Enantiopure Dimagnesium(I) and Magnesium(II) Hydride Complexes Incorporating Chiral Amidinate or β-Diketiminate Ligands

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Electronic Supplementary Information (22 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. Pentane and diethyl ether were distilled over Na/K alloy (50:50), while hexane, toluene and THF were distilled over molten potassium. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on either Bruker DPX300, Bruker AvanceIII 600 or Bruker AvanceIII 400 spectrometers and were referenced to the resonances of the solvent used. Mass spectra were collected using an Agilent Technologies 5975D inert MSD with a solid-state probe. FTIR spectra were collected for solid samples or Nujol mulls on an Agilent Cary 630 attenuated total reflectance (ATR) spectrometer. Microanalyses were carried out at the Science Centre, London Metropolitan University, or using a PerkinElmer- 2400 CHNS/O Series II System. Melting points were determined in sealed glass capillaries under dinitrogen, and are uncorrected. The starting materials L^{1}H,[1] Ar*NCClBu^{t} [2] and 5% w/w Na/NaCl[3] were prepared by literature procedures. All other reagents were used as received.

L^{2}H. Ar*NCClBu^{t} (26 g, 40 mmol) and (*S*)-α-methylbenzylamine (7.1 g, 40 mmol) were combined in a Schlenk flask. Toluene (30 mL) and triethylamine (7.5 mL, 53 mmol) were added, resulting in formation of a white precipitate. The mixture was heated at reflux overnight, cooled, and treated with 1 M $NaHCO_3$ (30 mL). The mixture was then transferred to a separating funnel and the organic layer was washed with water (2 x 30 mL). The organic layer was separated and volatiles removed *in vacuo* to give a sticky solid which was washed with methanol, then redissolved in isopropanol (50 mL) to give the title compound as colourless crystals after storage at room temperature overnight (26 g, 82%). $[\alpha]_D^{25}$ = -243 (c 1.00, $CHCl_3$); m.p. 201-204 °C; ^{1}H NMR (600 MHz, C_6D_6, 298 K): δ = 0.85 (overlapping, 12H, C(C*H*$_3$)$_3$ and CHC*H*$_3$), 1.94 (s, 3H, *p*-C*H*$_3$), 4.30 (m, 1H, NH), 4.39, (m, 1H, C*H*PhCH$_3$), 5.37 (s, 1H, C*H*Ph$_2$), 5.82 (s, 1H, C*H*Ph$_2$), 6.72-7.33 (m 27H, Ar*H*); ^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298 K): δ = 21.3 (CH*C*H$_3$(Ph), 25.3 (Ar-*C*H$_3$), 29.0 (C(*C*H$_3$)$_3$), 38.9 (*C*(CH$_3$)$_3$), 51.3 (*C*H(Ph)Me), 52.4, (*C*HPh$_2$), 52.9 (*C*HPh$_2$), 126.0, 126.0, 126.1, 126.2, 126.4, 127.2, 128.4, 128.6, 128.9, 129.1, 129.2, 129.7, 129.9, 130.0, 130.3, 130.5, 132.4, 132.8, 137.2, 142.6, 144.6, 144.6, 145.3, 145.4, 145.5, 146.0 (Ar-*C*), 156.1 (N*C*N); IR ν/cm^{-1} (ATR): 3463 (w, br, *ν*(N-H)), 1655 (vs, *ν*(C=N)), 1167 (m), 1076 (m), 1030 (m), 909 (w), 858 (m), 759 (s), 746 (s), 730 (s), 695 (vs).

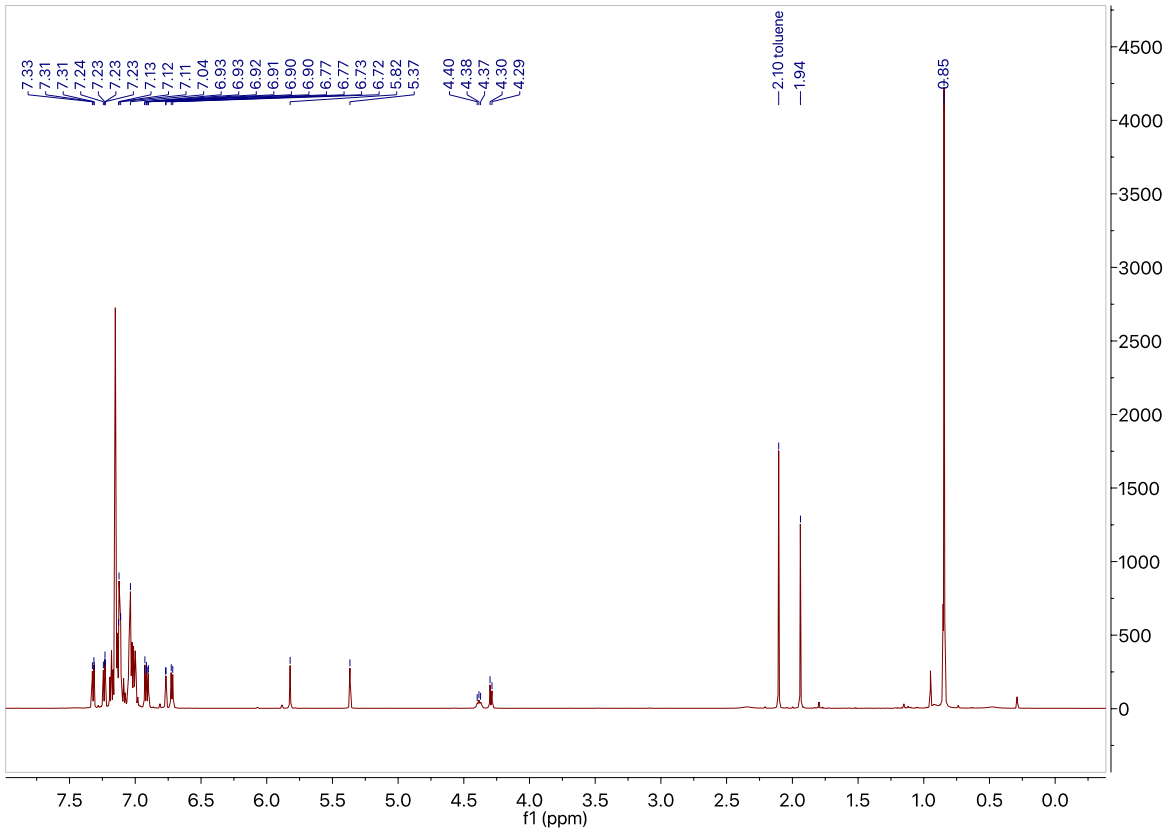

Figure S1. ^{1}H NMR spectrum (600 MHz, 298 K, C_6D_6) of L^{2}H.

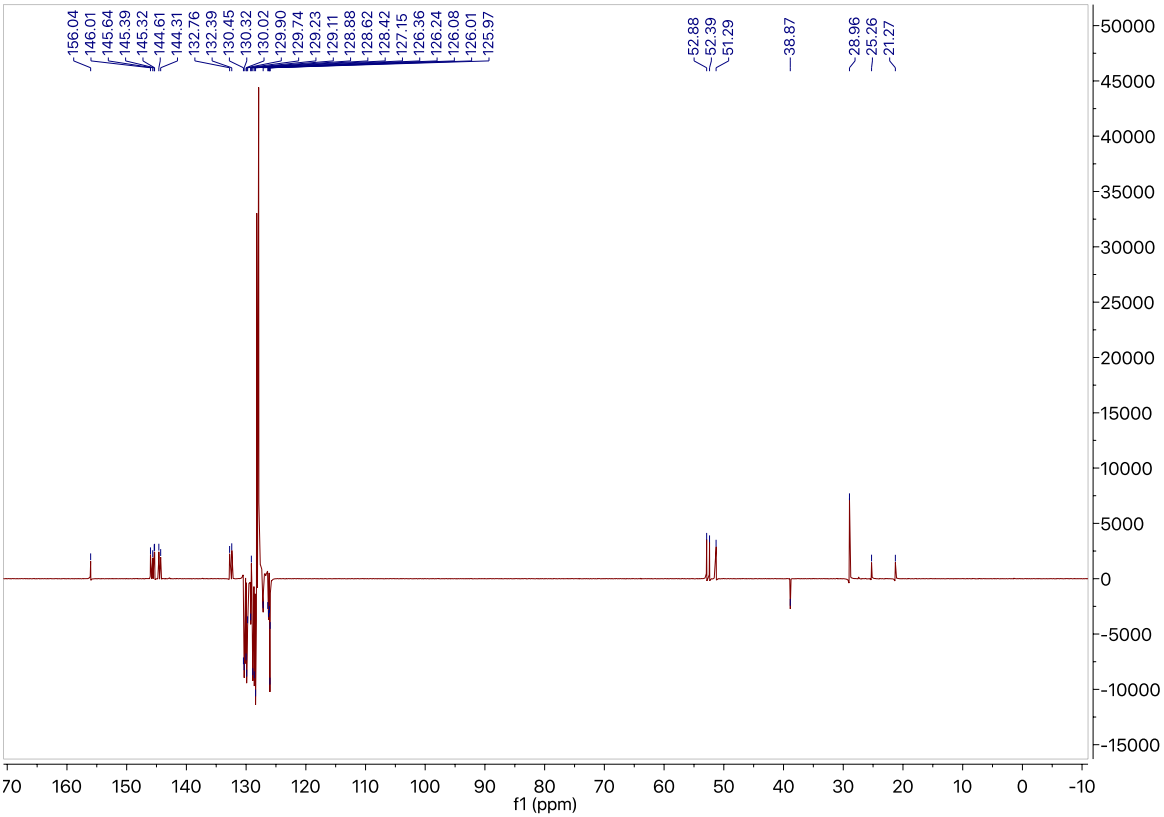

Figure S2. ^{13}C{^{1}H} NMR spectrum (151 MHz, 298 K, C_6D_6) of L^{2}H.

[(L^1)MgI(OEt$_2$)] 1. To a solution of L^{1}H (5.00 g, 13.8 mmol) dissolved in diethyl ether (15 ml) was added a freshly prepared solution of MeMgI in diethyl ether (MeI 1.2 mL, 17.9 mmol, Mg 0.50 g, 20.7 mmol) at -30 °C. The mixture was slowly warmed to room temperature and stirred for 12 hours, resulting in formation of a white suspension. The mixture was filtered and the precipitate dried *in vacuo*, yielding **1** as an analytically pure off-white power. The mother liquor was concentrated *in vacuo* and stored at -30 °C, yielding a second crop of the product. Colorless crystals suitable for crystallographic characterisation were grown from diethyl ether at -30 °C (5.98 g, 74%). M.p. 148-152; ^{1}H NMR (600 MHz, C_6D_6, 298 K): δ = 0.88 (br, 6H, OCH$_2$C*H*$_3$), 1.17 (d, $^3J_{H\text{-}H}$ = 7 Hz, 3H, CH(C*H*$_3$)$_2$), 1.23 (d, $^3J_{H\text{-}H}$ = 7 Hz, 3H, CH(C*H*$_3$)$_2$), 1.40 (br, 3H, CH(C*H*$_3$)$_2$), 1.65 (br, 6H, NCC*H*$_3$ & CH(C*H*$_3$)$_2$), 1.75 (br, 3H, NCC*H*$_3$), 1.86 (br, 3H, CH(Ph)C*H*$_3$), 3.21 (br, 3H, OC*H*$_2$CH$_3$ & C*H*Me$_2$), 3.63 (br, 3H, OC*H*$_2$CH$_3$ & C*H*Me$_2$), 4.64 (br, 2H, NCH$_3$C*H* & C*H*(Ph)(Me)), 7.10-7.47 (m, 8H, Ar-*H*); ^{13}C{1H} NMR (151 MHz, C_6D_6, 298 K): δ = 13.9 (OCH$_2$*C*H$_3$), 23.9, 24.0 (CH(*C*H$_3$)$_2$), 24.4, 25.0 (NC*C*H$_3$), 25.3, 25.4 (CH(*C*H$_3$)$_2$), 27.5 (CH(Ph)*C*H$_3$), 28.5 (br, *C*H(CH$_3$)$_2$), 59.0 (*C*H(Ph)(Me)), 65.7 (O*C*H$_2$), 95.6 (NCH$_3$*C*H), 123.3, 124.4, 125.7, 127.0, 128.9, 141.7, 143.0, 145.0, 147.2 (Ar-*C*), 169.0, 169.4 (*C*N); IR (Nujol): $\tilde{\nu}$/cm^{-1} = 1625 (w), 1560 (m), 1261 (s), 1093 (br), 1020 (br), 799 (s); Mass/ESI *m/z* (%): 513.2 (L^{1}MgI+H$^+$, 5), 385.2 (L^{1}Mg$^+$, 12), 362.3 (L^{1}H$^+$, 12); anal. calc. for $C_{29}H_{43}IMgN_2O$: C, 59.35 % H, 7.39 %, N, 4.77 %; found C, 59.28 %, H, 7.51 %, N, 4.78 %.

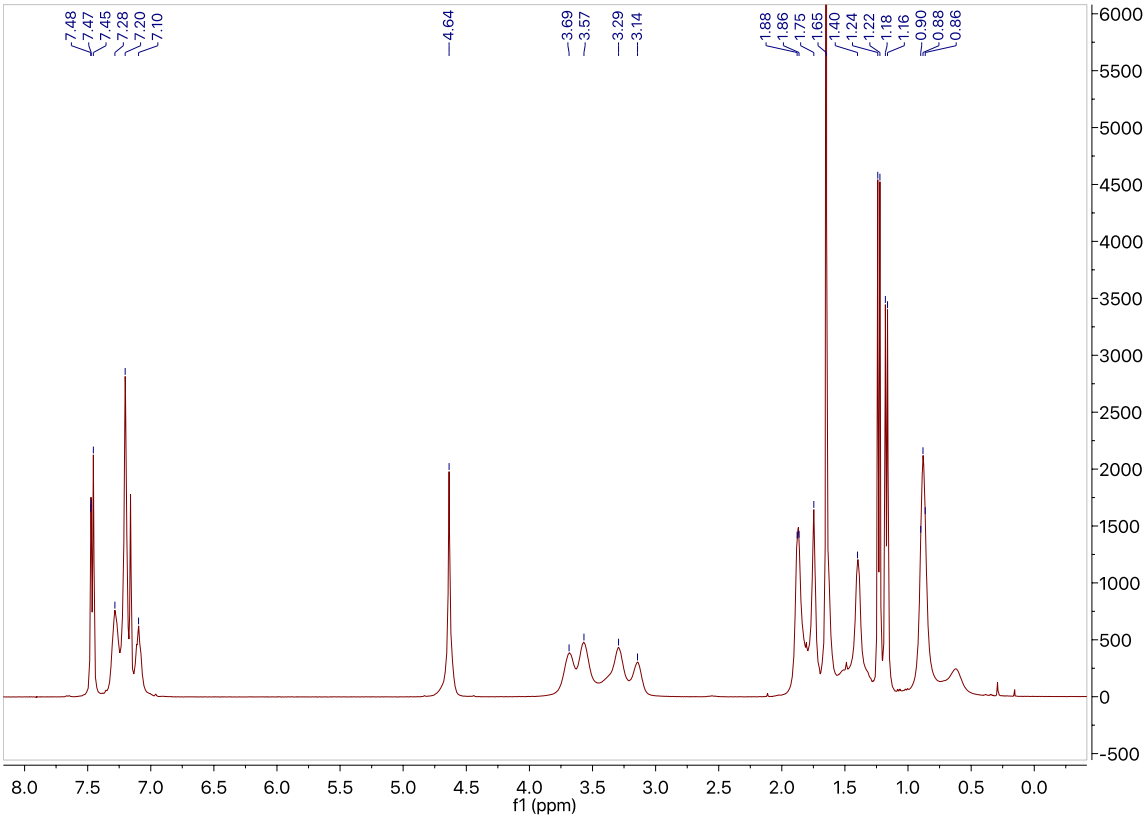

Figure S3. ^{1}H NMR spectrum (600 MHz, 298 K, C_6D_6) of **1**.

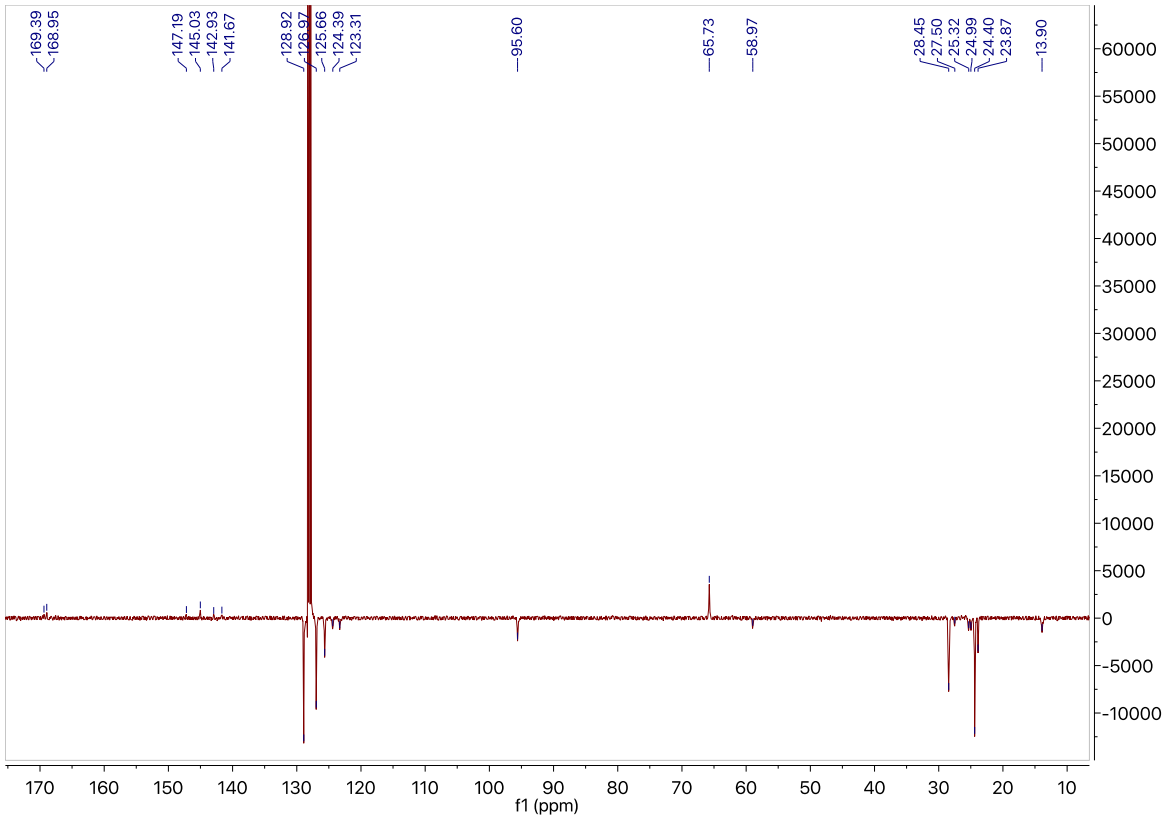

Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, 298 K, C_6D_6) of **1**.

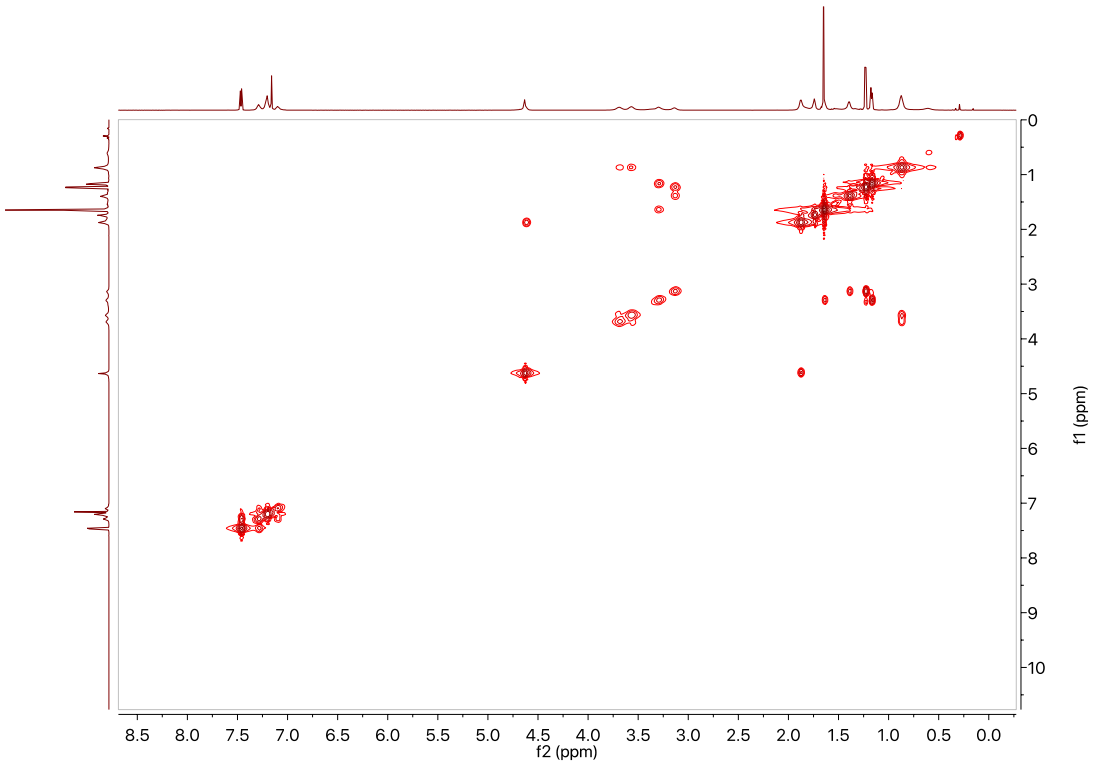

Figure S5. COSY NMR spectrum (600 MHz, 298 K, C_6D_6) of **1**.

[(L^1)Mg–Mg(L^1)] 2. [(L^1)MgI(OEt$_2$)] (4.00 g, 6.82 mmol) and 5% w/w Na/NaCl powder (16 g, 0.8 g of Na, 34.8 mmol) were combined in a Schlenk flask and a mixture of toluene (90 mL) and diethyl ether (10 mL) was added. The mixture was stirred vigorously for 2 days yielding a yellow suspension, which was allowed to settle before filtration. Volatiles were then removed from the filtrate *in vacuo* and the resultant dark yellow oil was dissolved in pentane, and the solution stored at -30 °C overnight, yielding yellow crystals of **2**. A second crop of crystals was obtained by filtration and concentration of the mother liquor *in vacuo* and storage at -30 °C (626 mg, 24 %). Yellow crystals suitable for crystallographic characterisation were grown from hexane at room temperature. M.p.: 153–158 °C (decomp. 180 °C); ^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K): δ = 1.10 (d, $^3J_{H\text{-}H}$ = 7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.14 (d, $^3J_{H\text{-}H}$ = 7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.20 (d, $^3J_{H\text{-}H}$ = 7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.23 (d, $^3J_{H\text{-}H}$ = 7 Hz, 6H, CH(Ph)C*H*$_3$), 1.36 (d, $^3J_{H\text{-}H}$ = 7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.63 (s, 6H, NCC*H*$_3$) 1.73 (s, 6H, NCC*H*$_3$), 3.10 (sept, $^3J_{H\text{-}H}$ = 7 Hz, 2H, C*H*(CH$_3$)$_2$), 3.38 (sept, $^3J_{H\text{-}H}$ = 7 Hz, 2H, C*H*(CH$_3$)$_2$), 4.58 (q, $^3J_{H\text{-}H}$ = 7 Hz, 2H, C*H*(Ph)Me), 4.65 (s, 2H, NCH$_3$C*H*), 7.10-7.19 (m, 16H, Ar-*H*); ^{13}C{^{1}H} NMR (151 MHz, C$_6$D$_6$, 298 K): δ = 23.5, 23.7, 23.9, 24.4 (CH(*C*H$_3$)$_2$), 25.2, 25.3 (NC*C*H$_3$), 25.4 (CH(Ph)*C*H$_3$), 28.2, 28.8 (*C*H(CH$_3$)$_2$), 57.7 (*C*H(Ph)(Me)), 96.1 (NCH$_3$*C*H), 123.5, 124.0, 124.9, 125.2, 126.4, 127.0, 128.6, 142.3, 142.5, 146.1, 147.6 (Ar-*C*), 165.6, 167.7 (*C*-N); IR (Nujol): *ν*/cm^{-1} = 1600 (w), 1521 (w), 1459 (m), 1389 (s), 1366 (s) 1315 (m), 1020 (br), 935 (m), 759 (s), 699 (vs); anal. calc. for C$_{50}$H$_{66}$Mg$_2$N$_4$: C, 77.82 %, H, 8.62 %, N, 7.26 %; found: C, 77.09 %, H, 8.97 %, N, 7.03 %.

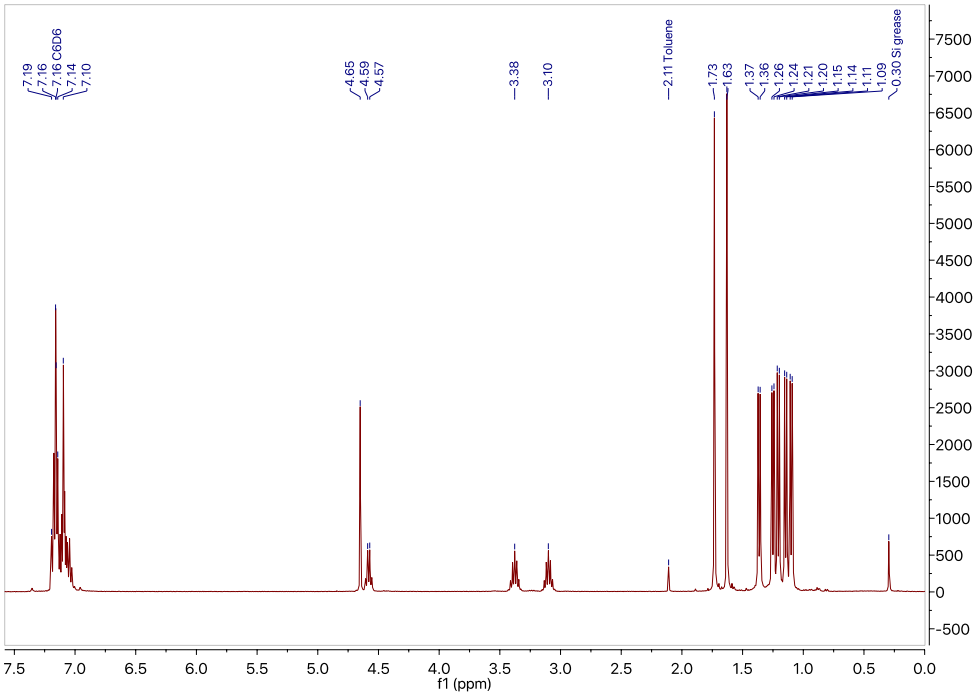

Figure S6. ^{1}H NMR spectrum (400 MHz, 298 K, C$_6$D$_6$) of **2**

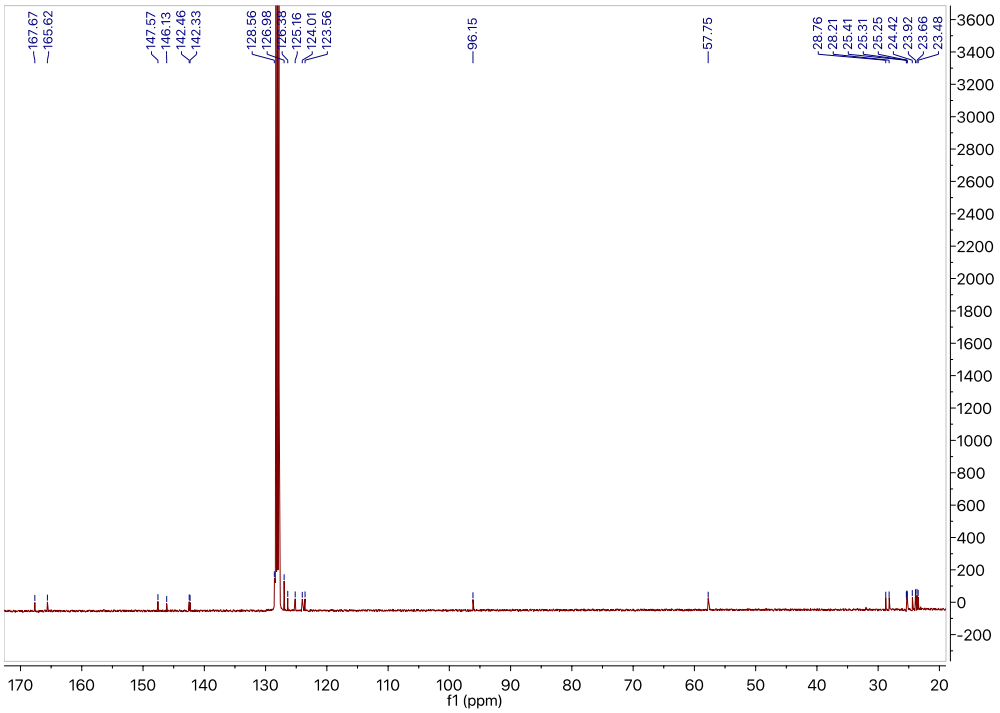

Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, 298 K, C_6D_6) of **2**

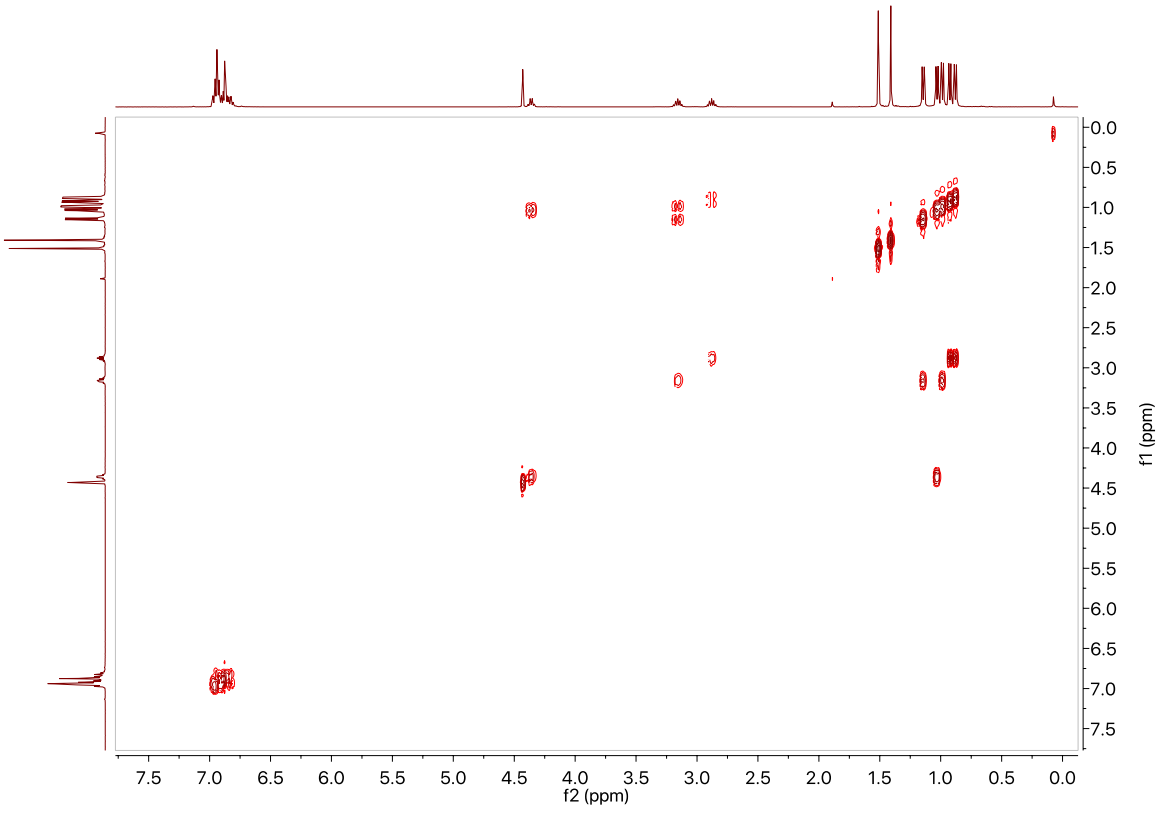

Figure S8. COSY NMR spectrum (600 MHz, 298 K, C_6D_6) of **2**

***in situ* formation of [(L^1)MgBu^n] 3.** To a solution of L^{1}H (1.00 g, 2.8 mmol) dissolved in toluene (10 ml) was added a solution of MgBu$^n_2$ in heptanes (6.4 mL, 2.8 mmol, 0.44 M). The mixture was heated at 60 °C for 24 h resulting in a bright orange solution. The solution was warmed to room temperature, and volatiles removed *in vacuo* to give a mobile, colourless, very air sensitive oil. Attempts to obtain **3** as a solid material by dissolving this oil in a small volume of pentane or hexane, then placing the solution at -30 °C or -78 °C, were not successful. Accordingly, the compound was prepared and used *in situ* in subsequent reactions, assuming quantitative conversion. NMR spectroscopic data presented here are of an aliquot of the total reaction mixture, at completion of the reaction, and are tentatively assigned. ^{1}H NMR (600 MHz, C_6D_6, 298 K): δ = -0.19 (br, 2H, MgC*H*$_2$), 0.95 (br, 5H, MgCH$_2$CH$_2$CH$_2$C*H*$_3$ and MgCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.16 (m, 6H, CH(C*H*$_3$)$_2$), 1.26 (d, $^3J_{H\text{-}H}$ = 7 Hz, 3H, CH(C*H*$_3$)$_2$), 1.30 (br, 3H, CH(C*H*$_3$)$_2$), 1.40 (br, 2H, MgCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.58 (br, 3H, CH(C*H*$_3$)Ph), 1.64 (br, 3H, NCC*H*$_3$), 1.78 (br, 3H, NCC*H*$_3$), 3.20 (br, 2H, C*H*Me$_2$), 4.57 (br, 1H, C*H*(Ph)Me), 4.73 (br, 1H, NCH$_3$C*H*), 7.06-7.21 (m, 8H, Ar-*H*); ^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298 K): δ = 1.4 (Mg*C*H$_2$), 14.0 (MgCH$_2$CH$_2$CH$_2$*C*H$_3$), 14.3 (MgCH$_2$*C*H$_2$), 23.4, 23.7, 23.9, 24.6 (CH(*C*H$_3$)$_2$), 25.2 (CH(Ph)*C*H$_3$), 28.5 (*C*H(CH$_3$)$_2$), 28.6 (MgCH$_2$CH$_2$*C*H$_2$CH$_3$), 29.2, 29.8 (NC*C*H$_3$) 31.5 (*C*H(CH$_3$)$_2$), 57.3 (*C*H(Ph)(Me)), 95.8 (NCH$_3$*C*H), 123.9, 124.0, 125.6, 125.7, 126.3, 127.0, 128.5, 129.3, 142.0, 142.3, 144.9, 147.0 (Ar-*C*), 168.1, 169.2 (*C*N).

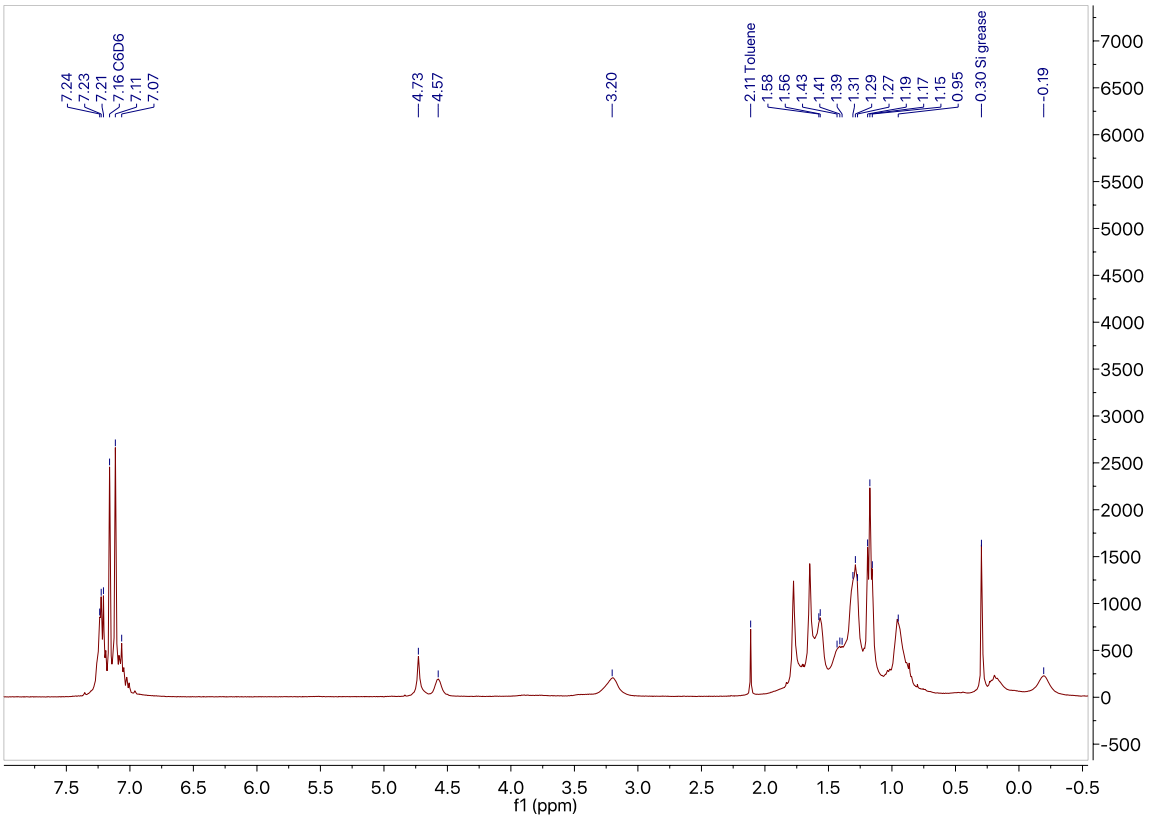

Figure S9. ^{1}H NMR spectrum (600 MHz, 298 K, C_6D_6) of an aliquot taken from the reaction mixture containing **3**.

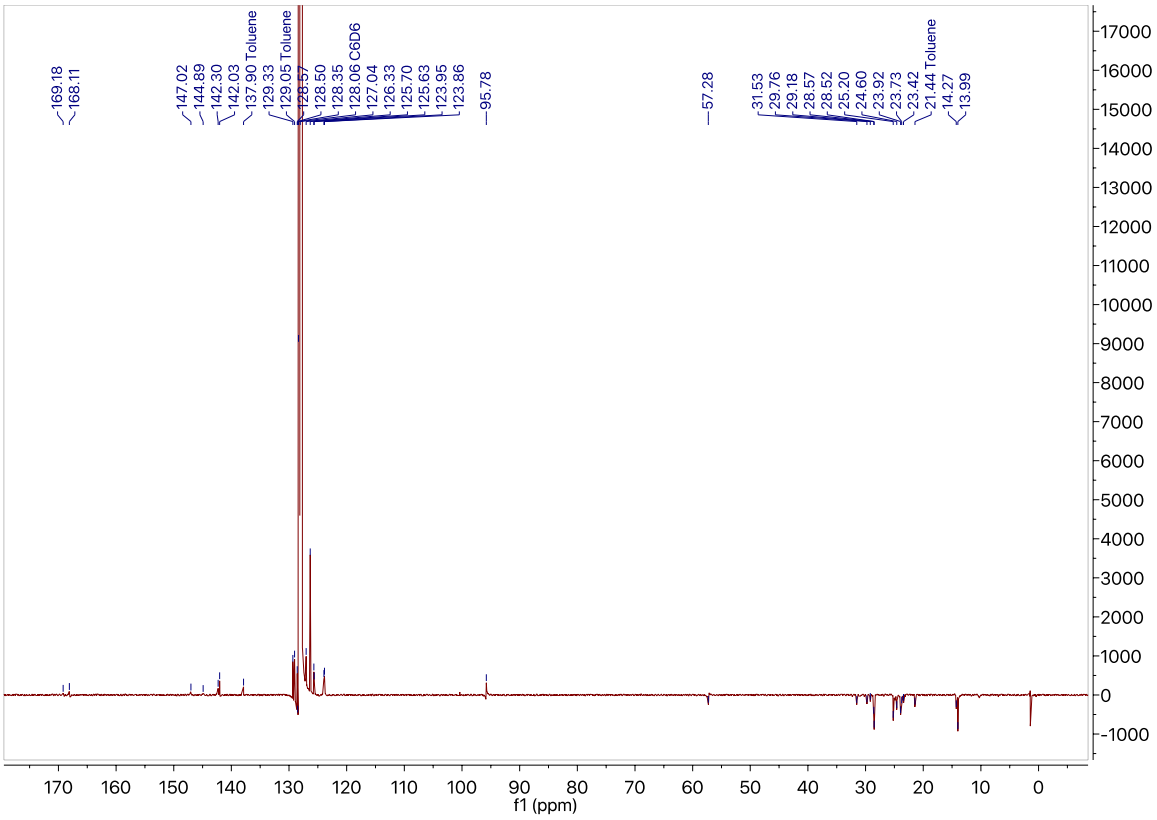

Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, 298 K, C_6D_6) of an aliquot taken from the reaction mixture containing **3**.

[(L^2)MgBu^n] 4. L^{2}H (500 mg, 0.80 mmol) was dissolved in toluene and treated with MgBu$^n_2$ (0.96 mL, 0.96 mmol, 1M). After heating at 60 °C overnight, a yellow solution had formed. Volatiles were removed *in vacuo*, and the residue was washed with ice cold hexane (5 mL) to give **4** as a colorless solid (404 mg, 78 %). M.p. 178-198 °C (decomp.); ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = -0.84 (br, 2H, MgC*H*$_2$), 1.09 (m, 3H, Mg(CH$_2$)$_3$C*H*$_3$), 1.08 (br, 2H, MgCH$_2$C*H*$_2$), 1.20 (s, 9H, C(C*H*$_3$)$_3$), 1.37 (d, $^{3}J_{H\text{-}H}$ = 6 Hz, 3H, CHPhC*H*$_3$), 1.45 (br, 2H, Mg(CH$_2$)$_2$C*H*$_2$), 1.92 (s, 3H, p-C*H*$_3$), 4.97 (q, $^{3}J_{H\text{-}H}$ = 6 Hz, 1H, C*H*PhCH$_3$), 5.79 (br, 2H, C*H*Ph$_2$), 6.81 (m, 2H, *m*-Ar*H), 7.02-7.29 (m, 25H, Ar*H*); $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6, 298 K): δ = 14.5 (br, Bu^n*C*H$_3$), 21.3 (CH(*C*H$_3$)Ph) 25.2 (*C*H$_2$), 26.8 (Ar**C*H$_3$), 30.6(C(*C*H$_3$)$_3$), 32.1 (br, *C*H$_2$ x 2) 40.6 (*C*(CH$_3$)$_3$), 53.9 (br, *C*HPh$_2$), 54.6 (*C*H(CH$_3$)Ph), 125.7, 126.5, 126.6, 126.7, 128.6, 128.7 (2 peaks), 128.8 (2 peaks), 129.3, 129.6, 129.7, 130.1, 138.5, 138.6, 143.6, 143.6, 145.4, 148.1 (Ar*C*), no resonances attributable to Mg*C*H$_2$ or N*C*N were observed; IR ν/cm^{-1} (Nujol mull): 1600 (vs), 1584 (w), 1550 (m), 1071 (s), 1032 (s), 1030 (s), 982 (w), 956 (w), 910 (w), 863 (w), 801 (m), 762 (m), 700 (vs). A satisfactory microanalysis could not be obtained as the compound could not be purified by recrystallisation.

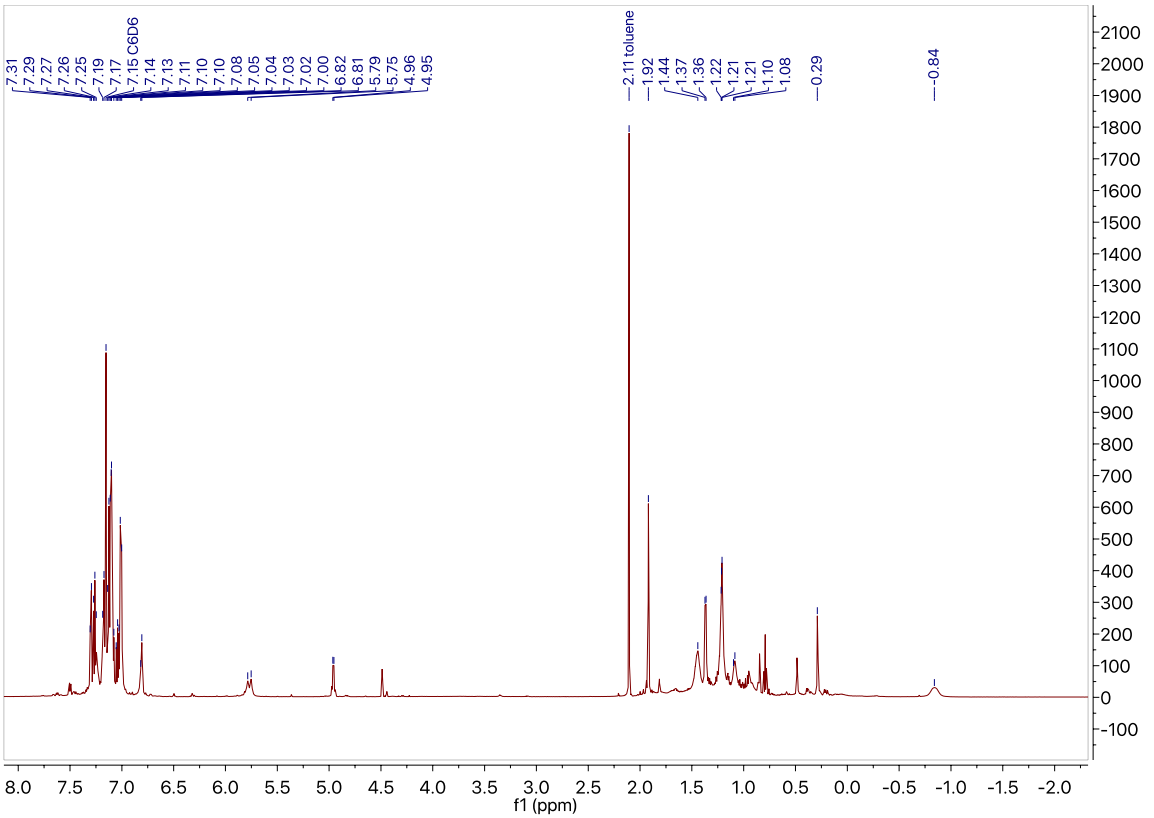

Figure S11. ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of an impure sample of **4**.

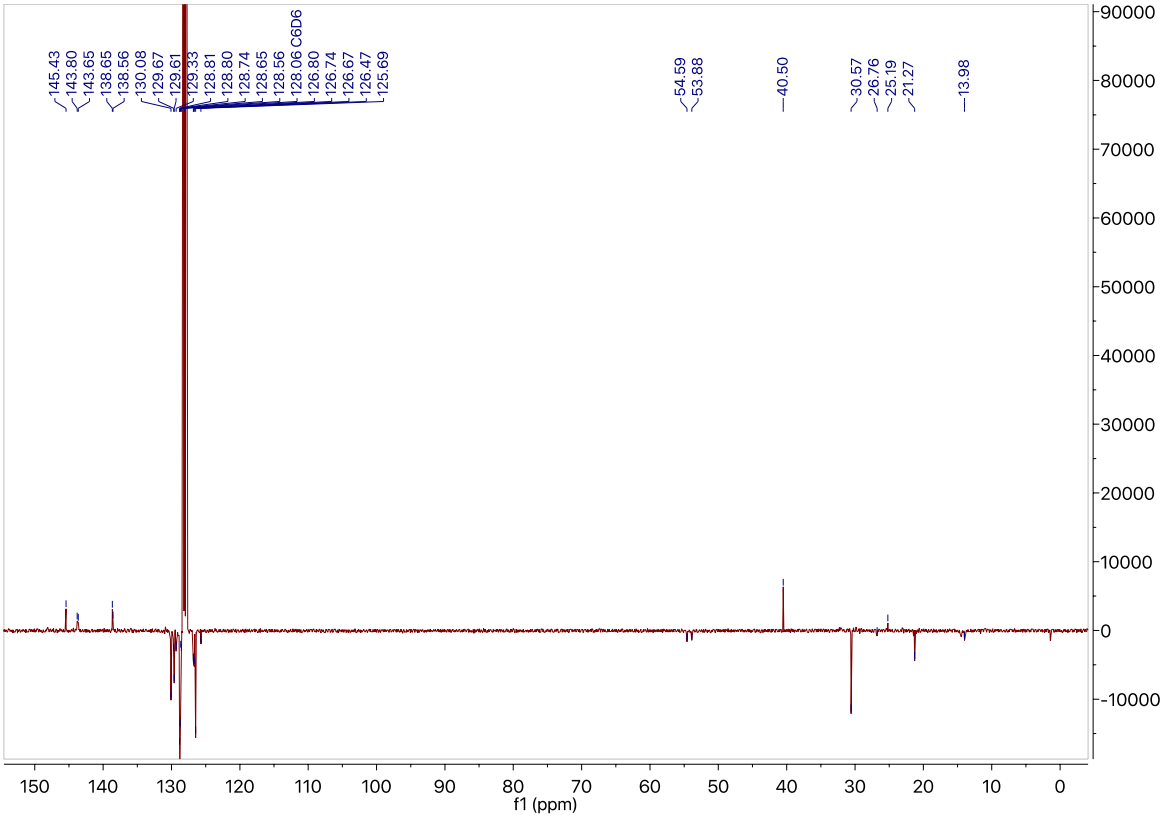

Figure S12. ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K, C_6D_6) of an impure sample of **4**.

[(L^1)$_4$Mg$_5$H$_6$] 5. An *in situ* generated solution of **3** (2.76 mmol) in toluene (10 mL) was treated with $PhSiH_3$ (0.48 mL, 3.31 mmol), and the mixture heated at 60 °C for 24 h resulting in a golden yellow solution. Upon warming to room temperature, pentane (20 mL) was added to the reaction solution, resulting in the precipitation of **5** as an analytically pure white solid. The solution was filtered and the filtrate concentrated *in vacuo* to 5 mL, then stored at -30 ºC, resulting in a second crop of **5** (114 mg, 31% yield). Crystals suitable for crystallographic characterisation were grown from toluene. M.p. 158-163 ºC; ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.40 (d, $^3J_{H\text{-}H}$ = 7 Hz, 12H, CH(CH_3)$_2$), 0.94 (m, 24H, CH(Ph)CH_3 and CH(CH_3)$_2$), 1.27 (d, $^3J_{H\text{-}H}$ = 7 Hz, 12H, CH(CH_3)$_2$), 1.57 (d, $^3J_{H\text{-}H}$ = 7 Hz, 12H, CHCH_3), 1.62 (s, 12H, CNCH_3), 1.79 (s, 12H, CNCH_3), 2.60 (sept, $^3J_{H\text{-}H}$ = 7 Hz, 4H, CHMe$_2$), 3.36 (br, 6H, MgH), 3.63 (sept, $^3J_{H\text{-}H}$ = 7 Hz, 4H, CHMe$_2$), 4.33 (q, $^3J_{H\text{-}H}$ = 7 Hz, 4H, CH(Ph)(Me)), 4.65 (s, 4H, NCH$_3$CH), 7.00-7.49 (m, 32H, Ar-H); ^{1}H NMR (400 MHz, C_7D_8, 298 K): δ = 0.33 (d, $^3J_{H\text{-}H}$ = 7 Hz, 12H, CH(CH_3)$_2$), 0.86 (d, $^3J_{H\text{-}H}$ = 7 Hz, 12H, CH(Ph)CH$_3$), 0.91 (d, $^3J_{H\text{-}H}$ = 7 Hz, 12H, CH(CH_3)$_2$), 1.24 (d, $^3J_{H\text{-}H}$ = 7 Hz, 12H, CH(CH_3)$_2$), 1.52 (d, $^3J_{H\text{-}H}$ = 7 Hz, 12H, CH(CH_3)$_2$), 1.59 (s, 12H, NCCH_3), 1.77 (s, 12H, NCCH_3), 2.54 (sept, $^3J_{H\text{-}H}$ = 7 Hz, 4H, CHMe$_2$), 3.29 (br, 6H, MgH), 3.57 (sept, $^3J_{H\text{-}H}$ = 7 Hz, 4H, CHMe$_2$), 4.27 (q, $^3J_{H\text{-}H}$ = 7 Hz, 4H, CH(Ph)(Me)), 4.61 (s, 4H, NCH$_3$CH), 7.03-.43 (m, 32H, Ar-H); ^{13}C{^{1}H}NMR (151 MHz, C_6D_6, 298 K): δ = 23.7, 24.1, 25.2, 25.3 (CH(*C*H$_3$)$_2$), 25.5 (CH(Ph)*C*H$_3$), 26.3, 26.5 (NC*C*H$_3$), 27.5, 28.5 (*C*H(Me)$_2$), 60.6 (*C*H(Ph)Me), 94.7 (NCH$_3$*C*H), 123.7, 124.4, 125.5, 125.7, 127.0, 127.0, 129.0, 143.1, 144.3, 145.7, 149.2 (Ar-*C*), 168.0, 171.3 (*C*-N); IR (Nujol): ν/cm^{-1} = 1625 (w), 1516 (w), 1188 (w), 1153 (w), 1089 (s), 1025 (s), 969 (w), 939 (w), 849 (w), 799 (s), 767(w), 699 (s); mass/ESI *m/z* (%): 385.3 (L^{1}Mg$^+$, 20); anal. calc. for $C_{100}H_{138}N_8Mg_5$: C, 76.32 % H, 8.84 %, N, 7.12 %; found C, 76.42 %, H, 9.49 %, N, 6.62 %.

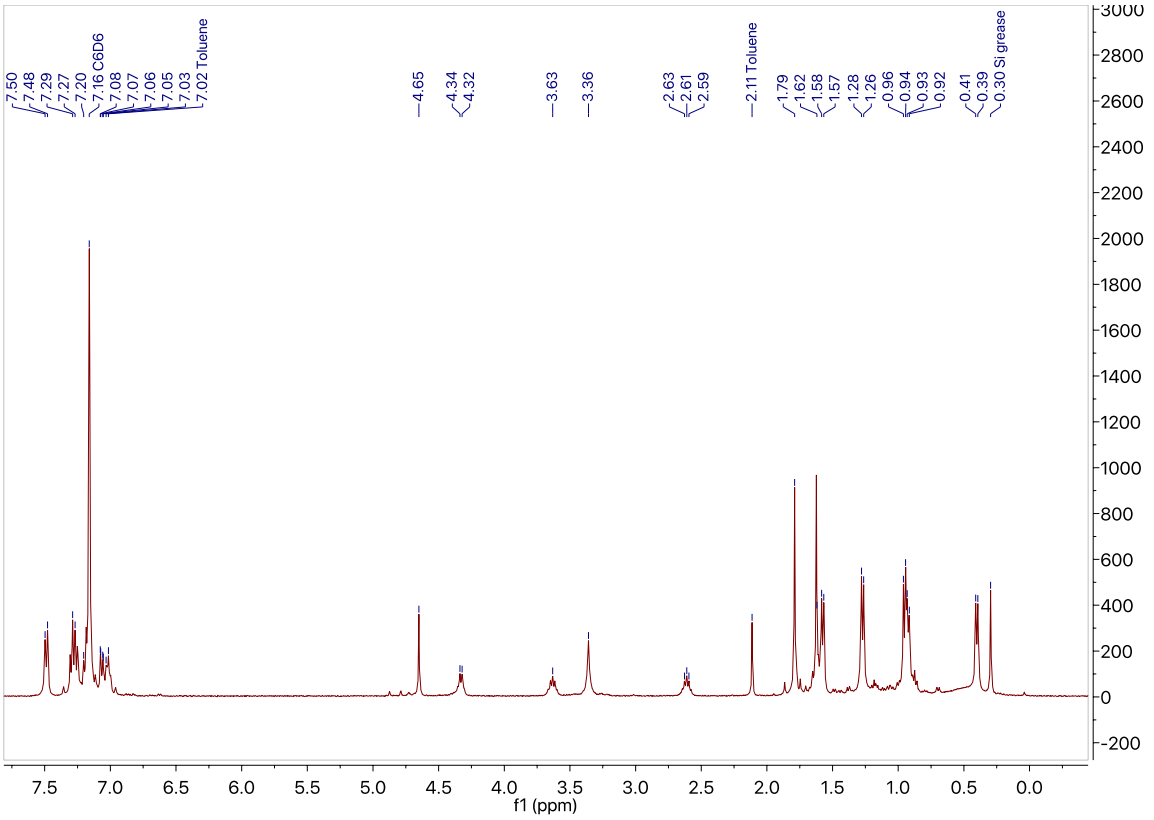

Figure S13. ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of **5**.

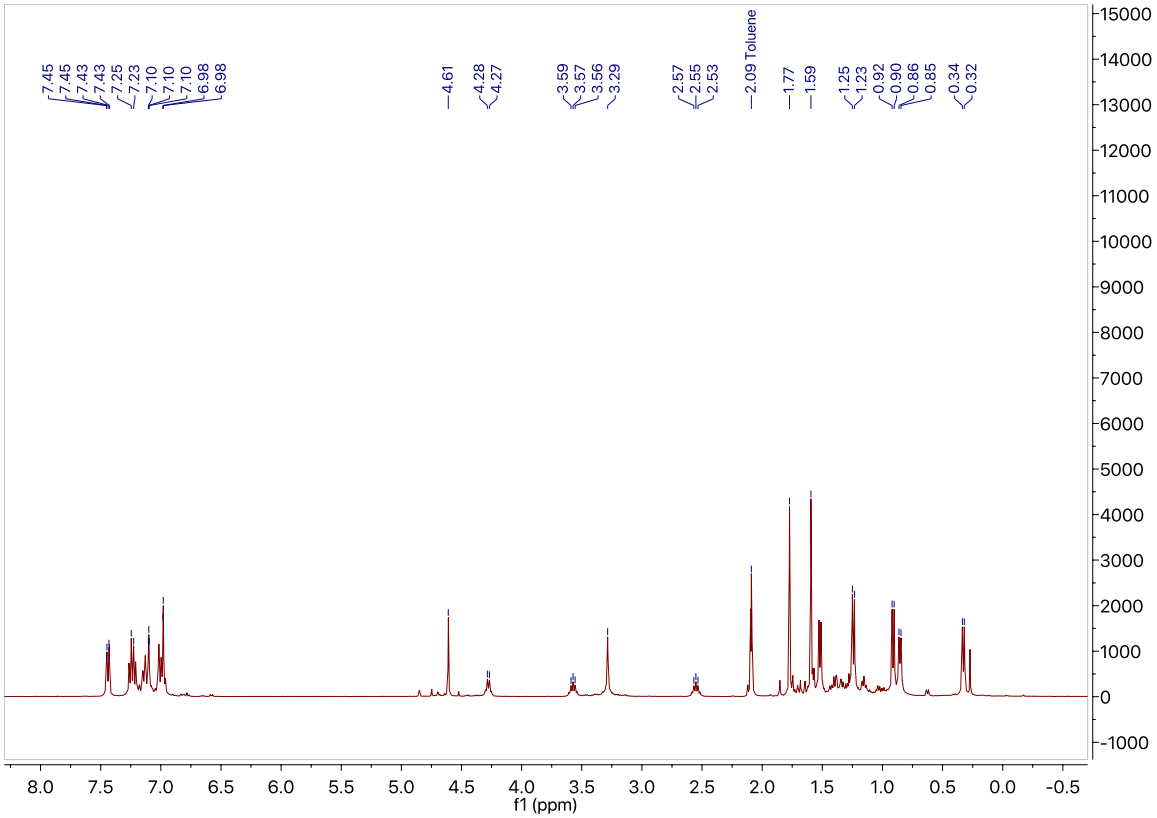

Figure S14. ^{1}H NMR spectrum (400 MHz, 298 K, C_7D_8) of **5**.

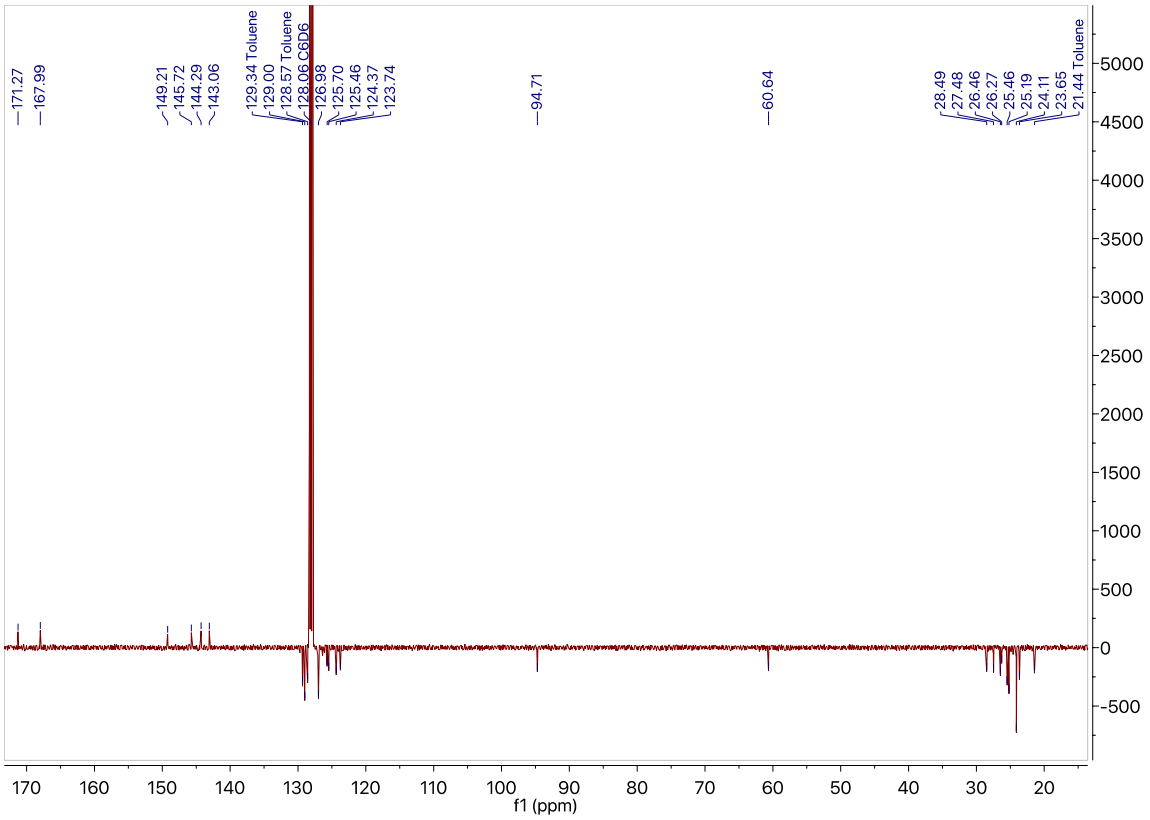

Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, 298 K, C_6D_6) of **5**.

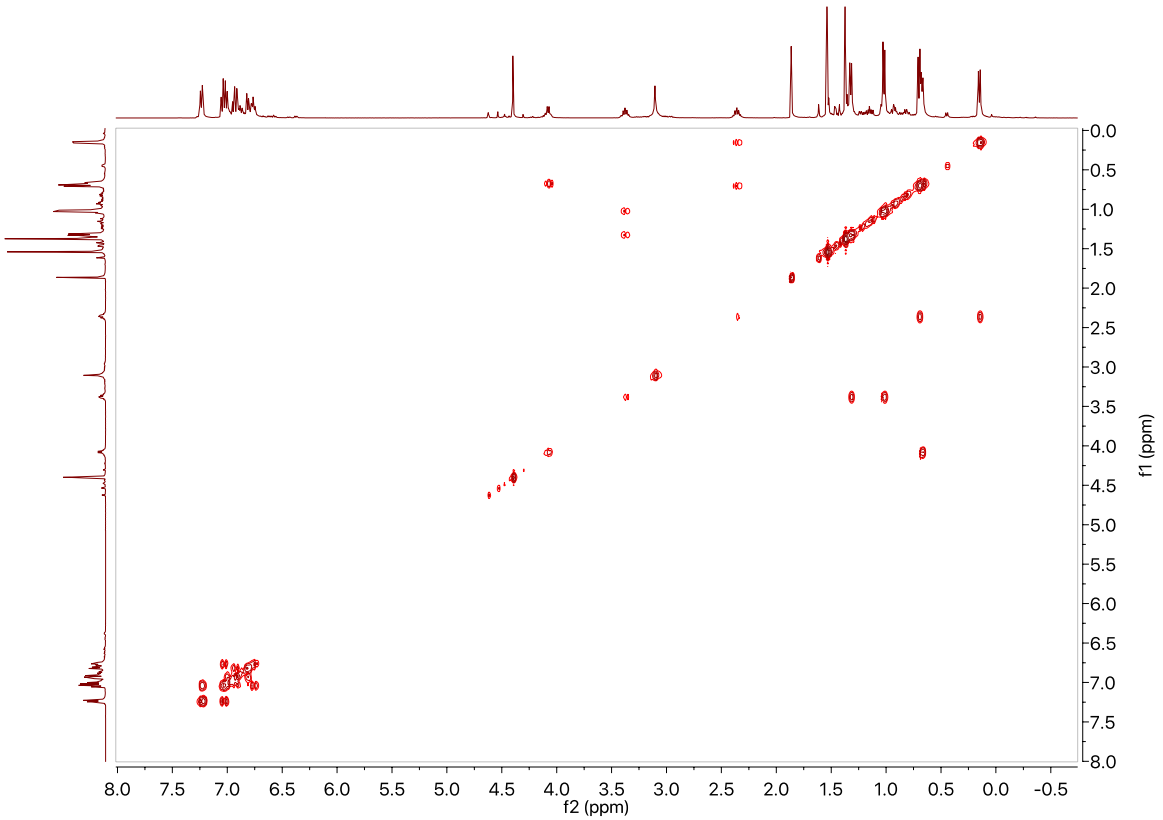

Figure S16. COSY NMR spectrum (600 MHz, 298 K, C_6D_6) of **5**.

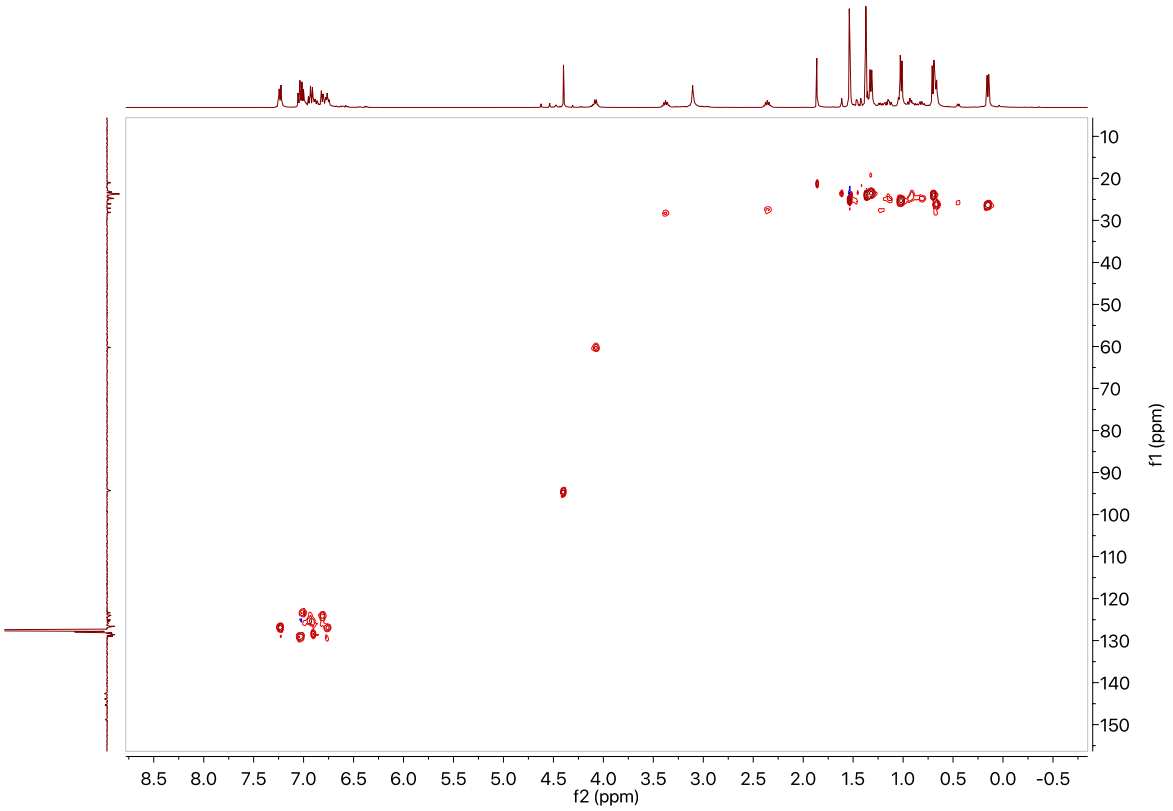

Figure S17. HMQC spectrum (^{1}H: 600 MHz; ^{13}C: 151 MHz; 298 K, C_6D_6) of **5**.

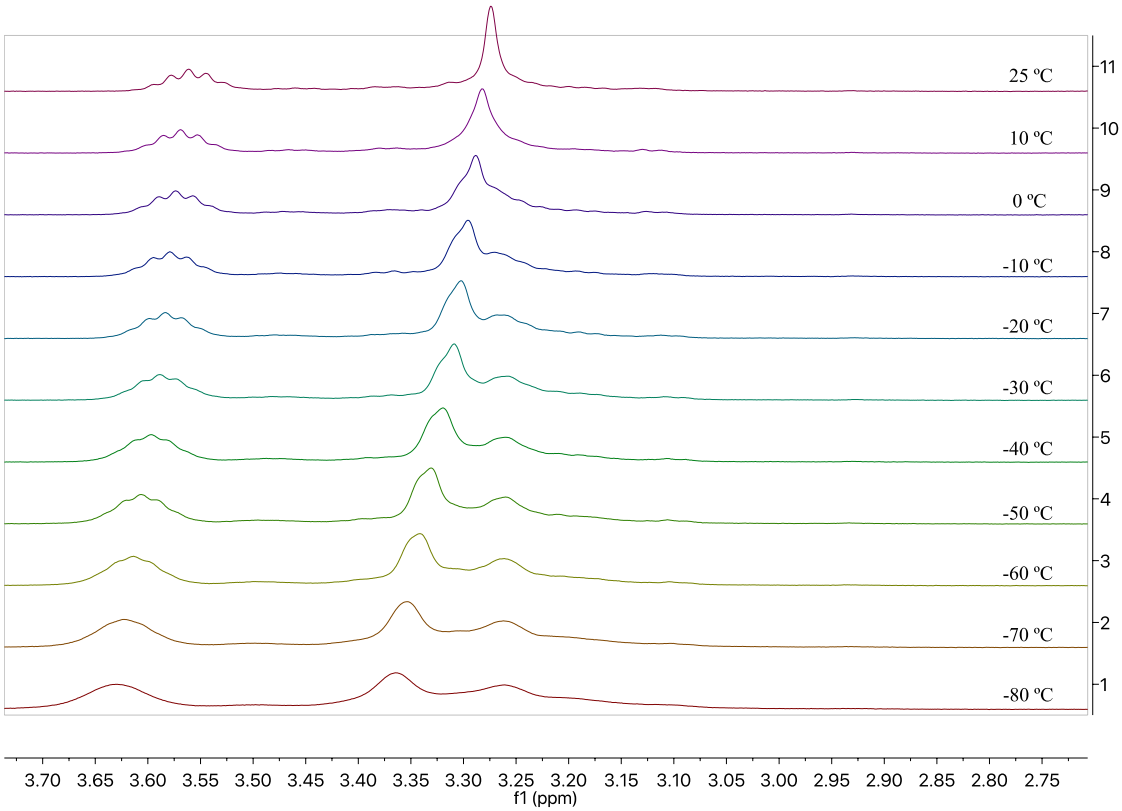

Figure S18. Variable temperature (25 to -80 °C) ^{1}H NMR spectra (400 MHz, 298 K, C_7D_8) of **5**, highlighting magnesium hydride resonances.

[Mg(L^1)$_2$]. A by-product that formed during the synthesis of **5** was presumed to be the homoleptic complex [Mg(L^1)$_2$]. This was rationally synthesised to confirm the identity of the by-product. To a solution of L^{1}H (1.00 g, 2.70 mmol) in toluene (10 mL) was added a solution of MgBu$^n{}_2$ (1.35 mL, 1M, 1.35 mmol) in heptanes. The mixture was then heated at 70 °C for 48 h, resulting in the formation of an orange solution. Volatiles were removed from the mixture *in vacuo*, leaving a dark yellow oil. Attempts were made to isolate the product as a solid by rectystallising it from a range of solvents, however this was unsuccessful, as the product was always obtained as an oil. As a result, NMR spectroscopic data could only be obtained on the impure oil, though these corresponded to the signals seen in the total reaction mixture that gave **5**. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 1.24-1.30 (m, 18H, CH(C*H*$_3$)$_2$), 1.40-1.45 (m, 18H, CH(C*H*$_3$)$_2$, CHPhC*H*$_3$, NC(C*H*$_3$)), 1.70 (s, 6H, NC(C*H*$_3$)) 3.25 (sept, $^3J_{H\text{-}H}$ = 7 Hz, 2H, C*H*(CH$_3$)$_2$), 3.38 (sept, $^3J_{H\text{-}H}$ = 7 Hz, 2H, C*H*(CH$_3$)$_2$), 4.45 (q, $^{3J}_{H\text{-}H}$ = 7 Hz, 2H, C*H*Me(Ph)), 4.54 (s, 2H, C*H* backbone), 7.03-7.22 (m, 16H, Ar-*H*); ^{13}C{^{1}H} NMR: δ = 24.2, 25.0, 25.1, 25.3 (CH(*C*H$_3$)$_2$), 25.7, 25.9 (NC*C*H$_3$) 27.6 (CH(Ph)*C*H$_3$), 28.3, 29.3 (*C*H(Me)$_2$), 58.1 (*C*H(Ph)(Me)), 97.2 (NCH$_3$*C*H), 123.6, 124.0, 125.0, 126.0, 126.2, 128.4, 142.4, 143.5, 147.8, 148.3 (Ar-*C*), 168.6, 170.8 (*C*N).

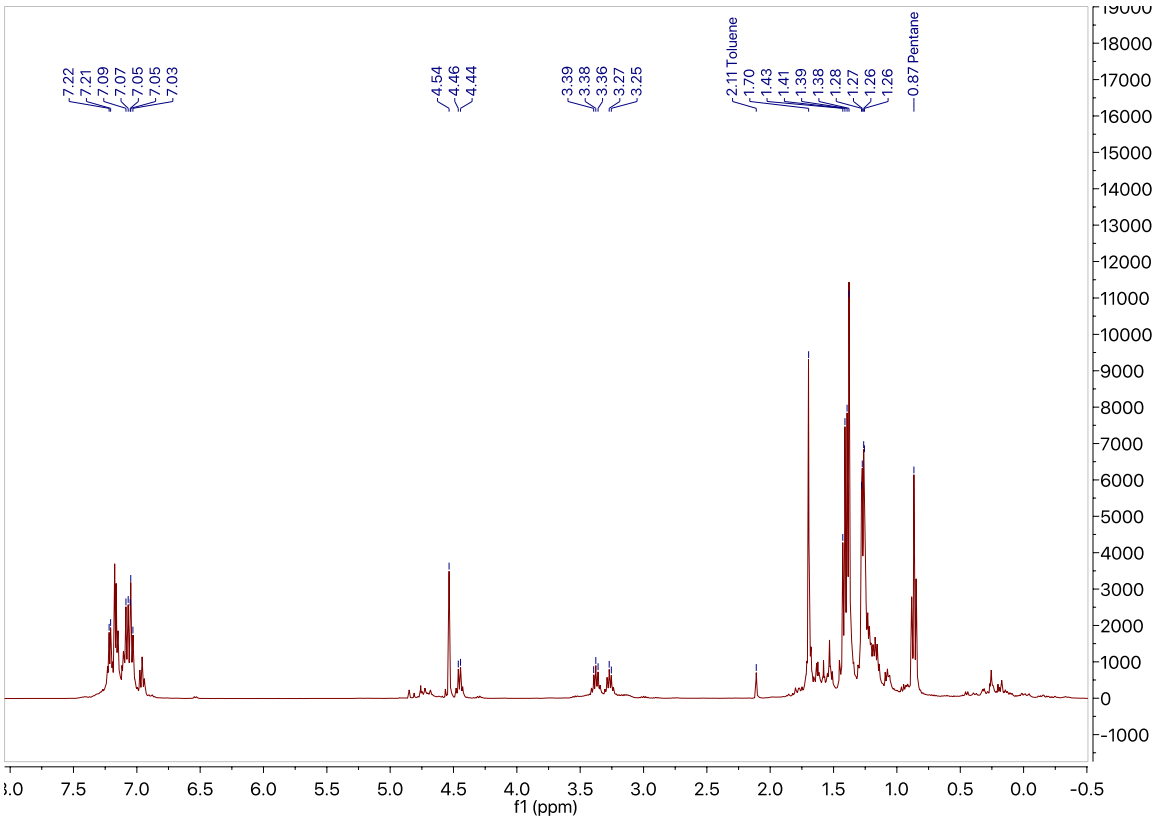

Figure S19. ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of an impure sample of [Mg(L^1)$_2$].

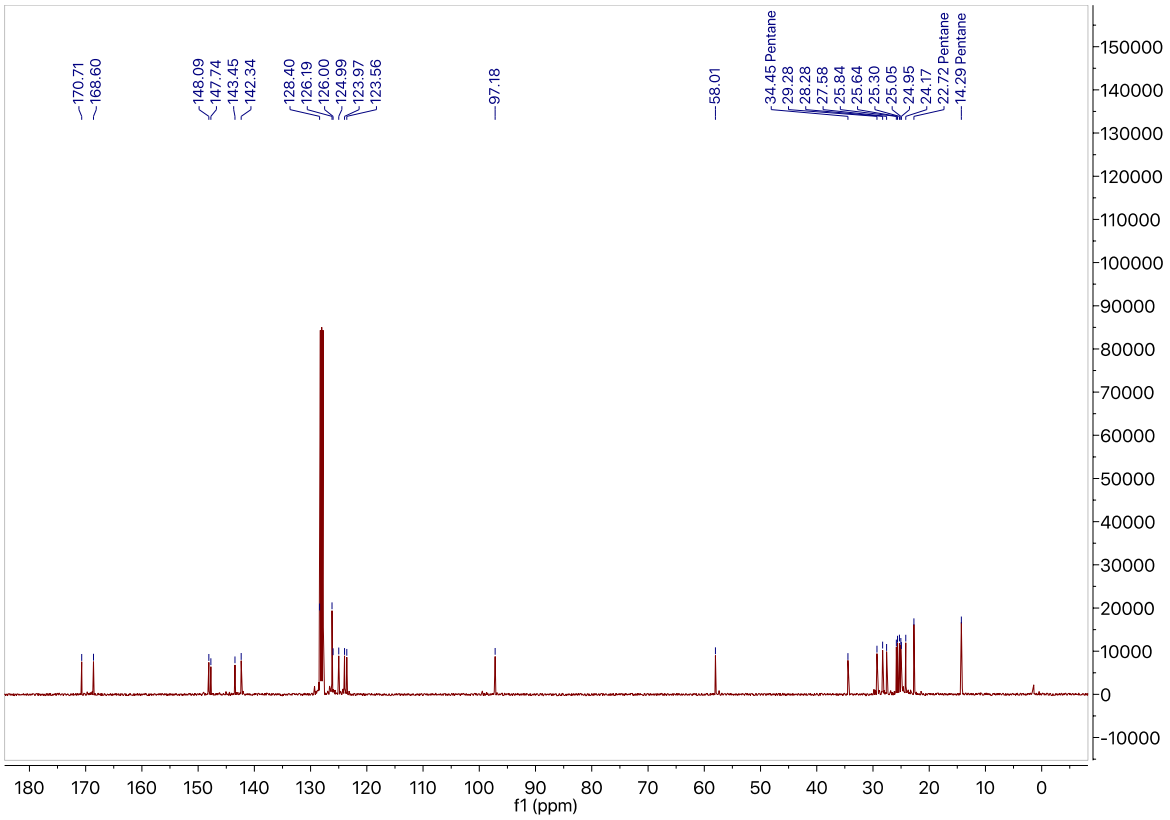

Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, C_6D_6) of an impure sample of $[Mg(L^1)_2]$.

$[(L^2)Mg(\mu\text{-}H)_2Mg(L^2)]$ 6. Compound **4** (1.77 g, 2.52 mmol) was dissolved in toluene (10 mL) and $PhSiH_3$ (1 mL, 8.07 mmol) added to the solution. The mixture was heated at 60 °C for 4 h, before volatiles were removed *in vacuo*, leaving a yellow oil. The oil was redissolved in pentane (1 mL) and stored at –30 °C overnight. Volatiles were then removed from the solution, and the residue washed with a small amount of cold pentane. This gave **6** as a white solid, contaminated with some of the reaction by-product $PhSiH_2Bu^n$, which could not otherwise be easily removed (1.55 g, 95 %). M.p. 220-224 °C (decomp.); ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 1.02 (s, 18H, C(C*H*$_3$)$_3$), 1.62 (d, $^{3}J_{H\text{-}H}$ = 6 Hz, 6H, CHPhC*H*$_3$), 1.99 (s, 6H, *p*-ArC*H*$_3$), 3.28 (s, 2H, Mg*H*), 5.10 (q, $^{3}J_{H\text{-}H}$ = 6 Hz, 2H. C*H*PhCH$_3$), 5.73 (s, 2H, C*H*Ph$_2$), 6.29 (s, 2H, C*H*Ph$_2$), 6.73-7.62 (m, 54H, Ar*H*); $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6, 298 K): δ = 21.2 (CH(*C*H$_3$)Ph), 27.6 (*p*-Ar*C*H$_3$), 30.5 (C(*C*H$_3$)$_3$), 39.9 (*C*(CH$_3$)$_3$), 52.4, 53.6 (*C*HPh$_2$), 55.3 (*C*H(CH$_3$)Ph), 126.2, 126.6, 126.6, 126.8, 127.1, 128.8, 128.9, 128.9, 129.5, 129.8, 129.8, 130.1, 130.1, 130.6, 130.7, 130.8, 131.0, 131.1, 132.9, 135.6, 138.3, 139.1, 142.6, 143.6, 144.1, 145.7, 146.5, 148.0 (Ar-*C*), 177.8 (N*C*N); IR ν/cm^{-1} (Nujol mull): 1183 (m), 1079 (m), 1032 (s), 930 (m), 894 (m), 837 (m), 762 (m), 702 (s). A satisfactory microanalysis could not be obtained for the compound as traces of $PhSiH_2Bu^n$ could not be completely removed, and the compound could not be recrystallised.

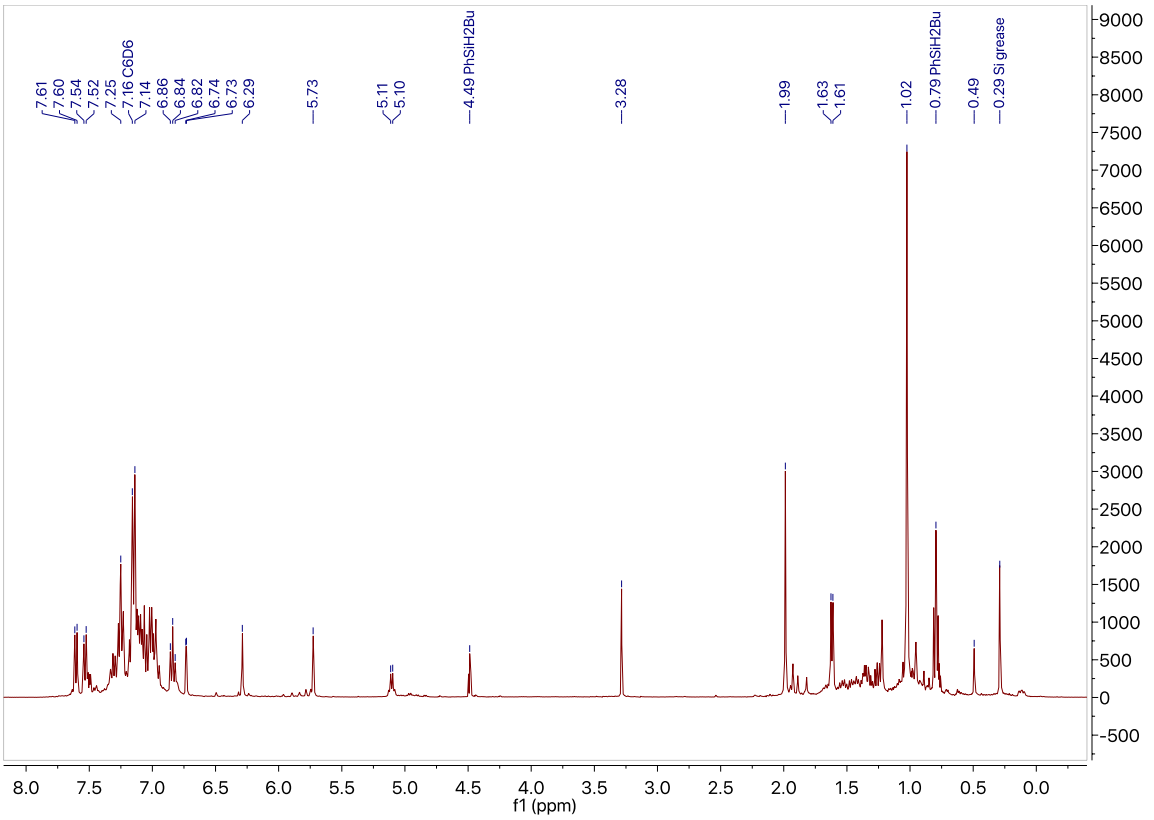

Figure S21. ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of **6**.

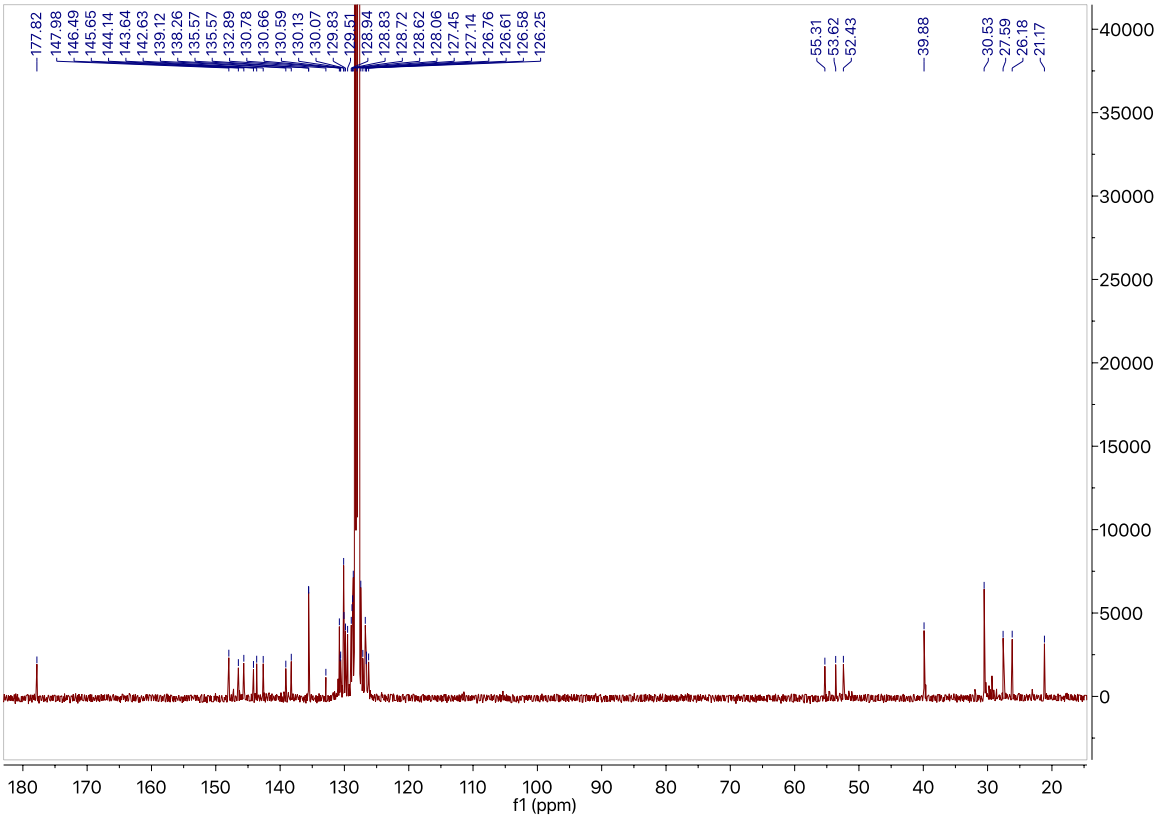

Figure S22. ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K, C_6D_6) of **6**.

[(L^2)(THF)Mg(μ-H)$_2$Mg(THF)(L^2)] 7. Compound **6** (200 mg, 0.30 mmol) was dissolved in THF (0.5 mL). The solution was stored at –30°C overnight, yielding colourless crystals of **7** (180 mg, 81 %). M.p. 162-164 °C; ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.86 (s, 18H, C(C*H*$_3$)$_3$), 1.30 (m, 8H, OCH$_2$C*H*$_2$), 1.65 (d, $^3J_{H\text{-}H}$ = 6 Hz, 6H, CHPhC*H*$_3$), 2.03 (s, 6H, *p*-ArC*H*$_3$), 3.52 (br, 8H, OC*H*$_2$CH$_2$), 4.48 (s, 2H, Mg*H*), 5.10 (q, $^3J_{H\text{-}H}$ = 6 Hz, 2H. C*H*PhCH$_3$), 6.53 (s, 2H, C*H*Ph$_2$), 6.90 (s, 2H, C*H*Ph$_2$), 6.65-7.47 (m, 54H, Ar*H*); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 21.2 (CH(*C*H$_3$)Ph), 25.7 (OCH$_2$*C*H$_2$), 27.4 (*p*-Ar*C*H$_3$), 30.6 (C(*C*H$_3$)$_3$), 39.9 (*C*(CH$_3$)$_3$), 52.4 (*C*HPh$_2$ – two signals), 55.5 (*C*H(CH$_3$)Ph), 126.3, 126.5 (2 signals), 126.6, 128.3, 128.5, 128.6, 126.7, 128.8, 128.9, 127.8, 130.1, 130.2, 130.3, 130.5, 130.9, 131.0, 137.7, 137.9, 143.2, 147.3, 148.6 (Ar*C*), 178.8 (N*C*N); IR ν/cm^{-1} (Nujol mull): 1196 (m), 1080 (m), 1068 (s), 1030 (s), 958 (w), 912 (w), 883 (m), 832 (m), 757 (s), 746 (s), 689 (vs); anal. calc. for $C_{100}H_{108}Mg_2N_4O_2$: C, 83.03 % H, 7.53 %, N, 3.87 %; found C, 82.45 %, H, 7.58 %, N, 3.97 %.

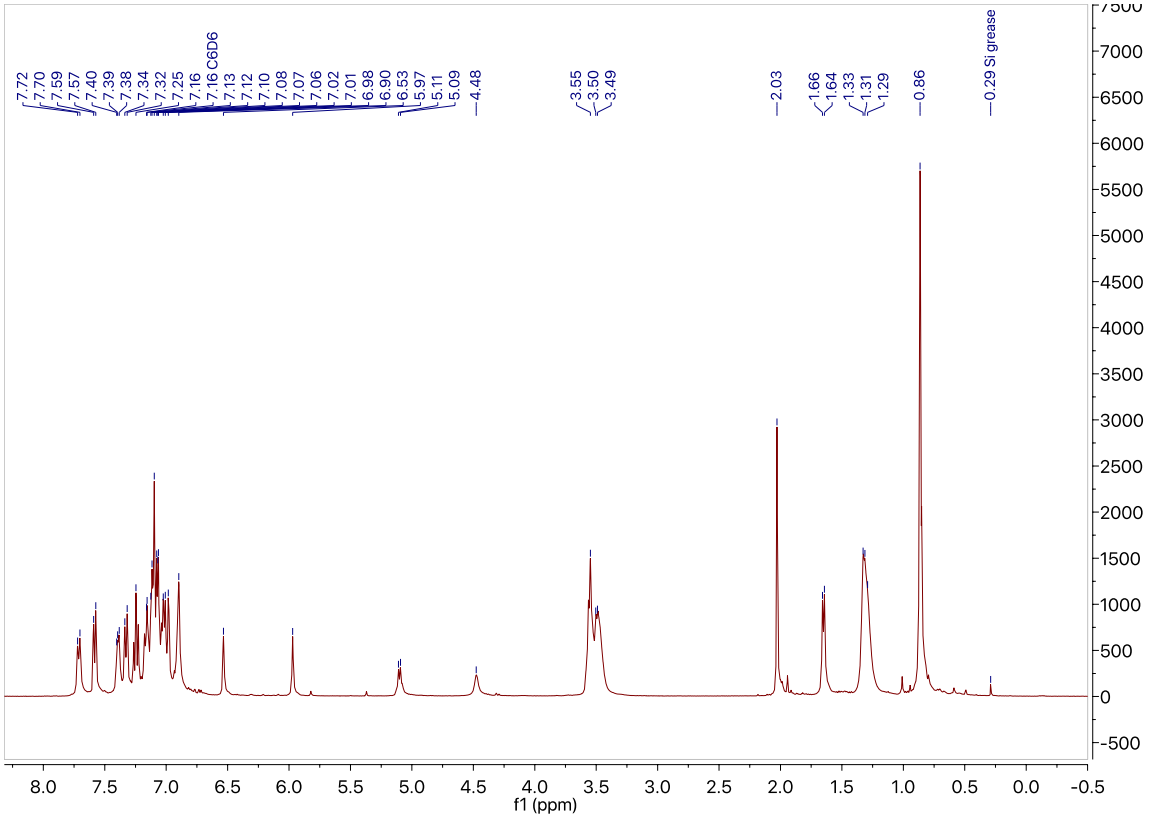

Figure S23. ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of **7**.

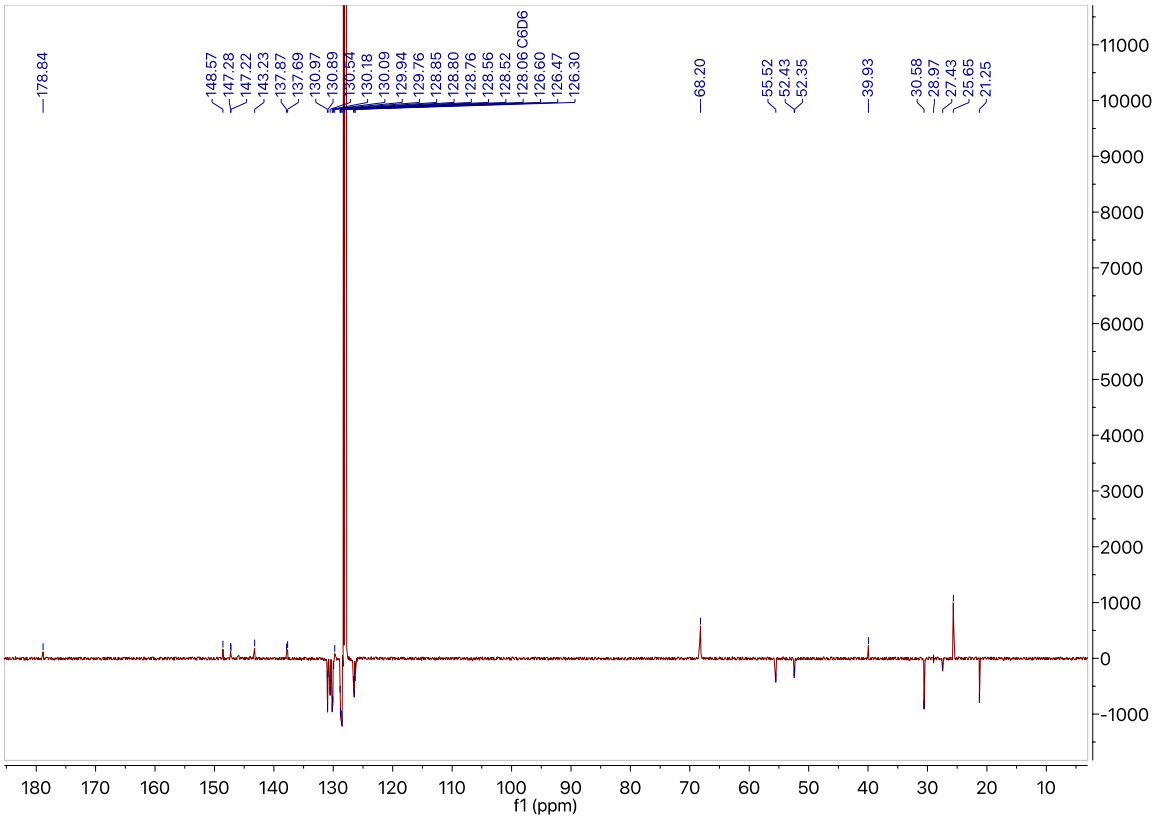

Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, C_6D_6) of **7**.

2. X-Ray Crystallography

Crystals of compounds 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 (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 (SHELX97[4]) using all unique data. Hydrogen atoms are typically included in calculated positions (riding model), except the hydride ligands, the atomic displacement and positional parameters a of which were refined isotropically. 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. Summary of Crystallographic Data for Compounds L^1H, L^2H, **1**, **2**, **5**, and **7**.

	L^1H	L^2H	**1**	**2**	**5**·(toluene)2	**7**·(THF)2
empirical formula	$C_{25}H_{34}N_2$	$C_{46}H_{46}N_2$	$C_{29}H_{43}IMgN_2O$	$C_{50}H_{66}MgN_4$	$C_{114}H_{154}Mg_5N_8$	$C_{108}H_{124}Mg_2N_4O_4$
formula weight	362.54	626.85	586.86	771.68	1757.99	1590.72
crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic	Orthorhombic	Monoclinic
space group	$P2_1$	$P2_1$	$P2_12_12_1$	$P1$	$I222$	$P2_1$
a (Å)	8.3950(2)	17.043(1)	8.5021(3)	9.3482(1)	14.8055(4)	13.2573(8)
b (Å)	12.0810(3)	10.6510(7)	18.0429(6)	11.4823(2)	18.0071(4)	23.7844(17)
c (Å)	11.1318(2)	20.5830(13)	19.2698(7)	12.0801(2)	19.8803(6)	14.6312(11)
α (º)	90	90	90	109.948(2)	90	90
β (º)	96.590(2)	96.752(2)	90	97.683(1)	90	105.348(2)
γ (º)	90	90	90	99.626(1)	90	90
V (Å^3)	1121.53(4)	3710.4(4)	2956.04(18)	1175.98(3)	5300.2(2)	4448.9(5)
Z	2	4	4	1	2	2
T (K)	123(2)	123(2)	123(2)	123(2)	123(2)	123(2)
ρ_{calcd} (g×cm^3)	1.074	1.122	1.319	1.090	1.102	1.187
μ (mm^{-1})	0.466	0.064	1.127	0.087	0.090	0.084
F(000)	396	1344	1216	418	1908	1712
reflns collected	11635	34525	17827	35181	20136	39019
unique reflns	3728	13709	5499	8512	4938	16478
R_{int}	0.0861	0.0755	0.0617	0.0258	0.0370	0.1718
R1 [I > 2σ(I)]	0.0496	0.0683	0.0384	0.0278	0.0307	0.0843
wR2 (all data)	0.1308	0.1334	0.0584	0.0760	0.0764	0.2204
Flack parameter	0.1(5)	-1.6(10)	-0.019(16)	0.05(5)	0.04(8)	-0.1(4)
largest peak and hole (e×Å^{-3})	0.17, -0.20	0.22, -0.26	0.47, -0.45	0.21, -0.17	0.19, -0.19	0.47, -0.43
CCDC No.	2047964	2047967	2047963	2047968	2047966	2047965

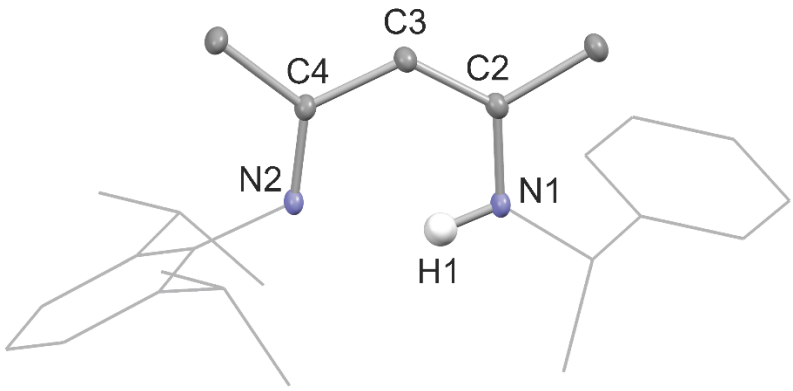

Figure S25. Molecular structure of L^1H (20% ellipsoids; *N*-substituents shown as wire frame for clarity; hydrogen atoms, except amine proton, omitted). Selected bond lengths (Å) and angles (°): N(1)-C(2) 1.351(4), N(2)-C(4) 1.292(4), C(2)-C(3) 1.368(4), C(3)-C(4) 1.440(4), C(2)-C(3)-C(4) 125.8(3).

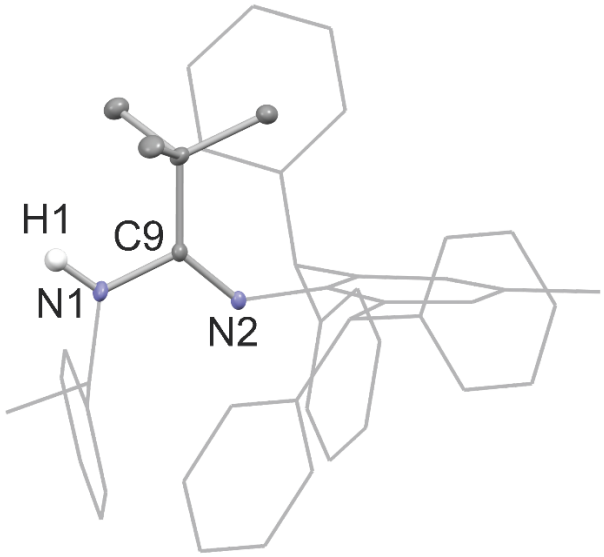

Figure S26. Molecular structure of L^2H (20% ellipsoids; *N*-substituents shown as wire frame for clarity; hydrogen atoms, except amine proton, omitted). Selected bond lengths (Å) and angles (°): N(1)-C(9) 1.382(6), N(2)-C(9) 1.271(6), N(2)-C(9)-N(1) 115.1(5).

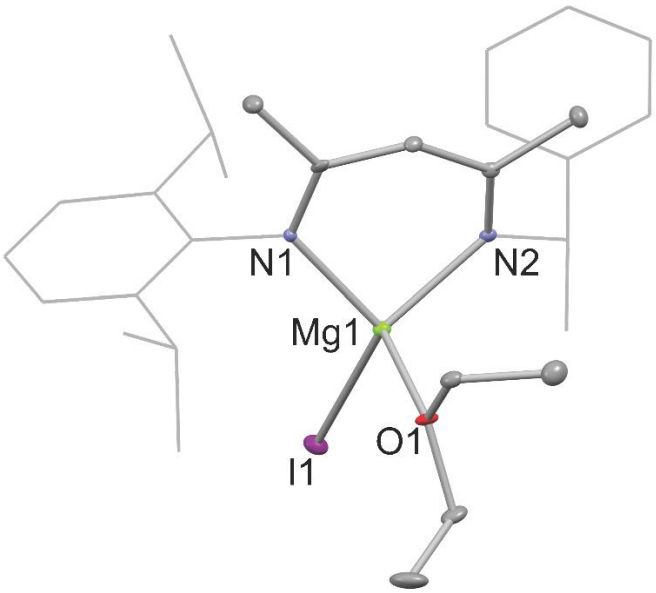

Figure S27. Molecular structure of **1** (20% ellipsoids; *N*-substituents shown as wire frame for clarity; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): I(1)-Mg(1) 2.6865(16), Mg(1)-O(1) 2.026(4), Mg(1)-N(1) 2.035(5), Mg(1)-N(2) 2.044(5), N(1)-Mg(1)-N(2) 93.51(18), O(1)-Mg(1)-I(1) 101.06(11).

4. References

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