Supplementary Material for:

Synthetic and catalytic intermediates in a magnesium promoted Tishchenko reaction

Benjamin M. Day,[a] William Knowelden[a] and Martyn P. Coles,*[b]

---

a Department of Chemistry, University of Sussex, Falmer, Brighton BN1 9QJ, UK.

b School of Chemical and Physical Sciences, Victoria University of Wellington, PO Box 600, Wellington, New Zealand. Fax: +64 (0)4 463 5237; Tel: +64 (0)4 463 6357; E-mail: martyn.coles@vuw.ac.nz

Contents

Mg(mes)(OAr)(THF)$_2$ (1) A solution of LiOAr (0.49 g, 2.30 mmol) in THF was added dropwise to a stirring THF solution of mesMgBr (2.5 mL of a 1.0 M solution, 2.5 mmol). After stirring for 24 h, volatiles were removed in vacuo leaving a white solid. The product was extracted in hot hexane. Slow cooling of the hot hexane solution to ambient temperature resulted in the formation of colourless crystals of Mg(mes)(OAr)(THF)$_2$. Yield: 0.25 g, 20.3 %.

^{1}H NMR (400 MHz, C_6D_6): δ 7.49 (d, $^3J_{HH}$ = 7.7 Hz, 2H, Ar *m*-C*H*), 7.05 (s, 2H, mesityl *m*-C*H*), 6.86 (t, $^3J_{HH}$ = 7.7 Hz, 1H, Ar *p*-C*H*), 3.52 (m, 12H, THF-CH_2), 2.56 (s, 6H, mesityl *o*-CH_3), 2.40 (s, 3H, mesityl *p*-CH_3), 1.61 (s, 18H, C(CH_3)$_3$), 1.16 (m, 12H, THF-CH_2).

Mg(mesC{NCy}$_2$)Br(OEt$_2$) (2) A solution of dicyclohexylcarbodiimide (0.50 g, 2.42 mmol) in Et$_2$O was added dropwise to a stirring Et$_2$O solution of mesMgBr (2.5 mL of a 1.0 M solution in Et$_2$O, 2.50 mmol). The resultant solution was allowed to stir for 18 h by which time a white precipitate of Mg(mesC{NCy}$_2$)Br(OEt$_2$) had formed and was isolated by filtration. Colourless crystal of [Mg(mesC{NCy}$_2$)Br(OEt$_2$)]$_2$ were obtained after storage of the supernatant at –20 °C for 3 days. Yield: 0.85 g, 70.0 %.

Anal. calcd. for $C_{26}H_{43}BrMgN_2O$ (*503.85*): C, 61.98; H, 8.60; N, 5.56 %. Found: C, 61.95; H, 8.71; N, 5.51 %. ^{1}H NMR (400 MHz, C_6D_6): δ 6.81(s, 2H, C$_6$*H*$_2$), 3.65 (q, 4H, $^3J_{HH}$ = 7.0 Hz, C*H*$_2$CH$_3$), 2.82 (m, 2H, Cy *α*-C*H*), 2.43 (s, 6H, *o*-C*H*$_3$), 2.11 (s, 3H, *p*-C*H*$_3$), 2.00-1.00 (m, 20 H, Cy-C*H*$_2$), 1.20 (t, 6H, $^3J_{HH}$ = 7.0 Hz , CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 175.8 (*C*N$_2$), 137.2, 134.8, 128.8, 128.7 (*C*$_6$H$_2$), 66.2 (*C*H$_2$CH$_3$), 56.2 (Cy *α*-*C*H), 38.0, 26.7, 25.5 (*C*H$_2$, Cy), 21.5 (*p*-*C*H$_3$), 20.9 (*o*-*C*H$_3$), 15.1 (CH$_2$*C*H$_3$).

Mg(mesC{NCy}$_2$)(OAr)(THF) (3) A solution of dicyclohexylcarbodiimide (1.36 g, 6.6 mmol) in THF was added drop wise to a stirring THF solution of mesMgBr (11.0 mL of a 0.6 M solution, 6.6

mmol). After stirring for 24 h, a THF solution of LiOAr (1.40 g, 6.6 mmol) was added drop wise and the resultant solution was left to stir for an additional 24 h. Removal of volatiles *in vacuo* left a white solid, from which the product was extracted in hot hexane. Slow cooling of this hexane solution yielded platelet crystals of Mg(mesC{NCy}$_2$)(OAr)(THF). Yield: 2.91 g, 70.3 %.

^{1}H NMR (400 MHz, C_6D_6): δ 7.51 (d, $^3J_{\mathrm{HH}}$ = 7.6, 2H, Ar *m*-C*H*), 6.90 (t, $^3J_{\mathrm{HH}}$ = 7.6, 1H, Ar *p*-C*H*), 6.80 (s, 2H, $C_6\mathit{H_2}$), 3.71 (br m, 4H, THF-$C\mathit{H_2}$), 2.71 (m, 2H, Cy *α*-C*H*), 2.31 (s, 6H, *o*-$C\mathit{H_3}$), 2.10 (s, 3H, *p*-$C\mathit{H_3}$), 1.79 (s, 18H, C($C\mathit{H_3}$)$_3$), 1.74-1.41 (m, 20H, Cy-$C\mathit{H_2}$), 1.23 (m, THF-$C\mathit{H_2}$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 175.8 (*C*N$_2$), 163.8 (Ar *i-C*), 138.1 (*C$_6$*H$_2$), 137.5 (Ar *o-C*), 134.5, 133.6, 128.9 (*C$_6$*H$_2$), 125.5, 114.41 (C$_6$*H$_3$*), 69.9 (THF-*C*H$_2$), 55.9 (Cy *α*-*C*H), 38.2 (Cy-*C*H$_2$), 36.0 (*C*(CH$_3$)$_3$), 32.1 (C(*C*H$_3$)$_3$), 26.6, 26.5 (Cy-*C*H$_2$), 25.4 (THF-*C*H$_2$), 21.5 (*p*-*C*H$_3$), 21.0 (*o*-*C*H$_3$).

Mg(mesC{NCy}$_2$)(N{SiMe$_3$}$_2$)(THF) (4) 6.1 mL of a 0.6 M solution of mesMgBr in Et_2O (3.7 mmol) was added to a clear, colourless solution of *N,N*-dicyclohexylcarbodiimide (0.76 g, 3.7 mmol) in Et_2O (15 mL). The resultant pale orange solution was left to stir for 2 h, during which time a white precipitate had formed. The solution was filtered and the precipitate was dissolved in THF (15 mL), giving slightly cloudy, colourless solution. A solution of LiN{SiMe$_3$}$_2$ (0.619 g, 3.7 mmol) in THF (15 mL) was added drop wise. The resultant clear, colourless solution was left to stir for approximately 48 h followed by removal of the volatiles *in vacuo*, leaving behind a white solid. Extraction of the product in hot hexane with slow cooling to ambient temperature yielded colourless crystals of **4**. Further crops of crystal of **4** were obtained after concentration of the mother liquor and storage at –20 °C. Yield 2.0 g, 82.2 %.

Anal. calcd. for $C_{32}H_{59}MgN_3OSi_2$ (*582.31*): C, 66.00; H, 10.21; N, 7.22 %. Found: C, 65.89; H, 10.16; N, 7.11 %. ^{1}H NMR (500 MHz, C_6D_6): δ 6.79 (s, 2H, *m*-$C_6\mathit{H_2}$), 3.83 (m, 4H, THF-$C\mathit{H_2}$), 2.68 (m, 2H, Cy *α*-C*H*), 2.34 (s, 6H, *o*-$C\mathit{H_3}$), 2.10 (s, 3H, *p*-$C\mathit{H_3}$), 0.51 (s, 18H, Si*Me$_3$*), §. ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ□175.4 (*C*N$_2$), 137.3, 134.5, 133.9, 128.8 (*C$_6$*H$_2$), 69.3 (THF-*C*H$_2$), 56.1 (Cy *α*-

*C*H), 38.2, 26.7, 26.6 (Cy-*C*H$_2$), 25.5 (THF-*C*H$_2$), 21.5 (*p*-Me), 21.0 (*o*-Me), 6.97 (Si*Me$_3$*).

§ the remaining THF-C*H$_2$* and Cy-C*H$_2$* resonances appear as a broad, ill-defined feature.

Mg(mesC{NCy}$_2$)(OAr)(mesCHO)$_2$ (5) A colourless solution of mesCHO (0.096 g, 0.65 mmol) in hexane was added drop wise to a colourless hexane solution of Mg(mesC{NCy}$_2$)(OAr)(THF) (0.204 g, 0.325 mmol) resulting in slightly cloudy orange/red solution. This solution was allowed to stir for 30 minutes before removal of volatiles in vacuo leaving an orange/red solid that was redissolved in pentane. The resultant orange/red solution was filtered and stored at -50 °C. After 3 days, red/orange floret-like crystals of Mg(mesC{NCy}$_2$)(OAr)(mesCHO)$_2$ formed. Yield 0.13 g, 47.0 %.

Anal. calcd. for $C_{56}H_{78}MgN_2O_3$ (*851.55*): C, 78.98; H, 9.23; N, 3.28 %. Found: C, 78.87; H, 9.33; N 3.33 %. ^{1}H NMR (400 MHz, C_6D_6): δ 10.50 (s, 2H, C*HO*), 7.51 (d, $^3J_{HH}$ = 7.7, 2H, Ar *m*-C*H*), 6.88 (t, $^3J_{HH}$ = 7.7, Ar *p*-C*H*), 6.83 (s, 2H, C$_6$*H$_2$* amidinate), 6.47 (s, 4H, C$_6$*H$_2$* aldehyde), 2.82 (m, 2H, Cy *α*-C*H*), 2.41 (s, 6H, *o*-C*H*$_3$ amidinate), 2.39 (s, 12H, *o*-C*H*$_3$ aldehyde), 2.11 (s, 3H, *p*-C*H*$_3$ amidinate), 1.87 (s, 6H, *p*-C*H*$_3$ aldehyde), 1.84 (s, 18H, C(C*H$_3$*)$_3$), 1.76-1.09 (m, 20H, Cy-C*H$_2$*). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 197.2 (*C*HO), 174.3 (*C*N$_2$), 164.2 (Ar *i-C*), 146.1, 143.8, 137.7, 136.9, 134.4, 133.9, 131.1, 129.4, 128.4, 125.2, 113.5 (*C$_6$*H$_2$ amidinate/aldehyde and Ar-*C$_6$*H$_3$), 55.8 (Cy *α*-*C*H), 38.1 (Cy-*C*H$_2$), 35.7 (*C*(CH$_3$)$_3$), 32.0 (C(*C*H$_3$)$_3$), 26.4, 26.3 (Cy-*C*H$_2$), 21.4 (*p*-*C*H$_3$), 21.2 (*p*-*C*H$_3$), 20.8 (*o*-*C*H$_3$), 20.6 (*o*-*C*H$_3$).

General Procedure for the Dimerisation of Benzaldehyde

In an inert atmosphere glovebox, an NMR tube fitted with a J. Young's tap were charged with 1 or 10 mol % of pre-catalyst followed by the addition of 0.5 mL of a D$_6$-benzene solution of 1,4-dimethoxybenzene (0.11 M). The NMR instrument was locked and shimmed to this sample and an experiment set up to record ^{1}H NMR spectra (1 scan every 30 s) for the duration of the experiment. 0.1 mL of a D_6-benzene solution of benzaldehyde (4.77 M) was then added to the sample, again in the glovebox, and was immediately taken and inserted into the NMR instrument. The experiment was started as soon as the sample was in the probe (maximum time elapsed after mixing = 2 min).

General Procedure for the Dimerisation of Trimethylacetaldehyde, Cyclohexanecarboxaldehyde, Isobutyraldehyde and Acetaldehdye

Similar method to the dimerisation of benzaldehyde using 1 mol % of pre-catalyst and 100 μL of aldehyde.

Solvent Free Dimerisation of Benzaldehyde by Compound 4

In an inert atmosphere glovebox, a vial was charged with finely ground **4** (5.3 mg, 0.009 mmol, 1 equiv.) and a magnetic stirrer bar. Benzaldehyde (0.966 g, 9.1 mmol, 1000 equiv.) was added with heat given off immediately. The resultant sample stirred for 24 h before analysis of a 24 mg sample by ^{1}H NMR spectroscopy.

Workup of Raw Data From NMR Experiments

The data was worked up by comparison of integrals of the methylene protons, $RC(O)OC\underline{H}_2R$, of the ester against the aryl or methyl protons of the 1,4-dimethoxybenzene standard. The concentrations of ester in solution were calculated using the following equation:

$$[\text{aldehyde}] = ([\text{standard}] \text{ x } I_{\text{aldehdye}} \text{ x } n) / I_{\text{standard}}$$

n = 2 if using integrals of the aryl protons of the standard
n = 3 if using integrals of the methyl protons of the standard

Figure S1 ^{1}H NMR spectrum (400 MHz, C_6D_6, 300 K) of Mg(mesC{NCy}$_2$)(OAr)(THF) (**3**)

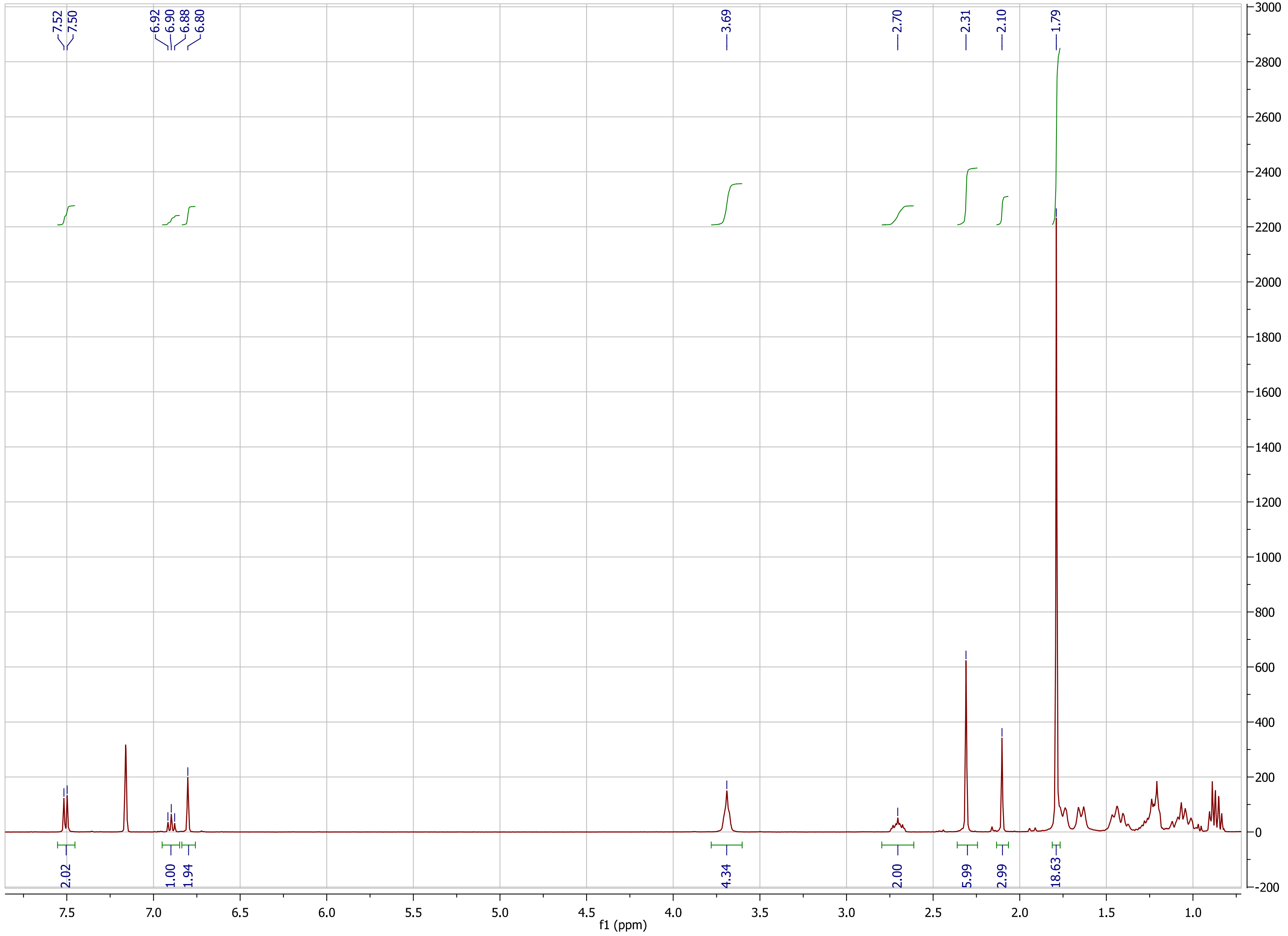

Figure S2 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR spectrum (100 MHz, C_6D_6, 300 K) of Mg(mesC$\{$NCy$\}_2$)(OAr)(THF) (**3**)

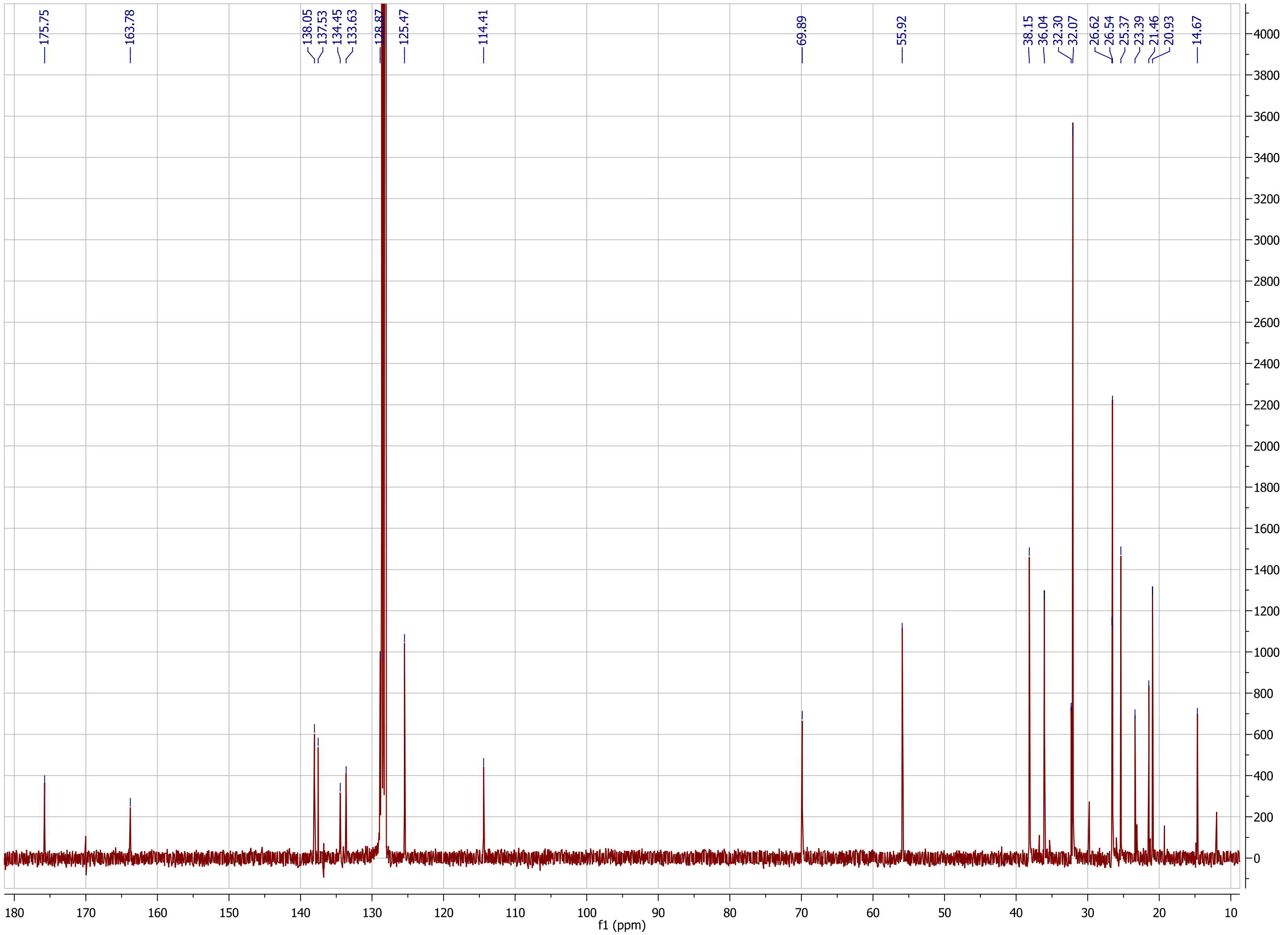

Figure S3 ORTEP of Mg(mes)(OAr)(THF)$_2$ (**1**) (ellipsoids at 30%, hydrogen atoms omitted)

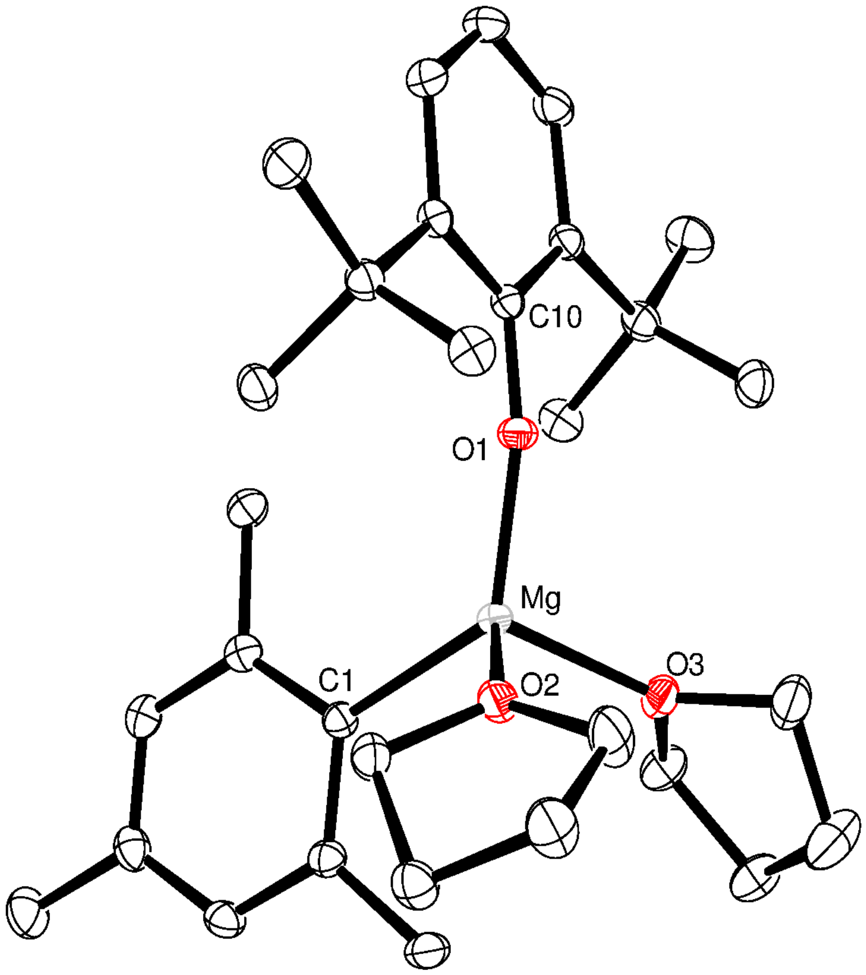

Figure S4 ORTEP of [Mg(mesC{NCy}$_2$)Br(OEt$_2$)]$_2$ ([**2**]$_2$) (ellipsoids at 30%, hydrogen atoms omitted)

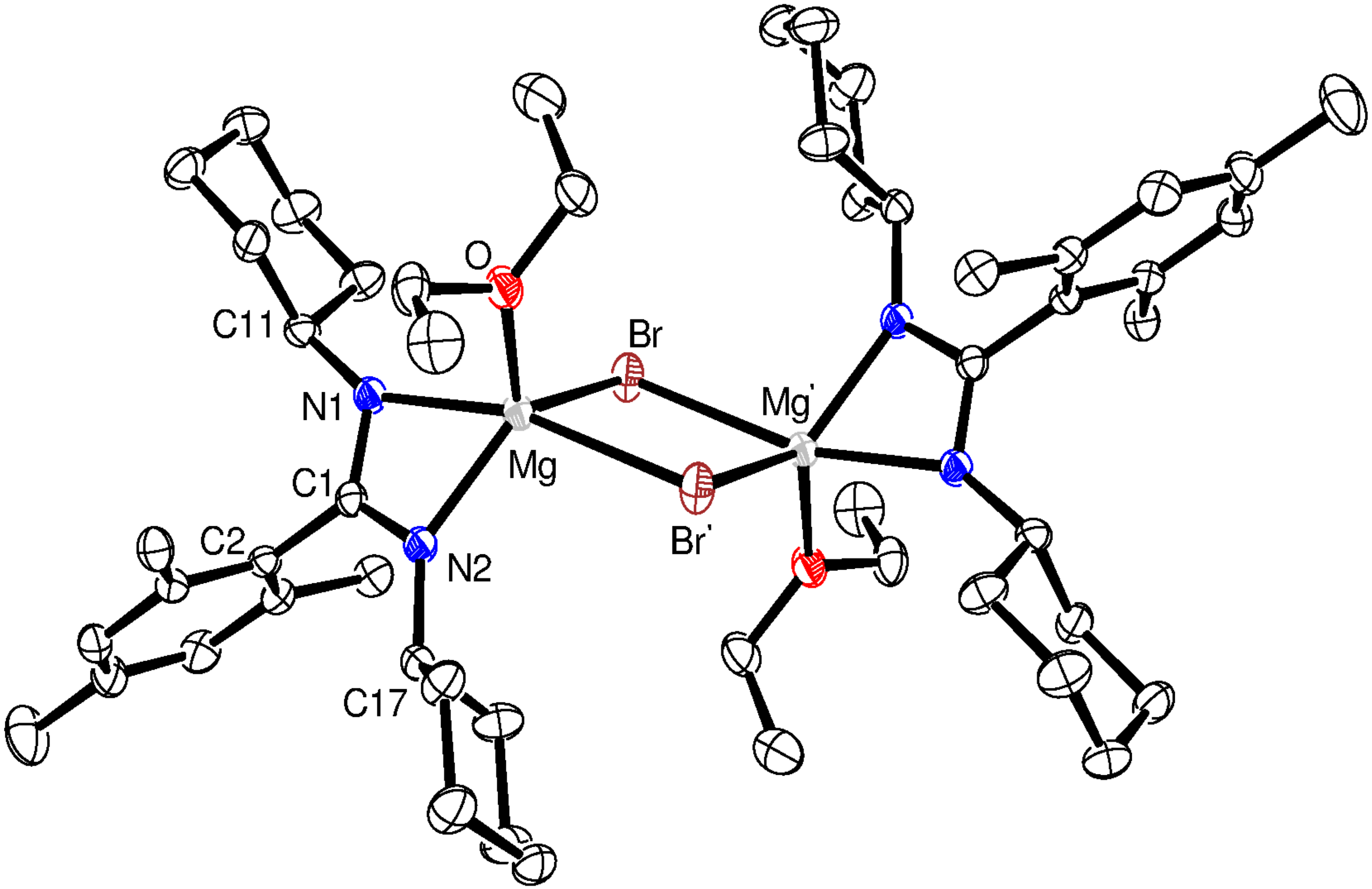

Figure S5 Mg(mesC{NCy}$_2$)(N{SiMe$_3$}$_2$)(THF) (**4**)