

SUPPLEMENTARY INFORMATION:

Nucleophilic displacement of ammonia from ammonia borane for the preparation of alkylamine-, pyridine- and phosphine-boranes

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General information:

Unless otherwise noted, all manipulations were carried out under inert atmosphere in flame-dried glassware, cooled under nitrogen. All solvents were distilled prior to use, unless otherwise noted: Diethyl ether (Et₂O) and Tetrahydrofuran (THF) from Na/Benzophenone. ¹¹B NMR spectra were recorded at room temperature, on a Varian INOVA 300 MHz NMR spectrophotometer. Chemical shifts (δ values) are reported in parts per million and are referenced to BF₃·Et₂O. Data are reported as: δ value, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, p=pentet, h=hextet, m=multiplet, br=broad) and integration. All amines and phosphines were purchased from commercial sources. The liquid amines were freshly distilled before use; however the solid amines and phosphines were used as such.

Optimization of reaction temperature for trans-amination of ammonia borane (1) with *N,N,N*-triethylamine (**2a**):

entry	solvent	temperature	reaction completion (¹¹ B NMR)	
			4 h	19 h
1	Ether	Reflux	26%	70%
2	THF	40°C	9%	28%
3	THF	50°C	28%	60%
4	THF	60°C	53%	85%
5*	THF	Reflux	98%	100%

*The reaction was complete in 6hrs.

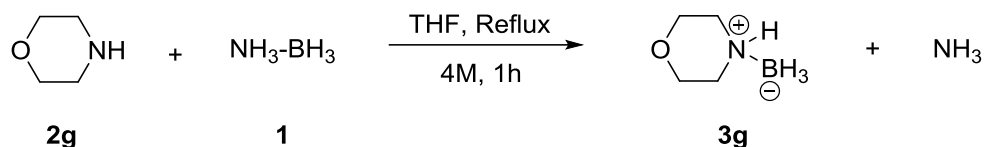
Kinetics studies for trans-amination of ammonia borane (1) with *N,N,N*-triethylamine (**2a**):

entry	amine (equiv)	reaction completion (¹¹ B NMR)						
		30 min	60 min	120 min	180 min	255 min	315 min	390 min
1	1	40%	61%	84%	92%	98%	99%	100%
2	2	62%	81%	97%	100%	-	-	-
3	4	84%	97%	100%	-	-	-	-

Plotting the inverse of concentration against time gave a linear curve suggesting an S_N2B mechanism.

Representative procedure for trans-amination:

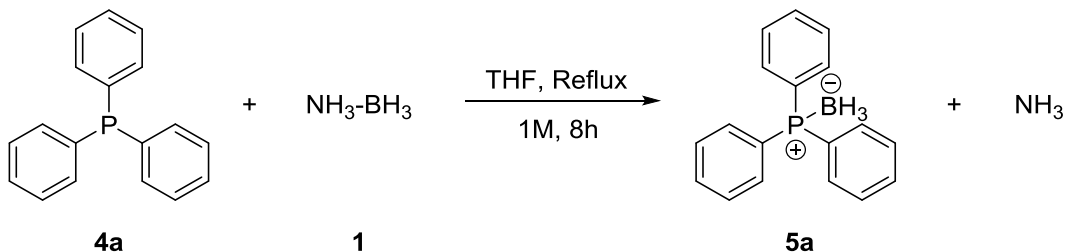
Preparation of morpholine-borane (**3g**):



Ammonia-borane (**1**, 0.31 gms, 10 mmol) was weighed and transferred to a 25 mL oven-dried round bottom flask, fitted with a water cooled reflux condenser. The flask was flushed with a stream of nitrogen and charged with anhydrous THF (2.5 mL) using syringe techniques.¹ The solution was stirred and morpholine (**2g**, 0.865 mL, 10 mmol) was added dropwise to the solution at room temperature. The reaction mixture was then refluxed and the progress was monitored by ¹¹B NMR spectroscopy. Upon completion of the reaction (1 h), the solution was cooled to room temperature and cannulated into another clean 25 mL oven dried round bottom flask. The solvent was removed under reduced pressure to obtain pure morpholine-borane as a white solid (**3g**, 0.98 gms, 97%). ¹¹B NMR (96 MHz, THF) δ (ppm): -14.8 (q, $J = 96$ Hz), mp 95-97 °C (lit. 93-95 °C).²

Representative procedure for phosphination:

Preparation of triphenylphosphine-borane (**5a**):



Ammonia-borane (**1**, 0.31gms, 10 mmol) and triphenylphosphine (**4a**, 2.62gms, 10 mmol) were weighed and transferred to a 50 mL oven dried round bottom flask fitted with a water cooled reflux condensor. The flask was flushed with a stream of nitrogen and charged with anhydrous THF (10 mL) using syringe techniques. The reaction mixture was stirred and brought to reflux. Reaction progress was monitored by ¹¹B NMR spectroscopy. Upon completion (8 h), the

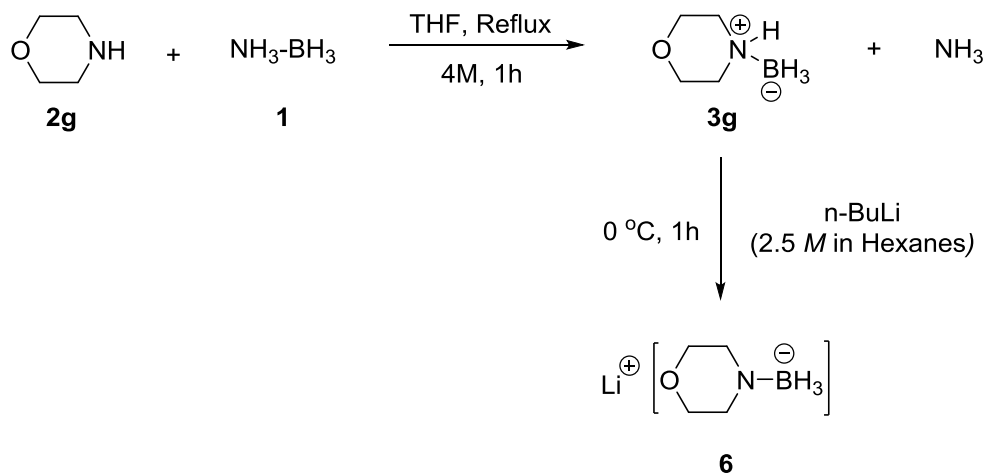
¹ H. C. Brown, *Organic Syntheses Via Boranes*, Wiley, New York, **1975**.

² Brown, H. C.; Murray, L. T. *Inorg. Chem.* **1984**, 23, 2746.

solution was cooled to room temperature and the solvent was evaporated under reduced pressure to obtain pure triphenylphosphine-borane as a white solid (**5a**, 2.65 gms, 96%). ^{11}B NMR (96 MHz, THF) δ (ppm): -38.1 (m). mp 187–189 °C (lit. 189-191 °C).³

Representative procedure for the one-pot preparation of lithium aminoborohydride:

Preparation of lithium morpholinoborohydride:



Ammonia-borane (**1**, 3.1gms, 100 mmol) was weighed and transferred to a 250 mL oven-dried round bottom flask fitted with a water cooled reflux condensor. The flask was flushed with a stream of nitrogen and charged with anhydrous THF (100 mL) using syringe techniques. The solution was stirred and morpholine (**2g**, 8.65 mL, 100 mmol) was added dropwise to the solution at room temperature. The reaction mixture was refluxed and the reaction progress was monitored by ^{11}B NMR. Upon complete trans-amination (1 h), the solution was cooled to room temperature and was charged, dropwise over a 30 min period at 0 °C, with n-butyllithium (2.5 M, 40 mL, 100 mmol) using a cannula. The reaction was stirred at 0 °C for 1 h and then allowed to warm to room temperature. The reaction mixture was stirred for an additional 1 h at 25 °C to afford lithium morpholinoborohydride (**6**), which was used as such for further reactions. ^{11}B NMR (96 MHz, THF) δ (ppm): -16 (q, J = 85.4 Hz).

³ Brodie, N.; Juge, S. *Inorg. Chem.* **1998**, 37, 2438.

***N,N,N*-triethylamine-borane (3a):**

Colourless Liquid. ^{11}B NMR (96 MHz, THF) δ (ppm): -12.90 (q, $J = 98.0$ Hz), bp 100 °C/12 mmHg (lit. 76 °C/4 torr).⁴

***N*-methylpyrrolidine-borane (3b):**

Colourless Liquid. ^{11}B NMR (96 MHz, THF) δ (ppm): -10.00 (q, $J = 98.0$ Hz).

***N,N*-diethylamine-borane (3d):**

Colourless Liquid. ^{11}B NMR (96 MHz, THF) δ (ppm): -16.64 (q, $J = 96.0$ Hz), bp 89-91 °C/12 mmHg (lit. 84 °C/4 torr).⁵

Piperidine-borane (3e):

White Solid. ^{11}B NMR (96 MHz, THF) δ (ppm): -14.90 (q, $J = 96.0$ Hz), mp 80-82 °C (lit. 81-83 °C).²

Pyrrolidine-borane (3f):

Colourless Liquid. ^{11}B NMR (96 MHz, THF) δ (ppm): -16.50 (q, $J = 95.0$ Hz).

Morpholine-borane (3g):

White Solid. ^{11}B NMR (96 MHz, THF) δ (ppm): -14.85 (q, $J = 96.0$ Hz), mp 93-95 °C (lit. 93-95 °C).²

***N,N*-diisopropylamine-borane (3h):**

Colourless Liquid. ^{11}B NMR (96 MHz, THF) δ (ppm): -21.10 (q, $J = 97.0$ Hz).

1-propanamine-borane (3j):

White Solid. ^{11}B NMR (96 MHz, THF) δ (ppm): -19.60 (q, $J = 95.0$ Hz), mp 44-46 °C (lit. 45 °C).⁵

⁴ Matsumura S.; Tokura, N. *Tetrahedron Lett.* **1968**, 4703.

⁵ Noth, H.; Beyer, H. *Chem. Ber.* **1960**, 93, 928.

Cyclohexylamine-borane (3k):

White Solid. ^{11}B NMR (96 MHz, THF) δ (ppm): -20.89 (q, $J = 95.0$ Hz), mp 96-98 °C (lit. 92-95 °C).⁶

Pyridine-borane (3l):

Colourless Liquid. ^{11}B NMR (96 MHz, THF) δ (ppm): -11.62 (q, $J = 99.0$ Hz).

Triphenylphosphine-borane (5a):

White solid. ^{11}B NMR (96 MHz, THF) δ (ppm): -38.1 (m), mp 187–189 °C (lit. 189-191 °C).³

Tricyclohexylphosphine-borane (5b):

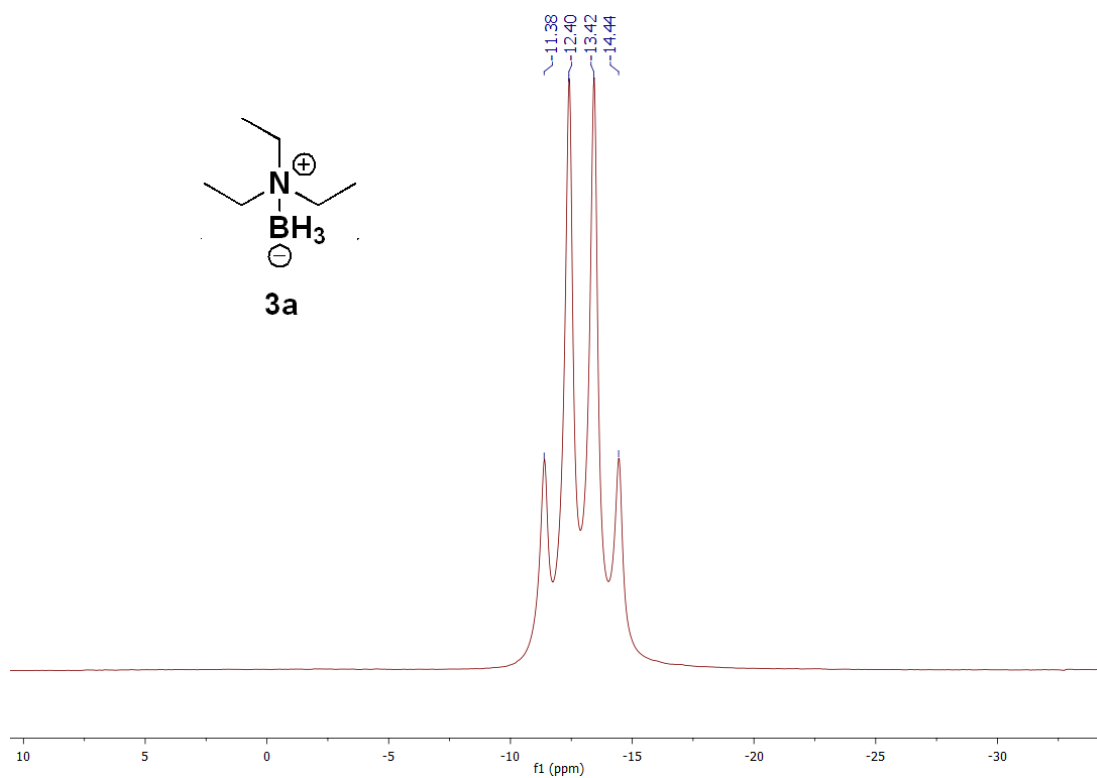
White solid. ^{11}B NMR (96 MHz, THF) δ (ppm): -43.59 (m), mp 177–179 °C (lit. 179 °C).⁷

Diphenylphosphine-borane (5c):

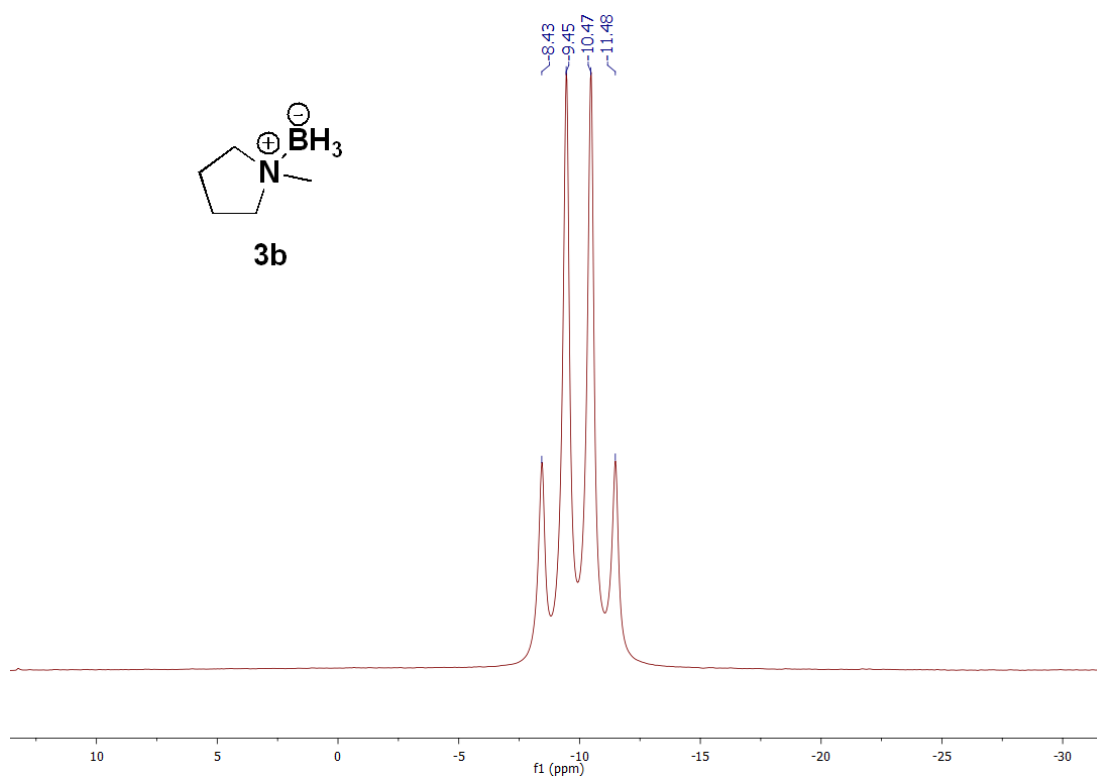
White solid. ^{11}B NMR (96 MHz, THF) δ (ppm): -40.23 (m), mp 45-47 °C (lit. 40 °C).⁷

⁶ Bragdon, R. W. (Metal Hydrides Inc.). Preparation of amine boranes, US Patent 2,927,133, **1960**.

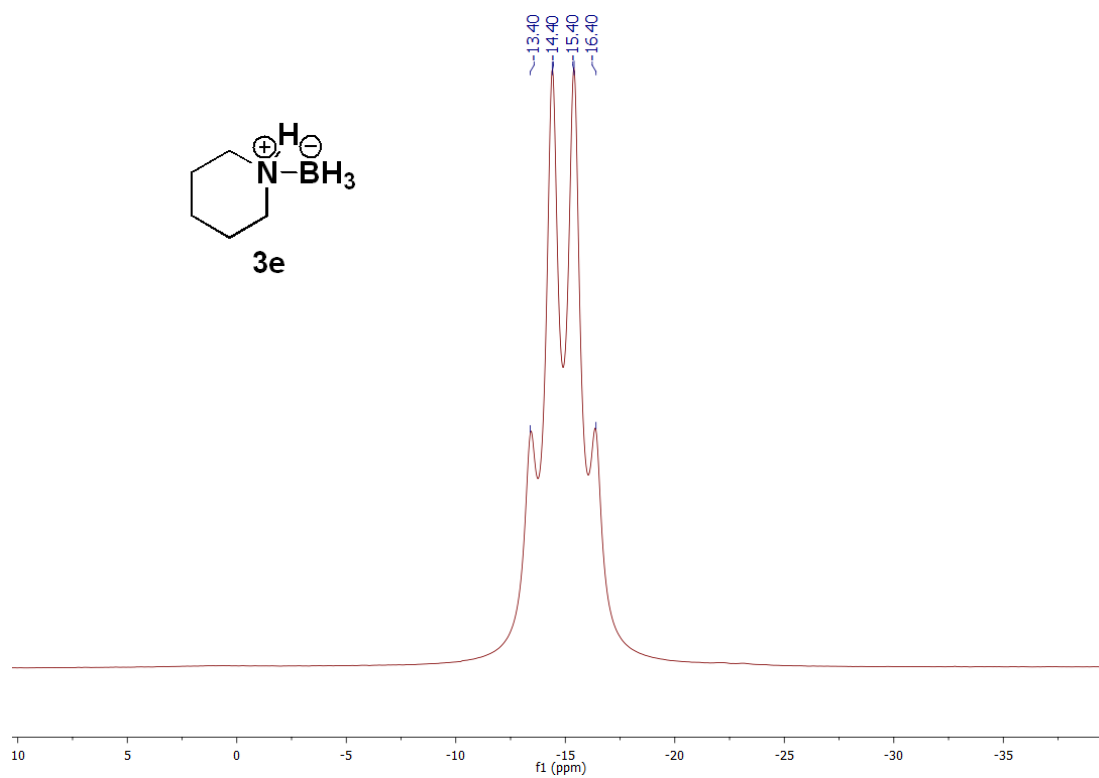
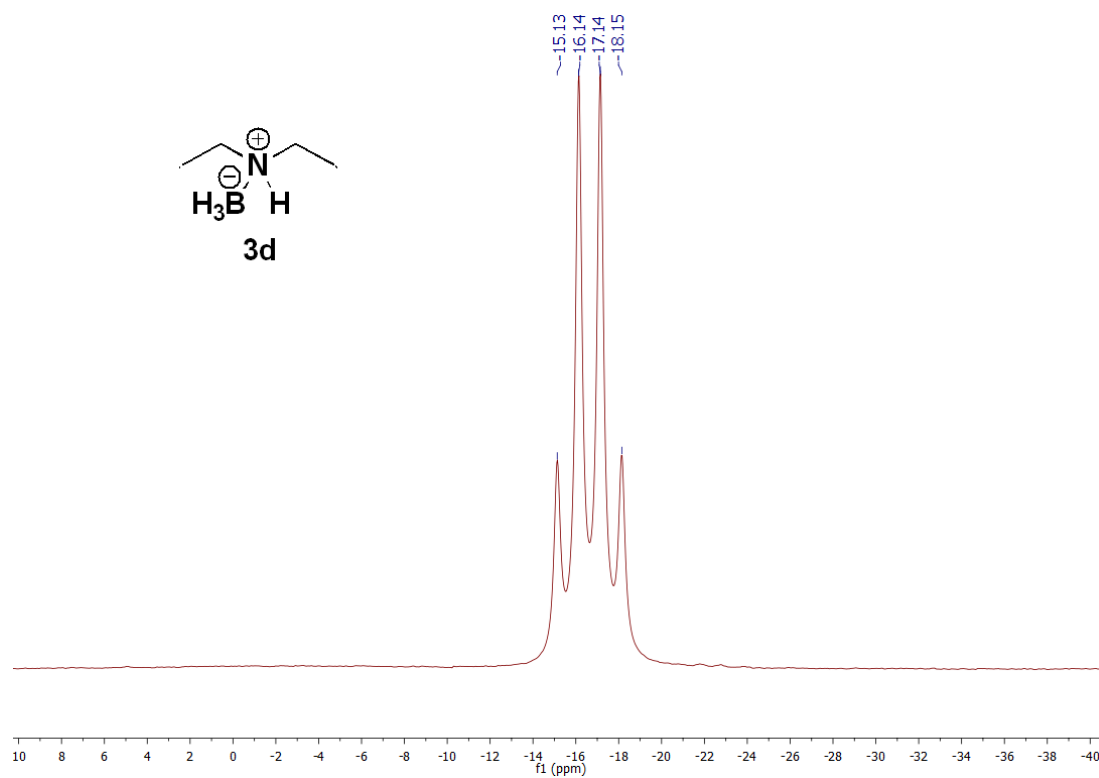
⁷ Cogen, S.; Van Overschelde, M.; Van der Eycken, J.; Vervecken, E.; Modha, S. G.; Van der Eycken, E. *Tetrahedron* **2009**, 65, 6410.

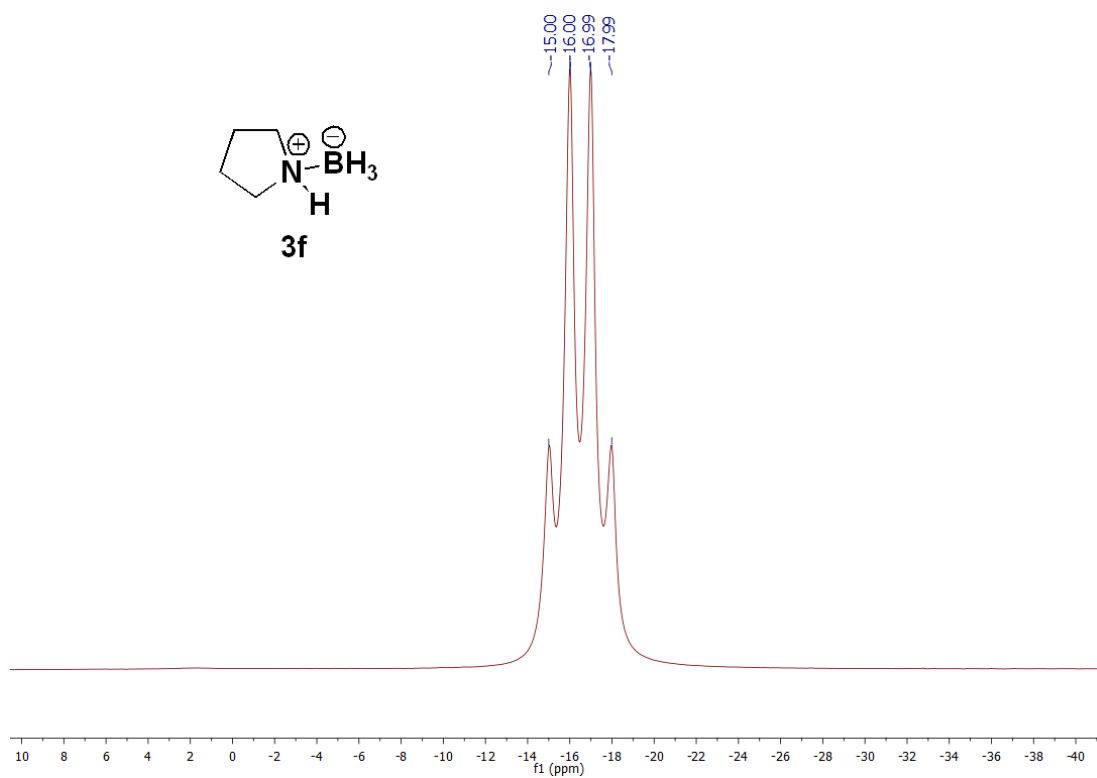


^{11}B NMR (96 MHz, THF) *N,N,N*-triethylamine-borane (Table 3, Entry 2)

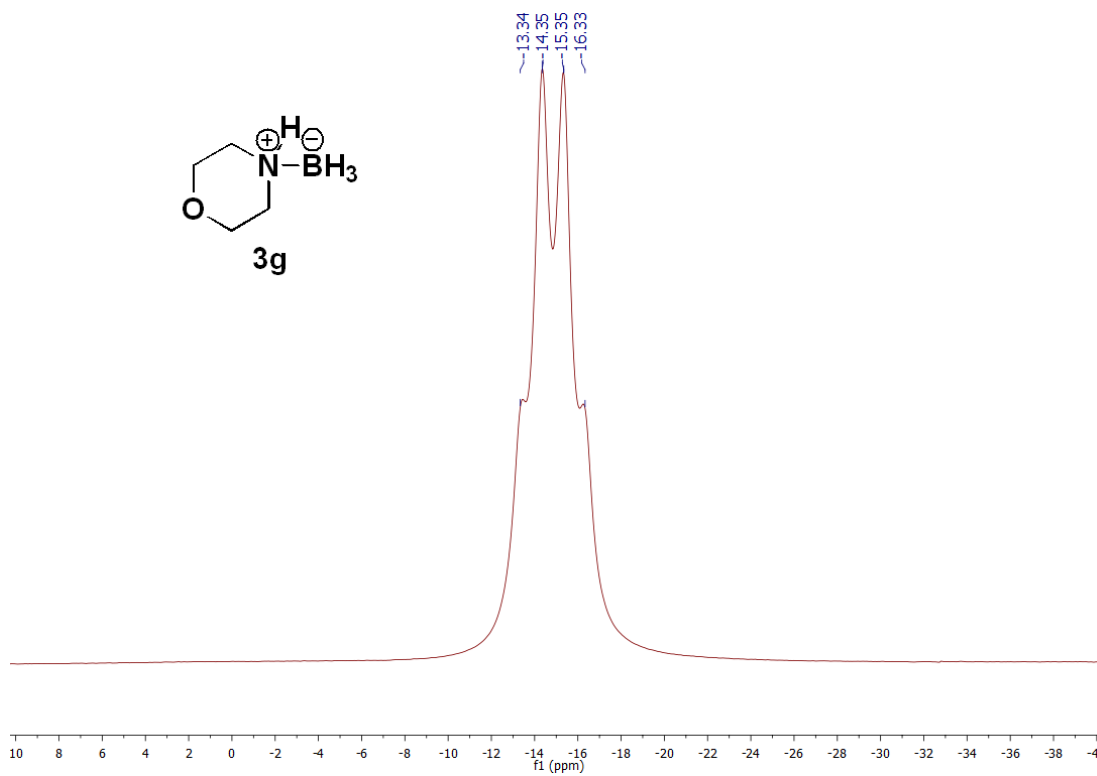


^{11}B NMR (96 MHz, THF) *N*-methylpyrrolidine-borane (Table 3, Entry 3)

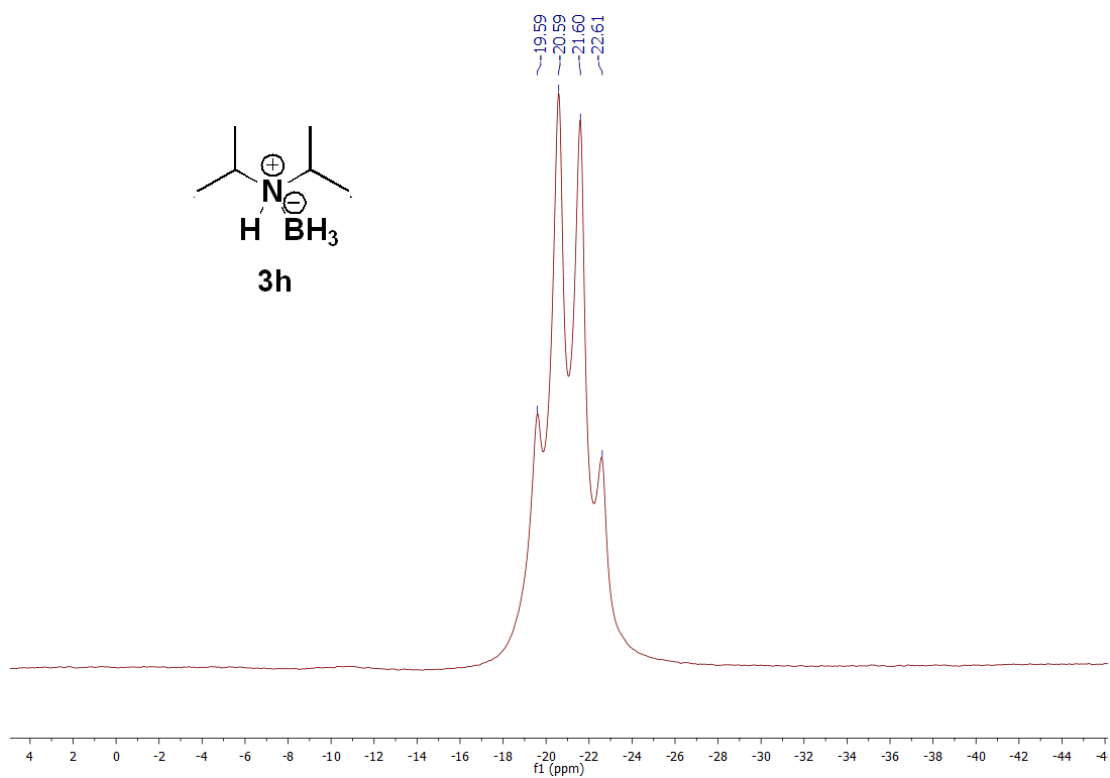




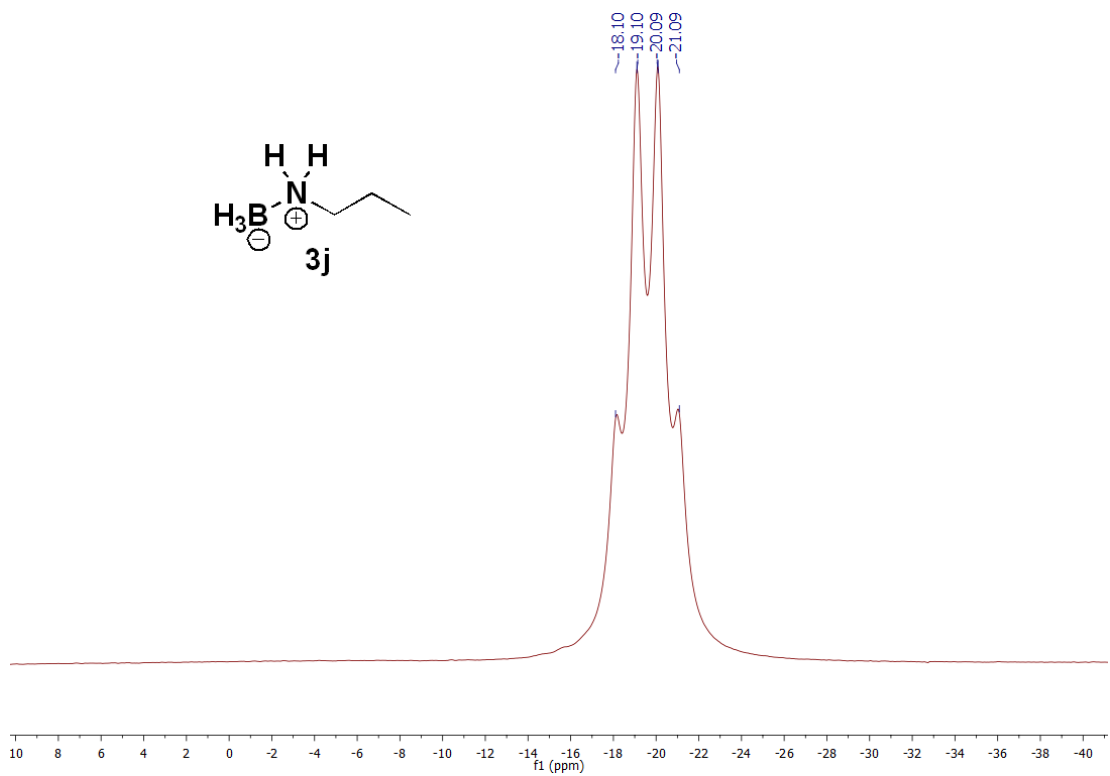
^{11}B NMR (96 MHz, THF) **Pyrrolidine-borane** (Table 3, Entry 7)



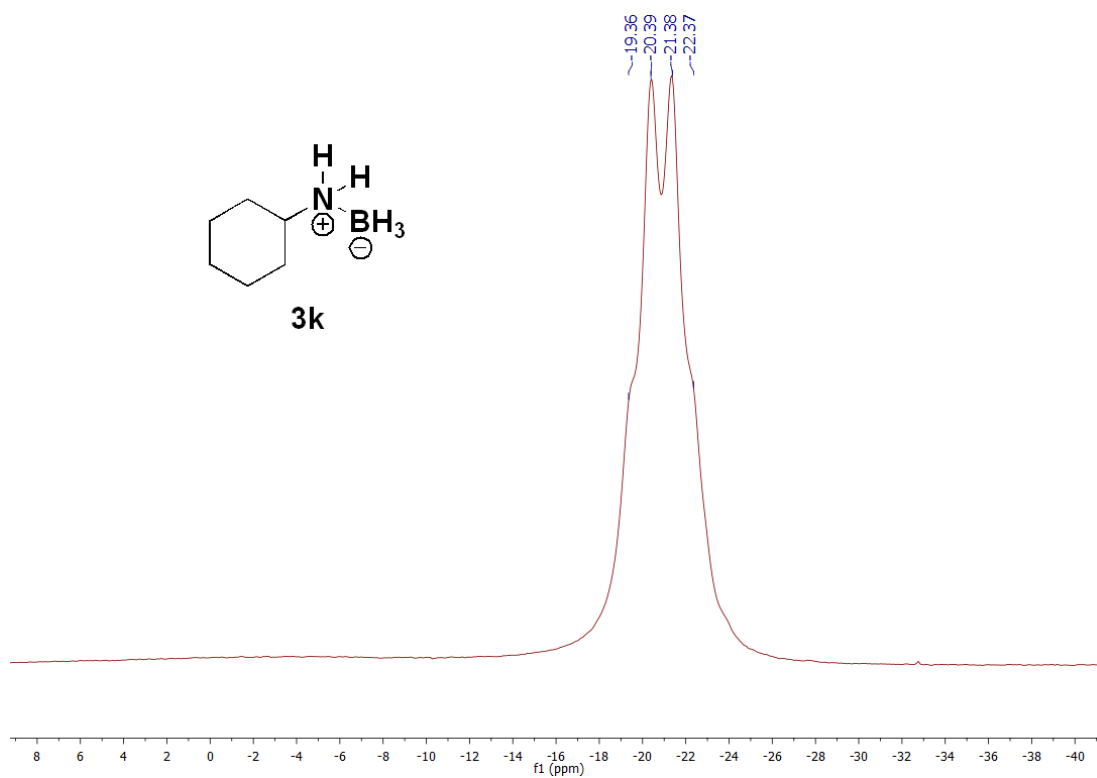
^{11}B NMR (96 MHz, THF) **Morpholine-borane** (Table 3, Entry 8)



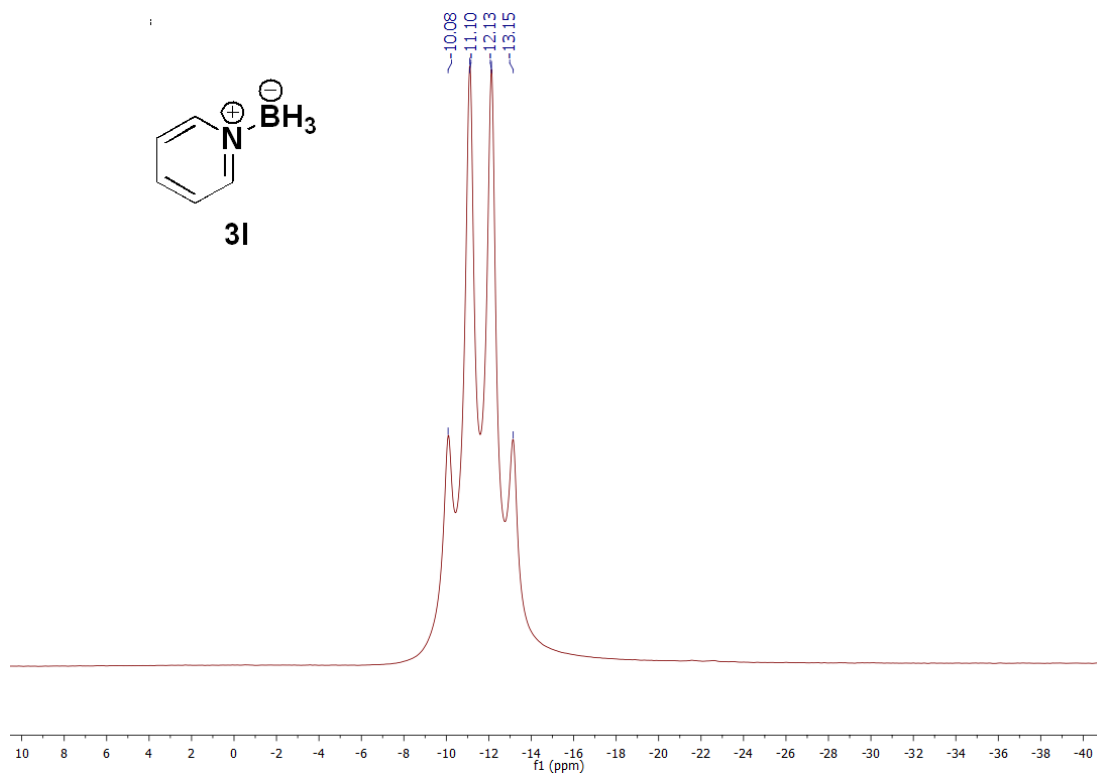
¹¹B NMR (96 MHz, THF) *N,N*-diisopropylamine-borane (Table 3, Entry 9)



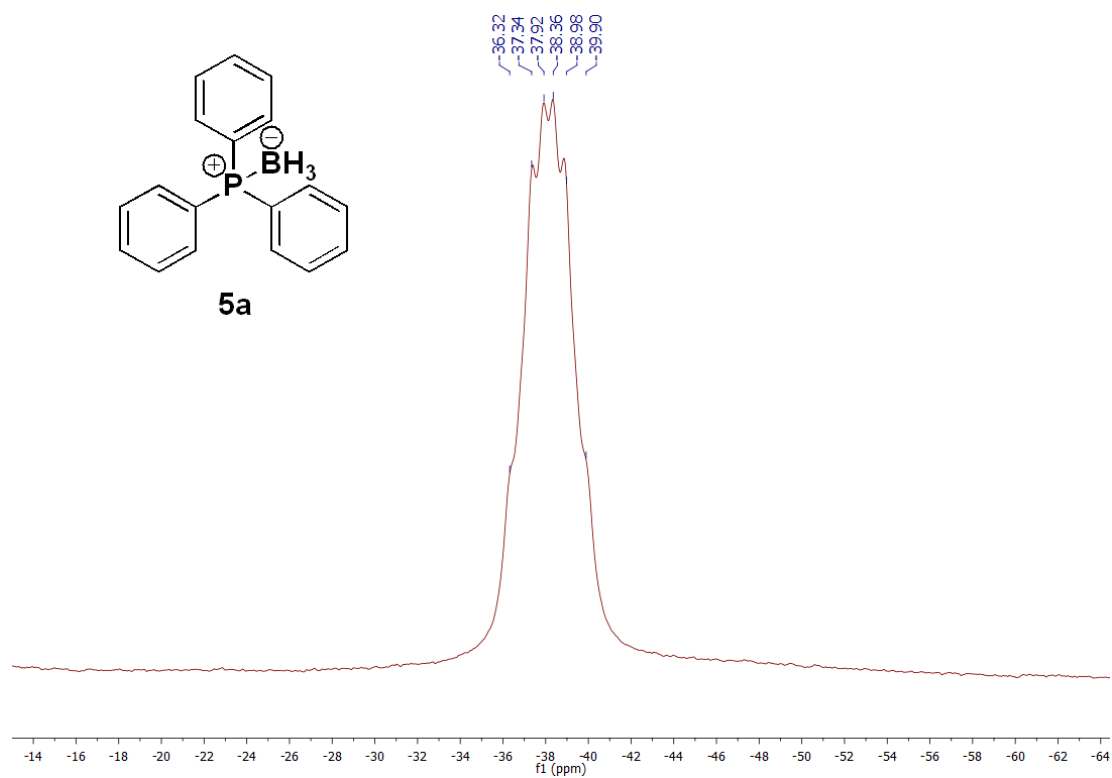
¹¹B NMR (96 MHz, THF) **1-propanamine-borane** (Table 3, Entry 11)



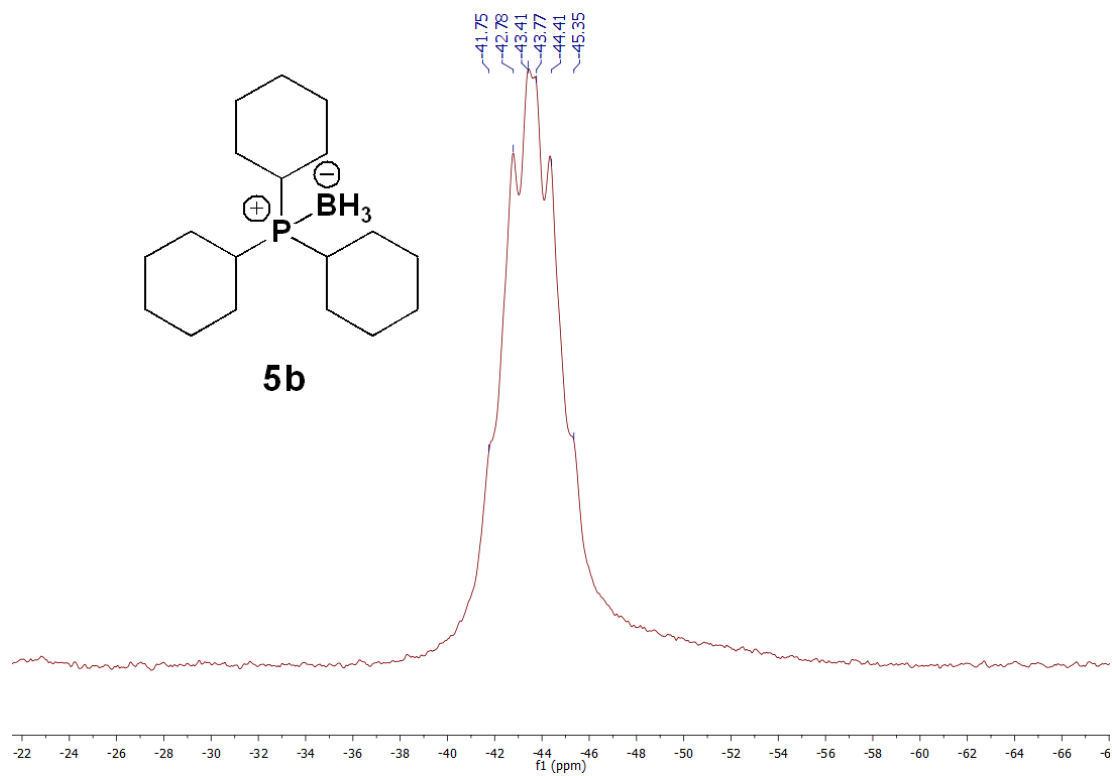
¹¹B NMR (96 MHz, THF) **Cyclohexylamine-borane** (Table 3, Entry 12)



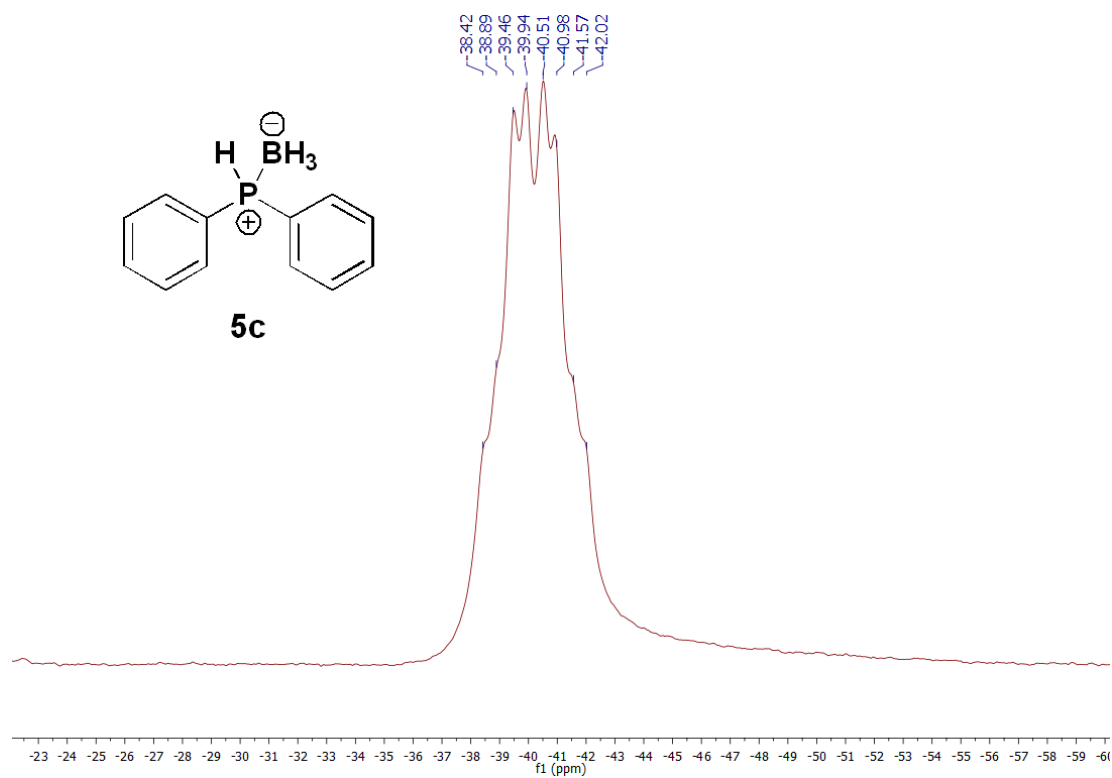
¹¹B NMR (96 MHz, THF) **Pyridine-borane** (Table 3, Entry 13)



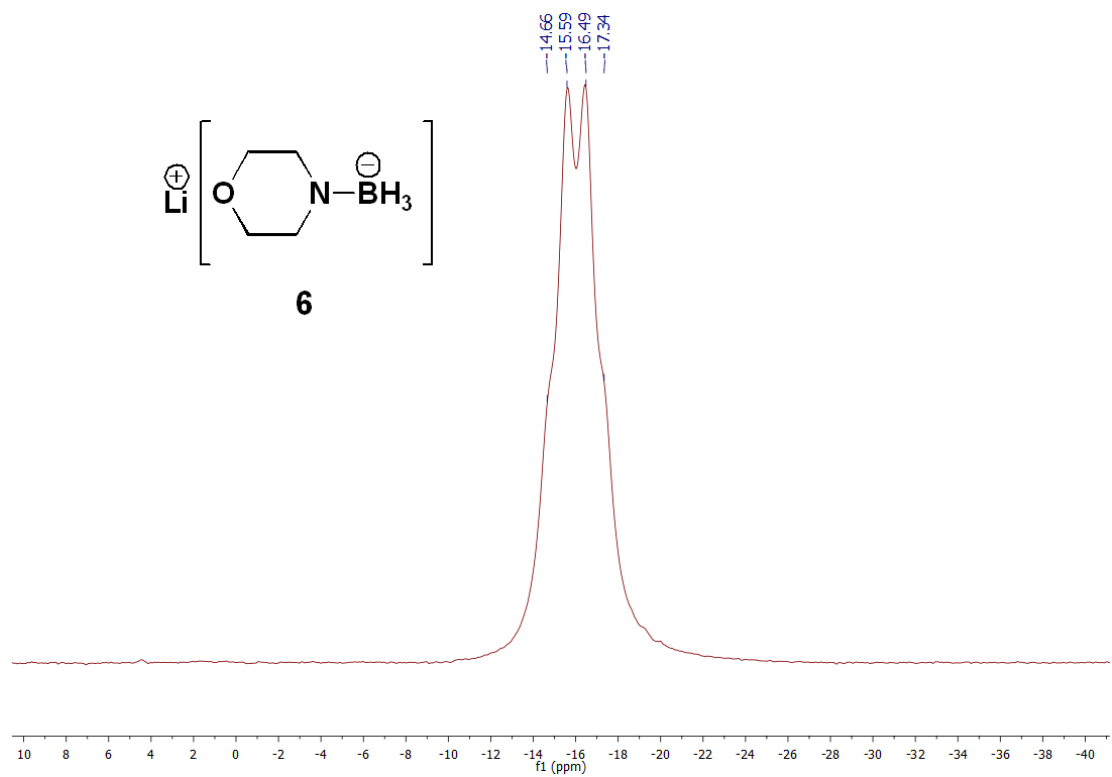
¹¹B NMR (96 MHz, THF) **Triphenylphosphine-borane** (Table 2, Entry 1)



¹¹B NMR (96 MHz, THF) **Tricyclohexylphosphine-borane** (Table 2, Entry 2)



^{11}B NMR (96 MHz, THF) **Diphenylphosphine-borane** (Table 2, Entry 3)



^{11}B NMR (96 MHz, THF) **Lithium Morpholinoborohydride (6)**