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1 Introduction

The literature on boron-containing heterocycles which have at least one other heteroatom within the six-membered ring system has been reviewed in the appropriate chapters of the first, second, and third editions of Comprehensive Heterocyclic Chemistry (CHEC I-III) and in earlier reviews quoted therein.[1–3] For the present edition, this chapter follows the same format as that used in CHEC-III and covers new developments reported from 2008. Since publication of CHEC-III, the field covered by this chapter has expanded enormously. The development is driven mainly by an extensive use of a BN/C = C isostere conception in the construction of a variety of novel boron-containing hetero π-conjugated molecules.[4] The most common systems were studied to be 1,2-, 1,3-, and 1,4-azaborines,[5–8] and their 1,2- and 1,4-oxaborine analogues [9]. A variety of π-extended BN-polycyclic aromatic hydrocarbons (PAHs) including BN-naphthalenes, BN-phenanthrenes, BN-anthracenes, BN-pyrene, BN-indenes, BN-coronenes, and higher BN-doped PAHs have also been synthesized and well characterized.[10–12] 1,9-dihydro-1,9-diboranaphthalenes and their fused analogues containing Hückel-anti-aromatic central B_2C_4 ring were also extensively covered in the literature.[10] Finally, a large number of boracycles that contain heavy heteroatoms, such as S, Se, P, and Te, have been synthesized and studied during the past decade.[7]

A *Chemical Abstracts* search between 2008 and the end of 2018 revealed that there are about 450 publications and more than 120 ring systems that come under the title of this article. The purpose of this survey is to summarize the most important data published over the last decade. Partially or totally saturated boracycles such as 1,3,2-diaza- or 1,2,3-dioxaboranes which were extensively covered in the first and second edition of *Comprehensive Heterocyclic Chemistry* are dealt with only briefly, as little new information is available beyond their standard preparative application. Boron dipyrroles (BODIPY) and related chelate systems as well as substitution with BN units in cluster systems and graphitic materials are beyond the scope of this review.

2 Theoretical methods

Many B,N-containing six-membered heterocycles have been studied theoretically.[13–17] The replacement of a single CC unit of benzene by a boron and nitrogen results in compounds isoelectronic to benzene, comprising of isomers 1,2-dihydro-1,2-azaborine (**1**), 1,4-dihydro-1,4-azaborine (**2**) and 1,3-dihydro-1,3-azaborine (**3**) as shown in **Fig. 1**. Generally, ab initio studies suggest that all three isomers have planar rings with bond lengths intermediate between single and double bonds, referring to their aromatic character and electron delocalization. The 1,3-azaborine ring is delocalized more than the 1,2-isomer, while 1,4-isomer was described as a partly delocalized 3-aza-1,4-pentadiene. Interestingly, thermodynamic stability in the series **1**–**3** does not go hand in hand with aromaticity. The less aromatic 1,2-azaborine is energetically more stable than 1,4-azaborine and 1,3-azaborine. Along with azaborines, aromaticity of diazaborines and their protonated forms has been examined on the basis of bond length changes occurring upon CH → N substitution and further nitrogen protonation, and with the aid of aromaticity indices belonging to four groups: energy (ECRE), structure (HOMA), electron delocalization (PDI) and magnetic properties (NICS(0)$_{\pi zz}$). Authors predict that the extent of the π-electron delocalization of the three isomeric azaborines would be slightly affected by CH replacement with nitrogen, meaning that molecular properties associated with aromaticity would more or less resemble those of parent azaborines.[18]

Following the monocyclic BN substituted benzenes, electronic properties of a variety of BN-aromatics, including BN-naphthalenes[19–22], BN-phenanthrenes[23–26], BN-anthracenes[26–28], BN-pyrenes[13,29,30], aryl-fused bis-BN dihydropyrenes[31], bis-BN-ullazine derivatives[32], BN-helicenes[33], BN-coronenes and nanographene[34–38] have been studied using theoretical methods. The relative orders of the topological and local aromaticity depend strongly on the position of the heteroatoms in the structure. In general, more ring shared BN containing molecules are less aromatic than the less ring shared BN molecules. Replacement of CC units of naphthalene by the isoelectronic BN combination is most favorable when the B and N atoms are kept adjacent to one another and disposed on the α and β positions, avoiding the fused-ring location.[19,39] It was suggested that energetic order of isomers is largely influenced by σ-orbital contribution that by π-orbital. Energetic stability is also perfectly correlated with HOMO-LUMO energy gaps.[13] Calculations are also presented on six-π-electron ionic N—B—N and B—N—B-substituted benzene rings.[40]

To evaluate the aromatic properties of benzene, 1,2-azaborine, 1,3-azaborine, 1,3,2,5-diazadiborine and $B_3N_3H_6$ ring, the nucleus independent chemical-shift (NICS) values were calculated at the B3LYP/6-311 + G(d,p) level of theory. It was predicted that 1,3,2,5-diazadiborine features aromaticity, which seems smaller than those of benzene and 1,3-azaborine, but greater than that of $B_3N_3H_6$ (**Fig. 2**).[41]

DFT calculations at M06L/6-311 ++G(d,p) level have been carried out on several 1,4-azaborine annulated linear polyacenes **4**–**6** to reveal their stability, aromaticity, electronic character, HOMO-LUMO energy gap and singlet-triplet energy gap (**Fig. 3**). The computed values of aromaticity indices and dehydrogenation energy of heterocycles suggest strong aromatic character for each six-membered ring in the linear polyacene mimics.[42]
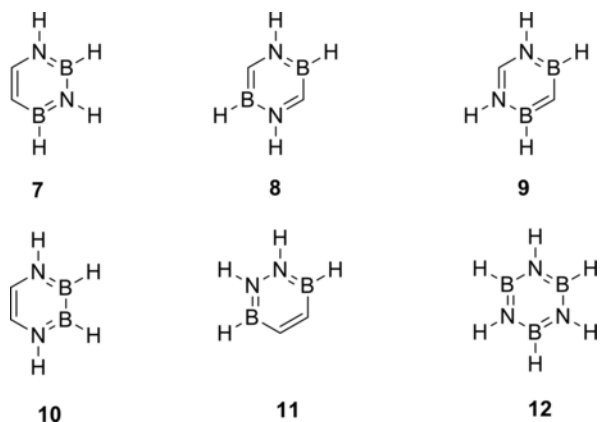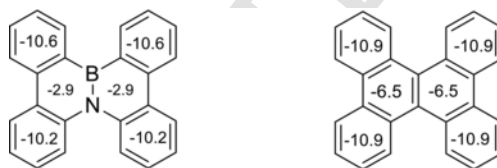
Fig. 1

NICS(0)	-8.0	-4.9	-6.2	-4.3	-1.6
NICS(1)	-10.2	-7.1	-8.6	-6.5	-2.7

Fig. 2

Fig. 3

An ab initio study has been carried out to investigate the effect of replacing [HC-CH]$_n$ linkages in benzene by the isoelectronic [HN-BH]$_n$ linkages for $n = 2$, and 3 (**Fig. 4**). Such replacements give rise to a set of diazadiborines (**7–11**) and borazine (**12**).[17] Among these molecules, the most stable isomer (**7**) contains an N—B—N—B linkage, while the two least stable isomers (**10,11**) have B—B or N—N bonds. The nucleus-independent chemical shift (NICS) and *para*-delocalization indexes (PDI) show a decrease in aromaticity going from benzene to diazadiborine **7**. The B—N orders in **10** and **11** (1.13 and 1.14, respectively) are intermediate between H$_2$BNH$_2$ (1,257) and borazine **12** (1.02).

Computations at the B3LYP/6-311 + G level of theory were performed to shed light on the influence of a boron—nitrogen—boron (BNB) zigzag edged benzo[*fg*]tetracene motif. The three benzene rings on the periphery of the NBN-benzo[*fg*]tetracene have relatively negative NICS(0) values of − 6.9 and − 7.6 and can be identified as aromatic rings. The rings with BN substitution show positive NICS(0) values (+ 1.5), indicating that they are nonaromatic. NICS computations for benzo[*fg*]tetracene carbocation give a qualitatively similar picture of the aromatic nature of individual rings (**Fig. 5**).[43]

The aromaticity of six-membered rings in 4b-aza-12b-boradibenzo[*g,p*]chrysene and dibenzo[*g,p*]chrysene are evaluated by NICS calculations at the B3LYP/6-31G∗ level (**Fig. 6**). As shown by the values of NICS(1), the BNC$_4$ rings have low aromaticity (− 2.9), whereas the C6 rings in dibenzo[*g,p*]chrysene have moderate aromaticity (− 6.5). However, BN substitution does not significantly affect

Fig. 4

Fig. 5

Fig. 6

the aromaticity of surrounding benzene rings in 4b-aza-12b-boradibenzo[g,p]chrysene (cf. benzene: − 11.2).[36] Dispersion-corrected DFT data on the low-lying conformations and stacking interactions of a set of saddle-shaped contorted B—N substituted polycyclic aromatic compounds are presented in ref.[44]

Advances have also been made in understanding the electronic structure of , which are 9,10-dihydroanthracene derivatives containing a boron atom and another main group element (**Fig. 7**). These molecules were shown to have a planar framework, as determined from X-ray crystallographic analysis. UV/Vis and fluorescence spectroscopy as well as theoretical calculations at B3LYP/6-311 + G(d,p)//B3LYP/6-31 + G(d) level proved that the nature of chalcogen atoms at the bridging position strongly affects their optical and electronic properties.[45]

Electronic structure of 1,3,2-benzodiazaborininones (**13**), 1,3,2-benzoxazaborininones (**14**), and 3,1,2-benzoxazaborininones (**15**) was evaluated using Gaussian 09 at the B3LYP/6-311 + G(2d,p) level of theory. Computationally derived pK_a values, NICS aromaticity calculations, and electrostatic potential surfaces revealed a unique isoelectronic/isostructural relationship between these azaborines and

Dibenzoheteraborines
(X = RP, O, S, Se)
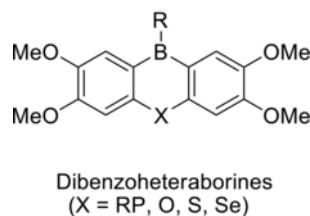
Fig. 7

their possible carbon-based heterocyclic systems.[46] The nucleus independent chemical shift indices of aromaticity have also been calculated for 5,6-dihydroborauracil (**16**), borauracil (**17**) and benzoborauracil (**18**) (**Fig. 8**).[47]

Quantum-chemical ab initio calculations were performed at different level of theory on three possible structural isomers of diborabenzene ($C_4H_4B_2$).[48] All three molecules were found to be local minima on the $C_4H_4B_2$ energy surface and to have closed shell singlet ground states. Planar 1,3- and 1,4-diborabenzene have three doubly occupied π orbitals while non-planar 1,2-diborabenzene has also three doubly occupied orbitals lower in energy than the 1,3- and the 1,4-isomer. The least stable compound in this series is 1,2- diborabenzene. The BB bond length in this structure is 1.544 Å. The length of BB bond in the planar form (1.572 Å) is much closer to the BB double bond in HB═BH (1.533 Å) than to the BB single bond in H_2B—BH_2 (1.659 Å). The energetically most favorable 1,3-diborabenzene was found to be about 19 and 36 kcal mol^{-1} lower in energy than the 1,2- and the 1,4-isomer. The most effective stabilization energy of about 24 kcal mol^{-1} was found for the energetically lowest 1,3-isomer. This value amounts to approximately one third of the experimental value for the bond separation energy of pyridine. In all cases the energetically lowest triplet states are significantly (16–24 kcal mol^{-1}) higher in energy than the singlet ground states.

9,10-Dihydro-9,10-diboraanthracenes (DBA) and related compounds, which provide two vicinal boron atoms embedded in a rigid, π-conjugated cyclic scaffold, also attracted much theoretical attention in the past decade.[49,50] According to NICS(0)/NICS(1) calculations, 9,10-dihydro-9,10diboraanthracene derivatives contain Hückel-anti-aromatic central B_2C_4 rings. Two-electron reduction of these compounds leads to their transformation into the Hückel-aromatic dianions.[51]

The borazine radical cation [1,2-B_2\{1,2-$(Me_2N)_2C_6H_4$\}$_2$]$^{•+}$ has been synthesized and its bonding have been studied using a combination of X-ray crystallography, EPR spectroscopy and DFT calculations. The electronic and structural features of the radical cation indicate that two N-heterocyclic units joined by a B_2 linker but with only a minor contribution from boron-based orbitals.[52]

3   Experimental structural methods

^{1}H, ^{13}C, ^{11}B NMR and UV-vis spectroscopy, mass-spectrometry and X-ray diffraction studies have been extensively used in order to establish structural features of new polyheteroatom six-membered boracycles. However, due to the vast amount of the available experimental data, a detailed analysis of the structural assignments seems impossible in a short review article. The present subsection attempts to cover the most important aspects of the topic.

An IR spectrum of 1,2-dihydro-1,2-azaborine in low-temperature neon matrices has been obtained and analyzed. The observed spectrum compared well with that of the DFT calculation.[53]

The gas phase microwave spectroscopy was applied for the identification and the first characterization of 1,2-BN cyclohexene which was produced from 1,2-BN cyclohexane through the loss of H_2 (i.e., heating sample in a Ne gas stream prior to insertion into microwave cavity) (**Scheme 1**).[54] This work presented the opportunity to compare the rotational constants and quadrupole coupling strengths for 1,2-BN cyclohexene with the aromatic, planar 1,2-dihydro-1,2-azaborine. The high level calculations were also applied to   estimate   structural
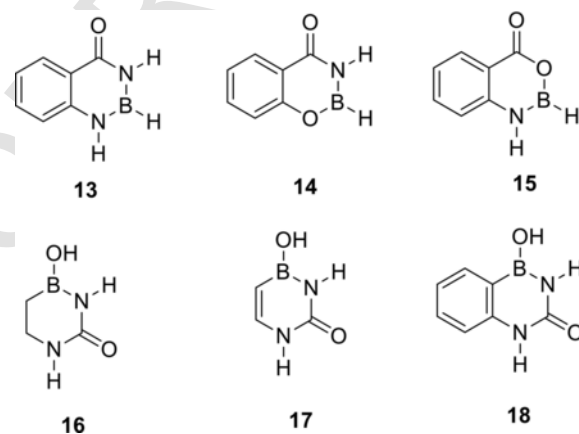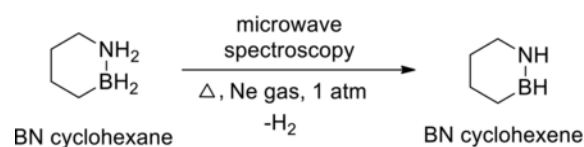

Fig. 8

Scheme 1

parameters for 1,2-BN cyclohexene and 1,2-BN cyclohexane. Particularly, the calculated B—N bond length for 1,2-BN cyclohexene is 1.40 Å, for 1,2-BN cyclohexane, 1.66 Å, and for the aromatic 1,2-dihydro-1,2-azaborine, 1.45 Å.

Chrostowska, Liu and co-workers presented a comprehensive electronic structure analysis of structurally simple BN heterocycles using a combined UV-photoelectron spectroscopy (UV-PES)/computational chemistry approach (Fig. 9).[46] Gas-phase He I photoelectron spectra of 1,2-dihydro- 1,2-azaborine 1, N-Me-1,2-BN-toluene 19, and N-Me-1,3-BN-toluene 20 have been recorded, assessed by density functional theory calculations, and compared with their corresponding carbonaceous analogues benzene and toluene. This analysis provided an in-depth look into the electronic structure changes associated with BN/CC isosterism of the classic arenes benzene and toluene. Authors determined the following trends: (i) HOMO energies (via UV-PES) are in the order: 20 (− 8.0 eV) > 19 (− 8.45 eV) > 1 (− 8.6 eV) > toluene (− 8.83 eV) > benzene (− 9.25 eV); (ii) the computationally determined molecular dipole moments are in the order 3 (4.577 D) > 19 (2.209 D) > 1 (2.154 D) > toluene (0.349 D) > benzene (0 D); (iii) the λ_{max} in the UV-vis absorption spectra are in the order 20 (297 nm) > 19 (278 nm) > 1 (269 nm) > toluene (262 nm) > benzene (255 nm). Noteworthy is also the prediction that for the 1,2-BN isostere, the negative charge is more localized at the C(3), C(5), and at the B—H hydride positions, while the positive charge is located at the N-substituent. For the 1,3-BN isostere, the negative charge is concentrated at the vicinity of the boron atom, whereas the positive charge is again localized at the N-substituent.

UV-Photoelectron spectroscopy (UV-PES) in concert with DFT calculations was also used to match experimentally determined ionization energies with occupied molecular orbitals of parental BN naphthalenes BN-9,1-Naph, BN 1,9-Naph, BN-9,10-Naph, and BN-1,2-Naph (Fig. 10). The trend with respect to the HOMO energy levels is as follows: BN-9,1-Naph (− 7.44 eV) > BN-1,9-Naph (− 7.78 eV) > BN-9,10-Naph (− 8.42 eV) > BN-1,2-Naph (− 8.45 eV). The trend for the optical HOMO-LUMO gap (BN-9,10-Naph > BN-1,2-Naph > BN-1,9-Naph ∼ BN-9,1-Naph) is consistent with the trend predicted by TD-DFT calculations.[20] With regard to the tricyclic BN isosteres of PAHs, gas-phase UV-PES studies revealed the following HOMO energy trend: anthracene, − 7.4 eV; BN anthracene BN-Anth, − 7.7 eV; bis-BN anthracene bis-BN-Anth, − 8.0 eV. The λ_{max} of the lower energy band in the UV-vis absorption spectrum is as follows: anthracene, 356 nm; BN-Anth, 359 nm; bis-BN-Anth, 357 nm.[27]

Microwave spectra and quadrupole coupling constants were reported for 1-ethyl-1,2-dihydro-1,2-azaborine,[55] 1,2-dihydro-1,2-azaborine,[56] and 4a,8a-azaboranaphthalene[21]. Results of the microwave measurements and calculations provided clear evidence for the aromatic character of BN heteroaromatics.

Spectroscopic and X-ray crystallographic analysis as well as the luminescence measurements were performed for a series of novel π-extended oxaborines 21,[57] 22,[58] 23,[59] and 24[9] (Fig. 11). All these compounds exhibited strong fluorescence with high quantum yields and are considered to be promising candidates for UV-OLED material.

The structure and bonding of the radical cation $[1,2—B_2(1,2-Me_2N)_2C_6H_4)_2]^+$ have been probed using a combination of X-ray crystallography, EPR spectroscopy and DFT calculations. It represents a new type of radical centered primarily on two N-heterocyclic units joined by a B_2 linker.[52]
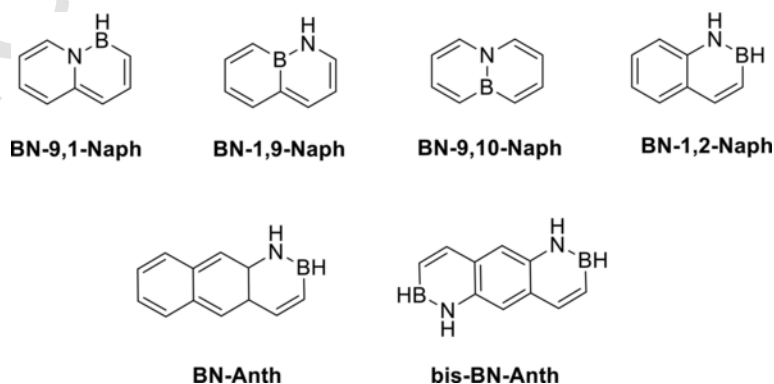

1
1,2-dihydro-
1,2-azaborine

19
N-Me-1,2-BN-
toluene

20
N-Me-1,3-BN-
toluene

Fig. 9

BN-9,1-Naph   **BN-1,9-Naph**   **BN-9,10-Naph**   **BN-1,2-Naph**

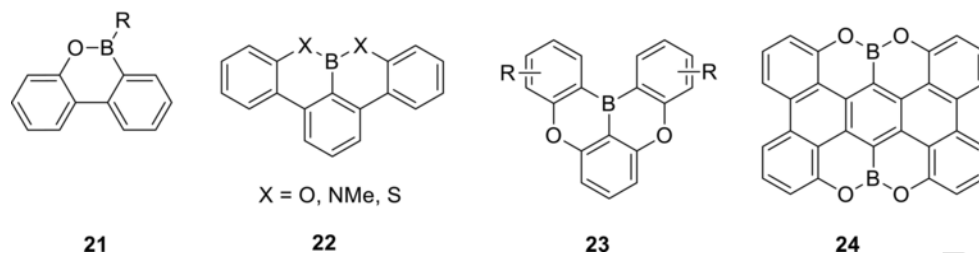**BN-Anth**   **bis-BN-Anth**

Fig. 10

X = O, NMe, S
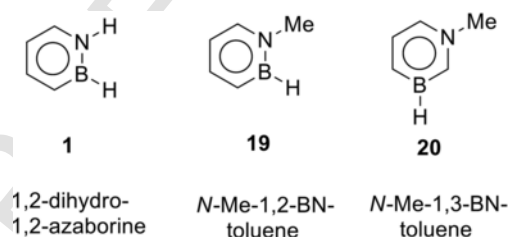
Fig. 11

4   Thermodynamic aspects

According calculated relative thermodynamic stabilities of 1,2-, 1,3-, and 1,4-azaborines, 1,2-azaborine is considerably more thermodynamically stable than either 1,3- and 1,4-isomers (**Fig. 12**).[14] The trend with respect to aromatic character, however, is less clear: while different indicators of π electron cyclic delocalization support 1,3-azaborine as the most aromatic isomer,[13,15,16] the current literature features discrepant evaluations of the relative aromaticities of 1,2- and 1,4-isomers.[5,60]

Liu and co-workers have experimentally determined by reaction calorimetry the resonance stabilization energy (RSE) of 1,2-azaborines (17 kcal mol^{-1}), which is lower than that of benzene (~ 32 kcal mol^{-1}), but on par with other aromatic heterocycles, such as pyrrole (~ 21 kcal mol^{-1}), thiophene (~ 20 kcal mol^{-1}), and furan (~ 15 kcal mol^{-1}).[14,61] The same group found that the thermodynamic parameters of the reversible Diels-Alder reaction between 1,2-azaborines and methyl acrylate correlate with aromaticity trends and thus place 1,2-azaborines between furan and thiophene on the aromaticity scale of heterocycles.[62]

Of the 6 parental BN isosteres of naphthalene bearing one BN unit, **BN-9,1-Naph** is the least thermodynamically stable, while in each pair of orientational isomers the more thermodynamically stable compound (with the smaller ΔH_f value) has the more stable HOMO energy of the two (**Fig. 13**). Calculations for the BN anthracene series suggest that these principles may be general for higher BN acenes as well.[20]

Thermodynamic stability

1,2-azaborine	1,4-azaborine	1,3-azaborine
ΔE_{rel} (kcal mol^{-1}): 0.0	+21.5	+29.8

Fig. 12

BN-1,2-Naph	BN-2,1-Naph	BN-1,9-Naph	BN-2,3-Naph	BN-9,10-Naph	BN-9,1-Naph
ΔH_f: 12.6	13.0	21.7	23.8	25.5	31.3

(Heat of formation numbers (in kcal/mol) are G3MP2 values at 298K)

thermodynamic stability
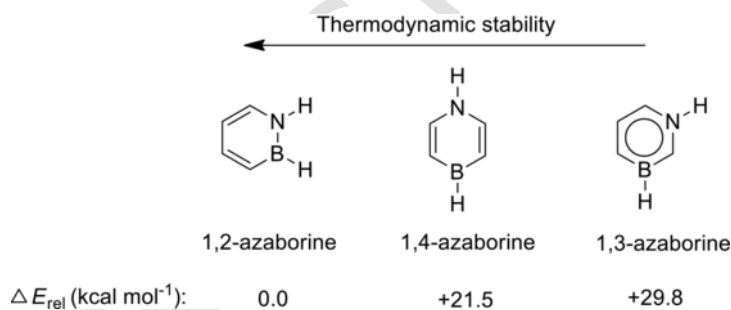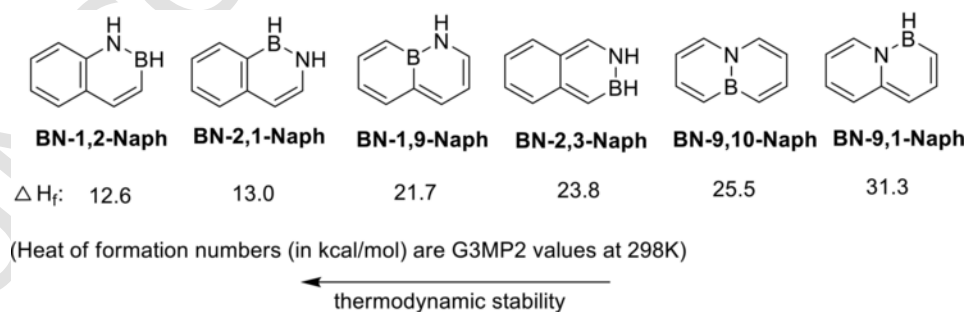
Fig. 13

The results of computer simulation of conformational transformations of 1,3-dioxanes and 1,3,2-dioxaborinanes in terms of HF, DFT, MP2 quantum chemical approximations have recently been reported.[63]

5   Reactivity of fully conjugated rings

5.1   Electrophilic aromatic substitution

In the last decade, numerous electrophilic aromatic substitution (EAS) reactions have been described in a series of unsaturated polyheteroatom boracycles. Selected examples of such reactions are given below.

In 2007, Ashe and co-workers reported that the BN analogue of benzene, 1,2-dihydro-1,2-azaborine **25**, easily undergoes classical electrophilic substitution. These EAS reactions allow the preparation of a variety of 3- and 5-substituted derivatives (**Scheme 2**). Competition experiments have shown that **25** is more reactive than furan and thiophene but less reactive than 1-methylindole.[64] Electrophilic aromatic substitution of 1,2-azaborine **26** with elemental bromine occurs as outlined in **Scheme 3** to give the C(3)-brominated 1,2-azaborine **27**.[65] EAS reaction was also used to introduce bromine in the azaborine core of 1-*t*-butyldimethylsilyl-2-chloro-1,2-azaborine.[66]

1,3-Azaborine **28a** resembles an electron rich aromatic nucleus capable of undergoing EAS reactions. Thus, treatment of **28a** with dimethyl(methylene)ammonium chloride afforded the azaborine **28b** regioselectively in 75% yield (**Scheme 4**).[67]
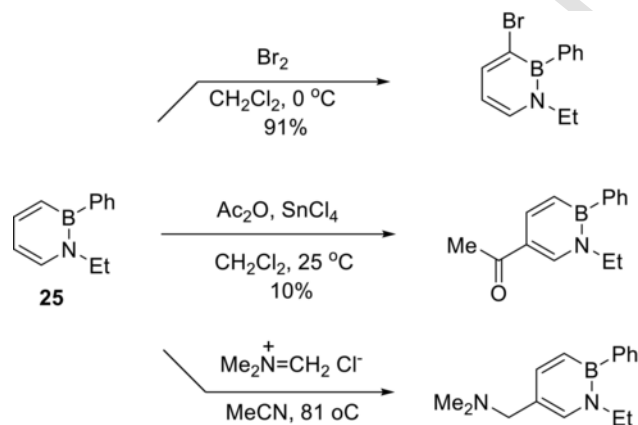
Scheme 2

Scheme 3
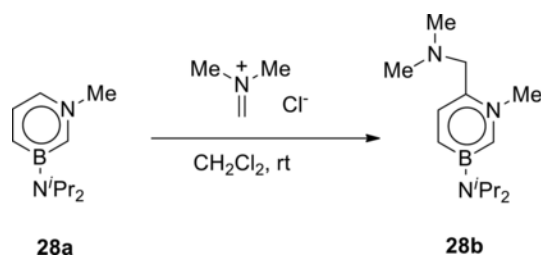
Scheme 4

Halogenation of 2,1-borazaronaphthalenes with bromine also proceeds regioselectively. The desired 3-bromo-2,1-borazaronaphthalenes were synthesized with aryl, heteroaryl, alkynyl, and alkyl substituents (**Scheme 5**). The addition of two equivalents of bromine to the 2-methyl-2,1-borazaronaphthalene resulted in site-selective dibromination at the 3- and 6-positions.[68,69]

A practical and effective electrophilic halogenation of 4a,8a-azaboranaphthalene **29** with *N*-halogenosuccinimides (NXS) was carried out using catalytic AlCl₃, AlBr₃, or BF₃·Et₂O. The electrophilic substitution takes place exclusively at the α-carbon positions next to boron affording compounds **30–32**. Further halogenation reaction occurs at the other ring providing disubstituted products **33–36** (**Scheme 6**).[22]

A completely regioselective halogenation has also been observed in the similar reaction of 4a-aza-10a-boraphenanthrene **37**. The use of propanal as an electrophile under analogous conditions provided a high yield of **40**, which incorporate 2 units of BN-phenanthrene (**Scheme 7**).[23]

It is worth noting that a new concept has recently been proposed for the selective late-stage functionalization of BN-aromatics promoted by coordination of organolithium compounds to the boron atom. This coordination increases the nucleophilicity of the system in the β position to the nitrogen atom and is therefore a useful tool for regioselective electrophilic substitution in the β position to the nitrogen atom.[70]

A number of EAS reactions of a "BN-fused" indole have been reported.[71] Thus, *N-t*-Bu-BN indole **41** is more nucleophilic in EAS than its carbonaceous counterpart and displays the classical indole-type regioselectivity (i.e., at the 3-position) (**Scheme 8**).

R¹ = H, alkyl
R² = alkyl, aryl, (hetero)aryl

Scheme 5

29

30, X = Cl (86%)
31, X = Br (86%)
32, X = I (75%)

33, X = Cl, Y = Cl (71%)
34, X = Cl, Y = Br (75%)
35, X = Br, Y = Br (80%)
36, X = I, Y = Cl (65%)

Scheme 6

37

38, X = Br (99%)
39, X = Cl (72%)

40 (80%)
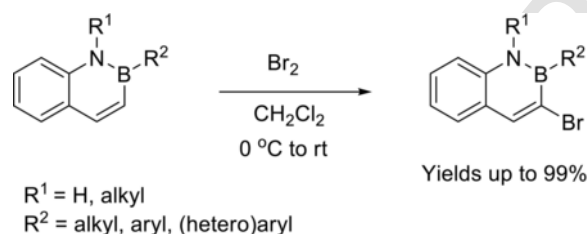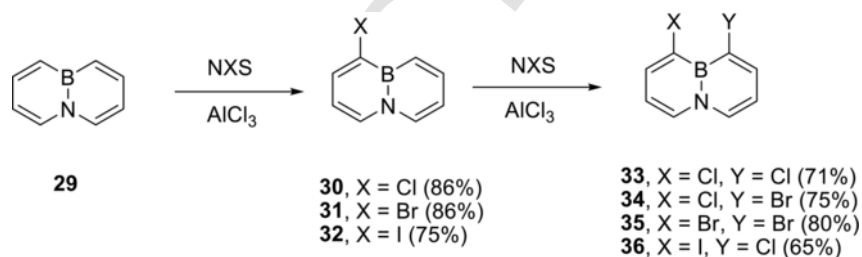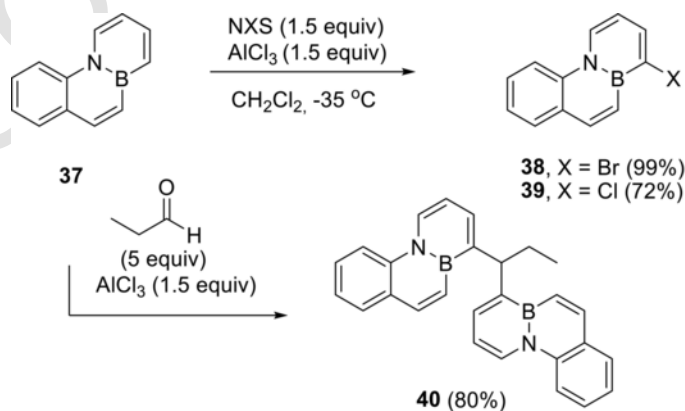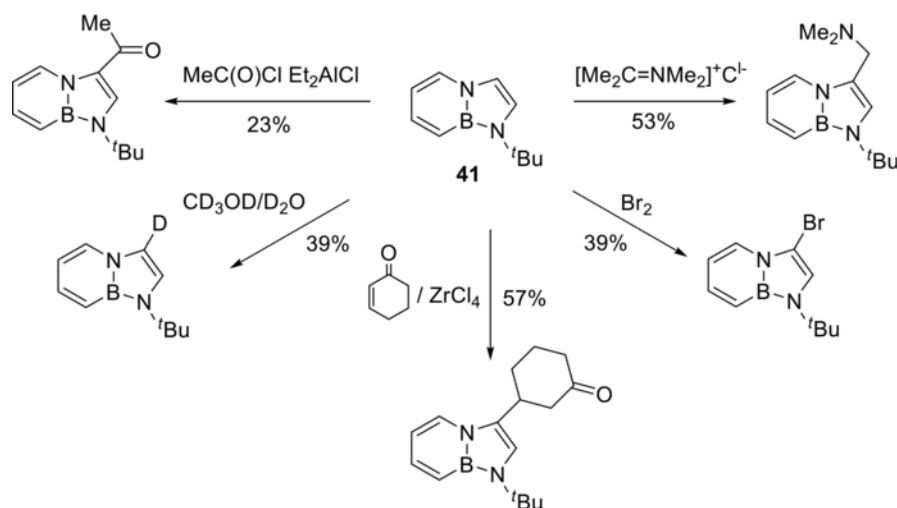
Scheme 7

Scheme 8

5.2   Addition and cycloaddition reactions

The first examples to demonstrate the cycloaddition reactions of 1,2-azaborines are illustrated in **Scheme 9**. *N*-TBS-*B*-Me-1,2-azaborine (TBS = *tert*-butyl-dimethylsilyl) **42** undergoes Diels-Alder reaction with various electron-deficient dienophiles. Both the *N*- and the *B*-substituent on the 1,2-azaborine exert significant influence on the [4 + 2]-cycloaddition reactivity and the aromatic character of the BN heterocycle.[62] Factors controlling the reactivity and selectivity of the Diels-Alder reactions involving 1,2-heteroborines [$H_4C_4B(H)X$, X = NH, PH, AsH; O, S, Se] has been computationally explored by means of density functional theory (DFT) calculations.[72,73]

1-Bora-4-tellurocyclohexa-2,5-diene **43** whose spectral parameters indicate some degree of π-electron delocalization over the Te/B rings, can be converted into a series of Te-containing heterocycles **44** via sequential [4 + 2] cycloaddition/alkyne-elimination reactions (**Scheme 10**).[74] More recently, the same authors demonstrated further reactivity of these heterocycles, providing access to unsymmetrically substituted tellurium-boron based heterocycle.[75]

Unusual reactivity has been noted for 1,3,2,5-diazadiborine **45** containing a formal B(+ 1)/B(+ III) mixed valence system in the aromatic six-membered $B_2C_2N_2$ ring. This compound readily forms the adduct **46** and **47** with methyl trifluoromethanesulfonate and phenylacetylene without any catalyst. Reacting the diazadiborine **45** with carbon dioxide afforded the bicyclo[2,2,2] product **48** (**Scheme 11**).[41]

5.3   Cross-coupling reactions

Diverse substitution at ring carbon of BN-heteroarenes was achieved by initial selective halogenation, followed by a variety of cross-coupling reactions, including Heck,[22] Negishi,[76] Suzuki-Miyaura,[22,76–79] and Sonogashira[22,23] processes. Thus, it was found that C(3)-brominated 1,2-azaborine **49** could be used in Negishi coupling reaction that is tolerant of a labile B—Cl bond.[76] A series of 1,2-azaborine derivatives **50** were thus prepared. [Pd(PtBu₃)₂] was found to be the most effective catalyst for the coupling reaction (**Scheme 12**). Similar strategy was used to prepare BN isosteres of indenyl and naphthalene.[76]

C(6)-Functionalization of 1,2-azaborines has been realized via Ir-catalyzed C—H borylation and subsequent Suzuki-Miyaura cross-coupling reaction (**Scheme 13**).[78]

A Pd-catalyzed borylation of 3-bromo-2,1-borazaronaphthalenes **51** allows the formation of umpolung reagents **52** for subsequent Pd-mediated cross-coupling. This strategy opens route to the rapid derivatization of these scaffolds (**Scheme 14**).[77]

Recently, Fang and co-workers demonstrated that 4-iodo-4*a*,8*a*-azanaphthalene **53** is excellent partner in various Pd-catalyzed cross-coupling reactions as shown in **Scheme 15**.[22]

The Pd-catalyzed cross-coupling reactions of 4-bromo-4a-aza-10a-boraphenathrene **38** were used to prepare BN-phenanthrenes **54**–**56** in a straightforward manner (**Scheme 16**).[23]

Recently, the Pd-catalyzed Suzuki-Miyaura cross-coupling of *N*—H and *N*-alkyl 3-bromo-2,1-borazaronaphthalenes and potassium (hetero)aryltrifluoroborates was used to synthesize a library of 3-(hetero)aryl and 3,6-diaryl-2,1-borazaronaphthalenes.[69] Of the palladium sources and ligands tested, the commercially available (*t*-Bu₃P)(aminobiphenyl)palladium chloride (commercially available *t*-Bu₃P—Pd—G2) was chosen as a best catalyst (**Scheme 17**).

Molander and co-workers have carried out extensive study in the area of a Ni-catalyzed reductive cross coupling of 3-bromo-2,1-borazaronaphthalenes with primary and secondary alkyl iodides. The method allows the coupling of azaborine cores bearing aryl and alkyl substituent on boron and also tolerates alkyl substituents on nitrogen (**Scheme 18**).[68]

dienophile	cycloadduct	yield (%)
(maleic anhydride)		96[a] >95:5 d.r.
(N-methylmaleimide)		95[a] >95:5 d.r.
(dimethyl maleate)		9[b] >95:5 d.r.
(dimethyl fumarate)		43[b] 1:1:1 d.r.
(methyl CF3-acrylate)		90[b] 1:1:1 d.r. single regioisomer
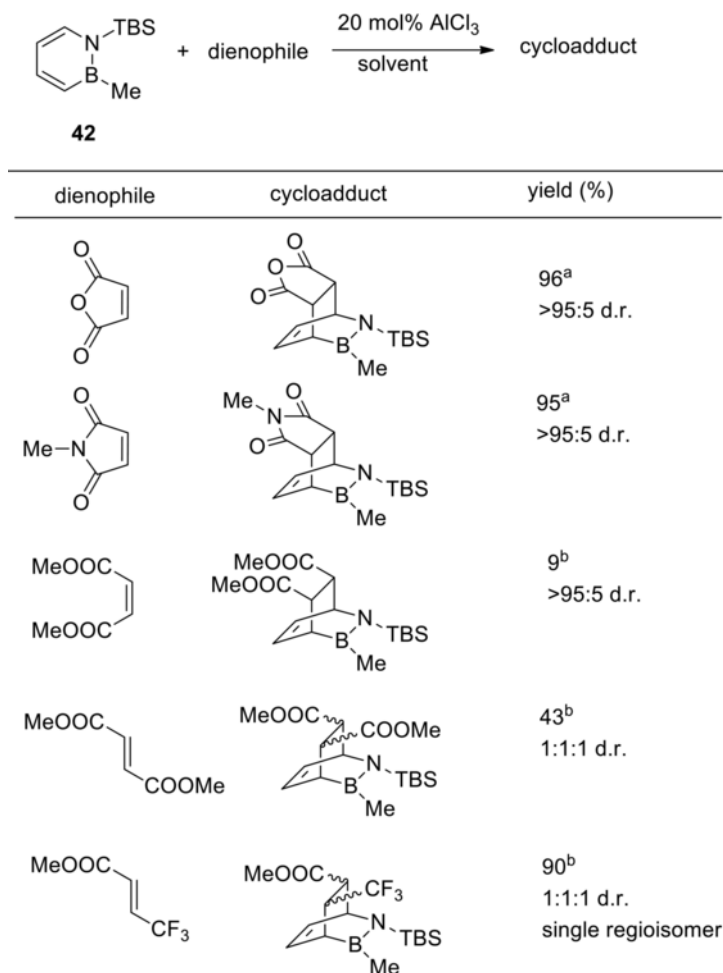
[a]Yield determined by ^{1}H NMR after 12 h at 20 °C in toluene;
[b]Yield determined by ^{1}H NMR after 12 h at 50 °C in CH$_2$Cl$_2$

Scheme 9
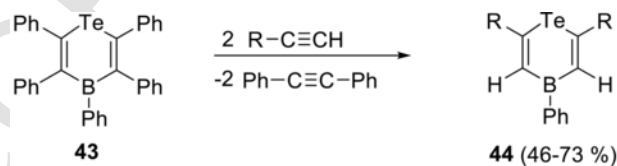
R = 4-BrC$_6$H$_4$, 4-MeOC$_6$H$_4$, 4-t-BuOC$_6$H$_4$, 4-F$_3$CC$_6$H$_4$, 3-ClC$_6$H$_4$,
3,5-F$_2$C$_6$H$_4$, 4-PhC$_6$H$_4$, 3-thienyl, Ph, ferrocenyl, fluoren-2-yl

Scheme 10

In 2014, Liu and co-workers described the first examples of rhodium-catalyzed B—H activation of azaborines leading to a new family of stilbene derivatives through dehydrogenative borylation.[80] Phosphine-free rhodium alkene complexes such as [Rh(cod)$_2$]BF$_4$ or [Rh(nbd)(Cl)]$_2$ were found to be suitable catalysts for these reactions providing the desired products in up to 83% isolates yield (**Scheme 19**).
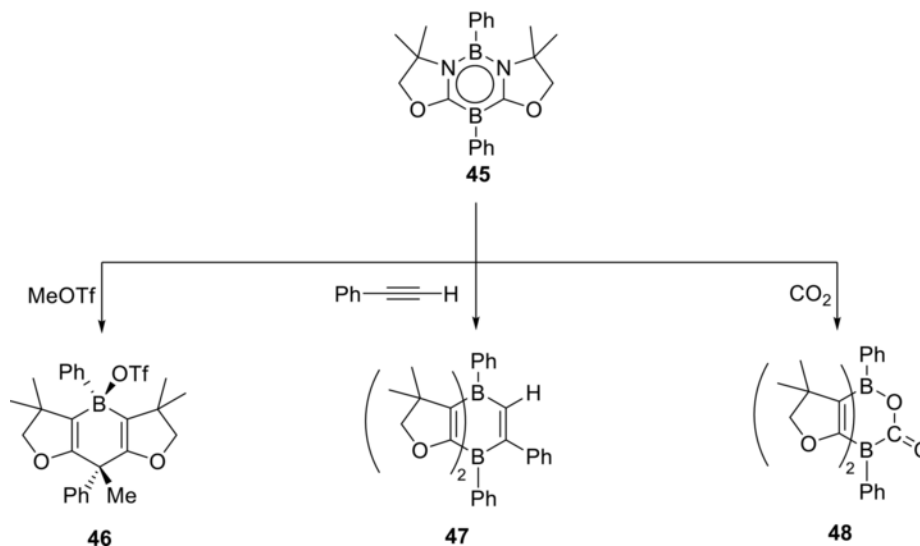
Scheme 11
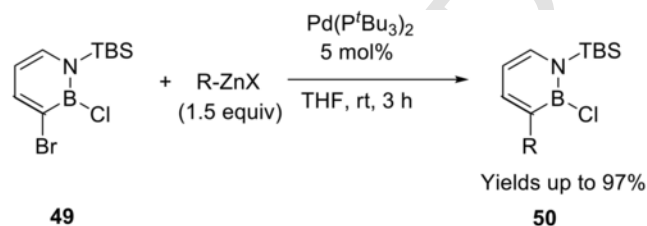
Scheme 12

R = ^{n}Pr, 1-phenylvilyl, vinyl, 2-(1,3-dioxan-2-yl)ethyl, 4-chlorophenyl, 3,4,5-trifluorophenyl
X = Br, I

Scheme 13
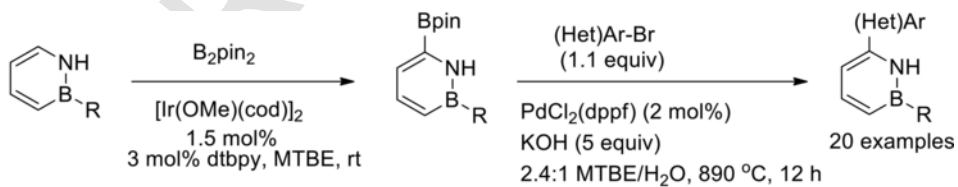
R = Me, n-Bu, Mes, n-BuO

Abbreviations: cod = 1,5-cyclooctadiene, dtbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine, MTBE = methyl *tert*-butyl ether
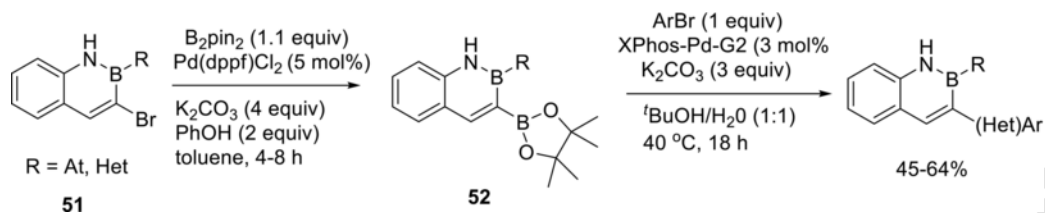
Scheme 14
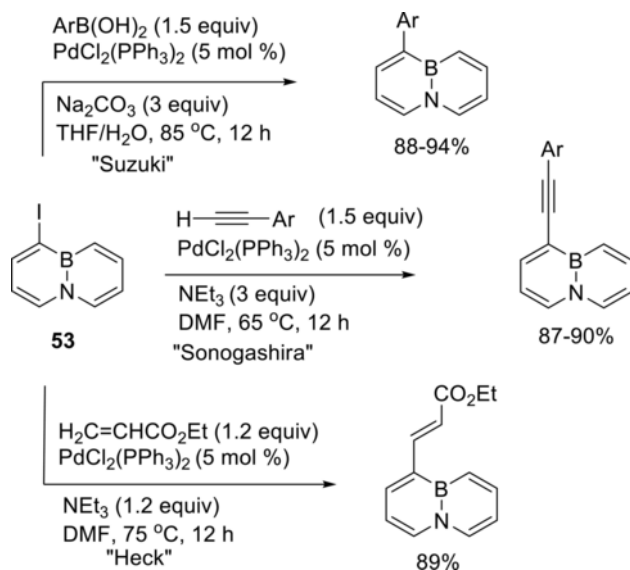
Scheme 15
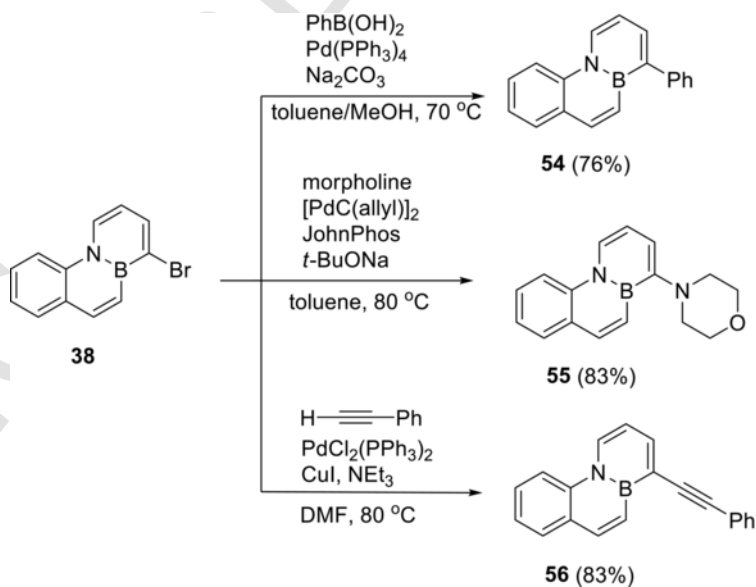
Scheme 16
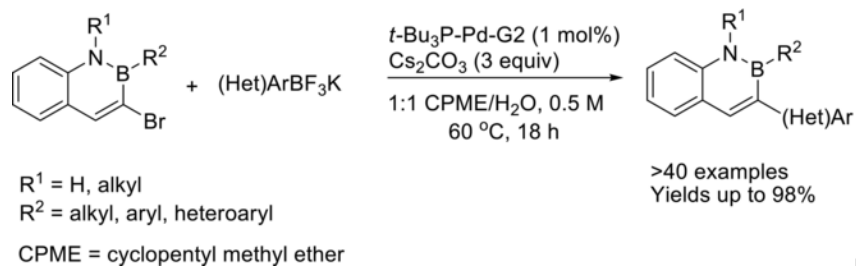
Scheme 17
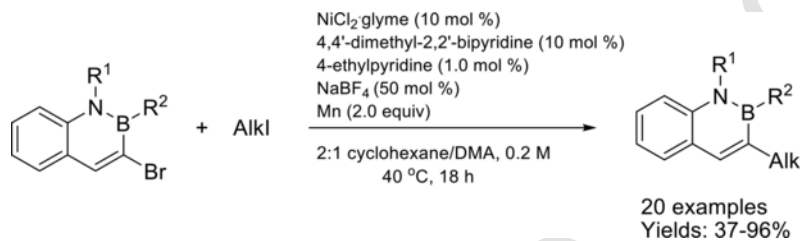
Scheme 18
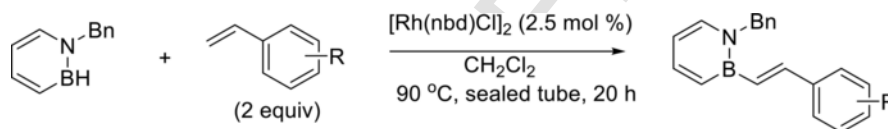
Scheme 19

5.4   Complexation with transition metal derivatives

The synthesis of boron-containing heteroarenes allowed exploration of their coordination chemistry. Thus, tricarbonylchromium complex **58** in which chromium is η^6-bound to the heterocyclic ring was prepared by heating **57** with $Cr(CO)_3(MeCN)_3$ in THF at 50 °C. Heating **58** in THF to 101 °C causes it to undergo a clean isomerization to its regioisomer **59**. The thermal conversion of **58** to **59** is favorable, apparently because phenyl is a better ligand toward $Cr(CO)_3$ than is 1,2- dihydro-1,2-azaborinyl. However, the $Cr(CO)_3$ group of **59** may be switched back to the heterocyclic ring by base conversion to the anion 60, followed by thermal isomerization to anion 61. Protonation of **61** reforms **58** (**Scheme 20**).[81] The corresponding reactions of chromium tricarbonyl complexes of 1,2-dihydro-1,2-benzazaborines, which are ring-fused analogues of **57**, have also been studied.[82] In this context it is important to emphasize that the reaction of 1,2-dihydro-1,2-oxaborine **62** with $Cr(CO)_3(MeCN)_3$ in THF at 70 °C gave thermodynamically stable complex **63** (**Scheme 21**). Apparently the 1,2-oxaborine ring is a poorer ligand than phenyl ring.[83]

3a,7a-Azaborindenyl-$Cr(CO)_3$ complex **65** is especially interesting because haptotropic migration from the six- to the five-membered ring is possible for this compound. Indeed, when 3a,7a-azaborindene (**64**) is treated with $Cr(CO)_3(CH_3CN)_3$ in THF at 25 °C, azaborindenyl-$Cr(CO)_3$ complex **65** is formed via η^6-complexation to the six membered ring. The latter can be quantitatively deprotonated by treatment with potassium bis(trimethylsilylamide) in THF at −60 °C to afford a solution of the potassium salt of η^6-3a,7a-azaborindenyl-$Cr(CO)_3$ (**66**). Allowing THF solutions of **66** to warm to 25 °C causes it to undergo a clean isomerization to its η^5-regioisomer **67** (**Scheme 22**).[84]

Incorporating additional functional groups into azaborine ring increases the number of possible modes of coordination and structural arrangements. Thus, it has been shown that the boron-2-pyridyl-substituted monobenzofused 1,4-azaborine **68** can serve as η^2-L-type ligand. Thus, complex **69** was prepared through reaction of **68** with $[\{PtMe_2(\mu\text{-}SMe_2)\}_2]$ and featured an η^2-coordination to the Pt atom by the B—C(3) component of the 1,4-azaborine ring (**Scheme 23**).[85]

The reaction of lithium 2-vinyl-1,2-azaboratabenzene **70** with one equivalent of $[\{Cp^*RuCl\}_4]$ afforded complex **71** in which BN-styrene is η^6-bound to ruthenium. When two equivalents of $[\{Cp^*RuCl\}_4]$ were added, diruthenium complex **72** was formed, in which η^6-binding occurs between one ruthenium atom and the azaborine ring, while the second ruthenium binds η^1 to the azaborine nitrogen and η^2 to the B-vinyl group (**Scheme 24**).[86]
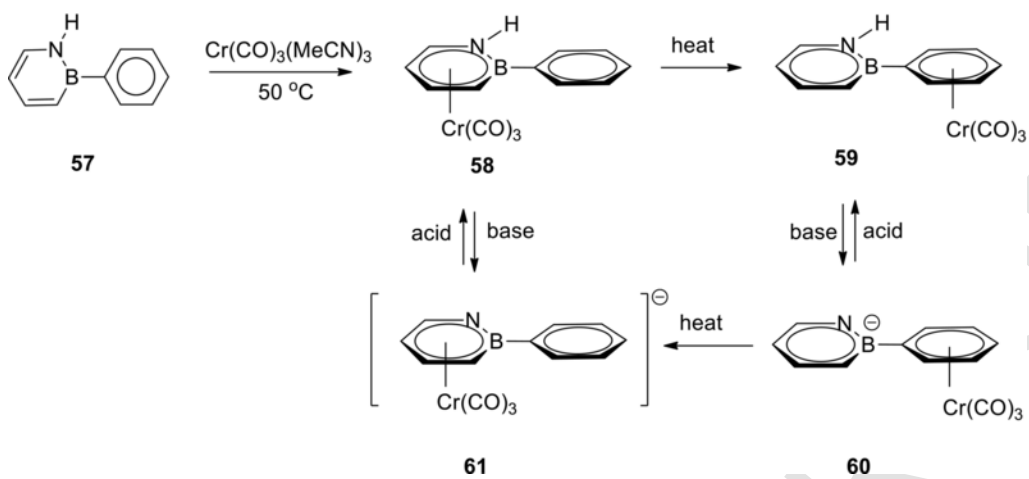
Scheme 20
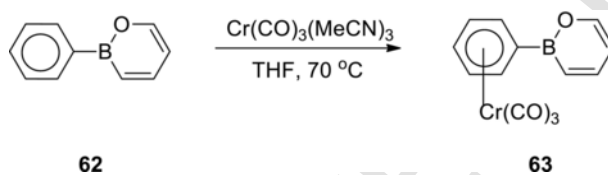
Scheme 21
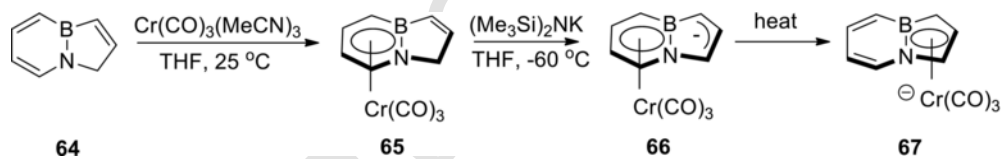
Scheme 22
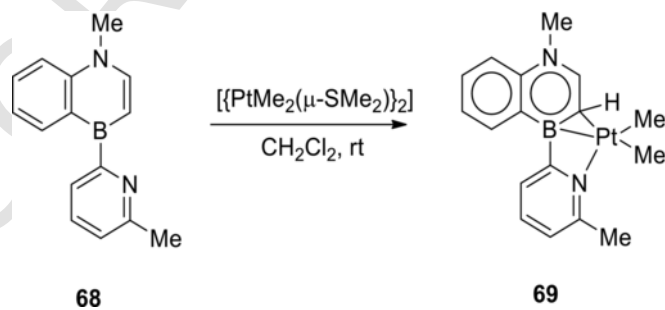
Scheme 23
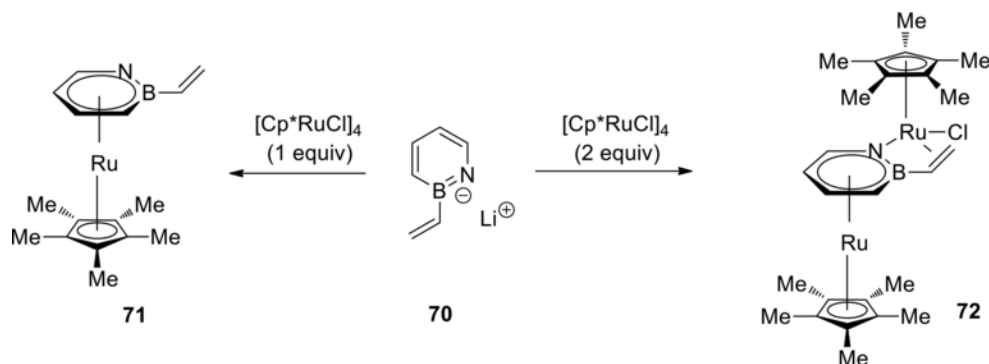
Scheme 24

6   Reactivity of nonconjugated rings

Liu's group reported the first synthesis and characterization of the parent 1,2-BN cyclohexane **76** (**Scheme 25**).[87] Reaction of the bis(trimethylsilyl)-substituted homoallylamine **73** with $BH_3\cdot THF$ afforded an intermediate consistent with structure **74**. The latter was reacted with KH to give cyclic amido borane **75** which produced the target 1,2-BN-cyclohexane **76** after treatment with HF·pyridine. In contrast to 1,2-dihydro-1,2-azaborine the B—H bond of which has been shown not to exhibit strong hydridic character, the B—H bond in 1,2-BN cyclohexane is hydridic in nature. Thus, the treatment of **76** with 1 equiv. of HCl led to the boracycle **77**. Similarly, reaction of **76** with 2 equiv. of HCl furnished compound **78**. The same research group investigated the potential of 1,2-BN cyclohexane to release H_2 under thermal activation. It was found that when **76** is heated as a solution in toluene for 2 h, trimer **79** is formed quantitatively with
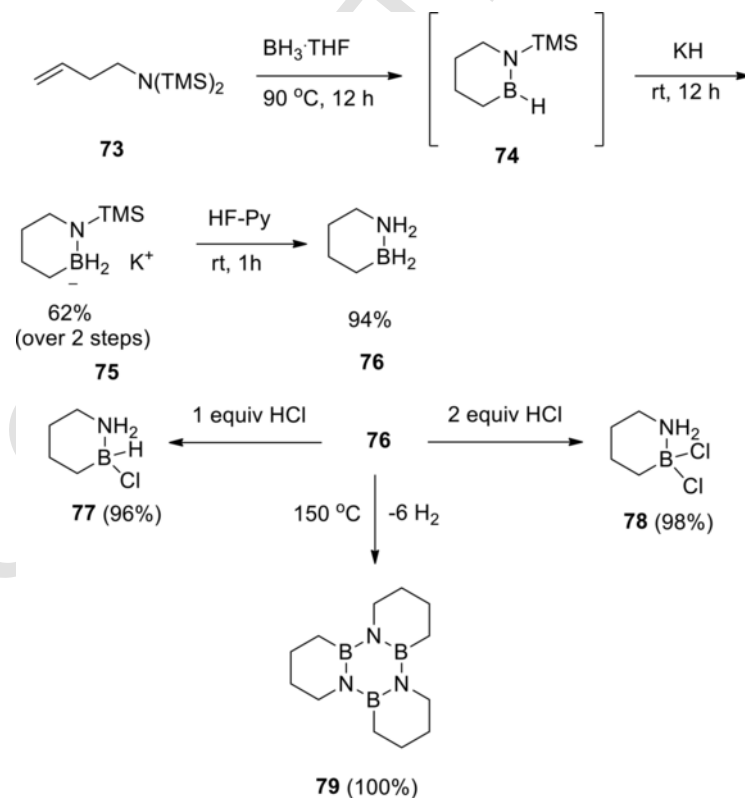
Scheme 25

concomitant release of 6 equiv. of H_2. More recently, the metal-catalyzed dehydrogenation of σ-complexes of BN-cyclohexanes has been developed. This route operates at a significantly lower temperature than non-catalyzed alternatives.[88]

In the 1,2-BN cyclohexane series, the reversible covalent binding of 1,2-, 1,3-, and 1,4-diols to an *N*-Bn 1,2-BN cyclohexane **80** has been studied by ^{11}B and ^{1}H NMR spectroscopy and single-crystal X-ray diffraction analysis. Thus, addition of 1,3-propanediol proceeded cleanly to afford the air- and moisture-stable complex **81** in 96% isolated yield. Addition of 1 equiv. of triflic acid to a solution of 80 in methylene chloride afforded acyclic ammonium salt **82** (**Scheme 26**). Competitive binding experiments show that the 1,2-BN cyclohexane framework possesses an inherent thermodynamic preference for a five-membered chelate ring size, *cis*-binding geometry, and acidic diol ligands.[89]

In order to generate boron-containing hetero π-conjugated molecules, Wang and co-workers used photoelimination process.[25] Upon UV-irradiation of B,N-heterocyclic compounds shown in **Scheme 27** in which the R group can be either an alkyl or an aryl group and N heterocycle can be either a pyridyl or a benzothiazolyl, the breaking of a C—H bond and of a C—B bond occurs to give the azaborines **83**–**90**.

7   Reactivity of substituents attached to ring carbon atoms

3-Allyl-substituted 1,2-azaborine **91** was used as a common precursor for the synthesis of new BN-heterocycles via ring-closing metathesis (RCM) as a key strategy. Thus, treatment of **91** with allylmagnesium bromide or 3-butenylmagnesium bromide gives rise to azaborines **92** and **93** in excellent yield. Subsequent RCM with Grubbs' first-generation RCM catalysis provided bicyclic compounds **94** and **95** (**Scheme 28**).[76]

Scheme 26

83, R' = H, R = Mes
84, R' = Me, R = Mes
85, R' = R = Me

86, R' = H, R = Mes
87, R' = Me, R = Mes
88, R' = R = Me

89

90
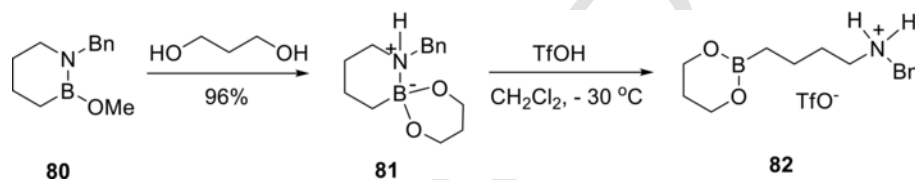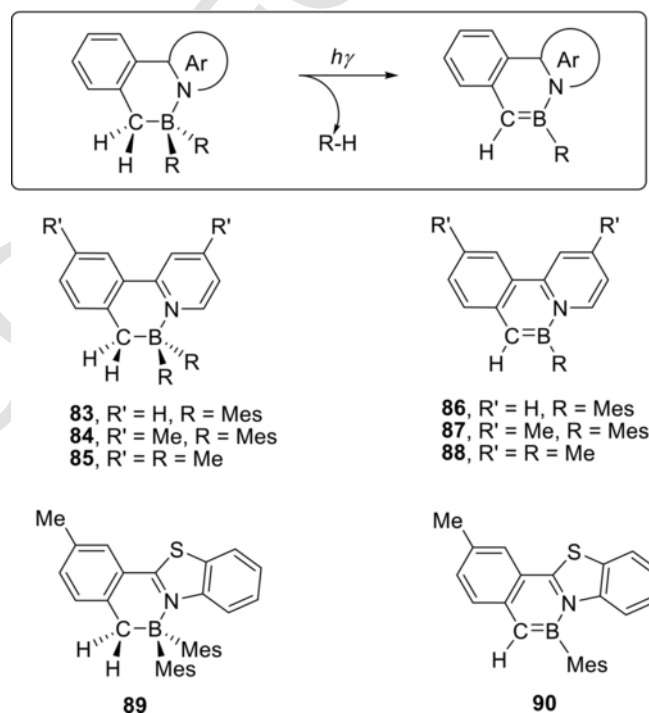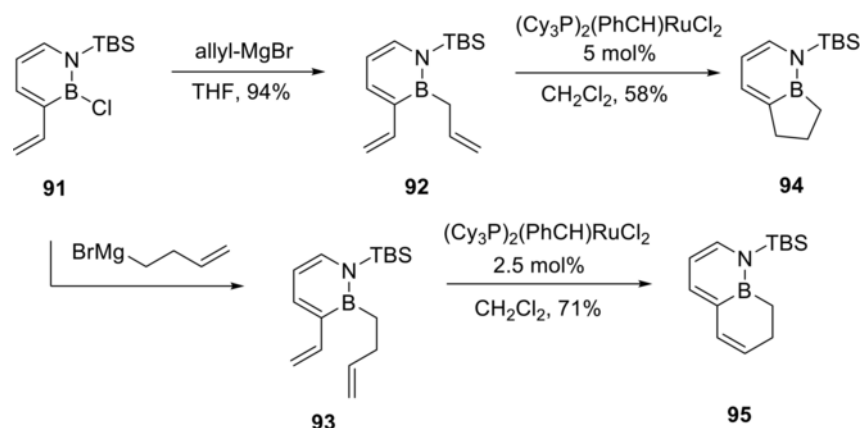
Scheme 27

Scheme 28

A late-stage functionalization of 1,2-azaborines at C(6) position was described by the Liu group.[78] Under catalytic conditions, borylation reaction of *B*-substituted 1,2-azaborines selectively afforded the *C*(6)-borylated azaborines. The latter were demonstrated to be an interesting substrates giving access to various C(6)-substituted azaborines via the Suzuki cross-coupling reactions (**Scheme 29**).

In order to evaluate the anion-recognition performance of bis(dimesitylboryl)dibenzoazaborine **96**, complexation of the latter with fluoride and cyanide ions has been studied. It was found that **96** formed Lewis acid-base type complexes with up to two anions in stepwise fashion (**Scheme 30**). Interestingly, the complex formation constants for CN ion were larger than those for F ion, despite the higher affinity of fluoride ion to boron atoms than that of cyanide ion.[90]

8   Reactivity of substituents attached to ring heteroatom

Nucleophilic displacement of halogen in the series of B-Hlg -heteroaromatics has been a subject of a number of reviews.[5,6,10] Additionally, reactivity and synthetic application of 1,1-diborylalkanes bearing five- and six-membered boracycles such as shown in **Fig. 14** have been recently reviewed by Fernández and co-workers.[91]

Except for η[6]-complexation with transition metals, the reactivity of the boron center in BN-heteroaromatics is mainly associated with nucleophilic substitution, which is in contrast to the reactivity of benzene for which the reactions of electrophilic substitution are more typical. The first substitution of various nucleophiles at the reactive B—Cl unit of boron-containing heteroarenes was described by Dewar and co-workers in the late 1950s.[3] Since then, many new nucleophilic substitution reactions of BN-heteroaromatics have been reported in literature. Thus, displacement of the chloride in 2-chloro-1,2-dihydro-1,2-azaborine **97** occurs readily in the presence of alkyl-, vinyl-, aryl-, and alkynyl-based nucleophiles. Moreover, heteroatom substitution also proceeded smoothly, resulting in the isolation of nitrogen-, oxygen-, and sulfur-substituted 1,2-azaborines (**Scheme 31**).[92]
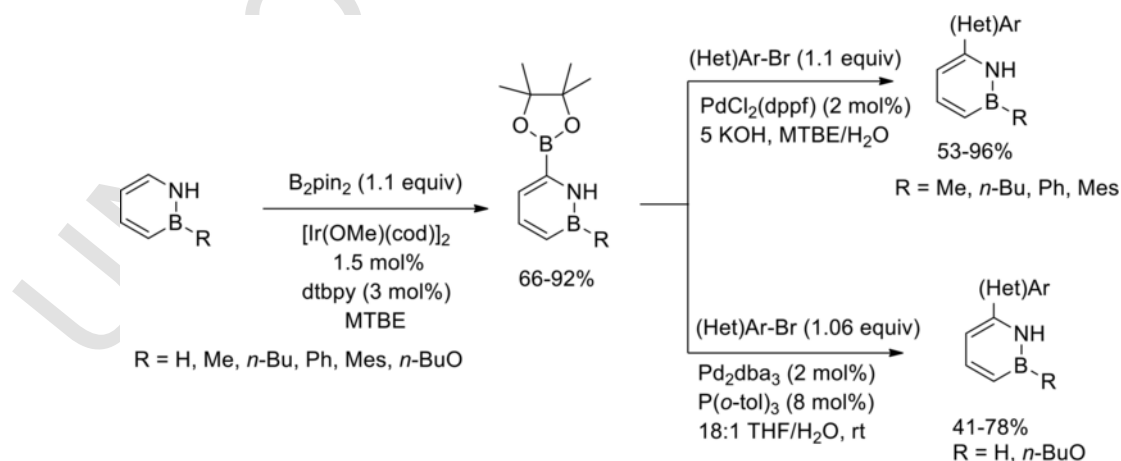
Scheme 29
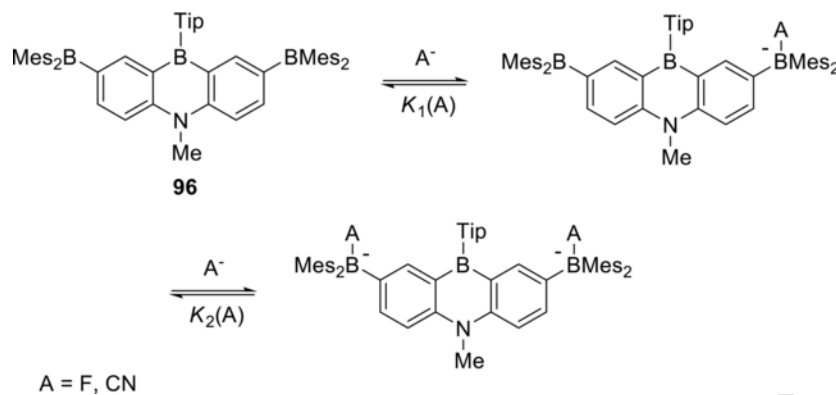
Scheme 30
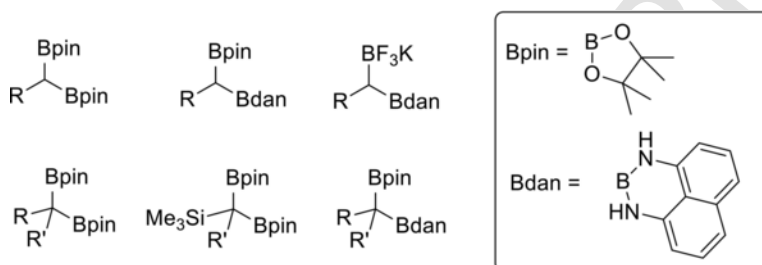
Fig. 14
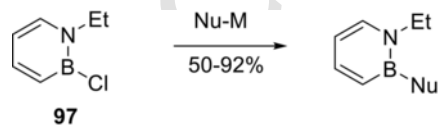
Nu-M: BuLi, vinylLi, PhMgBr, Ph━━━MgBr,
Me$_2$N, t-BuOK, BnSK

Scheme 31

2-Butoxy-1,2-dihydro-1,2-diazaborine **98** was found to be an excellent synthon which can be readily functionalized at both the nitrogen and boron position (**Scheme 32**).[93]

When 1,2-dihydro-1,2-azaborine (**1**) was treated with 2 equivalents of nucleophile (Nu-M) followed by 2 equivalents of electrophile (E-X), the substituted 1,2-azaborine heterocycle was formed in a good yield (**Scheme 33**).[94] The formation of 1,2-azaborine derivatives is consistent with nucleophilic aromatic substitution in which the hydride on boron is serving as a leaving group.

A general functional group-tolerant synthesis of BN biphenyls through a rhodium-catalyzed cross-coupling reaction of B━Cl substituted 1,2-azaborines with arylstannanes is shown in **Scheme 34**. The chlorobis(ethene)rhodium(I) dimer complex, [Rh(C$_2$H$_4$)$_2$Cl]$_2$, in combination with 2,2′-bis(diphenylphosphino)-1,1′-biphenyl (BIPHEP) was employed as the catalyst. This method dramatically expanded the scope of aryl substituents on the boron in the azaborine ring.[95]

Under basic and neutral conditions, 1,3-azaborine **28** exhibited very low reactivity when it was treated with a variety of nucleophiles (e.g., vinylmagnesium bromide, CsF, LiAlH$_4$, LiOAc, MeOH). The diisopropylamino group might be too strong of a donor to serve as a leaving group. However, substitution at boron occurred readily with acetic acid, furnishing a B━OAc substituted 1,3-azaborine **99** in 73% yield (**Scheme 35**). Authors postulate that under acidic conditions, protonation of nitrogen lone pair renders the diisopropylamino substituent a much better leaving group, thus promoting the substitution reaction.[67]

9-Chloro-9,10-BN-phenanthrene **100** was found to be suitable substrate for modifying the substitution at boron. It reacts readily with phenyllithium in n-Bu$_2$O at −78 °C to give B-phenyl-substituted BN-phenanthrene **101** (**Scheme 36**).[96]
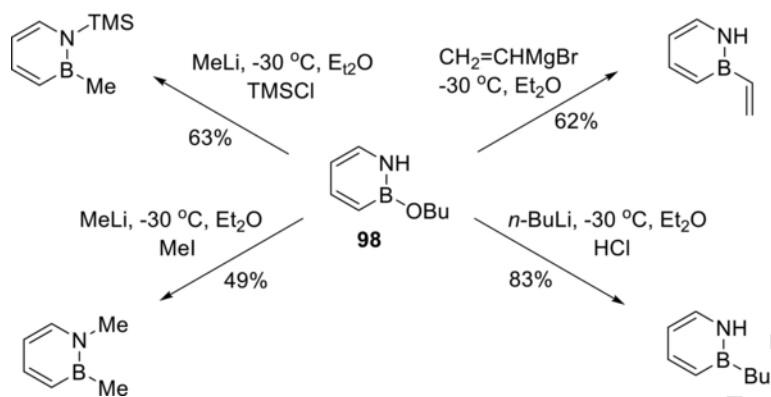
Scheme 32
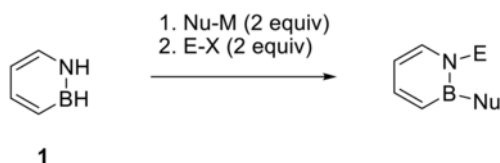
Scheme 33

Nu-M ; *t*-BuONa, *t*-BuLi, *n*-BuLi, PhLi; H₂C=CHMgBr, PhC≡CMgBr, AllOK

E-X: HCl, Me₃SiCl, MeI, BnBr

Scheme 34
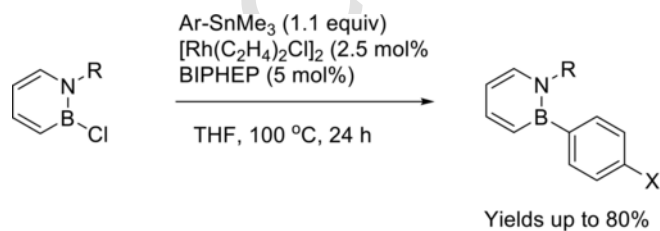
R = Et, *t*-butyldimethylsilyl
X = H, Me, OMe, CN, F, CF₃, C(O)OEt, C₆F₅, C(O)H, C(O)Me

BIPHEP = 2,2'-bis(diphenylphosphino)-1,1'-biphenyl
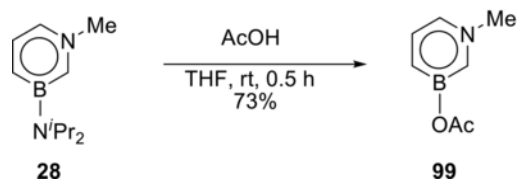
Scheme 35
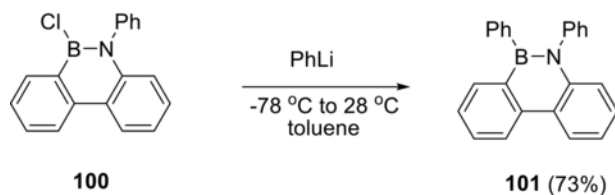
Scheme 36

A similar approach has also been described for the synthesis of 9-substituted 10,9-oxaboraphenanthrenes starting from 9-chloro-oxaboraphenanthrene **102**. The reaction of **102** with Grignard reagents resulted in the formation of the corresponding *B*-substituted derivatives **103** as shown in **Scheme 37**. 9-Trisyl- (**104**) and 9-supersilyl-10,9-oxaboraphenanthrene (**105**) were obtained selectively employing Li[C(SiMe$_3$)$_3$] or Na[Si^{t}Bu$_3$] as reactants.[57]

Substitution reactions of 2-chloromethyl-2,1-borazaronaphthalene **106** were studied in detail. This BN naphthalene isostere has been shown to be a suitable electrophile in reactions with a large variety of nucleophiles (**Scheme 38**).[97] It was also found that this building block can serve as the electrophile in palladium-catalyzed cross-coupling reactions to form sp^3-sp and sp^3-sp^3 bonds.[98]

Hall's group reported the preparation of chiral boronate derivatives via catalytic enantioselective conjugate addition of Grignard reagents on the 1,8-diaminonaphthalene (dan) derivatives **107** (**Scheme 39**).[99] In optimized conditions, this methodology affords chiral products **108** in excellent yield (up to 94%) and enantioselectivity (up to 98%).

New synthetic approaches to elaborate 2,1-borazaronaphthalene cores have also recently been suggested. They are based on the formation of C—C bonds via (i) nucleophilic substitution, (ii) Pd catalyzed cross-coupling, (iii) Ni catalyzed reductive cross-coupling, and (iv) visible light photoredox-Ni dual catalysis. These approaches enable the rapid construction of a library of naphthalene isosteres with numerous types of functional groups.[68,69,97,98,100,101]

9   Ring synthesis from acyclic compounds classified by number of ring atoms contributed by each component

9.1   One component synthesis

Reactions of this type are mainly represented by the Grubbs ring-closing metathesis (RCM). Ashe and co-workers were the first to apply RCM to the synthesis of 1,2-azaborines.[3] Later on several research groups extended the RCM methodology as a key synthetic strategy for
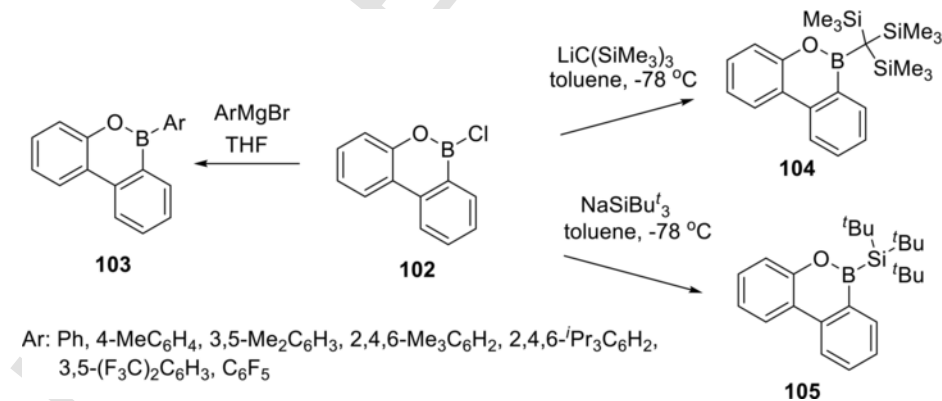
Scheme 37
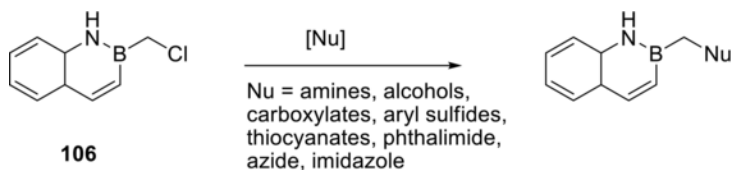
Scheme 38
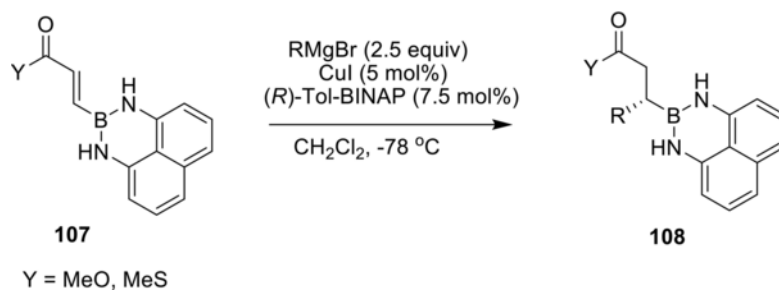
Scheme 39

a wide range of boracycles including 1,2-,[46,61,92,102] 1,3-,[67] 1,4-azaborines[85] and the fused BN-heterocycles[21–23,103–105]. Selected examples are shown in Schemes 40–44.

An efficient catalytic method for the generation of enolates from unactivated alkynes was reported by Sheppard and co-workers.[106] Thus, boron enolate **110** could be prepared by the treatment *ortho*-alkynylbenzene boronic acid **109** with PPh_3AuNTf_2 in 85% yield (**Scheme 45**). This method was found to be applicable to a range of alkynes.
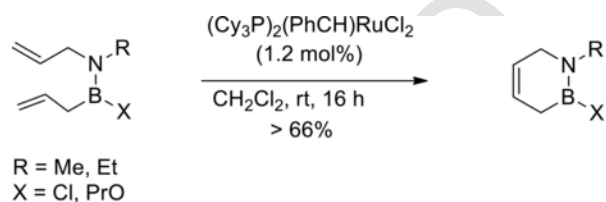
Scheme 40   (Ref. [92,102])
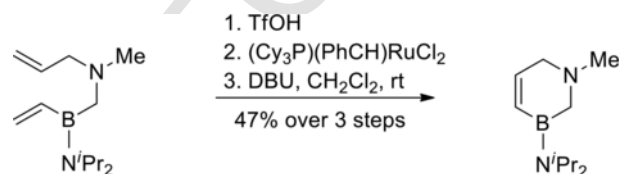
Scheme 41   (Ref. [67])
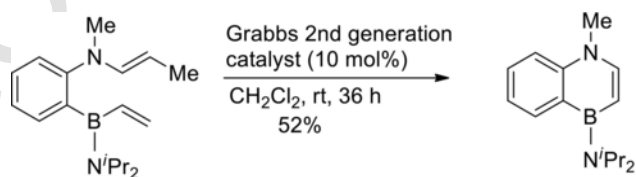
Scheme 42   (Ref. [85])
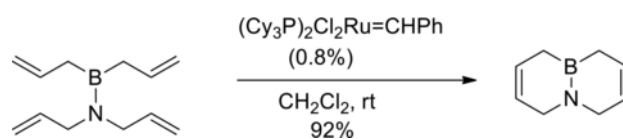
Scheme 43   (Ref. [22,103])
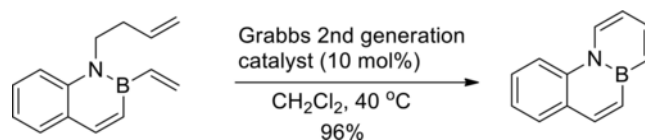
Scheme 44   (Ref. [23])
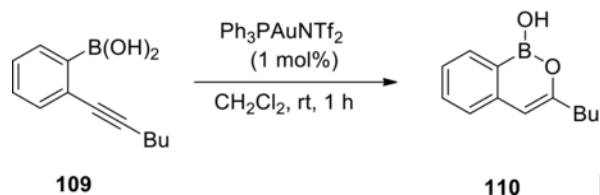
Scheme 45

Boron-fused double [5]helicenes **111** were synthesized from hexabromobenzene in a two-step protocol via Hart reaction and demethylative cyclization (**Scheme 46**). The helical structure of **111** was supported by X-ray crystallography.[107]

9.2   [5 + 1] Two component synthesis

The main methods available to synthesize six-membered boracycles containing C-B-X and X-B-Y linkages are of this type and were covered in CHEC-II and CHEC-III.[2,3] During the last decade many new examples of such syntheses have been reported and these are summarized in **Table 1**.

9.3   [4 + 2] Two component synthesis

In the last decade, considerable attention has been paid to new polycyclic aromatic 1,2-azaborine derivatives containing the N—B(OH) moiety. Interest in these air-stable and relatively nontoxic compounds arises from their vast biological activities.[136,137] A set of 2-acylated 2,3,1-diazaborines **112** were prepared by condensation of 2-formyl- or 2-acetylbenzeneboronic acid with acyl hydrazides. Depending on the substitution pattern or conditions of synthesis, products were isolated in open (A), monomer (B), or anhydro dimer (C) form (**Scheme**

R = H, ^{t}Bu
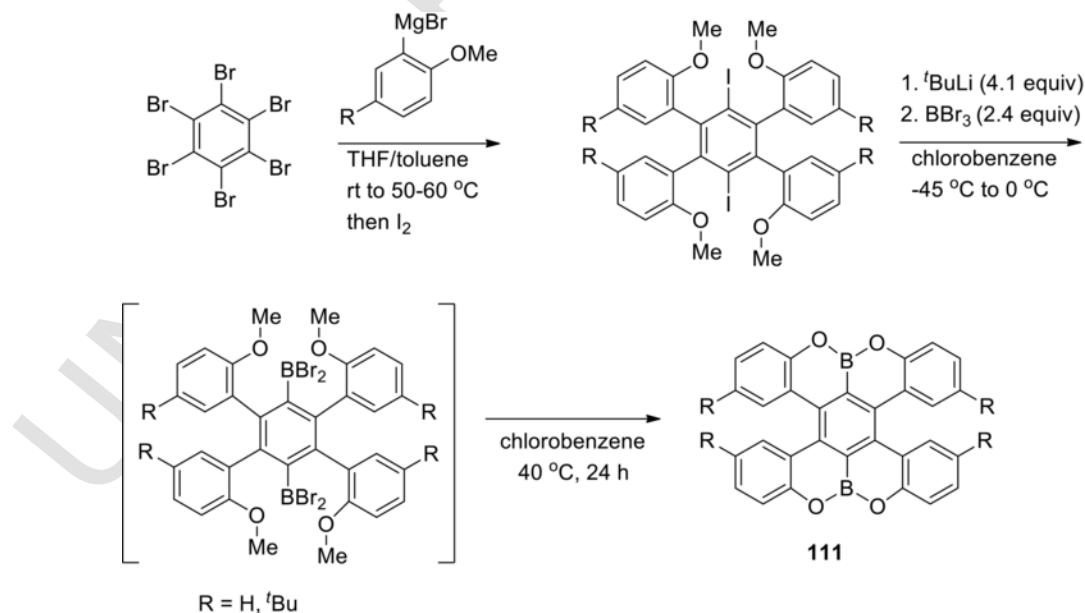
Scheme 46

Table 1 Two component synthesis of polyheteroatom six-membered boracycles from 5 + 1 atom fragments.
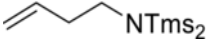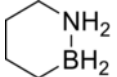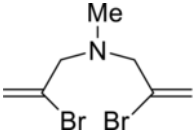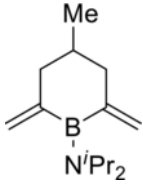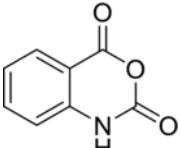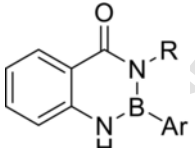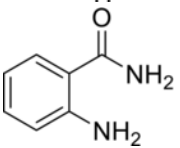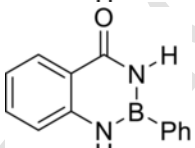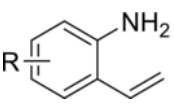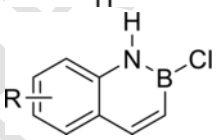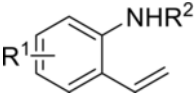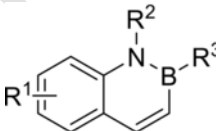
Substrate	Boron reagent	Boracycle	References
	BH$_3$ THF		**87**
	^{i}Pr$_2$NBCl$_2$		**60**
	RNH$_2$/ArB(OH)$_2$		**108**
	PhBF$_3$K		**109**
	BCl$_3$		110,111
	R^{3}BF$_3$K		69,97,100,101,111

Table 1   (Continued)
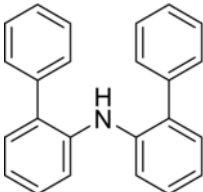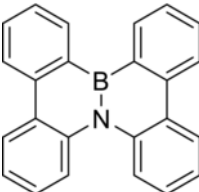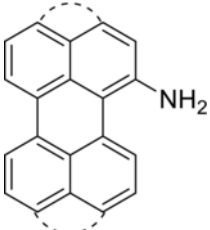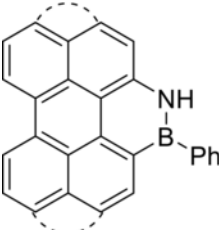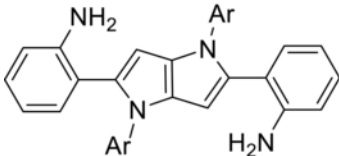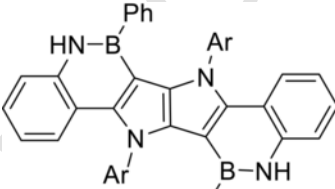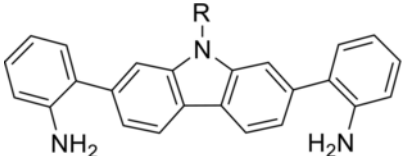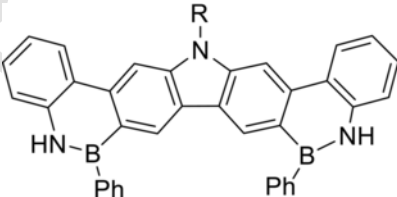
Substrate	Boron reagent	Boracycle	References
	BCl₃		36,112
	PhBCl₂		30
	PhBCl₂/Et₃N		113
	PhBCl₂/Et₃N		114

Table 1   (Continued)
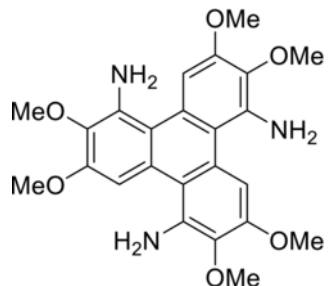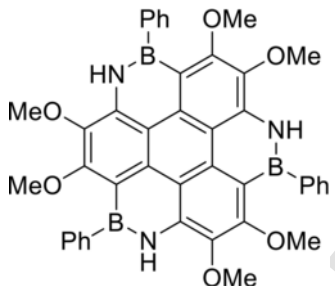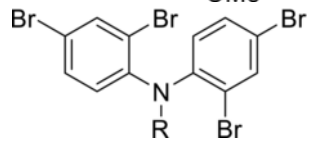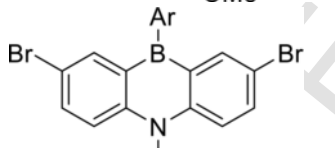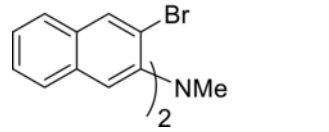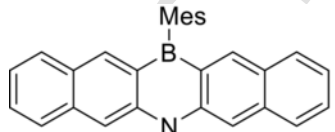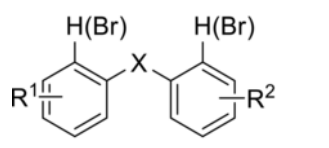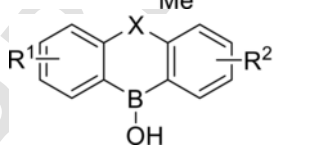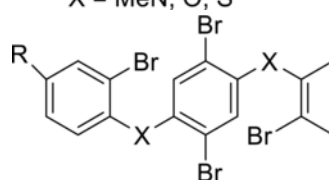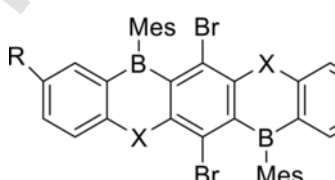
Substrate	Boron reagent	Boracycle	References
	PhBCl$_2$/Et$_3$N		34
	ArB(OMe)$_2$		115,116
	MesB(OMe)$_2$		117
\nX = MeN, O, S	B(OMe)$_3$		43,118–120
\nX = NMe, S	MesB(OMe)$_2$		121,122

Table 1   (Continued)
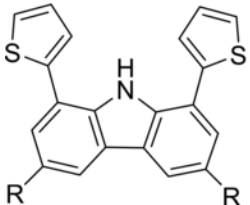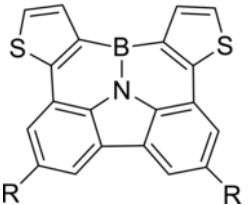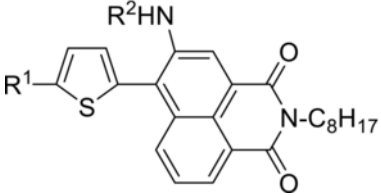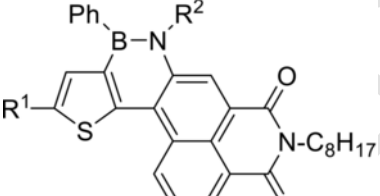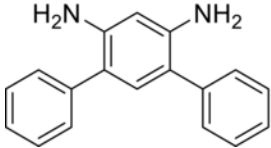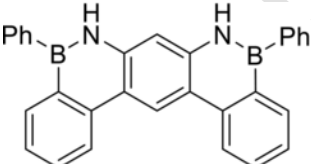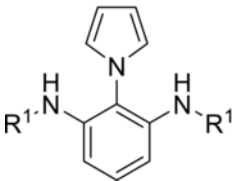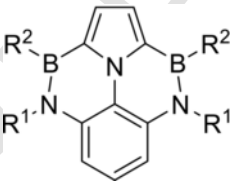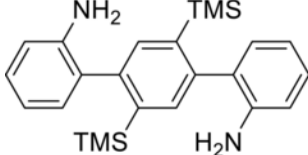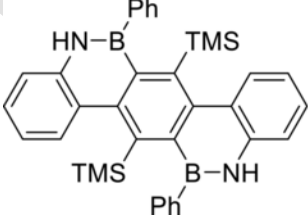
Substrate	Boron reagent	Boracycle	References
	BBr$_3$		**123**
	PhBCl$_2$		**124**
	PhBCl$_2$/FeCl$_3$		**125**
	BCl$_3$ or R^{2}BCl$_2$		**32**
	PhBCl$_2$/Et$_3$N		**126**

Table 1   (Continued)
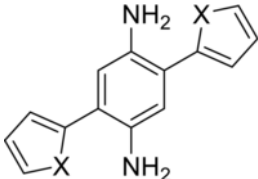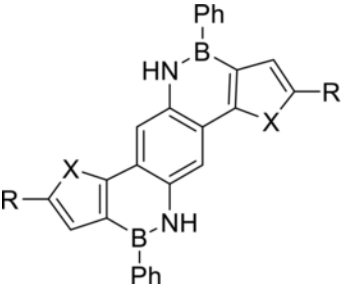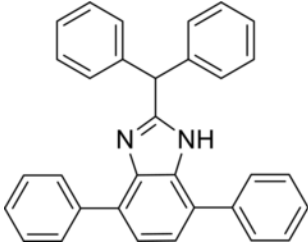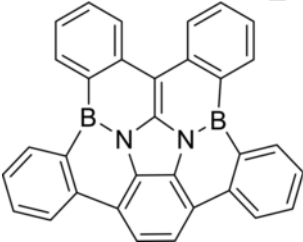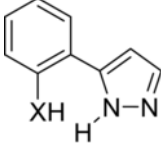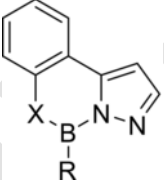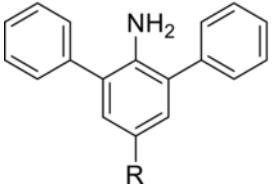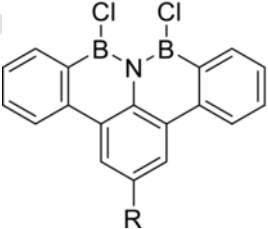
Substrate	Boron reagent	Boracycle	References
X = O, S	PhBCl₂/Et₃N		**127**
	BBr₃		**128**
X = NH, O	RB(OH)₂		129,130
	BCL₃/AlCl₃		**43**

Table 1   (Continued)
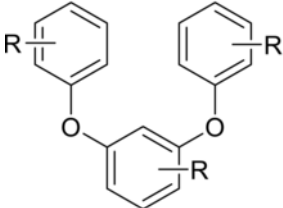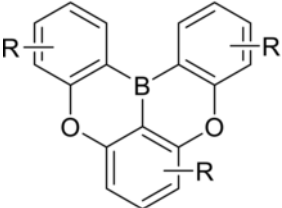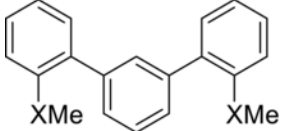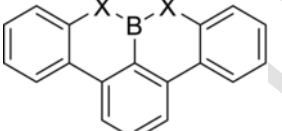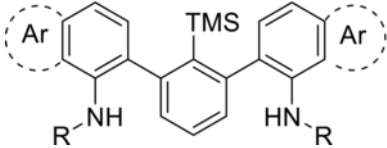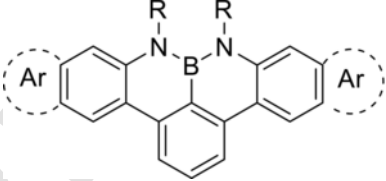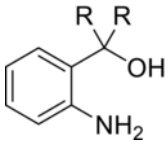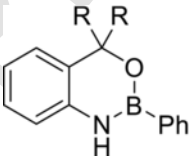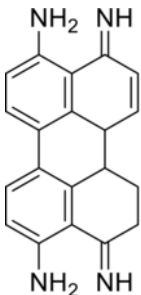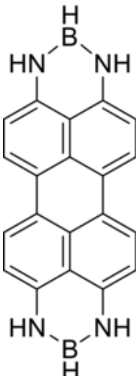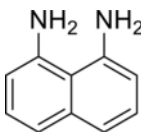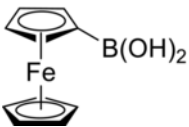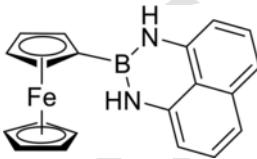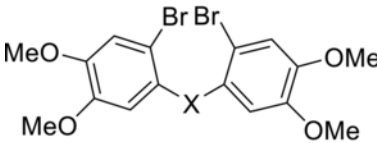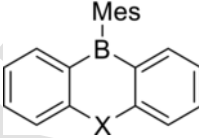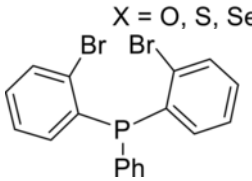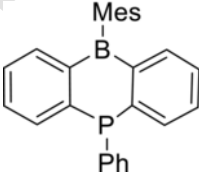
Substrate	Boron reagent	Boracycle	References
	BBr$_3$		59
 X = NMe, O, S	BBr$_3$/Base		58
	BCl$_3$/Et$_3$N		131
	PhB(OH)$_2$		132

Table 1   (Continued)

Substrate	Boron reagent	Boracycle	References
	BH$_3$ THF		133
	ferrocenyl-B(OH)$_2$		134
X = O, S, Se	MesB(OMe)$_2$		45
	MesB(OMe)$_2$		135

47).[138,139] Condensation of thiosemicarbazides with 2-formylphenylboronic acid affords the corresponding cyclic 2,3,2-benzodiazaborines.[140,141]

This methodology was extended to the salicyloyl and anthraniloyl hydrazines. The corresponding 1-hydroxy-2,3,1-benzodiazaborines are readily formed and ring closed to dibenzo-fused heterocycles **113** and **114** (**Scheme 48**).[142]

1-Hydroxy-2,3,1-benzodiazaborine **116** conjugated with 1,8-naphthalimide was prepared by the condensation of hydrazine-appended 1,8-naphthalimide **115** with 2-formylphenylboronic acid in dry ethanol (**Scheme 49**). The optical properties of this compound were rationalized using time-dependent density functional theory (TD-DFT) at the B3LYP/9-31G(d,p) level of theory.[143]

New aromatic BN 1,2-azaborine derivatives containing a fused pyrrolidinone ring have been prepared via a base catalyzed condensation of the substituted isoindolinones with the appropriate 2-formylboronic acids. For example, the reaction of 6-bromoisoindolinone with 2-formylphenylboronic acid using DBU in ethanol gave azaborine **117** in 84% yield (**Scheme 50**).[144]

The synthesis of 10b-aza-10c-borapyrene **118** has been performed via the combination of 2,6-diethynylpyridine with a cyclic borane using a microwave reactor and carefully controlling reaction conditions (**Scheme 51**).[29,145]

The polycyclic borazine **120** containing alternating BR and NR units has been prepared from diborate(4) anion, derived from the diborane **119**, and two equivalents of $B_2Cl_2(NMe_2)_2$ (**Scheme 52**). An analogous reaction starting with 1,1-$B_2\{1,8$-N_2naph$\}_2$ and $B_2Cl_2(NMe_2)_2$ afforded a similar species 1,1-$B_2\{1,8$-N_2naph$\}_2\{B_2(NMe_2)_2\}_2$.[146]

The synthesis of a B—B containing dithieno-1,2-dihydro-1,2-diborine **121** and its dianion **122** was accomplished using diaminoborane as the B—B source (**Scheme 53**). X-ray structural analysis of **121** revealed that the 1,2-diborine ring has a twisted nonplanar structure with a C—B—B—C dihedral angle of 44.5 degrees. The NICS(0) value calculated for the diborine ring at the HF/6-31 + G(d,p)//B3LYP/6-31G(d) level was + 8.3 ppm.[147]

R^1 = H, Me; R^2 = Ar, pyridin-2(3,4)-yl, NH_2, $NHNH_2$
R^2 = H, Alk. Ar

Scheme 47

113, X = O (80%)
114, X = NH (84%)

Scheme 48

Scheme 49

115 + → **116**

dry-EtOH
reflux, 5 h
44%

Scheme 50

DBU, ethanol
84%

117

Scheme 51

2 h, 160 °C
MW

1 h, 160 °C
2% Pd
MW

118 (78%)

Scheme 52

(i) 4 ^{n}BuLi
(ii) 2 B$_2$Cl$_2$(NMe$_2$)$_2$

119   **120**

Scheme 53

1. ^{n}BuLi, toluene, rt
2. Br$_2$B$_2$(NMe$_2$)$_2$

1. K/C$_8$, THF
2. [2.2.2]cryptand

121 (32%)

2(K$^+$-cryptand)

122
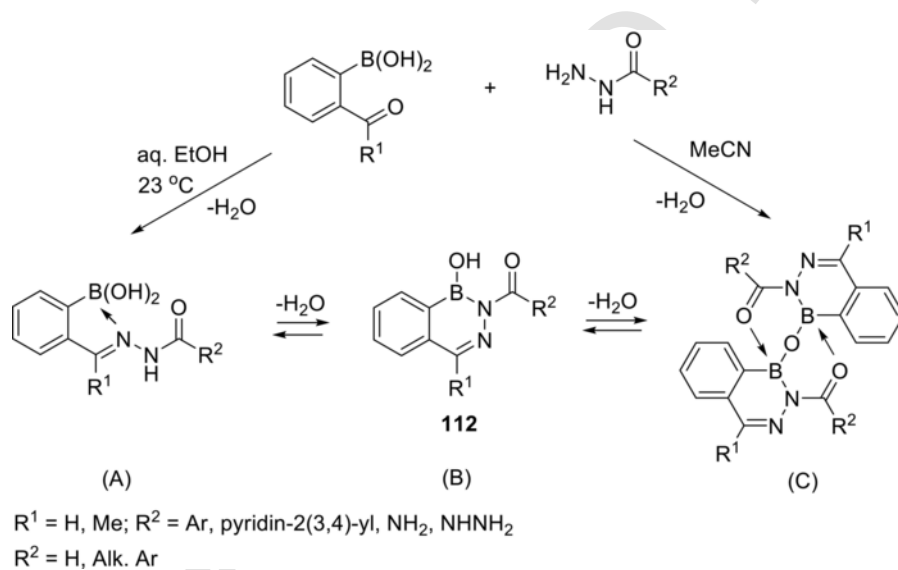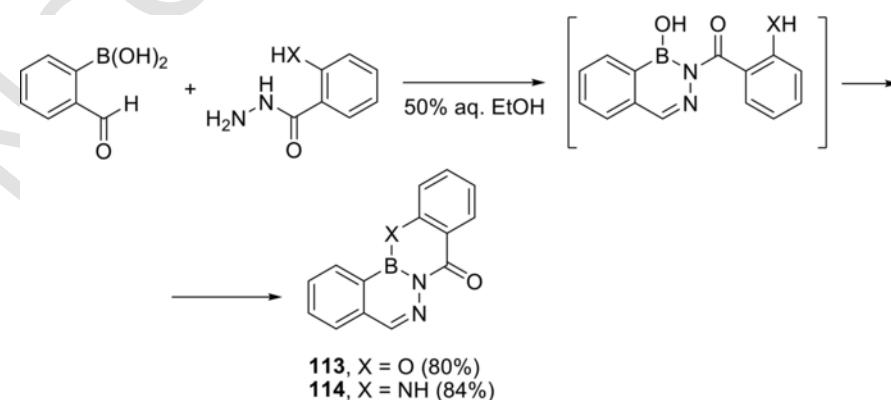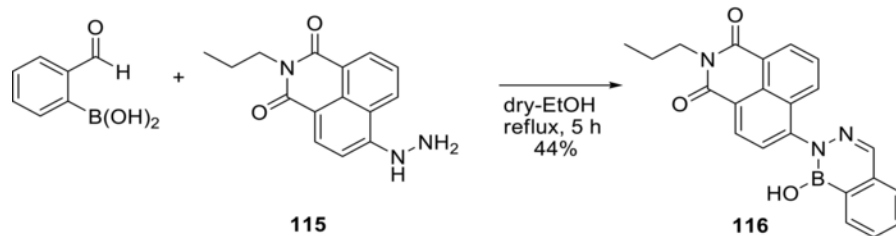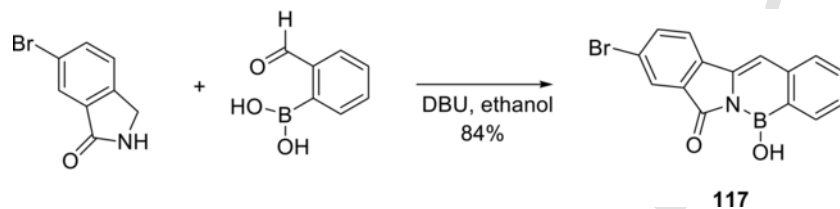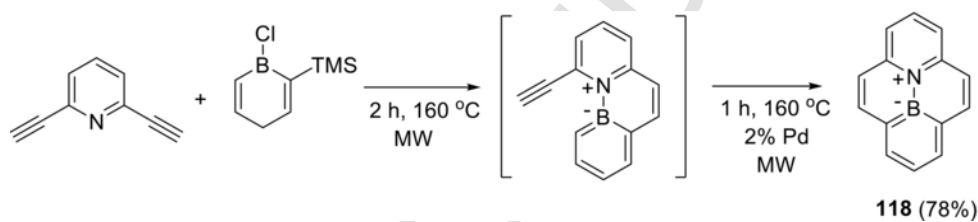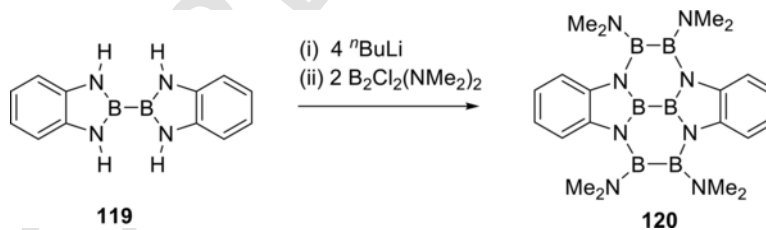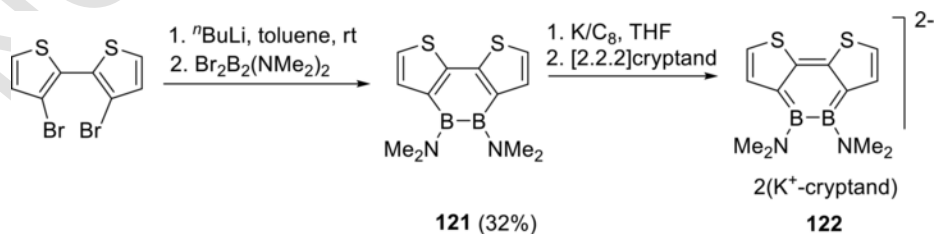
9.4   [3 + 3] Two component synthesis

A useful method for the preparation of 6-hydroxy-6H-dibenz[c,e][1,2]oxaborines **123** that serve as a building block for constructing versatile π-conjugated systems has recently been reported.[148] It involves boron-selective Suzuki-Miyaura cross-coupling between *ortho*-borylphenols and aryl halides or triflates bearing a 1,8-diaminonaphthalene (dan)-protected boryl group, followed by deprotection of the dan group and intramolecular dehydrative cyclization (**Scheme 54**).

Phenylene-containing oligoacenes and their functionalized analogues are generally obtained from the corresponding disilyl or distannyl precursors and hazardous boron halides.[3,49] A new approach to 9,10-dihydroxy-9,10-diboraanthracenes **124** employs the reaction of the appropriate substituted (2-halophenyl)boronates with *tert*-butyllithium (**Scheme 55**).[149]
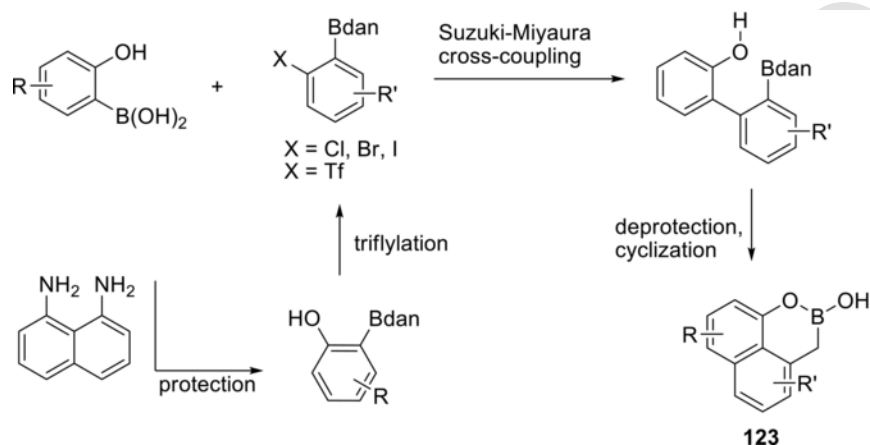
Scheme 54
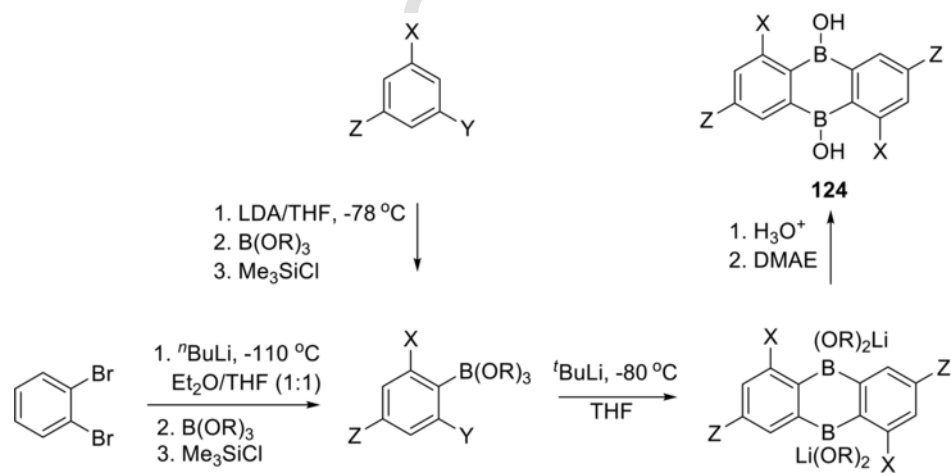
Scheme 55

10   Ring synthesis by transformation of another ring

Among the ring syntheses by transformation of another ring, reactions of five-membered antiaromatic boroles appear most prominently in the literature. Braunschweig's group[150–154] and other workers[96,155,156] have exploited the reactivity of antiaromatic boroles, a class of π-conjugated five-membered boracycles, gaining access to 1,2-heteraborine derivatives. Examples are the preparation of highly substituted monocyclic 1,2-azaborines **125** (**Scheme 56**)[150] and 1,2-phosphaborines **126** (**Scheme 57**)[157] by ring expansion of boroles. These reactions involve formal 1,1-insertion of a nitrene or phenylphosphinidene fragment into an endocyclic C—B bond. Addition of S_8 to pentaphenylboroles occurs readily in benzene at 65 °C to give 1,2-thiaborines **127** via insertion of the sulfur atom into endocyclic B—C bond (**Scheme 58**).[157] The mechanism of the borole ring expansion using computational methods was studied by Martin and co-workers.[158]

A novel route to the formation of six-membered BN-boracycles involves the rearrangement from aminoboroles to the aromatic BN-benzenes.[159,160] For example, the reaction between 9-chloro-9-borafluorene **128** with *N,O*-bis(trimethylsilyl)hydroxylamine results in 9-aza-10-boraphenanthrene **130**. The expected 9-(trimethylsilyloxyamino)-9-borafluorene **129** rearranges to the formally aromatic BN-phenanthrene at room temperature (**Scheme 59**).[159]

The thermal decomposition of 9-azido-9-borafluorene **131** in heptane solution results in N_2 elimination and yields the tetramer of a BN-phenanthryne **132** (**Scheme 60**). According to computations, loss of nitrogen and ring enlargement proceeds in a concert reaction, with the cyclotetramerization of BN-phenanthryne being an exothermic process.[155]

R^1 = Ph, Mes; R^2 = Me_3Si, Ph, 4-^{i}PrC$_6$H$_4$

Scheme 56

R = H, Me

Scheme 57

R = Ph, 4-PhC$_6$H$_4$
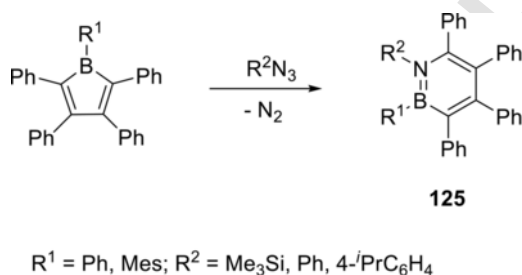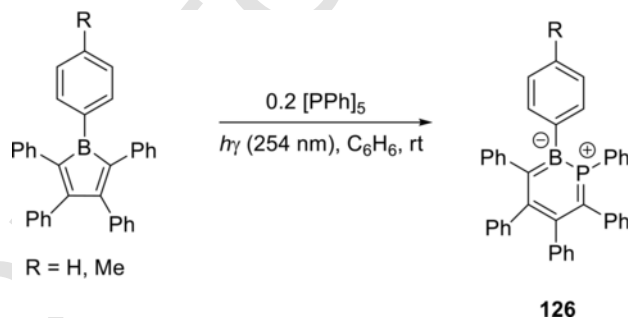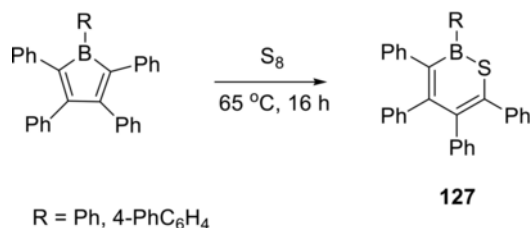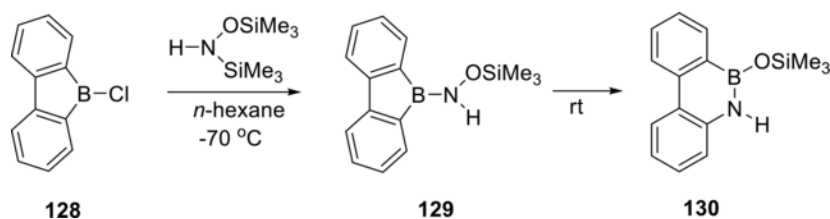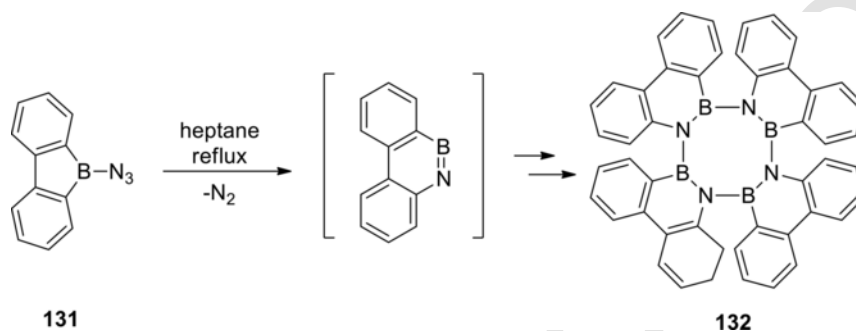
Scheme 58

Scheme 59

Scheme 60

The ring expansion method through 1,1- or 1,2-insertion reactions was found to be an effective strategy for synthesizing other types of six-membered boron heterocycles. Thus, 1,2-dihydro-1,2-heteraborines may be generally prepared using a carbenoid ring expansion from 1,2-heteraborolides. For example, 1,2-dihydro-2-phenyl-1,2-oxaborine **62** has been synthesized by the reaction of the appropriate 1,2-oxaborolide **133** with KN(SiMe$_3$)$_2$ and methylene chloride, as illustrated in **Scheme 61**. The reaction proceeds through the intermediacy of chlorocarbene generated from CH$_2$Cl$_2$ and base.[83] Similar approach was used to prepare 2-(diisopropylamino)-2H-1,2-thiaborine **134** (**Scheme 62**).[161]
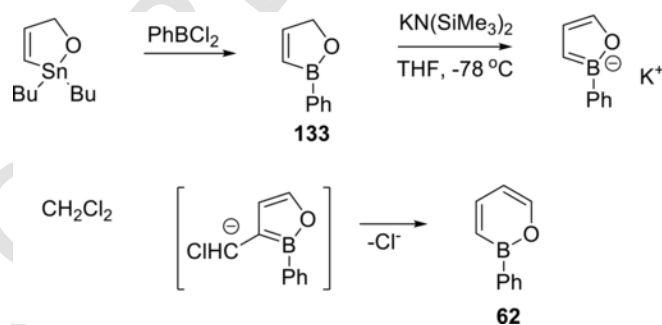
Scheme 61
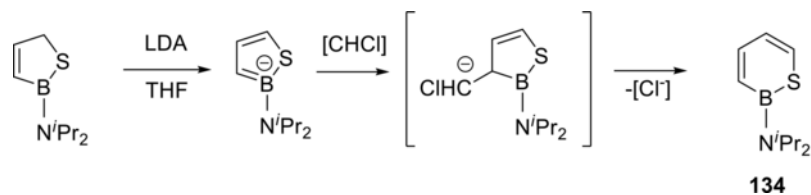
Scheme 62

Piers and co-workers explored the ring-expansion chemistry of the potassium salts of the dianions of bis-benzocycloborabutylidene **135** and diborole **136** using carbon dioxide as the agents of expansion.[162] Both dianions react with carbon dioxide to form the same insertion product **137** (**Scheme 63**).

A convenient preparation of 1,2-oxaborines **140** from pentaarylboroles **138** involves an oxygen insertion process (**Scheme 64**). Reaction of **138** with *N*-methylmorpholine *N*-oxide (NMO) afforded 1,2-oxaborines **140** in good yields. The reaction proceeds through the intermediates **139**, which are supported by the ^{11}B NMR spectroscopy.[156]

The first nickel-catalyzed boron insertion into the C(2)—O bond of benzofurans to construct benzoxaborine skeleton in one step was described by Yorimitsu and co-workers using bis(pinacolato)diboron as a borylating reagent and $NiCl_2(PPh_3)IPr$ (IPr = 1,3-bis(diisopropylphenyl)imidazole-2-ylidene) as a catalyst (**Scheme 65**). π-Extended naphthofurans were also applicable to the boron insertion to afford tricyclic naphthoxaborines such as **141**–**143**.[163] Report concerning manganese-catalyzed ring opening of benzofurans affording dianionic intermediates and their subsequent trapping with $B(OMe)_3$ has also appeared recently.[164]

11   Synthesis of particular classes of compounds

11.1   1,4-Diborabenzene

In 2016, Braunschweig and co-workers described the first example of an isolated neutral 6π-aromatic diborabenzene species.[165] Cycloaddition reaction of acetylene and cyclic (alkyl)(amino)carbene (CAAC)-stabilized boracumulene **144** resulted in the product **145** which proved to be diamagnetic and presented a single ^{11}B NMR resonance at 24.8 ppm (**Scheme 66**). X-ray diffraction analysis of **145** revealed a perfectly planar B_2C_4 ring is supported by two boron-coordinated CAAC ligands.
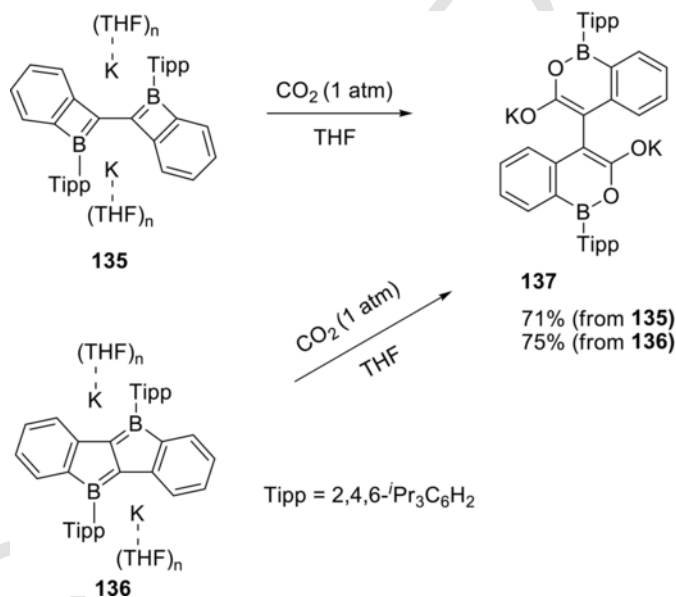
Scheme 63

Scheme 64

Scheme 65

Dipp = 2,6-diisopropylphenyl
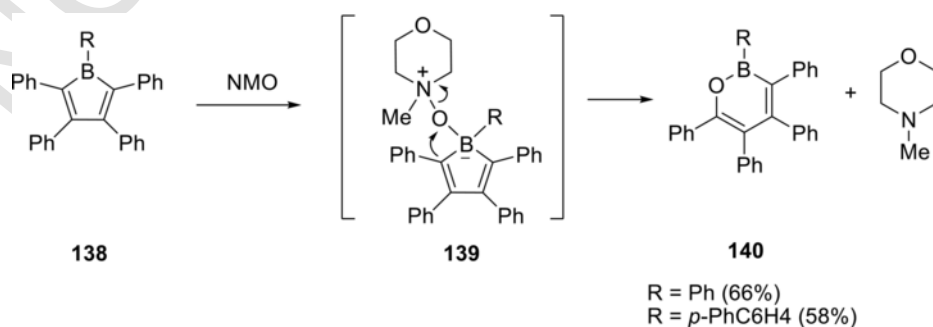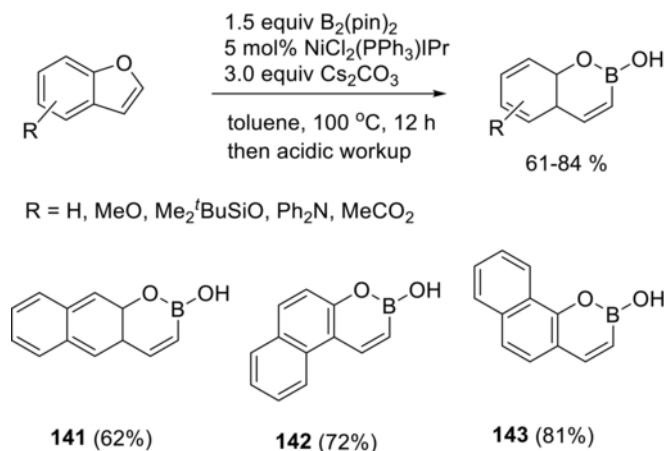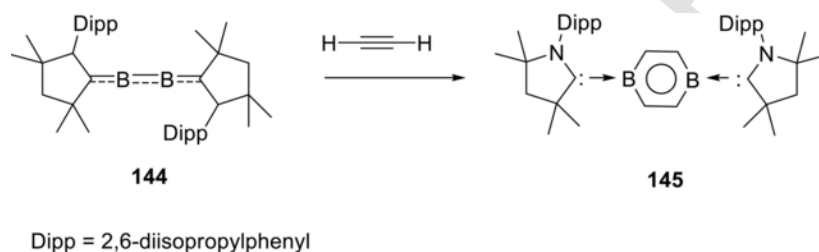
Scheme 66

11.2   9,10-Dihydro-9,10-diboraanthracenes

According to NICS(0)/NICS(1) calculations 9,10-dihydro-9,10-diboraanthracenes (DBAs) contain Hückel-anti-aromatic central B_2C_4 rings; upon two-electron reduction, they are transformed into the Hückel-aromatic dianions $(DBA)^{2-}$.[51] Interest in these boracycles stems from the peculiar structure and possible applications ranging from catalysis to materials science.[166] In particular, DBAs act as strong electron acceptors which offer new opportunities for the reductive activation of H_2 and terminal alkynes. Due to the fact that properly modified DBAs show strong photoluminescence, they are also being investigated as candidate materials for organic light-emitting devices (OLEDs).[49] Moreover, unsymmetrically substituted 9,10-dihydro-9,10-diboraanthracenes were shown to be versatile building blocks for the preparation of boron-doped π-conjugated systems via the hydroboration of arylalkynes.[167]

Synthesis of 9,10-dihydro-9,10-diboraanthracene derivatives has been studied by several groups of workers and a number of different preparative routes are available.[3] A novel synthetic method which has recently been developed for the preparation of unsymmetrically substituted DBAs is shown in **Scheme 67**.[168]

9,10-Dibromo-9,10-diboraanthracene **146** represents one of the best suited building blocks for constructing boron-doped polycyclic aromatic compounds.[10] The most practical way to synthesize this compound involves cyclocondensation of 1,2-$(Me_3Si)_2$-benzene with BBr_3 at an elevated temperature of 120 °C. A similar approach has been used for the preparation of 6,13-dibromo-6,13-diborapentacene **147**.[169] Nucleophilic substitution of these bromoboranes by organomagnesium or organolithium reagents has proved to be a useful route to the corresponding B,B'-diorganyl substituted derivatives.[51,170,171] Note that B,B'-bis(1,8-dichloro-9-anthryl-substituted DBA **148** represents a special class of a pentacoordinate boron-containing π-electron system. In this skeleton, with aid of the orthogonal arrangement of the anthryl substituent, the B and Cl atoms can form a three-carbon four electron (3c-4e) Cl—B—Cl bond. The antibonding interaction in the Cl—B—Cl bond significantly elevates the p-π* MO localized on the DBA skeleton and thereby perturbs the photophysical properties (**Fig. 15**).[172]

Wagner's group has recently introduced DBA **149** as novel ditopic hydroboration reagent.[173,174] The latter possesses a B—H—B bridged polymeric structure and can be used as a building block for luminescent conjugated polymers. Thus, hydroboration polymerization of **149** with 1,4-diethynyl-2,5-bis(hexyloxy)benzene affords boron-doped π-conjugated system **150** showing an intense photoluminescence (**Scheme 68**).

Dilithio 9,10-diboraanthracene **152** was obtained from the reaction of 9,10-dihydro-9,10-diboraanthracene and its SMe_2 adduct with excess lithium ion THF. An X-ray crystal structure of this compound revealed monomeric inverse sandwich complexes, each of them

Scheme 67

146   **147**   **148**

Fig. 15

146   **149**

150

R = C$_6$H$_{13}$O
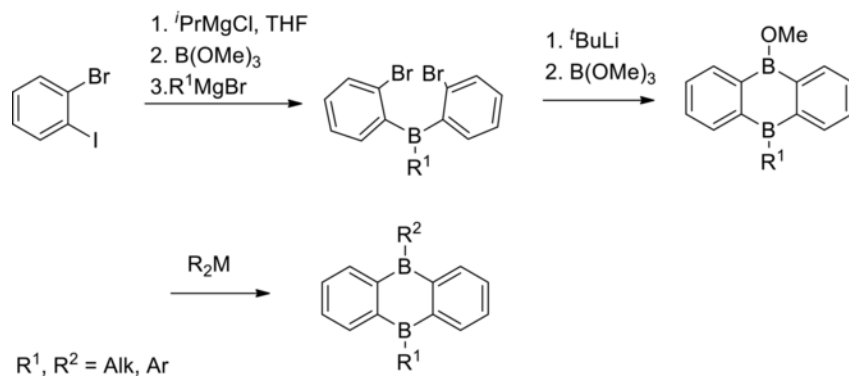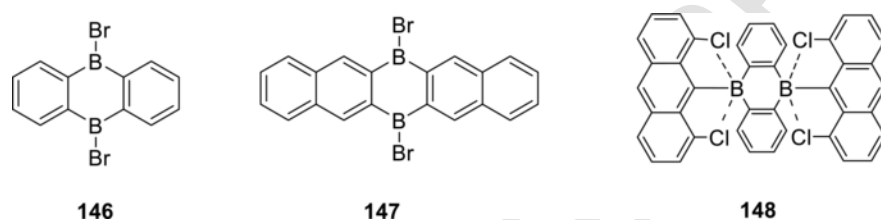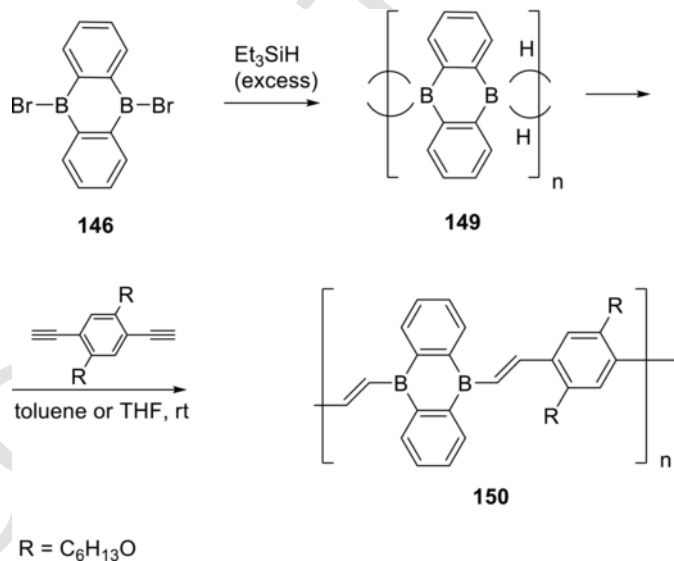
Scheme 68

containing two Li(thf)$_2$ moieties coordinated to both sides of the central B$_2$C$_4$ ring. This compound reacts with 4,4′-dimethylbenzophenone as a B＝C^{Ar}—C^{Ar}＝B diene and undergoes a [4 + 2] cycloaddition reaction with formation of a bicyclic product **153**. In contrast, *tert*-butylacetylene reacts with **152** under formal 1,4-addition of its methinic C—H group to give **154** and **155** (**Scheme 69**).[175]

In another interesting reaction, alkali metal salts (M = Li, Na) of doubly reduced 9,10-dimethyl-9,10-diboraanthracene **156** add CO$_2$ to furnish formal [4 + 2]-cycloadducts **158**. In the presence of excess CO$_2$ the reactions do not stop at the stage of [4 + 2]-cycloadducts but proceed further to furnish CO and [CO$_3$]$^{2-}$. With M = Li, Li$_2$CO$_3$ precipitates and the neutral **157** is liberated such that it can be reduced again to establish a catalytic cycle (**Scheme 70**).[176]
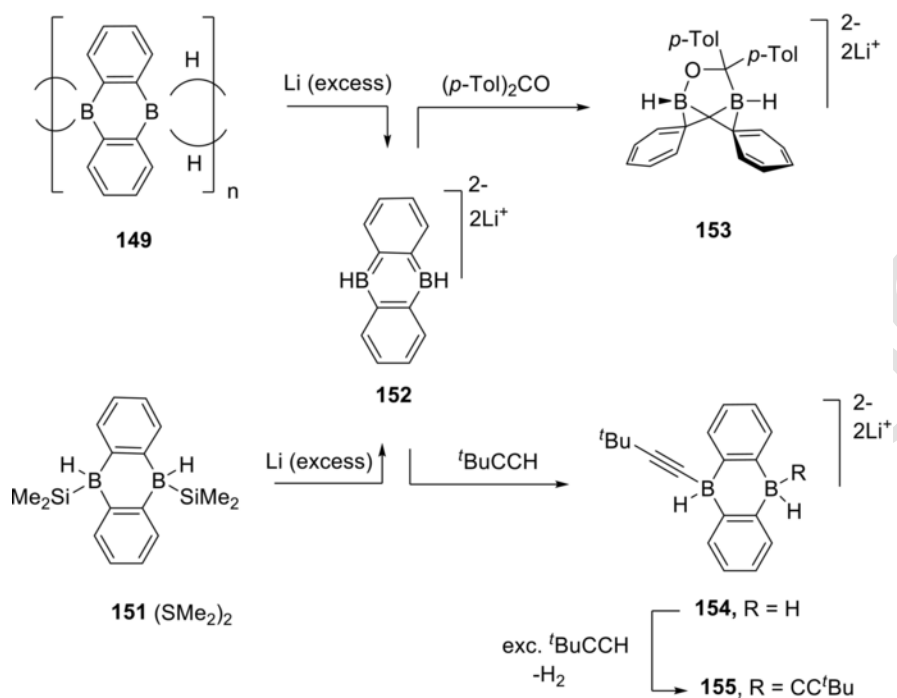
Scheme 69
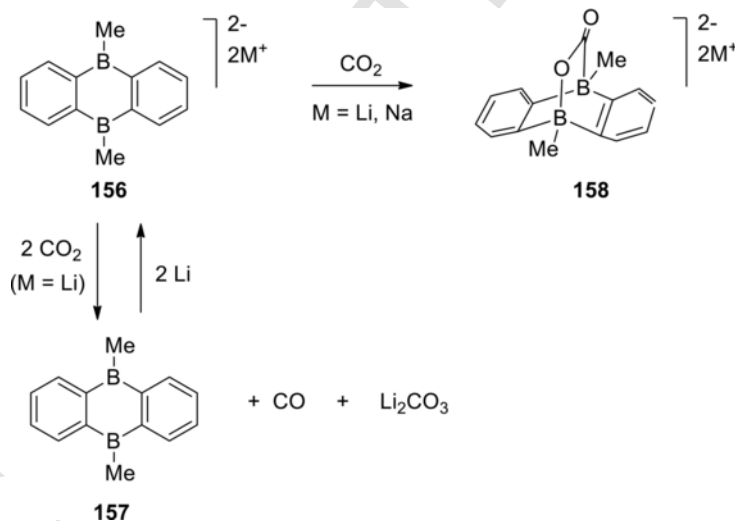
Scheme 70

11.3   Aromatic heterocycles based on the $B_2C_2N_2$ skeleton

In 2015, the Kinjo group developed a novel aromatic six-membered BN-heterocycle, namely 1,3,2,5-diazadiborine. The key steps of the synthesis are the condensation of borates **159** with $PhBCl_2$ followed by reduction of compound **160** with six equivalents of KC_8 (**Scheme 71**). 1,3,2,5-Diazaborine **45** was fully characterized by standard spectroscopic methods and X-ray diffraction analysis. The compound is thermally stable, but readily reacts with various substrates such as phenylacetylene, ethylene, styrene derivatives, CO_2 and MeOTf.[177]

1,4,2,5-Diazadiborine **162** was prepared by reduction of compound **161** with excess KC_8 in benzene (**Scheme 72**). In ^{11}B NMR spectrum of **162** a singlet appears at $\delta = 18.3$ ppm indicating that two boron atoms are magnetically equivalent. X-Ray diffraction analysis confirmed the coplanar $B_2C_2N_2$ ring. DFT calculations performed on **162** revealed the HOMO is mainly a π-orbital over the six-
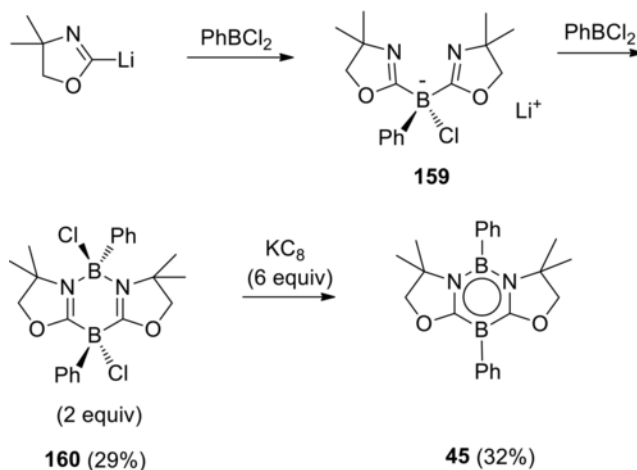
Scheme 71
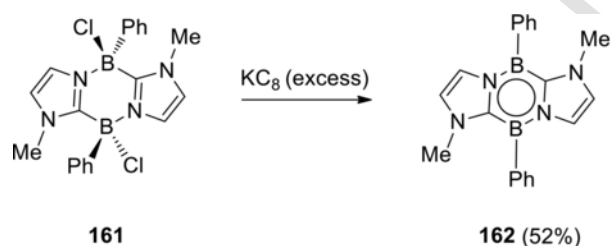
Scheme 72

membered $B_2C_2N_2$ ring, and the NICS values are comparable to those of benzene. 1,4,2,5-Diazadiborine **162** undergoes [4 + 2]-cycloaddition reactions with non-activated unsaturated bonds such as C=C, C=O, C≡C, and C≡N bonds.[178]

12   Important compounds and applications

Six-membered boracycles with two or more heteroatoms are of great importance due to their various roles such as reagents and carbon-boron synthons in organic synthesis,[5] building blocks,[7] functional materials,[6] and biorelated agents[5,61,79]. From a viewpoint of preparative use, most of the work in the decade 2008–18 has centered on the application of boron-containing heterocyclic π-conjugated molecules as new aromatic structures that are uniquely polarized, allowing access to complex molecular architectures not available to their all-carbon analogues. Examples are Diels-Alder cycloaddition[62] and photoisomerization[53] of BN-heteroaromatics that open the way to heteroatom-substituted cyclohexane and cyclobutane derivatives. The azaborine unit has also recently been used in the synthesis of new ligands for transition-metal-based catalysis.[179,180] A particular utility of 1,3-dioxa-5-aza-2,4,6-triborinate featuring a B_3NO_2 heterocycle in dehydrative amidation of carboxylic acids and in catalytic oligopeptide synthesis was described.[181,182]. Significant advances have been made in the field of Hückel antiaromatic 9,1- dihydro-9,10-diboraanthracenes. These compounds have been introduced as a novel ditopic building block for the hydroboration polymerization of aromatic dialkynes.[167,173–175,183,184] Moreover, the bisborane Lewis acids such as 9,10-dihydro-9,10-diboraanthracenes were shown to be efficient catalysts for inverse electron-demand Diels-Alder reactions (IEDDA).[185–188]

Saturated polyheteroatom six-membered boracycles are efficient reagents for synthesizing organoboron derivatives through selective C—C bond-forming reactions.[189–191] Thus, methods using bis(pinacolato)diboron (B_2Pin_2) and unsymmetrical diboron reagent PinB-BDan (Pin: pinacolato; Dan: naphthalene-1,8-diaminato) have been widely used for the diboration of alkenes and alkynes with excellent selectivity and broad functional group tolerance.[91] Japan chemists have demonstrated a new Ugi-type reaction of secondary amines using a six-membered aminoborane as an iminium generator under nonacidic conditions.[192]

Applications of BN-polycyclic aromatic hydrocarbons (PAHs) in the context of material chemistry have been reviewed.[10,11,193,194] Their rich optoelectronic properties may have potential applications in electric devices such as organic light-emitting diodes (OLEDs),[36,112,125,127,195] organic field effect transistors (OFETs),[196,197] and organic solar cells[198].

In 2011, Nakamura's group demonstrated that BN isosteres of polycyclic aromatic hydrocarbons (PAHs) have favorable charge transport properties.[36] Time-resolved microwave conductivity measurements prove that the intrinsic hole mobility of BN-fused PAH **163**

is comparable to that of rubrene, one of the most commonly used organic semiconductors. Following this, Pei and co-workers synthesized BN-isosteres **164** and reported a hole mobility of up to $0.15 \, cm^2 V^{-1} s^{-1}$ for organic field effect transistor (OFET) devices based on those compounds.[196,197] In 2014, the same group prepared BN-coronene derivative **165** and fabricated OFET devices which exhibit a hole mobility of up to $0.23 \, cm^2 V^{-1} s^{-1}$ (**Fig. 16**).[11,194]

The concept of using the empty *p*-orbital of boron to gain electron affinity has been applied to macromolecular systems. Especially, some of the π-conjugated boracycles can serve as "boron-doped" organic materials that utilize the vacant *p*-orbital of boron for dramatic electronic alteration. Thus, π-conjugated dendrons and dendrimers based on dibenzoazaborines exhibited strong light absorption and photoluminescence.[116] Several electron-deficient polymers containing the 9,10-diboraanthracene fragment have been synthesized and characterized.[183] Examples of free radical polymerization of functionalized 1,2-azaborines were also reported.[5,199–201] A BN aromatic ring strategy for preparation of poly(vinyl alcohol) derivatives via organoborane oxidation has recently been developed.[202]

Six-membered CBN heterocycles have received considerable attention as potential hydrogen storage materials owing to favorable kinetics of H_2 release.[203] Moreover, the Lewis acidity of three-coordinate borone-containing heterocycles has prompted chemists to investigate the optical sensing of anions such as fluoride and cyanide ions.[204–206]

BN/C = C isosterism has attracted the particular attention of medicinal chemists because it can be explored as a strategy for expanding the scope of core scaffold in bioactive molecules and may enhance the potency of biologically active compounds leading to new therapeutics.[104,207–210] Powerful examples of such applications are the synthesis of isosteres of biologically active carbonaceous biphenyl carboxamides **166–168** which were prepared from BN isostere of non-steroidal anti-inflammatory drug felbinac (**Fig. 17**). The isosteres displayed biological activities comparable to their carbonaceous analogues but exhibit better aqueous solubilities and in vivo oral availabilities.[207]

163 (n = 0, 1)   **164**   **165**

Fig. 16

Felbinac BN-isostere

166
Dopamine D3 receptor antagonist

167
PPAR γ antagonist
PPAR δ antagonist

168
CDK2 inhibitor

Fig. 17

169

HNE inhibitor

170

Antibacterial agent

171

Phosphodiesterase inhibitor (PDE10A)

172

β-Blocker
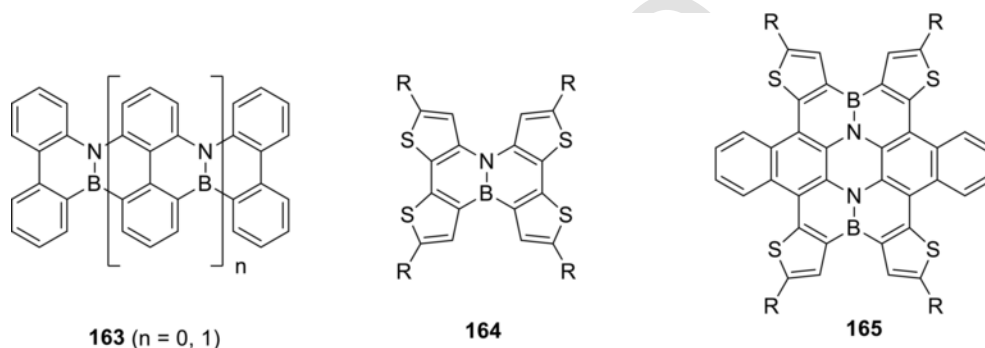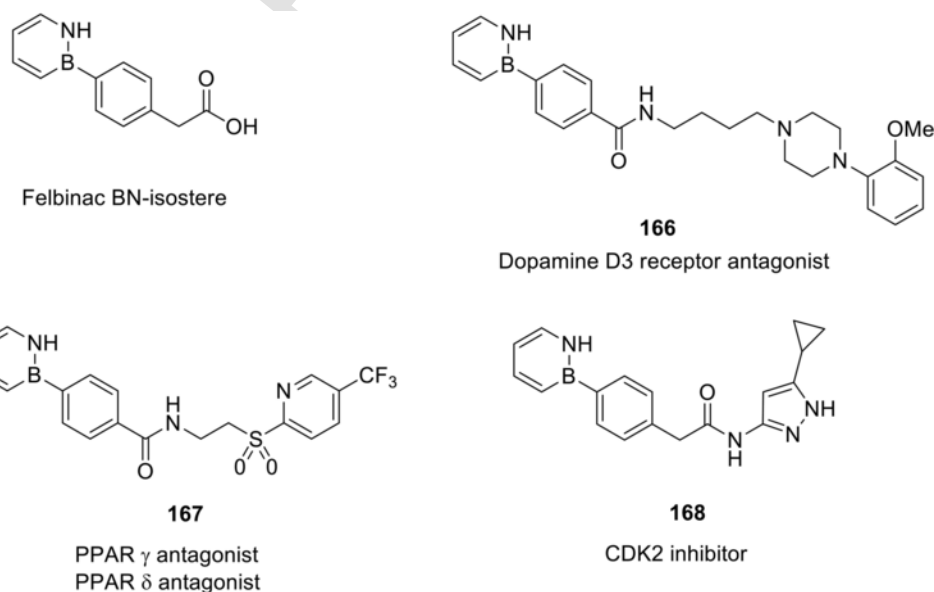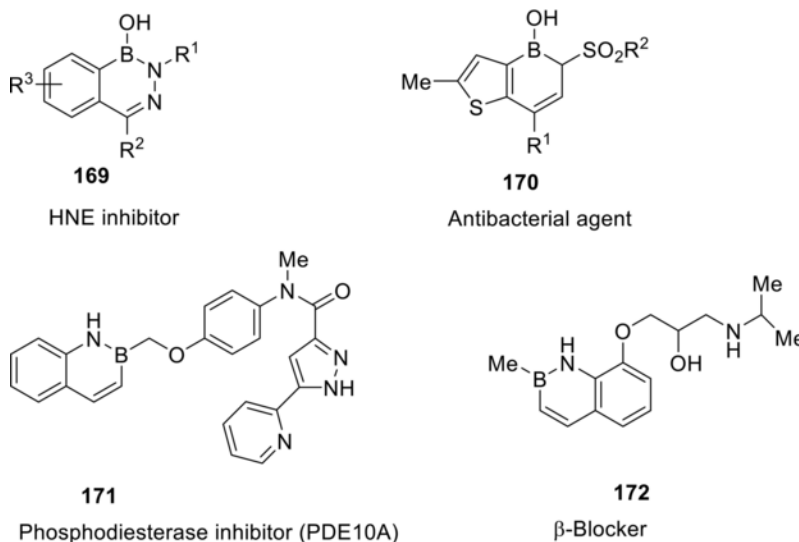
Fig. 18

The potential of aromatic boracycles as bioisosteric replacements of benzene and naphthalene in drug discovery programs can be illustrated by azaborine derivatives. Thus, recently diazaborines **169** are presented as serine protease inhibitors. These compounds reversibly inhibit human neutrophil elastase (HNE) serine protease with IC50 values in the low μM range.[136] The thieno-diazaborine **170** are the potent inhibitors of *Escherichia coli* enoyl-ACP reductase.[211,212] The borazaronaphthalene **171** was identified as an efficient inhibitor of the phosphodiesterase enzyme PDE10A.[210] Finally, a propranolol analogue **172** containing the 2,1-borazaronaphthalene fragment has shown potency as a β-blocker with a high bioactivity and low toxicity (**Fig. 18**).[213]

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