Chemical Science

ROYAL SOCIETY OF CHEMISTRY

EDGE ARTICLE

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Cite this: *Chem. Sci.*, 2024, **15**, 5674

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

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Received 12th December 2023
Accepted 2nd March 2024

DOI: 10.1039/d3sc06676b

rsc.li/chemical-science

The synthesis of BN-containing molecules, which have an interesting isosteric relationship to their parent all-C cores, has drawn a great deal of attention as an avenue to alter and tune molecular function. Nevertheless, many cores with embedded BN are still hard to synthesize, and thus, further effort is required in this direction. Herein, we present an integrated approach to BN-containing polycycles rooted in an exceptionally clean B–N condensation of amines with a tri-allylborane. Having released propene as the only byproduct, the resulting BN precursors are seamlessly telescoped into BN-containing polycyclic cores *via* a set of additional methodologies, either developed here ad-hoc or applied for the first time for the synthesis of BN-cycles. As the "sharpening stone" of the process, BN-embedded naphthalene, which has previously only been obtained in low yield, can now be synthesized efficiently through propenolysis, ring-closing metathesis and a new high-yielding aromatization. As a more advanced application, an analogously obtained BN-containing bis-enyne is readily converted to BN-containing non-aromatic tetra-, penta- and hexacyclic structures *via* ring-closing enyne metathesis, followed by the Diels–Alder cycloaddition. The resulting air-sensitive structures are easily handled by preventive hydration (quaternization) of their B–N bridge; reverting this hydration restores the original B_{sp^2}–N_{sp^2} structure. In the future, these structures may pave the way to BN-anthracenes and other π-extended BN-arenes.

Introduction

The notion of BN-isosterism refers to the kinship existing between an organic molecule and a derivative containing a boron-nitrogen (BN) pair in place of a carbon–carbon (CC) unit. Such BN derivative tends to be isostructural and isoelectronic with its all-carbon parent as a consequence of an electron counting formalism, with combinations B–N (3 + 5) and C–C (4 + 4) contributing a sum total of 8 valence electrons.[1] Although B/N replacement at mutually remote C-sites may produce, among others, interesting 1,3 or 1,4-BN-isosteres, the lion's share of research in this field is focused on 1,2-isosterism, which maps carbon–carbon single, double or even triple bonds onto their equivalent boron–nitrogen pairs. Hence, the C=C bond in ethylene maps onto an isosteric H_2N–BH_2 aminoborane (**A**, Fig. 1A), while the aromatic benzene ring is recast as the unsaturated 6-membered 1,2-azaborinine cycle (**B**, Fig. 1B), as demonstrated in the pioneering study launched by the Dewar laboratory in the late 1950's.[2]

BN isosteric replacement thus allows for even a small molecular core to be mapped onto a range of BN isosteres to potentially give diverse physical and chemical properties. This

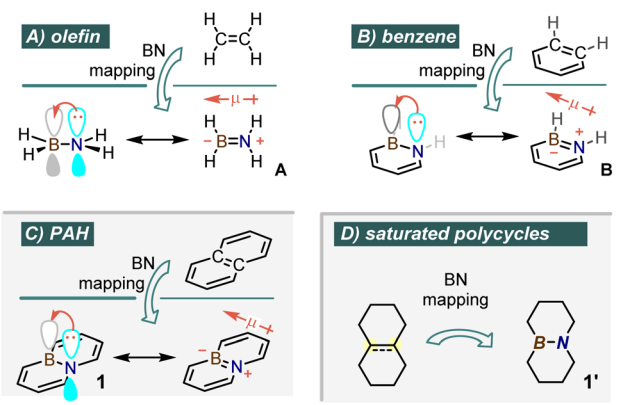

Fig. 1 (A) BN-isosterism illustrated through BN-mapping of ethylene, and (B–D) some common unsaturated ring structures.

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† Electronic supplementary information (ESI) available. CCDC 2297111 and 2297112. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d3sc06676b

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has sparked a great deal of interest from groups working in areas ranging from medicinal chemistry[3] to new organic electronic materials, as the mapping of BN onto polycyclic aromatic (or heteroaromatic) ring structures (PAH) can lead to cores with improved optoelectronic properties.[4] Taking naphthalene as the smallest PAH archetype, the energy levels of π-type molecular orbitals have been altered by mapping the all-carbon core onto several possible BN-isosteres,[5] including the historically important bicyclic azaborine **1** (Fig. 1C).[6] Potentially very interesting but much less explored are the BN isosteres of fully or partially saturated polycyclic molecules, such as the decaline-type derivative **1′** (Fig. 1D).[7]

The need for new synthetic tools to unlock the full potential of BN-isosterism is reflected in game-changing advances from several laboratories for the production of BN-containing mono- and polycyclic aromatic cores,[1,8] including impactful N-directed electrophilic borylation protocols,[9] ring-closing metathesis (RCM) of diolefinic aminoboranes,[10] or late-stage diversification of BN heterocycles.[8b] Nevertheless, efforts are ongoing to find more efficient ways to produce certain classes of polycyclic BN-containing cores, with challenges including the poor yield (see below) of the synthesis of BN-containing naphthalene **1** (shown in Fig. 1C), difficulties in accessing BN-containing acene-type cores, or the synthesis – and handling – of non-aromatic BN-containing cycles.

We now show how such aromatic and non-aromatic polycycles can be prepared and handled through a combination of virtually quantitative proto-deallylation of the B-allyl moiety, norbornene-aided aromatization, core extension *via* ring-closing enyne metathesis/Diels–Alder manifold, and product handling *via* interim B–N hydration.

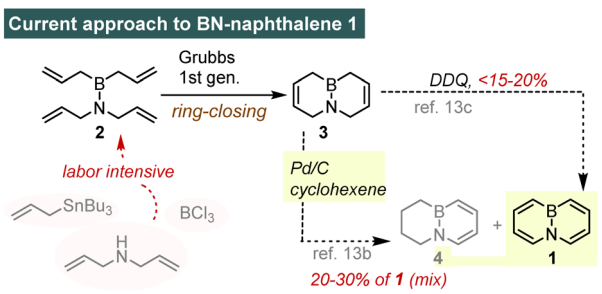
Results and discussion

Leveraging propenolysis with B(allyl)$_3$ for clean formation of aminoboranes

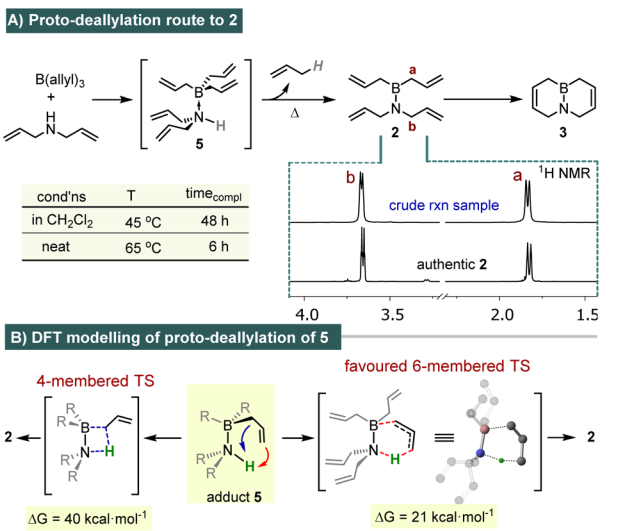
Following the group's recent foray into the development of BN-inspired methods (a collaborative effort with the Liu laboratory),[11] we became interested in exploiting the proto-deallylation reactivity of tri-allylboranes, which was originally documented by Mikhailov and Tutorskaya in the 1950s,[12] as an entry point into 6-membered BN-heterocycles. BN-naphthalene **1** was chosen as a test case due to the shortcomings of current routes to access this compound.[13] While the reported synthesis of **1** relies on a robust ring-closing metathesis (RCM) of tetra-allyl aminoborane **2** to bicycle **3** (see Scheme 1), the process suffers from the rather inefficient aromatization of **3** to **1**. Specifically, while the Pd-catalyzed dehydrogenation of **3** in cyclohexene leads to a hard-to-separate mixture of **1** and BN-tetralin **4**,[13b] the alternative entails an even lower-yielding, albeit cleaner, week-long oxidation of **3** with dichloro-dicyano-1,4-benzoquinone (DDQ, Scheme 1).[13c] In our hands, the latter route meant that the considerable effort (and cost) to produce a 4.8 g batch of **3** ultimately resulted in a meager ∼600 mg of **1**. Importantly, even the synthesis of the initial precursor **2** leaves a wide margin for improvement, particularly considering the cost and waste removal issues stemming from the use of the allyl-tin reagent[13b] or labor-intensive (filtration, distillations) sequence based on the allyl Grignard reagent.[13c]

With **1** serving as a building block for a wide range of BN targets, from simple BN-mapped naphthalene derivatives to extended BN-perylenes[14] to emissive core candidates (Samsung Display Ltd),[15] we envisage that improving its synthesis might have a positive impact in a number of areas in the field.

Hence, as an alternative path to **2**, we proceeded to expose B(allyl)$_3$ to a solution of *N*,*N*-diallylamine in CH_2Cl_2 at 0 °C, resulting in a species tentatively identified (*via* ^{1}H NMR, see ESI†) as the acid–base adduct **5** (Scheme 2A). When heated to 45 °C, this adduct gradually evolved to tetra-allyl aminoborane **2**, reaching complete conversion after ∼48 h. Seeking to shorten the reaction time, we opted for a solvent-free approach in hopes of enabling a higher-temperature process and doing away with the subsequent solvent switch in the RCM step. Gratifyingly, dropwise addition of *N*,*N*-diallylamine to neat triallylborane at 0 °C, followed by heating the resulting adduct to 65 °C, led to visible bubbling, and after ∼6 h, the formation of a clear liquid, shown by ^{1}H NMR to be the remarkably clean neat tetra-allyl species **2** (Scheme 2A).



Scheme 1 Current approach to prepare BN-naphthalene **1**.



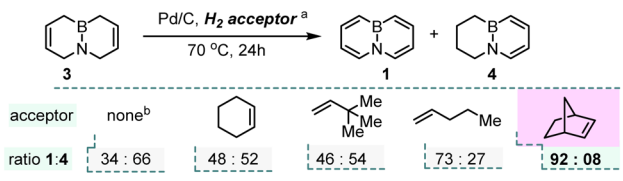
Scheme 2 (A) One-pot two-stage sequence to convert B(allyl)$_3$ to bicycle **3**. (B) Comparison of DFT barriers for 4- and 6-membered transition states for the proto-deallylation step.

This efficient reaction of an N–H substrate with organoborane appears to be unique for $B(allyl)_3$ and does not extend to non-allylic trialkylboron derivatives.[12] In the original 1961 report, this reactivity difference was rationalized through the low $B–C_{allyl}$ bond energy.[12b] It is important to note, however, that while any NH amine-organoborane adduct could in principle undergo proto-dealkylation *via* a 4-membered transition state (*i.e.* NH proton transferred to B–C carbon), allylic boranes are uniquely capable of propene elimination *via* a 6-membered transition state. In line with this reasoning, DFT modelling revealed a barrier of ~40 kcal mol^{-1} for converting **5** to **2** *via* a 4-membered transition state, which would be common to allyl- and alkyl boranes. However, this activation energy was nearly halved ($\Delta G^{\ddagger}$ = 21 kcal mol^{-1}) for the propene elimination *via* a 6-membered TS, which we believe to be the real reason for the enhanced reactivity of $B(allyl)_3$ adducts in this process (see Scheme 2B).

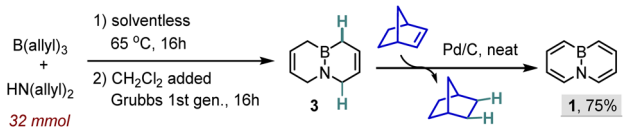
As propylene gas was the only by-product, the freshly obtained tetra-allyl precursor **2** was employed directly in the subsequent metathesis step. In a 16 mmol run, newly formed **2** was simply dissolved in CH_2Cl_2 and treated with the Grubbs first-generation catalyst for 16 h, leading to bicycle **3** in a 72% overall yield (1.53 g) upon distillation.

Having established one-pot access to **3**, we briefly turned our attention to the final aromatization step, in which losses of up to 80–90% (!) in yield are generally incurred. The large quantities of undesired BN-tetralin **4** formed when using the Pd/C-cyclohexene system[13b] (see Scheme 1) not only divert a large share of the precursor away from the target but also hamper the product purification. Since **4** presumably arises from the shuttling of an H_2 molecule between two unsaturated rings in substrate **3** rather than H_2 being passed off to the sacrificial acceptor, we wondered whether this side process might be suppressed by uncovering a more efficient H_2 acceptor. To put this into practice, the catalytic aromatization of **3** with Pd/C was tested in the presence of a range of olefins (6.5 equiv.) at 70 °C for 24 h (Scheme 3). While simple cyclic and linear olefins still led to significant amounts of undesired **4**, the use of norbornene led to BN-naphthalene being formed with an unprecedented 92 : 8 selectivity (see ESI Fig. S1†). We note that the chemoselectivity of reaction tracks with the enthalpy of hydrogenation ($\Delta H°$) of the acceptor in the order cyclohexene (−28 kcal mol^{-1}) < 1-hexene ≈ *t*-Bu-ethene (−30 kcal mol^{-1}) < norbornene (−33 kcal mol^{-1}).[16]

Following additional optimization, the aromatization of **3** was conducted at 110 °C in the presence of catalytic Pd/C and 3.5 equiv. of norbornene (neat), affording **1** in an 76% yield,



Scheme 3 Evaluation of hydrogen acceptors in the Pd-catalyzed aromatization of **3** to **1**. [a] Conducted in neat olefin acceptor. [b] Using cyclohexane as solvent.



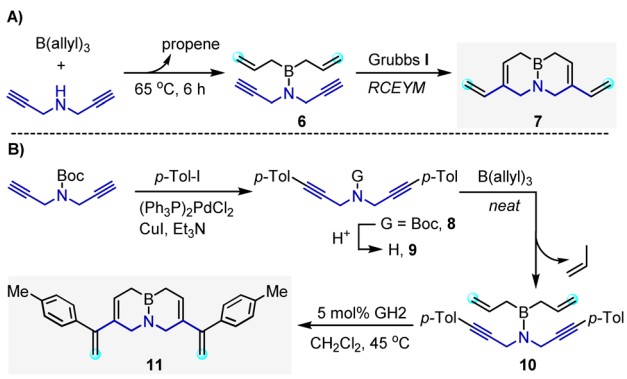
Scheme 4 Streamlined multi-gram synthesis of BN-naphthalene **1**.

a major improvement over the prior art. The streamlined process was then carried out on a multi-gram (32 mmol) scale (Scheme 4). A neat 1 : 1 mixture of $B(allyl)_3$ and diallylamine was heated to 65 °C for 16 h; the as-obtained **2** was then diluted with CH_2Cl_2 and treated with the Grubbs first-generation catalyst to afford 3.1 g of **3** (72% over 2 steps) upon distillation. Finally, the aromatization over Pd/C in norbornene (3.5 equiv.) produced 2.33 g of target BN-naphthalene **1** upon column chromatography (75%), representing an overall yield of 54% based on starting $B(allyl)_3$.

Integrated approach towards polycyclic BN-containing cores

Seeing how the proto-deallylation reaction enabled the facile and clean assembly of aminoborane **2**, this process was exploited to accelerate the discovery of new BN-containing polycyclic cores. $B(allyl)_3$ was allowed to react with neat *N*,*N*-dipropargyl amine, leading after ~6 h to clean formation of neat aminoborane **6** containing two 1,7-enyne groups (Scheme 5A). This product offers an interesting opportunity to access polycyclic BN products *via* the ring-closing enyne metathesis reaction (RCEYM).[17] Indeed, exposing **6** to the first-generation Grubbs catalyst (sealed tube, 3 days) afforded the expected bicyclic di-vinyl aminoborane **7**, which was isolated in 40% overall yield *via* low-pressure bulb-to-bulb distillation as a colorless moisture-sensitive low-melting crystalline solid. The structure of the compound was confirmed, in part, by ^1H NMR resonances for the newly formed vinyl group at 6.35, 4.98 and 4.92 ppm.

Encouraged by this result, we also sought to extend this approach to substituted bicyclic BN-cores by applying the RCM reaction to more challenging internal alkynes. To this end,

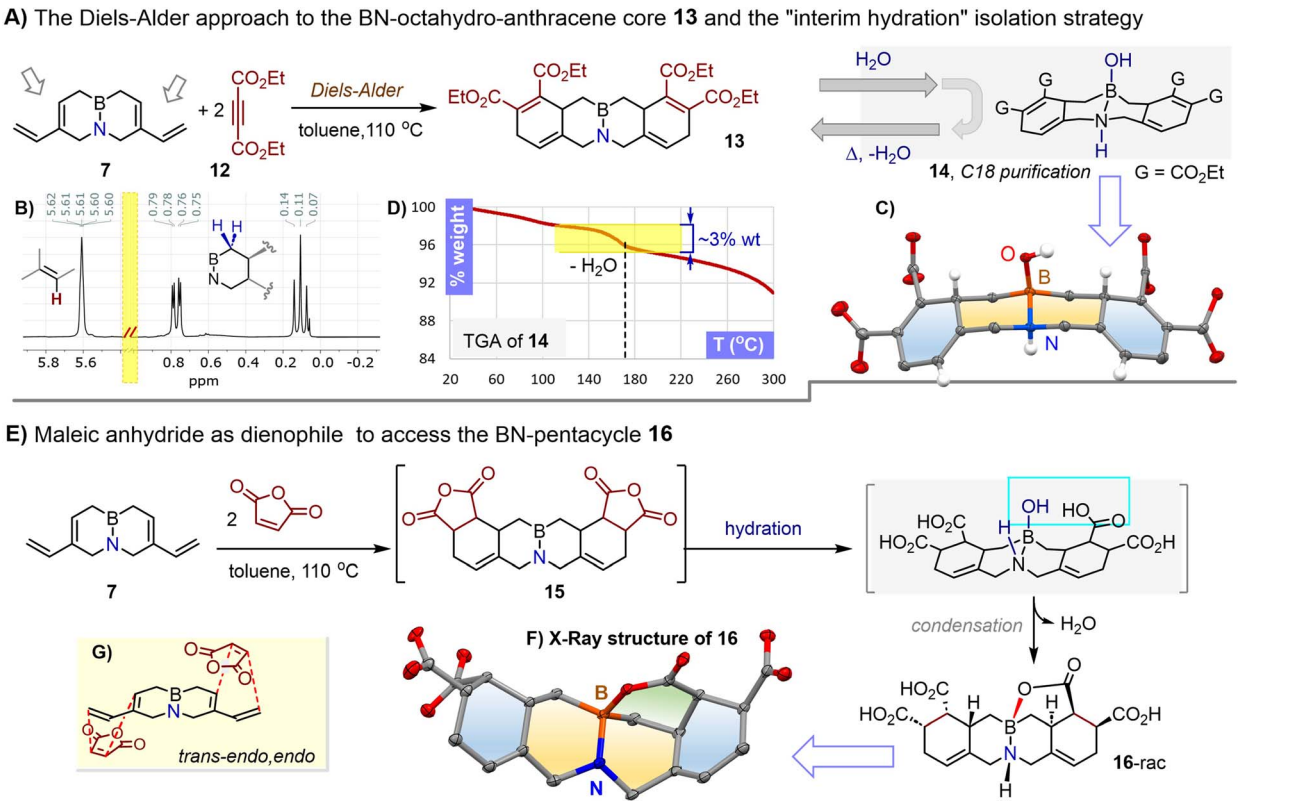


Scheme 5 (A) Access to bis-enyne aminoborane **6** and enyne metathesis ring closure towards 1,3-diene core **7**. (B) Access to internal bis-alkyne **9** and its RCEYM to form bicycle **11** (GH2 = Grubbs–Hoveyda second-generation catalyst).

doubly arylated precursor **8** was prepared *via* Sonogashira coupling and subsequently deprotected to dipropargylamine **9** (Scheme 5B). This compound reacted smoothly with $B(allyl)_3$ to afford new aminoborane **10** in good purity. As anticipated, enyne metathesis in this case proved to be more challenging, with initial attempts using the Grubbs first-generation catalyst leading to little-to-no conversion. Nevertheless, we were pleased to find that switching to the more active Grubbs–Hoveyda second-generation catalyst and raising the temperature to 45 °C led to the selective formation of the target bicyclic structure **11**, as confirmed by GC-MS and ^{1}H NMR analyses (Scheme 5B).

With the new bis-diene aminoborane **7** in hand, we proceeded to explore double Diels–Alder reaction as a way to access new BN-doped polycyclic cores.[18] Our initial test involved heating **7** with 2.4 equiv. of acetylene dicarboxylate (**12**) as dienophile in toluene at 80 °C (Scheme 6A). After 12 h, the GC-MS analysis of the mixture showed nearly complete consumption of **7** and formation of a new major species with $m/z = 355$, which would be consistent with the mono Diels–Alder adduct. A small peak with $m/z = 525$ was also observed, hinting at the possible formation of the target double-Diels–Alder product **13**. Fortunately, increasing the amount of dienophile to 4.0 equiv. and temperature to 110 °C led, after 15 h, to the formation of the target tetracyclic aminoborane **13** as the major product (Scheme 6A). We note that given the hydroscopic nature of the product, unequivocal determination of the stereochemistry of the compound (*i.e.*, *cis- vs. trans*-adduct) *via* NMR was hampered by the difficult purification of the crude mixture. After a number of unsuccessful attempts, we wondered whether product manipulation might be facilitated by temporary quaternization of the boron atom. The addition of H_2O to a solution of crude **13** in Et_2O led to the precipitation of hydrate **14** with a B–N bridge present in HN···B(OH) form.[19] Compound **14** proved to be air-stable and could now be readily purified using reversed-phase (C18) column chromatography or simply by repeated washing.

The clean ^{1}H NMR spectrum of **14** now clearly revealed the presence of a single diastereomer with a symmetry element at the B–N bridge, as evidenced by a single characteristic set of diastereotopic B–CHH signals (0.78 and 0.11 ppm, J_{gem} = 13.7 Hz), along with a sole olefinic resonance at 5.61 ppm (2H) (see Scheme 6B). Given that the hydrated (H)N–B(OH) bridge precludes the possibility of a C_2 symmetry axis, the two halves of bicycle **14** must be related by a mirror symmetry (C_s), which is only possible if **14**—and, by extension, **13**—is a Diels–Alder *cis*-adduct. This conclusion was confirmed by single crystal X-ray diffraction analysis of **14**, which not only showed the *cis*-



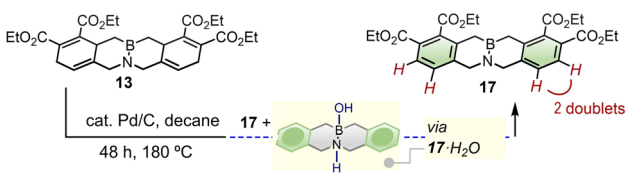
Scheme 6 Synthesis of non-aromatic BN-containing tetra-, penta- and hexacycles *via* double Diels–Alder reaction. (A) Synthesis of BN-tetracycle **13** and its interim hydration *via* B-quaternized derivative **14**. (B) Selected region of the ^{1}H NMR spectrum of **14** showing the olefinic resonance and diastereotopic B–CHH′ group. (C) ORTEP diagram of the X-ray structure of **14** at 50% thermal ellipsoids; most H atoms have been omitted for clarity. (D) TGA analysis trace for **14** showing the possible water loss at ~162 °C. (E) Synthesis of BN-containing non-aromatic pentacycle **16** *via* hexacycle **15**. (F) X-ray structure of **16**; all H atoms have been omitted for clarity. (G) Diagram showing the *trans-endo, endo* approach of maleic anhydride during the Diels–Alder step.

adduct configuration but also revealed the *trans* disposition of H and OH groups on the hydrated B–N bridge (Scheme 6C).[20]

At this point, we wondered whether the BN-hydration could be reversed to recover pure adduct **13**. Initial attempts to chemically remove the water molecule, including with Burgess reagents, met with little success. However, thermogravimetric analysis (TGA) of **14** revealed a well-defined endothermic weight loss of ~3% at 162 °C, in line with the release of a water molecule (Scheme 6D). Translating this knowledge to the preparatory scale, a sample of **14** was heated under vacuum to ~160 °C, which indeed resulted in the formation of BN-tetracycle **13** in >90% purity. This transformation was accompanied a change in the ^{11}B NMR chemical shift from ~0.0 ppm for **14** (quaternized borane) to 40 ppm for **13**. The latter value is typical for related B_{sp^2} aminoboranes, including **3** (41.2 ppm) and **7** (40.6 ppm). We believe that this approach, which we dubbed "interim hydration," may prove useful for the purification of other moisture-sensitive non-aromatic cyclic aminoboranes through temporary protection of the BN unit *via* the reversible addition of water or other protic agents.

Continuing with our exploration, the double Diels–Alder addition between **7** and maleic anhydride led to the formation of hexa-cyclic species **15**, as evidenced by a GC-MS peak with m/z = 381 (Scheme 6E). Although the compound was not isolated, subsequent reaction with H_2O led not only to the hydration of the BN bond but also the hydrolytic opening of two anhydride rings. The ^{1}H NMR spectrum of resulting species was complicated by the apparent lack of any symmetry and included two olefinic CH resonances at 5.60 and 5.42 ppm, along with three discernible COOH resonances in the 11–13 ppm region. Fortunately, X-ray-quality crystals of the product could be grown *via* slow diffusion of Et_2O into a MeOH solution.[20] The solid-state structure revealed that this lack of symmetry was due to one of the carboxylic acid moieties undergoing condensation with the B–OH group to form a 6-membered mixed B–O–C(O) anhydride ring, resulting in an overall pentacyclic core (**16**, Scheme 6F). The 3D structure also revealed a *trans-endo-endo* configuration, indicating that the initial Diels–Alder cycloaddition took place with two dienophile molecules approaching opposing sides of bicyclic precursor **7** in an *endo* configuration.[21]

Having successfully applied the newly developed sequence to polycyclic targets **13**/**14** and **15**/**16**, a number of future applications can now be envisioned. For example, this opens the door to BN isosteres of certain natural polycycles and of course, to the preparation of BN-containing polycyclic aromatic compounds, including access to new BN-tetracenes *via* 4-fold aromatization. En route to the latter goal, preliminary experiments show that heating **13** with Pd/C in decane (180 °C, 48 h)[22] produces new species **17** with aromatized external rings (Scheme 7), as observed from two characteristic ^{1}H NMR doublets at 7.81 and 7.20 ppm. The product was found to be hydroscopic, with ^{1}H NMR spectra typically presenting varying amounts of BN-hydrate, observed as a second set of doublets at 7.66 and 7.16 ppm. Similarly to the isolation of a BN-hydrate shown earlier, purification *via* reversed-phase column chromatography (C18) produced a mixture of **17** and **17**·$\mathbf{H_2O}$, which could be fully converted to the rather clean hydrate form (see ESI†) through the addition of water. In line with our interim hydration strategy, the dehydration of **17**·$\mathbf{H_2O}$ at 160 °C under vacuum led to clean **17**, which was characterized by a peak with m/z = 522 (M + H, ESI$^+$).[23] The ^{1}H NMR spectrum of the product showed, in addition to aforementioned aromatic doublets (2H each), two broad singlets arising from N–CH_2 (4.38 ppm, 4H) and B–CH_2 (2.28 ppm, 4H) groups of central rings.



Scheme 7 Semi-aromatization of tetracycle **13** (un-optimized).

Conclusions

In conclusion, this study contributes to the area of BN-isosterism through an integrated synthetic approach to a series of BN-containing cyclic cores. Owing to the highly efficient assembly of BN-containing precursors using the proto-deallylation of B(allyl)$_3$, which produces propylene as the only by-product, the B–N formation step is seamlessly integrated with the subsequent olefin or enyne metathesis stages. When combined with a newly developed high-performing aromatization, the approach gives rise to the first efficient synthesis of BN-naphthalene **1**. Furthermore, the manifold in which the proto-deallylation leads into the enyne metathesis/Diels–Alder ring core extension is shown to be a potentially versatile entry point into interesting new non-aromatic B–N embedded systems containing 4, 5 or 6 six-membered rings. It is also shown that the addition of water converts air-sensitive non-aromatic B–N cores to BN-hydrates suitable for handling and purification, following which the water molecule can be removed to recover original polycycles, thus converting this interim hydration strategy into a potentially interesting synthetic tool. Although beyond the scope of this work, based on our preliminary results with partial aromatization (product **17**), one can easily imagine further applications of strategies presented here, including the potential conversion of tetracyclic cores such as **13** into new π-extended cores, such as hitherto unreported BN-containing tetracene.[24]

Data availability

The datasets supporting this article have been uploaded as part of the ESI.†

Author contributions

The manuscript was written through contributions of all authors. F. R. and G. S. were primarily responsible for designing and conducting most of the experimental work, hypothesis validation and data analysis. P. R. contributed to initial experiments on proto-deallylation and enyne metathesis. V. M. was

responsible for the preparation and metathesis of the enyne **10**, while N. M. carried out a part of method development for the synthesis of **1**. R. P. B. helped design, validate and supervise synthetic efforts towards BN-naphthalene. A. S. and A. C. were responsible for project conceptualization and overall coordination, supervised the experimental work and wrote the first draft of the manuscript. A. S. was also responsible for DFT calculations.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported through MICINN grants (PID2020-113661GB-I00 and PDC2023-145801-I00) and AGAUR (2021 SGR 00520). We thank CSIC for the JAE-Intro scholarship to V. M. and the Generalitat de Cataluña (AGAUR) for the Investigo contract to G. S.-L. (2023 INV-2 00014G1). We thank Sonia Pérez from the «Josep Carilla» Thermal Analysis and Calorimetry service at IQAC for conducting thermogravimetric analyses used in this work.

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21 Unlike the cis addition observed in the case of **13**, the addition of the two molecules of maleic anhydride to the same side of the diene **7** (prod. **15**) is disfavored by steric repulsion between the two inward-disposed (endo) dienophiles.

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