Supplementary Information (SI) for Chemical Science.

Electronic Supporting Information for

Synthesis of symmetrical and unsymmetrical cyclic diborenes via NHC-directed C–H borylation

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Contents

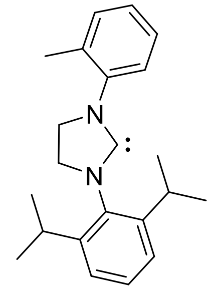
Methods and materials

All manipulations were performed either under an atmosphere of dry argon or in vacuo using standard Schlenk-line or glovebox techniques. The synthesized compounds were stored in a glovebox. Deuterated solvents were dried over molecular sieves and degassed *via* three freeze-pump-thaw cycles prior to use. All other solvents were distilled and degassed from appropriate drying agents. Both deuterated and non-deuterated solvents were stored under argon over activated 4 Å molecular sieves. Liquid-phase NMR spectra were acquired on a Bruker Avance 500 (^{1}H: 500.1 MHz, ^{11}B: 160.5 MHz, ^{13}C: 125.8 MHz), Bruker Avance Neom I 600 (^{1}H: 600.2 MHz, ^{11}B: 192.7 MHz, ^{13}C: 150.9 MHz, ^{13}C{^{11}B}: 276.0 MHz) or a Bruker Advance 400 (^{11}B: 128.5 MHz, ^{13}C: 100.7 MHz) NMR spectrometer. Chemical shifts (δ) are reported in ppm and internally referenced to the carbon nuclei (^{13}C{^{1}H}) (C_6D_6: 128.1; C_6D_5Br: 122.3, 126.3, 129.5, 131.1) or residual protons (^{1}H) (C_6D_6: 7.16; C_6D_5Br: 6.94, 7.01, 7.29) of the solvent. Heteronuclei NMR spectra are referenced to an external standard (^{11}B: $BF_3{\cdot}OEt_2$). Resonances are given as singlet (s), doublet (d), triplet (t), septet (sept), multiplet (m) or broad (br). High-resolution mass spectrometry (HRMS) data were obtained from a Thermo Scientific Exactive Plus spectrometer. UV-vis spectra were acquired on a METTLER TOLEDO UV-vis-Excellence UV5 spectrophotometer. Solid-state IR spectra were recorded on a Bruker FT-IR spectrometer ALPHA II inside a glovebox.

Solvents and reagents were purchased from Sigma-Aldrich, BLDpharm, ABCR or Alfa Aesar. 1-(2,6-diisopropylphenyl)-3-(2-methylphenyl)-imidazolinium chloride ([SIDippTolH]Cl),[1] $B_2Cl_4(SMe_2)_2$,[2] $B_2Br_4(SMe_2)_2$,[2] I*i*Pr[3] and KC_8[4] were synthesized according to reported procedures.

Synthetic procedures

Synthesis of 1-(2,6-diisopropylphenyl)-3-(2-methylphenyl)-imidazolin-ylidene (1)



1: SIDippTol

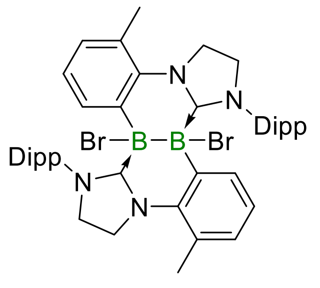
[SIDippTolH]Cl (3.5 g, 9.81 mmol, 1.00 equiv) was dissolved in ethanol (150 mL) and a solution of $NaBPh_4$ (3.69 g, 10.8 mmol, 1.10 equiv) in ethanol (150 mL) was added dropwise. A white precipitate formed, which was collected by filtration and dried *in vacuo*, yielding quantitatively [SIDippTolH]BPh_4 and was used without any further purification. A Schlenk tube was charged with [SIDippTolH]BPh_4 (6.0 g, 9.4 mmol, 1.00 equiv), KH (413.0 mg, 10.3 mmol, 1.10 equiv) and KO*t*Bu (53.0 mg, 470 µmol, 0.05 equiv). 30 mL THF was added and the resulting suspension was stirred at rt for 16 h. All volatiles were removed *in vacuo* and the resulting residue was extracted with warm hexane (4 x 60 mL). The solution was concentrated to around 50 mL. Cooling the concentrated solution to –78 °C afforded the carbene as a white powder (1.7 g, 5.3 mmol, 57%).

^{1}H NMR (500.1 MHz, C_6D_6): δ = 7.26 – 7.23 (m, 1H, H^{Dipp}), 7.15 – 7.13 (m, 3H, H^{Dipp}, H^{Tol}) 7.10 – 7.08 (m, 2H, H^{Tol}), 7.00 – 6.97 (m, 1H, H^{Tol}), 3.42 – 3.38 (m, 2H, NCH_2), 3.32 – 3.27 (m, 2H, NCH_2), 3.21 (sept, 2H, ^3J = 6.9 Hz, C$H^{i\mathrm{Pr}}$), 2.63 (s, 3H, CH_3), 1.27 (d, 6H, ^3J = 6.9 Hz, C$H_3{}^{i\mathrm{Pr}}$), 1.23 (d, 6H, ^3J = 7.0 Hz, C$H_3{}^{i\mathrm{Pr}}$) ppm.

^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 245.6 (C^{Carbene}), 147.2 (C^{q}), 143.9 (C^{q}) 139.3 (C^{q}), 133.1 (C^{q}), 132.2 (C^{Tol}), 128.4 (C^{Dipp}), 126.5 (C^{Tol}), 124.7 (C^{Dipp}), 124.1 (C^{Dipp}), 122.7 (C^{Tol}), 53.5 (NCH$_2$), 50.6 (NCH$_2$), 28.8 (CH$^{i\mathrm{Pr}}$) 25.2 (CH$_3{}^{i\mathrm{Pr}}$), 23.9 (CH$_3{}^{i\mathrm{Pr}}$), 21.4 (CH$_3$) ppm.

HRMS (LIFDI): calcd. for $[C_{22}H_{29}N_2]^+$ = $[M + H]^+$: m/z = 321.2325; found: 321.2310.

Synthesis of diborane 2



2

To a solution of $B_2Br_4(SMe_2)_2$ (310.0 mg, 666 µmol, 1.00 equiv) in benzene (2 mL) a solution of SIDippTol (853.7 mg, 2.66 mmol, 4.00 equiv) in benzene (2 mL) was added dropwise and the mixture was stirred at rt for 16 h, resulting in a pale-yellow suspension. After filtration, the off-white solid was washed with benzene (2 x 5 mL) and hexane (2 x 6 mL) and dried *in vacuo*. The crude product, contaminated with [SIDippTolH]Br, was used for subsequent reduction without further purification (crude yield: 470.0 mg, 573 µmol, 86%). Single crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a saturated solution of **2** in toluene at rt.

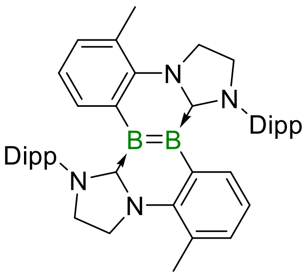
^{1}H{^{11}B} NMR (600.2 MHz, C_6D_5Br): δ = 7.33 (d, 2H, $^3J_{HH}$ = 6.9 Hz, H^{Tol}), 7.17 (t, 2H, $^3J_{HH}$ = 7.6 Hz, H^{Dipp}), 7.08 (d, 2H, $^3J_{HH}$ = 7.6 Hz, H^{Dipp}), 7.03 (d, 2H, $^3J_{HH}$ = 7.8 Hz, H^{Dipp}), 6.87 (t, 2H, $^3J_{HH}$ = 7.2 Hz, H^{Tol}), 6.58 (d, 2H, $^3J_{HH}$ = 7.5 Hz, H^{Tol}), 4.61 – 4.56 (m, 2H, NCH_2), 4.07 – 4.03 (m, 2H, NCH_2), 3.94 – 3.87 (m, 4H, NCH_2 + CH^{iPr}), 3.79 – 3.74 (m, 2H, NCH_2), 3.03 (sept, 2H, $^3J_{HH}$ = 6.7 Hz, CH^{iPr}), 2.01 (s, 6H, CH_3), 1.53 (d, 6H, ^3J = 6.5 Hz, CH_3^{iPr}), 1.21 – 1.20 (*two overlapping* d, 12H, ^3J = 6.8 Hz, ^3J = 6.5 Hz, CH_3^{iPr}), 0.79 (d, 6H, ^3J = 6.8 Hz, CH_3^{iPr}) ppm.

^{13}C{^{1}H,^{11}B} NMR (150.9 MHz, C_6D_5Br): δ = 195.1 ($C^{Carbene}$), 147.8 (C^q), 146.7 (C^q), 139.8 (C^q), 136.0 (C^q), 129.1 (CH^{Dipp}), 127.5 (CH^{Tol}), 126.1 (CH^{Tol}), 123.8 (CH^{Dipp}), 123.4 (CH^{Dipp}), 122.1 (CH^{Tol}), 118.5 (C^q), 59.2 (NCH$_2$), 45.3 (NCH$_2$), 29.6 (CH^{iPr}), 29.5 (CH^{iPr}), 27.5 (CH$_3^{iPr}$), 26.5 (CH$_3^{iPr}$), 24.0 (CH$_3^{iPr}$), 22.9 (CH$_3^{iPr}$), 17.6 (CH$_3$) ppm.

^{11}B{^{1}H} NMR (192.6 MHz, C_6D_5Br): δ = −7.8 ppm.

HRMS(LIFDI): calcd. for $C_{44}H_{54}N_4B_2Br_2$ $[M]^+$: *m/z* = 820.2875; found: 820.2874.

Synthesis of diborene 3



3

Route A: A suspension of **2** (80.0 mg, 97.5 µmol, 1.00 equiv) was combined with KC_8 (27.7 mg, 205 µmol, 2.10 equiv) in THF (1 mL) and benzene (1 mL). The reaction mixture instantly turned from pale yellow to red orange and was stirred at rt for 6 h. The suspension was filtered, and all volatiles were removed *in vacuo*. The residue was washed with pentane (3 x 0.6 mL) and extracted with warm *n*-hexane (6 x 1 mL). The filtrate dried *in vacuo* was yielding **3** as a dark red powder (42.0 mg, 63.6 µmol, 65%).

Route B: A solution of **4** (40.0 mg, 68.5 µmol, 1.00 equiv) and dimethylsulfide (0.5 mL) in benzene (1.5 mL) were combined with KC_8 (18.5 mg, 137.0 µmol, 2.00 equiv) and stirred at rt for 16 h, resulting in a green suspension showed a new ^{11}B NMR resonance at 20.3 ppm. The suspension was filtered, and all volatiles were removed *in vacuo.* Dark-green single crystals of **5** suitable for X-ray diffraction analysis were obtained by evaporation of a saturated diethyl ether solution at –30 °C. By leaving the diethyl ether solution of **5** for 3 d at rt or for 10 d at –30 °C, the solution turned from green to dark red, indicating the formation of **3**. Crystallization of the reaction mixture yielded red single crystals of **3**, contaminated with co-crystallized [SIDippTol]BHI. The obtained data serves solely as confirmation of connectivity due to whole molecule disorder. Recrystallization from hexane (0.6 mL) afforded **3** as a dark-red powder (7.60 mg, 11.5 µmol, 34%).

^{1}H{^{11}B} NMR (500.1 MHz, C_6D_6): δ = 7.22 (t, 2H, $^3J_{HH}$ = 7.7 Hz, H^{Dipp}), 7.07 (d, 4H, $^3J_{HH}$ = 7.7 Hz, H^{Dipp}), 6.89 (dd, 2H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.6 Hz, H^{Tol}), 6.87 (d, 2H, $^3J_{HH}$ = 6.6 Hz, H^{Tol}), 6.75 (t,

$^{3}J_{HH}$ = 7.3 Hz, H^{Tol}), 4.18 – 4.14 (m, 4H, NCH_2), 3.51 – 3.48 (m, 4H, NCH_2), 3.29 (sept, 4H, $^{3}J_{HH}$ = 6.8 Hz, C$H^{i\text{Pr}}$), 2.33 (s, 6H, CH_3^{Tol}), 1.77 (d, $^{3}J_{HH}$ = 6.9 Hz, C$H_3^{i\text{Pr}}$), 1.08 (d, $^{3}J_{HH}$ = 6.8 Hz, C$H_3^{i\text{Pr}}$) ppm.

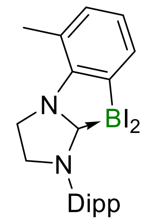
^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 169.4 (C^{Carbene})*, 147.8 (C^{q}), 140.2 (C^{q}), 138.4 (C^{q}), 138.1 (C^{q})*, 130.1 (CH$^{\text{Tol}}$), 129.0 (CH$^{\text{Dipp}}$), 127.4 (CH$^{\text{Tol}}$), 124.8 (CH$^{\text{Dipp}}$), 124.7 (C^{q}), 120.2 (CH$^{\text{Tol}}$), 52.7 (NCH$_2$), 51.7 (NCH$_2$), 28.4 (CH$^{i\text{Pr}}$), 26.3 (CH$_3^{i\text{Pr}}$), 24.1 (CH$_3$), 23.0 (CH$_3^{i\text{Pr}}$) ppm. *Note: the boron-bound carbon nuclei were detected by ^{1}H,^{13}C-HMBC NMR spectroscopy.*

^{11}B{^{1}H} NMR (128.5 MHz, C_6D_6): δ = 31.7 (br) ppm.

HRMS(LIFDI): calcd. for $C_{44}H_{54}N_4B_2$ [M]$^{+}$: *m/z* = 660.4529; found: 660.4512.

UV/Vis (C_6H_6): λ_{max} = 359, 416, 516 nm.

Synthesis of cyclic diodoborane 4



4

BI_3 (305.4 mg, 780 µmol, 1.00 equiv) in toluene (5 mL) was added dropwise to a solution of SIDippTol (**1**) (500.0 mg, 1.56 mmol, 2.00 equiv) in toluene (10 mL) under exclusion of light. The initially dark-red solution gradually formed a beige suspension within 16 hours at room temperature. The by-product ([SIDippTolH]I) was separated by filtration and further product was extracted with warm toluene (2 x 5 mL). After the removal of all volatiles, the colorless crude product was washed with pentane (3 x 5 mL) and diethyl ether (3 x 5 mL), yielding **4** as a colorless powder (240.0 mg, 411 µmol, 53%). Colorless single crystals of **4** suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated toluene solution at rt.

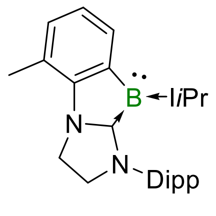
^{1}H{^{11}B} NMR (500.1 MHz, C_6D_6): δ = 7.82 – 7.81 (m, 1H, H^{Tol}), 7.20 – 7.16 (m, 1H, H^{Dipp}), 7.09 – 7.08 (m, 2H, H^{Dipp}), 6.97 – 6.94 (m, 1H, H^{Tol}), 6.67 – 6.65 (m, 1H, H^{Tol}), 3.59 – 3.54 (m, 2H, NCH_2), 3.28 (sept, $^{3}J_{HH}$ = 6.7 Hz, 2H, C$H^{i\text{Pr}}$), 3.03 – 2.99 (m, 2H, NCH_2), 1.88 (s, 3H, CH_3^{Tol}), 1.56 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, C$H_3^{i\text{Pr}}$), 1.01 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, C$H_3^{i\text{Pr}}$) ppm.

^{13}C{^{1}H,^{11}B} NMR (150.9 MHz, C_6D_6): δ = 185.4 (C^{Carbene}), 147.1 (C^{q}), 145.0 (C^{q}), 138.6 (C^{q}), 131.8 (CH$^{\text{Tol}}$), 131.0 (CH$^{\text{Dipp}}$), 130.7 (CH$^{\text{Tol}}$), 128.4 (C^{q}), 126.0 (CH$^{\text{Tol}}$), 125.0 (CH$^{\text{Dipp}}$), 119.4 (C^{q}), 58.6 (NCH$_2$), 45.7 (NCH$_2$), 29.1 (CH$^{i\text{Pr}}$), 27.2 (CH$_3^{i\text{Pr}}$), 23.8 (CH$_3^{i\text{Pr}}$), 17.8 (CH$_3$) ppm.

^{11}B{^{1}H} NMR (160.5 MHz, C_6D_6): δ = −36.6 ppm.

HRMS(LIFDI): calcd. for $C_{22}H_{27}N_2BI$ [M − I]$^{+}$: *m/z* = 457.1306; found: 457.1302.

Synthesis of borylene 6



6

C,C-(SIDippTol)BI_2 (**4**) (65.0 mg, 111 µmol, 1.00 equiv) and I*i*Pr (18.2 mg, 117 µmol, 1.05 equiv) were combined in benzene (2.0 mL) and stirred at rt for 20 minutes, followed by addition of KC_8 (30.1 mg, 222 µmol, 2.00 equiv) and stirring for further 16 h. The orange suspension was filtered, and all volatiles were removed *in vacuo*. The residue was recrystallized at –30 °C in diethyl ether (0.8 mL), yielding **6** as orange crystals (38.0 mg, 79 µmol, 71%). Orange crystals of **6** suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated diethyl ether solution at –30 °C.

^{1}H NMR (600.2 MHz, C_6D_6): δ = 7.47 (d, 1H, $^{3}J_{HH}$ = 7.4 Hz, H^{Tol}), 7.22 (t, 1H, $^{3}J_{HH}$ = 7.3 Hz, H^{Dipp}), 7.14 – 7.11 (m, 1H, H^{Tol}), 7.08 – 7.07 (m, 2H, H^{Dipp}), 7.00 (d, 1H, $^{3}J_{HH}$ = 6.9 Hz, H^{Tol}), 6.14 (s, 2H, $\mathrm{NC}H^{\mathrm{I}i\mathrm{Pr}}$), 4.91 (sept, 2H, $^{3}J_{HH}$ = 6.7 Hz, $\mathrm{C}H^{\mathrm{I}i\mathrm{Pr}}$), 4.30 – 4.28 (m, 2H, $\mathrm{NC}H_2$), 3.94 – 3.92 (m, 2H, $\mathrm{NC}H_2$), 3.76 (sept, 2H, $^{3}J_{HH}$ = 6.9 Hz, $\mathrm{C}H^{i\mathrm{Pr}}$), 2.69 (s, 3H, $\mathrm{C}H_3$), 1.28 (d, 6H, $^{3}J_{HH}$ = 6.9 Hz, $\mathrm{C}H_3{}^{i\mathrm{Pr}}$), 0.94 (d, 6H, $^{3}J_{HH}$ = 6.6 Hz, $\mathrm{C}H_3{}^{\mathrm{I}i\mathrm{Pr}}$), 0.93 (m, 12H, $^{3}J_{HH}$ = 6.7 Hz, $\mathrm{C}H_3{}^{i\mathrm{Pr}}$), 0.51 (d, 6H, $^{3}J_{HH}$ = 6.7 Hz, $\mathrm{C}H_3{}^{\mathrm{I}i\mathrm{Pr}}$) ppm.

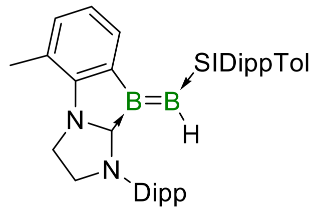
^{13}C{^{1}H,^{11}B} NMR (276.0 MHz, C_6D_6): δ = 162.1 ($C^{\mathrm{Carbene,\ I}i\mathrm{Pr}}$)*, 149.8 ($C^{q}$), 141.9 ($C^{q}$), 136.3 ($C^{q}$), 127.1 ($C\mathrm{H}^{\mathrm{Tol}}$), 124.4 ($C\mathrm{H}^{\mathrm{Dipp}}$), 123.9 ($C\mathrm{H}^{\mathrm{Tol}}$), 119.3 ($C\mathrm{H}^{\mathrm{Tol}}$), 118.0 ($C^{q}$), 117.1 ($C\mathrm{H}^{\mathrm{Dipp}}$), 115.3 (), 58.1 ($\mathrm{N}C\mathrm{H}_2$) 50.6 ($C\mathrm{H}^{\mathrm{I}i\mathrm{Pr}}$), 46.5 ($\mathrm{N}C\mathrm{H}_2$), 28.1 ($C\mathrm{H}^{i\mathrm{Pr}}$) 26.1 ($C\mathrm{H}_3{}^{i\mathrm{Pr}}$) 23.6 ($C\mathrm{H}_3{}^{i\mathrm{Pr}}$) 23.1 ($C\mathrm{H}_3{}^{i\mathrm{Pr}}$), 21.5 ($C\mathrm{H}_3{}^{i\mathrm{Pr}}$), 20.1 ($C\mathrm{H}_3$) ppm. *Note: Two boron-bound carbon nuclei were not detected due to broadening. The labelled signal set (*) is detected by ^{1}H,^{13}C-HSQC or ^{1}H,^{13}C-HMBC NMR spectroscopy.*

^{11}B NMR (192.6 MHz, C_6D_6): δ = −4.5 ppm.

HRMS(LIFDI): calcd. for $C_{31}H_{43}N_4B_1$ $[M]^+$: *m/z* = 482.3575; found: 482.3569.

UV/Vis (C_6H_6): λ_{max} = 371, 450 nm.

Synthesis of diborene 7



7

To a solution of $B_2Cl_4(SMe_2)_2$ (100.0 mg, 348 µmol, 1.00 equiv) in benzene (1.5 mL) and THF (0.6 mL) a solution of SIDippTol (**1**) (233.9 mg, 730 µmol, 2.10 equiv) in benzene (2 mL) was added dropwise and the mixture was stirred at rt for 5 h, resulting in a pale yellow suspension. The suspension was combined with KC_8 (197.4 mg, 1.46 mmol, 4.20 equiv) and the reaction mixture instantly turned dark green and showed a new ^{11}B NMR resonance at 30.1 ppm (assigned to the diborene $B_2Cl_2(SIDippTol)_2$). The reaction mixture was stirred at rt for further 10 h, after which it turned from green to dark purple. The suspension was filtered, and all volatiles were removed *in vacuo*. The residue was washed with pentane (3 x 3.0 mL) and diethyl ether (2 x 0.6 mL), yielding diborene **7** as a dark-purple powder (112.0 mg, 169 µmol, 49%). Dark purple single crystals of **7** suitable for X-ray diffraction analysis were obtained by diffusion of pentane into a saturated benzene solution at rt.

^{1}H{^{11}B} NMR (500.1 MHz, C_6D_6): δ = 7.97 (d, 1H, $^{3}J_{HH}$ = 7.3 Hz, H^{Tol}), 7.81 – 7.79 (m, 1H, H^{Tol}), 7.35 (t, 1H, $^{3}J_{HH}$ = 7.2 Hz, H^{Tol}), 7.28 (t, 1H, $^{3}J_{HH}$ = 7.6 Hz, H^{Dipp}) 7.16 – 7.14 (m, 2H, H^{Dipp}), 7.11 (t, 1H, $^{3}J_{HH}$ = 7.7 Hz, H^{Dipp}), 6.99 (d, 1H, $^{3}J_{HH}$ = 7.2 Hz, H^{Tol}), 6.96 (d, 2H, $^{3}J_{HH}$ = 7.7 Hz, H^{Dipp}), 6.86 – 6.84 (m, 1H, H^{Tol}), 6.75 – 6.70 (m, 2H, H^{Tol}), 4.12 (s, 1H, BH), 3.61 – 3.54 (m, 4H, NCH_2), 3.30 (br, 4H, NCH_2), 3.17 (sept, 4H, $^{3}J_{HH}$ = 6.9 Hz, C$H^{i\mathrm{Pr}}$), 2.31 (s, 3H, CH_3^{Tol}), 2.15 (s, 3H, CH_3^{Tol}), 1.23 (d, 6H, $^{3}J_{HH}$ = 6.9 Hz, C$H_3^{i\mathrm{Pr}}$), 1.16 (d, 6H, $^{3}J_{HH}$ = 6.9 Hz, C$H_3^{i\mathrm{Pr}}$), 1.08 (d, 6H, $^{3}J_{HH}$ = 6.4 Hz, C$H_3^{i\mathrm{Pr}}$), 0.89 – 0.86 (br, 6H, C$H_3^{i\mathrm{Pr}}$) ppm.

^{13}C{^{1}H}-NMR (100.7 MHz, C_6D_6): δ = 148.9 (C^{q}), 147.2 (C^{q}), 139.9 (C^{q}), 139.8 (C^{q}), 137.9 (C^{q}), 134.6 (C^{q}), 134.4 (C^{q}), 130.9 (CH$^{\mathrm{Tol}}$), 129.1 (CH$^{\mathrm{Dipp}}$), 128.6 (C^{q})*, 128.2 (CH$^{\mathrm{Tol}}$)*, 127.9 (CH$^{\mathrm{Tol}}$)*, 127.1 (CH$^{\mathrm{Tol}}$), 127.0 (CH$^{\mathrm{Tol}}$), 124.5 (CH$^{\mathrm{Dipp}}$), 124.3 (CH$^{\mathrm{Dipp}}$), 122.5 (CH$^{\mathrm{Tol}}$), 118.9 (CH$^{\mathrm{Tol}}$), 117.4 (C^{q}), 57.0 (NCH$_2$), 52.6 (NCH$_2$), 51.7 (NCH$_2$), 46.0 (NCH$_2$), 28.6 (CH$^{i\mathrm{Pr}}$), 28.4 (CH$^{i\mathrm{Pr}}$), 25.5 (CH$_3^{i\mathrm{Pr}}$), 25.2 (CH$_3^{i\mathrm{Pr}}$), 24.0 (CH$_3^{i\mathrm{Pr}}$), 19.1 (CH$_3$), 18.7 (CH$_3$) ppm. *Note: The carbene carbon nuclei were not detected due to broadening. The labelled signal sets (*) are partially superimposed by the solvent resonance and were detected by ^{1}H,^{13}C-HSQC or ^{1}H,^{13}C-HMBC NMR spectroscopy.*

^{11}B{^{1}H} NMR (128.5 MHz, C_6D_6): δ = 37.3 (BH), 17.7 (ArB) ppm.

FT-IR (solid-state): $\tilde{\nu}$(B–H) = 2432 cm^{-1}.

HRMS(LIFDI): calcd. for $C_{44}H_{54}N_4B_2$ [M]$^{+}$: m/z = 660.4529; found: 660.4529.

UV/Vis (C_6H_6): λ_{max} = 359, 416, 516 nm.

NMR spectra of isolated compounds

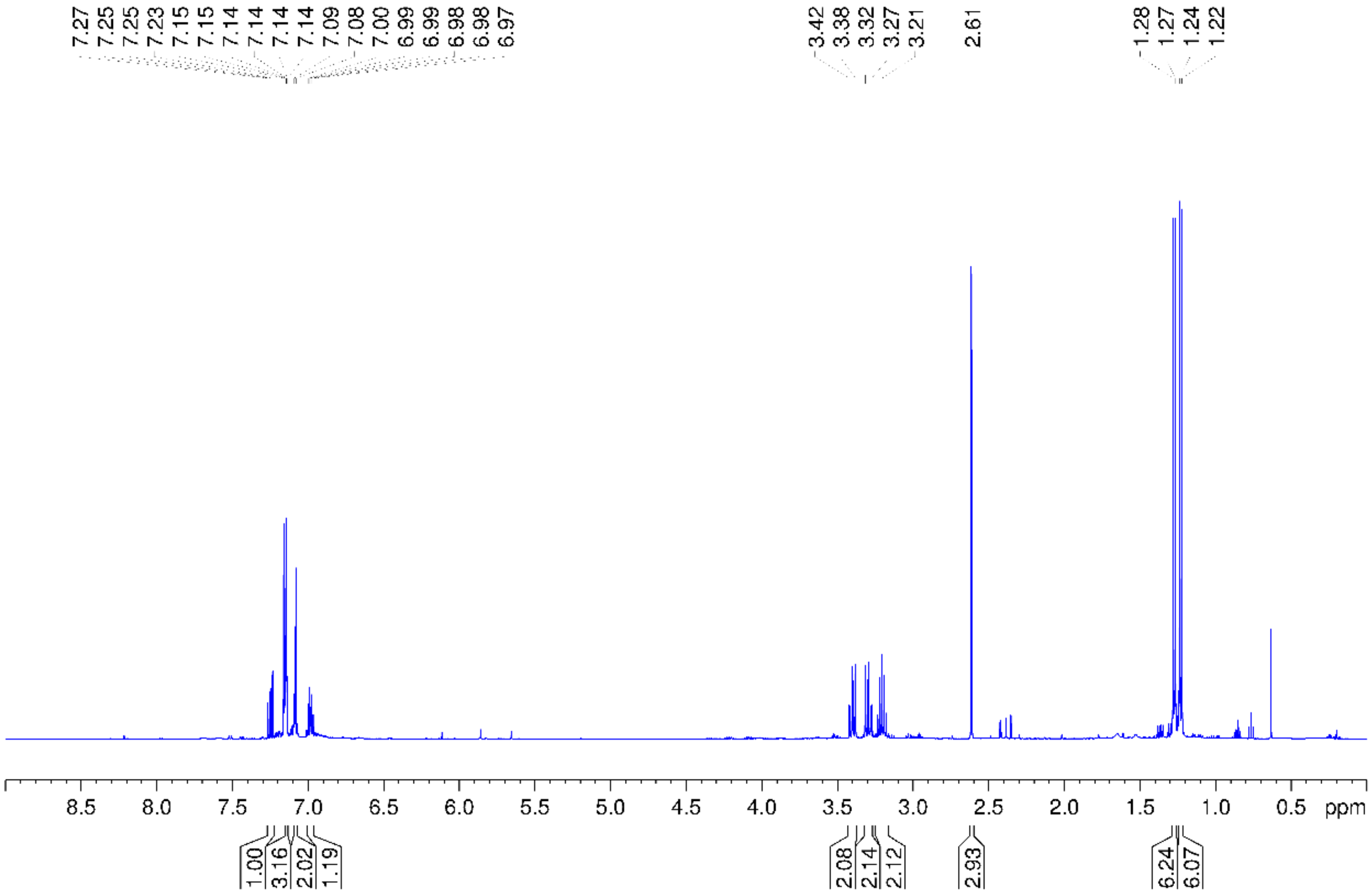


Fig. S1 ^{1}H NMR spectrum of 1-(2,6-diisopropylphenyl)-3-(2-methylphenyl)-imidazolin-ylidene (**1**).

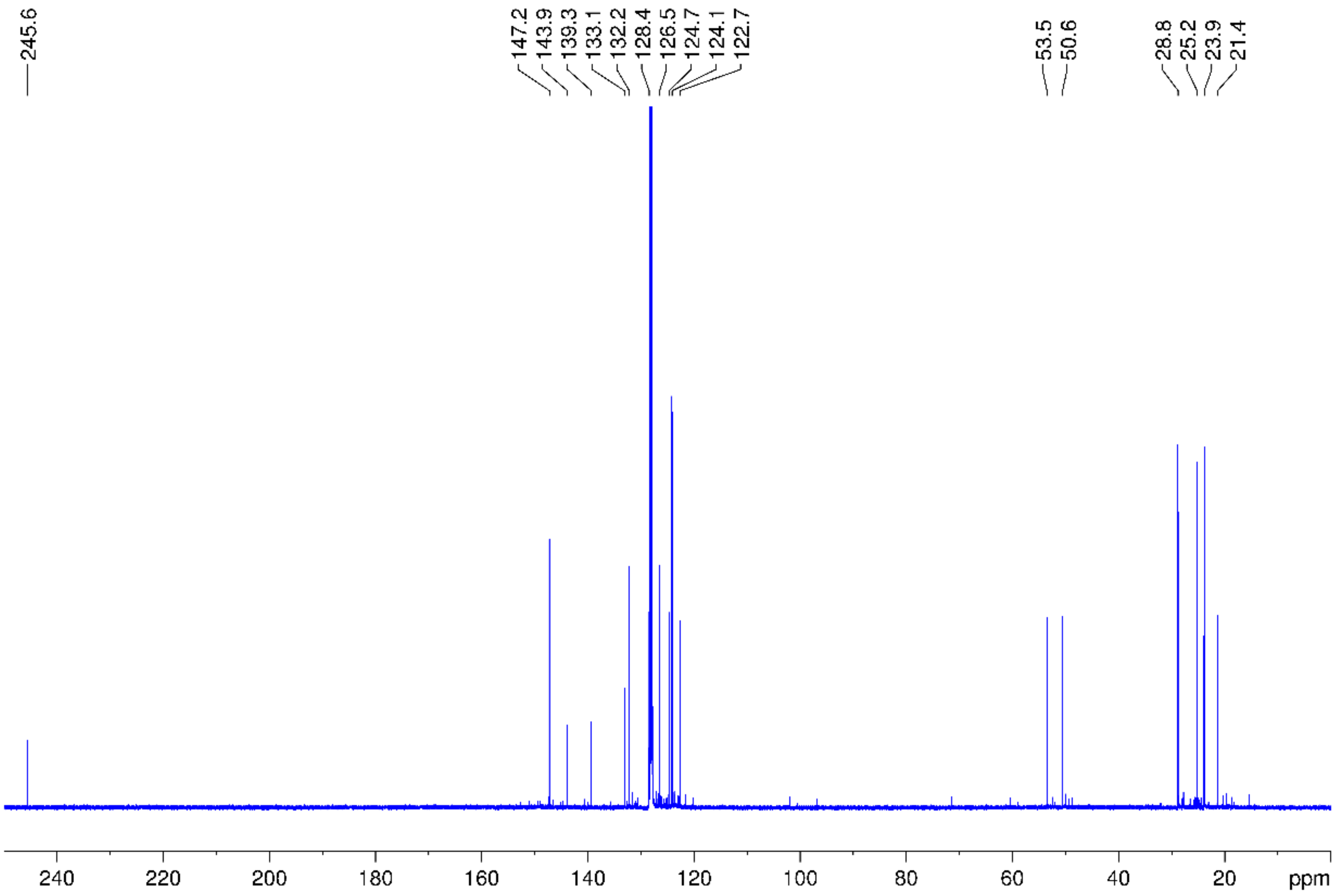


Fig. S2 ^{13}C NMR spectrum of 1-(2,6-diisopropylphenyl)-3-(2-methylphenyl)-imidazolin-ylidene (**1**).

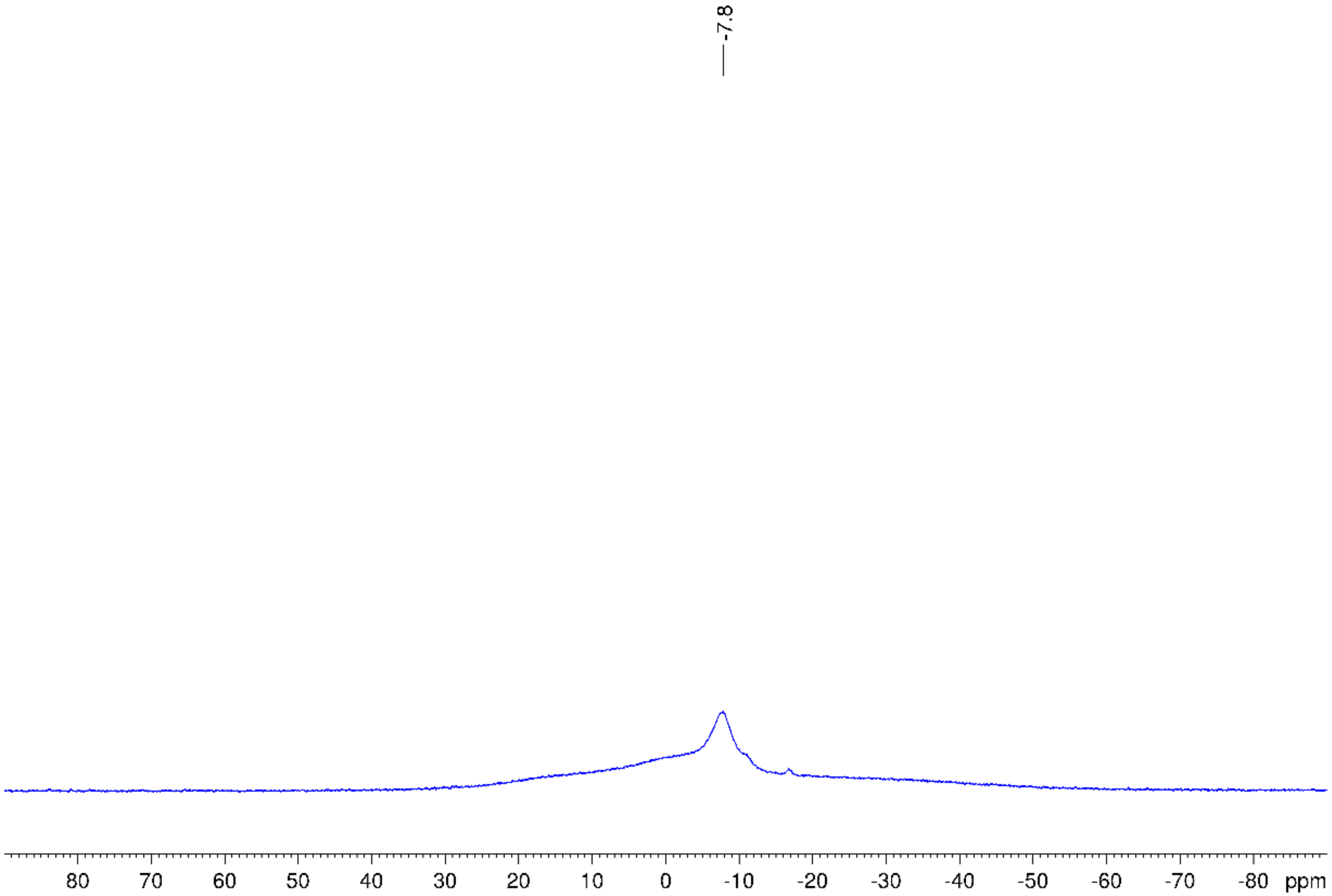


Fig. S3 ^{11}B NMR spectrum of diborane **2** in C_6D_5Br.

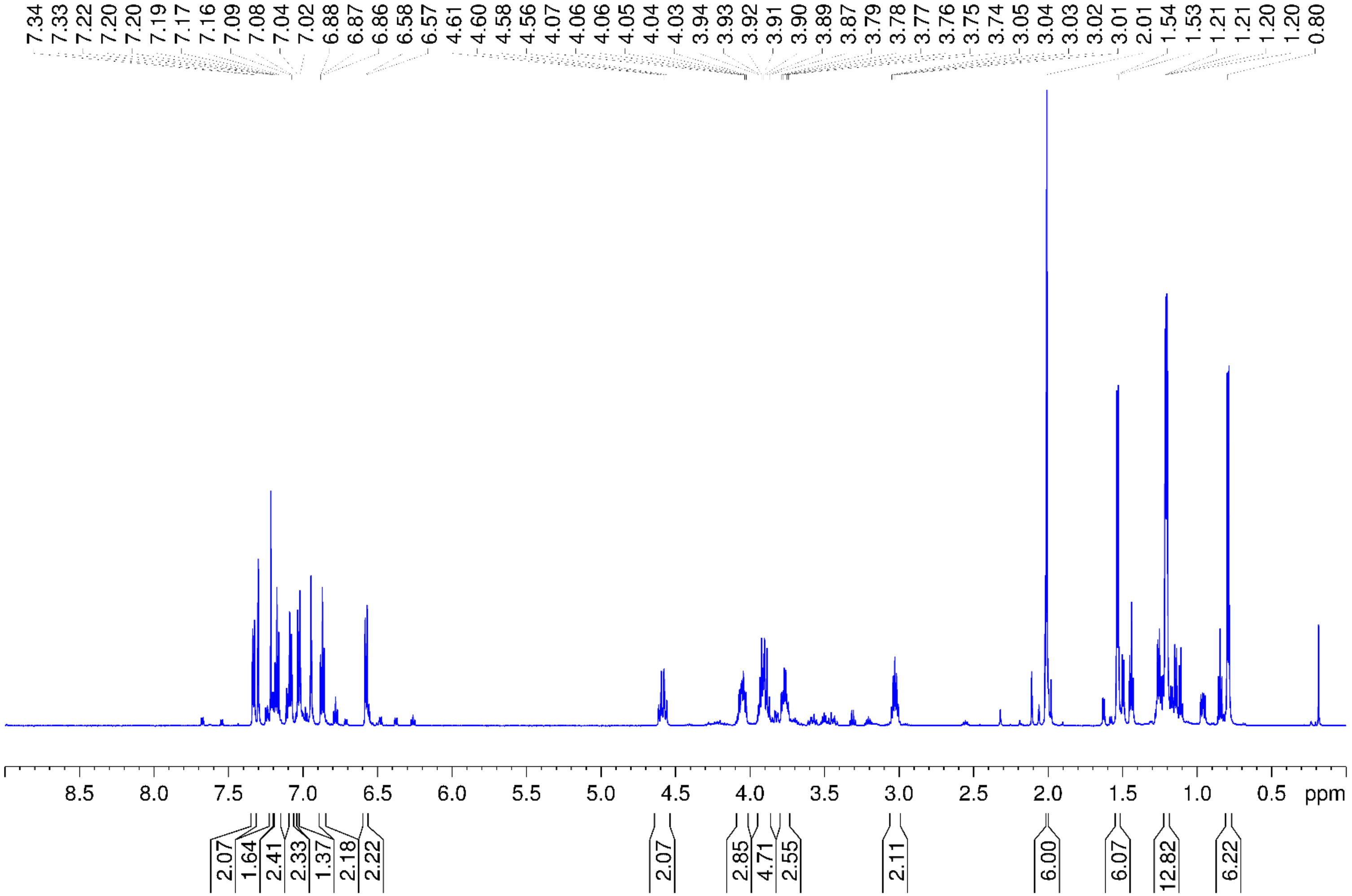


Fig. S4 ^{1}H NMR spectrum of diborane **2** in C_6D_5Br (contaminated with [SIDippTolH]Br).

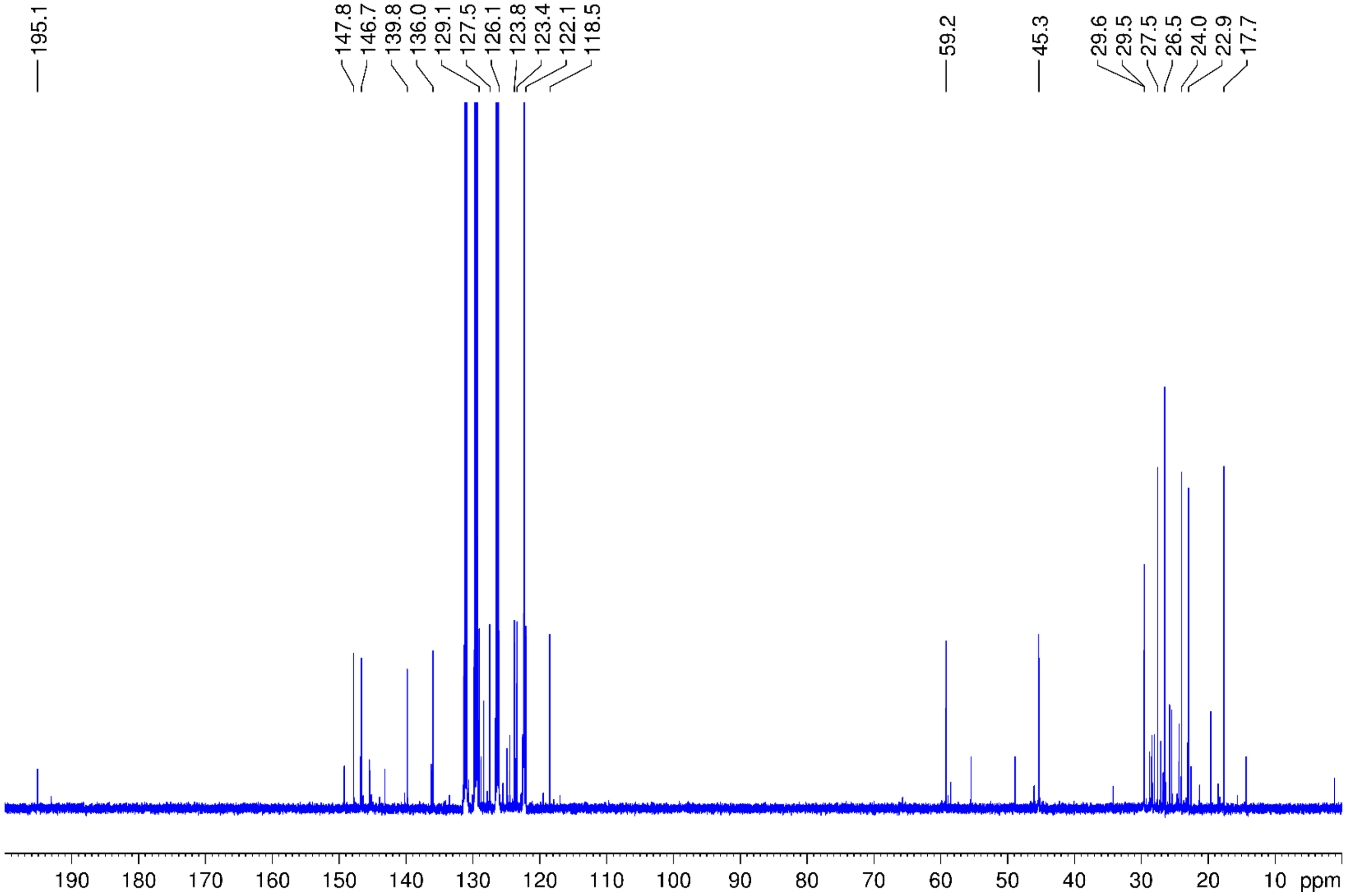


Fig. S5 $^{13}C\{^{1}H,^{11}B\}$ NMR spectrum of diborene **2** in C_6D_5Br.

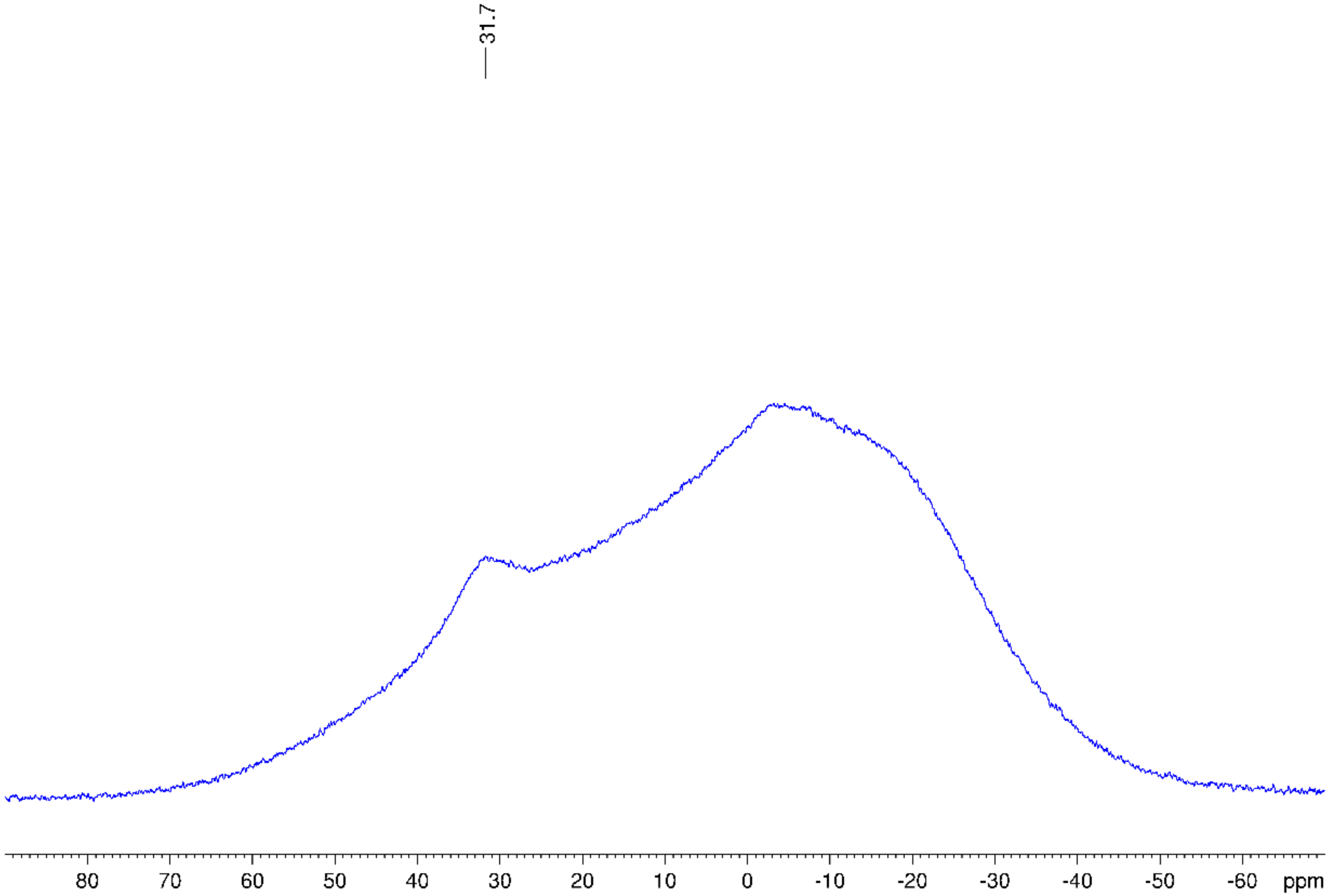


Fig. S6 $^{11}B\{^{1}H\}$ NMR spectrum of diborene **3** in C_6D_6.

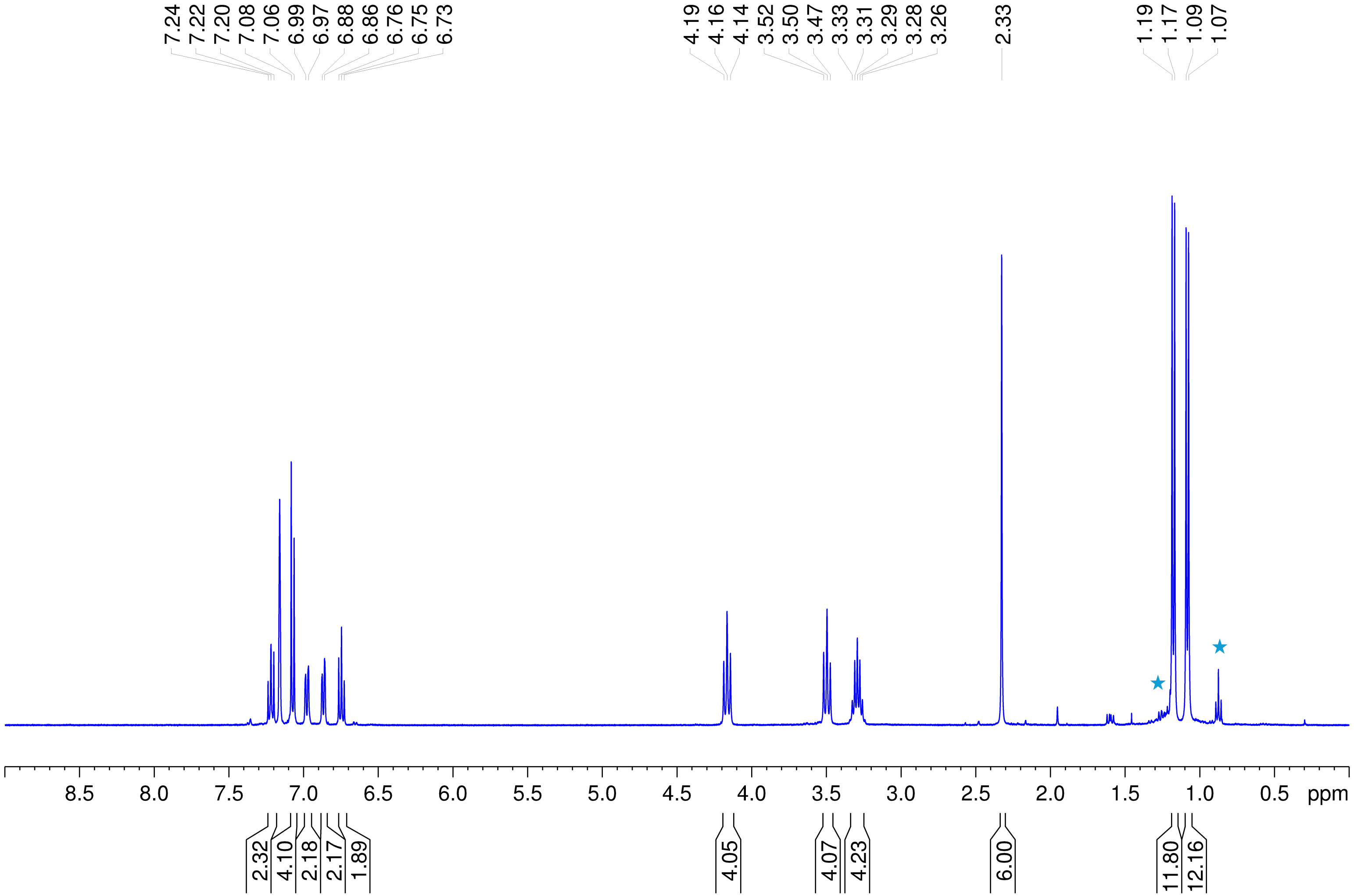


Fig. S7 $^{1}H\{^{11}B\}$ NMR spectrum of diborene **3** in C_6D_6 (★ = *n*-hexane).

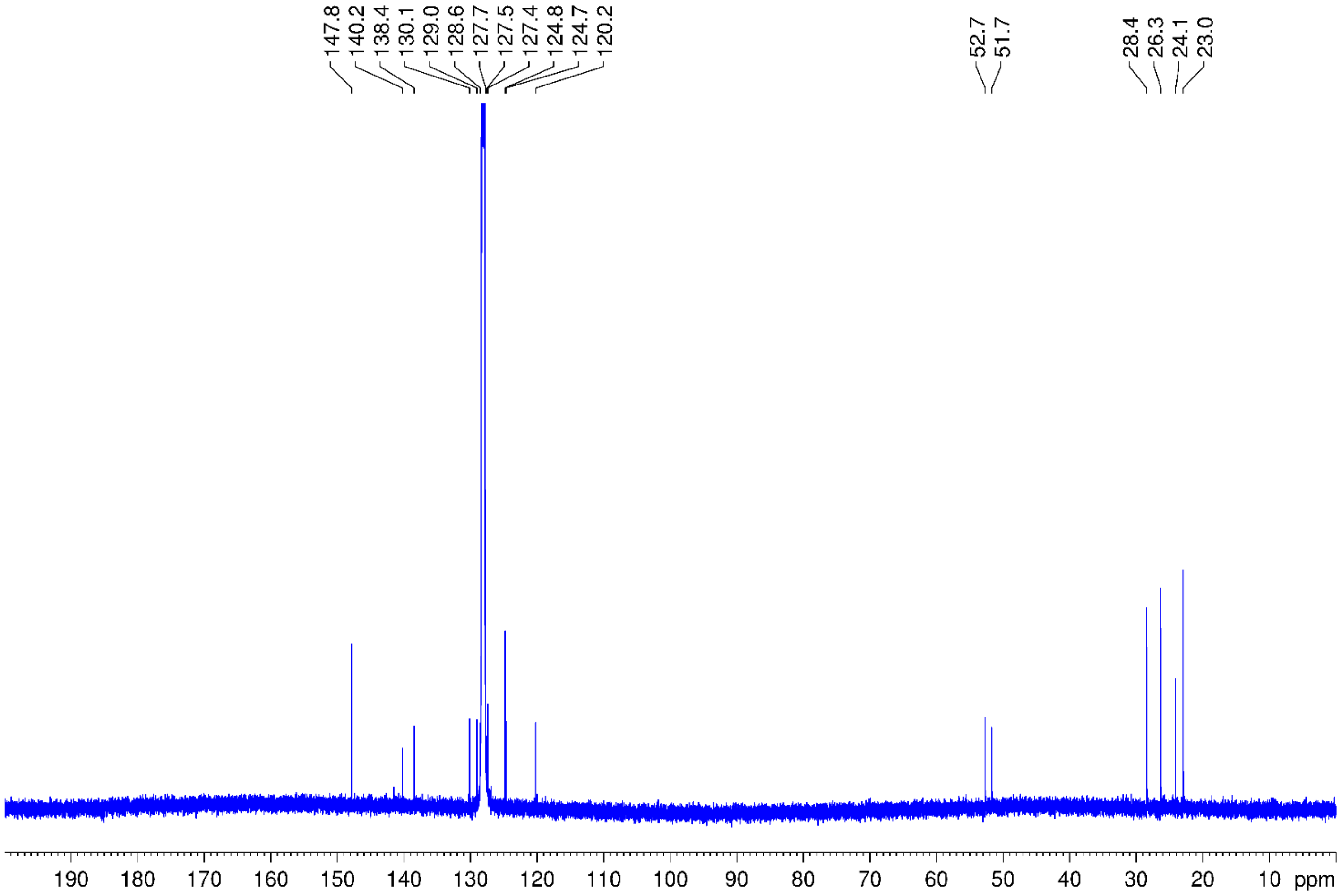


Fig. S8 $^{13}C\{^1H\}$ spectrum of **3** in C_6D_6.

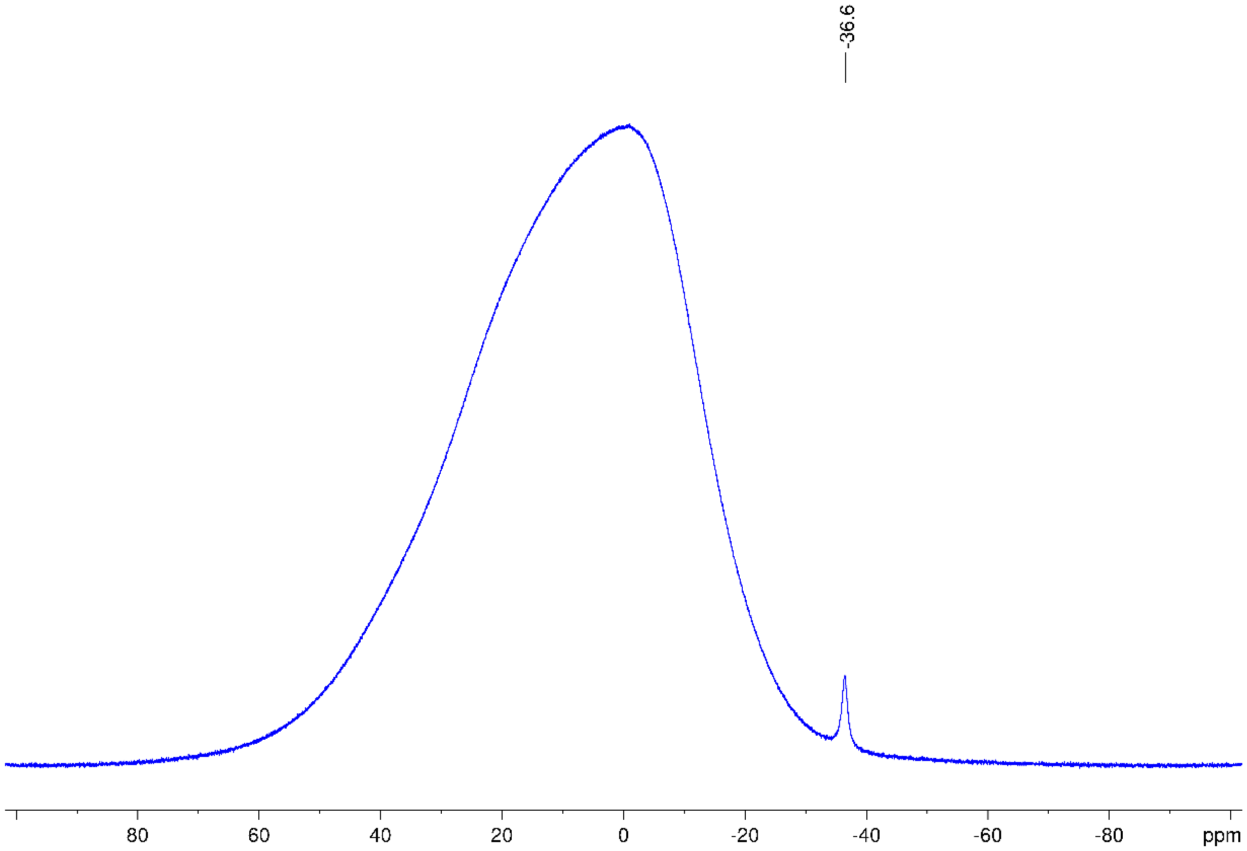


Fig. S9 ^{11}B NMR spectrum of **4** in C_6D_6.

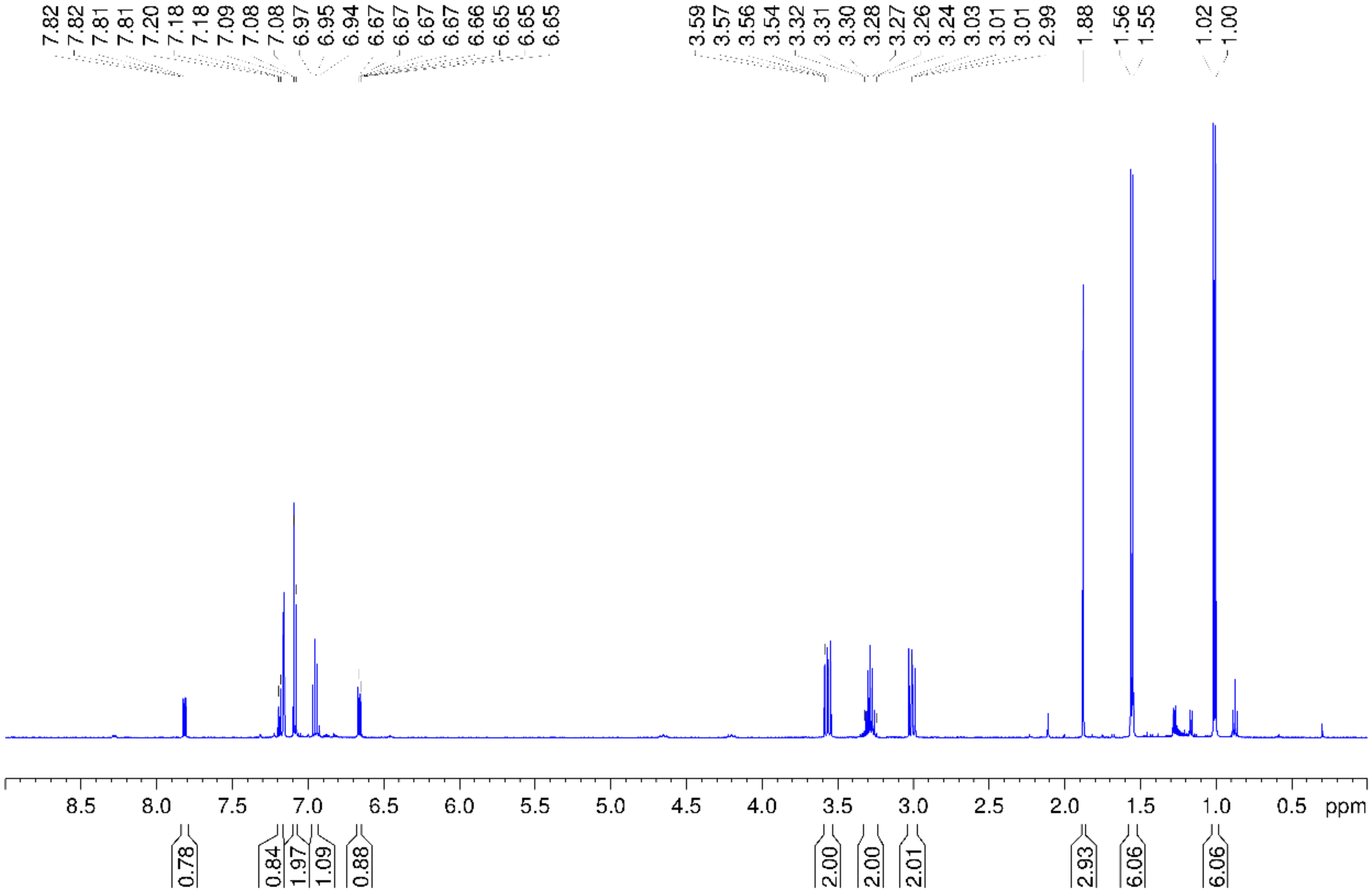


Fig. S10 ^{1}H NMR spectrum of **4** in C_6D_6.

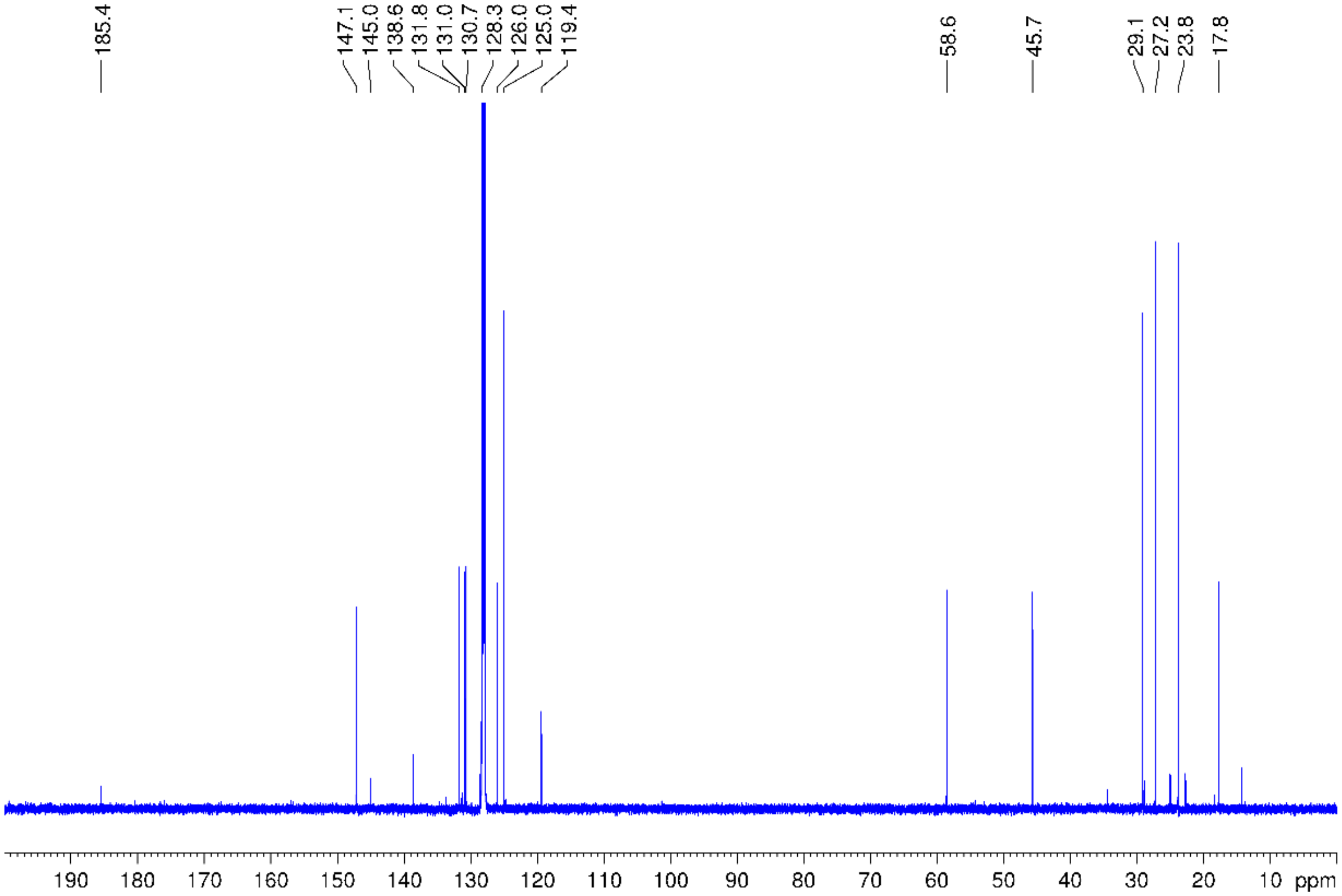


Fig. S11 $^{13}C\{^{1}H,^{11}B\}$ NMR spectrum of **4** in C_6D_6.

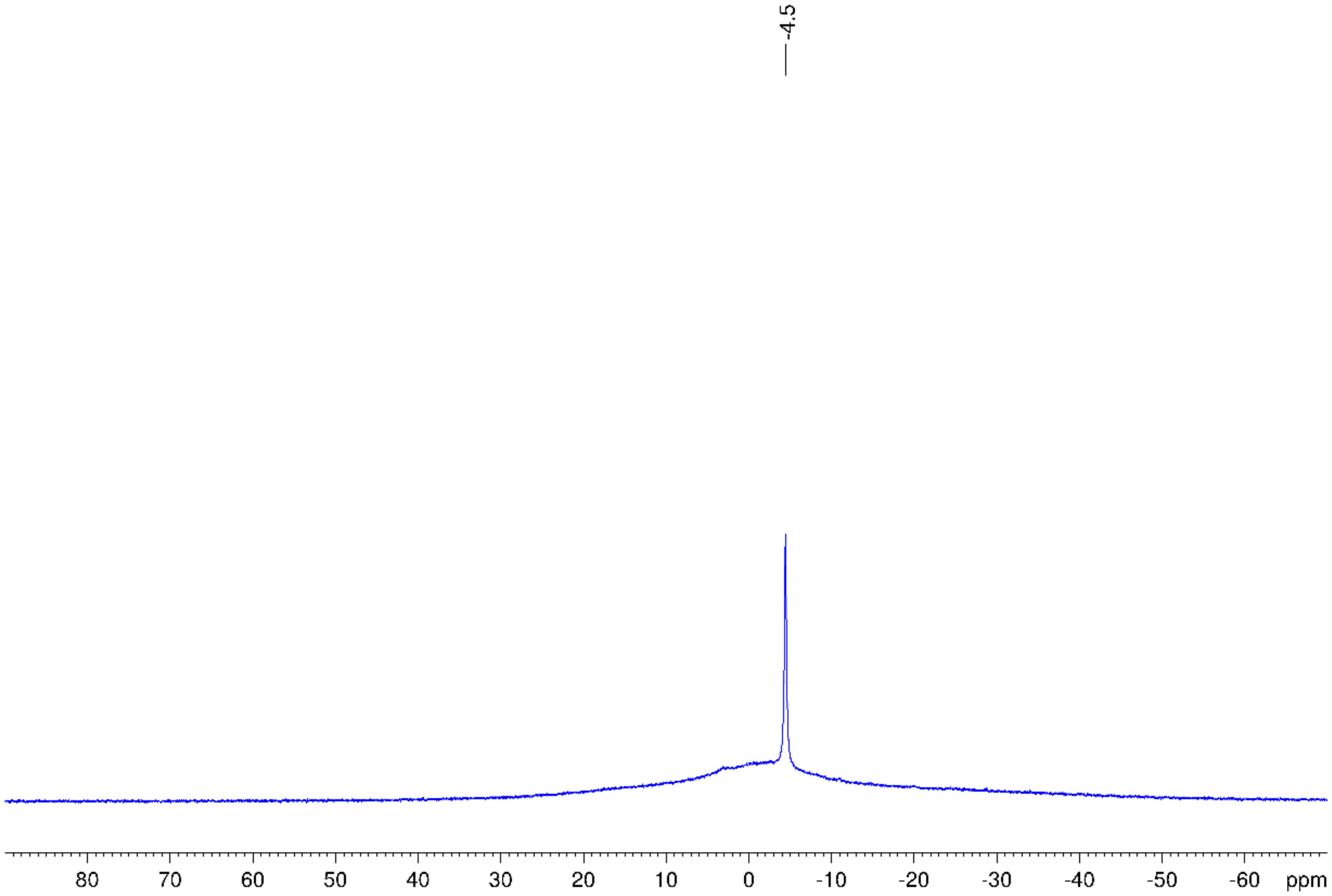


Fig. S12 ^{11}B NMR spectrum of **6** in C_6D_6.

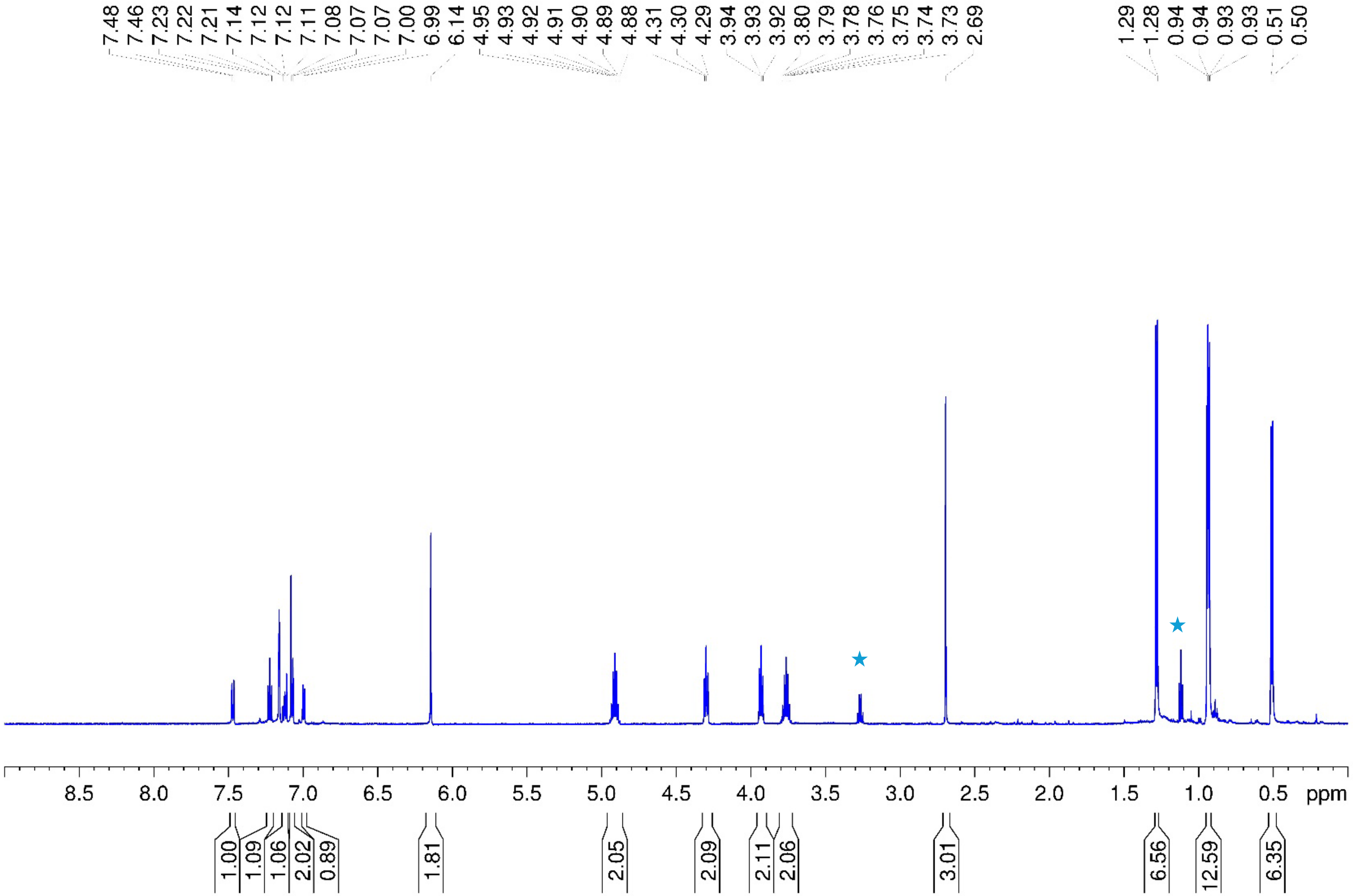


Fig. S13 $^{1}H\{^{11}B\}$ NMR spectrum of **6** in C_6D_6 (★ = diethyl ether).

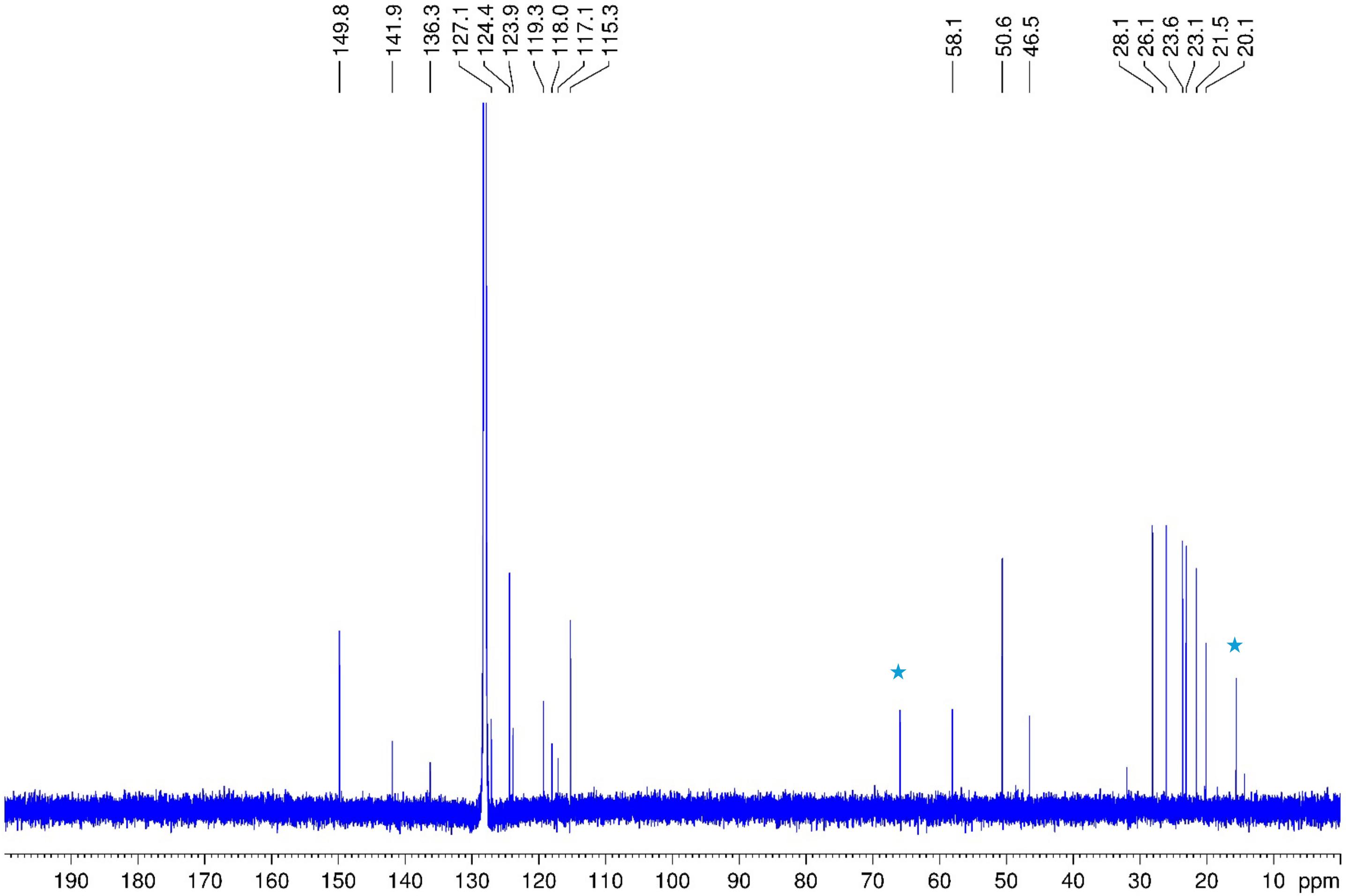


Fig. S14 $^{13}C\{^{1}H,^{11}B\}$ NMR spectrum of **6** in C_6D_6 (★ = diethyl ether).

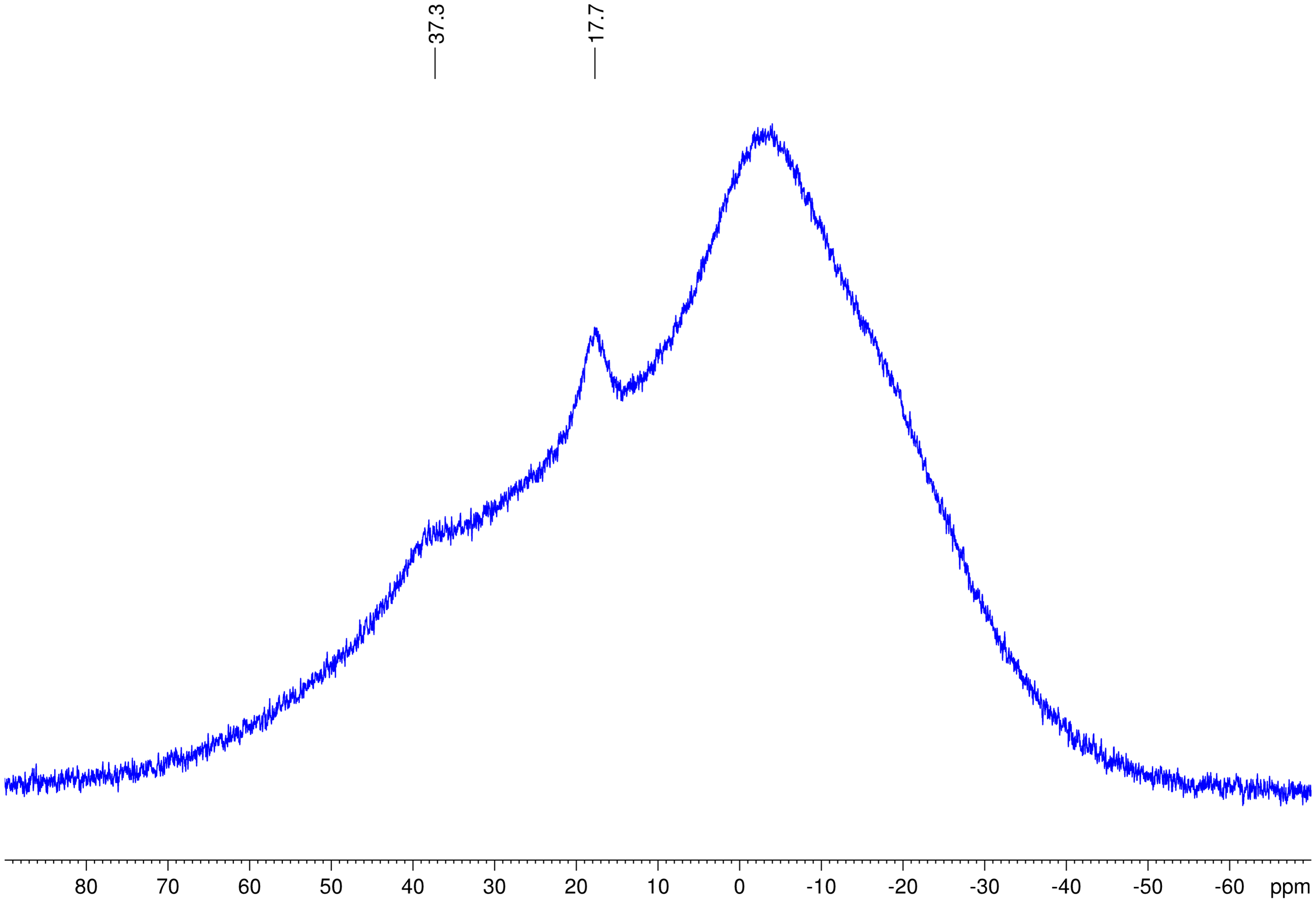


Fig. S15 $^{11}B\{^1H\}$ NMR spectrum of purple diborene **7** in C_6D_6.

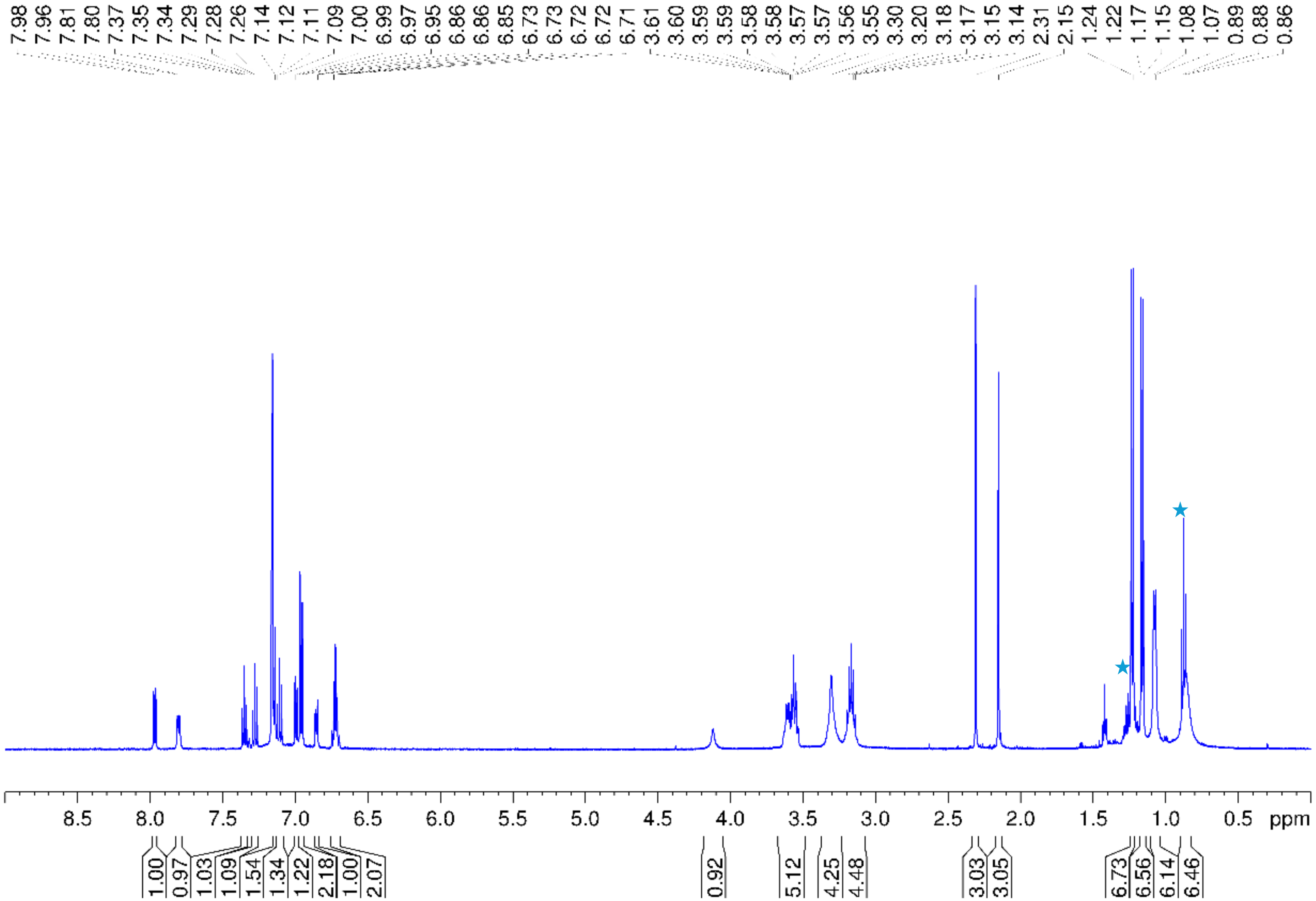


Fig. S16 ^{1}H{^{11}B} NMR spectrum of diborene **7** in C_6D_6 (★ = *n*-pentane).

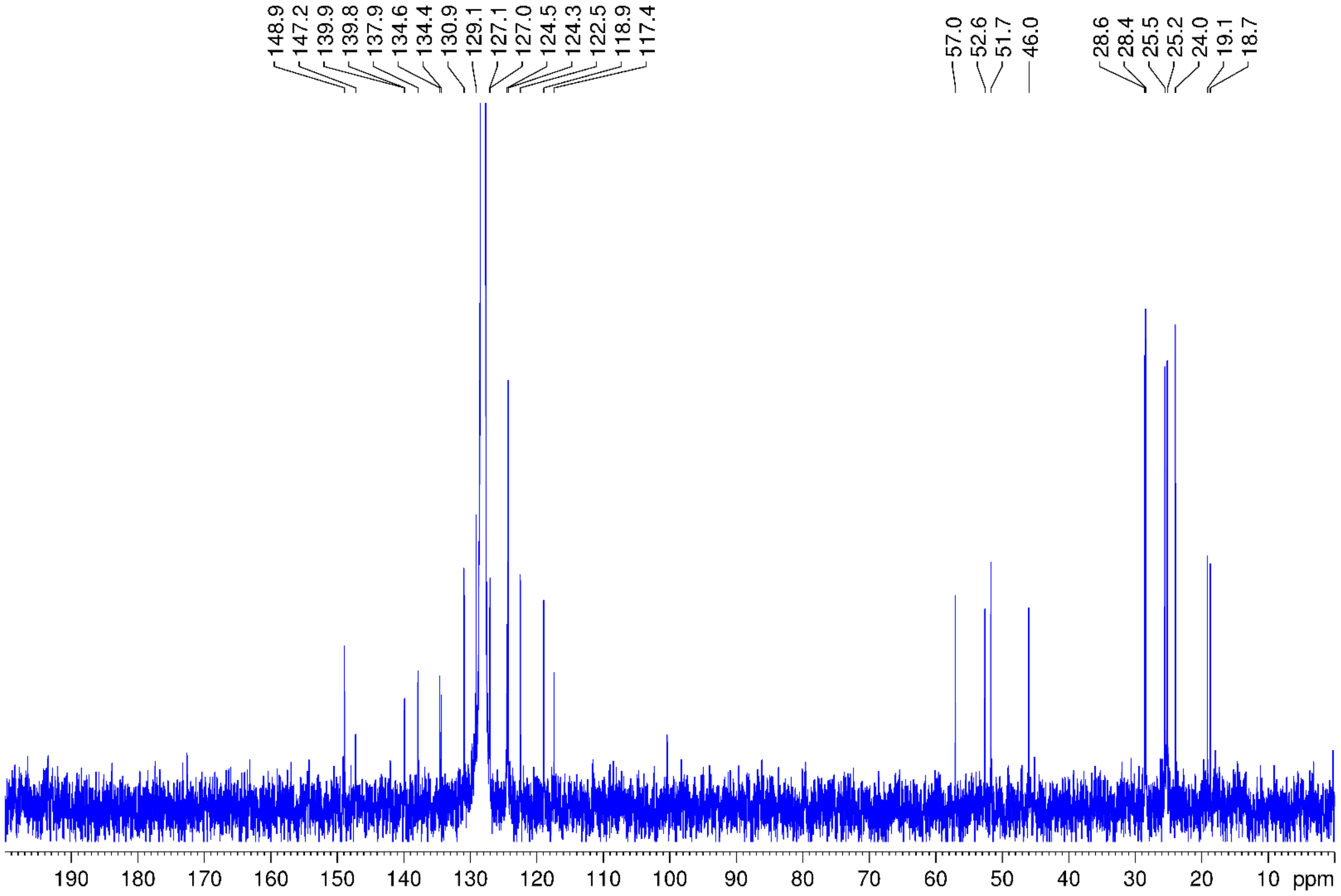


Fig. S17 $^{13}C\{^{1}H\}$ NMR spectrum of diborene **7** in C_6D_6.

NMR spectra of the reduction and isomerization to form diborene 3

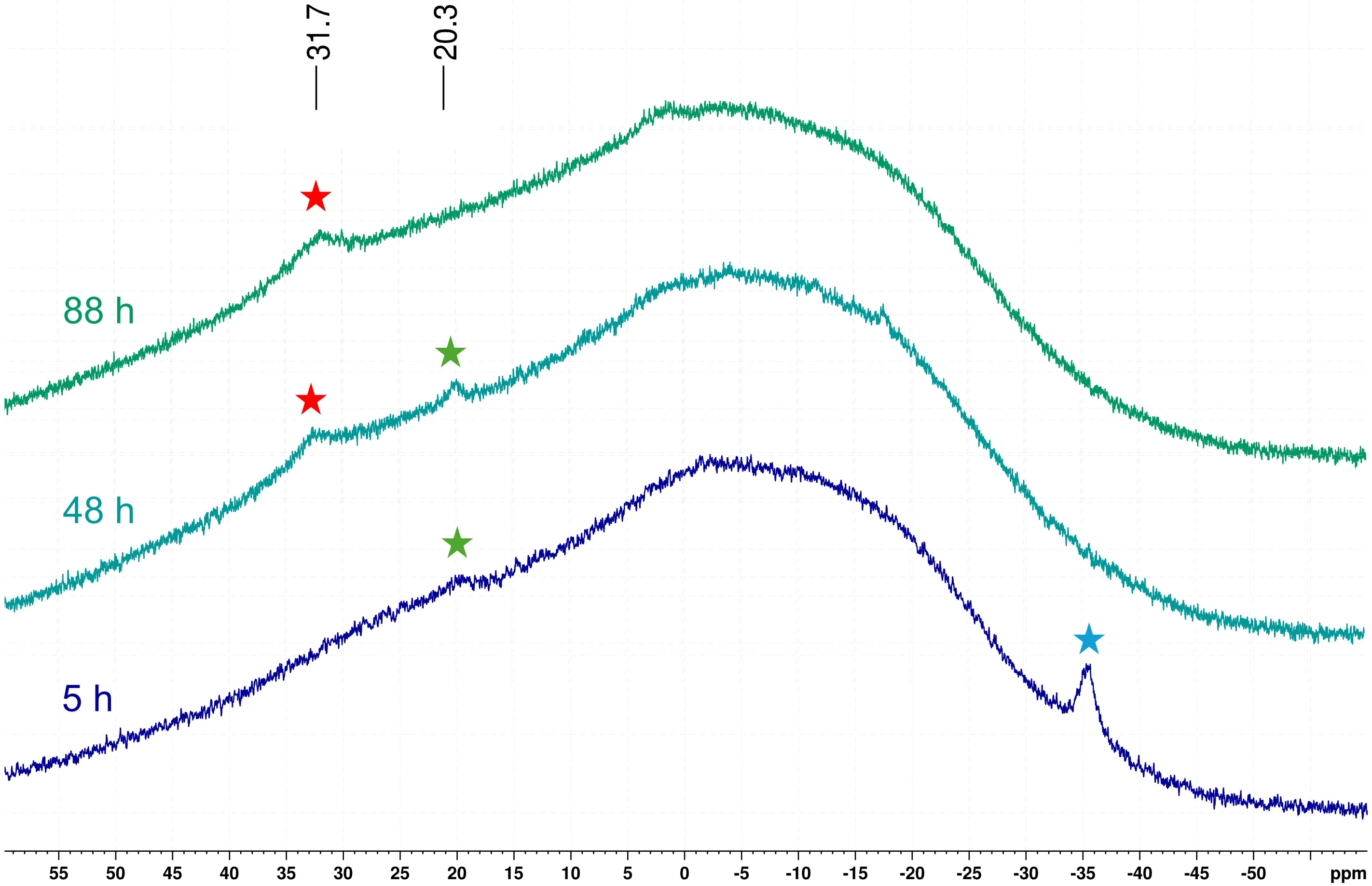


Fig. S18 ^{11}B NMR spectra of reduction of **4** and isomerization forming diborene **3** (★) from **5** (★) in benzene (★ = **4**).

NMR spectrum of reduction mixture to form 7 (^{11}B NMR resonance for dichlorodiborene)

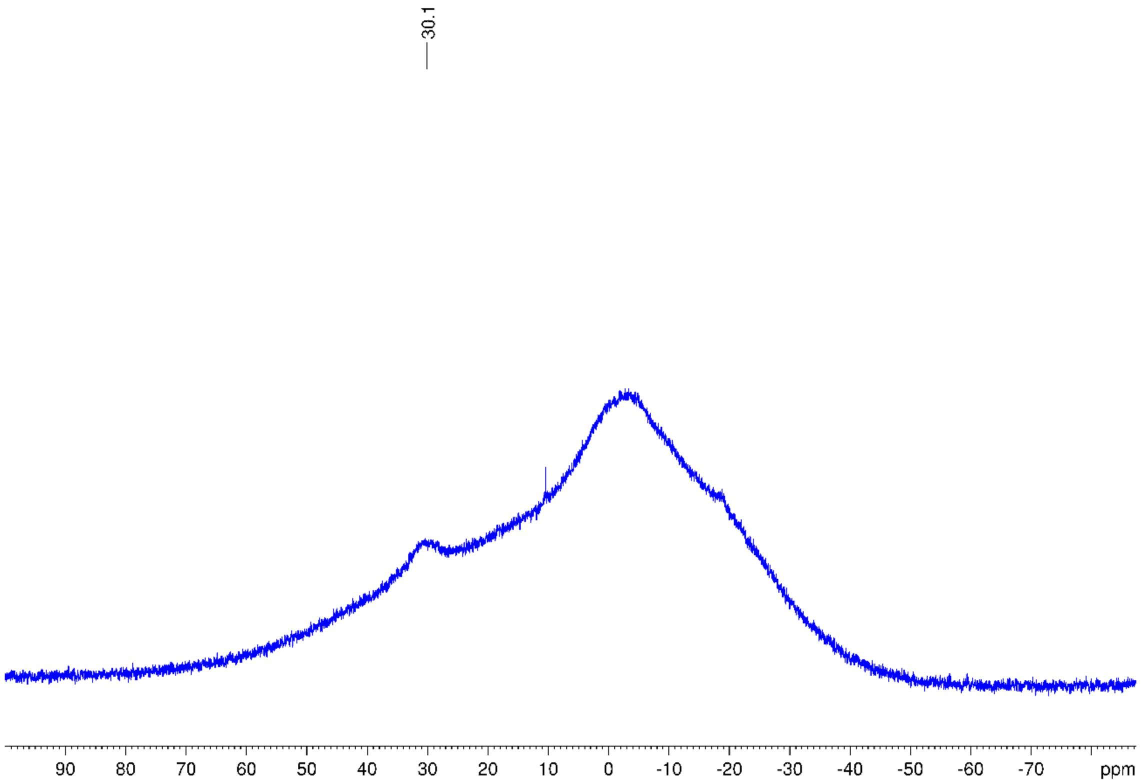


Fig. S19 ^{11}B NMR spectrum of reduction forming diborene **7**, 2 h after adding KC_8, indicating the presence of the diborene B_2Cl_2(SIDippTol)$_2$.

NMR spectra plot of C–H borylation to form cyclic diiodoborane 4

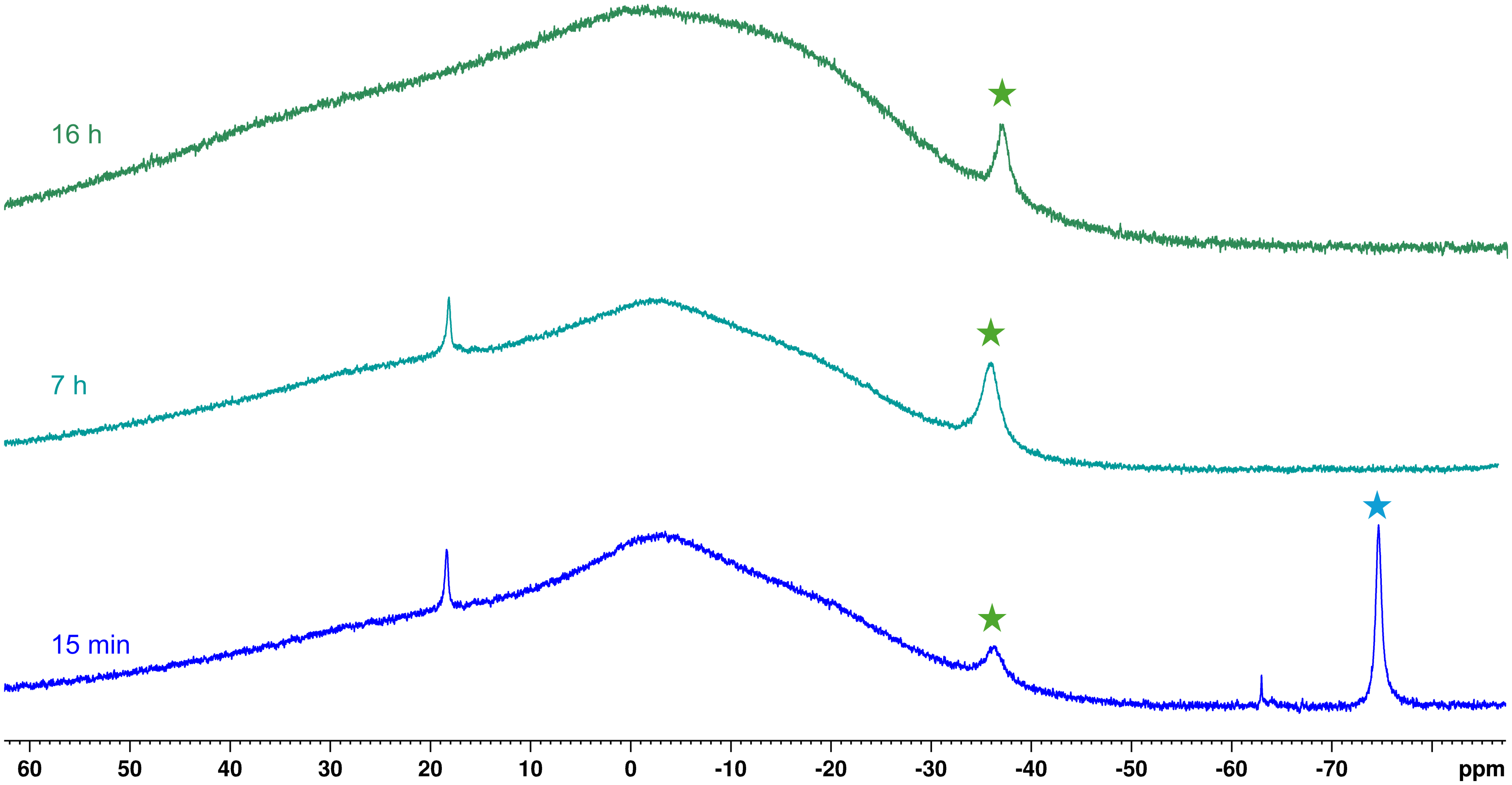


Fig. S20 ^{11}B NMR spectra of C–H borylation to form **4** at various time intervals after adding SIDippTol to BI$_3$. (★= (SIDippTol)BI$_3$;★ = **4**).

UV-vis spectra

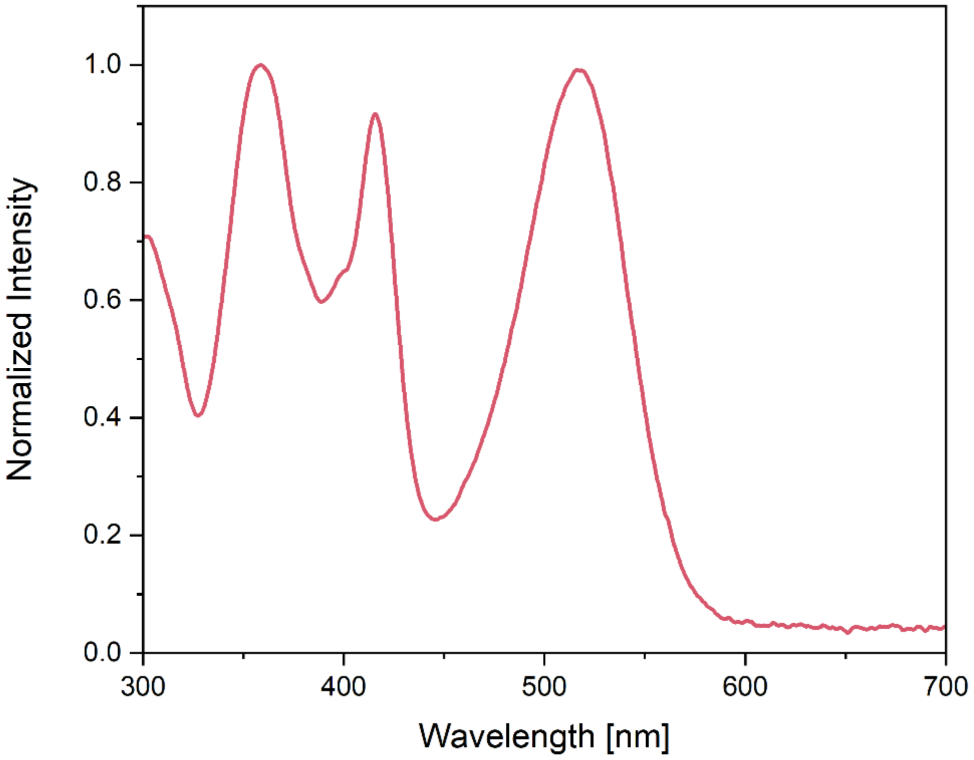


Fig. S21 UV–vis spectrum of **3** in C_6H_6.

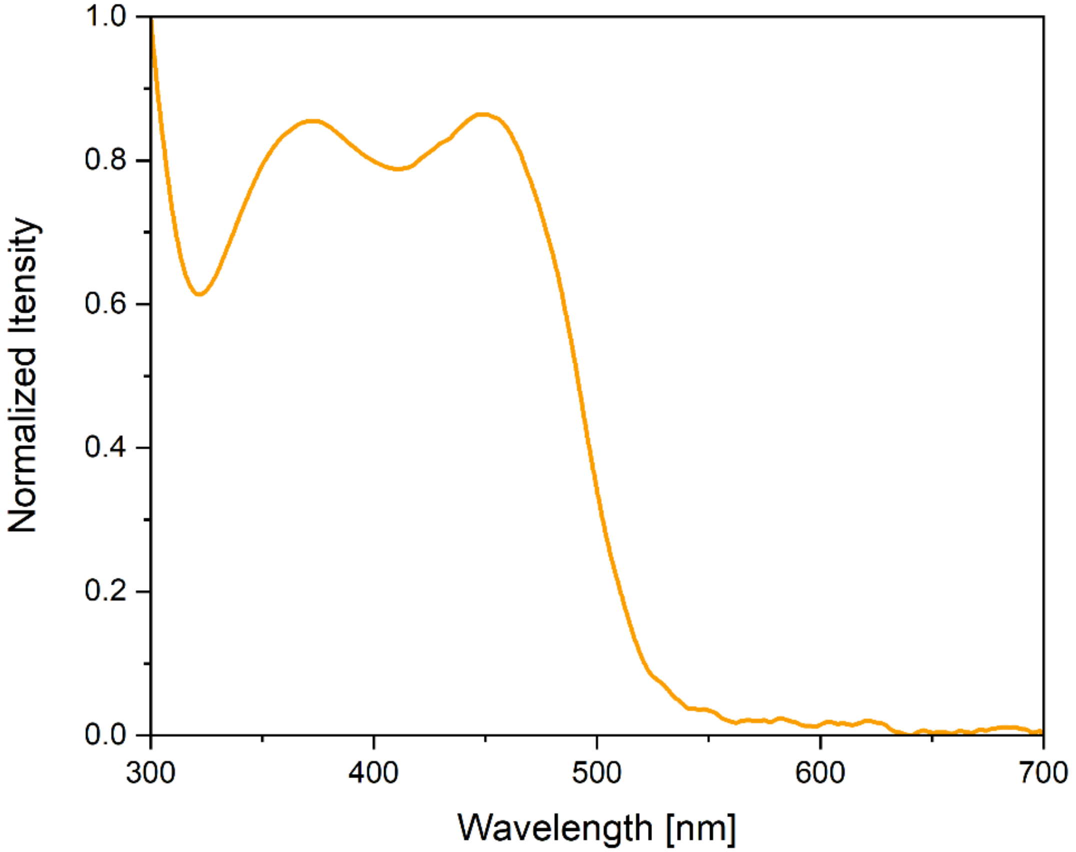


Fig. S22 UV-vis spectrum of **6** in C_6H_6.

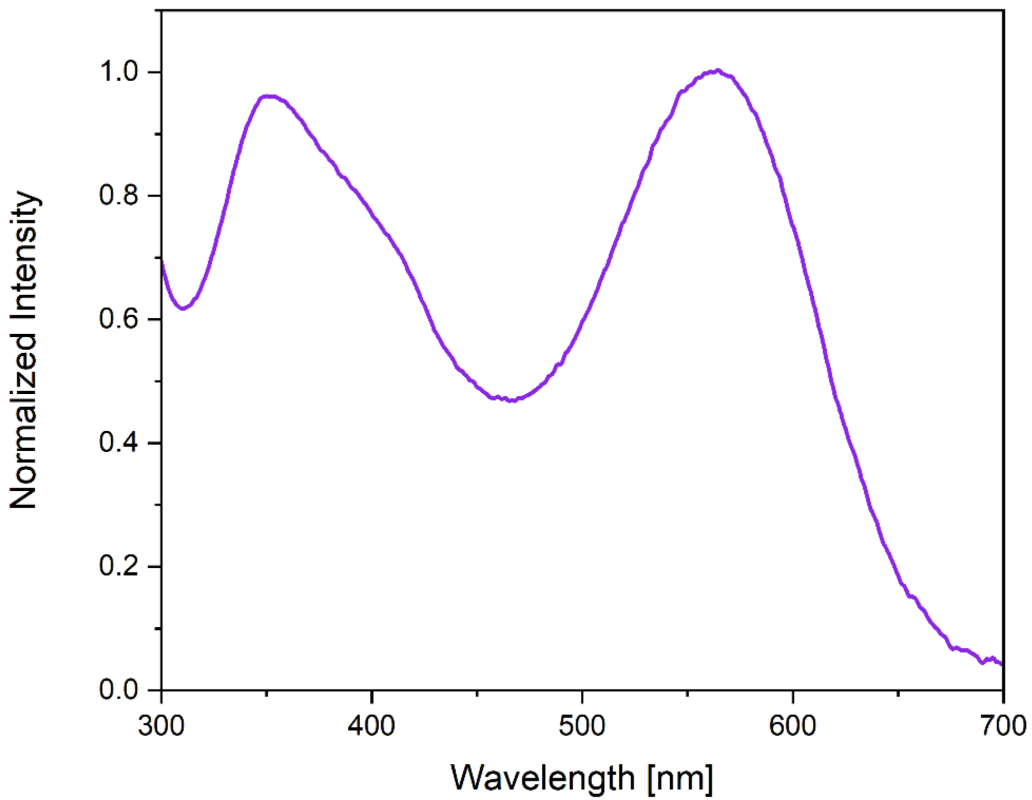


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Fig. S23 UV-vis spectrum of **7** in C_6H_6.

IR spectrum

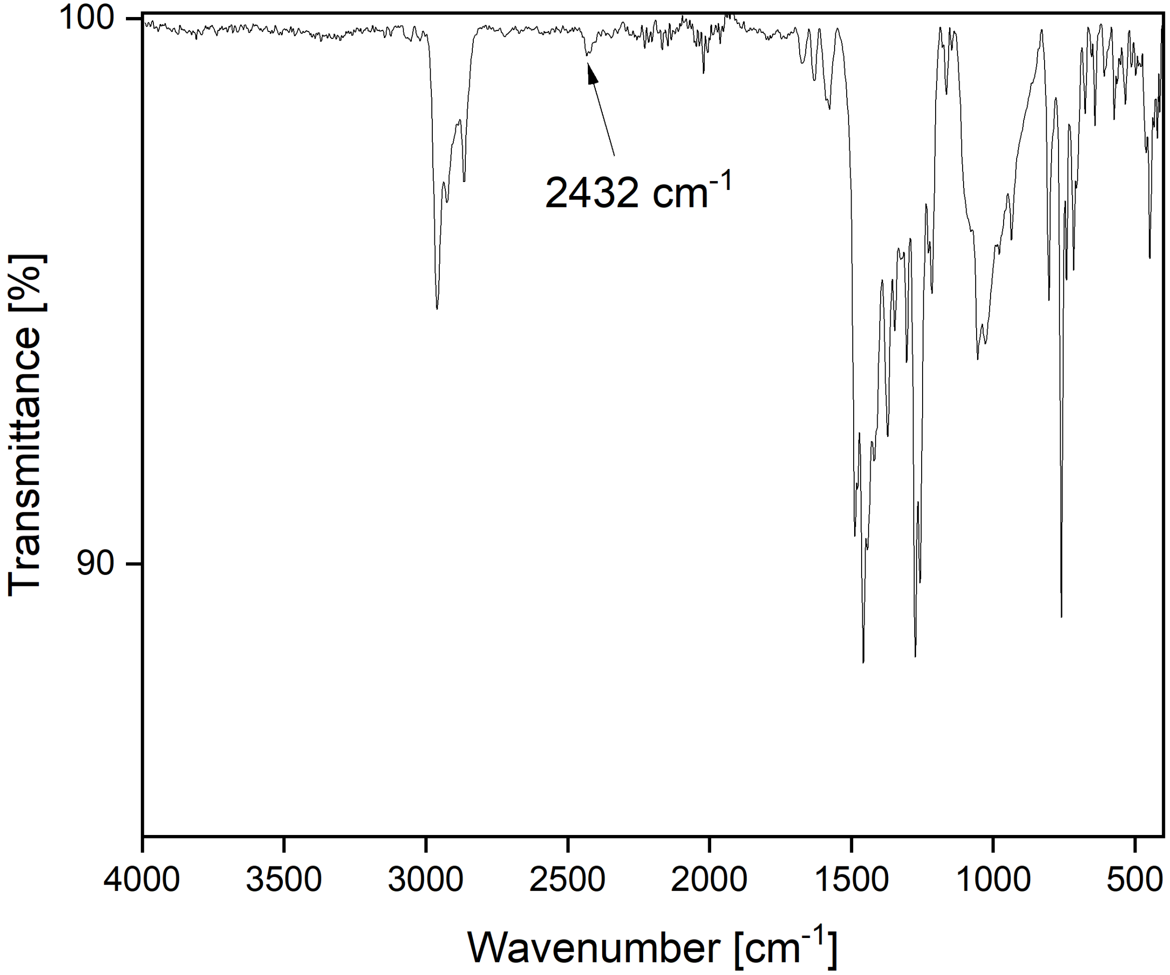


Fig. S24 Solid-state IR spectrum of **7**.

HRMS spectrum of reduction to diborene 7

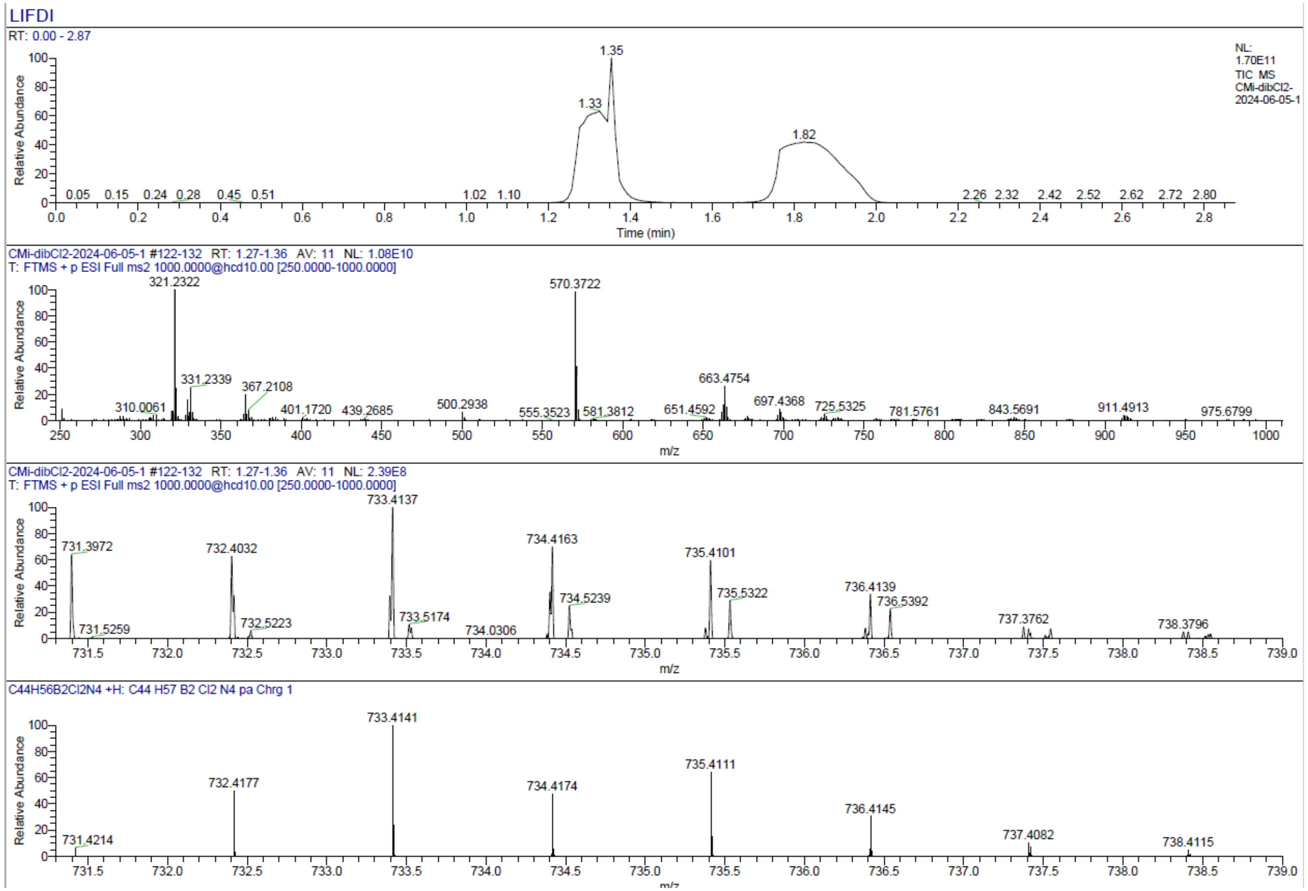


Fig. S25 HRMS (LIFDI) spectrum of reaction mixture reduction to diborene **7**: calcd. for $C_{44}H_{57}N_4B_2Cl_2$ $[M + H]^+$: *m/z* = 733.4141; found: 733.4137.

X-ray crystallographic data

The crystal data were collected on a *XtaLAB Synergy Dualflex HyPix* diffractometer with a Hybrid Pixel array detector and multi-layer mirror monochromated $Cu_{K\alpha}$ radiation. The structures were solved using the intrinsic phasing method,[5] refined with the ShelXL program[6] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealized positions, except those bound to boron, which were refined freely. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center under CCDC numbers 2447648 (**2**), 2447649 (**3**), 2447646 (**4**), 2447647 (**5**), 2447650 (**6**), 2447651 (**7**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

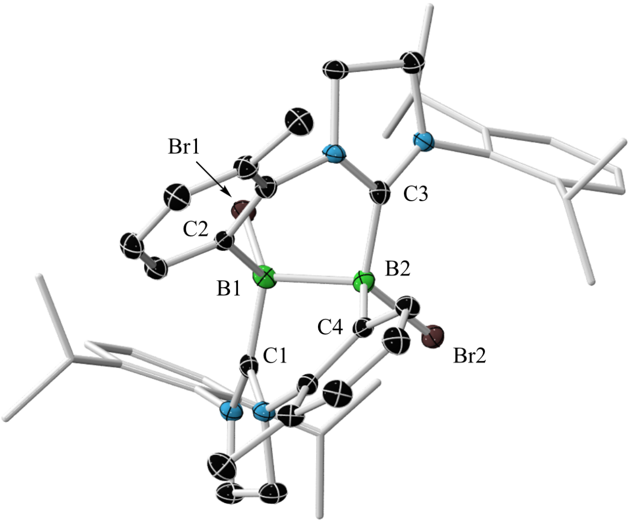


Fig. S26 Crystallographically-derived structure of **2**. Ellipsoids are shown at the 50% probability level. Ellipsoids of hydrogen atoms and the carbon atoms of Dipp and the toluene molecules were omitted for clarity.

Crystal data for **2**: $C_{51}H_{62}B_2Br_2N_4$, $M_r = 912.48$, colourless needle, 0.340×0.050×0.030 mm^3, monoclinic space group $P2_1/c$, $a = 7.85310(10)$ Å, $b = 15.44900(10)$ Å, $c = 37.9294(3)$ Å, $\beta = 91.6920(10)$°, $V = 4599.69(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.318$ g·cm^{-3}, $\mu = 2.522$ mm^{-1}, $F(000) = 1904$, $T = 100(2)$ K, $R_1 = 0.0436$, $wR_2 = 0.1011$, 9333 independent reflections [$2\theta \leq 150.428$°] and 508 parameters.

Refinement details for 2: Two reflektions (h,k,l = 3, 5, 7; -4, 4, 13) were removed from refinement as outliers.

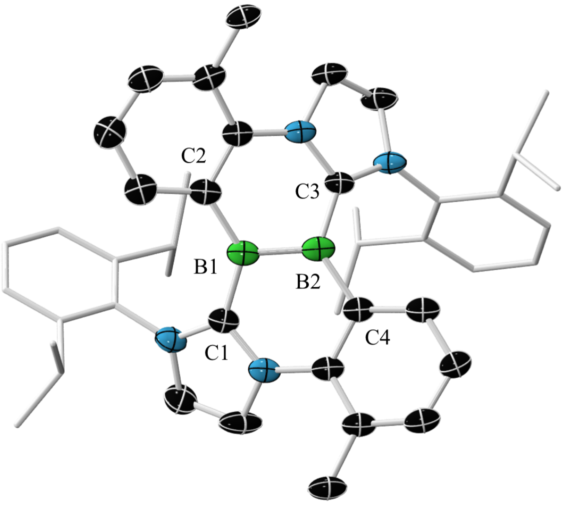


Fig. S27 Crystallographically-derived structure of **3**. Ellipsoids are shown at the 30% probability level. The unit cell contains co-crystallised [SIDippTol]BHI. The data obtained serves only as proof of connectivity due to whole molecule disorder.

Crystal data for 3: $C_{66}H_{82}B_3IN_6$, $M_r = 1118.70$, red block, 0.120×0.100×0.060 mm^3, monoclinic space group $P2_1/c$, $a = 15.6024(3)$ Å, $b = 21.2733(2)$ Å, $c = 21.6009(3)$ Å, $\beta = 93.274(2)$°, $V = 7157.95(18)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.038$ g·cm^{-3}, $\mu = 3.792$ mm^{-1}, $F(000) = 2352$, $T = 100(2)$ K, $R_1 = 0.0907$, $wR_2 = 0.2109$, 14662 independent reflections [$2\theta \leq 153.288$°] and 1085 parameters.

Refinement details for 3: The unit cell contains solvent molecules (diethyl ether) which have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.[7] There is a whole molecule disorder on the diborene molecule with an occupancy factor of 0.5. Idealized geometry of three otolyl-substituents were applied using AFIX 6. The displacement parameters of atoms C1_2 to C12_61 were restrained with RIGU keyword (esd = 0.004) in ShelXL input ('enhanced rigid bond' restraint). The U_{ij} displacement parameters of atoms C1_2 to C12_61 were restrained with a similarity restraint SIMU (esd = 0.009) and ISOR (esd = 0.018). Idealized geometry of NHC ligand were applied using SADI (N5 to C6; C3 to C4).

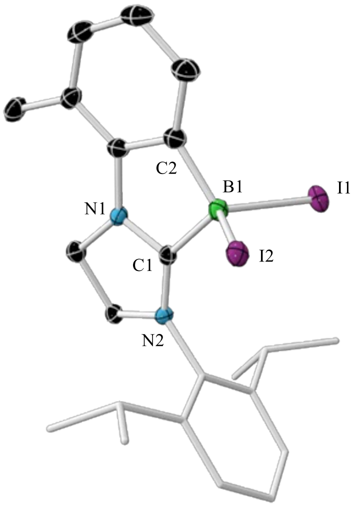


Fig. S28 Crystallographically-derived structure of **4**. Ellipsoids are shown at the 50% probability level. Ellipsoids of hydrogen atoms and the carbon atoms of Dipp and the toluene molecules were omitted for clarity.

Crystal data for 4: $C_{29}H_{35}BI_2N_2$, $M_r = 676.22$, colourless block, $0.100\times0.090\times0.050$ mm^3, triclinic space group $P\overline{1}$, $a = 8.20520(10)$ Å, $b = 10.8597(2)$ Å, $c = 16.6641(3)$ Å, $\alpha = 81.4500(10)°$, $\beta = 76.195(2)°$, $\gamma = 82.5200(10)°$, $V = 1419.00(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.583$ g·cm^{-3}, $\mu = 17.536$ mm^{-1}, $F(000) = 668$, $T = 100(2)$ K, $R_1 = 0.0247$, $wR_2 = 0.0607$, 5517 independent reflections [$2\theta \leq 150.172°$] and 291 parameters.

Refinement details for 4: The displacement parameters of the solvent molecules (RESI 2 and RESI 21 and RESI 211) were restrained to the same value with similarity restraint SIMU. The molecule structure was fixed with AFIX 6 to idealized geometry of toluene.

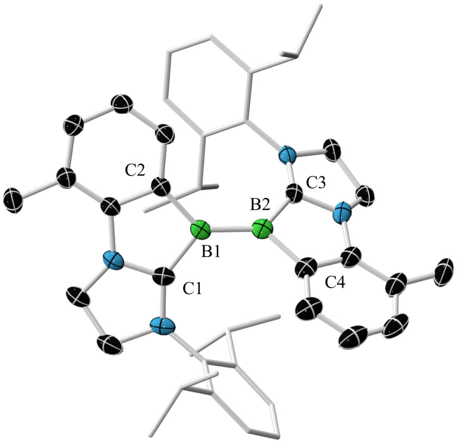


Fig. S29 Crystallographically-derived structure of **5**. Ellipsoids are shown at the 30% probability level. Ellipsoids of hydrogen atoms and the carbon atoms of Dipp and were omitted for clarity.

Crystal data for **5**: $C_{44}H_{54}B_2N_4$, M_r = 660.53, green block, 0.140×0.100×0.080 mm^3, monoclinic space group $P2_1/n$, a = 13.9101(2) Å, b = 15.7838(2) Å, c = 17.8930(3) Å, β = 104.378(2)°, V = 3805.44(10) Å^3, Z = 4, ρ_{calcd} = 1.153 g·cm^{-3}, μ = 0.501 mm^{-1}, F(000) = 1424, T = 100(2) K, R_1 = 0.0775, wR_2 = 0.1802, 7830 independent reflections [$2\theta \leq 150.694°$] and 461 parameters.

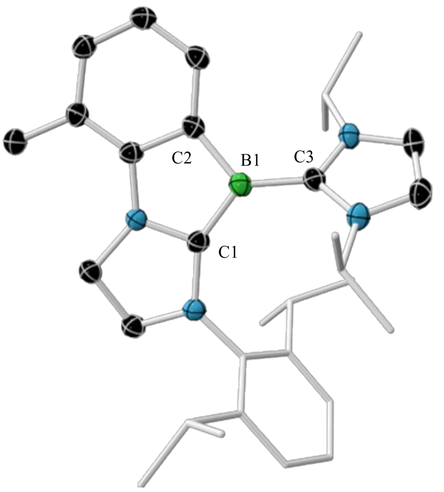


Fig. S30 Crystallographically-derived structure of **6**. Ellipsoids are shown at the 50% probability level. Ellipsoids of hydrogen atoms and the Dipp and *i*Pr carbon atoms were omitted for clarity. The unit cell contains two molecules.

Crystal data for **6**: $C_{31}H_{43}BN_4$, M_r = 482.50, orange plate, 0.180×0.160×0.050 mm^3, triclinic space group $P\overline{1}$, a = 14.1122(2) Å, b = 14.2169(2) Å, c = 16.8130(2) Å, α = 97.5520(10)°, β = 101.3590(10)°, γ = 101.8450(10)°, V = 3184.39(8) Å^3, Z = 4, ρ_{calcd} = 1.006 g·cm^{-3}, μ = 0.446 mm^{-1}, F(000) = 1048, T = 100(2) K, R_1 = 0.0680, wR_2 = 0.1602, 12833 independent reflections [$2\theta \leq 150.954°$] and 667 parameters.

Refinement details for 6: The unit cell contains solvent molecules (diethyl ether) which have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.[7] Some reflections were assigned to a twin component (0.6%) and were removed from refinement as outliers.

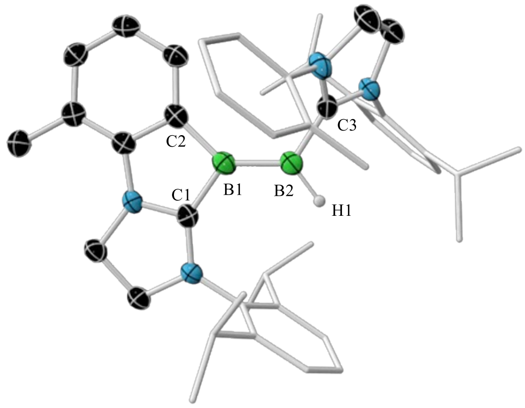
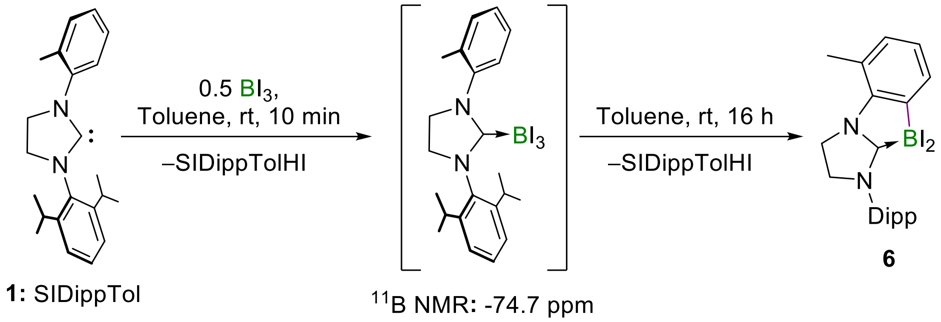


Fig. S31 Crystallographically-derived structure of **7**. Ellipsoids are shown at the 50% probability level. Ellipsoids of hydrogen atoms and Dipp and Tol carbon atoms were omitted for clarity.

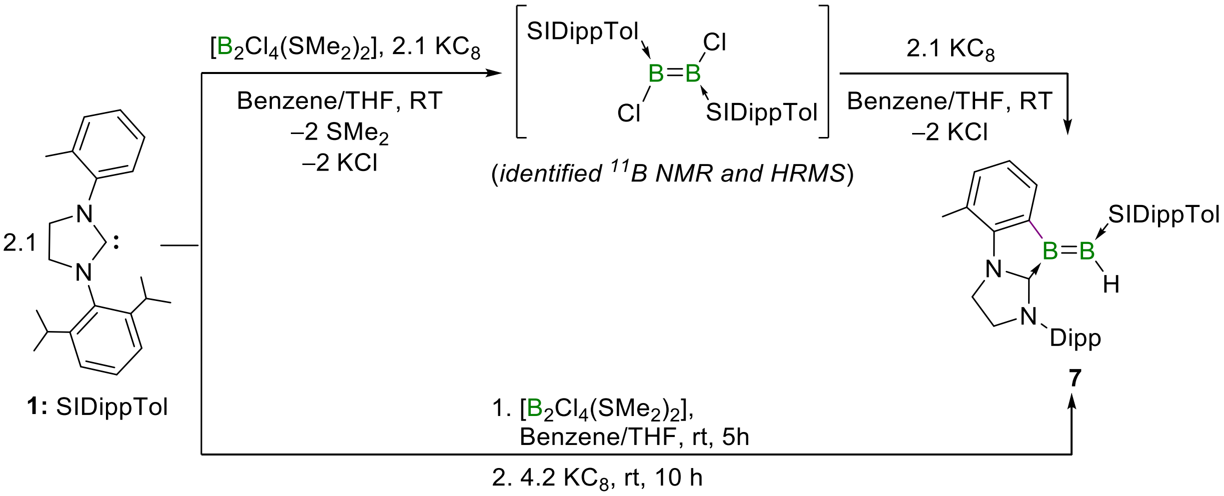
Crystal data for **7**: $C_{44}H_{56}B_2N_4$, $M_r = 662.54$, purple block, 0.220×0.170×0.080 mm^3, tetragonal space group $P\bar{4}2_1c$, $a = 18.90630(10)$ Å, $b = 18.90630(10)$ Å, $c = 23.2427(3)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 8308.06(14)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.059$ g·cm^{-3}, $\mu = 0.459$ mm^{-1}, $F(000) = 2864$, $T = 100(2)$ K, $R_1 = 0.0482$, $wR_2 = 0.1197$, Flack parameter = 0.06(11), 8485 independent reflections [$2\theta \leq 149.964°$] and 464 parameters.

Refinement details for 7: The unit cell contains solvent molecules (pentane) which have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.[7] All Hydrogen atoms except H1 were assigned to idealized positions. The coordinate of H1 was refined freely.

Schemes for the identification of intermediates



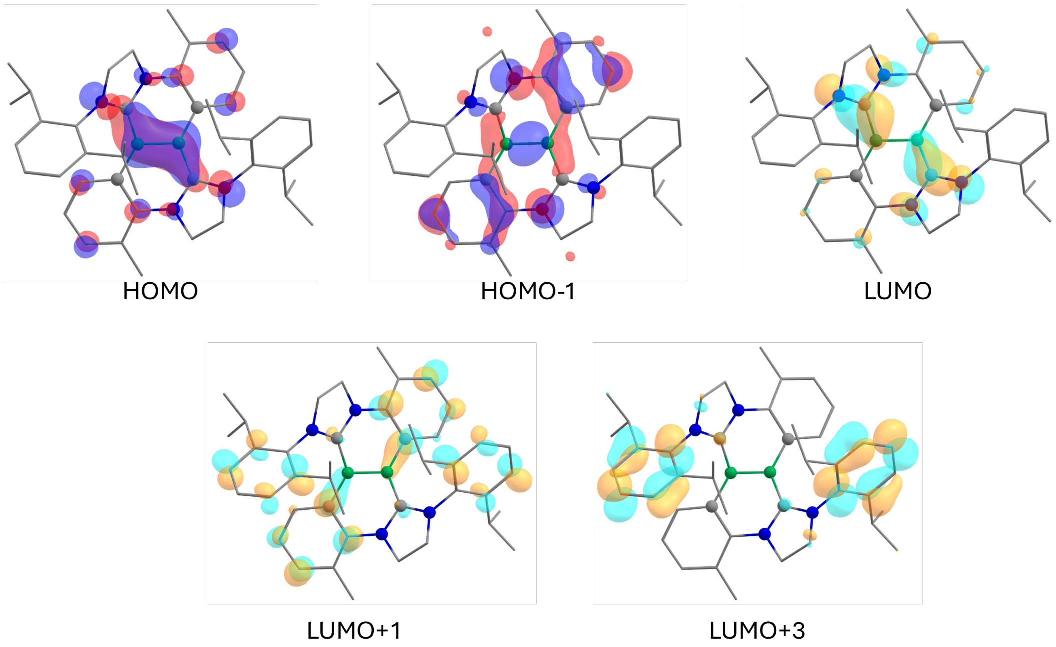
Scheme S1. Synthesis of **6** via an BI_3•SIDippTol intermediate.



Scheme S2. Synthesis of **7** via a diborene intermediate.

Computational details

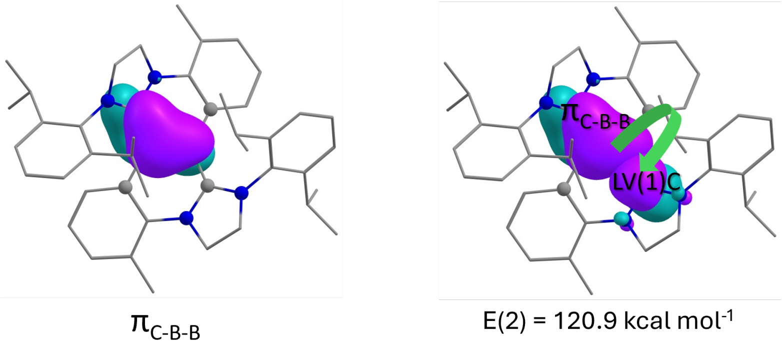
All molecules were fully optimized using the Gaussian 16, Rev. C.01[8] quantum chemistry program package at the ωB97X-D[9]/Def2-SVP[10] level of theory. The model compounds were fully optimised in gaseous state (no solvent effects) starting from the X-ray crystallographic structural coordinates. Frequency calculations were performed at the same level of theory to verify the nature of the stationary states and the absence of any imaginary frequencies to confirm that all structures represent minima on the potential energy hypersurface. Further single-point energy calculations were carried out with the ORCA 5.0.4 program[11] based on ωB97X-D/Def2-SVP structures using the domain-based local pair natural orbital approximation of CCSD(T)[12] as well as the solvation model based on density (SMD) continuum[13] (solvent: diethyl ether). The Def2-SVP basis set in combination with the resolution of identity approximation for Coulomb integrals (RI-J) and the numerical chain-of-spheres integration for the Hartree–Fock exchange integrals (COSX)[14] was chosen for these calculations. For this purpose, Def2/J and Def2-SVP/C were used as auxiliary basis sets. The gauge-including atomic orbital (GIAO)[15] method was employed to compute the ^{11}B chemical shifts. The NMR chemical shifts were calculated using the hybrid B3LYP functional[16] and def2-SVP basis set on the optimized geometries. The ^{11}B NMR chemical shifts were calculated relative to B_2H_6 (B3LYP, δ_{11B} shielding constant 93.38 ppm) and converted to the usual [$BF_3.OEt_2$] scale using the experimental $\delta(^{11}B)$ value of B_2H_6, 16.6 ppm. Natural bonding analyses were performed with the natural bond orbital (NBO 7.0)[17] partitioning scheme as implemented in the Gaussian 16 suite of programs. Natural charges were obtained from a natural bond orbital analysis. To analyse the bonding situation, the Wiberg bond indices (WBIs)[18] and Mayer bond orders (MBOs)[19] were obtained from NBO analysis and using the Multiwfn V.3.8 package.[20] Pictures of MOs and NBOs were generated by means of the ChemCraft1.8 program.[21]



HOMO HOMO-1 LUMO

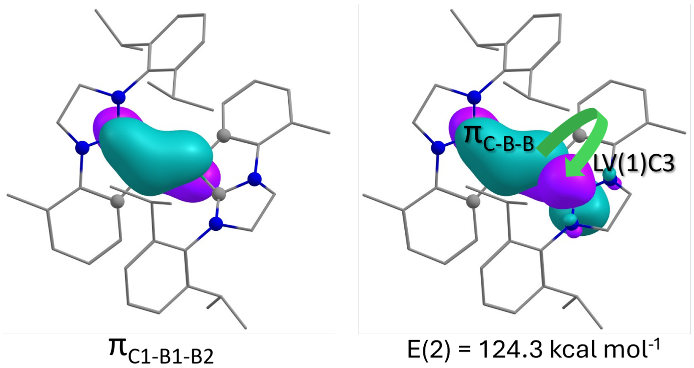
LUMO+1 LUMO+3

Fig. S32 Selected molecular orbitals of **3** (isosurface plot at 0.043 a.u.).



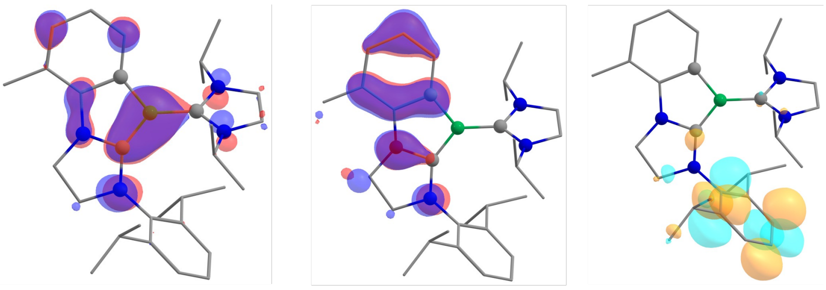
$\pi_{C\text{-}B\text{-}B}$ E(2) = 120.9 kcal mol^{-1}

Fig. S33 Selected natural bonding orbitals (NBOs) of **3** (isosurface plot at 0.043 a.u.).

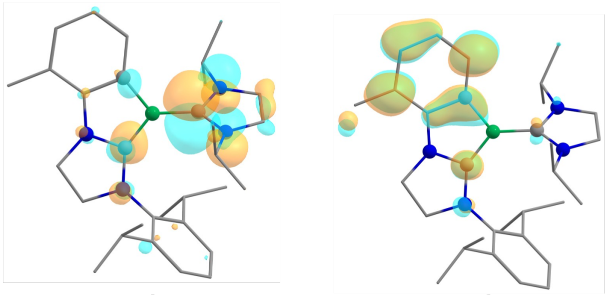


$\pi_{C1\text{-}B1\text{-}B2}$ E(2) = 124.3 kcal mol^{-1}

Fig. S34 Selected natural bonding orbitals (NBOs) of **5** (isosurface plot at 0.043 a.u.).

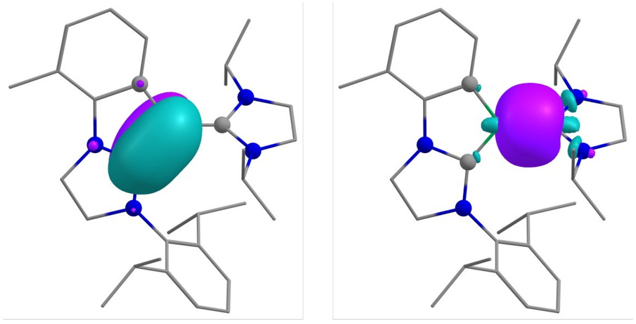


HOMO HOMO-1 LUMO



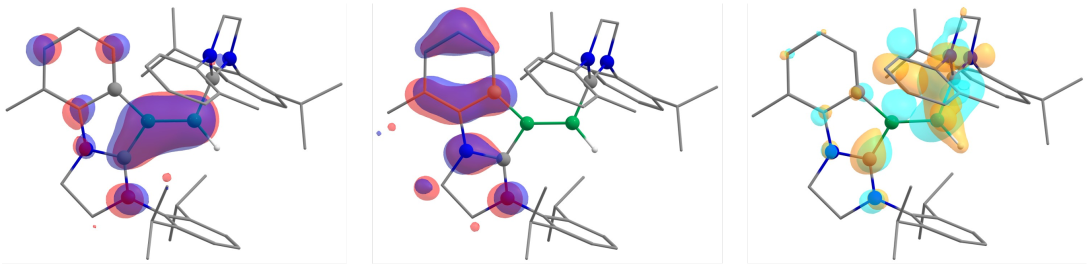
LUMO+2 LUMO+4

Fig. S35 Selected molecular orbitals of **6** (isosurface plot at 0.043 a.u.).



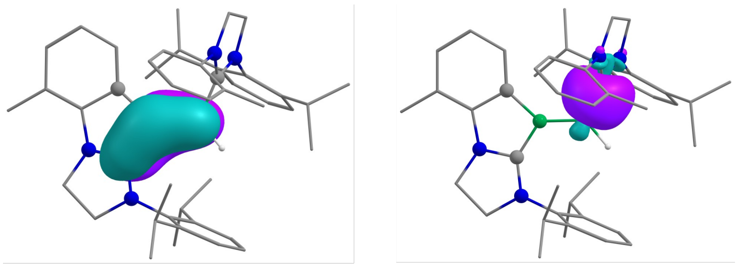
$\pi_{C1\text{-}B1}$ $\sigma_{C3\text{-}B1}$

Fig. S36 Selected natural bonding orbitals (NBOs) of **6** (isosurface plot at 0.043 a.u.).



HOMO HOMO-1 LUMO

Fig. S37 Selected molecular orbitals of **7** (isosurface plot at 0.043 a.u.).



$\pi_{C1\text{-}B1\text{-}B2}$ $\sigma_{C3\text{-}B2}$

Fig. S38 Selected natural bonding orbitals (NBOs) of **7** (isosurface plot at 0.043 a.u.).

Table S1. TD-DFT calculated energies (excitation energy (eV), λ_{calc} (nm)), oscillator strength (f), and main composition of the first UV−vis electronic excitations for **3**. Experimental absorption wavelengths (λ_{exp}, nm) of **3** are given for comparison.

No.	Transition Configurations (%)[a]	Excitation Energy (ev)	Calcd. Wavelength λ (nm)	Osc. Strength
1	HOMO → LUMO (95)	2.51	493.5	0.2288
2	HOMO → LUMO+2 (99)	3.02	410.4	0.001
3	HOMO → LUMO+1 (82) HOMO → LUMO+3 (15)	3.03	409.6	0.0736
4	HOMO → LUMO+1 (13) HOMO → LUMO+3 (84)	3.07	402.9	0.0572
5	HOMO → LUMO+4 (99)	3.12	397.3	0.0008
6	HOMO-1 → LUMO (13) HOMO → LUMO+5 (85)	3.31	374.4	0.0853
7	HOMO → LUMO+6 (98)	3.48	355.3	0.0035
8	HOMO-1 → LUMO (68) HOMO → LUMO+5 (12)	3.51	352.6	0.3897
9	HOMO → LUMO+7 (94)	3.67	337.6	0.0475
10	HOMO-2 → LUMO (82) HOMO → LUMO+8 (17)	3.86	320.6	0.0147

[a]components with greater than 10% contribution shown

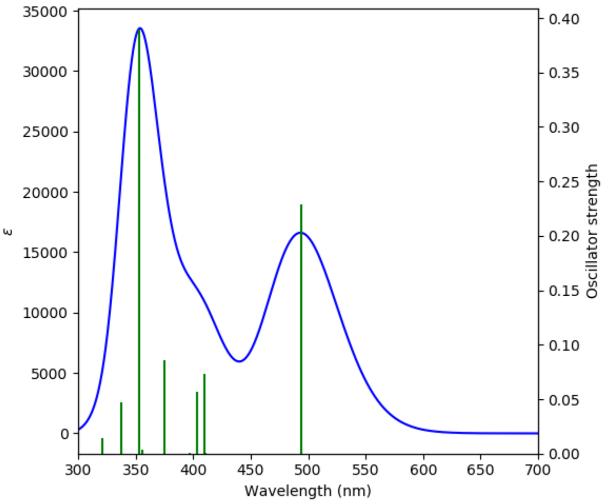


Fig. S39 Absorption spectrum of **3** computed at the TD-DFT-B3LYP/Def2-SVP level of theory (ε in $LM^{-1}cm^{-1}$).

Table S2. TD-DFT calculated energies (excitation energy (eV), λcalc (nm)), oscillator strength (f), and main composition of the first UV−vis electronic excitations for **6**. Experimental absorption wavelengths (λ_{exp}, nm) of **6** are given for comparison.

No.	Transition configurations (%)[a]	Excitation Energy (ev)	Calcd. (nm)	Wavelength λ	Osc. Strength
1	HOMO → LUMO (92)	2.42	512.2		0.0343
2	HOMO → LUMO+1 (92)	2.47	500.2		0.0046
3	HOMO → LUMO+2 (97)	2.76	449.1		0.1827
4	HOMO → LUMO+3 (100)	3.22	384.2		0.0065
5	HOMO → LUMO+4 (91)	3.36	368.3		0.0501
6	HOMO → LUMO+5 (80)	3.81	325.2		0.0991
7	HOMO-1 → LUMO (80)	3.90	317.2		0.0779
8	HOMO → LUMO+6 (81)	3.94	314.3		0.0497
9	HOMO-1 → LUMO+1 (86)	3.97	311.5		0.027
10	HOMO-1 → LUMO+2 (88)	4.09	302.6		0.1039

[a]components with greater than 10% contribution shown

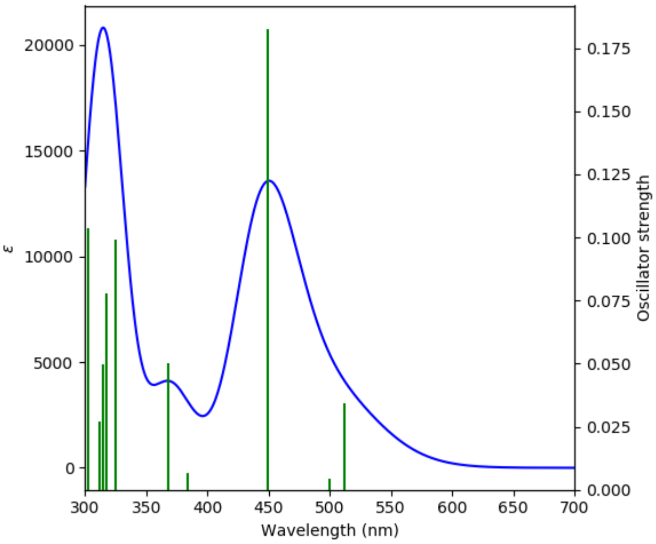


Fig. S40 Absorption spectrum of **6** computed at the TD-DFT-B3LYP/Def2-SVP level of theory (ε in $LM^{-1}cm^{-1}$).

Table S3. TD-DFT calculated energies (excitation energy (eV), λ_{calc} (nm)), oscillator strength (f), and main composition of the first UV−vis electronic excitations for **7**. Experimental absorption wavelengths (λ_{exp}, nm) of **7** are given for comparison.

No.	Transition Configurations (%)[a]	Excitation Energy (ev)	Calcd. (nm)	Wavelength λ	Osc. Strength
1	HOMO → LUMO (86)	2.22	558.2		0.0688
2	HOMO → LUMO+1 (87)	2.55	484.5		0.0565
3	HOMO → LUMO+2 (71) HOMO → LUMO+3 (26)	2.64	468.5		0.0049
4	HOMO → LUMO+2 (24) HOMO → LUMO+3 (73)	2.66	465.4		0.0006
5	HOMO → LUMO+4 (48) HOMO → LUMO+5 (48)	2.77	446.1		0.0028
6	HOMO → LUMO+4 (28) HOMO → LUMO+5 (44) HOMO → LUMO+7 (20)	2.84	435.2		0.0173
7	HOMO → LUMO+6 (96)	2.89	428.6		0.0156
8	HOMO → LUMO+4 (16) HOMO → LUMO+7 (65)	3.30	375.2		0.2033
9	HOMO → LUMO+8 (88)	3.38	366.4		0.0457
10	HOMO-1 → LUMO (89)	3.68	336.8		0.045

[a]components with greater than 10% contribution shown

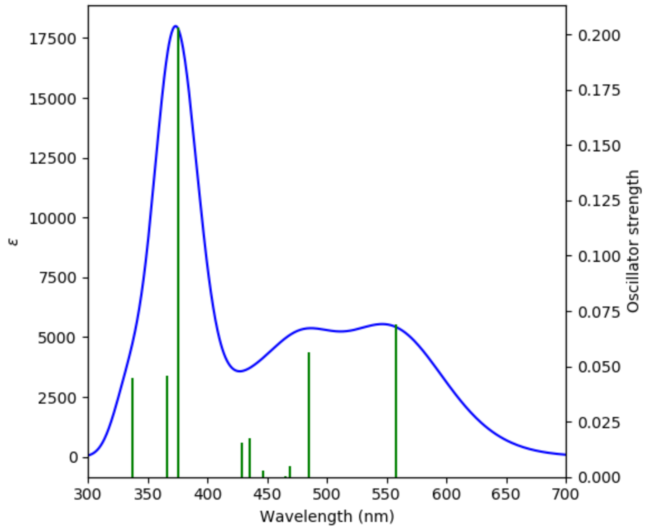


Fig. S41 Absorption spectrum of **7** computed at the TD-DFT-B3LYP/Def2-SVP level of theory (ε in $LM^{-1}cm^{-1}$).

Coordinates of optimized geometries

Compound 3, ωB97X-D/Def2-SVP

Energy = – 1975.996252 Eh

Imaginary frequency = 0

N	0.863996000000	-2.396192000000	-0.623684000000
N	-0.864118000000	2.396445000000	-0.623204000000
N	-2.572189000000	1.313471000000	0.269362000000
N	2.572579000000	-1.313662000000	0.268461000000
C	-1.459610000000	1.166108000000	-0.517135000000
C	-0.426964000000	-2.645415000000	-1.141209000000
C	0.426858000000	2.645769000000	-1.140710000000
C	1.459607000000	-1.165907000000	-0.517513000000
C	-1.345288000000	-1.559502000000	-1.204974000000
C	1.345207000000	1.559890000000	-1.204643000000
C	2.660839000000	1.859034000000	-1.605314000000
C	3.130020000000	0.669043000000	1.606136000000
C	3.487838000000	-0.288156000000	0.638973000000
C	3.064784000000	3.140624000000	-1.930817000000
C	4.759019000000	-0.282555000000	0.031834000000
C	2.120909000000	4.167440000000	-1.938768000000
C	4.056775000000	1.666498000000	1.917716000000
C	1.808374000000	0.600299000000	2.353242000000
C	-3.487753000000	0.287987000000	0.639155000000
C	-0.791249000000	-3.944065000000	-1.582703000000
C	0.791070000000	3.944494000000	-1.582005000000
C	-2.660945000000	-1.858525000000	-1.605676000000
C	-3.130149000000	-0.669960000000	1.605680000000
C	1.076805000000	1.943574000000	2.398530000000
C	5.658708000000	0.725067000000	0.386522000000
C	0.185190000000	-5.077676000000	-1.810265000000
C	5.165199000000	-1.343118000000	-0.980097000000
C	2.037062000000	0.046982000000	3.765911000000
C	-0.185462000000	5.078063000000	-1.809372000000
C	-2.121100000000	-4.166892000000	-1.939489000000
C	-1.808441000000	-0.602018000000	2.352740000000
C	-2.036780000000	-0.048712000000	3.765471000000
C	5.641382000000	-0.741751000000	-2.306299000000
C	-4.057138000000	-1.667406000000	1.916579000000
C	-1.077567000000	-1.945681000000	2.397907000000
C	-1.624813000000	3.410119000000	0.115335000000
C	5.306955000000	1.701418000000	1.311150000000
C	1.624875000000	-3.410104000000	0.114300000000
C	-3.064941000000	-3.140045000000	-1.931374000000
B	-0.787106000000	-0.123398000000	-1.021342000000
C	2.571183000000	-2.583252000000	0.970274000000
C	-5.307297000000	-1.701650000000	1.309923000000
C	-4.758886000000	0.283057000000	0.031933000000

C	-5.658789000000	-0.724633000000	0.385901000000
B	0.787063000000	0.123718000000	-1.021271000000
C	-2.570951000000	2.583008000000	0.971278000000
C	-5.640179000000	0.743813000000	-2.306284000000
C	6.226028000000	-2.280194000000	-0.388916000000
C	-5.164783000000	1.344307000000	-0.979398000000
C	-6.226046000000	2.280748000000	-0.388004000000

Compound 5, ωB97X-D/Def2-SVP

Energy = – 1975.980562 Eh

Imaginary frequency = 0

N	2.295039000000	1.704220000000	0.341553000000
N	-0.625179000000	-3.030905000000	-0.195025000000
B	0.003119000000	0.806609000000	-0.911270000000
N	0.625247000000	3.030959000000	-0.195111000000
N	-2.295040000000	-1.704277000000	0.341718000000
C	1.135355000000	-1.880416000000	-1.119366000000
C	0.699903000000	-3.145906000000	-0.664355000000
C	1.113343000000	1.762932000000	-0.319784000000
C	-1.113351000000	-1.762902000000	-0.319657000000
C	1.472758000000	-4.309235000000	-0.729065000000
C	4.337837000000	0.642986000000	-0.476238000000
C	3.226320000000	0.624806000000	0.386463000000
C	-0.699841000000	3.146062000000	-0.664419000000
C	2.394040000000	-1.815503000000	-1.718420000000
C	3.046432000000	-0.394663000000	1.341501000000
C	-1.135423000000	1.880591000000	-1.119381000000
C	4.529564000000	1.720218000000	-1.535277000000
C	2.662170000000	3.008675000000	0.892155000000
C	-1.361263000000	-3.811409000000	0.781958000000
C	3.203590000000	-2.946600000000	-1.789695000000
C	2.749532000000	-4.168357000000	-1.291502000000
C	-3.226392000000	-0.624924000000	0.386454000000
C	1.849403000000	-0.389167000000	2.277533000000
C	-1.472580000000	4.309463000000	-0.729164000000
C	1.361300000000	3.811299000000	0.782038000000
C	-4.337777000000	-0.643228000000	-0.476385000000
C	-3.046700000000	0.394614000000	1.341471000000
C	-1.849784000000	0.389229000000	2.277648000000
C	5.294281000000	-0.367345000000	-0.338978000000
C	-2.662129000000	-3.008770000000	0.892224000000
C	-2.749406000000	4.168684000000	-1.291518000000
C	0.986827000000	-5.660565000000	-0.267605000000
C	-2.394146000000	1.815781000000	-1.718361000000
C	1.329299000000	-1.791993000000	2.594583000000
C	-4.529223000000	-1.720516000000	-1.535414000000
C	4.016491000000	-1.394122000000	1.424515000000
C	-3.203599000000	2.946953000000	-1.789631000000

C	2.166041000000	0.374241000000	3.568974000000
C	-4.016833000000	1.394011000000	1.424296000000
C	5.137038000000	-1.376531000000	0.601150000000
C	-5.294328000000	0.367035000000	-0.339300000000
C	-1.329547000000	1.792078000000	2.594402000000
C	-0.986477000000	5.660769000000	-0.267821000000
C	-5.137281000000	1.376282000000	0.600787000000
C	-2.166633000000	-0.373860000000	3.569220000000
C	5.738374000000	2.605547000000	-1.205324000000
C	4.650796000000	1.137802000000	-2.947640000000
C	-5.738094000000	-2.605867000000	-1.205769000000
C	-4.650053000000	-1.138157000000	-2.947839000000
B	-0.003252000000	-0.806510000000	-0.911183000000

Compound 6, ωB97X-D/Def2-SVP

Energy = – 1449.641644 Eh

Imaginary frequency = 0

N	0.088080000000	-2.040721000000	-1.334550000000
B	-1.191514000000	0.019580000000	-0.334368000000
N	-1.048216000000	2.178168000000	0.575977000000
N	0.970455000000	1.256717000000	0.825391000000
N	-1.750023000000	-2.518004000000	-0.297056000000
C	-0.942934000000	-1.480252000000	-0.648377000000
C	-2.332059000000	2.103299000000	0.067080000000
C	-0.314016000000	1.020872000000	0.324239000000
C	3.183792000000	0.933409000000	-0.130757000000
C	-2.524134000000	0.803811000000	-0.496157000000
C	1.035844000000	-1.263795000000	-2.146023000000
C	4.374509000000	0.203849000000	-0.186145000000
C	2.251835000000	-0.767703000000	1.371844000000
C	2.127580000000	0.458503000000	0.681578000000
C	-0.073726000000	-3.409939000000	-1.406790000000
C	-3.775670000000	0.533896000000	-1.080154000000
C	-2.947195000000	-2.397832000000	0.545688000000
C	-3.334350000000	3.089686000000	0.074705000000
C	0.980555000000	2.479368000000	1.611875000000
C	-1.222516000000	-3.708630000000	-0.752686000000
C	3.456351000000	-1.471435000000	1.273228000000
C	1.137338000000	-1.270551000000	2.275649000000
C	3.047021000000	2.205324000000	-0.953768000000
C	4.518393000000	-0.985095000000	0.517930000000
C	-0.217583000000	3.257664000000	1.057209000000
C	-4.779197000000	1.494218000000	-1.087786000000
C	-4.555243000000	2.753671000000	-0.514201000000
C	0.999196000000	-2.793922000000	2.260982000000
C	-4.113585000000	-3.168524000000	-0.059862000000
C	3.191301000000	1.926165000000	-2.453891000000
C	0.411748000000	-0.957516000000	-3.504100000000
C	-2.636973000000	-2.804089000000	1.981070000000
C	2.381863000000	-1.962349000000	-2.246977000000

C	4.035085000000	3.285756000000	-0.499804000000
C	1.337440000000	-0.749589000000	3.704156000000
C	-3.141526000000	4.451227000000	0.695953000000

Compound 7, ωB97X-D/Def2-SVP

Energy = – 1977.174080 Eh

Imaginary frequency = 0

B	0.227538000000	-0.259369000000	0.546647000000
H	0.327211000000	-1.462248000000	0.424678000000
B	-0.842186000000	0.721286000000	-0.115362000000
C	-1.058721000000	2.283957000000	-0.187283000000
C	-0.426309000000	3.395746000000	0.386287000000
C	-0.829215000000	4.694495000000	0.080472000000
C	-1.877552000000	4.911519000000	-0.817824000000
C	-2.549019000000	3.846955000000	-1.433053000000
C	-2.125685000000	2.556802000000	-1.092984000000
N	-2.608202000000	1.341466000000	-1.606522000000
C	-1.950624000000	0.278663000000	-1.056619000000
N	-2.546376000000	-0.865726000000	-1.484274000000
C	-3.567782000000	-0.582803000000	-2.480880000000
C	-3.826920000000	0.925051000000	-2.276888000000
C	-2.004535000000	-2.150132000000	-1.212278000000
C	-0.949692000000	-2.639758000000	-2.004466000000
C	-0.398879000000	-3.881431000000	-1.678083000000
C	-0.864941000000	-4.604888000000	-0.585395000000
C	-1.898360000000	-4.098914000000	0.195764000000
C	-2.487723000000	-2.867220000000	-0.102603000000
C	-3.576219000000	-2.299241000000	0.792234000000
C	-4.714704000000	-3.294599000000	1.032234000000
C	-2.977628000000	-1.788904000000	2.108341000000
C	-0.394743000000	-1.845654000000	-3.175203000000
C	1.106989000000	-1.594141000000	-3.025977000000
C	-0.728919000000	-2.521047000000	-4.509928000000
C	-3.645863000000	4.112456000000	-2.434100000000
C	1.347304000000	0.465055000000	1.370429000000
N	2.574535000000	0.749740000000	0.924351000000
C	3.352383000000	1.534280000000	1.880885000000
C	2.336303000000	1.798442000000	3.006098000000
N	1.181984000000	1.006794000000	2.583197000000
C	0.032543000000	0.820393000000	3.407943000000
C	-0.845364000000	1.885135000000	3.605874000000
C	-1.956045000000	1.726933000000	4.427863000000
C	-2.181001000000	0.501378000000	5.051111000000
C	-1.299499000000	-0.557115000000	4.847783000000
C	-0.176591000000	-0.423829000000	4.025451000000
C	0.745932000000	-1.586206000000	3.779173000000
C	3.150268000000	0.264914000000	-0.290615000000
C	3.747245000000	-1.009305000000	-0.294547000000
C	4.392435000000	-1.425301000000	-1.461784000000
C	4.440582000000	-0.605554000000	-2.583555000000

C	3.811959000000	0.634019000000	-2.568332000000
C	3.142007000000	1.089599000000	-1.430266000000
C	3.682700000000	-1.939369000000	0.905954000000
C	2.920234000000	-3.225250000000	0.565948000000
C	5.077159000000	-2.237287000000	1.467287000000
C	2.402679000000	2.414234000000	-1.458579000000
C	1.341476000000	2.438626000000	-2.563195000000
C	3.362886000000	3.602461000000	-1.569828000000

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