

Supplementary Information

A hydrido-iridium- β -diketone as efficient and robust homogeneous catalyst for the hydrolysis of ammonia-borane or amine-borane adducts in air to produce hydrogen.

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General Procedures. The hydrolytic dehydrogenation reactions were carried out at room temperature under air. $[\text{IrHCl}\{(\text{PPh}_2(o\text{-C}_6\text{H}_4\text{CO}))_2\text{H}\}]$ (**1**)¹ was prepared as previously reported by the reaction of $[\text{IrCl}(\text{Cod})]_2$ ² (Cod = 1,5-cyclooctadiene) and *o*-(diphenylphosphine)benzaldehyde.³ Ammonia-borane and amino-boranes were purchased and used as received. The preparation of the metal complexes was carried out at room temperature under nitrogen by standard Schlenk techniques. Microanalysis was carried out with a Leco CHNS-932 microanalyser. ¹H and ¹³C{¹H} (TMS internal standard), ³¹P{¹H} (H₃PO₄ external standard) and ¹¹B{¹H} (BF₃·OEt₂ external standard) spectra were recorded with a Bruker Avance DPX 300 spectrometer.

Dehydrogenation of RR'R''N—BH₃ with catalyst 1. A typical dehydrogenation experiment is described here for the hydrolysis of H₃N—BH₃ using THF/H₂O = 1/1 mixtures and 0.5 mol% catalyst loading: A solution of 42.5 mg (1.38 mmol) of H₃N—BH₃ in 1.5 ml of H₂O was prepared in a round bottom 40 ml flask fitted with a gas outlet and with a side arm sealed with a tight-fitting septum cap. The flask was connected via the gas outlet to a water-filled gas burette. A solution of 5.5 mg (0.0068 mmol) of **1** in 1.5 ml of dry THF was then syringed through the septum, magnetic stirring was connected and timing started. Gas evolution began immediately and the amount of gas evolved was determined periodically by measuring the displacement of water in the burette. 3.0 equivalents of hydrogen occupy 100 ml at atmospheric pressure. Volumes were measured at atmospheric pressure and corrected for water vapor pressure at 20°C. The procedure was repeated at different THF/H₂O ratios using always a total volume of 3 ml. Figure S1 shows the release of hydrogen using different THF/H₂O mixtures. The procedure was repeated at different catalyst loadings by modifying the amount of iridium.

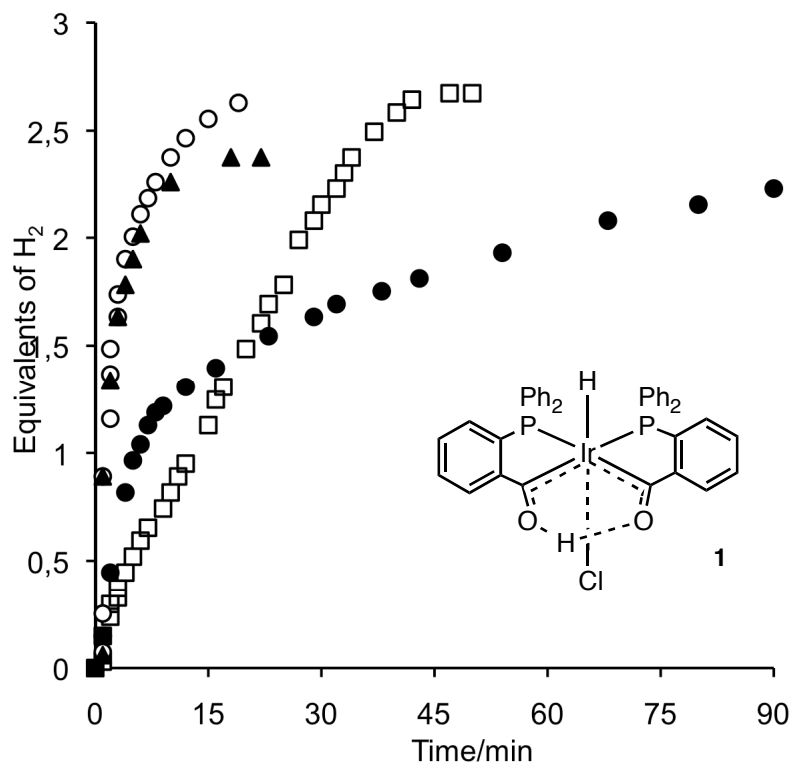


FIGURE S1. Hydrogen release from H₃NBH₃ using 0.5 mol% of **1** as catalyst in THF/H₂O mixtures: 85/15 (□); 50/50 (○); 40/60 (▲) or 30/70 (●).

- (1) M. A. Garralda, R. Hernández, L. Ibarlucea, E. Pinilla and M. R. Torres, *Organometallics*, 2003, **22**, 3600
- (2) J. L. Herde, J. C. Lambert and C. V. Senoff, *Inorg. Synth.*, 1974, **15**, 18;
- (3) S. Laue, L. Greiner, J. Wöltinger and A. Liese, *Adv. Synth. Catal.*, 2001, **343**, 711.

NMR Identification of iridium species after the catalytic reaction.

a) After completion of the catalytic reaction using THF/H₂O = 1/1 mixtures, elimination of THF afforded a yellow solid that was decanted and vacuum dried. The ¹H and ³¹P{¹H} NMR spectra of this solid in THF-d₈ solution were recorded (see Figure S2).

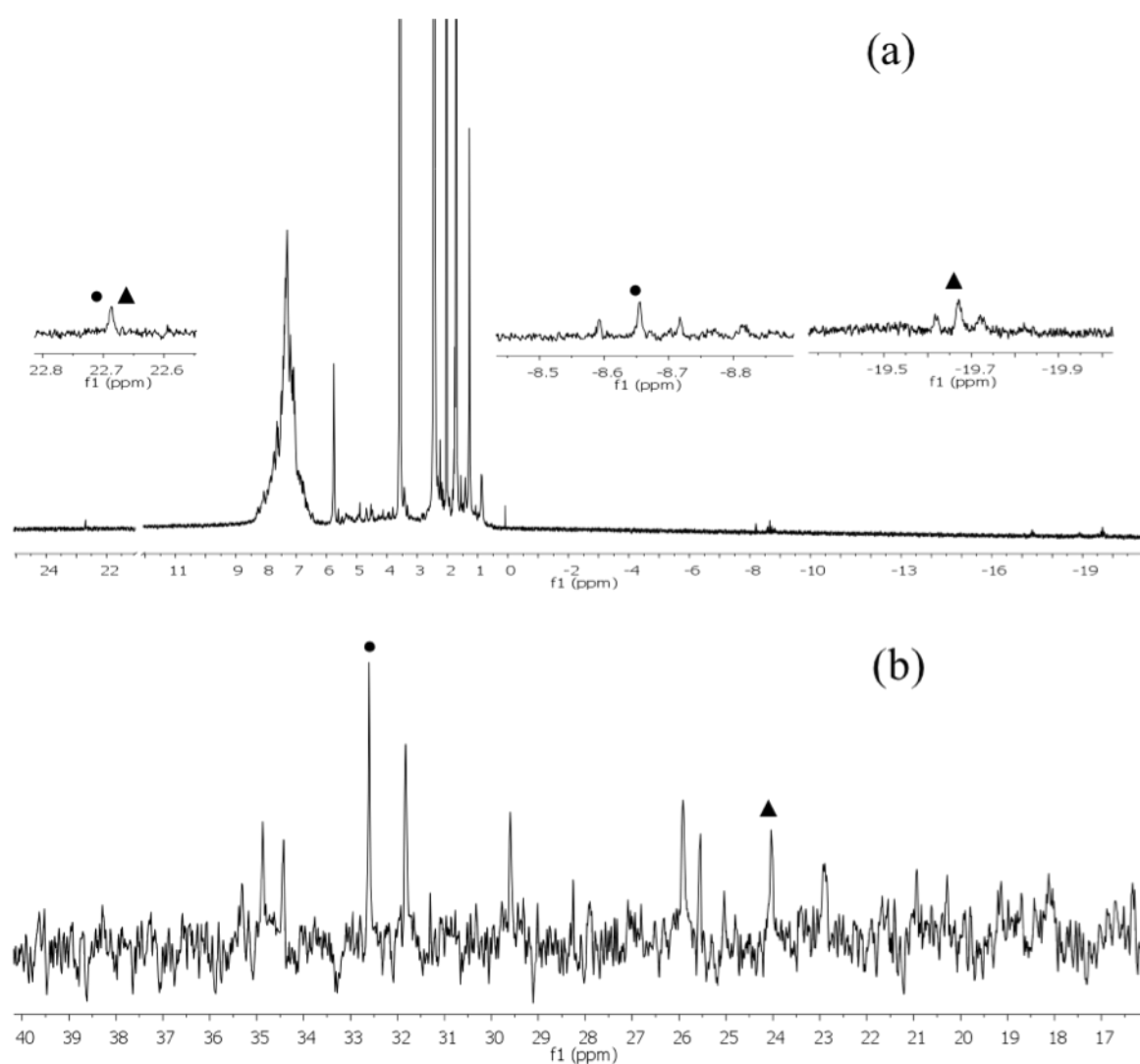


Figure S2. ¹H (a) and ³¹P{¹H} (b) NMR spectra (THF-d₈) of the yellow solid recovered after the dehydrogenation of NH₃BH₃ with **1** (THF/H₂O = 1/1), upon elimination of THF. (▲) [IrHCl{(PPh₂(o-C₆H₄CO)₂H)}]; (●) [IrH₂{(PPh₂(o-C₆H₄CO)₂H)}].

b) When the catalytic reaction was performed using THF/H₂O = 4/6 mixtures, a solid was formed, which was decanted and vacuum dried. The ¹H and ³¹P{¹H} NMR spectra of this solid in THF-d₈ solution were recorded (see Figure S3).

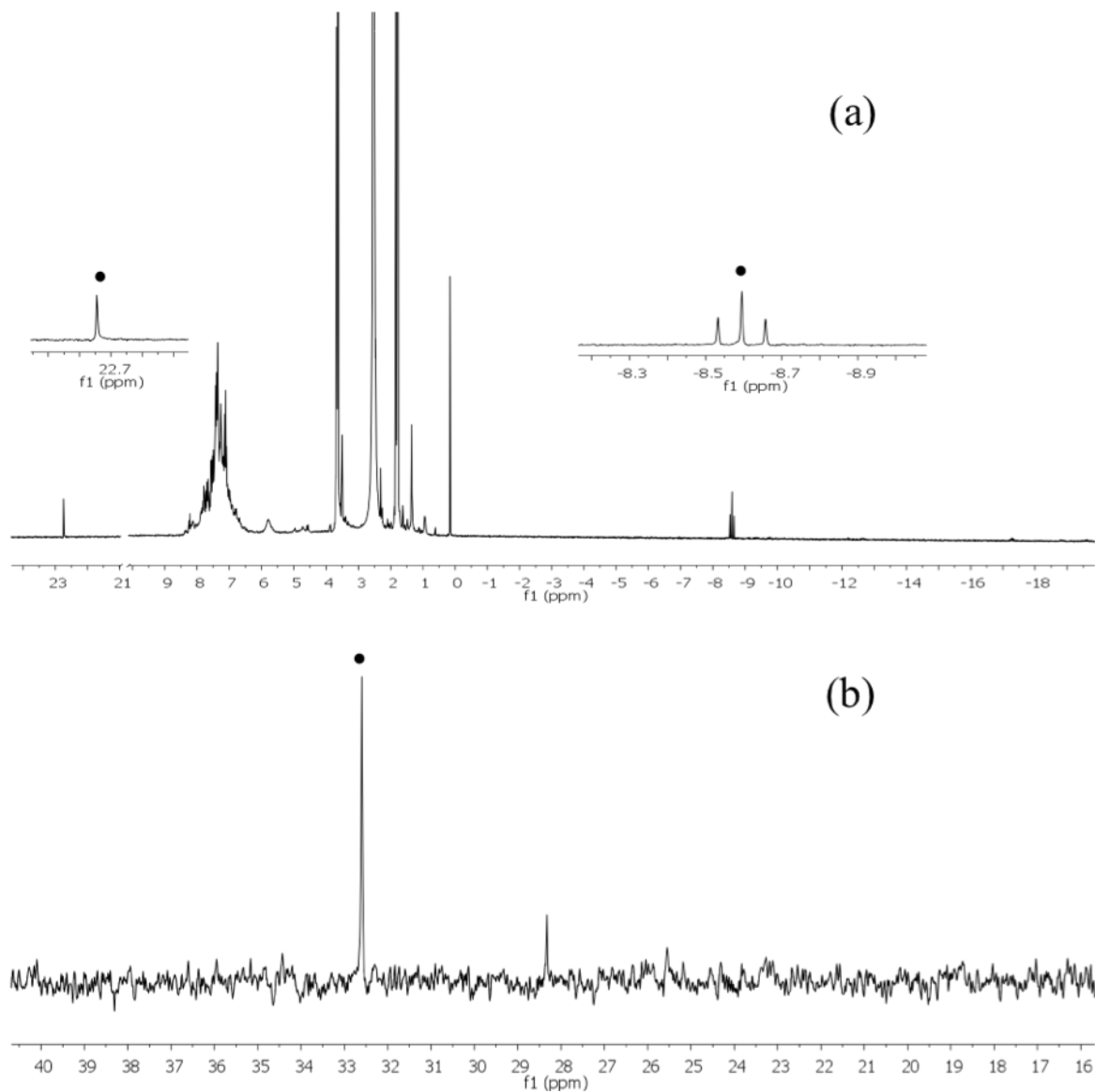


Figure S3. ¹H (a) and ³¹P{¹H} (b) NMR spectra (THF-d₈) of the yellow solid formed during the dehydrogenation of NH₃BH₃ with **1** THF/H₂O = 4/6, (•) [IrH₂{(PPh₂(o-C₆H₄CO)₂H)}].

NMR Characterization of boron species after the catalytic reaction. After completion of the catalytic reactions, a sample of the reaction mixture was transferred into a NMR tube and the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum was recorded. The spectrum obtained was compared with that of a sample prepared by mixing 85.3 mg (1.38 mmol) of H_3BO_3 with 0.110 ml of aqueous ammonia solution (25% in NH_3) (1.38 mmol) in 3 ml of $\text{THF}/\text{H}_2\text{O} = 1/1$ (See Figure S4).

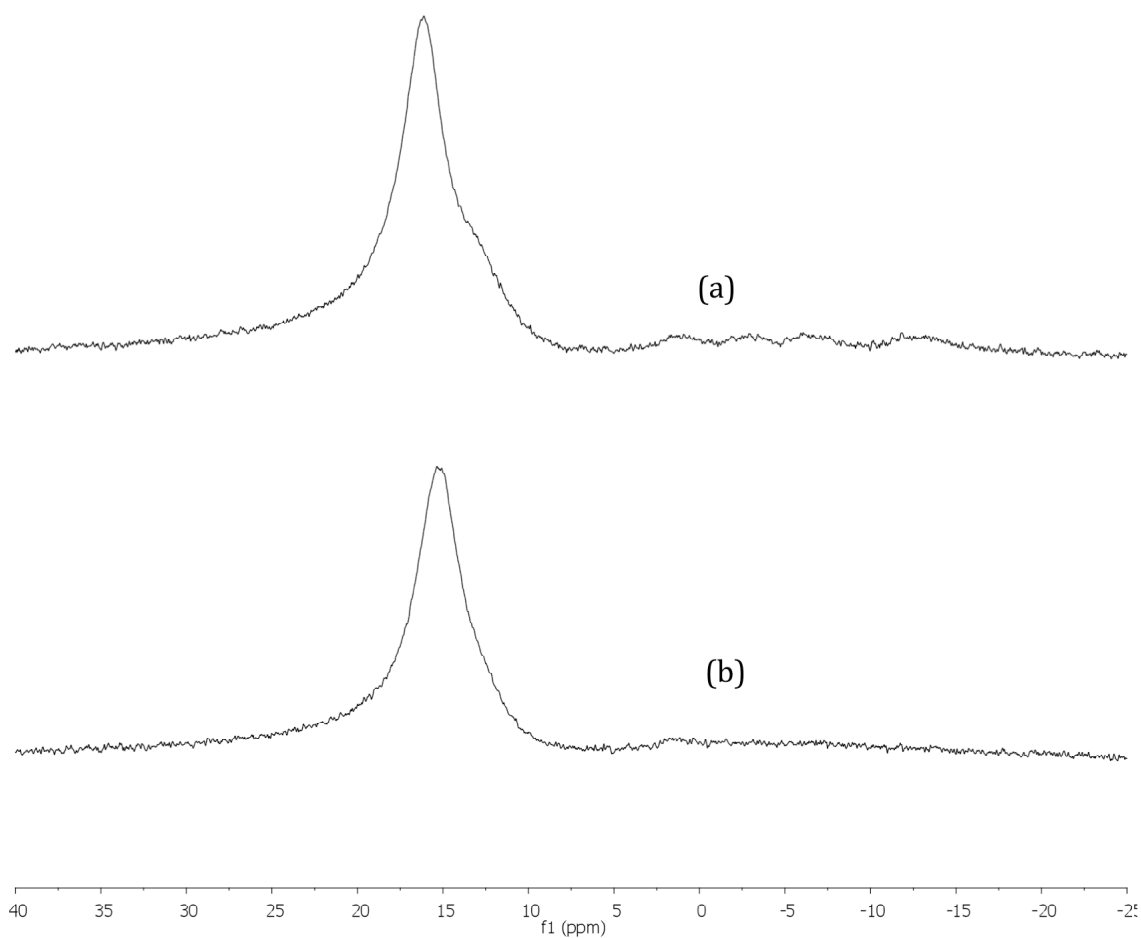


Figure S4. (a) $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of the reaction mixture after catalytic dehydrogenation of $\text{H}_3\text{N}-\text{BH}_3$. (b) $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of the sample prepared by mixing equimolar amounts of boric acid and ammonia in $\text{THF}/\text{H}_2\text{O}$.

Reaction of **1** with amines.

Formation and characterization of [IrHCl{(PPh₂(*o*-C₆H₄CO)(PPh₂(*o*-C₆H₄CNCH₃)H)] (3). To a THF suspension of **1** (30 mg, 0.037 mmol) was added 2.0M MeNH₂ solution in THF (0.15 ml, 0.074 mmol) whereupon a dissolution was obtained. Stirring during 17 h and evaporation of the solvent gave a yellow solid that was washed with diethyl ether and vacuum dried. Yield: 80%. Anal. calc. for C₃₉H₃₃ClIrOP₂·THF: C, 57.81; H, 4.63; N, 1.57. Found: C, 57.84; H, 4.73; N, 1.46. ¹H NMR (CDCl₃): δ –20.67 (t, 1H, ²J(P,H) = 14.0 Hz, IrH), 13.22 (s, 1H, N··H··O), 3.70 (s, 3H, CH₃). ³¹P{¹H} NMR (CDCl₃): δ 30.8 (d), 15.0 (d, ²J(P,P) = 7 Hz). ¹³C{¹H} NMR (CDCl₃): δ 243.9 (d, ²J(P,C) = 106 Hz, C=O), 221.8 (d, ²J(P,C) = 103 Hz, C=N); 37.3 (s, CH₃).

Reaction of **3 with H₂O.** To a THF solution of **3** (15 mg, 0.018 mmol) was added H₂O (1 ml). Stirring during 48 h and evaporation of THF gave a yellow solid, identified by NMR as an equimolar mixture of **3** and **4**.

Formation and characterization of [IrH(PPh₂(*o*-C₆H₄CO)₂(CH₃NH₂)] (4). To a THF/H₂O = 1/1 suspension of **1** (30 mg, 0.037 mmol) was added 2.0M MeNH₂ solution in THF (0.15 ml, 0.074 mmol). Stirring during 30 min gave a yellow solid that was decanted. The solid was recrystallised from dichloromethane/diethyl ether and vacuum dried. Yield: 70%. Anal. calc. for C₃₉H₃₄NIrO₂P₂·CH₂Cl₂: C, 54.12; H, 4.09; N, 1.58. Found: C, 54.44; H, 3.76; N, 1.52. ¹H NMR (CDCl₃): δ –7.94 (dd, 1H, ²J(P,H)_{cis} = 20.0 Hz, ²J(P,H)_{trans} = 130.0 Hz, IrH), 1.39 (s, 2H, NH), 2.31 (s, 3H, CH₃). ³¹P{¹H} NMR (CDCl₃): δ 30.5 (d), 25.7 (d, ²J(P,P) = 4 Hz). ¹³C{¹H} NMR (CDCl₃): δ 239.9 (d, ²J(P,C) = 102 Hz, C=O), 213.9 (d, ²J(P,C) = 5 Hz, C=O); 37.3 (s, CH₃).

Reaction of **1 with NEt₃.** a) To a THF suspension of **1** (20 mg, 0.025 mmol) was added NEt₃ (0.0068 ml, 0.050 mmol). Stirring during 24 h and evaporation of THF gave

a yellow solid identified by NMR as **1**. b) To a THF/H₂O = 1/1 suspension of **1** (20 mg, 0.025 mmol) was added NEt₃ (0.0068 ml, 0.050 mmol). Stirring during 24 h and evaporation of THF gave a yellow solid identified by NMR as [Ir₂H₂(PPh₂(*o*-C₆H₄CO))₂(μ-PPh₂(*o*-C₆H₄CO))₂].⁴

(4) F. Acha, R. Ciganda, M. A. Garralda, R. Hernández, L. Ibarlucea, E. Pinilla and M. R. Torres, *Dalton Trans.*, 2008, 4602–4611.

NMR Spectroscopy of the catalyzed reaction. Glass equipment was oven-dried and cooled in a desiccator provided with P₂O₅ before use. A pressure valve sample tube was charged with a solution of 7.5 mg (0.243 mmol) of H₃N—BH₃ in 0.25 ml of D₂O (99.96%D) and a solution of 3 mg (0.0037 mmol) of **1** in 0.75 ml of THF-d₈ whereupon some gas evolution was observed. The tube was introduced immediately in the spectrometer and the ¹H, ¹¹B{¹H} and ³¹P{¹H} NMR spectra were monitored over time. (see Figure S5).

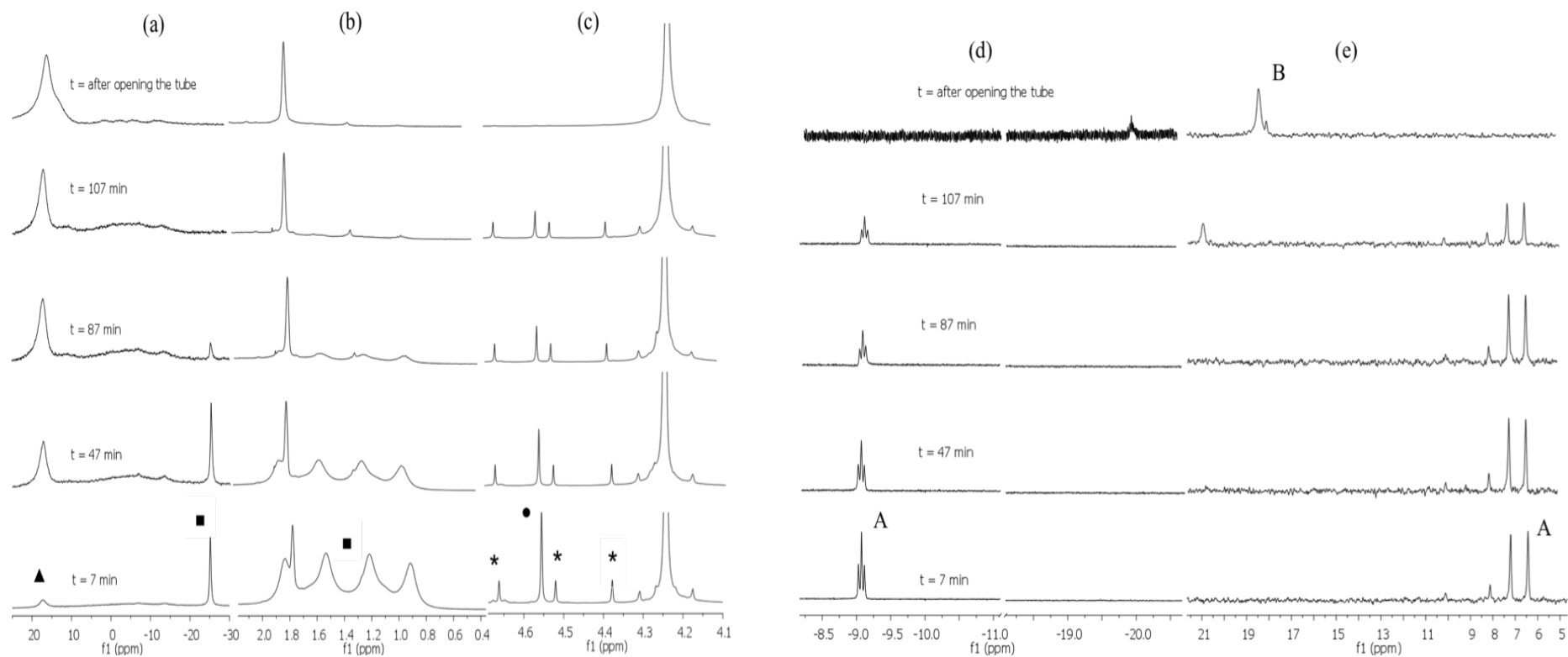


Figure S5. $^{11}\text{B}\{^1\text{H}\}$ NMR (a), ^1H NMR (b, c and d) and $^{13}\text{P}\{^1\text{H}\}$ NMR (e) spectra of the “in situ” catalytic NH_3BH_3 hydrolysis showing the gradual disappearance of NH_3BH_3 (■) (a and b), the formation of borate (▲) (a) and the evolution of HD (*) and H_2 (●) (c); the initial formation of species (A) and its transformation into (B) after completion of the catalytic reaction (d and e).

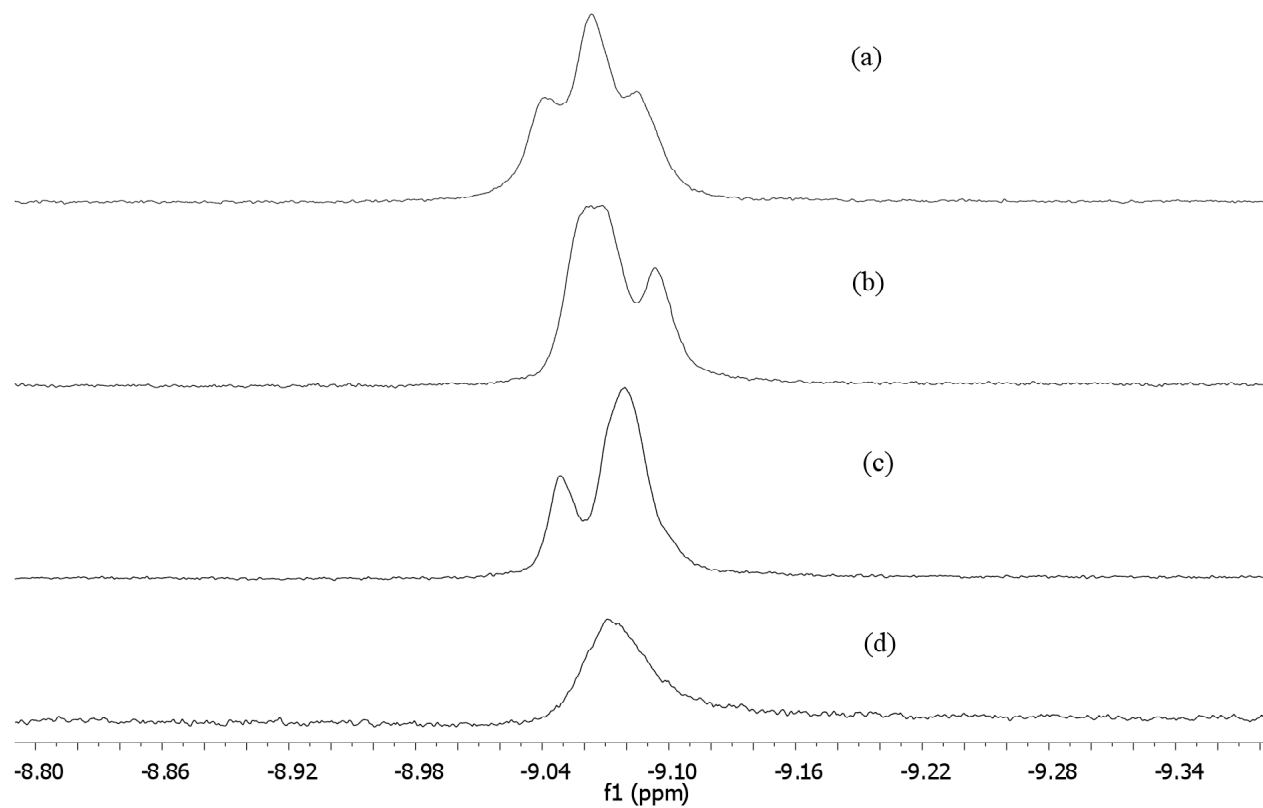


Figure S6. ^1H NMR spectra of the “in situ” catalytic NH_3BH_3 hydrolysis in the hydride region.
(a) ^1H NMR spectrum; (b) ^{31}P irradiated at 7.31 ppm; (c) ^{31}P irradiated at 6.20 ppm; (d) $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum