Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information for:

Magnesium hydrides bearing sterically demanding amidinate ligands: synthesis, reactivity and catalytic application

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1. General Experimental Section

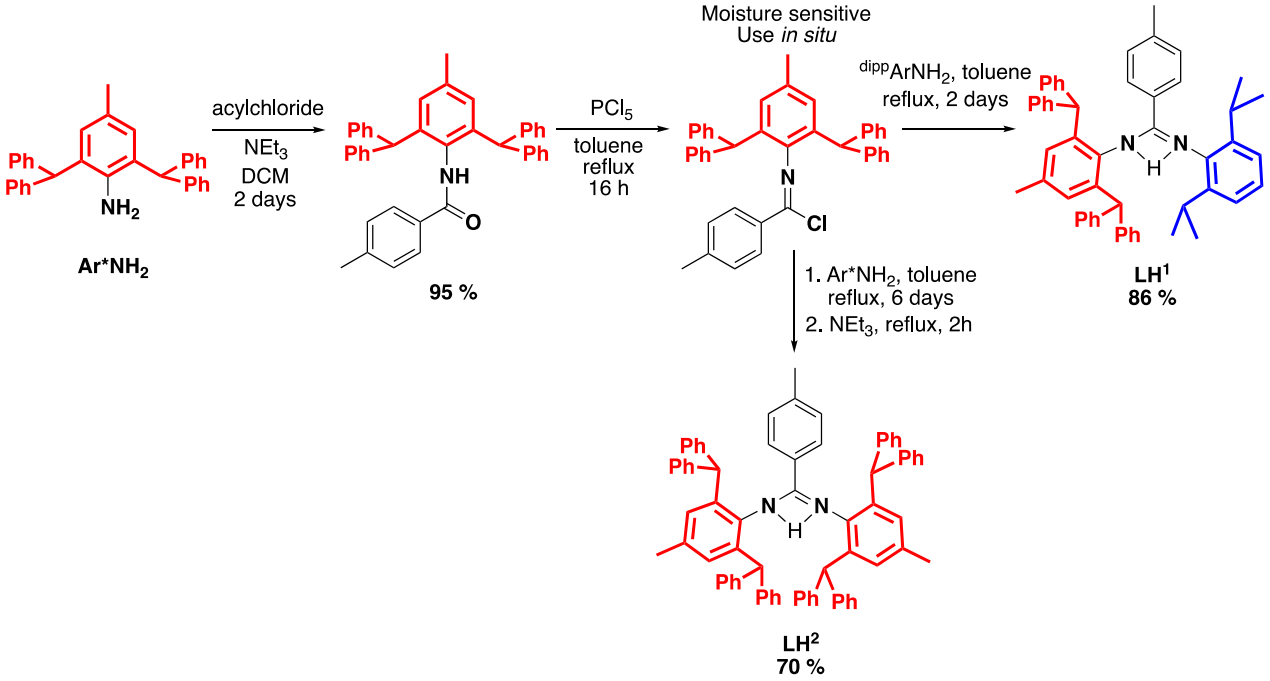
All manipulations were carried out using standard Schlenk-line and glovebox techniques under an inert atmosphere of argon or dinitrogen. A MBraun Labmaster glovebox was employed, operating at < 0.1 ppm O_2 and < 0.1 ppm H_2O. Solvents were dried over activated alumina from an SPS (solvent purification system) based upon the Grubbs design and degassed before use. Glassware was dried for 12 h at 120 °C prior to use. Benzene-d_6 was stored over activated 3Å molecular sieves. NMR-scale reactions were conducted in J. Young's tap tubes and prepared in a glovebox. All heating mentioned was done using silicone oil baths. ^{1}H (tetramethylsilane; 0 ppm) and ^{13}C (tetramethylsilane; 0 ppm) spectra were obtained on BRUKER 400 MHz or 500 MHz machines unless otherwise stated; all peak intensities are derived from internal standard peaks with values quoted in ppm. Data was processed using the MestReNova or Topsin software. C^{IV} refers to quaternary carbons.

Phosphorus pentachloride and *p*-toluoyl chloride were purchased from Sigma Aldrich and used without purification. Ar*NH_2 was prepared according to literature procedure.[1] HBpin, phenylsilane and DIC were purchased from Sigma Aldrich and used without further purification. The alkenes and benzaldehyde were purchased from Sigma Aldrich or Alfa Aeser, distilled and stored over 3Å molecular sieves prior to use. Other chemicals were purchased from Sigma Aldrich, Fluorochem or Alfa Aeser. $Mg[N(SiMe_3)_2]_2$ was prepared according to literature procedure.[2]

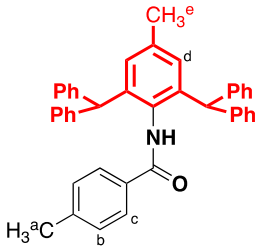
2. Synthetic Procedures

2.1 Pro-ligand synthesis

Figure S1: Synthesis of the pro-ligands **LH^1** and **LH^2.**

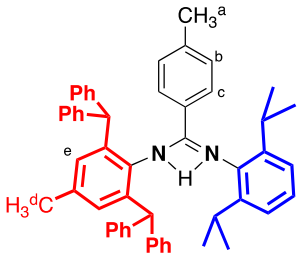


Ar*NCH(O)-*p*-tol: Ar*NH_2 (6.0 g, 13.6 mL), *p*-toluoyl chloride (1.8 mL, 13.6 mmol) and triethylamine (1.55 mL, 13.6 mmol) were added to dichloromethane (300 mL) and stirred at room temperature for 3 days after which time a white precipitate was observed. The organic fraction was diluted with dichloromethane (300 mL), washed with sodium hydrogen carbonate (3 x 400 mL) and dried ($MgSO_4$). The solvent was removed in vacuo to yield the product as a white powder in good purity (7.2 g, 95%).



^{1}H NMR (400 MHz, $CDCl_3$, 298 K): 2.15 (s, 3H, CH_3^e), 2.36 (s, 3H, CH_3^a), 5.63 (s, 2H, CHPh$_2$), 6.38 (s, 1H, NH), 6.59 (s, 2H, CH^d), 6.90-7.12 (m, 10H, ArH), 7.13-7.25 (m, 14H, ArH). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K): 21.5 (CH_3), 21.7 (CH_3), 52.7 (CHPh$_2$), 126.4 (CH), 127.1 (CH), 128.4 (CH), 129.1 (CH), 129.4 (CH), 131.0 (C^{IV}). 131.4 (C^{IV}), 137.1 (C^{IV}), 142.1 (C^{IV}), 142.4 (C^{IV}), 143.1 (C^{IV}), 165.7 (OCNH); Anal. Calc. ($C_{41}H_{35}NO$): C, 88.29; H, 6.63; N, 2.51. Found: C, 88.13; H, 6.56; N, 2.45.

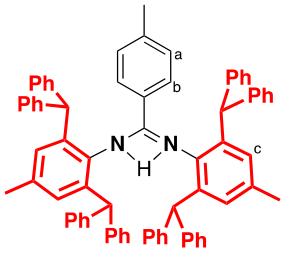
LH^1: Ar*NCH(O)-*p*-tol (7.2 g, 12.9 mmol) and phosphorus pentachloride (3.23 g, 15.5 mmol) were combined in a Schlenk flask which was then placed under nitrogen. Dry toluene (40 mL) was added and the reaction was heated at 110 °C overnight. The solvent was removed *in vacuo* using a secondary trap and the solid residues were heated at 130 °C for 1 hour to drive of residual PCl_5 and the $OPCl_3$ by-product. Full conversion of Ar*NCH(O)-*p*-tol to the imidoyl chloride was confirmed by ^{1}H NMR; the intermediate was not isolated, but used directly in the next step. The residues were dissolved in toluene (30 mL) and 2,6-diisopropylaniline (2.43 mL, 12.9 mmol) and triethylamine (2.34 mL, 16.8 mmol) was added. The reaction was heated at 110 °C for 48 hours, after which time the organic layer was diluted with 50:50 toluene:diethylether (70 mL) and



washed with sodium hydrogen carbonate (1 x 100 mL), followed by water (2 x 100 mL). The organic layer was dried ($MgSO_4$) and the solvent removed in vacuo. The resulting sticky brown residue was triturated with hot methanol to yield a colourless crystalline precipitate (8.0 g, 86%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): 0.82 (d, 6H, CH(CH_3)$_2$, $^3J_{HH}$ = 6.6 Hz), 1.10 (d, 6H, CH(CH_3)$_2$, $^3J_{HH}$ = 6.6 Hz), 2.15 (s, 3H, CH_3^d), 2.19 (s, 3H, CH_3^a), 3.30 (sept, 2H, CH(CH$_3$)$_2$, $^3J_{HH}$ = 6.6 Hz), 4.76 (bs, 1H, NH), 5.93 (s, 2H, CHPh$_2$), 6.51 (d, 2H, ArH^c, $^3J_{HH}$ = 7.2 Hz), 6.55 (s, 2H, ArH^e), 6.79 (d, 2H, ArH^b, $^3J_{HH}$ = 7.2 Hz), 6.85-7.00 (m, 8H, ArH), 7.03-7.11 (m, 4H, ArH), 7.12-7.29 (m, 11H, ArH); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K): 21.2 (CH_3), 21.8 (CH_3), 22.8 (CH(CH_3)$_2$), 24.5 (CH(CH_3)$_2$), 28.3 (CH(CH$_3$)$_2$), 52.7 ($CHPh_2$), 122.0 (CH), 122.8 (CH), 126.2 (CH), 127.5 (CH), 128.1 (CH), 128.4 (CH), 128.6 (CH), 128.9 (CH), 129.3 (CH), 130.0 (CH), 134.8 (C^{IV}), 136.1 (C^{IV}), 138.4 (C^{IV}), 139.0 (C^{IV}), 143.0 (C^{IV}), 143.4 (C^{IV}), 143.8 (C^{IV}), 153.0 (NC(Ar)N); Anal. Calc. ($C_{53}H_{52}N_2$): C, 88.78; H, 7.31; N, 3.91. Found: C, 88.89; H, 7.26; N, 3.84.

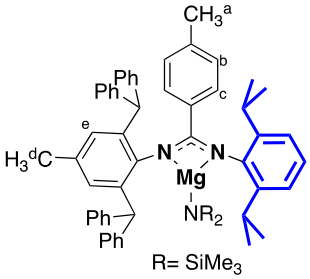
LH^2: Ar*NCH(O)-*p*-tol (3.5 g, 6.7 mmol) and phosphorus pentachloride (1.67 g, 8.0 mmol) were combined in a Schlenk flask which was then placed under nitrogen. Dry toluene (20 mL) was added and the reaction was heated at 110 °C overnight. The solvent was removed *in vacuo* using a secondary trap and the solid residues were heated at 130 °C for 1 hour to drive of residual PCl_5 and the $OPCl_3$ by-product. Full conversion of Ar*NCH(O)-*p*-tol to the imidoyl chloride was confirmed by ^{1}H NMR; the intermediate was not isolated, but used directly in the next step. The residues were dissolved in toluene (30 mL) and Ar*NH_2 (2.64 g, 6.0 mmol) was added. The reaction was heated at 110 °C for 6 days after which time triethylamine (1.21 mL, 8.7 mmol) was added and the reaction heated for a further 2 hours at 110 °C. The organic layer was then diluted with toluene (70 mL) and washed with sodium hydrogen carbonate (1 x 100 mL), followed by water (2 x 100 mL). The organic layer was dried ($MgSO_4$) and the solvent removed in vacuo. The resulting sticky brown residue was triturated with methanol to yield a white precipitate which could be further recrystallized from a mixture of dichloromethane and methanol. The product was isolated as a colourless crystalline solid (4.6 g, 70%).



^{1}H NMR (500 MHz, $CDCl_3$, 298 K): 2.12 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 5.03 (s,1H, NH), 5.89 (s, 4H, CHPh$_2$), 6.48-7.18 (m, 48H, ArH); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): 21.3 (CH_3), 21.5 (CH_3), 21.8 (CH_3), 51.4 ($CHPh_2$), 53.1 ($CHPh_2$), 125.4 (CH), 125.5 (CH), 126.0 (CH), 126.3 (CH), 126.8 (CH), 127.9 (CH), 128.1 (CH), 128.3 (CH), 128.8 (CH), 129.1 (CH), 129.4 (CH), 129.5 (CH), 129.7 (CH), 130.0 (CH), 132.0 (C^{IV}), 134.1 (C^{IV}), 135.9 (C^{IV}), 138.7 (C^{IV}), 142.7 (C^{IV}), 142.9 (C^{IV}), 143.4 (C^{IV}), 143.9 (C^{IV}), 144.7 (C^{IV}), 145.2 (C^{IV}), 154.8 (C^{IV}); Anal. Calc. ($C_{74}H_{62}N_2$): C, 90.76; H, 6.38; N, 2.86. Found: C, 90.59; H, 6.41; N, 2.83.

2.2 Complex synthesis

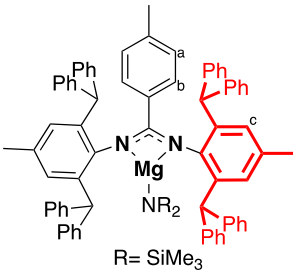
1a: LH^1 (200 mg, 0.28 mmol) and Mg[N(SiMe$_3$)$_2$]$_2$ (96.2 mg, 0.28 mmol) were dissolved in toluene (10 ml) and transferred to a J. Young's ampoule. The reaction was stirred at room temperature overnight, after which time the solvent was removed *in vacuo*. The off white residue was washed with *n*-hexane (5 ml) and the resulting precipitated isolated and dried to yield a white solid (150 mg, 60%).



^{1}H NMR (600 MHz, benzene-d_6, 298 K): 0.02 (s, 18H, N(Si(CH_3)$_3$)$_2$), 0.97 (d, 6H, CH(CH_3)$_2$, $^3J_{HH}$ = 6.8 Hz), 1.35 (d, 6H, CH(CH_3)$_2$, $^3J_{HH}$ = 6.8 Hz), 1.81 (s, 3H, CH_3^a), 1.86 (s, 3H, CH_3^d), 3.49 (sept, 2H, CH(CH$_3$)$_2$, $^3J_{HH}$

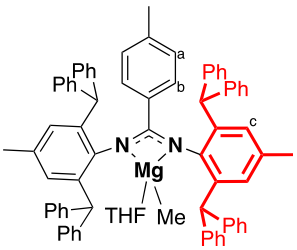
= 6.8 Hz), 6.08 (s, 2H, C*H*Ph$_2$), 6.37 (d, 2H, Ar*H*^{b}, $^3J_{HH}$ = 8.0 Hz), 6.82 (m, 4H, Ar*H*), 6.92 (d, 2H, Ar*H*^{c}, $^3J_{HH}$ = 8.0 Hz), 6.94 (s, 2H, Ar*H*^{e}), 6.95-7.06 (m, 11H, Ar*H*), 7.25 (m, 4H, Ar*H*), 7.39 (m, 4H, Ar*H*). ^{13}C{^{1}H} NMR (125 MHz, benzene-d_6, 298 K): 5.5 (N(Si(*C*H$_3$)$_3$)$_2$), 20.9 (*C*H$_3$^{a}), 21.2 (*C*H$_3$^{d}), 23.4 (CH(*C*H$_3$)$_2$), 25.3 (CH(*C*H$_3$)$_2$), 28.9 (*C*H(CH$_3$)$_2$), 53.3 (*C*HPh$_2$), 123.7 (*C*H), 125.0 (*C*H), 126.5 (*C*H), 128.3(*C*H), 128.5 (*C*H), 128.8 (*C*H), 129.2 (*C*H), 129.3 (*C*H), 129.7 (*C*H), 130.1 (*C*H), 130.7 (*C*H), 132.8 (C^{IV}), 139.0 (C^{IV}), 139.2 (C^{IV}), 142.0 (C^{IV}), 142.3 (C^{IV}), 142.4 (C^{IV}), 143.9 (C^{IV}), 144.3 (C^{IV}), 172.9 (N*C*(Ar)N).

1b: LH^2 (200 mg, 0.20 mmol) and Mg[N(SiMe$_3$)$_2$]$_2$ (70.5 mg, 0.20 mmol) were dissolved in toluene (10 ml) and transferred to a J. Young's ampoule. The reaction was heated at reflux for 3 days after which time the solvent was removed *in vacuo*. The off white residue was washed with *n*-hexane (5 ml) and the resulting precipitated isolated and dried to yield a white solid (180 mg, 76%).



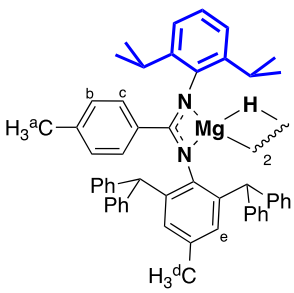
^{1}H NMR (500 MHz, benzene-d_6, 298 K): -0.15 (s, 18H, N(Si(C*H*$_3$)$_3$)$_2$), 1.80 (s, 6H, C*H*$_3$), 1.83 (s, 3H, C*H*$_3$), 6.23 (d, 2H, Ar*H*^{b}, $^3J_{HH}$ = 8.0 Hz), 6.26 (s, 4H, C*H*Ph$_2$), 6.82-6.86 (m, 10H, Ar*H*), 6.90-6.95 (m, 12H, Ar*H*), 7.07 (s, 4H, Ar*H*^{C}), 6.95-7.14 (m, 4H, Ar*H*), 7.24 (t, 8H, Ar*H*, $^3J_{HH}$ = 7.5 Hz), 7.44 (d, 8H, Ar*H*, $^3J_{HH}$ = 7.5 Hz); ^{13}C{^{1}H} NMR (125 MHz, benzene-d_6, 298 K): 5.2 (N(Si(*C*H$_3$)$_3$)$_2$), 20.8 (*C*H$_3$), 21.0 (*C*H$_3$), 52.1 (*C*HPh$_2$), 126.2 (*C*H), 127.3 (*C*H), 128.2 (*C*H), 128.9 (*C*H), 129.7 (*C*H), 129.7 (*C*H), 130.0 (*C*H), 130.7 (*C*H^C), 138.6 (C^{IV}), 139.4 (C^{IV}), 143.0 (C^{IV}), 144.0 (C^{IV}), 144.5 (C^{IV}), 175.7 (N*C*(Ar)N).

2b: LH^2 (200 mg, 0.20 mmol) and MgMe$_2$ (12.2 mg, 0.22 mmol) were dissolved in THF (10 ml) and the reaction was stirred at room temperature overnight. The solvent was removed *in vacuo* and the off white residue was recrystallised from a toluene:*n*-hexane mix (5 ml). The resulting crystals were isolated and dried to yield a white solid (160 mg, 72%).



^{1}H NMR (500 MHz, benzene-d_6, 298 K): -1.11 (Mg-C*H*$_3$), 0.92 (4H, m, O(CH$_2$)$_2$(C*H*$_2$)$_2$), 1.82 (s, 6H, C*H*$_3$), 1.88 (s, 3H, C*H*$_3$), 2.60 (4H, m, O(C*H*$_2$)$_2$(CH$_2$)$_2$), 6.15 (d, 2H, Ar*H*^{a}, $^3J_{HH}$ = 8.0 Hz), 6.49 (s, 4H, C*H*Ph$_2$), 6.94-7.14 (m, 38H, Ar*H*), 7.42 (d, 8H, Ar*H*, $^3J_{HH}$ = 7.5 Hz); ^{13}C{^{1}H} NMR (125 MHz, benzene-d_6, 298 K): -13.9 (Mg-*C*H$_3$), 20.9 (*C*H$_3$), 21.0 (*C*H$_3$), 25.0 (O(CH$_2$)$_2$(*C*H$_2$)$_2$), 51.9 (*C*HPh$_2$), 68.1 (O(*C*H$_2$)$_2$(CH$_2$)$_2$), 125.9 (*C*H), 126.2 (*C*H), 128.1 (*C*H), 128.5 (*C*H), 128.7 (*C*H), 130.1 (*C*H), 130.2 (*C*H), 130.7 (*C*H), 130.8 (*C*H), 131.5 (C^{IV}), 137.8 (C^{IV}), 138.4 (C^{IV}), 144.4 (C^{IV}), 145.1 (C^{IV}), 145.4 (C^{IV}), 172.3 (N*C*(Ar)N).

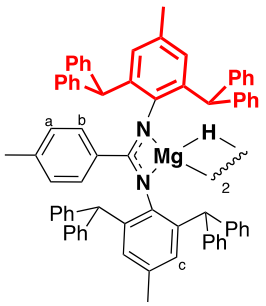
3a: LH^1 (400 mg, 0.56 mmol) and Mg[N(SiMe$_3$)$_2$]$_2$ (192.5 mg, 0.56 mmol) were dissolved in toluene (10 ml) and transferred to a J. Young's ampoule. The reaction was stirred at room temperature overnight, after which time the solvent was removed *in vacuo*. The residue was re-dissolved in toluene (10 ml), phenylsilane (137 µl, 1.11 mmol) was added and the reaction was heated to 80 °C overnight. The solvent was concentrated to approximated 5 ml, n-hexane (10 ml) was added and the flask was transferred to the fridge. Colourless crystals form after standing overnight which were isolated and dried *in vacuo* (240 mg, 58%).



^{1}H NMR (500 MHz, benzene-d_6, 298 K): 0.93 (d, 6H, CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.8 Hz), 1.07 (d, 6H, CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.8 Hz), 1.75 (s, 3H, C*H*$_3$^{a}), 1.85 (s, 3H, C*H*$_3$^{d}), 3.39 (sept, 2H, C*H*(CH$_3$)$_2$, $^3J_{HH}$ = 6.8 Hz), 3.64 (s, 1H, Mg-*H*), 6.22 (s, 2H, C*H*Ph$_2$), 6.39 (d,

2H, ArH^b, $^3J_{HH}$ = 8.0 Hz), 6.81 (d, 2H, ArH^c, $^3J_{HH}$ = 8.1 Hz), 6.90 (s, 2H, ArH^e), 6.93-7.10 (m, 17H, Ar*H*), 7.13 (d, 2H, Ar*H*, $^3J_{HH}$ = 7.5 Hz), 7.31 (d, 4H, Ar*H*, $^3J_{HH}$ = 7.5 Hz). $^{13}C\{^1H\}$ NMR (125 MHz, benzene-d_6, 298 K): 20.8 (CH_3), 21.0 (CH_3), 22.5 ($CH(CH_3)_2$), 25.1 ($CH(CH_3)_2$), 28.2 ($CH(CH_3)_2$), 52.5 ($CHPh_2$), 123.3 (*C*H), 124.1 (*C*H), 126.4 (*C*H), 126.7 (*C*H), 128.3 (*C*H), 128.4 (*C*H), 129.1 (*C*H), 129.6 (*C*H), 129.7 (C^{IV}), 129.9 (*C*H), 130.1 (*C*H), 132.1 (C^{IV}), 138.4 (C^{IV}), 139.0 (C^{IV}), 142.2 (C^{IV}), 142.3 (C^{IV}), 142.9 (C^{IV}), 144.1 (C^{IV}), 144.8 (C^{IV}), 173.6 (N*C*(Ar)N). IR υ/cm^{-1} (ATR): 1599 (w), 1443 (m), 1396 (w), 1360 (w), 1325 (w), 1242 (w), 1076 (w), 1032 (w), 841 (w), 820 (w), 760 (w), 714 (w), 698 (s), 606 (m), 555 (w), 530 (w).

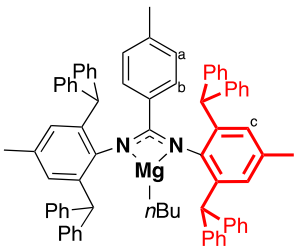
3b; Route 1: LH^2 (200 mg, 0.2 mmol) and Mg[N(SiMe$_3$)$_2$]$_2$ (70.5 mg, 0.2 mmol) were dissolved in toluene (10 ml) and transferred to a J. Young's ampoule. The reaction was heated at reflux for 3 days after which time the solvent was removed *in vacuo*. The white residue was re-dissolved in toluene (10 ml), phenylsilane (75 µl, 0.61 mmol) was added and the solution was heated at 110 °C for 3 days. The solvent was removed *in vacuo* and ^{1}H NMR analysis showed the formation of the product, however, it was difficult to isolated the product cleanly, free from minor impurities.



3b; Route 2: LH^2 (500 mg, 0.51 mmol) was dried under vacuum for 1 hour and dissolved in toluene (5 ml). Di-n-butylmagnesium (1 M in heptane, 0.61 ml, 0.61 mmol) was added dropwise and the solution was stirred at room temperature for 5 hours after which time the solvent was removed *in vacuo*. The white residue was re-dissolved in toluene (10 ml), phenylsilane (143 µl, 1.16 mmol) was added and the solution was heated at 80 °C overnight. The precipitate that formed was isolated and dried *in vacuo* to yield the pure product as a white powder (300 mg, 58%).

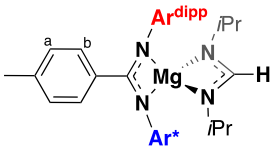
^{1}H NMR (500 MHz, benzene-d_6, 298 K): 1.83 (s, 3H, CH_3), 1.92 (s, 6H, CH_3), 5.03 (s, 1H, Mg-*H*), 6.08 (d, 2H, ArH^a, $^3J_{HH}$ = 8.0 Hz), 6.33 (d, 2H, ArH^b, $^3J_{HH}$ = 8.0 Hz), 6.36 (s, 4H, CHPh$_2$), 6.73 (bs, 8H, Ar*H*), 6.83-7.04 (m, 24H, Ar*H*), 7.07 (s, 4H, ArH^c), 7.50 (d, 8H, Ar*H*, $^3J_{HH}$ = 6.7 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, benzene-d_6, 298 K): 20.9 (CH_3), 51.9 ($CHPh_2$), 125.9 (*C*H), 126.6 (*C*H), 128.0 (*C*H), 128.2 (*C*H), 128.4 (*C*H), 129.3 (*C*H), 129.9 (*C*H), 130.2 (*C*H), 131.0 (*C*H), 132.1 (C^{IV}), 138.7 (C^{IV}), 138.7 (C^{IV}), 139.2 (C^{IV}), 143.2 (C^{IV}), 143.7 (C^{IV}), 145.6 (C^{IV}), 178.4 (N*C*(Ar)N). IR υ/cm^{-1} (ATR): 1624 (w), 1599 (w), 1493 (m), 1445 (m), 1392 (w), 1340 (w), 1078 (w), 1032 (w), 856 (w), 827 (w), 760 (m) 745 (m), 729 (m), 696 (s), 606 (m), 557 (m), 464 (m); Anal. Calc. ($C_{74}H_{62}MgN_2$): C, 88.56; H, 6.63; N, 2.79. Found: C, 88.35; H, 6.48; N, 2.65.

NMR data for LMg(*n*Bu) intermediate: ^{1}H NMR (500 MHz, benzene-d_6, 298 K): -1.09 (m, 2H, Mg-CH_2(CH$_2$)$_2$CH$_3$), 1.09-1.20 (m, 5H, CH_2 and CH_3), 1.37 (sept, 2H, CH_2, $^3J_{HH}$ = 7.2 Hz), 1.77 (s, 6H, CH_3), 1.82 (s, 3H, CH_3), 6.32 (s, 4H, CHPh$_2$), 6.54 (d, 2H, ArH^a, $^3J_{HH}$ = 8.0 Hz), 6.84 (s, 4H, ArH^C), 6.98-7.21 (m, 40H, Ar*H*), 7.39 (d, 2H, ArH^b, $^3J_{HH}$ = 8.0 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, benzene-d_6, 298 K): 6.5 (Mg-CH_2), 14.4 (CH_3), 20.9 (CH_3), 21.0 (CH_3), 31.8 (CH_2), 32.0 (CH_2), 52.4 ($CHPh_2$), 126.4 (*C*H), 127.1 (*C*H), 128.2 (*C*H), 128.5 (*C*H), 129.0 (*C*H), 129.3 (*C*H), 129.7 (*C*H), 130.3 (*C*H), 130.5 (*C*H), 132.6 (C^{IV}), 138.5 (C^{IV}), 139.7 (C^{IV}), 143.1 (C^{IV}), 144.1 (C^{IV}), 144.5 (C^{IV}), 173.9 (N*C*(Ar)N).

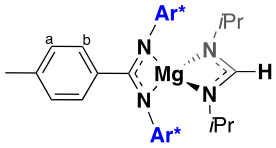


General NMR scale procedure for the insertion of DIC: Compound **3a** or **3b** (0.02 mmol) was dissolved in benzene-d_6 (0.6 ml) and *N,N'*-diisopropylcarbodiimide (3 µl, 0.02 mmol) was added using a micro pipette. The reactions were monitered by ^{1}H NMR. Compound **3a** was fully converted to **4a** within 15 minutes at room temperature, whereas full

formation of **4b** required 16 hours at 298 K. *Note:* The reactions could also be performed on a larger scale, but due to relative instabilities and problems with isolation, compounds **4a** and **4b** were formed and analysed *in situ*.

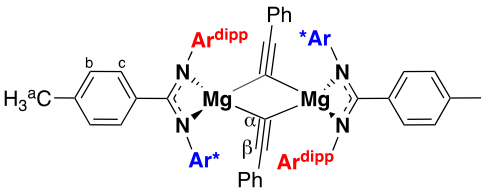


4a: ^{1}H NMR (600 MHz, benzene-d_6, 298 K): 0.87 (d, 12H, N(CH(C*H*)$_3$), $^{3}J_{HH}$ = 6.5 Hz), 0.91 (d, 6H, CH(C*H*)$_3$, $^{3}J_{HH}$ = 6.8 Hz), 1.32 (d, 6H, CH(C*H*)$_3$, $^{3}J_{HH}$ = 6.8 Hz), 1.77 (s, 3H, C*H*$_3$), 1.84 (s, 3H, C*H*$_3$), 3.08 (sept, 2H, N(C*H*(CH)$_3$), $^{3}J_{HH}$ = 6.5 Hz), 3.50 (sept, 2H, C*H*(CH)$_3$, $^{3}J_{HH}$ = 6.8 Hz), 6.28 (d, 2H, Ar*H*^{a}, $^{3}J_{HH}$ = 8.0 Hz), 6.31 (s, 2H, C*H*Ph$_2$), 6.61 (d, 2H, Ar*H*^{b}, $^{3}J_{HH}$ = 8.0 Hz), 6.95 (s, 2H, Ar*H*), 6.98-7.13 (m, 13H, Ar*H*), 7.20 (t, 4H, Ar*H*, $^{3}J_{HH}$ = 7.6 Hz), 7.35 (d, 4H, Ar*H*, $^{3}J_{HH}$ = 7.6 Hz), 7.91 (s, 1H, C*H*(N*i*Pr)$_2$); ^{13}C{^{1}H} NMR (150 MHz, benzene-d_6, 298 K): 20.9 (*C*H$_3$), 21.1 (*C*H$_3$), 22.8 (CH(*C*H)$_3$), 25.7 (CH(*C*H)$_3$), 26.3 (N(CH(*C*H)$_3$)), 28.6 (*C*H(CH)$_3$), 49.7 (N(*C*H(CH)$_3$)), 52.4 (*C*HPh$_2$), 123.5 (*C*H), 124.3 (*C*H), 126.3 (*C*H), 126.6 (*C*H), 128.4 (*C*H), 128.6 (*C*H), 128.8 (*C*H), 129.8 (*C*H), 130.0 (*C*H), 130.3 (*C*H), 130.8 (*C*H), 131.8 (C^{IV}), 138.3 (C^{IV}), 138.7 (C^{IV}), 142.5 (C^{IV}), 142.6 (C^{IV}), 143.3 (C^{IV}), 144.2 (C^{IV}), 145.4 (C^{IV}), 169.0 (*C*H(N*i*Pr)$_2$), 173.7 (N*C*(Ar)N).



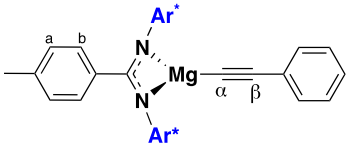
4b: ^{1}H NMR (600 MHz, benzene-d_6, 298 K): 0.77 (d, 12H, CH(C*H*)$_3$, $^{3}J_{HH}$ = 6.5 Hz), 1.77 (s, 6H, C*H*$_3$), 1.87 (s, 3H, C*H*$_3$), 2.87 (sept, 2H, CH(C*H*)$_3$, $^{3}J_{HH}$ = 6.5 Hz), 6.09 (d, 2H, Ar*H*^{a}, $^{3}J_{HH}$ = 8.0 Hz), 6.31 (s, 4H, C*H*Ph$_2$), 6.76 (d, 2H, Ar*H*^{b}, $^{3}J_{HH}$ = 8.0 Hz), 6.88-7.19 (m, 36H, Ar*H*), 7.36 (d, 8H, Ar*H*, $^{3}J_{HH}$ = 7.5 Hz), 7.86 (s, 1H, C*H*(N*i*Pr)$_2$); ^{13}C{^{1}H} NMR (150 MHz, benzene-d_6, 298 K): 21.1 (*C*H$_3$), 21.2 (*C*H$_3$), 25.9 (CH(*C*H$_3$)$_2$), 48.5 (*C*H(CH$_3$)$_2$), 52.1 (*C*HPh$_2$), 126.1 (*C*H), 126.6 (*C*H), 128.4 (*C*H), 128.8 (*C*H), 129.0 (*C*H), 129.8 (*C*H), 130.2 (*C*H), 130.3 (*C*H), 130.9 (*C*H), 131.8 (C^{IV}), 135.6 (C^{IV}), 137.9 (C^{IV}), 138.8 (C^{IV}), 143.3 (C^{IV}), 144.7 (C^{IV}), 145.7 (C^{IV}), 166.6 (*C*H(N*i*Pr)$_2$), 173.6 (N*C*(Ar)N).

5a: 1a or **3a** (0.01 mmol) was dissolved in benzene-d_6 (0.6 ml) and transferred to a J. Young's NMR tube. Phenylacetylene (1.1 µl, 0.01 mmol) was added, and the reaction was monitored by ^{1}H NMR spectroscopy. Due to issues with stability, **5a** was generated in situ and fully characterised without further isolation.



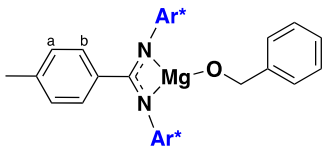
^{1}H NMR (500 MHz, benzene-d_6, 298 K): 0.84 (d, 12H, CH(C*H*$_3$)$_2$, $^{3}J_{HH}$ = 6.7 Hz), 1.20 (d, 12H, CH(C*H*$_3$)$_2$, $^{3}J_{HH}$ = 6.7 Hz), 1.64 (s, 6H, C*H*$_3^{a}$), 1.75 (s, 6H, C*H*$_3$), 3.63 (sept, 4H, C*H*(CH$_3$)$_2$, $^{3}J_{HH}$ = 6.7 Hz), 5.87 (d, 4H, Ar*H*^{b}, $^{3}J_{HH}$ = 8.2 Hz), 6.19 (d, 4H, Ar*H*^{c}, $^{3}J_{HH}$ = 8.2 Hz), 6.72 (t, 4H, Ar*H*, $^{3}J_{HH}$ = 7.5 Hz), 6.79 (s, 4H, C*H*Ph$_2$), 6.80-7.15 (m, 44H, Ar*H*), 7.24 (d, 8H, Ar*H*, $^{3}J_{HH}$ = 7.4 Hz), 7.29 (d, 4H, Ar*H*, $^{3}J_{HH}$ = 7.1 Hz); ^{13}C{^{1}H} NMR (125 MHz, benzene-d_6, 298 K): 20.9 (*C*H$_3$), 21.1 (*C*H$_3$), 22.8 (CH(*C*H)$_3$), 26.3 (CH(*C*H)$_3$), 28.6 (*C*H(CH)$_3$), 51.8 (*C*HPh$_2$), 105.2 (Mg*C*$_\alpha$≡C), 122.1 (MgC≡*C*$_\beta$), 123.7 (*C*H), 124.1 (*C*H), 126.0 (*C*H), 126.0 (*C*H), 127.4 (*C*H), 128.3 (*C*H), 128.5 (*C*H), 129.5 (*C*H), 129.7 (*C*H), 130.0 (*C*H), 130.3 (*C*H), 131.5 (*C*H), 132.1 (C^{IV}), 132.4 (C^{IV}), 134.0 (*C*H), 137.6 (C^{IV}), 138.7 (C^{IV}), 142.2 (C^{IV}), 142.9 (C^{IV}), 143.0 (C^{IV}), 143.6 (C^{IV}), 148.0 (C^{IV}), 175.7 (N*C*(Ar)N).

5b: 1b or **3b** (0.01 mmol) was dissolved in benzene-d_6 (0.6 ml) and transferred to a J. Young's NMR tube. Phenylacetylene (1.1 µl, 0.01 mmol) was added, and the reaction was monitored by ^{1}H NMR spectroscopy. Due to issues with stability, **5b** was generated in situ and fully characterised without further isolation.



^{1}H NMR (500 MHz, benzene-d_6, 298 K): 1.79 (s, 6H, CH_3), 1.86 (s, 3H, CH_3), 6.24 (s, 4H, CHPh$_2$), 6.41 (d, 2H, ArH^a, $^3J_{HH}$ = 7.8 Hz), 6.85 (s, 4H, ArH), 6.97 (d, 2H, ArH^b, $^3J_{HH}$ = 7.8 Hz), 7.01 (m, 4H, ArH), 7.04 (m, 16H, ArH), 7.09 (m, 4H, ArH), 7.13 (m, 2H, ArH), 7.17 (m, 9H, ArH), 7.23 (m, 8H, ArH), 7.56 (m, 2H, ArH). ^{13}C{^{1}H} NMR (125 MHz, benzene-d_6, 298 K): 21.1 (CH_3), 21.2 (CH_3), 52.5 (CHPh$_2$), 109.8 (MgC≡C_β), 116.6 (MgC_α≡C), 126.2 (CH), 126.4 (CH), 127.8 (CH), 128.3 (CH), 128.5 (CH), 128.8 (CH), 129.2 (CH), 129.5 (CH), 129.9 (CH), 130.0 (CH), 130.4 (CH), 132.1 (CH), 132.8 (C^{IV}), 138.9 (C^{IV}), 139.4 (C^{IV}), 142.4 (C^{IV}), 143.5 (C^{IV}), 145.4 (C^{IV}), 172.6 (NC(Ar)N).

6b: 3b (0.01 mmol) was dissolved in benzene-d_6 (0.6 ml) and transferred to a J. Young's NMR tube. Benzaldehyde (1.1 μl, 0.01 mmol) was added, and the reaction was monitored by ^{1}H NMR spectroscopy. Due to issues with stability, **6b** was generated in situ. Benzyl benzoate (0.8 equivs) was formed at the same time and thus only the compounds' ^{1}H NMR data is reported and assigned as best as possible.



^{1}H NMR (500 MHz, benzene-d_6, 298 K): 1.67 (s, 3H, CH_3), 1.96 (s, 6H, CH_3), 5.49 (d,), 5.67 (d, 2H, ArH^a, $^3J_{HH}$ = 6.7 Hz), 5.67 (s, 2H, OCH_2Ph), 6.23 (d, 2H, ArH^b, $^3J_{HH}$ = 6.7 Hz), 6.56-7.25 (broad signal and multiplets corresponding to ArH and CHPh$_2$).

2.3 Catalytic Methods

Hydroboration of carbodiimide: In a glovebox, a J. Young's was loaded with **1a-b**, **3a-b** (0.025 mmol) in C_6D_6 (0.6 mL). Compounds **3a** and **3b** required heating into solution before the addition of substrates. *N,N′*-Diisopropylcarbodiimide (37.3 μl, 0.25 mmol) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (34.8 μl, 0.25 mmol) were added to the tube and mesitylene was added as an internal standard, a t=0 ^{1}H NMR spectrum was recorded. The tube was heated to either 60 or 80 °C and the progress of the reaction was monitored by taking ^{1}H NMR spectra at regular intervals, with conversions calculated versus the internal standard.

Hydroboration of Phenylacetylene: In a glovebox, a J. Young's was loaded with **1a-b**, **3b** (0.015 mmol) in C_6D_6 (0.6 mL). Compounds **3a** and **3b** required heating into solution before the addition of substrates. Phenylacetylene (16.3 μl, 0.15 mmol) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (21.7 μl, 0.15 mmol) were added to the tube and mesitylene was added as an internal standard, a t=0 ^{1}H NMR spectrum was recorded. The tube was either left at room temperature or heated to 80 °C and the progress of the reaction was monitored by taking ^{1}H NMR spectra at regular intervals, with conversions calculated versus the internal standard.

Tishchenko Reaction: In a glovebox, a J. Young's was loaded with **1b** or **3b** (0.006 mmol) in C_6D_6 (0.6 mL). Compounds **3b** required heating into solution before the addition of the substrate. Benzaldehyde (61 μl, 0.6 mmol) was added to the tube. The reaction started immediately, with the progress monitored by taking ^{1}H NMR spectra at regular intervals. The ratio of benzaldehyde to benzyl benzoate was used to calculate the conversion.

3. Additional Spectroscopic Data

3.1 Diffusion Ordered NMR Spectroscopy

DOSY experiments were conducted using a DSTE (double stimulated echo for convection compensation) pulse sequence according to literature procedure on either a 500 or 600 MHz NMR spectrometer.[3]

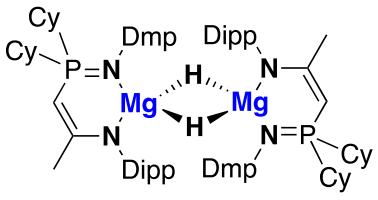
Table S1: DOSY data for magnesium complexes

Compound	**Diffusion Coefficient**	**Hydrodynamic radius (r_s) Å**	**Spherical volume Å^3**
1a	4.95 x 10^{-10}	7.74	1600
3a	4.72 x 10^{-10}	7.61	1850
1b	4.64 x 10^{-10}	7.24	1950
3b	4.04 x 10^{-10}	8.89	2950
2b	5.37 x 10^{-10}	6.69	1250

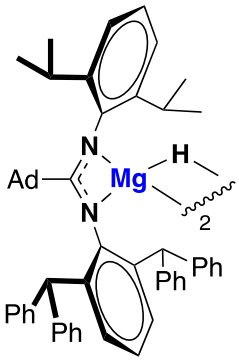
3.2 Magnesium Hydrides

Figure S2: A selection of monomeric and dimeric magnesium hydrides and their associated Mg–*H* ^{1}H NMR shifts (ppm).[4-17]

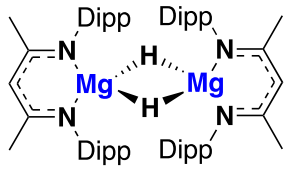
Dimers



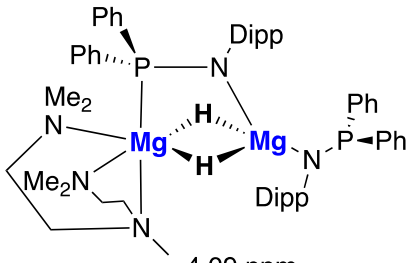
3.84 ppm



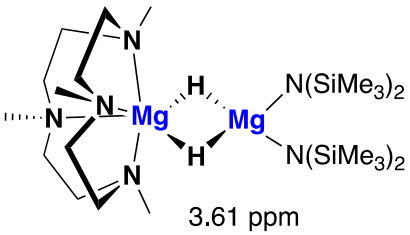
3.84 ppm



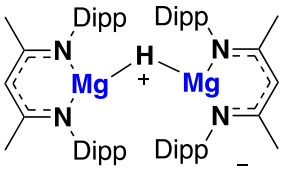
4.03 ppm



4.09 ppm

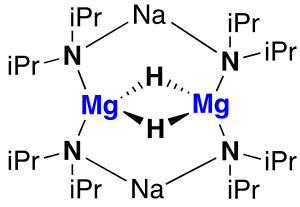


3.61 ppm

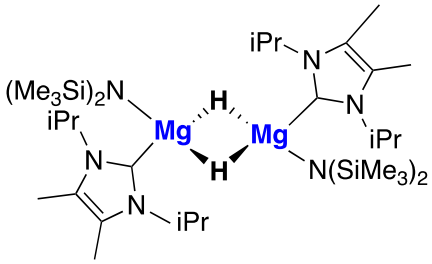


$^{-}$ [Al(OHCH4(CHF$_3$)$_3$)$_4$]

4.76 ppm

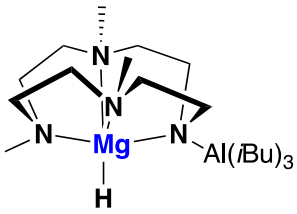


3.70 ppm

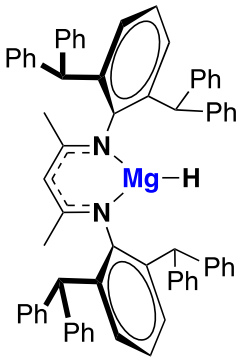


4.28 ppm

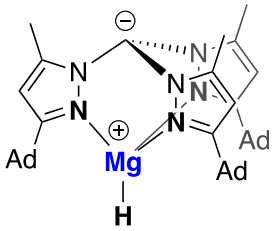
Monomers



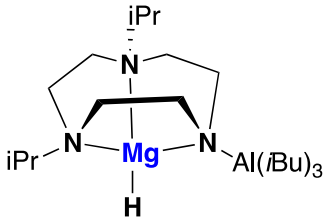
3.55 ppm



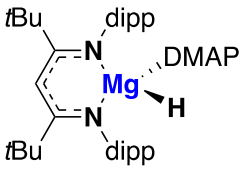
4.07 ppm



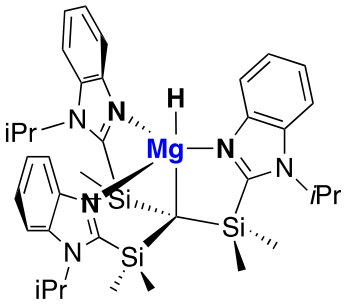
5.68 ppm



4.15 ppm



4.65 ppm



6.78 ppm

4. Stoichiometric Reactions

Figure S3: Stack plot of the reaction of **3b** with an excess of *N,N'*-diisopropylcarbodiimide (DIC) over time to form the insertion product **4b**.

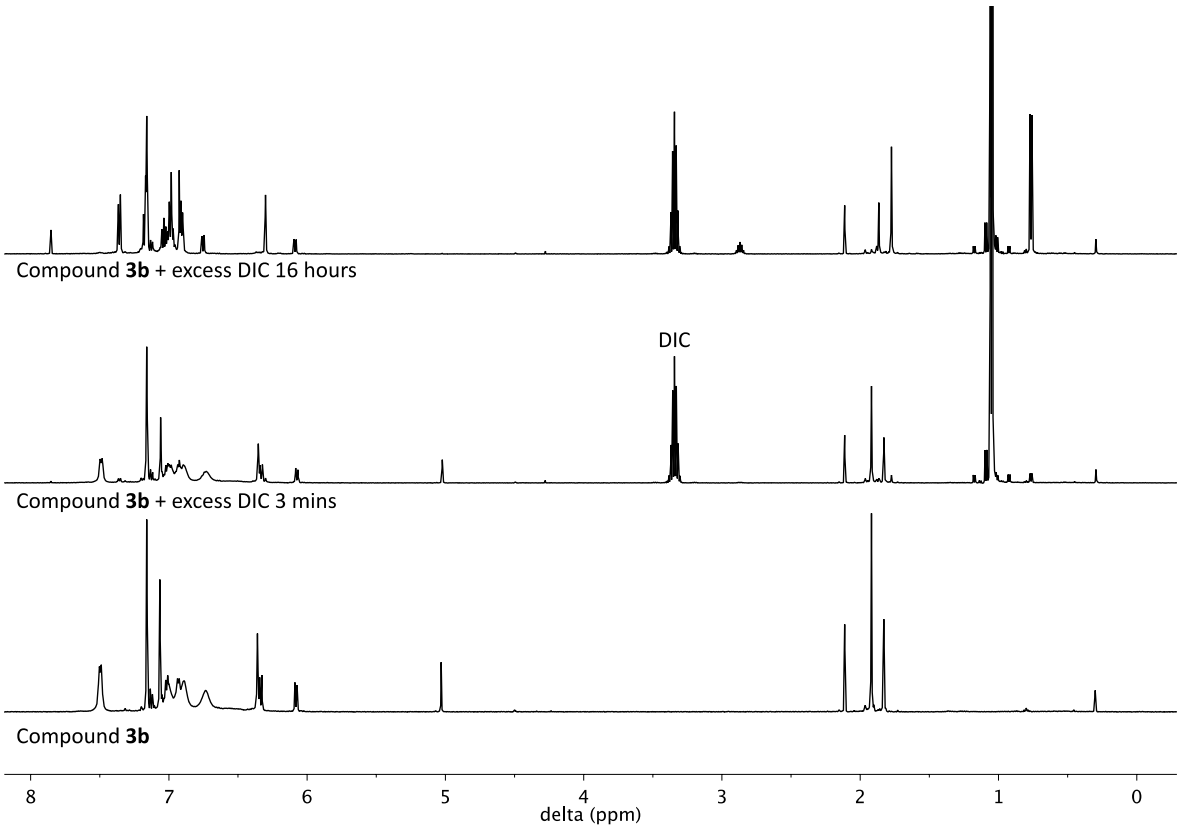


Figure S4: Stack plot of the reaction of **3a** with phenylacetylene to form product **5a**.

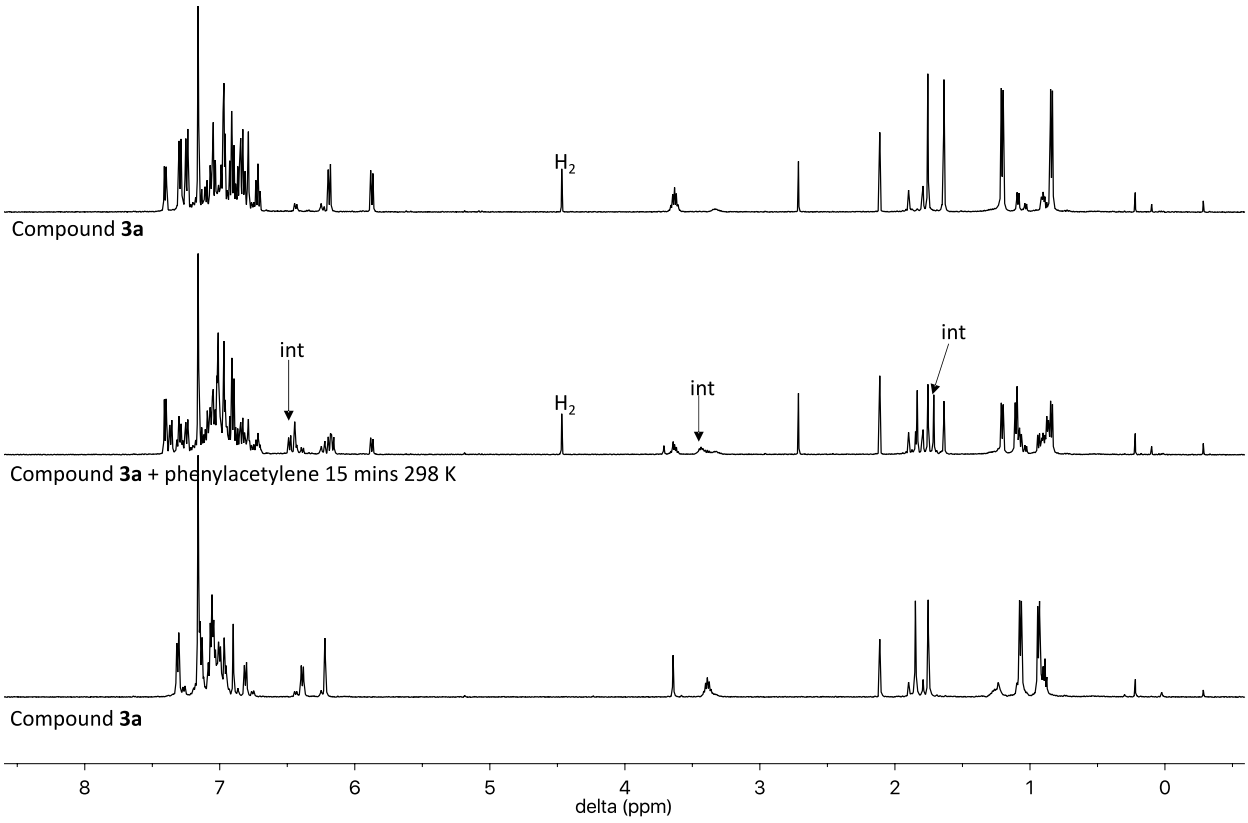
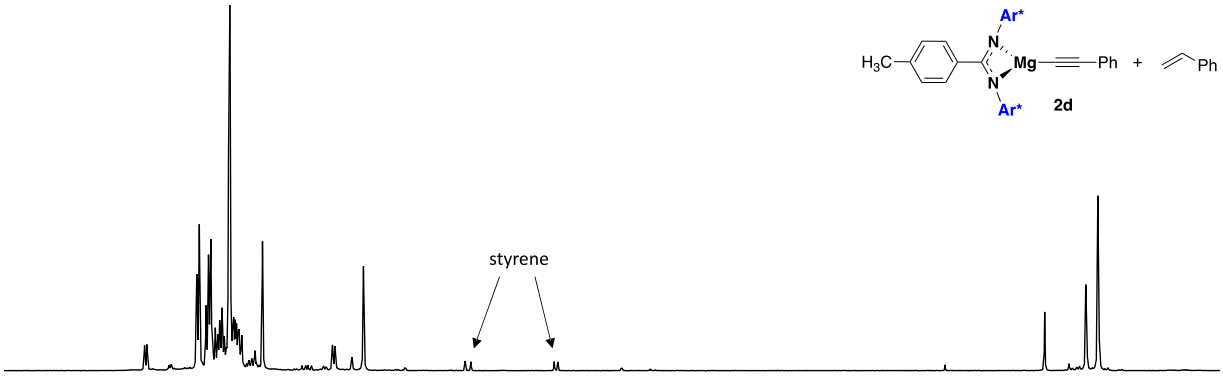
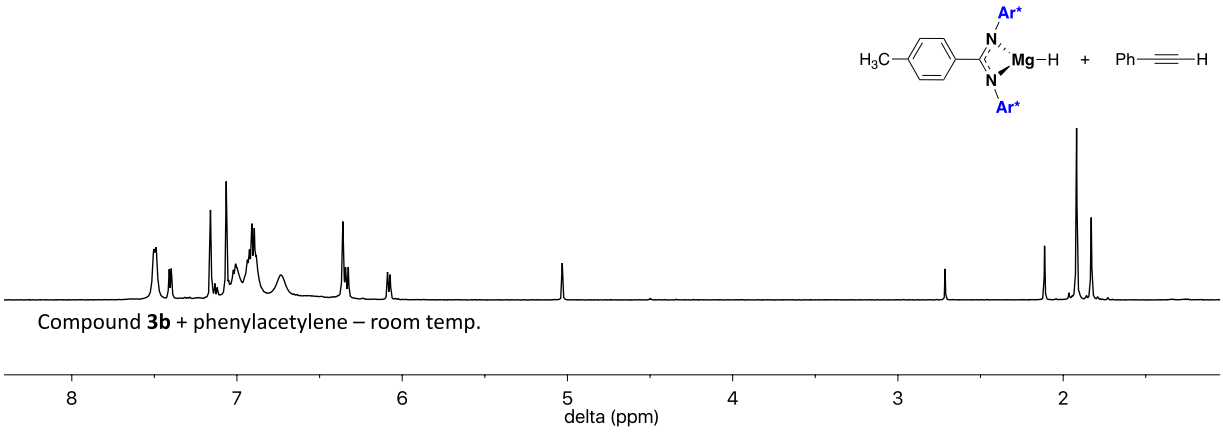


Figure S5: Stack plot of the reaction of **3b** with phenylacetylene to form product **5b**.



Compound **3b** + phenylacetylene – 2h at 80 °C



Compound **3b** + phenylacetylene – room temp.

5. Catalysis Data

Figure S6: Plot of [(iPr)NCN(iPr)] versus time for **1a** (black triangles) and **3a** (red circles).

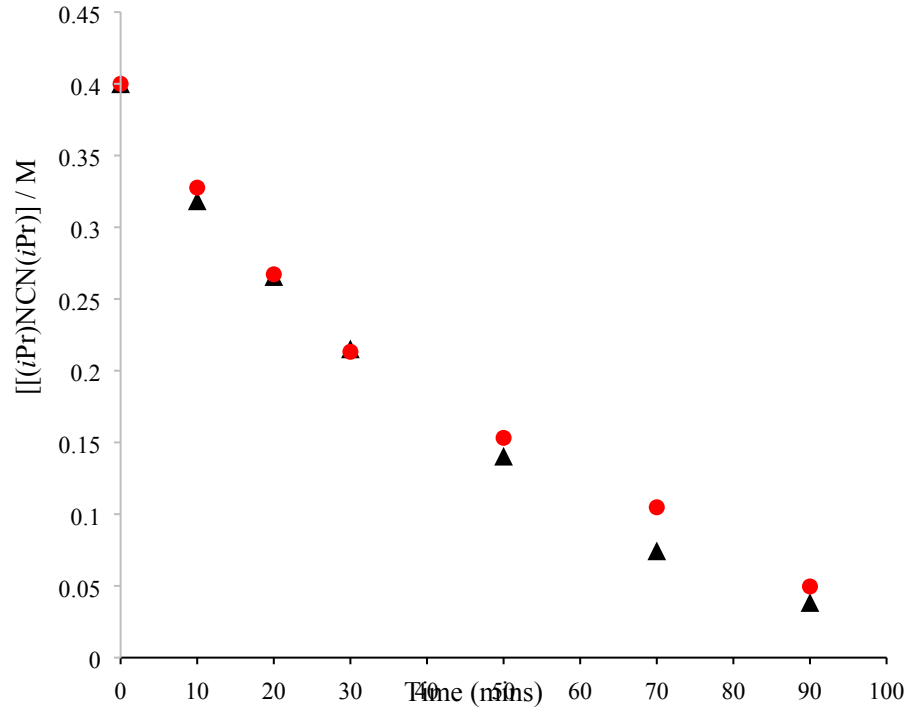


Figure S7: Attempted first order fit of hydroboration of *N,N′*-diisopropylcarbodiimide using **1a** and **3a**. Plot of ln[(iPr)NCN(iPr)] versus time for **1a** (black triangles) and **3a** (red circles).

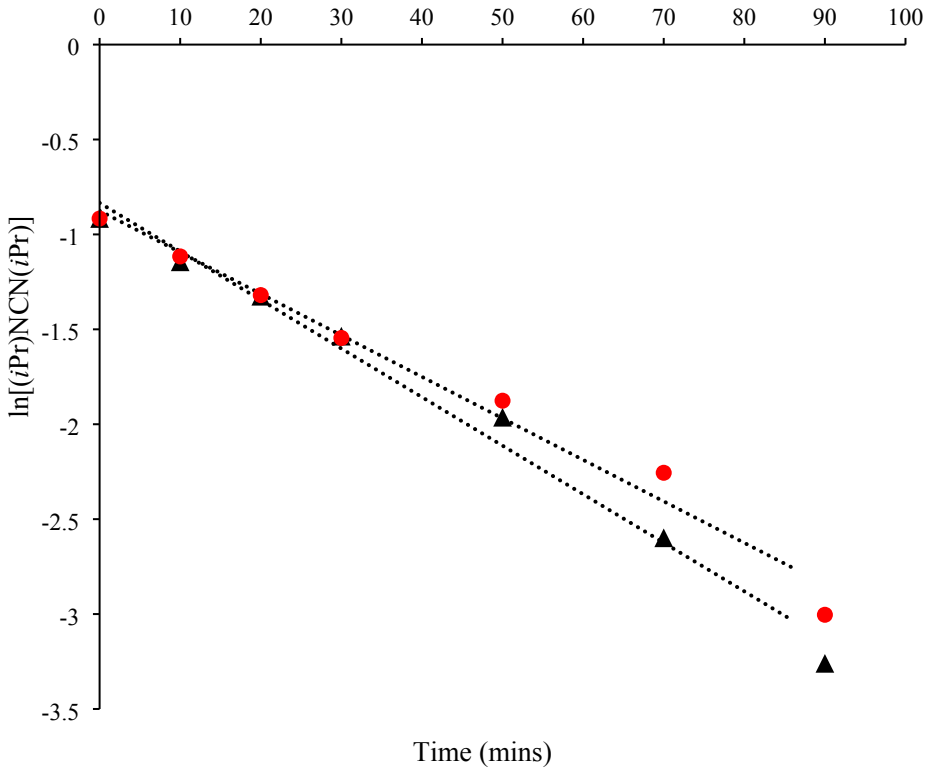


Figure S8: Attempted first order fit of hydroboration of *N,N′*-diisopropylcarbodiimide using **3b**. Plot of ln[(iPr)NCN(iPr)] versus time.

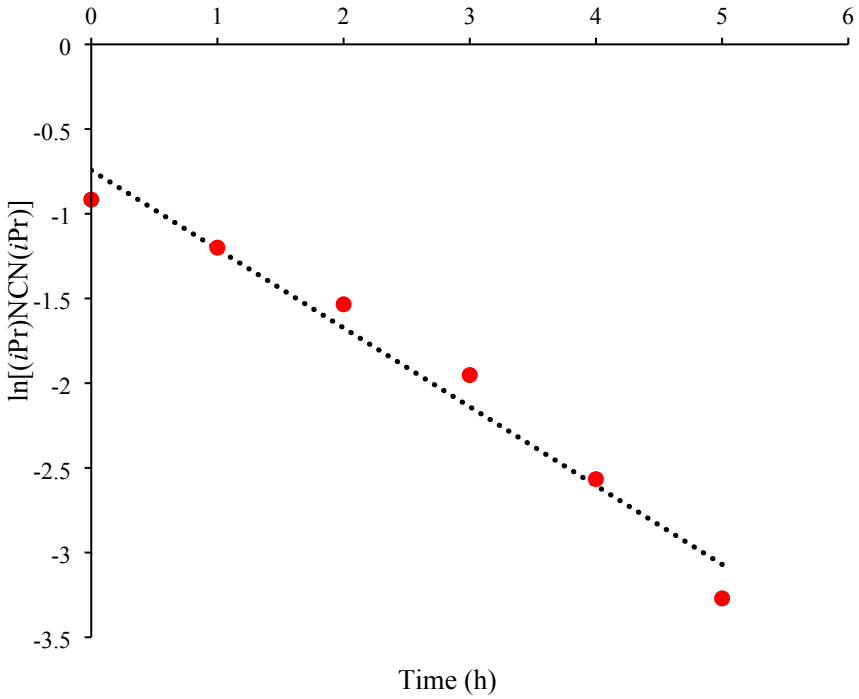
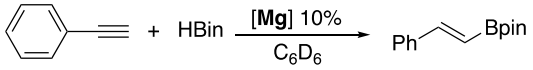


Table S2: Catalytic hydroboration of phenylacetylene



Complex	t (h)	T (°C)	Conversion (%)
1a	96	25	26
1a	16	80	86
1b	96	25	6
1b	16	80	88
3b	16	80	88

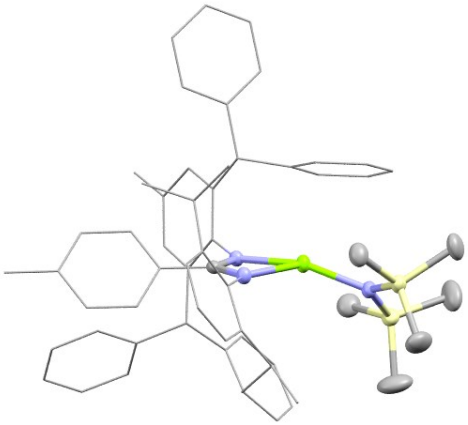
Reaction conditions: [HBpin]=[phenylactylene]= 0.25 M in benzene-d_6. Conversions determined by ^{1}H NMR spectroscopy.

6. X-ray Crystallographic Data

All crystals were ran on a Agilent Oxford Diffraction SuperNova equipped with a microfocus Cu Kα X-ray source and an Atlas CCD detector. Full spheres of data were collected to 0.84 Å resolution with each 1° scan frame in ω collected twice. Total collection time varied depending on size and quality of crystal, and sample temperature. The Cryojet5® used for these measurement is the original prototype device developed by Oxford Instruments and the Pt-resistance sensor is located in the copper-block heat exchanger and not in the nozzle of the instrument close to the sample (in contrast to the CryojetHT® used in the PXRD experiments). Thus the temperatures quoted in these SXD experiments should be treated as nominal (despite stability to much better than 0.1 °C). Using Olex2,[18] the structure was solved with the ShelXT[19] structure solution program using Intrinsic Phasing and refined with the ShelXL[20] refinement package using Least Squares minimisation.

*The X-ray crystal structure of **1a***

Figure S9: The X-ray crystal structure of **1a**. Hydrogen atoms and solvent molecules omitted for clarity.

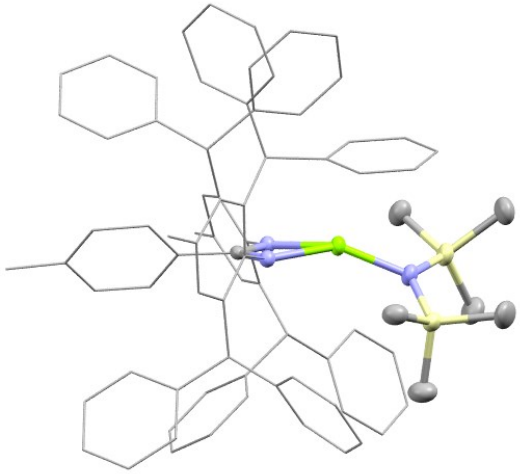


Single crystals of **1a** were grown from toluene/hexane solution. **1a** was found to crystallise in a P-1 space group.

Crystal Data for **1a:** $C_{59}H_{69}N_3MgSi_2$, M =900.66, triclinic, P-1, a = 12.3496(3) Å, b = 12.7732(3) Å, c = 19.2070(4) Å, α = 97.5417(18), β = 99.133(2)°, γ = 116.233(3), V = 2612.97(12) Å^3, Z = 2, ρ_{calc}g/cm^3 = 1.145, μ(CuKα) = 1.54184 mm^{-1}, T = 150.00(10), colourless blocks, 41210 reflections measured (7.924° ≤ 2Θ ≤ 147.028°), 10353 unique (R_{int} = 0.0307, R_{sigma} = 0.0248) which were used in all calculations. The final R_1 was 0.0385 (I > 2σ(I)) and wR_2 was 0.1381 (all data), 598 parameters. CCDC 2016833.

*The X-ray crystal structure of **1b***

Figure S10: The X-ray crystal structure of **1b**. Hydrogen atoms omitted for clarity.



Single crystals of **1b** were grown from toluene/hexane solution. **1b** was found to crystallise in a P-1 space group. The unit cell contained one molecule of toluene that could be modelled. Two further disordered molecules of toluene were modelled using a solvent mask (SQUEEZE).

Crystal Data for **1b:** $C_{87}H_{87}N_3MgSi_2$, M =1255.08, triclinic, P-1, a = 15.6130(3) Å, b = 17.0913(3) Å, c = 17.1689(3) Å, α = 84.511(2), β = 69.542(2)°, γ = 64.578(2), V = 3868.85(14) Å^3, Z = 2, ρ_{calc}g/cm^3 = 1.077, μ(CuKα) = 1.54184 mm^{-1}, T = 150.41(14), colourless blocks, 66096 reflections measured (6.704° ≤ 2Θ ≤ 145.538°), 15170 unique (R_{int} = 0.0319, R_{sigma} = 0.0240) which were used in all calculations. The final R_1 was 0.0413 (I > 2σ(I)) and wR_2 was 0.1091 (all data), 1018 parameters. CCDC 2016832.

*The X-ray crystal structure of **3a***

Figure S11: The major and minor components arising from the single crystal XRD of **3a**.

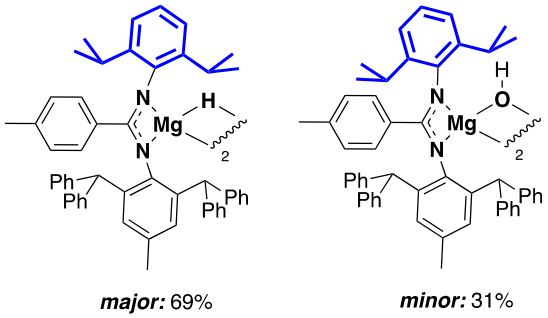
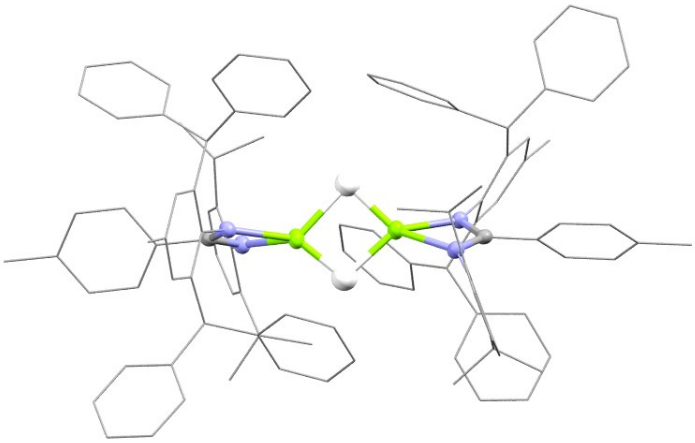


Figure S12: The X-ray crystal structure of **3a** where the magnesium hydrides were found to have 69% occupancy. Additional hydrogen atoms omitted for clarity.



Single crystals of **3a** were grown from toluene/hexane solution. **3a** was found to crystallise in a P-1 space group. The structure of **3a** was found to be disordered with significant unresolved residual electron density near the hydrides (HD,HE). This was interpreted as co-crystallised **3a-OH** and the crystal was modelled as a mixture of **3a** (69%) and **3a-OH** (31%). It was not possible to locate the H atom of the OH group in the minor component. The thermal parameters of adjacent atoms in the major and minor components of the disordered fragment were then restrained to be similar and all atoms were refined isotropically. The asymmetric unit also contained two disordered molecules of toluene, which were modelled using a solvent mask (SQUEEZE).

Crystal Data for **3a:** $C_{106}H_{103.395}Mg_2N_4O_{0.605}$, M =1491.62 g/mol), triclinic, P-1, a = 13.5273(2) Å, b = 13.5524(2) Å, c = 28.3251(4) Å, α = 95.5850(10)°, β = 97.1380(10)°, γ = 112.921(2)°, V = 4684.98(13) Å^3, Z = 2, ρ_{calc}g/cm^3 = 1.057, μ(CuKα) = 0.585 mm^{-1}, T = 149.95(10) K, colourless blocks, 79427 reflections measured (7.174° ≤ 2Θ ≤ 145.546°), 18287 unique (R_{int} = 0.0294, R_{sigma} = 0.0179) which were used in all calculations. The final R_1 was 0.0436 (I > 2σ(I)) and wR_2 was 0.1157 (all data). CCDC 2016830.

*The X-ray crystal structure of **3b***

Figure S13: The major and minor components arising from the single crystal XRD of **3b**.

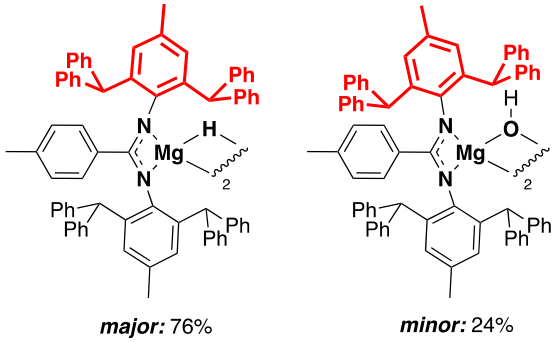
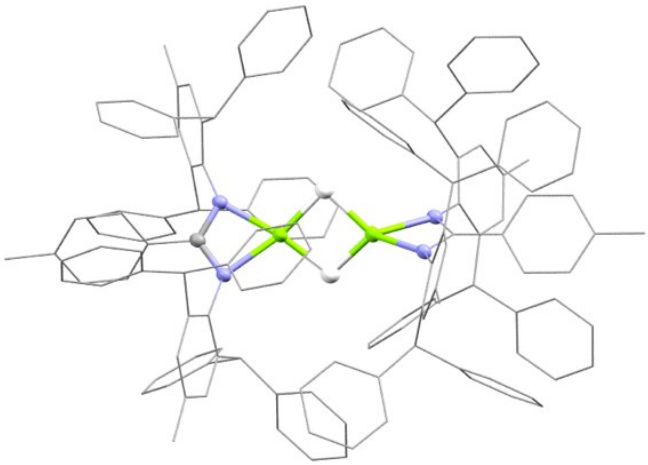


Figure S14: The X-ray crystal structure of **3b** where the magnesium hydrides were found to have 76% occupancy. Additional hydrogen atoms omitted for clarity.

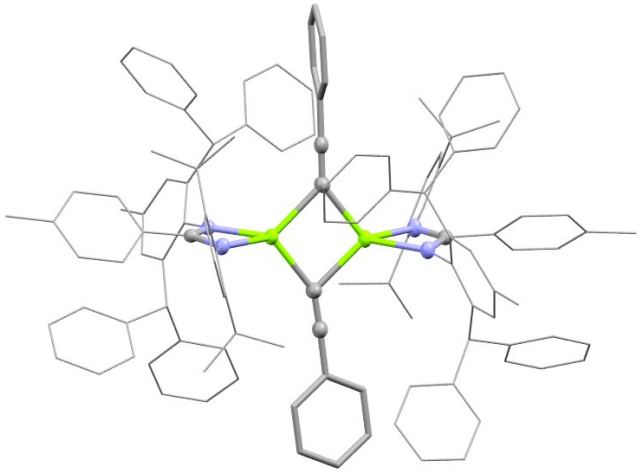


Single crystals of **3b** were grown from a benzene solution. **3b** was found to crystallise in a $P2_1/n$ space group. The structure of **3b** was found to be disordered with significant unresolved residual electron density near the hydrides (H,HA). This was interpreted as co-crystallised **3b-OH** and the crystal was modelled as a mixture of **3b** (76%) and **3b-OH** (24%). It was not possible to locate the H atom of the OH group in the minor component. The thermal parameters of adjacent atoms in the major and minor components of the disordered fragment were then restrained to be similar and all atoms were refined isotropically. The asymmetric unit also contained seven disordered molecules of benzene, which were modelled using a solvent mask (SQUEEZE).

Crystal Data for **3b:** $C_{168}H_{145}Mg_2N_5O_{0.25}$, M =2286.50 g/mol), monoclinic, $P2_1/n$, a = 23.3074(3) Å, b = 23.7367(2) Å, c = 24.8704(3) Å, β = 111.7680(10)°, V = 12778.2(3) Å^3, Z = 4, T = 154.4(8) K, μ(CuKα) = 0.606 mm^{-1}, ρ_{calc}g/cm^3 = 1.189, 92563 reflections measured (7.448° ≤ 2Θ ≤ 145.58°), 25118 unique (R_{int} = 0.0639, R_{sigma} = 0.0482) which were used in all calculations. The final R_1 was 0.0538 (I > 2σ(I)) and wR_2 was 0.1527 (all data). CCDC 2016829.

*The X-ray crystal structure of **5a***

Figure S15: The X-ray crystal structure of **5a**. Hydrogen atoms and solvent omitted for clarity.



Single crystals of **5a** were grown from benzene solution. **5a** was found to crystallise in a P-1 space group. The unit cell contained two molecule of benzene that could be modelled. Five further molecules of benzene were modelled using a solvent mask (SQUEEZE).

Crystal Data for **5a:** $C_{134}H_{124}N_4Mg_2$, M =1838.98, triclinic, P-1, a = 15.3790(4) Å, b = 17.8137(5) Å, c = 23.3393(5) Å, α = 88.579(2), β = 74.671(2)°, γ = 79.266(2), V = 6056.6(3) Å^3, Z = 2, ρ_{calc}g/cm^3 = 1.008, μ(CuKα) = 0.530 mm^{-1}, T = 150.00(10), colourless blocks, 45049 reflections measured (7.134° ≤ 2Θ ≤ 145.498°), 23357 unique reflections (R_{int} = 0.0282, R_{sigma} = 0.0347) which were used in all calculations. The final R_1 was 0.0451 (I > 2σ(I)) and wR_2 was 0.1297 (all data), 1273 parameters. CCDC 2016831.

7. NMR Spectra

Figure S16: ^{1}H NMR spectrum of compound **LH^{1}**.

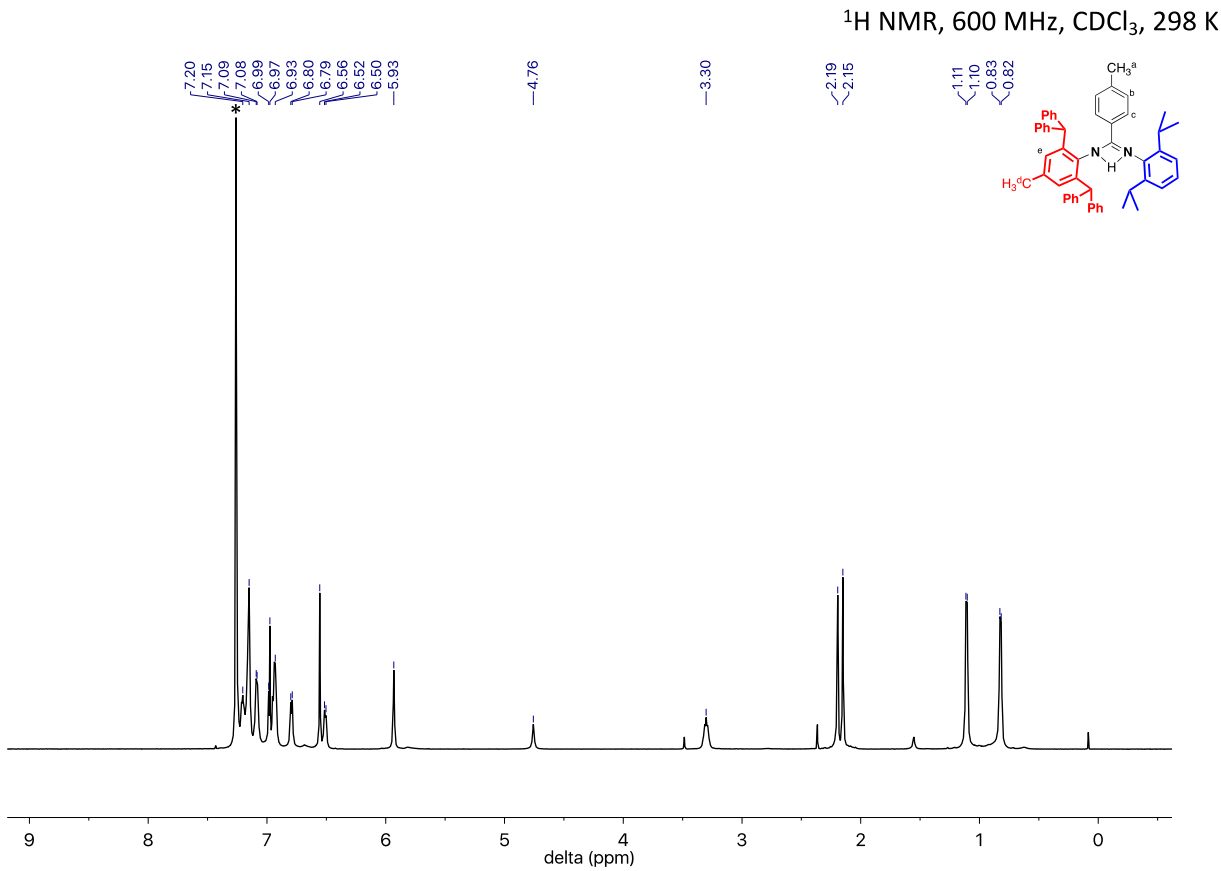


Figure S17: $^{13}C\{^{1}H\}$ NMR spectrum of compound **LH^{1}**.

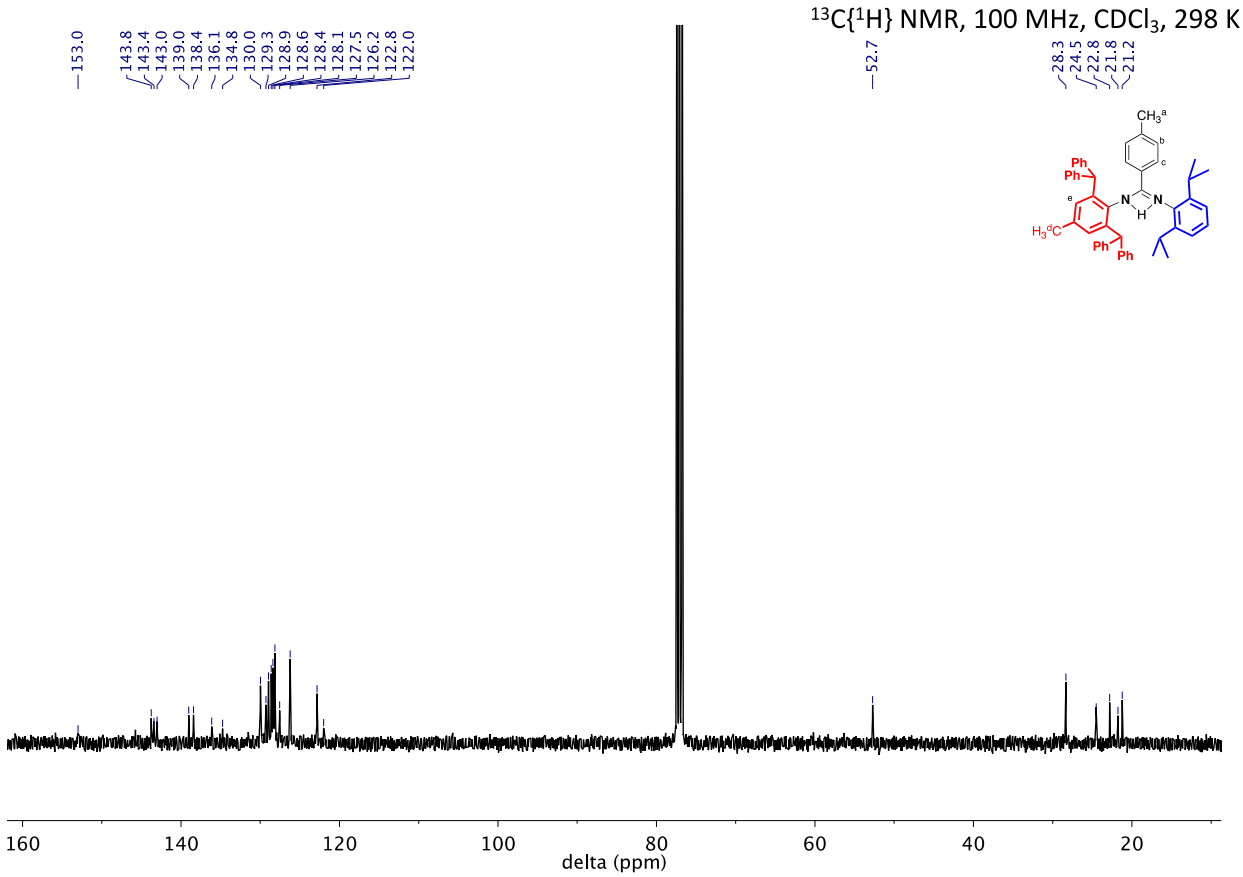


Figure S18: ^{1}H NMR spectrum of compound **LH^{2}**.

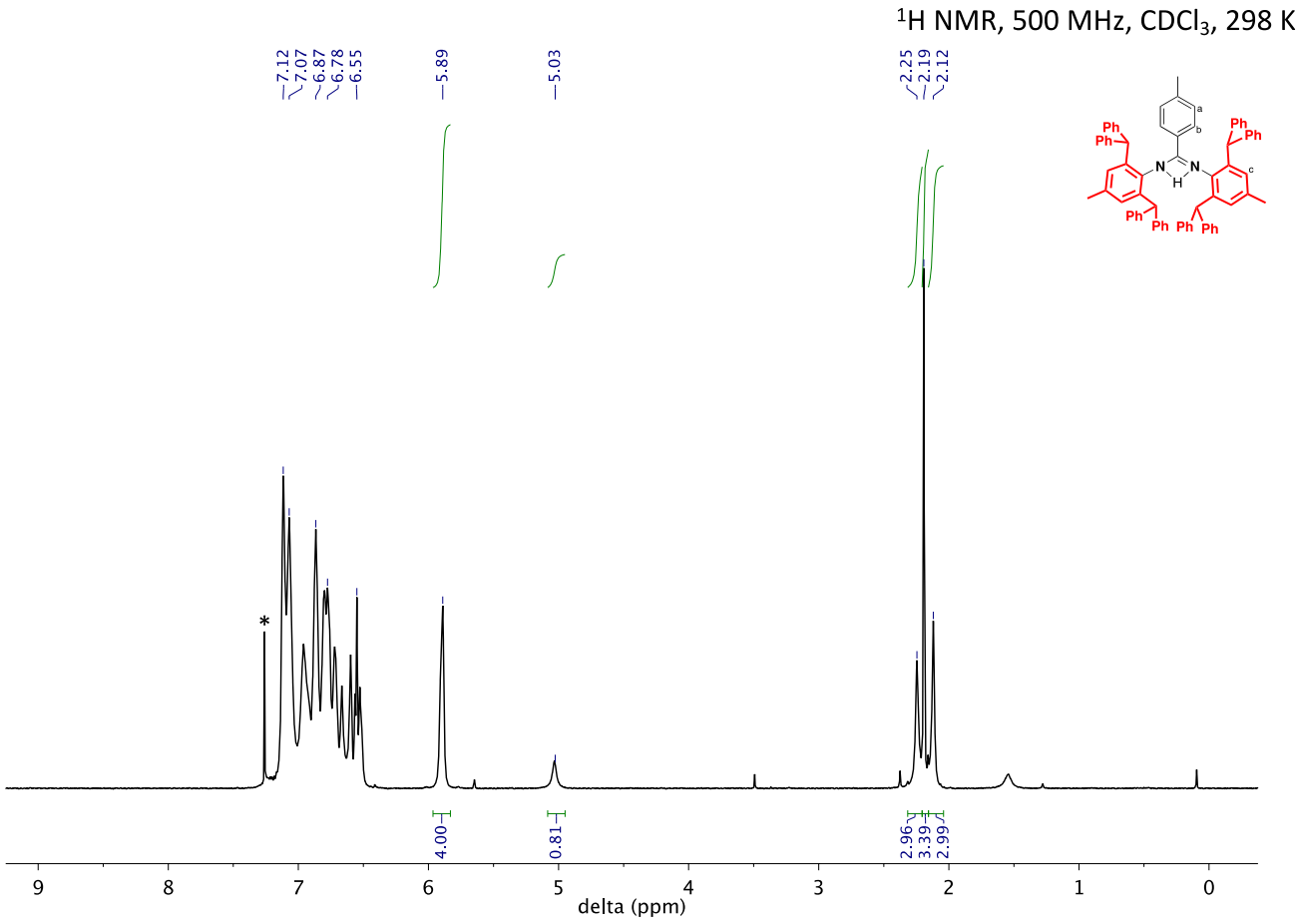


Figure S19: $^{13}C\{^{1}H\}$ NMR spectrum of compound **LH²**.

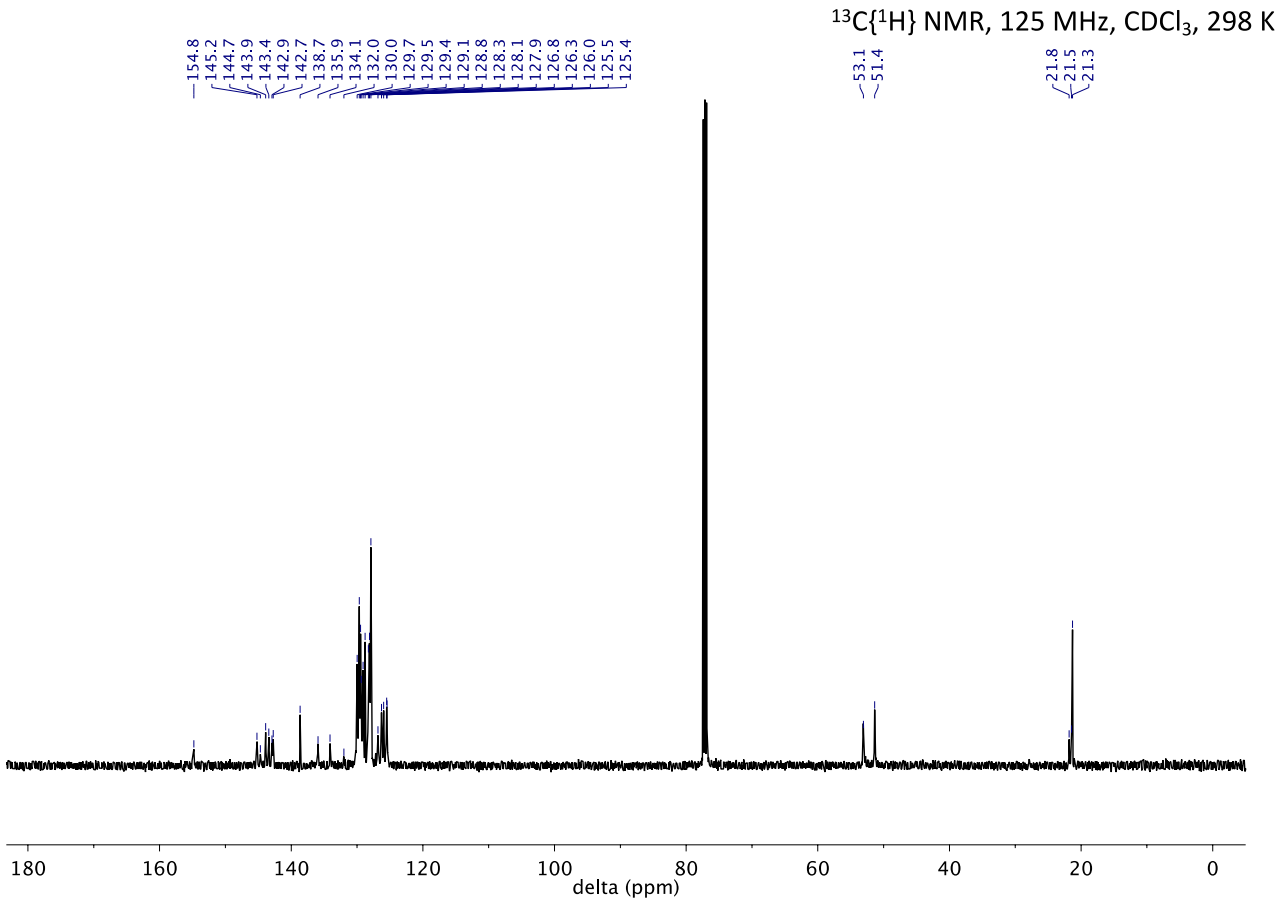


Figure S20: ^{1}H NMR spectrum of compound **1a**.

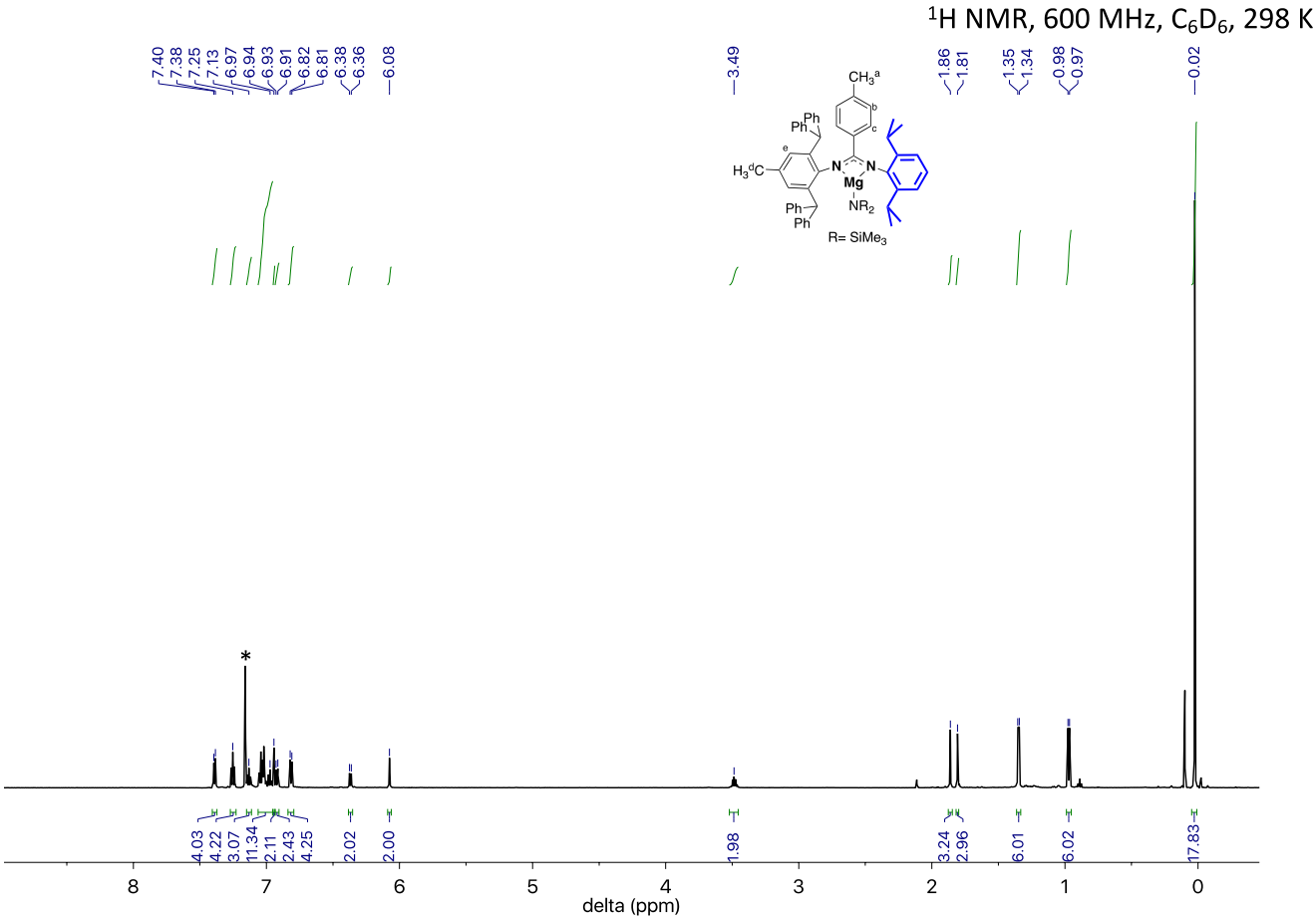


Figure S21: $^{13}C\{^1H\}$ NMR spectrum of compound **1a**.

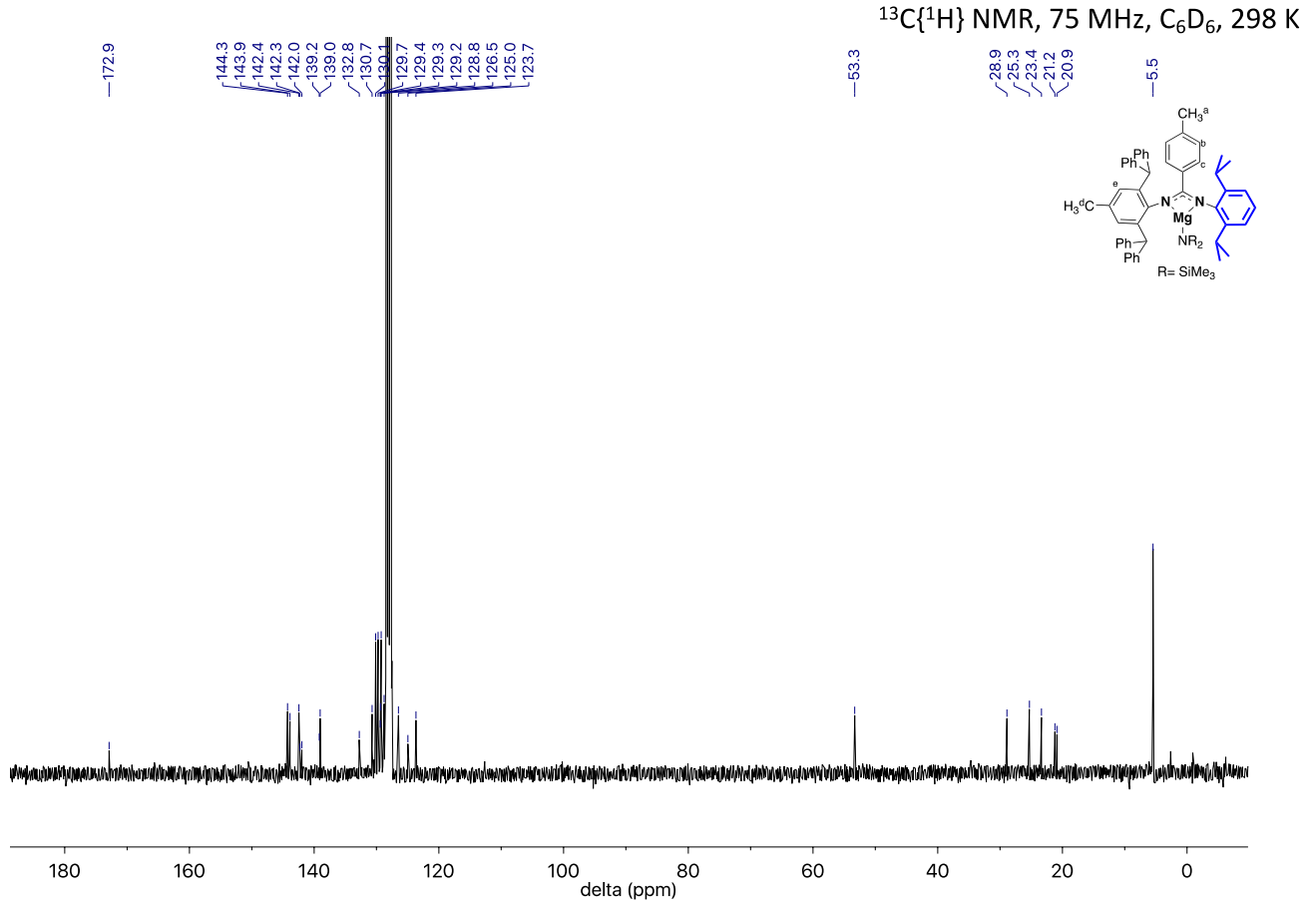


Figure S22: ^{1}H NMR spectrum of compound **1b**.

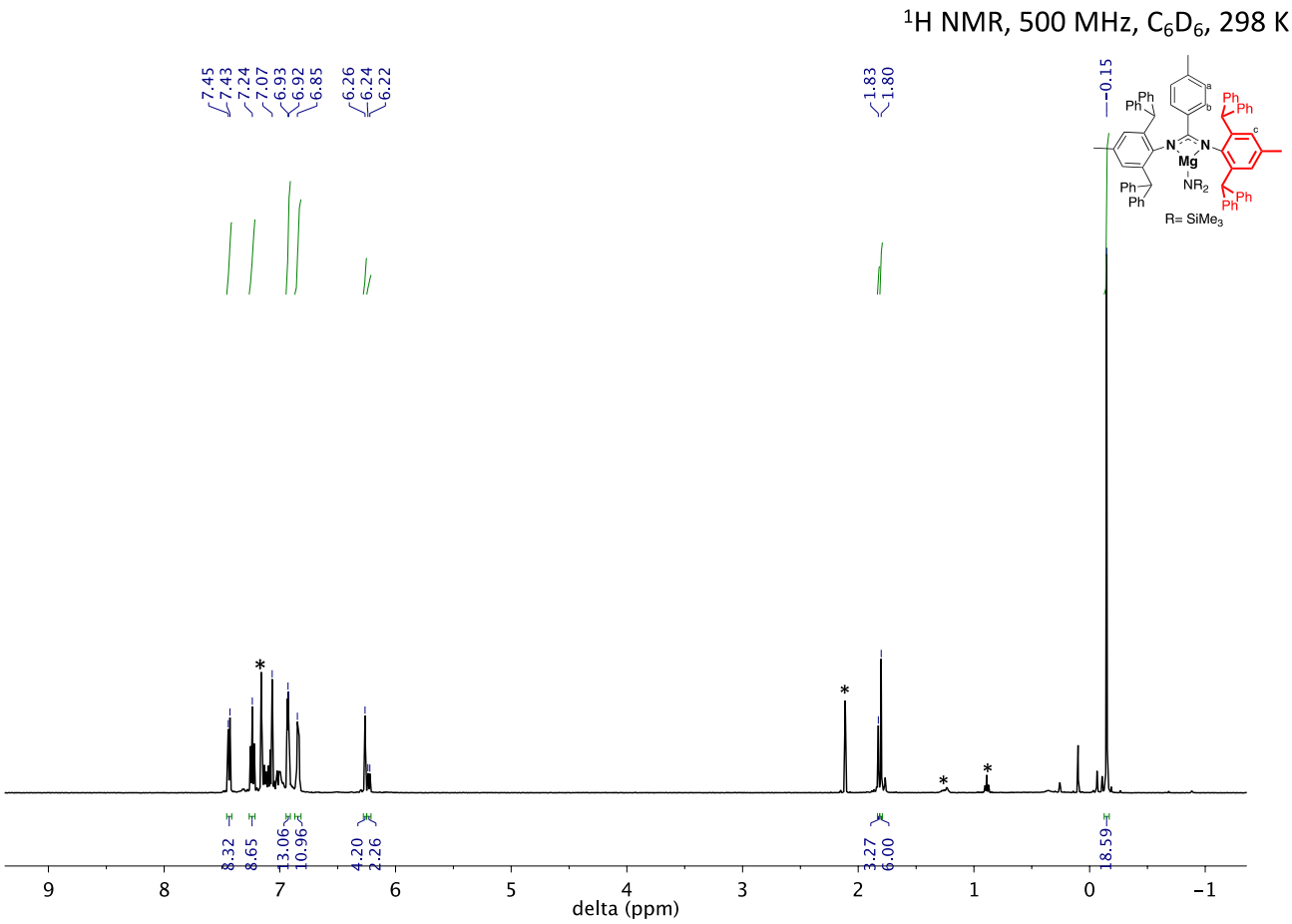


Figure S23: ^{13}C{^{1}H} NMR spectrum of compound **1b**.

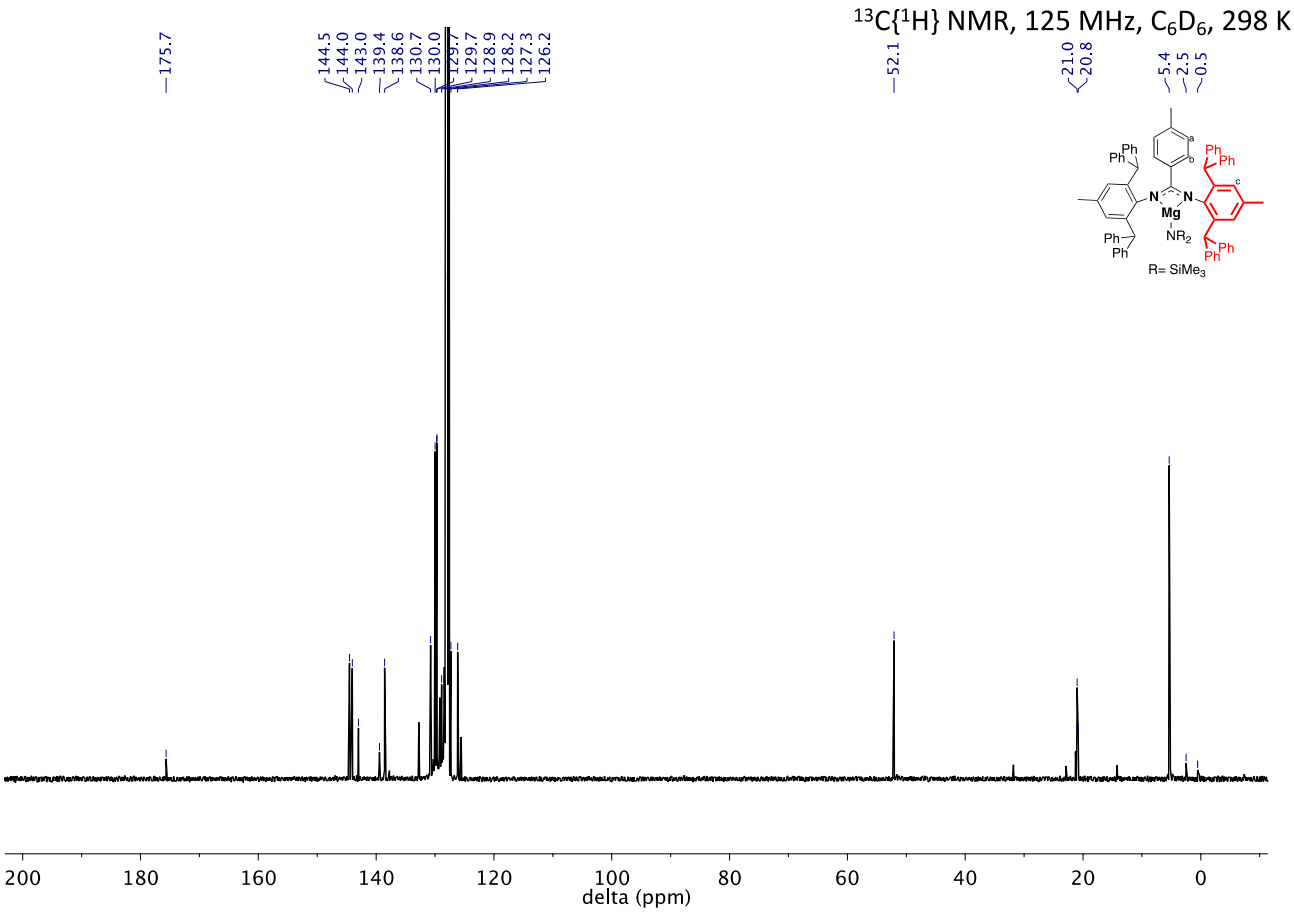


Figure S24: ^{1}H NMR spectrum of compound **2b**.

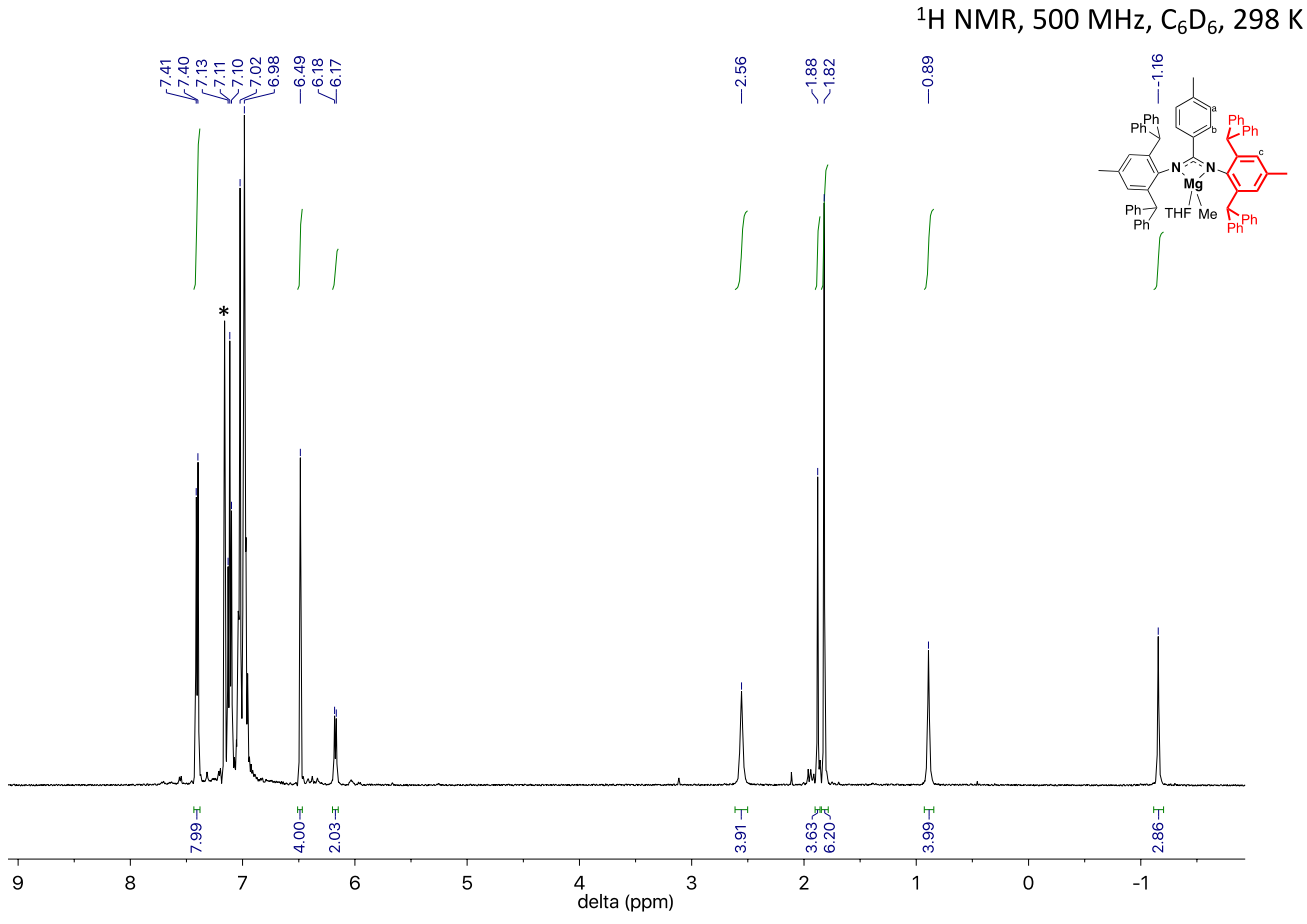


Figure S25: $^{13}C\{^{1}H\}$ NMR spectrum of compound **2b**.

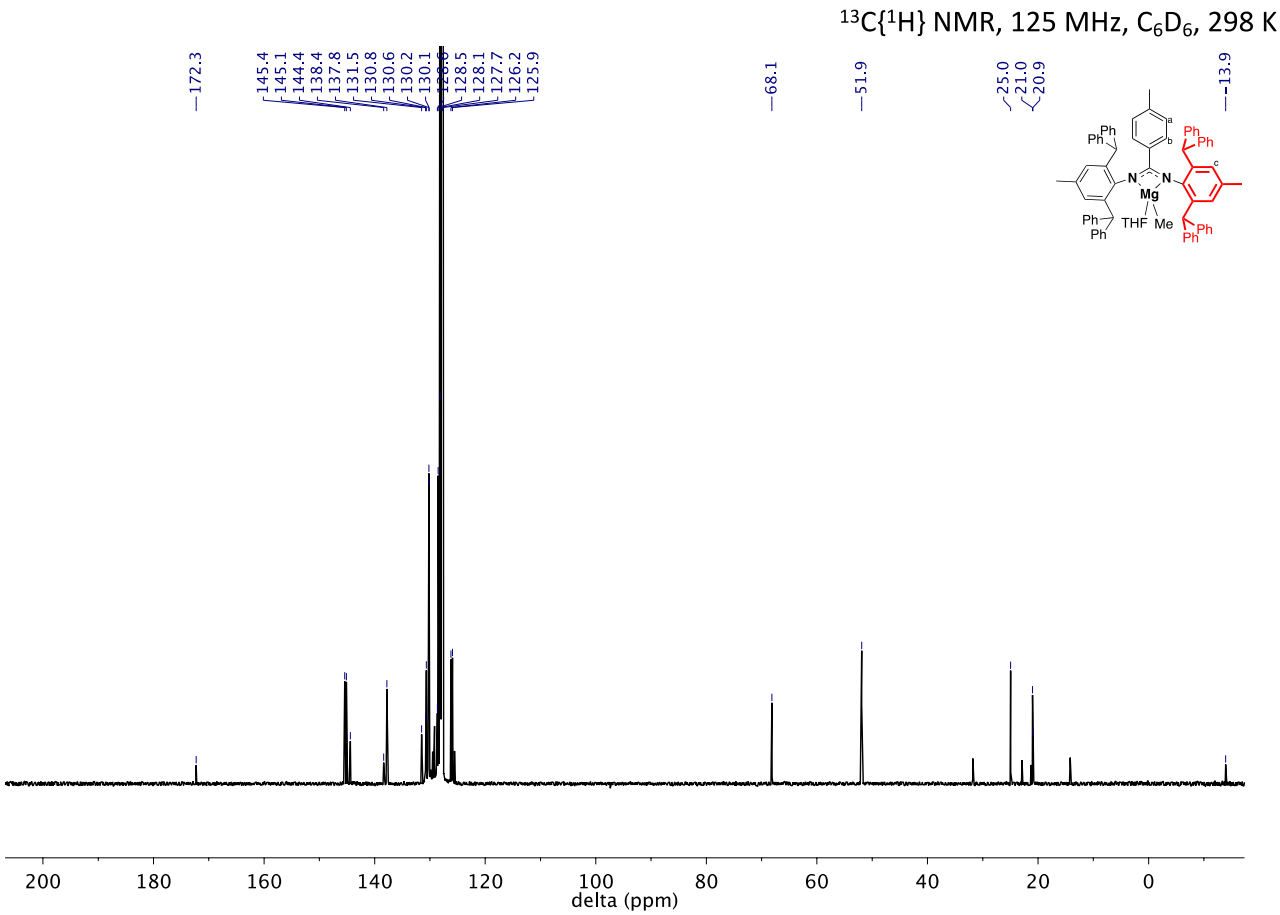


Figure S26: ^{1}H NMR spectrum of compound **3a**.

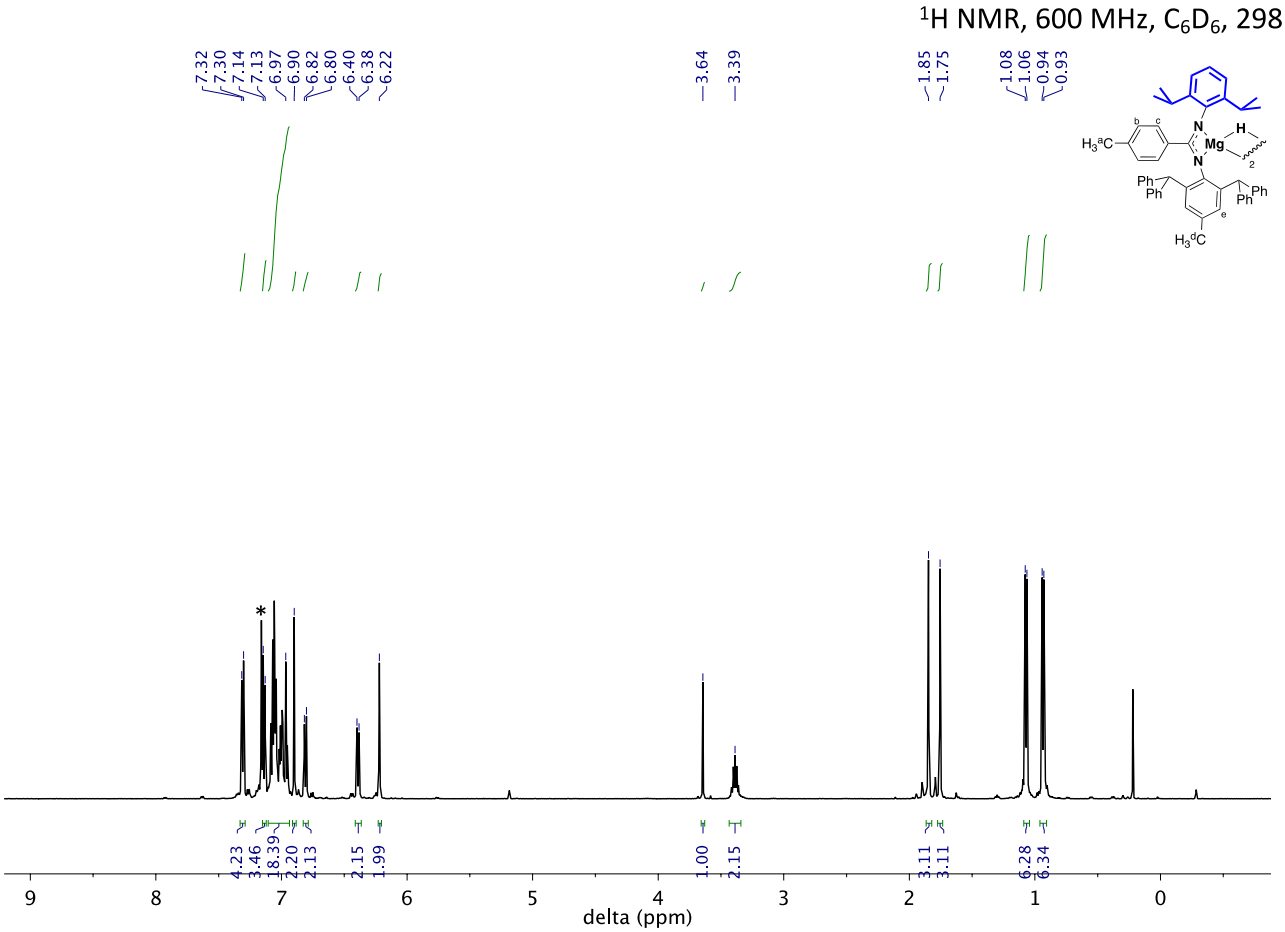


Figure S27: $^{13}C\{^1H\}$ NMR spectrum of compound **3a**.

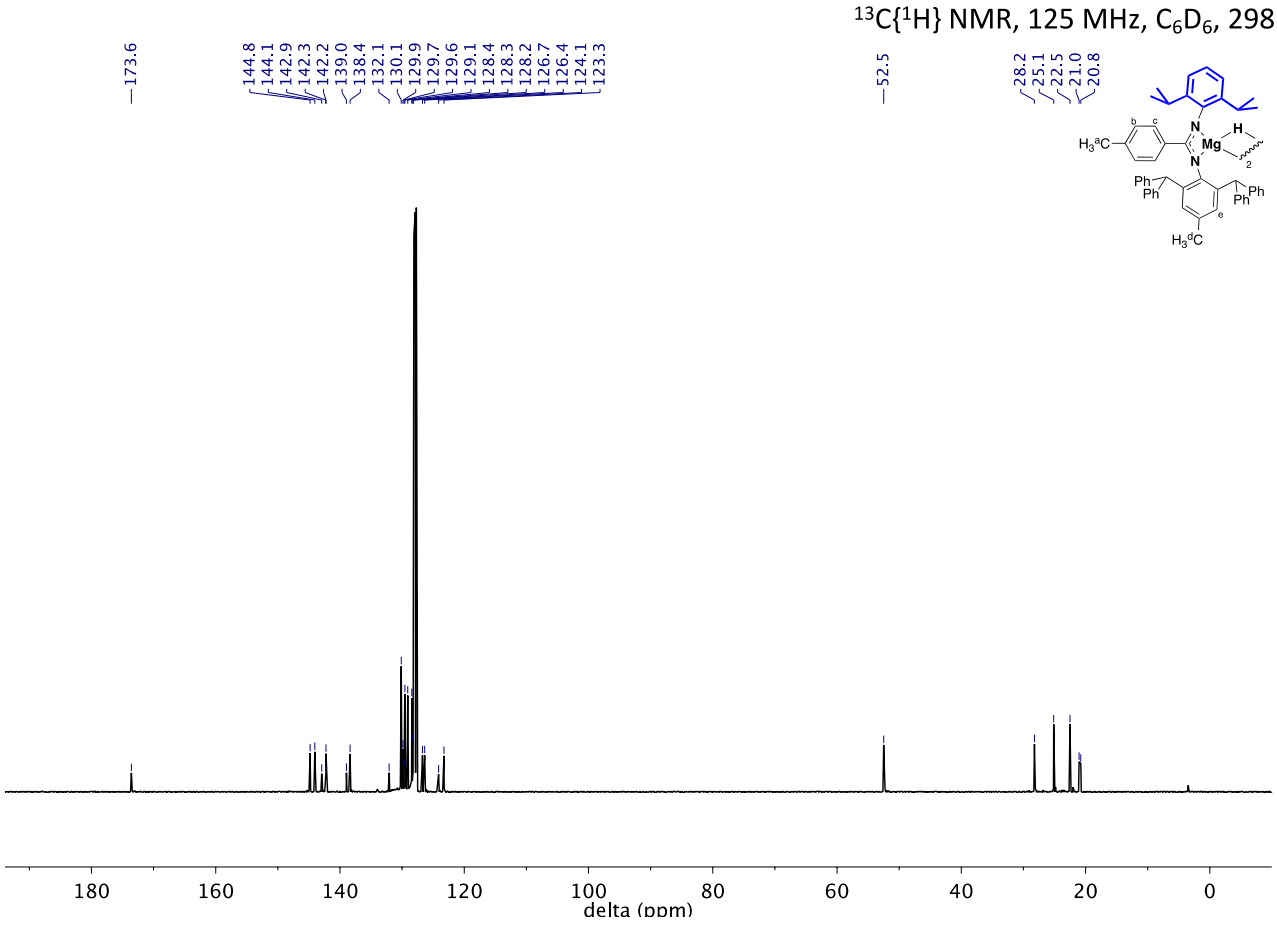


Figure S28: ^{1}H NMR spectrum of compound **LMg(*n*Bu)** intermediate.

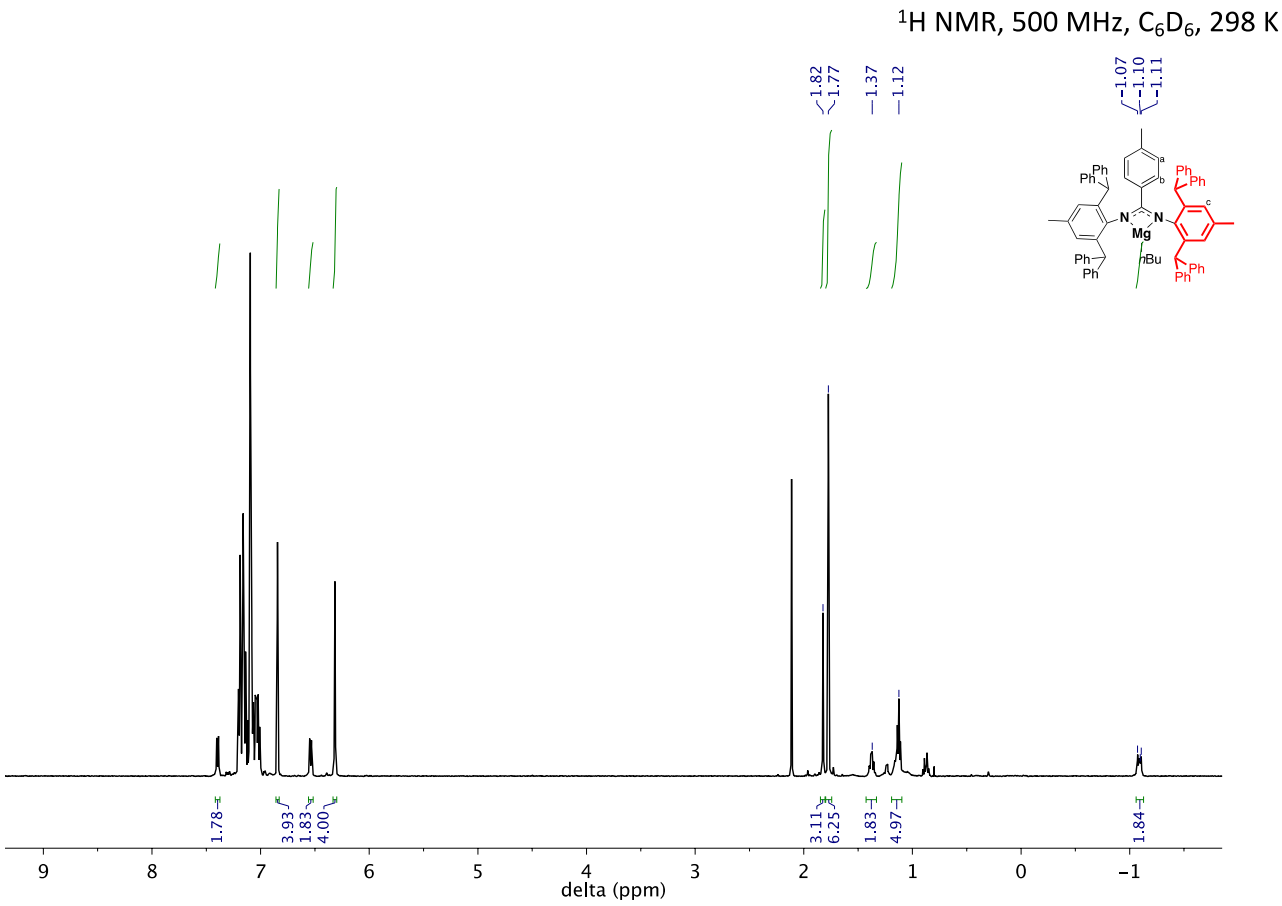


Figure S29: ^{13}C{^{1}H} NMR spectrum of compound **LMg(*n*Bu)** intermediate.

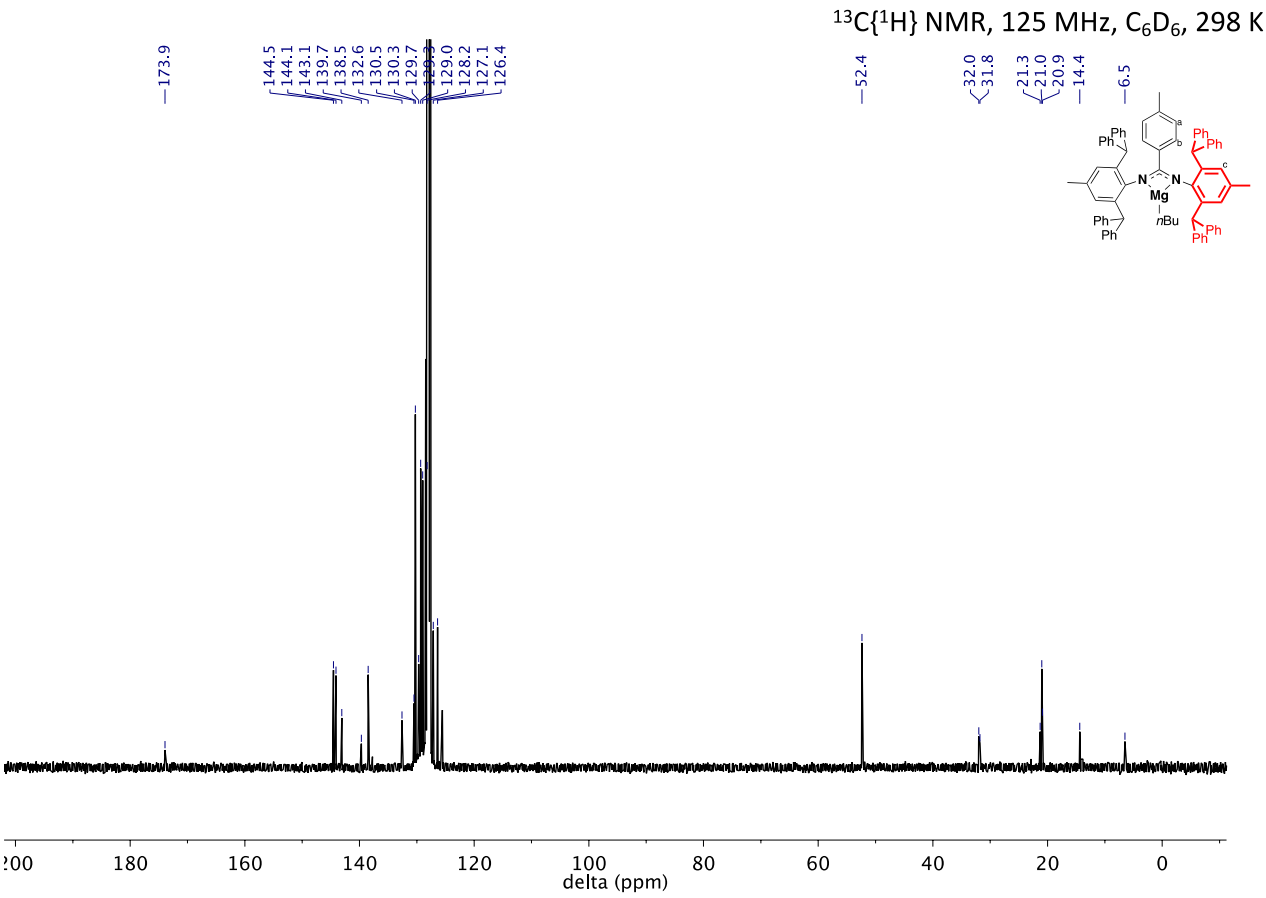


Figure S30: ^{1}H NMR spectrum of compound **3b**.

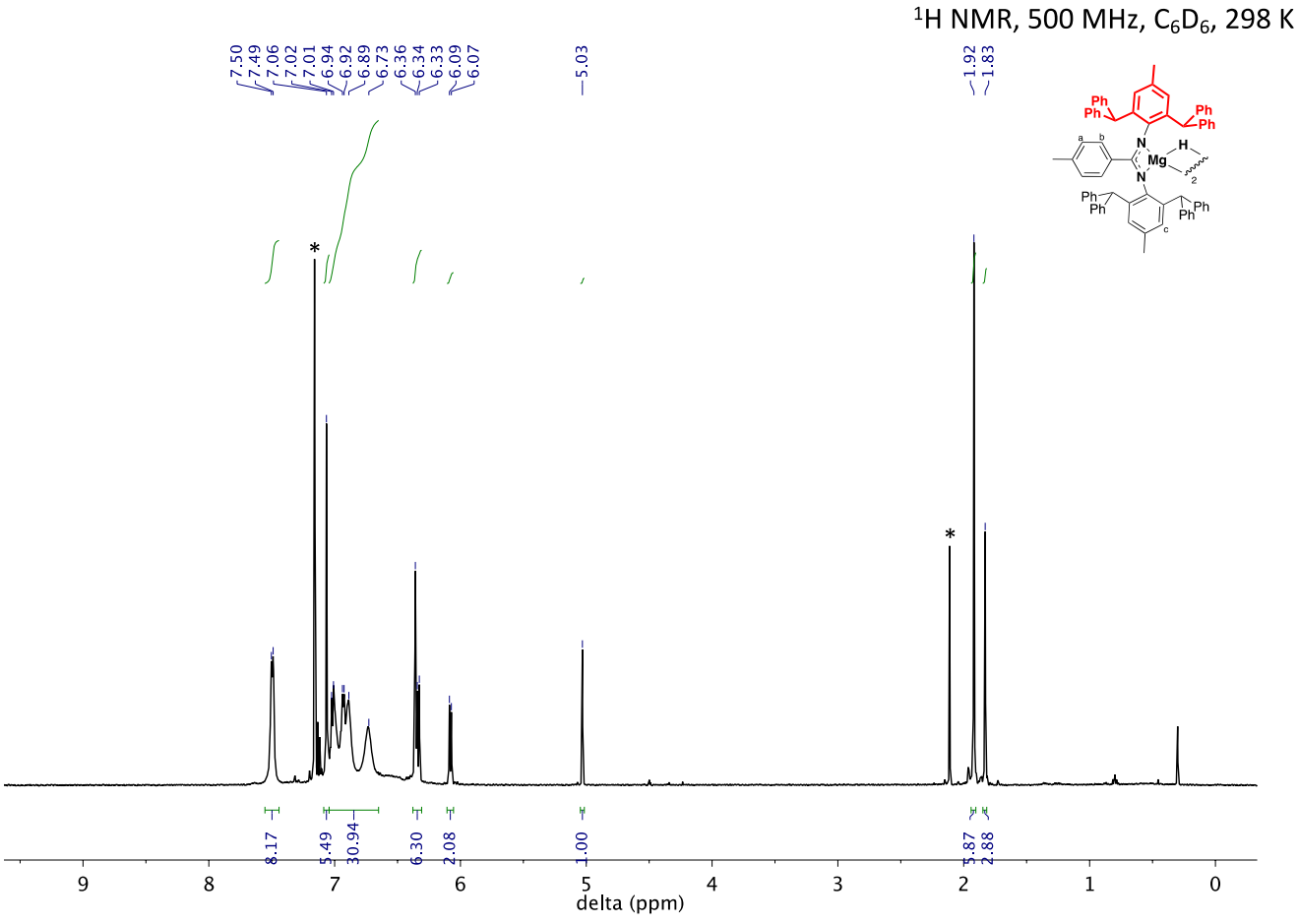


Figure S31: $^{13}C\{^{1}H\}$ NMR spectrum of compound **3b**.

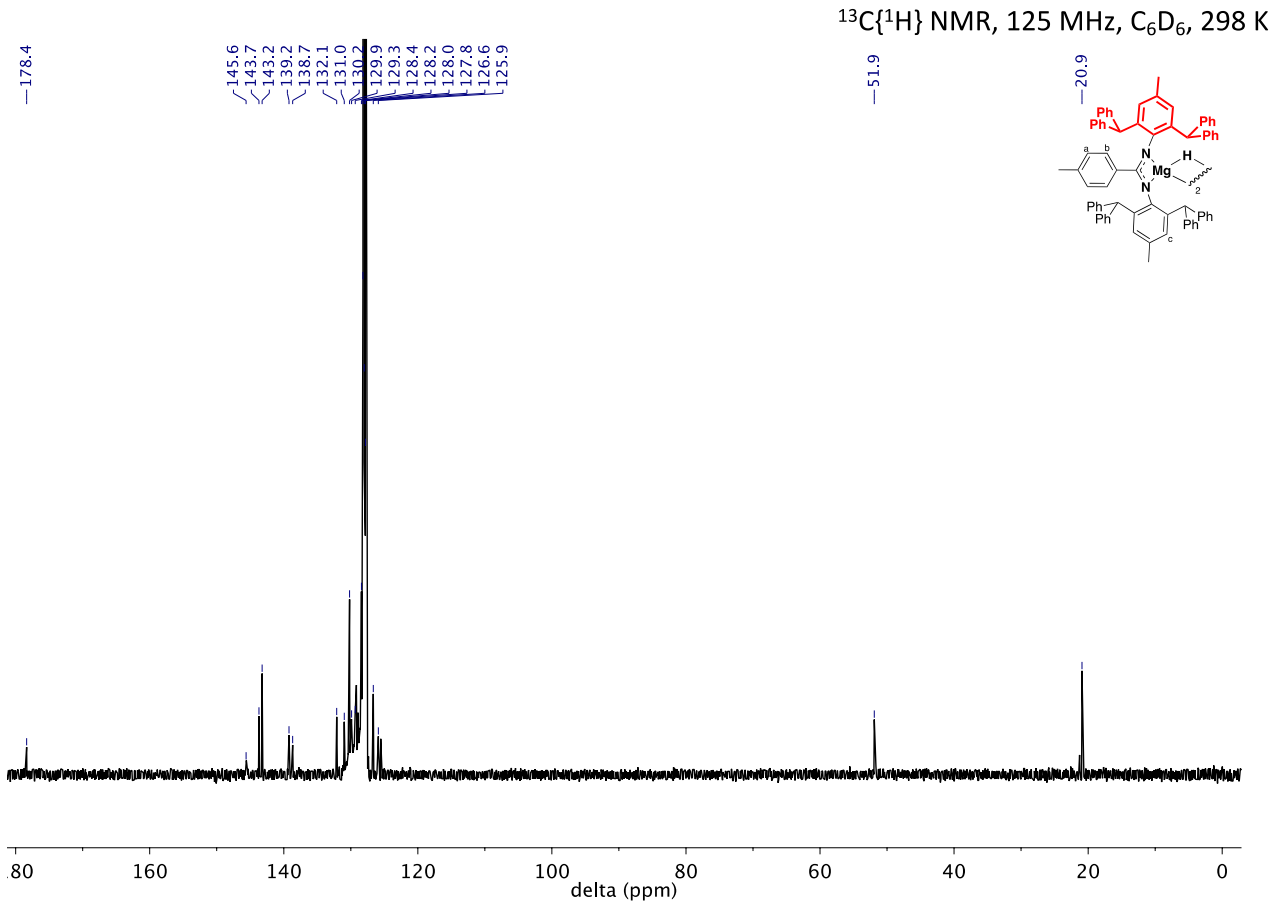


Figure S32: ^{1}H NMR spectrum of compound **4a**.

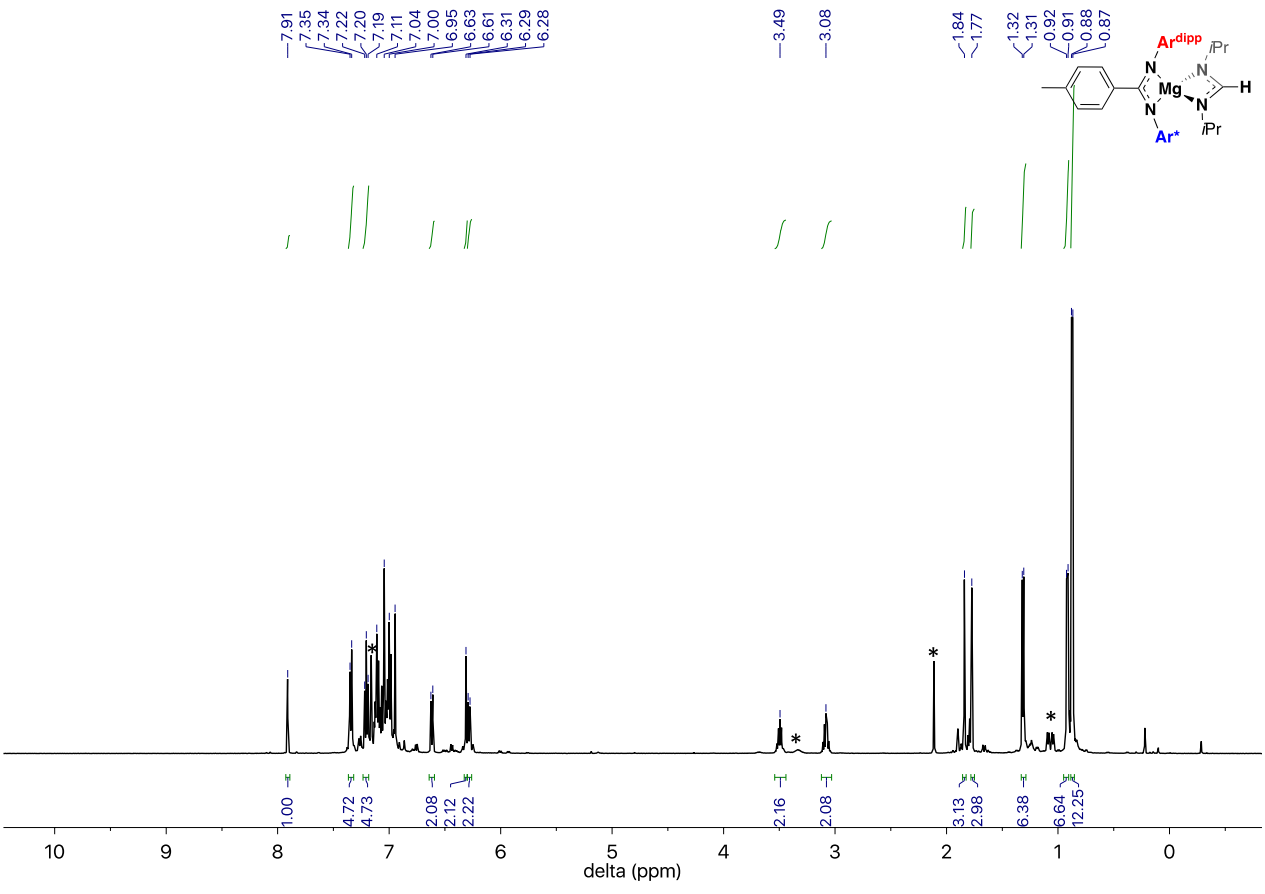


Figure S33: $^{13}C\{^{1}H\}$ NMR spectrum of compound **4a**.

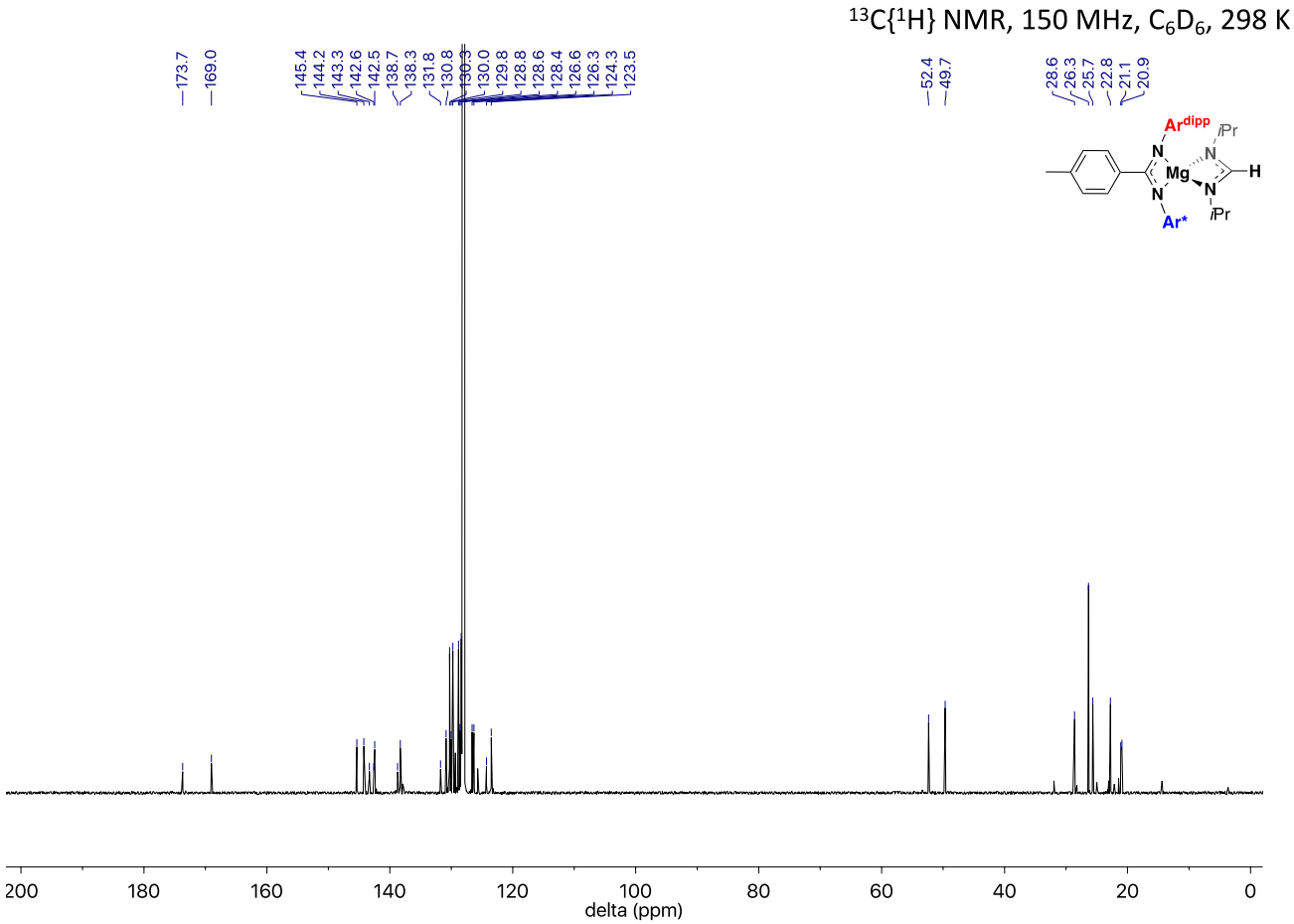


Figure S34: ^{1}H NMR spectrum of compound **4b**.

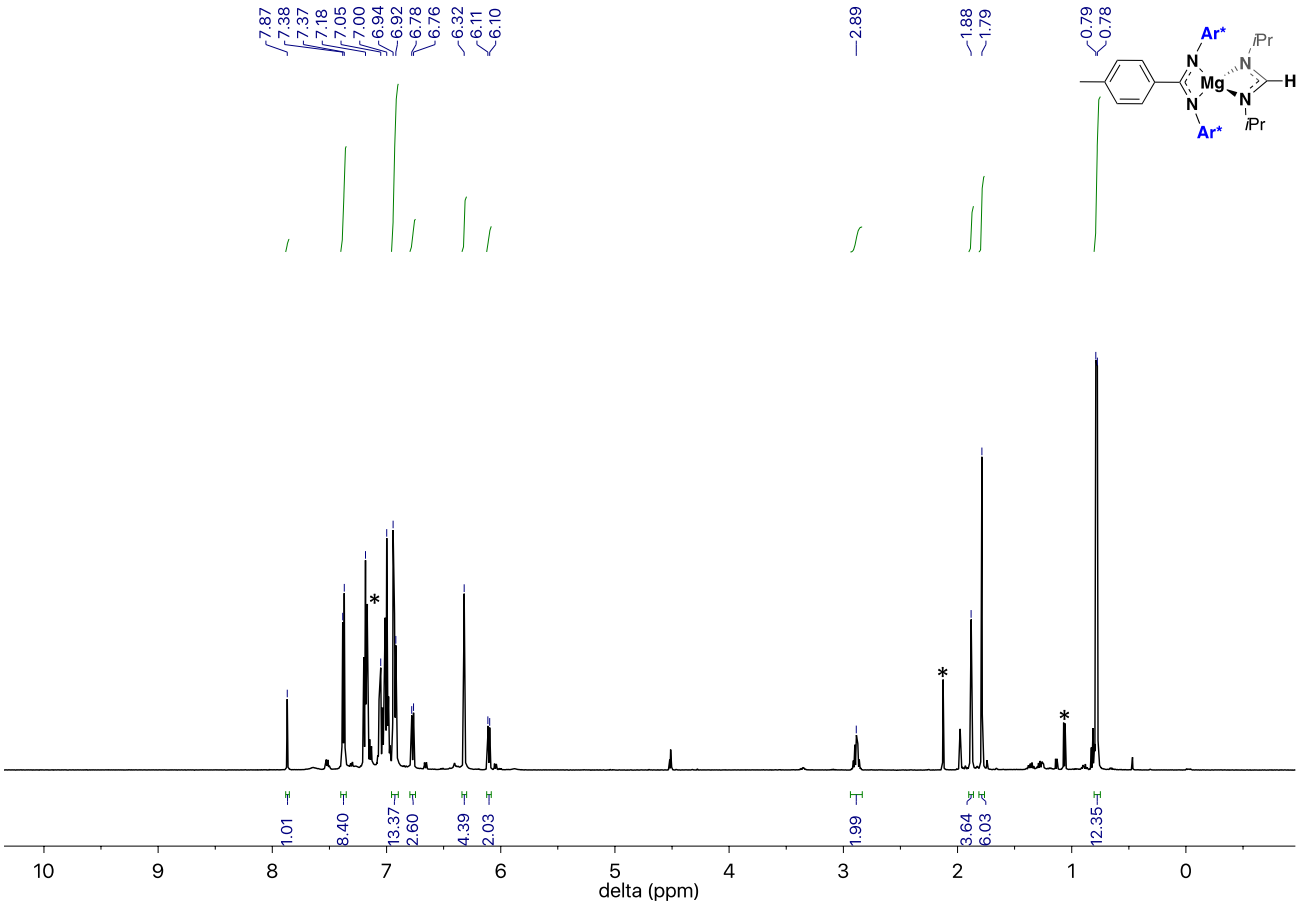


Figure S35: $^{13}C\{^{1}H\}$ NMR spectrum of compound **4b**.

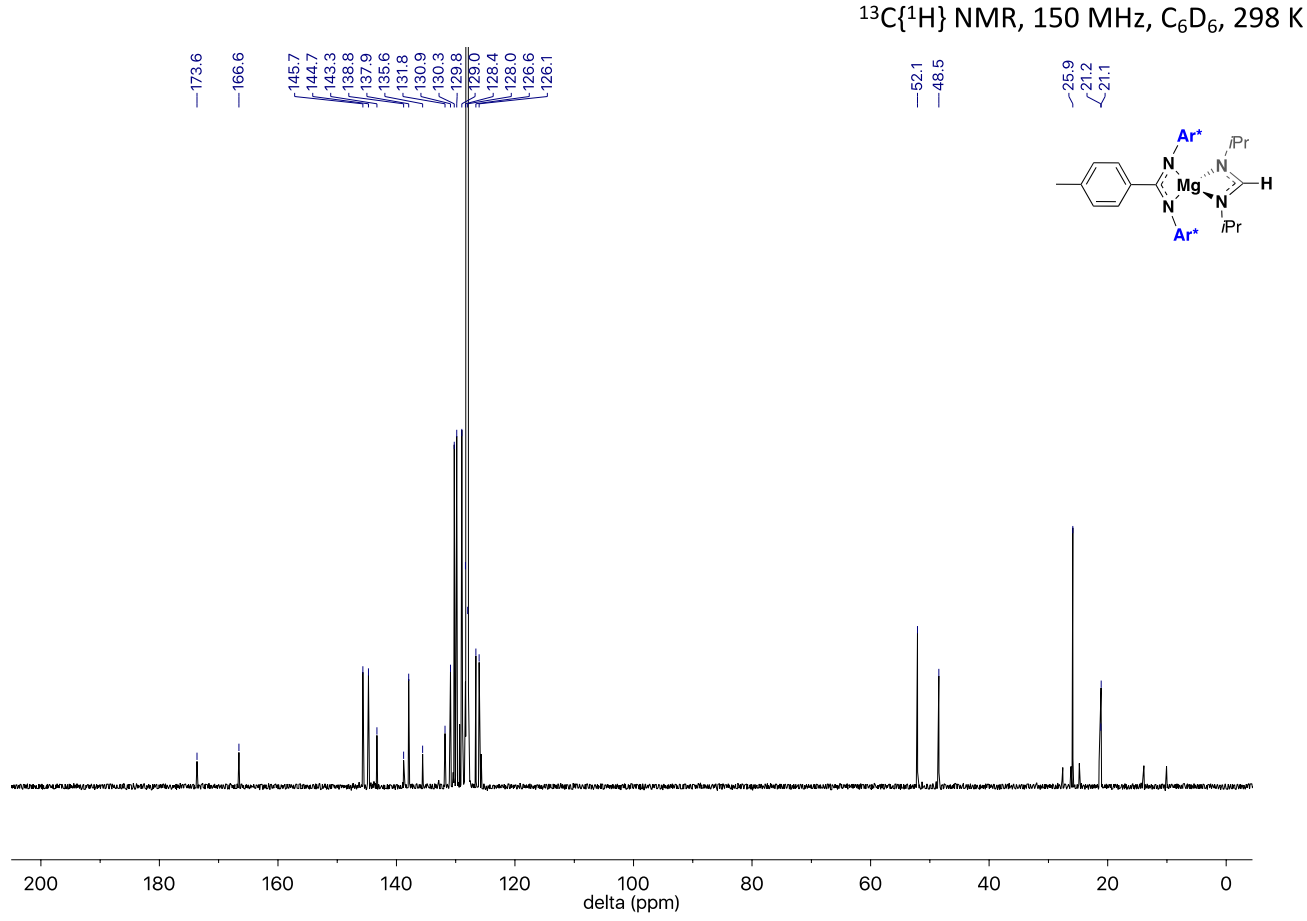


Figure S36: ^{1}H NMR spectrum of compound **5a**.

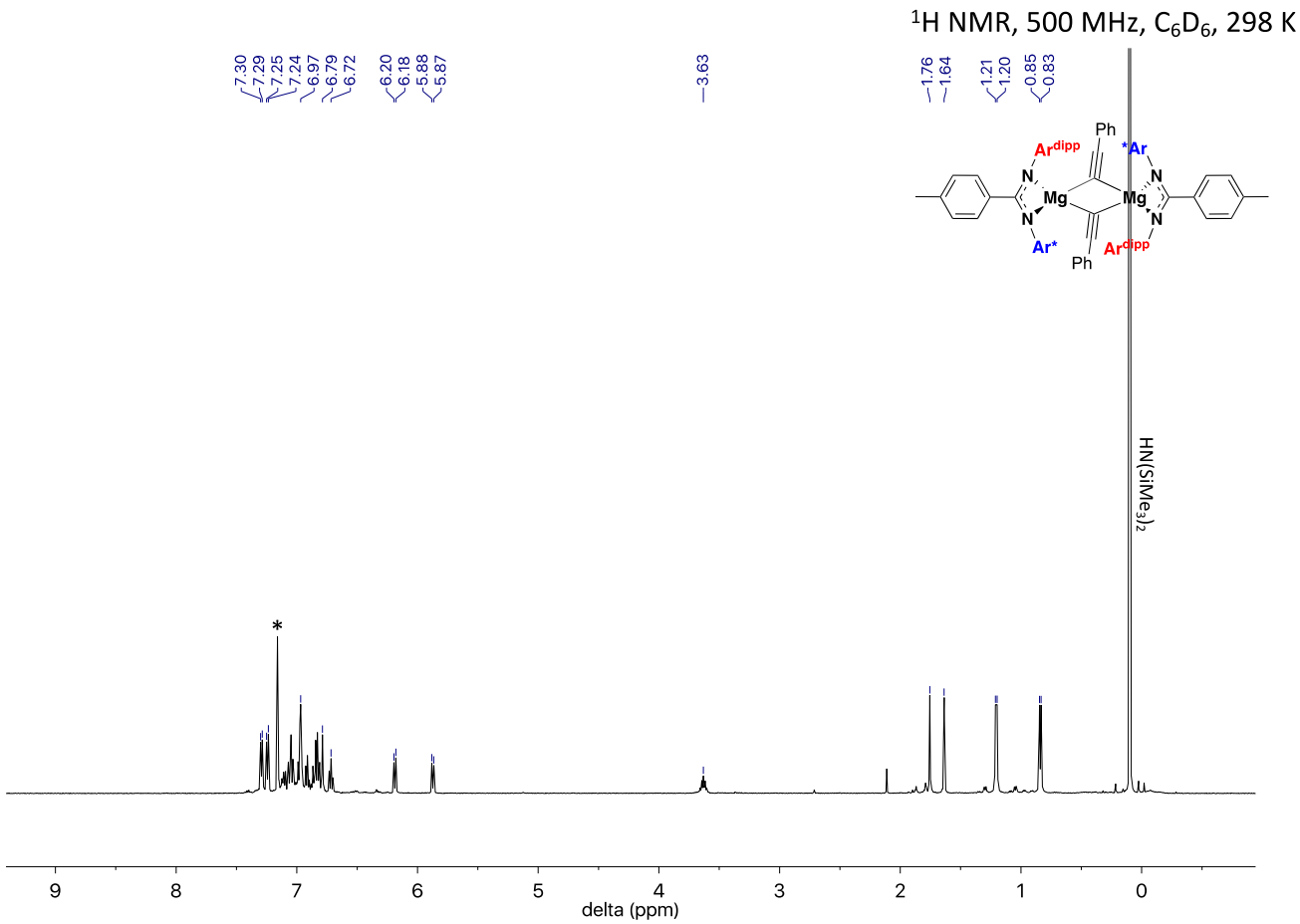


Figure S37: $^{13}C\{^{1}H\}$ NMR spectrum of compound **5a**.

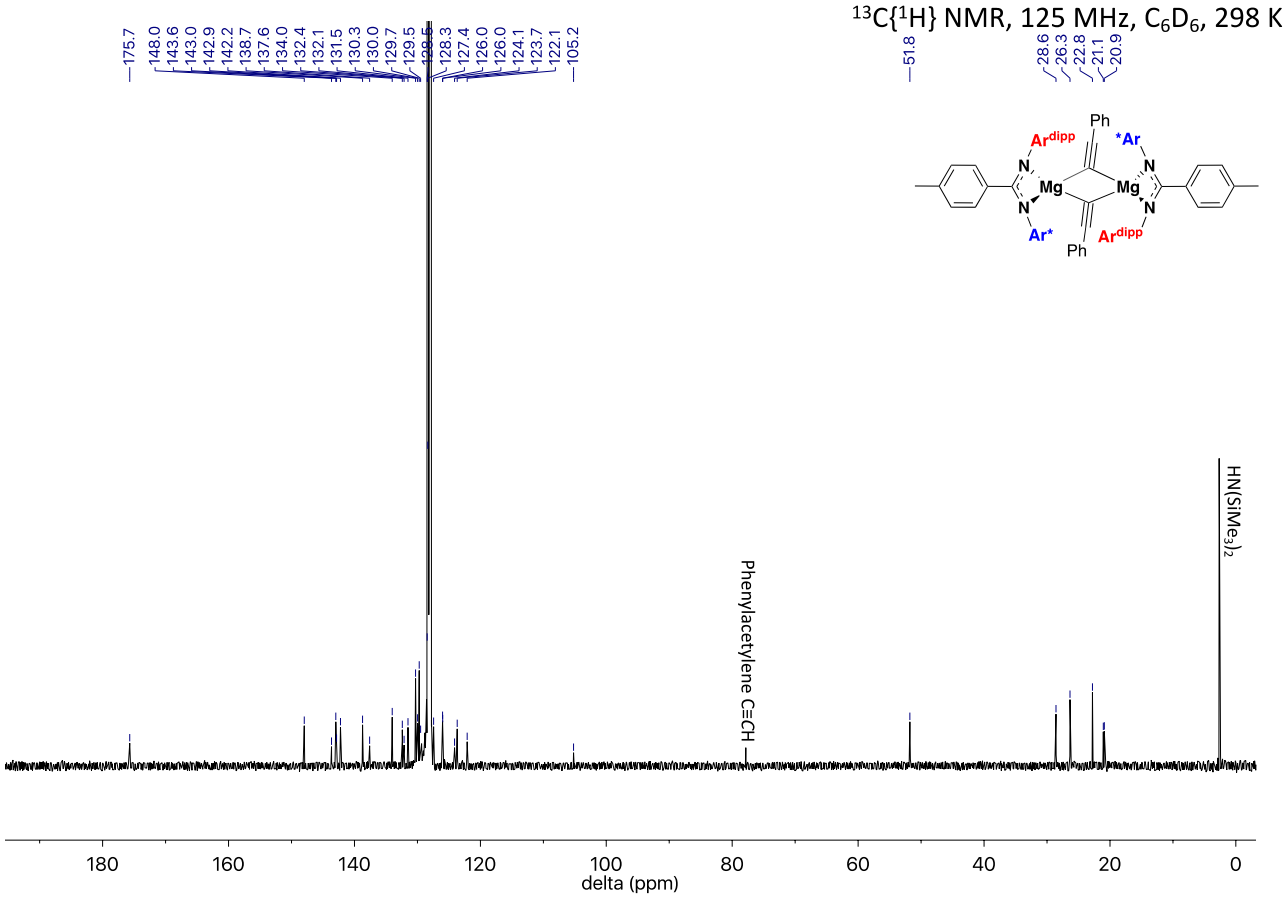


Figure S38: ^{1}H NMR spectrum of compound **5b**.

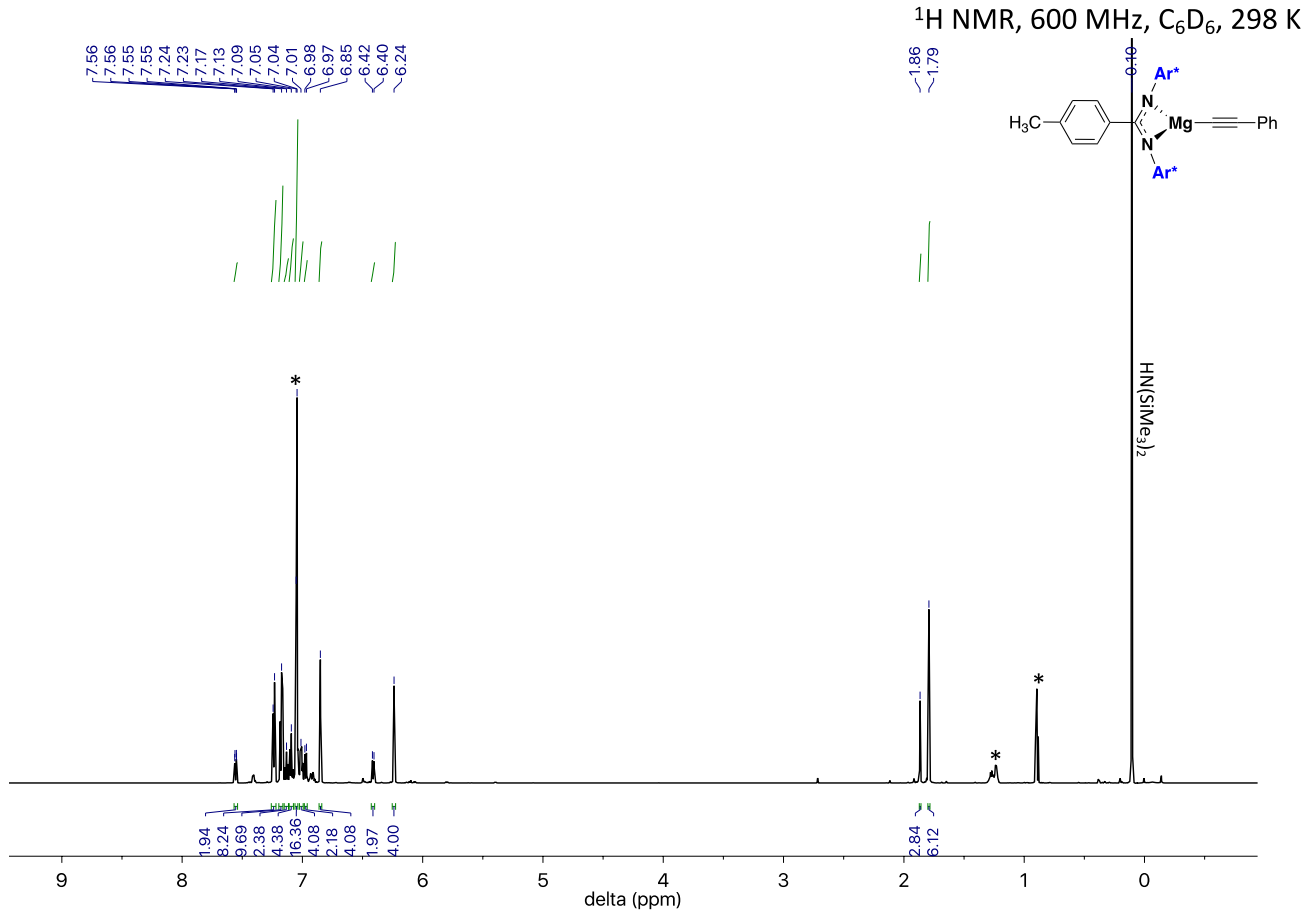


Figure S39: $^{13}C\{^{1}H\}$ NMR spectrum of compound **5b**.

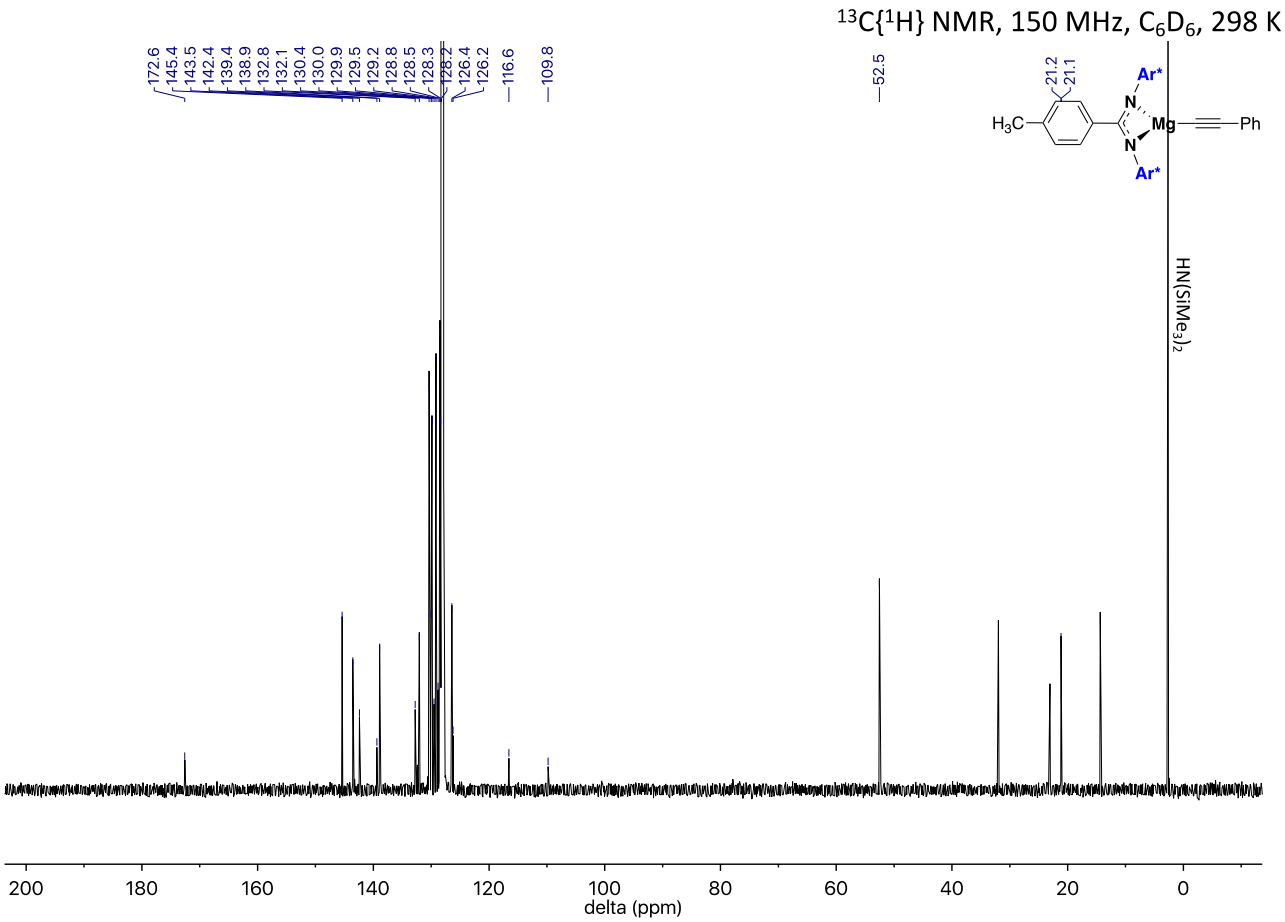
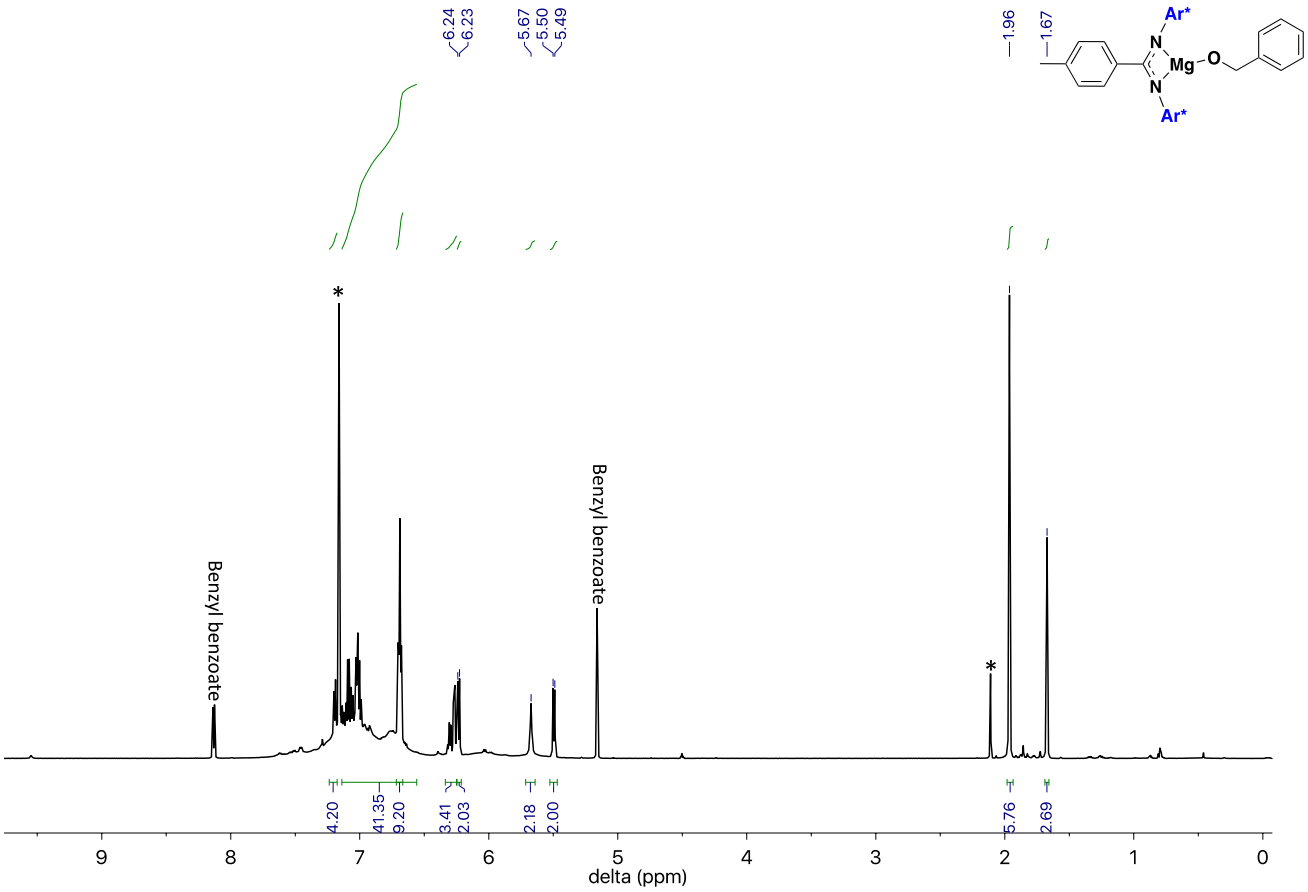


Figure S40: ^{1}H NMR spectrum of compound **6b**.

^{1}H NMR, 500 MHz, C_6D_6, 298 K



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