Electronic Supplementary Material (ESI) for Dalton Transactions.

Synthesis and Reactivity of Boryl Substituted Silaimines

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Supplementary Information (25 pages)

Contents

1. Experimental

General considerations.

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. Pentane was distilled over Na/K alloy (50:50), while hexane, toluene and THF were distilled over molten potassium. ^{1}H, ^{13}C{^{1}H}, ^{11}B{^{1}H} and ^{29}Si{^{1}H} NMR spectra were recorded on a Bruker AvanceIII 400 spectrometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to the resonances of the solvent used. The ^{29}Si{^{1}H} and ^{11}B{^{1}H} NMR spectra were referenced to the external $SiMe_4$ and $BF_3.OEt_2$ respectively. Mass spectra were collected using an Agilent Technologies 5975D inert MSD with a solid-state probe. High resolution mass spectra (ESI) were recorded by the Monash Analytical Platform using an Agilent 6220 Accurate Mass LC-TOF system with Agilent 1200 Series HPLC. FTIR spectra were recorded as Nujol mulls, using a Agilent Cary 630 spectrometer operating in attenuated total reflectance (ATR) or transmission modes. Microanalyses were carried out at the Science Centre, London Metropolitan University. Melting points were determined in sealed glass capillaries under dinitrogen, and are uncorrected. The starting materials $(HCNDip)_2Si$:[1], $(HCNBu^t)_2Si$:[2] and $(HCNDip)_2BN_3$[3] were prepared by literature procedures. All other reagents were used as received, except CO_2 gas which was dried over P_2O_5 in prior to use.

Synthesis of $(HCNDip)_2Si{=}N\{B(DipNCH)_2\}$ 1. $(HCNDip)_2Si$: (100 mg, 0.247 mmol) and $(HCNDip)_2BN_3$ (106 mg, 0.247 mmol) were dissolved in 8 mL of benzene, generating a yellow solution. This was stirred for 10 min before volatiles were removed *in vacuo* and the residue extracted with hexane (5 mL) and filtered. The filtrate was then placed at -30 °C for 3 d, after which time colourless needles of **1** had deposited. These were isolated and a second crop obtained from the mother liquor (172 mg, 86 %). M.p. 228–232 °C; ^{1}H NMR (400 MHz, C_6D_6) δ 0.99 (d, J = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 1.05 (d, J = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 1.12 (d, J = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 1.22 (d, J = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 3.14 (sept, J = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 3.30 (sept, J = 6.9 Hz, 4H, C*H*(CH$_3$)$_2$), 5.38 (s, 2H, C*H*), 5.82 (s, 2H, C*H*), 7.07-7.20 (m, 12H, Ar*H*); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 23.9, 24.1, 24.4, 24.6 (CH(*C*H$_3$)$_2$), 28.6, 29.3 (*C*H(CH$_3$)$_2$), 117.9, 118.6 (*C*H), 123.2, 123.7, 124.0, 126.0, 126.7, 137.5, 141.8, 146.1, 146.9 (Ar*C*); ^{11}B{^{1}H} NMR (128 MHz, C_6D_6) δ 21.0; ^{29}Si{^{1}H} NMR (80 MHz, THF-d_8) δ -48.0; IR ν/cm^{-1} (Nujol): 1449 (m), 1261 (m), 1229 (s), 755 (s), 698 (vs); MS (EI, 70 eV): m/z (%) = 805.9 (M^+, 100), 402.4 ({(HCNDip)$_2$BNH}$^+$, 34); HRMS (ESI): calc. for $C_{52}H_{73}BN_5Si$ (M^++H): 8065728, found 806.5680.

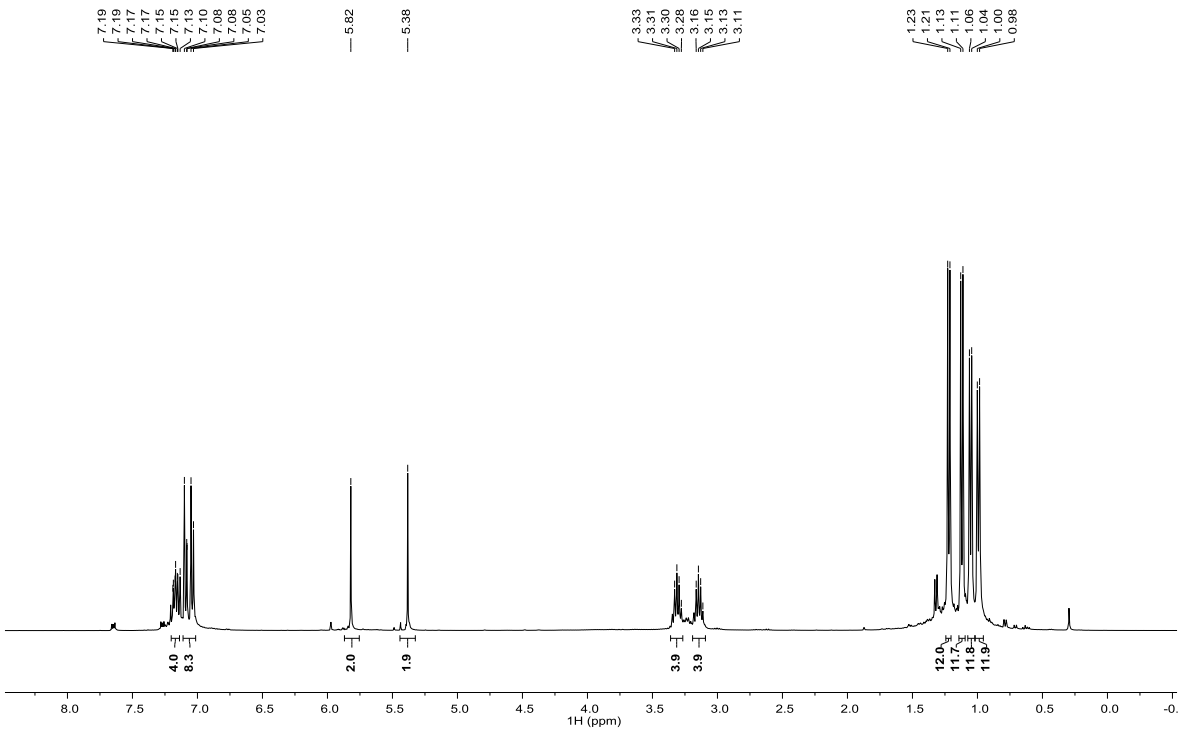

Figure S1. ^{1}H NMR specturm (400 MHz, 298 K, C_6D_6) of **1**.

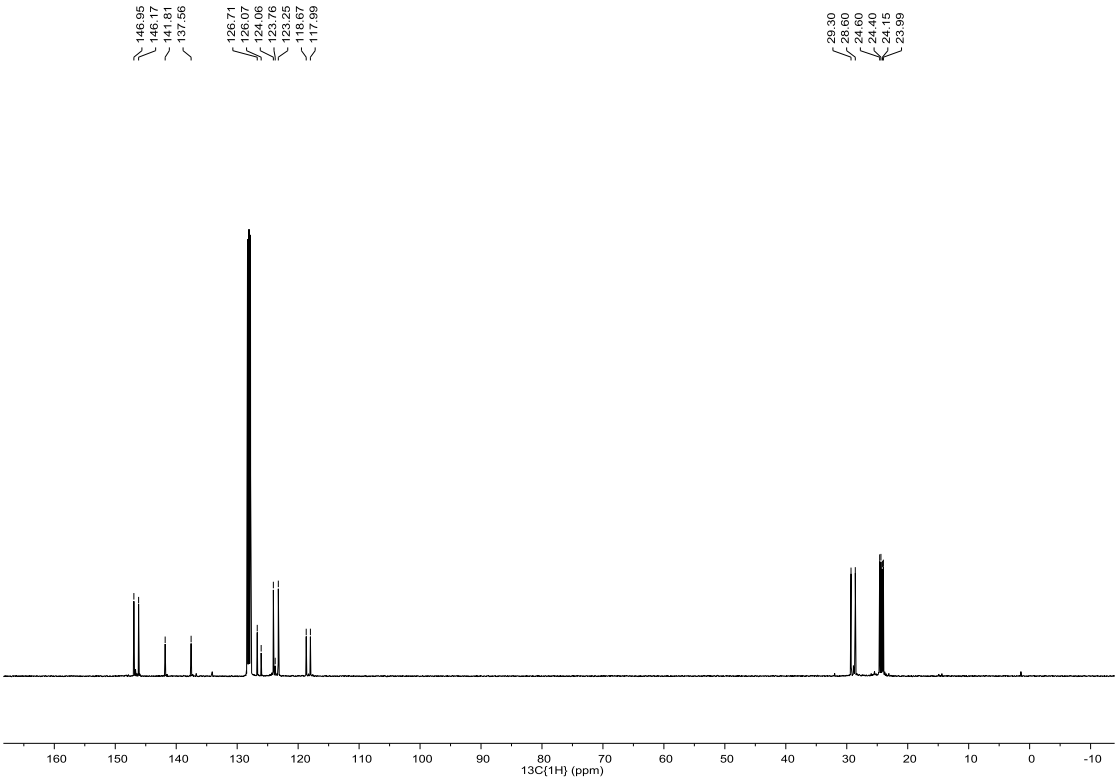

Figure S2. $^{13}C\{^{1}H\}$ NMR specturm (101 MHz, 298 K, C_6D_6) of **1**.

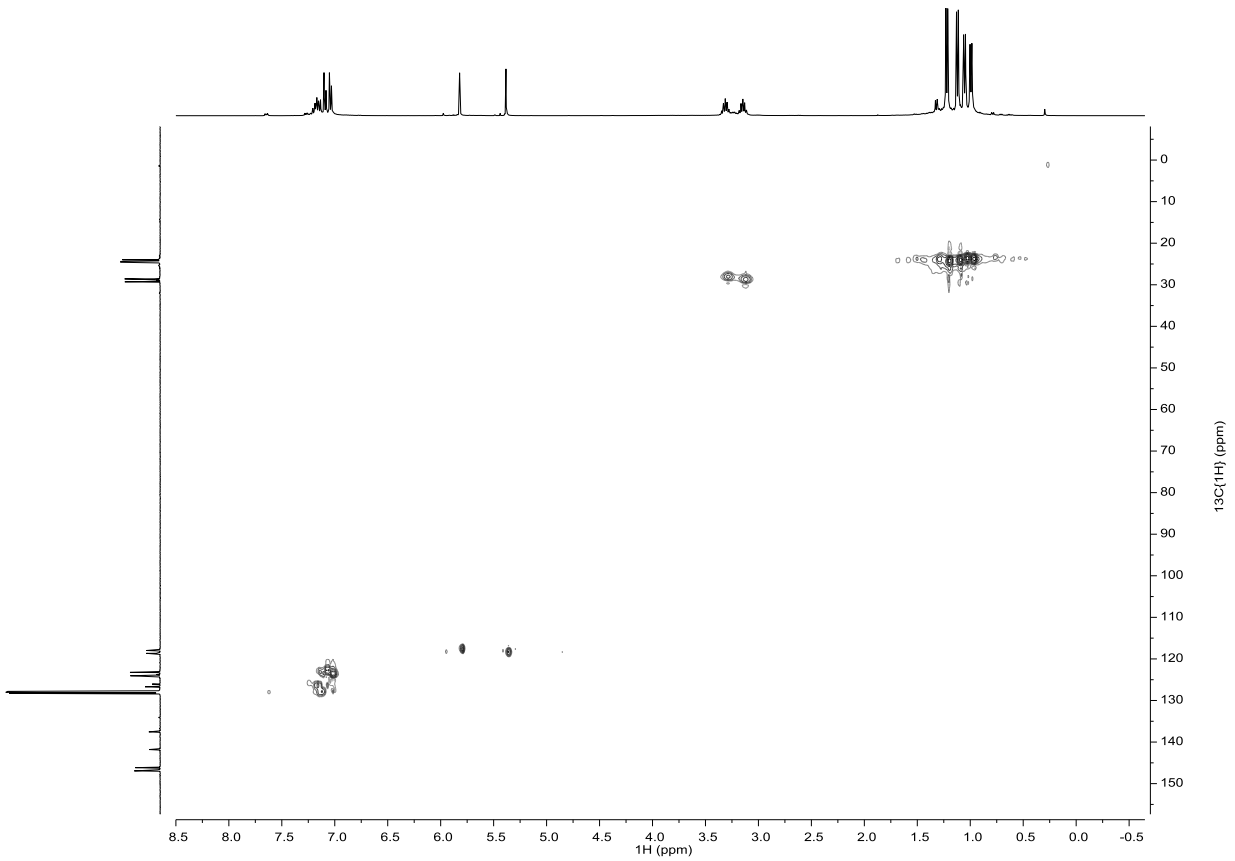

Figure S3. HMQC specturm (^{1}H: 400 MHz; ^{13}C: 101 MHz, 298 K, C_6D_6) of **1**.

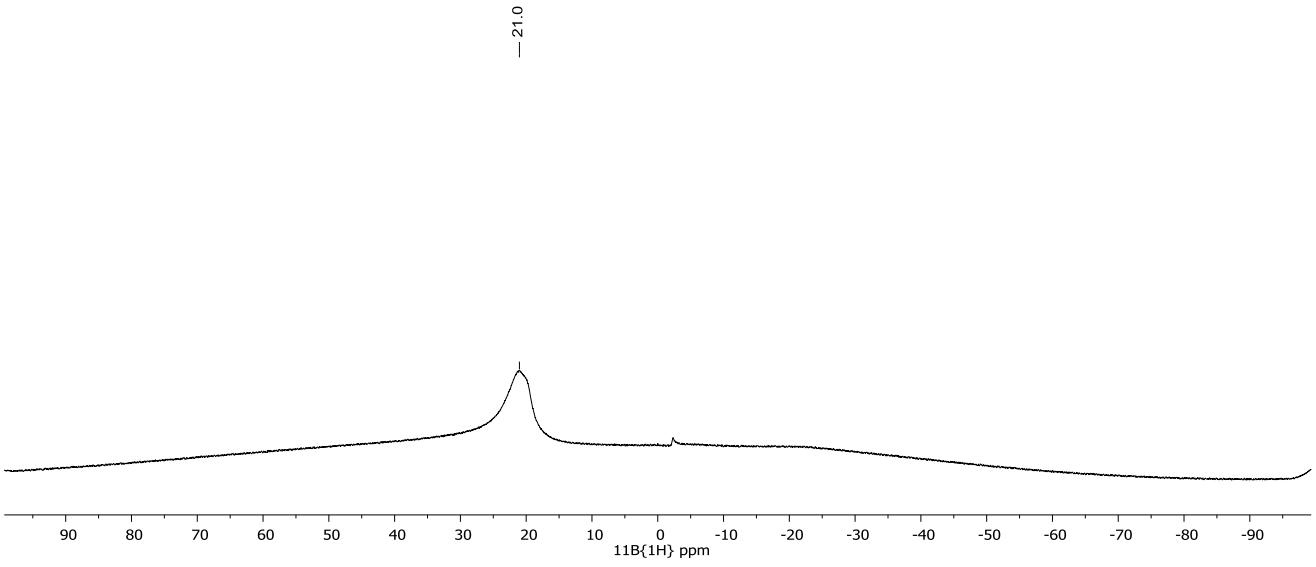

Figure S4. ^{11}B{^{1}H} NMR specturm (128 MHz, 298 K, C_6D_6) of **1**.

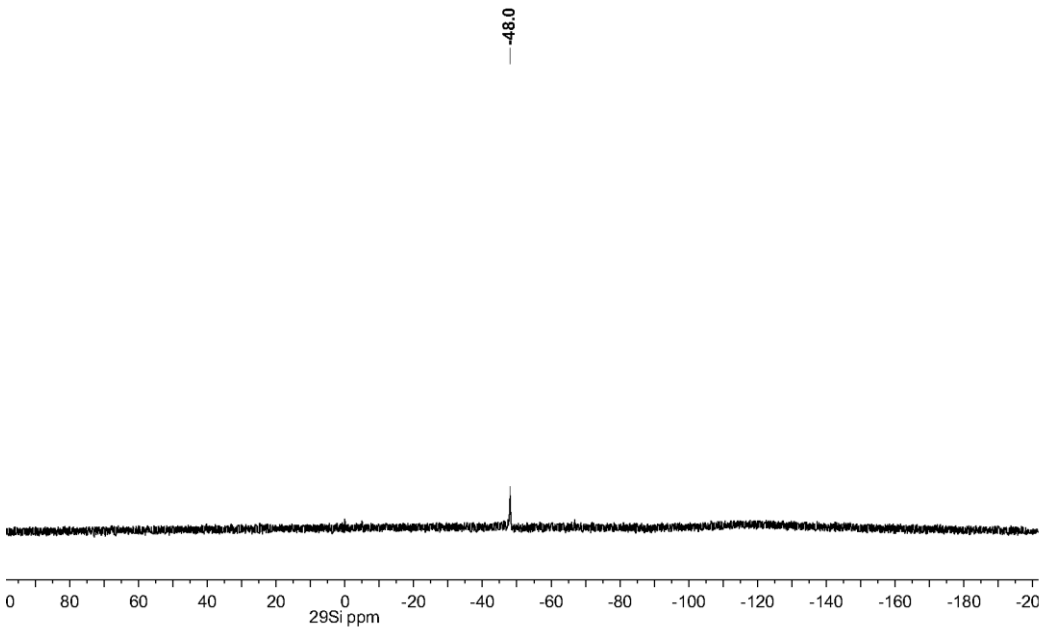

Figure S5. $^{29}Si\{^{1}H\}$ NMR specturm (80 MHz, 298 K, THF-d_8) of **1**.

Synthesis of (HCNBu^t)$_2$Si=N{B(DipNCH)$_2$} 2. (HCNBu^t)$_2$Si: (92 mg, 0.468 mmol) and (HCNDip)$_2$BN$_3$ (201 mg, 0.468 mmol) were dissolved in 8 mL of benzene, yielding a yellow solution. This was stirred for 10 min before volatiles were removed *in vacuo*, the residue extracted with hexane (5 mL), and the extract filtered. The filtrate was then placed at -30 °C for 3d, after which time colourless rods of **2** had deposited. These were isolated and a second crop obtained from the mother liquor (246 mg, 88 %). M.p: 143–146 °C. ^{1}H NMR (400 MHz, C_6D_6) δ 1.02 (s, 18H, C(C*H*$_3$)$_3$), 1.31 (d, *J* = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 1.38 (d, *J* = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 3.74 (sept, 4H, C*H*(CH$_3$)$_2$), 5.60 (s, 2H, C*H*), 6.24 (s, 2H, C*H*), 7.21-7.23 (m, 6H, Ar*H*); $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6) δ 23.8, 25.8 (CH(*C*H$_3$)$_2$), 28.5 (*C*H(CH$_3$)$_2$), 31.1 (C(*C*H$_3$)$_3$), 53.2 (*C*(CH$_3$)$_3$), 110.5, 117.3 (*C*H), 123.5, 126.3, 127.4, 141.5, 146.6 (Ar*C*); $^{11}B\{^{1}H\}$ NMR (128 MHz, C_6D_6) δ 20.9; $^{29}Si\{^{1}H\}$ NMR (80 MHz, C_6D_6) δ -57.6; IR *v*/cm^{-1} (Nujol): 1441 (m), 1270 (vs), 1224 (s), 1117 (s), 949 (s), 757 (s); MS (EI, 70 eV): *m*/*z* (%) = 597.4 (M$^+$, 11), 57.0 (Bu^{t+}, 100); anal. calc. for $C_{36}H_{56}BN_5Si$: C 72.33 %, H 9.44 %, N 11.72%: found: C 72.17 %, H 9.59 %, N 11.61 %.

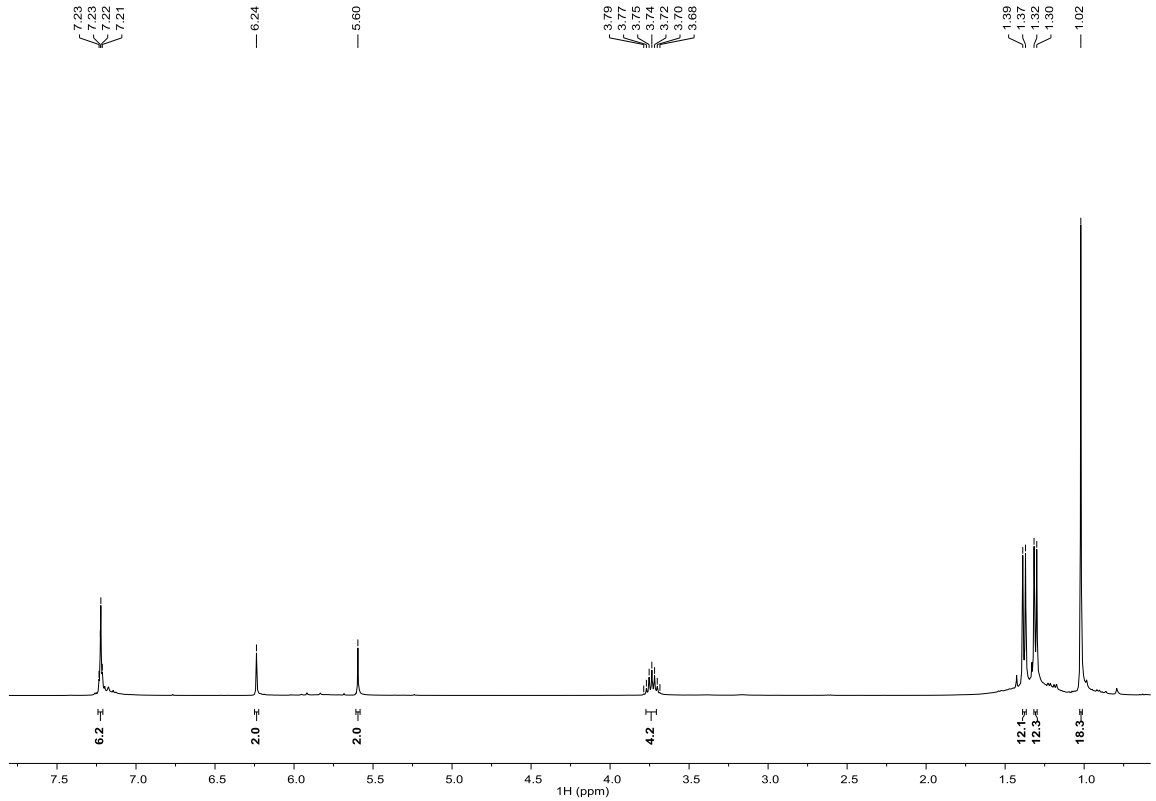

Figure S6. ^{1}H NMR specturm (400 MHz, 298 K, C_6D_6) of **2**.

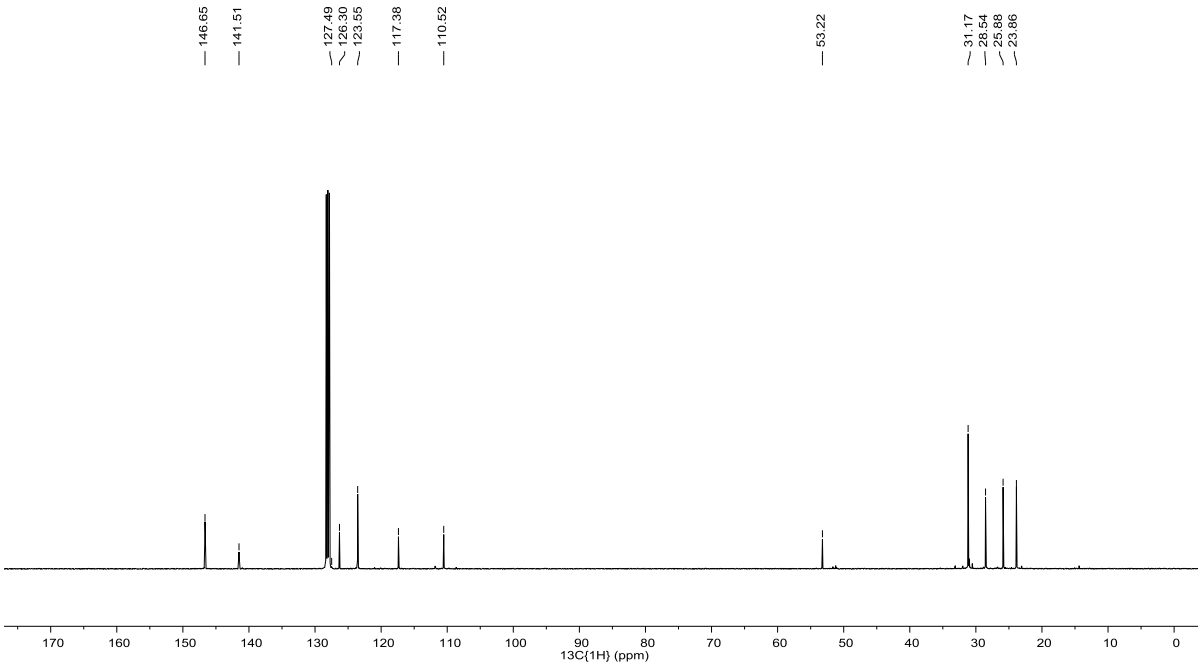

Figure S7. ^{13}C{^{1}H} NMR specturm (101 MHz, 298 K, C_6D_6) of **2**.

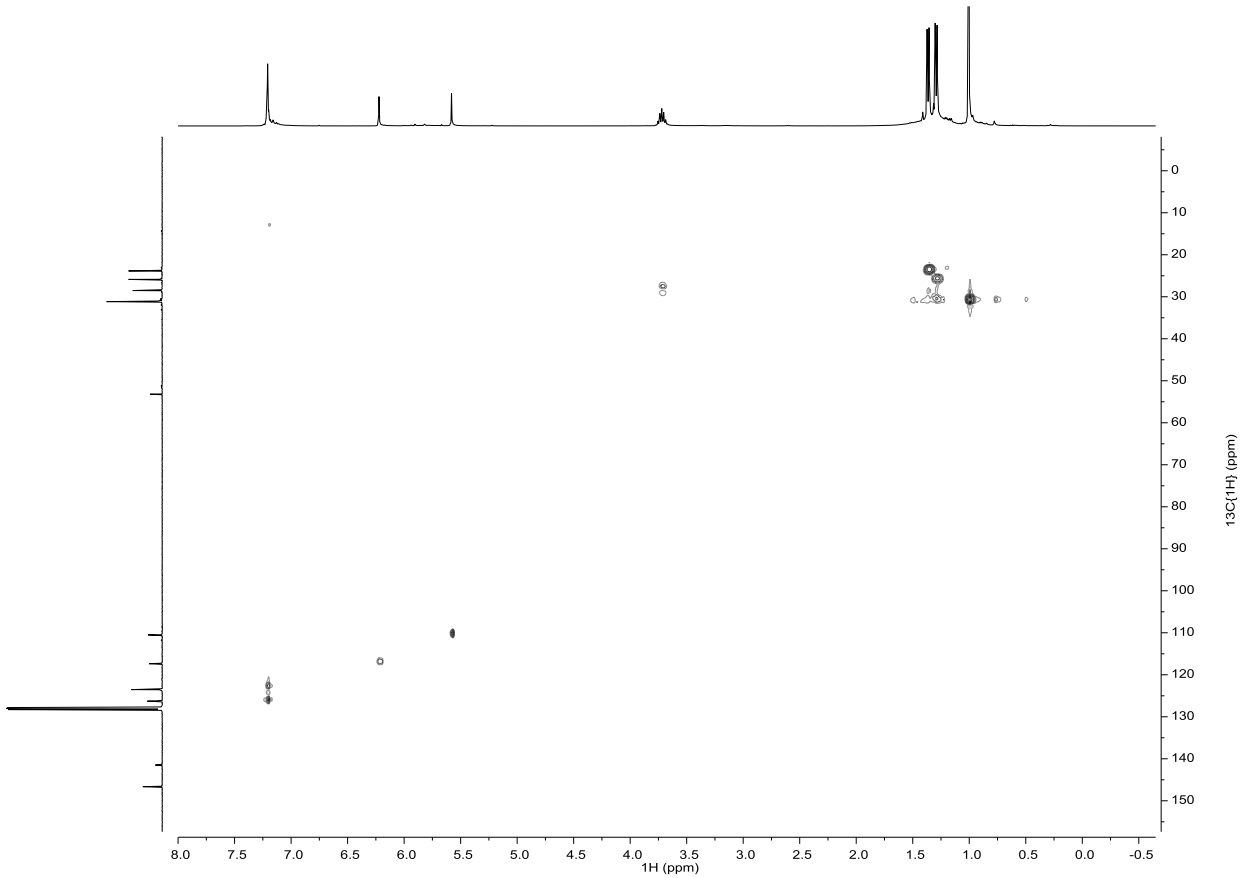

Figure S8. HMQC specturm (^{1}H: 400 MHz; ^{13}C: 101 MHz, 298 K, C_6D_6) of **2**.

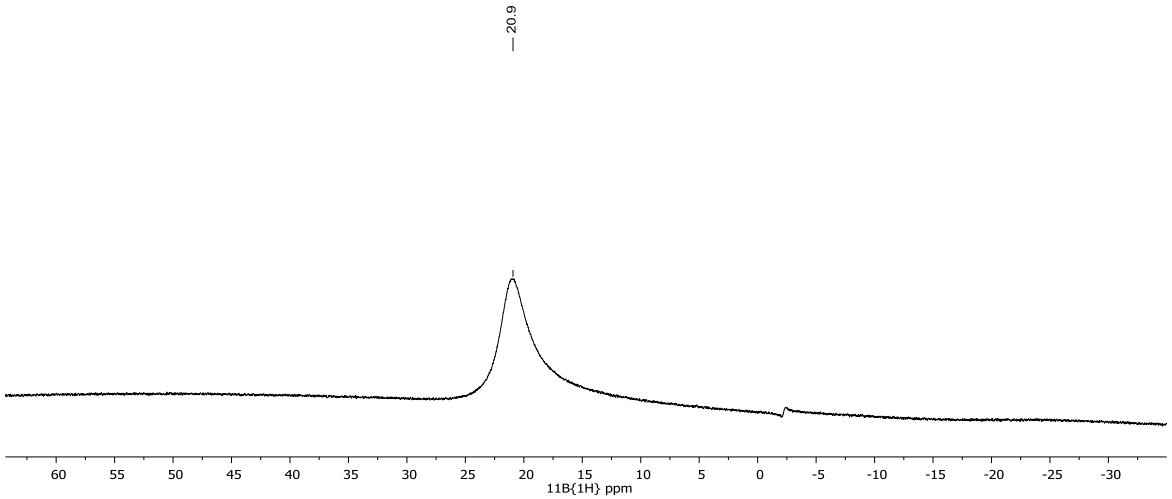

Figure S9. ^{11}B{^{1}H} NMR specturm (128 MHz, 298 K, C_6D_6) of **2**.

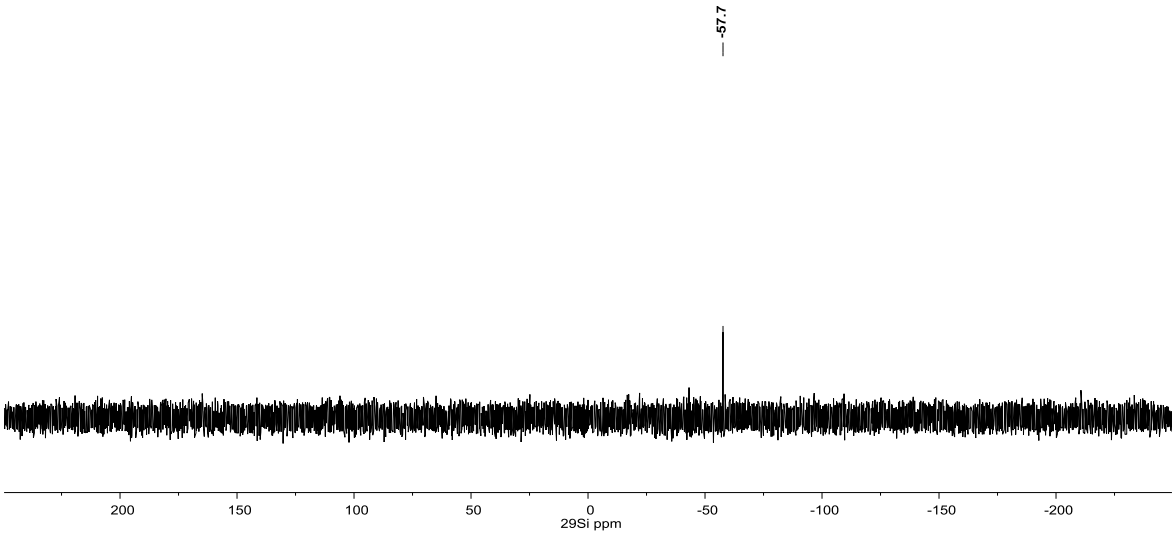

Figure S10. $^{29}Si\{^{1}H\}$ NMR specturm (80 MHz, 298 K, C_6D_6) of **2**.

Synthesis of (HCNDip)$_2$Si{OC(=O)N[B(DipNCH)$_2$]} 3. Compound **1** (100 mg, 0.124 mmol) was dissolved in 8 mL of benzene in a Schlenk flask which was cooled to -78 °C, placed under vacuum, then backfilled with CO_2 gas (*ca.* 50 mL). The reaction mixture was slowly warmed to room temperature, resulting in a solution colour change from yellow to pale yellow. The reaction mixture was stirred for 12h at room temperature, all volatiles then removed *in vacuo*, and the residue extracted with hexane (5 mL). The extract was filtered and the filtrate placed at -30 °C for 1d, after which time colourless plates of **3** had deposited. These were isolated and a second crop obtained from the mother liquor (76 mg, 72 %). M.p: 191–194 °C; ^{1}H NMR (400 MHz, C_6D_6) δ 1.11 (d, *J* = 6.6 Hz, 12H, CH(C*H*$_3$)$_2$), 1.15 (d, *J* = 6.6 Hz, 12H, CH(C*H*$_3$)$_2$), 1.19 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.26 (d, *J* = 7.1 Hz, 12H, CH(C*H*$_3$)$_2$), 2.82-3.08 (m, 4H, C*H*(CH$_3$)$_2$), 3.24 (m, 4H, C*H*(CH$_3$)$_2$), 5.42 (s, 2H, C*H*), 5.74 (s, 2H, C*H*), 7.06-7.23 (m, 12H, Ar*H*); $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6) δ 24.3, 26.3, 26.5, 26.8 (CH(*C*H$_3$)$_2$), 28.5, 28.8, 28.9, 29.0 (*C*H(CH$_3$)$_2$), 120.5, 120.9 (*C*H), 123.4, 124.5, 124.9, 125.5, 137.4, 139.6, 145.1, 146.8, 148.0, 148.7, 151.7 (Ar*C*); $^{11}B\{^{1}H\}$ NMR (128 MHz, C_6D_6) δ 21.0; $^{29}Si\{^{1}H\}$ NMR (80 MHz, C_6D_6) δ -49.2; IR ν/cm^{-1} (Nujol): 1804 (s, CO str.), 1255 (m), 1228 (m), 1198 (s), 1102 (s), 1059 (m), 950 (s), 935 (s), 805 (s,) 760 (vs); MS (EI, 70 eV): *m*/*z* (%) = 429.4 ({(HCNDip)$_2$BNCO}, 52); anal. calc. for $C_{53}H_{72}BN_5SiO_2$: C 74.88 %, H 8.54 %, N 8.24 %: found: C 74.60 %, H 8.45 %, N 8.03 %.

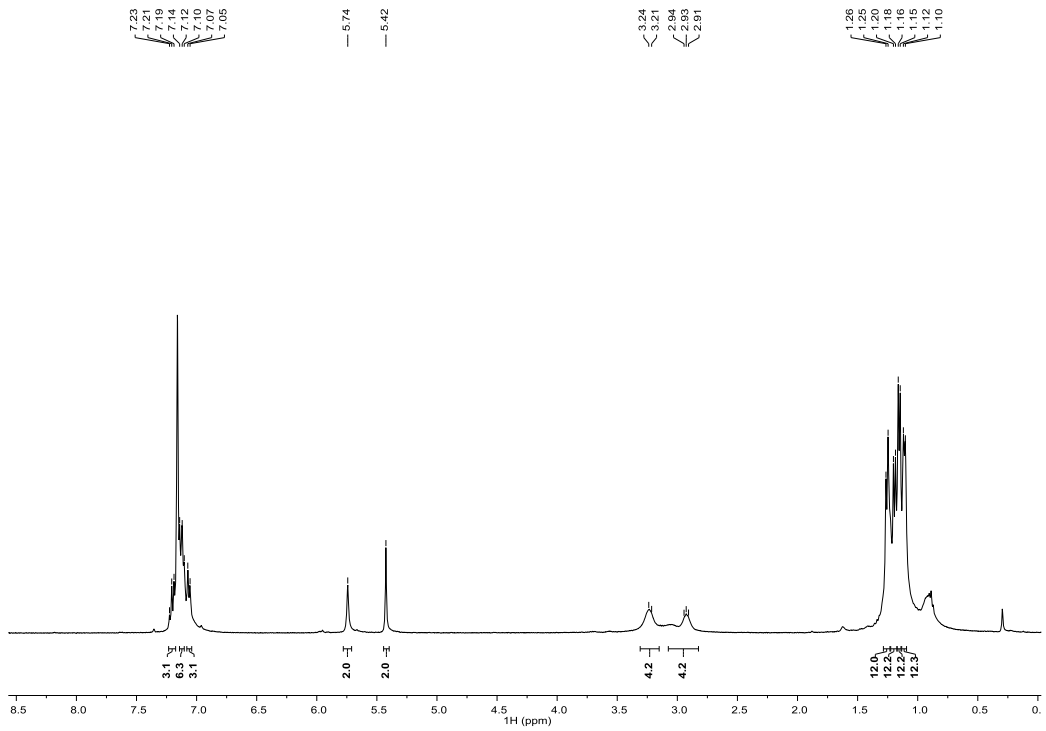

Figure S11. ^{1}H NMR specturm (400 MHz, 298 K, C_6D_6) of **3**.

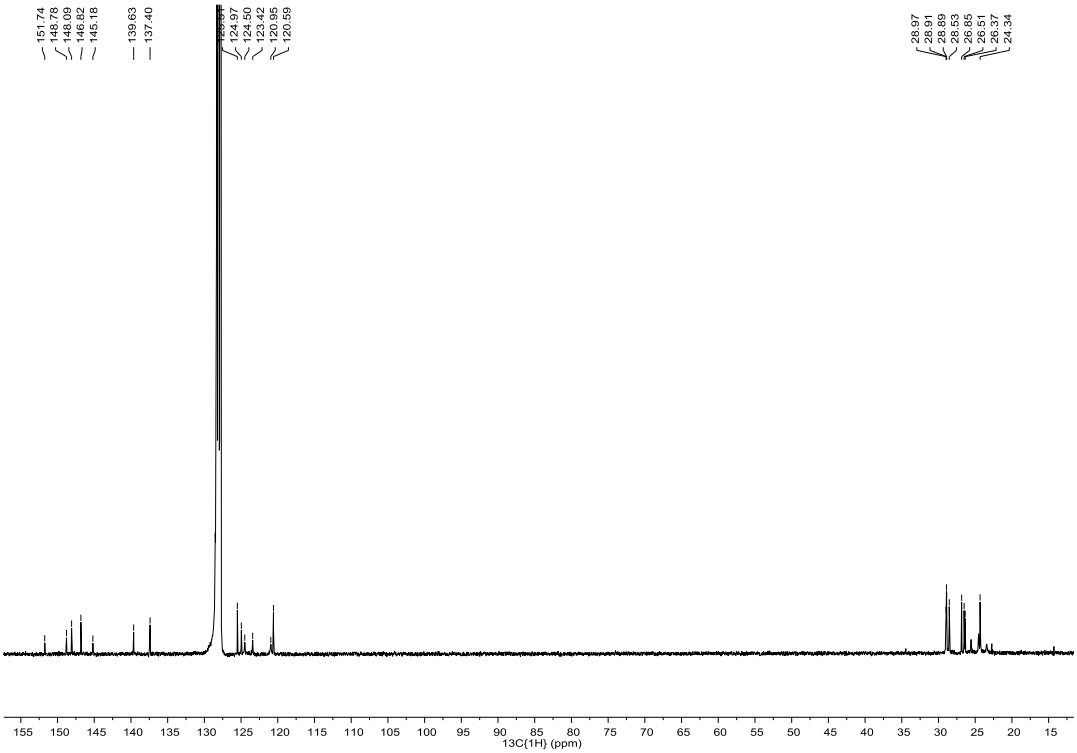

Figure S12. $^{13}C\{^{1}H\}$ NMR specturm (101 MHz, 298 K, C_6D_6) of **3**.

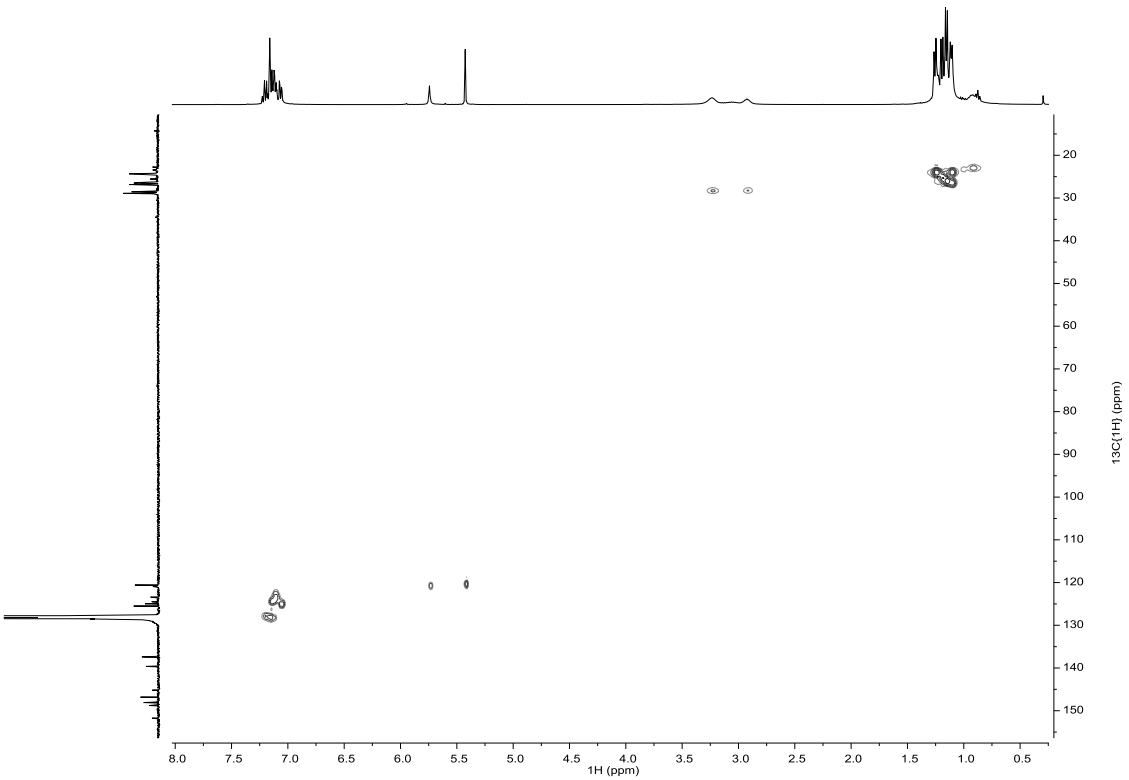

Figure S13. HMQC specturm (^{1}H: 400 MHz; ^{13}C: 101 MHz, 298 K, C_6D_6) of **3**.

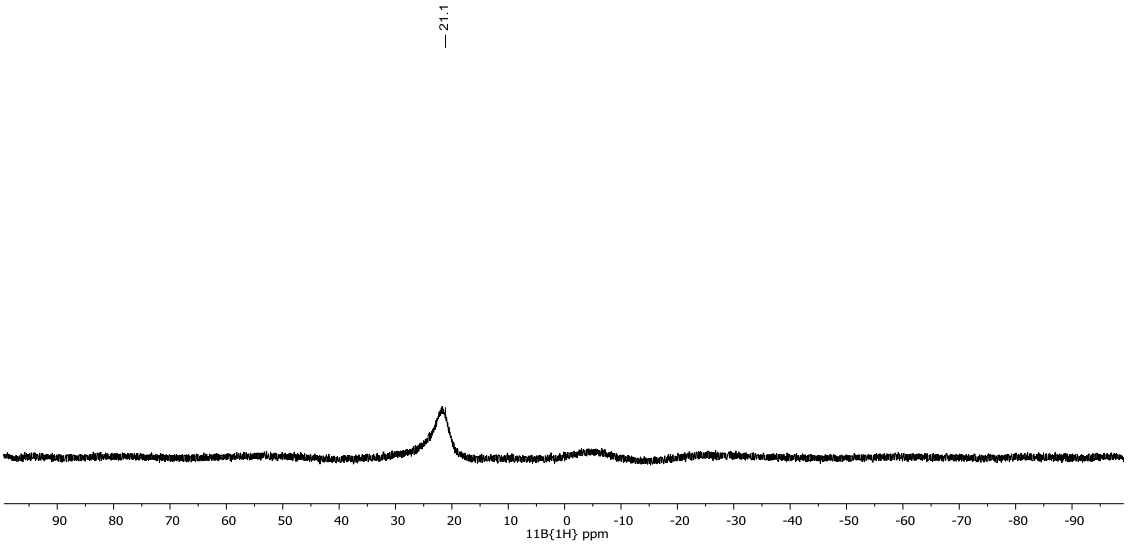

Figure S14. ^{11}B{^{1}H} NMR specturm (128 MHz, 298 K, C_6D_6) of **3**.

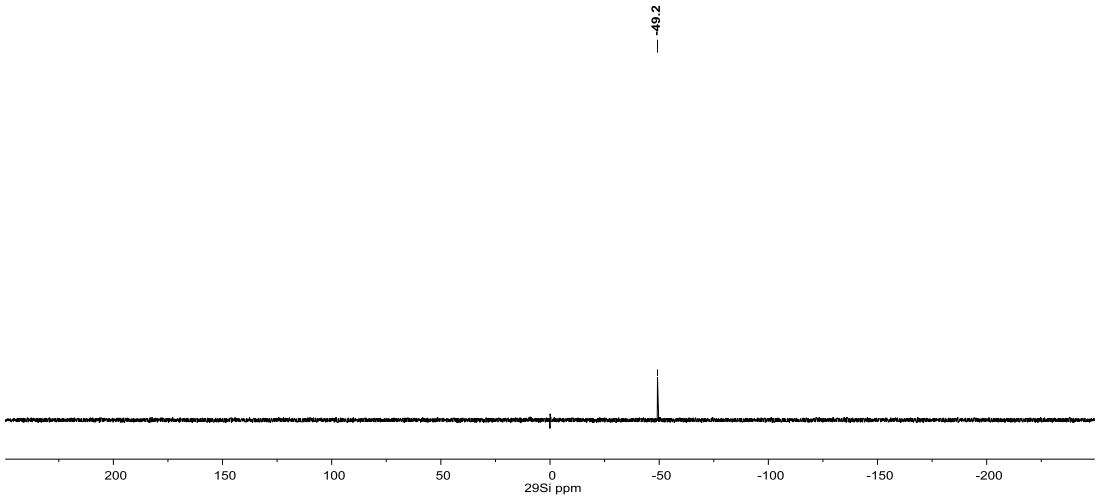

Figure S15. $^{29}Si\{^{1}H\}$ NMR specturm (80 MHz, 298 K, C_6D_6) of **3**.

Synthesis of (HCNDip)$_2$B(NCO) 4. Compound **2** (120 mg, 0.100 mmol) was dissolved in 8 mL of benzene in a Schlenk flask, which was cooled to -78 °C, placed under vacuum, the backfilled with *ca.* 50 mL CO_2 gas. The reaction mixture was slowly warmed to room temperature, then placed in an oil bath at 80 °C for 14h, resulting in a slow colour change from yellow to pale yellow. All the volatiles were then removed *in vacuo* and the residue extracted with hexane (5 mL). The extract was filtered, and the filtrate placed at -30 °C for 4h, after which time colourless blocks of **4** had deposited. These were isolated and a second crop obtained from the mother liquor (36 mg, 41 %) M.p: 105–108 °C; ^{1}H NMR (400 MHz, C_6D_6) δ 1.19 (d, J = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$), 1.26 (d, J = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 3.14 (s, J = 7.0 Hz, 4H, C*H*(CH$_3$)$_2$), 5.95 (s, 2H, C*H*), 7.12-7.21 (m, 6H, Ar*H*); $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6) δ 24.0, 24.3 (CH(*C*H$_3$)$_2$), 28.8 (*C*H(CH$_3$)$_2$), 118.2 (*C*H), 123.9, 127.9, 128.1, 128.4, 136.8, 146.4 (Ar*C*); $^{11}B\{^{1}H\}$ NMR (128 MHz, C_6D_6) δ 17.7; IR ν/cm^{-1} (Nujol): 2301 (vs), 1535 (m), 1406 (vs), 1275 (s), 1116 (s), 1084 (s), 1059 (m), 937 (m), 910 (s), 759 (vs); MS (EI, 70 eV): m/z (%) = 429.5 (M^+, 100); anal. calc. for $C_{27}H_{36}BN_3O$: C 75.52 %, H 8.45 %, N 9.79 %: found: C 75.21 %, H 8.69 %, N 9.80 %.

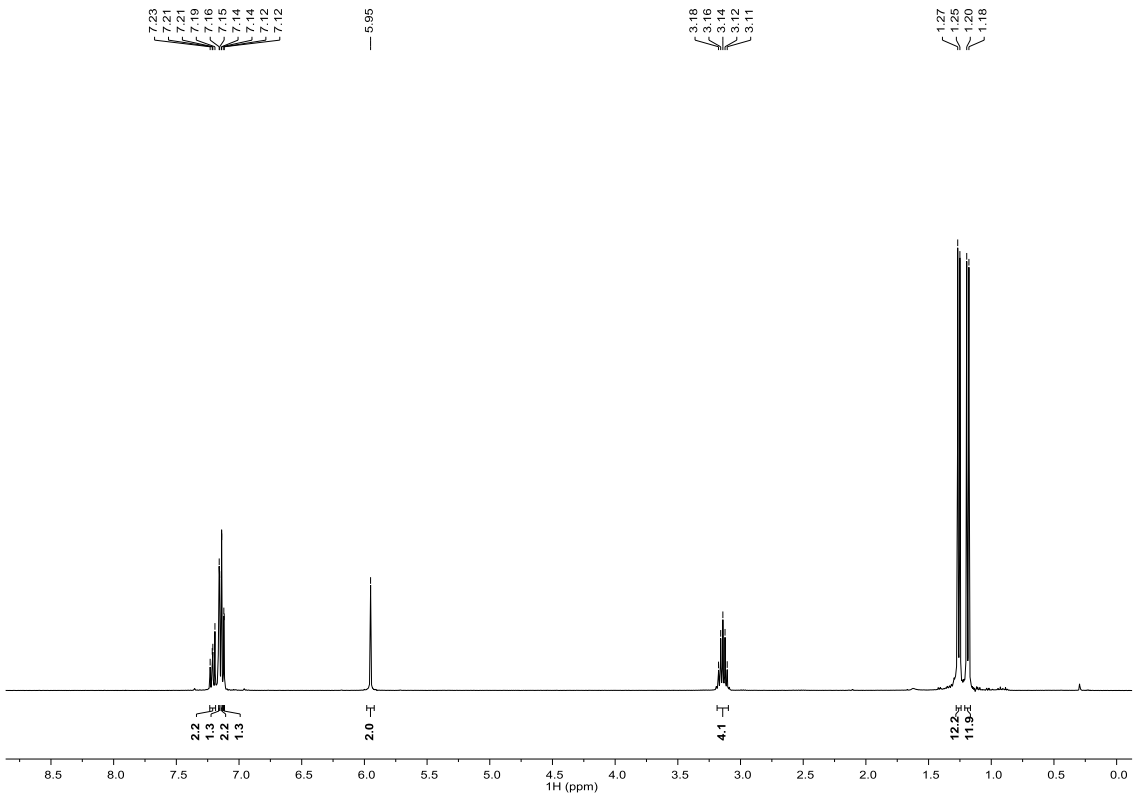

Figure S16. ^{1}H NMR specturm (400 MHz, 298 K, C_6D_6) of **4**.

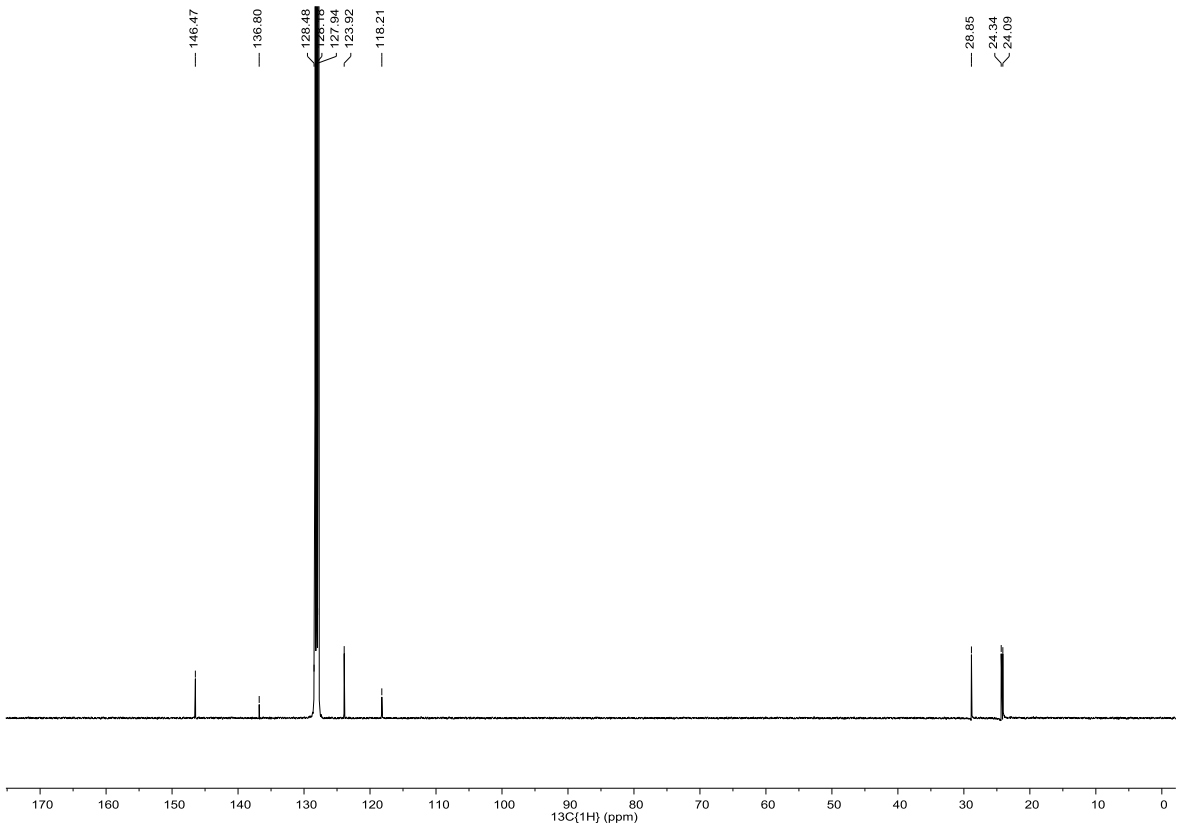

Figure S17. ^{13}C{^{1}H} NMR specturm (101 MHz, 298 K, C_6D_6) of **4**.

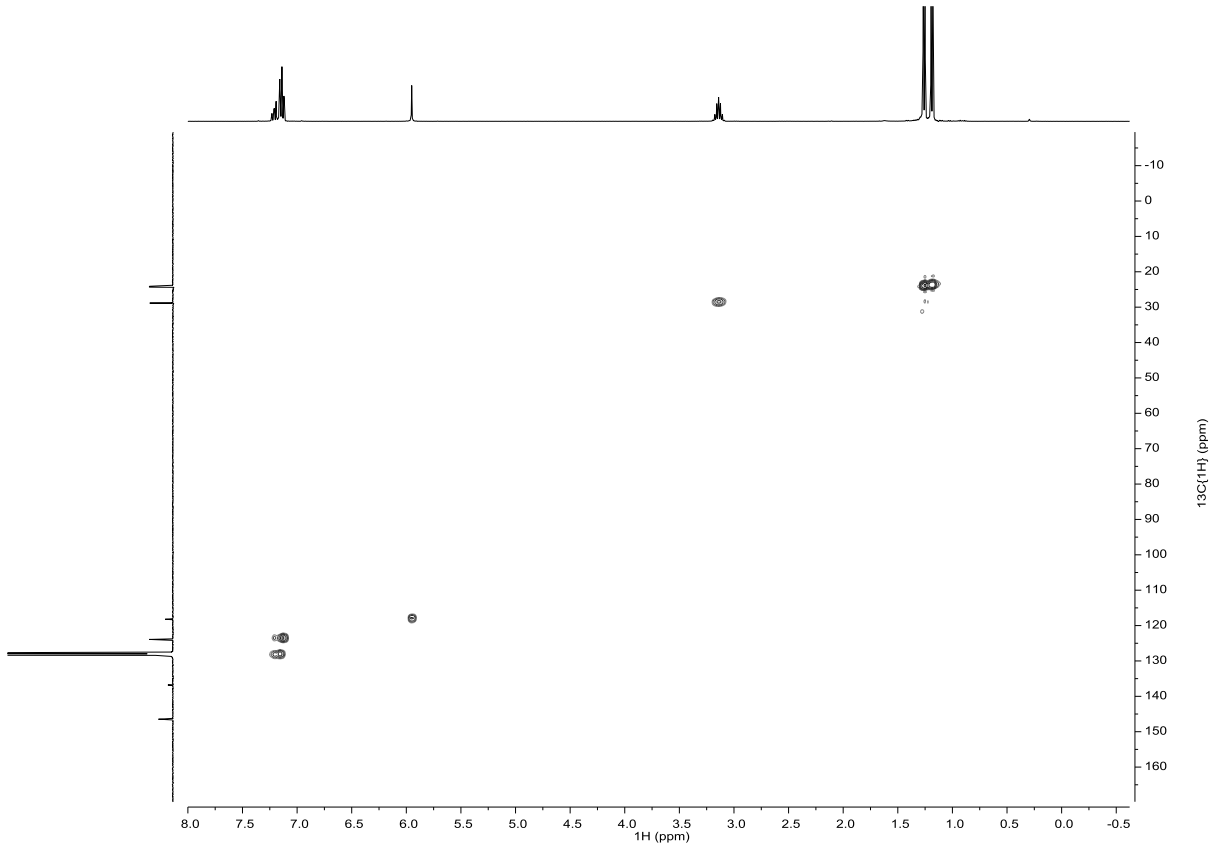

Figure S18. HMQC specturm (^{1}H: 400 MHz; ^{13}C: 101 MHz, 298 K, C_6D_6) of **4**.

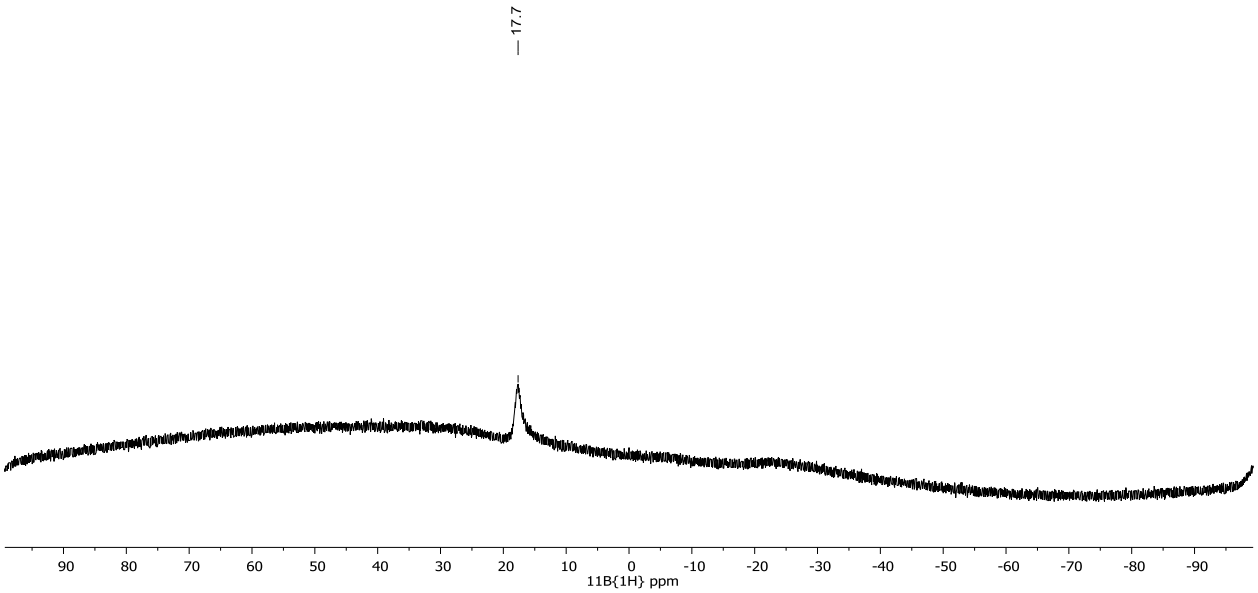

Figure S19. ^{11}B{^{1}H} NMR specturm (128 MHz, 298 K, C_6D_6) of **4**.

Synthesis of (HCNDip)$_2$Si(OH)−(H)N{B(DipNCH)$_2$} 5. Compound **1** (100 mg, 0.124 mmol) was dissolved in benzene (4 mL) and 2.5 mL of an 0.05 M solution of water in THF was added, resulting in a solution colour change from yellow to pale yellow. The solution was stirred for 1h, volatiles removed *in vacuo*, and the residue extracted with hexane (5 mL). The extract was filtered and the filtrate placed at room temperature for 3d, after which colourless needles of **5** had deposited. These were isolated and a second crop obtained from the mother liquor (72 mg, 70 %); M.p: >260 °C. ^{1}H NMR (400 MHz, C_6D_6) δ 0.93 (m, 12H, CH(C*H*$_3$)$_2$), 1.11 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.14-1.22 (m, 24H, CH(C*H*$_3$)$_2$), 2.09 (s, 1H, N*H*), 2.26 (s, 1H, SiO*H*), 3.09 (sept, *J* = 6.9 Hz, 4H, C*H*(CH$_3$)$_2$), 3.42 (sept, 2H, *J* = 6.9 Hz, C*H*(CH$_3$)$_2$), 3.69 (sept, *J* = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 5.45 (s, 2H, C*H*), 5.75 (s, 2H, C*H*), 7.04-7.18 (m, 12H, Ar*H*); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 23.3, 23.3, 23.9, 25.3, 25.8, 26.1 (CH(*C*H$_3$)$_2$), 28.1, 28.5, 28.7 (*C*H(CH$_3$)$_2$), 118.8, 118.9 (*C*H), 123.9, 124.1, 124.4, 126.9, 127.9, 128.5, 140.1, 147.2, 147.7, 148.6 (Ar*C*); ^{11}B{^{1}H} NMR (128 MHz, C_6D_6) δ 22.4; ^{29}Si{^{1}H} NMR (80 MHz, C_6D_6) δ -51.9; IR *ν*/cm^{-1} (Nujol): 3572 (br), 3348 (m), 1206 (s), 1069 (s), 980 (s), 698 (s); MS (EI, 70 eV): *m*/*z* (%) = 823.8 (M$^+$, 42); HRMS (ESI): calc. for $C_{52}H_{73}BN_5OSi$ (M$^+$-H): 822.5677, found 822.5668.

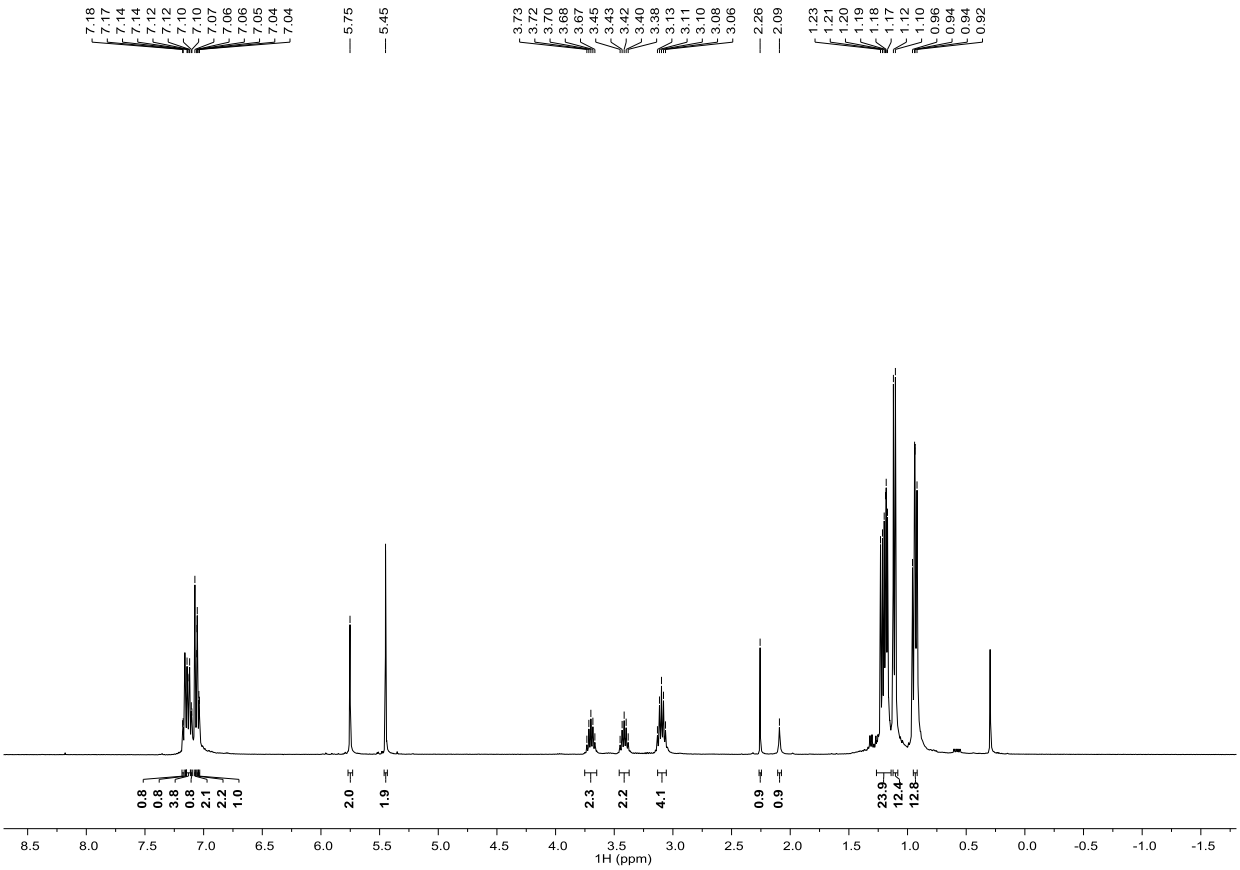

Figure S20. ^{1}H NMR specturm (400 MHz, 298 K, C_6D_6) of **5**.

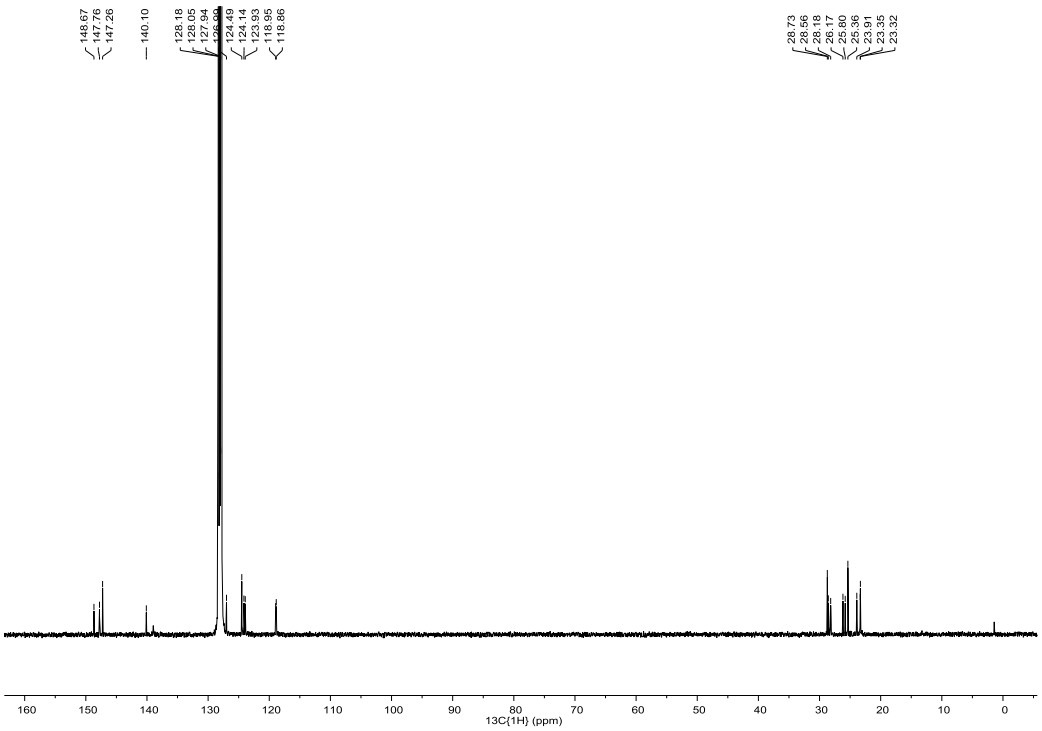

Figure S21. $^{13}C\{^{1}H\}$ NMR specturm (101 MHz, 298 K, C_6D_6) of **5**.

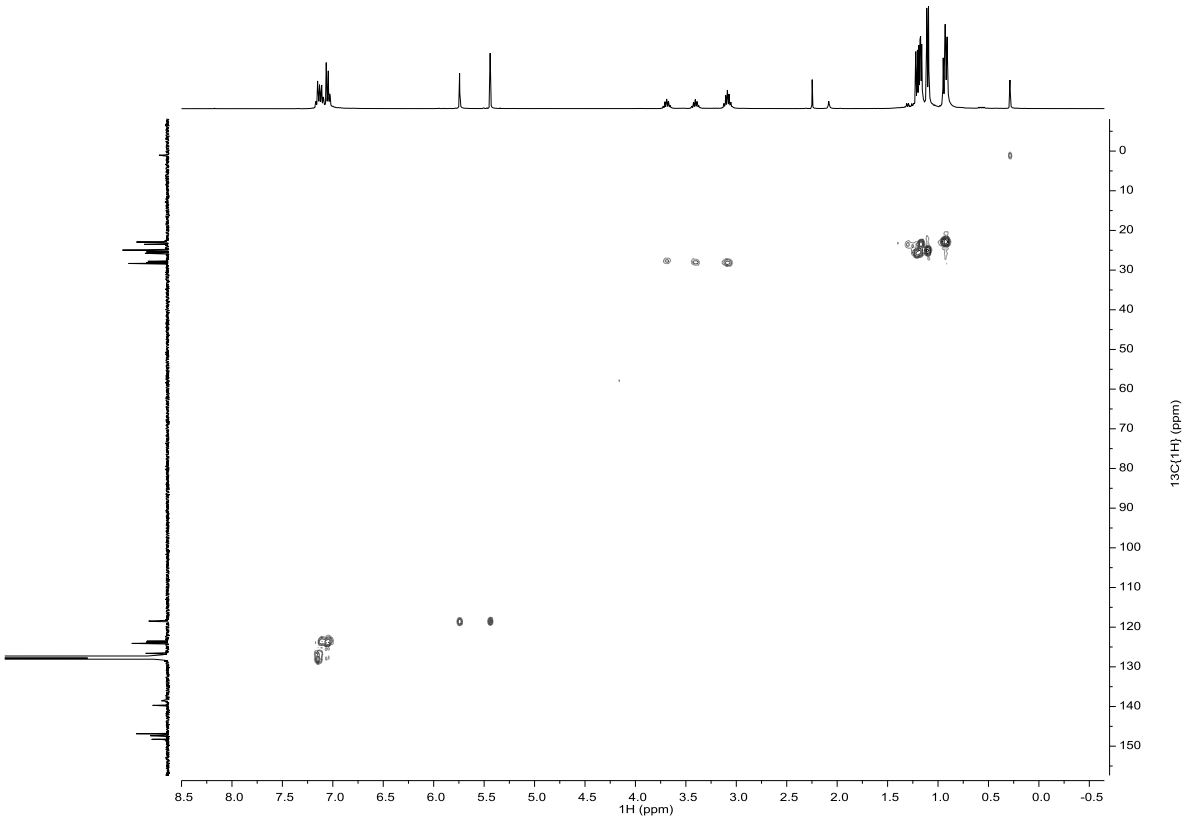

Figure S22. HMQC specturm (^{1}H: 400 MHz; ^{13}C: 101 MHz, 298 K, C_6D_6) of **5**.

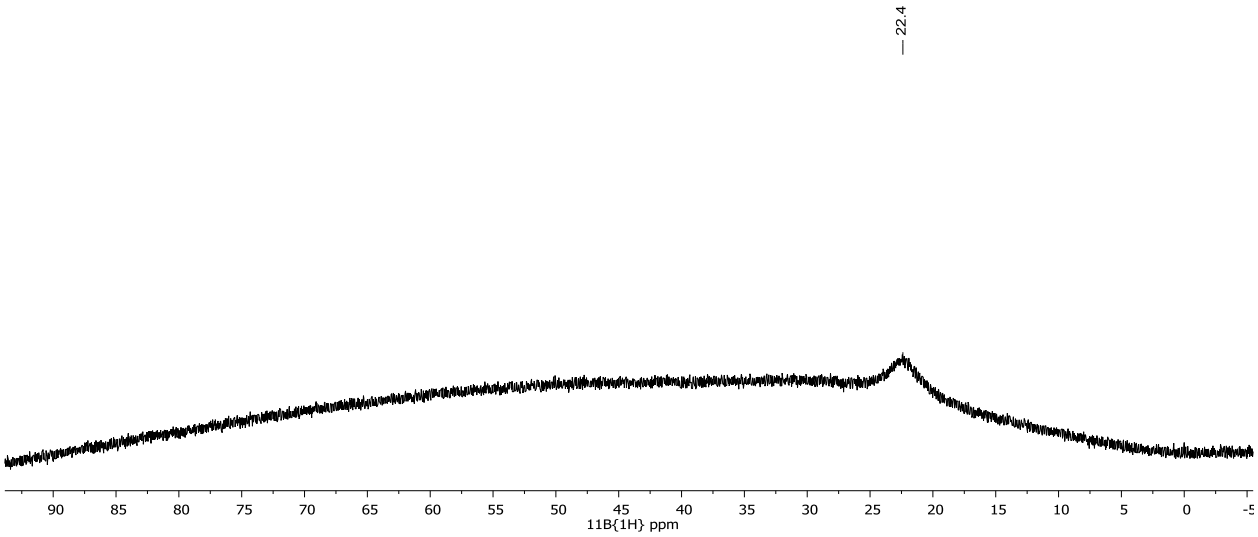

Figure S23. $^{11}B\{^{1}H\}$ NMR specturm (128 MHz, 298 K, C_6D_6) of **5**.

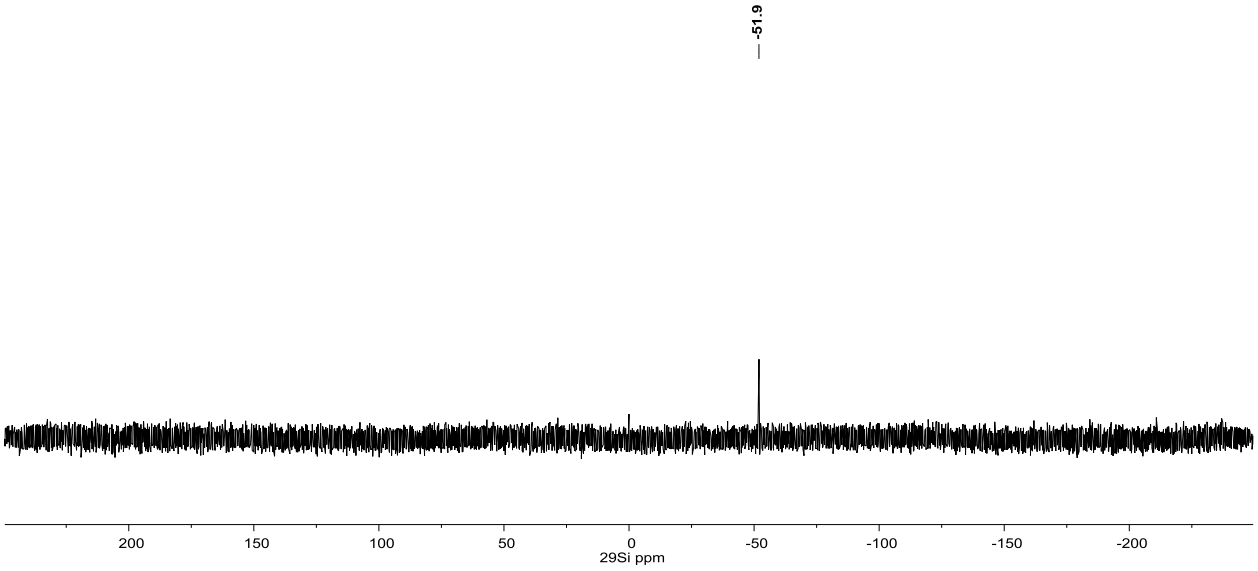

Figure S24. $^{29}Si\{^{1}H\}$ NMR specturm (80 MHz, 298 K, C_6D_6) of **5**.

Synthesis of $(HCNBu^{t})_2Si(OH)-(H)N\{B(DipNCH)_2\}$ 6. Compound **2** (90 mg, 0.150 mmol) was dissolved in benzene (4 mL), and 3 mL of an 0.05 M solution of water in THF was added. This resulted in a solution colour change from yellow to pale yellow. The mixture was allowed to stir for 1h, then volatiles were removed *in vacuo* and the residue was extracted with hexane (5 mL). The extract was filtered and the filtrate placed at room temperature for 4d, after which time colourless crystals of **6** had deposited. These were isolated and a second crop obtained from the mother liquor (66 mg, 71 %); M.p: 154–159 °C; ^{1}H NMR (400 MHz, C_6D_6) δ 1.19 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.26 (s, 18H, C(C*H*$_3$)$_3$), 1.36 (d, *J* = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 1.90 (s, 1H, N*H*), 1.94 (s, 1H, SiO*H*), 3.45 (sept, *J* = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 5.65 (s, 2H, C*H*), 6.00 (s, 2H, C*H*), 7.13-7.19 (m, 6H, Ar*H*); $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6) δ 23.1, 25.9 (CH(*C*H$_3$)$_2$), 28.2 (*C*H(CH$_3$)$_2$), 30.8 (C(*C*H$_3$)$_3$), 50.7 (*C*(CH$_3$)$_3$), 110.0, 118.2 (*C*H), 123.9, 127.4, 138.4, 146.9 (Ar*C*); $^{11}B\{^{1}H\}$ NMR

(128 MHz, C_6D_6) δ 22.3; $^{29}Si\{^1H\}$ NMR (80 MHz, C_6D_6) δ -47.4; IR ν/cm^{-1} (Nujol): 3579 (br), 3335 (m), 1229 (s), 1096 (s), 909 (m), 761 (s); MS (EI, 70 eV): *m*/*z* (%) = 615.5 (M^+, 36), 57.1 (Bu^{t+}, 100); anal. calc. for $C_{36}H_{58}BN_5OSi$: C 70.22 %, H 9.49 %, N 11.37 %: found: C 70.01 %, H 9.34%, N 11.12 %.

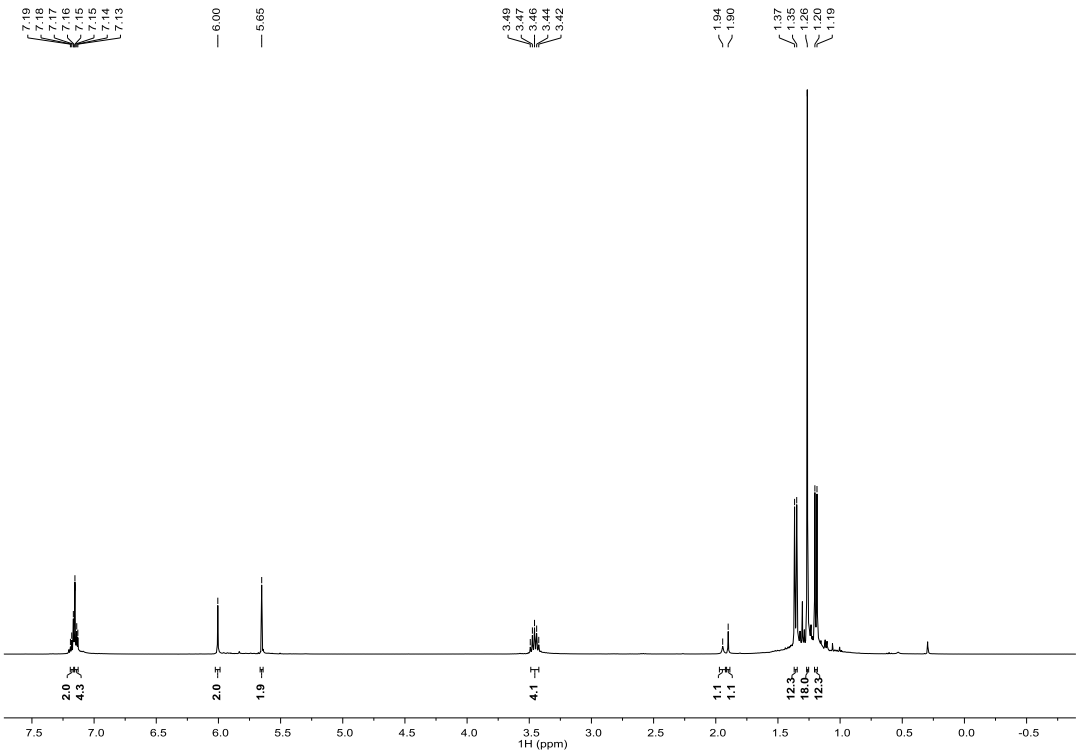

Figure S25. ^1H NMR specturm (400 MHz, 298 K, C_6D_6) of **6**.

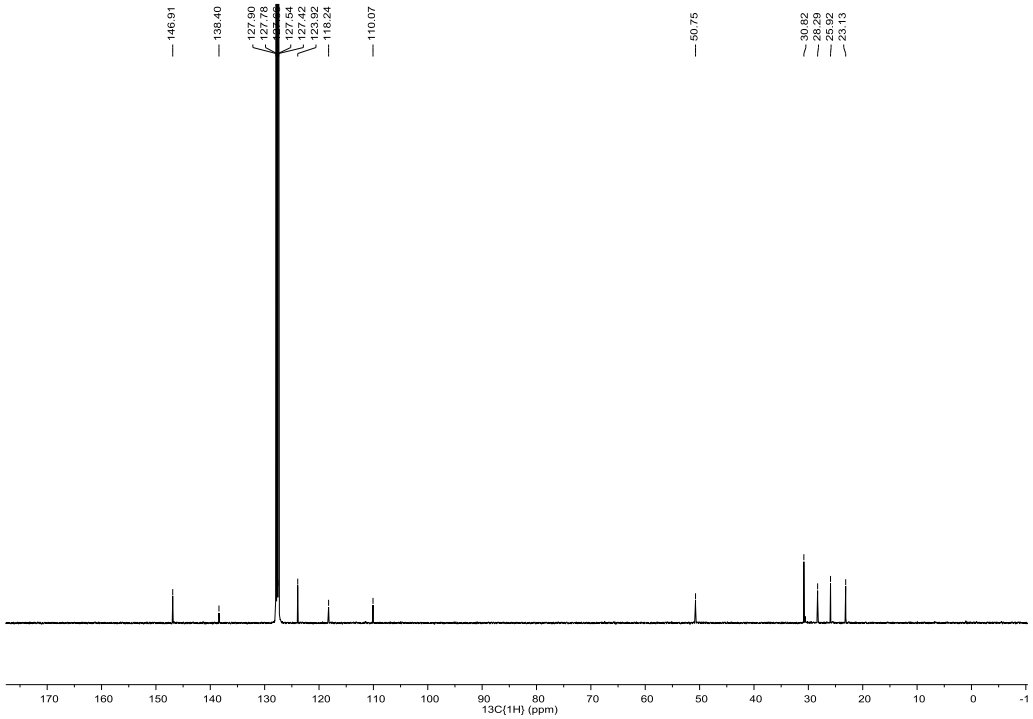

Figure S26. $^{13}C\{^1H\}$ NMR specturm (101 MHz, 298 K, C_6D_6) of **6**.

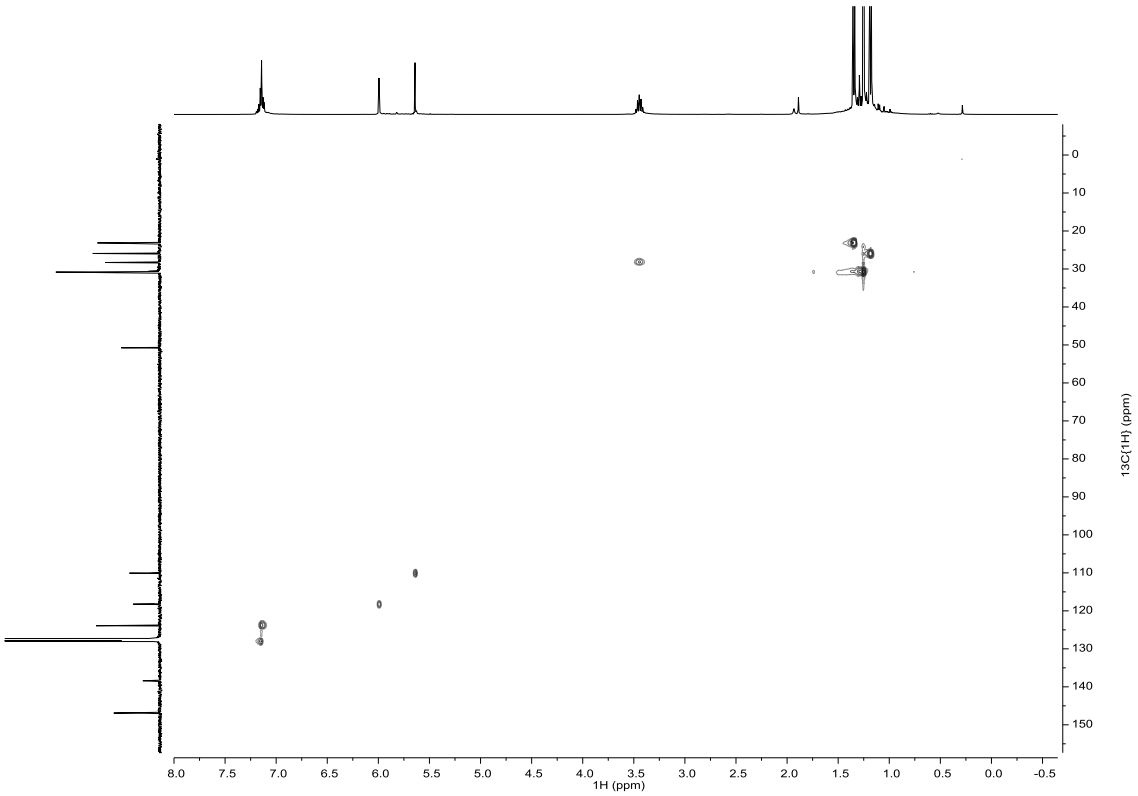

Figure S27. HMQC specturm (^{1}H: 400 MHz; ^{13}C: 101 MHz, 298 K, C_6D_6) of **6**.

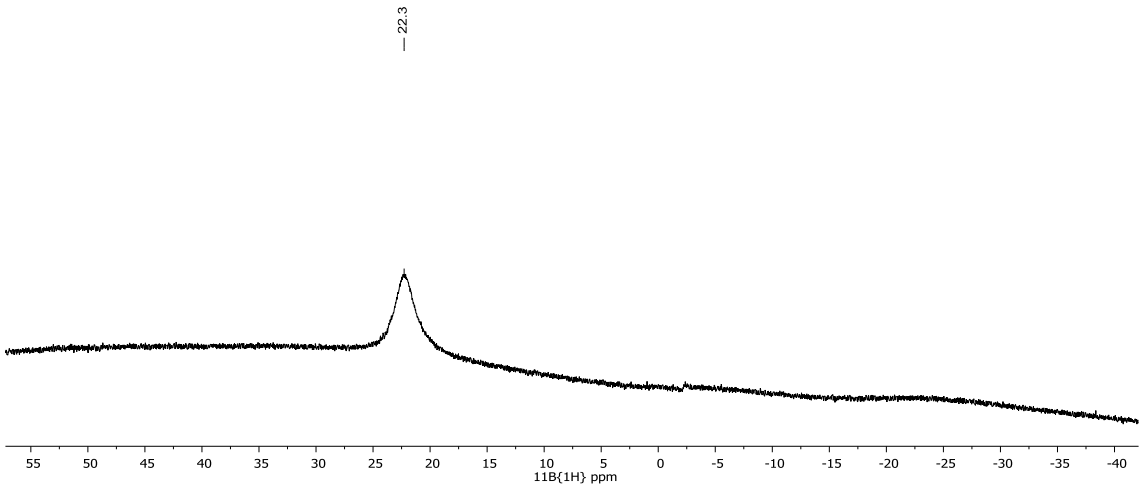

Figure S28. ^{11}B{^{1}H} NMR specturm (128 MHz, 298 K, C_6D_6) of **6**.

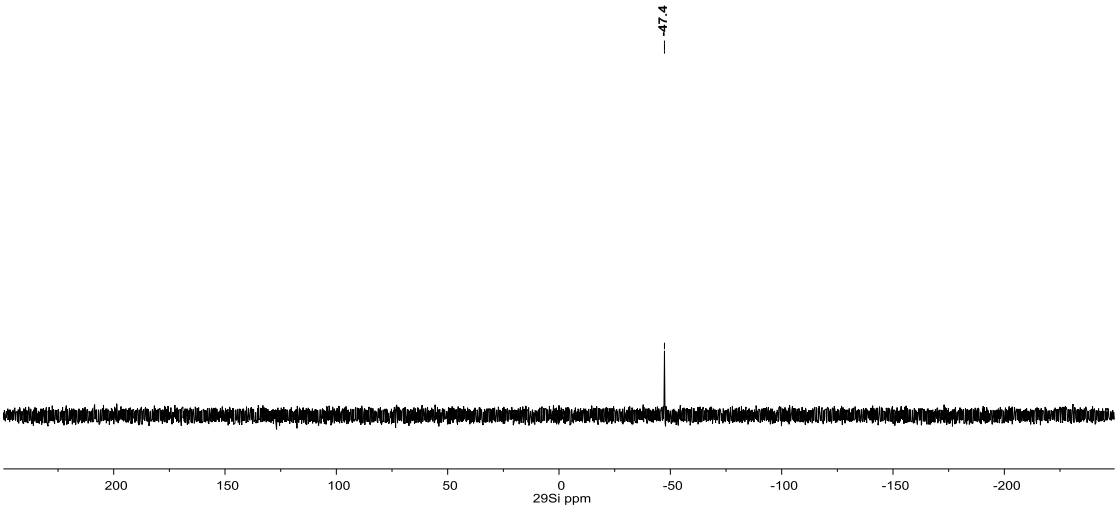

Figure S29. $^{29}Si\{^{1}H\}$ NMR specturm (80 MHz, 298 K, C_6D_6) of **6**.

Synthesis of $(HCNBu^t)_2Si\{[(HCNDip)_2B]NN\}_2$ 7. Compound **2** (120 mg, 0.100 mmol) and $(HCNDip)_2BN_3$ (89 mg, 0.200 mmol) were dissolved in benzene (8 mL), and the reaction mixture heated at 80 °C for 6 d, leading to the slow formation of **7**. Volatiles were then removed *in vacuo* and the residue was extracted with hexane (5 mL). The extract was filtered and the filtrate placed at -30 °C for 3d, after which colourless crystals of **7** had deposited. These were isolated and a second crop obtained from the mother liquor (140 mg, 68 %). M.p: 207–210 °C; ^{1}H NMR (400 MHz, C_6D_6) δ 0.79 (s, 18H, C(C*H*$_3$)$_3$), 1.18 (d, *J* = 6.7 Hz, 24H, CH(C*H*$_3$)$_2$), 1.21 (d, *J* = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$), 3.15 (sept, *J* = 7.0 Hz, 8H, C*H*(CH$_3$)$_2$), 5.23 (s, 2H, C*H*), 5.92 (s, 4H, C*H*), 7.12-7.24 (m, 12H, Ar*H*); $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6) δ 23.0, 26.7 (CH(*C*H$_3$)$_2$), 28.8 (*C*H(CH$_3$)$_2$), 31.1 (C(*C*H$_3$)$_3$), 51.0 (*C*(CH$_3$)$_3$), 109.7, 120.9 (*C*H), 123.5, 127.4, 127.9, 140.9 (Ar*C*); $^{11}B\{^{1}H\}$ NMR (128 MHz, C_6D_6) δ 23.6; $^{29}Si\{^{1}H\}$ NMR (80 MHz, C_6D_6) δ -43.0; IR *ν*/cm^{-1} (Nujol): 1401 (vs), 1250 (vs), 1152 (m), 1071 (m), 980 (m), 879 (vs), 758 (s); MS (EI, 70 eV): *m*/*z* (%) = 429.4 ((HCNDip)$_2$BNSi$^+$, 81), ((HCNDip)$_2$B$^+$, 65), 57.2 (Bu^{t+}, 100); HRMS (ESI/APCI): calc. for $C_{62}H_{93}B_2N_{10}Si$ (M^++H): 1027.7540, found 1027.7356.

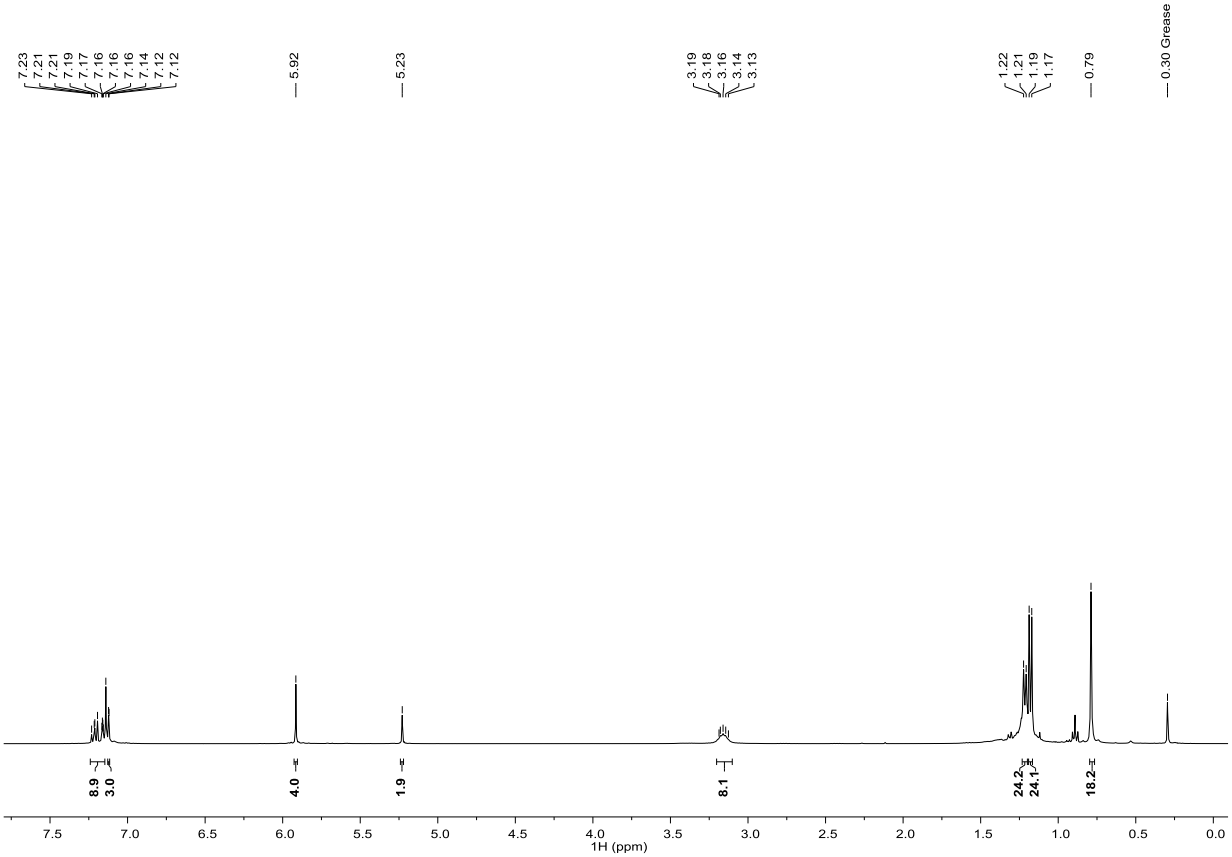

Figure S30. ^{1}H NMR specturm (400 MHz, 298 K, C_6D_6) of **7**.

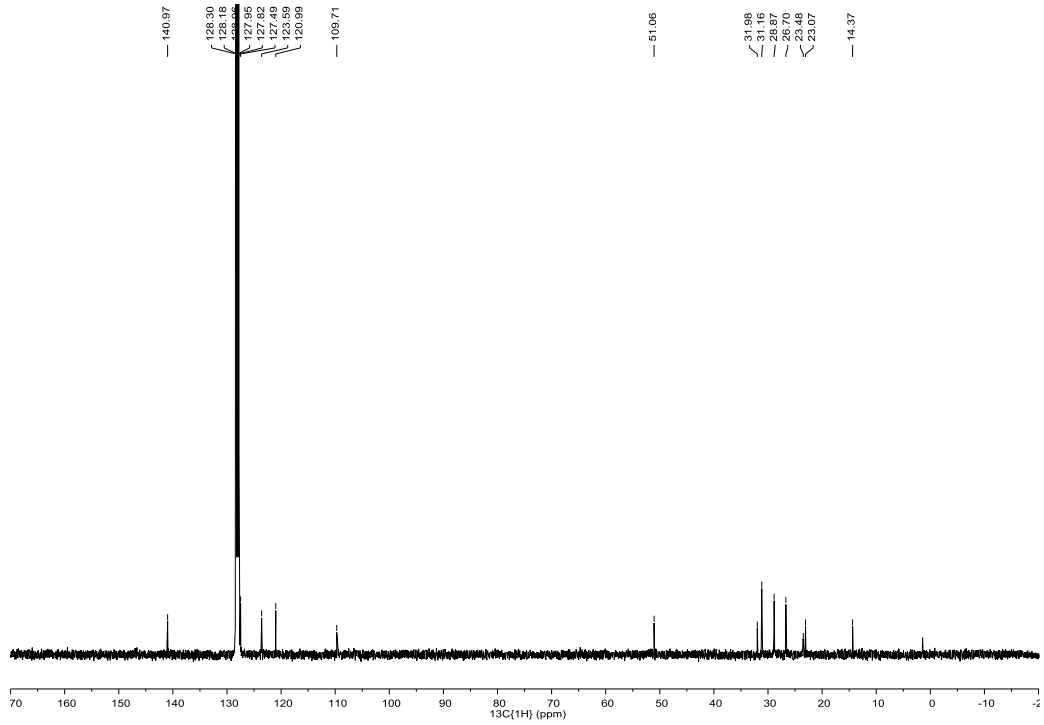

Figure S31. ^{13}C{^{1}H} NMR specturm (101 MHz, 298 K, C_6D_6) of **7**.

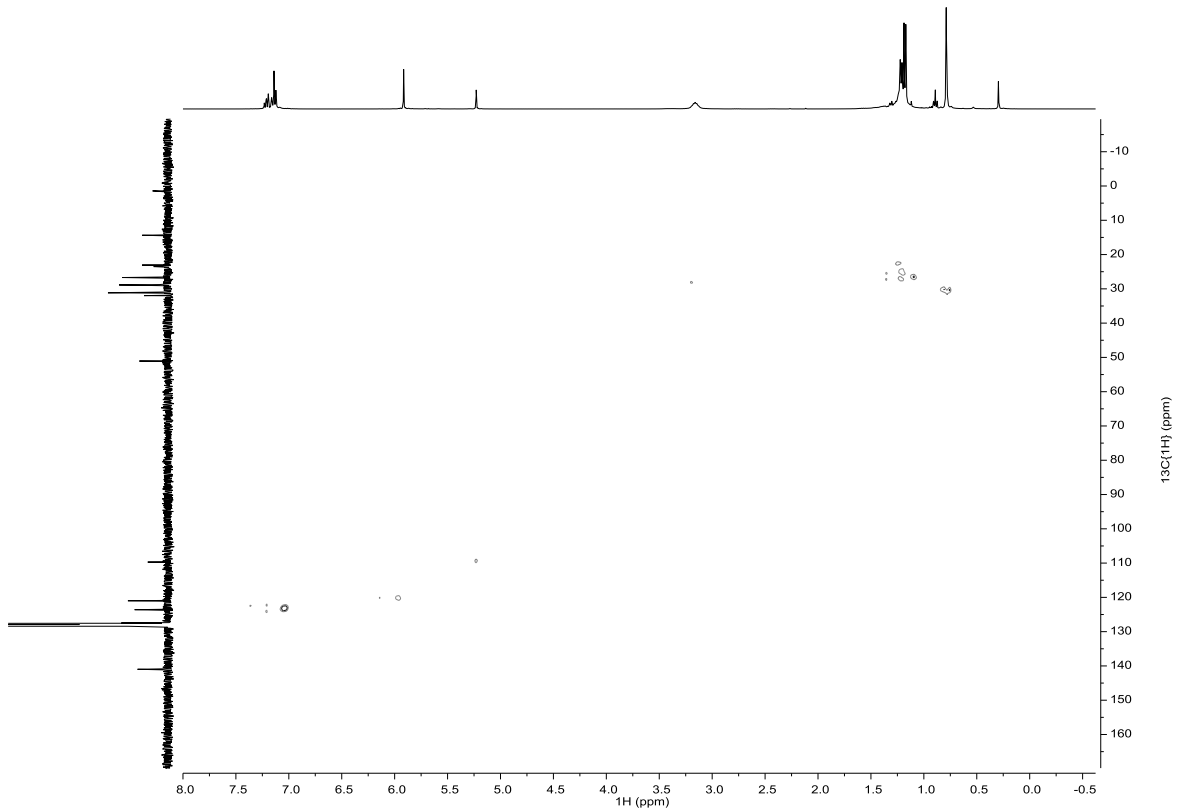

Figure S32. HMQC specturm (^{1}H: 400 MHz; ^{13}C: 101 MHz, 298 K, C_6D_6) of **7**.

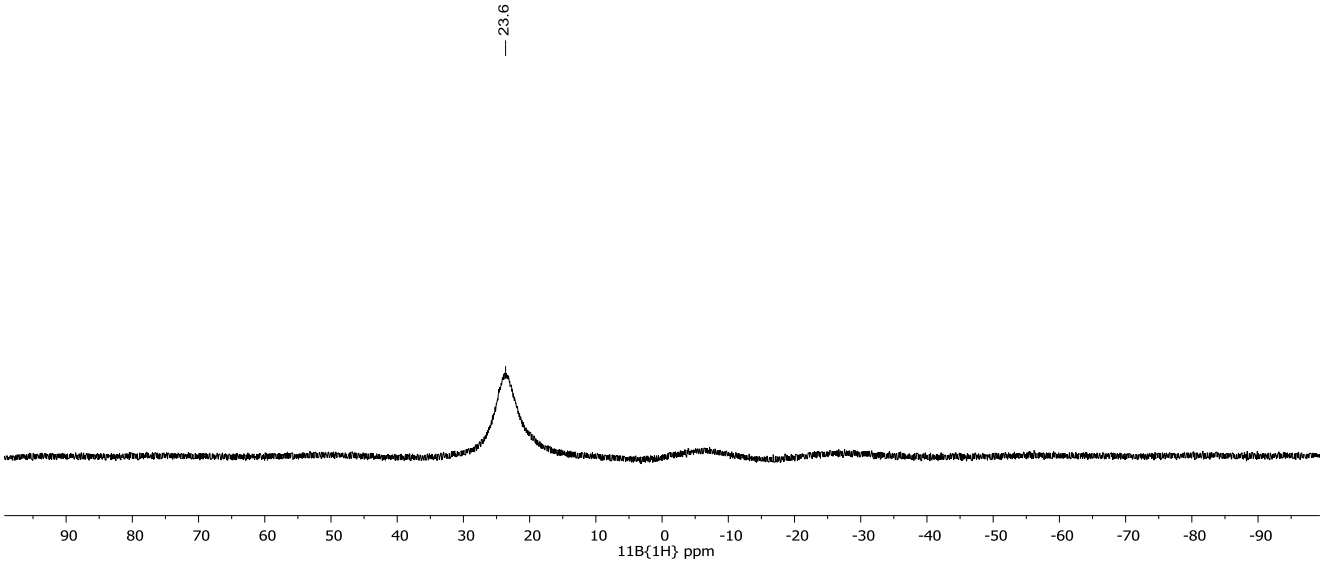

Figure S33. ^{11}B{^{1}H} NMR specturm (128 MHz, 298 K, C_6D_6) of **7**.

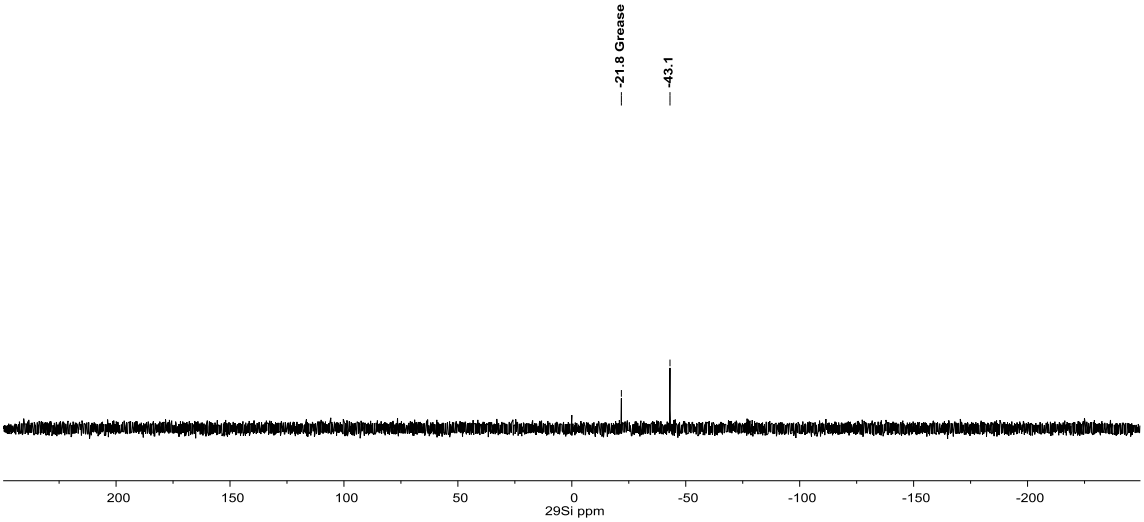

Figure S34. $^{29}Si\{^{1}H\}$ NMR specturm (80 MHz, 298 K, C_6D_6) of **7**.

2. X-Ray Crystallography

Crystals of **1-7** 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 Mo Kα radiation (λ = 0.71073 Å) or Cu Kα radiation (1.54180 Å), or the MX2 beamline of the Australian Synchrotron (λ = 0.71090 Å). The software package Blu-Ice[4] was used for synchrotron data acquisition, while the program XDS[5] was employed for synchrotron data reduction.. All structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX-16[6]) using all unique data. Hydrogen atoms are typically 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. Crystal data for **1**-**7**.

	1 $(hexane)_{0.5}$	**2**	**3**	**4**
empirical formula	$C_{55}H_{79}BN_5Si$	$C_{36}H_{56}BN_5Si$	$C_{53}H_{72}BN_5O_2Si$	$C_{27}H_{36}BN_3O$
formula weight	849.13	597.75	850.05	429.40
crystal system	Triclinic	Orthorhombic	Orthorhombic	Monoclinic
space group	*P*-1	*Pbca*	$P2_12_12_1$	$P2_1/c$
a (Å)	12.776(3)	20.0450(5)	9.94260(10)	12.69160(10)
b (Å)	20.405(4)	12.0661(2)	20.1639(3)	9.19770(10)
c (Å)	21.920(4)	29.3699(6)	24.4987(3)	22.4558(2)
α (º)	114.35(3)	90	90	90
β (º)	91.65(3)	90	90	96.8040(10)
γ (º)	93.08(3)	90	90	90
V ($Å^3$)	5191(2)	7103.6(3)	4911.54(11)	2602.88(4)
Z	4	8	4	4
T (K)	100(2)	123(2)	123(2)	123(2)
ρ_{calcd} ($g \cdot cm^3$)	1.087	1.118	1.150	1.096
μ (mm^{-1})	0.084	0.805	0.757	0.509
F(000)	1852	2608	1840	928
reflns collected	19415	36803	92483	26554
unique reflns	19256	6608	9123	4838
R_{int}	0.0796	0.0982	0.1196	0.0386
R1 [$I > 2\sigma(I)$]	0.0612	0.0770	0.0485	0.0445
wR2 (all data)	0.1724	0.2121	0.1269	0.1166
largest peak and hole ($e \cdot Å^{-3}$)	0.480, -0.410	0.914, -0.293	0.359, -0.413	0.308, -0.294
CCDC no.	1936048	1936049	1936051	1936047

Table S1 (contd.). Crystal data for **1**-**7**.

	5	**6**	**7** $(benzene)_{1.5}$
empirical formula	$C_{52}H_{74}BN_5OSi$	$C_{36}H_{58}BN_5OSi$	$C_{71}H_{101}B_2N_{10}Si$
formula weight	824.06	615.77	1144.32
crystal system	Monoclinic	Monoclinic	Triclinic
space group	$P2_1/c$	$P2_1/n$	P-1
a (Å)	19.7295(15)	12.6357(2)	12.25400(10)
b (Å)	12.4632(9)	20.6176(3)	13.34060(10)
c (Å)	19.9618(15)	14.6141(3)	23.45660(10)
α (º)	90	90	76.3140(10)
β (º)	96.766(4)	99.935(2)	81.4680(10)
γ (º)	90	90	66.8400(10)
V ($Å^3$)	4874.3(6)	3750.14(11)	3418.88(5)
Z	4	4	2
T (K)	123(2)	123(2)	123(2)
ρ_{calcd} ($g \cdot cm^3$)	1.123	1.091	1.112
μ (mm^{-1})	0.090	0.795	0.657
F(000)	1792	1344	1242
reflns collected	26161	33263	67124
unique reflns	9035	8701	12702
R_{int}	0.1697	0.0584	0.0526
R1 [$I > 2\sigma(I)$]	0.1066	0.0686	0.0428
wR2 (all data)	0.3216	0.2249	0.1143
largest peak and hole ($e \cdot Å^{-3}$)	1.070, -1.024	0.716, -0.426	0.528, -0.353
CCDC no.	1936046	1936050	1936052

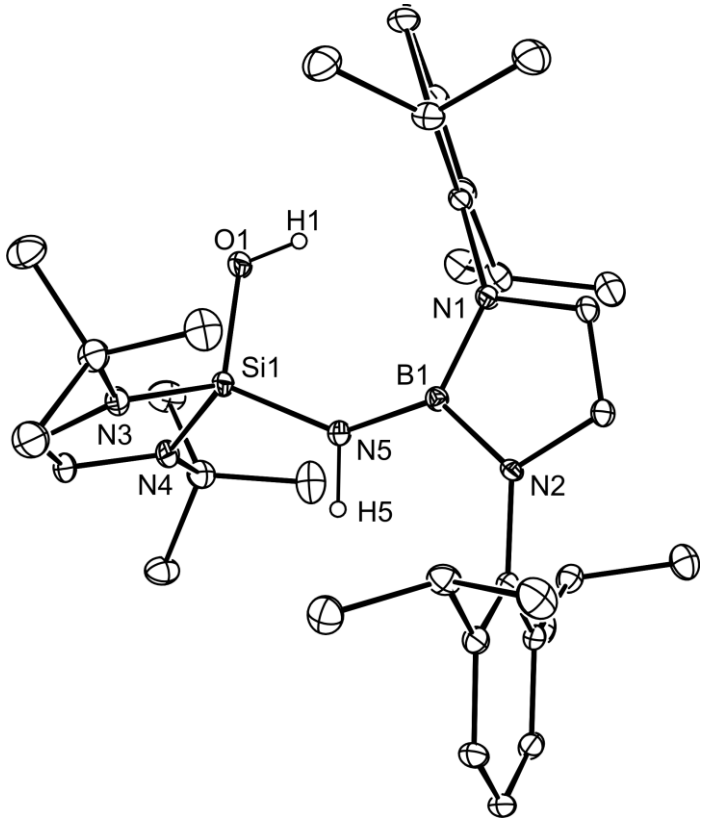

Figure S35. ORTEP diagram of compound **6** (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (º): Si(1)-O(1) 1.6301(18), Si(1)-N(5) 1.715(2), N(5)-B(1) 1.445(3), O(1)-Si(1)-N(5)1 07.78(10), B(1)-N(5)-Si(1) 139.63(17).

3. References

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