Electronic Supplementary Material (ESI) for Dalton Transactions.

Reaction of Diborylstannylene with CO_2 and N_2O: Diboration of Carbon Dioxide by a Main Group Bis(boryl) Complex

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SUPPORTING INFORMATION

(21 pages total)

1. Synthetic procedures

(i) General methods and instrumentation. All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon or dinitrogen. Hydrocarbon solvents were degassed by sparging with dinitrogen and dried by passing through a column of the appropriate drying agent and stored over Na or K mirror.[S1] THF was refluxed over potassium-sodium alloy and distilled prior to use. NMR spectra were measured in C_6D_6 which was dried over potassium, distilled under reduced pressure and stored under dinitrogen in Teflon valve ampoules. NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Bruker Avance III HD nanobay 400 MHz or Bruker Avance III 500 MHz spectrometer at ambient temperature unless stated otherwise and referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane (δ = 0 ppm). ^{11}B{^{1}H} NMR spectra were referenced to external $Et_2O{\cdot}BF_3$. 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. Coupling to $^{203/205}$Tl nuclei was confirmed by measuring the spectrum of the same sample at different spectrometer frequency. Elemental analyses were carried out by London Metropolitan University.

(ii) Starting materials. Sn{B(NDippCH)$_2$}$_2$ (Dipp = 2,6-$C_6H_3{}^i Pr_2$) (**1**) and (thf)$_2$Li{B(NDippCH)$_2$} were synthesised according to published procedures.[S2, S3] Carbon dioxide was stored in a Young's tap ampoule at 1 atm over P_2O_5 before use. {(HCDippN)$_2$B}CO_2H was made by the route similar to that described in ref.[S3] but we have found that it was necessary to use a strong acid (*p*-toluenesulfonic acid monohydrate, Aldrich) before flash chromatography in order to convert initially formed lithium carboxylate into free borylcarboxilic acid.

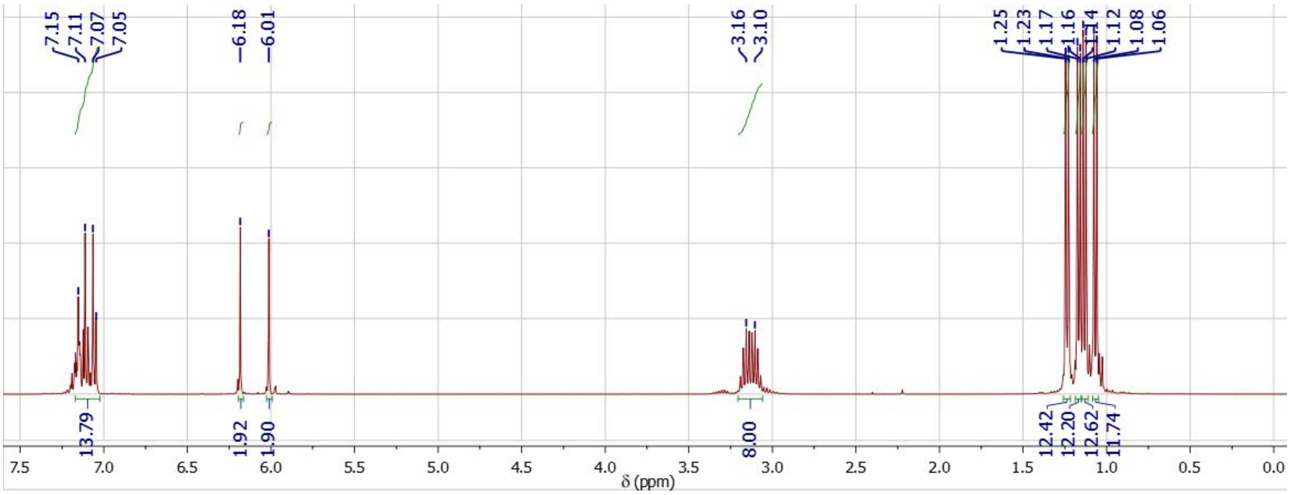
Reaction of Sn{B(NDippCH)$_2$}$_2$ with 1 equiv CO_2: Solution of Sn{B(NDippCH)$_2$}$_2$ (27 mg, 0.030 mmol) in C_6D_6 (0.5 mL) was degassed by freeze/pump/thaw procedure, then the tube was filled with CO_2 and gently shaken. The solution colour changed from yellow-green to light orange. Immediately ^{1}H NMR showed formation of a single asymmetrical product, but the starting stannylene was not completely consumed. After shaking for 10 min the reaction was complete. All volatiles were removed *in vacuo*, the oily residue was dissolved in pentane (0.5 mL), transferred into crystallisation tube, concentrated to a smaller volume and stored at −30 °C overnight producing orange-yellow (depending on viewing angle) crystals of Sn{B(NDippCH)$_2$}{O_2CB(NDippCH)$_2$} (**2**) suitable for X-ray diffraction.

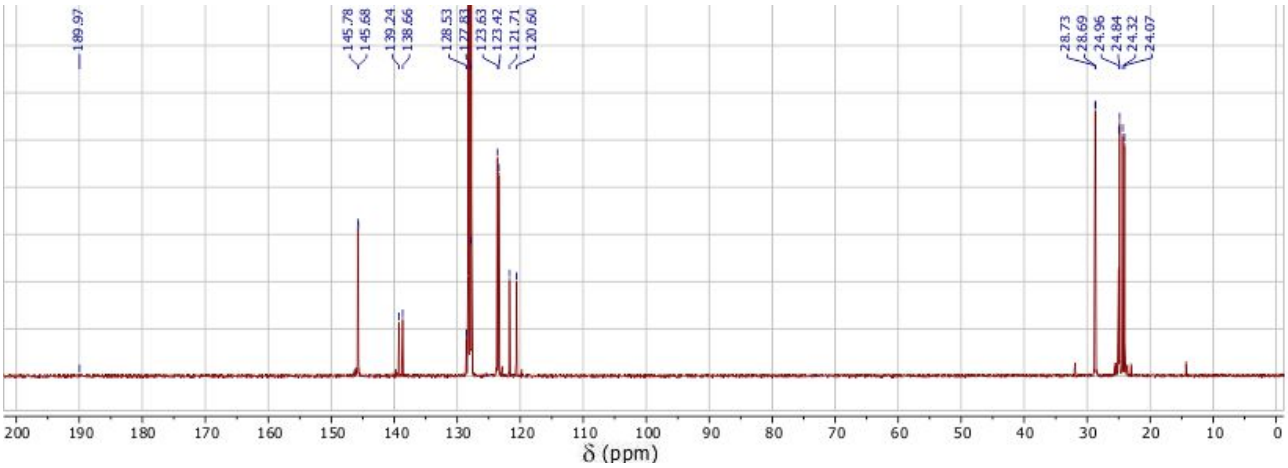
Compound **2** was highly soluble (and thermally unstable, *vide infra*) in aliphatic hydrocarbon solvents even at low temperature so that only few crystals could be isolated; however, the ^{1}H NMR spectrum of the crystals was nearly identical (apart from signals of the crystallisation solvent pentane and minor decomposition products) to the spectrum of *in situ* prepared sample.

^{1}H NMR (C_6D_6): δ 7.05-7.19 (12H, m, CH of Ar + C_6D_5H), 6.18 (2H, s, NCH), 6.01 (2H, s, NCH), 3.16 (4H, septet, ^3J = 6.9 Hz, C*H*Me$_2$), 3.10 (4H, septet, ^3J = 6.9 Hz, C*H*Me$_2$), 1.24 (12H, septet, ^3J = 6.9 Hz, CH*Me*$_2$), 1.17 (12H, septet, ^3J = 6.9 Hz, CH*Me*$_2$), 1.17 (12H, septet, ^3J = 6.9 Hz, CH*Me*$_2$), 1.13 (12H, septet, ^3J = 6.9 Hz, CH*Me*$_2$), 1.07 (12H, septet, ^3J = 6.9 Hz, CH*Me*$_2$).

^{13}C-NMR (C_6D_6): δ 190 (br, BCO_2), 145.78 (*o*-C of Ar), 145.68 (*o*-C of Ar), 139.24 (*ipso*-C of Ar), 138.66 (*ipso*-C of Ar), 128.53 (*p*-CH of Ar), 127.83 (*p*-CH of Ar, overlapping with C_6D_5H), 123.63 (*m*-CH of Ar), 123.42 (*m*-CH of Ar), 121.71 (NCH), 120.60 (NCH), 28.73 (*C*HMe$_2$), 28.69 (*C*HMe$_2$), 24.96 (CH*Me*$_2$), 24.84 (CH*Me*$_2$), 24.32 (CH*Me*$_2$), 24.07 (CH*Me*$_2$).

^{11}B{^{1}H} (C_6D_6): δ 58.1 (BSn), 19.8 (BCO_2).





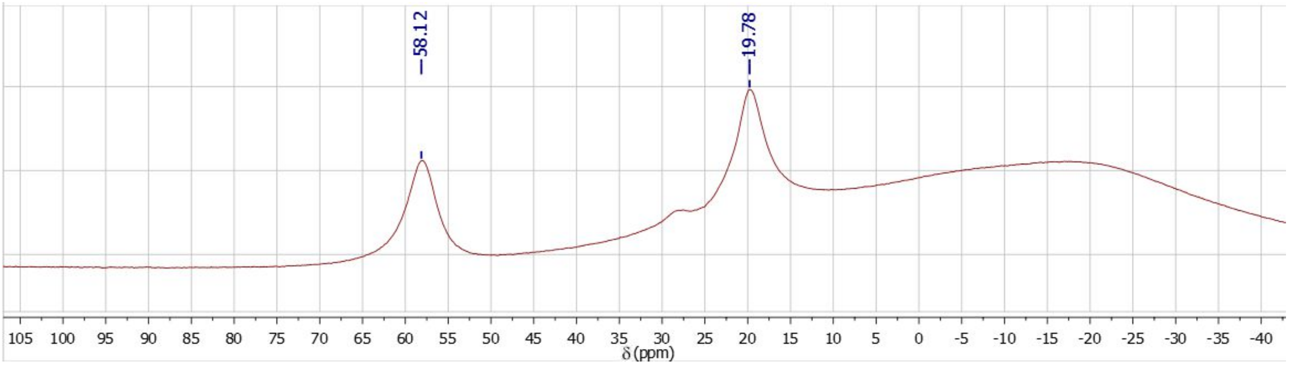


Fig. s1. ^{1}H, ^{13}C{^{1}H} and ^{11}B{^{1}H} NMR spectra of *in situ* prepared **2**.

Decomposition of 2. Similarly to the previous experiment, solution of Sn{B(NDippCH)$_2$}$_2$ (34 mg, 0.038 mmol) in C_6D_6 (0.5 mL) was degassed by freeze/pump/thaw procedure, then the tube was filled with CO_2 and gently shaken for 10 min. The colour gradually changed from yellow-green to orange-yellow and the ^{1}H NMR spectrum showed clean formation of a single product. The mixture was transferred into a two-section crystallization tube and all volatiles removed *in vacuo*. The residue was dissolved in hexane (0.5 mL) and the tube was sealed under vacuum. The concentrated solution failed to produce crystals at −30 °C for several days, so it was stored at room temperature. Initially, after 1 d, a small amount (less than 5%) of very well shaped rhombic colourless crystals was formed, which were identified by X-ray diffraction as Sn$_3${O$_2$CB(NDippCH)$_2$}$_4$(μ$_3$-O) (**5**).

The remaining solution was stored for two weeks, while slowly darkening to brown and almost black, then concentrated again producing large colourless blocks, which were washed with a small amount of cold hexane and dried *in vacuo* yielding {(HCDippN)$_2$B}C(O)O{B(NDippCH)$_2$} (**3**) (21 mg, 0.025 mmol, 67%). Anal. found (calcd. for $C_{53}H_{72}B_2N_4O_2$): C, 77.82 (77.75); H, 9.05 (8.86); N, 6.80 (6.84) %. From the mother liquor black (dark brown when crushed) crystals precipitated which were of insufficient quality/size for X-ray diffraction.

^{1}H NMR (C_6D_6) for **3**: δ 7.14-7.20 (4H, m, *p*-CH of Ar + C_6D_5H), 7.02-7.05 (8H, m, *m*-CH of Ar), 5.89 (2H, s, NCH), 5.88 (2H, s, NCH), 3.15 (4H, septet, ^{3}J = 6.9 Hz, C*H*Me$_2$), 2.94 (4H, septet, ^{3}J = 6.9 Hz, C*H*Me$_2$), 1.24 (12H, septet, ^{3}J = 6.9 Hz, CH*Me*$_2$), 1.13 (12H, septet, ^{3}J = 6.9 Hz, CH*Me*$_2$), 1.10 (12H, septet, ^{3}J = 6.9 Hz, CH*Me*$_2$), 0.97 (12H, septet, ^{3}J = 6.9 Hz, CH*Me*$_2$), 0.95 (12H, septet, ^{3}J = 6.9 Hz, CH*Me*$_2$).

^{13}C{^{1}H} NMR (C_6D_6) for **3**: δ 175.5 (very broad, only observed in HMBC, BCO$_2$), 146.66 (*o*-C of Ar), 146.71 (*o*-C of Ar), 138.58 (*ipso*-C of Ar), 138.02 (*ipso*-C of Ar), 127.88 (*p*-CH of Ar), 127.61 (*p*-CH of Ar), 123.55 (*m*-CH of Ar), 123.43 (*m*-CH of Ar), 120.62 (NCH), 118.64 (NCH), 28.67 (*C*HMe$_2$), 28.52 (*C*HMe$_2$), 25.29 (CH*Me*$_2$), 24.68 (CH*Me*$_2$), 23.93 (CH*Me*$_2$), 23.77 (CH*Me*$_2$).

$^{11}B\{^1H\}$ (C_6D_6) for **3**: δ 21.4 (br), 19.5 (br).

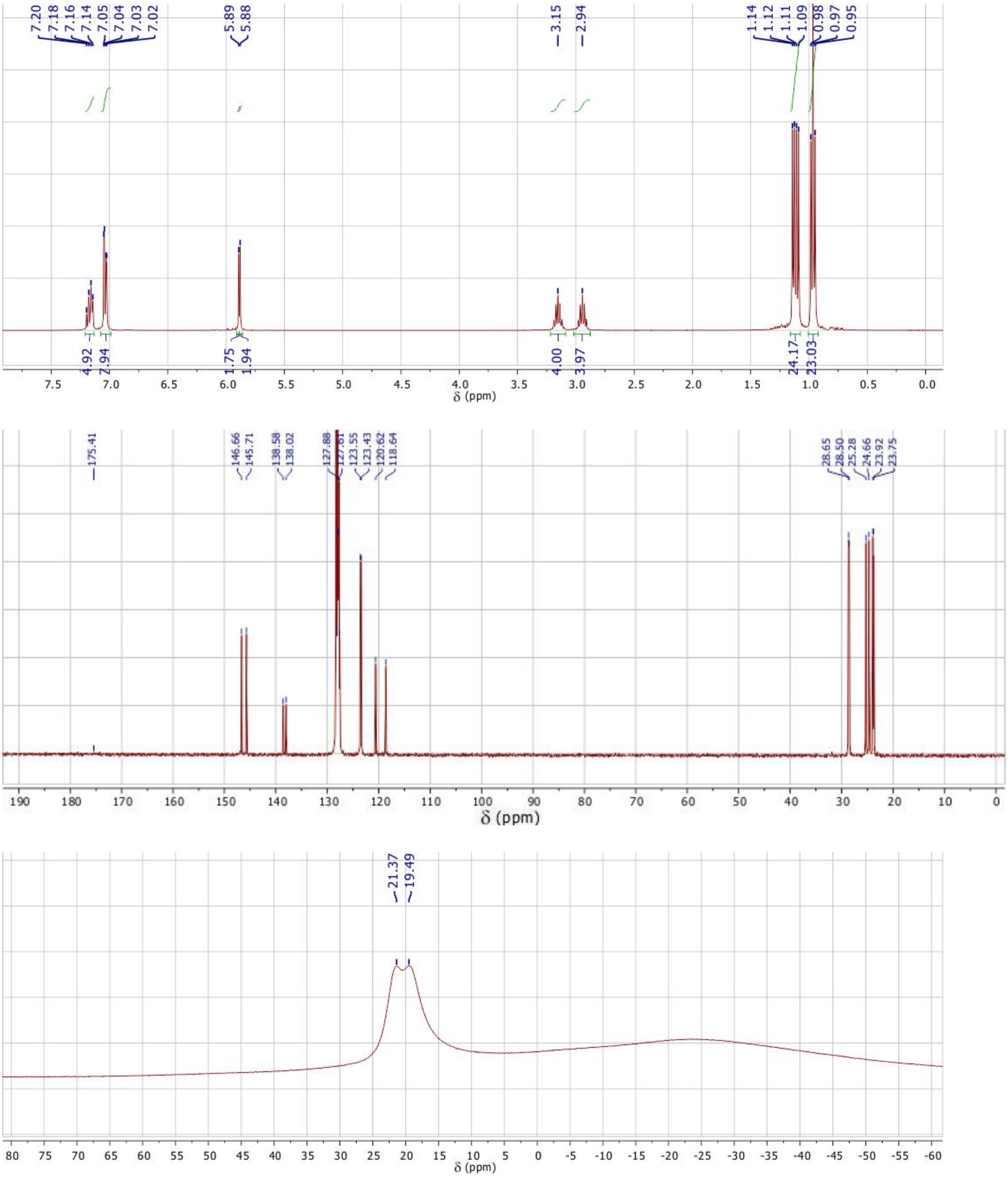


Fig. s2. ^1H, $^{13}C\{^1H\}$ and $^{11}B\{^1H\}$ NMR spectra of crystalline **3**.

Alternative synthesis of {(HCDippN)$_2$B}C(O)O{B(NDippCH)$_2$} (3): Initial attempts to make 4 by nucleophilic substitution of bromoborane Br{B(NDippCH)$_2$} using Li or K borylcarboxylates were unsuccessful (no reaction with Li salt in C_6D_6/thf or MeCN at 80 °C, slow reaction with K salt giving a mixture of unidentified products). However, use of neutral nucleophile HO_2C\{B(NDippCH)$_2$\} in the presence of amine base (similar approach to the large-scale synthesis of HO\{B(NDippCH)$_2$\} where water and pyridine reacted with bromoborane[S4]) produced the desired product.

HO_2C\{B(NDippCH)$_2$\} (15.5 mg, 0.035 mmol) and Br\{B(NDippCH)$_2$\} (16.5 mg, 0.035 mmol) were dissolved in C_6D_6 (0.5 mL) followed by the addition of NEt_3 (5 µL, 0.036 mmol). The mixture was heated at 80 °C for 3 h showing 25% conversion by ^{1}H NMR. After 2 d at 80 °C the reaction slowed down at 70% conversion, so more NEt_3 (5 µL, 0.036 mmol) was added and the mixture was heated for another 2 d at 80 °C when the conversion reached more than 90%. Solution was transferred into crystallisation tube (leaving crystalline [Et_3NH]Br), all volatiles removed *in vacuo* and the residue was recrystallized from hexane yielding colourless plates of **3** (18 mg, 0.022 mmol, 63%), identified by ^{1}H and ^{11}B NMR.

Reaction of Sn{B(NDippCH)$_2$}$_2$ with 2 equiv CO$_2$: Solution of Sn\{B(NDippCH)$_2$\}$_2$ (27 mg, 0.030 mmol) in C_6D_6 (0.5 mL) was degassed by freeze/pump/thaw procedure, then the tube was filled with CO_2 and shaken for 10 min. The ^{1}H NMR spectrum showed clean formation of a single product. The tube was reconnected to the CO_2 ampoule to top up the gas pressure. Monitoring by ^{1}H NMR showed formation of one major product after 10 days, as the colour changed to pale brown.

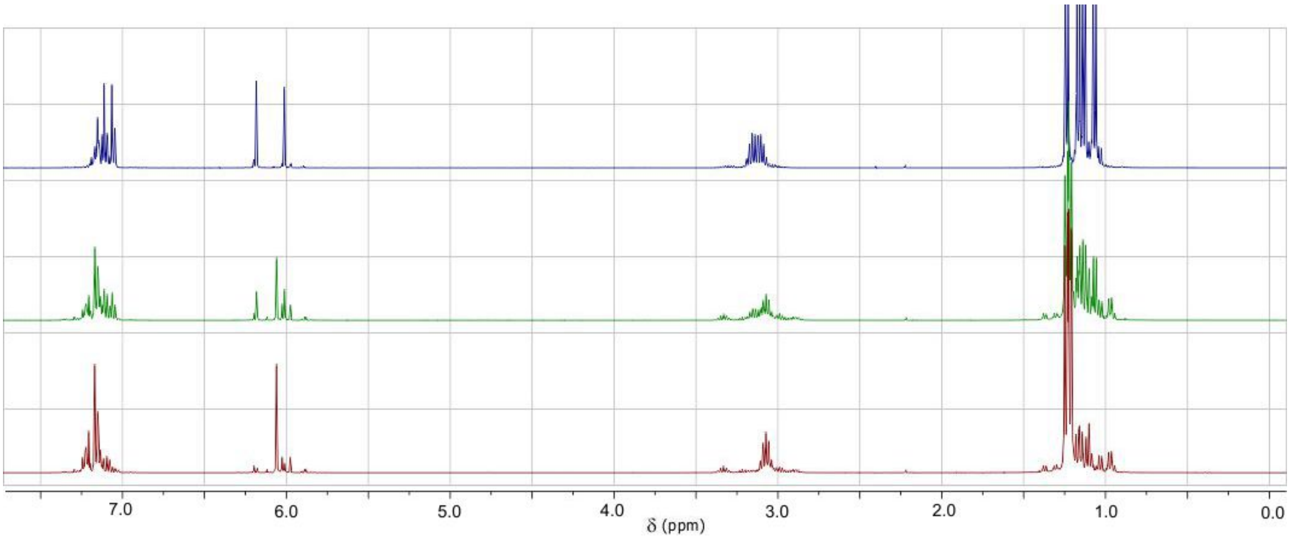


Fig. s3. ^{1}H NMR spectrum of the reaction mixture Sn\{B(NDippCH)$_2$\}$_2$ + CO_2: 10 min after addition (top); after 3 d (middle); after 10 d (bottom).

Volatiles were removed *in vacuo* but attempted crystallisation of the oily residue from hexane or pentane gave only small amount of colourless crystals identified as **5** by X-ray diffraction. The oily product was transferred into NMR tube with C_6D_6 (0.5 mL) and solid 4-$Me_2NC_5H_4N$ (DMAP) (6.0

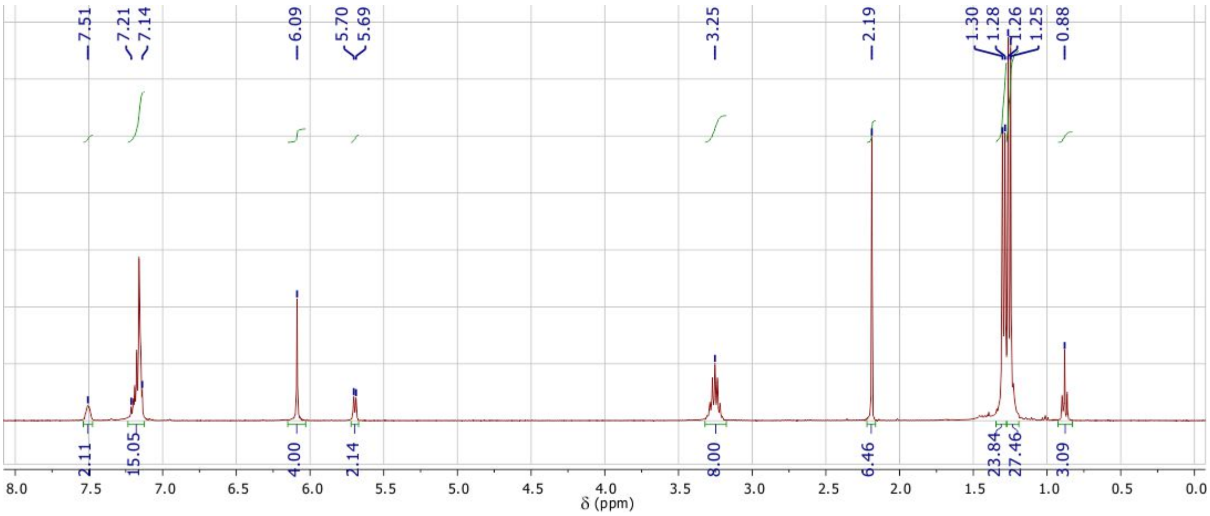
mg, 0.049 mmol) was added resulting in mainly one product. Removal of volatiles and extraction with warm hexane (the product was sparingly soluble) produced off-white needles and plates of Sn$\{O_2CB(NDippCH)_2\}_2$(DMAP) (**4**(DMAP)) (18 mg, 0.016 mmol, 54%). X-ray quality crystals of Sn$\{O_2CB(NDippCH)_2\}_2$(DMAP)·1/2C_6H_{14} were obtained by slow evaporation of hexane solution. Anal. found (calcd. for $C_{61}H_{82}B_2N_6O_4Sn$): C, 66.08 (66.38); H, 7.43 (7.49); N, 7.42 (7.61) %.

^{1}H NMR (C_6D_6): δ 7.51 (br m, 2H, *o*-H of DMAP), 7.14-7.21 (m, 12H, *m*- and *p*-H of Ar + C_6D_5H), 6.09 (s, 4H, NCH), 5.69 (d, ^3J = 6.2 Hz, 2H, *m*-H of DMAP), 3.25 (sept, ^3J = 6.9 Hz, 8H, C*H*Me$_2$), 2.19 (s, 6H, NMe$_2$), 1.29 (d, ^3J = 6.9 Hz, 24H, CH*Me*$_2$), 1.26 (d, ^3J = 6.9 Hz, 24H, CH*Me*$_2$ + CH$_2$ of hexane), 0.88 (t, 3H, CH$_3$ of hexane).

^{13}C-NMR (C_6D_6): δ 154.40 (*p*-C of DMAP), 147.54 (*o*-CH of DMAP), 146.20 (*o*-C of Ar), 139.30 (*ipso*-C of Ar), 127.40 (*p*-CH of Ar), 123.25 (*m*-CH of Ar), 119.78 (NCH), 106.31 (*m*-CH of DMAP), 38.17 (NMe$_2$), 31.92 (CH$_2$ of hexane), 28.71 (*C*HMe$_2$), 24.71 (CH*Me*$_2$), 24.46 (CH*Me*$_2$), 23.01 (CH$_2$ of hexane), 14.31 (CH$_3$ of hexane), (BCO$_2$ was not observed).

^{11}B NMR (C_6D_6): δ 20.9 (br).

^{119}Sn NMR (C_6D_6): δ −375.3.



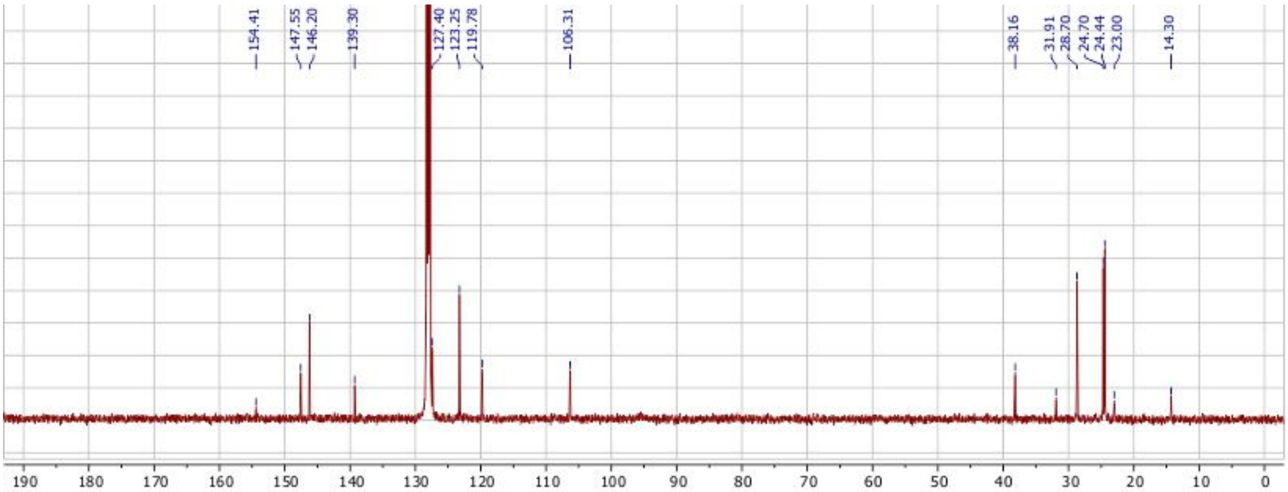


Fig. s4. ^{1}H and ^{13}C{^{1}H} NMR spectra of crystalline Sn{$O_2CB(NDippCH)_2$}$_2$(DMAP).

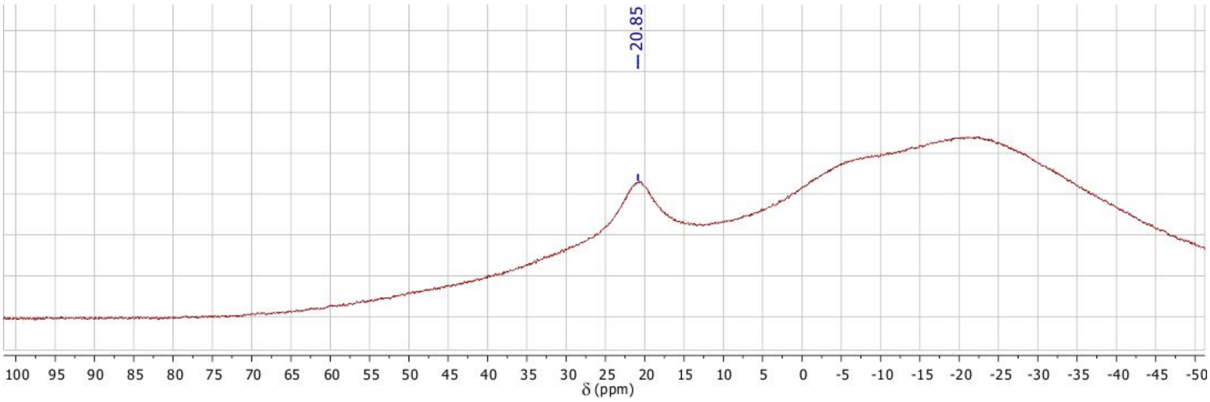


Fig. s5. ^{11}B NMR spectrum of crystalline Sn{$O_2CB(NDippCH)_2$}$_2$(DMAP).

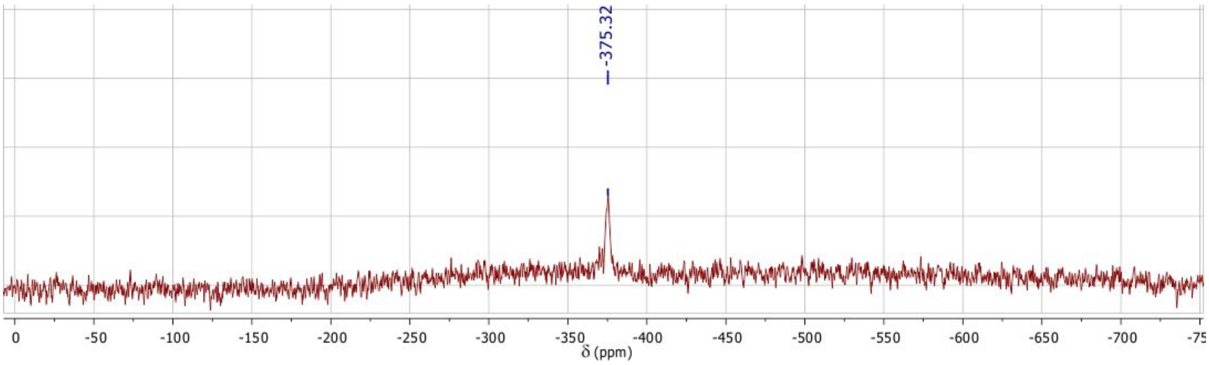


Fig. s6. ^{119}Sn NMR spectrum of crystalline Sn{$O_2CB(NDippCH)_2$}$_2$(DMAP).

Alternative routes towards tin(II) bis(borylcarboxilate)

Via reaction of $SnBr_2$ with 2 equiv of Li{$O_2CB(NDippCH)_2$}:

Solution of $(thf)_2$Li{$B(NDippCH)_2$} (45 mg, 0.083 mmol) in C_6D_6 (0.5 mL) was degassed by freeze/pump/thaw procedure, then the tube was backfilled with CO_2 and gently shaken. ^{1}H NMR spectrum showed clean formation of a single product. Excess CO_2 was removed from the headspace, the tube was taken into the glovebox and solid $SnBr_2$ (11.5 mg, 0.042 mmol) was added. The mixture was sonicated for 10 min until all solid dissolved forming clear solution showing a single set of ^{1}H NMR signals. The mixture was transferred into a two-section crystallization tube and all volatiles removed *in vacuo* at 50 °C. When hexane was added to the oily residue, a white powder (assumed to be LiBr) precipitated. The clear solution was decanted into the second section, concentrated to almost dryness and stored at room temperature overnight forming colourless blocks of **4·LiBr(thf)** (28 mg, 0.025 mmol, 58%). Anal. found (calcd. for $C_{58}H_{80}B_2BrLiN_4O_5Sn$): C, 61.24 (61.08); H, 7.21 (7.07); N, 4.99 (4.91) %.

^{1}H NMR (C_6D_6): δ 7.05-7.13 (m, 12H, *m*- and *p*-H of Ar), 6.08 (s, 4H, NCH), 3.08 (br sept, 8H, C*H*Me_2), 2.99 (br m, 4H, OCH_2 of thf), 1.30 (br m, 4H, CH_2 of thf), 1.18-1.28 (m, 48H, CH*Me*$_2$).

$^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 181.0 (very broad, only observed in HMBC, BCO_2), 145.78 (*o*-C of Ar), 145.69 (*o*-C of Ar), 139.54 (*ipso*-C of Ar), 127.36 (*p*-CH of Ar), 123.18 (*m*-CH of Ar), 120.08 (NCH), 67.56 (OCH_2 of thf), 28.70 (*C*HMe_2), 25.44 (CH_2 thf), 24.52 (CH*Me*$_2$), 24.48 (CH*Me*$_2$).

$^{11}B\{^{1}H\}$ NMR (C_6D_6): δ 20.0 (br).

^{7}Li NMR (C_6D_6): δ 0.22 (s).

^{119}Sn NMR (C_6D_6): δ −408.3.

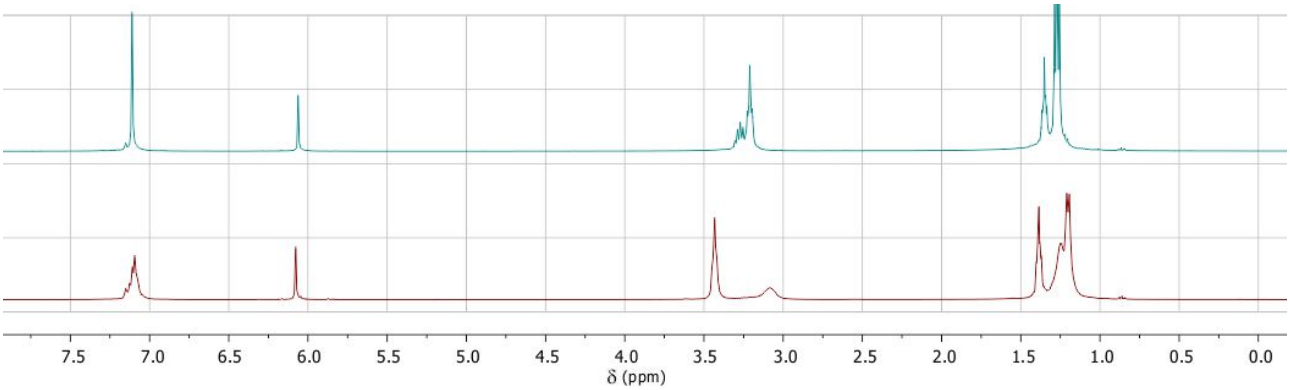


Fig. s7. ^{1}H NMR spectra of the reaction mixture $(thf)_2Li\{B(NDippCH)_2\}$ + CO_2 (top) and after addition of $SnBr_2$ (bottom)

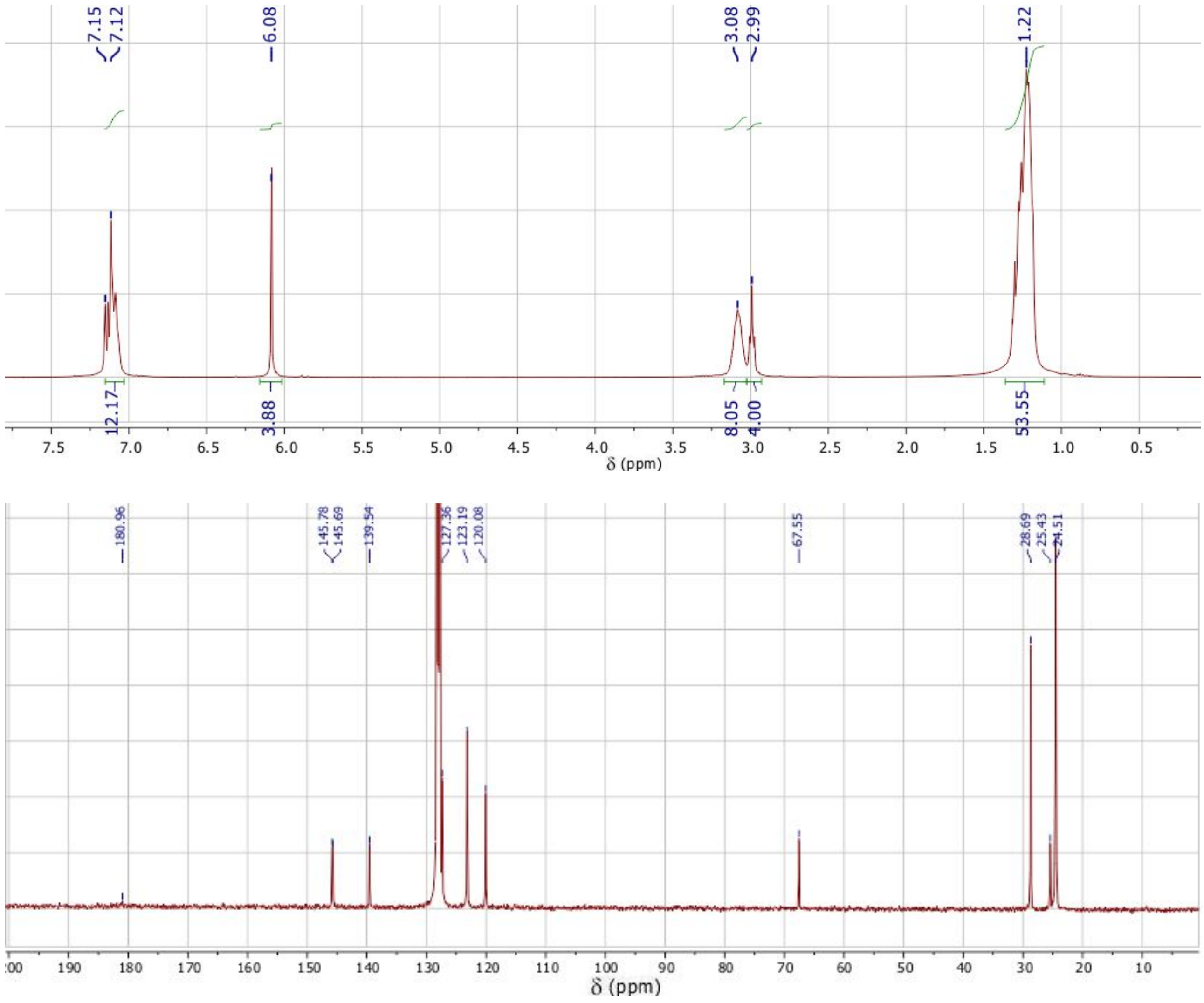


Fig. s8. ^{1}H and ^{13}C{^{1}H} NMR spectra of crystalline Sn{$O_2CB(NDippCH)_2$}$_2$(LiBr)(thf).

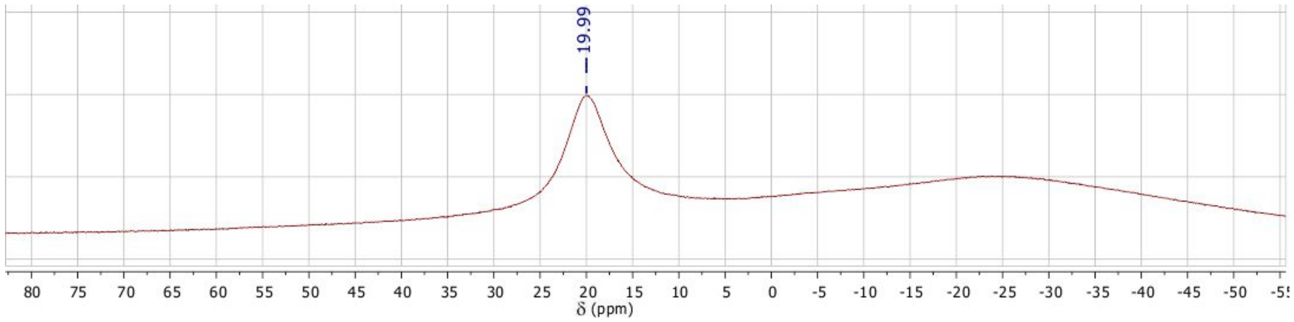


Fig. s9. ^{11}B NMR spectrum of crystalline Sn{$O_2CB(NDippCH)_2$}$_2$(LiBr)(thf).

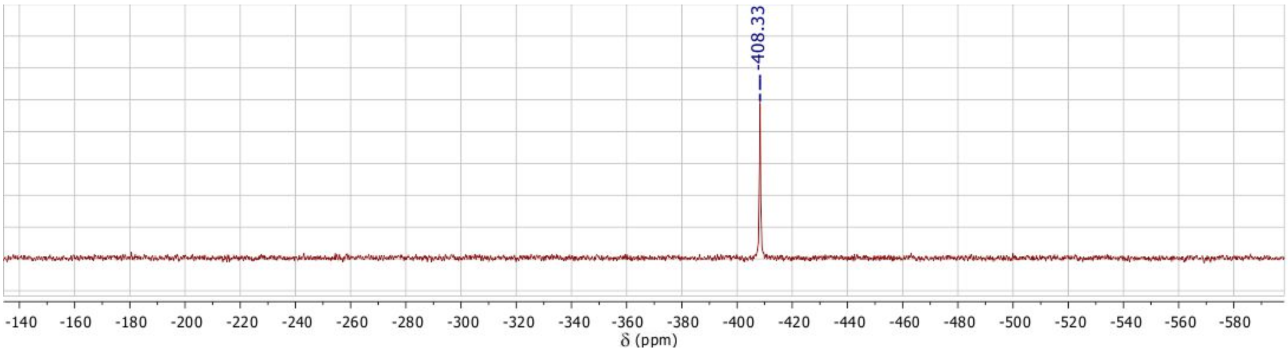


Fig. s10. ^{119}Sn NMR spectrum of crystalline Sn{O_2CB(NDippCH)$_2$}$_2$(LiBr)(thf).

Via reaction of SnBr$_2$ with 2 equiv of K{O$_2$CB(NDippCH)$_2$}:

(1) Preparation of [K{O$_2$CB(NDippCH)$_2$}]$_4$(C$_6$H$_6$)$_x$ (7)

Solid potassium hydride (5.5 mg, 0.138 mmol) was added to a solution of HO$_2$C{B(NDippCH)$_2$} (54 mg, 0.125 mmol) in benzene (1.0 mL) and the mixture was sonicated for 1 h until no more hydrogen was evolving (excess pressure was removed when the initial vigorous reaction slowed down after ~10 min); light brown colour developed by the end of the reaction. Solution was filtered and concentrated to half of its volume when small colourless crystals started precipitating. Precipitation was completed by addition of equal volume of hexane and storing overnight. Washing with hexane and drying under vacuum yielded white powder (still containing some benzene of crystallisation) of **7** (34 mg, 0.072 mmol, 57.8%). Large colourless blocks suitable for X-ray diffraction were obtained by careful layering benzene solution of **7** with hexane.

^{1}H NMR (C_6D_6): δ 7.21 (br t, ^{3}J = 7.4 Hz, 2H, *p*-H of Ar), 7.12 (br d, ^{3}J = 7.4 Hz, 4H, *m*-H of Ar), 6.07 (s, 2H, NCH), 3.26 (br s, 4H, C*H*Me$_2$), 1.25 (d, ^{3}J = 6.9 Hz, overlapping with br s, 24H, CH*Me*$_2$).

^{13}C{^{1}H} NMR (C_6D_6): δ 146.34 (*o*-C of Ar), 140.78 (*ipso*-C of Ar), 126.93 (*p*-CH of Ar), 123.00 (*m*-CH of Ar), 118.50 (NCH), 28.25 (*C*HMe$_2$), 24.52 (CH*Me*$_2$), 24.21 (CH*Me*$_2$), (BCO$_2$ was not observed).

^{11}B{^{1}H} NMR (C_6D_6): δ 20.9 (v br).

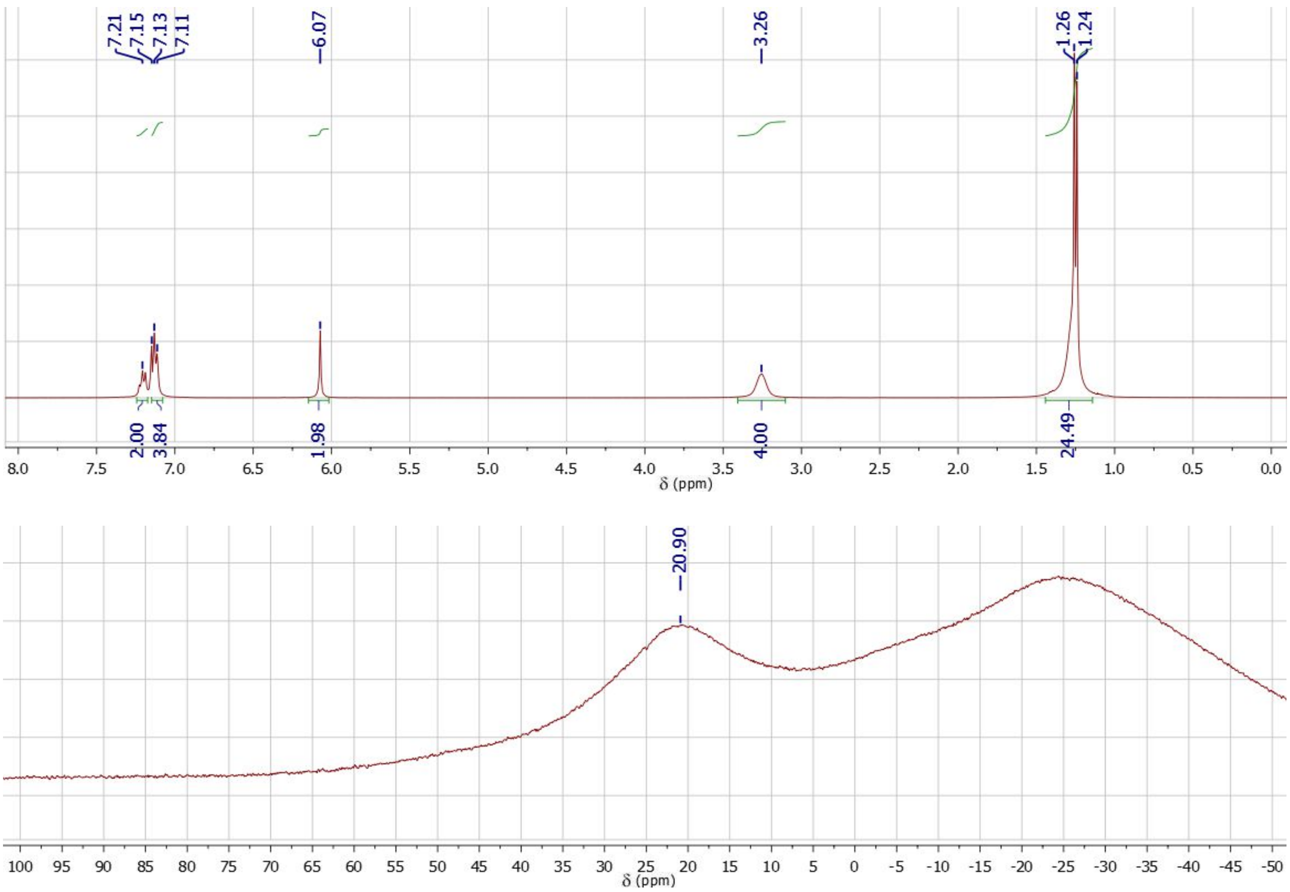


Fig. s11s ^{1}H and ^{11}B NMR spectra of crystalline $[\mathrm{K}\{\mathrm{O_2CB(NDippCH)_2}\}]_4(\mathrm{C_6H_6})_x$ (**7**).

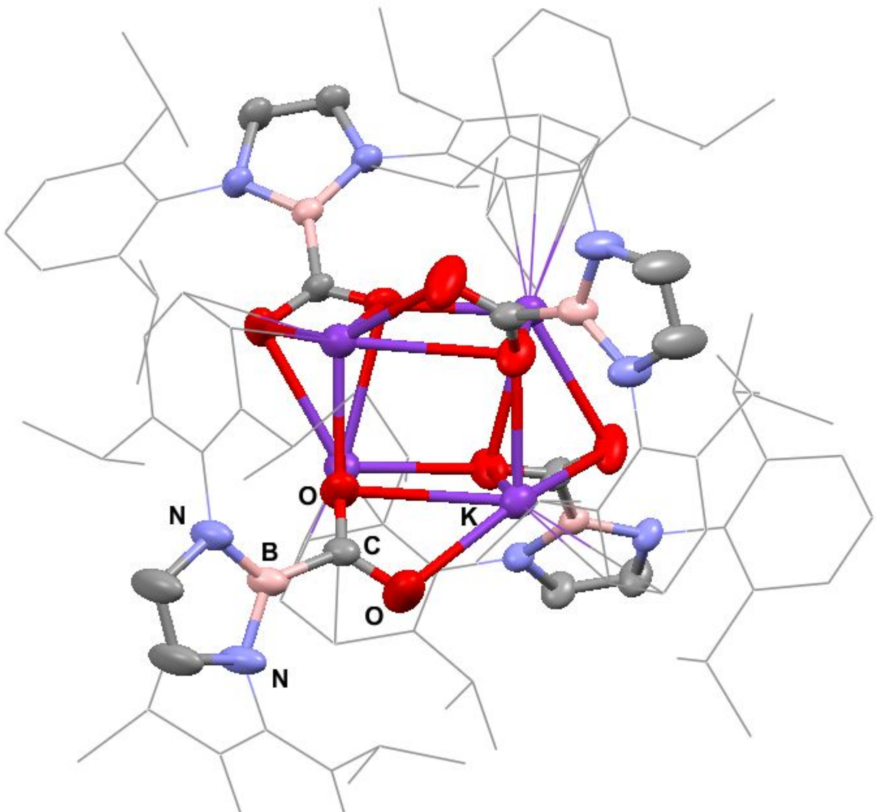


Figure s12. Molecular structure of **7** in the solid state as determined by X-ray crystallography. Hydrogen atoms omitted and Dipp groups shown in wireframe format for clarity.

(2) Preparation of Sn{O_2CB(NDippCH)$_2$}$_2$ (4) from 7:

Solid potassium hydride (3.0 mg, 0.075 mmol) was added to a solution of HO_2C\{B(NDippCH)$_2$\} (23 mg, 0.053 mmol) in C_6D_6 (0.4 mL) and the mixture was sonicated for 1 h until no more hydrogen was evolving and ^{1}H NMR spectrum showed disappearance of the starting compound and formation of **7**. The solution was transferred into a new NMR tube and the residue was washed with C_6D_6 (0.1 mL). Solid $SnBr_2$ (7.2 mg, 0.026 mmol) was added, but no reaction was observed after sonication for 30 min. Then thf (0.15 mL) was vacuum-transferred to the tube and sonication continued for another 30 min resulting in clear solution with a single new set of ^{1}H NMR signals, but no KBr precipitate. All volatiles were removed *in vacuo*, the residue was extracted with hexane (0.5 mL), leaving white powder of KBr. Attempted crystallisation from the extract was unsuccessful, removing the solvent gave pale brown oil, which showed similar ^{1}H NMR spectrum to that of **4** obtained via CO_2 insertion. Addition of DMAP (3.4 mg, 0.028 mmol) resulted in the formation of **4·(DMAP)** by comparison of its ^{1}H NMR spectrum to the reported above.

Experiment demonstrating decarbonylative instability of *in situ* prepared solution of (thf)$_2$Li{O_2CB(NDippCH)$_2$}

Solution of (thf)$_2$Li{B(NDippCH)$_2$} (45 mg, 0.083 mmol) in C_6D_6 (0.5 mL) was degassed by freeze/pump/thaw procedure, then the tube was backfilled with CO_2 and gently shaken. ^{1}H and ^{13}C NMR spectra showed clean formation of a single product. Next day (after ~17 h) the sample showed unexpectedly complex spectra, particularly ^{13}C NMR spectrum, in which a small sharp peak at 184 ppm indicated CO formation. Solid $SnBr_2$ (11.5 mg, 0.042 mmol) was added and the mixture was sonicated for 10 min until all solid dissolved forming cloudy solution. ^{1}H NMR spectrum showed that a mixture of products was formed with a major component having two backbone CH peaks at 5.88 and 6.05 ppm (corresponding to BCO_2 and BO moieties). All volatiles were removed *in vacuo*, the residue was extracted with hexane (0.5 mL), leaving white powder of LiBr. Crystallisation from concentrated solution at room temperature still gave a mixture with a major product **6** forming large colourless blocks, suitable for X-ray diffraction. Additional recrystallisation yielded almost pure Sn{O_2CB(NDippCH)$_2$}{OB(NDippCH)$_2$}(LiBr)(thf) (**6**) (27 mg, 0.024 mmol, 58%).

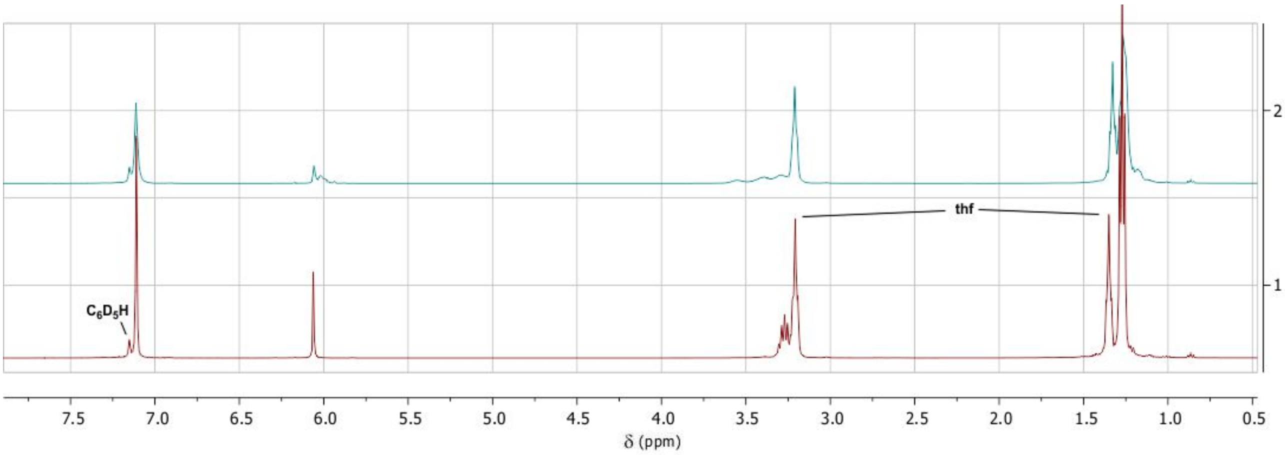


Fig. s13. ^{1}H NMR spectra of the reaction mixture $(thf)_2Li\{B(NDippCH)_2\}$ + CO_2 (lower) and after 17 h at room temperature (upper).

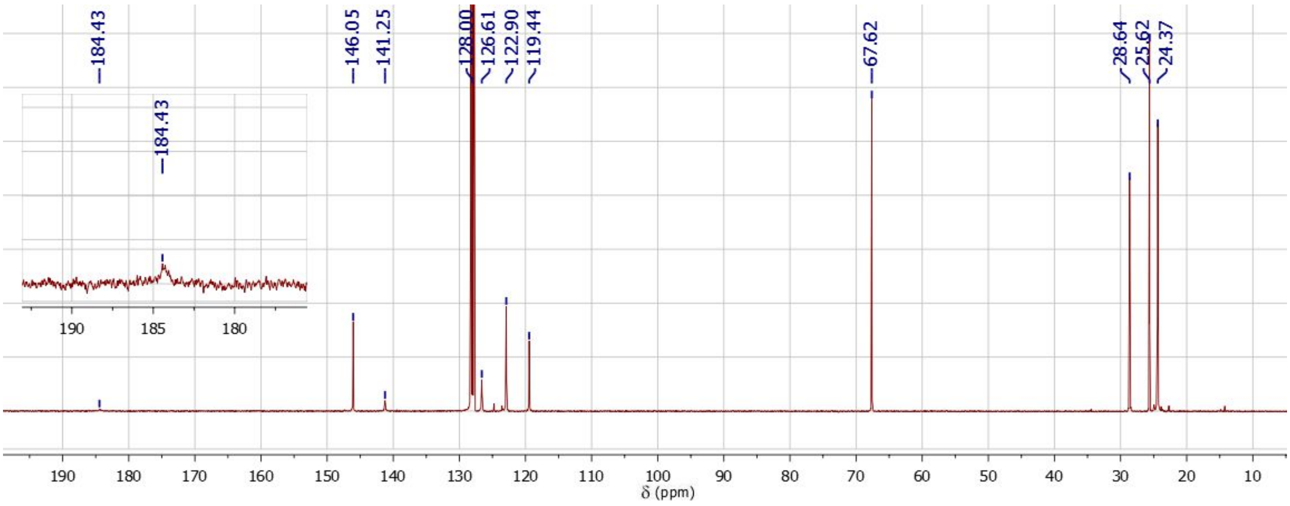


Fig. s14. ^{13}C NMR spectrum of freshly prepared $(thf)_2Li\{O_2CB(NDippCH)_2\}$ showing broad signal of BCO_2 moiety at 184 ppm (inset).

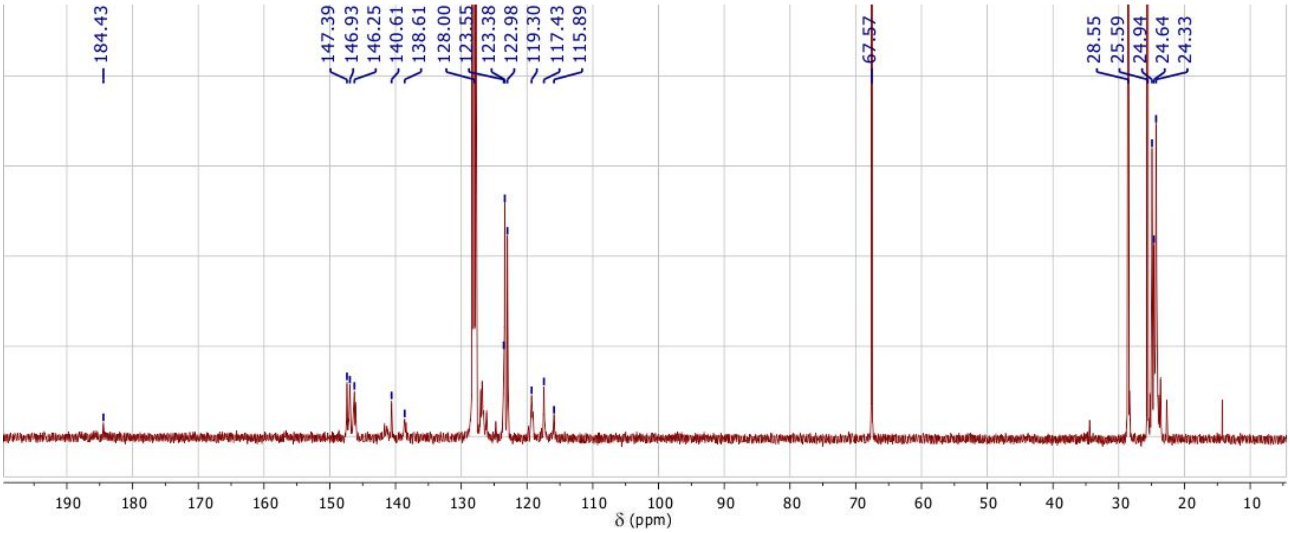


Fig. s15. ^{13}C NMR spectrum of the reaction mixture $(thf)_2Li\{B(NDippCH)_2\}$ + CO_2 after 17 h at room temperature.

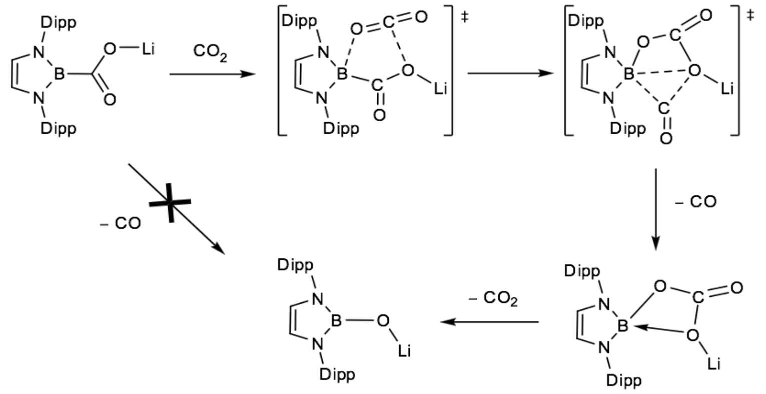


Fig. s16. Proposed mechanism for the decomposition of (thf)$_2$Li{O$_2$CB(NDippCH)$_2$} in the presence of added CO$_2$ (the isolated carboxylate was stable in C$_6$D$_6$ solution).

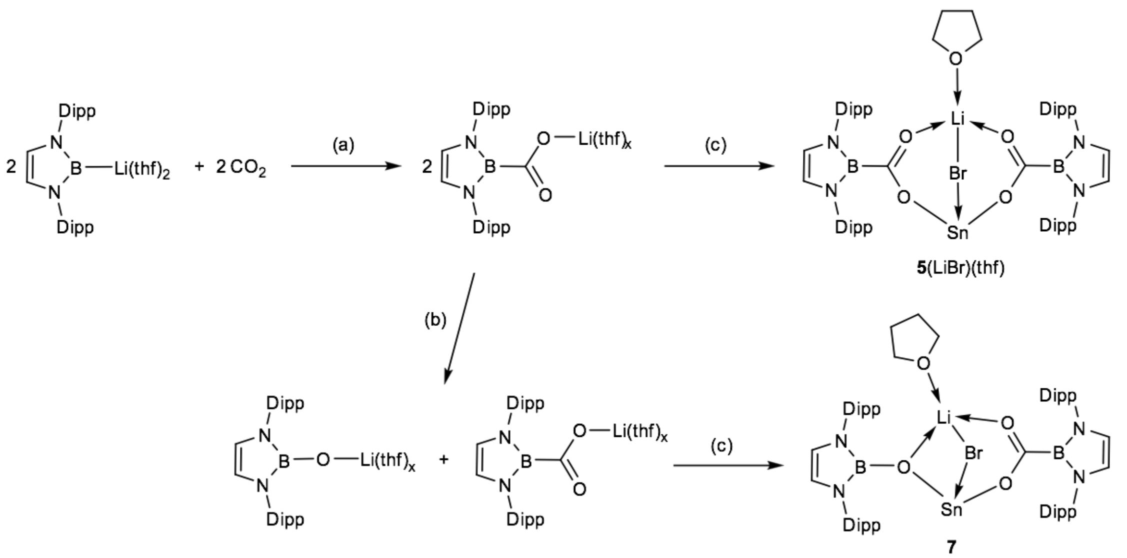


Fig. s17. Reactions of lithium borylcarboxylate with SnBr$_2$. Reagents and conditions: (a) benzene, 1 atm CO$_2$, 10 min; (b) benzene, 1 atm CO$_2$, 17 h; (c) SnBr$_2$, benzene, sonication 30 min, hexane extraction

^{1}H NMR (C$_6$D$_6$) for **7**: δ 7.13-7.21 (2H, m, *p*-CH of Ar + C$_6$D$_5$H), 7.01-7.11 (10H, m, *m*- and *p*-CH of Ar), 6.05 (2H, s, NCH), 5.88 (2H, s, NCH), 3.34 (2H, septet, ^3J = 6.8 Hz, C*H*Me$_2$), 3.29 (2H, septet, ^3J = 6.8 Hz, C*H*Me$_2$), 3.22 (2H, septet, ^3J = 6.8 Hz, C*H*Me$_2$), 3.06 (2H, septet, ^3J = 6.8 Hz, C*H*Me$_2$), 2.84 (4H, br m, OCH$_2$ of thf), 1.29-1.32 (16H, br m, CH*Me$_2$* + CH$_2$ of thf), 1.15-1.27 (36H, m, CH*Me$_2$*).

^{13}C{^{1}H} NMR (C$_6$D$_6$) for **7**: δ 183.0 (very broad, only observed in HMBC, BCO$_2$), 147.60 (*o*-C of Ar), 147.45 (*o*-C of Ar), 145.94 (*o*-C of Ar), 145.66 (*o*-C of Ar), 139.80 (*ipso*-C of Ar), 139.36

(*ipso*-C of Ar), 127.63 (*p*-CH of Ar), 127.28 (*p*-CH of Ar), 124.18 (*m*-CH of Ar), 124.12 (*m*-CH of Ar), 123.18 (*m*-CH of Ar), 123.06 (*m*-CH of Ar), 120.40 (NCH), 116.46 (NCH), 67.88 (OCH_2 of thf), 28.76 (*C*HMe$_2$), 28.69 (*C*HMe$_2$), 28.65 (*C*HMe$_2$), 25.22 (CH_2 thf), 24.99 (CH*Me*$_2$), 24.87 (CH*Me*$_2$), 24.84 (CH*Me*$_2$), 24.65 (CH*Me*$_2$), 24.49 (CH*Me*$_2$), 24.45 (CH*Me*$_2$), 24.17 (CH*Me*$_2$), 23.81 (CH*Me*$_2$).

$^{11}B\{^1H\}$ (C_6D_6) for **7**: δ 21.5 (br).

^7Li NMR (C_6D_6) for **7**: δ −0.30.

^{119}Sn NMR (C_6D_6) for **7**: δ −287.5.

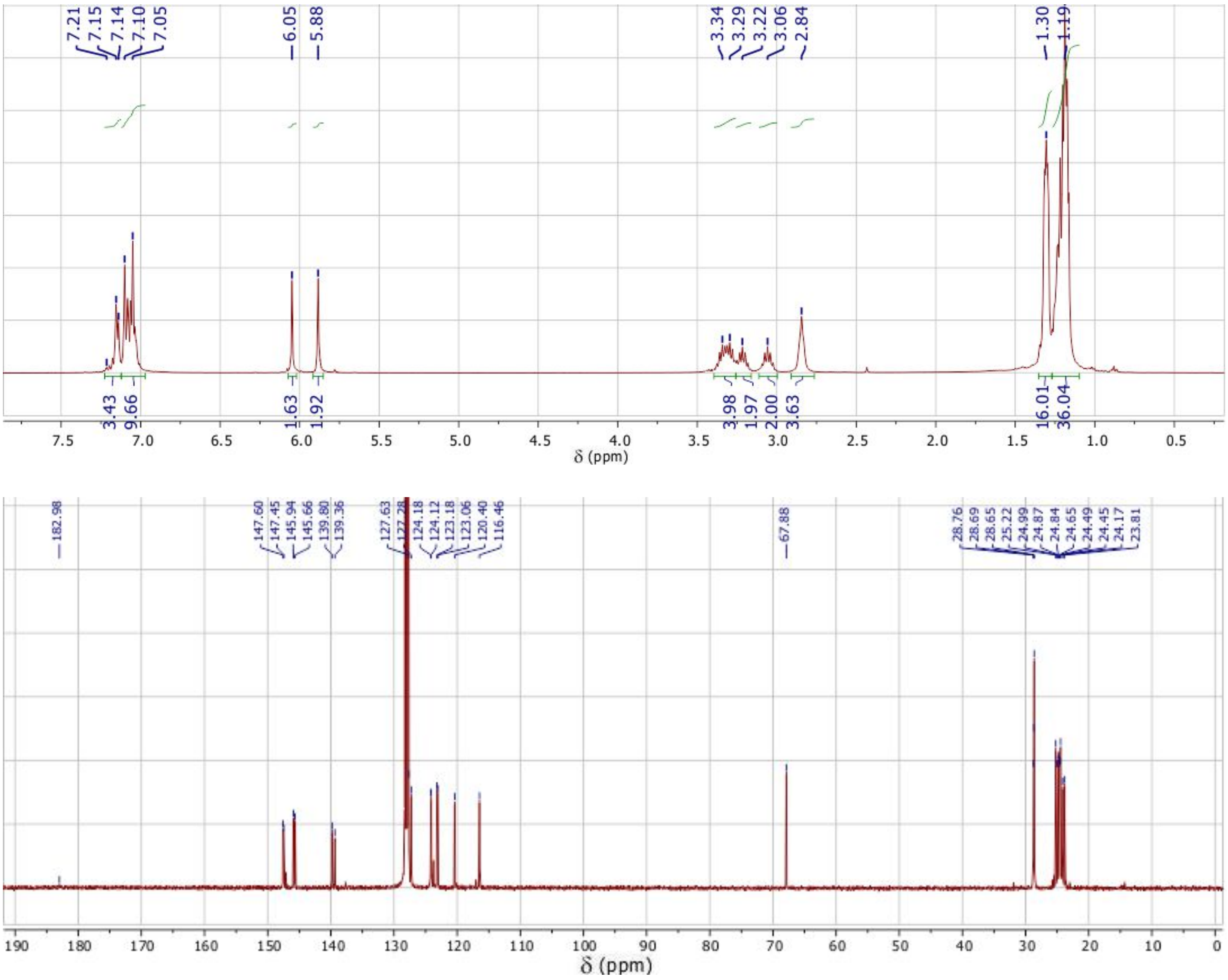


Fig. s18. ^1H and $^{13}C\{^1H\}$ NMR spectra of crystalline $Sn\{O_2CB(NDippCH)_2\}\{OB(NDippCH)_2\}$-(LiBr)(thf).

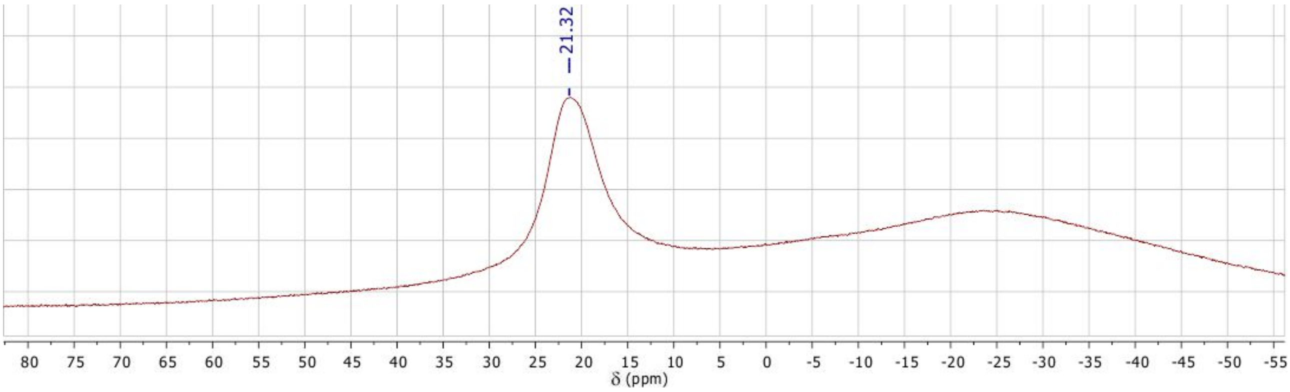


Fig. s19. ^{11}B NMR spectrum of crystalline Sn{O_2CB(NDippCH)$_2$}{OB(NDippCH)$_2$}(LiBr)(thf).

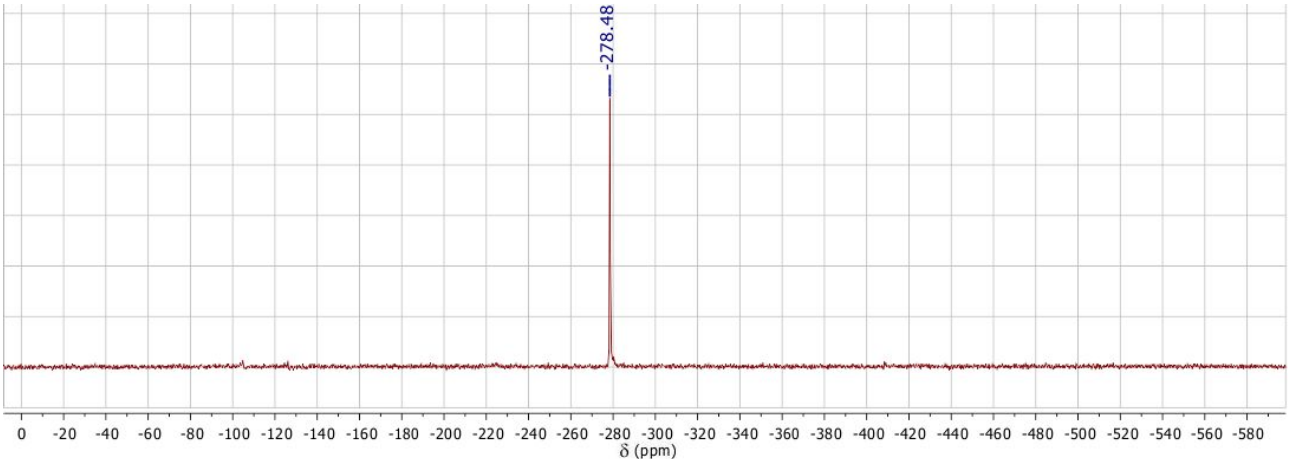


Fig. s20. ^{119}Sn NMR spectrum of crystalline Sn{O_2CB(NDippCH)$_2$}{OB(NDippCH)$_2$}(LiBr)(thf).

Reaction of Sn{B(NDippCH)$_2$}$_2$ with N_2O: Solution of Sn{B(NDippCH)$_2$}$_2$ (15 mg, 0.017 mmol) in C_6D_6 (0.5 mL) was degassed by freeze/pump/thaw procedure, then the tube was filled with N_2O and gently shaken. The solution colour changed from yellow-green to dark purple. Immediately ^{1}H NMR showed formation of a single asymmetrical product. After staying at room temperature for 12 h the colour changed to light yellow and a complex mixture (including free diazadiene DippN=CHCH=NDipp with backbone CH signal at 8.17 ppm) was formed due to overoxidation.

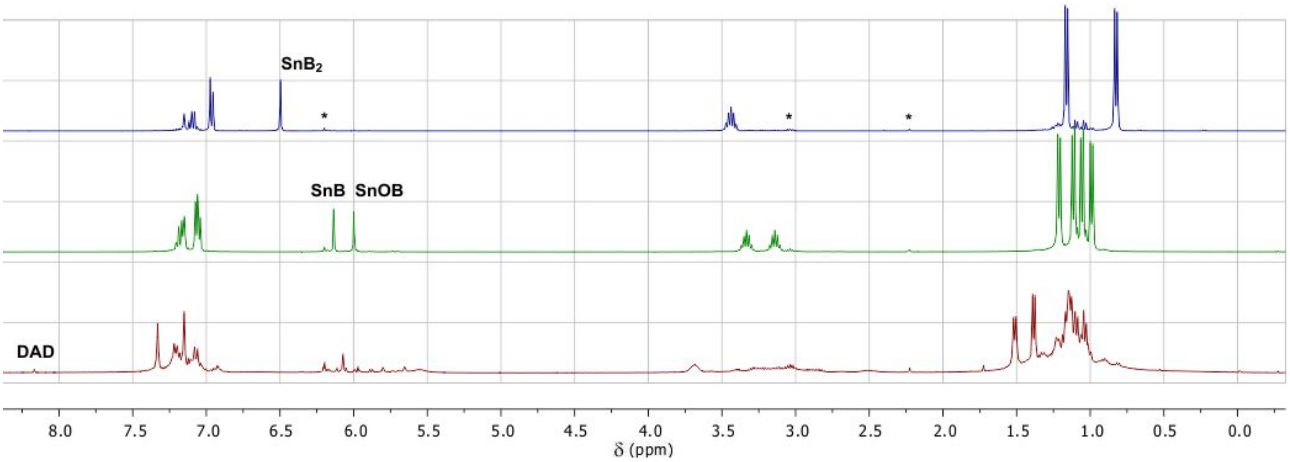


Fig. s21. ^{1}H NMR spectrum of the reaction Sn{B(NDippCH)$_2$}$_2$ + N_2O: before the N_2O addition (top); immediately after addition (middle); after 12 h (bottom) (star indicates signals of H_2Sn{B(NDippCH)$_2$}$_2$ impurity).

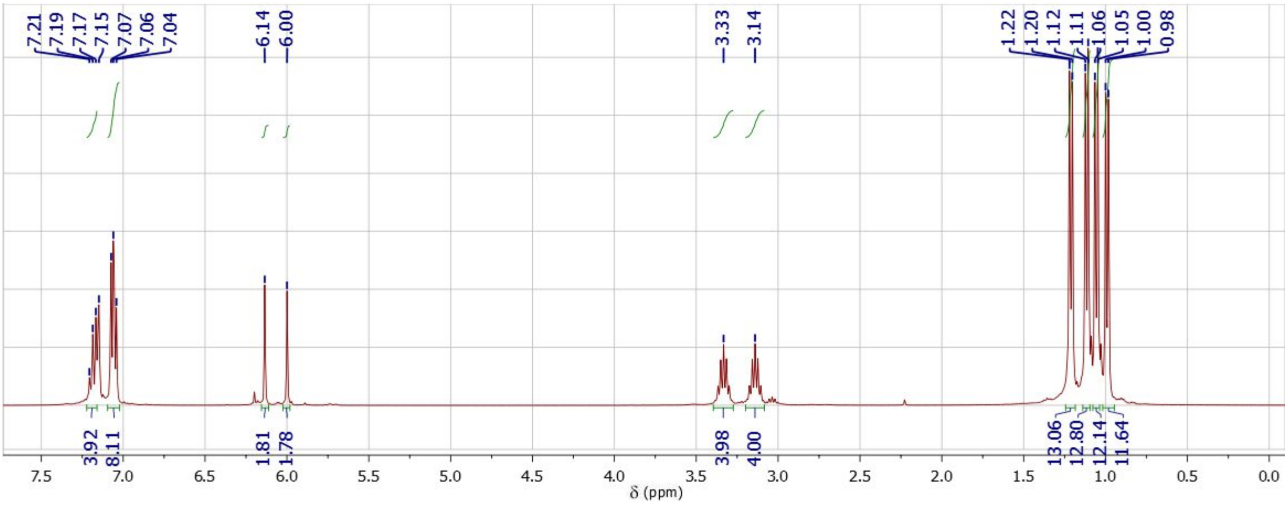
In order to crystallise the initial product, reaction was carried out in a two-section tube. Solution of [Sn{B(NDippCH)$_2$}$_2$] (25 mg, 0.028 mmol) in C_6H_6 (0.5 mL) was degassed by freeze/pump/thaw procedure and treated with N_2O until the colour turned dark purple. The tube was then quickly degassed by freeze/pump/thaw to avoid further oxidation and sealed under vacuum. The solution was concentrated to ¼ volume and stored at room temperature overnight producing deep red-purple crystals of [Sn{B(NDippCH)$_2$}{OB(NDippCH)$_2$}] (**8**) suitable for X-ray diffraction.

The crystalline material isolated after picking crystals **8** for crystallographic study contained also some starting [Sn{B(NDippCH)$_2$}$_2$] and [Sn{OB(NDippCH)$_2$}$_2$] (identified by comparison of its ^{1}H NMR spectrum with that of the reported compound[S4]).

^{1}H NMR (C_6D_6): δ 7.15-7.21 (m, 4H, *p*-H of Ar), 7.04-7.07 (m, 8H, *m*-H of Ar), 6.14 (s, 2H, NCH), 6.00 (s, 2H, NCH), 3.33 (septet, ^3J = 6.9 Hz, 4H, C*H*Me$_2$), 3.14 (septet, ^3J = 6.9 Hz, 4H, C*H*Me$_2$), 1.21 (d, ^3J = 6.9 Hz, 12H, CH*Me*$_2$), 1.11 (d, ^3J = 6.9 Hz, 12H, CH*Me*$_2$), 1.06 (d, ^3J = 6.9 Hz, 12H, CH*Me*$_2$), 0.99 (d, ^3J = 6.9 Hz, 12H, CH*Me*$_2$).

^{13}C{^{1}H} NMR (C_6D_6): δ 147.27 (*o*-C of Ar), 145.85 (*o*-C of Ar), 139.34 (*ipso*-C of Ar), 138.74 (*ipso*-C of Ar), 127.92 (*p*-CH of Ar), 127.00 (*p*-CH of Ar), 123.74 (*m*-CH of Ar), 123.48 (*m*-CH of Ar), 122.13 (NCH), 116.60 (NCH), 28.74 (*C*HMe$_2$), 28.65 (*C*HMe$_2$), 24.85 (CH*Me*$_2$), 24.68 (CH*Me*$_2$), 24.41 (CH*Me*$_2$), 24.16 (CH*Me*$_2$).

^{11}B{^{1}H} NMR (C_6D_6): δ 79.4 (SnB), 24.6 (SnOB).



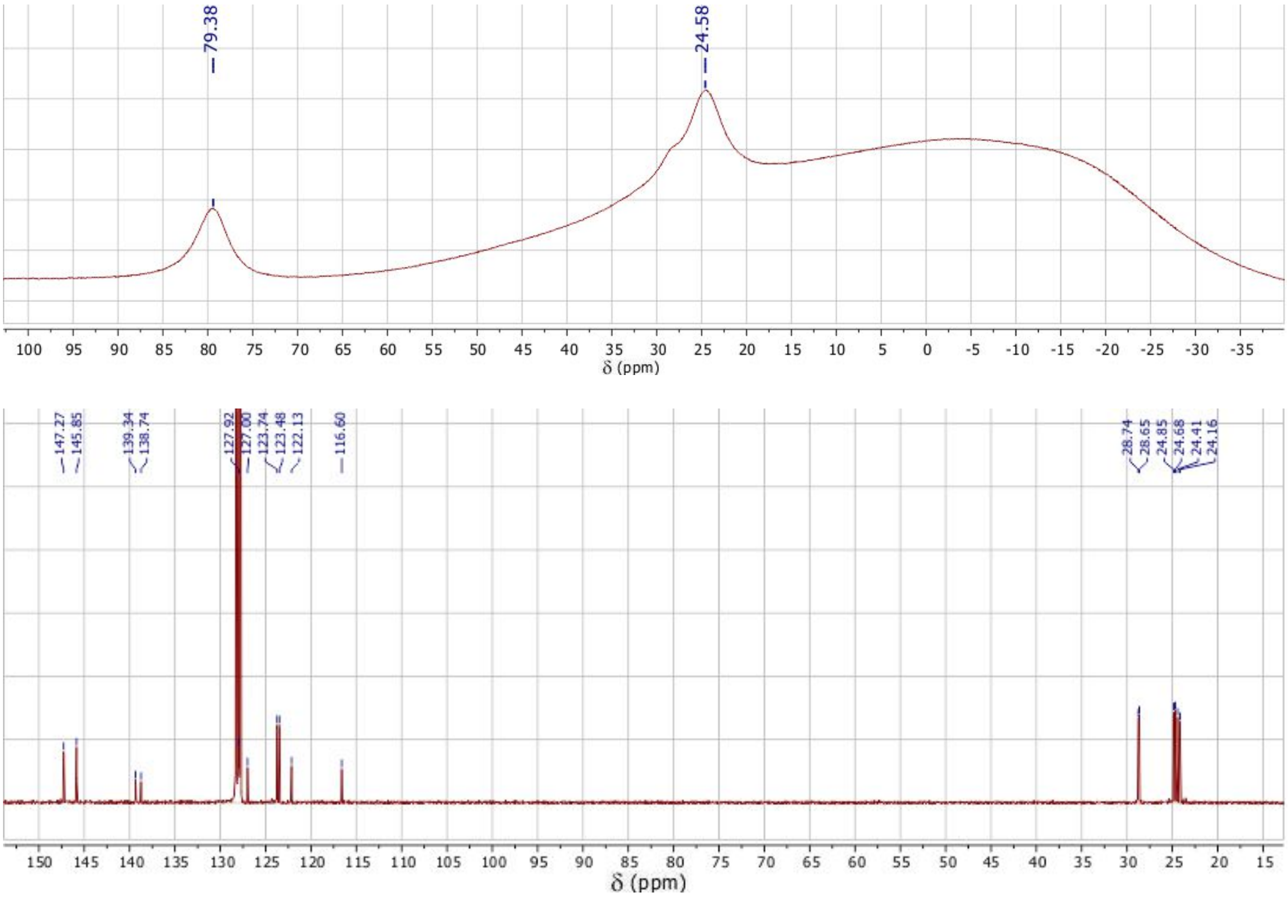


Fig. s22. ^{1}H, $^{11}B\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectra of *in situ* prepared **8**.

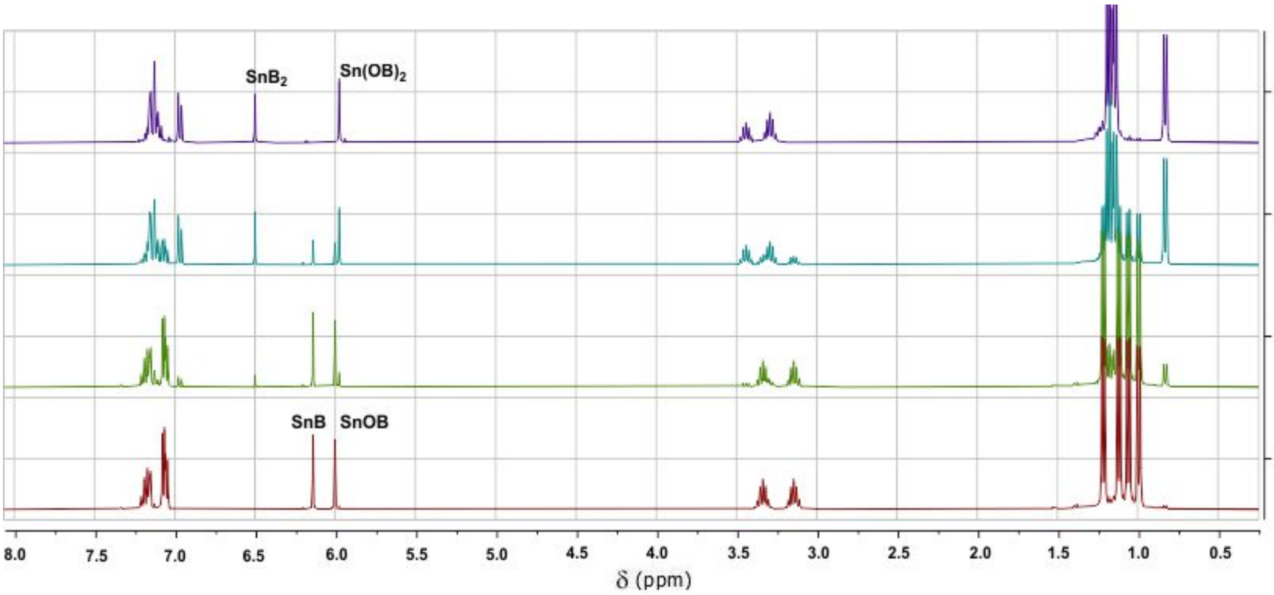


Fig. s23. ^{1}H NMR spectra showing conversion of **8** into a mixture of bis(boryl)- and bis(boryloxy)tin. Bottom: freshly prepared **8**; successive spectra measured after 1 day, 10 days and 3 months at room temperature.

2. X-ray crystallographic studies

2: $C_{53}H_{72}B_2N_4O_2Sn$, C_5H_{12}, monoclinic, *P*2$_1$/*c*, M_r = 1009.60, *a* = 20.0173(2), *b* = 12.9464(1), *c* = 24.1828(2) Å, β = 111.287(1)°, V = 5839.44(10) Å^3, ρ_x = 1.148 Mg m^{-3}, *Z* = 4, R_1 = 0.0380 (10492 observed reflections), wR_2 = 0.1062 (12081 total reflections). CCDC ref: 2077134.

3: $C_{106}H_{144}B_4N_8O_4$, orthorhombic, *P*2$_1$2$_1$2$_1$, M_r = 1637.60, *a* = 12.4748(3), *b* = 20.5322(4), *c* = 39.6202(9) Å, V = 10148.1(4) Å^3, ρ_x = 1.072 Mg m^{-3}, *Z* = 4, R_1 = 0.0714 (17328 observed reflections), wR_2 = 0.1889 (20233 total reflections). CCDC ref: 2077137.

5: $C_{108}H_{144}B_4N_8O_9Sn_3$, triclinic, *P*-1, M_r = 2097.61, *a* = 14.3697(3), *b* = 14.8194(3), *c* = 28.2627(6) Å, α = 77.969(2)°, β = 78.949(2)°, γ = 67.924(2)°, V = 5388.7(2) Å^3, ρ_x = 1.293 Mg m^{-3}, *Z* = 2, R_1 = 0.0307 (19556 observed reflections), wR_2 = 0.790 (21962 total reflections). CCDC ref: 2077136.

4(DMAP): $C_{61}H_{82}B_2N_6O_4Sn$, $0.5C_6H_{14}$, monoclinic, *P*2$_1$/*c*, M_r = 1146.75, *a* = 9.9561(1), *b* = 22.1784(3), *c* = 29.1176(3) Å, β = 97.887(1)°, V = 6368.65(13) Å^3, ρ_x = 1.196 Mg m^{-3}, *Z* = 4, R_1 = 0.0419 (11243 observed reflections), wR_2 = 0.1156 (13211 total reflections). CCDC ref: 2077140.

4(LiBr)(thf): $C_{58}H_{80}B_2BrLiN_4O_5Sn$, monoclinic, *P*2$_1$/*c*, M_r = 1140.42, *a* = 10.3410(1), *b* = 21.4584(1), *c* = 27.4349(1) Å, β = 92.851(1)°, V = 6080.31(7) Å^3, ρ_x = 1.246 Mg m^{-3}, *Z* = 4, R_1 = 0.0343 (11777 observed reflections), wR_2 = 0.0887 (12634 total reflections). CCDC ref: 2077135.

6: $C_{57}H_{80}B_2BrLiN_4O_4Sn$, monoclinic, *P*2$_1$/*c*, M_r = 1112.41, *a* = 19.7798(9), *b* = 16.8149(5), *c* = 19.3768(9) Å, β = 117.717(6)°, V = 5705.1(5) Å^3, ρ_x = 1.295 Mg m^{-3}, *Z* = 4, R_1 = 0.0497 (9830 observed reflections), wR_2 = 0.1441 (11843 total reflections). CCDC ref: 2077133.

7: $C_{108}H_{144}B_4K_4N_8O_8$, $3C_6H_6$, monoclinic, *C*2/*c*, M_r = 2116.27, *a* = 29.0119(2), *b* = 15.7055(1), *c* = 28.1694(3) Å, β = 103.568(1)°, V = 12477.08(18) Å^3, ρ_x = 1.127 Mg m^{-3}, *Z* = 4, R_1 = 0.0654 (11308 observed reflections), wR_2 = 0.2100 (13016 total reflections). CCDC ref: 2077139.

8: $C_{58}H_{78}B_2N_4OSn$, C_6H_6, tetragonal, *I*4$_1$/*a*, M_r = 987.55, *a* = 12.7358(2), *b* = 12.7358(2), *c* = 69.4576(16) Å, V = 11266.1(4) Å^3, ρ_x = 1.164 Mg m^{-3}, *Z* = 8, R_1 = 0.0781 (5467 observed reflections), wR_2 = 0.1745 (5886 total reflections). CCDC ref: 2077138.

3. References

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s2 A. V. Protchenko, K. H. Birjkumar, D. Dange, A. D. Schwarz, D. Vidovic, C. Jones, N. Kaltsoyannis, P. Mountford and S. Aldridge, *J. Am. Chem. Soc.*, 2012, **134**, 6500.

s3 Y. Segawa, Y. Suzuki, M. Yamashita and K. Nozaki, *J. Am. Chem. Soc.*, 2008, **47**, 16069.

s4 Y. K. Loh, L. Ying, M. Á. Fuentes, D. C. H. Do and S. Aldridge, *Angew. Chem. Int. Ed.*, 2019, **58**, 4847.