Supporting Information for:

Reactivity of a Magnesium Diboranate with Organic Nitriles

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General experimental considerations

All reactions and manipulations were performed under an inert atmosphere of argon using standard Schlenk and glovebox techniques. Any glassware required for synthetic procedures was stored in an oven at 150 °C for at least 1 hour prior to use. All solvents were dried by passage through an Innovative Technologies solvent purification system under argon and stored over 4 Å molecular sieves or potassium. d_8-toluene was purchased from Sigma-Aldrich Ltd., dried over a potassium mirror and vacuum distilled under argon prior to use. Di-*n*-butylmagnesium (1.0 M solution in *n*-heptane) and bis(pinacolato)diborane (B_2pin_2) were purchased from Sigma-Aldrich Ltd. Di-*n*-butylmagnesium solution was used without further purification and B_2pin_2 was sublimed under vacuum at 80 °C before use. NMR experiments were conducted in J. Young NMR tubes and prepared in a glovebox. ^{1}H, ^{13}C{^{1}H}, ^{11}B{^{1}H}, COSY and HSQC NMR spectra were recorded on an Agilent ProPulse spectrometer operating at 500 MHz (^{1}H), 126 MHz (^{13}C), 160.4 MHz (^{11}B) and at a temperature of 298 K unless stated otherwise. The spectra were referenced to residual solvent resonances (d_8-Toluene: ^{1}H, δ = 2.09, 6.98, 7.00, 7.09 and ^{13}C, δ = 20.4, 125.5, 128.3, 129.2 ppm) or an external $BF_3.OEt_2$ standard for ^{11}B experiments. Elemental (CHN) analysis was performed by Elemental Microanalysis Ltd., Okehampton, Devon, UK. [(BDI)Mg*n*Bu] (**VI**) and [(BDI) Mg{pinBB(*n*-Bu)pin}] (**V**) (BDI = HC{(Me)CN(2,6-^{i}Pr$_2$C$_6$H$_3$)}$_2$ were synthesised by literature procedures.[1,2]

Synthetic, spectroscopic and analytical data for new compounds

Compound 1: In a J. Young NMR tube, d_8-toluene (*ca*. 0.5 mL) was added to **V** (75.6 mg, 0.10 mmol) and *i*-PrCN, (6.94 mg, 0.10 mmol), and the resulting colourless solution was left at room temperature for 7 h. Slow removal of toluene *in-vacuo* resulted in the formation of compound **1** as colourless block crystals (0.07 g, 79%). ^{1}H NMR (500 MHz, 298 K, d_8-Tol): δ 7.09 (m, 6H, Ar-*H*), 4.83 (s, 1H, NC(CH$_3$)C*H*), 3.43 (hept, 3H, $^3J_{HH}$ = 7.3 Hz, C*H*(CH$_3$)$_2$), 3.33 (hept, 1H, $^3J_{HH}$ = 6.7 Hz, C*H*(CH$_3$)$_2$), 3.15 (hept, 1H, $^3J_{HH}$ = 6.5 Hz, C*H*(CH$_3$)$_2$), 1.71 (s, 3H,

NC(CH_3)CH), 1.66 (s, 3H, NC(CH_3)CH), 1.48 (d, 3H, $^3J_{HH}$ = 6.9 Hz, CH_3) 1.41 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH_3), 1.18 (m, 36H, CH_3) 1.10 (s, 3H, CH_3), 1.05 (s, 3H, CH_3), 1.01 (s, 3H, CH_3), 0.92 (m, 4H, CH_2), 0.68 (s, 3H, CH_3), 0.39 (s, 3H, CH_3), -0.36 (m, 1H, CH_2-B), -0.54 (m, 1H, CH_2-B) ppm. ^{13}C{^{1}H} NMR (126 MHz, 298 K, d_8-Tol) : δ 169.5, 168.6 (N*C*(CH$_3$)CH), 146.9, 145.8, 143.1, 143.0, 142.5, 141.2, 125.7, 125.5, 124.8, 124.5, 124.1, 123.2 (*C* Ar), 95.6 (NC(CH$_3$)*C*H), 84.9 (B(O*C*(CH$_3$)$_2$)$_2$), 79.6 (B(O*C*(CH$_3$)$_2$)$_2$), 78.3 (B(O*C*(CH$_3$)$_2$)$_2$), 37.7, 29.8 (*C*H(CH$_3$)$_2$), 29.0 (*C*H$_3$), 29.0 (*C*H(CH$_3$)$_2$), 28.7, 27.0 (*C*H$_2$), 26.8, 26.7 (*C*H(CH$_3$)$_2$), 26.6 (*C*H$_2$), 26.1, 25.9, 25.8, 25.7, 25.7, 25.7, 25.3, 25.3, 25.0 (*C*H$_3$), 24.9 (NC(*C*H$_3$)CH), 24.6, 24.6 (*C*H$_3$), 24.3 (NC(*C*H$_3$)CH), 23.7, 19.9, 19.1, 14.7 (*C*H$_3$) ppm. ^{11}B{^{1}H} NMR (96 MHz, 298 K, d_8-Tol): δ 34.2 (*B*pin), 8.8 (*n*-Bu*B*pin) ppm. CHN analysis; Calculated: $C_{49}H_{81}B_2MgN_3O_4$, C: 71.59%, H: 9.93%, N: 5.11%. Found: C: 71.27%, H: 9.56%, N: 5.24%.

Compound 2: In a J. Young'NMR tube, d_8-toluene (*ca*. 0.5 mL) was added to **V** (75.6 mg, 0.10 mmol) and *t*-BuCN, (8.35 mg, 0.10 mmol) and the resulting colourless solution was then heated at 40 °C for 15 h. The toluene was removed *in-vacuo* and the resulting white solid was crystallised from pentane at –35 °C to provide compound **2** as colourless block crystals (0.03 g, 28%). ^{1}H NMR (500 MHz, 298 K, d_8-Tol): δ 7.12 (m, 6H, Ar-*H*), 4.85 (s, 1H, NC(CH$_3$)C*H*), 3.40 (hept, 3H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 3.29 (hept, 1H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 3.17 (hept, 1H, $^3J_{HH}$ = 6.6 Hz, C*H*(CH$_3$)$_2$), 3.13 (hept, 1H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 1.63 (s, 6H, NC(CH_3)CH), 1.47 (d, 3H, $^3J_{HH}$ = 6.9 Hz, CH_3), 1.38 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH_3), 1.31 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH_3), 1.30 (s, 9H, CH_3), 1.28 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH_3), 1.23 (s, 9H, CH_3), 1.23 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH_3), 1.21 (d, 3H, $^3J_{HH}$ = 6.7 Hz, CH_3), 1.19 (s, 6H, CH_3), 1.16 (d, 3H, $^3J_{HH}$ = 6.9 Hz, CH_3), 1.12 (s, 3H, CH_3), 0.99 (m, 6H, CH_3), 0.88 (m, 4H, CH_2), 0.30 (s, 3H, CH_3), 0.04 (m, 1H, CH_2-B), -0.61 (m, 1H, CH_2-B) ppm. ^{13}C{^{1}H} NMR (126 MHz, 298 K, d_8-Tol) : δ 170.4, 169.8 (N*C*(CH$_3$)CH), 148.2, 146.3, 143.6, 143.0, 142.1, 141.3, 129.2, 128.2, 126.0, 125.7, 125.7, 124.8, 124.8, 123.8, 123.4 (*C*(Ar)), 96.0 (NC(CH$_3$)*C*H), 83.7 (B(O*C*(CH$_3$)$_2$)$_2$), 80.7 (B(O*C*(CH$_3$)$_2$)$_2$), 78.8 (B(O*C*(CH$_3$)$_2$)$_2$), 40.6 (*C*(CH$_3$)$_3$), 32.0 (*C*H$_3$), 29.8, 29.4, 29.3, 28.1 (*C*H(CH$_3$)$_2$), 27.6 (*C*H$_3$), 27.0 (*C*H$_2$-CH$_3$), 26.7 (*C*H$_3$), 26.6 (*C*H$_2$), 26.3, 26.2, 25.7 (*C*H$_3$), 25.5 (*C*H$_2$), 25.4 (*C*H$_2$), 25.4, 25.0 (*C*H$_3$), 24.9, 24.9 (NC(*C*H$_3$)CH), 24.9, 24.8, 24.6, 24.5, 24.1, 23.5, 23.1, 22.8, 15.0 (*C*H$_3$) ppm. ^{11}B{^{1}H} NMR (96 MHz, 298 K, d_8-Tol): δ 34.4 (*B*pin), 9.5 (*n*-Bu*B*pin) ppm. CHN analysis; Calculated: $C_{50}H_{83}B_2MgN_3O_4$, C: 71.82%, H: 10.01%, N: 5.03%. Found: C: 72.25%, H: 9.79%, N: 4.96%.

Compound 3: In a J. Young NMR tube, d_8-toluene (*ca*. 0.5 mL) was added to **V** (75.6 mg, 0.10 mmol) and *i*-PrCN, (13.9 mg, 0.20 mmol), and the resulting colourless solution was then heated at 60 °C for 12 h. To avoid premature crystallisation, the solution was gradually cooled to room temperature by placing the NMR tube into a Dewar flask of warm water covered in aluminium foil, upon which a crop of colourless crystals was obtained and washed with *n*-hexane (0.03 g, 19%).

^{1}H NMR (500 MHz, 298 K, d_8-Tol): δ 7.07 (m, 6H, Ar-*H*), 4.82 (s, 1H, NC(CH$_3$)C*H*), 3.26 (hept, 2H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 3.18 (hept, 2H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 3.01 (hept, 1H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 2.93 (hept, 1H, $^3J_{HH}$ = 6.9 Hz, C*H*(CH$_3$)$_2$), 1.61 (s, 6H, NC(C*H*$_3$)CH), 1.40 (d, 6H, $^3J_{HH}$ = 6.9 Hz, C*H*$_3$), 1.28 (d, 6H, $^3J_{HH}$ = 6.7 Hz, C*H*$_3$), 1.24 (d, 6H, $^3J_{HH}$ = 7.0 Hz, C*H*$_3$), 1.17 (d, 6H, $^3J_{HH}$ = 7.0 Hz, C*H*$_3$), 1.16 (d, 6H, $^3J_{HH}$ = 7.1 Hz, C*H*$_3$), 1.13 (d, 6H, $^3J_{HH}$ = 6.7 Hz, C*H*$_3$), 1.05 (s, 12H, C*H*$_3$) ppm. Once isolated, this compound was insufficiently soluble to allow to enable the recording of a meaningful ^{13}C NMR spectrum. ^{11}B{^{1}H} NMR (96 MHz, 298 K, d_8-Tol): δ 10.7 (*B*pin) ppm. CHN analysis; Calculated: $C_{49}H_{81}B_2MgN_3O_4$, C: 71.59%, H: 9.93%, N: 5.11%. Found: C: 71.27%, H: 9.56%, N: 5.24%.

Compound 4: In a J. Young NMR tube, d_8-toluene (*ca*. 0.5 mL) was added to **V** (30.2 mg, 0.04 mmol) and cooled to –35 °C, before the addition of *o*-tolunitrile, (4.70 mg, 0.04 mmol). The resulting colourless solution was then left at –35 °C for 48 hours. The toluene was removed *in-vacuo* and the resultant colourless solid crystallised from anhydrous n-hexane at –35 °C to provide compound **4** as colourless block crystals (0.02 g, 41%). ^{1}H NMR (400 MHz, 298 K, d_8-Tol): δ 7.07 (m, 6H, Ar-*H*), 4.82 (s, 1H, NC(CH$_3$)C*H*), 3.26 (hept, 2H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 3.18 (hept, 2H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 3.01 (hept, 1H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 2.93 (hept, 1H, $^3J_{HH}$ = 6.9 Hz, C*H*(CH$_3$)$_2$), 1.61 (s, 6H, NC(C*H*$_3$)CH), 1.40 (d, 6H, $^3J_{HH}$ = 6.9 Hz, C*H*$_3$), 1.28 (d, 6H, $^3J_{HH}$ = 6.7 Hz, C*H*$_3$), 1.24 (d, 6H, $^3J_{HH}$ = 7.0 Hz, C*H*$_3$), 1.17 (d, 6H, $^3J_{HH}$ = 7.0 Hz, C*H*$_3$), 1.16 (d, 6H, $^3J_{HH}$ = 7.1 Hz, C*H*$_3$), 1.13 (d, 6H, $^3J_{HH}$ = 6.7 Hz, C*H*$_3$), 1.05 (s, 12H, C*H*$_3$) ppm. Once isolated, this compound was insufficiently soluble to allow to enable the recording of a meaningful ^{13}C NMR spectrum. ^{11}B{^{1}H} NMR (96 MHz, 298 K, d_8-Tol): δ 10.0 (*B*pin) ppm. Despite repeated attempts an accurate CHN microanalysis could not be obtained for this compound.

Compound 5: In a J. Young NMR tube, d_8-toluene (*ca*. 0.5 mL) was added to **V** (75.6 mg, 0.10 mmol) and *o*-tolunitrile, (23.5 mg, 0.20 mmol), and the resultant colourless solution was then left at room temperature for 24 h. The toluene was removed *in-vacuo* and the resultant colourless solid crystallised from hexane at −35 °C whereupon compound **5** was obtained as a crop of colourless block crystals (0.06 g, 67%). ^{1}H NMR (500 MHz, 298 K, d_8-Tol): δ 7.97 (d, 1H, $^3J_{HH}$ = 7.7 Hz, Ar-*H*), 7.66 (d, 1H, $^3J_{HH}$ = 7.2 Hz, Ar-*H*), 7.23 (t, 1H, $^3J_{HH}$ = 7.4 Hz, Ar-*H*), 7.17 (t, 1H, $^3J_{HH}$ = 7.3 Hz, Ar-*H*), 7.06 (m, 8H, Ar-*H*), 6.89 (m, 1H, Ar-*H*), 6.83 (d, 1H, $^3J_{HH}$ = 7.7 Hz, Ar-*H*), 5.04 (s, 1H, NC(CH$_3$)C*H*), 3.32 (sept, 2H, $^3J_{HH}$ = 6.7 Hz, C*H*(CH$_3$)$_2$), 3.10 (sept, 2H, $^3J_{HH}$ = 6.7 Hz, C*H*(CH$_3$)$_2$), 2.84 (s, 3H, Ar-C*H*$_3$), 2.51 (s, 3H, Ar-C*H*$_3$), 1.69 (s, 6H, NC(C*H*$_3$)CH), 1.29 (d, 6H, $^3J_{HH}$ = 6.9 Hz, C*H*$_3$), 1.18 (d, 6H, $^3J_{HH}$ = 6.6 Hz, C*H*$_3$), 1.11 (d, 6H, $^3J_{HH}$ = 6.7 Hz, C*H*$_3$), 0.92 (d, 6H, $^3J_{HH}$ = 6.7 Hz, C*H*$_3$), 0.74 (s, 6H, C*H*$_3$), 0.59 (s, 6H, C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (126 MHz, 298 K, d_8-Tol) : δ 181.7, 170.3 (N*C*(CH$_3$)CH), 145.3, 144.0, 141.5, 139.9, 135.6, 132.0, 130.8, 130.5, 130.2, 128.4, 125.8, 125.7, 124.6, 124.5, 123.3 (*C* Ar), 94.7 (NC(CH$_3$)*C*H), 80.3 (B(O*C*(CH$_3$)$_2$)$_2$), 29.2, 28.3 (*C*H(CH$_3$)$_2$), 26.6, 25.8, 25.1, 25.0, 24.6 (*C*H$_3$), 24.4 (NC(*C*H$_3$)CH), 23.9 (*C*H$_3$), 23.1 (NC(*C*H$_3$)CH), 22.6, 21.0 (*C*H$_3$) ppm. ^{11}B{^{1}H} NMR (96 MHz, 298 K, d_8-Tol): δ 11.0 (*B*pin) ppm. CHN analysis; Calculated: $C_{59}H_{74}BMgN_5O_2$, C: 76.99%, H: 8.10%, N: 7.61%. Experimental: C: 76.11%, H: 8.28%, N: 7.21%. CHN analysis provides a better match with the calculated values for the molecule with no coordinated nitrile, which is labile and may be removed during the drying process to provide the following values. CHN analysis; Calculated: $C_{51}H_{67}BMgN_4O_2$, C: 76.26%, H: 8.41%, N: 6.98%. Found: C: 76.11%, H: 8.28%, N: 7.21%.

Compound 6: In a J. Young NMR tube, d_8-toluene (*ca*. 0.5 mL) was added to **V** (151.2 mg, 0.20 mmol) and *o*-tolunitrile, (94.1 mg, 0.80 mmol). The resultant dark orange solution was heated at 60 °C for 12 hours. The toluene was removed *in-vacuo* and the resultant yellow solid crystallised from hexane at −35 °C to yield compound **6** as a crop of colourless block crystals (0.15 g, 71%). ^{1}H NMR (500 MHz, 298 K, d_8-Tol): δ 7.86 (d, 1H, $^3J_{HH}$ = 7.7 Hz, Ar-*H*), 7.20 (d, 4H, $^3J_{HH}$ = 7.2 Hz, Ar-*H*), 7.09 (t, 3H, $^3J_{HH}$ = 7.6 Hz, Ar-*H*), 6.86 (m, 6H, Ar-*H*), 6.65 (t, 2H, $^3J_{HH}$ = 7.6 Hz, Ar-*H*), 6.28 (t, 1H, $^3J_{HH}$ = 6.9 Hz, Ar-*H*), 6.15 (t, 1H, $^3J_{HH}$ = 7.2 Hz, Ar-*H*), 4.91 (s, 1H, NC(CH$_3$)C*H*), 3.68 (hept, 2H, $^3J_{HH}$ = 6.7 Hz, C*H*(CH$_3$)$_2$), 3.53 (hept, 2H, $^3J_{HH}$ = 6.7 Hz, C*H*(CH$_3$)$_2$), 2.38 (s, 3H, Ar-C*H*$_3$), 2.15 (s, 3H, Ar-C*H*$_3$), 1.68 (s, 6H, NC(C*H*$_3$)CH), 1.59 (d, 6H, $^3J_{HH}$ = 6.1 Hz, C*H*$_3$), 1.29 (d, 6H, $^3J_{HH}$ = 6.6 Hz, C*H*$_3$), 1.16 (d, 6H, $^3J_{HH}$ = 6.4 Hz, C*H*$_3$), 1.16 (d, 6H, $^3J_{HH}$ = 6.4 Hz, C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (126 MHz, 298 K, d_8-Tol) : δ

167.9, 162.4 (N*C*(CH_3)CH), 147.3, 144.7, 144.4, 142.6, 142.4, 139.7, 137.2, 134.7, 132.9, 132.8, 131.0, 128.8, 128.4, 126.8, 125.7, 125.0, 124.8, 124.5, 124.3, 123.3, 119.5, 117.6 (*C* Ar), 96.3 (NC(CH_3)*C*H), 82.8, 82.6 (B(O*C*(CH_3)$_2$)$_2$), 28.4, 27.1 (*C*H(CH_3)$_2$), 26.7, 26.6, 25.7, 25.4, 25.1, 25.0 (*C*H_3), 24.9 (NC(*C*H_3)CH), 22.1, 20.5 (*C*H_3) ppm. $^{11}B\{^1H\}$ NMR (96 MHz, 298 K, d_8-Tol) : δ 24.3 (*B*pin) ppm. Despite repeated attempts, a meaningful CHN microanalysis could not be obtained for this compound.

Compound 7: In a J. Young NMR tube, d_8-toluene (*ca*. 0.5 mL) was added to **V** (75.6 mg, 0.10 mmol) and *m*-tolunitrile, (23.5 mg, 0.20 mmol), and the resultant colourless solution was then heated at 60 °C for 48 h. The toluene was removed *in-vacuo* and the resultant yellow solid crystallised from anhydrous hexane at –35 °C to provide compound **7** as a crop of yellow block crystals (0.06 g, 70%). ^1H NMR (500 MHz, 298 K, d_8-Tol): δ 8.72 (d, 1H, $^3J_{HH}$ = 7.3 Hz, Ar-*H*), 8.51 (s, 1H, Ar-*H*), 8.16 (s, 1H, Ar-*H*), 8.13 (d, 1H, $^3J_{HH}$ = 7.3 Hz, Ar-*H*), 7.27 (t, 1H, $^3J_{HH}$ = 5.1 Hz, Ar-*H*), 7.19 (t, 1H, $^3J_{HH}$ = 5.0 Hz, Ar-*H*), 7.12 (s, 1H, Ar-*H*), 7.05 (m, 6H, Ar-*H*), 7.00 (s, 1H, Ar-*H*), 5.02 (s, 1H, NC(CH_3)C*H*), 3.31 (hept, 3H, $^3J_{HH}$ = 6.7 Hz, C*H*(CH_3)$_2$), 3.18 (hept, 1H, $^3J_{HH}$ = 6.5 Hz, C*H*(CH_3)$_2$), 2.34 (s, 3H, Ar-C*H*$_3$), 2.21 (s, 3H, Ar-C*H*$_3$), 1.70 (s, 6H, NC(C*H*$_3$)CH), 1.26 (d, 6H, $^3J_{HH}$ = 6.7 Hz, C*H*$_3$), 1.20 (d, 12H, $^3J_{HH}$ = 6.3 Hz, C*H*$_3$), 0.93 (s, 6H, C*H*$_3$), 0.92 (s, 6H, C*H*$_3$), 0.62 (s, 6H, C*H*$_3$) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, 298 K, d_8-Tol) : δ 178.3, 170.0 (N*C*(CH_3)CH), 145.3, 143.9, 141.6, 133.2, 130.6, 130.2, 129.2, 128.2, 127.8, 125.7, 124.4, 123.5 (*C* Ar), 95.3 (NC(CH_3)*C*H), 80.4 (B(O*C*(CH_3)$_2$)$_2$), 28.9, 28.8 (*C*H(CH_3)$_2$), 27.0, 25.8, 25.0, 25.0, 24.6, 24.5, 24.3 (*C*H_3), 21.4, 21.3 (NC(*C*H_3)CH) ppm. $^{11}B\{^1H\}$ NMR (96 MHz, 298 K, d_8-Tol): δ 11.6 (*B*pin) ppm. CHN analysis; Calculated: $C_{51}H_{67}BMgN_4O_2$, C: 76.26%, H: 8.41%, N: 6.98%. Found: C: 76.16%, H: 8.40%, N: 6.98%.

NMR Spectra

Compound 1

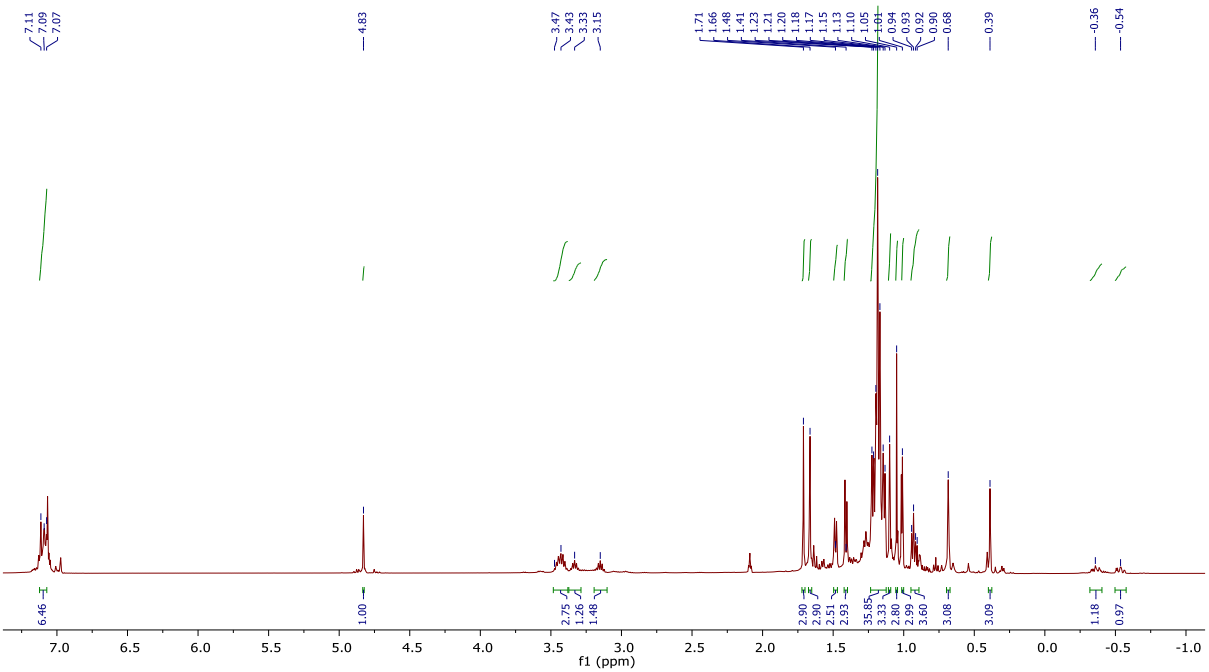

Figure S1: ^{1}H NMR spectrum (500 MHz, 298 K, d_8-Tol) of **1**.

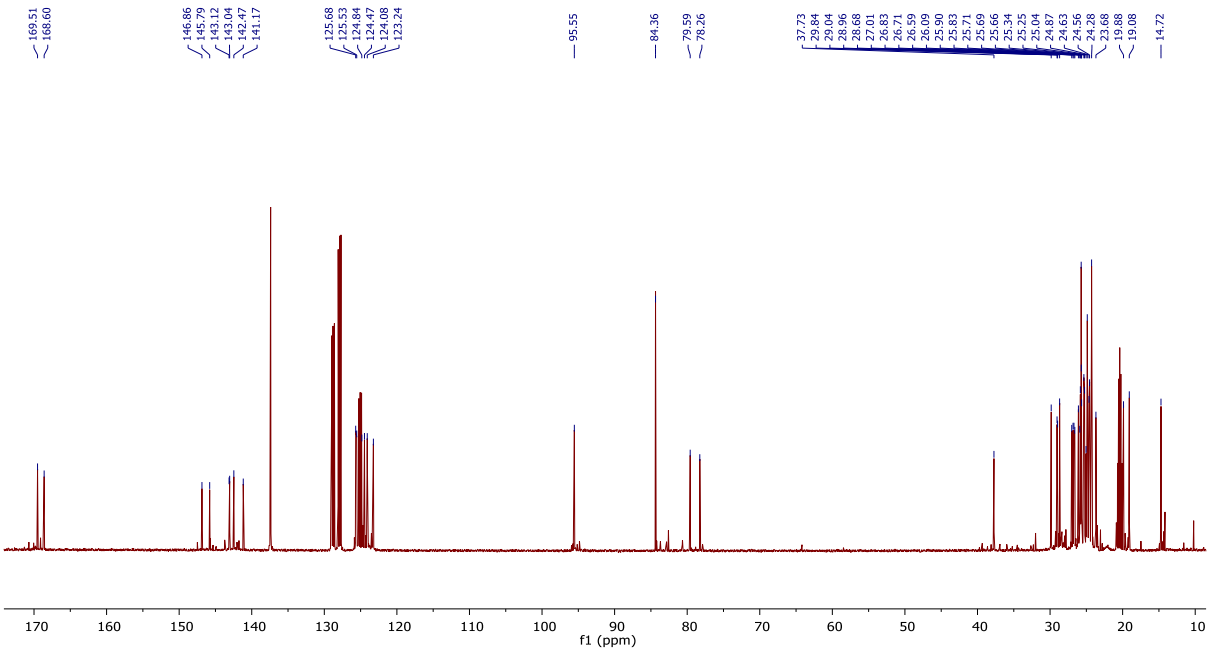

Figure S2. ^{13}C{^{1}H} NMR spectrum (126 MHz, 298 K, d_8-Tol) of **1**.

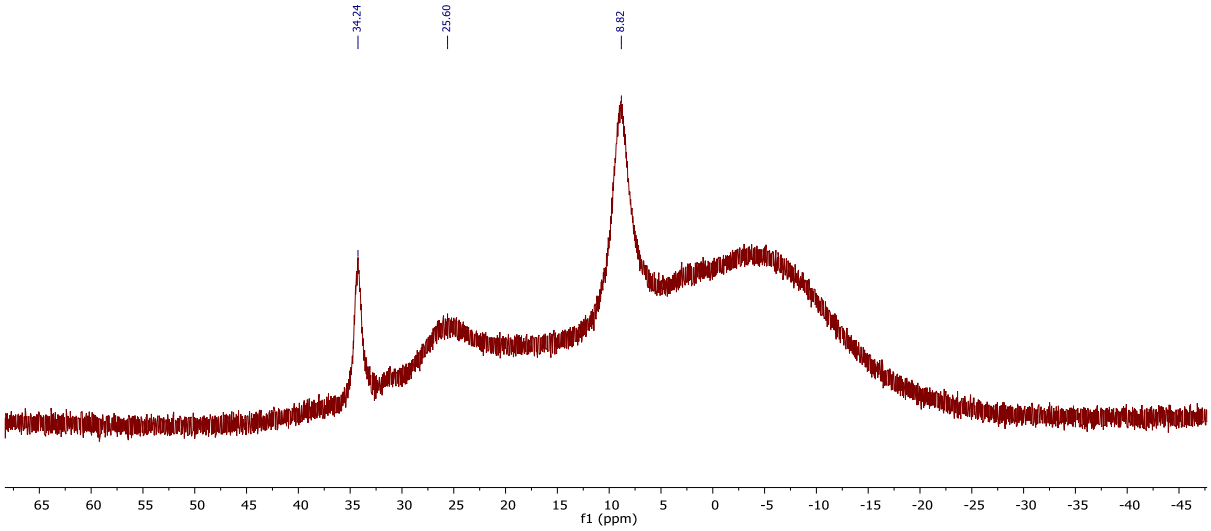

Figure S3: $^{11}B\{^{1}H\}$ NMR spectrum (96 MHz, 298 K, d_8-Tol) of **1**.

Compound 2

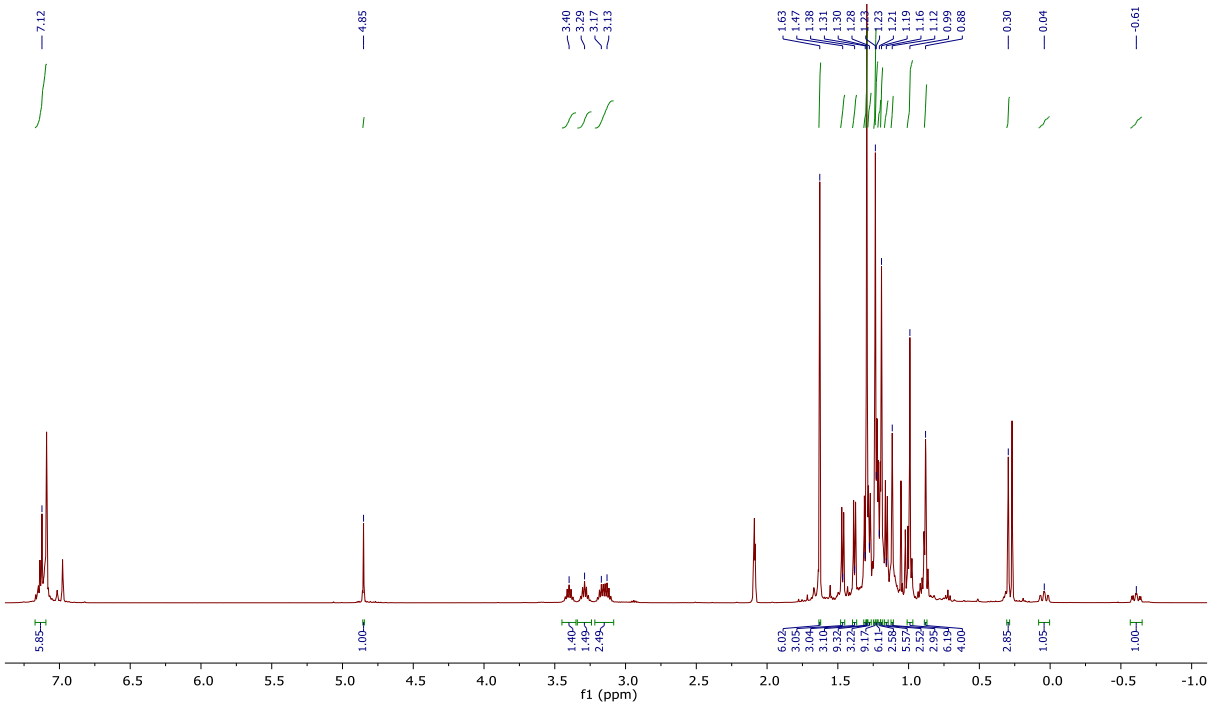

Figure S4: ^{1}H NMR spectrum (500 MHz, 298 K, d_8-Tol) of **2**.

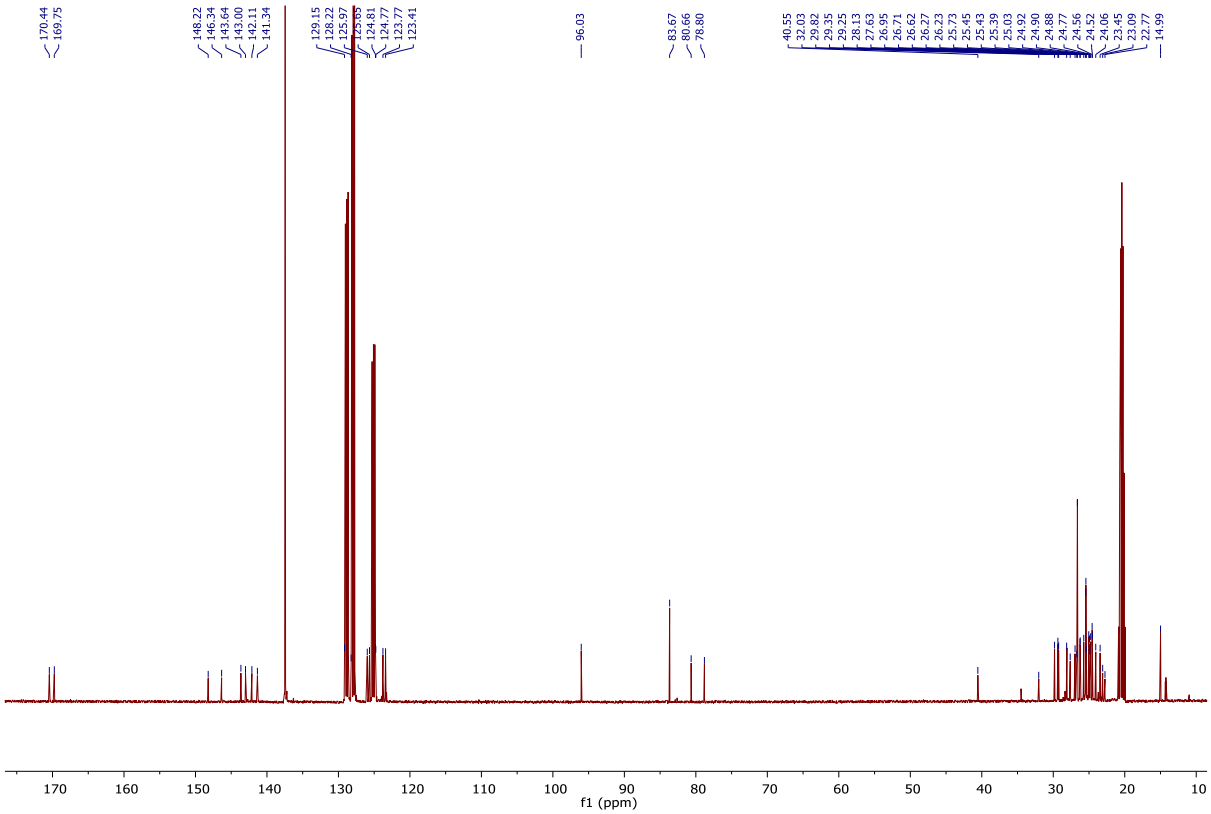

Figure S5: $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, 298 K, d_8-Tol) of **2**.

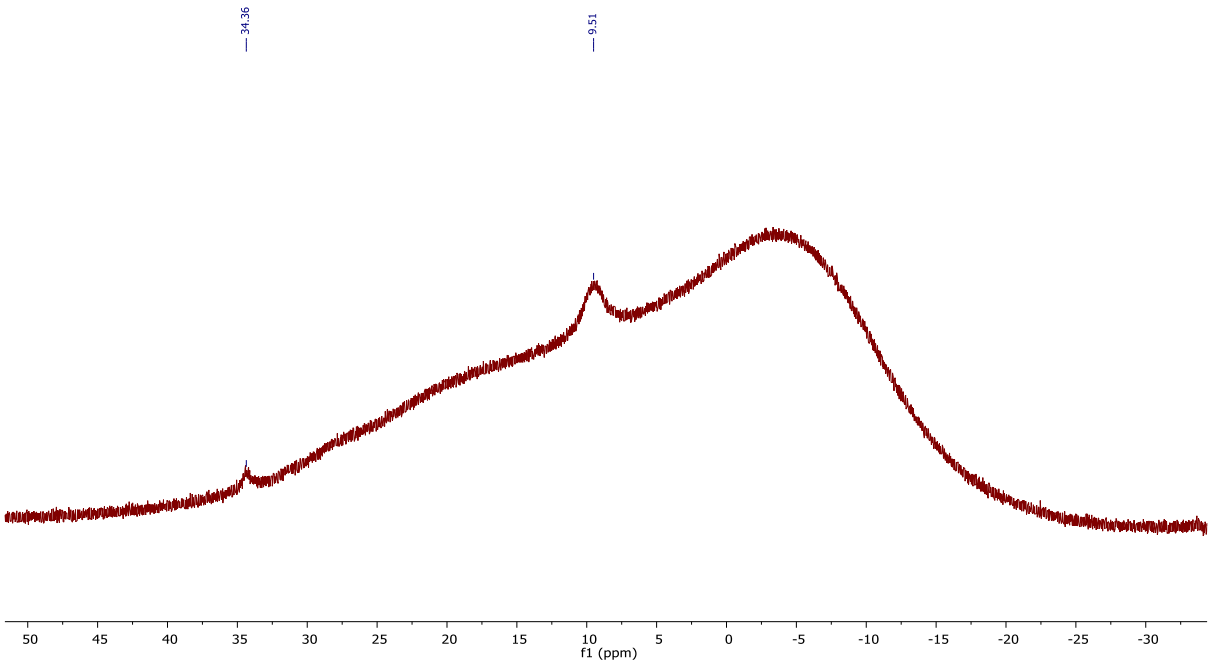

Figure S6: $^{11}B\{^{1}H\}$ NMR spectrum (96 MHz, 298 K, d_8-Tol) of **2**.

Compound 3

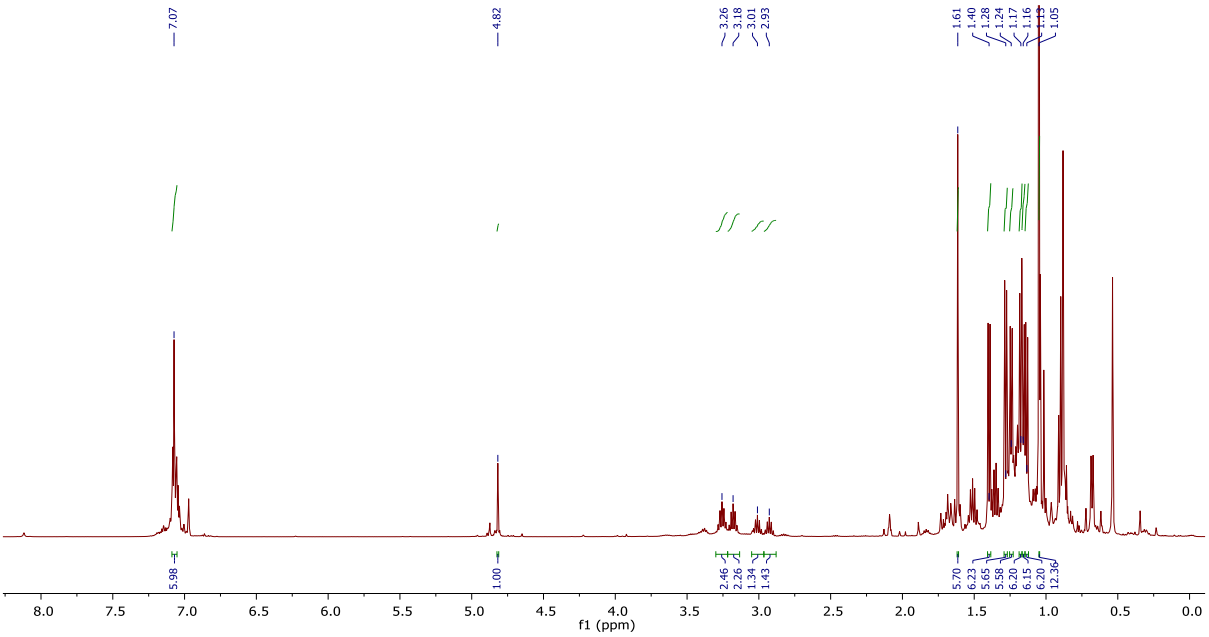

Figure S7: ^{1}H NMR spectrum (500 MHz, 298 K, d_8-Tol) of **3** (with residual *n*-BuBpin).

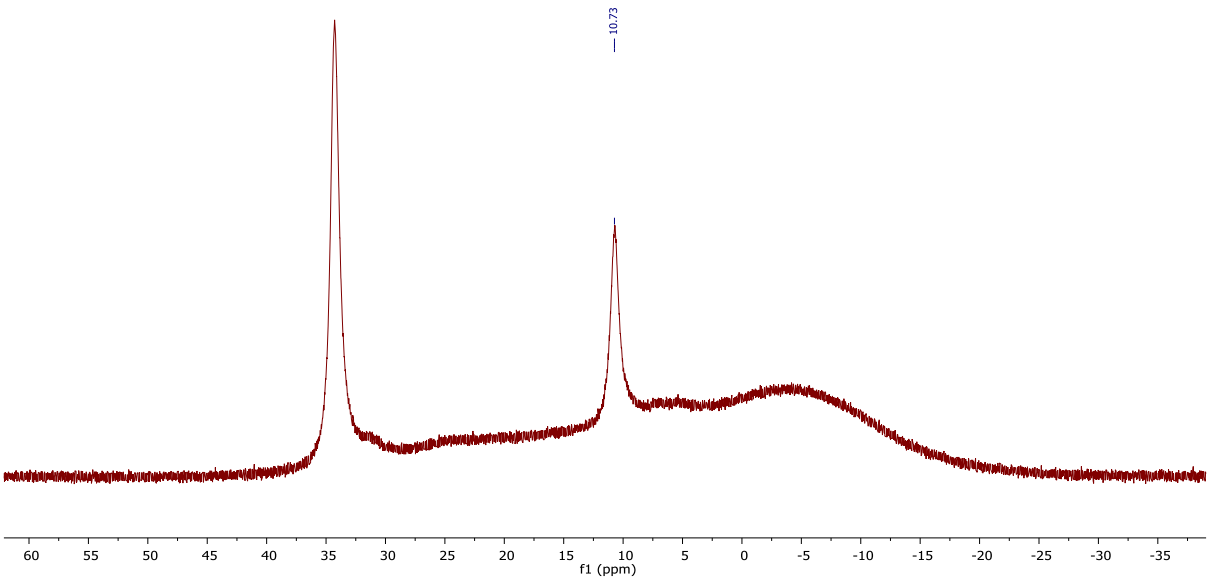

Figure S8: ^{11}B{^{1}H} NMR spectrum (96 MHz, 298 K, d_8-Tol) of **3** (with residual *n*-BuBpin).

Compound 4

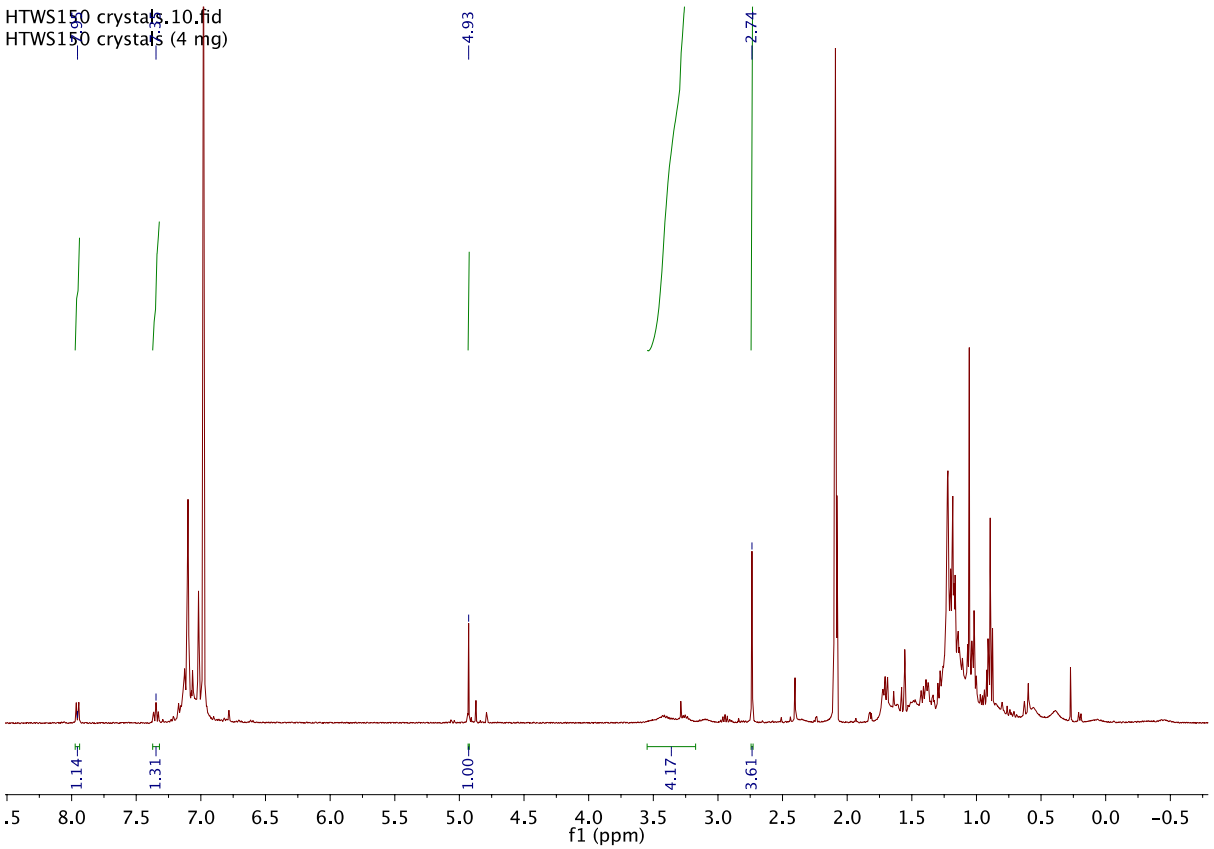

Figure S9: ^{1}H NMR spectrum (400 MHz, 298 K, d_8-Tol) of **4**.

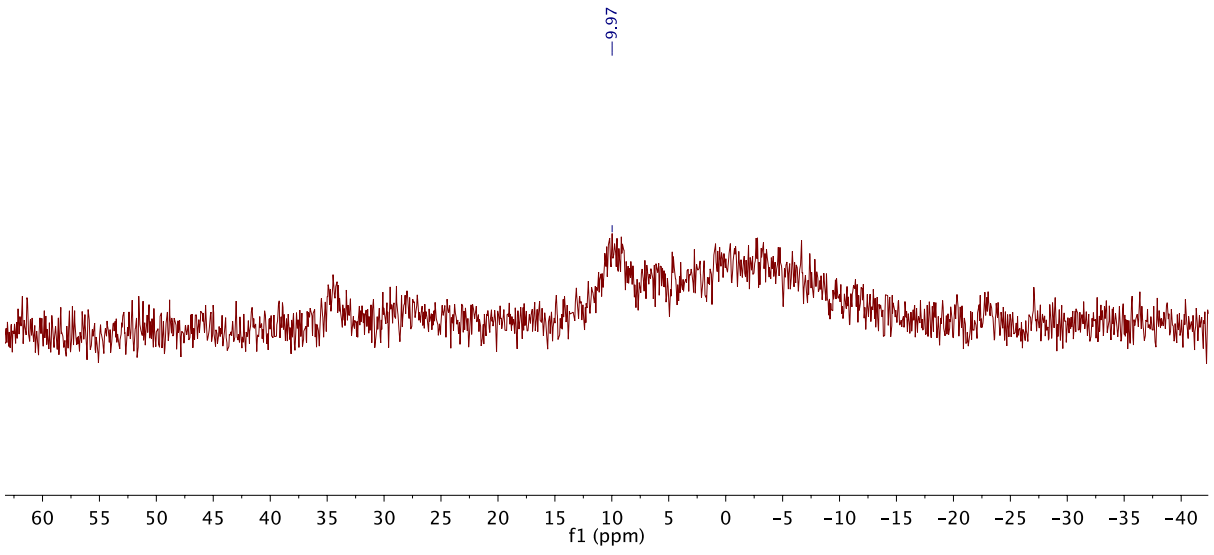

Figure S10: ^{11}B{^{1}H} NMR spectrum (96 MHz, 298 K, d_8-Tol) of **4**.

Compound 5

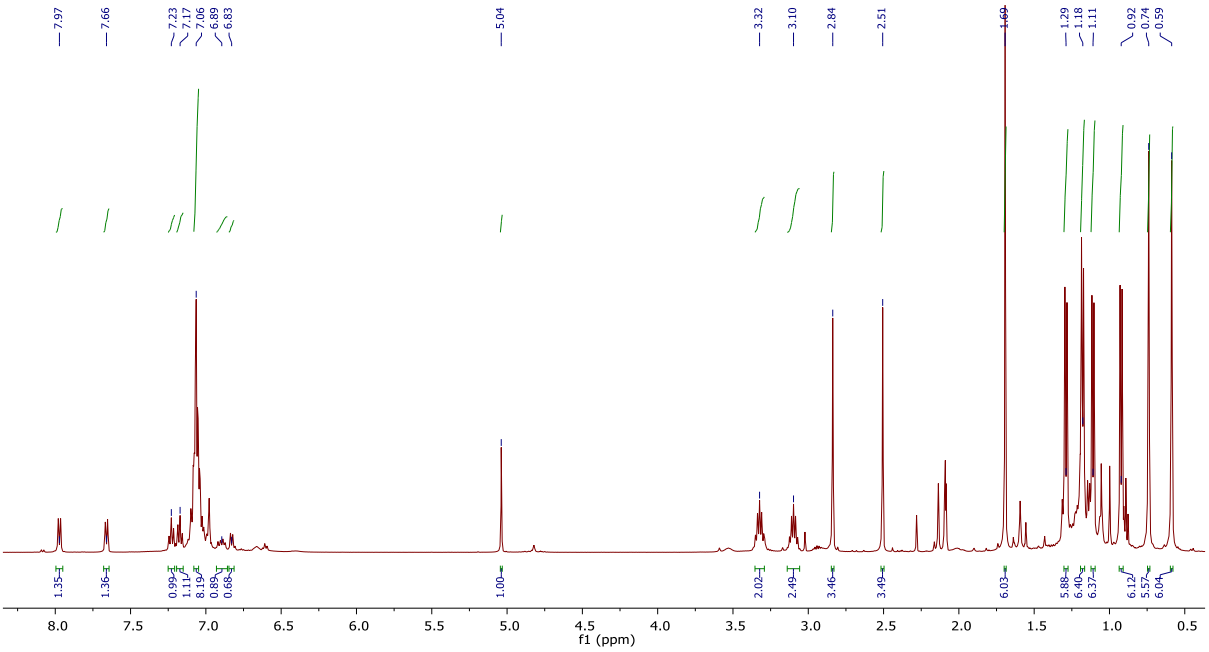

Figure S11: ^{1}H NMR spectrum (500 MHz, 298 K, d_8-Tol) of **5**.

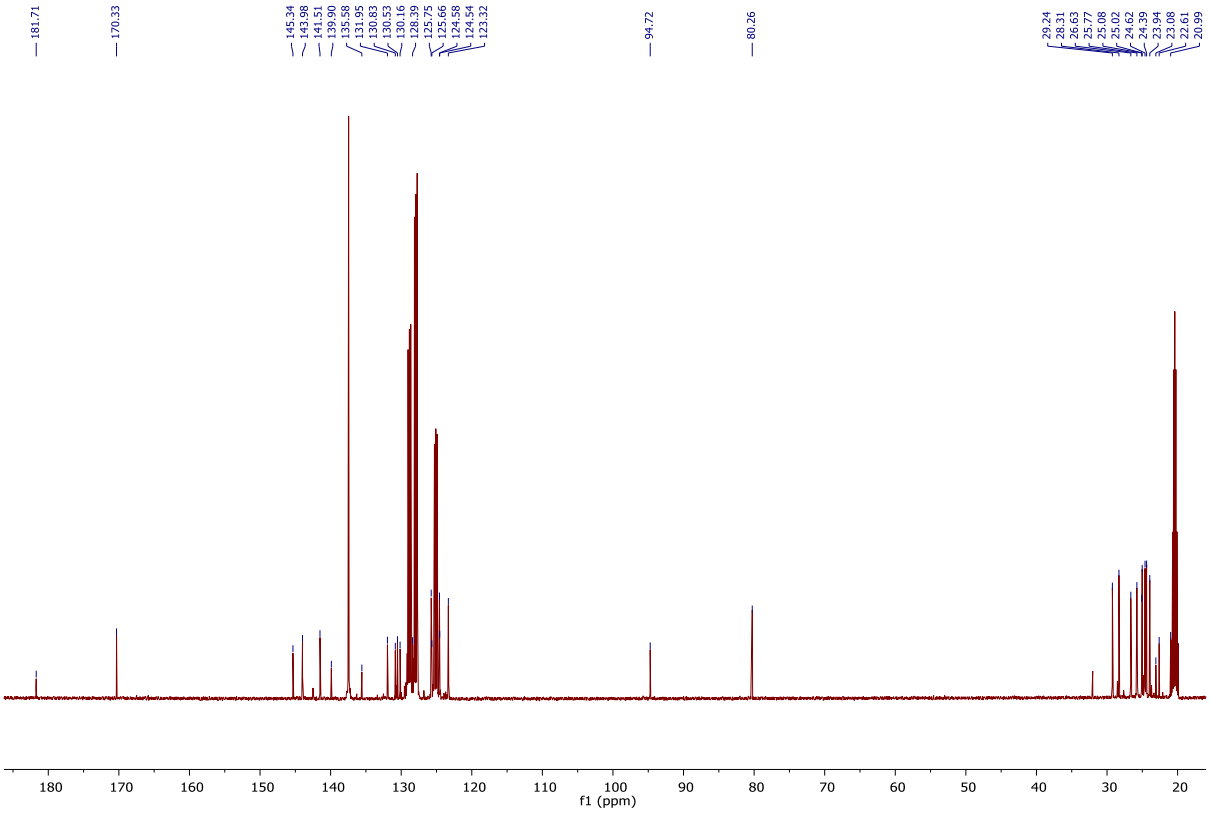

Figure S12: ^{13}C{^{1}H} NMR spectrum (126 MHz, 298 K, d_8-Tol) of **5**.

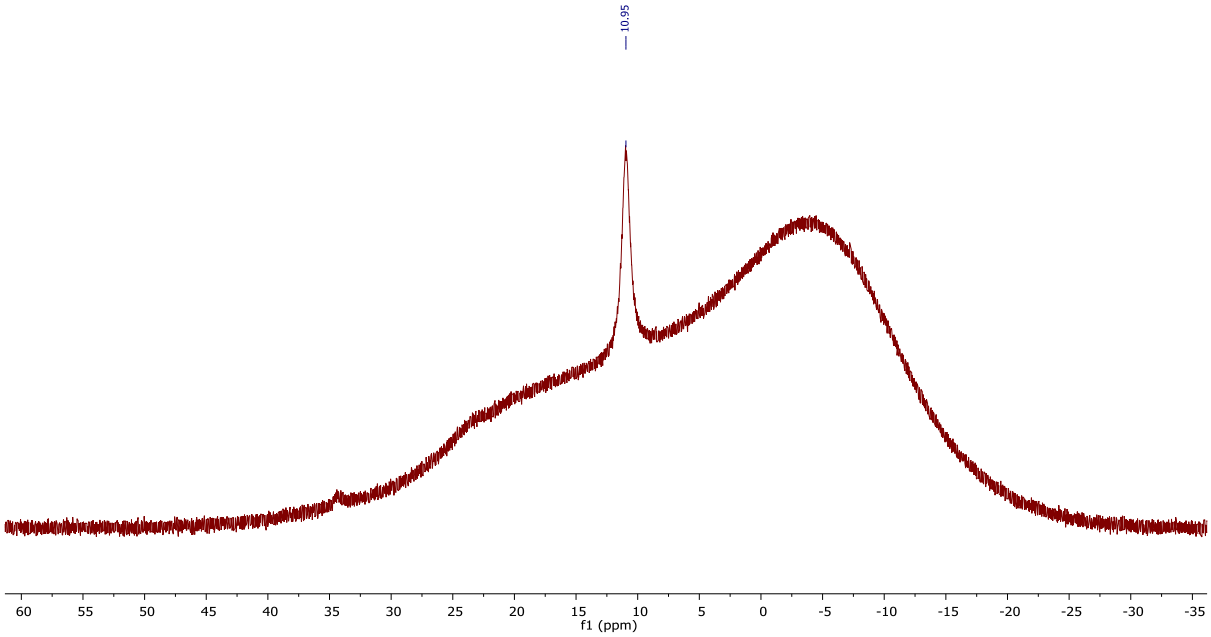

Figure S13: $^{11}B\{^{1}H\}$ NMR spectrum (96 MHz, 298 K, d_8-Tol) of **5**.

Compound 6

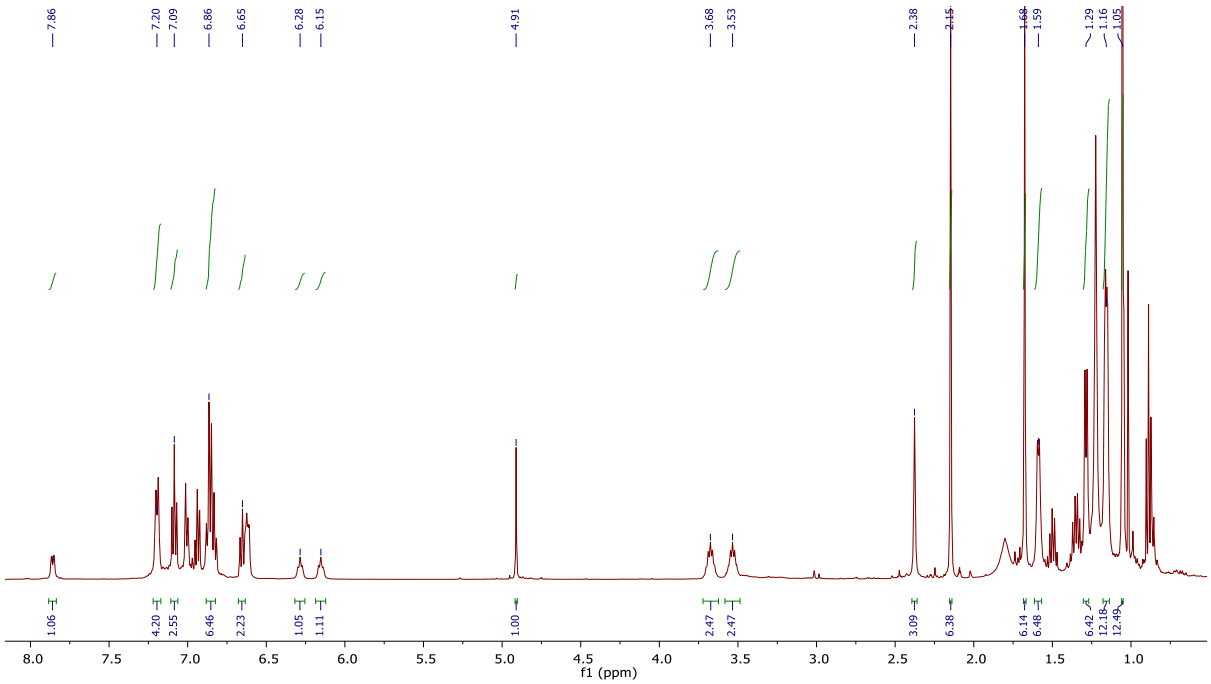

Figure S14: ^{1}H NMR spectrum (500 MHz, 298 K, d_8-Tol) of **6** (and *n*-BuBpin).

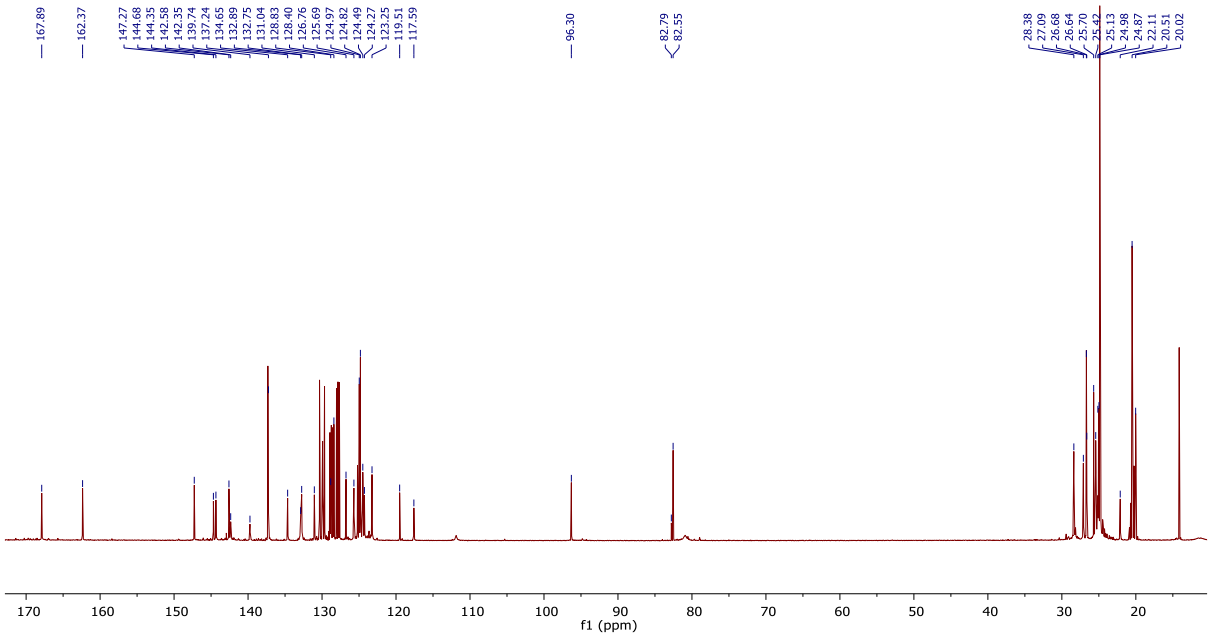

Figure S15: $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, 298 K, d_8-Tol) of **6** (and *n*-BuBpin).

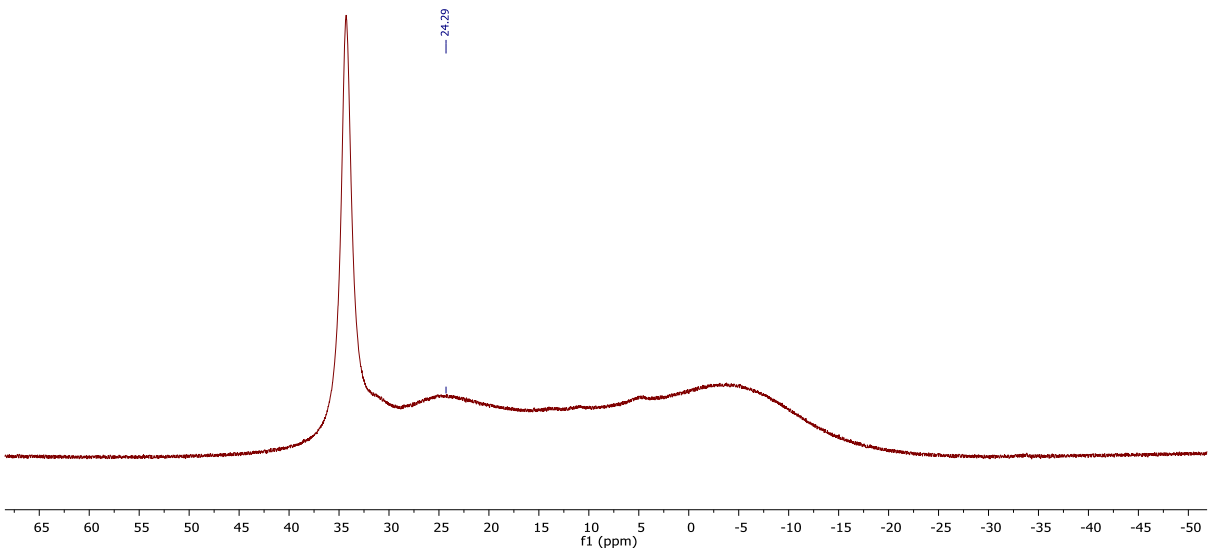

Figure S16: $^{11}B\{^{1}H\}$ NMR spectrum (96 MHz, 298 K, d_8-Tol) of **6** (and *n*-BuBpin).

Compound 7

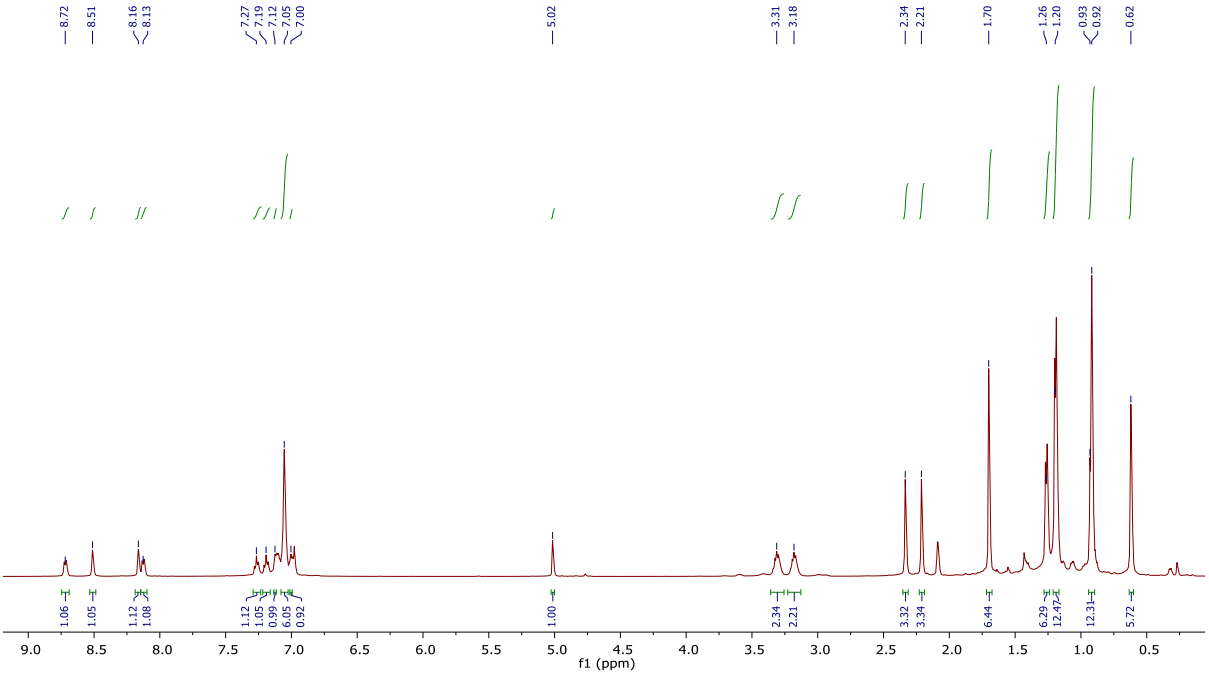

Figure S17:. ^{1}H NMR spectrum (500 MHz, 298 K, d_8-Tol) of **7**.

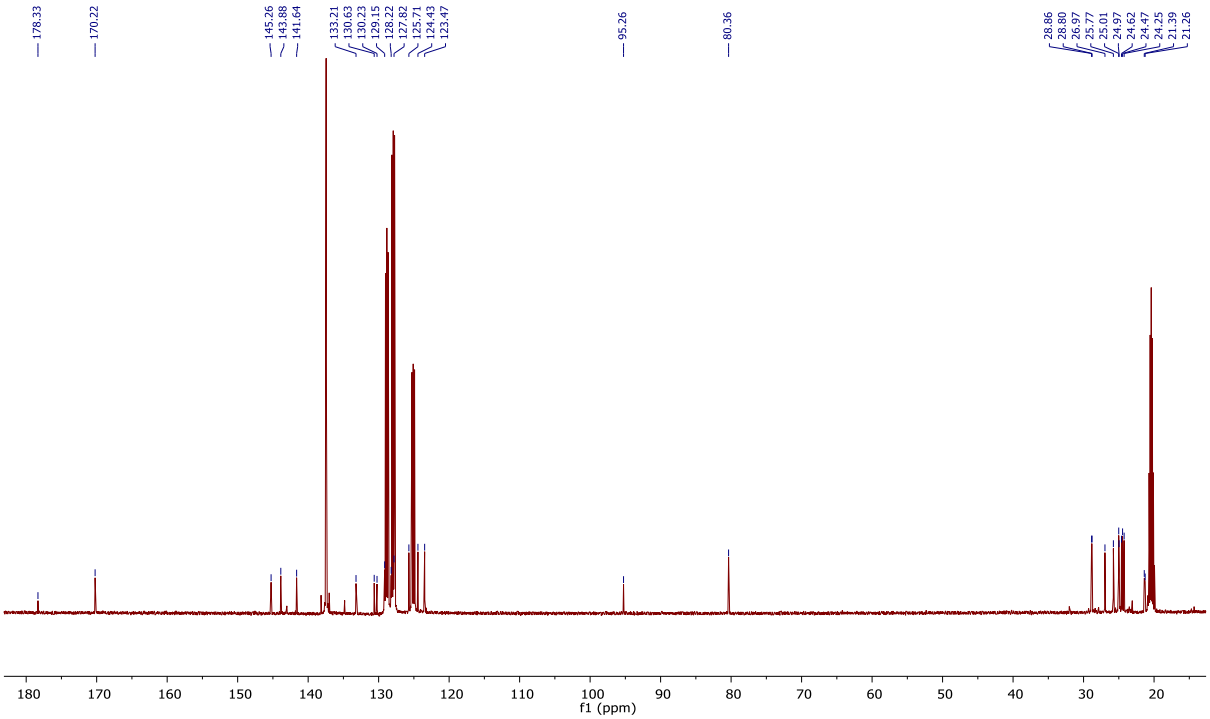

Figure S18:^{13}C{^{1}H} NMR spectrum (126 MHz, 298 K, d_8-Tol) of **7**.

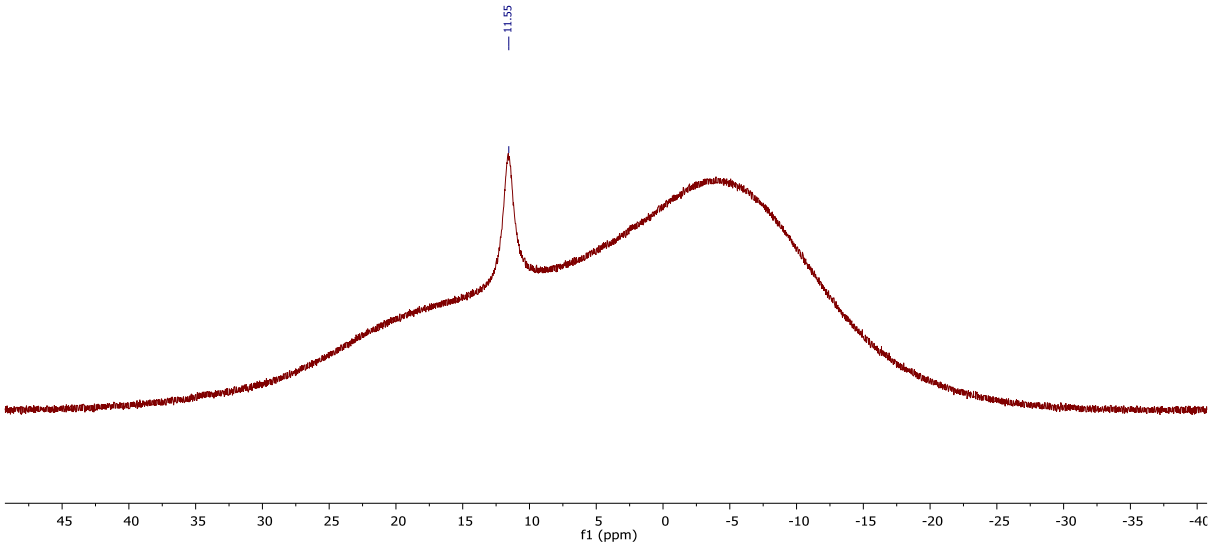

Figure S19: $^{11}B\{^{1}H\}$ NMR spectrum (96 MHz, 298 K, d_8-Tol) of **7**.

X-ray diffraction Analysis

Single crystal X-ray diffraction was performed for compounds **1** – **7** on a Supernova, EosS2 diffractometer using Cu-Kα (λ = 1.54184 Å) radiation at 150(2) K throughout. All structures were refined on F^2 data, *via* Olex2,[3] using ShelXL[4] to implement Least Squares minimisation. The asymmetric unit in **1** contains one molecule of the magnesium complex and one half-occupancy toluene moiety. The latter straddles a crystallographic inversion centre in a disordered manner and this was ultimately modelled using the FragmentDB plugin for Olex2, which is a GUI-specific implementation of the invaluable DSR refinement package by Kratzert et al.[5] Disorder also prevailed in the main feature. In particular, B1, O1, O2, B2, O3, O4 and C30-C41 were modelled to take account of 50:50 disorder, C28 and C29 for 55:45 disorder while C47, C48, and C49 were treated for 75:25 disorder. Chemically equivalent distances were restrained to being similar in disordered regions. Additionally, ADP restraints were also applied to fractional occupancy atoms on merit.

In addition to one molecule of the magnesium complex, the asymmetric unit in **2** contains half of a molecule of pentane. There was some minimal disorder in the main feature in that C36 and C38-C1 were modeled to take account of each being averaged at two sites in the structure in a 75:25 ratio. Chemically comparable distance restraints were included across both components. The central carbon in the solvent is located on a crystallographic 2-fold rotation axis. The associated hydrogen content was located and refined subject to distance and ADP restraints. The terminal pentane carbon was also treated for 50:50 disorder. Clearly, this disorder should have extended to the neighbouring methylene carbon but crystallographic symmetry appears to have averaged this out in a manner that would have made modelling rather artificial.

In the structure of **3**, the asymmetric unit comprises half of a molecule of the magnesium complex and half of a molecule of toluene. In each case, the remainder of the molecular entity is generated *via* a crystallographic inversion centre. This necessarily means that the toluene methyl group is disordered with the hydrogen atom which is *para* to it. The isopropyl methyl group attached to both C15 and C27 were also treated for disorder, in a 55:45 ratio. Bond distance and ADP restraints were included in the model, to assist convergence, in relation to these fractional occupancy methyl carbons.

The asymmetric unit in **4** comprises one molecule of the complex and half of a hexane fragment with an occupancy of 85%. The latter is proximate to a crystallographic inversion centre, which serves to generate the remainder. However, while said solvent is lies predominantly within a structural void and there is evidence of additional proximate residual electron density. This

diffuse electron density was treated the solvent mask algorithm available in Olex2 and is accounted for in the formula presented herein, as 15% of half of a hexane per asymmetric unit. The asymmetric unit in **5** contains 2 regions of solvent in addition to one molecule of the main feature. Both solvent regions contained disordered hexane moieties which were treated with the solvent mask algorithm available in Olex2 in preference to multi-component modelling accompanied by a large number of restraints. Based on the electron density present, a guest solvent allowance of one molecule of hexane per motif has been made in the formula as presented.

The motif in **6** contains two solvent regions in addition to one molecule of the target compound. The first solvent region contains a half of a hexane molecule which was ordered, while the second observed to contain one exceedingly disordered hexane molecule. Efforts to model the latter without over parameterisation were unsuccessful and it was, therefore, treated using the solvent mask algorithm available *via* the Olex2 interface. Allowance for this solvent has been made in the formula unit. Indeed, inspection of the gross structure reveals channels which are essentially packed with this disordered solvent, so it is not at all surprising that it is randomly disordered in the structure.

Table S1: X-ray crystallographic data for compounds **1** – **7**.

Compound	**1**	**2**	**3**	**4**	**5**	**6**	7
Empirical formula	$C_{52.5}H_{85}B_2MgN_3O_4$	$C_{52.5}H_{89}B_2MgN_3O_4$	$C_{46.5}H_{71}BMgN_4O_2$	$C_{56}H_{88}B_2MgN_3O_4$	$C_{65}H_{88}BMgN_5O_2$	$C_{76}H_{102}BMgN_6O_2$	$C_{51}H_{67}BMgN_4O_2$
Formula weight	868.16	872.19	753.19	913.22	1006.52	1166.75	803.20
Crystal system	monoclinic	monoclinic	triclinic	triclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$C2/c$	P-1	P-1	$P2_1/c$	P-1	$P2_1/n$
a/Å	11.6153(1)	36.7820(6)	11.7365(2)	11.2114(2)	18.4280(5)	11.9955(3)	11.3884(1)
b/Å	23.5122(2)	15.5738(2)	12.6432(3)	12.0585(2)	13.0574(3)	14.4571(2)	16.7959(1)
c/Å	19.4842(2)	19.0103(3)	16.8901(4)	21.9245(3)	27.8233(9)	20.6837(4)	24.2385(2)
α/°	90	90	90.694(2)	89.0540(10)	90	82.187(2)	90
β/°	99.398(1)	99.660(1)	108.261(2)	82.7760(10)	106.588(3)	86.300(2)	95.3360(10)
γ/°	90	90	105.976(2)	72.506(2)	90	82.390(2)	90
U/Å^3	5249.74(8)	10735.4(3)	2274.81(9)	2803.79(8)	6416.3(3)	3518.42(12)	4616.21(6)
Z	4	8	2	2	4	2	4
ρ_{calc} g cm^{-3}	1.098	1.079	1.100	1.082	1.042	1.101	1.156
μ/mm^{-1}	0.625	0.612	0.631	0.608	0.563	0.580	0.657
F(000)	1900.0	3832.0	822.0	998.0	2184.0	1266.0	1736.0
Crystal size/mm^3	0.208 × 0.189 × 0.106	0.14 × 0.094 × 0.092	0.315 × 0.216 × 0.166	0.128 × 0.076 × 0.064	0.211 × 0.1 × 0.055	0.257 × 0.136 × 0.113	0.236 × 0.133 × 0.098
2θ range for data collection/°	5.938 to 146.858	6.176 to 146.252	5.542 to 146.186	7.69 to 146.088	7.538 to 146.286	6.22 to 147.242	19.182 to 146.618
Index ranges	−14 ≤ h ≤ 12, −24 ≤ k ≤ 29, −22 ≤ l ≤ 24	−45 ≤ h ≤ 45, −19 ≤ k ≤ 19, −23 ≤ l ≤ 20	−14 ≤ h ≤ 14, −15 ≤ k ≤ 14, −20 ≤ l ≤ 20	−13 ≤ h ≤ 12, −14 ≤ k ≤ 14, −27 ≤ l ≤ 25	−18 ≤ h ≤ 22, −16 ≤ k ≤ 8, −33 ≤ l ≤ 34	−14 ≤ h ≤ 14, −17 ≤ k ≤ 14, −25 ≤ l ≤ 25	−10 ≤ h ≤ 14, −20 ≤ k ≤ 18, −29 ≤ l ≤ 24
Reflections collected	72525	45878	25194	35411	26516	45242	24175
Independent reflections, R_{int}	10505, 0.0406	10690, 0.0473	9038, 0.0240	11153, 0.0369	12194, 0.0426	14095, 0.0423	8994, 0.0293
Data/restraints/parameters	10505/246/780	10690/14/650	9038/28/555	11153/0/616	12194/0/630	14095/0/740	8994/0/548
Goodness-of-fit on F^2	1.038	1.022	1.036	1.028	0.986	1.049	1.042
Final $R1$, wR_2[I>=2σ (I)]	0.0727, 0.1934	0.0509, 0.1311	0.0395, 0.1041	0.0560, 0.1520	0.0621, 0.1665	0.0466, 0.1210	0.0396, 0.1028
Final $R1$, wR_2[all data]	0.0835, 0.2045	0.0652, 0.1417	0.0437, 0.1076	0.0649, 0.1615	0.0887, 0.1854	0.0586, 0.1295	0.0450, 0.1075
Largest diff. peak/hole / e Å^{-3}	0.66/−0.59	0.54/−0.30	0.26/−0.21	0.45/−0.29	0.42/−0.30	0.46/−0.26	0.34/−0.24

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