Supplementary Information

C–H and C–F coordination of arenes in neutral alkaline earth metal complexes

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Materials and Methods

Synthetic and characterising data for new compounds

General considerations. All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon. Solvents were degassed by sparging with argon and dried by passing through a column of the appropriate drying agent. NMR spectra were measured in benzene-d_6 or cyclohexane-d_{12}, which were both dried over potassium, distilled under reduced pressure and stored under argon in Teflon valve ampoules. NMR samples were prepared under argon in 5 mm Norell Select Series NMR Tube fitted with J. Young Teflon valves. ^{1}H, ^{13}C{^{1}H} and ^{19}F{^{1}H} NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer at various temperatures as described in the experimental below. ^{1}H and ^{13}C{^{1}H} spectra were referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane (δ = 0 ppm). ^{19}F{^{1}H} spectra were referenced externally to $CFCl_3$ (δ = 0 ppm). Assignments were confirmed using two-dimensional ^{1}H-^{1}H and ^{13}C-^{1}H NMR correlation experiments. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. Elemental analyses were carried out by Dr Remi Rouquette at the Macquarie Analytical & Workshop Facility (MAWF), Macquarie University. Due to the highly sensitive nature of some of the compounds reported here, achieving reproducible elemental analysis data was challenging. That said, all compounds apart from **3** and **5** have been successfully characterised by elemental analysis. H_2(**NON**) and K_2(**NON**) were prepared by literature methods.[S1] All other reagents were used as received.

Preparation A of (NON)Mg(OEt$_2$) (1): To a suspension of MgI_2 (0.767 g, 2.76 mmol) in diethyl ether (5 mL) was added a solution of K_2(**NON**) (2.00 g, 2.67 mmol) in diethyl ether (5 mL) at –78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight whereupon volatiles were removed *in vacuo*. The residual was extracted with toluene (10 mL), volatiles from the filtrate were removed *in vacuo* to give **1** as an off-white powder (1.91 g, 93%). N.B. X-ray quality crystals were obtained by dissolving this solid in minimal warm toluene and leaving the solution to slowly cool to room temperature overnight giving large colourless blocks.

Preparation B of (NON)Mg(OEt$_2$) (1): A solution of *n*-butyl-sec-butyl magnesium in hexane (0.70 M, 11.0 mL, 7.7 mmol) was added dropwise to a solution of H_2(**NON**) (4.78 g, 7.10 mmol) in diethyl ether (40 mL) at room temperature. The reaction was left to stir at room temperature for 2 hours under a stream of argon. The solvent was removed under reduced pressure and the resulting solid was heated to 150 °C under reduced pressure for 2 hours to yield **1** as a white solid. **Yield:** 5.26 g (6.84 mmol, 96%). **^{1}H NMR** (400 MHz, C_6D_6, 298 K): 0.78 (br, 6H, OEt_2-CH_3), 1.14 (d, $^{3}J_{HH}$ = 6.9 Hz, 12H, Dipp-^{i}Pr-CH_3), 1.24 (d, $^{3}J_{HH}$ = 6.6 Hz, 12H, Dipp-^{i}Pr-CH_3), 1.34 (s, 18H, ^{t}Bu-CH_3), 1.64 (s, 6H, CMe_2-CH_3), 2.82 (br, 4H, OEt_2-CH_2), 3.56 (sept., $^{3}J_{HH}$ = 6.4 Hz, 4H, Dipp-^{i}Pr-C*H*), 6.26 (d, $^{4}J_{HH}$ = 2.0 Hz, 2H, Xanth-C_{ortho}*H*) 6.66 (d, $^{4}J_{HH}$ = 2.1 Hz, 2H, Xanth-C_{para}*H*), 7.19-7.29 (m, 6H, Dipp-C_6H_3-C*H*); **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6, 298 K): 13.3 (OEt_2-*C*H_3), 24.7, 26.1, 28.2 (Dipp-^{i}Pr-*C*H), 29.6 (CMe_2-

CH_3), 32.1 (^{t}Bu-CH_3), 35.1 (^{t}Bu-CMe_3), 36.1 (CMe_2), 65.0 (OEt_2-CH_2), 103.7, 109.6, 124.0, 124.1, 131.0, 138.6, 146.4, 146.8, 147.9, 148.6 (Ar-*C*); **IR** ν_{max} (cm^{-1}) (Nujol): 1616(m), 1575(m), 1305(s), 1253(s), 1201(s), 1189(s), 1054(m), 1016(m), 892(m), 792(s), 774(s), 682(s), 530(m), 459(m), 425(m); **anal. calc.** for $C_{51}H_{72}MgN_2O_2$: N, 3.64; C, 79.61; H, 9.43%, found: N, 3.80; C, 79.53; H, 9.43%.

Preparation of (NON)Ca(OEt$_2$)$_2$ (2) To a suspension of CaI_2 (0.588 g, 2.00 mmol) in diethyl ethyl (20 mL) was added a solution of K_2(**NON**) (1.00 g, 1.33 mmol) in diethyl ether (20 mL) at room temperature. The reaction mixture was stirred for 2 days at room temperature whereupon volatiles were removed *in vacuo*. The residual was extracted with warm toluene (30 mL, ca. 60 °C), volatiles from the filtrate were removed *in vacuo* to give **2** as a colourless powder. **Yield:** 0.920 g (1.06 mmol, 80%). N.B. X-ray quality crystals were obtained by dissolving this solid in minimal warm toluene and leaving the solution to slowly cool to room temperature overnight giving large colourless blocks. **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ = 0.60 (t, $^3J_{HH}$ = 7.1 Hz, 12H, OEt_2-CH_3), 1.19 (d, $^3J_{HH}$ = 7.1 Hz, 12H, Dipp-^{i}Pr-CH_3), 1.33 (d, $^3J_{HH}$ = 6.6 Hz, 12H, Dipp-^{i}Pr-CH_3), 1.36 (s, 18H, ^{t}Bu-CH_3), 1.80 (s, 6H, CMe_2-CH_3), 3.07 (q, $^3J_{HH}$ = 7.1 Hz, 8H, OEt_2-CH_2), 3.57 (sept., $^3J_{HH}$ = 6.8 Hz, 4H, Dipp-^{i}Pr-C*H*), 6.16 (s, 2H, Xanth-C_{ortho}*H*), 6.65 (s, 2H, Xanth-C_{para}*H*), 7.15 (t, $^3J_{HH}$ = 7.6 Hz, 2H, Dipp-*p*-C*H*), 7.28 (d, $^3J_{HH}$ = 7.6 Hz, 4H, Dipp-*m*-C*H*); **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6, 298 K): δ = 13.7 (OEt_2-CH_3), 24.9, 25.6 (Dipp-^{i}Pr-*C*H), 28.8 (Dipp-^{i}Pr-*C*H), 31.9 (CMe_2-CH_3), 32.0 (^{t}Bu-CH_3), 35.0 (^{t}Bu-CMe_3), 35.2 (CMe_2), 64.5 (OEt_2-CH_2), 103.5, 108.4, 122.7, 123.9, 128.0, 128.6, 129.4, 138.9, 145.3, 146.3, 148.9, 150.5 (Ar-*C*); **IR** υ/cm^{-1} (Nujol): 2957(s), 2863(m), 1625(m), 1605(m), 1575(s), 1481(s), 1430(s), 1410(s), 1388(m), 1334(s), 1307(s), 1247(s), 1198(s), 1187(s), 1147(m), 1117(m), 1087(s), 1044(s), 1016(s), 942(m), 876(s), 802(m), 791(s), 774(s), 660(s), 547(m), 511(m), 459(m), 421(m); **anal. calc.** for $C_{55}H_{82}CaN_2O_3$: C 76.87%, H 9.62%, N 3.26%, found: C 76.80%, H 9.38%, N 3.79%.

Preparation of [(NON)Mg]$_2$ (3): A solution of *n*-butyl-sec-butyl magnesium in hexane (0.70 M, 2.56 mL, 1.79 mmol) was added dropwise to a solution of H_2(**NON**) (1.15 g, 1.71 mmol) in benzene (5 mL) in J. Youngs flask at room temperature. The reaction solution was heated to 95 °C and left to stir under a stream of argon for 60 minutes. The reaction flask was sealed and the reaction was stirred for 2 days at 95 °C. The pressure in the reaction flask was released under argon every 10–16 hours. After two days, the reaction solution was cooled to room temperature and concentrated under reduced pressure (*ca.* 1 mL). With the reaction stirring vigorously, *n*-hexane (20 mL) was added to the solution resulting in the precipitation of **3** as a white powder. The reaction mixture was concentrated under reduced pressure to approximately 5 mL to ensure complete precipitation. The white powder was isolated *via* cannula filtration and dried under reduced pressure. **Yield:** 1.05 g (1.51 mmol, 88%). **^{1}H NMR** (400 MHz, C_6D_6, 298 K): 1.18–1.24 (m, 48H, Dipp–^{i}Pr–CH_3), 1.31 (s, 36H, ^{t}Bu–CH_3), 1.66 (s, 12H, CMe_2–CH_3), 3.31 (br, 8H, Dipp–^{i}Pr–C*H*), 6.22 (s, 4H, Xanth–C_{ortho}*H*), 6.70 (d, 4H, $^4J_{HH}$ = 2.1 Hz, 2H, Xanth–C_{para}*H*), 7.16 (m, 12H, Dipp–C*H*); **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6, 298 K): 24.4, 26.0 (Dipp–^{i}Pr–CH_3), 28.8 (Dipp–^{i}Pr–*C*H), 29.1 (CMe_2–CH_3), 32.0 (^{t}Bu–CH_3), 35.1 (^{t}Bu–CMe_3), 36.2 (CMe_2), 105.1, 110.4, 124.2, 124.6 , 128.6, 131.6, 138.7, 146.0, 146.8, 147.2 (Ar–*C*); **IR** ν_{max} (cm^{-1}) (Nujol): 1620(s), 1580(m), 1481(s),

1420(s), 1411(s), 1379(m), 1359(m), 1325(s), 1309(s), 1248(m), 1183(s), 1139(m), 1109(m), 1015(s), 895(m), 889(m), 809(s), 782(m), 761(m), 662(m), 630(m), 528(m), 463(m), 418(m). Reproducible elemental analysis results (CHN) for this compound could not be obtained, likely due its high sensitivity towards air and moisture.

Preparation of (NON)Ca(C_6H_6)$_2$ (4): A crystalline sample of **2** (0.500 g, 0.582 mmol) was heated to 150 °C under high vacuum (1 x 10^{-2} mbar) for 1 hour. This resulted in an obvious colour change of the sample from colourless to bright yellow. Once cooled to room temperature, the bright yellow powder was dissolved in the minimum volume of boiling benzene (ca. 50 mL), after which the solution was slowly cooled to room temperature overnight to give **4** as large yellow crystals. **Yield:** 0.480 g (0.553 mmol, 95%). N.B. compound **4** does not dissolve in benzene (or C_6D_6) at room temperature, therefore NMR data has been recorded at 353 K. However, at this temperature exchange of coordinated C_6H_6 with C_6D_6 is present. As such, no resonances for coordinated benzene are observed. **^{1}H NMR** (400 MHz, C_6D_6, 353K): δ = 1.24 (d, $^3J_{HH}$ = 6.7 Hz, 12H, Dipp–^{i}Pr–CH_3), 1.26 (d, $^3J_{HH}$ = 6.6 Hz, 12H, Dipp–^{i}Pr–CH_3), 1.32 (s, 18H, ^{t}Bu–CH_3), 1.74 (s, 6H, CMe$_2$–CH_3), 3.28 (sept., $^3J_{HH}$ = 6.9 Hz, 4H, Dipp–^{i}Pr–C*H*), 5.99 (d, $^4J_{HH}$ = 2.2 Hz, 2H, Xanth–C$_{ortho}$*H*), 6.61 (d, $^4J_{HH}$ = 2.32 Hz, 2H, Xanth–C$_{para}$*H*), 7.23 (t, $^3J_{HH}$ = 6.8 Hz, 2H, Dipp-*p*-C*H*), 7.31 (d, $^3J_{HH}$ = 6.8 Hz, 4H, Dipp-*m*-C*H*); **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6, 353 K): δ = 24.8, 25.9 (Dipp–^{i}Pr–*C*H$_3$), 28.6 (Dipp–^{i}Pr–*C*H), 31.6 (CMe$_2$–*C*H$_3$), 32.1 (^{t}Bu–*C*H$_3$), 35.0 (^{t}Bu–*C*Me$_3$), 35.3 (*C*Me$_2$), 104.5, 109.3, 123.6, 124.0, 128.3, 128.6, 130.1, 139.1, 145.7, 146.6, 148.4, 150.8 (Ar-*C*); **IR** υ/cm^{-1} (Nujol): 1607(m), 1575(m), 1476(s), 1429(s), 1409(m), 1355(m), 1328(s), 1308(s), 1254(m), 1244(s), 1194(s), 1184(s), 1120(m), 1096(m), 1033(m), 1016(m), 941(m), 876(m), 857(m), 811(m), 800(m), 790(m), 773(m), 760(m), 710(s), 700(s), 674(s), 659(m), 547(m), 512(m), 432(m); **anal. calc.** for $C_{53}H_{67}CaN_2O$: C 80.76%, H 8.57%, N 3.55%, found: C 80.63%, H 9.11%, N 3.68%.

Preparation of (NON)Mg(PhF)$_2$ (5): Compound **3** (0.315 g, 0.453 mmol) was dissolved in fluorobenzene (3 mL) and stirred for 30 minutes at room temperature. The solvent of the reaction mixture was removed under reduced pressure to yield **5** as an off-white powder. **Yield:** 0.270 g (0.303 mmol, 67%). N.B. X-ray quality crystals of **5** were grown by dissolving this powder in the minimum volume of boiling fluorobenzene and allowing the solution to slowly cool to room temperature overnight. **^{1}H NMR** (400 MHz, C_6D_6, 298 K): 0.99 (d, $^3J_{HH}$ = 6.9 Hz, 12H, Dipp–^{i}Pr–CH_3), 1.22 (d, $^3J_{HH}$ = 6.8 Hz, 12H, Dipp–^{i}Pr–CH_3), 1.34 (s, 18H, ^{t}Bu–CH_3), 1.70 (s, 6H, CMe$_2$–CH_3), 3.61 (hept, $^3J_{HH}$ = 6.9 Hz, 4H, Dipp–^{i}Pr–C*H*), 6.38 (s, 2H, Xanth–C$_{ortho}$*H*), 6.41–6.46 (m, 4H, PhF–C$_{ortho}$*H*), 6.61–6.65 (m, 2H, PhF–C$_{para}$*H*), 6.70–6.76 (m, 6H, PhF–C$_{meta}$*H* & Xanth–C$_{para}$*H*), 7.25–7.32 (m, 6H, Dipp–C$_6$H$_3$–C*H*); **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6, 298 K): 24.6, 25.5 (Dipp–^{i}Pr–*C*H$_3$), 28.2 (Dipp–^{i}Pr–*C*H), 30.1 (CMe$_2$–*C*H$_3$), 32.1 (^{t}Bu–*C*H$_3$), 35.2 (^{t}Bu–*C*Me$_3$), 36.2 (*C*Me$_2$), 104.7, 108.9 (Ar–*C*), 115.0 (d, $^2J_{CF}$ = 22.0 Hz, PhF–*C*$_{ortho}$H) 124.2, 124.3 (Ar–*C*), 125.9 (PhF–*C*$_{para}$H), 130.5 (d, $^3J_{CF}$ = 10.3 Hz, PhF–*C*$_{meta}$H), 130.5 (Ar–*C*), 137.7, 146.8, 146.9, 147.1, 147.8 (Ar–*C*), 164.0 (d, $^1J_{CF}$ = 229.3 Hz, PhF–*C*$_{ipso}$); **^{19}F{^{1}H} NMR** (376 MHz, C_6D_6, 298 K): –124.9 (Ph–*F*); **IR** ν_{max} (cm^{-1}) (Nujol): 1619(m), 1575(m), 1483(s), 1436(s), 1412(s), 1335(s), 1302(s), 1252(s), 1200(s), 1188(s), 1172(m), 1138(m), 1127(s), 1110(m), 1015(s), 895(m), 852(m), 790(s), 779(s), 753(s),

679(m), 529(m), 430(m). Reproducible elemental analysis results (CHN) for this compound could not be obtained, likely due its high sensitivity towards air and moisture.

Preparation of (NON)Ca(FPh)$_3$ (6): Compound **4** (0.200 g, 0.231 mmol) was dissolved in fluorobenzene (10 mL) and stirred for 30 mins at room temperature. This dissolution proceeded with an obvious colour change from the bright yellow crystalline solid **4** to a pale yellow solution. The reaction mixture was concentrated (ca. 3 mL) and slowly cooled to –20 °C overnight to give **6** as colourless crystals. **Yield:** 0.150 g (150 mmol, 65%). N.B. NMR data collected on a sample of **6** in C_6D_6 was found to be identical to that of **4**, with exactly 3 molecules of fluorobenzene present in solution. The NMR data reported below was collected in C_6H_{12} at 70 °C due to the low solubility of the complex in the solvent at room temperature. The NMR spectra reported are fairly broad, consistent with a fluxional process – likely due to the coordination/decoordination of the fluorobenzene molecules. **^{1}H NMR** (400 MHz, C_6D_{12}, 343 K): δ = 1.27 (br., 24H, Dipp–^{i}Pr–CH_3), 1.61 (s, 18H, ^{t}Bu–CH_3), 1.77 (s, 6H, CMe$_2$–CH_3), 3.40 (br., 4H, Dipp–^{i}Pr–CH), 5.71 (br., 2H, Xanth–C$_{ortho}H$), 6.61 (br., 2H, Xanth–C$_{para}H$), 7.11-7.47 (m, 21H, ArH); **^{13}C{^{1}H} NMR** (101 MHz, C_6D_{12}, 343 K): δ = 24.8, 25.5 (Dipp–^{i}Pr–CH$_3$), 28.6 (Dipp–^{i}Pr–CH), 29.8 (CMe$_2$–CH$_3$), 31.8 (^{t}Bu–CH$_3$), 34.9 (^{t}Bu–CMe$_3$), 35.7 (CMe$_2$), 105.3, 109.3 (Ar–C), 115.7 (d, $^2J_{CF}$ = 22 Hz, PhF–C_{ortho}H) 123.8, 124.1, 125.2 (Ar–C), 130.1 (d, $^3J_{CF}$ = 7.6 Hz), 128.3, 128.6, 130.1, 136.7 141.5, 146.7, 151.6 (Ar–C), 164.0 (d, $^1J_{CF}$ = 247 Hz, PhF–C_{ipso}); **^{19}F{^{1}H} NMR** (376 MHz, C_6D_6, 343 K): –111.2 (Ph–F); **IR** υ/cm^{-1} (Nujol): 1609(m), 1574(m), 1488(s), 1480(s), 1459(s), 1431(s), 1411(s), 1357(m), 1338(s), 1304(s), 1247(s), 1200(s), 1178(s), 1140(m), 1114(m), 1016(m), 875(m), 847(m), 802(m), 790(s), 748(s), 680(m), 660(m), 525(m), 490(m), 418(m); **anal. calc.** for $C_{65}H_{77}CaF_3N_2O$: C 78.12%, H 7.77%, N 2.80%, found: C 77.89%, H 7.72%, N 2.76%.

^{1}H NMR spectra of new compounds

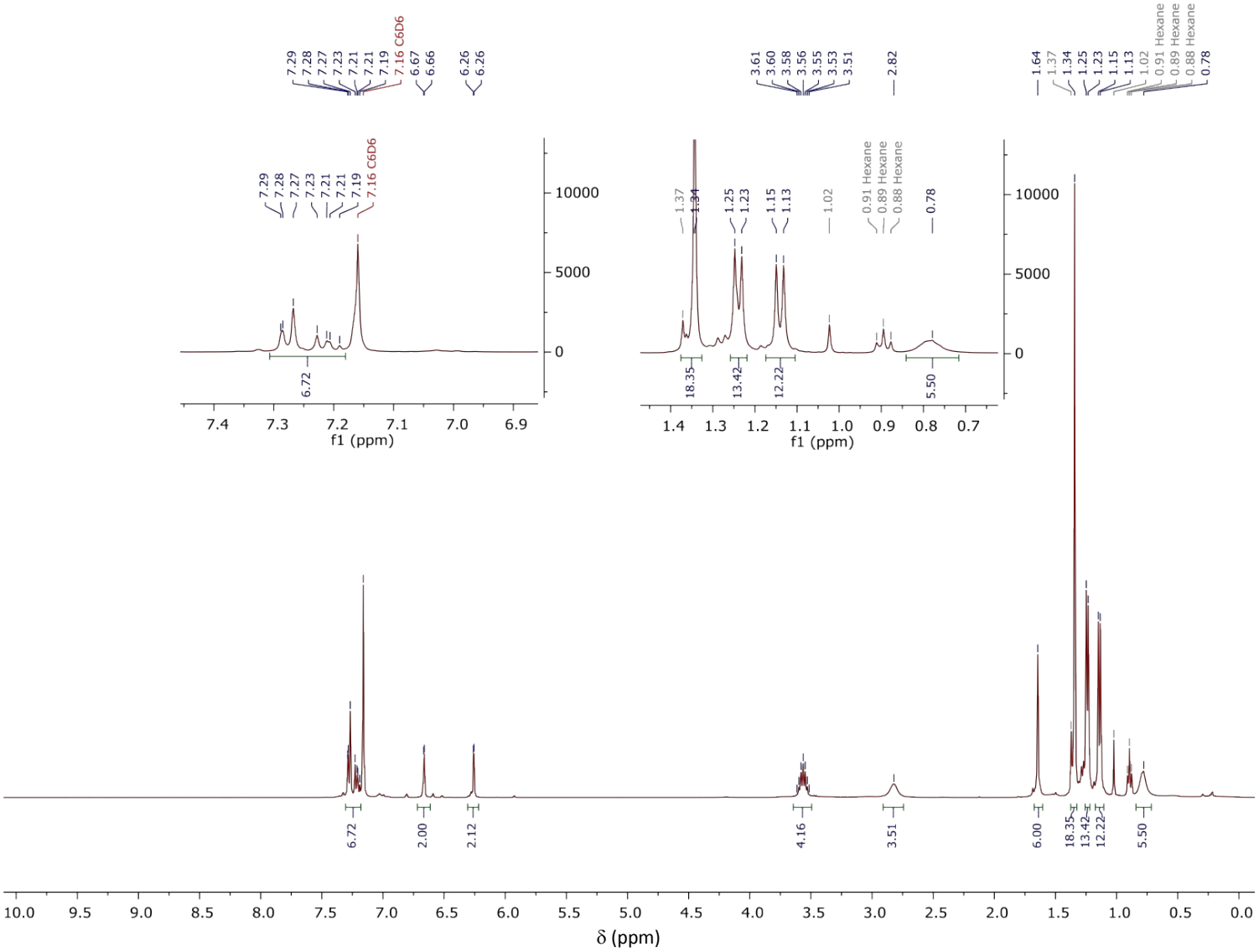

Figure S1: ^{1}H NMR spectrum of (**NON**)Mg(OEt_2) (**1**) (400 MHz, C_6D_6, 298 K)

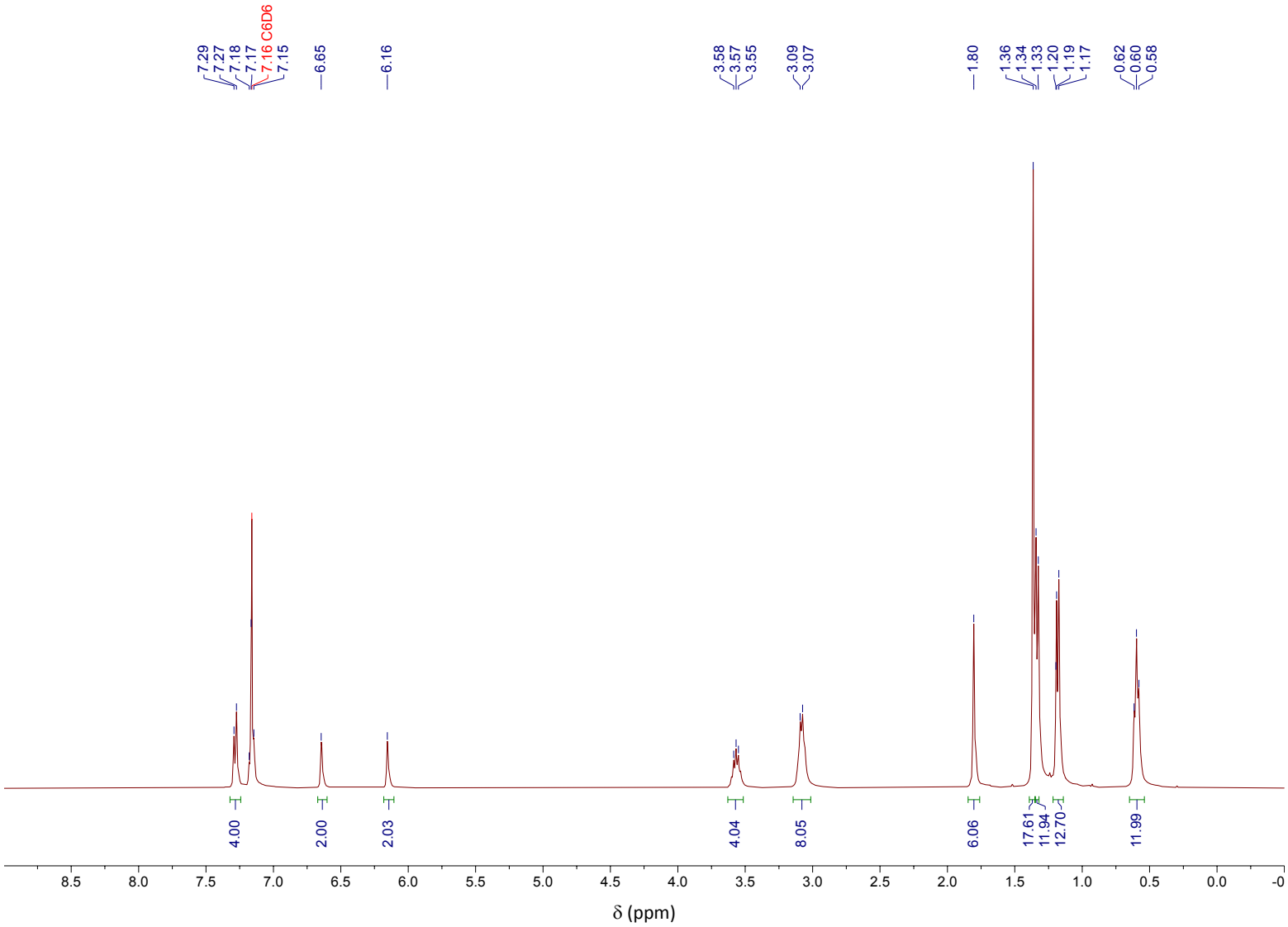

Figure S2: ^{1}H NMR spectrum of (**NON**)Ca(OEt$_2$)$_2$ (**2**) (400 MHz, C_6D_6, 298 K)

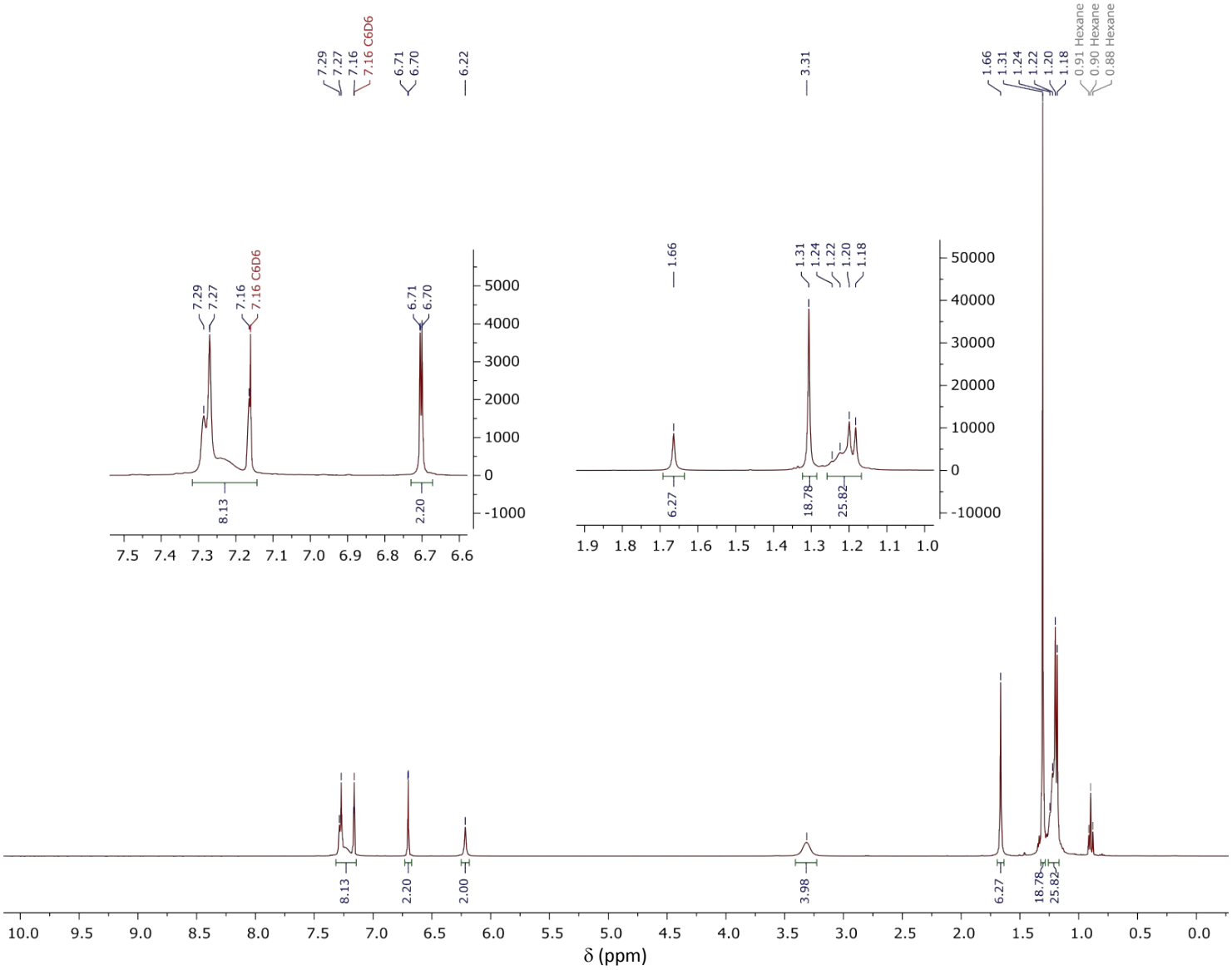

Figure S3: ^{1}H NMR spectrum of [(**NON**)Mg]$_2$ (**3**) (400 MHz, C_6D_6, 298 K)

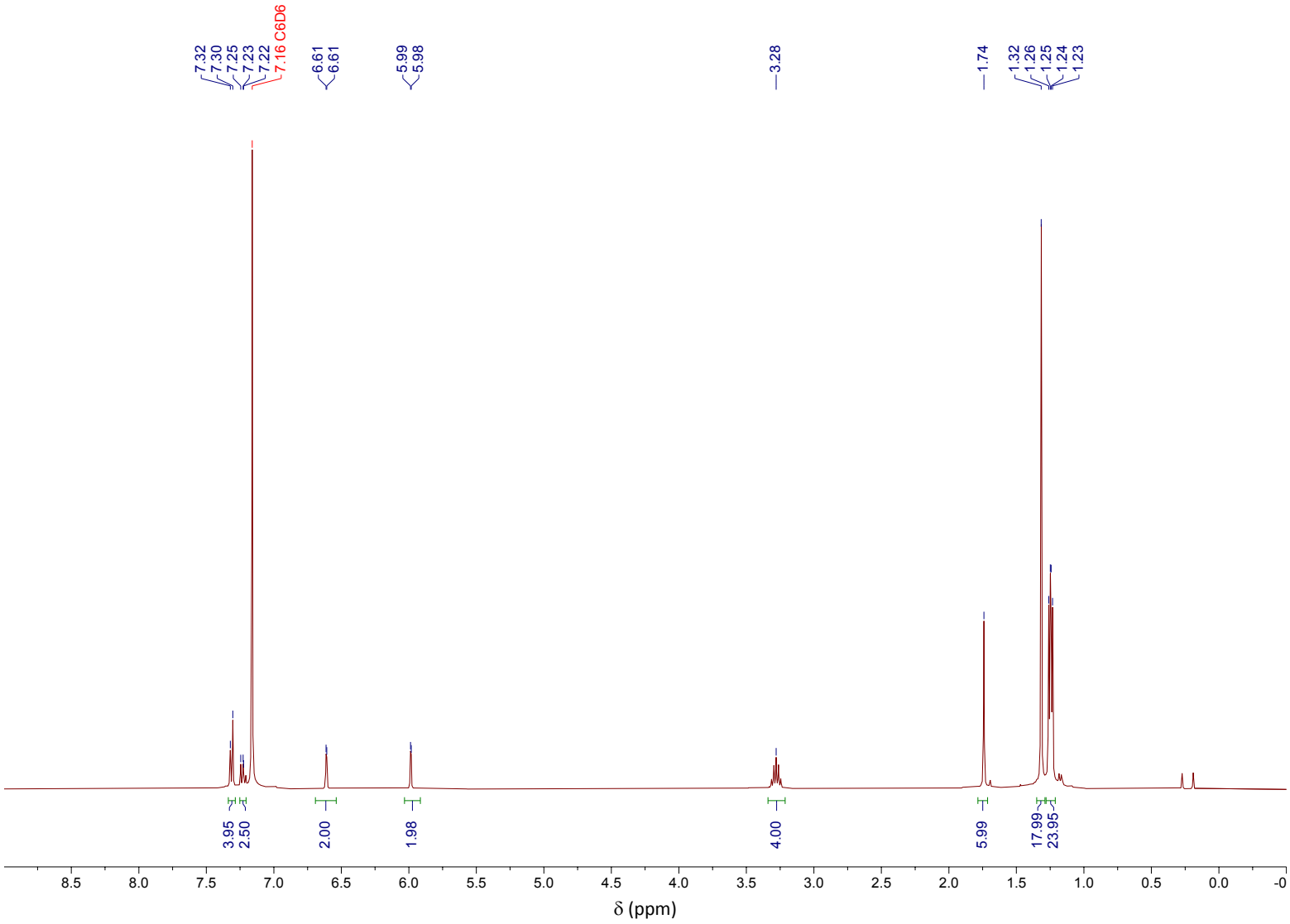

Figure S4: ^{1}H NMR spectrum of (**NON**)Ca(C_6H_6)$_2$ (**4**) (400 MHz, C_6D_6, 353 K)

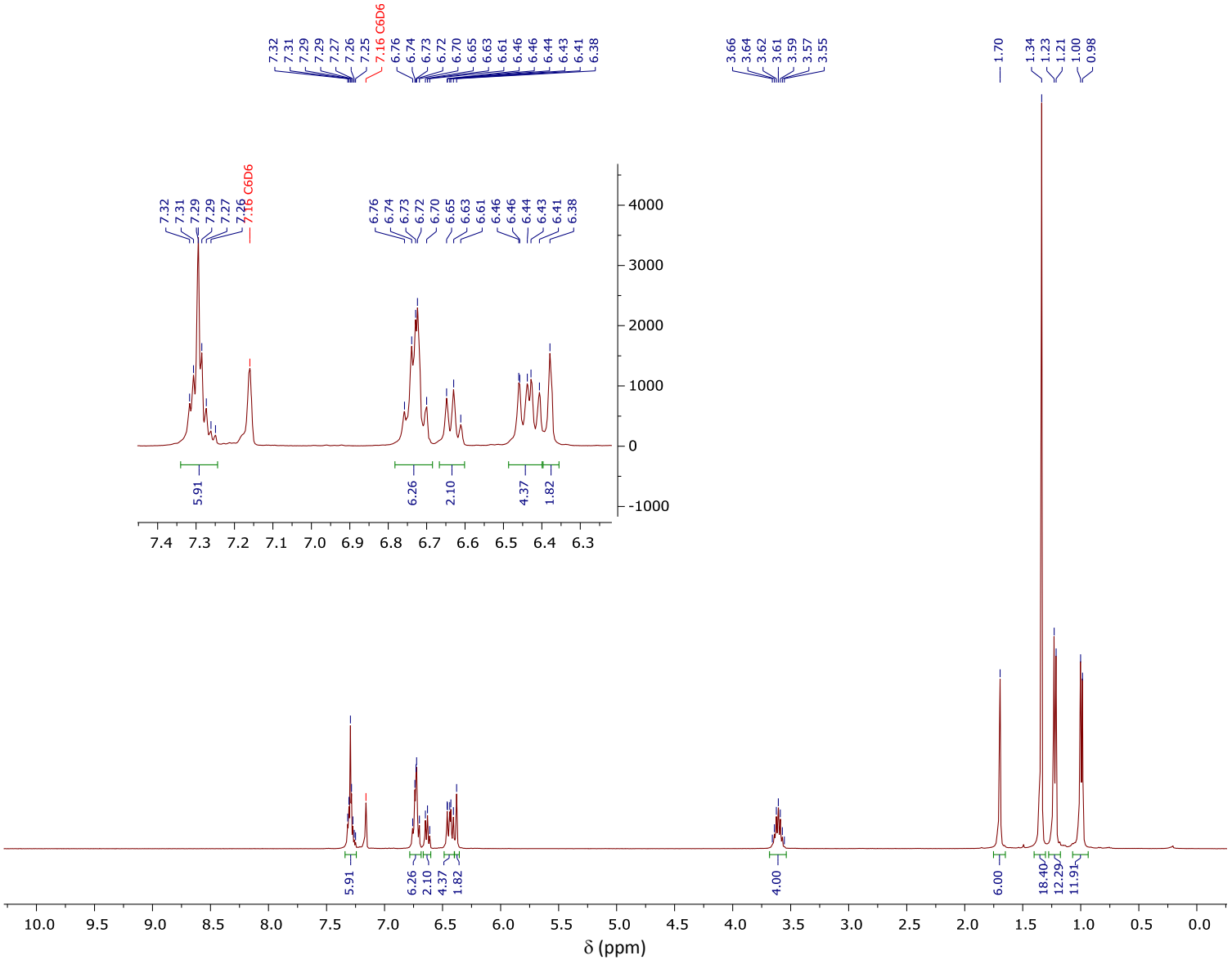

Figure S5: ^{1}H NMR spectrum of (**NON**)Mg(PhF)$_2$ (**5**) (400 MHz, C_6D_6, 298 K)

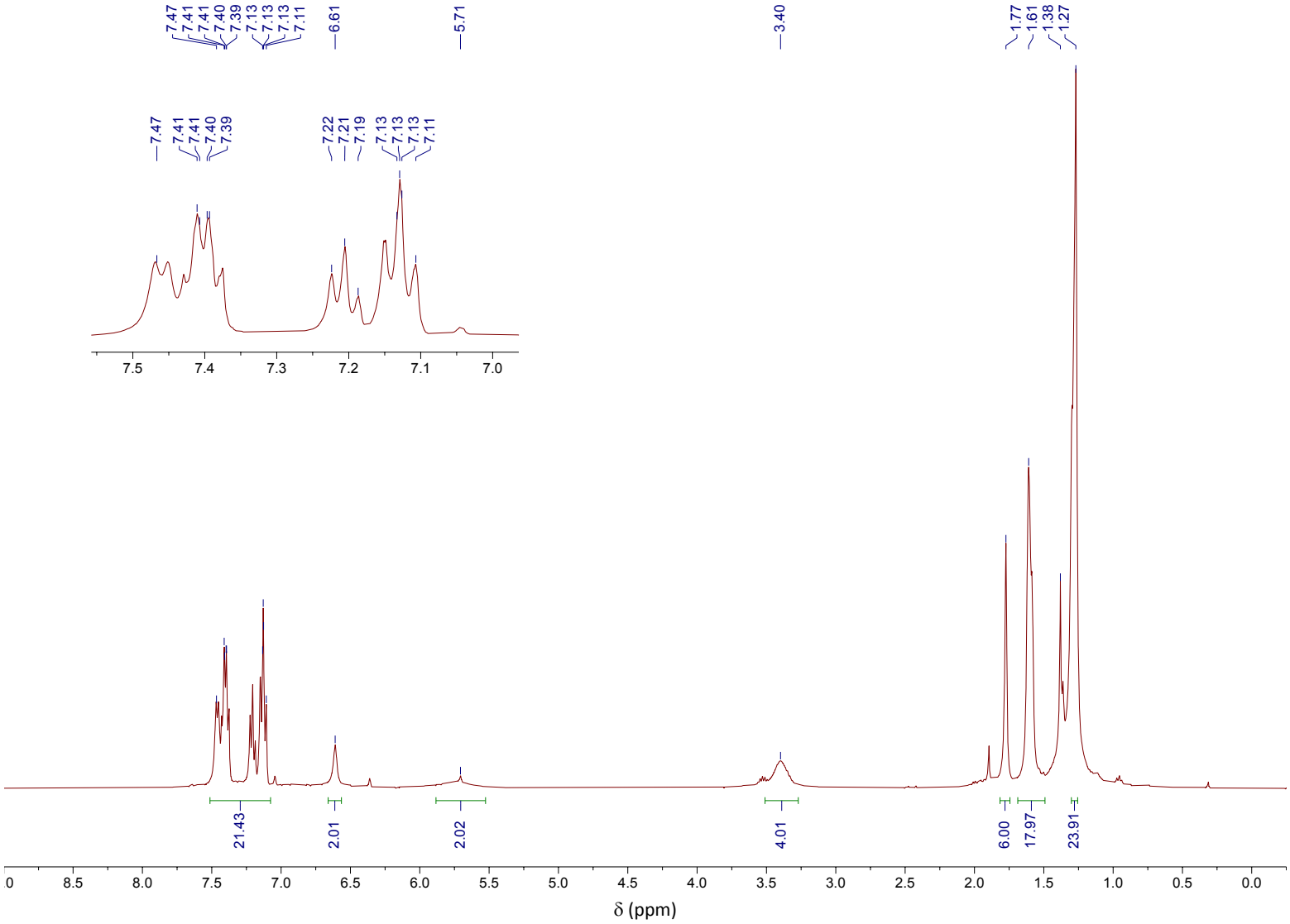

Figure S6: ^{1}H NMR spectrum of (**NON**)Ca(PhF)$_3$ (**6**) (400 MHz, C_6D_{12}, 343 K)

Diffusion ordered NMR spectroscopy (DOSY) experimental details

Diffusion Ordered Spectroscopy (DOSY) experiments were carried out on a Bruker Avance 400 MHz spectrometer at 298 K. Compounds **1** and **3** were analysed at a 20 mg/mL concentration in C_6D_6. To avoid distorted diffusion coefficients, the spectra were collected without sample spinning. The Bruker dstebpgp3s convection corrected pulse sequence was used, with a diffusion delay of Δ = 100 ms and gradient pulse length of δ = 2 ms. Spectra were obtained over a 16 step gradient range from 2-95%. Spectra were processed using the MestReNova Bayesian DOSY transform function at a resolution factor of 0.1 and 128 points in the diffusion dimension over a range of $1x10^{-11}$ – $1x10^{-8}$ m^2s^{-1} (Figures S7 and S8).

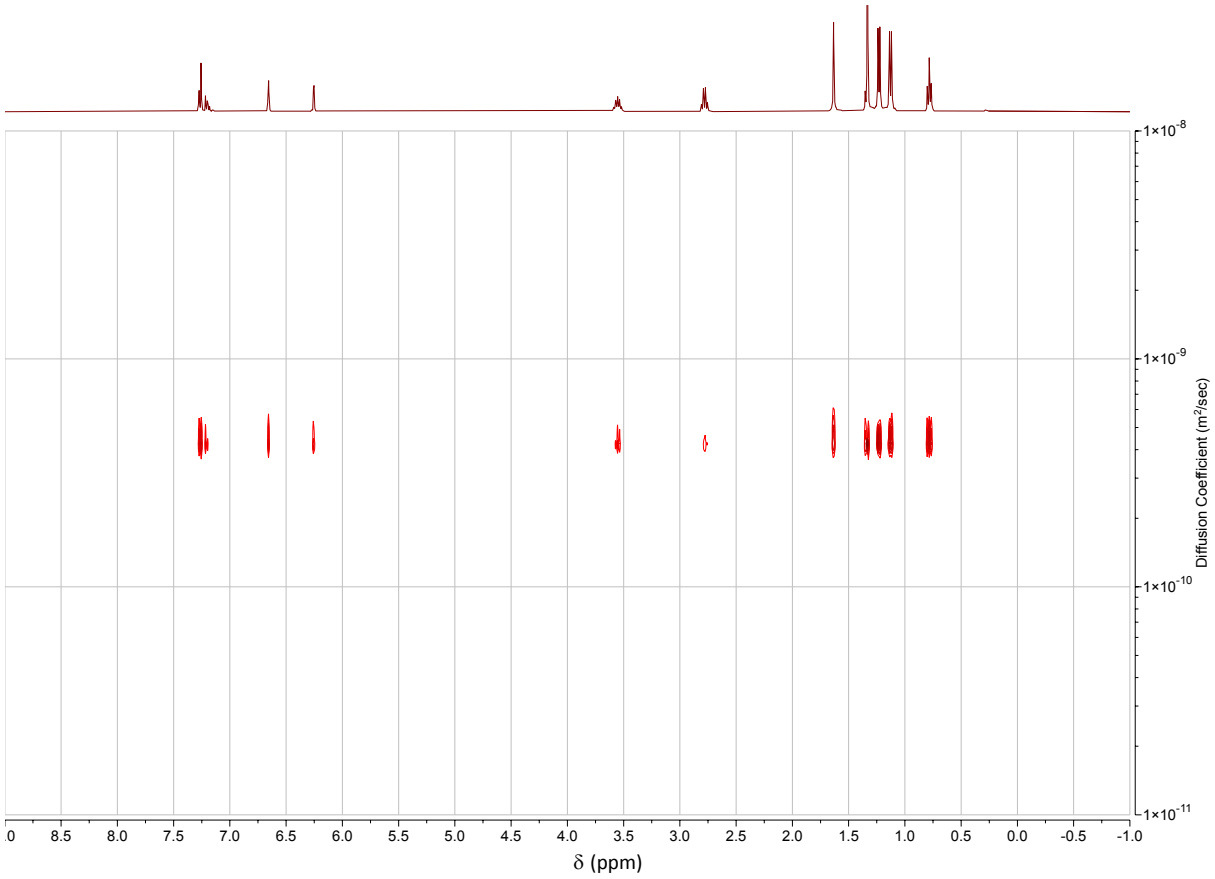

Figure S7: Processed ^{1}H NMR data of **1** in C_6D_6 using the Bayesian DOSY transform function.

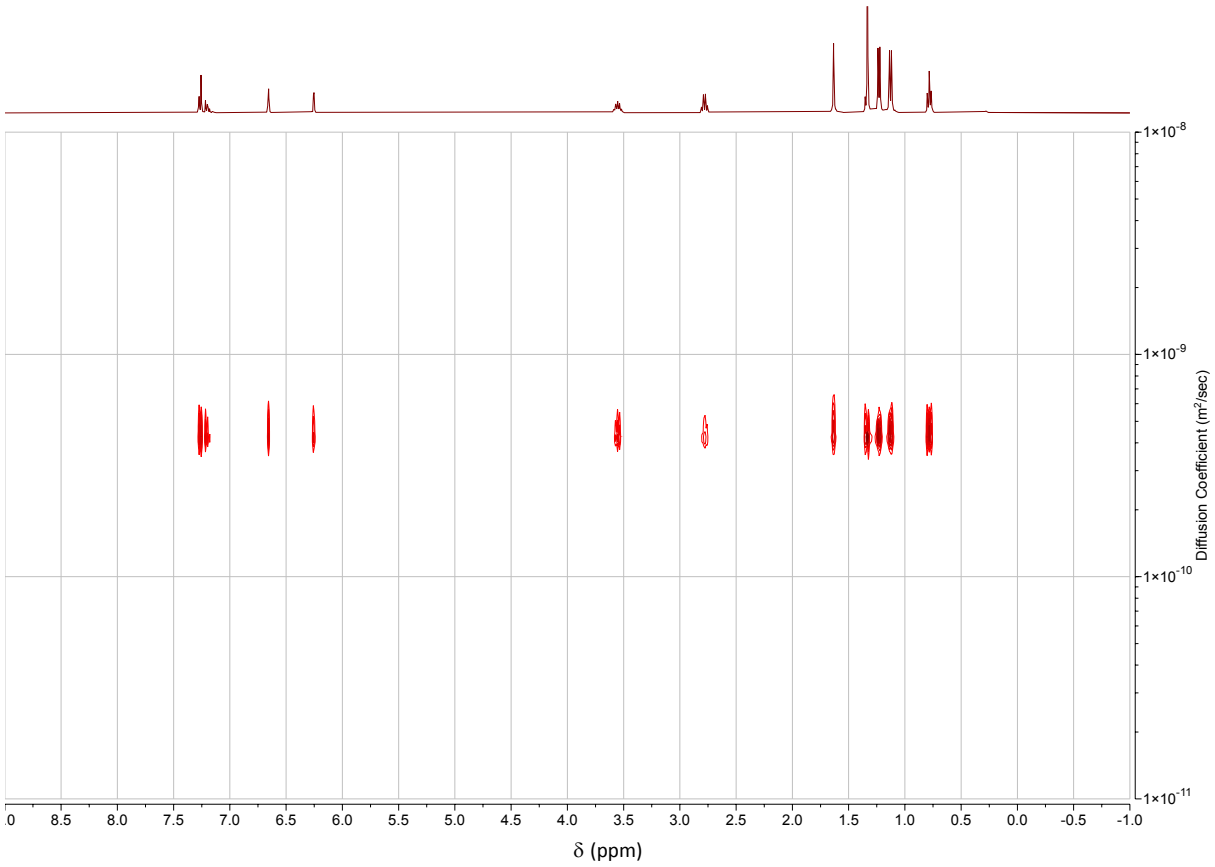

Figure S8: Processed ^{1}H NMR data of **3** in C_6D_6 using the Bayesian DOSY transform function.

The hydrodynamic radii (r_H) of **1** and **3** were then calculated using the Stokes–Einstein equation (for diffusion of spherical particles through a liquid with low Reynolds number) shown below.

$$r_H = \frac{k_B T}{6\pi f \eta D}$$

$r_H = hydrodynamic\ radius,\ \ 7.731 \times 10^{-10}\ m\ for\ 1;\ 7.683 \times 10^{-10}\ m\ for\ 3$

$k_B = Boltzmann\ constant,\ 1.38064 \times 10^{-23}\ m^2\ kg\ s^{-2}\ K^{-1}$

$T = Temperature,\ 298\ K$

$f = shape\ correct\ factor,\ 1\ for\ a\ sphereical\ particle$

$\eta = viscosity\ of\ solvent,\ 0.000601\ N\ s\ m^2\ (C_6H_6)$

$D = diffusion\ coefficient,\ 4.70 \times 10^{-10}\ m^2\ s^{-1}\ for\ 1;4.73 \times 10^{-10}\ m^2\ s^{-1}\ for\ 3$

X-ray crystallographic studies

Single-crystal X-ray diffraction data were collected using either using a Rigaku Supernova dual-source diffractometer (compounds **1-5**) or a Rigaku Xcaliber single-source (Mo) diffractometer (compound **6**). Crystals were selected under Paratone-N oil, mounted on Micromount loops and quench-cooled using an Oxford Cryosystems open flow N_2 cooling device.[S2] Data were collected at 150 K using mirror monochromated Cu K_α (λ = 1.5418 Å) or Mo K_α (λ = 0.71073 Å) radiation. Data collected were processed using the CrysAlisPro package, including unit cell parameter refinement and inter-frame scaling (which was carried out using SCALE3 ABSPACK within CrysAlisPro).[S3] Equivalent reflections were merged and diffraction patterns processed with the CrysAlisPro suite.[S3] Structures were subsequently solved using SHELXT-2018 and refined on F^2 using the SHELXL 2018 package and the graphical interface X-Seed.[S4-S6]

Finalised CIFs for all structures have been deposited at the Cambridge Crystallographic Data Centre (2082997-2083002). These can be obtained free-of-charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Table S1: Crystallographic and refinement parameters for the structures of compounds **1-3**.

	1·C_7H_8	**2**·C_6H_6	**3**·$2C_6H_6$
Formula	$C_{51}H_{72}MgN_2O_2$	$C_{55}H_{82}CaN_2O_3$	$C_{106}H_{136}Mg_2N_4O_2$
M	861.55	937.41	1546.80
Cell Setting	Triclinic	Monoclinic	Monoclinic
Space Group	*P*–1	$P2_1/c$	$P2_1/c$
a/Å	11.4770(3)	13.69890(10)	15.7995(2)
b/Å	11.6476(3)	21.4450(2)	26.2202(2)
c/Å	22.1930(6)	19.4889(2)	22.4868(2)
α/°	102.158(2)	90	90
β/°	93.494(2)	94.2990(10)	90.2910(10)
γ/°	112.779(3)	90	90
V/Å^3	2640.38(13)	5709.20(9)	9315.40(16)
Z	2	4	4
Unique/$I > 2\sigma I$	10374/9260	11154/9872	18659/13982
R_{int}	0.0174	0.0265	0.0421
Parameters	587	664	1121
R_1 (all data/ $I > 2\sigma I$)	0.0494/0.0442	0.0462/0.0406	0.0767/0.0553
wR_2 (all data/ $I > 2\sigma I$)	0.1218/0.1165	0.1112/0.1065	0.1659/0.1514
GooF	1.028	1.041	1.072
Residual max/min	0.568/–0.274	0.492/–0.278	0.738/–0.460
T/K	150(2)	150(2)	150(2)
Radiation, λ (Å)	Cu Kα, (1.54184)	Cu Kα, (1.54184)	Cu Kα, (1.54184)
CCDC number	2082997	2082998	2082999

Table S2: Crystallographic and refinement parameters for the structures of compounds **4-6**.

	4·2C_6H_6	**5**·1.5C_6H_5F	**6**·C_6H_5F
Formula	$C_{59}H_{74}CaN_2O$	$C_{59}H_{72}F_2MgN_2O_3$	$C_{65}H_{77}Ca\ F_3N_2O_O$
M	1023.49	1031.64	1095.46
Cell Setting	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_1$	$P2_1/c$	$P2_1/c$
a/Å	10.11790(10)	24.1012(14)	21.3549(14)
b/Å	11.36910(10)	19.7730(11)	26.9800(11)
c/Å	26.1145(3)	26.1381(16)	22.6462(11)
α/°	90	90	90
β/°	90.0050(10)	104.791(6)	108.370(6)
γ/°	90	90	90
V/Å^3	3003.99(5)	12043.4(13)	12382.8(12)
Z	2	8	8
Unique/$I > 2\sigma I$	11788/11596	23638/15707	29707/14216
R_{int}	0.0258	0.0303	0.0536
Parameters	724	1498	1755
R_1 (all data/ $I > 2\sigma I$)	0.0481/0.0472	0.1356/0.1066	0.1723/0.0775
wR_2 (all data/ $I > 2\sigma I$)	0.1186/0.1177	0.3330/0.3029	0.2324/0.1740
GooF	1.043	1.049	1.017
Residual max/min	0.342/–0.393	0.775/–0.594	0.547/–0.578
T/K	150(2)	150(2)	150(2)
Radiation, λ (Å)	Cu Kα, (1.54184)	Mo Kα, (0.71073)	Mo Kα, (0.71073)
CCDC number	2083000	2083002	2083003

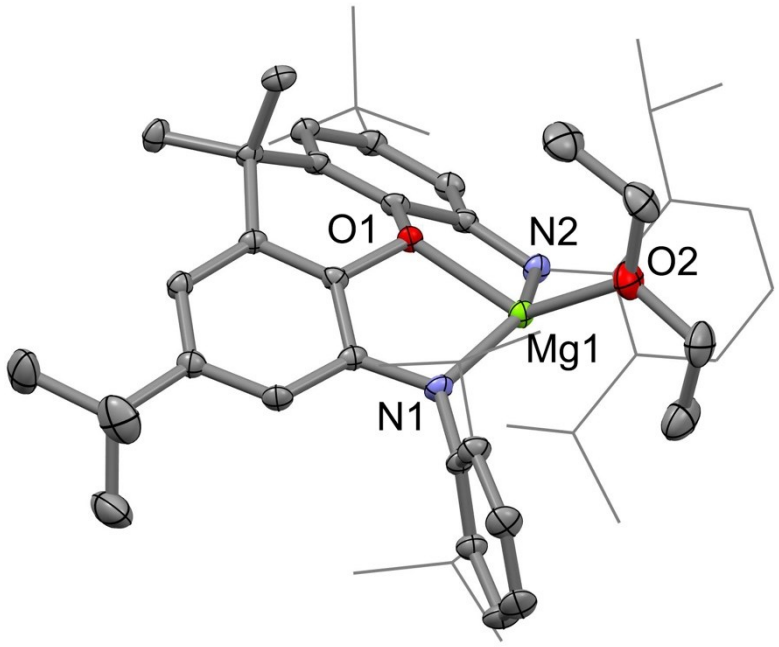

Figure S9. Molecular structures of **1** as determined by X-ray crystallography. Non-coordinating solvent molecules and hydrogen atoms have been removed, and selected groups of the **NON** ligand are shown in wireframe for clarity. Displacement ellipsoids set at the 50% probability level.

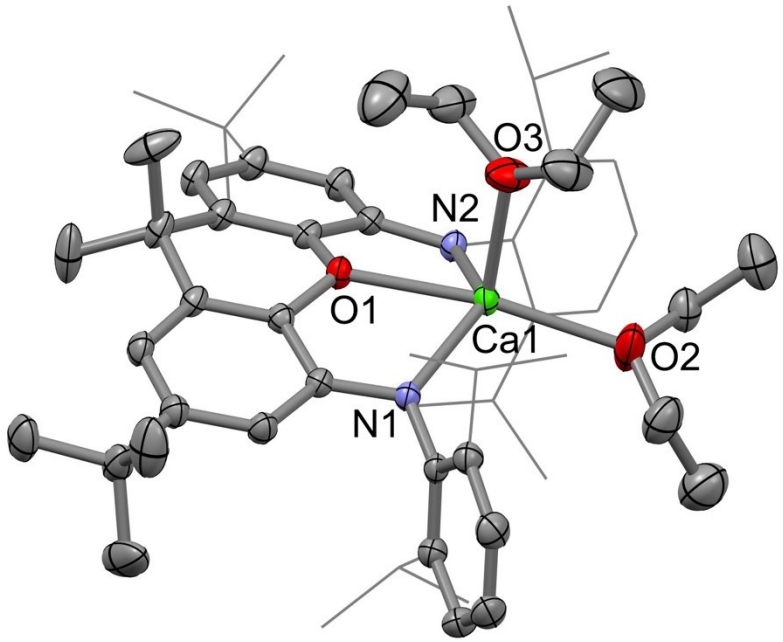

Figure S10. Molecular structures of **2** as determined by X-ray crystallography. Non-coordinating solvent molecules and hydrogen atoms have been removed, and selected groups of the **NON** ligand are shown in wireframe for clarity. Displacement ellipsoids set at the 50% probability level.

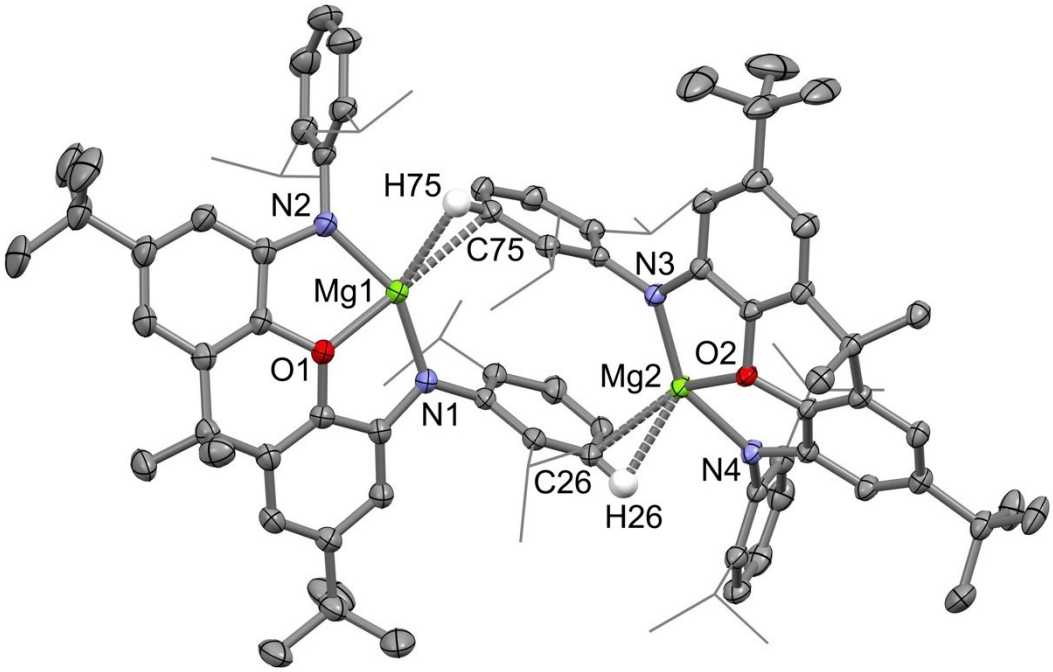

Figure S11. Molecular structures of **4** as determined by X-ray crystallography. Non-coordinating solvent molecules and most hydrogen atoms have been removed, and selected groups of the **NON** ligand are shown in wireframe for clarity. Displacement ellipsoids set at the 50% probability level.

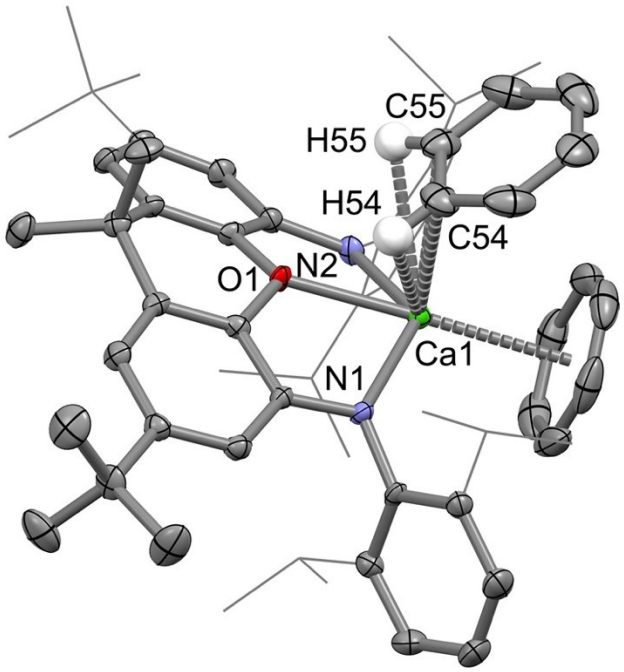

Figure S12. Molecular structures of **4** as determined by X-ray crystallography. Non-coordinating solvent molecules and most hydrogen atoms have been removed, and selected groups of the **NON** ligand are shown in wireframe for clarity. Displacement ellipsoids set at the 50% probability level.

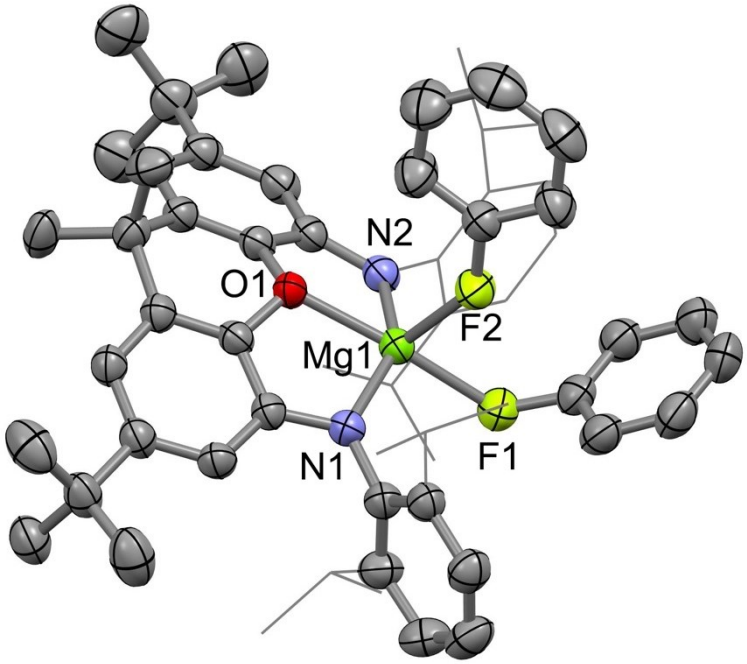

Figure S13. Molecular structures of **5** as determined by X-ray crystallography. Non-coordinating solvent molecules and hydrogen atoms have been removed, and selected groups of the **NON** ligand are shown in wireframe for clarity. Displacement ellipsoids set at the 50% probability level.

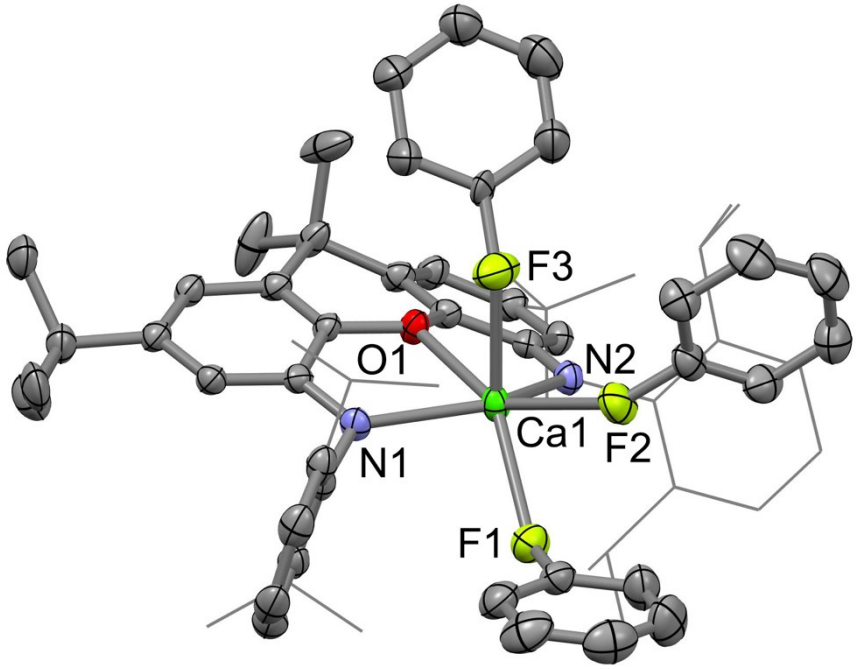

Figure S14. Molecular structures of **6** as determined by X-ray crystallography. Non-coordinating solvent molecules and hydrogen atoms have been removed, and selected groups of the **NON** ligand are shown in wireframe for clarity. Displacement ellipsoids set at the 50% probability level.

Neutron Laue diffraction experiment details

The structure of compound **4** was investigated using single-crystal neutron Laue diffraction. The unit-cell employed is as for the X-ray determination as this cannot be reliably determined using Laue neutron diffraction – related data such as space group are unchanged although the extent of the twinning inherent in the crystal grown for neutron diffraction is potentially greater than that for the crystals used for the X-ray diffraction experiment. Care was taken to ensure that the temperature of the experiment was matched to the X-ray experiment using an Oxford Cryosystems COBRA^{TM} cryostream which also served to protect the crystal from moisture and oxygen, the sample was handled immersed in argon to ensure compound stability while the crystal was transferred to the coldstream.

Neutron Laue data were collected on the KOALA instrument at ANSTO. Data were collected from a yellow single-crystal (2.8 x 0.8 x 0.6 mm^3) mounted to the phi axis of the KOALA diffractometer which stands at an end guide position of TG3 - a supermirror thermal neutron guide at the OPAL nuclear reactor at ANSTO. A total 33 Laue diffraction images (2000s per exposure) were collected in two different orientations (8 in run 1 and 25 in run 2) with 17° rotation of the crystal around the phi axis occurring between exposures. The crystal was manually reorientated by 102.6° between runs. A total of 57518 reflections with wavelengths between 0.85 and 1.70 Å covering the full sphere of reciprocal space to a maximum resolution of 0.90 Å were reduced [L4R(int) = 10.7(7.4) for 4σ observations] to yield 3709 independent reflections; 2610 with I > 3σ(I). Data reduction was by means of the LAUEG suite.[S7,S8]

Structural refinement: The neutron diffraction data obtained for **4** has been modelled using the CRYSTALS[S9] software package. Initial refinements were complicated by the near 90 beta value of the monoclinic cell which had to be resolved before progress towards an acceptable final model was possible. The crystal is a true merohedral twin and it is not possible to assess the scale (microscopic or macroscopic) of the twinning with multiple ways in which it can occur summed over the whole volume of the crystal. It should be noted that the twin operator is 100% correlated to any parameter which might usually (with X-rays) be considered to be capable of indicating whether the chiral structure is resolved and if refined, alongside a twin operator, any enantiomer sensitive parameter should give rise to an alert to the analyst of a matrix singularity. In the case of neutrons, there are no anomalous scatterers which can be employed to determine the extent of resolution of the chirality and here yields an assessment of the overall contributions to the scattering of the multiple ways in which the twinning can occur. It is notable that the twin fraction is very well determined 0.591(4).

With the depletion of the already somewhat limited data, due to the chiral space group, it has been necessary to choose carefully which parameters are included in the refinement and how restraints can best be employed to extract the chemical information which is the purpose of this study. Phenyl and benzene groups have been restrained to have carbon atoms coplanar and bond lengths similar while the solvating benzenes have been modelled only isotropically and further idealised. Displacement-similarity and vibrational restraints have been employed across the structure to supplement the data and a convergent refinement results which is fully detailed in the CIF. A clearly disordered *t*-Butyl group is well modelled across two sets of sites with a common displacement parameter for the methyl carbons (and a related riding isotropic displacement parameter for the H atoms) clearly improving the overall fit of the model to the data. The final R and Rw for this model converged to 0.073 and 0.084 and the goodness of fit was 1.523 for 866 parameters with 1233 restraints and 2226 reflections which met a 3 sigma criterion

of observability. A final difference map was featureless with minimum and maximum residual nuclear densities of -0.59 and 0.65 fm.

The finalised CIF has been deposited at the Cambridge Crystallographic Data Centre (2083003). This can be obtained free-of-charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

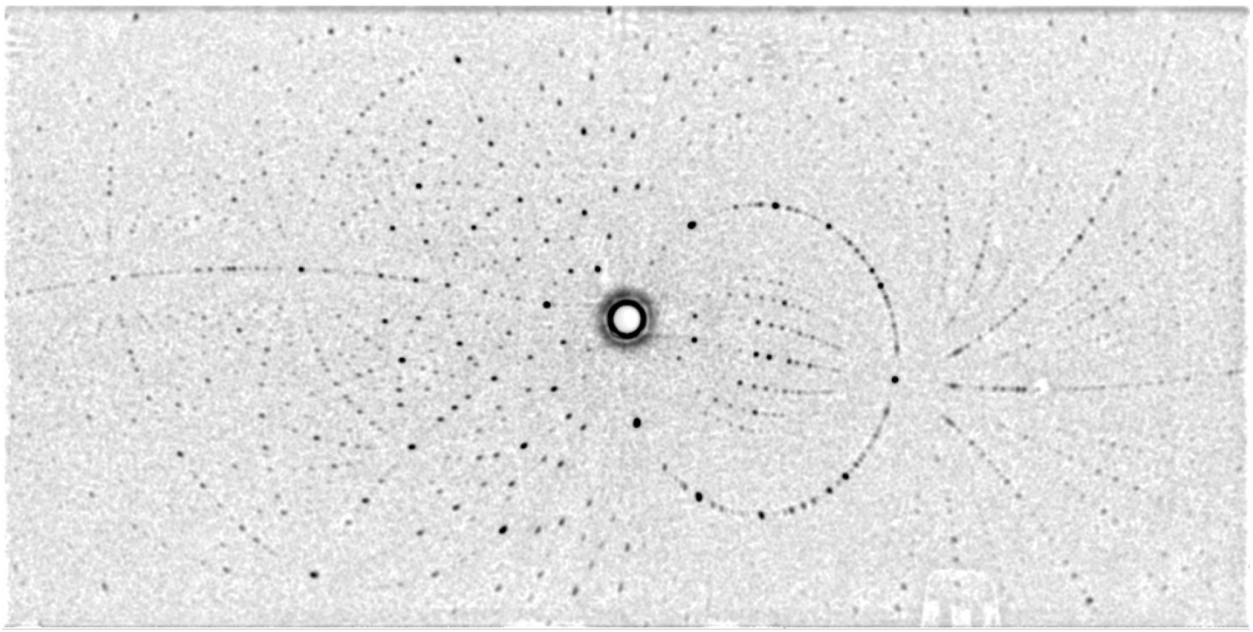

Figure S15. A representative Laue neutron diffraction image from a single-crystal of (**NON**)Ca(C_6H_6)$_2$ (**4**) from which data have been extracted for refinement of the neutron diffraction study reported here.

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