Supplementary Information for

# Diborane Heterolysis: Breaking and Making B-B bonds at Magnesium

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**General Experimental Procedures:** All manipulations were carried out using standard Schlenk line and glovebox techniques under an inert atmosphere of argon. NMR experiments were conducted in J Young tap NMR tubes made up and sealed in a Glovebox. NMR spectra were collected on a Bruker AV300 spectrometer operating at 300.2 MHz ($^1$H), 75.5 MHz ($^{13}$C), 96.3 MHz ($^{11}$B) or an Agilent ProPulse spectrometer operating at 500 MHz ($^1$H), 126 MHz ($^{13}$C), 160.4 MHz ($^{11}$B). The spectra were referenced relative to residual solvent resonances or an external $BF_3.OEt_2$ standard ($^{11}$B). Solvents (toluene, hexane) were dried by passage through a commercially available (Innovative Technologies) solvent purification system, under nitrogen and stored in ampoules over molecular sieves. $d_8$-Toluene was purchased from Fluorochem Ltd. and Sigma-Aldrich Ltd. and dried over molten potassium before distilling under argon and storing over molecular sieves. Di-*n*-butylmagnesium (1.0 M solution in *n*-heptane) and the diborane reagents were purchased from Sigma-Aldrich Ltd. [HC{(Me)CN(2,6-$^i$Pr$_2$C$_6$H$_3$)}$_2$Mg*n*Bu] (**2**) and [HC{(Me)CN(2,6-$^i$Pr$_2$C$_6$H$_3$)}$_2$MgH]$_2$ (**6**) were synthesised by literature procedures.[1,2] Elemental analysis was carried out Mr Stephen Boyer of London Metropolitan Enterprises.

**[(BDI)MgBpin(H$_2$)BOC(Me)$_2$C(Me)$_2$OMg(BDI)], Compound 7:** In a J Youngs NMR tube, $d_8$-toluene (0.5 mL) was added to a mixture of compound **6** (100 mg, 0.11 mmol) and bis(pinacolato)diboron (28.7 mg, 0.11 mmol). The solution was heated for 5 minutes at 60 ˚C to provide a colourless solution and compound **7** crystallised on cooling to room temperature. The crystals were filtered and dried under reduced pressure to afford compound **7** in 70 % yield (90 mg). Colourless crystals suitable for X-ray diffraction analysis were obtained from a saturated toluene solution of compound **7** at room temperature. $^1$H NMR (500 MHz, toluene) δ 7.17-7.03 (m, 12H, Ar-*H*) 4.92 (s, 1H, NC(CH$_3$)C*H*), 4.76 (s, 1H, NC(CH$_3$)C*H*), 3.54 (br s, 2H, B*H*$_2$), 3.07 (m, 6H, C*H*(CH$_3$)$_2$), 2.94 (hept, 2H, $J_{HH}$ = 7.0 Hz, C*H*(CH$_3$)$_2$), 1.75 (s, 6H, NC(C*H*$_3$)CH), 1.60 (s, 3H, C*H*$_3$), 1.57 (s, 3H, C*H*$_3$), 1.45 (d, 6H, C*H*$_3$), 1.38 (d, 6H, C*H*$_3$), 1.25 (s, 3H, C*H*$_3$), 1.20 (s, 3H, C*H*$_3$), 1.19 (m, 12H, C*H*$_3$), 1.14 (m, 12H, C*H*$_3$), 1.09 (s, 3H, C*H*$_3$), 1.06 (s, 3H, C*H*$_3$), 1.05 (d, 6H, C*H*$_3$), 0.98 (s, 3H, C*H*$_3$), 0.87 (s, 3H, C*H*$_3$), 0.85 (s, 3H, C*H*$_3$), 0.83 (s, 3H, C*H*$_3$), 0.26(s, 3H, C*H*$_3$), 0.21 (s, 3H, C*H*$_3$) ppm. $^{13}$C{$^1$H} NMR (126 MHz, d$_8$-toluene) $\delta$ 170.54 (N$\underline{C}$(CH$_3$)CH), 169.94 (N$\underline{C}$(CH$_3$)CH), 168.19, 144.19, 144.05, 142.42, 142.32, 142.30, 141.09, 125.76 (CH ar), 125.68 (CH ar), 124.35 (CH ar), 124.22 (CH ar), 124.15 (CH ar), 124.05 (CH ar), 124.01 (CH ar), 123.29 (CH ar), 123.09 (CH ar), 123.06 (CH ar), 95.09 (NC(CH$_3$)$\underline{C}$H), 93.49 (NC(CH$_3$)$\underline{C}$H), 88.05 (B(O$\underline{C}$(CH$_3$)$_2$)$_2$), 82.80 (B(O$\underline{C}$(CH$_3$)$_2$)$_2$), 81.80 (B(O$\underline{C}$(CH$_3$)$_2$)$_2$), 73.52 (B(O$\underline{C}$(CH$_3$)$_2$)$_2$), 32.13 (CH$_3$), 28.86 (CH$_3$), 28.13 ($\underline{C}$H(CH$_3$)$_2$), 27.97 ($\underline{C}$H(CH$_3$)$_2$), 27.90 ($\underline{C}$H(CH$_3$)$_2$), 27.76 ($\underline{C}$H(CH$_3$)$_2$), 27.30 (CH$_3$), 27.14 (CH$_3$), 26.61 (CH$_3$), 26.45 (CH$_3$), 26.03 (CH$_3$), 25.93 (CH$_3$), 25.56 (CH$_3$), 25.18 (CH$_3$), 24.96 (CH$_3$), 24.71 (CH$_3$), 24.67 (CH$_3$), 24.65 (CH$_3$), 24.58 (CH$_3$), 24.49 (CH$_3$), 24.44 (CH$_3$), 24.40 (CH$_3$), 24.20 (CH$_3$), 24.18 (CH$_3$), 23.16 (CH$_3$)ppm. $^{11}$B{$^1$H} (160 MHz, d$_8$-toluene) $\delta$ –16.68 ppm. Despite multiple attempts an accurate microanalysis could not be obtained for this compound.

**[(BDI)Mg(hex)B-B(hex)(*n*-Bu)], Compound 8:** In a J Youngs NMR tube, d$_8$-toluene (0.5 mL) was added to a mixture of compound **2** (50 mg, 0.1 mmol) and bis(hexyleneglycolato)diboron (25.4 mg, 0.1 mmol). After 2 hours at room temperature, the NMR spectra demonstrated the formation of [(BDI)Mg(hex)B-B(hex)(*n*-Bu)], compound **8**. The solvent was removed under reduced pressure to afford compound **8** as a colourless solid in 93% yield (70mg). Colourless crystals suitable for X-ray diffraction analysis were obtained from a saturated hexane solution at –35°C. $^1$H NMR (500 MHz, d$_8$-toluene) $\delta$ 7.11 (m, 6H, CH ar), 4.95 (m, 1H, NC(CH$_3$)C*H*), 4.10-3.93 (m, 2H, BOC*H*(CH$_3$)CH$_2$), 3.27-3.15 (m, 4H, C*H*(CH$_3$)$_2$), 1.66,-1.61 (m, 9H, CH$_3$), 1.46-1.34 (m, 8H, CH$_3$ and CH$_2$), 1.30-1.14 (m, 24H, CH$_3$ and CH$_2$), 1.14-1.00 (m, 9H, CH$_3$ and CH$_2$), 0.98- 0.73 (m, 3H, CH$_3$), 0.73-0.52 (m, 5H, CH$_3$ and CH$_2$), 0.52- -0.22 (m, 3H, CH$_3$) ppm. $^{13}$C{$^1$H} NMR (126 MHz, d$_8$-toluene) $\delta$ 169.92 (N$\underline{C}$(CH$_3$)CH), 169.77 (N$\underline{C}$(CH$_3$)CH), 169.66 (N$\underline{C}$(CH$_3$)CH), 169.47 (N$\underline{C}$(CH$_3$)CH), 169.38 (N$\underline{C}$(CH$_3$)CH), 169.29 (N$\underline{C}$(CH$_3$)CH), 169.13 (N$\underline{C}$(CH$_3$)CH), 169.05 (N$\underline{C}$(CH$_3$)CH), 145.41 (C$^{IV}$ Ar), 145.36 (C$^{IV}$ Ar), 145.12 (C$^{IV}$ Ar), 145.05 (C$^{IV}$ Ar), 142.41 (C$^{IV}$ Ar), 142.31 (C$^{IV}$ Ar), 142.15 (C$^{IV}$ Ar), 142.08 (C$^{IV}$ Ar), 141.97 (C$^{IV}$ Ar), 141.84 (C$^{IV}$ Ar), 141.74 (C$^{IV}$ Ar), 141.66 (C$^{IV}$ Ar), 141.65 (C$^{IV}$ Ar), 141.60 (C$^{IV}$ Ar), 125.51 (CH Ar), 125.45 (CH Ar), 125.43 (CH Ar), 125.14 (CH Ar), 124.99 (CH Ar), 124.89 (CH Ar), 124.70 (CH Ar), 124.51 (CH Ar), 124.24 (CH Ar), 124.09 (CH Ar), 123.95 (CH Ar), 123.93 (CH Ar), 123.88 (CH Ar), 123.85 (CH Ar), 123.79 (CH Ar), 123.76 (CH Ar), 123.71 (CH Ar), 123.65 (CH Ar), 123.61 (CH Ar), 123.55 (CH Ar), 123.52 (CH Ar), 96.90 (NC(CH$_3$)$\underline{C}$H), 96.65 (NC(CH$_3$)$\underline{C}$H), 96.27 (NC(CH$_3$)$\underline{C}$H), 96.01 (NC(CH$_3$)$\underline{C}$H), 69.61 (BO$\underline{C}$(CH$_3$)$_2$CH$_2$), 68.76 (BO$\underline{C}$(CH$_3$)$_2$CH$_2$), 68.53 (BO$\underline{C}$(CH$_3$)$_2$CH$_2$), 68.48 (BO$\underline{C}$(CH$_3$)$_2$CH$_2$), 68.31 (BO$\underline{C}$H(CH$_3$)CH$_2$), 67.24 (BO$\underline{C}$H(CH$_3$)CH$_2$), 66.85 (BO$\underline{C}$H(CH$_3$)CH$_2$), 66.73

($BO\underline{C}H(CH_3)CH_2$), 66.61($BO\underline{C}H(CH_3)CH_2$), 65.86 ($BO\underline{C}H(CH_3)CH_2$), 65.79 ($BO\underline{C}H(CH_3)CH_2$), 65.70 ($BO\underline{C}H(CH_3)CH_2$), 65.61 ($BO\underline{C}H(CH_3)CH_2$), 65.01 ($BO\underline{C}H(CH_3)CH_2$), 64.81 ($BO\underline{C}H(CH_3)CH_2$), 63.97 ($BO\underline{C}H(CH_3)CH_2$), 61.43 ($BO\underline{C}H(CH_3)CH_2$), 49.39 ($CH_3$), 49.21 ($CH_3$), 45.95($CH_3$ and $CH_2$), 45.76 ($CH_3$ and $CH_2$), 45.67 ($CH_3$ and $CH_2$), 45.55 ($CH_3$ and $CH_2$), 44.60 ($CH_3$ and $CH_2$), 44.53 ($CH_3$ and $CH_2$), 34.81 ($CH_3$), 34.59 ($CH_3$), 33.63 ($CH_3$), 33.59 ($CH_3$), 31.63 ($CH_3$), 31.36 ($CH_3$), 31.26 ($CH_3$), 31.22 ($CH_3$), 31.02 ($CH_3$), 30.98 ($CH_3$), 30.93 ($CH_3$), 29.47 ($CH_3$), 29.28 ($CH_3$), 29.06 ($CH_3$), 29.03 ($CH_3$), 28.63 ($CH_3$), 28.59 ($CH_3$), 28.52 ($CH_3$), 28.34 ($CH_3$), 28.27 ($CH_3$), 28.25 ($CH_3$), 28.22 ($CH_3$), 27.91 ($CH_3$), 27.82 ($CH_3$), 27.80 ($CH_3$), 27.72 ($CH_3$), 27.31 ($CH_3$), 27.15 ($CH_3$), 26.67 ($CH_3$), 26.04 ($CH_3$), 25.71 ($CH_3$), 25.54 ($CH_3$), 25.47 ($CH_3$), 25.32 ($CH_3$), 25.28 ($CH_3$), 25.17 ($CH_3$), 25.09 ($CH_3$), 25.02 ($CH_3$), 24.95 ($CH_3$), 24.85 ($CH_3$), 24.83 ($CH_3$), 24.82 ($CH_3$), 24.77 ($CH_3$), 24.72 ($CH_3$), 24.66 ($CH_3$), 24.65 ($CH_3$), 24.55 ($CH_3$), 24.51 ($CH_3$), 24.48 ($CH_3$), 24.42 ($CH_3$), 24.33 ($CH_3$), 24.28 ($CH_3$), 24.21 ($CH_3$), 24.17 ($CH_3$), 24.05 ($CH_3$), 24.00 ($CH_3$), 23.91 ($CH_3$), 23.01 ($CH_3$), 22.67 ($CH_3$), 22.46 ($CH_3$), 22.38 ($CH_3$), 22.28 ($CH_3$), 22.09 ($CH_3$), 22.05 ($CH_3$) ppm. $^{11}B\{^1H\}$ NMR (160 MHz, toluene) δ 30.50, 3.96 ppm. Elemental analysis: Found C, 71.67; H, 9.80; N, 3.36 %. $C_{45}H_{74}B_2MgN_2O_4$ requires: C, 71.78; H, 9.91; N, 3.72 %.

**[(BDI)Mg{B(hex)}DMAP], Compound 9:** In a J Youngs NMR tube, $d_8$-toluene (0.5 mL) was added to a mixture of compound **2** (200 mg, 0.4 mmol) and bis(hexyleneglycolato)diboron (101 mg, 0.4 mmol). After 2 hours at room temperature, one equivalent of 2-dimethylaminopyridine (DMAP) (48.95 mg, 0.4 mmol) was added. After a further 2 hours at 40˚C, the NMR spectra revealed the formation of compound **9** and *n*-BuB(hex). Colourless crystals suitable for X-ray diffractions studies were obtained from a saturated hexane solution of compound **9** at –35˚C. $^1H$ NMR (500 MHz, toluene) δ 8.75(s, 1.4H, DMAP), 8.33 (s, 0.6H, DMAP), 7.23 (m, 2H, CH ar), 7.08 (m, 2H, CH ar), 6.99 (m, 2H, CH ar), 6.06 (s, 2H , DMAP), 4.96 (s, 1H, $NC(CH_3)C\mathit{H}$) , 3.88 (Bu-Bhex), 3.71 (m, 3H, $C\mathit{H}(CH_3)_2$ + $BOC\mathit{H}(CH_3)CH_2$), 2.98(m, 2H, $C\mathit{H}(CH_3)_2$), 2.24 (s, 6H, $N(CH_3)_2$ DMAP), 1.80 (s, 6H, $NC(C\mathit{H}_3)CH$), 1.67(m, 6H, $CH_3$), 1.65 (m, 6H, $CH_3$), 1.56 (m, 2H, $CH_2$), 1.41 (Bu-Bhex), 1.12 (Bu-Bhex), 1.04( (m, 15H, $CH_3$), 0.96 (m, Bu-Bhex), 0.91 (m, 3H, $CH_3$), 0.60 (m, 6H, $CH_3$). The extreme air sensitivity of this compound precluded the acquisition of an elemental analysis.

**[(BDI)Mg{(hex)BB(hex)Bpin}], Compound 10:** In a J Youngs NMR tube, $d_8$-toluene (0.5 mL) was added to a mixture of compound **2** (200 mg, 0.4 mmol) and bis(pinacolato)diboron (107 mg, 0.4 mmol). After 2 hours at room temperature, one equivalent of bis(hexyleneglycolato)diboron (101 mg, 0.4 mmol) was added. After 2 hours at room temperature, analysis by NMR spectroscopy revealed the formation of the complex [(BDI)Mg {(hex)BB(hex)Bpin}]. The solvent was removed under reduced pressure and the resultant solid was washed with hexane to afford compound **10** as a colourless solid in 69% yield (226.6 mg). Colourless crystals suitable for X-ray diffraction analysis were obtained from a saturated hexane solution at -35˚C. $^{1}$H NMR (500 MHz, d$_8$-toluene) δ 7.20 (m, 2H, CH Ar), 7.11 (m, 4H, CH Ar), 4.95 (m, 1H, NC(CH$_3$)C*H*), 4.11-3.90 (m, 2H, BOC*H*(CH$_3$)CH$_2$), 3.36-3.20 (m, 4H, C*H*(CH$_3$)$_2$), 1.70-1.51 (m, 12H, CH$_3$), 1.42-1.36 (m, 4H, BOCH(CH$_3$)C*H*$_2$), 1.32-1.10 (m, 33H, CH$_3$), 1.07-1.03 (m, 3H, CH$_3$), 0.92-0.90 (m, 3H, CH$_3$), 0.73-0.60 (m, 6H, CH$_3$), 0.50-0.36 (m, 3H, CH$_3$) ppm. $^{13}$C{$^{1}$H} NMR (126 MHz, d$_8$-toluene) δ 169.85 (N$\underline{C}$(CH$_3$)CH), 169.68 (N$\underline{C}$(CH$_3$)CH), 169.47 (N$\underline{C}$(CH$_3$)CH), 169.30 (N$\underline{C}$(CH$_3$)CH), 169.13 (N$\underline{C}$(CH$_3$)CH), 168.65 (N$\underline{C}$(CH$_3$)CH), 145.44 (C$^{IV}$ Ar), 145.34 (C$^{IV}$ Ar), 145.29 (C$^{IV}$ Ar), 145.23 (C$^{IV}$ Ar), 143.00 (C$^{IV}$ Ar), 142.78 (C$^{IV}$ Ar), 142.61 (C$^{IV}$ Ar), 142.57 (C$^{IV}$ Ar), 142.28 (C$^{IV}$ Ar), 142.23 (C$^{IV}$ Ar), 142.09 (C$^{IV}$ Ar), 141.86 (C$^{IV}$ Ar), 141.81 (C$^{IV}$ Ar), 141.63 (C$^{IV}$ Ar), 141.43 (C$^{IV}$ Ar), 141.38 (C$^{IV}$ Ar) , 141.24 (C$^{IV}$ Ar), 125.47 (CH Ar), 125.41 (CH Ar), 125.27 (CH Ar), 125.15 (CH Ar), 125.00 (CH Ar), 124.42 (CH Ar), 124.09 (CH Ar), 123.83 (CH Ar), 123.80 (CH Ar), 123.72 (CH Ar), 123.67 (CH Ar), 123.55 (CH Ar), 123.48 (CH Ar), 123.09 (CH Ar), 96.95 (NC(CH$_3$)$\underline{C}$H), 96.83 (NC(CH$_3$)$\underline{C}$H), 96.42 (NC(CH$_3$)$\underline{C}$H), 96.38 (NC(CH$_3$)$\underline{C}$H), 80.15 (B(O$\underline{C}$(CH$_3$)$_2$)$_2$), 80.11 (B(O$\underline{C}$(CH$_3$)$_2$)$_2$), 80.06 (B(O$\underline{C}$(CH$_3$)$_2$)$_2$), 79.92 (B(O$\underline{C}$(CH$_3$)$_2$)$_2$), 79.90 (B(O$\underline{C}$(CH$_3$)$_2$)$_2$), 69.15 (BO$\underline{C}$H(CH$_3$)CH$_2$), 68.76 (BO$\underline{C}$H(CH$_3$)CH$_2$), 68.50 (BO$\underline{C}$H(CH$_3$)CH$_2$), 68.21 (BO$\underline{C}$H(CH$_3$)CH$_2$), 67.91 (BO$\underline{C}$H(CH$_3$)CH$_2$), 66.87 (BO$\underline{C}$H(CH$_3$)CH$_2$), 66.15 (BO$\underline{C}$H(CH$_3$)CH$_2$), 66.01 (BO$\underline{C}$H(CH$_3$)CH$_2$), 49.71 (CH$_3$), 49.66 (CH$_3$), 46.23 (CH$_3$), 45.77 (CH$_3$), 43.63 (CH$_3$), 34.06 (CH$_3$), 33.52 (CH$_3$), 31.40 (CH$_3$), 30.93 (CH$_3$ and $\underline{C}$H(CH$_3$)$_2$), 30.89 (CH$_3$ and $\underline{C}$H(CH$_3$)$_2$), 30.74 (CH$_3$ and $\underline{C}$H(CH$_3$)$_2$), 30.60 (CH$_3$ and $\underline{C}$H(CH$_3$)$_2$), 30.25 (CH$_3$ and $\underline{C}$H(CH$_3$)$_2$), 28.82 (CH$_3$ and $\underline{C}$H(CH$_3$)$_2$), 28.71 (CH$_3$ and $\underline{C}$H(CH$_3$)$_2$), 28.62 (CH$_3$ and $\underline{C}$H(CH$_3$)$_2$), 28.52 (CH$_3$ and $\underline{C}$H(CH$_3$)$_2$), 28.48 (CH$_3$ and $\underline{C}$H(CH$_3$)$_2$), 28.38 (CH$_3$ and $\underline{C}$H(CH$_3$)$_2$), 28.34 (CH$_3$ and $\underline{C}$H(CH$_3$)$_2$), 28.27 (CH$_3$ and $\underline{C}$H(CH$_3$)$_2$), 28.23(CH$_3$ and $\underline{C}$H(CH$_3$)$_2$), 28.15 (CH$_3$ and $\underline{C}$H(CH$_3$)$_2$), 28.12 (CH$_3$ and $\underline{C}$H(CH$_3$)$_2$), 28.02 (CH$_3$ and $\underline{C}$H(CH$_3$)$_2$), 27.98 (CH$_3$ and $\underline{C}$H(CH$_3$)$_2$), 27.90 (CH$_3$ and $\underline{C}$H(CH$_3$)$_2$), 27.71 (CH$_3$ and $\underline{C}$H(CH$_3$)$_2$), 25.72 (CH$_3$), 25.52 (CH$_3$), 25.37 (CH$_3$), 25.28 (CH$_3$), 25.24 (CH$_3$), 25.11 (CH$_3$), 25.09 (CH$_3$), 25.02 (CH$_3$), 24.94 (CH$_3$), 24.82 (CH$_3$), 24.80 (CH$_3$), 24.76 (CH$_3$), 24.73 (CH$_3$), 24.51 (CH$_3$), 24.48 (CH$_3$), 24.45 (CH$_3$), 24.43 (CH$_3$), 24.35 (CH$_3$), 24.23 (CH$_3$), 24.19 (CH$_3$), 24.14 (CH$_3$), 24.10 (CH$_3$), 23.95 (CH$_3$), 23.93 (CH$_3$), 23.16 (CH$_3$), 22.99 (CH$_3$), 22.70 (CH$_3$), 22.32 (CH$_3$), 22.13 (CH$_3$) ppm. $^{11}$B{$^{1}$H} NMR (160 MHz, d$_8$-toluene) δ 34.38, 30.41, 1.68 ppm. Elemental analysis: Found C, 68.75; H, 9.58; N, 3.52 %. $C_{47}H_{77}B_3MgN_2O_6$ requires: C, 68.60; H, 9.43; N, 3.40 %.

**[(BDI)Mg{(neo)BB(neo)Bpin}], Compound 11:** In a J Youngs NMR tube, d$_8$-toluene (0.5 mL) was added to a mixture of compound **2** (100 mg, 0.2 mmol) and bis(pinacolato)diboron (50.8 mg, 0.2 mmol). After 2 hours at room temperature, one equivalent of bis(neopentylglycolato)diboron (50.8 mg, 0.2 mmol) was added. After 2 hours at 40˚C, analysis by NMR spectroscopy indicted the formation of [(BDI)Mg{(neo)BB(neo)Bpin}]. The solvent was removed under reduced pressure and the resultant solid was rcrystallised from hexane to afford compound **11** as a colourless solid (95 mg, 60%). Colourless crystals suitable for X-ray diffraction analysis were obtained from a saturated hexane solution at room temeprature. $^1$H NMR (500 MHz, d$_8$-toluene) δ 7.14 (m, 6H, CH Ar), 4.79 (m, 1H, NC(CH$_3$)C*H*), 3.70-3.64 (m, 4H, BOC*H*$_2$C(CH$_3$)$_2$), 3.32 (m, 6H, BOCH$_2$C(C*H*$_3$)$_2$ + C*H*(CH$_3$)$_2$), 3.10 (m, 2H, C*H*(CH$_3$)$_2$), 1.63 (s, 6H, CH$_3$), 1.54 (d, 6H, CH$_3$), 1.37 (d, 6H, CH$_3$), 1.29 (d, 6H, CH$_3$), 1.18 (d, 6H, CH$_3$), 1.05 (s, 12H, B(OC(C*H*$_3$)$_2$)$_2$, 0.74 (s, 6H , BOCH$_2$C(C*H*$_3$)$_2$), 0.44 (s, 3H, BOCH$_2$C(C*H*$_3$)$_2$), 0.40 (s, 3H, BOCH$_2$C(C*H*$_3$)$_2$) ppm. $^{13}$C{$^1$H} NMR (126 MHz, d$_8$-toluene) δ 170.06 (N$\underline{C}$(CH$_3$)CH), 144.69, 142.47, 141.52, 125.46 (CH Ar), 124.03 (CH Ar), 123.47 (CH Ar), 94.35 (NC(CH$_3$)$\underline{C}$H), 80.19 (B(O$\underline{C}$(CH$_3$)$_2$)$_2$), 76.48 (BO$\underline{C}$H$_2$C(CH$_3$)$_2$), 72.71 (BO$\underline{C}$H$_2$C(CH$_3$)$_2$), 68.80 (BO$\underline{C}$H$_2$C(CH$_3$)$_2$), 32.78 (BOCH$_2\underline{C}$(CH$_3$)$_2$), 31.01 (BOCH$_2\underline{C}$(CH$_3$)$_2$), 28.57 ($\underline{C}$H(CH$_3$)$_2$), 27.90 ($\underline{C}$H(CH$_3$)$_2$), 25.27 (CH($\underline{C}$H$_3$)$_2$), 24.98 (B(OC($\underline{C}$H$_3$)$_2$), 24.57 (CH($\underline{C}$H$_3$)$_2$), 24.11 (CH($\underline{C}$H$_3$)$_2$), 24.03 (NC($\underline{C}$H$_3$)CH), 22.52 (BOCH$_2$C($\underline{C}$H$_3$)$_2$), 22.44 (BOCH$_2$C($\underline{C}$H$_3$)$_2$), 22.38 (BOCH$_2$C($\underline{C}$H$_3$)$_2$) ppm. $^{11}$B{$^1$H} NMR (160 MHz, toluene) δ 36.51, 4.68 ppm. Elemental analysis: Found C, 67.98; H, 9.35; N, 3.61 %. $C_{45}H_{73}B_3MgN_2O_6$ requires: C, 68.00; H, 9.26; N 3.52 %.

**[(BDI)Mg{pinBB(hex)Bpin}], Compound 12:** In a J Youngs NMR tube, d$_8$-toluene (0.5 mL) was added to a mixture of compound **2** (100 mg, 0.2 mmol) and bis(hexyleneglycolato)diboron (50.1 mg, 0.2 mmol). After 2 hours at room temperature, one equivalent of bis(pinacolato)diboron (50.8 mg, 0.2 mmol) was added. After 2 hours at 40˚C (or 3days at RT), analysis by NMR spectroscopy demonstrated the formation of [(BDI)Mg{pinBB(hex)Bpin}] (**12**). The solvent was removed under reduced pressure and the resultant solid was washed with hexane to afford **12** as a colourless compound in 67% yield (111 mg). Colourless crystals suitable for X-ray diffraction analysis were obtained from a saturated hexane solution at –35˚C. $^1$H NMR (500 MHz, d$_8$-toluene) δ 7.20 (m, 2H, CH Ar), 7.11 (m, 4H, CH Ar), 4.84 (m, 1H, NC(CH$_3$)C*H*), 4.02 (m, 1H, BOC*H*(CH$_3$)CH$_2$), 3.34-3.19 (m, 4H, C*H*(CH$_3$)$_2$), 1.68 (s, 6H, CH$_3$), 1.63 (m, 6H, CH$_3$), 1.29-1.15 (m, 41H, CH$_3$ and CH$_2$), 0.90 (m, 6H, CH$_3$), 0.72 (m, 6H, CH$_3$) ppm. $^{13}$C{$^1$H} NMR (126 MHz, toluene) δ 170.17 (N$\underline{C}$(CH$_3$)CH), 169.93 (N$\underline{C}$(CH$_3$)CH), 161.00 (C$^{IV}$ Ar), 144.83 (C$^{IV}$ Ar), 144.67 (C$^{IV}$ Ar), 143.17 (C$^{IV}$ Ar), 142.30 (C$^{IV}$ Ar), 141.90

($C^{IV}$ Ar), 141.59 ($C^{IV}$ Ar), 140.89 ($C^{IV}$ Ar), 128.75 (CH Ar), 127.82 (CH Ar), 125.41 (CH Ar), 125.33 (CH Ar), 125.32 (CH Ar), 124.39 (CH Ar), 123.56 (CH Ar), 123.53 (CH Ar), 123.09 (CH Ar), 94.40 ($NC(CH_3)\underline{C}H$), 93.91 ($NC(CH_3)\underline{C}H$), 80.16 ($B(O\underline{C}(CH_3)_2)_2$), 69.99 ($B(O\underline{C}(CH_3)_2CH_2$), 66.11 ($BO\underline{C}H(CH_3)CH_2$), 49.34 ($CH_3$), 33.77 ($CH_3$), 31.63 ($CH_3$), 28.27 ($\underline{C}H(CH_3)_2$), 28.23 ($\underline{C}H(CH_3)_2$), 28.18 ($\underline{C}H(CH_3)_2$), 27.66 ($\underline{C}H(CH_3)_2$), 27.46 ($\underline{C}H(CH_3)_2$), 25.44 ($CH_3$), 25.30 ($CH_3$), 25.18 ($CH_3$), 25.11 ($CH_3$), 25.04 ($CH_3$), 24.93 ($CH_3$), 24.88 ($CH_3$), 24.86 ($CH_3$), 24.66 ($CH_3$), 24.59 ($CH_3$), 24.53 ($CH_3$), 24.51 ($CH_3$), 24.47 ($CH_3$), 24.28 ($CH_3$), 24.08 ($CH_3$), 22.96 ($CH_3$), 22.69 ($CH_3$), 13.93 ($CH_3$) ppm. $^{11}B\{^1H\}$ NMR (160 MHz, toluene) δ 30.42, 1.37 ppm. Elemental analysis: Found C, 68.47; H, 9.52; N, 3.41 %. $C_{47}H_{77}B_3MgN_2O_6$ requires: C, 68.60; H, 9.43; N, 3.40 %.

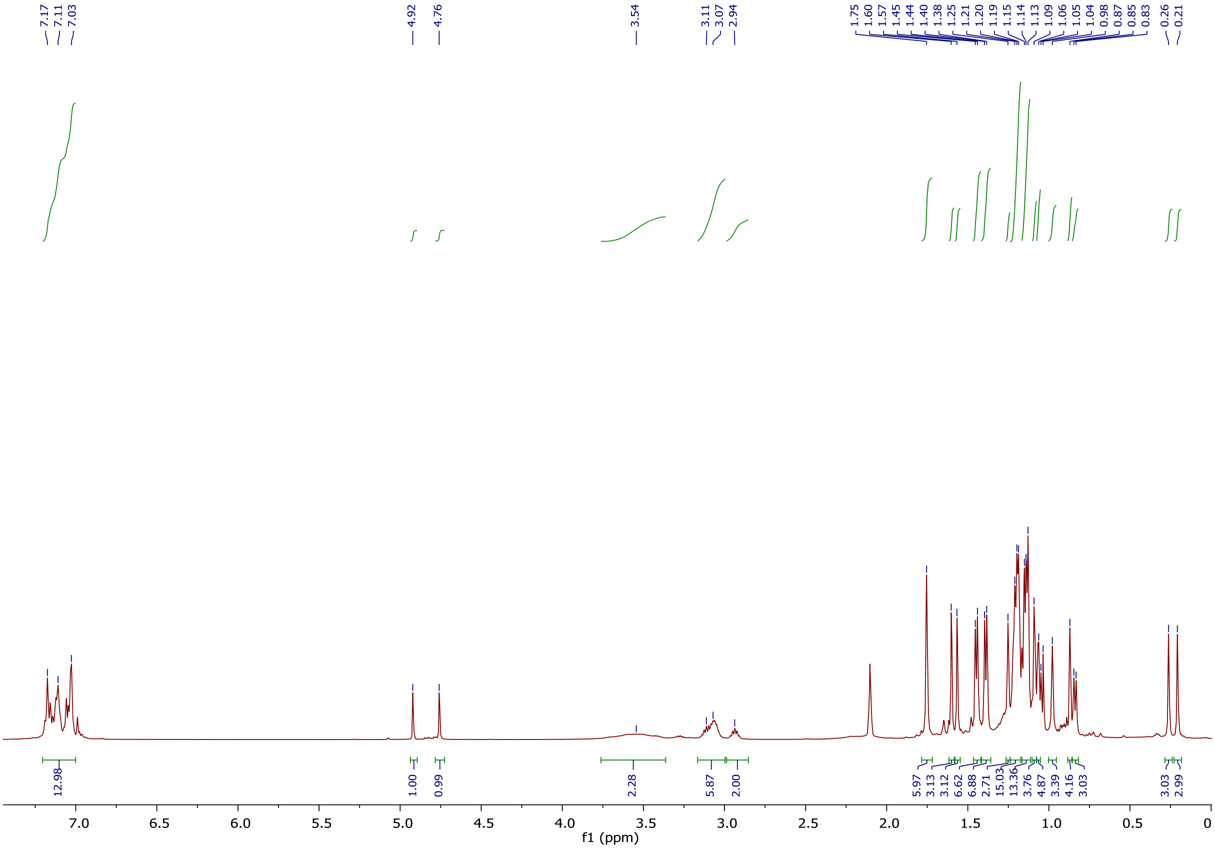

**Figure S1:** $^{1}$H NMR spectrum (500 MHz) of compound **7**.

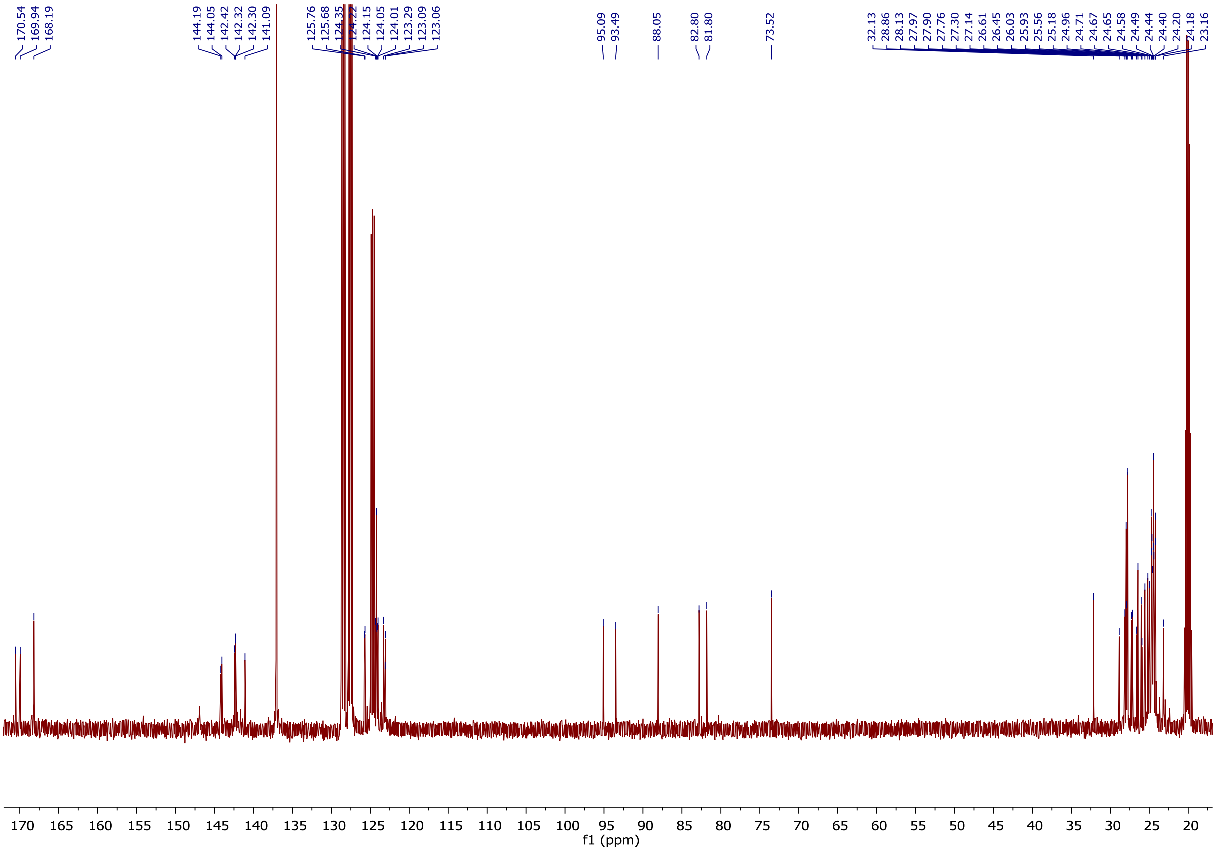

**Figure S2:** $^{13}$C{$^{1}$H} NMR spectrum (126 MHz) of compound **7**.

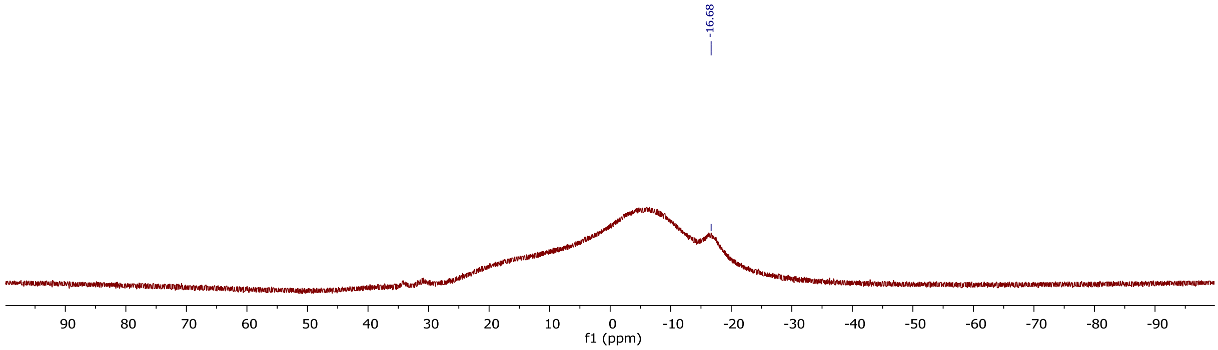

**Figure S3:** $^{11}B\{^{1}H\}$ NMR spectrum (160 MHz) of compound **7**.

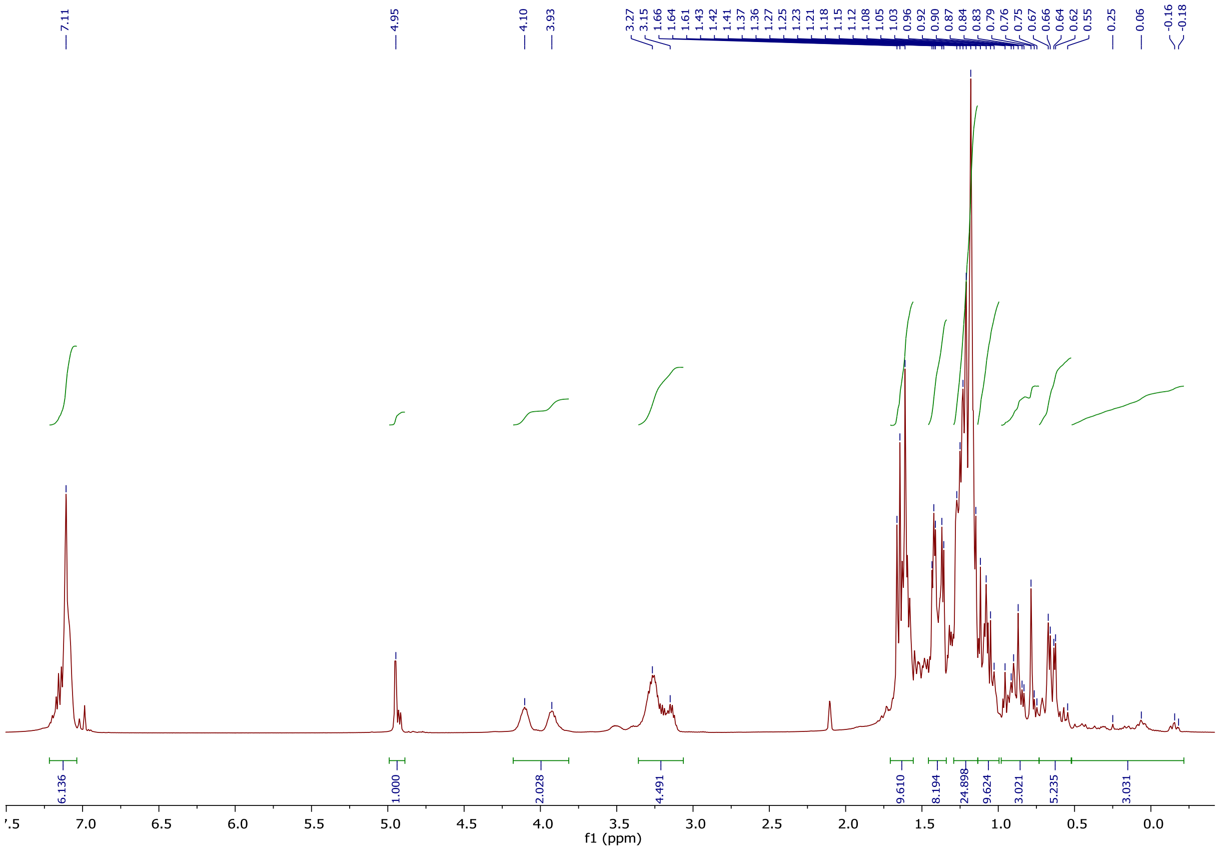

**Figure S4:** $^{1}H$ NMR spectrum (500 MHz) of compound **8**.

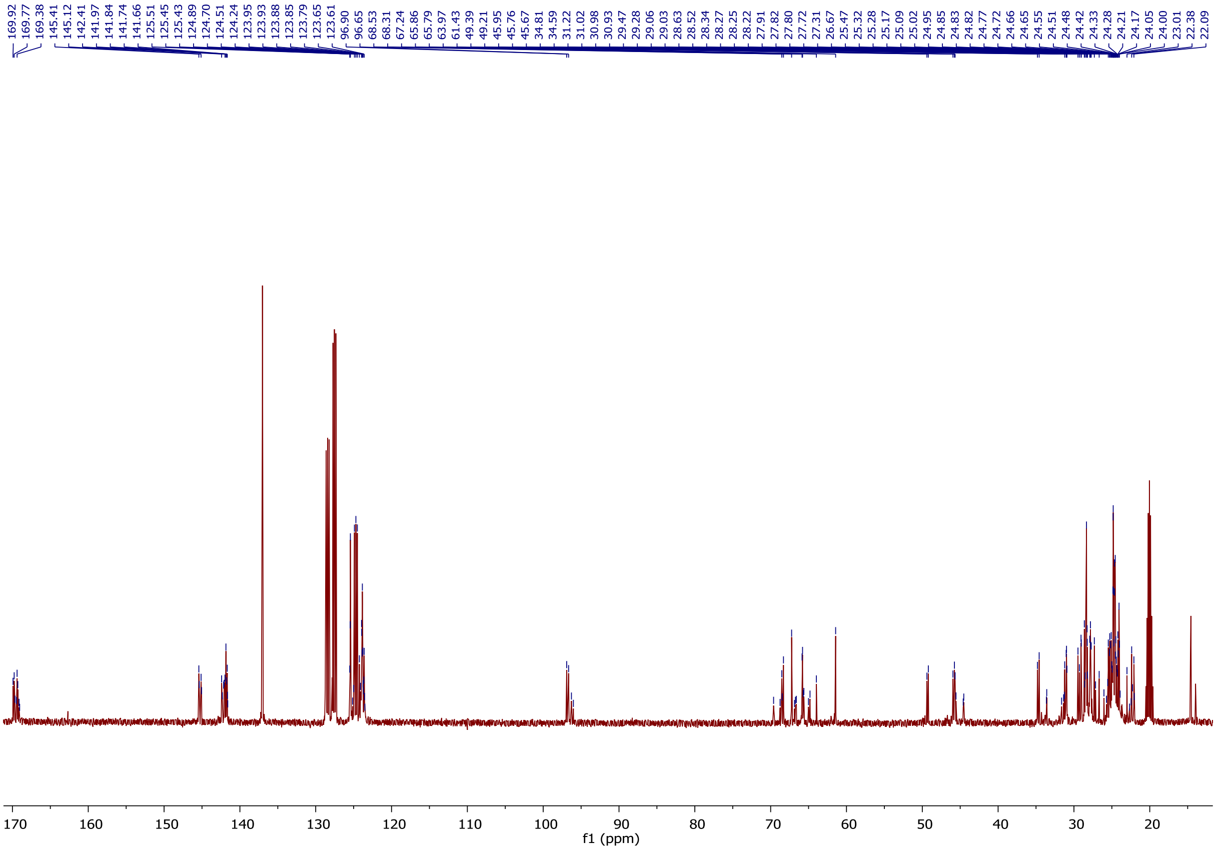

**Figure S5:** $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz) of compound **8**.

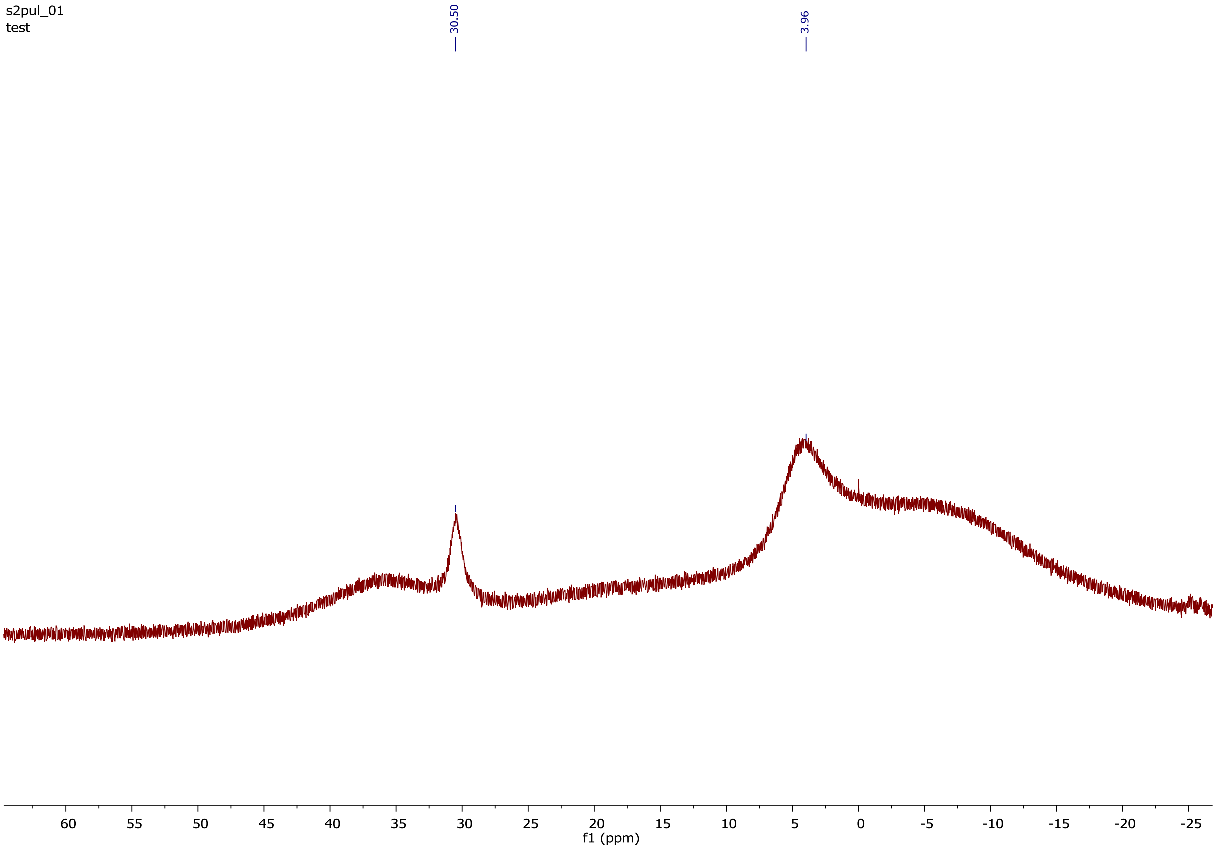

**Figure S6:** $^{11}B\{^{1}H\}$ NMR spectrum (160 MHz) of compound **8**.

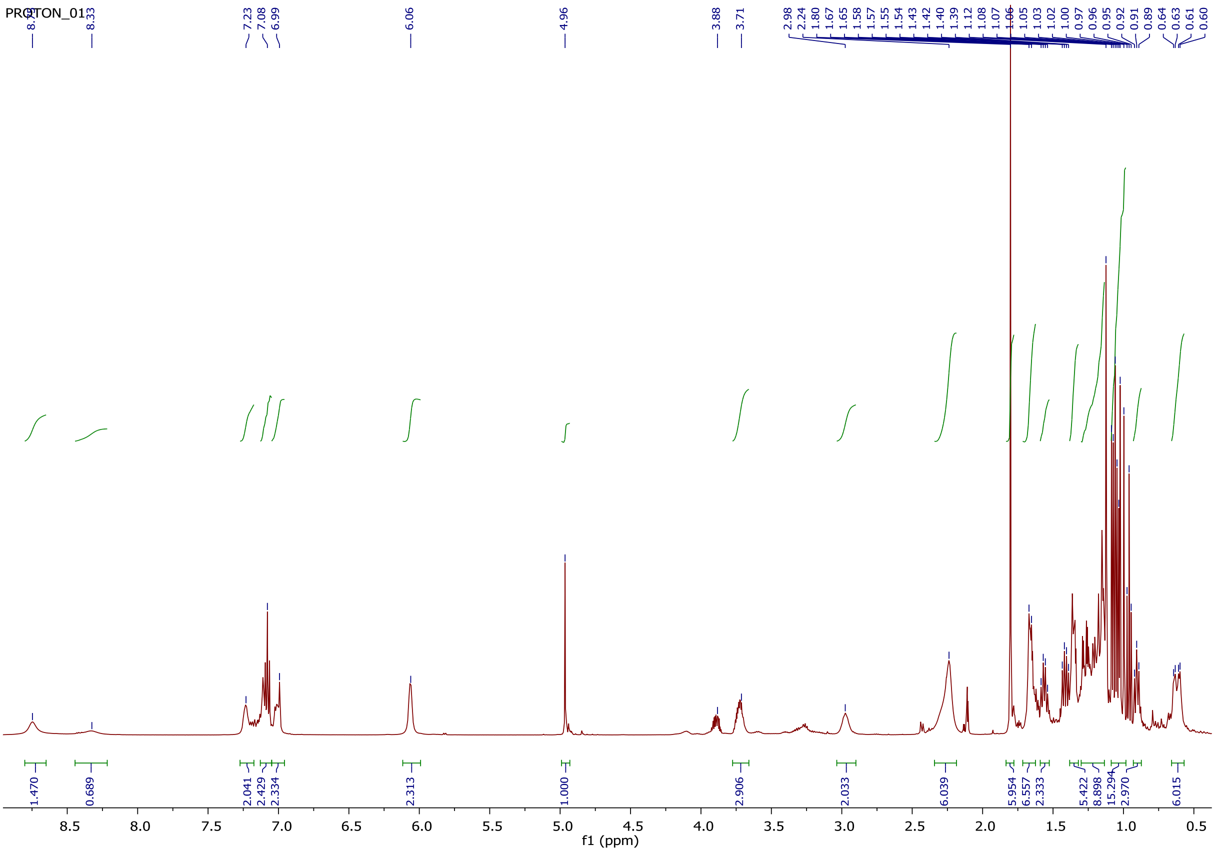

**Figure S7:** $^{1}$H NMR spectrum (500 MHz) of compound **9** generated *in situ* by addition of DMAP to a solution of compound **8**.

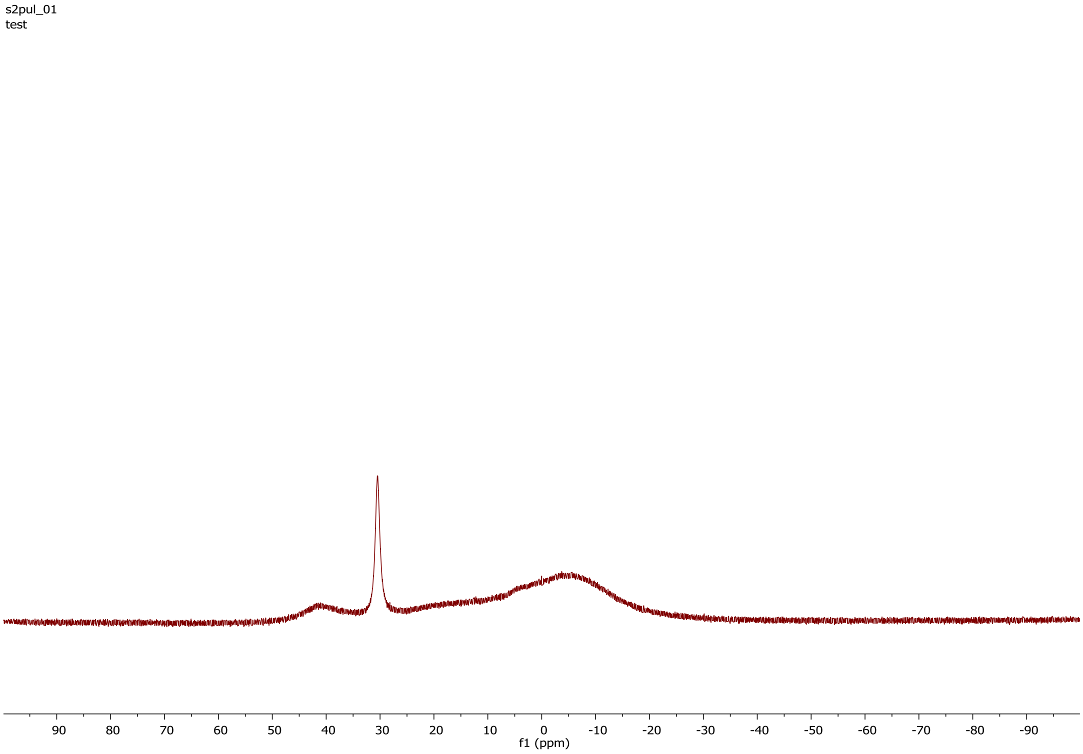

**Figure S8:** $^{11}$B{$^{1}$H} NMR spectrum (160 MHz) of compound **9** generated *in situ* by addition of DMAP to a solution of compound **8**.

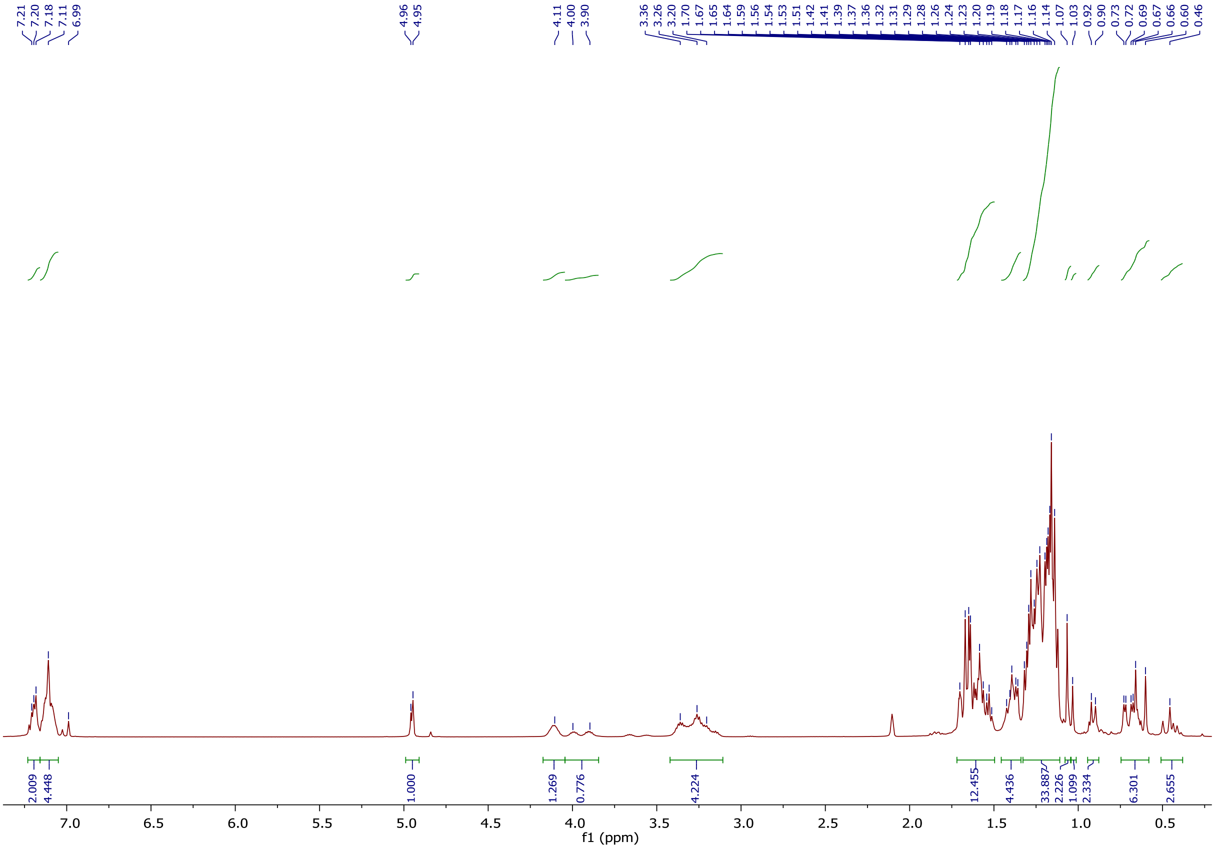

**Figure S9:** $^1$H NMR spectrum (500 MHz) of compound **10**.

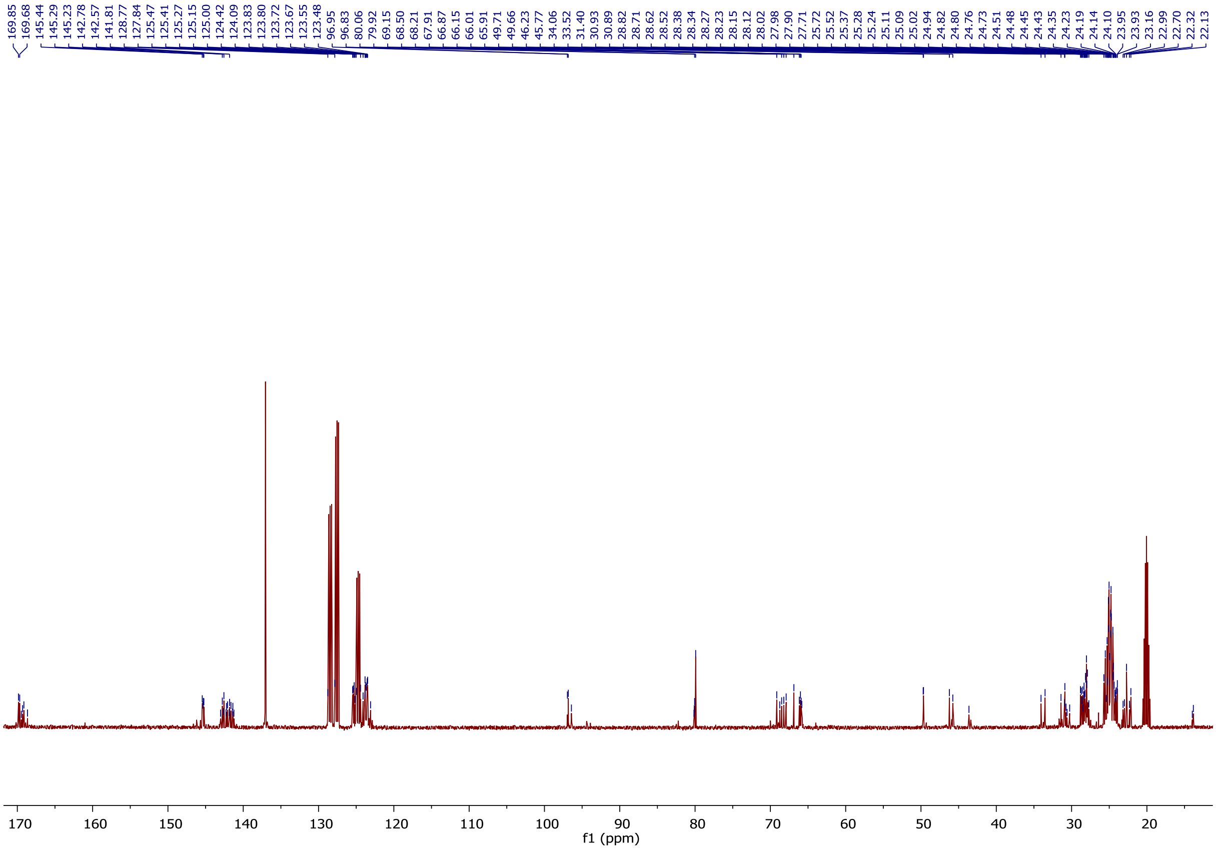

**Figure S10:** $^{13}$C{$^1$H} NMR spectrum (126 MHz) of compound **10**.

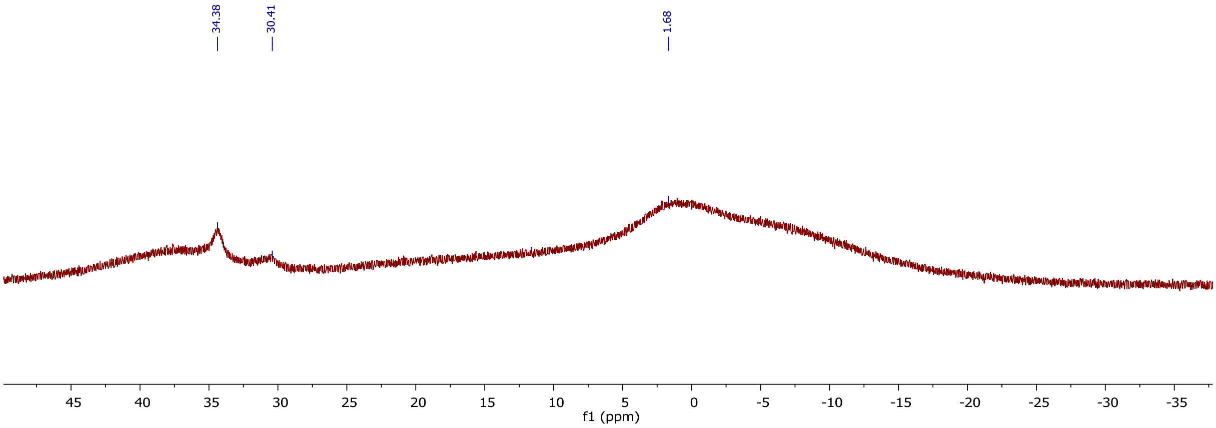

**Figure S11:** $^{11}B\{^{1}H\}$ NMR spectrum (160 MHz) of compound **10**.

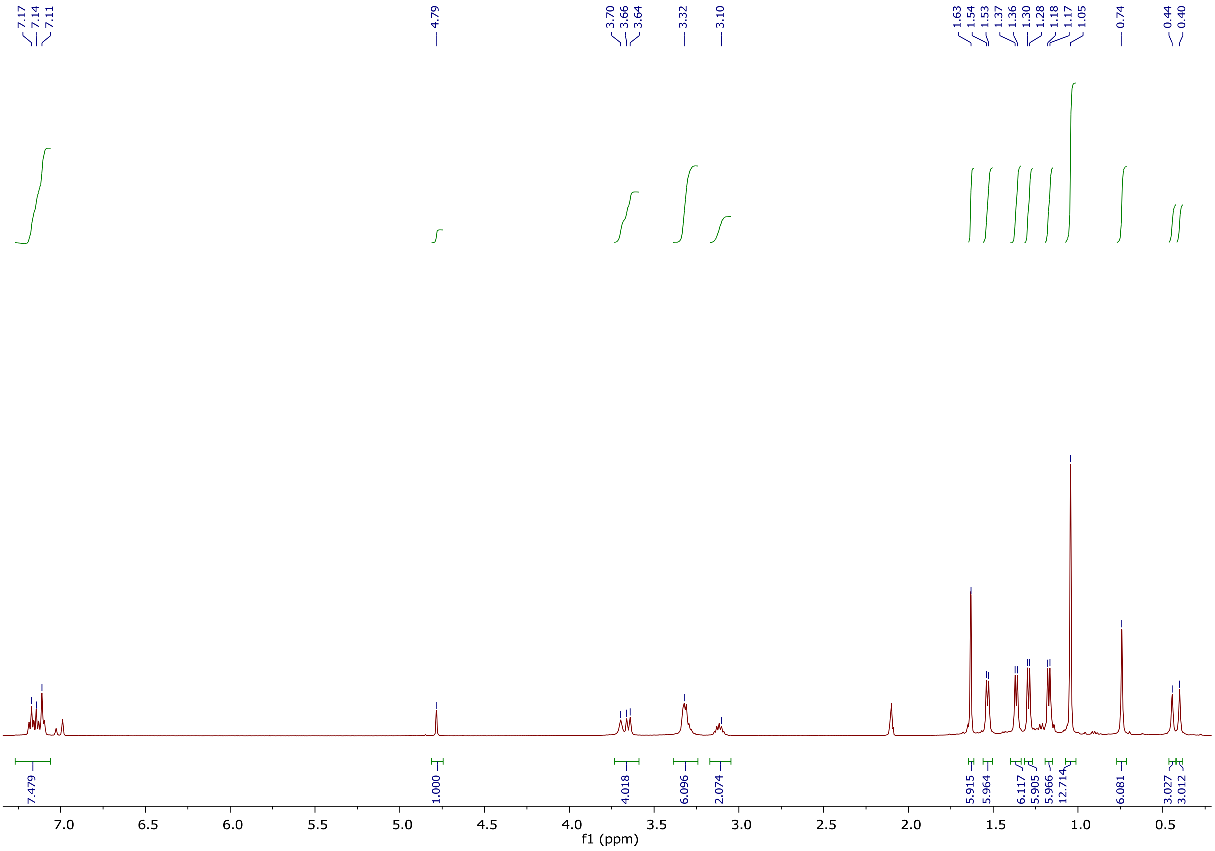

**Figure S12:** $^{1}H$ NMR spectrum (500 MHz) of compound **11**.

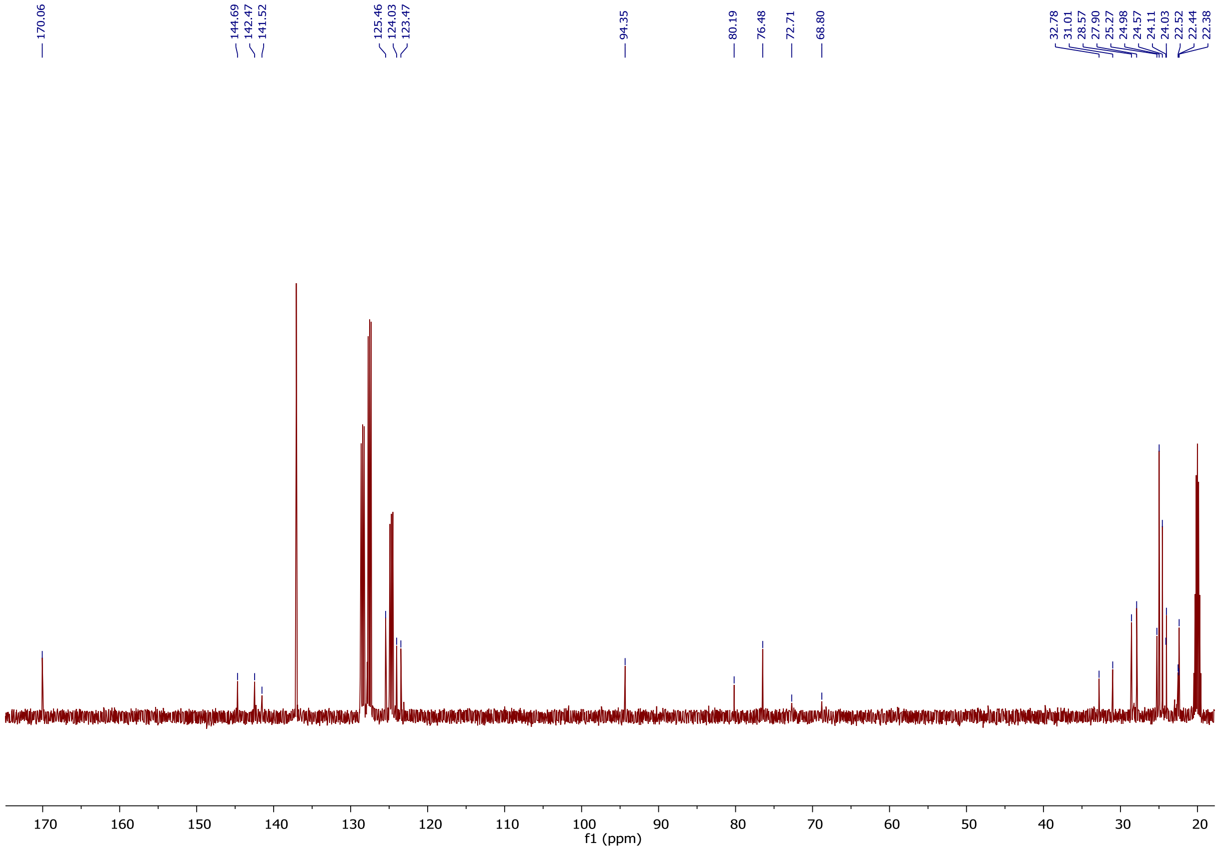

**Figure S13:** $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz) of compound **11**.

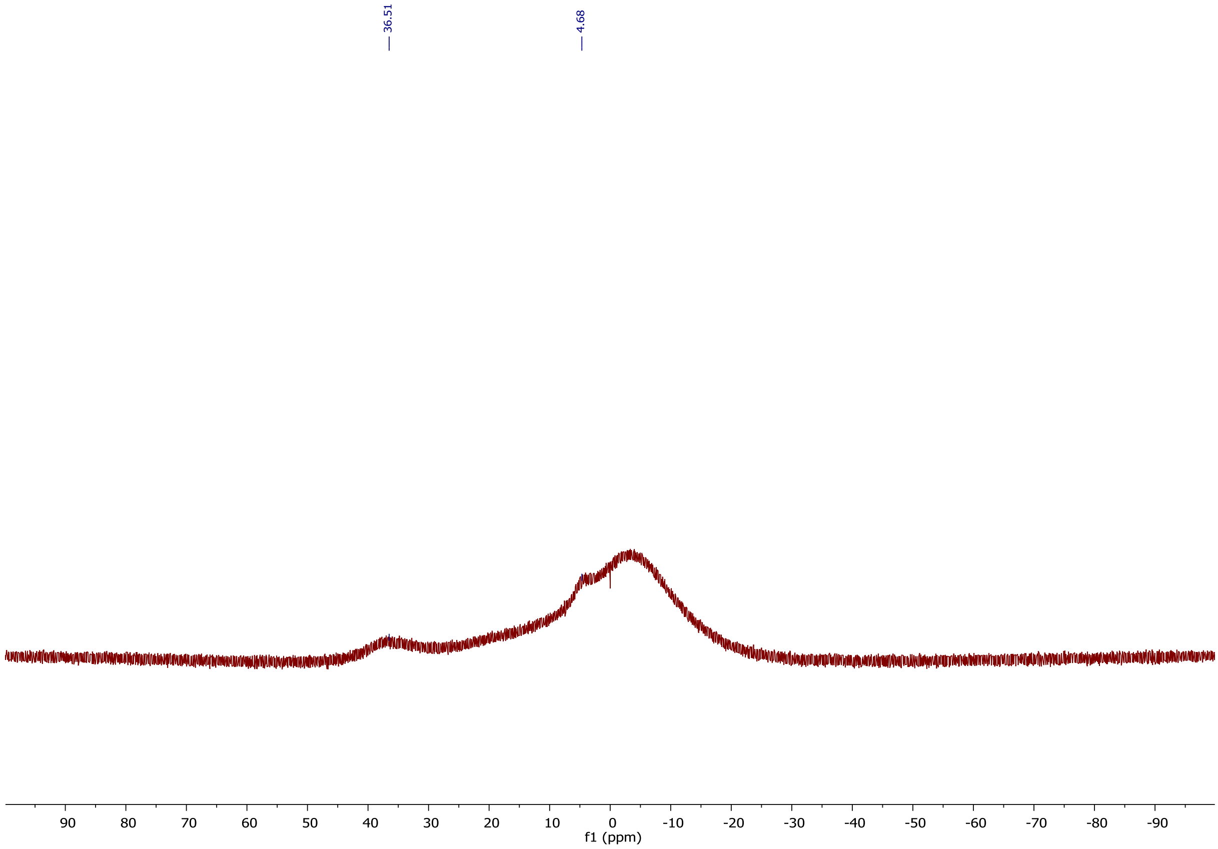

**Figure S14:** $^{11}B\{^{1}H\}$ NMR spectrum (160 MHz) of compound **11**.

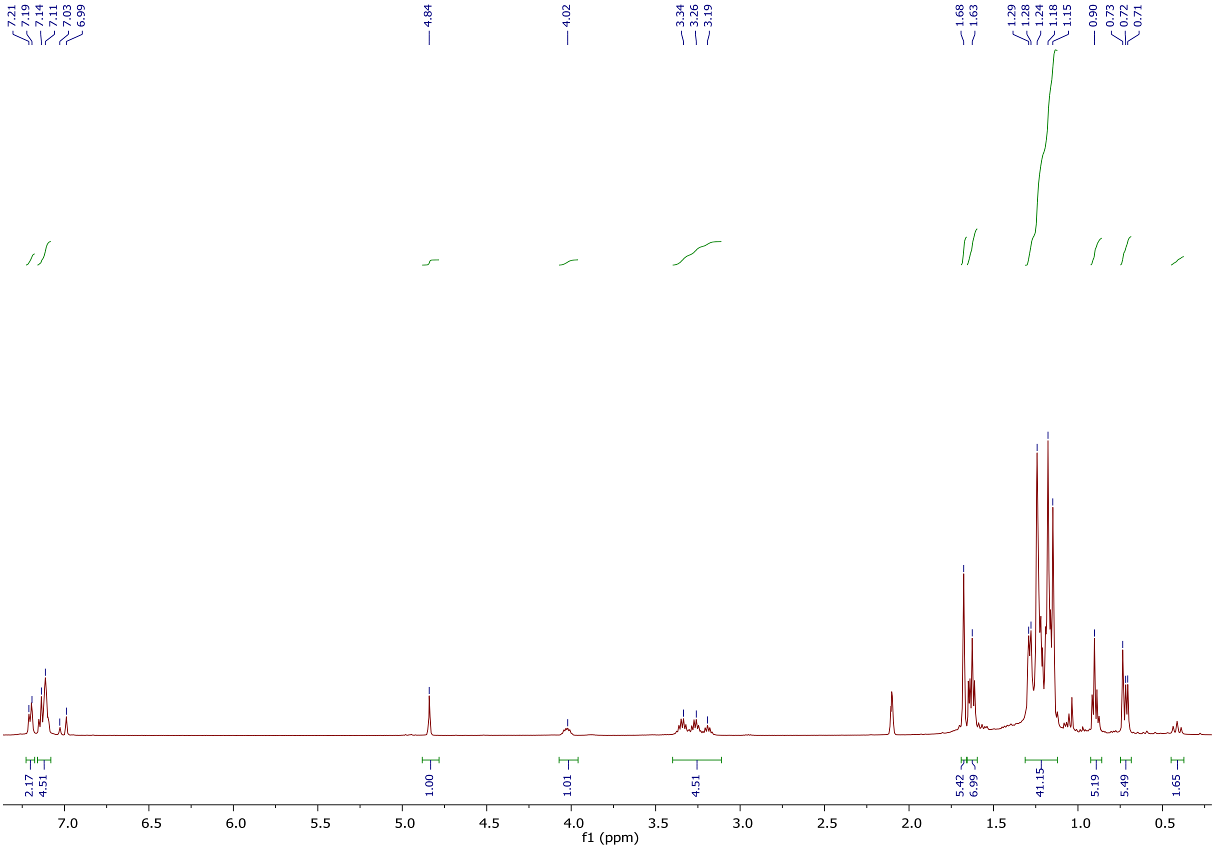

**Figure S15:** $^{1}$H NMR spectrum (500 MHz) of compound **12**.

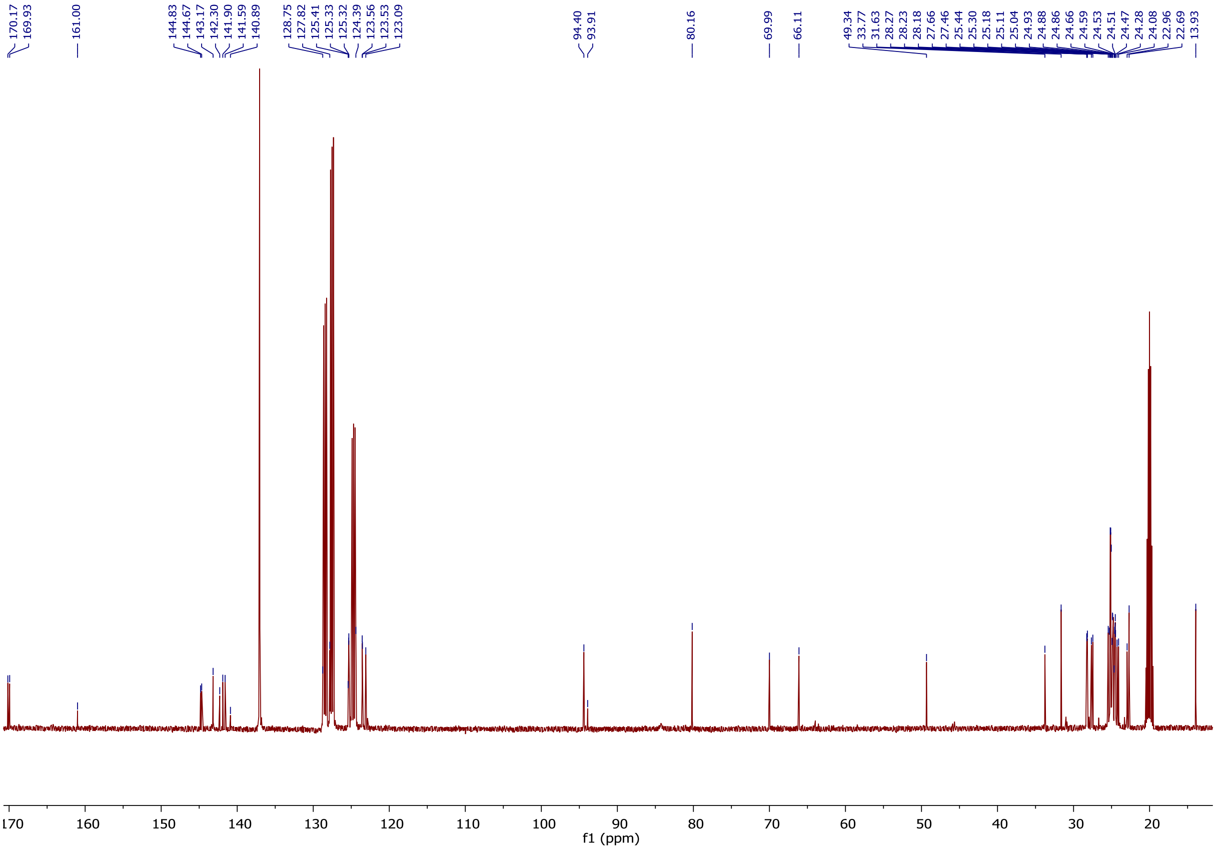

**Figure S16:** $^{13}$C{$^{1}$H} NMR spectrum (126 MHz) of compound **12**.

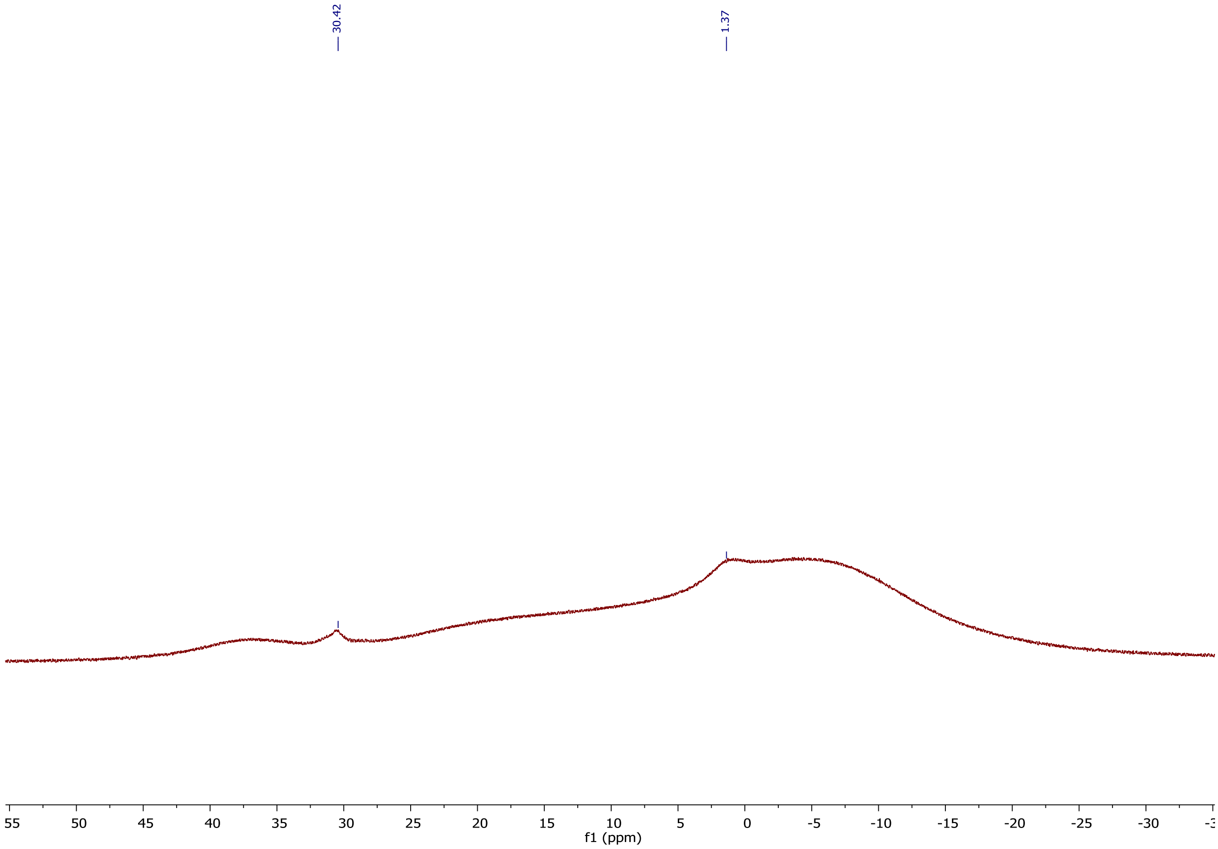

**Figure S17:** $^{11}$B{$^{1}$H} NMR spectrum (160 MHz) of compound **12**.

**Single Crystal X-ray Diffraction analysis:** Single Crystal X-ray diffraction data for compounds **7** – 12 were collected using Cu*K*α (*λ* = 1.54184 Å) on a SuperNova, Dual Cu at zero, EosS2 diffractometer. The crystals were kept at 150(2) K during data collections. Using Olex2,[3] the structures were solved *via* SHELXS[4] and refined with the ShelXL refinement package using Least Squares minimisation. For compound **7** H2a and H2b were located and refined without restraints. The isopropyl carbons 24-C26 and all carbons in the boron-based ligand in compound **8** were seen to exhibit disorder in a 55:45 ratio. ADP and comparable distance similarity restraints were employed, on merit, in the latter region in order to assist convergence. The asymmetric unit in compound **9** contains 2 molecules of the magnesium complex. Disorder modelling was necessary in the region of the B(hex) ligands in order to secure a chemically sensible refinement. In particular, the atoms in the ligand based on B1 (with the exceptions of O2 and C40) were seen to be disordered in a 55:45 ratio, while those in the moiety based on B2 (O3 excepted) were split over 2 positions in a 50:50 ratio. O-B, B-C and chemically equivalent C-C bond lengths were restrained to being similar for fractional occupancy atoms in the final least-squares run. ADP restraints were also included in disordered regions to assist convergence. In compound **10** C36 and C37 disordered in a 75:25 ratio. Chemically equivalent distances involving these fractional occupancy carbons atoms were restrained to being similar in the final least-squares refinement. The asymmetric unit in compound **12** contains 2 molecules of the magnesium complex and some solvent. Disorder modelling was necessitated for some atoms in the boryl ligands of the main features. In particular, C37-C39, C42-C47, C89-C94 and O6 were each split, in a 50:50 ratio, over 2 positions. O-B, B-C and chemically equivalent C-C bond lengths were restrained to being similar for fractional occupancy atoms in the final least-squares run. ADP restraints were also included in disordered regions to assist convergence. The guest solvent was diffuse and hence was addressed using the solvent mask algorithm in Olex2. An allowance of one molecule of hexane (per asymmetric unit) has been made in the formula as presented herein, to account for same.

CCDC 1824654-1824659 contain the supplementary crystallographic data for compounds **7** – **12**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.ca.ac.uk/data_request/cif.

**Table S1:** Single Crystal X-ray Data Parameters for compounds **7** – **12**.

| Compound | **7** | **8** | **9** | **10** | **11** | **12** |
|---|---|---|---|---|---|---|
| Empirical formula | $C_{70}H_{108}B_2Mg_2N_4O_4$ | $B_2C_{45}MgN_2O_4H_{0.13}$ | $C_{84}H_{126}B_2Mg_2N_8O_4$ | $C_{47}H_{77}B_3MgN_2O_6$ | $C_{45}H_{73}B_3MgN_2O_6$ | $C_{100}H_{168}B_6Mg_2N_4O_{12}$ |
| Formula weight | 1139.84 | 678.53 | 1382.16 | 822.84 | 794.79 | 1731.85 |
| Temperature/K | 150.00(10) | 150.00(10) | 150.00(10) | 150.01(10) | 150.01(10) | 150.01(10) |
| Crystal system | monoclinic | orthorhombic | monoclinic | tetragonal | monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $Pbcn$ | $P2_1/c$ | $I4_1/a$ | $P2_1/c$ | $C/2c$ |
| $a$/Å | 22.6369(3) | 15.16029(17) | 23.0365(7) | 37.2496(5) | 12.8409(4) | 45.271(3) |
| $b$/Å | 12.3776(2) | 27.6648(3) | 19.3651(4) | 37.2496(5) | 35.1364(8) | 18.2367(7) |
| $c$/Å | 25.1115(3) | 21.7294(2) | 21.5333(6) | 14.5258(2) | 11.0846(2) | 37.898(2) |
| $\alpha$/° | 90 | 90 | 90 | 90 | 90 | 90 |
| $\beta$/° | 104.8410(10) | 90 | 116.442(4) | 90 | 105.051(3) | 122.981(8) |
| $\gamma$/° | 90 | 90 | 90 | 90 | 90 | 90 |
| Volume/Å$^3$ | 6801.28(17) | 9113.46(16) | 8601.2(4) | 20155.0(6) | 4829.6(2) | 26246(3) |
| $Z$ | 4 | 8 | 4 | 16 | 4 | 8 |
| $\rho_{calc}$ g/cm$^3$ | 1.113 | 0.989 | 1.067 | 1.085 | 1.093 | 0.877 |
| $\mu$/mm$^{-1}$ | 0.681 | 0.641 | 0.630 | 0.649 | 0.662 | 0.515 |
| $F$(000) | 2488.0 | 2705.0 | 3008.0 | 7168.0 | 1728.0 | 7568.0 |
| Crystal size/mm$^3$ | 0.167×0.089×0.064 | 0.246×0.161×0.091 | 0.242×0.096×0.073 | 0.272×0.064×0.058 | 0.233×0.078×0.066 | 0.229×0.197×0.16 |
| 2Θ range for data collection/° | 7.284 to 147.172 | 6.39 to 146.322 | 6.26 to 147.072 | 6.532 to 147.182 | 5.03 to 146.51 | 5.44 to 140.152 |
| Reflections collected | 113576 | 62560 | 67284 | 77992 | 33036 | 95419 |
| Independent reflections | 13681 [$R_{int}$=0.0837, $R_{sigma}$= 0.0401] | 9102 [$R_{int}$=0.0544, $R_{sigma}$=0.0333] | 17110 [$R_{int}$=0.0445, $R_{sigma}$=0.0433] | 10099 [$R_{int}$=0.0586, $R_{sigma}$=0.0382] | 9514 [$R_{int}$=0.0559, $R_{sigma}$=0.0572] | 24859 [$R_{int}$=0.0598, $R_{sigma}$=0.0677] |
| Data/restraints/parameters | 13681/0/775 | 9102/87/646 | 17110/236/1054 | 10099/3/569 | 9514/0/540 | 24859/234/1260 |
| Goodness-of-fit on $F^2$ | 1.014 | 1.047 | 1.020 | 1.035 | 1.057 | 0.945 |
| Final R indexes [$I$>=2σ ($I$)] | $R_1$=0.0422, $wR_2$=0.0989 | $R_1$=0.0646, $wR_2$=0.1671 | $R_1$=0.0575, $wR_2$=0.1449 | $R_1$=0.0557, $wR_2$=0.1311 | $R_1$=0.0574, $wR_2$=0.1361 | $R_1$=0.0781, $wR_2$=0.2155 |
| Final R indexes [all data] | $R_1$=0.0607, $wR_2$=0.1085 | $R_1$=0.0746, $wR_2$=0.1759 | $R_1$=0.0883, $wR_2$=0.1623 | $R_1$=0.0793, $wR_2$=0.1444 | $R_1$=0.0868, $wR_2$=0.1507 | $R_1$=0.1381, $wR_2$=0.2621 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.26/-0.24 | 0.62/-0.50 | 0.60/-0.32 | 0.35/-0.26 | 0.40/-0.20 | 0.25/-0.23 |

## References

1 A. P. Dove, V. C. Gibson, P. Hormnirun, E. L. Marshall, J. A. Segal, A. J. P. White, D. J. Williams, *Dalton. Trans.* 2003, 3088.

2 S. J. Bonyhady, C. Jones, S. Nembenna, A. Stasch, A. J. Edwards, G. J. McIntyre, *Chem.-Eur. J.*, 2010, **16**, 938.

3 L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard, H. Puschmann, *Acta Cryst. A* 2015, **71**, 59-75.

4 G. M. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112-122.