Supporting Information for

Alkali Metal Catalyzed Dehydro-coupling of Boranes and Amines Leading to the Formation of B-N Bond

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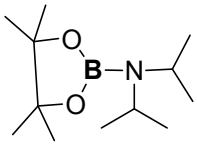
A1. Experimental section

General: All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame dried Schlenk-type glassware, either on a dual manifold Schlenk line interfaced with a high vacuum (10^{-4} torr) line, or in an argon-filled M. Braun glovebox. The ^{1}H NMR (400 MHz), $^{11}B\{^{1}H\}$ (128 MHz), $^{13}C\{^{1}H\}$ (100 MHz), spectra were recorded on a BRUKER AVANCE III-400 spectrometer. All catalytic substrates amines and boranes were purchased from either Sigma Aldrich or Alfa Aesar. Amines were distilled over CaH_2 prior to use. $LiN(SiMe_3)_2$, $NaN(SiMe_3)_2$ and $KN(SiMe_3)_2$ were purchased from Sigma Aldrich and used as received. $CDCl_3$ was purchased from Sigma Aldrich.

A2. Typical procedure for CDC reactions: Catalyzed cross-dehydrocoupling (CDC) reactions were carried out by using the following standard protocol. In the glove-box, the pre-catalyst chosen (0.05 mmol) was loaded into a Schleck tube and subsequently the amine (n × 0.05 mmol, n equi) followed by borane (n × 0.05 mmol, n equi) were added to the Schleck tube. The reaction

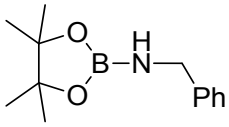
was stirred in an oil bath at desired temperature (25°C). After the required amount of time, the reaction was quenched by adding $CDCl_3$ to the reaction mixture. Substrate conversion was monitored by the ^1H NMR spectrum of the reaction mixture, comparing integrations characteristic of the substrates and products. Novel compounds characterized here after.

Product – **E**



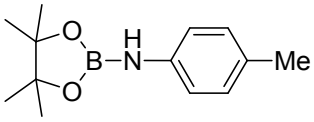
C_6H_{14}NBpin:- ^1H NMR (400 MHz, $CDCl_3$) δ 3.34 (m, 2H, CH), 1.18 (s, 12H), 1.10 (s, 12H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 80.9 (O attached C), 44.5 (CH), 24.5 (CH_3-C), 23.2 (CH_3-C) ppm. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ 23.8 ppm.

Product – **G**



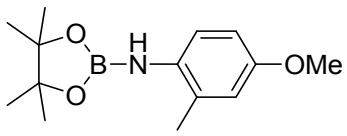
C_7H_7NBpin:- ^1H NMR (400 MHz, $CDCl_3$) δ 7.23-7.17 (m, 3H, Ar-H), 7.15 - 7.10 (m, 2H, Ar-H) 4.01 (d, 2H, *J* =7.7 Hz, CH_2), 1.15 (s, 12H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.8 (Ar-C), 128.3 (Ar-C), 126.7 (Ar-C) 82.1 (O attached C), 45.2 (CH_3), 24.6 (CH_3-C) ppm. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ 24.8 ppm.

Product – **I**



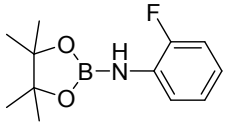
$C_7H_7N(H)Bpin$:- ^1H NMR (400 MHz, $CDCl_3$) δ 7.01-6.95 (m, 4H, Ar-H), 4.53 (br, 1H, NH), 2.25 (s, 3H), 1.29 (s, 12H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 140.6 (N attached Ar-C), 129.4 (Ar-C), 117.5 (Ar-C), 121.3 (Ar-C), 119.3 (Ar-C), 118.9 (Ar-C), 83.6 (O attached C), 24.6 (CH_3-C), 20.5 (CH_3-C) ppm.$^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ 23.9 ppm.

Product – **J**



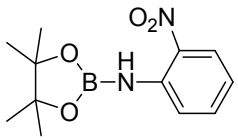
$C_8H_9ON(H)Bpin$:- ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, 1H, J = 8.4 Hz, Ar-H), 6.71-6.67 (m, 2H, Ar-H), 4.37 (br, 1H, NH), 3.75 (s, 3H), 2.18 (s, 3H), 1.31 (s, 12H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.6 (N attached Ar-C), 129.4 (Ar-C), 117.5 (Ar- C), 121.3 (Ar- C), 119.3 (Ar- C), 118.9 (Ar- C), 82.6 (O attached C), 55.5 (O attached C), 24.6 (CH_3-C), 18.1 (CH_3- C) ppm. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ 24.1 ppm.

Product - **K**



$C_6H_4FN(H)Bpin$:- ^1H NMR (400 MHz, $CDCl_3$) δ 7.61-7.57 (d, 1H, Ar-H), 7.02 - 6.95 (m, 2H, Ar-H), 6.80-6.74 (m, 1H, Ar-H), 4.97 (br, 1H, NH), 1.32 (s, 12H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.4 (F attached Ar-C), 151.0 (N attached Ar-C), 131.6 (Ar-C), 124.3 (Ar-C), 119.1 (Ar-C), 114.5 (Ar-C), 83.0 (O attached C), 24.6 (CH_3-C). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ 24.04 ppm.

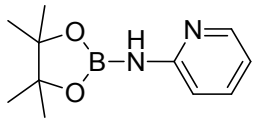
Product - **L**



$C_6H_4NO_2N(H)Bpin$:- ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (br, 1H, NH), 7.93-7.87 (m, 2H, Ar-H), 7.72 (d, 1H, J = 8.4), 7.14 (t, 1H, J = 7.8 Hz, Ar-H), 1.16 (s, 12H, CH_3 – H) ppm . $^{13}C\{^1H\}$

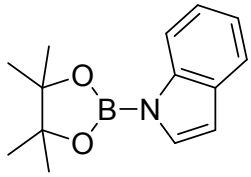
NMR (100 MHz, $CDCl_3$) δ 145.0 (N attached Ar-C), 135.6 (Ar-C), 135.2 (Ar-C), 121.3 (Ar-C), 119.3 (Ar-C), 118.9 (Ar-C), 83.6 (O attached C), 24.5 (CH_3-C) ppm. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ 24.32 ppm.

Product – **M**



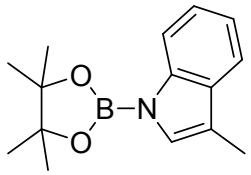
$C_5H_4N_2$(H)Bpin:- ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, 1H, *J* = 3.9 Hz Ar-H), 7.51 - 7.47 (m, 1H, Ar-H), 7.41-7.33 (m, 1H, Ar-H), 6.77-6.72 (m, 1H, Ar-H), 5.76 (br, 1H, NH), 1.29 (s, 12H) ppm.$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 156.3 (N attached Ar-C), 147.8 (N attached Ar-C), 137.2 (Ar-C), 111.5 (Ar-C), 108.5 (Ar-C), 83.1 (O attached C), 24.6 (CH_3-C) ppm. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ 23.99 ppm.

Product – **N**



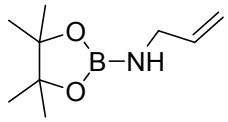
C_8H_6NBpin:- ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, 1H, *J* = 7.9, C=CH), 7.41 (d, 1H, *J* = 7.3 Hz), 7.20 (d, 1H, *J* = 3.2 Hz), 7.06-7.04 (m, 1H, Ar-H), 7.00 - 6.97 (m, 1H, Ar-H), 6.41 (d, 1H, *J* = 3.3 Hz, C=CH), 1.21 (s, 12H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 135.8 (N attached Ar-C), 135.0 (Ar-C), 134.8 (Ar-C), 133.7 (Ar-C), 131.6 (Ar-C), 130.3 (Ar-C), 130.4 (Ar-C), 127.9 (Ar-C), 127.8 (Ar-C) ppm. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ 24.5 ppm.

Product - **O**



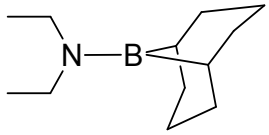
$C_9H_8N(H)Bpin$:- ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, 1H, *J* = 8.1 Hz, C = CH), 7.65 (d, 1H, *J* = 7.8 Hz), 7.58 (d, 1H, *J* = 7.5 Hz), 7.38 (d, 1H, *J* = 7.9 Hz) 7.31 - 7.19 (m, 6H, Ar-H), 6.99 (d, 1H, Ar-H), 2.36 (s, 3H), 1.40 (s, 12H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 139.6 (N attached Ar-C), 136.2 (Ar-C), 131.9 (Ar-C), 126.0 (Ar-C), 122.6 (Ar-C), 120.8 (Ar-C), 118.5 (Ar-C), 114.6 (Ar-C), 110.9 (Ar-C), 84.1 (O attached C), 24.7 (CH_3-C), 9.71 (CH_3-C) ppm. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ 24.35 ppm.

Product – **P**



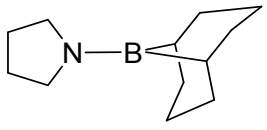
$C_3H_5N(H)Bpin$:- ^1H NMR (400 MHz, $CDCl_3$) δ 5.86 - 5.79 (m, 1H, CH) 5.09 - 5.04 (d, *J* = 1.7, 17.1 Hz, 1H, CH), 4.95 - 4.92 (m, 1H, CH), 3.45 (m, 1H), 3.45 (m, 2H, CH_2), 2.25 (br, 1H, NH), 1.16 (s, 12H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 81.9 (O attached C), 43.4 (CH), 24.5 (CH_3 - C), 24.4 (CH_3-C) ppm. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ 24.35 ppm.

Product – **Q**



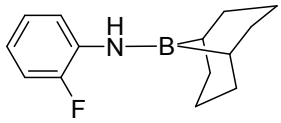
$C_4H_{10}NBR_2$: ^1H NMR (400 MHz, $CDCl_3$) δ 3.05 - 3.00 (q, *J* = 7.1, 7.0 Hz, 4H, CH_2), 1.83 - 1.57 (m, 5H, CH_2), 1.32 - 1.25 (m, 2H, C*H*), 0.99 (t, 6H, *J* = 7.0 Hz, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) 40.4, 30.9, 21.0, 14.5 ppm. $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ 47.7 ppm.

Product – **R**

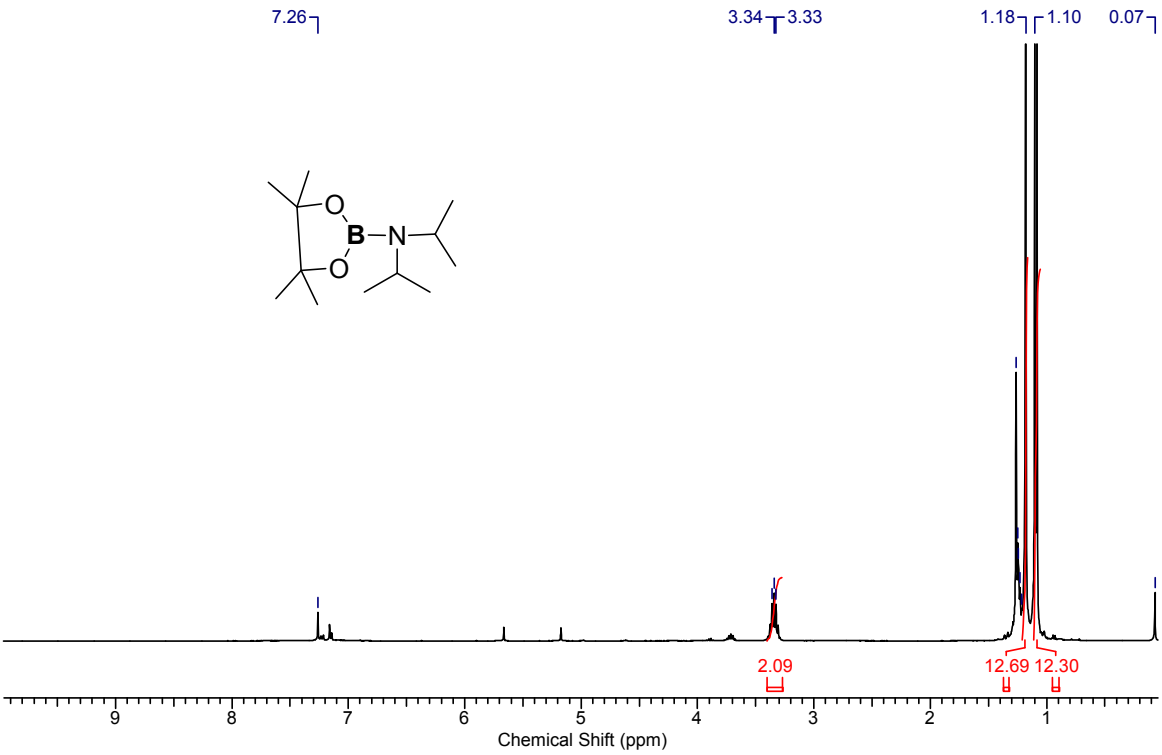


$C_4H_8NBR_2$: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.29 - 3.26 (m, 4H, C*H*$_2$), 1.89 - 1.63 (m, 14H, C*H*,C*H*$_2$), 1.37 - 1.36 (m, 4H, C*H*$_2$), 3.45 (m, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) 44.6, 30.5, 23.7, 21.2 ppm. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ 48.4 ppm.

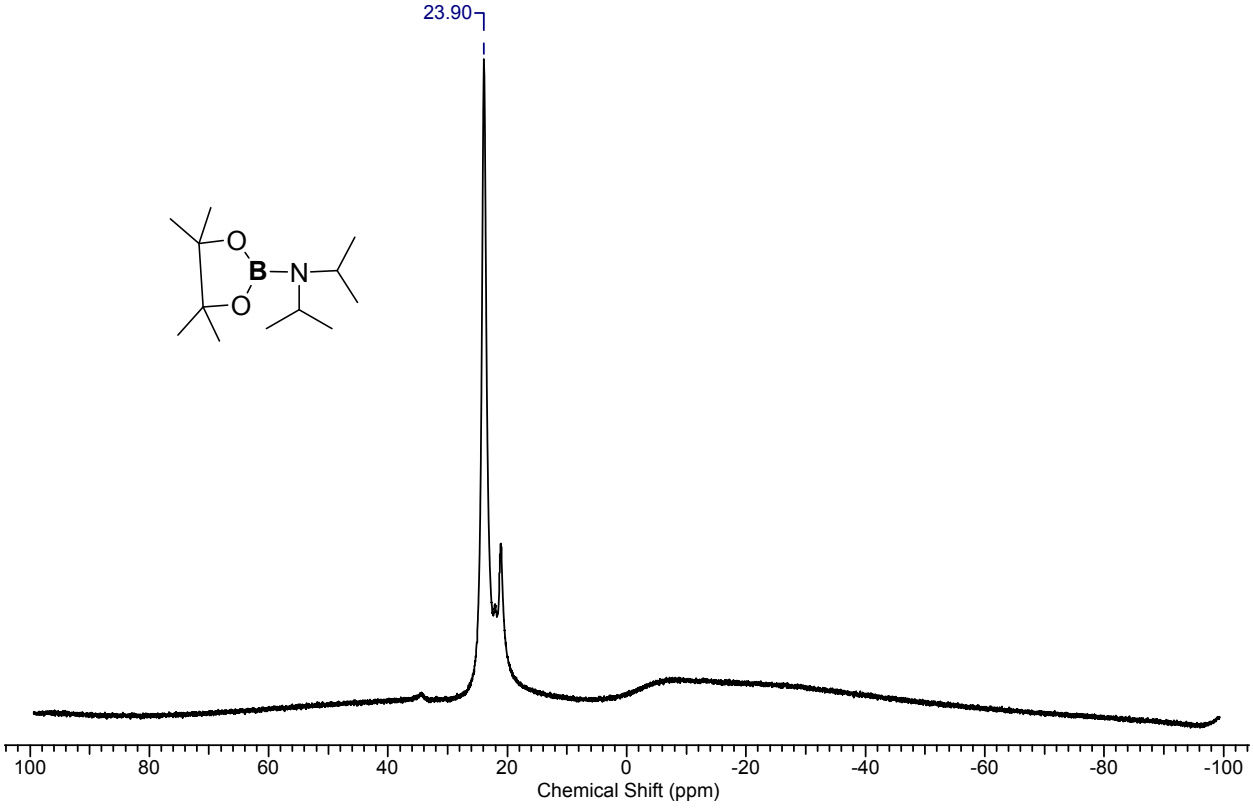
Product – **U**



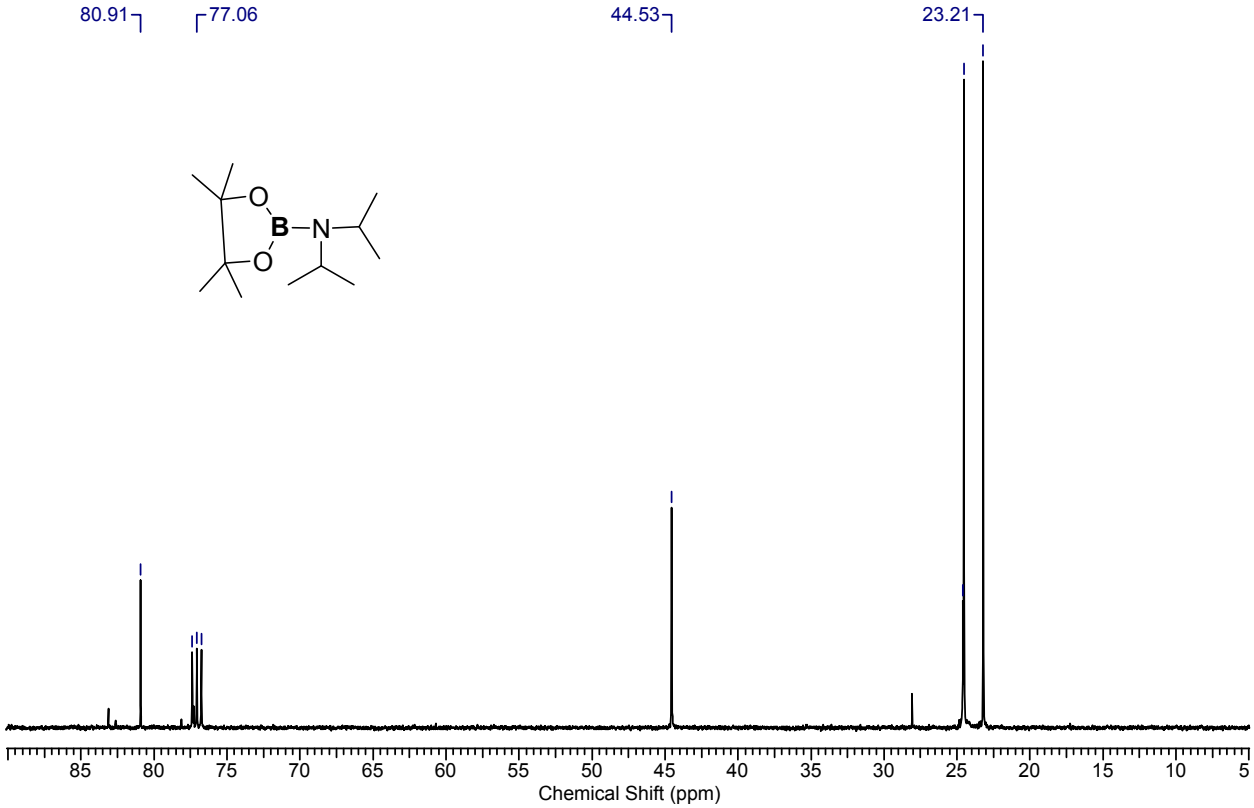
$C_6H_4FN(H)BR_2$: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14-7.08 (m, 1H, Ar-*H*), 7.01 - 6.87 (m, 2H, Ar-*H*), 6.70-6.57 (m, 1H, Ar-*H*), 5.97 (br, 1H, N*H*), 1.90 -1.03 (m, 14H) ppm. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ 52.8 ppm.



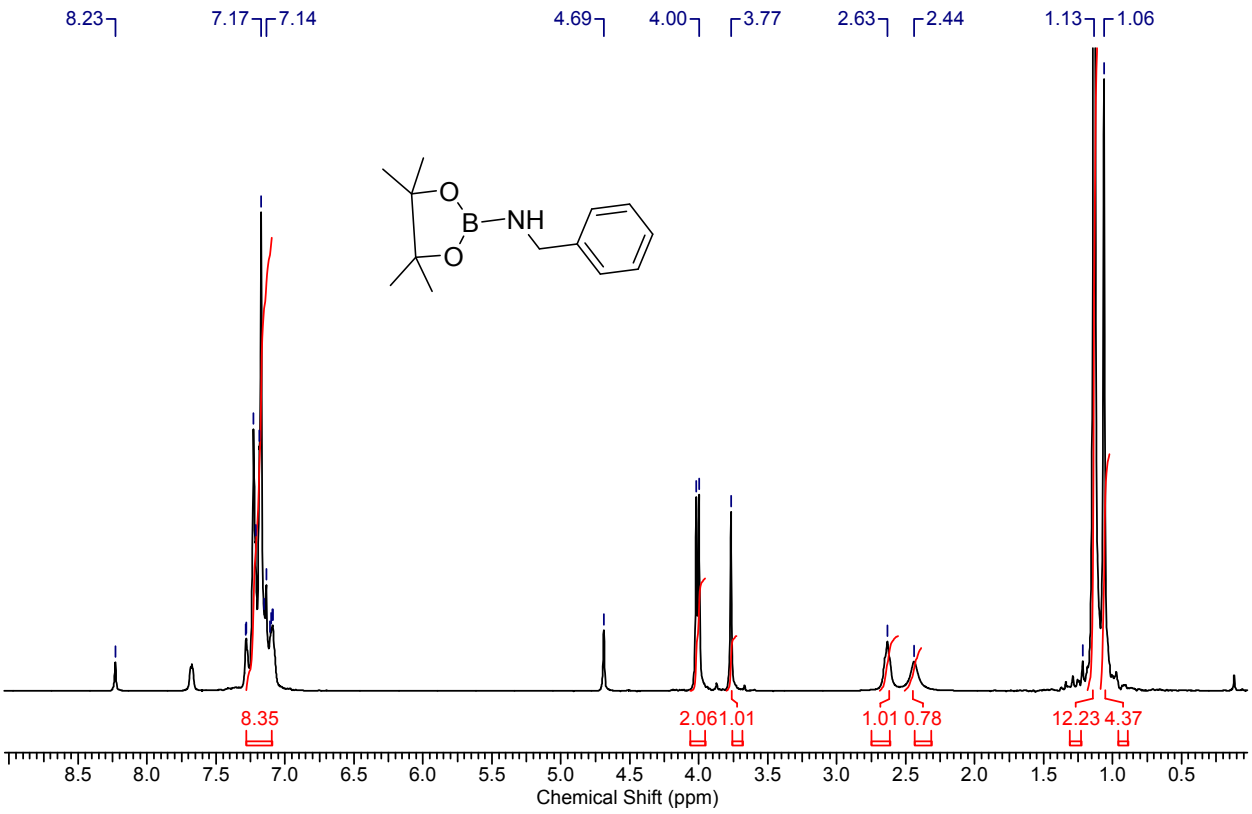
S1.[1]H NMR spectrum (400 MHz, 25°C, $CDCl_3$) of [$(CH_3)_2$CHNBpin] (**E**)



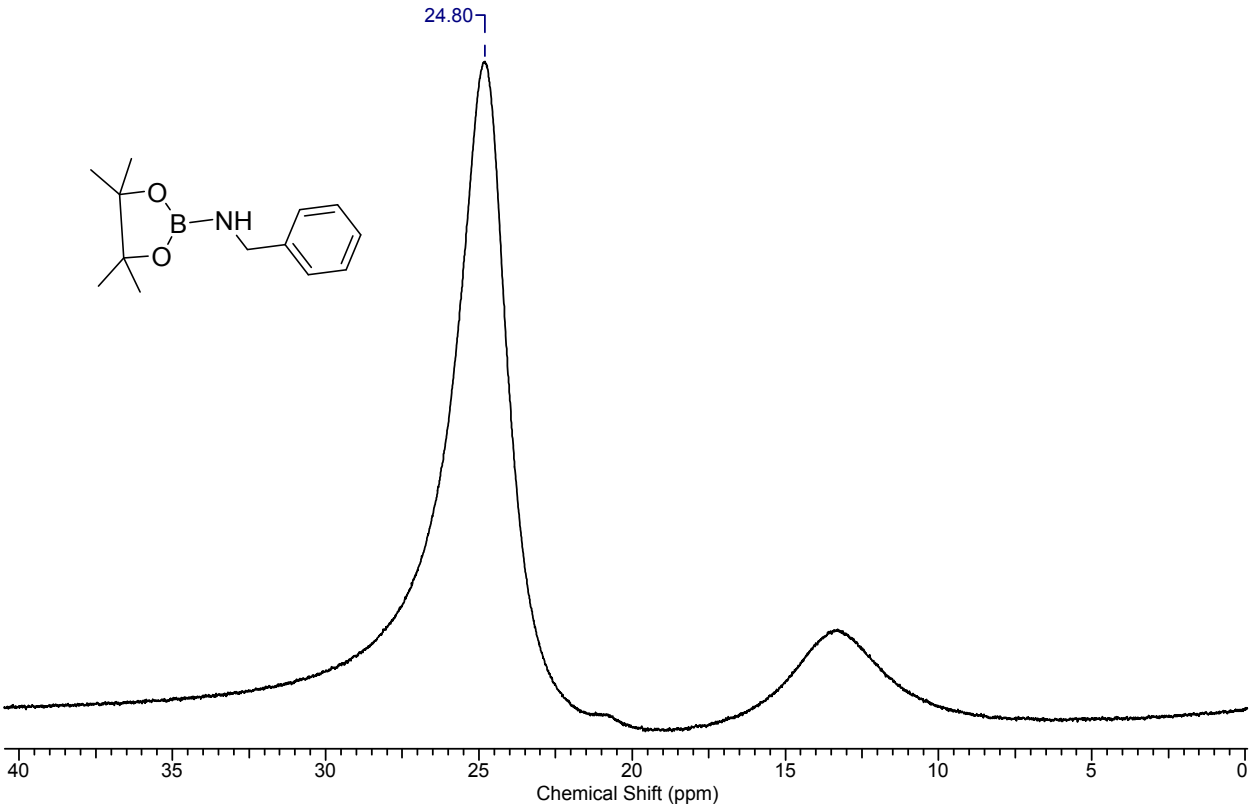
S2.[11]B NMR spectrum (128.4 MHz, 25°C, $CDCl_3$) of [$(CH_3)_2$CHNBpin] (**E**)



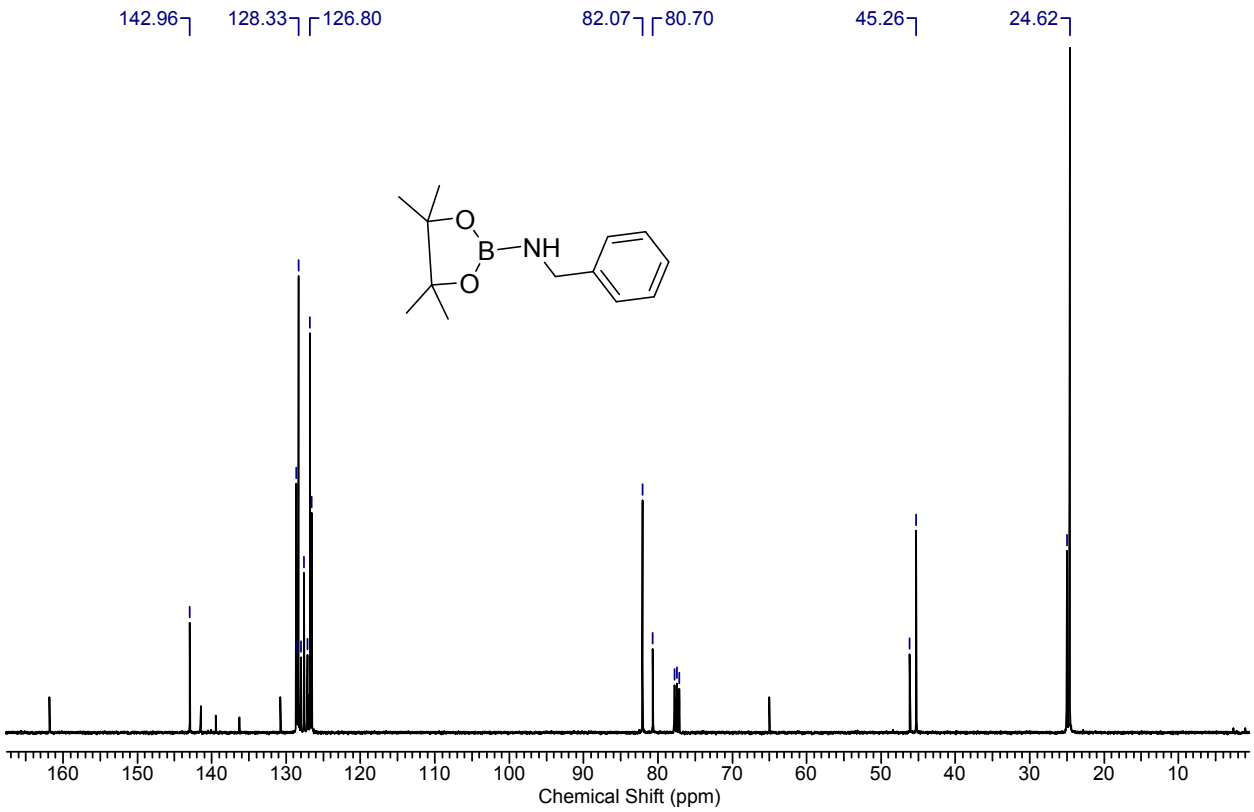
S3.^{13}C NMR spectrum (100 MHz, 25°C, $CDCl_3$) of $[(CH_3)_2CHNBpin]$ (**E**)



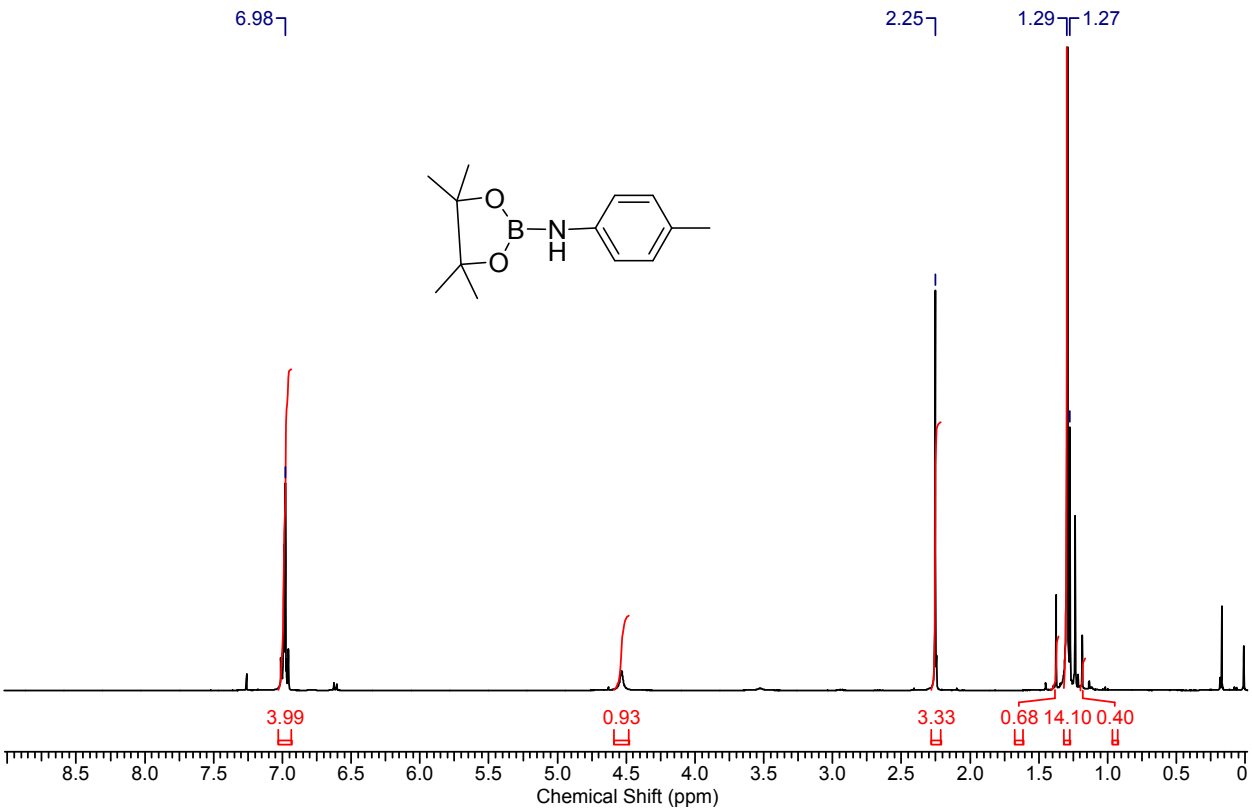
S4. ^{1}H NMR spectrum (400 MHz, 25°C, $CDCl_3$) of [C_7H_7N(H)Bpin] (**G**)



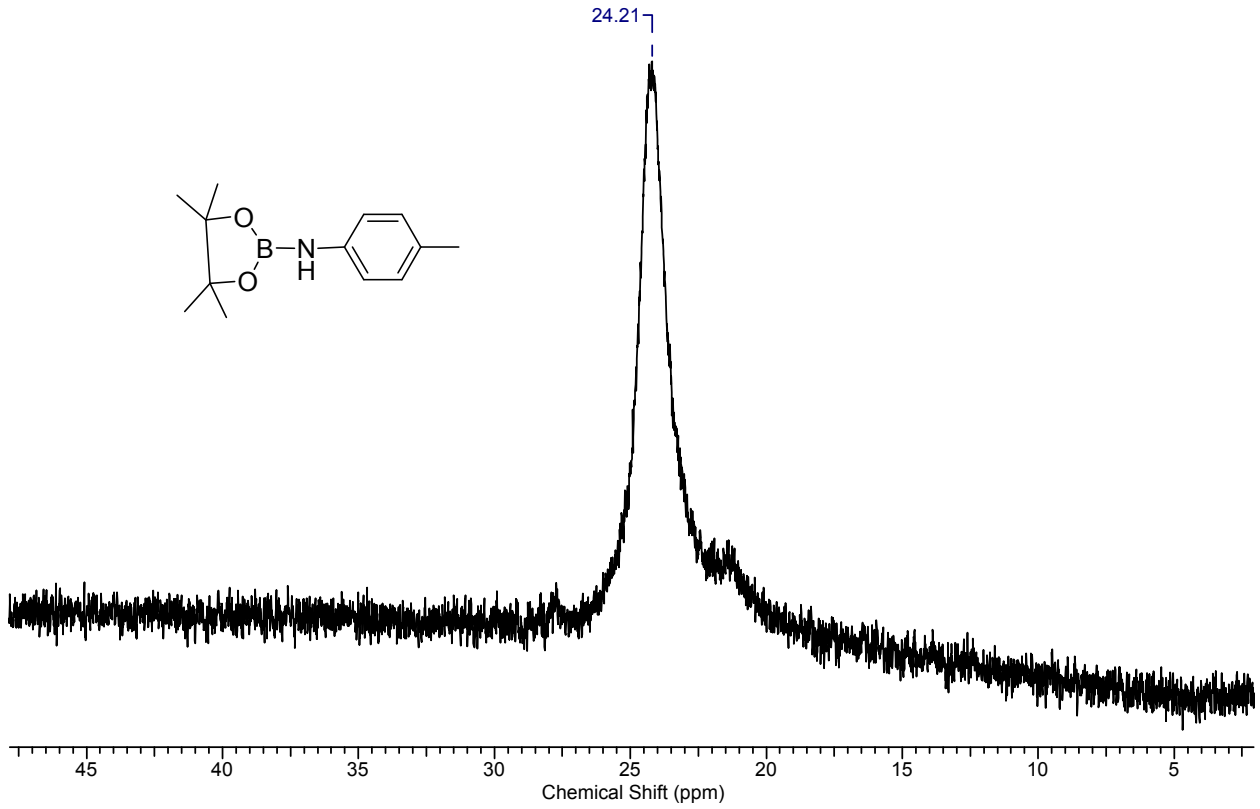
S5.^{11}B NMR spectrum (128.4 MHz, 25°C, $CDCl_3$ of $[C_7H_7N(H)Bpin]$ (**G**)



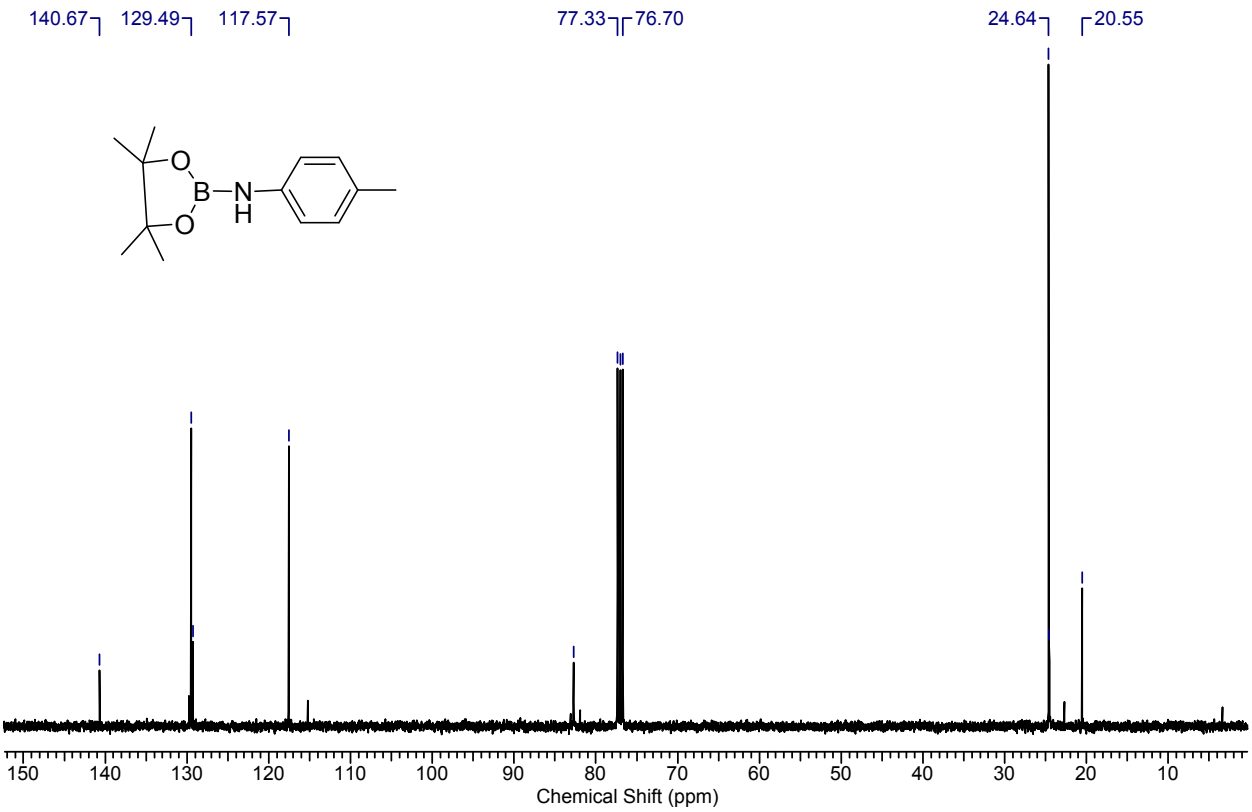
S6.^{13}C NMR spectrum (100 MHz, 25°C, $CDCl_3$ of $[C_7H_7N(H)Bpin]$ (**G**)



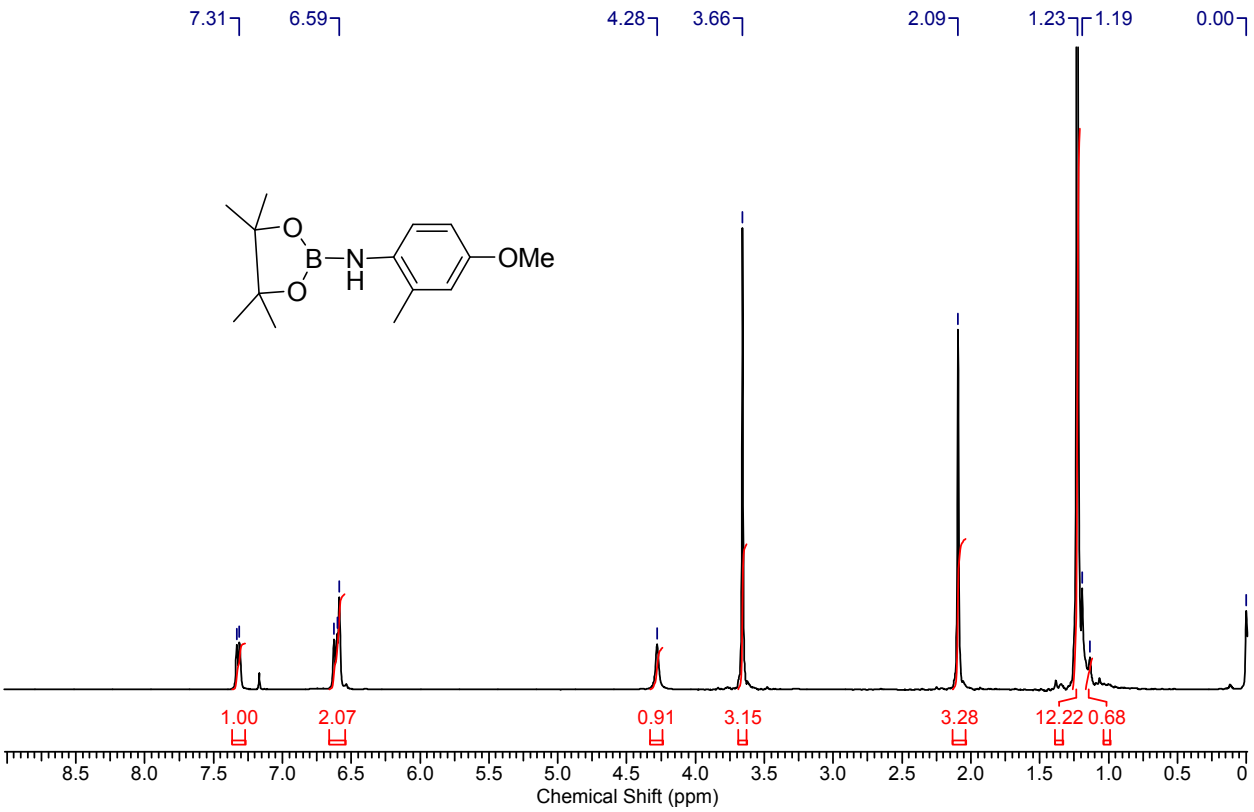
S7.^{1}H NMR spectrum (400 MHz, 25°C, $CDCl_3$) of [C_7H_7N(H)Bpin] **(I)**



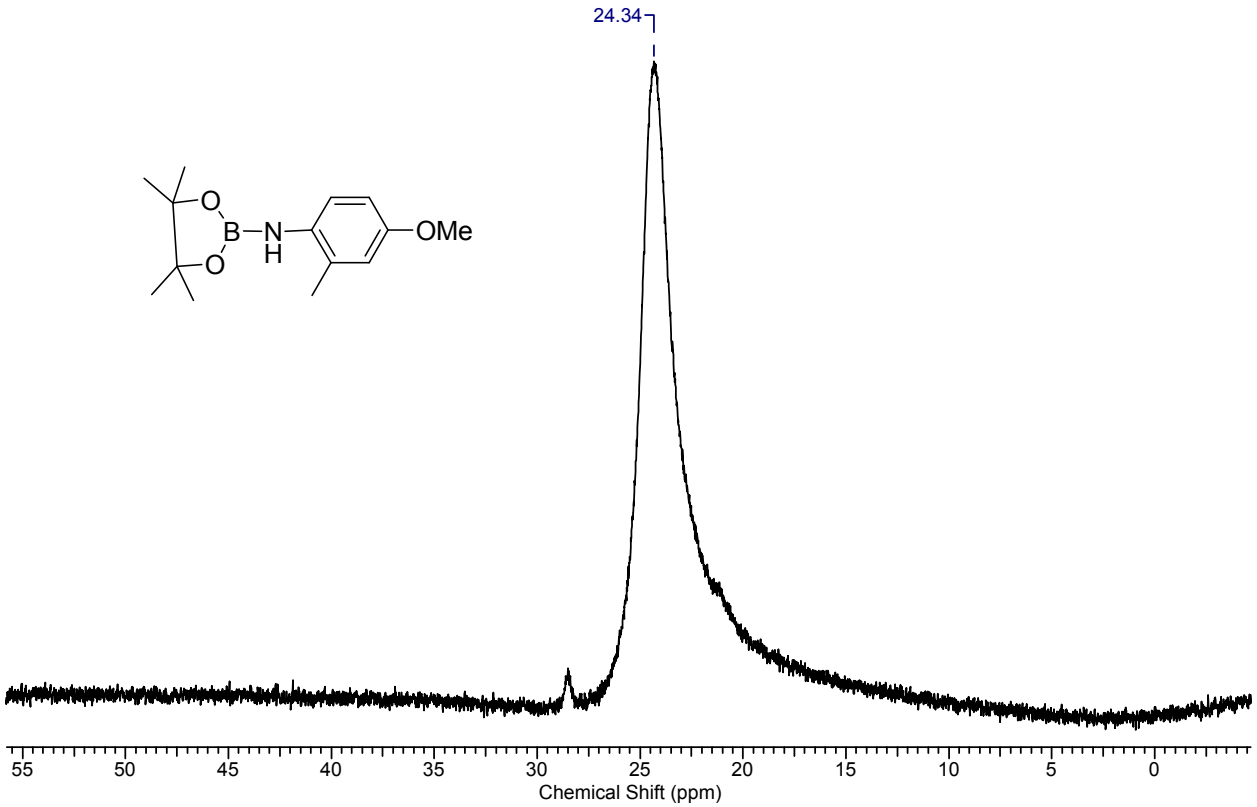
S8.^{11}B NMR spectrum (128.4 MHz, 25°C, $CDCl_3$ of $[C_7H_7N(H)Bpin]$ (**I**)



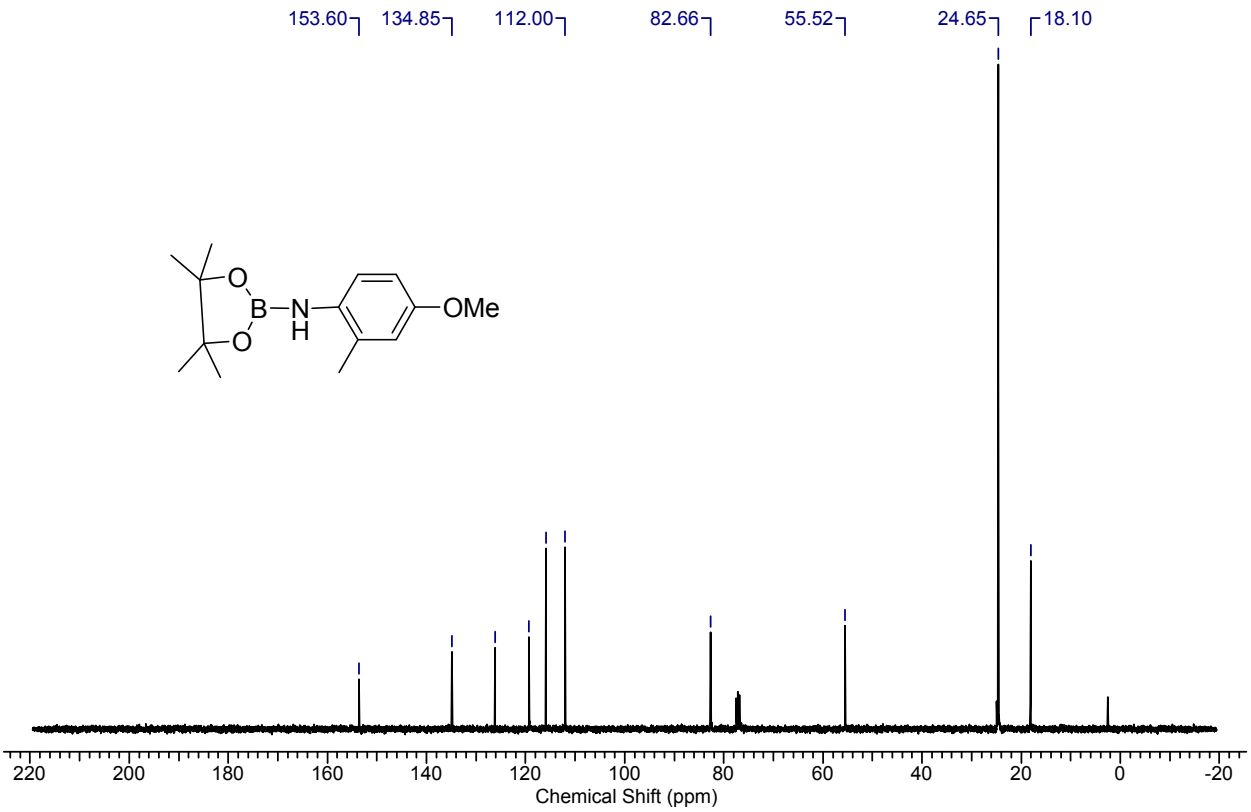
S9.^{13}C NMR spectrum (100 MHz, 25°C, $CDCl_3$ of $[C_7H_7N(H)Bpin]$ (**I**)



S10. ^{1}H NMR spectrum (400 MHz, 25°C, $CDCl_3$) of [$C_8H_{10}ON(H)Bpin$](**J**)

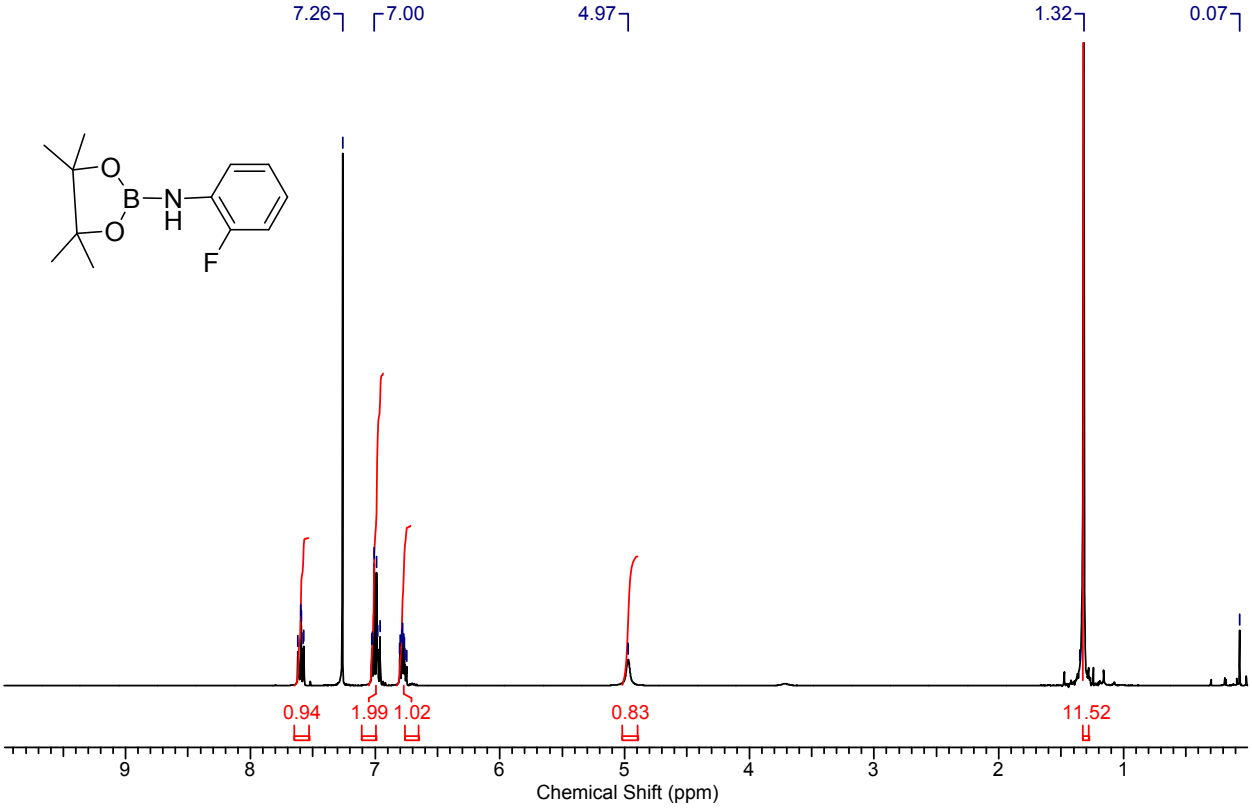


S11.^{11}B NMR spectrum (128.4 MHz, 25°C, $CDCl_3$ of $[C_8H_{10}ON(H)Bpin]$(**J**)



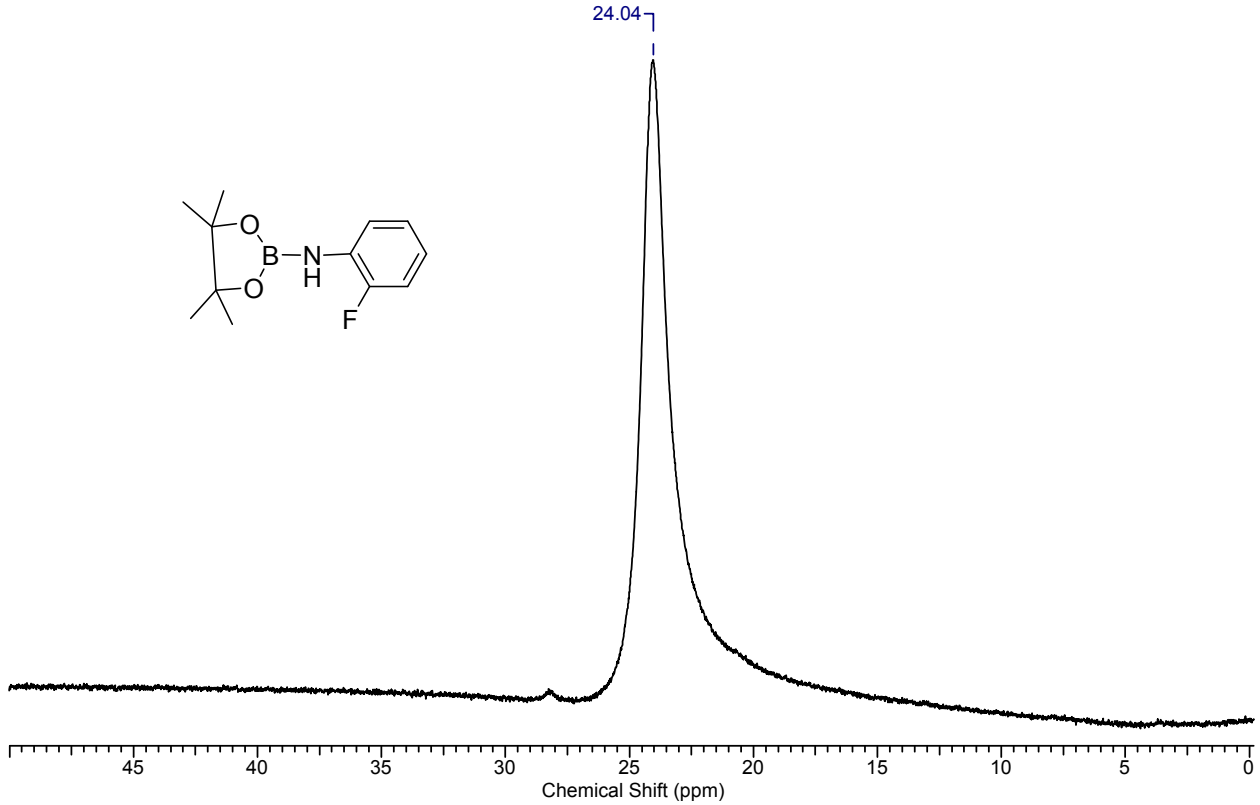
S12. ^{13}C NMR spectrum (100 MHz, 25°C, $CDCl_3$ of $[C_8H_{10}ON(H)Bpin]$ (**J**)

Fig-S4

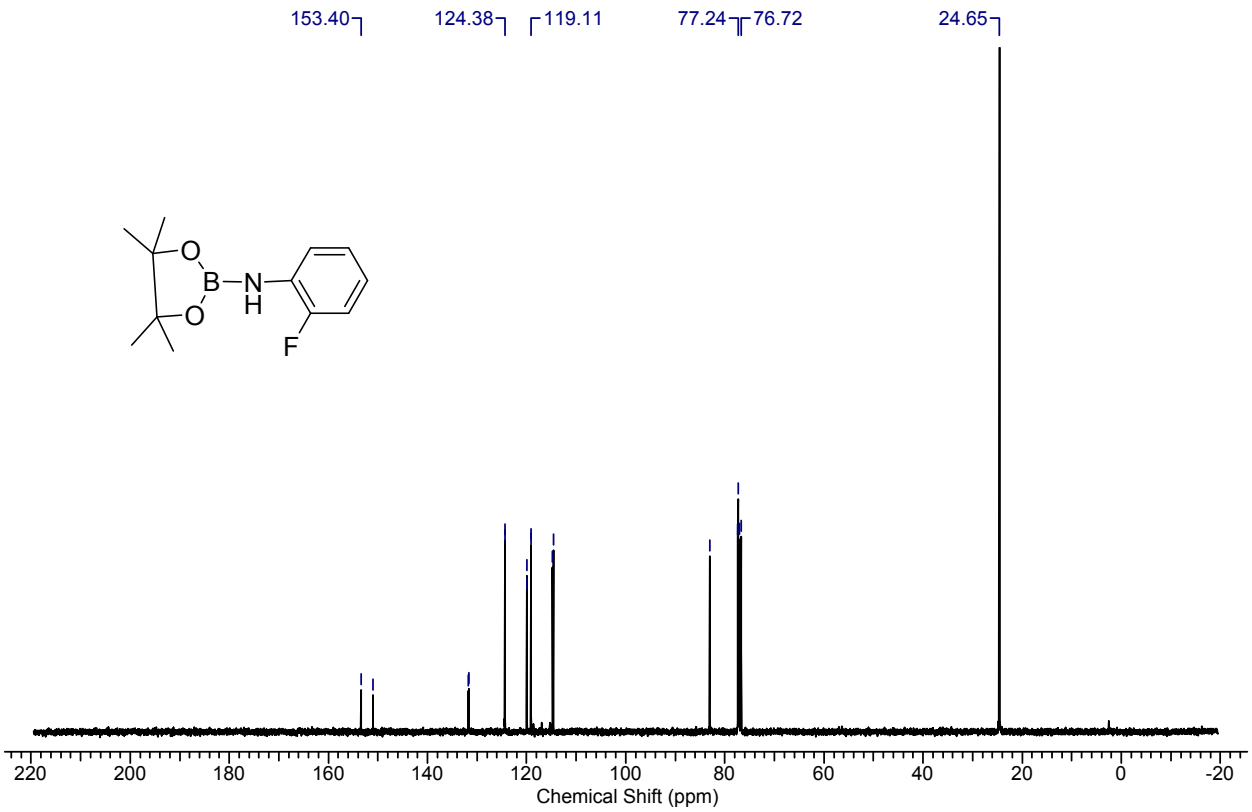


S13. ^{1}H NMR spectrum (400 MHz, 25°C, $CDCl_3$) of $[C_6H_4FN(H)Bpin]$ (**K**)

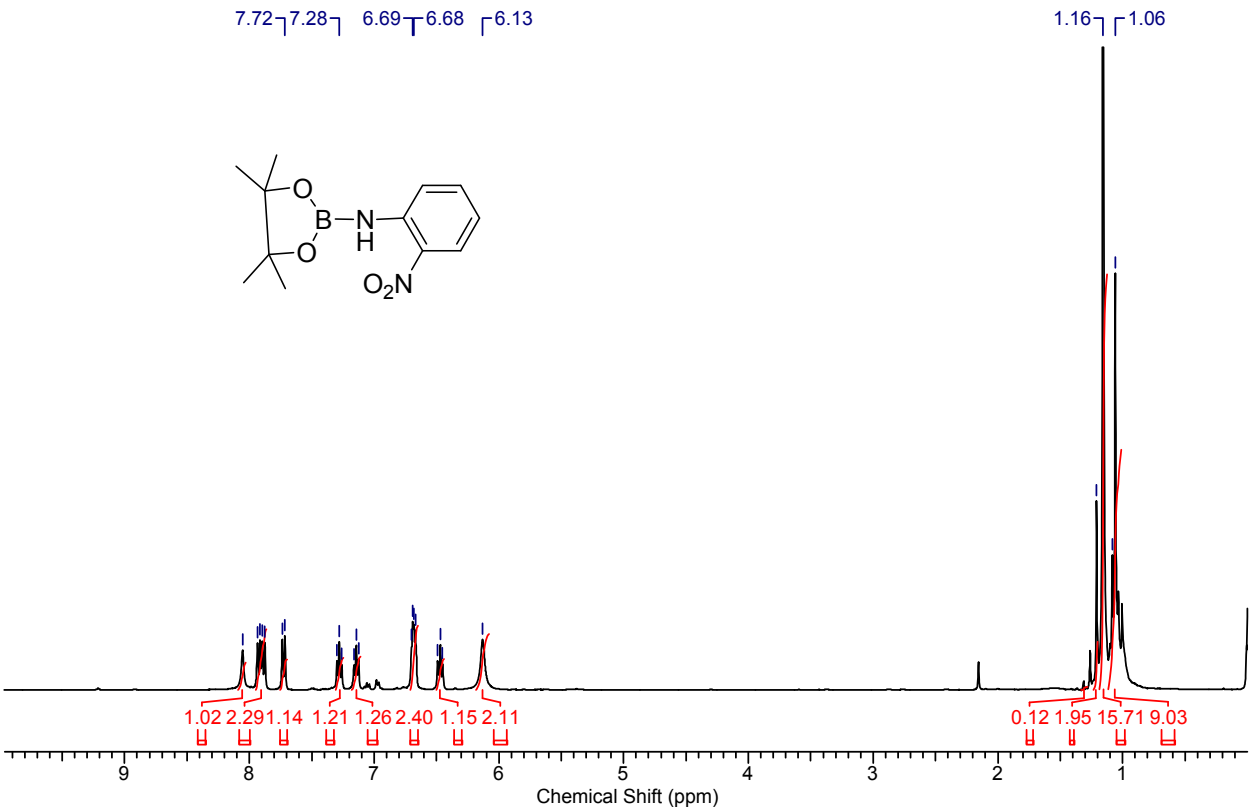
Fig-S5



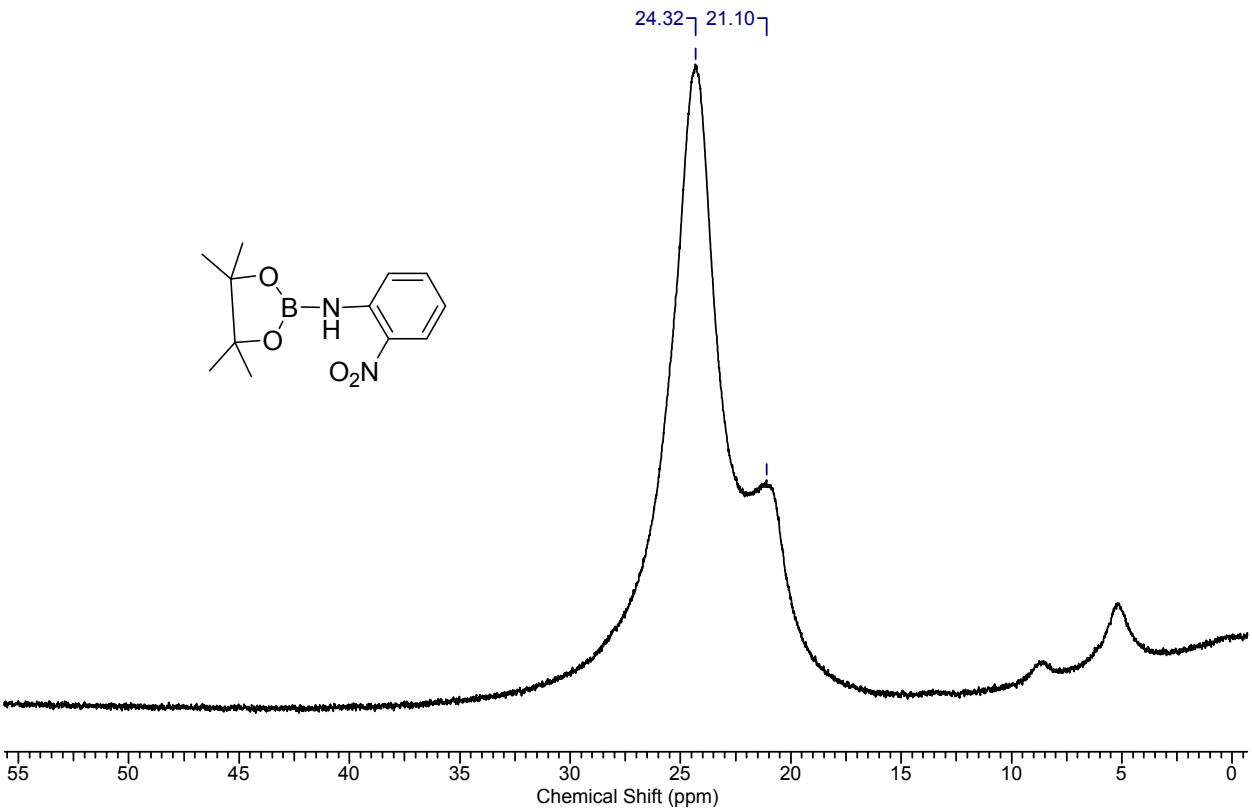
S14.^{11}B NMR spectrum (128.4 MHz, 25°C, $CDCl_3$ of $[C_6H_4FN(H)Bpin]$ (**K**)



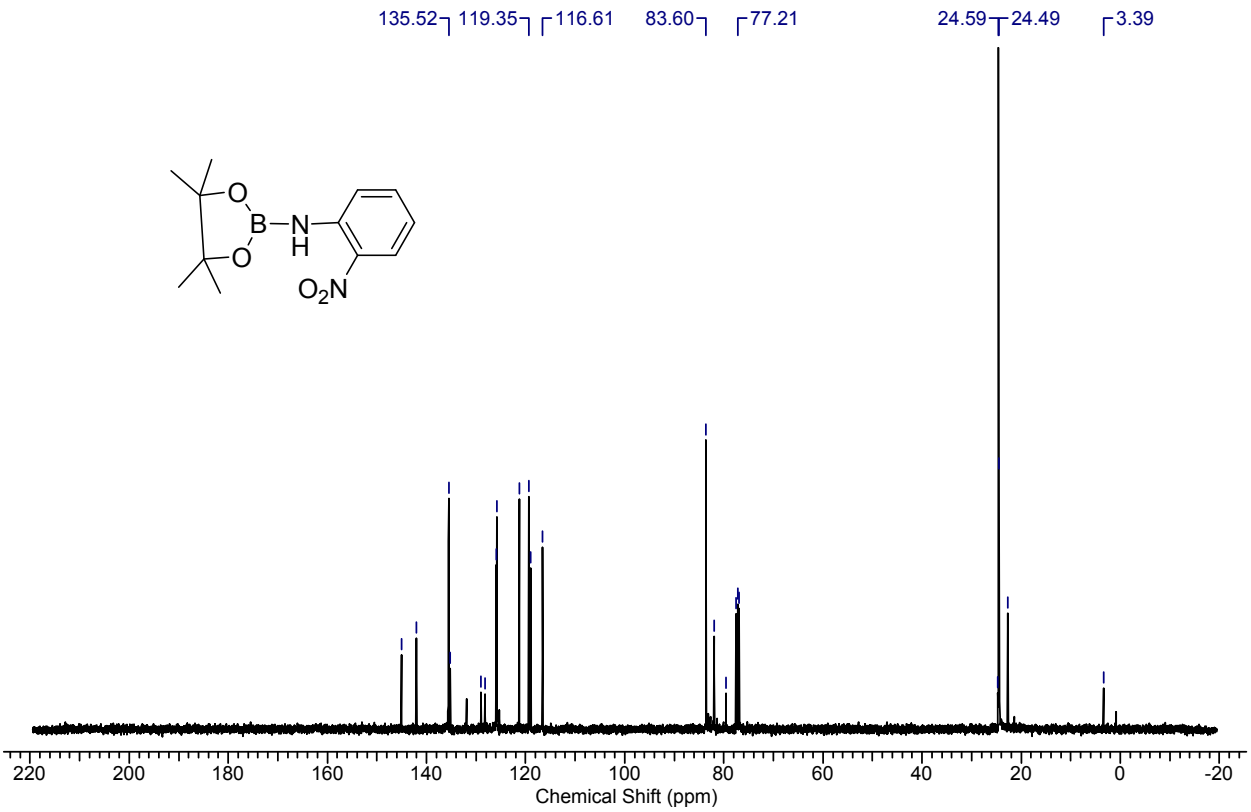
S15.^{13}C NMR spectrum (100 MHz, 25°C, $CDCl_3$ of $[C_6H_4FN(H)Bpin]$ (**K**)



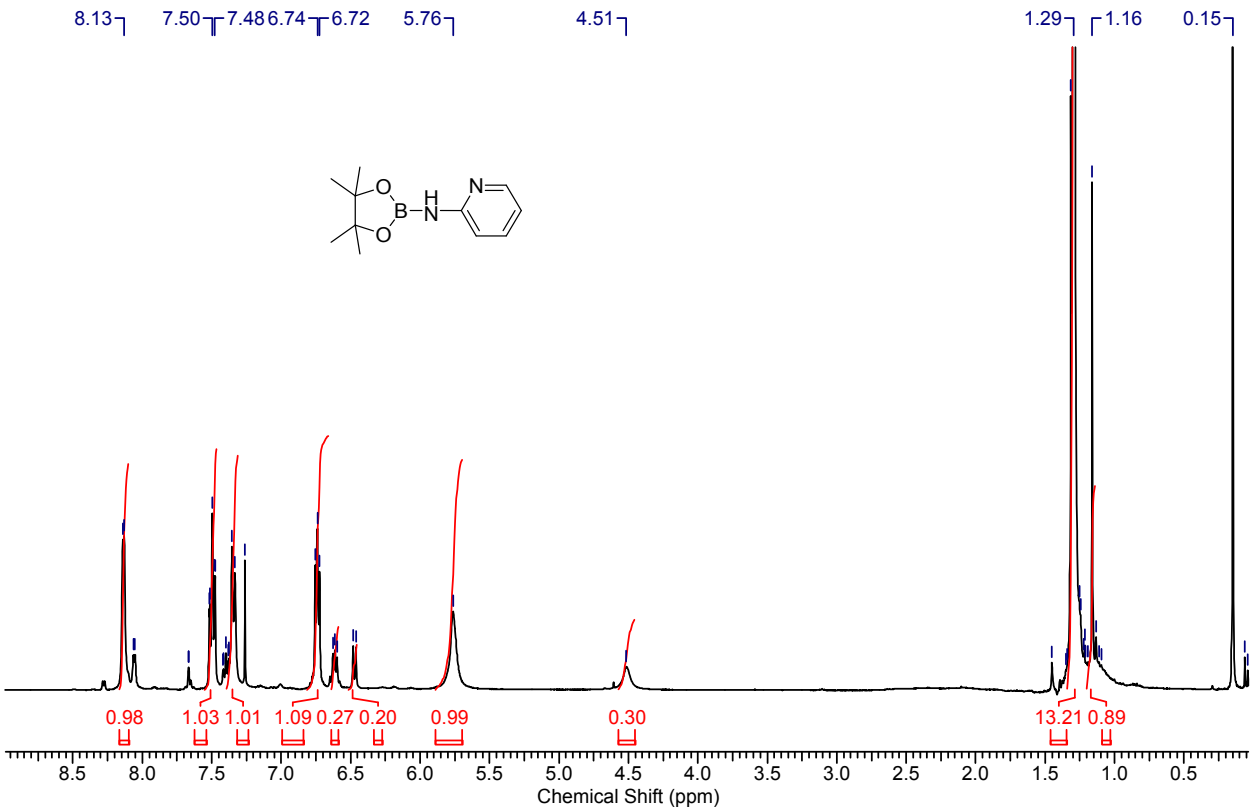
S16. ^{1}H NMR spectrum (400 MHz, 25°C, $CDCl_3$) of $[C_6H_4NO_2N(H)Bpin]$ (**L**)



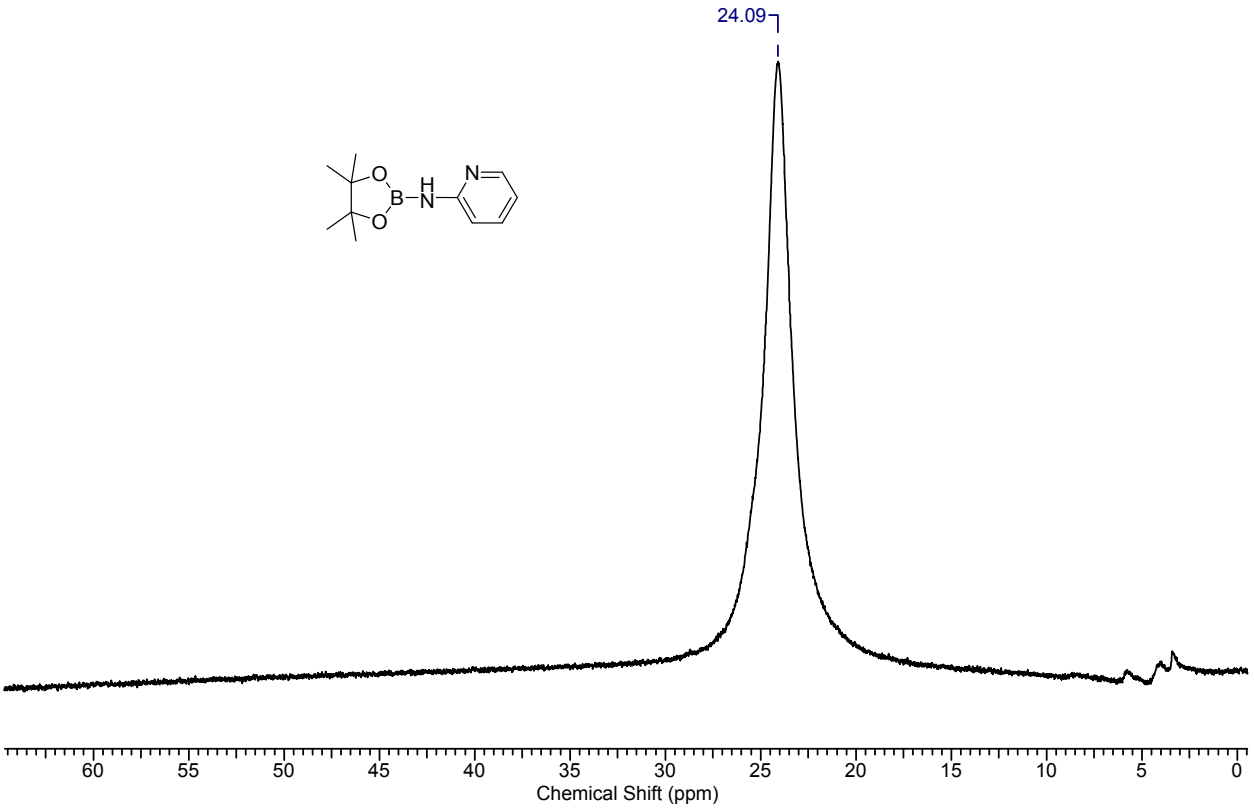
S17.^{11}B NMR spectrum (128.4 MHz, 25°C, $CDCl_3$ of $[C_6H_4NO_2N(H)Bpin]$ (**L**)



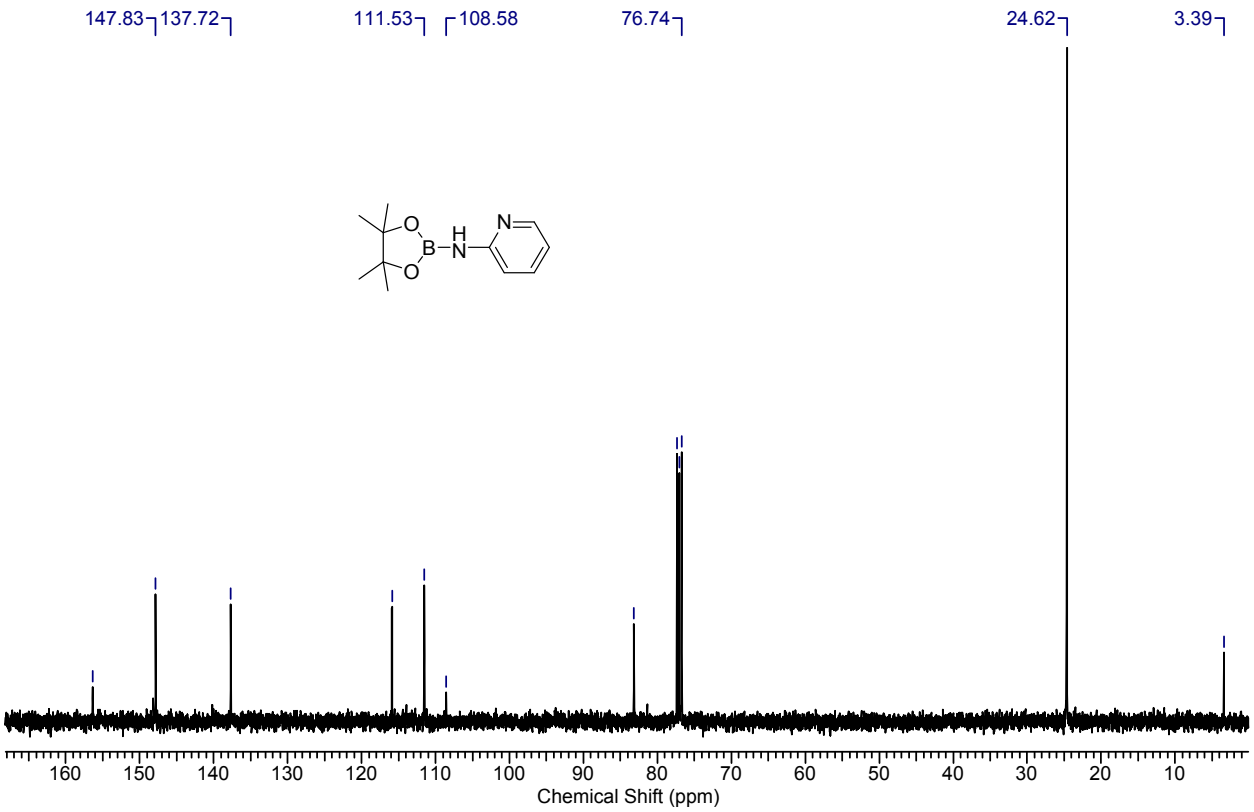
S18. ^{13}C NMR spectrum (100 MHz, 25°C, $CDCl_3$ of $[C_6H_4NO_2N(H)Bpin]$ (**L**)



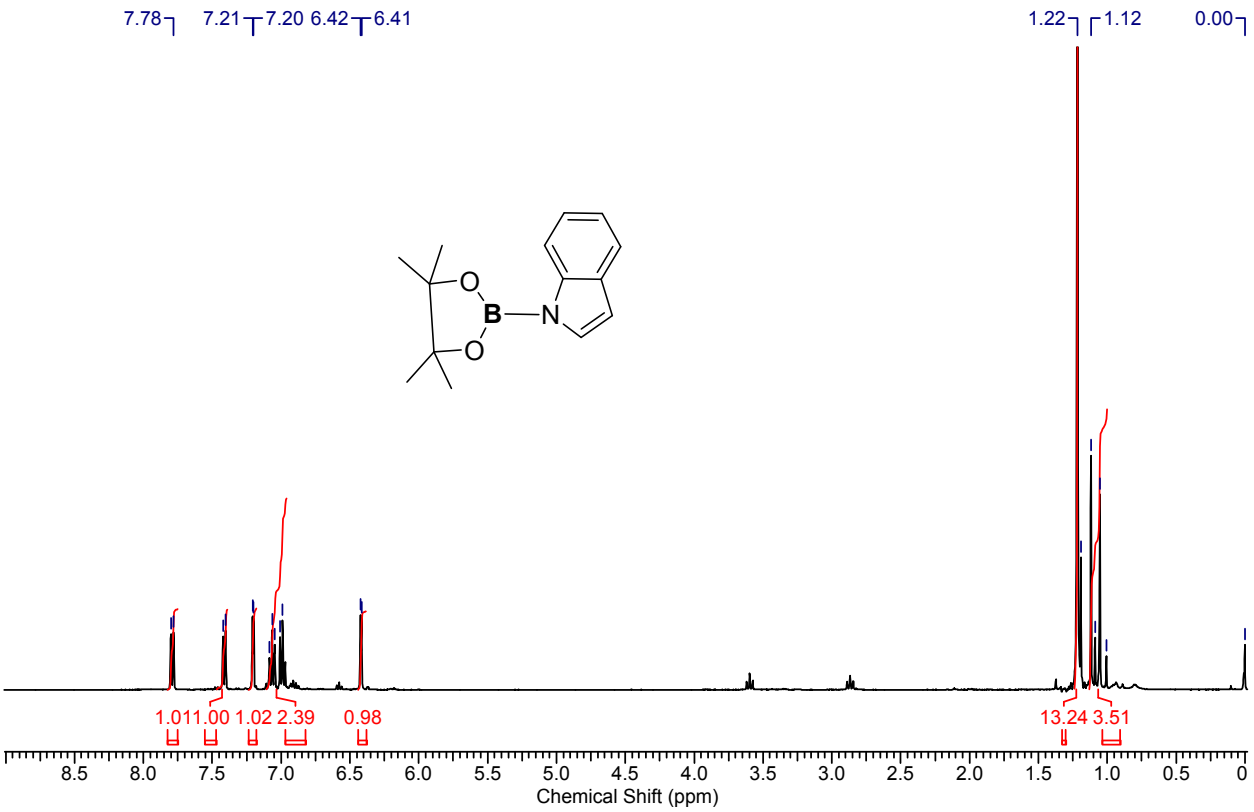
S19.^{1}H NMR spectrum (400 MHz, 25°C, $CDCl_3$) [$C_5H_4N_2$(H)Bpin] (**M**)



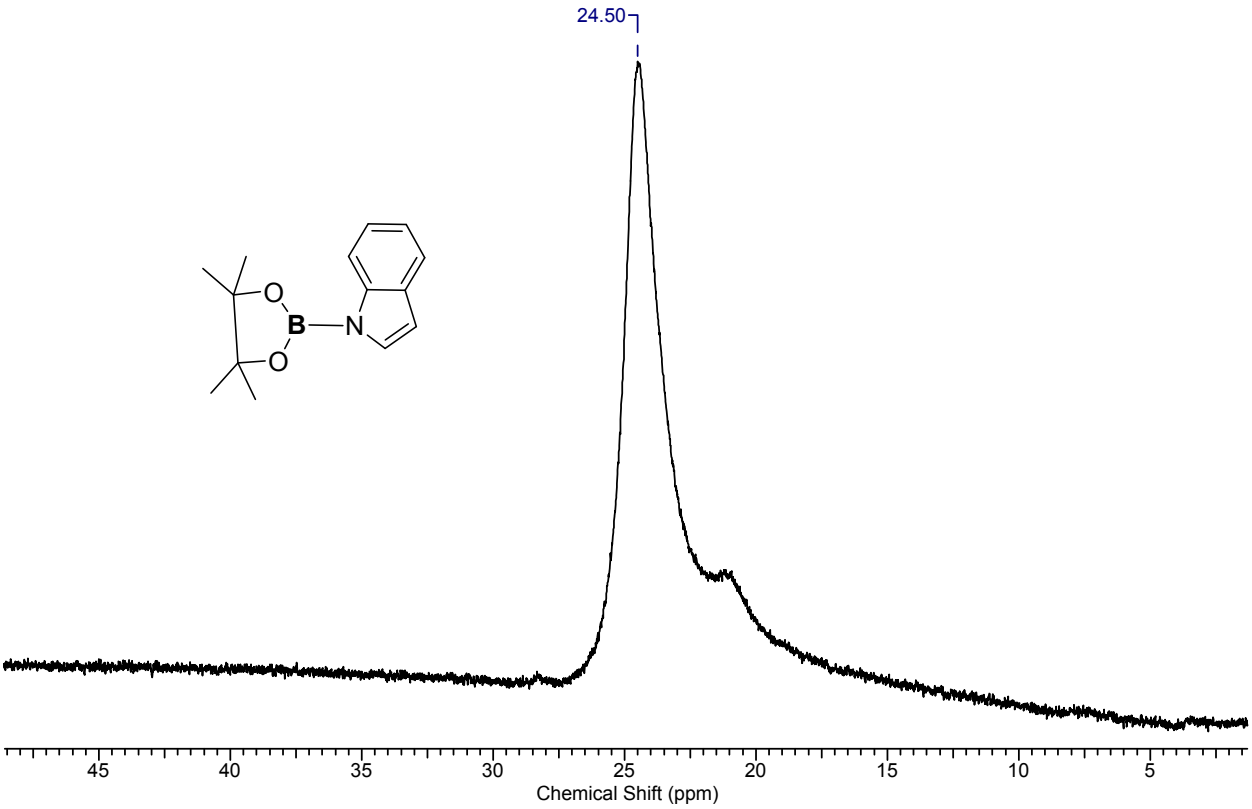
S20. ^{11}B NMR spectrum (128.4 MHz, 25°C, $CDCl_3$) of $[C_5H_4N_2(H)Bpin]$ (**M**)



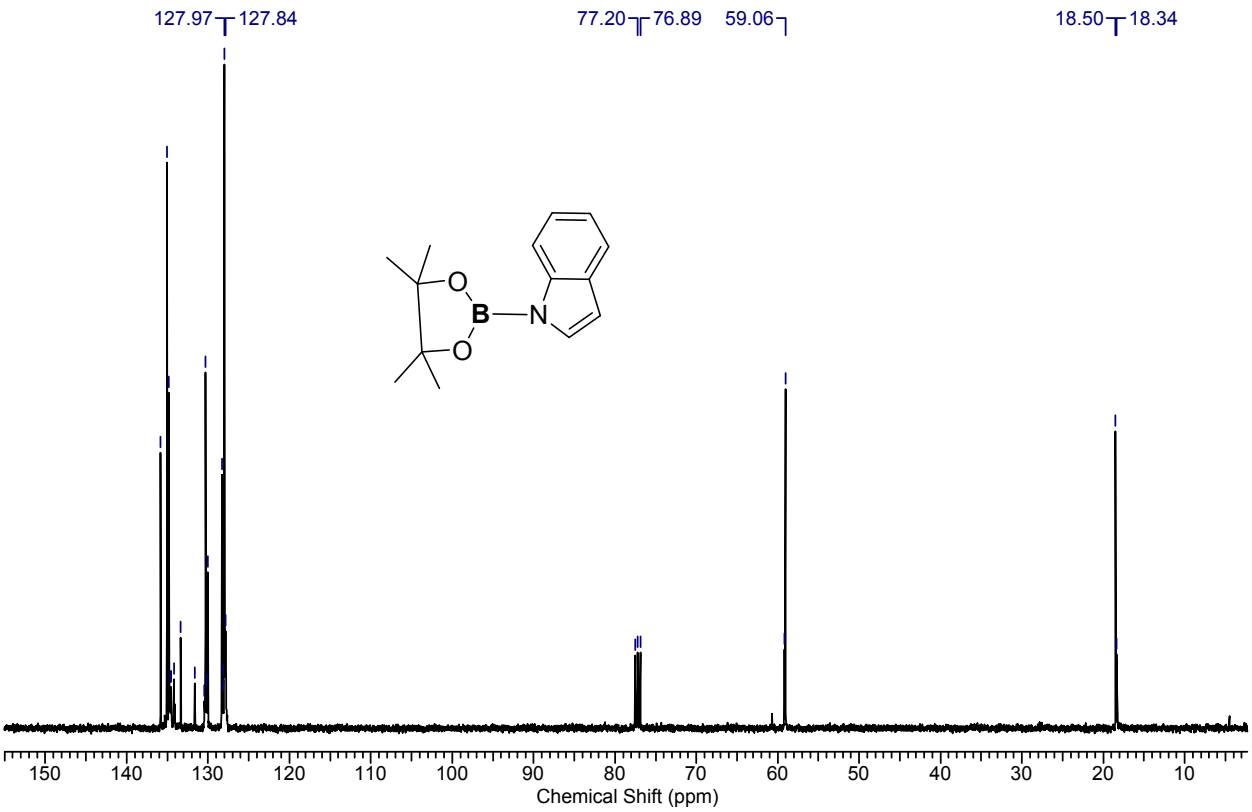
S21. ^{13}C NMR spectrum (100 MHz, 25°C, $CDCl_3$ of $[C_5H_4N_2(H)Bpin]$ (**M**)



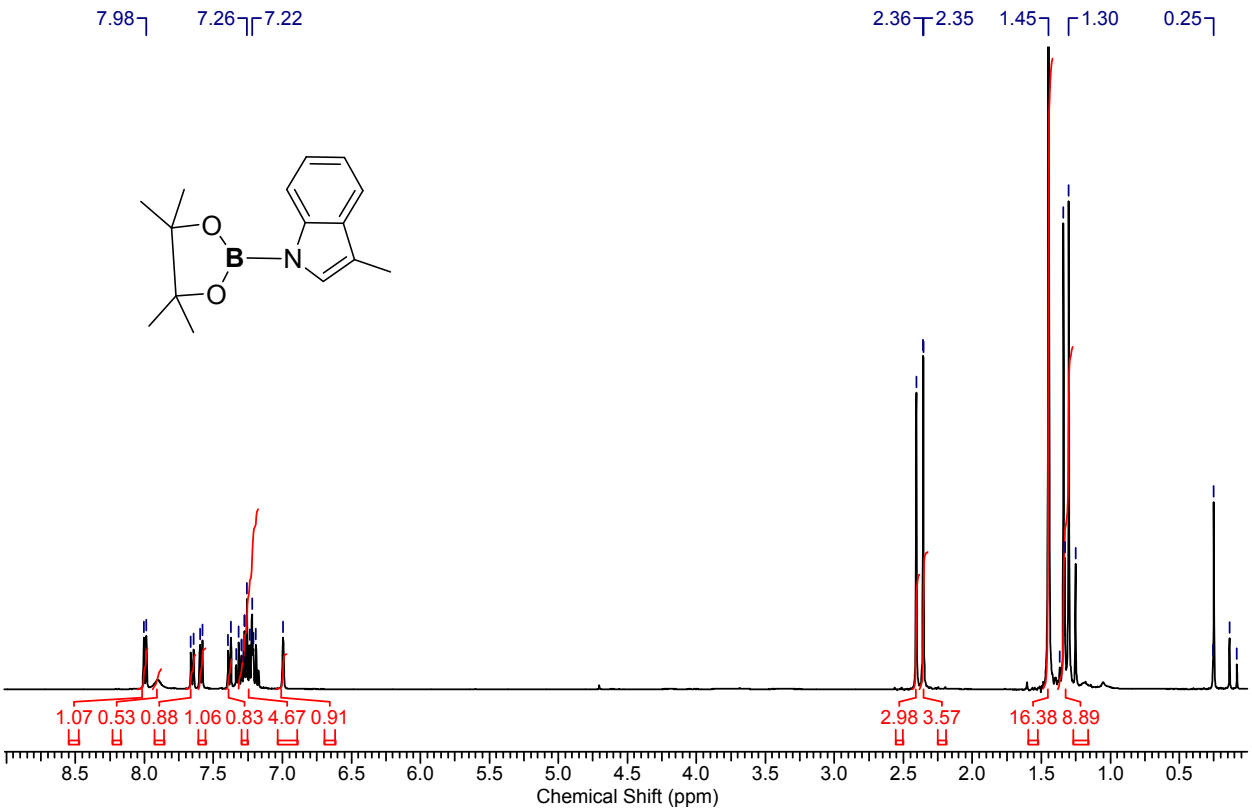
S22. ^{1}H NMR spectrum (400 MHz, 25°C, $CDCl_3$) of [C_8H_6NBpin] (**N**)



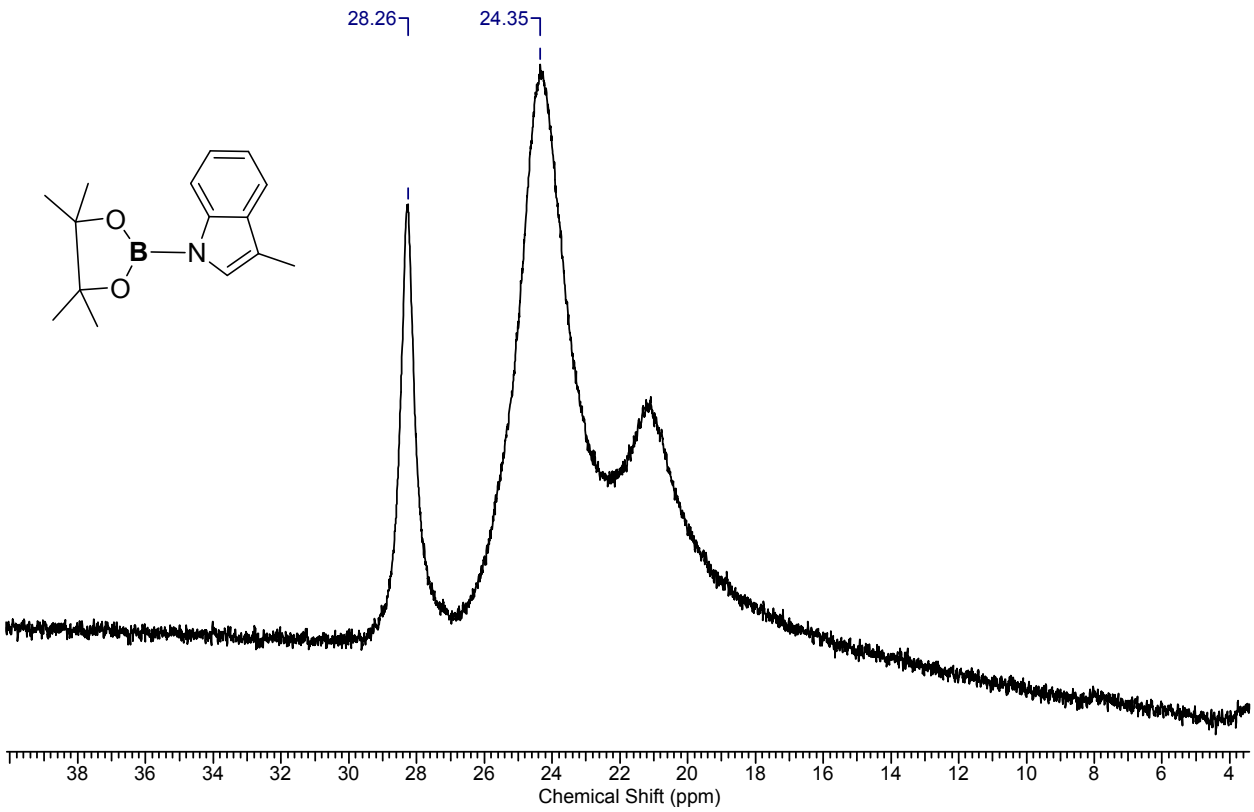
S23.^{11}B NMR spectrum (128.4 MHz, 25°C, $CDCl_3$ of [C_8H_6NBpin] (**N**)



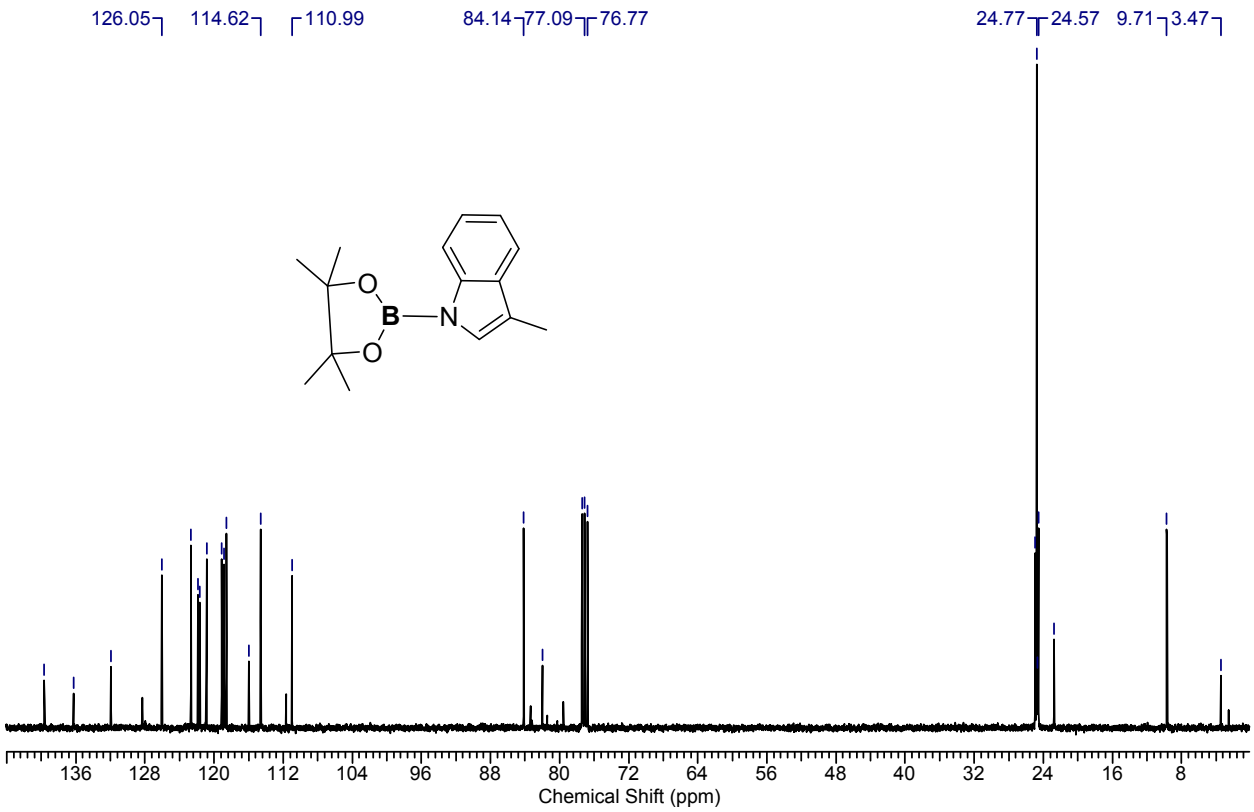
S24.^{13}C NMR spectrum (100 MHz, 25°C, $CDCl_3$ of $[C_8H_6NBpin]$ (**N**)



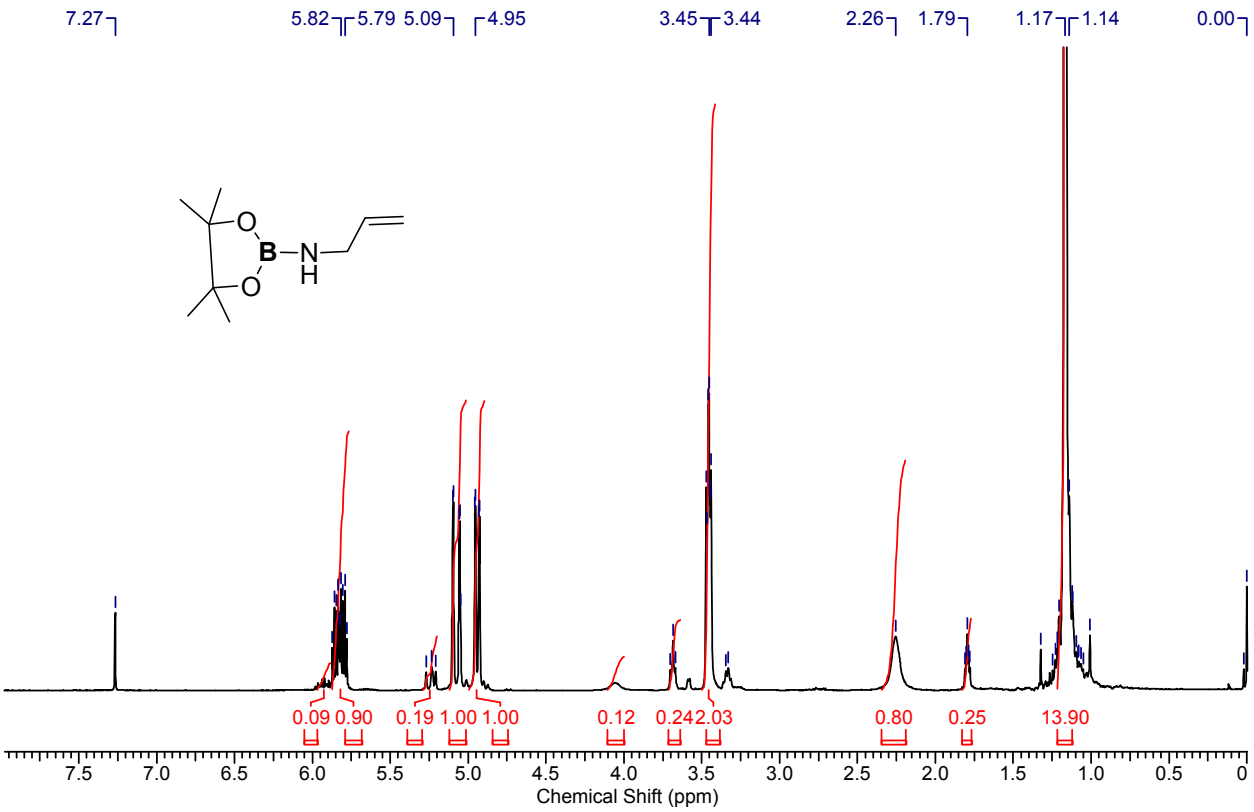
S25.^{1}H NMR spectrum (400 MHz, 25°C, $CDCl_3$) of [C_8H_8NBpin] (**O**)



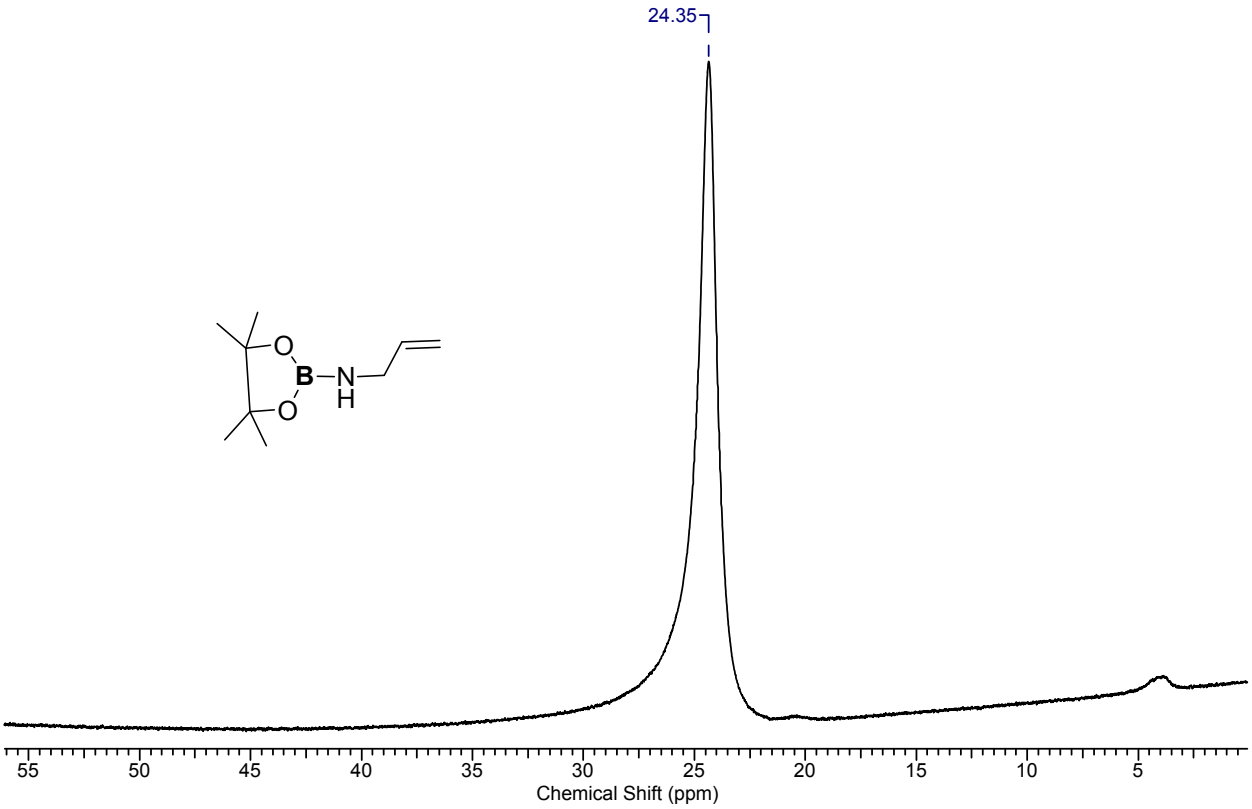
S26.^{11}B NMR spectrum (128.4 MHz, 25°C, $CDCl_3$ of [C_8H_8NBpin] (**O**)



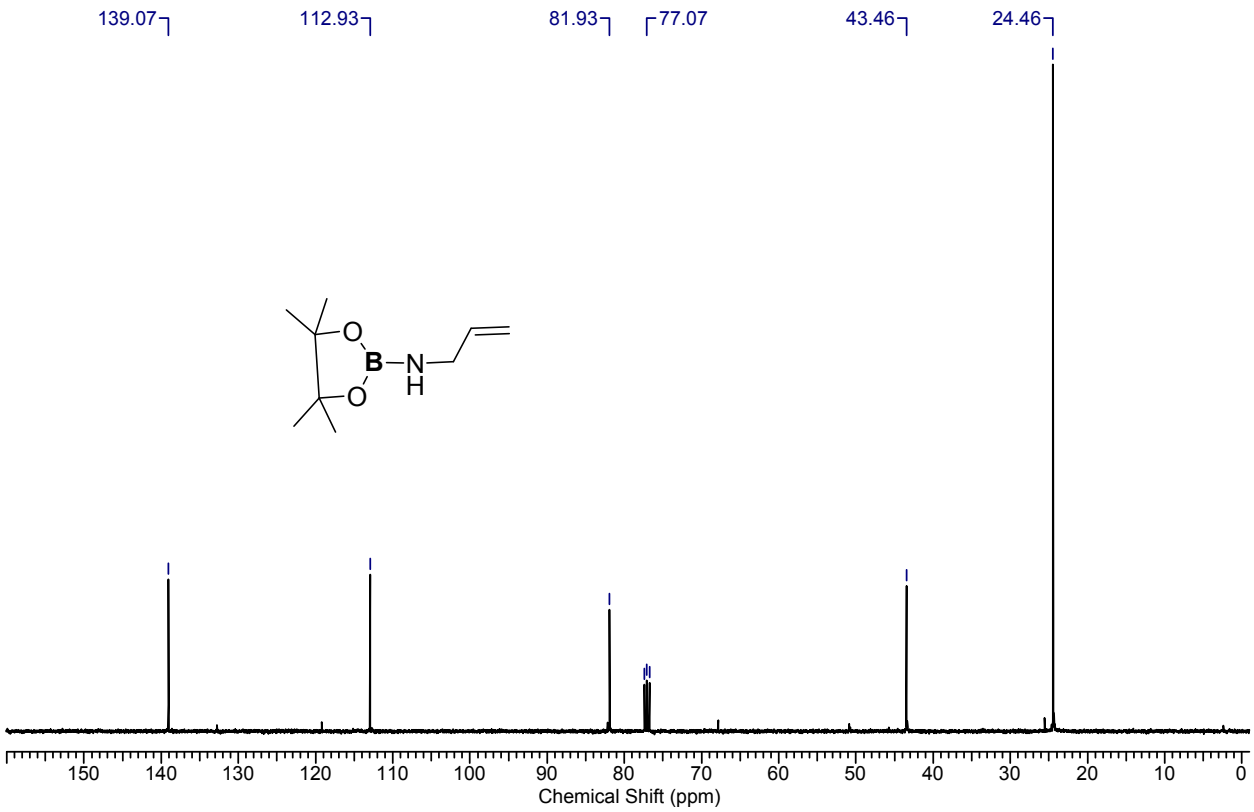
S27.^{13}C NMR spectrum (100 MHz, 25°C, $CDCl_3$ of [C_8H_8NBpin] (**O**)



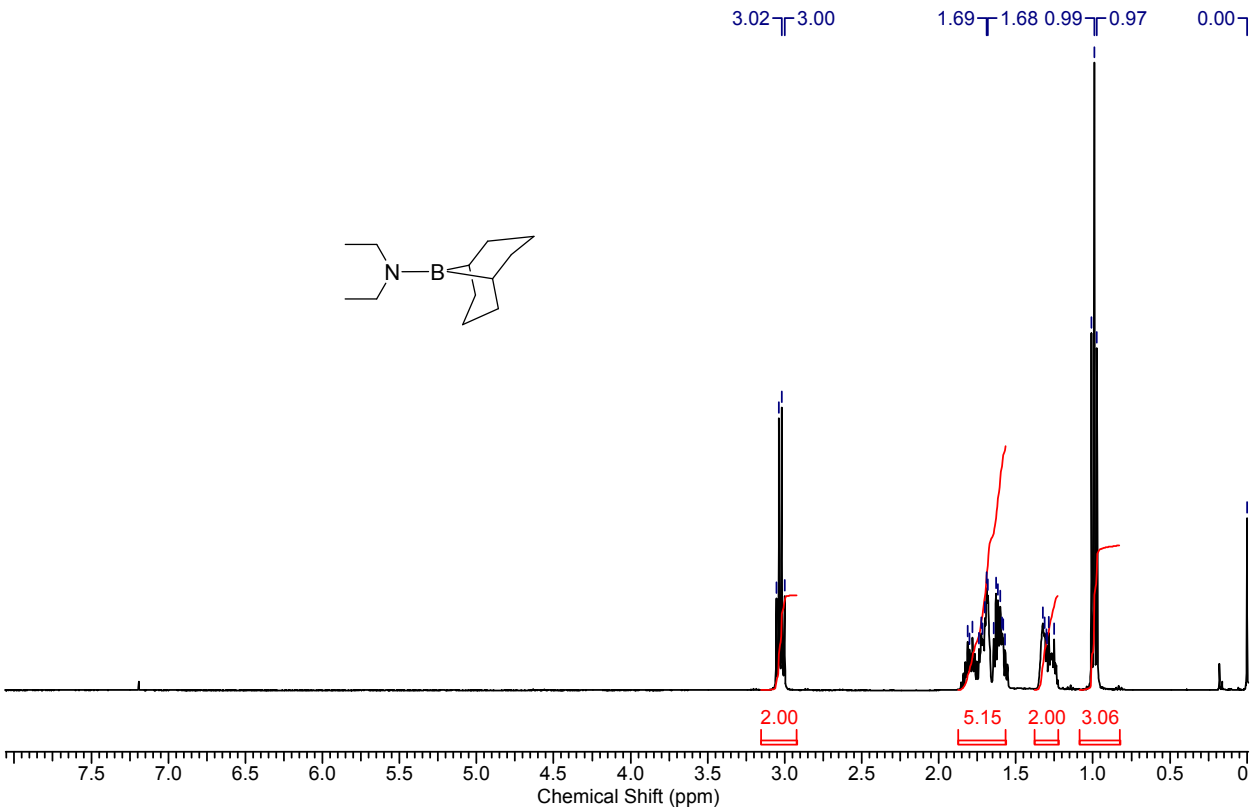
S28.[1]H NMR spectrum (400 MHz, 25°C, $CDCl_3$) of $[C_3H_5N(H)Bpin]$ (**P**)



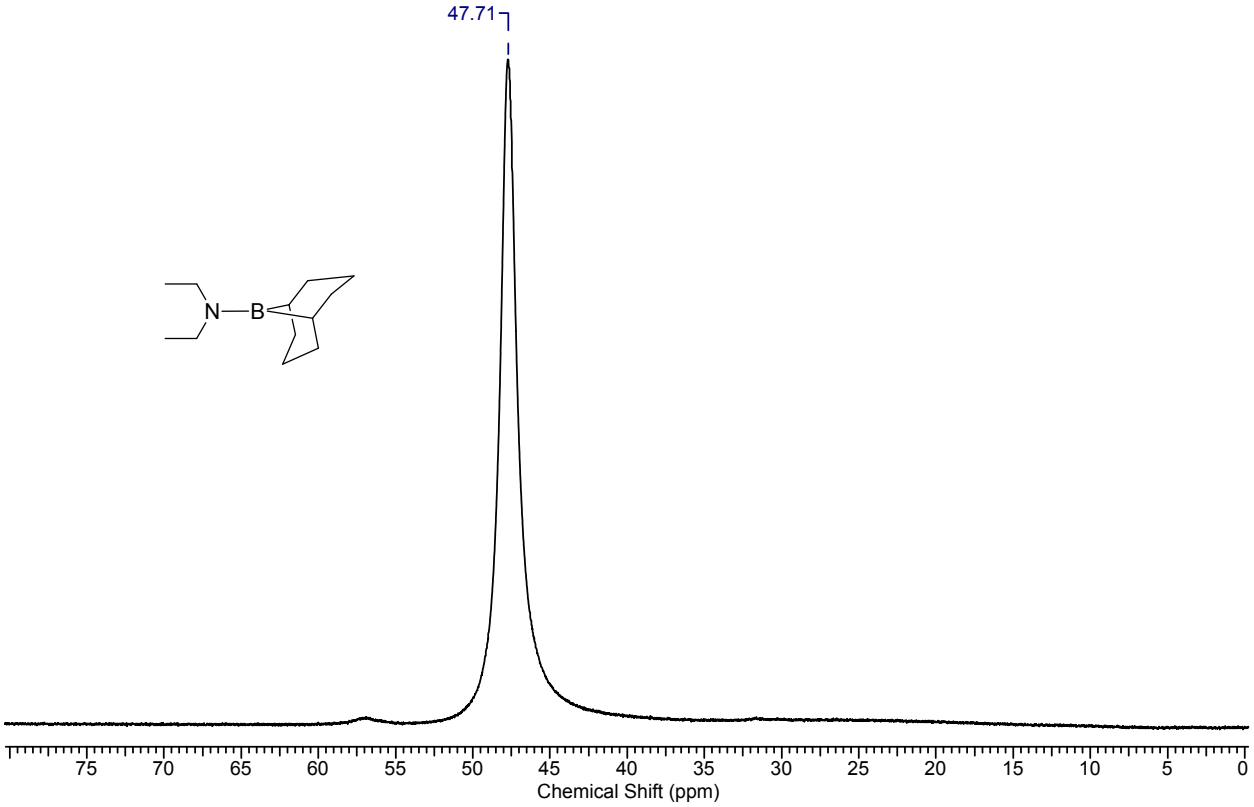
S29.^{11}B NMR spectrum (128.4 MHz, 25°C, $CDCl_3$ of $[C_3H_5N(H)Bpin]$ (**P**)



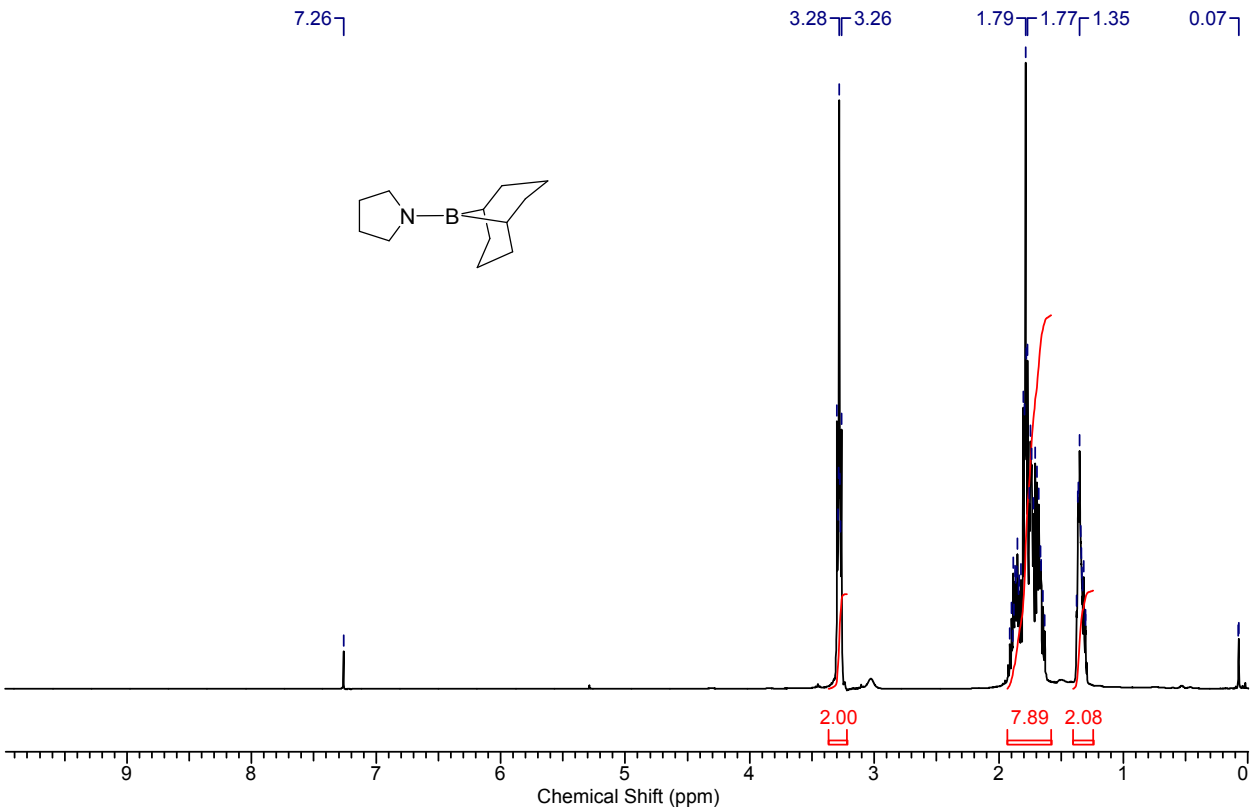
S30. ^{13}C NMR spectrum (100 MHz, 25°C, $CDCl_3$ of $[C_3H_5N(H)Bpin]$ (**P**)



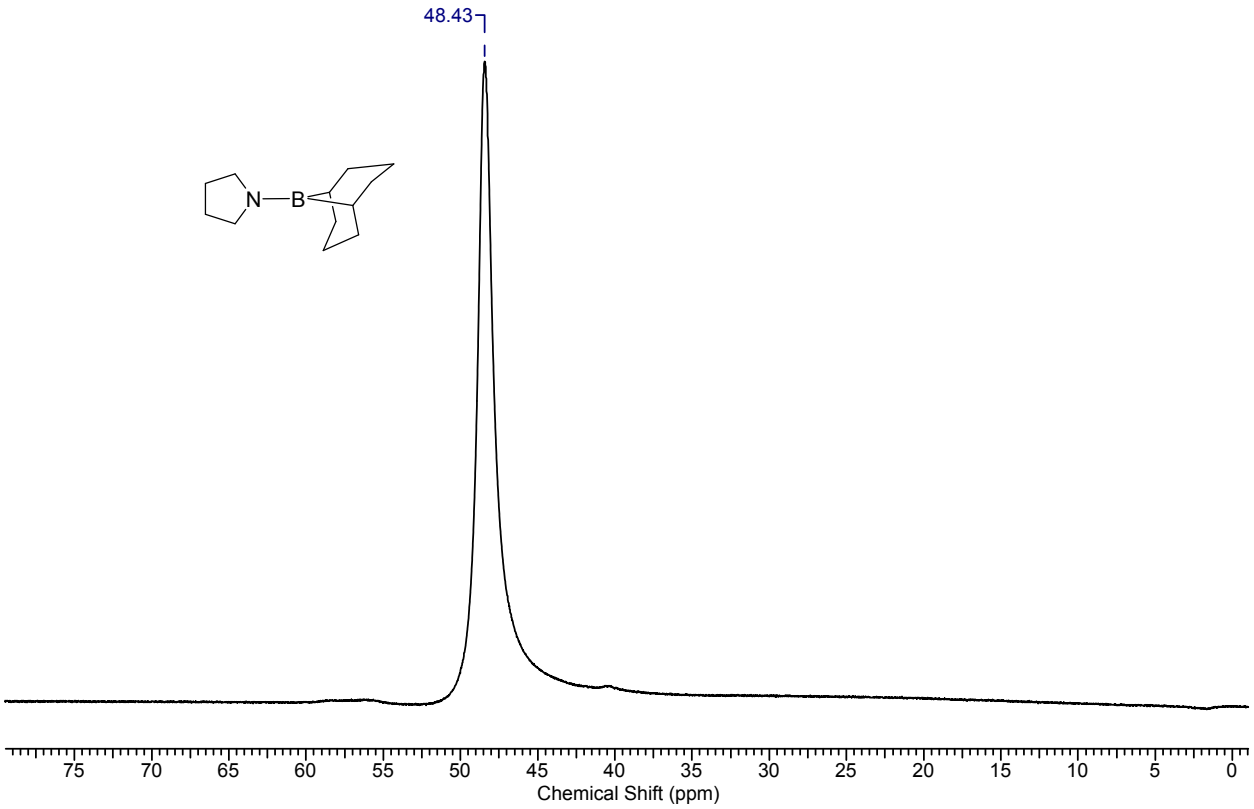
S31.^{1}H NMR spectrum (400 MHz, 25°C, $CDCl_3$) of $[(CH_3)_2NBR_2]$ (**Q**)



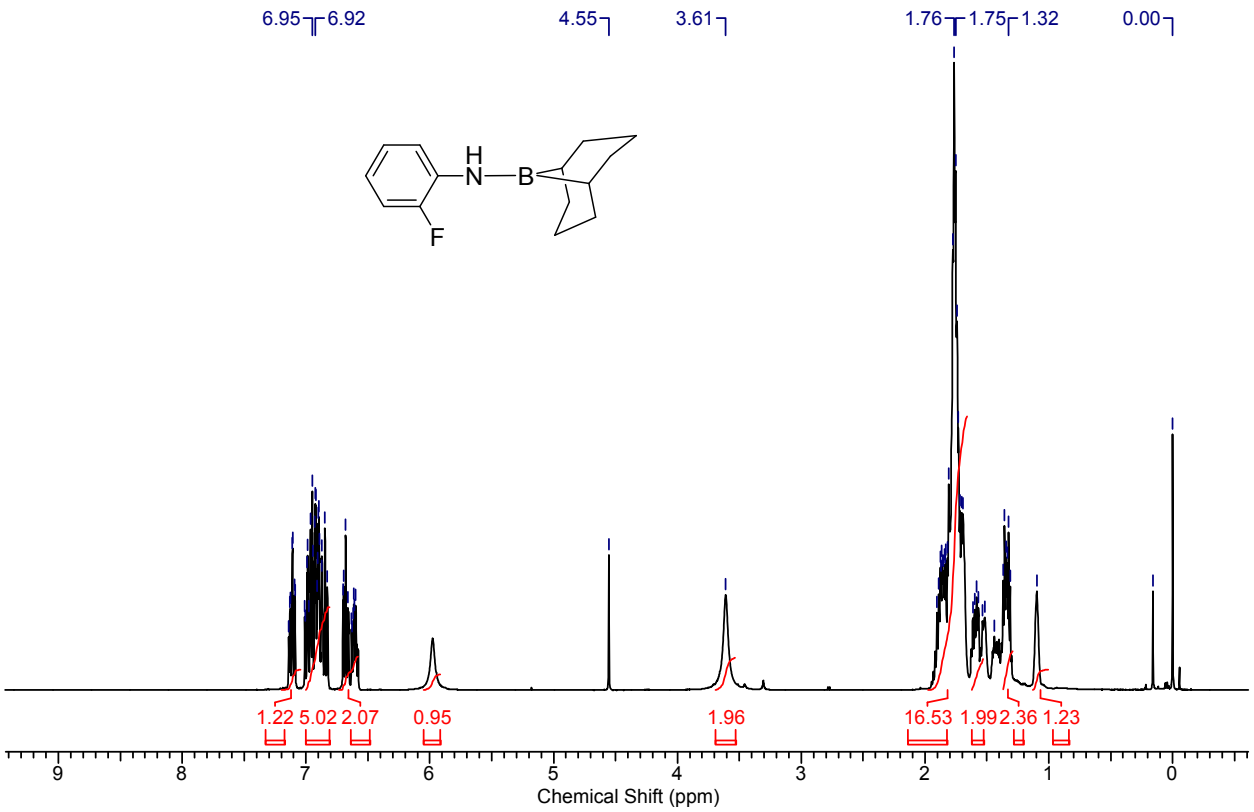
S32.^{11}B NMR spectrum (128.4 MHz, 25°C, $CDCl_3$) of $[(CH_3)_2NBR_2]$ (**Q**)



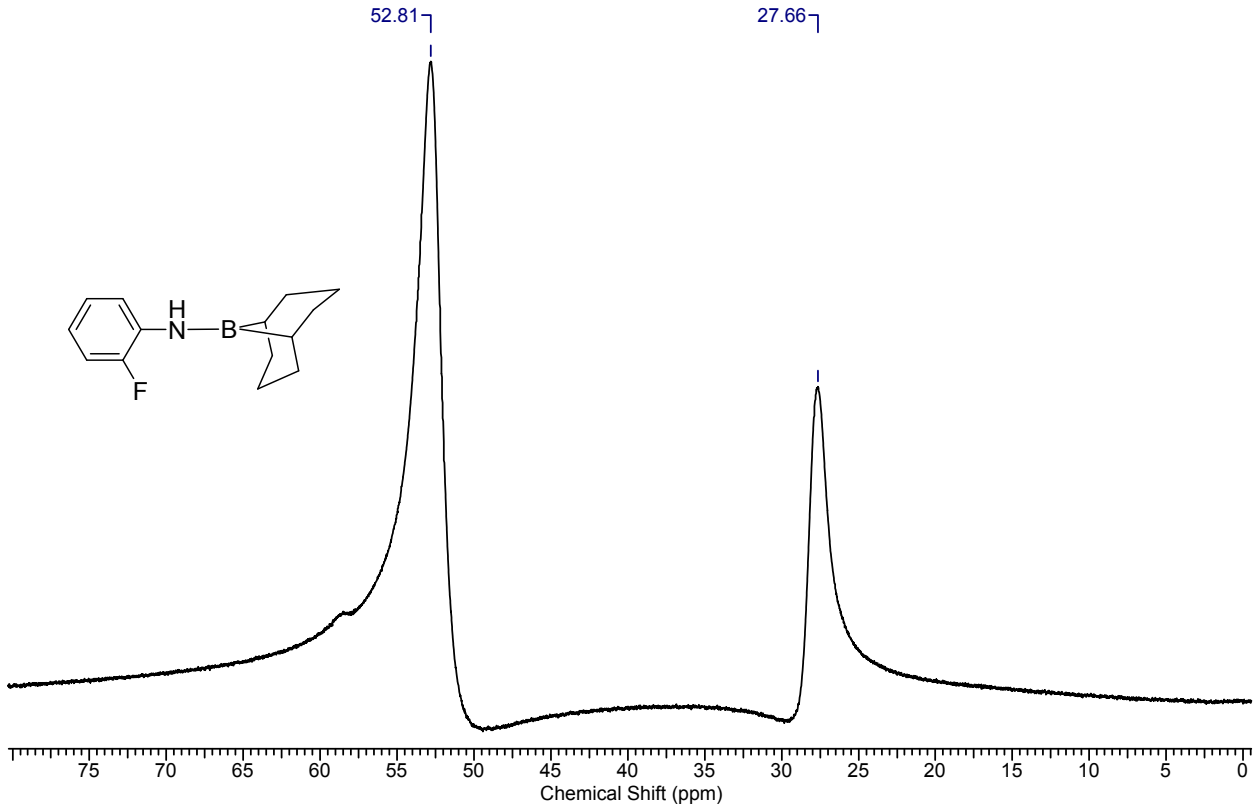
S33.^{1}H NMR spectrum (400 MHz, 25°C, $CDCl_3$) of $[(CH_2)_4NBR_2]$ (**R**)



S34. ^{11}B NMR spectrum (128.4 MHz, 25°C, $CDCl_3$) of $[(CH_2)_4NBR_2]$ (**R**)



S35.^{1}H NMR spectrum (400 MHz, 25°C, $CDCl_3$) of $[C_6H_4FN(H)BR_2]$ (**U**)



S36.^{11}B NMR spectrum (128.4 MHz, 25°C, $CDCl_3$) of $[C_6H_4FN(H)BR_2]$ (**U**)