Supplementary Information for:

The Significance of Secondary Interactions during Alkaline Earth-promoted Dehydrogenation of Dialkylamine-Boranes

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Experimental

All reactions were carried out using standard Schlenk line and glovebox techniques under an inert argon atmosphere. NMR experiments were conducted in J. Youngs tap NMR tubes prepared and sealed in a glovebox. NMR spectra were collected on Bruker AV300 and AV500 spectrometers operating at 75.5 MHz (^{13}C), 96.3 MHz (^{11}B). Solvents (toluene, THF, hexane) were dried by a commercially available solvent purification system (Innovative Technologies) under nitrogen before storage in ampoules over molecular sieves. C_6D_6 and d_8-toluene were purchased from Goss Scientific Instruments Ltd., dried over molten potassium before distillation under nitrogen and storage over molecular sieves. $Me_2NH.BH_3$ and KH, were purchased from Sigma-Aldrich Ltd. and used without further purification. Compounds **2**, **3**, **5**, **11**, **12**, [(2,6-*i*-$Pr_2C_6H_3$)NH(*o*-C_6H_4)C(H)=N(2,6-*i*-$Pr_2C_6H_3$)] and [$KNMe_2BH_3$] were synthesised by literature procedures.[1-5] CHN microanalysis was conducted by Mr. Stephen Boyer of London Metropolitan University.

Compound 4: Toluene (ca. 10ml) was added to the solid [(2,6-*i*-$Pr_2C_6H_3$)NH(*o*-C_6H_4)C(H)=N(2,6-*i*-$Pr_2C_6H_3$)] ligand precursor (1000 mg, 2.4 mmol) and 1 molar equivalent of $MgBu_2$ (331.5 mg, 2.4 mmol) in a Schlenk tube and the resultant solution was stirred at room temperature for ca. 18 hours, allowing butane gas to vent under an inert atmosphere. The deep yellow solution was concentrated *in vacuo* and stored at -32°C overnight giving a yellow microcrystalline powder. Filtration and drying *in vacuo* provided compound **4** as a yellow solid (Yield: 1154 mg, 92%). ^{1}H NMR (C_6D_6 , 298 K, 300 MHz) δ = -0.07 (t, $^3J_{HH}$ = 7.54 Hz, 2H, MgC*H*$_2$), 0.82 (t, $^3J_{HH}$ = 7.54 Hz, 2H, $CH_2CH_2CH_3$) 1.06 (d, $^3J_{HH}$ = 6.78 Hz, 6H, $CH(CH_3)_2$), 1.13 (d, $^3J_{HH}$ = 6.78 Hz, 6H, $CH(CH_3)_2$), 1.21 (d, $^3J_{HH}$ = 6.78 Hz, 6H, $CH(CH_3)_2$), 1.27(d, $^3J_{HH}$ = 6.78 Hz, 6H, $CH(CH_3)_2$), 1.47 (qt, $^3J_{HH}$ = 7.54 Hz, 2H, $MgCH_2CH_2CH_2$), 3.05 (spt, $^3J_{HH}$ = 6.78 Hz, 2H, $CH(CH_3)_2$), 3.32 (spt, $^3J_{HH}$ = 6.78 Hz, 2H, $CH(CH_3)_2$), 6.31 (m, 1H, arom-*H*), 6.43 (m, 1H, arom-*H*), 6.90 (m, 2H, arom-*H*), 7.08 (m, 3H, arom-*H*), 7.24 (m, 3H, arom-*H*), 7.95 (s, 1H, C*H*=N). ^{13}C{^{1}H} NMR (C_6D_6 , 298 K, 125.76 MHz) δ = 5.81 ($MgCH_2$), 14.7 ($CH_2CH_2CH_3$), 23.8, 24.6, 24.7, 25.2 ($CH(CH_3)_2$), 28.9 ($CH(CH_3)_2$), 29.7 ($CH(CH_3)_2$), 31.4 ($CH_2CH_2CH_2$), 31.8 ($CH_2CH_2CH_3$), 113.5, 115.8, 117.8, 124.6, 125.0, 126.2, 127.4, 135.5, 138.9, 141.3, 144.5 (Ar-*C*), 160.5

(*i*-N=CHC_6H_4), 173.0 (*C*H=N). Anal. Calcd. for $C_{35}H_{48}MgN_2.(H_2O)_2$: C, 75.46; H, 9.41; N, 5.03%. Found: C, 75.99; H, 8.86; N, 5.78%. The sample was highly hydroscopic and sequestered two water molecules on exposure to atmosphere. ^{1}H, ^{13}C{^{1}H} and HSQC spectra are thus included as Figures S1-S3 as corroborative evidence of purity.

Compound 6: D_8-toluene (ca. 0.5 ml) was added to a solid mixture of compound **4** (40 mg, 0.058 mmol) and two molar equivalents of $Me_2NH.BH_3$ (6 mg, 0.115 mmol) and the solution sealed in a J. Youngs tap NMR tube before standing at RT for ca. 2 hours. Compound **6** was isolated by slow evaporation and crystallisation from the reaction mixture. ^{1}H NMR (d_8-tol, 298 K, 300 MHz) δ = 1.07 - 1.12 (m, 12H, 2 x CH(CH_3)$_2$), 1.26 – 1.30 (m, 12H, 2 x CH(CH_3)$_2$), 1.81 (s, 3H, N(CH_3)), 2.17 (s, 3H, N(CH_3)), 2.23 (s, 3H, N(CH_3)), 2.31 (s, 3H, N(CH_3)), 3.13 (spt, m, 2H, C*H*(CH$_3$)$_2$), 3.33 (m, 2H, C*H*(CH$_3$)$_2$), 6.25 (m, 2H, arom-*H*), 6.75 (m, 1H, arom-*H*), 6.89 (m, 1H, arom-*H*), 7.13 (m, 3H, arom-*H*), 7.17 (m, 1H, arom-*H*), 7.19 – 7.23 (m, 2H, arom-*H*), 7.99 (s, 1H, C*H*=N). ^{13}C{^{1}H} NMR (d_8-tol, 298 K, 75.5 MHz) δ = 23.4 (CH(*C*H$_3$)), 24.8 (CH(*C*H$_3$)), 26.3 (CH(*C*H$_3$)), 26.4 (CH(*C*H$_3$)), 28.8 (*C*H(CH$_3$)$_2$), 28.9 (*C*H(CH$_3$)$_2$), 29.0 (*C*H(CH$_3$)$_2$), 29.1 (*C*H(CH$_3$)$_2$), 32.4 (N(*C*H$_3$)), 46.1 (N(*C*H$_3$)), 48.3 (N(*C*H$_3$)), 52.8 (N(*C*H$_3$)), 112.8 (*C*$_6$H$_4$), 116.8 (*i*-N*C*$_6$H$_4$), 120.4 (*C*$_6$H$_4$), 124.3 (*m*-N*C*$_6$H$_4$), 124.8 (*p*-N*C*$_6$H$_4$), 127.0 (*m*-N*C*$_6$H$_4$), 127.4 (*p*-N*C*$_6$H$_4$), 133.8 (*C*$_6$H$_4$), 138.4 (*C*$_6$H$_4$), 141.9 (*o*-N*C*$_6$H$_4$), 144.7 (*o*-N*C*$_6$H$_4$), 147.9 (*i*-N*C*$_6$H$_4$), 149.5 (*i*-N*C*$_6$H$_4$), 161.8 (*i*-N=CH*C*$_6$H$_4$), 172.6 (*C*H=N). ^{11}B NMR (d_8-tol, 298 K, 96.3 MHz) δ = –16.0 (q, *B*H$_3$, $^1J_{BH}$ = 86 Hz), 3.3 (t, *B*H$_2$, $^1J_{BH}$ = 99 Hz). A single crystal of **4** suitable for X-ray diffraction analysis was isolated from a concentrated toluene solution at –30 °C. Anal. Calc. for $C_{35}H_{56}B_2MgN_4$: C: 72.63; H: 9.75; N: 9.68 %. Found: C: 72.62, 72.71; H: 9.82, 9.90; N: 9.71, 9.73%.

Compound 7: D_8-toluene (ca. 0.5 ml) was added to a solid mixture of compound **5** (71 mg, 0.1 mmol) and one molar equivalent of $Me_2NH.BH_3$ (6 mg, 0.1 mmol) and the solution sealed in a J. Youngs tap NMR tube before standing at RT for ca. 2 hours. Compound **7** was isolated by slow evaporation and crystallisation from the reaction mixture. ^{1}H NMR (d_8-tol, 298 K, 300 MHz) δ = 1.12 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.16 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(CH_3)$_2$), coincident with THF ca. 1.26 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(CH_3)$_2$), coincident with THF ca. 1.29 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.88 (br. s, 6H, N(CH_3)$_2$), 3.55 (THF), 3.09 (spt, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.27 (spt, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 6.22 (m, 2H, arom-*H*), 6.82 (m, 1H, arom-*H*), 6.98 (m, 1H, arom-*H*), 7.14 (m, 3H, arom-*H*), 7.22 (t, $^3J_{HH}$ = 8.7 Hz, 1H, arom-*H*), 7.24 (m, 2H, arom-*H*), 7.95 (s, 1H, C*H*=N). ^{13}C{^{1}H} NMR (d_8-tol, 298 K, 75.5 MHz) δ = 23.7 (CH(*C*H$_3$)$_2$), 25.3 (CH(*C*H$_3$)$_2$), 25.7 (THF), 26.1 (CH(*C*H$_3$)$_2$), 26.2 (CH(*C*H$_3$)$_2$), 28.8 (*C*H(CH$_3$)$_2$), 29.2 (*C*H(CH$_3$)$_2$), 46.7 (N(*C*H$_3$)$_2$), 70.3 (THF), 111.9 (*C*$_6$H$_4$), 117.1 (*i*-N*C*$_6$H$_4$), 118.7 (*C*$_6$H$_4$), 124.3 (*m*-N*C*$_6$H$_4$), 125.0 (*p*-N*C*$_6$H$_4$), 125.8 (*m*-N*C*$_6$H$_4$), 126.5 (*p*-N*C*$_6$H$_4$), 133.9 (*C*$_6$H$_4$), 139.3 (*C*$_6$H$_4$), 141.1 (*o*-N*C*$_6$H$_4$), 144.3 (*o*-N*C*$_6$H$_4$), 148.2 (*i*-N*C*$_6$H$_4$), 149.3 (*i*-N*C*$_6$H$_4$), 159.6 (*i*-N=CH*C*$_6$H$_4$),

171.0 (*C*H=N). ^{11}B NMR (d_8-tol, 298 K, 96.3 MHz) δ = –12.4 (q, *B*H$_3$, $^1J_{BH}$ = 80 Hz). A single crystal of **7** suitable for X-ray diffraction analysis was isolated from a concentrated toluene solution at –30°C. Anal. Calc. for $C_{37}H_{56}BCaN_3O$: C: 72.88; H: 9.26; N: 6.89 %. Found: C: 72.69, 72.73; H, 9.15, 9.13; N: 6.75, 6.82 %.

Characterisation of compound 8 (Reaction of 7 with DMAB): D_8-toluene (ca. 0.5 ml) was added to solid compound **7** (0.122 g, 0.2 mmol) and one molar equivalent of $Me_2NH.BH_3$ (11.8 mg, 0.2 mmol) and the solution sealed in a J. Youngs tap NMR tube before heating at 30°C for ca. 16 hours. Removal of solvent under vacuum provided a yellow solid. ^{1}H NMR (d_8-tol, 298 K, 300 MHz) δ = 1.10 (d, J_{HH} = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.13 (d, J_{HH} = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.18 (d, J_{HH} = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.75 (s, 3H, N(C*H*$_3$)$_2$), 1.84 (s, 3H, N(C*H*$_3$)$_2$), 2.30 (s, 3H, N(C*H*$_3$)$_2$), 2.37 (s, 3H, N(C*H*$_3$)$_2$), 3.22 (spt, J_{HH} = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.35 (spt, J_{HH} = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 6.19 - 6.35 (m, 2H, arom-*H*), 6.53 (m, 1H, arom-*H*), 6.93 (m, 1H, arom-*H*), 7.07 (m, 3H, arom-*H*), 7.16 (m, 1H, arom-*H*), 7.21 – 7.26 (m, 2H, arom-*H*), 8.20 (s, 1H, C*H*=N). ^{13}C{^{1}H} NMR (d_8-tol, 298 K, 75.5 MHz) δ = 23.7 (CH(*C*H$_3$)$_2$), 24.1 (CH(*C*H$_3$)$_2$), 25.2 (CH(*C*H$_3$)$_2$), 26.6 (CH(*C*H$_3$)$_2$), 28.9 (*C*H(CH$_3$)$_2$), 29.3 (*C*H(CH$_3$)$_2$), 43.7 (N(*C*H$_3$)$_2$), 44.2 (N(*C*H$_3$)$_2$), 51.6 (N(*C*H$_3$)$_2$), 52.6 (N(*C*H$_3$)$_2$), 112.7 (*C*$_6$H$_4$), 117.2 (*i*-N*C*$_6$H$_4$), 118.2 (*C*$_6$H$_4$), 123.8 (*m*-N*C*$_6$H$_4$), 124.6 (*p*-N*C*$_6$H$_4$), 125.3 (*m*-N*C*$_6$H$_4$), 128.5 (*p*-N*C*$_6$H$_4$), 133.0 (*C*$_6$H$_4$), 138.8 (*C*$_6$H$_4$), 141.3 (*o*-N*C*$_6$H$_4$), 144.2 (*o*-N*C*$_6$H$_4$), 148.2 (*i*-N*C*$_6$H$_4$), 149.8 (*i*-N*C*$_6$H$_4$), 160.2 (*i*-N=CH*C*$_6$H$_4$), 170.3 (*C*H=N). ^{11}B NMR (d_8-tol, 298 K, 96.3 MHz) δ = –11.2 (q, *B*H$_3$, $^1J_{BH}$ = 89 Hz), 1.8 (t, *B*H$_2$, $^1J_{BH}$ = 96 Hz). Conversion by integration of ^{11}B NMR spectrum: 78.2 % **7**, 13.6 % [Me_2N-BH_2]$_2$, 8.2 % HB(NMe_2)$_2$.

Compound 9: D_8-toluene (ca. 0.5 ml) was added to a solid mixture of compound **2** (29.4 mg, 0.05 mmol) and one molar equivalent of $Me_2NH.BH_3$ (2.9 mg, 0.05 mmol) and the solution sealed in a J. Youngs tap NMR tube before heating at 30°C for ca. 72 hours. ^{1}H NMR (d_8-tol, 298 K, 300 MHz) δ = 1.13 (d, *J* = 7.2 Hz, 12H, CH(C*H*$_3$)$_2$), 1.20 (d, *J* = 7.2 Hz, 12H, CH(C*H*$_3$)$_2$), 1.64 (s, 6H, N(C*H*$_3$)$_2$), 1.70 (s, 6H, NC(C*H*$_3$)), 1.80 (s, 3H, N(C*H*$_3$)), 1.92 (s, 3H, N(C*H*$_3$)), 3.26 (m, 4H, C*H*(CH$_3$)$_2$), 4.80 (s, 1H, C-*H*), 6.95 – 7.16 (m, 6H, arom-*H*). ^{13}C{^{1}H} NMR (d_8-tol, 298 K, 75.5 MHz) δ = 23.8 (CH(*C*H$_3$)), 24.9 (CH(*C*H$_3$)), 25.8 (*C*H(CH$_3$)), 29.0 (NC(*C*H$_3$)), 44.2 (N(*C*H$_3$)), 51.5 (N(*C*H$_3$)), 94.7 (*C*H), 123.9 (*m*-*C*$_6$H$_3$), 126.2 (*p*-*C*$_6$H$_3$), 141.7 (*o*-*C*$_6$H$_3$), 143.1 (*i*-*C*$_6$H$_3$), 161.8 (*C*N). ^{11}B NMR (d_8-tol, 298 K, 96.3 MHz) δ = –11.2 (q, *B*H$_3$, $^1J_{BH}$ = 99 Hz), 2.1 (t, *B*H$_2$, $^1J_{BH}$ = 96 Hz). A single crystal of **9** suitable for X-ray diffraction analysis was isolated from a concentrated toluene solution at –30 °C. Anal. Calc. for $C_{37}H_{66}B_2CaN_4O$: C: 68.94; H: 10.32; N: 8.64 %. Found: C: 68.87; H: 10.26; N: 8.69%.

Compound 10: A THF (ca. 10 ml) solution of compound **11** (0.4 g, 0.61 mmol) was added to a THF solution of (ca. 5 ml) K(NMe_2BH_3) (59.1 mg, 0.61 mmol) in a Schlenk tube cooled to –76 °C and stirred at room temperature for ca. 18 hours. Filtration to remove KI and removal of solvent under vacuum

provided compound **10** as a colourless solid. ^{1}H NMR (d_8-tol, 298 K, 300 MHz) δ = 1.10 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.21 (d, *J* = 7.2 Hz, 12H, CH(C*H*$_3$)$_2$), 1.56 (s, 6H, NC(C*H*$_3$)), 1.60 (s, 6H, N(C*H*$_3$)$_2$), 3.16 (m, 4H, C*H*(CH$_3$)$_2$), 4.78 (s, 1H, C-*H*), 6.95 – 7.16 (m, 6H, arom-*H*). ^{13}C{^{1}H} NMR (d_8-tol, 298 K, 75.5 MHz) δ = 24.9 (CH(*C*H$_3$)), 25.1 (CH(*C*H$_3$)), 25.6 (*C*H(CH$_3$)), 28.5 (NC(*C*H$_3$)), 48.5 (N(*C*H$_3$)), 95.8 (*C*H), 124.1 (*m*-*C*$_6$H$_3$), 125.5 (*p*-*C*$_6$H$_3$), 142.8 (*o*-*C*$_6$H$_3$), 147.4 (i-*C*$_6$H$_3$), 168.9 (*C*N). ^{11}B NMR (d_8-tol, 298 K, 96.3 MHz) δ = –11.8 (q, *B*H$_3$, $^{1}J_{BH}$ = 91 Hz). Decomposition of compound **10** upon storage prevented characterisation by X-ray diffraction analysis or CHN microanalysis.

Compound 13: A Youngs tap NMR tube charged with compound **12**, (0.05.mmol, 30mg) dissolved in 0.5ml of C_6D_6 and $Me_2NH.BH_3$ (0.05mmol, 3mg) was left at room temperature for 1hour. Colourless crystals suitable for X-ray crystallographic analysis precipitated from solution at room temperature. ^{1}H NMR (C_6D_6, 298 K 500 MHz): 7.11 – 6.99 (6H, s, Ar-*H*), 5.39 (1H, s, NC*H*CN), 3.33 (4H, sept, J_{HH} = 6.8 Hz, NC*H*(CH$_3$)$_2$), 3.03 (br q, NB*H*$_3$), 1.49 (6H, s, BN(C*H*$_3$)$_2$), 1.36 (12H, d, J_{HH} = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.25 (12H, d, J_{HH} = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.22 (18H, s, NCC(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 298 K, 125.76 MHz): 177.8 (N*C*), 146.3, 142.3 (Ar-quart), 126.0, 124.6 (CH-arom) 96.0 (NC(*C*(CH$_3$)$_3$)CH), 48.0 (N(*C*H$_3$)$_2$), 44.8 (*C*(CH$_3$)$_3$), 33.6 (*C*(CH$_3$)$_3$), 28.9, 25.43, 24.80 (CH(*C*H$_3$)$_2$). ^{11}B NMR (C_6D_6, 298 K, 96.3 MHz) -15.4 (q, 91 Hz, H$_3$*B*N(Me)$_2$). A meaningful microanalysis could not be obtained for this compound. ^{1}H, ^{13}C{^{1}H} and ^{11}B NMR spectra are thus included as Figures S6-S8 as corroborative evidence of purity.

Kinetic Experiments

All kinetic experiments were carried out on an NMR-scale in J. Youngs tap NMR tubes. Compounds were weighed out and added to 0.5 ml d_8-toluene inside a glovebox under an inert argon atmosphere, before being sealed inside a J. Youngs tap NMR tube. On removal from the glovebox the sample was frozen in liquid nitrogen and thawed before insertion into the NMR spectrometer. Reactions were monitored by ^{11}B NMR spectroscopy on a Bruker AV500 spectrometer, with concentration of boron-containing species determined using integration across all ^{11}B resonances. Boron-containing species were identified using chemical shift values obtained from literature reports of known compounds. Reactions requiring elevated temperatures were heated inside the NMR spectrometer and equilibrated for ca. 10 minutes prior to use. The internal temperature of the NMR spectrometer deviated from the temperature at which it was set by a relationship characterised using methanol chemical shifts. The resulting calibration curve was utilised to set the NMR spectrometer to a temperature at which the desired internal temperature for heating of the NMR tube was achieved. Reactions requiring prolonged heating times (>ca. 13 hours) were heated in thermostatically controlled oil baths, monitored periodically by ^{11}B NMR spectroscopy, with spectra taken on a Bruker AV300 spectrometer. Kinetic

experiments were conducted until 3 half-lives had passed, unless the reaction prohibited this. To determine values of kinetic isototpe effect (KIE) isolated experiments were conducted similar to the method adopted by Manners.[6] D_8-toluene (0.5 ml) was added to a solid mixture of compound **2** (58.8 mg, 0.1 mmol) and one molar equivalent of (i) $Me_2NH.BH_3$ (5.9 mg, 0.1 mmol), (ii) $Me_2NH.BD_3$ (6.1 mg, 0.1 mmol), or (iii) $Me_2ND.BH_3$ (6.0 mg, 0.1 mmol), and each solution was sealed in a J. Youngs tap NMR tube before the reactions at 308 K were monitored using a Bruker AV400 spectrometer. The results of these reactions are shown in Figure 5, a second-order kinetic data plot for the consumption of DMAB.

X-ray diffraction analysis

All data collections were performed at 150 K, using MoKα radiation. Data for compounds **6**, **7** and **9** were attained using a Nonius kappaCCD diffractometer while those for **13** were attained on an Agilent Xcalibur machine. For compound **6** all hydrogen atoms bonded to B(1) and B(2) have been located and freely refined. Although crystal movement during data collection resulted in a lower than ideal data completeness during the data collection of compound **7**, the structure is unambiguous. For compound **9** C(31) and C(32) in the THF ligand are disordered over two sites in the ratio 60:40. All hydrogen atoms bonded to B(1) and B(2) have been located and freely refined. For compound **13** B(1), C(37) and C(38) are disordered in a 60:40 ratio. Hydrogen atoms attached to B(1) and B(1A) were located and refined subject to having similar B-H distances and H...H distances within each fractional BH_3 moiety. In addition to one molecule of the complex, the asymmetric unit has a guest in the guise of one molecule of benzene. Crystallographic data for compounds **6**, **7**, **9** and **13** are available as CCDC 1488814-1488817 respectively.

Figure S1: ^{1}H NMR spectrum of compound **4** (C_6D_6, 298 K, 300 MHz).

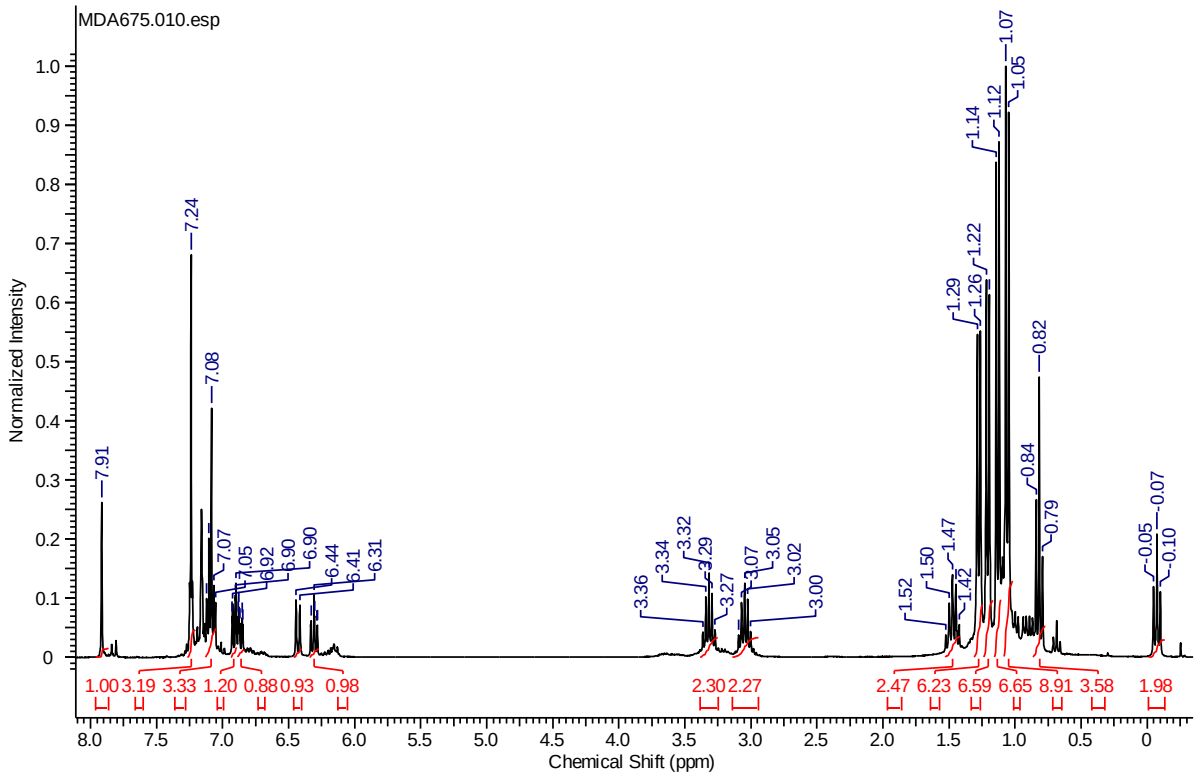


Figure S2: ^{13}C{^{1}H} NMR spectrum of compound **4** (C_6D_6 , 298 K, 125.76 MHz).

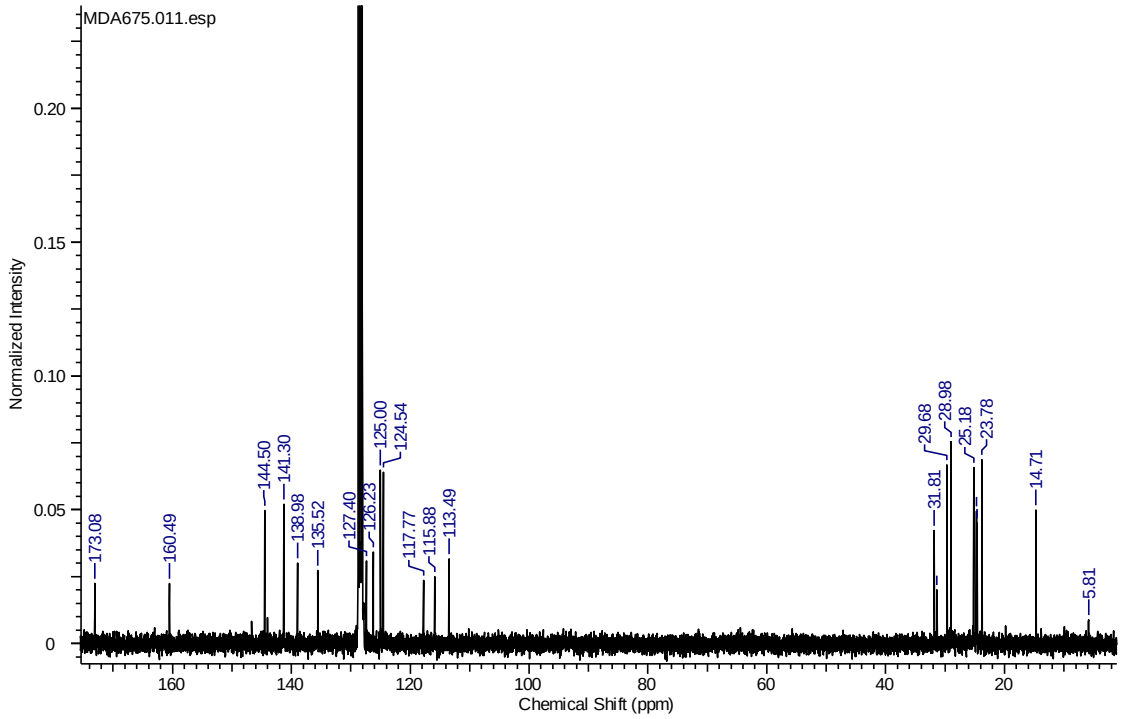


Figure S3: HSQC NMR spectrum of compound **4**.

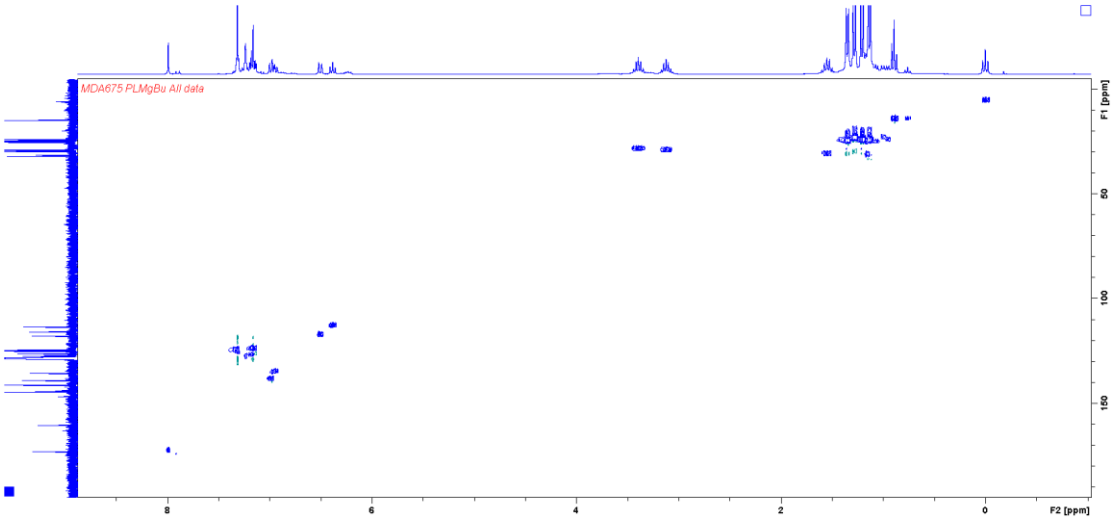


Figure S4: ^{1}H NMR spectrum (C_6D_6, 298K, 300 MHz) of the reaction of compound **3** and 2 molar equivalents of DMAB in a sealed NMR tube after 72 hours at 25°C. The resonance attributed to molecular H_2 is observed at δ 4.49 ppm whilst the signal at δ 4.78 ppm is assigned to the re-formation of compound **3**.

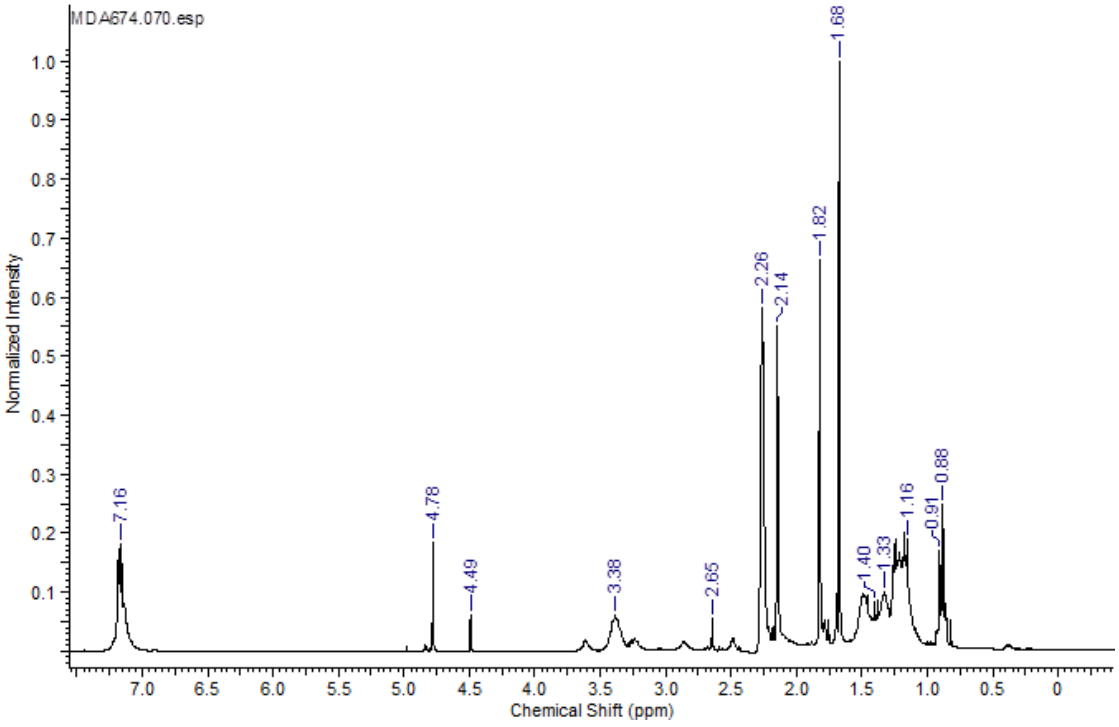


Figure S5: ^{11}B NMR spectrum (C_6D_6, 298K, 96.3 MHz) of the reaction of compound **3** and 2 molar equivalents of DMAB in a sealed NMR tube after 72 hours at 25°C showing the production of $[Me_2N\text{-}BH_2]_2$ and **3**.

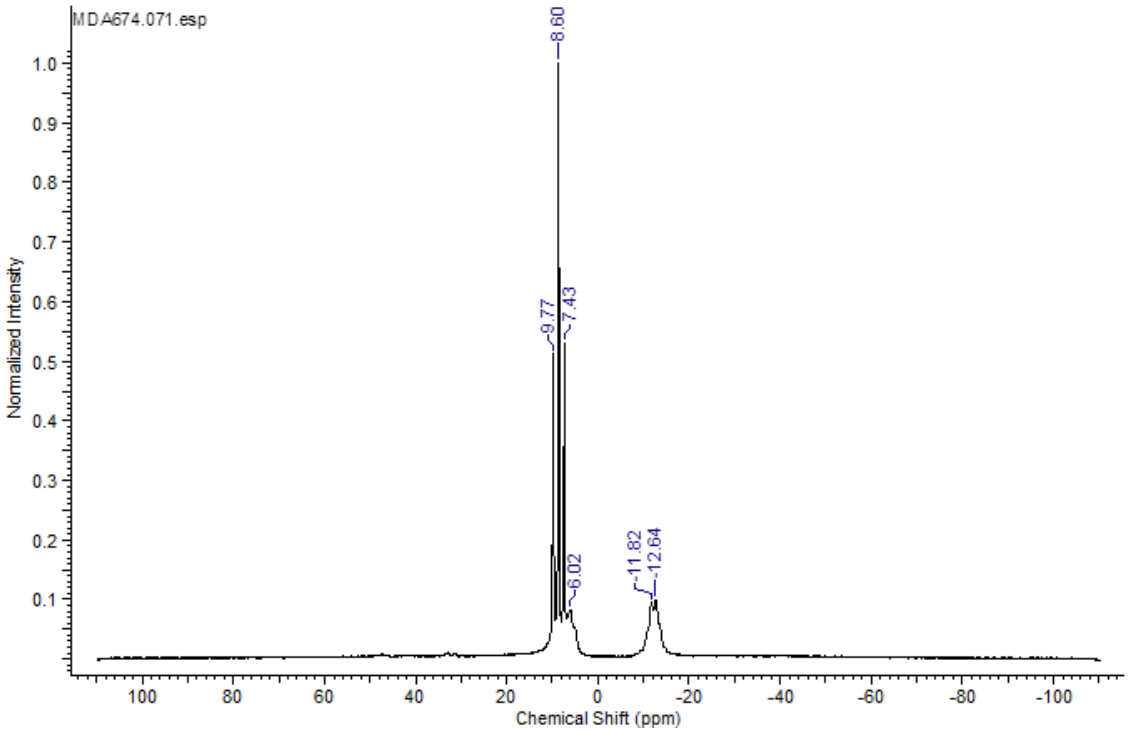


Figure S6: : ^1H NMR spectrum of compound **13** (C_6D_6, 298 K, 500 MHz).

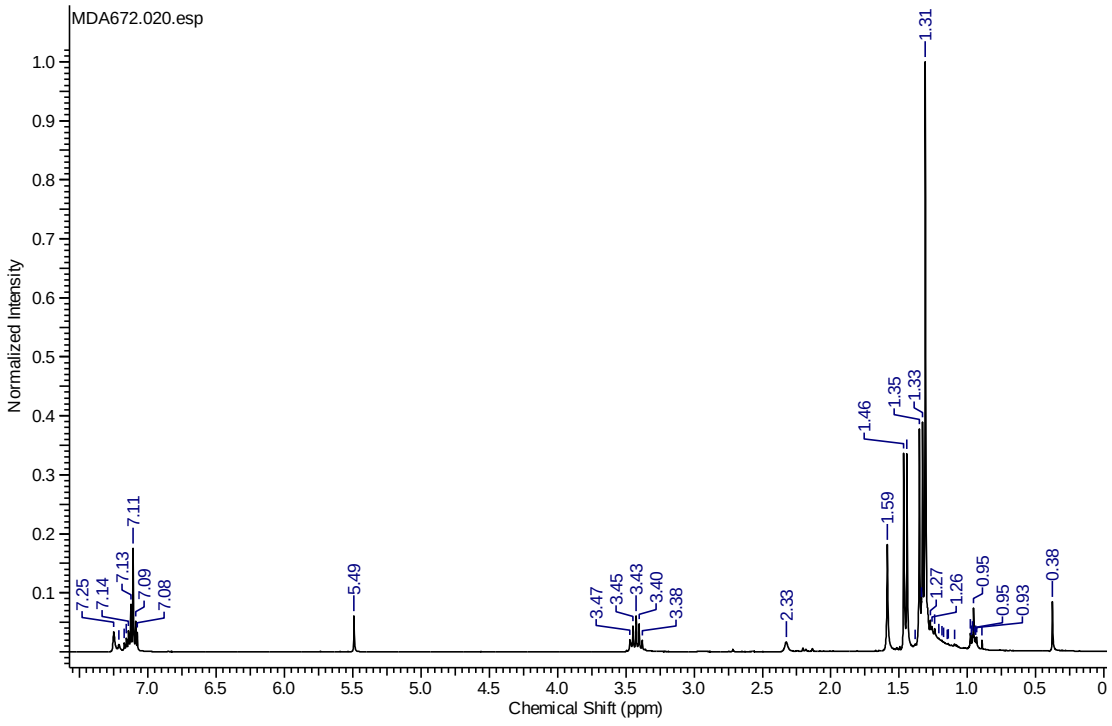


Figure S7: $^{13}C\{^{1}H\}$ NMR spectrum of compound **13** (C_6D_6, 298 K 125.76 MHz).

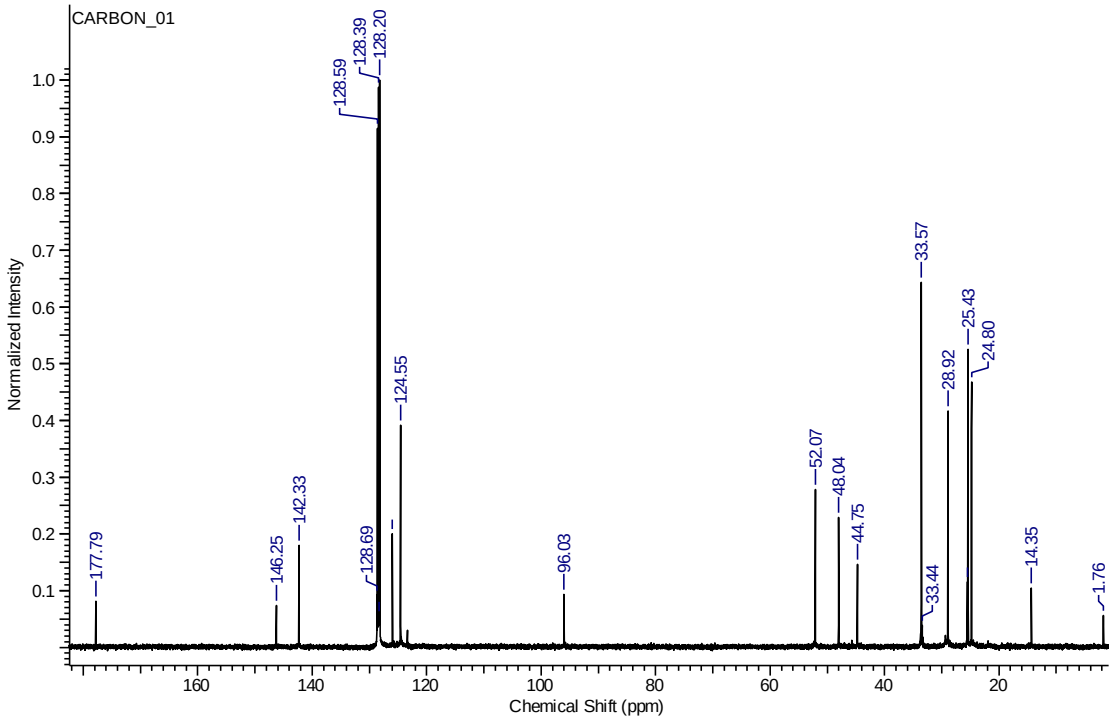
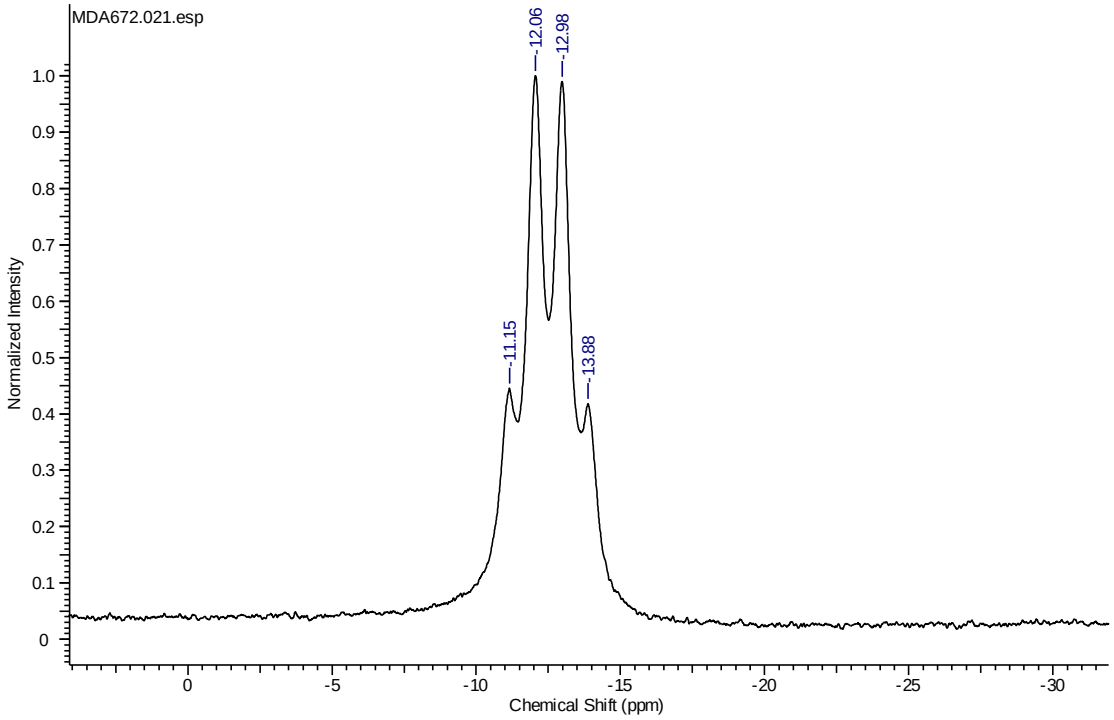


Figure S8: ^{11}B NMR spectrum of compound **13** (C_6D_6, 298 K 96.3 MHz).



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