ASSOCIATED CONTENT

SUPPORTING INFORMATION

Unsymmetrical Bis(anilido)xanthene Ligands: Development and Use in the Preparation of Magnesium Diamide Complexes

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Contents

1. Syntheses and Spectra

General Experimental

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. Pentane and diethyl ether were distilled over Na/K alloy (50:50), while hexane, toluene and THF were distilled over molten potassium. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on either Bruker DPX300, Bruker AvanceIII 600 or Bruker AvanceIII 400 spectrometers and were referenced to the resonances of the solvent used. FTIR spectra were collected for solid samples or Nujol mulls on an Agilent Cary 630 attenuated total reflectance (ATR) spectrometer. Microanalyses were carried out at by the Elemental Analysis Service at London Metropolitan University. Melting points were determined in sealed glass capillaries under dinitrogen and are uncorrected. 4,5-dibromo-2,7-diethyl-9,9-dimethylxanthene,[S1] 2,4,6–tricyclohexylbromide,[S2] $Mg\{CH_2(SiMe_3)\}_2$[S3] and K/KI (5% w/w)[S4] were prepared according to their literature procedures. Unless otherwise stated, all other chemicals were purchased from Sigma-Aldrich and used as received.

Preparation of 4,5-diazido-2,7-diethyl-9,9-dimethyl-xanthene (B)

4,5-dibromo-2,7-diethyl-9,9-dimethylxanthene (2.20 g, 5.19 mmol) was dissolved in THF (~10 mL) and *ⁿ*BuLi (6.65 mL, 10.63 mmol, 2.05 eqv) added dropwise at –78 °C. The reaction mixture was stirred at –78 °C for 2 hours to give a dark yellow-brown suspension and tosyl azide (2.09 g, 10.63 mmol, 2.05 eqv) was then added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 18 hours to give a beige suspension (ensure sufficient solvent to enable stirring). A 1M NaOH solution was added to give a biphasic mixture. The organic layer was separated and the aqueous layer extracted with Et_2O (3 x 100 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and filtered to give a red solution. The volatiles were removed in vacuo to give a red oil which was allowed to stand for 2 hours to give an off-white solid. The solid was washed with minimum EtOH (10 mL) to give a pale yellow-pink solid. **Yield**: 1.49 g, 82%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (t, J = 7.6 Hz, 6H, $CH_2C\underline{H}_3$), 1.60 (s, 6H, $C(C\underline{H}_3)_2$), 2.63 (q, J = 7.6 Hz, 4H, $C\underline{H}_2CH_3$), 6.83 (d, J = 2.0 Hz, 2H, $_{xanth}Ar–\underline{H}$), 6.98 (d, J = 2.0 Hz, 2H, $_{xanth}Ar–\underline{H}$).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 15.8 ($CH_2\underline{C}H_3$), 28.7 ($\underline{C}H_2CH_3$), 32.1 ($C(\underline{C}H_3)_2$), 34.7 ($\underline{C}(CH_3)_2$), 117.4, 121.5, 127.6, 131.3, 139.7, 140.2 ($_{xanth}Ar–\underline{C}$).

I.R. (solid, cm^{-1}): 701 (m), 741 (m), 814 (m), 845 (s), 881 (w), 915 (w), 979 (m), 1064 (w), 1087 (w), 1123 (w), 1167 (s), 1258 (s), 1297 (s), 1347 (m), 1374 (m), 1440 (s), 1459 (s), 1579 (m), 1607 (m), 1622 (m), 2100 (s), 2873 (w), 2932 (w), 2963 (m).

Melting point and HRMS were not obtained due to the explosive nature of azides towards thermal decomposition.

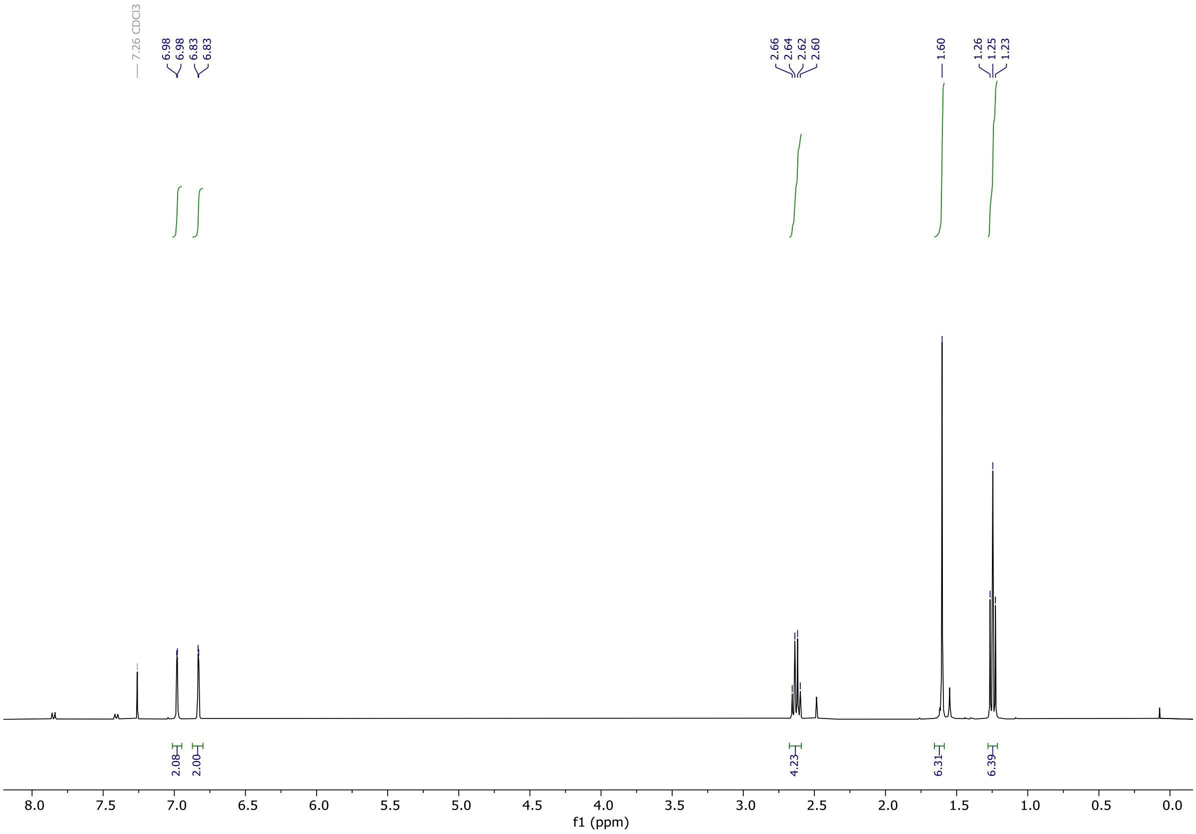


Figure S1: ^{1}H NMR spectrum (400 MHz, 298 K, CDCl$_3$) of **B**.

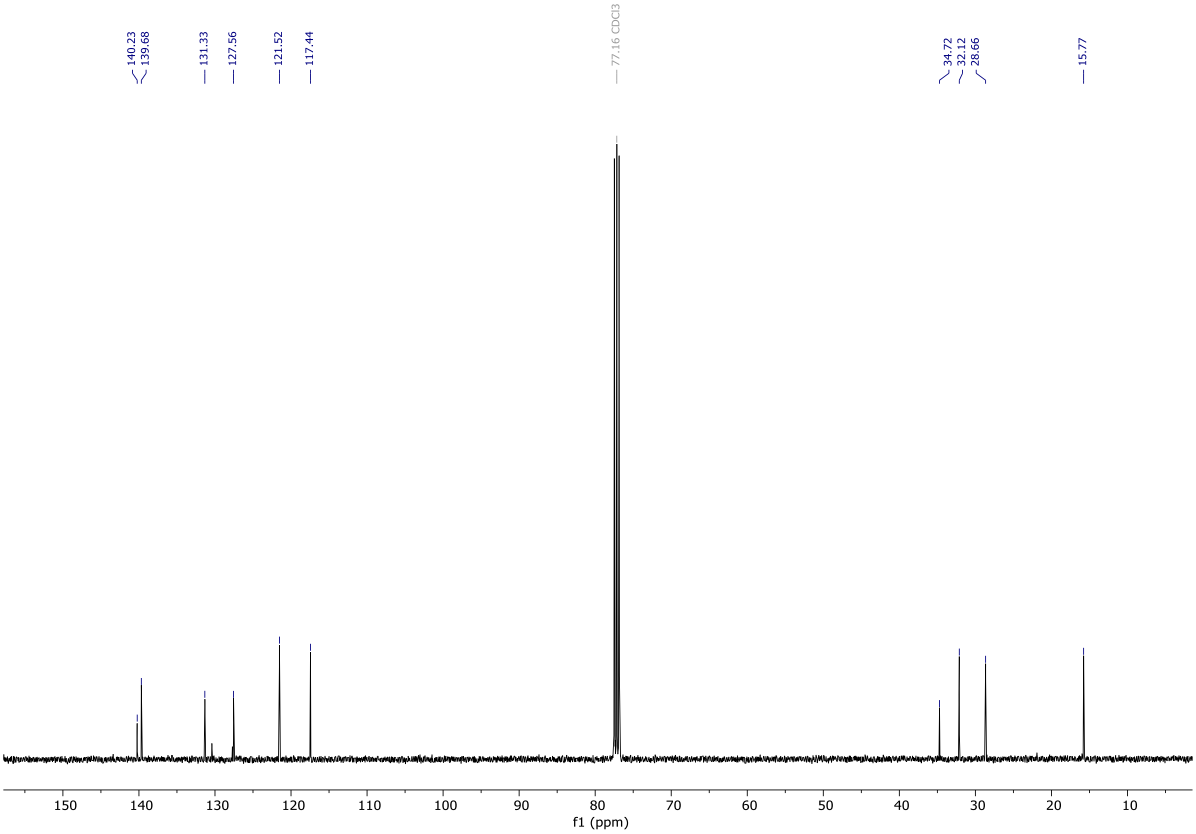


Figure S2: ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K, CDCl$_3$) of **B**.

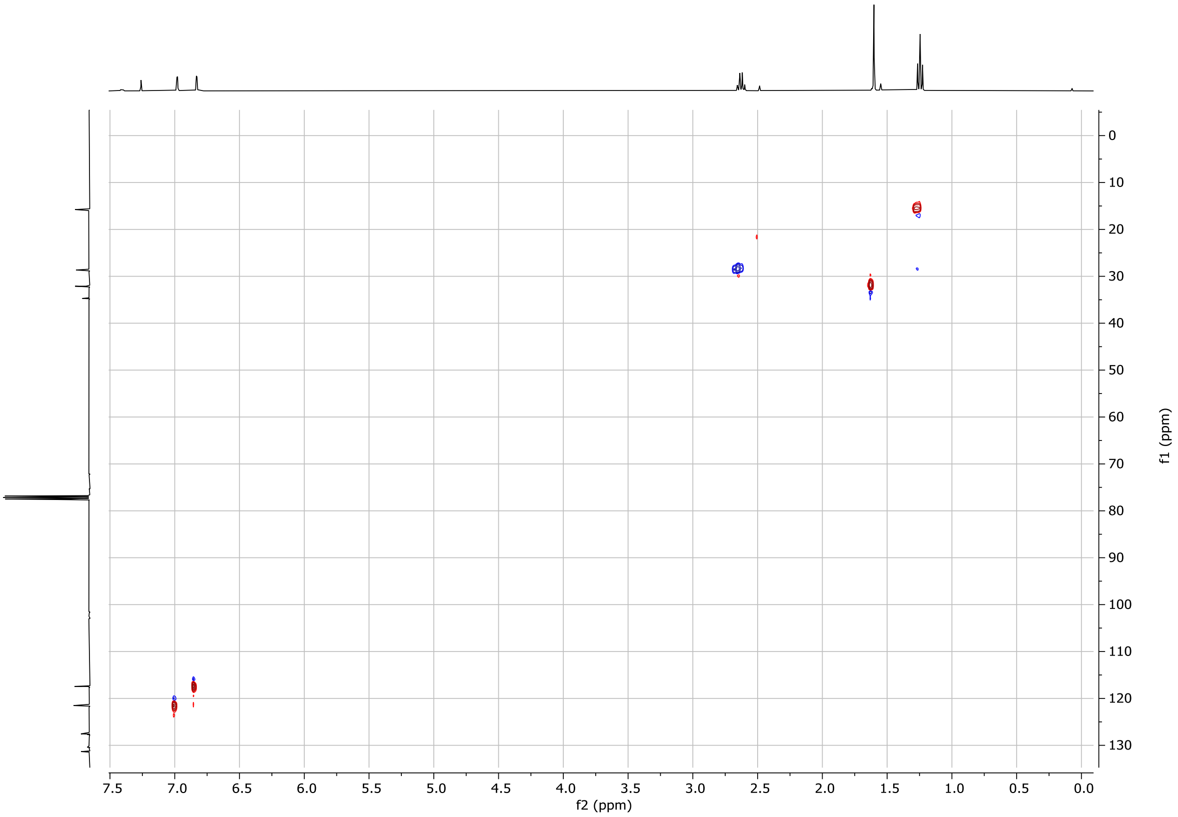


Figure S3: HSQC NMR spectrum (298 K, $CDCl_3$) of **B**.

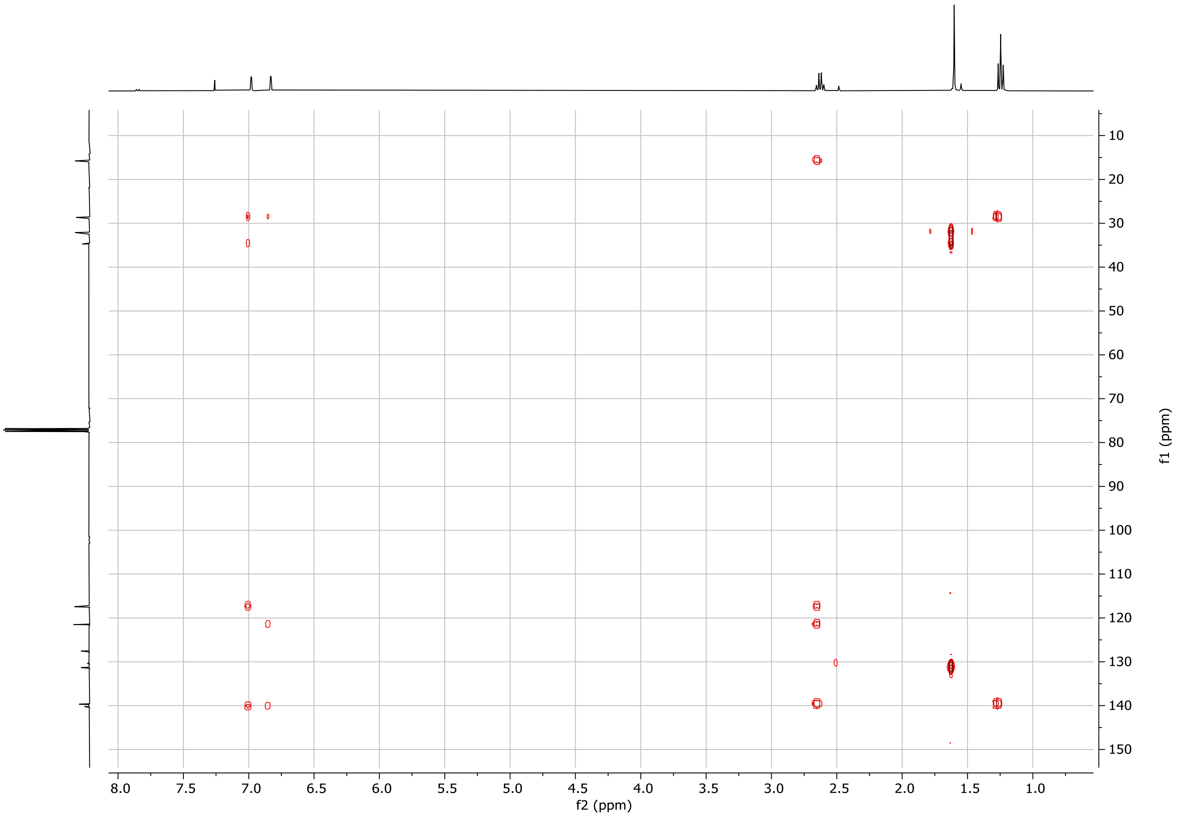


Figure S4: HMBC NMR spectrum (298 K, $CDCl_3$) of **B**.

Preparation of 4,5-diamino-2,7-diethyl-9,9-dimethyl-xanthene (C)

4,5-diazido-2,7-diethyl-9,9-dimethyl-xanthene (1.49 g, 4.28 mmol) and lithium aluminium hydride (0.49 g, 12.8 mmol, 3 eqv) were charged to a round-bottomed Schlenk and dissolved in Et_2O (100 mL). The reaction mixture was stirred at reflux for 2 hrs and the excess lithium aluminium hydride quenched with H_2O (~25 mL). The biphasic mixture was filtered through a frit and the remaining solid washed with Et_2O (100 mL). The organic layer was separated, washed with brine and 1M NaOH, dried over $MgSO_4$ and filtered. The solvent was removed in vacuo to give the product as a colourless solid that could be used without further purification. Crystallisation of the product is possible from hexane to give the title compound as colourless crystals. **Yield**: 1.49 g, 89%.

Large-scale (10 g scale) 2-step synthesis from 4,5-dibromo-2,7-diethyl-9,9-dimethylxanthene:

4,5-dibromo-2,7-diethyl-9,9-dimethylxanthene (10.00 g, 23.6 mmol) was dissolved in THF (~150 mL) and ^{n}BuLi (25.9 mL, 51.9 mmol, 2.2 eqv) added dropwise at –78 °C. The reaction mixture was stirred at –78 °C for 2 hours to give a dark yellow-brown suspension and tosyl azide (9.29 g, 47.1 mmol, 2.0 eqv) was then added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 18 hours to give a beige suspension. A 1M NaOH solution was added to give a biphasic mixture. The organic layer was separated and the aqueous layer extracted with Et_2O (3 x 100 mL). The separating funnel was not sealed at any point during this process. The combined organic layers were washed with brine, dried over $MgSO_4$ and filtered to give a red solution. The volatiles were removed (preferably at ambient pressure and temperature) to give a red waxy solid. The solid was dissolved in dry Et_2O (~250 mL) and added to a round-bottomed Schlenk containing lithium aluminium hydride (1.33 g, 35.3 mmol, 1.5 eqv). The reaction mixture was stirred at reflux for 2 hrs and the excess lithium aluminium hydride quenched with H_2O (~25 mL). The biphasic mixture was filtered through a frit and the remaining solid washed with Et_2O (250 mL). The organic layer was separated, washed with brine and 1M NaOH, dried over $MgSO_4$ and filtered. The solvent was removed in vacuo to give the product as a colourless solid that could be used without further purification. **Yield**: 6.55 g, 93 % (over 2 steps).

m.p. 105 – 106 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 (t, J = 7.6 Hz, 6H, $CH_2C\underline{H}_3$), 1.60 (s, 6H, $C(C\underline{H}_3)_2$), 2.56 (q, J = 7.6 Hz, 4H, $C\underline{H}_2CH_3$), 3.81 (s, 4H, $_{xanth}$Ar–N$\underline{H}_2$), 6.51 (d, J = 2.0 Hz, 2H, $_{xanth}$Ar–$\underline{H}$), 6.65 (d, J = 2.0 Hz, 2H, $_{xanth}$Ar–$\underline{H}$).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 15.9 ($CH_2\underline{C}H_3$), 28.8 ($\underline{C}H_2CH_3$), 32.0 ($C(\underline{C}H_3)_2$), 34.5 ($\underline{C}(CH_3)_2$), 113.2, 115.1, 130.3, 134.2, 137.0, 138.8 ($_{xanth}$Ar–$\underline{C}$).

I.R. (solid, cm^{-1}): 692 (w), 737 (w), 794 (w), 934 (w), 1030 (m), 1090 (w), 1162 (m), 1214 (s), 1261 (m), 1276 (m), 1300 (w), 1360 (w), 1445 (s), 1477 (s), 1625 (s), 2861 (w), 2926 (w), 2963 (m), 3024 (w), 3299 (w), 3345 (w), 3410 (w).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{19}H_{25}N_2O$: 297.1961; Found: 297.1952.

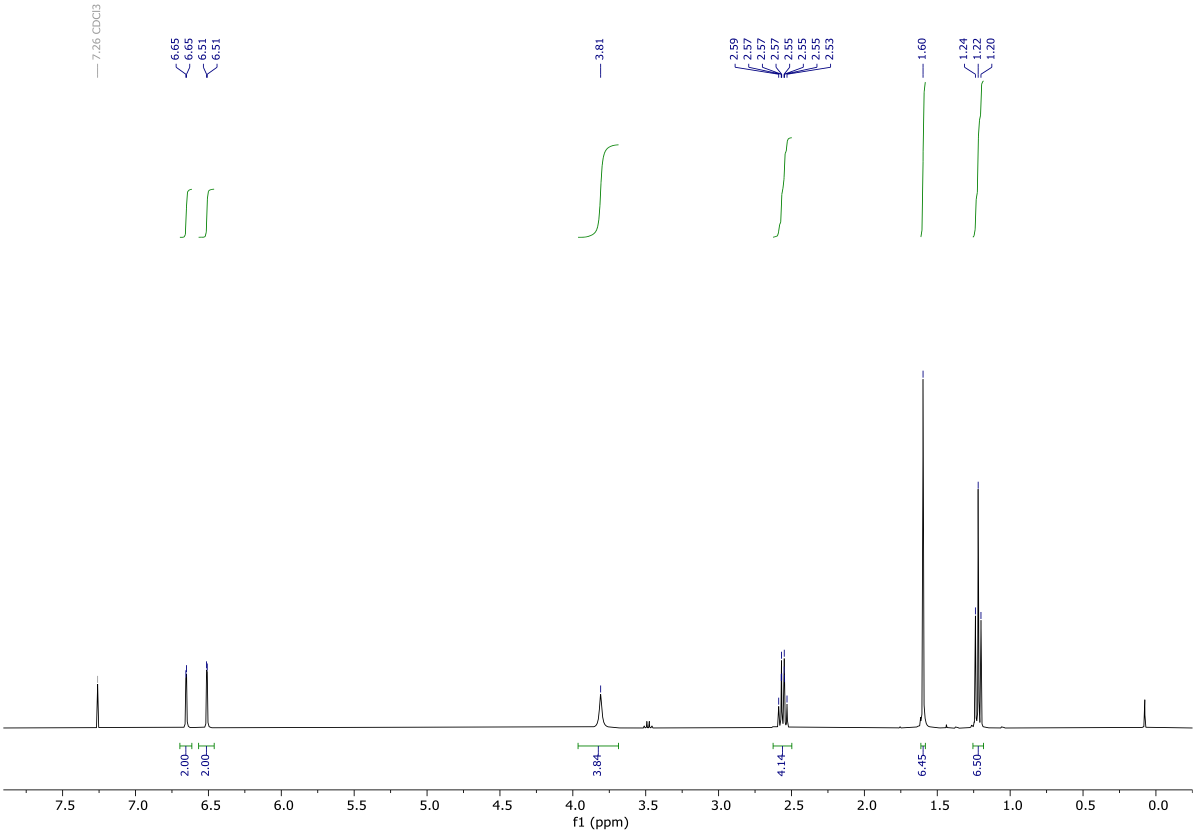


Figure S5: ^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of **C**.

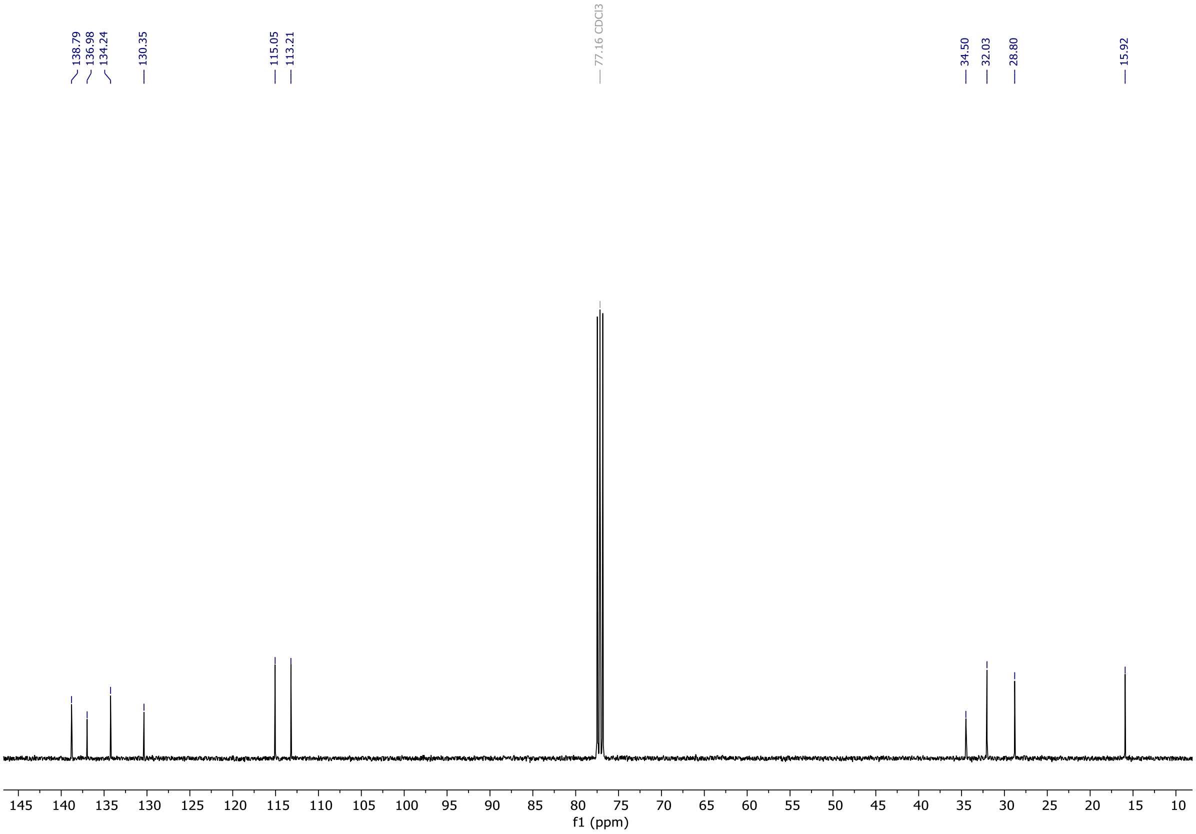


Figure S6: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, $CDCl_3$) of **C**.

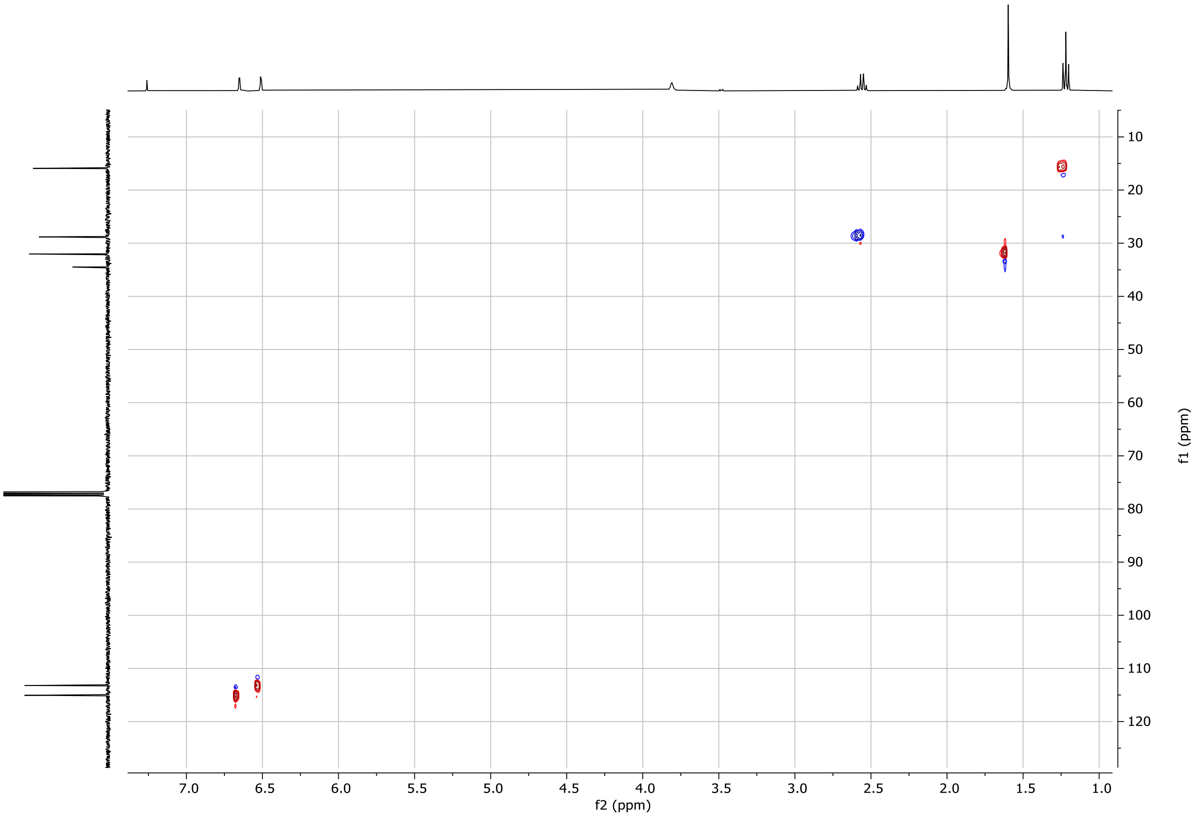


Figure S7: HSQC NMR spectrum (298 K, $CDCl_3$) of **C**.

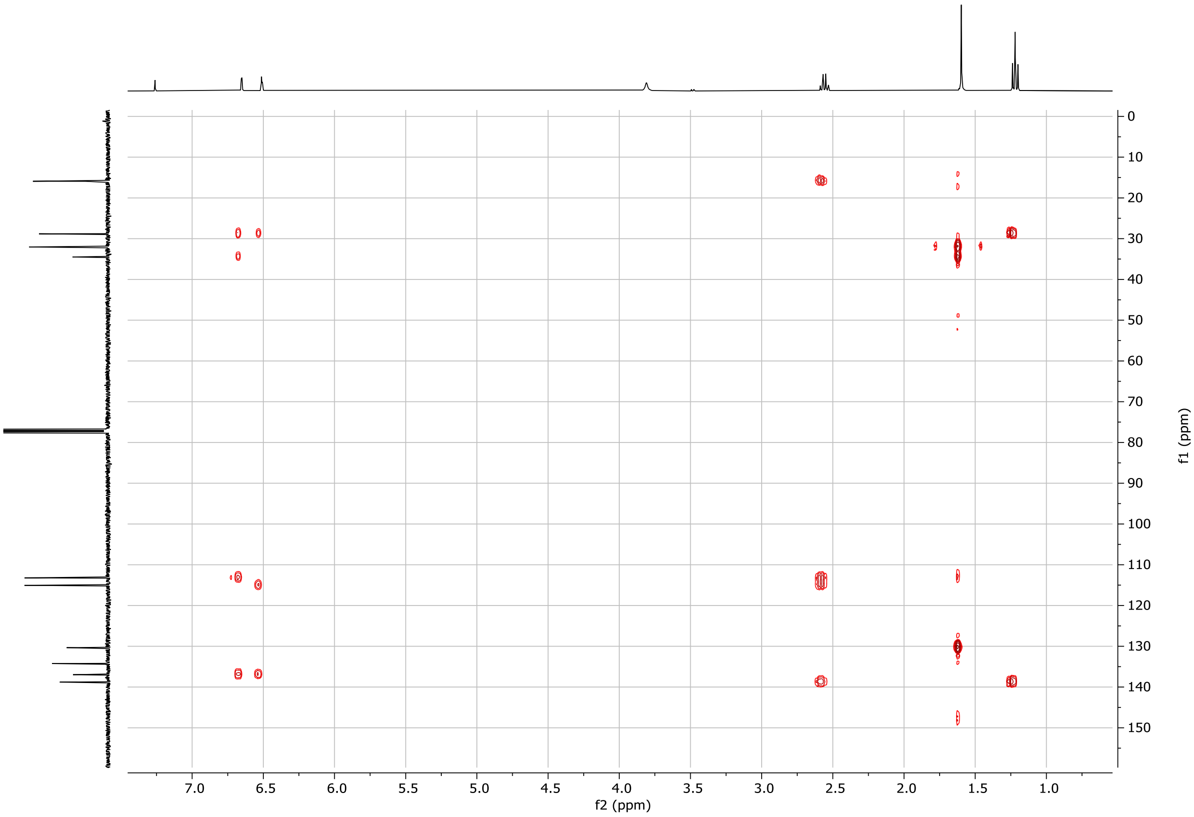


Figure S8: HMBC NMR spectrum (298 K, $CDCl_3$) of **C**.

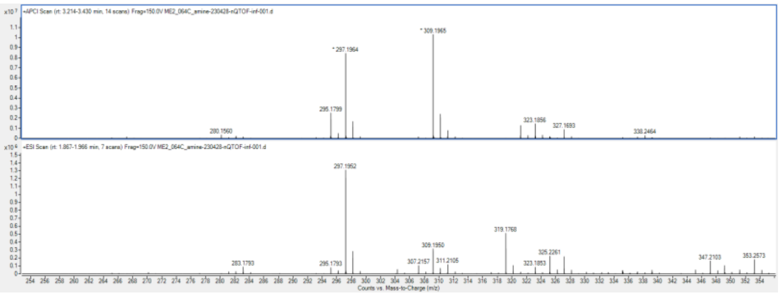


Figure S9: HRMS Spectrum of **C**.

Preparation of 4-(2,4,6-tricylcohexylanilido)-5-amino-2,7-diethyl-9,9-dimethylxanthene (D)

2,4,6–tricyclohexylphenyl bromide (2.04 g, 5.06 mmol) and 4,5-diamino-2,7-diethyl-9,9-dimethyl-xanthene (1.50 g, 5.06 mmol) were charged to a flame-dried Schlenk containing Pd(OAc)$_2$ (45 mg, 0.10 mmol), NaO^{t}Bu (681 mg, 6.8 mmol) and DPEPhos (164 mg, 0.14 mmol). Toluene (~50 mL) was added and the reaction mixture was allowed to stir for 18 hours at 90 °C under an atmosphere of N$_2$. The mixture was diluted with hexane (~200 mL) and filtered through celite. The organic layer was then washed with water (~100 mL) and brine (~100 mL) and dried over MgSO$_4$. The volatiles were removed in vacuo to give the crude product as a dark red oily residue. The crude material contains a mixture of the mono- (85%, elutes in diethyl ether) and bis-substituted (15%, elutes in hexane) xanthene products which can be separated by column chromatography over silica (hexane, 500 mL → diethyl ether, 500 mL). The diethyl ether fraction was dried and the product obtained as an off-white solid that could be used without further purification. Crystallisation of the product is possible from toluene to give colourless crystals of the title compound. **Yield**: 1.73 g, 56%.

m.p. 108 – 110 °C

^{1}H NMR (600 MHz, CDCl$_3$): δ 1.09 (t, J = 7.6 Hz, 3H, CH$_2$C$\underline{H}_3$), 1.11 – 1.21 (m, 4H, Cy–$\underline{H}$), 1.24 (t, J = 7.6 Hz, 3H, CH$_2$C$\underline{H}_3$), 1.26 – 1.51 (m, 14H, Cy–$\underline{H}$), 1.59 – 1.62 (m, 2H, Cy–$\underline{H}$), 1.64 (s, 6H, C(C$\underline{H}_3$)$_2$), 1.71 – 2.01 (m, 12H, Cy–$\underline{H}$), 2.43 (q, J = 7.6 Hz, 2H, C$\underline{H}_2$CH$_3$), 2.48 – 2.55 (m, 1H, Cy–$\underline{H}$), 2.58 (q, J = 7.6 Hz, 2H, C$\underline{H}_2$CH$_3$), 2.75 – 2.83 (m, 2H, Cy–$\underline{H}$), 3.76 (s, 2H, $_{\mathrm{xanth}}$Ar–N$\underline{H}_2$), 5.50 (s, 1H, $_{\mathrm{xanth}}$Ar–N$\underline{H}$), 5.97 (d, J = 1.8 Hz, 1H, $_{\mathrm{xanth}}$Ar–$\underline{H}$), 6.54 (d, J = 1.8 Hz, 1H, $_{\mathrm{xanth}}$Ar–$\underline{H}$), 6.57 (d, J = 1.8 Hz, 1H, $_{\mathrm{xanth}}$Ar–$\underline{H}$), 6.70 (d, J = 1.8 Hz, 1H, $_{\mathrm{xanth}}$Ar–$\underline{H}$), 7.01 (s, 2H, $_{\mathrm{TCHP}}$Ar–$\underline{H}$).

^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$): δ 16.0, 16.2 (CH$_2\underline{C}$H$_3$), 26.4, 26.4, 27.0, 27.2, 27.2, 28.8 (Cy–$\underline{C}$), 29.1 (CH$_2\underline{C}$H$_3$), 32.0 (C($\underline{C}$H$_3$)$_2$), 33.7 (Cy–$\underline{C}$), 34.6 (C($\underline{C}$H$_3$)$_2$), 34.8, 35.5, 39.2, 44.8 (Cy–$\underline{C}$), 110.2, 113.2, 113.3, 115.0, 122.9, 129.4, 130.7, 134.0, 134.3, 136.1, 136.6, 137.2, 138.7, 138.8, 145.9 ($_{\mathrm{xanth}}$Ar–$\underline{C}$, $_{\mathrm{TCHP}}$Ar–$\underline{C}$).

I.R. (solid, cm^{-1}): 691 (s), 742 (m), 842 (m), 1027 (w), 1058 (w), 1131 (w), 1159 (m), 1213 (s), 1258 (w), 1360 (w), 1437 (s), 1508 (w), 1588 (w), 1618 (m), 2580 (s), 2922 (s), 2960 (m), 3343 (br).

HRMS (ESI) m/z: [M + H]$^+$ calc. for $C_{43}H_{58}N_2O$: 619.4622; Found: 619.4642.

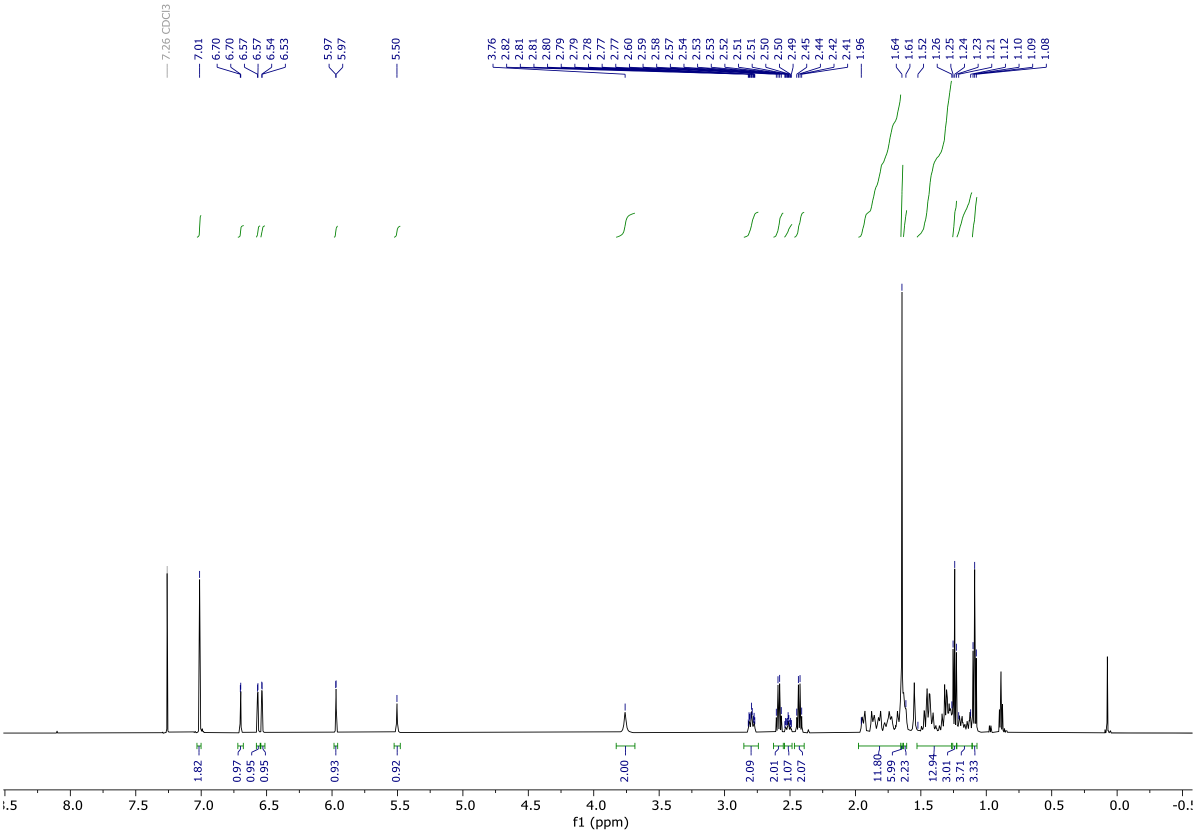


Figure S10: ^{1}H NMR spectrum (600 MHz, 298 K, $CDCl_3$) of **D**.

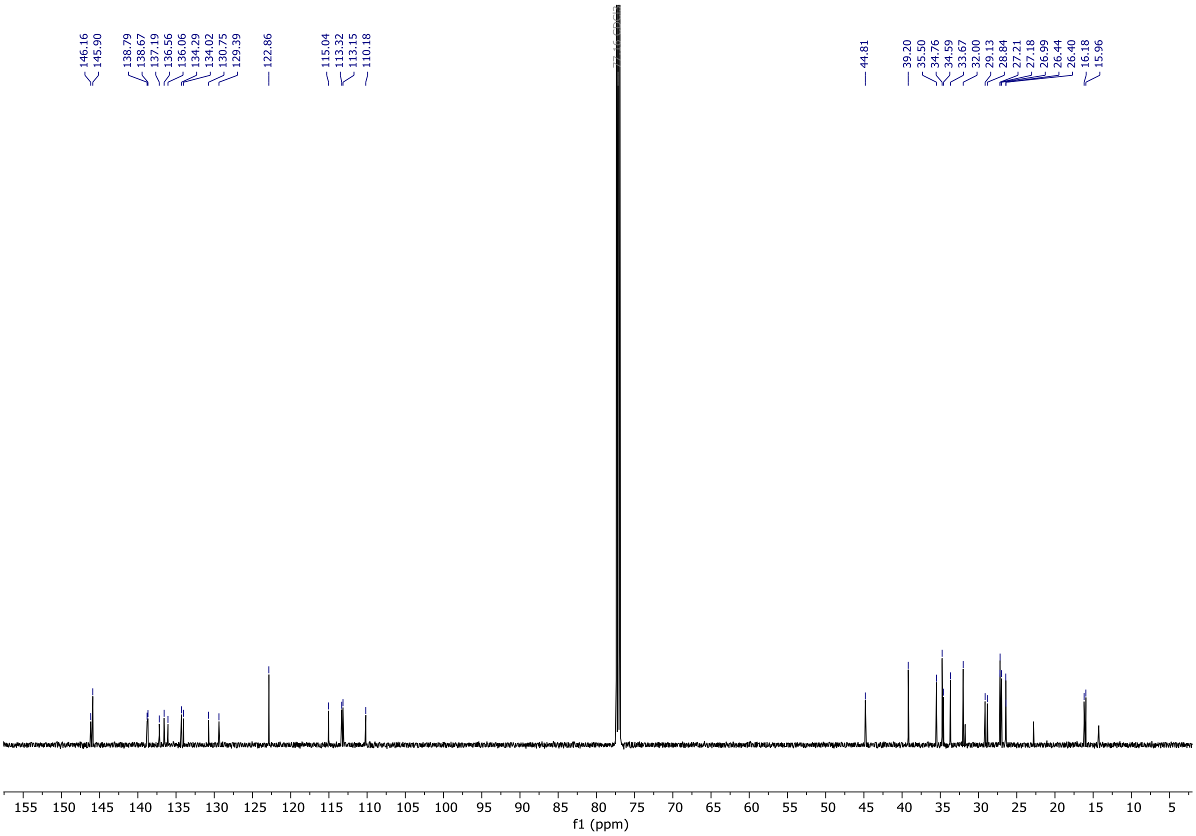


Figure S11: $^{13}C\{^1H\}$ NMR spectrum (151 MHz, 298 K, $CDCl_3$) of **D**.

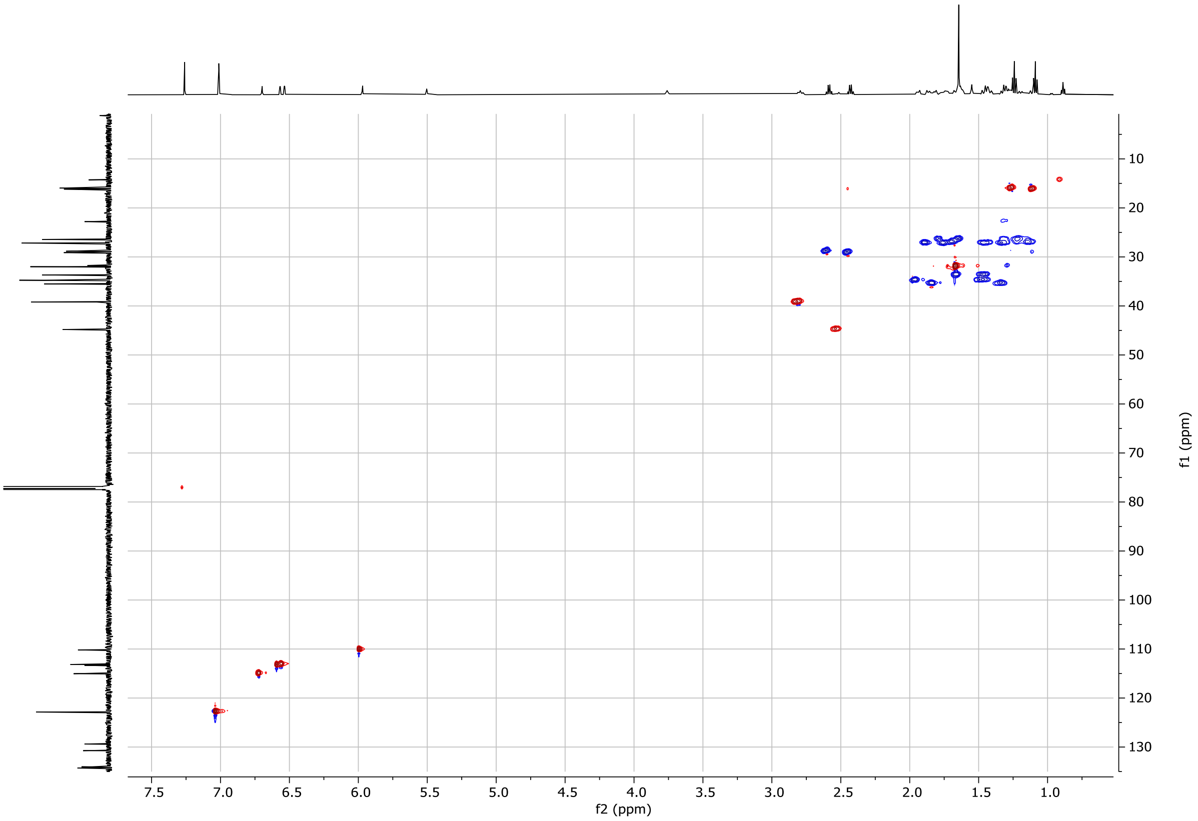


Figure S12: HSQC NMR spectrum (298 K, $CDCl_3$) of **D**.

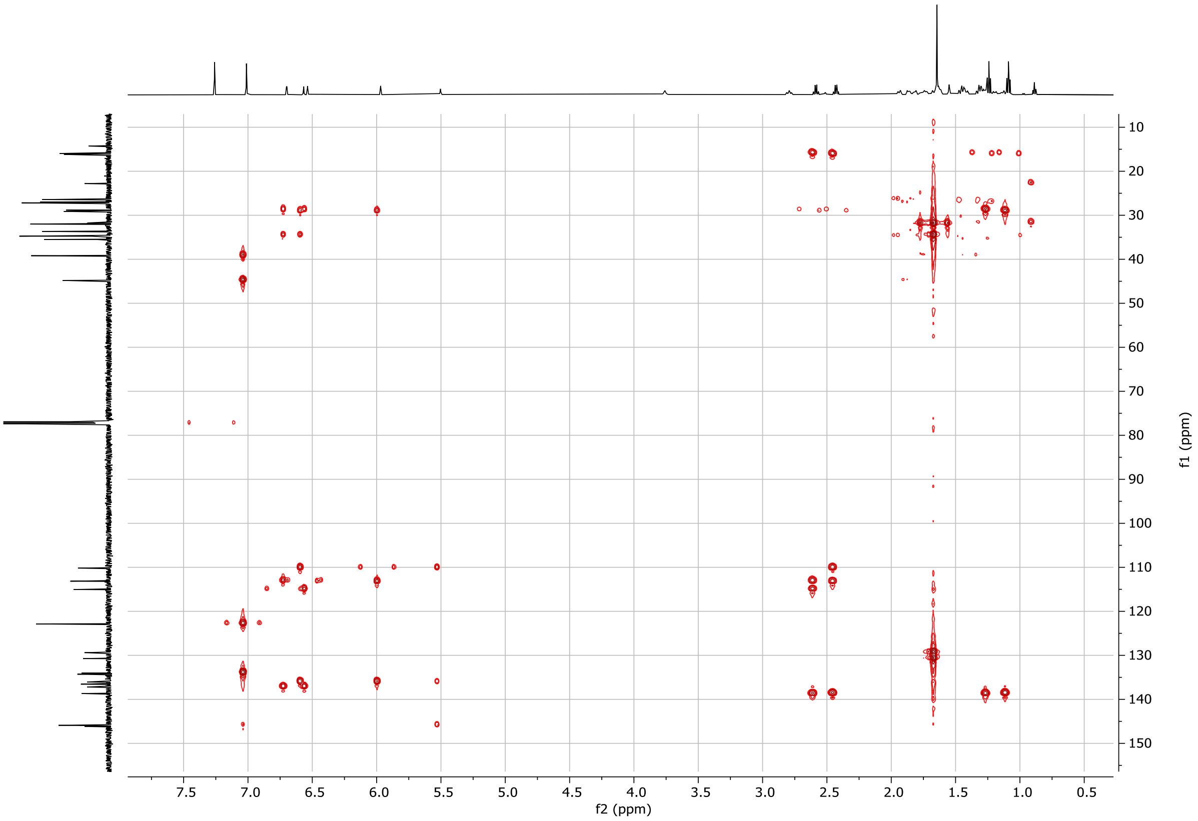


Figure S13: HMBC NMR spectrum (298 K, $CDCl_3$) of **D**.

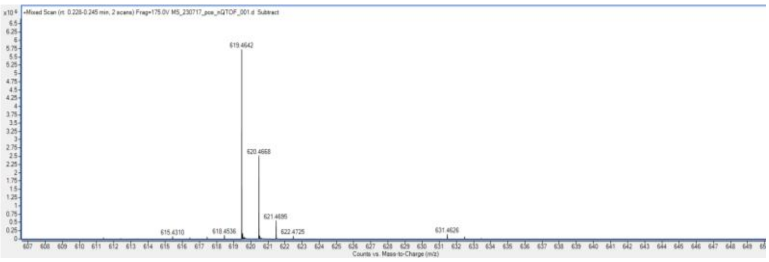


Figure S14: HRMS Spectrum of **D**.

Preparation of 4-(2,4,6-tricylcohexylanilido)-5-(2,4,6-trimethylanilido)-2,7-diethyl-9,9-dimethylxanthene, (NON$^{TCHP/Mes}$)H$_2$.

2,4,6–trimethylphenyl bromide (457 mg, 2.29 mmol) and 4-(2,4,6-tricylcohexylanilido)-5-amino-2,7-diethyl-9,9-dimethylxanthene (1.42 g, 2.29 mmol) were charged to a flame-dried Schlenk containing Pd(OAc)$_2$ (21 mg, 0.09 mmol), NaO^{t}Bu (309 mg, 3.20 mmol) and DPEPhos (75 mg, 0.14 mmol). Toluene (~50 mL) was added and the reaction mixture was allowed to stir for 18 hours at 90 °C under an atmosphere of N$_2$. The mixture was diluted with hexane (~200 mL) and filtered through celite. The organic layer was then washed with water (~100 mL) and brine (~100 mL) and dried over MgSO$_4$. The volatiles were removed *in vacuo* to give a dark red oily residue. The oil was purified by column chromatography over silica (hexane) to give the product as a colourless solid. Crystallisation of the product is possible (but not necessary) from toluene. **Yield**: 792 mg, 47%.

m.p. 57 – 59 °C.

^{1}H NMR (600 MHz, C$_6$D$_6$) δ 1.06 (t, J = 7.6 Hz, 6H, $CH_2C\underline{H}_3$), 1.13 – 1.60 (m, 18H, Cy–$\underline{H}$), 1.65 – 1.73 (m, 4H, Cy–$\underline{H}$), 1.76 – 1.82 (m, 2H, Cy–$\underline{H}$), 1.92 – 1.96 (m, 2H, Cy–$\underline{H}$), 1.98 – 2.03 (m, 4H, Cy–$\underline{H}$), 2.17 (s, 3H, ${}_{Mes}Ar–C\underline{H}_3$), 2.25 (s, 6H, ${}_{Mes}Ar–C\underline{H}_3$), 2.29 (q, J = 7.6 Hz, 2H, $C\underline{H}_2CH_3$), 2.37 (q, J = 7.6 Hz, 2H, $C\underline{H}_2CH_3$), 2.58 (tt, J = 12.0, 3.2 Hz, 1H, Cy–$\underline{H}$), 3.19 (tt, J = 12.0, 3.2 Hz, 2H, Cy–$\underline{H}$), 5.70 (s, 1H, N$\underline{H}$), 5.93 (s, 1H, N$\underline{H}$), 6.69 (d, J = 2.0 Hz, 1H, ${}_{xanth}Ar–\underline{H}$), 6.72 (d, J = 2.0 Hz, 1H, ${}_{xanth}Ar–\underline{H}$), 6.86 (s, 2H, ${}_{TCHP}Ar–\underline{H}$), 7.28 (s, 2H, ${}_{Mes}Ar–\underline{H}$).

^{13}C{^{1}H} NMR (151 MHz, C$_6$D$_6$) δ 16.3, 16.7 ($CH_2\underline{C}H_3$), 18.4, 21.4 (${}_{Mes}Ar–\underline{C}$), 26.6, 26.7, 27.3, 27.4, 27.4 (Cy–$\underline{C}$), 29.4, 29.5 ($\underline{C}H_2CH_3$), 32.3 ($C(\underline{C}H_3)_2$), 34.6 (Cy–$\underline{C}$), 34.8 ($\underline{C}(CH_3)_2$), 35.2, 35.5, 39.8, 45.3 (Cy–$\underline{C}$), 110.1, 110.6, 114.4, 114.6, 123.4, 129.7, 130.2, 130.4, 134.7, 135.2, 135.4, 136.0, 136.6, 136.7, 137.1, 137.4, 139.3, 139.4, 146.5, 146.9 (${}_{xanth}Ar–\underline{C}$, ${}_{Mes}Ar–\underline{C}$, ${}_{TCHP}Ar–\underline{C}$).

I.R. (solid, cm^{-1}): 696 (m), 732 (s), 769 (w), 816 (w), 848 (m), 924 (w), 951 (w), 998 (w), 1031 (m), 1062 (w), 1083 (w), 1136 (w), 1165 (m), 1209 (s), 1240 (w), 1275 (m), 1293 (m), 1314 (m), 1351 (m), 1390 (m), 1445 (s), 1482 (m), 1508 (m), 1609 (m), 1622 (m), 2847 (s), 2922 (s), 2962 (m), 3024 (w), 3397 (w).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{52}H_{68}N_2O$: 737.5405; Found: 737.5398.

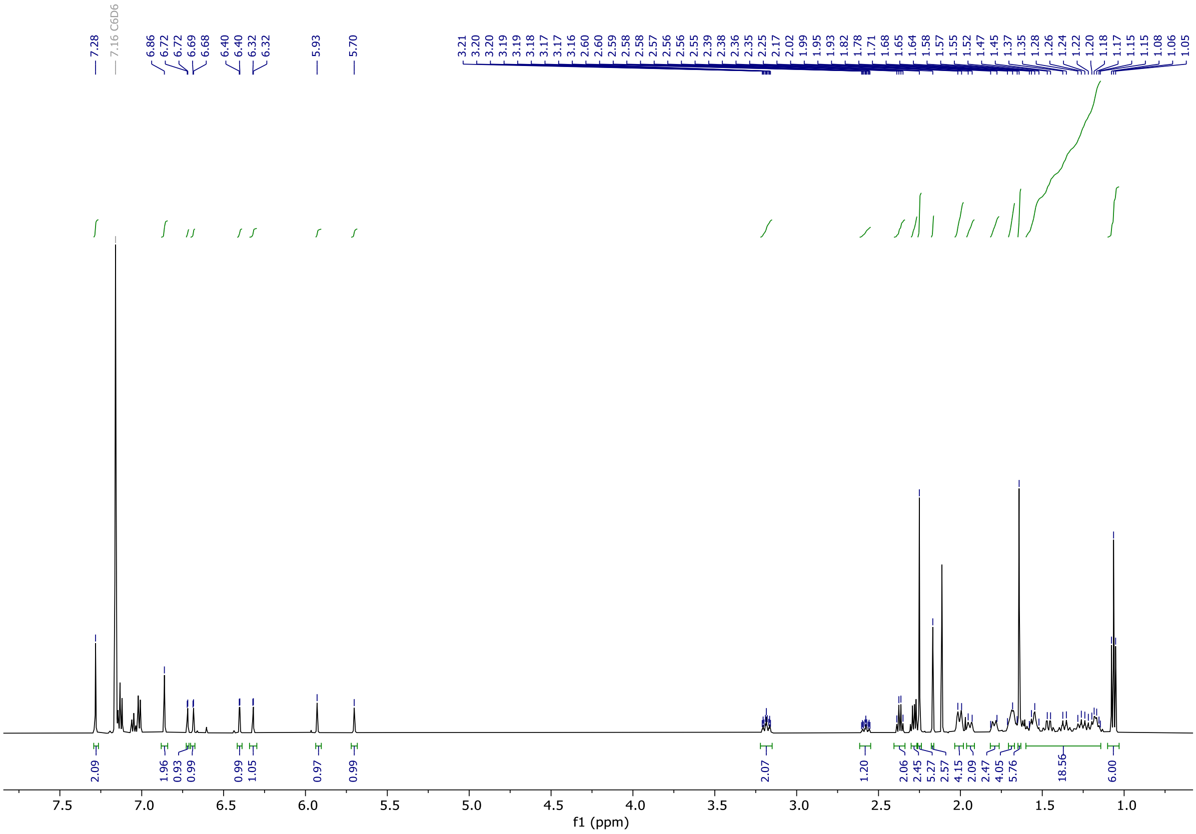


Figure S15: ^{1}H NMR spectrum (600 MHz, 298 K, C_6D_6) of $(NON^{TCHP/Mes})H_2$.

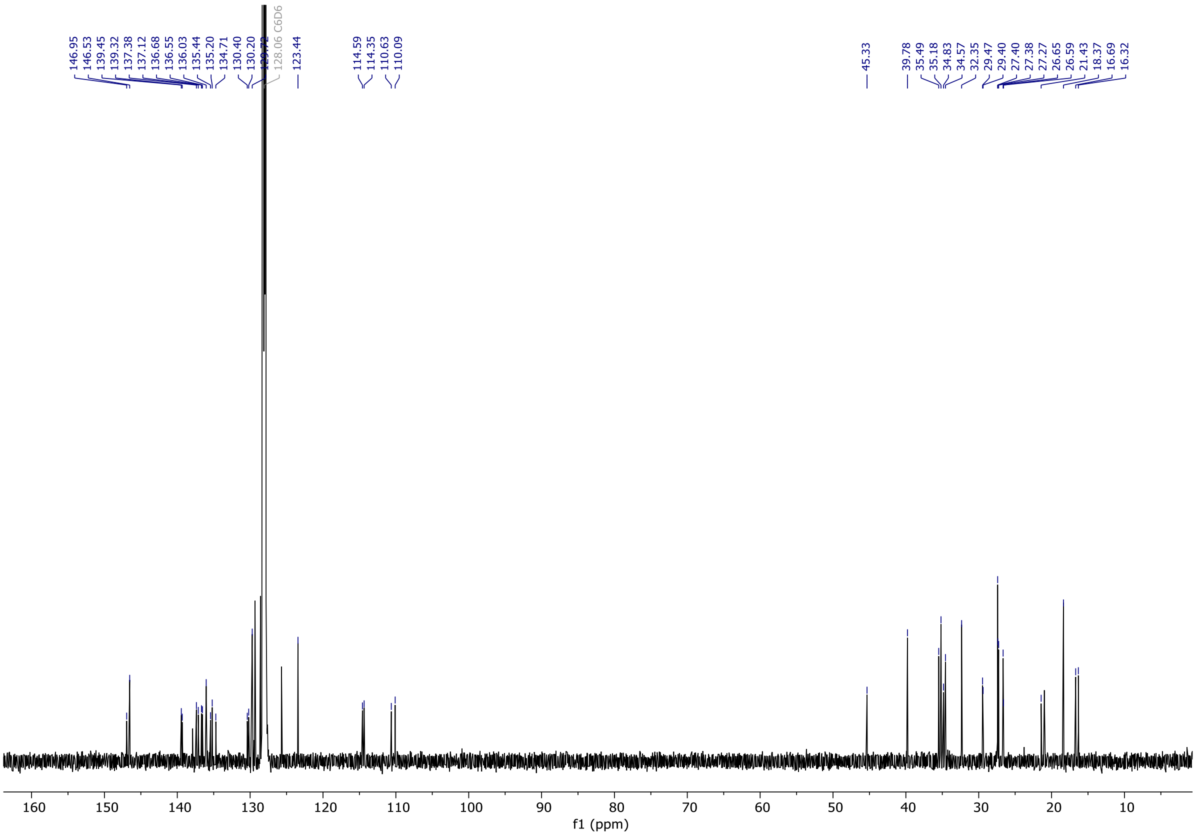


Figure S16: $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, 298 K, C_6D_6) of $(NON^{TCHP/Mes})H_2$.

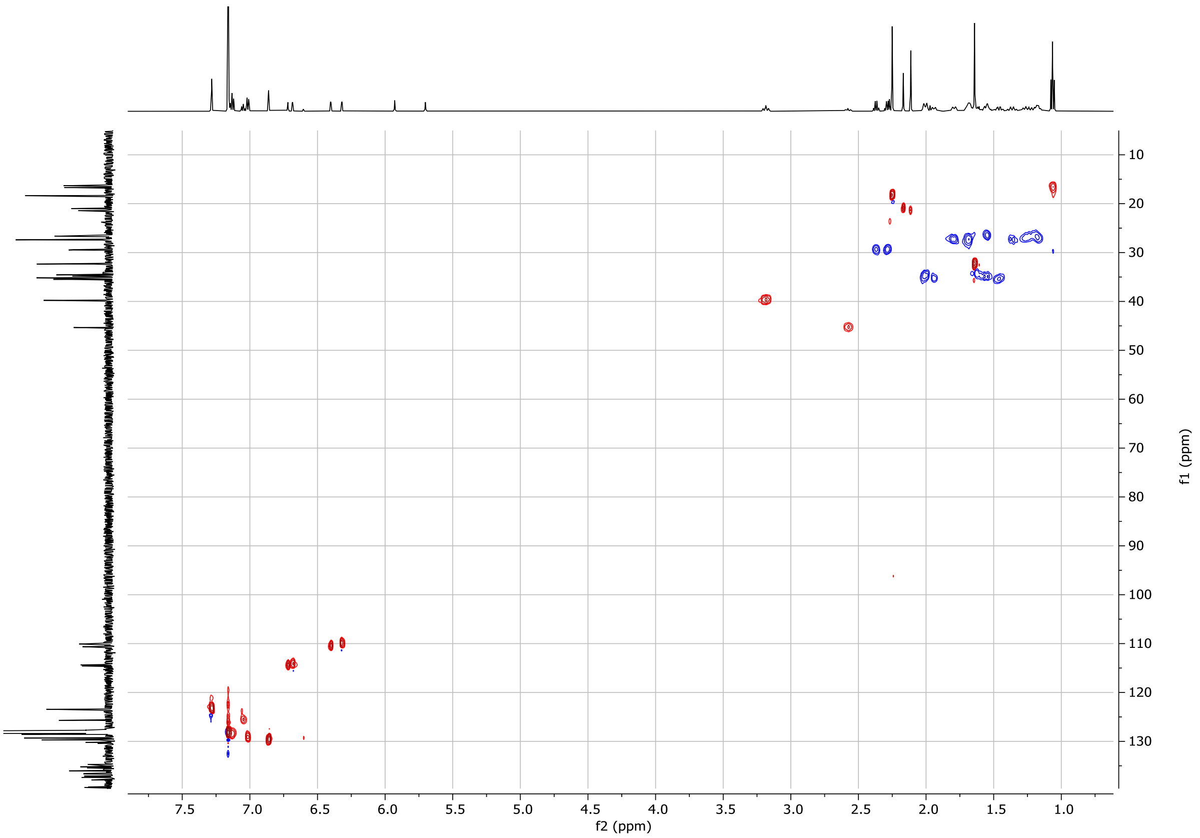


Figure S17: HSQC NMR spectrum (298 K, C_6D_6) of $(NON^{TCHP/Mes})H_2$.

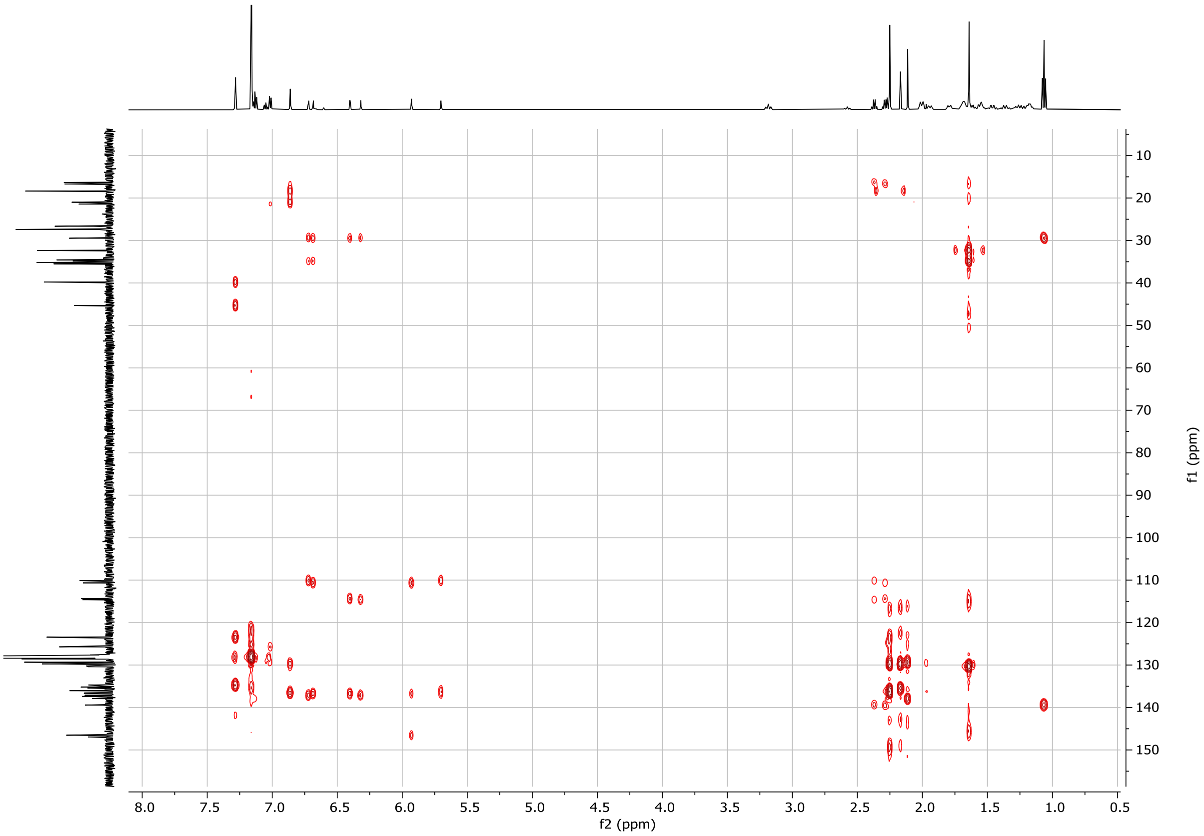


Figure S18: HMBC NMR spectrum (298 K, C_6D_6) of $(NON^{TCHP/Mes})H_2$.

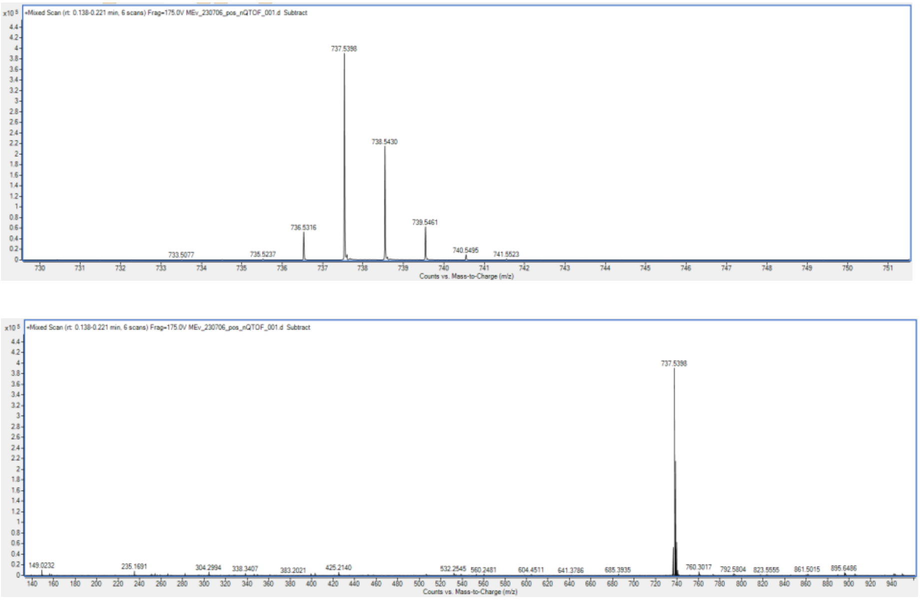


Figure S19: HRMS Spectrum of (NON$^{TCHP/Mes}$)H$_2$.

Preparation of 4-(2,4,6-tricylcohexylanilido)-5-(2,4,6-triisopropylanilido)-2,7-diethyl-9,9-dimethylxanthene, (NON$^{TCHP/Trip}$)H$_2$.

2,4,6–triisopropylphenyl bromide (483 mg, 2.42 mmol) and 4-(2,4,6-tricylcohexylanilido)-5-amino-2,7-diethyl-9,9-dimethylxanthene (1.50 g, 2.42 mmol) were charged to a flame-dried Schlenk containing Pd(OAc)$_2$ (22 mg, 0.09 mmol), NaO^{t}Bu (309 mg, 3.39 mmol) and DPEPhos (78 mg, 0.15 mmol). Toluene (~50 mL) was added and the reaction mixture was allowed to stir for 18 hours at 90 °C under an atmosphere of N$_2$. The mixture was diluted with hexane (~200 mL) and filtered through celite. The organic layer was then washed with water (~100 mL) and brine (~100 mL) and dried over MgSO$_4$. The volatiles were removed *in vacuo* to give a dark red oily residue. The oil was purified by column chromatography over silica (hexane) to give the product as a colourless solid. Crystallisation of the product is possible (but not necessary) from hexane. **Yield**: 1.07 g, 54%.

m.p. 180 – 182 °C.

^{1}H NMR (600 MHz, C$_6$D$_6$): δ 1.05 (t, J = 7.6 Hz, 3H, CH$_2$C$\underline{H}_3$), 1.06 (t, J = 7.6 Hz, 3H, CH$_2$C$\underline{H}_3$), 1.16 – 1.25 (m, 6H, Cy–$\underline{H}$), 1.24 (d, J = 6.8 Hz, 6H, CH(C$\underline{H}_3$)$_2$), 1.29 (d, J = 6.8 Hz, 12H, CH(C$\underline{H}_3$)$_2$), 1.31 – 1.46 (m, 6H, Cy–$\underline{H}$), 1.53 – 1.63 (m, 4H, Cy–$\underline{H}$), 1.59 (s, 6H, C(C$\underline{H}_3$)$_2$), 1.64 – 1.76 (m, 6H, Cy–$\underline{H}$), 1.77 – 1.83 (m, 2H, Cy–$\underline{H}$), 1.92 – 1.97 (m, 2H, Cy–$\underline{H}$), 1.98 – 2.06 (m, 4H, Cy–$\underline{H}$), 2.26 (q, J = 7.6 Hz, 2H, C$\underline{H}_2$CH$_3$), 2.31 (q, J = 7.6 Hz, 2H, C$\underline{H}_2$CH$_3$), 2.60 (tt, J = 12.0, 3.3 Hz, 1H, Cy–$\underline{H}$), 2.88 (hept, J = 7.4 Hz, 1H, C$\underline{H}$(CH$_3$)$_2$), 3.22 (tt, J = 12.0, 3.3 Hz, 2H, Cy–$\underline{H}$), 3.53 (hept, J = 7.4 Hz, 2H, C$\underline{H}$(CH$_3$)$_2$), 5.91 (s, 1H, N$\underline{H}$), 5.96 (s, 1H, N$\underline{H}$), 6.37 (d, J = 1.9 Hz, 1H, $_{xanth}$Ar–$\underline{H}$), 6.42 (d, J = 1.9 Hz, 1H, $_{xanth}$Ar–

H), 6.65 (d, J = 1.9 Hz, 1H, $_{\text{xanth}}$Ar–H), 6.67 (d, J = 1.9 Hz, 1H, $_{\text{xanth}}$Ar–H), 7.26 (s, 2H, $_{\text{TCHP}}$Ar–H), 7.29 (s, 2H, $_{\text{Trip}}$Ar–H).

^{13}C{^{1}H} NMR (151 MHz, C_6D_6): δ 16.8, 16.8 ($CH_2\underline{C}H_3$), 23.4, 24.5, 24.9 ($CH(\underline{C}H_3)_2$), 26.7, 27.3, 27.4, 27.5 (Cy–C), 29.0 ($\underline{C}H(CH_3)_2$), 29.5 ($\underline{C}H_2CH_3$), 32.5 ($C(\underline{C}H_3)_2$), 34.1 (Cy–C), 34.8 ($\underline{C}(CH_3)_2$), 34.9 ($\underline{C}H(CH_3)_2$), 35.2, 35.9, 39.9, 45.4 (Cy–C), 109.8, 110.4, 114.4, 114.6, 122.2, 123.4, 130.0, 133.9, 134.8, 136.3, 136.5, 136.9, 137.3, 139.5, 139.6, 146.6, 147.0, 147.6, 148.1 ($_{\text{xanth}}$Ar–C, $_{\text{Trip}}$Ar–C, $_{\text{TCHP}}$Ar–C).

I.R. (solid, cm^{-1}): 742 (w), 844 (m), 861 (w), 876 (w), 923 (w), 941 (w), 997 (w), 1031 (w), 1062 (w), 1165 (w), 1219 (s), 1239 (w), 1273 (w), 1292 (w), 1316 (w), 1359 (m), 1396 (m), 1448 (s), 1513 (s), 1612 (m), 1627 (m), 2850 (s), 2920 (s), 2958 (m), 3424 (w).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{58}H_{80}N_2O$: 821.6344; Found: 821.6349.

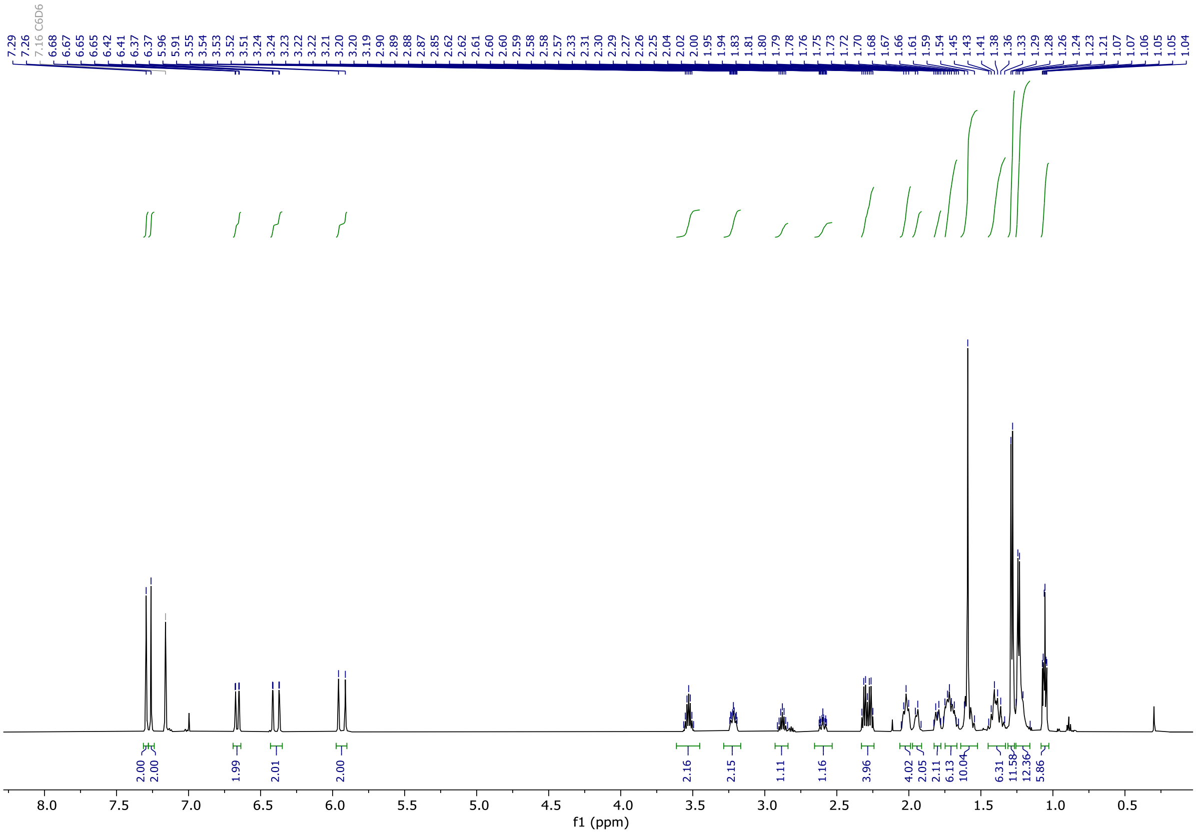


Figure S20: ^{1}H NMR spectrum (600 MHz, 298 K, C_6D_6) of $(NON^{TCHP/Trip})H_2$.

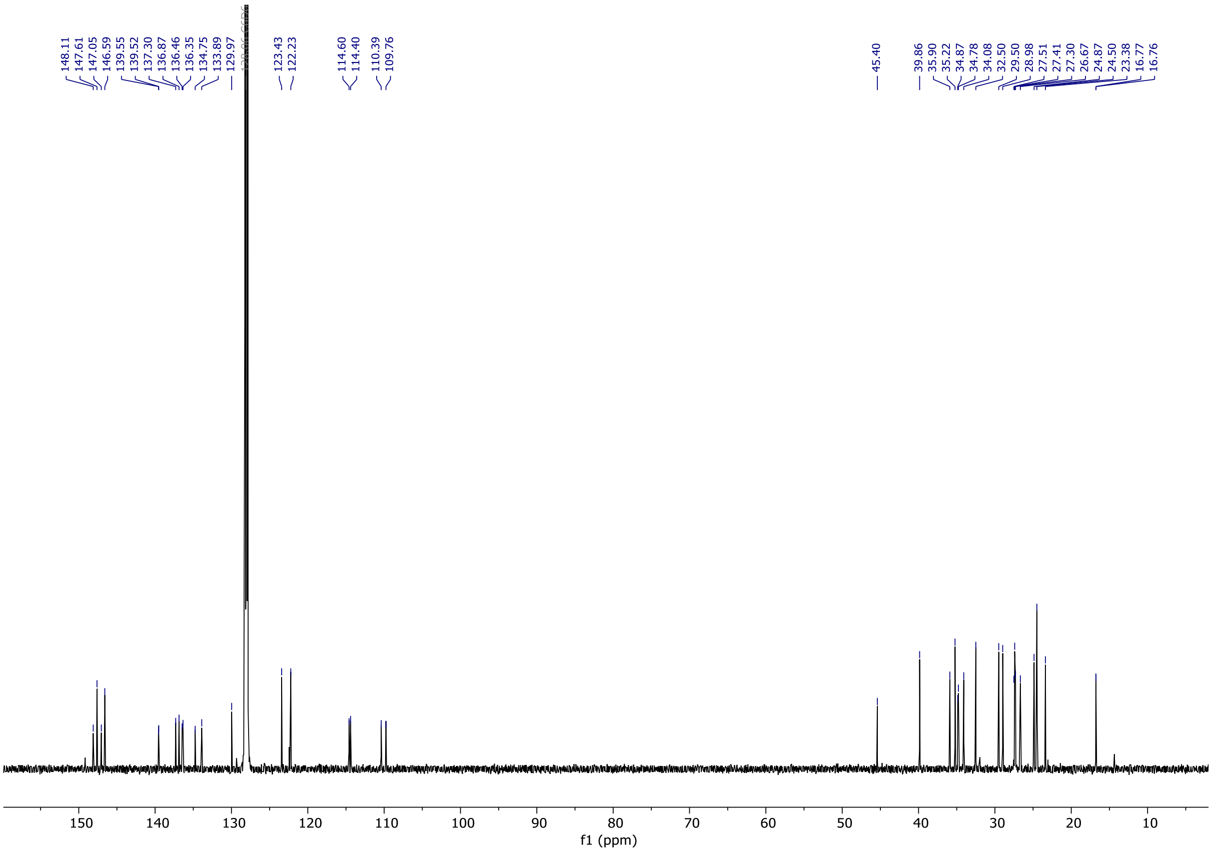


Figure S21: $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, 298 K, C_6D_6) of $(NON^{TCHP/Trip})H_2$.

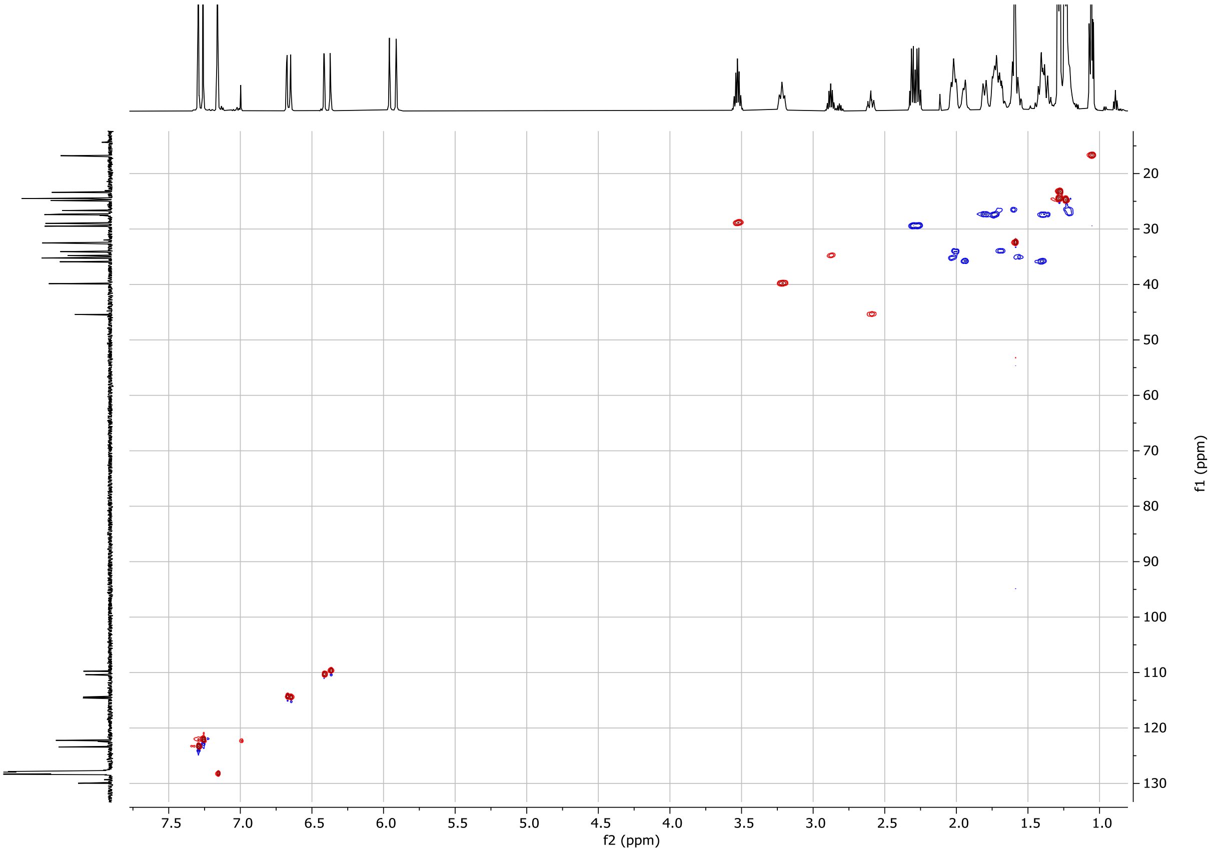


Figure S22: HSQC NMR spectrum (298 K, C_6D_6) of $(NON^{TCHP/Trip})H_2$.

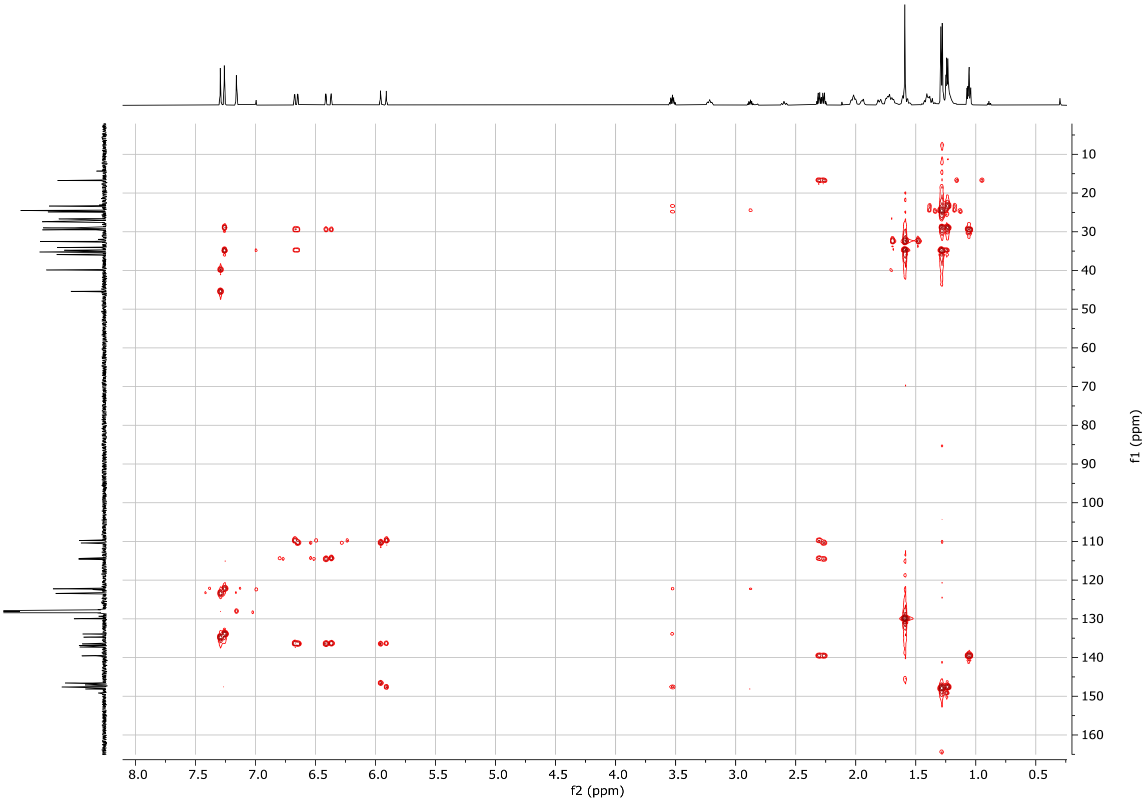


Figure S23: HMBC NMR spectrum (298 K, C_6D_6) of $(NON^{TCHP/Trip})H_2$.

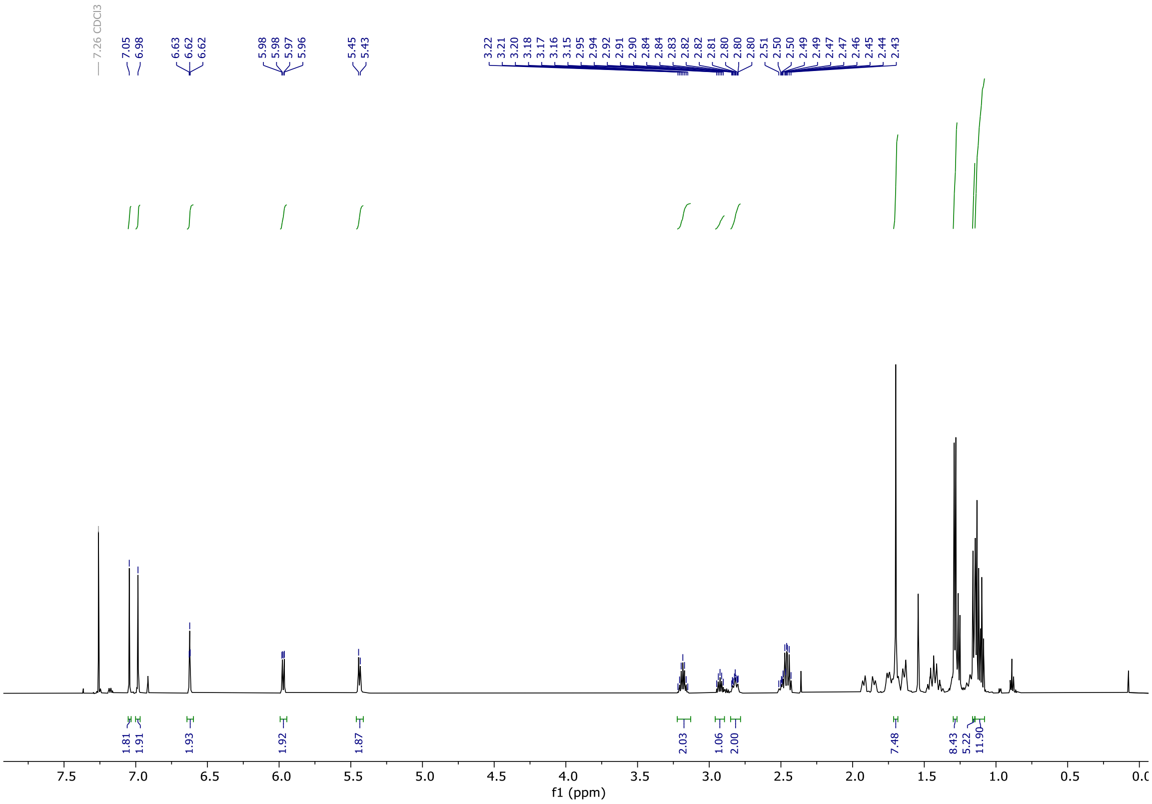


Figure S24: ^{1}H NMR spectrum (600 MHz, 298 K, $CDCl_3$) of $(NON^{TCHP/Trip})H_2$.

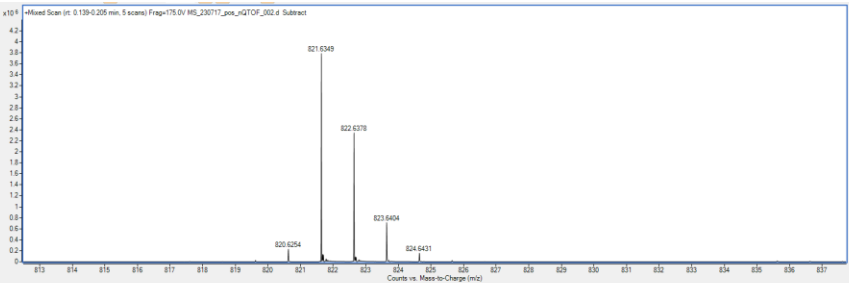


Figure S25: HRMS Spectrum of $(NON^{TCHP/Trip})H_2$.

Preparation of 4,5-bis(2,4,6-tricyclohexylanilido)-2,7-diethyl-9,9-dimethyl-xanthene, $(NON^{TCHP})H_2$.

2,4,6–tricyclohexylphenyl bromide (1.95 g, 4.82 mmol) and 4,5-diamino-2,7-diethyl-9,9-dimethyl-xanthene (0.72 g, 2.41 mmol) were charged to a flame-dried Schlenk containing $Pd(OAc)_2$ (22 mg, 0.10 mmol), NaO^tBu (650 mg, 6.8 mmol) and DPEPhos (78 mg, 0.14 mmol). Toluene (~50 mL) was added and the reaction mixture was allowed to stir for 18 hours at 90 °C under an atmosphere of N_2. The mixture was diluted with hexane (~200 mL) and filtered through celite. The organic layer was then washed with water (~100 mL) and brine (~100 mL) and dried over $MgSO_4$. The volatiles were removed in vacuo to give the crude product as a dark red oily residue. Purification was by means of flash chromatography on alumina (2 cm x 10 cm) using hexane (~500 mL) as the eluent. The product was isolated as white fluffy solid. **Yield**: 1.68 g, 74 %.

Spectral data match with previous literature reports.[S5]

Preparation of $[Mg(NON^{TCHP/Mes})]_2$ (1)

A 50 mL oven-dried Schlenk flask was charged with $NON^{TCHP/Mes}$–H_2 (90 mg, 0.12 mmol) and $Mg\{CH_2(SiMe_3)\}_2$ (25 mg, 0.12 mmol). Benzene (1 mL) was added and the suspension was boiled for 30 mins to give a clear yellow solution. The reaction mixture was cooled to room temperature, solvent reduced *in vacuo* and pentane (1 mL) added to give a white precipitate. The solid was collected *via* cannula filtration and dried *in vacuo* to give the title compound as an off-white powder. **Yield**: 60 mg, 65%. The title compound can be crystallized from a concentrated benzene solution stored at 8 °C for 18 hours.

m.p. >300 °C (dec).

^{1}H NMR (600 MHz, C_6D_6): δ 1.01 (t, J = 7.6 Hz, 6H, $CH_2C\underline{H}_3$), 1.09 (s, 3H, $C(C\underline{H}_3)_2$), 1.16 – 1.28 (m, 6H, Cy–$\underline{H}$), 1.36 (s, 3H, ${}_{Mes}Ar$–$C\underline{H}_3$), 1.38 – 1.63 (m, 14H, Cy–$\underline{H}$), 1.66 (s, 3H, $C(C\underline{H}_3)_2$), 1.70 – 1.92 (m, 8H, Cy–$\underline{H}$), 1.97 (s, 3H, ${}_{Mes}Ar$–$C\underline{H}_3$), 2.01 – 2.10 (m, 2H, Cy–$\underline{H}$), 2.15 – 2.29 (m, 4H, $C\underline{H}_2CH_3$, Cy–

$\underline{H}$), 2.46 (s, 3H, ${}_{\text{Mes}}$Ar–C$\underline{H}_3$), 2.51 – 2.64 (m, 3H, C$\underline{H}_2$CH$_3$, Cy–$\underline{H}$), 2.80 – 2.93 (m, 1H, Cy–$\underline{H}$), 3.30 – 3.42 (m, 1H, Cy–$\underline{H}$), 5.99 (d, J = 1.8 Hz, 1H, ${}_{\text{xanth}}$Ar–$\underline{H}$), 6.18 (d, J = 1.8 Hz, 1H, ${}_{\text{xanth}}$Ar–$\underline{H}$), 6.21 (d, J = 2.2 Hz, 1H, ${}_{\text{Mes}}$Ar–$\underline{H}$), 6.50 (d, J = 2.2 Hz, 1H, ${}_{\text{Mes}}$Ar–$\underline{H}$), 6.82 (d, J = 1.8 Hz, 1H, ${}_{\text{xanth}}$Ar–$\underline{H}$), 7.26 (d, J = 1.8 Hz, 1H, ${}_{\text{xanth}}$Ar–$\underline{H}$), 7.32 (d, J = 2.2 Hz, 1H, ${}_{\text{TCHP}}$Ar–$\underline{H}$), 7.38 (d, J = 2.2 Hz, 1H, ${}_{\text{TCHP}}$Ar–$\underline{H}$).

^{13}C{^{1}H} NMR (151 MHz, C_6D_6): δ 16.8, 18.1 (CH$_2\underline{C}$H$_3$), 19.4, 20.1, 22.0 (${}_{\text{Mes}}$Ar–$\underline{C}$H$_3$), 24.8 (C($\underline{C}$H$_3$)$_2$), 25.5, 26.5, 26.5, 26.6, 26.7, 26.9, 27.1, 27.5 (Cy–$\underline{C}$), 29.6, 30.0 ($\underline{C}$H$_2$CH$_3$), 33.8 (C($\underline{C}$H$_3$)$_2$), 35.0, 35.1, 35.3, 35.4, 36.1 (Cy–$\underline{C}$), 36.4 ($\underline{C}$(CH$_3$)$_2$), 37.0, 38.0, 38.1, 44.9 (Cy–$\underline{C}$), 105.9, 111.7, 119.0, 123.2, 123.8, 124.1, 124.3, 129.9, 130.1, 130.3, 131.2, 135.0, 135.2, 138.2, 141.5, 142.5, 143.1, 143.6, 145.0, 145.5, 145.7, 146.1, 148.2, 150.9 (${}_{\text{xanth}}$Ar–$\underline{C}$, ${}_{\text{TCHP}}$Ar–$\underline{C}$, ${}_{\text{Mes}}$Ar–$\underline{C}$).

I.R. (solid, cm^{-1}): 624 (w), 644 (w), 688 (m), 745 (m), 805 (w), 852 (s), 863 (m), 923 (w), 993 (w), 1025 (s), 1154 (s), 1185 (w), 1210 (s), 1236 (m), 1262 (m), 1292 (m), 1347 (m), 1426 (s), 1448 (s), 1569 (m), 1618 (m), 2850 (s), 2920 (s), 2961 (m).

Anal. Calcd. for $C_{104}H_{132}Mg_2N_4O_2$ (1518.84): C 82.24, H 8.76, N 3.69. Found: C 82.25, H 9.07, N 3.26.

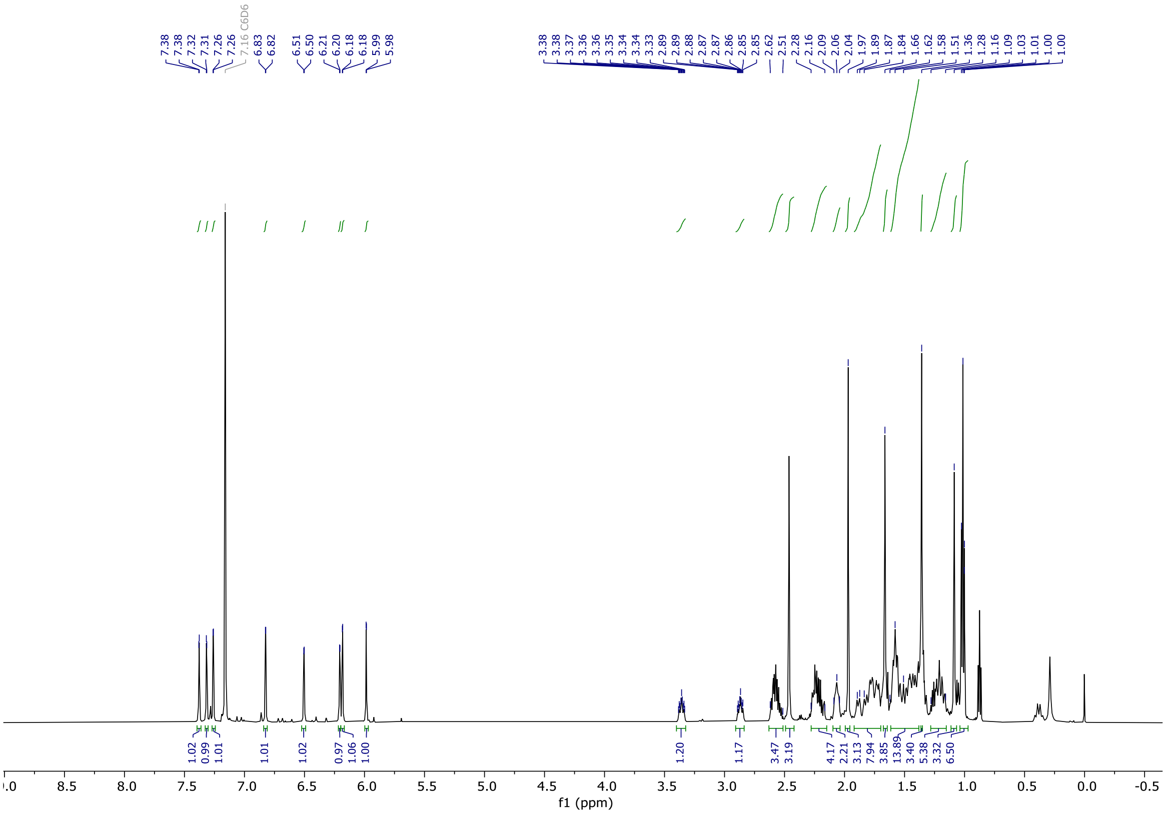


Figure S26: ^{1}H NMR spectrum (600 MHz, 298 K, C_6D_6) of **1**.

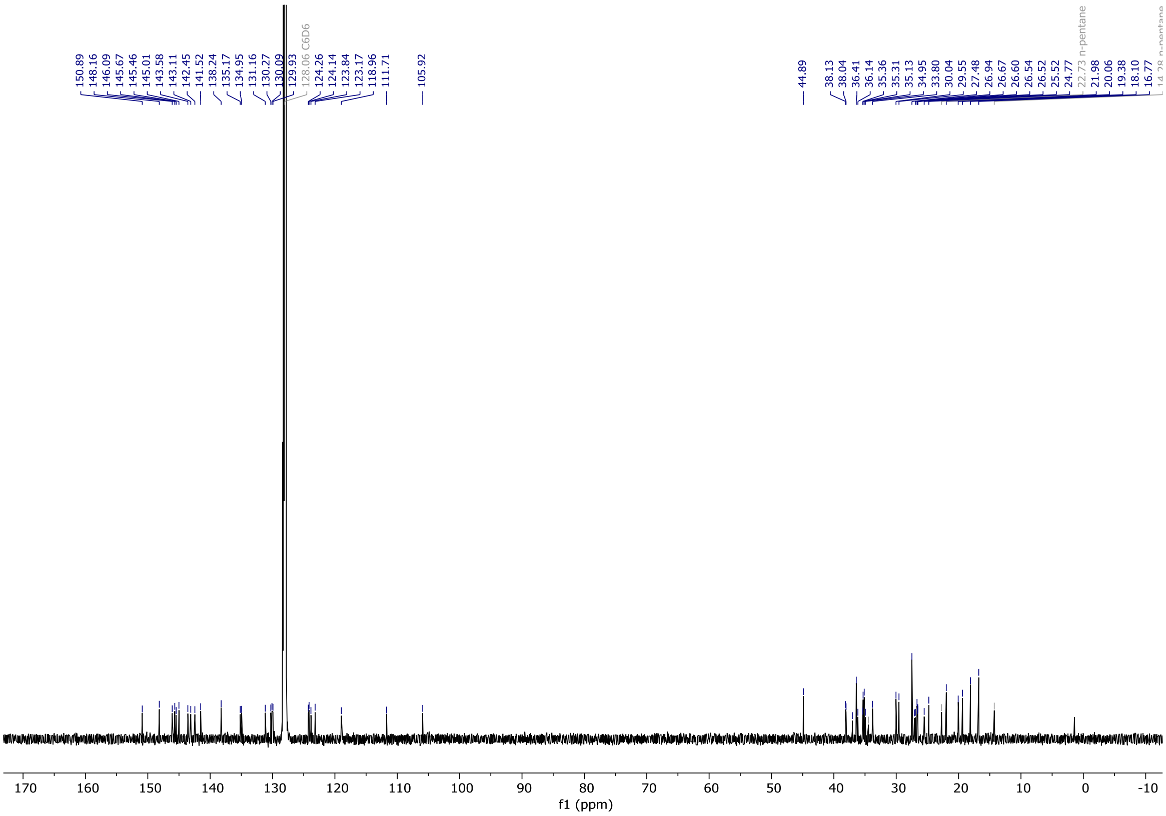


Figure S27: $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, 298 K, C_6D_6) of **1**.

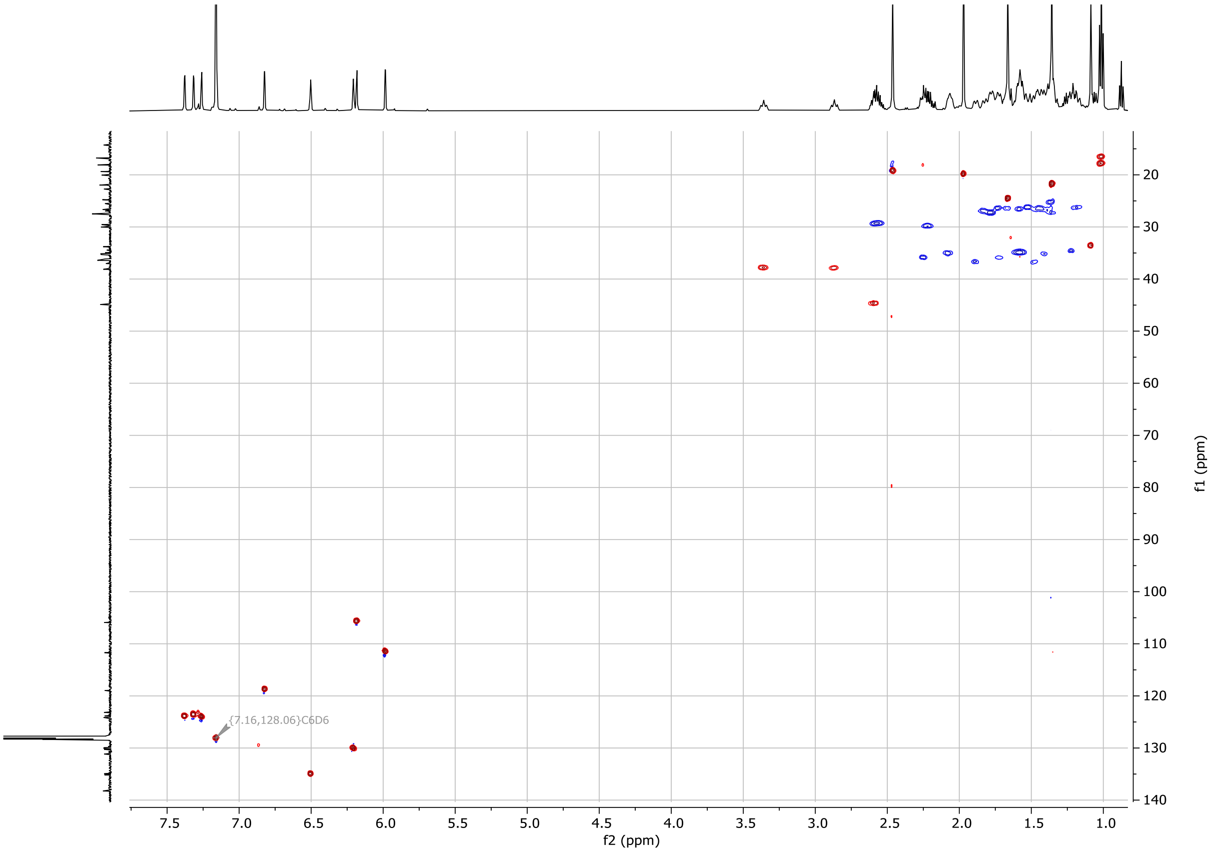


Figure S28: HSQC NMR spectrum (298 K, C_6D_6) of **1**.

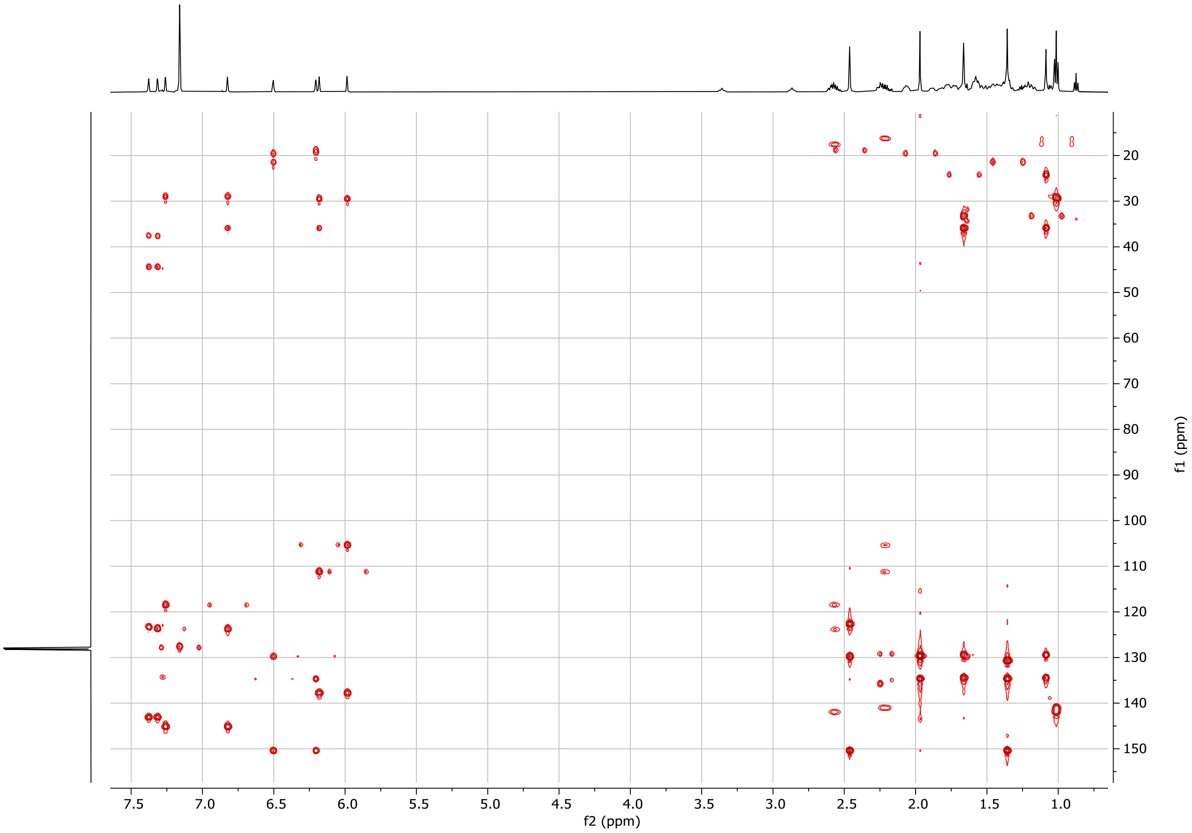


Figure S29: HMBC NMR spectrum (298 K, C_6D_6) of **1**.

Preparation of "Mg(NON$^{TCHP/Trip}$)" (2)

A 50 mL oven-dried Schlenk flask was charged with NON$^{TCHP/Trip}$–H_2 (1.00 g, 1.22 mmol) and Mg{$CH_2(SiMe_3)$}$_2$ (242 mg, 1.22 mmol). Methylcyclohexane (10 mL) was added and the suspension was heated at 80 °C for 30 mins to give a clear yellow solution. The reaction mixture was cooled to room temperature, filtered *via* cannula and dried *in vacuo* to give the title compound as a pale-yellow powder. **Yield**: 1.012 g, 98%.

m.p. 106 – 108 °C (dec).

^{1}H NMR (400 MHz, C_6D_6): δ 0.88 (d, J = 6.8 Hz, 6H, $CH(C\underline{H}_3)_2$), 1.04 – 1.13 (m, 6H, $CH_2C\underline{H}_3$), 1.14 – 1.27 (m, 18H, $CH(C\underline{H}_3)_2$, Cy–$\underline{H}$), 1.33 (d, J = 6.8 Hz, 6H, $CH(C\underline{H}_3)_2$), 1.39 – 1.51 (m, 4H, Cy–$\underline{H}$), 1.59 (s, 6H, $C(C\underline{H}_3)_2$), 1.61 – 1.68 (m, 4H, Cy–$\underline{H}$), 1.71 – 1.89 (m, 6H, Cy–$\underline{H}$), 2.00 – 2.14 (m, 4H, Cy–$\underline{H}$), 2.20 – 2.40 (m, 4H, $C\underline{H}_2CH_3$), 2.56 – 2.68 (m, 1H, Cy–$\underline{H}$), 2.94 (hept, J = 6.8 Hz, 1H, $C\underline{H}(CH_3)_2$), 2.99 – 3.12 (m, 2H, Cy–$\underline{H}$), 3.33 (hept, J = 6.8 Hz, 2H, $C\underline{H}(CH_3)_2$), 6.09 (br d, 1H, $_{xanth}$Ar–$\underline{H}$), 6.10 (br d, 1H, $_{xanth}$Ar–$\underline{H}$), 6.37 (br d, 1H, $_{xanth}$Ar–$\underline{H}$), 6.41 (br d, 1H, $_{xanth}$Ar–$\underline{H}$), 7.25 (s, 2H, $_{Trip}$Ar–$\underline{H}$), 7.26 (s, 2H, $_{TCHP}$Ar–$\underline{H}$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 17.2 ($CH_2\underline{C}H_3$), 23.2, 24.2, 24.8 ($CH(\underline{C}H_3)_2$), 25.9, 26.7, 26.8, 27.4, 27.5, 27.8 (Cy–$\underline{C}$), 29.0 ($\underline{C}H(CH_3)_2$), 29.9 ($C(\underline{C}H_3)_2$), 30.2 ($\underline{C}H_2CH_3$), 33.0, 34.7 (Cy–$\underline{C}$), 34.8 ($\underline{C}H(CH_3)_2$), 35.5 (Cy–$\underline{C}$), 35.7 ($\underline{C}(CH_3)_2$), 36.5, 40.0, 45.3 (Cy–$\underline{C}$), 108.3, 112.0, 112.3, 122.2, 123.4, 130.8, 130.9, 137.8, 140.9, 143.5, 144.4, 144.6, 144.9, 145.6, 147.1, 147.3 ($_{\text{xanth}}$Ar–$\underline{C}$, $_{\text{TCHP}}$Ar–$\underline{C}$, $_{\text{Trip}}$Ar–$\underline{C}$).

I.R. (solid, cm^{-1}): 643 (w), 677 (s), 844 (w), 861 (w), 941 (w), 1027 (m), 1060 (w), 1133 (w), 1180 (w), 1215 (m), 1293 (w), 1360 (w), 1381 (w), 1446 (s), 1508 (w), 1579 (m), 1608 (m), 2850 (s), 2922 (s), 2958 (m).

Anal. Calcd. for $C_{58}H_{78}MgN_2O$ (843.58): C 82.58, H 9.32, N 3.32. Found: C 82.79, H 9.28, N 2.84.

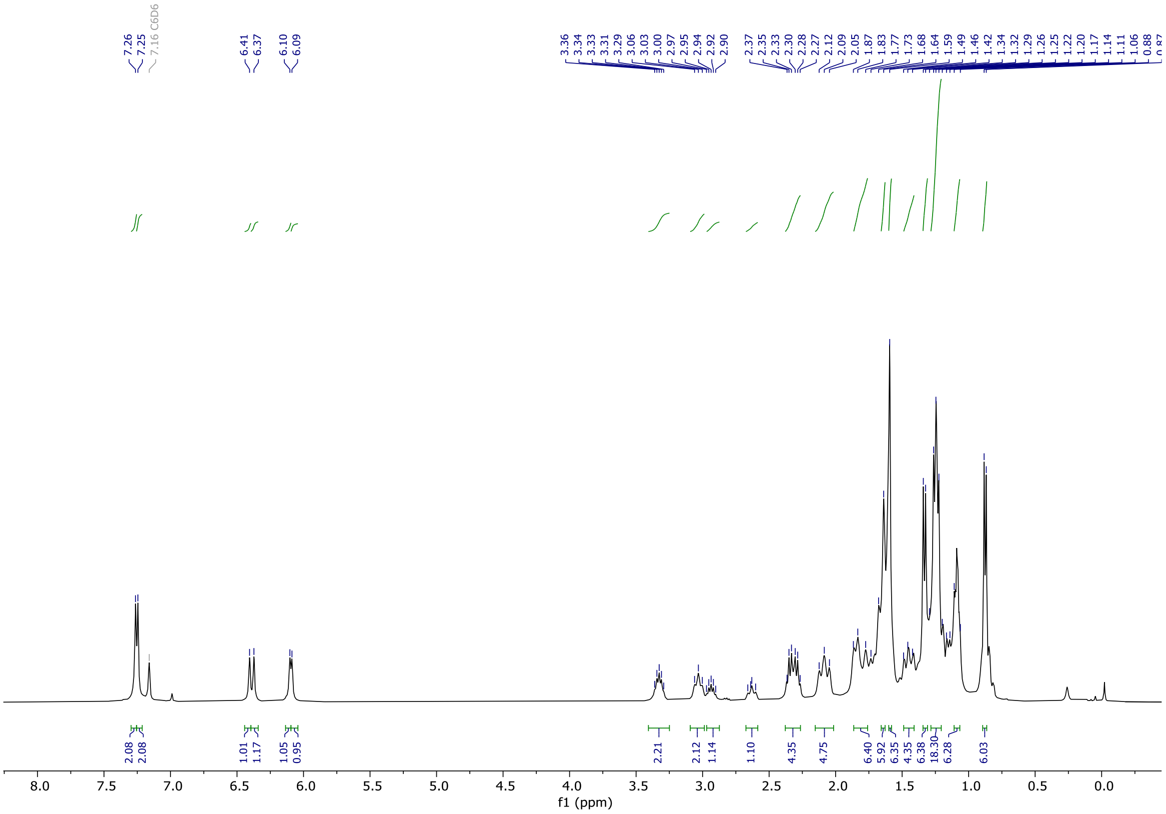


Figure S30: ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of **2**.

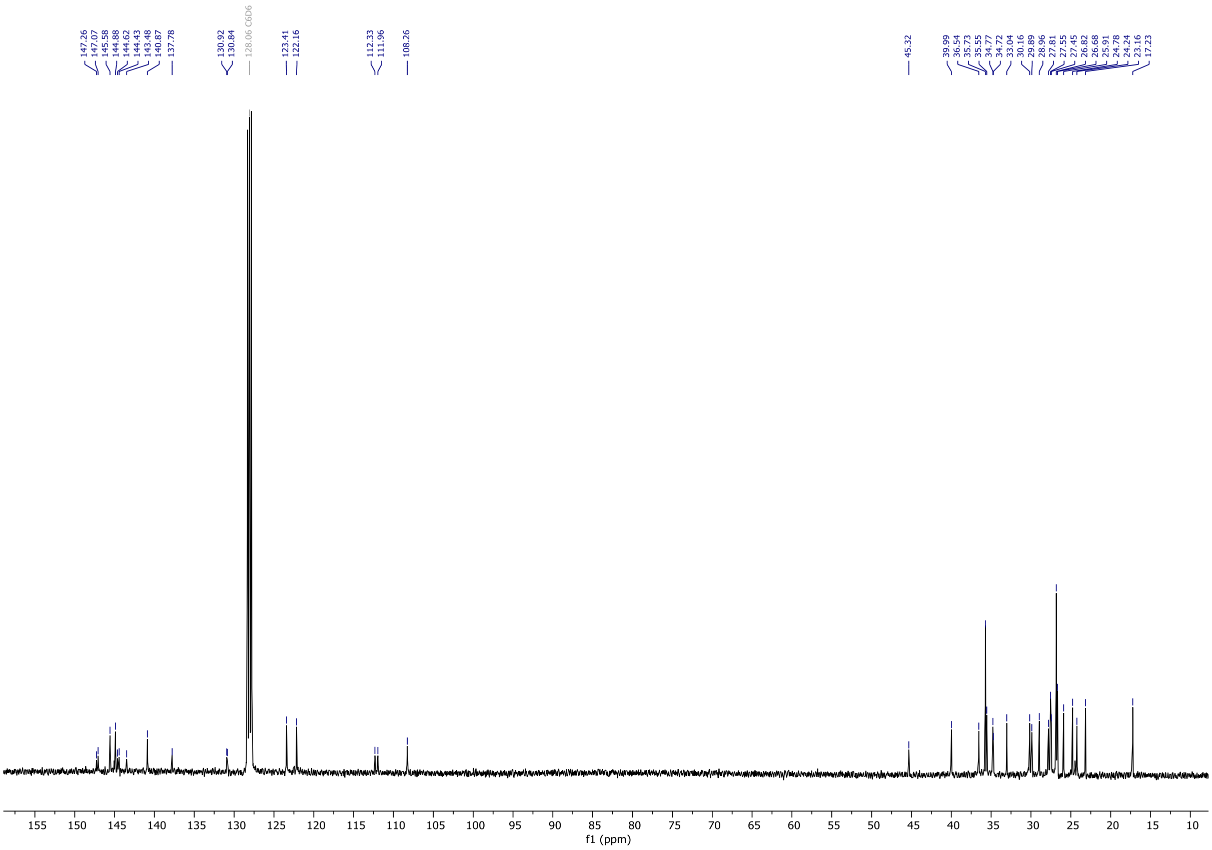


Figure S31: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, C_6D_6) of **2**.

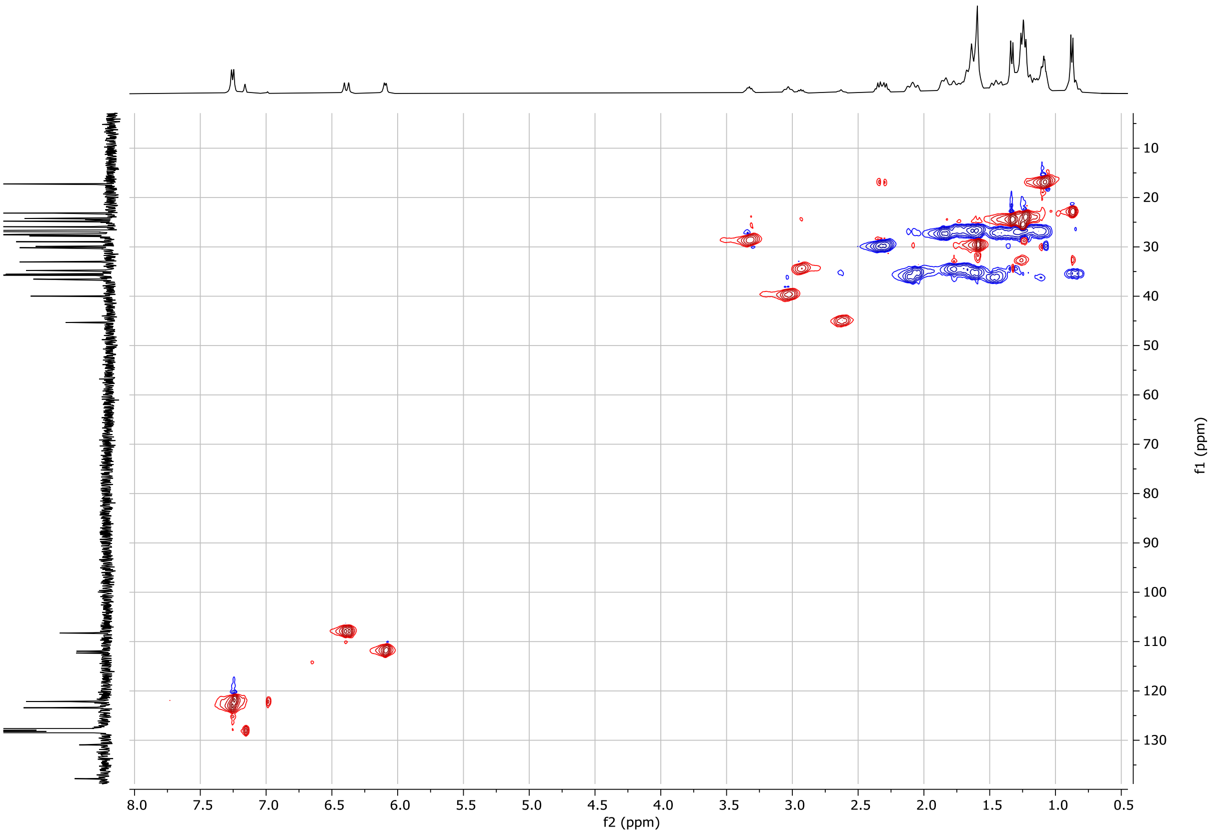


Figure S32: HSQC NMR spectrum (298 K, C_6D_6) of **2**.

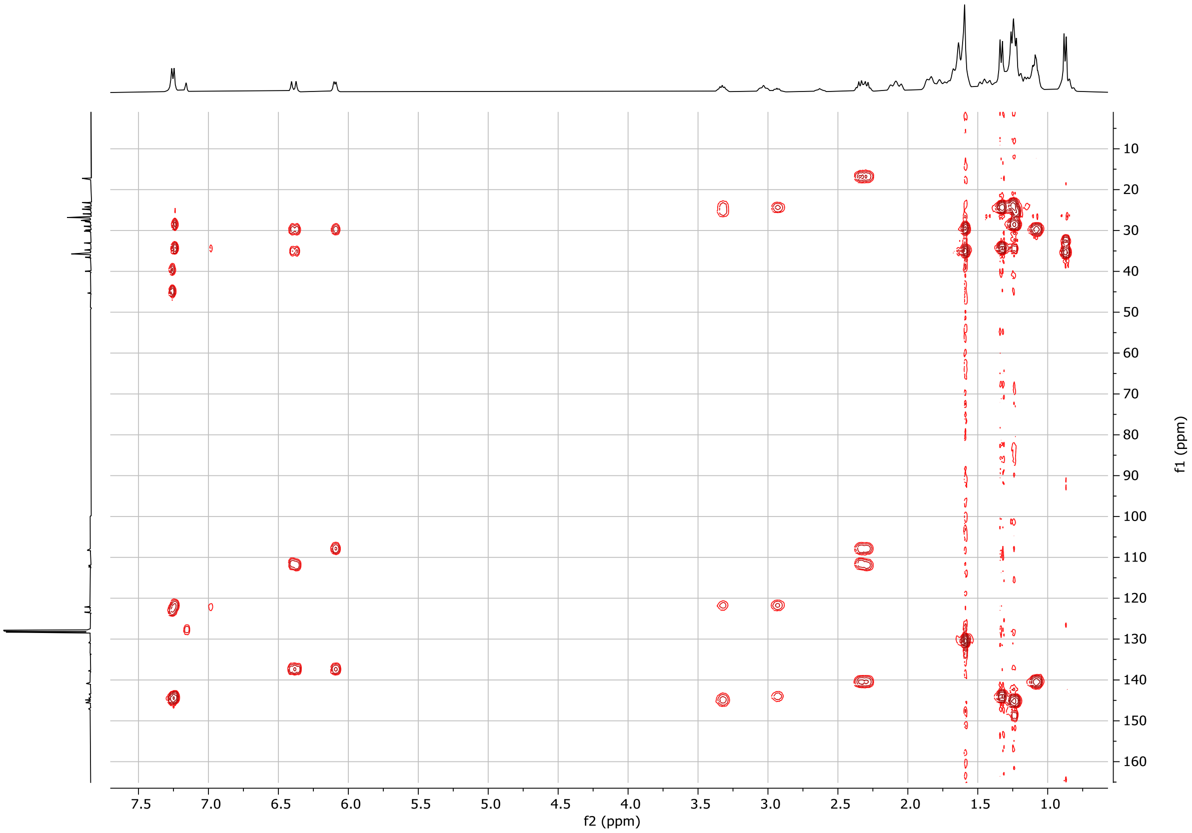


Figure S33: HMBC NMR spectrum (298 K, C_6D_6) of **2**.

Preparation of Mg(NON$^{TCHP/Trip}$)(THF)$_2$ (3)

A 50 mL oven-dried Schlenk flask was charged with NON$^{TCHP/Trip}$–H_2 (100 mg, 0.12 mmol) and Mg{$CH_2(SiMe_3)$}$_2$ (24 mg, 0.12 mmol). Benzene (10 mL) was added and the suspension was heated at 70 °C for 30 mins to give a clear yellow solution. THF (1 mL) was added and the volatiles were removed *in vacuo*. Hexane was added and the solution was stored at room temperature to give colourless crystals of the title compound. The supernatant was decanted and the crystals dried *in vacuo*. **Yield**: 78 mg, 65%.

m.p. 207 – 209 °C (dec).

^{1}**H NMR** (600 MHz, C_6D_6): δ 1.13 – 1.19 (m, 6H $CH_2C\underline{H}_3$), 1.23 (d, J = 6.8 Hz, 6H, $CH(C\underline{H}_3)_2$), 1.24 – 1.30 (m, 8H, Cy–$\underline{H}$), 1.32 (d, J = 6.8 Hz, 6H, $CH(C\underline{H}_3)_2$), 1.39 (d, J = 6.8 Hz, 6H, $CH(C\underline{H}_3)_2$), 1.41 – 1.51 (m, 8H, Cy–$\underline{H}$), 1.53 – 1.64 (m, 6H, Cy–$\underline{H}$), 1.66 – 1.74 (m, 4H, THF), 1.78 (s, 6H, $C(C\underline{H}_3)_2$), 1.79 – 1.86 (m, 4H, Cy–$\underline{H}$), 1.96 – 2.05 (m, 2H, Cy–$\underline{H}$), 2.15 – 2.32 (m, 2H, Cy–$\underline{H}$), 2.36 – 2.46 (m, 4H, $C\underline{H}_2CH_3$), 2.54 – 2.62 (m, 1H, Cy–$\underline{H}$), 2.93 (hept, J = 6.8 Hz, 1H, $C\underline{H}(CH_3)_2$), 3.19 – 3.30 (m, 2H, Cy–$\underline{H}$), 3.62 (hept, J = 6.8 Hz, 2H, $C\underline{H}(CH_3)_2$), 3.77 – 3.94 (m, 4H, THF), 6.02 (d, J = 1.8 Hz, 1H, $_{xanth}$Ar–

$\underline{H}$), 6.13 (d, J = 1.8 Hz, 1H, $_{\text{xanth}}$Ar–$\underline{H}$), 6.38 (d, J = 1.8 Hz, 1H, $_{\text{xanth}}$Ar–$\underline{H}$), 6.39 (d, J = 1.8 Hz, 1H, $_{\text{xanth}}$Ar–$\underline{H}$), 7.20 (s, 2H, $_{\text{TCHP}}$Ar–$\underline{H}$), 7.23 (s, 2H, $_{\text{Trip}}$Ar–$\underline{H}$).

^{13}C{^{1}H} NMR (151 MHz, C_6D_6): δ 17.0, 17.0 ($CH_2\underline{C}H_3$), 24.6, 24.8, 26.6 ($CH(\underline{C}H_3)_2$), 26.7, 26.9 (Cy–$\underline{C}$), 27.6 ($\underline{C}H(CH_3)_2$), 27.6 (Cy–$\underline{C}$), 27.8 ($C(\underline{C}H_3)_2$), 28.0 (Cy–$\underline{C}$), 30.3, 30.3 ($\underline{C}H_2CH_3$), 34.4 (THF), 34.6 ($\underline{C}H(CH_3)_2$), 35.2 (Cy–$\underline{C}$), 35.6 ($\underline{C}(CH_3)_2$), 37.1, 38.6, 45.2 (Cy–$\underline{C}$), 70.3 (THF), 106.0, 106.1, 110.7, 111.9, 121.6, 123.0, 129.3, 129.4, 136.8, 136.9, 139.9, 140.1, 141.8, 143.2, 145.1, 145.9, 147.6, 148.6, 148.7, 149.3 ($_{\text{xanth}}$Ar–$\underline{C}$, $_{\text{TCHP}}$Ar–$\underline{C}$, $_{\text{Trip}}$Ar–$\underline{C}$).

I.R. (solid, cm^{-1}): 643 (w), 677 (w), 803 (s), 844 (w), 861 (w), 876 (w), 923 (w), 1027 (s), 1060 (m), 1096 (m), 1213 (s), 1262 (m), 1293 (w), 1351 (w), 1396 (w), 1446 (s), 1511 (m), 1577 (w), 1621 (m), 2850 (s), 2922 (s), 2958 (m).

A reproducible microanalysis could not be obtained due to inherent sensitivity of the complex towards decomposition.

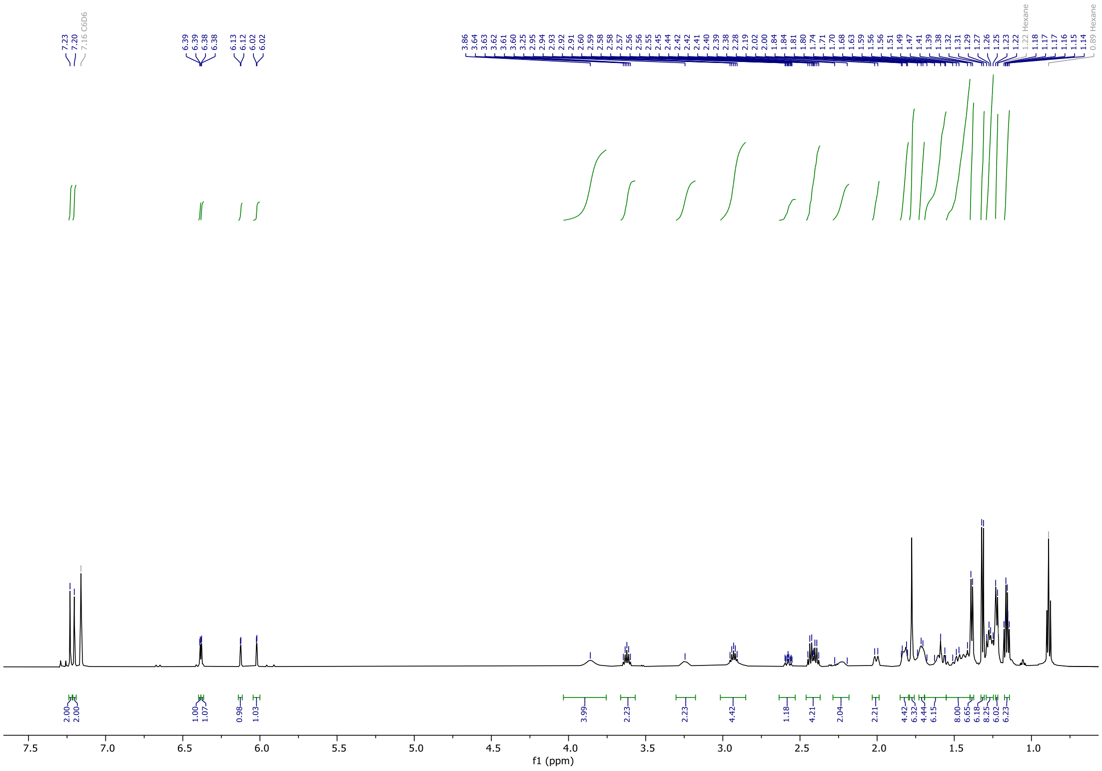


Figure S34: ^{1}H NMR spectrum (600 MHz, 298 K, C_6D_6) of **3**.

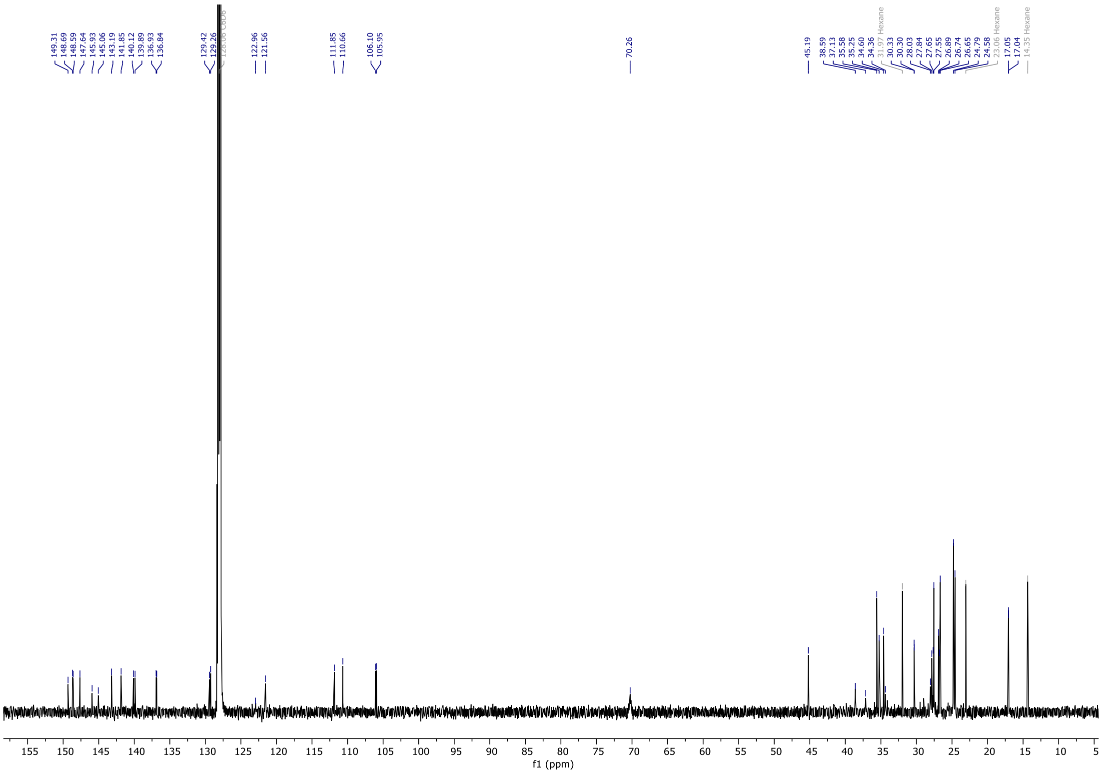


Figure S35: $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, 298 K, C_6D_6) of **3**.

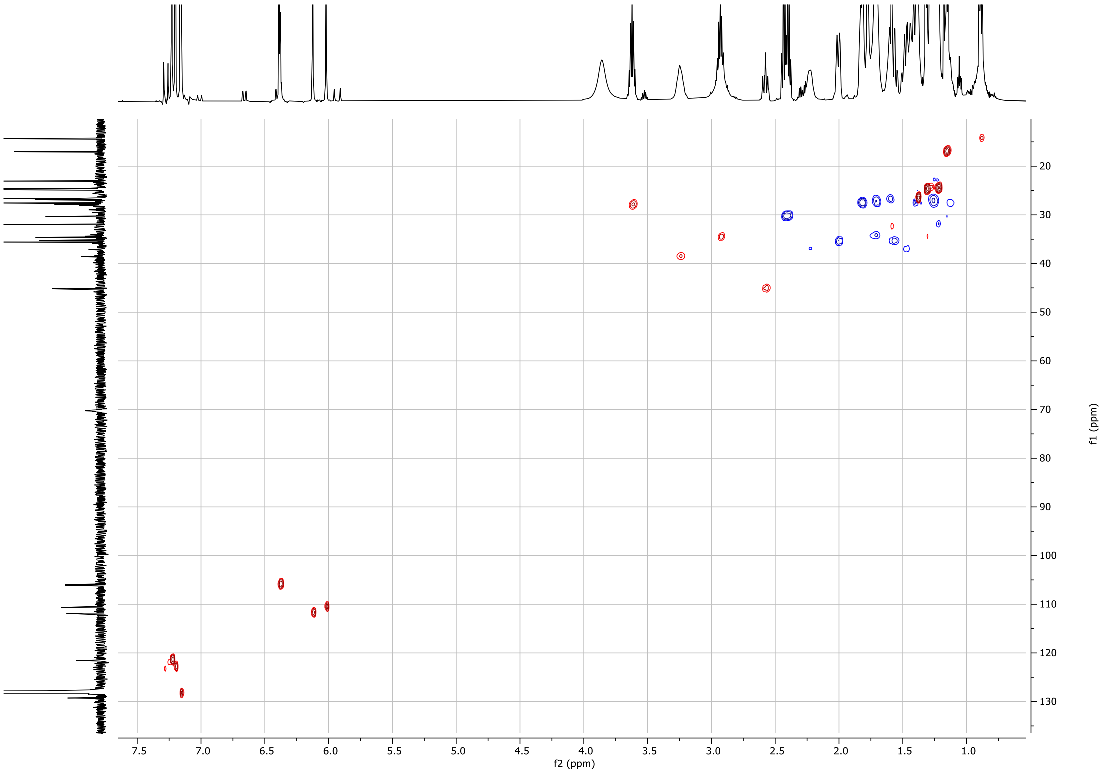


Figure S36: HSQC NMR spectrum (298 K, C_6D_6) of **3**.

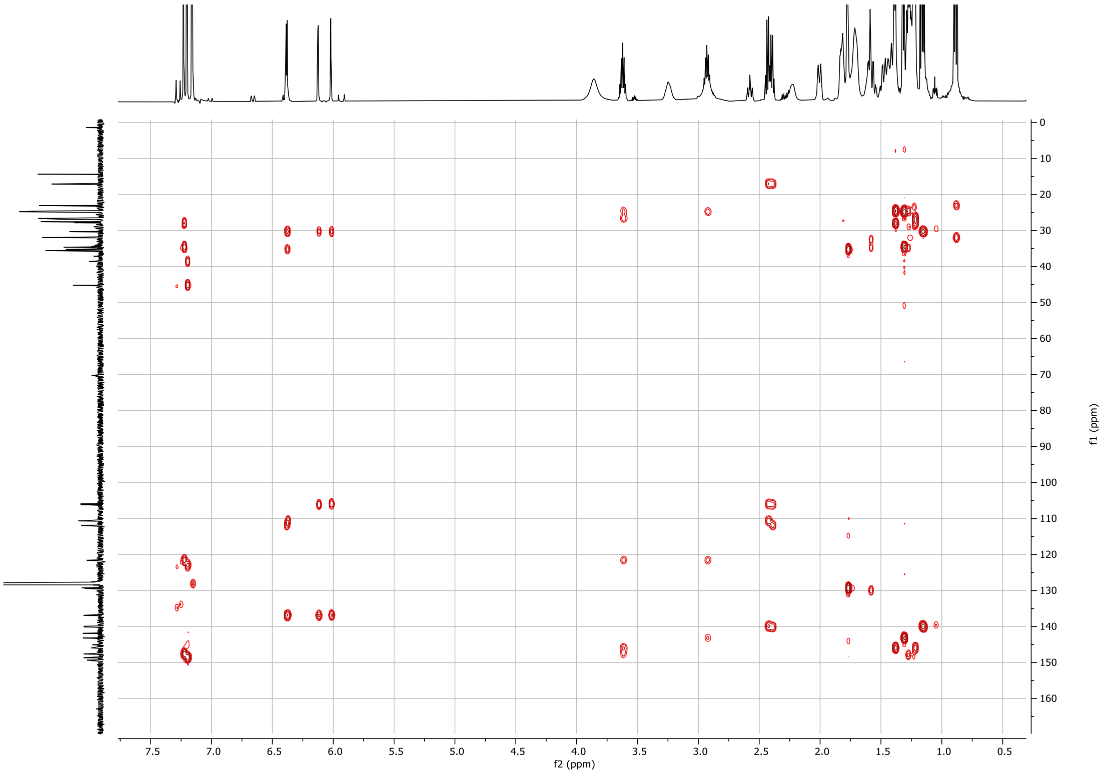


Figure S37: HMBC NMR spectrum (298 K, C_6D_6) of **3**.

Preparation of $\mathbf{Mg(NON^{TCHP/Trip})(TMC)_2}$ (4)

A 10 mL oven-dried Schlenk flask was charged with $Mg(NON^{TCHP/Trip})$ (65 mg, 0.08 mmol) and 1,3,4,5-tetramethylimidazol-2-ylidene (20 mg, 0.16 mmol). Toluene (1 mL) was added and the solution was allowed to sit at room temperature for 5 days to give colourless crystals of the title compound. The supernatant was decanted and the crystals dried *in vacuo*. **Yield**: 21 mg, 25%.

m.p. 186 – 188 °C (dec).

^{1}H NMR (600 MHz, C_6D_6): δ 0.59 (d, J = 6.8 Hz, 6H, $CH(C\underline{H}_3)_2$), 1.20 (t, J = 7.6 Hz, 3H, $CH_2C\underline{H}_3$), 1.22 (t, J = 7.6 Hz, 3H, $CH_2C\underline{H}_3$), 1.24 – 1.28 (m, 2H, Cy–$\underline{H}$), 1.30 (d, J = 6.8 Hz, 6H, $CH(C\underline{H}_3)_2$), 1.31 (d, J = 6.8 Hz, 6H, $CH(C\underline{H}_3)_2$), 1.31 – 1.39 (m, 6H, Cy–$\underline{H}$), 1.45 (br s, 12H, TMC–$C\underline{H}_3$), 1.47 – 1.70 (m, 10H, Cy–$\underline{H}$), 1.70 – 1.89 (m, 8H, Cy–$\underline{H}$), 1.94 – 2.01 (m, 2H, Cy–$\underline{H}$), 2.02 (s, 6H, $C(C\underline{H}_3)_2$), 2.24 – 2.31 (m, 2H, Cy–$\underline{H}$), 2.42 (q, J = 7.6 Hz, 2H, $C\underline{H}_2CH_3$), 2.47 (q, J = 7.6 Hz, 2H, $C\underline{H}_2CH_3$), 2.50 – 2.55 (m, 1H, Cy–$\underline{H}$), 2.80 – 3.20 (m, 15H, $C\underline{H}(CH_3)_2$, Cy–$\underline{H}$, TMC–$C\underline{H}_3$), 3.31 – 3.40 (m, 2H, $C\underline{H}(CH_3)_2$), 6.10 (d, J = 1.9 Hz, 1H, $_{xanth}$Ar–$\underline{H}$), 6.18 (d, J = 1.8 Hz, 1H, $_{xanth}$Ar–$\underline{H}$), 6.39 – 6.43 (m, 2H, $_{xanth}$Ar–$\underline{H}$), 6.98 – 7.00 (m, 4H, $_{TCHP}$Ar–$\underline{H}$, $_{Trip}$Ar–$\underline{H}$).

^{13}C{^{1}H} NMR (151 MHz, C_6D_6): δ 8.3 (TMC–$\underline{C}H_3$), 16.4, 16.6 ($CH_2\underline{C}H_3$), 23.2, 25.0 ($CH(\underline{C}H_3)_2$), 26.8 (Cy–$\underline{C}$), 27.2 ($CH(\underline{C}H_3)_2$), 27.5, 27.6, 27.7 (Cy–$\underline{C}$), 27.8 ($\underline{C}H(CH_3)_2$), 30.0, 30.0 ($\underline{C}H_2CH_3$), 33.5

(C(<u>C</u>H$_3$)$_2$), 33.7 (<u>C</u>(CH$_3$)$_2$), 34.5 (TMC–<u>C</u>H$_3$), 34.6 (<u>C</u>H(CH$_3$)$_2$), 34.8, 35.8, 38.1, 38.3, 45.2 (Cy–<u>C</u>), 105.7, 105.9, 112.6, 113.7, 120.9, 122.6 ($_{\text{xanth}}$Ar–<u>C</u>, $_{\text{TCHP}}$Ar–<u>C</u>, $_{\text{Trip}}$Ar–<u>C</u>), 124.1 (TMC–<u>C</u>), 136.2, 136.7, 137.9, 139.3, 139.4, 139.4, 140.8, 145.0, 145.8, 150.1, 150.6, 150.9 ($_{\text{xanth}}$Ar–<u>C</u>, $_{\text{TCHP}}$Ar–<u>C</u>, $_{\text{Trip}}$Ar–<u>C</u>).

I.R. (solid, cm^{-1}): 742 (w), 839 (m), 861 (w), 874 (w), 923 (w), 950 (w), 997 (w), 1031 (w), 1165 (w), 1211 (s), 1241 (w), 1271 (w), 1295 (w), 1316 (w), 1359 (m), 1400 (w), 1446 (s), 1511 (s), 1577 (w), 1620 (s), 1662 (s), 2850 (m), 2920 (s), 2958 (m).

A reproducible microanalysis could not be obtained due to inherent sensitivity of the complex towards decomposition.

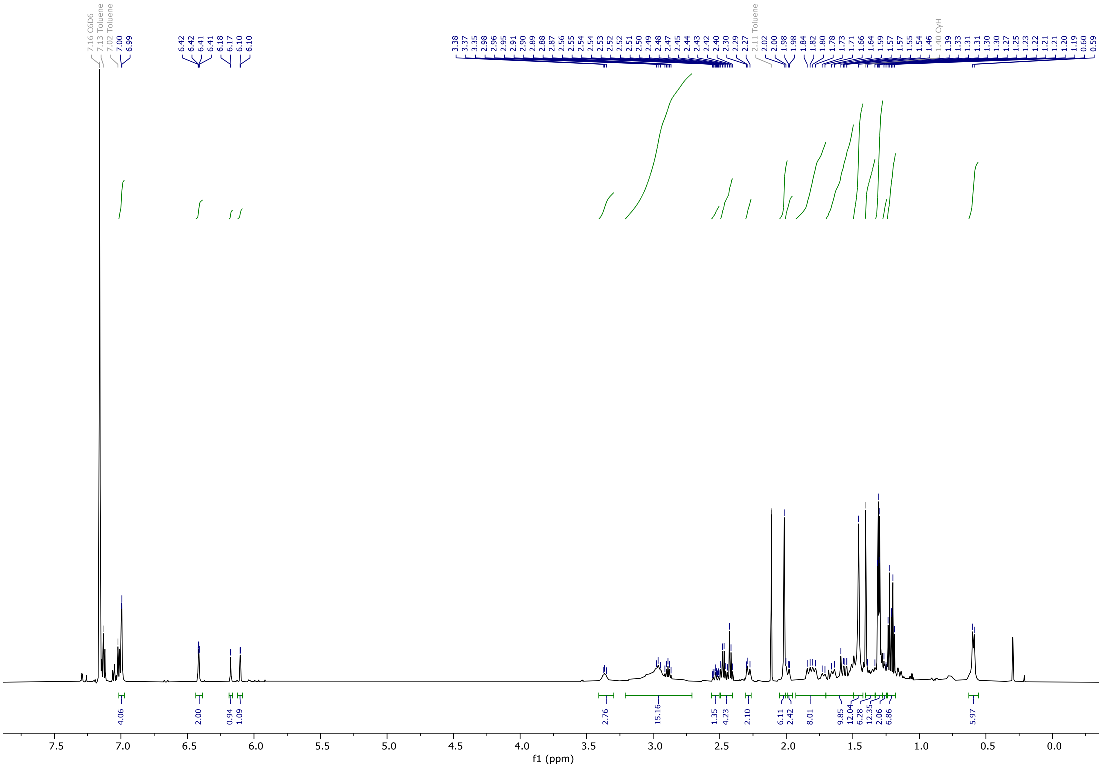


Figure S38: ^{1}H NMR spectrum (600 MHz, 298 K, C_6D_6) of **4**.

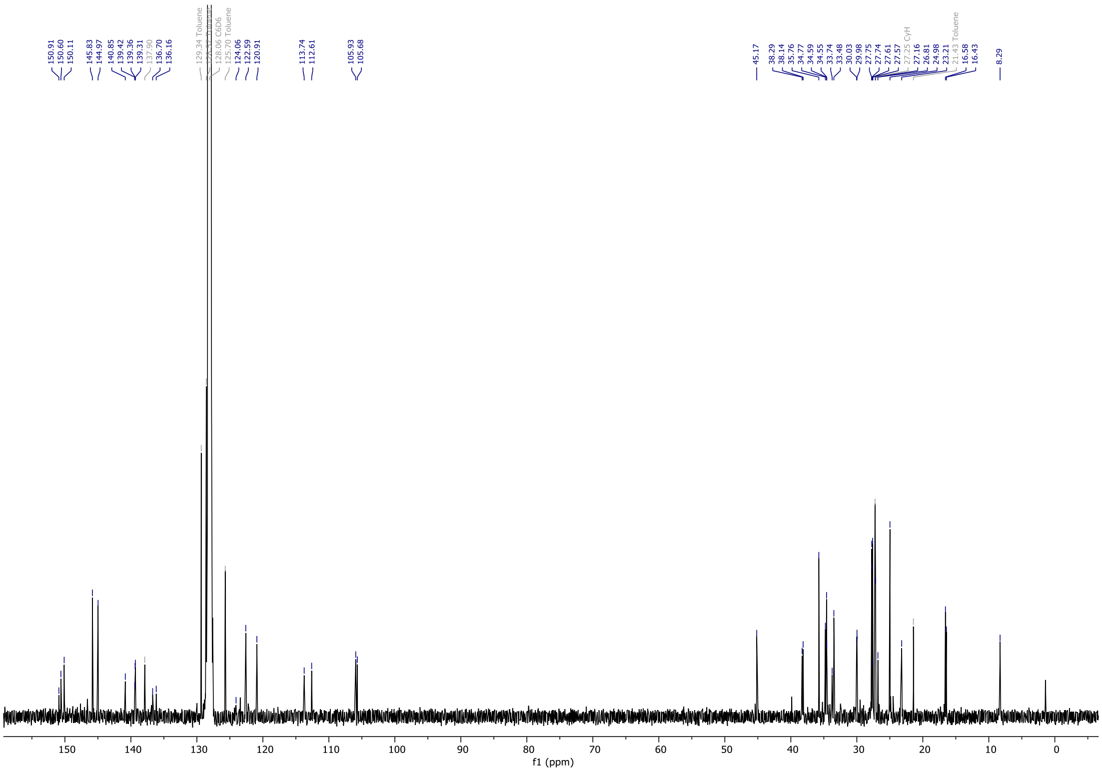


Figure S39: $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, 298 K, C_6D_6) of **4**.

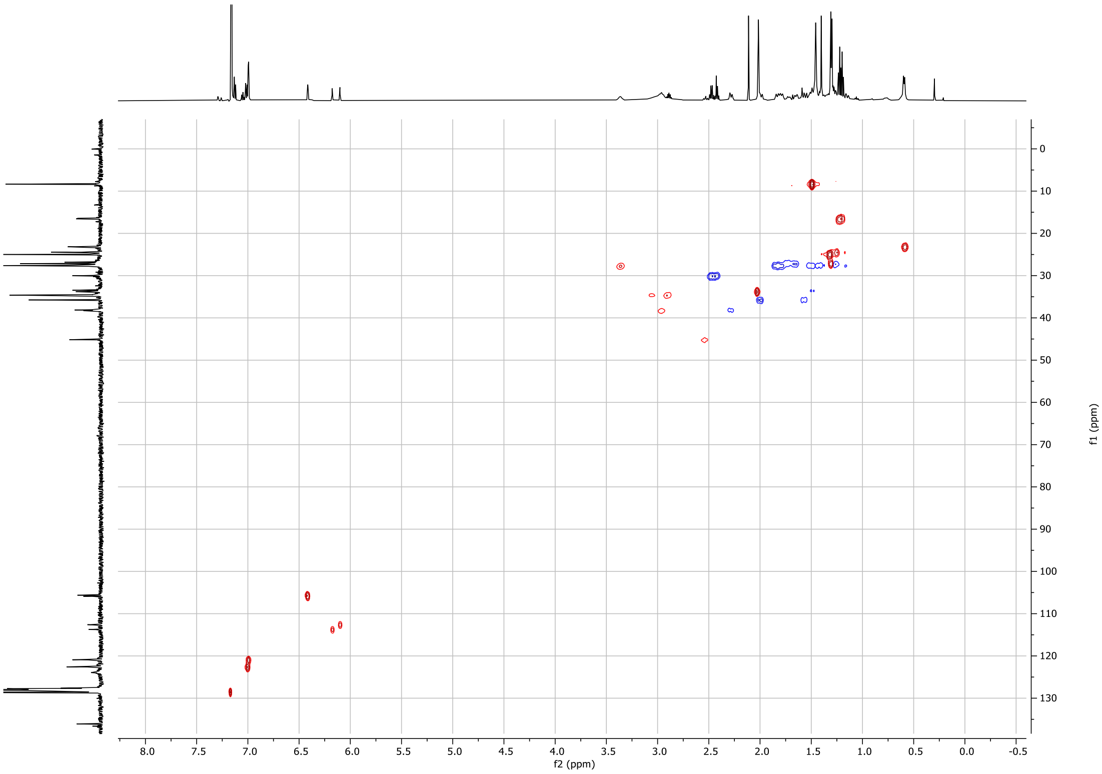


Figure S40: HSQC NMR spectrum (298 K, C_6D_6) of **4**.

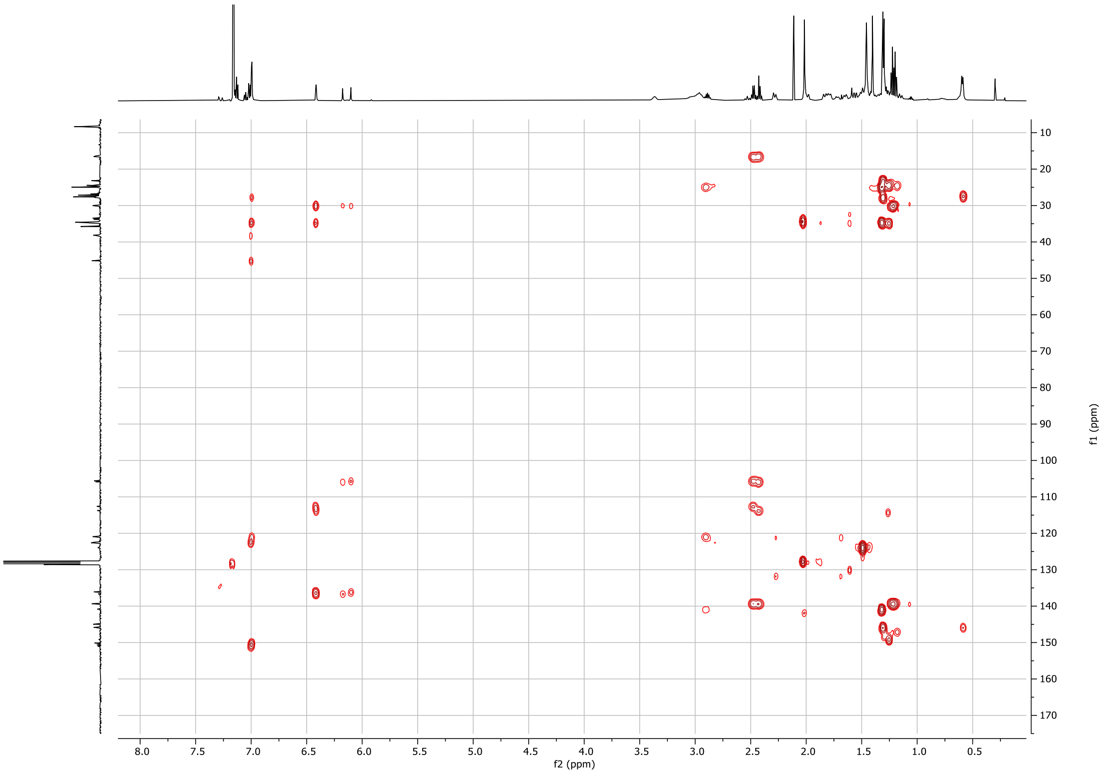


Figure S41: HMBC NMR spectrum (298 K, C_6D_6) of **4**.

Preparation of $[K(C_6H_6)]_2[Mg(NON^{TCHP/Trip})(Ph)(H)]_2[K_4(C_{12}H_{10})]$ (5)

A 50 mL oven-dried Schlenk flask was charged with $NON^{Trip/TCHP}$–H_2 (200 mg, 0.24 mmol) and $Mg\{CH_2(SiMe_3)\}_2$ (48 mg, 0.24 mmol). Benzene (10 mL) was added and the suspension was heated at 70 °C for 30 mins to give a clear yellow solution. The solution was transferred to a 50 mL oven-dried Schlenk flask charged with K/KI (5 wt%, 760 mg, 0.97 mmol) and a stir bar. The reaction mixture was stirred for 18 hours to give an intense dark red colored solution that was settled and subsequently filtered *via* cannula. The volatiles were reduced in vacuo (to ca. 3 mL) and the solution was stored at 8 °C for several days to give a small crop of dark red crystals. **Yield**: 16 mg, 5%.

m.p. >300 °C (dec).

I.R. (solid, cm^{-1}): 677 (m), 699 (m), 736 (m), 794 (m), 844 (m), 861 (w), 876 (w), 923 (w), 952 (w), 997 (w), 1029 (m), 1055 (w), 1135 (w), 1165 (w), 1213 (s), 1243 (w), 1293 (w), 1318 (w), 1360 (m), 1396 (m), 1446 (s), 1508 (m), 1623 (m), 2850 (s), 2922 (s), 2960 (m).

Dissolving crystals of the title compound in C_6D_6 resulted in a rapid colour change from dark red to yellow-orange. The only species that could be determined from the ^1H NMR spectrum were dihydrogen, biphenyl, and an unknown bis(anilido)xanthene magnesium product. A ^1H NMR spectrum of this solution is provided. Satisfactory microanalysis data for this compound could not be obtained due to its inherent sensitivity to air and moisture.

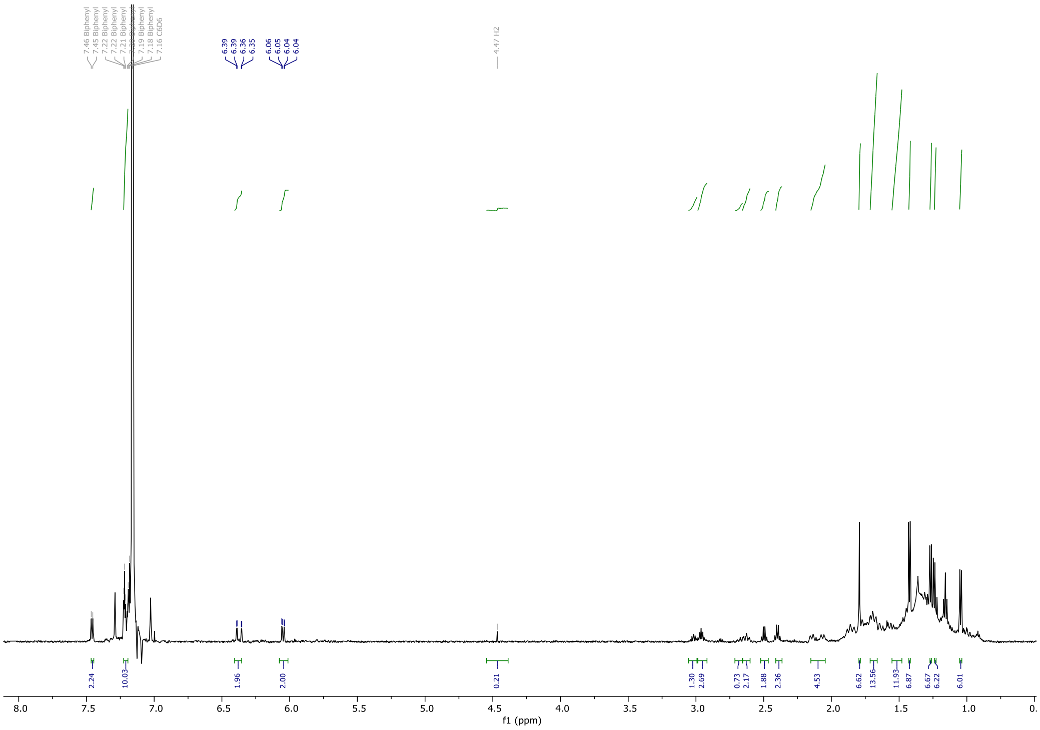
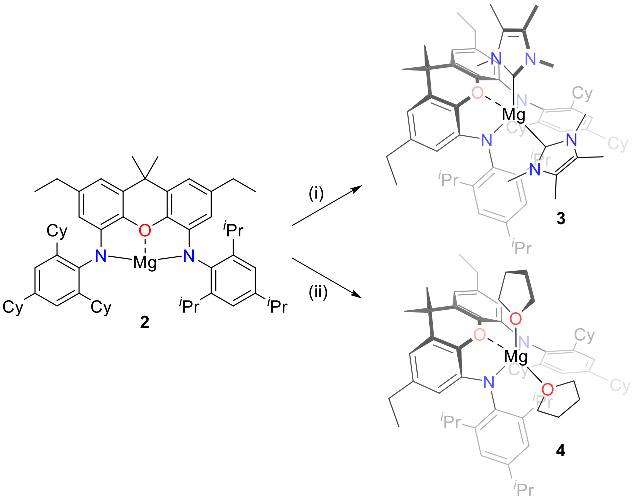
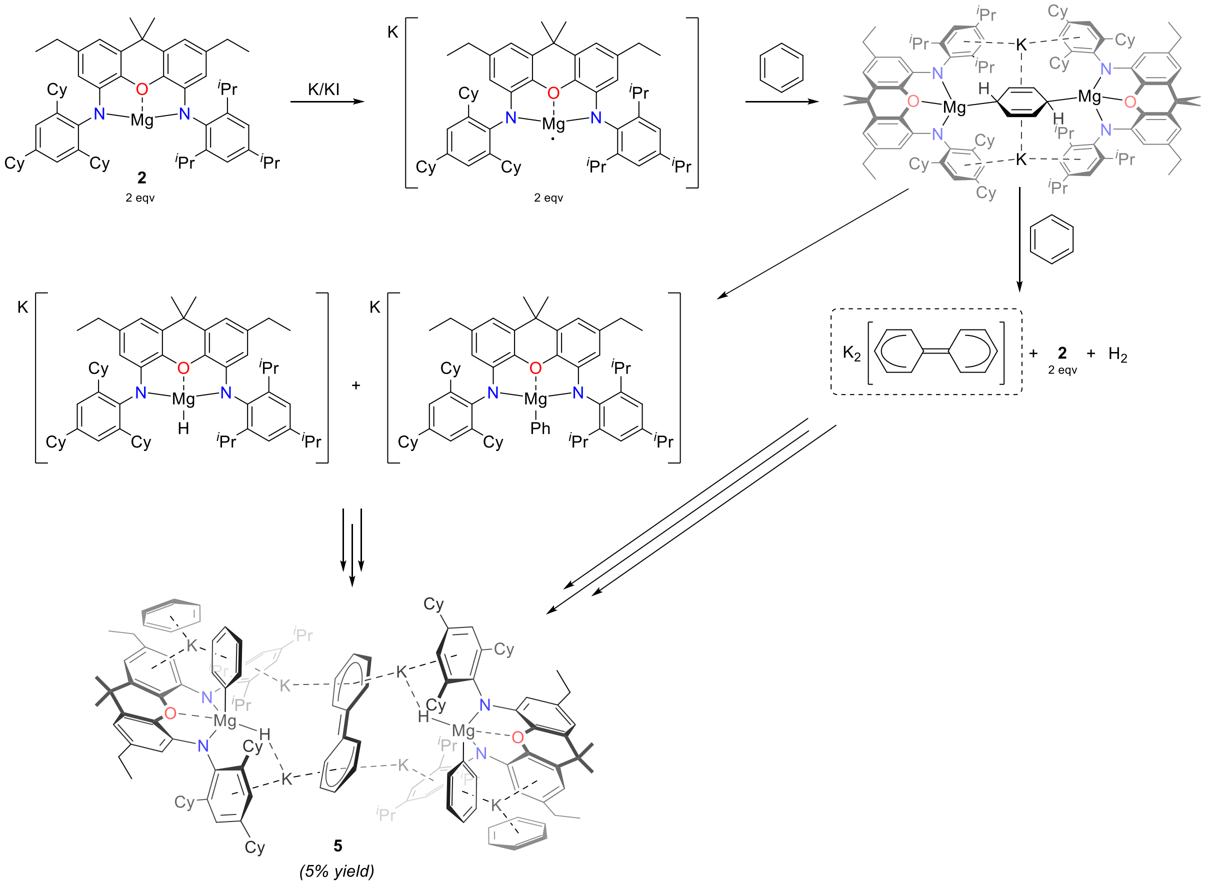


Figure S42: ^{1}H NMR spectrum (600 MHz, 298 K, C_6D_6) of decomposition products generated upon dissolution of **5**.

2. Additional Schemes



Scheme S1: Synthesis of Lewis adducts **3** and **4** from “Mg(NON$^{\mathrm{TCHP/Trip}}$)” (**2**).
(i) TMC (2 eqv), C_6H_6. (ii) THF (excess), C_6H_6.



Scheme S2: Tentative mechanism for the formation of **5**.

3. X-ray Crystallography

Crystals suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using a Rigaku Xtalab Synergy Dualflex using a graphite monochromator with Cu Kα (1.54180 Å) or Mo Kα (0.71073 Å), or the MX1/MX2 beamlines of the Australian Synchrotron (λ = 0.71090 Å).[S6,S7] The software package Blu-Ice[S8] was used for synchrotron data acquisition, while the program XDS[S9] was employed for synchrotron data reduction. All structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX-18)[S10] using all unique data. Hydrogen atoms were included in calculated positions (riding model). Crystal data, details of data collections, and refinements for all structures can be found in their CIF files and are summarized in Table S1.

Table S1: Crystallographic Data for Isolated Compounds

Compound	**Xanth–$(NH_2)_2$**		**Xanth–(NHTCHP)(NH_2)**		**$(NON^{TCHP/Mes})H_2$**	
Empirical formula	$C_{19}H_{24}N_2O$		$C_{43}H_{58}N_2O$		$C_{62.5}H_{80}N_2O$	
Formula weight	296.4		618.91		875.28	
Temperature	122.9(2) K		123.00(10) K		123.01(10) K	
Crystal system	Monoclinic		Triclinic		Triclinic	
Space group	$P2_1/c$		P-1		P-1	
Unit cell dimensions	a = 16.4224(3) Å	α = 90°	9.99070(10)	103.3550(10)	a = 12.43860(10) Å	α= 89.6690(10)°
	b = 26.1026(3) Å	β = 117.172(2)°	17.0201(2)	102.2380(10)	b = 19.1066(2) Å	β= 87.3360(10)°
	c = 17.6208(3) Å	γ = 90°	23.3184(2)	103.6610(10)	c = 21.5188(3) Å	γ = 89.3550(10)°
Volume	6719.9(2) Å^3		3596.71(7) Å^3		5108.22(10) Å^3	
Z	16		4		4	
Density (calculated)	1.172 Mg/m^3		1.143 Mg/m^3		1.138 Mg/m^3	
Absorption coefficient	0.565 mm^{-1}		0.506 mm^{-1}		0.495 mm^{-1}	
F(000)	2560		1352		1908	
Crystal size	0.400 x 0.250 x 0.100 mm^3		0.61 × 0.26 × 0.18 mm^3		0.300 x 0.250 x 0.160 mm^3	
Theta range for data collection	3.490 to 80.128°		7.828 to 160.72		3.557 to 80.121°	
Index ranges	$-16<=h<=20$, $-33<=k<=27$, $-22<=l<=20$		$-12 \leq h \leq 12$, $-21 \leq k \leq 21$, $-29 \leq l \leq 29$		$-11<=h<=15$, $-24<=k<=24$, $-27<=l<=27$	
Reflections collected	54341		84525		115683	
Independent reflections	14255 [R(int) = 0.0542]		15546 [R_{int} = 0.0510, R_{sigma} = 0.0374]		21944 [R(int) = 0.0619]	
Completeness to theta = 67.684 °	99.50%		99.80%		99.80%	
Absorption correction	Semi-empirical from equivalents		Gaussian		Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.38281		1.000 and 0.212		1.00000 and 0.74947	
Data / restraints / parameters	14255 / 338 / 949		15546 / 144 / 893		21944 / 0 / 1197	
Goodness-of-fit on F^2	1.057		1.033		1.068	
Final R indices [I > 2sigma(I)]	R_1 = 0.0670, wR_2 = 0.1877		R_1 = 0.0589, wR_2 = 0.1509		R1 = 0.0639, wR2 = 0.1845	
R indices (all data)	R_1 = 0.0769, wR_2 = 0.1989		R_1 = 0.0654, wR_2 = 0.1562		R1 = 0.0716, wR2 = 0.1945	
Largest diff. peak and hole	1.979 and -0.641 e.Å^{-3}		0.65 and -0.65 e.Å^{-3}		1.451 and -0.621 e.Å^{-3}	
CCDC Number	2456735		2456737		2456739	

Table S1 (contd.): Crystallographic Data for Isolated Compounds

Compound	**$(\mathrm{NON}^{\mathrm{TCHP/Trip}})\mathrm{H}_2$**	**$[\mathrm{Mg}(\mathrm{NON}^{\mathrm{TCHP/Mes}})]_2$ (1)**	**$[\mathrm{Mg}(\mathrm{NON}^{\mathrm{TCHP/Trip}})(\mathrm{TMC})_2]$ (3)**
Empirical formula	$C_{58} H_{80} N_2 O$	$C_{110} H_{138} Mg_2 N_4 O_2$	$C_{79} H_{110} Mg N_6 O$
Formula weight	821.24	1596.86	1184.03
Temperature	123.01(10) K	100(2) K	123.00(10) K
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P2₁/*c*	C2/*c*	P-1
Unit cell dimensions	a = 12.7070(2) Å α= 90°	a = 29.100(6) Å α= 90°	a = 12.61880(10) Å α= 87.7400(10)°
	b = 28.0723(3) Å β= 98.6530(10)°	b = 11.070(2) Å β= 97.90(3)°	b = 14.43510(10) Å β= 84.0810(10)°
	c = 14.6372(2) Å γ = 90°	c = 29.060(6) Å γ = 90°	c = 39.6972(2) Å γ = 88.1770(10)°
Volume	5161.87(12) Å^3	9273(3) Å^3	7184.04(9) Å^3
Z	4	4	4
Density (calculated)	1.057 Mg/m^3	1.144 Mg/m^3	1.095 Mg/m^3
Absorption coefficient	0.458 mm^{-1}	0.079 mm^{-1}	0.564 mm^{-1}
F(000)	1800	3464	2584
Crystal size	0.380 x 0.140 x 0.100 mm^3	0.120 x 0.100 x 0.070 mm^3	0.670 x 0.530 x 0.360 mm^3
Theta range for data collection	3.518 to 80.503°.	1.413 to 26.371°	3.523 to 80.729°
Index ranges	-16<=*h*<=16, -13<=*k*<=35, -17<=*l*<=18	-35<=*h*<=35, -12<=*k*<=13, -36<=*l*<=36	-16<=*h*<=16, -18<=*k*<=18, -38<=*l*<=50
Reflections collected	55342	81581	150012
Independent reflections	10992 [R(int) = 0.0505]	9286 [R(int) = 0.0644]	30789 [R(int) = 0.0394]
Completeness to theta = 67.684 °	99.30%	99.40%	99.90%
Absorption correction	Gaussian	Semi-empirical from equivalents	Gaussian
Max. and min. transmission	1.000 and 0.572	Value not reported by XDS	1.000 and 0.101
Data / restraints / parameters	10992 / 967 / 756	9286 / 0 / 550	30789 / 276 / 1700
Goodness-of-fit on F^2	1.048	1.037	1.011
Final R indices [I > 2sigma(I)]	R_1 = 0.0972, wR_2 = 0.2770	R_1 = 0.0522, wR_2 = 0.1365	R_1 = 0.0728, wR_2 = 0.1981
R indices (all data)	R_1 = 0.1144, wR_2 = 0.2954	R_1 = 0.0717, wR_2 = 0.1510	R_1 = 0.0807, wR_2 = 0.2057
Largest diff. peak and hole	0.631 and -0.294 e.Å^{-3}	0.271 and -0.304 e.Å^{-3}	1.024 and -0.392 e.Å^{-3}
CCDC Number	2456736	2456738	2456733

Table S1 (contd.): Crystallographic Data for Isolated Compounds

Compound	$[\mathrm{Mg(NON^{TCHP/Trip})(THF)_2}]$ (4)	$\mathrm{K_4[Mg(NON^{TCHP/Trip})(Ph)(H)]_2{\cdot}K_2[C_6H_6]_2}$ (5)
Empirical formula	$C_{80}H_{110}MgN_2O_3$	$C_{164}H_{202}K_6Mg_2N_4O_2$
Formula weight	1172.00	2544.5
Temperature	100(2) K	100(2) K
Crystal system	Orthorombic	Triclinic
Space group	$P2_1$	P-1
Unit cell dimensions	a = 17.500(4) Å α = 90°	a = 13.650(3) Å α = 103.86(3)°
	b = 17.780(4) Å β = 104.86(3)°	b = 16.680(3) Å β = 104.61(3)°
	c = 22.860(5) Å γ = 90°	c = 24.090(5) Å γ = 93.90(3)°
Volume	6875(3) Å^3	5105(2) Å^3
Z	4	1
Density (calculated)	1.132 Mg/m^3	0.828 Mg/m^3
Absorption coefficient	0.075 mm^{-1}	0.172 mm^{-1}
F(000)	2560	1368
Crystal size	0.120 x 0.050 x 0.030 mm^3	0.110 x 0.070 x 0.050 mm^3
Theta range for data collection	0.922 to 26.372°.	0.906 to 26.372°
Index ranges	$-21<=h<=21, -22<=k<=22, -28<=l<=28$	$-17<=h<=16, -20<=k<=20, -30<=l<=28$
Reflections collected	188359	97564
Independent reflections	[R(int) = 0.0]	20409 [R(int) = 0.0372]
Completeness to theta = 67.684 °		99.00%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	Value not reported by XDS	Value not reported by XDS
Data / restraints / parameters	28099 / 174 / 1573	20409 / 12 / 816
Goodness-of-fit on F^2	1.032	1.03
Final R indices [I > 2sigma(I)]	R_1 = 0.0367, wR_2 = 0.0960	R_1 = 0.0890, wR_2 = 0.2691
R indices (all data)	R_1 = 0.0376, wR_2 = 0.0969	R_1 = 0.1092, wR_2 = 0.2946
Largest diff. peak and hole	0.544 and -0.281 e.Å^{-3}	0.759 and -0.331 e.Å^{-3}
CCDC Number	2456740	2456734

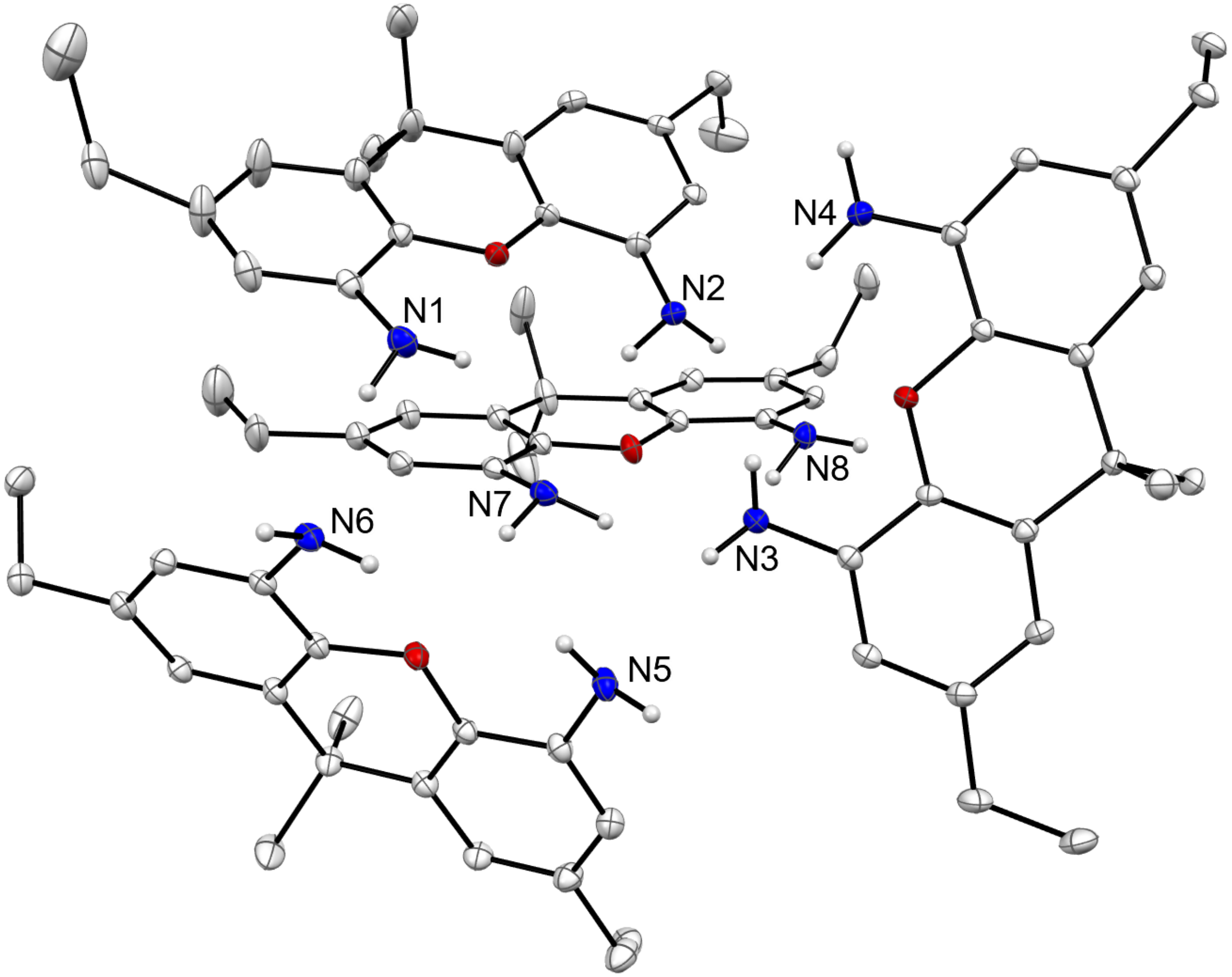


Figure S43: Molecular structure of **C**. Thermal ellipsoids shown at 20% probability; hydrogen atoms omitted.

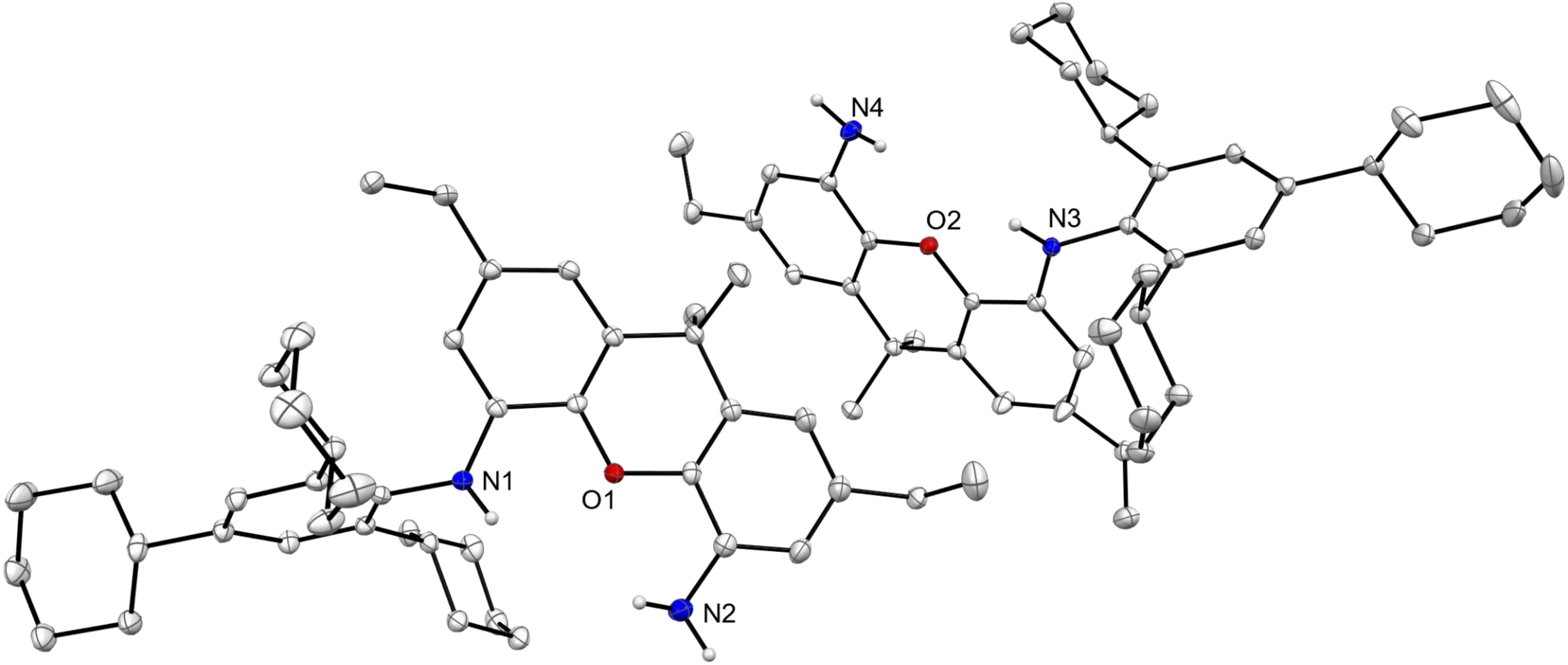


Figure S44: Molecular structure of **D**. Thermal ellipsoids shown at 20% probability; hydrogen atoms omitted.

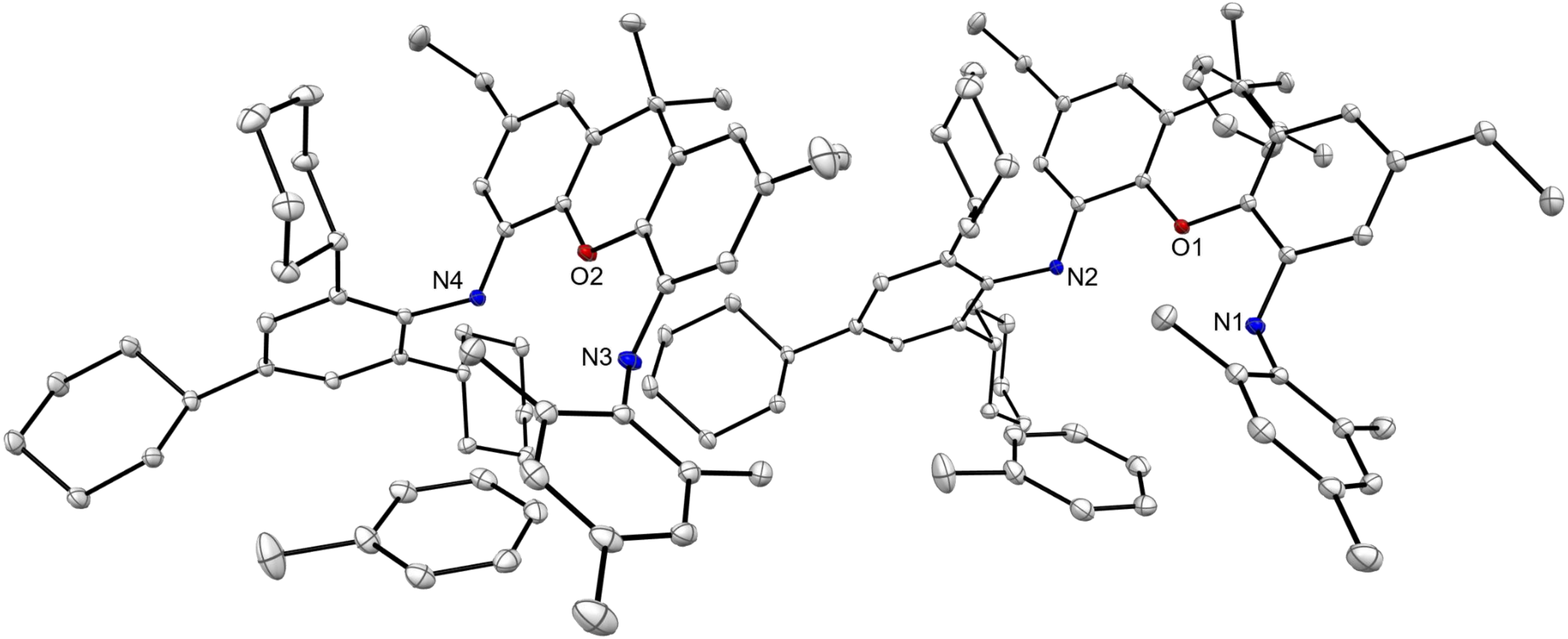


Figure S45: Molecular structure of $(NON^{TCHP/Mes})H_2$. Thermal ellipsoids shown at 20% probability; hydrogen atoms omitted.

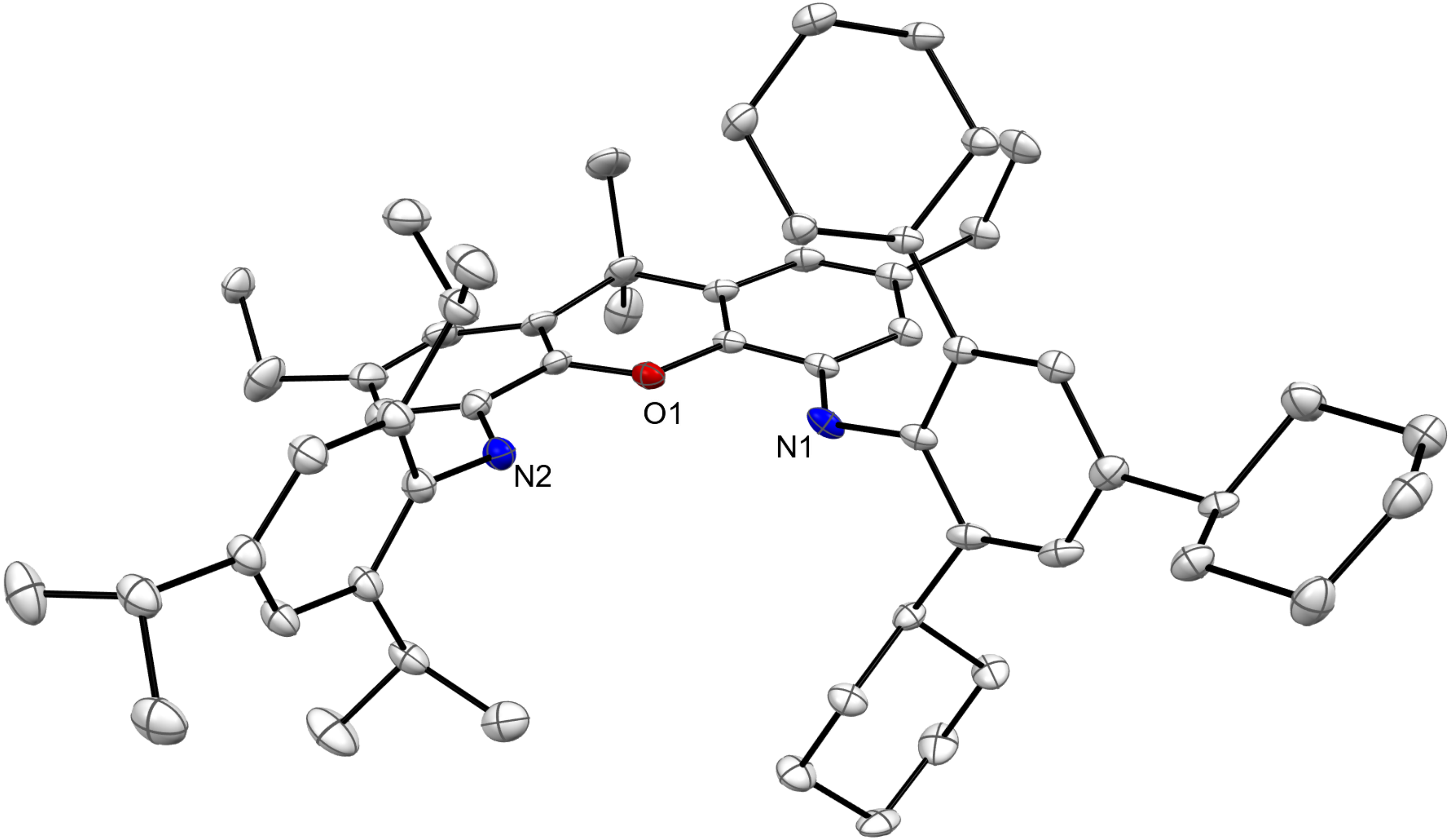


Figure S46: Molecular structure of $(NON^{TCHP/Trip})H_2$. Thermal ellipsoids shown at 20% probability; hydrogen atoms omitted.

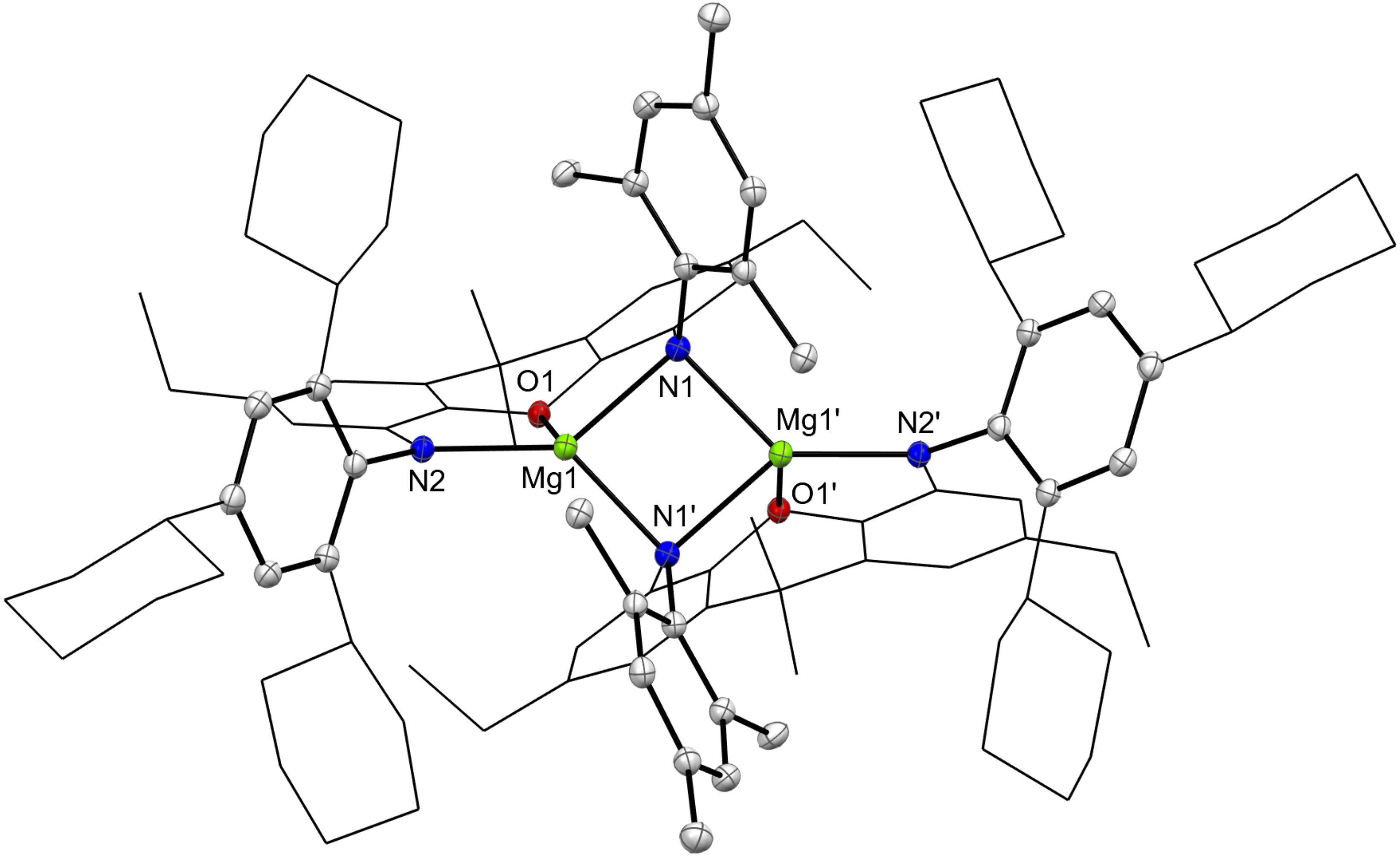


Figure S47: Molecular structure of **1**. Thermal ellipsoids shown at 20% probability; benzene solvate and hydrogen atoms omitted.

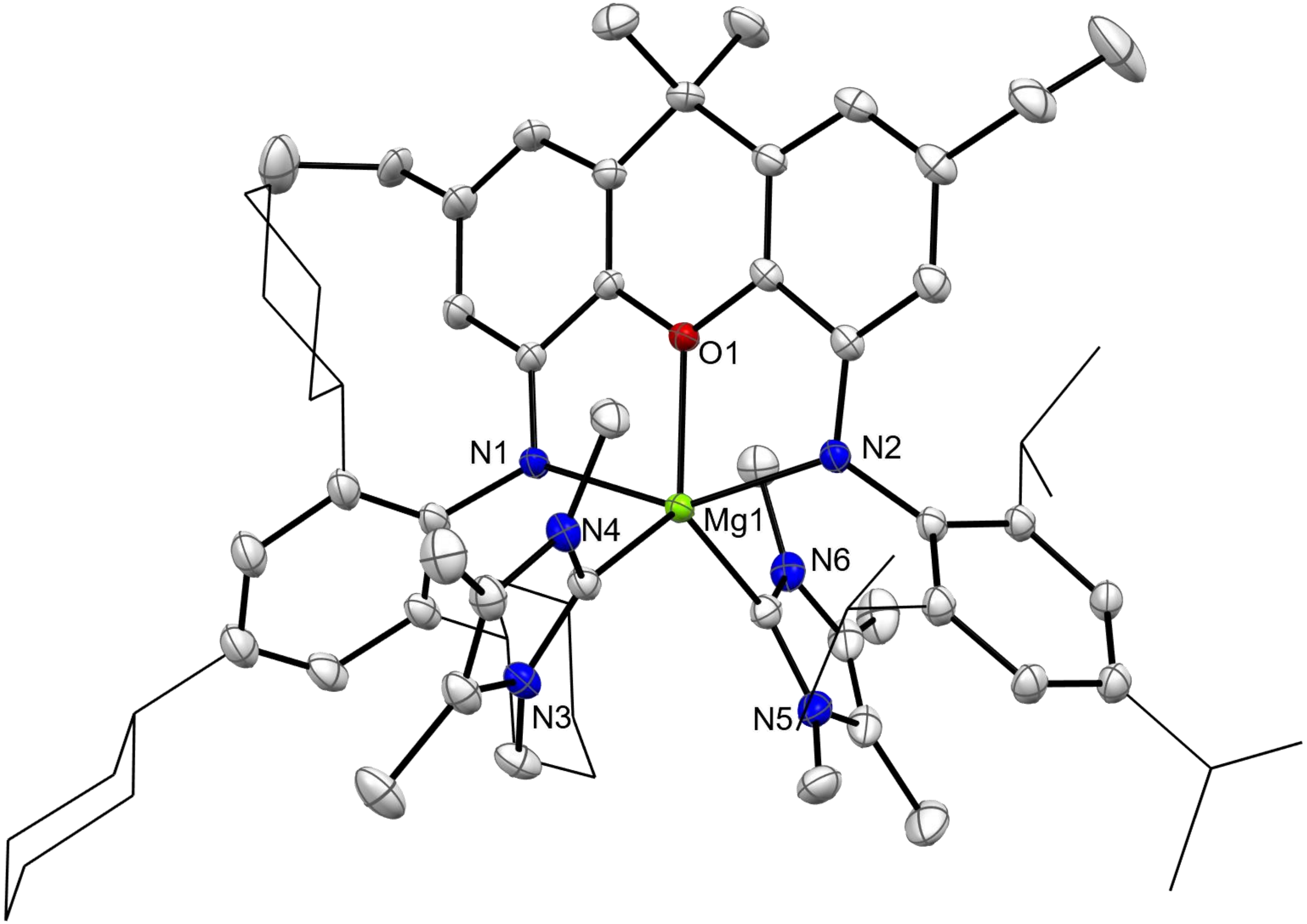


Figure S48: Molecular structure of **3**. Thermal ellipsoids shown at 20% probability; only one molecular unit visualised; hydrogen atoms and toluene solvate omitted.

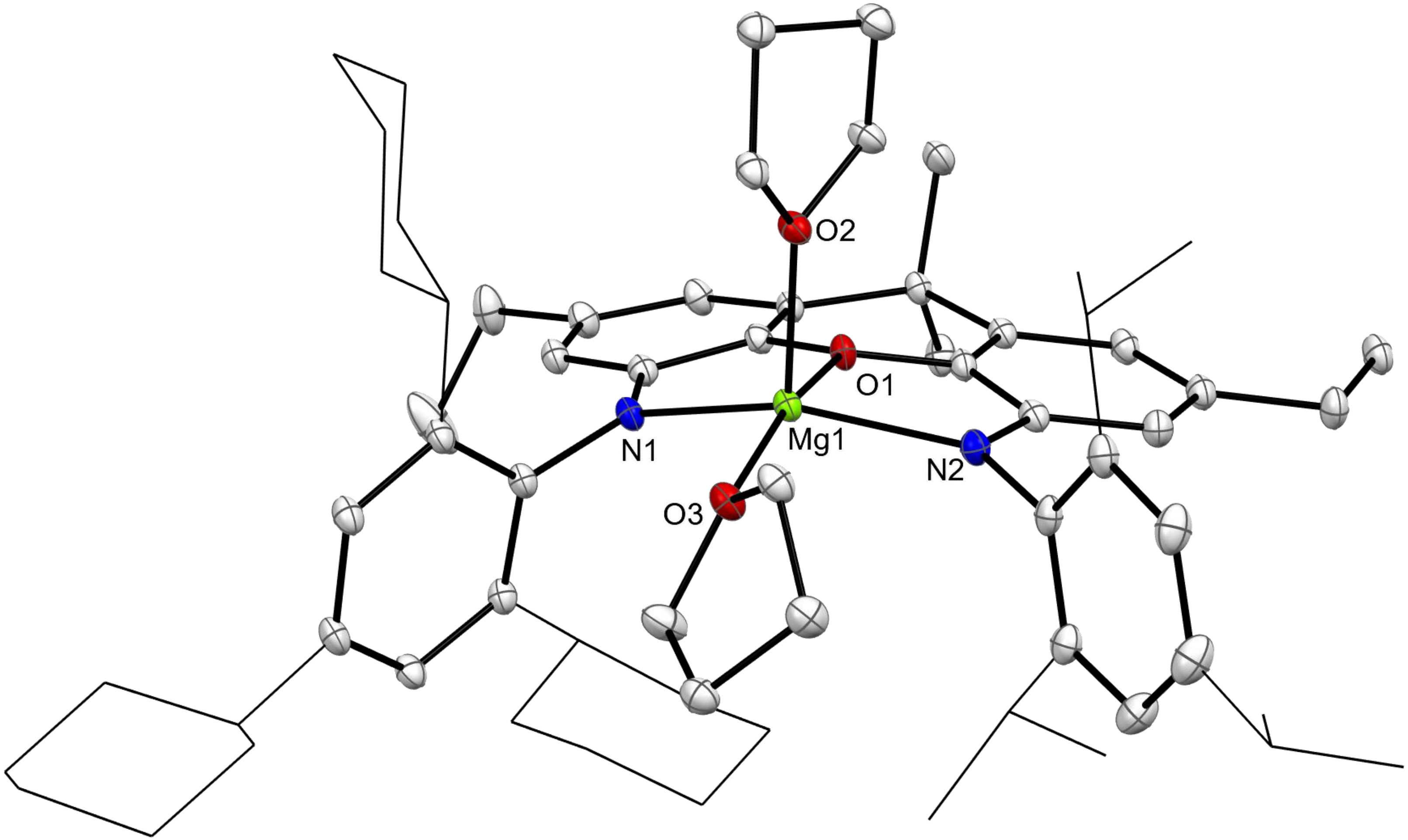


Figure S49: Molecular structure of **4**. Thermal ellipsoids shown at 20% probability; only one molecular unit visualised; hydrogen atoms and toluene solvate omitted.

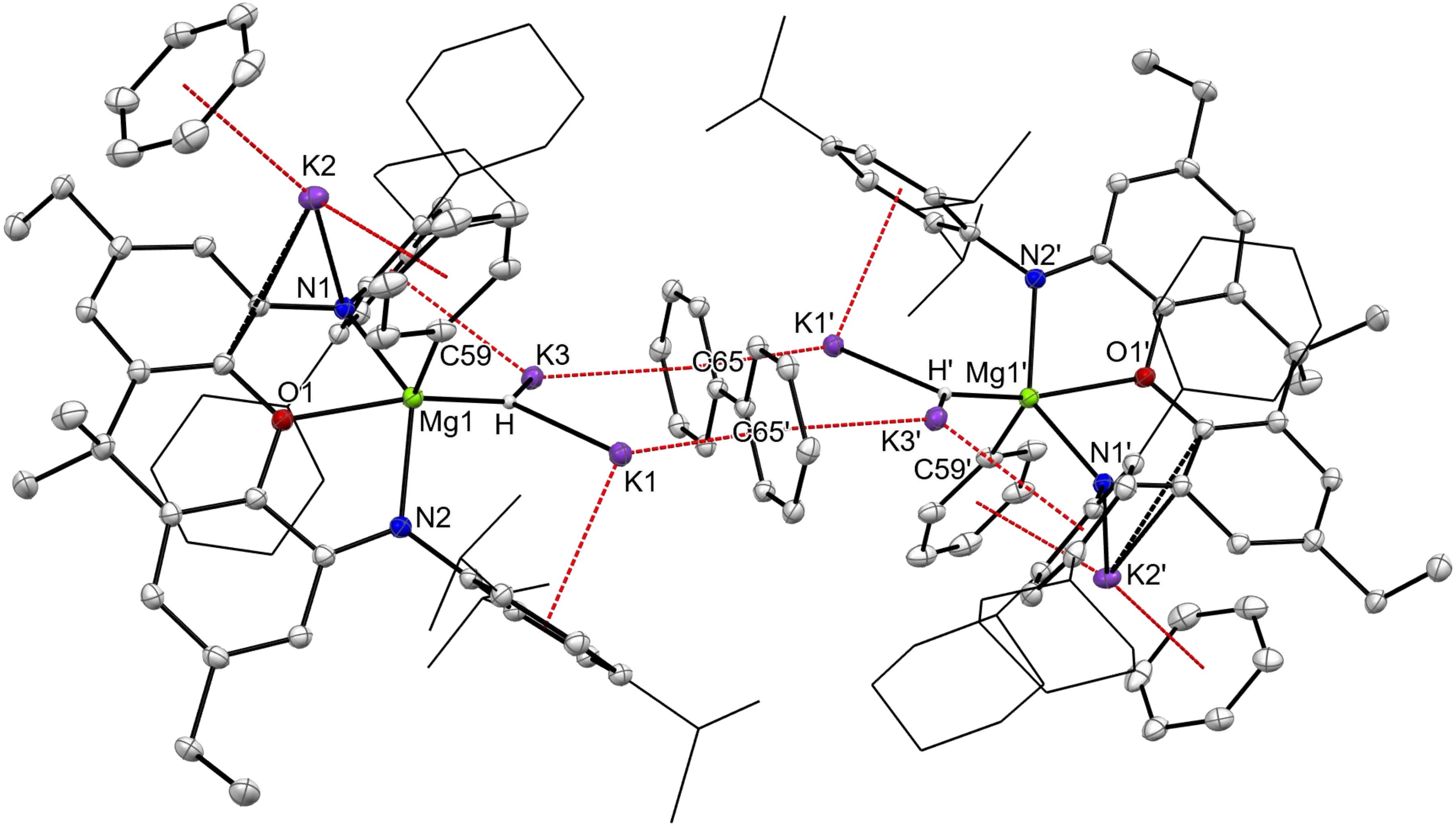


Figure S50: Molecular structure of **5**. Thermal ellipsoids shown at 20% probability; hydrogen atoms omitted.

4. References

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