

Supporting Information

B–B Bond Nucleophilicity in a Tetraaryl μ -Hydridodiborane(4) Anion

*Timo Trageser, Michael Bolte, Hans-Wolfram Lerner, and Matthias Wagner**

anie_202000292_sm_miscellaneous_information.pdf

Table of contents

1.	Experimental details and characterization data	S1
2.	Plots of NMR spectra	S10
3.	X-ray crystal structure determinations	S24
4.	Computational details	S30
5.	References	S40

1. Experimental details and characterization data

General considerations. All reactions and manipulations were carried out in an argon-filled glovebox or by applying standard Schlenk techniques under an argon atmosphere. Pentane and hexane were dried over Na, THF and benzene were dried over Na/benzophenone, [D₈]THF was dried over Na-K alloy. Prior to use, the solvents were distilled from the respective drying agent, degassed by applying three freeze-pump-thaw cycles, and stored over activated molecular sieves (3 Å). Compounds **2**H₂, **2**^HH₂, M[**2**H] (M⁺ = Li⁺, K⁺), and Li₂[**2**] were synthesized according to literature procedures.^[S1-S55] *Note:* The compounds M[**2**H] crystallize from THF as solvates [Li(thf)₃][**2**H] and [K(thf)₂][**2**H]; according to ¹H NMR spectroscopy, the amounts of coordinated solvent molecules remain unchanged even after drying under a dynamic vacuum. Prior to use, all liquid reactants were degassed by applying three freeze-pump-thaw cycles. NMR: Bruker Avance 300 and Avance III 500 HD; NMR samples were investigated in flame-sealed NMR tubes. Chemical shifts are referenced to (residual) solvent signals (¹H; ¹H{¹¹B}/¹³C{¹H}); [D₈]THF: δ = 3.58/67.2 ppm), external BF₃·Et₂O (¹¹B; ¹¹B{¹H}) or Me₄Si (²⁹Si{¹H}). Abbreviations: s = singlet, d = doublet, dd = doublet of doublets, m = multiplet, br = broad.

Reaction of [Li(thf)₃][2H] with 1 equiv of 1. An NMR tube was charged at room temperature with [Li(thf)₃][2H] (9.0 mg, 11.6 μmol), **1** (3.2 mg, 11.6 μmol), and [D₈]THF (0.6 mL). An ¹H NMR spectrum recorded after 30 min revealed that Li[2H] had vanished and one new compound, Li[3], had quantitatively formed. Li[3] gives rise to two sets of resonances with an integral ratio of 1:2. A dilute [D₈]THF solution of Li[3] remains stable for at least 7 d under inert conditions. However, if the solvent is removed *in vacuo* and the solid residue re-dissolved in [D₈]THF, a partial rearrangement of Li[3] to furnish the known C₁-symmetric B₃ cluster Li[3a]^[55] was observed by NMR spectroscopy.

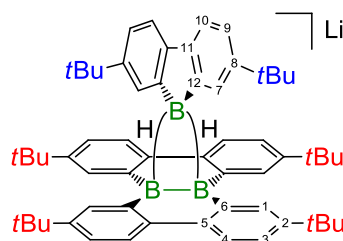


Figure S1. NMR numbering scheme for Li[3].

NMR shifts of compound Li[3]

¹H NMR (300.0 MHz, [D₈]THF): δ = 7.84 (d, ⁴J(H,H) = 2.4 Hz, 4H; H-1), 7.75 (d, ³J(H,H) = 8.3 Hz, 4H; H-4), 7.22 (d, ³J(H,H) = 7.8 Hz, 2H; H-10), 7.02 (dd, ³J(H,H) = 8.3 Hz, ⁴J(H,H) = 2.4 Hz, 4H; H-3), 6.85 (dd, ³J(H,H) = 7.8 Hz, ⁴J(H,H) = 2.0 Hz, 2H; H-9), 6.13 (d, ⁴J(H,H) = 2.0 Hz, 2H; H-7), 3.28 (br, 2H[†]; BH), 1.21 (s, 36H; CH₃), 0.95 (s, 18H; CH₃). [†] The relative integral value of 2H was further confirmed by means of an ¹H{¹¹B} NMR experiment.

¹¹B NMR (96.3 MHz, [D₈]THF): δ = 4.8 (br, *h*_{1/2} ≈ 905 Hz), -17.6 (br, *h*_{1/2} ≈ 190 Hz).

¹³C{¹H} NMR (75.4 MHz, [D₈]THF): δ = 151.2* (br, C-12), 146.7 (C-8), 146.6 (C-11), 145.9* (br, C-6), 145.7 (C-2), 140.8 (C-5), 137.1 (C-1), 130.7 (C-7), 123.3 (C-4), 122.7 (C-9), 122.0 (C-3), 117.0 (C-10), 34.8 (CCH₃), 34.6 (CCH₃), 32.2 (CH₃), 32.0 (CH₃).

* These resonances were detected through cross-peaks in the ¹H-¹³C-HMBC NMR experiment.

Reaction of $[K(thf)_2][2H]$ with 1 equiv of **1.** An NMR tube was charged at room temperature with $[K(thf)_2][2H]$ (11 mg, 14.2 μ mol), **1** (3.9 mg, 14.2 μ mol), and $[D_8]THF$ (0.6 mL). An 1H NMR spectrum recorded after 30 min revealed that $K[2H]$ had vanished and one new compound, $K[3]$, had quantitatively formed. $K[3]$ gives rise to two sets of resonances with an integral ratio of 1:2. A dilute $[D_8]THF$ solution of $K[3]$ remains stable for at least 5 d under inert conditions. However, if the solvent is removed *in vacuo* and the solid residue re-dissolved in $[D_8]THF$, a partial rearrangement of $K[3]$ to furnish the C_1 -symmetric B_3 cluster $K[3a]$ was observed by NMR spectroscopy. Colorless single crystals of $[K(thf)_{2.5}][3]$ suitable for single-crystal X-ray diffraction analysis were grown through gas-phase diffusion of hexane into a concentrated THF solution of $K[3]$ with subsequent slow evaporation of the solvents at room temperature. The mother liquor was removed via syringe and the solid residue washed with hexane (3 x 0.5 mL). Yield of $[K(thf)_{2.5}][3]$: 24 mg (23 μ mol, 70%).

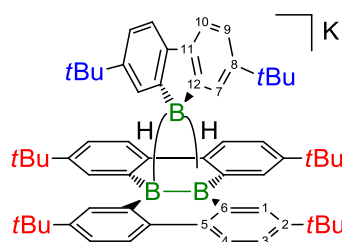


Figure S2. NMR numbering scheme for $K[3]$.

NMR shifts of compound $K[3]$

1H NMR (300.0 MHz, $[D_8]THF$): δ = 7.85 (d, $^4J(H,H)$ = 2.3 Hz, 4H; H-1), 7.75 (d, $^3J(H,H)$ = 8.3 Hz, 4H; H-4), 7.22 (d, $^3J(H,H)$ = 7.9 Hz, 2H; H-10), 7.04 (dd, $^3J(H,H)$ = 8.3 Hz, $^4J(H,H)$ = 2.3 Hz, 4H; H-3), 6.86 (dd, $^3J(H,H)$ = 7.9 Hz, $^4J(H,H)$ = 2.0 Hz, 2H; H-9), 6.12 (d, $^4J(H,H)$ = 2.0 Hz, 2H; H-7), 3.32 (br, 2H[†]; BH), 1.20 (s, 36H; CH_3), 0.95 (s, 18H; CH_3). [†] The relative integral value of 2H was further confirmed by means of an $^1H\{^{11}B\}$ NMR experiment.

^{11}B NMR (96.3 MHz, $[D_8]THF$): δ = 4.8 (br, $h_{1/2} \approx 970$ Hz), -17.6 (br, $h_{1/2} \approx 170$ Hz).

$^{13}C\{^1H\}$ NMR (75.4 MHz, $[D_8]THF$): δ = 151.0* (br, C-12), 146.7 (C-8), 146.6 (C-11), 146.1* (br, C-6), 146.1 (C-2), 140.6 (C-5), 137.2 (C-1), 130.7 (C-7), 123.4 (C-4), 122.7 (C-9), 122.2 (C-3), 117.1 (C-10), 34.8 (CCH_3), 34.6 (CCH_3), 32.2 (CH_3), 32.0 (CH_3).

* These resonances were detected through cross-peaks in the 1H - ^{13}C -HMBC NMR experiment.

The chemical shift values of the minor and major set of signals in the $^{13}C\{^1H\}$ NMR spectrum of $K[3]$ coincide within ± 2 ppm with those of **1**·THF and $K[2H]$,^[S4] respectively (the only exception is the signal of the C–H atom *ortho* to the boron atom of the $[2H]^-$ subunit in $[3]^-$, which appears 9.4 ppm downfield of the corresponding resonance in $K[3]$).

Reaction of [Li(thf)₃][2H] with exc. H₃C-I. In an NMR tube, [Li(thf)₃][2H] (10 mg, 12.9 μmol) was dissolved in [D₈]THF (0.6 mL) and excess neat H₃C-I (2.4 μl, 5.5 mg, 38.7 μmol) was added at room temperature. An ¹H NMR spectrum recorded after 30 min revealed that Li[2H] had vanished and two new compounds, Li[3] and **4**, had selectively formed in a stoichiometric ratio of 1:1. After 2 d, also Li[3] had completely been consumed and the reaction mixture contained equimolar amounts of **1**·THF and **4**.

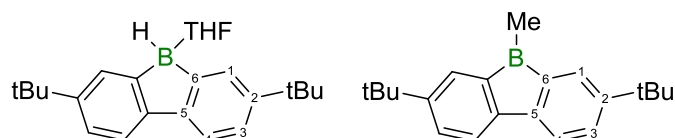


Figure S3. NMR numbering schemes for **1**·THF (left) and **4** (right).

NMR shifts of compound 1·THF

¹H{¹¹B} NMR (500.2 MHz, [D₈]THF): δ = 7.55 (d, ⁴J(H,H) = 2.0 Hz, 2H; H-1), 7.39* (d, ³J(H,H) = 7.9 Hz, 2H; H-4), 7.16* (dd, ³J(H,H) = 7.9 Hz, ⁴J(H,H) = 2.0 Hz, 2H; H-3), 3.78 (br, 1H; BH), 1.33* (s, 18H; CCH₃).

¹¹B NMR (160.5 MHz, [D₈]THF): δ = 8.0 (br, *h*_{1/2} ≈ 320 Hz).

¹³C{¹H} NMR (125.8 MHz, [D₈]THF): δ = 150.8 (br, C-6), 148.3 (C-2), 148.0 (C-5), 128.9 (C-1), 124.4 (C-3), 118.6* (C-4), 34.9* (CCH₃), 31.9* (CH₃).

NMR shifts of compound 4

¹H{¹¹B} NMR (500.2 MHz, [D₈]THF): δ = 7.50 (dd, ⁴J(H,H) = 2.0 Hz, 2H; H-1), 7.38* (d, ³J(H,H) = 7.9 Hz, 2H; H-4), 7.16* (dd, ³J(H,H) = 7.9 Hz, ⁴J(H,H) = 2.0 Hz, 2H; H-3), 1.33* (s, 18H; CCH₃), 0.31 (s, 3H; BCH₃).

¹¹B NMR (160.5 MHz, [D₈]THF): δ = 13.9 (br, *h*_{1/2} ≈ 260 Hz).

¹³C{¹H} NMR (125.8 MHz, [D₈]THF): δ = 152.6 (br, C-6), 148.6 (C-2), 147.4 (C-5), 127.3 (C-1), 124.6 (C-3), 118.6* (C-4), 34.9* (CCH₃), 31.9* (CH₃), 3.2 (br, BCH₃).

*These resonances overlap either partially or completely with those of the other product.

All NMR resonances compiled for **1**·THF and **4** are in accordance with the literature.^[S4,S6]

Reaction of $[\text{Li}(\text{thf})_3][\mathbf{2H}]$ with 1 equiv of allyl bromide. In an NMR tube, $[\text{Li}(\text{thf})_3][\mathbf{2H}]$ (11 mg, 14.2 μmol) was dissolved in $[\text{D}_8]\text{THF}$ (0.6 mL) and neat allyl bromide (1.2 μl , 1.7 mg, 14.2 μmol) was added at room temperature. An ^1H NMR spectrum recorded after 30 min revealed that $\text{Li}[\mathbf{2H}]$ had vanished and three new compounds, $\text{Li}[\mathbf{3}]$ and $\mathbf{9}$ and $\mathbf{5}$, had selectively formed. After 3 d, also $\text{Li}[\mathbf{3}]$ and $\mathbf{9}$ had completely been consumed and the reaction solution contained only the known^[S6] 1,3-propylene-bridged bis(borafluorene) $\mathbf{5}$.

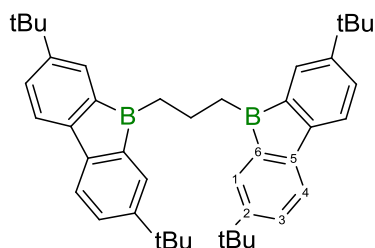


Figure S4. NMR numbering scheme for $\mathbf{5}$.

NMR shifts of compound 5

^1H NMR (500.2 MHz, $[\text{D}_8]\text{THF}$): δ = 7.48 (d, $^4J(\text{H,H})$ = 2.0 Hz, 2H; H-1), 7.37 (d, $^3J(\text{H,H})$ = 7.9 Hz, 2H; H-4), 7.13 (dd, $^3J(\text{H,H})$ = 7.9 Hz, $^4J(\text{H,H})$ = 2.0 Hz, 2H; H-3), 1.53-1.47 (m, 2H; CCH_2C), 1.30 (s, 18H; CH_3), 0.96-0.91 (m, 4H; BCH_2).

^{11}B NMR (160.5 MHz, $[\text{D}_8]\text{THF}$): δ = 14.8 (br, $h_{1/2} \approx 1115$ Hz).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, $[\text{D}_8]\text{THF}$): δ = 152.7 (br, C-6), 148.3 (C-2), 147.6 (C-5), 128.1 (C-1), 124.3 (C-3), 118.4 (C-4), 34.9 (CCH_3), 32.0 (CH_3), 25.9 (br, BCH_2), 23.0 (CCH_2C).

All NMR resonances compiled for $\mathbf{5}$ are in accordance with the literature.^[S6]

Synthesis of an authentic sample of 9 through the reaction of [Li(thf)₃]₂[2] with exc. allyl iodide. In an argon-filled glovebox, a dark red solution of [Li(thf)₃]₂[2] (15.0 mg, 15.1 μmol) in [D₈]THF (0.3 mL) was added at room temperature with stirring to a solution of allyl iodide (5.0 μl, 9.2 mg, 55 μmol) in [D₈]THF (0.2 mL; screw-capped vial). The resulting yellow solution was stirred for 1 h and the completeness of the conversion confirmed by ¹H NMR spectroscopy (selectivity for **9** ≈ 82%). Excess allyl iodide was removed *in vacuo* to afford a yellow solid.

Note: The synthesis of **9** requires 2 equiv of allyl iodide for a quantitative conversion and can indeed be carried out using this stoichiometry. However, when working on a small scale we found it advantageous to use excess allyl iodide in order to avoid impurities originating from unwanted C–H activation reactions if accidentally less than the required amount is added.

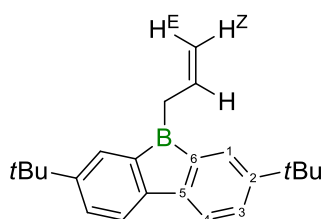


Figure S5. NMR numbering scheme for **9**.

NMR shifts of compound **9**

¹H NMR (500.2 MHz, [D₈]THF): δ = 7.56 (d, ⁴J(H,H) = 2.0 Hz, 2H; H-1), 7.39 (d, ³J(H,H) = 7.9 Hz, 2H; H-4), 7.17 (dd, ³J(H,H) = 7.9 Hz, ⁴J(H,H) = 2.0 Hz, 2H; H-3), 6.19-6.10 (m, 1H; CH), 4.81 (d, ³J(H,H) = 17.3 Hz, 1H; H^E), 4.70 (d, ³J(H,H) = 10.5 Hz, 1H; H^Z), 1.80 (d, ³J(H,H) = 7.9 Hz, 2H; CH₂), 1.33 (s, 18H; CH₃).

¹¹B NMR (160.5 MHz, [D₈]THF): δ = 11.9 (br, *h*_{1/2} ≈ 275 Hz).

¹³C{¹H} NMR (125.8 MHz, [D₈]THF): δ = 151.6 (br, C-6), 148.5 (C-2), 147.4 (C-5), 142.0 (CH=CH₂), 128.0 (C-1), 124.5 (C-3), 118.6 (C-4), 110.9 (CH=CH₂), 34.9 (CCH₃), 31.9 (CH₃), 29.0 (br, BCH₂).

Reaction of $[K(\text{thf})_2][\mathbf{2H}]$ with exc. Me_3SiCl . In an NMR tube, $[K(\text{thf})_2][\mathbf{2H}]$ (15 mg, 20.4 μmol) was dissolved in $[\text{D}_8]\text{THF}$ (0.6 mL) and excess neat Me_3SiCl (9.1 μl , 7.8 mg, 71.5 μmol) was added at room temperature. An ^1H NMR spectrum recorded after 30 min revealed that $K[\mathbf{2H}]$ had vanished and two new compounds, $K[\mathbf{3}]$ and $\mathbf{6}$, had selectively formed in a stoichiometric ratio of 1:1. After 2 d, also $K[\mathbf{3}]$ had completely been consumed and the reaction mixture contained equimolar amounts of $\mathbf{1}\cdot\text{THF}$ and $\mathbf{6}$. KCl formed as byproduct partially precipitates from the THF solution, which constitutes one driving force for the reaction.

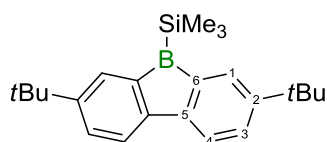


Figure S6. NMR numbering scheme for $\mathbf{6}$.

NMR shifts of compound $\mathbf{6}$

^1H NMR (500.2 MHz, $[\text{D}_8]\text{THF}$): δ = 7.52 (dd, $^4J(\text{H,H}) = 2.0$ Hz, $^5J(\text{H,H}) = 0.7$ Hz, 2H; H-1), 7.38* (dd, $^3J(\text{H,H}) = 7.8$ Hz, $^5J(\text{H,H}) = 0.7$ Hz, 2H; H-4), 7.18-7.15* (m, 2H; H-3), 1.33* (s, 18H; CCH_3), 0.01 (s, 9H; SiCH_3).

^{11}B NMR (160.5 MHz, $[\text{D}_8]\text{THF}$): δ = 12.6 (br, $h_{1/2} \approx 530$ Hz).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, $[\text{D}_8]\text{THF}$): δ = 152.0 (br, C-6), 148.5 (C-2), 147.7 (C-5), 127.7 (C-1), 124.5* (C-3), 118.6* (C-4), 34.9* (CCH_3), 31.9* (CCH_3), -0.5 (SiCH_3).

$^{29}\text{Si}\{^1\text{H}\}$ NMR (99.4 MHz, $[\text{D}_8]\text{THF}$): δ = 14.4 (detected through a cross-peak in the ^1H - ^{29}Si -HMBC NMR experiment).

*These resonances overlap either partially or completely with those of $\mathbf{1}\cdot\text{THF}$.

Reaction of $[K(thf)_2][2H]$ with exc. 2,3-dimethylbutadiene. In an NMR tube, $[K(thf)_2][2H]$ (12 mg, 16.3 μ mol) was dissolved in $[D_8]THF$ (0.6 mL) and excess neat 2,3-dimethylbutadiene (3.7 μ l, 2.7 mg, 32.7 μ mol) was added at room temperature. An 1H NMR spectrum recorded after 30 min revealed that $K[2H]$ had vanished and three new compounds, $K[7]$, $K[3]$ and **8**, had selectively formed. After 2 d, also $K[3]$ had completely been consumed and the reaction mixture contained $K[7]$ and **8** in a stoichiometric ratio of 2:1.

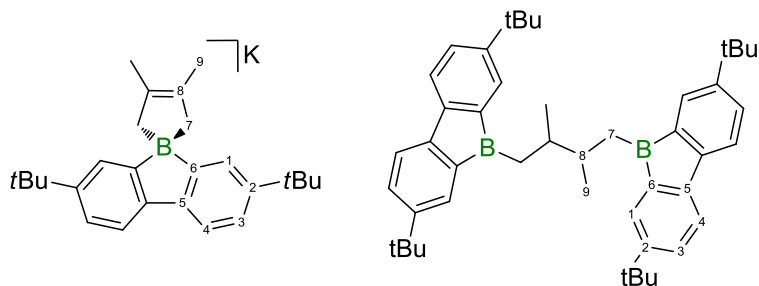


Figure S7. NMR numbering schemes for $K[7]$ (left) and **8** (right).

NMR shifts of compound $K[7]$

1H NMR (500.2 MHz, $[D_8]THF$): δ = 7.60 (d, $^4J(H,H)$ = 2.0 Hz, 2H; H-1), 7.40 (d, $^3J(H,H)$ = 7.9 Hz, 2H; H-4), 7.00 (dd, $^3J(H,H)$ = 7.9 Hz, $^4J(H,H)$ = 2.0 Hz, 2H; H-3), 1.71 (s, 6H; H-9), 1.31 (s, 18H; CH_3), 1.27-1.26 (m, 4H; H-7).

^{11}B NMR (160.5 MHz, $[D_8]THF$): δ = -10.7 (s).

$^{13}C\{^1H\}$ NMR (125.8 MHz, $[D_8]THF$): δ = 173.8* (br, C-6), 147.3 (C-2), 145.2 (C-5), 134.4 (C-8), 127.1 (C-1), 120.6 (C-3), 117.5 (C-4), 39.0* (br, C-7), 35.0 (CCH_3), 32.3 (CH_3), 18.5 (C-9).

* These signals are split into poorly resolved multiplets.

*NMR shifts of the major diastereomer of compound **8***

1H NMR (500.2 MHz, $[D_8]THF$): δ = 7.54 (d, $^4J(H,H)$ = 2.0 Hz, 4H; H-1), 7.36 (d, $^3J(H,H)$ = 7.9 Hz, 4H; H-4), 7.26 (dd, $^3J(H,H)$ = 7.9 Hz, $^4J(H,H)$ = 2.0 Hz, 4H; H-3), 1.42-1.39 (m, 2H; H-8), 1.31 (s, 36H; CH_3), 1.27-1.23[#] (m, 2H; H-7), 0.90-0.85[#] (m, 2H; H-7), 0.55 (d, $^3J(H,H)$ = 6.5 Hz, 6H; H-9).

^{11}B NMR (160.5 MHz, $[D_8]THF$): δ = 22.1 (br, $h_{1/2} \approx 900$ Hz).

$^{13}C\{^1H\}$ NMR (125.8 MHz, $[D_8]THF$): δ = 151.5 (br, C-6), 148.5 (C-2), 148.1 (C-5), 128.7 (C-1), 124.9 (C-3), 118.5 (C-4), 38.9 (C-8), 34.9 (CCH_3), 31.9 (CH_3), 24.2 (br, C-7), 19.6 (C-9).

[#] These signals belong to diastereotopic protons; note that one of the two expected diastereomers is strongly dominant (approximately 10:1).

Note: An authentic sample of **8**, prepared from **1**·THF and 2,3-dimethylbutadiene in $[D_8]THF$, gave identical NMR shift values. The atom connectivity in **8** has also been confirmed by means of an X-ray crystal structure determination (see below).^[S7]

Synthesis of $[\text{Li}(\text{thf})_4][\mathbf{2}^{\text{H}}\text{H}]$. In an argon-filled glovebox, THF (4.0 mL) was added at room temperature to a glass vial, charged with a solid mixture of yellow $\mathbf{2}^{\text{H}}\text{H}_2$ (100 mg, 0.31 mmol) and colorless $(\text{Me}_3\text{Si})_3\text{Cl}\cdot 2\text{THF}$ (140 mg, 0.37 mmol). The resulting clear, dark-red solution was stirred for 1 h. The uncapped vial was placed into a larger glass vessel containing hexane (15 mL). The vessel was closed and stored for 3 d to allow for gas-phase diffusion of the solvents. It was next kept at $-30\text{ }^\circ\text{C}$ overnight, whereupon an orange precipitate formed. The mother liquor was removed via syringe and the solid residue washed with pentane (3 x 0.5 mL). Yield of $[\text{Li}(\text{thf})_4][\mathbf{2}^{\text{H}}\text{H}]$: 83 mg (0.13 mmol, 42%).

Orange single crystals of $[\text{Li}(\text{thf})_4][\mathbf{2}^{\text{H}}\text{H}]$ suitable for single-crystal X-ray diffraction analysis were grown through gas-phase diffusion of hexane into a concentrated THF solution of $\text{Li}[\mathbf{2}^{\text{H}}\text{H}]$ at room temperature.

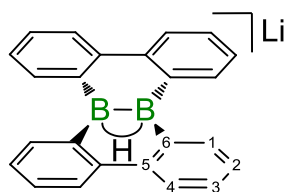


Figure S8. NMR numbering scheme for $\text{Li}[\mathbf{2}^{\text{H}}\text{H}]$.

NMR shifts of compound $\text{Li}[\mathbf{2}^{\text{H}}\text{H}]$

^1H NMR (500.2 MHz, $[\text{D}_8]\text{THF}$): $\delta = 8.61$ (dd, $^3J(\text{H},\text{H}) = 7.3$ Hz, $^4J(\text{H},\text{H}) = 1.5$ Hz, 4H; H-1), 8.43 (d, $^3J(\text{H},\text{H}) = 7.6$ Hz, 4H; H-4), 7.23-7.16 (m, 8H; H-2, H-3), -1.26 (br, 1H; BH).

^{11}B NMR (160.5 MHz, $[\text{D}_8]\text{THF}$): $\delta = 21.2$ (br, $h_{1/2} \approx 500$ Hz).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, $[\text{D}_8]\text{THF}$): $\delta = 146.8$ (br, C-6), 141.3 (C-5), 131.3 (C-1), 125.9 (C-4), 124.0 (C-2), 123.0 (C-3).

2. Plots of NMR spectra

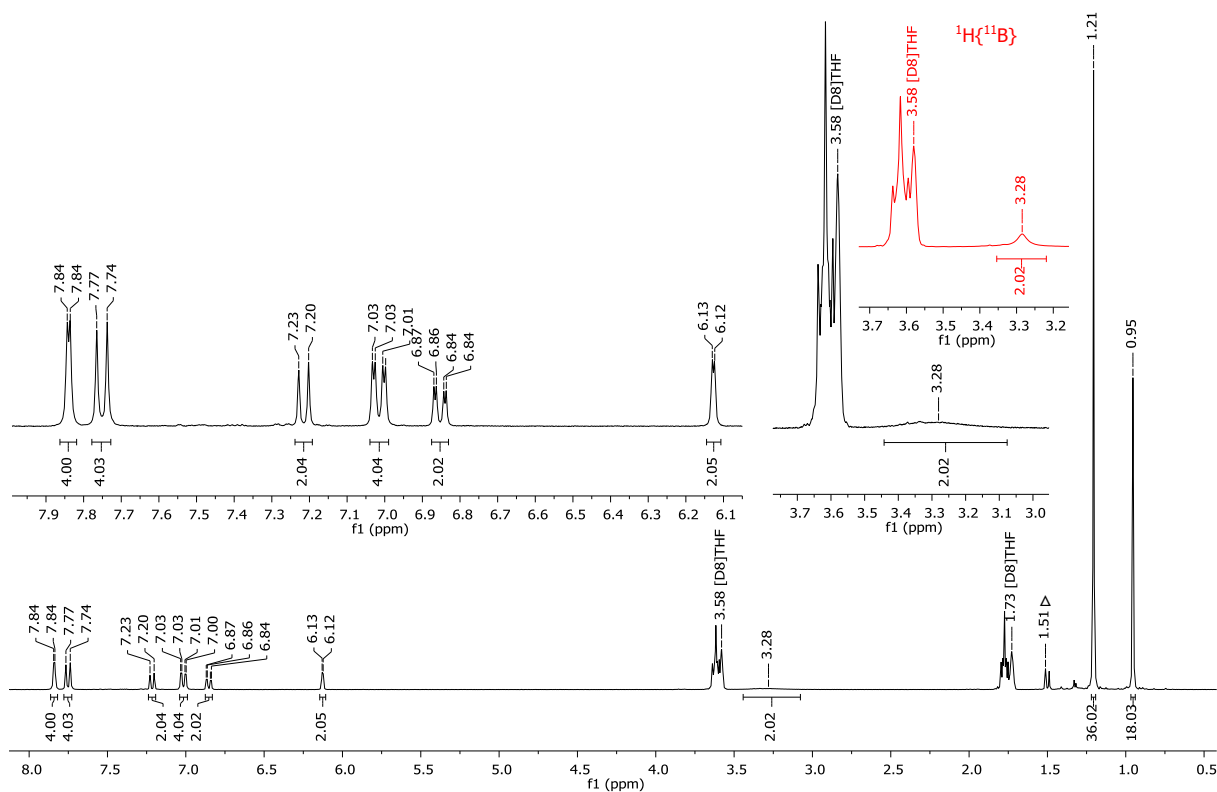


Figure S9: ^1H NMR spectrum of $\text{Li}[3]$ (300.0 MHz, $[\text{D}_8]\text{THF}$). One signal of residual $\text{Li}[2\text{H}]$ is marked with Δ (small excess due to unavoidable weighing errors on a 1 mg scale).

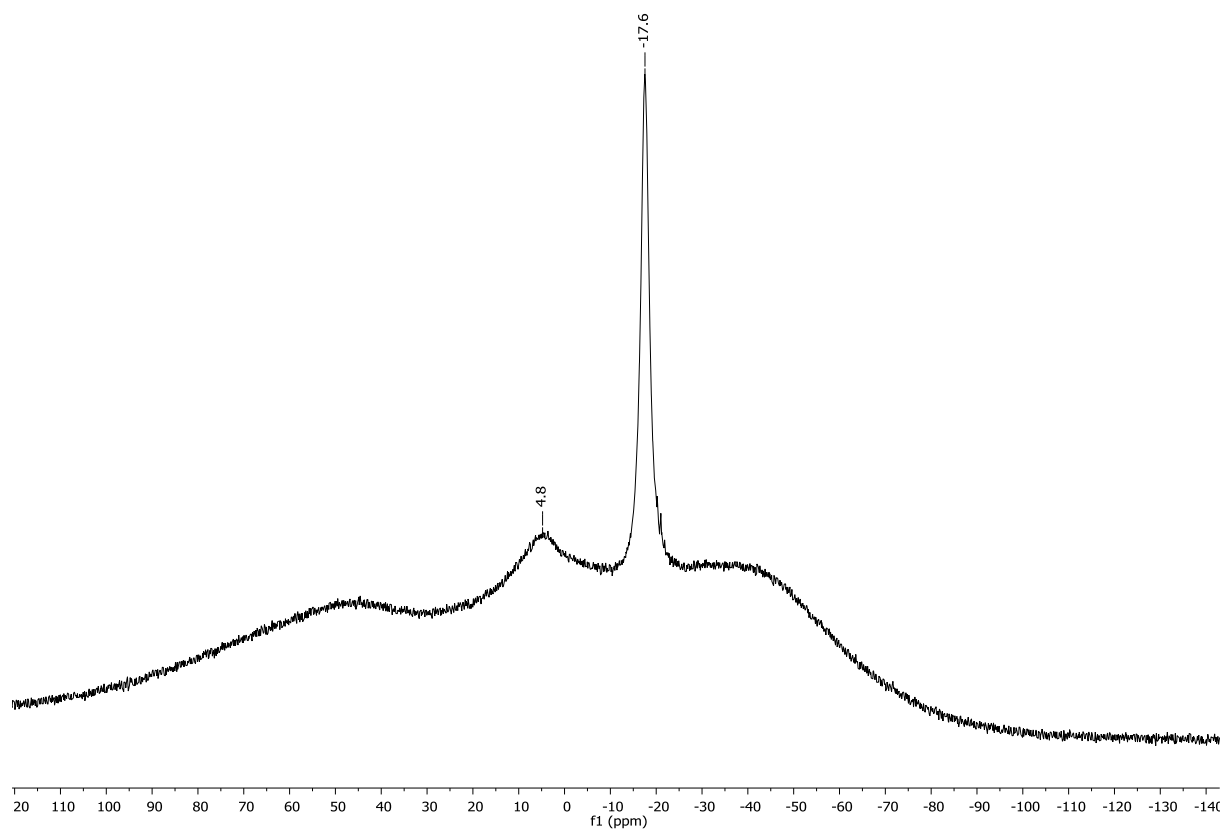


Figure S10: ^{11}B NMR spectrum of $\text{Li}[3]$ (96.3 MHz, $[\text{D}_8]\text{THF}$).

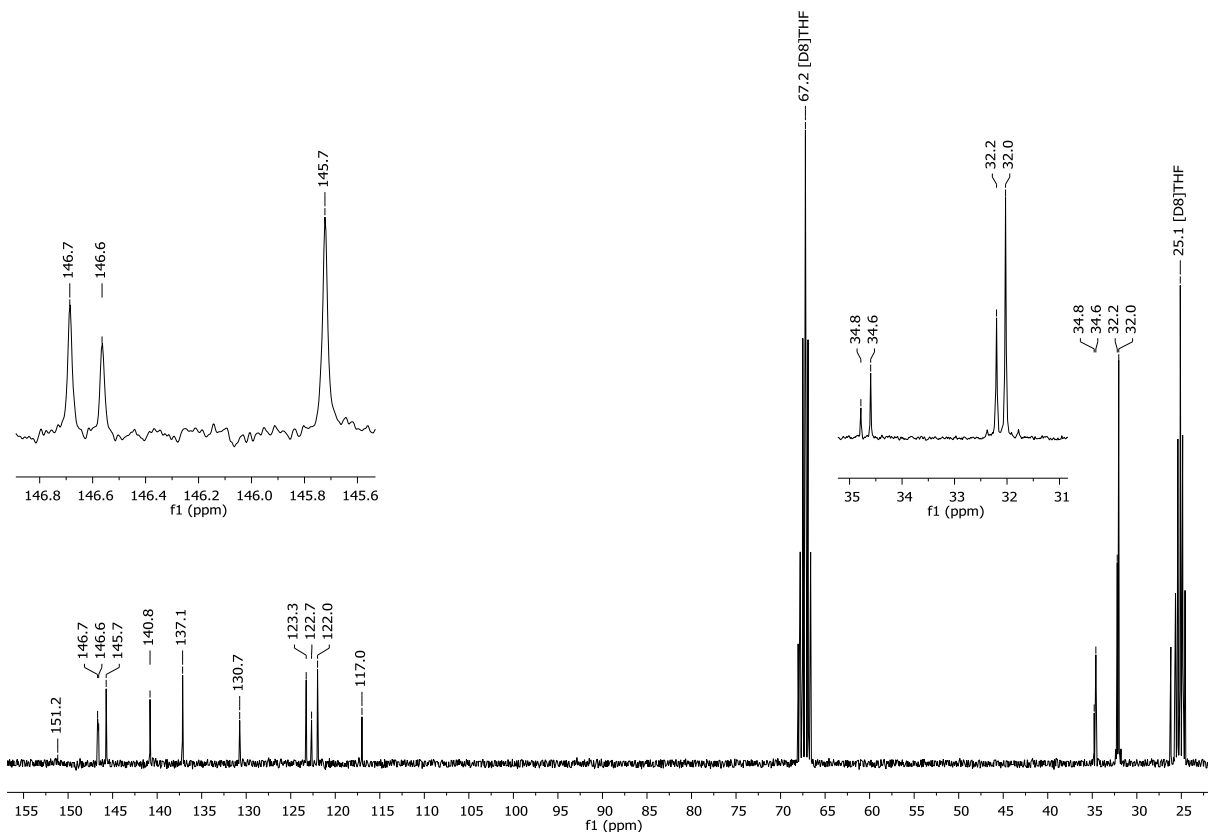


Figure S11: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of Li[3] (75.4 MHz, $[\text{D}_8]\text{THF}$).

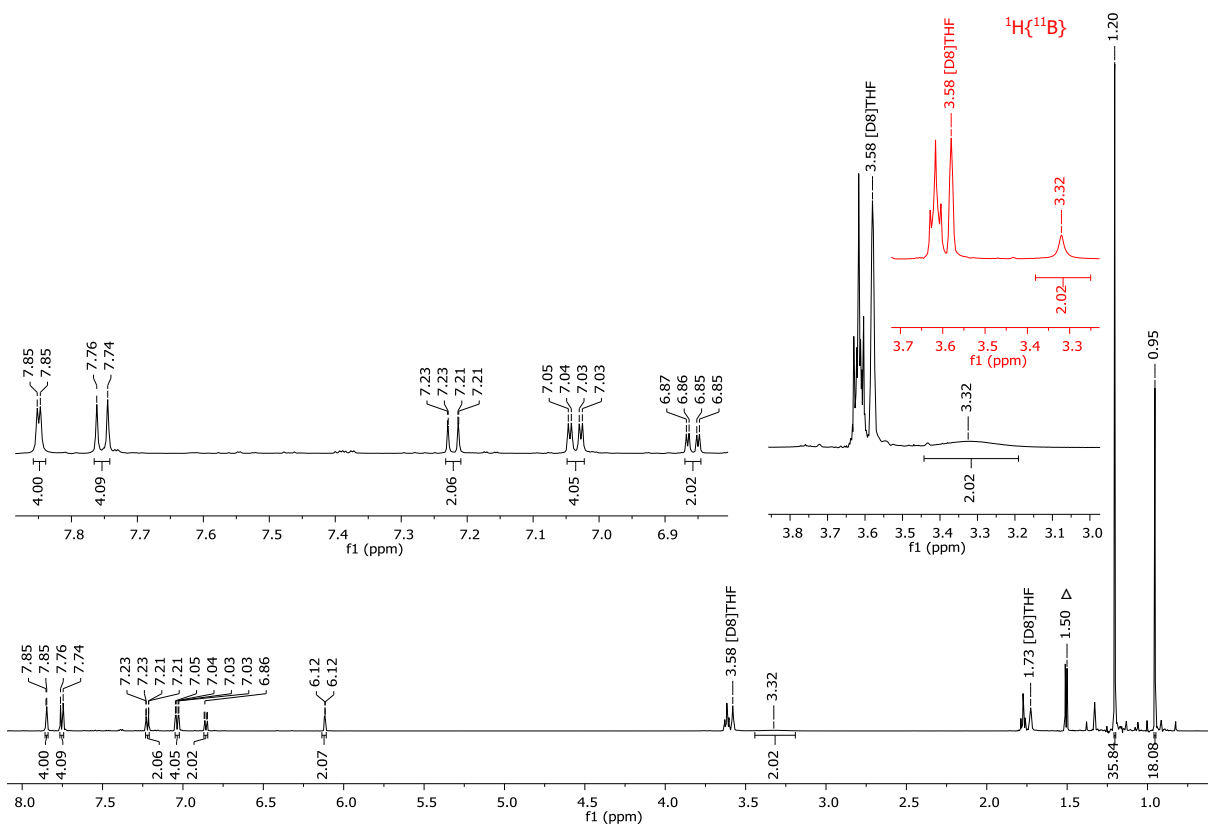


Figure S12: ^1H NMR spectrum of K[3] (300.0 MHz, $[\text{D}_8]\text{THF}$). One signal of residual K[2H] is marked with Δ (small excess due to unavoidable weighing errors on a 1 mg scale).

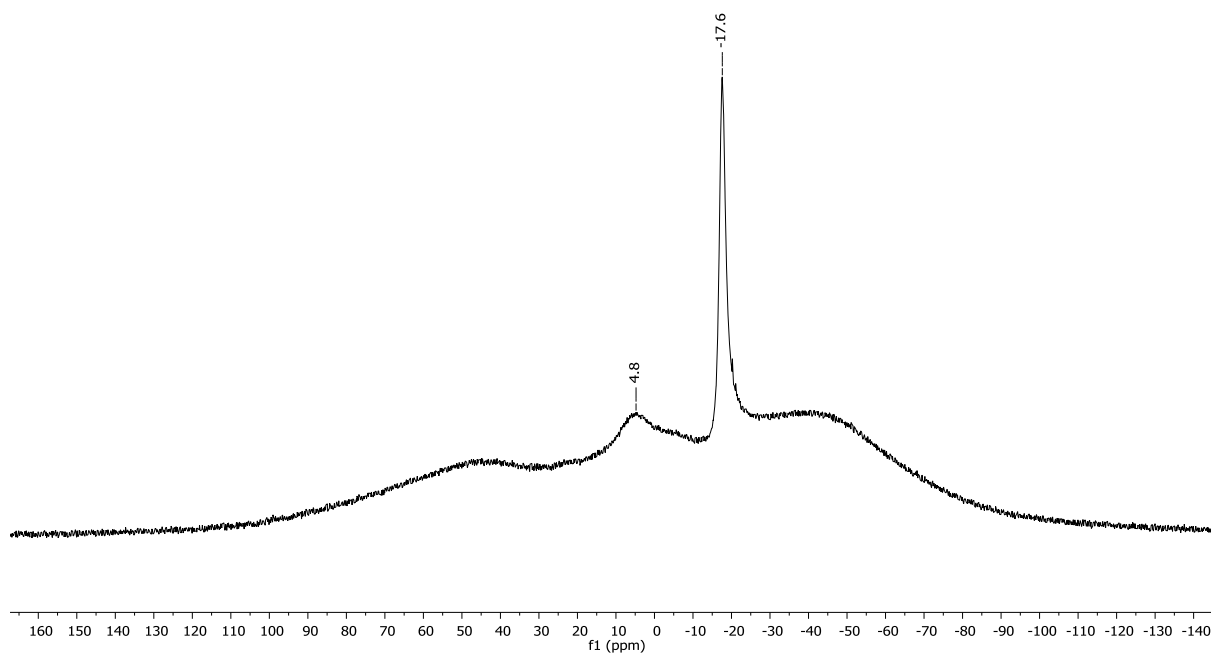


Figure S13: ^{11}B NMR spectrum of $\text{K}[\mathbf{3}]$ (96.3 MHz, $[\text{D}_8]\text{THF}$).

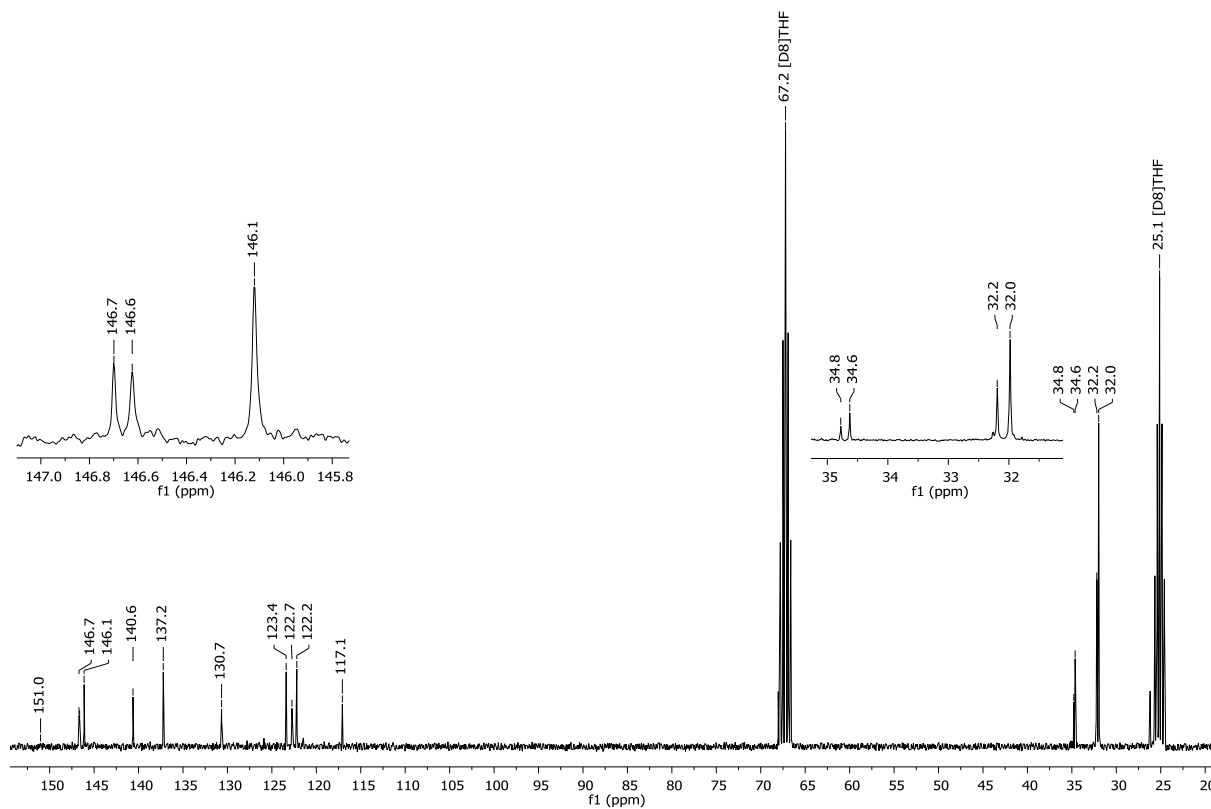


Figure S14: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{K}[\mathbf{3}]$ (75.4 MHz, $[\text{D}_8]\text{THF}$).

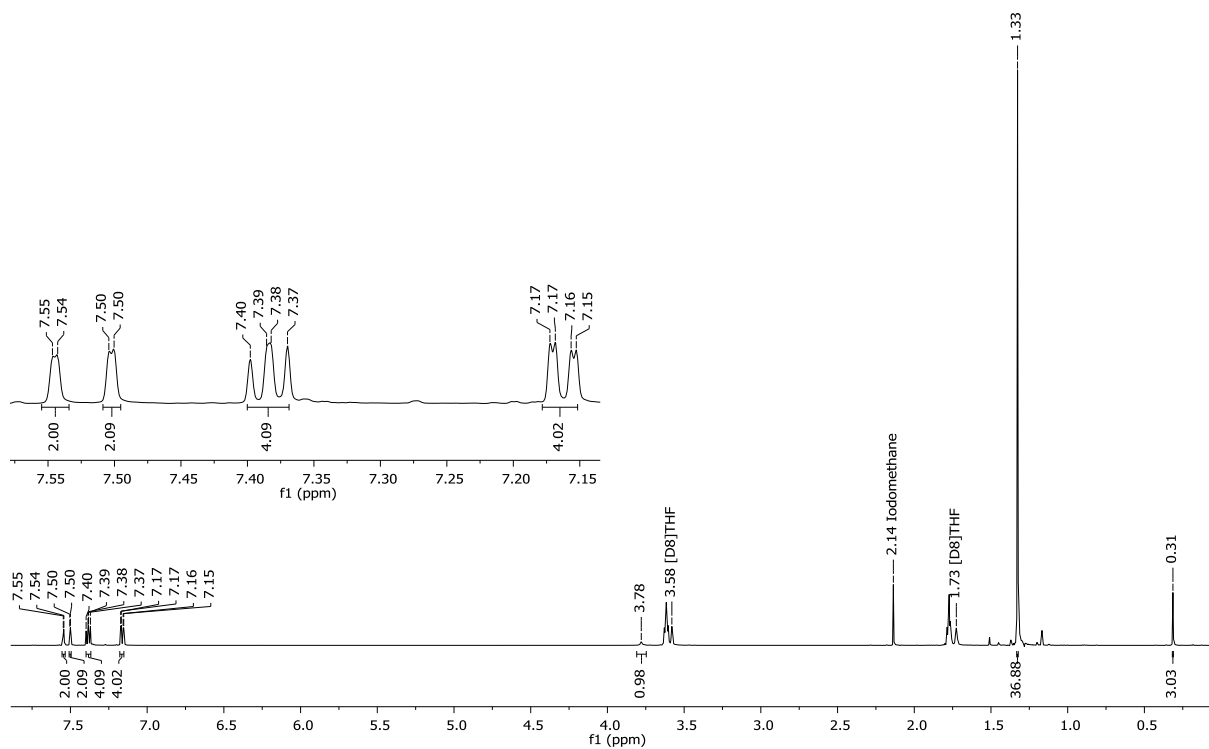


Figure S15: $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum of a mixture of **1**·THF and **4** (500.2 MHz, $[\text{D}_8]\text{THF}$).

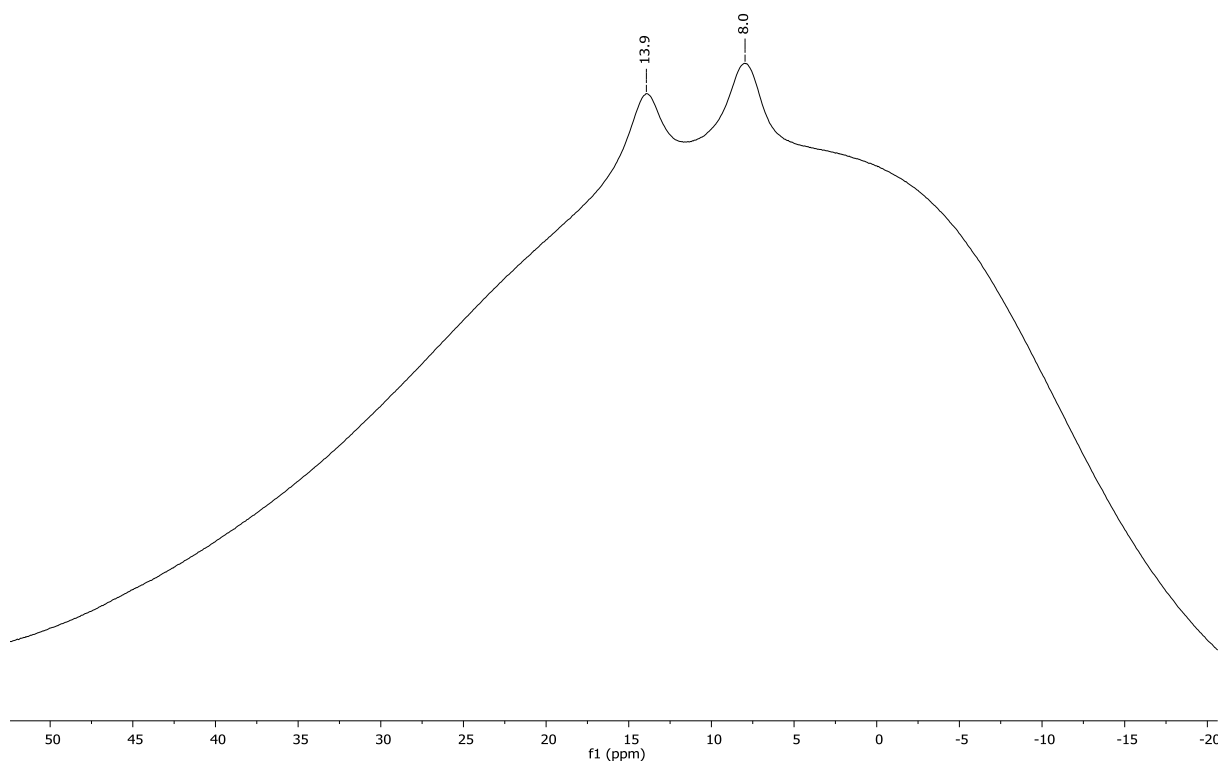


Figure S16: ^{11}B NMR spectrum of a mixture of **1**·THF and **4** (160.5 MHz, $[\text{D}_8]\text{THF}$).

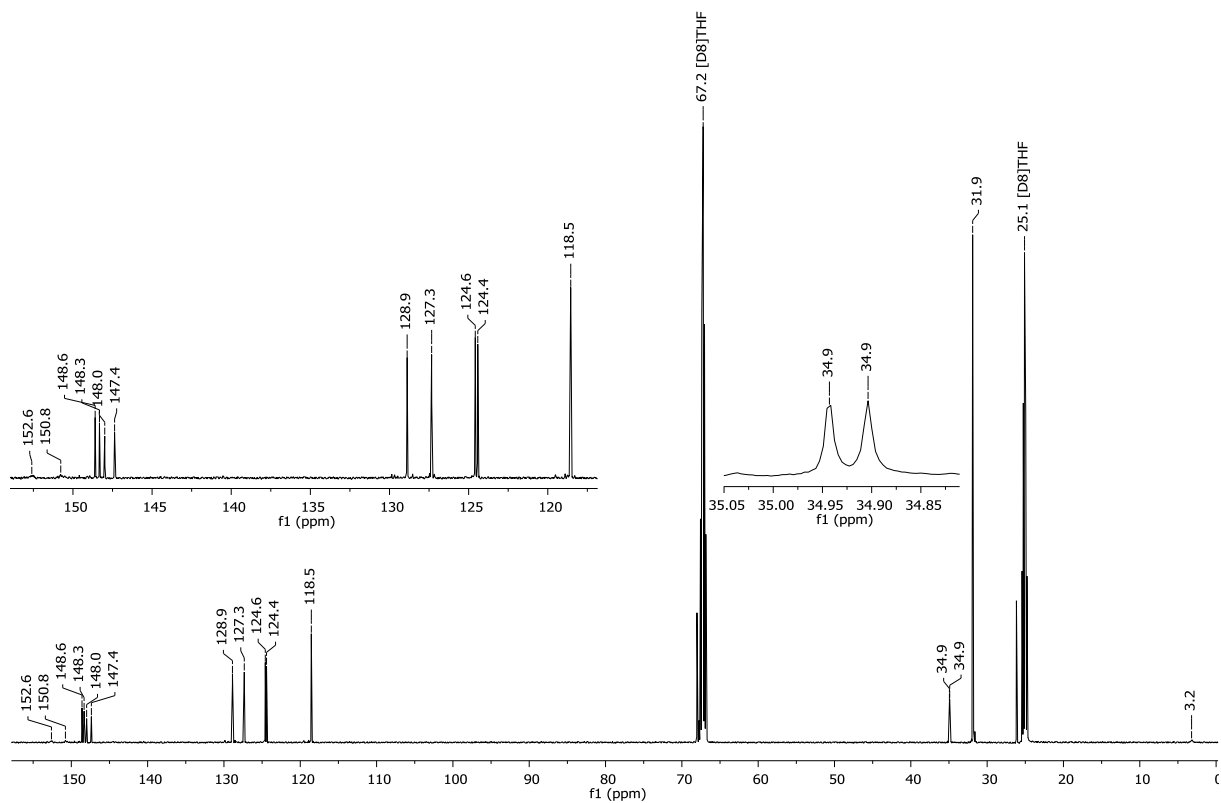


Figure S17: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of a mixture of **1**·THF and **4** (125.8 MHz, $[\text{D}_8]\text{THF}$).

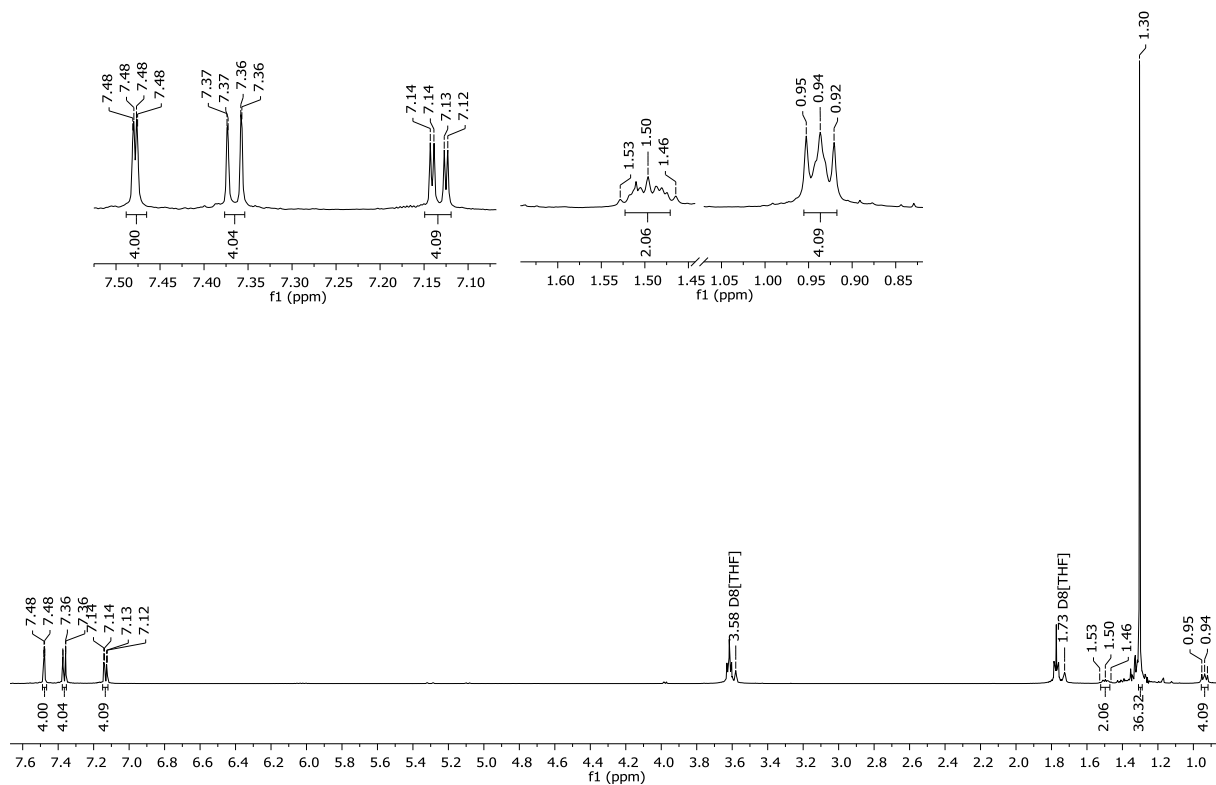


Figure S18: ^1H NMR spectrum of **5** (500.2 MHz, $[\text{D}_8]\text{THF}$).

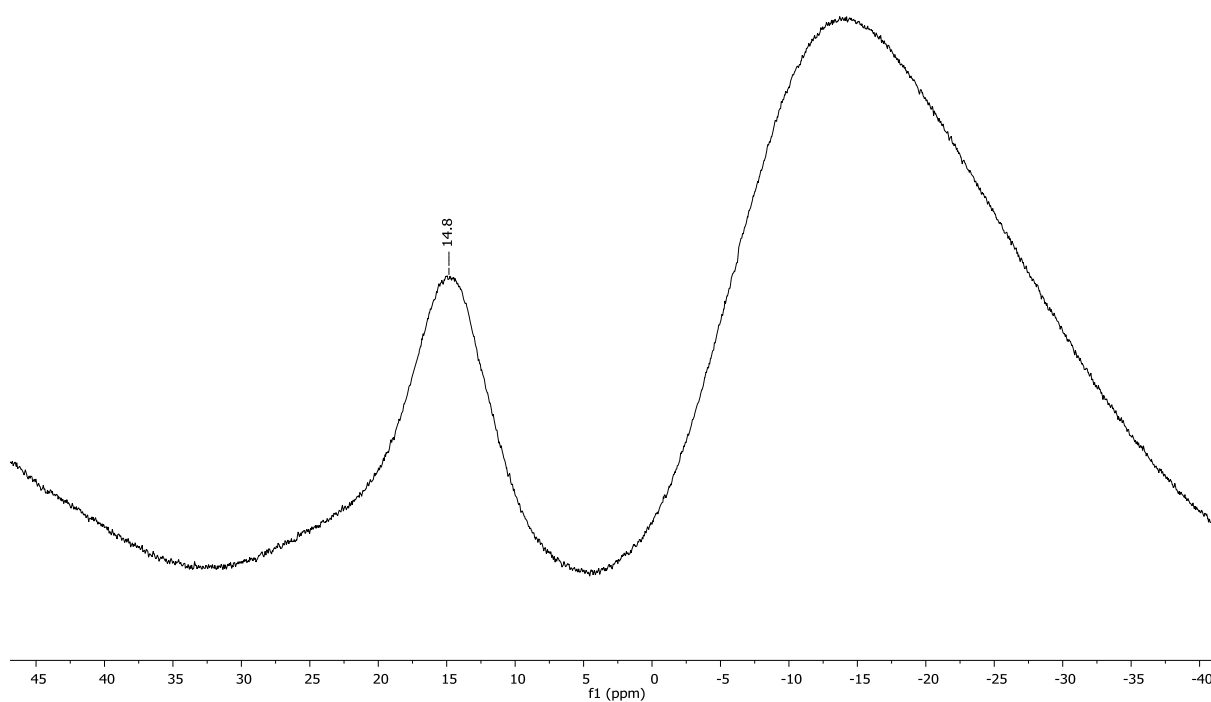


Figure S19: ^{11}B NMR spectrum of **5** (160.5 MHz, $[\text{D}_8]\text{THF}$).

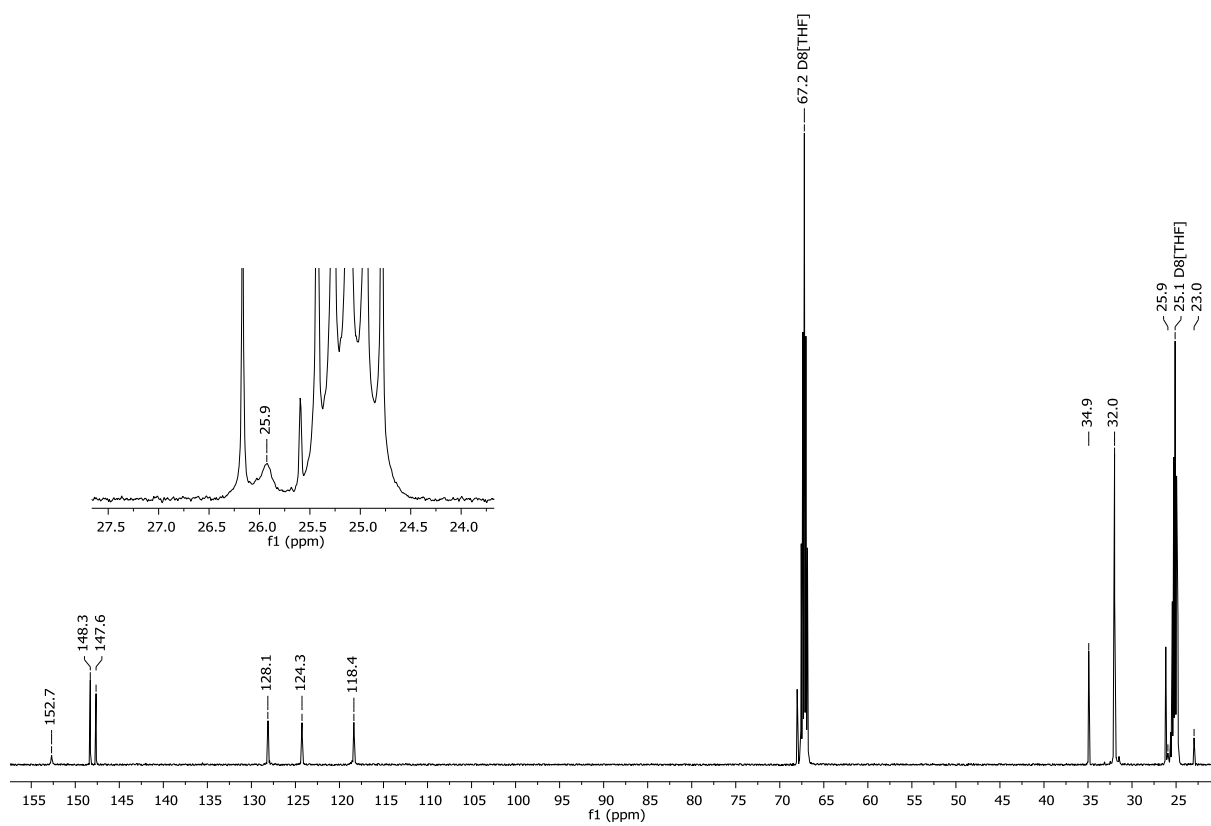


Figure S20: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5** (125.8 MHz, $[\text{D}_8]\text{THF}$).

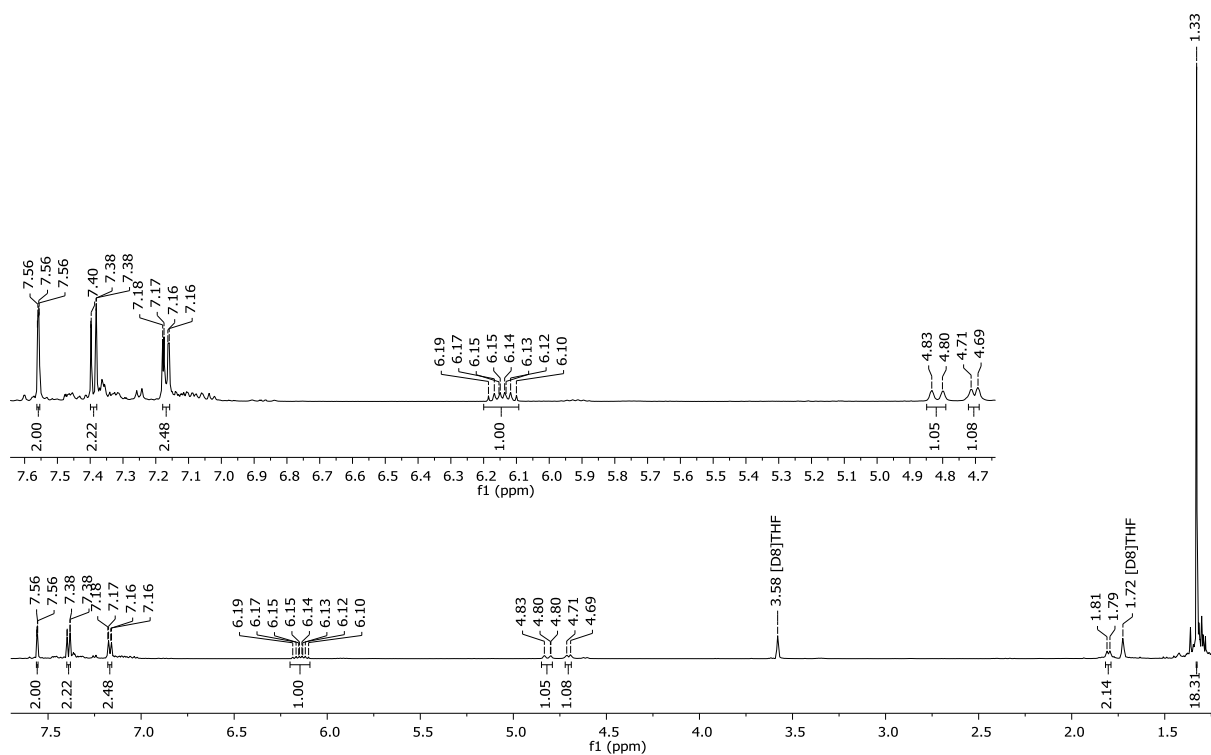


Figure S21: ^1H NMR spectrum of **9** (500.2 MHz, $[\text{D}_8]\text{THF}$).

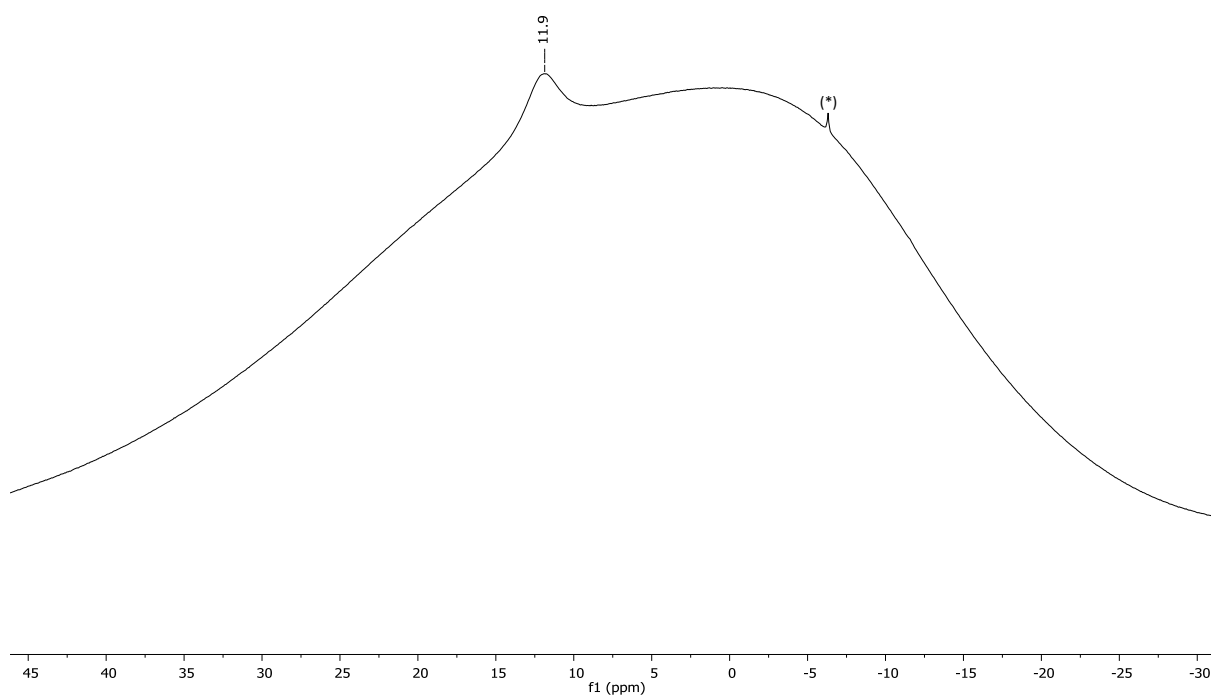


Figure S22: ^{11}B NMR spectrum of **9** (160.5 MHz, $[\text{D}_8]\text{THF}$). The signal marked with (*) corresponds to a minor impurity.

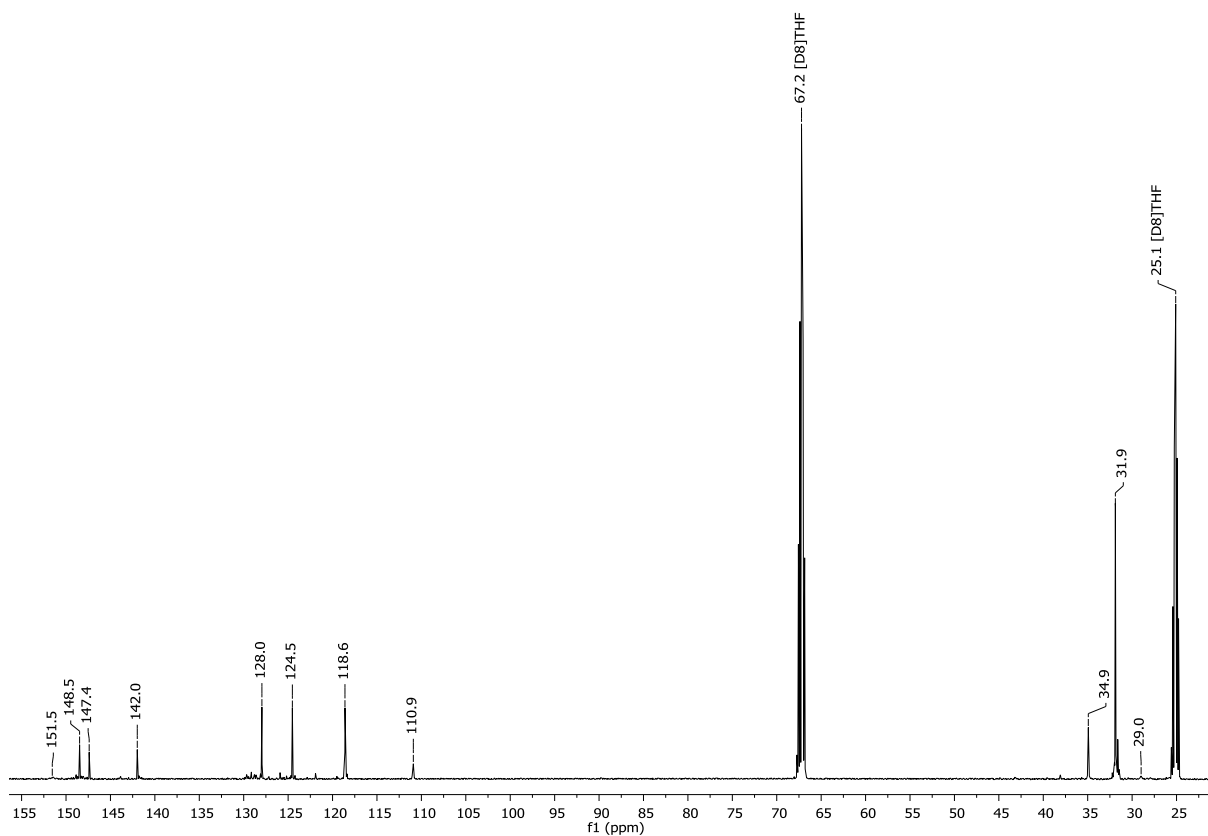


Figure S23: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **9** (125.8 MHz, $[\text{D}_8]$ THF).

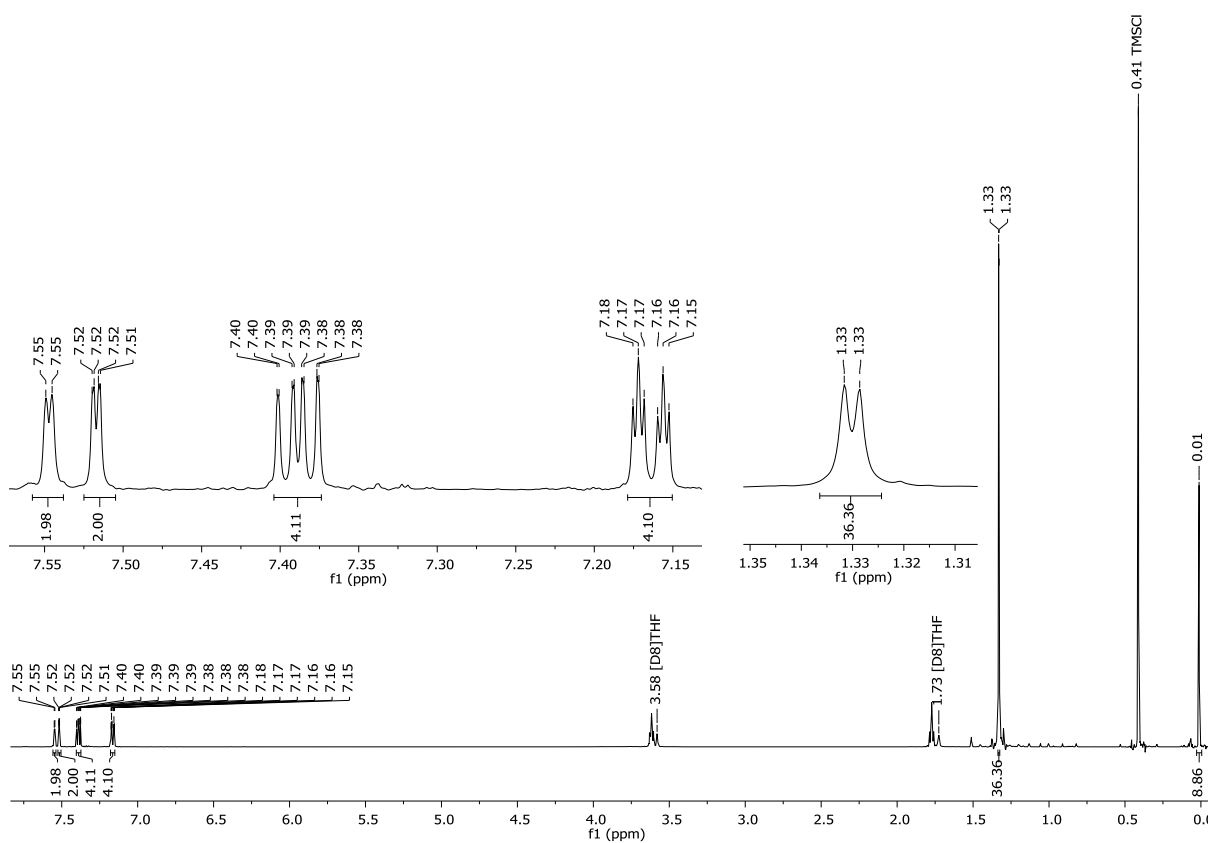


Figure S24: ^1H NMR spectrum of a mixture of **1**·THF and **6** (500.2 MHz, $[\text{D}_8]$ THF).

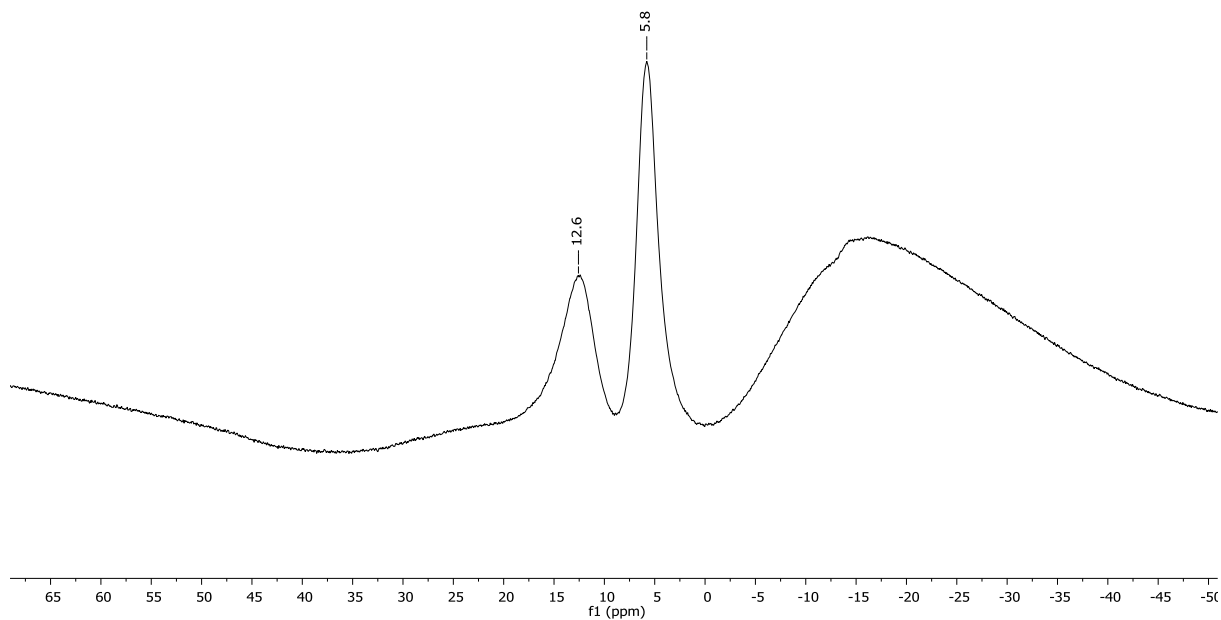


Figure S25: ^{11}B NMR spectrum of a mixture of **1**-THF and **6** (160.5 MHz, $[\text{D}_8]\text{THF}$).

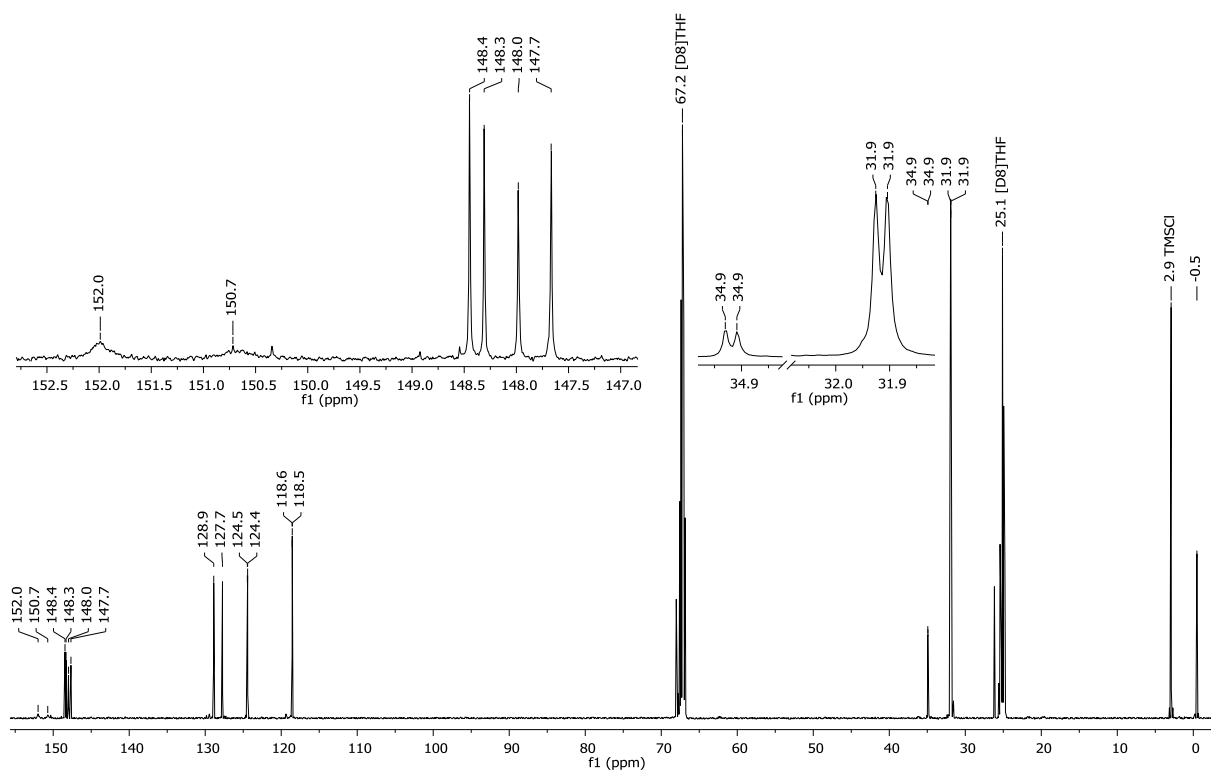


Figure S26: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of a mixture of **1**-THF and **6** (125.8 MHz, $[\text{D}_8]\text{THF}$).

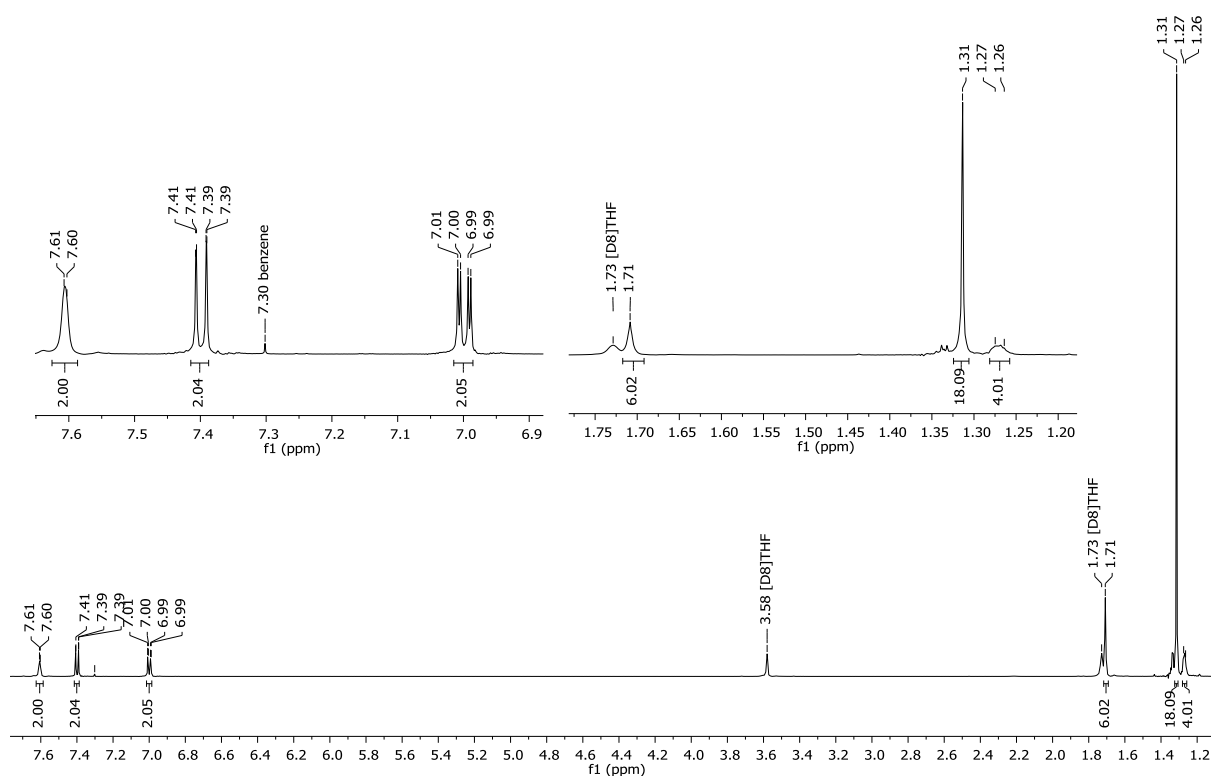


Figure S27: ^1H NMR spectrum of K[7] (500.2 MHz, $[\text{D}_8]\text{THF}$).

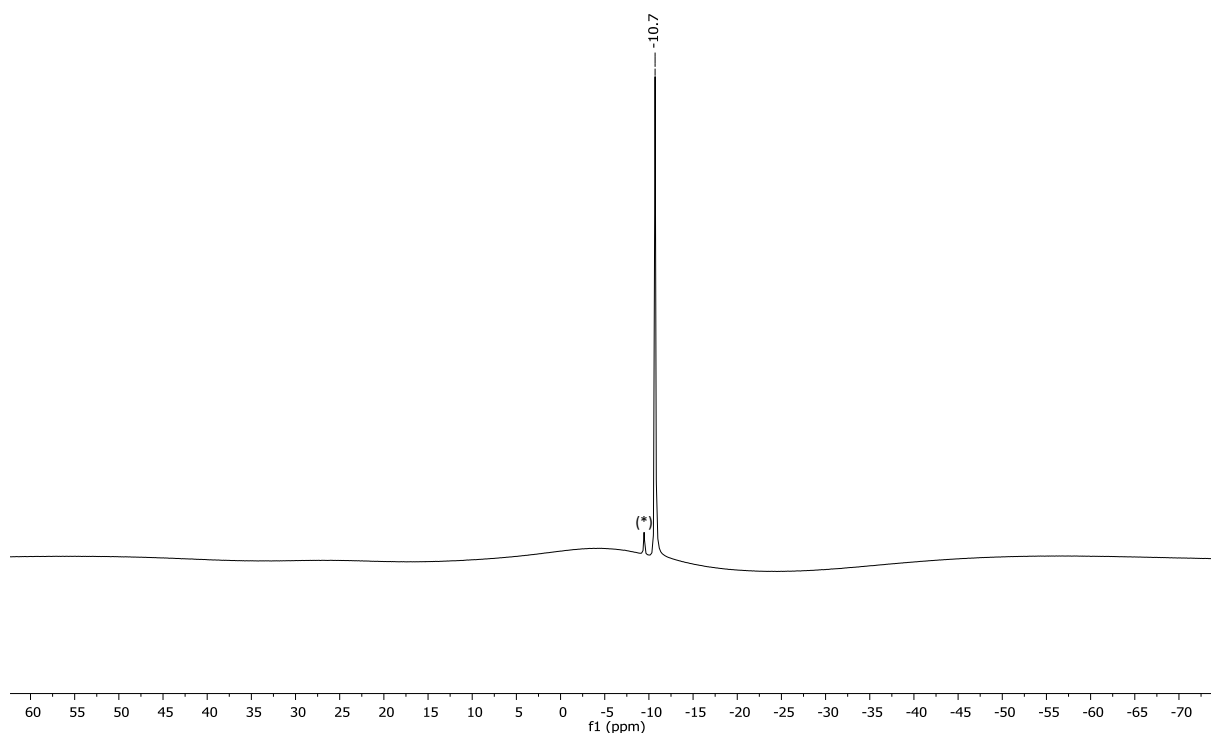


Figure S28: ^{11}B NMR spectrum of K[7] (160.5 MHz, $[\text{D}_8]\text{THF}$). The signal marked with (*) corresponds to a minor impurity.

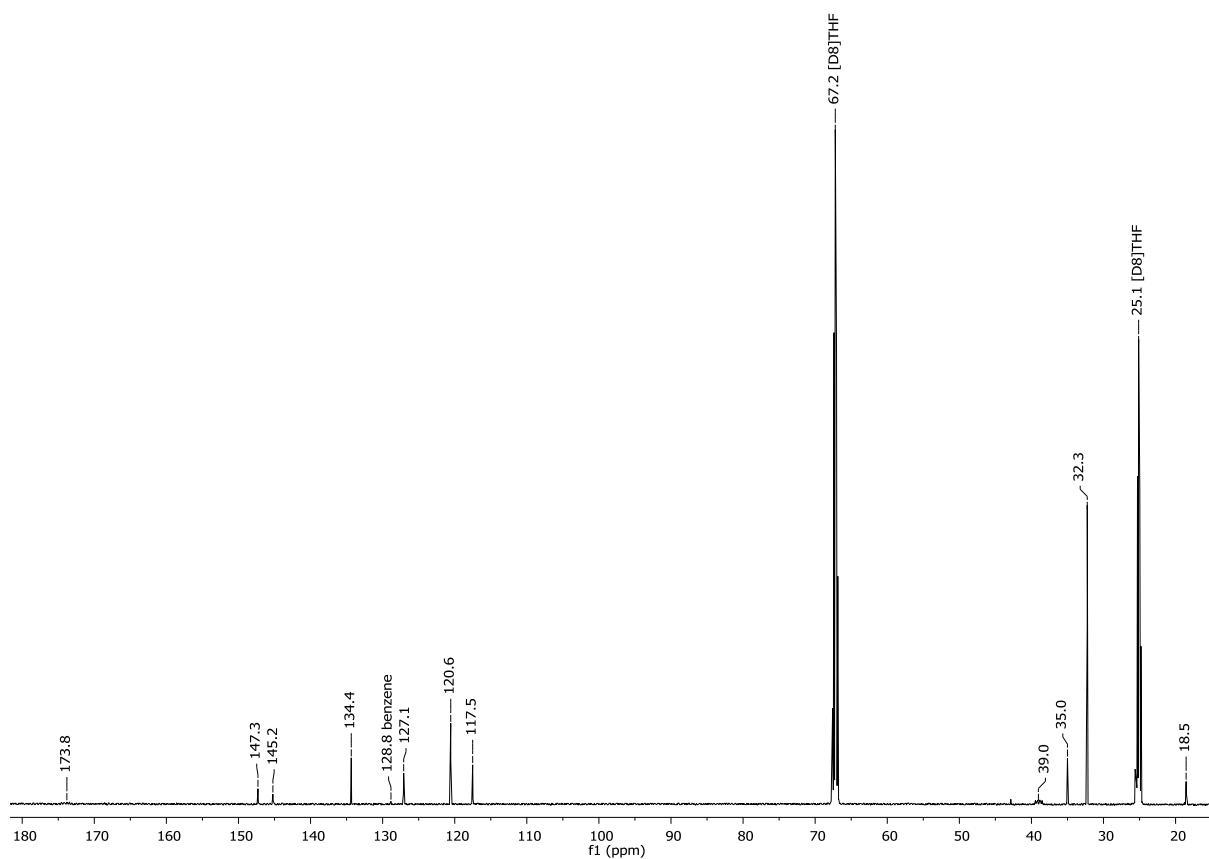


Figure S29: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **K[7]** (125.8 MHz, $[\text{D}_8]\text{THF}$).

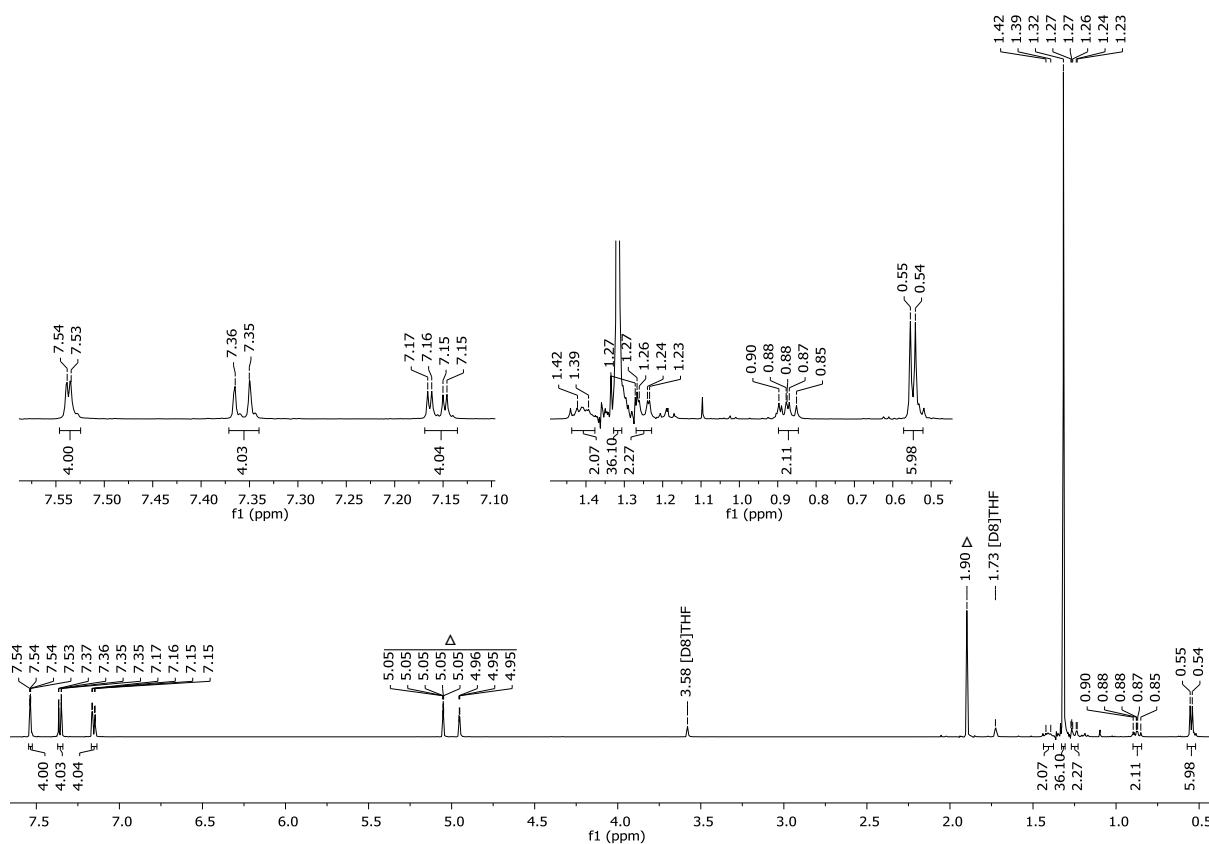


Figure S30: ^1H NMR spectrum of **8** (500.2 MHz, $[\text{D}_8]\text{THF}$). Signals of excess 2,3-dimethylbutadiene are marked with Δ .

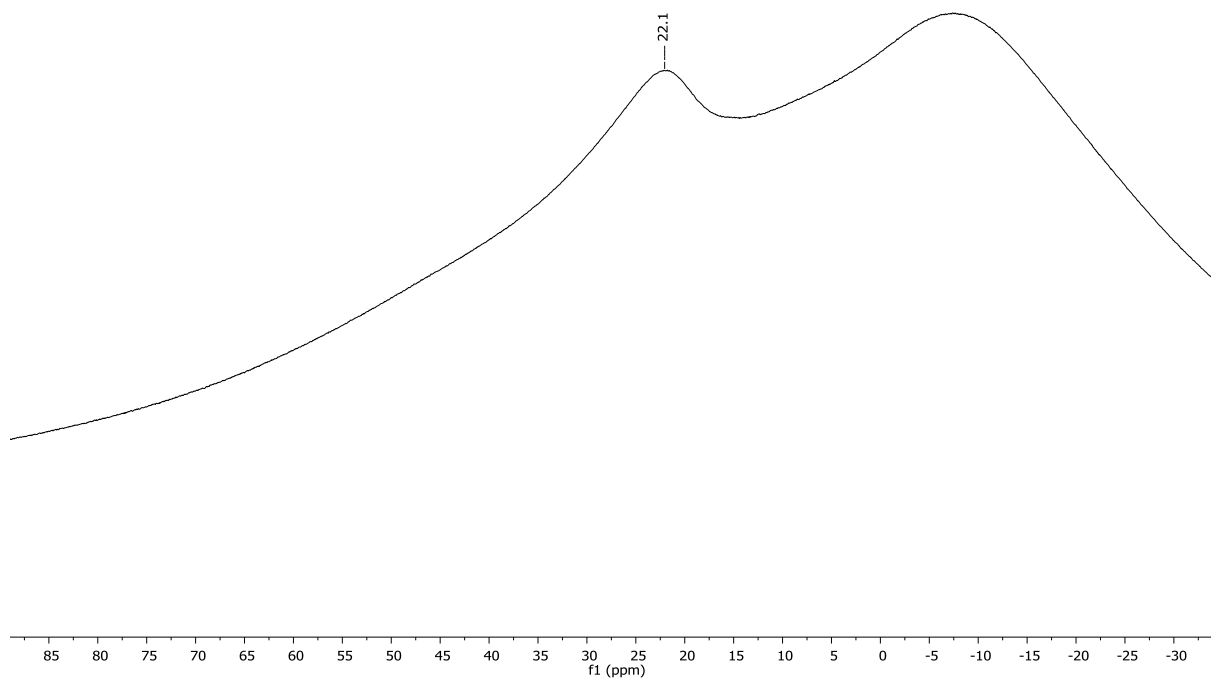


Figure S31: ^{11}B NMR spectrum of **8** (160.5 MHz, $[\text{D}_8]\text{THF}$).

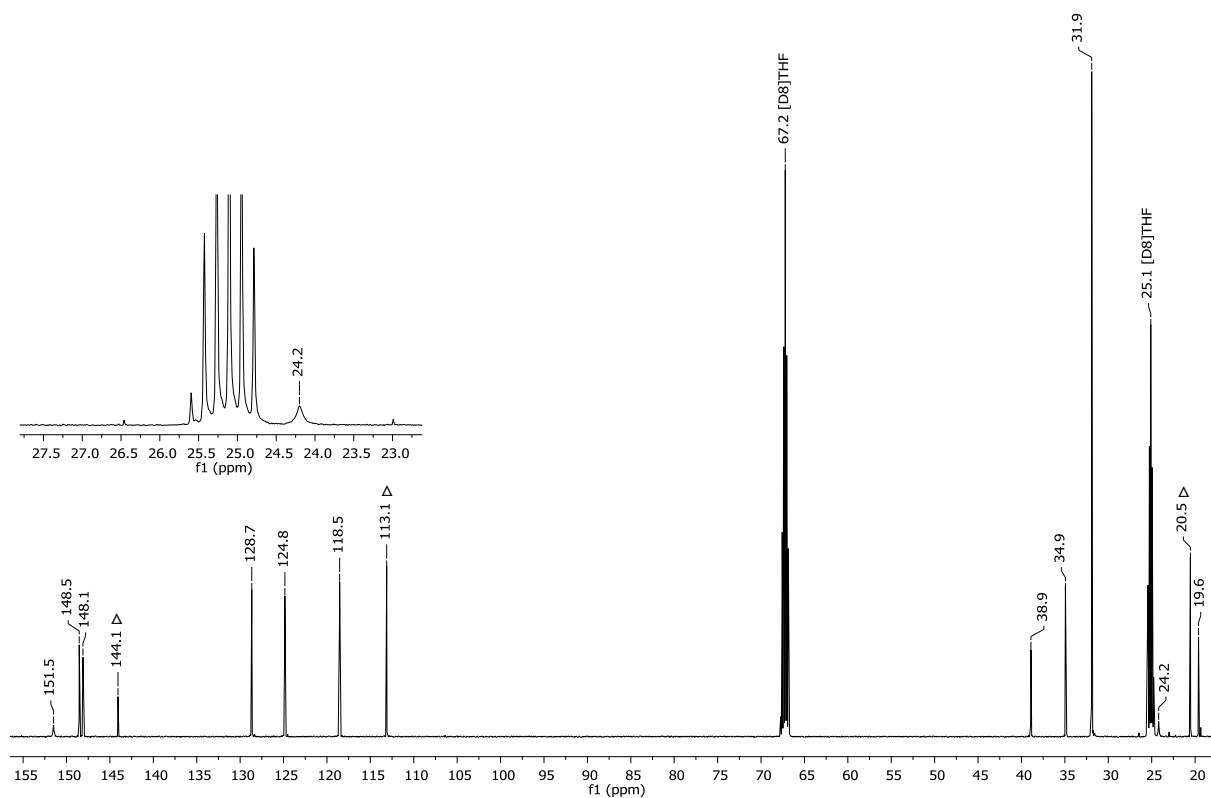


Figure S32: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **8** (125.8 MHz, $[\text{D}_8]\text{THF}$). Signals of excess 2,3-dimethylbutadiene are marked with Δ .

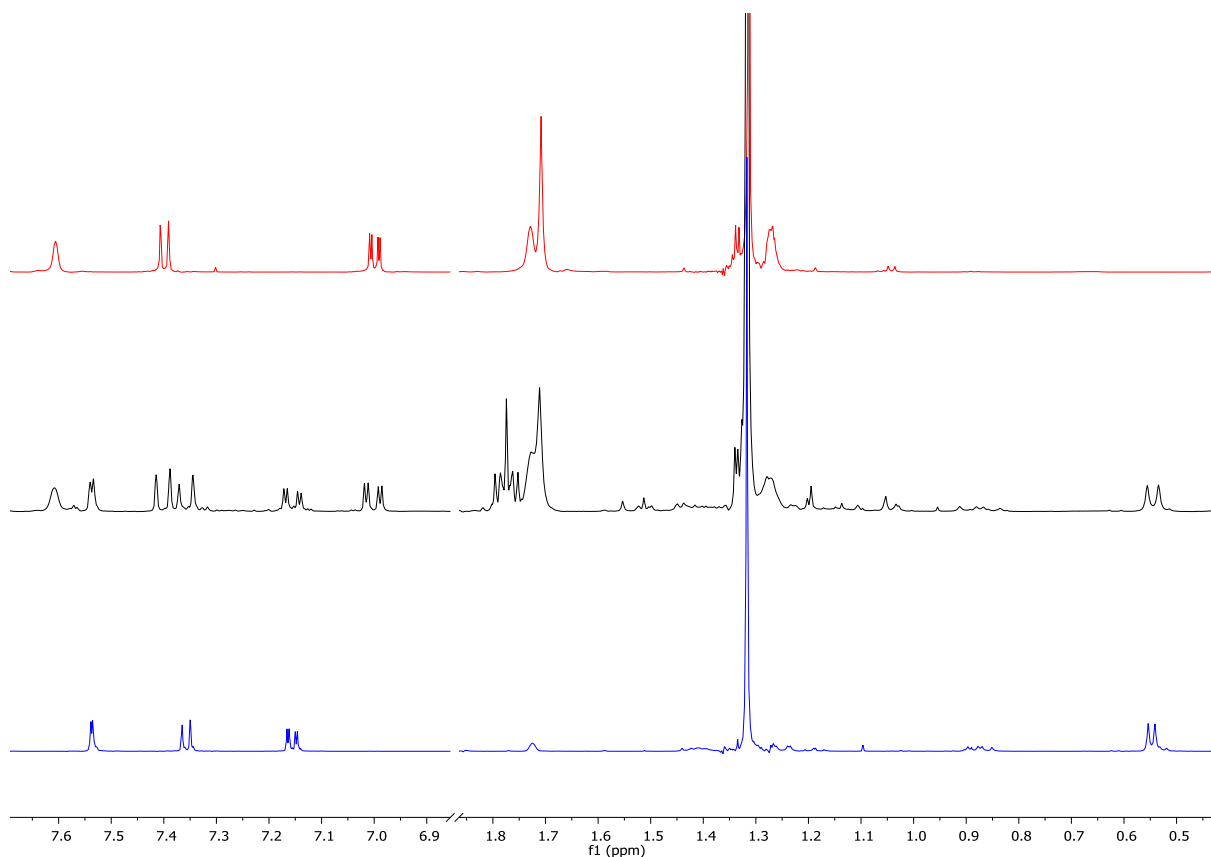


Figure S33: Stack of the ¹H NMR spectra of K[7] (500.2 MHz, [D₈]THF; red), the reaction of K[3] with 2,3-dimethylbutadiene (300.1 MHz, [D₈]THF; black), and **8** (500.2 MHz, [D₈]THF; blue).

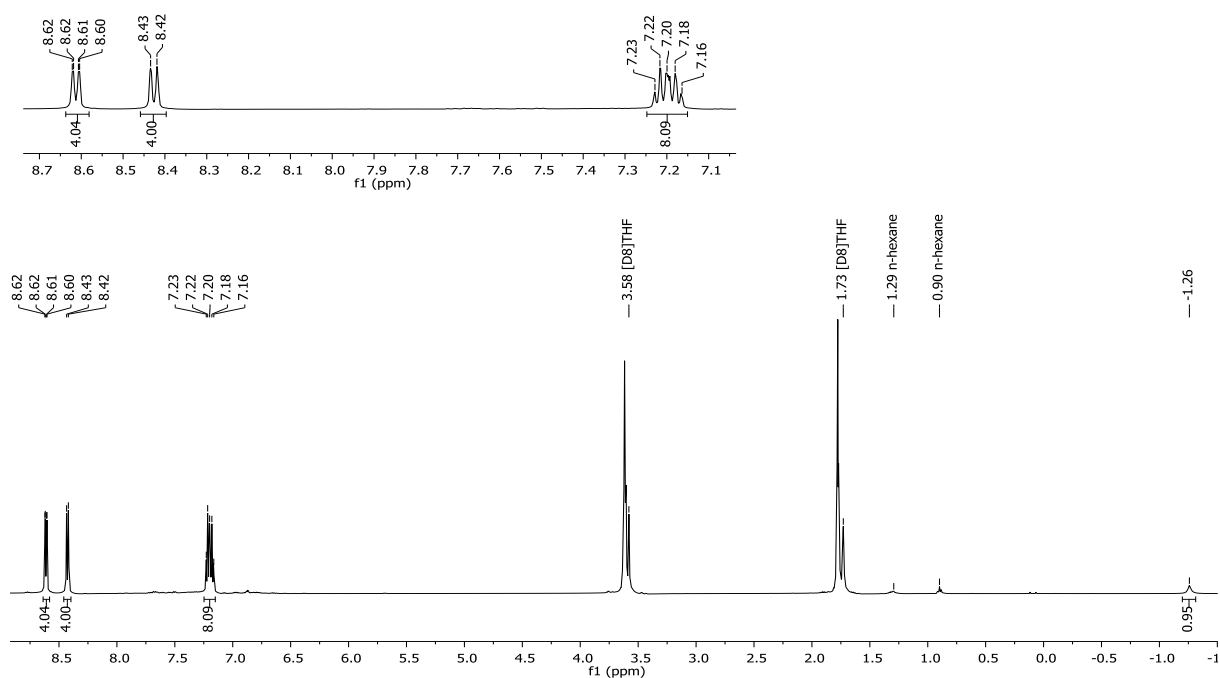


Figure S34: ¹H NMR spectrum of Li[2^H] (500.2 MHz, [D₈]THF).

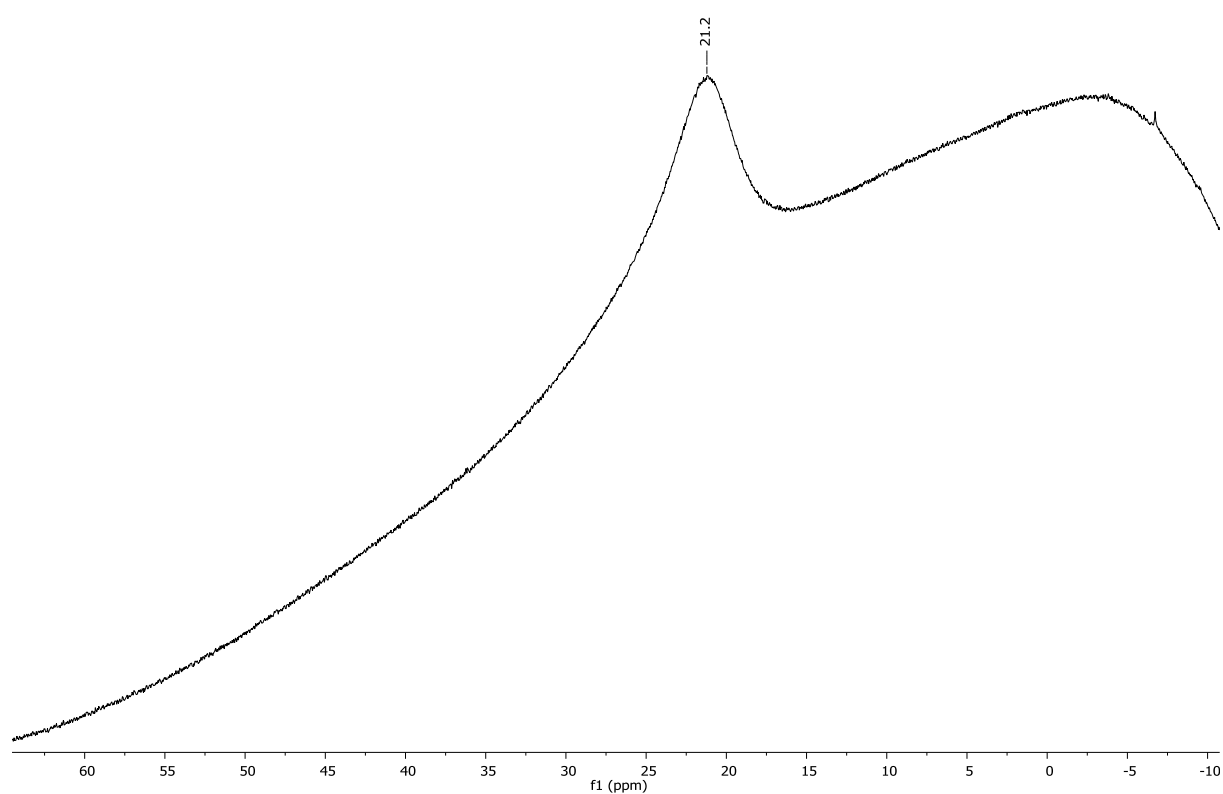


Figure S35: ^{11}B NMR spectrum of $\text{Li}[\mathbf{2}^{\text{H}}]$ (160.5 MHz, $[\text{D}_8]\text{THF}$).

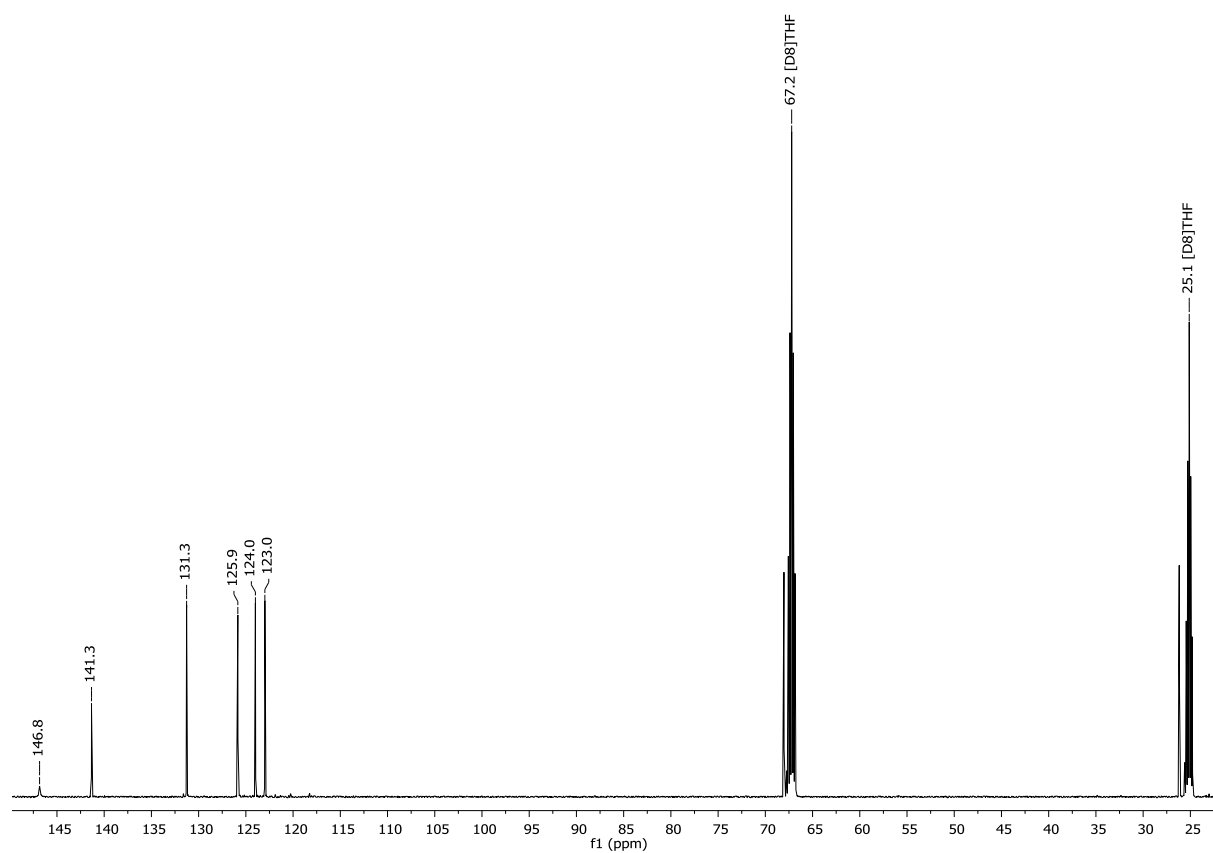


Figure S36: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Li}[\mathbf{2}^{\text{H}}]$ (125.8 MHz, $[\text{D}_8]\text{THF}$).

3. X-ray crystal structure determinations

Data for all structures were collected on a STOE IPDS II two-circle diffractometer with a Genix Microfocus tube with mirror optics using MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). The data were scaled using the frame-scaling procedure in the *X-AREA* program system.^[S8] The structures were solved by direct methods using the program *SHELXS* and refined against F^2 with full-matrix least-squares techniques using the program *SHELXL*.^[S9]

Structure	Internal code	CCDC reference number
$\{[\text{K}_{1.5}(\text{thf})_{3.5}][\mathbf{3}_{1.5}]\}_2$	wa2888	1971559
$[\text{K}(\text{thf})_2][\mathbf{3a}]$	wa2883	1971560
$\text{K}[\mathbf{7}]$	wa2818	1971561
$[\text{Li}(\text{thf})_4][\mathbf{2}^{\text{H}}\text{H}]$	wa2711	1971562

$\{[K_{1.5}(thf)_{3.5}][3_{1.5}]\}_2$

Colorless single crystals of $\{[K_{1.5}(thf)_{3.5}][3_{1.5}]\}_2$ were grown through slow evaporation of the solvent from a THF solution of $K[3]$ (3 d, room temperature).

The crystal lattice consists of one molecule of $[K(thf)_2][3]^A$ and half a molecule of $[K(thf)_3][3]^B$ in the asymmetric unit. $[K(thf)_3][3]^B$ is located on a two-fold rotation axis.

In $[K(thf)_2][3]^A$, three *t*-butyl groups are disordered over two positions with site occupation factors of 0.671(13), 0.525(12), and 0.526(12) for the respective major occupied sites. In the thf ring containing O71, two methylene groups are disordered over two positions with a site occupation factor of 0.58(2) for both major occupied sites. In the thf ring containing O81, three methylene groups are disordered over two positions with a site occupation factor of 0.500(12) for all three major occupied sites.

In $[K(thf)_3][3]^B$, the K^+ ion is disordered over four equally occupied sites. In two aromatic rings, the atoms C2A, C3A, C4A and C2B, C3B, C4B are disordered over two equally occupied sites. One *t*-butyl group is disordered over two positions with a site occupation factor of 0.55(3) for the major occupied site. In the thf ring containing O71A, one methylene group is disordered over two equally occupied sites. In the thf ring containing O81A, two methylene groups are disordered over two positions with a site occupation factor of 0.71(2) for both major occupied sites. Equivalent atoms were generated by the symmetry operator $1-x, y, -z+(3/2)$.

The displacement ellipsoids of the disordered atoms were restrained to an isotropic behavior. Symmetry-equivalent bond lengths and angles in the thf rings of $[K(thf)_3][3]^B$ were restrained to be equal.

The H atoms bonded to B atoms were freely refined.

Although the quality of the data is good ($R_{int} = 0.059$; $R_{\sigma} = 0.041$), the residual values are slightly elevated ($R1 = 0.1346$ for all data; $wR2 = 0.3093$ for all data). This is due to multiple disorders in various parts of the structure.

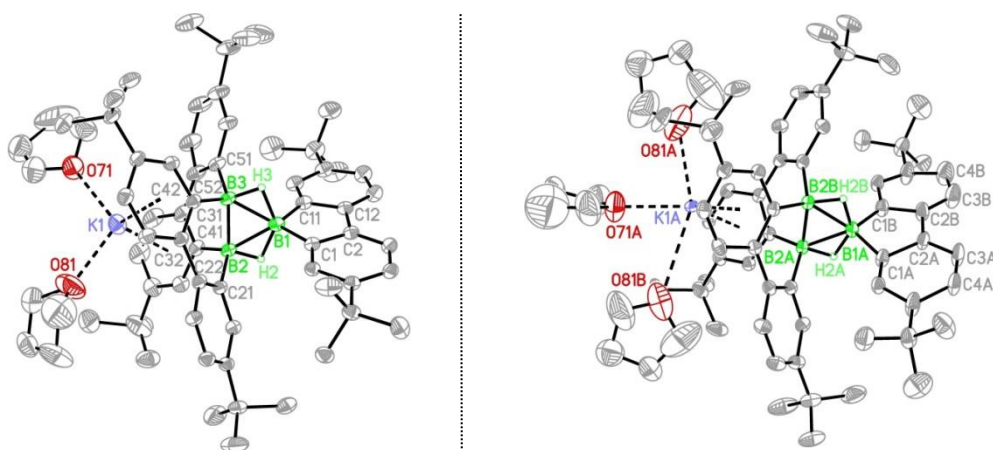


Figure S37: Molecular structure of $[K(thf)_2][3]^A$ (left) and $[K(thf)_3][3]^B$ (right) in the solid state. Carbon-bonded hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level. Selected B...B distances and bond lengths [Å]: B(1)···B(2) = 1.797(6), B(1)···B(3) = 1.833(6); B(2)–B(3) = 1.833(5), B(1)–H(2) = 1.47(3), B(1)–H(3) = 1.56(4), B(2)–H(2) = 1.21(4), B(3)–H(3) = 1.20(4); B(1A)···B(2A) = 1.811(6), B(1A)···B(2B) = 1.811(6); B(2A)–B(2B) = 1.838(8), B(1A)–H(2A) = 1.51(4), B(1A)–H(2B) = 1.51(4), B(2A)–H(2A) = 1.24(4), B(2B)–H(2B) = 1.24(4).

[K(thf)₂][3a]

Colorless single crystals of [K(thf)₂][3a] were grown through slow evaporation of the solvent from a concentrated THF solution of K[3a] (4 d, room temperature).

There are two molecules [K(thf)₂][3a]^A and [K(thf)₂][3a]^B in the asymmetric unit, which possess almost identical structural parameters, as becomes evident from the superposition shown in Figure S38 (right). In [K(thf)₂][3a]^A, two t-butyl groups are disordered over two positions with site occupation factors of 0.884(10) and 0.623(11) for the respective major occupied site. Additionally, in one thf ligand one methylene group is disordered over two positions with a site occupation factor of 0.55(2) for the major occupied site.

In [K(thf)₂][3a]^B, one t-butyl group is disordered over two positions with a site occupation factor of 0.649(10) for the major occupied site. Furthermore, in one thf ligand one methylene group is disordered over two positions with a site occupation factor of 0.58(4) for the major occupied site. In the other thf ligand, two methylene groups are disordered over two positions with a site occupation factor of 0.67(4) for both major occupied sites.

The H atoms bonded to B atoms were freely refined.

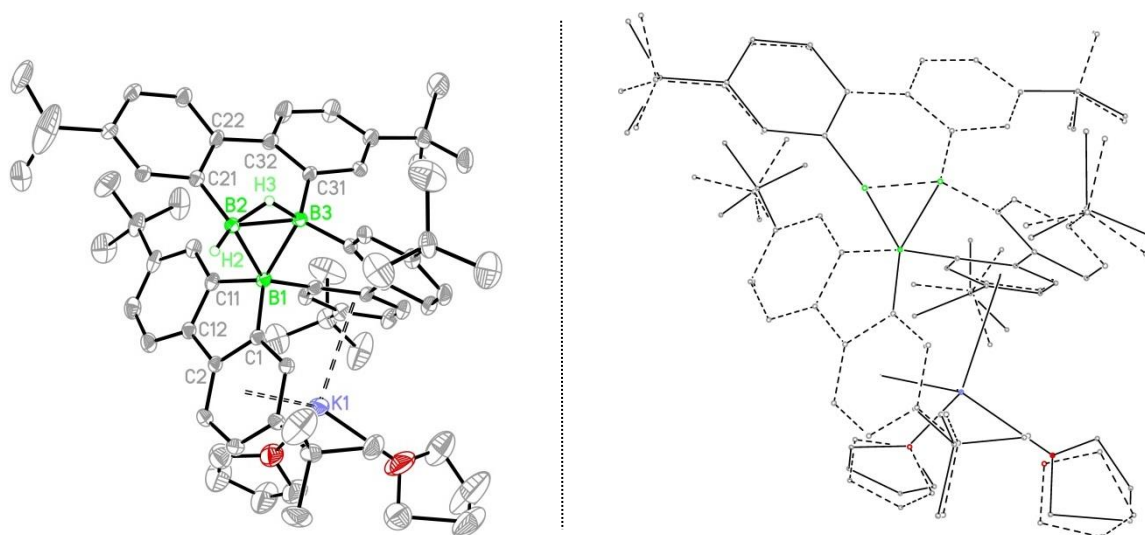


Figure S38: Left: Molecular structure of [K(thf)₂][3a]^A in the solid state. Carbon-bonded hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level. Selected bond lengths [Å]: B(1)–B(2) = 1.971(6), B(1)–B(3) = 1.949(7), B(2)–B(3) = 1.717(7), B(2)–H(2) = 1.06(4), B(2)–H(3) = 1.26(4), B(3)–H(3) = 1.33(4). Right: Superposition of [K(thf)₂][3a]^A and [K(thf)₂][3a]^B.

K[7]

Colorless single crystals of K[7] were grown through slow evaporation of the solvent from a benzene solution containing a mixture of K[7] and **8** at room temperature.

In K[7], both *t*-butyl groups are disordered over two positions with site occupation factors of 0.612(7) and 0.638(16) for the respective major occupied sites. The displacement ellipsoids of the disordered atoms were restrained to an isotropic behavior.

K[7] forms a coordination polymer in the crystal lattice. The [7][−] ions within the polymer chain are parallel aligned and possess the same orientation. The individual anions are linked through the K⁺ cations, which form contact-ion pairs with the top side of one *o*-phenylene ring and the bottom side of the other.

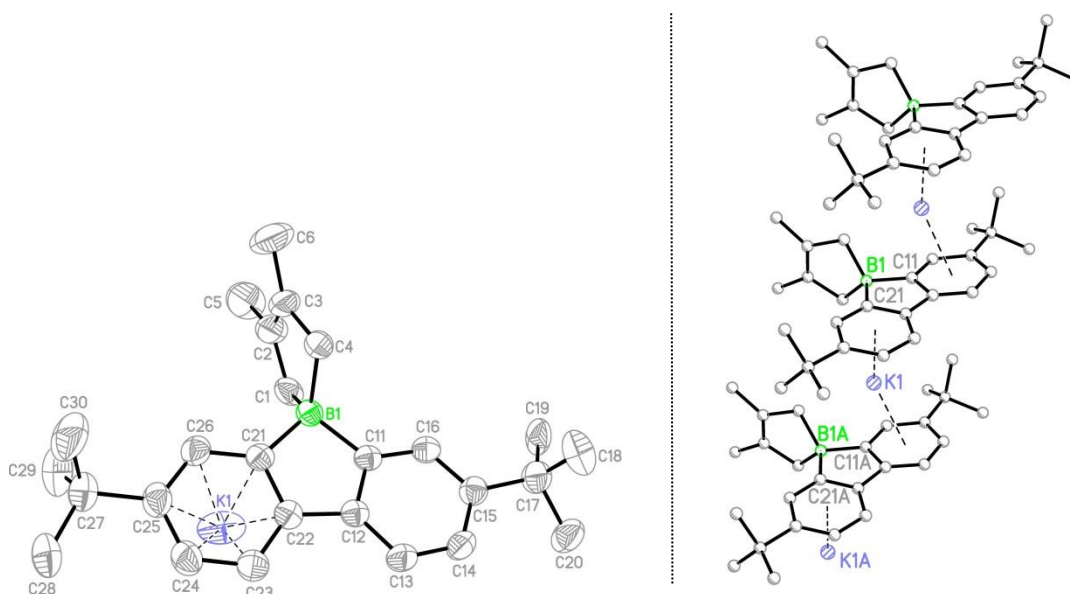


Figure S39: Left: Monomeric unit of K[7] in the solid state. Hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å], and bond angles [°]: B(1)–C(1) = 1.648(3), B(1)–C(4) = 1.663(3), B(1)–C(11) = 1.630(3), B(1)–C(21) = 1.636(3), C(2)–C(3) = 1.337(4); C(1)–B(1)–C(4) = 100.14(17), C(11)–B(1)–C(21) = 97.91(16).

Right: Molecular structure of K[7] in the solid state. Hydrogen atoms are omitted for clarity. Selected intermolecular distances [Å] and bond angle [°]: K(1)⋯COG(C(11A)) = 2.9296(11), K(1)⋯COG(C(21)) = 2.8541(11); COG(C(11A))⋯K(1)⋯COG(C(21)) = 151.8 (no standard deviation can be calculated here due to software issues). Dihedral angle between the best planes of adjacent borafluorene moieties: 0.0. COG(C(X)): centroid of the phenylene ring containing C(X). Equivalent atoms were generated by the symmetry operator $x-1, y, z$.

[Li(thf)₄][2^HH]

Orange single crystals of [Li(thf)₄][2^HH] were grown by gas-phase diffusion of hexane into a concentrated THF solution of Li[2^HH] (3 d, room temperature).

In one thf ligand of [Li(thf)₄][2^HH], one CH₂ group is disordered over two positions with a site occupation factor of 0.70(2) for the major occupied site. In two thf ligands, two CH₂ groups are disordered over two positions with site occupation factors of 0.55(3) or 0.66(3) for the major occupied sites. In one thf ring, all CH₂ groups are disordered over two positions with a site occupation factor of 0.530(12) for each major occupied site. The displacement ellipsoids of all atoms constituting the [Li(thf)₄]⁺ cation were restrained to an isotropic behavior.

The H atom bonded to the B atoms was freely refined.

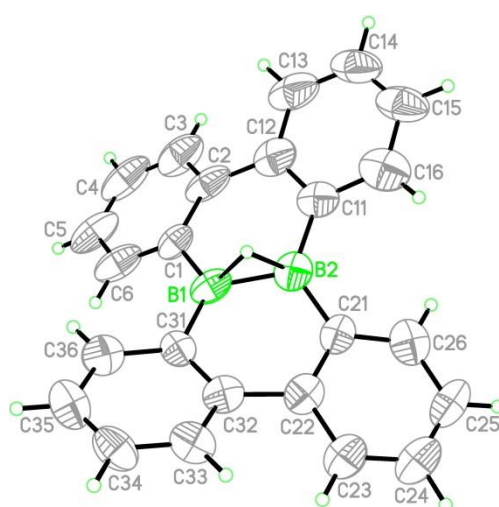


Figure S40: Molecular structure of [Li(thf)₄][2^HH] in the solid state. The solvent-separated [Li(thf)₄]⁺ cation is omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å], and torsion angles [°]: B(1)–B(2) = 1.619(9), B(1)–H(1) = 1.25(7), B(2)–H(1) = 1.16(7), B(1)–C(1) = 1.552(8), B(1)–C(31) = 1.598(8), B(2)–C(11) = 1.559(8), B(2)–C(21) = 1.567(8); C(1)–B(1)–B(2)–C(11) = 21.8(6), C(31)–B(1)–B(2)–C(21) = 21.7(6), C(1)–C(2)–C(12)–C(11) = 19.4(7), C(21)–C(22)–C(32)–C(31) = 22.4(7).

Table S1. Selected crystallographic data for $\{[K_{1.5}(\text{thf})_{3.5}][\mathbf{3}_{1.5}]\}_2$, $K(\text{thf})_2[\mathbf{3a}]$, $K[\mathbf{7}]$, and $[\text{Li}(\text{thf})_4][\mathbf{2}^{\text{H}}\text{H}]$.

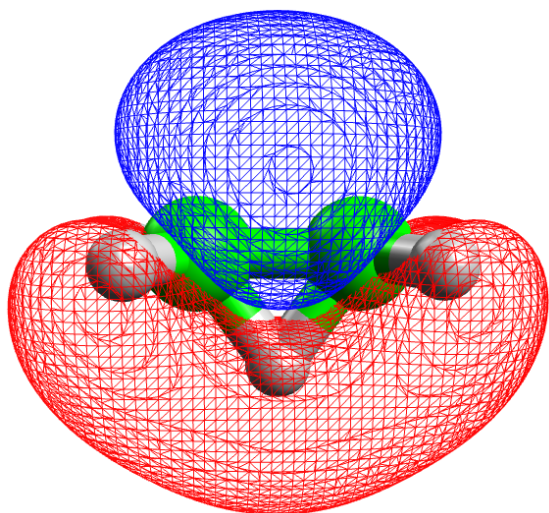
	$\{[K_{1.5}(\text{thf})_{3.5}][\mathbf{3}_{1.5}]\}_2$	$K(\text{thf})_2[\mathbf{3a}]$	$K[\mathbf{7}]$	$[\text{Li}(\text{thf})_4][\mathbf{2}^{\text{H}}\text{H}]$
formula	$\text{C}_{208}\text{H}_{278}\text{B}_9\text{K}_3\text{O}_7$	$\text{C}_{68}\text{H}_{90}\text{B}_3\text{KO}_2$	$\text{C}_{26}\text{H}_{34}\text{BK}$	$\text{C}_{40}\text{H}_{49}\text{B}_2\text{LiO}_4$
<i>M</i>	3104.88	1010.92	396.44	622.35
color, shape	colorless, block	colorless, block	colorless, block	orange, plate
<i>T</i> [K]	173(2)	173(2)	173(2)	173(2)
radiation, λ [Å]	MoK α , 0.71073	MoK α , 0.71073	MoK α , 0.71073	MoK α , 0.71073
crystal system	monoclinic	triclinic	triclinic	orthorhombic
space group	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>Pbca</i>
<i>a</i> [Å]	25.3076(5)	13.3225(7)	6.3711(3)	17.8756(14)
<i>b</i> [Å]	20.8846(6)	22.0531(11)	13.9000(8)	19.8294(11)
<i>c</i> [Å]	37.9056(7)	23.8906(11)	14.3367(8)	20.1619(11)
α [°]	90	112.197(4)	106.606(4)	90
β [°]	98.174(2)	101.377(4)	97.326(5)	90
γ [°]	90	92.082(4)	95.101(4)	90
<i>V</i> [Å ³]	19831.1(8)	6323.5(6)	1196.21(11)	7146.6(8)
<i>Z</i>	4	4	2	8
<i>D</i> _{calcd} [g cm ⁻³]	1.040	1.062	1.101	1.157
μ [mm ⁻¹]	0.121	0.125	0.230	0.071
F(000)	6736	428	428	2672
crystal size [mm]	0.26 x 0.25 x 0.23	0.29 x 0.27 x 0.27	0.29 x 0.27 x 0.27	0.19 x 0.12 x 0.04
rflns collected	90961	2192	21106	64192
independent rflns (<i>R</i> _{int})	18282 (0.0590)	23718 (0.0833)	4477 (0.0262)	6745 (0.1684)
data/restraints/parameters	18282 / 319 / 1263	23718 / 168 / 1472	4477 / 72 / 311	6745 / 180 / 513
GOF on <i>F</i> ²	1.186	1.063	1.162	1.224
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.1097, 0.2863	0.0948, 0.1724	0.0627, 0.1440	0.1364, 0.2356
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1346, 0.3093	0.1922, 0.2196	0.0701, 0.1486	0.2134, 0.2678
largest diff peak and hole [e Å ⁻³]	1.038, -0.502	0.844, -0.435	0.328, -0.464	0.299, -0.153

4. Computational details

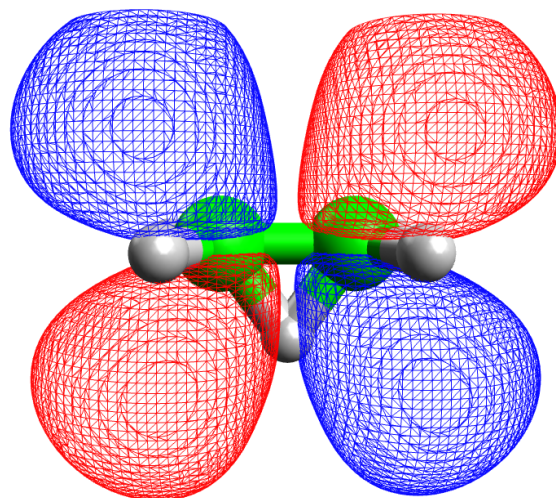
DFT calculations were carried out with the Gaussian program package.^[S10] The PBE0^[S11–S14] hybrid functional was used and combined with the D3BJ atom-pairwise dispersion correction with Becke-Johnson damping as devised by Grimme.^[S15,S16] Geometry optimizations and harmonic frequency calculations were generally computed with the SMD solvation model^[S17] (to account for effects of the THF solvent) using the TZVP basis set.^[S18] For the B₃ cluster isomers, [2H·1]⁻, [3]⁻, and [3a]⁻, geometry optimizations and harmonic frequency calculations were computed under gas-phase conditions with the TZVP basis set^[S18] followed by single point calculations with the SMD solvation model^[S17]. All Gibbs free energies reported correspond to the total energies of the system calculated with the SMD solvation model^[S17], corrected by thermal contributions from the frequency analyses. All stationary points reported were characterized as minima or first order saddle points by eigenvalue analysis of the diagonalized Hessians. The graphics were produced with Avogadro 1.1.1.

non-classical $[\text{B}_2\text{H}_5]^-$

HOMO



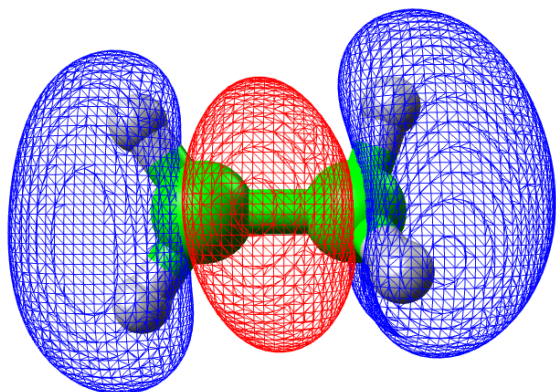
LUMO



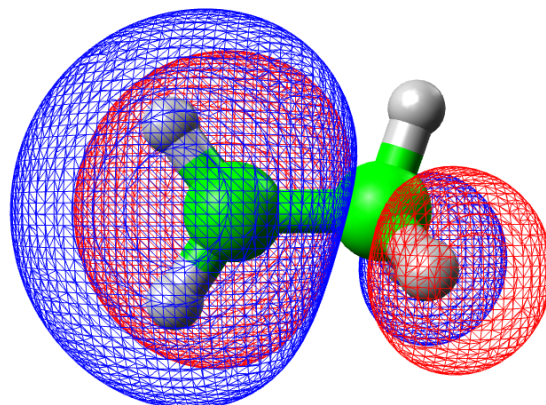
H	-1.46490	1.02428	-0.03605
H	-1.46490	-1.02428	-0.03605
B	-0.80814	0.00000	-0.08769
H	1.46490	1.02428	-0.03604
H	1.46490	-1.02428	-0.03605
B	0.80814	0.00000	-0.08769
H	-0.00000	-0.00000	1.02106

classical $[\text{B}_2\text{H}_5]^-$

HOMO



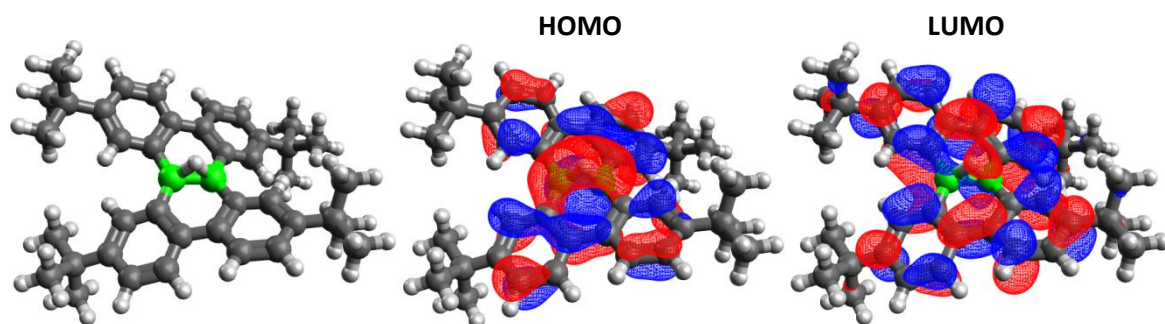
LUMO



H	-1.21115	-0.60225	0.99103
H	-1.21115	-0.60226	-0.99102
B	-0.79502	0.01093	-0.00000
H	-1.19991	1.17818	-0.00000
B	0.88671	0.00095	-0.00000
H	1.55871	-1.01950	0.00000
H	1.60502	0.98642	0.00000

[2H]⁻

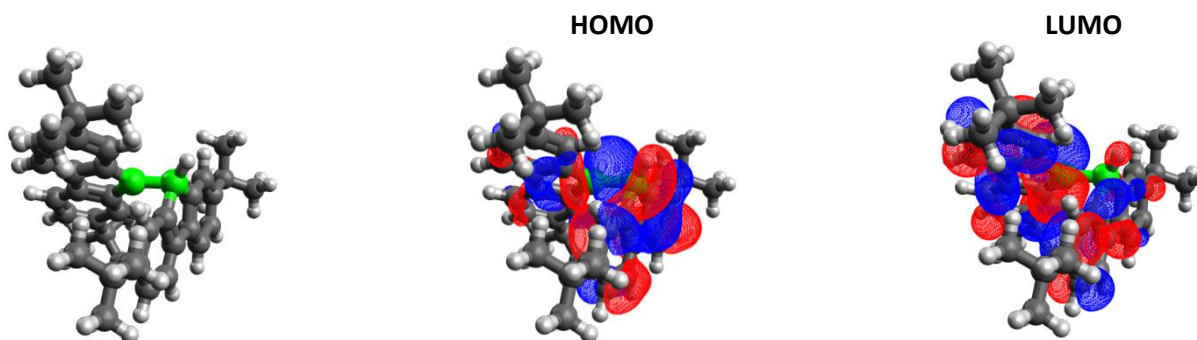
Gibbs free energy = -1602.32949113 Hartree



C	2.74183	-1.58888	0.65022	H	-3.18992	-4.69012	-1.51347	H	4.00206	-2.98366	3.62665
C	3.30481	-2.81116	0.97716	H	-3.47888	-0.52747	-0.64646	C	5.41402	-1.61362	1.71672
C	2.52023	-3.94961	0.76010	H	0.84686	4.65576	-0.88171	H	6.40788	-1.77182	2.14393
C	1.23410	-3.83480	0.27757	H	3.19793	4.73704	-1.38437	H	4.86952	-0.93585	2.37892
C	0.65410	-2.59626	-0.04313	H	3.50172	0.55359	-0.62224	H	5.54081	-1.11919	0.75082
C	1.44690	-1.42690	0.11370	H	-3.30802	0.66844	0.83564	C	5.55232	-3.84774	0.65596
C	-0.76671	-2.54930	-0.43996	H	-2.89297	4.90138	1.14591	H	5.64654	-3.40407	-0.33884
C	-1.53779	-1.35476	-0.35662	H	-0.62674	4.729j20	0.36519	H	5.11164	-4.84036	0.54157
B	-0.80997	0.01411	-0.09811	C	-4.72358	2.82263	1.58101	H	6.55660	-3.97081	1.07297
B	0.83131	-0.00934	-0.09429	C	-4.81315	1.96432	2.84777	C	-5.04446	-2.59497	-1.35265
C	-1.40783	-3.71400	-0.88500	H	-4.54929	0.92414	2.64604	C	-5.55987	-3.96162	-1.79586
C	-2.75974	-3.75515	-1.17491	H	-5.83146	1.98285	3.24835	H	-5.07306	-4.29708	-2.71524
C	-3.54837	-2.61139	-1.05346	H	-4.13444	2.33957	3.61821	H	-6.63415	-3.90227	-1.98956
C	-2.90220	-1.44425	-0.66424	C	-5.68693	2.26451	0.52676	H	-5.40096	-4.72145	-1.02632
C	-1.43131	1.42147	0.15188	H	-5.43807	1.23408	0.26543	C	-5.80529	-2.18235	-0.08697
C	-0.63627	2.59872	0.04162	H	-5.64823	2.86105	-0.38849	H	-5.62290	-2.89268	0.72381
C	0.78532	2.56196	-0.35361	H	-6.71439	2.27864	0.90344	H	-6.88183	-2.15119	-0.28149
C	1.55714	1.37028	-0.30821	C	-5.16831	4.24063	1.92970	H	-5.49606	-1.19392	0.25888
C	1.42234	3.74459	-0.76709	H	-4.53187	4.68537	2.69905	C	-5.34017	-1.58525	-2.46757
C	2.76690	3.79323	-1.06550	H	-6.19157	4.21900	2.31410	H	-4.80764	-1.85331	-3.38378
C	3.56231	2.64516	-0.98317	H	-5.15523	4.89479	1.05401	H	-5.03694	-0.57475	-2.18628
C	2.92606	1.46880	-0.61944	C	5.04424	2.71923	-1.33463	H	-6.41225	-1.56613	-2.68678
C	-2.72622	1.56864	0.67703	C	5.72873	3.75781	-0.43841	H	5.64128	3.47711	0.61447
C	-3.29894	2.78200	1.03546	C	5.20004	3.13890	-2.80115	H	5.28648	4.74880	-0.56049
C	-2.51376	3.92366	0.87468	H	6.25950	3.20760	-3.06675	H	6.79205	3.83097	-0.68653
C	-1.21727	3.82143	0.40257	H	4.74154	4.11198	-2.99062	C	5.75475	1.38323	-1.13882
H	0.01228	0.01875	-1.15020	H	4.72735	2.40904	-3.46362	H	6.81334	1.49141	-1.38964
H	3.31627	-0.69302	0.84194	C	4.70297	-2.95548	1.56849	H	5.68948	1.04580	-0.10159
H	2.90229	-4.93575	1.00360	C	4.60267	-3.60264	2.95501	H	5.33853	0.60194	-1.77965
H	0.64526	-4.74082	0.19735	H	5.59842	-3.71896	3.39389				
H	-0.83643	-4.62341	-1.03036	H	4.13931	-4.59036	2.90414				

[2aH⁺]⁻

Gibbs free energy = -1602.32141377 Hartree



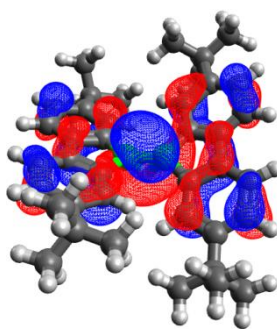
C	-1.75230	1.75530	-0.70783	H	-5.37093	0.73608	-1.70079	H	-4.43386	4.48559	0.85989
C	-1.99200	0.79106	-1.71351	H	-3.47340	-0.32561	-2.82296	H	-4.39832	3.22357	2.10033
C	-0.73706	0.23489	-2.19949	H	1.02520	-3.19579	3.05524	H	-5.90451	4.07827	1.75133
C	0.37031	0.84439	-1.54417	H	-1.21350	-4.11460	2.69428	C	-3.30737	-3.03663	1.20496
B	-0.19018	1.86531	-0.41109	H	-2.25924	-0.70878	0.31103	C	-4.35048	-2.02920	1.70185
C	-0.53209	-0.77061	-3.13250	H	2.88547	2.25618	0.59210	H	-4.24814	-1.86219	2.77757
C	0.76096	-1.20326	-3.42010	H	5.15710	-0.54388	2.91425	H	-5.36078	-2.40261	1.50767
C	1.87025	-0.63641	-2.79156	H	3.20295	-2.00106	3.10430	H	-4.24628	-1.06668	1.19810
C	1.64677	0.38654	-1.86731	C	3.29949	-1.11801	-3.02294	C	-3.48740	-3.23556	-0.30534
C	-2.86055	2.34068	-0.09027	C	3.86263	-1.64484	-1.69571	H	-4.48807	-3.62368	-0.52010
C	-4.16924	1.99729	-0.42680	H	4.88838	-2.00212	-1.83248	H	-2.75254	-3.94645	-0.69252
C	-4.36355	1.02841	-1.42301	H	3.25556	-2.47372	-1.32255	H	-3.36579	-2.29468	-0.84596
C	-3.29150	0.42868	-2.06198	H	3.87171	-0.86895	-0.92700	C	-3.55377	-4.37194	1.90064
C	1.84890	0.50277	1.21325	C	3.37689	-2.23682	-4.05788	H	-3.46281	-4.28528	2.98677
C	1.93759	-0.70630	1.92663	H	2.80991	-3.11663	-3.74288	H	-2.85623	-5.14086	1.55792
C	0.66078	-1.43855	1.85970	H	4.41846	-2.54218	-4.18978	H	-4.56638	-4.71830	1.67755
C	-0.27253	-0.72755	1.07256	H	2.99726	-1.91407	-5.03113	C	5.43951	1.82168	1.60914
B	0.38723	0.63882	0.59070	C	4.16907	0.04775	-3.50792	C	6.54050	1.00326	0.92348
C	0.31692	-2.64508	2.44274	H	4.18532	0.86395	-2.78224	H	6.79472	0.10961	1.49748
C	-0.96289	-3.16454	2.23768	H	3.79315	0.44606	-4.45432	H	7.44865	1.60411	0.81566
C	-1.90763	-2.49007	1.46849	H	5.19996	-0.28631	-3.66156	H	6.22046	0.68370	-0.07201
C	-1.53981	-1.25933	0.90629	C	-5.38709	2.62039	0.25179	C	5.91671	2.24258	3.00370
C	2.96591	1.32495	1.14183	C	-6.26639	3.30809	-0.79935	H	6.82342	2.85046	2.92723
C	4.18136	0.96659	1.73125	H	-5.71002	4.09687	-1.31251	H	6.14419	1.37602	3.62824
C	4.23027	-0.23845	2.43929	H	-7.14271	3.76047	-0.32461	H	5.15060	2.83328	3.51277
C	3.12262	-1.07088	2.54921	H	-6.61981	2.60163	-1.55362	C	5.20185	3.08229	0.78191
H	0.35440	2.95268	-0.30822	C	-6.20188	1.52396	0.94773	H	4.44131	3.72539	1.23154
H	-1.37375	-1.23891	-3.63577	H	-6.54232	0.76556	0.23930	H	4.88677	2.84221	-0.23678
H	0.89263	-2.00397	-4.13795	H	-7.08384	1.95519	1.43167	H	6.12988	3.65659	0.71822
H	2.49868	0.82329	-1.36003	H	-5.60191	1.02369	1.71213				
H	-2.68793	3.07554	0.68906	C	-5.00012	3.66087	1.29988				

[2aH]⁻

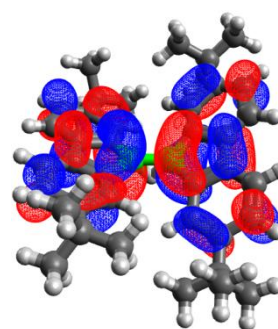
Gibbs free energy = -1602.31890598 Hartree



HOMO



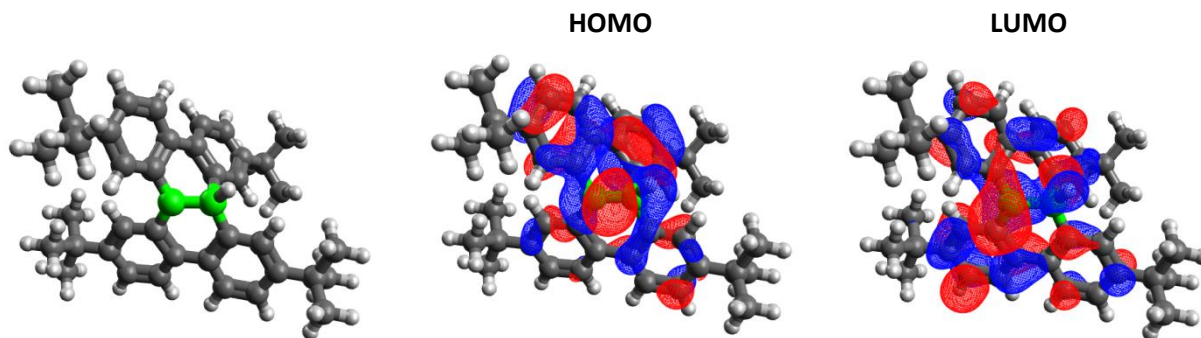
LUMO



C	1.08153	1.88079	-0.07117	H	3.06218	4.92891	-1.44547	H	-4.90985	-2.04479	0.96417
C	0.44675	3.12016	-0.31336	H	0.66888	5.15631	-0.99284	C	-5.04889	-1.49246	-1.75488
C	-0.98433	3.04888	-0.01185	H	-0.53969	-5.03705	-1.41575	H	-4.61264	-1.43896	-2.75562
C	-1.34732	1.74290	0.37967	H	-2.95864	-4.89123	-1.73948	H	-4.70707	-0.61890	-1.19743
B	-0.06032	0.81775	0.25616	H	-2.96499	-0.93455	-0.10826	H	-6.13645	-1.42141	-1.85051
C	-1.92281	4.07347	-0.03897	H	2.84912	-0.58644	1.34900	C	5.29315	-3.53250	2.40523
C	-3.22314	3.81853	0.36937	H	4.02556	-4.53150	0.16553	H	4.54554	-3.61376	3.19868
C	-3.60923	2.55299	0.82646	H	1.78911	-4.95108	-0.72878	H	6.27280	-3.39239	2.87206
C	-2.65424	1.53473	0.82206	C	-4.66544	-2.80646	-1.06523	H	5.31571	-4.48096	1.86541
C	2.44173	1.77820	-0.36936	C	4.97872	-2.35052	1.48009	C	6.03588	-2.28770	0.37140
C	3.17902	2.85617	-0.86295	C	-5.04398	2.33897	1.30320	H	6.03179	-3.20064	-0.22887
C	2.51605	4.07300	-1.06229	C	4.66099	2.75417	-1.21709	H	7.03548	-2.16787	0.80111
C	1.16212	4.20755	-0.80126	C	-5.27731	0.92483	1.82579	H	5.84626	-1.44436	-0.29678
C	1.35786	-1.71990	0.31874	H	-5.11544	0.17769	1.04657	C	5.06976	-1.07724	2.31812
C	1.04733	-2.98950	-0.21208	H	-6.31129	0.82669	2.16681	H	4.91493	-0.17796	1.72004
C	-0.37905	-3.07766	-0.53440	H	-4.62149	0.68876	2.66747	H	6.06390	-1.00710	2.76743
C	-1.05790	-1.89006	-0.15818	C	-5.36628	3.32285	2.43371	H	4.33271	-1.07684	3.12527
B	0.05456	-0.82015	0.23079	H	-4.69197	3.17199	3.28079	C	5.21515	1.35163	-0.99085
C	-1.06485	-4.13689	-1.10887	H	-6.39296	3.17582	2.78284	H	5.14255	1.05893	0.05792
C	-2.44097	-4.05042	-1.29433	H	-5.26847	4.36010	2.10700	H	6.27166	1.32441	-1.27118
C	-3.14863	-2.90766	-0.92121	C	-6.00716	2.58022	0.13455	H	4.68859	0.60446	-1.58962
C	-2.43061	-1.83923	-0.37005	H	-5.80435	1.88355	-0.68320	C	4.86011	3.10927	-2.69541
C	2.62708	-1.53043	0.86567	H	-5.91360	3.59521	-0.25754	H	4.29583	2.42550	-3.33467
C	3.59926	-2.53187	0.84915	H	-7.04277	2.43634	0.45820	H	5.91854	3.03498	-2.96378
C	3.28195	-3.74364	0.22300	C	-5.25130	-3.95306	-1.88649	H	4.52827	4.12609	-2.91437
C	2.01743	-3.98125	-0.29552	H	-4.82093	-3.98831	-2.89083	C	5.46394	3.73169	-0.35119
H	-0.01405	-0.02016	1.34379	H	-6.33092	-3.81359	-1.98801	H	5.34706	3.49348	0.70937
H	-1.64637	5.07494	-0.35658	H	-5.08875	-4.92248	-1.40905	H	5.13687	4.76268	-0.50253
H	-3.94599	4.62768	0.34841	C	-5.29428	-2.84814	0.33310	H	6.52832	3.67520	-0.59983
H	-2.93051	0.55581	1.19446	H	-5.06989	-3.79687	0.82796				
H	2.92959	0.82137	-0.23726	H	-6.38192	-2.74237	0.26920				

[2H⁺]⁻

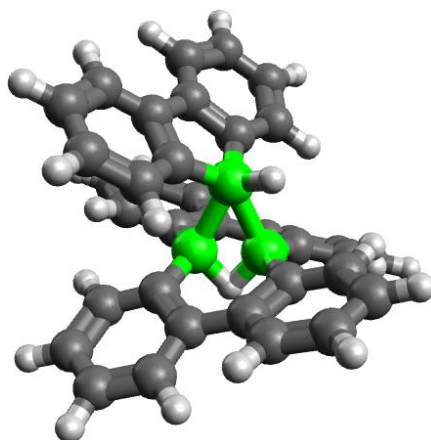
Gibbs free energy = -1602.31389682 Hartree



C	2.01436	-1.60357	0.72303	H	-4.44504	-3.92999	-0.85658	H	2.94401	-1.34228	4.12116
C	2.24035	-2.52566	1.74140	H	-3.46115	0.13994	-1.74417	C	4.60090	-1.62286	1.95589
C	1.18727	-3.37587	2.08070	H	2.45727	3.83169	0.07893	H	5.53500	-1.73614	2.51302
C	-0.02886	-3.28259	1.42591	H	4.61053	3.41658	-0.89360	H	4.26116	-0.59129	2.07571
C	-0.24228	-2.35630	0.40256	H	3.23238	-0.39292	-2.26749	H	4.81916	-1.78551	0.89730
C	0.80813	-1.49367	0.02021	H	-2.92566	1.12585	0.47881	C	4.14690	-4.03400	2.31089
C	-1.57360	-2.23777	-0.23491	H	-1.13596	4.61864	2.16330	H	4.32162	-4.25599	1.25478
C	-1.92516	-0.98325	-0.78013	H	0.96440	4.01314	1.19614	H	3.46880	-4.79340	2.70638
B	-0.77634	0.07301	-0.77267	C	-3.59267	3.28314	1.98555	H	5.09961	-4.12260	2.84214
B	0.71771	-0.43673	-1.26133	C	-4.00044	2.16942	2.95768	C	-5.50911	-1.60898	-1.98331
C	-2.49569	-3.27424	-0.28161	H	-4.06743	1.20360	2.45218	C	-6.41265	-2.83706	-1.91198
C	-3.75899	-3.09206	-0.84148	H	-4.97751	2.38947	3.39888	H	-5.99205	-3.68064	-2.46531
C	-4.13478	-1.86369	-1.37221	H	-3.27203	2.07498	3.76725	H	-7.38458	-2.60113	-2.35323
C	-3.19350	-0.82777	-1.32798	C	-4.64215	3.38588	0.87299	H	-6.58245	-3.15400	-0.87972
C	-0.87251	1.40742	0.02091	H	-4.73275	2.44779	0.32165	C	-6.19630	-0.46369	-1.22967
C	0.27120	2.23238	0.18521	H	-4.37711	4.17208	0.16125	H	-6.32580	-0.71668	-0.17398
C	1.57560	1.92739	-0.45791	H	-5.62245	3.62289	1.29745	H	-7.18314	-0.26491	-1.65866
C	1.81165	0.71778	-1.15146	C	-3.56861	4.60511	2.74762	H	-5.61428	0.45849	-1.28476
C	2.61120	2.87581	-0.40723	H	-2.86533	4.57709	3.58386	C	-5.34644	-1.21638	-3.45640
C	3.84768	2.64905	-0.97679	H	-4.56177	4.81007	3.15573	H	-4.86550	-2.02040	-4.01961
C	4.11448	1.45661	-1.65618	H	-3.29542	5.44046	2.09732	H	-4.73542	-0.31817	-3.56556
C	3.07518	0.54048	-1.73781	C	5.49911	1.20669	-2.24328	H	-6.32385	-1.01836	-3.90705
C	-2.07843	1.79128	0.61471	C	6.53069	1.20919	-1.10855	H	6.30347	0.42615	-0.38000
C	-2.23820	2.94502	1.37381	C	5.84619	2.31589	-3.24264	H	6.54283	2.16529	-0.58055
C	-1.09582	3.72110	1.55724	H	6.84392	2.15128	-3.66120	H	7.53457	1.02885	-1.50559
C	0.11869	3.37004	0.98802	H	5.83878	3.30037	-2.76999	C	5.59006	-0.13425	-2.96657
H	0.84895	-1.12230	-2.27526	H	5.12820	2.33268	-4.06679	H	6.59758	-0.26217	-3.37173
H	2.81415	-0.93346	0.43454	C	3.57223	-2.62270	2.48002	H	5.39175	-0.97054	-2.29166
H	1.30218	-4.10522	2.87621	C	3.34940	-2.34619	3.97123	H	4.88365	-0.19332	-3.79824
H	-0.84310	-3.92842	1.74004	H	4.29518	-2.41970	4.51718				
H	-2.23640	-4.25129	0.11437	H	2.64976	-3.06079	4.41040				

[2H·1]⁻

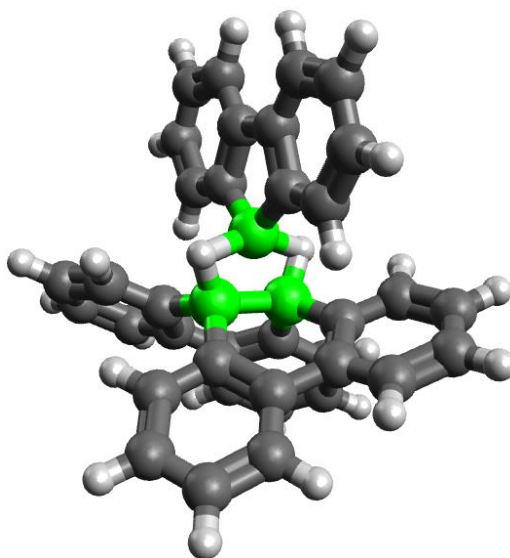
Gibbs free energy = -1461.03432325 Hartree



C	2.09480	-2.66389	-1.74504	C	-2.50662	2.04285	2.28764	C	-0.73724	3.87163	-1.48677
C	3.30573	-2.90201	-2.36970	C	-3.48317	1.06080	2.37766	C	1.57568	2.33731	-1.21523
C	4.42916	-2.20203	-1.95045	C	-3.18519	-0.23628	2.00424	C	1.66025	3.72061	-1.33508
C	4.31237	-1.28886	-0.92042	H	1.21422	-3.15417	-2.14233	C	0.50545	4.48938	-1.45644
C	3.09704	-1.05937	-0.25312	H	5.38523	-2.34219	-2.44343	C	-2.69808	-0.64378	-1.59979
C	1.94820	-1.76597	-0.68043	H	5.18776	-0.70919	-0.65660	C	-4.00403	-0.23304	-1.85112
C	3.07021	-0.04106	0.82991	H	5.18784	-0.22201	1.19388	C	-4.31944	1.12189	-1.89811
C	1.87950	0.60334	1.25152	H	5.30732	1.51854	2.88628	C	-3.32053	2.07089	-1.72588
B	0.50870	-1.39275	-0.12880	H	1.08739	2.04726	2.62209	H	-2.47735	-1.70499	-1.56242
C	4.27850	0.30507	1.45359	H	-3.34431	-2.73514	2.28847	H	-5.34098	1.43636	-2.08688
C	4.35246	1.28278	2.42847	H	-3.26452	-5.02700	1.48555	H	-3.55985	3.12804	-1.79613
C	3.19423	1.93311	2.82849	H	0.13489	-4.06548	-0.89395	H	-1.63708	4.46838	-1.60334
C	1.98681	1.57233	2.25494	H	-0.52228	2.48590	1.67558	H	0.57784	5.56906	-1.53966
C	-0.91417	0.39043	1.45538	H	-4.48659	1.30843	2.70759	H	2.48721	1.76001	-1.10855
C	-1.91325	-0.61003	1.54427	H	-3.98948	-0.96033	2.01569	H	0.40723	-0.48334	-2.04295
C	-1.70977	-2.01071	1.08723	B	-0.10167	0.13769	-1.13069	H	2.63195	4.20462	-1.33134
C	-0.68050	-2.40170	0.18461	B	0.46365	0.06438	0.77279	H	-4.78264	-0.97287	-2.01065
C	-2.60084	-2.99250	1.54501	C	-1.68555	0.28456	-1.37593	H	3.22625	2.69342	3.60190
C	-2.55366	-4.30195	1.10361	C	0.34103	1.69493	-1.21499	H	3.36689	-3.60088	-3.19738
C	-1.58023	-4.67735	0.18963	H	0.70230	-1.15821	1.13952	H	-1.51895	-5.70118	-0.16430
C	-0.65590	-3.73645	-0.23352	C	-2.01589	1.65110	-1.48258	H	-2.73344	3.07287	2.54226
C	-1.25079	1.69828	1.82220	C	-0.81664	2.48528	-1.37805				

[3]⁻

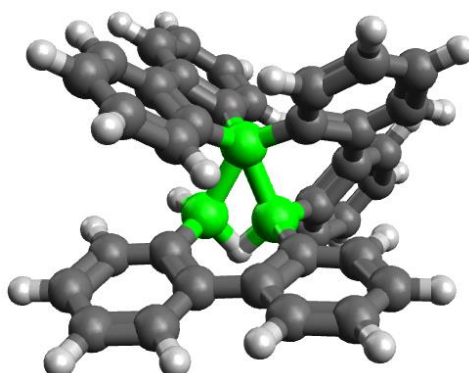
Gibbs free energy = -1461.03381702 Hartree



C	0.13065	2.53288	-2.10113	C	0.26442	-3.90443	2.24924	C	-2.01055	2.56609	0.52321
C	0.25606	3.90507	-2.25003	C	0.93032	-4.62875	1.27115	C	-3.11518	3.39076	0.71759
C	0.91918	4.63109	-1.27132	C	1.46946	-3.96605	0.18163	C	-4.40354	2.88034	0.61683
C	1.45926	3.96973	-0.18144	H	-0.43504	1.97195	-2.84043	C	-2.00438	-2.57132	-0.52418
C	1.36334	2.57891	-0.04448	H	0.99918	5.71121	-1.34353	C	-3.10704	-3.39861	-0.71863
C	0.66436	1.83969	-1.01224	H	1.92976	4.55433	0.60100	C	-4.39662	-2.89129	-0.61788
C	1.94564	1.91301	1.14066	H	3.41407	3.45905	1.41395	C	-4.59244	-1.54701	-0.33081
C	1.47201	0.66831	1.60337	H	4.38680	2.51242	3.45046	H	-1.00962	-2.99082	-0.60746
B	0.39275	0.27123	-0.85886	H	1.72774	-0.81293	3.12576	H	-5.25116	-3.54384	-0.76896
C	3.00213	2.53976	1.81450	H	3.42463	-3.45006	-1.41097	H	-5.59931	-1.14554	-0.26450
C	3.56518	2.00262	2.95710	H	4.39755	-2.50092	-3.44628	H	-5.60203	1.13168	0.26347
C	3.07756	0.80045	3.44745	H	1.72874	0.81703	-3.12552	H	-5.25964	3.53081	0.76796
C	2.06422	0.15140	2.76171	H	-0.43235	-1.97319	2.83904	H	-1.01677	2.98790	0.60652
C	0.66812	-1.83810	1.01163	H	1.01325	-5.70863	1.34358	H	-2.96606	4.44098	0.94797
C	1.36984	-2.57552	0.04452	H	1.94227	-4.54939	-0.60036	H	-2.95538	-4.44847	-0.94904
C	1.95161	-1.90804	-1.13988	B	-1.14914	-0.00158	-0.00014	H	3.50274	0.35461	4.34144
C	1.47507	-0.66468	-1.60326	B	0.39328	-0.27041	0.85766	H	-0.18713	4.40733	-3.10415
C	3.01071	-2.53196	-1.81221	C	-2.17495	-1.22736	-0.21850	H	3.50862	-0.34567	-4.33864
C	3.57382	-1.99341	-2.95408	C	-2.17792	1.22172	0.21752	H	-0.17801	-4.40783	3.10308
C	3.08351	-0.79263	-3.44518	C	-3.48816	-0.72479	-0.14060	H	-0.72064	0.09498	-1.43915
C	2.06742	-0.14631	-2.76087	C	-3.48990	0.71603	0.13946	H	-0.72133	-0.09676	1.43703
C	0.13541	-2.53259	2.10016	C	-4.59614	1.53561	0.32972				

[3a]⁻

Gibbs free energy = -1461.034323252 Hartree



B	0.28444	0.66591	0.18601	C	-2.74754	-1.33068	-0.96145	H	5.67581	-1.15200	-2.13544
B	-0.75049	0.30738	-1.45846	C	-4.12399	-1.59119	-1.05947	C	3.68048	-1.16535	-2.93953
B	0.32601	-0.91445	-0.97232	H	-4.52437	-2.54940	-0.75477	C	2.32537	-1.11030	-2.63740
C	1.12529	1.99815	-0.24672	C	-5.01219	-0.65476	-1.55593	H	1.60371	-1.13896	-3.44911
C	0.38680	3.14424	0.12020	H	-6.06910	-0.89402	-1.61059	C	1.11020	-0.18061	1.33269
C	0.85987	4.43080	-0.11896	C	-4.54618	0.58146	-1.98881	C	2.33438	-0.83936	1.08686
H	0.27356	5.29786	0.17127	C	-3.18839	0.83703	-1.93382	C	3.05580	-1.41609	2.13352
C	2.09327	4.60263	-0.73384	H	-2.80853	1.79268	-2.28204	H	3.97721	-1.94548	1.91382
H	2.47209	5.60121	-0.92645	C	-0.42528	-2.19686	-0.41143	C	2.59870	-1.36093	3.44010
C	2.83886	3.48773	-1.10048	C	-1.83343	-2.33565	-0.36922	H	3.16812	-1.82317	4.23949
C	2.36095	2.20178	-0.85566	C	-2.37245	-3.46839	0.26417	C	1.39674	-0.72142	3.70152
H	2.96616	1.35666	-1.15881	H	-3.44467	-3.57665	0.36117	C	0.67726	-0.14721	2.66070
C	-1.02522	1.38150	0.82404	C	-1.57727	-4.46411	0.79741	H	-0.25342	0.35498	2.89385
C	-0.88494	2.77760	0.74782	H	-2.03670	-5.31813	1.28392	H	-0.18059	-0.64430	-2.16264
C	-1.86847	3.63366	1.24128	C	-0.19518	-4.36022	0.70513	H	-0.48820	1.29306	-2.08655
H	-1.75244	4.71104	1.16936	C	0.35196	-3.24005	0.10765	H	4.00629	-1.23412	-3.97212
C	-3.00203	3.09791	1.83559	H	1.43080	-3.15099	0.05236	H	1.01390	-0.66668	4.71577
H	-3.77465	3.75483	2.22186	C	1.87038	-1.01130	-1.32289	H	0.44629	-5.13805	1.10593
C	-3.14540	1.71581	1.94128	C	2.82336	-0.97237	-0.29435	H	-5.23408	1.32545	-2.37663
C	-2.16440	0.86967	1.43946	C	4.18442	-1.03023	-0.59754	H	-4.03024	1.29990	2.41272
H	-2.29949	-0.20392	1.51886	H	4.91680	-0.96144	0.19971	H	3.80368	3.61951	-1.58102
C	-2.26918	-0.08959	-1.42945	C	4.61449	-1.12402	-1.91251				

5. References

- [S1] A. Hübner, M. Diefenbach, M. Bolte, H.-W. Lerner, M. C. Holthausen, M. Wagner, *Angew. Chem. Int. Ed.* **2012**, *51*, 12514–12518; *Angew. Chem.* **2012**, *124*, 12682–12686.
- [S2] A. Hübner, A. M. Diehl, M. Bolte, H.-W. Lerner, M. Wagner, *Organometallics* **2013**, *32*, 6827–6833.
- [S3] T. Kaese, H. Budy, M. Bolte, H.-W. Lerner, M. Wagner, *Angew. Chem. Int. Ed.* **2017**, *56*, 7546–7550; *Angew. Chem.* **2017**, *129*, 7654–7658.
- [S4] T. Kaese, A. Hübner, M. Bolte, H.-W. Lerner, M. Wagner, *J. Am. Chem. Soc.* **2016**, *138*, 6224–6233.
- [S5] A. Hübner, M. Bolte, H.-W. Lerner, M. Wagner, *Angew. Chem. Int. Ed.* **2014**, *53*, 10408–10411; *Angew. Chem.* **2014**, *126*, 10576–10579.
- [S6] T. Kaese, T. Trageser, H. Budy, M. Bolte, H.-W. Lerner, M. Wagner, *Chem. Sci.* **2018**, *9*, 3881–3891.
- [S7] T. Trageser, M. Bolte, H.-W. Lerner, M. Wagner, 2019, Private communication to the Cambridge Structural Database; deposition number: CCDC 1971556.
- [S8] Stoe & Cie, *X-AREA. Diffractometer control program system*. Stoe & Cie, Darmstadt, Germany, **2002**.
- [S9] G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112–122.
- [S10] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, 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, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09, Revision D.01*, Gaussian, Inc., Wallingford, CT, USA, **2013**.
- [S11] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- [S12] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1997**, *78*, 1396–1396.
- [S13] J. P. Perdew, M. Ernzerhof, K. Burke, *J. Chem. Phys.* **1996**, *105*, 9982–9985.
- [S14] C. Adamo, V. Barone, *J. Chem. Phys.* **1999**, *110*, 6158–6170.
- [S15] L. Goerigk, S. Grimme, *J. Chem. Theory Comput.* **2011**, *7*, 291–309.
- [S16] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456–1465.
- [S17] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378–6396.
- [S18] A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829–5835.