

Supporting Information

The interconversion between THF·B₃H₇ and B₃H₈⁻: an efficient synthetic method for MB₃H₈ (M = Li and Na)

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1. Experimental Section:

1.1. General Remarks.

All manipulations were carried out on a Schlenk line or in a glovebox filled with high purity nitrogen. The ^{11}B NMR spectra were recorded using either a 128 MHz or a 193 MHz spectrometer and externally referenced to $\text{BF}_3\cdot\text{OEt}_2$ in C_6D_6 ($\delta = 0.00$ ppm). The ^1H NMR spectra was recorded using either a 400 MHz or a 600 MHz spectrometer. X-ray diffraction (XRD) data were obtained with a Rigaku D/max 2500 diffractometer using $\text{Cu}/\text{K}\alpha$ radiation, $\lambda = 0.1542$ nm, 40 kV, 100 mA. IR spectra were measured by a Spectrum 400F.

The $\text{THF}\cdot\text{BH}_3$ tetrahydrofuran (THF) solution, HCl diethyl ether solution, and ammonia borane (NH_3BH_3) were purchased from United Boron (Zhengzhou) Energy Materials S&T LLC and used as received. K, LiH, NaH, LiBH_4 , NaBH_4 , NH_4Cl and $\text{N}(\text{C}_4\text{H}_9)_4\text{Br}$ were purchased from Sinopharm Chemical Reagents Co., Ltd. NH_4Cl was recrystallized from methanol and NBu_4Br was recrystallized from tetrahydrofuran (THF). Dichloromethane was dried over calcium hydride, THF and toluene were dried over sodium and freshly distilled prior to use. LiNH_2BH_3 and NaNH_2BH_3 were prepared according the literature methods.^{S1}

1.2. Reaction of KB_3H_8 with HCl.

A solution of KB_3H_8 (0.40 g, 5 mmol) in 25 mL of THF was added to a 50 mL flask. A solution of 1 M HCl in diethyl ether (5 mL, 5 mmol) was added dropwisely to the flask at room temperature and stirred for 20 min. After KCl was filtered (Fig. S1), the solution of $\text{THF}\cdot\text{B}_3\text{H}_7$ was obtained. ^{11}B NMR (128 MHz, THF): δ -8.23 (*br*, 2B of *BHB*), -12.99 (*br*, *BH*₂) ppm (Fig. 1).

In another batch of reaction, KB_3H_8 (0.40 g, 5 mmol) was added to a 100 mL flask and then 25 mL of THF was condensed. A solution of 1 M HCl in diethyl ether (5 mL, 5 mmol) was added dropwisely to the flask at room temperature and stirred for 20 min. The ^{11}B NMR showed the formation of B_3H_7 (Fig. 2b). Then 5 mL, 10 mL, 15 mL of 1 M HCl diethyl ether solution was added dropwisely to above reaction mixture in turn. Reaction mixture was stirring for 20 min after each addition of HCl and then monitored by ^{11}B NMR. The results are listed in Fig. 2c, d, and e.

1.3. Reaction of $\text{THF}\cdot\text{B}_3\text{H}_7$ with LiNH_2BH_3 .

A $\text{THF}\cdot\text{B}_3\text{H}_7$ solution (30 mL, 5 mmol) and LiNH_2BH_3 (0.19 g, 5 mmol) were added to a 50 mL flask. The mixture was stirred for 20 min at room temperature. The formed precipitate was filtered and dried under dynamic vacuum to give the $[\text{NH}_2\text{BH}_2]_n$ white product, which was confirmed by XRD and IR (Figs. S2 and S3). Removal of THF from the filtrate under dynamic vacuum to give

Li(THF)_{1.5}B₃H₈ as a clear oily product (0.64 g, 82%). ¹¹B NMR (193 MHz, CD₃CN): δ -30.8 (*nonet*, *J* = 33 Hz) ppm. ¹H NMR (600 MHz, CD₃CN): δ 3.64 (*m*, 4α-H of THF), 1.79 (*m*, 4β-H of THF), 0.14 (*decet*, *J* = 33 Hz, 8H of B₃H₈) ppm. ¹H{¹¹B} (600 MHz, CD₃CN): δ 3.65 (*m*, 4α-H of THF), 1.80 (*m*, 4β-H of THF), 0.13 (*s*, 8H of B₃H₈) ppm (Figs. S4, S5 and S6). [NH₂BH₂]_n: IR (cm⁻¹): 3300 (*s*, *br*), 3248 (*w*), 2398 (*s*, *br*), 1560 (*s*), 1405 (*s*), 1209 (*s*, *br*), 1081 (*m*), 846 (*w*), 708 (*w*).

1.4 Reaction of THF·B₃H₇ with NaNH₂BH₃.

A THF·B₃H₇ (30 mL, 5 mmol) solution and NaNH₂BH₃ (0.27 g, 5 mmol) were added to a 50 mL flask. The reaction was stirred for 30 min at room temperature. The formed precipitate was filtered. Then THF in the filtrate was pumped to give an oily product, which was dissolved in 20 mL CH₂Cl₂ and converted into suspension under stirring. After filtration, the solid was dried under dynamic vacuum, unsolvated NaB₃H₈ was obtained (0.24 g, 76%). NaB₃H₈: ¹¹B NMR (193 MHz, CD₃CN): δ -30.0 (*nonet*, *J* = 33 Hz) ppm. ¹H NMR (600 MHz, CD₃CN): δ 0.14 (*decet*, *J* = 33 Hz) ppm (Figs. S7 and S8).

1.5. Reaction of THF·B₃H₇ with LiBH₄.

In a 50 mL flask, LiBH₄ (0.11 g, 5 mmol) was added and then THF·B₃H₇ (30 mL, 5 mmol) was injected. The reaction was stirred 1 h at room temperature, B₃H₇ was completely consumed and the formed B₃H₈⁻ and BH₃ signals, and a small amount of BH₄⁻ signal were observed in ¹¹B NMR (Fig. S9). The THF solvent and the formed THF·BH₃ solution was removed under dynamic vacuum to produce a sticky solid, into which 20 mL of THF was added and then 20 μL of H₂O was injected. After stirring 10 min, a small amount of precipitate was formed which was filtered. Removal of THF from the filtrate produced Li(THF)_{1.5}B₃H₈ as a clear oily product (0.61 g, 79%). ¹¹B NMR (128 MHz, CD₃CN): δ -31.2 (*nonet*, *J* = 33 Hz) ppm. ¹H NMR (600 MHz, CD₃CN): δ 3.64 (*m*, 4α-H of THF), 1.80 (*m*, 4β-H of THF), 0.14 (*decet*, *J* = 33 Hz, 8H of B₃H₈) ppm (Figs. S10 and S11).

1.6. Reaction of THF·B₃H₇ with NaBH₄.

In a 50 mL flask, NaBH₄ (0.19 g, 5 mmol) was added and then THF·B₃H₇ (30 mL, 5 mmol) was injected. The reaction was stirred for 12 h at room temperature, B₃H₇ was completely consumed and the formed B₃H₈⁻ and BH₃ signals, and a small amount of BH₄⁻ signal were observed in the ¹¹B NMR (Fig. S12). The formed THF·BH₃ and the THF solvent were removed under dynamic vacuum to produce a sticky solid, into which 20 mL of THF was added and then 30 μL H₂O was injected. After stirring 50 min, a small amount of precipitate was formed which was filtered. Removal of THF from the filtrate produced an oily product. The oily product was dissolved in 20 mL CH₂Cl₂ to convert into

suspension under stirring. After filtration, the solid was dried under dynamic vacuum to produce unsolvated NaB_3H_8 (0.23 g, 73%).

1.7. Synthesis of $\text{NH}_4\text{B}_3\text{H}_8$.

The prepared unsolvated KB_3H_8 (0.80 g, 10 mmol) and NH_4Cl (0.54 g, 10 mmol) were added into a 50 mL Schlenk flask and then 30 mL liquid ammonia was condensed at $-78\text{ }^\circ\text{C}$. After 50 min stirring, ammonia was removed and the flask was warmed to room temperature. The prepared $\text{NH}_4\text{B}_3\text{H}_8$ was extracted using dry THF. The KCl residue was washed with THF ($3 \times 10\text{ mL}$), which was confirmed by XRD (Fig. S13). The combined filtrate and the wash solution was then evaporated to produce a white solid, which was dried under dynamic vacuum to give the $\text{NH}_4\text{B}_3\text{H}_8$ white powder (0.57 g, 96%). ^{11}B NMR (193 MHz, CD_3CN): δ -30.6 (*nonet*, $J = 33\text{ Hz}$) ppm (Fig. S14). ^1H NMR (400 MHz, CD_3CN): δ 5.85 (*s*, 4H of NH_4), 0.14 (*decet*, $J = 33\text{ Hz}$, 8H of B_3H_8) ppm (Fig. S15).

1.8. Synthesis of $\text{NBu}_4\text{B}_3\text{H}_8$.

The prepared unsolvated KB_3H_8 (0.80 g, 10 mmol) and NBu_4Br (3.22 g, 10 mmol) were added into a 50 mL flask and then 30 mL of THF was condensed. After the reaction mixture stirring for 6 hours at room temperature, the reaction solution was filtered and the KBr frit was washed with THF ($3 \times 10\text{ mL}$), which was confirmed by XRD (Fig. S16). The filtrate was evaporated to produce a sticky solid, which was washed with diethyl ether ($3 \times 30\text{ mL}$) and dried under vacuum to give a free-flowing $\text{NBu}_4\text{B}_3\text{H}_8$ white powder (2.69 g, 95%). ^{11}B NMR (193 MHz, CD_3CN): δ -31.4 (*nonet*, $J = 33\text{ Hz}$) ppm (Fig. S17). ^1H NMR (600 MHz, CD_3CN): δ 3.09 (*t*, 2H of CH_2), 1.58 (*m*, 2H of CH_2), 1.35 (*m*, 2H of CH_2), 0.97 (*t*, $J = 7\text{ Hz}$, 3H of CH_3), 0.14 (*decet*, $J = 33\text{ Hz}$, 8H of B_3H_8) ppm (Fig. S18).

2. Supporting Results:

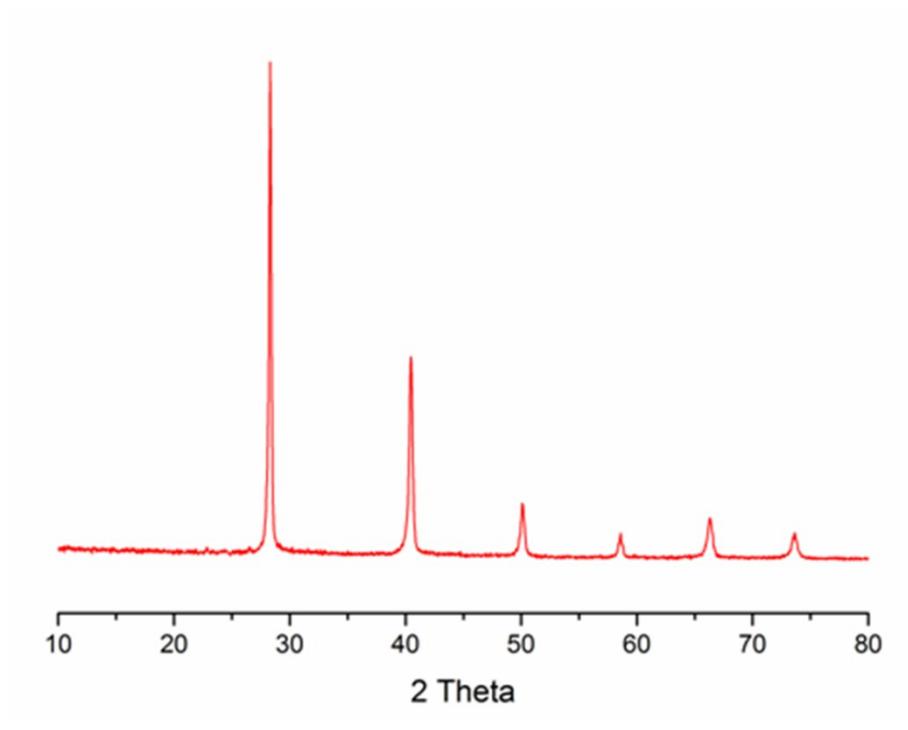


Fig. S1 X-ray powder diffraction data of KCl.

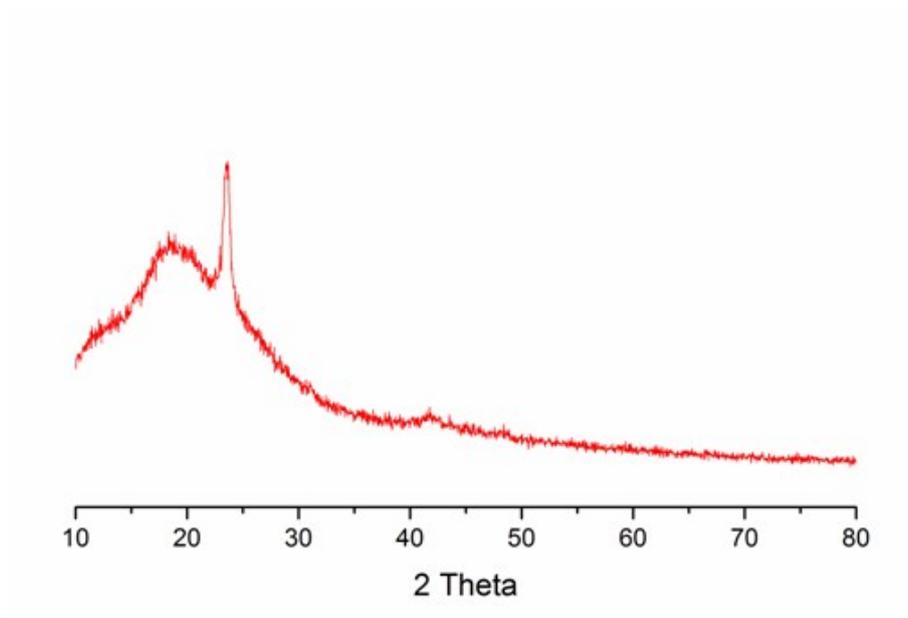


Fig. S2 X-ray powder diffraction data of the formed $[\text{NH}_2\text{BH}_2]_n$.

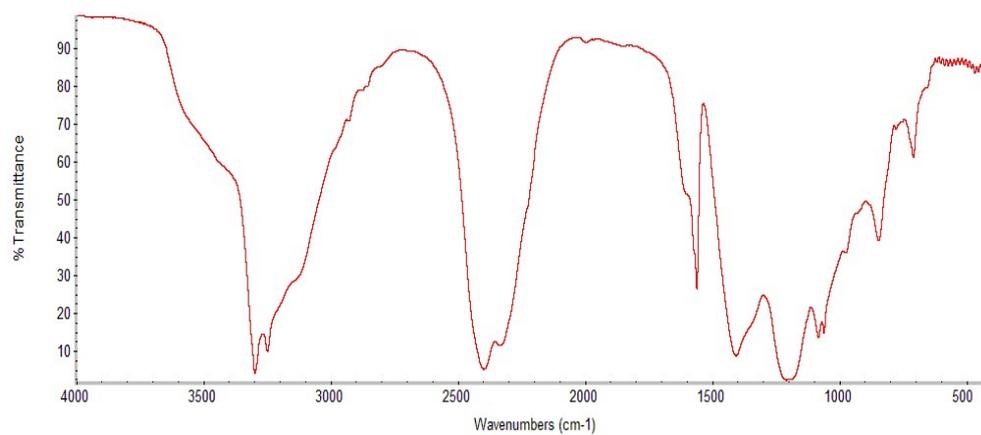


Fig. S3 IR spectrum of the formed $[\text{NH}_2\text{BH}_2]_n$.

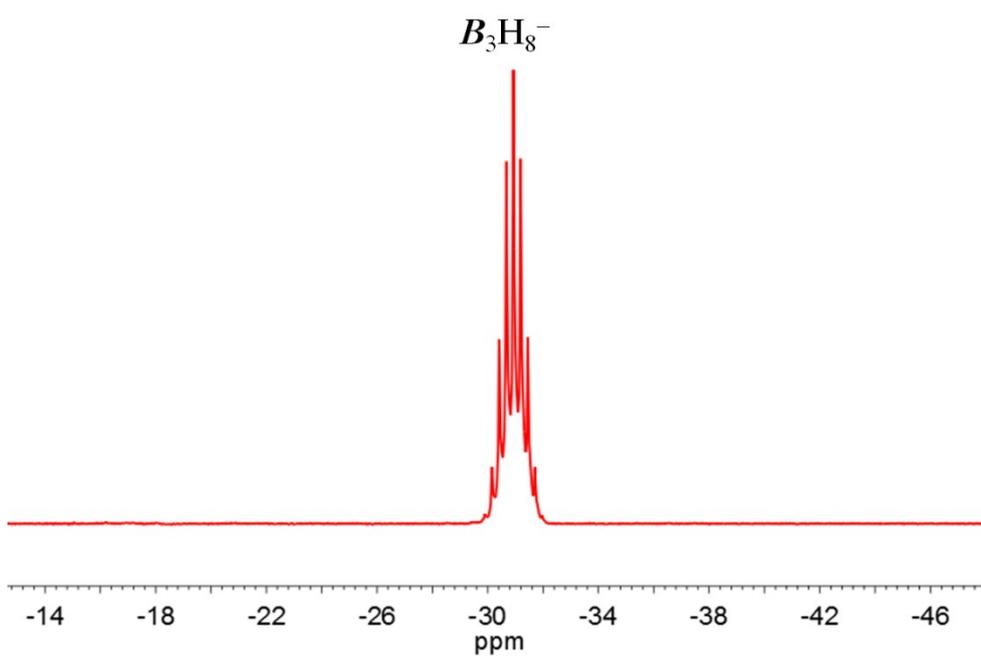


Fig. S4 ^{11}B NMR spectrum of the prepared $\text{Li}(\text{THF})_{1.5}\text{B}_3\text{H}_8$ in CD_3CN .

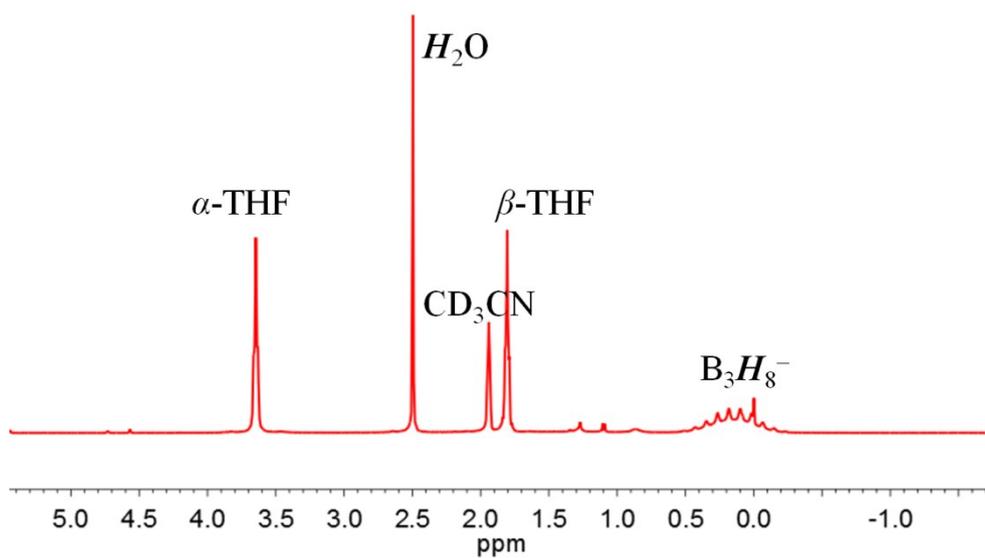


Fig. S5 ^1H spectrum of the prepared $\text{Li}(\text{THF})_{1.5}\text{B}_3\text{H}_8$ in CD_3CN .

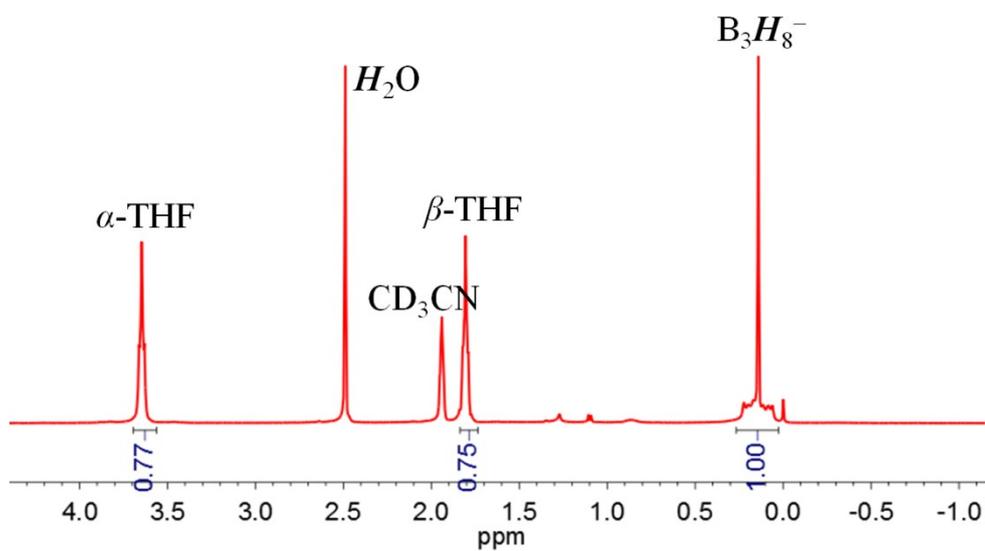


Fig. S6 $^1\text{H}\{^{11}\text{B}\}$ spectrum of the prepared $\text{Li}(\text{THF})_{1.5}\text{B}_3\text{H}_8$ in CD_3CN .

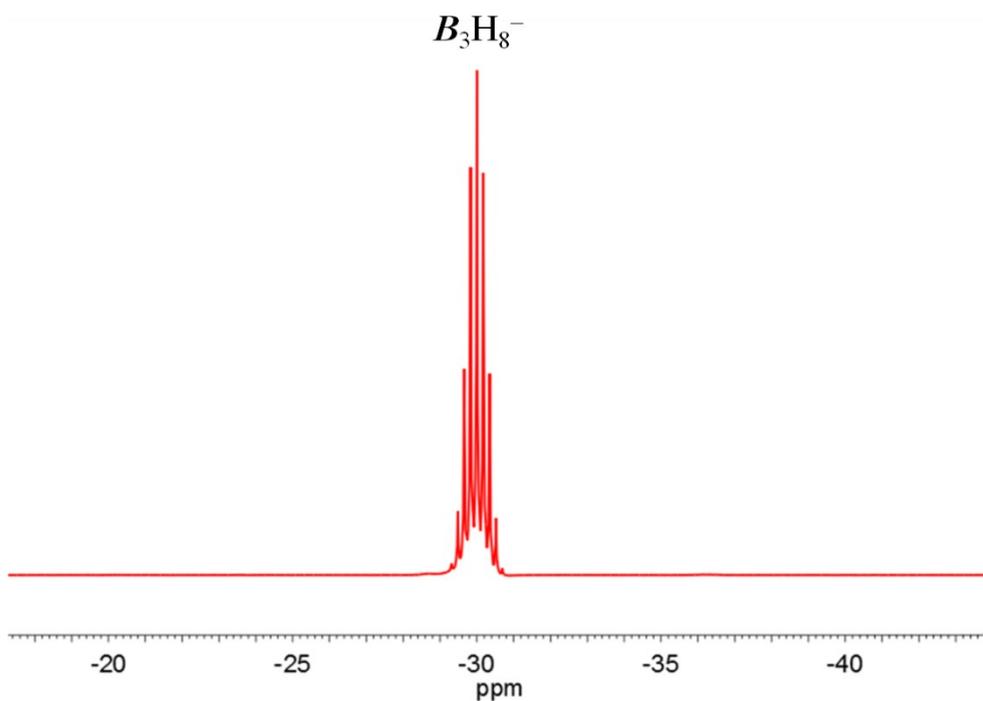


Fig. S7 ^{11}B NMR spectrum of the prepared unsolvated NaB_3H_8 in CD_3CN .

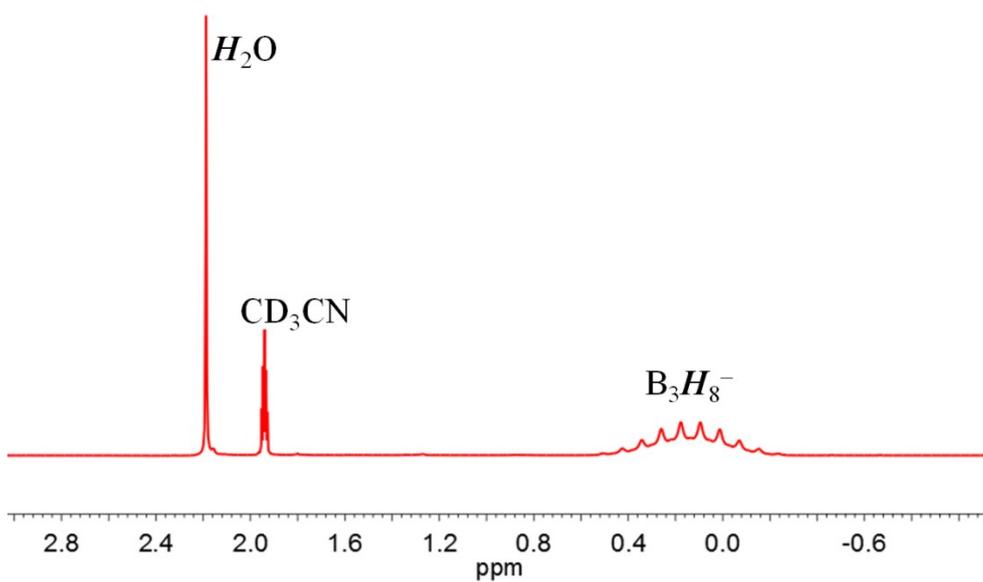


Fig. S8 ^1H NMR spectrum of the prepared unsolvated NaB_3H_8 in CD_3CN .

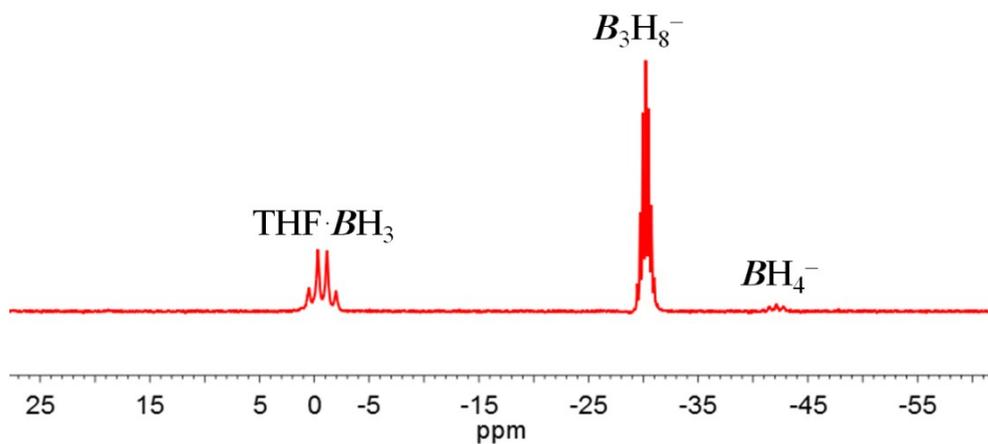


Fig. S9 ^{11}B NMR spectrum of the reaction solution of LiBH_4 and $\text{THF}\cdot\text{B}_3\text{H}_7$ in THF at room temperature.

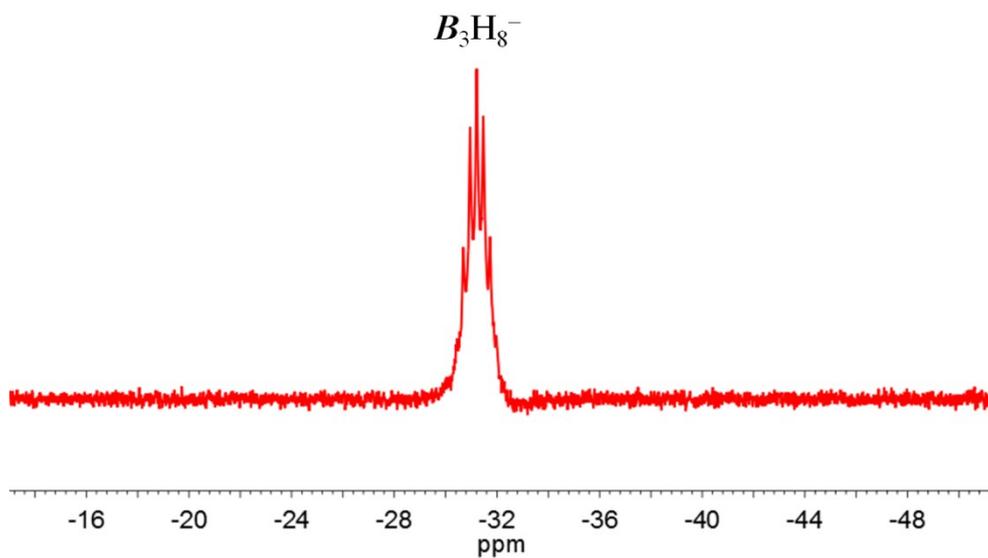


Fig. S10 ^{11}B NMR spectrum of the prepared $\text{Li}(\text{THF})_{1.5}\text{B}_3\text{H}_8$ in CD_3CN .

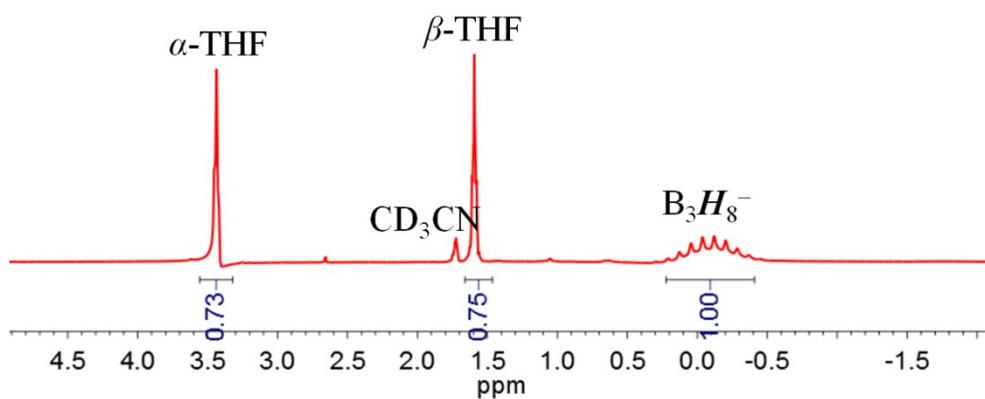


Fig. S11 ^1H NMR spectrum of the prepared $\text{Li}(\text{THF})_{1.5}\text{B}_3\text{H}_8$ in CD_3CN .

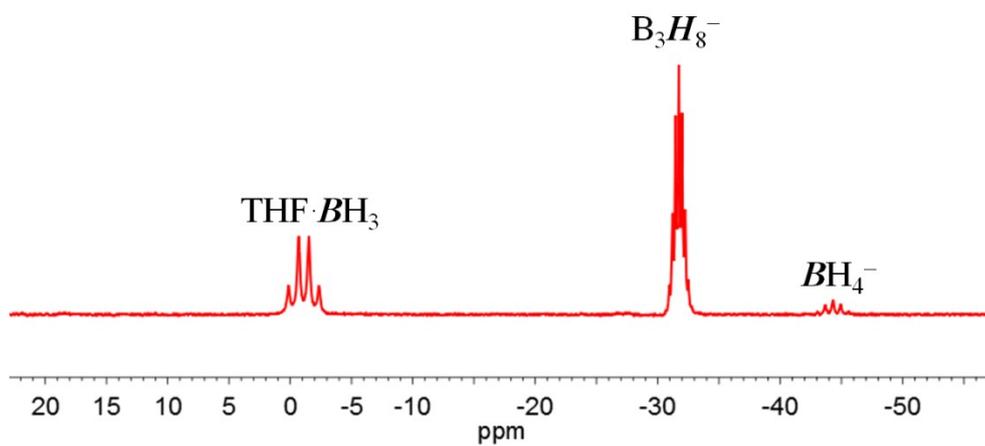


Fig. S12 ^{11}B NMR spectrum of the reaction solution of NaBH_4 and $\text{THF}\cdot\text{B}_3\text{H}_7$ in THF at room temperature.

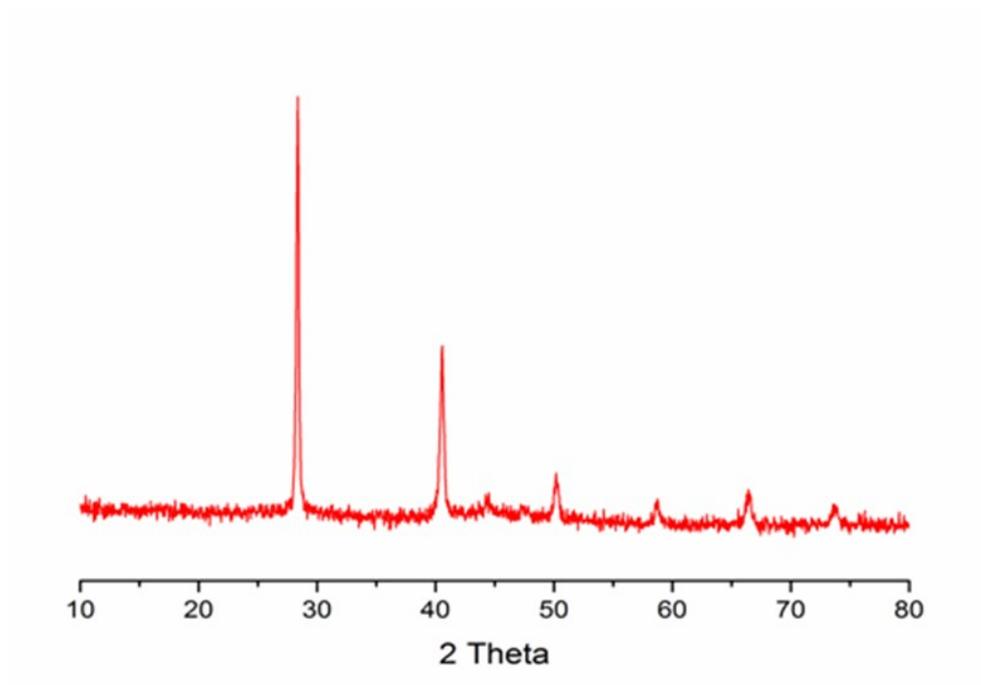


Fig. S13 X-ray powder diffraction data of the formed KCl.

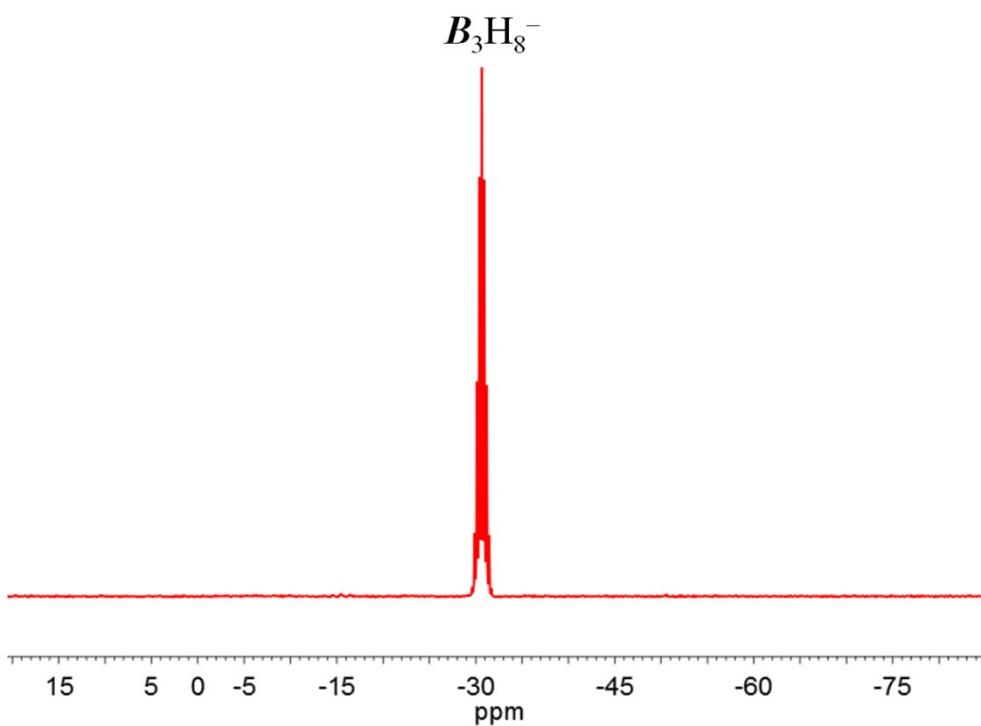


Fig. S14 ^{11}B NMR spectrum of the prepared $\text{NH}_4\text{B}_3\text{H}_8$ in CD_3CN .

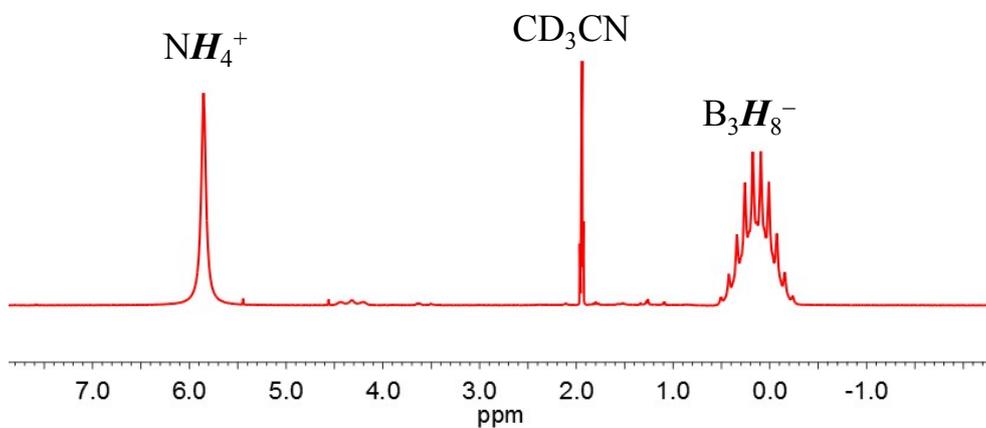


Fig. S15 ^1H NMR spectrum of the prepared $\text{NH}_4\text{B}_3\text{H}_8$ in CD_3CN .

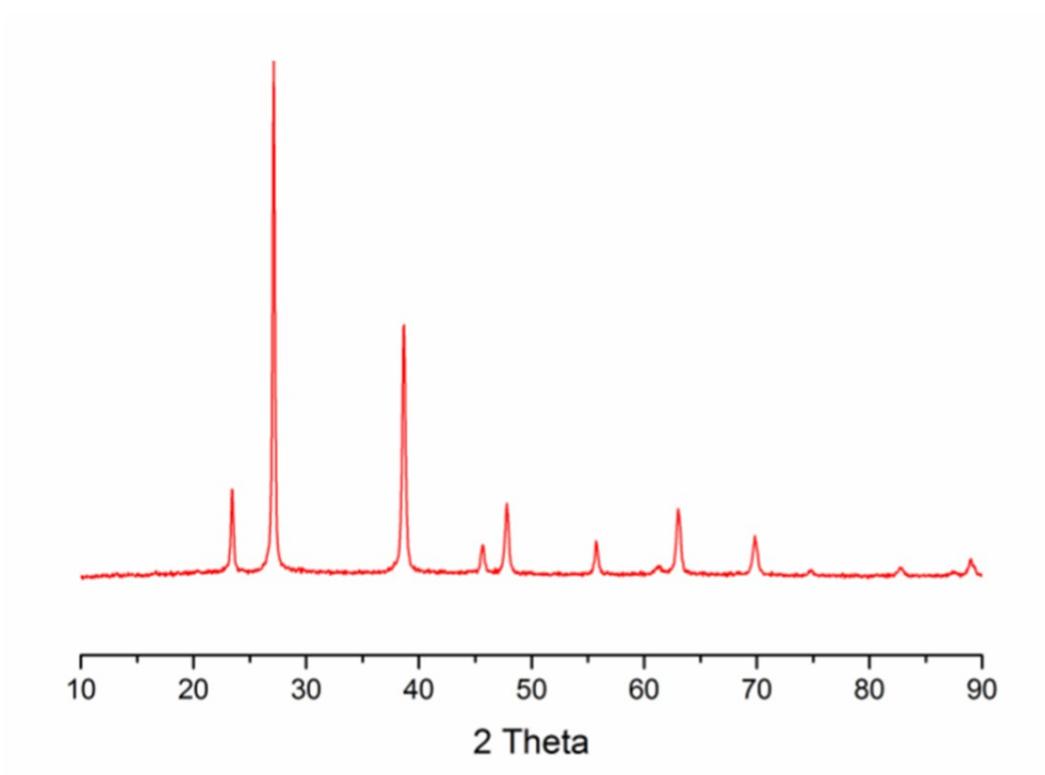


Fig. S16 X-ray powder diffraction data of the formed KBr.

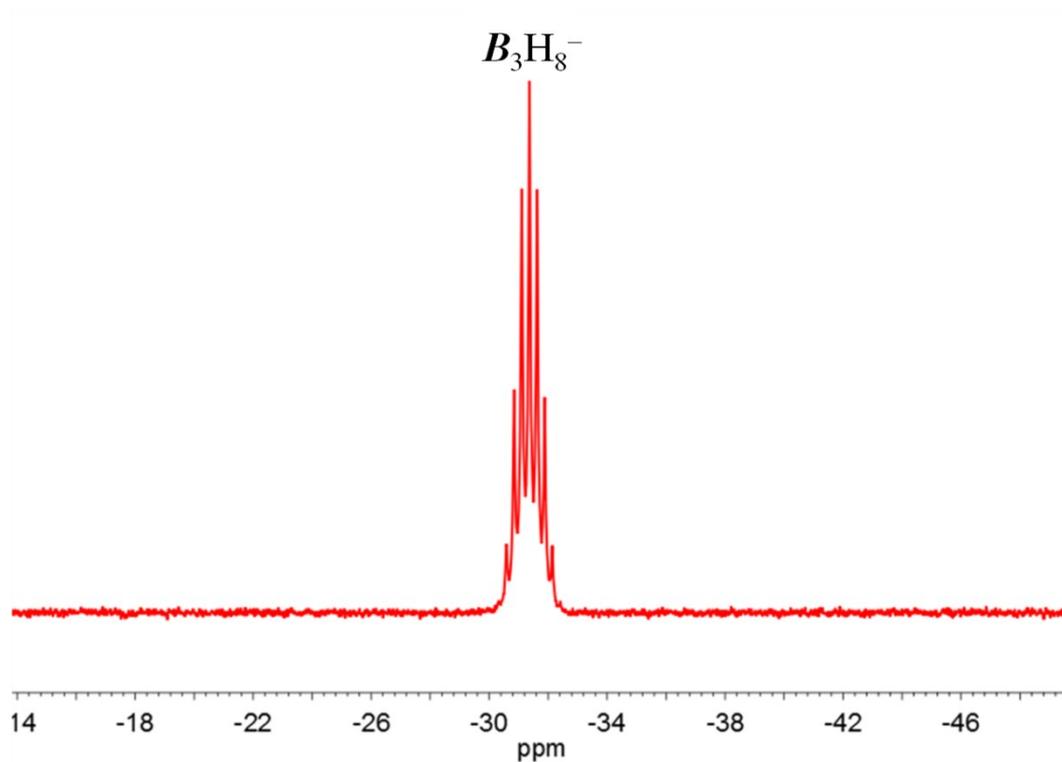


Fig. S17 ^{11}B NMR spectrum of the prepared $\text{NBu}_4\text{B}_3\text{H}_8$ in CD_3CN .

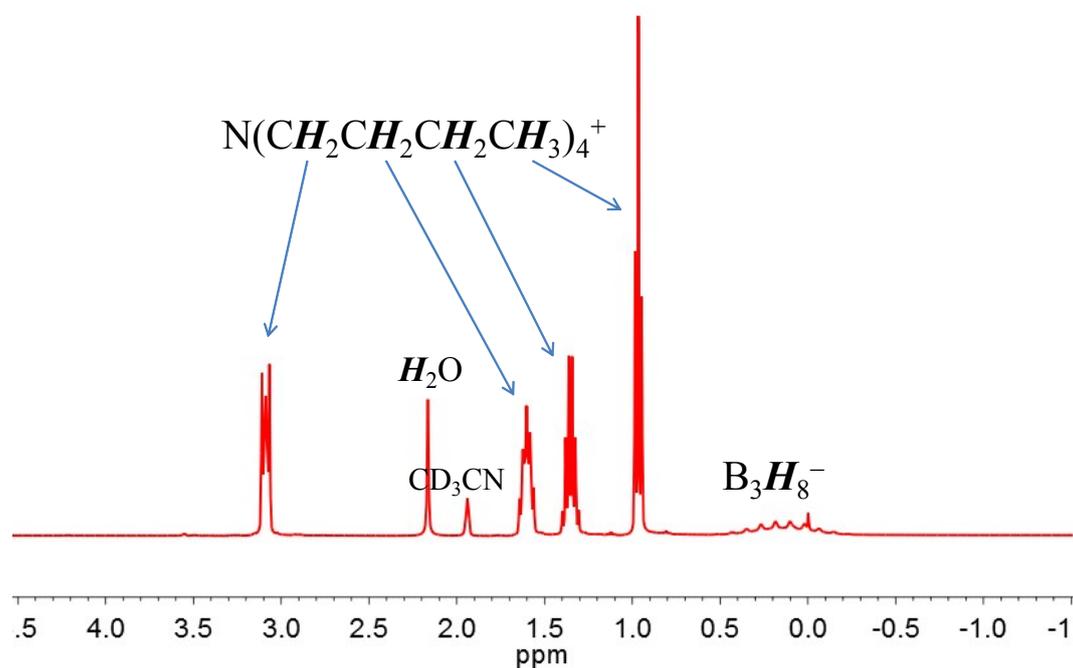
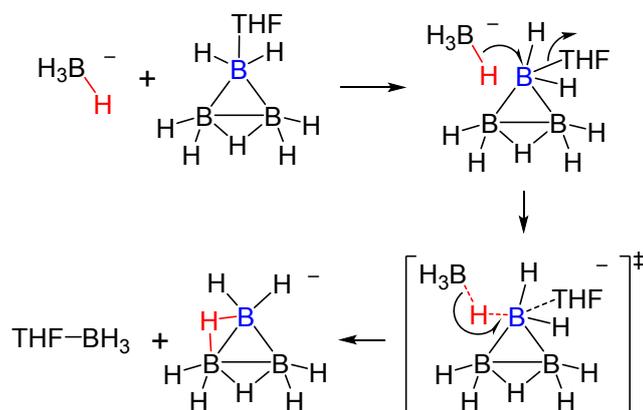


Fig. S18 ^1H NMR spectrum of the prepared $\text{NBu}_4\text{B}_3\text{H}_8$ in CD_3CN .

3. Supporting Scheme:



Scheme S1 The reaction of MBH_4 ($\text{M} = \text{Li}, \text{Na}$) with $\text{THF} \cdot \text{B}_3\text{H}_7$.

4. References:

- S1. (a) Y. S. Chua, P. Chen, G. Wu, Z. Xiong, *Chem. Commun.*, 2011, **47**, 5116-5129; (b) W. Xu, H. Fan, G. Wu and P. Chen, *New J. Chem.*, 2012, **36**, 1496-1501; (c) H. V. K. Diyabalanage, T. Nakagawa, R. P. Shrestha, T. A. Semelsberger, B. L. Davis, B. L. Scott, A. K. Burrell, W. I. F. David, K. R. Ryan, M. O. Jones and P. P. Edwards, *J. Am. Chem. Soc.*, 2010, **132**, 11836-11837; (d) Z. Xiong, C. K. Yong, G. Wu, P. Chen, W. Shaw, A. Karkamkar, T. Autrey, M. O. Jones, S. R. Johnson, P. P. Edwards, W. I. F. David, *Nat. Mater.*, 2008, **7**, 138-141; (e) Z. Xiong, G. Wu, Y. S. Chua, J. Hu, T. He, W. Xu and P. Chen, *Energy Environ. Sci.*, 2008, **1**, 360-363.