Supporting Information for:

Hydrosilylation of B≡B Triple Bonds: Catalyst- and Reductant-Free Construction of B–Si bonds and B_2Si Heterocycles

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Synthetic Details

General Considerations. All manipulations were performed either under an atmosphere of dry argon or *in vacuo* using standard Schlenk line or glovebox techniques. Deuterated solvents were dried over molecular sieves and degassed by three freeze-pump-thaw cycles prior to use. All other solvents were distilled and degassed from appropriate drying agents. Solvents (both deuterated and non-deuterated) were stored under argon over activated 4 Å molecular sieves. NMR spectra were acquired on a Bruker Avance 500 NMR spectrometer (^{1}H: 500.1 MHz, ^{11}B: 160.5 MHz, ^{13}C{^{1}H}: 125.8 MHz, ^{29}Si{^{1}H}: 99.4 MHz) or on a Bruker Avance 400 NMR spectrometer (^{1}H: 400.1 MHz, ^{11}B: 128.4 MHz, ^{13}C{^{1}H}: 125.8 MHz,) at 298 K unless otherwise stated. Chemical shifts (δ) are given in ppm and internally referenced to the carbon nuclei (^{13}C{^{1}H}) or residual protons (^{1}H) of the solvent. ^{11}B NMR spectra were referenced to [$BF_3{\cdot}OEt_2$] as an external standard. ^{29}Si NMR spectra were referenced to $SiMe_4$ as an external standard. High-resolution mass spectrometry data was obtained from a Thermo Scientific Exactive Plus spectrometer in ASAP or LIFDI mode. H_3SiPh and $HSiMe_2Ph$ were purchased from Sigma-Aldrich. SIDep[1] and $B_2(SIDep)_2$[2] were synthesized following a modified literature procedure.

Synthesis of 2

30 mg (44 µmol) $B_2(SIDep)_2$ was dissolved in 0.6 mL benzene and 5.9 mg (44 µmol) $HSiMe_2Ph$ was added by cannula. Within 6 d at 40 °C the solution turned from red to purple with complete consumption of the diboryne. The solvent was removed under reduced pressure and the yellow residue was washed with pentane (3 x 0.6 mL). After drying under vacuum the product was isolated in 99% yield (35.9 mg) as a purple solid. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated hexane solution.

$^{1}H\{^{11}B\}$ NMR (500.1 MHz, C_6D_6, 298 K): 7.55 – 7.52 (m, 2H, CH_{Ar}), 7.30 – 7.27 (m, 2H, CH_{Ar}), 7.26 – 7.22 (m, 1H, CH_{Ar}), 7.18 (t, 2H, $^{3}J_{H,H}$ = 7.5 Hz, CH_{Ar}, *overlapping with the solvent signal*), 7.01 – 6.99 (m, 6H, CH_{Ar}), 6.83 (s, 2H, CH_{Ar}), 6.81 (s, 2H, CH_{Ar}), 4.48 (br. s, 1H, B*H*), 3.17 (s, 4H, NCH_2), 3.08 (s, 4H, NCH_2), 2.74 (q, 2H, $^{3}J_{H,H}$ = 7.5 Hz, CH_{2Et}), 2.65 – 2.47 (three overlapping q, 2H, $^{3}J_{H,H}$ = 7.5 Hz, CH_{2Et}), 1.23 – 1.20 (two overlapping t, 24H, $^{3}J_{H,H}$ = 7.5 Hz, CH_{3Et}), −0.11 (s, 6H, SiCH_3) ppm.

$^{13}C\{^{1}H\}$ NMR (125.8 MHz, C_6D_6, 298 K): 194.1 ($C_{Carbene}$), 194.1 ($C_{Carbene}$), 152.4 (C_q), 141.4 (C_q), 141.1 (C_q), 140.6 (C_q), 138.8 (C_q), 135.4 (CH$_{Ar}$), 128.6 (CH$_{Ar}$), 127.6 (CH$_{Ar}$), 127.4 (CH$_{Ar}$), 127.0 (CH$_{Ar}$), 126.6 (CH$_{Ar}$), 126.0 (CH$_{Ar}$), 125.8 (CH$_{Ar}$), 52.1 (NCH$_2$), 51.7 (NCH$_2$), 24.8 (CH$_{2Et}$), 24.7 (CH$_{2Et}$), 14.4 (CH$_{3Et}$), 14.3 (CH$_{3Et}$), 5.4 (SiCH$_{3Et}$) ppm.

$^{11}B\{^{1}H\}$ NMR (160.5 MHz, C_6D_6, 298 K): 35.3 (*B*Si), 21.0 (*B*H) ppm.

$^{29}Si\{^{1}H\}$ NMR (99.4 MHz, C_6D_6, 298 K): −18.9 ppm.

HRMS(LIFDI): m/z ($C_{54}H_{72}B_2N_4Si$) = calc.: 826.5707, found: 826.5694.

Synthesis of 3

Starting from 1: 30 mg (44 µmol) $B_2(SIDep)_2$ was dissolved in 0.6 mL benzene and 5.9 mg (44 µmol) $HSiMe_2Ph$ was added by cannula. Within three days at 80 °C the solution turned from red to purple and then to yellow with complete consumption of the starting materials and intermediates.

Starting from 2: 30 mg (41 µmol) **2** was dissolved in 0.6 mL benzene and heated to 80 °C for three days, whereupon the solution turned from purple to yellow with complete consumption of the diborene.

Workup details for both routes: The solvent was removed under reduced pressure and the yellow residue was washed with TMS_2O (3 x 0.6 mL). After drying in vacuum the product was isolated in 51% yield (18.2 mg, Route 1) or 72% (25.8 mg, Route 2) as a colourless solid. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated hexane solution.

$^1H\{^{11}B\}$ NMR (500.1 MHz, C_6D_6, 298 K): 7.37 – 7.35 (m, 2H, C*H*$_{Ar}$), 7.27 – 7.20 (m, 3H, C*H*$_{Ar}$), 7.14 (m, 2H, C*H*$_{Ar}$), 7.11 – 7.06 (m, 5H, C*H*$_{Ar}$), 7.02 – 7.01 (m, 2H, C*H*$_{Ar}$), 6.94 – 6.93 (m, 1H, C*H*$_{Ar}$), 6.88 – 6.85 (m, 1H, C*H*$_{Ar}$), 6.72 – 6.71 (m, 1H, C*H*$_{Ar}$), 6.56 – 6.55 (m, 1H, C*H*$_{Ar}$), 3.98 – 3.96 (m, 1H,BC(*H*)N), 3.76 – 3.69 (m, 1H, C*H*CH$_{3Et}$), 3.55 – 3.49 (m, 2H, NC*H*$_2$), 3.37 – 3.27 (m, 2H, NC*H*$_2$), 3.18 – 3.10 (m, 2H, C*H*$_{2Et}$), 3.01 – 2.86 (m, 6H, NC*H*$_2$+C*H*$_{2Et}$), 2.81 – 2.73 (m, 1H, C*H*$_{2Et}$), 2.70 – 2.35 (m, 7H, NC*H*$_2$+C*H*$_{2Et}$), 2.27 – 2.19 (m, 1H, C*H*$_{2Et}$), 2.17 – 2.10 (m, 1H, C*H*$_{2Et}$), 1.46 – 1.38 (m, 9H, C*H*$_{3Et}$), 1.27 – 1.25 (m, 3H, CHC*H*$_{3Et}$), 1.18 – 1.15 (m, 3H, C*H*$_{3Et}$), 1.02 – 0.93 (m, 9H, C*H*$_{3Et}$), 0.87 (br. s, 1H, B*H*), −0.08 (s, 3H, SiC*H*$_3$), −0.29 (s, 3H, SiC*H*$_3$) ppm.

$^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6, 298 K): 152.8 (*C*$_q$), 149.2 (*C*$_q$), 149.2 (*C*$_q$), 148.6 (*C*$_q$), 142.1 (*C*$_q$), 141.4 (*C*$_q$), 141.1 (*C*$_q$), 140.5 (*C*$_q$), 139.9 (*C*$_q$), 139.8 (*C*$_q$), 138.9 (*C*$_q$), 136.4 (*C*$_q$), 133.8 (*C*H$_{Ar}$), 129.4 (*C*H$_{Ar}$), 128.7 (*C*H$_{Ar}$), 127.2 (*C*H$_{Ar}$), 127.1 (*C*H$_{Ar}$), 126.9 (*C*H$_{Ar}$), 126.9 (*C*H$_{Ar}$), 126.6 (*C*H$_{Ar}$), 126.5 (*C*H$_{Ar}$), 126.2 (*C*H$_{Ar}$), 125.9 (*C*H$_{Ar}$), 125.9 (*C*H$_{Ar}$), 124.0 (*C*H$_{Ar}$), 63.7 (B*C*(H)N), 56.3 (N*C*H$_2$), 55.6 (N*C*H$_2$), 52.7 (N*C*H$_2$), 51.2 (N*C*H$_2$), 41.2 (*C*HCH$_{3Et}$), 24.8 (*C*H$_{2Et}$), 24.7 (*C*H$_{2Et}$), 24.0 (*C*H$_{2Et}$), 24.0 (*C*H$_{2Et}$), 23.5 (*C*H$_{2Et}$), 21.4 (CH*C*H$_{3Et}$), 16.0 (*C*H$_{3Et}$), 15.6 (*C*H$_{3Et}$), 15.4 (*C*H$_{3Et}$), 15.3 (*C*H$_{3Et}$), 15.1 (*C*H$_{3Et}$), 14.0 (*C*H$_{3Et}$), 13.5 (*C*H$_{3Et}$), 4.7 (Si*C*H$_3$), 2.9 (Si*C*H$_3$) ppm. Note: the signals for the carbenes could not be found due to broadening.

$^{11}B\{^1H\}$ NMR (160.5 MHz, C_6D_6, 298 K): 56.0, −34.4 ppm.

$^{29}Si\{^1H\}$ NMR (99.4 MHz, C_6D_6, 298 K): −8.8 ppm (detected indirectly by $^{29}Si,^1H$-HMQC).

HRMS(LIFDI): m/z ($C_{54}H_{72}B_2N_4Si$) = calc.: 826.5707, found: 826.5694.

Synthesis of 4

30 mg (44 µmol) of $B_2(SIDep)_2$ was dissolved in 0.6 mL benzene and a small excess of H_3SiPh (ca. 3 equiv) was added by syringe. Within 2 min at room temperature the solution turned from red to yellow and new ^{11}B signals at –29 and –33 ppm were found. All volutiles were removed under reduced pressure and the orange residue was washed with pentane (3 x 0.6 mL). After drying under vacuum the product was isolated in 83% yield (28.7 mg) as an off-white solid. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated hexane solution.

$^1H\{^{11}B\}$ NMR (500.1 MHz, C_6D_6, 298 K): 7.20 (q, 4H, $^3J_{H,H}$ = 7.5 Hz, CH_{Ar}, *overlapping with the solvent signal*), 7.14 – 7.11 (m, 3H, CH_{Ar}), 7.07 – 7.06 (m, 4H, CH_{Ar}), 7.02 – 6.99 (m, 4H, CH_{Ar}), 3.38 – 3.33 (m, 3H, Si*H* + NCH_2), 3.17 – 2.99 (m, 8H, NCH_2 + CH_{2Et}), 2.75 – 2.52 (m, 10H, CH_{2Et}), 2.21 (q, 2H, $^3J_{H,H}$ = 7.5 Hz, CH_{2Et}), 2.01 (q, 2H, $^3J_{H,H}$ = 7.5 Hz, CH_{2Et}), 1.33 (t, 6H, $^3J_{H,H}$ = 7.5 Hz, CH_{3Et}), 1.22 (br. t, 6H, $^3J_{H,H}$ = 7.5 Hz, CH_{3Et}), 1.11 (br. t, 6H, $^3J_{H,H}$ = 7.5 Hz, CH_{3Et}) *overlapping with* 1.08 (t, 6H, $^3J_{H,H}$ = 7.5 Hz, CH_{3Et}), –0.13 – –0.16 (m, 1H, B*H*), –0.36 – –0.40 (m, 1H, B*H*) ppm. *Note: The signal for the silicon-bound proton can be found within the 3.38 - 3.33 multiplet at 3.45 as a sharp singlet.*

$^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6, 298 K): 144.5 (C_q), 142.9 (C_q), 142.4 (C_q), 142.0 (C_q), 139.8 (C_q), 139.0 (C_q), 137.2 (C_q), 127.4 (CH_{Ar}), 127.3 (CH_{Ar}), 126.4 (CH_{Ar}), 125.9 (CH_{Ar}), 125.6 (CH_{Ar}), 125.4 (CH_{Ar}), 50.5 (NCH_2), 50.3 (NCH_2), 24.7 (CH_{2Et}), 24.5 (CH_{2Et}), 23.8 (CH_{2Et}), 14.4 (CH_{3Et}), 14.3 (CH_{3Et}), 14.2 (CH_{3Et}), 13.8 (CH_{3Et}) ppm. *Note: The signals for the carbenes could not be identified due to broadening.*

$^{11}B\{^1H\}$ NMR (160.5 MHz, C_6D_6, 298 K): –29.0, –32.9 ppm.

$^{29}Si\{^1H\}$ NMR (99.4 MHz, C_6D_6, 298 K): –28.5 ppm.

HRMS(LIFDI): m/z ($C_{52}H_{68}B_2N_4Si$) = calc.: 798.5394, found: 798.5385.

Synthesis of (SIDep)B_2($H_3SiPhSiH_3$)B_2(SIDep) (5)

15 mg (22 µmol) of B_2(SIDep)$_2$ was dissolved in 0.6 mL benzene and an excess of $H_3SiPhSiH_3$ (ca. 4 eq.) was added by syringe. Within 5 min at room temperature the solution turned from red to yellow and new ^{11}B signals at –29 and –33 ppm were found. All volutiles were removed under reduced pressure, the light-yellow residue was redissolved in C_6D_6 and 16 mg of (23 µmol) B_2(SIDep)$_2$ was added. After 1 h at room temperature the product began to crystallize, with complete consumption of the starting material noted after 2d. These crystals were washed with C_6D_6 (2 x 0.6mL) and the product was isolated in 74% yield (24.4 mg) as an orange solid. Single crystals suitable for X-ray diffraction were obtained from the reaction solution.

^{1}H{^{11}B} NMR (500.1 MHz, C_6D_6, 298 K): 7.30 – 7.23 (m, 8H, C*H*$_{Ar}$), 7.14 – 7.09 (m, 12H, C*H*$_{Ar}$), 7.02 – 7.01 (m, 4H, C*H*$_{Ar}$), 6.79 (s, 4H, C*H*$_{Ar,\ Si\text{-}Ph\text{-}Si}$), 3.40 – 3.37 (m, 4H, Si*H* + NC*H*$_2$), 3.33 – 3.26 (m, 4H, NC*H*$_2$), 3.20 – 3.14 (m, 8H, NC*H*$_2$), 3.08 – 3.01 (m, 4H, C*H*$_{2Et}$), 2.81 – 2.55 (m, 22H, NC*H*$_2$ + C*H*$_{2Et}$), 2.33 – 2.19 (m, 8H, C*H*$_{2Et}$), 1.42 (t, 12H, $^3J_{H,H}$ = 7.66 Hz, C*H*$_{3Et}$), 1.27 – 1.25 (m, 24H, C*H*$_{3Et}$), 1.13 – 1.07 (m, 12H, C*H*$_{3Et}$), –0.15 – –0.17 (m, 2H, B*H*), –0.40 – –0.41 (m, 2H, B*H*) ppm. *Note: The signal for the silicon-bound proton can be found within the multiplet at 3.38 – 3.33 ppm.*

^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 298 K): 142.5 (*C*$_q$), 142.0 (*C*$_q$), 141.9 (*C*$_q$), 139.5 (*C*$_q$), 139.0 (*C*$_q$), 134.0 (*C*$_{Ar,\ SiCCH}$), 127.2 (*C*H$_{Ar}$), 127.1 (*C*H$_{Ar}$), 126.9 (*C*H$_{Ar}$), 125.6 (*C*H$_{Ar}$), 125.3 (*C*H$_{Ar}$), 125.1 (*C*H$_{Ar}$), 50.2 (N*C*H$_2$), 50.1 (N*C*H$_2$), 24.5 (*C*H$_{2Et}$), 24.0 (*C*H$_{2Et}$), 23.6 (*C*H$_{2Et}$), 14.2 (*C*H$_{3Et}$), 14.0 (*C*H$_{3Et}$), 13.9 (*C*H$_{3Et}$) ppm. *Note: The signals for the carbenes could not be identified due to broadening.*

^{11}B{^{1}H} NMR (160.5 MHz, C_6D_6, 298 K): –28.8, –32.7 ppm.

^{29}Si{^{1}H} NMR (99.4 MHz, C_6D_6, 298 K): –25.9 ppm.

HRMS(LIFDI): m/z ($C_{98}H_{130}B_4N_8Si_2$) = calc.: 1519.0394, found: 1519.0347.

NMR Spectra

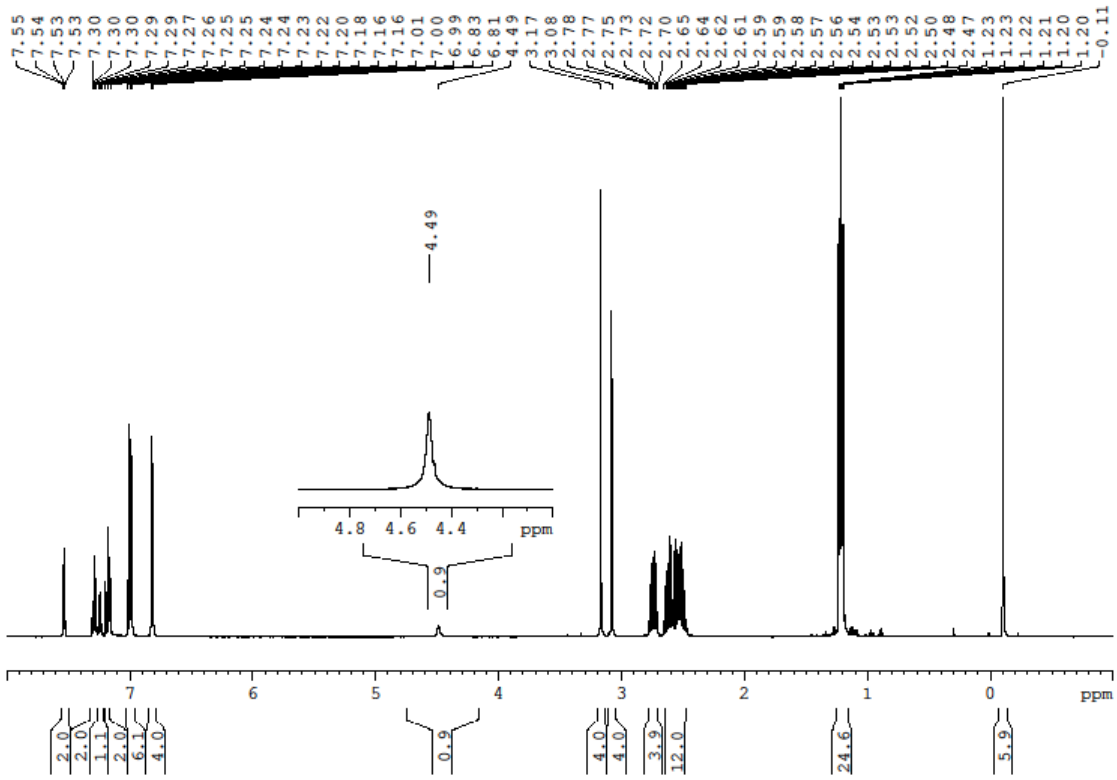

Figure S1. $^{1}H\{^{11}B\}$ NMR spectrum of **2**.

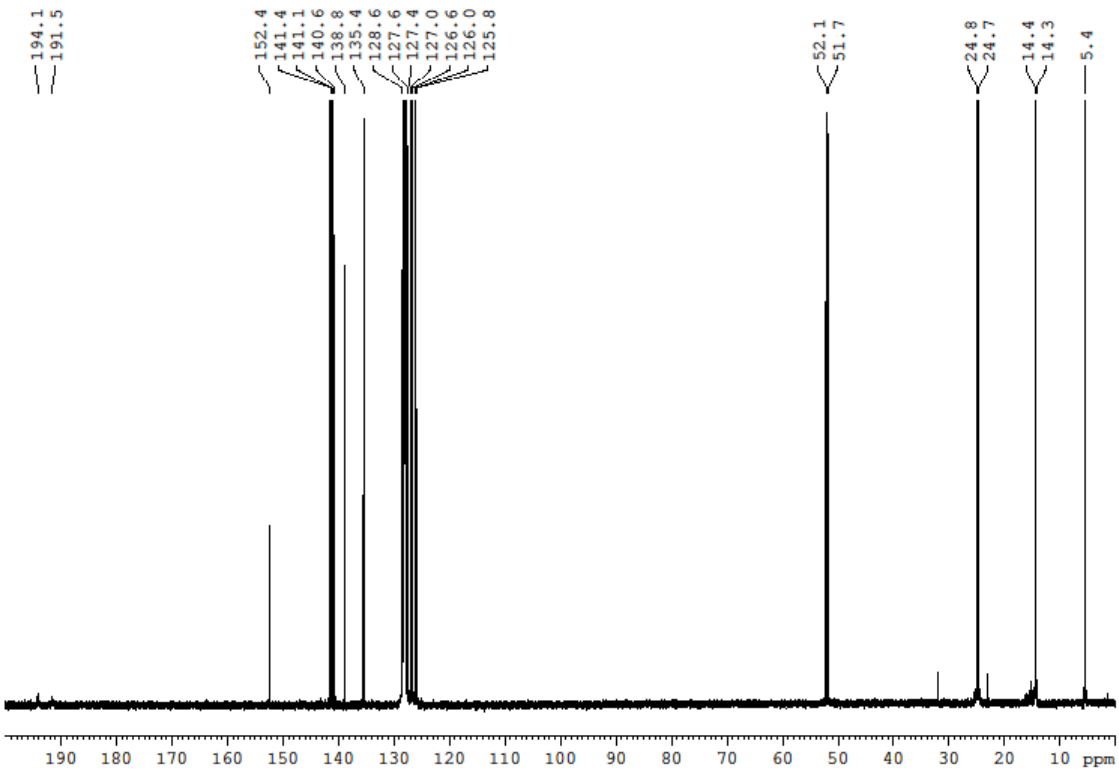

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **2**.

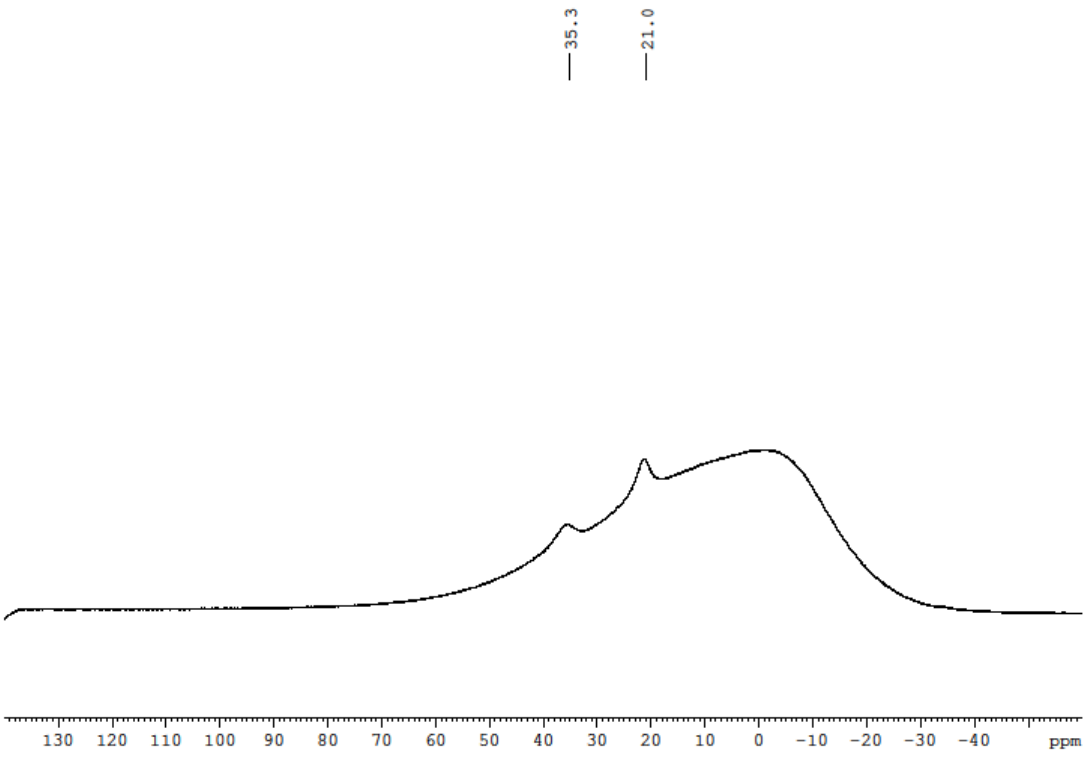

Figure S3. $^{11}B\{^{1}H\}$ NMR spectrum of **2**.

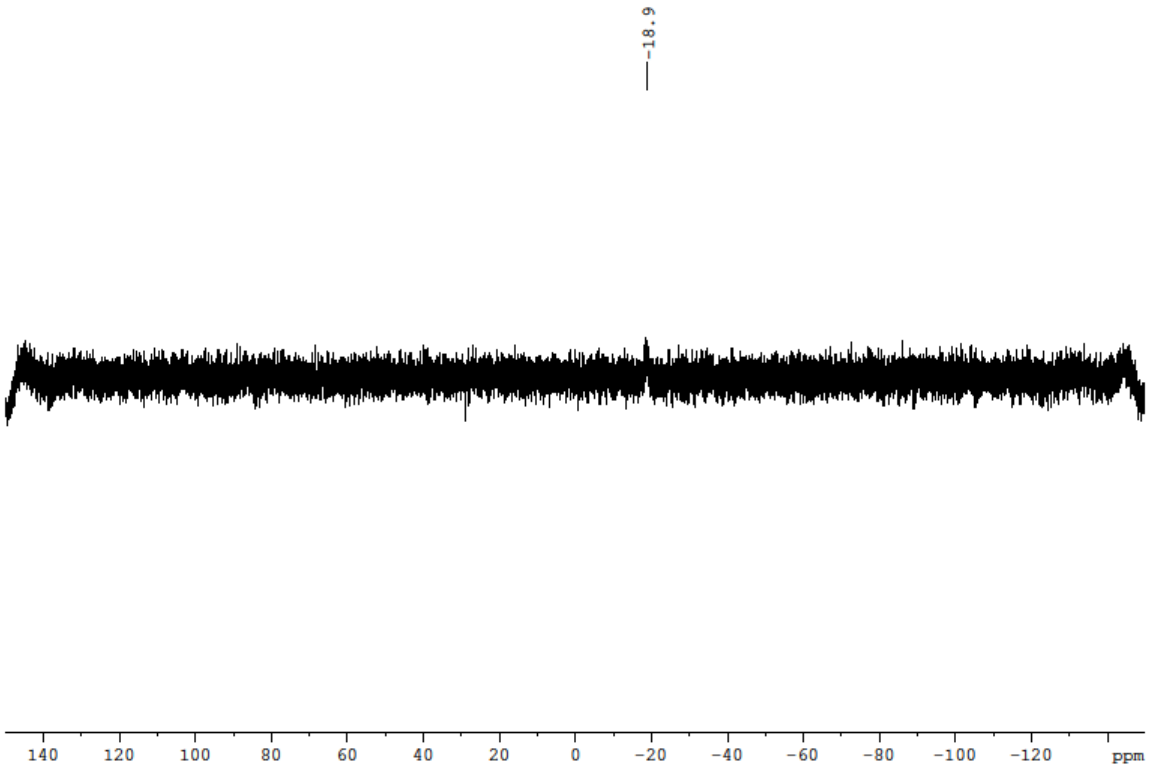

Figure S4. $^{29}Si\{^{1}H\}$ NMR spectrum of **2**.

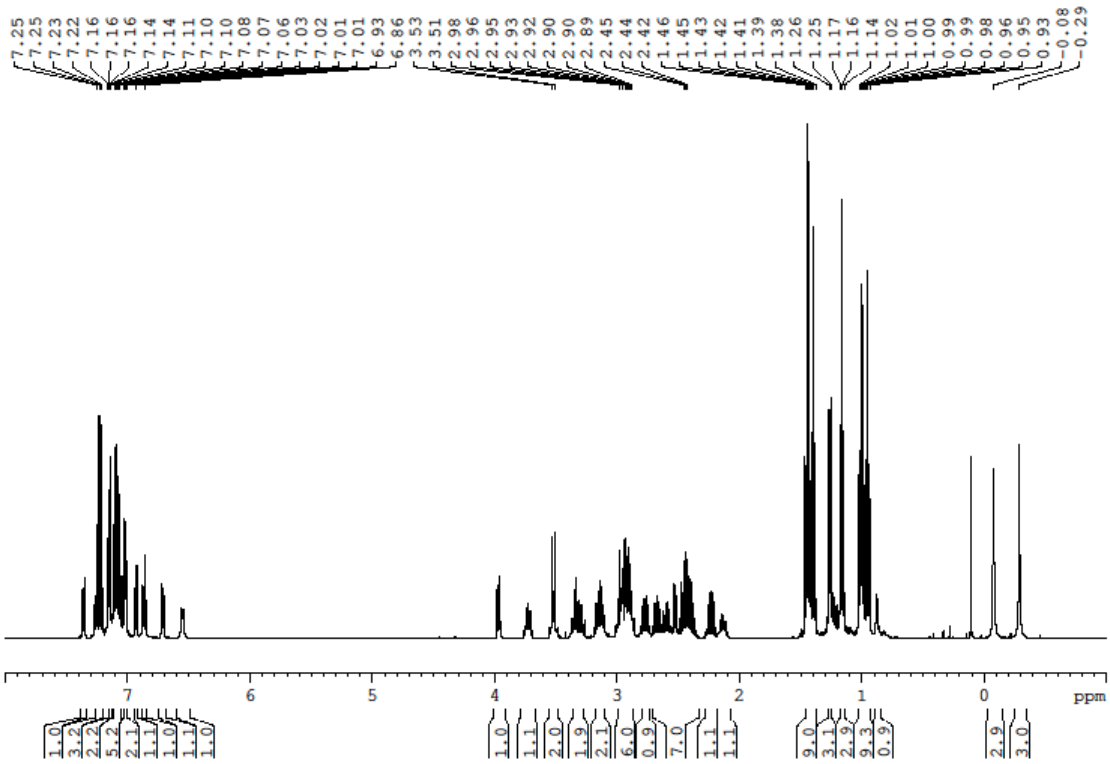

Figure S5. $^{1}H\{^{11}B\}$ NMR spectrum of **3**.

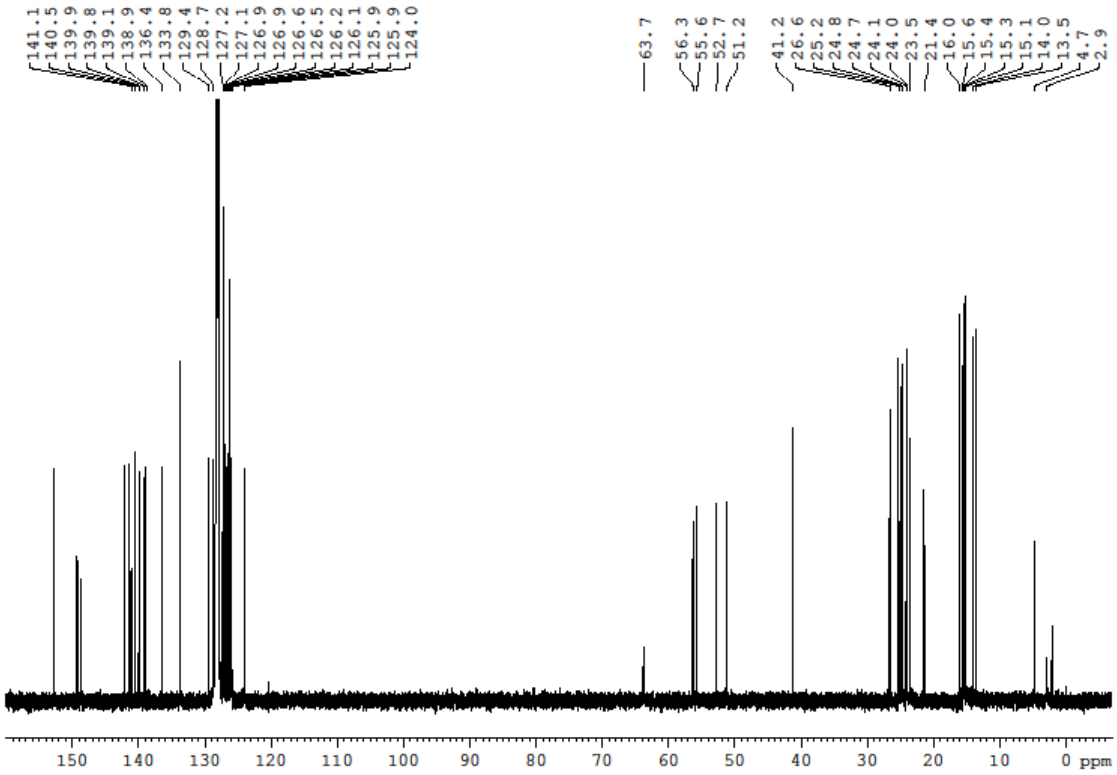

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **3**.

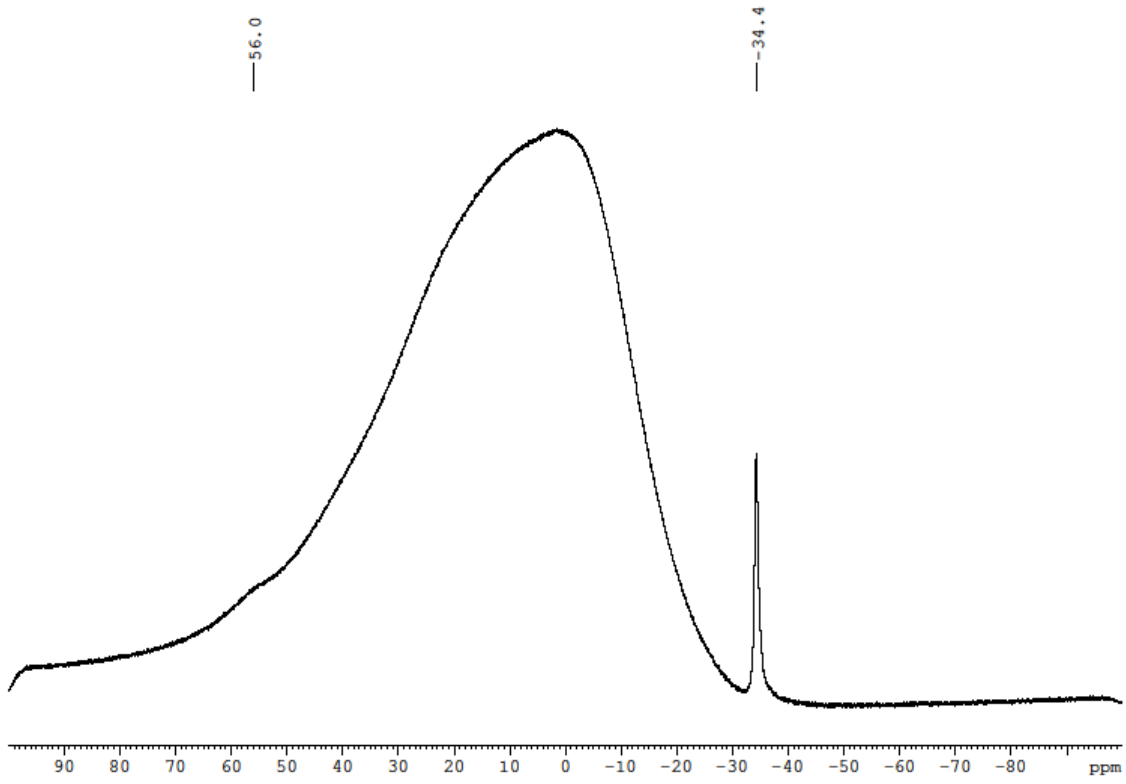

Figure S7. $^{11}B\{^{1}H\}$ NMR spectrum of **3**.

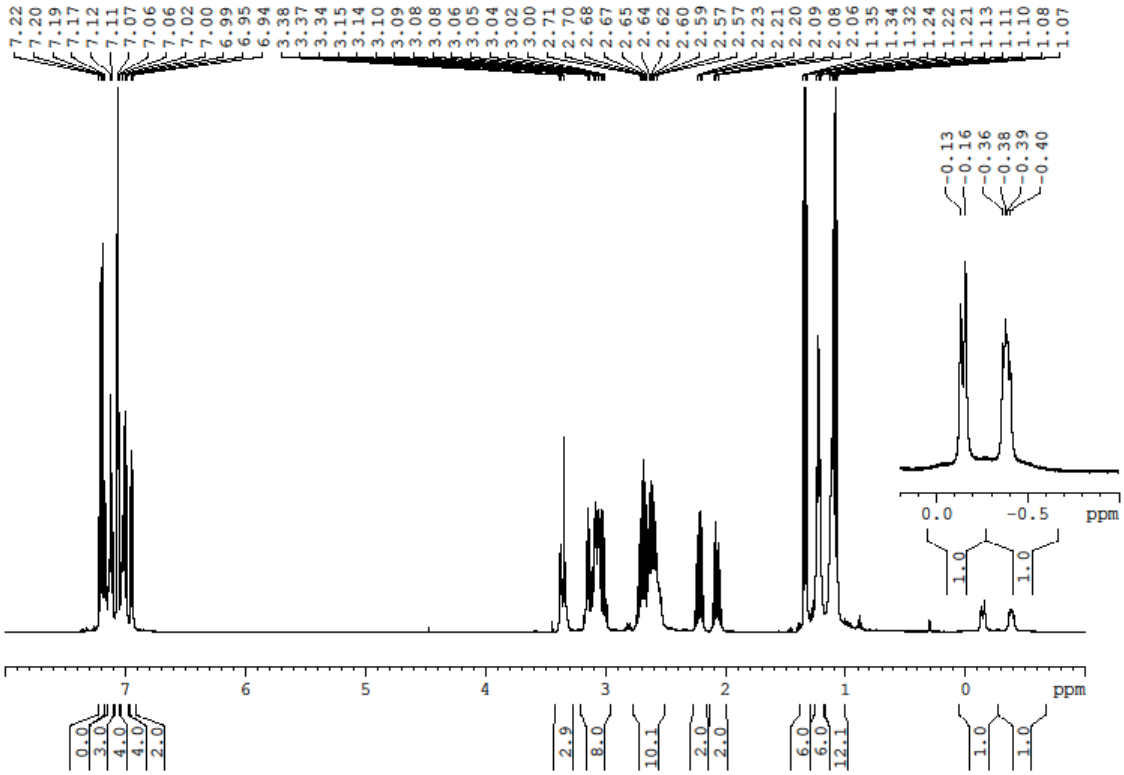

Figure S8. $^{1}H\{^{11}B\}$ NMR spectrum of **4**.

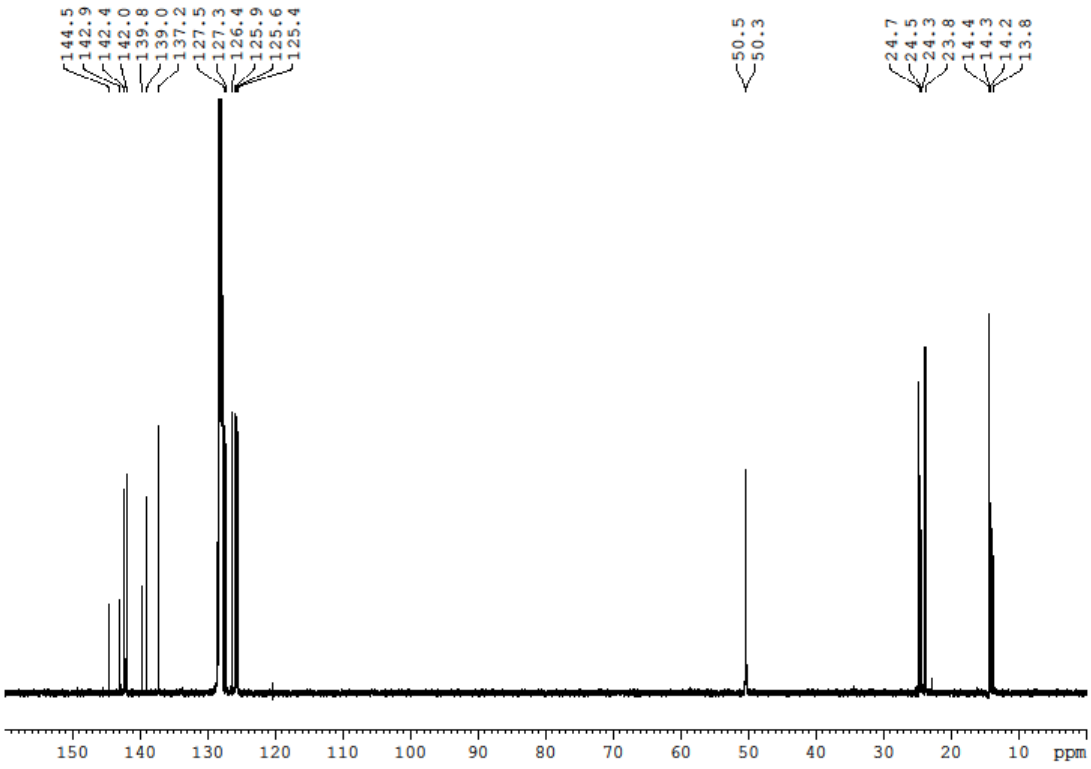

Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of **4**.

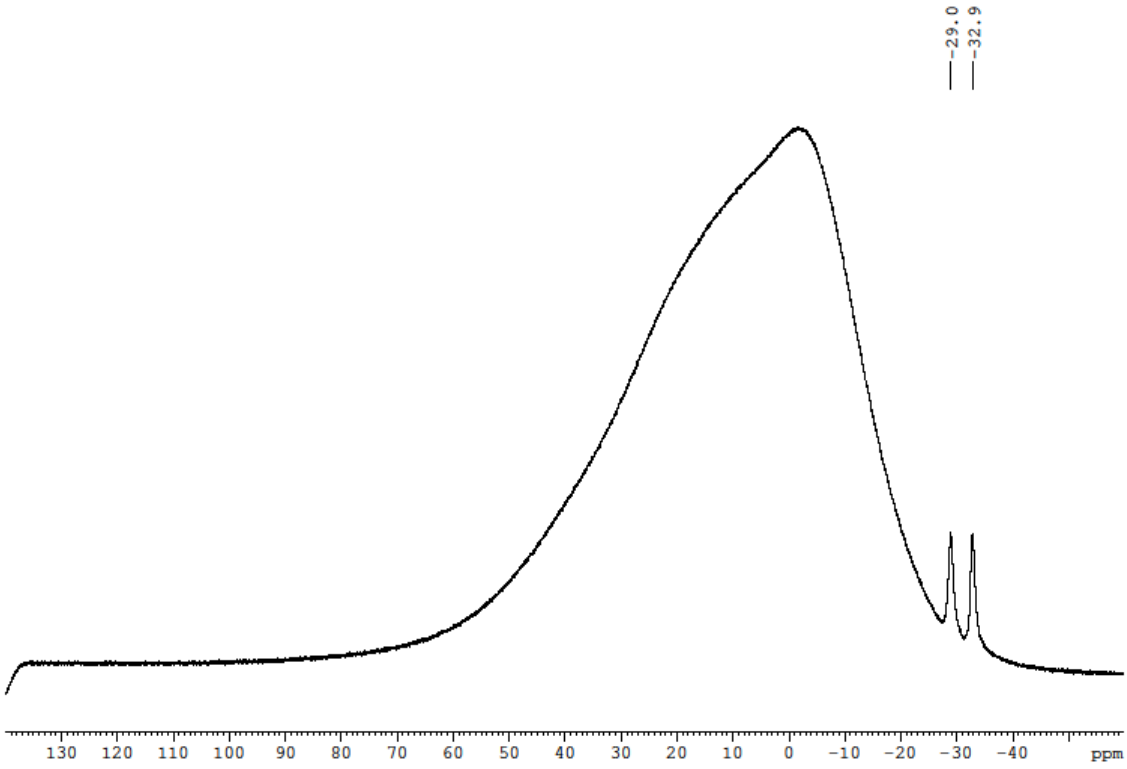

Figure S10. $^{11}B\{^{1}H\}$ NMR spectrum of **4**.

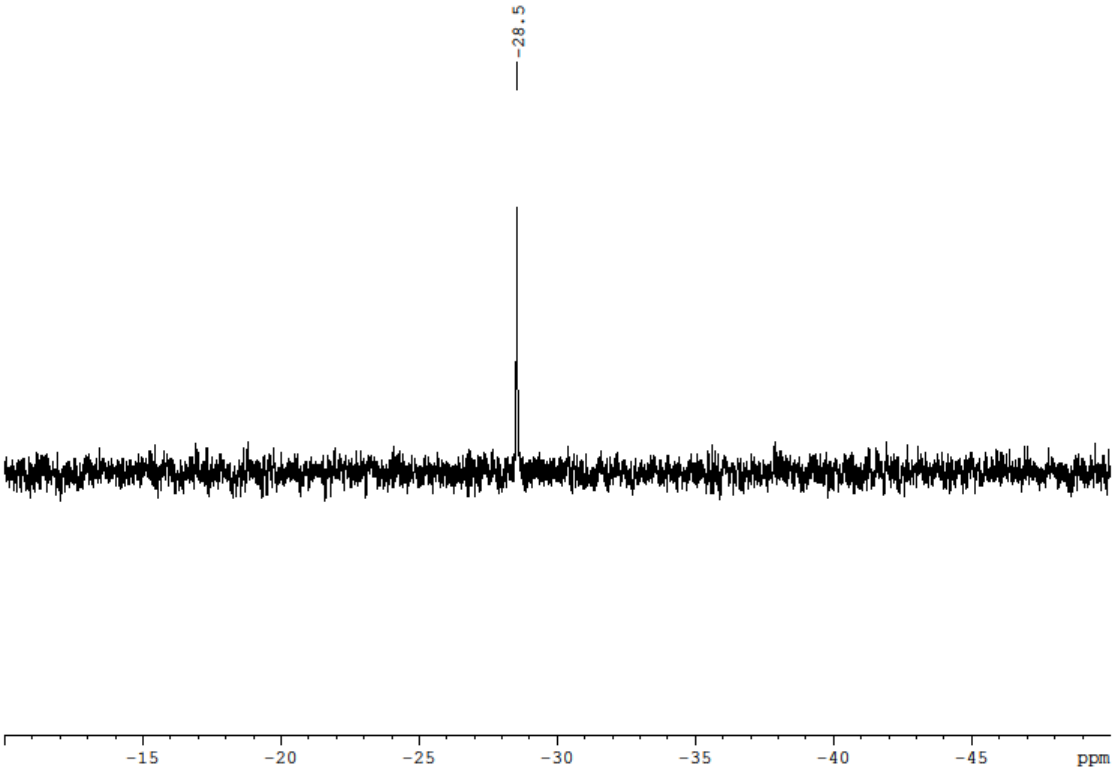

Figure S11. $^{29}Si\{^{1}H\}$ NMR spectrum of **4**.

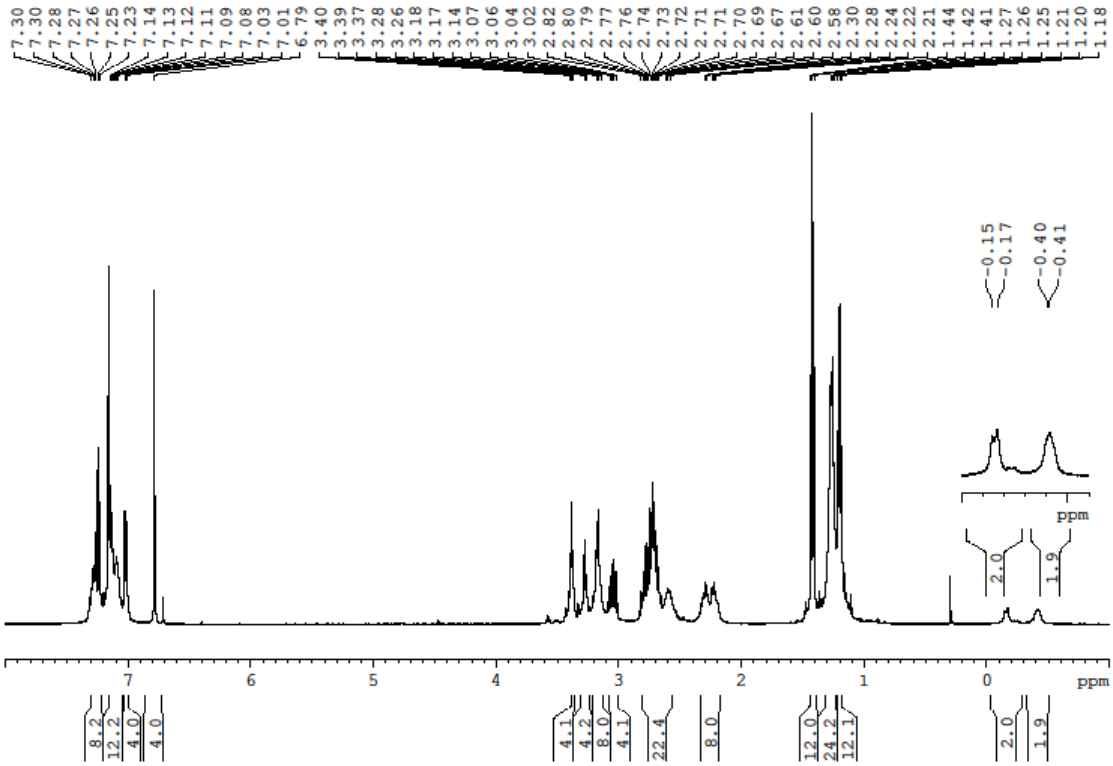

Figure S12. $^{1}H\{^{11}B\}$ NMR spectrum of **5**.

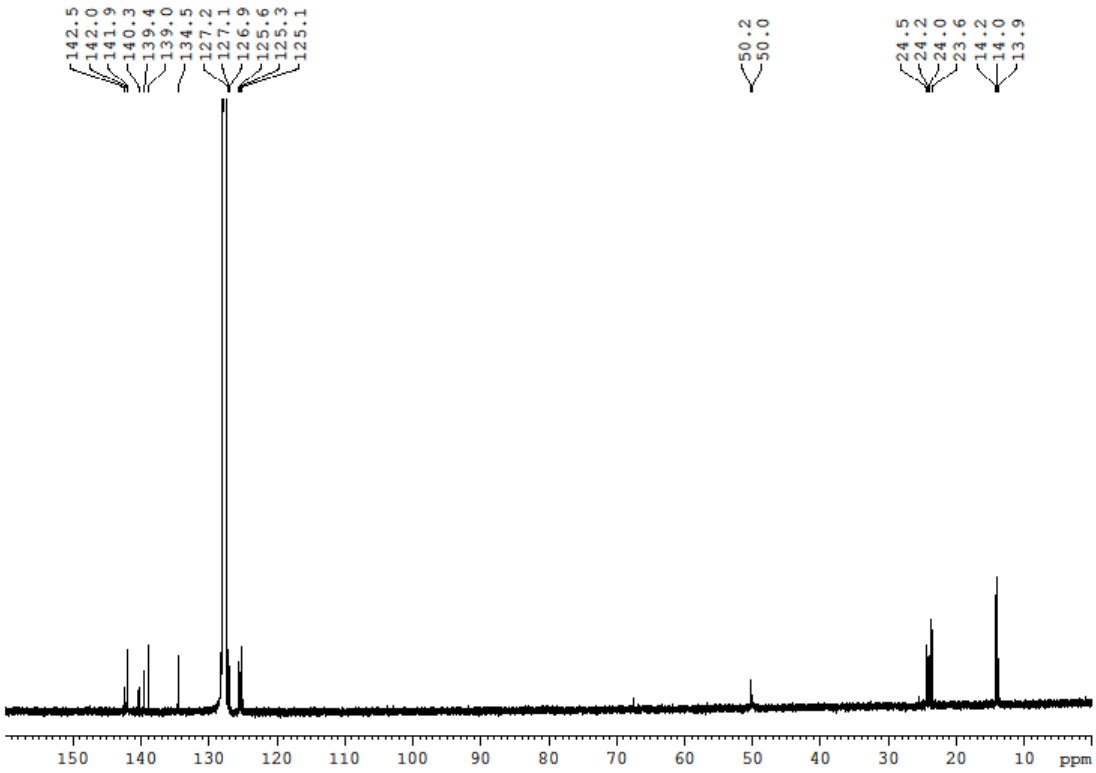

Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum of **5**.

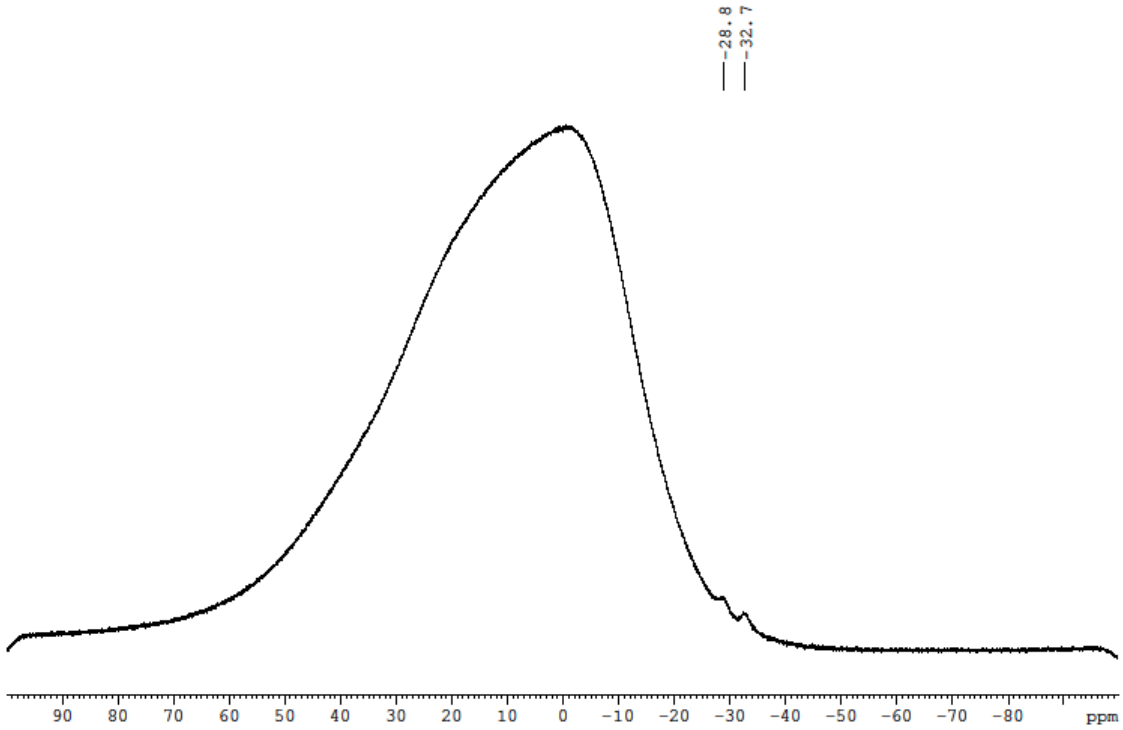

Figure S14. $^{11}B\{^{1}H\}$ NMR spectrum of **5**.

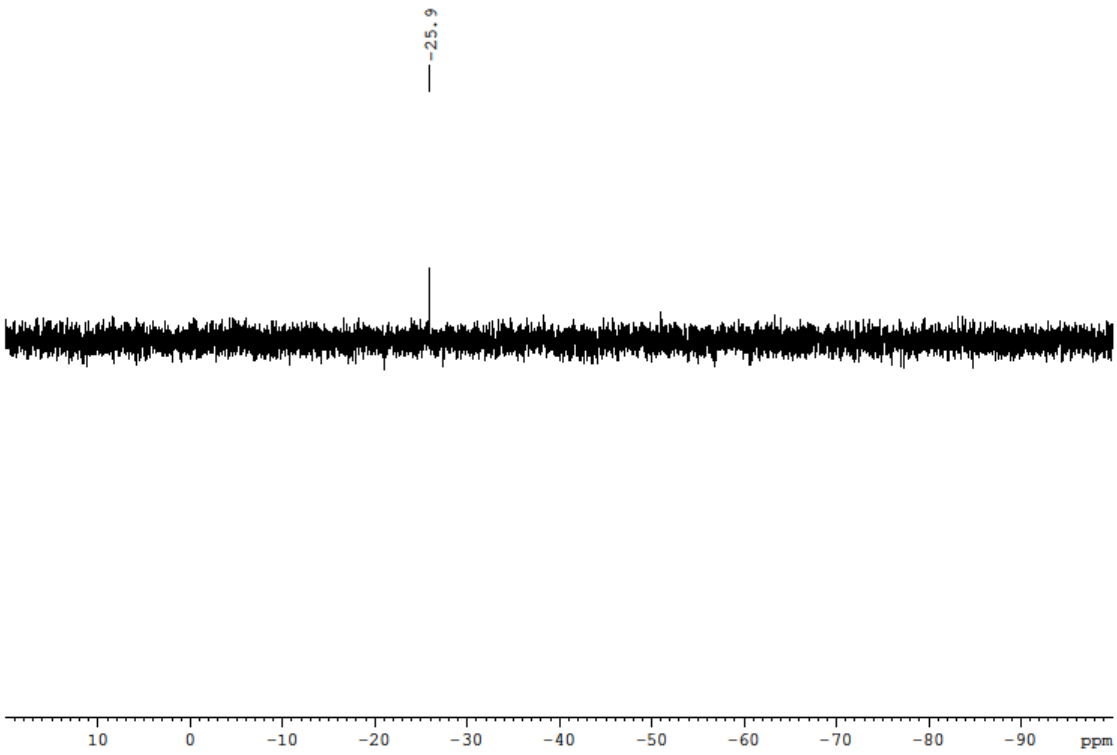

Figure S15. $^{29}Si\{^{1}H\}$ NMR spectrum of **5**.

UV-vis Spectra

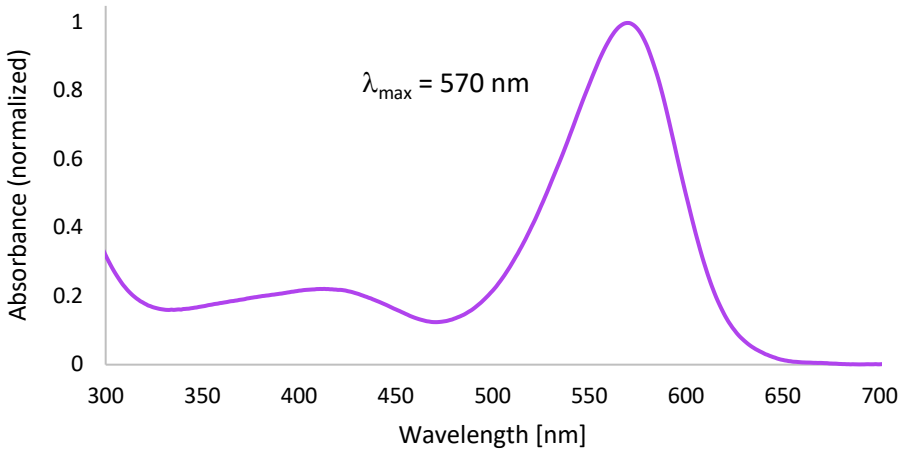

Figure S16. UV-vis spectrum of **2** (C_6H_6)

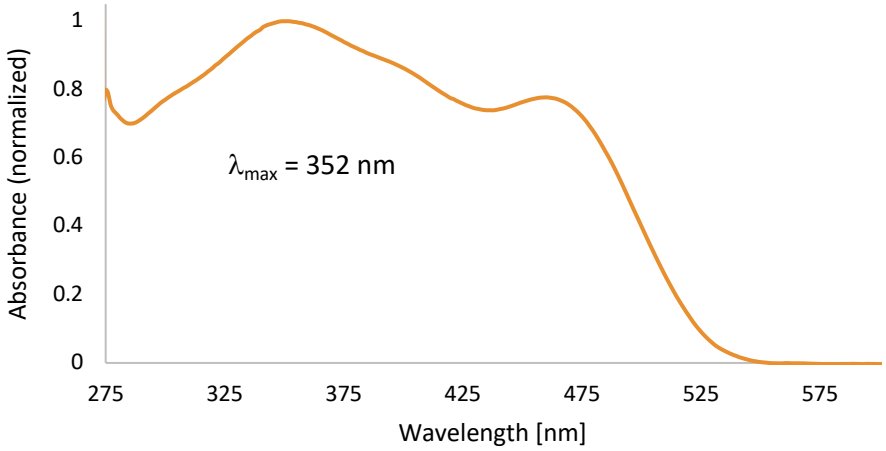

Figure S17. UV-vis spectrum of **5** (C_6H_6).

Crystallographic Details

The crystal data of **2** were collected on a BRUKER D8 QUEST diffractometer with a CMOS area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using the intrinsic phasing method,[3] refined with the SHELXL program[4] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms except H1 were assigned to idealized positions. The coordinates of H1 were refined freely. Crystal data for **2**: $C_{54}H_{72}B_2N_4Si$, M_r = 826.86, purple block, 0.421×0.396×0.272 mm^3, monoclinic space group $P2_1/c$, a = 12.4737(3) Å, b = 14.9710(4) Å, c = 26.1547(7) Å, β = 92.7860(10)°, V = 4878.5(2) Å^3, Z = 4, ρ_{calcd} = 1.126 g·cm^{-3}, μ = 0.088 mm^{-1}, $F(000)$ = 1792, T = 130(2) K, R_1 = 0.0583, wR^2 = 0.1175, 9588 independent reflections [$2\theta \leq 52.042°$] and 564 parameters.

The crystal data of **3** were collected on a Rigaku XtaLAB Synergy-S diffractometer with an HPA area detector and multi-layer mirror monochromated $Cu_{K\alpha}$ radiation. The structure was solved using the intrinsic phasing method,[3] refined with the ShelXL program[4] 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 geometric positions. The crystal was integrated as a twin with a second domain rotated 138° around the [0.91 0.36 -0.20] real vector. However, as reflections of this second domain were very weak ($F2/\sigma < 1$ and R_{int} higher than 90%) only the HKLF4 file based on the first domain was used in refinement. One of the ethyl groups of the 2,6-diethylphenyl unit was rotationally disordered. U_{ij} parameters of all atoms belonging to disordered residues (6 and 106) were restrained with similarity restraint SIMU and rigid body restraint RIGU. The distances of C1 atoms to the phenyl groups were restrained to the same value using the SADI command. Crystal data for **3**: $C_{54}H_{72}B_2N_4Si$, M_r = 826.86, colorless plate, 0.166×0.081×0.024 mm^3, space group $I2/a$, a = 24.18452(19) Å, b = 11.44862(12) Å, c = 68.9173(7) Å, α = 90°, β = 90.4985(8)°, γ = 90°, V = 19081.1(3) Å^3, Z = 16, ρ_{calcd} = 1.151 g·cm^{-3}, μ = 0.725 mm^{-1}, $F(000)$ = 7168, T = 100.00(10) K, R_1 = 0.0634, wR_2 = 0.1427, 19783 independent reflections [$2\theta \leq 155.008°$] and 1139 parameters.

The crystal data of **4** were collected on a BRUKER D8 QUEST diffractometer with a CMOS area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using the intrinsic phasing method,[3] refined with the SHELXL program[4] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms, except these bound to silicon and boron atoms in the central SiB_2 ring, were assigned to idealized positions. One of carbenes

shows disorder in the ring (residues SIME 10 and 11). Geometries of all NHC units were restrained with SAME keyword. The atomic displacement parameters of atoms belonging to residues 10 and 11 were restrained with similarity restraint SIMU, 'enhanced rigid bond' restraint RIGU and to approximate isotropic behavior with ISOR. Crystal data for **4**: $C_{52}H_{68}B_2N_4Si$, M_r = 798.81, yellow block, 0.286×0.214×0.154 mm^3, monoclinic space group $P2_1/c$, a = 22.4231(5) Å, b = 11.6708(2) Å, c = 19.4398(5) Å, β = 113.0050(10)°, V = 4682.72(18) Å^3, Z = 4, ρ_{calcd} = 1.133 g·cm^{-3}, μ = 0.089 mm^{-1}, F(000) = 1728, T = 100(2) K, R_1 = 0.0891, wR_2 = 0.1234, 9208 independent reflections [2θ≤52.042°] and 595 parameters.

The crystal data of **5** were collected on a RIGAKU XTALAB SYNERGY-S diffractometer with a HPA area detector and multi-layer mirror monochromated CuK_α radiation. The structure was solved using the intrinsic phasing method,[3] refined with the SHELXL program[4] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms, except those bound to silicon and boron atoms in the central SiB_2 ring, were assigned to idealized positions. One of the ethyl groups was rotationally disordered (residues 12 and 112). The geometry of both these residues was constrained using the DFIX restraint on 1–2 and 1–3 distances. The displacement parameters of disordered atoms were restrained to the same value with similarity restraint SIMU, 'enhanced rigid bond' restraint RIGU and isotropic restraint ISOR. Crystal data for **5**: $C_{110}H_{142}B_4N_8Si_2$, M_r = 1675.73, colorless plate, 0.173×0.068×0.026 mm^3, space group P–1, a = 11.6410(2) Å, b = 12.3141(3) Å, c = 17.9847(3) Å, α = 95.791(2)°, β = 101.108(2)°, γ = 104.877(2)°, V = 2414.05(9) Å^3, Z = 1, ρ_{calcd} = 1.153 g·cm^{-3}, μ = 0.724 mm^{-1}, F(000) = 906, T = 100.00(10) K, R_1 = 0.0746, wR_2 = 0.1579, 10145 independent reflections [2θ≤155.932°] and 583 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-2301095 (**2**), -2301097 (**3**) -2301098 (**4**), and -2301096 (**5**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

Computational Details

All computational work was conducted using two quantum chemistry program packages, Gaussian 16 (Revision C.01)[5] and ORCA 5.0.4.[6] Geometry optimizations for compounds **1** to **5** employed the ωB97X-D[7]/6-31G(d,p) level of theory. Vibrational frequency calculations were performed to verify that the optimized geometries correspond to minima on their respective potential energy surfaces, as indicated by all positive eigenvalues of the Hessian matrices. Solvent corrections were included considering implicit solvation by the solvent model based on density (SMD; solvent = benzene; ε = 2.2706).[8] Gibbs free energies (*G*) for compounds **2** and **3** were calculated using single-point calculations (*E*) at the SMD/ωB97X-D/6-311++G(d,p) level of theory. Zero-point energy and thermal corrections to the free energy, collectively termed G_{corr}, were obtained at the ωB97X-D/6-31G(d,p) level. For Kohn–Sham molecular orbitals (MOs) and their corresponding energies, calculations were carried out at the PBE0[9]/def2-SVP[10] level. To analyze the bonding situations in the different systems, Mayer bond orders[11] were calculated using the Multiwfn 3.8 software,[12] while intrinsic bond orbital (IBO)[13] calculations were performed with IBOView.

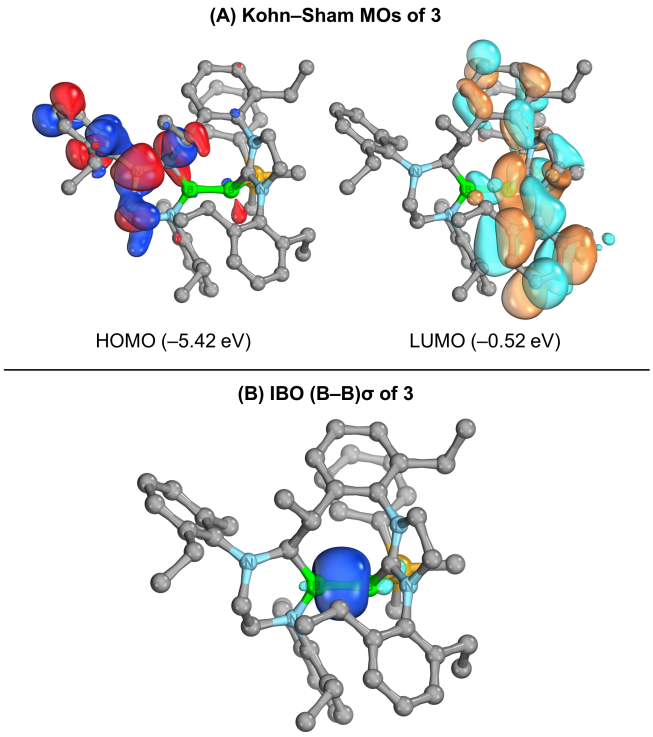

Figure S18. (A) Kohn–Sham MOs of **3**. All hydrogen atoms are omitted for clarity. Orbital threshold: 80.0. A HOMO-LUMO gap of 4.90 eV is obtained for 3 at the PBE0/def2-SVP level. (B) IBO of **3** depicting its B–B σ bond.

Table S1. Thermochemistry of compounds **2** and **3**.

Compound	*E* (Hartree)	G_{corr} (Hartree)	*G* (Hartree)	Δ*G* (kcal mol^{-1})
2	-2659.283359	1.075365	-2658.207994	0.0
3	-2659.361710	1.079831	-2658.281879	-46.4

Cartesian Coordinates

Cartesian coordinates are given in Å.

1			
N	-1.125696000	0.162330000	2.953600000
B	-0.606470000	0.112577000	0.485683000
B	0.326194000	0.082649000	-0.640283000
N	-2.804535000	-0.383051000	1.625166000
N	1.806823000	1.035543000	-2.471933000
N	1.978293000	-1.136297000	-2.090675000
C	-1.485302000	-0.028323000	1.646069000
C	-3.329827000	-0.593865000	2.965800000
H	-3.394000000	-1.664837000	3.207177000
H	-4.329663000	-0.162387000	3.071579000
C	-2.283276000	0.119532000	3.837897000
H	-2.613285000	1.130133000	4.118232000
H	-2.055942000	-0.430453000	4.755723000
C	1.191975000	-0.065926000	3.620407000
C	0.111873000	0.776226000	3.303588000
C	2.522116000	1.909308000	4.049398000
H	3.464161000	2.354056000	4.355372000
C	2.396030000	0.523499000	3.997016000
H	3.246917000	-0.097929000	4.255028000
C	1.458481000	2.721500000	3.688983000
H	1.572953000	3.802371000	3.696142000
C	-0.853467000	3.083208000	2.773406000
H	-1.034373000	3.877062000	3.508366000
H	-1.790805000	2.532865000	2.662266000
C	0.239062000	2.170525000	3.286499000
C	3.333295000	2.878839000	-0.903574000
H	4.051851000	3.705997000	-0.933168000
H	3.803580000	2.030908000	-1.409928000
C	-0.492591000	3.705127000	1.416675000
H	-0.317333000	2.921250000	0.673857000
H	0.411829000	4.317489000	1.486881000
H	-1.304659000	4.346343000	1.059722000
C	3.043923000	2.498743000	0.554710000
H	2.288302000	1.708555000	0.614078000
H	2.660490000	3.359509000	1.109933000
H	3.952481000	2.151597000	1.057463000
C	1.022893000	-1.563742000	3.477357000
H	0.867557000	-1.775455000	2.410474000
H	0.091858000	-1.863885000	3.971210000
C	2.172361000	-2.413941000	4.006806000
H	1.945756000	-3.474741000	3.869773000
H	2.348672000	-2.239331000	5.073235000
H	3.107902000	-2.209725000	3.475318000
C	-3.463770000	-0.775975000	0.425379000
C	-3.281470000	-2.069496000	-0.085395000
C	-3.949462000	-2.399189000	-1.265398000
H	-3.839229000	-3.391573000	-1.689080000
C	-4.750025000	-1.467296000	-1.913764000
H	-5.262221000	-1.743569000	-2.830512000

C	-4.884687000	-0.178201000	-1.411476000
H	-5.487193000	0.544556000	-1.950640000
C	-4.232530000	0.191923000	-0.236850000
C	-4.259589000	1.603894000	0.311307000
H	-3.218963000	1.946367000	0.378627000
H	-4.631354000	1.583482000	1.343568000
C	-5.071159000	2.611422000	-0.495458000
H	-4.687055000	2.704104000	-1.516004000
H	-5.014137000	3.598562000	-0.029189000
H	-6.127656000	2.330438000	-0.554520000
C	-2.324399000	-3.025703000	0.594025000
H	-1.305747000	-2.676368000	0.376853000
H	-2.433474000	-2.936542000	1.680066000
C	-2.462916000	-4.492854000	0.201398000
H	-2.229099000	-4.654442000	-0.855466000
H	-3.475468000	-4.867733000	0.383323000
H	-1.763032000	-5.100172000	0.781559000
C	1.325008000	0.013466000	-1.703131000
C	3.121436000	-0.807263000	-2.935953000
H	3.285142000	-1.574303000	-3.696770000
H	4.044972000	-0.697431000	-2.348708000
C	2.681898000	0.538730000	-3.523078000
H	3.518319000	1.221190000	-3.696025000
H	2.136248000	0.406763000	-4.469584000
C	1.320158000	2.368121000	-2.374059000
C	2.077273000	3.291797000	-1.635124000
C	1.604849000	4.598019000	-1.523826000
H	2.180136000	5.322302000	-0.953171000
C	0.407217000	4.973542000	-2.120766000
H	0.050715000	5.994746000	-2.026790000
C	-0.335410000	4.042479000	-2.833827000
H	-1.274742000	4.337230000	-3.294133000
C	0.102231000	2.723788000	-2.971982000
C	-0.755962000	1.728815000	-3.722337000
H	-0.953003000	2.122393000	-4.727241000
H	-0.213913000	0.788182000	-3.849851000
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H	-2.678850000	2.354606000	-2.900230000
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C	0.918300000	-4.442444000	-0.825018000
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H	1.687544000	-5.497430000	0.883709000
C	2.618566000	-3.577560000	0.638575000
H	3.231557000	-3.677945000	1.530034000
C	2.705482000	-2.405711000	-0.116606000
C	3.603857000	-1.284958000	0.357951000
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H	5.391986000	-1.845473000	-0.757274000
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H	-0.428520000	-2.083263000	-2.661222000
H	-0.827621000	-3.791157000	-2.612658000
C	0.608108000	-3.286573000	-4.135859000
H	1.065640000	-4.276417000	-4.229070000
H	1.376515000	-2.536461000	-4.338545000
H	-0.160715000	-3.192482000	-4.908473000

2

Si	1.796935000	0.051235000	-1.518294000
C	0.895064000	0.198784000	-3.205678000
H	-0.065411000	0.716385000	-3.148242000
H	0.707912000	-0.799649000	-3.611277000
H	1.527539000	0.726513000	-3.928190000
N	0.134406000	-1.654278000	2.170947000
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B	-1.005326000	0.276037000	-0.034426000
H	-1.847317000	-0.010389000	0.777411000
N	2.195707000	-0.984036000	1.852416000
C	3.041175000	1.491729000	-1.492613000
H	3.384619000	1.734276000	-2.505884000
H	3.922068000	1.245606000	-0.894929000
H	2.597701000	2.390831000	-1.055567000
N	-2.819906000	0.708392000	-1.788890000
C	4.160544000	-1.449715000	-2.360254000
H	4.640664000	-0.483741000	-2.497235000
N	-1.427238000	2.381354000	-1.570099000
C	2.851475000	-1.505748000	-1.865932000
C	2.990142000	-3.941137000	-2.004253000
H	2.524917000	-4.912651000	-1.858865000
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C	0.926177000	-0.942016000	1.303847000
C	2.193851000	-1.553769000	3.199768000
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C	-1.203444000	-5.037073000	-0.211687000
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C	-2.587551000	0.737731000	4.506175000
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H	-3.067520000	0.171732000	5.310786000
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C	3.243747000	-0.040874000	1.610179000
C	3.049848000	1.319508000	1.914106000
C	4.132872000	2.185186000	1.754578000
H	4.006824000	3.242598000	1.960002000
C	5.371107000	1.713311000	1.346338000
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C	4.504006000	-0.545486000	1.238295000
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H	-1.012525000	-1.414016000	-2.168632000
C	-1.380979000	-3.072590000	-3.489241000
H	-2.100570000	-3.419005000	-4.238452000
H	-1.279876000	-3.852645000	-2.728777000
H	-0.407944000	-2.970520000	-3.977134000
C	-0.579289000	3.329154000	-0.907578000
C	0.455705000	3.929973000	-1.635223000
C	1.254928000	4.878991000	-0.992760000
H	2.082788000	5.322454000	-1.538851000
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H	-1.791970000	2.097911000	1.421132000
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H	-1.712308000	3.822194000	3.204094000
H	-3.379746000	3.399517000	2.834479000
C	0.730477000	3.628487000	-3.089217000
H	0.172941000	2.747973000	-3.406351000
H	1.787586000	3.365288000	-3.196478000
C	0.407559000	4.815313000	-4.004811000
H	1.012047000	5.690578000	-3.749402000
H	-0.642885000	5.113821000	-3.920295000
H	0.606484000	4.562027000	-5.049989000

3

B	-1.283397000	0.343938000	0.125702000
H	-2.192169000	-0.332454000	0.564725000
B	0.168562000	-0.552770000	0.403392000
N	0.267647000	-1.423720000	1.531084000
C	1.263292000	-2.493854000	1.623934000
H	0.792725000	-3.368436000	2.088269000
H	2.115261000	-2.213353000	2.259944000
C	1.760135000	-2.851475000	0.237381000
H	2.509415000	-3.642508000	0.311798000
H	0.915948000	-3.250888000	-0.345768000
N	2.339397000	-1.708227000	-0.435992000
C	1.493046000	-0.521852000	-0.536908000

H	2.015479000	0.315289000	-0.062526000
Si	-1.640583000	2.089848000	1.112089000
C	-2.136821000	1.821571000	2.920933000
H	-2.758650000	0.930018000	3.048958000
H	-2.696565000	2.692796000	3.280400000
H	-1.260999000	1.705745000	3.561900000
C	-3.159598000	2.969782000	0.363460000
H	-4.060944000	2.505974000	0.775516000
H	-3.213427000	2.886459000	-0.725283000
H	-3.207100000	4.033867000	0.617251000
C	-0.215233000	3.351624000	1.220560000
C	-0.423947000	4.736680000	1.277579000
H	-1.430298000	5.135837000	1.176865000
C	0.628111000	5.629542000	1.466732000
H	0.432467000	6.697752000	1.501036000
C	1.926788000	5.154525000	1.626979000
H	2.748032000	5.847383000	1.784675000
C	2.161113000	3.784012000	1.584149000
H	3.170502000	3.398861000	1.703693000
C	1.103587000	2.905582000	1.370993000
H	1.312749000	1.842219000	1.305206000
C	-0.647296000	-1.444177000	2.635703000
C	-1.830709000	-2.191156000	2.555290000
C	-2.684398000	-2.217465000	3.660335000
H	-3.615271000	-2.775326000	3.592059000
C	-2.352310000	-1.560236000	4.834613000
H	-3.021602000	-1.593983000	5.688722000
C	-1.157077000	-0.855280000	4.915556000
H	-0.907489000	-0.339646000	5.836364000
C	-0.295337000	-0.777125000	3.823521000
C	-2.192979000	-2.994360000	1.331991000
H	-1.565790000	-2.687483000	0.495882000
H	-3.223482000	-2.760895000	1.045032000
C	-2.059330000	-4.505052000	1.544449000
H	-2.693305000	-4.851237000	2.366782000
H	-1.028211000	-4.784169000	1.784481000
H	-2.356091000	-5.044126000	0.639136000
C	0.987159000	0.026645000	3.881403000
H	1.021999000	0.670953000	2.998315000
H	1.843643000	-0.652044000	3.782145000
C	1.188045000	0.889268000	5.122965000
H	1.263463000	0.286880000	6.033702000
H	0.368081000	1.602326000	5.253385000
H	2.112356000	1.466250000	5.029515000
C	3.758335000	-1.607203000	-0.446682000
C	4.478934000	-2.466903000	-1.307495000
C	5.862326000	-2.338579000	-1.409501000
H	6.402424000	-2.990897000	-2.091679000
C	6.549201000	-1.377380000	-0.682968000
H	7.623946000	-1.269625000	-0.789458000
C	5.847813000	-0.565613000	0.195678000
H	6.391760000	0.162371000	0.789304000

C	4.465001000	-0.681401000	0.358221000
C	3.799789000	-3.530589000	-2.144467000
H	4.102613000	-3.401487000	-3.190749000
H	2.718041000	-3.388058000	-2.111113000
C	4.144529000	-4.957629000	-1.703141000
H	5.220587000	-5.144260000	-1.768958000
H	3.635431000	-5.693470000	-2.332920000
H	3.846557000	-5.136797000	-0.665511000
C	3.783232000	0.169299000	1.414974000
H	3.578626000	1.169736000	1.008526000
H	2.810829000	-0.262309000	1.652794000
C	4.554639000	0.316822000	2.727688000
H	4.801461000	-0.662684000	3.148505000
H	3.940033000	0.855787000	3.455220000
H	5.486765000	0.876316000	2.611874000
C	-1.663974000	0.568075000	-1.394853000
N	-1.192710000	1.506266000	-2.252007000
C	-1.680514000	1.301723000	-3.616882000
H	-0.895627000	0.822575000	-4.217737000
H	-1.944895000	2.251810000	-4.085437000
C	-2.879085000	0.386337000	-3.390173000
H	-3.830676000	0.932031000	-3.388003000
H	-2.947598000	-0.425320000	-4.117987000
N	-2.605969000	-0.140842000	-2.050705000
C	0.029847000	2.226659000	-2.073991000
C	1.225994000	1.505922000	-1.969225000
C	2.410738000	2.223276000	-1.798640000
H	3.345140000	1.682531000	-1.675107000
C	2.407588000	3.610021000	-1.771052000
H	3.335047000	4.152091000	-1.618235000
C	1.216588000	4.304040000	-1.924069000
H	1.212499000	5.389219000	-1.884795000
C	0.008876000	3.628170000	-2.083531000
C	1.268317000	-0.009773000	-2.001518000
H	0.303774000	-0.371410000	-2.359822000
C	2.291393000	-0.500927000	-3.030627000
H	3.322925000	-0.277949000	-2.749221000
H	2.095519000	-0.031526000	-4.000188000
H	2.212702000	-1.582375000	-3.151423000
C	-1.259507000	4.425372000	-2.266311000
H	-1.356593000	5.117645000	-1.422586000
H	-2.126067000	3.764329000	-2.217653000
C	-1.281835000	5.208430000	-3.583378000
H	-0.450542000	5.917100000	-3.639033000
H	-2.213390000	5.772617000	-3.684835000
H	-1.194003000	4.537182000	-4.444352000
C	-3.286076000	-1.334786000	-1.647132000
C	-2.685542000	-2.567024000	-1.968234000
C	-3.420499000	-3.730521000	-1.766243000
H	-2.984834000	-4.693310000	-2.008782000
C	-4.710233000	-3.676383000	-1.245121000
H	-5.273806000	-4.592684000	-1.101090000

C	-5.263445000	-2.457475000	-0.890567000
H	-6.259496000	-2.418292000	-0.458549000
C	-4.560027000	-1.263248000	-1.080061000
C	-1.253435000	-2.594773000	-2.455570000
H	-0.643857000	-2.082009000	-1.702931000
H	-1.160541000	-1.989480000	-3.366801000
C	-0.650671000	-3.972765000	-2.700777000
H	-0.665237000	-4.579939000	-1.789737000
H	0.392638000	-3.868881000	-3.011626000
H	-1.181376000	-4.521502000	-3.484904000
C	-5.166945000	0.033665000	-0.604570000
H	-6.160993000	0.155703000	-1.050836000
H	-4.557968000	0.878498000	-0.933896000
C	-5.282084000	0.062728000	0.925097000
H	-5.913051000	-0.753602000	1.289614000
H	-5.723835000	1.004063000	1.264003000
H	-4.294921000	-0.042467000	1.383582000

4

Si	0.531821000	0.543663000	-1.516892000
H	0.125516000	0.061048000	-2.870825000
B	0.569256000	-0.603181000	0.116130000
H	1.514152000	-0.221342000	0.751525000
B	-0.860186000	0.369593000	-0.098303000
H	-1.806799000	-0.127037000	-0.646851000
C	1.969612000	1.740555000	-1.738001000
C	3.161471000	1.584136000	-1.016222000
H	3.233486000	0.800546000	-0.269582000
C	4.256664000	2.413028000	-1.241240000
H	5.170561000	2.255000000	-0.675462000
C	4.182564000	3.429283000	-2.190471000
H	5.036472000	4.076110000	-2.369435000
C	3.004940000	3.608717000	-2.913403000
H	2.937462000	4.399249000	-3.655285000
C	1.916376000	2.770289000	-2.689806000
H	1.008175000	2.917983000	-3.270293000
C	0.707715000	-2.043036000	-0.373670000
N	1.900479000	-2.710182000	-0.495539000
C	1.754390000	-4.050541000	-1.052657000
H	1.973987000	-4.813501000	-0.295041000
H	2.437130000	-4.209116000	-1.890790000
C	0.287635000	-4.068872000	-1.489247000
H	0.180921000	-3.974103000	-2.577711000
H	-0.238692000	-4.972474000	-1.171887000
N	-0.262612000	-2.895750000	-0.811043000
C	3.182310000	-2.102753000	-0.360464000
C	3.861824000	-1.680613000	-1.515923000
C	5.133995000	-1.127802000	-1.365414000
H	5.676270000	-0.784274000	-2.239238000
C	5.698060000	-0.965580000	-0.107085000
H	6.682939000	-0.519038000	-0.009175000
C	4.995235000	-1.355604000	1.025389000

H	5.427875000	-1.211824000	2.011800000
C	3.732806000	-1.938108000	0.918560000
C	3.210905000	-1.796213000	-2.879612000
H	2.128464000	-1.697297000	-2.750228000
H	3.382967000	-2.804911000	-3.281888000
C	3.675183000	-0.769151000	-3.912381000
H	3.060066000	-0.845689000	-4.813046000
H	4.715122000	-0.928017000	-4.213672000
H	3.580801000	0.247789000	-3.522205000
C	3.008385000	-2.390160000	2.163421000
H	1.942074000	-2.169099000	2.072991000
H	3.374754000	-1.795233000	3.006072000
C	3.218227000	-3.876640000	2.466312000
H	2.717388000	-4.158680000	3.397563000
H	4.282651000	-4.110279000	2.567090000
H	2.812779000	-4.503030000	1.667157000
C	-1.653161000	-2.873934000	-0.498021000
C	-2.070580000	-3.173950000	0.809792000
C	-3.434235000	-3.338722000	1.043640000
H	-3.771692000	-3.575386000	2.049381000
C	-4.360302000	-3.198164000	0.016475000
H	-5.418157000	-3.345829000	0.213442000
C	-3.932714000	-2.842838000	-1.253555000
H	-4.661866000	-2.689159000	-2.043104000
C	-2.576404000	-2.664751000	-1.531128000
C	-1.094683000	-3.313042000	1.955245000
H	-1.641378000	-3.141911000	2.889347000
H	-0.345391000	-2.519141000	1.889470000
C	-0.406465000	-4.678692000	2.024500000
H	0.251088000	-4.736809000	2.896631000
H	0.207761000	-4.857707000	1.138603000
H	-1.141347000	-5.486601000	2.093637000
C	-2.132339000	-2.213694000	-2.904923000
H	-2.299133000	-3.020974000	-3.630350000
H	-1.057248000	-2.018592000	-2.883545000
C	-2.842534000	-0.939619000	-3.372703000
H	-2.440656000	-0.613072000	-4.336466000
H	-2.691522000	-0.136664000	-2.647647000
H	-3.920461000	-1.085487000	-3.489080000
C	-1.278126000	1.636554000	0.678110000
N	-2.491194000	2.231943000	0.514356000
C	-2.724036000	3.320303000	1.456182000
H	-3.414856000	3.001125000	2.249386000
H	-3.162064000	4.186315000	0.952844000
C	-1.314772000	3.588674000	1.978637000
H	-0.870336000	4.461766000	1.489236000
H	-1.272044000	3.741801000	3.059844000
N	-0.606507000	2.364106000	1.605739000
C	-3.587203000	1.709188000	-0.232474000
C	-3.897325000	2.285784000	-1.468383000
C	-5.018076000	1.811008000	-2.153060000
H	-5.274080000	2.246206000	-3.115443000

C	-5.796191000	0.794308000	-1.620583000
H	-6.665067000	0.435024000	-2.163678000
C	-5.468156000	0.232168000	-0.390962000
H	-6.081272000	-0.567002000	0.010648000
C	-4.362772000	0.680219000	0.327846000
C	-3.040214000	3.363327000	-2.091133000
H	-2.349847000	3.767258000	-1.346078000
H	-3.685491000	4.187771000	-2.417244000
C	-2.229830000	2.844002000	-3.284077000
H	-1.631112000	3.647932000	-3.723679000
H	-2.884836000	2.441843000	-4.063378000
H	-1.557068000	2.044057000	-2.963129000
C	-3.951660000	0.052328000	1.640332000
H	-3.459593000	0.803518000	2.265007000
H	-3.176523000	-0.691361000	1.417635000
C	-5.074274000	-0.593407000	2.446382000
H	-4.686867000	-0.949910000	3.405391000
H	-5.502781000	-1.456689000	1.931060000
H	-5.881811000	0.117533000	2.648426000
C	0.671714000	2.054648000	2.158961000
C	1.785010000	2.817562000	1.787588000
C	3.023776000	2.492649000	2.346114000
H	3.899546000	3.057799000	2.038848000
C	3.146740000	1.454706000	3.255685000
H	4.117997000	1.208194000	3.673684000
C	2.022778000	0.724045000	3.626591000
H	2.118029000	-0.092885000	4.336476000
C	0.771456000	1.002391000	3.085493000
C	1.699586000	3.977916000	0.823540000
H	0.799223000	3.893375000	0.209054000
H	2.538056000	3.913429000	0.125587000
C	1.756693000	5.335523000	1.534873000
H	1.676795000	6.154902000	0.814416000
H	2.704113000	5.449268000	2.070664000
H	0.954877000	5.447872000	2.271718000
C	-0.418795000	0.153489000	3.467176000
H	-0.046103000	-0.754017000	3.954856000
H	-0.923568000	-0.177455000	2.554441000
C	-1.414459000	0.845735000	4.401947000
H	-2.228747000	0.164220000	4.667457000
H	-1.863616000	1.722963000	3.927593000
H	-0.929957000	1.175660000	5.326061000

5

Si	-0.344769000	0.190427000	3.278647000
C	-0.175599000	0.098885000	1.415456000
N	3.097179000	1.595158000	3.995370000
B	0.615812000	1.368851000	4.564574000
H	0.906170000	0.662507000	5.490339000
B	-1.001439000	1.852827000	4.208519000
H	-1.243963000	2.683932000	3.374875000
N	1.882650000	3.332565000	3.406348000

C	0.566294000	1.045034000	0.696745000
H	1.028007000	1.864835000	1.238918000
N	-2.217318000	0.786945000	6.240882000
C	1.840170000	2.100147000	3.991512000
N	-3.512513000	1.582582000	4.657556000
C	0.735266000	0.955700000	-0.679403000
H	1.307860000	1.725665000	-1.193321000
C	3.209813000	3.627215000	2.850672000
H	3.547933000	4.612476000	3.181121000
H	3.178599000	3.629247000	1.755294000
C	4.082353000	2.482994000	3.390024000
H	4.626576000	1.969054000	2.592131000
H	4.811560000	2.817027000	4.139231000
C	3.703566000	0.131811000	5.855118000
C	3.461823000	0.300609000	4.480736000
C	4.087387000	-1.129562000	6.303795000
H	4.280258000	-1.290071000	7.358733000
C	4.225865000	-2.189967000	5.416000000
H	4.523470000	-3.167279000	5.783611000
C	3.981681000	-2.004097000	4.064341000
H	4.085140000	-2.839272000	3.379647000
C	3.596092000	-0.755961000	3.570282000
C	3.340334000	-0.557086000	2.094729000
H	4.297556000	-0.357055000	1.591647000
H	2.730007000	0.337678000	1.957908000
C	2.637866000	-1.726484000	1.408398000
H	2.331957000	-1.446580000	0.396919000
H	1.738582000	-2.004038000	1.964453000
H	3.278505000	-2.608683000	1.320947000
C	3.508448000	1.287472000	6.807211000
H	2.429420000	1.442630000	6.923963000
H	3.894338000	2.197836000	6.338452000
C	4.134355000	1.129939000	8.188314000
H	5.209468000	0.932090000	8.129012000
H	3.667631000	0.315784000	8.750717000
H	3.987729000	2.046036000	8.768002000
C	0.975423000	4.412297000	3.677986000
C	0.308171000	5.042093000	2.618192000
C	-0.489595000	6.156187000	2.894774000
H	-0.999012000	6.649926000	2.071489000
C	-0.646318000	6.628000000	4.186449000
H	-1.273516000	7.491492000	4.383514000
C	0.003396000	5.980879000	5.229656000
H	-0.116005000	6.339412000	6.248643000
C	0.832539000	4.885021000	4.998499000
C	1.566069000	4.290264000	6.176342000
H	1.520504000	3.201160000	6.142663000
H	1.032687000	4.578590000	7.086830000
C	3.014205000	4.773511000	6.291328000
H	3.618219000	4.442553000	5.441609000
H	3.480495000	4.381945000	7.200439000
H	3.060340000	5.866362000	6.326351000

C	0.373206000	4.568447000	1.184625000
H	1.140195000	3.802211000	1.069159000
H	0.678617000	5.410690000	0.551499000
C	-0.966897000	4.016760000	0.684315000
H	-1.754822000	4.773982000	0.741338000
H	-1.287204000	3.161733000	1.284358000
H	-0.879200000	3.688429000	-0.354586000
C	-2.211962000	1.423446000	5.032291000
C	-4.462476000	1.128046000	5.663285000
H	-5.233639000	0.490965000	5.221050000
H	-4.963772000	1.983299000	6.138277000
C	-3.559261000	0.363517000	6.639872000
H	-3.746975000	0.629419000	7.683436000
H	-3.669190000	-0.723580000	6.537552000
C	-1.173805000	0.849158000	7.213258000
C	-0.916095000	2.079908000	7.845191000
C	0.064607000	2.119605000	8.832605000
H	0.287414000	3.054771000	9.335534000
C	0.753184000	0.967187000	9.198568000
H	1.505723000	1.013247000	9.979929000
C	0.485033000	-0.235606000	8.563669000
H	1.036913000	-1.127543000	8.845240000
C	-0.476940000	-0.315662000	7.553692000
C	-0.718155000	-1.623242000	6.832307000
H	-1.407188000	-1.445873000	6.002713000
H	-1.214508000	-2.325199000	7.515641000
C	0.559341000	-2.263316000	6.278448000
H	0.316095000	-3.182230000	5.736987000
H	1.266810000	-2.522273000	7.071791000
H	1.064684000	-1.584346000	5.587156000
C	-1.673704000	3.316997000	7.419546000
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H	-1.301715000	3.615035000	6.431200000
C	-1.619012000	4.507988000	8.370373000
H	-0.606163000	4.908978000	8.476860000
H	-1.978366000	4.244138000	9.370194000
H	-2.247075000	5.316485000	7.985238000
C	-3.945645000	2.171952000	3.434840000
C	-4.019713000	3.568954000	3.336515000
C	-4.491122000	4.116476000	2.143677000
H	-4.561726000	5.193101000	2.033682000
C	-4.874750000	3.296824000	1.090594000
H	-5.241692000	3.737364000	0.168314000
C	-4.782649000	1.915898000	1.204397000
H	-5.068306000	1.294519000	0.363306000
C	-4.309270000	1.327339000	2.375894000
C	-4.169585000	-0.173173000	2.528841000
H	-4.936797000	-0.538379000	3.225720000
H	-3.206147000	-0.373778000	3.010594000
C	-4.256518000	-0.976237000	1.233473000
H	-5.241724000	-0.894502000	0.762210000
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H	-2.455434000	4.371442000	4.520809000
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B	1.001439000	-1.852827000	-4.208519000
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H	1.214508000	2.325199000	-7.515641000
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H	-0.316095000	3.182230000	-5.736987000
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H	-1.064684000	1.584346000	-5.587156000
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H	2.247075000	-5.316485000	-7.985238000
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References

1 Z. Ouyang, J. Du, L. Wang, J. L. Kneebone, M. L. Neidig and L. Deng, *Inorg. Chem.*, 2015, **54**, 8808–8816.

2 M. Arrowsmith, J. Böhnke, H. Braunschweig, M. A. Celik, T. Dellermann and K. Hammond, *Chem. Eur. J.*, 2016, **22**, 17169–17172.

3 G. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3–8.

4 G. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112–122.

5 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, 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, Ö. Farkas, J. B. Foresman, J. V Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 16, Revision C.01*, Gaussian, Inc., Wallingford CT, 2016.

6 (*a*) F. Neese, *Wiley Interdiscip. Rev. Comput. Mol. Sci.*, 2012, **2**, 73–78; (*b*) F. Neese, *WIREs Comput. Mol. Sci.*, 2022, **12**, e1606.

7 J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615.

8 A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378–6396.

9 (*a*) M. Ernzerhof and G. E. Scuseria, *J. Chem. Phys.*, 1999, **110**, 5029–5036; (*b*) C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158–6170.

10 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.

11 (*a*) I. Mayer, *Chem. Phys. Lett.*, 1983, **97**, 270–274; (*b*) I. Mayer, *Int. J. Quantum Chem.*, 1984, **26**, 151–154; (*c*) A. J. Bridgeman, G. Cavigliasso, L. R. Ireland and J. Rothery, *J. Chem. Soc. Dalton Trans.*, 2001, 2095–2108.

12 T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580–592.

13 G. Knizia, *J. Chem. Theory Comput.*, 2013, **9**, 4834–4843.