Zinc borylation and reduction by a diborane(4) species via B-O bond formation

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Supporting Information (47 pages total)

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1. General considerations

All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon or dinitrogen. Solvents were degassed by sparging with argon and dried by passing through a column of the appropriate drying agent. Toluene and hexane were purified using an MBraun SPS-800 solvent purification system and stored over a potassium mirror. THF and Et_2O were purified using an MBraun SPS-800 and stored over activated molecular sieves. NMR spectra were measured in benzene-d_6 (which was dried over potassium, with the solvent then being distilled under reduced pressure), or THF-d_8 (dried by storage over activated molecular sieves and degassed by three freeze pump thaw cycles) and stored under argon in Teflon valve ampoules. NMR samples were prepared under argon in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ^{1}H, $^{13}C\{^{1}H\}$, ^{31}P and ^{11}B NMR spectra were recorded on a Bruker Avance III HD nanobay 400 MHz or Bruker Avance III 500 MHz spectrometer at ambient temperature and referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane or $Et_2O{\cdot}BF_3$ (δ = 0 ppm). Assignments were confirmed using two-dimensional ^{1}H-^{1}H and ^{13}C-^{1}H NMR correlation experiments. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. Elemental analyses were carried out by London Metropolitan University. B_2pin_2, HOBpin, DMAP, CO_2 and KO^{t}Bu were used as received. MeI was degassed and stored over molecular sieves. (Nacnac^{Mes})ZnI,[S1] (Nacnac^{Mes})ZnMe,[S2] {(HCDippN)$_2$}BOH[S3] were prepared according to literature procedures.

2. X-ray crystallographic details

Single-crystal X-ray diffraction data for compounds (Nacnac^{Mes})Zn(DMAP)Bpin (**2**), (Nacnac^{Mes})Zn(DMAP)I (**3**), [(Nacnac^{Mes})ZnOBpin]$_2$ (**4**), (Nacnac^{Mes})ZnOB{(NDippCH)$_2$} (**5**) and [(Nacnac^{Mes})Zn]$_2$ (**VII**) were collected on an Oxford Diffraction/Agilent SuperNova diffractometer equipped with a 135 mm Atlas CCD area detector or a Rigaku XtaLAB Synergy-DW VHF equipped with a PhotonJet-R dual wavelength rotating anode and HyPix-Arc 150° detector. Crystals were selected under Paratone-N oil, mounted on MiTeGen Micromount loops and quench-cooled using an Oxford Cryosystems open flow N2 cooling device.[S4] Data were collected at 150 K using mirror monochromated Cu Kα radiation (λ = 1.5418 Å; Oxford Diffraction Supernova) or Mo Kα radiation (λ = 0.71073 Å; Oxford Diffraction Supernova). Data collected were processed using the CrysAlisPro package, including unit cell parameter refinement and inter-frame scaling (which was carried out using SCALE3 ABSPACK within CrysAlisPro).[S5] Equivalent reflections were merged and diffraction patterns processed with the CrysAlisPro suite.[S5] Structures were solved ab initio from the integrated intensities using SHELXT[S6] and refined on F^2 using SHELXL[S7] with the graphical interface OLEX2.[S8] Selected crystallographic data are summarised in Table S1 and full details are given in the supplementary deposited CIF files (CCDC 2385165-2385169). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/ data_request/cif.

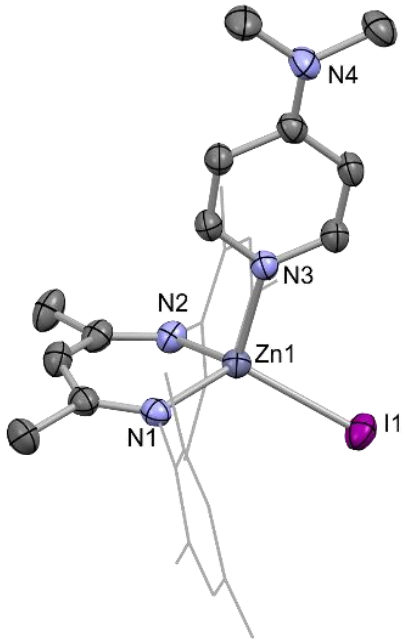

Fig S1. *Molecular structure of (Nacnac^{Mes})Zn(DMAP)I, as determined by single crystal X-ray crystallography. Hydrogen atoms omitted and some residues displayed as wireframe for clarity. Key bond lengths (Å) and bond angles (°): Zn1-N1 2.000(2), Zn1-N2 1.989(2), Zn1-N3 2.047(2), Zn1-I1 2.5572(5), N1-Zn1-N1 96.88(7), N3-Zn1-I1 106.46(5).*

Table S1. *Crystallographic data for compounds (Nacnac^{Mes})Zn(DMAP)Bpin (**2**), (Nacnac^{Mes})Zn(DMAP)I (**3**), [(Nacnac^{Mes})ZnOBpin]$_2$ (**4**), (Nacnac^{Mes})ZnOB{(NDippCH)$_2$} (**5**) and [(Nacnac^{Mes})Zn]$_2$ (**VII**).*

Compound	**2**	**3**	**4**
Formula	$C_{36}H_{51}BN_4O_2Zn$	$C_{30}H_{39}IN_4Zn(C_6H_{14})$	$C_{58}H_{82}B_2N_4O_6Zn_2$
Fw (g mol^{-1})	647.98	734.09	1083.63
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P 2_1/c	P 2_1/n	P 2_1/n
a (Å)	13.88904(6)	8.60930(10)	14.94854(6)
b (Å)	26.07802(12)	29.1368(3)	11.80920(5)
c (Å)	2016258(9)	14.2475(2)	16.28848(6)
α (°)	90	90	90
β (°)	92.9187(4)	91.3760(10)	91.3130(4)
γ (°)	90	90	90
V (Å^{-3})	7293.39(5)	3572.92(7)	2874.654(19)
Z	8	4	2
ρ_{calc} (g cm^{-3})	1.180	1.365	1.252
Radiation, λ (Å)	1.54184	1.54184	1.54184
Absorption	Multi-scan	Multi-scan	Multi-scan
μ (mm^{-1})	1.196	7.943	1.423
Reflections collected	325188	79811	100530
Independent reflections	15080	7460	5915
$R_{(int)}$	0.0730	0.0466	0.0397
Parameters	821	335	414
R_1 (all data/I>2σ(I))	0.0386	0.0250	0.0316
ωR_2 (all data/I >2σ(I))	0.1124	0.0622	0.0864
GooF	1.079	1.039	1.095
T (K)	100.00(10)	149.98(16)	100.00(10)
CCDC reference number	2385165	2385169	2385167

Table S1 contd.

	5	**VIII**
Formula	$C_{49}H_{65}BN_4OZn$	$C_{46}H_{58}N_4Zn_2$
Fw (g mol^{-1})	802.23	797.70
Crystal system	Monoclinic	Orthorhombic
Space group	P 1 2_1/c 1	P b c a
a (Å)	16.1404(2)	21.7767(2)
b (Å)	15.15920(10)	10.91670(10)
c (Å)	19.0592(2)	36.1028(4)
α (°)	90	90
β (°)	101.4280(10)	90
γ (°)	90	90
V (Å^{-3})	4570.87(8)	8582.71(15)
Z	4	8
ρ_{calc} (g cm^{-3})	1.166	1.235
Radiation, λ (Å)	1.54184	1.54184
Absorption	Multi-scan	Multi-scan
μ (mm^{-1})	1.030	1.626
Reflections collected	103585	130609
Independent reflections	9545	8834
$R_{(int)}$	0.0488	0.0747
Parameters	542	485
R_1 (all data/I>2σ(I))	0.0319	0.0803
ωR_2 (all data/I >2σ(I))	0.0921	0.1829
GooF	1.033	1.162
T (K)	149.98(11)	100.00(10)
CCDC reference number	2385168	2385166

3. Synthesis of novel compounds

(Nacnac^{Mes})ZnBpin (1)

To an NMR tube fitted with a J-Youngs valve was added KO^{t}Bu (0.004 g, 0.04 mmol) and B_2pin_2 (0.01 g, 0.04 mmol) and C_6D_6 (0.5 ml). The suspension was heated to 80 °C for 1 h with occasional ultrasonication to yield a homogeneous mixture. To this was added (Nacnac^{Mes})ZnI (0.02 g, 0.038 mmol) before further heating at 80 °C for 12 h. The resulting solution was filtered to remove precipitated KI and the product was characterised by multinuclear NMR spectroscopy. This indicated quantitative conversion. Also present were signals corresponding to the by-product ^{t}BuOBpin.[S9]

(Nacnac^{Mes})ZnBpin

^{1}H NMR (500 MHz, benzene-d_6, 298 K): δ_H 1.02 (12 H, s, {OC(C*H*$_3$)$_2$}$_2$), 1.64 (6 H, s, Nacnac-C*H*$_3$), 2.17 (6 H, s, *p*-C*H*$_3$), 2.20 (12 H, s, *o*-C*H*$_3$), 4.99 (1 H, s, C*H*), 6.82 (4 H, s, Ar-*H*) ppm.

^{13}C{^{1}H} NMR (101 MHz, benzene-d_6): δ_C 19.0 (*o*-*C*H$_3$), 21.0 (*p*-*C*H$_3$), 22.6 (Nacnac-*C*H$_3$), 25.2, ({OC(*C*H$_3$)$_2$}$_2$), 83.1 (O*C*(CH$_3$)$_2$), 96.1 (Nacnac-*C*H), 129.3 (Ar-*C*H), 131.2 (Ar-*C*CH$_3$), 133.4 (Ar-*C*CH$_3$), 146.1 (Ar-*C*N), 166.4 (Nacnac-*C*N) ppm.

^{11}B NMR (128 MHz, benzene-d_6, 298 K): δ_B 38.8 (br) ppm

^{t}BuOBpin

^{1}H NMR (500 MHz, benzene-d_6, 298 K): δ_H 1.06 (12 H, s, {OC(C*H*$_3$)$_2$}$_2$), 1.38 (9 H, s, C(C*H*$_3$)$_3$) ppm.

^{13}C{^{1}H} NMR (101 MHz, benzene-d_6): δ_C 24.6 ({OC(*C*H$_3$)$_2$}$_2$), 30.3 (C(*C*H$_3$)$_3$, 73.5 (*C*(CH$_3$)$_3$), 81.76 (O*C*(CH$_3$)$_2$) ppm.

^{11}B NMR (128 MHz, benzene-d_6, 298 K): δ_B 21.7 ppm

(Nacnac^{Mes})Zn(DMAP)Bpin (2)

To an *in situ* generated solution of (Nacnac^{Mes})ZnBpin (0.1 mmol, 0.7 mL) in C_6D_6 (ca. 1 mL) was added DMAP (0.012 g, 0.1 mmol). The sample was sonicated briefly to aid dissolution of the DMAP, at which point NMR spectroscopy indicated that conversion was complete. Removal of volatiles *in vacuo*, extraction into hexane and filtration yielded a colourless solution. Single crystals suitable for X-ray crystallography were obtained by slow evaporation of the hexane solution. Yield 0.047 g (73 %).

^{1}H NMR (500 MHz, benzene-d_6, 298 K): δ_H 0.97 (12 H, s, {OC(C*H*$_3$)$_2$}$_2$), 1.81 (6 H, s, Nacnac-C*H*$_3$), 2.13 (6 H, s, N(C*H*$_3$)$_2$), 2.18 (6 H, s, *p*-C*H*$_3$), 2.27 (12 H, s, *o*-C*H*$_3$), 5.00 (1 H, s, C*H*), 6.02 (2 H, d, $^3J_{HH}$ = 6.24 Hz, DMAP-*m*-C*H*), 6.84 (4 H, s, Ar-*H*), 8.64 (2 H, d, $^3J_{HH}$ = 6.24 Hz, DMAP-*o*-C*H)* ppm.

^{13}C{^{1}H} NMR (101 MHz, benzene-d_6): δ_C 19.2 (*o*-*C*H$_3$), 21.0 (*p*-*C*H$_3$), 23.1 (Nacnac-*C*H$_3$), 25.7, ({OC(*C*H$_3$)$_2$}$_2$), 38.2 (N(*C*H$_3$)$_2$), 80.3 (O*C*(CH$_3$)$_2$), 93.7 (Nacnac-*C*H), 106.6 (DMAP-m-*C*H), 129.2 (Ar-*C*CH$_3$), 131.7 (Ar-*C*H), 132.3 (Ar-*C*CH$_3$), 147.6 (Ar-*C*N), 150.5 (DMAP-*o*-*C*H), 154.4 (DMAP-*p*-*C*N), 165.2 (Nacnac-*C*N) ppm.

^{11}B NMR (128 MHz, benzene-d_6, 298 K): δ_B 40.1 (br.) ppm

Elemental Microanalysis – Expected for $C_{36}H_{51}BN_4O_2Zn$: C 66.73, H 7.93, N 8.65 %. Found: C 67.04, H 8.00, N 8.27 %.

Reaction of (Nacnac^{Mes})ZnBpin (1) with MeI

To an *in situ* generated C_6D_6 solution of **1** (0.038 mmol, 0.5 mL) was added MeI (0.02 mL, excess). Immediate reaction yielded the known species (Nacnac^{Mes})ZnI and MeBpin, as determined by *in situ* NMR spectroscopy.

Reaction of (Nacnac^{Mes})Zn(DMAP)Bpin (2) with MeI

To a solution of **2** (0.01 g, 0.015 mmol) in C_6D_6 (0.5 mL) was added MeI (0.02 mL, excess). Immediate reaction yielded the known species MeBpin, as well as a new species. Removal of volatiles, extraction into hexane and filtration yielded a colourless solution, from which colourless single crystals could be obtained when left to stand. Single crystal crystallographic measurements showed that this new species was (Nacnac^{Mes})Zn(DMAP)I, for which an alternative synthesis was conducted by analogy to the reported chloride analogue, yielding a clean sample for the measurement of characterising data.[S10]

(Nacnac^{Mes})Zn(DMAP)I

^{1}H NMR (500 MHz, benzene-d_6, 298 K): δ_H 1.63 (6 H, s (br.), *o*-C*H*$_3$), 1.65 (6 H, s, Nacnac-C*H*$_3$), 2.18 (6 H, s, *p*-C*H*$_3$), 2.21 (6 H, s (br.), *o*-C*H*$_3$), 3.05 (6 H, s, N(C*H*$_3$)$_2$), 4.84 (1 H, s, C*H*), 6.66 (2 H, s, Ar-*H*), 6.67 (2 H, br., DMAP-*m*-C*H*), 6.79 (2 H, s, Ar-*H*), 8.20 (2 H, d (br.), $^3J_{HH}$ = 4.86 Hz, DMAP-*o*-C*H)* ppm.

^{13}C{^{1}H} NMR (101 MHz, benzene-d_6): δ_C 18.9, 20.1 (*o*-*C*H$_3$), 21.1 (*p*-*C*H$_3$), 23.8 (Nacnac-*C*H$_3$), 39.2 (N(*C*H$_3$)$_2$), 93.9 (Nacnac-*C*H), 107.5 (DMAP-*m*-*C*H), 129.4, 130.0 (Ar-*C*H), 132.0, 133.1, 133.7 (Ar-*C*CH$_3$), 146.3 (Ar-*C*N), 149.6 (DMAP-*o*-*C*H), 156.6 (DMAP-*p*-*C*N), 167.9 (Nacnac-*C*N) ppm.

Reaction of (Nacnac^{Mes})ZnBpin (1) with CO_2

An *in situ* generated C_6D_6 solution of **1** (0.5 mmol, 0.6 mL) was degassed by three freeze-pump-thaw cycles before the addition of one atmosphere of CO_2. Heating to 80 °C for 16 h led to the formation of one predominant species by *in situ* ^{1}H NMR spectroscopy (and CO by ^{13}C{^{1}H} NMR). Removal of volatiles, extraction into hexane and filtration yielded a colourless solution, from which colourless single crystals could be obtained when left to stand. These crystals were suitable for X-ray crystallographic measurements. The minor species observed by NMR exactly matches the signals of the known species [(Nacnac^{Mes})Zn]$_2$. An alternative direct synthesis of [(Nacnac^{Mes})ZnOBpin]$_2$ (**4**) is given below.

[(Nacnac^{Mes})ZnOBpin]$_2$ (4)

To a mixture of (Nacnac^{Mes})ZnMe (0.02 g, 0.048 mmol) and HOBpin (0.007 g, 0.049 mmol) was added benzene (0.5 mL), leading to immediate bubbling of the solution, which ceased after ca. 1 min. The resulting solution was left to stand, resulting in the formation of large colourless crystals of [(Nacnac^{Mes})ZnOBpin]$_2$. The supernatant solution was decanted, and the crystals were washed with hexane (0.5 mL), before removal of all remaining volatiles *in vacuo*.

^{1}H NMR (500 MHz, THF-d_8, 298 K): δ_H 1.01 (12 H, s, {OC(C*H*$_3$)$_2$}$_2$), 1.37 (6 H, s, Nacnac-C*H*$_3$), 1.78 (12 H, s, *o*-C*H*$_3$), 2.37 (6 H, s, *p*-C*H*$_3$), 4.69 (1 H, s, C*H*), 6.72 (4 H, s, Ar-*H*) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, THF-d_8): δ_C 18.8 (*o*-CH_3), 21.4 (*p*-CH_3), 23.3 (Nacnac-CH_3), 25.4 ({OC(CH_3)$_2$}$_2$), 81.8 (O*C*(CH_3)$_2$), 95.0 (Nacnac-*C*H), 130.0 (Ar-*C*H), 132.9 (Ar-*C*CH_3), 133.1 (Ar-*C*CH_3), 146.5 (Ar-*C*N), 168.1 (Nacnac-*C*N) ppm.

^{11}B NMR (128 MHz, THF-d_8, 298 K): δ_B 22.6 (br.) ppm

(Nacnac^{Mes})ZnOB{(NDippCH)$_2$} (5)

To a mixture of (Nacnac^{Mes})ZnMe (0.2 g, 0.48 mmol) and {(HCDippN)$_2$}BOH (0.195 g, 0.48 mmol) in a J-Young ampoule was added toluene (5 mL) before stirring at 80 °C for 16 h, during which gas evolution could be observed. Evaporation of volatiles *in vacuo* yielded a sticky solid. Extraction into hexane (5 mL), filtration and removal of solvent *in vacuo* afforded an off-white powder. Single crystals could be obtained by recrystallisation of a portion of this material by slow evaporation from hexane. These crystals were suitable for single crystal X-ray crystallographic measurements. Yield 0.311 g (80 %).

^1H NMR (500 MHz, benzene-d_6, 298 K): δ_H 1.00 (12 H, d, $^3J_{HH}$ = 6.91 Hz, CH(C*H*$_3$)$_2$), 1.21 (12 H, d, $^3J_{HH}$ = 6.91 Hz, CH(C*H*$_3$)$_2$), 1.36 (6 H, s, Nacnac-C*H*$_3$), 1.78 (12 H, s, *o*-C*H*$_3$), 2.24 (6 H, s, *p*-C*H*$_3$), 3.37 (4 H, sept., $^3J_{HH}$ = 7.01 Hz, C*H*(CH_3)$_2$) 4.73 (1 H, s, C*H*), 5.90 (2 H, s, {DippNC*H*}$_2$) 6.65 (4 H, s, Ar-*H*), 7.11 (4 H, d (br.), $^3J_{HH}$ = 7.57 Hz, Ar-*m*-*H*), 7.21 (2 H, d (br.), $^3J_{HH}$ = 7.57 Hz, Ar-*p*-*H*) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, benzene-d_6): δ_C 18.1 (*o*-CH_3), 21.1 (*p*-CH_3), 23.0 (Nacnac-CH_3), 23.7 (CH(*C*H$_3$)$_2$), 23.9 (CH(*C*H$_3$)$_2$), 28.7 (*C*H(CH_3)$_2$), 95.6 (Nacnac-*C*H), 115.6 ({DippN*C*H}$_2$), 123.3 (Dipp-*m*-*C*H), 129.9 (Mes-*m*-*C*H), 131.0 (Mes-*C*CH_3), 133.9 (Mes-*C*CH_3), 141.1 (Dipp-*C*N), 143.9 (Mes-*C*N), 146.6 (Dipp-*C*CH(CH_3)$_2$), 170.0 (Nacnac-*C*N) ppm.

^{11}B NMR (128 MHz, benzene-d_6, 298 K): δ_B 21.5 ppm

Elemental Microanalysis – Expected for $C_{49}H_{65}BN_4OZn$: C 73.36, H 8.17, N 6.98 %. Found: C 73.72, H 8.00, N 6.63 %.

Reaction of (Nacnac^{Mes})ZnBpin (1) with (Nacnac^{Mes})ZnOB{(NDippCH)$_2$} (5)

To an *in situ* generated C_6D_6 solution of **1** (0.38 mmol, 0.5 mL) was added **5** (0.03 g, 0.037 mmol), before heating to 80 °C for 12 h. NMR spectroscopy indicates clean conversion to the known species [(Nacnac^{Mes})Zn]$_2$ and one new species, which gives rise to signals consistent with the proposed complex {(HCDippN)$_2$}BOBpin.[1] Attempts at crystallisation yielded only crystals of [(Nacnac^{Mes})Zn]$_2$, as well as a stickly gel-like substance assigned to the {(HCNDipp)$_2$}BOBpin by-product.

{(HCDippN)$_2$}BOBpin

^1H NMR (500 MHz, benzene-d_6, 298 K): δ_H 0.69 (12 H, s, {OCC*H*$_3$}$_2$), 1.25 (12 H, d, $^3J_{HH}$ = 7.00 Hz, CH(C*H*$_3$)$_2$), 1.39 (12 H, d, $^3J_{HH}$ = 7.00 Hz, CH(C*H*$_3$)$_2$), 3.40 (4 H, sept., $^3J_{HH}$ = 7.00 Hz, C*H*(CH_3)$_2$), 6.01 (2 H, s, {DippNC*H*}$_2$), 7.15 (4 H, br., Ar-*m*-*H*), 7.20 (2 H, m, Ar-*p*-*H*) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, benzene-d_6): δ_C 24.3 ({OC(*C*H$_3$)$_2$}$_2$), 24.6 (CH(*C*H$_3$)$_2$), 24.8 (CH(*C*H$_3$)$_2$), 30.3 (*C*H(CH_3)$_2$), 82.2 (O*C*(CH_3)$_2$), 117.0 ({DippN*C*H}$_2$), 123.7, 129.3, 138.0 (Ar-*C*), 146.9 (Ar-*C*N) ppm.

^{11}B NMR (128 MHz, benzene-d_6, 298 K): δ_B 20.8, 21.7 ppm

4. NMR Spectra of novel compounds

(Nacnac^{Mes})ZnBpin (1)

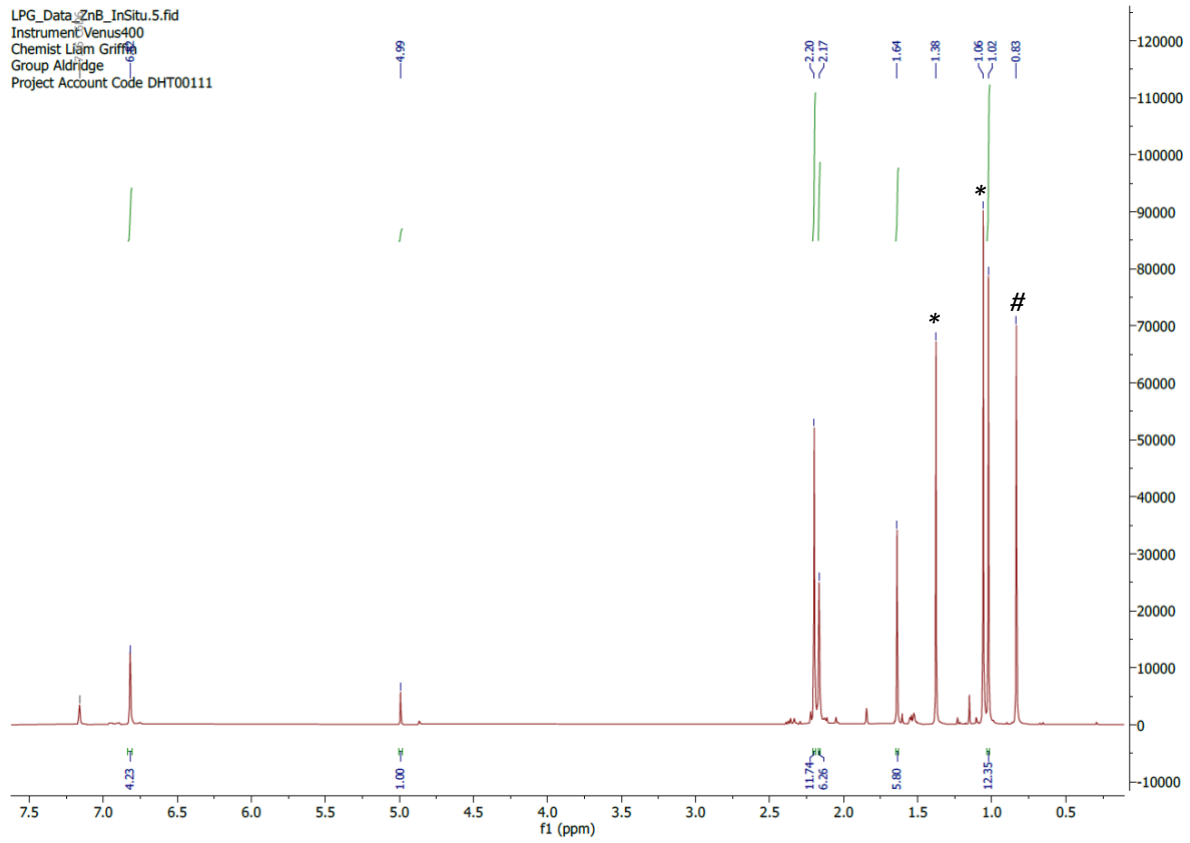

Fig S2. *In situ ^{1}H NMR spectrum of (Nacnac^{Mes})ZnBpin (**1**). ^{t}BuOBPin by-product marked * and residual B_2pin_2 marked #.*

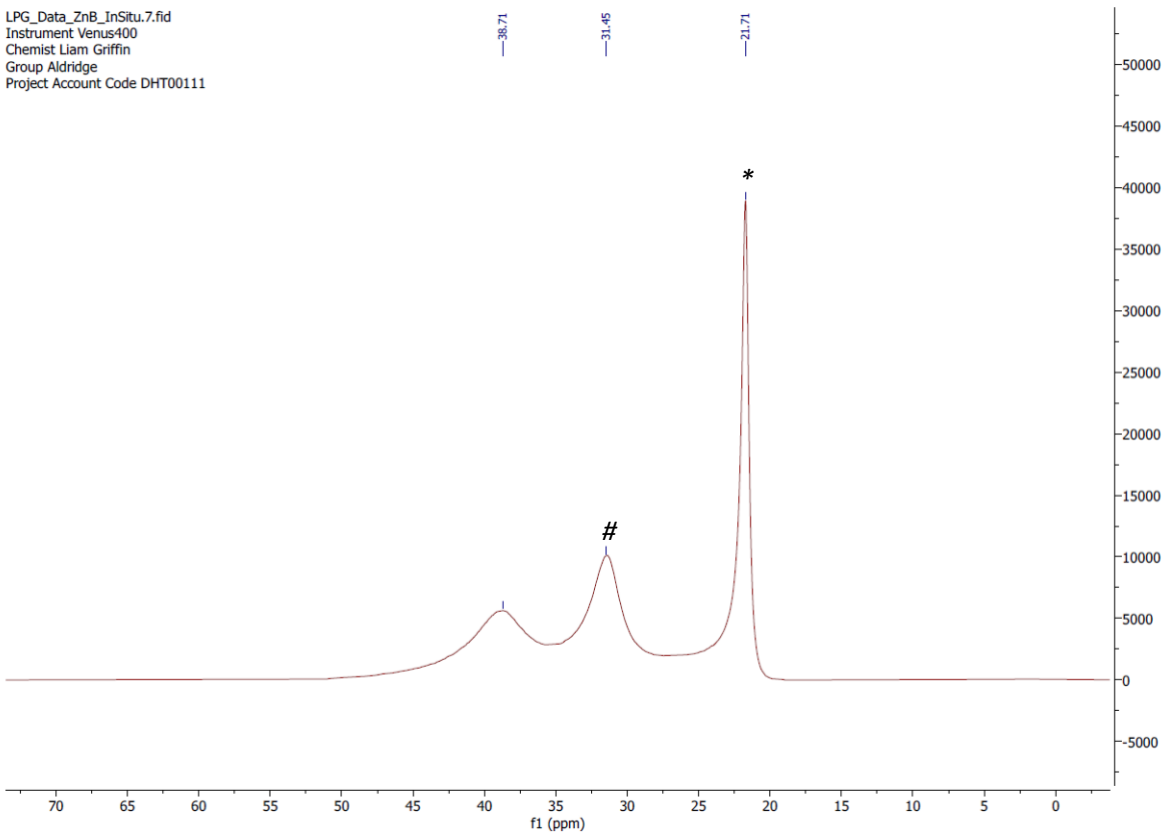

Fig S3. *In situ ^{11}B NMR spectrum of (Nacnac^{Mes})ZnBpin (**1**). ^{t}BuOBPin by-product marked * and residual B_2pin_2 marked #.*

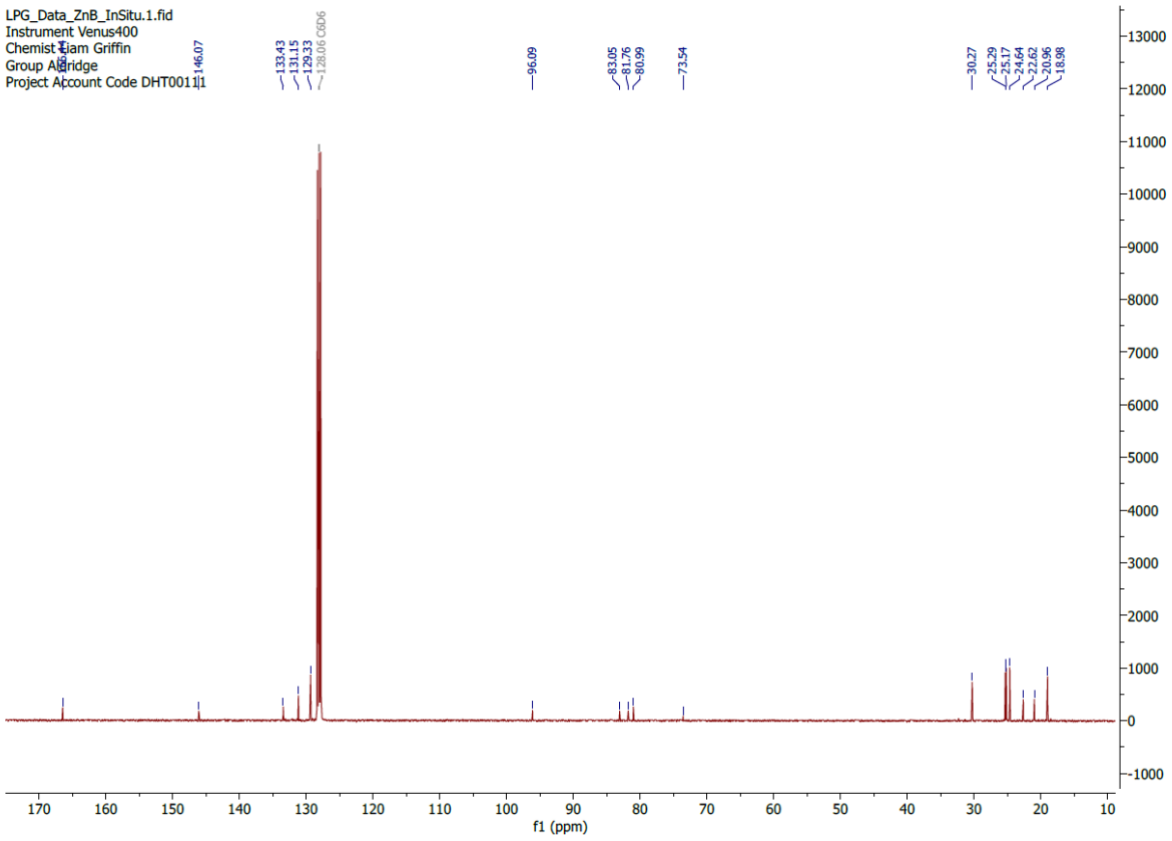

Fig S4. *In situ* ^{13}C *NMR spectrum of (Nacnac*^{Mes}*)ZnBpin (**1**).*

(Nacnac^{Mes})Zn(DMAP)Bpin (2)

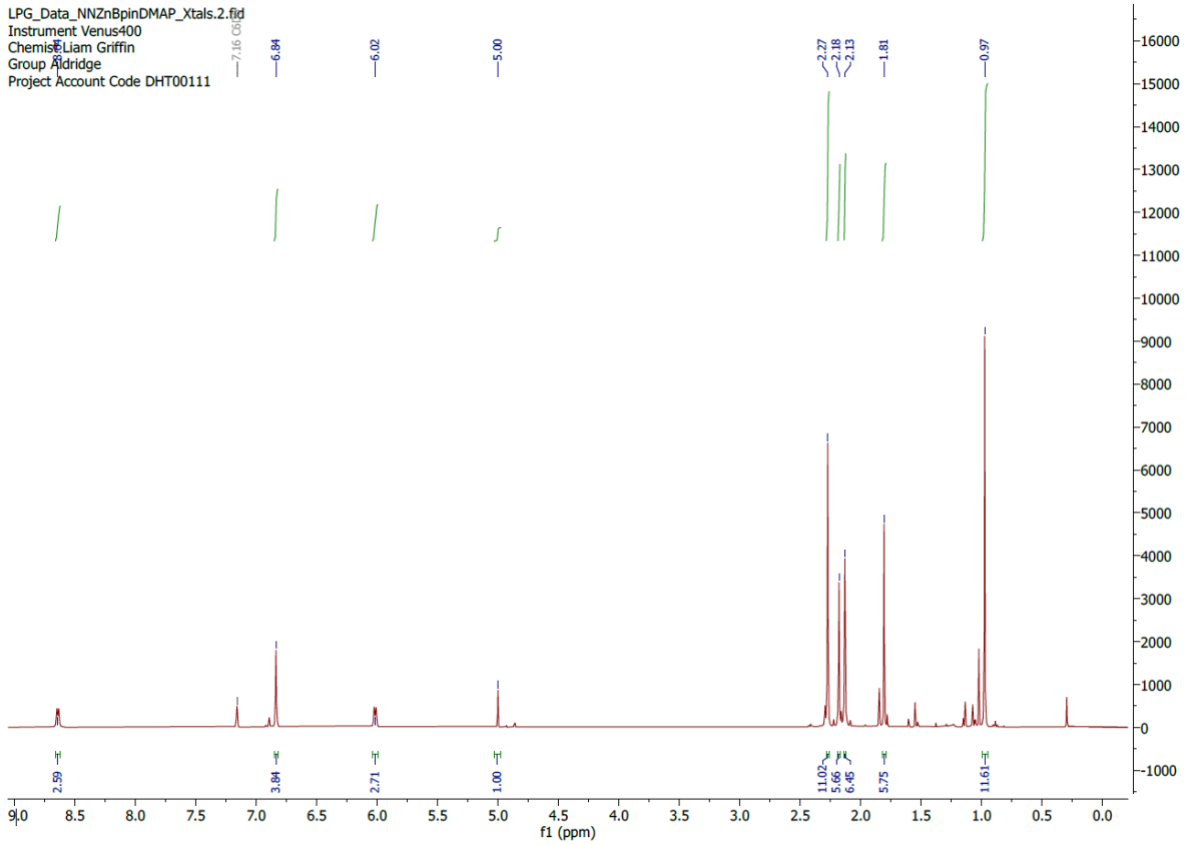

Fig S5. *^{1}H NMR spectrum of (Nacnac^{Mes})Zn(DMAP)Bpin (**2**).*

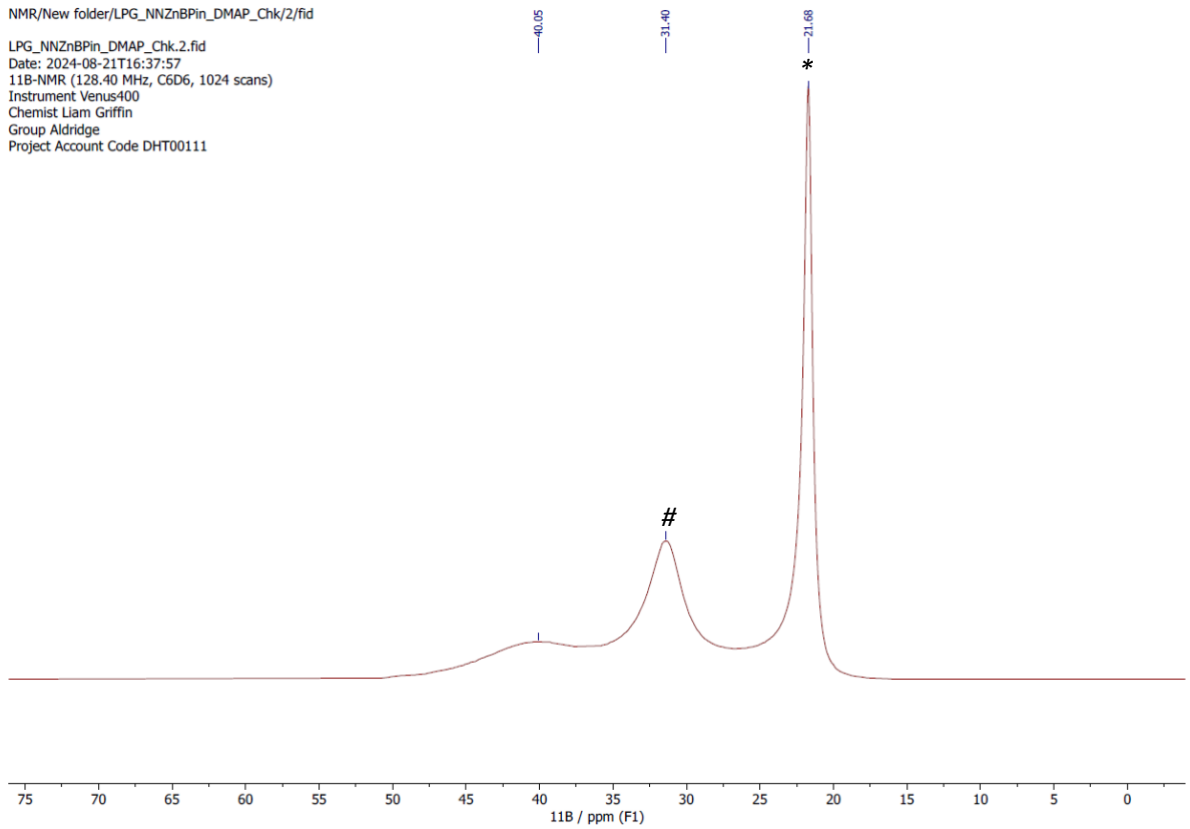

Fig S6. *In situ ^{11}B NMR spectrum of (Nacnac^{Mes})Zn(DMAP)Bpin (**2**). ^{t}BuOBPin by-product marked * and residual B_2pin_2 marked #.*

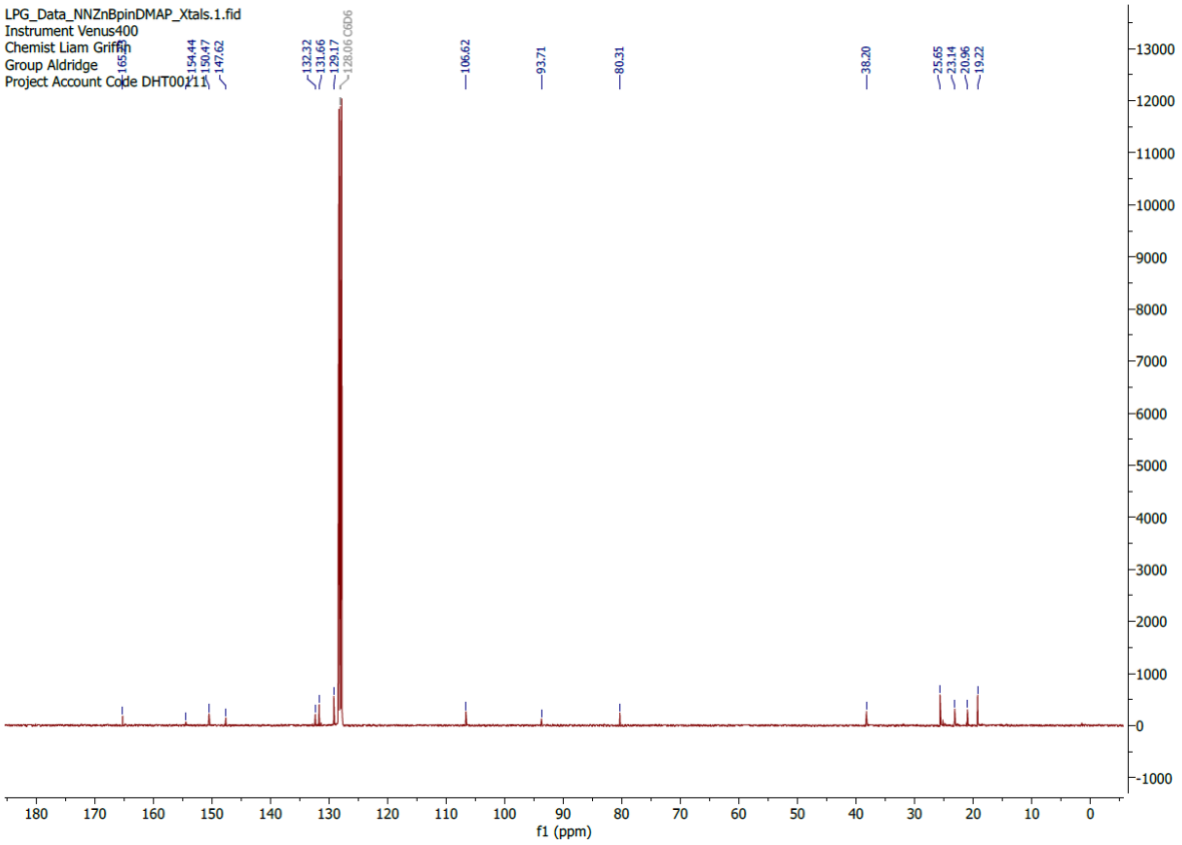

Fig S7. *^{13}C NMR spectrum of (Nacnac^{Mes})Zn(DMAP)Bpin (**2**).*

(Nacnac^{Mes})Zn(DMAP)I (3)

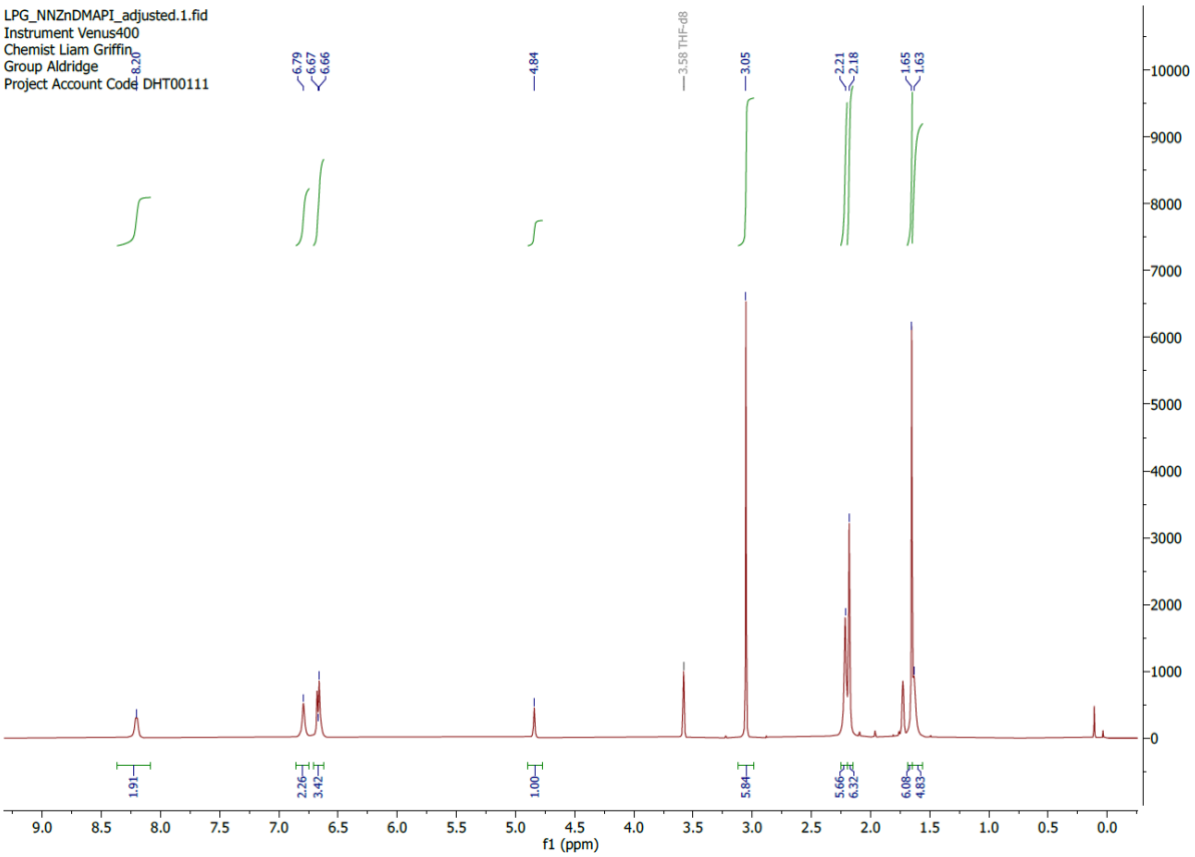

Fig S8. *^{1}H NMR spectrum of (Nacnac^{Mes})Zn(DMAP)I (**3**).*

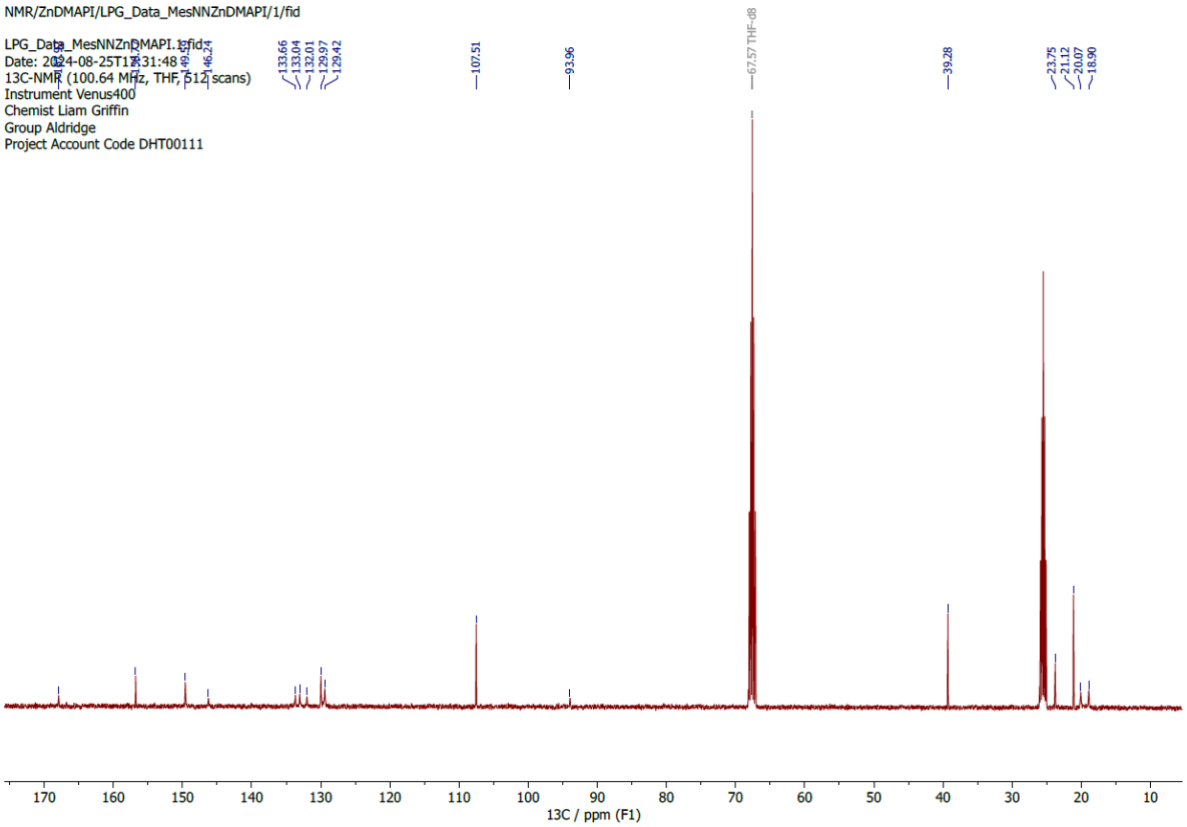

Fig S9. *^{13}C NMR spectrum of (Nacnac^{Mes})Zn(DMAP)I (**3**).*

[(Nacnac^{Mes})ZnOBpin]$_2$ (4)

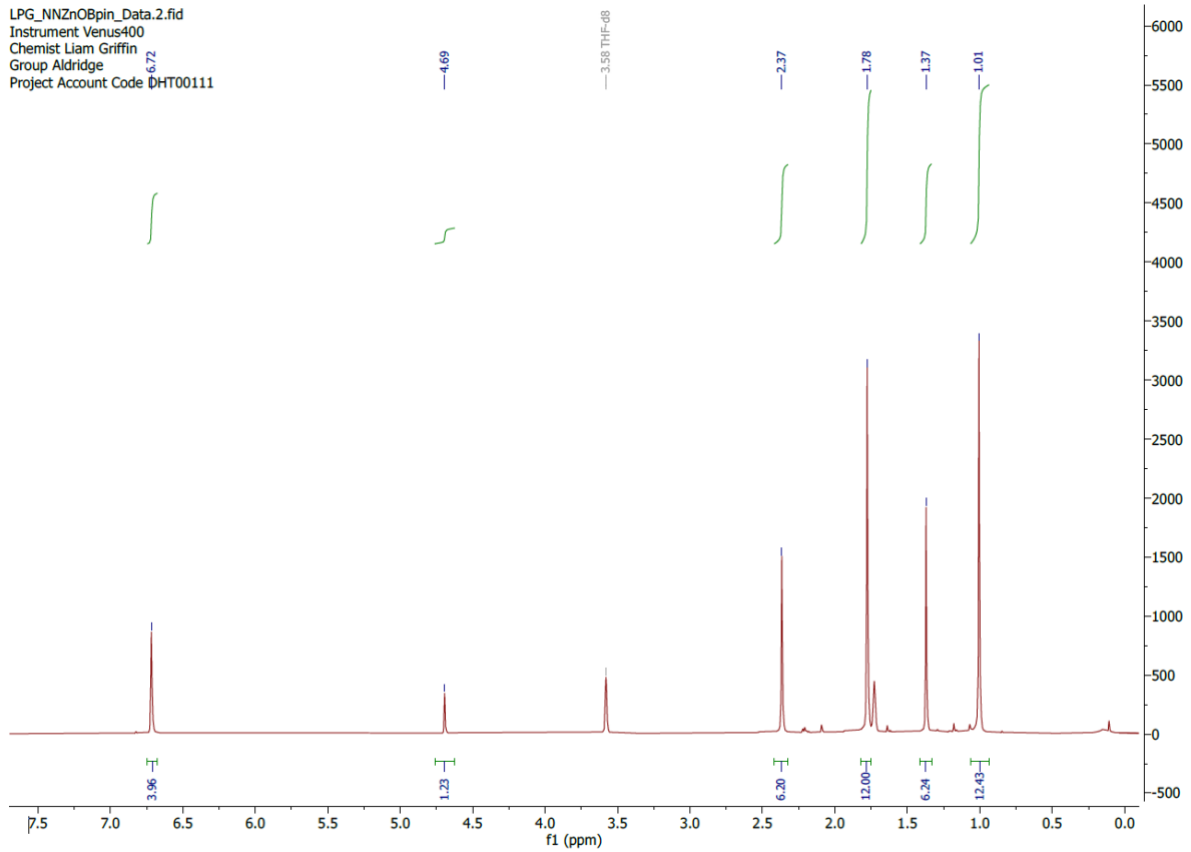

Fig S10. *^{1}H NMR spectrum of [(Nacnac^{Mes})ZnOBpin]$_2$ (**4**).*

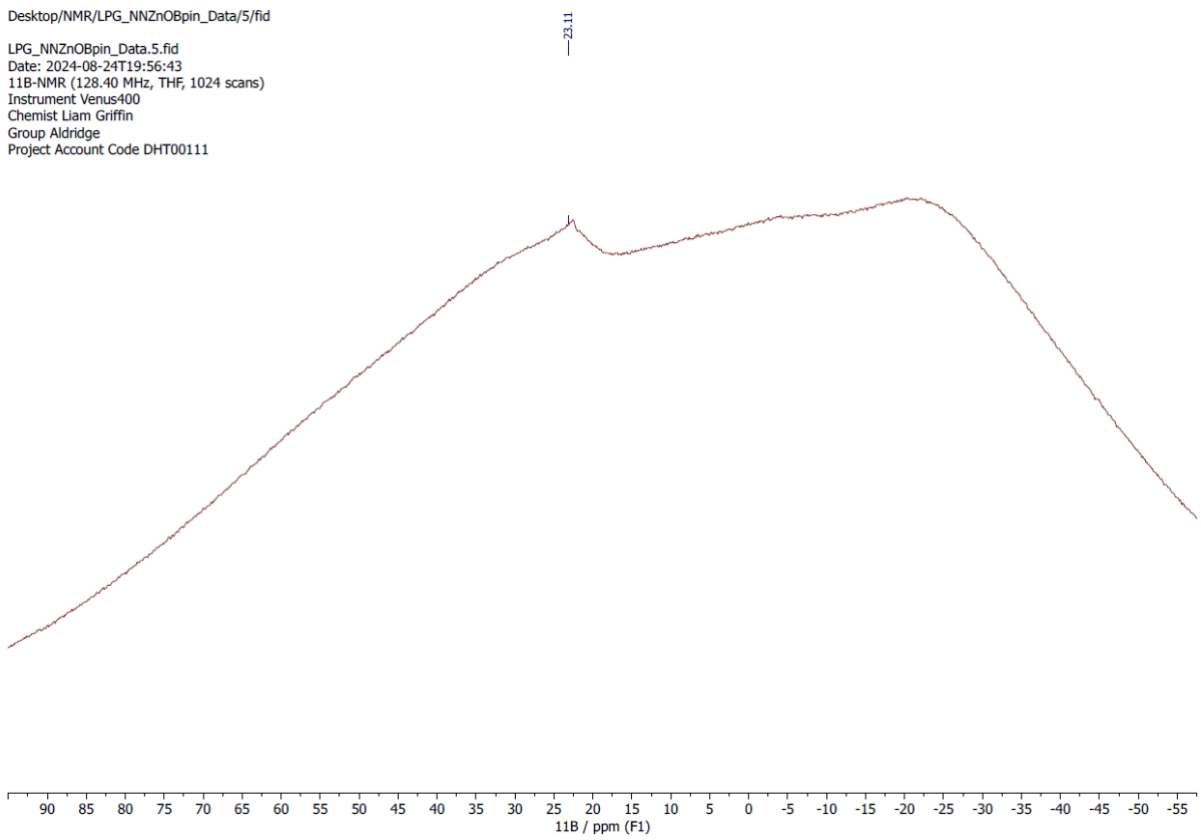

Fig S11. *^{11}B NMR spectrum of [(Nacnac^{Mes})ZnOBpin]$_2$ (**4**).*

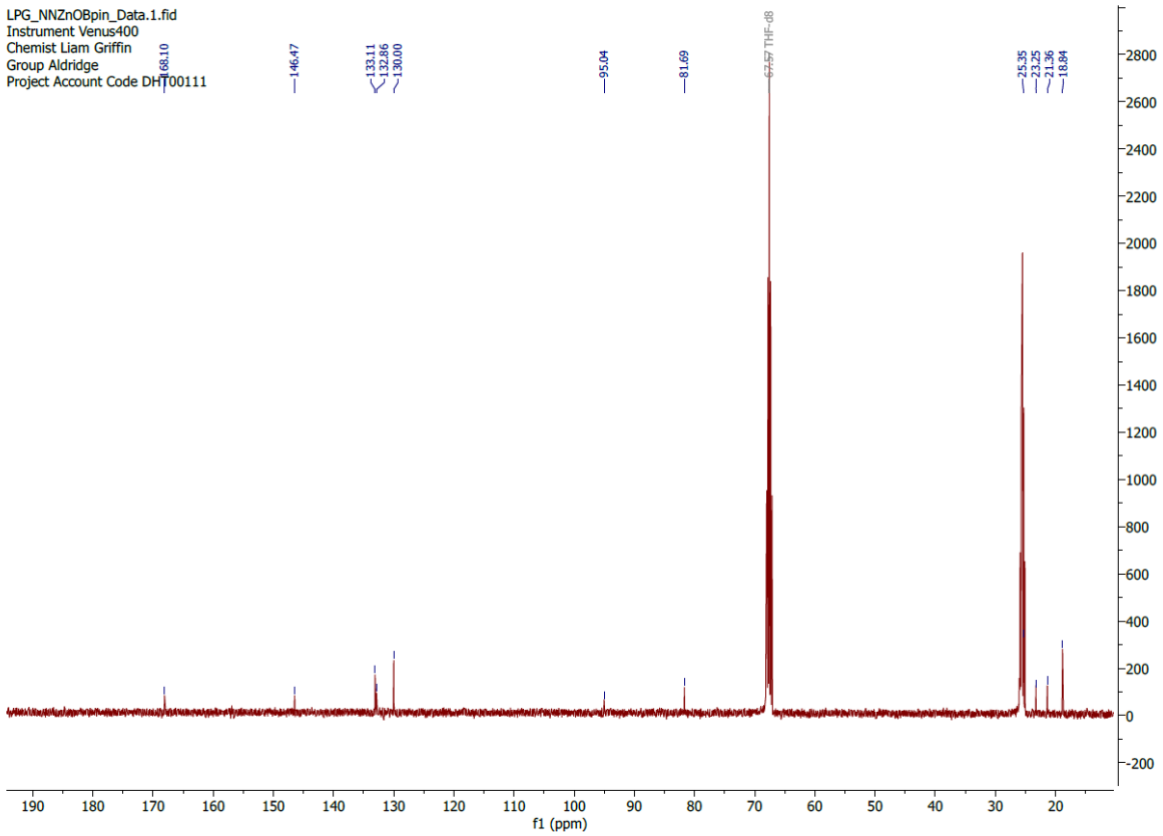

Fig S12. *^{13}C NMR spectrum of [(Nacnac^{Mes})ZnOBpin]$_2$ (**4**).*

(Nacnac^{Mes})ZnOB{(NDippCH)$_2$} (5)

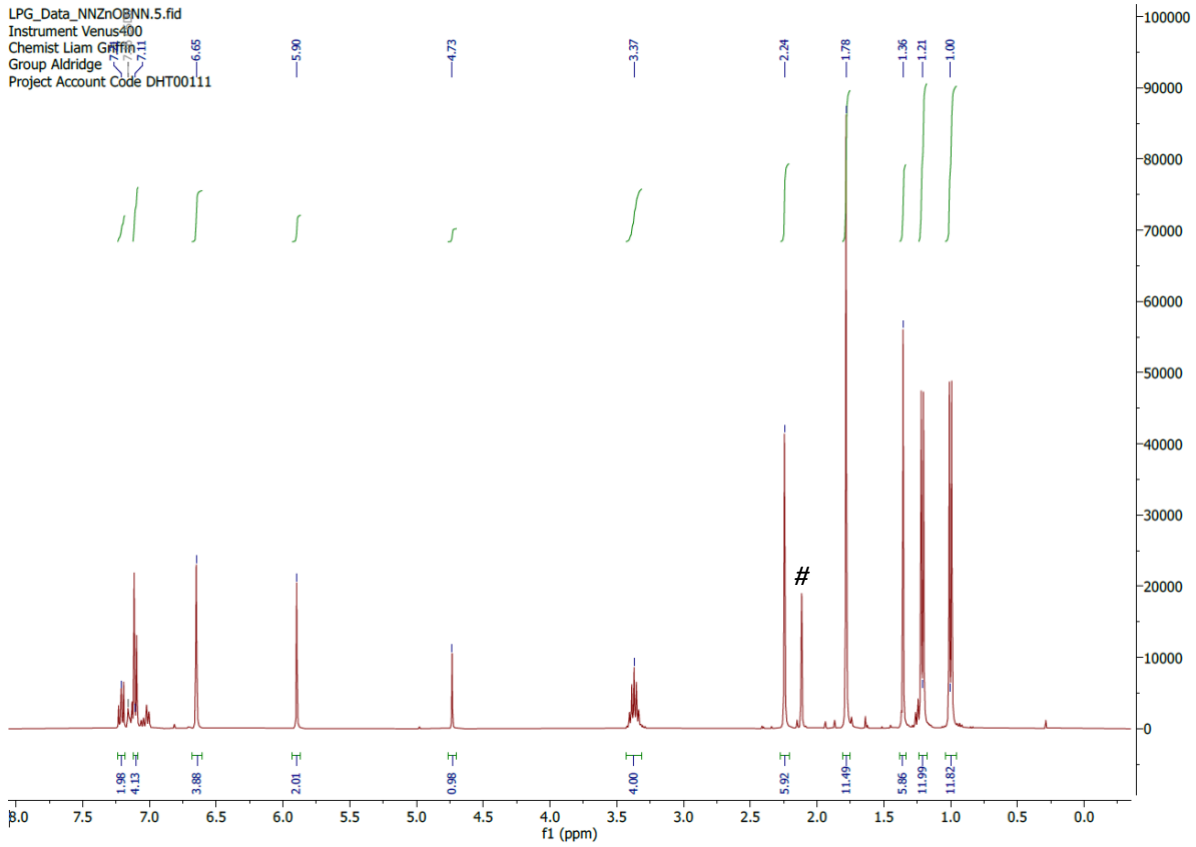

Fig S13. *^{1}H NMR spectrum of (Nacnac^{Mes})ZnOB{(NDippCH)$_2$}. Residual toluene marked #.*

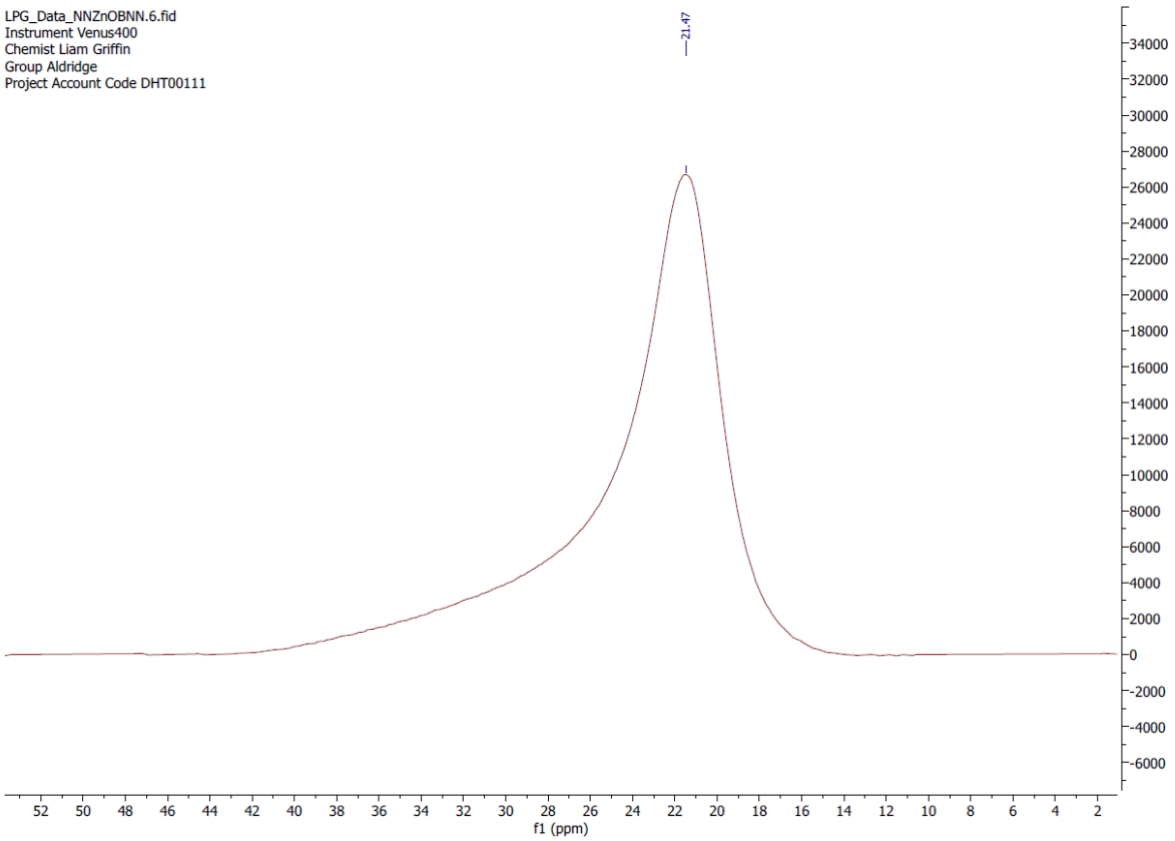

Fig S14. *^{11}B NMR spectrum of (Nacnac^{Mes})ZnOB{(NDippCH)$_2$}.*

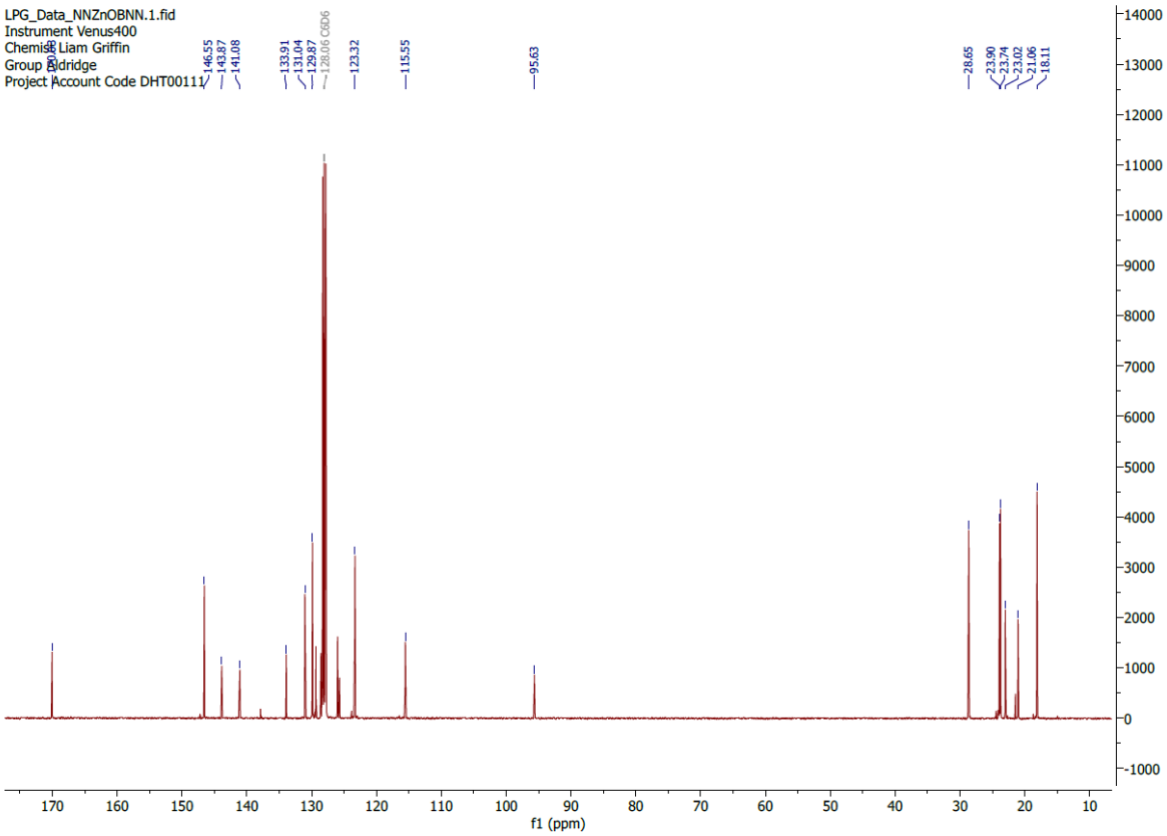

Fig S15. *^{13}C NMR spectrum of (Nacnac^{Mes})ZnOB{(NDippCH)$_2$}.*

{(HCDippN)$_2$}BOBpin (6)

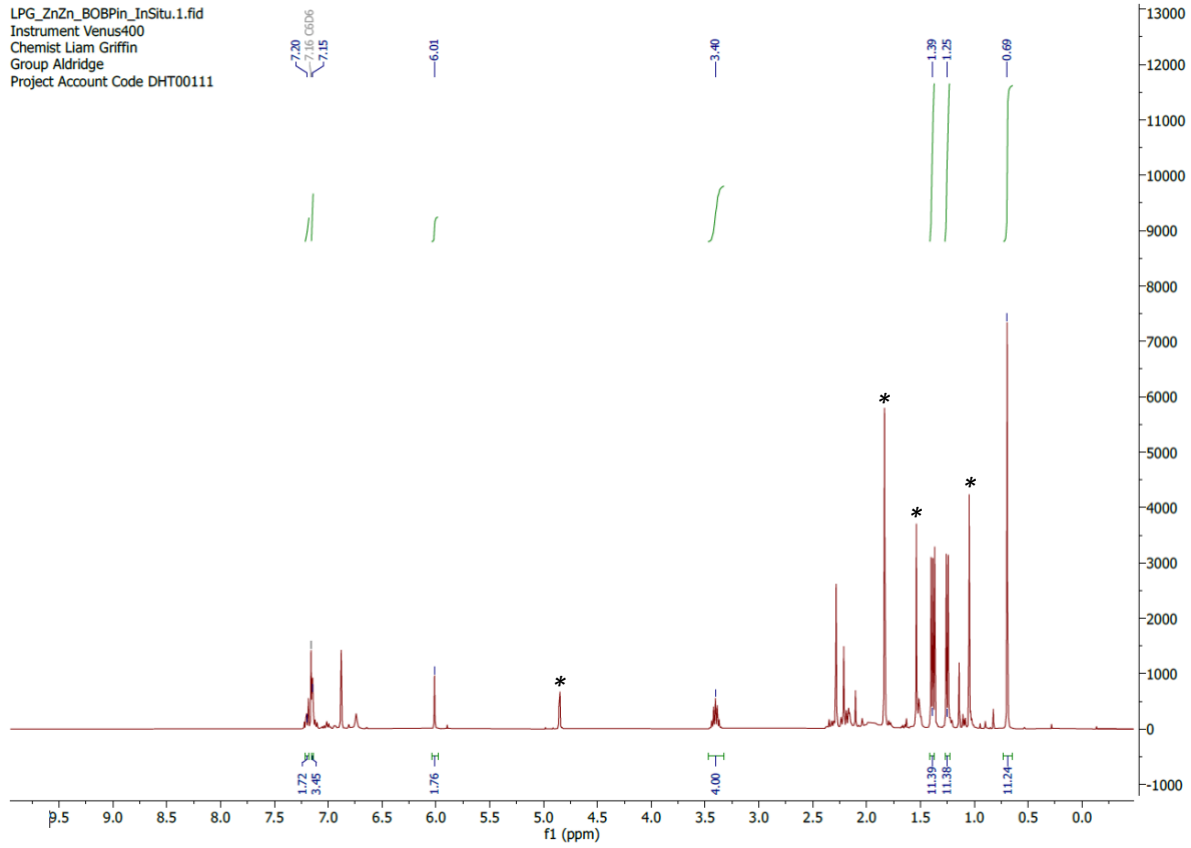

Fig S16. *In situ ^{1}H NMR spectrum of {(HCDippN)$_2$}BOBpin (**6**). Diagnostic signals of [(Nacnac^{Mes})Zn]$_2$ are marked *.*

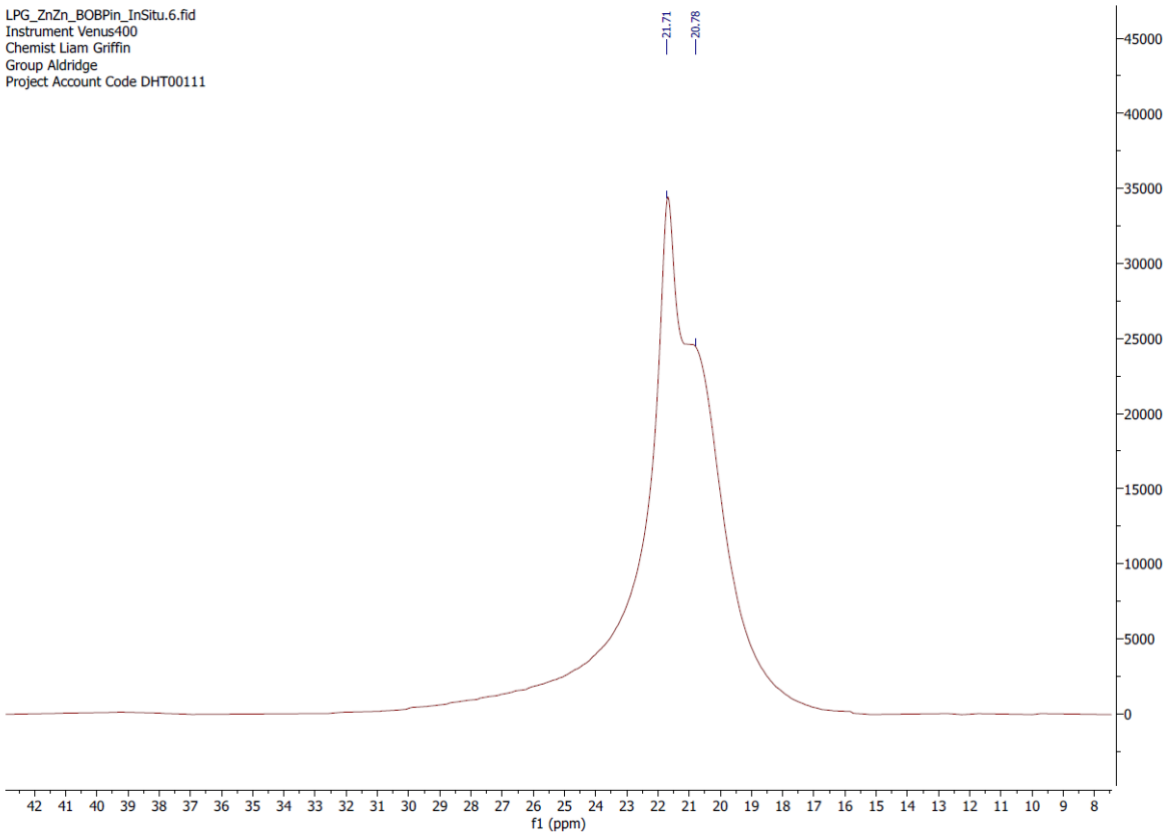

Fig S17. *In situ ^{11}B NMR spectrum of {(HCDippN)$_2$}BOBpin (**6**).*

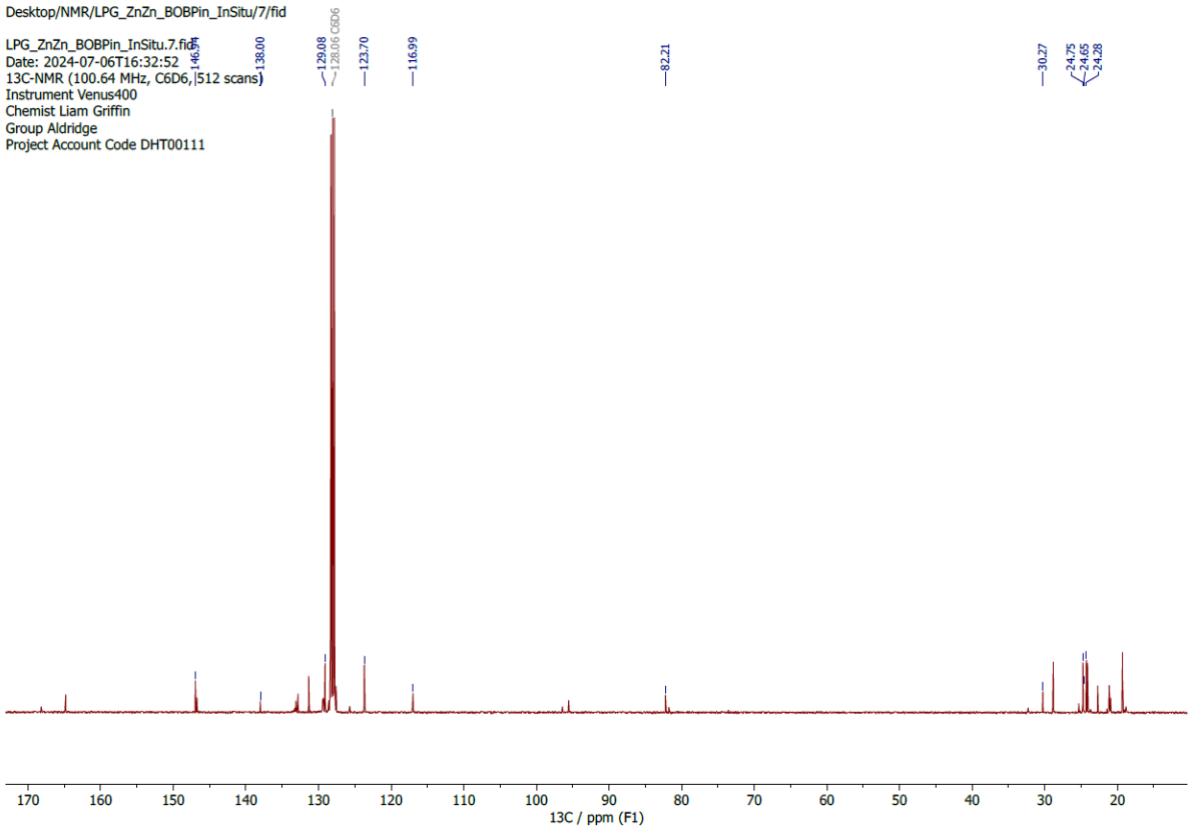

Fig S18. *In situ ^{13}C NMR spectrum of {(HCDippN)$_2$}BOBpin (**6**), in the presence of [(Nacnac^{Mes})Zn]$_2$.*

5. Computational details

Gas phase geometry optimizations and frequency analyses were carried out using the ORCA (5.0.4) software package,[S11,S12] using the R2-Scan-3C method.[S13] The optimized structures were confirmed to be minima on the potential energy surface by the absence of imaginary frequencies. Single point calculations were performed using the ωB97X-D4 functional and Def2-TZVP basis set.[S14-S16] Natural bonding orbital (NBO) analyses were carried out using the NBO 7.0 program.[S17,S18] Atoms in molecules (AIM) analyses were conducted using Multiwfn software package.[S19] AIM bonding classifications have been made in accordance with the literature precedent.[S20] All iso-surfaces have been rendered at 0.05, unless otherwise stated.

(Nacnac^{Mes})ZnBpin

LUMO

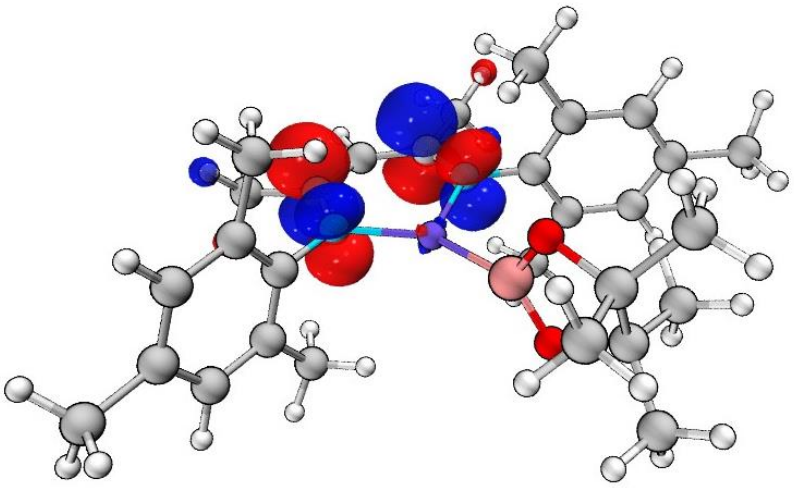

Fig S19. *Ligand based LUMO of (Nacnac^{Mes})ZnBpin (**1**), E = 1.2292 eV.*

HOMO

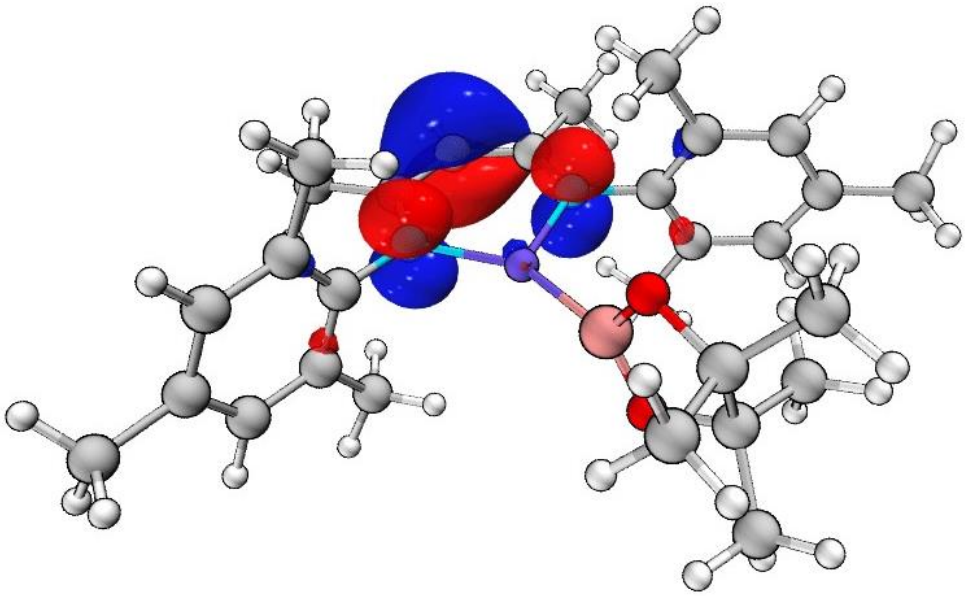

Fig S20. *Ligand based HOMO of (Nacnac^{Mes})ZnBpin (**1**), E = -7.8818 eV.*

Zn-B bonding contributions

HOMO-2

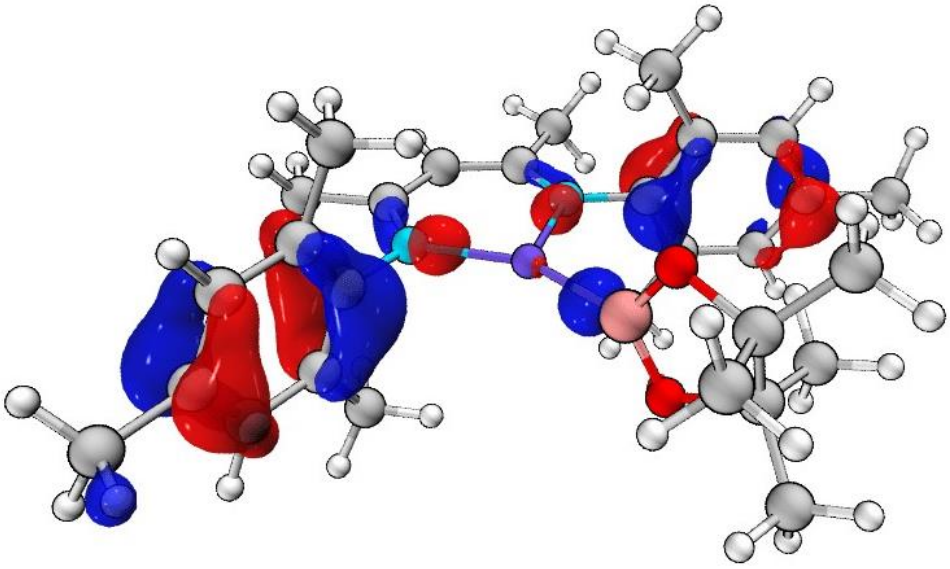

Fig S21. *HOMO-2 of (Nacnac^{Mes})ZnBpin (**1**), featuring a small region of electron density between B and Zn, E = -8.6125 eV.*

HOMO-3

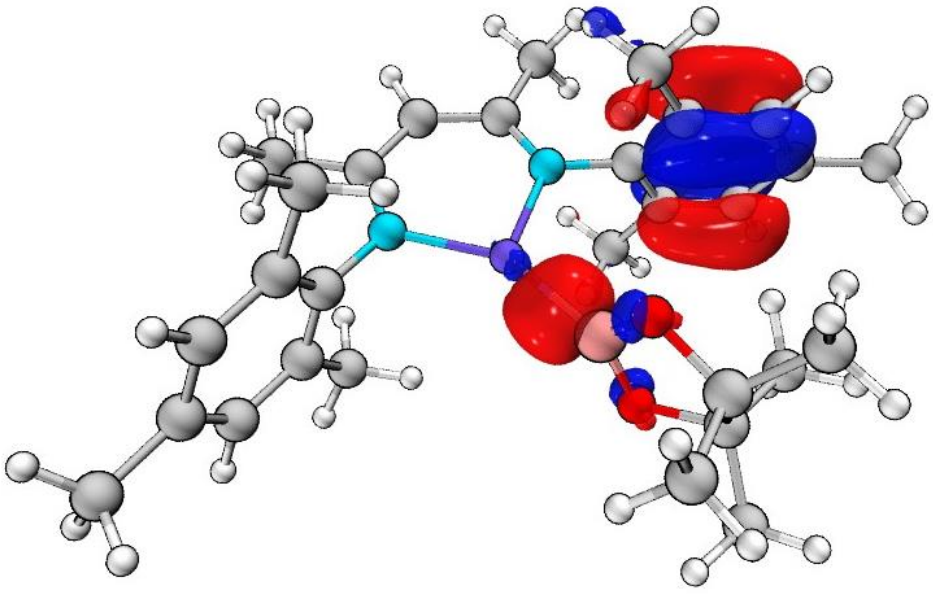

Fig S22. *HOMO-3 of (Nacnac^{Mes})ZnBpin (**1**), featuring a significant region of electron density between B and Zn, E = -8.8903 eV.*

HOMO-4

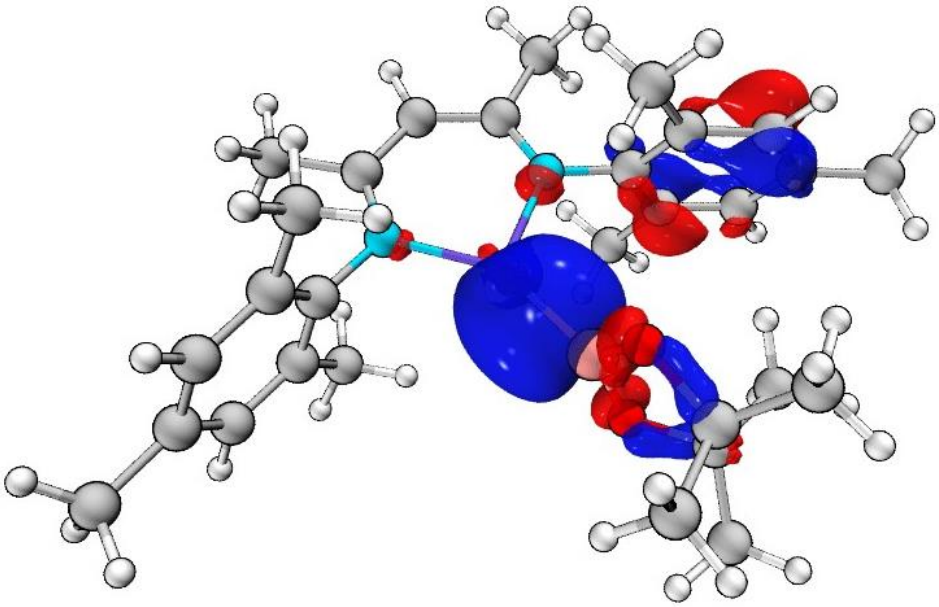

Fig S23. *HOMO-4 of (Nacnac^{Mes})ZnBpin (**1**), featuring the most significant region of electron density between B and Zn, E = -8.9182 eV.*

NBO analysis

One conventional NBO was located for the Zn-B interaction.

1.96172 electrons

21.75% (0.4664 electrons) Zn: s 96.5%, p 2.4%, d 1.1%

78.25% (0.8846 electrons) B: s 47.6%, p 52.4%

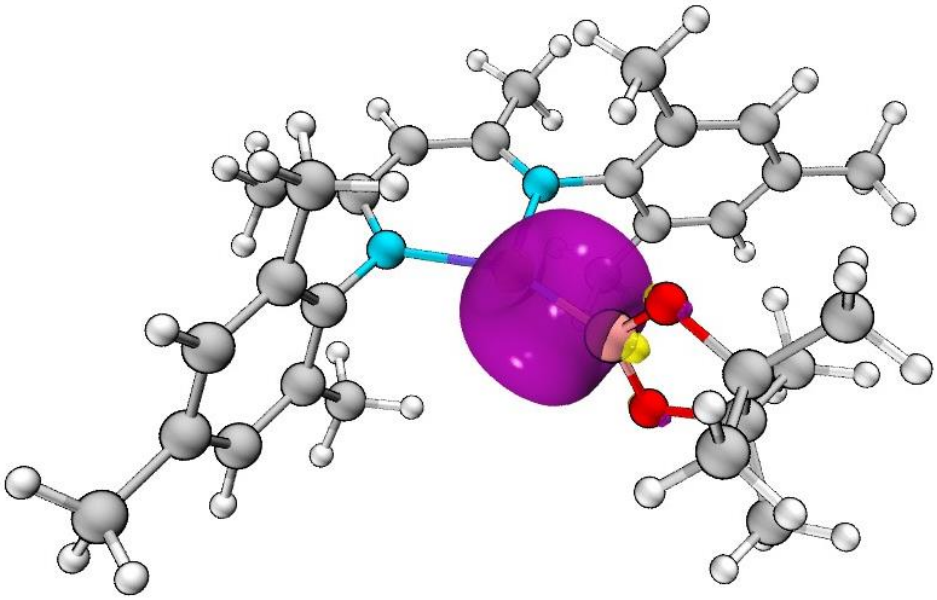

Fig S24. *NBO corresponding to the Zn-B bonding interaction in (Nacnac^{Mes})ZnBpin (**1**).*

WBI: 0.592

NPA charges

Zn: 1.47012 e

B: 0.46825 e

Bader charges

Zn: 0.879 e

B: 1.352 e

QTAIM

ρ	0.1001319145E+00
$\nabla^2\rho$	0.5864727743E-01
G(r)	0.5672856343E-01
K(r)	0.4206674407E-01
V(r)	-0.9879530750E-01
E(r)	-0.4206674407E-01
ELF	0.5441836390E+00
ε	0.084374

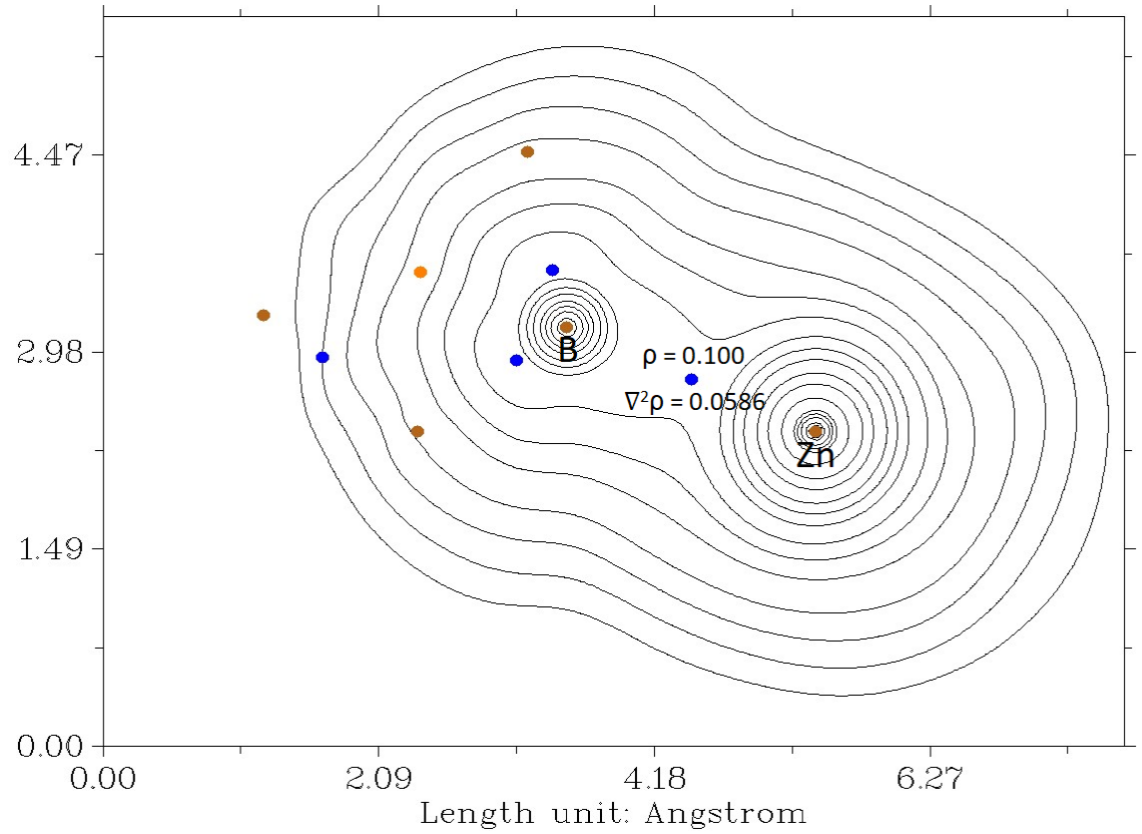

Fig S25. *Contour plot of electron density in the region around the Zn-B bond in (Nacnac^{Mes})ZnBpin (**1**).*

(Nacnac^{Mes})Zn(DMAP)Bpin (2)

LUMO

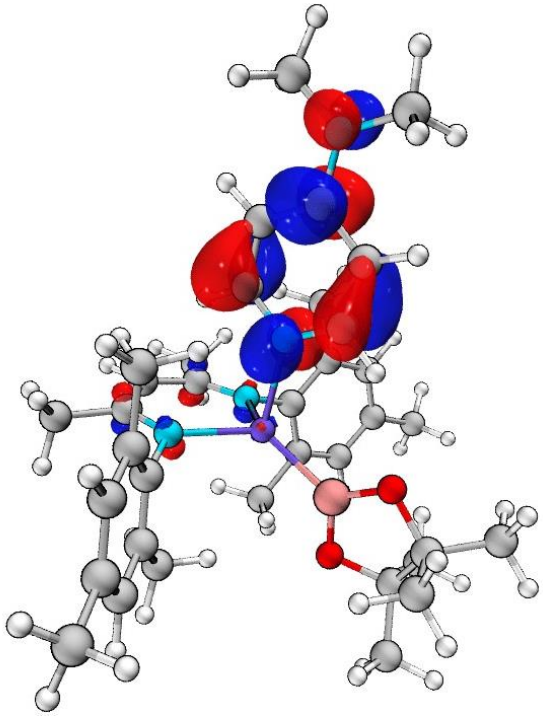

Fig S26. *DMAP-based LUMO of (Nacnac^{Mes})Zn(DMAP)Bpin (**2**), E = 1.3777 eV*

HOMO

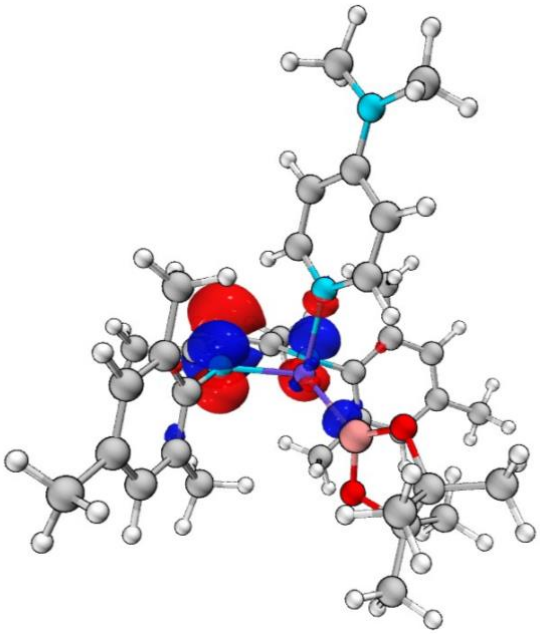

Fig S27. *Primarily ligand-based HOMO of (Nacnac^{Mes})Zn(DMAP)Bpin (**2**), with a small amount of electron density between B and Zn, E = -7.1873 eV.*

Zn-B bonding contributions

HOMO-2

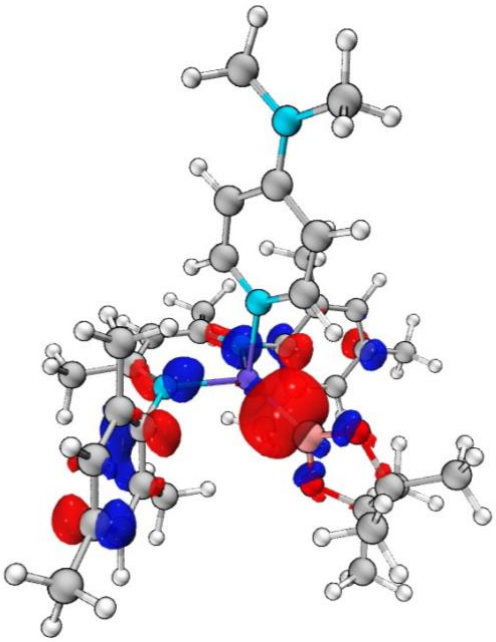

Fig S28. *HOMO-2 of (Nacnac^{Mes})Zn(DMAP)Bpin (**2**), featuring a significant contribution to Zn-B σ-bonding, E = -8.1452 eV.*

HOMO-3

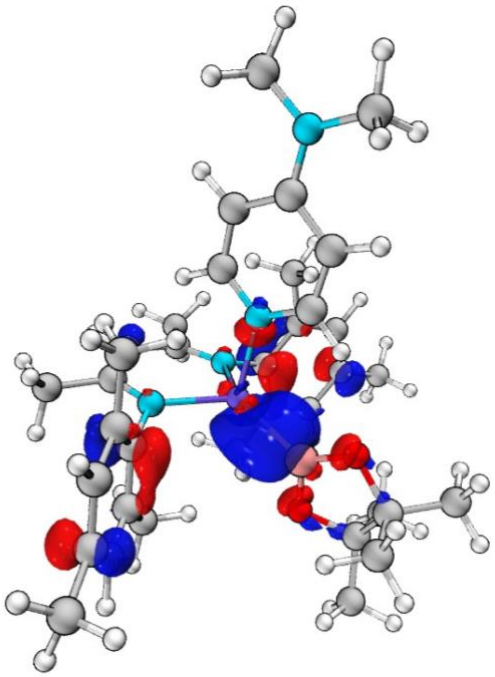

Fig S29. *HOMO-3 of (Nacnac^{Mes})Zn(DMAP)Bpin (**2**), featuring a significant contribution to Zn-B σ-bonding, E = -8.2358 eV.*

NBO analysis

No NBO was located for the Zn-B bonding interaction. This is instead described as a second-order perturbation interaction between a B-based lone pair and a Zn based vacant orbital, with an overall stabilization energy of 232.81 kcal/mol.

B-based lone pair – 1.64650 electrons: s 49.3%, p 50.67%

Zn vacant orbital – 0.44130 electrons: s 98.7%, p 1.0%, d 0.3%

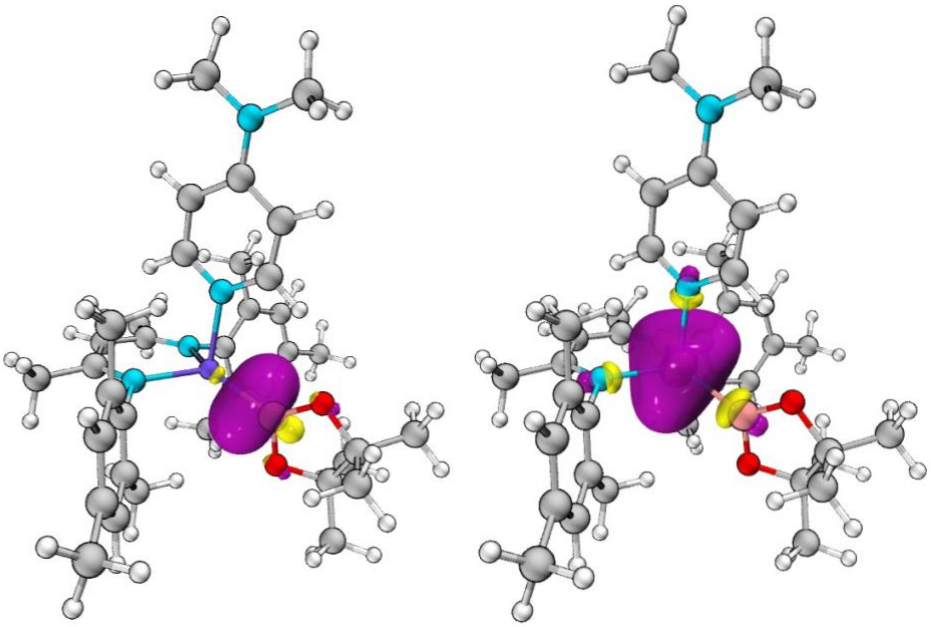

Fig S30. *NBO orbitals for (Nacnac^{Mes})Zn(DMAP)Bpin (**2**) calculated to interact by Second Order Perturbation Theory, leading to a Zn-B σ-bonding interaction. Left, B-based lone pair, Right, Zn-based vacant orbital.*

WBI: 0.496

NPA charges

Zn: 1.56613 e

B: 0.41854 e

Bader charges

Zn: 0.975 e

B: 1.272 e

QTAIM

ρ	0.9544211041E-01
$\nabla^2\rho$	0.9014936624E-01
G(r)	0.6015711525E-01
K(r)	0.3761977370E-01
V(r)	-0.9777688895E-01
E(r)	-0.3761977370E-01
ELF	0.4750102996E+00
ε	0.058560

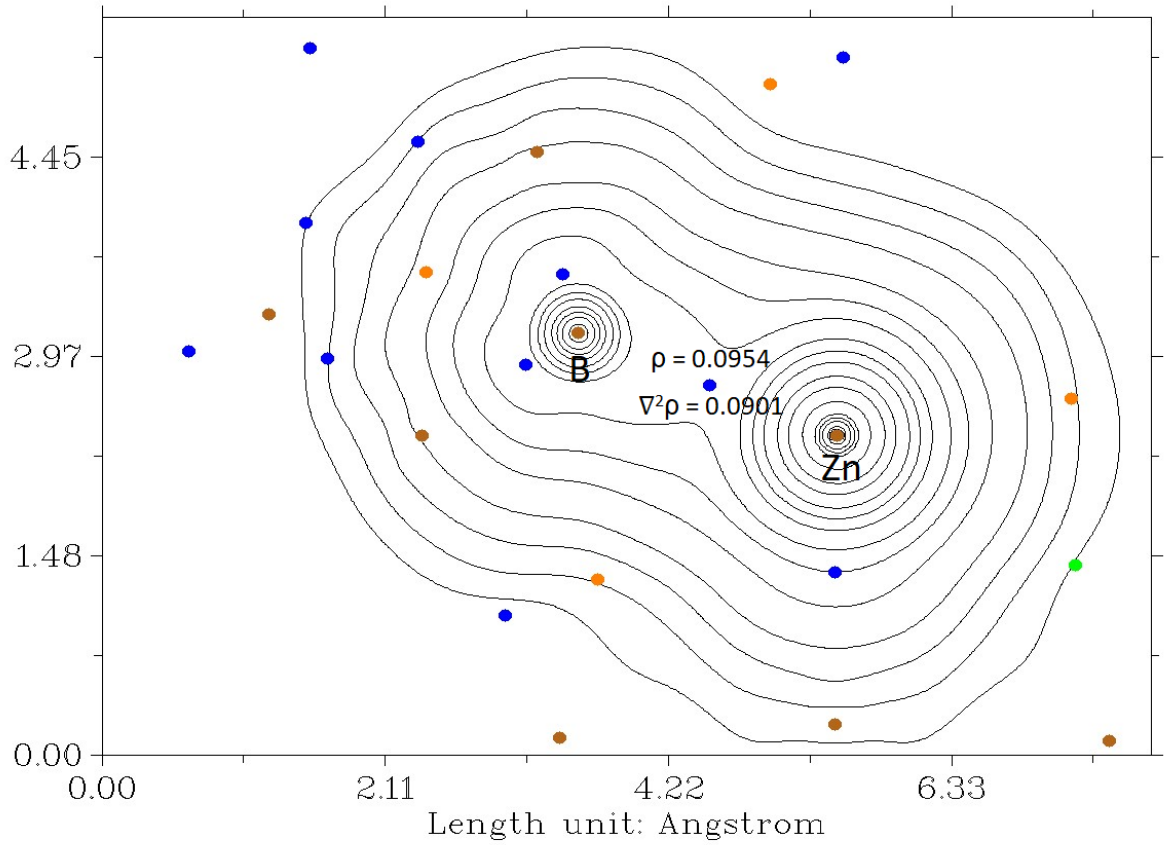

Fig S31. *Contour plot of electron density in the region around the Zn-B bond in (Nacnac^{Mes})Zn(DMAP)Bpin (**2**).*

Table S2. *Key QTAIM parameters (in a.u.) relating to the BCPs of the Zn-B bonding interactions for zinc-boryl species **1** and **2**.*

	(Nacnac^{Mes})ZnBpin (**1**)	(Nacnac^{Mes})Zn(DMAP)Bpin (**2**)
ρ	0.1001	0.09544
$\nabla^2\rho$	0.05865	0.09015

7. Optimised XYZ coordinates

Nacnac^{Mes}ZnBpin (1): -3195.348038663298 E_h			
Zn	-1.00569597992652	8.36829931809950	15.63429840251350
O	0.23312213009687	8.82138844931929	12.91695432176124
O	0.52007541007981	6.66428836442517	13.61985128564829
N	-1.00132060882704	8.98680513854936	17.48706083474262
N	-2.98397560074018	8.17560082294936	15.52626010096209
C	-3.82584362761764	8.48661489253424	16.50201497363231
C	0.27947824933209	9.24194269732946	18.05966785395151
C	-3.46404433021647	7.68090421113294	14.28142371969911
C	-2.09955684484563	9.18168116580471	18.21976143433770
C	0.86515508562621	10.50775852417875	17.91062008689743
C	-3.40577565560078	8.95756409529206	17.75964034207281
H	-4.19559568496607	9.17288776875349	18.46873064547313
C	0.96903761986552	8.20356947631389	18.70082616086399
C	-5.31030102528431	8.34069367031991	16.26740517725800
H	-5.62208463098462	8.94142523664205	15.40560004437338
H	-5.88284359683960	8.65155586413264	17.14269733518252
H	-5.56550887310249	7.30293616430865	16.02633832431562
C	0.98883870833172	8.15462424257073	11.85552865940697
C	-3.64647705186926	8.56705293370207	13.20887074662354
C	2.12870611863673	10.72821612053757	18.45538848032458
H	2.58266030170770	11.71221954637801	18.35024483314607
C	2.82588523452401	9.72211164650550	19.12392416834940
C	-3.35937440624044	10.03143294109755	13.38047222482478
H	-2.28290962635983	10.18931165992444	13.53062775621891
H	-3.86960279493573	10.45249679558921	14.25332004757756
H	-3.66177085846881	10.59461133397619	12.49374523406720
C	2.23170623746087	8.46600218474290	19.23138906501148
H	2.76606100526013	7.66423628153838	19.73788484041198
C	-3.63946841055333	6.29994085257612	14.10533858610848
C	4.20210410669543	9.97759265939289	19.67750303863014
H	4.96499938477502	9.86933477596887	18.89661662063115
H	4.44673722145007	9.27179505412282	20.47645313837126
H	4.28795363921820	10.99223159360665	20.07871758419871
C	-1.94189946723816	9.67975989421774	19.63715538683082
H	-1.33342618185558	8.98590239961452	20.22745636879637
H	-2.91203616060652	9.79933243346003	20.12135277569335
H	-1.41468466011727	10.63992671532522	19.65507029765383
C	0.73778903605291	6.64510792256562	12.17264868152541
C	0.14709628785161	11.59027223124144	17.15500716485876
H	0.71435088699354	12.52422152384613	17.17935720872944
H	-0.85367516445567	11.78192751575098	17.55761340447506
H	0.00837957513403	11.30265187491263	16.10435787225475
C	0.36244534525873	6.83121960931995	18.78743644526742
H	1.00078531357699	6.15846248631201	19.36579675140064
H	0.23327981850129	6.40125201527618	17.78547917198924

H	-0.63186491435181	6.84660215836907	19.24738622244431
C	-4.06062734999684	8.05480853953977	11.97976339516872
H	-4.21032914424376	8.74183593281979	11.14847199228339
C	-3.32804713498226	5.34782570386731	15.22523578652070
H	-3.59362019477010	4.32362007682671	14.95098716579851
H	-3.85143537262757	5.60608696496562	16.15209415423432
H	-2.25462285626204	5.37161412988234	15.45576953485031
B	0.07304448756951	7.92702078893298	13.95840084221468
C	-4.05920697301049	5.83025511932885	12.86182836852453
H	-4.20118919368124	4.75946534422299	12.72531708326651
C	2.44717334875777	8.57193069660631	12.02548239821174
H	2.50886617339186	9.66350991338173	11.98765709434612
H	3.07651032636746	8.16148502024486	11.22885191362045
H	2.83878400900518	8.24260417030653	12.99255647722442
C	0.45080207650664	8.62408617740779	10.51437488118228
H	-0.63061134178426	8.48404400542419	10.44969500250764
H	0.92828452643038	8.07644501509085	9.69388056646429
H	0.66704568073475	9.68894959713337	10.38562408499210
C	-4.27870160251624	6.69111208084301	11.78765328700445
C	1.90288007569518	5.72087170226832	11.86398665901859
H	2.79574565993803	5.99527596060713	12.42946067267719
H	2.14065537036363	5.74717890579368	10.79440644423122
H	1.63379180553312	4.69358449202173	12.12732160136328
C	-4.68118532347664	6.15632897055789	10.43970265670045
H	-5.28049991822012	6.88387713391947	9.88410960345592
H	-5.26214419480631	5.23405474856243	10.53358303092309
H	-3.79661350826854	5.92678277334761	9.83177579487694
C	-0.55189104368806	6.10996662259340	11.55342687561135
H	-0.77000315874329	5.13040721296623	11.98944954521262
H	-0.45902216422676	5.99436058083086	10.46809608281842
H	-1.39884362541463	6.76814635717840	11.77174318518715

Nacnac^{Mes}ZnOB{(NDippCH)$_2$} (5): -4007.029880121355 E_h

Zn	1.77209368059339	8.07311725809021	15.09667972475072
O	1.36650550644669	8.30270856516209	13.34274955456828
N	3.61564948723860	7.80273374126823	15.68911459300305
N	0.82016550544546	7.62751184508411	16.71614580906611
N	-0.01990301896639	10.00950916287920	12.06662725842504
N	1.28556264005621	8.56357797229134	10.86541686442202
C	4.69001897398264	7.94824184130176	14.75962943057442
C	5.51515992922284	9.08146830864706	14.80962973594603
C	1.49197808428461	7.26148499284366	17.81424249839451
C	3.86720329345713	7.31729339118173	16.90203945706116
C	-0.75423942721806	10.73291543767099	13.04317901783591
C	4.87702005432260	6.96195722069282	13.78052830224434
C	-0.60775639293589	7.59650064149891	16.75924920628608
C	-1.31662306328746	8.76434727189238	17.06268246041562
C	2.88504888430707	7.12585638269352	17.89098868138104
H	3.25806796598992	6.77854170036045	18.84623406512002
C	5.27650494980375	10.16843909914266	15.82106079840106

H	4.21590483169879	10.43242473453470	15.87629222814001
H	5.84341412043759	11.06637740538387	15.56152537920866
H	5.57546894438557	9.86926717318692	16.83337432328468
C	5.27588502102586	6.89636462914789	17.24649101398751
H	5.61864914838416	6.13456862342055	16.53693268794416
H	5.32587052360669	6.48687568061776	18.25613988782268
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C	1.61176475786661	8.27158563620232	10.71382409595862
H	0.61181576734759	8.20996263023565	10.27937439068170
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C	2.70897416462438	1.67859941902235	8.70442870141882
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H	2.82233750268491	6.65959978474801	9.37753454021103

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