# From propenolysis to enyne metathesis: tools for expedited assembly to 4a,8a-azaboranaphthalene and extended embedded BN-polycycles

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# **1. Materials and Methods**

Reagents. All commercially acquired reagents were used as received unless indicated otherwise. The triallylborane was synthesized employing  $BF_3 \cdot Et_2O$  as boron source following the procedure initially developed by Brown and Racherla<sup>1</sup> and subsequently implemented on multi-gram scales by Staubitz and co-workers.<sup>2</sup>

Reaction conditions. Reactions requiring inert atmosphere were conducted under Argon atmosphere using standard Schlenk-line techniques. When indicated, reactions were conducted in standard tube-shaped Schlenk flasks sealable with a screw-on Teflon stopper valve. All other reactions were performed employing standard organic synthesis protocols.

Chromatography. Thin layer chromatography (TLC) was performed using Merck aluminiumbacked plates of TLC Silica gel 60 F254; the plates were revealed using UV light at 254 nm or by staining using potassium permanganate stain. Standard Flash Column chromatography was accomplished using silica gel (60 Å pore size, 230-400  $\mu$ m mesh size). Also, *EZ*-Prep and CombiFlash automated chromatography instruments using the Biotage C18 column or Buchi silica gel column were used when necessary. Routine GC-MS measurements were recorded on an Agilent 6890 chromatograph equipped with an Agilent 5973 Network MS detector and using a 30 m-long HP-5MS column.

Gas Chromatography coupled to High Resolution Mass Spectrometry. Analyses were carried out at the IQAC Mass Spectrometry Facility, using a Thermo Scientific Trace 1310 Gas Chromatograph equipped with MS/MS Q Exactive GC Orbitrap.

Liquid Chromatography coupled to a High-Resolution Mass Spectrometry. Analyses were carried out at Institut Químic de Sarrià IQS-SCIEX DEMO LAB Facility, using a EXION LC (Sciex) chromatograph coupled to a QTOF X500B (Hybrid LC/MS/Ms quadrupole time-of-flight mass spectrometer). Direct injections were performed using as mobile phase A Milli-Q water (w/o 0.1% of Formic acid) and as mobile phase B  $CH_3CN$  (w/o 0.1% of Formic acid) (50:50).

Nuclear Magnetic Resonance. Spectroscopic experiments for the characterization of compounds were carried out at the *Servicio de Resonancia Magnética Nuclear* at IQAC-CSIC using a Bruker Avance NEO 400 MHz instrument, as well as at the Structural Determination facility at IQS on a Varian Mercury 400 MHz (9.3950 T) instrument (400 MHz for <sup>1</sup>H and 101 MHz for <sup>13</sup>C). The 1H and 13C chemical shifts ( $\delta$ ) are quoted in parts per million (ppm) and referenced to the appropriate NMR solvent peak(s), which for <sup>1</sup>H measurements would correspond to the residual *proteo* component of the deuterated solvent. The <sup>11</sup>B chemical shifts are referenced relative to the external BF<sub>3</sub>·Et<sub>2</sub>O resonance which is set to 0.0 ppm. 2D-NMR experiments COSY, HSQC and HMBC were used where necessary in assigning NMR spectra. Spin-spin coupling constants (*J*) are reported in Hertz (Hz).

# 2. Synthetic approach to BN-naphthalene 1



#### 2.1 Streamlined synthesis of tetrahydro-BN-naphthalene 3

Steps  $I_a$  and  $I_b$ : Synthesis of **2** via proto-deallylation.

The reaction was conducted under Argon atmosphere. Caution: the triallylborane must be handled with care because of its pyrophoric nature.

Triallylborane (4.28 g, 5.95 mL, 32.0 mmol) was charged via syringe into a 50 mL oven-dried Schlenk tube equipped with a Teflon screw-on valve. The tube was then cooled to 0 °C in an ice/water bath, and the *N*,*N*-diallylamine (3.11 g, 3.95 mL, 32.0 mmol) was added dropwise. The mixture was then allowed to reach room temperature and then heated to 65 °C, resulting in a rather vigorous gas evolution. The mixture was allowed to stir at this temperature, initially with the valve cracked opened to argon so as to prevent pressure build up. Once the gas evolution subsided ( $\approx$  30 min), the valve was sealed, and the stirring continued at 65 °C for a total of 16 h. Upon cooling, the resulting colorless liquid was shown by <sup>1</sup>H and <sup>11</sup>B NMR to be the target **2** with >95% purity, and so could be used without further purification.



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  5.89 (ddt, *J* = 16.8, 10.0, 7.7 Hz, 2H, C=CH-CH<sub>2</sub>-N), 5.74 (ddt, *J* = 17.0, 10.6, 5.3 Hz, 2H, C=CH-CH<sub>2</sub>-B), 5.13-5.04 (m, 4H), 4.91 (apparent dd, *J* = 17.0, 1.7 Hz, 2H, CH<sub>2</sub>(trans)-CH (B)), 4.85 (ddt, *J* = 10.0, 2.4, 1.2 Hz, 2H, CH<sub>2</sub>(cis)-CH (B)), 3.67 (dt, *J* = 4.9 Hz, 4H, CH<sub>2</sub>-N), 1.84 (d, *J* = 7.7 Hz, 4H, CH<sub>2</sub>-B). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  136.9, 136.3, 115.5, 113.7, 50.9, 26.0 (C-B, obtained from HSQC). <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  43.9 ppm. Data in agreement with literature values.<sup>3</sup>

Step II: Synthesis of **3** by ring-closing metathesis

This procedure was adapted from that described by groups of Ashe and Fang.<sup>3,4</sup> The stoichiometry for this step is taken assuming the quantitative formation of **2** in previous step. The reaction was conducted under argon atmosphere.

The as-obtained neat liquid of the tetraallyl derivative, **2** (assuming that 6.05 g, 32.0 mmol are obtained in step  $I_b$ ) was transferred via syringe to a 350 mL oven-dried Schlenk tube, and the original flask was rinsed with a portion of anhydrous dichloromethane (15 mL) which was then added to the reaction flask. Next, 1<sup>st</sup> generation Grubbs catalyst (790 mg, 0.96 mmol, 3 mol %) was added carefully as solid leading to intense bubbling. An additional portion of anhydrous dichloromethane (16 mL) was carefully added so as to wash down any catalyst remaining on the tube walls. The resulting dark-purple solution was left stirring at room temperature, initially with the valve crack-opened to argon to avoid ethylene pressure build up, and, once the intensity of bubbling subsided (after  $\approx$  15 min), with the tube sealed. The stirring continued for a total of 16 h. At this stage, the solvent was removed using the Schlenk-line vacuum, and the liquid residue was subjected to a short-path vacuum distillation (80-100 °C,  $1 \cdot 10^{-1}$  mbar) using a Kugelrohr distillator. The target **3** was obtained as a colorless to off-white liquid (3.1 g, 72% over the two steps).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  5.85-5.73 (m, 2H), 5.62-5.55 (m, 2H), 3.51 (apparent tt, *J* = 5.4, 2.6 Hz, 4H, CH<sub>2</sub>-N), 1.41 (d, *J* = 5.4 Hz, 4H, CH<sub>2</sub>-B). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  126.03, 124.29, 50.13, 16.6 (C-B, obtained from HSQC). <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  41.1 ppm. Data in agreement with literature values.<sup>3</sup>



# 2.2 The hydrogen acceptor effect in the Pd/C-catalyzed dehydrogenation of 3 to 1

An oven-dried Schlenk tube was allowed to cool under argon and was charged with a magnetic stir bar, palladium on carbon (10% wt Pd/C, 53 mg, 5 mol % Pd, 0.05 mmol Pd) and precursor **3** (133 mg, 1.0 mmol). The hydrogen acceptor (6.5 mmol, 6.5 equiv.), or, for **run 1**, cyclohexane (0.70 mL) was added via syringe and the reaction mixture was heated to 70 °C with stirring for 21 h. At this point, the mixture was allowed to cool to room temperature and 1,2-dimethoxyethane (DME) (90 mg, 134  $\mu$ L, 1.0 mmol) was added as internal standard. The resulting suspension was shaken to ensure homogeneity. Next, 5 drops of the suspension were added to 1 mL of CDCl<sub>3</sub>, and subsequently, filtered with a syringe filter to remove the Pd/C. Finally, the resulting clear solution was analyzed by <sup>1</sup>H NMR and <sup>11</sup>B NMR.

For **Run 5** (with norbornene), due to incomplete conversion after 21 h, heating was continued, and addition samples were analyzed overtime until full conversion was reached.

**Table S1**. Comparison of products distributions obtained in Pd/C-catalyzed dehydrogenation of **3** using different acceptors.<sup>[a]</sup> Quantities: **Run 1**: cyclohexane (0.70 mL); **Run 2**: cyclohexene (0.67 mL); **Run 3**: neoxene (0.83 mL); **Run 4**: 1-hexene (0.80 mL), **Run 5**: Norbornene (0.66 mL).

Run	acceptor	% <b>3</b> <sup>[a]</sup>	% <b>1</b> <sup>[a]</sup>	% <b>4</b> <sup>[a]</sup>	% <b>S1</b> <sup>[a],[c]</sup>	% <b>S2</b> <sup>[a],[c]</sup>	Ratio <b>3:4</b>
1	None <sup>[b]</sup>	0	24	45	0	< 5%	34:66
2	Cyclohexene	0	39	42	0	0	48:52
3	Neohexene	18	27	31	0	0	46:54
4	1-Hexene	6	53	20	0	0	73:27
5	Norbornene	34	36	3	20	0	92:8
5'	Norbornene <sup>[d]</sup>	4	80	5	7	0	94:6

[a] Yields determined by <sup>1</sup>H NMR using DME as an internal standard; [b] Reaction conducted in cyclohexane (0.7 mL); [c] Detected by <sup>11</sup>B NMR and GC-MS; [d] Reaction after 72 h.



**Figure S1**. <sup>1</sup>H NMR traces of the aromatic region of the crude reaction mixtures in the dehydrogenation of **3** after 21 h at 70 °C.

#### 2.3 Optimized aromatization from 3 to form 1



Note: in order to prevent norbornene from condensing and solidifying in the colder upper part of the tube, the reaction vessel was submerged almost fully in oil and the protruding part was covered with foil.

An oven-dried Schlenk tube was allowed to cool under inert atmosphere, and then charged with palladium on carbon (1.58 g, 10% wt Pd/C, this amounts to 5 mol % Pd loading, 1.48 mmol).

Next, the tetrahydro-BN-naphthalene **3** (3.95 g, 29.73 mmol) and norbornene (9.84 g, 104.05 mmol, 3.5 equiv.) were added. Subsequently, the tube was sealed, and the mixture was heated to 110 °C for 21 h. After this time, the resulting mixture was diluted with dichloromethane (20 mL) and filtered through a plug of celite. <sup>1</sup>H NMR analysis of the crude mixture showed a  $\approx$  95:5 ratio of **1** to the semi-aromatized **4**. After the cake with additional portions of dichloromethane, the combined filtrate was concentrated under reduced pressure. Finally, the obtained orange oil was purified by column chromatography on silica gel, eluting with neat hexane. Target **1** obtained as colorless solid, (2.91 g, 76%) as a white solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.82 (d, *J* = 6.9 Hz, 2H, N-*alfa-H*), 7.70 (dd, *J* = 11.2, 6.4 Hz, 2H, N-*beta-H*), 7.43 (d, *J* = 11.1 Hz, 2H, B-*alfa-H*) 6.74 (apparent td, *J* = 6.7, 1.5 Hz, 2H, B-*beta-H*). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  138.3, 133.9, 114.3. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  28.5 ppm. Data in agreement with literature values.<sup>3</sup>

# 3. Enyne metathesis for the synthesis of BN-polycycles

# 3.1 Streamlined synthesis of the bis-diene bicyclic aminoborane 6



Steps  $I_a$  and  $I_b$ : Synthesis of **6** via proto-deallylation.

The reaction was conducted under argon atmosphere. Caution: the triallylborane must be handled with care because of its pyrophoric nature.

Triallylborane (2.07 g, 2.87 mL, 15.46 mmol) was charged *via* syringe into a 25 mL oven-dried Schlenk tube equipped with a Teflon screw-on valve. The tube was then cooled at 0 °C in an ice/water bath and the *N*,*N*-dipropargylamine (1.44 g, 1.60 mL, 15.46 mmol) was added dropwise. The mixture was then allowed to reach room temperature and then warmed up to 65 °C, leading to visible gas evolution. The mixture was allowed to stir at this temperature, initially with the valve crack open to argon ( $\approx$  30 min so as to prevent pressure build up). The Schlenk tube was then sealed, and the stirring continued at 65 °C for a total of 16 h. The resulting reddish liquid presented a set of NMR signals that were coherent with the target double enyne **6** (90 % by NMR, 2.57 g, 13.9mmol).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  5.86 (ddt, *J* = 17.4, 10.0, 7.6 Hz, 2H, CH<sub>2</sub>=CH-C), two overlapping signals: (CH<sub>2</sub>=CH: 4.95 (apparent dq, *J* = ~17.2, 2.0 Hz, 2H) and 4.91 (ddt, *J* = 10.0, 2.4, 1.3 Hz, 2H), 4.03 (d, *J* = 2.4 Hz, 2H, CH<sub>2</sub>-N), 2.20 (t, *J* = 2.3 Hz, consistently only a 1.3-1.5H integral observed in place of the expected 2H for the terminal alkyne CCH), 1.88 (apparent d, *J* = 7.6 Hz, 4H, CH<sub>2</sub>-B). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  135.7, 114.6, 80.9, 71.4, 37.7, 26.3 (C-B, obtained from HSQC). <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  44.8 ppm.

Step II: Synthesis of **7** by ring-closing enyne metathesis.

*Stoichiometry calculations for this step assumed the quantitative formation of 6 in the previous step. The reaction was conducted under argon atmosphere.* 

The liquid  ${\bf 6}$  (2.86 g, 15.46 mmol obtained in step I<sub>b</sub>) was transferred via syringe to a 50 mL oven

dried Schlenk tube; and the original flask was rinsed with a portion of anhydrous dichloromethane (17 mL) which was also added to the reaction flask. Next, 1<sup>st</sup>-generation Grubbs catalyst (382 mg, 0.46 mmol, 3 mol %) was added carefully (as powder). An additional portion of dichloromethane (6 mL) was carefully added so as to wash down any catalyst remaining on the walls, and at this point the valve was quickly closed. This was done taking into account that small amounts of ethylene are commonly generated during this process, and that this ethylene may be crucial to maintain the activity of the catalyst.<sup>\*,5</sup> The resulting dark-purple solution was left stirring at room temperature for a total of 64 h. At this stage, the solvent was removed using the Schlenk-line vacuum, and the liquid residue was subjected to a short-path vacuum distillation (90-110 °C,  $1 \cdot 10^{-1}$  mbar) using a Kugelrohr distillation apparatus. The target **7** was obtained as a colorless to off-white liquid which rapidly solidifies upon standing (1.15 g, 40% combined yield over the step I and step II).

**\*Note**: We have observed that opening the flask before the process is complete may lead to reaction stalling, which we tentatively attribute to the escape of ethylene.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.35 (dd, *J* = 17.8, 11.0 Hz, 2H, CH<sub>2</sub>=CH-), 5.90 (m, 2H), 4.98 (apparent d, *J* = 17.8 Hz, 2H, CH<sub>4</sub>(trans)=CH-), 4.92 (d, *J* = 11.0 Hz, 2H, CH<sub>4</sub>(cis)=CH-), 3.73 (apparent td, *J* = 4.8, 1.7 Hz, 4H, CH<sub>2</sub>-N), 1.57 (apparent q, *J* = 5.1 Hz, 4H, CH<sub>2</sub>-B). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  138.4, 133.3, 129.4, 109.3, 49.8, 17.4 (C-B obtained from HSQC). <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  40.8 ppm. HRMS (EI) m/z calcd. for C<sub>12</sub>H<sub>16</sub>BN<sup>+</sup> [M<sup>+</sup>] 185.1370, found 185.1370.

#### 3.2 Synthesis of the bis-diene aminoborane 11



Bis(3-(p-tolyl)prop-2-yn-1-yl)amine formation

Adapted from a reported procedure.<sup>6</sup> Di-*tert*-butyl dicarbonate (Boc<sub>2</sub>O, 10.9 g, 50.0 mmol) was added dropwise at 0 °C to a solution of prop-2-yn-1-amine (3.18 mL, 50.0 mmol) in dichloromethane (100 mL). After 1 h of stirring, the solvent was removed under reduced pressure giving a colourless oil which, when placed in a refrigerator, eventually turned into a white solid. This solid was then purified by column chromatography on silica gel using Hex/EtOAc (9:1,  $R_F = 0.43$ ) to afford *tert*-butyl prop-2-yn-1-ylcarbamate as a white solid. (6.95 g, 90%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  4.69 (br s, 1H, NH), 3.92 (d, *J* = 3.5 Hz, 2H, CH<sub>2</sub>-N), 2.22 (t, *J* = 2.5 Hz, 1H, CH=C-), 1.45 (s, 9H, <sup>t</sup>Bu). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  155.3, 85.3, 80.2, 71.3, 30.5, 28.4. Data in agreement with literature values.<sup>6</sup>

Adapted from a reported procedure.<sup>6</sup> NaH (60% in mineral oil) (4.37 g, 109 mmol) was added in a 250 mL round bottom flask followed by the addition of anhydrous DMF (110 mL). Parallelly, *tert*-butyl prop-2-yn-1-ylcarbamate (6.78 g, 43.7 mmol) was dissolved in anhydrous THF (30 mL) in a round bottom flask. Then, the latter solution was added to the NaH suspension dropwise at 0 °C and it was left stirring for 1 h at room temperature. Next, 3-bromoprop-1-yne (3.95 mL, 52.4 mmol) was added dropwise and the reaction mixture was left stirring for 2 h at room temperature. After this time, the mixture was quenched with water (400 mL) and extracted with Et<sub>2</sub>O (3 x 100 mL). The combined organic layers were washed with brine (3 x 100 mL), dried over anhydrous magnesium sulphate and the solvent was removed under reduced pressure. Finally, the oil is purified through a silica column chromatography using Hex/EtOAc (100:1  $\rightarrow$  9:1, R<sub>F</sub> = 0.51 with Hex/EtOAc 9:1) as eluent phase to afford *tert*-butyl di(prop-2-yn-1yl)carbamate as an orange oil (7.04 g, 83%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.17 (br s, 4H, CH<sub>2</sub>-N), 2.22 (t, *J* = 2.5 Hz, 2H, CH≡C-), 1.47 (s, 9H, <sup>t</sup>Bu). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 154.3, 81.2, 78.9, 72.0, 35.3, 28.4. Data in agreement with literature values.<sup>6</sup>

Boc

p-Tol 1

p-Tol p-Tol (8): The Sonogashira reaction protocol is adapated from a published procedure for a related N-propagyl substrate.<sup>7</sup> The 4-iodotoluene (3.09 g, 16.0 mmol), bis(triphenylphosphine) palladium (II) dichloride (0.449 g, 2 mol %,) and copper (I) iodide (0.244 g, 4 mol %) were introduced in a 350 mL oven-dried Schlenk tube equipped with a Teflon screwon stopper. Then, the tert-butyl di(prop-2-yn-1-yl)carbamate obtained in the previous step (3.09 g, 16.0 mmol) and triethylamine (6.46 g, 6.5 mL, 64.0 mmol) were added. Finally, anhydrous THF (6.4 mL) was added, and the reaction was left stirring at room temperature for 12 h. At this point, the crude mixture was diluted in ethyl acetate ( $\approx$  15 mL), filtered through a pad of Celite<sup>\*</sup>. The organic solution was then washed with brine (4 x 30 mL) and dried with anhydrous magnesium sulphate. The solvent was then removed under reduced pressure the resulting oil is purified through a silica column chromatography using Hex/EtOAc (9:1,  $R_F$  = 0.34) as eluent phase to afford tert-butyl di(prop-2-yn-1-yl)carbamate 8 as a yellow/brown oil (0.62 g, 42%, unoptimized procedure).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.34 (d, *J* = 8.1 Hz, 4H), 7.11 (d, *J* = 8.0 Hz, 4H), 4.46 (s, 4H, CH<sub>2</sub>-N), 2.35 (s, 6H, CH<sub>3</sub>-Ar), 1.54 (s, 9H, <sup>t</sup>Bu). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 154.6, 138.4, 131.7, 129.0, 119.8, 53.5, 83.8, 80.8, 36.1, 28.4, 21.5.

p-Tol (9): The *N*,*N*-bis-propargyl derivative **8** (2.51 g, 6.73 mmol) was dissolved in dichloromethane (12 mL), and to this solution the trifluoroacetic acid (7.67 g, 5.18 mL, 67.3 mmol) was added. After 1 h of stirring, the reaction was quenched with a saturated aqueous solution of K<sub>2</sub>CO<sub>3</sub> (38 mL) and the product was extracted with dichloromethane (3 x 38 mL), dried

over anhydrous magnesium sulphate, filtered and the solvent was removed under reduced pressure to give the amine **9** as a dark orange oil (1.73 g, 94%). *The product was sufficiently pure to be used as obtained in the next step.* 

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.33 (d, J = 8.2 Hz, 4H), 7.10 (d, J = 8.0 Hz, 4H), 3.79 (s, 4H, CH<sub>2</sub>-N), 2.34 (s, 6H, Me). The N-H proton is not observed. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  138.3, 131.7, 129.1, 120.1, 86.2, 84.0, 38.1, 21.5.

Steps  $I_a$  and  $I_b$ : Synthesis of **10** via proto-deallylation.

The reaction was conducted under argon atmosphere. Caution: the triallylborane must be handled with care because of its pyrophoric nature.

Triallylborane (134 mg, 0.186 mL, 1.0 mmol) was charged *via* syringe into a 15 mL oven-dried Schlenk tube equipped with a Teflon screw-on valve. The tube was then cooled at 0 °C in an ice/water bath and the amine **9** (273.0 mg, 1.0 mmol) was added dropwise. The mixture was then allowed to reach room temperature and then warmed up to 65 °C, leading to visible gas evolution. The mixture was allowed to stir at this temperature for a total of 16 h. The resulting brown oil presented a set of NMR signals that were coherent with the target **10**, which was obtained in more than 90% purity (NMR) and was used without any additional purification (70% by NMR, 255.72 mg, .0.7 mmol).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 7.33 (d, *J* = 7.8 Hz, 4H), 7.11 (d, *J* = 7.8 Hz, 4H), 5.94 (ddt, *J* = 17.6, 10.3, 7.7 Hz, 2H, CH<sub>2</sub>=CH-), 5.01 (apparent dq, *J* = 17.0, 1.8 Hz, 2H, CHH<sub>(trans)=</sub>CH-), 4.93 (apparent ddt, *J* = 10.1, 2.4, 1.2 Hz 2H, CHH<sub>(trans)=</sub>CH-), 4.29 (s, 4H, CH<sub>2</sub>-N), 2.35 (s, 6H, CH<sub>3</sub>-Ar), 1.96 (apparent d, *J* = 7.4, Hz, 4H, CH<sub>2</sub>-B). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 138.2, 136.0, 131.7, 129.1, 120.1, 114.4, 85.9, 83.3, 38.8, 26.5 (C-B from HSQC), 21.5. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 44.1.

Step II: Synthesis of **11** by ring-closing enyne metathesis.

*Stoichiometry calculations for this step assumed the quantitative formation of* **10** *in the previous step. The reaction was conducted under argon atmosphere.* 

The oil **10** (365 mg, 1.0 mmol, as obtained in step  $I_b$ ) was diluted in anhydrous dichloromethane (0.75 mL). Next, 2<sup>nd</sup>-generation Hoveyda-Grubbs catalyst (18.8 mg, 0.03 mmol, 3 mol %) was added carefully (as powder). An additional portion of dichloromethane (0.75 mL) was carefully added so as to wash down any catalyst remaining on the walls. The valve was quickly closed to avoid any ethylene loss. The resulting dark-green solution was left stirring at room temperature for a total of 64 h. At this stage, the solvent was removed using the Schlenk-line vacuum, and the NMR spectroscopic analysis of the resulting residue (reaction crude) showed the formation of the target product **11** (98 % by NMR, 359.78 mg, 0.98 mmol)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.18 (d, *J* = 8 Hz, 4H), 7.12 (d, *J* = 8 Hz, 4H), 5.83 – 5.79 (m, 2H, CH=CH<sub>2</sub>-B), 5.09 (d, *J* = 1.4 Hz, 2H, CHH'=C-*tol*), 5.01 (d, *J* = 1.4 Hz, 2H, CHH'=C-*tol*), 3.73 (apparent td, *J* = 4.8, 1.7 Hz, 4H, CH<sub>2</sub>-N), 2.35 (s, 6H, CH<sub>3</sub>-Ar), 1.55 (apparent q, *J* = 4.6 Hz, 4H, CH<sub>2</sub>-B). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  149.7, 138.7, 136.9, 134.8, 128.7, 128.4, 128.1, 110.8, 51.6, 21.2, 17.1 (C-B from HSQC). <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  40.0. HRMS (EI) m/z calcd. for C<sub>26</sub>H<sub>28</sub>BN<sup>+</sup> [M<sup>+</sup>] 365.2309, found 365.2303.

# 4. Obtention of BN-polycycles via Diels-Alder reaction

# 4.1. Synthesis of BN tetracycles 13 (and its hydrate 14)



# The reaction was conducted under argon atmosphere.

The Diels-Alder stage. The bicyclic core **7** (27.8 mg, 0.15 mmol) was charged in an oven-dried Schlenk flask equipped with a Teflon screw-on valve; this substrate was then dissolved in anhydrous toluene (1.0 mL). Subsequently, diethyl 2-butynedioate (102 mg, 96  $\mu$ L, 0.60 mmol, 4.0 equiv.) were added. The tube was sealed, and the mixture was heated to 110 °C for 12 h. At this stage the GC-MS analysis of the reaction mixture showed the complete consumption of the starting material and the formation of the BN-tetracycle **13** as the major product. The solvent was removed under reduced pressure to obtain a dark-orange oil.

The interim hydration stage. The crude oil was suspended in ether (0.3 mL). Subsequently, 43  $\mu$ L of water and the resulting mixture was allowed to stir at room temperature until precipitation of an orangish solid ( $\approx$  3h). This solid is separated by centrifugation, and then purified by washing with ether (2 x 0.5 mL) to obtain a white solid which was shown by NMR to be the hydrate **14** in pure form (30 % after the double DA and the hydration, 24.45 mg, 0.045mmol). Heating **14** at 162 °C for 35 min under vacuum in a Schlenk flask returned to the target (dehydrated) **13** now pure by NMR (80 %, 18.9 mg, 0.036mmol).

**14** (hydrated form): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.61 (apparent broad singlet, 2H, CH<sub>2</sub>-CH-CR<sub>2</sub>), 4.30-4.14 (m, ~9H, CO<sub>2</sub>CH<sub>2</sub>), 3.63 (t, *J* = 11.7, Hz, 2H, CHH'-N), 3.36-3.27 (m, 2H, CH-CH<sub>2</sub>-B), 3.13-2.83 (m, 6H, 2 overlapped signals: CHH'-CH=C, CHH'-N. Furthermore, N-H could be located in this zone), 1.31 (t, *J* = 7.2 Hz, 6H), 1.26 (t, *J* = 7.1 Hz, 6H), 0.77 (dd, *J* = 13.7, 4.0 Hz, 2H, CHH'-B), 0.11 (apparent t, *J* = 13.4 Hz, 2H, CHH'-B). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 169.17, 166.89, 144.21, 133.75, 124.32, 121.45, 61.15, 61.13, 54.59, 36.62, 29.04, 27.33, 14.23, 14.17. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 0.20 ppm.

	HR-MS data, QTOF			
Mode	ESI-	ESI+		
Structure	EtOOC	EtOOC		
Formula	C <sub>28</sub> H <sub>37</sub> BNO <sub>9</sub> <sup>-</sup>	$C_{28}H_{37}BNO_8^+$		
Calculated	542.2567	526.2607		
Found	542.2569	526.2587		

**13**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.56 (broad, 2H, C**H**=CR<sub>2</sub>), 4.31-4.14 (m, 8H, CO<sub>2</sub>C**H**<sub>2</sub>), 3.82 (d, *J* = 13.5 Hz, 2H, C**H**H'-N), two overlapping signals: 3.24 (d, *J* = 13.4 Hz, 2H, CH**H'**-N) and 3.26-3.16 (m, 2H), 3.10 (ddt, J = 23.0, 7.4, 2.6 Hz, 2H, C**H**-CH<sub>2</sub>-B), 2.88 (ddt, J = 23.0, 6.6, 3.3 Hz, 2H), 1.34-

1,26 (m, 14H + extra integral for impurities – up to 20H,  $CO_2CH_2CH_3$  + CHH'B), 0.78 (dd, *J* = 16.4, 12.3 Hz, 2H, CHH'-B. *The other diastereotopic CHB proton overlaps with the "1.34-1.26 multiplet" (COSY, HSQC)*. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.9, 167.4, 140.8, 134.4, 127.4, 116.6, 61.2, 61.1, 57.2, 35.3, 27.3, 24.3 (CH<sub>2</sub>-B, obtained from HSQC), 14.2, 14.1. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  41.2 ppm. GC-MS (EI): 525 (M<sup>+</sup>), 480 (M<sup>+</sup>-OEt).

#### 4.2. Synthesis of BN tetracycle 16



The bicyclic core **7** (0.15 mmol, 27.8 mg) was charged in an oven-dried Schlenk flask equipped with a Teflon screw-on valve and then dissolved in anhydrous toluene (1.0 mL). Maleic anhydride (59 mg, 96  $\mu$ L, 0.60 mmol, 4.0 equiv.) was added, the tube was sealed, and the mixture was heated to 110 °C for 12 h. After this reaction time, the GC-MS analysis of the reaction mixture showed the complete consumption of the starting material and the presence of the tetracycle **15** as the major product. GC-MS (EI): 381 (M<sup>+</sup>), 353 (M<sup>+</sup>-CO).

Hydration of **15** to **16**. The solvent was removed under reduced pressure to obtain a heterogeneous solid which was suspended in ether (0.5 mL). Subsequently, 43  $\mu$ L of water were added to the resulting suspension and the mixture was allowed to stir at room temperature for 12 h. This solid was washed with acetonitrile (2 x 0.5 mL) to obtain a brownish solid (77 % of **16**, 48.1 mg, 0.11 mmol). Then, 10 mg of the obtained solid were solved in MeOH (0.7 mL, not all the product was dissolved) and transferred to a 5 ml vial using a syringe equipped with a syringe filter. Finally, the vial was placed in a bigger vial ( $\approx$  10 mL) which was filled with ether (5 mL) and was subsequently closed. After one-week, suitable crystals for X-ray diffraction appeared in the small vial and the structure of **16** was thus confirmed.

	HR-MS data, QTOF		
Mode	ESI-	ESI+	
Structure	$HO_2C$ $HO_2C$ , $H \rightarrow H$ $HO_2C$ , $H \rightarrow H$ $H \rightarrow H$ $H \rightarrow H$ $H \rightarrow CO_2H$	$HO_2C$ $HO_2C_2H$ $H$	
Formula	$C_{20}H_{23}BNO_8^-$	$C_{20}H_{25}BNO_8^+$	
Calculated	416.1522	418.1668	
Found	416.1521	418.1665	

# 5. Synthesis of the semi-aromatized product 17 (and its hydrate 17-H<sub>2</sub>O)



The H<sub>2</sub>O adduct **14** (27mg, 0.05 mmol) were charged in a Schlenk tube equipped with a Teflon screw-on vale. The flask was placed under vacuum and then was heated to 162 °C for 35 min using a sand bath. After this time, the reaction vessel was removed from the sand and allowed to cooldown under an Argon flow. After the dehydration protocol, Pd/C (10.6 mg, 10% wt Pd/C) and decane (2.20 mL) were added to the reaction tube containing the newly formed Diels-Alder adduct **13**. Subsequently, the tube was sealed, and the mixture was heated to 180 °C for 24h.<sup>8</sup> After this time, the resulting mixture was diluted with dichloromethane (8 mL) and filtered through a plug of celite. After washing the cake with additional portions of dichloromethane the filtrate was concentrated under reduced pressure (first rotavap, then Schlenk line) to obtain a yellowish solid. HPLC analysis of the obtained solid showed the formation of a new species with m/z m+1 = 522, consistent with the semi-aromatized product **17** (*note:* **17** *and* **17\_H<sub>2</sub>O are** *observed with the same m+1 in the HPLC*). Finally, the obtained solid was purified by reverse phase column chromatography using H<sub>2</sub>O:CH<sub>3</sub>CN (95:5 to 50:50) as an eluent. Target **17** and its hydrated form **17-H<sub>2</sub>O** were obtained as a white solid. (5mg, 17%, 70:30 **17-H<sub>2</sub>O:17** by NMR).

The interim hydration stage. The obtained solid was solved in deuterated chloroform (0.7 mL). Subsequently, 1  $\mu$ L of water was added to the solution and it was allowed to stir for 5 min. After this time, <sup>1</sup>H NMR analysis of the mixture showed a  $\approx$  94:6 ratio of **17-H<sub>2</sub>O**: **17**. Heating **17-H<sub>2</sub>O** at 162 °C for 35 min under vacuum in a Schlenk flask returned to the target (dehydrated) **17** (9:1 product: starting material by NMR)

**17-H2O:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 7.66 (d, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 4.36 (m, ~11H, CO<sub>2</sub>CH<sub>2</sub>), 3.88 (dd, J = 13.0, 3.8 Hz, 2H, Ar-CHH'-N), 3.52 (dd, J = 13.0, 7.3 Hz,2H, Ar-CHH'-N), 1.72 (d, *J* = 14.7 Hz, 2H, Ar-CHH'-B), 1.65 (d, *J* = 14.7 Hz, 2H, Ar-CHH'-B), 1.39 (t, *J* = 7.2 Hz, ~7H), 1.34 (t, *J* = 7.1 Hz, ~8H).

**17:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 7.81 (d, J = 8.1 Hz, 2H), 7.20 (d, J = 7.20 Hz, 2H), 4.46 (q, J = 7.2 Hz, 4H), 4.38 (s, 4H, Ar-CH<sub>2</sub>-N), 4.34 (q, J = 7.2 Hz, 4H), 2.28 (s, 4H, Ar-CH<sub>2</sub>-B), 1.41 (t, J = 7.1 Hz, 7H), 1.37 (t, J = 7.1 Hz, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  169.72, 166.76, 140.23, 137.17, 132.71, 127.05, 127.00, 126.34, 61.61, 61.48, 53.20, 17.84 (C- B, from HSQC), 14.35, 14.29.

# 6. References

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# 7. Computational details

All calculations were performed using Gaussian 09.<sup>[1]</sup>

Calculations were performed at the DFT level using the B3LYP functional with an ultrafine integration grid and employing the 6-31+G(d,p) basis set for all atoms. Empirical dispersion was applied using the D3 version of Grimme dispersion with Becke-Johnson damping (gd3BJ keyword). All structures were fully optimized in dichloromethane using the SMD continuum model. Transition states were identified by having one imaginary frequency in the Hessian matrix. It was confirmed that transition states connect with the corresponding intermediates by means of application of the eigenvector corresponding to the imaginary frequency and subsequent optimization of the resulting structures. All energies collected in the text are Gibbs energies in solvent at 298 K.

Reaction path 1: via 6-membered transition state



Reaction path 2: via 4-membered transition state



Species: neutral (allyl)₂NH···B(allyl)₃ (5)
Stoichiometry: C15H26BN
Charge: 0 Multiplicity: 1



Coordinates (xyz)

В	0.85675232	-0.09653326	-0.08880310
Ν	-0.78092500	-0.44188549	0.11432537
С	1.46226885	-1.31218309	-1.02895069
с	1.10367944	1.34703460	-0.83087101
С	1.47169089	-0.14354731	1.44229315
С	-1.59409484	0.59126807	0.85606885
с	-1.52871413	-0.95576425	-1.08081170
С	2.95615803	-1.37821752	-0.99067148
С	3.79030672	-0.99829779	-1.96891835
С	1.25470795	-1.45874913	2.11242521
С	1.17454543	2.56516515	0.03809705
С	-2.80976419	-1.64395399	-0.70335262
С	-2.15474549	1.67591630	-0.01836873
С	-3.43906133	2.03789532	0.00460661
С	-4.00910133	-1.32614743	-1.19431282

С	0.30560982	-1.73666324	3.02312515
С	2.28632814	3.26103692	0.31536226
н	1.06572044	-2.28469154	-0.69534259
н	1.14547174	-1.17793217	-2.07239396
н	0.34774879	1.48648510	-1.61943729
Н	2.06342428	1.25119378	-1.35511861
Н	2.54486295	0.06410287	1.34502333
н	1.06441678	0.66539261	2.06107688
Н	-2.41233782	0.08068794	1.37062101
н	-0.93368212	1.01413734	1.61477437
Н	-1.70995429	-0.11804506	-1.75597067
Н	-0.87134826	-1.66154677	-1.58748823
Н	3.39803907	-1.74075621	-0.06124444
н	4.86937547	-1.04395461	-1.84917626
Н	3.41549553	-0.62488784	-2.92009113
Н	1.87792068	-2.28602728	1.76848543
Н	0.25090910	2.89545641	0.51576910
Н	-2.71425036	-2.47605662	-0.00472157
Н	-1.46316095	2.20653722	-0.66432738
Н	-3.80349906	2.86183195	-0.60123284
н	-4.16553482	1.52371911	0.62876942
Н	-4.89944128	-1.88424805	-0.92092913
н	-4.13643390	-0.49786262	-1.88620321
Н	0.16871553	-2.73932621	3.41813673
н	-0.34634777	-0.96006847	3.41982549
Н	2.27406452	4.11443807	0.98818434
н	3.24694218	2.98816559	-0.11789375
Н	-0.71328674	-1.22963546	0.77031765

Imaginary frequencies: none

E(RB3LYP)=-666.909258752 HartreesThermal correction to Gibbs Free Energy=0.331151Sum of electronic and thermal Free Energies=-666.57811

#### **Species: neutral tetra-allyl aminoborane (allyl)<sub>2</sub>N-B(allyl)<sub>2</sub> (2)** Stoichiometry: C<sub>12</sub>H<sub>20</sub>BN Charge: 0 Multiplicity: 1

≶∕\_<mark>B</mark>∕∕∕∕

Coordinates (xyz)

-0.91224069	-0.04693960	-0.12016854
0.48481894	-0.13491335	-0.00449004
-1.79651208	-1.29448037	-0.59595663
-1.69430640	1.30506570	0.22827701
1.33840175	0.99730049	0.39196920
1.25799475	-1.36005237	-0.26372276
-1.83691567	2.14516521	-1.01123648
-2.24194125	-2.06055498	0.62040492
1.92632689	-1.32960411	-1.61345433
1.72243758	0.92795871	1.84653161
2.97800801	0.83416593	2.29333595
3.24684325	-1.39367016	-1.80467517
-1.32708923	3.37067478	-1.19148930
-3.46780310	-2.02881379	1.15910760
-1.25405915	-1.95832077	-1.27961863
-2.67779629	-0.92278924	-1.13309718
-2.69363923	1.02145594	0.58795161
-1.22202215	1.89145830	1.02377994
2.23888195	0.99977566	-0.23245885
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2.01049340	-1.48069084	0.52404641
0.58900028	-2.22043605	-0.19881770
-2.38221111	1.68534653	-1.83727007
-1.47225867	-2.65111792	1.11987953
1.25633611	-1.23249622	-2.46776016
0.89300884	0.94125255	2.55372952
3.20522779	0.78695304	3.35445099
	-0.91224069 0.48481894 -1.79651208 -1.69430640 1.33840175 1.25799475 -1.83691567 -2.24194125 1.92632689 1.72243758 2.97800801 3.24684325 -1.32708923 -3.46780310 -1.25405915 -2.67779629 -2.69363923 -1.22202215 2.23888195 0.80548788 2.01049340 0.58900028 -2.38221111 -1.47225867 1.25633611 0.89300884 3.20522779	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$

н н н н н	3.82154475 3.68211183 3.93583352 -1.44712124 -0.77749184 -3.70431524 -4.27220756	0.80716170 -1.36894506 -1.47831968 3.90385526 3.87997056 -2.57696603 -1.45365455	1.60669199 -2.79949868 -0.96690844 -2.13030353 -0.40244383 2.06664552 0.70523867	
Imaginary frequ	uencies: none			
E(RB3LYP)= Thermal correc Sum of electro	ction to Gibbs Fronting and thermal	ee Energy= Free Energies=	-548.988651480 Hartrees 0.248207 -548.740444	
Species: proper Stoichiometry: Charge: 0	n <b>e</b> C₃H₀ Multiplicity: 1			
~	,			
Coordinates (x)	γz)			
С Н Н С Н С Н Н	$\begin{array}{r} 1.23562670\\ 1.80980560\\ 1.18037418\\ 1.80980145\\ -0.13180048\\ -0.16279036\\ -1.28510620\\ -1.30495505\\ -2.24455600 \end{array}$	-0.16429849 0.15236462 -1.25735766 0.15233334 0.45625389 1.54648901 -0.22088022 -1.30892226 0.28864191	0.0000032 -0.87963998 -0.0002075 0.87965297 0.00000329 -0.00000681 -0.00000259 0.00000259 0.00000285 0.00000557	
Imaginary frequ	uencies: none			
E(RB3LYP)= Thermal correc Sum of electro	ction to Gibbs Front	ee Energy= Free Energies=	-117.931979648 Hartrees 0.0544 -117.8776	

**Species: 6-membered TS in proto-deallylation in 5** Stoichiometry: C<sub>15</sub>H<sub>26</sub>BN Charge: 0 Multiplicity: 1



Coordinates (xyz)

В	0.79640311	-0.14578422	-0.11967262
Ν	-0.72416448	-0.29438253	0.10828353
С	1.40936508	-1.39650453	-0.99035833
С	1.35737528	1.28100082	-0.73080599
С	1.55143172	-0.15990773	1.58309385
С	-1.47641104	0.89327472	0.57797109
С	-1.53859426	-1.10357041	-0.83229904
С	2.89864977	-1.53530878	-0.93548385
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С	1.07579806	-1.38772475	2.07712866
С	1.27094360	2.55427983	0.04992359
С	-2.81901278	-1.60422630	-0.21898659
С	-1.97548502	1.78541133	-0.52841661
С	-3.23406382	2.22062881	-0.62333715
С	-4.03066791	-1.42755802	-0.75045564
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С	2.27938462	3.11516304	0.73335497
н	0.97140019	-2.34529272	-0.64886296
Н	1.10186589	-1.26916075	-2.03870575

н	0.85025464	1.40804133	-1.70002968	
Н	2.41148492	1.09133803	-0.96270391	
н	2.61799170	-0.07682999	1.38597333	
н	1.13791893	0.74398171	2.03027516	
н	-2.33087092	0.56118892	1.17944033	
н	-0.81622066	1.45397784	1.24477648	
н	-1.75961595	-0.52333189	-1.73712569	
Н	-0.94154443	-1.96354610	-1.13692658	
н	3.31043162	-1.91033023	0.00326712	
Н	4.83565092	-1.33239636	-1.77967040	
Н	3.41965225	-0.84496960	-2.87213383	
н	1.65875352	-2.28355459	1.86307360	
Н	0.30841635	3.06484715	0.07257936	
Н	-2.71396273	-2.17100148	0.70589582	
Н	-1.24925548	2.08462442	-1.28020767	
Н	-3.54667185	2.88540406	-1.42331855	
Н	-3.99258029	1.92381361	0.09726044	
н	-4.92065383	-1.84720503	-0.29060822	
Н	-4.16919292	-0.85555173	-1.66474470	
н	-0.61931226	-2.55282223	2.71387297	
н	-0.73411054	-0.75927177	3.04396849	
Н	2.14433941	4.03398743	1.29751348	
Н	3.27136810	2.66769954	0.75025391	
Н	-0.68381880	-1.13305803	1.28473764	
Imaginarv	frequencies: one: -11d	80.38 cm <sup>-1</sup>		
5 5	•			

E(RB3LYP)=	-666.870561233 Hartrees
Thermal correction to Gibbs Free Energy=	0.326496
Sum of electronic and thermal Free Energies=	-666.54407

**Species: 4-membered TS in proto-deallylation in 5** Stoichiometry: C<sub>15</sub>H<sub>26</sub>BN Charge: 0 Multiplicity: 1

Coordinates (xyz)

В	0.70903216	0.48987138	-0.23101124
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С	1.37540787	0.01221283	-1.62248725
с	0.90412023	2.05880932	0.11889015
с	-1.87266619	0.79071272	0.29834465
С	-1.09883506	-1.39737806	-0.52371390
c	1.86707317	-1.93965961	1.05478815
C	1,48206112	-2.87083359	1,93936433
c	0.71083562	2.55130970	1.52388161
C	2.80806098	0.40126305	-1.82790525
с	-2.03006038	-2.19375804	0.34800105
с	-2.42036085	1.32945300	-0.99776898
с	-3.66741298	1.12602202	-1.43189680
с	-3.22179910	-2.65547026	-0.03919594
с	-0.13317127	3.51412570	1.91609143
С	3.84120972	-0.44694588	-1.91423305
Н	2.54077659	0.08869006	0.88578473
Н	1.47115494	-0.20011688	2.25113589
Н	0.75611243	0.49602841	-2.39627494
Н	1.27296190	-1.06518948	-1.78559554
Н	1.94028696	2.29538574	-0.16056489
Н	0.27494708	2.64532099	-0.56537408
Н	-2.65813575	0.24470386	0.83059322
Н	-1.54887302	1.60768132	0.94334168
Н	-1.54490023	-1.23961158	-1.51437809
н	-0.18409151	-1.97650834	-0.66455909
Н	2.34283084	-2.26463482	0.13040397
н	1.63159057	-3.92973224	1.75070616

Н	1.00535069	-2.59921935	2.87913625	
Н	1.34191449	2.08851145	2.28239967	
Н	3.01729679	1.46930501	-1.89370891	
Н	-1.66288649	-2.40278496	1.35293075	
н	-1.72641485	1.90781757	-1.60722992	
Н	-4.01970519	1.53877323	-2.37292919	
н	-4.37730470	0.53919385	-0.85315149	
Н	-3.84320171	-3.25402512	0.62056893	
н	-3.61234497	-2.44888158	-1.03309079	
н	-0.20090559	3.82243336	2.95552680	
Н	-0.78634549	4.02189196	1.20870138	
н	4.86055561	-0.09281841	-2.03924753	
н	3.69863903	-1.52455837	-1.86245372	
н	0.30703908	-0.31467592	0.92378397	
Imaginar	y frequencies: one: -1585	5.34 cm-1		
E(RB3LYP)=		-666.838572063	Hartrees	
Thermal correction to Gibbs Free Energy=			0.32182	
Sum of electronic and thermal Free Energies=		-666.51675		

# **Species: weak adduct between 2 and propene (initially obtained after proto-deallylation)** Stoichiometry: C<sub>15</sub>H<sub>26</sub>BN Charge: 0 Multiplicity: 1

*∕*∼<sup>H</sup> / R ~<sup>Ń</sup>~~ 1

weak propene complex

Coordinates (xyz)

B N C C C C	0.39851487 -0.89622061 1.47954025 0.89517102 0.74004026 -1.95288672	0.52850300 -0.01648657 -0.25617923 1.91458618 -0.70463754 0.47486691	-0.69561526 -0.58594401 -1.59692472 -0.07190292 2.36700848 0.30877585
C	-1.30375132	-1.24640359	-1.28851393
C	2.90650009	0.17734583	-1.43789690
C	3.65456411	0.77746094	-2.3/131554
C	1.99001974	-1.05008728	2.04505052
	-0.00354892	2.86135864	0.66198529
	-1.1593/1/9	-2.40/82//6	-0.418589/9
	-3.03033410	1.10/99921	-0.43535002
	-4.33014291		
C C	2 17280204	-3.23178743	1 60985022
C	0 16316092	3 26986252	1 92654523
н	1 41624234	-1 32974104	-1 37279147
н	1.18819564	-0.15079402	-2.65337978
н	1.31554711	2.44616412	-0.94244762
Н	1.77105573	1.68759136	0.55084254
н	0.48585613	0.31115566	2,65389683
Н	-0.07532634	-1.42290565	2.32994039
Н	-2.37209174	-0.37427240	0.86246832
Н	-1.50376013	1.14375760	1.04262069
Н	-2.34591265	-1.14049318	-1.60973273
Н	-0.70292052	-1.35699346	-2.19371848
Н	3.35545019	-0.01157911	-0.46187664
Н	4.68104033	1.07458065	-2.17533298
Н	3.25900230	0.99438324	-3.36188463
Н	2.77066453	-0.28947141	2.08049792
Н	-0.84803466	3.26166571	0.09939285
Н	-0.14987240	-2.68576165	-0.07433784
Н	-2.73768246	2.05181192	-1.02234828
H	-5.092/2152	1.3/939365	-0.9/048936
H	-4.6/292494	-0.040356/4	0.14443666
H	-2.U1/64386	-4.12069/81	0.59242016
Н	-3.19352027	-3.04920309	-0.35855642

Н	3.21544932	-2.80968533	2.26085907	
Н	1.58914953	-3.12787930	1.62446131	
н	-0.52354506	3.96875474	2.39571069	
н	0.99095792	2.90889061	2.53387933	
н	2.83701466	-2.39554961	0.59356994	
Imaginary frequencies: none				
E(RB3LYP)=			-666.92428725 Hartrees	
Thermal correction to Gibbs Free Energy=		0.321273		
Sum of electronic and thermal Free Energies=			-666.60301425	

[1] Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

# 8. Characterization data

<sup>№</sup> В <sup>№</sup> <sup>№</sup> <sup>1</sup>Н NMR (400 MHz, CDCl<sub>3</sub>)

# $\begin{array}{c} 5.5 \\$



Zoom-in regions





# HSQCEDETGPSISP experiment (CDCl<sub>3</sub>)







S24











S29

#### HSQCEDETGPSISP experiment (CDCl<sub>3</sub>)



HRMS (EI) m/z calcd. for  $C_{12}H_{16}BN^+$  [M<sup>+</sup>] 185.1370, found 185.1370.











HSQCEDETGPSISP experiment (CDCl<sub>3</sub>)





S37

#### HSQCEDETGPSISP experiment (CDCl<sub>3</sub>)



#### **GC-HRMS**



HRMS (EI) m/z calcd. for  $C_{26}H_{28}BN^+$  [M<sup>+</sup>] 365.2309, found 365.2303.





# HSQCEDETGPSISP experiment (CDCl<sub>3</sub>)



HMBCGP experiment (CDCl<sub>3</sub>)









HSQCEDETGPSISP experiment (CDCl<sub>3</sub>) M -0 0 20  $CH_2-B$ 80 •8= 60 09 0 40 00 . 60 80 (mdd) 100 IJ - 120 - 140 - 160 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm









HPLC-MS (ESI+) m/z calcd. for  $C_{28}H_{33}BNO_8^+$  [M-OH]<sup>+</sup> 522.38, found 522.36.





# 9. X-Ray diffraction structural determination details

Table S2. Crystal data and structure refinement for 3ANZB133\_0m\_a.

In all cases, a prismatic crystal was selected and used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a D8 Venture system equipped with a multilayer monochromator and a Mo microfocus ( $\lambda = 0.71073$  Å). The frames were integrated with the Bruker SAINT software package<sup>9</sup> using a narrow-frame algorithm. Data were corrected for absorption effects using the multi-scan method (SADABS),<sup>10</sup> and the structure was solved and refined using the Bruker SHELXTL software package.<sup>11</sup>

# References

9) Data reduction with Bruker SAINT versions V7.60A. Bruker **2007**. Bruker AXS Inc., Madison, Wisconsin, USA.

10) G. M. Sheldrick, (1996). SADABS. Program for Empirical Absorption Correction. University of Gottingen, Germany.

11) G. M. Sheldrick, Acta Crystallographica Section C-Structural Chemistry 2015, 71, 3-8.

Identification code:	3ANABB45	
Chemical formula:	C22H29BNO8.50	
Formula weight:	454.27 g/mol	
Temperature:	100(2) K	
Wavelength:	0.71073 Å	
Crystal system:	triclinic	
Space group:	P -1	
Unit cell dimensions:	a = 7.0333(3) Å	α = 79.685(2)°
	b = 11.0537(5) Å	β = 85.884(2)°
	c = 15.3641(7) Å	γ = 82.938(2)°
Volume:	1164.73(9) ų	
Z:	2	
Density (calculated):	1.295 g/cm <sup>3</sup>	
Absorption coefficient:	0.098 mm <sup>-1</sup>	
F(000):	482	

Crystal size: Theta range for data collection: Index ranges: Reflections collected: Independent reflections: Refinement method: Data / restraints / parameters: Goodness-of-fit on F<sup>2</sup>: Final R indices [I>2σ(I)]:

Weighting scheme:

Largest diff. peak and hole: R.M.S. deviation from mean: 0.229 mm x 0.197 mm x 0.059 mm 1.88 to 30.64° -9<=h<=10, -15<=k<=15, -22<=l<=21 60033 7146 [R(int) = 0.0936] Full-matrix least-squares on F<sup>2</sup> 7146 / 5 / 334 1.080 R1 = 0.0726, wR2 = 0.1831 all data R1 = 0.1061, wR2 = 0.2026 w=1/[ $\sigma^2$ (F<sub>o</sub><sup>2</sup>)+(0.0937P)<sup>2</sup>+0.8888P] where P=(F<sub>o</sub><sup>2</sup>+2F<sub>c</sub><sup>2</sup>)/3 0.929 and -0.373 eÅ<sup>-3</sup> 0.097 eÅ<sup>-3</sup>

 Table S3. Crystal data and structure refinement for 3ANZB133\_0m\_a.



Identification code:	3ANABB85
Chemical formula:	$C_{56}H_{76}B_2N_2O_{18}\\$
Formula weight:	1086.80 g/mol
Temperature:	100(2) K
Wavelength:	0.71073 Å
Crystal system:	triclinic
Space group:	P-1
Unit cell dimensions:	a = 7.7013(3) Å α = 68.809(2)°
	b = 13.3036(6) Å β = 86.831(2)°
	c = 14.8499(6) Å γ = 82.254(2)°
Volume:	1405.59(10) Å <sup>3</sup>
Ζ:	1
Density (calculated):	1.284 g/cm <sup>3</sup>
Absorption coefficient:	0.095 mm <sup>-1</sup>
F(000):	580
Crystal size:	0.208 mm x 0.122 mm x 0.039 mm
Theta range for data collection:	1.65 to 30.63°
Index ranges:	-11<=h<=10, -19<=k<=19, -21<=l<=21
Reflections collected:	64172
Independent reflections:	8615 [R(int) = 0.0851]
Refinement method:	full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters:	8615 / 0 / 419
Goodness-of-fit on F <sup>2</sup> :	1.077
Final R indices [I>2σ(I)]	R1 = 0.0649, wR2 = 0.1359
	all data R1 = 0.0992, wR2 = 0.1505
Weighting scheme	$w=1/[\sigma^2 (F_o^2)+(0.0490P)^2+0.9547P]$
	where $P=(F_0^2 + 2F_c^2)/3$
Largest diff. peak and hole	0.403 and -0.384 eÅ-3
R.M.S. deviation from mean:	0.060 eÅ <sup>-3</sup>