Supplementary Material for:

# Catalytic C-C Bond Formation Promoted by Organo- and Amido-Magnesium(II) Compounds

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**Experimental Procedures**

*General*

All manipulations were carried out under dry nitrogen using standard Schlenk-line and cannula techniques, or in a conventional nitrogen-filled glovebox. Solvents were dried using a PureSolv. system (Innovative Technologies). NMR spectra were recorded in $C_6D_6$ at 298 K (unless otherwise stated), using a Varian INOVA system at 300 MHz ($^1$H) or 75 MHz ($^{13}$C{$^1$H}). Proton and carbon chemical shifts were referenced internally to residual solvent resonances. Elemental analyses were performed S. Boyer at London Metropolitan University. All compounds were purchased from Sigma-Aldrich chemical company. Liquids were subjected to 3 x freeze-pump-thaw cycles, and stored under nitrogen in the glovebox. Compound **1** was made according to literature procedures.[1]

**Mg(mesC{NCy}$_2$)$_2$(THF) (2)**

Compound **2** was isolated from the attempted preparation of **A** (see below for details). Anal. Calcd. for $C_{48}H_{74}N_4MgO$ (*747.43*): C, 77.13; H, 9.98; N, 7.50 %. Found: C, 76.86; H, 10.12; N, 7.56 %. $^1$H NMR: δ 6.85 (s, 4H, C$_6$*H$_2$*), 3.74 (m, 4H, THF-C*H$_2$*), 2.87 (m, 4H, *α*-C$_6$*H$_{11}$*), 2.47 (s, 12H, 2,6-*Me$_2$*), 2.13 (s, 6H, *4*-Me), 2.13-1-23 (m, 40H, C$_6$*H$_{11}$*), 1.45 (THF-C*H$_2$*). $^{13}$C NMR: δ 174.3 (*C*N$_2$), 136.7, 134.2, 134.1, 128.4 (*C$_6$*H$_2$), 67.9 (THF-*C*H$_2$), 54.7 (*α*-*C$_6$*H$_{11}$), 37.8, 26.5, 25.9 (*C$_6$*H$_{11}$), 25.8 (THF-*C*H$_2$), 21.2 (4-*Me*), 20.7 (2,6-*Me*).

**Mg({Me$_3$Si}$_2$NC{N*i*-Pr}$_2$)$_2$(THF) (3)**

A solution of *N,N'*-di*iso*propylcarbodiimide (0.12 mL, 0.73 mmol.) in THF (5 mL) was added dropwise to a stirring solution of Mg(N{SiMe$_3$}$_2$)$_2$ (0.25 g, 0.73 mmol.) in THF (5 mL). The resulting solution was stirred at room temperature for 24 h followed by concentration of the solution *in vacuo*. Clear, colourless crystals suitable for X-ray diffraction were obtained upon storage of the solution at –

30 °C for 24 h. Yield 0.31 g, 78 %. Anal. Calcd. for $C_{30}H_{72}N_6MgOSi_4$ (*669.58*): C, 53.81; H, 10.84; N, 12.55 %. Found: C, 53.60; H, 10.77; N, 12.54 %. $^1$H NMR: δ 3.69 (sept, $J_{HH}$ = 6.2 Hz, 4H, C*H*$(CH_3)_2$), 3.59, 1.41 (m, 4H, THF-C*H*$_2$), 1.17 (d, $J_{HH}$ = 6.2 Hz, 24H, CH(C*H*$_3$)$_2$), 0.32 (s, 36H, N{Si*Me*$_3$}$_2$). $^{13}$C NMR: δ 167.2 (*C*$N_2$), 67.9 (THF-*C*$H_2$), 44.7 (*C*H$(CH_3)_2$), 27.4 (CH(*C*$H_3$)$_2$), 25.7 (THF-*C*$H_2$), 2.5 (Si*Me*$_3$).

**Mg(C≡CPh)$_2$(THF)$_4$ (4)**

A solution of $MgBu_2$ in heptane (1.2 mL of a 1.0M solution, 1.2 mmol.) was added dropwise to a stirring solution of phenyl acetylene (0.31 mL, 2.4 mmol.) in THF (5 mL). The resultant solution was stirred for 24 h followed by removal of the solvent *in vacuo* to give a white powder. Clear colourless crystals were obtained by recrystallisation from a hexane/THF solution. Yield 0.54 g, 84 %. $^1$H NMR: δ 7.89 (d, $J_{HH}$ = 7.2 Hz, 2H, *o*-C$_6$*H*$_5$), 7.10 (t, $J_{HH}$ = 7.2 Hz, 2H, *p*-C$_6$*H*$_5$), 7.00 (d, $J_{HH}$ = 7.2 Hz, 4H, *m*-C$_6$*H*$_5$), 3.61, 1.40 (m, THF-C*H*$_2$). $^{13}$C NMR: δ* 132.2, 129.3, 128.5, 127.0 (*C*$_6$H$_5$), 68.0, 25.8 THF-*C*$H_2$). * Resonances for the C≡C carbons not observed.

**Mg(PhC≡CC{N*i*-Pr}$_2$)$_2$(THF)$_2$ (5)**

A solution of $MgBu_2$ in heptane (0.88 mL of a 1.0 M solution, 0.88 mmol.) was added drop wise to a stirring solution of PhC≡CC{N*i*-Pr}{NH*i*-Pr} (0.40 g, 1.8 mmol.) in THF (5 mL). The solution was allowed to stir for 24 h followed by removal of the volatiles. Clear yellow crystals suitable for X-ray analysis were obtained by recrystallization from hexane at -30 °C. Yield 0.36 g, 66 %. Anal. Calcd. for $C_{38}H_{54}N_4MgO_2$ (*623.17*): C, 73.24; H, 8.73; N, 8.99 %. Found: C, 73.15; H, 8.61; N, 9.05 %. $^1$H NMR: δ 7.48 (m, 4H, *o*-C$_6$*H*$_5$), 6.95 (m, 6H, *m*- and *p*-C$_6$*H*$_5$), 4.38 (sept, $J_{HH}$ = 6.4 Hz, 4H, C*H*$(CH_3)_2$), 3.62 (m, THF-C*H*$_2$), 1.44 (d, $J_{HH}$ = 6.4 Hz, 24H, CH(C*H*$_3$)$_2$), 1.34 (m, THF-C*H*$_2$). $^{13}$C NMR: δ 157.9 (*C*$N_2$), 132.3, 128.9, 128.7, 123.1 (*C*$_6$H$_5$), 95.9, 80.8 (*C*≡*C*), 68.0 (THF-*C*$H_2$), 48.9 (*C*H$(CH_3)_2$), 26.7 (CH(*C*$H_3$)$_2$), 25.6 (THF-*C*$H_2$).

**Mg(PhC≡CC{N-*i*-Pr}$_2$)Br(OEt$_2$) (6)**

A solution of MeMgBr in $Et_2O$ (0.48 mL of a 3.0 M solution, 1.45 mmol.) was added drop wise to a stirring solution of PhC≡CC{N*i*-Pr}{NH*i*-Pr} (0.33 g, 1.45 mmol.) in $Et_2O$ (5 mL). The resultant solution was left to stir for 24 h, followed by concentration to ca. 1 mL and storage at -30 °C. Yellow crystals of **6** were obtained after 24 h. Yield 0.47 g, 81 %. Anal. Calcd. for $C_{19}H_{29}MgN_2OBr$ (*405.66*): C, 56.26; H, 7.21; N, 6.91 %. Found: C, 56.05; H, 7.27; N, 6.75 %. $^1$H NMR: δ 7.38 (br, 2H, *o*-$C_6H_5$), 6.94 (m, 3H, *m*- and *p*-$C_6H_5$), 4.35 (br sept, 2H, C*H*$(CH_3)_2$), 3.53 (q, $J_{HH}$ = 6.9 Hz, 4H, C$H_2CH_3$), 1.73, 1.52 (br d, 12H, CH(C$H_3$)$_2$), 1.07 (t, $J_{HH}$ = 6.9 Hz, 6H, $CH_2CH_3$). $^{13}$C NMR ($C_6D_6$, 75 MHz, 298K) δ 158.9 (*C*$N_2$), 132.3, 129.3, 128.7, 122.5 (*C*$_6$H$_5$), 97.1, 80.1 (*C*≡C), 65.6 (*C*$H_2CH_3$), 49.1 (*C*H$(CH_3)_2$), 26.1 (CH(*C*$H_3$)$_2$), 14.7 ($CH_2$*C*$H_3$).

**Mg(mesC{NCy}$_2$)(C≡CPh)(THF) (A)**

*NMR scale*

Phenylacetylene (0.0045 mL, 0.034 mmol.) was added to a J. Young NMR tube charged with a solution of **1** (20 mg, 0.034 mmol.) in $C_6D_6$ (0.5 mL). The solution was allowed to sit for 10 mins at room temperature followed by $^1$H NMR analysis.

$^1$H NMR: δ 7.84 (d, $J_{HH}$ = 7.2 Hz, 2H, *o*-$C_6H_5$), 7.10 (t, $J_{HH}$ = 7.2 Hz, 2H, *m*-$C_6H_5$), 7.02 (d, $J_{HH}$ = 7.2 Hz, 1H, *p*-$C_6H_5$), 6.84 (s, 2H, $C_6H_2$), 3.96 (m, THF-C$H_2$), 2.81 (br m, 2H, α-$C_6H_{11}$), 2.46 (br s, 6H, 2,6-*Me*$_2$), 2.13 (br s, 3H, 4-*Me*), 1.95-1.00 (m, 24H, $C_6H_{11}$ + THF-C$H_2$), 0.09 (s, 18H, HN(Si*Me*$_3$)$_2$). $^{13}$C NMR ($C_6D_6$, 75 MHz, 298K) δ 173.9 (*C*$N_2$), 136.6, 134.5, 134.3, 132.2, 129.3, 128.40, 127.4, 126.4 (*C*$_6$H$_5$ and *C*$_6$H$_2$), 120.1, 117.7 (*C*≡*C*), 68.9 (THF-*C*$H_2$), 55.9, 55.2 (α-*C*$_6$H$_{11}$), 37.9, 26.4 (br), 26.1, 25.6 (*C*$_6$H$_{11}$), 21.2 (*4*-Me), 20.8 (2,6-*Me*), 2.7 (HN(Si*Me*$_3$)$_2$).

*Attempted isolation of **A** - preparative scale*

Phenylacetylene (0.065 mL, 0.62 mmol.) was added drop wise to a rapidly stirring solution of **1** (0.36g, 0.62 mmol.) in toluene (10 mL). The resulting solution was left to stir for 24 h at room temperature, followed by removal of volatiles *in vacuo* to give a yellow oil. The addition of hexane (5 mL) and THF (1 mL) to the oil, followed by storage at –30 °C for 24 h yielded a white powder, identified as **4** by $^1$H NMR spectroscopy. Yield 0.027 g, 16 %. Additional crops of clear, colourless crystals were obtained by further concentration of the solution identified as **2**. Yield 0.060 g, 26 %.

**Mg(mesC{NCy}$_2$)({Me$_3$Si}$_2$NC{N*i*-Pr}$_2$)(THF)$_n$ (B)**

*NMR scale*

*N,N'*-di*iso*propylcarbodiimide (0.0056 mL, 0.034 mmol.) was added to a J. Young NMR tube charged with a solution of **1** (20 mg, 0.034 mmol.) in $C_6D_6$ (0.5 mL). The solution was allowed to sit for 2 h at room temperature followed by $^1$H NMR analysis, showing formation of a mixture of **2**, **3** and **B**.

$^1$H NMR: δ 6.85 (s, $C_6H_2$ {**2**}), 6.82 (s, $C_6H_2$ {**B**}), 3.79, 3.51, 3.39 (overlapping sept, C*H*$(CH_3)_2$ {**3**/**B**}), 3.71 (m, THF-C$H_2$ {**2**/**3**/**B**}), 2.87 (m, *α*-$C_6H_{11}$ {**2**}), 2.87 (m, *α*-$C_6H_{11}$ {**B**}), 2.47 (s, 2,6-*Me*$_2$ {**2**}), 2.42, 2.41 (s, 2,6-*Me*$_2$ {**B**}), 2.13 (s, 4-*Me* {**2**}), 2.12 (s, 4-*Me* {**2**}), 1.90-1.38 (overlapping m, $C_6H_{11}$ {**2**/**B**}), 1.42 (m, THF-C$H_2$ {**2**/**3**/**B**}), 1.30, 1.27, 1.26, 1.22, 1.20, 1.18 (overlapping d, CH(C$H_3$)$_2$ {**3**/**B**}), 1.17 (d, CH(C$H_3$)$_2$ {**3**}), 1.07 (d, CH(C$H_3$)$_2$ {**B**}), 0.37, 0.36, 0.32 (s, N{Si*Me*$_3$}$_2$ {**B**}), 0.32 (s, N{Si*Me*$_3$}$_2$ {**3**}). $^{13}$C NMR ($C_6D_6$, 75 MHz, 298K) δ 174.0 (*C*$N_2$ {**2**}), 173.8 (*C*$N_2$ {**B**}), 166.4 (*C*$N_3$ {**3**/**B**}), 136.5, 136.4, 134.6, 134.3, 134.2, 128.4 ($C_6H_2$ {**2**/**B**}), 68.1 (THF-*C*$H_2$ {**2**/**3**/**B**}), 55.3 (*α*-$C_6H_{11}$ {**B**}), 54.9 (*α*-$C_6H_{11}$ {**2**}), 45.3 (overlapping *C*H$(CH_3)_2$), {**3**/**B**}), 37.9, 37.8, 27.5, 27.4, 27.0, 26.5, 26.4, 26.3, 26.2, 26.1, 25.9, 25.6, 25.3, 24.9, 24.8 ($C_6H_{11}$, CH(*C*$H_3$)$_2$ and THF-*C*$H_2$ {**2**/**3**/**B**}), 21.2 (4-*Me* {**2**/**B**}), 20.8 (2,6-*Me*$_2$ {**B**}), 20.7 (2,6-*Me* {**2**}).

**Mg(mesC{NCy}$_2$)(PhC≡CC{N*i*-Pr}$_2$) (THF) (C)**

*NMR scale*

Phenylacetylene (0.0045 mL, 0.034 mmol.) was added to a J. Young NMR tube charged with a solution of **1** (20 mg, 0.034 mmol.) in $C_6D_6$ (0.5 mL). The solution was allowed to sit for 2 h at room temperature followed by the addition of *N,N'*-di*iso*propylcarbodiimide (0.0056 mL, 0.034 mmol.). $^1$H NMR analysis showed formation of a mixture of **2**, **5** and **C**.

$^1$H NMR: δ 7.48 (m, *o*-C$_6$*H$_5$* {**5**}), 7.46 (m, *o*-C$_6$*H$_5$* {**C**}), 6.98 (m, *m*- and *p*-C$_6$*H$_5$* {**C**}), 6.95 (m, *m*- and *p*-C$_6$*H$_5$* {**5**}), 6.84 (s, C$_6$*H$_2$* {**2**}), 6.81 (s, C$_6$*H$_2$* {**C**}), 4.37 (overlapping sept, C*H*(CH$_3$)$_2$, {**5**/**C**}), 3.77 (m, THF-C*H$_2$* {**2**/**5**/**C**}), 2.79 (m, *α*-C$_6$*H$_{11}$* {**5**/**C**}), 2.45 (s, 2,6-*Me$_2$* {**2**}), 2.44 (s, 2,6-*Me$_2$* {**C**}), 2.13 (s, 4-*Me* {**5**/**C**}), 1.84-1.12 (m, C$_6$*H$_{11}$* {**2**/**C**} and THF-C*H$_2$* {**2**/**5**/**C**}), 1.44 (d, CH(C*H$_3$*)$_2$ {**5**}), 1.41, 1.05 (d, CH(C*H$_3$*)$_2$ {**C**}), 0.09 (s, HN{Si*Me$_3$*}$_2$). $^{13}$C NMR: δ 174.0 (*C*N$_2$ {**2**}), 173.8 (*C*N$_2$ {**C**}), 157.9 (*C*N$_2$ {**5**}), 157.7 (*C*N$_2$ {**C**}), 136.5, 136.4, 134.7, 134.4, 132.3, 132.2, 128.9, 128.7, 123.1 (*C$_6$*H$_5$ and *C$_6$*H$_2$ {**2**/**5**/**C**}), 95.9 (*C*≡*C* {**5**}), 95.8 (*C*≡*C* {**C**}), 81.0 (*C*≡*C* {**C**}), 80.8 (*C*≡*C* {**5**}), 68.0 (THF-*C*H$_2$ {**2**/**5**/**C**}), 55.7, 55.1 (*α*-*C$_6$*H$_{11}$ {**2**/**C**}), 48.9, 48.8 (*C*H(CH$_3$)$_2$ {**5**/**C**}), 37.9, 37.8, 27.5, 27.3, 26.9, 26.7, 26.5, 26.4, 26.1, 25.6, 24.8 (*C$_6$*H$_{11}$, CH(*C*H$_3$)$_2$ and THF-*C*H$_2$ {**2**/**5**/**C**}), 21.2, 20.8, 20.7 (2,6-*Me$_2$* and 4-*Me* {**2**/**C**}), 2.7 (HN(Si*Me$_3$*)$_2$).

*Preparative scale*

Phenylacetylene (0.065 mL, 0.62 mmol.) was added drop wise to a rapidly stirring solution of **1** (0.36 g, 0.62 mmol.) in toluene (10 mL). The solution was allowed to stir for 4 h at room temperature, followed by the addition of *N,N'*-di*iso*propylcarbodiimide (0.10 mL, 0.62 mmol.). The resulting solution was stirred for 24 h followed by removal of volatiles *in vacuo* to give a crude yellow solid. The addition of hexane (5 mL) to the solid, followed by storage at –30 °C for 24 h yielded clear colourless crystals, identified as **2**. Yield 0.11 g, 47 %. Additional crops of clear, yellow crystals were

obtained by further concentration of the solution and storage at –30 °C, identified as **5**(THF) by $^{1}$H NMR spectroscopy. Yield 0.070 g, 36 %.

**General procedure for catalytic study**

*NMR scale*

To a J. Young NMR tube charged with a mixture of phenyl acetylene (0.022 mL, 0.17 mmol.) and *N,N'*-di*iso*propylcarbodiimide (0.028 mL, 0.17 mmol) was added a solution of **1** in $C_6D_6$ (0.5 mL of a 0.0034 M standard solution, 1.7 μmol). The NMR tube was heated to 80 °C for 24 h with regular monitoring of the progress of the catalysis using $^{1}$H NMR spectroscopy. Yields of the propargylamidine were determined using peaks corresponding to the THF from **1** as an internal standard.

*Preparative scale*

A solution of **1** (10 mg, 0.017 mmol.) in toluene (2.5 mL) was added to a stirring solution of phenyl acetylene (0.22 mL, 1.7 mmol.) and *N,N'*-di*iso*propylcarbodiimide (0.28 mL, 1.7 mmol.) in toluene (2.5 mL). The solution was heated to 80 °C and allowed to stir for 24 h, followed by removal of the volatiles *in vacuo* to give a yellow oil. Clear, yellow crystals of propargylamidine were obtained by recrystallisation from hexane. Yield 0.28 g, 73 %.

**References**

1. Day, B. M.; Knowelden, W.; Coles, M. P., *Dalton Trans.* **2012,** *41*, 10930-10933.

**Figure S1** $^{1}$H NMR Spectrum of Mg(mesC{NCy}$_2$)(N{SiMe$_3$}$_2$)(THF) (**1**) ($C_6D_6$, 300 MHz).

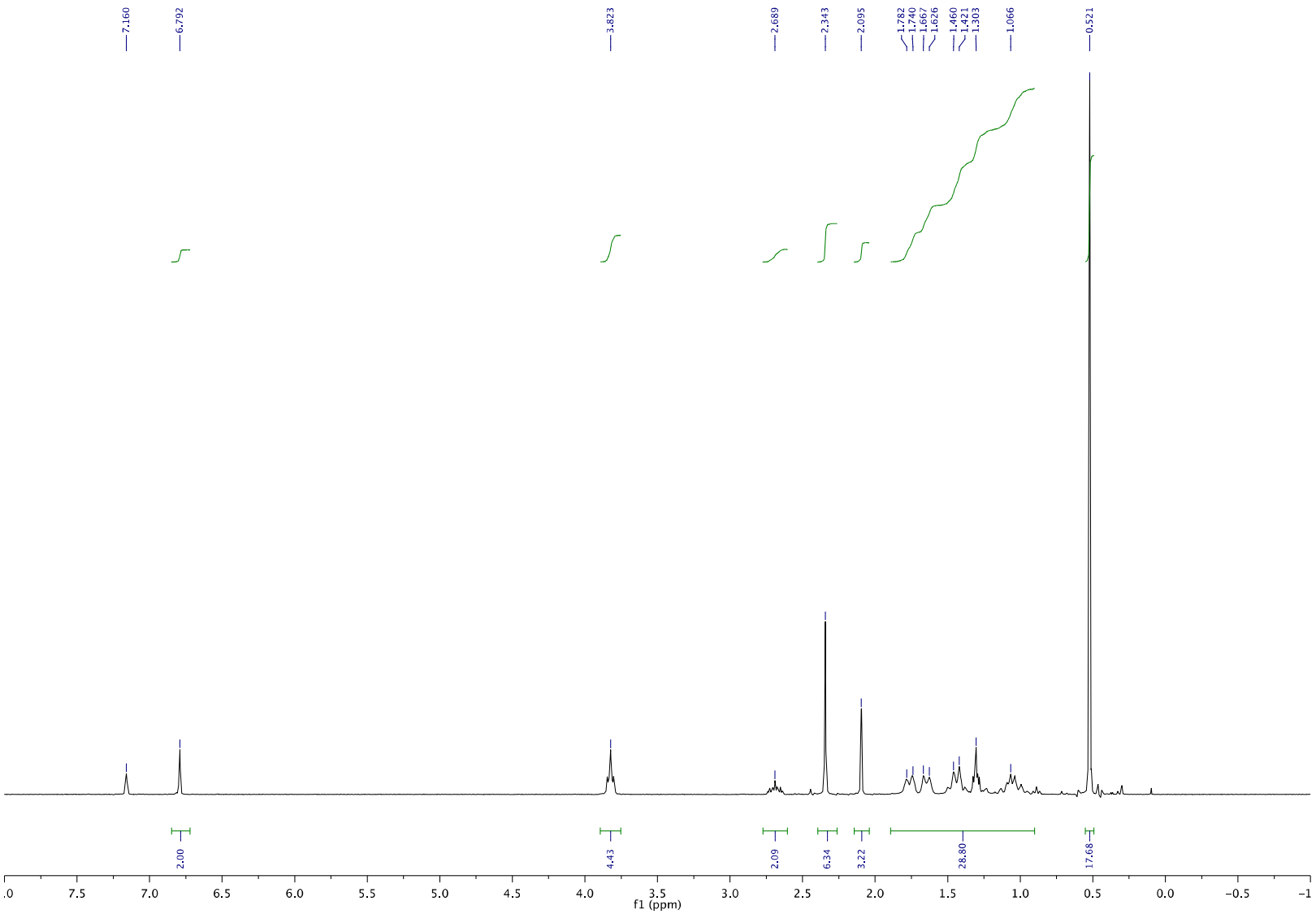

**Figure S2** $^{1}$H NMR Spectrum of Mg(mesC{NCy}$_2$)$_2$(THF) (**2**) ($C_6D_6$, 300 MHz).

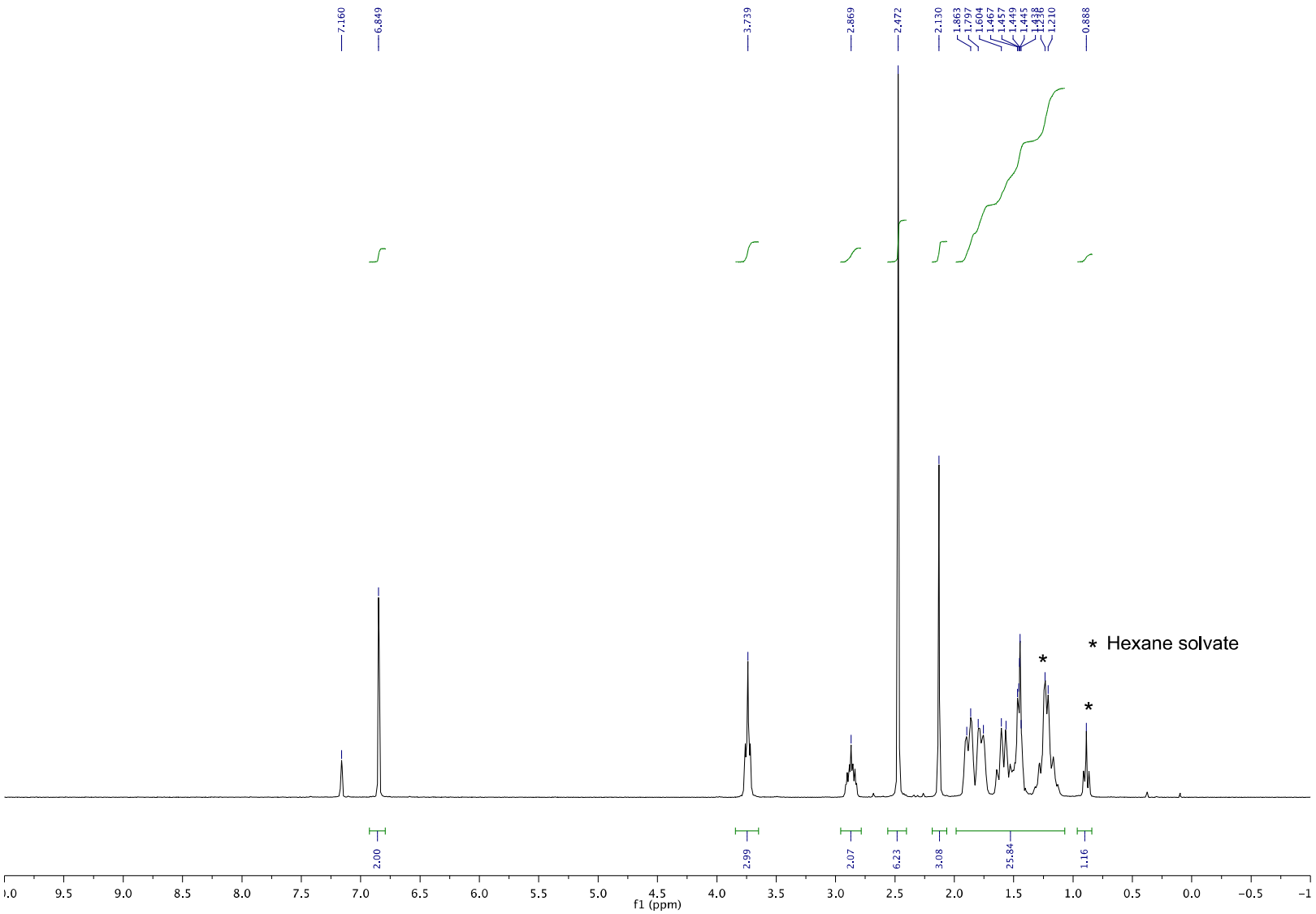

**Figure S3** $^{13}C\{^{1}H\}$ NMR Spectrum of $Mg(mesC\{NCy\}_2)_2(THF)$ (**2**) ($C_6D_6$, 75 MHz).

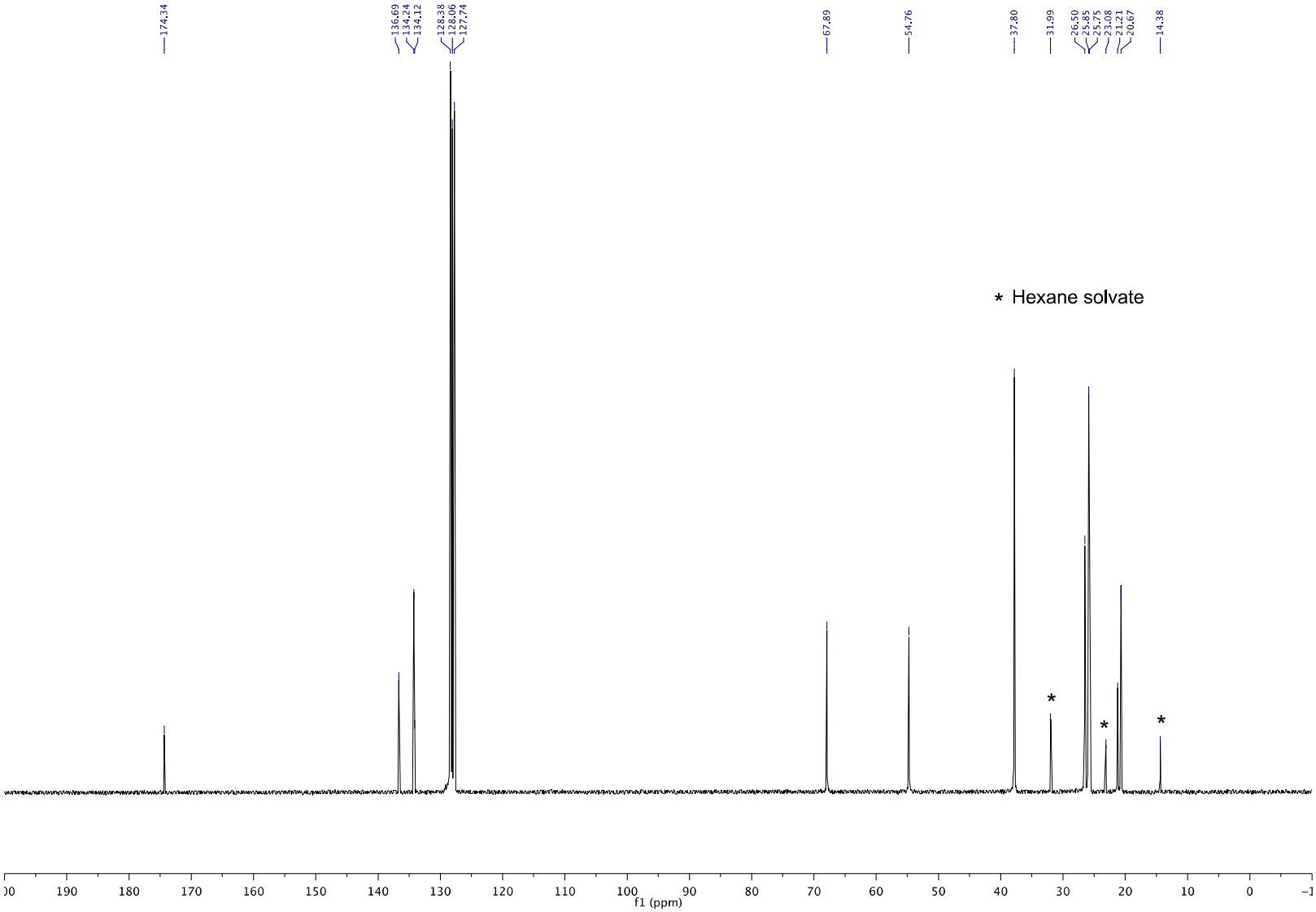

**Figure S4** $^{1}$H NMR Spectrum of Mg({$Me_3Si$}$_2$NC{N*i*-Pr}$_2$)$_2$(THF) (**3**) ($C_6D_6$, 300 MHz).

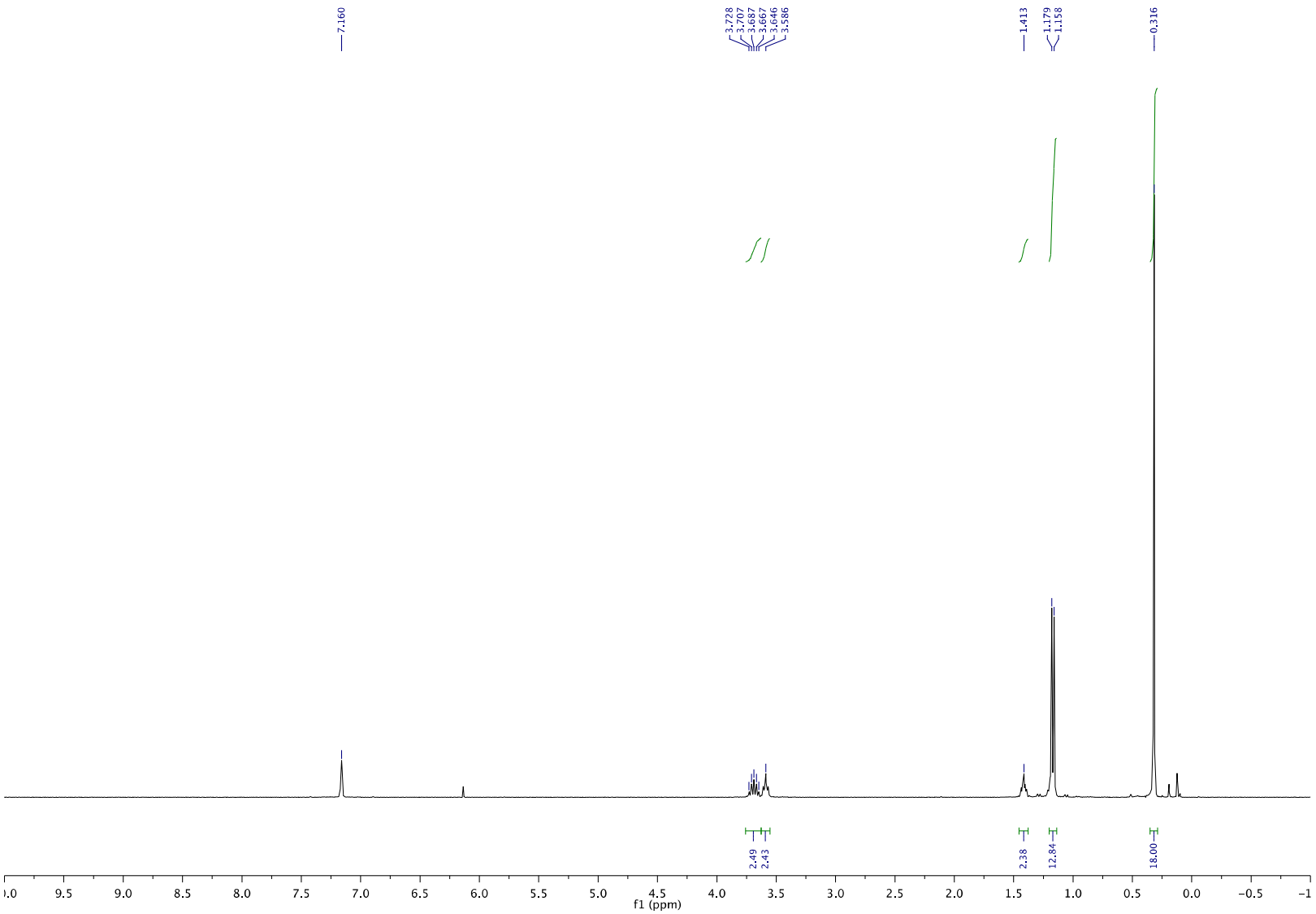

**Figure S5** $^{13}C\{^{1}H\}$ NMR Spectrum of $Mg(\{Me_3Si\}_2NC\{N\textit{i}\text{-}Pr\}_2)_2(THF)$ (**3**) ($C_6D_6$, 75 MHz).

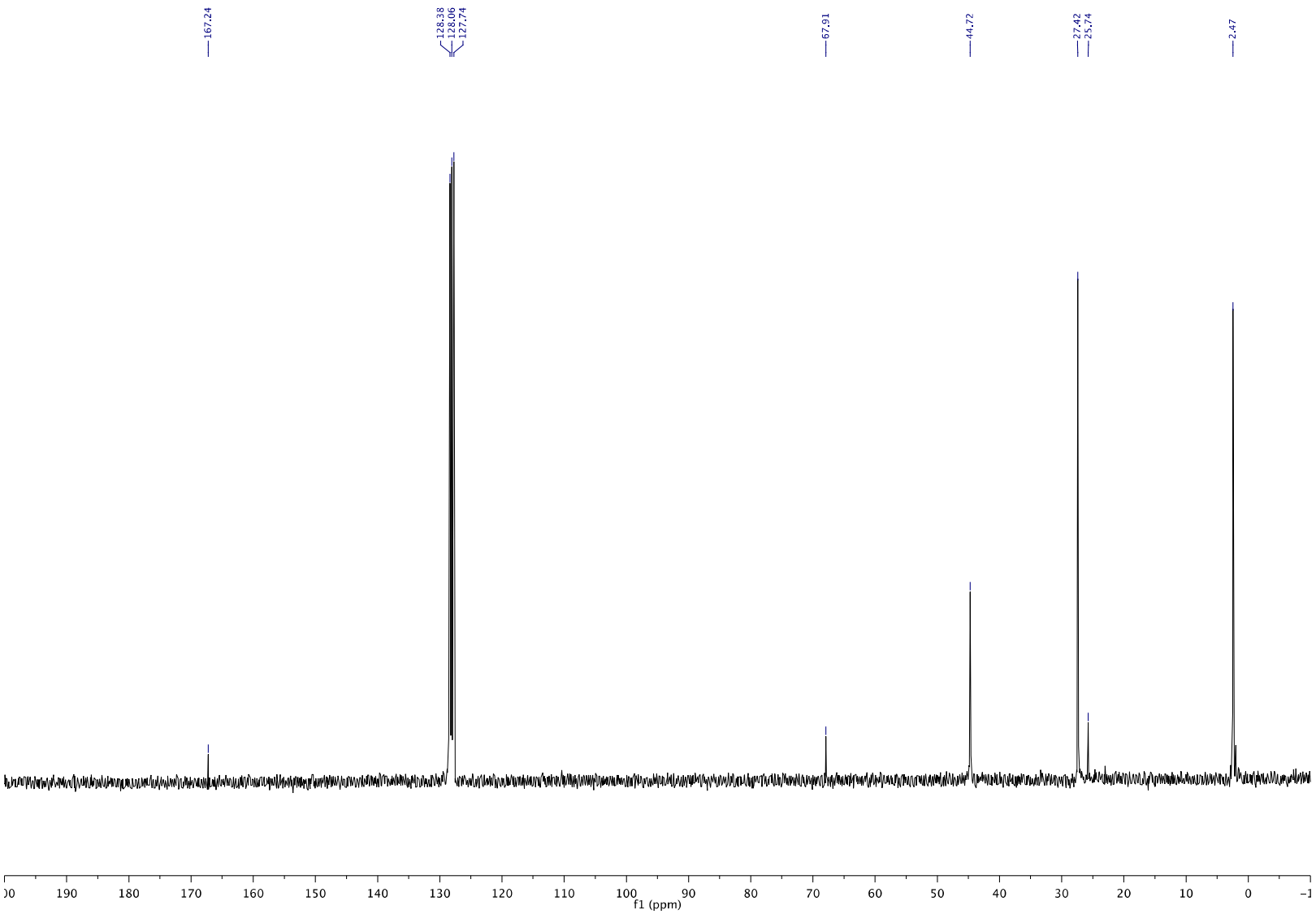

**Figure S6** $^{1}H$ NMR Spectrum of $Mg(C{\equiv}CPh)_2(THF)_4$ (**4**) ($C_6D_6$, 300 MHz).

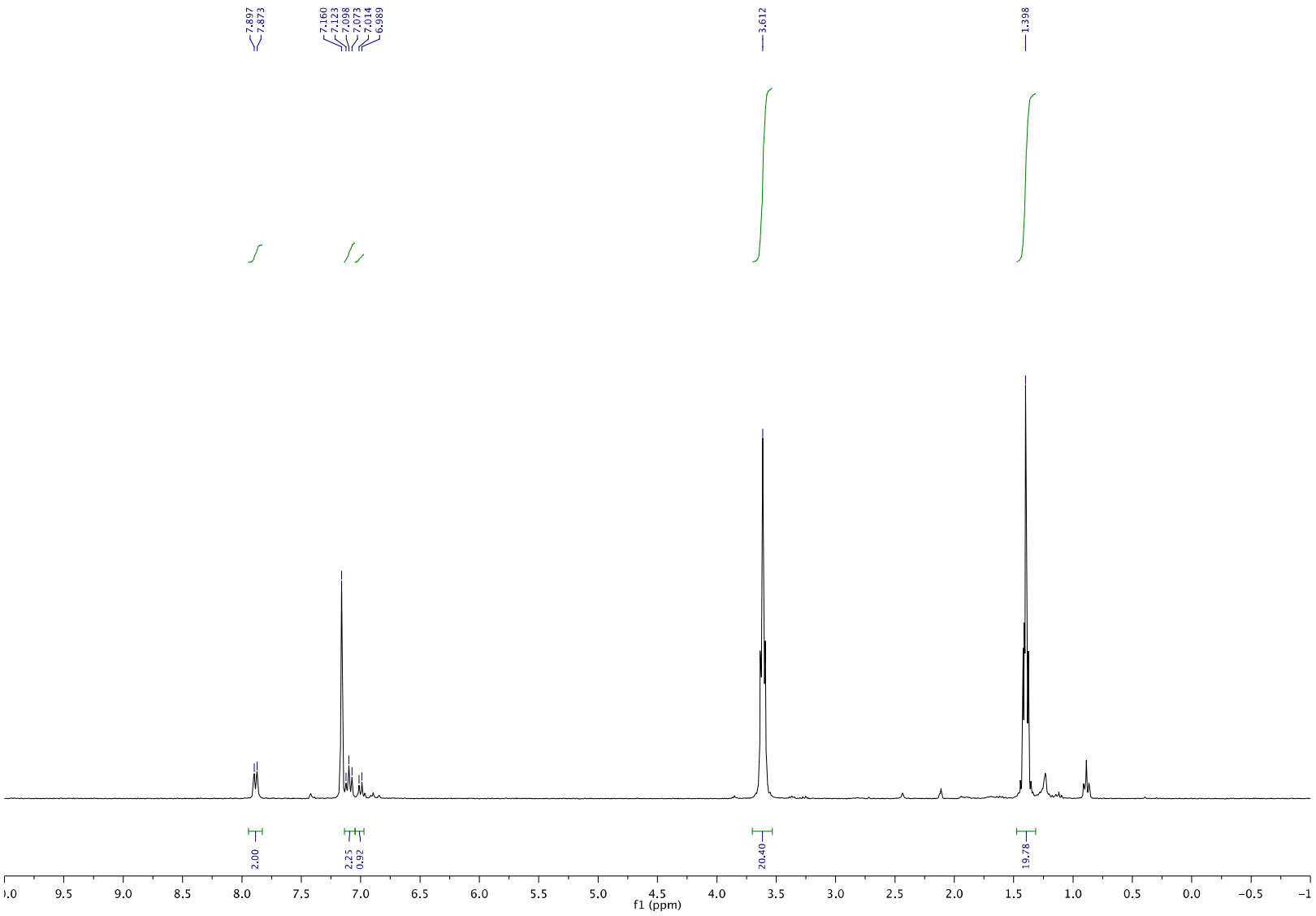

**Figure S7** $^{13}C\{^{1}H\}$ NMR Spectrum of $Mg(C{\equiv}CPh)_2(THF)_4$ (**4**) ($C_6D_6$, 75 MHz).

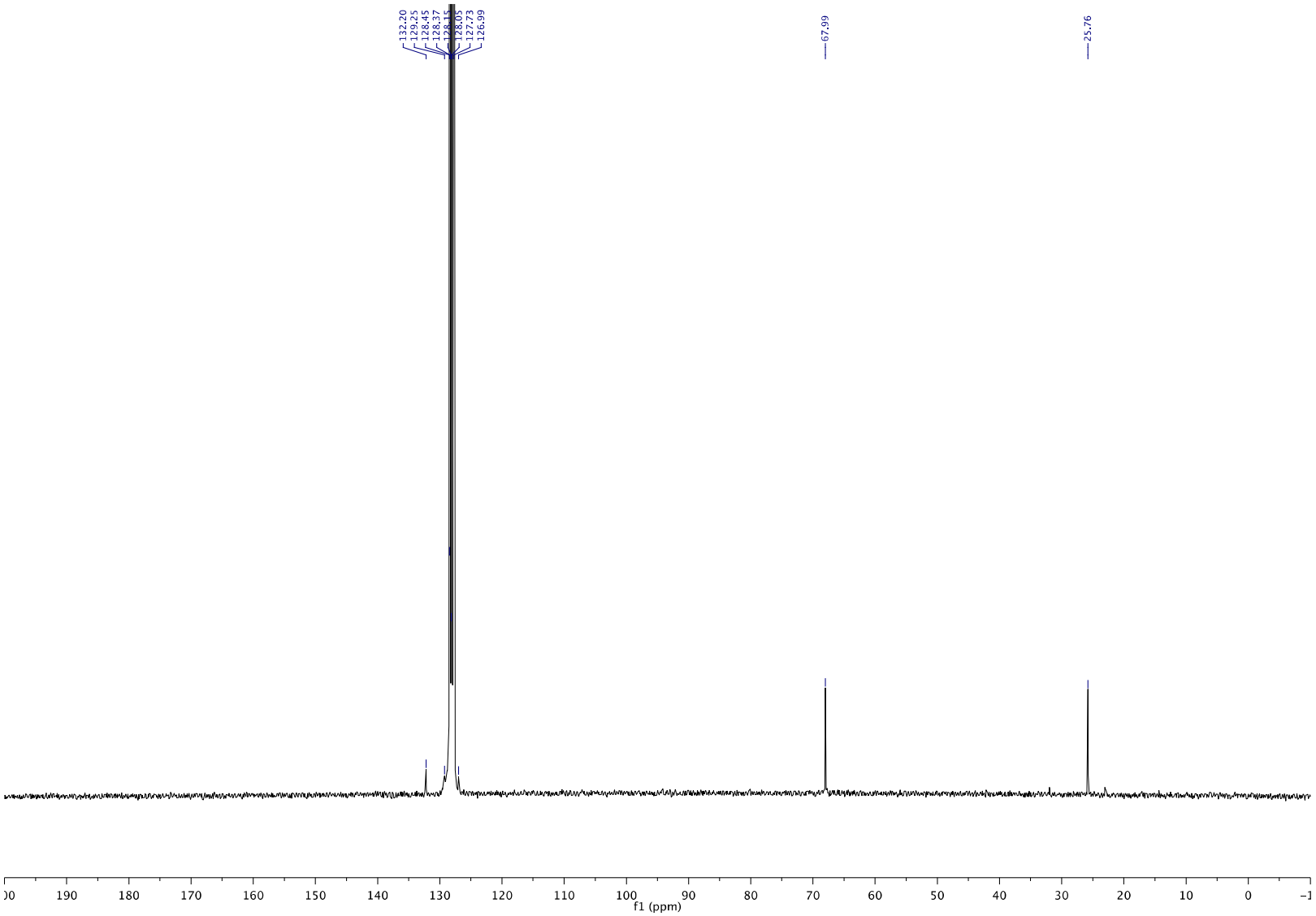

**Figure S8** $^{1}$H NMR Spectrum of Mg(PhC≡CC{N*i*-Pr}$_2$)$_2$(THF)$_2$ (**5**) ($C_6D_6$, 300 MHz).

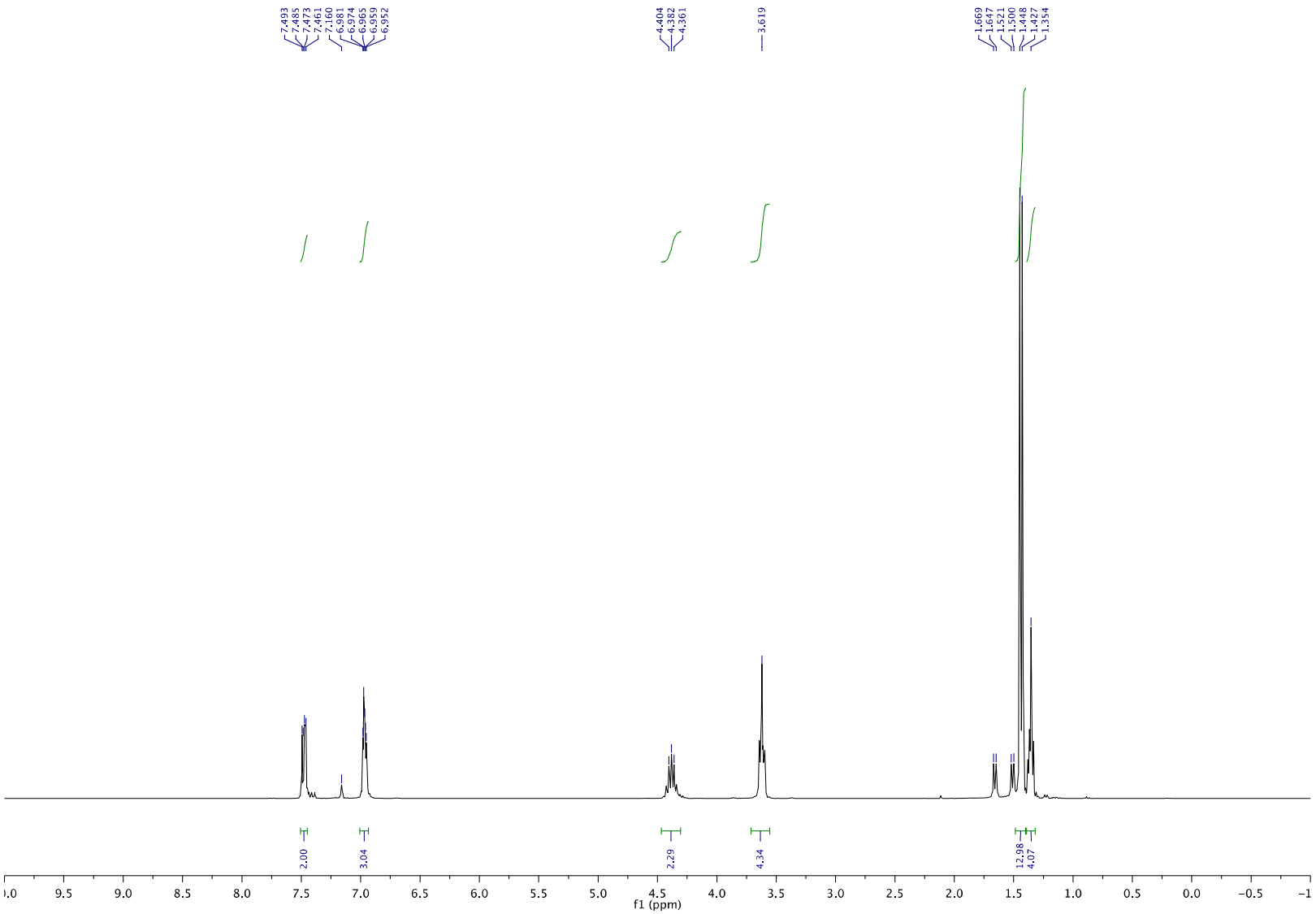

**Figure S9** $^{13}C\{^{1}H\}$ NMR Spectrum of $Mg(PhC{\equiv}CC\{N\textit{i}\text{-}Pr\}_2)_2(THF)_2$ (**5**) ($C_6D_6$, 75 MHz).

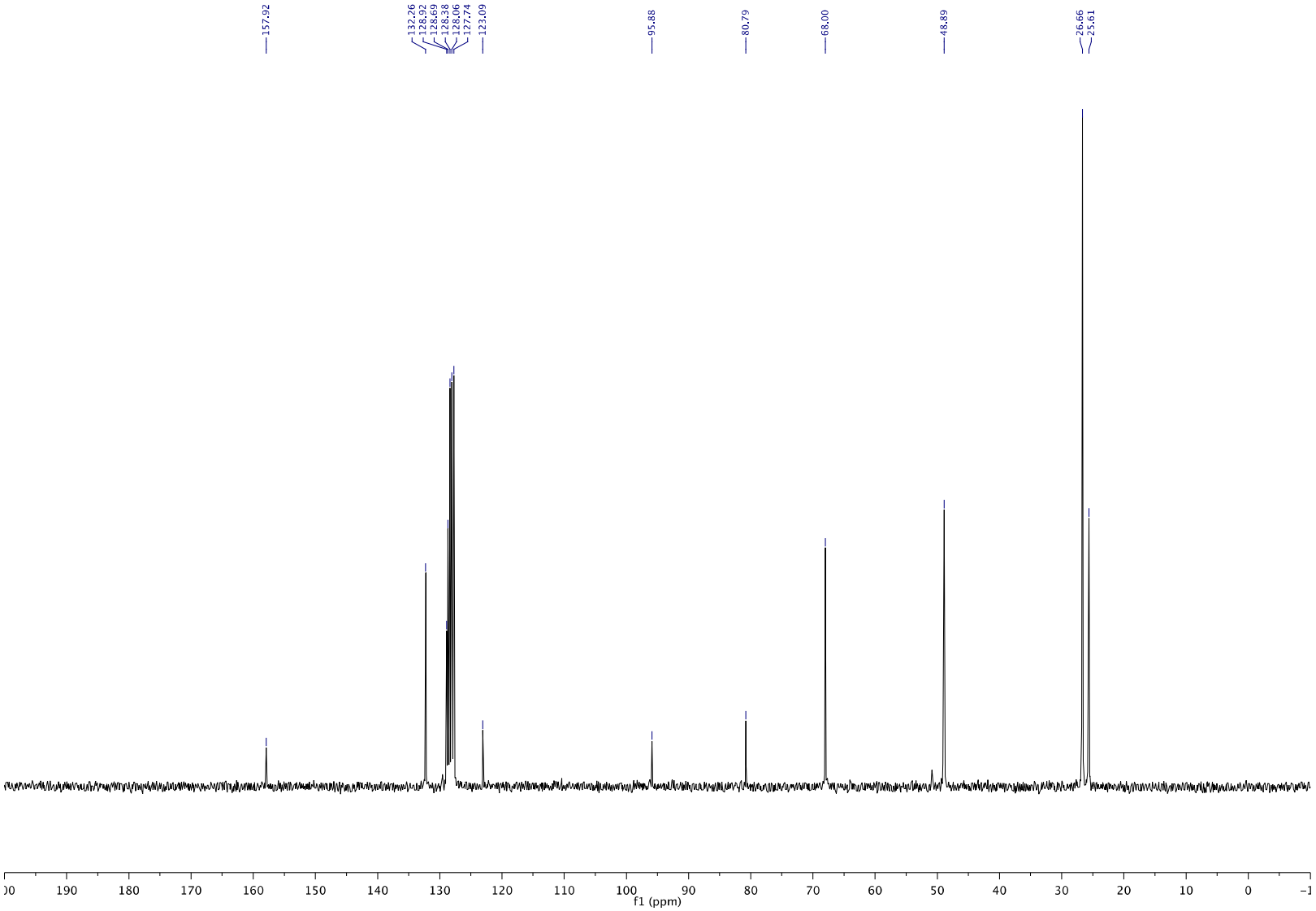

**Figure S10** $^{1}$H NMR Spectrum of Mg(PhC≡CC{N*i*-Pr}$_2$)Br(Et$_2$O) (**6**) ($C_6D_6$, 300 MHz).

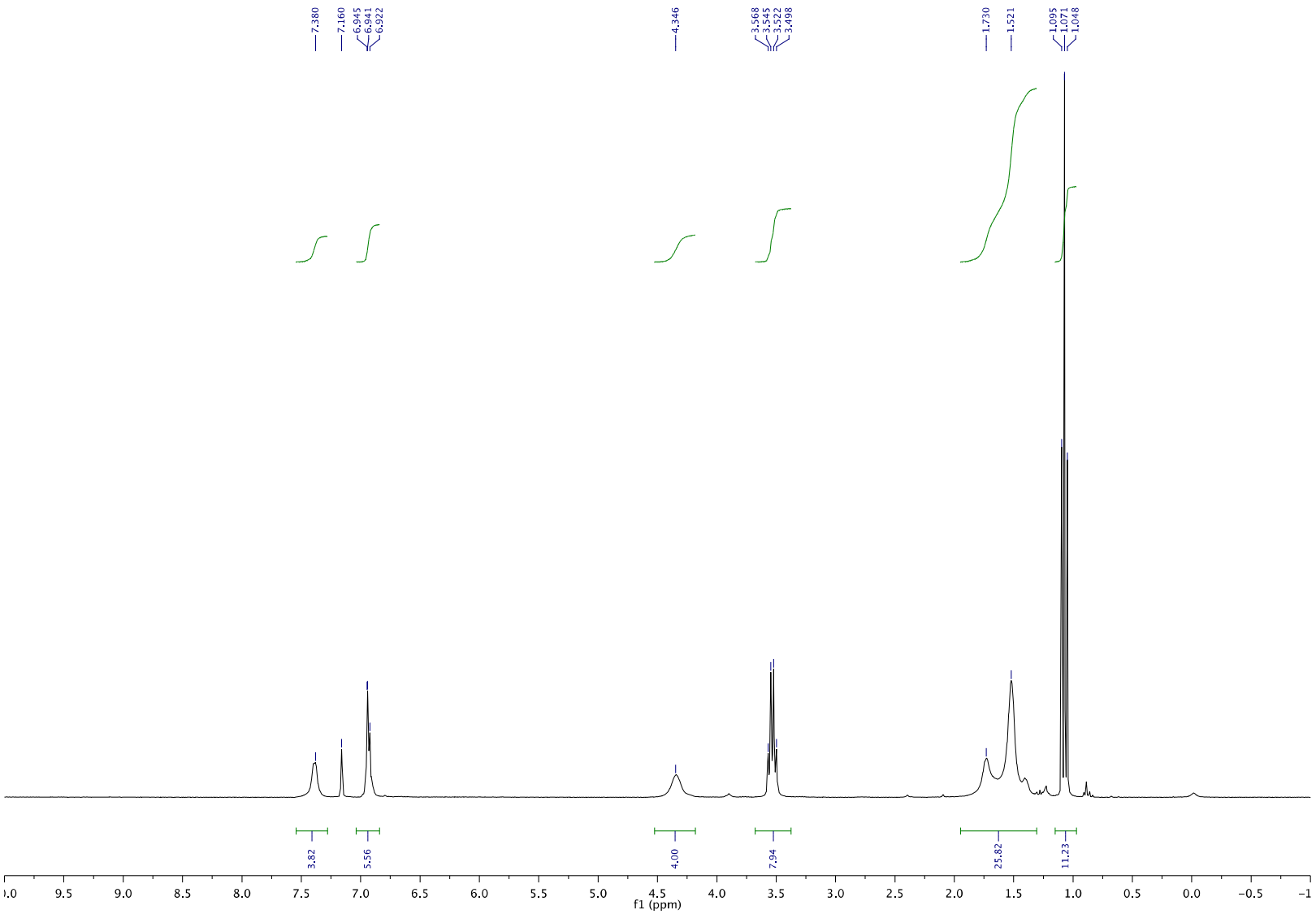

**Figure S11** $^{13}C\{^{1}H\}$ NMR Spectrum of Mg(PhC≡CC{N*i*-Pr}$_2$)Br(Et$_2$O) (**6**) ($C_6D_6$, 75 MHz).

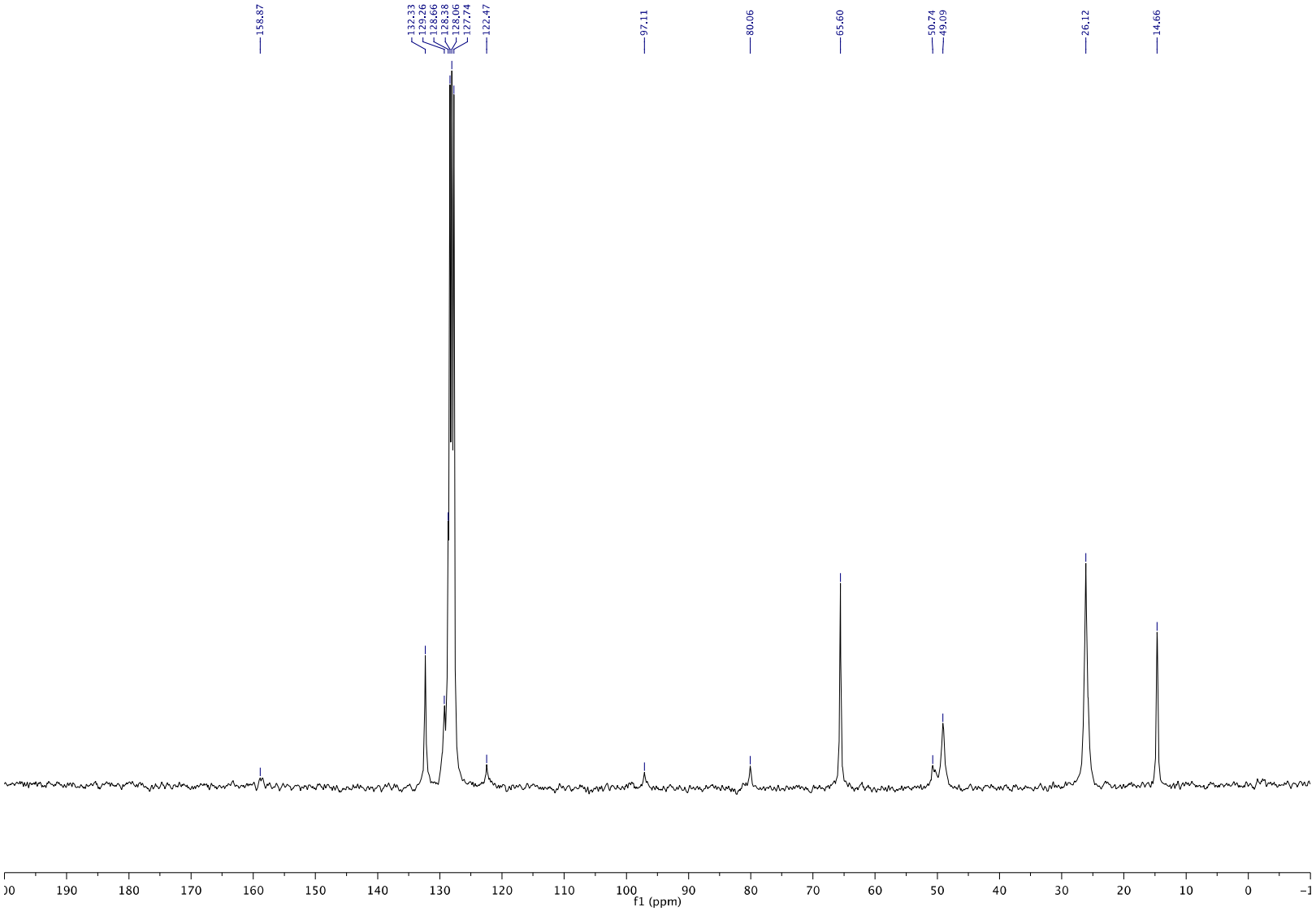

**Figure S12** $^{1}$H NMR Spectrum of the NMR scale reaction of **1** with one equivalent PhC≡CH ($C_6D_6$, 300 MHz), affording Mg(mesC{NCy}$_2$)(C≡CPh)(THF) (**A**).

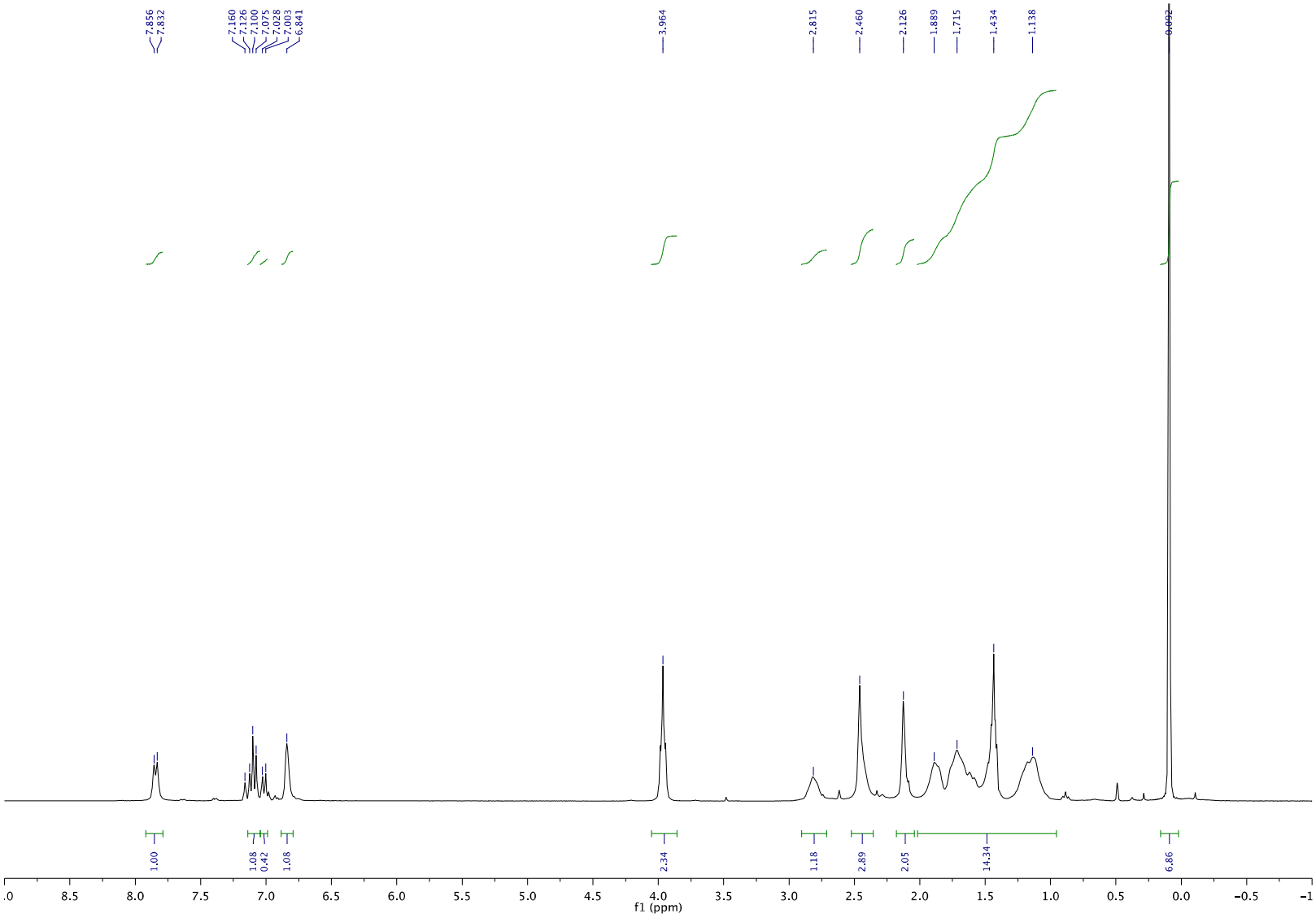

**Figure S13** $^{13}C\{^{1}H\}$ NMR Spectrum of the NMR scale reaction of **1** with one equivalent PhC≡CH ($C_6D_6$, 75 MHz), affording Mg(mesC{NCy}$_2$)(C≡CPh)(THF) (**A**).

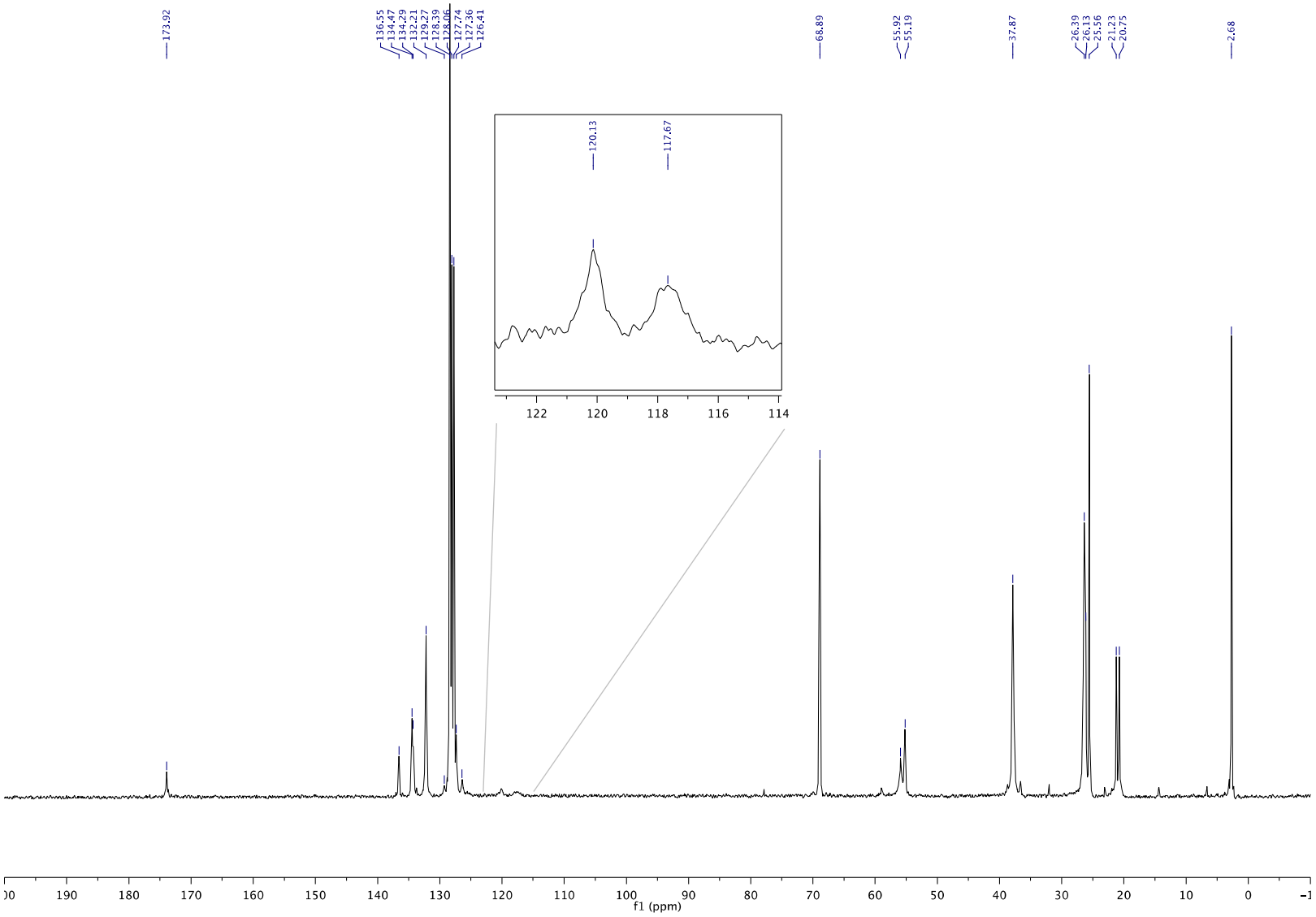

**Figure S14** $^{1}$H NMR Spectrum of the NMR scale reaction of **1** with one equivalent *i*Pr-N=C=N*i*-Pr ($C_6D_6$, 300 MHz). Peaks corresponding to Mg(mesC{NCy}$_2$)$_2$(THF) (**2**) and Mg({$Me_3Si$}$_2$NC{N*i*-Pr}$_2$)$_2$(THF) (**3**) identified.

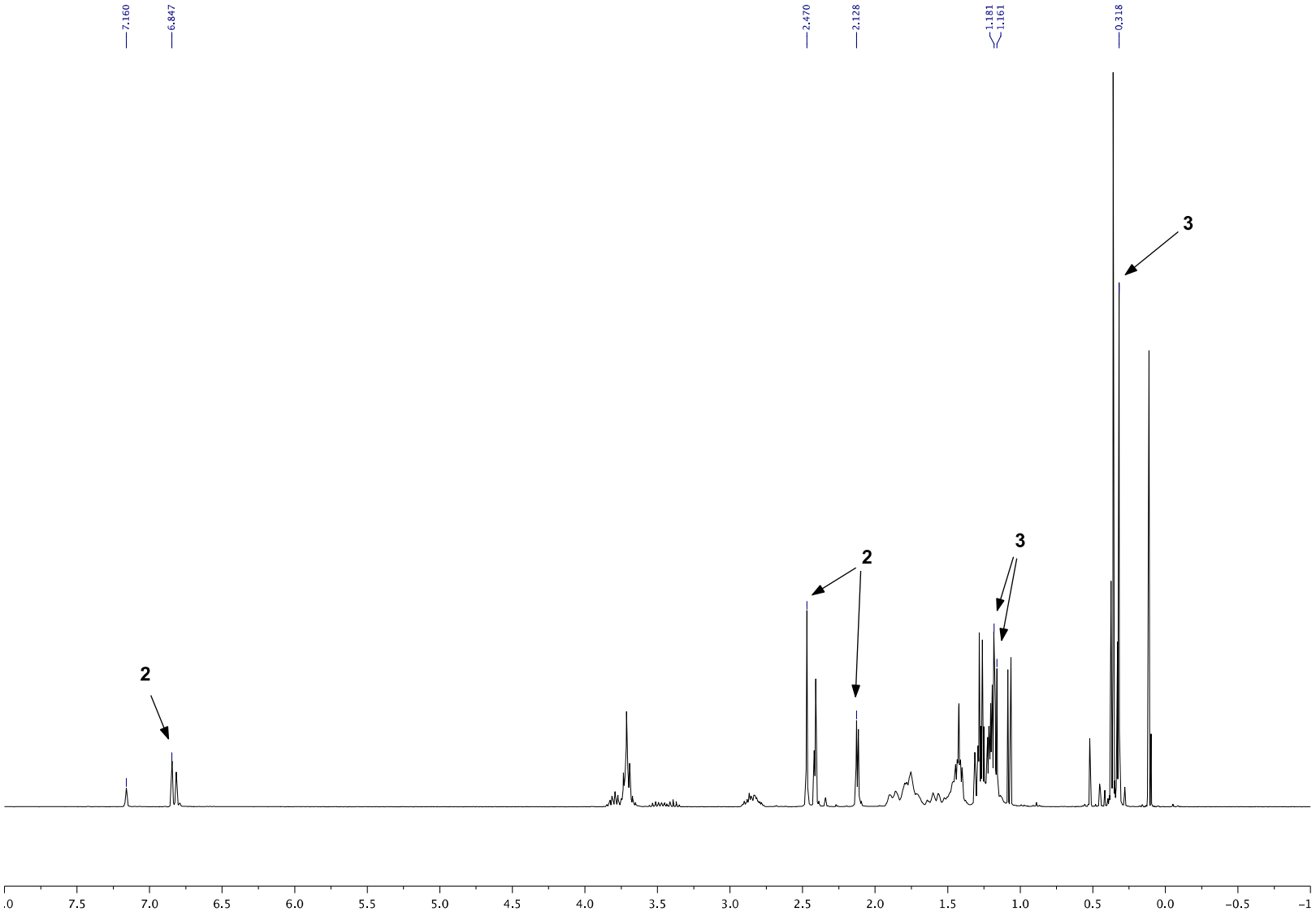

**Figure S15** $^{13}C\{^{1}H\}$ NMR Spectrum of the NMR scale reaction of **1** with one equivalent *i*Pr-N=C=N*i*-Pr ($C_6D_6$, 75 MHz). Low-field peaks corresponding to Mg(mesC{NCy}$_2$)$_2$(THF) (**2**), Mg({Me$_3$Si}$_2$NC{N*i*-Pr}$_2$)$_2$(THF) (**3**) and Mg(mesC{NCy}$_2$)({Me$_3$Si}$_2$NC{N*i*-Pr}$_2$)(THF)$_n$ (**B**) shown (expansion).

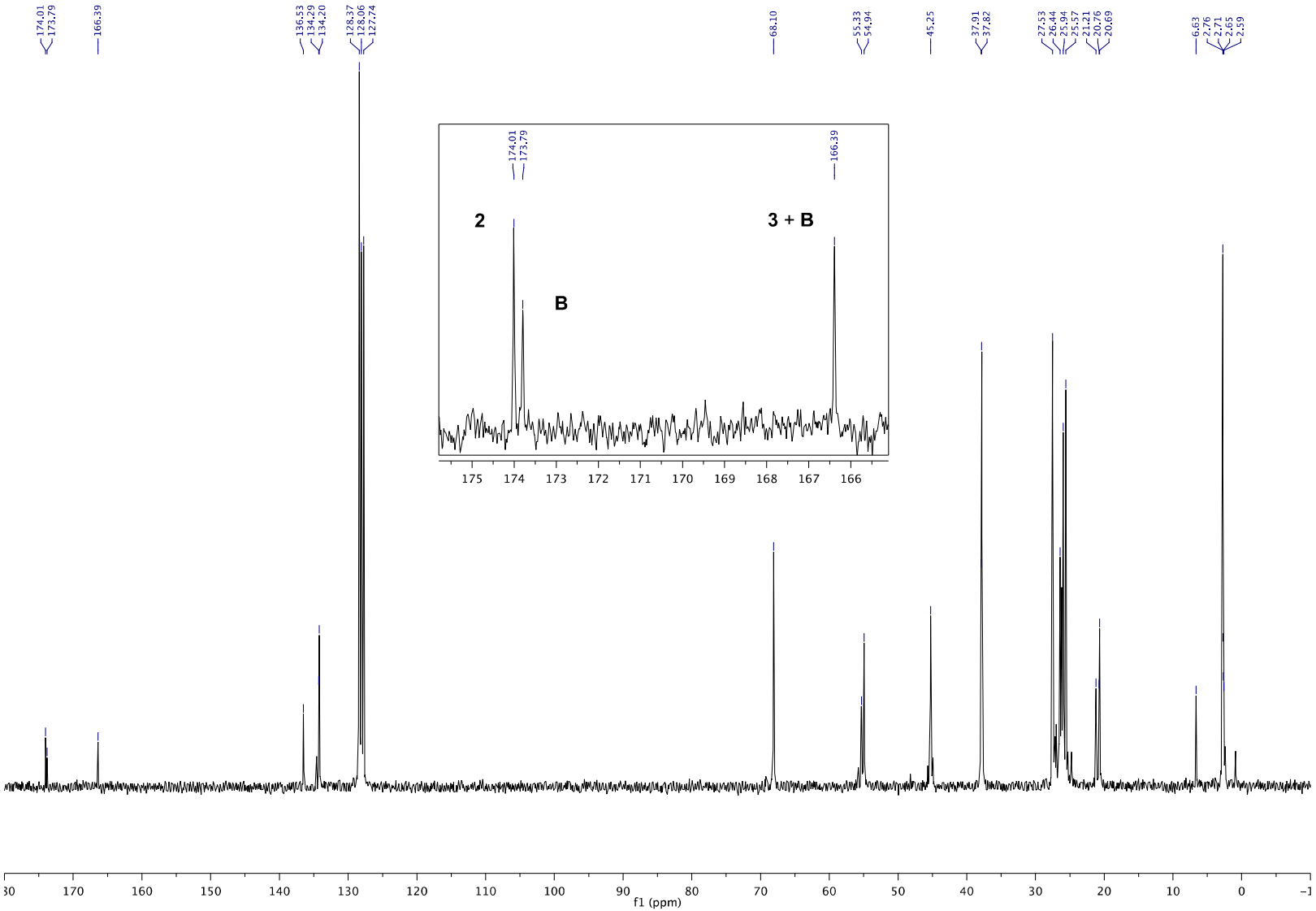

**Figure S16** $^1$H NMR Spectrum of the NMR scale reaction of *in situ* generated **A** with one equivalent *i*Pr-N=C=N*i*-Pr ($C_6D_6$, 300 MHz). Peaks corresponding to Mg(mesC{NCy}$_2$)$_2$(THF) (**2**) and Mg(PhC≡CC{N*i*-Pr}$_2$)$_2$(THF)$_2$ (**5**) identified.

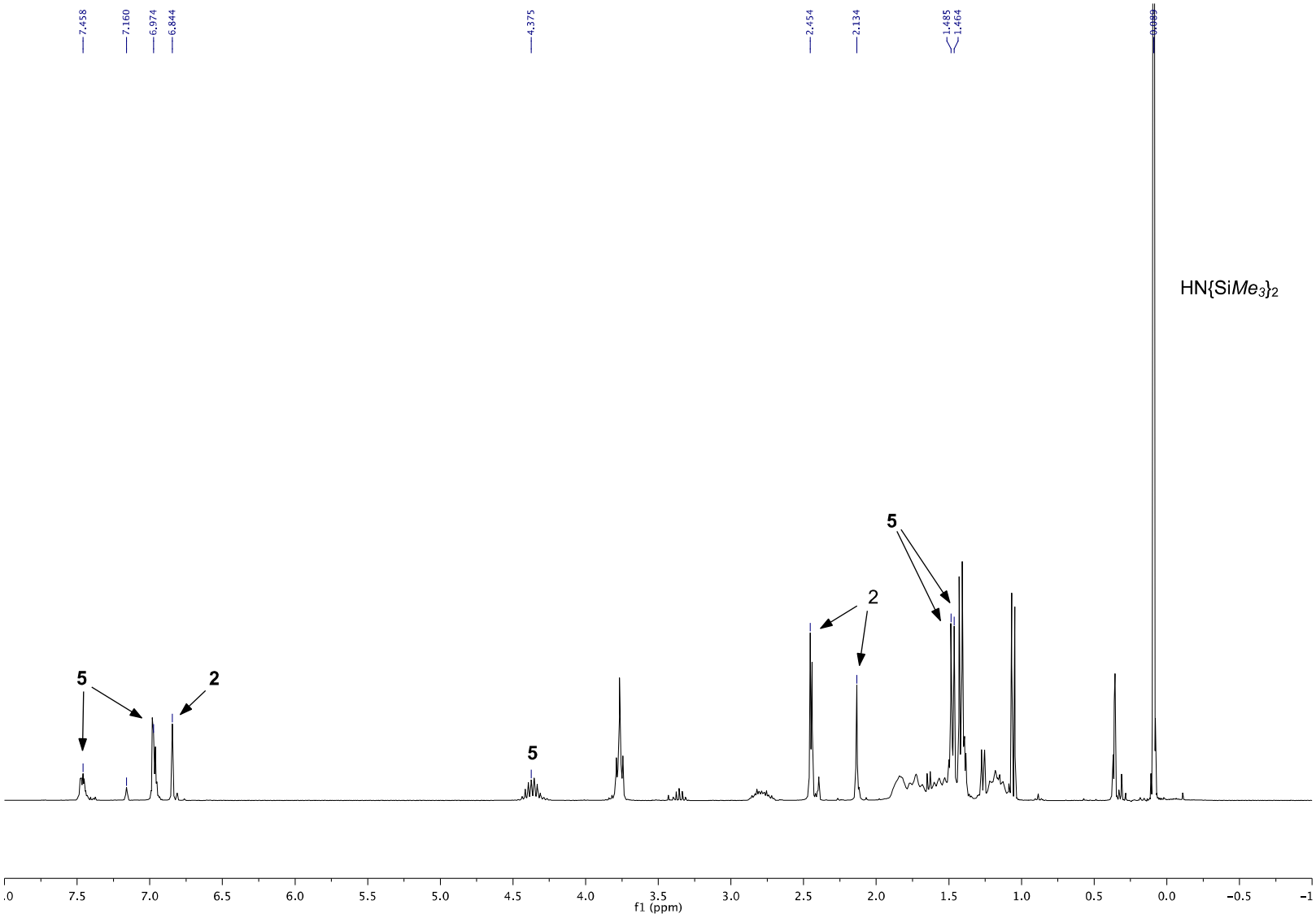

**Figure S17** $^{13}C\{^{1}H\}$ NMR Spectrum of the NMR scale reaction of of *in situ* generated **A** with one equivalent *i*Pr-N=C=N*i*-Pr ($C_6D_6$, 75 MHz). Low-field peaks corresponding to Mg(mesC{NCy}$_2$)$_2$(THF) (**2**), Mg(PhC≡CC{N*i*-Pr}$_2$)$_2$(THF)$_2$ (**5**) and Mg(mesC{NCy}$_2$)(PhC≡CC{N*i*-Pr}$_2$)(THF)$_n$ (**C**) and acetylenic peaks for **5** and **C** shown (expansions).

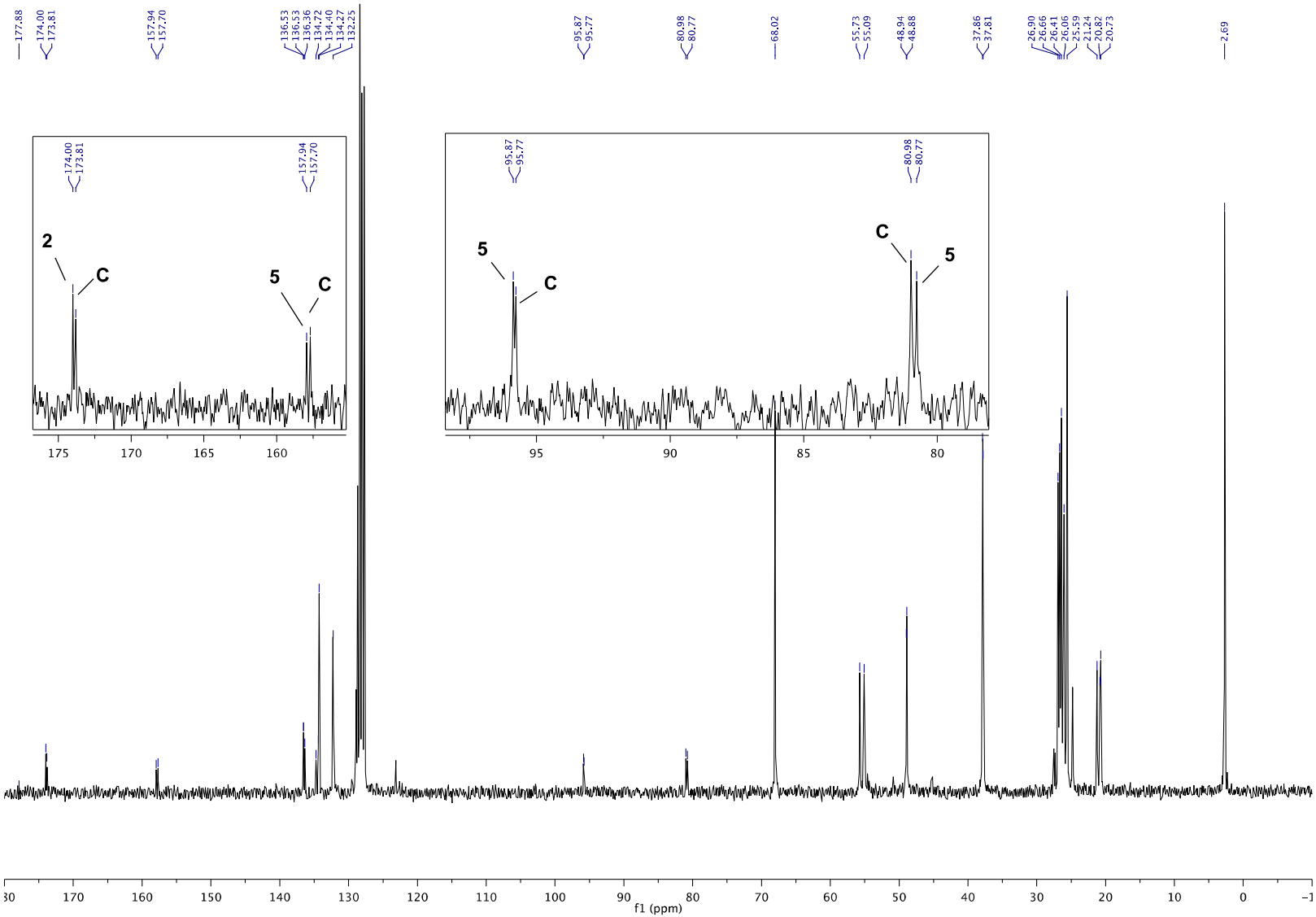

**Figure S18** Stacked $^1$H NMR spectra of a representative catalytic coupling of PhC≡CH and *i*-PrN=C=N*i*-Pr using **1** at Room Temperature ($C_6D_6$, 300 MHz).

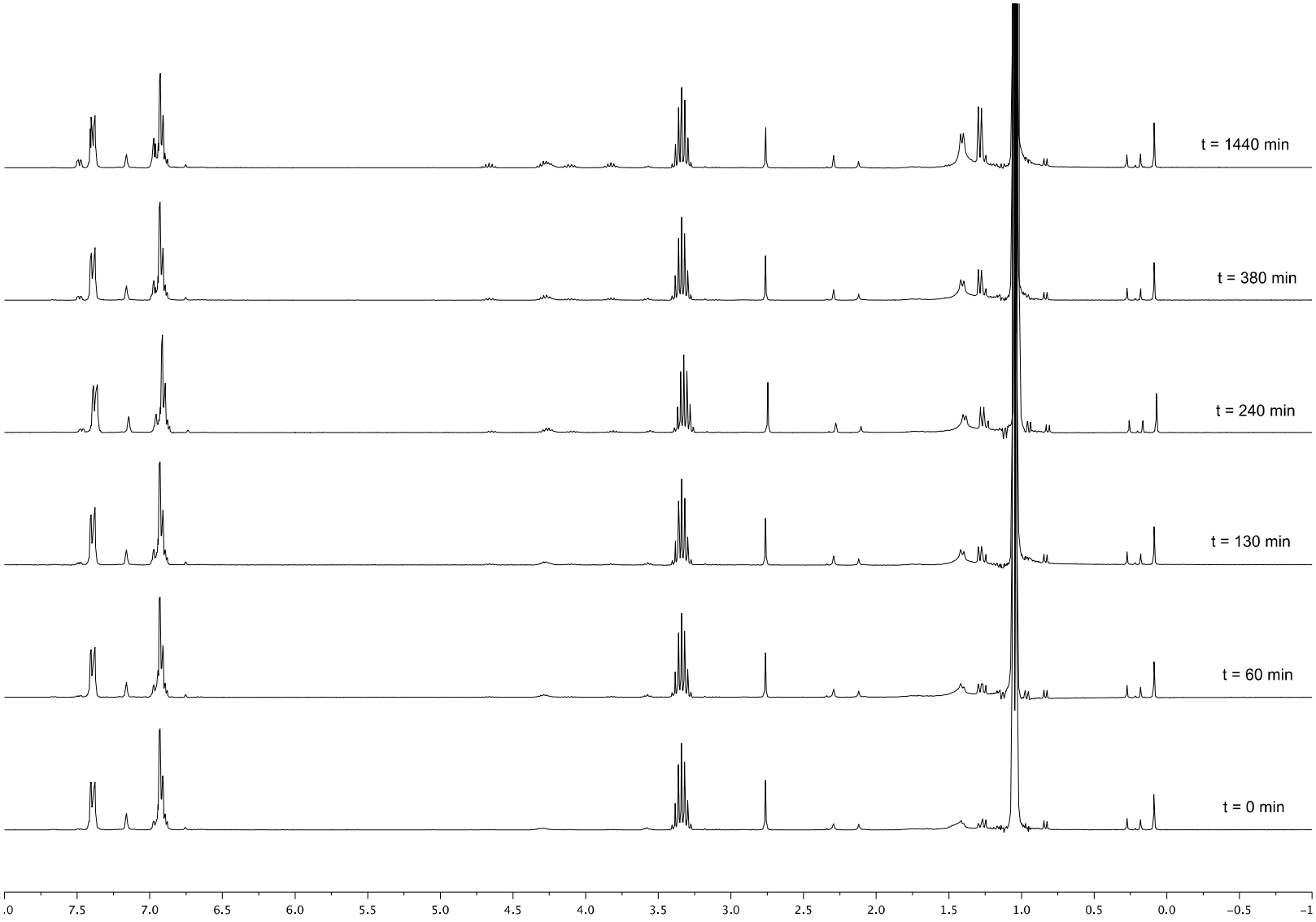

**Figure S19** Stacked $^{1}H$ NMR spectra of a representative catalytic coupling of PhC≡CH and *i*-PrN=C=N*i*-Pr using **1** at 50 °C ($C_6D_6$, 300 MHz).

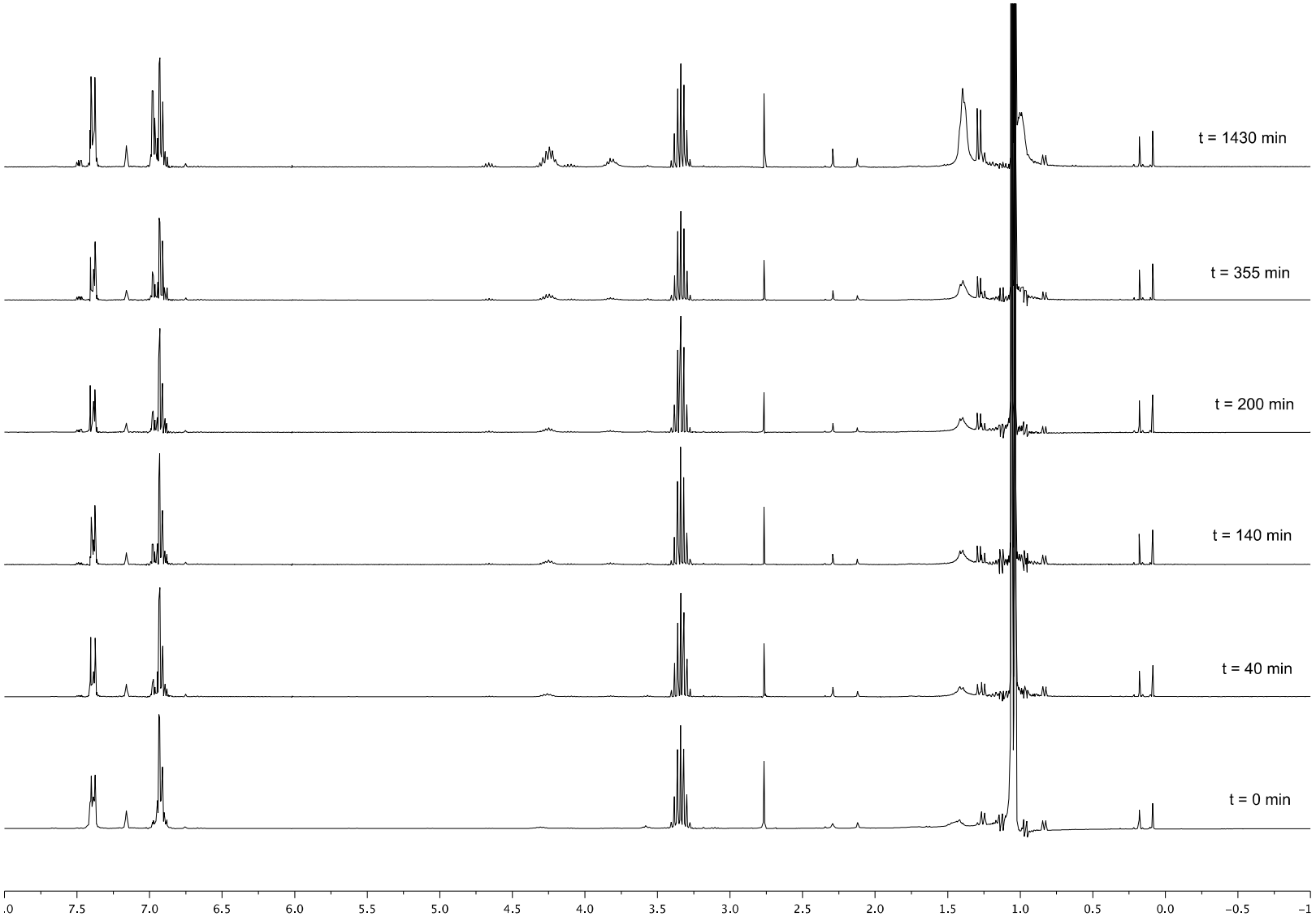

**Figure S20** Stacked $^{1}H$ NMR spectra of a representative catalytic coupling of PhC≡CH and *i*-PrN=C=N*i*-Pr using **1** at 80 °C ($C_6D_6$, 300 MHz).

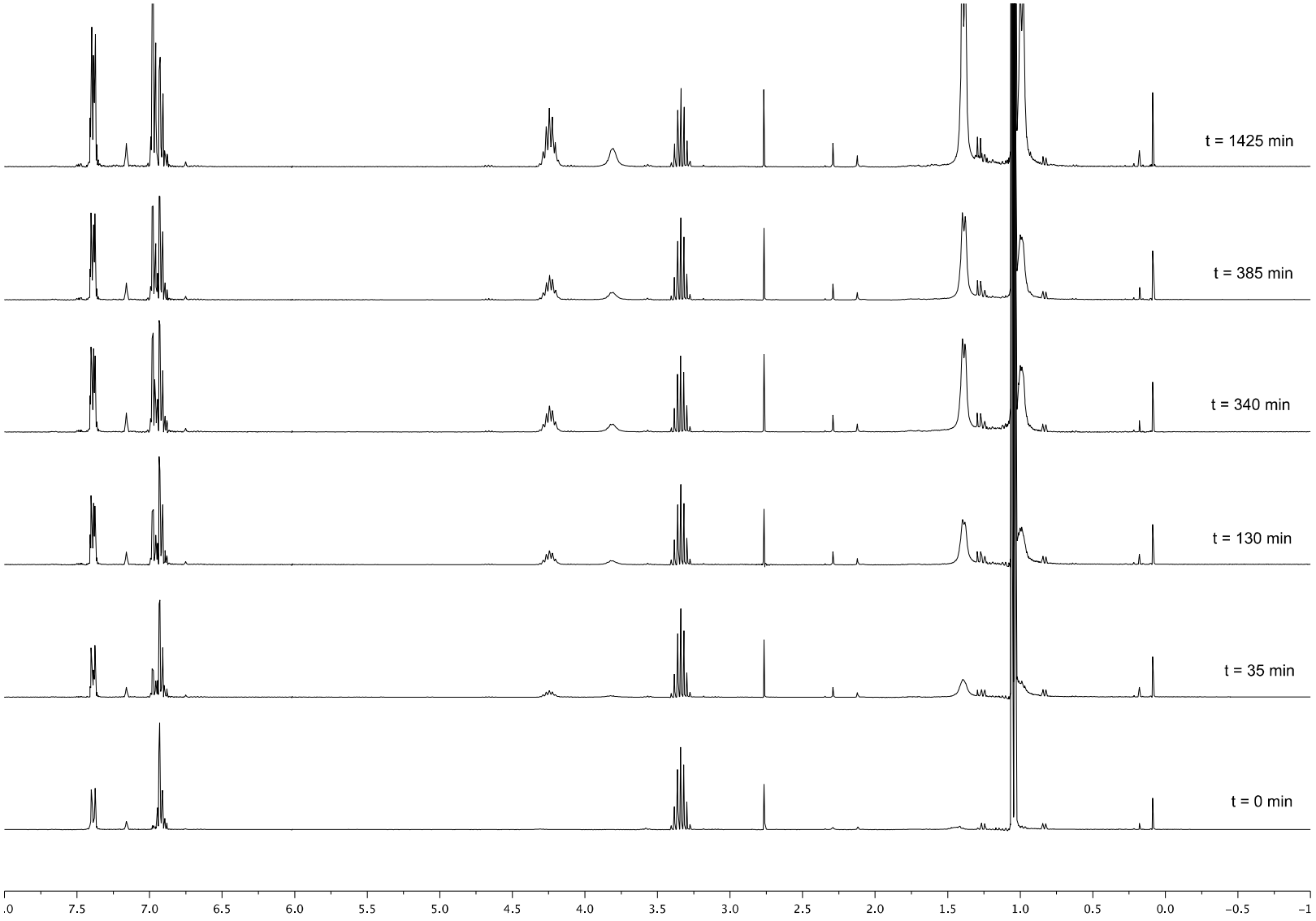

**Figure S21** Assigned $^1$H NMR spectrum of the catalytic coupling of PhC≡CH and *i*-PrN=C=N*i*-Pr using **1** at 80 °C (after 1876 min) ($C_6D_6$, 300 MHz). Inset shows peak for non-coordinated THF (1 equiv from **1**).

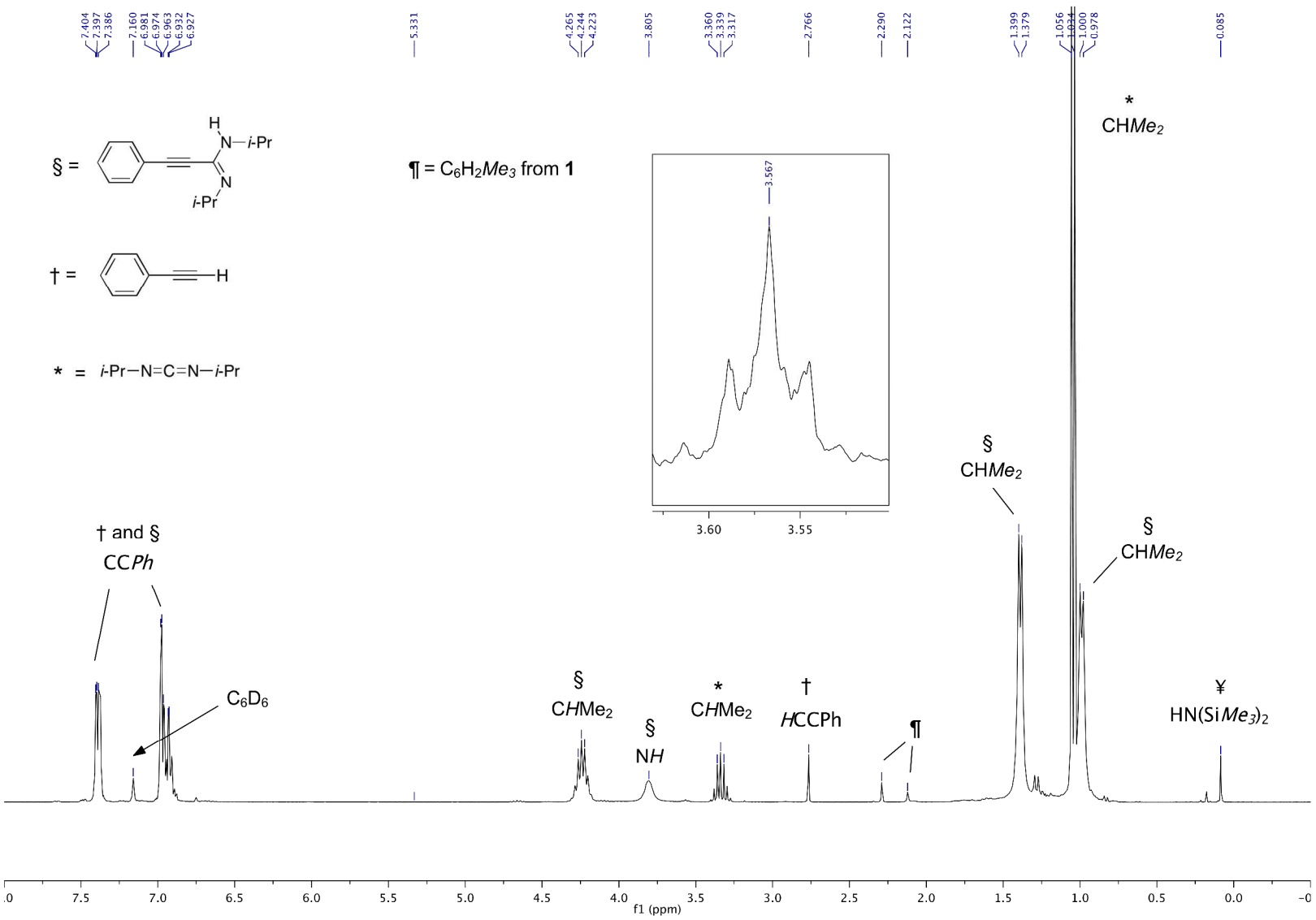

**Figure S22** $^{1}$H NMR spectrum of isolated PhC≡C{N*i*-Pr}{NH*i*-Pr} ($C_6D_6$, 300 MHz).

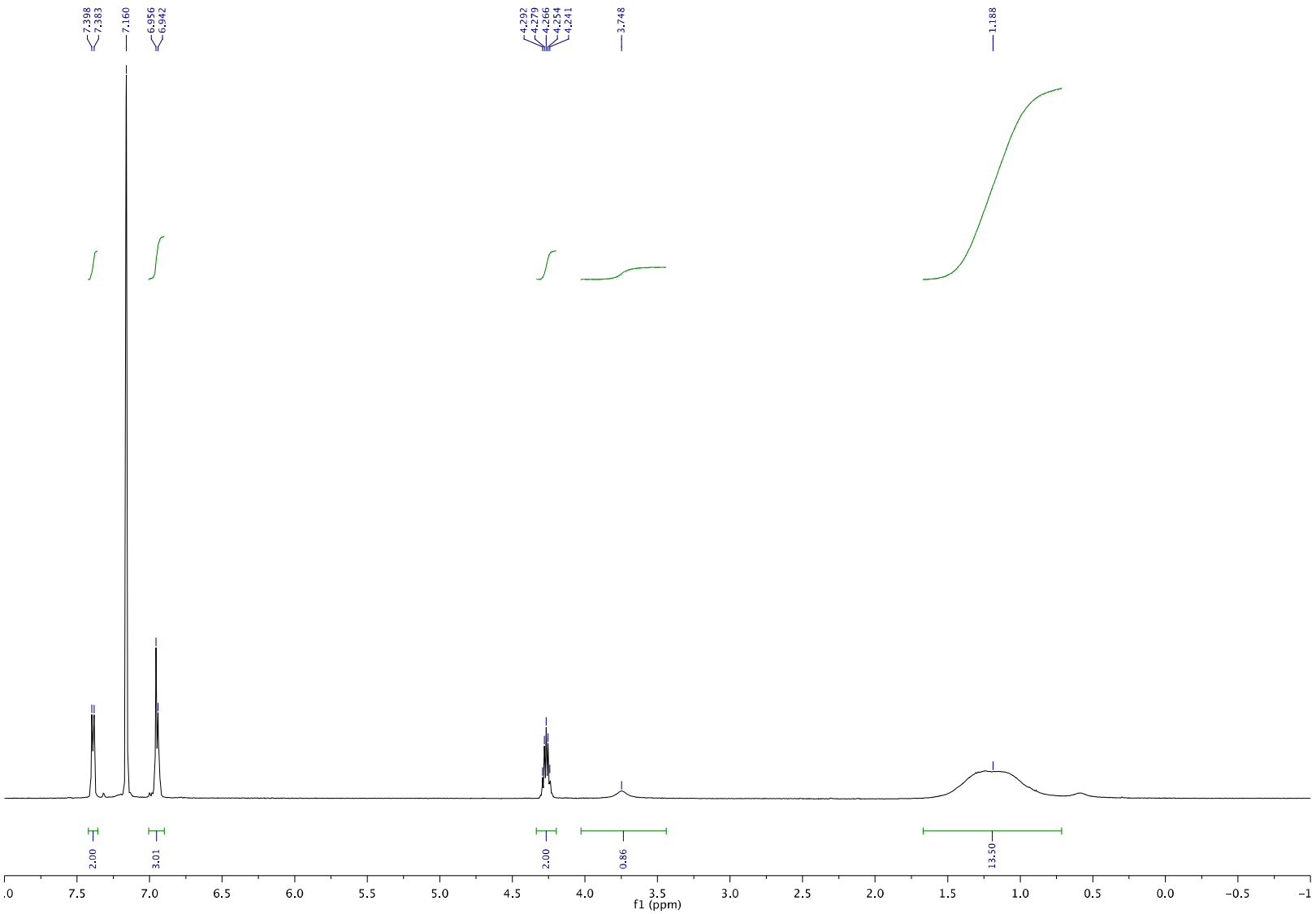

**Table S1** Crystal structure and refinement data for Mg(mesC{NCy}$_2$)$_2$(THF) (**2**)

| | | |
|---|---|---|
| Identification code | RJS047C | |
| Empirical formula | C48 H74 Mg N4 O | |
| Formula weight | 747.42 | |
| Temperature | 120(1) K | |
| Wavelength | 1.54180 Å | |
| Crystal system | Tetragonal | |
| Space group | $P\,4_3\,2_1\,2$ (No.96) | |
| Unit cell dimensions | a = 10.24350(13) Å | α= 90°. |
| | b = 10.24350(13) Å | β= 90°. |
| | c = 43.7040(7) Å | γ = 90°. |
| Volume | 4585.83(11) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.08 Mg/m$^3$ | |
| Absorption coefficient | 0.608 mm$^{-1}$ | |
| F(000) | 1640 | |
| Crystal size | 0.25 x 0.09 x 0.05 mm$^3$ | |
| Theta range for data collection | 4.05 to 73.79°. | |
| Index ranges | -12<=h<=12, -12<=k<=12, -54<=l<=32 | |
| Reflections collected | 33678 | |
| Independent reflections | 4630 [R(int) = 0.058] | |
| Completeness to theta = 73.79° | 99.9 % | |
| Absorption correction | Gaussian | |
| Max. and min. transmission | 1.782 and 0.924 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 4630 / 0 / 248 | |
| Goodness-of-fit on F$^2$ | 1.044 | |
| Final R indices [I>2sigma(I)] | R1 = 0.037, wR2 = 0.092 | |
| R indices (all data) | R1 = 0.040, wR2 = 0.094 | |
| Absolute structure parameter | -0.02(5) | |
| Largest diff. peak and hole | 0.24 and -0.21 e.Å$^{-3}$ | |

Data collection SuperNova, Dual, Cu at zero, Atlas , Program package WinGX , Abs. correction 'GAUSSIAN'
Refinement using SHELXL-97 , Drawing using ORTEP-3 for Windows

**Figure S23** ORTEP (ellipsoids 30 %, H-atoms omitted) of Mg(mesC{NCy}$_2$)$_2$(THF) (**2**)

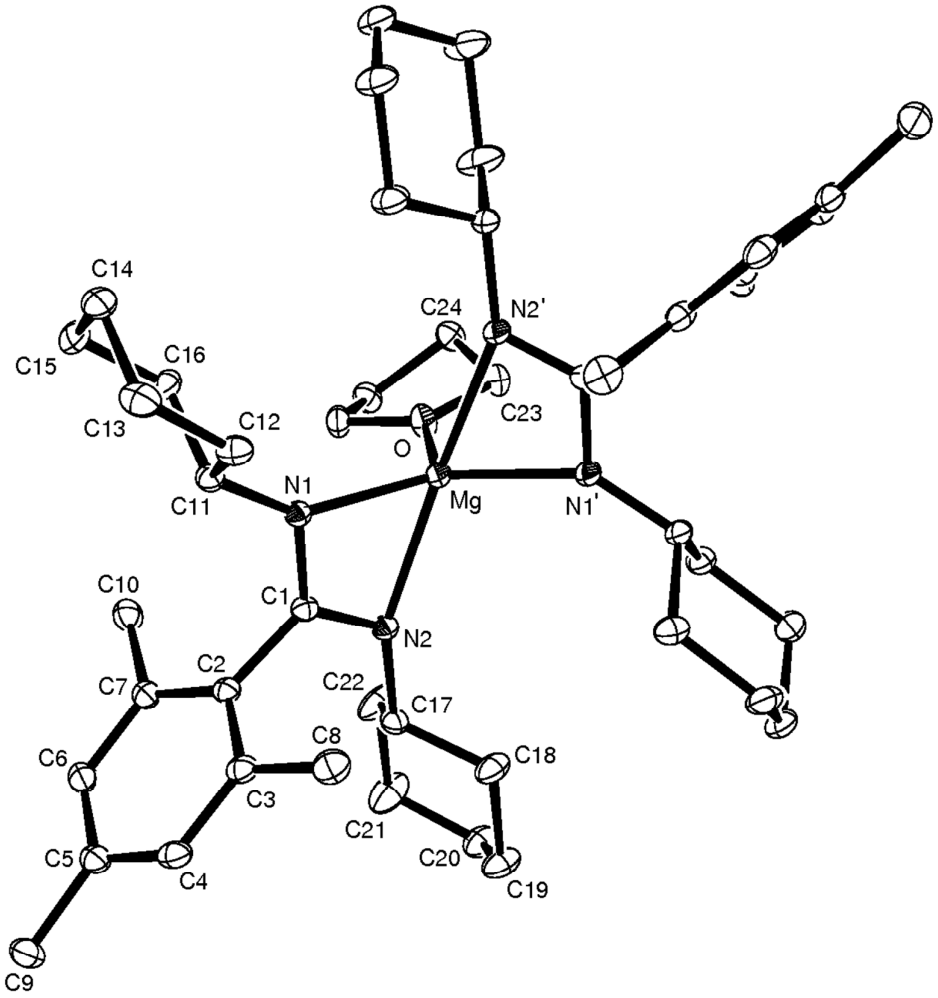

**Table S2** Crystal structure and refinement data for $Mg(\{Me_3Si\}_2NC\{N\textit{i}\text{-}Pr\}_2)_2(THF)$ (**3**)

| | | |
|---|---|---|
| Identification code | rjs121 | |
| Empirical formula | C30 H72 Mg N6 O Si4 | |
| Formula weight | 669.61 | |
| Temperature | 120.01(10) K | |
| Wavelength | 1.5418 Å | |
| Crystal system | Monoclinic | |
| Space group | $P\ 2_1/c$ (No.14) | |
| Unit cell dimensions | a = 9.9306(2) Å | α= 90°. |
| | b = 24.2870(4) Å | β= 114.059(2)°. |
| | c = 18.9646(4) Å | γ = 90°. |
| Volume | 4176.61(14) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.07 Mg/m$^3$ | |
| Absorption coefficient | 0.186 mm$^{-1}$ | |
| F(000) | 1480 | |
| Crystal size | 0.32 x 0.27 x 0.11 mm$^3$ | |
| Theta range for data collection | 3.13 to 73.81°. | |
| Index ranges | -12<=h<=12, -29<=k<=29, -21<=l<=21 | |
| Reflections collected | 50946 | |
| Independent reflections | 8369 [R(int) = 0.114] | |
| Reflections with I>2sigma(I) | 7105 | |
| Completeness to theta = 66.97° | 98.6 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 1.00 and 0.899 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 8369 / 0 / 379 | |
| Goodness-of-fit on F$^2$ | 1.055 | |
| Final R indices [I>2sigma(I)] | R1 = 0.080, wR2 = 0.125 | |
| R indices (all data) | R1 = 0.088, wR2 = 0.130 | |
| Largest diff. peak and hole | 0.34 and -0.35 e.Å$^{-3}$ | |

Data collection SuperNova, Dual, Cu at zero, Atlas , Program package WinGX , Abs. correction 'MULTISCAN'
Refinement using SHELXL-97 , Drawing using ORTEP-3 for Windows

**Figure S24** ORTEP (ellipsoids 30 %, H-atoms omitted) of Mg({$Me_3Si$}$_2$NC{N*i*-Pr}$_2$)$_2$(THF) (**3**)

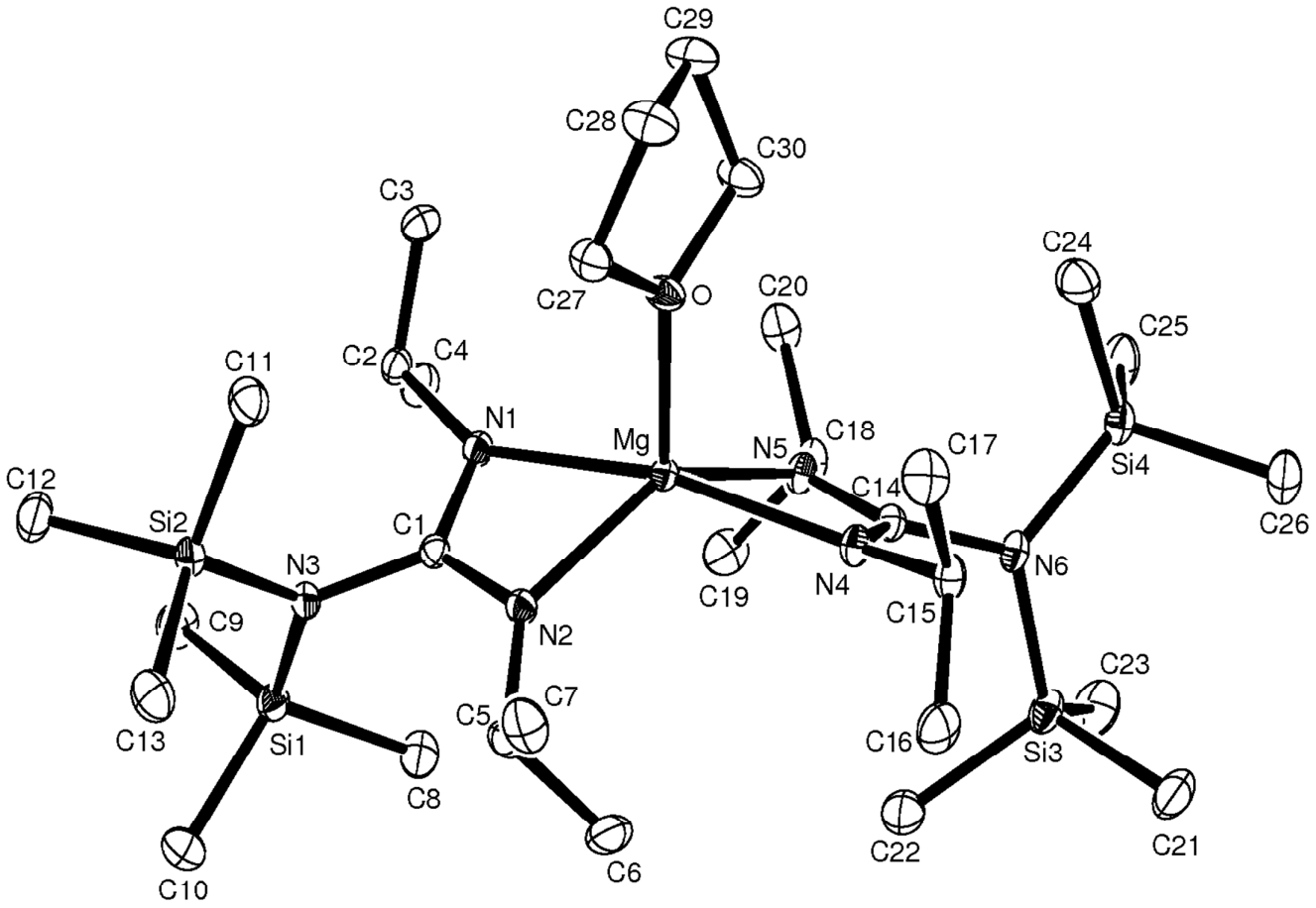

**Table S3** Crystal structure and refinement data for $Mg(CCPh)_2(THF)_4$ (**4**)

| | | |
|---|---|---|
| Identification code | rjs084 | |
| Empirical formula | C32 H42 Mg O4 | |
| Formula weight | 514.97 | |
| Temperature | 120.01(10) K | |
| Wavelength | 1.54180 Å | |
| Crystal system | Monoclinic | |
| Space group | *C* 2/c (No.15) | |
| Unit cell dimensions | a = 11.0212(6) Å | α= 90°. |
| | b = 22.0516(10) Å | β= 105.758(7)°. |
| | c = 12.0459(8) Å | γ = 90°. |
| Volume | 2817.6(3) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.21 $Mg/m^3$ | |
| Absorption coefficient | 0.814 $mm^{-1}$ | |
| F(000) | 1112 | |
| Crystal size | 0.55 x 0.41 x 0.24 $mm^3$ | |
| Theta range for data collection | 4.01 to 73.82°. | |
| Index ranges | -13<=h<=13, -26<=k<=27, -14<=l<=14 | |
| Reflections collected | 16457 | |
| Independent reflections | 2836 [R(int) = 0.059] | |
| Completeness to theta = 73.82° | 99.3 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 1.00 and 0.63 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 2836 / 3 / 191 | |
| Goodness-of-fit on $F^2$ | 0.994 | |
| Final R indices [I>2sigma(I)] | R1 = 0.075, wR2 = 0.221 | |
| R indices (all data) | R1 = 0.078, wR2 = 0.229 | |
| Largest diff. peak and hole | 1.385 and -0.341 $e.Å^{-3}$ | |

The large residual electron density is the result of poor data, leading to a spurious peak. One of the THF molecules is disordered over two positions and was modeled with loose (SADI) constraints. The molecule lies on a 2-fold rotation axis.

Data collection SuperNova, Dual, Cu at zero, Atlas , Program package WinGX , Abs. correction 'MULTISCAN' Refinement using SHELXL-97 , Drawing using ORTEP-3 for Windows

**Figure S25** ORTEP (ellipsoids 30 %, H-atoms omitted) of $Mg(CCPh)_2(THF)_4$ (**4**)

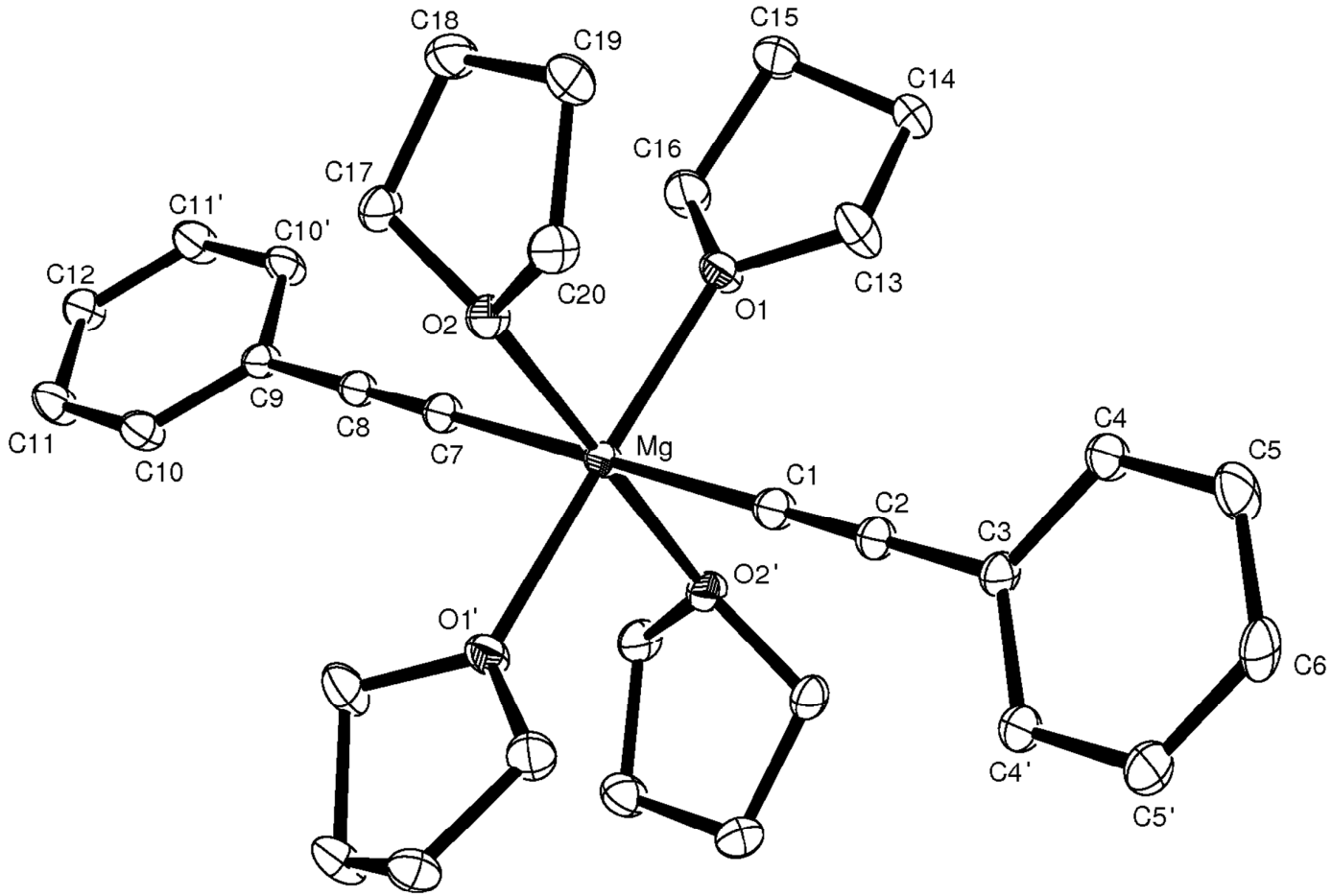

**Table S4** Crystal structure and refinement data for $Mg(PhC{=}C\{N\textit{i}\text{-}Pr\}_2)_2(THF)_2$ (**5**(THF))

able 1. Crystal data and structure refinement for $Mg(PhCCC\{N^iPr\}_2)_2(THF)_2$.

| | | |
|---|---|---|
| Identification code | rjs163 | |
| Empirical formula | C38 H54 Mg N4 O2 | |
| Formula weight | 623.16 | |
| Temperature | 120.01(10) K | |
| Wavelength | 1.5418 Å | |
| Crystal system | Triclinic | |
| Space group | $P\bar{1}$ (No.2) | |
| Unit cell dimensions | a = 9.3730(3) Å | α= 78.282(3)°. |
| | b = 10.0360(4) Å | β= 70.533(4)°. |
| | c = 10.5466(4) Å | γ = 77.850(3)°. |
| Volume | 904.86(6) $Å^3$ | |
| Z | 1 | |
| Density (calculated) | 1.14 $Mg/m^3$ | |
| Absorption coefficient | 0.703 $mm^{-1}$ | |
| F(000) | 338 | |
| Crystal size | 0.34 x 0.30 x 0.21 $mm^3$ | |
| Theta range for data collection | 4.55 to 73.91°. | |
| Index ranges | -11<=h<=11, -12<=k<=11, -13<=l<=11 | |
| Reflections collected | 10124 | |
| Independent reflections | 3565 [R(int) = 0.016] | |
| Completeness to theta = 66.97° | 99.8 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 1.000 and 0.632 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3565 / 0 / 205 | |
| Goodness-of-fit on $F^2$ | 1.025 | |
| Final R indices [I>2sigma(I)] | R1 = 0.035, wR2 = 0.090 | |
| R indices (all data) | R1 = 0.036, wR2 = 0.091 | |
| Largest diff. peak and hole | 0.19 and -0.17 $e.Å^{-3}$ | |

The molecule lies on an inversion centre

Data collection SuperNova, Dual, Cu at zero, Atlas , Program package WinGX , Abs. correction 'MULTISCAN' Refinement using SHELXL-97 , Drawing using ORTEP-3 for Windows

**Figure S26** ORTEP (ellipsoids 30 %, H-atoms omitted) of Mg(PhC≡ C{N*i*-Pr}$_2$)$_2$(THF)$_2$ (**5**(THF))

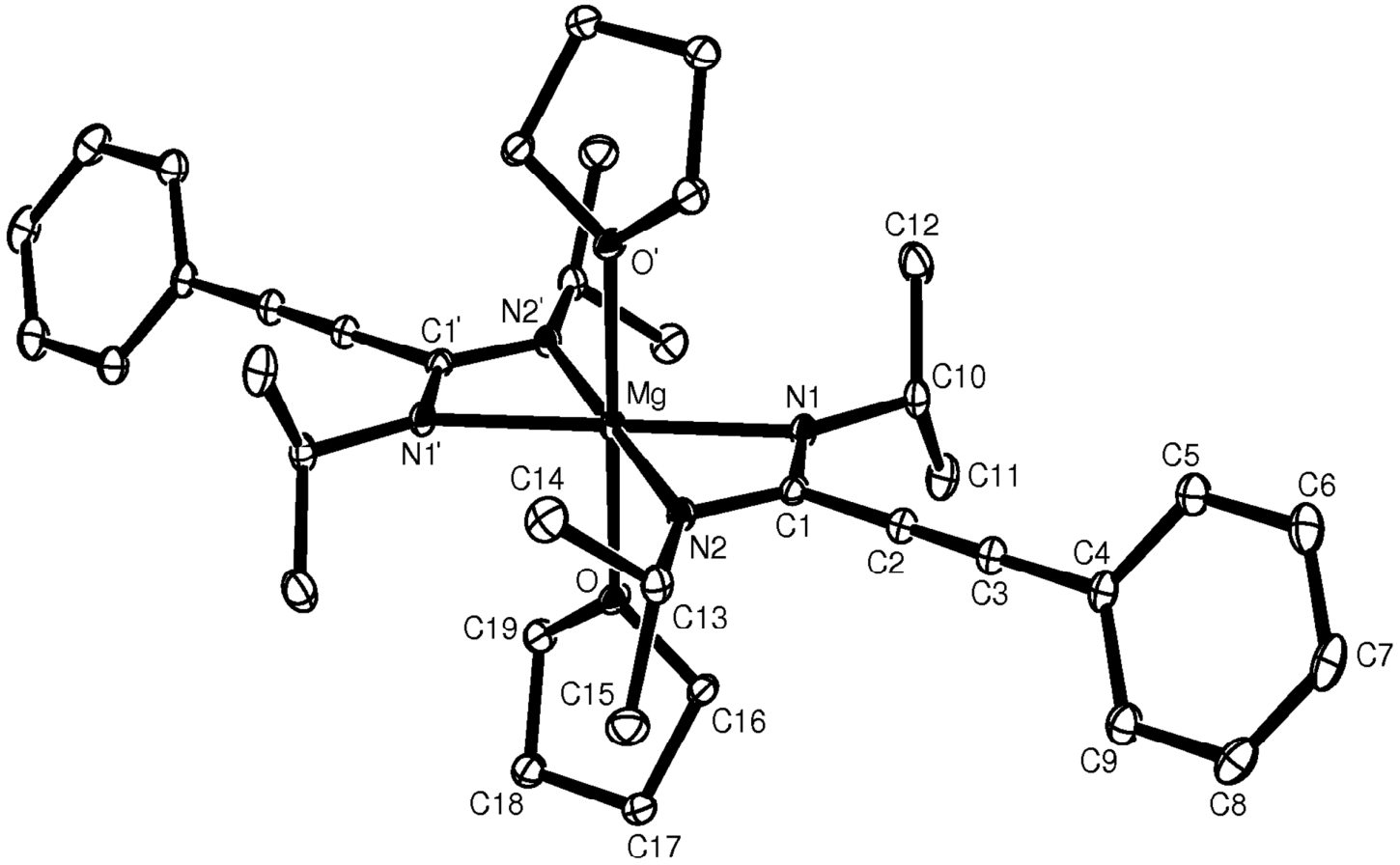

**Table S5** Crystal structure and refinement data for $[Mg(PhC{=}CC\{N\textit{i}\text{-}Pr\}_2)Br(Et_2O)]_2$ ($[\mathbf{6}]_2$)

| | | |
|---|---|---|
| Identification code | RJS037 | |
| Empirical formula | C19 H29 Br Mg N2 O | |
| Formula weight | 405.66 | |
| Temperature | 120(1) K | |
| Wavelength | 1.54180 Å | |
| Crystal system | Orthorhombic | |
| Space group | $Pca2_1$ (No.29) | |
| Unit cell dimensions | a = 18.05830(13) Å | α= 90°. |
| | b = 12.40280(8) Å | β= 90°. |
| | c = 19.33740(13) Å | γ = 90°. |
| Volume | 4331.06(5) Å$^3$ | |
| Z | 8 | |
| Density (calculated) | 1.24 Mg/m$^3$ | |
| Absorption coefficient | 2.916 mm$^{-1}$ | |
| F(000) | 1696 | |
| Crystal size | 0.65 x 0.57 x 0.41 mm$^3$ | |
| Theta range for data collection | 3.56 to 73.91°. | |
| Index ranges | -22<=h<=20, -15<=k<=10, -24<=l<=24 | |
| Reflections collected | 29431 | |
| Independent reflections | 8510 [R(int) = 0.029] | |
| Completeness to theta = 73.91° | 98.7 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 1.00000 and 0.70232 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 8510 / 1 / 434 | |
| Goodness-of-fit on F$^2$ | 1.058 | |
| Final R indices [I>2sigma(I)] | R1 = 0.034, wR2 = 0.089 | |
| R indices (all data) | R1 = 0.034, wR2 = 0.089 | |
| Absolute structure parameter | 0.00(7) | |
| Largest diff. peak and hole | 0.52 and -0.69 e.Å$^{-3}$ | |

`Racemic Twin (TWIN -1 0 0 0 -1 0 0 0 -1, BASF 0.41743)`

Data collection SuperNova, Dual, Cu at zero, Atlas , Program package WinGX , Abs. correction 'MULTISCAN'

Refinement using SHELXL-97 , Drawing using ORTEP-3 for Windows

**Figure S27** ORTEP (ellipsoids 30 %, H-atoms omitted) of [Mg(PhC≡ CC{N*i*-Pr}$_2$)Br(Et$_2$O)]$_2$ ([**6**]$_2$)