ASSOCIATED CONTENT

ELECTRONIC SUPPLEMENTARY INFORMATION

Magnesium(0) Complexes and their Reduction Reactions with Binary Transition Metal Carbonyls

Yixiao Jiang,[a] Maryam Niksefat,[a] Sophie G. Unsworth,[a] Joseph M. Parr,[a] Matthew J. Evans,[a,b]

Cameron Jones[a,*]

[a] *School of Chemistry, PO Box 23, Monash University, VIC, 3800, Australia.*

[b] *College of Science and Engineering, Flinders University, Bedford Park, SA, 5042, Australia.*

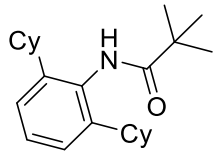
Contents (115 pages)

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. 2,6–Dicyclohexylaniline,[S1] 2,4,6–tricyclohexylaniline,[S2] Na/NaCl[S3] (5 wt%), *N*-(2,6-diisopropylphenyl)-3,3-dimethylbutan-2-imine[S4] were prepared according to their literature procedures. Unless otherwise stated, chemicals were purchased from Sigma-Aldrich and used as received.

Preparation of *N*-(2,6-dicyclohexylphenyl)pivalamide



2,6-dicyclohexylaniline (20.00 g, 77.7 mmol) and triethylamine (10.80 mL, 77.7 mmol) were suspended in dichloromethane (250 mL) and transferred to a 500 mL round bottom flask fitted with a reflux condenser (under anaerobic conditions). Pivaloyl chloride (9.51 mL, 77.7 mmol) was added dropwise with vigorous stirring. Upon complete addition, the resultant mixture was heated at reflux (in a 50 °C oil bath) for 3 hours. A white precipitate formed during this period. The mixture was cooled, the reaction volume reduced by half *in vacuo*, then filtered through a glass frit. The solid material was then washed with water (3 x 75 mL), hexane (3 x 50 mL) and dried *in vacuo*. The product was obtained as a white solid that was sufficiently pure for the following synthetic procedure. **Yield**: 21.5 g, 81 %.

M.p.: > 260 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.16 – 1.44 (m, 10H, Cy–*H*), 1.38 (s, 9H, $C(CH_3)_3$), 1.65 – 1.89 (m, 10H, Cy–*H*), 2.63 – 2.50 (m, 2H, Cy–*H*), 6.81 (s, 1H, N*H*CO), 7.12 (d, J = 7.8 Hz, 2H, $_{DCHP}$Ar–*H*), 7.21 – 7.27 (m, 1H, $_{DCHP}$Ar–*H*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 26.4, 27.4 (Cy–*C*), 28.0 ($C(CH_3)_3$), 34.0, 39.4 (Cy–*C*), 39.8 ($C(CH_3)_3$), 124.0, 128.1, 131.8, 145.3 ($_{DCHP}$Ar–*C*), 177.3 (NH*C*O).

I.R. (solid, cm^{-1}): 3295 (m), 2922 (s), 2848 (s), 1640 (s), 1502 (s), 1446 (s), 1360 (m), 1308 (w), 1256 (w), 1170 (m), 1133 (w), 1103 (w), 1025 (w), 943 (m), 887 (w), 790 (m), 738 (m).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{23}H_{35}NO$: 342.2792; Found: 342.2795.

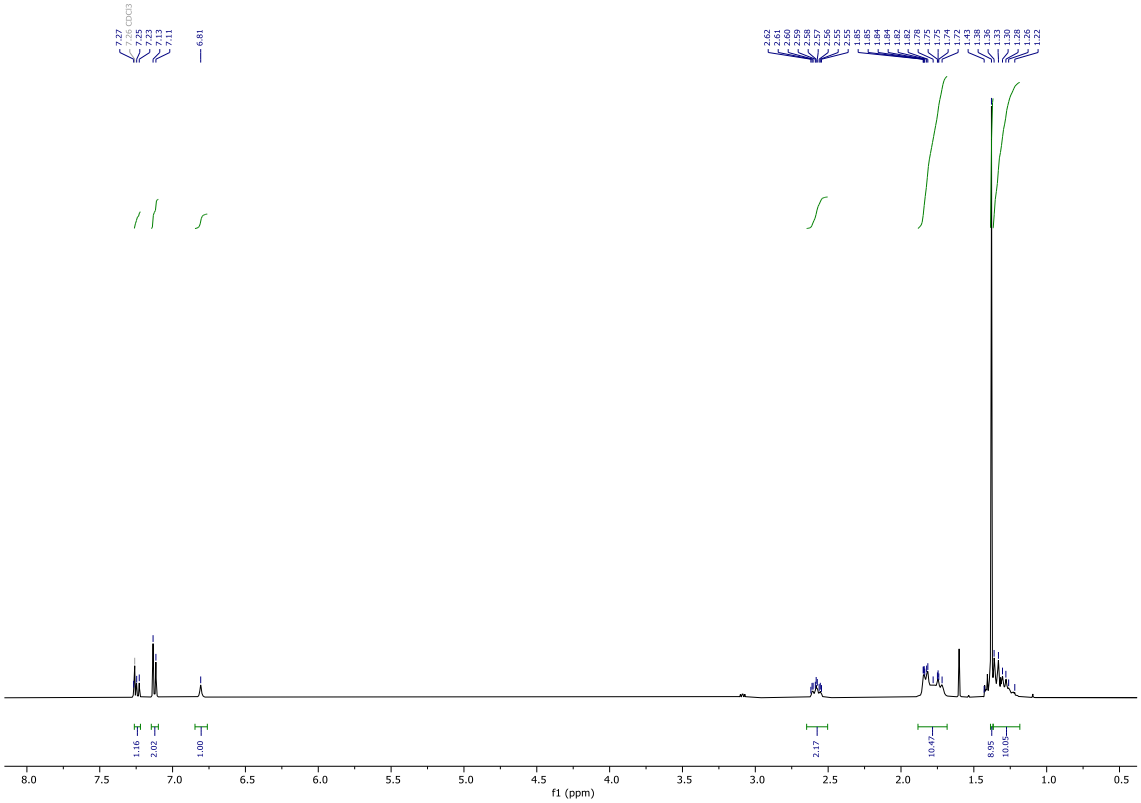


Figure S1: ^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of *N*-(2,6-dicyclohexylphenyl)pivalamide.

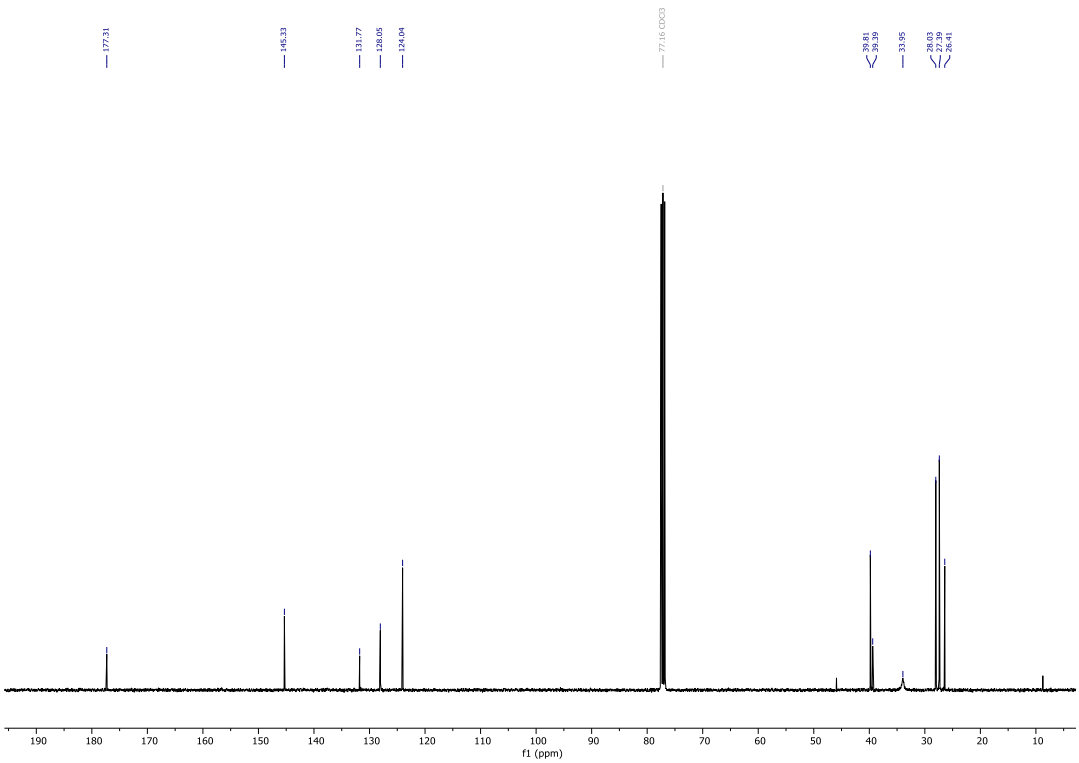


Figure S2: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, $CDCl_3$) of *N*-(2,6-dicyclohexylphenyl)pivalamide.

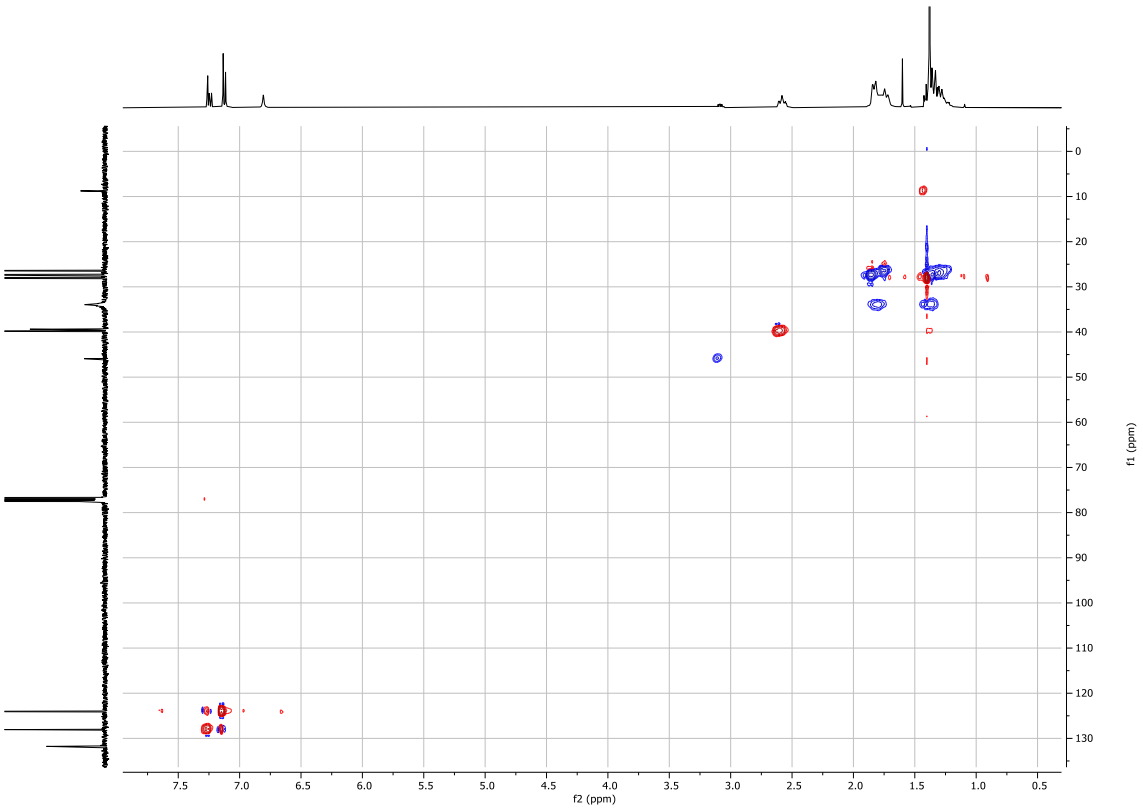


Figure S3: HSQC NMR spectrum (298 K, $CDCl_3$) of *N*-(2,6-dicyclohexylphenyl)pivalamide.

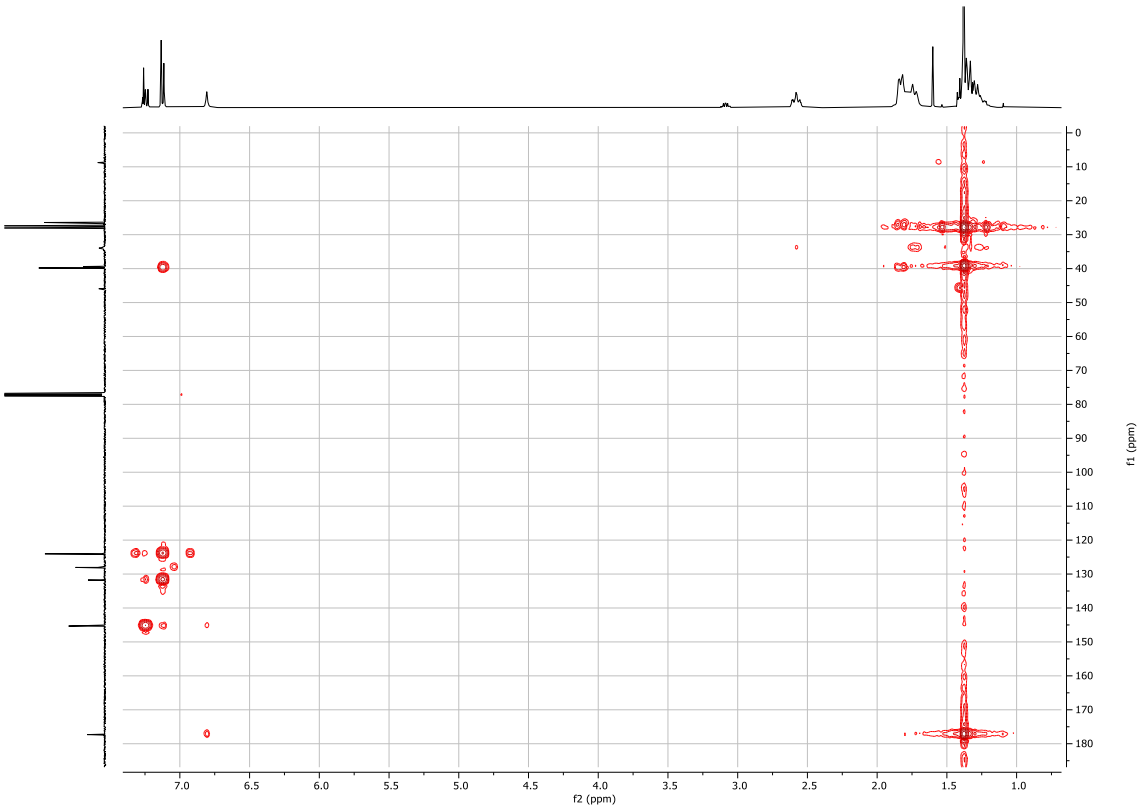


Figure S4: HMBC NMR spectrum (298 K, $CDCl_3$) of *N*-(2,6-dicyclohexylphenyl)pivalamide.

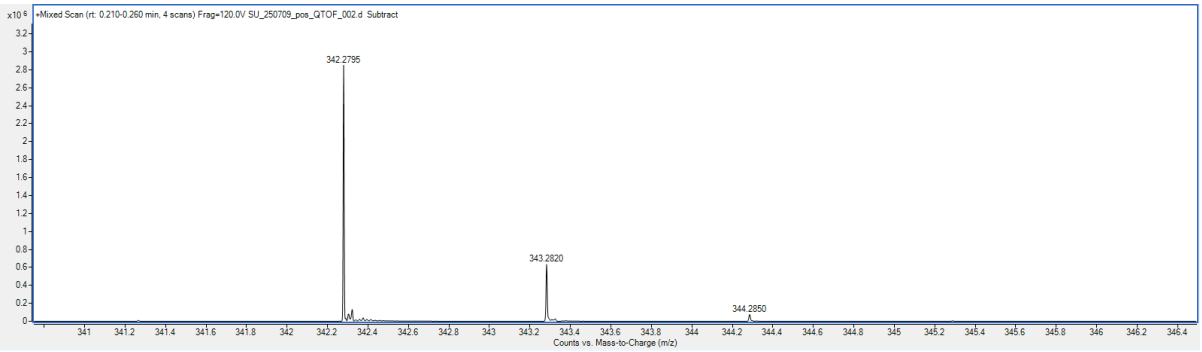
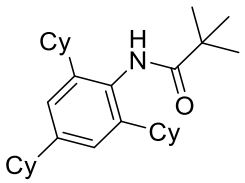


Figure S5: HRMS spectrum of *N*-(2,6-dicyclohexylphenyl)pivalamide.

Preparation of *N*-(2,4,6-tricyclohexylphenyl)pivalamide



2,4,6-tricyclohexylaniline (5.00 g, 14.7 mmol) and triethylamine (2.10 mL, 15.0 mmol) were suspended in dichloromethane (150 mL) and transferred to a 500 mL round bottom flask fitted with a reflux condenser (under anaerobic conditions). Pivaloyl chloride (1.86 mL, 15.0 mmol) was added dropwise with vigorous stirring. Upon complete addition, the resultant mixture was heated at reflux (in a 50 °C oil bath) for 3 hours. A white precipitate formed during this time. The mixture was cooled and filtered through a glass frit. The solid material was washed with water (3 x 75 mL), hexane (3 x 50 mL) and then dried *in vacuo*. The product was obtained as a white solid that was sufficiently pure for the following synthetic procedure. **Yield**: 6.00 g, 96 %.

M.p.: > 260 °C.

^{1}H NMR (400 MHz, C_6D_6): δ 1.20 (s, 9H, C(C$\underline{H}_3$)$_3$), 1.22 – 1.53 (m, 14H, Cy–$\underline{H}$), 1.59 – 2.05 (m, 16H, Cy–$\underline{H}$), 2.52 (tt, J = 11.8, 3.4 Hz, 1H, Cy–$\underline{H}$), 2.73 (tt, J = 11.8, 3.4 Hz, 2H, Cy–$\underline{H}$), 6.29 (s, 1H, N$\underline{H}$CO), 7.14 (s, 3H, $_{TCHP}$Ar–$\underline{H}$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 26.6, 26.8, 27.4 (Cy–$\underline{C}$), 27.8 (C($\underline{C}$H$_3$)$_3$), 28.0, 34.4, 35.0 (Cy–$\underline{C}$), 39.2 ($\underline{C}$(CH$_3$)$_3$), 40.3, 45.2 (Cy–$\underline{C}$), 122.6, 130.5, 145.5, 147.5 ($_{TCHP}$Ar–$\underline{C}$), 176.7 (NH$\underline{C}$O).

I.R. (solid, cm^{-1}): 3293 (m), 2920 (s), 2845 (s), 2588 (w), 2485 (w), 1635 (s), 1506 (s), 1471 (s), 1438 (s), 1396 (w), 1361 (m), 1240 (w), 1170 (w), 1032 (w), 957 (m), 935 (m), 854 (w), 806 (w), 656 (s).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{29}H_{45}NO$: 423.3574; Found: 424.3606.

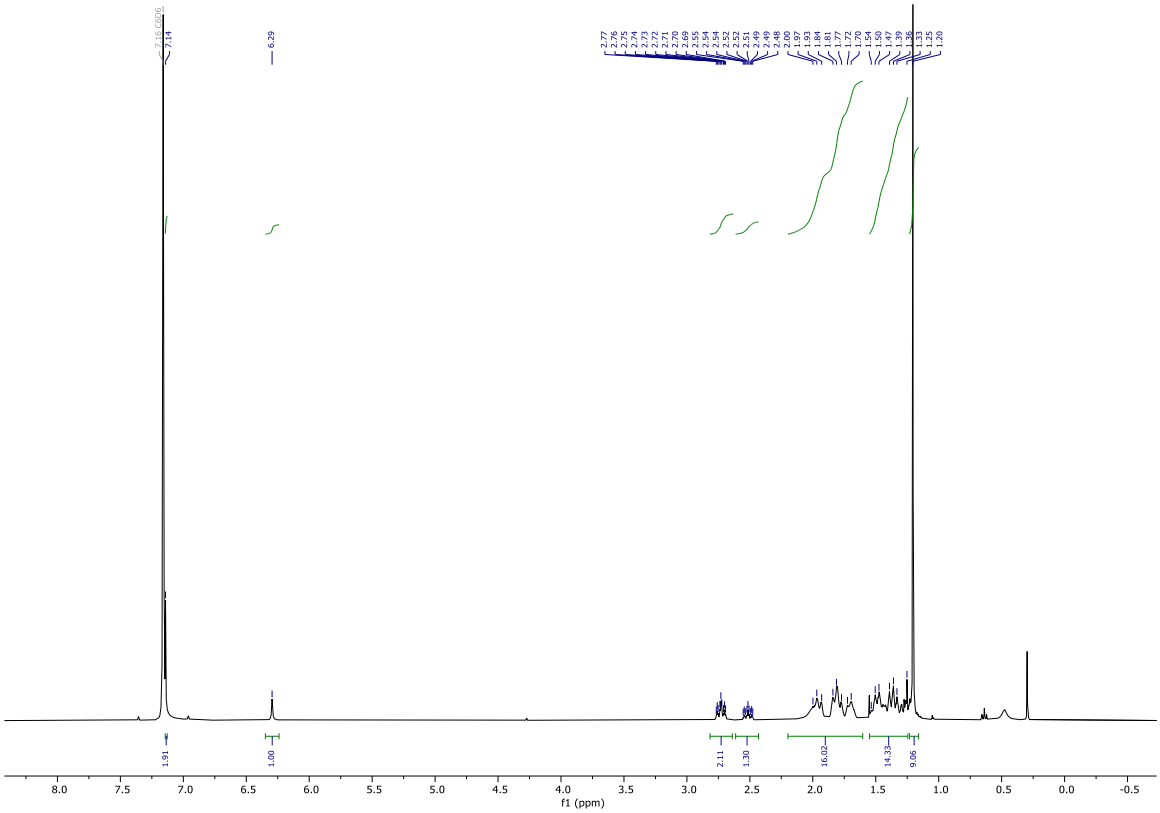


Figure S6: ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of *N*-(2,4,6-tricyclohexylphenyl)pivalamide.

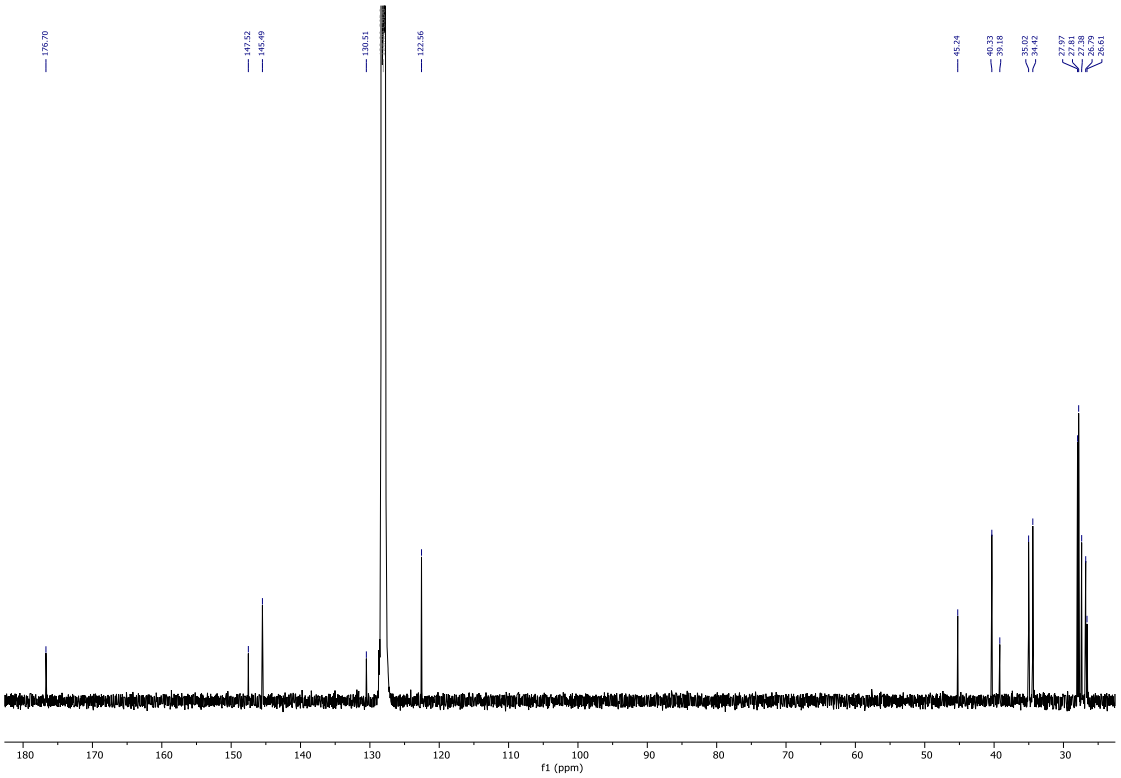


Figure S7: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, C_6D_6) of *N*-(2,4,6-tricyclo hexylphenyl)pivalamide.

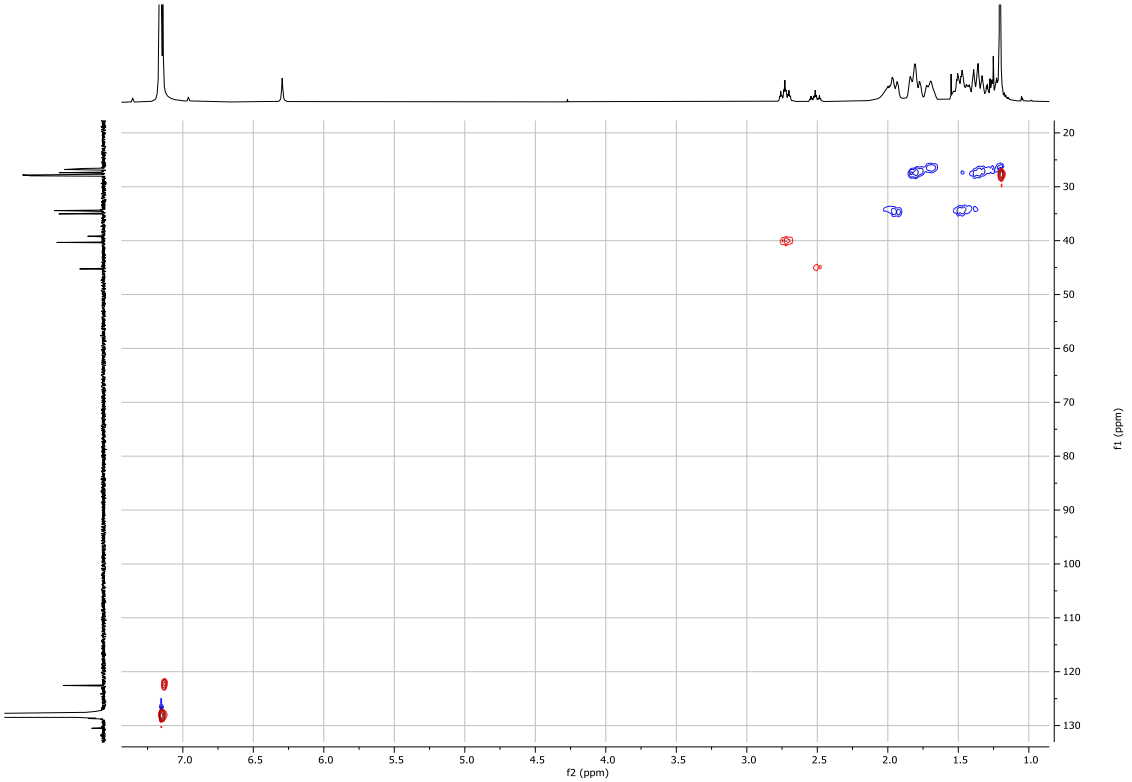


Figure S8: HSQC NMR spectrum (298 K, C_6D_6) of *N*-(2,4,6-tricyclohexylphenyl)pivalamide.

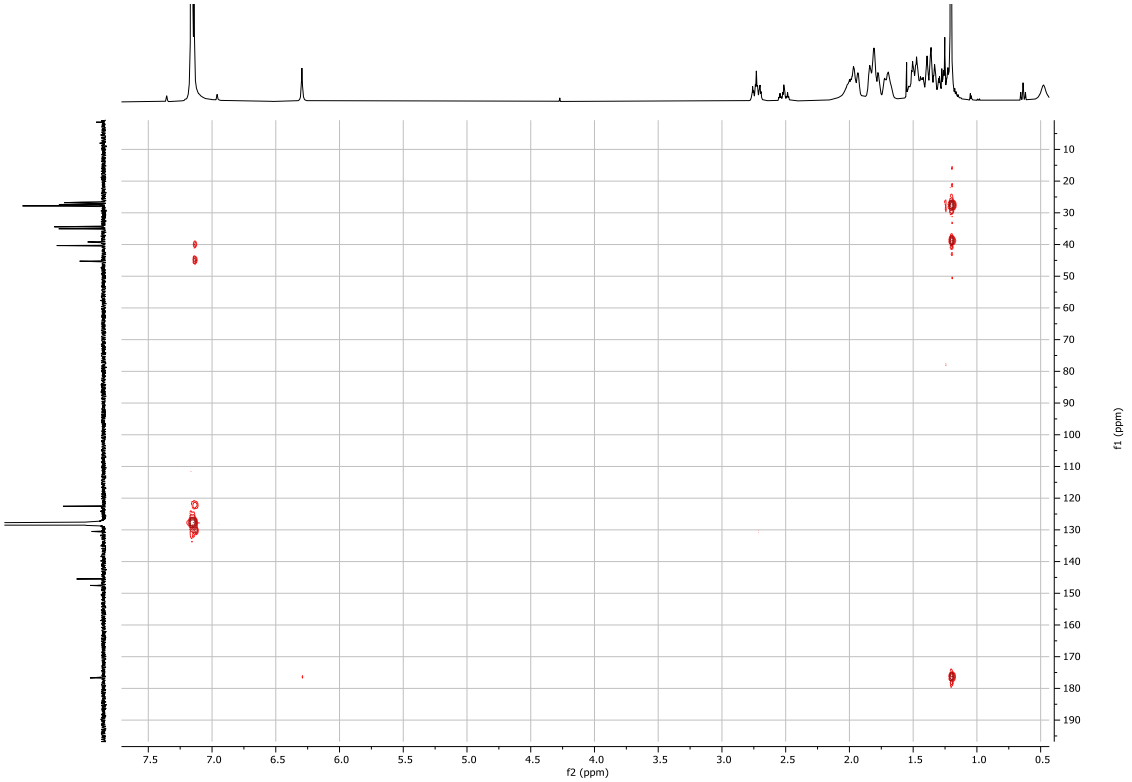


Figure S9: HMBC NMR spectrum (298 K, C_6D_6) of *N*-(2,4,6-tricyclohexylphenyl)pivalamide.

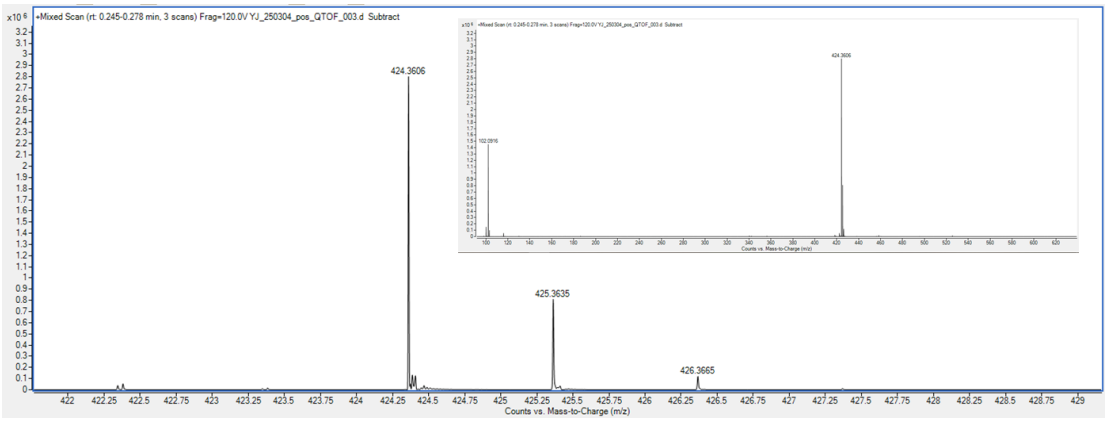
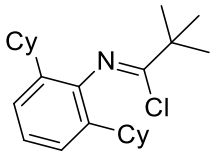


Figure S10: HRMS spectrum of *N*-(2,4,6-tricyclohexylphenyl)pivalamide.

Preparation of *N*-(2,6-dicyclohexylphenyl)pivalimidoyl chloride



N-(2,6-dicyclohexylphenyl)pivalamide (21.50 g, 0.063 mol) was dissolved in toluene (~200 mL) and stirred under an inert atmosphere. To this suspension was added phosphorus pentachloride (19.66 g, 0.094 mol) in one portion. The reaction mixture was heated at reflux for 16 hours to give a clear yellow solution. Volatiles were removed *in vacuo* and the residue heated under vacuum at 90 °C for 2 hours. The residue was then dissolved in diethyl ether (~100 mL) and the product obtained as a pale-yellow solid by fractional crystallisation. **Yield**: 17.95 g, 79 %.

M.p.: 94–95 °C.

^{1}H NMR (400 MHz, C_6D_6): δ 1.06 – 1.34 (m, 8H, Cy–*H*), 1.36 (s, 9H, C(C*H*$_3$)$_3$), 1.40 – 1.54 (m, 2H, Cy–*H*), 1.61 – 1.83 (m, 6H, Cy–*H*), 1.89 – 2.04 (m, 4H, Cy–*H*), 2.44 – 2.61 (m, 2H, Cy–*H*), 7.12 – 7.15 (m, 3H, $_{DCHP}$Ar–*H*).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 26.7, 27.7 (Cy–*C*), 28.6 (C(*C*H$_3$)$_3$), 33.5, 33.8, 39.9 (Cy–*C*), 44.1 (*C*(CH$_3$)$_3$), 124.1, 125.0, 135.8, 143.9 ($_{DCHP}$Ar–*C*), 154.5 (N*C*Cl).

I.R. (solid, cm^{-1}): 2972 (w), 2920 (s), 2843 (s), 1981 (w), 1700 (s), 1460 (m), 1441 (s), 1360 (w), 1243 (w), 1031 (w), 995 (w), 931 (m), 856 (s), 818 (s), 629 (m).

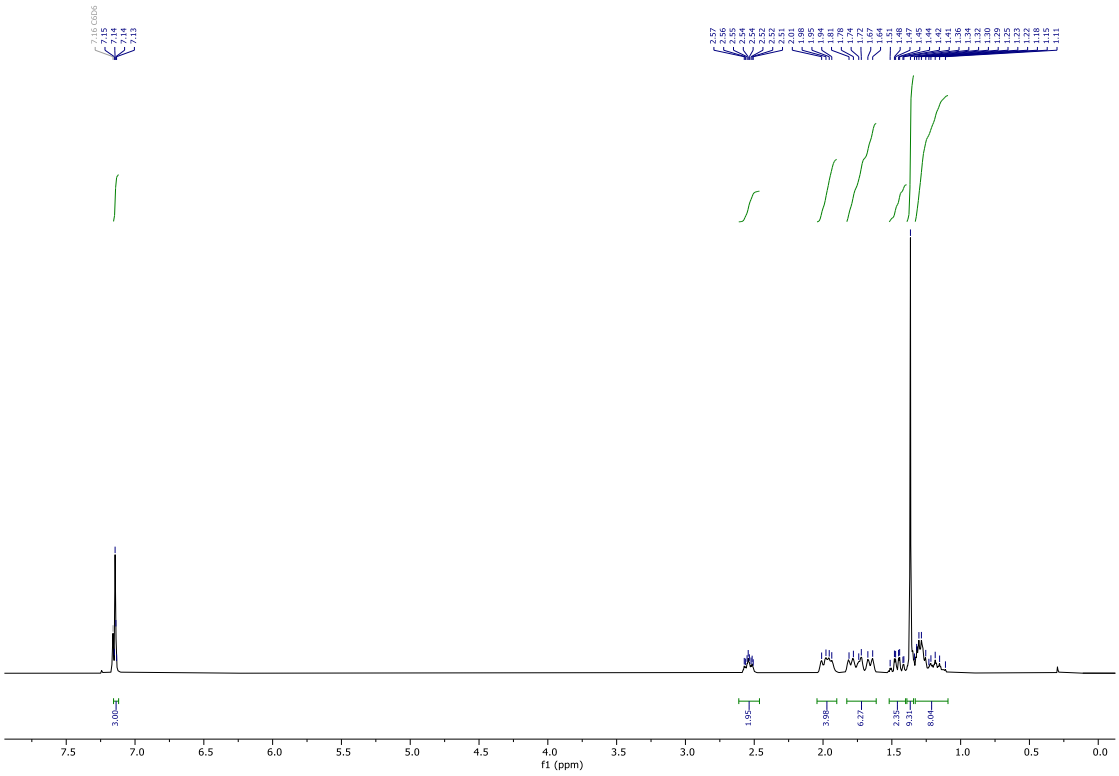


Figure S11: ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of *N*-(2,6-dicyclohexylphenyl)pivalimidoyl chloride.

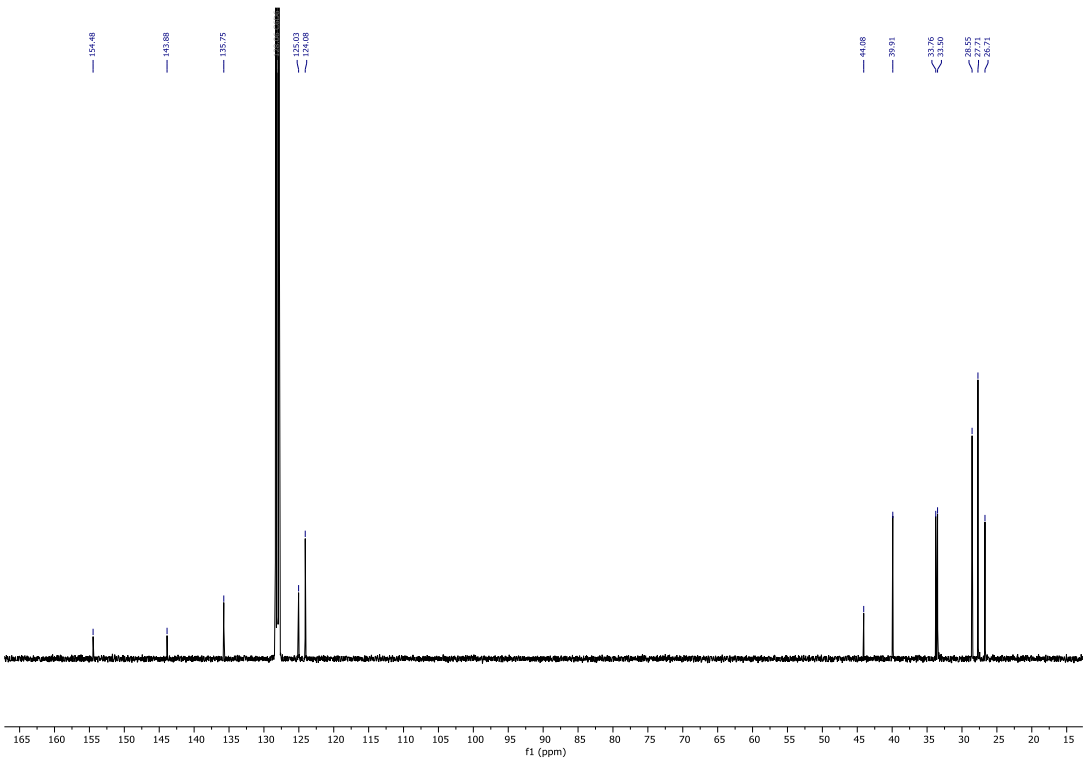


Figure S12: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, C_6D_6) of *N*-(2,6-dicyclohexylphenyl)pivalimidoyl chloride.

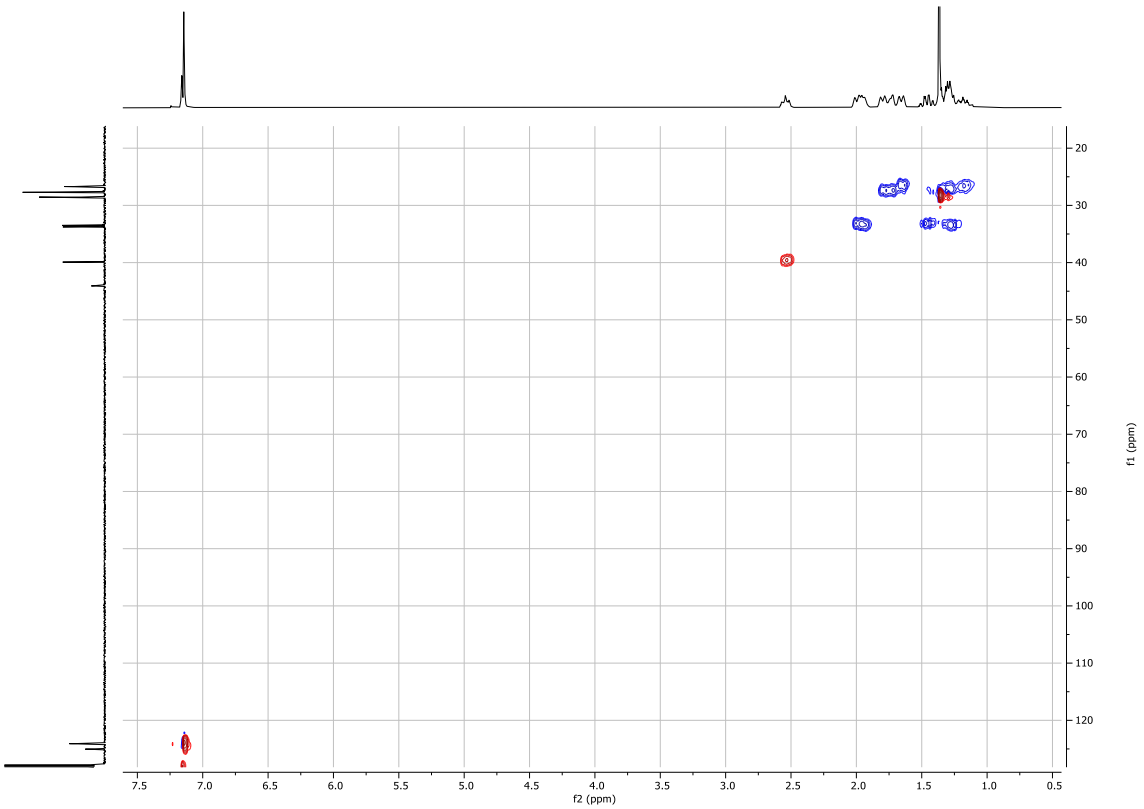


Figure S13: HSQC NMR spectrum (298 K, C_6D_6) of *N*-(2,6-dicyclohexylphenyl)pivalimidoyl chloride.

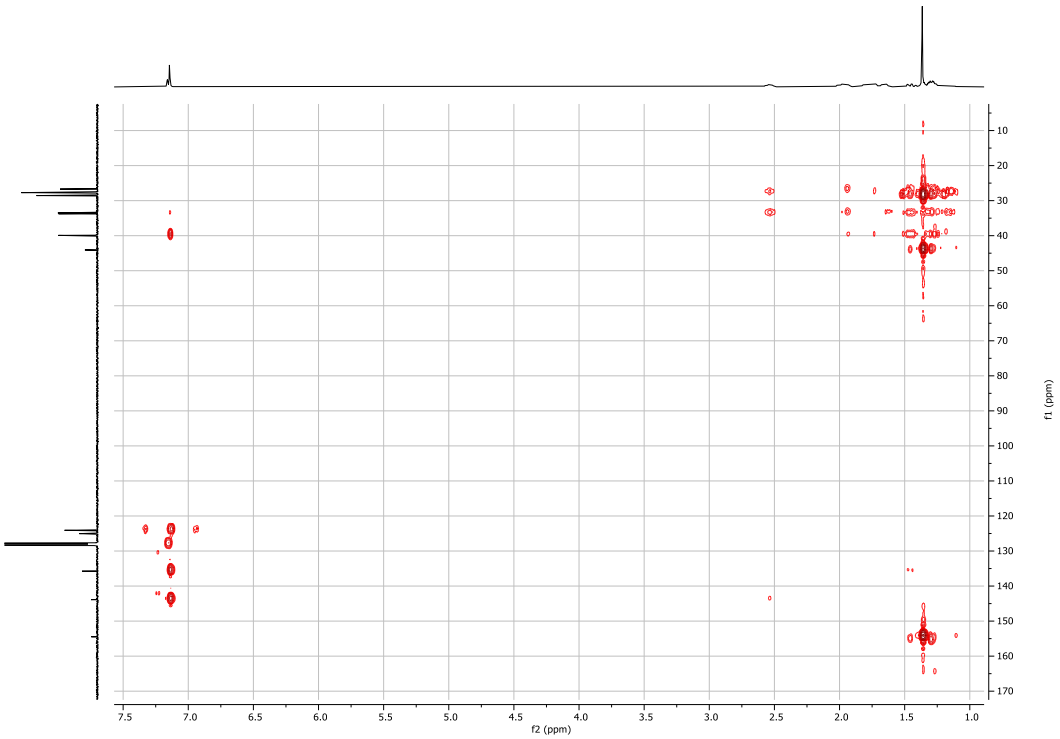
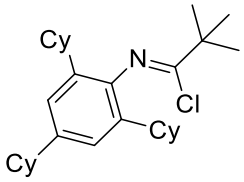


Figure S14: HMBC NMR spectrum (298 K, C_6D_6) of *N*-(2,6-dicyclohexylphenyl)pivalimidoyl chloride.

Preparation of *N*-(2,4,6-tricyclohexylphenyl)pivalimidoyl chloride



N-(2,4,6-tricyclohexylphenyl)pivalamide (5.00 g, 0.011 mol) was dissolved in toluene (~200 mL) and stirred under an inert atmosphere. To this suspension was added phosphorus pentachloride (3.53 g, 0.017 mol) in one portion. The reaction mixture was heated at reflux for 16 hours to give a clear yellow solution. Volatiles were removed *in vacuo* and the residue heated under vacuum at 90 °C for 2 hours. The residue was then dissolved in diethyl ether (~100 mL) and the product obtained as a pale-yellow solid by fractional crystallisation. **Yield**: 4.50 g, 87%.

M.p.: > 260 °C

^{1}H NMR (400 MHz, C_6D_6) δ 1.18 – 1.36 (m, 8H, Cy–*H*), 1.38 (s, 9H, C(C*H*$_3$)$_3$), 1.44 – 2.12 (m, 22H, Cy–*H*), 2.40 – 2.67 (m, 3H, Cy–*H*), 7.15 (s, 2H, $_{TCHP}$Ar–*H*).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6): *δ* 26.7, 26.8, 27.4, 27.8 (Cy–*C*), 28.6 (C(*C*H$_3$)$_3$), 33.7, 33.9, 35.2, 40.1 (Cy–*C*), 44.1 (*C*(CH$_3$)$_3$), 45.2 (Cy–*C*), 122.4, 135.5, 141.9, 144.3 ($_{TCHP}$Ar–*C*), 154.2 (N*C*Cl).

I.R. (solid, cm^{-1}): 2972 (w), 2920 (s), 2843 (s), 1981 (w), 1700 (s), 1460 (m), 1441 (s), 1360 (w), 1243 (w), 1031 (w), 995 (w), 931 (m), 856 (s), 818 (s), 629 (m).

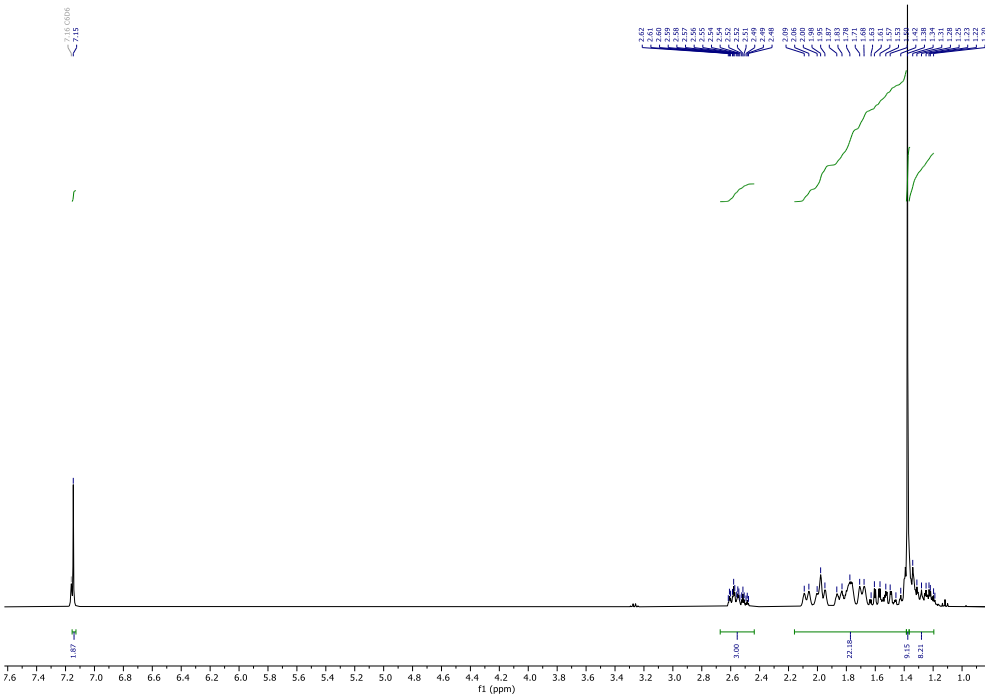


Figure S15: ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of *N*-(2,4,6-tricyclohexylphenyl)pivalimidoyl chloride.

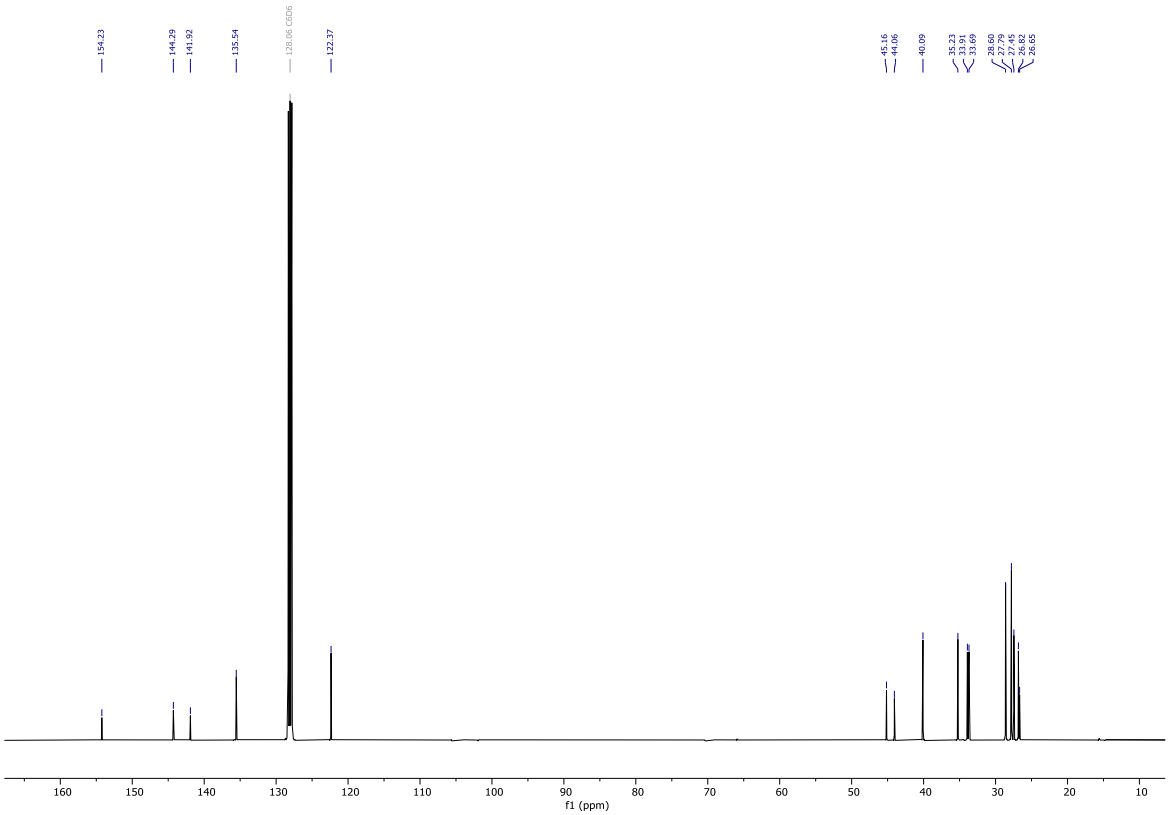


Figure S16: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, C_6D_6) of *N*-(2,4,6-tricyclohexylphenyl)pivalimidoyl chloride.

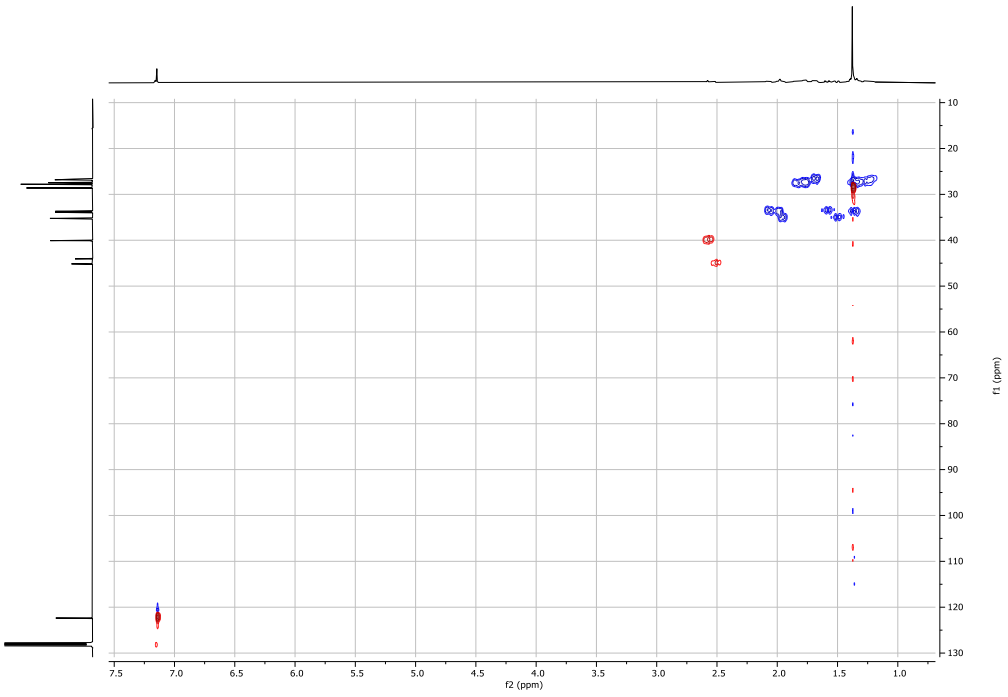


Figure S17: HSQC NMR spectrum (298 K, C_6D_6) of *N*-(2,4,6-tricyclohexylphenyl)pivalimidoyl chloride.

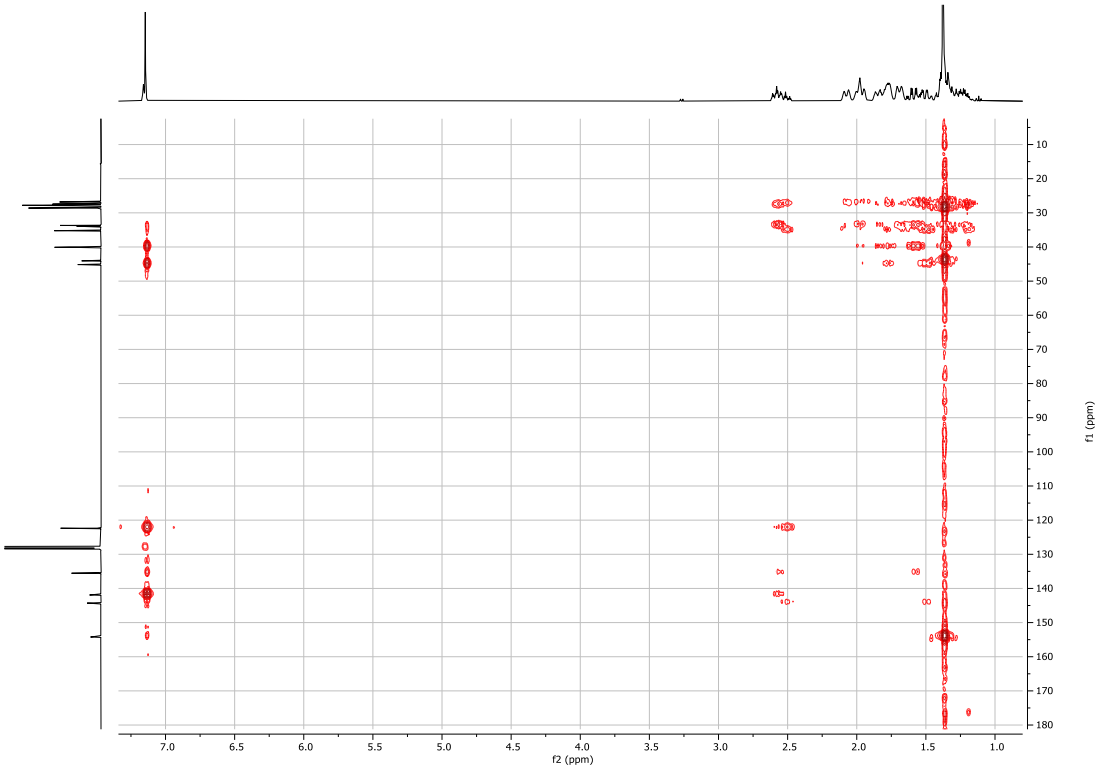
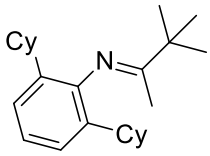


Figure S18: HMBC NMR spectrum (298 K, C_6D_6) of *N*-(2,4,6-tricyclohexylphenyl)pivalimidoyl chloride.

Preparation of *N*-(2,6-dicyclohexylphenyl)-3,3-dimethylbutan-2-imine



N-(2,6-dicyclohexylphenyl)pivalimidoyl chloride (11.00 g, 0.031 mol) was dissolved in diethyl ether (~200 mL) and cooled to –78 °C. To this mixture was added a solution of methyl magnesium bromide (3M in Et_2O, 13.3 mL, 0.040 mol). The mixture was allowed to warm to room temperature and stirred for 16 hours. The mixture was then cooled to 0 °C in an ice bath and water (~50 mL) added slowly. The organic layer was extracted with diethyl ether (3 x 100 mL), dried over anhydrous $MgSO_4$ and filtered. Volatiles were removed *in vacuo* and the obtained off-white solid used without further purification. **Yield**: 10.01 g, 96 %.

M.p.: 84–86 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.17 – 1.28 (m, 8H, Cy–*H*), 1.29 (s, 9H, C(C*H*$_3$)$_3$), 1.52 – 1.63 (m, 4H, Cy–*H*), 1.65 (s, 3H, NCC*H*$_3$), 1.68 – 1.92 (m, 8H, Cy–*H*), 2.20 – 2.31 (m, 2H, Cy–*H*), 6.94 – 7.01 (m, 1H, $_{DCHP}$Ar–*H*), 7.02 – 7.07 (m, 2H, $_{DCHP}$Ar–*H*).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 16.1 (NC$\underline{C}H_3$), 26.5, 27.3, 27.5 (Cy–$\underline{C}$), 28.3 (C($\underline{C}H_3)_3$), 33.3, 33.4, 39.0 (Cy–$\underline{C}$), 40.6 ($\underline{C}(CH_3)_3$), 122.7, 123.5, 135.0, 146.9 ($_{DCHP}$Ar–$\underline{C}$), 176.6 (N$\underline{C}$).

I.R. (solid, cm^{-1}): 2918 (s), 2847 (s), 1647 (s), 1442 (s), 1364 (s), 1308 (w), 1259 (w), 1230 (m), 1181 (w), 1140 (s), 1092 (w), 1028 (w), 943 (w), 887 (w), 793 (m), 760 (s), 700 (w).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{24}H_{37}N$: 340.2999; Found: 340.3004.

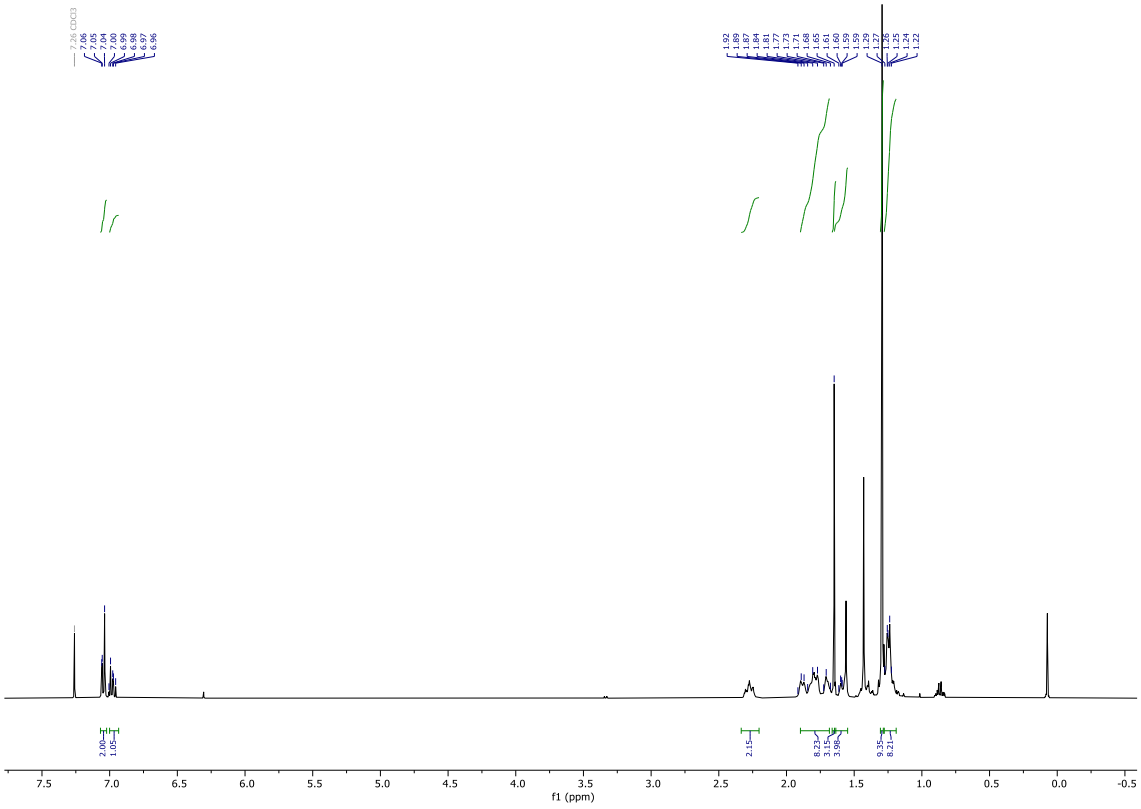


Figure S19: ^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of *N*-(2,6-dicyclohexylphenyl)-3,3-dimethylbutan-2-imine.

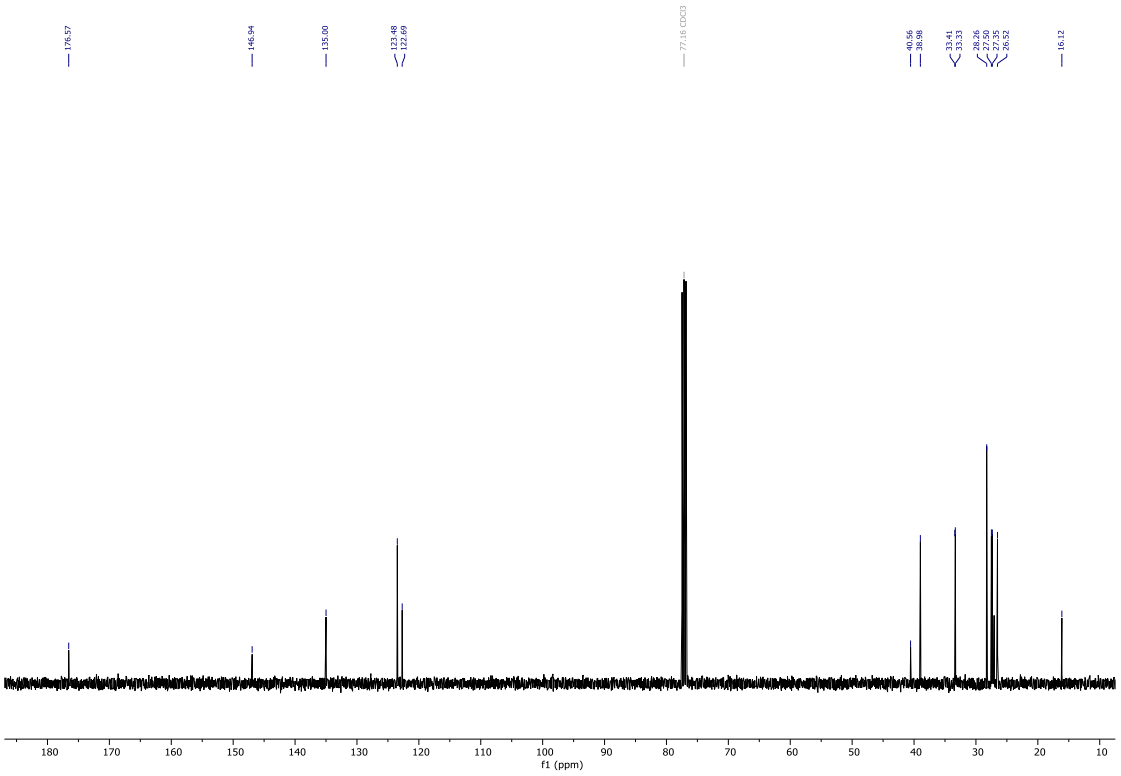


Figure S20: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, $CDCl_3$) of *N*-(2,6-dicyclohexylphenyl)-3,3-dimethylbutan-2-imine.

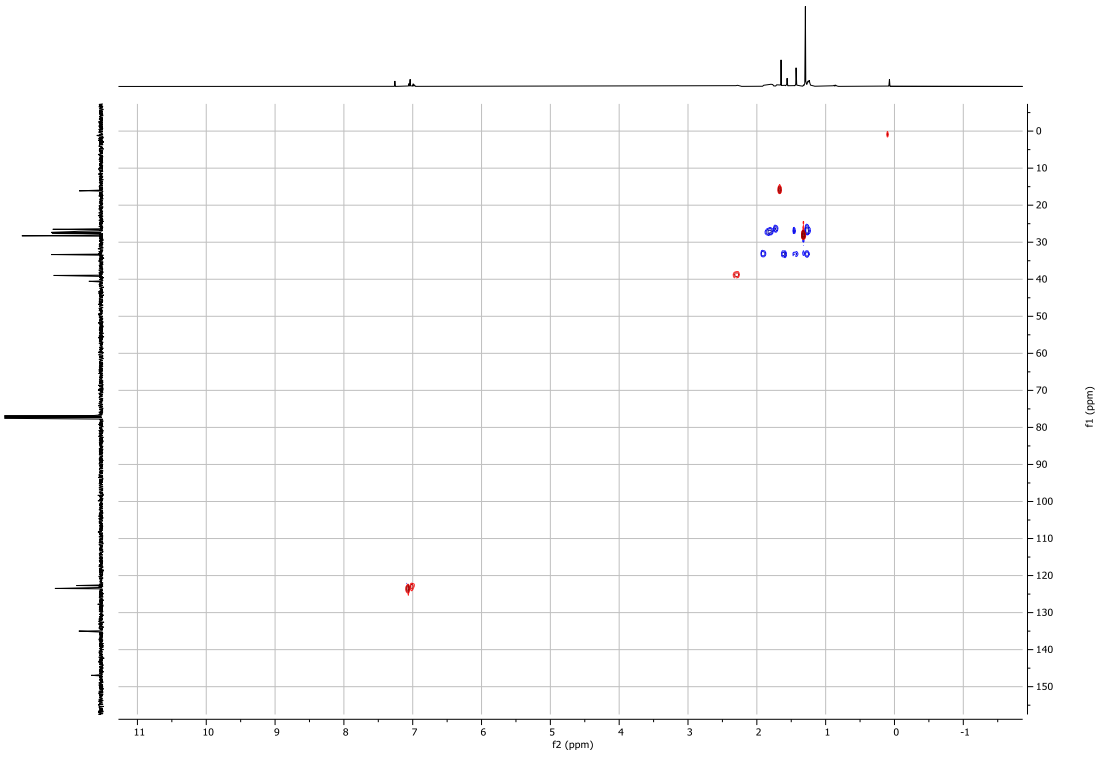


Figure S21: HSQC NMR spectrum (298 K, $CDCl_3$) of *N*-(2,6-dicyclohexylphenyl)-3,3-dimethylbutan-2-imine.

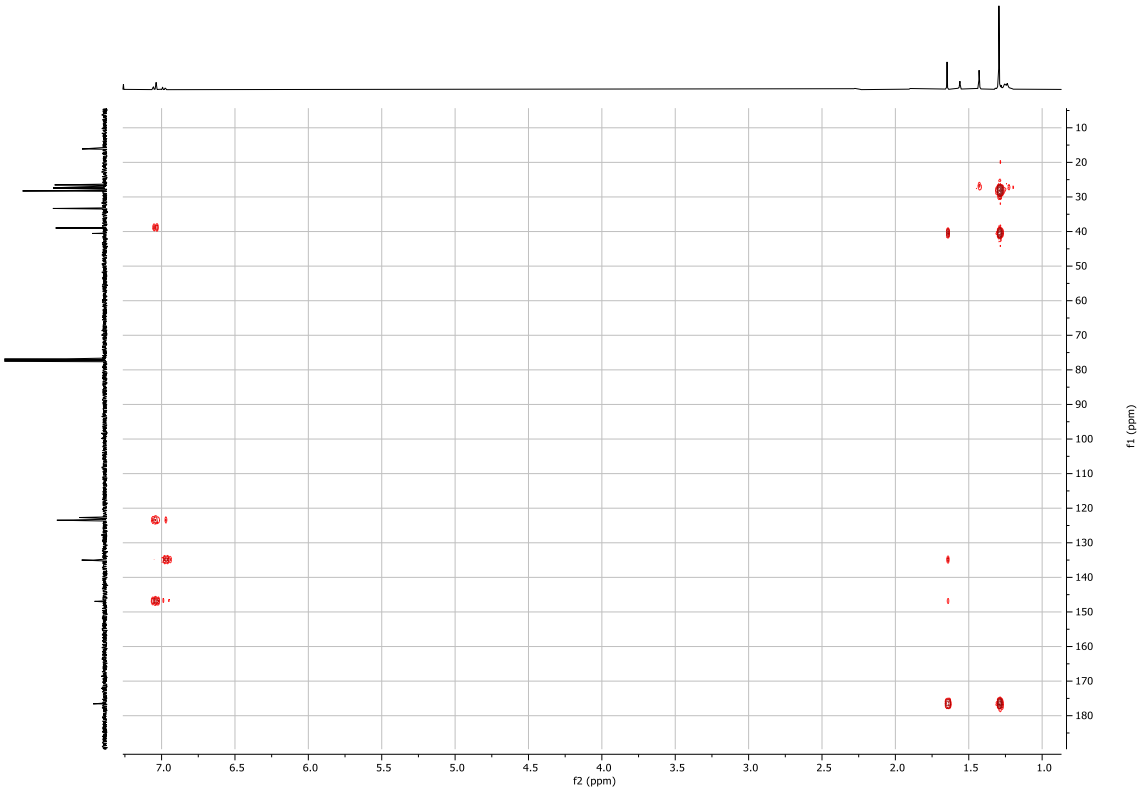


Figure S22: HMBC NMR spectrum (298 K, $CDCl_3$) of *N*-(2,6-dicyclohexylphenyl)-3,3-dimethylbutan-2-imine.

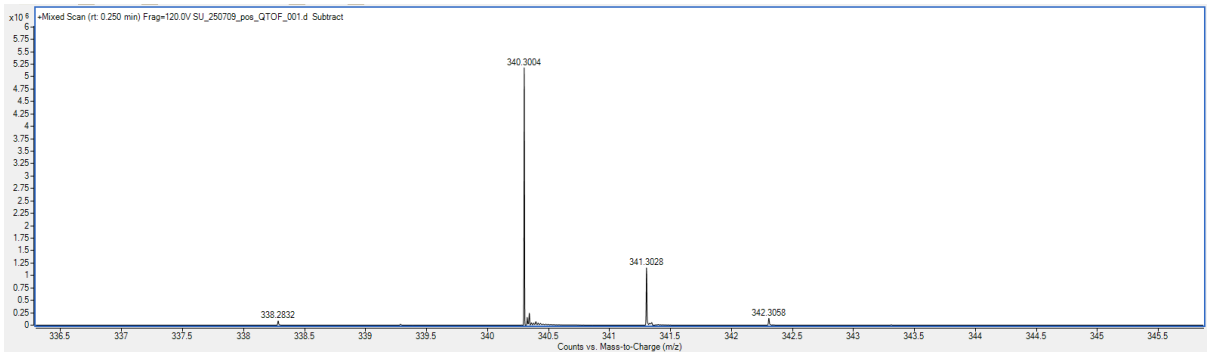
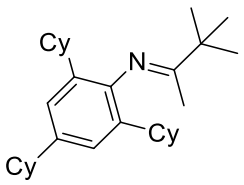


Figure S23: HRMS spectrum of *N*-(2,6-dicyclohexylphenyl)-3,3-dimethylbutan-2-imine.

Preparation of *N*-(2,4,6-tricyclohexylphenyl)-3,3-dimethylbutan-2-imine



N-(2,4,6-tricyclohexylphenyl)pivalimidoyl chloride (4.00 g, 0.009 mol) was dissolved in diethyl ether (~200 mL) and cooled to –78 °C. To this mixture was added a solution of methyl magnesium bromide (3M in Et_2O, 6.45 mL, 0.019 mol). The mixture was allowed to warm to room temperature and stirred for 16 hours. The mixture was then cooled to 0 °C in an ice bath and water (~50 mL) added slowly. The organic layer was extracted with diethyl ether (3 x 100 mL), dried over anhydrous $MgSO_4$ and filtered. Volatiles were removed *in vacuo* and the obtained off-white solid used without further purification. **Yield**: 3.50 g, 92%.

M.p.: 150–152 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.14 – 1.25 (m, 8H, Cy–*H*), 1.28 (s, 9H, C(C*H*$_3$)$_3$), 1.34 – 1.50 (m, 6H, Cy–*H*), 1.53 – 1.62 (m, 2H, Cy–*H*), 1.65 (s, 3H, C*H*$_3$), 1.67 – 1.94 (m, 14H, Cy–*H*), 2.15 – 2.32 (m, 2H, Cy–*H*), 2.36 – 2.48 (m, 1H, Cy–*H*), 6.86 (s, 2H, $_{TCHP}$Ar–*H*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 16.1 (*C*H$_3$), 26.5, 26.6, 27.2, 27.4, 27.6 (Cy–*C*), 28.3 (C(*C*H$_3$)$_3$), 33.4, 33.5, 34.9, 39.1 (Cy–*C*), 40.5 (*C*(CH$_3$)$_3$), 44.6 (Cy–*C*), 121.8, 134.4, 142.0, 144.5 ($_{TCHP}$Ar–*C*), 176.3 (N*C*).

I.R. (solid, cm^{-1}): 2965 (w), 2919 (s), 2846 (s), 1654 (s), 1444 (s), 1360 (m), 1240 (w), 1146 (s), 1031 (w), 952 (w), 885 (m), 843 (m), 808 (s), 706 (w), 629 (w).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{30}H_{47}N$: 422.3782; Found: 422.3813.

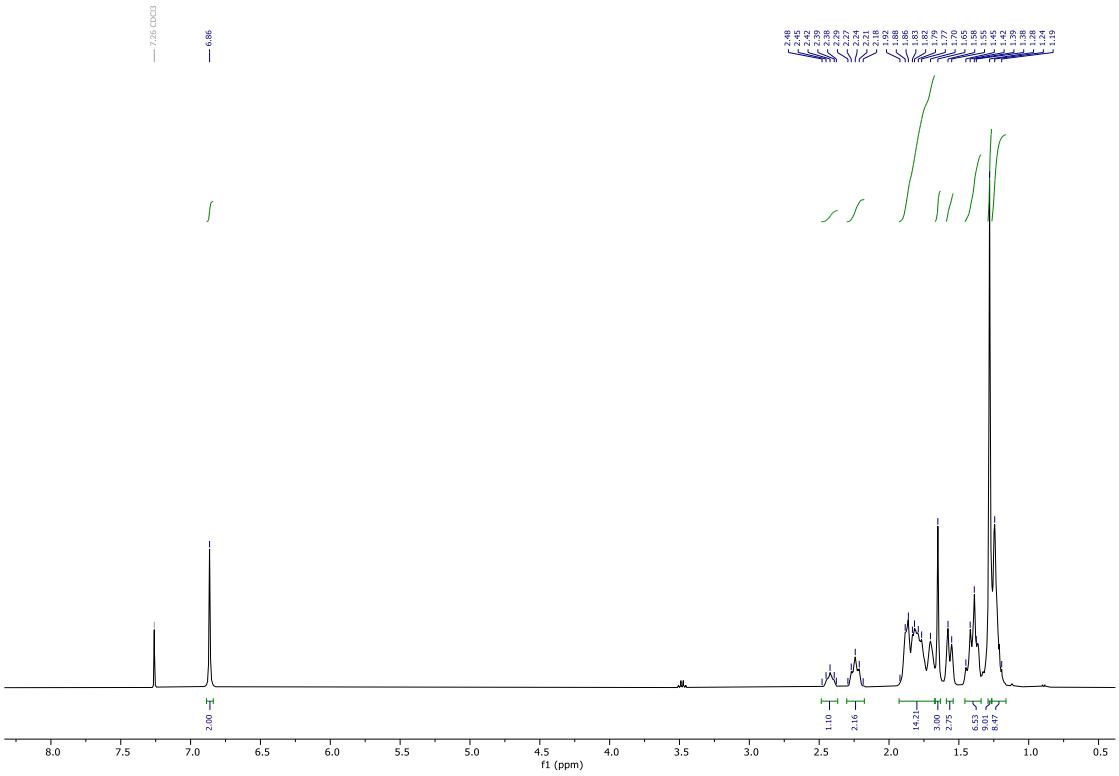


Figure S24: ^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of *N*-(2,4,6-tricyclohexylphenyl)-3,3-dimethylbutan-2-imine

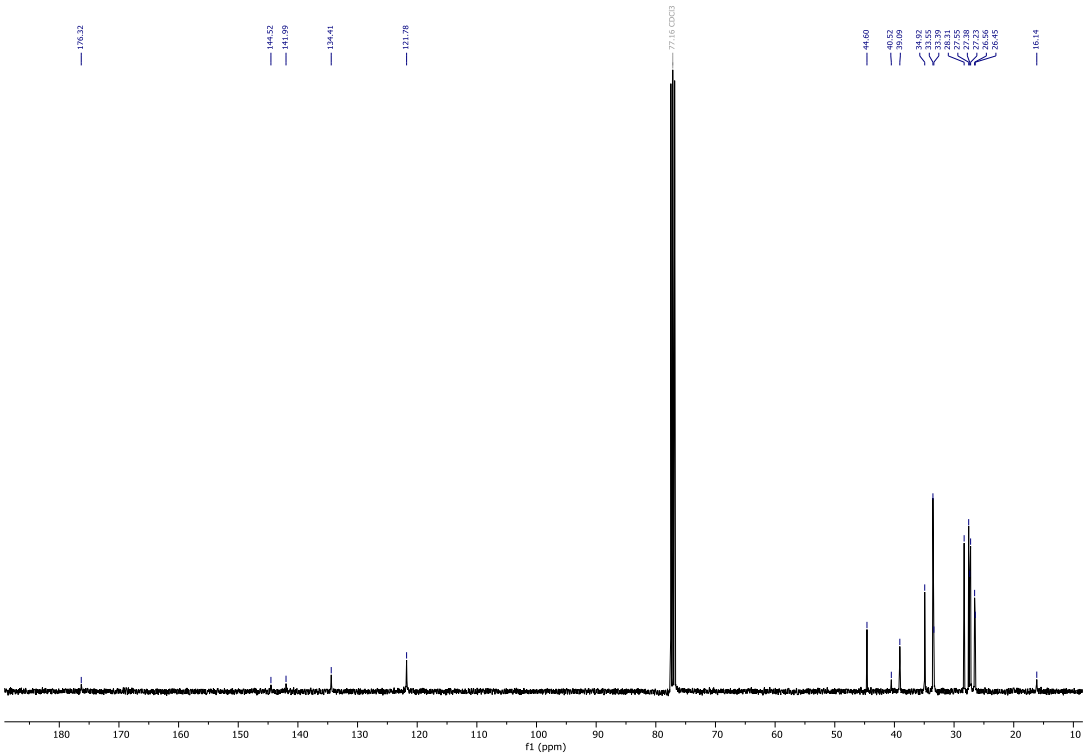


Figure S25: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, $CDCl_3$) of *N*-(2,4,6-tricyclohexylphenyl)-3,3-dimethylbutan-2-imine

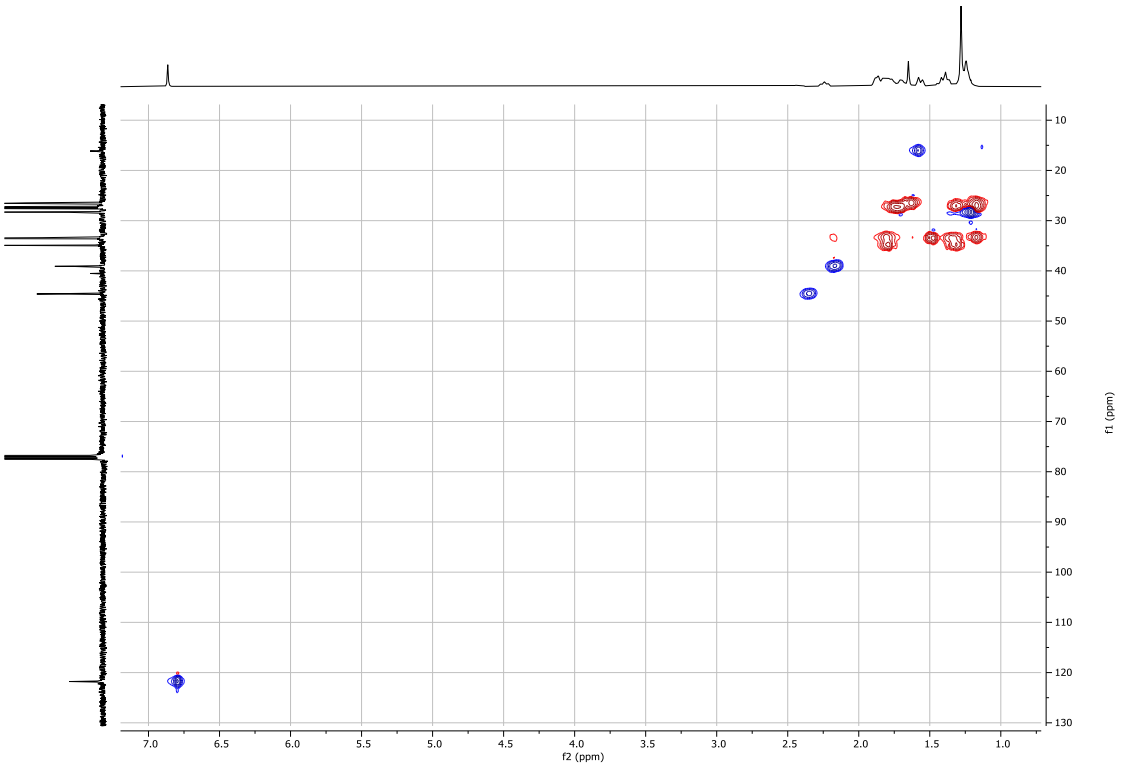


Figure S26: HSQC NMR spectrum (298 K, $CDCl_3$) of *N*-(2,4,6-tricyclohexylphenyl)-3,3-dimethylbutan-2-imine

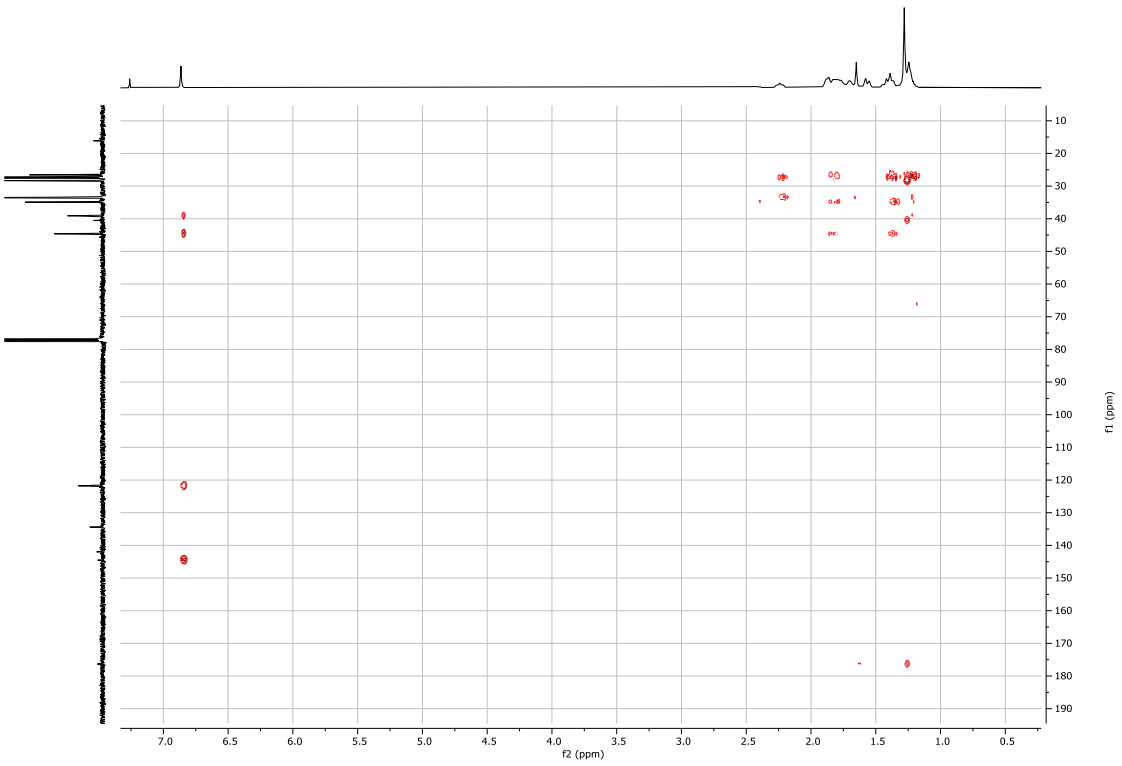


Figure S27: HMBC NMR spectrum (298 K, $CDCl_3$) of *N*-(2,4,6-tricyclohexylphenyl)-3,3-dimethylbutan-2-imine

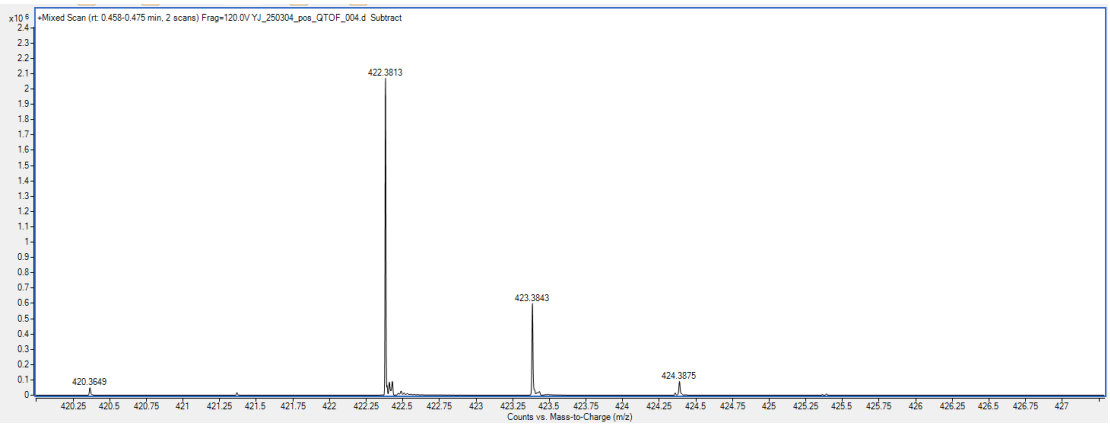
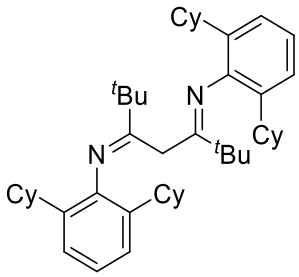


Figure S28: HRMS spectrum of *N*-(2,4,6-tricyclohexylphenyl)-3,3-dimethylbutan-2-imine

Preparation of ^{DCHP}NacnacH



N-(2,6-dicyclohexylphenyl)-3,3-dimethylbutan-2-imine (7.55 g, 0.022 mol) was dissolved in hexane (~150 mL) and TMEDA (3.34 mL, 0.022 mol) was added. The solution was cooled to –78 °C and *n*-butyllithium (1.6 M in hexanes, 13.9 mL, 0.022 mol) was then added dropwise. The resultant mixture was allowed to warm to room temperature and stirred for 16 hours to give a yellow suspension. *N*-(2,6-dicyclohexylphenyl)pivalimidoyl chloride (8.00 g, 0.022 mol) was dissolved in hexane (~100 mL) and transferred to the reaction mixture which was stirred at reflux for 5 hours. The solution was cooled to room temperature and quenched with water (~100 mL) to give a clear biphasic mixture. The organic layer was extracted with diethyl ether (3 x 100 mL) and then washed with brine (2 x 100 mL). The organic layer was then dried with $MgSO_4$, filtered and the volatiles removed *in vacuo*. The oily residue was dissolved in hexane and the product isolated as a solid by fractional crystallisation. **Yield**: 10.21 g, 69%.

M.p.: 204–208 °C.

^{1}H NMR (400 MHz, C_6D_6): δ 0.89 – 1.16 (m, 8H, Cy–*H*), 1.21 (s, 18H, C(C*H*$_3$)$_3$), 1.33 – 1.98 (m, 32H, Cy–*H*), 2.37 – 2.56 (m, 2H, Cy–*H*), 2.63 – 2.81 (m, 2H, Cy–*H*), 3.35 (s, 1H, C*H*$_2$), 7.03 – 7.20 (m, 6H, ^{DCHP}Ar–*H*).

$^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6): δ 26.8, 27.3, 27.6, 27.8 (Cy–*C*), 29.3 (C(*C*H$_3$)$_3$), 30.9, 31.3 (Cy–*C*), 32.2 (*C*H$_2$), 34.9, 35.3, 39.3, 40.4 (Cy–*C*), 41.8 (*C*(CH$_3$)$_3$), 123.5, 124.0, 134.1, 136.9, 145.2 ($_{DCHP}$Ar–*C*), 172.7 (N*C*).

I.R. (solid, cm^{-1}): 3302 (br), 2914 (s), 2847 (s), 1640 (s), 1617 (m), 1502 (m), 1446 (s), 1360 (w), 1308 (w), 1259 (w), 1170 (w), 1103 (m), 1021 (m), 943 (m), 887 (w), 790 (w), 760 (s).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{47}H_{70}N_2$: 663.5612; Found: 663.5602.

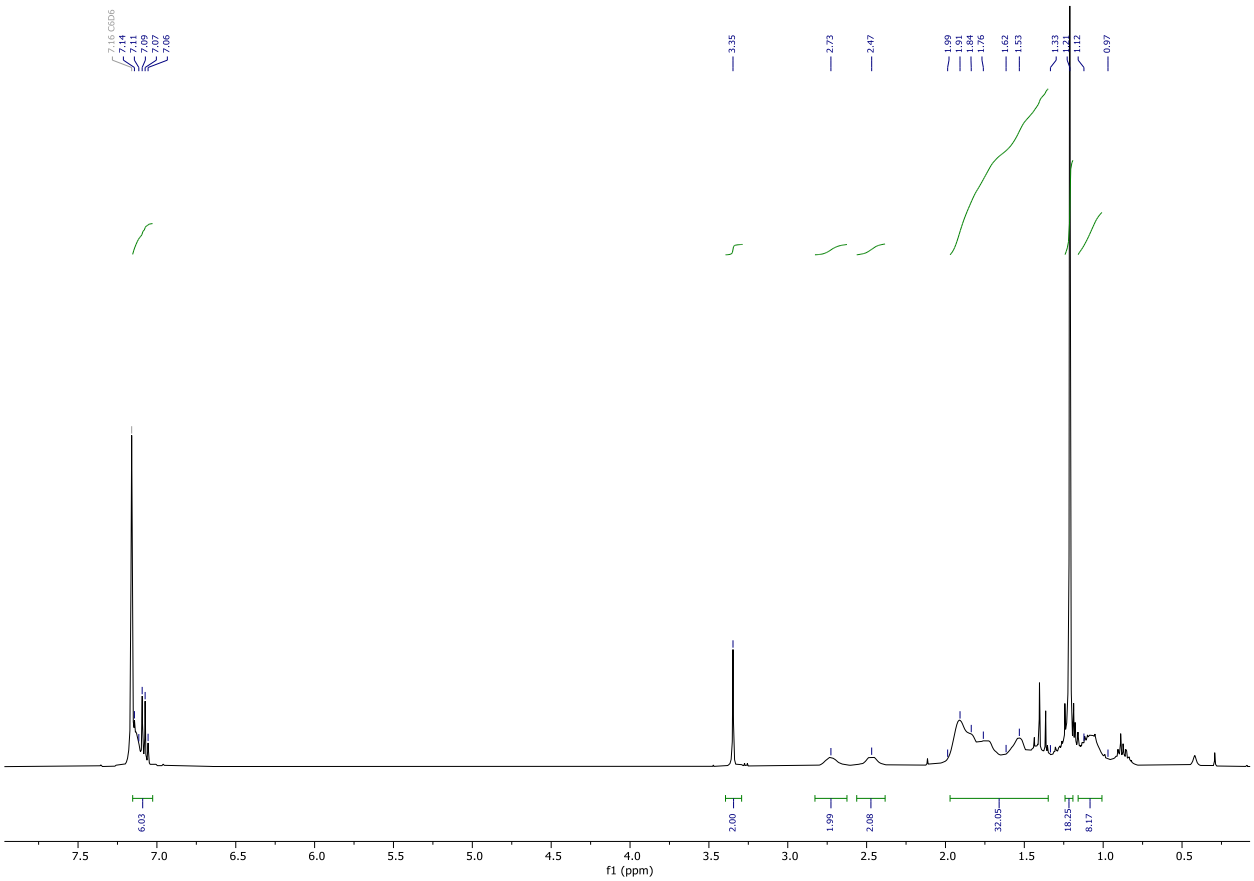


Figure S29: ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of **^{DCHP}NacnacH**.

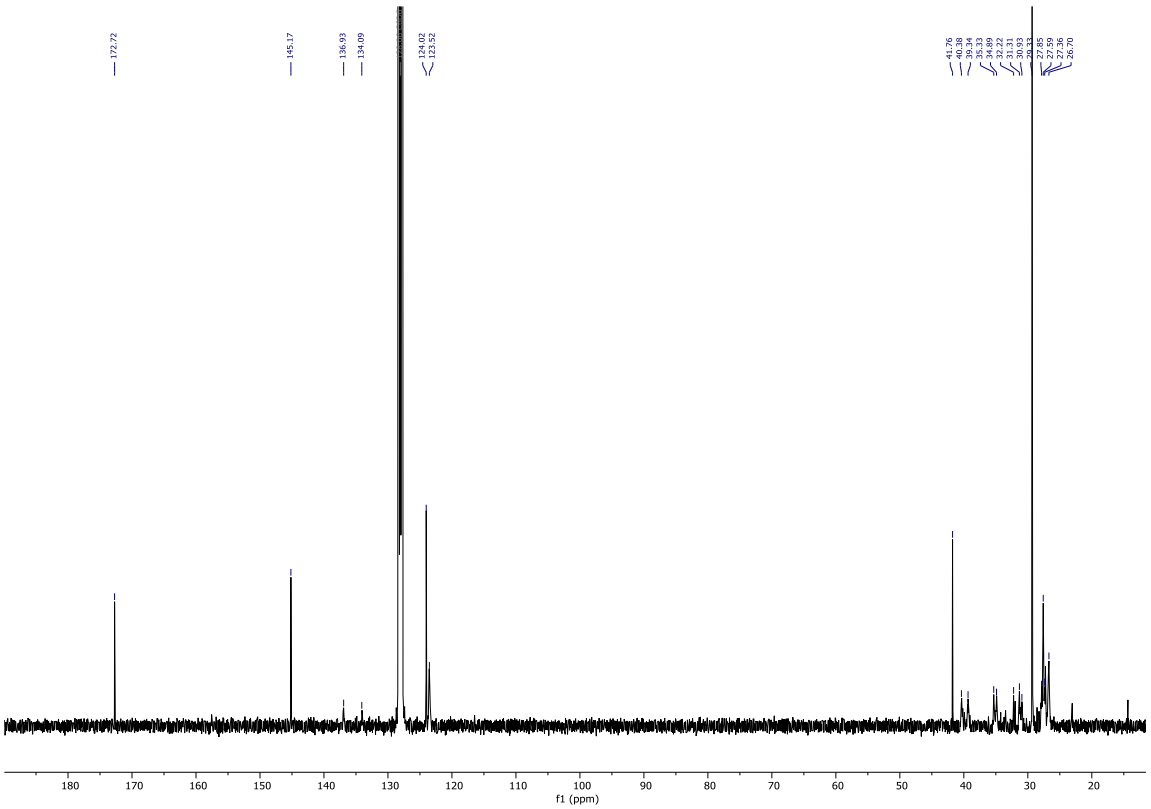


Figure S30: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, C_6D_6) of ^{DCHP}**NacnacH**.

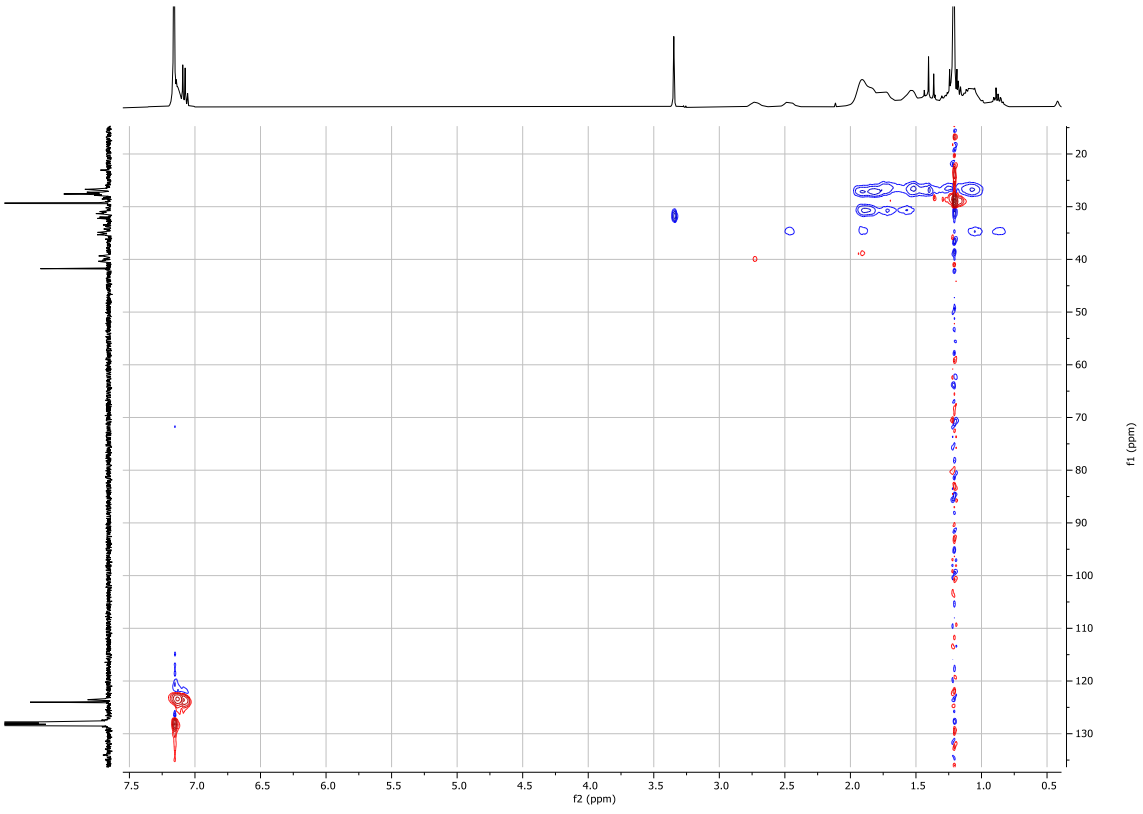


Figure S31: HSQC NMR spectrum (298 K, C_6D_6) of ^{DCHP}**NacnacH**.

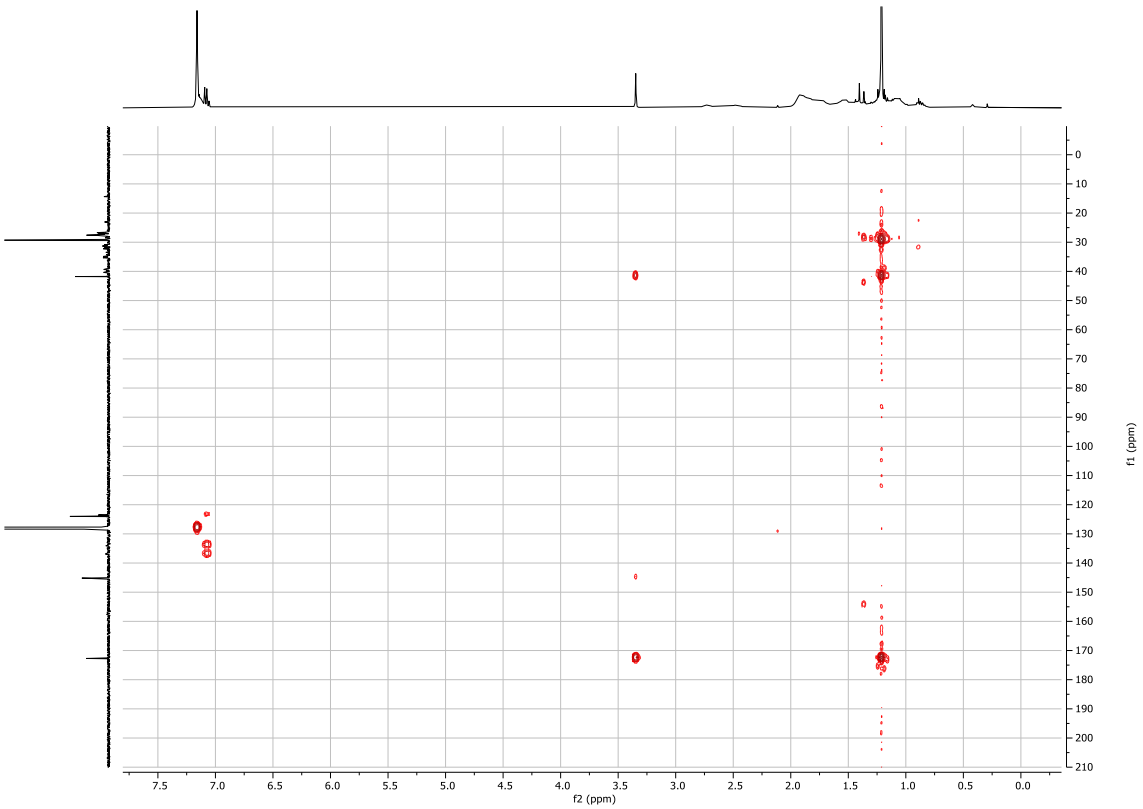


Figure S32: HMBC NMR spectrum (298 K, C_6D_6) of ^{DCHP}**NacnacH**.

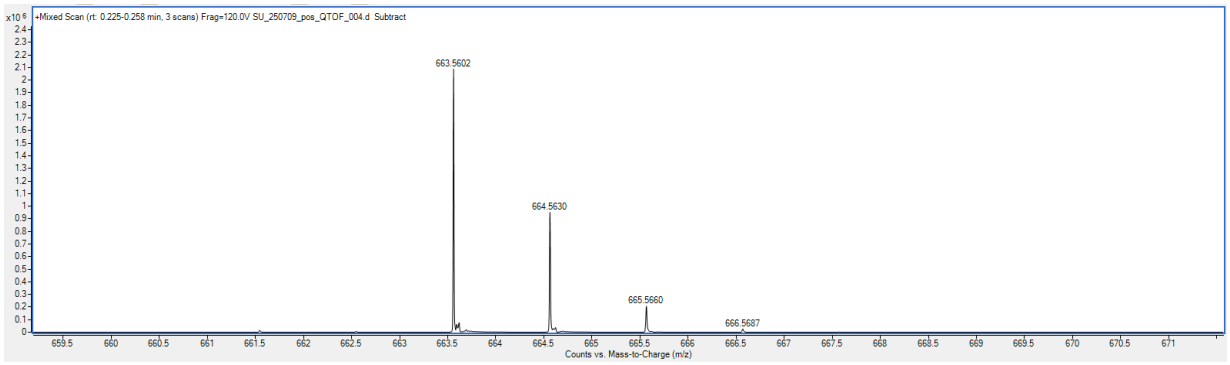
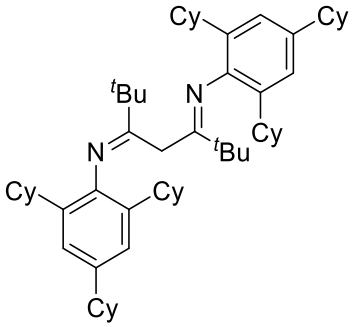


Figure S33: HRMS Spectrum of ^{DCHP}**NacnacH**.

Preparation of ^{TCHP}NacnacH

Bis(imine) Tautomer



N-(2,4,6-tricyclohexylphenyl)-3,3-dimethylbutan-2-imine (3.00 g, 0.007 mol) was dissolved in hexane (~150 mL) and TMEDA (3.00 mL, 0.020 mol) was added. The solution was cooled to –78 °C and *n*-butyllithium (1.6 M in hexanes, 5.00 mL, 0.008 mol) was added dropwise. The resulting mixture was allowed to warm to room temperature and stirred for 16 hours to give a yellow suspension. *N*-(2,4,6-tricyclohexylphenyl)pivalimidoyl chloride (3.15 g, 0.007 mol) was dissolved in hexane (~100 mL) and transferred to the reaction mixture was then heated at reflux for 5 hours. The solution was cooled to room temperature and quenched with water (~100 mL) to give a clear biphasic mixture. The organic layer was extracted with diethyl ether (3 x 100 mL) and then washed with brine (2 x 100 mL). The organic layer was dried with $MgSO_4$, filtered and the volatiles removed *in vacuo*. The oily residue was dissolved in hexane and the product isolated as a solid by fractional crystallisation. **Yield**: 5.00 g, 84%.

M.p.: 174–177 °C.

^{1}H NMR (400 MHz, C_6D_6): δ 1.25 (s, 18H, C(C$\underline{H}_3$)$_3$), 1.38 – 1.42 (m, 16H, Cy–$\underline{H}$), 1.43 – 1.61 (m, 12H, Cy–$\underline{H}$), 1.64 – 2.09 (m, 32H, Cy–$\underline{H}$), 2.45 – 2.60 (m, 4H, Cy–$\underline{H}$), 2.69 – 2.87 (m, 2H, Cy–$\underline{H}$), 3.38 (s, 2H, C$\underline{H}_2$), 7.05 – 7.15 (m, 4H, $_{TCHP}$Ar–$\underline{H}$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 26.7, 26.8, 27.0, 27.3, 27.5, 27.7, 27.8, 27.9 (Cy–$\underline{C}$), 29.4 (C($\underline{C}$H$_3$)$_3$), 31.2, 31.6 (Cy–$\underline{C}$), 32.4 ($\underline{C}$H$_2$), 34.4, 35.0, 35.2, 35.4, 35.6, 39.5, 40.5 (Cy–$\underline{C}$), 41.8 ($\underline{C}$(CH$_3$)$_3$), 45.0 (Cy–$\underline{C}$), 121.6, 121.9, 133.9, 136.7, 143.1, 143.4 ($_{TCHP}$Ar–$\underline{C}$), 173.1 (N$\underline{C}$).

I.R. (solid, cm^{-1}): 2918 (s), 2845 (s), 1643 (w), 1614 (s), 1439 (s), 1358 (w), 1293 (w), 1235 (w), 1175 (w), 1107 (m), 1000 (w), 952 (w), 862 (m), 625 (w).

HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{59}H_{90}N_2$: 827.7177; found: 827.7162.

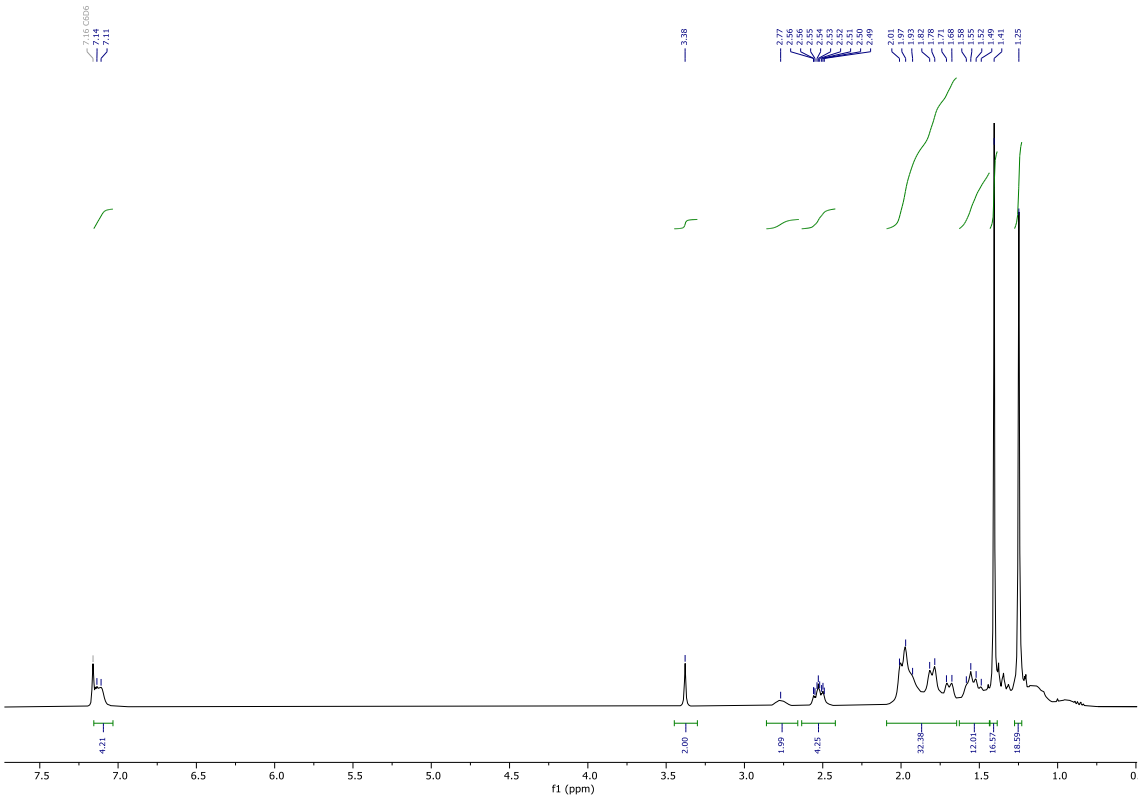


Figure S34: ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of ^{TCHP}**NacnacH** (bis(imine) tautomer).

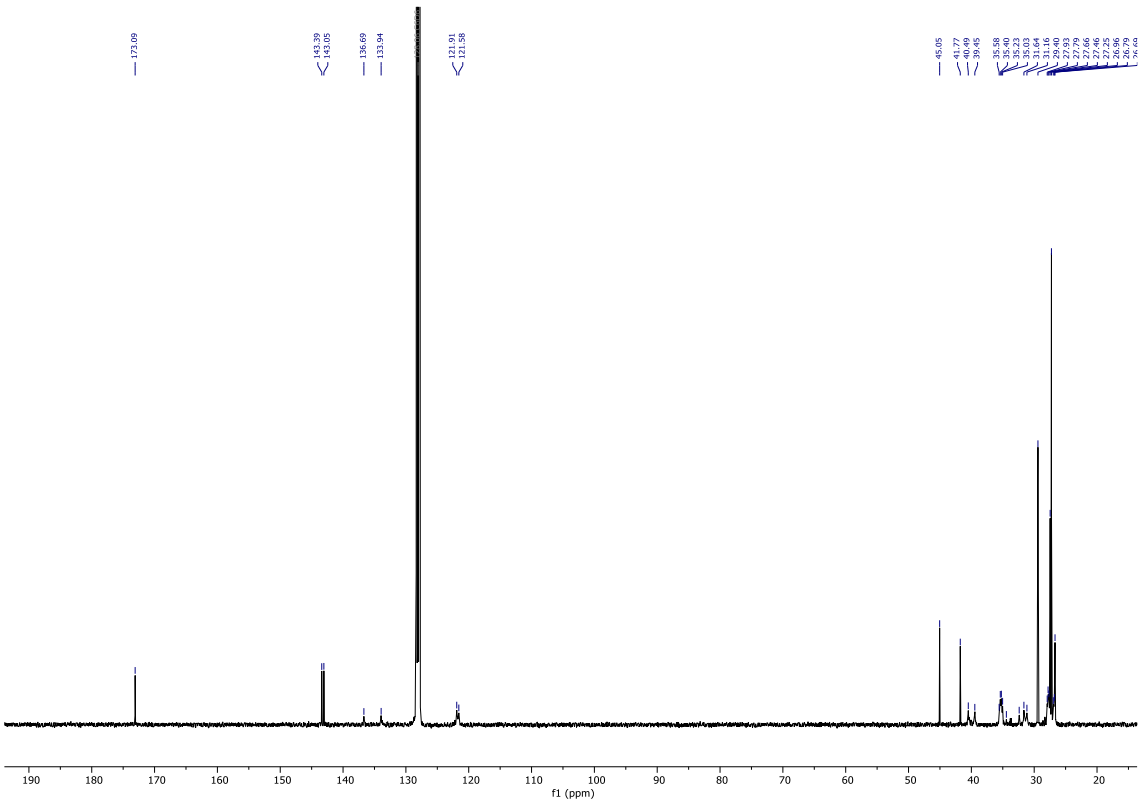


Figure S35: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, C_6D_6) of ^{TCHP}**NacnacH** (bis(imine) tautomer).

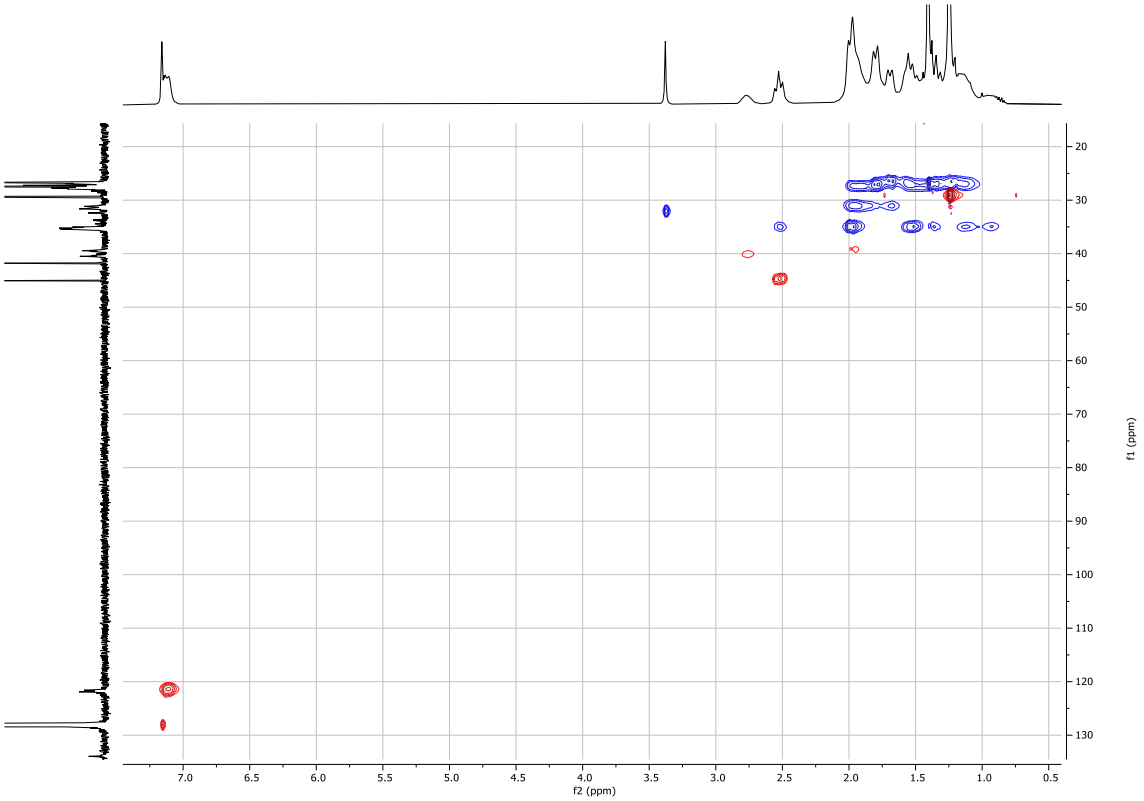


Figure S36: HSQC NMR spectrum (298 K, C_6D_6) of ^{TCHP}**NacnacH** (bis(imine) tautomer).

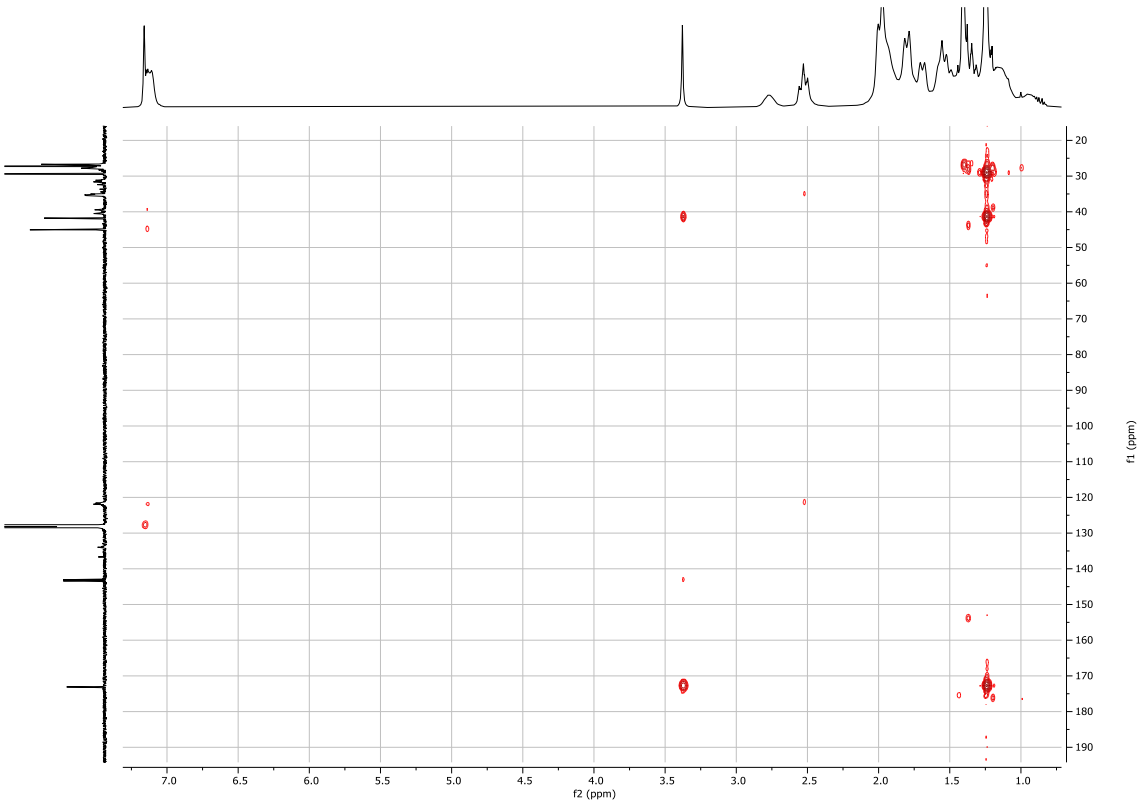


Figure S37: HMBC NMR spectrum (298 K, C_6D_6) of ^{TCHP}**NacnacH** (bis(imine) tautomer).

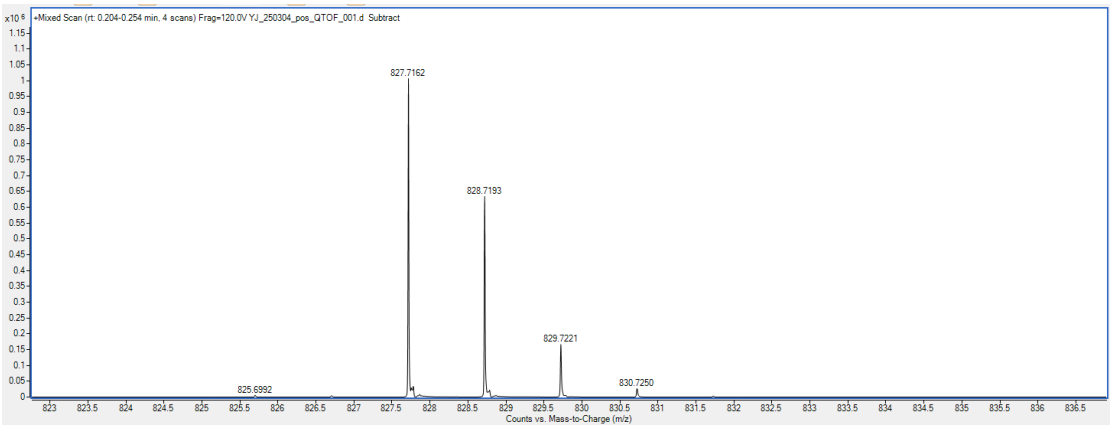
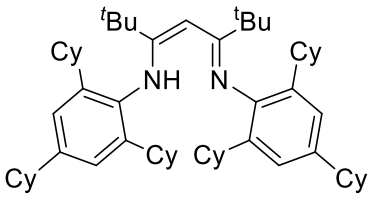


Figure S38: HRMS spectrum of ^{TCHP}**NacnacH** (bis(imine) tautomer).

Enamine Tautomer



A diethyl ether solution (~20 mL) of [(^{TCHP}Nacnac)Li(OEt$_2$)] (see below, 1.00 g, 1.10 mol) was carefully quenched by the dropwise addition of cold water (~10 mL). The aqueous layer was discarded and the organic layer washed with water (2 x 10 mL) and brine (1 x 10 mL), dried with $MgSO_4$, filtered, and the volatiles removed *in vacuo* to afford a yellow oil. Bright yellow crystals were obtained from a hexane solution of the crude product. **Yield**: 850 mg, 93%.

M.p.: 174–177 °C.

^{1}H NMR (400 MHz, C_6D_6): δ 1.21 (s, 18H, C(C*H*$_3$)$_3$), 1.25 – 1.55 (m, 22H, Cy–*H*), 1.63 – 1.82 (m, 18H, Cy–*H*), 1.85 – 2.12 (m, 20H, Cy–*H*), 2.39 – 2.52 (m, 2H, Cy–*H*), 2.95 – 3.08 (m, 4H, Cy–*H*), 5.64 (s, 1H, NCC*H*), 7.06 (s, 4H, $_{TCHP}$Ar–*H*), 12.01 (s, 1H, N*H*).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 26.7, 26.9, 27.2, 27.5, 27.6 (Cy–*C*), 31.4 (C(*C*H$_3$)$_3$), 33.0, 35.2, 35.8, 39.3 (Cy–*C*), 41.6 (*C*(CH$_3$)$_3$), 45.0 (Cy–*C*), 96.0 (NC*C*H), 122.1, 139.0, 141.2, 143.0 ($_{TCHP}$Ar–*C*), 170.4 (N*C*).

I.R. (solid, cm^{-1}): 2918 (s), 2847 (s), 1612 (m), 1547 (s), 1447 (s), 1391 (w), 1354 (w), 1291 (w), 1264 (m), 1208 (w), 1104 (s), 1020 (m), 989 (w), 947 (w), 856 (s), 781 (w), 725 (w), 677 (m).

HRMS (ESI) m/z: [M + H]$^+$ calc. for $C_{59}H_{90}N_2$: 827.7177; 827.7169.

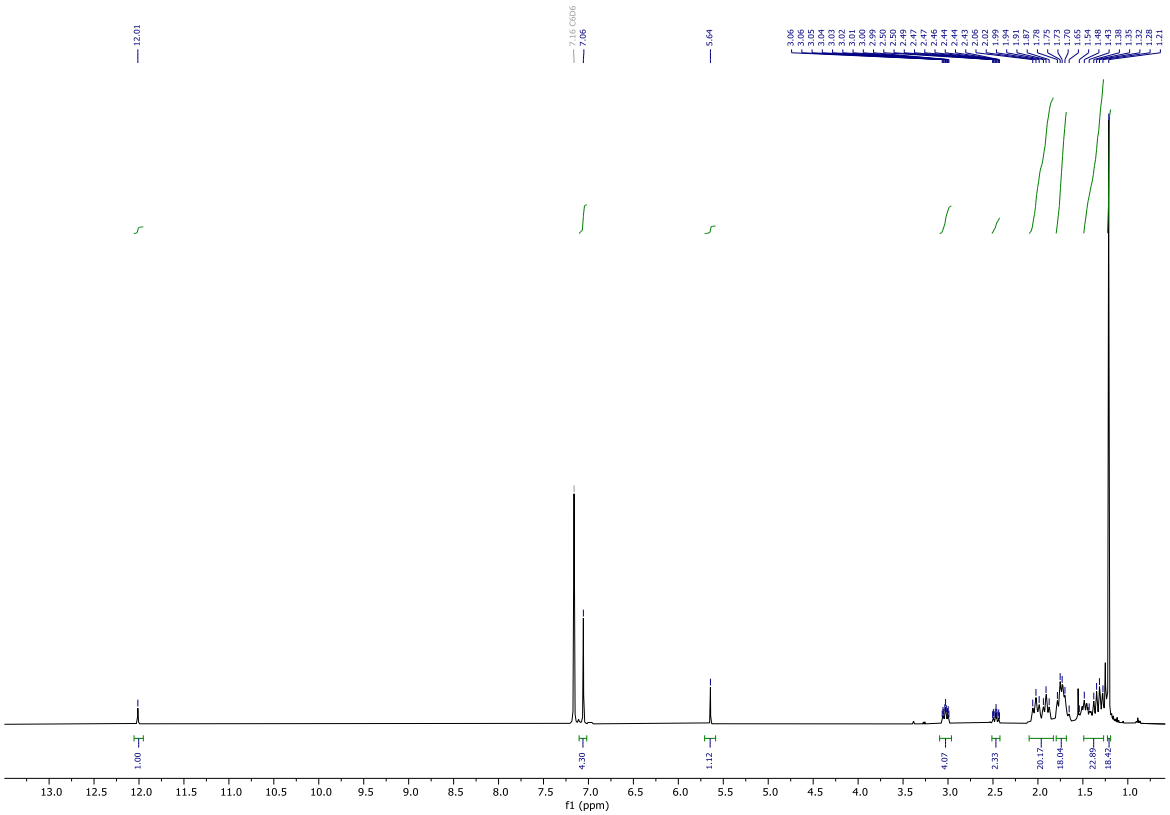


Figure S39: ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of ^{TCHP}**NacnacH** (eneamine tautomer).

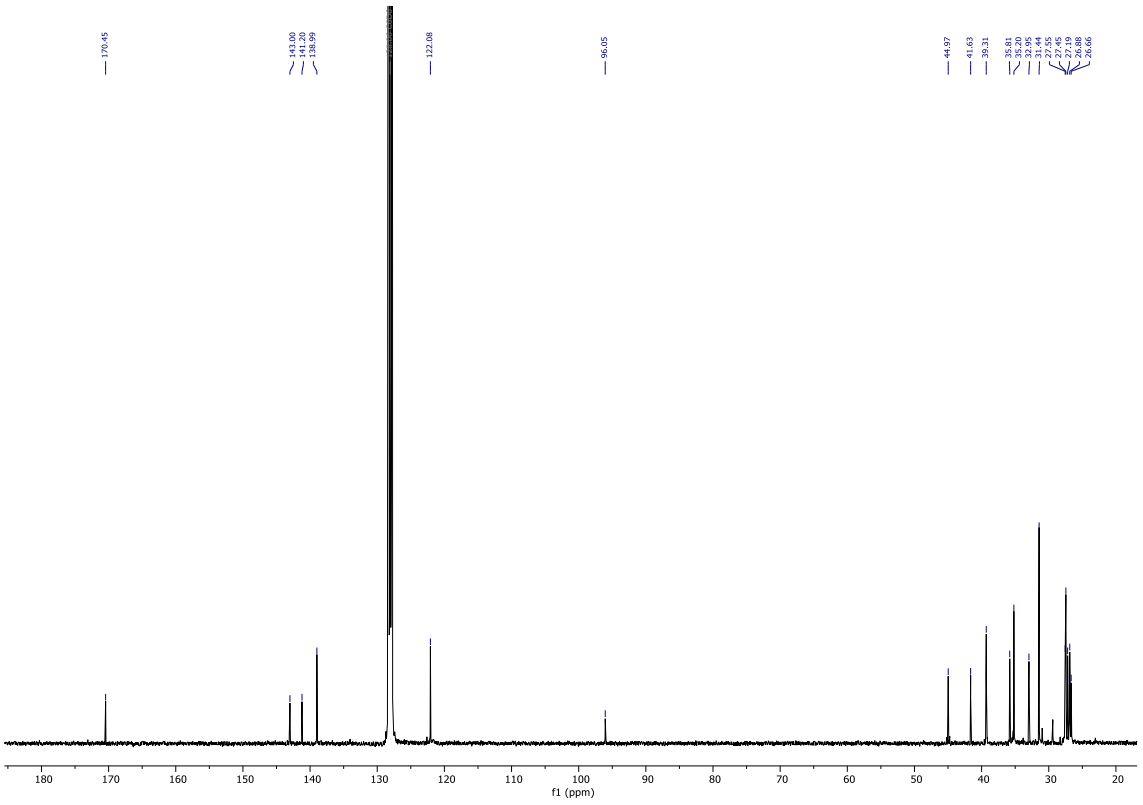


Figure S40: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, C_6D_6) of ^{TCHP}**NacnacH** (eneamine tautomer).

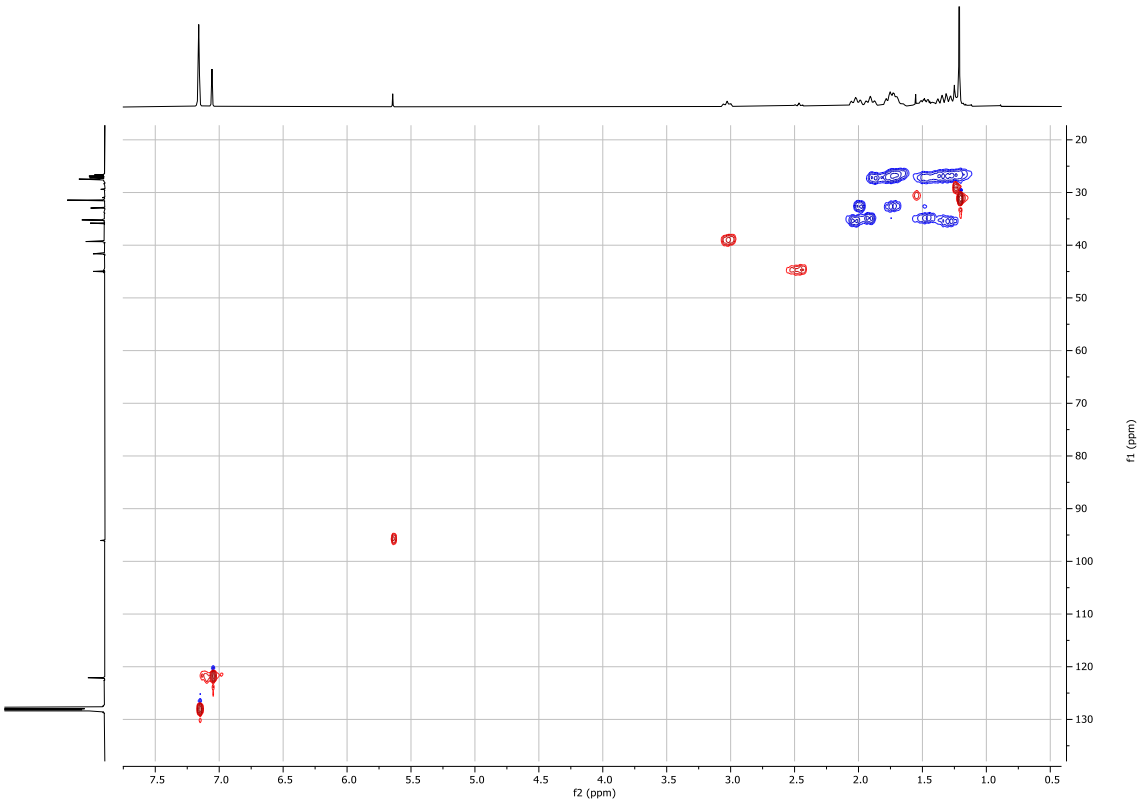


Figure S41: HSQC NMR spectrum (298 K, C_6D_6) of ^{TCHP}**NacnacH** (eneamine tautomer).

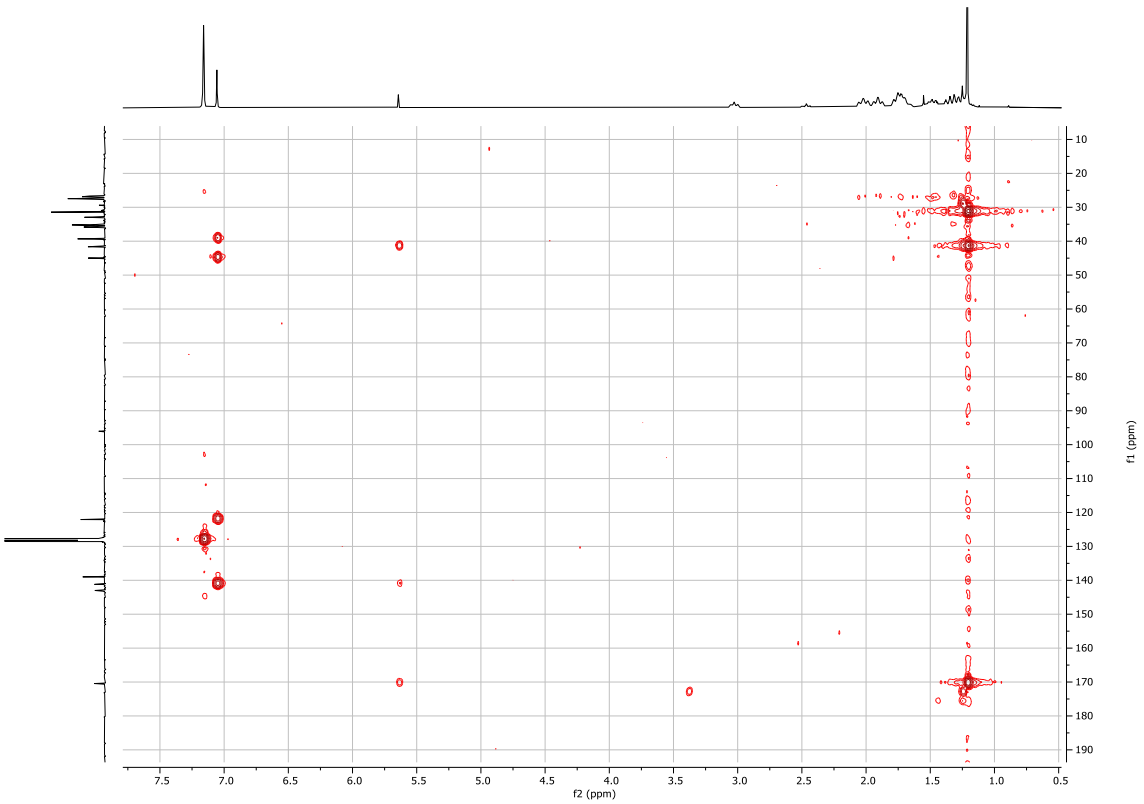


Figure S42: HMBC NMR spectrum (298 K, C_6D_6) of ^{TCHP}**NacnacH** (eneamine tautomer).

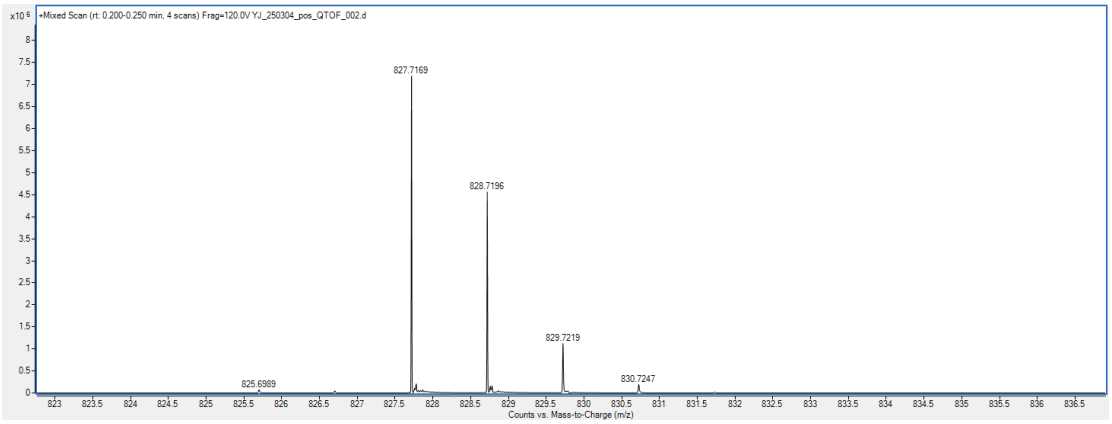
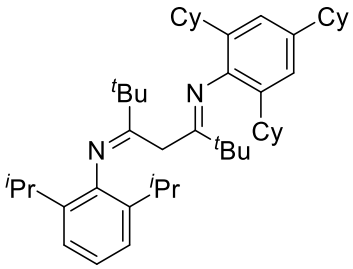


Figure S43: HRMS spectrum of ^{TCHP}**NacnacH** (eneamine tautomer).

Preparation of $^{TCHP/Dip}$NacnacH.



N-(2,6-diisopropylphenyl)-3,3-dimethylbutan-2-imine (13.00 g, 0.050 mol) was dissolved in diethyl ether (~150 mL) and TMEDA (10.28 mL, 0.069 mol) was added. The solution was cooled to –78 °C and *n*-butyllithium (2 M in hexanes, 24.66 mL, 0.049 mol) was added dropwise. The resultant mixture was allowed to warm to room temperature and stirred for 16 hours to give a yellow suspension. *N*-(2,4,6-tricyclohexylphenyl)pivalimidoyl chloride (21.50 g, 0.049 mol) was dissolved in diethyl ether (~100 mL) and transferred to the reaction mixture, then heated at reflux for 5 hours. The solution was then cooled to room temperature and quenched with water (~100 mL) to give a clear biphasic mixture. The organic layer was extracted with diethyl ether (3 x 100 mL) and then washed with brine (2 x 100 mL). The organic layer was dried with $MgSO_4$, filtered and the volatiles removed *in vacuo*. The oily residue was dissolved in hexane and the product isolated as a solid by fractional crystallisation. **Yield**: 27.20 g, 84%.

M.p.: 208–210 °C.

^{1}H NMR (400 MHz, C_6D_6): δ 1.18 (s, 9H, C(C$\underline{H}_3$)$_3$), 1.23 (s, 9H, C(C$\underline{H}_3$)$_3$), 1.26 – 1.38 (m, 12H, CH(C$\underline{H}_3$)$_2$), 1.42 – 2.04 (m, 30H, Cy–$\underline{H}$), 2.24 – 2.41 (m, 1H, C$\underline{H}$(CH$_3$)$_2$), 2.50 (tt, J = 11.9, 3.4 Hz, 2H,

Cy–*H*), 2.64 – 2.81 (m, 1H, Cy–*H*), 3.04 – 3.21 (m, 1H, C*H*(CH_3)$_2$), 3.29 – 3.46 (m, 2H, C*H*$_2$), 7.06 (t, J = 7.6 Hz, 1H, $_{Dipp}$Ar–*H*), 7.09 – 7.15 (m, 4H, $_{TCHP}$Ar–*H*, $_{Dipp}$Ar–*H*).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 20.8, 24.1, 24.6 (CH(*C*H_3)$_2$), 26.7, 26.8, 27.4, 27.7, 27.8 (Cy–*C*), 29.0, 29.4 (C(*C*H_3)$_3$), 31.7 (Cy–*C*), 32.3 (*C*H_2), 34.4, 35.3, 35.3, 39.3, 40.3 (Cy–*C*), 41.9 (*C*(CH_3)$_3$), 45.0 (Cy–*C*), 121.9, 122.6, 122.9, 123.3, 124.0, 143.1, 143.2, 145.2 ($_{TCHP}$Ar–*C*, $_{Dipp}$Ar–*C*), 172.8, 173.0 (N*C*).

I.R. (solid, cm^{-1}): 3302 (w), 3058 (m), 2960 (s), 2920 (s), 2846 (s), 1638 (s), 1612 (s), 1498 (w), 1446 (s), 1381 (w), 1362 (m), 1325 (w), 1295 (w), 1256 (w), 1241 (w), 1217 (w), 1180 (w), 1109 (m), 1044 (w), 1025 (w), 952 (w), 934 (w), 893 (w), 859 (m), 842 (w), 814 (w), 796 (w), 760 (s), 708 (w).

HRMS (ESI) m/z: [M + H]+ calc. for $C_{47}H_{73}N_2$: 665.5769; Found: 665.5768.

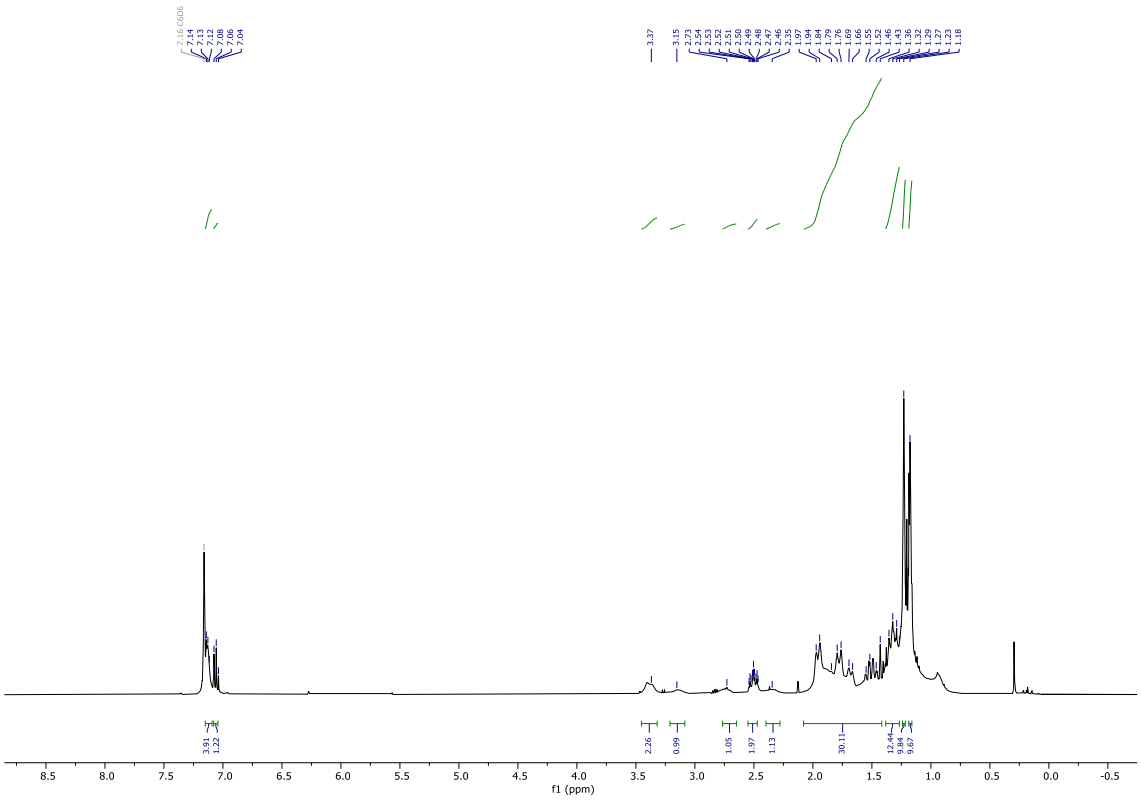


Figure S44: ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of **$^{TCHP/Dip}$NacnacH**.

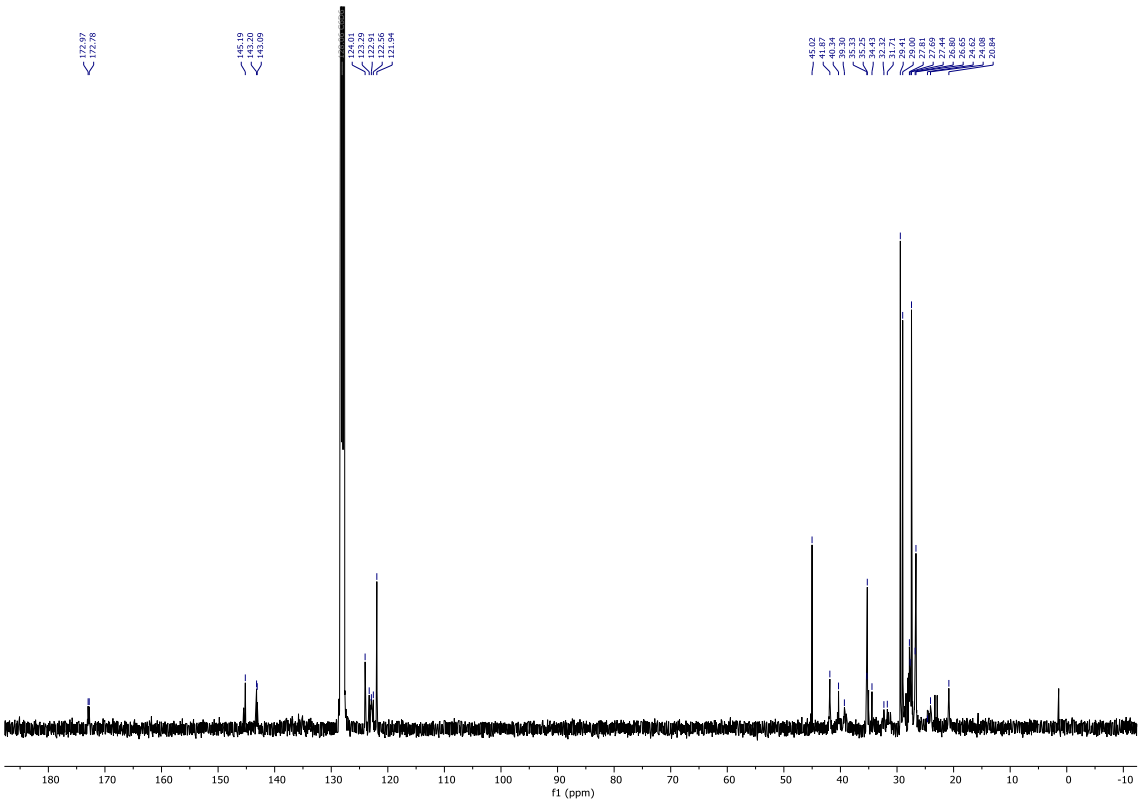


Figure S45: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, C_6D_6) of $^{TCHP/Dip}$**NacnacH**.

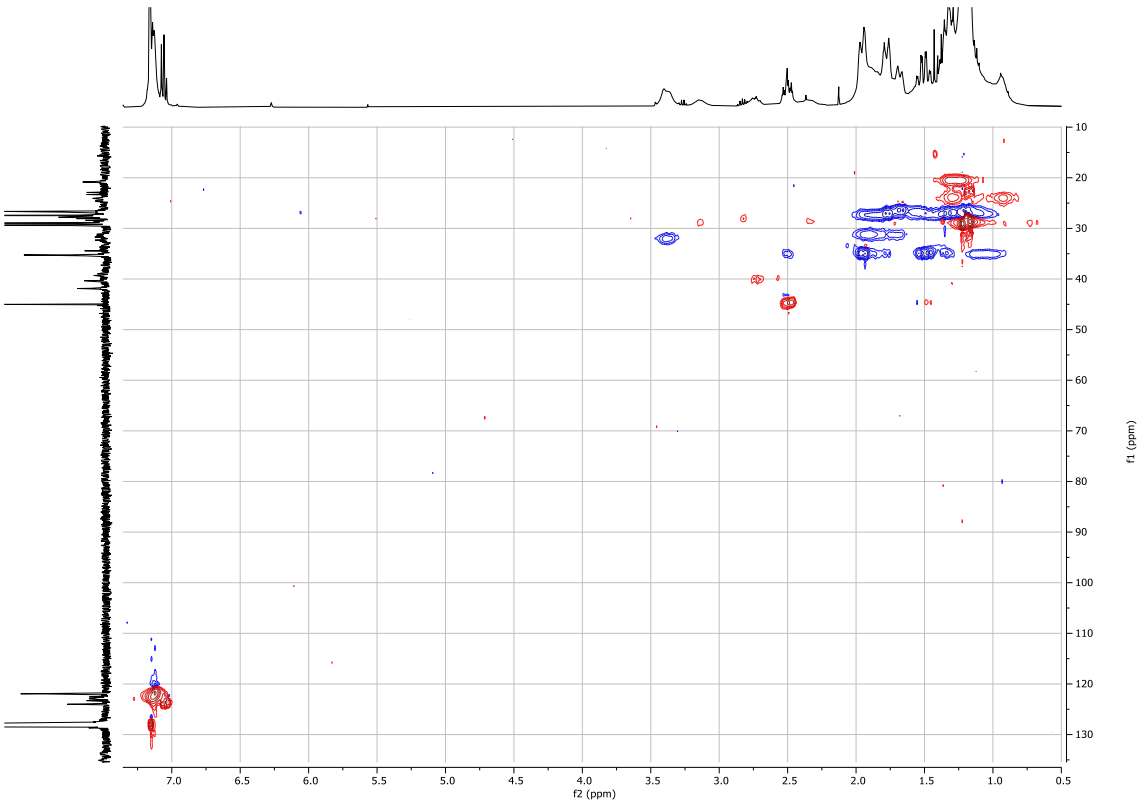


Figure S46: HSQC NMR spectrum (298 K, C_6D_6) of $^{TCHP/Dip}$**NacnacH**.

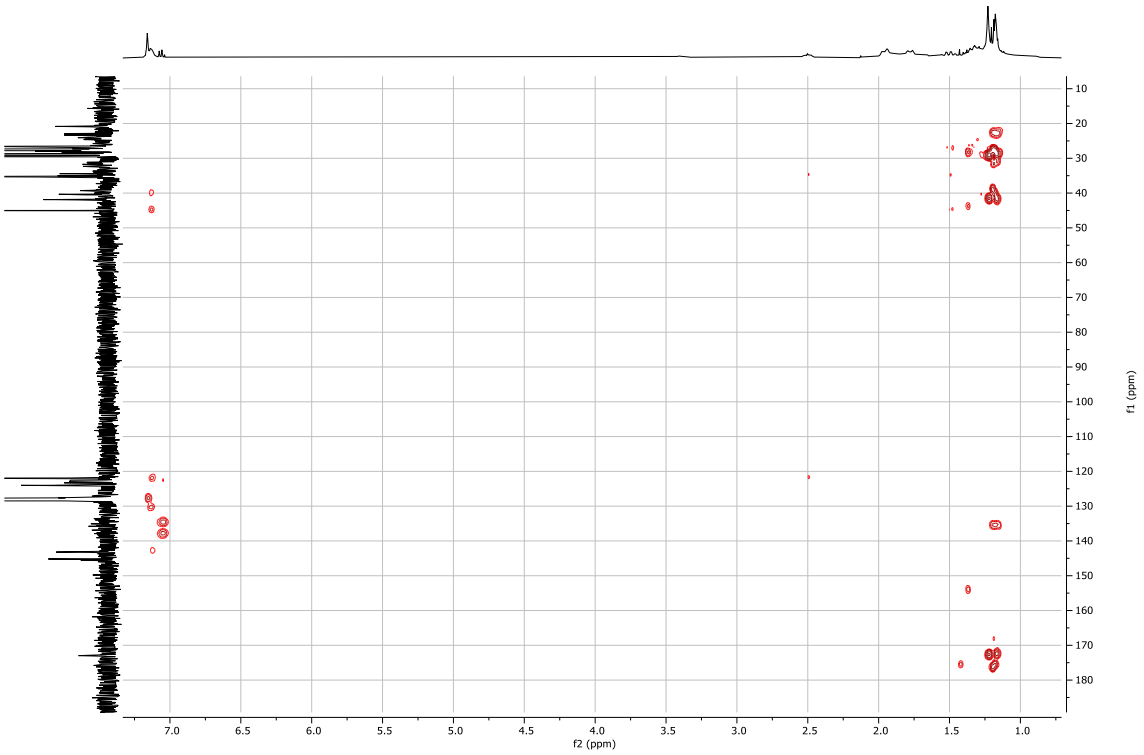


Figure S47: HMBC NMR spectrum (298 K, C_6D_6) of $^{TCHP/Dip}$**NacnacH**.

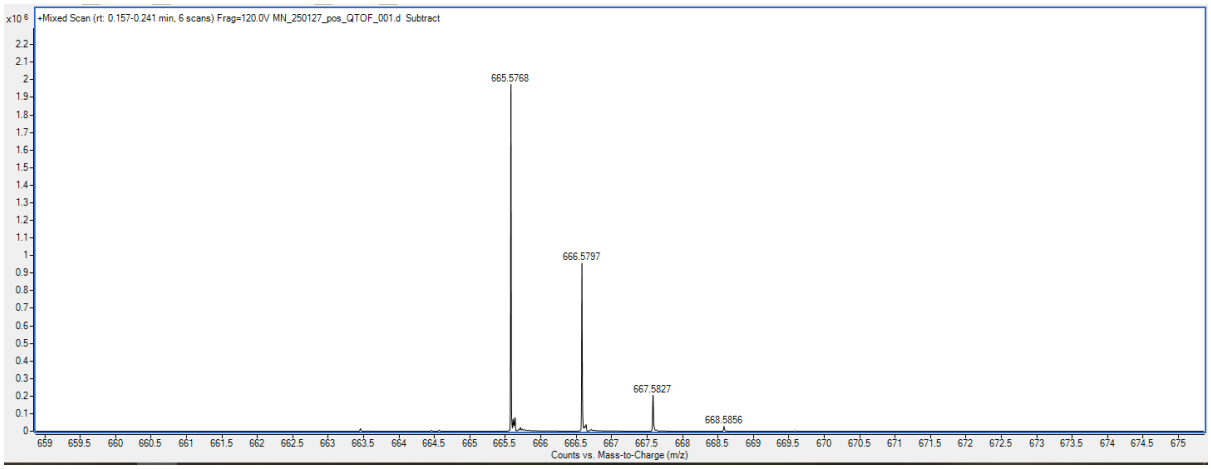
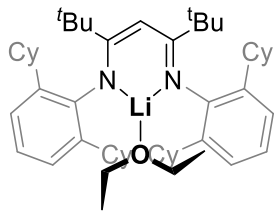


Figure S48: HRMS spectrum of $^{TCHP/Dip}$**NacnacH**.

Preparation of [(^{DCHP}Nacnac)Li(OEt$_2$)]



^{DCHP}NacnacH (500 mg, 0.75 mmol) was charged to a flame-dried ampule and toluene (~5 mL) was added. To this stirred suspension was added methyl lithium/lithium bromide (1.5 M in Et_2O, 0.98 mmol, 0.65 mL) at room temperature. The mixture was allowed to stir at room temperature for 1 hour and then sealed and stirred at 120 °C for 16 hours. The formed yellow solution was filtered via cannula and the volatiles removed *in vacuo*. The oily residue was suspended in hexane (~5 mL) to give an off-white solid, which was collected by filtration and washed with hexane (3 x 3 mL). The supernatant was reduced in volume under vacuum to provide a second yield of pale-yellow crystals. **Yield**: 374 mg, 66 %.

M.p.: 222–226 °C (dec).

^{1}H NMR (400 MHz, C_6D_6): δ 0.42 (t, J = 7.0 Hz, 6H, $\underline{Et}_2O$), 1.13 – 1.35 (m, 3H, Cy–$\underline{H}$), 1.37 (s, 18H, C(C$\underline{H}_3$)$_3$), 1.45 – 1.65 (m, 12H, Cy–$\underline{H}$), 1.71 – 1.96 (m, 20H, Cy–$\underline{H}$), 2.04 – 2.13 (m, 5H, Cy–$\underline{H}$), 2.44 (q, J = 7.0 Hz, 4H, $\underline{Et}_2O$), 2.98 – 3.10 (m, 4H, Cy–$\underline{H}$), 5.38 (s, 1H, NCC$\underline{H}$), 6.92 – 6.98 (m, 2H, $_{DCHP}$Ar–$\underline{H}$), 7.03 (d, J = 7.6 Hz, 4H, $_{DCHP}$Ar–$\underline{H}$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 13.5 ($\underline{Et}_2O$), 27.0, 27.7, 27.9 (Cy–*C*), 33.4 (C($\underline{C}$H$_3$)$_3$), 33.8, 34.7, 38.9 (Cy–*C*), 44.7 ($\underline{C}$(CH$_3$)$_3$), 64.0 ($\underline{Et}_2O$), 93.1 (NC$\underline{C}$H), 121.1, 124.2, 138.2, 151.9 ($_{DCHP}$Ar–$\underline{C}$), 172.1 (N$\underline{C}$).

^{7}Li NMR (156 MHz, C_6D_6): δ 1.18 ($\underline{Li}OEt_2$).

I.R. (solid, cm^{-1}): 2918 (s), 2851 (s), 1621 (w), 1457 (s), 1375 (s), 1344 (w), 1310 (w), 1209 (w), 1138 (w), 1105 (w), 846 (w), 723 (w).

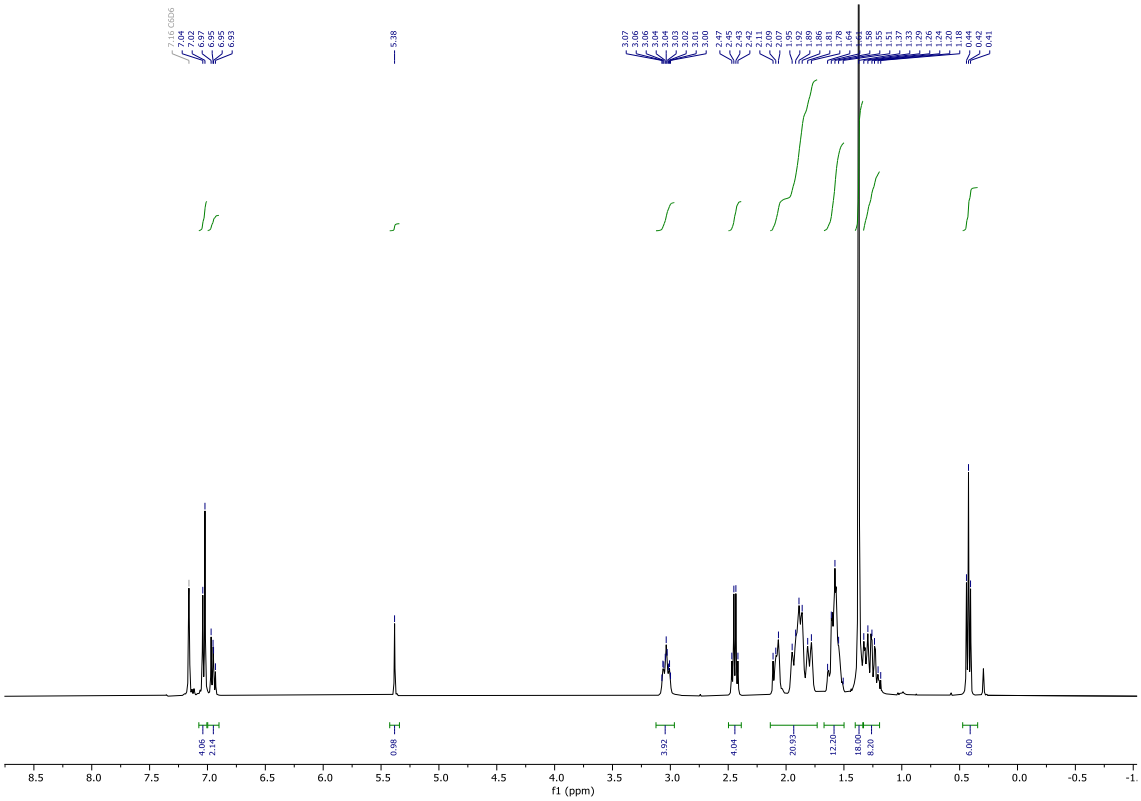


Figure S49: ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of **[(^{DCHP}Nacnac)Li(OEt$_2$)]**.

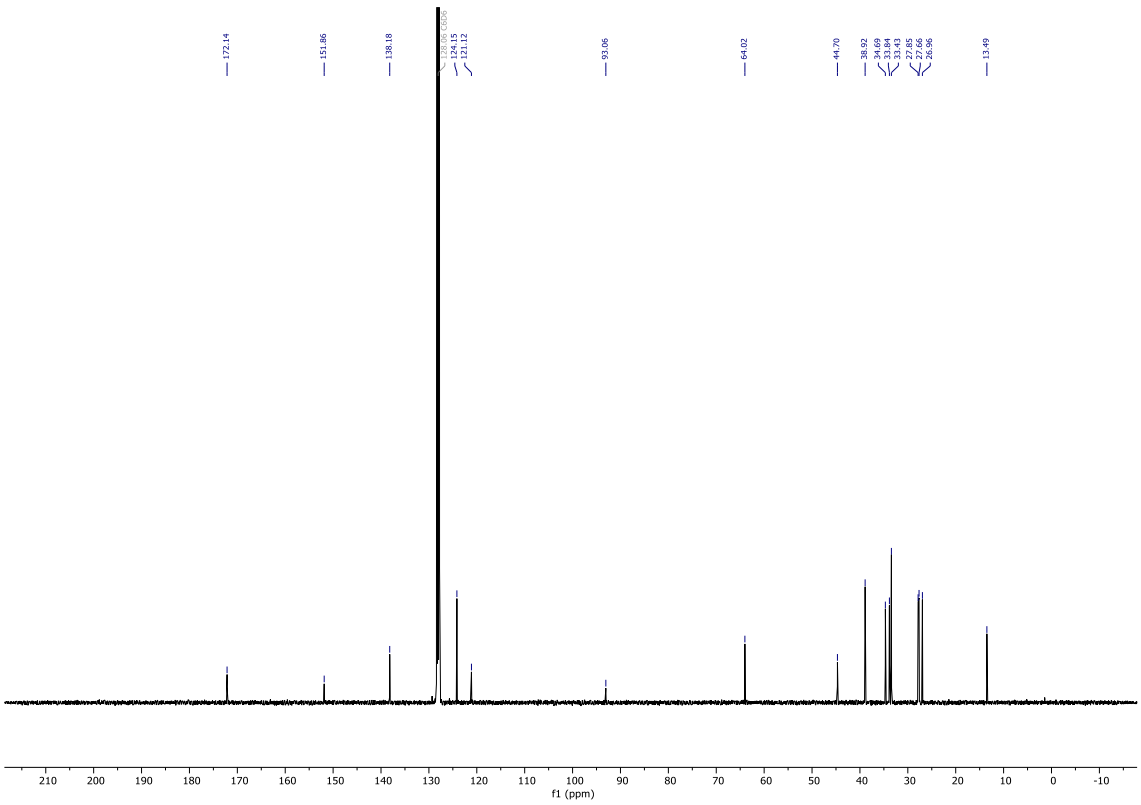


Figure S50: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, C_6D_6) of **[(^{DCHP}Nacnac)Li(OEt$_2$)]**.

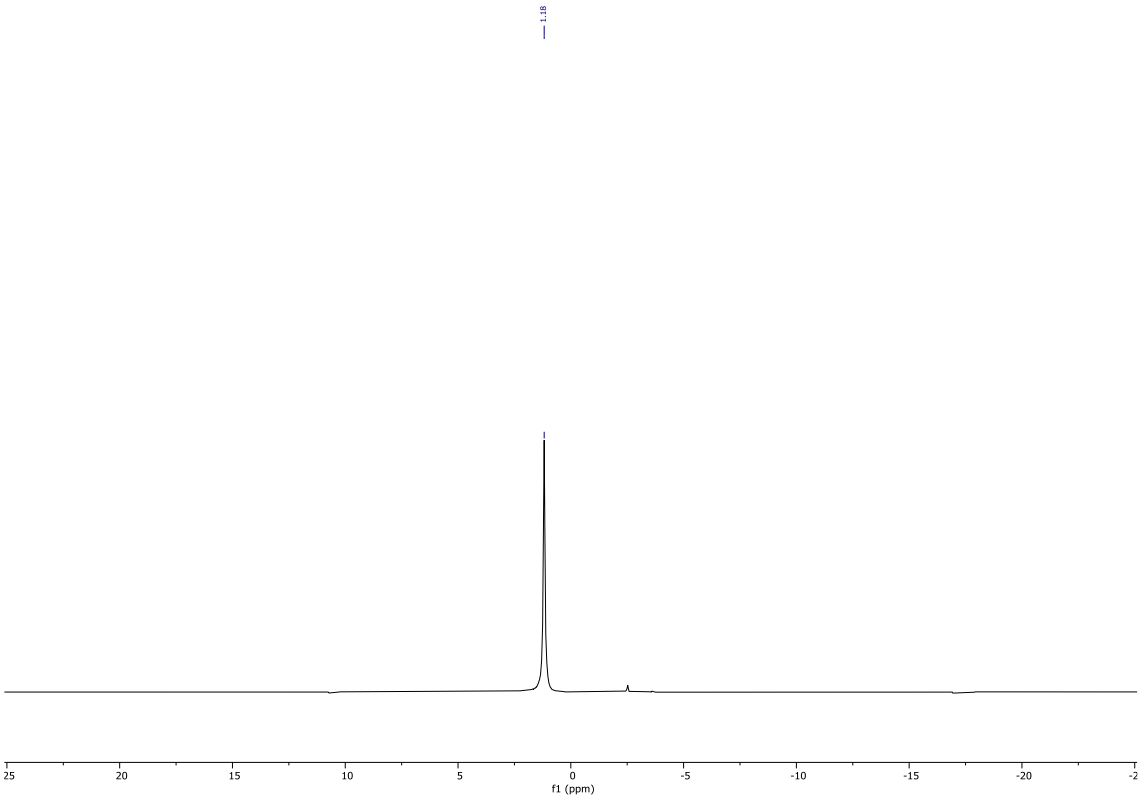


Figure S51: ^{7}Li NMR spectrum (101 MHz, 298 K, C_6D_6) of **[(^{DCHP}Nacnac)Li(OEt$_2$)]**.

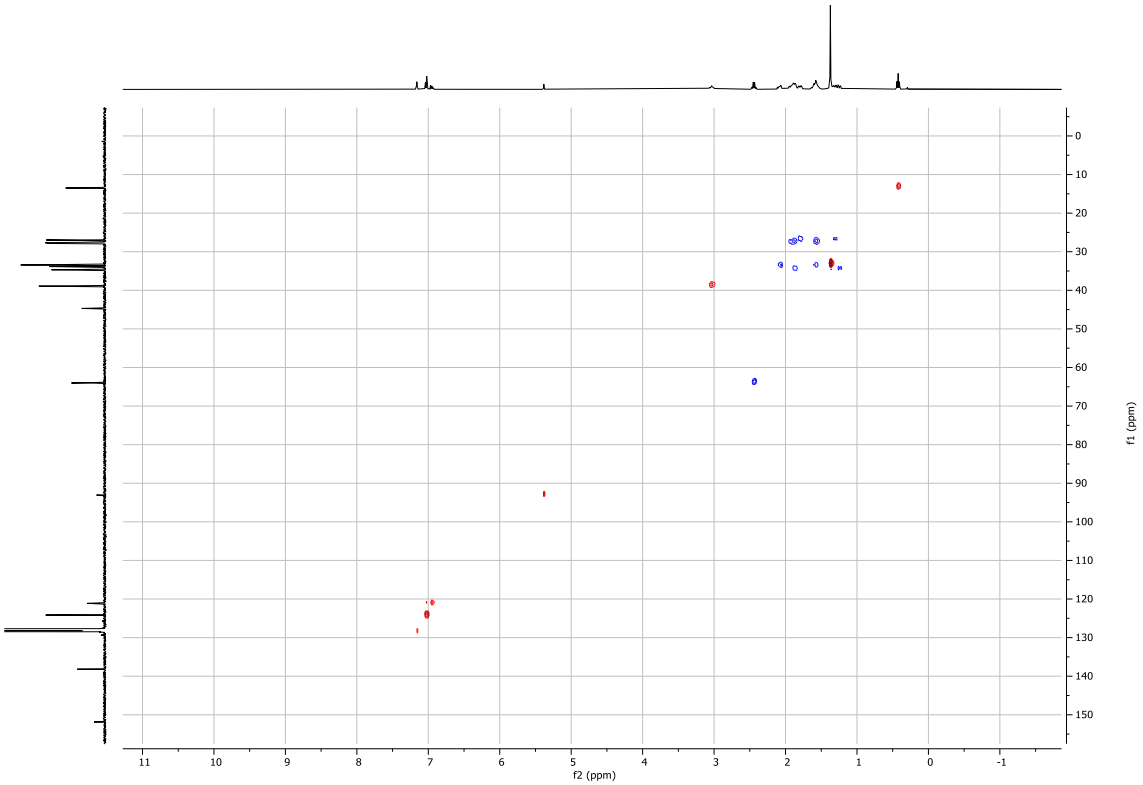


Figure S52: HSQC NMR spectrum (298 K, C_6D_6) of **[(^{DCHP}Nacnac)Li(OEt$_2$)]**.

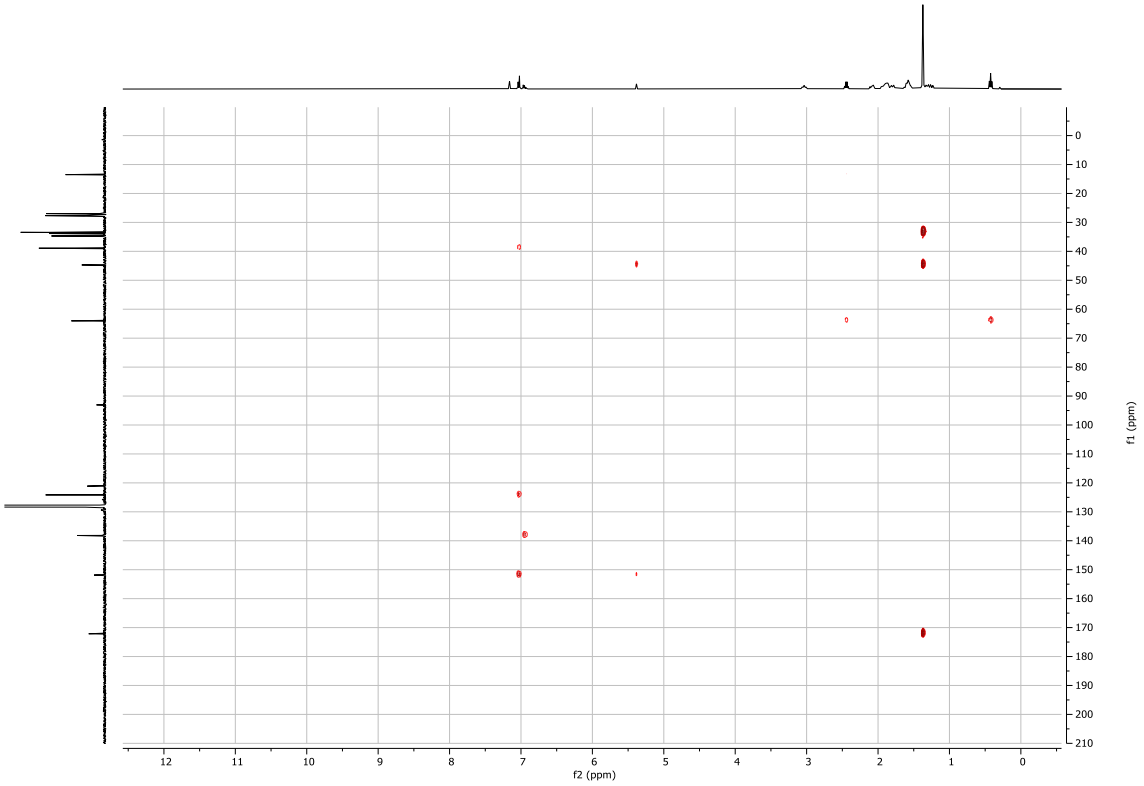
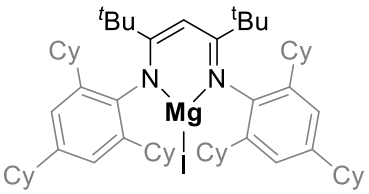


Figure S53: HMBC NMR spectrum (298 K, C_6D_6) of **[(DCHPNacnac)Li(OEt$_2$)]**.

Preparation of [(TCHPNacnac)MgI] 1



Method A:

TCHPNacnacH (4.00 g, 4.83 mmol) was charged to a flame-dried ampule and toluene (~10 mL) was added. To this stirred suspension was added methyl magnesium iodide (3M in Et_2O, 5.30 mmol, 1.76 mL) at room temperature. The mixture was stirred at room temperature for 1 hour and then sealed and stirred at 120 °C for 3 days. The formed yellow-orange solution was filtered *via* cannula and the volatiles removed *in vacuo*. The oily residue was suspended in hexane (~10 mL) and stored at -30 °C to give an off-white solid which was collected by filtration and washed with hexane (3 x 5 mL). The supernatant was reduced in volume under vacuum to provide a second yield of pale-yellow crystals. **Yield**: 3.80 g, 80%.

Method B:

[(^{TCHP}Nacnac)Li(OEt$_2$)] **2** (see below) (1.00 g, 1.10 mmol) and $MgI_2(OEt_2)_2$ (470 mg, 1.10 mmol) were charged to a flame-dried ampule and toluene (~5 mL) was added. The mixture was stirred at room temperature for 1 hour and then sealed and stirred at 120 °C for a further 18 hours. The formed yellow-orange solution was filtered *via* cannula and the volatiles removed *in vacuo*. The oily residue was suspended in hexane (~10 mL) and stored at -30 °C to give an off-white solid which was collected by filtration. **Yield**: 520 mg, 50%.

M.p.: 182–184 °C (dec).

^{1}H NMR (400 MHz, C_6D_6): δ 1.24 (s, 18H, C(C$\underline{H}_3$)$_3$), 1.27 – 1.40 (m, 8H, Cy–$\underline{H}$), 1.40 – 1.80 (m, 32H, Cy–$\underline{H}$), 1.82 – 2.17 (m, 18H, Cy–$\underline{H}$), 2.40 – 2.55 (m, 6H, Cy–$\underline{H}$), 2.79 – 2.94 (m, 4H, Cy–$\underline{H}$), 5.55 (s, 1H, NCC$\underline{H}$), 7.10 (s, 4H, $_{TCHP}$Ar–$\underline{H}$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 26.6, 26.7, 27.4, 27.5, 28.1 (Cy–$\underline{C}$), 32.9 (C($\underline{C}$H$_3$)$_3$), 34.3, 35.1, 35.7, 40.1 (Cy–$\underline{C}$), 44.5 ($\underline{C}$(CH$_3$)$_3$), 44.9 (Cy–$\underline{C}$), 96.0 (NC$\underline{C}$H), 123.5, 139.5, 142.2, 144.9 ($_{TCHP}$Ar–$\underline{C}$), 179.3 (N$\underline{C}$).

I.R. (Nujol, cm^{-1}): 2918 (s), 2847 (s), 1497 (s), 1447 (s), 1389 (s), 1347 (s), 1295 (s), 1214 (m), 1181 (m), 1131 (m), 1025 (m), 995 (m), 945 (w), 858 (s), 795 (w), 704 (m).

Anal calcd. for $C_{59}H_{89}MgN_2I$: C 72.49 %, H 9.18 %, N 2.87 %; found: C 72.14 %, H 9.82 %, N 2.32 %.

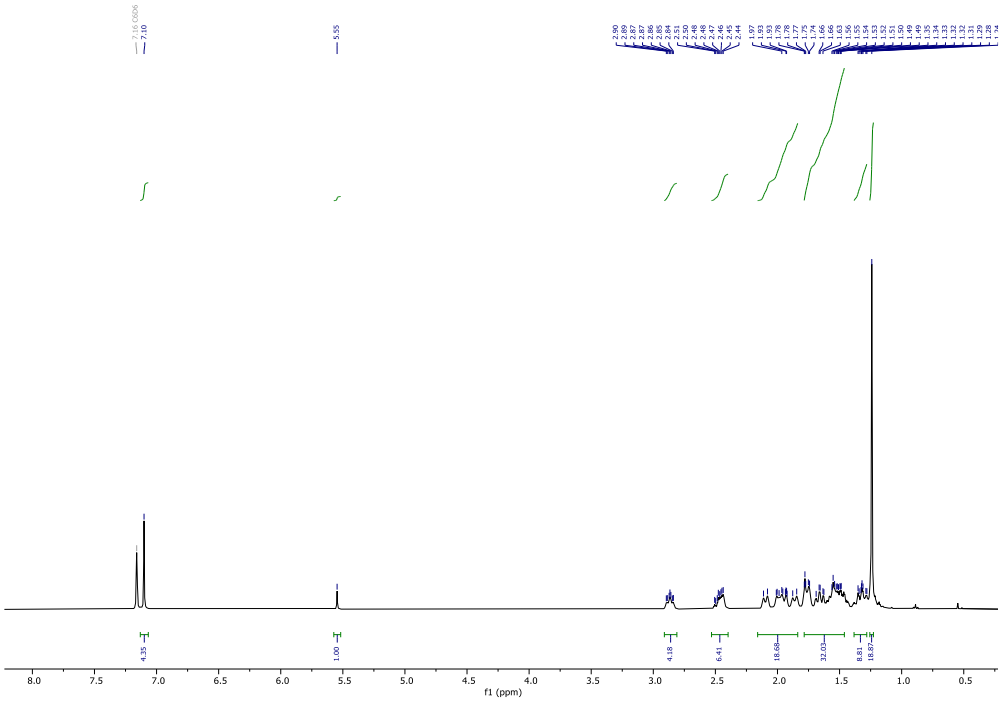


Figure S54: ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of **1**.

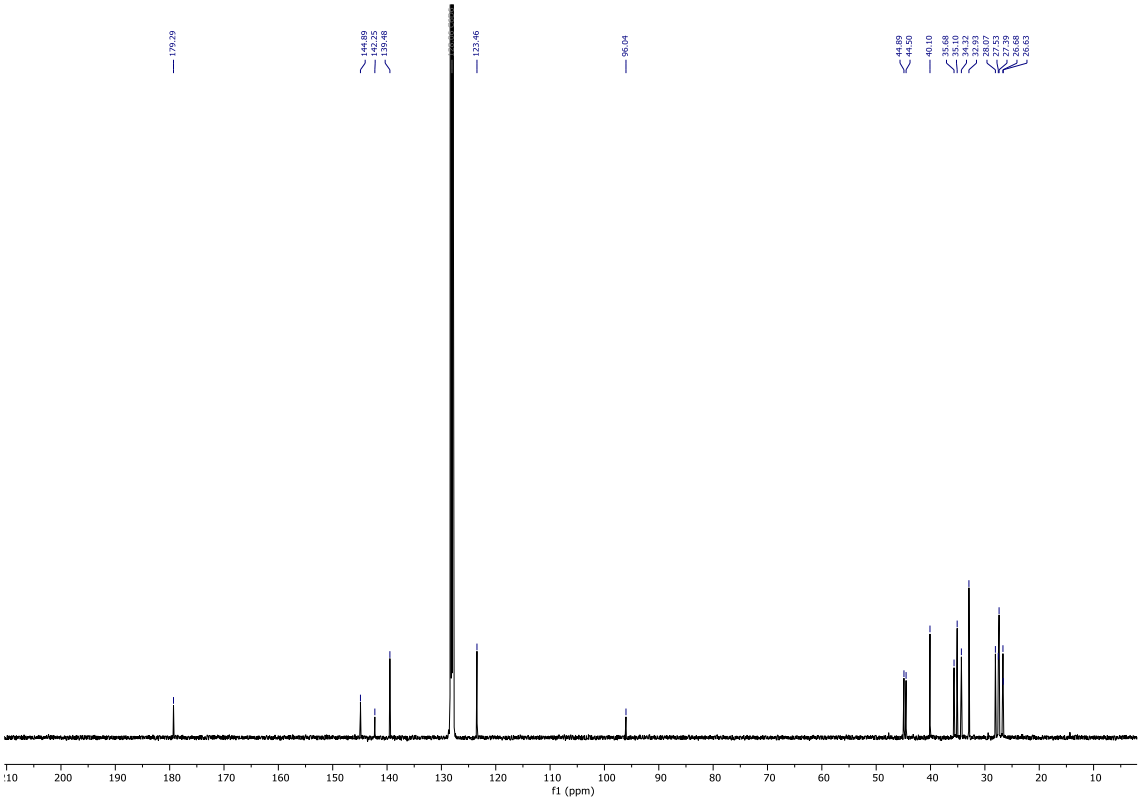


Figure S55: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, C_6D_6) of **1**.

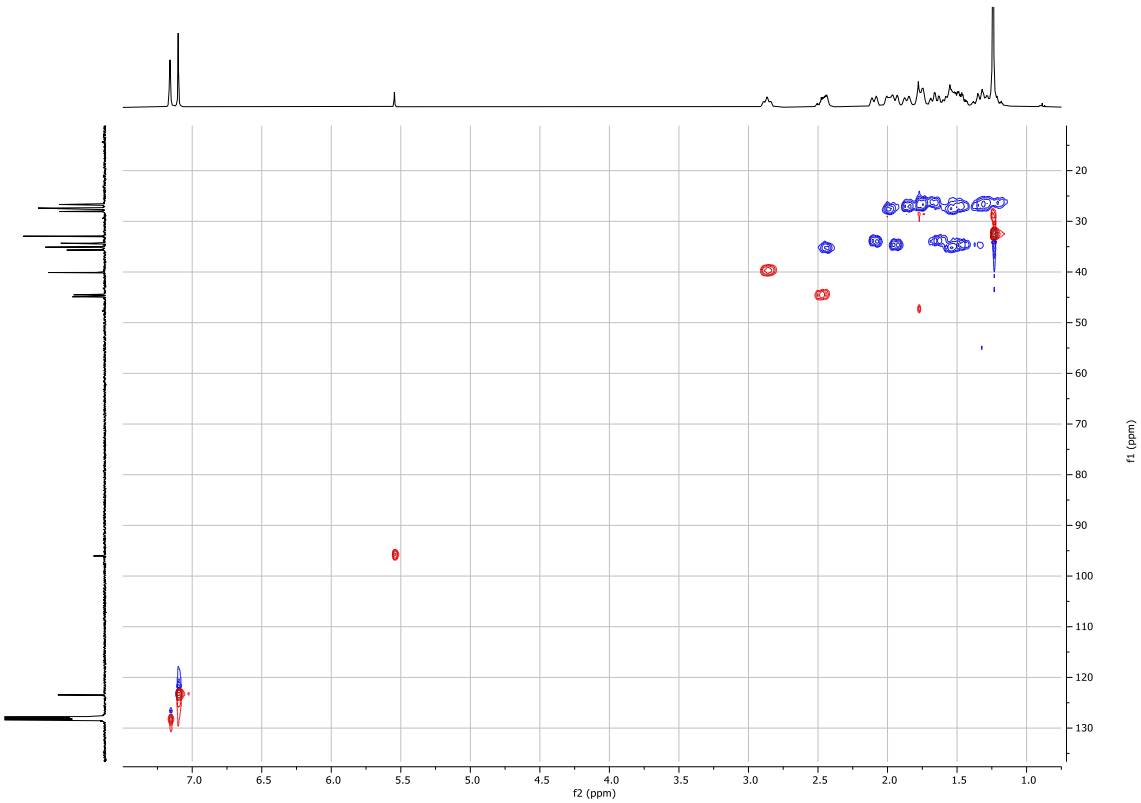


Figure S56: HSQC NMR spectrum (298 K, C_6D_6) of **1**.

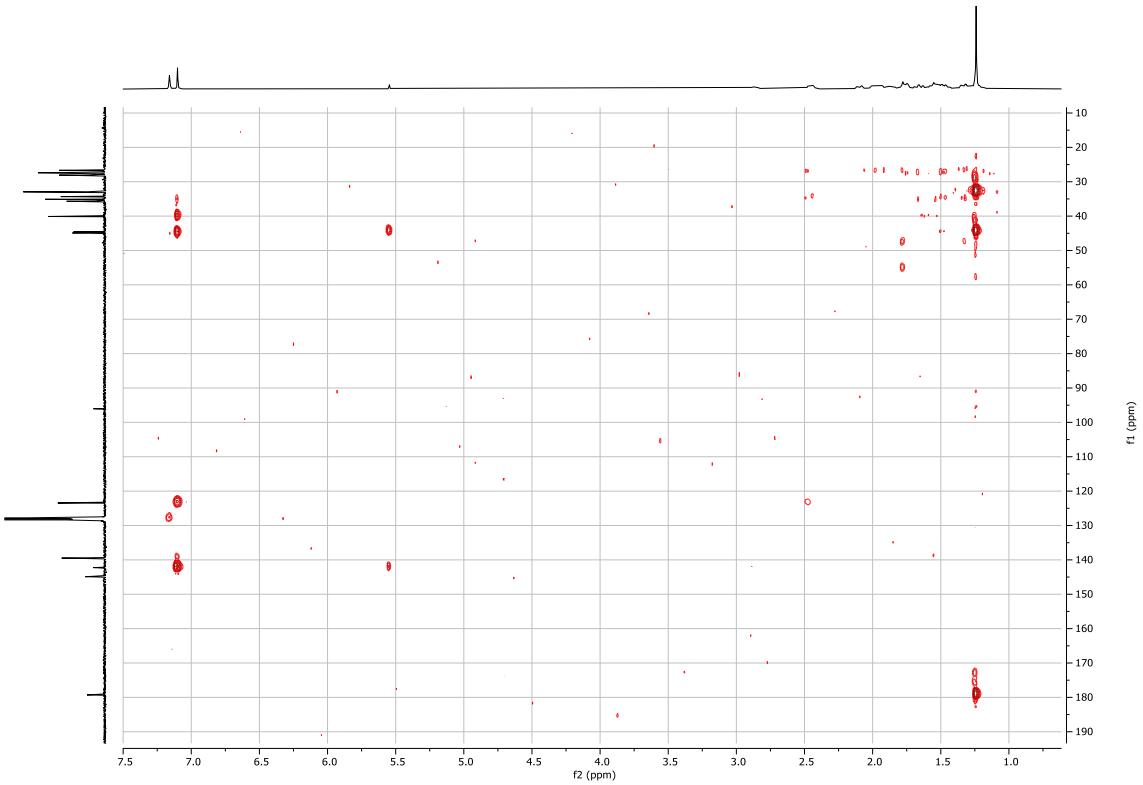
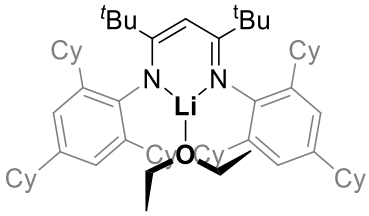


Figure S57: HMBC NMR spectrum (298 K, C_6D_6) of **1**.

Preparation of [(^{TCHP}Nacnac)Li(OEt$_2$)] 2



^{TCHP}NacnacH (2.00 g, 2.42 mmol) was charged to a flame-dried ampule and toluene (~5 mL) was added. To this suspension was added methyl lithium (3 M in Et_2O, 2.54 mmol, 0.85 mL) with stirring at room temperature. The mixture was stirred at room temperature for 1 hour, then sealed and stirred at 120 °C for a further 16 hours. The formed yellow solution was filtered *via* cannula and the volatiles removed *in vacuo*. The oily residue was suspended in hexane (~5 mL) and stored at –30 °C for 18 hours to give pale-yellow crystals. **Yield**: 2.19 g, 95%.

M.p.: 150–152 °C (dec).

^{1}H NMR (400 MHz, C_6D_6): δ 0.46 (t, J = 7.0 Hz, 6H, $\underline{Et}_2O$), 1.21 – 1.37 (m, 10H, Cy–$\underline{H}$), 1.39 (s, 18H, $C(C\underline{H}_3)_3$), 1.44 – 2.17 (m, 50H, Cy–$\underline{H}$), 2.42 (q, J = 7.2 Hz, 4H, $\underline{Et}_2O$), 2.46 – 2.54 (m, 2H, Cy–$\underline{H}$), 3.00 – 3.12 (m, 4H, Cy–$\underline{H}$), 5.37 (s, 1H, NCC$\underline{H}$), 6.96 (s, 4H, $_{TCHP}$Ar–$\underline{H}$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 13.7 ($\underline{Et}_2O$), 26.8, 27.1, 27.5, 27.6, 27.7, 27.9 (Cy–$\underline{C}$), 33.5 ($C(\underline{C}H_3)_3$), 34.0, 34.9, 35.6, 39.0 (Cy–$\underline{C}$), 44.6 ($\underline{C}(CH_3)_3$), 45.0 (Cy–$\underline{C}$), 63.9 ($\underline{Et}_2O$), 93.0 (NC$\underline{C}$H), 122.3, 137.7, 140.0, 149.8 ($_{TCHP}$Ar–$\underline{C}$), 172.1 (N$\underline{C}$).

^{7}Li NMR (156 MHz, C_6D_6): δ 1.39 ($\underline{Li}OEt_2$).

I.R. (solid, cm^{-1}): 2922 (s), 2845 (s), 1656 (m), 1608 (w) 1520 (m), 1441 (s), 1400 (m), 1360 (m), 1233 (w), 1141 (m), 1097 (m), 993 (w), 943 (w), 858 (s), 708 (w), 604 (w).

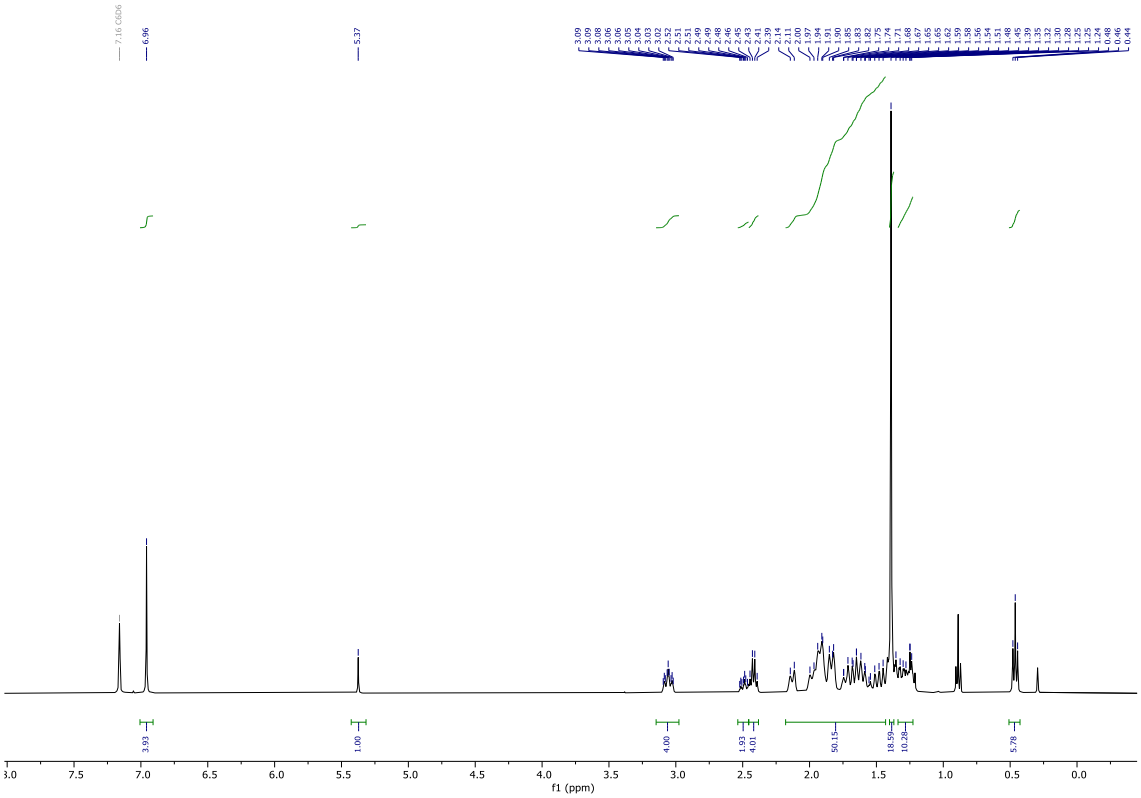


Figure S58: ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of **2**.

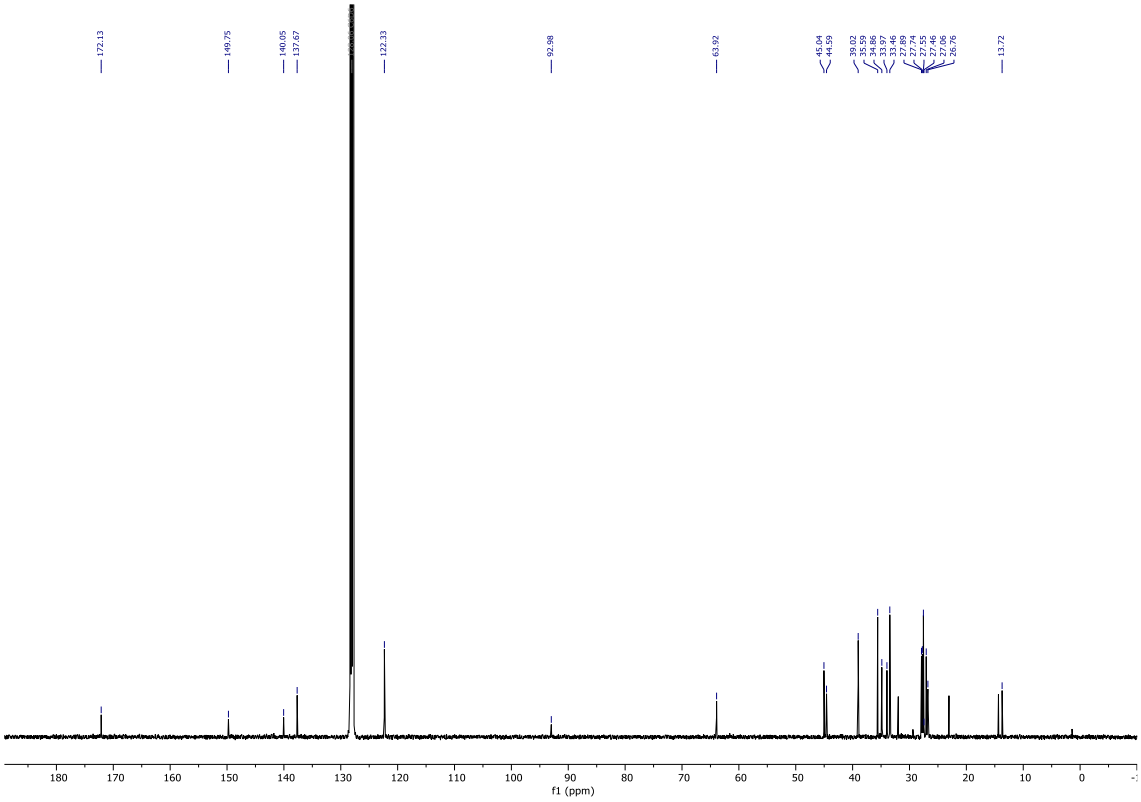


Figure S59: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, C_6D_6) of **2**.

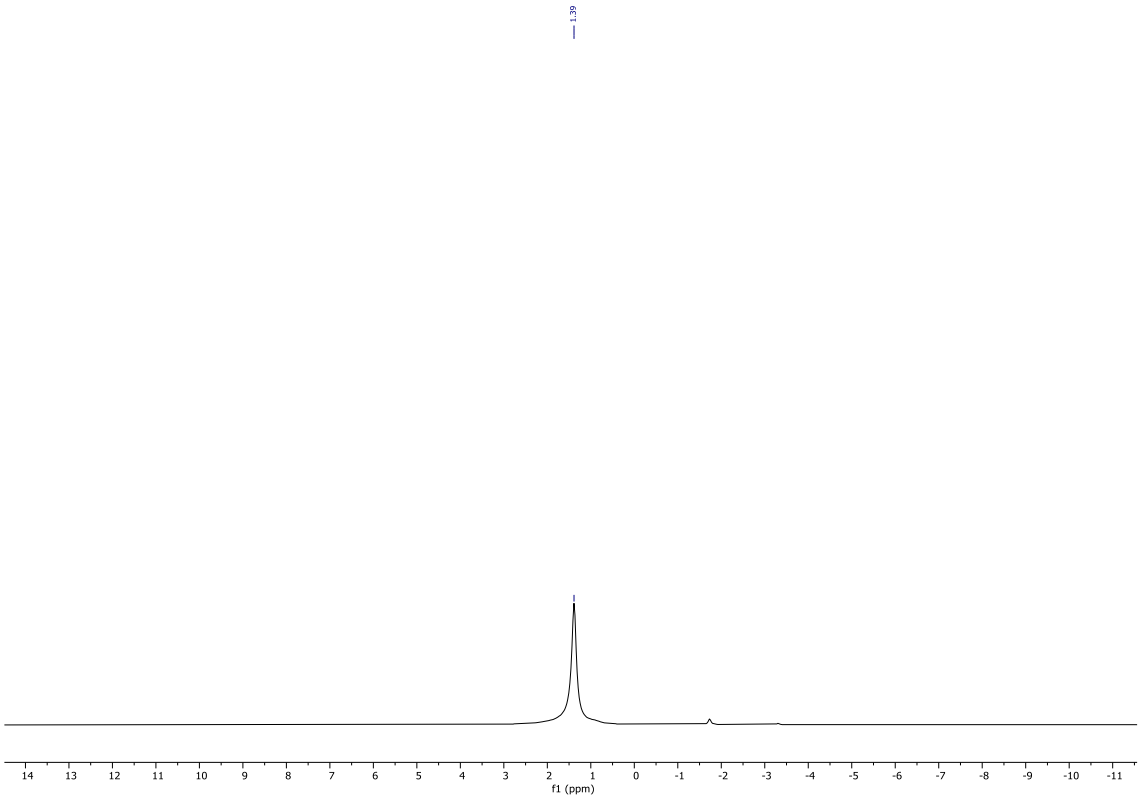


Figure S60: ^{7}Li NMR spectrum (101 MHz, 298 K, C_6D_6) of **2**.

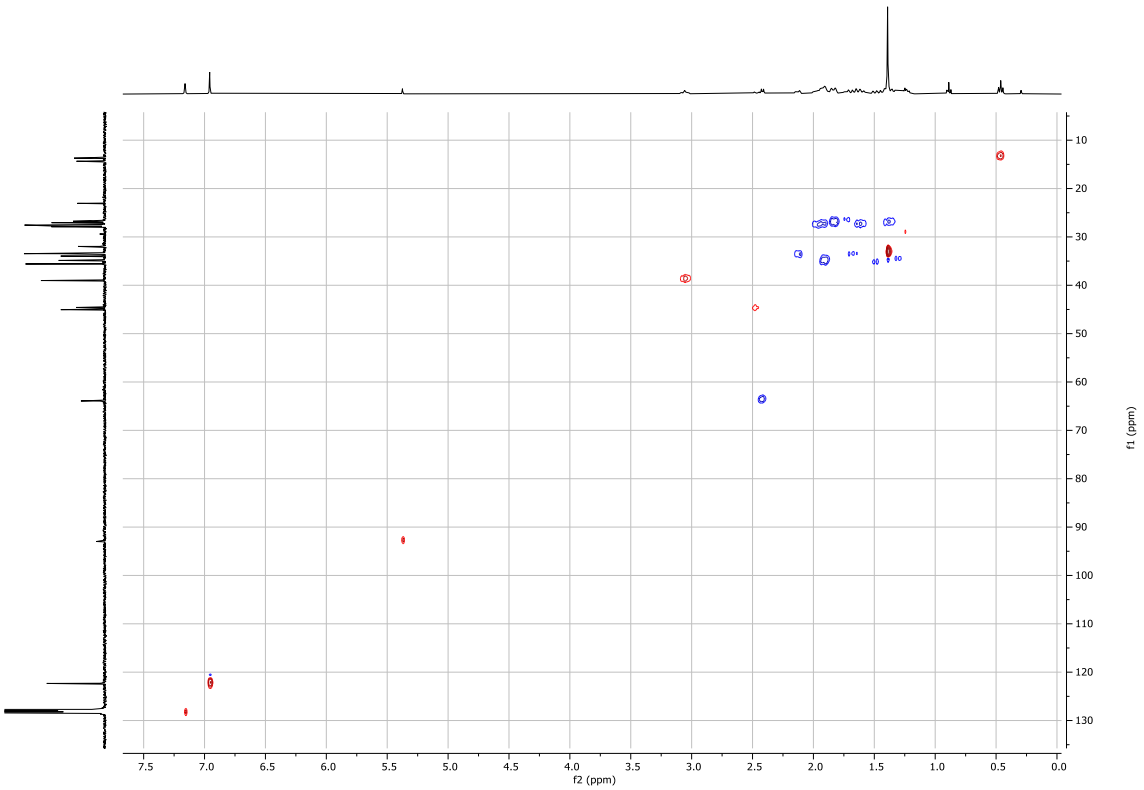


Figure S61: HSQC NMR spectrum (298 K, C_6D_6) of **2**.

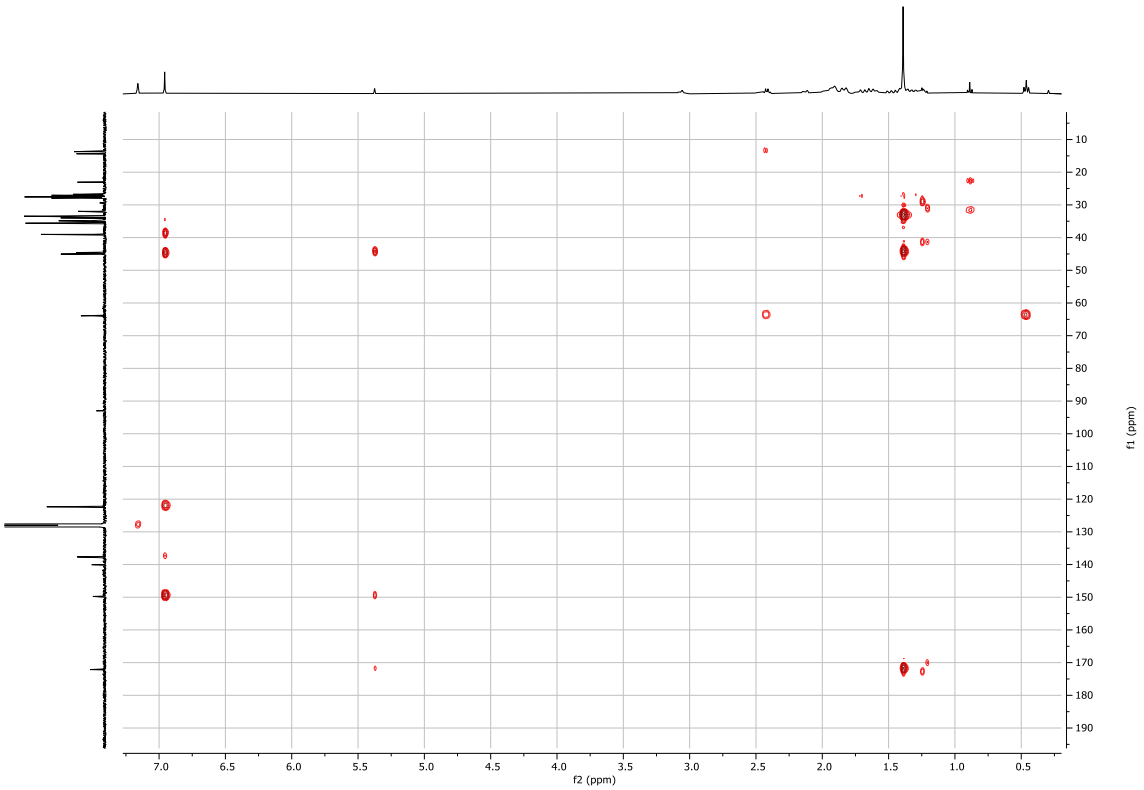
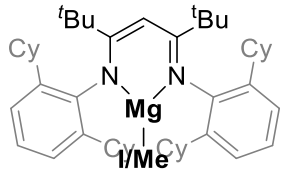


Figure S62: HMBC NMR spectrum (298 K, C_6D_6) of **2**.

Preparation of [(^{DCHP}Nacnac)MgI] 3 and [(^{DCHP}Nacnac)MgMe] 3-Me



^{DCHP}NacnacH (1.50 g, 2.26 mmol) was charged to a flame-dried ampule and toluene (~5 mL) was added. To the resultant suspension was added methyl magnesium iodide (3M in Et_2O, 3.39 mmol, 1.13 mL) at room temperature. The mixture was stirred at room temperature for 1 hour, then sealed and stirred at 120 °C for 3 days. The formed orange solution was filtered *via* cannula and the volatiles removed *in vacuo*. The oily residue was suspended in hexane (~10 mL) to give an off-white solid which was collected by filtration and washed with hexane (3 x 5 mL). The supernatant was reduced in volume to provide a second crop of pale yellow crystals. **Yield**: 1.596 g (crystalline mixture of **3** and **3-Me** in an approx. 50:50 ratio).

M.p.: 294–296 °C (dec).

^{1}H NMR (400 MHz, C_6D_6): δ -1.39 (br s, 3H, ~50%, C$\underline{H}_3$) 0.86* (t, J = 7.2 Hz, 3H, $\underline{Et}_2O$), 1.21 (s, 18H, C(C$\underline{H}_3$)$_3$), 1.23 – 1.29 (m, 4H, Cy–$\underline{H}$), 1.34 – 1.57 (m, 16H, Cy–$\underline{H}$), 1.64 – 1.85 (m, 8H, Cy–$\underline{H}$), 1.91 – 2.05 (m, 8H, Cy–$\underline{H}$), 2.13 – 2.56 (m, 4H, Cy–$\underline{H}$), 2.71 – 2.94 (m, 4H, Cy–$\underline{H}$), 3.51* (q, J = 7.2 Hz, 2H, $\underline{Et}_2O$), 5.54 (s, 1H, NCC$\underline{H}$), 7.00 – 7.14 (m, 6H, $_{DCHP}$Ar–$\underline{H}$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ -18.1 ($\underline{C}H_3$), 14.0* ($\underline{Et}_2O$), 26.6, 27.5, 28.0 (Cy–$\underline{C}$), 32.9 (C($\underline{C}H_3$)$_3$), 34.1, 35.3, 39.9 (Cy–$\underline{C}$), 44.6 ($\underline{C}(CH_3)_3$), 66.6* ($\underline{Et}_2O$), 96.0 (NC$\underline{C}$H), 125.1, 134.9, 139.9, 144.6 ($_{DCHP}$Ar–$\underline{C}$), 178.0 (N$\underline{C}$).

I.R. (solid, cm^{-1}): 2922 (s), 2850 (s), 1618 (w), 1534 (w), 1498 (m), 1465 (w), 1444 (m), 1383 (s), 1364 (s), 1349 (s), 1303 (m), 1211 (m), 1182 (m), 1150 (w), 1131 (m), 1079 (w), 1023 (w), 995 (w), 937 (m), 891 (w), 878 (w), 841 (w), 794 (w), 762 (s), 714 (s), 699 (w), 669 (w).

*N.B. residual diethyl ether was difficult to fully remove from the bulk material which may suggest weak coordination of diethyl ether to the magnesium centre of **3** or **3-Me**. However, ether coordination was not observed in the crystal structure of the co-crystallised mixture.

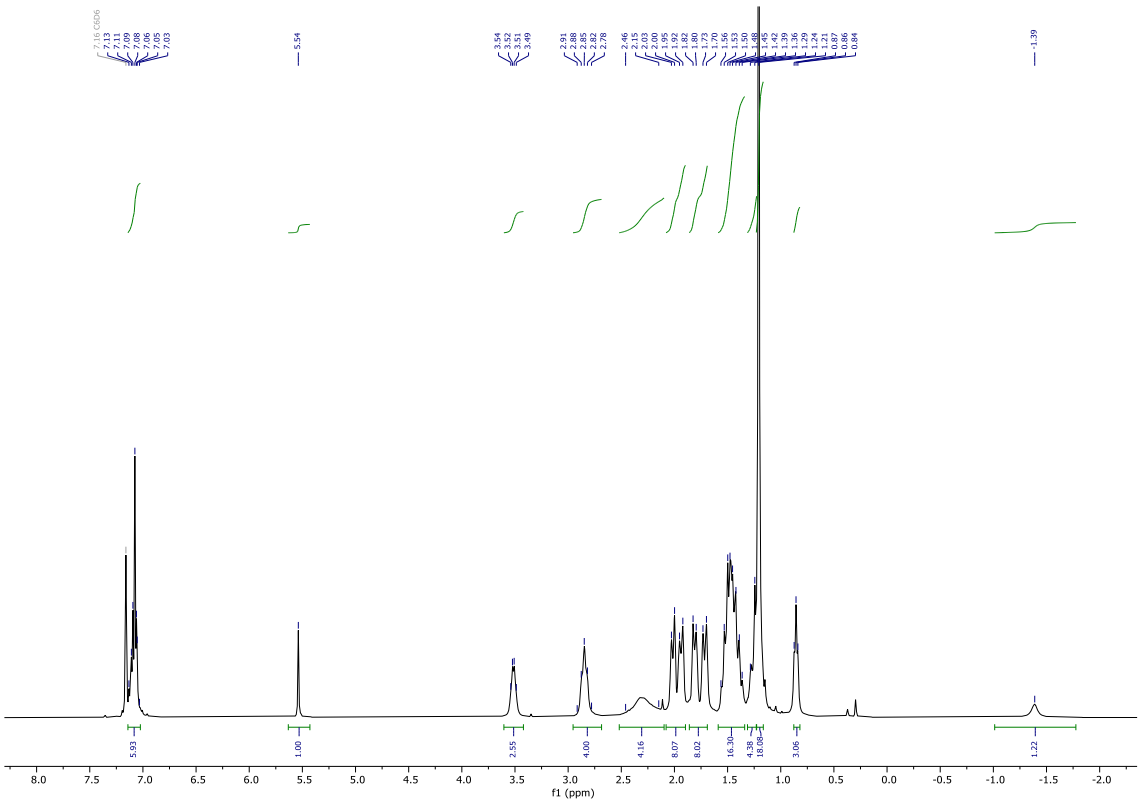


Figure S63: ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of a co-crystallised mixture of **3** and **3-Me**.

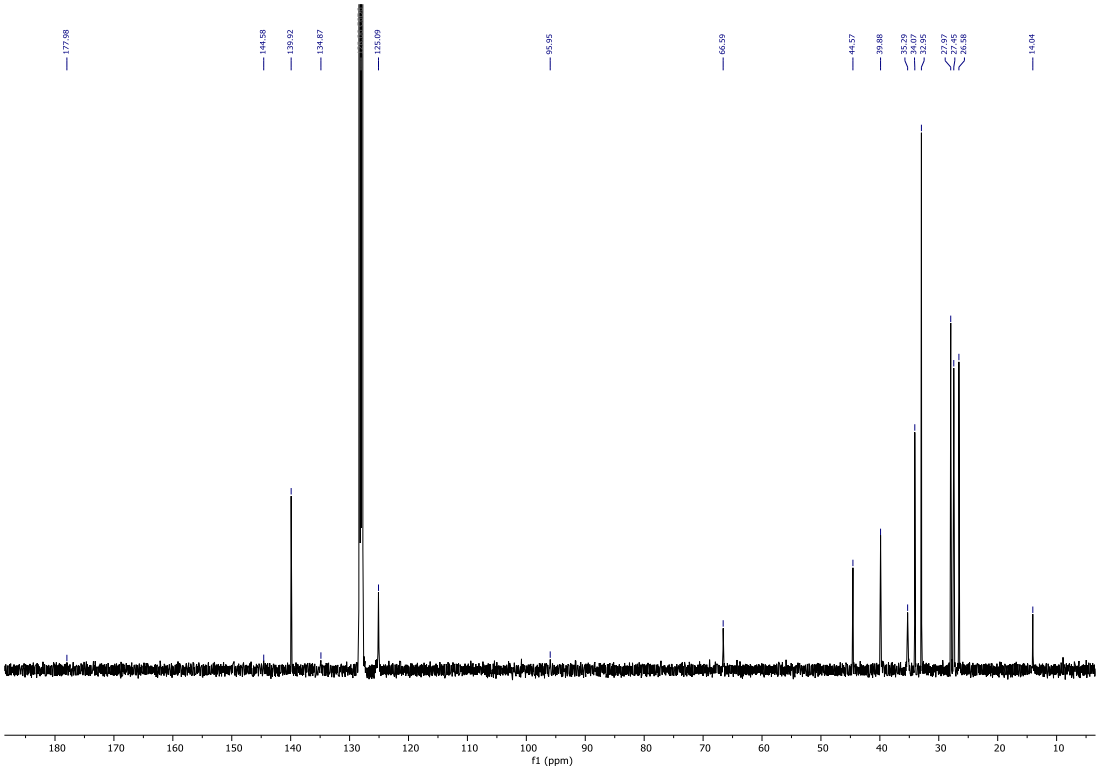


Figure S64: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, C_6D_6) of a co-crystallised mixture of **3** and **3-Me**.

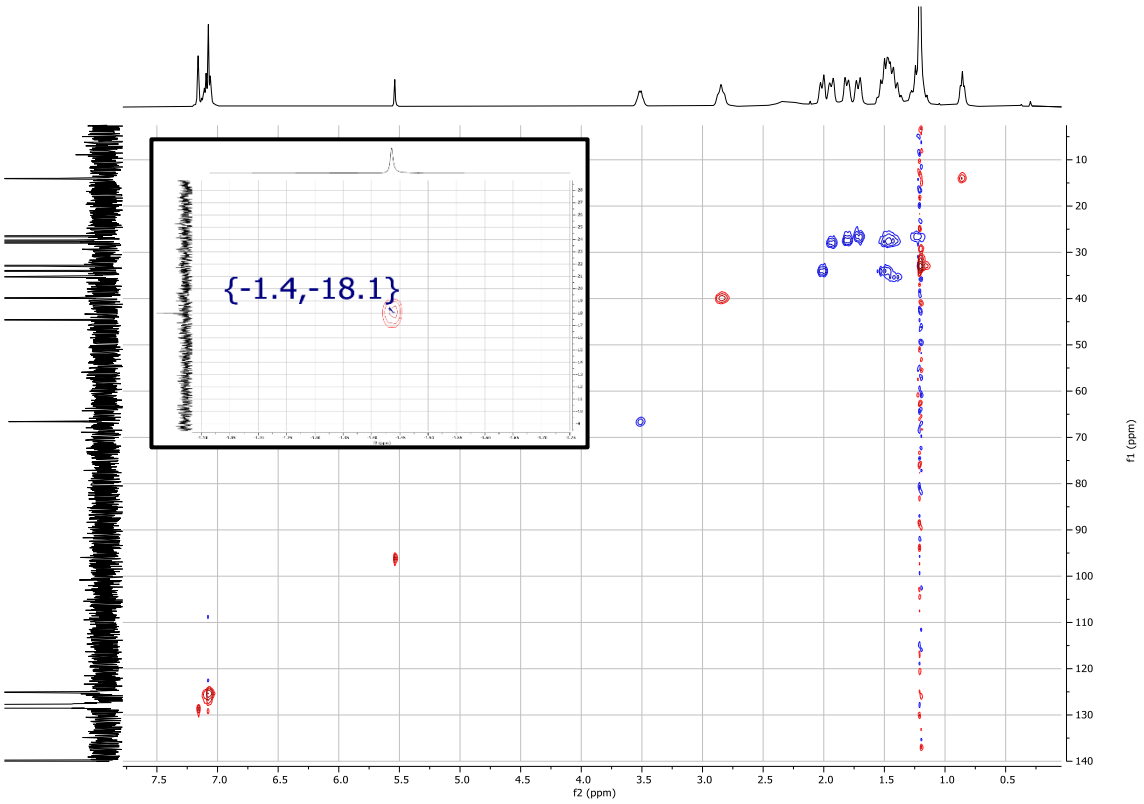


Figure S65: HSQC NMR spectrum (298 K, C_6D_6) of a co-crystallised mixture of **3** and **3-Me**. Inset: HSQC NMR spectrum including negative ppm range.

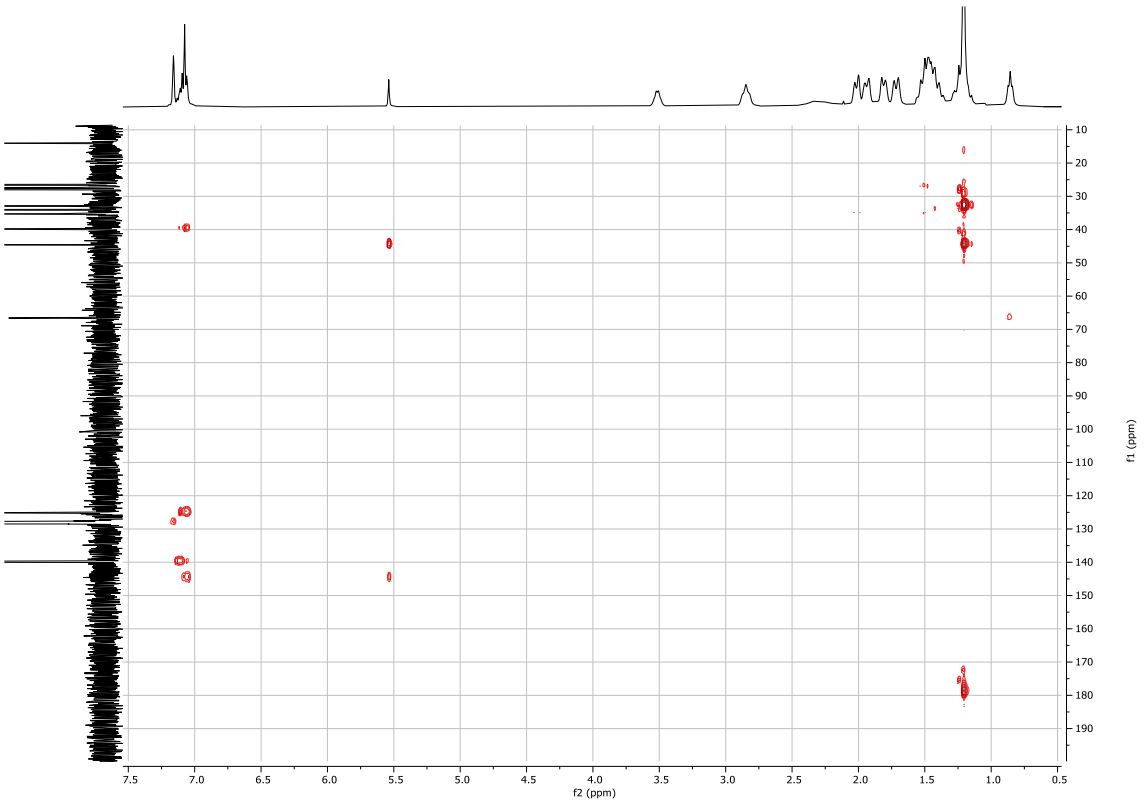
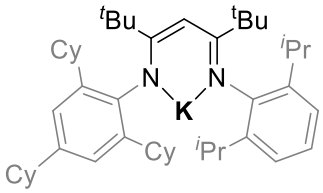


Figure S66: HMBC NMR spectrum (298 K, C_6D_6) of a co-crystallised mixture of **3** and **3-Me**.

Preparation of [($^{TCHP/Dip}$Nacnac)K] 4



$^{TCHP/Dip}$NacnacH (3.00 g, 4.51 mmol) and benzyl potassium (0.881 g, 6.77 mmol) were charged to a flame-dried ampule and toluene (~20 mL) was added. The mixture was allowed to stir at room temperature for 1 hour and then sealed and stirred at 120 °C for 16 hours. The reaction mixture was cooled to room temperature, filtered *via* cannula, and the solvent removed under vacuum. The resultant oily solid residue was suspended in hexane (~20 mL), sonicated for 10 minutes, and then stored at –30 °C for 24 hours. The resultant yellow-red precipitated solid was collected by filtration and dried under vacuum. **Yield**: 2.92 g, 92%.

M.p.: > 260 °C (dec).

^{1}H NMR (400 MHz, C_6D_6): δ 0.80 (d, J = 6.8 Hz, 6H, CH(C$\underline{H}_3$)$_2$), 0.93 – 1.12 (m, 8H, Cy–$\underline{H}$), 1.16 (s, 18H, C(C$\underline{H}_3$)$_3$), 1.17 – 1.20 (m, 6H, CH(C$\underline{H}_3$)$_2$), 1.22 – 1.47 (m, 8H, Cy–$\underline{H}$), 1.47 – 1.74 (m, 10H, Cy–$\underline{H}$), 1.76 – 1.94 (m, 4H, Cy–$\underline{H}$), 2.26 – 2.37 (m, 1H, Cy–$\underline{H}$), 2.59 – 2.74 (m, 2H, Cy–$\underline{H}$), 3.02 (hept, J = 7.0 Hz, 2H, C$\underline{H}$(CH$_3$)$_2$), 4.77 (s, 1H, NCC$\underline{H}$), 6.62 (t, J = 7.6 Hz, 1H, $_{Dipp}$Ar–$\underline{H}$), 6.74 (s, 2H, $_{TCHP}$Ar–$\underline{H}$), 6.82 (d, J = 7.6 Hz, 2H, $_{Dipp}$Ar–$\underline{H}$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 23.6, 24.4 (CH(C$\underline{H}_3$)$_2$), 26.8 (C$\underline{H}$(CH$_3$)$_2$), 27.0, 27.5, 27.6, 27.7, 27.7 (Cy–$\underline{C}$), 32.9, 32.9 (C(C$\underline{H}_3$)$_3$), 34.1, 35.5, 35.6, 38.5 (Cy–$\underline{C}$), 44.4, 44.5 ($\underline{C}$(CH$_3$)$_3$), 44.9 (Cy–$\underline{C}$), 90.4 (NC$\underline{C}$H), 118.3, 122.8, 123.7, 134.4, 135.9, 137.0, 150.1, 152.0 ($_{TCHP}$Ar–$\underline{C}$, $_{Dipp}$Ar–$\underline{C}$), 166.9, 167.5 (N$\underline{C}$).

I.R. (solid, cm^{-1}): 2920 (s), 2850 (s), 1558 (m), 1472 (s), 1435 (s), 1390 (m), 1336 (m), 1314 (s), 1295 (w), 1258 (w), 1210 (s), 1172 (m), 1120 (w), 1087 (m), 1023 (w), 997 (w), 941 (w), 915 (m), 867 (m), 839 (w), 822 (w), 802 (w), 773 (m).

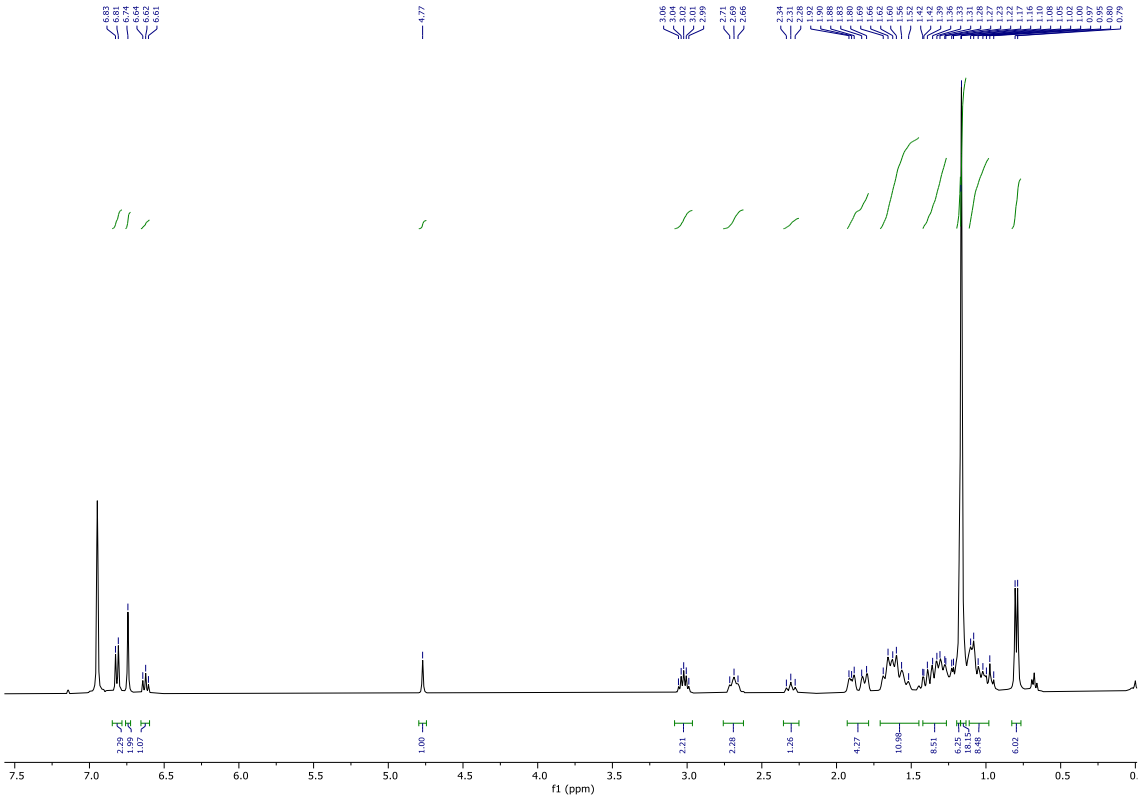


Figure S67: ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of **4**.

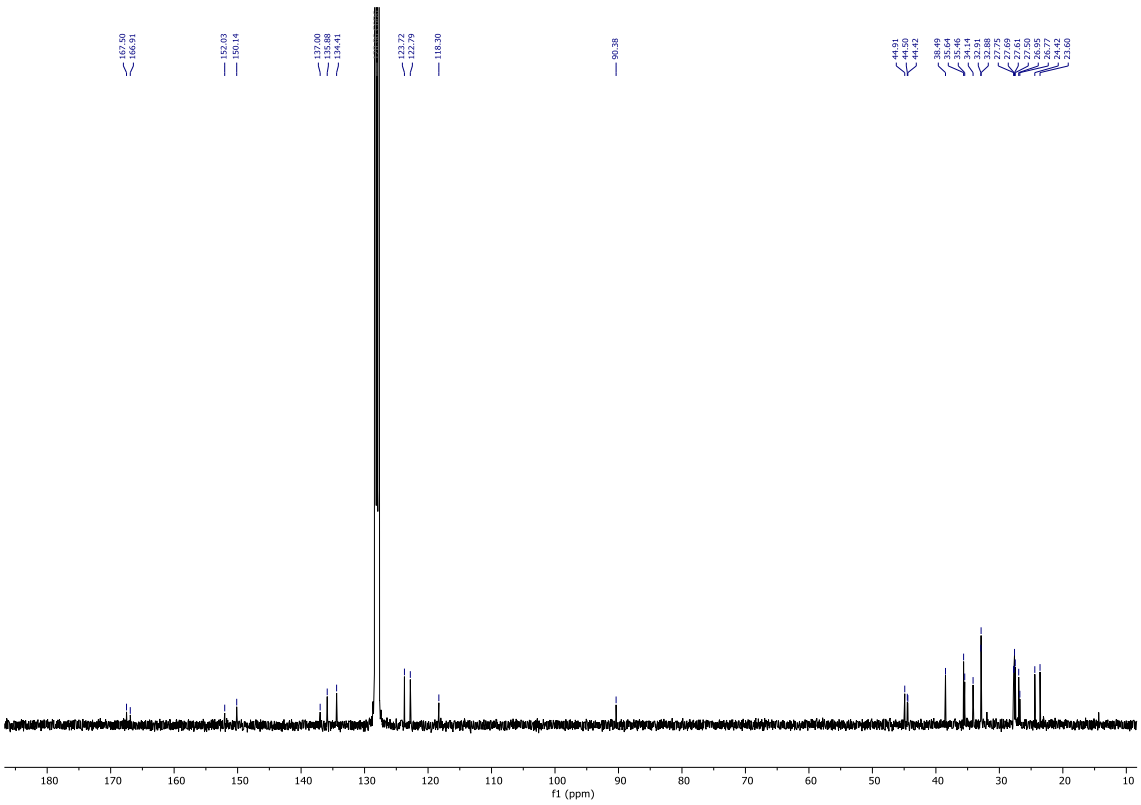


Figure S68: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, C_6D_6) of **4**.

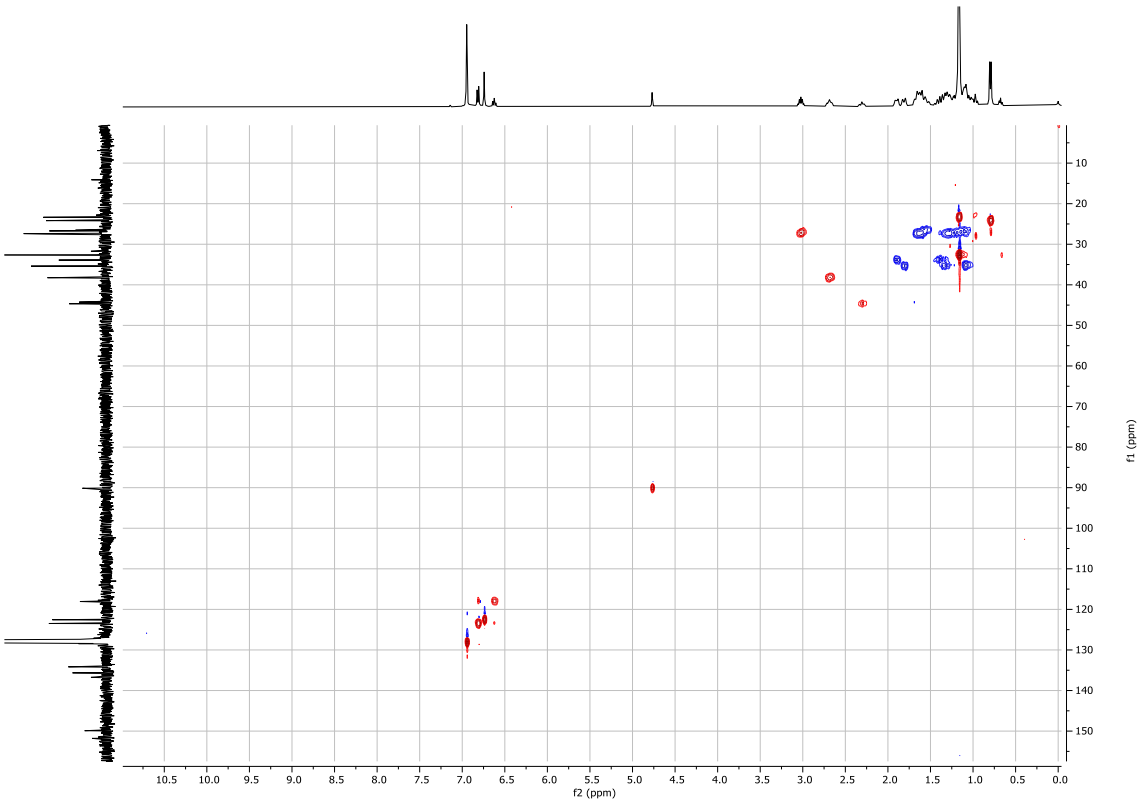


Figure S69: HSQC NMR spectrum (298 K, C_6D_6) of **4**.

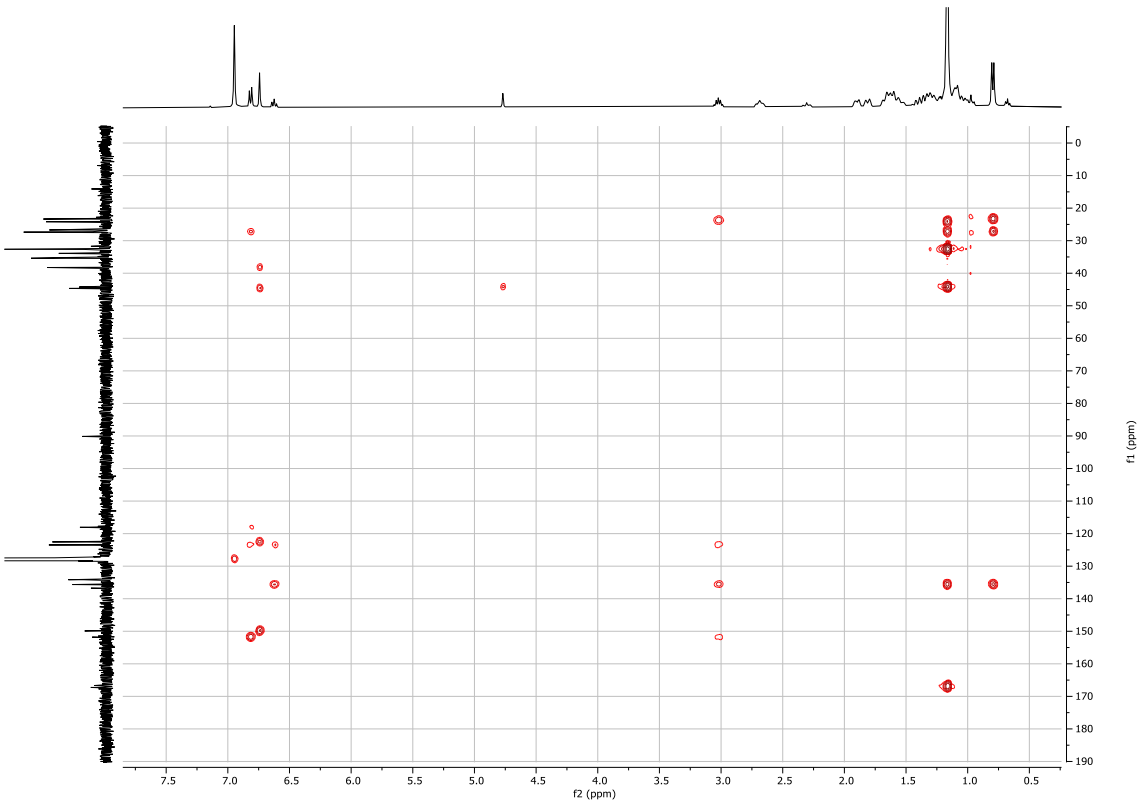
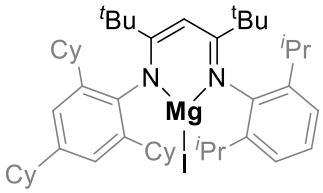


Figure S70: HMBC NMR spectrum (298 K, C_6D_6) of **4**.

Preparation of [($^{TCHP/Dip}$Nacnac)MgI] 5



[($^{TCHP/Dip}$Nacnac)K] (704 mg, 1.00 mmol) and $MgI_2(OEt_2)_2$ (469 mg, 1.10 mmol, 1.1 eqv) were charged to a flame-dried ampule and toluene (~10 mL) was added. The mixture was allowed to stir at room temperature for 1 hour and then sealed and stirred at 120 ℃ for 18 hours. The formed pale-yellow solution was filtered *via* cannula and the volatiles removed *in vacuo*. The oily solid residue was dissolved in hexane (~10 mL) and stored at –30 ℃ to give an off-white solid precipitate which was collected by filtration. **Yield**: 540 mg, 66%.

M.p.: 188–190 ℃ (dec).

^{1}H NMR (400 MHz, C_6D_6): δ 1.16 (s, 9H, C(C$\underline{H}_3$)$_3$), 1.22 (s, 9H, C(C$\underline{H}_3$)$_3$), 1.32 (d, J = 6.8 Hz, 6H, CH(C$\underline{H}_3$)$_2$), 1.34 – 1.44 (m, 8H, Cy–$\underline{H}$), 1.48 (d, J = 6.8 Hz, 6H, CH(C$\underline{H}_3$)$_2$), 1.58 – 2.07 (m, 20H, Cy–$\underline{H}$), 2.22 – 2.33 (m, 2H, Cy–$\underline{H}$), 2.39 – 2.55 (m, 1H, Cy–$\underline{H}$), 2.77 – 2.91 (m, 2H, Cy–$\underline{H}$), 3.23 (hept, J = 6.9 Hz, 2H, C$\underline{H}$(CH$_3$)$_2$), 5.42 (s, 1H, NCC$\underline{H}$), 7.01 – 7.13 (m, 6H, $_{TCHP}$Ar–$\underline{H}$, $_{Dipp}$Ar–$\underline{H}$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 23.4, 25.6 (CH(C$\underline{H}_3$)$_2$), 26.6, 27.4, 27.6, 28.0 (Cy–$\underline{C}$), 28.7 (C$\underline{H}$(CH$_3$)$_2$), 32.8, 33.7 (C(C$\underline{H}_3$)$_3$), 35.1, 36.5, 40.1 (Cy–$\underline{C}$), 44.1, 44.2 (C$\underline{C}$(CH$_3$)$_3$), 44.9 (Cy–$\underline{C}$), 95.6 (NC$\underline{C}$H), 123.3, 124.0, 126.1, 139.2, 141.4, 142.1, 143.8, 145.2 ($_{TCHP}$Ar–$\underline{C}$, $_{Dipp}$Ar–$\underline{C}$), 177.9, 178.0 (N$\underline{C}$).

I.R. (solid, cm^{-1}): 2920 (s), 2850 (s), 1608 (w), 1508 (m), 1446 (m), 1381 (s), 1362 (s), 1316 (m), 1258 (w), 1217 (w), 1195 (m), 1128 (w), 1098 (w), 1027 (m), 997 (w), 936 (w), 878 (w), 863 (w), 841 (w), 801 (w), 762 (m), 727 (w).

A reproducible microanalysis could not be obtained due to the extreme air and moisture sensitivity of the complex, and the inability to remove traces of $^{TCHP/Dip}$NacnacH after repeated recrystallizations.

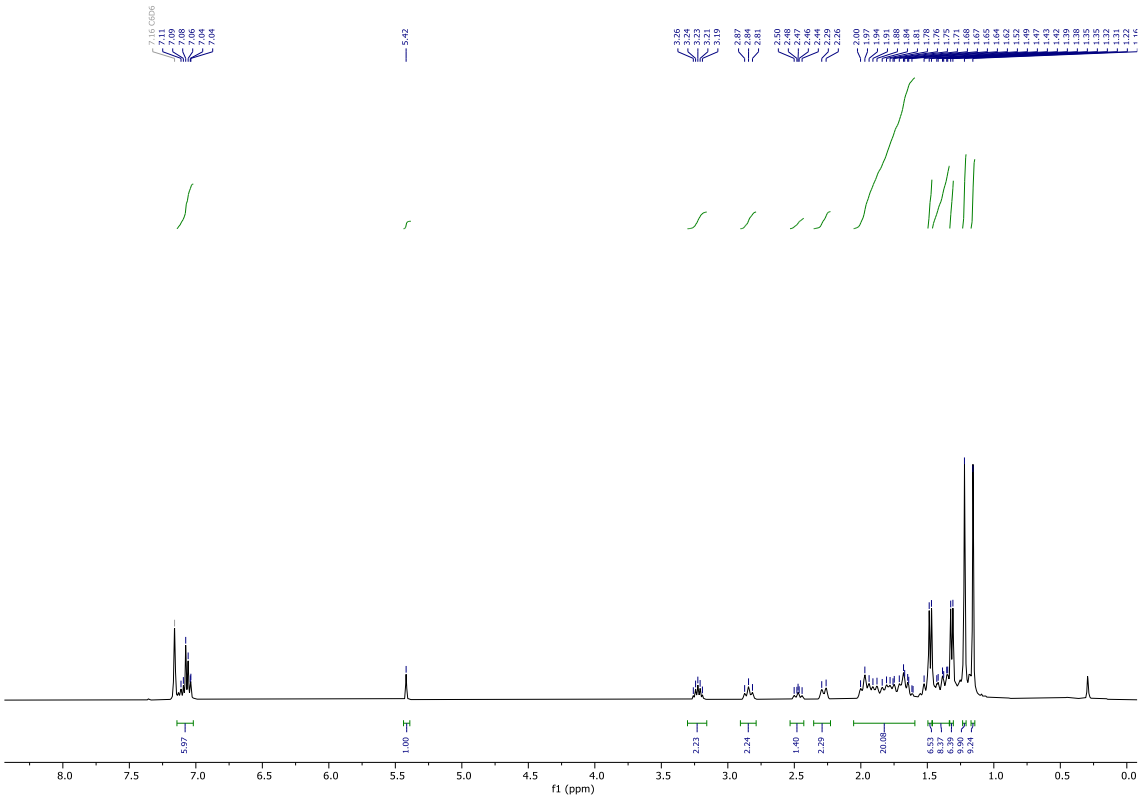


Figure S71: ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of **5**.

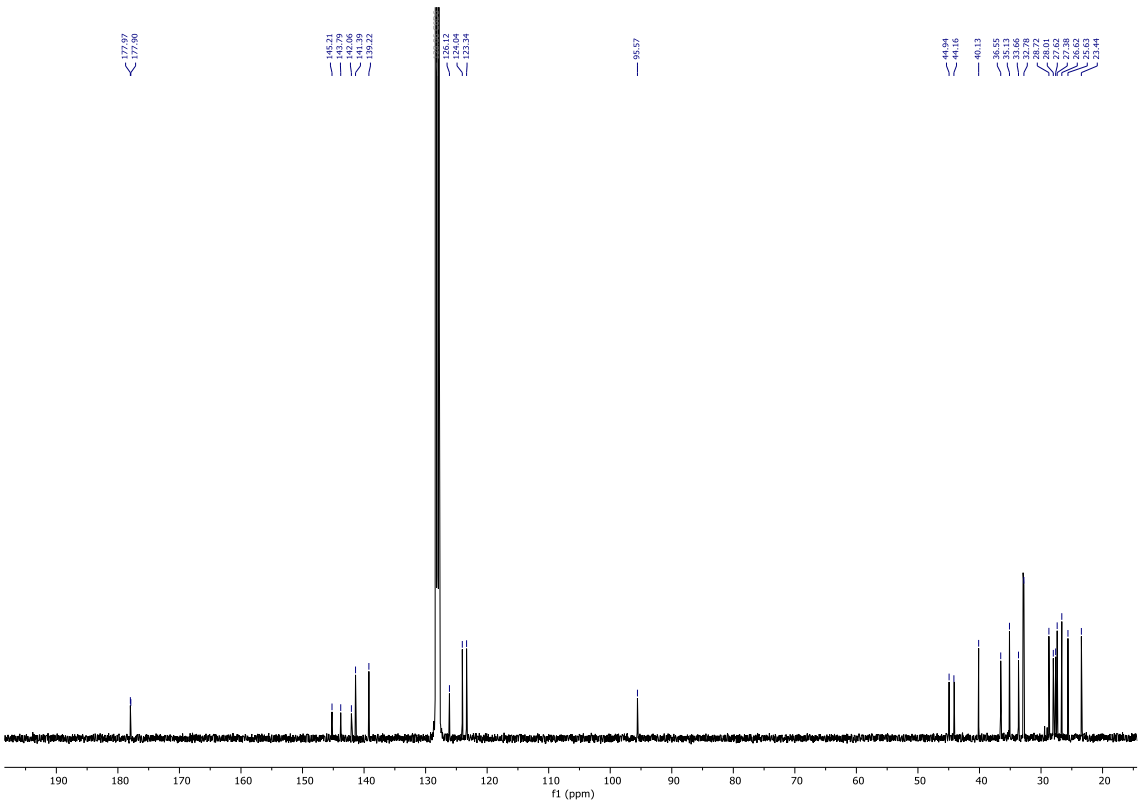


Figure S72: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, C_6D_6) of **5**.

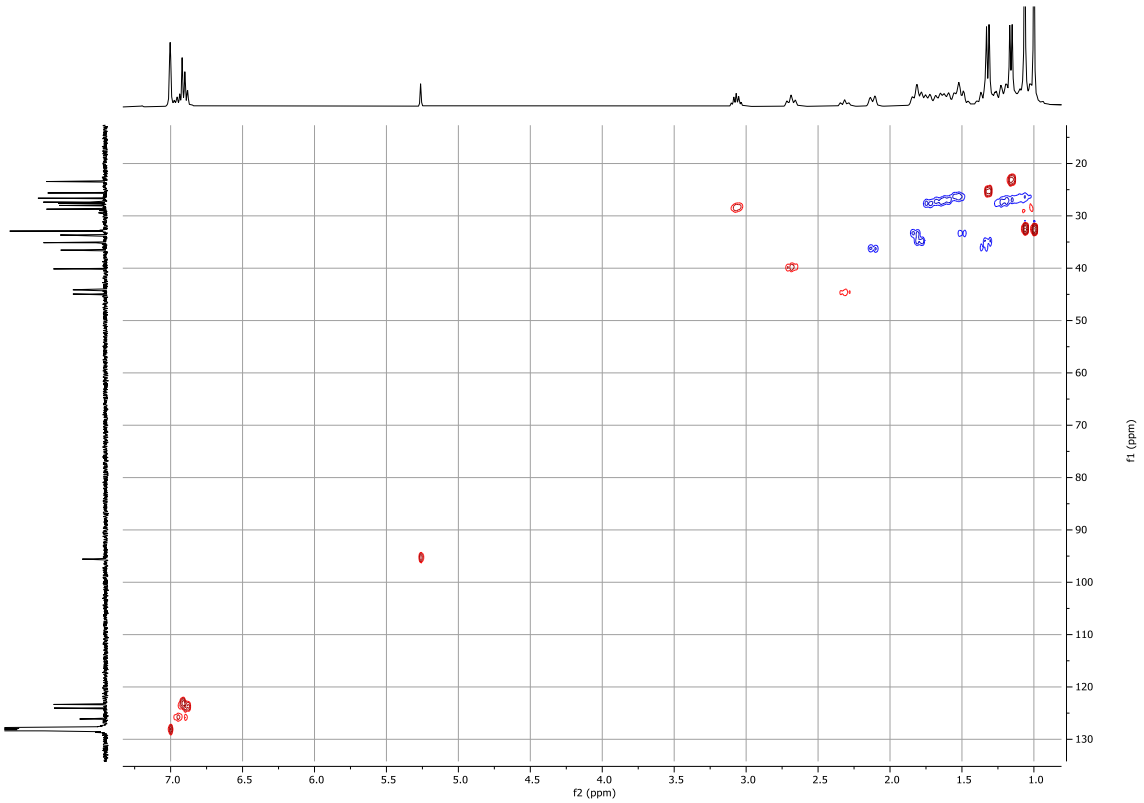


Figure S73: HSQC NMR spectrum (298 K, C_6D_6) of **5**.

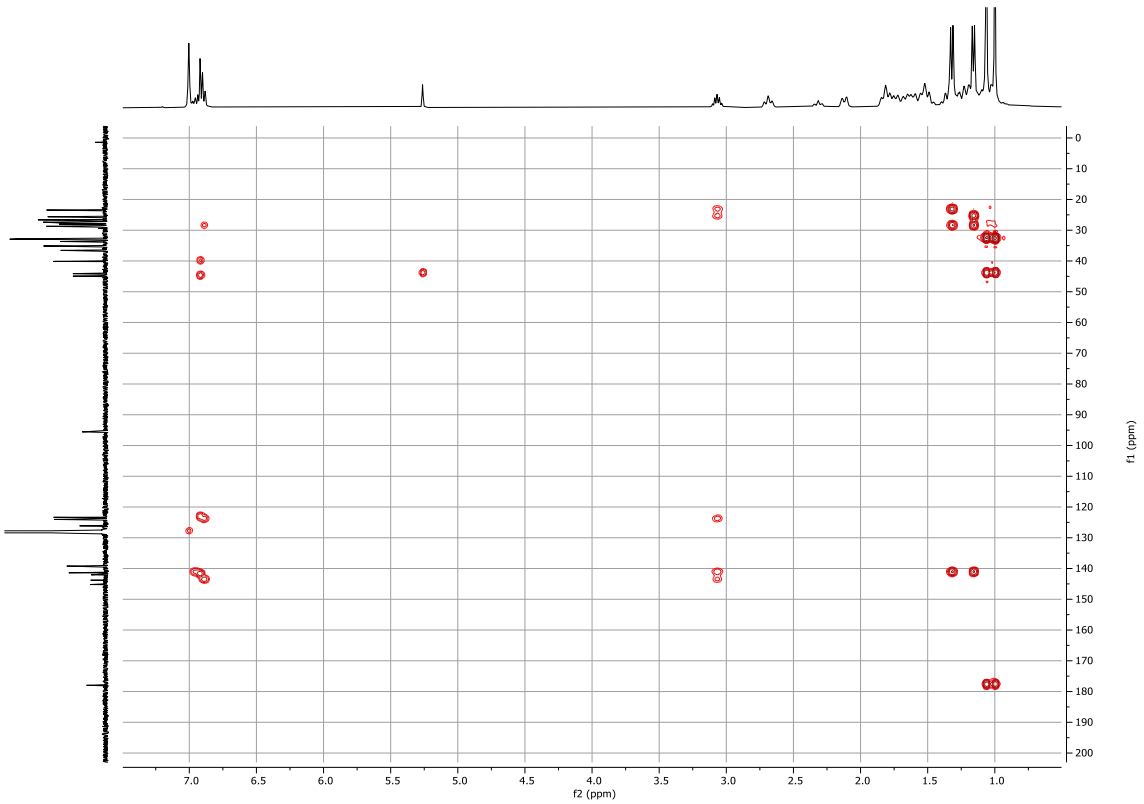
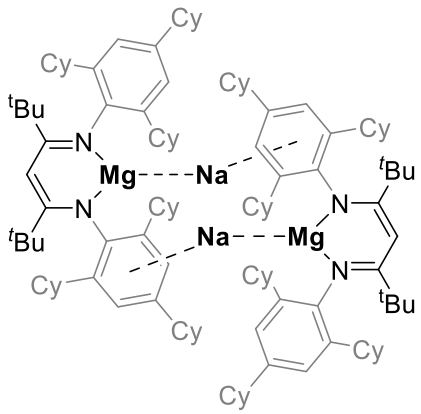


Figure S74: HMBC NMR spectrum (298 K, C_6D_6) of **5**.

Preparation of [{(^{TCHP}Nacnac)Mg}Na]$_2$ 6



Compound **1** (2.00 g, 2.45 mmol) and Na/NaCl (5% w/w, 4.92 g, 10.70 mmol) were charged to a 50 mL ampule and methylcyclohexane (20 mL) was added. The reaction mixture was allowed to stir for 18 hours at room temperature. The volatiles were removed *in vacuo*, the residue extracted with hexane (50 mL) and filtered to give a dark red solution. The filtrate was concentrated to *ca.* 5 mL and then stored at room temperature for 18 hours, resulting in the formation of dark red block-shaped crystals. **Yield**: 1.52 g, 85 %.

M.p.: 170–172 °C (dec).

^{1}H NMR (400 MHz, C_6D_6): δ 1.26 (s, 18H, C(C$\underline{H}_3$)$_3$), 1.32 – 1.73 (m, 30H, Cy–$\underline{H}$), 1.73 – 2.17 (m, 26H, Cy–$\underline{H}$), 2.44 – 2.56 (m, 2H, Cy–$\underline{H}$), 2.63 – 2.76 (m, 4H, Cy–$\underline{H}$), 2.86 – 3.05 (m, 4H, Cy–$\underline{H}$), 5.41 (s, 1H, NCC$\underline{H}$), 7.04 (s, 4H, $_{TCHP}$Ar–$\underline{H}$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 26.8, 27.1, 27.5, 27.6, 27.8 (Cy–$\underline{C}$), 33.4 (C($\underline{C}$H$_3$)$_3$), 34.3, 35.2, 35.5, 39.3 (Cy–$\underline{C}$), 44.0 ($\underline{C}$(CH$_3$)$_3$), 44.5 (Cy–$\underline{C}$), 95.3 (NC$\underline{C}$H), 121.9, 140.5, 142.3, 148.1 ($_{TCHP}$Ar–$\underline{C}$), 173.8 (N$\underline{C}$).

I.R. (Nujol, cm^{-1}): 1510 (m), 1135 (m), 1110 (w), 1025 (w), 993 (w), 954 (w), 889 (w), 866 (m), 781 (m) 706 (m), 608 (w).

Anal. calcd. for $C_{118}H_{178}Mg_2N_4Na_2$: C 81.11 %, H 10.27 %, N 3.21 %; found: C 81.17 %, H 10.65 %, N 3.17 %.

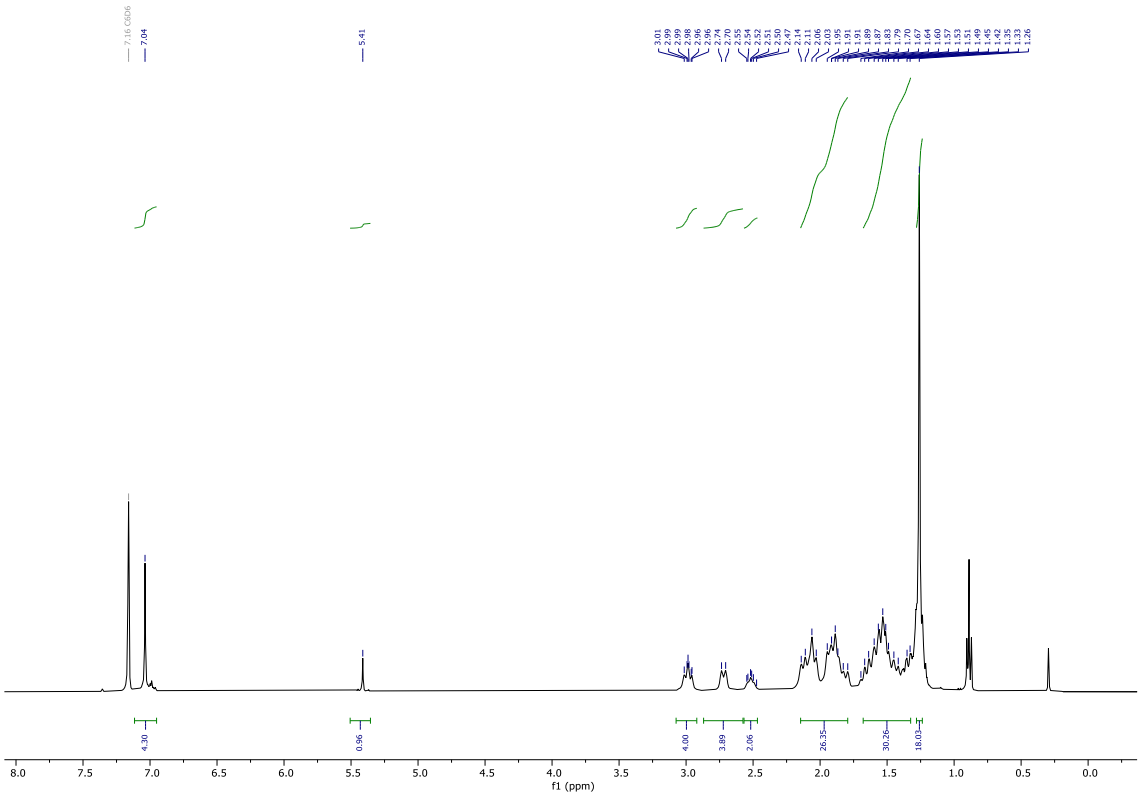


Figure S75: ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of **6**.

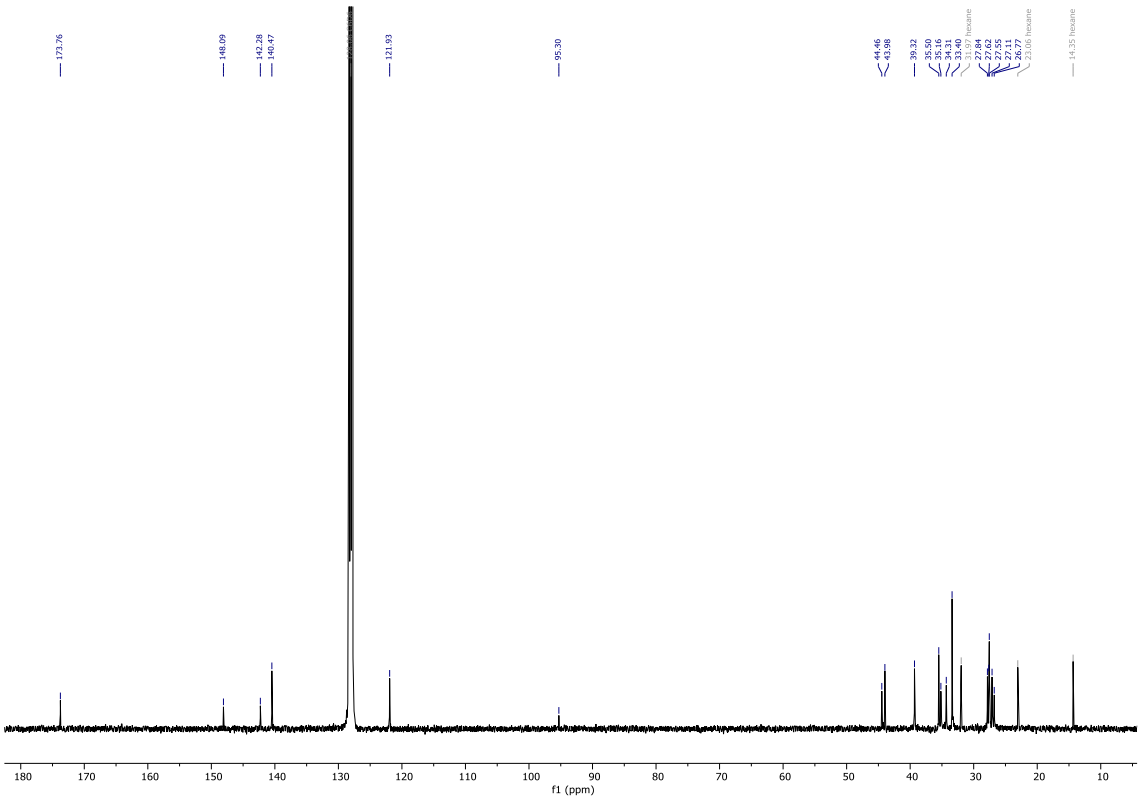


Figure S76: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, C_6D_6) of **6**.

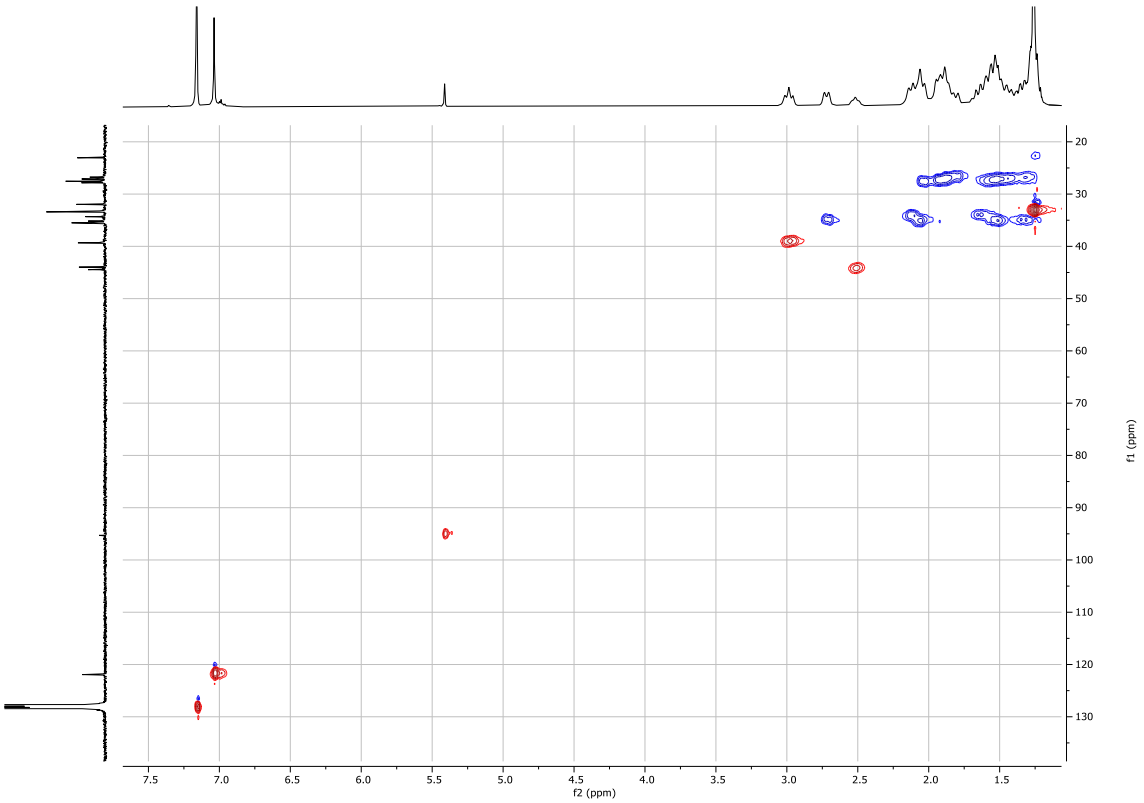


Figure S77: HSQC NMR spectrum (298 K, C_6D_6) of **6**.

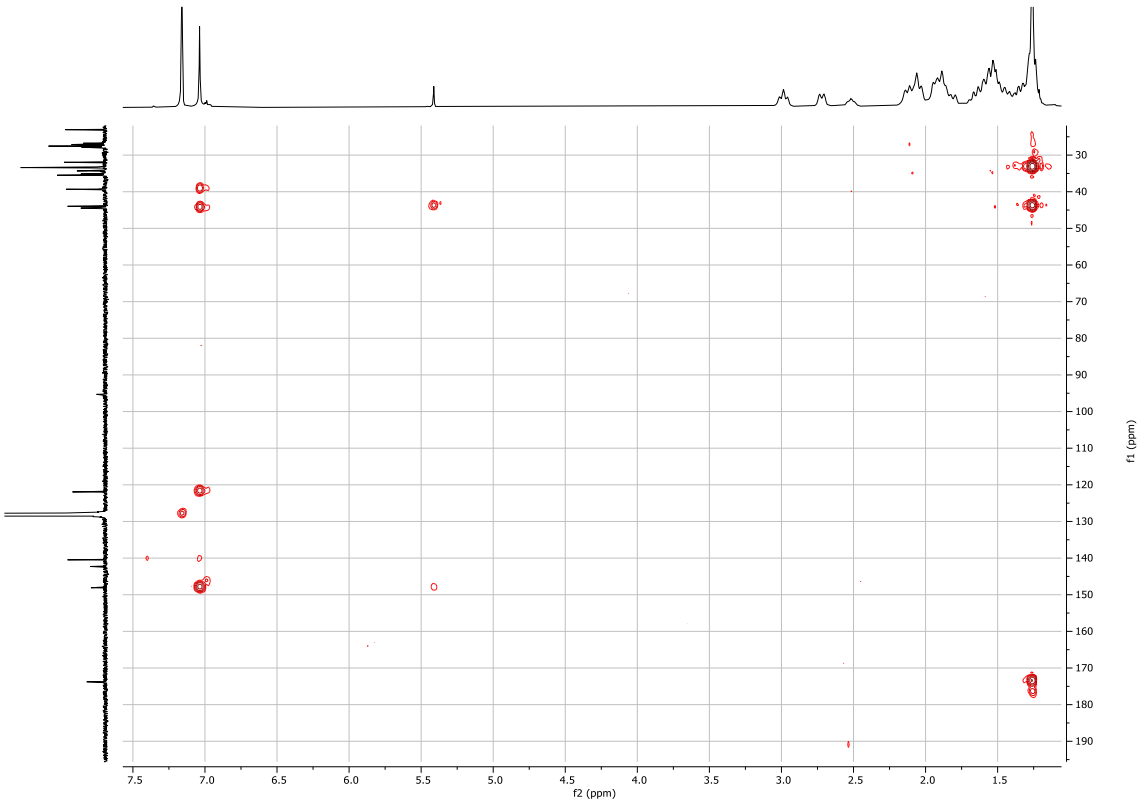
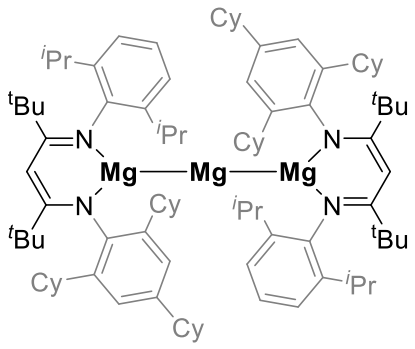


Figure S78: HMBC NMR spectrum (298 K, C_6D_6) of **6**.

Preparation of [{($^{TCHP/Dip}$Nacnac)Mg}$_2$Mg] 7



Compound **5** (250 mg, 0.31 mmol) and Na/NaCl (5% w/w, 1.025 g, 2.23 mmol) were charged to a 50 mL ampule and hexane (10 mL) was added. The reaction mixture was allowed to stir for 18 hours at room temperature. The volatiles were then removed *in vacuo*, the residue extracted with hexane (10 mL) and filtered to give a dark red solution. The filtrate was concentrated to *ca.* 2 mL and then stored at room temperature for several days resulting in the formation of red-brown crystals. **Yield**: 130 mg, 60 %.

M.p.: 138 – 140 °C (dec).

^{1}H NMR (400 MHz, C_6D_6): δ 1.21 (s, 18H, C(C$\underline{H}_3$)$_3$), 1.22 (s, 18H, C(C$\underline{H}_3$)$_3$), 1.31 (d, J = 6.8 Hz, 12H, CH(C$\underline{H}_3$)$_2$), 1.39 (d, J = 6.8 Hz, 12H, CH(C$\underline{H}_3$)$_2$), 1.45 – 2.18 (m, 60H, Cy–$\underline{H}$), 2.52 – 2.63 (m, 2H, Cy–$\underline{H}$), 2.70 – 2.83 (m, 4H, Cy–$\underline{H}$), 3.15 (hept, J = 6.8 Hz, 4H, C$\underline{H}$(CH$_3$)$_2$), 5.26 (s, 2H, NCC$\underline{H}$), 6.95 – 7.03 (m, 6H, $_{Dipp}$Ar–$\underline{H}$), 7.10 (s, 4H, $_{TCHP}$Ar–$\underline{H}$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 23.8, 25.2 (CH(C$\underline{H}_3$)$_2$), 26.8, 27.0, 27.4 (Cy–$\underline{C}$), 27.6 (C$\underline{H}$(CH$_3$)$_2$), 28.0, 28.4, 29.4 (Cy–$\underline{C}$), 33.1, 33.2 (C(C$\underline{H}_3$)$_3$), 34.0, 35.3, 35.5, 39.7, 43.7 (Cy–$\underline{C}$), 43.7 (C(CH$_3$)$_3$), 44.9 (Cy–$\underline{C}$), 94.7 (NC$\underline{C}$H), 122.3, 123.0, 123.4, 124.6, 133.2, 139.6, 140.3, 141.2 ($_{Dipp}$Ar–$\underline{C}$, $_{TCHP}$Ar–$\underline{C}$), 174.2, 174.6 (N$\underline{C}$).

I.R. (Nujol, cm^{-1}): 1654 (w), 1609 (m), 1598 (m), 1056 (m), 1028 (m), 955 (m), 877 (m), 819 (m), 802 (m), 780 (m), 691 (m), 648 (m).

A reproducible microanalysis could not be obtained due to the extreme air and moisture sensitivity of the complex, and the inability to remove traces of $^{TCHP/Dip}$NacnacH after repeated recrystallizations.

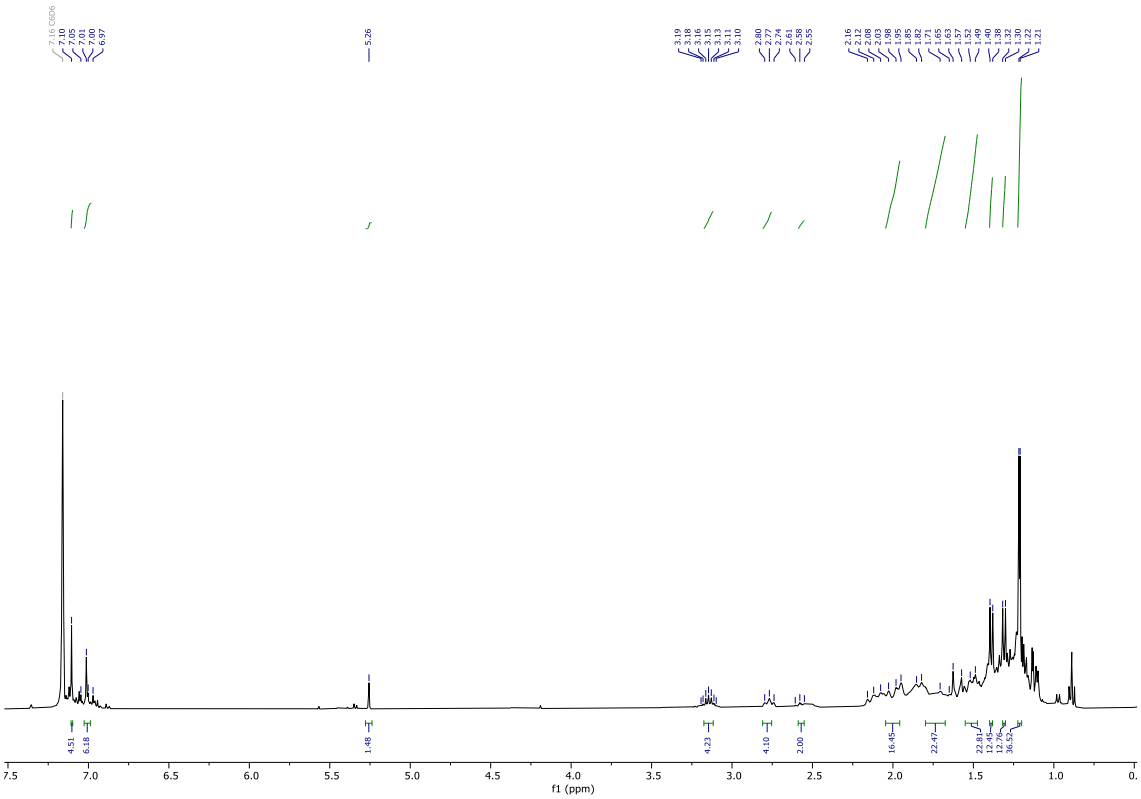


Figure S79: ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of **7**.

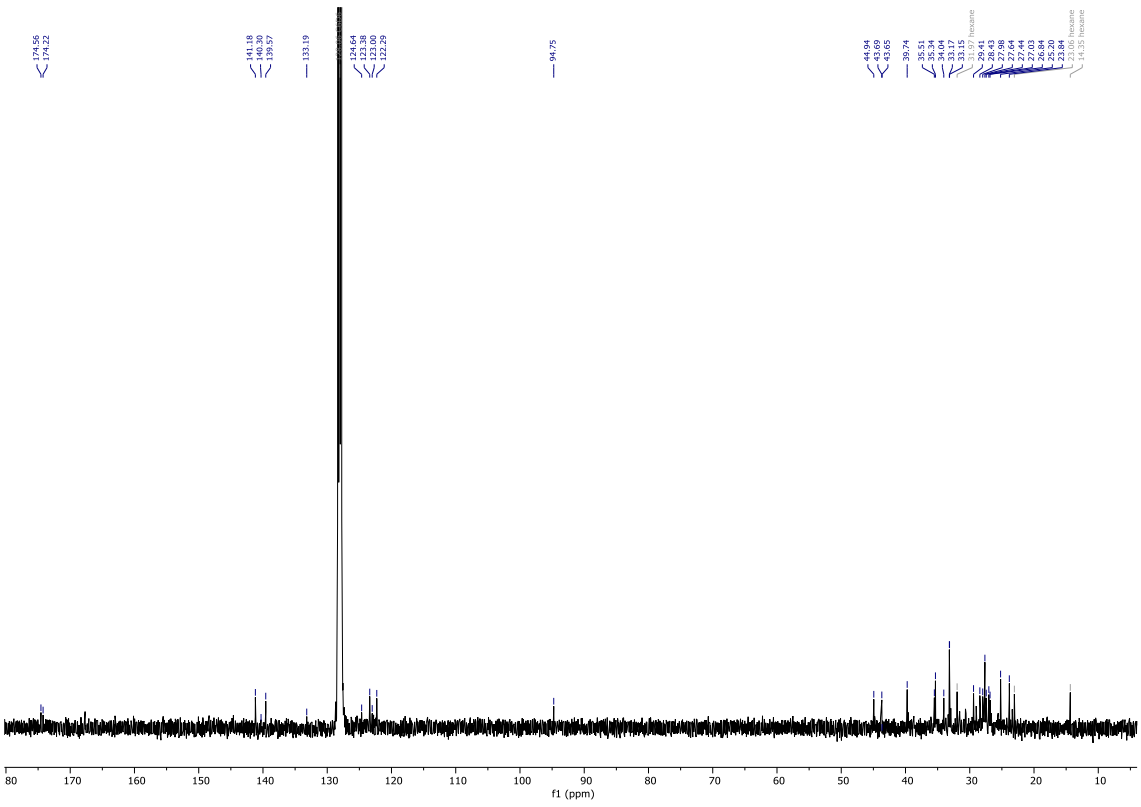


Figure S80: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, C_6D_6) of **7**.

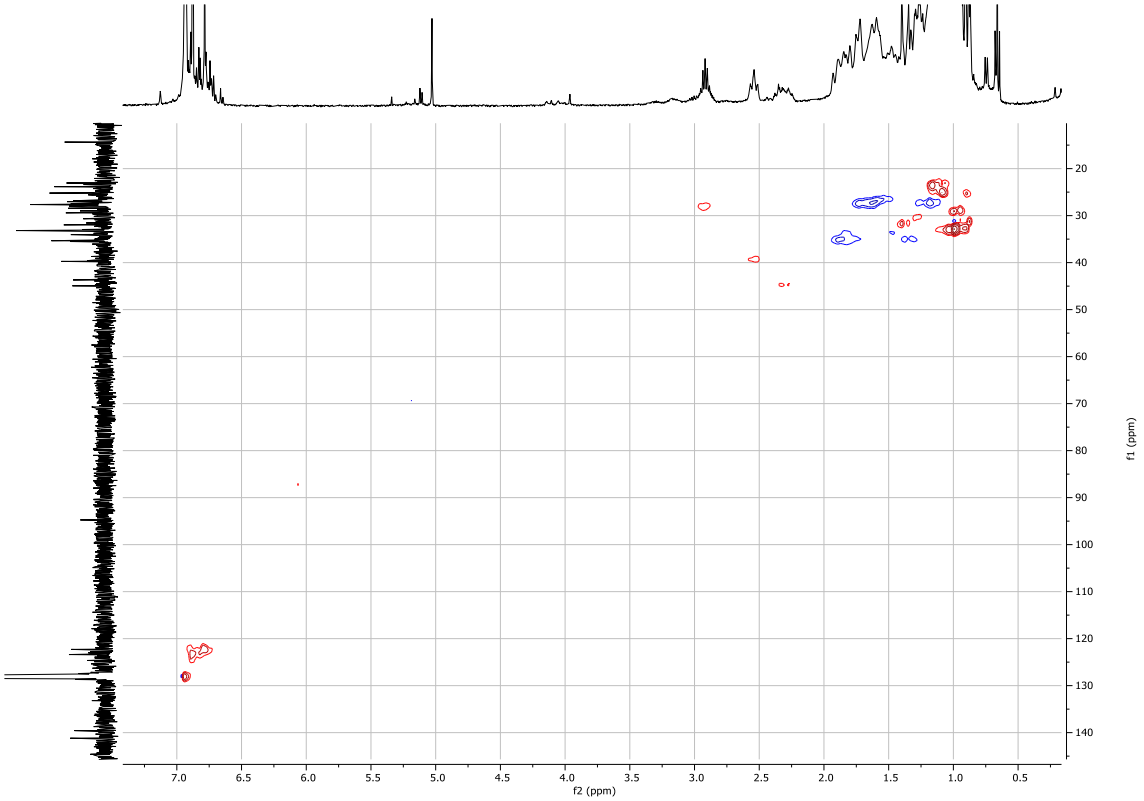


Figure S81: HSQC NMR spectrum (298 K, C_6D_6) of **7**.

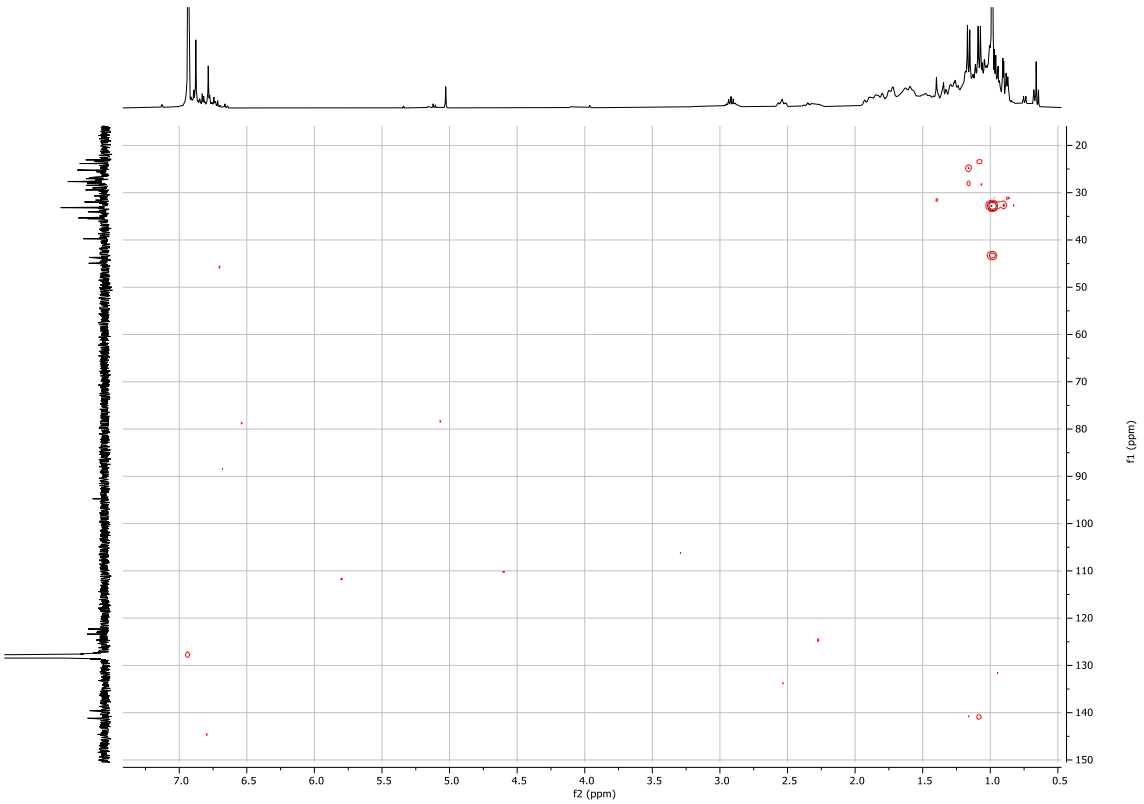
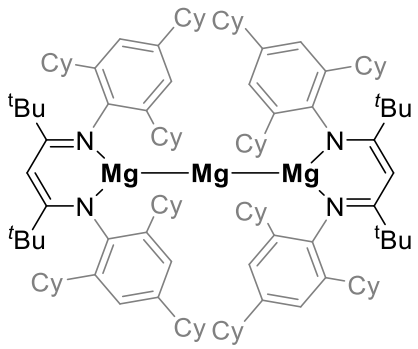


Figure S82: HMBC NMR spectrum (298 K, C_6D_6) of **7**.

Preparation of [{(^TCHP^Nacnac)Mg}$_2$Mg] 8



Compound **1** (2.00 g, 2.05 mmol), MgI_2 (284 mg, 1.03 mmol) and Na/NaCl (5% w/w, 6.89 g, 14.98 mmol) were charged to a 50 mL ampule and methylcyclohexane (20 mL) was added. The reaction mixture was allowed to stir for 18 hours at room temperature. The volatiles were removed *in vacuo*, the residue extracted with hexane (50 mL), then filtered to give a dark red solution. The filtrate was concentrated to *ca.* 5 mL and stored at room temperature for 18 hours, resulting in the formation of dark red block-shaped crystals. **Yield**: 1.34 g, 76 %.

M.p.: 120–122 °C (dec).

^{1}H NMR (400 MHz, C_6D_6): δ 1.20 (s, 36H, C(C$\underline{H}_3$)$_3$), 1.32 – 1.73 (m, 62H, Cy–$\underline{H}$), 1.77 – 2.22 (m, 58H, Cy–$\underline{H}$), 2.62 – 2.72 (m, 4H, Cy–$\underline{H}$), 2.81 – 2.92 (m, 8H, Cy–$\underline{H}$), 5.45 (s, 2H, NCC$\underline{H}$), 7.06 (s, 8H, $_{TCHP}$Ar–$\underline{H}$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 26.9, 27.0, 27.7, 27.8 (Cy–$\underline{C}$), 33.2 (C($\underline{C}$H$_3$)$_3$), 34.3, 35.4, 35.7, 39.9 (Cy–$\underline{C}$), 43.9 ($\underline{C}$(CH$_3$)$_3$), 44.7 (Cy–$\underline{C}$), 95.8 (NC$\underline{C}$H), 122.2, 140.0, 142.9, 144.7 ($_{TCHP}$Ar–$\underline{C}$), 176.1 (N$\underline{C}$).

I.R. (Nujol, cm^{-1}): 1510 (m), 1025 (w), 997 (w), 862 (m), 787 (w), 708 (w), 658 (w).

Anal. calcd. for $C_{118}H_{178}Mg_3N_4$: C 82.14 %, H 10.40 %, N 3.25 %; found: C 81.54 %, H 11.15 %, N 2.78 %.

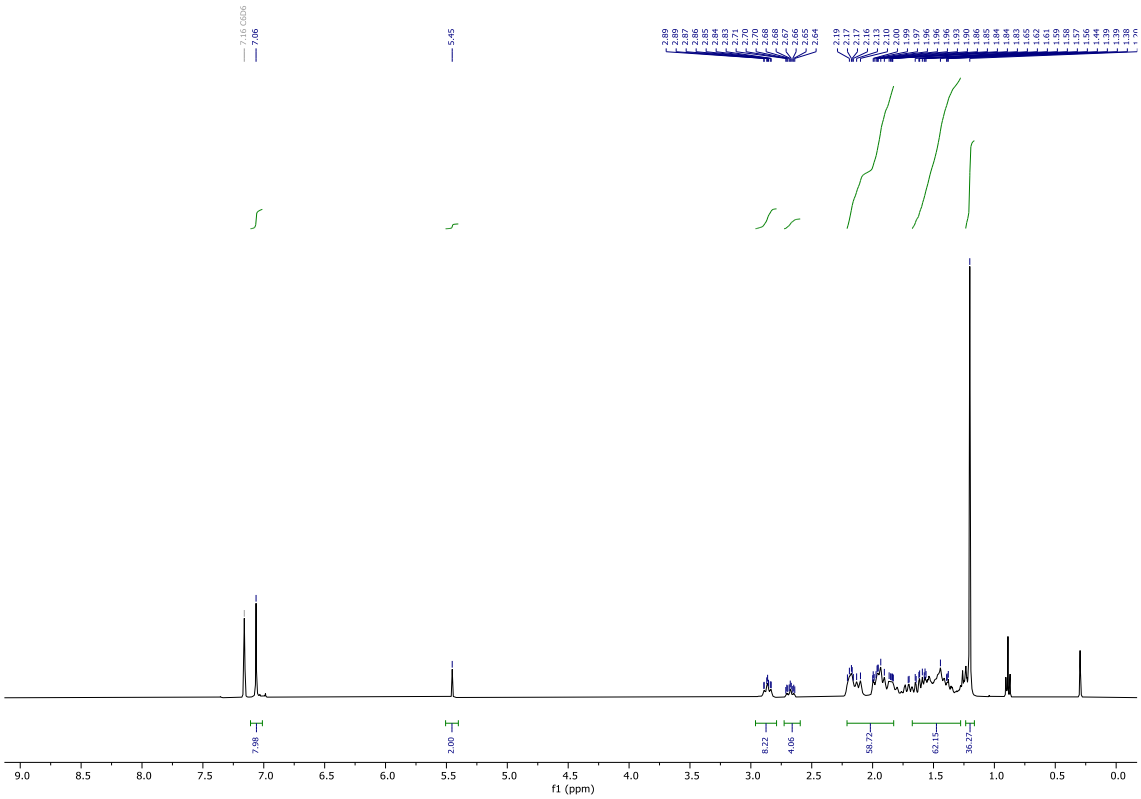


Figure S83: ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of **8**.

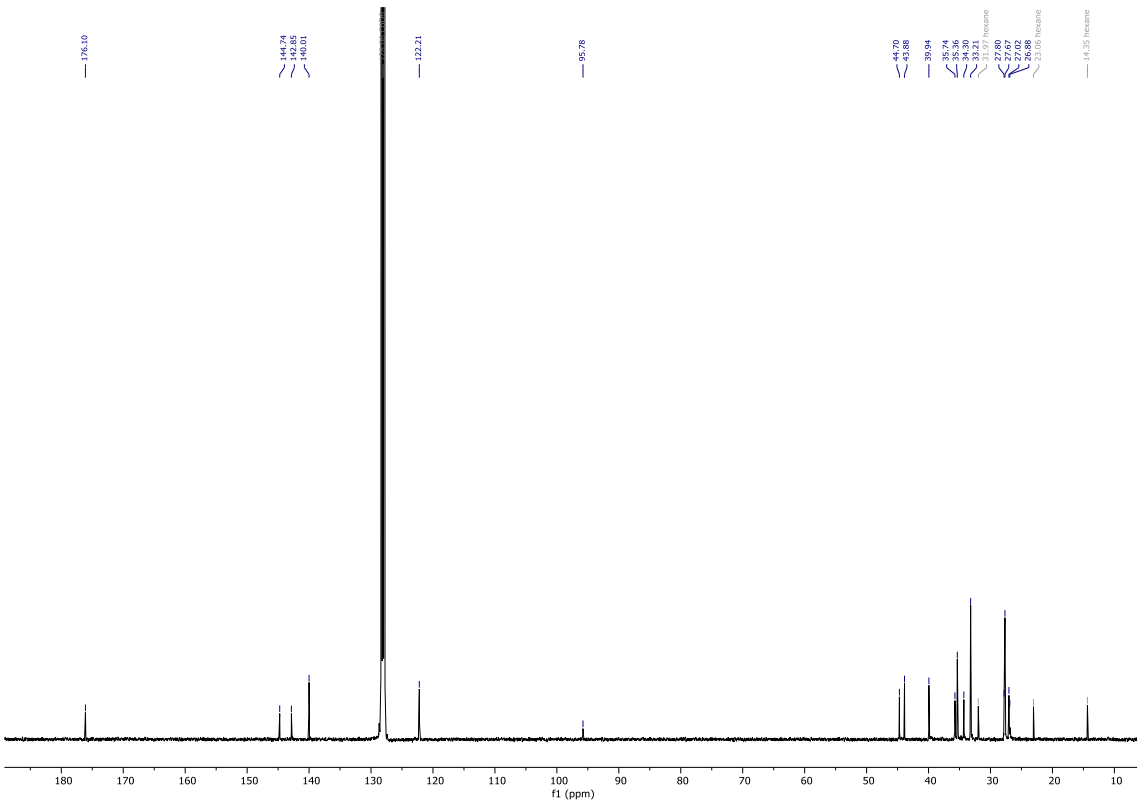


Figure S84: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, C_6D_6) of **8**.

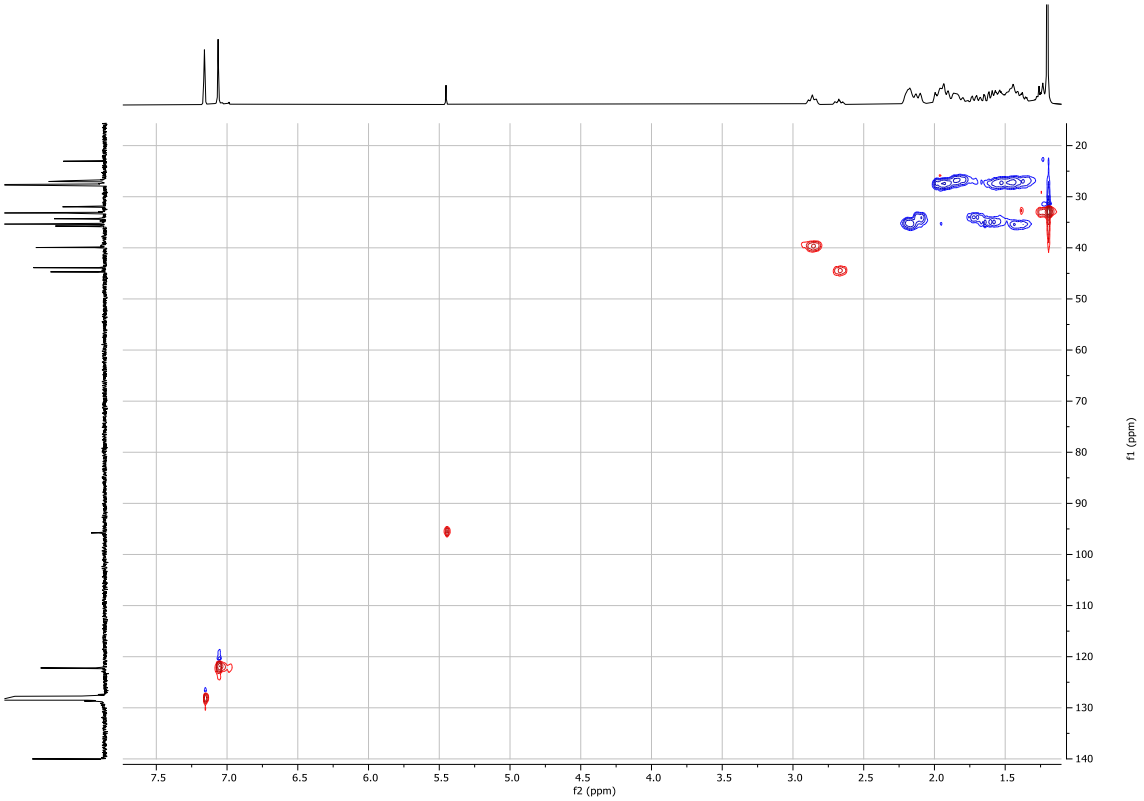


Figure S85: HSQC NMR spectrum (298 K, C_6D_6) of **8**.

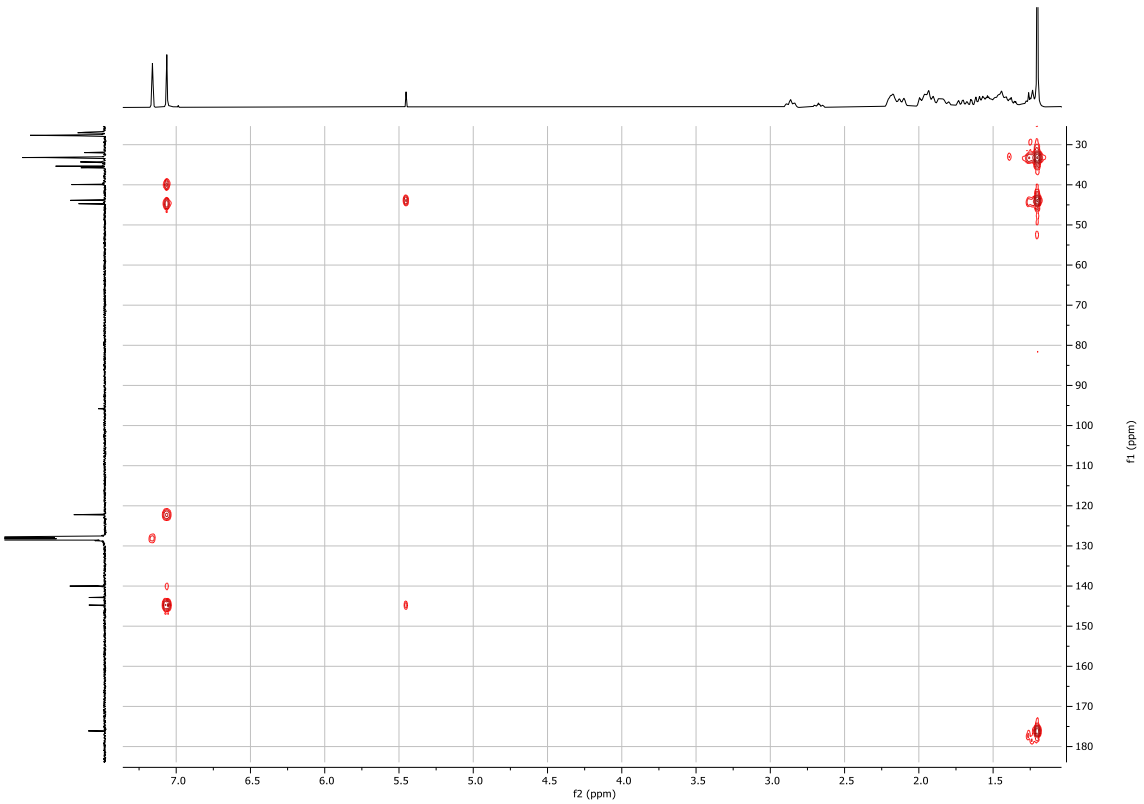
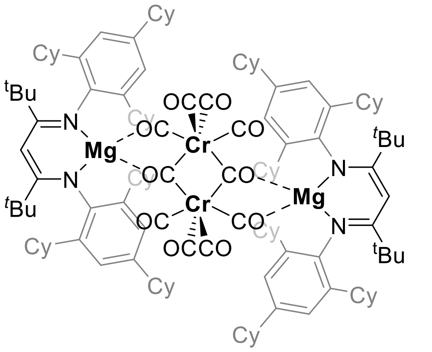


Figure S86: HMBC NMR spectrum (298 K, C_6D_6) of **8**.

Preparation of [{(^{TCHP}Nacnac)Mg}$_2${μ-$Cr_2(CO)_{10}$}] 9



Compound **6** (300 mg, 0.17 mmol) and $Cr(CO)_6$ (75 mg, 0.34 mmol) were charged to a 50 mL ampule and benzene (10 mL) was added. The reaction mixture was stirred at room temperature for 18 hours. The volatiles were removed *in vacuo*, the residue extracted with hexane (10 mL), and filtered *via* cannula. The filtrate was concentrated (~1 mL) and allowed to sit at room temperature for 18 hours resulting in the deposition of red crystals. **Yield**: 75 mg, 21%.

Note: The negligible solubility of the complex in both aliphatic and arene solvents, once crystallised, prevented the collection of meaningful NMR spectroscopic data. Attempts to dissolve the complex in ethereal solvents resulted in decomposition.

M.p.: 126-128 °C (dec).

I.R. (Nujol, cm^{-1}): 2000 (w), 1985 (w), 1955 (s), 1936 (s), 1851 (w), 1731 (s), 1661 (w), 1532 (w), 1500 (s), 1019 (m), 997 (m), 949 (w), 889 (w), 874 (w), 854 (m), 839 (w), 788 (m), 708 (w), 658 (s).

Anal. calcd. for $C_{128}H_{178}Mg_2Cr_2N_4O_{10}$: C 73.72 %, H 8.60%, N 2.69 %; found: C 73.50 %, H 9.10 %, N 2.37 %.

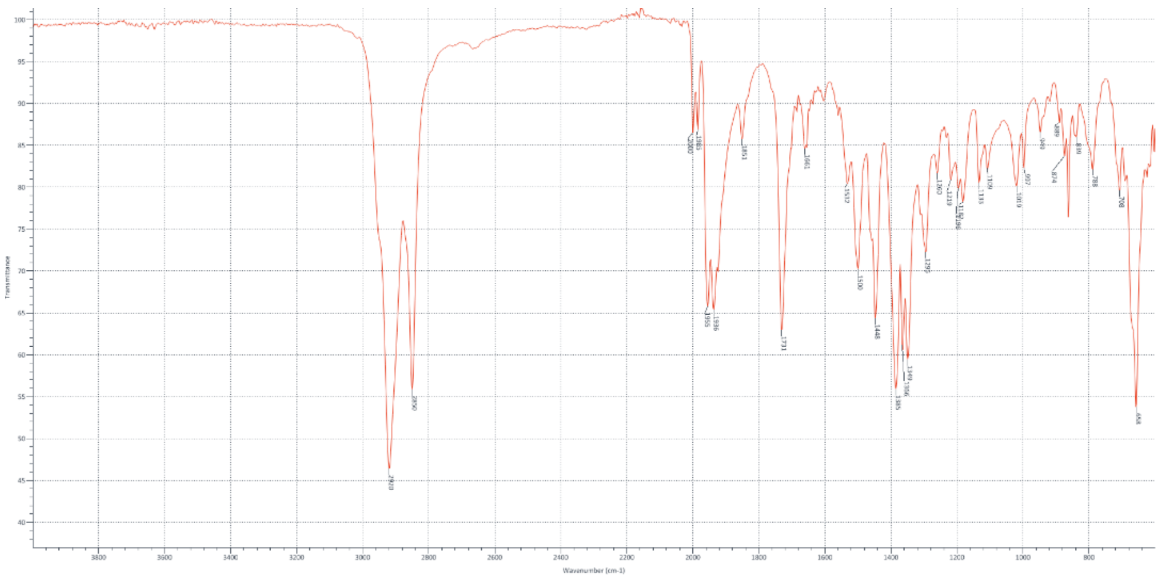
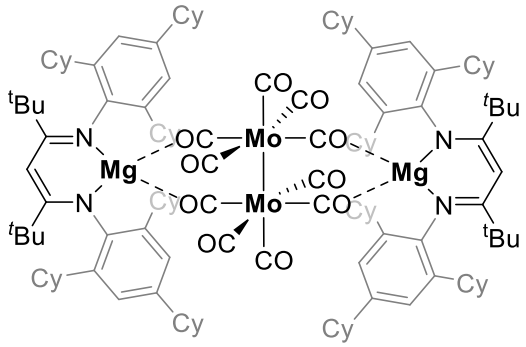


Figure S87: FTIR spectrum (Nujol mull) of **9**.

Preparation of [{(^{TCHP}Nacnac)Mg}$_2${μ-Mo$_2$(CO)$_{10}$}] 10



Compound **6** (300 mg, 0.17 mmol) and $Mo(CO)_6$ (90 mg, 0.34 mmol) were charged to a 50 mL ampule and benzene (10 mL) was added. The reaction mixture was stirred at room temperature for 18 hours. The volatiles were removed *in vacuo*, the residue extracted with hexane (10 mL), and filtered *via* cannula. The filtrate was concentrated (~1 mL) and allowed to sit at room temperature for 18 hours resulting in the formation of red crystals. **Yield**: 50 mg, 13%.

Note: The negligible solubility of the complex in both aliphatic and arene solvents, once crystallised, prevented the collection of meaningful NMR spectroscopic data. Attempts to dissolve the complex in ethereal solvents resulted in decomposition.

M.p.: 134–136 °C (dec).

I.R. (Nujol, cm^{-1}): 1983 (s), 1931 (s), 1892 (s), 1702 (w), 1608 (w), 1073 (w), 1019 (w), 999 (w), 926 (m), 861 (s), 807 (w), 790 (m), 706 (w).

Anal. Calcd. for $C_{128}H_{178}Mg_2Mo_2N_4O_{10}$: C 70.74 %, H 8.26%, N 2.58 %; found: C 69.30 %, H 8.54 %, N 2.57 %.

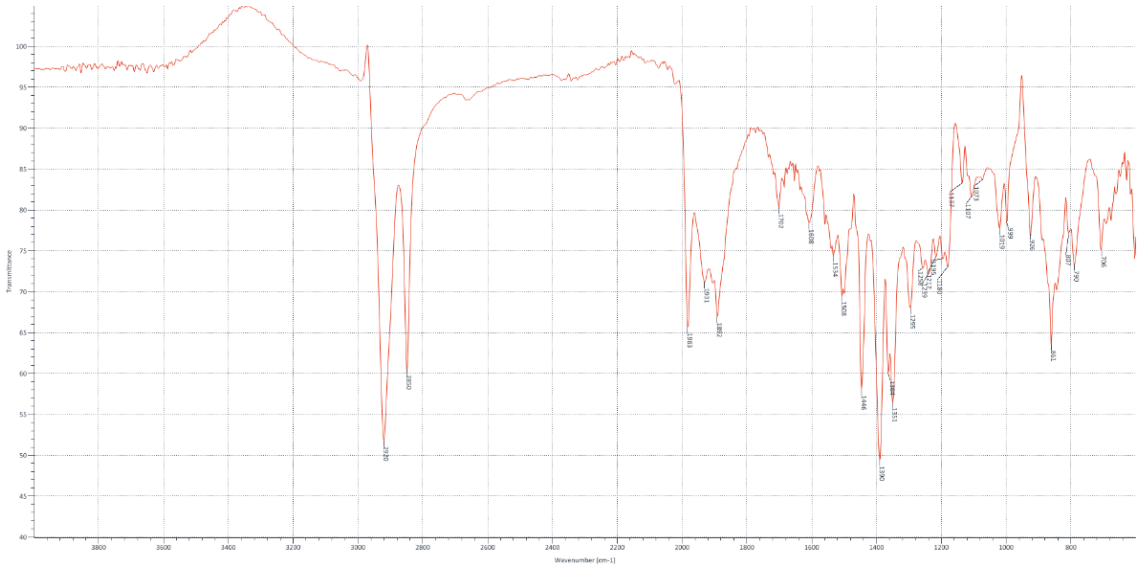
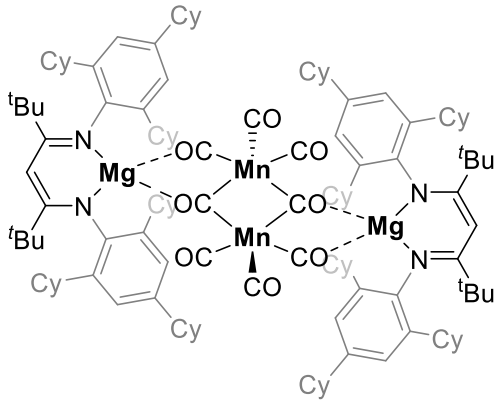


Figure S88: FTIR spectrum (Nujol mull) of **10**.

Preparation of [{(^{TCHP}Nacnac)Mg}$_2${μ-Mn$_2$(CO)$_8$}] 11



Method A:

Compound **6** (300 mg, 0.17 mmol) and $Mn(CO)_5Br$ (94 mg, 0.34 mmol) were charged to a 50 mL ampule and benzene (10 mL) was added. The reaction mixture was stirred at room temperature for 18 hours. The volatiles were removed *in vacuo*, the residue extracted with hexane (10 mL), and filtered *via* cannula. The filtrate was concentrated (~1 mL) and allowed to sit at room temperature for 18 hours, resulting in the formation of brown crystals. **Yield**: 50 mg, 14%.

Method B:

Compound **6** (300 mg, 0.17 mmol) and $Mn_2(CO)_{10}$ (66 mg, 0.17 mmol) were charged to a 50 mL ampule and benzene (10 mL) was added. The reaction mixture was stirred at room temperature for 18 hours. The volatiles were removed *in vacuo*, the residue extracted with hexane (10 mL), and filtered *via* cannula. The filtrate was concentrated (~1 mL) and allowed to sit at room temperature for 18 hours, resulting in the formation of brown crystals. **Yield**: 78 mg, 22%.

Note: The negligible solubility of the complex in both aliphatic and arene solvents, once crystallised, prevented the collection of meaningful NMR spectroscopic data. Attempts to dissolve the complex in ethereal solvents resulted in decomposition.

M.p.: 181–182 °C (dec).

I.R. (Nujol, cm^{-1}): 1981 (s), 1929 (s), 1729 (m), 1608 (m), 1019 (m), 997 (w), 950 (w), 889 (w), 861 (m), 792 (w), 662 (s).

Anal. calcd. for $C_{126}H_{178}Mg_2Mn_2N_4O_8$: C 74.36 %, H 8.82 %, N 2.75 %; found: C 74.23 %, H 9.22 %, N 2.39 %.

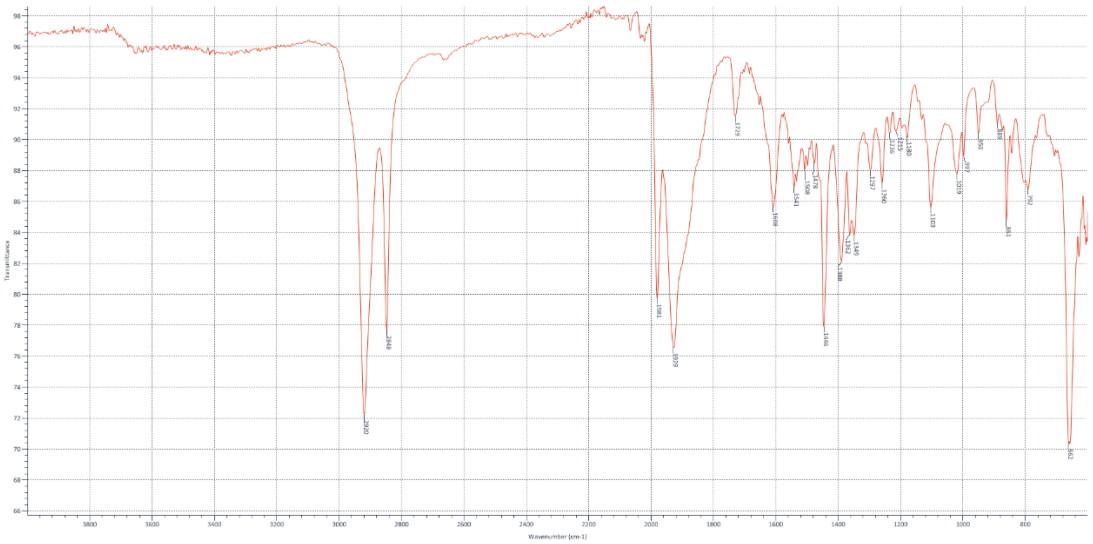
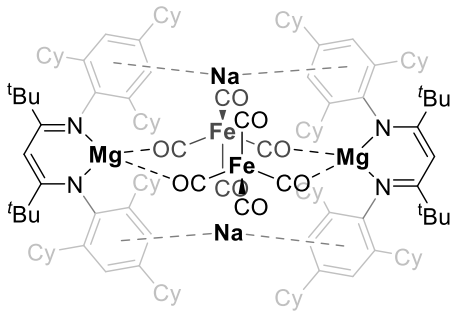


Figure S89: FTIR spectrum (Nujol mull) of **11**.

Preparation of [{(^TCHP^Nacnac)Mg}Na{Fe(CO)$_4$}]$_2$ 12



Compound **6** (300 mg, 0.17 mmol) and Fe(CO)$_5$ (67 mg, 46 µL, 0.34 mmol) were charged to a 50 mL ampule and benzene (10 mL) was added. The reaction mixture was stirred at room temperature for 18 hours. The volatiles were removed *in vacuo*, the residue extracted with hexane (10 mL), and filtered *via* cannula. The filtrate was concentrated (~1 mL) and allowed to sit at room temperature for 18 hours, resulting in the formation of yellow crystals. **Yield**: 120 mg, 34%.

Note: The negligible solubility of the complex in both aliphatic and arene solvents, once crystallised, prevented the collection of meaningful NMR spectroscopic data. Attempts to dissolve the complex in ethereal solvents resulted in decomposition.

M.p.: 144–147 °C (dec).

I.R. (Nujol, cm^{-1}): 2018 (m), 1992 (m), 1934 (m), 1784 (w), 1608 (m), 1103 (m), 1019 (m), 999 (w), 949 (w), 919 (w), 891 (w), 861 (m), 792 (m), 706 (w), 690 (w), 641 (w), 611 (w).

Anal. calcd. for $C_{126}H_{178}Mg_2Fe_2N_4O_8Na_2$: C 72.65 %, H 8.61 %, N 2.69 %; found: C 71.29 %, H 8.89 %, N 2.40 %.

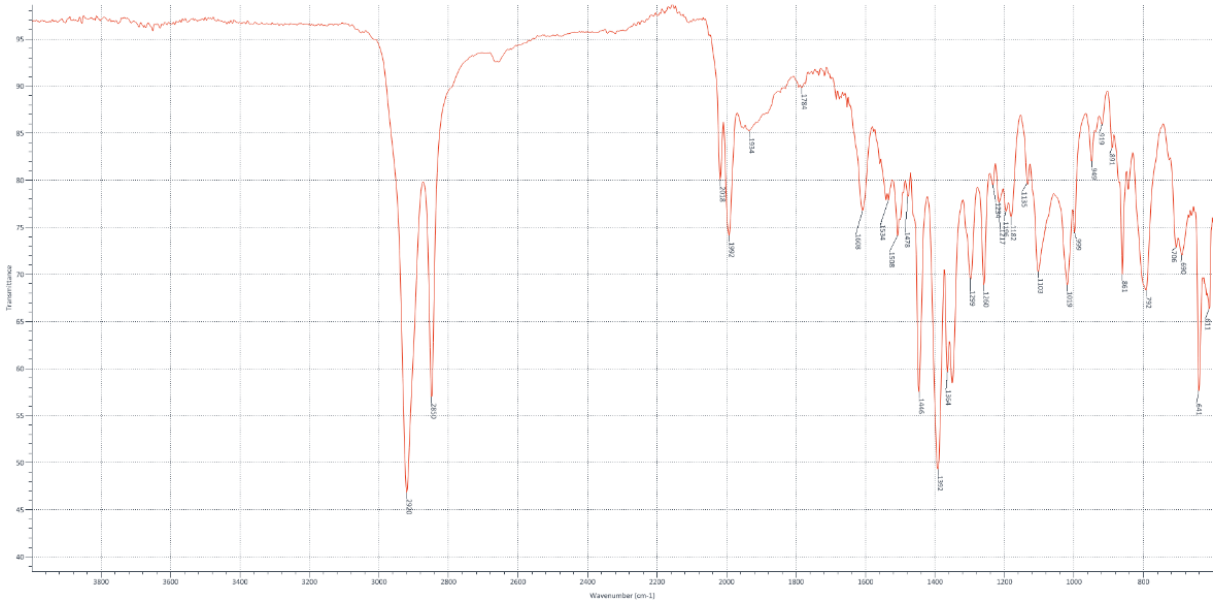


Figure S90: FTIR spectrum (Nujol mull) of **12**.

2. 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) radiation, or the MX1/MX2 beamlines of the Australian Synchrotron (λ = 0.71090 Å).[S5],[S6] The software package Blu-Ice[S7] was used for synchrotron data acquisition, while the program XDS[S8] 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)[S9] 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	(TCHP)NC(Cl)Bu^t	(TCHP)NC(Me)Bu^t	^{DCHP}NacnacH
Empirical formula	C_{29} H_{44} Cl N	C_{30} H_{47} N	C_{47} H_{70} N_2
Formula weight	442.1	421.68	663.05
Temperature	123.0(2) K	100(2) K	123.0(1) K
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$
Unit cell dimensions	a = 10.64740(10) Å α = 90°	a = 6.2000(12) Å α = 90°	a = 20.1744(2) Å α = 90°
	b = 11.33190(10) Å β = 93.0700(10)°	b = 16.190(3) Å β = 91.56(3)°	b = 10.27740(10) Å β = 113.8260(10)°
	c = 21.9748(3) Å γ = 90°	c = 26.470(5) Å γ = 90°	c = 21.3777(2) Å γ = 90°
Volume	2647.57(5) Å^3	2656.0(9) Å^3	4054.71(7) Å^3
Z	4	4	4
Density (calculated)	1.109 Mg/m^3	1.055 Mg/m^3	1.086 Mg/m^3
Absorption coefficient	1.367 mm^{-1}	0.059 mm^{-1}	0.455 mm^{-1}
F(000)	968	936	1464
Crystal size	0.240 x 0.130 x 0.080 mm^3	0.120 x 0.080 x 0.060 mm^3	0.650 x 0.410 x 0.290 mm^3
Theta range for data collection	4.029 to 79.743°	1.475 to 26.370°	4.175 to 79.937°
Index ranges	-13<=*h*<=12, -14<=*k*<=14, -17<=*l*<=27	-7<=*h*<=7, -20<=*k*<=19, -33<=*l*<=33	-23<=*h*<=25, -8<=*k*<=12, -26<=*l*<=27
Reflections collected	22636	62956	35972
Independent reflections	5653 [R(int) = 0.0291]	5385 [R(int) = 0.0445]	8644 [R(int) = 0.0236]
Completeness to theta = 67.684 °	100.00%	99.90%	99.90%
Absorption correction	Gaussian	Semi-empirical from equivalents	Gaussian
Max. and min. transmission	0.745 and 0.183	Value not reported by XDS	1.000 and 0.135
Data / restraints / parameters	5653 / 0 / 283	5385 / 0 / 285	8644 / 0 / 448
Goodness-of-fit on F^2	1.056	1.073	1.027
Final R indices [I > 2sigma(I)]	R_1 = 0.0411, wR_2 = 0.1106	R_1 = 0.0387, wR_2 = 0.0988	R_1 = 0.0447, wR_2 = 0.1191
R indices (all data)	R_1 = 0.0432, wR_2 = 0.1124	R_1 = 0.0446, wR_2 = 0.1045	R_1 = 0.0474, wR_2 = 0.1216
Largest diff. peak and hole	0.486 and -0.251 e.Å^{-3}	0.228 and -0.177 e.Å^{-3}	0.309 and -0.221 e.Å^{-3}
CCDC Number	2534925	2534941	2534934

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

Compound	^{TCHP}NacnacH	$^{TCHP/Dip}$NacnacH	(^{DCHP}Nacnac)Li(OEt$_2$)
Empirical formula	$C_{59}H_{90}N_2$	$C_{47}H_{70}N_2$	$C_{51}H_{79}LiN_2O$
Formula weight	827.32	663.05	743.1
Temperature	100(2) K	100(2) K	122.97(12) K
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$C2/c$
Unit cell dimensions	a = 21.780(4) Å α = 90°	a = 20.1744(2) Å α = 90°	a = 18.12080(10) Å α = 90°
	b = 24.420(5) Å β = 90.77(3)°	b = 10.2774(1) Å β = 113.826(1)	b = 15.59790(10) Å β = 94.2790(10)°
	c = 9.7100(19) Å γ = 90°	c = 21.3777(2) Å γ = 90°	c = 16.06980(10) Å γ = 90°
Volume	5164.0(18) Å^3	4054.71(7) Å^3	4529.41(5) Å^3
Z	4	4	4
Density (calculated)	1.064 Mg/m^3	1.086 Mg/m^3	1.090 Mg/m^3
Absorption coefficient	0.060 mm^{-1}	0.455 mm^{-1}	0.467 mm^{-1}
F(000)	1832	1464	1640
Crystal size	0.120 x 0.110 x 0.040 mm^3	0.650 x 0.410 x 0.290 mm^3	0.280 x 0.190 x 0.150 mm^3
Theta range for data collection	0.935 to 26.371°	4.175 to 79.937°	3.744 to 80.268°
Index ranges	-27<=*h*<=27, -30<=*k*<=30, -12<=*l*<=12	-23<=*h*<=25, -8<=*k*<=12, -26<=*l*<=27	-23<=*h*<=20, -19<=*k*<=18, -20<=*l*<=19
Reflections collected	121840	35972	47235
Independent reflections	10480 [R(int) = 0.0495]	8644 [R(int) = 0.0236]	4921 [R(int) = 0.0300]
Completeness to theta = 67.684 °	99.40%	99.9%	100.00%
Absorption correction	Semi-empirical from equivalents	Gaussian	Gaussian
Max. and min. transmission	Value not reported by XDS	1.000 and 0.543	1.000 and 0.416
Data / restraints / parameters	10480 / 0 / 556	8644 / 0 / 448	4921 / 0 / 256
Goodness-of-fit on F^2	1.069	1.027	1.068
Final R indices [I > 2sigma(I)]	R_1 = 0.0721, wR_2 = 0.2157	R_1 = 0.0447, wR_2 = 0.1191	R_1 = 0.0368, wR_2 = 0.0945
R indices (all data)	R_1 = 0.0841, wR_2 = 0.2282	R_1 = 0.0474, wR_2 = 0.1216	R_1 = 0.0390, wR_2 = 0.0962
Largest diff. peak and hole	0.526 and -0.415 e.Å^{-3}	0.309 and -0.221 e.Å^{-3}	0.283 and -0.181 e.Å^{-3}
CCDC Number	2534939	2534934	2534927

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

Compound	**1**	**2**	**3/3-Me**
Empirical formula	C_{59} H_{89} I Mg N_2	$C_{65.5}$ H_{105} Li N_2 O	$C_{47.5}$ $H_{70.5}$ $I_{0.5}$ Mg N_2
Formula weight	977.53	943.45	757.31
Temperature	100(2) K	123.0(1) K	123.0(1) K
Crystal system	Trigonal	Monoclinic	Monoclinic
Space group	$P3_221$	$P2_1/c$	$P2_1/n$
Unit cell dimensions	a = 10.9500(15) Å α = 90°	a = 19.46810(10) Å α = 90°	a = 10.1795(2) Å α = 90°
	b = 10.9500(15) Å β = 90°	b = 15.83380(10) Å β = 105.7560(10)°	b = 23.0996(4) Å β = 99.324(2)°
	c = 39.160(8) Å γ = 120°	c = 20.11950(10) Å γ = 90°	c = 18.9134(3) Å γ = 90°
Volume	4066.3(14) Å^3	5968.89(6) Å^3	4388.58(14) Å^3
Z	3	4	4
Density (calculated)	1.198 Mg/m^3	1.050 Mg/m^3	1.146 Mg/m^3
Absorption coefficient	0.640 mm^{-1}	0.443 mm^{-1}	3.338 mm^{-1}
F(000)	1566	2092	1632
Crystal size	0.210 x 0.130 x 0.040 mm^3	0.440 x 0.220 x 0.090 mm^3	0.180 x 0.150 x 0.060 mm^3
Theta range for data collection	1.560 to 26.371°	3.606 to 80.403°	3.827 to 80.854°
Index ranges	-13<=*h*<=13, -13<=*k*<=13, -48<=*l*<=48	-24<=*h*<=24, -20<=*k*<=20, -25<=*l*<=21	-12<=*h*<=12, -29<=*k*<=20, -23<=*l*<=23
Reflections collected	103219	125181	47139
Independent reflections	5576 [R(int) = 0.0315]	12940 [R(int) = 0.0363]	9414 [R(int) = 0.0540]
Completeness to theta = 67.684 °	100.00%	99.80%	100.00%
Absorption correction	Semi-empirical from equivalents	Gaussian	Gaussian
Max. and min. transmission	Value not reported by XDS	1.000 and 0.343	0.771 and 0.140
Data / restraints / parameters	5576 / 0 / 291	12940 / 164 / 710	9414 / 7 / 476
Goodness-of-fit on F^2	1.076	1.066	1.051
Final R indices [I > 2sigma(I)]	R_1 = 0.0223, wR_2 = 0.0642	R_1 = 0.0475, wR_2 = 0.1297	R_1 = 0.0450, wR_2 = 0.1170
R indices (all data)	R_1 = 0.0224, wR_2 = 0.0643	R_1 = 0.0518, wR_2 = 0.1343	R_1 = 0.0570, wR_2 = 0.1268
Largest diff. peak and hole	0.308 and -0.357 e.Å^{-3}	0.676 and -0.393 e.Å^{-3}	0.453 and -0.467 e.Å^{-3}
CCDC Number	2534940	2534936	2534926

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

Compound	5	6	7
Empirical formula	C_{50} H_{74} I Mg N_2	C_{124} H_{184} Mg_2 N_4 Na_2	C_{94} H_{142} Mg_3 N_4
Formula weight	854.32	1825.34	1401.04
Temperature	123.0(1) K	100(2) K	100(2) K
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	*P*-1	*P*-1	$P2_1/n$
Unit cell dimensions	a = 12.7396(3) Å α = 92.684(2)°	a = 15.708(3) Å α = 86.06(3)°	a = 10.960(2) Å α = 90°
	b = 14.1682(3) Å β = 107.429(2)°	b = 16.044(3) Å β = 86.00(3)°	b = 19.800(4) Å β = 93.46(3)°
	c = 14.5489(4) Å γ = 109.246(2)°	c = 22.901(5) Å γ = 76.73(3)°	c = 20.060(4) Å γ = 90°
Volume	2334.36(10) $Å^3$	5596(2) $Å^3$	4345.2(15) $Å^3$
Z	2	2	2
Density (calculated)	1.215 Mg/m^3	1.083 Mg/m^3	1.071 Mg/m^3
Absorption coefficient	5.757 mm-1	0.078 mm-1	0.080 mm^{-1}
F(000)	906	2004	1540
Crystal size	0.310 x 0.210 x 0.170 mm^3	0.120 x 0.100 x 0.040 mm^3	0.080 x 0.050 x 0.020 mm^3
Theta range for data collection	3.899 to 79.617°	0.893 to 28.806°	1.446 to 26.371°
Index ranges	-16<=*h*<=16, -18<=*k*<=16, -15<=*l*<=18	-20<=*h*<=21, -21<=*k*<=21, -30<=*l*<=30	-13<=*h*<=13, -24<=*k*<=24, -25<=*l*<=25
Reflections collected	29075	68112	101682
Independent reflections	9690 [R(int) = 0.0541]	19715 [R(int) = 0.0682]	8690 [R(int) = 0.1530]
Completeness to theta = 67.684 °	99.10%	87.80%	98.10%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.56875	Value not reported by XDS	Value not reported by XDS
Data / restraints / parameters	9690 / 0 / 501	19715 / 0 / 1201	8690 / 240 / 522
Goodness-of-fit on F^2	1.103	1.075	0.946
Final R indices [I > 2sigma(I)]	R_1 = 0.0389, wR_2 = 0.1030	R_1 = 0.0916, wR_2 = 0.2593	R_1 = 0.0783, wR_2 = 0.2104
R indices (all data)	R_1 = 0.0424, wR_2 = 0.1050	R_1 = 0.1245, wR_2 = 0.2974	R_1 = 0.2076, wR_2 = 0.2972
Largest diff. peak and hole	0.952 and -0.821 e.$Å^{-3}$	0.917 and -0.492 e.$Å^{-3}$	0.347 and -0.230 e.$Å^{-3}$
CCDC Number	2534933	2534928	2534938

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

Compound	8	9	10
Empirical formula	$C_{130}H_{206}Mg_3N_4$	$C_{138}H_{202}Cr_2Mg_2N_4O_{10}$	$C_{152}H_{234}Mg_2Mo_2N_4O_{10}$
Formula weight	1897.91	2229.64	2517.92
Temperature	100(2) K	100(2) K	100(2) K
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	$P2_1/c$	*P*2/*n*
Unit cell dimensions	a = 28.460(6) Å α = 90°	a = 28.490(6) Å α = 90°	a = 21.490(4) Å α = 90°
	b = 15.350(3) Å β = 112.19(3)°	b = 16.970(3) Å β = 97.79(3)°	b = 13.590(3) Å β = 100.63(3)°
	c = 30.730(6) Å γ = 90°	c = 26.340(5) Å γ = 90°	c = 25.000(5) Å γ = 90°
Volume	12430(5) $Å^3$	12617(4) $Å^3$	7176(3) $Å^3$
Z	4	4	2
Density (calculated)	1.014 Mg/m^3	1.174 Mg/m^3	1.165 Mg/m^3
Absorption coefficient	0.071 mm-1	0.241 mm^{-1}	0.240 mm^{-1}
F(000)	4200	4840	2724
Crystal size	0.080 x 0.050 x 0.020 mm^3	0.110 x 0.090 x 0.030 mm^3	0.110 x 0.100 x 0.020 mm^3
Theta range for data collection	1.535 to 26.371°	0.721 to 26.372°	1.382 to 26.373°
Index ranges	-35<=*h*<=35, -19<=*k*<=19, -38<=*l*<=38	-35<=*h*<=33, -21<=*k*<=21, -32<=*l*<=32	-26<=*h*<=26, -16<=*k*<=16, -31<=*l*<=31
Reflections collected	111398	227507	190732
Independent reflections	12466 [R(int) = 0.0866]	25662 [R(int) = 0.1366]	14647 [R(int) = 0.0570]
Completeness to theta = 67.684 °	99.70%	99.90%	99.80%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	Value not reported by XDS	Value not reported by XDS	Value not reported by XDS
Data / restraints / parameters	12466 / 662 / 720	25662 / 409 / 1383	14647 / 593 / 819
Goodness-of-fit on F^2	0.99	1.028	1.047
Final R indices [I > 2sigma(I)]	R_1 = 0.0759, wR_2 = 0.2144	R_1 = 0.0869, wR_2 = 0.2290	R_1 = 0.0445, wR_2 = 0.1297
R indices (all data)	R_1 = 0.1436, wR_2 = 0.2629	R_1 = 0.1588, wR_2 = 0.2880	R_1 = 0.0486, wR_2 = 0.1338
Largest diff. peak and hole	0.293 and -0.253 e.$Å^{-3}$	0.767 and -0.486 e.$Å^{-3}$	0.794 and -0.370 e.$Å^{-3}$
CCDC Number	2534929	2534937	2534935

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

Compound	**11**		**12**	
Empirical formula	C_{144} H_{220} Mg_2 Mn_2 N_4 O_8		C_{150} H_{234} Fe_2 Mg_2 N_4 Na_2 O_8	
Formula weight	2293.73		2427.7	
Temperature	123.0(1) K		100(2) K	
Crystal system	Monoclinic		Orthorhombic	
Space group	$P2_1$		*Pbcn*	
Unit cell dimensions	a = 12.5782(5) Å	α = 90°	a = 22.520(5) Å	α = 90°
	b = 36.5924(17) Å	β = 93.938(3)°	b = 30.790(6) Å	β = 90°
	c = 14.8905(5) Å	γ = 90°	c = 20.820(4) Å	γ = 90°
Volume	6837.4(5) $Å^3$		14436(5) $Å^3$	
Z	2		4	
Density (calculated)	1.114 Mg/m^3		1.117 Mg/m^3	
Absorption coefficient	2.008 mm^{-1}		0.270 mm^{-1}	
F(000)	2500		5296	
Crystal size	0.280 x 0.210 x 0.190 mm^3		0.210 x 0.100 x 0.090 mm^3	
Theta range for data collection	3.522 to 81.308°		1.120 to 26.372°	
Index ranges	-16<=*h*<=15, -43<=*k*<=46, -14<=*l*<=19		-28<=*h*<=28, -38<=*k*<=38, -25<=*l*<=25	
Reflections collected	75283		338054	
Independent reflections	24636 [R(int) = 0.1442]		14741 [R(int) = 0.1215]	
Completeness to theta = 67.684 °	99.90%		99.80%	
Absorption correction	Semi-empirical from equivalents		Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.52544		Value not reported by XDS	
Data / restraints / parameters	24636 / 1841 / 1401		14741 / 266 / 711	
Goodness-of-fit on F^2	1.02		1.028	
Final R indices [I > 2sigma(I)]	R_1 = 0.1041, wR_2 = 0.2556		R_1 = 0.0605, wR_2 = 0.1596	
R indices (all data)	R_1 = 0.1571, wR_2 = 0.2940		R_1 = 0.0941, wR_2 = 0.1795	
Largest diff. peak and hole	1.075 and -0.523 e.$Å^{-3}$		0.668 and -0.400 e.$Å^{-3}$	
CCDC Number	2534930		2534932	

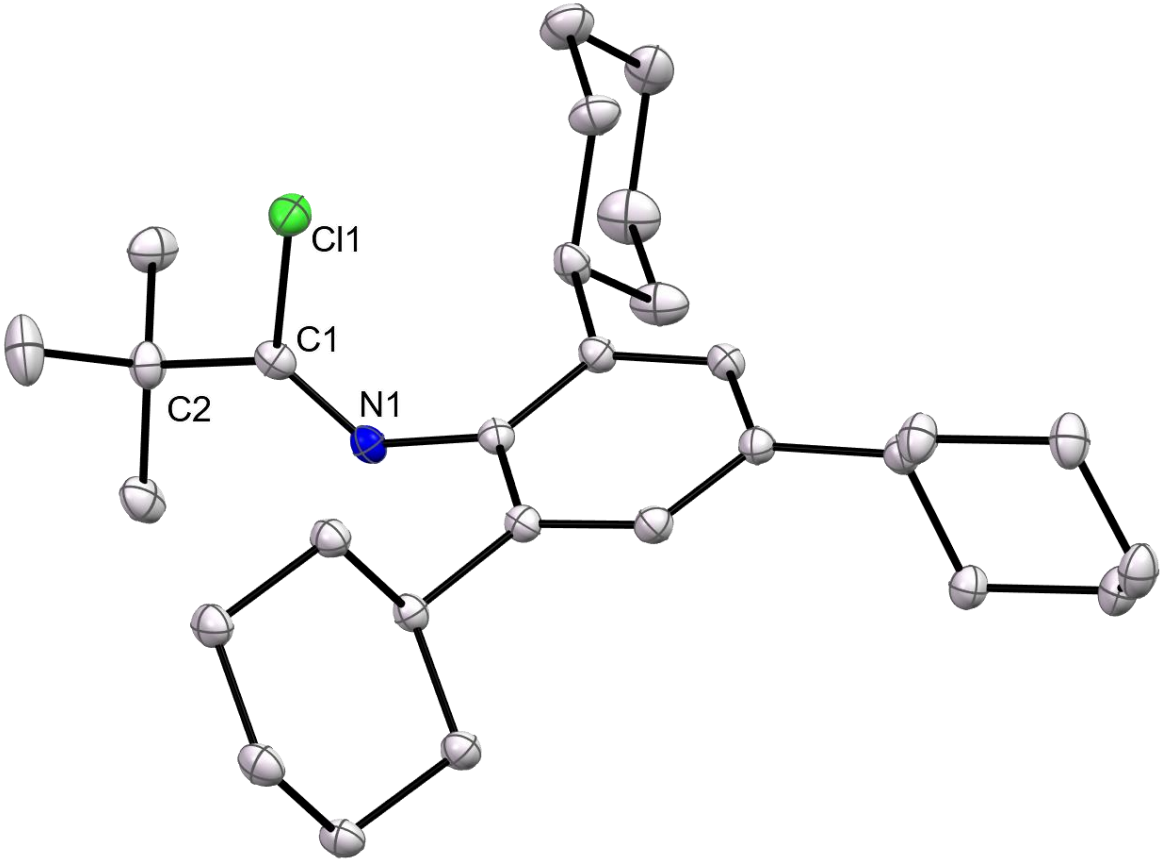


Figure S91: Molecular structure of (TCHP)NC(Cl)Bu^t (thermal ellipsoids shown at 30% probability; hydrogen atoms omitted).

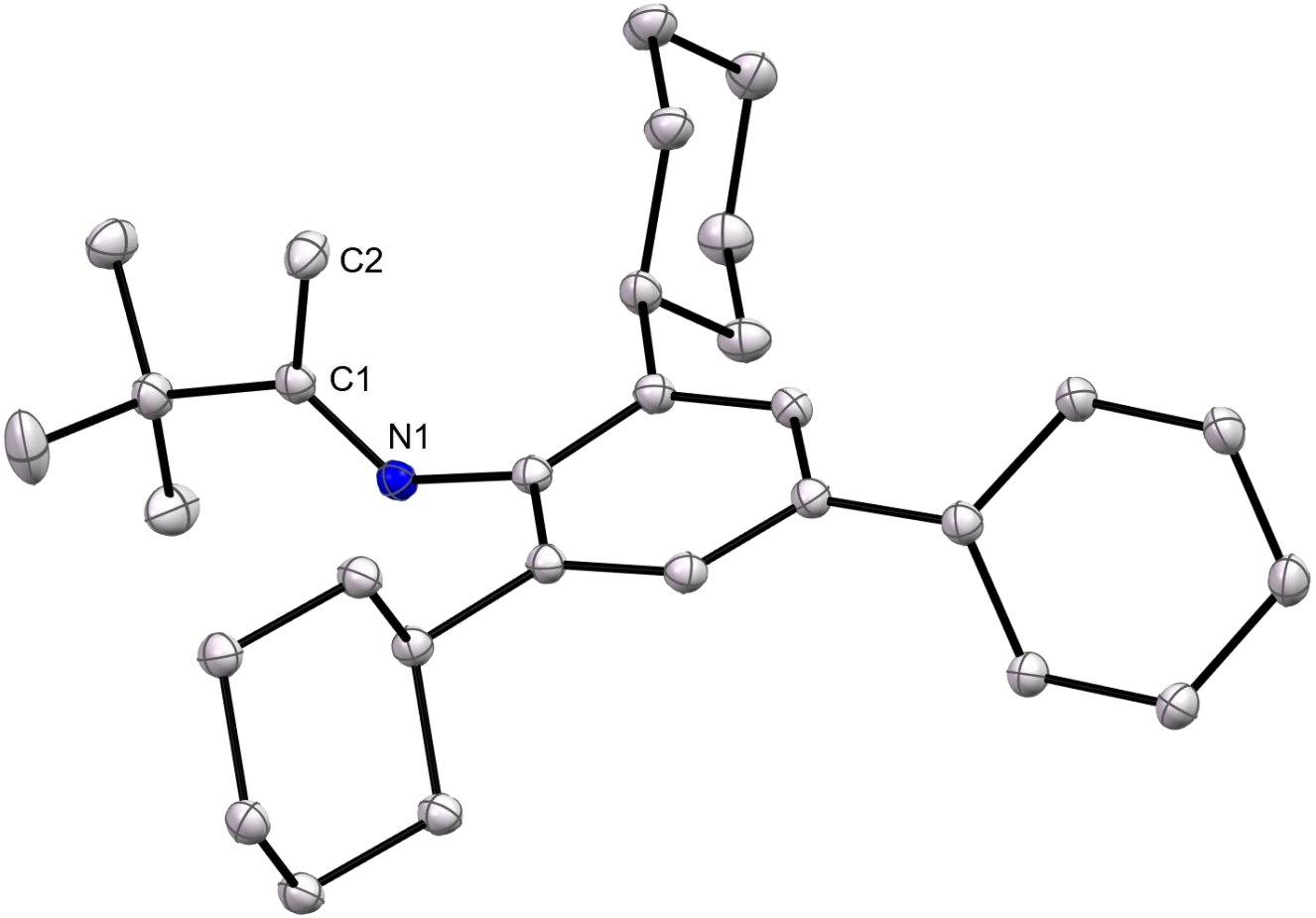


Figure S92: Molecular structure of (TCHP)NC(Me)Bu^t (thermal ellipsoids shown at 30% probability; hydrogen atoms omitted).

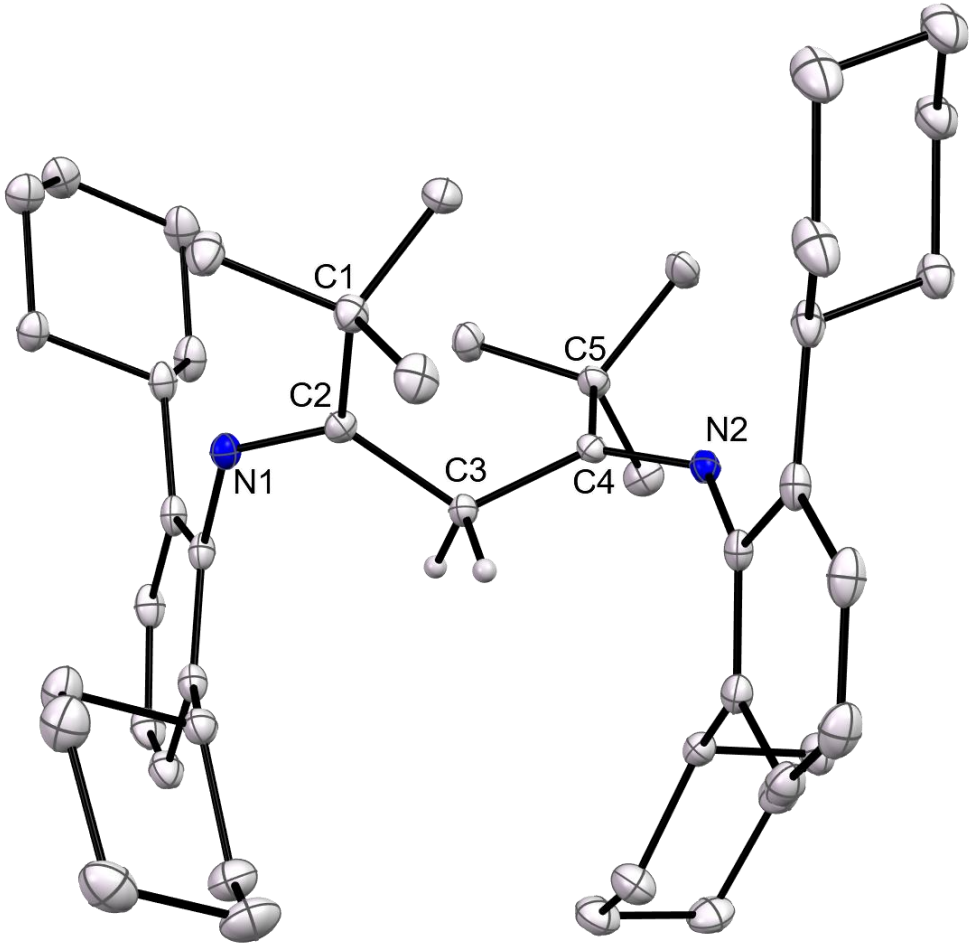


Figure S93: Molecular structure of the bis(imine) tautomer of ^{DCHP}NacnacH (thermal ellipsoids shown at 30% probability; hydrogen atoms, except backbone methylene protons, omitted).

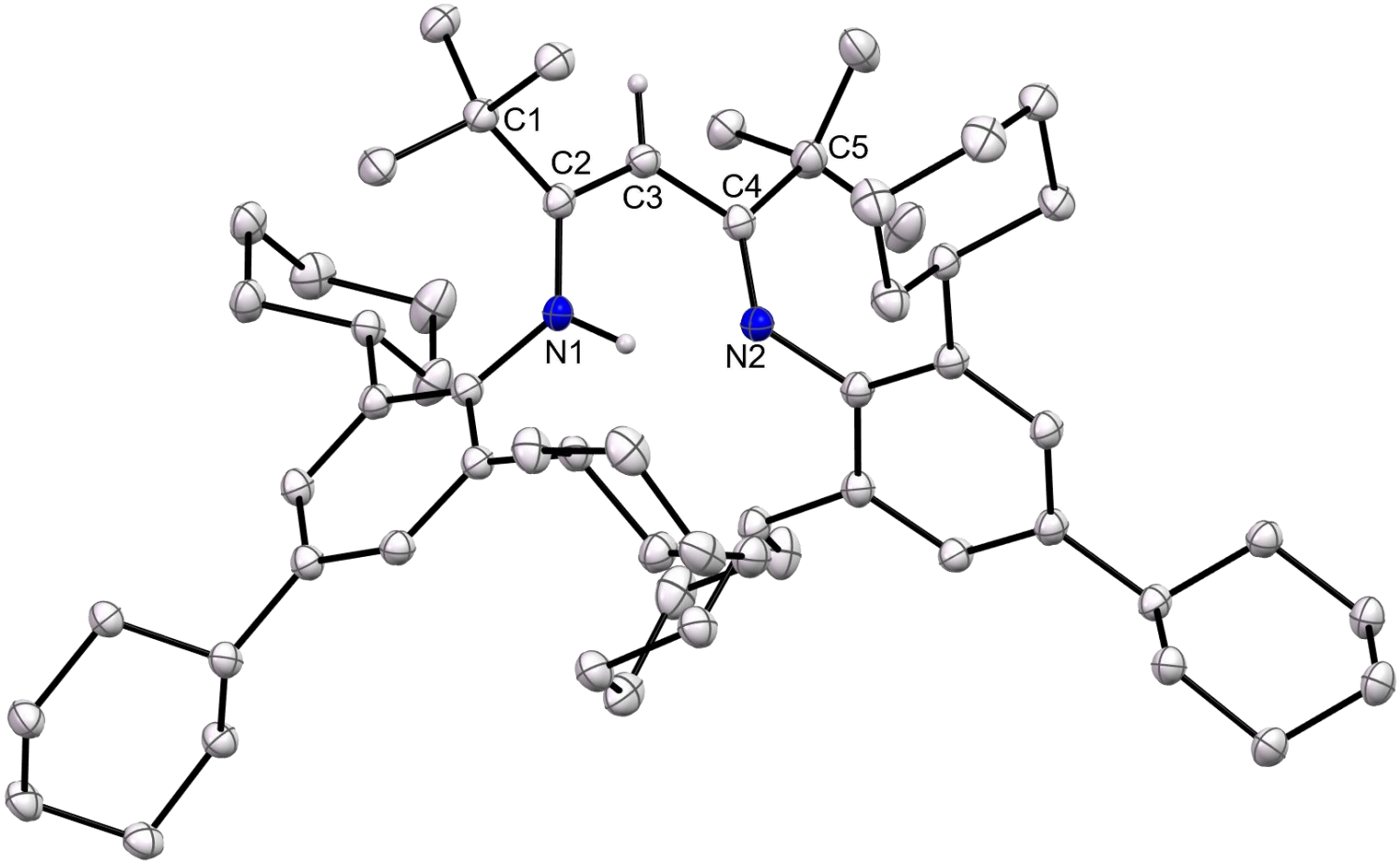


Figure S94: Molecular structure of the eneamine tautomer of ^{TCHP}NacnacH (thermal ellipsoids shown at 30% probability; hydrogen atoms, except amine and backbone methine protons, omitted).

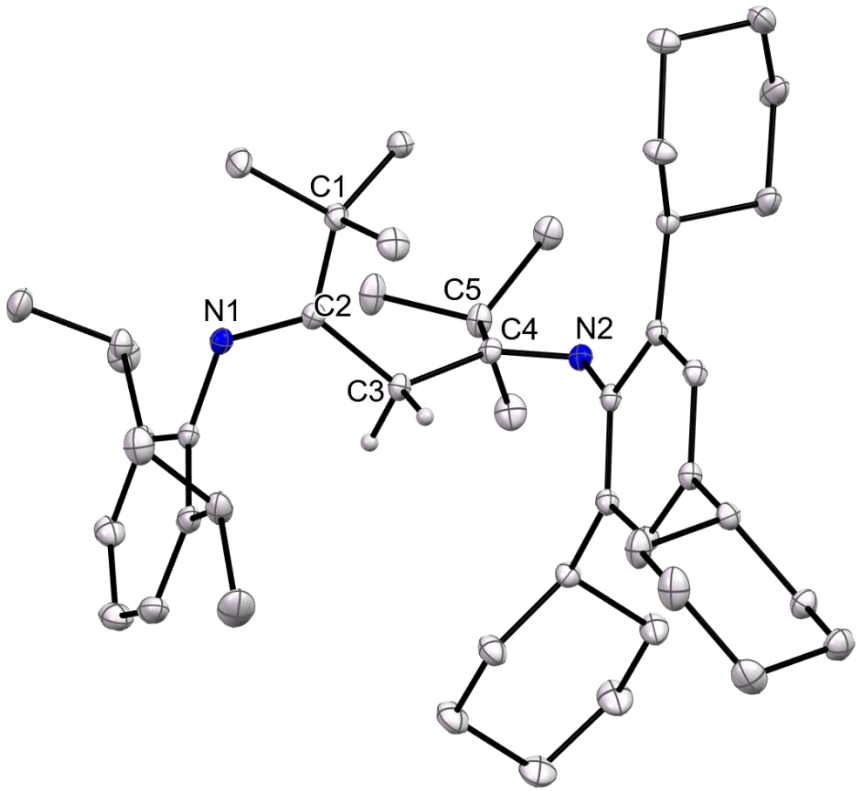


Figure S95: Molecular structure of the bis(imine) tautomer of $^{TCHP/Dip}$NacnacH (thermal ellipsoids shown at 30% probability; hydrogen atoms, except backbone methylene protons, omitted).

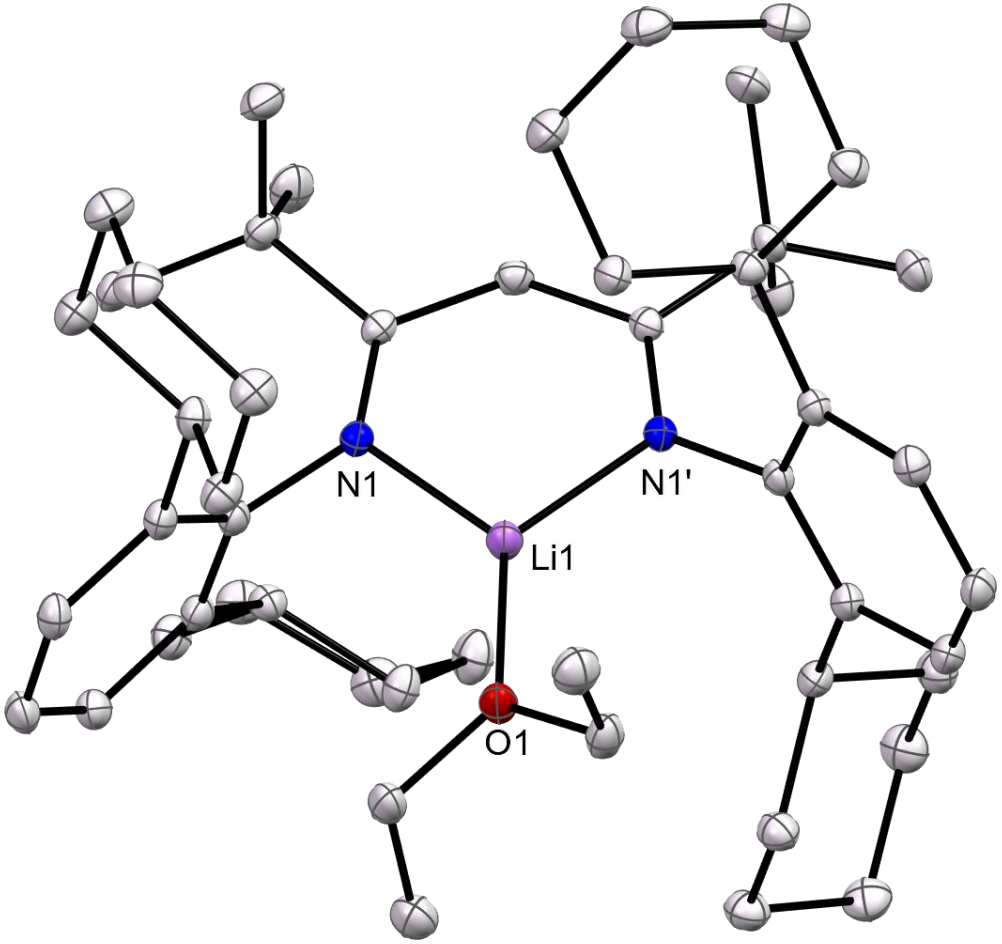


Figure S96: Molecular structure of [(^{DCHP}Nacnac)Li(OEt_2)] (thermal ellipsoids shown at 30% probability; hydrogen atoms omitted).

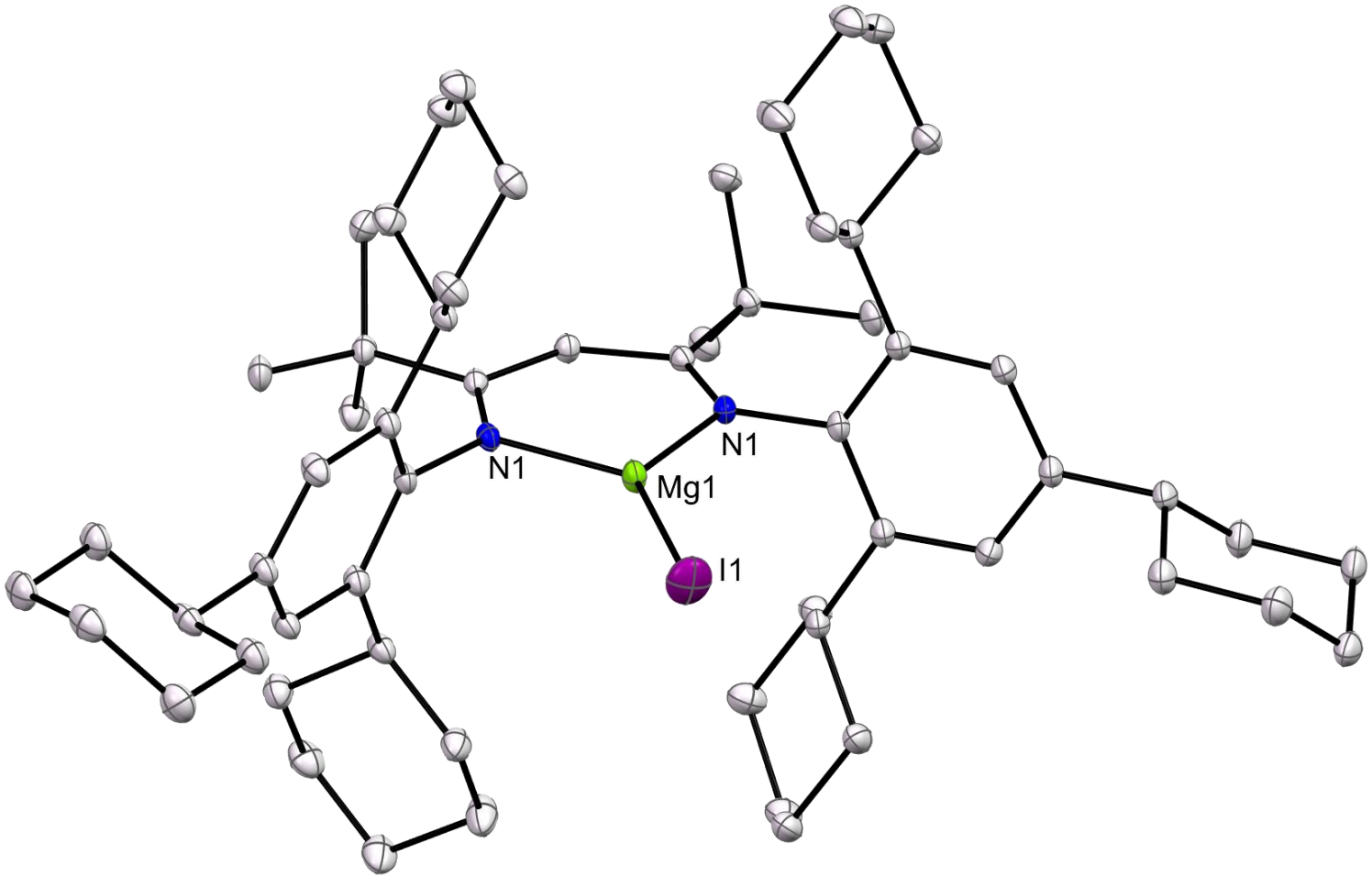


Figure S97: Molecular structure of compound **1** (thermal ellipsoids shown at 25% probability; hydrogen atoms omitted).

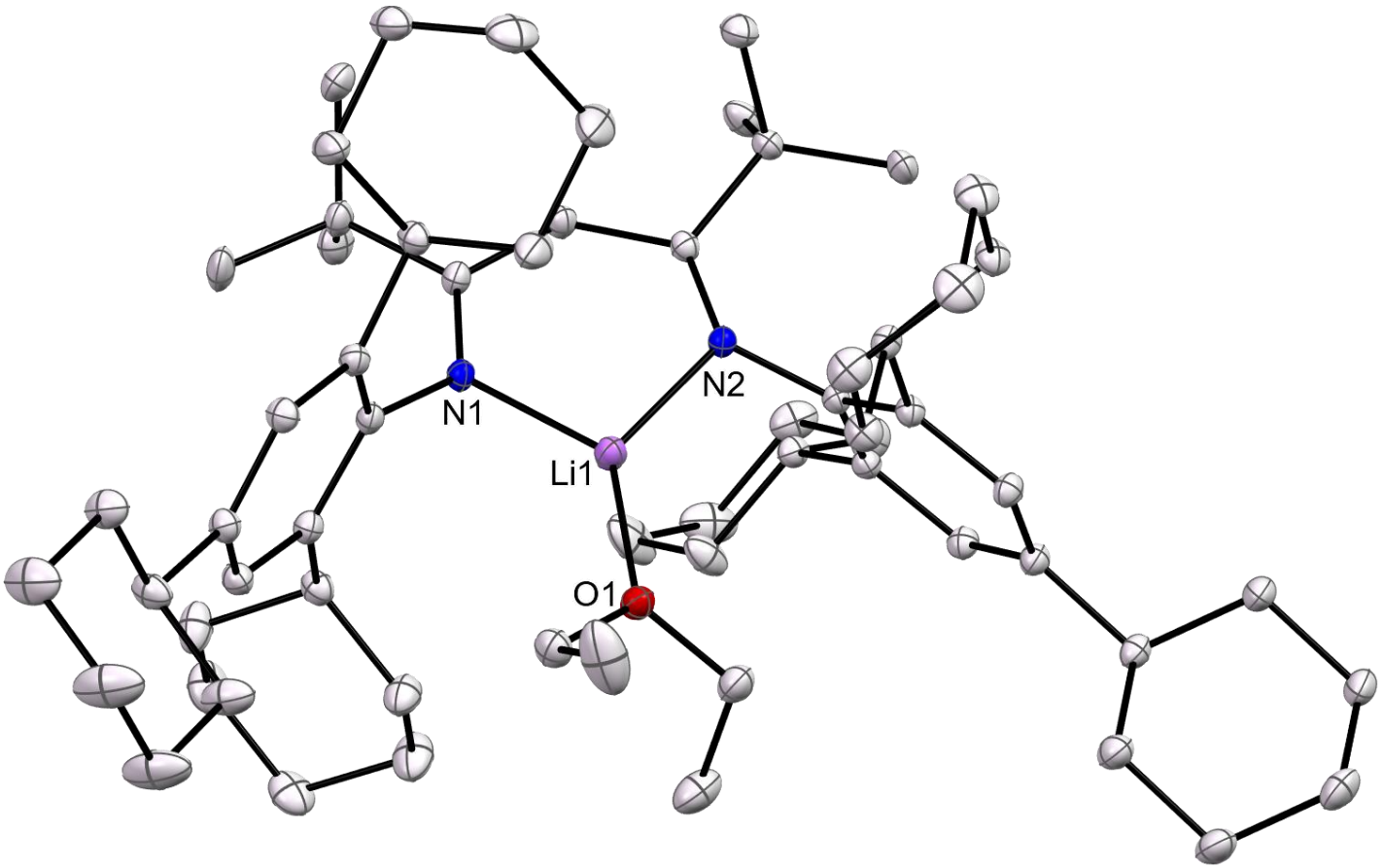


Figure S98: Molecular structure of compound **2** (thermal ellipsoids shown at 30% probability; hydrogen atoms omitted).

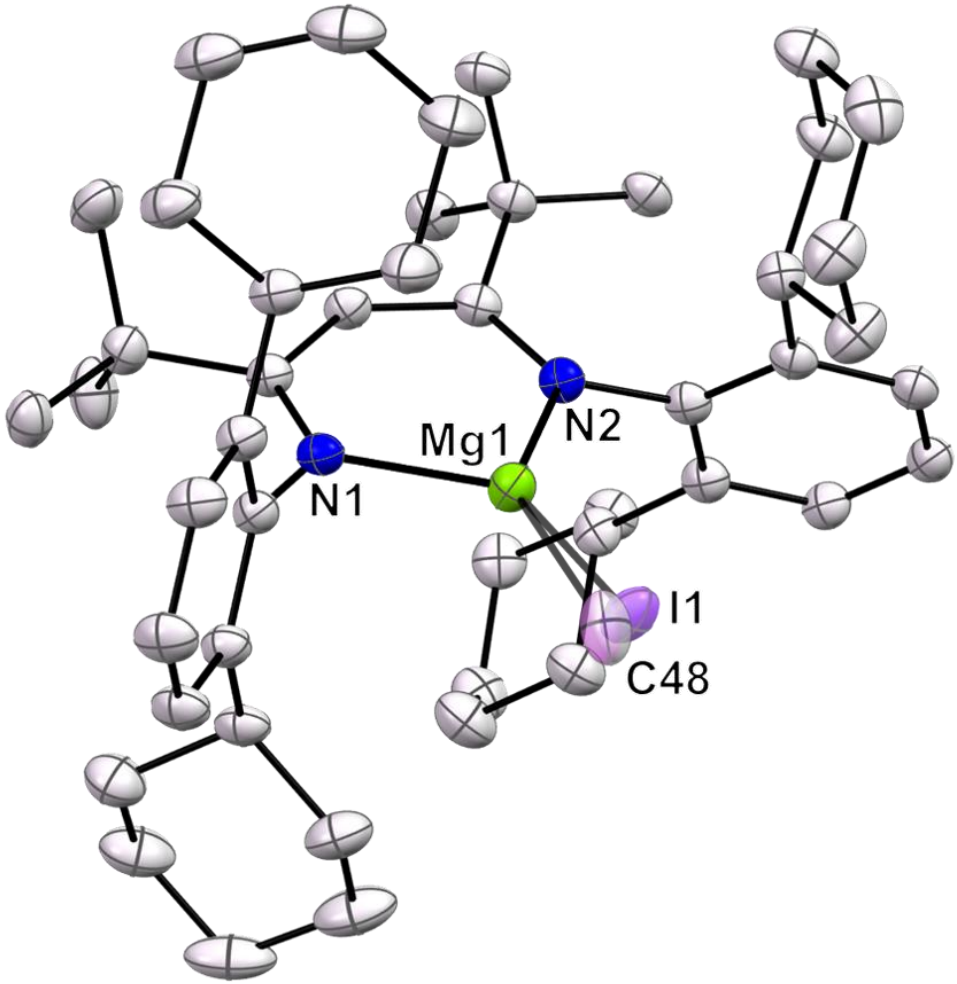


Figure S99: Molecular structure of the co-crystallised mixture of compounds **3** and **3-Me** (thermal ellipsoids shown at 30% probability; hydrogen atoms omitted).

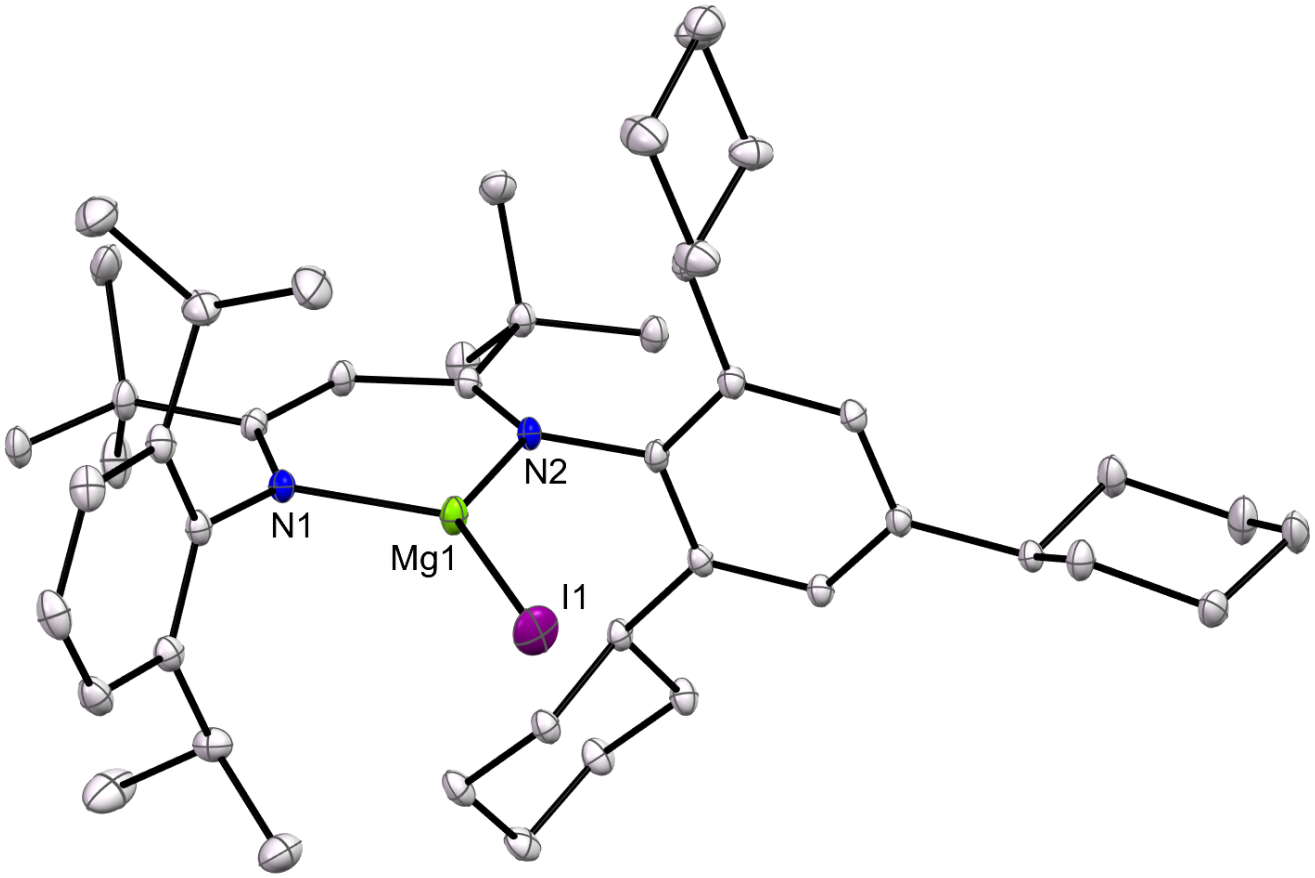


Figure S100: Molecular structure of compound **5** (thermal ellipsoids shown at 25% probability; hydrogen atoms omitted).

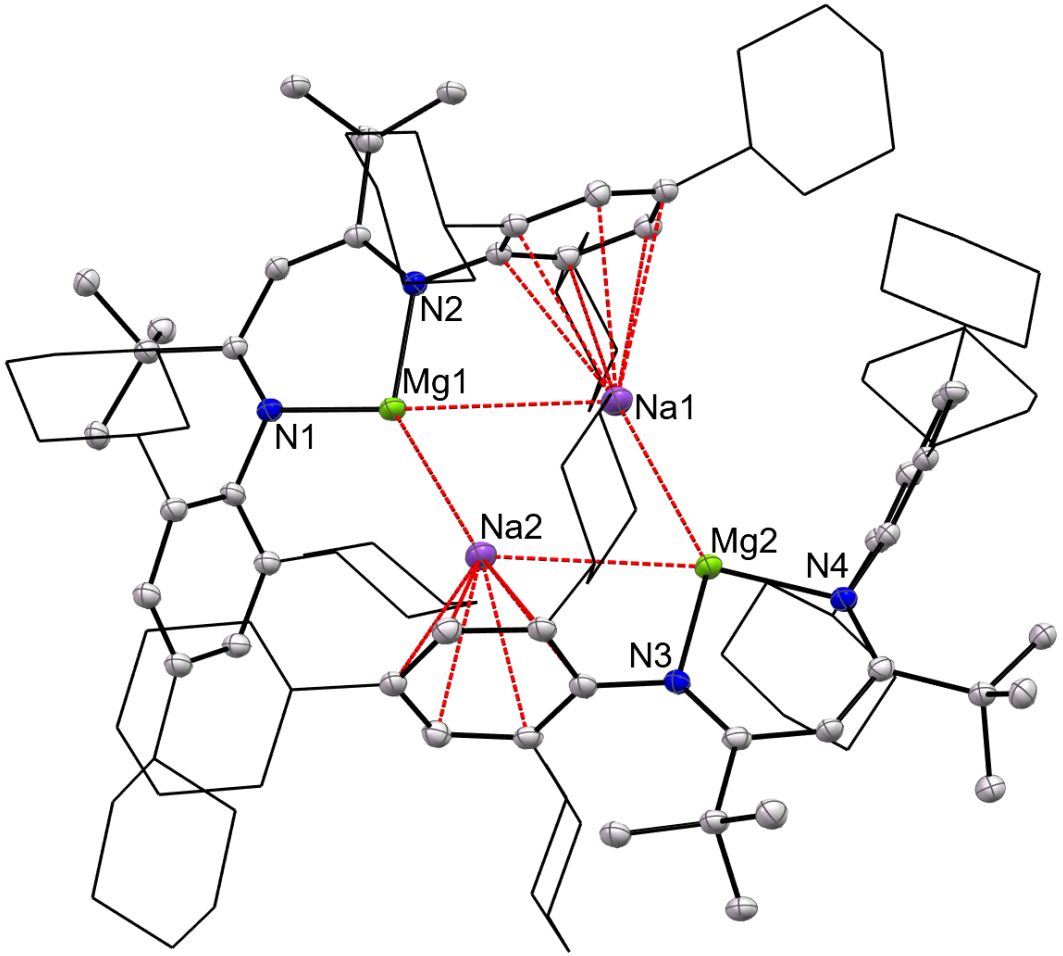


Figure S101: Molecular structure of **6** (25% thermal ellipsoids; hydrogen atoms omitted; cyclohexyl groups shown as wireframe for clarity).

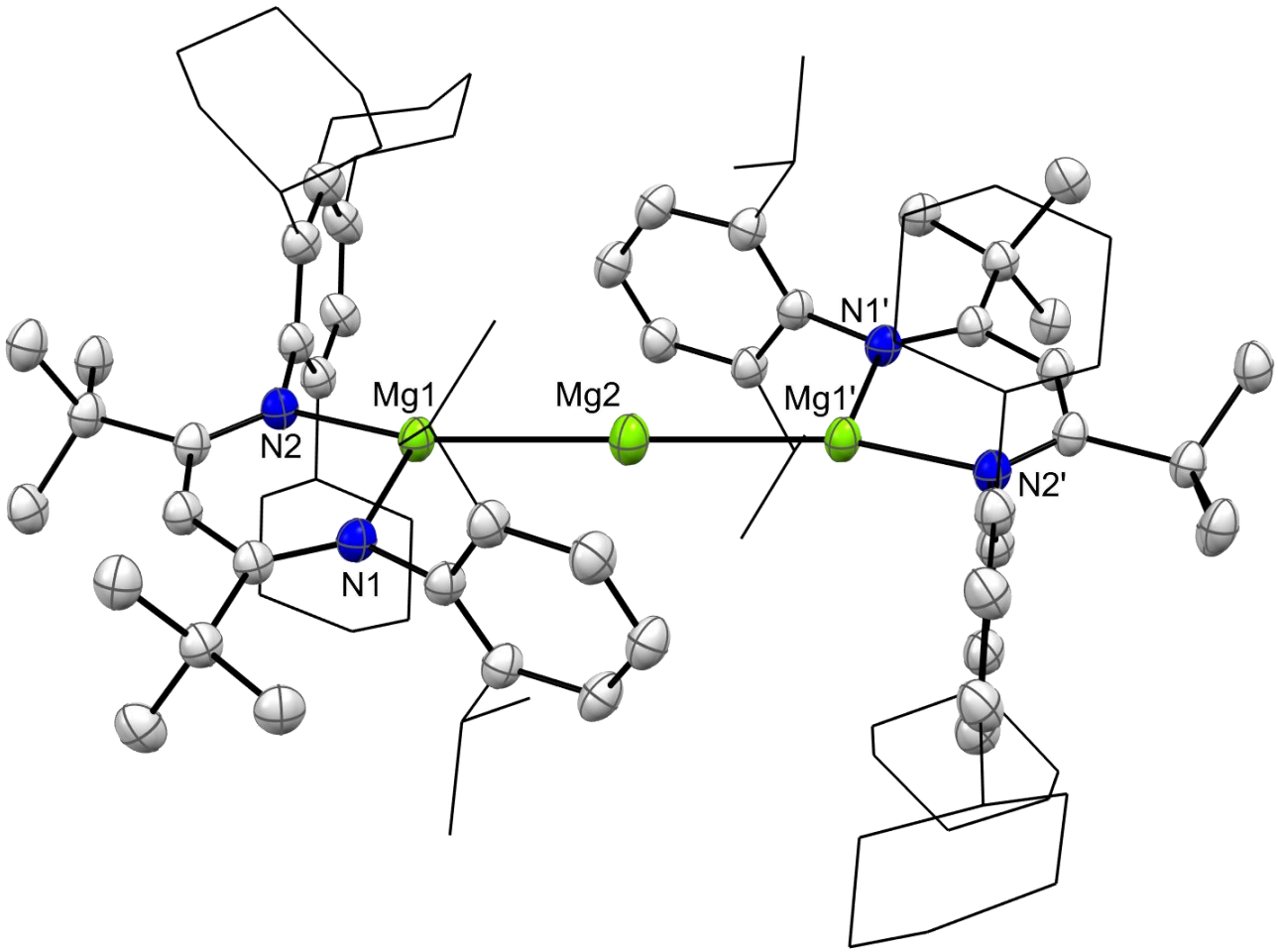


Figure S102: Molecular structure of **7** (25% thermal ellipsoids; hydrogen atoms omitted; cyclohexyl and isopropyl groups shown as wireframe for clarity).

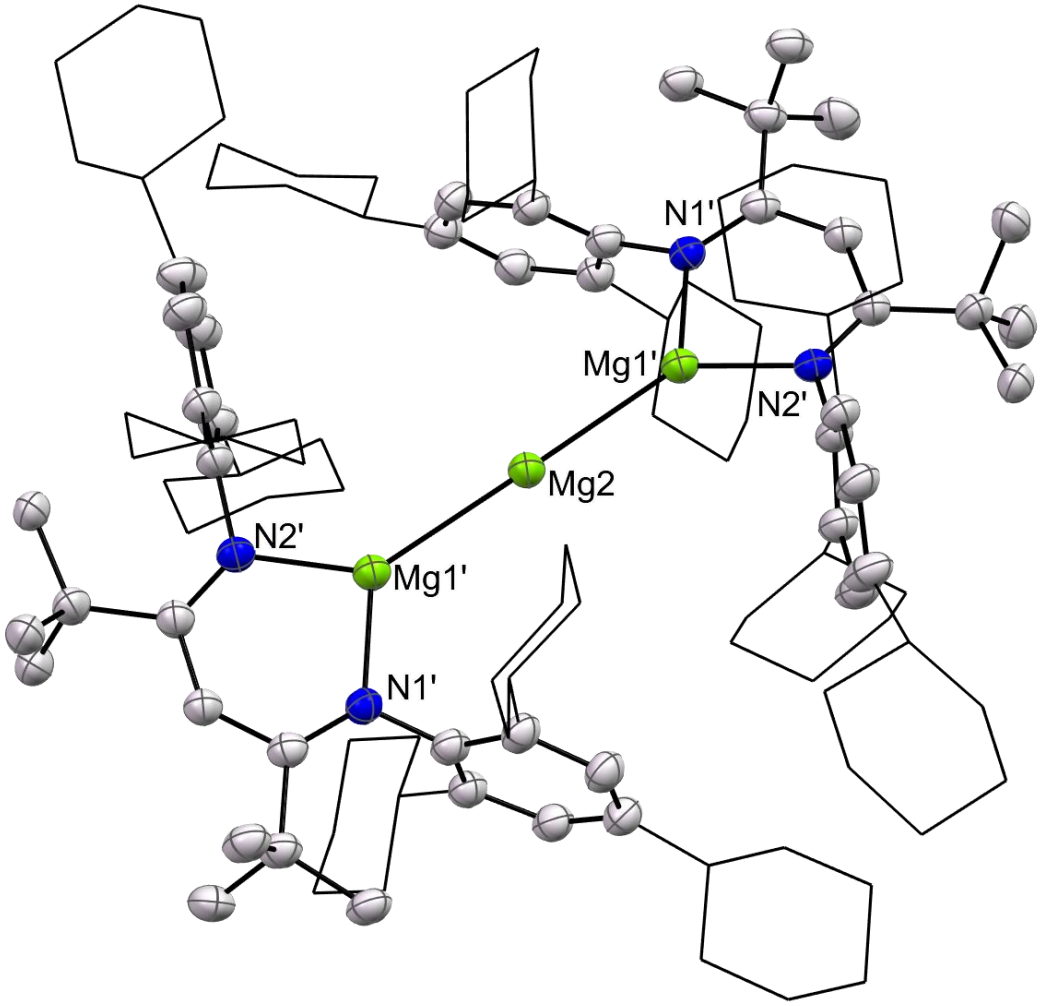


Figure S103: Molecular structure of **8** (25% thermal ellipsoids; hydrogen atoms omitted; cyclohexyl groups shown as wireframe for clarity).

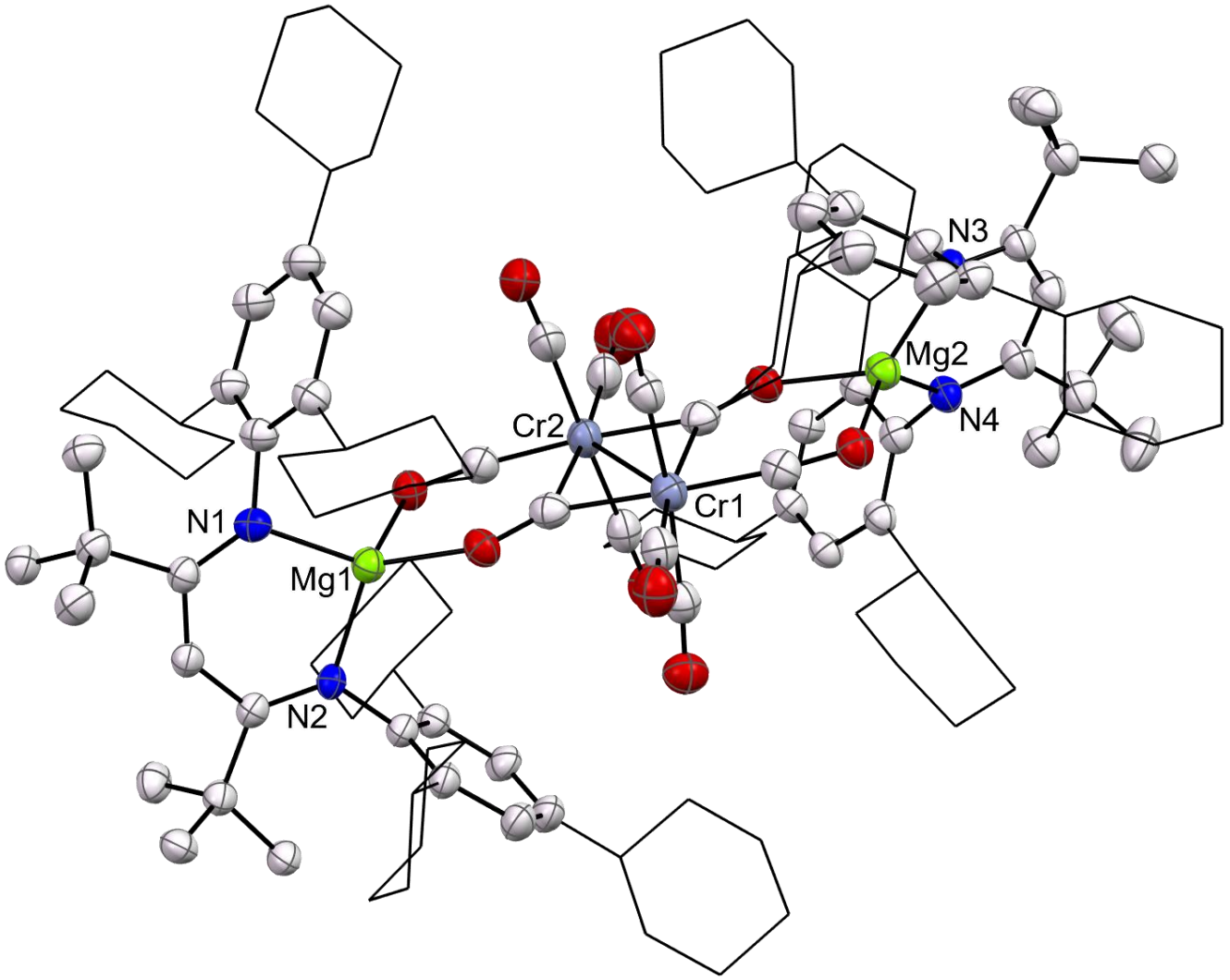


Figure S104: Molecular structure of **9** (25% thermal ellipsoids; hydrogen atoms omitted; cyclohexyl groups shown as wireframe for clarity).

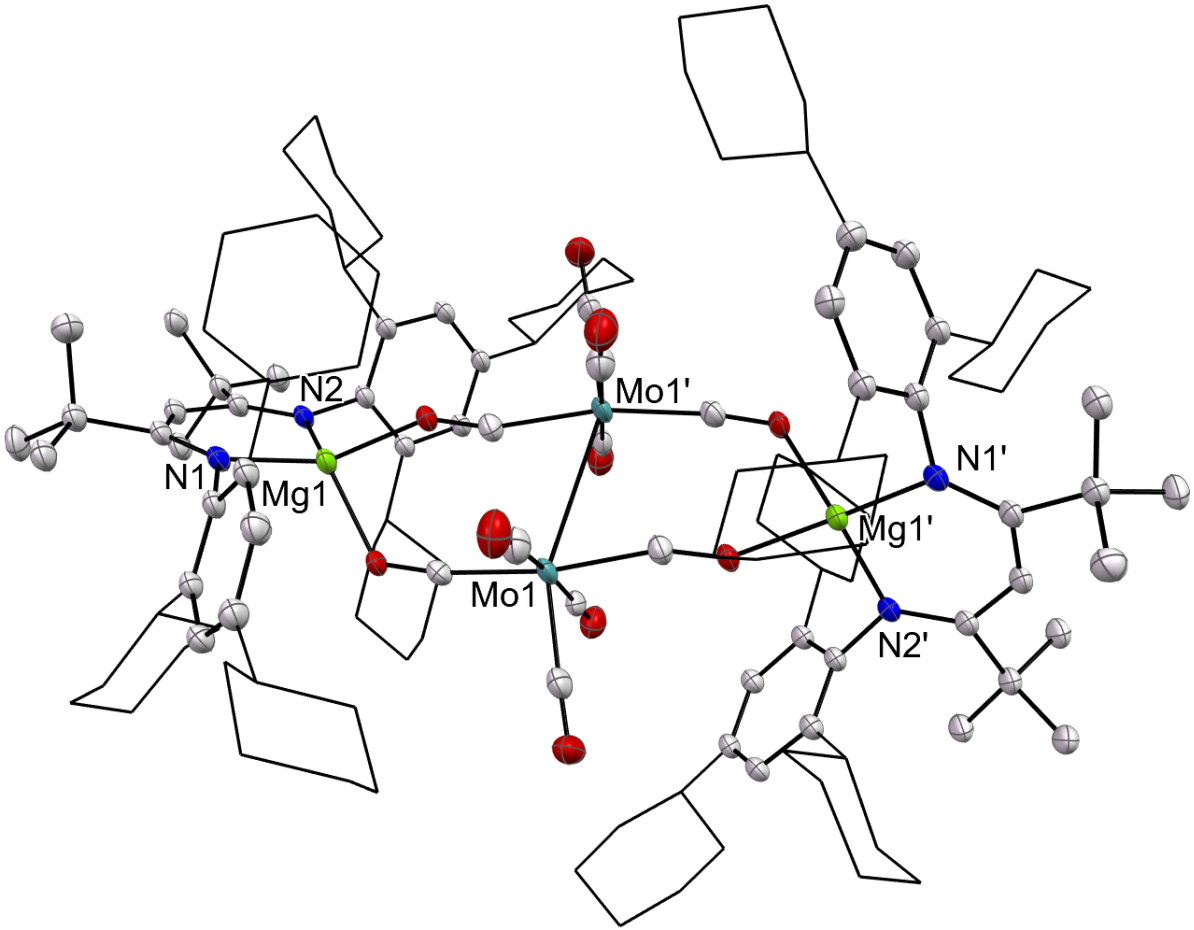


Figure S105: Molecular structure of **10** (25% thermal ellipsoids; hydrogen atoms omitted; cyclohexyl groups shown as wireframe for clarity).

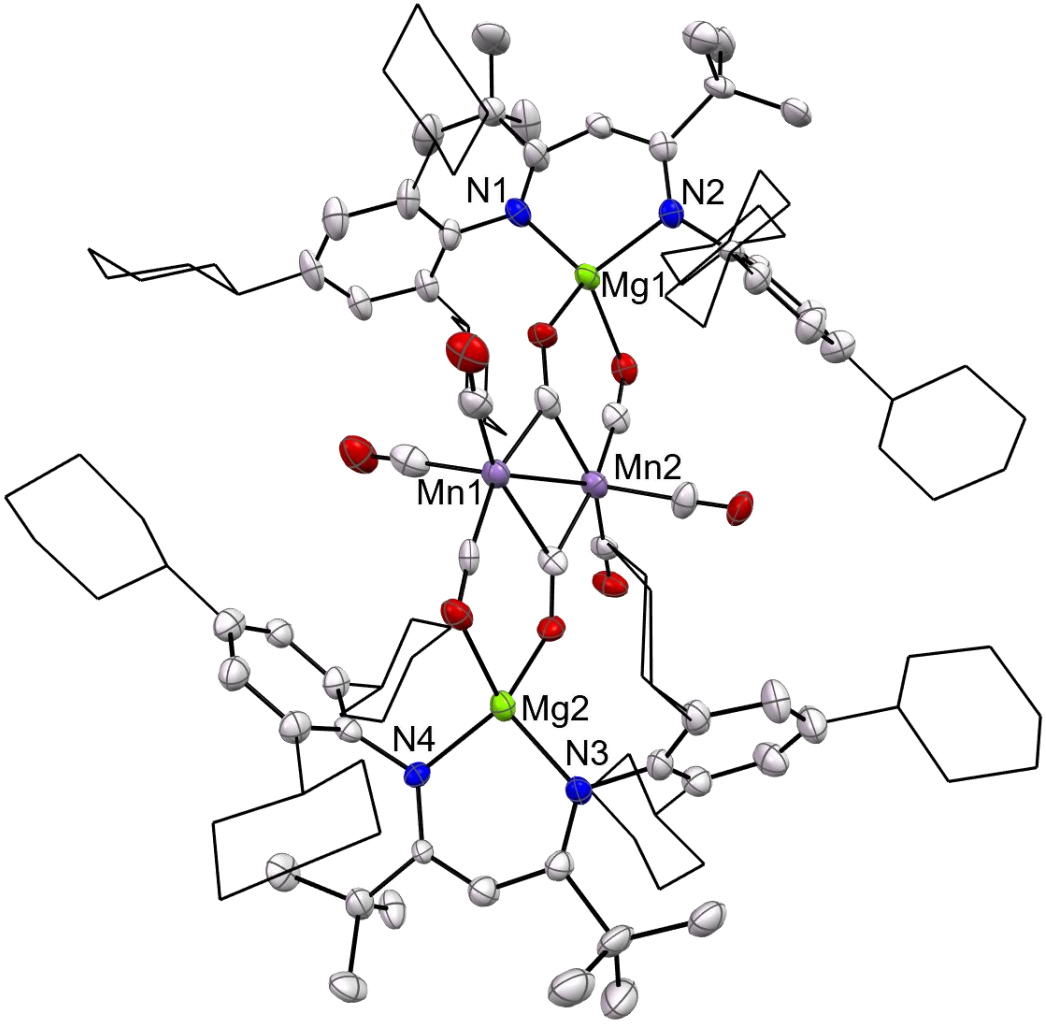


Figure S106: Molecular structure of **11** (25% thermal ellipsoids; hydrogen atoms omitted; cyclohexyl groups shown as wireframe for clarity).

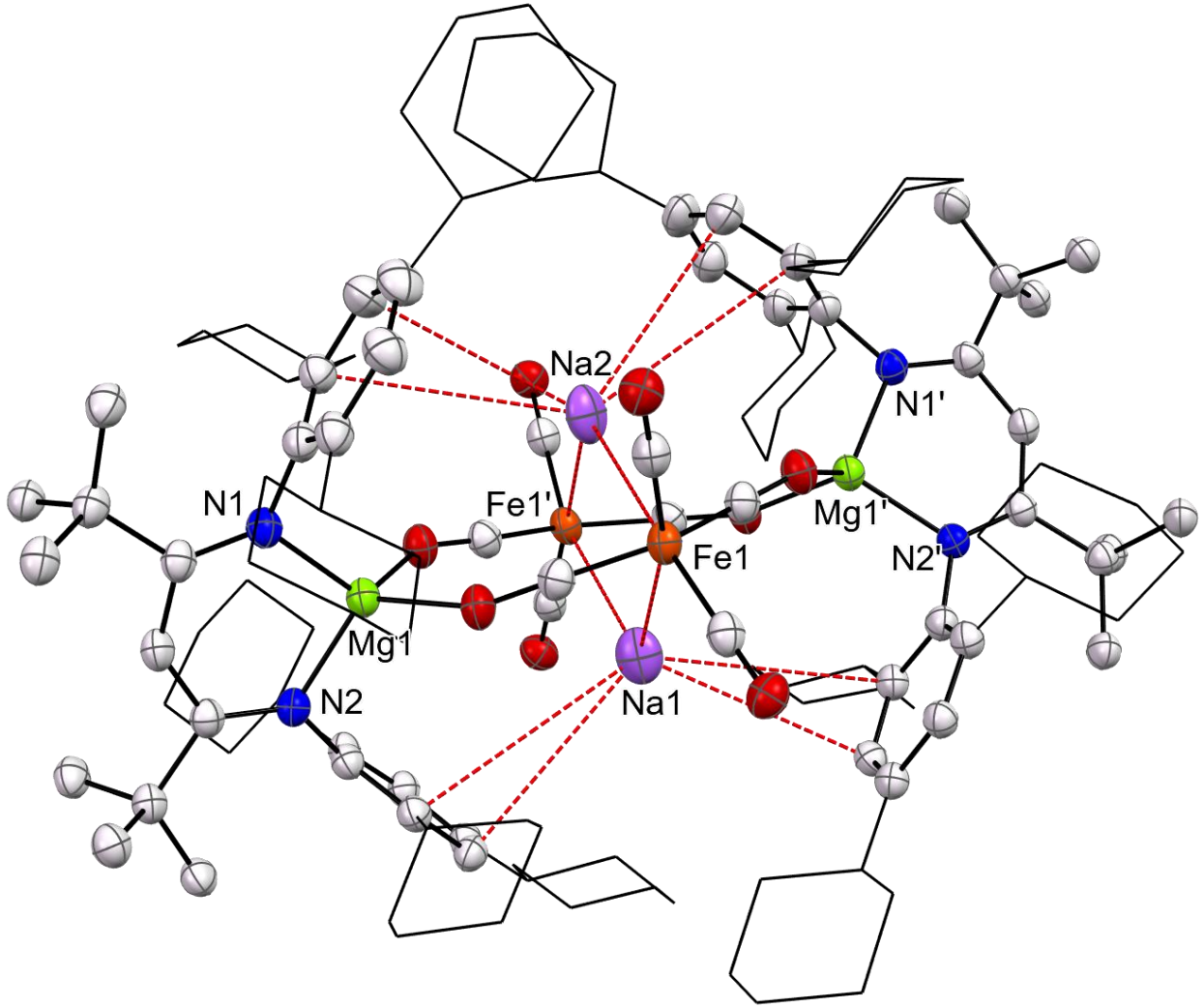


Figure S107: Molecular structure of **12** (25% thermal ellipsoids; hydrogen atoms omitted; cyclohexyl groups shown as wireframe for clarity).

3. Computational

All calculations were carried out using Gaussian 09 (Revision D01).[S10] All structures were fully optimised without the use of symmetry constraints (keyword: nosymm) at a B3PW91/def2svp level of theory.[S11–13] Grimme 3D dispersion corrections were included in the optimisation process using Becke-Johnson dampening (GD3BJ).[S14] Frequency analyses were performed on all stationary points to confirm their nature as minima. Energies were determined at the updated B3PW91/def2tzvp level of theory including Grimme 3D dispersion corrections (GD3BJ). This computational model was used by Harder and co-workers on the only other reported magnesium(0) complex.[S15] The calculated structure matched the experimental data well, with the comparison tabulated below. Charges and key bonding metrics were calculated at the B3PW91-D3BJ/def2tzvp//def2svp level of theory using NBO 6.0.[S16] Non-Covalent Interaction (NCI) plots were performed using the DFT optimised geometry of **6** in the NCIPLOT 6.0 program.[S17] Atoms-In-Molecules (AIM) analysis was performed in the Multiwfn software package.[S18]

Comparison of Computational Model to Solid State Data

Table S2: Comparison of selected bond lengths and angles between the experimental and computational data for **6-8**.

			XRD	DFT
Bond length (Å)	**6**	Mg–Na	3.154(2), 3.528(2), 3.479(2), 3.217(2)	3.061, 3.365, 3.021, 3.572
		Mg–Mg	5.812(2)	5.752
		Na–Na	3.303(3)	3.063
		Mg–N	2.108(3), 2.118(3), 2.136(3), 2.107(3)	2.125, 2.154, 2.141, 2.137
		N–N	2.998(5), 2.997(4)	3.054, 2.998
	7	Mg–Mg	2.828, 2.828	
		Mg–N	2.053, 2.066, 2.053, 2.066	
	8	Mg–Mg	2.840, 2.840	
		Mg–N	2.043, 2.050, 2.043, 2.050	
Bond Angles (°)	**6**	N–Mg–N	89.9(1), 90.4(1)	88.9, 91.1
	7	N–Mg–N	93.14, 93.14	
		Mg–Mg–Mg	180.00	
	8	N–Mg–N	93.25	
		Mg–Mg–Mg	177.89	

Molecular Orbitals

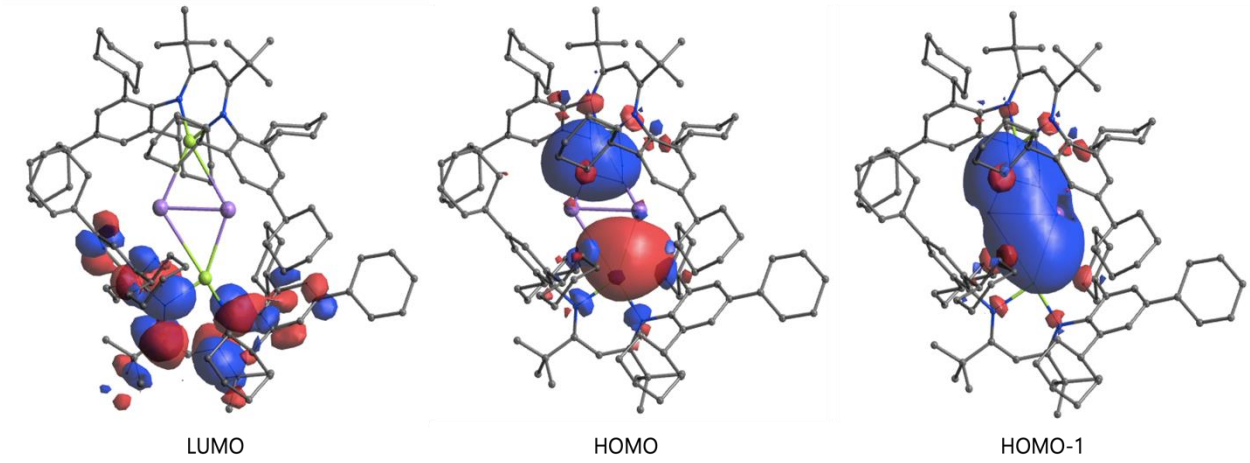


Figure S108: Selected frontier molecular orbitals of **6.** Energies calculated at the B3PW91(GD3BJ)/def2tzvp level of theory: LUMO = -0.949; HOMO = -2.724; HOMO-1 = -3.742 eV.

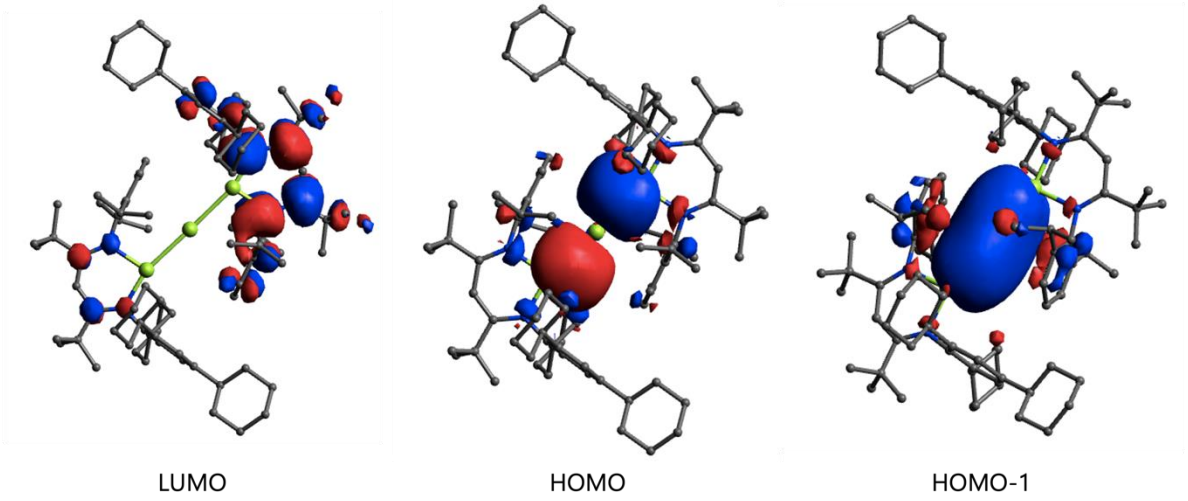


Figure S109: Selected frontier molecular orbitals of **7** Energies calculated at the B3PW91(GD3BJ)/def2tzvp level of theory: LUMO = -0.820; HOMO = -3.209; HOMO-1 = -4.900 eV.

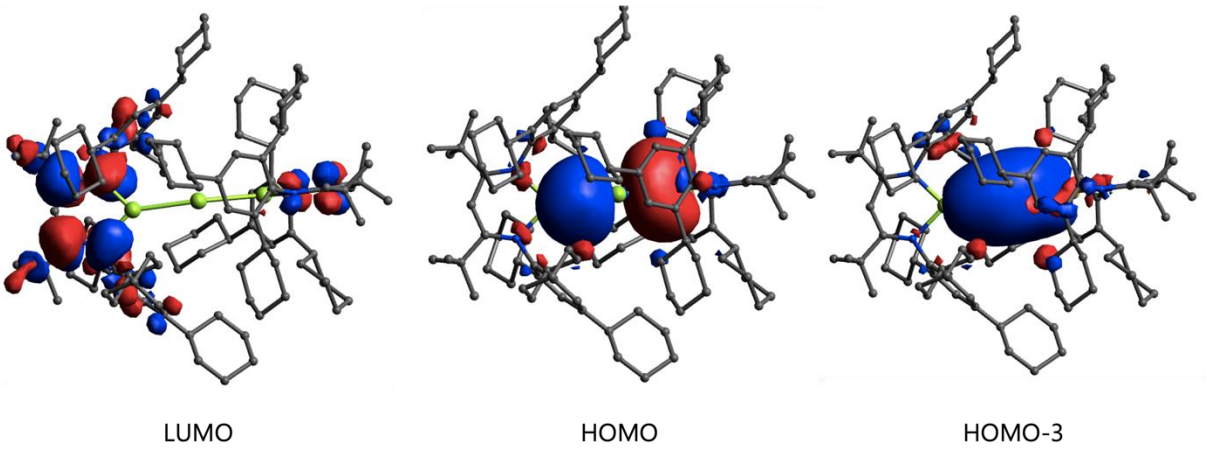


Figure S110: Selected frontier molecular orbitals of **8.** Energies calculated at the B3PW91(GD3BJ)/def2tzvp level of theory: LUMO = -0.929; HOMO = -3.337; HOMO-3 = -5.074 eV.

Non-Covalent Interaction (NCI) Plot

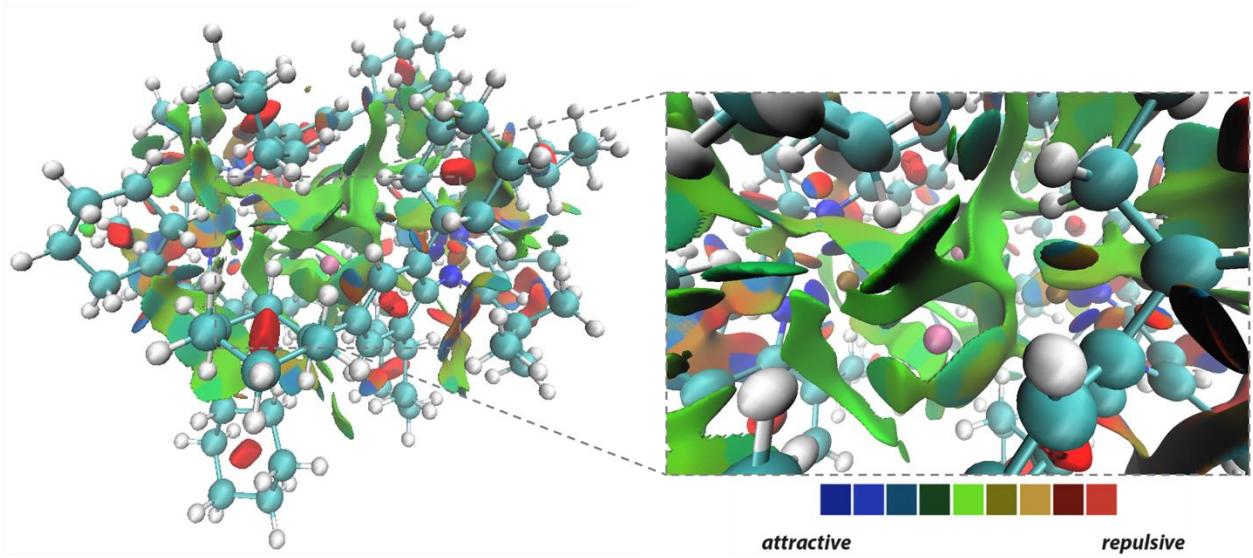


Figure S111: NCI plot of **6.**

Atoms-In-Molecules (AIM) Calculations

	Bond	*Density of all electrons ρ(r)*	*Laplacian of electron density ∇ 2ρ(r)*	*Lagrangian kinetic energy G(r)*	*Potential energy density V(r)*	*Energy density H(r)*	*Ellipticity of electron density ε*
6	Mg1–Na1	0.016	0.019	0.0009	-0.0035	-0.0025	0.065
	Mg2–Na1	0.009	0.012	0.0007	-0.0018	-0.0011	0.072
	Mg2–Na2	0.015	0.019	0.0009	-0.0032	-0.0023	0.075
	Mg1–Na2	0.008	0.0076	0.0022	-0.0025	-0.0003	0.072
7	Mg1–Mg2	0.030	-0.0069	0.0007	-0.0107	-0.0100	0.038
	Mg2–Mg3	0.030	-0.0067	0.0007	-0.0105	-0.0099	0.040
8	Mg1–Mg2	0.028	-0.0082	0.0005	-0.0092	-0.0087	0.023
	Mg2–Mg3	0.028	-0.0084	0.0005	-0.0093	-0.0087	0.027

Table S3: Summary of select data from the QTAIM calculations of Bond Critical Points (BCPs).

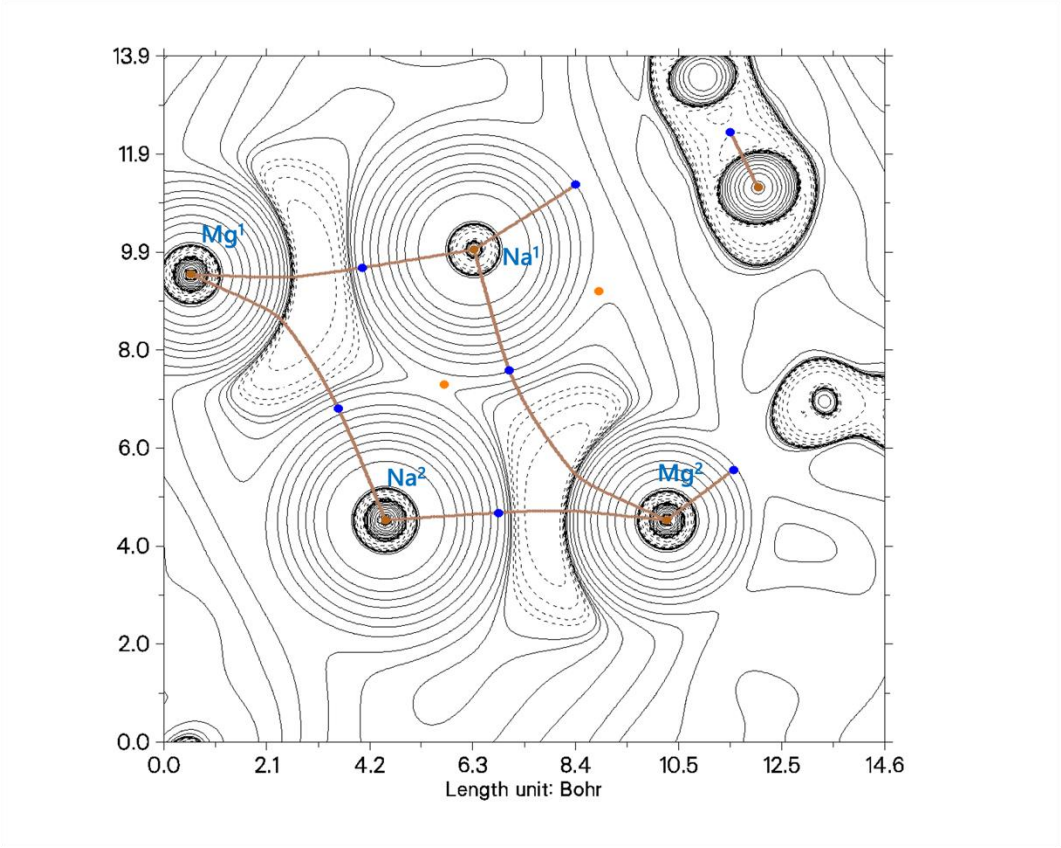


Figure S112: Laplacian distribution plot for **6**, from the AIM calculations. Bond- and ring critical points are shown as blue and orange dots respectively.

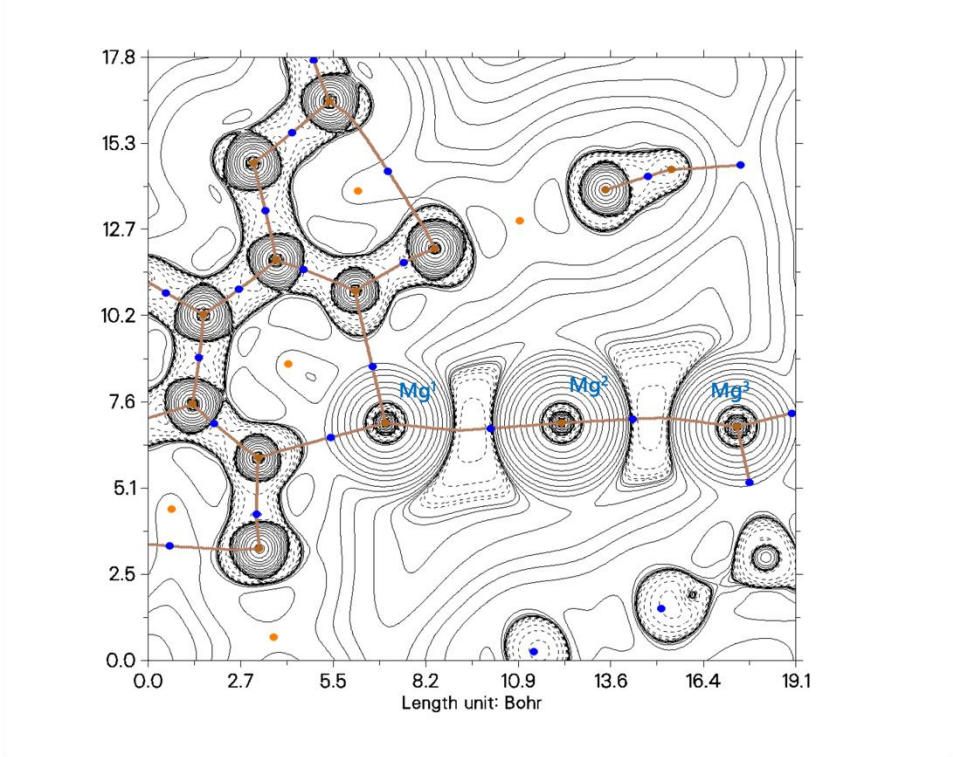


Figure S113: Laplacian distribution plot for **7**, from the AIM calculations. Bond- and ring critical points are shown as blue and orange dots respectively.

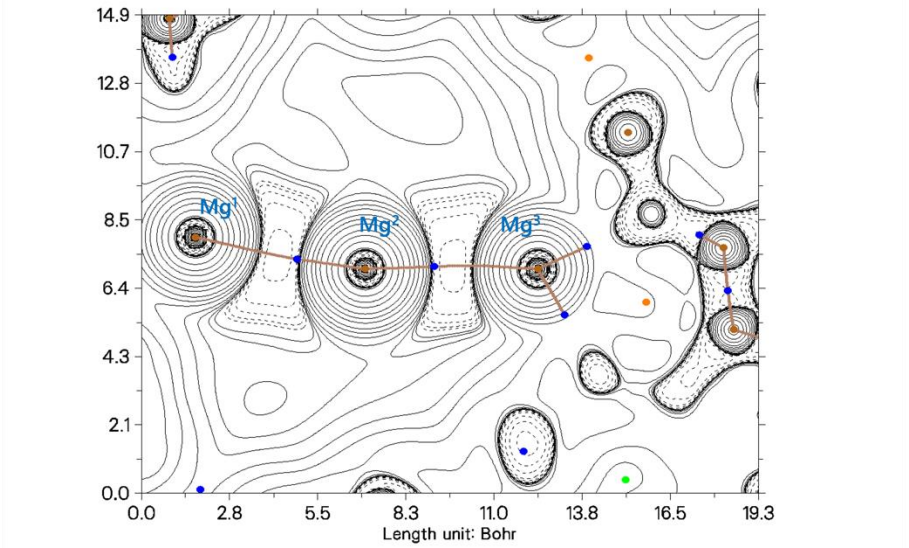


Figure S114: Laplacian distribution plot for **8**, from the AIM calculations. Bond- and ring critical points are shown as blue and orange dots respectively.

Natural Bonding Orbital (NBO) Calculations

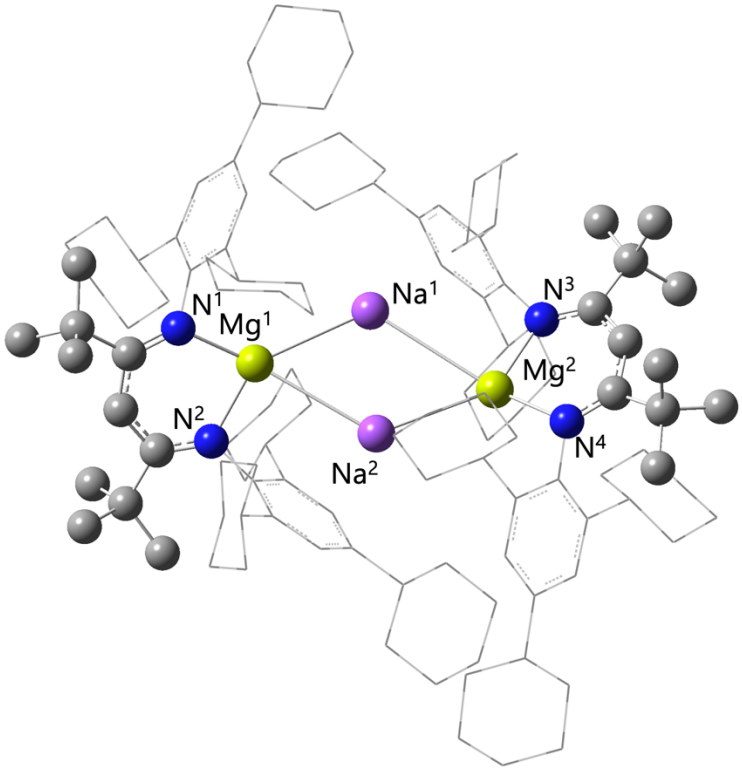


Figure S115: Labelled image of compound **6** used for NBO analysis. Hydrogen atoms omitted and tricyclohexylphenyl groups shown in wireframe for clarity.

Table S4: Select Natural population Analysis charges, and Bader charges (in parentheses), from the NBO and QTAIM analyses on compound **6**.

Atom	Charge	Atom	Charge
Mg1	+0.61 (+0.46)	N1	-0.76
Mg2	+0.57 (+0.44)	N2	-0.76
Na1	+0.37 (+0.69)	N3	-0.76
Na2	+0.49 (+0.73)	N4	-0.76

Table S5: Select Wiberg Bond Index (WBI) data from the NBO analysis on compound **6**.

Bond	WBI	Bond	WBI
Mg1–N1	0.036	Mg1–Na1	0.452
Mg1–N2	0.035	Mg1–Na2	0.071
Mg2–N3	0.033	Mg2–Na1	0.105
Mg2–N4	0.035	Mg2–Na2	0.396
Mg1–Mg2	0.143	Na1–Na2	0.190

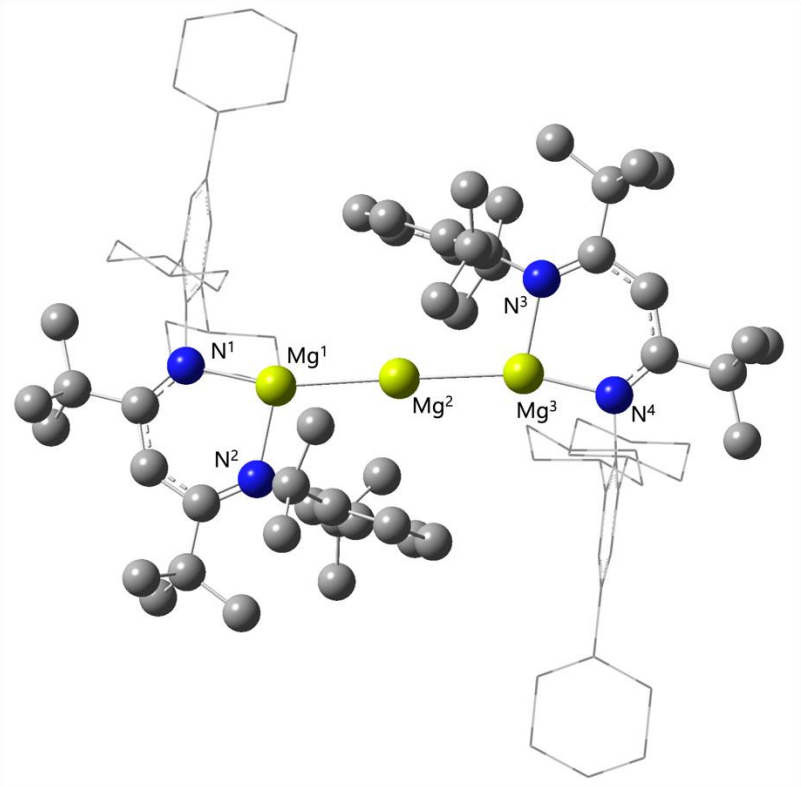


Figure S116: Labelled image of compound **7** used for NBO analysis. Hydrogen atoms omitted and tricyclohexylphenyl groups shown in wireframe for clarity.

Table S6: Select Natural population Analysis (NPA) charge and Wiberg Bond Index (WBI) data from the NBO analysis on compound **7**.

Atom	NPA Charge	Bond	WBI
Mg1	+0.803	Mg1–Mg2	0.508
Mg2	+0.337	Mg2–Mg3	0.506
Mg3	+0.800	-	-

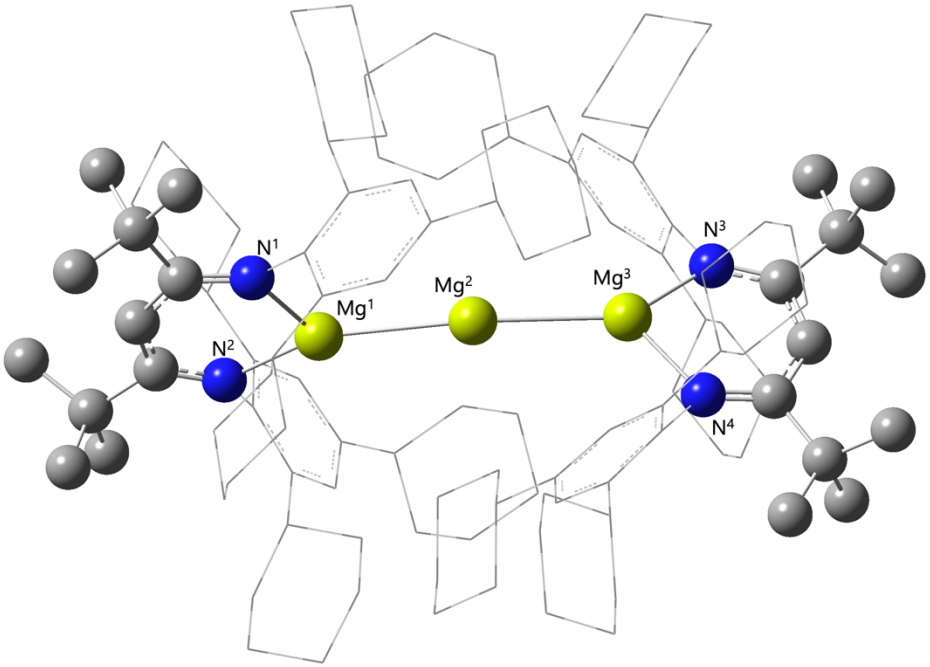


Figure S117: Labelled image of compound **8** used for NBO analysis. Hydrogen atoms omitted and tricyclohexylphenyl groups shown in wireframe for clarity.

Table S7: Select Natural population Analysis (NPA) charge and Wiberg Bond Index (WBI) data from the NBO analysis on compound **8**.

Atom	NPA Charge	Bond	WBI
Mg1	+0.774	Mg1–Mg2	0.498
Mg2	+0.408	Mg2–Mg3	0.495
Mg3	+0.801	Mg1–N1	0.0316
N1	-0.761	Mg1–N3	0.0334
N2	-0.778	Mg3–N3	0.0331
N3	-0.762	Mg3–N4	0.0496
N4	-0.778	-	

Cartesian Coordinates

6

Mg	6.420201	11.495701	3.073608
N	5.951253	10.022205	1.593510
N	7.180531	12.817569	1.576592
C	6.280669	8.896844	-0.691374
C	6.345288	10.087681	0.326327
C	6.960612	11.236857	-0.219439
H	7.195053	11.132399	-1.271252
C	7.292508	12.511840	0.289973
C	7.729921	13.515572	-0.825354
C	5.482309	7.665879	-0.242846

H	5.630191	6.869854	-0.989576
H	4.406134	7.865043	-0.178573
H	5.801525	7.273012	0.727622
C	7.740832	8.450698	-0.920470
H	8.212425	8.126747	0.018582
H	8.353982	9.262648	-1.335165
H	7.769558	7.602728	-1.623353
C	5.688899	9.331319	-2.045401
H	5.614505	8.454576	-2.707144
H	6.302392	10.078331	-2.566350
H	4.677574	9.747087	-1.930271
C	6.523261	13.693230	-1.769180
H	6.198520	12.745122	-2.217663
H	6.781277	14.389309	-2.583144
H	5.666828	14.115349	-1.221876
C	8.927048	12.950787	-1.610547
H	9.782223	12.763828	-0.944557
H	9.247775	13.678510	-2.372494
H	8.693887	12.010963	-2.128769
C	8.122060	14.923024	-0.361184
H	7.334423	15.404361	0.229487
H	8.292896	15.542472	-1.255697
H	9.041514	14.940119	0.234525
C	4.963240	9.173614	2.132811
C	3.615132	9.310741	1.706102
C	2.627163	8.542555	2.317818
H	1.595354	8.629090	1.970905
C	2.901255	7.669622	3.374743
C	4.220678	7.585191	3.810646
H	4.459401	6.918406	4.637645
C	5.258903	8.315238	3.219010
C	3.261407	10.303040	0.622438
H	4.064349	10.280321	-0.127635
C	3.235484	11.742117	1.151466
H	2.431711	11.834158	1.900949
H	4.179048	11.961977	1.676279
C	3.026316	12.731829	0.013390
H	3.898494	12.678242	-0.660475
H	2.998833	13.759811	0.403173
C	1.753677	12.428491	-0.770765
H	0.878499	12.588767	-0.114710
H	1.643150	13.130289	-1.613846
C	1.744155	10.986670	-1.271848
H	2.546382	10.858844	-2.020938
H	0.797742	10.764026	-1.791357
C	1.963881	9.999857	-0.128063
H	1.107402	10.066741	0.565756
H	1.980786	8.964239	-0.506436
C	6.675584	8.148845	3.721984
H	7.142586	9.155579	3.704191
C	6.767288	7.667053	5.169265
H	6.148231	8.311875	5.819516
H	6.343024	6.652343	5.260523
C	8.211685	7.638787	5.647665
H	8.607504	8.669609	5.642600
H	8.265959	7.288794	6.690490
C	9.073572	6.756594	4.750734
H	8.726745	5.710386	4.835468
H	10.120417	6.763791	5.094180
C	8.981301	7.202206	3.295682

H	9.427132	8.207226	3.198793
H	9.572102	6.535158	2.646359
C	7.534733	7.261680	2.815648
H	7.100042	6.245913	2.783528
H	7.497629	7.654876	1.792327
C	1.787539	6.837932	3.966164
H	0.872164	7.459752	3.938380
C	2.005831	6.423342	5.422721
H	2.908673	5.791612	5.492623
H	2.201807	7.313390	6.042179
C	0.815424	5.636510	5.965011
H	0.999537	5.340417	7.010695
H	-0.074788	6.291055	5.980948
C	0.523596	4.408554	5.105814
H	-0.360264	3.872192	5.488327
H	1.372205	3.704445	5.183026
C	0.323752	4.790530	3.641099
H	-0.596494	5.395738	3.547151
H	0.165877	3.889542	3.025747
C	1.504203	5.596080	3.105020
H	2.414146	4.969215	3.089244
H	1.324307	5.903410	2.062351
C	7.733351	13.928929	2.237425
C	9.126116	13.963580	2.518209
C	9.645477	15.020253	3.276566
H	10.720043	15.058141	3.463684
C	8.832824	16.022539	3.823509
C	7.458186	15.931745	3.587981
H	6.795582	16.685460	4.018839
C	6.892769	14.923447	2.797416
C	10.036009	12.834119	2.086800
H	9.539666	12.287388	1.270954
C	10.218449	11.830399	3.237292
H	10.694243	12.349415	4.090816
H	9.227432	11.482871	3.591807
C	11.074612	10.640454	2.823357
H	11.211510	9.959724	3.678318
H	10.534867	10.067675	2.048444
C	12.424236	11.091767	2.272053
H	13.013737	10.223210	1.935705
H	13.004781	11.566783	3.084234
C	12.250242	12.092425	1.131523
H	11.760316	11.588290	0.278868
H	13.232210	12.435538	0.766959
C	11.402662	13.286471	1.562689
H	11.271276	13.993393	0.727058
H	11.944114	13.835757	2.352380
C	9.423503	17.127017	4.668057
H	10.506365	17.154813	4.451187
C	9.270594	16.845710	6.171808
H	9.715175	15.869268	6.431215
H	8.195468	16.764644	6.412207
C	9.909373	17.943673	7.015041
H	9.754155	17.733187	8.083506
H	11.002238	17.925977	6.854239
C	9.368303	19.324021	6.657087
H	8.297169	19.373145	6.925783
H	9.874169	20.101428	7.252818
C	9.524119	19.606412	5.165344
H	10.599547	19.658815	4.915718

H	9.097964	20.590487	4.910528
C	8.867036	18.514779	4.325957
H	8.999422	18.711383	3.249730
H	7.779097	18.530025	4.513385
C	5.403496	14.962241	2.529881
H	5.166347	14.133623	1.842265
C	4.594280	14.754945	3.817445
H	4.872735	13.783153	4.263579
H	4.888226	15.528130	4.548073
C	3.092310	14.830724	3.577911
H	2.785285	13.985952	2.938078
H	2.553746	14.702743	4.530993
C	2.698939	16.147828	2.914072
H	1.614986	16.174343	2.714419
H	2.907713	16.979012	3.612482
C	3.481964	16.372592	1.623210
H	3.230359	17.352449	1.185339
H	3.176589	15.618495	0.878406
C	4.987714	16.277820	1.848617
H	5.306196	17.123983	2.481963
H	5.526528	16.392438	0.894271
Mg	8.093036	12.651564	8.453973
Na	6.290577	11.109490	6.067336
N	6.592457	12.169652	9.922700
N	9.542174	12.696897	10.007727
C	5.627712	11.981277	12.276623
C	6.784003	12.077487	11.231431
C	8.064080	12.178482	11.818659
H	8.059000	12.033132	12.890198
C	9.347801	12.448493	11.292170
C	10.502162	12.294905	12.328958
C	4.237414	11.652558	11.720562
H	3.903631	12.363681	10.958267
H	3.516505	11.693910	12.552138
H	4.180922	10.647027	11.285256
C	5.541500	13.375141	12.929751
H	5.329087	14.143432	12.170889
H	6.482206	13.647769	13.427777
H	4.731477	13.398541	13.676472
C	5.927174	10.921328	13.352186
H	5.062552	10.830586	14.027668
H	6.798285	11.165728	13.974349
H	6.102804	9.933868	12.897885
C	10.151981	12.956369	13.674015
H	9.883791	14.015552	13.537734
H	11.025939	12.914724	14.342321
H	9.323556	12.464000	14.200622
C	11.861686	12.864766	11.908045
H	12.229455	12.445858	10.966737
H	12.596082	12.620145	12.691435
H	11.845195	13.956433	11.799367
C	10.671043	10.775166	12.527455
H	9.746191	10.313821	12.901924
H	11.480468	10.569509	13.246382
H	10.928218	10.287314	11.575180
C	5.464015	11.782219	9.183120
C	5.220486	10.398388	8.952263
C	4.229808	10.023582	8.036715
H	4.042689	8.961745	7.855975
C	3.472462	10.967065	7.319126

C	3.729546	12.317360	7.567666
H	3.160565	13.075370	7.027791
C	4.707460	12.746497	8.475606
C	6.070507	9.369070	9.666376
H	6.279648	9.762517	10.673783
C	7.436195	9.187668	8.991708
H	7.280289	8.779448	7.979051
H	7.927788	10.165430	8.857101
C	8.339745	8.260223	9.794102
H	8.573482	8.744818	10.758392
H	9.301724	8.125922	9.274482
C	7.672988	6.909862	10.040366
H	7.559343	6.383600	9.074844
H	8.315022	6.270396	10.668004
C	6.296045	7.075495	10.679809
H	6.414495	7.494211	11.695651
H	5.809731	6.094210	10.804259
C	5.405871	8.004707	9.857766
H	4.420983	8.127269	10.337969
H	5.219887	7.538523	8.873930
C	2.398802	10.509853	6.355009
H	2.770358	9.593435	5.858853
C	1.117462	10.138317	7.121874
H	1.349589	9.375042	7.882726
H	0.775887	11.031136	7.676540
C	0.009747	9.650520	6.194328
H	-0.900969	9.429352	6.774904
H	0.322035	8.699428	5.731752
C	-0.286273	10.662970	5.091694
H	-1.057588	10.271464	4.407714
H	-0.706764	11.580160	5.543516
C	0.981855	11.015712	4.320017
H	0.764778	11.774877	3.550922
H	1.348448	10.126238	3.783679
C	2.084141	11.517176	5.245164
H	1.756908	12.471357	5.693550
H	3.003631	11.730402	4.673929
C	4.894554	14.229613	8.709938
H	5.761318	14.349746	9.381745
C	5.196282	14.995945	7.417532
H	6.090582	14.552144	6.946316
H	4.364137	14.855713	6.707925
C	5.402413	16.483377	7.669396
H	6.305569	16.621004	8.289198
H	5.600237	17.003824	6.717325
C	4.197098	17.100342	8.374187
H	3.326618	17.064048	7.693882
H	4.377317	18.166068	8.592050
C	3.859365	16.346119	9.657997
H	2.953706	16.766893	10.124750
H	4.675604	16.489451	10.387390
C	3.674478	14.851724	9.410019
H	2.781840	14.690791	8.779281
H	3.476086	14.329910	10.359308
C	10.631779	13.328360	9.380498
C	10.784862	14.730838	9.517668
C	11.696217	15.391502	8.692389
H	11.819938	16.471145	8.788386
C	12.450931	14.721331	7.725426
C	12.299632	13.339145	7.625849

H	12.891934	12.790221	6.889161
C	11.406240	12.626039	8.428530
C	9.956999	15.479457	10.541353
H	9.875632	14.832361	11.429703
C	10.584455	16.789856	11.022208
H	11.619683	16.610221	11.356013
H	10.647940	17.502826	10.181870
C	9.759812	17.423319	12.139287
H	10.221206	18.370579	12.463253
H	9.769721	16.755517	13.019840
C	8.316012	17.653629	11.700133
H	8.300332	18.407380	10.891574
H	7.722270	18.074038	12.528460
C	7.684023	16.362206	11.191414
H	7.597351	15.639631	12.021426
H	6.658662	16.548927	10.836864
C	8.513314	15.725836	10.082880
H	8.519098	16.364705	9.184195
H	8.049227	14.773744	9.782512
C	13.348501	15.471985	6.772702
H	13.321978	16.538765	7.062026
C	12.811149	15.377180	5.338188
H	12.780064	14.313915	5.039108
H	11.769610	15.726324	5.325191
C	13.663712	16.159335	4.346455
H	13.598754	17.237173	4.583181
H	13.265263	16.043908	3.324425
C	15.123163	15.714494	4.406457
H	15.738973	16.313389	3.715712
H	15.193973	14.667597	4.058572
C	15.673561	15.806713	5.828808
H	16.715189	15.447360	5.861073
H	15.702715	16.867957	6.136644
C	14.814046	15.023356	6.819040
H	15.202123	15.129974	7.844805
H	14.869217	13.946759	6.577892
C	11.342022	11.119258	8.312829
H	10.474245	10.778728	8.904706
C	11.138211	10.631616	6.873722
H	10.195057	11.054688	6.485827
H	11.948491	11.019301	6.231908
C	11.115564	9.111713	6.786044
H	10.225455	8.738291	7.318579
H	10.998808	8.798541	5.737129
C	12.360704	8.477577	7.395381
H	13.246074	8.760947	6.797231
H	12.293256	7.377872	7.350483
C	12.557540	8.946045	8.833632
H	13.479130	8.517324	9.260671
H	11.724089	8.572112	9.455519
C	12.598165	10.467924	8.917238
H	13.485317	10.843782	8.376658
H	12.720858	10.788748	9.962446
Na	8.276740	13.367016	5.483942

7

Mg	5.475901	7.925828	8.094275
N	6.351742	6.400026	9.256522
N	5.535897	6.785678	6.384040
C	6.406214	6.909801	10.573964

C	5.296780	6.741718	11.439786
C	5.277568	7.418509	12.664411
H	4.419484	7.289229	13.328078
C	6.305958	8.275411	13.040295
H	6.257576	8.827764	13.979959
C	7.372029	8.470941	12.168014
H	8.161789	9.172010	12.447607
C	7.441724	7.812270	10.934142
C	4.098118	5.898864	11.044063
H	4.337153	5.415064	10.084717
C	3.789069	4.797284	12.060327
H	4.658644	4.146483	12.233870
H	2.959093	4.165561	11.706485
H	3.490489	5.218414	13.033340
C	2.876284	6.794622	10.823271
H	2.607449	7.332289	11.746017
H	2.001954	6.207283	10.505809
H	3.081098	7.554318	10.050217
C	8.622326	8.085258	10.017483
H	8.424829	7.560786	9.068228
C	9.927868	7.531396	10.596154
H	10.180913	8.028840	11.546046
H	10.763959	7.695582	9.897969
H	9.861194	6.452209	10.794850
C	8.761021	9.577131	9.709278
H	7.865322	9.951233	9.188002
H	9.629801	9.766065	9.062646
H	8.888300	10.173327	10.624981
C	7.352422	4.080778	9.632856
C	6.694544	5.211688	8.787130
C	6.507336	4.857213	7.427405
H	6.840341	3.851500	7.199122
C	6.000685	5.545166	6.302480
C	6.048848	4.709036	4.989043
C	7.588216	4.403924	11.111474
H	8.229675	5.279589	11.257094
H	8.089344	3.540838	11.577302
H	6.658708	4.585294	11.660632
C	6.450746	2.833743	9.582368
H	5.451125	3.058847	9.983970
H	6.888517	2.030709	10.196323
H	6.322020	2.445207	8.563273
C	8.730624	3.761533	9.021748
H	8.661560	3.392939	7.989595
H	9.236486	2.989224	9.622685
H	9.369914	4.657639	9.013455
C	5.198785	3.440213	5.187138
H	5.571293	2.801597	5.999079
H	5.196248	2.842682	4.261675
H	4.155976	3.705497	5.420560
C	7.513545	4.329441	4.702376
H	8.134503	5.232056	4.595263
H	7.576375	3.762222	3.760089
H	7.954988	3.712940	5.496720
C	5.515153	5.402838	3.730970
H	4.458674	5.679257	3.816089
H	5.609173	4.701336	2.887148
H	6.073370	6.309484	3.472455
C	5.050846	7.646163	5.370422
C	5.931964	8.575598	4.770902

C	5.410666	9.559339	3.929052
H	6.100198	10.275967	3.474584
C	4.043523	9.661834	3.658065
C	3.192786	8.736427	4.265971
H	2.118438	8.809425	4.073740
C	3.663394	7.739191	5.125118
C	7.415898	8.532397	5.050422
H	7.609699	7.652661	5.685668
C	8.258298	8.363079	3.778659
H	7.934247	7.462632	3.232988
H	8.075644	9.215453	3.100650
C	9.747103	8.286340	4.103284
H	9.939157	7.376116	4.700412
H	10.335230	8.180064	3.177021
C	10.206895	9.509538	4.892323
H	10.109427	10.407530	4.255181
H	11.275947	9.424482	5.147768
C	9.370688	9.698322	6.155636
H	9.684742	10.605463	6.696583
H	9.552622	8.849686	6.838857
C	7.880749	9.764424	5.839882
H	7.285417	9.854755	6.766902
H	7.663701	10.673465	5.250884
C	2.693907	6.815272	5.824909
H	3.286916	6.025724	6.314721
C	1.938585	7.559192	6.936026
H	2.659249	8.035014	7.626392
H	1.367818	8.389307	6.482798
C	0.994586	6.633628	7.693368
H	1.592663	5.870966	8.222215
H	0.451514	7.195103	8.471063
C	0.019885	5.935093	6.749550
H	-0.647631	6.688700	6.293327
H	-0.629896	5.242055	7.308864
C	0.763667	5.192371	5.641995
H	0.049861	4.720963	4.946640
H	1.351553	4.369464	6.088125
C	1.704071	6.123089	4.880176
H	1.104963	6.884140	4.350329
H	2.253235	5.567487	4.102845
Mg	5.062396	9.939464	9.900319
C	3.503465	10.751994	2.763562
C	3.745508	12.151514	3.349874
C	4.058807	10.666785	1.334659
H	2.408995	10.611280	2.698015
C	3.187985	13.251620	2.451351
H	4.832566	12.300574	3.480277
H	3.303477	12.214324	4.355802
C	3.496428	11.767599	0.439053
H	5.159431	10.754146	1.372247
H	3.842954	9.671155	0.914539
C	3.743699	13.152497	1.033117
H	3.406498	14.241332	2.884836
H	2.086524	13.166142	2.416162
H	3.933845	11.696749	-0.570408
H	2.408544	11.614774	0.316593
H	3.303183	13.932040	0.390058
H	4.831781	13.346421	1.056676
Mg	4.701664	11.944437	11.742578
N	3.543156	13.357488	10.683112

N	4.751219	13.121697	13.431486
C	3.304496	12.772705	9.419295
C	2.191782	11.914085	9.240205
C	2.081766	11.177536	8.055086
H	1.224734	10.513655	7.920258
C	3.053705	11.243635	7.063280
H	2.975771	10.631451	6.163549
C	4.164440	12.058148	7.260334
H	4.942835	12.082953	6.494954
C	4.316497	12.822257	8.423888
C	1.152005	11.719858	10.328589
H	1.393408	12.420031	11.142983
C	-0.268287	12.029212	9.849856
H	-0.346516	13.044083	9.432982
H	-0.983359	11.949812	10.683748
H	-0.593780	11.323718	9.069029
C	1.240181	10.299908	10.893991
H	1.050672	9.548469	10.111633
H	0.505744	10.144551	11.698030
H	2.245857	10.100869	11.301043
C	5.561692	13.677124	8.588077
H	5.537388	14.094200	9.607962
C	5.577588	14.849339	7.602186
H	5.608691	14.489952	6.561095
H	6.463928	15.482589	7.765519
H	4.685747	15.483415	7.706991
C	6.837767	12.844875	8.452165
H	6.876402	12.062684	9.227575
H	7.731612	13.474936	8.565578
H	6.899004	12.349582	7.471618
C	2.268876	15.553746	10.413193
C	3.125595	14.507068	11.186133
C	3.439449	14.906388	12.509471
H	3.029515	15.874895	12.771096
C	4.179803	14.313495	13.556034
C	4.249560	15.193725	14.839952
C	1.908673	15.186318	8.970446
H	2.790424	15.024705	8.341166
H	1.335296	16.019999	8.535527
H	1.289979	14.285798	8.902312
C	0.943691	15.760547	11.169630
H	0.388030	14.813894	11.249483
H	0.310171	16.479187	10.625744
H	1.093325	16.146294	12.186887
C	3.055750	16.876778	10.351730
H	3.256686	17.297725	11.345809
H	2.485742	17.624575	9.777834
H	4.023684	16.729593	9.848910
C	2.815128	15.420346	15.353250
H	2.180220	15.936816	14.621132
H	2.836893	16.028086	16.271780
H	2.333945	14.460162	15.595788
C	4.904065	16.539580	14.475933
H	5.916621	16.381394	14.073852
H	4.991942	17.168537	15.376042
H	4.331404	17.102155	13.726663
C	5.051757	14.616051	16.010898
H	4.644010	13.668453	16.379254
H	5.015617	15.339858	16.840242
H	6.105618	14.447511	15.762961

C	5.551370	12.399418	14.348929
C	6.959518	12.508156	14.279386
C	7.745218	11.645893	15.044968
H	8.832882	11.735601	14.982943
C	7.188685	10.677612	15.885709
C	5.796728	10.585604	15.933106
H	5.343372	9.827561	16.578334
C	4.965769	11.416069	15.174911
C	7.611388	13.526238	13.373371
H	6.812944	14.175236	12.978498
C	8.610889	14.433524	14.101991
H	8.116527	14.928319	14.953499
H	9.421832	13.819295	14.531076
C	9.213479	15.468572	13.156402
H	8.413698	16.145643	12.804530
H	9.939061	16.100001	13.694976
C	9.874620	14.802497	11.952513
H	10.739650	14.208393	12.299698
H	10.276773	15.563020	11.263133
C	8.897582	13.884535	11.222340
H	9.397640	13.376093	10.382531
H	8.089437	14.494846	10.781112
C	8.279638	12.857378	12.163907
H	7.538812	12.233006	11.630589
H	9.057951	12.159792	12.522271
C	3.466876	11.233483	15.215429
H	3.017518	12.073304	14.660442
C	3.047342	9.944905	14.493010
H	3.448981	9.947040	13.463237
H	3.521058	9.084098	14.997876
C	1.533316	9.771589	14.485291
H	1.085344	10.585472	13.888939
H	1.259272	8.830919	13.980300
C	0.956476	9.815845	15.897603
H	1.325649	8.944698	16.469125
H	-0.141851	9.725567	15.868337
C	1.367816	11.097402	16.618639
H	0.972655	11.106023	17.647673
H	0.914500	11.964087	16.103699
C	2.884735	11.263932	16.634484
H	3.330081	10.451347	17.234786
H	3.165950	12.204945	17.134031
C	8.062948	9.766556	16.713486
C	8.967795	8.874239	15.850352
C	8.898583	10.550971	17.735364
H	7.393258	9.096522	17.283173
C	9.841511	7.958773	16.704039
H	9.613476	9.515569	15.223762
H	8.352480	8.284162	15.153676
C	9.773089	9.633595	18.585388
H	9.541012	11.268377	17.194194
H	8.230280	11.154713	18.370367
C	10.665737	8.752018	17.714923
H	10.498692	7.352790	16.059055
H	9.194802	7.244187	17.245231
H	10.382569	10.229939	19.284191
H	9.126134	8.990763	19.209823
H	11.265953	8.072344	18.341824
H	11.385356	9.391655	17.171665

8

Mg	7.584440	4.845971	19.423719
N	7.331729	5.068260	17.339397
N	9.649176	4.699151	19.090875
C	5.935386	4.929817	17.239920
C	5.093944	6.007831	17.591765
C	3.735362	5.758450	17.795112
H	3.081991	6.592205	18.063626
C	3.172451	4.488572	17.648321
C	4.023396	3.441873	17.278074
H	3.614686	2.440718	17.145190
C	5.391045	3.636214	17.066322
C	5.618557	7.425313	17.674323
H	6.706314	7.387166	17.499926
C	4.999057	8.295030	16.566103
H	5.222389	7.857121	15.581059
H	3.899666	8.271734	16.667915
C	5.473348	9.741978	16.628692
H	6.562409	9.779363	16.444914
H	5.003565	10.330120	15.823388
C	5.169021	10.355089	17.991495
H	4.073159	10.395057	18.131300
H	5.527826	11.396374	18.041190
C	5.789269	9.527814	19.111806
H	6.886997	9.605190	19.053437
H	5.508083	9.942059	20.090273
C	5.377853	8.062913	19.047521
H	5.911350	7.480707	19.820707
H	4.309202	7.980392	19.293355
C	6.299866	2.504729	16.636053
H	7.074985	2.951755	15.993781
C	7.066232	1.838635	17.786949
H	6.350531	1.347902	18.469002
H	7.593446	2.598817	18.385102
C	8.078654	0.832151	17.249210
H	8.835548	1.379543	16.659746
H	8.624184	0.354618	18.078267
C	7.407590	-0.224332	16.377177
H	8.156679	-0.921496	15.967658
H	6.730496	-0.829571	17.006426
C	6.600327	0.415864	15.250957
H	7.291021	0.918765	14.550127
H	6.074660	-0.357084	14.666641
C	5.603363	1.438604	15.787870
H	4.847624	0.916019	16.397697
H	5.055337	1.917284	14.959677
C	7.973047	5.331808	14.892862
C	8.258308	5.050950	16.397545
C	9.626562	4.876390	16.705963
H	10.277707	4.868062	15.841285
C	10.298194	4.720398	17.936758
C	8.705550	4.324038	13.989870
H	9.799082	4.392562	14.060974
H	8.435075	4.508091	12.938556
H	8.416516	3.290420	14.235026
C	8.500575	6.754969	14.622802
H	7.986013	7.485719	15.265210
H	8.319896	7.036878	13.572936
H	9.578362	6.834120	14.822630
C	6.497649	5.302434	14.481915

H	6.044003	4.310586	14.599695
H	6.430367	5.574491	13.416885
H	5.887134	6.014948	15.045038
C	10.121843	4.927563	20.398453
C	10.071632	3.896382	21.357283
C	10.217997	4.224099	22.710413
H	10.173483	3.418611	23.445184
C	10.398518	5.537927	23.139632
C	10.513526	6.534239	22.160343
H	10.691722	7.562591	22.484084
C	10.393265	6.261692	20.800002
C	9.874812	2.455991	20.933718
H	9.754346	2.452630	19.836730
C	11.091640	1.579058	21.265059
H	11.997018	1.995385	20.796485
H	11.269558	1.606354	22.354938
C	10.878412	0.134186	20.822897
H	11.762878	-0.474628	21.072469
H	10.781732	0.103921	19.722132
C	9.623925	-0.462751	21.455937
H	9.765897	-0.517230	22.550865
H	9.470224	-1.498183	21.110073
C	8.395405	0.389742	21.153126
H	8.165389	0.332104	20.076665
H	7.511934	-0.013090	21.675077
C	8.610050	1.845517	21.545729
H	8.687737	1.914555	22.643009
H	7.738980	2.459809	21.259055
C	10.542146	7.338859	19.746461
H	11.040156	6.869496	18.882633
C	9.205081	7.866264	19.206823
H	8.647244	8.354114	20.023979
H	8.585730	7.028672	18.851725
C	9.429277	8.832645	18.048741
H	9.890025	8.274977	17.214788
H	8.465780	9.206544	17.669955
C	10.331501	9.993583	18.452746
H	10.509637	10.661896	17.594406
H	9.816681	10.600235	19.219085
C	11.655559	9.486036	19.018310
H	12.282195	10.329290	19.351897
H	12.220317	8.978122	18.215453
C	11.435010	8.508124	20.168980
H	12.398296	8.125800	20.544575
H	10.967406	9.048679	21.009247
Mg	5.260854	4.858482	21.088074
C	10.385672	5.938069	24.597357
C	9.001859	6.501306	24.970488
C	10.792858	4.831855	25.572683
H	11.111496	6.764396	24.719162
C	8.935864	6.956785	26.423285
H	8.243451	5.721482	24.786386
H	8.749548	7.330264	24.291861
C	10.739134	5.307057	27.022238
H	10.107543	3.974436	25.464554
H	11.798895	4.460432	25.317990
C	9.353481	5.841588	27.377027
H	7.918898	7.306855	26.661713
H	9.604085	7.825656	26.564807
H	11.020726	4.485290	27.700820

H	11.487109	6.106300	27.174605
H	9.329421	6.195216	28.420773
H	8.621438	5.016852	27.309188
C	1.676559	4.328858	17.803443
C	0.937546	4.994037	16.630030
C	1.210114	2.885248	17.971519
H	1.384164	4.874041	18.719628
C	-0.577287	4.899856	16.779691
H	1.254665	4.498420	15.694529
H	1.252178	6.046057	16.540189
C	-0.305297	2.785825	18.107332
H	1.525707	2.292655	17.094995
H	1.707766	2.446414	18.849971
C	-1.028745	3.450903	16.940804
H	-1.075482	5.367905	15.914854
H	-0.888016	5.477812	17.669273
H	-0.608672	1.730304	18.202277
H	-0.614305	3.280178	19.042441
H	-2.120287	3.399008	17.086838
H	-0.811672	2.896216	16.009754
C	11.825264	4.450309	17.803813
C	12.489785	5.440351	16.831931
C	12.620623	4.510063	19.112228
C	11.949788	3.015879	17.251625
H	12.119305	5.352062	15.802194
H	12.333347	6.480234	17.157812
H	13.575014	5.256762	16.804155
H	12.250820	3.805332	19.863274
H	13.667431	4.246329	18.894591
H	12.617862	5.509325	19.564955
H	13.011108	2.739888	17.144424
H	11.478027	2.294682	17.936626
H	11.464245	2.914100	16.270884
Mg	3.278097	4.949161	23.146520
N	2.449927	3.335067	24.215035
N	2.346642	6.256679	24.492970
C	2.737202	2.272402	23.337090
C	4.041865	1.737496	23.286708
C	4.398328	0.946096	22.193924
H	5.420328	0.565166	22.137150
C	3.500288	0.618652	21.174460
C	2.195809	1.114453	21.280244
H	1.460078	0.855655	20.519661
C	1.798975	1.946404	22.331195
C	5.026457	1.972356	24.412697
H	4.496174	2.526994	25.205098
C	5.509889	0.642698	25.015406
H	4.646817	0.068156	25.388387
H	5.962623	0.028400	24.217646
C	6.539399	0.847776	26.121305
H	6.071881	1.394839	26.960233
H	6.858254	-0.126489	26.526640
C	7.740895	1.637726	25.610409
H	8.252828	1.048067	24.827704
H	8.478242	1.793475	26.415373
C	7.298025	2.975446	25.029309
H	6.916324	3.610026	25.844532
H	8.152532	3.515307	24.595993
C	6.223005	2.815896	23.964518
H	5.868549	3.809758	23.636129

H	6.660979	2.348940	23.071719
C	0.401536	2.521441	22.417260
H	0.153897	2.599838	23.487086
C	0.305457	3.953152	21.872164
H	0.546380	3.952727	20.796676
H	1.060951	4.594001	22.353461
C	-1.072296	4.552095	22.132901
H	-1.199387	4.662148	23.224179
H	-1.131572	5.568887	21.712469
C	-2.188813	3.677442	21.569602
H	-3.173602	4.095712	21.834806
H	-2.137017	3.689190	20.466732
C	-2.075323	2.235645	22.060054
H	-2.272364	2.207013	23.147094
H	-2.850743	1.609306	21.589542
C	-0.689534	1.650741	21.792033
H	-0.533342	1.575466	20.703566
H	-0.619918	0.624697	22.189135
C	1.142058	2.130979	26.033476
C	1.624544	3.383980	25.245879
C	1.179758	4.612786	25.785092
H	0.479615	4.506471	26.603734
C	1.498123	5.948457	25.465066
C	-0.382342	2.157604	26.237971
H	-0.721525	3.013342	26.836754
H	-0.700244	1.243068	26.762362
H	-0.911738	2.191409	25.273663
C	1.848196	2.183097	27.402904
H	2.941217	2.159750	27.275772
H	1.558104	1.311820	28.011771
H	1.594206	3.094844	27.961285
C	1.491113	0.783069	25.396182
H	0.996396	0.627678	24.429723
H	1.159441	-0.018337	26.074743
H	2.568516	0.660609	25.240691
C	3.104705	7.431698	24.318914
C	2.969720	8.191561	23.135756
C	3.934442	9.164035	22.840948
H	3.829282	9.739385	21.918858
C	5.020716	9.405803	23.683461
C	5.102856	8.670107	24.872111
H	5.939503	8.867012	25.546887
C	4.173320	7.692555	25.212922
C	1.763344	7.990240	22.242938
H	1.242047	7.090201	22.614180
C	0.768920	9.156885	22.355297
H	0.510629	9.335028	23.409911
H	1.259894	10.080234	21.998945
C	-0.493938	8.894217	21.540348
H	-1.187168	9.747408	21.622783
H	-1.021221	8.023853	21.971251
C	-0.168090	8.610689	20.076317
H	0.247509	9.525797	19.616621
H	-1.086437	8.371175	19.515066
C	0.849178	7.481206	19.941120
H	0.393448	6.532969	20.274894
H	1.114568	7.335500	18.881811
C	2.101951	7.744847	20.769736
H	2.624469	8.629237	20.365884
H	2.804210	6.896636	20.693728

C	4.294280	6.895621	26.492266
H	3.273391	6.645263	26.818887
C	4.999312	5.548995	26.288836
H	6.040723	5.732533	25.974388
H	4.515304	4.993959	25.469944
C	4.955683	4.716567	27.565418
H	3.902214	4.469022	27.781087
H	5.472820	3.755390	27.416676
C	5.559505	5.468346	28.747870
H	5.477261	4.867997	29.668744
H	6.638753	5.615849	28.567631
C	4.895087	6.829549	28.938048
H	5.376360	7.381103	29.762243
H	3.841870	6.680820	29.237868
C	4.935785	7.655599	27.655176
H	4.427862	8.623623	27.797691
H	5.987347	7.889856	27.416509
C	6.144089	10.356676	23.342103
C	7.277054	9.610767	22.615973
C	5.724309	11.600041	22.554987
H	6.564566	10.712683	24.301427
C	8.462302	10.522371	22.319668
H	6.881264	9.190859	21.676640
H	7.592640	8.746882	23.220880
C	6.916133	12.510436	22.265988
H	5.270003	11.298756	21.595987
H	4.941914	12.144113	23.108714
C	8.033210	11.762360	21.540669
H	9.234630	9.967531	21.764388
H	8.929588	10.833393	23.271865
H	6.592312	13.383728	21.676353
H	7.308005	12.908335	23.219804
H	8.894888	12.428260	21.369518
H	7.674645	11.454184	20.542659
C	3.967281	-0.260634	20.029830
C	4.509676	-1.608305	20.535012
C	2.914766	-0.499811	18.947669
H	4.813450	0.267116	19.547435
C	5.047762	-2.473278	19.399698
H	3.691597	-2.138309	21.055868
H	5.295662	-1.442740	21.287654
C	3.445967	-1.368104	17.811054
H	2.038020	-0.996106	19.401749
H	2.557407	0.461769	18.550742
C	3.993281	-2.697744	18.320202
H	5.409138	-3.436724	19.794942
H	5.925716	-1.973399	18.951363
H	2.655536	-1.534941	17.061154
H	4.254123	-0.825269	17.291140
H	4.410741	-3.287034	17.487245
H	3.164658	-3.295421	18.741782
C	0.662554	7.011943	26.238326
C	0.516178	6.657886	27.728295
C	1.194115	8.448201	26.178024
C	-0.724836	6.996348	25.564678
H	-0.078421	5.751293	27.902887
H	1.499901	6.514840	28.200938
H	0.007496	7.481136	28.252897
H	1.310613	8.816362	25.154402
H	0.474086	9.105879	26.689471

H	2.162165	8.560591	26.681812
H	-1.385600	7.745190	26.030382
H	-0.638372	7.235286	24.494097
H	-1.202239	6.009688	25.651269

4. References

[S1] G. M. Richardson, M. J. Evans, T. Rajeshkumar, J. A. J. McCone, S. A. Cameron, L. Maron, C. Jones, M. D. Anker, *Chem. Eur. J.*, 2024, **30**, e202400681.

[S2] R. Savka, H. Plenio, *Eur. J. Inorg. Chem.*, 2014, **2014**, 6246–6253.

[S3] J. Hicks, M. Juckel, A. Paparo, D. Dange, C. Jones, *Organometallics*, 2018, **37**, 24, 4810–4813.

[S4] P. H. M. Budzelaar, A. B. van Oort, A. G. Orpen, *Eur. J. Inorg. Chem.*, 1998, **1998**, 1485-1494.

[S5] N. P. Cowieson, D. Aragao, M. Clift, D. J. Ericsson, C. Gee, S. J. Harrop, N. Mudie, S. Panjikar, J. R. Price, A. Riboldi-Tunnicliffe, R. Williamson, and T. Caradoc-Davies. *J. Synchrotron Rad.*, 2015, **22**, 187–190.

[S6] D. Aragão, J. Aishima, H. Cherukuvada, R. Clarken, M. Clift, N. P. Cowieson, D. J. Ericsson, C. L. Gee, S. Macedo, N. Mudie, S. Panjikar, J. R. Price, A. Riboldi-Tunnicliffe, R. Rostan, R. Williamson, and T. T. Caradoc-Davies. *J. Synchrotron Rad.*, 2018, **25**, 885–891.

[S7] T. M. McPhillips, S. E. McPhillips, H.-J. Chiu, A. E. Cohen, A. M. Deacon, P. J. Ellis, E. Garman, A. Gonzalez, N. K. Sauter, R. P. Phizackerley, S. M. Soltis, and P. Kuhn. *J. Synchrotron Rad.*, 2002, **9**, 401– 406.

[S8] W. Kabsch, *J. Appl. Crystallogr.*, 1993, **26**, 795– 800.

[S9] G. M. Sheldrick. SHELX-18, **2018**, University of Göttingen.

[S10] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09*, *Revision D.01*, **2013**, Gaussian Inc., Wallingford CT,.

[S11] A. D. Becke, *J. Chem. Phys.,* 1993, **98**, 1372-1377.

[S12] J. P. Perdew in, Electronic Structures of Solids '91, P. Ziesche and H. Eschrig (eds), Akademie, Berlin, **1991**.

[S13] F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys*., 2005, **7**, 3297-3305.

[S14] S. Grimme, J. Antony, S. Ehrlich and H. Kreig, *J. Chem. Phys*., 2010, **132**, 154104.

[S15] B. Rösch, T. X. Gentner, J. Eyselein, J. Langer, H. Elsen and S. Harder, *Nature*, 2021, **592**, 717-721.

[S16] E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis and F. Weinhold, NBO 6.0., 2013; F. Weinhold and C. R. Landis, *Chem. Educ. Res. Pr*., 2001, **2**, 91–104.

[S17] E. R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García, A. J. Cohen and W. Yang, *J. Am. Chem. Soc*., 2010, **132**, 6498–6506.

[S18] T. Lu, and F. Chen. *J. Comput. Chem*., 2012, **33**, 580-592.