The Complex Reactivity of β-Diketiminato Magnesium(I) Dimers Towards Pinacolborane: Implications for Catalysis

Dafydd D. L. Jones,[a] Aidan J. R. Matthews[a] and Cameron Jones*[,a]

[a] School of Chemistry, PO Box 23, Monash University, VIC, 3800, Australia.

Supplementary Information (25 pages)

Contents

1. Experimental

General considerations.

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. Hexane and toluene were distilled over molten potassium. ^{1}H, $^{13}C\{^{1}H\}$, and $^{11}B\{^{1}H\}$ NMR spectra were recorded on either Bruker DPX300 or Bruker AvanceIII 400 spectrometers and were referenced to the resonances of the solvent used, or external $BF_3.OEt_2$. Mass spectra were recorded on an Agilent Technologies 5975D inert MSD with a solid state probe. IR spectra were recorded as Nujol mulls, using a Agilent Cary 630 spectrometer operating in attenuated total reflectance (ATR) or transmission modes. Melting points were determined in sealed glass capillaries under dinitrogen, and are uncorrected. The compounds [{(^{Ar}Nacnac)Mg–}$_2$] (Ar = Xyl, Mes or Dep) were prepared by literature procedures.[1-3] HBpin was distilled prior to use, and its purity confirmed by NMR spectroscopy. All other reagents were used as received.

NMR scale reactions between [{(^{Ar}Nacnac)Mg–}$_2$] and 2, 5 or 20 equivs of HBpin

ca. 20 mg of the corresponding magnesium(I) dimer[{(^{Ar}Nacnac)Mg–}$_2$] (Ar = Xyl, Mes or Dep) was dissolved in 2 mL of toluene. The solutions were cooled to -78 °C after which 2, 5 or 20 equivalents of pinacolborane (HBpin) was added *via* micro-syringe or syringe. The reaction mixtures were warmed to room temperature and stirred overnight, after which time volatiles were removed *in vacuo* and the residue extracted with C_6D_6 (0.7 mL). ^{1}H and $^{11}B\{^{1}H\}$ NMR spectra of the total non-volatile residues are depicted below.

Reactions involving [{(Xyl Nacnac)Mg–}$_2$]

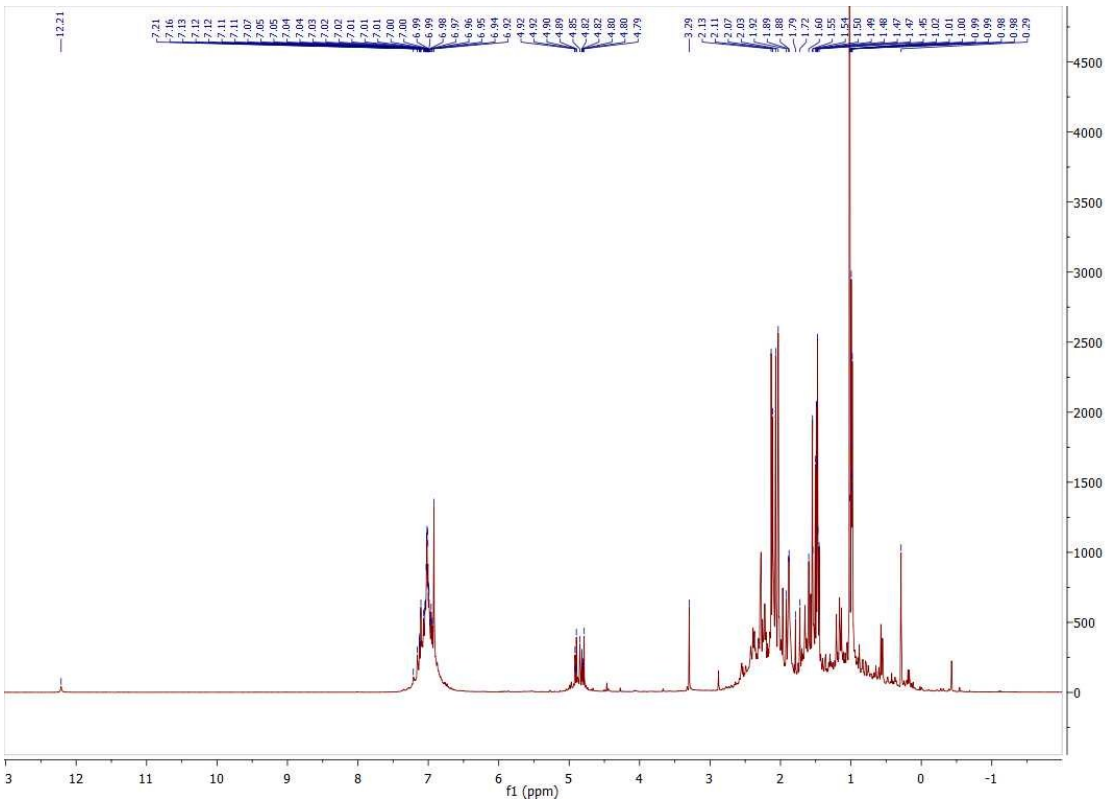

Figure S1. ^{1}H NMR spectrum of the total non-volatile residue remaining after preliminary work-up of the reaction between [{(^{Xyl}Nacnac)Mg–}$_2$] and 2 equivalents of HBpin.

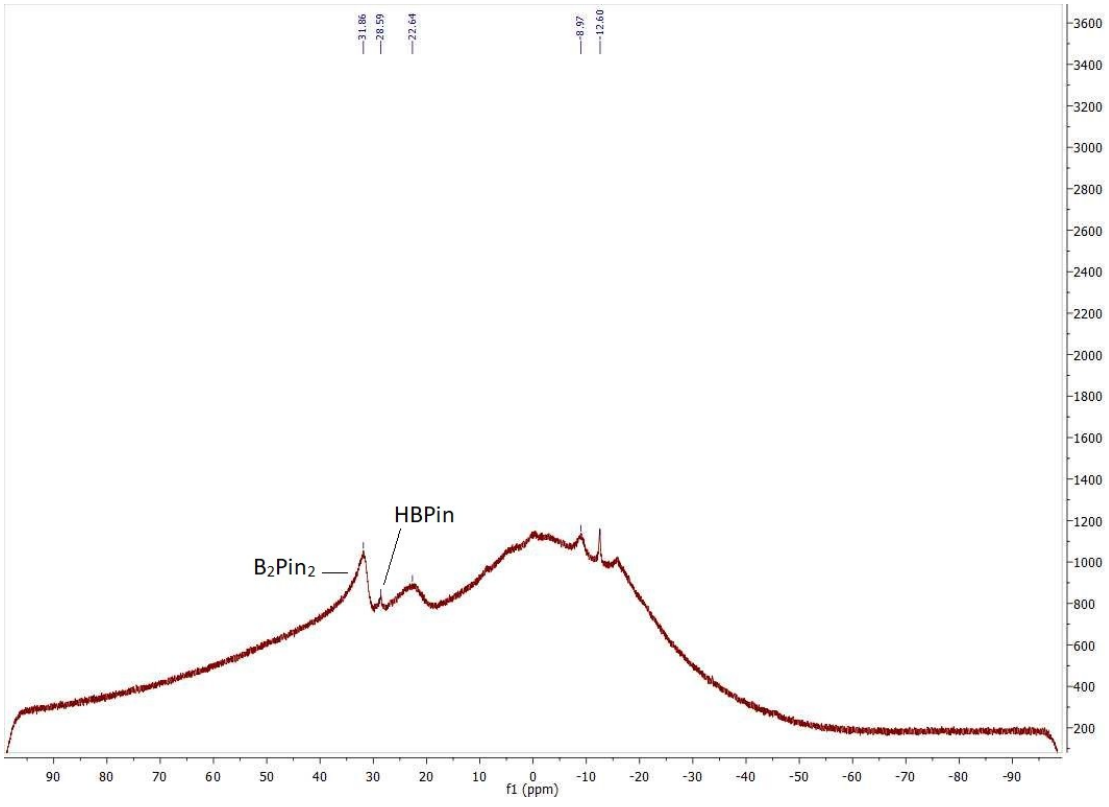

Figure S2. ^{11}B{^{1}H} NMR spectrum of the total non-volatile residue remaining after preliminary work-up of the reaction between [{(^{Xyl}Nacnac)Mg–}$_2$] and 2 equivalents of HBpin.

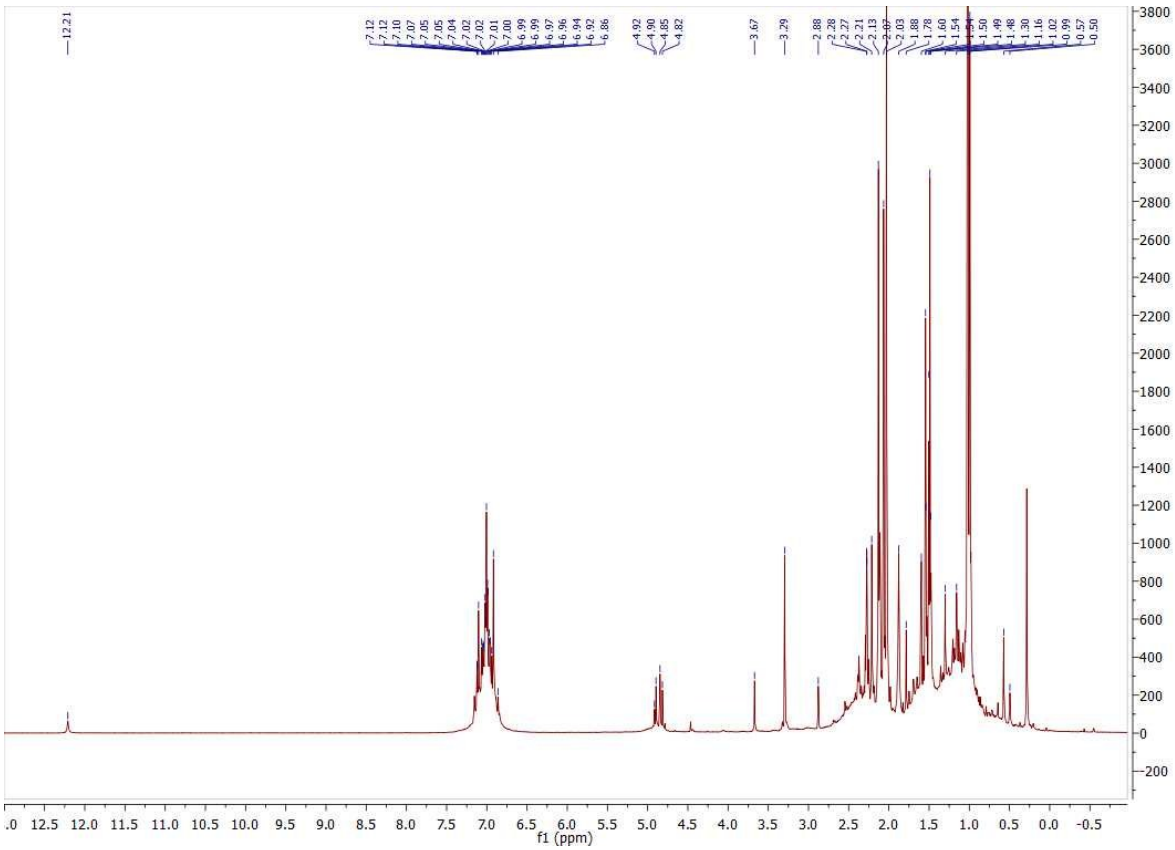

Figure S3. ^{1}H NMR spectrum of the total non-volatile residue remaining after preliminary work-up of the reaction between [{(^{Xyl}Nacnac)Mg–}$_2$] and 5 equivalents of HBpin.

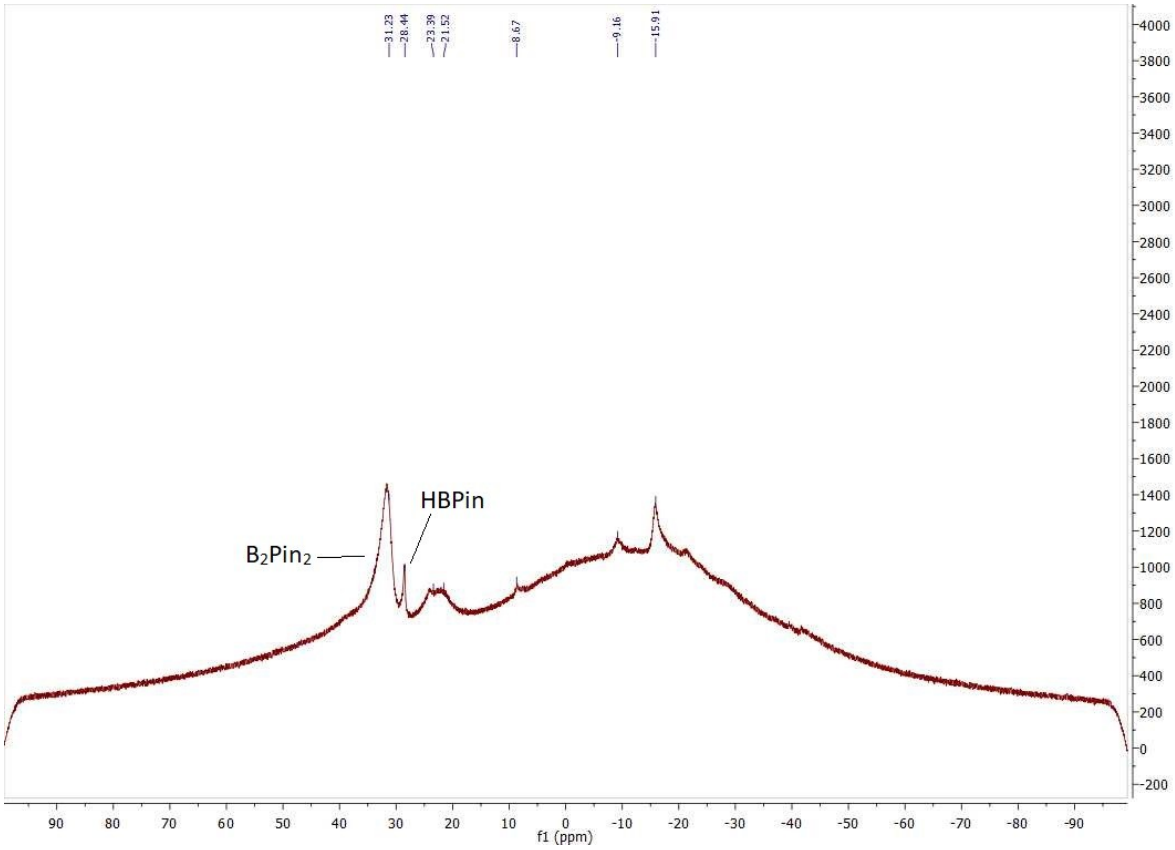

Figure S4. ^{11}B{^{1}H} NMR spectrum of the total non-volatile residue remaining after preliminary work-up of the reaction between [{(^{Xyl}Nacnac)Mg–}$_2$] and 5 equivalents of HBpin.

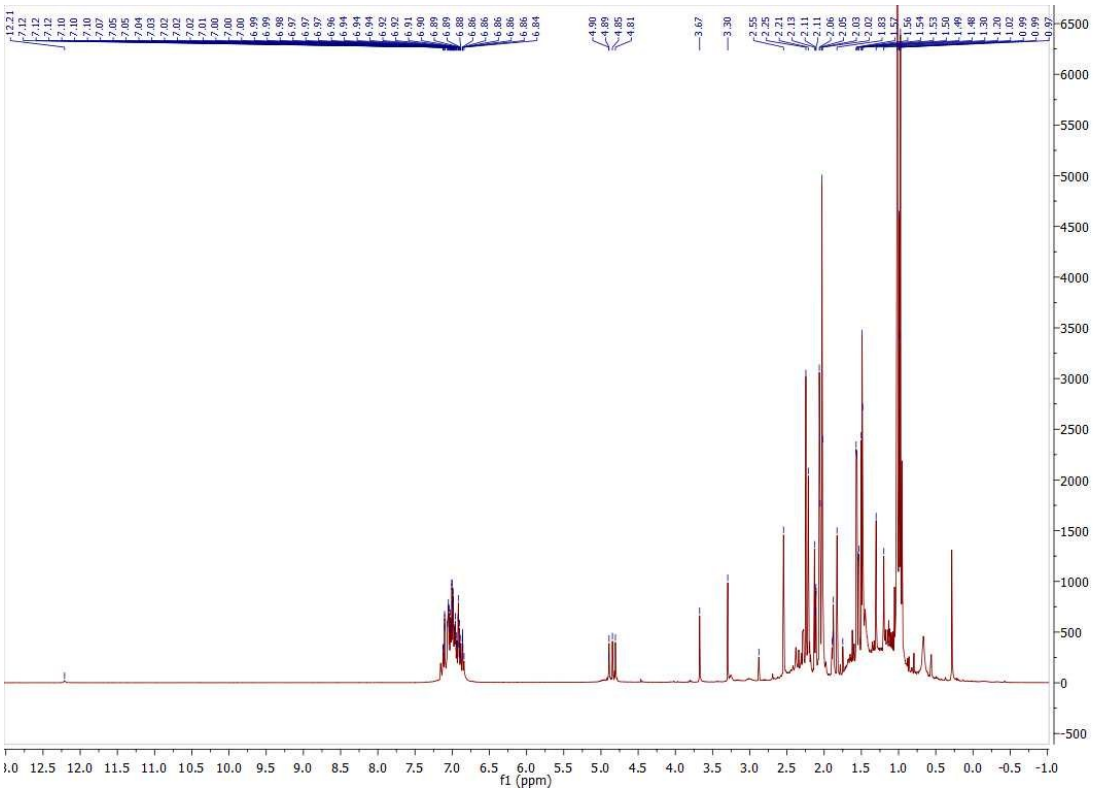

Figure S5. ^{1}H NMR spectrum of the total non-volatile residue remaining after preliminary work-up of the reaction between [{(^{Xyl}Nacnac)Mg–}$_2$] and 20 equivalents of HBpin.

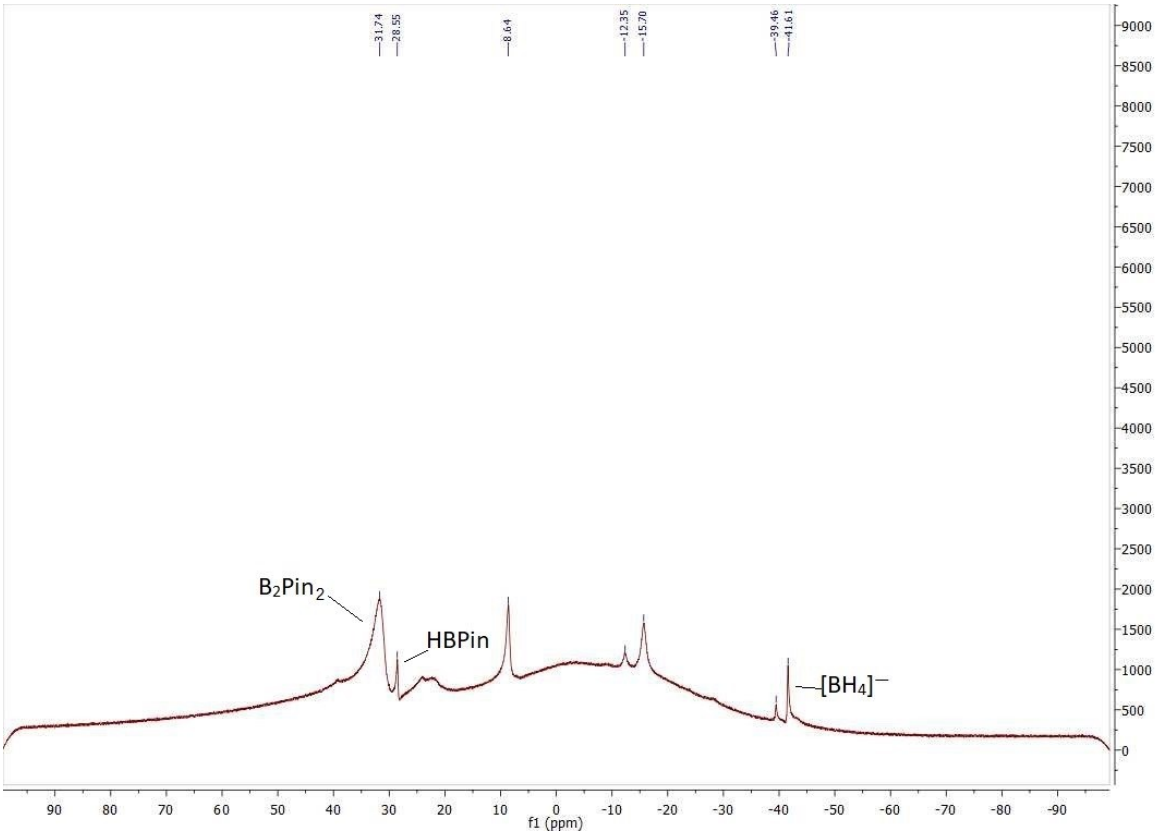

Figure S6. ^{11}B{^{1}H} NMR spectrum of the total non-volatile residue remaining after preliminary work-up of the reaction between [{(^{Xyl}Nacnac)Mg–}$_2$] and 20 equivalents of HBpin.

Reactions involving [{(^Mes^Nacnac)Mg–}$_2$]

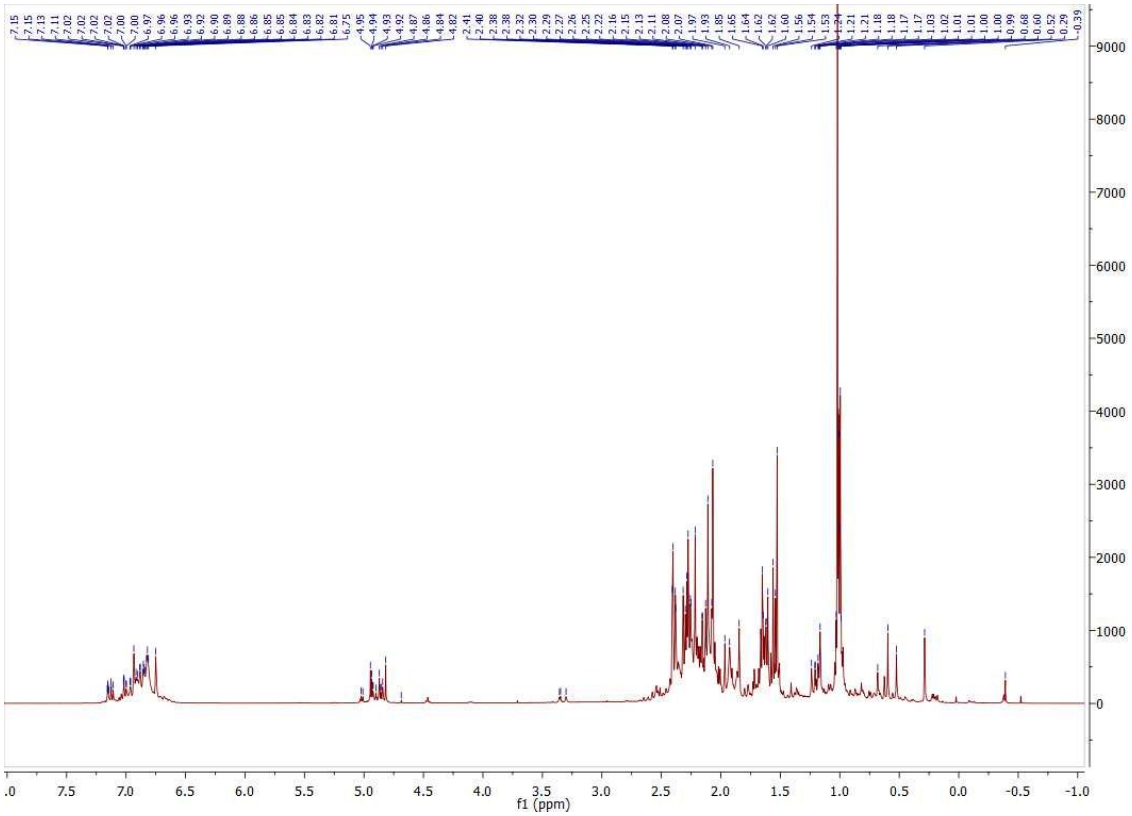

Figure S7. ^{1}H NMR spectrum of the total non-volatile residue remaining after preliminary work-up of the reaction between [{(^{Mes}Nacnac)Mg–}$_2$] and 2 equivalents of HBpin.

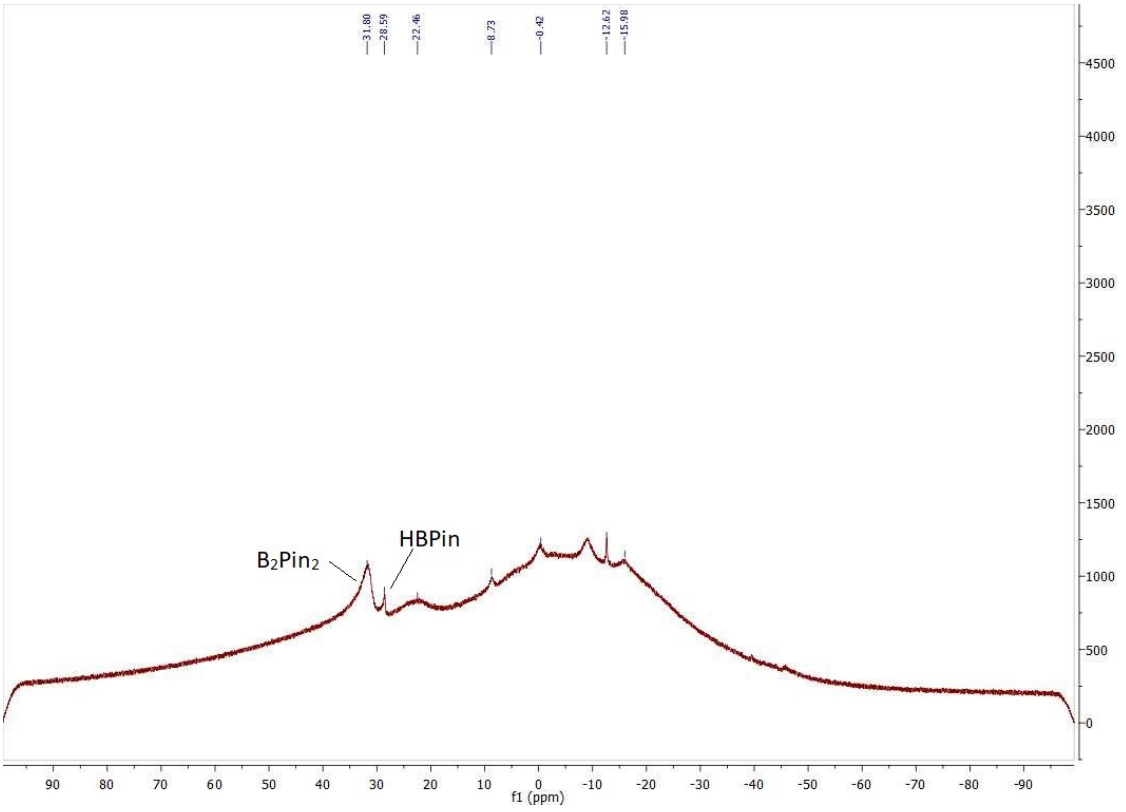

Figure S8. ^{11}B{^{1}H} NMR spectrum of the total non-volatile residue remaining after preliminary work-up of the reaction between [{(^{Mes}Nacnac)Mg–}$_2$] and 2 equivalents of HBpin.

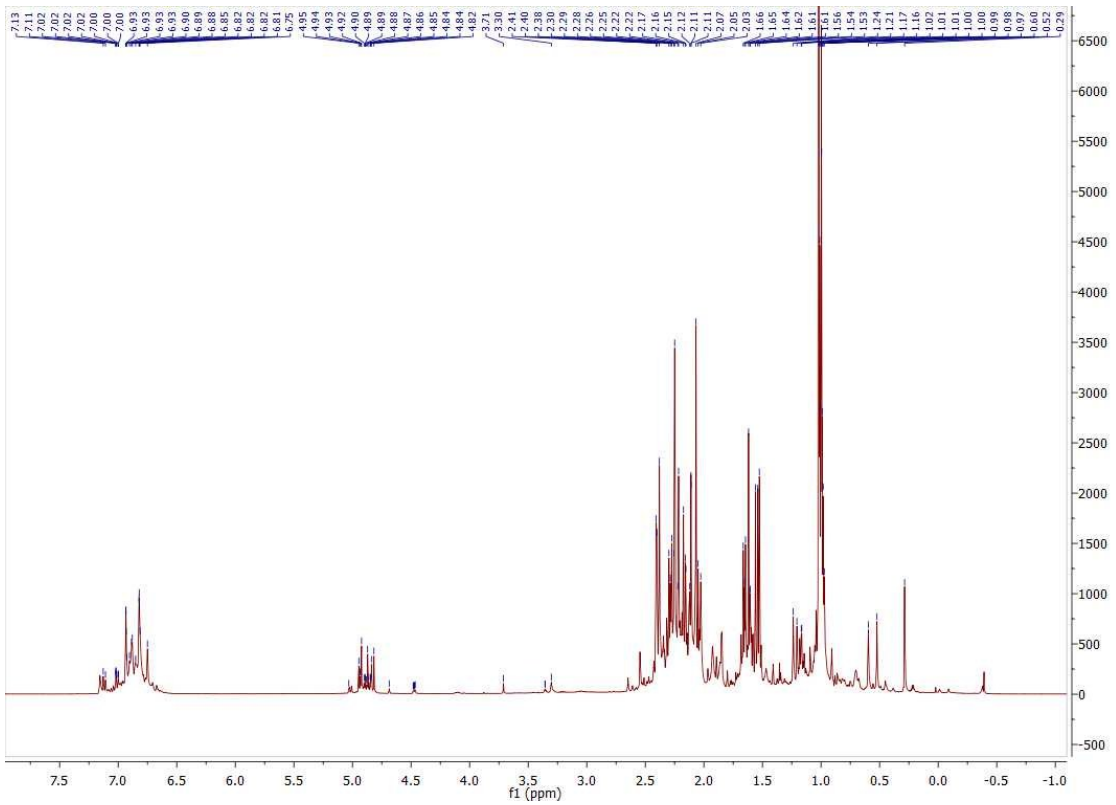

Figure S9. ^{1}H NMR spectrum of the total non-volatile residue remaining after preliminary work-up of the reaction between [{(^{Mes}Nacnac)Mg–}$_2$] and 5 equivalents of HBpin.

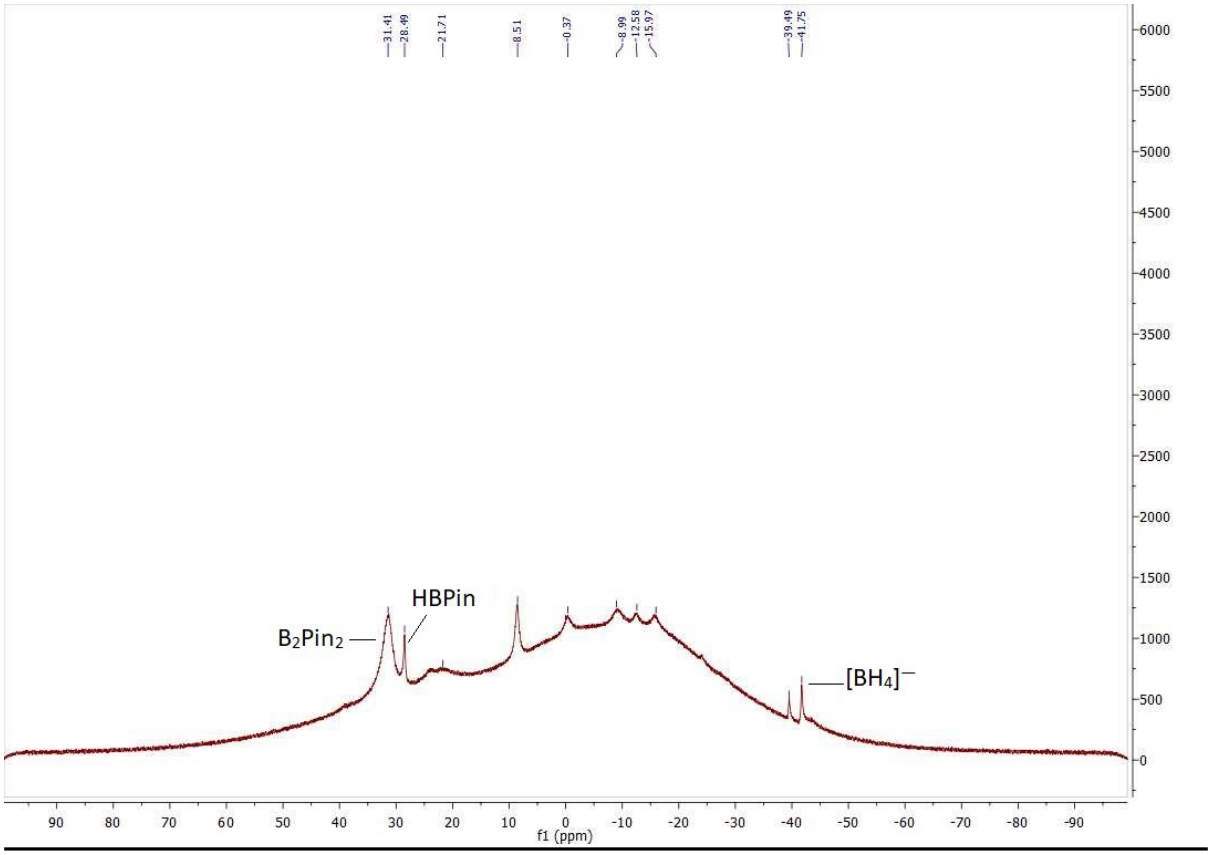

Figure S10. ^{11}B{^{1}H} NMR spectrum of the total non-volatile residue remaining after preliminary work-up of the reaction between [{(^{Mes}Nacnac)Mg–}$_2$] and 5 equivalents of HBpin.

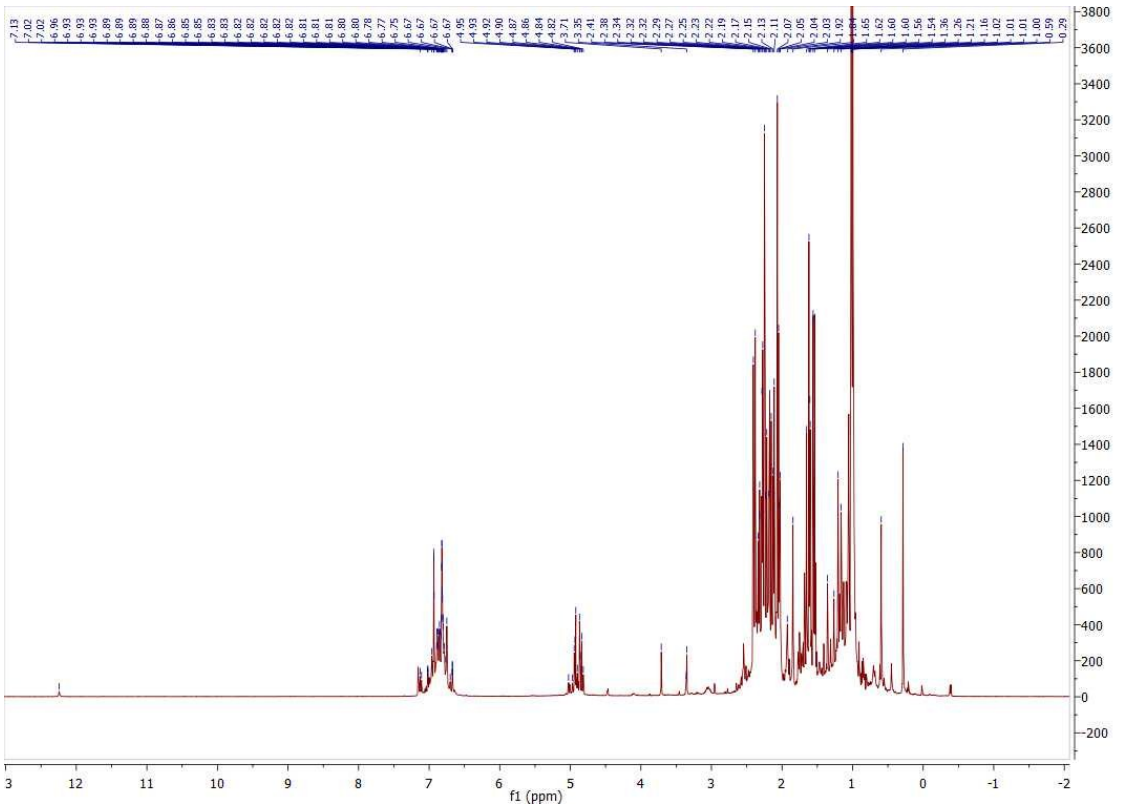

Figure S11. ^{1}H NMR spectrum of the total non-volatile residue remaining after preliminary work-up of the reaction between [{(^{Mes}Nacnac)Mg–}$_2$] and 20 equivalents of HBpin.

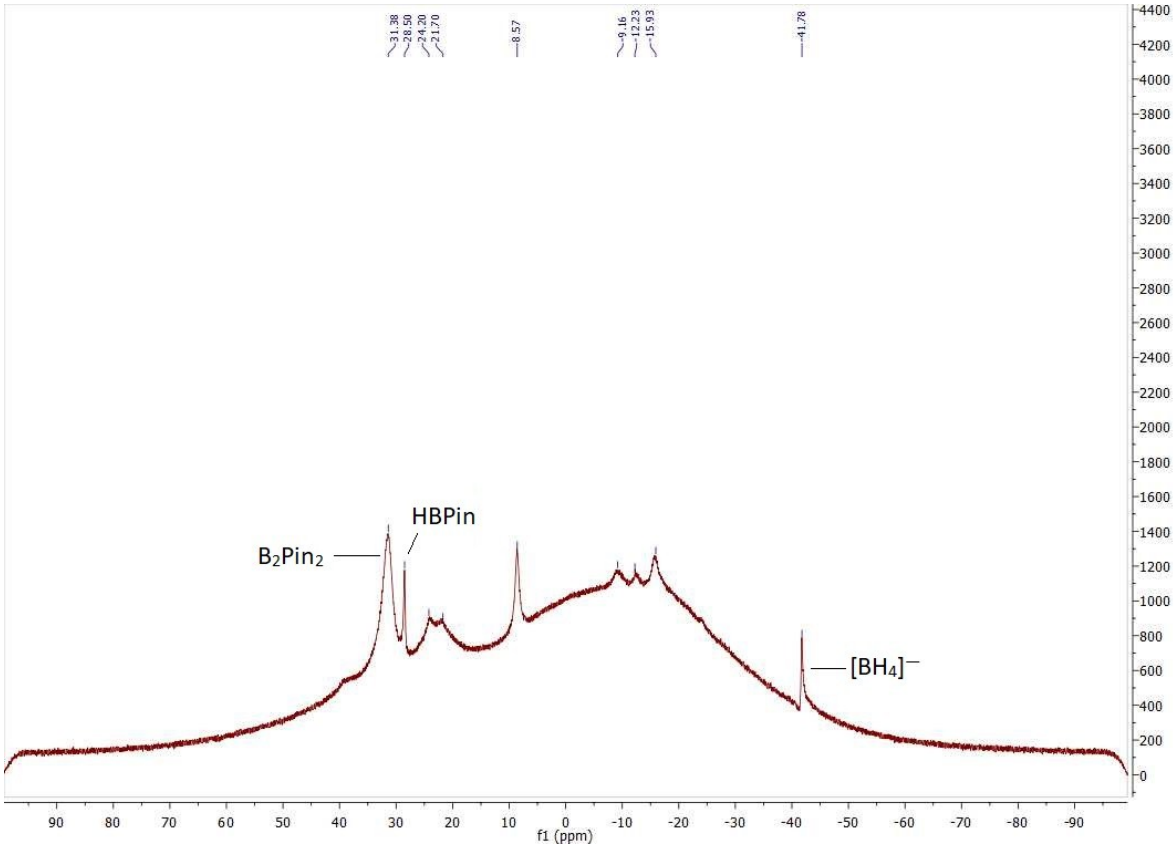

Figure S12. ^{11}B{^{1}H} NMR spectrum of the total non-volatile residue remaining after preliminary work-up of the reaction between [{(^{Mes}Nacnac)Mg–}$_2$] and 20 equivalents of HBpin.

Reactions involving [{(DepNacnac)Mg–}2]

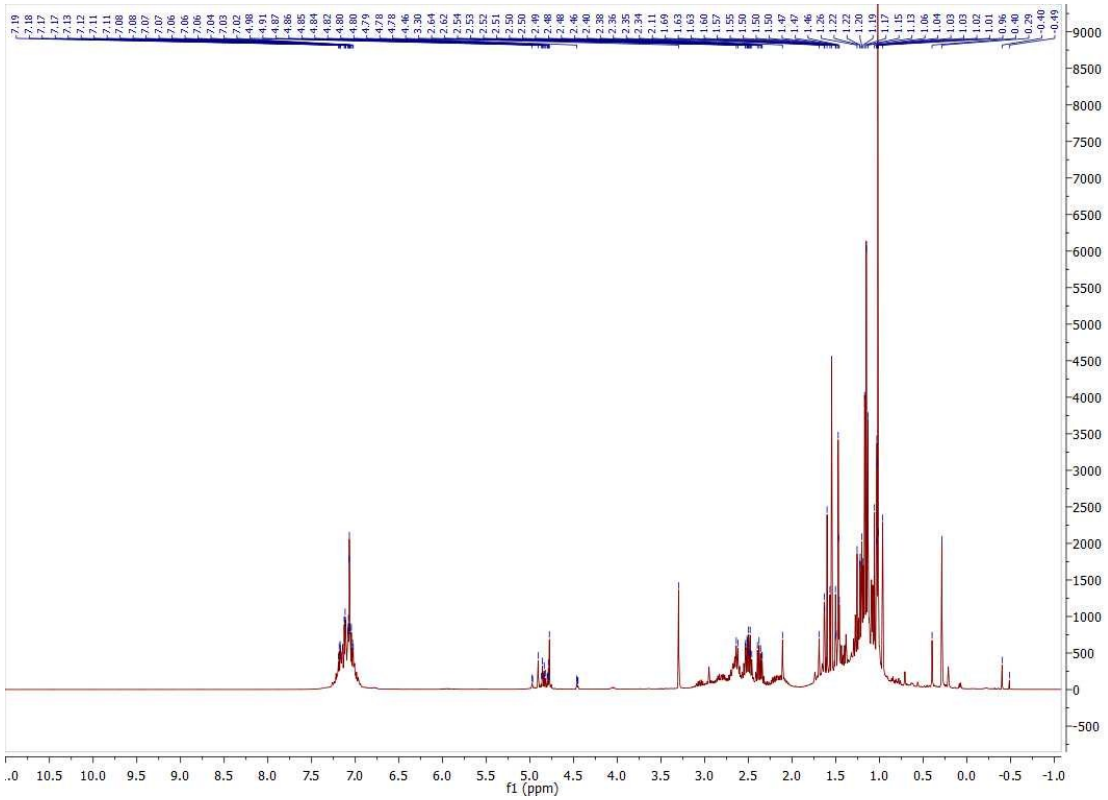

Figure S13. ^{1}H NMR spectrum of the total non-volatile residue remaining after preliminary work-up of the reaction between [{(DepNacnac)Mg–}$_2$] and 2 equivalents of HBpin.

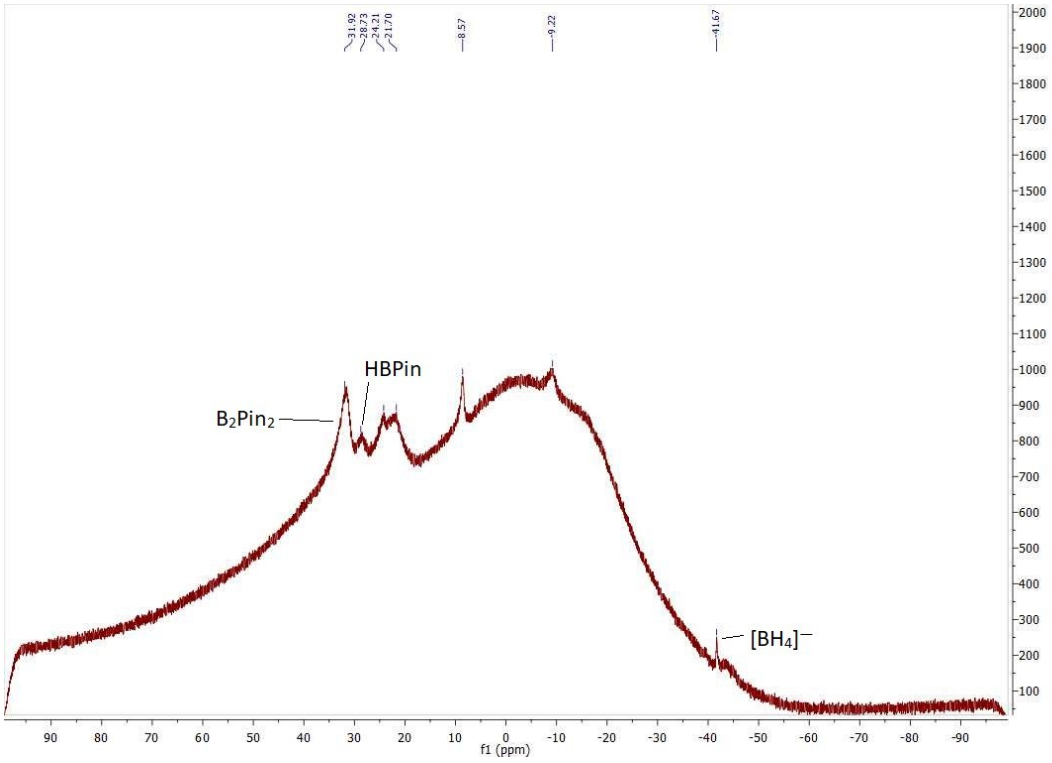

Figure S14. ^{11}B{^{1}H} NMR spectrum of the total non-volatile residue remaining after preliminary work-up of the reaction between [{(DepNacnac)Mg–}$_2$] and 2 equivalents of HBpin.

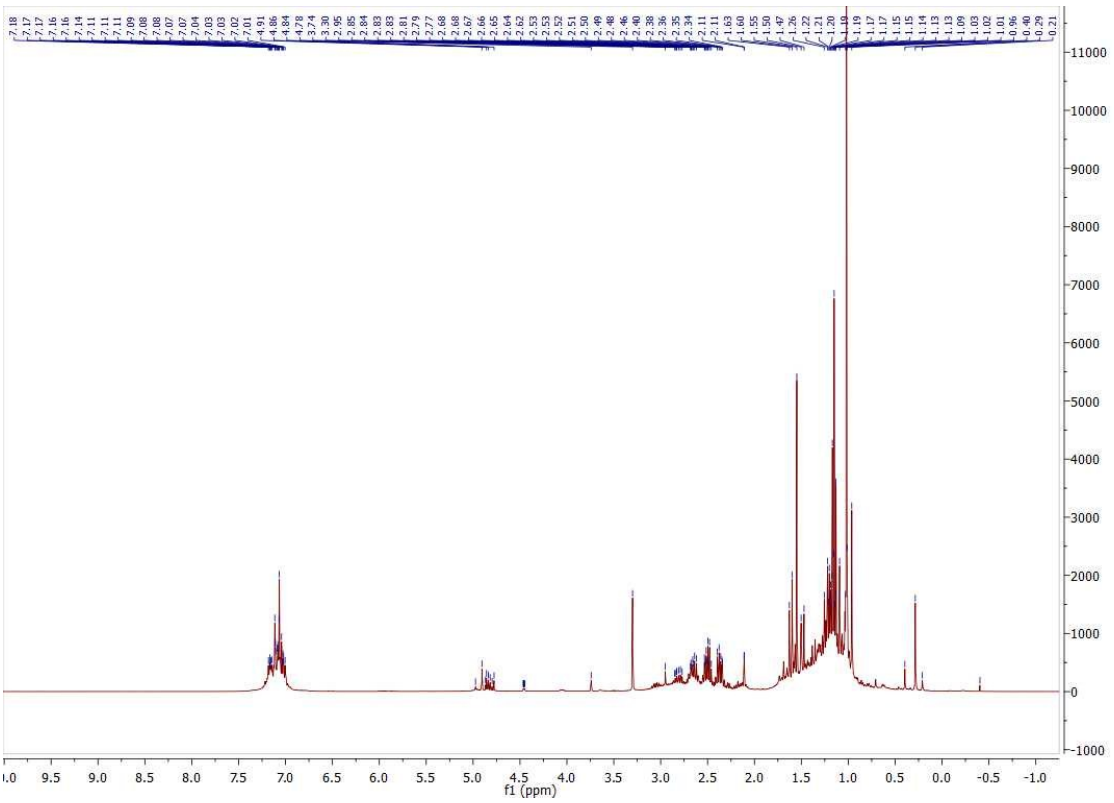

Figure S15. ^{1}H NMR spectrum of the total non-volatile residue remaining after preliminary work-up of the reaction between [{(^{Dep}Nacnac)Mg–}$_2$] and 5 equivalents of HBpin.

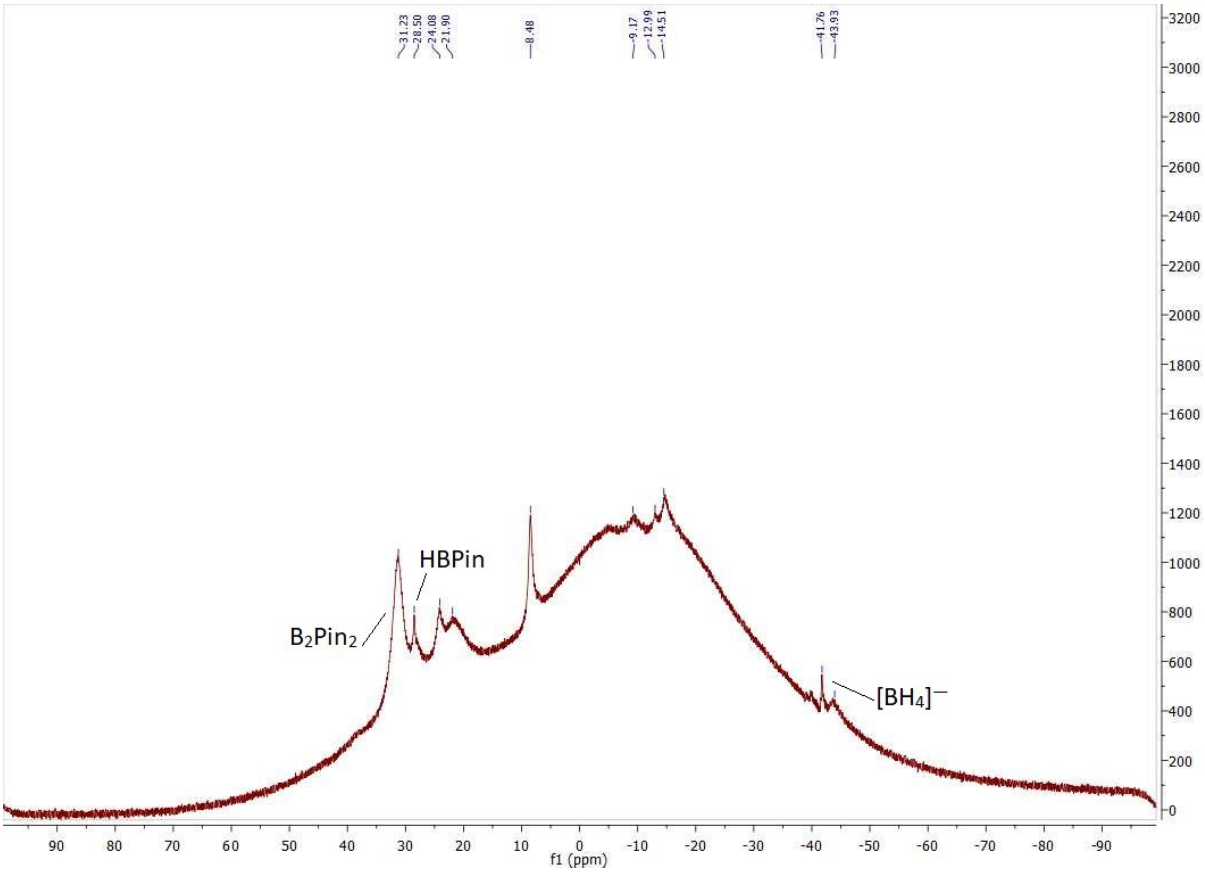

Figure S16. ^{11}B{^{1}H} NMR spectrum of the total non-volatile residue remaining after preliminary work-up of the reaction between [{(^{Dep}Nacnac)Mg–}$_2$] and 5 equivalents of HBpin.

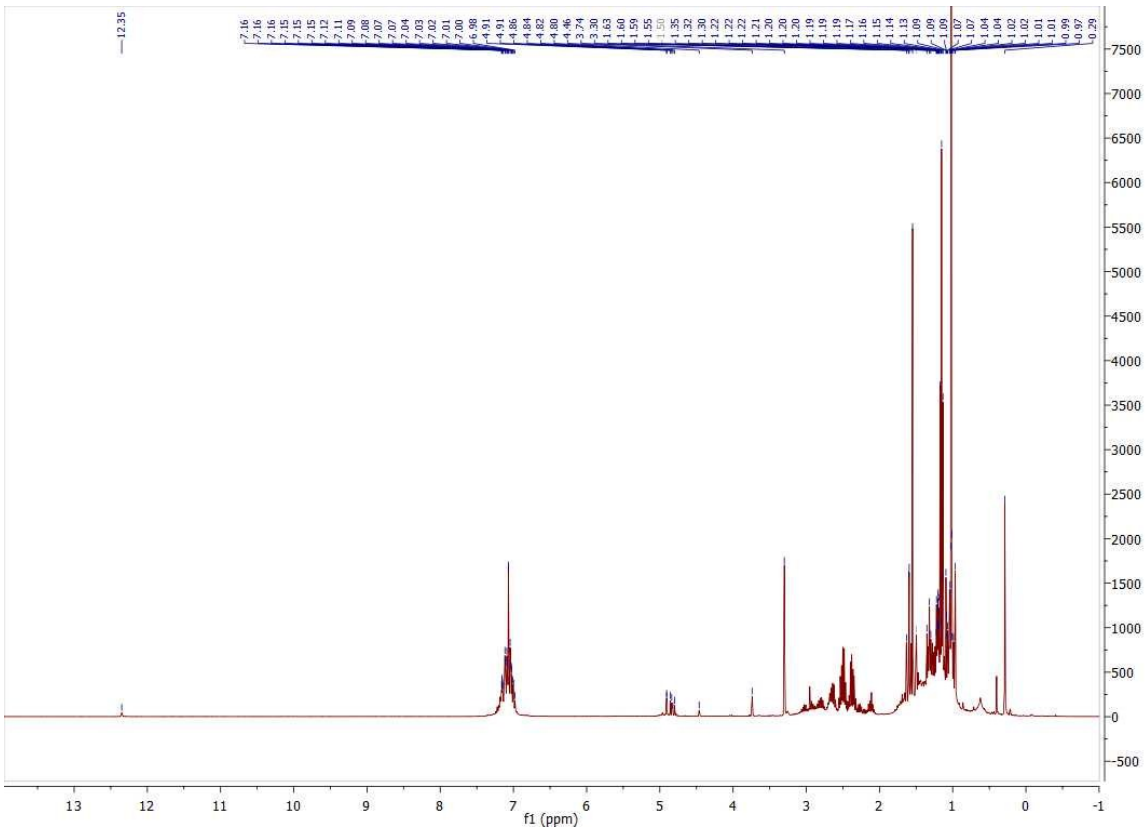

Figure S17. ^{1}H NMR spectrum of the total non-volatile residue remaining after preliminary work-up of the reaction between [{(^{Dep}Nacnac)Mg–}$_2$] and 20 equivalents of HBpin.

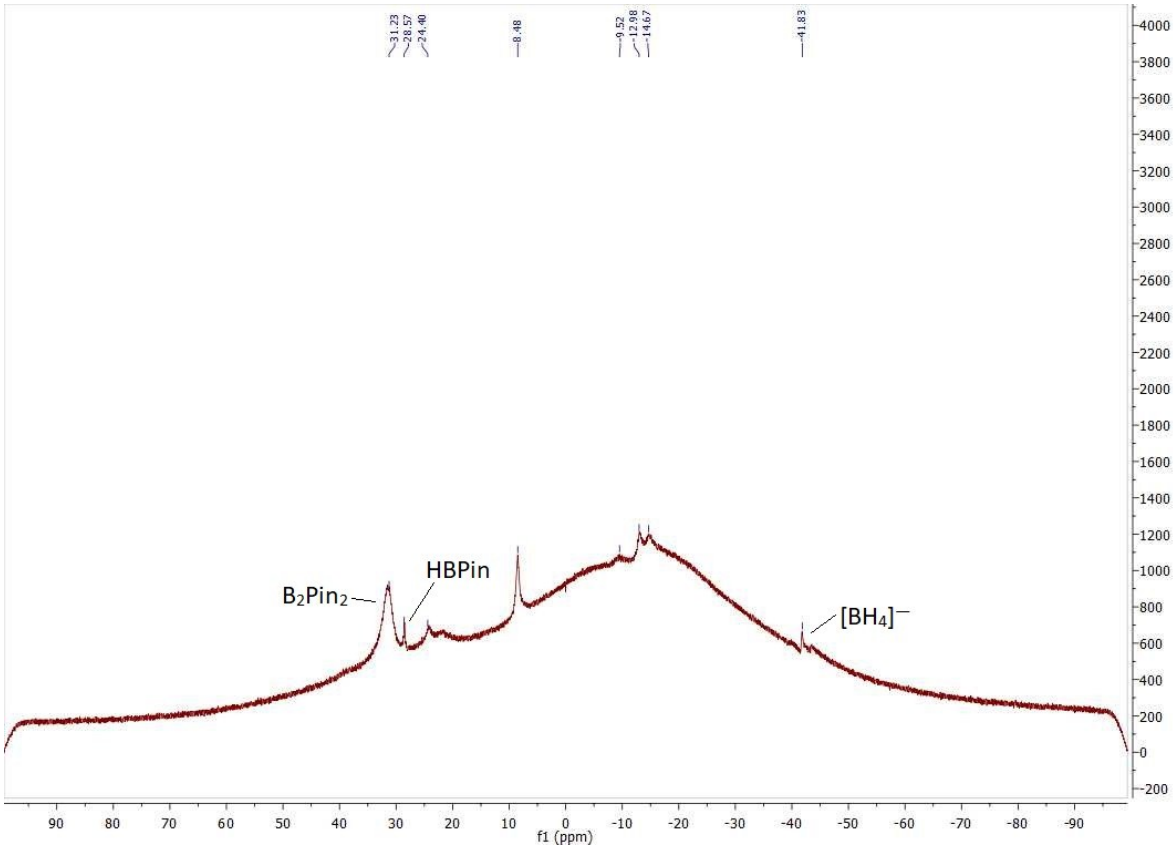

Figure S18. ^{11}B{^{1}H} NMR spectrum of the total non-volatile residue remaining after preliminary work-up of the reaction between [{(^{Dep}Nacnac)Mg–}$_2$] and 20 equivalents of HBpin.

Synthesis of compound 5. [{(^{Xyl}Nacnac)Mg–}$_2$] (100 mg, 0.151 mmol) was dissolved in toluene (20 mL) and cooled to -78 °C. HBpin (44µL, 0.302 mmol) was added *via* a micro-syringe and the resultant solution was allowed to warm to room temperature and stirred overnight. Volatiles were then removed *in vacuo* and the residue extracted with n-hexane (2 x 15 mL). The extract was concentrated to *ca.* 5 mL, filtered and the filtrate stored at -30 °C overnight, yielding a few small colourless crystals of **5**. Spectrosciopic data could not be obtained on the compound due to its very low yield.

Synthesis of compound 6. [{(^{Mes}Nacnac)Mg–}$_2$] (100 mg, 0.140 mmol) was dissolved in toluene (20 mL) and cooled to -78 °C. HBpin (41µL, 0.280 mmol) was added *via* a micro-syringe and the resultant solution was allowed to warm to room temperature and stirred overnight. Volatiles were then removed *in vacuo* and the residue extracted with n-hexane (2 x 15 mL). The extract was concentrated to *ca.* 5 mL, filtered and the filtrate stored at -30 °C overnight, yielding a few small colourless crystals of **6**. Spectrosciopic data could not be obtained on the compound due to its very low yield.

Synthesis of compound 8 and 10. [{(^{Xyl}Nacnac)Mg–}$_2$] (100 mg, 0.151 mmol) was dissolved In toluene (20 mL) and cooled to -78 °C. HBpin (110µL, 0.758 mmol) was added *via* micro-syringe and the resultant solution was allowed to warm to room temperature and stirred overnight. Volatiles were then removed *in vacuo* and the residue extracted with n-hexane (2 x 15 mL). The solution was concentrated to *ca.* 5 mL, filtered, and the filtrate stored at -30 °C overnight, yielding small colourless crystals of compound **8** (7 mg, 5%). Filtration and further concentration of the mother liquor yielded colourless crystals of compound **10** (37 mg, 27%). Further concentration allowed the isolation of crystalline B_2pin_2 (18 mg) which was confirmed by x-ray crystallography.

Data for compound **8**: ^{1}H NMR (400 MHz, 298 K, C_6D_6) assigned from a sample containg some impurities δ = 0.99 (s, 24H, OC(C*H*$_3$)$_2$), 1.50 (s, 12H, NCC*H*$_3$), 2.07 (s, 24H, *o*-ArC*H*$_3$), 4.85 (s, 2H, NCC*H*), 6.86-7.15 (m, 12H, Ar*H*). ^{13}C{^{1}H} NMR (75 MHz, 298 K, C_6D_6); δ = 18.6 (C(*C*H$_3$)$_2$), 23.3 (NC*C*H$_3$), 24.8 (Ar*C*H$_3$), 81.2 (O*C*(CH$_3$)$_2$), 95.4 (NC*C*H), 123.7, 129.0, 132.6, 148.8 (Ar*C*), 168.0 (N*C*CH); ^{11}B{^{1}H} NMR: no signals observed.

Data for compound **10**: 121-124 °C (decomp). ^{1}H NMR (400 MHz, 298 K, C_6D_6) δ = 0.51 (s, 6H, C*H*$_3$), 0.99 (s, 6H, C*H*$_3$), 1.03 (s, 6H, C*H*$_3$), 1.22 (s, 6H, C*H*$_3$), 1.60 (s, 6H, NCC*H*$_3$), 1.61 (s, 6H, NCC*H*$_3$), 2.06 (s, 6H, ArC*H*$_3$), 2.16 (s, 6H, ArC*H*$_3$), 2.22 (s, 6H, ArC*H*$_3$), 2.39 (s, 6H, ArC*H*$_3$), 3.27 (s, 1H, C(BH$_2$)*H*), 4.90 (s, 1H, NCC*H*), 6.98 – 7.15 (m, 12H, Ar*H*), signals for BH fragments were not observed; ^{13}C{^{1}H} NMR (75 MHz, 298 K, C_6D_6) δ = 18.8 (*C*H$_3$), 20.0 (*C*H$_3$), 20.5 (*C*H$_3$), 20.9 (*C*H$_3$), 23.3 (NC*C*H$_3$), 24.2 (overlapping signals for NC*C*H$_3$ and Ar*C*H$_3$), 24.3 (Ar*C*H$_3$), 24.5

(Ar*C*H_3), 24.9 (Ar*C*H_3), 26.5 (*C*(BH_2)H), 75.8 (BO*C*(CH_3)$_2$), 77.7 (BO*C*(CH_3)$_2$), 79.7 (BO*C*(CH_3)$_2$), 83.4 (BO*C*(CH_3)$_2$), 97.1 (NC*C*H), 124.0, 125.0, 128.5, 128.7, 128.8, 128.9, 130.2, 131.6, 132.0, 133.2, 146.8, 148.8 (Ar*C*), 168.7 (N*C*CH), 184.4 ((N*C*)$_2$CBH_2); $^{11}B\{^1H\}$ NMR (128 MHz, 298 K, C_6D_6), δ = -9.36 ((NC)$_2$C*B*H_2), -0.32 (*B*H_2Mg); IR ν/cm^{-1} (ATR): 2312 (B-H str), 2116 (B-H str), 1598 (w), 1566 (w), 1543 (m), 1458 (s), 1388 (m), 1366 (s), 1331 (m), 1229 (m), 1179 (m), 1159 (m), 1144 (m), 1095 (m), 1041 (m), 1009 (m), 953 (m), 919 (w), 851 (w), 830 (m), 756 (s), 698 (s); EI/MS (70e/V) m/s (%): 146.1 (MeCNXyl$^+$, 100), 329.2 (^{Xyl}NacnacMg$^+$, 70); accurate elemental analysis could not be obtained due to residual HBpin in the sample which could not be removed from the sample.

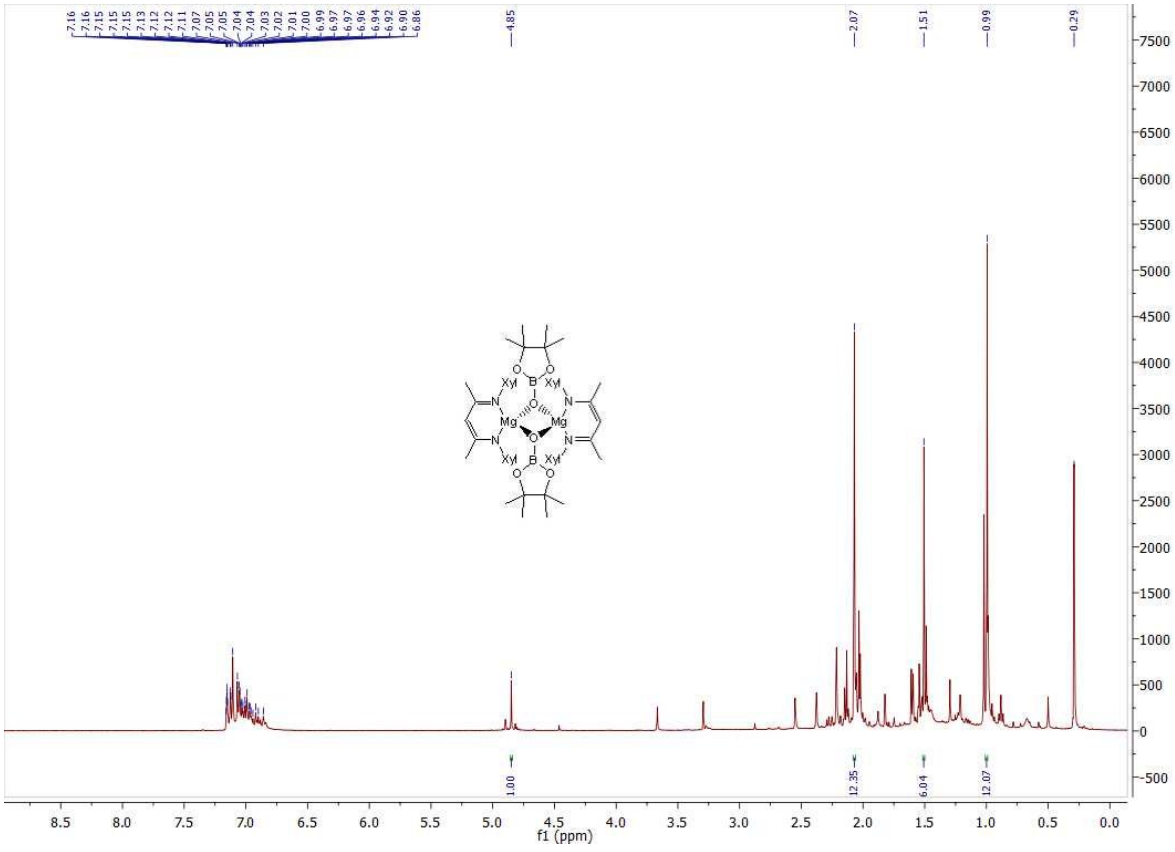

Figure S19. ^1H NMR spectrum (C_6D_6, 298 K) of a sample of **8**, containing impurities.

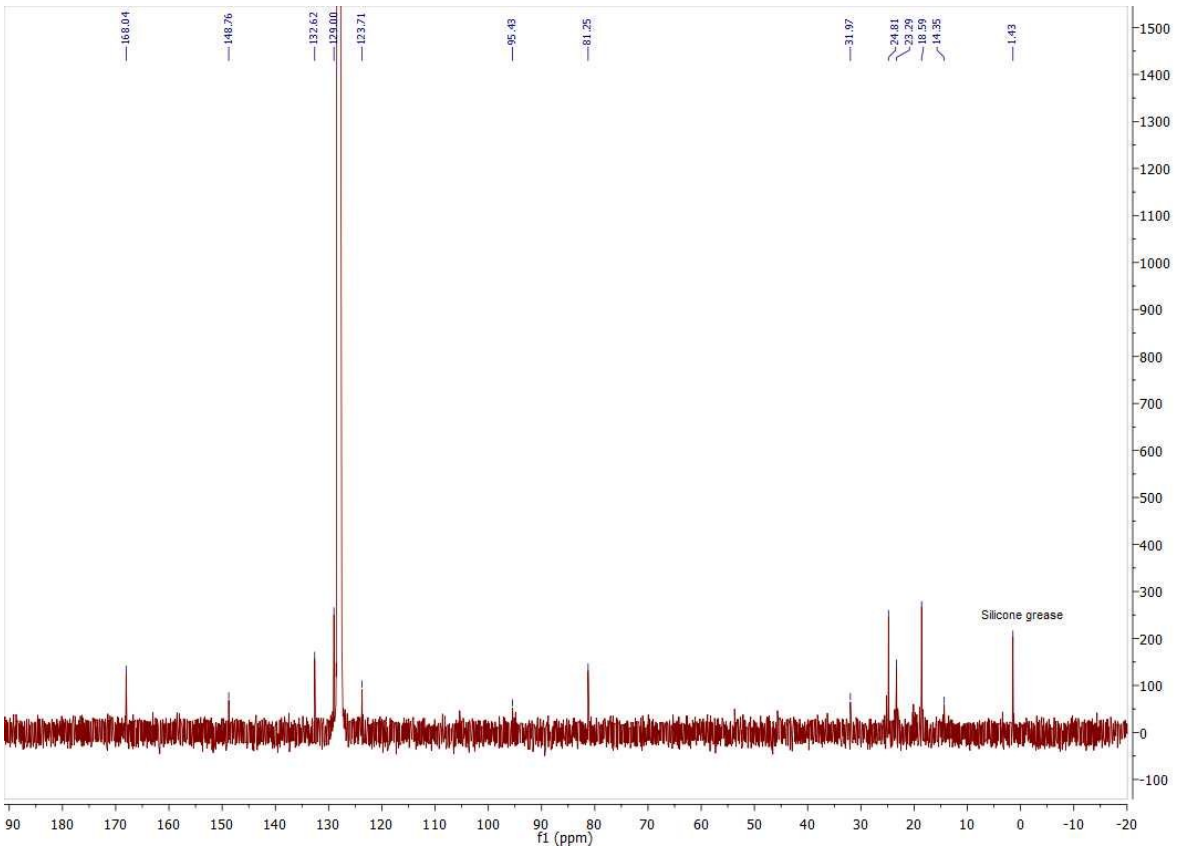

Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 298 K) of a sample of **8**, containing impurities.

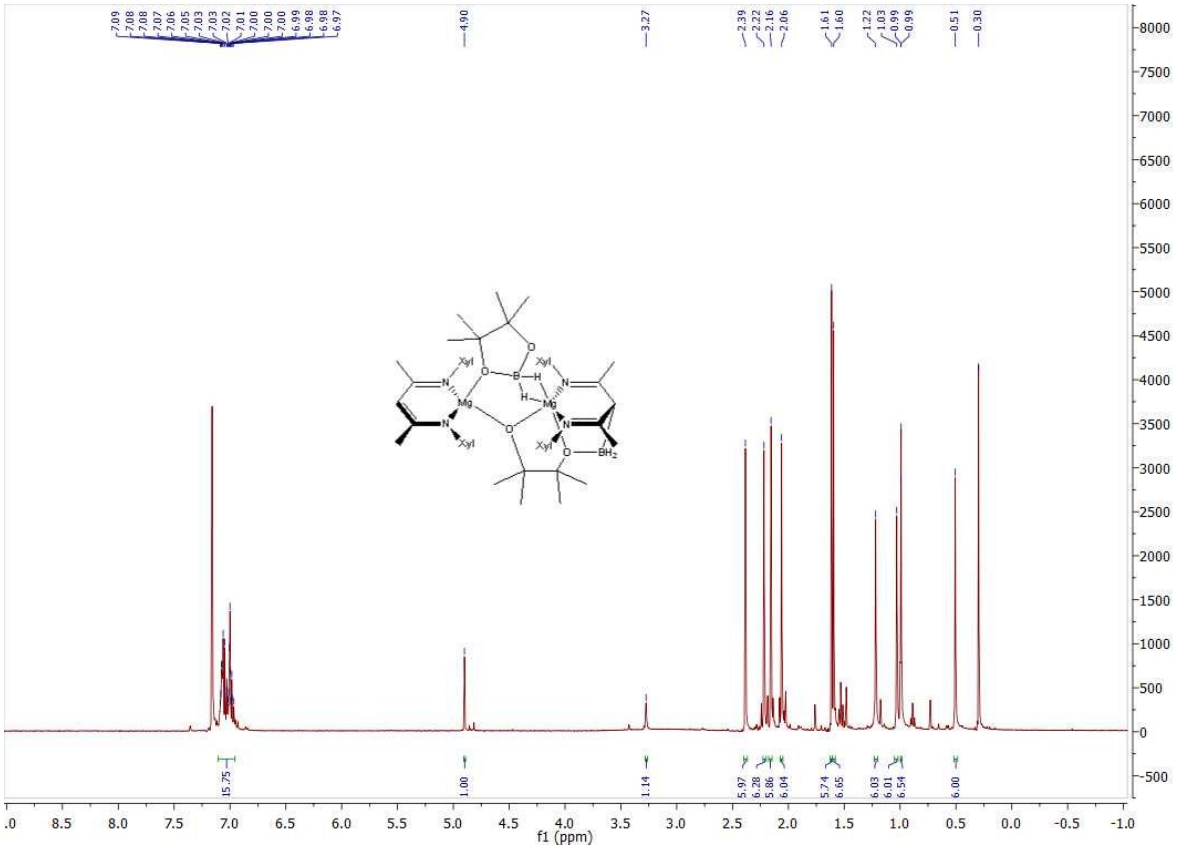

Figure S21. ^{1}H NMR spectrum (C_6D_6, 298 K) of a sample of **10**.

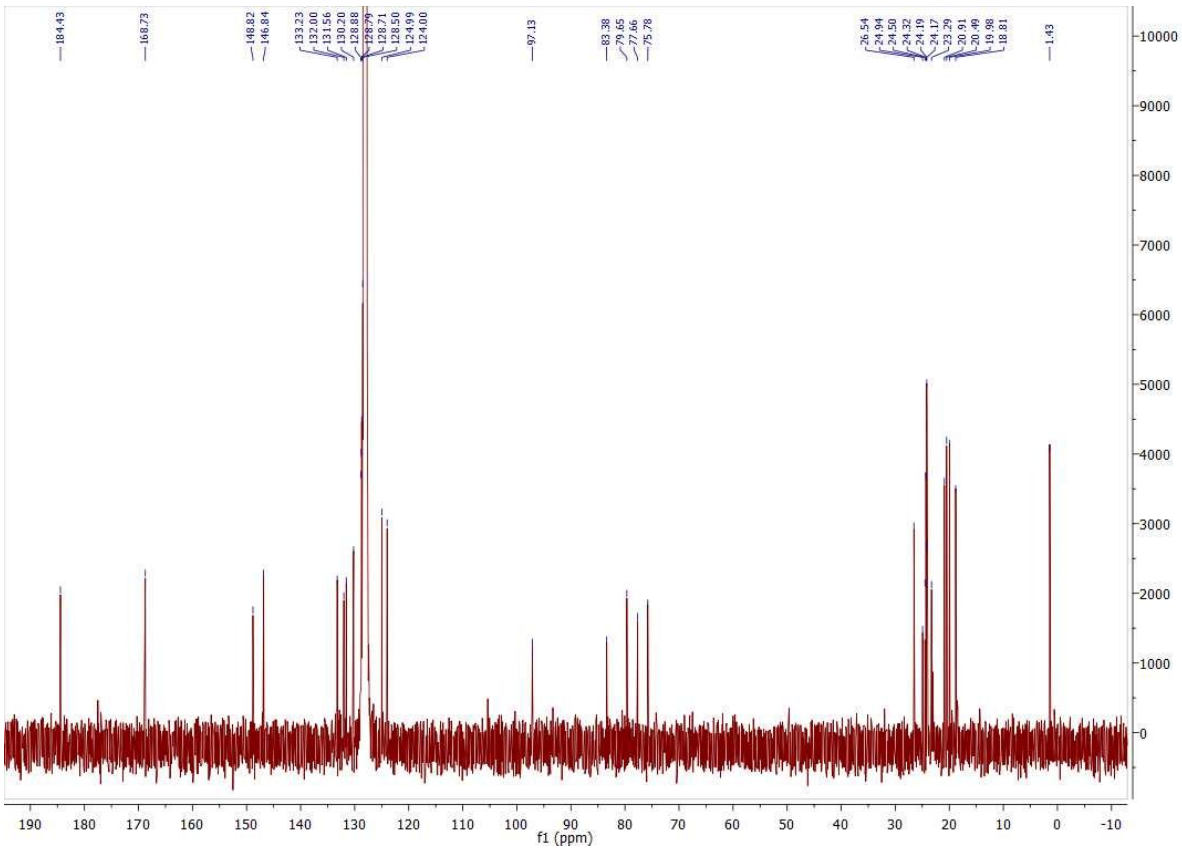

Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 298 K) of a sample of **10**.

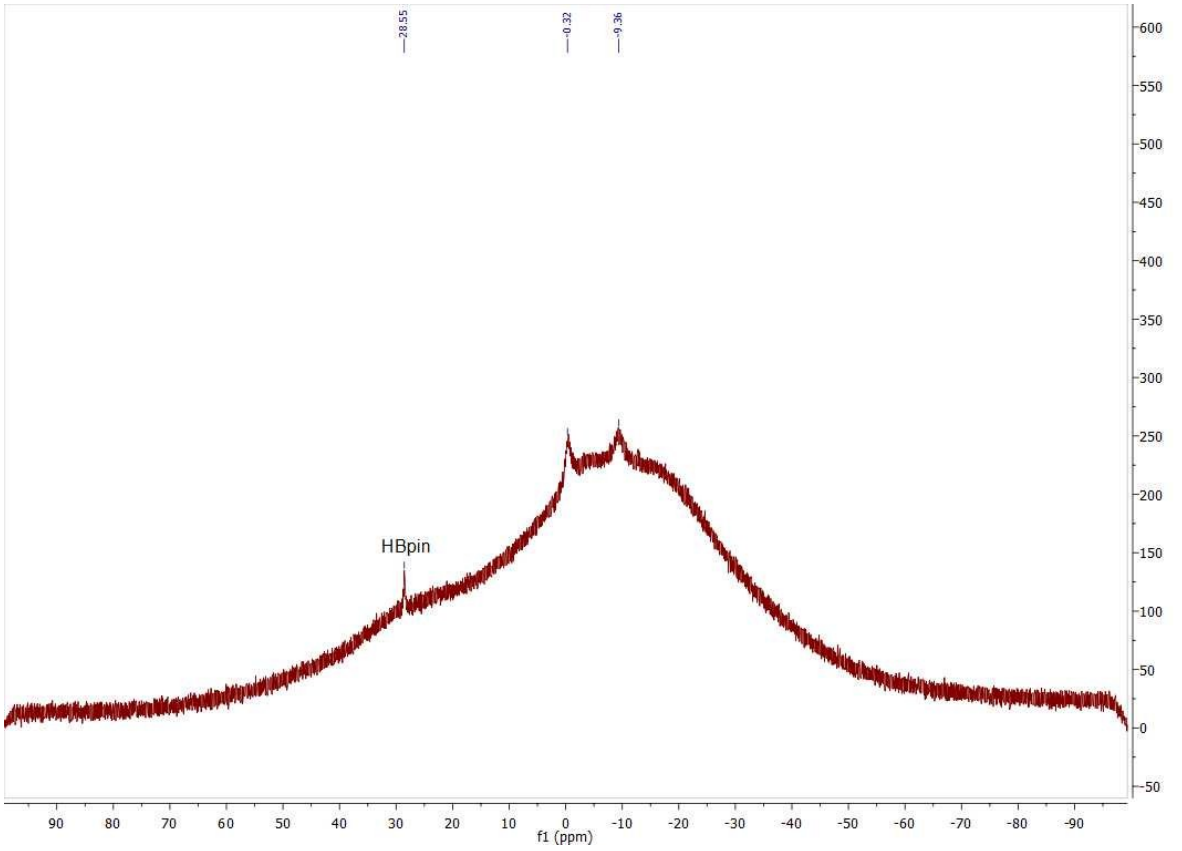

Figure S23. $^{11}B\{^{1}H\}$ NMR spectrum (C_6D_6, 298 K) of a sample of **10**.

Synthesis of compound 9 and 11. [{(^{Mes}Nacnac)Mg–}$_2$] (100 mg, 0.140 mmol) was dissolved In toluene (20 mL) and cooled to -78 °C. HBpin (101µL, 0.700 mmol) was added *via* micro-syringe and the resultant solution warmed to room temperature and stirred overnight. Volatiles were then removed *in vacuo* and the residue extracted with n-hexane (2 x 15 mL). The extract was concentrated, filtered, and the filtrate stored at -30 °C, yielding small colourless crystals of compound **9** (4 mg, 3 % yield). Filtration and further concentration of the mother liquor yielded another crop of colourless crystals of compound **11** (43 mg, 32 % yield).

Data for compound **9**: ^{1}H NMR (400 MHz, 298 K, C_6D_6); assigned from a sample containg some impurities δ = 1.02 (s, 24H, BOC(C*H*$_3$)$_2$), 1.57 (s, 12H, NCC*H*$_3$), 2.08 (s, 24H, *o*-ArC*H*$_3$), 2.42 (s, 12H, *p*-ArC*H*$_3$), 4.88 (s, 1H, NCC*H*), 6.95 (s, 8H, Ar*H*); ^{13}C{^{1}H} NMR (75 MHz, 298 K, C_6D_6) δ = 18.6 (BOC(*C*H$_3$)$_2$), 21.2 (Ar*C*H$_3$), 23.3 (NC*C*H$_3$), 24.8 (Ar*C*H$_3$), 81.2 (BO*C*(CH$_3$)$_2$), 95.3 (NC*C*H), 129.6, 132.0, 132.3, 146.1 (Ar*C*), 168.2 (N*C*CH); ^{11}B{^{1}H} NMR: no signals observed.

Data for compound **11**: M.p. 160-163 °C (decomp). ^{1}H NMR (400 MHz, 298 K, C_6D_6); δ = 0.53 (s, 6H, C*H*$_3$), 0.98 (s, 6H, C*H*$_3$), 1.05 (s, 6H, C*H*$_3$), 1.24 (s, 6H, C*H*$_3$), 1.65 (s, 6H, NCC*H*$_3$), 1.67 (s, 6H, NCC*H*$_3$), 2.07 (s, 6H, ArC*H*$_3$), 2.16 (s, 6H, ArC*H*$_3$), 2.22 (s, 6H, ArC*H*$_3$), 2.26 (s, 6H, ArC*H*$_3$), 2.30 (s, 6H, ArC*H*$_3$), 2.38 (s, 6H, ArC*H*$_3$), 3.30 (s, 1H, C(BH$_2$)*H*), 4.93 (s, 1H, NCC*H*), 6.81 (s, 2H, Ar*H*), 6.88 (s, 2H, Ar*H*), 6.91 (s, 2H, Ar*H*), 6.93 (s, 2H, Ar*H*); signals for BH fragments were not observed; ^{13}C{^{1}H} NMR (75 MHz, 298 K, C_6D_6) δ = 18.8 (*C*H$_3$), 20.0 (*C*H$_3$), 20.4 (*C*H$_3$), 20.9 (*C*H$_3$), 23.1 (NC*C*H$_3$), 23.2 (NC*C*H$_3$), 24.1 (Ar*C*H$_3$), 24.2 (Ar*C*H$_3$), 24.3 (Ar*C*H$_3$), 24.5 (Ar*C*H$_3$), 25.0 (Ar*C*H$_3$), 26.6 (Ar*C*H$_3$), 27.5 (*C*(BH$_2$)H), 75.8 (BO*C*(CH$_3$)$_2$), 77.7 (BO*C*(CH$_3$)$_2$), 79.7 (BO*C*(CH$_3$)$_2$), 83.2 (BO*C*(CH$_3$)$_2$), 97.1 (NC*C*H), 129.1, 129.4, 129.5, 129.6, 129.9, 131.3, 131.7, 132.7, 132.9, 133.7, 144.5, 146.4 (Ar*C*), 168.7 (N*C*CH), 184.5 ((N*C*)$_2$C(BH$_2$)H); ^{11}B{^{1}H} NMR (128 MHz, 298 K, C_6D_6) δ = -9.34 (C(*B*H$_2$)H), -0.22 (*B*H$_2$Mg). IR ν/cm^{-1} (ATR): 2292 (B-H str), 2120 (B-H str), 1621 (w), 1593 (w), 1508 (m), 1474 (m), 1447 (m), 1385 (s), 1363 (s), 1251 (m), 1195 (s), 1144 (s), 1059 (m), 1012 (m), 954 (m), 916 (w), 890 (w), 853 (s), 815 (w), 761 (w), 733 (m), 700 (m); EI/MS (70e/V) m/s (%): 160.1 (MeCNMes$^+$, 100), (^{Mes}NacnacMg$^+$, 52), 500.4 (^{Mes}NacnacMgH$_2$Bpin$^+$, 7); accurate elemental analysis could not be obtained due to residual HBpin in the sample which could not be removed from the sample.

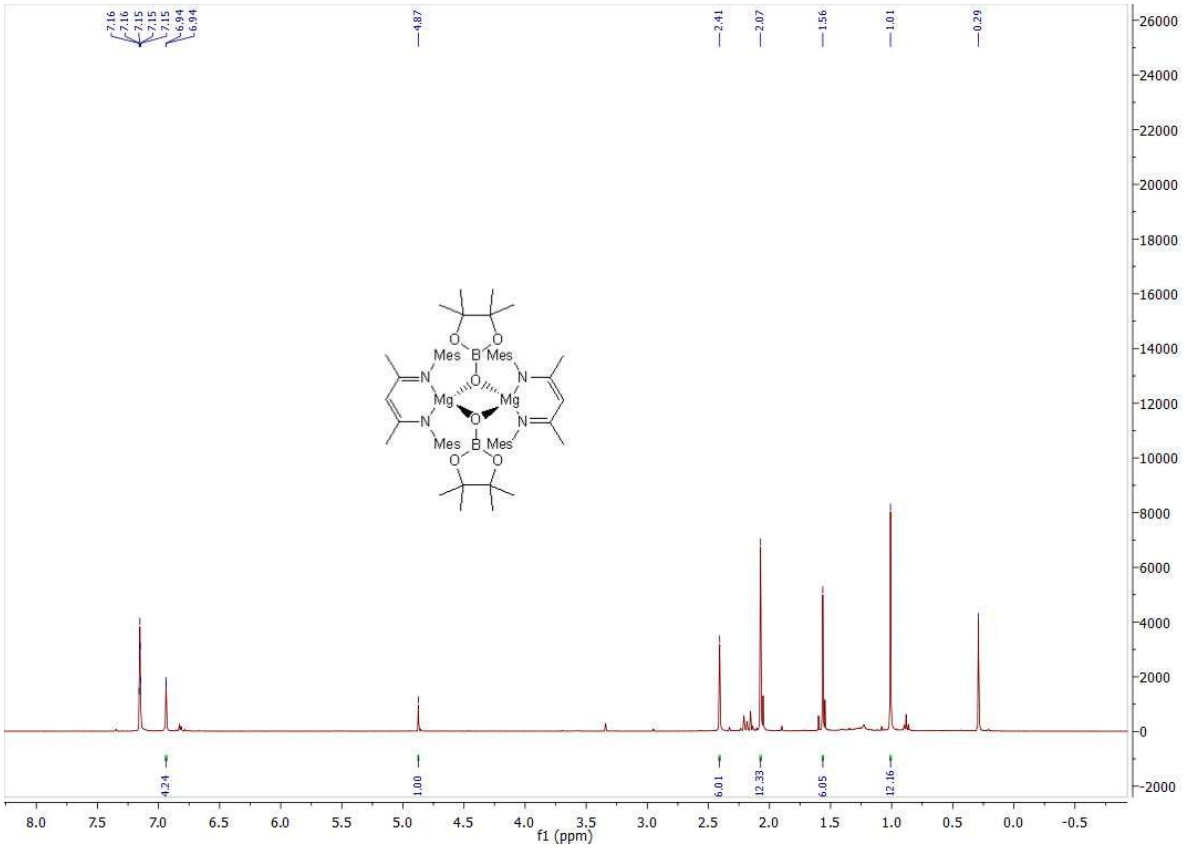

Figure S24. ^{1}H NMR spectrum (C_6D_6, 298 K) of a sample of **9**, containing impurities.

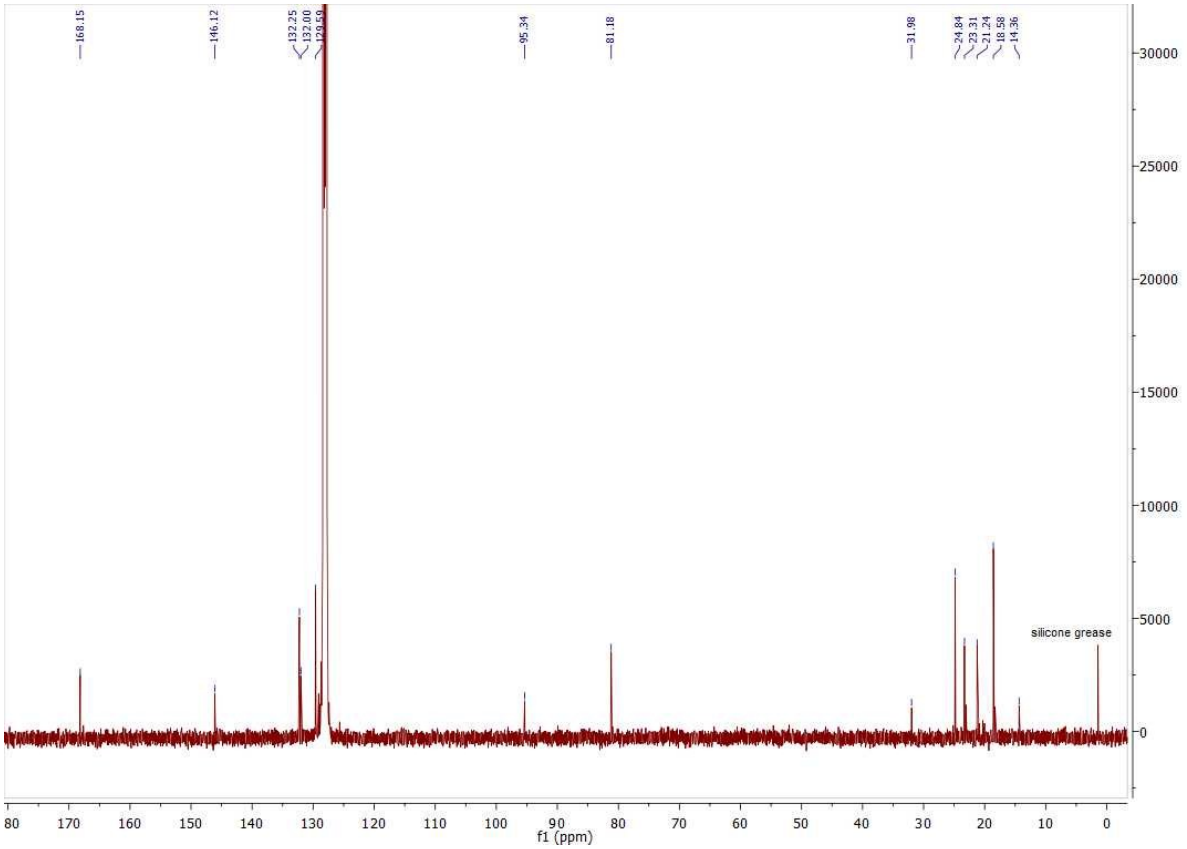

Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 298 K) of a sample of **9**, containing impurities.

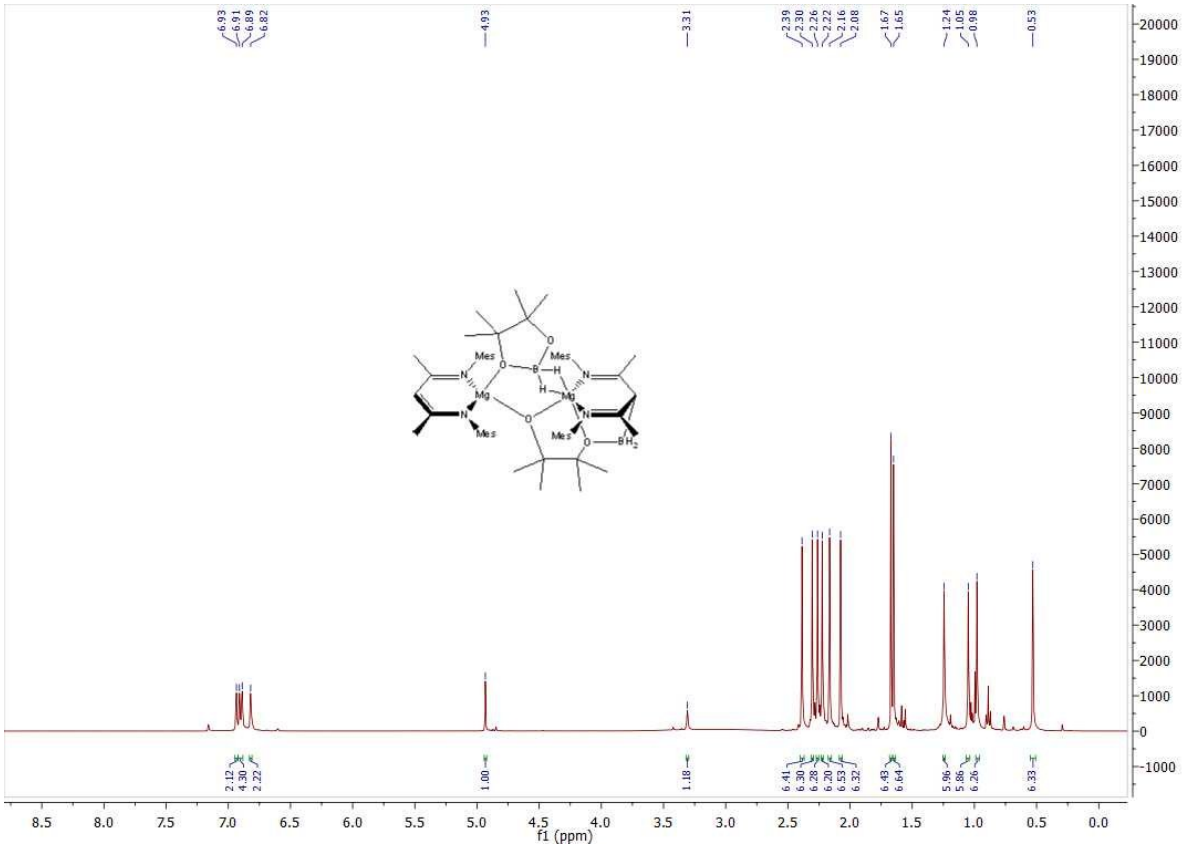

Figure S26. ^{1}H NMR spectrum (C_6D_6, 298 K) of a sample of **11**.

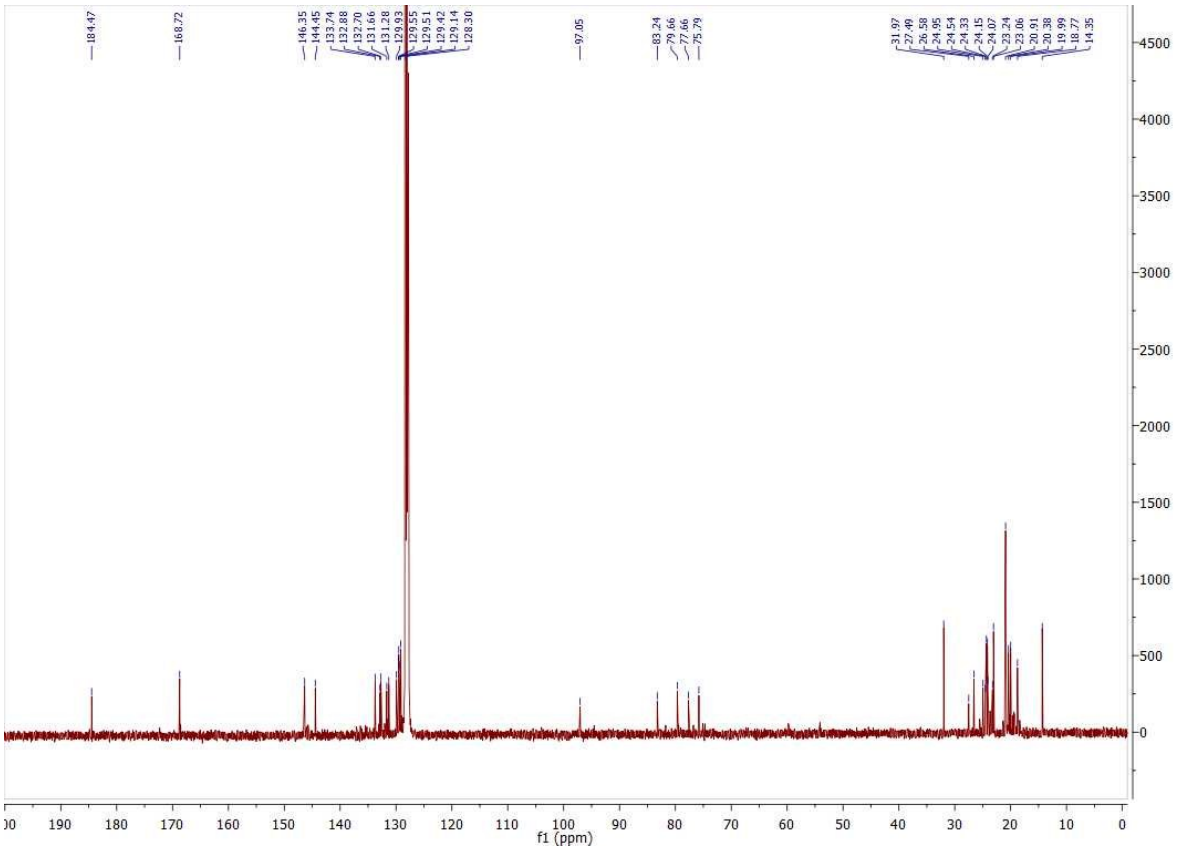

Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 298 K) of a sample of **11**.

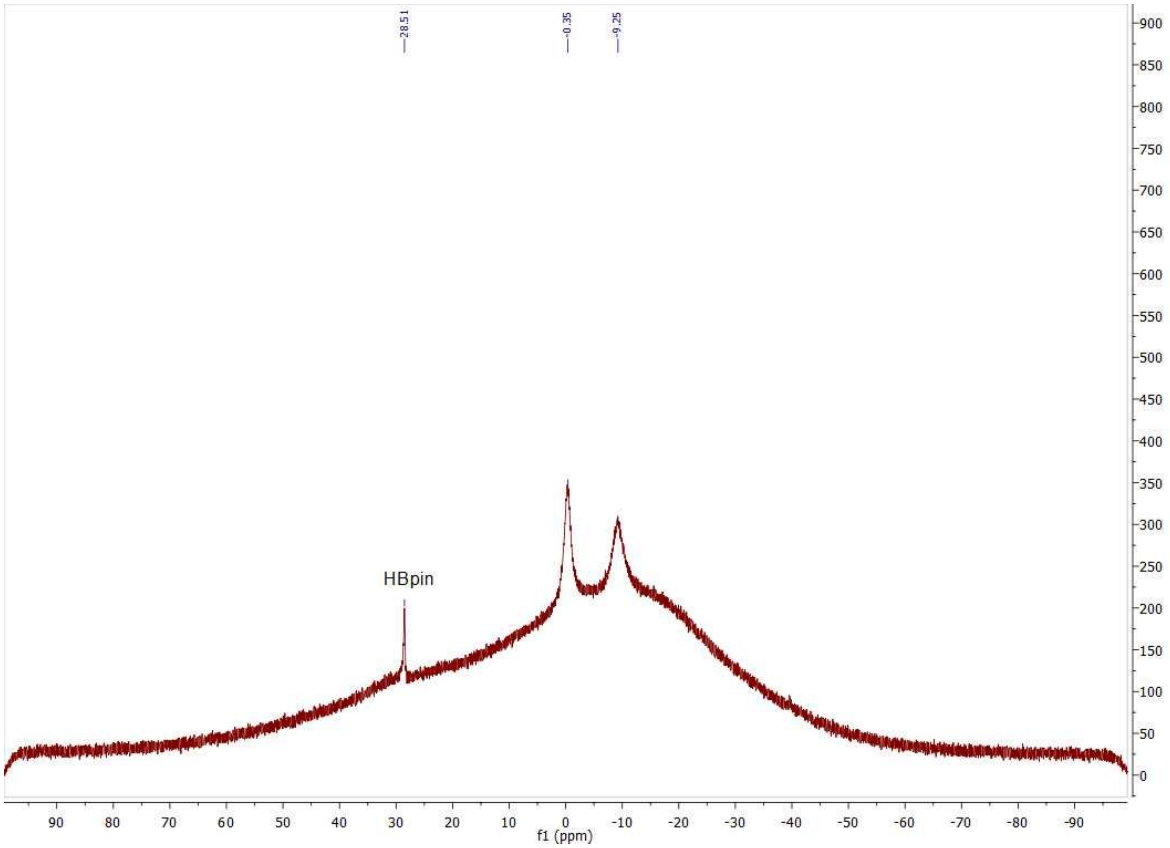

Figure S28. $^{11}B\{^{1}H\}$ NMR spectrum (C_6D_6, 298 K) of a sample of **11**.

Synthesis of compound 12. [{(^{Mes}Nacnac)Mg–}$_2$] (100 mg, 0.140 mmol) was dissolved in toluene (20 mL) and the solution cooled to -78 °C. HBpin (0.41 mL, 2.82 mmol) was added dropwise *via* syringe and the resultant solution was allowed to warm to room temperature and stirred overnight. Volatiles were then removed *in vacuo* and the residue extracted with n-hexane (2 x 15 mL). The extract was concentrated, filtered, and the filtrate stored at -30 °C overnight, yielding a few small colourless crystals of **12**. Spectrosciopic data could not be obtained on the compound due to its very low yield.

Synthesis of compound 13. [{(^{Dep}Nacnac)Mg–}$_2$] (100 mg, 0.130 mmol) was dissolved in toluene (20 mL) and the solution cooled to -78 °C. HBpin (0.38 mL, 2.62 mmol) was added dropwise *via* syringe and the resultant solution was allowed to warm to room temperature and stirred overnight. Volatiles were then removed *in vacuo* and the residue extracted with n-hexane (2 x 15 mL). The extract was concentrated, filtered, and the filtrate stored at -30 °C overnight, yielding a few small colourless crystals of **13**. Spectrosciopic data could not be obtained on the compound due to its very low yield.

Synthesis of compound 14 and 15. [{(^{Xyl}Nacnac)Mg–}$_2$] (100 mg, 0.151 mmol) was dissolved in toluene (20 mL) and the solution cooled to -78 °C. HBpin (0.47 mL, 3.03 mmol) was added dropwise *via* syringe and the resultant solution was allowed to warm to room temperature and stirred overnight. Volatiles were then removed *in vacuo* and the residue extracted with n-hexane (2 x 15 mL). The extract was concentrated, filtered, and the filtrate stored at -30 °C overnight, yielding a few small colourless crystals of **14**. This compound could not be isolated cleanly but an ^{1}H NMR spectrum of an impure sample of the compound could be tentatively assigned. During one preparation of the compound, several crystals of **15** were isolated and crystallographically characterised. Spectrosciopic data could not be obtained for **15** due to its very low yield.

Data for compound **14**: ^{1}H NMR (400 MHz, 298 K, C_6D_6) assigned from a sample containg some impurities δ = 0.67 (br, 12H, BOC(C*H*$_3$)$_2$), 1.06 (s, 3H, B*H*$_3$) 1.45 (Br, 12H, BOC(C*H*$_3$)$_2$), 1.55 (s, 6H, NCC*H*$_3$), 1.83 (s, 6H, ArC*H*$_3$), 2.55 (s, 6H, ArC*H*$_3$), 3.25 (br, 1H, (C(BH$_3$)*H*), 6.84-6.99 (m, 6H, Ar*H*);); EI/MS (70e/V) *m/s* (%): 146.1 (MeCNXyl$^+$, 100), 306.2 (^{Xyl}Nacnac$^+$, 43), 329.2 (^{Xyl}NacnacMg$^+$, 55), 344.3 (Mg{(XylNCMe)$_2$(BH$_3$)CH}$^+$, 11); accurate elemental analysis could not be obtained due to several impurities present.

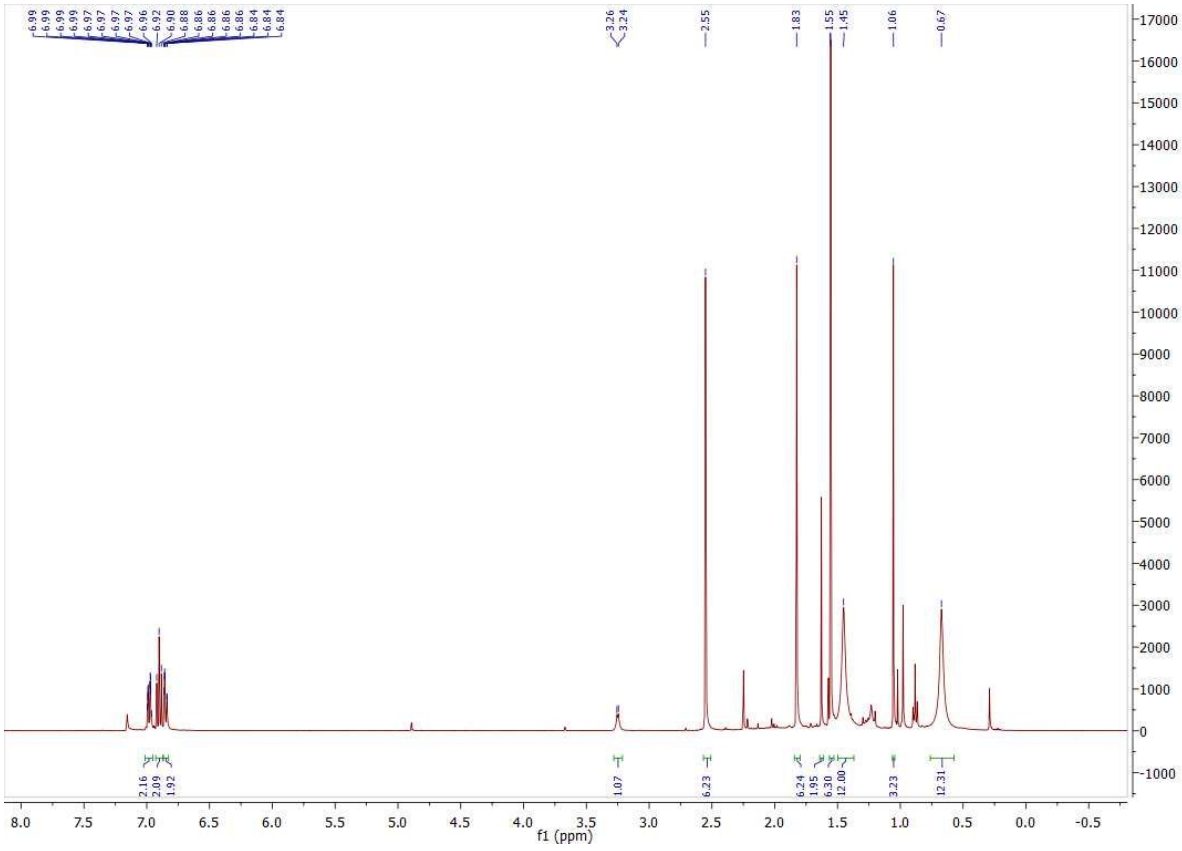

Figure S29. ^{1}H NMR spectrum (C_6D_6, 298 K) of an impure sample of **14**.

2. X-Ray Crystallography

Crystals of **5** and **8-15** suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using a Rigaku Xtalab Synergy Dualflex using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å) or Cu Kα radiation (1.54180 Å). All structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX-16[4]) using all unique data. Hydrogen atoms are typically included in calculated positions (riding model), with the exception of some hydride ligands, which were freely isotropically refined. Crystal data, details of data collections and refinements for all structures can be found in their CIF files and are summarized in Table S1.

Table S1. Crystal data for **5** and **8**-**15**.

	5	**8**	**9**	**10**·(hexane)	**11**·(hexane)$_{0.5}$
empirical formula	$C_{54}H_{76}B_2Mg_2N_4O_4$	$C_{54}H_{74}B_2Mg_2N_4O_6$	$C_{58}H_{82}B_2Mg_2N_4O_6$	$C_{60}H_{92}B_2Mg_2N_4O_4$	$C_{61}H_{93}B_2Mg_2N_4O_4$
formula weight	915.42	945.41	1001.51	1003.61	1016.63
crystal system	Triclinic	Orthorhombic	Monoclinic	Triclinic	Monoclinic
space group	*P*-1	*Pcba*	$P2_1/n$	*P*-1	$P2_1/c$
a (Å)	11.4535(7)	18.7772(2)	15.0677(3)	11.9366(2)	16.8368(2)
b (Å)	15.0953(8)	13.77780(10)	11.9199(2)	14.5020(2)	13.1697(2)
c (Å)	16.8124(10)	20.9610(2)	16.2820(4)	18.0950(3)	28.4900(2)
α (°)	78.411(5)	90	90	74.5840(10)	90
β (°)	74.116(5)	90	91.400(2)	84.6270(10)	102.4760(10)
γ (°)	73.622(5)	90	90	76.9510(10)	90
V (Å^3)	2658.1(3)	5422.79(9)	2923.46(10)	2939.77(8)	6168.07(13)
Z	2	4	2	2	4
T (K)	123(2)	123(2)	123(2)	123(2)	123(2)
ρ_{calcd} (g·cm^3)	1.144	1.158	1.138	1.134	1.095
μ (mm^{-1})	0.761	0.791	0.758	0.726	0.698
F(000)	988	2032	1080	1092	2212
reflns collected	37622	28499	28382	42346	51622
unique reflns	9552	4988	5315	10680	11421
R_{int}	0.1295	0.0456	0.1020	0.0379	0.0613
R1 [I > 2σ(I)]	0.1136	0.0484	0.0664	0.0425	0.0557
wR2 (all data)	0.2763	0.1368	0.1958	0.1163	0.1574
largest peak and hole (e·Å^{-3})	0.77, -0.77	0.38, -0.22	0.46, -0.24	0.47, -0.34	0.81, -0.29
CCDC no.	1902610	1902609	1902608	1902614	1902616

	12	**13**	**14**·(hexane)$_{0.33}$	**15**
empirical formula	$C_{35}H_{53}BMgN_2O_4$	$C_{37}H_{57}BMgN_2O_4$	$C_{35}H_{56.67}B_2MgN_2O_4$	$C_{54}H_{76}B_2Mg_2N_4O_5$
formula weight	600.91	628.96	615.42	931.42
crystal system	Orthorhombic	Orthorhombic	Triclinic	Triclinic
space group	*Fdd*2	*Pcba*	*P*-1	*P*-1
a (Å)	29.445(6)	19.8525(9)	10.05420(10)	13.8511(3)
b (Å)	70.806(14)	17.9603(9)	19.51950(10)	14.1433(3)
c (Å)	9.946(2)	20.4433(10)	28.2699(2)	27.5193(4)
α (º)	90	90	84.5010(10)	83.1000(10)
β (º)	90	90	81.4220(10)	82.2860(10)
γ (º)	90	90	85.5530(10)	84.312(2)
V (Å^3)	20736(7)	7289.2(6)	5449.46(7)	5284.66(18)
Z	24	8	6	4
T (K)	100(2)	123(2)	123(2)	123(2)
ρ_{calcd} (g·cm^3)	1.155	1.146	1.125	1.171
μ (mm^{-1})	0.090	0.722	0.709	0.789
F(000)	7824	2736	2008	2008
reflns collected	39551	35782	84461	78885
unique reflns	11264	6480	19775	19197
R_{int}	0.0358	0.0995	0.1074	0.1128
R1 [I > 2σ(I)]	0.0322	0.1017	0.0567	0.0738
wR2 (all data)	0.0837	0.3304	0.1636	0.2125
largest peak and hole (e·Å^{-3})	0.18, -0.29	0.78, -0.36	0.75, -0.40	1.18, -0.47
CCDC no.	1902615	1902611	1902612	1902613

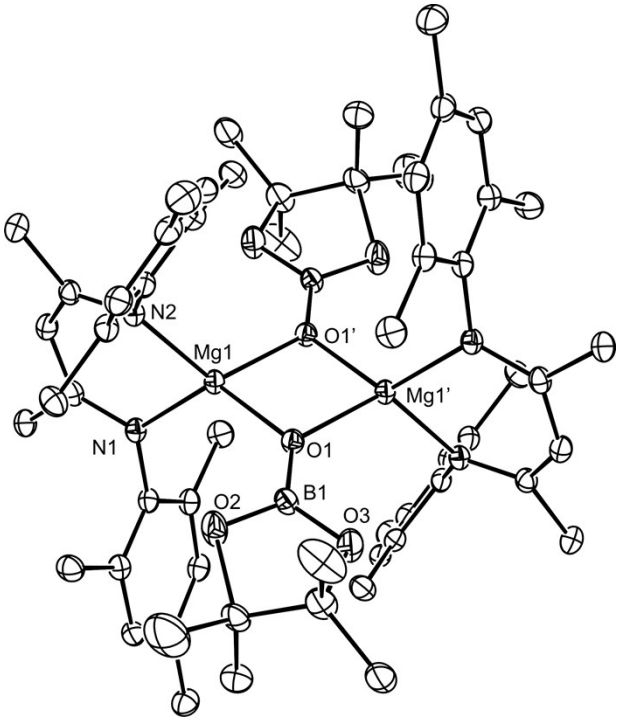

Figure S30. ORTEP diagram of compound **9** (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (º): Mg(1)-O(1) 1.9607(13), Mg(1)-O(1)' 1.9767(14), O(1)-B(1) 1.328(3), O(1)-Mg(1)-O(1)' 82.51(6), Mg(1)-O(1)-Mg(1)' 97.48(6).

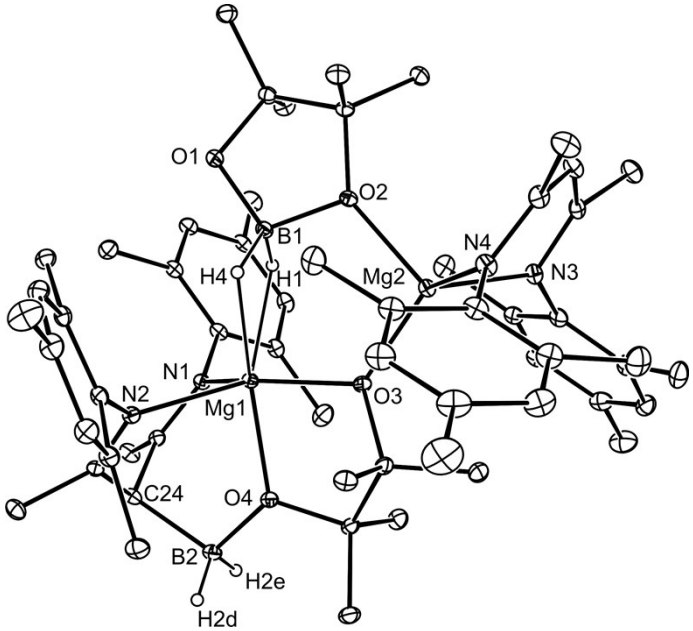

Figure S31. ORTEP diagram of compound **11** (25% thermal ellipsoids; hydrogen atoms, except hydrides, omitted). Selected bond lengths (Å) and angles (º): Mg(1)-O(3) 2.0057(14), Mg(1)-O(4) 2.0196(13), Mg(1)-H(1) 2.05(2), Mg(1)-H(4) 2.18(2), Mg(2)-O(3) 1.9482(13), Mg(2)-O(2) 2.0086(14), B(2)-O(4) 1.500(2), Mg(1)-O(3) 2.0057(14), Mg(1)-O(4) 2.0196(13), Mg(1)-H(1) 2.05(2), Mg(1)-H(4) 2.18(2), Mg(2)-O(3) 1.9482(13), Mg(2)-O(2) 2.0086(14), B(2)-O(4) 1.500(2), O(3)-Mg(1)-O(4)81.33(5), H(1)-Mg(1)-H(4)53.3(8), O(3)-Mg(2)-O(2)100.60(6).

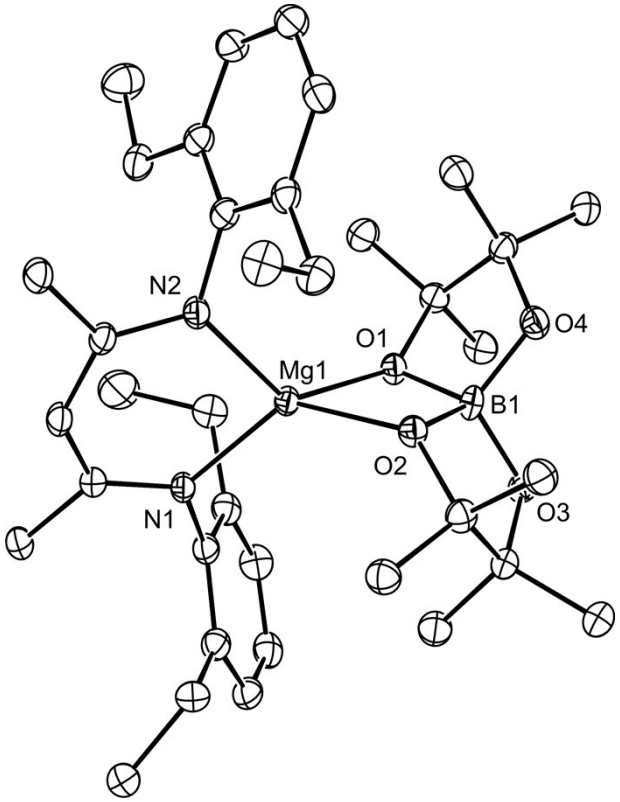

Figure S32. ORTEP diagram of compound **13** (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (º): Mg(1)-O(2) 2.000(3), Mg(1)-O(1) 2.029(3), O(1)-B(1) 1.528(6), B(1)-O(2) 1.502(6), O(2)-Mg(1)-O(1) 69.96(14), O(2)-B(1)-O(1) 99.4(3).

3. References

1. S. J. Bonyhady, D. Collis, N. Holzmann, A. J. Edwards, R. O. Piltz, G. Frenking, A. Stasch, C. Jones, *Nat. Commun.*, 2018, **9**, 3079.
2. S. J. Bonyhady, C. Jones, S. Nembenna, A. Stasch, A. J. Edwards, G. J. McIntyre, *Chem. Eur. J.*, 2010, **16**, 938.
3. R. Lalrempuia, C. E. Kefalidis, S. J. Bonhady, B. Schwarze, L. Maron, A. Stasch, C. Jones, *J. Am. Chem. Soc.*, 2015, **137**, 8944.
4. G.M. Sheldrick, *SHELX-16*, University of Göttingen, 2016.