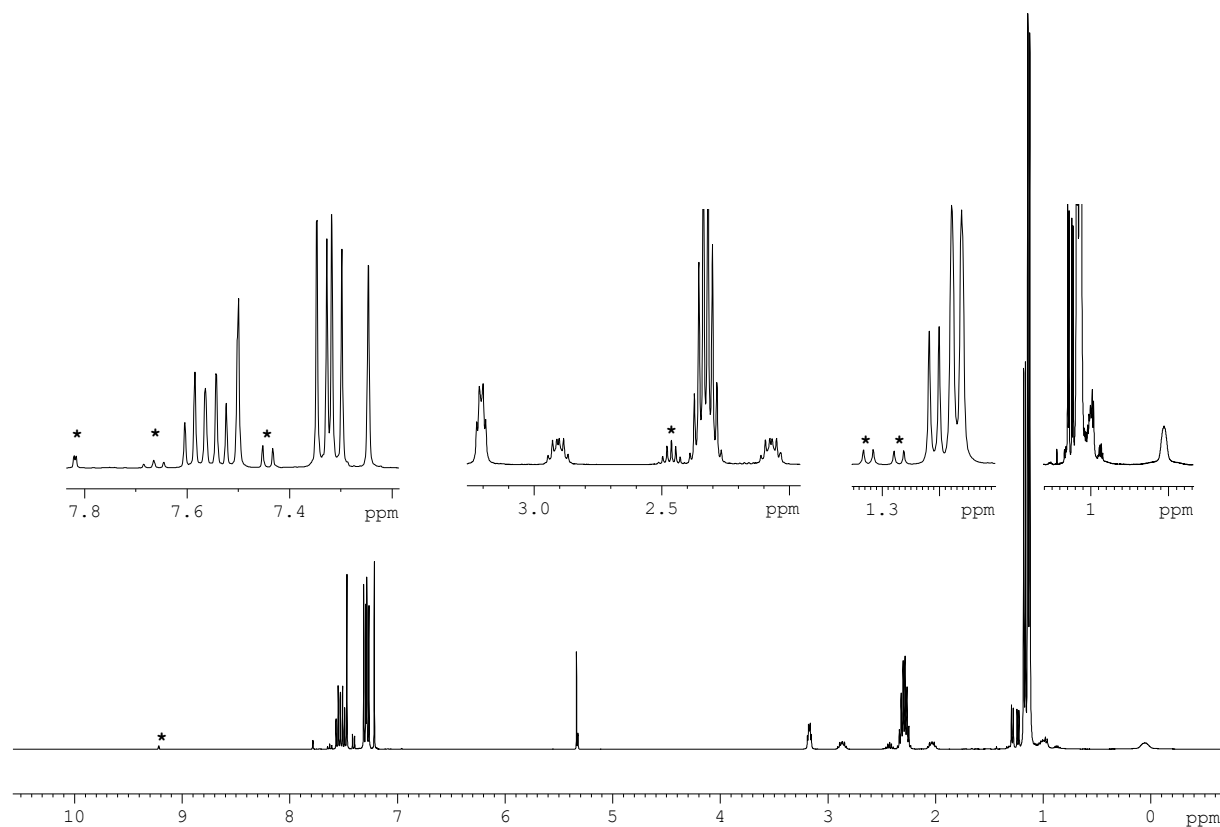


Figure S42: ¹H{¹¹B} NMR spectrum of **5a** in CD₂Cl₂ at 298 K. * = [IDippH][OTf].

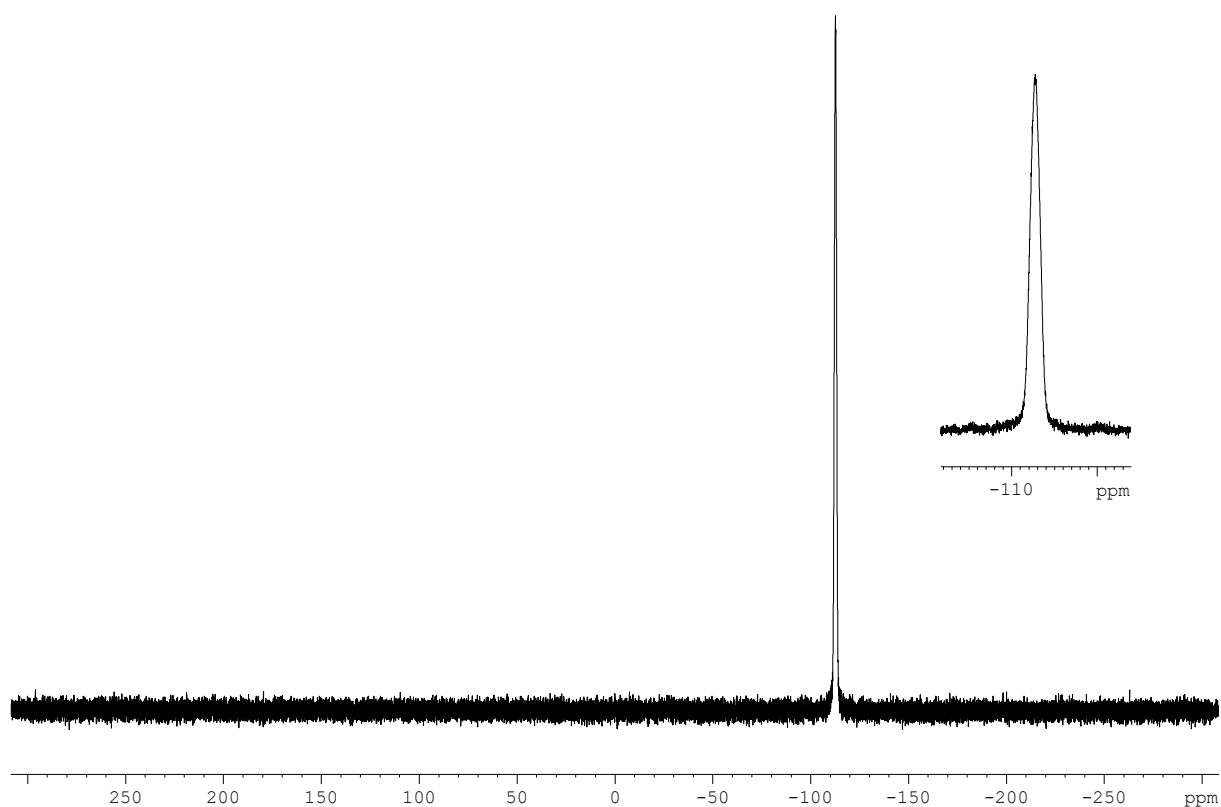


Figure S43: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5a** in CD_2Cl_2 at 298 K.

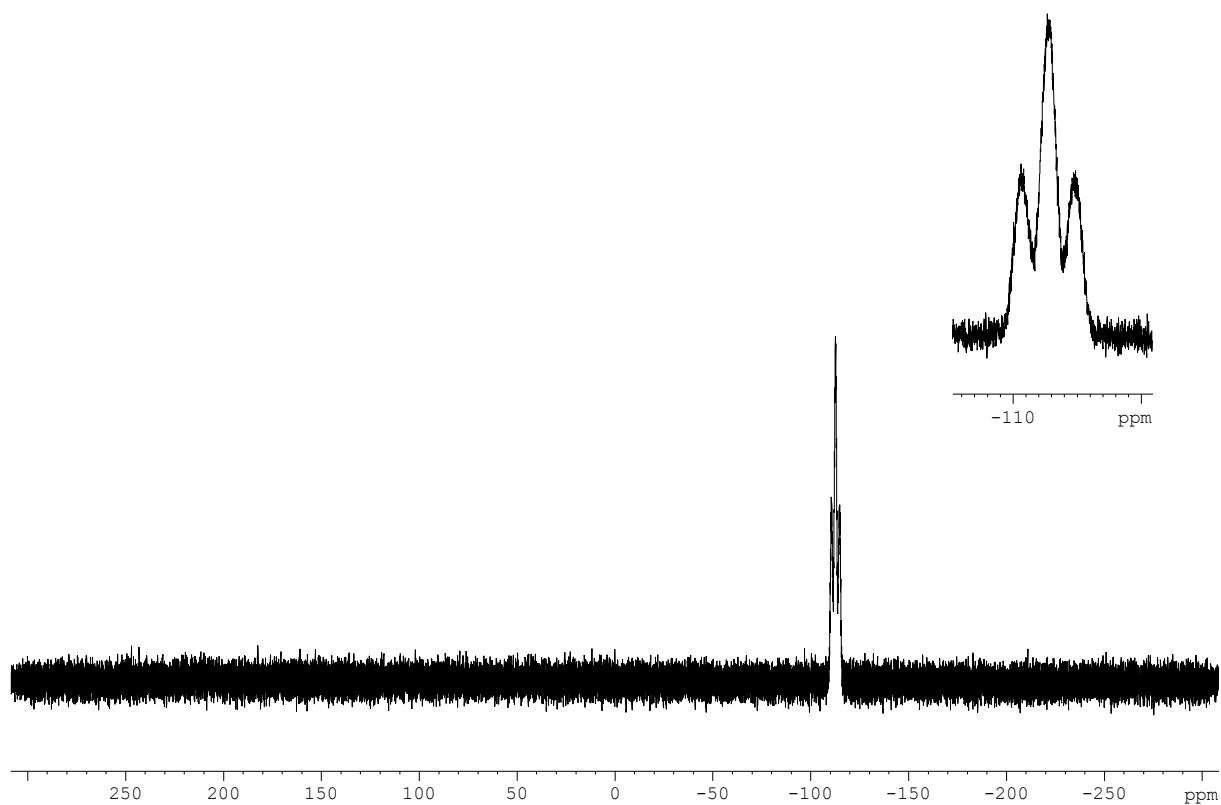


Figure S44: ^{31}P NMR spectrum of **5a** in CD_2Cl_2 at 298 K.

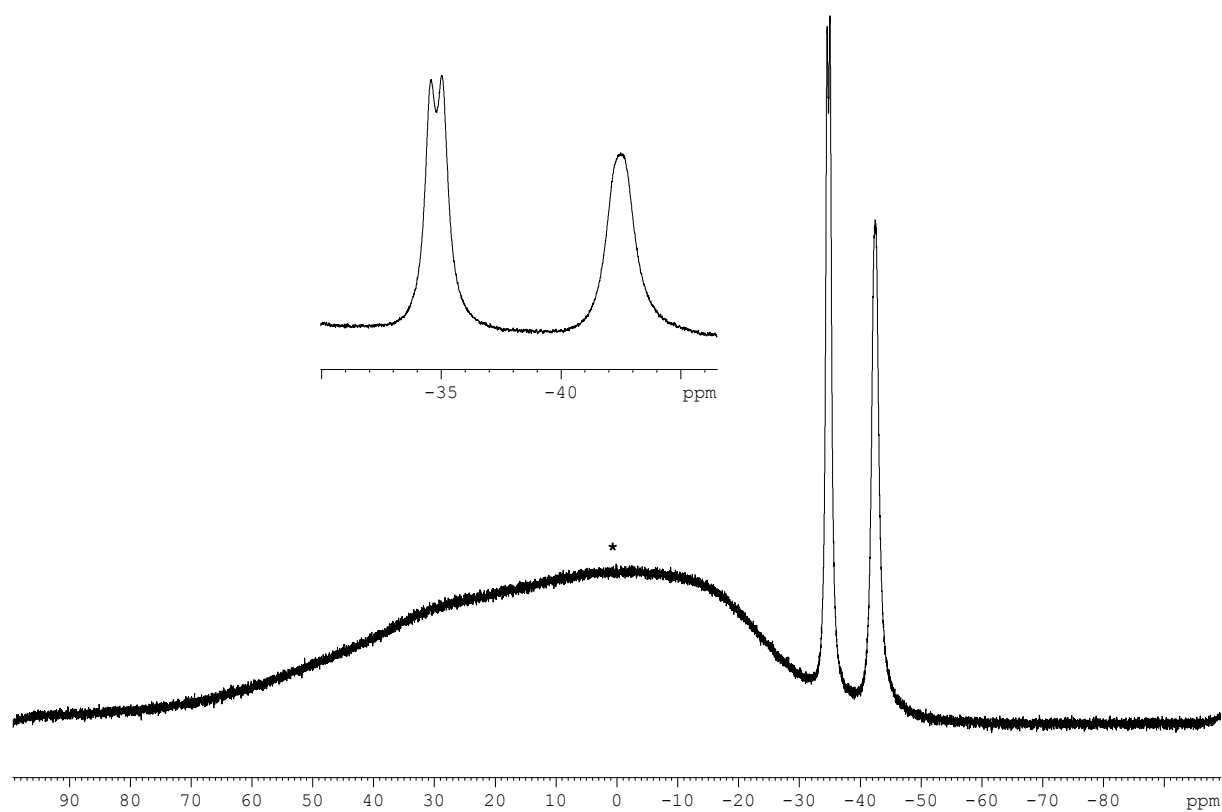


Figure S45: $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **5a** in CD_2Cl_2 at 298 K. * = signal from the NMR probe.

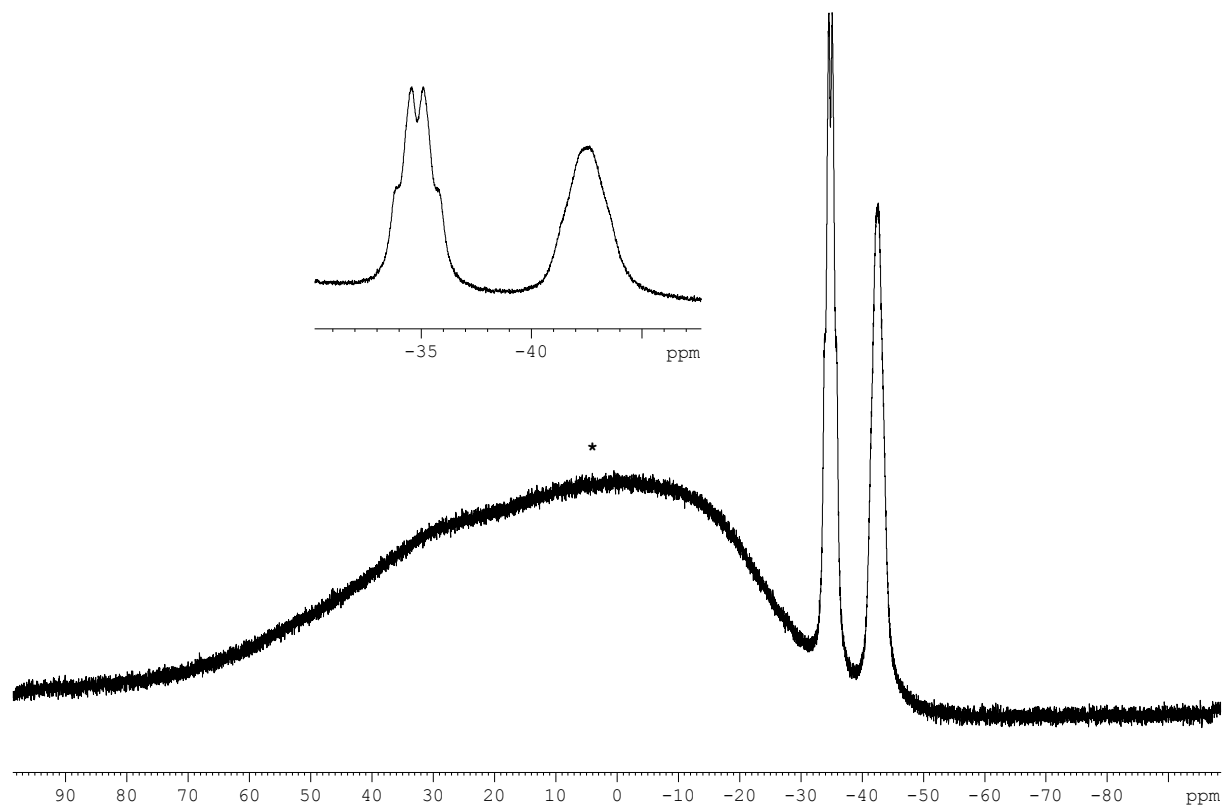


Figure S46: ^{11}B NMR spectrum of **5a** in CD_2Cl_2 at 298 K. * = signal from the NMR probe.

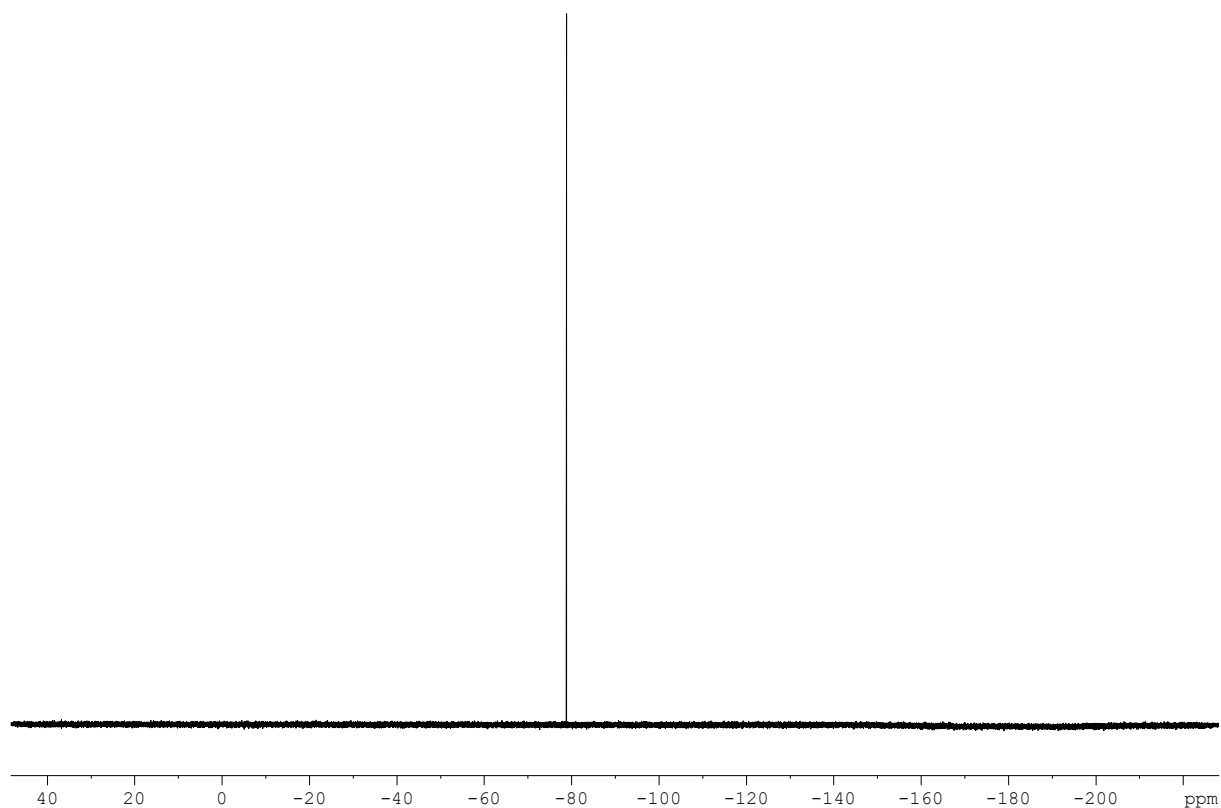


Figure S47: ^{19}F NMR spectrum of **5a** in CD_2Cl_2 at 298 K.

$[\text{IDipp} \cdot \text{GeH}_2\text{BH}_2\text{AsH}_2\text{BH}_2 \cdot \text{IDipp}][\text{OTf}]$ (**5b**)

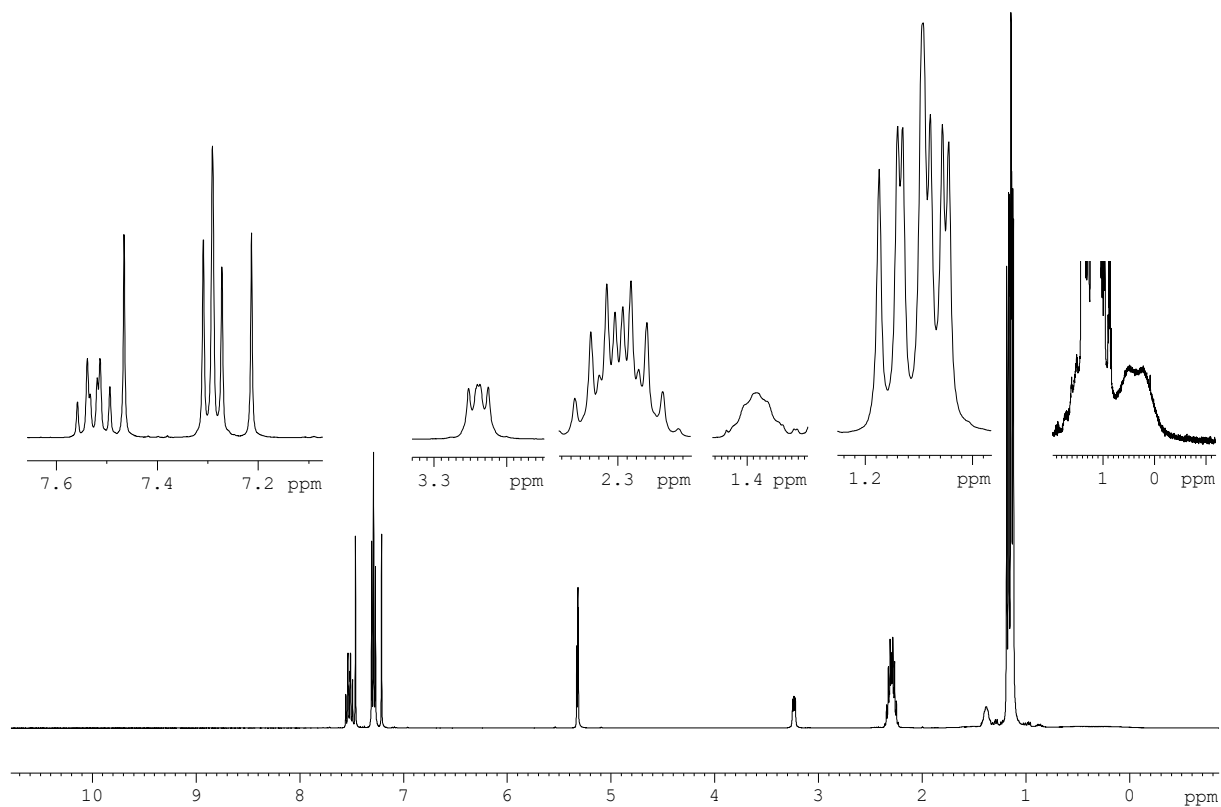


Figure S48: ^1H NMR spectrum of **5b** in CD_2Cl_2 at 298 K.

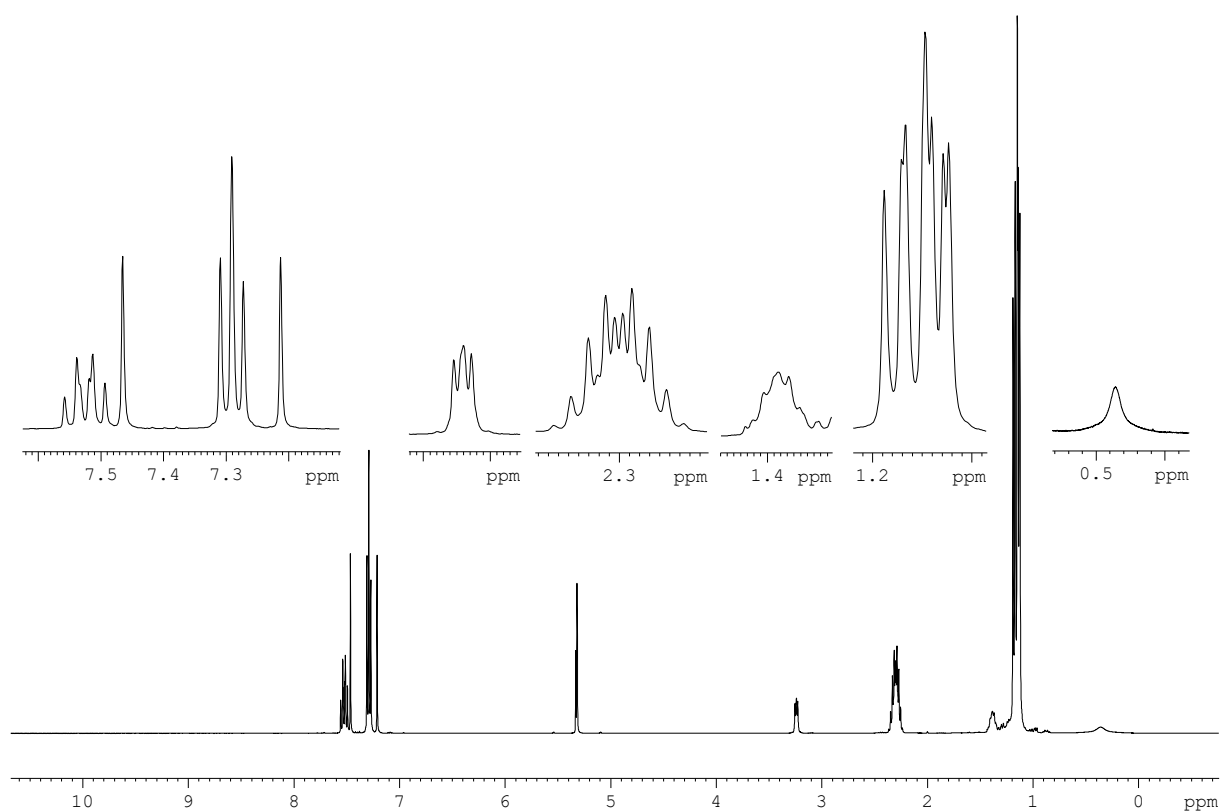


Figure S49: $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum of **5b** in CD_2Cl_2 at 298 K.

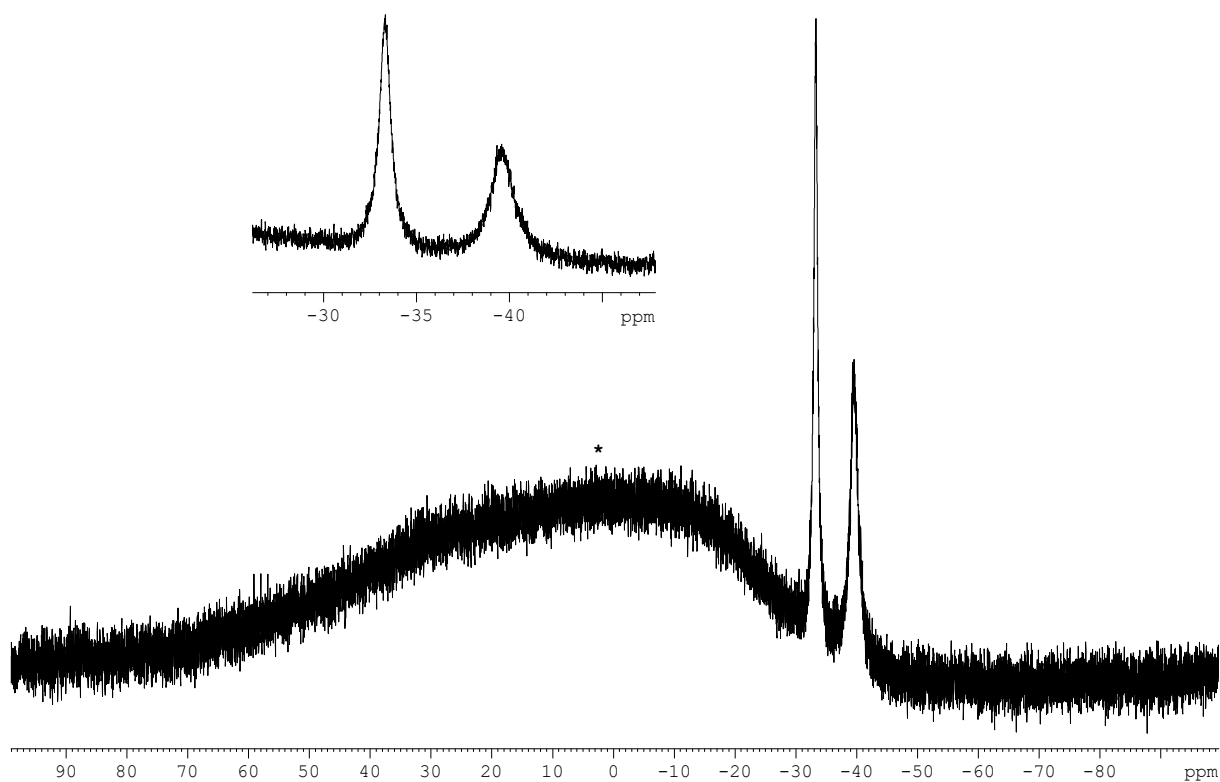


Figure S50: $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **5b** in CD_2Cl_2 at 298 K. * = signal from the NMR probe.

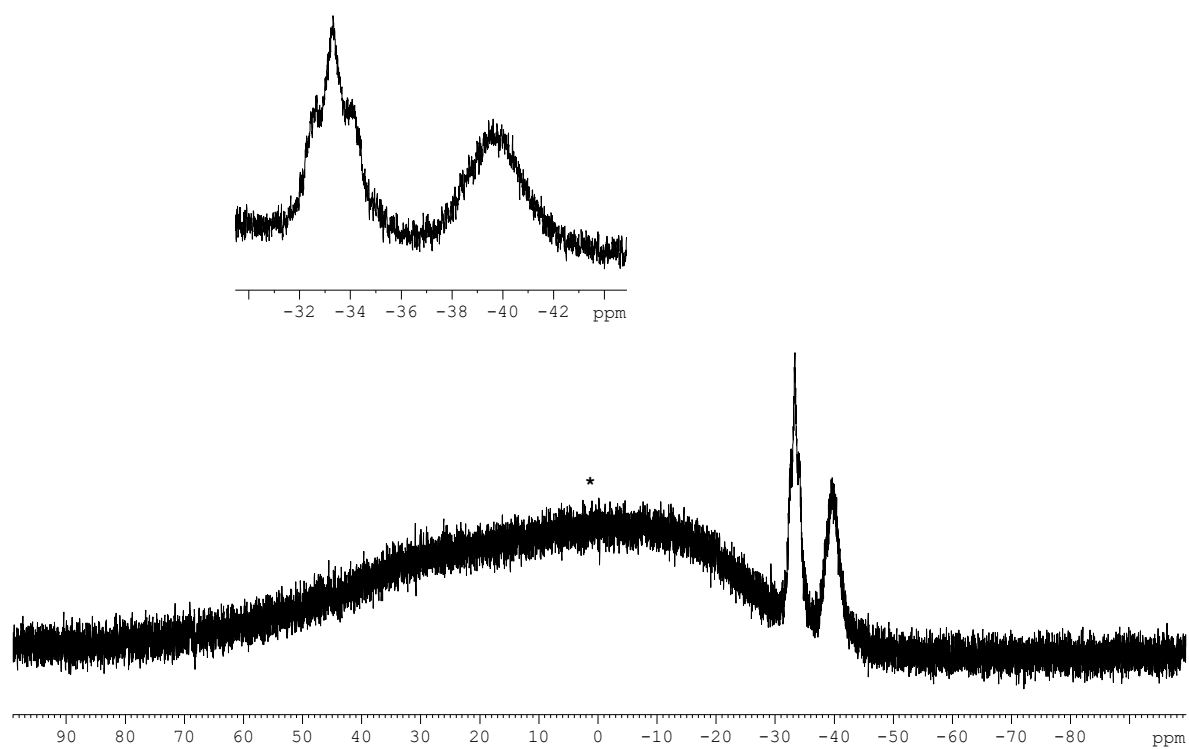


Figure S51: ^{11}B NMR spectrum of **5b** in CD_2Cl_2 at 298 K. * = signal from the NMR probe.

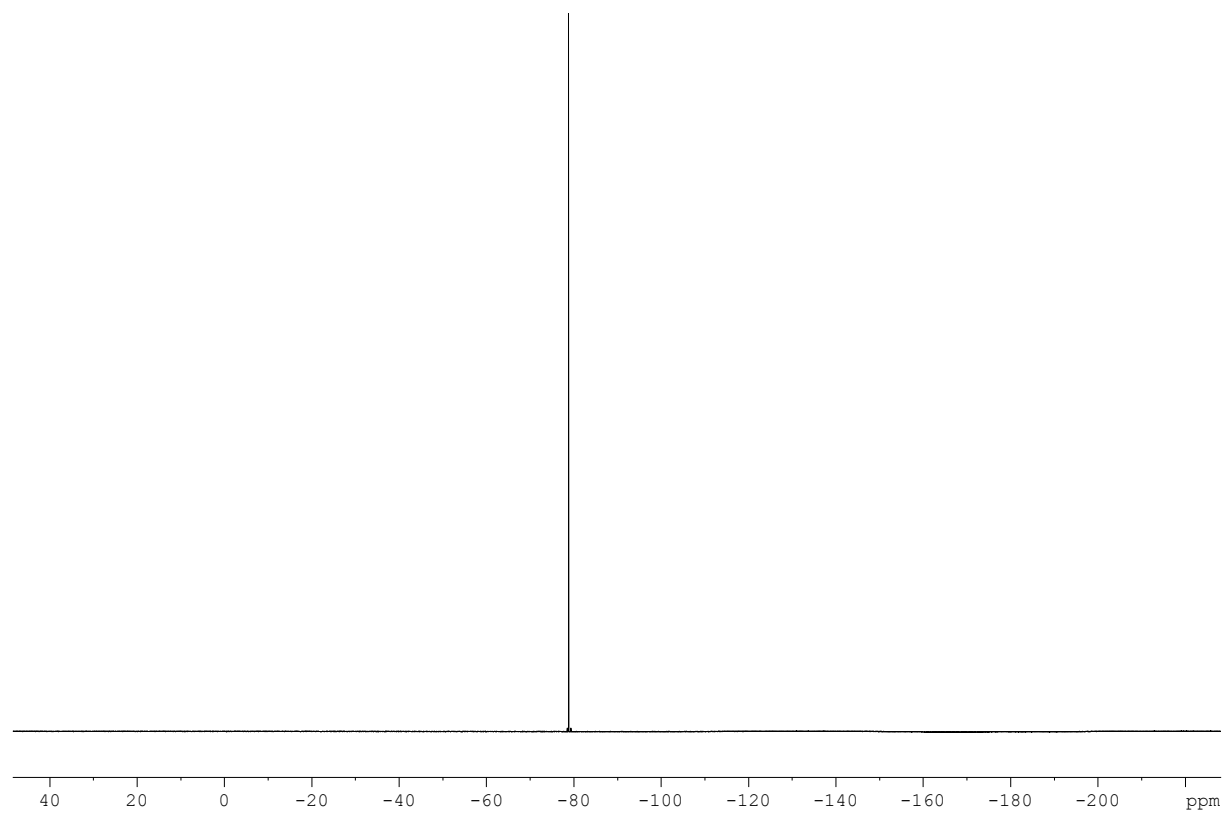


Figure S52: ^{19}F NMR spectrum of **5b** in CD_2Cl_2 at 298 K.

3 Crystallographic data

Single-crystal X-ray diffraction experiments were performed on a Bruker D8 diffractometer equipped with an APEX II CCD detector (**2a**, **2b**) and on a XtaLAB Synergy R DW system (Rigaku) equipped with a HyPix-Arc 150 detector (**5a**, **5b**). Data were collected using Cu- $K\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) (**2b**, **5a**, **5b**) or Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) (**2a**), respectively. The crystals were kept in a cold nitrogen stream at a steady temperature of 193 K (**2a**), 173 K (**2b**), 100 K (**5a**, **5b**) during the measurement. Data reduction was performed using Bruker SAINT⁹ or CrysAlisPro (Rigaku),¹⁰ respectively. An absorption correction based on a gaussian integration over a multifaceted crystal was applied. Using Olex2¹¹ as the graphical interface, the structures were solved with ShelXT¹² using dual methods. The models were refined with ShelXL¹³ using full matrix least squares minimisation on F^2 .

Crystallographic data and details of the experiments are given in Tables S1 and S2.

CIF files with comprehensive information on the details of the diffraction experiments and full tables of bond lengths and angles are deposited in Cambridge Crystallographic Data Centre under the deposition codes CCDC 2219857-2219860. These data can be obtained free of charge at www.ccdc.cam.ac.uk/contents/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 **2a** and **2b**.

Compound	2a	2b
Internal naming	riv1959	riv1963
CCDC number	2219857	2219858
Formula	C ₄₃ H ₆₁ B ₂ N ₃ O ₃ F ₃ SGeP	C ₄₃ H ₆₁ B ₂ N ₃ O ₃ F ₃ SGeAs
Dcalc	1.231	1.285
μ/mm^{-1}	0.771	2.453
Formula Weight	882.18	926.13
Color	colorless	colorless
Shape	rod-shaped	block-shaped
Size/mm ³	0.75×0.17×0.15	0.39×0.08×0.06
T/K	193.15	173.15
Crystal System	monoclinic	monoclinic
Space Group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	9.9956(10)	10.0247(4)
<i>b</i> /Å	14.6178(15)	14.6574(6)
<i>c</i> /Å	32.816(3)	32.8291(14)
α /°	90	90
β /°	96.941(2)	97.0402(17)
γ /°	90	90
<i>V</i> /Å ³	4759.8(8)	4784.4(3)
<i>Z</i>	4	4
<i>Z'</i>	1	1
Wavelength/Å	0.71073	1.54178
Radiation type	MoK α	CuK α
$\theta_{\text{min}}/^\circ$	1.527	2.712
$\theta_{\text{max}}/^\circ$	27.171	72.635
Measured Refl's.	128412	32668
Indep't Refl's	10494	9484
Refl's $I \geq 2 \sigma(I)$	7761	9005
<i>R</i> _{int}	0.0774	0.0334
Parameters	549	538
Restraints	0	0
Largest Peak	0.488	0.825
Deepest Hole	-0.365	-1.080
GooF	1.036	1.059
<i>wR</i> ₂ (all data)	0.1216	0.1072
<i>wR</i> ₂	0.1077	0.1054
<i>R</i> ₁ (all data)	0.0661	0.0411
<i>R</i> ₁	0.0438	0.0397

Table S2: Crystallographic data for compounds **5a** and **5b**.

Compound	5a · 1.65 CH ₂ Cl ₂	5b · 0.8 CH ₂ Cl ₂
Internal naming	MA295	MA376
CCDC number	2219859	2219860
Formula	C _{111.65} H _{163.3} B ₄ F ₆ Ge ₂ N ₈ O ₆ P ₂ S ₂ Cl _{3.3}	C _{55.8} H _{81.6} AsB ₂ Cl _{1.6} F ₃ GeN ₄ O ₃ S
Dcalc	1.187	1.228
μ/mm^{-1}	2.251	2.569
Formula Weight	2259.06	1171.36
Color	clear colorless	clear colorless
Shape	plate-shaped	block-shaped
Size/mm ³	0.17×0.08×0.02	0.17×0.09×0.03
T/K	100.00(10)	100.00(10)
Crystal System	monoclinic	monoclinic
Space Group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	35.1849(3)	35.2609(2)
<i>b</i> /Å	10.44010(10)	10.43718(8)
<i>c</i> /Å	35.7996(3)	35.8116(3)
α /°	90	90
β /°	105.9250(10)	105.9603(7)
γ /°	90	90
<i>V</i> /Å ³	12645.7(2)	12671.53(16)
<i>Z</i>	4	8
<i>Z'</i>	1	2
Wavelength/Å	1.54184	1.54184
Radiation type	Cu K α	Cu K α
θ_{min} /°	2.567	2.539
θ_{max} /°	70.072	75.046
Measured Refl's.	122947	130860
Indep't Refl's	23845	25685
Refl's $I \geq 2 \sigma(I)$	17054	21418
<i>R</i> _{int}	0.0655	0.0497
Parameters	1680	1756
Restraints	972	1150
Largest Peak	0.905	0.744
Deepest Hole	-1.283	-0.939
GooF	1.038	1.067
<i>wR</i> ₂ (all data)	0.2096	0.1992
<i>wR</i> ₂	0.1957	0.1925
<i>R</i> ₁ (all data)	0.1081	0.0857
<i>R</i> ₁	0.0762	0.0734

3.1 Crystal Structures

[IDipp·GeH₂BH₂PPh₂BH₂·NMe₃][OTf] (**2a**)

2a was crystallized from a THF solution layered with three times the amount of *n*-hexane at room temperature as clear colorless rods in the monoclinic space group *P*2₁/*c*. The structure of **2a** in the solid state is shown in Figure S53. The asymmetric unit contains one molecule of the cation [IDipp·GeH₂BH₂PPh₂BH₂·NMe₃]⁺ and a [OTf][−] anion. The hydrogen atom positions located on the Ge and B atoms were located from the difference Fourier map and refined freely.

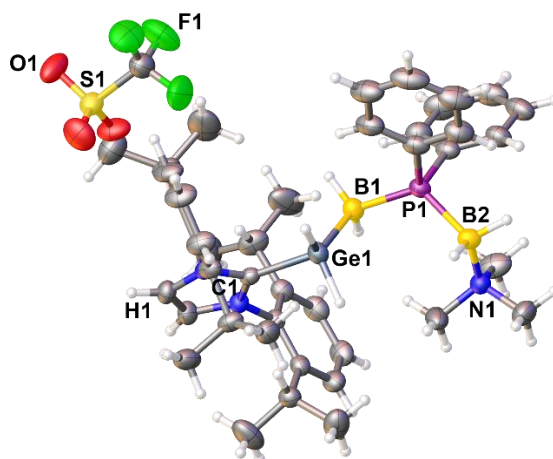
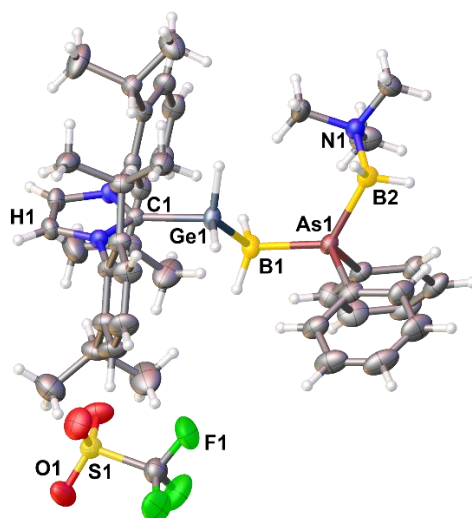


Figure S53: Molecular structure of **2a** in the solid state. Anisotropic displacement parameters are set to 50% probability level. Selected bond lengths [Å] and angles [°]: C1-Ge1 2.009(2), Ge1-B1 2.051(3), B1-P1 1.937(3), P1-B2 1.969(3), B2-N1 1.609(3); C1-Ge1-B1 111.86(10), Ge1-B1-P1 112.17(14), P1-B2-N1 116.50(18).

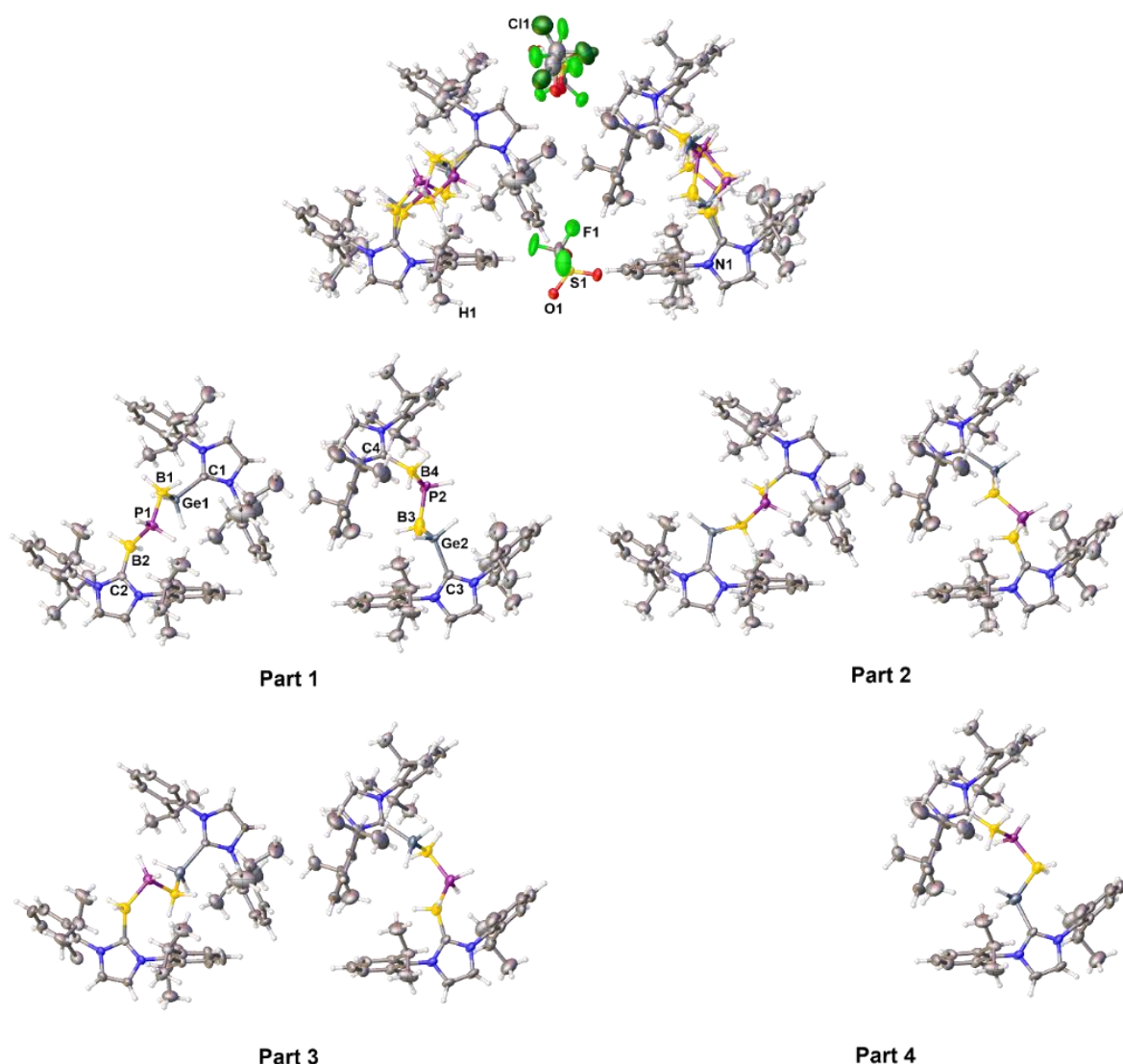
2b was crystallized from a THF solution layered with three times the amount of *n*-hexane at room temperature as clear colorless blocks in the monoclinic space group $P2_1/c$. The structure of **2b** in the solid state is shown in Figure S54. The asymmetric unit contains one molecule of the cation [IDipp·GeH₂BH₂AsPh₂BH₂·NMe₃]⁺ and a [OTf][−] anion. The hydrogen atom positions located on the Ge and B atoms were located from the difference Fourier map and refined freely.



S39

[IDipp·GeH₂BH₂PH₂BH₂·IDipp][OTf] (5a) • 1.65 CH₂Cl₂

5a was crystallized from a CH₂Cl₂ solution layered with three times the amount of *n*-hexane at room temperature as clear colorless plates in the monoclinic space group *P*2₁/*c*. The structure of **5a** in the solid state is shown in Figure S55. The asymmetric unit contains two molecules of the cation [IDipp·GeH₂BH₂PH₂BH₂·IDipp]⁺, two molecules of the anion [OTf][−] and 1.65 CH₂Cl₂ solvent molecules. The GeH₂BH₂PH₂BH₂ chains of both cations are heavily disordered (left molecule: disordered over three positions (occupancies: 0.66:0.28:0.06); right molecule: disordered over four positions (occupancies: 0.45:0.25:0.15:0.15)). Further are four *i*Pr-Groups, one [OTf][−] anion and the CH₂Cl₂ solvent molecule disordered over two positions. Additionally, was one CH₂Cl₂ molecule heavily disordered. Therefore, a solvent mask was calculated, and 172 electrons were found in a volume of 984 Å³ in 3 voids per unit cell. This is consistent with the presence of one CH₂Cl₂ per asymmetric unit, which accounts for 168 electrons per unit cell. The EADP constraint and the DFIX, DANG, ISOR, SADI and SIMU restraints were applied to model these disorders.



[IDipp·GeH₂BH₂AsH₂BH₂·IDipp][OTf] (5b) • 0.8 CH₂Cl₂

5b was crystallized from a CH₂Cl₂ solution layered with three times the amount of *n*-hexane at room temperature as clear colorless blocks in the monoclinic space group *P*2₁/*c*. The structure of **5b** in the solid state is shown in Figure S56. The asymmetric unit contains two molecules of the cation [IDipp·GeH₂BH₂AsH₂BH₂·IDipp]⁺, two molecules of the anion [OTf][−] and 0.8 CH₂Cl₂ solvent molecules. The GeH₂BH₂AsH₂BH₂ chains of both cations are heavily disordered (left molecule: disordered over four positions (occupancies: 0.55:0.2:0.18:0.07); right molecule: disordered over three positions (occupancies: 0.55:0.37:0.08)). Further are five *i*Pr-Groups, one [OTf][−] anion and two CH₂Cl₂ solvent molecule disordered over two or in case of the second CH₂Cl₂ molecule over three positions. The EADP constraint and the DFIX, DANG, ISOR, SADI and SIMU restraints were applied to model these disorders.

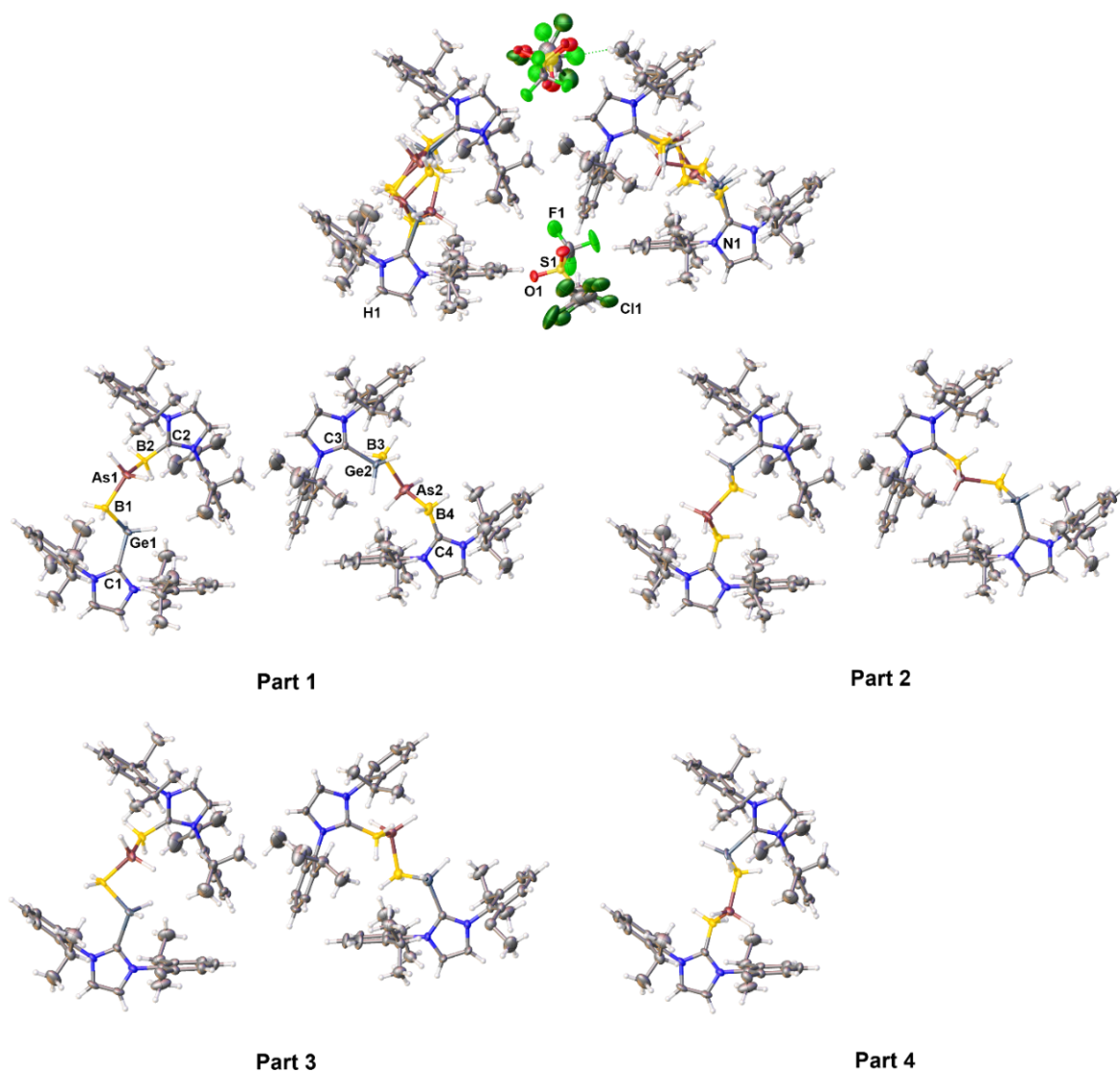


Figure S56: Molecular structure of **5b** in the solid state. Anisotropic displacement parameters are set to 50% probability level. Top: Combined disordered parts; middle left: part 1 of the cations (occupancy left molecule: 55%; occupancy right molecule: 55%) middle right: part 2 of the cations (occupancy left molecule: 20%; occupancy right molecule: 37%) bottom left: part 3 of the cations (occupancy left molecule: 18%; occupancy right molecule: 8%) bottom right: part 4 of the cations (occupancy left molecule: 7%). Selected bond lengths [Å] and angles [°] for part 1, molecule A: C1-Ge1 1.994(3), Ge1-B1 2.055(8), B1-As1 2.076(6), As1-B2 2.034(10), B2-C2 1.595(9); C1-Ge1-B1 112.1(2), Ge1-B1-As1 103.4(3), B1-As1-B2 119.0(4), As1-B2-C2 112.2(7). Part 1, molecule B: C3-Ge2 1.932(3), Ge2-B3 1.995(15), B3-As2 2.007(10), As2-B4 2.01(1), B4-C4 1.594(13); C3-Ge2-B3 113.3(3), Ge2-B3-As2 107.3(5), B3-As2-B4 114.5(6), As2-B4-C4 120.9(8).

4 Computational details

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 B3LYP¹⁴ with def2-TZVP all electron basis set.¹⁵ Gaussian 09 program package¹⁶ was used throughout. All structures correspond to minima on their respective potential energy surfaces as verified by computation of second derivatives. Basis sets were obtained from the EMSL basis set exchange database.¹⁷ Computed thermodynamic characteristics are summarized in Table S3.

Table S3. Reaction energies ΔE°_0 , standard reaction enthalpies ΔH°_{298} , Gibbs energies ΔG°_{298} (kJ mol⁻¹) and standard reaction entropies ΔS°_{298} (J mol⁻¹ K⁻¹) for the processes in the gas phase. B3LYP/def2-TZVP level of theory.

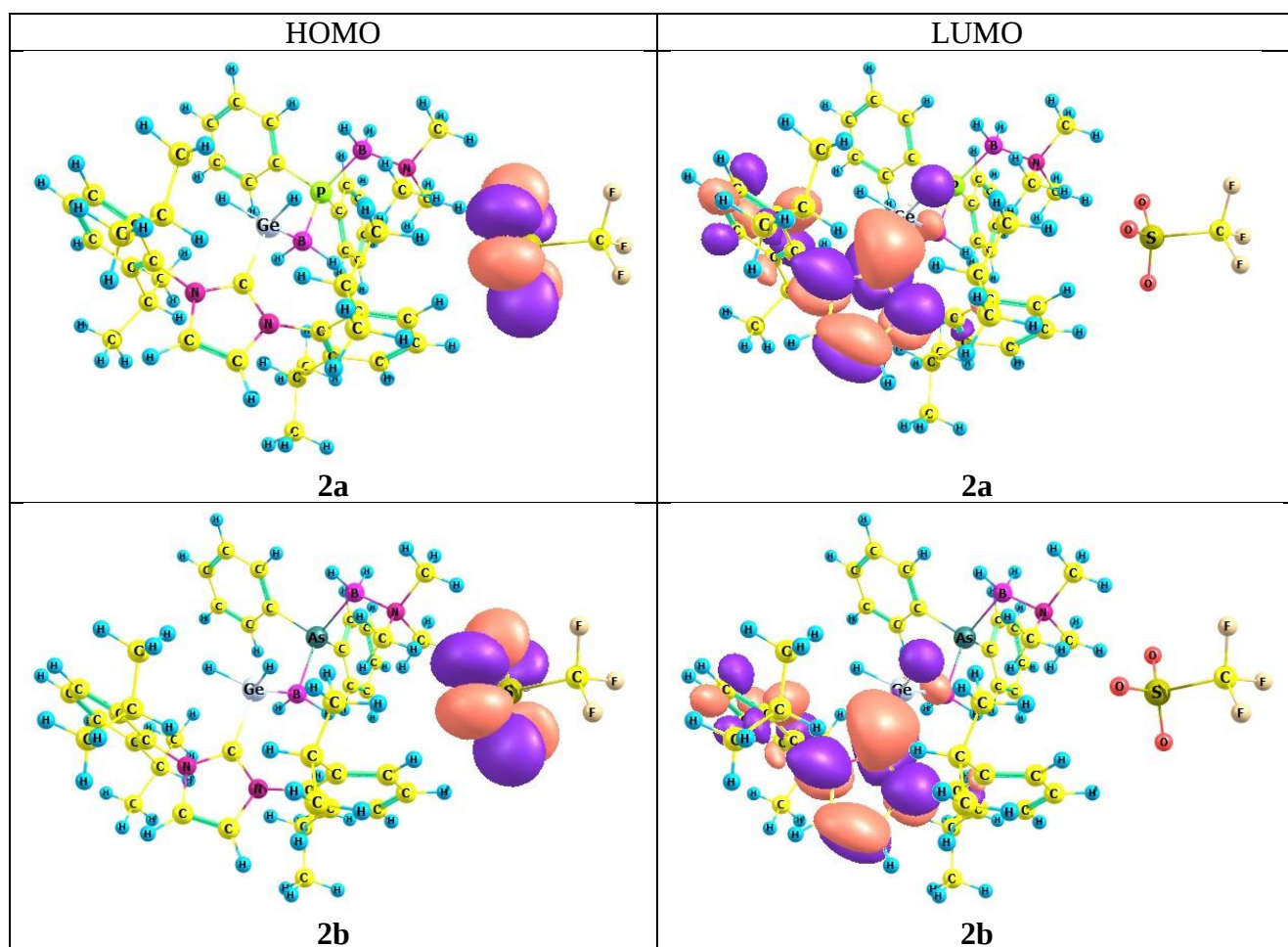
Process	ΔE°_0	ΔH°_{298}	ΔS°_{298}	ΔG°_{298}
IDipp·GeH ₂ BH ₂ OTf + PPh ₂ BH ₂ ·NMe ₃ = IDipp·GeH ₂ BH ₂ PPh ₂ BH ₂ ·NMe ₃ ⁺ ...OTf ⁻	-77.9	-69.0	-183.6	-14.3
IDipp·GeH ₂ BH ₂ OTf + PH ₂ BH ₂ ·NMe ₃ = IDipp·GeH ₂ BH ₂ PH ₂ BH ₂ ·NMe ₃ ⁺ ...OTf ⁻	-67.5	-58.1	-173.9	-6.2
IDipp·GeH ₂ BH ₂ OTf + PH ₂ BH ₂ ·IDipp = IDipp·GeH ₂ BH ₂ PH ₂ BH ₂ ·IDipp ⁺ ...OTf ⁻	-122.8	-113.8	-151.0	-68.7
IDipp·GeH ₂ BH ₂ OTf + AsPh ₂ BH ₂ ·NMe ₃ = IDipp·GeH ₂ BH ₂ AsPh ₂ BH ₂ ·NMe ₃ ⁺ ...OTf ⁻	-51.3	-43.8	-168.9	6.6
IDipp·GeH ₂ BH ₂ OTf + AsH ₂ BH ₂ ·NMe ₃ = IDipp·GeH ₂ BH ₂ AsH ₂ BH ₂ ·NMe ₃ ⁺ ...OTf ⁻	-39.9	-31.8	-168.5	18.4
IDipp·GeH ₂ BH ₂ OTf + AsH ₂ BH ₂ ·IDipp = IDipp·GeH ₂ BH ₂ AsH ₂ BH ₂ ·IDipp ⁺ ...OTf ⁻	-88.1	-80.0	-146.7	-36.3
IDipp·GeH ₂ BH ₂ PH ₂ BH ₂ ·NMe ₃ ⁺ ...OTf ⁻ + IDipp = IDipp·GeH ₂ BH ₂ PH ₂ BH ₂ ·IDipp ⁺ ...OTf ⁻ + NMe ₃	-79.4	-82.0	-33.7	-72.0
IDipp·GeH ₂ BH ₂ AsH ₂ BH ₂ ·NMe ₃ ⁺ ...OTf ⁻ + IDipp = IDipp·GeH ₂ BH ₂ AsH ₂ BH ₂ ·IDipp ⁺ ...OTf ⁻ + NMe ₃	-75.8	-78.2	-35.4	-67.6

Table S4. Total energies E°_0 , sum of electronic and thermal enthalpies H°_{298} (Hartree) and standard entropies S°_{298} (cal mol⁻¹K⁻¹). B3LYP/def2-TZVP level of theory.

Compound	E°_0	H°_{298}	S°_{298}
NMe ₃	-174.5440634	-174.417903	68.894
IDipp	-1160.453853	-1159.85478	201.948
IDipp·GeH ₂ BH ₂ OTf (1)	-4226.5937589	-4225.911610	264.687
PH ₂ BH ₂ ·IDipp	-1529.126212	-1528.480323	209.039
PH ₂ BH ₂ ·NMe ₃	-543.2072814	-543.033406	89.525
PPh ₂ BH ₂ ·NMe ₃	-1005.475369	-1005.126986	141.765
AsH ₂ BH ₂ ·IDipp	-3423.662289	-3423.018066	212.05

AsH ₂ BH ₂ ·NMe ₃	-2437.741976	-2437.569768	92.673
AsPh ₂ BH ₂ ·NMe ₃	-2900.007591	-2899.660075	145.212
IDipp·GeH ₂ BH ₂ PPh ₂ BH ₂ ·NMe ₃ ⁺ ...OTf (2a)	-5232.098816	-5231.064877	362.579
IDipp·GeH ₂ BH ₂ PH ₂ BH ₂ ·NMe ₃ ⁺ ...OTf (3a)	-4769.826734	-4768.967143	312.646
IDipp·GeH ₂ BH ₂ PH ₂ BH ₂ ·IDipp ⁺ ...OTf (5a)	-5755.766748	-5754.435266	437.634
IDipp·GeH ₂ BH ₂ AsPh ₂ BH ₂ ·NMe ₃ ⁺ ...OTf (2b)	-7126.620875	-7125.588353	369.521
IDipp·GeH ₂ BH ₂ AsH ₂ BH ₂ ·NMe ₃ ⁺ ...OTf (3b)	-6664.350945	-6663.493495	317.091
IDipp·GeH ₂ BH ₂ AsH ₂ BH ₂ ·IDipp ⁺ ...OTf (5b)	-7650.289599	-7648.960151	441.675

Figure S57. HOMO and LUMO of computationally studied ion pairs.



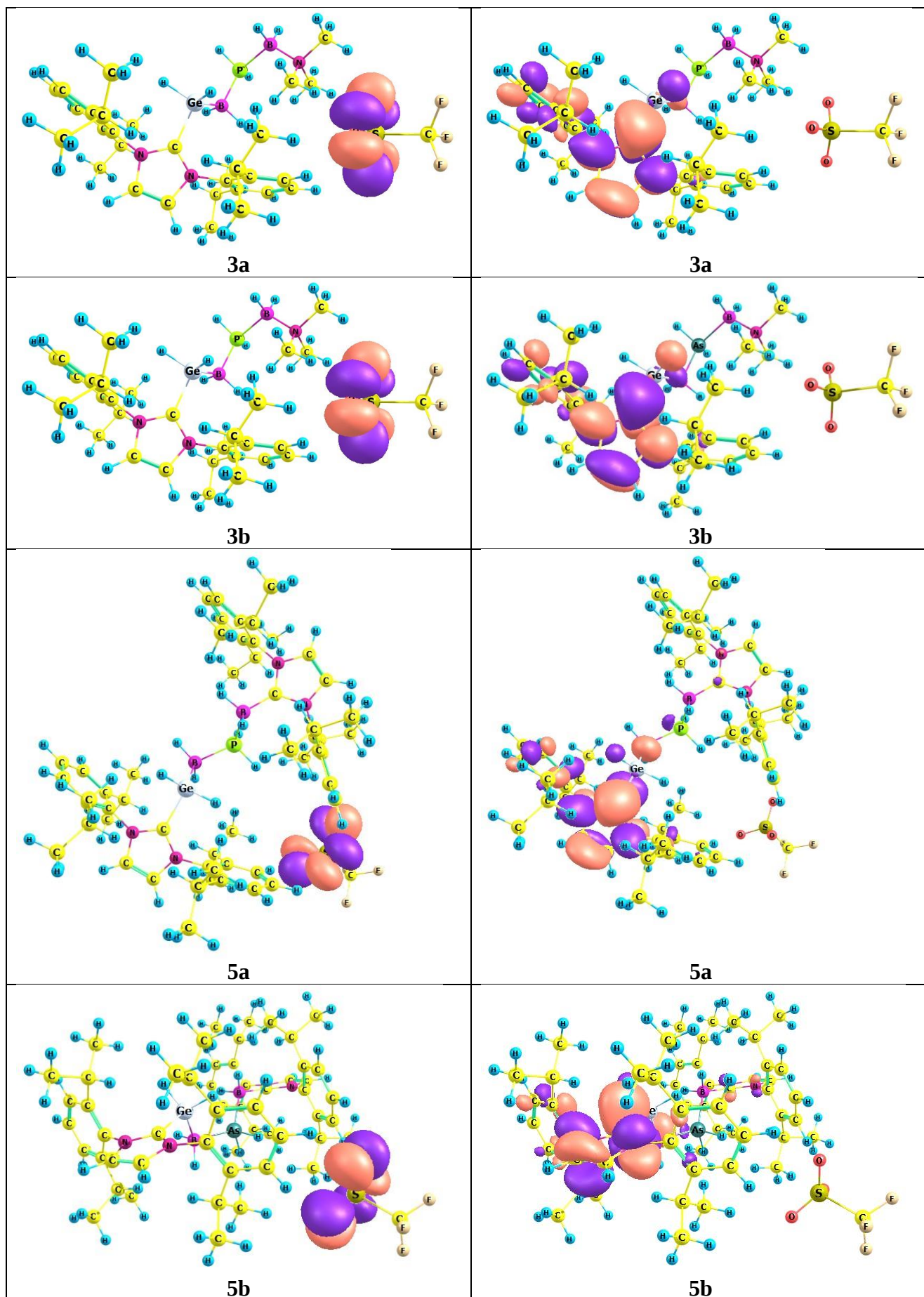


Table S5. Optimized geometries of theoretically studied compounds. xyz coordinates in angstroms. B3LYP/def2-TZVP level of theory.

NMe ₃				1	3.367911000	-1.795661000	2.100446000
7	0.000000000	0.000000000	0.364251000	1	4.301039000	-2.726052000	0.896102000
6	0.000000000	1.388115000	-0.059243000	1	1.999683000	-3.510320000	-0.792051000
6	-1.202143000	-0.694058000	-0.059243000	1	3.532998000	-2.831401000	-1.399328000
6	1.202143000	-0.694058000	-0.059243000	1	1.971265000	-2.080841000	-1.838616000
1	-2.082978000	-0.182263000	0.332167000	1	3.356559000	0.170758000	0.677365000
1	-1.199333000	-1.712780000	0.332167000	1	2.853824000	0.025670000	-1.014925000
1	-1.302051000	-0.751740000	-1.158793000	1	4.369760000	-0.738864000	-0.477085000
1	-0.883645000	1.895043000	0.332167000	6	0.600105000	4.205790000	0.288009000
1	0.000000000	1.503479000	-1.158793000	6	0.285705000	1.949816000	1.081858000
1	0.883645000	1.895043000	0.332167000	6	0.395196000	2.383942000	-1.273766000
1	2.082978000	-0.182263000	0.332167000	6	0.568246000	3.741990000	-1.020988000
1	1.302051000	-0.751740000	-1.158793000	6	0.456042000	3.304848000	1.339304000
1	-1.199333000	-1.712780000	0.332167000	1	0.176449000	1.260119000	1.908335000
IDipp				1	0.367458000	2.027238000	-2.296731000
6	0.674960000	-0.000061000	1.853488000	1	0.676013000	4.434976000	-1.846647000
6	-0.674915000	0.000151000	1.853504000	1	0.476103000	3.659518000	2.362981000
7	-1.062430000	0.000181000	0.517812000	1	0.734448000	5.261414000	0.489850000
6	-0.000003000	-0.000080000	-0.342280000	6	-4.390347000	-1.339521000	0.275324000
7	1.062444000	-0.000158000	0.517787000	6	-2.139066000	-2.014836000	-0.264412000
1	1.379343000	-0.000152000	2.666568000	6	-2.633687000	0.305136000	0.078384000
1	-1.379279000	0.000280000	2.666601000	6	-3.965457000	-0.018218000	0.319932000
6	2.435809000	-0.000373000	0.090009000	6	-3.466108000	-2.337548000	-0.019836000
6	3.085267000	1.227701000	-0.111259000	1	-1.438783000	-2.807387000	-0.497209000
6	3.084594000	-1.228644000	-0.112192000	1	-2.329837000	1.342304000	0.120224000
6	4.416080000	1.199376000	-0.527433000	1	-4.671784000	0.771775000	0.546213000
6	4.415415000	-1.200728000	-0.528378000	1	-3.780800000	-3.373598000	-0.061438000
6	5.077373000	-0.000779000	-0.734658000	1	-5.426502000	-1.590225000	0.464915000
1	4.940696000	2.131057000	-0.697180000	AsPh ₂ BH ₂ -NMe ₃			
1	4.939506000	-2.132569000	-0.698867000	33	0.037237000	-0.328397000	-0.771678000
6	-2.435805000	0.000376000	0.090067000	6	0.315038000	1.551027000	-0.203006000
6	-3.084599000	1.228638000	-0.112164000	5	1.021240000	-1.434643000	0.732190000
6	-4.415430000	1.200704000	-0.528315000	6	-1.822871000	-0.623770000	-0.180355000
6	-5.077391000	0.000746000	-0.734534000	1	0.480670000	-2.506245000	0.820529000
1	-4.939527000	2.132537000	-0.698825000	1	1.096847000	-0.846952000	1.778936000
6	-4.416091000	-1.199400000	-0.527282000	7	2.579832000	-1.768995000	0.300646000
1	-4.940708000	-2.131088000	-0.696980000	6	2.633971000	-2.608536000	-0.927000000
6	-3.085267000	-1.227707000	-0.111139000	6	3.204073000	-2.523359000	1.421659000
6	-2.379919000	2.563741000	0.074073000	6	3.354132000	-0.518522000	0.075801000
1	-1.393576000	2.364550000	0.491176000	1	2.625063000	-3.425085000	1.603380000
6	-3.116585000	3.476910000	1.064890000	1	3.185235000	-1.905473000	2.315369000
6	-2.165994000	3.265466000	-1.276204000	1	4.234208000	-2.784960000	1.169210000
1	-1.598665000	2.631072000	-1.957893000	1	2.087143000	-3.530237000	-0.743968000
1	-3.118903000	3.508866000	-1.751899000	1	3.671847000	-2.836137000	-1.178109000
1	-1.614358000	4.198245000	-1.137505000	1	2.161458000	-2.072105000	-1.746051000
1	-4.107294000	3.755953000	0.700388000	1	3.273381000	0.109166000	0.959617000
1	-2.551805000	4.398959000	1.219408000	1	2.937223000	0.014264000	-0.775061000
1	-3.243448000	2.991921000	2.034677000	1	4.401629000	-0.756924000	-0.119686000
6	-2.381271000	-2.563037000	0.076099000	6	0.778376000	4.238974000	0.466676000
1	-1.394748000	-2.364031000	0.492864000	6	0.283065000	1.972310000	1.129271000
6	-3.118247000	-3.474983000	1.067808000	6	0.580987000	2.501621000	-1.190832000
6	-2.167978000	-3.266026000	-1.273622000	6	0.814068000	3.835043000	-0.861964000
1	-3.121111000	-3.509351000	-1.748906000	6	0.508862000	3.303588000	1.461747000
1	-1.600472000	-2.632523000	-1.955991000	1	0.078283000	2.255352000	1.913914000
1	-1.616794000	-4.198969000	-1.134232000	1	0.601276000	2.196570000	-2.230895000
1	-3.244707000	-2.989116000	2.037209000	1	1.017884000	4.556140000	-1.644512000
1	-2.553925000	-4.397197000	1.223016000	1	0.475090000	3.612037000	2.500071000
1	-4.109161000	-3.753816000	0.703698000	1	0.955597000	5.275327000	0.726879000
6	2.381278000	2.563038000	0.075947000	6	-4.513818000	-1.131005000	0.454423000
1	1.394759000	2.364048000	0.492731000	6	-2.315846000	-1.931317000	-0.132493000
6	3.118270000	3.475011000	1.067620000	6	-2.705433000	0.424857000	0.085238000
6	2.167970000	3.265989000	-1.273791000	6	-4.037187000	0.173130000	0.401842000
1	3.121097000	3.509298000	-1.749094000	6	-3.645289000	-2.183364000	0.183950000
1	1.600454000	2.632467000	-1.956135000	1	-1.656506000	-2.765645000	-0.338451000
1	1.616789000	4.198937000	-1.134421000	1	-2.357193000	1.448813000	0.049417000
1	3.244740000	2.989172000	2.037034000	1	-4.702864000	1.003059000	0.607740000
1	2.553955000	4.397232000	1.222809000	1	-4.002944000	-3.205638000	0.220344000
1	4.109181000	3.753828000	0.703489000	1	-5.549945000	-1.326108000	0.701476000
6	2.379915000	-2.563739000	0.074108000	PH ₂ BH ₂ -NMe ₃			
1	1.393589000	-2.364532000	0.491243000	15	2.149785000	0.047509000	0.097514000
6	2.165939000	-3.265500000	-1.276141000	5	0.488216000	-0.794213000	-0.607586000
6	3.116612000	-3.476885000	1.064923000	1	2.997052000	-1.075262000	-0.052779000
1	4.107306000	-3.755945000	0.700393000	1	2.632277000	0.708111000	-1.061387000
1	3.243515000	-2.991870000	2.034692000	7	-0.850734000	-0.009493000	-0.007391000
1	2.551832000	-4.398925000	1.219489000	1	0.396795000	-1.918946000	-0.181678000
1	1.598586000	-2.631124000	-1.957827000	1	0.365848000	-0.726643000	-1.803985000
1	1.614307000	-4.198275000	-1.137397000	6	-0.915624000	-0.112414000	1.474654000
1	3.118831000	-3.508913000	-1.751864000	6	-2.055134000	-0.658301000	-0.587498000
1	-6.110357000	0.000889000	-1.060192000	6	-0.836092000	1.423325000	-0.400560000
1	6.110332000	-0.000936000	-1.060341000	1	-1.807021000	0.396796000	1.847084000
PPh ₂ BH ₂ -NMe ₃				1	-0.022935000	0.339454000	1.900027000
15	0.055497000	-0.324539000	-0.666833000	1	-0.947684000	-1.163741000	1.750170000
6	0.252058000	1.463699000	-0.230465000	1	-2.960739000	-0.179981000	-0.207108000
5	1.068851000	-1.347537000	0.700622000	1	-2.050098000	-1.711386000	-0.318043000
6	-1.691728000	-0.686893000	-0.213038000	1	-2.015089000	-0.572044000	-1.670121000
1	0.534056000	-2.413099000	0.865947000	1	-1.747944000	1.918433000	-0.059757000
1	1.255613000	-0.750838000	1.730309000	1	-0.761529000	1.488601000	-1.483538000
7	2.587612000	-1.717680000	0.144176000	1	0.029446000	1.905829000	0.048498000
6	2.523798000	-2.594925000	-1.055975000	AsH ₂ BH ₂ -NMe ₃			
6	3.300286000	-2.442216000	1.229564000	33	1.703144000	0.026768000	0.054701000
6	3.347281000	-0.483749000	-0.190754000	5	-0.108557000	-0.893213000	-0.533422000
1	2.730598000	-3.329842000	1.492660000	1	2.551734000	-1.202723000	-0.228147000

1	2.074287000	0.687246000	-1.271125000
7	-1.407581000	-0.011545000	-0.007955000
1	-0.198595000	-1.952371000	0.033917000
1	-0.242631000	-0.968681000	-1.725955000
6	-1.441235000	0.071477000	1.476782000
6	-2.639699000	-0.701558000	-0.475918000
6	-1.379358000	1.360772000	-0.578401000
1	-2.318017000	0.635865000	1.800851000
1	-0.535218000	0.559612000	1.826869000
1	-1.479356000	-0.936904000	1.881365000
1	-3.526043000	-0.160254000	-0.136851000
1	-2.646811000	-1.713036000	-0.078130000
1	-2.624961000	-0.749966000	-1.561428000
1	-2.280556000	1.907107000	-0.292239000
1	-1.316985000	1.288115000	-1.661489000
1	-0.502995000	1.885370000	-0.204748000

PH₂BH₂-IDipp

15	-1.350031000	-0.227991000	3.146333000
5	0.112378000	0.072902000	1.850412000
1	-2.417553000	0.558464000	2.638557000
1	-1.925684000	-1.443442000	2.683862000
1	0.573380000	1.167790000	2.100783000
6	-0.034177000	-0.004290000	0.247574000
1	0.967424000	-0.737342000	2.133130000
7	1.061465000	-0.092610000	-0.560900000
6	0.687296000	-0.177245000	-1.890955000
6	-0.658212000	-0.132799000	-1.921546000
7	-1.094673000	-0.014247000	-0.610160000
6	2.450816000	-0.033056000	-0.152510000
1	1.410648000	-0.252472000	-2.681884000
1	-1.345707000	-0.154004000	-2.745897000
6	-2.508050000	0.052408000	-0.283166000
5	5.138783000	0.092152000	0.483844000
6	3.148190000	-1.228368000	0.081938000
6	3.070381000	1.224570000	-0.070619000
6	4.426498000	1.256839000	0.252039000
6	4.502528000	-1.134910000	0.399273000
6	2.497049000	-2.598526000	-0.006414000
6	2.339537000	2.531154000	-0.338757000
1	4.931476000	2.211147000	0.323569000
1	5.065811000	-2.039548000	0.587234000
1	6.191246000	0.141150000	0.734114000
6	-5.207925000	0.163558000	0.359139000
6	-3.233866000	-1.148286000	-0.169613000
6	-3.128653000	1.313361000	-0.152647000
6	-4.484722000	1.328307000	0.178006000
6	-4.585553000	-1.054397000	0.171576000
6	-2.752524000	-2.575993000	-0.454220000
6	-2.490699000	2.695691000	-0.330557000
1	-4.977505000	2.284962000	0.298172000
1	-5.153891000	-1.968709000	0.290520000
1	-6.254658000	0.207075000	0.632375000
6	2.685993000	-3.413125000	1.281584000
6	3.001529000	-3.786950000	-1.231315000
1	1.427147000	-2.451027000	-0.129981000
1	2.320889000	-2.862756000	2.148618000
1	3.734806000	-3.664374000	1.452286000
1	2.130858000	-4.351257000	1.214599000
1	4.073452000	-3.576124000	-1.161218000
1	2.826196000	-2.829139000	-2.158422000
1	2.489277000	-4.340365000	-1.307266000
6	2.490136000	3.527838000	0.819428000
1	1.277117000	2.311306000	-0.427602000
6	2.792889000	3.158656000	-1.667337000
1	3.852489000	3.421714000	-1.638293000
1	2.227394000	4.070779000	-1.870160000
1	2.643821000	2.475812000	-2.506084000
1	3.523793000	3.859332000	0.936402000
1	2.164268000	3.085292000	1.760611000
1	1.881264000	4.414450000	0.630549000
6	-1.327723000	-2.975201000	-0.065226000
6	-3.033688000	-2.953160000	-1.921468000
1	-3.412211000	-3.200358000	0.154028000
6	-1.678049000	3.156724000	0.887293000
1	-3.352008000	3.366516000	-0.385177000
6	-1.726172000	2.924068000	-1.641618000
1	-1.063858000	-2.632375000	0.933466000
1	-0.591789000	-2.599970000	-0.774552000
1	-1.253547000	-4.064957000	-0.077413000
1	-2.396171000	-2.389700000	-2.605607000
1	-4.072445000	-2.760238000	-2.192997000
1	-2.831484000	-4.014704000	-2.081860000
1	-1.559989000	3.995268000	-1.775312000
1	-2.294090000	2.568470000	-2.504017000
1	-0.750890000	2.442143000	-1.655607000
1	-1.369915000	4.196268000	0.750110000
1	-0.785257000	2.555462000	1.044774000
1	-2.272749000	3.099181000	1.799586000

AsH₂BH₂-IDipp

33	-1.456016000	-0.379660000	2.927586000
5	0.132244000	0.051272000	1.624482000
1	-2.600161000	0.440468000	2.332679000
1	-2.000896000	-1.673303000	2.316077000
1	0.510046000	1.157103000	1.945981000
6	0.067989000	0.023589000	0.018965000
1	1.000661000	-0.730518000	1.933808000
7	1.206240000	-0.050742000	-0.730967000
6	0.906030000	-0.076445000	-2.081896000
6	-0.434903000	-0.009911000	-2.184846000
7	-0.942986000	0.062825000	-0.896585000

6	2.571800000	-0.022152000	-0.245959000
1	1.671415000	-0.131287000	-2.833975000
1	-1.075693000	0.010418000	-3.045964000
6	-2.372502000	0.127345000	-0.648580000
6	5.222784000	0.048972000	0.536799000
6	3.244823000	-1.233159000	-0.021293000
6	3.197227000	1.224523000	-0.082579000
6	4.534396000	1.229441000	0.312747000
6	4.580921000	-1.166899000	0.371214000
6	2.586207000	-2.591428000	-0.195270000
6	2.493666000	2.548453000	-0.338356000
1	5.043431000	2.174732000	0.447564000
1	5.125043000	-2.084274000	0.553953000
1	6.260760000	0.076781000	0.844265000
6	-5.103754000	0.230834000	-0.156870000
6	-3.109547000	-1.071874000	-0.629275000
6	-2.993556000	1.386164000	-0.501466000
6	-4.366114000	1.396923000	-0.248113000
6	-4.477813000	-0.982446000	-0.360992000
6	-2.622750000	-2.489814000	-0.952097000
6	-2.341685000	2.770773000	-0.586944000
1	-4.860474000	2.351237000	-0.116374000
1	-5.056450000	-1.896764000	-0.313312000
1	-6.163971000	0.270313000	0.058962000
6	2.690157000	-3.450652000	1.073362000
6	3.154414000	-3.336225000	-1.414198000
1	1.527076000	-2.427189000	-0.376829000
1	2.279218000	-2.925381000	1.935464000
1	3.724621000	-3.718869000	1.297499000
1	2.131299000	-4.379672000	0.941922000
1	4.218093000	-3.549572000	-1.287879000
1	3.040297000	-2.753458000	-2.330523000
1	2.637290000	-4.288153000	-1.553242000
6	2.588735000	3.497166000	0.865124000
1	1.435877000	2.344018000	-0.494001000
6	3.025167000	3.222442000	-1.614098000
1	4.083928000	3.472082000	-1.516769000
1	2.480035000	4.148115000	-1.811111000
1	2.916122000	2.574622000	-2.486105000
1	3.617233000	3.812349000	1.051879000
1	2.207343000	3.021568000	1.768565000
1	1.999059000	4.397131000	0.678608000
6	-1.219779000	-2.917875000	-0.517650000
6	-2.838853000	-2.800711000	-2.445832000
1	-3.312958000	-3.134425000	-0.401654000
6	-1.610936000	3.182473000	0.698416000
1	-3.195969000	3.447107000	-0.674236000
6	-1.490285000	3.043698000	-1.834231000
1	-1.002941000	-2.624700000	0.507754000
1	-0.449380000	-2.516251000	-1.174053000
1	-1.151915000	-4.006496000	-0.577695000
1	-2.166903000	-2.213392000	-3.074891000
1	-3.862654000	-2.587438000	-2.756067000
1	-2.636135000	-3.855937000	-2.643052000
1	-1.313306000	4.118338000	-1.916718000
1	-1.999150000	2.722629000	-2.745625000
1	-0.517132000	2.558437000	-1.799907000
1	-1.297702000	4.226913000	0.624102000
1	-0.728592000	2.574998000	0.887277000
1	-2.262975000	3.086315000	1.567266000

1

32	0.383125000	-0.303497000	-0.865870000
1	0.613011000	1.026251000	-1.620510000
1	-0.304536000	-1.241328000	-1.887035000
16	4.031879000	-0.234705000	-0.964603000
9	6.110626000	-1.674070000	-1.680756000
9	4.577327000	-2.823802000	-0.665242000
9	5.867243000	-1.500174000	0.469515000
8	3.167892000	-0.293934000	0.294043000
8	4.849261000	0.938134000	-0.928470000
8	3.288082000	-0.571877000	-2.146871000
7	-2.321823000	-0.524380000	0.571202000
7	-1.544502000	1.481590000	0.708059000
6	-1.288736000	0.260183000	0.181309000
6	-3.221390000	0.205275000	1.328073000
1	-4.115698000	-0.235578000	1.727948000
6	-2.733828000	1.461555000	1.414116000
1	-3.117905000	2.337620000	1.903134000
6	5.216426000	-1.651895000	-0.687456000
6	-2.524274000	-1.918769000	0.231315000
6	-3.212013000	-2.221803000	-0.954954000
6	-3.431952000	-3.568592000	-1.238542000
1	-3.954198000	-3.842298000	-2.145540000
6	-2.991140000	-4.563285000	-0.380938000
1	-3.169191000	-5.603300000	-0.623927000
6	-2.321607000	-4.232221000	0.785587000
1	-1.983110000	-5.019984000	1.444258000
6	-2.071712000	-2.902695000	1.125100000
6	-3.744975000	-1.156504000	-1.902715000
1	-3.326671000	-0.195172000	-1.603803000
6	-5.275288000	-1.043886000	-1.795331000
1	-5.644931000	-0.247512000	-2.444717000
1	-5.759382000	-1.974607000	-2.098228000
1	-5.592716000	-0.822050000	-0.774694000
6	-3.315490000	-1.395402000	-3.357349000
1	-3.643549000	-0.563547000	-3.983864000
1	-2.231932000	-1.477701000	-3.441980000
1	-3.758337000	-2.305389000	-3.766078000
6	-1.379377000	-2.572262000	2.440158000
1	-1.021188000	-1.543692000	2.385794000
6	-2.373096000	-2.660027000	3.612366000

1	-1.881508000	-2.382672000	4.547028000	6	6.219015000	-1.042107000	2.610762000
1	-3.229531000	-1.997688000	3.473572000	1	6.035249000	-0.694281000	3.629234000
1	-2.755110000	-3.677300000	3.722620000	1	7.224679000	-0.725614000	2.326905000
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1	-0.430697000	-4.495167000	2.881692000	1	2.755450000	-3.367867000	-1.744556000
1	0.555468000	-3.415357000	1.881409000	6	4.232488000	-4.696581000	-2.517868000
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1	-0.476869000	5.349605000	-1.515363000	6	3.171584000	-2.744812000	-3.733838000
6	0.697284000	5.005939000	0.235185000	1	2.401903000	-3.398044000	-4.148789000
1	1.273009000	5.914701000	0.113307000	1	3.989767000	-2.701746000	-4.455062000
6	0.954234000	4.165229000	1.305647000	1	2.750824000	-1.743356000	-3.639803000
1	1.731003000	4.427207000	2.010346000	6	-0.089757000	-2.258550000	1.561960000
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6	-3.315523000	4.172074000	-1.419190000	6	-2.716809000	-1.791160000	2.237054000
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1	0.517530000	-2.104445000	5.162995000
6	-0.417257000	-2.483924000	-0.960710000
1	0.624695000	-2.279071000	-1.215957000
6	-0.581907000	-4.013928000	-0.907635000
1	-0.320484000	-4.459019000	-1.870172000
1	-1.614777000	-4.283513000	-0.681164000
1	0.054514000	-4.463045000	-0.141972000
6	-1.283905000	-1.888650000	-2.078359000
1	-1.026313000	-2.354003000	-3.032388000
1	-1.18932000	-0.815641000	-2.175027000
1	-2.348488000	-2.044338000	-1.905454000
5	-1.624361000	4.129020000	-1.076445000
1	-0.139050000	1.771526000	1.481956000
1	1.603361000	2.748637000	1.657375000
5	0.722549000	2.389244000	0.919363000
1	-1.147485000	3.880386000	-2.153033000
1	-2.010584000	5.264841000	-0.987463000
16	-5.607681000	-0.380550000	-0.034266000
9	-7.323977000	-2.317651000	-0.647865000
9	-8.261359000	-0.517525000	0.118946000
9	-7.490325000	-0.559420000	-1.908411000
8	-5.531237000	-0.904535000	1.315538000
8	-4.664281000	-0.963276000	-0.981456000
8	-5.721211000	1.072142000	-0.132209000
6	-7.262781000	-0.976229000	-0.650843000
1	0.825058000	4.847309000	-0.366360000
1	-0.441498000	4.773918000	1.351454000

3b			
33	-0.154467000	3.911405000	0.110238000
32	1.596472000	1.028181000	-0.554964000
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7	1.708650000	-1.684471000	0.843290000
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1	4.673850000	-2.988268000	0.508280000
6	0.327109000	-1.638798000	1.295251000
6	0.076007000	-1.225824000	2.614194000
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6	-0.683806000	-2.050297000	0.411404000
6	1.183764000	-0.882608000	3.603034000
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6	0.910272000	0.399315000	4.401502000
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1	0.050191000	0.287265000	5.063618000
1	0.726065000	1.245703000	3.741714000

6	1.439391000	-2.061135000	4.559837000
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1	1.689548000	-2.977627000	4.022638000
1	0.553782000	-2.266966000	5.164267000
6	-0.400255000	-2.644576000	-0.962466000
1	0.641306000	-2.441620000	-1.220788000
6	-1.269616000	-2.041226000	-2.073813000
1	-1.104108000	-0.967573000	-2.163515000
1	-2.333747000	-2.197868000	-1.898925000
1	-1.014843000	-2.500125000	-3.031726000
6	-0.569432000	-4.174220000	-0.915920000
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1	-1.602088000	-4.441775000	-0.686118000
6	4.715889000	-0.524028000	-0.702408000
6	5.569258000	0.297714000	0.049026000
6	6.637971000	0.889031000	-0.623840000
1	7.317080000	1.532038000	-0.080041000
6	6.846373000	0.667791000	-1.975619000
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6	5.987667000	-0.153900000	-2.688145000
1	6.162539000	-0.317139000	-3.743385000
6	4.900861000	-0.771795000	-2.071140000
6	5.385979000	0.548593000	1.539211000
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6	5.269994000	2.045717000	1.862531000
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1	4.454679000	2.511933000	1.308896000
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1	7.484000000	0.335517000	2.110308000
1	6.579924000	-1.177336000	2.161910000
6	3.987250000	-1.678034000	-2.883458000
1	3.146348000	-1.969567000	-2.253577000
6	3.399486000	-0.958594000	-4.106766000
1	2.688236000	-1.610379000	-4.617277000
1	4.174552000	-0.689790000	-4.826805000
1	2.876287000	-0.046522000	-3.818223000
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5a			
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5	-2.557990000	-1.295162000	0.179541000
1	-2.764217000	-2.413532000	-0.208227000
1	-1.979616000	-1.306019000	1.239090000
7	-4.174783000	0.736714000	0.809495000
7	-5.172016000	-1.029793000	0.075695000
7	4.257041000	-2.661060000	-0.458845000
7	4.252767000	-0.603041000	0.192711000
6	-3.942203000	-0.506972000	0.321317000
6	-3.176444000	1.715716000	1.199656000
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1	-5.919884000	1.916214000	1.237032000
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6	3.453025000	-1.676334000	0.009523000
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6	3.520993000	-3.14681000	-2.115834000
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1	-1.189097000	2.541910000	3.796902000
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1	6.354570000	-2.831226000	-0.911157000
6	5.552012000	-0.913537000	-0.154893000
1	6.343396000	-0.190247000	-0.084317000
6	-1.299231000	3.592269000	1.939871000
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6	3.854736000	0.705485000	0.685960000
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1	3.467503000	2.401682000	3.574632000
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1	-7.574653000	-2.796164000	2.367384000
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1	2.392592000	-2.545067000	-4.892361000
1	1.422563000	-3.345614000	-3.657292000
1	6.427009000	0.238192000	2.842170000
1	3.204459000	0.583471000	4.841617000
6	5.683945000	0.169345000	3.638851000
1	6.001307000	-0.613069000	4.332235000
1	5.690130000	1.118970000	4.177197000
6	3.270767000	-0.311405000	4.220852000
1	3.573633000	-1.136808000	4.869066000
1	2.273788000	-0.527969000	3.836110000

6	4.885978000	-3.373093000	-4.009497000	1	-4.970405000	1.506299000	4.101187000
1	5.753182000	-3.245815000	-3.359757000	6	3.638192000	1.651335000	-1.745039000
1	4.927905000	-2.600184000	-4.779360000	1	3.839339000	0.594493000	-1.934076000
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15	-1.248245000	-0.571810000	-1.075823000	6	-5.894817000	-4.843796000	0.011043000
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16	0.885698000	5.990916000	-0.753252000	6	-2.754090000	3.069076000	-2.180832000
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9	0.400285000	8.533021000	-0.117080000	6	3.112043000	3.352602000	1.616600000
6	1.261251000	7.814677000	-0.858577000	1	2.751307000	4.313711000	1.959209000
				6	-6.840815000	-1.168633000	-3.350863000
5b				1	-6.738067000	-0.318184000	-4.027885000
32	1.658237000	-1.708041000	0.377589000	1	-7.547774000	-0.891302000	-2.566977000
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5	-2.576249000	-1.398142000	0.287362000	6	4.428526000	0.095712000	3.097695000
1	-2.737104000	-2.535503000	-0.057051000	1	4.546116000	-0.860344000	2.584730000
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7	-4.253376000	0.598811000	0.852641000	1	6.206016000	-5.960079000	1.897042000
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1	3.970566000	-6.869108000	0.729628000	8	1.694247000	5.429376000	-1.606327000
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1	-4.397051000	0.334549000	5.294121000				

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