

## Selective Dehydrogenation of Ammonia Borane to Polycondensated BN Rings Catalysed by Ruthenium Olefin Complexes

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## I. GENERAL REMARKS

All experiments were performed under Ar atmosphere using standard Schlenk and vacuum-line techniques or in an MBraun glove box. Glassware was flame dried on a Schlenk line or kept at 120 °C overnight prior to use. Solvents were dried and stored over 4 Å molecular sieves under Ar. Deuterated solvents were purchased from Eurisotop, degassed and distilled from the proper drying agent, and stored over 4 Å molecular sieves under Ar. The argon was provided by PANGAS and further purified with an MBraun >99 HP gas purification system. Air sensitive compounds were handled in a glovebox (MBraun lab master 130 or 150B-G). Chemicals were received from ABCR, Acros, Aldrich, Fluka, Lancaster, STREM or Boron Specialties. The following compounds were prepared by previously reported methods: diammoniate of diborane<sup>[S1]</sup> and complex **1** <sup>[S2]</sup>. IR spectra were recorded on a Perkin-Elmer-Spectrum 2000 FT-IR-Raman spectrometer with KBr beam splitter (range 500 - 4000 cm<sup>-1</sup>). For solid compounds the ATR technique was used. The absorption bands are described as follows: very strong (vs), strong (s), middle (m), weak (w), or broad (br). Samples were prepared in open glass capillaries. Solution NMR measurements were carried out on Bruker Avance 200, 300, 400, 500 MHz and 500 MHz cryoprobe spectrometers at room temperature (unless indicated otherwise). Solid state NMR measurements were carried out on Bruker Avance 700 MHz spectrometers equipped with a 2.5 mm two channel probe at room temperature. The sample spun at 20 kHz. For <sup>11</sup>B solid state MAS NMR, a Hahn echo pulse-sequence was used with an echo delay of 1.6 ms. Chemical shifts  $\delta$  are given as dimensionless numbers and the absolute values of the coupling constants are given in Hertz (Hz), the first atom mentioned in the subscript always refers to the atom that was used to observe the coupling. Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), quartet (q), virtual triplet (vt), virtual doublet of doublets (vdd) and broad (br). NMR spectra were referenced to TMS (<sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si), BF<sub>3</sub>·OEt<sub>2</sub> (<sup>11</sup>B), CFCl<sub>3</sub> (<sup>19</sup>F), H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P) and Rh(acac)<sub>3</sub> (<sup>103</sup>Rh). Quaternary carbons are indicated as C<sub>quat</sub>, aromatic carbon and hydrogens as C<sub>ar</sub> and CH<sub>ar</sub>, benzylic carbons and hydrogens as CH<sub>benz</sub>, olefinic carbons and hydrogens as CH<sub>olefin</sub>. Single crystals suitable for X-ray diffraction analysis were coated with polyisobutylene oil in a glovebox, transferred to a nylon loop and then transferred to the goniometer of a Bruker X8 APEX2 or D8-Venture diffractometer equipped with a molybdenum X-ray tube ( $\lambda = 0.71073$  Å) and a copper X-ray tube ( $\lambda = 1.5406$  Å). Preliminary data was collected to determine the crystal system. The space group was identified, and the data was processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structure was solved using direct methods (SHELXT) on OLEX2 completed by Fourier transformation and refined by full-matrix least-squares procedures. The DLS measurements were performed with a Zetasizer Nano ZS

(Malvern Instruments Ltd., Malvern, UK) equipped with a max 4 mW He–Ne laser (emitting at 633 nm). Each measurement was performed at the non-invasive backscatter angle (NIBS) of 173° at a temperature of 25 °C and was preceded by a 30 s equilibration time. Agilent 7890A gas chromatograph (Agilent Technologies) equipped with a HP Molsieve column (15 m x 0.32 mm x 25 µm) and combined with a thermal conductivity detector was used for the analysis the gas phase in the experiment of AB dehydrogenation.

## II. SYNTHESIS AND CHARACTERIZATION DATA

**Ammonia borane:** To a solution of sodium borohydride (1.00 g, 26.4 mmol, 1.0 equiv) in THF (50 ml) ammonium sulfate (6.99 g, 52.9 mmol, 2.0 equiv) was added. The reaction mixture was placed in an ultrasonic bath at 40°C overnight. The precipitate was filtered off and the solvent was removed under reduced pressure giving a white solid. The product was recrystallized from diethyl ether.

<sup>11</sup>B-NMR (96 MHz, THF-d<sub>8</sub>, 298K): δ (ppm) –24.1 (q, *J* = 95.4 Hz).

**<sup>15</sup>N ammonia borane:** <sup>15</sup>N labelled AB was synthesized following the previous protocol using (<sup>15</sup>NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.

**Complex 2:** A 50 mL Schlenk flask (with a glass ground joint and an additional side arm with a needle valve gas inlet) equipped with a stirring bar was charged under Ar with K(dme)<sub>2</sub>[RuH(trop<sub>2</sub>dad)] (100 mg, 0.132 mmol, 1.0 equiv) and dried and degassed THF (10 mL). To the dark brown solution was added H<sub>2</sub>O (8 µL, 0.44 mmol, 3.4 equiv.) and stirred at 70 °C during 5 h forming a clear red solution and a red crystalline precipitate. The reaction mixture was cooled down for 12 h and a dark red crystalline product was isolated by filtration. Single crystals suitable for X-ray diffraction analysis were obtained from the red solid. The clear filtrate was concentrated to half of its volume and after 48h a second crop of dark red crystals was obtained. After drying under vacuum, the title compound was isolated as crystalline red solid. Combined yield: 52 mg, 35 %. Due to the low solubility of the complex in common organic solvents a complete NMR spectroscopic characterization was not possible.

Mp > 220 °C (dec)

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298K) δ [ppm] = 7.99 (t, 2H, <sup>3</sup>*J*<sub>HH</sub> = 8.5 Hz, 2 N=CH), 7.85 (t, 1H, <sup>3</sup>*J*<sub>HH</sub> = 7.6 Hz, CH<sub>ar</sub>), 7.59 – 6.48 (m, 31H), 6.23 (m, 2H, CH<sub>olefin</sub>), 5.01 (s, 1H, CH<sub>benz</sub>), 4.97 (s, 1H, CH<sub>benz</sub>), 4.88 (d, 1H, <sup>3</sup>*J*<sub>HH</sub> = 11.1 Hz, CH<sub>olefin</sub>), 4.35 (d, 1H, <sup>3</sup>*J*<sub>HH</sub> = 8.9 Hz, CH<sub>olefin</sub>), 3.73-3.65 (m, 3H, overlapped 2CH<sub>olefin</sub> and residual THF), 3.51 (s, 1H, CH<sub>benzyl</sub>), 3.29 (s, 1H, CH<sub>benz</sub>), 3.22 (br, 1H, NH), 3.11-2.97 (m, 3H, overlapped 2CH<sub>olefin</sub> + 1 NCH<sub>2</sub>), 2.02 (br, 1H, NH), 1.87 (THF), 1.01 (br, 2H, NCH<sub>2</sub>), 0.40 (d, 1H, <sup>3</sup>*J*<sub>HH</sub> = 13.2 Hz, NCH<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298K) δ [ppm] = 143.0 (C<sub>ar</sub>), 141.0 (C<sub>ar</sub>), 137.8 (CH<sub>ar</sub>), 133.3 (CH<sub>ar</sub>),

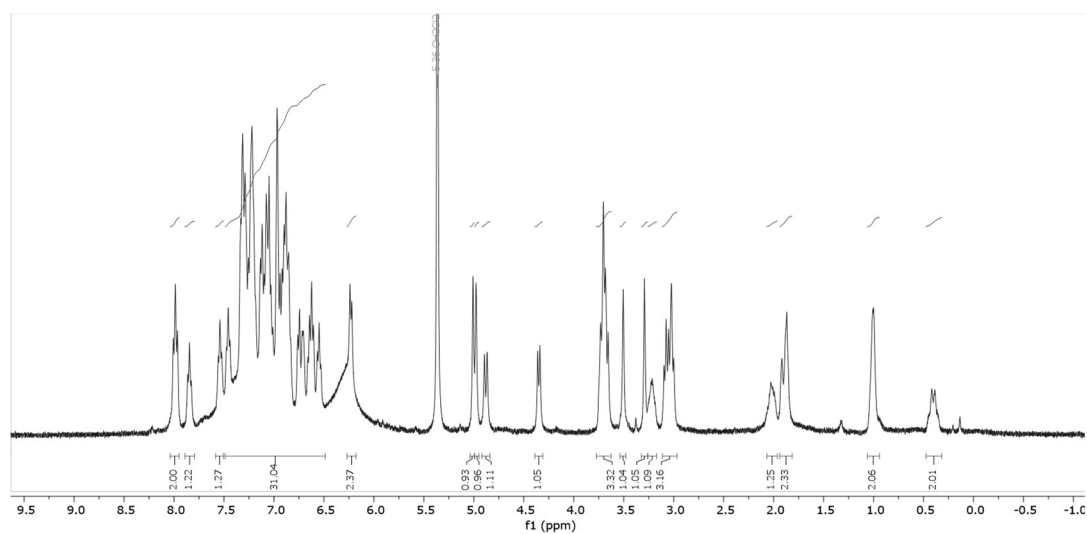
132.3 (CH<sub>ar</sub>), 130.9 (CH<sub>ar</sub>), 129.5 (CH<sub>olefin</sub>), 129.0 (CH<sub>ar</sub>), 128.7 (CH<sub>ar</sub>), 128.4 (CH<sub>ar</sub>), 128.1 (CH<sub>ar</sub>), 127.8(CH<sub>ar</sub>), 127.5 (CH<sub>ar</sub>), 127.3 (CH<sub>ar</sub>), 127.1 (CH<sub>ar</sub>), 126.8 (CH<sub>ar</sub>), 126.3 (CH<sub>ar</sub>), 124.4 (CH<sub>ar</sub>), 123.2 (CH<sub>ar</sub>), 121.9 (CH<sub>ar</sub>), 121.8 (CH<sub>ar</sub>), 121.5(CH<sub>ar</sub>), 121.2 (CH<sub>ar</sub>), 75.1 (CH<sub>benz</sub>), 72.3 (CH<sub>benz</sub>), 72.1 (CH<sub>benz</sub>), 70.2 (CH<sub>benz</sub>), 69.9 (CH<sub>olef</sub>), 64.4 (CH<sub>olef</sub>), 61.9 (CH<sub>olef</sub>), 53.9 (NCH<sub>2</sub>), 53.6 (CH<sub>olef</sub>), 53.4 (CH<sub>olef</sub>), 48.1 (NCH<sub>2</sub>), 44.5 (CH<sub>olef</sub>), 25.6 (NCH<sub>2</sub>). Note: Due to the low solubility of the complex a complete elucidation of all <sup>13</sup>C signals corresponding to some of the CH<sub>ar</sub> and quaternary aromatic carbon atoms was not possible.

IR (ATR, cm<sup>-1</sup>): 2947.6 (s, ν<sub>CH</sub>), 1593.3 (m, ν<sub>C=C</sub> or ν<sub>C=N</sub>), 1481.7 (m, ν<sub>C=C</sub> or ν<sub>C=N</sub>), 1454.8 (m, ν<sub>C=C</sub> or ν<sub>C=N</sub>), 794.3 (s), 748.9 (s), 723.8 (s).

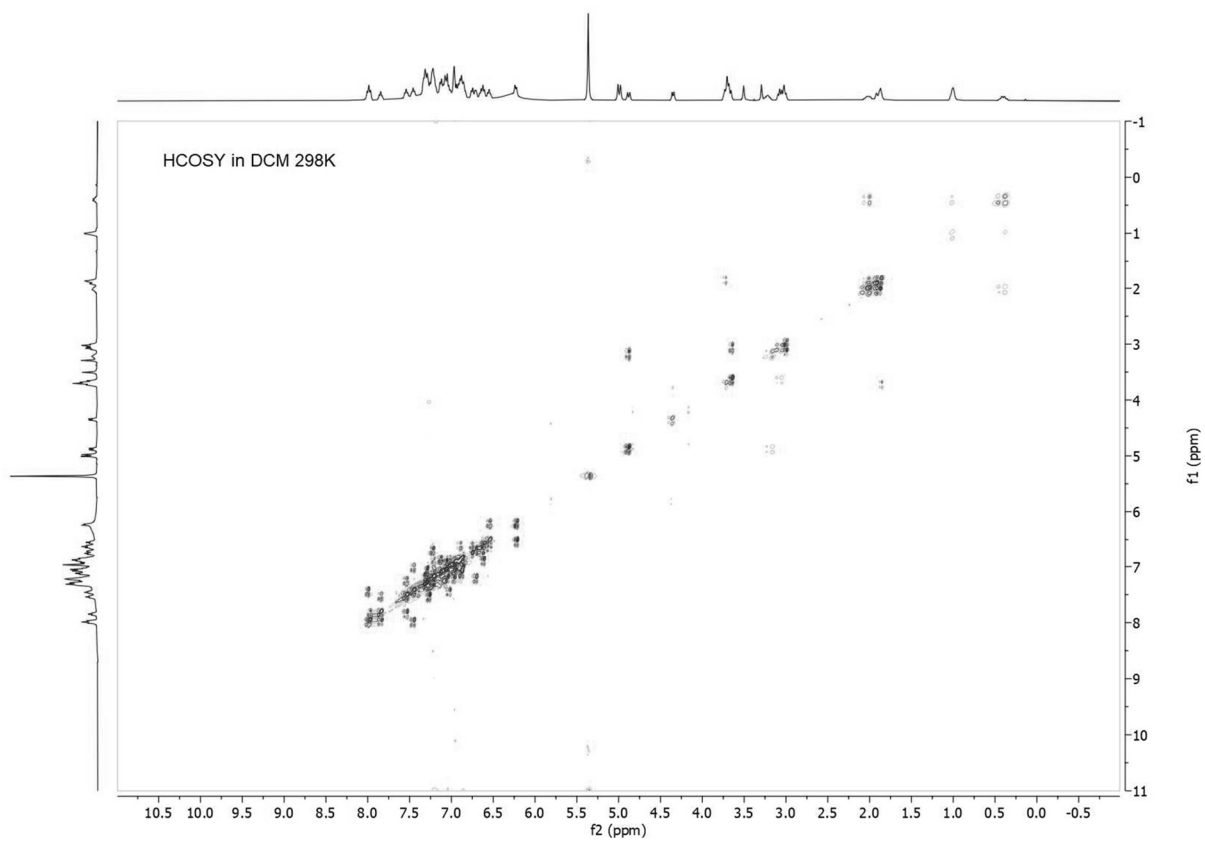
HRMS (MALDI-TOF solid) Calc for C<sub>64</sub>H<sub>52</sub>N<sub>4</sub>Ru<sub>2</sub> [M+1H]<sup>+</sup> m/z = 1081.2352, Found 1081.2381

The X-ray crystallographic coordinates for the structure of complex **2** have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number CCDC 2108631. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

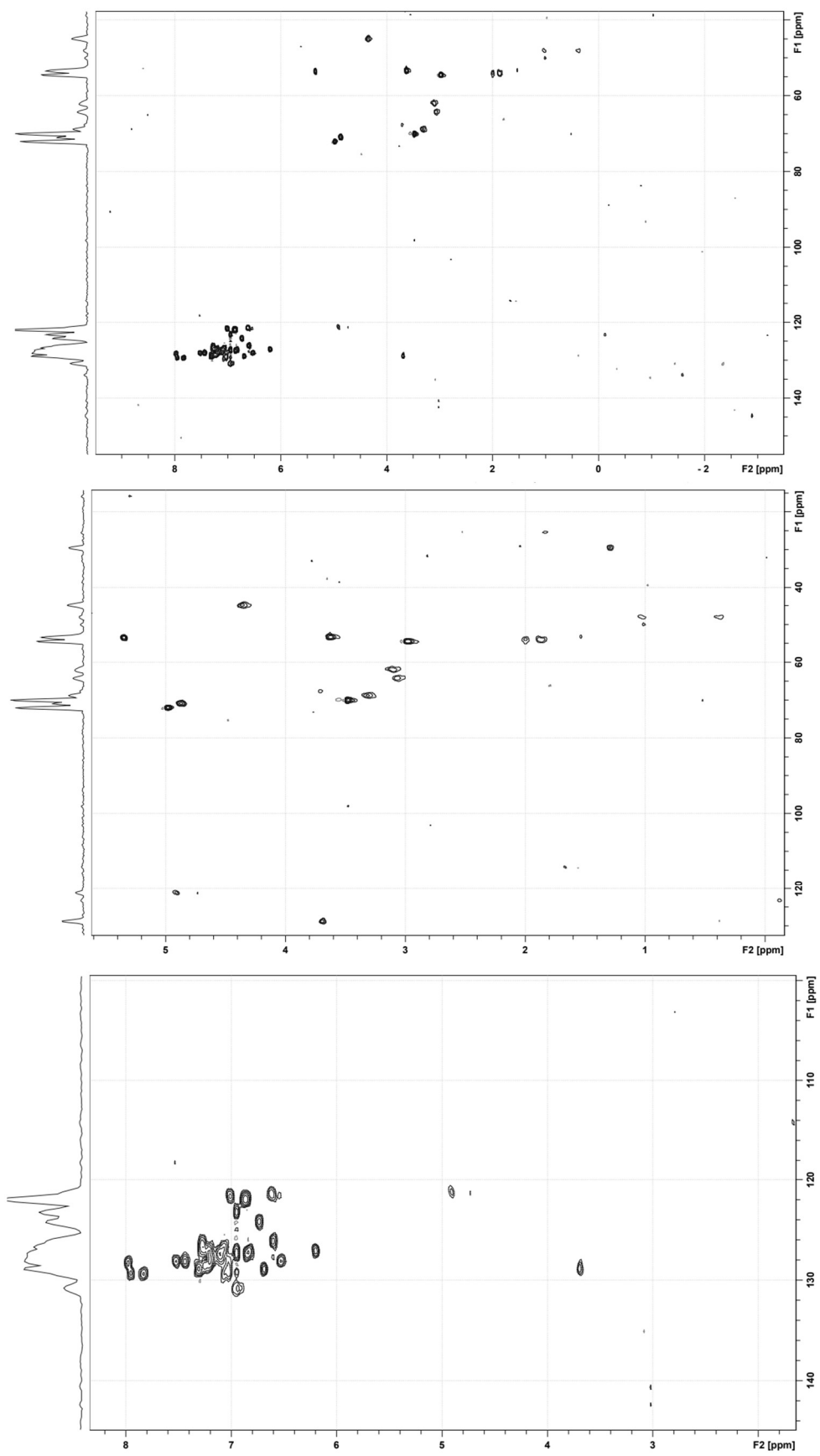
## Selected NMR spectra



**Figure S1.**  $^1\text{H}$  NMR spectrum of complex 2 (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298K)

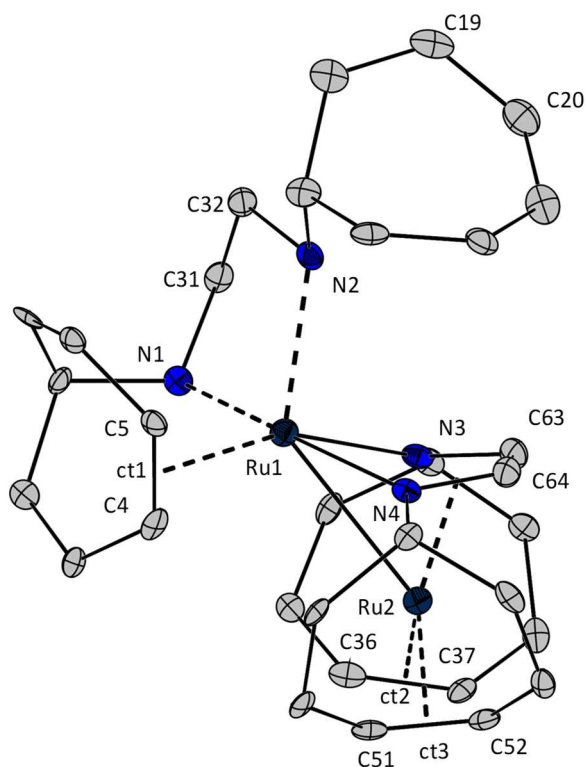


**Figure S2.**  $^1\text{H}$  COSY spectrum complex 2



**Figure S3.**  $^1\text{H}$ - $^{13}\text{C}$  HSQC spectrum complex 2 (with zoom sections)

### Crystallographic data of Complex 2 (CCDC 2108631)



**Figure S4.** Molecular structure of complex 2. Ellipsoids are drawn at a 50 % probability level. Non-relevant hydrogen atoms, benzofused rings and 3 molecules of co-crystallized THF have been removed for clarity. Ct is the centroid of the C=C<sub>trop</sub> bond. Selected bond distances [Å] and angles [°]: Ru1-N1 2.142(2), Ru1-N2 2.252(2), Ru1-N3 2.119(2), Ru1-N4 2.157(2), Ru1-Ru2 2.7119(6), Ru2-N3 2.095(2), Ru2-N4 2.086(2), Ru1-ct1 1.998(2), Ru2-ct2 1.996(2), Ru2-ct3 2.012(2), N1-C31 1.488(4), N2-C32 1.499(4), C31-C32 1.510(4), N3-C63 1.390(4), N4-C64 1.397(4), C63-C64 1.390(4), C4-C51.447(4), C19-C20 1.344(4), C36-C37 1.452(4), C51-C52 1.457(4), N3-Ru2-Ru1 51.41(9), N3-Ru2-N4 77.9(1), N3-Ru2-ct3 91.9(1), N3-Ru2-ct3 169.8(1), N3-Ru1-ct1 50.8(1), N4-Ru2-Ru1 50.20(8), N4-Ru2-ct2 166.8(1), N4-Ru2-ct3 92.6(1), N4-Ru1-ct1 51.0(1), ct2-Ru2-Ru1 116.7(1), ct2-Ru2-ct3 98.0(1), ct3-Ru2-Ru1 124.7(1), ct1-Ru1-Ru2 71.4(3), N3-Ru1-N4 75.8(1), N3-Ru1-N1 94.5(1), N3-Ru1-N2 92.9(1), N1-Ru1-N4 170.3(1), N2-Ru1-N4 102.3(1), N1-Ru1-N2 79.3(1).



**Table S1** Crystal data and structure refinement for complex **2 x 3(THF)**

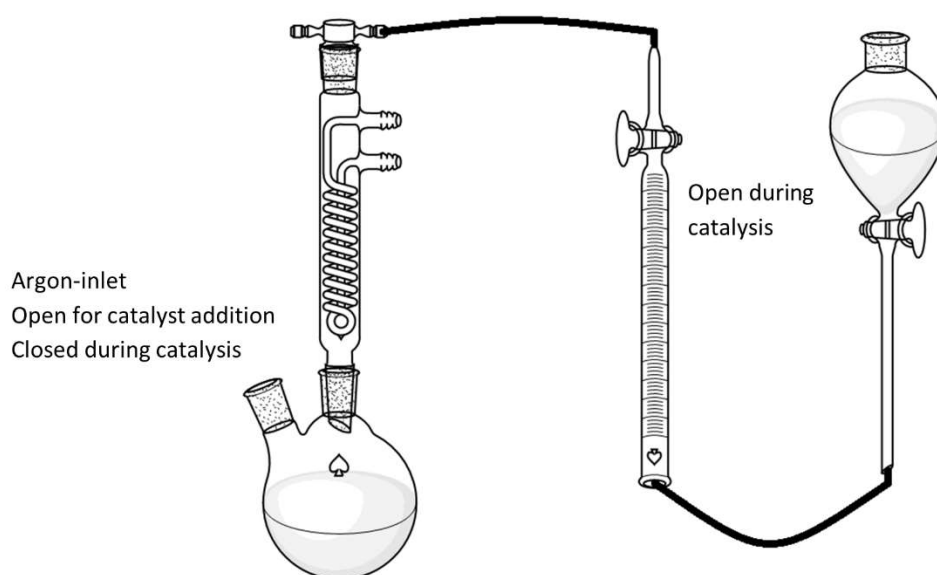
Empirical formula	C <sub>7</sub> H <sub>7</sub> 6N <sub>4</sub> O <sub>3</sub> Ru <sub>2</sub>
Formula weight	1295.54
Temperature/K	100.00
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /n
a/Å	10.47460(10)
b/Å	23.4500(2)
c/Å	23.6481(2)
α/°	90
β/°	91.9100(10)
γ/°	90
Volume/Å <sup>3</sup>	5805.44(9)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.482
μ/mm <sup>-1</sup>	0.577
F(000)	2688.0
Crystal size/mm <sup>3</sup>	0.35 × 0.06 × 0.05
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	3.446 to 52.744
Index ranges	-13 ≤ h ≤ 13, -29 ≤ k ≤ 29, -29 ≤ l ≤ 29
Reflections collected	81371
Independent reflections	11859 [R <sub>int</sub> = 0.0677, R <sub>sigma</sub> = 0.0374]
Data/restraints/parameters	11859/0/766
Goodness-of-fit on F <sup>2</sup>	1.064
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0411, wR <sub>2</sub> = 0.0902
Final R indexes [all data]	R <sub>1</sub> = 0.0543, wR <sub>2</sub> = 0.0953
Largest diff. peak/hole / e Å <sup>-3</sup>	0.88/-0.46

### III. CATALYTIC DEHYDROGENATION OF AB BY Ru COMPLEXES: SYNTHESIS OF BN NANOSHEETS.

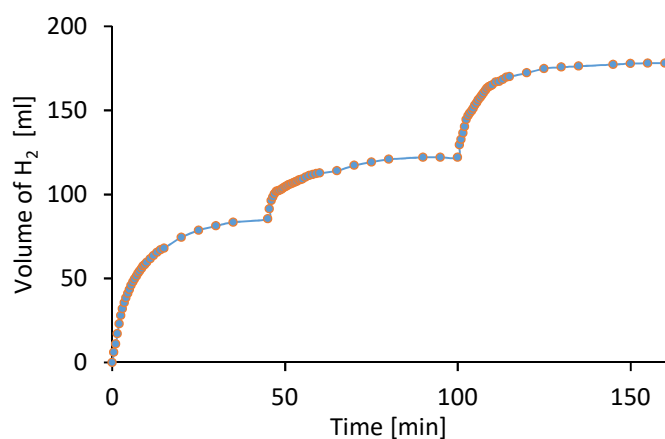
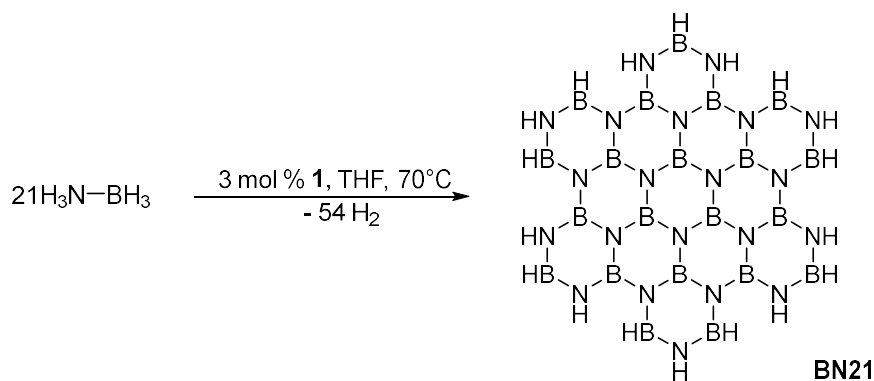
#### A) GENERAL PROCEDURE AND HYDROGEN EVOLUTION EXPERIMENTS

In a two-neck 50 mL flask, a solution of AB (92 mg, 3.0 mmol) in THF (10 mL) was heated to 70 °C in an open system under argon (Figure S5). Catalyst **1** (22.7 mg, 0.03 mmol, 1.0 mol %) was added as a solid to the reaction mixture. After 50 and 100 minutes at 70 °C, the same amount of catalyst **1** (1 mol%), was added. The resulting solution was stirred at 70 °C for 1h, cooled to ambient temperature and filtered over a plug of Florisil®. The solvent was removed under vacuum and product was obtained as a light brown solid (78 mg). Analysis by <sup>11</sup>B-NMR spectroscopy of a solution in THF of the solid indicated formation of polyborazine as only boron containing material.

The reaction using catalyst **2** (0.09 mmol, 3.0 mol%) followed the same protocol with exception that the catalyst was added at once. Complete conversion of ammonia borane was observed after 2.5 h. In both catalytic experiments, once the catalyst was added to the heated mixture the measurement of gas evolution was started. The displacement of water in the burette (Figure S5) was continuously monitored at regular time intervals, collecting upon completion 183.0 mL (2.52 equiv) of hydrogen. All catalytic runs were measured twice and the composition of the gas formed was analyzed by GC-TCD. Molecular hydrogen was the only gas detected.



**Figure S5.** Setup for the synthesis of BN nanosheets by Ru-catalyzed AB dehydrogenation and hydrogen evolution measurement.



**Figure S6.** Hydrogen evolution measured in the dehydrogenation of ammonia borane catalyzed by **1**, added at the beginning of the set up, and after 50 and 100 minutes. The experiments were repeated twice. The two experiments released upon completion 180.0 mL of hydrogen (2.48 equiv) and 185.0 mL of hydrogen (2.55 equiv).

## B) EXPERIMENTS WITH MERCURY AND TRIPHENYLPHOSPHINE AS ADDITIVES

Several poisoning test were performed to assure the homogeneity of the catalysis.

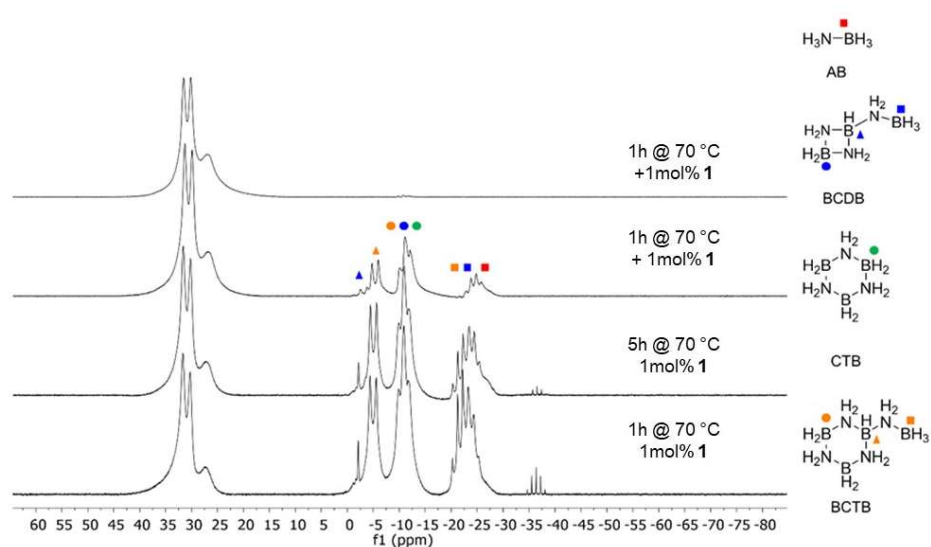
To a solution of AB (31 mg, 1.0 mmol) in THF (1 mL), one drop of Hg, 5 equivalents or 0.5 equivalents of PPh<sub>3</sub> (with respect to the amount of catalyst) were added. The solution was heated to 70°C and catalyst **2** (72 mg, 3 mol%) was added following the same protocol described in section A.

The addition of Hg to the dehydrogenation with catalyst **2** had no influence on the catalyst activity (no change in conversion or reaction time observed). This is an indication for the existence of a homogenous catalyst. This assumption is strengthened by the influence of adding an excess of triphenylphosphine (15 mol%) to the reaction mixture. In this case, the homogeneous catalyst was deactivated and no catalyzed dehydrogenation of AB was observed. Adding a sub-stoichiometric

amount of phosphine (0.5 equivalents of  $\text{PPh}_3$  with respect to the amount of catalyst) a proportional loss of catalytic activity (change in conversion is proportional to using half of the amount of catalyst) was observed, which is an indication for the existence of a homogenous catalyst

### C) $^{11}\text{B}$ NMR MONITORING OF AB DEHYDROGENATION CATALYZED BY COMPLEX 1

Complex **1** (24 mg, 0.032 mmol, 1.0 mol %) was added to a solution of AB (100 mg, 3.2 mmol) in THF (5 mL) in a 50 mL Schlenk flask (containing a ground glass joint and an additional side arm with a needle-valve gas inlet) under argon. The reaction mixture was stirred in the closed system for 1h at 70 °C. After cooling down the reaction mixture to room temperature, an aliquot (0.1 mL) was taken and analyzed by  $^{11}\text{B}$  NMR. A second aliquot was taken after 5h and analyzed. Two more additional analysis were made after addition of a second and third load of catalyst **1** (1 mol%) and heating for two additional hours (Figure S7).

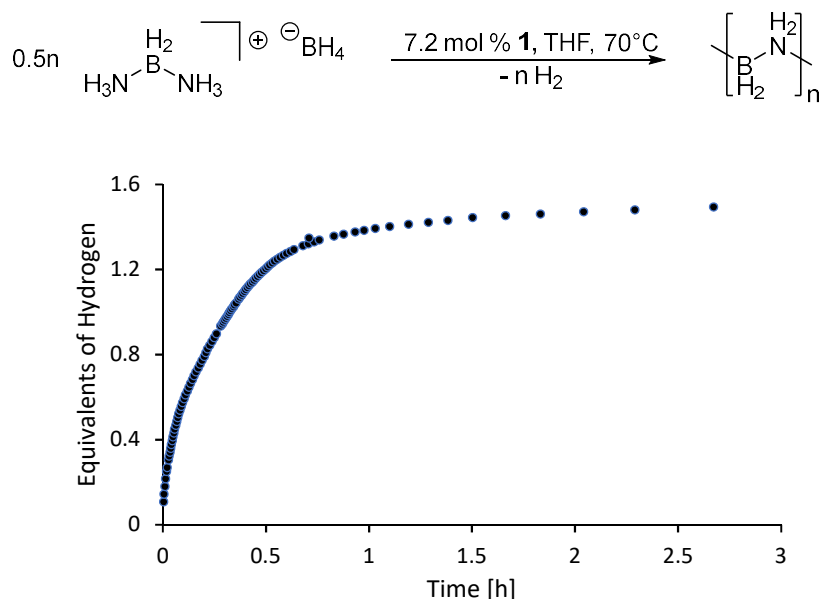


**Figure S7.** Intermediates observed by  $^{11}\text{B}$  NMR spectroscopic analysis during the dehydrogenation reaction of AB catalyzed by **1**. **BCDB**: B-(cyclodiborazanyl)amine-borane, **CTB**: cyclotriborazane and **BCTB**: B-(cyclotriborazanyl)amine-borane.

### D) DEHYDROGENATION OF DIAMMONIATE OF DIBORANE (DADB) CATALYZED BY COMPLEX 1

Diammoniate of diborane (DADB) (138.7 mg, 2.25 mmol, 1.0 equiv) and complex **1** (122 mg, 161  $\mu\text{mol}$ , 7.2 mol%) were dissolved in THF (8 mL). The reaction mixture was heated at 70 °C and the hydrogen evolution monitored with the time (Figure S8). The reaction mixture was stirred for 3 h, observing the formation of a white precipitate. The reaction solution was analyzed by  $^{11}\text{B}$  NMR spectroscopy, indicating the absence of boron containing compounds. The precipitated was filtrated and dried under

vacuum, affording an off-white solid (101.6 mg, 78 %) identified by  $^{11}\text{B}$ -MAS-NMR as linear polyaminoborane.<sup>[S3]</sup>

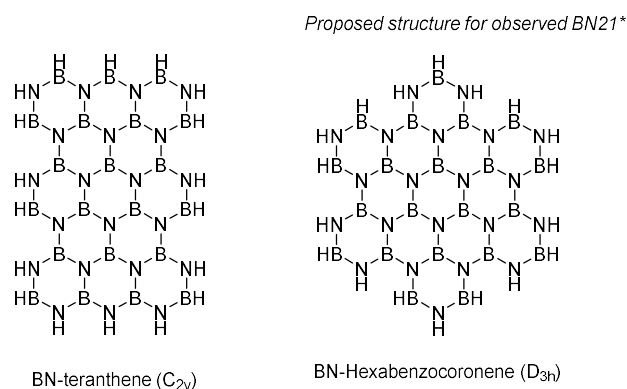


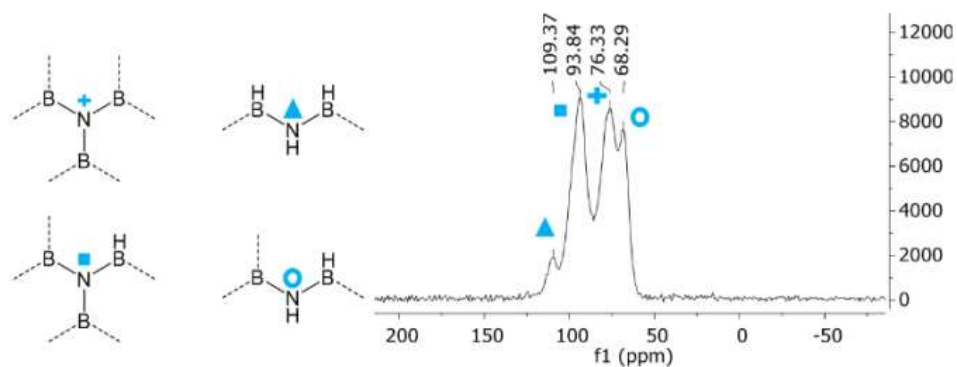
**Figure S8.** Hydrogen evolution measured with the setup shown in Figure S5. Secondary axis: equivalents of hydrogen formed with respect to diammoniate of diborane, DADB.

#### D) SELECTED NMR AND MASS SPECTRA OF THE BN NANOSHEETS FORMED IN THE Ru CATALYZED DEHYDROGENATION OF AB.

##### 1) NMR analysis

$^{15}\text{N}$  labelled AB was prepared from the reaction of  $(^{15}\text{NH}_4)\text{SO}_4$  and  $\text{NaBH}_4$  in THF, following the previously described protocol. The experimentally determined  $^{15}\text{N}$  NMR shifts (Figure S10) are in agreement with the calculated NMR shifts by Gastreich, shown in Table S2.<sup>[S4]</sup> The proposed BN21 compound contains four nitrogen atoms in different chemical environments, which makes them magnetically inequivalent;  $\text{NB}_3$  (6x),  $\text{NB}_2(\text{BH})$  (6x),  $\text{NH}(\text{BH})_2$  (3x) and  $\text{NHB}(\text{BH})$  (6x). The peak intensities correspond to the ratio of nitrogen atoms in their distinct chemical environment (Figure S9).



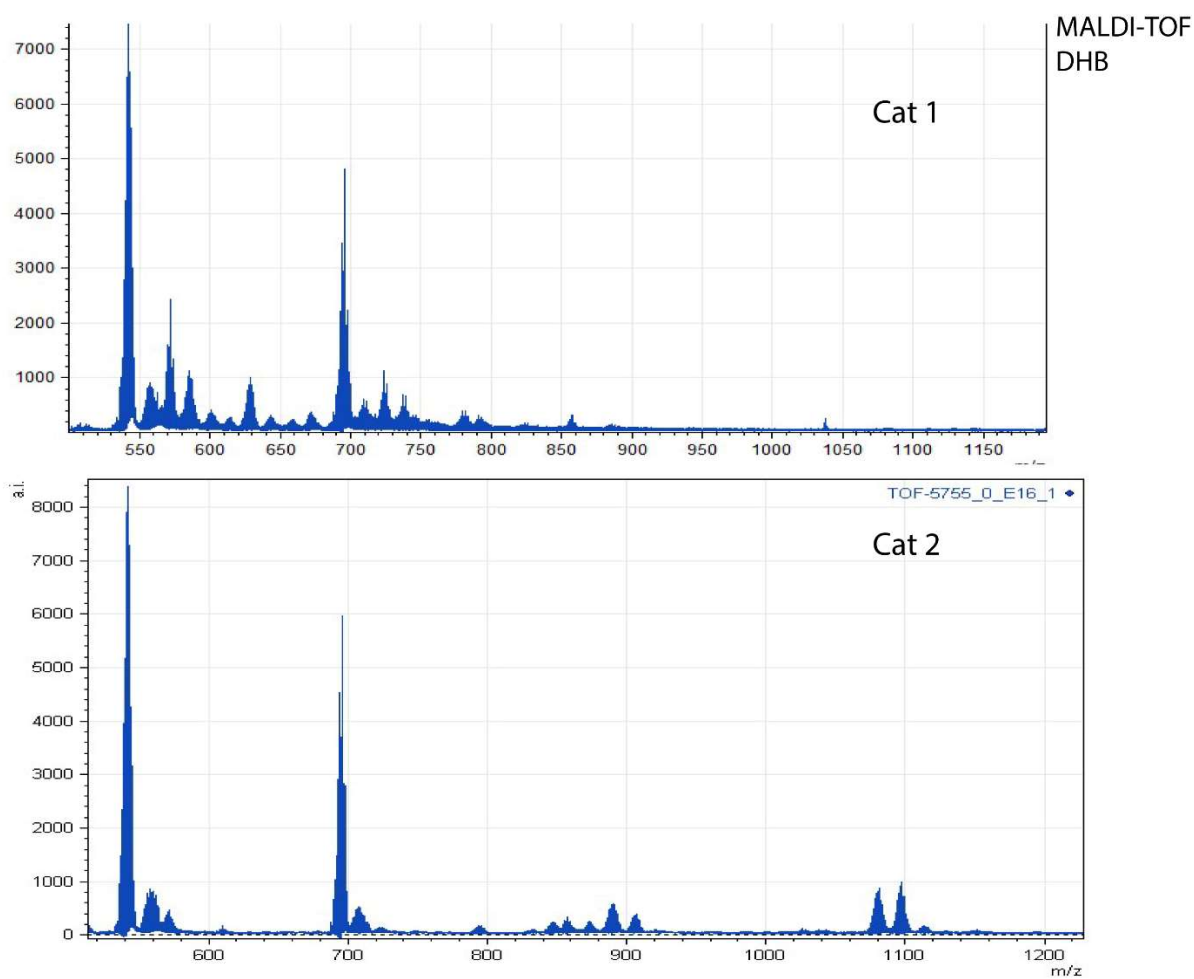


**Figure S9.** Proposed structure for BN<sub>21</sub> product and <sup>15</sup>N NMR spectrum of the compound with assignation of the magnetically inequivalent nitrogen atoms.

**Table S2.** Comparison of calculated<sup>[S4]</sup> with experimentally determined <sup>15</sup>N-NMR shifts of polyborazylene.

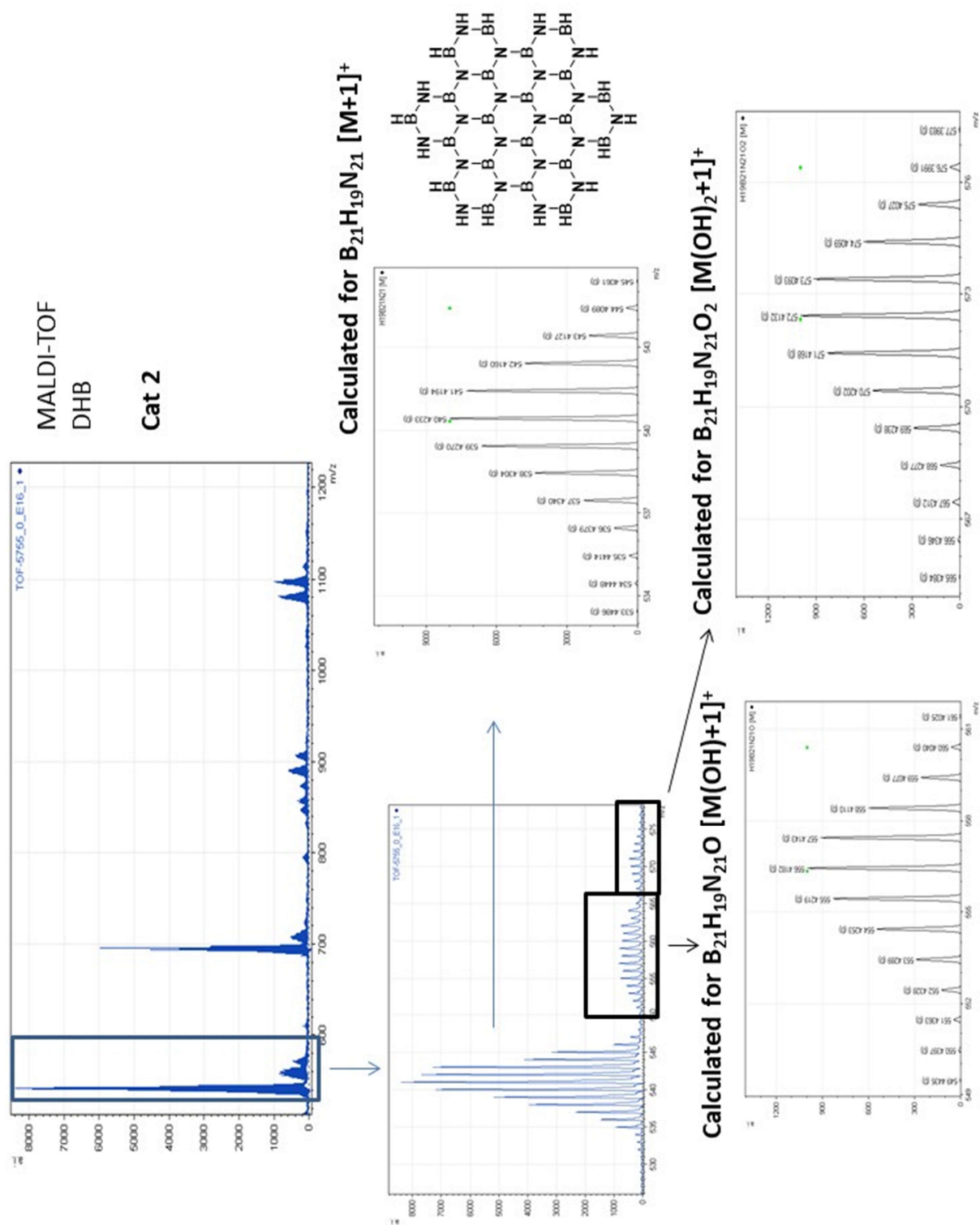
	calculated shift	experimental shift
▲	115.7 ppm	109.37 ppm
■	108.7 ppm	93.84 ppm
+	96.7 ppm	76.33 ppm
○	94.7 ppm	68.29 ppm

## 2) MS Spectra



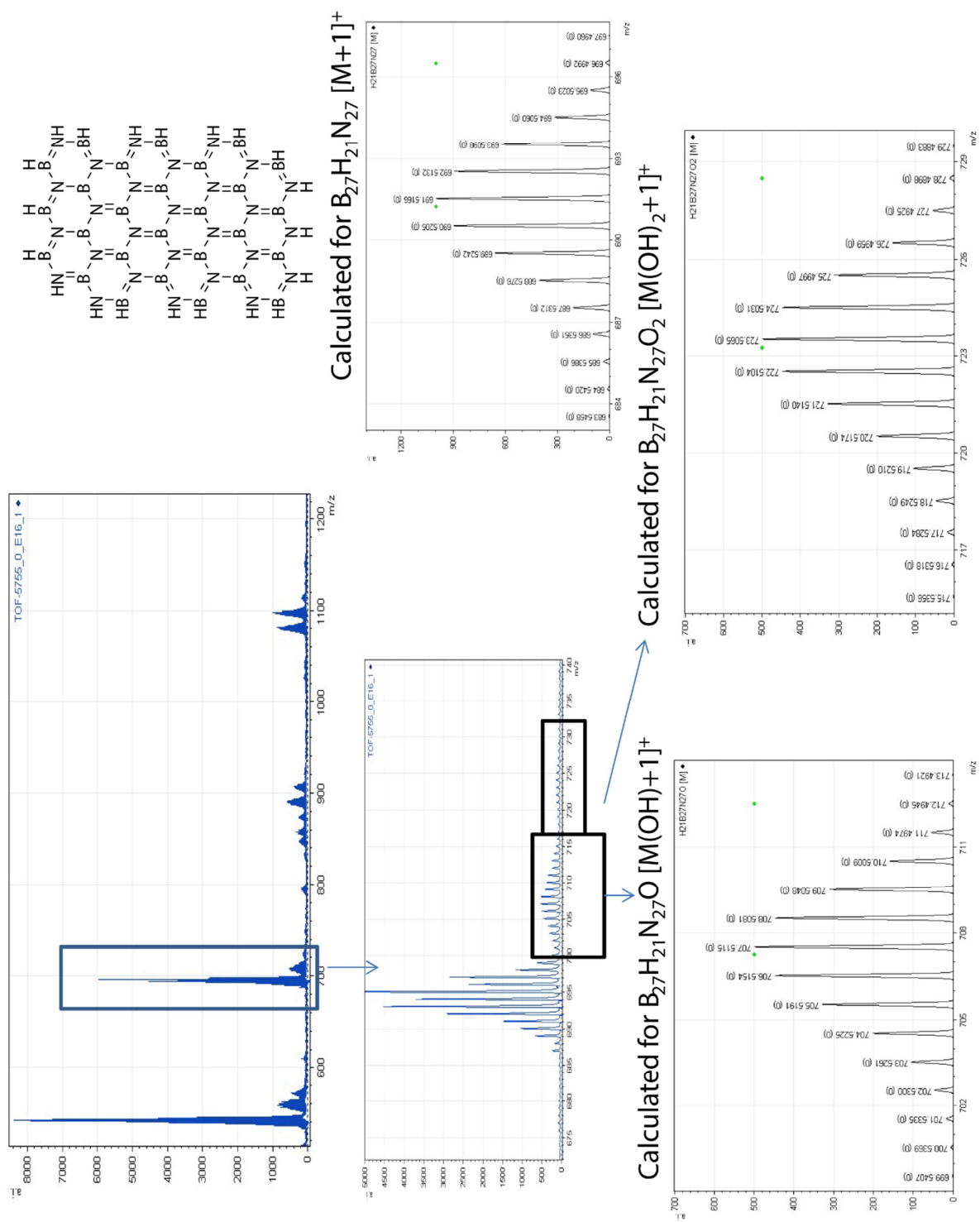
**Figure S10.** MALDI-TOF mass spectra of BN product obtained by AB decomposition catalyzed by complex **1** (top) or complex **2** (bottom). Samples were dissolved in THF and DHB was used as matrix for the analysis.

(See Figures S11-S15 for amplified views and comparison of isotope patterns of found and calculated peaks and proposed isomers).

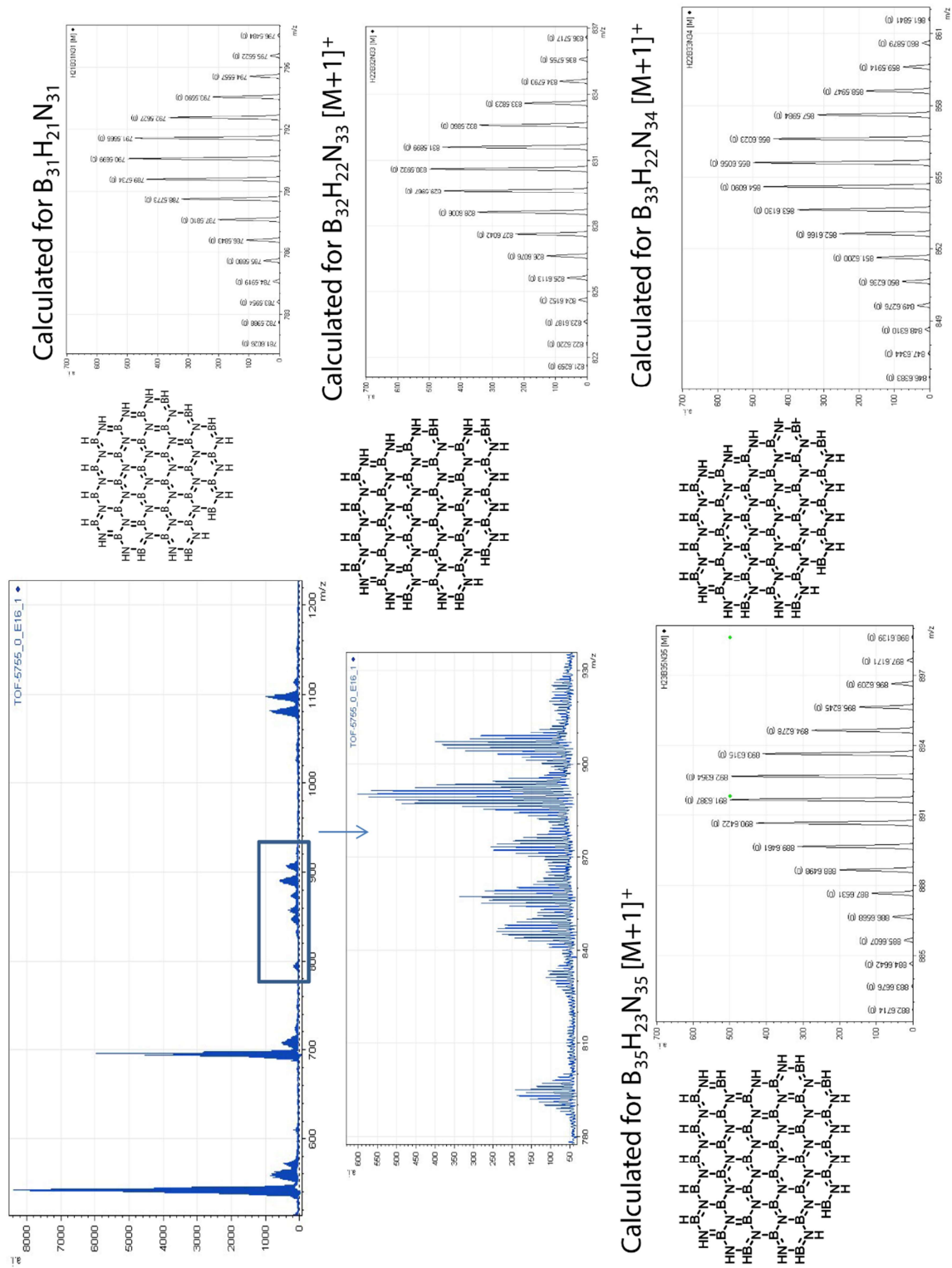


**Figure S11.** Comparison of found and calculated mass peaks and isotope pattern assigned to  $\text{B}_{21}\text{N}_{21}\text{H}_{18}$ .

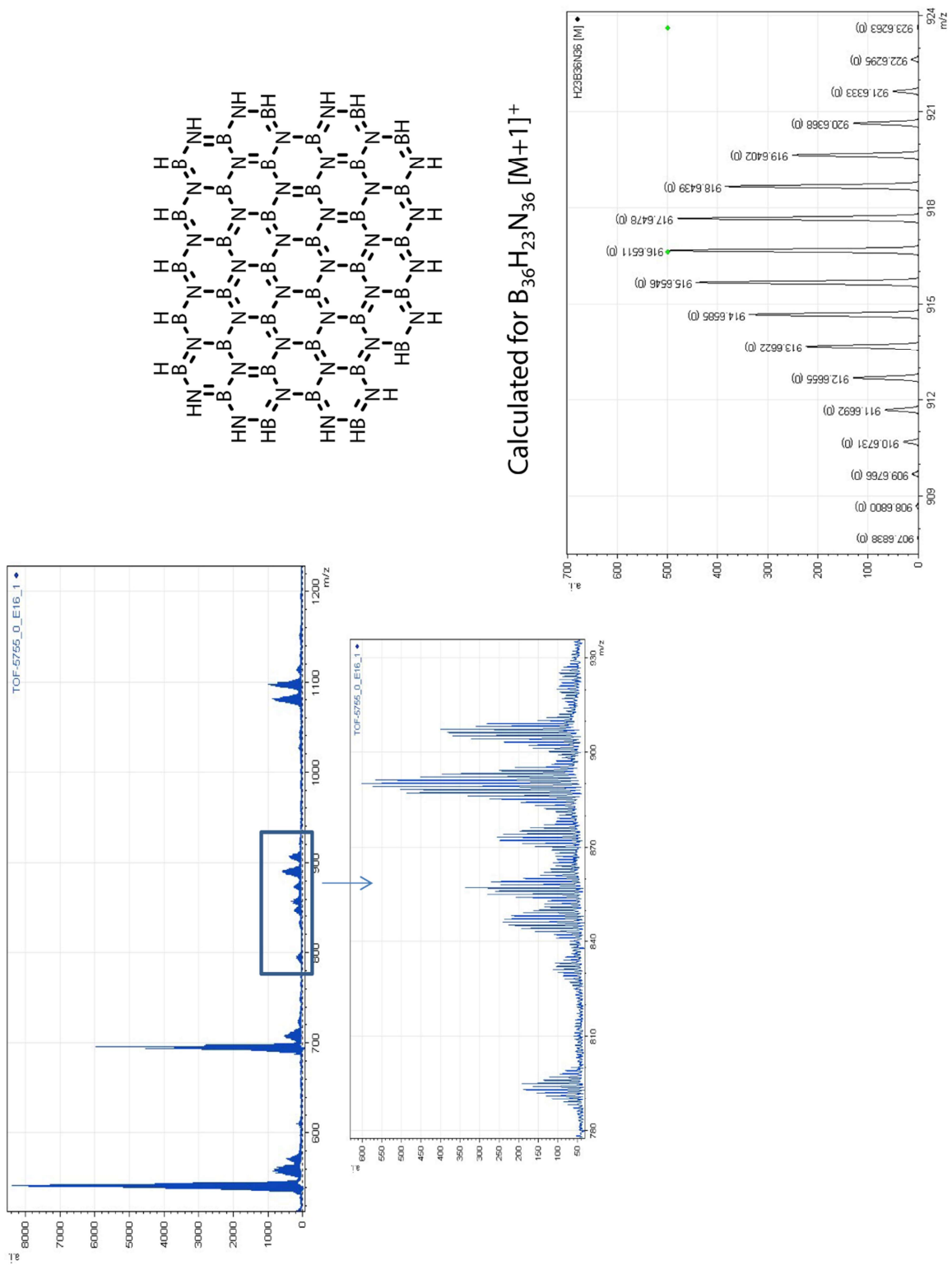




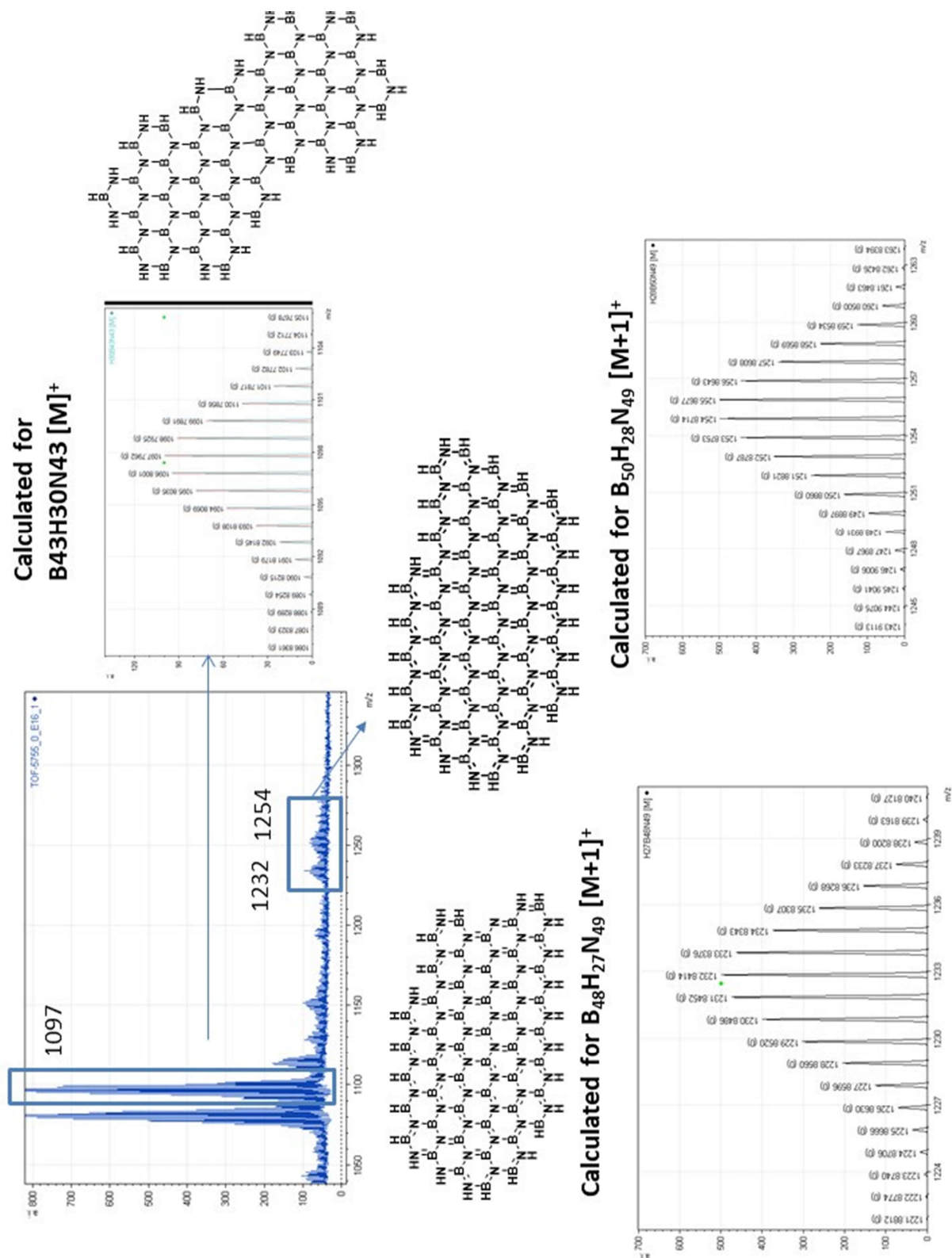
**Figure S12.** Comparison of found and calculated mass peaks and isotope pattern assigned to  $B_{27}N_{27}H_{21}$ .



**Figure S13.** Comparison of found and calculated mass peaks and isotope pattern assigned to  $B_{31-35}N_{31-35}H_{22-23}$ .

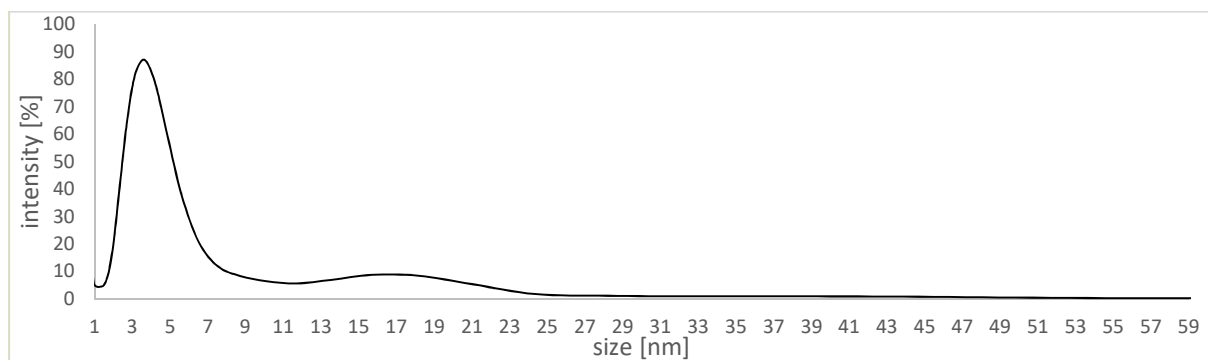


**Figure S14.** Comparison of found and calculated mass peaks and isotope pattern assigned to  $B_{36}N_{36}H_{23}$ .



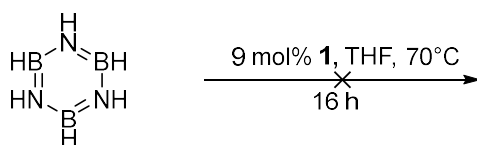
**Figure S15.** Comparison of found and calculated mass peaks and isotope pattern assigned to B<sub>43</sub>N<sub>43</sub>H<sub>30</sub>, B<sub>48</sub>N<sub>49</sub>H<sub>26</sub> and B<sub>50</sub>N<sub>49</sub>H<sub>28</sub> and proposed isomers. (m/z = 1081 is assigned to complex 2)

### E) DYNAMIC LIGHT SCATTERING EXPERIMENT OF THE BN NANOSHEETS FORMED IN THE Ru CATALYZED DEHYDROGENATION OF AB.



**Figure S16.** DLS spectra of the BN nanosheets formed in the Ru catalyzed dehydrogenation of AB. This spectrum is the average sum of 10 consecutive measurements. A BN nanosheet THF solution (0.5 mg/ml) was prepared and before measurement filtered over a syringe filter (with a GHP membrane) into a glass cuvette.

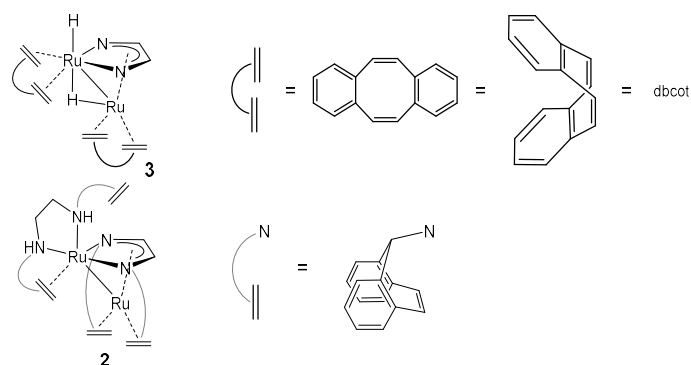
### F) REACTION OF BORAZINE AND COMPLEX 1



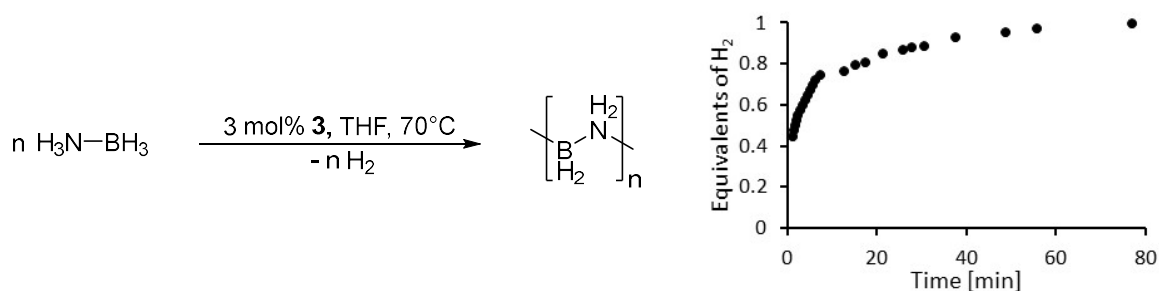
Complex **1** (26.7 mg, 35.3  $\mu\text{mol}$ , 9 mol%) was added to a stock solution of borazine in dimethoxyethane (0.5 mL, 0.8 M) and the solution was heated at 70°C for 16h. Analysis by  $^{11}\text{B}$  NMR spectroscopy of an aliquot of the solution showed no significant conversion of borazine.

### G) CATALYTIC DEHYDROGENATION OF AB BY COMPLEX 3

To a solution of ammonia borane (25.1 mg, 813  $\mu\text{mol}$ ) in THF (1 mL) heated to 70°C was added  $[\text{Ru}_2\text{H}(\mu\text{-H})(\text{Me}_2\text{dad})(\text{dbcot})_2]$  (**3**) (17.0 mg, 24.4  $\mu\text{mol}$ , 3 mol%) as a solid following the same protocol described in section A. The reaction mixture was stirred at 70 °C over a period of 2h and the hydrogen evolution monitored with the time (Figure S17). An insoluble white solid was formed in the reaction mixture, no boron containing compounds were detected by  $^{11}\text{B}$  NMR analysis of the solution. Upon filtration and drying under reduced pressure, polyaminoborane was isolated as insoluble off-white powder (19 mg, 81% yield).



**Figure S17.** Comparison of molecular structure of complex  $[\text{Ru}_2\text{H}(\mu\text{-H})(\text{Me}_2\text{dad})(\text{dbcot})_2]$  **3** (top) and **2** (bottom).



**Figure S18.** Hydrogen evolution of the dehydrogenation of ammonia borane catalyzed by  $[\text{Ru}_2\text{H}_2^{\text{Me}_2\text{dad}}(\text{dbcot})_2]$  **3**.

#### IV. REFERENCES

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