Electronic Supporting Information for

Transition metal catalysed dehydrogenation of amine-borane fuel blends

Sib Sankar Mal, Frances H. Stephens and R. Tom Baker*

1.0 General Experimental:

Unless otherwise stated, all synthetic manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk line or glovebox techniques using an MBraun Labmaster glove box. All solvents were purchased from Sigma Aldrich and were dried and thoroughly deaerated. Toluene and hexanes (both HPLC grade), were dried with activated alumina using either a Glass Contour or MBraun solvent purification system and then stored over 4 Å molecular sieves. Alternately, THF and 1,2-dimethoxyethane (both HPLC grade) were distilled from Na and benzophenone prior to use. Sulfolane was dried *via* azeotropic distillation with toluene or by addition of molecular sieves and borane-dimethylsulfide was purged with N_2 before use. All other chemicals were purchased from Sigma Aldrich, with the exception of ammonia-borane (GFS Chemicals), sulfolane (Alfa Aesar), $[RhCl(1,5\text{-cod})]_2$ (Strem), and $[RuCl_2\{^tBuPCH_2CH_2NH_2\}_2]$ (Kanata Chemical Company, Canada). These reagents were used as received and $RuCl_2(PMe_3)_4$ was prepared using standard literature procedures.[1] The NMR solvent C_6D_6 was purchased from Cambridge Isotope Laboratories and distilled from Na and benzophenone. All ^{11}B NMR measurements were performed using either a 400 MHz or 500 MHz Bruker instrument.

1.1 Gas Burette Measurements:

The volume of H_2 was quantitatively measured using a gas burette with pressure equalizing against atmospheric pressure. Standard atmospheric pressure was assumed alongside ideal gas behavior. As in previous investigations the burette was filled with water,[2] or mineral oil, with near identical H_2 release being obtained. When water displacement was recorded, the vapor pressure of water was considered when calculating the partial pressure of H_2.

In a typical procedure, AB (83 mg, 2.66 mmol), SBAB (232 mg, 2.66 mmol), and either $[RhCl(1,5\text{-cod})]_2$ (**1**) (13 mg, 0.03 mmol), $[RuCl_2\{^tBuPCH_2CH_2NH_2\}_2]$ (**2**) (15 mg, 0.03 mmol), $RuCl_2(PMe_3)_4$ (**3**) (13 mg, 0.03 mmol), Ni/BN (10 mg) or Fe/TiO_2 (10 mg) were weighed into a round bottom Schlenk flask fitted with a side arm. The Schlenk flask was attached to the hydrogen burette *via* tubing and the vessel was lowered into a preheated oil bath. Agitation was provided using a stirrer bar and care was taken to ensure that the rate of agitation was comparable in each run, with the same type of stir bar used in each instance. After a short reaction period (*ca* 30 seconds) the reaction vessel was opened up to the burette enabling readings to commence. The start of the reaction was assumed to be the moment the flask was lowered into the oil bath and pressure was equalized before each reading.

2.0 Preparation of *sec*-butylamine borane:[3]

1st Method:

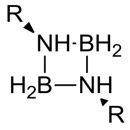
Sec-butylamine (10 ml, 101 mmol) was added dropwise at room temperature to a solution of $BH_3{}^{\cdot}SMe_2$ (10 ml, 100 mmol) in hexanes (20 mL). After a 3-4 h period the ^{11}B NMR spectrum of this mixture demonstrated that complete consumption of $BH_3{}^{\cdot}SMe_2$ had occurred. All the volatile components of the reaction mixture were removed *in vacuo* to afford the product as a colourless liquid (7.9 g, 95.2 %). Further purification of the product can be achieved using distillation at 30-40 °C to a cold trap (-80 °C) under high vacuum. mp 2 °C. ^{1}H NMR(C_6D_6): δ 3.84, 3.71 (N*H*), 2.59 (mult, 1H, C*H*), 1.7 (br, 3H, BH_2),1.50, 1.21 (mult, 1H, CH_2), 1.01 (d, 6, 3H, CH_3), 0.66 (tr, 7.5, 3H, CH_3). ^{13}C: 55.6, 28.6, 18.1, 10.1 ppm. ^{11}B: -19.5 ppm (q, 97).

2nd Method:

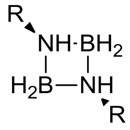
Sec-butylamine (8 ml, 81 mmol) was added dropwise at 0 ^{o}C to a solution of $BH_3{}^{\cdot}SMe_2$ (9 mL, 91 mmol) and the reaction mixture allowed to warm to room temperature. The ^{11}B NMR spectrum demonstrated that complete consumption of $BH_3{}^{\cdot}SMe_2$ had occurred. All the volatile components of the reaction mixture were removed *in vacuo* to afford the product as a colourless liquid (6.53 g, 98.3 %).

2.1 Thermolysis of *sec*-butylamine borane:

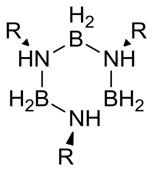
Sec-butylamine borane (106 mg, 1.2 mmol) was heated at 85 ^{o}C using a preheated sand bath and the reaction was monitored using ^{11}B NMR spectroscopy with samples taken from the reaction solution at 4 and 24 h and dissolved in C_6D_6 (Figure S1). In a separate experiment, this procedure was repeated at 60 ^{o}C (Figure S2). Tri(*N*-*sec*-butyl)borazine: ^{1}H NMR (C_6D_6): δ 4.84 (br, 1H, BH), 3.43 (mult, 1H, C*H*), 1.62, 1.55 (ov mult, 1H, CH_2), 1.28 (d, 6.5, 3H, CH_3), 0.83 (tr, 7.5, 3H, CH_3). ^{13}C: 58.7, 33.3, 25.2, 11.9 ppm. ^{11}B: 32.8 ppm (br). Cyclodi(*N*-*sec*-butyl)borazane isomers: ^{1}H: 3.1, 2.95 (major), 2.73, 2.39, 2.29, 2.2 (br, BH), 2.9, 2.8, 2.7, 2.5, (br, NH), 1.45-1.15 (ov mult, CH_2), 0.924, 0.921, 0.89, 0.88 (tr, 6.5, CH_3),0.78, 0.77 (ov), 0.69 (tr, 7.5, CH_3). ^{13}C: 60.38, 58.63 (ov), 28.7, 28.5, 27.4, 18.1, 18.0, 10.44, 10.37 ppm. ^{11} B: -4.4, -5.3(tr, 109.39) ppm. Cyclotri(*N*-*sec*-butyl)borazane isomers: ^{1}H NMR (C_6D_6): δ 2.8-2.3 (ov br, NH_2), 0.8-0.68 (ov tr, CH_3).BH at 2.35, 2.24, 1.95. ^{13}C: 57.61, 57.56, 57.47, 57.44, 57.22, 57.15, 57.10, 57.04 (minor), 56.69, 56.62 (major), 28.19 (br), 27.87 (major), 27.56, 27.55, 27.52, 27.46, 27.42 (minor), 18.01, 17.14, 17.10, 17.05, 16.98, 16.93 (major), 16.32, 16.31, 16.21, 16.18, 11.54, 11.51, 11.50. 11.48, 11.42, 11.40, 11.33, 11.32 ppm. ^{11}B: -7.8, -9.4, -10.0, -11.0 ppm (tr, 115, BH_2). (μ-*sec*-butylamino)diborane: ^{1}H NMR (C_6D_6): δ 3.65, 3.52 (br, NH), 2.64 (ov mult, 1H, C*H*), 1.1, 0.8 (mult, 1H, CH_2), 0.68 (d, 6.5, 3H, CH_3), 0.40 (tr, 7.5, 3H, CH_3), 0.18, 0.15 (br tr d, 10, 4). ^{13}C: 52.6, 28.7, 18.1, 9.7 ppm. ^{11}B: -23.1, -23.7 (tr d, 128, 28) ppm.



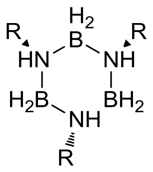
ee-meso



ee-C_2



eee (C_3 and C_s)



eea-multiple diastereomers

In proposing structures for the aminoborane oligomers, the singlets at –4.4 and –5.3 ppm in the ^{11}B NMR spectrum, together with the ^{1}H and ^{13}C NMR spectra and product evolution with time (Figure S3), are consistent with the two diastereoisomers of the equatorial-equatorial (ee) cyclic dimers. Similarly the four overlapping resonances between -8 and -11 ppm are consistent with the eee and eea cyclic trimer diastereoisomers as confirmed by mass spectrometry (Figure S4). The *sec*-butylaminodiborane compound was identified by its ^{11}B NMR chemical shift and coupling constants.[4] Spectroscopic and MS characterization of the crude reaction mixture was consistent with formation of N’, N’’,N”’-tri(sec-butyl)borazine in high yield (Figures S5-8). Measured hydrogen release over time at 60 °C is shown in Figure S16.

2.2 Thermolysis of SBAB/AB mixtures:

Solid NH_3BH_3 (83 mg, 2.66 mmol) was added to *sec*-butylamine borane (232 mg, 2.66 mmol) and the resulting mixture was heated at 85 ^{o}C using a preheated oil bath. The reaction was monitored using ^{11}B NMR spectroscopy by dissolving a sample in THF/C_6D_6/4:1 (Figure S9). Measured hydrogen release over time at 60 °C is shown in Figure S17.

2.3 Thermolysis of AB and SBAB/AB mixtures in sulfolane:

Solid NH_3BH_3 (100 mg, 3.22 mmol) was added to sulfolane (2.52 g, 21.0 mmol) and the resulting mixture was heated at 80 ^{o}C using a preheated oil bath. The reaction was monitored using ^{11}B NMR spectroscopy (Figure S10). After 24 h the reaction was complete and products included borazine (major, 30.5), polyborazylene (28), *B-(*cyclodiborazanyl)amine-borane[5] (-3, -11, -26) and trace amounts of cyclotriborazane (-10.5) and μ-aminodiborane[4] (-27 ppm).

In a separate reaction vessel, solid NH_3BH_3 (100 mg, 3.22 mmol) was added to *sec*-butylamine borane (280 mg, 3.22 mmol) followed by sulfolane (2.52 g, 21.0 mmol). The resulting mixture was heated at 80 ^{o}C using a preheated oil bath and the reaction was monitored using ^{11}B NMR spectroscopy by dissolving a sample in THF/C_6D_6/4:1 (Figure S11).

2.4 General Procedure for catalysed dehydrogenation of *sec*-butylamine-borane:

Sec-butylamine-borane (232 mg, 2.66 mmol) was mixed with a given pre-catalyst (1 mol %) and the mixture was heated at 60 ^{o}C in a preheated oil bath. The resulting reaction was monitored using ^{11}B NMR spectroscopy with samples taken for analysis at approximately 1 h, 3 h, and 5 h and dissolved in C_6D_6. Catalysts used in this procedure were $[RhCl(1,5\text{-cod})]_2$ (**1**) (13 mg, 0.03 mmol), $[RuCl_2\{^tBuPCH_2CH_2NH_2\}_2]$ (**2**) (15 mg, 0.03 mmol), $RuCl_2(PMe_3)_4$ (**3**) (13 mg, 0.03 mmol). One example is shown in Figure S12.

2.5 General Procedure for catalysed dehydrogenation of SBAB/AB mixtures:

Solid NH_3BH_3 (83 mg, 2.66 mmol) was added to *sec*-butylamine borane (232 mg, 2.66 mmol) and the catalyst (1 mol % **1, 2** or **3**) was then added to the resulting mixture. The reaction solution was heated at 60 ^{o}C using a preheated oil bath and monitored using ^{11}B NMR spectroscopy by dissolving a sample in THF/C_6D_6/4:1; one example is shown in Figure S13. Measured hydrogen release over time at 60 °C is shown in Figure S17.

2.6 General Procedure for catalysed dehydrogenation of SBAB/AB mixture in ILs:

Solid NH_3BH_3 (83 mg, 2.66 mmol) was added to *sec*-butylamine borane (232 mg, 2.66 mmol) forming a homogeneous solution. After addition of (EMIM)[$EtSO_4$] (200 mg, 0.85 mmol) and 1 mol % catalyst **1**, the resulting solution was heated at 80 ^{o}C using a preheated oil bath and monitored using ^{11}B NMR spectroscopy; examples at 60 °C and 80 °C are shown in Figures S14 and S15. Measured hydrogen release over time at 60 °C is shown in Figure S18.

2.7 Preparation of Fe/TiO_2 catalyst

Solid $FeCl_3 \cdot 6H_2O$ (1 mmol, 0.270 g), TiO_2 (10 mmol, 0.798 g) and $NaBH_4$ (100 mmol, 3.783 g) were added to a 500 mL round-bottom flask. To these solids was cautiously added distilled water (25 mL) which induced the formation of H_2 gas in a vigorous and exothermic reaction. The solution was allowed to stir overnight (approximately 24 hours) and was then filtered, washed with water, and dried over a 24 hour period. The collected particles were reacted with a second aliquot of $NaBH_4$ (100 mmol, 3.783 g) and H_2O (25 mL) to ensure that all the $FeCl_3$ had been reduced. After stirring for an additional 24 hours the solution was filtered and the catalyst particles were dried *in vacuo* to afford 0.53 g of brown solid.

2.8 Preparation of Ni/BN catalyst

A similar procedure as for $FeCl_3$ on TiO_2 was applied with BN (10 mmol, 0.248 g) in place of TiO_2, and $NiCl_2 \cdot 6H_2O$ in place of $FeCl_3 \cdot 6H_2O$ (1 mmol, 0.238 g) to give 0.187 g black solid.

2.9 General Procedure for heterogeneous catalysed dehydrogenation of SBAB/AB mixture:

Solid NH_3BH_3 (83 mg, 2.66 mmol) was added to *sec*-butylamine borane (232 mg, 2.66 mmol) forming a homogeneous solution and the catalysts (Ni/BN, 10 mg or Fe/TiO_2, 10 mg) were added to the resulting mixture. The reaction solution was heated at 80 °C using a preheated oil bath and monitored using ^{11}B NMR. Measured hydrogen release over time at 60 °C is shown in Figures S19 and S20.

2.10 Hg-test for catalysed dehydrogenation of SBAB/AB mixture using [RhCl(1,5-cod)]$_2$ precatalyst:

Solid NH_3BH_3 (83 mg, 2.66 mmol) was added to *sec*-butylamine borane (235 mg, 2.67 mmol) forming a homogeneous solution and 1 mol % of [RhCl(1,5-cod)]$_2$ precatalyst was added to the resulting mixture followed by 736 mg of Hg. The reaction solution was heated at 80 °C using a preheated oil bath. Measured hydrogen release over time at 60 °C is shown in Figure S21.

3.0 Figures:

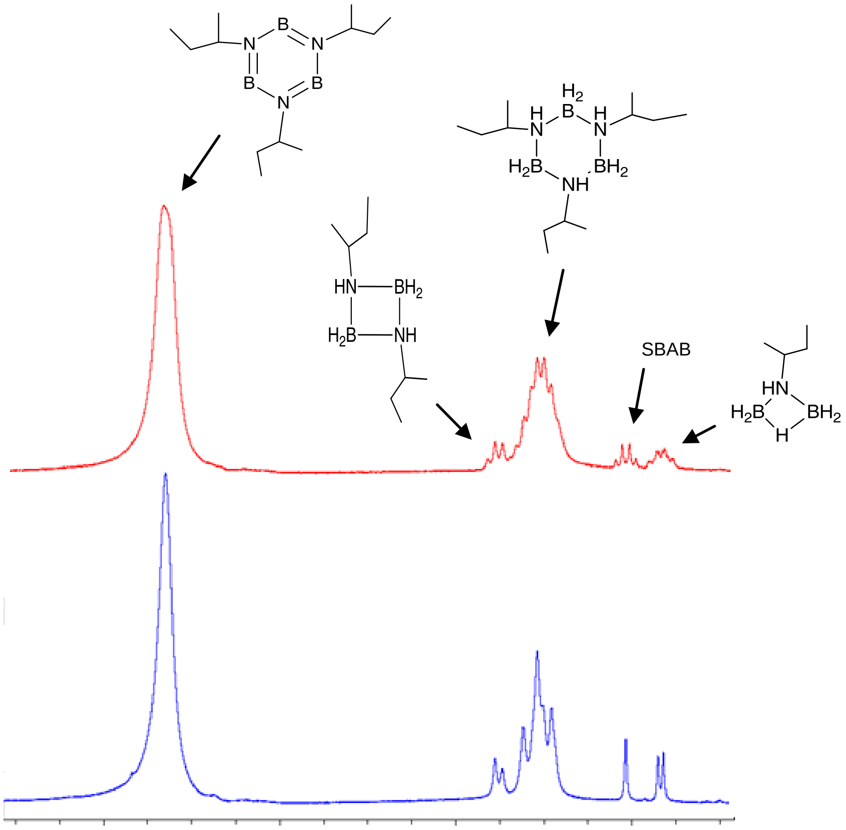


Figure S1: ^{11}B NMR spectra (RT, sample dissolved in C_6D_6) of neat SBAB after 4 h thermolysis at 85 °C. Bottom spectrum is proton-decoupled.

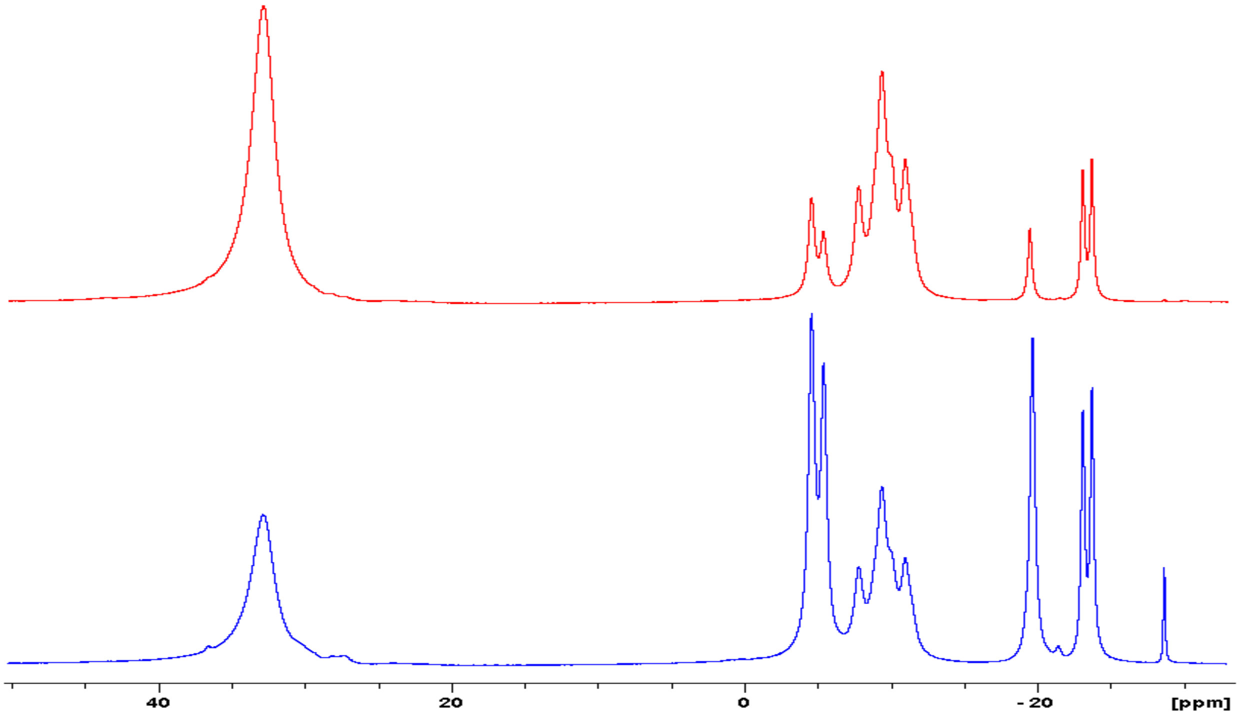


Figure S2: ^{11}B{^{1}H} NMR spectra (RT, sample dissolved in C_6D_6) of neat SBAB after 3 (bottom) and 24 h (top) thermolysis at 60 ^{o}C.

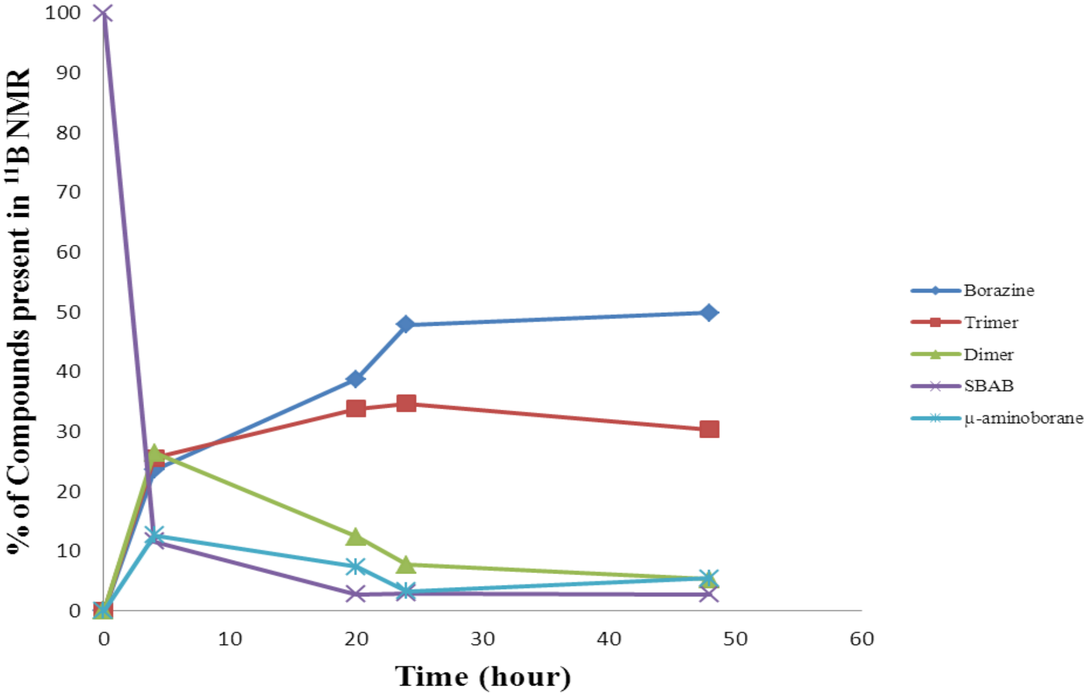


Figure S3: Product distribution *vs*. time for SBAB thermolysis at 60 ^{o}C determined from integration of ^{11}B NMR spectra.

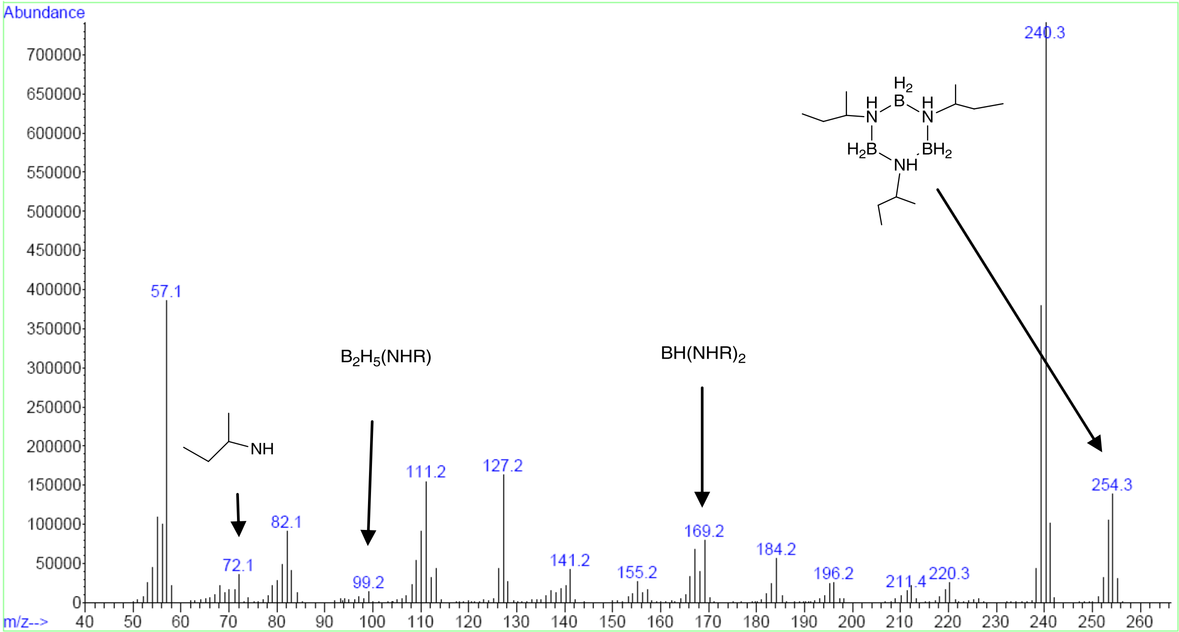


Figure S4: Mass spectrum of SBAB thermolysis mixture after 3 h at 60 °C.

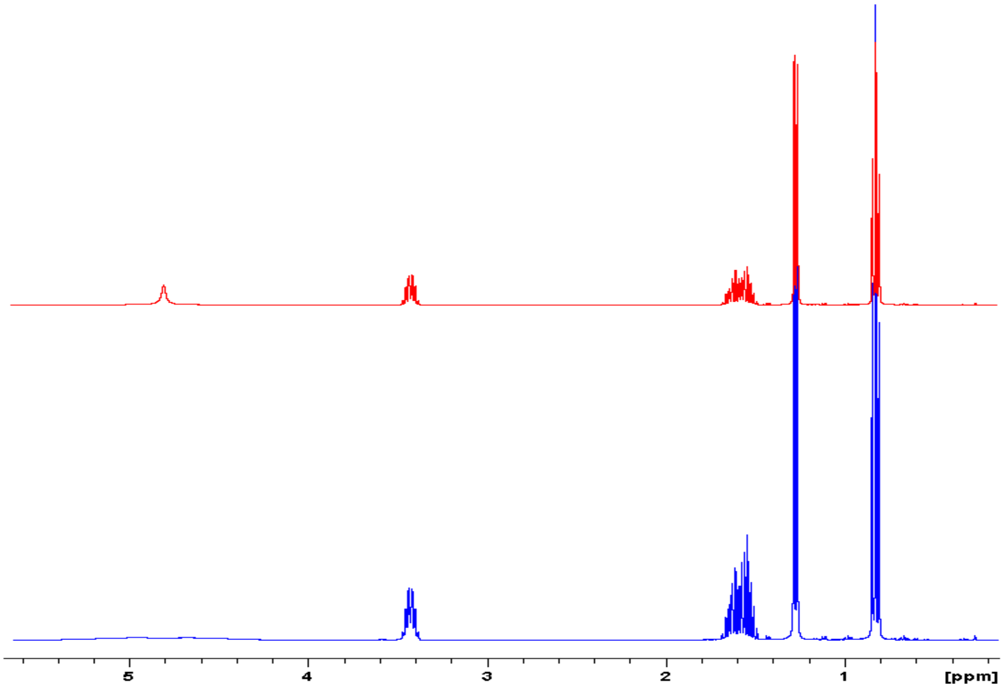


Figure S5: ^{1}H NMR spectra (RT, sample dissolved in C_6D_6) of N’,N’’,N’’’-tri(*sec*-butyl)borazine from crude reaction mixture of SBAB thermolysis after 40 h at 85 °C). Bottom spectrum is boron-decoupled.

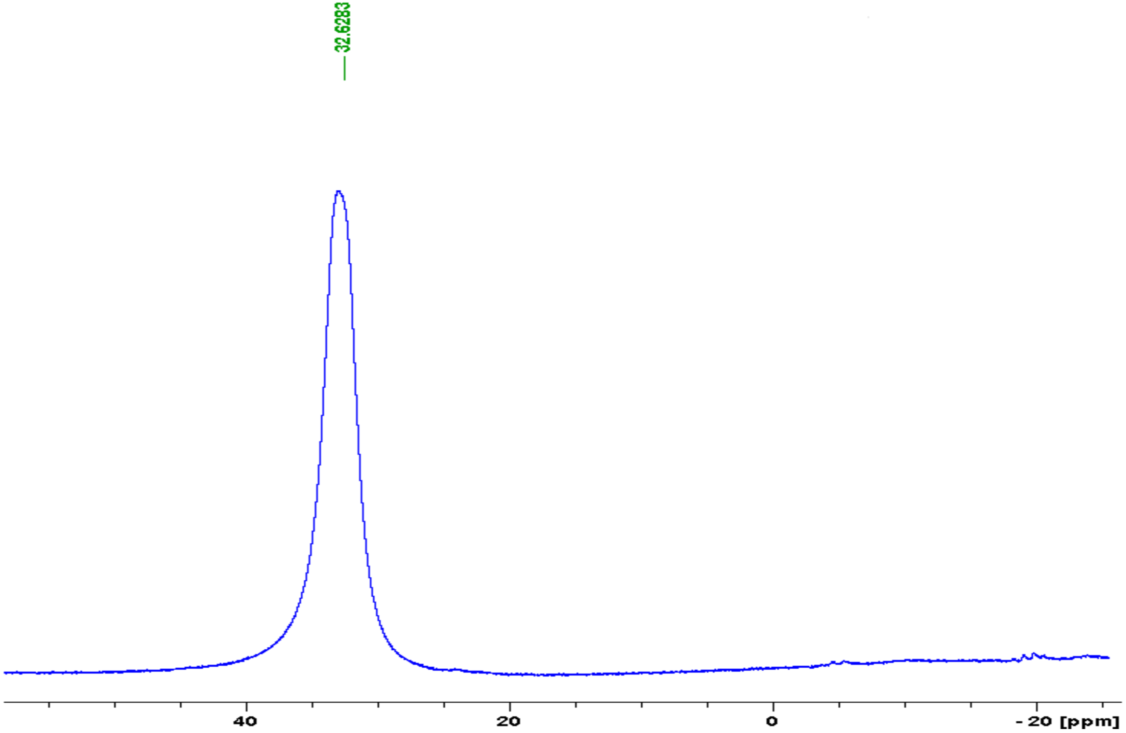


Figure S6: ^{11}B NMR spectrum (RT, sample dissolved in C_6D_6) of N’,N’’,N’’’-tri(*sec*-butyl)borazine from crude reaction mixture of SBAB thermolysis after 40 h at 85 ^{o}C).

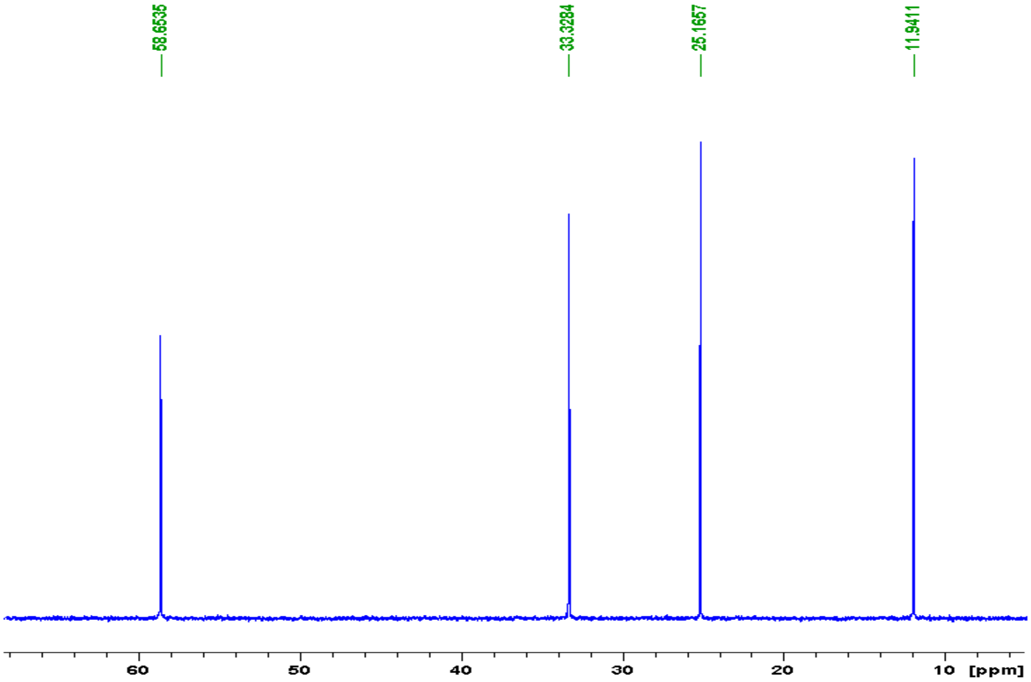


Figure S7: ^{13}C NMR spectrum (RT, sample dissolved in C_6D_6) of N’,N’’,N’’’-tri(*sec*-butyl)borazine from crude reaction mixture of SBAB thermolysis after 40 h at 85 ^{o}C).

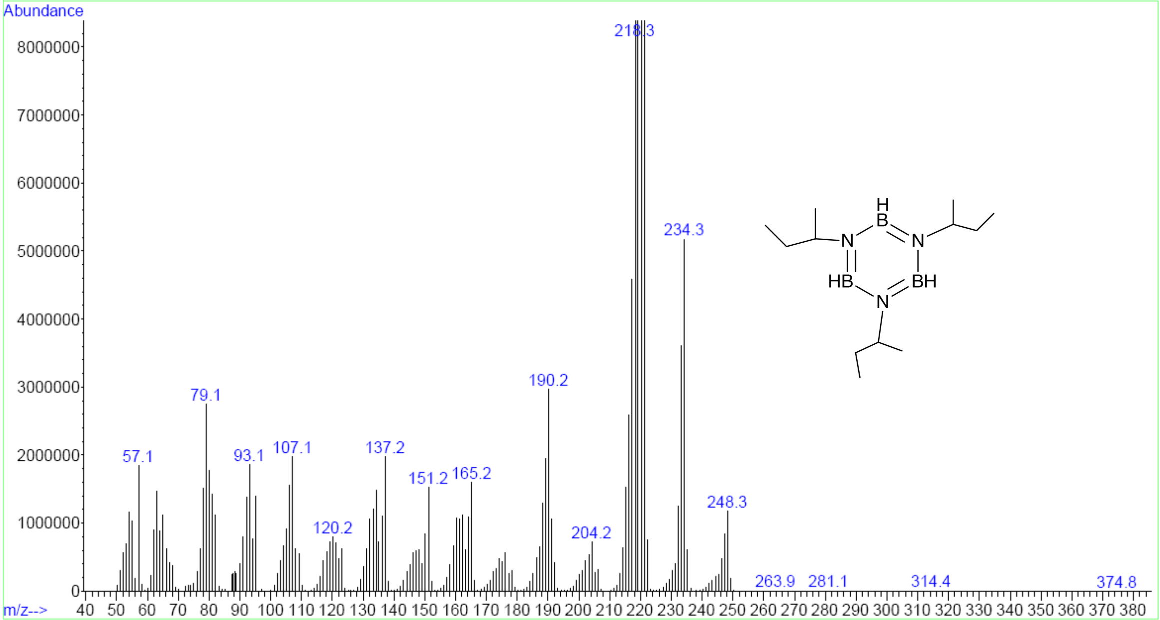


Figure S8: Mass spectrum of N’,N’’,N’’’-tri(*sec*-butyl)borazine from crude reaction mixture of SBAB thermolysis after 40 h at 85 °C)..

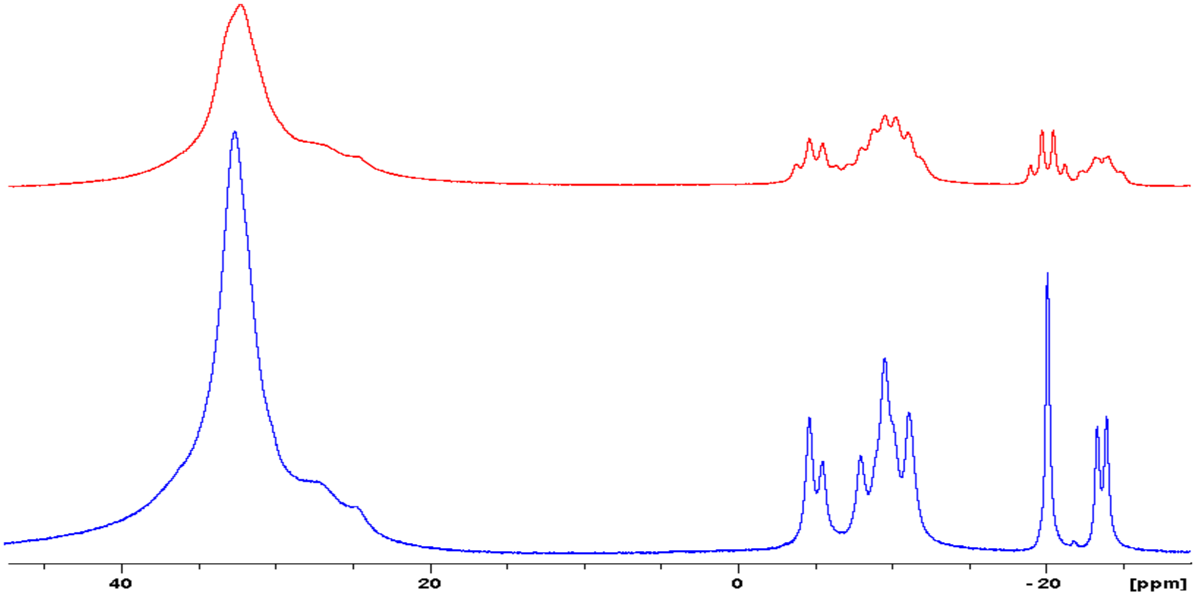


Figure S9: ^{11}B NMR spectra (RT, sample dissolved in 4:1 THF/C_6D_6) of SBAB/AB mixture after 4 h thermolysis at 60 °C. Bottom spectrum is proton-decoupled.

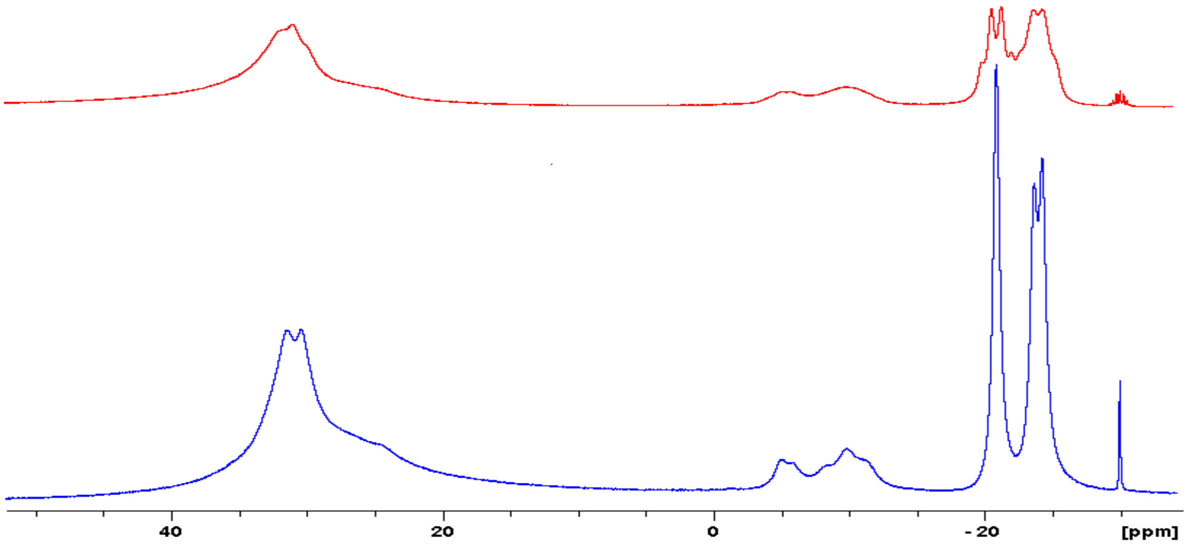


Figure S10: ^{11}B NMR spectra (RT, sample dissolved in THF/C_6D_6) of SBAB/AB mixture after 24 h thermolysis in sulfolane at 80 °C. Bottom spectrum is proton-decoupled.

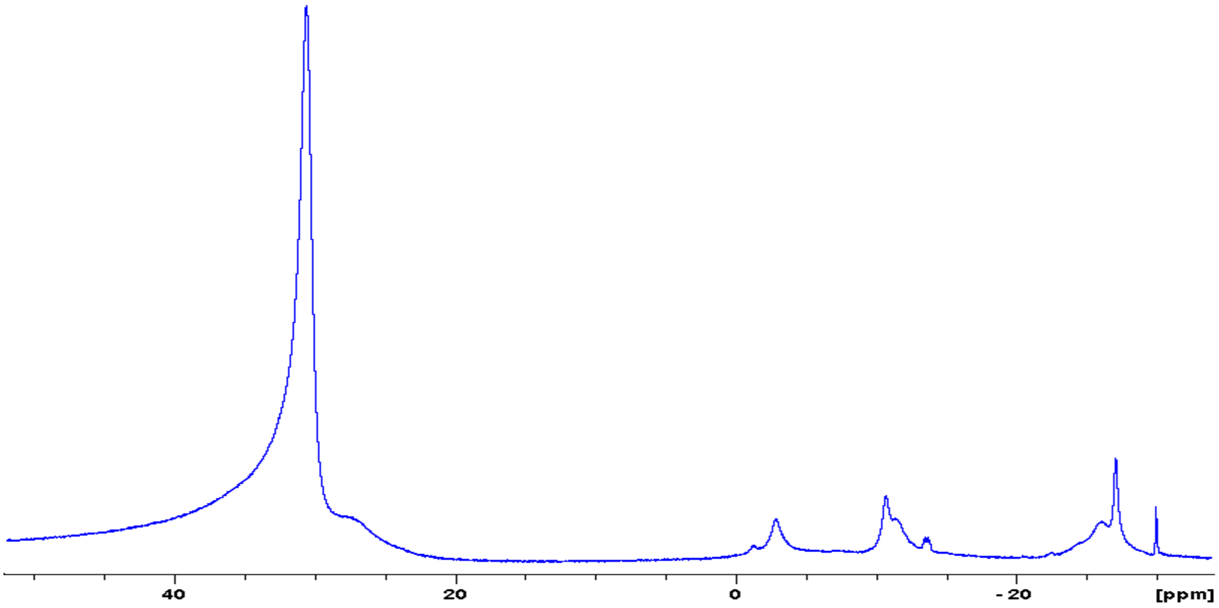


Figure S11: ^{11}B{^{1}H} NMR spectra (RT, sample dissolved in THF/C_6D_6) of AB after 24 h thermolysis at 80 °C in sulfolane.

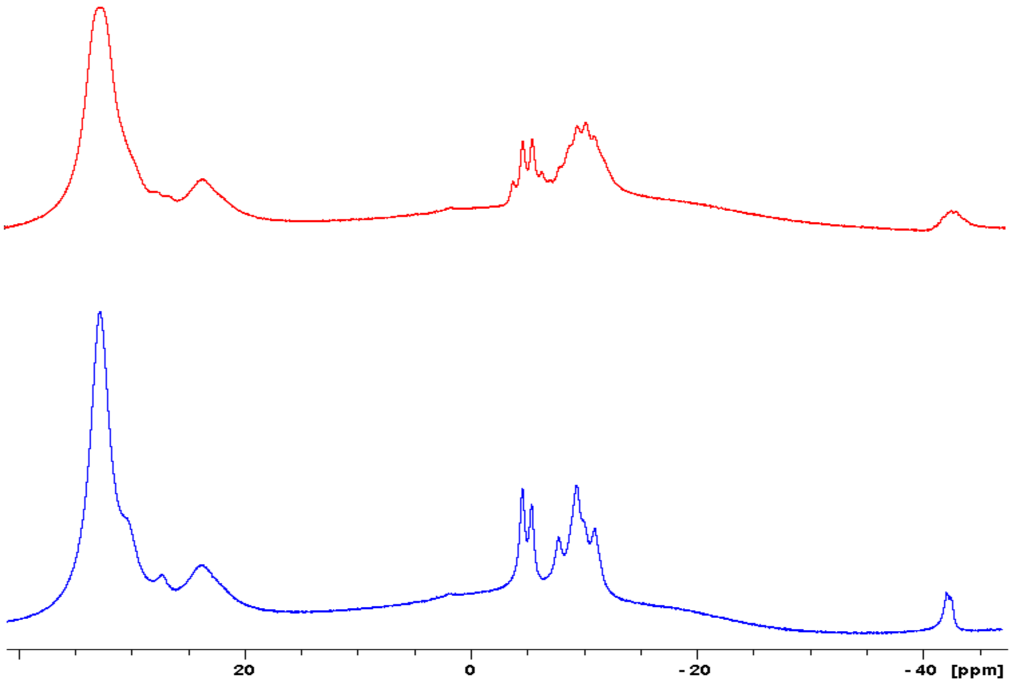


Figure S12: ^{11}B NMR spectra (RT, sample dissolved in C_6D_6) of neat SBAB catalyzed by 2 mol% [$RuCl_2\{^tBuPCH_2CH_2NH_2\}_2$] after 21 h at 50 °C. Bottom spectrum is proton-decoupled.

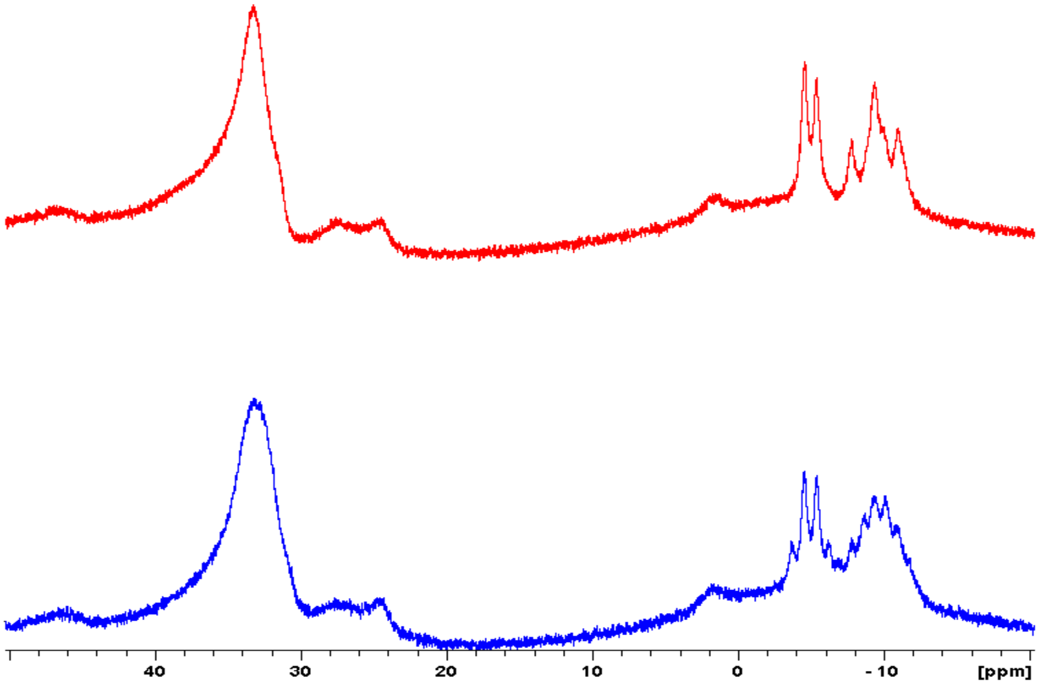


Figure S13: ^{11}B NMR spectra (RT, sample dissolved in C_6D_6) of SBAB/AB mixture catalyzed by 2 mol% [RhCl(1,5-cod)]$_2$ after 50 h at 50 °C. Top spectrum is proton-decoupled.

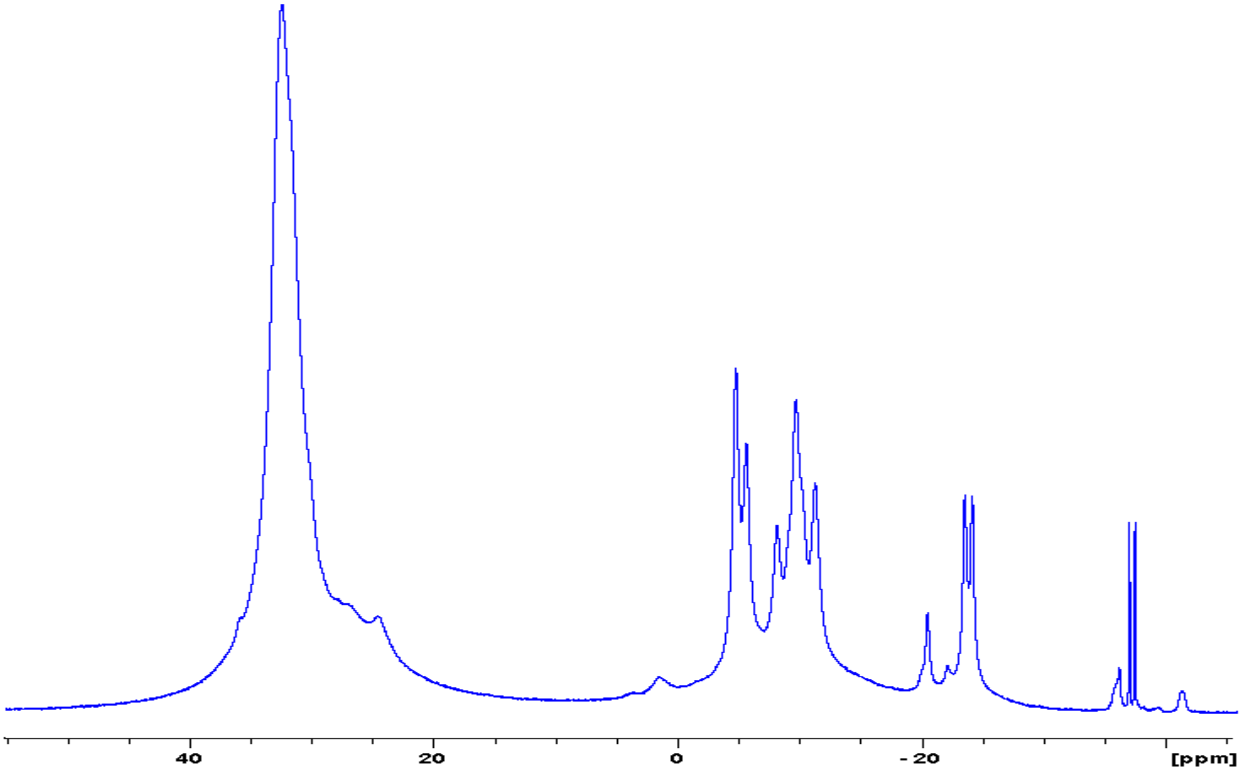


Figure S14: $^{11}B\{^{1}H\}$ NMR spectra (RT, sample dissolved in C_6D_6) of SBAB/AB mixture catalyzed by 2 mol% [Ru $Cl_2(PMe_3)_4$] in (EMIM)$EtSO_4$ after 23 h at 60 °C.

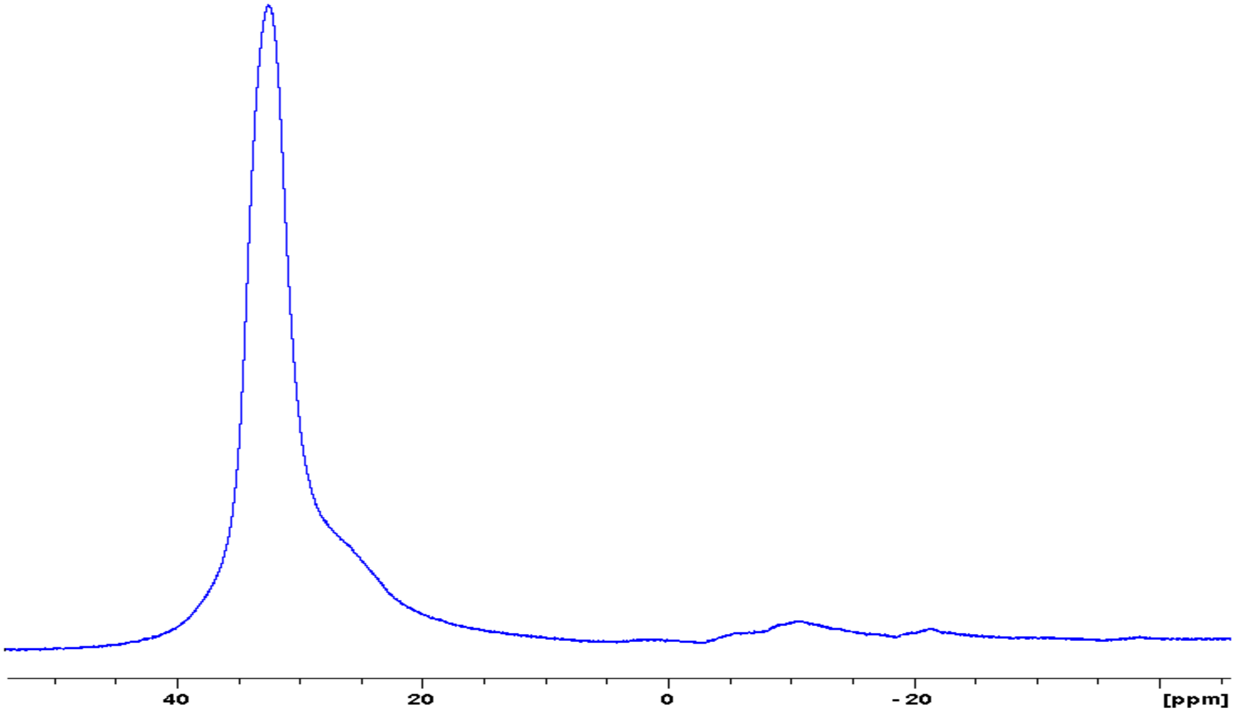


Figure S15: $^{11}B\{^{1}H\}$ NMR spectra (RT, sample dissolved in C_6D_6) of SBAB/AB mixture catalyzed by 2 mol% [Ru $Cl_2(PMe_3)_4$] in (EMIM)$EtSO_4$ after 23 h at 80 °C.

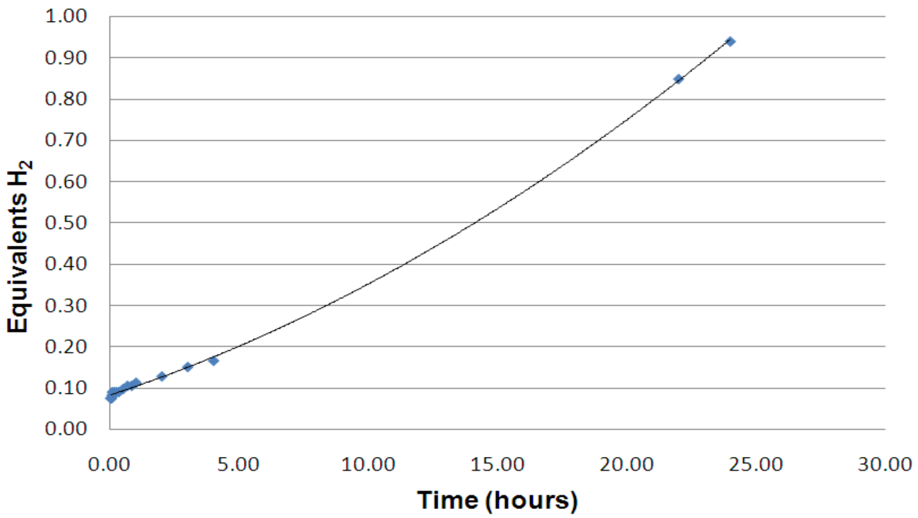


Figure S16: H_2 release from neat SBAB thermolysis at 60 °C

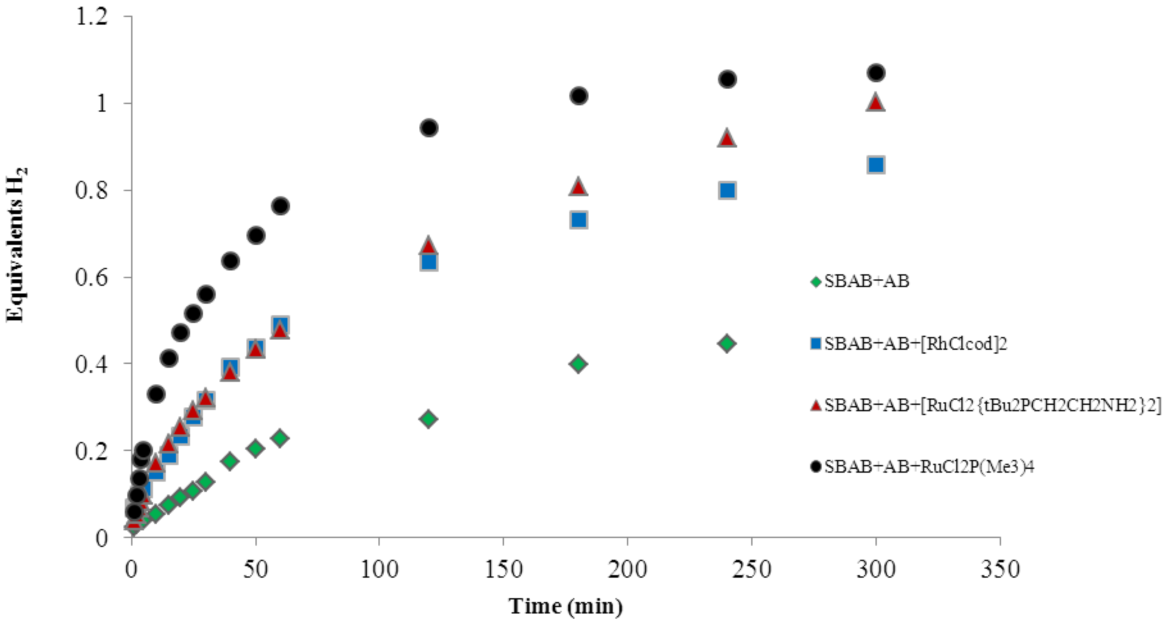


Figure S17: H_2 release from SBAB/AB solution using 1 mol% catalyst at 60 °C

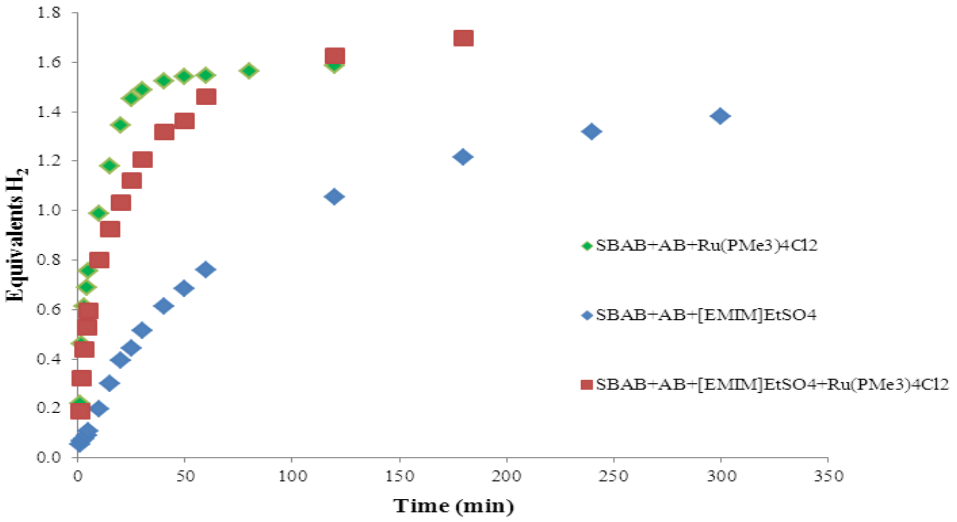


Figure S18: H_2 release from SBAB/AB mixture in ionic liquid using 1 mol% catalyst at 80 ^oC

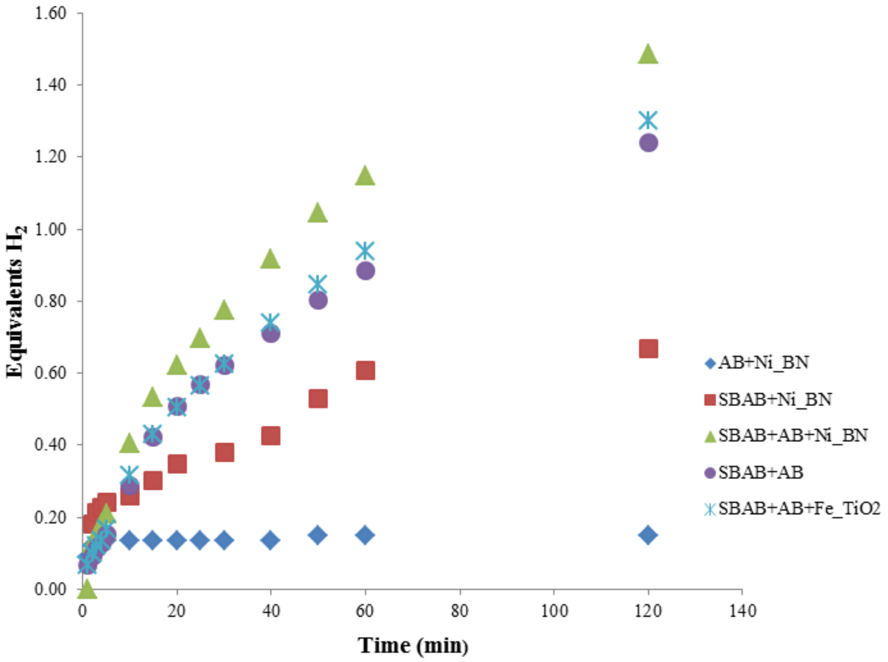


Figure S19: H_2 release from SBAB/AB mixture using heterogeneous catalysts at 80 ^oC

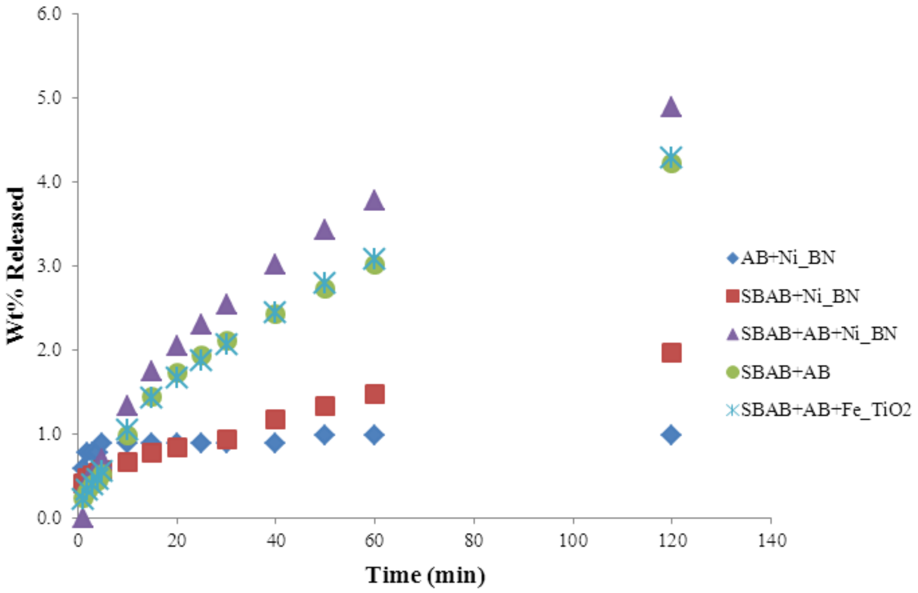


Figure S20: Dehydrogenation of SBAB and SBAB/AB mixture using base metal heterogeneous catalysts at 80 °C

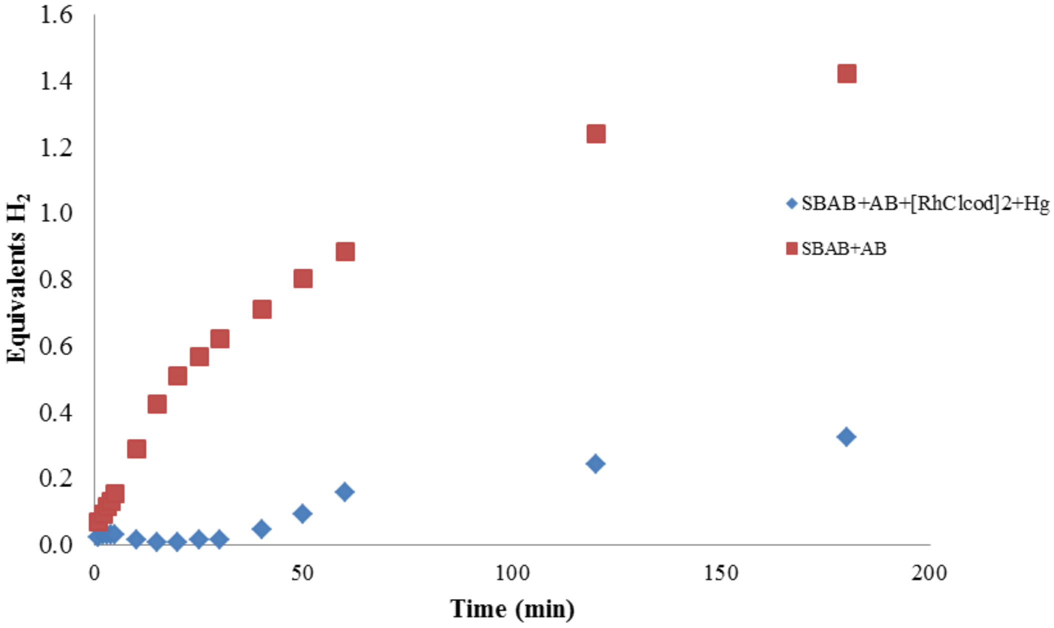


Figure S21: Dehydrogenation of SBAB/AB mixture using 1 mol% catalyst at 80 °C and the Hg-test.

Table S1. Metal-catalysed dehydrogenation of equimolar SBAB/AB mixture at 60 °C

Catalyst	Time (h)	Equivalents H_2
$[Rh(\mu\text{-}Cl)](1,5\text{-}cod)]_2$(**1**)	23	1.38
$[RuCl_2\{^tBu_2PCH_2CH_2NH_2\}_2]$ (**2**)	20	1.31
$RuCl_2(PMe_3)_4$ (**3**)	23	1.15

4.0 References:

1 J. A. Staler and G. Wilkinson *J. Chem. Soc., Dalton Trans.*, 1984, 1731; J. Gotzig, R. Werner and H. Werner *J. Organomet. Chem.* 1985, **285**, 99.

2 N. Blaquiere, S. Diallo-Garcia, S. I. Gorelsky, D. A. Black and K. Fagnou, *J. Am. Chem. Soc.*, 2008, **130**, 14034-14035.

3 Y. Yamamoto, K. Miyamoto, J. Umeda, Y. Nakatani, T. Yamamoto and N. Miyaura, *J. Organomet. Chem.*, 2006, **691**, 4909-4917.

4 D. F. Gaines and R. Schaeffer, *J. Am. Chem. Soc*. 1964, **86**, 1505-1507; L. D. Schwartz and P. C. Keller, *J. Am. Chem. Soc*. 1972, **94**, 3015-3018; X. Chen, J.-C. Zhao and S. G. Shore, *J. Am. Chem. Soc.* 2010, **132**, 13332-13345.

5 V. Pons, R. T. Baker, N. K. Szymczak, D. J. Heldebrant, J. C. Linehan, M. H. Matus, D. J. Grant and D. A. Dixon, *Chem. Commun.*, 2008, 6597-6599.