Studies on the New Synthetic Approaches to Lewis Acidity-Diminished Organoboron Compounds

（ルイス酸性抑制型有機ホウ素化合物の新規合成法開発に関する研究）

LI JIALUN

March 2024
Hiroshima University

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Contents

Chapter 1

General Introduction

1-1 Cross-Coupling

Coupling reactions are an important type of reaction in organic chemistry, in which metal catalysis leads to the formation of a new carbon–carbon bond between two chemical units, resulting in the production of a new organic molecule. One of earliest explorations in this field dates back to the 19th century when sodium-induced synthesis of aliphatic hydrocarbons was first reported by Wurtz.[1] However, palladium-catalyzed coupling reactions quickly gained prominence as the reaction conditions and mechanisms were studied in detail. Today, palladium-catalyzed coupling reactions are highly regarded for their mild reaction conditions, high productivity, and ease of handling, and have become one of the most important methods for the construction of carbon–carbon and carbon–heteroatom bonds.

These palladium-catalyzed reactions, often named after pioneers, couple electrophilic reagents (e.g., organic halides and pseudohalides, X=F, Cl, Br, I, etc.) and nucleophilic reagents (e.g., organometallic reagents, alkenes,[2] alkynes, etc.), in which Grignard's reagents,[3] organozinc reagents,[4] organostannanes[5] and organosilanes[6] are generally used as the organometallic reagents (Figure 1).

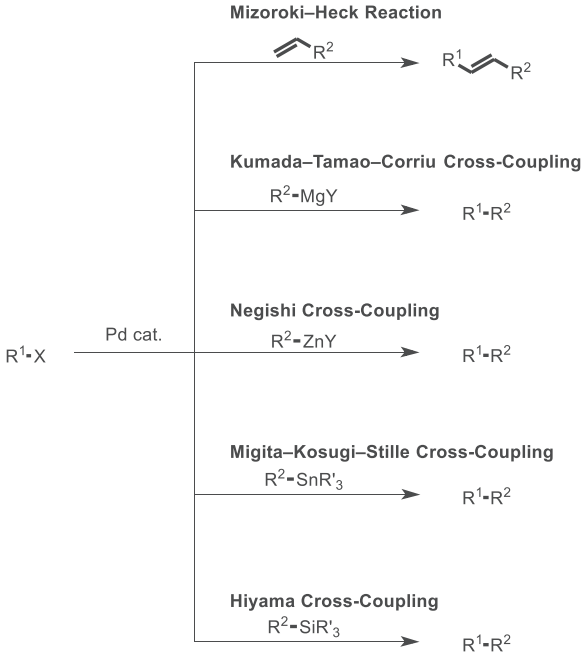


Figure 1

In addition to carbon–carbon bond-froming reactions, palladium-catalyzed carbon–heteroatom bond-forming reactions are also an important branch of organometallic chemistry, such as the Buchwald–Hartwig Cross-Coupling reaction[7] and the Larock indole synthesis reaction[8] (Figure 2).

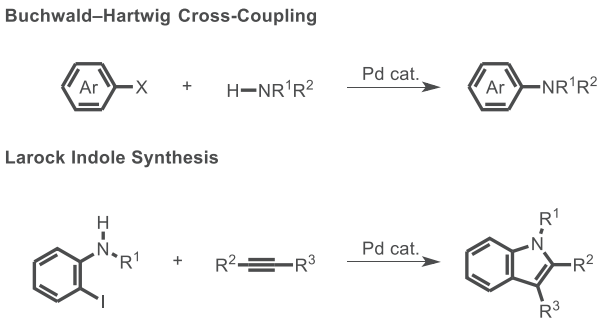


Figure 2

Among them, Suzuki–Miyaura Cross-Coupling (SMC) is the most widely used reaction (Figure 3).[9] The main advantages of SMC are that the reaction conditions are mild, and various boronic acids are readily available.[10] In addition, the handling and removal of boron-containing by-products are easy as compared to those associated with other organometallic reagents, and boronic acids are much safer for the environment. Cross-Coupling based on Grignard reagents has several disadvantages, including their high reactivity to damage some functional groups present in the starting materials, whereas the SMC process is tolerant of a wide range of functional groups. While the low functional group tolerance can be minimized through the use of organostannanes (Migita–Kosugi–Stille Coupling), the toxicity of some organostannanes and the difficulty in removing tin by-products make them a less attractive option. Other named cross-couplings are also less convenient and practical because of the limited availability of required organometallic reagents.

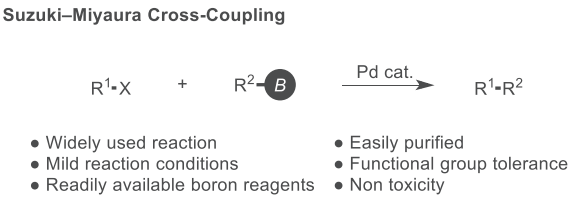


Figure 3

In this regard, SMC plays a crucial role not only in organic synthesis but also in pharmaceutical industries, being utilized for the synthesis of natural products, polymers, functional materials, liquid crystals, and pharmaceutically important molecules. Its contribution to chemical synthesis lies in providing reliable and flexible strategies for the efficient construction of complex molecules as well as in methodological innovations.

1-2 Lewis Acidity and Stability of Organoboron Compounds

Organoboronic acids [R–B(OH)$_2$][11] and diol-derived cyclic boronates such as R–B(pin) (pin = pinacolato)[12] and R–B(neop) (neop = neopentyl glycolato),[13] have consistently served as pivotal reagents in boron-based synthetic organic chemistry;[14] their boron-Lewis acidity strongly influences reactivity and stereoselectivity in various boron-based transformations (Figure 4). Furthermore, the Lewis acidity often impacts the stability of organoboron compounds employed;[15] most of the organoboron-based transformations, regardless of catalytic/non-catalytic ones, proceed through donor–acceptor interaction between Lewis basic moieties and the Lewis acidic 2p empty orbital of

the boron centers.

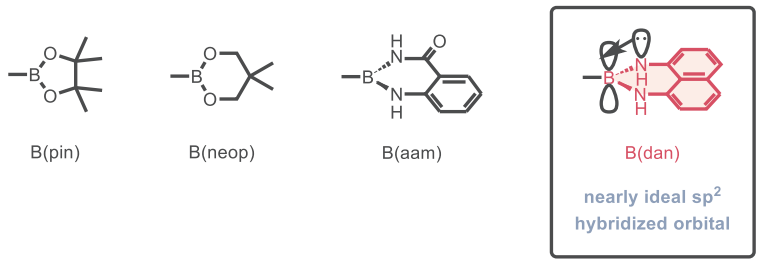


Figure 4

Therefore, diminishing the inherent Lewis acidity of organoboron compounds by introducing suitable substituents on the boron center leads to a drastic change in the properties and behavior of the corresponding organoboron compounds. In particular, anthranilamide (aam)[16] and 1,8-diaminonaphthalene (dan)[17] are representative substituents for diminishing boron Lewis acidity since these boryl groups [B(aam) and B(dan)] can form a nearly ideal B(sp^2)-hybridized orbital derived from its planar six-membered ring structure, with effective electron donation to the empty p orbital of the boron center from the adjacent nitrogen atoms.[18] The Lewis acidity-diminishment with the B(dan) moieties was demonstrated to significantly improve air- and/or water-resistant properties of some organoboron compounds, being quite unstable in their Lewis acidic B(pin)-forms. For example, 2-pyridyl–B(dan) becomes significantly resistant towards protodeborylation, allowing its isolation even by column chromatography, in stark contrast to the fact that its $B(OH)_2$- and B(pin)-counterparts suffer serious decomposition under aqueous conditions (Figure 5).[19]

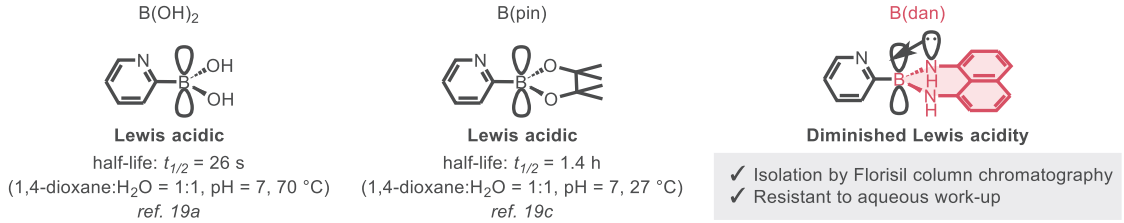


Figure 5

On the other hand, Yoshida and coworkers have recently demonstrated the Lewis acidity of boronamides and boronates can uniformly be assessed by computed ammonia affinity (AA).[20] As illustrated in Figure 6, the calculated Lewis acidity hierarchy [B(aromatic diol) > B(aliphatic diol) > B(mdan) ≈ B(aam) > B(dan)] aligned well with experimental findings. Hence, various B(dan) compounds that show the least calculated AA values are generally much more stable in comparison to other boronamide- and boronate-counterparts.

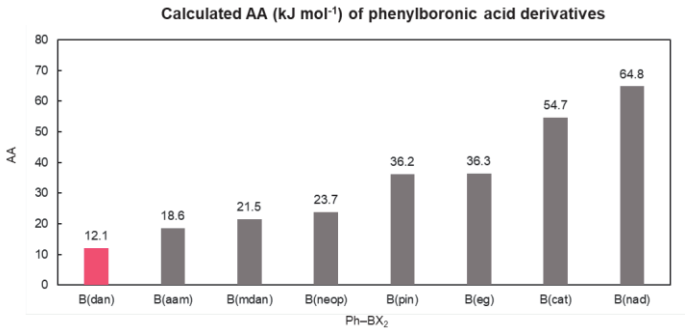


Figure 6

1-3 Borylation Reactions for Synthesizing R–B(dan)

The strongly diminished B(dan)-Lewis acidity provides a significantly robust nature to dan-substituted organoboron compounds [R–B(dan)]. The typical synthetic application therewith is the boron-masking strategy in SMC developed by Suginome in 2007, where the carbon–B(dan) bonds remain completely intact even under strongly basic aqueous conditions (Figure 7).[21]

On the other hand, Yoshida and Saito first demonstrated that a variety of R(sp^2)–B(dan) (R = aryl, alkenyl) can be efficaciously activated by *t*-BuOK or $Ba(OH)_2$, leading to direct SMC without in situ deprotection of the dan moiety (Figure 8).[22] In addition, Tsuchimoto found that the R(sp)–B(dan) bond of alkynyl–B(dan) can be directly used for SMC with aryl(alkenyl) halides and allylic carbonates as electrophiles.[23]

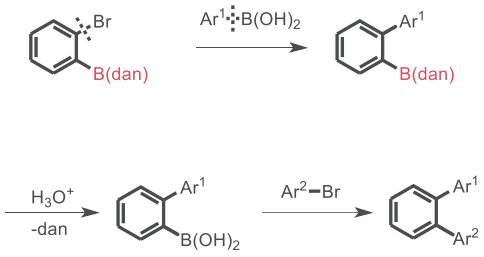


Figure 7

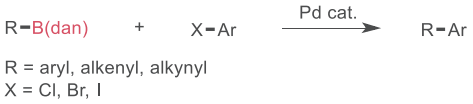


Figure 8

As depicted in Figure 9, the number of papers related to B(dan) has steadily increased over the past decade, indicating a growing acknowledgment of the synthetic utility of R–B(dan). The following describes several typical synthetic routes for accessing R–B(dan).

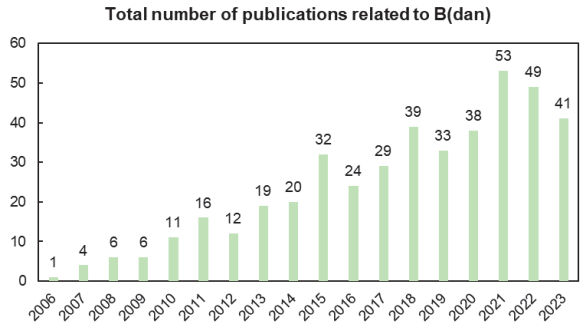


Figure 9

1-3-1 Conventional synthesis: dehydration condensation

Ar–B(dan) were conventionally synthesized through dehydration condensation of Ar–$B(OH)_2$ with 1,8-diaminonaphthalene ($danH_2$).[21a] Although a variety of Ar–B(dan) compounds are available by this route, the structural diversity is totally dependent on those of starting Ar–$B(OH)_2$, and thus relatively unstable, protodeborylation-prone Ar–$B(OH)_2$ cannot be used for this method (Figure 10).

Figure 10

1-3-2 Catalytic B(dan)-installing reactions with C=C or C≡C bonds

In 2014, Yoshida first demonstrated that chemoselective σ-bond metathesis between (pin)B–B(dan) and a copper catalyst occurs to give a dan-substituted borylcopper species, which serving as a pivotal catalytic intermediate for the three-component hydroboration of alkynes (Figure 11).[24] The copper-catalyzed hydroboration of internal alkynes exhibited regio- and stereoselective outcomes. Specifically, alkyl(aryl)alkynes experienced the B(dan)-addition at the geminal position to the alkyl group with $(Ph_3P)_3CuCl$ catalyst, while the use of (SIPr)CuCl catalyst resulted in inverse regioselectivity.

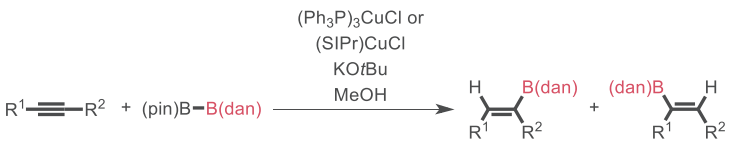


Figure 11

The catalytic cycle is initiated by the exclusive formation of a dan-substituted borylcopper species, Cu–B(dan), which could be logically explained by the selective interaction between the Lewis acidic B(pin) moiety of (pin)B–B(dan) and the alkoxy moiety of Cu–OR during the σ-bond metathesis step (Figure 12). Subsequent alkyne insertion into the Cu–B(dan) bond (borylcupration) generated a borylalkenylcopper species, which, upon protonation with MeOH, yielded the hydroboration product while regenerating Cu–OR. The regioselectivity in the borylcupration step was governed by the orientation of Cu–B(dan), and the strategic selection of ligands, along with the diminished boron-Lewis acidity, played a crucial role in achieving Markovnikov selectivity or the opposite: the

steric repulsion between a sterically demanding alkyne substituent and the bulkier copper moiety [(SIPr)CuCl] directed the introduction of the B(dan) moiety into a less sterically hindered position of the alkyne (Figure 13). Conversely, the less sterically hindered copper moiety in $(Ph_3P)_nCu$–B(dan) favored addition to the α position of the aryl group, guided by the electronic directing effect of the aryl group in alkyl(aryl)alkynes.

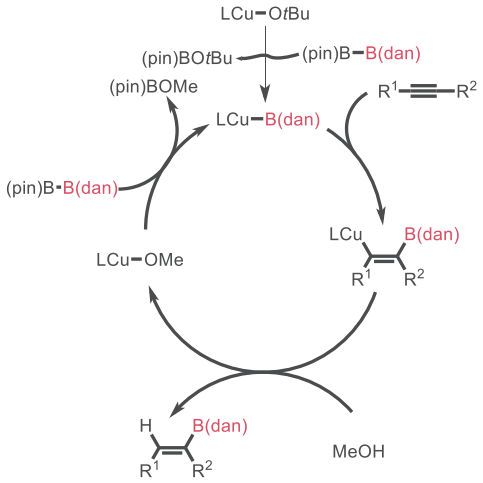


Figure 12

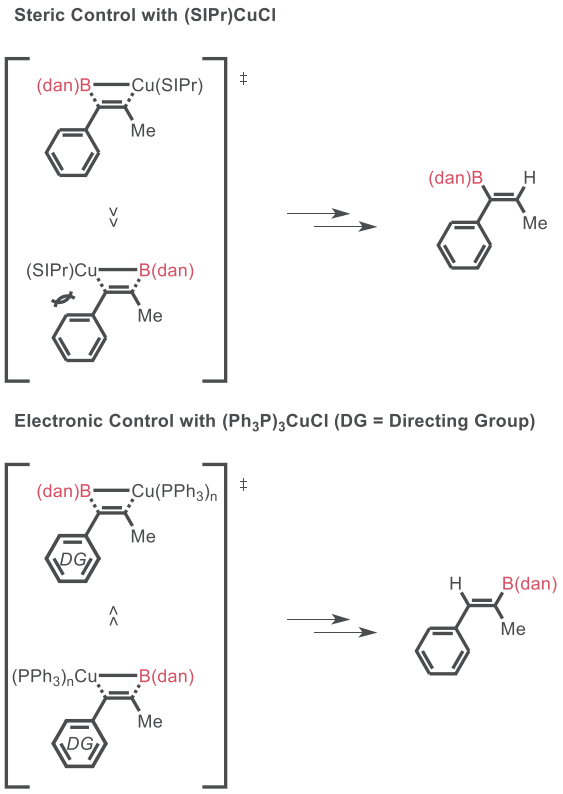


Figure 13

The use of other electrophiles including alkyl, benzyl, stannyl and amino group, allowed the copper-catalyzed B(dan)-installing carboboration[25], borylstannylation[26] and aminoboration[27] of C=C or C≡C bonds to proceed regio- and stereoselectively, giving the corresponding multi-

substituted alkyl– and alkenyl–B(dan) compounds (Figure 14).

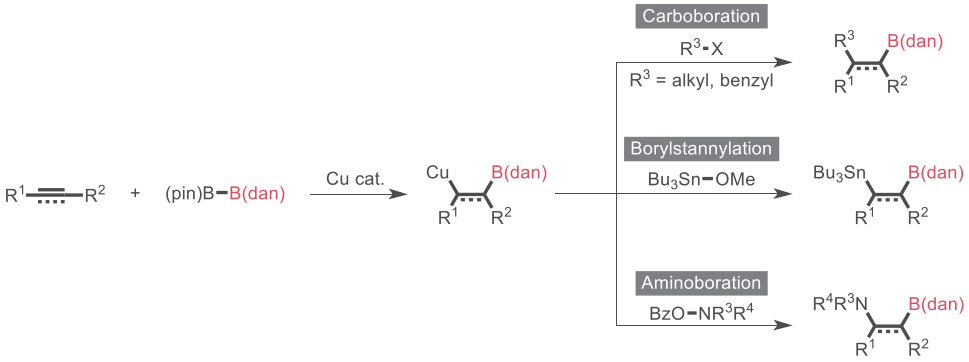


Figure 14

1-3-3 Catalytic B(dan)-installing reactions with organic halides

Li reported that (pin)B–B(dan) was coupled with carbon(aryl)–halogen bonds through the palladium-catalyzed Miyaura–Ishiyama-type borylation in 2015 (Figure 15).[28] The reaction showcased the exclusive transfer of the B(dan) moiety leading to the efficient synthesis of diverse aryl–B(dan) compounds in high yields.

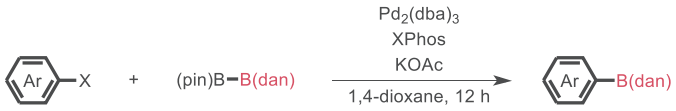


Figure 15

Yoshida found that various alkyl, alkenyl, aryl and heteroaryl halides were successfully coupled with (pin)B–B(dan) via copper-catalyzed borylative substitution, and the corresponding R–B(dan) were obtained in high yields (Figure 16).[29] The proposed catalytic cycle involves a one-electron transfer process: an electron-rich borylcuprate, generated by coordination of KO*t*Bu to a dan-substituted boryl copper species, should act as a one-electron reductant to organic halides (Figure 17). Subsequent elimination of X^- from the resulting radical anion species generates a radical, which is then combined with [*t*BuO–Cu(II)–B(dan)] to give a Cu(III) complex. Finally, R–B(dan) is generated from the Cu(III) complex through reductive elimination with regenerating a Cu–O*t*Bu complex.

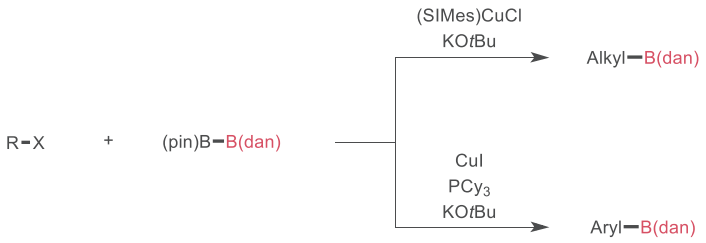


Figure 16

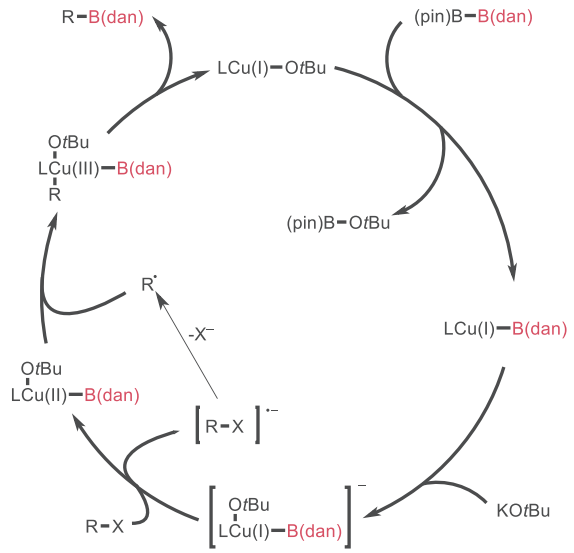


Figure 17

1-3-4 Catalytic B(dan)-installing reactions with C–H bonds

Efficiently facilitated by a DPPE-coordinated iridium catalyst, the dehydrogenative direct C(aryl)–H borylation of arenes using H–B(dan) resulted in the generation of various Ar–B(dan). In parallel with the typical Hartwig–Miyaura borylation,[30] the regioselective installation of the B(dan) moiety occurred at a less sterically hindered position (Figure 18).[31]

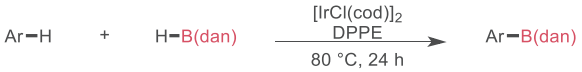


Figure 18

1-4 Application of Organic Materials Containing B(dan) Moiety

Nanographene shows fundamental importance in materials chemistry due to its unique electronic properties and supramolecular behavior, which become a promising option to be applied into organic field-effect transistors (OFETs), organic photovoltaics (OPVs), and organic light-emitting diodes (OLEDs).[32] Tuning the optical, electronic, and magnetic properties of nanographene through the introduction of heteroatoms has emerged as a versatile strategy.[33] The selection of heteroatom type, doping position, and doping concentration significantly influences the electronic energy band structure and charge carrier concentration in heteroatom-doped nanographene. While common dopants like nitrogen, oxygen, and sulfur have been extensively explored within the graphene carbon framework, boron introduces a unique dimension, characterized by its electron-deficient nature and Lewis acidic properties, providing diverse functionalities for nanographene.[34]

The replacement of C=C units with the isoelectronic polar B−N bonds in heteronanographene enables the resulting compound with similar geometric structures to have completely different electronic characteristic (Figure 19). In 2016, Feng reported a class of dibenzo-fused 1,9-diaza-9a-boraphenalenes NBN-DBP, in which the N–B–N subunit is decorated at the zigzag edge (Figure 20).[35] In 2018, a heptagonal ring embedded NBN-6 *via* oxidative coupling was reported by Wang's group.[36] In 2019, Feng reported pentagonal ring-fused NBN-doped nanographene NBN-penta

which possesses a planar structure.[37] In 2020, Zhang synthesized a new NBN-doped double [5]helicene Ph-NBNDH *via* highly regioselective intramolecular Scholl reactions.[38] Although NBN-doped nanographene has the expected optoelectronic performance, the synthesis of these compounds remains challenging mostly due to the limited synthetic methodology.

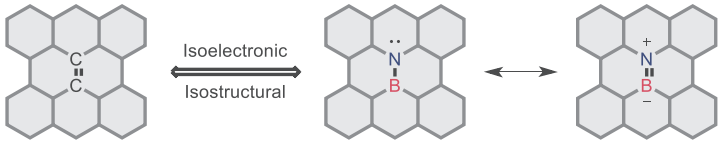
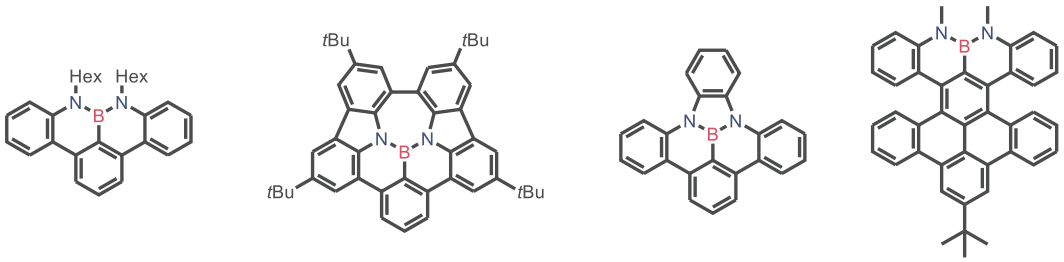


Figure 19



NBN-DBP 2016 | NBN-6 2018 | NBN-penta 2019 | Ph-NBNDH 2020

Figure 20

The unique characteristic of naphthalene-1,8-diaminato substituted B(dan), which readily takes planar structure, can be regarded as a partial structure of boron-doped nanographene containing an N–B–N bond. In 2018, Bao disclosed that B(dan)-doped aromatic species exhibited AIE behavior,[39] which have proven to be excellent in sensing TNT due to interaction between electron-rich Ar–B(dan) and electron-deficient TNT leading to a charge-transfer luminescence quenching effect.[40] Remarkably, Ph–B(dan) proved effective for sensing TNT at the ppb level. Upon the addition of TNT to a solution of Ph–B(dan) (0.05 mg/L) in an H_2O/MeOH solution, there was a noticeable decrease in luminescent intensity (Figure 21A and B). The luminescence of the Ph–B(dan) solution disappeared entirely with the addition of 70 ppb of TNT (Figure 21C). Additionally, the detection of TNT can be achieved using test paper under daylight conditions (Figure 21D).

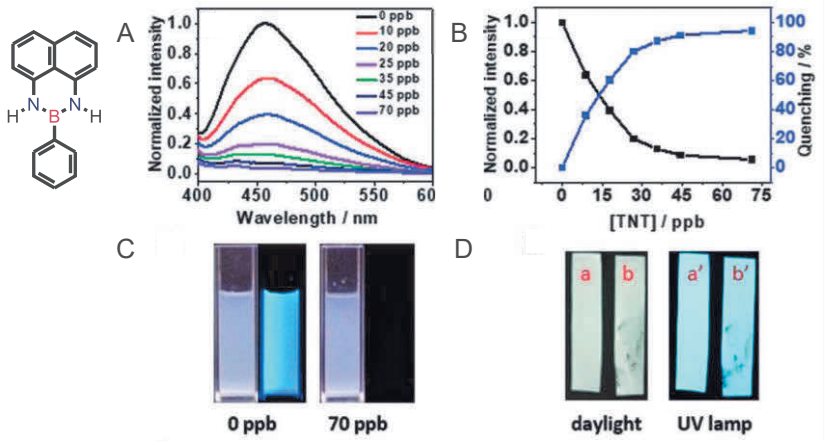


Figure 21

In 2021, Zhao demonstrated the synthesis of ring-fused B(dan)-doped phenalenes using a palladium-catalyzed cyclization/bicyclization strategy (Figure 22).[41] This innovative approach allowed for the modular assembly of structurally diverse B(dan)-doped phenalenes, marking the first instance of their construction *via* a palladium-catalyzed Larock-type cyclization, notably, the utilization of transition-metal catalysis for the direct construction of B(dan)-doped π-systems was unprecedented before. Subsequent investigations revealed that the incorporation of B(dan) moiety exerted significant influence on the geometry and optoelectronic properties of these fused π systems. Particularly noteworthy was the photo-induced structural planarization (PISP) character observed in B(dan)-doped phenalenes. These compounds exhibited both AIE and aggregation-induced excimer emission (AIEE) activities. Furthermore, this expanded B(dan) species demonstrated efficacy in the detection of TNT, boasting a remarkably low detection limit of 230 ppb.

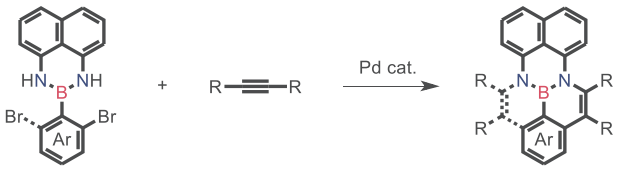


Figure 22

Building upon the previous approach, Huang utilized 2-bromophenylboronic acid and readily available phenylnaphthalene diazaboroles with halogen groups in neighboring positions as starting materials, through a palladium-catalyzed cyclization reaction invovling carbon–carbon and carbon–nitrogen bond-forming reactions, obtaining a series of novel B(dan)-doped naphthalenes (Figure 23).[42] Distinguishing from the Larock reaction involving internal alkynes, the cyclization module introducing bromophenylboronic acids presented distinct challenges: The reaction pathways and reactivity of potential intermediates differed significantly; uncertainties arose in the second oxidative addition of palladium catalyst to the C–Br bond. Significantly, these B(dan)-doped naphthalenes demonstrated a narrower HOMO-LUMO gap and reduced energy uptake compared to the hydrocarbon analogue, and the luminescent properties of the backbone could be effectively modulated by multiple substituents. The molecules within B(dan)-doped exhibited variable luminescence efficiency and high sensitivity for TNT detection, showcasing its potential for practical applications in sensing technologies.

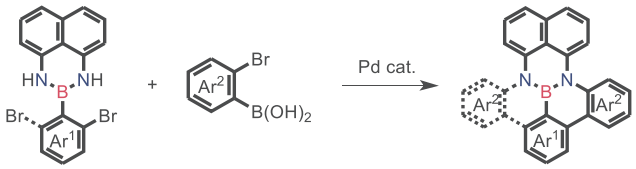


Figure 23

1-5 This thesis

The major objectives of this thesis are the development of new method of synthesizing highly stable organoboron compounds with diminished Lewis acidity, which are classified into three

chapters as follows:

In Chapter 2, the author reported that H–B(dan) could serve as a B(dan) electrophile despite its significantly diminished boron-Lewis acidity and thus readily underwent a direct reaction with nucleophilic Grignard reagents, resulting in the construction of new carbon–B(dan) bonds under transition metal-free conditions (Figure 24). The structural diversity of the resulting C(sp/sp^2/sp^3)–B(dan) compounds was enough broad because of the wide availability of the corresponding Grignard reagents. Additionally, stable 2-pyridyl–B(dan) were successfully obtained using the Turbo Grignard reagent, which could easily be purified by column chromatography. Iterative cross-coupling of the 5-bromo-2-pyridyl–B(dan), synthesized through the present method, was demonstrated to proceed chemoselectively.

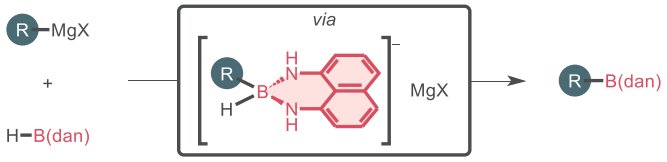


Figure 24

In Chapter 3, the author disclosed that ethynyl–B(dan) of remarkable stability acted as a versatile dipolarophile in [3+2] cycloaddition reactions, enabling the convenient and direct synthesis of a diverse array of B(dan)-containing isoxazoles and triazole with high regioselectivity (Figure 25). In addition, the successful application of Larock indole synthesis and related Pd/Cu-catalyzed heteroannulations to ethynyl–B(dan) resulted in the formation of indoles, benzofuran, and indanone bearing the B(dan) moiety. The exceptional resistance of the resulting heteroaryl–B(dan) compounds toward protodeborylation, arising from their highly diminished Lewis acidity, was rigorously confirmed by theoretical calculation-based assessments of AA. Furthermore, the synthetic utility of the heteroaryl–B(dan) compounds was showcased in direct SMC.

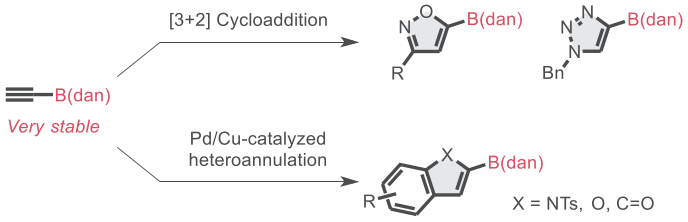


Figure 25

In Chapter 4, the author unfolded that the smooth addition of an unsymmetrical diboron, (pin)B–B(aam), took place across a carbon–carbon triple bond of various terminal alkynes under platinum catalysis, resulting in the regio- and stereoselective formation of *cis*-*vic*-diborylalkenes through B(aam)-installation at the terminal carbon (Figure 26). The use of a highly electron-deficient triarylphosphine ligand, P(BFPy)$_3$ was the key to the regiocontrol in this process, and the close correlation between the electron-deficiency in ligands and the observed regioselectivity was experimentally validated.

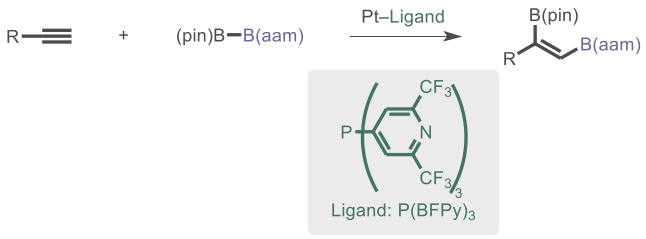


Figure 26

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Chapter 2

Transition Metal-free B(dan)-installing Reaction (dan: naphthalene-1,8-diaminato): H–B(dan) as a B(dan) Electrophile

H–B(dan) was demonstrated to serve as a B(dan) electrophile, despite its highly diminished boron-Lewis acidity, leading to direct and transition metal-free approach to R–B(dan) of high synthetic utility upon treatment with Grignard reagents. Iterative cross-coupling of 5-bromo-2-pyridyl–B(dan), synthesized by the present method, was also achieved.

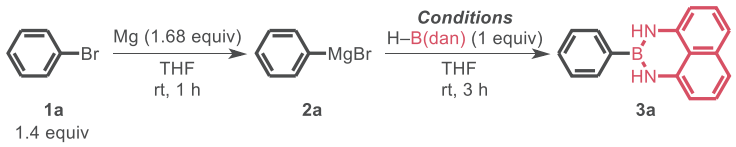
2-1 Introduction

Lewis acidity of organoboron compounds having a naphthalene-1,8-diaminato substituent on the boron center, R–B(dan), is highly diminished, owing to the effective electron-donation from the adjacent nitrogen atoms and the nearly ideal B(sp^2)-hybridized orbital arising from the planar six-membered ring structure.[1] This feature is well illustrated by boron-masking strategy in iterative Suzuki–Miyaura coupling (SMC) with Ar–B(dan), where they become inert toward transmetalation even with commonly used bases such as NaOH, K_3PO_4 and CsF.[2] Saito's and Yoshida's groups have independently reported, on the other hand, that the "protected" B(dan) moiety can be readily activated by *t*-BuOK to generate the respective borate species, which serves as a key intermediate in the actual direct SMC with Ar–B(dan).[3,4] In view of the synthetic significance derived from their base-dependent inactive/active modifiable character toward SMC, the development of a convenient and direct method of accessing Ar–B(dan) would be an important subject in synthetic organic chemistry. Previously, they have been synthesized by dehydrative condensation of Ar–$B(OH)_2$ with 1,8-diaminonaphthalene ($danH_2$),[2a,5] and by Cu[6]- or Pd[7]-catalyzed Miyaura–Ishiyama-type coupling of aryl halides with (pin)B–B(dan)[8]; the use of H–B(dan) as a B(dan)-installing reagent in Ir-catalyzed dehydrogenative coupling with Ar–H is another option for preparing them.[9] Based on the results that the B(dan) moiety can smoothly accept nucleophilic attack by *t*-BuOK, despite the diminished Lewis acidity, the author envisaged that a B(dan) reagent having a suitable leaving group should react with carbon nucleophiles, leading to transition metal-free B(dan)-installing reaction into organic frameworks.[10,11] Herein the author reports that H–B(dan) serves as a convenient B(dan) electrophile[12,13] in the reaction with various aryl Grignard reagents, which provides a direct way of synthesizing diverse Ar–B(dan) derivatives. Other Grignard reagents with alkyl, allyl, ethynyl or vinyl groups have also proven to be efficient nucleophiles in this reaction.

2-2 Results and Discussion

The author first carried out the reaction of H–B(dan) with phenylmagnesium bromide (**2a**), generated in situ from phenyl bromide (**1a**) and magnesium, in THF at room temperature, and found that H–B(dan) served as a B(dan) electrophile for capturing **2a** to afford Ph–B(dan) (**3a**) in 93% yield (Table 1, Entry 1). Lowering (0 °C) or raising (50 °C) the reaction temperature resulted in decrease in the yield (Entries 2 and 3) and the use of diethyl ether or toluene as a solvent was not effective for the formation of **3a** (Entries 4 and 5).

Table 1 Optimization of reaction conditions[a]



Entry	Changes from Standard Conditions	Yield (%)[b]
1	none	93 (87)[c]
2	0 °C	59
3	50 °C	40
4	Ether	37
5	Toluene	0

[a] Standard conditions: **1a** (1.40 mmol), Mg (1.68 mmol), THF (2 mL), H–B(dan) (1.00 mmol), rt. [b] GC yield. [c] Isolated yield.

With the optimized reaction conditions in hand, the author next investigated the B(dan)-installing reaction with various aryl Grignard reagents (Figure 27). The substrate scope has turned out to be sufficiently broad: arylmagnesium bromides bearing an electron-donating (**3b**–**3g**) or -withdrawing substituent (**3h** and **3i**) were readily convertible into the respective Ar–B(dan) in high yields within 3 hours. In addition, halogen-substituted Ar–B(dan) (**3j**–**3l**) could be synthesized by the present reaction, being utilizable for the iterative SMC.[2] The reaction was also applicable to polycyclic- and sterically bulky arylmagnesium bromides to furnish **3m**–**3p**, and 2-thienylmagnesium bromide could be transformed into 2-thienyl–B(dan) (**3q**) in 84% yield.

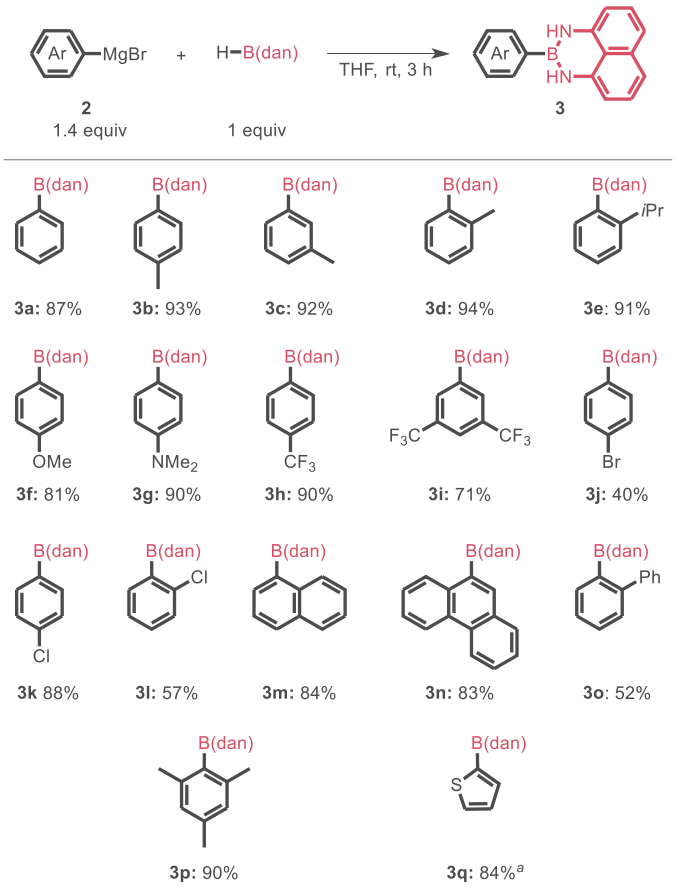


Figure 27 Substrate scope on aryl Grignard reagents

[a] 2-Thienylmagnesium bromide was prepared at reflux temperature.

The versatility of the present method was further enhanced by its application to pyridyl bromides (Figure 28). Thus, treatment of 3-pyridyl or 2-pyridyl bromides with Turbo Grignard reagent (*i*-PrMgCl•LiCl)[14] and H–B(dan) was found to provide the respective pyridyl–B(dan) (**3r**–**3w**) in good yields. It should be noted that the resulting 2-pyridyl–B(dan) are enough stable to be isolated even by silica gel column chromatography,[3,6,7] being in stark contrast to the strong propensity of their $B(OH)_2$/B(pin) counterparts to decompose by protodeborylation.[15] As compared with the existing synthesis of 2-pyridyl–B(dan) by use of (dan)B–B(pin) and a transition metal catalyst,[11] the present reaction has proven to be superior in efficacy and substrate scope; its combination with direct SMC would provide a promising option for "2-pyridyl problem".[16]

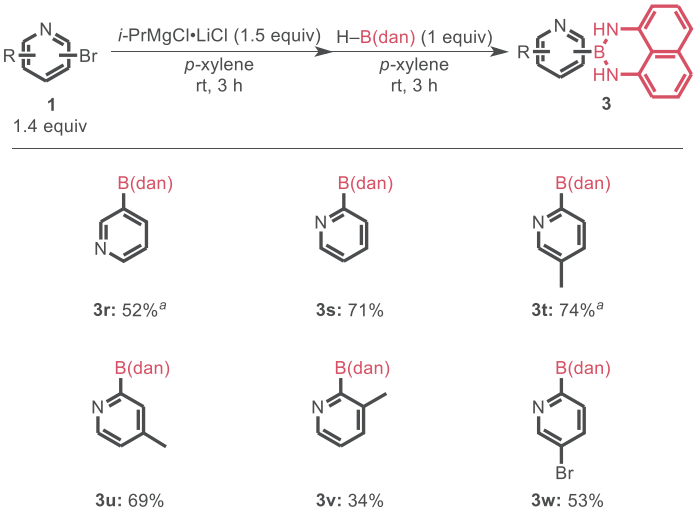


Figure 28 Synthesis of pyridyl–B(dan) with Turbo Grignard reagent

[a] Pyridyl–Br (1 equiv), Turbo Grignard reagent (1.4 equiv).

As shown in Figure 29, a variety of primary (Me, *n*-Bu, *i*-Bu, neopentyl), secondary (*i*-Pr, cyclopropyl) and tertiary (*t*-Bu) alkyl Grignard reagents could facilely be coupled with H–B(dan) to produce the corresponding alkyl–B(dan) (**4a**–**4g**) in a straightforward manner, and furthermore vinyl– (**4h**), ethynyl– (**4i**) and 3-hydroxypropyl–B(dan) (**4j**) were also readily accessible under the present reaction conditions. Moreover, allyl bromide was efficiently transformable into allyl–B(dan) (**4k**) in 95% yield by employing Barbier-type conditions, whereas the reaction of crotyl bromide (*E*:*Z* = 85:15) gave a mixture of *α*- (**4l**) and *γ*-adducts (**4'l**) in 42:58 ratio.

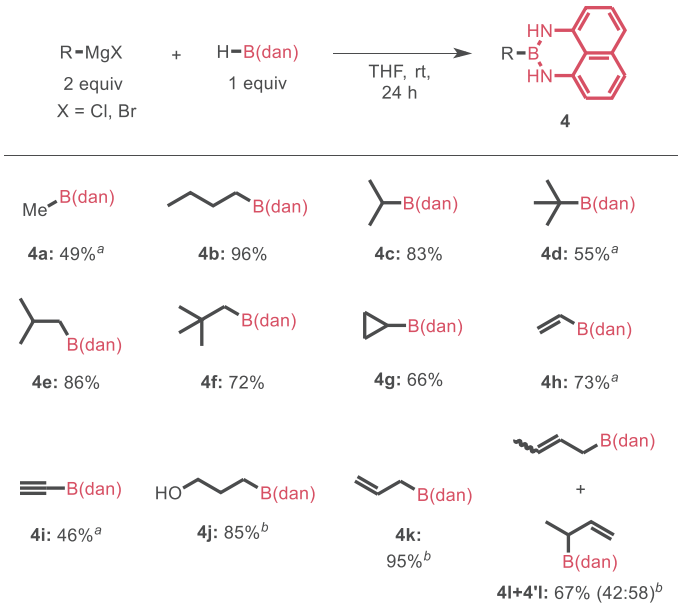


Figure 29 Substrate scope of other Grignard reagents

[a] Commercially available Grignard reagents were used. [b] The reaction was conducted according to modified procedures.

During the course of the reaction, the author observed vigorous evolution of gas from the reaction

mixture. On the assumption that the gas would be hydrogen, generated from a leaving group, a hydride (H–MgX) and a proton (H–N on the B(dan)), the author carried out its trapping experiment by using *trans*-stilbene as a hydrogen accepter in the presence of a palladium catalyst (Figure 30A). A reduced product, 1,2-diphenylethane, was found to form in 88% yield, which verifies the evolved gas is indeed hydrogen. Moreover, this result implies that R–B(dan) would exist as their anionic forms in the reaction mixture before aqueous work-up; quenching the reaction with methyl tosylate afforded a mixture of *N*-methylated (**3'a**) and *N*,*N'*-dimethylated (**3"a**) products (Figure 30B, Exp. 1), while *N*-methylation of isolated **3a** did not occur at all under similar conditions (Figure 30B, Exp. 2). In addition, the reaction with D_2O-quenching gave deuterated **3a** (Figure 30C). Based upon

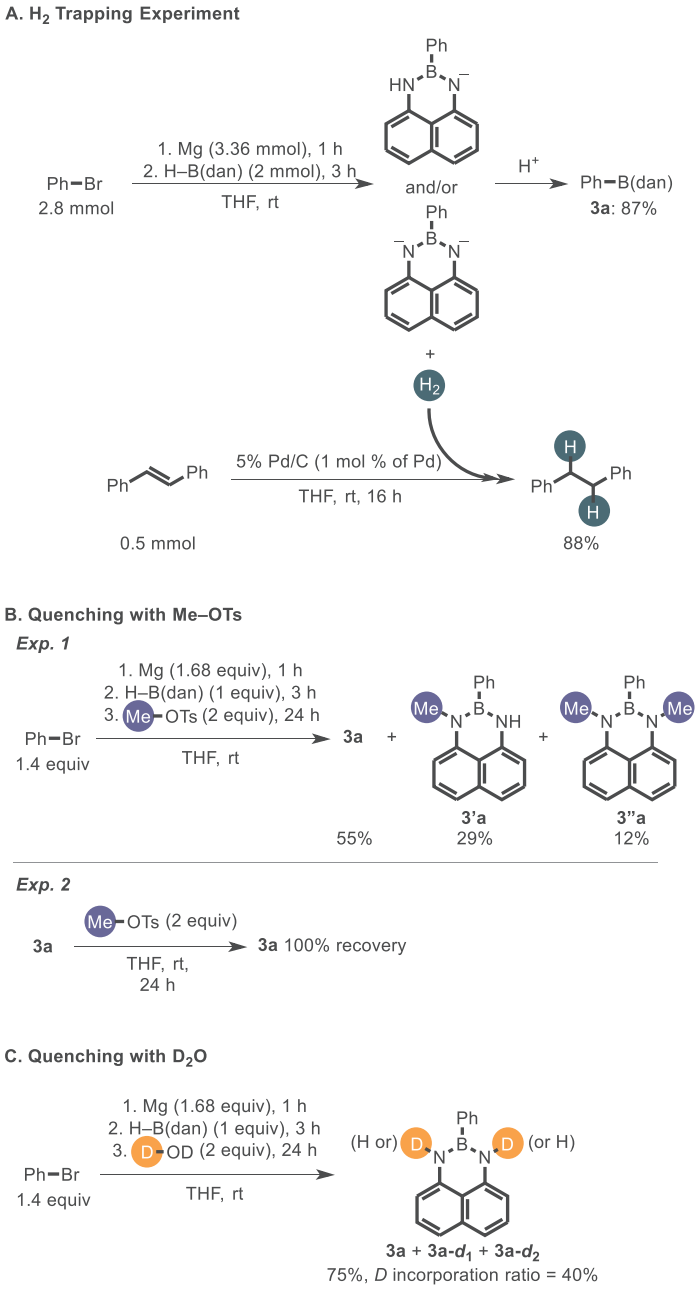


Figure 30 Mechanic studies

these, a plausible pathway for the B(dan)-installing reaction, where a hydride serves as a good leaving group, is depicted in Figure 31. First, a Grignard reagent of enough nucleophilicity attacks the boron center of H–B(dan) to lead to intermediary formation of a borate species (**5**). Subsequent elimination of H–MgX, which promptly reacts with the H–N on the B(dan) moiety to evolve H_2, followed by aqueous work-up finally gave the product.

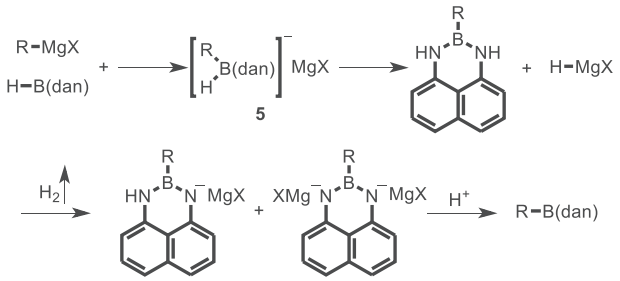


Figure 31 A plausible pathway for the B(dan)-installing reaction

The synthetic utility of the present reaction was well demonstrated by the iterative SMC with **3w** (Figure 32); the chemoselective SMC at the Br moiety of **3w** with *p*-TolB(OH)$_2$ offered **6** in 45% yield without damaging the 2-pyridyl–B(dan) bond. The resulting **6** was then cross-coupled with 4-iodobenzotrifluoride under direct SMC conditions to furnish oligoarene **7** in 52% yield.

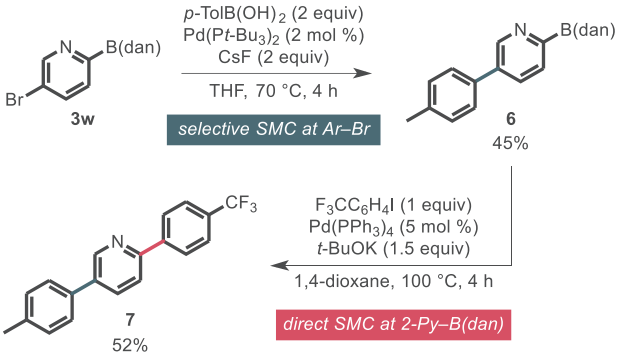


Figure 32 Iterative SMC with 5-bromo-2-pyridyl–B(dan)

In conclusion, the author has demonstrated that H–B(dan) can serve as a promising B(dan) electrophile for capturing such carbon nucleophiles as diverse Grignard reagents, leading to the convenient and practical method for synthesizing C(sp, sp^2 and sp^3)–B(dan) of high synthetic utility under the transition metal-free conditions. Moreover, the reaction pathway has been found to include the evolution of H_2 via the deprotonation of the H–N on the B(dan) moiety with H–MgX.

2-3 Experimental Section

2-3-1 General Remarks

All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under an argon atmosphere. Nuclear magnetic resonance spectra were taken on a Varian System 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz; ^{11}B, 186 MHz; ^{19}F, 470 MHz) or a Varian 400MR (^{1}H, 400 MHz) spectrometer using residual chloroform (^{1}H, δ = 7.26), $CDCl_3$ (^{13}C, δ = 77.16), a residual proton in DMSO-d_6 (^{1}H, δ = 2.50), DMSO-d_6 (^{13}C, δ = 39.52) or tetramethylsilane (^{1}H and ^{13}C, δ = 0) as an internal standard, and boron trifluoride diethyl etherate (^{11}B, δ = 0.00) or benzotrifluoride (^{19}F, δ = -63.72) as an external standard. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, m = multiplet), coupling constants (Hz), integration. GC analysis was performed on a Shimadzu GC-2014 (GC conditions: Column: TC-1 (GLScience), 30 m x 0.25 mm, film 0.25 μm; Flow rate: 1.89 mL/min; Injector temperature: 250 °C; Oven temperature: 100 °C to 250 °C at 20 °C/min, hold at 250 °C for 10 min; FID temperature: 250 °C). High-resolution mass spectra were obtained with a Thermo Fisher Scientific LTQ Orbitrap XL or JEOL JMS–T100GCV spectrometer. Melting points were measured with Yanaco Micro Melting Point apparatus and uncorrected. Column chromatography was carried out using Merck Kieselgel 60 or Florisil. Unless otherwise noted, commercially available reagents were used without purification. All solvents were dried over activated molecular sieve 4Å.

2-3-2 General Procedure

Procedure A: Reaction of aryl Grignard reagents with H–B(dan) using Mg.
A 25 mL of Schlenk tube was charged with magnesium turnings (1.68 mmol, 1.68 equiv). After the tube was heated under vacuum for 5 minutes with the aid of a heating gun, the tube was cooled to room temperature and back-filled with argon. Iodine (0.01 mmol, 1 mol %) and THF (2 mL) were then added. After stirring for 10 minutes at room temperature, an aryl bromide (1.4 mmol, 1.4 equiv) was added. After stirring for 1 h at room temperature, H–B(dan) (1 mmol, 1 equiv) was added to the mixture and the resulting mixture was stirred for additional 3 h. The reaction mixture was quenched with sat. NH_4Cl aq (5 mL). The layers were allowed to separate and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified on SiO_2 (10% to 25% EtOAc/Hexane) to afford the target compound.

Procedure B: Reaction of heteroaryl Grignard reagents with H–B(dan) using Turbo Grignard reagent.
To a flame dried 25 mL of Schlenk tube were added *i*-PrMgCl•LiCl (0.75 mmol, 1.5 equiv), a heteroaryl bromide (0.7 mmol, 1.4 equiv) and *p*-xylene (1 mL). After stirring for 3 h at room temperature, H–B(dan) (0.5 mmol, 1 equiv) was added and the resulting mixture was stirred for additional 3 h. The reaction mixture was quenched with sat. NH_4Cl aq. (5 mL). The layers were allowed to separate and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified on SiO_2 (10% to 25% EtOAc/Hexane) to afford the target compound.

Procedure C: Reaction of alkyl Grignard reagents with H–B(dan) using Mg.
A 25 mL of Schlenk tube was charged with magnesium turnings (2.4 mmol, 2.4 equiv). After the tube was heated under vacuum for 5 minutes with the aid of a heating gun, the tube was cooled to room temperature and back-filled with argon. Iodine (0.01 mmol, 1 mol %) and THF (2 mL) were then added. After stirring for 10 minutes at room temperature, an alkyl halide (2 mmol, 2 equiv) was added and then stirred for 2 h at reflux temperature. After returning to room temperature, H–B(dan) (1 mmol, 1 equiv) was added and the resulting mixture was stirred for additional 24 h. The reaction mixture was quenched with sat. NH_4Cl aq. (5 mL). The layers were allowed to separate and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified on SiO_2 (10% to 25% EtOAc/Hexane) to afford the target compound.

Procedure D: Reaction of commercially available Grignard reagents with H–B(dan).
To a flame dried 25 mL of Schlenk tube were added a Grignard reagent (2 mmol, 2 equiv), H–B(dan) (1 mmol, 1 equiv) and THF (2 mL). After stirring for 24 h at room temperature, the reaction mixture was quenched with sat. NH_4Cl aq. (5 mL). The layers were allowed to separate and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified on SiO_2 (10% to 25% EtOAc/Hexane) to afford the target compound.

2-phenyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3a)
Isolated in 87% yield as a brown solid (Procedure A)
^{1}H NMR ($CDCl_3$) δ 7.68-7.64 (m, 2H), 7.54-7.43 (m, 3H), 7.17 (t, J = 7.8 Hz, 2H), 7.09 (d, J = 8.2 Hz, 2H), 6.43 (d, J = 7.3 Hz, 2H), 6.03 (brs, 2H).
^{13}C NMR ($CDCl_3$) δ 141.18, 136.47, 131.55, 130.41, 128.39, 127.75, 119.97, 117.95, 106.16.

2-(*p*-tolyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3b)
Isolated in 93% yield as a brown solid (Procedure A)
^{1}H NMR ($CDCl_3$) δ 7.56 (d, J = 7.9 Hz, 2H), 7.28 (d, J = 7.5 Hz, 2H), 7.16 (dd, J = 8.3, 7.3 Hz, 2H), 7.07 (dd, J = 8.3, 1.0 Hz, 2H), 6.42 (dd, J = 7.2, 1.0 Hz, 2H), 6.03 (brs, 2H), 2.42 (s, 3H).
^{13}C NMR ($CDCl_3$) δ 141.28, 140.51, 136.47, 131.57, 129.17, 127.74, 119.91, 117.84, 106.08, 21.71.

2-(*m*-tolyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3c)
Isolated in 92% yield as a gray solid (Procedure A)
^{1}H NMR ($CDCl_3$) δ 7.52-7.46 (m, 2H), 7.41 (t, J = 7.3 Hz, 1H), 7.36 (d, J = 7.7 Hz, 1H), 7.23 (dd, J = 8.3, 7.2 Hz, 2H), 7.15 (d, J = 8.2 Hz, 2H), 6.46 (d, J = 7.3 Hz, 2H), 6.05 (brs, 2H), 2.49 (s, 3H).
^{13}C NMR ($CDCl_3$) δ 141.19, 137.67, 136.41, 132.22, 131.09, 128.56, 128.22, 127.69, 119.91, 117.80, 106.08, 21.60.

2-(*o*-tolyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3d)
Isolated in 94% yield as a gray solid (Procedure A)
^{1}H NMR ($CDCl_3$) δ 7.44 (d, J = 8.1 Hz, 1H), 7.31 (t, J = 7.3 Hz, 1H), 7.21 (d, J = 4.2 Hz, 2H), 7.12 (t, J = 7.8 Hz, 2H), 7.05 (d, J = 8.3 Hz, 2H), 6.33 (d, J = 7.3 Hz, 2H), 5.80 (brs, 2H), 2.48 (s, 3H).
^{13}C NMR ($CDCl_3$) δ 141.21, 140.76, 136.47, 132.36, 129.81, 129.44, 127.75, 125.41, 119.89, 117.95, 106.03, 22.53.

2-(2-isopropylphenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3e)
Isolated in 91% yield as a gray solid (Procedure A)
^{1}H NMR ($CDCl_3$) δ 7.43-7.34 (m, 3H), 7.22 (td, J = 7.2, 1.4 Hz, 1H), 7.17-7.10 (m, 2H), 7.06 (d, J = 8.3 Hz, 2H), 6.35 (d, J = 7.2 Hz, 2H), 5.80 (brs, 2H), 3.24-3.13 (m, 1H), 1.28 (dd, J = 6.9, 2.3 Hz, 6H).
^{13}C NMR ($CDCl_3$) δ 151.95, 141.09, 136.39, 132.20, 129.48, 127.66, 125.46, 124.83, 119.83, 117.88, 106.00, 33.78, 24.83.

2-(4-methoxyphenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3f)
Isolated in 81% yield as a gray solid (Procedure A)
^{1}H NMR ($CDCl_3$) δ 7.59 (d, J = 8.6 Hz, 2H), 7.14 (dd, J = 8.3, 7.3 Hz, 2H), 7.05 (d, J = 7.4 Hz, 2H), 6.98 (d, J = 8.5 Hz, 2H), 6.42 (dd, J = 7.3, 1.0 Hz, 2H), 5.99 (brs, 2H), 3.86 (s, 3H).
^{13}C NMR ($CDCl_3$) δ 161.54, 141.32, 136.48, 133.13, 127.75, 119.80, 117.81, 113.99, 106.05, 55.31.

***N,N*-dimethyl-4-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)aniline (3g)**
Isolated in 90% yield as a white solid (Procedure A): mp 164–165 °C
^{1}H NMR ($CDCl_3$) δ 7.55 (d, J = 8.6 Hz, 2H), 7.17 (t, J = 7.8 Hz, 2H), 7.07 (d, J = 8.3 Hz, 2H), 6.79 (d, J = 8.6 Hz, 2H), 6.43 (d, J = 6.2 Hz, 2H), 6.01 (brs, 2H), 3.02 (s, 6H).

^{13}C NMR ($CDCl_3$) δ 152.00, 141.61, 136.47, 132.78, 127.71, 119.64, 117.44, 111.90, 105.84, 40.25.
^{11}B NMR ($CDCl_3$) δ 28.86.
HRMS (APCI) Calcd for $C_{18}H_{18}BN_3$: $[M+H]^+$, 288.16665. Found: m/z 288.16702

2-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3h)
Isolated in 90% yield as a gray solid (Procedure A)
^{1}H NMR ($CDCl_3$) δ 7.71-7.63 (m, 4H), 7.19 (t, J = 7.7 Hz, 2H), 7.12 (d, J = 8.1 Hz, 2H), 6.42 (d, J = 7.2 Hz, 2H), 5.96 (brs, 2H).
^{13}C NMR ($CDCl_3$) δ 140.68, 136.36, 131.92 (q, J = 32.4 Hz), 131.73, 127.70, 124.86 (q, J = 3.8 Hz), 124.21 (q, J = 272.3 Hz), 119.99, 118.26, 106.36.

2-(3,5-bis(trifluoromethyl)phenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3i)
Isolated in 71% yield as a yellow solid (Procedure A)
^{1}H NMR ($CDCl_3$) δ 8.06 (s, 2H), 8.04-7.96 (m, 1H), 7.17 (dd, J = 8.3, 7.2 Hz, 2H), 7.11 (dd, J = 8.4, 1.1 Hz, 2H), 6.48 (dd, J = 7.2, 1.1 Hz, 2H), 6.02 (brs, 2H).
^{13}C NMR ($CDCl_3$) δ 140.30, 136.39, 131.57, 131.54 (q, J = 32.9 Hz), 127.81, 123.96, 123.60 (q, J = 273.1 Hz), 120.13, 118.80, 106.75.

2-(4-bromophenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3j)
Isolated in 40% yield as a dark green solid (Procedure A)
^{1}H NMR ($CDCl_3$) δ 7.58 (d, J = 7.9 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 7.15 (t, J = 7.8 Hz, 2H), 7.07 (d, J = 8.2 Hz, 2H), 6.42 (d, J = 7.2 Hz, 2H), 5.97 (brs, 2H).
^{13}C NMR ($CDCl_3$) δ 140.90, 136.44, 133.15, 131.58, 127.76, 125.04, 119.97, 118.19, 106.30.

2-(4-chlorophenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3k)
Isolated in 88% yield as a gray solid (Procedure A)
^{1}H NMR ($CDCl_3$) δ 7.55 (d, J = 7.8 Hz, 2H), 7.41 (d, J = 7.8 Hz, 2H), 7.15 (t, J = 7.8 Hz, 2H), 7.08 (d, J = 8.2 Hz, 2H), 6.41 (d, J = 7.3 Hz, 2H), 5.97 (brs, 2H).
^{13}C NMR ($CDCl_3$) δ 140.92, 136.53, 136.43, 132.92, 128.62, 127.75, 119.94, 118.15, 106.27.

2-(2-chlorophenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3l)
Isolated in 57% yield as a purple solid (Procedure A)
^{1}H NMR ($CDCl_3$) δ 7.53 (dd, J = 7.1, 2.1 Hz, 1H), 7.42-7.29 (m, 3H), 7.14 (dd, J = 8.3, 7.2 Hz, 2H), 7.06 (dd, J = 8.4, 1.0 Hz, 2H), 6.39 (dd, J = 7.3, 1.0 Hz, 2H), 6.08 (brs, 2H).
^{13}C NMR ($CDCl_3$) δ 140.99, 137.99, 136.46, 134.01, 131.13, 129.68, 127.75, 126.63, 120.00, 118.07, 106.20.

2-(naphthalen-1-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3m)
Isolated in 84% yield as a gray solid (Procedure A)
^{1}H NMR ($CDCl_3$) δ 8.26-8.20 (m, 1H), 7.97-7.91 (m, 2H), 7.71 (d, J = 5.5 Hz, 1H), 7.59-7.51 (m, 3H), 7.20 (dd, J = 8.3, 7.1 Hz, 2H), 7.15 (d, J = 7.2 Hz, 2H), 6.36 (d, J = 7.2 Hz, 2H), 5.99 (brs, 2H).
^{13}C NMR ($CDCl_3$) δ 141.20, 136.52, 135.52, 133.37, 130.78, 129.63, 128.89, 128.02, 127.78, 126.34, 125.95, 125.51, 120.05, 118.09, 106.16.

2-(phenanthren-9-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3n)

Isolated in 83% yield as a gray solid (Procedure A)

^{1}H NMR ($CDCl_3$) δ 8.77 (d, J = 8.3 Hz, 1H), 8.71 (d, J = 7.4 Hz, 1H), 8.25 (dd, J = 8.1, 1.3 Hz, 1H), 7.98 (s, 1H), 7.91 (dd, J = 7.8, 1.4 Hz, 1H), 7.66 (s, 4H), 7.17 (dd, J = 8.3, 7.2 Hz, 2H), 7.11 (dd, J = 8.4, 1.0 Hz, 2H), 6.42 (dd, J = 7.2, 1.1 Hz, 2H), 6.08 (brs, 2H).

^{13}C NMR ($CDCl_3$) δ 141.18, 136.53, 133.76, 132.49, 131.35, 130.91, 130.16, 128.86, 128.83, 127.80, 127.33, 126.89, 126.69, 126.65, 123.32, 122.68, 120.10, 118.14, 106.21.

2-([1,1'-biphenyl]-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3o)

Isolated in 52% yield as a brown solid (Procedure A)

^{1}H NMR ($CDCl_3$) δ 7.69 (d, J = 8.8 Hz, 1H), 7.55-7.36 (m, 8H), 7.08 (t, J = 7.2 Hz, 2H), 7.02 (d, J = 8.3 Hz, 2H), 6.13 (d, J = 7.0 Hz, 2H), 5.50 (brs, 2H).

^{13}C NMR ($CDCl_3$) δ 146.52, 142.78, 141.17, 136.32, 132.89, 129.81, 129.53, 129.20, 128.88, 128.49, 127.67, 127.57, 127.29, 127.03, 119.58, 117.63, 105.87.

2-mesityl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3p)

Isolated in 90% yield as a red solid (Procedure A)

^{1}H NMR ($CDCl_3$) δ 7.17 (ddd, J = 8.5, 7.2, 1.3 Hz, 2H), 7.10 (d, J = 8.3 Hz, 2H), 6.92 (s, 2H), 6.35 (d, J = 7.2 Hz, 2H), 5.78 (brs, 2H), 2.42 (s, 6H), 2.35 (s, 3H).

^{13}C NMR ($CDCl_3$) δ 141.28, 140.75, 138.62, 136.46, 127.72, 127.34, 119.89, 117.91, 105.99, 22.40, 21.32.

2-(thiophen-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3q)

Isolated in 84% yield as a gray solid

^{1}H NMR ($CDCl_3$) δ 7.58 (dd, J = 4.7, 0.9 Hz, 1H), 7.45 (dd, J = 3.4, 0.9 Hz, 1H), 7.21 (dd, J = 4.7, 3.4 Hz, 1H), 7.12 (dd, J = 8.3, 7.2 Hz, 2H), 7.04 (d, J = 7.2 Hz, 2H), 6.37 (d, J = 7.2 Hz, 2H), 5.92 (brs, 2H).

^{13}C NMR ($CDCl_3$) δ 140.81, 136.39, 132.97, 130.22, 128.68, 127.70, 119.85, 118.08, 106.24.

This compound was synthesized by a similar method to Procedure A: A 25 mL of Schlenk tube was charged with magnesium turnings (1.68 mmol, 1.68 equiv). After the tube was heated under vacuum for 5 minutes with the aid of a heating gun, the tube was cooled to room temperature and back-filled with argon. Iodine (0.01 mmol, 1 mol %) and THF (2 mL) were then added. After stirring for 10 minutes at room temperature, 2-bromothiophene (1.4 mmol, 1.4 equiv) was added and then stirred for 2 h at reflux temperature. After cooling to room temperature, H–B(dan) (1 mmol, 1 equiv) was added and the resulting mixture was stirred for additional 3 h. The reaction mixture was quenched with sat. NH_4Cl aq. (5 mL). The layers were allowed to separate and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified on SiO_2 (10% to 25% EtOAc/Hexane) to afford **3q**.

2-(pyridin-3-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3r)

Isolated in 52% yield as a black solid: mp 204–205 °C

^{1}H NMR (DMSO-*d6*) δ 9.07 (s, 1H), 8.64 (dd, J = 4.9, 1.8 Hz, 1H), 8.42 (brs, 2H), 8.27 (dt, J = 7.6, 1.9 Hz, 1H), 7.45 (dd, J = 7.6, 4.8 Hz, 1H), 7.10 (t, J = 7.8 Hz, 2H), 6.93 (d, J = 8.2 Hz, 2H), 6.59

(d, J = 7.5 Hz, 2H).
^{13}C NMR (DMSO-*d6*) δ 153.38, 150.82, 142.08, 140.22, 135.99, 127.74, 123.27, 119.84, 116.61, 105.85.
^{11}B NMR (DMSO-*d6*) δ 29.82.
HRMS (APCI) Calcd for $C_{15}H_{12}BN_3$: $[M+H]^+$, 246.1970. Found: m/z 246.12006
This compound was synthesized by a similar method to Procedure B: To a flame dried 25 mL of Schlenk tube were added *i*-PrMgCl•LiCl (0.7 mmol, 1.4 equiv), 3-bromopyridine (0.5 mmol, 1 equiv) and *p*-xylene (1 mL). After stirring for 3 h at room temperature, H–B(dan) (0.5 mmol, 1 equiv) was added and the resulting mixture was stirred for additional 3 h. The reaction mixture was quenched with sat. NH_4Cl aq. (5 mL). The layers were allowed to separate and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified on SiO_2 (10% to 25% EtOAc/Hexane) to afford **3r**.

2-(pyridin-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3s)
Isolated in 71% yield as a brown solid (Procedure B)
^{1}H NMR ($CDCl_3$) δ 8.82-8.77 (m, 1H), 7.69 (td, J = 7.6, 1.7 Hz, 1H), 7.61 (dt, J = 7.6, 1.2 Hz, 1H), 7.32 (ddd, J = 7.6, 4.8, 1.3 Hz, 1H), 7.15 (dd, J = 8.3, 7.3 Hz, 2H), 7.06 (dd, J = 8.4, 1.0 Hz, 2H), 6.57 (brs, 2H), 6.45 (dd, J = 7.3, 1.0 Hz, 2H).
^{13}C NMR ($CDCl_3$) δ 150.19, 141.10, 136.52, 134.98, 127.74, 126.82, 124.55, 120.47, 117.98, 106.31.

2-(5-methylpyridin-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3t)
Isolated in 74% yield as a yellow solid
^{1}H NMR ($CDCl_3$) δ 8.63 (s, 1H), 7.58-7.50 (m, 2H), 7.14 (dd, J = 8.3, 7.2 Hz, 2H), 7.05 (dd, J = 8.3, 1.0 Hz, 2H), 6.53 (brs, 2H), 6.45 (dd, J = 7.3, 1.0 Hz, 2H), 2.39 (s, 3H).
^{13}C NMR ($CDCl_3$) δ 150.97, 141.21, 136.56, 135.51, 134.43, 127.76, 126.48, 120.43, 117.92, 106.27, 18.88.
This compound was synthesized by a similar method to Procedure B: To a flame dried 25 mL of Schlenk tube were added *i*-PrMgCl•LiCl (0.7 mmol, 1.4 equiv), 3-bromopyridine (0.5 mmol, 1 equiv) and *p*-xylene (1 mL). After stirring for 3 h at room temperature, H–B(dan) (0.5 mmol, 1 equiv) was added and the resulting mixture was stirred for additional 3 h. The reaction mixture was quenched with sat. NH_4Cl aq. (5 mL). The layers were allowed to separate and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified on SiO_2 (10% to 25% EtOAc/Hexane) to afford **3t**.

2-(4-methylpyridin-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3u)
Isolated in 69% yield as a gray solid (Procedure B): mp 187–188 °C.
^{1}H NMR ($CDCl_3$) δ 8.64 (d, J = 5.9 Hz, 1H), 7.44 (s, 1H), 7.17-7.10 (m, 3H), 7.05 (dd, J = 8.3, 1.0 Hz, 2H), 6.57 (brs, 2H), 6.44 (dd, J = 7.3, 1.0 Hz, 2H), 2.37 (s, 3H).
^{13}C NMR ($CDCl_3$) δ 149.94, 145.91, 141.16, 136.51, 128.02, 127.72, 125.44, 120.45, 117.88, 106.25, 21.17.

^{11}B NMR ($CDCl_3$) δ 27.53.
HRMS (APCI) Calcd for $C_{16}H_{14}BN_3$: $[M+H]^+$, 260.13535. Found: m/z 260.13568

2-(3-methylpyridin-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3v)
Isolated in 34% yield as a gray solid (Procedure B)
^{1}H NMR ($CDCl_3$) δ 8.61 (dd, J = 4.7, 0.9 Hz, 1H), 7.48 (ddd, J = 7.8, 1.6, 0.8 Hz, 1H), 7.22 (dd, J = 7.8, 4.7 Hz, 1H), 7.13 (dd, J = 8.3, 7.3 Hz, 2H), 7.05 (dd, J = 8.3, 1.0 Hz, 2H), 6.44 (brs, 2H), 6.41 (dd, J = 7.3, 1.0 Hz, 2H), 2.59 (s, 3H).
^{13}C NMR ($CDCl_3$) δ 147.42, 141.24, 137.62, 137.16, 136.50, 127.75, 123.82, 120.25, 117.90, 106.29, 20.77.

2-(5-bromopyridin-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3w)
Isolated in 53% yield as a yellow solid (Procedure B): mp 158–159 °C
^{1}H NMR ($CDCl_3$) δ 8.85 (dd, J = 2.3, 0.8 Hz, 1H), 7.86 (dd, J = 8.1, 2.3 Hz, 1H), 7.53 (dd, J = 8.1, 0.8 Hz, 1H), 7.14 (dd, J = 8.3, 7.2 Hz, 2H), 7.06 (dd, J = 8.3, 1.0 Hz, 2H), 6.48 (brs, 2H), 6.45 (dd, J = 7.3, 1.1 Hz, 2H).
^{13}C NMR ($CDCl_3$) δ 151.40, 140.84, 137.58, 136.51, 127.75, 127.68, 122.47, 120.46, 118.20, 106.43.
^{11}B NMR ($CDCl_3$) δ 27.29.
HRMS (APCI) Calcd for $C_{15}H_{11}BBrN_3$: $[M+H]^+$, 324.03022. Found: m/z 324.03085

2-methyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (4a)
Isolated in 49% yield as a gray solid (Procedure D)
^{1}H NMR ($CDCl_3$) δ 7.13 (dd, J = 8.3, 7.3 Hz, 2H), 7.05 (dd, J = 8.3, 1.1 Hz, 2H), 6.30 (dd, J = 7.2, 1.1 Hz, 2H), 5.62 (brs, 2H), 0.37 (s, 3H).
^{13}C NMR ($CDCl_3$) δ 141.35, 136.41, 127.70, 119.52, 117.43, 105.49.

2-butyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (4b)
Isolated in 96% yield as a black liquid
^{1}H NMR ($CDCl_3$) δ 7.11 (t, J = 7.8 Hz, 2H), 7.02 (d, J = 8.3 Hz, 2H), 6.31 (d, J = 7.2 Hz, 2H), 5.61 (brs, 2H), 1.48-1.34 (m, 4H), 1.00-0.91 (m, 3H), 0.91-0.83 (m, 2H).
^{13}C NMR ($CDCl_3$) δ 141.35, 136.43, 127.67, 119.65, 117.41, 105.50, 27.13, 25.61, 14.11.
^{11}B NMR ($CDCl_3$) δ 31.95.
HRMS (APCI) Calcd for $C_{14}H_{17}BN_2$: M^+, 224.14793. Found: m/z 224.14804
This compound was synthesized by a similar method to Procedure C: A 25-mL of Schlenk tube was charged with magnesium turnings (2.4 mmol, 2.4 equiv). After the tube was heated under vacuum for 5 minutes with the aid of a heating gun, the tube was cooled to room temperature and back-filled with argon. Iodine (0.01 mmol, 1 mol %) and THF (2 mL) were then added. After stirring for 10 minutes at room temperature, 1-bromobutane (2 mmol, 2 equiv) was added and the mixture was stirred for 1 h. To the mixture was added H–B(dan) (1 mmol, 1 equiv), and the resulting mixture was stirred for additional 24 h. The reaction mixture was quenched with sat. NH_4Cl aq. (5 mL). The layers were allowed to separate and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified on SiO_2 (10% to 25% EtOAc/Hexane) to afford **4b**.

2-isopropyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (4c)

Isolated in 83% yield as a gray solid

^{1}H NMR ($CDCl_3$) δ 7.14 (t, 2H), 7.04 (dd, J = 8.3, 1.1 Hz, 2H), 6.34 (dd, J = 7.3, 1.1 Hz, 2H), 5.61 (brs, 2H), 1.23-1.12 (m, 1H), 1.10 (d, 6H).

^{13}C NMR ($CDCl_3$) δ 141.36, 136.44, 127.69, 119.69, 117.48, 105.66, 18.92.

This compound was synthesized by a similar method to Procedure C: A 25 mL of Schlenk tube was charged with magnesium turnings (2.4 mmol, 2.4 equiv). After the tube was heated under vacuum for 5 minutes with the aid of a heating gun, the tube was cooled to room temperature and back-filled with argon. Then THF (2 mL) was added (Iodine was not necessary in this case). After stirring for 10 minutes at room temperature, 2-isopropyl bromide (2 mmol, 2 equiv) was added and the mixture was stirred for 1 h. H–B(dan) (1 mmol, 1 equiv) was added and the resulting mixture was stirred for additional 24 h. The reaction mixture was quenched with sat. NH_4Cl aq. (5 mL). The layers were allowed to separate and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified on SiO_2 (10% to 25% EtOAc/Hexane) to afford **4c**.

2-(*tert*-butyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine(4d)

Isolated in 55% yield as a brown solid (Procedure D): mp 107–108 °C

^{1}H NMR ($CDCl_3$) δ 7.16 (dd, J = 8.3, 7.3 Hz, 2H), 7.06 (dd, J = 8.3, 1.0 Hz, 2H), 6.37 (dd, J = 7.3, 1.1 Hz, 2H), 5.64 (brs, 2H), 1.07 (s, 9H).

^{13}C NMR ($CDCl_3$) δ 141.37, 136.43, 127.71, 119.59, 117.52, 105.74, 27.83.

^{11}B NMR ($CDCl_3$) δ 33.17.

HRMS (APCI) Calcd for $C_{14}H_{17}BN_2$: $[M+H]^+$, 225.15576. Found: m/z 225.15550

2-neopentyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (4e)

Isolated in 86% yield as a purple solid (Procedure C)

^{1}H NMR ($CDCl_3$) δ 7.16 (dd, J = 8.3, 7.3 Hz, 2H), 7.07 (dd, J = 8.3, 1.1 Hz, 2H), 6.33 (dd, J = 7.3, 1.1 Hz, 2H), 5.63 (brs, 2H), 1.94-1.82 (m, 1H), 1.04 (d, J = 6.6 Hz, 6H), 0.84 (d, J = 7.3 Hz, 2H).

^{13}C NMR ($CDCl_3$) δ 141.33, 136.41, 127.65, 119.65, 117.41, 105.50, 25.65, 25.51.

2-isobutyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (4f)

Isolated in 72% yield as a purple solid (Procedure C): mp 91–92 °C

^{1}H NMR ($CDCl_3$) δ 7.13 (dd, J = 8.2, 7.3 Hz, 2H), 7.04 (d, J = 8.3 Hz, 2H), 6.32 (d, J = 7.3 Hz, 2H), 5.61 (s, 2H), 1.07 (brs, 9H), 0.89 (s, 2H).

^{13}C NMR ($CDCl_3$) δ 141.35, 136.43, 127.70, 119.67, 117.45, 105.53, 32.47, 30.56.

^{11}B NMR ($CDCl_3$) δ 31.13.

HRMS (APCI) Calcd for $C_{15}H_{19}BN_2$: M^+, 238.16358. Found: m/z 238.16386

2-cyclopropyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (4g)

Isolated in 66% yield as a purple solid (Procedure C): mp 64–65 °C

^{1}H NMR ($CDCl_3$) δ 7.10 (dd, J = 8.3, 7.2 Hz, 2H), 7.00 (dd, J = 8.4, 1.1 Hz, 2H), 6.29 (td, J = 7.1, 1.1 Hz, 2H), 5.44 (brs, 2H), 0.79-0.67 (m, 2H), 0.44 (td, J = 5.9, 3.9 Hz, 2H), -0.08 (tt, J = 9.4, 6.3 Hz, 1H).

^{13}C NMR ($CDCl_3$) δ 141.25, 136.41, 127.65, 119.52, 117.42, 105.52, 4.07.
^{11}B NMR ($CDCl_3$) δ 31.47.
HRMS (APCI) Calcd for $C_{13}H_{13}BN_2$: M^+, 208.11663. Found: m/z 208.11682

2-vinyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (4h)
Isolated in 73% yield as a purple liquid (Procedure D)
^{1}H NMR ($CDCl_3$) δ 7.11 (ddd, J = 8.4, 7.2, 2.3 Hz, 2H), 7.03 (dd, J = 7.7, 3.4 Hz, 2H), 6.34 (d, J = 7.3 Hz, 2H), 6.09-5.99 (m, 1H), 5.92 (d, J = 17.4 Hz, 2H), 5.75 (brs, 2H).
^{13}C NMR ($CDCl_3$) δ 141.10, 136.39, 130.85, 127.63, 119.96, 117.65, 105.84.

2-ethynyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (4i)
Isolated in 46% yield as a purple solid
^{1}H NMR ($CDCl_3$) δ 7.11 (dd, J = 8.3, 7.3 Hz, 2H), 7.05 (dd, J = 8.3, 1.1 Hz, 2H), 6.30 (dd, J = 7.3, 1.1 Hz, 2H), 5.85 (brs, 2H), 2.61 (s, 1H).
^{13}C NMR ($CDCl_3$) δ 140.38, 136.37, 127.66, 120.14, 118.19, 106.01, 90.78.
This compound was synthesized by a similar method to Procedure D: After a 25 mL of Schlenk tube were heated under vacuum for 5 minutes with the aid of a heating gun, the tube was cooled to room temperature and back-filled with argon. Ethynyl magnesium chloride (0.5 M in THF, 2 mmol, 2 equiv) and H–B(dan) (1 mmol, 1 equiv) were added and then stirred for 24 h at 0 °C. The reaction mixture was quenched with sat. NH_4Cl aq. (5 mL). The layers were allowed to separate and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified on SiO_2 (10% to 25% EtOAc/Hexane) to afford the target compound.

3-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)propan-1-ol (4j)
Isolated in 85% yield as a gray solid: mp 98–99 °C
^{1}H NMR ($CDCl_3$) δ 7.09 (dd, J = 8.3, 7.3 Hz, 2H), 7.00 (dd, J = 8.3, 1.0 Hz, 2H), 6.30 (dd, J = 7.3, 1.0 Hz, 2H), 5.70 (brs, 2H), 3.69 (td, J = 6.4, 4.0 Hz, 2H), 1.77-1.67 (m, 2H), 1.36 (t, J = 5.0 Hz, 1H), 0.96-0.89 (m, 2H).
^{13}C NMR ($CDCl_3$) δ 141.24, 136.41, 127.68, 119.67, 117.51, 105.60, 64.92, 27.88.
^{11}B NMR ($CDCl_3$) δ 31.68.
HRMS (APCI) Calcd for $C_{13}H_{15}BN_2O$: $[M+H]^+$, 227.13502. Found: m/z 227.13438
This compound was synthesized by a similar method to Procedure C: After a 25 mL of Schlenk tube was heated under vacuum for 5 minutes with the aid of a heating gun, the tube was cooled to room temperature and back-filled with argon. 3-Chloro-1-propanol (2 mmol, 2 equiv) and THF (2 mL) were then added. After cooling to -20 °C, *tert*-butyl magnesium chloride (2 mmol, 2 equiv) was added dropwise and then stirred for 1 h. After raising to room temperature, the mixture was heated to reflux for 15 minutes and cooled to room temperature. To the mixture were added magnesium turnings (2.4 mmol, 2.4 equiv) and 1,2-dibromoethane (1-2 drop), and the mixture was heated to reflux for 9 h. H–B(dan) (1 mmol, 1 equiv) was added after the mixture was cooled to room temperature. After stirring for additional 8 h at room temperature, the mixture was quenched with sat. NH_4Cl aq. (5 mL). The layers were allowed to separate and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified on SiO_2 (10% to 25%

EtOAc/Hexane) to afford **4j**.

2-allyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (4k)

Isolated in 95% yield as a gray liquid

^{1}H NMR ($CDCl_3$) δ 7.10 (dd, J = 8.3, 7.2 Hz, 2H), 7.02 (dd, J = 8.4, 1.0 Hz, 2H), 6.31 (dd, J = 7.3, 1.0 Hz, 2H), 5.97-5.85 (m, 1H), 5.62 (brs, 2H), 5.11-5.03 (m, 2H), 1.82 (d, J = 7.8 Hz, 2H).

^{13}C NMR ($CDCl_3$) δ 141.10, 136.42, 135.26, 127.67, 119.71, 117.70, 115.73, 105.73.

This compound was synthesized by a similar method to Procedure C: A 25 mL of Schlenk tube was charged with magnesium turnings (1.2 mmol, 1.2 equiv). After the tube was heated under vacuum for 5 minutes with the aid of a heating gun, the tube was cooled to room temperature and back-filled with argon. Iodine (0.01 mmol, 1 mol %) and THF (2 mL) were then added. After stirring for 10 minutes at room temperature, 3-bromoprop-1-ene (2 mmol, 2 equiv) and H–B(dan) (1 mmol, 1 equiv) were added and the resulting mixture was stirred for 24 h. The reaction mixture was quenched with sat. NH_4Cl aq. (5 mL). The layers were allowed to separate and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified on SiO_2 (10% to 25% EtOAc/Hexane) to afford **4k**.

2-(but-2-en-1-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine(4l) and 2-(but-3-en-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (4'l)

Isolated in 67% yield (42:58) as a black liquid

^{1}H NMR ($CDCl_3$) δ 7.13 (t, J = 8.5 Hz, 4H, **4l + 4'l**), 7.04 (d, J = 7.2 Hz, 4H, **4l + 4'l**), 6.33 (d, J = 7.0 Hz, 4H, **4l + 4'l**), 6.03-5.89 (m, 1H, **4'l**), 5.61 (s, 4H, **4l + 4'l**), 5.56-5.44 (m, 2H, **4l**), 5.12-5.03 (m, 2H, **4'l**), 1.97 (quint, J = 7.6 Hz, 1H, **4'l**), 1.77-1.64 (m, 5H, **4l**), 1.20 (d, J = 7.3 Hz, 3H, **4'l**).

^{13}C NMR ($CDCl_3$) δ 142.09, 141.21, 141.15, 136.42, 128.14, 127.06, 126.25, 126.16, 124.50, 119.70, 118.00, 117.69, 117.58, 112.76, 106.42, 106.01, 105.81, 105.66, 18.27, 14.89, 12.77.

These compounds were synthesized by a similar procedure to that for **4k**.

H_2 Trapping Experiment:

Two-chamber Schlenk tube (chamber I: left; chamber II: right)

The procedure for Figure 30A. As shown in the above photo, a two-chamber Schlenk tube was used for this experiment. At first, magnesium turnings (3.36 mmol, 1.68 equiv) was placed in the chamber I. After the tube was heated under vacuum for 5 minutes with the aid of a heating gun, the tube was cooled to room temperature and back-filled with argon. Iodine (0.02 mmol, 1 mol %) and THF (4 mL) were then added. After stirring for 10 minutes at room temperature, phenyl bromide (2.8 mmol, 1.4 equiv) was added and the mixture was stirred for 1 h at room temperature. Next, chamber II was charged with 5% Pd/C (5.00 μmol, 1 mol % of Pd), *trans*-stilbene (0.50 mmol, 0.5 equiv) and THF (0.50 mL). To the chamber I, H–B(dan) (2 mmol, 1 equiv) was added. After stirring at room temperature for 16 h, the resulting each solution was treated separately for subsequent work-up. Regarding the solution in the chamber I, the mixture was quenched with sat. NH_4Cl aq. (10 mL). The layers were allowed to separate and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified on SiO_2 (EtOAc/Hexane = 1/5) to afford **3a** in 87% yield. On the other hand, the solution in the chamber II was filtered through a pad of Celite (***CAUTION***: the Celite pad may not be dried up after the filtration due to possible ignition of the activated Pd/C), and then evaporation of the solvent followed by column chromatography on silica gel (EtOAc/Hexane = 1/20) gave 1,2-diphenylethane in 88% yield. Accordingly, only ^{1}H NMR data of 1,2-diphenylethane are provided here. ^{1}H NMR ($CDCl_3$) δ 7.35-7.28 (m, 4H), 7.26-7.19 (m, 6H), 2.96 (s, 4H).

Quenching with Me–OTs

The procedure for Figure 30B, Exp. 1. A 25 mL of Schlenk tube was charged with magnesium turnings (1.68 mmol, 1.68 equiv). After the tube was heated under vacuum for 5 minutes with the aid of a heating gun, the tube was cooled to room temperature and back-filled with argon. Iodine (0.01 mmol, 1 mol %) and THF (2 mL) were then added. After stirring for 10 minutes at room temperature, phenyl bromide (1.4 mmol, 1.4 equiv) was added. After stirring for 1 h at room temperature, H–B(dan) (1 mmol, 1 equiv) was added and the mixture was stirred for 3 h. To the resulting mixture was added MeOTs (2 mmol, 2 equiv) and stirring was continued at room temperature for additional 24 h. The reaction mixture was quenched with sat. NH_4Cl aq. (5 mL).

The layers were allowed to separate and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified on SiO_2 (EtOAc/Hexane = 1/20) to afford **3a** in 55% yield, **3'a** in 29% yield, and **3"a** in 12% yield (**3'a** and **3"a** were obtained as an inseparable mixture).

The procedure for Figure 30B, Exp. 2. A 25 mL of Schlenk tube was heated under vacuum for 5 minutes with the aid of a heating gun, and the tube was cooled to room temperature and back-filled with argon. Isolated **3a** (5 mmol, 1 equiv), MeOTs (0.5 mmol, 1 equiv) and THF (1 mL) were then added. After stirring for 24 h at room temperature, the reaction mixture was quenched with sat. NH_4Cl aq. (5 mL). The layers were allowed to separate and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was found to only contain **3a** (100% recovery) by ^1H NMR.

1-methyl-2-phenyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3'a) and 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3"a)

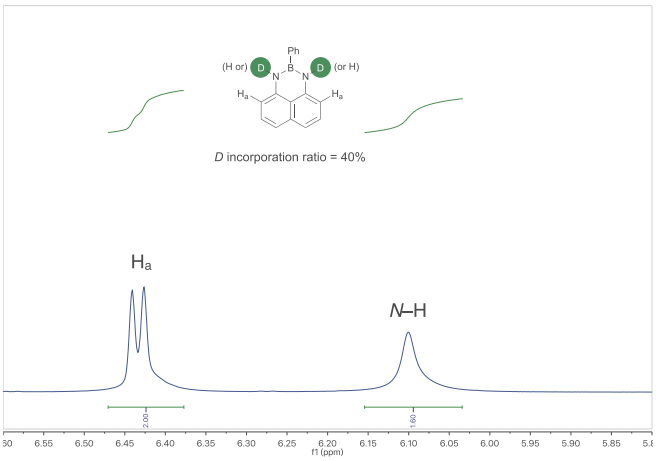
^1H NMR ($CDCl_3$) δ 7.63-7.56 (m, **3'a**), 7.49-7.43 (m, **3'a** + **3"a**), 7.38-7.10 (m, **3'a** + **3"a**), 6.52 (dd, J = 14.6, 7.7 Hz, **3'a**), 6.40 (dd, J = 7.1, 1.3 Hz, **3"a**), 5.92 (brs, **3'a**), 3.09 (s, **3"a)**, 2.92 (s, **3'a**).

^{13}C NMR ($CDCl_3$) δ 143.99, 143.21, 140.49, 136.26, 135.98, 132.45, 131.86, 129.09, 128.40, 128.24, 128.21, 127.81, 127.41, 127.38, 118.36, 118.29, 117.79, 105.94, 103.76, 103.69, 35.74, 34.84.

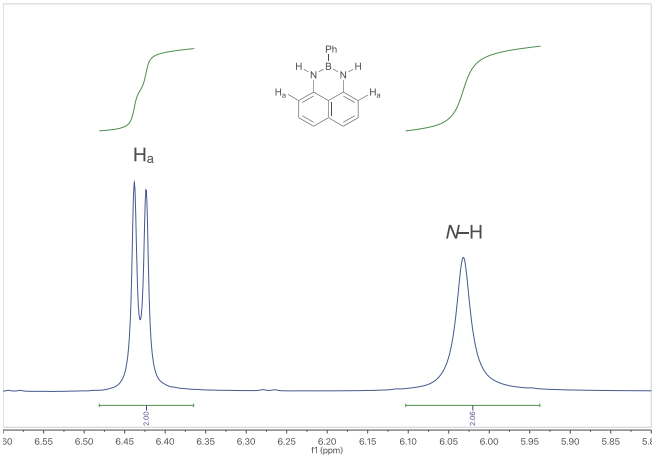
^{11}B NMR ($CDCl_3$) δ 30.89.

Quenching with D_2O

The procedure for Figure 30C. A 25 mL of Schlenk tube was charged with magnesium turnings (1.68 mmol, 1.68 equiv). After the tube was heated under vacuum for 5 minutes with the aid of a heating gun, the tube was cooled to room temperature and back-filled with argon. Iodine (0.01 mmol, 1 mol %) and THF (2 mL) were then added. After stirring for 10 minutes at room temperature, phenyl bromide (1.4 mmol, 1.4 equiv) was added. After stirring for 1 h at room temperature, H–B(dan) (1 mmol, 1 equiv) was added and the mixture was stirred for 3 h. To the resulting mixture was added D_2O (2 mmol, 2 equiv) and stirring was continued at room temperature for additional 24 h. The reaction mixture was concentrated by rotary evaporation. The deuterium incorporation ratio (40%, see below) and the NMR yield (75%, anisole as an internal standard) were determined by ^1H NMR spectrum of the crude material.



^{1}H NMR spectrum of **3a** + **3a**-d_1 + **3a**-d_2



^{1}H NMR spectrum of **3a**

Iterative SMC of 5-bromo-2-pyridyl–B(dan):
Selective SMC at the Ar–Br bond of 3w

After a 25 mL of Schlenk tube were heated under vacuum for 5 minutes with the aid of a heating gun, the tube was cooled to room temperature and back-filled with argon. $Pd(PtBu_3)_2$ (8 μmol, 2 mol %), CsF (0.8 mmol, 2 equiv), **3w** (0.4 mmol, 1 equiv), *p*-tolyl boronic acid (0.8 mmol, 2 equiv), and THF (1 mL) was added. The resulting mixture was stirred at reflux for 6 h. After quenching the mixture with brine (20 mL), the resulting mixture was extracted with EtOAc (15 mL × 3). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified on SiO_2 (EtOAc/Hexane as an eluent) to afford a cross-coupling product, **6** in 45% yield.

Direct SMC at the Ar–B(dan) bond of 6

After a 25-mL of Schlenk tube were heated under vacuum for 5 minutes with the aid of a heating gun, the tube was cooled to room temperature and back-filled with argon. $Pd(PPh_3)_4$ (5 μmol, 5 mol %), **6** (0.1 mmol, 1 equiv), 4-iodobenzotrifluoride (0.1 mmol, 1 equiv), and 1,4-dioxane (1 mL) was added. The mixture was stirred at 100 °C for 5 min before addition of *t*-BuOK (1 M in THF, 0.15 mL, 0.15 mmol). The resulting mixture was stirred at 100 °C for 4 h. After quenching the mixture with brine (20 mL), the resulting mixture was extracted with EtOAc (15 mL × 3). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified on SiO_2 (EtOAc/Hexane as an eluent) to afford a cross-coupling product, **7** in 52% yield.

2-(5-(*p*-tolyl)pyridin-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (6)

Isolated in 45% yield as a yellow solid: mp 182–183 °C

^{1}H NMR ($CDCl_3$) δ 9.03 (dd, J = 2.3, 0.9 Hz, 1H), 7.89 (dd, J = 7.8, 2.3 Hz, 1H), 7.69 (dd, J = 7.9, 1.0 Hz, 1H), 7.56-7.51 (m, 2H), 7.32 (d, J = 8.3 Hz, 2H), 7.15 (dd, J = 8.3, 7.3 Hz, 2H), 7.06 (dd, J = 8.3, 1.0 Hz, 2H), 6.58 (brs, 2H), 6.47 (dd, J = 7.3, 1.0 Hz, 2H), 2.43 (s, 3H).

^{13}C NMR ($CDCl_3$) δ 148.65, 141.16, 138.51, 137.19, 136.57, 134.90, 132.95, 130.03, 127.78, 127.14, 126.77, 120.50, 118.01, 106.34, 21.34.

^{11}B NMR ($CDCl_3$) δ 27.70.

HRMS (APCI) Calcd for $C_{22}H_{18}BN_3$: $[M+H]^+$, 336.16665. Found: m/z 336.16724

5-(*p*-tolyl)-2-(4-(trifluoromethyl)phenyl)pyridine (7)

Isolated in 52% yield as a white solid: mp 227–228 °C

^{1}H NMR ($CDCl_3$) δ 8.95 (dd, J = 2.4, 0.9 Hz, 1H), 8.16 (d, J = 8.8 Hz, 2H), 7.98 (dd, J = 8.2, 2.4 Hz, 1H), 7.83 (dd, J = 8.3, 0.9 Hz, 1H), 7.75 (d, J = 8.2 Hz, 2H), 7.55 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 7.9 Hz, 2H), 2.43 (s, 3H).

^{13}C NMR ($CDCl_3$) δ 154.35, 148.35, 142.50, 138.48, 135.91, 135.16, 134.53, 130.85 (q, J = 32.4 Hz), 130.06, 127.18, 127.03, 125.87 (q, J = 3.7 Hz), 124.36 (q, J = 272.2 Hz), 120.81, 21.35.

^{19}F NMR ($CDCl_3$) δ -63.82.

HRMS (APCI) Calcd for $C_{19}H_{14}F_3N$: $[M+H]^+$, 314.11511. Found: m/z 314.11526

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Chapter 3

Ethynyl–B(dan) in [3+2] Cycloaddition and Larock Indole Synthesis: Synthesis of Stable Boron-containing Heteroaromatic Compounds

The cycloaddition of nitrile oxides with ethynyl–B(dan) (dan = naphthalene-1,8-diaminato) allowed the facile preparation of diverse isoxazolyl–B(dan) compounds, all of which displayed excellent protodeborylation-resistant properties. The dan-installation on the boron center proves vital to the high stability of the products as well as the perfect regioselectivity arising from hydrogen bond-directed orientation in the cycloaddition. The diminished boron-Lewis acidity of ethynyl–B(dan) also renders it amenable to azide–alkyne cycloaddition, Larock indole synthesis and related heteroannulations. The obtained boron-containing triazole, indoles, benzofuran and indenone exhibit sufficient resistance toward protodeborylation. Despite the commonly accepted transmetalation-inactive property derived from the diminished Lewis acidity, the synthesized heteroaryl–B(dan) compound was still found to be convertible to the oligoarene via sequential Suzuki–Miyaura coupling.

3-1 Introduction

Suzuki–Miyaura coupling (SMC) stands out as one of the most efficient and versatile methods for constructing carbon frameworks of myriad organic compounds, wherein organoboron compounds are coupled with organic electrophiles.[1] Organoboronic acids [R–B(OH)$_2$][2] and boronates such as R–B(pin) (pin = pinacolato)[3] have been particularly important and frequently used reagents in such boron-based carbon–carbon bond-forming reaction; however, their inherent Lewis acidity, being a key for the smooth transmetalation,[4] occasionally becomes a double-edged sword, posing challenges in terms of instability arising from protodeborylation which depends on organic moieties attached to the boron center.[5] To address the issue, one strategy that has garnered increasing attention have relied on the use of a B(dan) group (dan = naphthalene-1,8-diaminato),[6-8] whose Lewis acidity is highly diminished[9] with its nearly ideal B(sp^2)-hybridized orbital and effective electron donation to the empty p orbital from the adjacent nitrogen atoms. The representative example of B(dan)-induced stabilization is found in heteroarylboron compounds; 2-pyridyl–B(dan), which is available straightforwardly by B(dan)-installing reactions,[10] becomes significantly resistant towards protodeborylation, in stark contrast to the fact that its B(OH)$_2$- and B(pin)-counterparts suffer serious decomposition.[5]

For over a century, the synthesis and functionalization of heterocyclic frameworks have been a central subject in chemical synthesis, owing to their ubiquitous occurrence in active pharmaceutical ingredients and other biologically relevant molecules.[11] In this context, the development of an efficient and reliable way of functionalizing the heterocyclic scaffolds has been of great importance, and therefore heteroarylboron compounds have emerged as the promising reagents for such functionalization, albeit their potentially protodeborylation-prone properties in the Lewis acidic forms as described above. The [3+2] cycloaddition of 1,3-dipoles with dipolarophiles represents one of the most well-established methods of constructing heterocyclic skeletons,[12] and the use of ethynylboron compounds as dipolarophiles would provide a convenient and direct approach to diverse five-membered heteroarylboron compounds. Yet, intriguingly, only a limited number of studies have been reported on this transformation. In 1966, Grünangera reported the first synthesis of 5-isoxazolylboronic acids from dibutyl ethynylboronate via the [3+2] cycloaddition with nitrile oxides, however, a critical limitation was the inability to isolate the products, largely due to their ease of the protodeborylation.[13*a*] On the other hand, the use of ethynyl–B(pin) in a similar reaction gave a moderate yield of isoxazolyl–B(pin) as a mixture of regioisomers.[13*b*] Beyond the instability of the Lewis acidic heteroarylboron compounds, another drawback of ethynyl–B(pin) is its water-sensitivity, limiting the synthetic utility of the ethynylboron-based [3+2] cycloadditions and accessibility to heteroarylboron motifs obtained therefrom. To address these chanlleges, Grob harnessed ethynyl–B(mida),[14] whose p orbital is protected by intramolecular coordination, for the [3+2] cycloadditions, leading to the formation of stable isoxazolyl/triazolyl–B(mida) that could undergo slow-release SMC through the in situ generation of cross-coupling-active boronic acid counterparts.[15] Herein, the author reports an alternative avenue for this synthetic paradigm by leveraging ethynyl–B(dan), less frequently utilized in chemical synthesis,[16] and directly converting it to isoxazolyl/triazolyl–B(dan). Notably, the diminished boron-Lewis acidity of ethynyl–B(dan) also enabled Pd-catalyzed coupling with *ortho*-iodoanilines known as Larock indole synthesis.[17,18] All the synthesized heteroaryl–B(dan) compounds exhibit excellent stability for standard handling, in sharp contrast to their Lewis acidic forms, and can undergo direct SMC,[19] regardless of the previous discovery that the diminished B(dan)-Lewis acidity could retard the transmetalation step.[6]

3-2 Results and Discussion

The requisite ethynyl–B(dan) (**4i**) was directly prepared by established one-pot procedure[10c] using ethynyl Grignard reagent, triethylborate and 1,8-diaminonaphthalene. Notably, the compound displayed sufficient stability to be isolated via silica gel column chromatography. The incorporation of the dan moiety led to a pronounced reduction in the boron-Lewis acidity, which, in turn, markedly enhanced its resistance to water. When exposed to water in DMSO-d_6 (*ca*. 9 vol% H_2O), no detectable decomposition was observed even after 16 days, whereas ethynyl–B(pin) was quite unstable under the same conditions (Figure 33).

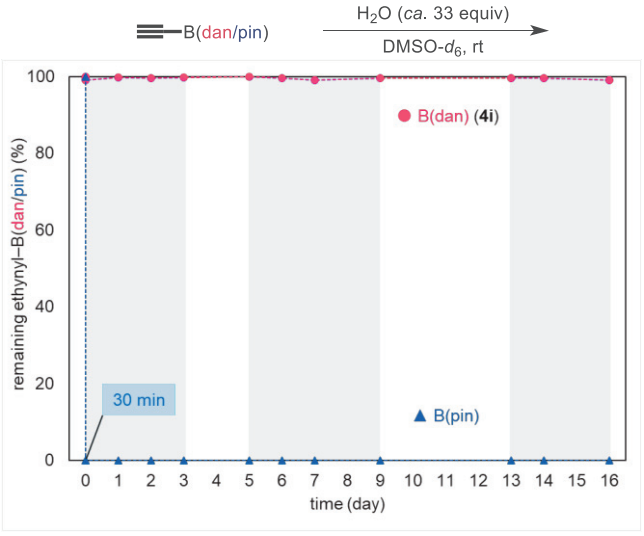


Figure 33 Stability of ethynyl–B(dan/pin) toward water

Having successfully synthesized stable ethynyl–B(dan) (**4i**), the author subsequently explored its reactivity with phenyl nitrile oxide generated *in situ* from phenyl chlorooxime (**8a**), and observed that the [3+2] cycloaddition proceeded smoothly to afford 3-phenylisoxazol-5-yl–B(dan) (**9a**) as the sole product in 85% yield (Figure 34). The perfect regioselectivity, which stands in contrast to the case with ethynyl–B(pin), can be potentially attributed to hydrogen bonding interaction between the oxygen anion of the nitrile oxide and the N–H moiety of the B (dan) (Figure 35).[20,21] The substrate scope proved to be sufficiently broad: aryl nitrile oxides bearing methoxy (**9b** and **9c**) or halogen substituent (**9d** and **9e**) were efficiently transformed to the corresponding isoxazol-5-yl–B(dan) in good yields, the latter of which was found to be utilizable for the sequential SMC (Figure 40, *vide infra*). The reaction was also viable to sterically demanding aryl nitrile oxides (from **8f** or **8g**) to efficiently produce **9f** and **9g**; however, the use of electron-deficient nitrile oxides (from **8h**–**9j**) resulted in decreased yields. In addition to (*E*)-β-styryl and 2-pyridyl nitrile oxides that produced the respective B(dan)-substituted isoxazoles (**9k** and **9l**) in high yields, alkyl (diphenylmethyl, *i*-Pr and Cy) nitrile oxides could also be readily coupled with **4i** to give 3-alkylisoxazol-5-yl–B(dan) (**9m**–**9o**) in a straightforward manner. Furthermore, terephthalonitrile oxide could participate in the title reaction smoothly, forming the diboryl product (**9p**) in 72% yield via the dual cycloaddition. It should be noted that the resulting isoxazole-5-yl–B(dan) (**9a**–**9p**) and other heteroaryl–B(dan) discussed below are sufficiently stable under ambient conditions, thus allowing for their isolation by silica gel column chromatography.

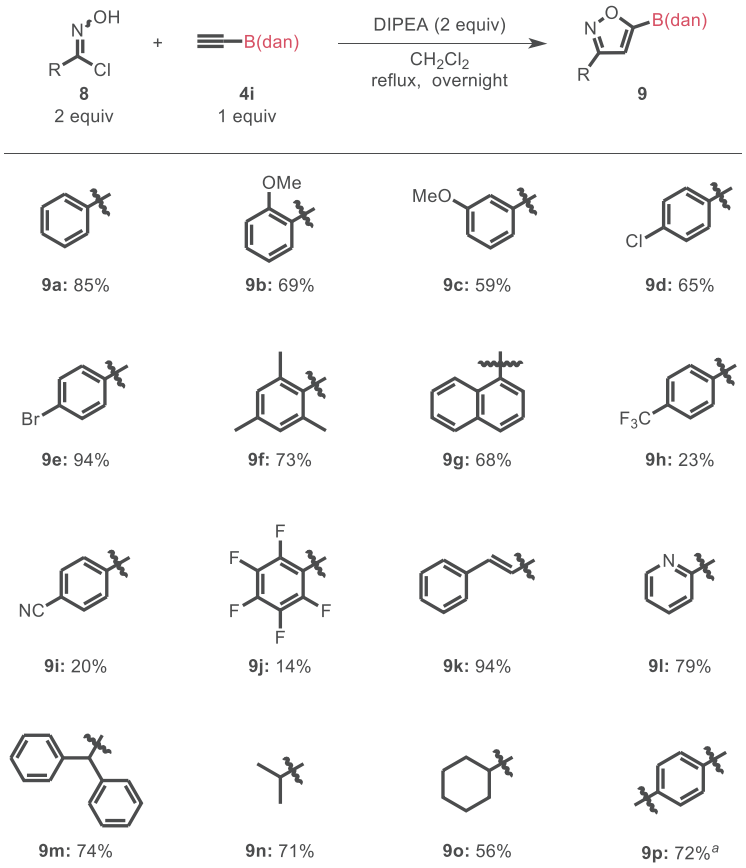


Figure 34 [3+2] Cycloaddition of nitrile oxides with ethynyl–B(dan)

[a] Chlorooxime (1 equiv), **4i** (2 equiv).

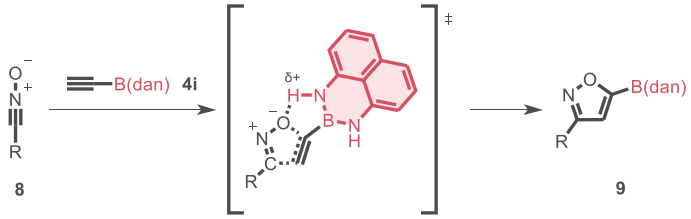


Figure 35 Hydrogen bond between nitrile oxides and ethynyl–B(dan)

Larock indole synthesis, a palladium-catalyzed coupling reaction of *ortho*-iodoaniline derivatives with alkynes, is one of the most popular ways of constructing variously substituted indole skeletons. In particular, the reaction with terminal alkynes in the presence of a copper cocatalyst can provide diverse 2-substituted indoles through a cascade comprising Sonogashira coupling and subsequent intramolecular heteroannulation. As such, synthetically important 2-borylindoles may become accessible by reacting it with ethynylboron compounds; however, this type of transformation has not yet been achieved, probably owing to concurrent SMC as well as the instability of the ethynylboron compounds (Figure 33). In this regard, **4i** with diminished Lewis acidity would emerge as a promising candidate. To delight, treating it with *N*-tosyliodoaniline (**10a**) under Pd/Cu co-catalysis afforded indol-2-yl–B(dan) (**11a**) in 76% yield (Figure 36), whereas the control experiment using ethynyl–B(pin) failed to provide the desired product (Figure 37A), further highlighting the unique reactivity of **4i**. This method was indeed amenable to a rich array of 2-

iodoaniline substrates bearing either electron-donating (**10b**) or -withdrawing (**10c** and **10d**) groups; the bromo moiety remained intact in the synthesis of **11d**. In addition, azaindol-2-yl–B(dan) (**11e**) could be prepared in 79% yield from *N*-tosylated 2-amino-3-iodopyridine (**10e**).

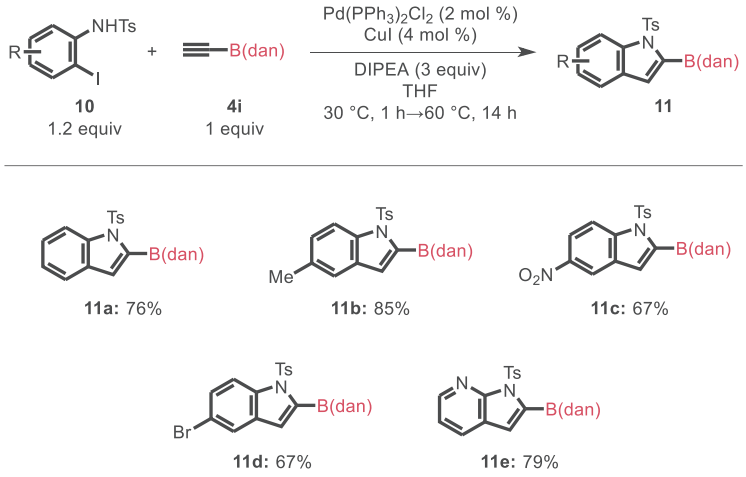


Figure 36 Larock indole synthesis with ethynyl–B(dan)

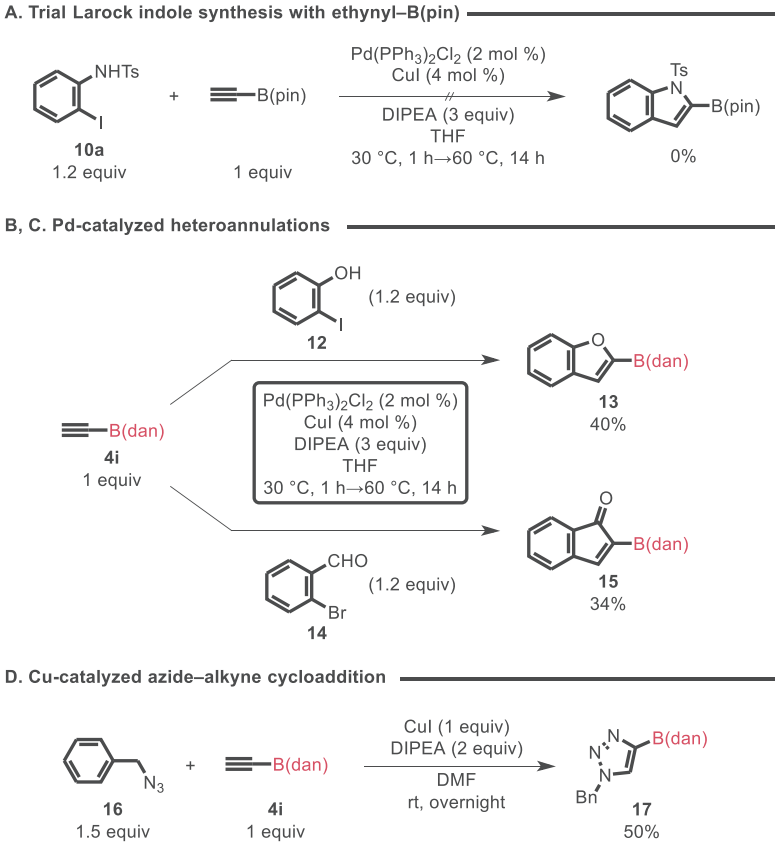


Figure 37 Synthesis of other heteraryl–B(dan)

The potential of ethynyl–B(dan) (**4i**) as a versatile synthon for constructing other heteroaryl–B(dan) compounds was demonstrated by the reaction with either 2-iodophenol (**12**)[22] or 2-bromobenzaldehyde (**14**)[23] under conditions similar to those of the indole synthesis, affording B(dan)-substituted benzofuran (**13**) and indenone (**15**), respectively (Figure 37B and 37C).

Furthermore, a copper-catalyzed azide–alkyne cycloaddition involving benzyl azide (**16**) and **4i** regioselectively furnished triazol-4-yl–B(dan) (**17**) in 50% yield (Figure 37D), whose structure was unambiguously determined via X-ray crystallographic analysis (Figure 38).

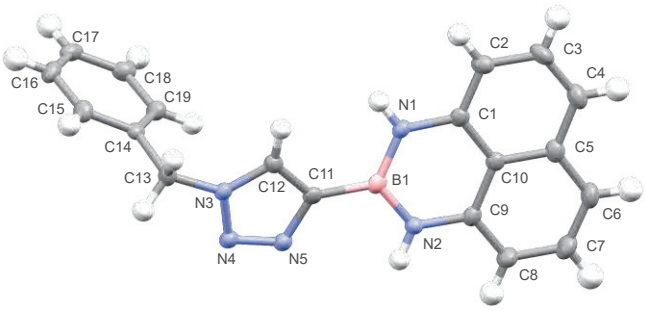


Figure 38 X-ray crystal structure of **17**

The data presented clearly showed that the dan-installation onto the boron centers considerably enhances the protodeborylation-resistant properties of both ethynyl- and heteroaryl-boron compounds, when compared with their B(pin) counterparts.[5] This highlighted property can be mainly attributed to the diminished Lewis acidity inherent to the B(dan) moieties, which was quantitatively evaluated by computed ammonia affinity (AA).[9b] As depicted in Figure 39, all the calculated AA values of the B(dan) compounds fall below those of the corresponding B(pin) compounds, which aligned well with the observed experimental behaviors.

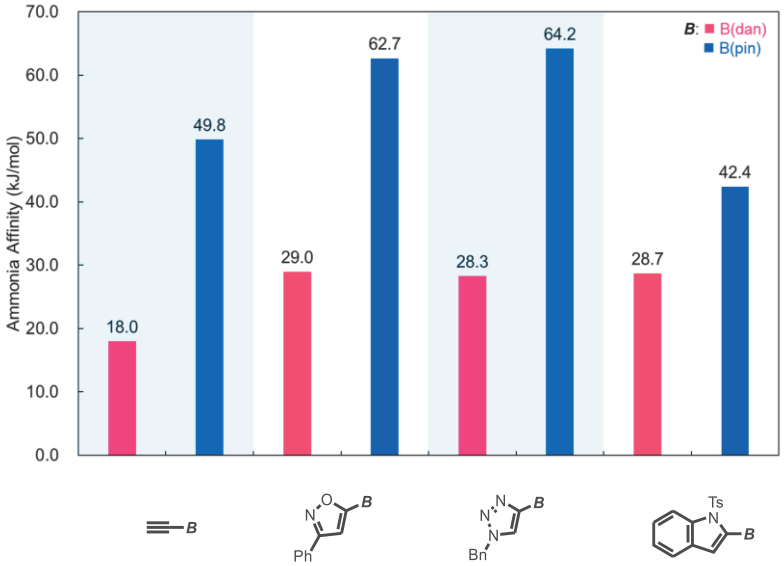


Figure 39 Calculated ammonia affinity (kJ/mol) of R–B(dan)

Although the B(dan)-derived Lewis acidity diminishment can greatly enhance the compound stability, it usually inhibits the transmetalation step of SMC, resulting its utilization as boron-masking strategy in the iterative cross-coupling.[6] Yoshida[19b,d] and Saito,[19c,e] on the other hand, independently disclosed that the use of a strong base, *t*-BuOK, as an activator enabled the direct SMC smoothly. Notably, $Ba(OH)_2$ conditions also turned out to promote the direct SMC of the heteroaryl–B(dan).[10c]

Based on these findings, the chemoselective SMC of **9e** with 4-iodoanisole in the presence of $Ba(OH)_2$ was accomplished to give **18** in 39% yield (Figure 40).[24] The remaining bromine moiety was then coupled with 3,5-dimethylphenyl boronic acid to furnish an isoxazole-containing π-extended compound (**19**) in 79% yield.

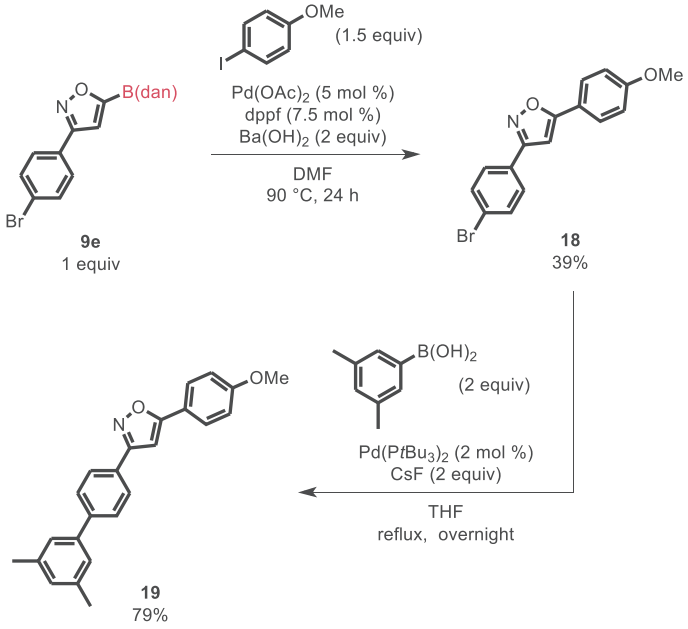


Figure 40 Sequential SMC with **9e**

In conclusion, the author has first demonstrated the prowess of the highly stable ethynyl–B(dan) in the [3+2] cycloadditions that produce various B(dan)-containing isoxazoles and triazole in a highly regioselective manner. Moreover, the diminished boron-Lewis acidity of ethynyl–B(dan) permits its participation in the selective Larock indole synthesis and related Pd/Cu-catalyzed heteroannulations. Importantly, these reactions proceed without damaging the boron functionality, leading to the direct formation of indoles, benzofuran and indenone with the B(dan) moiety at the 2 positions. The synthesized heteroaryl–B(dan) exhibited excellent protodeborylation-resistant properties, as supported by theoretical calculation-based ammonia affinity evaluations. In contrast to expectations set by their diminished Lewis acidity, the heteroaryl–B(dan) was demonstrated to be reactive towards the direct SMC under the $Ba(OH)_2$ conditions, which opens up an efficient and versatile route toward heteroaryl-containing π-extended systems. These findings have clearly exemplified the synthetic potential of the robust yet reactive B(dan) moiety, offering an attractive alternative to the commonly-used B(pin) and $B(OH)_2$ moieties.

3-3 Experimental Section

3-3-1 General Remarks

All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under an argon atmosphere. Nuclear magnetic resonance spectra were taken on a Varian System 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz; ^{11}B, 160 MHz) or Varian System 400 (^{1}H, 400 MHz) spectrometer using residual proton in DMSO-d_6 (^{1}H, δ = 2.50), Acetone-d_6 (^{1}H, δ = 2.05), residual chloroform (^{1}H, δ = 7.26) or $CDCl_3$ (^{13}C, δ = 77.0) as an internal standard and boron trifluoride diethyl etherate (^{11}B, δ = 0.00) as an external standard. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet), coupling constants (Hz), integration. High-resolution mass spectra were obtained with a Thermo Fisher Scientific LTQ Orbitrap XL spectrometer. Melting points were measured with Yanaco Micro Melting Point apparatus and uncorrected. Preparative recycling gel permeation chromatography was performed with GL Science PU 614 equipped with Shodex GPC H-2001L and -2002L columns (toluene as an eluent). Column chromatography was carried out using Merck Kieselgel 60. Unless otherwise noted, commercially available reagents were used without purification. All solvents were dried over activated molecular sieves 3Å.

3-3-2General Produce

Synthesis of ethynyl–B(dan) (4i)

A flame-dried 100 mL of two-necked flask equipped with a magnetic stirring bar was heated under vacuum for 5 minutes with the aid of a heating gun. After cooling to room temperature, the flask was back-filled with argon. It was then cooled further to -78 °C. Into this flask, ethynylmagnesium chloride (0.5 M in THF, 20 mmol, 1 equiv) was introduced, and the mixture was stirred for 10 minutes at -78 °C. Trimethylborate (24 mmol, 1.2 equiv) was then added dropwise maintaining the temperature. The mixture was allowed to warm to room temperature and was stirred for 24 hours. Subsequently, a THF solution (10 mL) of 1,8-diaminonaphthalene (24 mmol, 1.2 equiv) was added dropwise, followed by a dropwise addition of acetic acid (30 mmol, 1.5 equiv) after 10 minutes. The reaction was quenched using saturated $NaHCO_3$ aq. After phase separation, the aqueous layer was extracted with ethyl acetate. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated using rotary evaporation. The residue was subjected to column chromatography over silica gel, using a hexane/ethyl acetate (5:1) eluent, yielding ethynyl–B(dan) (**4i**) (7.69 mmol, 38% yield).

2-ethynyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (4i)

^{1}H NMR ($CDCl_3$) δ 7.11 (dd, J = 8.3, 7.2 Hz, 2H), 7.04 (dd, J = 8.3, 1.2 Hz, 2H), 6.30 (dd, J = 7.1, 1.2 Hz, 2H), 5.85 (s, 2H), 2.61 (s, 1H).

^{13}C NMR ($CDCl_3$) δ 140.38, 136.38, 127.66, 120.15, 118.39, 106.14, 90.78.

Synthesis of chlorooximes (8)

Step 1: Preparation of oximes: A general procedure

A 25-mL of Schlenk tube was heated under vacuum for 5 minutes with the aid of a heating gun, cooled to room temperature and back-filled with argon. An aldehyde (3 mmol, 1 equiv) was dissolved in water/ethanol (2:1, 3 mL:1.5 mL), and hydroxylamine chloridrate (6 mmol, 2 equiv) was introduced followed by a portionwise addition of sodium acetate (9 mmol, 3 equiv) at 0 °C. The reaction mixture was stirred and warmed to room temperature until all the aldehyde was fully consumed (TLC monitoring). After phase separation, the aqueous layer was extracted with ethyl acetate. The organic solution was washed with brine, dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The crude oxime was used directly in the subsequent step.

Step 2: Preparation of chlorooximes (**8**): A general procedure

A 25-mL of Schlenk tube was heated under vacuum for 5 minutes with the aid of a heating gun, cooled to room temperature and back-filled with argon. An oxime (2 mmol, 1 equiv) was dissolved in DMF (3 mL) and *N*-chlorosuccinimide (2 mmol, 1 equiv) was added portionwise at 0 °C. The reaction mixture was stirred and allowed to warm to room temperature until all the oxime was fully consumed (TLC monitoring). The mixture was quenched with water, and the aqueous phase was extracted with diethyl ether. The organic phase was washed with brine, dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The chlorooxime (**8**) was used directly in the subsequent reaction.

[3+2] Cycloaddition of nitrile oxides with ethynyl–B(dan): A general procedure

A 25-mL Schlenk tube was evacuated for 5 minutes using a heating gun, then cooled to room

temperature and purged with argon. Ethynyl–B(dan) (0.2 mmol, 1 equiv) and chlorooxime (0.4 mmol, 2 equiv) were dissolved in CH_2Cl_2 (1 mL). After stirring for 5 minutes at room temperature, *N*,*N*-diisopropylethylamine (0.8 mmol, 4 equiv) was added, and the mixture was stirred at 40 °C overnight. Then the mixture was diluted with ethyl acetate (20 mL) and brine (20 mL). After allowing the organic layer to separate, the aqueous phase was extracted with ethyl acetate. The organic phase was washed with brine, dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The residue was purified using column chromatography over silica gel (Hexane/EtOAc as an eluent) to give isoxazolyl–B(dan) (**9**).

5-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)-3-phenylisoxazole (9a)
Isolated in 85% yield as a gray solid: mp 158–159 ˚C
^{1}H NMR ($CDCl_3$) δ 7.85 (dd, J = 7.5, 2.2 Hz, 2H), 7.51 – 7.41 (m, 3H), 7.17 – 7.11 (m, 2H), 7.09 (d, J = 8.6 Hz, 2H), 6.96 (s, 1H), 6.42 (dd, J = 7.2, 1.1 Hz, 2H), 6.22 (s, 2H).
^{13}C NMR ($CDCl_3$) δ161.77, 139.96, 136.41, 130.16, 129.12, 128.85, 127.72, 127.11, 120.41, 118.77, 109.39, 106.78.
^{11}B NMR ($CDCl_3$) δ 24.66.
HRMS Calcd for $C_{19}H_{14}BN_3O$: $[M+H]^+$, 312.1303. Found: *m/z* 312.1308

3-(2-methoxyphenyl)-5-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)isoxazole (9b)
Isolated in 69% yield as a gray solid: mp 181–182 ˚C
^{1}H NMR ($CDCl_3$) δ 7.94 (dd, J = 7.7, 1.8 Hz, 1H), 7.44 (ddd, J = 8.7, 7.6, 1.8 Hz, 1H), 7.21 (s, 1H), 7.19 – 7.10 (m, 2H), 7.11 – 6.99 (m, 4H), 6.44 (d, J = 7.1 Hz, 2H), 6.24 (s, 2H), 3.93 (s, 3H).
^{13}C NMR ($CDCl_3$) δ 159.40, 157.30, 140.12, 136.44, 131.38, 129.94, 127.73, 121.15, 120.40, 118.67, 117.79, 112.90, 111.58, 106.70, 55.72.
^{11}B NMR ($CDCl_3$) δ 24.54.
HRMS Calcd for $C_{20}H_{16}BN_3O_2$: $[M+H]^+$, 342.1408. Found: *m/z* 342.1414

3-(3-methoxyphenyl)-5-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)isoxazole (9c)
Isolated in 59% yield as a gray solid: mp 142–143 ˚C
^{1}H NMR ($CDCl_3$) δ 7.47 – 7.35 (m, 3H), 7.15 (dd, J = 8.3, 7.2 Hz, 2H), 7.10 (dd, J = 8.4, 1.1 Hz, 2H), 7.01 (d, J = 6.6 Hz, 1H), 6.99 (s, 1H), 6.45 (dd, J = 7.1, 1.1 Hz, 2H), 6.21 (s, 2H), 3.88 (s, 3H).
^{13}C NMR ($CDCl_3$) δ 161.75, 160.17, 139.96, 136.46, 130.20, 130.14, 127.76, 120.45, 119.61, 118.86, 116.26, 112.15, 109.53, 106.81, 55.56.
^{11}B NMR ($CDCl_3$) δ 24.54.
HRMS Calcd for $C_{20}H_{16}BN_3O_2$: $[M+H]^+$, 342.1408. Found: *m/z* 342.1404

3-(4-chlorophenyl)-5-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)isoxazole (9d)
Isolated in 65% yield as a gray solid: mp 225–226 ˚C
^{1}H NMR (Acetone-d_6) δ 7.92 (m, 4H), 7.56 (d, J = 8.5 Hz, 2H), 7.42 (s, 1H), 7.12 (dd, J = 8.3, 7.3 Hz, 2H), 7.04 (dd, J = 8.3, 1.0 Hz, 2H), 6.64 (dd, J = 7.3, 1.1 Hz, 2H).
^{13}C NMR (Acetone-d_6) δ 161.25, 142.02, 137.44, 136.20, 130.11, 129.28, 128.92, 128.50, 121.52, 118.70, 110.78, 107.35.
^{11}B NMR (Acetone-d_6) δ 24.54.
HRMS Calcd for $C_{19}H_{13}BClN_3O$: $[M+H]^+$, 346.0913. Found: *m/z* 346.0922

3-(4-bromophenyl)-5-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)isoxazole (9e)

Isolated in 94% yield as a green solid: mp 208–209 °C

^{1}H NMR (Acetone-d_6) δ 7.91 (s, 2H), 7.83 (dd, J = 8.9, 2.2 Hz, 2H), 7.70 (d, J = 8.6 Hz, 2H), 7.41 (d, J = 1.1 Hz, 1H), 7.12 (t, J = 7.8 Hz, 2H), 7.03 (d, J = 8.2 Hz, 2H), 6.63 (dd, J = 7.4, 1.1 Hz, 2H).

^{13}C NMR (Acetone-d_6) δ 161.30, 141.99, 137.42, 133.09, 129.48, 129.29, 128.48, 124.45, 121.50, 118.68, 110.73, 107.34.

^{11}B NMR (Acetone-d_6) δ 25.07.

HRMS Calcd for $C_{19}H_{13}BBrN_3O$: $[M+H]^+$, 390.0408. Found: *m/z* 390.0412

3-mesityl-5-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)isoxazole (9f)

Isolated in 73% yield as a yellow solid: mp 213–214 °C

^{1}H NMR ($CDCl_3$) δ 7.15 (t, J = 7.3 Hz, 2H), 7.10 (d, J = 9.3 Hz, 2H), 6.96 (s, 2H), 6.63 (s, 1H), 6.43 (ddd, J = 7.1, 2.5, 1.1 Hz, 2H), 6.26 (d, J = 6.4 Hz, 2H), 2.34 (s, 3H), 2.14 (s, 6H).

^{13}C NMR ($CDCl_3$) δ 161.27, 140.04, 139.02, 137.35, 136.44, 128.56, 127.75, 125.89, 120.43, 118.77, 112.88, 106.75, 21.28, 20.45.

^{11}B NMR ($CDCl_3$) δ 24.54.

HRMS Calcd for $C_{22}H_{20}BN_3O$: $[M+H]^+$, 354.1772. Found: *m/z* 354.1781

3-(naphthalen-1-yl)-5-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)isoxazole (9g)

Isolated in 68% yield as a gray solid: mp 137–138 °C

^{1}H NMR (Acetone-d_6) δ 8.49 – 8.42 (m, 1H), 8.10 – 7.96 (m, 4H), 7.80 (dd, J = 7.1, 1.3 Hz, 1H), 7.68 – 7.55 (m, 3H), 7.41 (s, 1H), 7.14 (dd, J = 8.3, 7.3 Hz, 2H), 7.05 (dd, J = 8.3, 1.1 Hz, 2H), 6.66 (dd, J = 7.3, 1.1 Hz, 2H).

^{13}C NMR (Acetone-d_6) δ 162.25, 142.08, 137.45, 134.92, 131.84, 131.00, 129.46, 128.68, 128.51, 127.89, 127.84, 127.21, 126.43, 126.24, 121.53, 118.67, 114.27, 107.34.

^{11}B NMR (Acetone-d_6) δ 24.72.

HRMS Calcd for $C_{23}H_{16}BN_3O$: $[M+H]^+$, 362.1459. Found: *m/z* 362.1467

5-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)-3-(4-(trifluoromethyl)phenyl)isoxazole (9h)

Isolated in 23% yield as a gray solid: mp 237–238 °C

^{1}H NMR (Acetone-d_6) δ 8.13 (dq, J = 7.7, 0.8 Hz, 2H), 7.97 (s, 2H), 7.89 (dd, J = 8.0, 0.7 Hz, 2H), 7.52 (s, 1H), 7.13 (dd, J = 8.3, 7.3 Hz, 2H), 7.04 (dd, J = 8.4, 1.0 Hz, 2H), 6.64 (dd, J = 7.3, 1.0 Hz, 2H).

^{13}C NMR (Acetone-d_6) δ 160.28, 141.10, 136.55, 133.07, 131.15 (q, J = 32.3 Hz), 127.61, 127.47, 125.98 (q, J = 3.8 Hz), 122.94 (q, J = 271.5 Hz), 120.65, 117.83, 110.08, 106.47.

^{11}B NMR (Acetone-d_6) δ 25.42.

HRMS Calcd for $C_{20}H_{13}BF_3N_3O$: $[M+H]^+$, 380.1177. Found: *m/z* 380.1183

4-(5-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)isoxazol-3-yl)benzonitrile (9i)

Isolated in 20% yield as a green solid: mp 259–260 °C

^{1}H NMR (Acetone-d_6) δ 8.11 (d, J = 7.9 Hz, 2H), 7.99 – 7.90 (m, 4H), 7.52 (d, J = 0.8 Hz, 1H), 7.13 (t, J = 7.8 Hz, 2H), 7.04 (dt, J = 8.4, 1.0 Hz, 2H), 6.64 (dt, J = 7.3, 1.0 Hz, 2H).

^{13}C NMR (Acetone-d_6) δ 185.74, 160.16, 147.36, 141.07, 136.55, 133.46, 132.95, 127.61, 127.56, 117.85, 113.34, 110.07, 106.48.
^{11}B NMR (Acetone-d_6) δ 26.30.
HRMS Calcd for $C_{20}H_{13}BN_4O$: $[M+H]^+$, 337.1255. Found: *m/z* 337.1261

5-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)-3-(perfluorophenyl)isoxazole (9j)
Isolated in 14% yield as a yellow solid: mp 245–246 °C
^{1}H NMR (Acetone-d_6) δ 8.03 (s, 2H), 7.40 (q, J = 1.5 Hz, 1H), 7.13 (ddd, J = 8.4, 7.2, 1.2 Hz, 2H), 7.05 (dt, J = 8.3, 1.2 Hz, 2H), 6.63 (dt, J = 7.2, 1.2 Hz, 2H).
^{13}C NMR (Acetone-d_6) δ 160.00, 150.46, 146.05, 143.71, 141.02, 136.53, 127.61, 127.50, 120.66, 117.89, 112.93, 106.51. (F-bound carbon signals and F–C coupling constants could not be resolved due to the low yield of **9j**)
^{11}B NMR (Acetone-d_6) δ 25.48.
HRMS Calcd for $C_{19}H_9BF_5N_3O$: $[M+H]^+$, 402.0832. Found: *m/z* 402.0829

(*E*)-5-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)-3-styrylisoxazole (9k)
Isolated in 94% yield as a green solid: mp 92–93 °C
^{1}H NMR ($CDCl_3$) δ 7.57 – 7.50 (m, 2H), 7.43 – 7.32 (m, 3H), 7.22 (s, 2H), 7.15 (dd, J = 8.3, 7.1 Hz, 2H), 7.09 (dd, J = 8.3, 1.1 Hz, 2H), 6.93 (s, 1H), 6.43 (dd, J = 7.1, 1.2 Hz, 2H), 6.20 (s, 2H).
^{13}C NMR ($CDCl_3$) δ 160.96, 139.96, 136.43, 136.16, 135.85, 129.13, 129.02, 127.75, 127.13, 120.42, 118.82, 115.72, 108.49, 106.78.
^{11}B NMR ($CDCl_3$) δ 25.77.
HRMS Calcd for $C_{21}H_{16}BN_3O$: $[M+H]^+$, 338.1459. Found: *m/z* 338.1465

5-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)-3-(pyridin-2-yl)isoxazole (9l)
Isolated in 79% yield as a yellow solid: mp 222–223 °C
^{1}H NMR (Acetone-d_6) δ 8.71 (ddd, J = 4.9, 1.8, 1.0 Hz, 1H), 8.12 (d, J = 7.8 Hz, 1H), 8.00 – 7.93 (m, 3H), 7.63 (s, 1H), 7.48 (ddd, J = 7.6, 4.8, 1.2 Hz, 1H), 7.13 (dd, J = 8.3, 7.3 Hz, 2H), 7.04 (dd, J = 8.4, 1.0 Hz, 2H), 6.66 (dd, J = 7.4, 1.1 Hz, 2H).
^{13}C NMR (Acetone-d_6) δ 163.40, 150.80, 149.35, 142.12, 138.10, 137.49, 128.54, 125.58, 122.40, 121.56, 118.70, 111.90, 107.39.
^{11}B NMR (Acetone-d_6) δ 25.71.
HRMS Calcd for $C_{18}H_{13}BN_4O$: $[M+H]^+$, 313.1255. Found: *m/z* 313.1260

3-benzhydryl-5-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)isoxazole (9m)
Isolated in 75% yield as a gray solid: mp 137–138 °C
^{1}H NMR ($CDCl_3$) δ 7.37 – 7.31 (m, 4H), 7.30 – 7.27 (m, 2H), 7.24 – 7.21 (m, 4H), 7.12 (dd, J = 8.3, 7.1 Hz, 2H), 7.07 (dd, J = 8.3, 1.2 Hz, 2H), 6.52 (s, 1H), 6.39 (dd, J = 7.1, 1.2 Hz, 2H), 6.12 (s, 2H), 5.72 (s, 1H).
^{13}C NMR ($CDCl_3$) δ 164.96, 141.29, 139.96, 136.43, 128.93, 128.83, 127.74, 127.23, 120.40, 118.78, 111.83, 106.73, 48.40.
^{11}B NMR ($CDCl_3$) δ 25.77.
HRMS Calcd for $C_{26}H_{20}BN_3O$: $[M+H]^+$, 402.1772. Found: *m/z* 402.1769

3-isopropyl-5-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)isoxazole (9n)

Isolated in 71% yield as a gray solid: mp 132–133 °C

^{1}H NMR ($CDCl_3$) δ 7.13 (dd, J = 8.3, 7.1 Hz, 2H), 7.07 (dd, J = 8.3, 1.2 Hz, 2H), 6.58 (s, 1H), 6.41 (dd, J = 7.2, 1.2 Hz, 2H), 6.18 (s, 2H), 3.17 (hept, J = 6.9 Hz, 1H), 1.33 (d, J = 6.9 Hz, 6H).

^{13}C NMR ($CDCl_3$) δ 168.45, 140.07, 136.40, 127.71, 120.36, 118.66, 109.54, 106.66, 26.25, 22.10.

^{11}B NMR ($CDCl_3$) δ 25.30.

HRMS Calcd for $C_{16}H_{16}BN_3O$: $[M+H]^+$, 278.1459. Found: *m/z* 278.1465

3-cyclohexyl-5-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)isoxazole (9o)

Isolated in 56% yield as a gray solid: mp 172–173 °C

^{1}H NMR ($CDCl_3$) δ 7.14 (dd, J = 8.3, 7.2 Hz, 2H), 7.07 (dd, J = 8.4, 1.1 Hz, 2H), 6.57 (s, 1H), 6.41 (dd, J = 7.2, 1.2 Hz, 2H), 6.15 (s, 2H), 2.85 (tt, J = 11.4, 3.5 Hz, 1H), 2.08 – 1.93 (m, 2H), 1.89 – 1.66 (m, 4H), 1.46 – 1.29 (m, 4H).

^{13}C NMR ($CDCl_3$) δ 167.53, 140.08, 136.43, 127.73, 120.37, 118.69, 109.75, 106.67, 35.63, 32.43, 26.12, 26.02.

^{11}B NMR ($CDCl_3$) δ 24.19.

HRMS Calcd for $C_{19}H_{20}BN_3O$: $[M+H]^+$, 318.1772. Found: *m/z* 318.1777

1,4-bis(5-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)isoxazol-3-yl)benzene (9p)

Isolated in 72% yield as a gray solid: mp 284–284 °C

^{1}H NMR (DMSO-*d6*) δ 8.70 (s, 4H), 8.08 (s, 4H), 7.65 (s, 2H), 7.11 (dd, J = 8.2, 7.4 Hz, 4H), 6.97 (dd, J = 8.3, 1.0 Hz, 4H), 6.60 (dd, J = 7.4, 1.0 Hz, 4H).

^{13}C NMR (DMSO-*d6*) δ 160.42, 141.36, 135.99, 130.03, 127.72, 127.62, 120.24, 117.12, 110.81, 106.19.

^{11}B NMR (DMSO-*d6*) δ 26.01.

HRMS Calcd for $C_{32}H_{22}B_2N_6O_2$: $[M+H]^+$, 545.2063. Found: *m/z* 545.2070

Synthesis of *N*-tosyl-2-iodoaniline (10): A general procedure

A 25-mL of Schlenk tube was heated under vacuum for 5 minutes with the aid of a heating gun, cooled to room temperature and back-filled with argon. A 2-iodoaniline (2 mmol, 1 equiv) was introduced into a mixture of pyridine and CH_2Cl_2 (1:1 ratio, 1.5 mL:1.5 mL), and the solution was cooled to 0 °C. Then 4-methylbenzenesulfonyl chloride (2 mmol, 1 equiv) was added portionwise, and the mixture was allowed to stir overnight, gradually warming to room temperature. Once the reaction was complete, water (10 mL) and CH_2Cl_2 (10 mL) were added, followed by phase separation. The organic phase was successively washed with 1 N NaOH (2 ×10 mL), 1 N HCl (2 ×10 mL), and brine (2 × 10 mL). The solution was then dried over $MgSO_4$. Evaporation of the solvent followed by column chromatography on silica gel (Hexane/EtOAc = 2:1 as an eluent) gave *N*-tosyl-2-iodoaniline (**10**).

Larock indole synthesis with ethynyl–B(dan)

A 25-mL Schlenk tube was evacuated for 5 minutes using a heating gun, cooled to room temperature, and then purged with argon. *N*-Tosyl-2-iodoaniline (0.24 mmol, 1.2 equiv), ethynyl–B(dan) (0.2 mmol, 1 equiv), $Pd(PPh_3)_2Cl_2$ (0.004 mmol,2 mol %) and CuI (0.008 mmol, 4 mol %) were dissolved in THF (0.4 mL). After stirring for 5 minutes at room temperature, *N*,*N*-

diisopropylethylamine (0.6 mmol, 3 equiv) was added, and the resulting mixture was stirred at 30 °C for 1 h, followed by stirring at 60 °C for 14 h. The mixture was then diluted with ethyl acetate (20 mL) and brine (20 mL), allowing the organic layer to separate. The aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and the solvent was removed using rotary evaporation. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc = 5:1 as an eluent) to give indolyl–B(dan) (**11**).

2-(1-tosyl-1*H*-indol-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (11a)

Isolated in 76% yield as a yellow solid: mp 165–166 ˚C

^{1}H NMR ($CDCl_3$) δ 8.30 (d, J = 8.4 Hz, 1H), 7.67 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 7.8 Hz, 1H), 7.40 (t, J = 7.8 Hz, 1H), 7.29 (d, J = 7.5 Hz, 1H), 7.15 (t, J = 9.5 Hz, 4H), 7.08 (d, J = 8.2 Hz, 2H), 6.98 (s, 1H), 6.38 (d, J = 7.2 Hz, 2H), 6.16 (s, 2H), 2.31 (s, 3H).

^{13}C NMR ($CDCl_3$) δ 145.06, 140.97, 138.93, 136.47, 135.48, 130.63, 129.83, 127.77, 126.80, 125.75, 123.89, 121.33, 120.04, 118.07, 115.21, 112.18, 106.22, 21.67.

^{11}B NMR ($CDCl_3$) δ 28.12.

HRMS Calcd for $C_{25}H_{20}BN_3O_2S$: $[M+H]^+$, 438.1442. Found: *m/z* 438.1445

2-(5-methyl-1-tosyl-1*H*-indol-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (11b)

Isolated in 85% yield as a purple solid: mp 172–173 ˚C

^{1}H NMR ($CDCl_3$) δ 8.16 (d, J = 8.6 Hz, 1H), 7.65 (d, J = 7.1 Hz, 2H), 7.21 (d, J = 8.6 Hz, 1H), 7.18 – 7.11 (m, 4H), 7.08 (d, J = 8.3 Hz, 2H), 6.92 (s, 1H), 6.38 (d, J = 7.2 Hz, 2H), 6.18 (s, 2H), 2.44 (s, 3H), 2.30 (s, 3H).

^{13}C NMR ($CDCl_3$) δ 144.92, 141.02, 137.31, 136.47, 135.45, 133.56, 130.93, 129.79, 127.77, 127.29, 126.76, 121.13, 120.12, 120.10, 118.01, 114.92, 106.20, 21.66, 21.33.

^{11}B NMR ($CDCl_3$) δ 27.42.

HRMS Calcd for $C_{26}H_{22}BN_3O_2S$: $[M+H]^+$, 452.1599. Found: *m/z* 452.1602

2-(5-nitro-1-tosyl-1*H*-indol-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (11c)

Isolated in 67% yield as a yellow solid: mp 277–278 ˚C

^{1}H NMR (DMSO-*d6*) δ 8.75 (d, J = 2.6 Hz, 1H), 8.58 (s, 2H), 8.42 – 8.22 (m, 2H), 8.01 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 7.7 Hz, 2H), 7.42 (d, J = 0.8 Hz, 1H), 7.26 (dd, J = 8.2, 7.4 Hz, 2H), 7.11 (dd, J = 8.3, 1.0 Hz, 2H), 6.66 (dd, J = 7.4, 1.0 Hz, 2H).

^{13}C NMR (DMSO-*d6*) δ 145.72, 143.78, 142.01, 139.39, 135.97, 133.67, 131.04, 130.19, 127.53, 126.95, 119.93, 119.55, 117.27, 117.11, 116.41, 114.26, 105.53, 20.93.

^{11}B NMR (DMSO-*d6*) δ 28.48.

HRMS Calcd for $C_{25}H_{19}BN_4O_4S$: $[M+H]^+$, 483.1293. Found: *m/z* 483.1297

2-(5-bromo-1-tosyl-1*H*-indol-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (11d)

Isolated in 67% yield as a yellow solid: mp 224–225 ˚C

^{1}H NMR ($CDCl_3$) δ 8.15 (d, J = 8.9 Hz, 1H), 7.69 – 7.58 (m, 3H), 7.46 (dd, J = 8.9, 2.0 Hz, 1H), 7.20 – 7.12 (m, 4H), 7.08 (dd, J = 8.3, 1.1 Hz, 2H), 6.86 (d, J = 0.8 Hz, 1H), 6.37 (dd, J = 7.2, 1.1 Hz, 2H), 6.12 (s, 2H), 2.32 (s, 3H).

^{13}C NMR ($CDCl_3$) δ 145.40, 140.79, 137.59, 136.48, 135.33, 132.37, 129.94, 128.48, 127.77,

126.80, 123.88, 120.16, 118.67, 118.24, 117.32, 116.54, 106.32, 21.67.
^{11}B NMR ($CDCl_3$) δ 27.71.
HRMS Calcd for $C_{25}H_{19}BBrN_3O_2S$: $[M+H]^+$, 516.0547. Found: *m/z* 516.0556

2-(1-tosyl-1*H*-pyrrolo[2,3-*b*]pyridin-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (11e)
Isolated in 79% yield as a purple solid: mp 243–244 ˚C
^{1}H NMR (Acetone-*d6*) δ 8.36 (dt, J = 4.8, 1.4 Hz, 1H), 8.10 (d, J = 7.2 Hz, 1H), 7.97 (dt, J = 7.8, 1.4 Hz, 1H), 7.64 (s, 2H), 7.35 (d, J = 8.6 Hz, 2H), 7.24 (ddd, J = 7.7, 4.8, 1.1 Hz, 1H), 7.13 (ddd, J = 8.3, 7.2, 1.1 Hz, 2H), 7.02 (dt, J = 8.3, 1.1 Hz, 2H), 6.91 (d, J = 1.2 Hz, 1H), 6.58 (dt, J = 7.3, 1.2 Hz, 2H), 2.36 (s, 3H).
^{13}C NMR (Acetone-*d6*) δ 150.29, 146.01, 145.33, 143.05, 137.53, 136.68, 130.29, 130.03, 129.18, 128.46, 123.84, 121.29, 119.85, 117.90, 113.65, 106.68, 21.47.
^{11}B NMR (Acetone-*d6*) δ 27.91.
HRMS Calcd for $C_{24}H_{19}BN_4O_2S$: $[M+H]^+$, 439.1395. Found: *m/z* 439.1399

2-6. Larock indole synthesis with ethynyl–B(pin)
This reaction was carried out according to a method similar to that with ethynyl–B(dan).

2-7. Pd-catalyzed synthesis of benzofuran with ethynyl–B(dan)
This reaction was carried out by use of 2-iodophenol (0.24 mmol, 1.2 equiv), following a method analogous to the Larock indole synthesis with ethynyl–B(dan).

2-(benzofuran-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (13)
Isolated in 40% yield as a yellow solid.
^{1}H NMR ($CDCl_3$) δ 7.66 (dd, J = 7.7, 1.1 Hz, 1H), 7.57 (dt, J = 8.3, 1.0 Hz, 1H), 7.38 (ddt, J = 8.3, 7.1, 1.2 Hz, 1H), 7.27 (t, J = 7.5 Hz, 1H), 7.23 (d, J = 1.2 Hz, 1H), 7.16 (ddd, J = 8.3, 7.2, 1.0 Hz, 2H), 7.08 (dt, J = 8.4, 1.1 Hz, 2H), 6.45 (dt, J = 7.2, 1.2 Hz, 2H), 6.22 (s, 2H).
^{13}C NMR ($CDCl_3$) δ 157.01, 140.43, 136.37, 127.91, 127.62, 125.56, 122.84, 121.66, 120.06, 118.15, 114.91, 111.47, 106.26.

2-8. Pd-catalyzed synthesis of indenone with ethynyl–B(dan)
This reaction was carried out by use of 2-bromobenzaldehyde (0.24 mmol, 1.2 equiv), following a method analogous to the Larock indole synthesis with ethynyl–B(dan).

2-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)-1*H*-inden-1-one (15)
Isolated in 34% yield as a yellow solid: mp 217–218 ˚C
^{1}H NMR (DMSO-*d6*) δ 10.60 (s, 1H), 8.44 (s, 2H), 7.91 (dd, J = 7.8, 1.4 Hz, 1H), 7.77 (td, J = 7.4, 1.4 Hz, 1H), 7.71 (dd, J = 7.8, 1.4 Hz, 1H), 7.64 (td, J = 7.9, 1.1 Hz, 1H), 7.05 (t, J = 7.8 Hz, 2H), 6.91 (d, J = 8.2 Hz, 2H), 6.42 (d, J = 7.3 Hz, 2H).
^{13}C NMR (DMSO-*d6*) δ 192.16, 142.16, 136.55, 136.44, 134.92, 133.94, 130.29, 128.07, 127.55, 125.60, 120.44, 117.19, 105.99, 96.95.
^{11}B NMR (DMSO-*d6*) δ 23.60.
HRMS Calcd for $C_{19}H_{13}BN_2O$: $[M+H]^+$, 297.1194. Found: *m/z* 297.1195

2-8. Cu-catalyzed azide–ethynyl–B(dan) cycloaddition

A 25-mL Schlenk tube was evacuated for 5 minutes using a heating gun, then cooled to room temperature and purged with argon. Ethynyl–B(dan) (0.2 mmol, 38.4 1 equiv), CuI (0.2 mmol, 1 equiv) and benzyl azide (0.3 mmol, 1.5 equiv) were dissolved in DMF (1 mL) and stirred for 5 minutes at room temperature., *N*,*N*-diisopropylethylamine (0.4 mmol, 2 equiv) was added, and the resulting mixture was stirred at 30 °C for 1 h, followed by heating at 60 °C for 14 h. The mixture was then diluted with ethyl acetate (20 mL) and brine (20 mL), allowing the organic layer to separate. The aqueous layer was extracted with ethyl acetate, and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc = 5:1 as an eluent) to product **17** (32.7 mg, 50% yield).

2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (17)

Isolated as a gray solid: mp 157–158 ˚C

^{1}H NMR (Acetone-*d6*) δ 8.20 (s, 1H), 7.62 (s, 2H), 7.44 – 7.32 (m, 5H), 7.09 (t, J = 7.4 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 6.58 (dd, J = 7.3, 1.2 Hz, 2H), 5.69 (s, 2H).

^{13}C NMR (Acetone-*d6*) δ 142.67, 137.44, 137.03, 130.28, 129.74, 129.12, 128.92, 128.42, 121.07, 117.90, 106.74, 53.78.

^{11}B NMR (Acetone-*d6*) δ 26.89.

HRMS Calcd for $C_{19}H_{16}BN_5$: $[M+H]^+$, 326.1572. Found: *m/z* 326.1575

Chemoselective Cross-Coupling

Selective SMC at the B(dan) moiety of 9e

A 25 mL Schlenk tube was equipped with a magnetic stirring bar and loaded with $Ba(OH)_2$ (0.3 mmol, 2 equiv). The tube was then evacuated for 5 minutes using a heating gun, cooled to room temperature, and purged with argon. $Pd(OAc)_2$ (7.5 µmol, 5 mol %), 1,1'-bis(diphenylphosphino)ferrocene (11.3 µmol, 7.5 mol %), **9e** (0.15 mmol, 1 equiv), 4-iodoanisole (0.23 mmol, 1.5 equiv) and DMF (0.3 mL) were then added. The resulting mixture was stirred at 90 °C for 24 h and then quenched with brine. After the organic phase was allowed to separate, the aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and the solvent was removed using rotary evaporation. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc = 5:1 as an eluent) to **18** (19.4 mg, 39% yield).

SMC at the Br moiety of 18

A 25 mL of Schlenk tube was heated under vacuum for 5 minutes with the aid of a heating gun, cooled to room temperature, and back-filled with argon. $Pd(P{t}Bu_3)_2$ (0.003 mmol,2 mol %), CsF (0.3 mmol, 2 equiv), **18** (0.15 mmol, 1 equiv), 3,5-dimethylboronic acid (0.3 mmol, 2 equiv), and THF (0.5 mL) were added. After the resulting mixture was stirred at reflux overnight, it was diluted with ethyl acetate (20 mL) and brine (20 mL). The organic phase was allowed to separate, and the aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and the solvent was removed using rotary evaporation. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc = 5:1 as an eluent)

to give **19** (43.9 mg, 79% yield).

3-(4-bromophenyl)-5-(4-methoxyphenyl)isoxazole (18)

^{1}H NMR ($CDCl_3$) δ 7.75 (ddd, J = 17.8, 8.8, 2.1 Hz, 4H), 7.61 (d, J = 8.5 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H), 6.68 (d, J = 1.9 Hz, 1H), 3.87 (d, J = 2.0 Hz, 3H).

^{13}C NMR ($CDCl_3$) δ 170.88, 162.17, 161.39, 132.28, 128.45, 128.38, 127.61, 124.35, 120.24, 114.60, 96.05, 55.58.

3-(3',5'-dimethyl-[1,1'-biphenyl]-4-yl)-5-(4-methoxyphenyl)isoxazole (19)

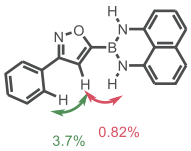
Isolated as a yellow solid: mp 170–171 ˚C

^{1}H NMR ($CDCl_3$) δ 7.91 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 2.9 Hz, 2H), 7.09 – 6.94 (m, 3H), 6.73 (s, 1H), 3.87 (s, 3H), 2.40 (s, 6H).

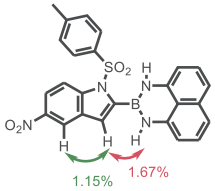
^{13}C NMR ($CDCl_3$) δ 170.38, 162.67, 161.15, 142.97, 140.33, 138.39, 129.37, 127.99, 127.56, 127.44, 127.09, 125.00, 120.37, 114.42, 96.11, 55.39, 21.38.

HRMS Calcd for $C_{24}H_{21}NO_2$: $[M+H]^+$, 356.1645. Found: *m/z* 356.1650

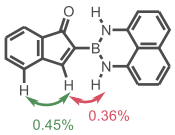
NOE Experiments for Determining Regiochemistry



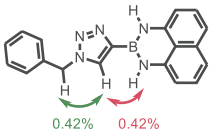
9a



11a



15



17

X-Ray Crystallography

The single crystal suitable for X-ray structural determination was mounted on a XtaLAB Synergy diffractometer. The sample was irradiated with graphite monochromated Mo-Kα radiation (λ= 0.71073 Å) at 100 K for data collection. The data were processed using the CrysAlisPro program suite (1.171.42.27a). The structure was solved by the SHELXT program (ver. 2018/2). Refinement on F^2 was carried out by full-matrix least-squares using the SHELXL in the SHELX software package (ver. 2018/3) and expanded using Fourier techniques. All non-hydrogen atoms were refined using anisotropic thermal parameters. The hydrogen atoms were assigned to idealized geometric positions and included in the refinement with isotropic thermal parameters. The SHELXL was interfaced with Olex 2 1,3-ac4. The pictures of molecules were prepared using Pov-Ray 3.7.0.0. The crystallographic data are summarized as follow and can be obtained from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystallographic details.

	Triazolyl–B(dan) 17		**Triazolyl–B(dan) 17**
CCDC number	2283889	F(000)	680.0
Empirical formula	$C_{19}H_{16}BN_5$	Crystal size / mm^3	0.263 x 0.041 x 0.038
Formula weight	325.18	θ range / °	2.568 to 25.023
T / K	100.04(11)	Index ranges	−18<=h<=18
λ / Å	0.71073		−11<=k<=12
Crystal system	Monoclinic		−11<=l<=11
Space group	$P2_1/c$	Refl. collected	16790
a / Å	15.8905(9)	Indep. Reflections/R_{int}	2859/0.0763
b / Å	10.7826(6)	Completeness to θ	100
c / Å	9.5146(6)	Absorption correction	None
α / °	90	Refinement method	Full-matrix least-squares on F^2
β / °	93.298(5)	Data/restraints /parameters	2859/0/226
γ / °	90	GOF	1.030
V / Å	1627.54(17)	Final R indices [I>2sigma(I)] R_1 / wR_2	0.0457/0.0997
Z	4	R indices (all data) R_1 / wR_2	0.0692/0.1081
ρ / Mg m^{-3}	1.327	Extinction coefficient	n/a
μ / mm^{-1}	0.082	Largest diff. peak and hole / e$Å^{-3}$	0.20and −0.23

Evaluation of Lewis Acidity by Computed Ammonia Affinity

Geometry optimizations and frequency calculations were conducted according to the reported method using M06-2X with def2-SVP basis set on Gaussian 16 Rev. A.03 program. All calculations were conducted in the gas phase at 298 K. All optimized structures were confirmed to be local minima by verifying the absence of imaginary frequencies. Enthalpies were obtained from geometry optimizations at this level of theory.

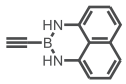
NH_3

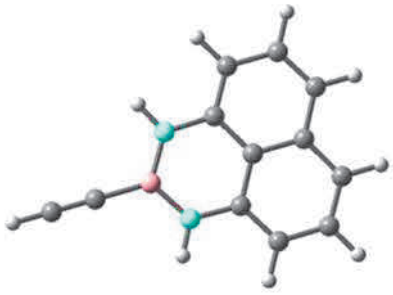
Charge = 0; Multiplicity = 1

Sum of electronic and thermal Enthalpies = -56.434971 (hartree)

N	0.00000000	0.00000000	0.11994100
H	0.00000000	0.93767700	-0.27986200
H	-0.81205200	-0.46883900	-0.27986200
H	0.81205200	-0.46883900	-0.27986200

Ethynyl–B(dan) (1)





Charge = 0; Multiplicity = 1

Dihedral angle = 174.8°

N–B–N angle = 116.9°

B–N bond: 1.41918 Å, 1.41918 Å

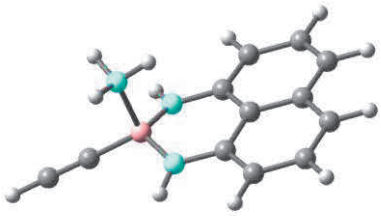
Sum of electronic and thermal Enthalpies = -596.242983 (hartree)

AA = 18.0 (kJ/mol)

B	-2.20169131	0.00000972	0.00000028
N	-1.45959204	-1.20968074	0.00006480
N	-1.45958335	1.20969483	-0.00006436
C	-0.06821509	-1.24549436	0.00000135
C	-0.06820612	1.24549839	-0.00000117
C	0.63574288	-2.43602374	-0.00000481
C	2.04637220	-2.42546733	-0.00001301
C	2.74874543	-1.24465757	-0.00001663
C	2.06099998	-0.00000565	-0.00000012
C	0.63735190	-0.00000053	0.00000002
C	2.74875440	1.24464132	0.00001626
C	2.04638967	2.42545613	0.00001280

C	0.63576043	2.43602270	0.00000487
H	-1.92722488	-2.10689157	-0.00004512
H	-1.92720970	2.10690904	0.00004572
H	0.09189864	-3.38215109	0.00001507
H	2.58115780	-3.37669985	-0.00002952
H	3.83956161	-1.24277235	-0.00002508
H	3.83957055	1.24274824	0.00002450
H	2.58118211	3.37668480	0.00002920
H	0.09192299	3.38215397	-0.00001490
C	-3.74646404	0.00001557	0.00000064
C	-4.95951760	0.00001456	0.00000042
H	-6.03445895	-0.00012535	-0.00000809

Ethynyl–B(dan)–NH_3

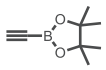


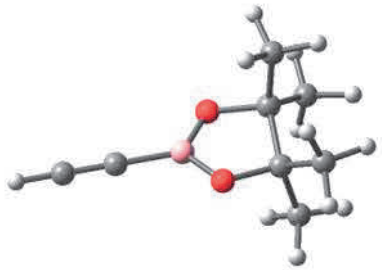
Charge = 0; Multiplicity = 1
Dihedral angle = 112.3°
(dan)N–B–N(dan) angle = 111.8°
B–N(dan) bond: 1.48049 Å, 1.48050 Å
Sum of electronic and thermal Enthalpies = -652.684797 (hartree)

B	2.01761794	0.00000236	0.01249013
N	1.23493034	-1.22630585	-0.26218239
N	1.23493058	1.22617896	-0.26272662
C	-0.13989406	-1.24915475	-0.17497374
C	-0.13987717	1.24910146	-0.17514152
C	-0.86185680	-2.43682628	-0.16912516
C	-2.26639246	-2.42239170	-0.06783200
C	-2.96338961	-1.24095593	0.02443243
C	-2.27012197	-0.00000254	-0.00227088
C	-0.84686772	-0.00001984	-0.09118340
C	-2.96335573	1.24098051	0.02444196
C	-2.26633594	2.42239439	-0.06781990
C	-0.86179601	2.43678967	-0.16919845
H	1.68521101	-2.11365222	-0.43927000
H	1.68522412	2.11352452	-0.43979333
H	-0.32570609	-3.38513983	-0.24153218
H	-2.80426076	-3.37253006	-0.06218355
H	-4.05168063	-1.23515260	0.09891741

H	-4.05164695	1.23520110	0.09893251
H	-2.80417435	3.37254928	-0.06212137
H	-0.32562949	3.38508830	-0.24168504
H	2.70146096	-0.82917109	2.11005262
H	2.70145642	0.82992051	2.10981866
H	1.26455667	0.00037626	2.18753699
N	2.20430927	0.00032723	1.78240720
C	3.52297258	-0.00008987	-0.47110052
C	4.69038812	-0.00018703	-0.80396589
H	5.71706854	-0.00025677	-1.12118832

Ethynyl–B(pin)

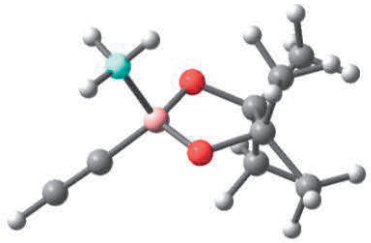




Charge = 0; Multiplicity = 1
Dihedral angle = 139.7°
O–B–O angle = 113.3°
B–O bond: 1.36361 Å, 1.36361 Å
Sum of electronic and thermal Enthalpies = -487.242408 (hartree)
AA = 49.8 (kJ/mol)

B	-1.30309323	-0.00000369	-0.00000128
O	-0.55335631	-1.06001703	0.41677013
C	0.81322534	-0.78219910	0.05504150
C	0.81322208	0.78220079	-0.05504104
O	-0.55336025	1.06001284	-0.41677164
C	1.06556677	1.46779036	1.28504587
C	1.73466770	1.34521471	-1.12296050
C	1.06557490	-1.46778755	-1.28504507
C	1.73467183	-1.34520915	1.12296228
H	0.41328214	1.05309174	2.06683306
H	2.11147426	1.35728688	1.60285014
H	0.83887652	2.53731401	1.18066884
H	1.66583142	2.44152522	-1.12397635
H	2.77819252	1.06368624	-0.91827505
H	1.45687408	0.98453133	-2.12038536
H	0.41328960	-1.05309170	-2.06683317
H	2.11148237	-1.35727955	-1.60284785
H	0.83888912	-2.53731219	-1.18066843
H	2.77819577	-1.06367642	0.91827820
H	1.45687539	-0.98452684	2.12038674
H	1.66584001	-2.44151993	1.12397810
C	-2.84330930	-0.00000712	-0.00000262
C	-4.05526725	-0.00000763	-0.00000293
H	-5.13001694	0.00005127	0.00002478

Ethynyl–B(pin)–NH_3



Charge = 0; Multiplicity = 1

Dihedral angle = 125.2°

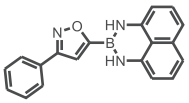
O–B–O angle = 107.9°

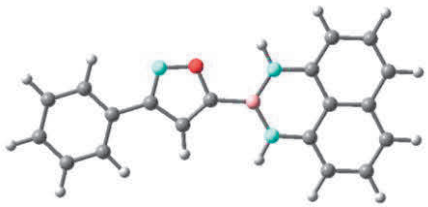
B–O bond: 1.43019 Å, 1.43473 Å

Sum of electronic and thermal Enthalpies = -543.696356 (hartree)

B	-1.14682793	0.30064825	-0.09889092
O	-0.32686349	-0.23311321	-1.14827108
C	0.88628202	-0.65858376	-0.54121545
C	1.05017867	0.38573309	0.61479904
O	-0.29681953	0.61640777	1.00710252
C	1.83832781	-0.11388895	1.81628545
C	1.65338847	1.70131920	0.11178344
C	2.00012397	-0.64240862	-1.57673935
C	0.68956911	-2.07667456	-0.00109749
H	1.32785815	-0.96211216	2.28777776
H	2.85320685	-0.42174890	1.52184013
H	1.92260613	0.68903265	2.56256653
H	1.48795211	2.47786894	0.87238557
H	2.73402209	1.61571427	-0.07155712
H	1.18250796	2.01704673	-0.83243668
H	2.05561460	0.32684913	-2.08821090
H	2.97309080	-0.85541666	-1.10863372
H	1.80595913	-1.41447972	-2.33440382
H	1.62079383	-2.49143683	0.41073923
H	-0.08384658	-2.08881763	0.78056840
H	0.34984686	-2.71780097	-0.82618805
H	-2.20459566	1.57079932	-1.60858773
H	-2.38174566	2.18353128	-0.07273647
H	-0.93898826	2.38266262	-0.88702121
N	-1.72520996	1.75145127	-0.72470993
C	-2.49068978	-0.48217993	0.26950829
C	-3.53651110	-1.04358478	0.52763334
H	-4.44822383	-1.55983882	0.76492695

Isoxazolyl–B(dan) (3a)





Charge = 0; Multiplicity = 1

Dihedral angle = 180.0°

N–B–N angle = 117.7°

B–N bond: 1.41458 Å, 1.41727 Å

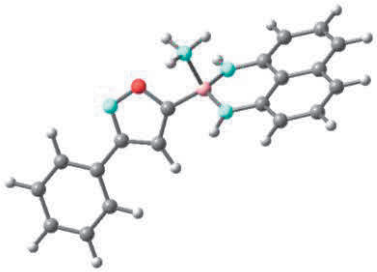
Sum of electronic and thermal Enthalpies = -995.427691 (hartree)

AA = 29.0 (kJ/mol)

B	-0.69994891	-0.14056139	-0.00025543
N	-1.32272368	1.13255105	-0.00040599
N	-1.53690016	-1.28097249	0.00002754
C	-2.70830057	1.28756643	-0.00025025
C	-2.92648595	-1.19592368	0.00012764
C	-3.30501533	2.53452733	-0.00035878
C	-4.71149667	2.64808915	-0.00021569
C	-5.51357391	1.53311624	0.00003814
C	-4.93711606	0.23292628	0.00014721
C	-3.51901708	0.10757996	0.00000683
C	-5.73173051	-0.94617651	0.00038417
C	-5.13643733	-2.18437614	0.00046355
C	-3.73215020	-2.31949439	0.00033955
H	-0.78938033	1.99217276	-0.00070653
H	-1.13953018	-2.21319531	0.00007663
H	-2.68091157	3.42994438	-0.00056342
H	-5.16094469	3.64243000	-0.00029988
H	-6.60039269	1.62623018	0.00015493
H	-6.81810552	-0.84804760	0.00049708
H	-5.75313366	-3.08460780	0.00063673
H	-3.27314272	-3.30942702	0.00041485
C	0.85775005	-0.31579512	-0.00029159
C	1.93206755	0.52532982	-0.00019437
O	1.31731538	-1.58217221	-0.00027908
H	1.92747811	1.61069160	-0.00020863
N	2.66728517	-1.60141790	-0.00018891
C	4.49832059	-0.00848083	0.00001949
C	5.46475482	-1.02328666	-0.00051791

C	4.91003711	1.32804387	0.00071392
C	6.81776076	-0.70037549	-0.00037132
H	5.13613863	-2.06298366	-0.00106151
C	6.26609142	1.64863531	0.00085023
H	4.16858805	2.12841021	0.00119284
C	7.22290702	0.63556100	0.00030421
H	7.56325419	-1.49684369	-0.00079349
H	6.57528476	2.69471528	0.00138581
H	8.28471535	0.88596521	0.00040287
C	3.06291335	-0.35186568	-0.00013619

Isoxazolyl–B(dan)–NH_3

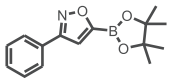


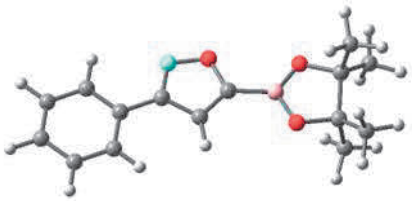
Charge = 0; Multiplicity = 1
Dihedral angle = 146.8°
(dan)N–B–N(dan) angle = 111.8°
B–N(dan) bond: 1.47843 Å, 1.48239 Å
Sum of electronic and thermal Enthalpies = -1051.873691 (hartree)

B	-0.69660635	-0.40110651	0.64308176
N	-1.43763545	-1.27240848	-0.29988047
N	-1.29158305	0.94985287	0.72469133
C	-2.77023062	-1.07434822	-0.59504683
C	-2.62537012	1.18563981	0.45660333
C	-3.52527148	-2.02067299	-1.27681265
C	-4.88596196	-1.78750589	-1.55598084
C	-5.50513353	-0.62364574	-1.16620783
C	-4.76779879	0.38219366	-0.48400536
C	-3.39182967	0.15559781	-0.18796018
C	-5.36202982	1.61986692	-0.11374241
C	-4.60694333	2.59228314	0.49703118
C	-3.24295311	2.38568167	0.78354113
H	-1.01509503	-2.09709740	-0.70476012
H	-0.78152255	1.72880210	1.11982189
H	-3.05139627	-2.95202222	-1.59308987
H	-5.45265851	-2.55196056	-2.09116302
H	-6.55877777	-0.44687333	-1.38639890
H	-6.41681502	1.78563167	-0.33709965

H	-5.06453139	3.54544413	0.76906836
H	-2.65893693	3.17062712	1.26838285
H	-0.44741576	-2.04376466	2.26484033
H	-0.61239539	-0.56329360	2.98562418
H	-1.94343204	-1.31017009	2.33142123
N	-0.94044085	-1.14891624	2.21582384
C	0.90310772	-0.43788140	0.52219056
C	1.84571254	0.35836401	-0.05494376
O	1.53682706	-1.48918528	1.08775183
C	3.08548560	-0.31003425	0.21098554
H	1.67380316	1.28044907	-0.60064127
C	4.45230849	0.09241472	-0.17591544
C	5.55308593	-0.67989608	0.21941986
C	4.66507382	1.24405917	-0.94044138
C	6.84097572	-0.30188712	-0.14530232
H	5.37868202	-1.57702176	0.81416907
C	5.95658819	1.62067235	-1.30442753
H	3.81634085	1.85137962	-1.25827617
C	7.04727711	0.84932204	-0.90781274
H	7.69174943	-0.90938394	0.16688432
H	6.10997392	2.52036686	-1.90194338
H	8.05835740	1.14367720	-1.19299849
N	2.87907772	-1.40811632	0.89389405

Isoxazolyl–B(pin)





Charge = 0; Multiplicity = 1

Dihedral angle = 176.8°

O–B–O angle = 113.9°

B–O bond: 1.35833 Å, 1.36303 Å

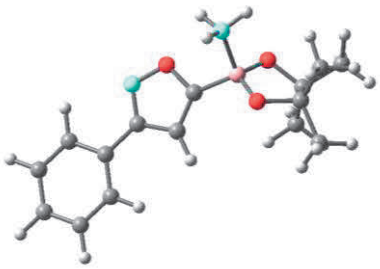
Sum of electronic and thermal Enthalpies = -886.428135 (hartree)

AA = 62.7 (kJ/mol)

B	-1.56871882	0.17071909	0.01558551
O	-2.09963829	-1.07373310	-0.14970679
C	-3.51344187	-0.96282784	0.11827561
C	-3.77973479	0.56177321	-0.14391307
O	-2.49797827	1.15097750	0.15919012
C	-4.07126213	0.86668624	-1.61035325
C	-4.83606360	1.18560146	0.75084000
C	-3.72060397	-1.35483728	1.57840338
C	-4.26904152	-1.90697287	-0.79998889
H	-3.31889836	0.40456354	-2.26539404
H	-5.06584544	0.50520982	-1.90550240
H	-4.03227109	1.95426925	-1.75737902
H	-4.95073970	2.24738396	0.49426674
H	-5.80581278	0.68698773	0.60602642
H	-4.55440157	1.11841241	1.80827659
H	-3.18812590	-0.66614995	2.24985619
H	-4.78597214	-1.35448046	1.84651770
H	-3.31841933	-2.36517165	1.73263469
H	-5.35419048	-1.77185399	-0.68118499
H	-4.00228559	-1.74139131	-1.85045786
H	-4.02006114	-2.94540897	-0.54235658
C	-0.02654506	0.40590337	0.03521293
C	1.02814312	-0.45649581	-0.03870553
O	0.45147662	1.65837528	0.13825012
C	2.17362896	0.39590522	0.03003811
H	0.98059816	-1.53681767	-0.12833670
C	3.60384675	0.03300494	-0.00191092
C	4.58531203	1.02947187	0.08660891

C	3.99605096	-1.30427331	-0.11995402
C	5.93349600	0.68819726	0.05732438
H	4.27116203	2.06962182	0.17845966
C	5.34743072	-1.64321815	-0.14897862
H	3.24162990	-2.08935551	-0.19025550
C	6.31925944	-0.64835376	-0.06038617
H	6.69057523	1.47067728	0.12706166
H	5.64128845	-2.68972720	-0.24136098
H	7.37735173	-0.91326926	-0.08300810
N	1.79775448	1.64865143	0.13532346

Isoxazolyl–B(pin)–NH_3

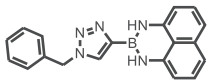


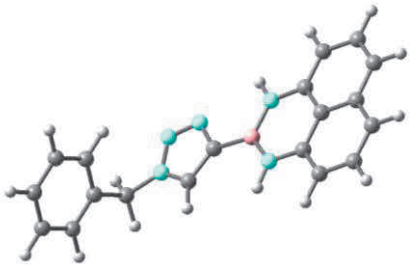
Charge = 0; Multiplicity = 1
Dihedral angle = 157.9°
O–B–O angle = 108.2°
B–O bond: 1.42623 Å, 1.43412 Å
Sum of electronic and thermal Enthalpies = -942.886975 (hartree)

B	-1.65124768	0.78720831	-0.29740980
O	-2.44471702	0.79636608	0.89716713
C	-3.16239021	-0.43090574	0.93245926
C	-3.35640284	-0.74193709	-0.59197498
O	-2.15726216	-0.22823456	-1.16167316
C	-3.46990686	-2.22127590	-0.92791568
C	-4.54807710	0.01355620	-1.18652933
C	-4.45607977	-0.23350433	1.70808363
C	-2.29329230	-1.48237484	1.62504758
H	-2.55217338	-2.75405863	-0.65109263
H	-4.32238812	-2.67959674	-0.40423525
H	-3.62150672	-2.34388052	-2.00978519
H	-4.47961351	-0.02786278	-2.28281433
H	-5.50780005	-0.42471979	-0.87806199
H	-4.54838928	1.06858303	-0.87247894
H	-5.02639907	0.62016460	1.32091229
H	-5.08475822	-1.13533808	1.65778085
H	-4.22263723	-0.03417320	2.76324723
H	-2.82626211	-2.43488021	1.75623158

H	-1.37350959	-1.66598529	1.05141163
H	-2.00535248	-1.09785824	2.61308367
H	-1.33958746	2.99285036	-0.47330397
H	-1.64245709	2.31049673	-1.95822878
H	-2.89697160	2.55309860	-0.88258579
N	-1.91092821	2.30513795	-0.97296103
C	-0.04238903	0.75884362	-0.14771361
C	0.92930819	-0.17891535	-0.32840250
O	0.55636229	1.90449993	0.24588930
C	2.14548004	0.50186296	0.00289581
H	0.78699348	-1.20299567	-0.65781705
C	3.52756086	-0.01789085	-0.00551741
C	3.79210062	-1.32951446	-0.41274608
C	4.59219885	0.80077450	0.39578842
C	5.09779929	-1.81703541	-0.42038042
H	2.97188685	-1.97607312	-0.72796805
C	5.89442267	0.31197623	0.38737486
H	4.37710822	1.82142442	0.71357790
C	6.15208521	-0.99817207	-0.02058122
H	5.29113918	-2.84193649	-0.74041229
H	6.71616307	0.95688534	0.70257326
H	7.17422102	-1.37975375	-0.02582239
N	1.90220848	1.74423225	0.33902403

Triazolyl–B(dan) (11)



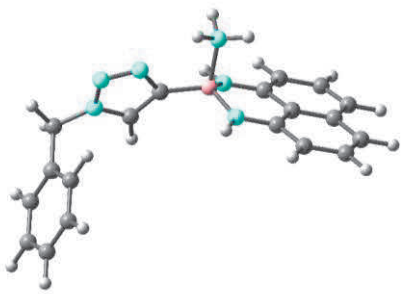


Charge = 0; Multiplicity = 1
Dihedral angle = 179.3°
N–B–N angle = 117.0°
B–N bond: 1.41661 Å, 1.42211 Å
Sum of electronic and thermal Enthalpies = -1030.849425 (hartree)
AA = 28.3 (kJ/mol)

B	-0.88976017	-0.36212192	-0.39741533
N	-1.79638077	-1.35537280	0.04787237
N	-1.41219464	0.94477505	-0.60111211
C	-3.14024424	-1.10825621	0.28689403
C	-2.75059973	1.26100249	-0.38050106
C	-4.00815858	-2.09467601	0.72213010
C	-5.36642723	-1.79332488	0.95105004
C	-5.85936674	-0.52611056	0.75029377
C	-5.00038660	0.51491882	0.30355679
C	-3.62688772	0.22157196	0.06924301
C	-5.46905835	1.83971935	0.08359225
C	-4.60665271	2.81796482	-0.34793796
C	-3.24416094	2.53758081	-0.58289608
H	-1.45766619	-2.29900826	0.20357651
H	-0.83381028	1.71343616	-0.91322391
H	-3.63080204	-3.10525708	0.88562315
H	-6.03216618	-2.58720479	1.29411128
H	-6.91133110	-0.29987995	0.92951018
H	-6.52173499	2.06179059	0.26398815
H	-4.97336725	3.83230620	-0.51432815
H	-2.57157270	3.32609708	-0.92556971
C	0.59972226	-0.76771424	-0.62925483
C	1.72592594	-0.09023648	-1.06010467
N	2.70748101	-1.01742421	-1.05309949
H	1.91213746	0.93876604	-1.35486357
C	4.12020051	-0.85153579	-1.34012902
H	4.23310200	-0.37412775	-2.32320057

H	4.52244789	-1.87182699	-1.40746912
C	4.83571822	-0.05340925	-0.27247874
C	5.79774542	0.89511581	-0.62324577
C	4.55395784	-0.27971208	1.07897006
C	6.47948341	1.60673663	0.36439132
H	6.01678268	1.08090597	-1.67743908
C	5.23105889	0.43398417	2.06421307
H	3.79779809	-1.01932796	1.35412462
C	6.19649546	1.37759662	1.70909249
H	7.22916951	2.34656786	0.08022036
H	5.00468640	0.25246400	3.11581708
H	6.72552993	1.93632964	2.48237109
N	2.24212758	-2.19519887	-0.63556242
N	0.99173922	-2.05802445	-0.38487611

Triazolyl–B(dan)–NH_3

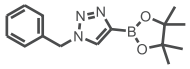


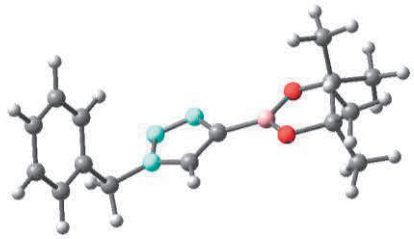
Charge = 0; Multiplicity = 1
Dihedral angle = 89.0°
(dan)N–B–N(dan) angle = 110.6°
B–N(dan) bond: 1.48973 Å, 1.48687 Å
Sum of electronic and thermal Enthalpies = -1087.295158 (hartree)

B	0.91464402	-0.91928794	-0.60976441
N	1.70216677	-1.35837200	0.57252305
N	1.26670756	0.47889132	-0.98450351
C	2.95039457	-0.84984001	0.85922583
C	2.50373428	1.02395412	-0.72795008
C	3.79930683	-1.44736706	1.78384981
C	5.06978655	-0.90088909	2.05065485
C	5.50627602	0.23561502	1.41232337
C	4.66479822	0.89377246	0.47368088
C	3.38147105	0.34394644	0.18513411
C	5.06154903	2.10102084	-0.16365549
C	4.20181105	2.73930811	-1.02639093
C	2.92791180	2.21260225	-1.31280956
H	1.42862720	-2.16747295	1.11428329

H	0.64867551	1.03866811	-1.55648628
H	3.47102711	-2.35147745	2.30094997
H	5.71459898	-1.39669383	2.77916976
H	6.48994948	0.65676581	1.62464893
H	6.04664823	2.51467841	0.05657815
H	4.50587809	3.67275315	-1.50449272
H	2.25985694	2.73358553	-2.00163811
H	1.61085943	-2.85750678	-1.68018523
H	0.63743581	-1.91104410	-2.62816528
H	2.25640000	-1.50120568	-2.38814944
N	1.41750919	-1.89516990	-1.95994826
C	-0.65495116	-1.24805842	-0.58249302
C	-1.61819604	-1.09964709	0.39627243
N	-2.77106370	-1.50663852	-0.18632170
H	-1.57840552	-0.73714946	1.41943513
C	-4.11718302	-1.49409251	0.35500726
H	-4.11001996	-1.98190603	1.33925108
H	-4.71313092	-2.11275400	-0.33011026
C	-4.68642280	-0.09599015	0.45745848
C	-5.41805969	0.29067739	1.58124848
C	-4.50153793	0.81407479	-0.58868008
C	-5.96760889	1.57070181	1.65933693
H	-5.55846745	-0.41322900	2.40500036
C	-5.04611576	2.09282168	-0.50872339
H	-3.92433304	0.51184826	-1.46609565
C	-5.78174024	2.47353359	0.61488643
H	-6.53592985	1.86415588	2.54308690
H	-4.89582505	2.79773315	-1.32768122
H	-6.20598683	3.47662798	0.67669064
N	-2.56284914	-1.87463716	-1.44456905
N	-1.30567376	-1.72647405	-1.68825563

Triazolyl–B(pin)



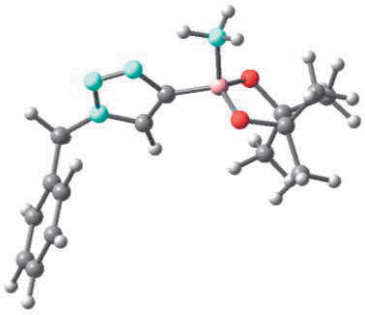


Charge = 0; Multiplicity = 1
Dihedral angle = 176.5°
O–B–O angle = 113.0°
B–O bond: 1.36244 Å, 1.37058 Å
Sum of electronic and thermal Enthalpies = -921.848514 (hartree)
AA = 64.2 (kJ/mol)

B	1.74623104	-0.38460946	-0.00722874
O	2.09769511	0.68063524	0.78030473
C	3.52899400	0.81096227	0.70251086
C	3.84870077	0.10610018	-0.66206101
O	2.77567576	-0.84539534	-0.77154273
C	3.73017863	1.05142836	-1.85491145
C	5.17518141	-0.63307216	-0.70051757
C	4.11161021	0.06482546	1.90016565
C	3.90101716	2.28245626	0.76088806
H	2.78011398	1.60383416	-1.82367085
H	4.55834292	1.77309700	-1.88216856
H	3.74904868	0.45513427	-2.77694474
H	5.30917549	-1.08998885	-1.69038387
H	6.00972330	0.06139474	-0.52270274
H	5.20846767	-1.43162844	0.05006547
H	3.86151991	-1.00475208	1.85372093
H	5.20426577	0.16963737	1.94831413
H	3.67665634	0.48054915	2.81922232
H	4.98217168	2.41332448	0.60535955
H	3.35960493	2.86056902	0.00265287
H	3.64287141	2.68688130	1.74927914
C	0.31122980	-0.97302961	0.00928544
C	-0.75877219	-0.60080067	0.80388772
N	-1.75910188	-1.42338481	0.43349198
H	-0.87257676	0.16171450	1.56901873
C	-3.14096435	-1.44207863	0.87167251
H	-3.16854060	-1.44528444	1.96991664

H	-3.54489280	-2.40040339	0.51652269
C	-3.94069611	-0.28133600	0.32132492
C	-4.87398494	0.37771201	1.12310301
C	-3.76801257	0.12328440	-1.00655594
C	-5.63487488	1.42586135	0.60467054
H	-5.00713446	0.07084800	2.16327120
C	-4.52439684	1.17246164	-1.52238769
H	-3.03447370	-0.39032011	-1.63308927
C	-5.46058792	1.82501074	-0.71865904
H	-6.36073361	1.93547003	1.24001530
H	-4.38283978	1.48271476	-2.55867269
H	-6.05143940	2.64742286	-1.12444017
N	-1.35366578	-2.25011985	-0.53860802
N	-0.12511608	-1.99189532	-0.79541747

Triazolyl–B(pin)–NH_3

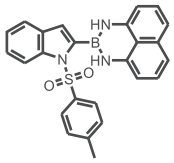


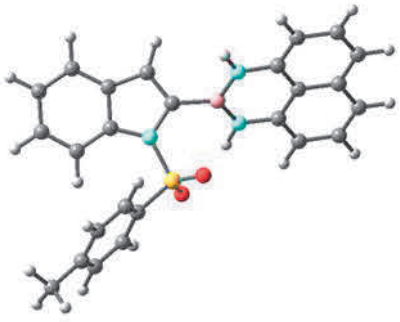
Charge = 0; Multiplicity = 1
Dihedral angle = 103.4°
O–B–O angle = 107.2°
B–O bond: 1.43802 Å, 1.44211 Å
Sum of electronic and thermal Enthalpies = -978.307936 (hartree)

B	-1.87091698	0.83664955	-0.22116393
O	-2.70588400	0.63809709	0.93775507
C	-3.18173983	-0.69782492	0.90577130
C	-3.22145632	-0.99586808	-0.63042346
O	-2.08927997	-0.28115091	-1.09908157
C	-3.07278461	-2.46424441	-1.00088839
C	-4.48689548	-0.42709522	-1.28309476
C	-4.52964336	-0.77282397	1.60729969
C	-2.16746852	-1.59366054	1.62157601
H	-2.09720754	-2.84954041	-0.68083040
H	-3.86837154	-3.07049865	-0.54149145
H	-3.13846569	-2.57715553	-2.09249647
H	-4.34548759	-0.41790343	-2.37399121

H	-5.37587283	-1.03181459	-1.05335959
H	-4.68345397	0.59960908	-0.93822026
H	-5.22719335	-0.02707773	1.20559353
H	-4.97492474	-1.77350809	1.49900862
H	-4.39715585	-0.56848823	2.67923339
H	-2.52928429	-2.62640966	1.72868281
H	-1.21915923	-1.61216385	1.06432846
H	-1.98115257	-1.17801779	2.62201481
H	-3.00287317	2.76289493	-0.32062238
H	-1.62325650	2.76961947	-1.27956629
H	-3.01723204	1.96485424	-1.78544178
N	-2.44456140	2.22158880	-0.98166264
C	-0.32335839	1.23297527	0.02322434
C	0.68629894	0.68516179	0.78985117
N	1.76468303	1.47528407	0.56852927
H	0.72811899	-0.17270576	1.45442988
C	3.12121968	1.31513519	1.05045163
H	3.10012839	1.17440335	2.14006849
H	3.62199463	2.27051004	0.83976125
C	3.84725469	0.16796214	0.38069660
C	3.60286748	-0.13734878	-0.96173011
C	4.79170844	-0.57573991	1.09138400
C	4.29919972	-1.17174899	-1.58256707
H	2.85963444	0.43877381	-1.51793173
C	5.49229950	-1.60784097	0.46806558
H	4.97988720	-0.34812076	2.14342761
C	5.24659917	-1.90796427	-0.87051923
H	4.09908370	-1.40518639	-2.62928724
H	6.22662310	-2.18379946	1.03319889
H	5.78936537	-2.71893335	-1.35822078
N	1.47206596	2.45132562	-0.28102597
N	0.23174744	2.31571517	-0.60533212

Indolyl–B(dan) (5a)



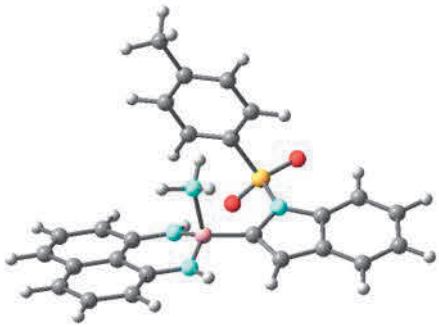


Charge = 0; Multiplicity = 1
Dihedral angle = 137.5°
N–B–N angle = 117.1°
B–N bond: 1.41883 Å, 1.41997 Å
Sum of electronic and thermal Enthalpies = -1700.465360 (hartree)
AA = 28.7 (kJ/mol)

B	1.58848752	0.73815057	0.01197933
N	2.55138820	1.27496738	0.90694637
N	2.02725041	-0.27633374	-0.87762703
C	3.87037054	0.83331646	0.95602874
C	3.32498857	-0.77484819	-0.86478671
C	4.79120802	1.36474224	1.84053968
C	6.11713326	0.88240663	1.85787117
C	6.52090312	-0.11702928	1.00644130
C	5.60234043	-0.69016534	0.08353692
C	4.26270889	-0.20845089	0.05665627
C	5.97739337	-1.72897910	-0.81100539
C	5.05609603	-2.25762981	-1.68361146
C	3.72764691	-1.78733403	-1.71834271
H	2.29370687	1.97822616	1.58735038
H	1.39058583	-0.72474400	-1.52865434
H	4.48408981	2.15757527	2.52486993
H	6.82749228	1.31601656	2.56390759
H	7.54695283	-0.48712599	1.02512735
H	7.00415938	-2.09684821	-0.79003264
H	5.35043803	-3.05676088	-2.36620642
H	3.00660017	-2.21724516	-2.41528228
C	0.15792681	1.39174211	-0.06439373
C	-0.10000176	2.73302064	-0.12086110
C	-1.49769940	2.92022271	-0.39840330

H	0.64921566	3.51572697	-0.02415928
C	-2.08062238	1.63343398	-0.51234386
C	-2.28942190	4.06621010	-0.57452663
C	-3.44269108	1.48061926	-0.81210771
C	-3.63526274	3.91540866	-0.86293461
H	-1.84077140	5.05714281	-0.48978368
C	-4.19870670	2.63254723	-0.98306115
H	-3.91177513	0.50700761	-0.92626914
H	-4.26438021	4.79453918	-1.00663264
H	-5.25791339	2.53293204	-1.22405410
S	-1.07373419	-0.99423479	-0.19180617
O	-0.21305336	-1.32135107	0.92641686
O	-0.78774545	-1.51957205	-1.51614897
C	-2.74028370	-1.37559514	0.22886592
C	-3.21314794	-1.01886338	1.49092179
C	-3.53277795	-2.04108354	-0.69943565
C	-4.53231686	-1.31270715	1.80878551
H	-2.55557670	-0.51281109	2.19987890
C	-4.85029431	-2.33590161	-0.35508743
H	-3.11731712	-2.30555882	-1.67268268
C	-5.36845408	-1.97236549	0.89358878
H	-4.92622303	-1.02897453	2.78664576
H	-5.48952449	-2.85518803	-1.07140881
C	-6.78720263	-2.30266113	1.26885103
H	-7.38194859	-2.57433443	0.38791805
H	-6.80974505	-3.15257291	1.96777276
H	-7.27062081	-1.45251336	1.76909274
N	-1.05331576	0.71130404	-0.28041256

Indolyl–B(dan)–NH_3

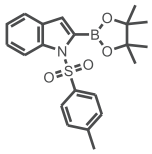


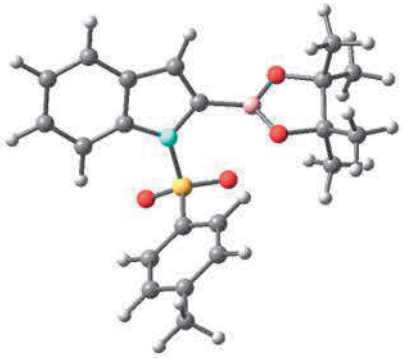
Charge = 0; Multiplicity = 1
Dihedral angle = 131.2°
(dan)N–B–N(dan) angle = 111.1°
B–N(dan) bond: 1.47609 Å, 1.49259 Å
Sum of electronic and thermal Enthalpies = -1756.911263 (hartree)

B	-0.51556750	-0.95315569	0.07712467
N	-1.33503298	-2.08539949	0.60088294
N	-1.19941946	-0.27662959	-1.04247628
C	-2.71012569	-1.98875690	0.62549536
C	-2.57074571	-0.18191826	-1.08917091
C	-3.49808325	-2.80881519	1.42581051
C	-4.90051756	-2.67867528	1.42853931
C	-5.53349748	-1.74610728	0.64111920
C	-4.77264661	-0.89781702	-0.20906521
C	-3.35012069	-1.00148405	-0.20238723
C	-5.39412352	0.02474116	-1.09409130
C	-4.62984313	0.77623653	-1.95640643
C	-3.22500274	0.68131264	-1.96221678
H	-0.95287069	-2.77365191	1.23550738
H	-0.68562743	0.11145056	-1.82290250
H	-3.01624834	-3.56215246	2.05260845
H	-5.48938987	-3.33760594	2.06977035
H	-6.62070585	-1.65691434	0.63992350
H	-6.48220074	0.10302907	-1.09495499
H	-5.11496895	1.46429769	-2.65177435
H	-2.63467923	1.28061703	-2.65868307
H	-0.31878210	-0.24421915	2.31243625
H	-0.19265174	1.10008243	1.34899830
H	-1.65766862	0.36114848	1.55350868
N	-0.65164003	0.19430481	1.45283504
C	1.06181469	-1.29220829	-0.01338388
C	1.59643467	-2.45824972	0.45218686
C	3.03106210	-2.39773099	0.38991025
H	1.02206256	-3.30916814	0.81015698
C	3.37314130	-1.13829370	-0.14661930
C	4.03596709	-3.30504044	0.75785407
C	4.71414304	-0.76472057	-0.31990016
C	5.36132591	-2.94007348	0.58830797
H	3.76823070	-4.27905569	1.17042294
C	5.68834215	-1.68128344	0.05584356
H	4.98902998	0.19693441	-0.74073730
H	6.15792219	-3.63092630	0.86718891
H	6.73731048	-1.41030030	-0.07233884
S	2.03251932	0.93818308	-1.33212639
O	1.12000116	0.69304112	-2.43199623
O	3.38291210	1.38582996	-1.58799524
C	1.26675738	2.10534702	-0.23600620
C	0.05551503	2.69058505	-0.59049908
C	1.91915826	2.43281558	0.95333433

C	-0.53210172	3.59985020	0.28857996
H	-0.42896412	2.41771214	-1.52761757
C	1.31619712	3.33924109	1.81883135
H	2.87663744	1.96821618	1.19957358
C	0.08340083	3.93457174	1.50122805
H	-1.49129446	4.05052836	0.02689834
H	1.80938911	3.59620755	2.75842331
C	-0.54199676	4.93797487	2.43129201
H	-0.32050972	4.70296164	3.48059359
H	-0.14407004	5.94369716	2.22617608
H	-1.63095683	4.97828835	2.30165352
N	2.15587823	-0.46031915	-0.38667296

Indolyl–B(pin)





Charge = 0; Multiplicity = 1

Dihedral angle = 117.6°

O–B–O angle = 112.9°

B–O bond: 1.36979 Å, 1.36106 Å

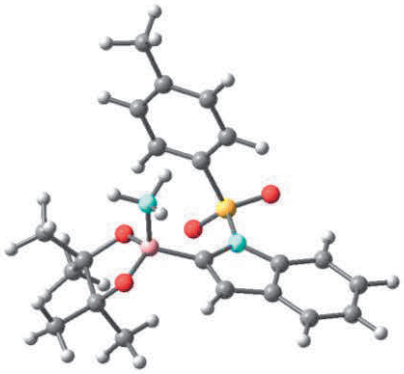
Sum of electronic and thermal Enthalpies = -1591.475966 (hartree)

AA = 42.4 (kJ/mol)

B	-1.84741884	0.67750597	-0.11312301
O	-2.00703279	-0.59463333	-0.59531057
C	-3.33797035	-1.01976260	-0.23549872
C	-4.08496873	0.35261136	-0.09421783
O	-3.01876749	1.24452773	0.28550303
C	-4.63605332	0.86516564	-1.42201867
C	-5.16042707	0.38064659	0.97742219
C	-3.23440276	-1.77516968	1.08577870
C	-3.87861243	-1.92482879	-1.32905761
H	-3.86376012	0.83421140	-2.20423199
H	-5.49985562	0.27375626	-1.75552683
H	-4.95275010	1.90881722	-1.29167594
H	-5.62493783	1.37578308	1.00341588
H	-5.94210148	-0.36162714	0.75798350
H	-4.73824359	0.17313995	1.96756184
H	-2.85073719	-1.12618871	1.88366886
H	-4.20885905	-2.18716326	1.38325416
H	-2.52214451	-2.60333978	0.96510127
H	-4.93222726	-2.17426125	-1.13483823
H	-3.80003456	-1.45325386	-2.31595914
H	-3.30341937	-2.86099390	-1.34742953
C	-0.50827753	1.49123765	-0.19988330
C	-0.29680309	2.61578781	-0.94673137

C	1.09173116	2.98488975	-0.83819461
H	-1.06101261	3.12775871	-1.52667266
C	1.70098425	2.04724250	0.02626168
C	1.86768624	4.01929453	-1.38618787
C	3.05659818	2.11740535	0.36821175
C	3.21322549	4.08917483	-1.06219237
H	1.41366415	4.75214348	-2.05490413
C	3.79761862	3.14761902	-0.19344050
H	3.50450993	1.40717769	1.06059707
H	3.83051294	4.88564849	-1.47965900
H	4.85737835	3.23184010	0.05113643
S	0.89363405	-0.11465106	1.51602315
O	-0.46363347	-0.49815680	1.85636048
O	1.83579724	0.32905344	2.52012368
C	1.65141113	-1.41206919	0.57889278
C	0.89724017	-2.07931624	-0.38842022
C	2.97474131	-1.74711765	0.84206786
C	1.50749203	-3.09525583	-1.11257056
H	-0.14422561	-1.79743698	-0.56454863
C	3.56356584	-2.77319398	0.10446832
H	3.52341813	-1.21780663	1.62198346
C	2.84437077	-3.45631859	-0.88058543
H	0.93501839	-3.62656464	-1.87599205
H	4.60099715	-3.04919313	0.30204081
C	3.47975127	-4.55603832	-1.68768567
H	4.49330113	-4.77990523	-1.33241535
H	2.88241709	-5.47732659	-1.63236626
H	3.54426799	-4.27003241	-2.74799423
N	0.71049400	1.14047868	0.40068447

Indolyl–B(pin)–NH_3



Charge = 0; Multiplicity = 1
Dihedral angle = 149.6°
O–B–O angle = 107.5°

B–O bond: 1.42906 Å, 1.43868 Å

Sum of electronic and thermal Enthalpies = -1647.927082 (hartree)

B	-0.84391903	0.92671635	-0.72227540
O	-1.22232876	2.19530452	-1.28556947
C	-1.83832514	2.92479317	-0.22899521
C	-2.58010670	1.78727519	0.55133331
O	-1.68289053	0.69261921	0.41066034
C	-2.79052996	2.06122060	2.03304710
C	-3.91019602	1.41571707	-0.11003164
C	-2.74807777	3.98924187	-0.82108428
C	-0.75133482	3.57478402	0.63039732
H	-1.82672786	2.12306980	2.55207667
H	-3.35333487	2.99453370	2.18708342
H	-3.36259128	1.23729212	2.48470762
H	-4.24937792	0.45136650	0.29615916
H	-4.68946049	2.16754382	0.08097422
H	-3.79522445	1.32215231	-1.20124612
H	-3.43629889	3.55873762	-1.55949036
H	-3.33369537	4.48566931	-0.03273536
H	-2.13870492	4.75062076	-1.32794658
H	-1.18324599	4.23528140	1.39576323
H	-0.13579709	2.81242218	1.12976368
H	-0.09671737	4.16926375	-0.02237543
H	-0.80664414	0.05241474	-2.77609899
H	-1.05201627	-1.14300548	-1.64399558
H	-2.29238406	-0.10661700	-2.03970303
N	-1.28253208	-0.17891554	-1.90194418
C	0.76838146	0.77594065	-0.56177425
C	1.64038715	1.48113820	-1.34356479
C	2.98833567	1.11417960	-1.00243891
H	1.32856148	2.21874998	-2.08012204
C	2.91039319	0.15142130	0.03094512
C	4.24277359	1.52460962	-1.48106686
C	4.06578948	-0.40161568	0.60283938
C	5.38634588	0.97464102	-0.92516693
H	4.30662107	2.26878091	-2.27672857
C	5.29136234	0.02339846	0.10620249
H	4.00594434	-1.13058716	1.40518369
H	6.36941677	1.28302416	-1.28373603
H	6.20364443	-0.39329124	0.53581771
S	0.90863335	-1.02698323	1.51437194
O	0.16397377	-0.22742463	2.45748714
O	2.00797848	-1.86073764	1.96010762
C	-0.21335056	-2.06574332	0.60525790

C	-1.56311400	-2.08016885	0.93344587
C	0.30945838	-2.88590507	-0.39613929
C	-2.41498016	-2.91990830	0.21487008
H	-1.92650479	-1.40793855	1.70950143
C	-0.55684825	-3.70921523	-1.10848451
H	1.37957746	-2.86553947	-0.61477534
C	-1.93054725	-3.73924662	-0.81183376
H	-3.48003505	-2.93566412	0.45545831
H	-0.16377971	-4.35024748	-1.90039044
C	-2.85055633	-4.66719116	-1.55887527
H	-2.54527720	-4.77521889	-2.60826459
H	-2.82918680	-5.66994033	-1.10511195
H	-3.88864353	-4.31186978	-1.52935074
N	1.54080631	-0.05210510	0.28140499

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Chapter 4

Platinum–P(BFPy)$_3$-catalyzed Regioselective Diboration of Terminal Alkynes with (pin)B–B(aam)

An unsymmetrical diboron, (pin)B–B(aam), is smoothly added across a carbon–carbon triple bond of various terminal alkynes under platinum catalysis, resulting in the regio- and stereoselective formation of *cis*-*vic*-diborylalkenes via the B(aam)-installation at the terminal carbon. The use of a highly electron-deficient triarylphosphine ligand, P(BFPy)$_3$, is indispensable for the regiocontrol, and electron-deficiency in ligands has proven to be closely correlated with the regioselectivity.

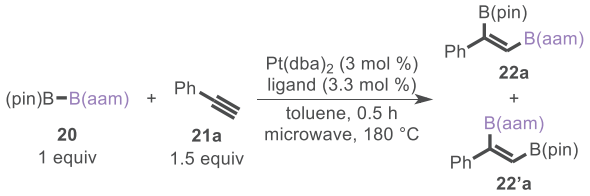
4-1 Introduction

Diborons have been a linchpin in a variety of transition metal-catalyzed and -free borylation reactions,[1,2] which provide direct access to diverse organoboron compounds of high synthetic significance.[3] Bis(pinacolato)diboron, (pin)B–B(pin), is the most used for this purpose, and to the best of the author's knowledge, platinum-catalyzed addition of its boron–boron bond across alkynes (diboration), which affords synthetically useful *cis*-*vic*-diborylalkenes,[4] triggered the flexible and broad-ranging utilization for boron-installing reactions. Besides this commonly used symmetrical diboron, recent attention has also been devoted to the use of unsymmetrical ones, especially having different boron-Lewis acidities.[2,5] In 2010, Suginome reported on platinum- or iridium-catalyzed diboration of terminal alkynes with (pin)B–B(dan) (dan = naphthalene-1,8-diaminato), where the B(dan) moiety was regioselectively attached to the terminal carbon of the triple bonds.[6] The difference in its boron-Lewis acidities also allowed σ-bond metathesis with a copper catalyst to occur chemoselectively to afford a boron-Lewis acidity-diminished Cu–B(dan) species that serve as a key catalytic intermediate in various B(dan)-installing reactions.[5,7] In this context, attention of Yoshida's groups has been directed toward developing unsymmetrical diborons with different boron-Lewis acidities including (pin)B–B(aam) (aam = anthranilamidato),[8] (neop)B–B(dan)[9] and (pin)B–B(mdan) (mdan = *N*,*N'*-dimethyl-naphthalene-1,8-diaminato),[8*b*] and their application to catalytic borylation reactions via the σ-bond metathesis as a key elementary step; the synthetic versatility of (pin)B–B(aam) was demonstrated by the palladium-catalyzed Miyaura–Ishiyama-type borylation of aryl halides[8*a*] and the copper-catalyzed internal-selective hydroboration of terminal alkynes[8*b*]. Regardless of the diminished boron-Lewis acidity, the resulting C(sp^2)–B(aam) bonds were also found to be directly convertible into C(sp^2)–C bonds by Suzuki–Miyaura coupling,[8,10] verifying the synthetic utility of the B(aam)-installing reactions.[11,12] Herein, the author discloses that (pin)B–B(aam) can also be catalytically activated by oxidative addition to a platinum complex, leading to *syn*-diboration of terminal alkynes, and that a highly electron-deficient triarylphosphine developed by Korenaga, $P(BFPy)_3$, is effective for regiocontrol.[13]

4-2 Results and Discussion

Initially, the author conducted a reaction of (pin)B–B(aam) (**20**) with phenylacetylene (**21a**) in toluene at 180 °C (microwave heating) using $Pt(dba)_2$ and highly electron-deficient tris[2,6-bis(trifluoromethyl)-4-pyridyl]phosphine, $P(BFPy)_3$ (Taft's σ* value[13a,14]: σ* (BFPy) = 1.66), and observed that *syn*-diboration of the triple bond took place to afford *vic*-diborylalkenes (**22a** and **22'a**) in 88% yield with regioselective attachment of the B(aam) moiety to the terminal carbon (ratio = 96:4, entry 1, Table 2). The reaction performed under conventional heating conditions (100 °C, oil bath) took a long time to complete (entry 2), while the use of DMF as a solvent resulted in poor yield and regioselectivity (entry 3). The electron-deficiency in triarylphosphines proved to be a key to the regiocontrol (Figure 41): the reaction with tris[3,5-bis(trifluoromethyl)phenyl]phosphine (σ*[3,5-$(F_3C)_2C_6H_3$] = 1.18), an optimum ligand for the diboration with (pin)B–B(dan), or tris[4-(trifluoromethyl)phenyl]phosphine (σ*(4-$F_3CC_6H_4$) = 0.96) proceeded with lower regioselectivity (entries 4 and 5). On the other hand, the use of more electron-rich phosphines such as PPh_3 (σ*(Ph) = 0.61) and tri(4-methoxyphenyl)phosphine (σ*(4-$MeOC_6H_4$) = 0.45) provided almost the same amount of **22a** and **22'a** (entries 6 and 7), and ligand-free conditions was ineffective (entry 8). The platinum catalysis was found to be indispensable for the present diboration, and thus $P(BFPy)_3$-coordinated nickel/palladium complex (entries 9 and 10) and even $[IrCl(cod)]_2$, which promoted the diboration with (pin)B–B(dan),[6] did not furnish **22a** and **22'a** (entry 11).

Table 2 Reaction conditions for diboration of phenylacetylene **21a** with **20**[a]



Entry	Ligand	σ*(Ar)[b]	**22a**:**22'a**	Yield (%)[c]
1	$P(BFPy)_3$	1.66	96:4	88
2[d]	$P(BFPy)_3$	1.66	95:5	85
3[e]	$P(BFPy)_3$	1.66	87:13	55
4	$P[3,5\text{-}(F_3C)_2C_6H_3]_3$	1.18	88:12	90
5	$P(4\text{-}F_3CC_6H_4)_3$	0.96	71:29	82
6	PPh_3	0.61	56:44	79
7	$P(4\text{-}MeOC_6H_4)_3$	0.45	45:55	51
8	–		69:31	55
9[f]	$P(BFPy)_3$	1.66		0
10[g]	$P(BFPy)_3$	1.66	–	0
11[h]	–	–	–	–

[a] Conditions: **20** (0.15 mmol), **21a** (0.225 mmol), $Pt(dba)_2$ (4.5 μmol), ligand (4.95 μmol), toluene (2 mL), microwave, 180 °C, 0.5 h. [b] Taft's σ* value of an Ar group of a ligand. [c] ^1H NMR yield. [d] 100 °C, 72 h. [e] DMF was used instead of toluene. [f] $Ni(cod)_2$ (3 mol %) was used instead of $Pt(dba)_2$. [g] $Pd_2(dba)_3$•$CHCl_3$ (1.5 mol %) was used instead of $Pt(dba)_2$. [h] $[IrCl(cod)]_2$ (1.5 mol %) was used instead of $Pt(dba)_2$.

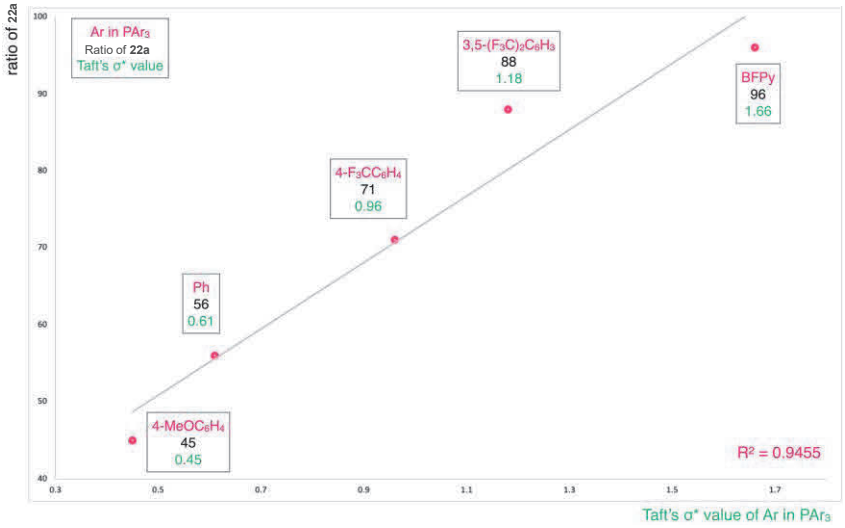


Figure 41 Relationship between Taft's σ* value and regioselectivity

The substrate scope of the regioselective diboration was sufficiently broad (Figure 42): a variety of aromatic terminal alkynes bearing an electron-donating (**21b**–**21d**) or -withdrawing substituent (**21e**–**21h**) smoothly underwent the diboration to afford the respective products (**22b**–**22h**) in high yields without damaging the reactive functionalities such as Ar–Br, cyano and carbonyl moieties. In addition to the successful reaction of an enyne (**21i**) and 1,4-diethynylbenzene (**21j**) that accepted dual addition of **20**, aliphatic terminal alkynes (**21k** and **21l**) were convertible into the diborated products (**22k** and **22l**) in 97% and 90% yield with similar regioselectivity. The high functional group compatibility was observed also with aliphatic alkynes: C(sp^3)–CN (**21m**), –Cl (**21n**) and –OTs (**21o**) moieties were remained intact throughout the diboration. The reaction was also applicable to a propargyl ether (**21p**), 4-bromo-1-butyne (**21q**) and ethynyl–B(mida) (**21r**), the latter of which furnished a differently substituted triborylalkene (**22r**), and regioselectivity became exceptionally reversed with trimethylsilylacetylene (**21s**). Furthermore, internal alkynes could participate in the reaction: treatment of diphenylacetylene (**21t**) or 4-octyne (**21u**) gave stereoselectively *syn* products (**22t** and **22u**). It should be noted that the high regiocontrol was achieved in the reaction of **21v** or **21w**, where the B(pin) moiety was preferentially installed into the α position of the phenyl group, whereas the reaction of 2-octyne (**21x**) led to the formation of a mixture of regioisomers (**22x** and **22'x**). Finally, a conjugated diene (**23**) was also readily transformable into a 1,4-diborated product (**24**) in a stereoselective fashion.[15]

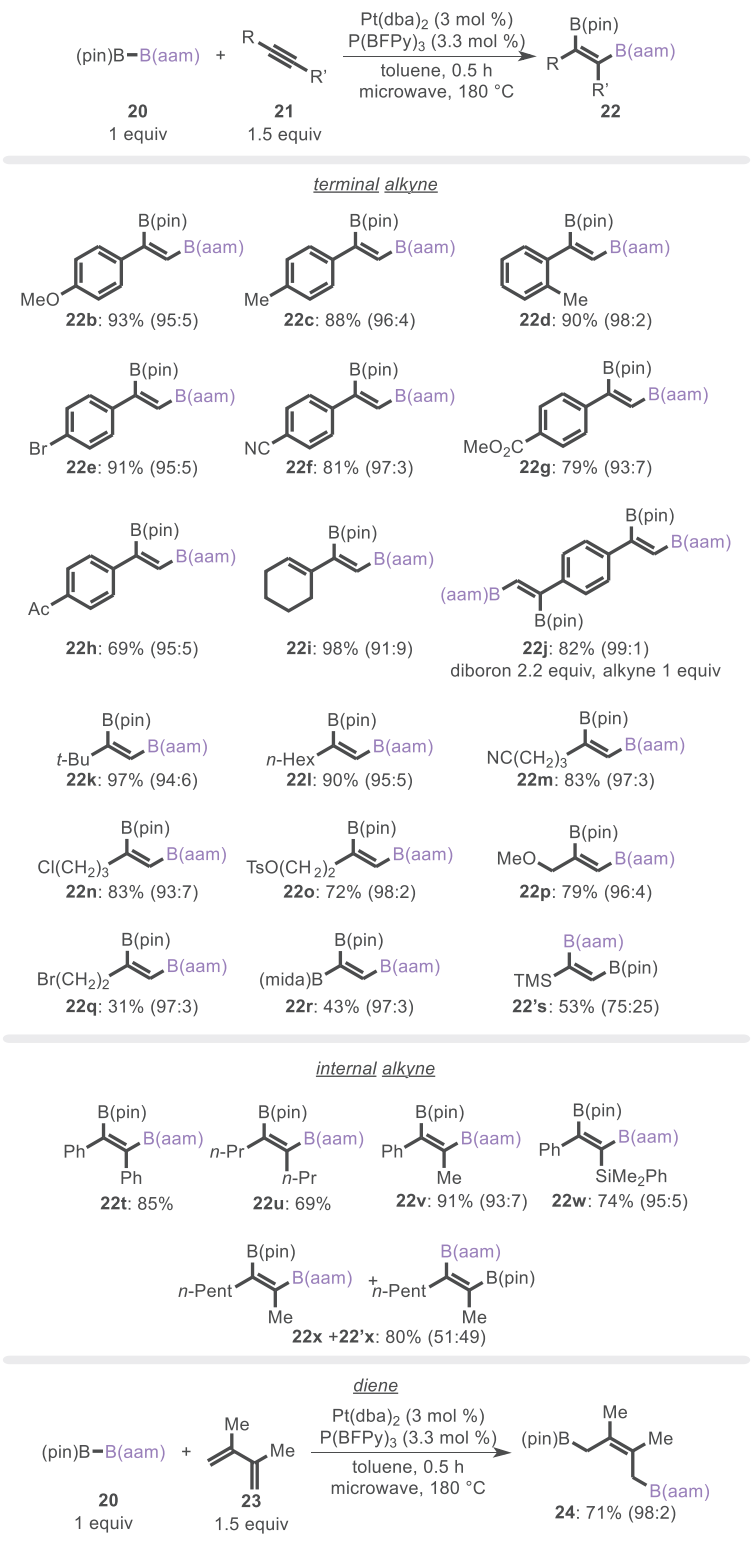


Figure 42 Substrate scope of the diboration

Synthetic utility of the resulting diborylalkene was demonstrated by site-selective cross-coupling (Figure 43); owing to the diminished Lewis acidity that retards transmetalation step,[16] the B(aam) moiety of **22a** remained intact during smooth cross-coupling with *p*-tolyl–Br at the sterically congested B(pin) moiety, giving **25** in 43% yield (60% NMR yield). In addition, the remaining

C(sp^2)–B(aam) bond could successively undergo the direct cross-coupling[8,10] with 4-bromoanisole to result in the stereoselective formation of triarylalkene **26**.

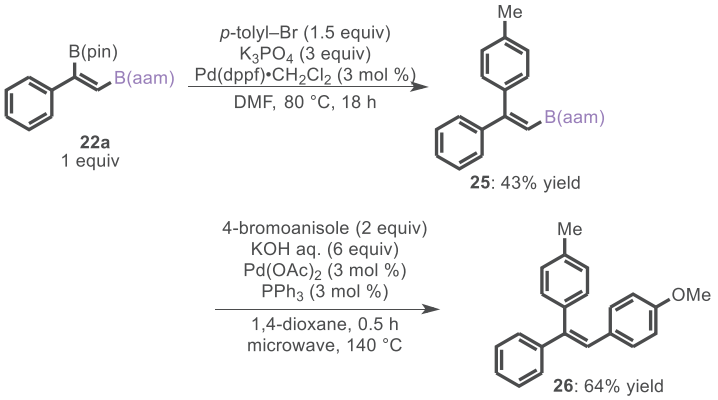


Figure 43 Chemoselective cross-coupling of the diboration product

The present diboration would be commenced by oxidative addition of the boron–boron bond of **20** to a Pt(0) catalyst in a similar fashion to the well-established diboration with bis(pinacolato)diboron (Figure 44).[4,17] The resulting oxidative adduct (**27**) then accepts insertion of an alkyne at the Pt–B(pin) bond and/or –B(aam) bond to provide an alkenyl platinum intermediate (**28** and/or **28'**), which finally affords the diboration product (**22**) through reductive elimination.

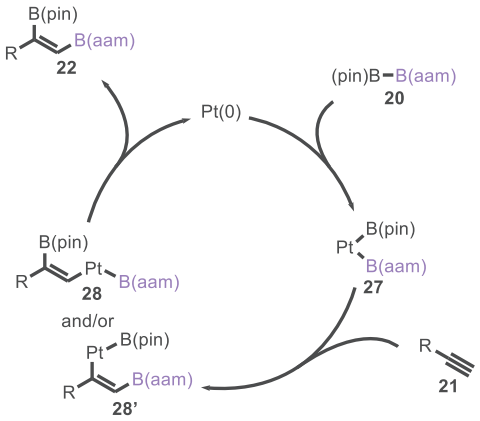


Figure 44 A plausible catalytic cycle for the diboration

In conclusion, the author has disclosed that (pin)B–B(aam) with different boron-Lewis acidity can be catalytically activated by oxidative addition to a platinum(0) complex to lead to regio- and stereoselective diboration of unsaturated carbon linkages including terminal alkynes, internal alkynes and a conjugated diene. Moreover, the regioselectivity with terminal alkynes has proven to be closely correlated with the electron-deficiency in triarylphosphine ligands that can be assessed by Taft's σ* values of the aryl moiety.

4-3 Experimental Section

4-3-1 General Remarks

All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under an argon atmosphere. Nuclear magnetic resonance spectra were taken on a Varian System 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz; ^{11}B, 160 MHz) or Varian System 400 (^{1}H, 400 MHz) spectrometer using residual proton in DMSO-d_6 (^{1}H, δ = 2.50), Acetone-d_6 (^{1}H, δ = 2.05), residual chloroform (^{1}H, δ = 7.26) or $CDCl_3$ (^{13}C, δ = 77.0) as an internal standard and boron trifluoride diethyl etherate (^{11}B, δ = 0.00) as an external standard. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet), coupling constants (Hz), integration. High-resolution mass spectra were obtained with a Thermo Fisher Scientific LTQ Orbitrap XL spectrometer. Melting points were measured with Yanaco Micro Melting Point apparatus and uncorrected. Preparative recycling gel permeation chromatography was performed with GL Science PU 614 equipped with Shodex GPC H-2001L and -2002L columns (toluene as an eluent). Column chromatography was carried out using Merck Kieselgel 60. All microwave reactions (Biotage, Initiator+) were conducted in a sealed tube, and the reaction temperature was maintained by an external infrared sensor. Unless otherwise noted, commercially available reagents were used without purification. All solvents were dried over activated molecular sieves 3Å.

4-3-2 General Procedure

Pt-Catalyzed Diboration of Alkynes

A reaction tube equipped with a magnetic stirring bar was charged with $Pt(dba)_2$ (4.5 μmol, 3 mol %), $P(BFPy)_3$ (4.95 μmol, 3.3 mol %), (pin)B–B(aam) (0.15 mmol, 1 equiv), an alkyne (0.225 mmol, 1.5 equiv) and toluene (2 mL), and the mixture was stirred at 180 °C for 30 min under microwave irradiation. The mixture was diluted with ethyl acetate and filtered through a Celite plug. The organic solution was washed with brine, dried over Na_2SO_4, and evaporated. Purification of the residue by boric acid impregnated silica gel-column chromatography (hexane/ethyl acetate as an eluent) or gel permeation chromatography (toluene as an eluent) gave the product.

(*E*)-2-(2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (22a)

Isolated in 88% yield as a pale yellow solid: mp 190–191 ˚C

^{1}H NMR ($CDCl_3$) δ 8.23 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.05 (s, 1H), 7.64 (s, 1H), 7.52 (dd, *J* = 8.1, 7.1 Hz, 1H), 7.44 (dd, *J* = 7.5, 2.1 Hz, 2H), 7.39 – 7.33 (m, 2H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.14 (ddd, *J* = 8.0, 7.2, 1.1 Hz, 1H), 7.03 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.60 (s, 1H), 1.40 (s, 12H).

^{13}C NMR ($CDCl_3$) δ 167.79, 144.62, 140.95, 133.79, 129.29, 128.47, 127.85, 127.23, 121.74, 118.86, 117.59, 84.95, 25.08.

^{11}B NMR ($CDCl_3$) δ 29.95, 27.65.

HRMS Calcd for $C_{21}H_{24}B_2N_2O_3$: $[M+Na]^+$, 397.1865. Found: *m*/*z* 397.1867

(*E*)-2-(2-(4-methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (22b)

Isolated in 93% yield as a pale yellow solid: mp 82–83 ˚C

^{1}H NMR ($CDCl_3$) δ 8.22 (d, *J* = 7.9 Hz, 1H), 7.98 (s, 1H), 7.56 (s, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 2H), 6.53 (s, 1H), 3.83 (s, 3H), 1.41 (s, 12H).

^{13}C NMR ($CDCl_3$) δ 166.76, 159.61, 144.67, 136.68, 133.74, 129.25, 128.46, 121.63, 119.23, 117.55, 113.90, 84.89, 55.43, 25.08.

^{11}B NMR ($CDCl_3$) δ 29.65, 22.19.

HRMS Calcd for $C_{22}H_{26}B_2N_2O_4$: $[M+Na]^+$, 427.1971. Found: *m*/*z* 427.1968

(*E*)-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(*p*-tolyl)vinyl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (22c)

Isolated in 88% yield as a pale yellow solid: mp 182–183 ˚C

^{1}H NMR ($CDCl_3$) δ 8.22 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.00 (s, 1H), 7.59 (s, 1H), 7.51 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.14 (dd, *J* = 18.8, 8.0 Hz, 3H), 7.01 (d, *J* = 8.2 Hz, 1H), 6.57 (s, 1H), 2.36 (s, 3H), 1.40 (s, 12H).

^{13}C NMR ($CDCl_3$) δ 166.73, 144.65, 141.46, 137.76, 133.74, 129.27, 129.21, 127.13, 121.66, 119.27, 117.57, 84.90, 25.08, 21.32.

^{11}B NMR ($CDCl_3$) δ 31.47.

HRMS Calcd for $C_{22}H_{26}B_2N_2O_3$: $[M+Na]^+$, 411.2022. Found: *m*/*z* 411.2025

(*E*)-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(*o*-tolyl)vinyl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (22d)

Isolated in 90% yield as a pale yellow solid: mp 142–143 ˚C

^{1}H NMR ($CDCl_3$) δ 8.23 (dd, *J* = 7.9, 1.6 Hz, 1H), 8.12 (s, 1H), 7.94 (s, 1H), 7.52 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.21 – 7.06 (m, 5H), 7.02 (d, *J* = 8.1 Hz, 1H), 6.34 (s, 1H), 2.28 (s, 3H), 1.36 (s, 12H).

^{13}C NMR ($CDCl_3$) δ 166.86, 146.26, 144.69, 134.37, 133.73, 129.79, 129.23, 128.09, 127.23, 126.13, 121.69, 119.31, 117.67, 84.75, 25.04, 20.42.

^{11}B NMR ($CDCl_3$) δ 29.24.

HRMS Calcd for $C_{22}H_{26}B_2N_2O_3$: $[M+Na]^+$, 411.2022. Found: *m*/*z* 411.2024

(*E*)-2-(2-(4-bromophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (22e)

Isolated in 91% yield as a pale yellow solid: mp 175–176 ˚C

^{1}H NMR ($CDCl_3$) δ 8.22 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.04 (s, 1H), 7.62 (s, 1H), 7.52 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.17 – 7.11 (m, 1H), 7.02 (d, *J* = 8.1 Hz, 1H), 6.58 (s, 1H), 1.39 (s, 12H).

^{13}C NMR ($CDCl_3$) δ 166.68, 144.53, 143.39, 133.82, 131.54, 129.29, 128.96, 122.00, 121.84, 119.31, 117.61, 85.07, 25.05.

^{11}B NMR ($CDCl_3$) δ 30.00.

HRMS Calcd for $C_{21}H_{23}B_2BrN_2O_3$: $[M+Na]^+$, 475.0970. Found: *m*/*z* 475.0971

(*E*)-4-(2-(4-oxo-3,4-dihydrobenzo[*d*][1,3,2]diazaborinin-2(1*H*)-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzonitrile (22f)

Isolated in 81% yield as a pale yellow solid: mp 229–230 ˚C

^{1}H NMR ($CDCl_3$) δ 8.23 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.03 (s, 1H), 7.64 (d, *J* = 8.1 Hz, 3H), 7.52 (dd, *J* = 8.7, 3.2 Hz, 3H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 8.1 Hz, 1H), 6.64 (s, 1H), 1.39 (s, 12H).

^{13}C NMR ($CDCl_3$) δ 166.64, 149.26, 144.41, 133.91, 132.23, 129.30, 128.05, 122.03, 119.35, 119.13, 117.67, 111.16, 85.27, 25.03.

^{11}B NMR ($CDCl_3$) δ 29.95.

HRMS Calcd for $C_{22}H_{23}B_2N_3O_3$: $[M+Na]^+$, 422.1818. Found: *m*/*z* 422.1818

methyl (*E*)-4-(2-(4-oxo-3,4-dihydrobenzo[*d*][1,3,2]diazaborinin-2(1*H*)-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzoate (22g)

Isolated in 79% yield as a pale yellow solid: mp 159–160 ˚C

^{1}H NMR ($CDCl_3$) δ 8.23 (dd, *J* = 8.1, 1.6 Hz, 1H), 8.05 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.62 (s, 1H), 7.56 – 7.46 (m, 3H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.66 (s, 1H), 3.92 (s, 3H), 1.39 (s, 12H).

^{13}C NMR ($CDCl_3$) δ 167.37, 166.97, 149.36, 144.76, 134.10, 130.02, 129.55, 127.56, 126.98, 122.15, 119.58, 117.89, 85.38, 52.51, 25.42.

^{11}B NMR ($CDCl_3$) δ 30.07.

HRMS Calcd for $C_{23}H_{26}B_2N_2O_5$: $[M+Na]^+$, 455.1920. Found: *m*/*z* 455.1919

(*E*)-2-(2-(4-acetylphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (22h)

Isolated in 69% yield as a pale yellow solid: mp 146–147 ˚C

^{1}H NMR ($CDCl_3$) δ 8.23 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.04 (s, 1H), 7.94 (d, *J* = 8.3 Hz, 2H), 7.63 (s, 1H), 7.52 (dd, *J* = 7.6, 4.4 Hz, 3H), 7.18 – 7.12 (m, 1H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.67 (s, 1H), 2.61 (s, 3H), 1.40 (s, 12H).

^{13}C NMR ($CDCl_3$) δ 166.65, 149.30, 144.50, 136.17, 133.84, 129.29, 128.58, 127.51, 121.90, 119.34, 117.64, 85.14, 26.80, 25.02.

^{11}B NMR ($CDCl_3$) δ 30.77.

HRMS Calcd for $C_{23}H_{26}B_2N_2O_4$: $[M+Na]^+$, 439.1971. Found: *m*/*z* 439.1970

(*E*)-2-(2-(cyclohex-1-en-1-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (22i)

Isolated in 98% yield as a pale yellow solid: mp 122–123 ˚C

^{1}H NMR ($CDCl_3$) δ 8.19 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.78 (s, 1H), 7.49 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.14 – 7.07 (m, 2H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.17 (s, 1H), 6.03 (d, *J* = 3.8 Hz, 1H), 2.22 (t, *J* = 5.3 Hz, 4H), 1.71 (dd, *J* = 6.1, 2.5 Hz, 2H), 1.61 (dd, *J* = 6.0, 2.6 Hz, 2H), 1.38 (s, 12H).

^{13}C NMR ($CDCl_3$) δ 166.65, 144.63, 140.29, 133.72, 132.21, 129.25, 121.54, 119.10, 117.41, 84.78, 26.60, 25.34, 25.20, 22.79, 22.27.

^{11}B NMR ($CDCl_3$) δ 29.77, 23.01.

HRMS Calcd for $C_{21}H_{28}B_2N_2O_3$: $[M+Na]^+$, 401.2178. Found: *m*/*z* 401.2180

2,2'-((1*E*,1'*E*)-1,4-phenylenebis(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene-2,1-diyl))bis(2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one) (22j)

A reaction tube equipped with a magnetic stirring bar was charged with $Pt(dba)_2$ (4.5 μmol, 6 mol %), $P(BFPy)_3$ (4.95 μmol, 6.6 mol %), (pin)B–B(aam) (0.165 mmol, 2.2 equiv), 1,4-diethynylbenzene (0.075 mmol, 1 equiv) and toluene (2 mL), and the mixture was stirred at 180 °C for 30 min under microwave irradiation. The mixture was diluted with ethyl acetate and filtered through a Celite plug. The organic solution was washed with brine, dried over Na_2SO_4, and evaporated. Purification of the residue by boric acid impregnated silica gel-column chromatography (hexane/ethyl acetate as an eluent) gave the product **22j**.

Isolated in 82% yield as a pale yellow solid: mp >300 ˚C (Melting point of **22j** could not be determined, because it is out of the measurable range of the melting point apparatus.)

^{1}H NMR (DMSO-d_6) δ 9.12 (s, 2H), 9.01 (s, 2H), 7.98 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.55 (dd, *J* = 7.6, 2.1 Hz, 2H), 7.44 (s, 4H), 7.24 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.08 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 2H), 6.84 (s, 2H), 1.25 (s, 24H).

^{13}C NMR (DMSO-d_6) δ 165.60, 145.29, 142.37, 133.32, 127.95, 126.78, 120.70, 118.64, 117.96, 84.11, 24.62.

^{11}B NMR (DMSO-d_6) δ 28.59, 21.72.

HRMS Calcd for $C_{36}H_{42}B_4N_4O_6$: $[M+H]^+$, 671.3549. Found: *m*/*z* 671.3563

(*E*)-2-(3,3-dimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-1-yl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (22k)

Isolated in 97% yield as a pale yellow solid: mp 129–130 ˚C

^{1}H NMR ($CDCl_3$) δ 8.19 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.69 (s, 1H), 7.48 (ddd, *J* = 8.4, 7.1, 1.6 Hz, 1H), 7.14 – 7.06 (m, 2H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.15 (s, 1H), 1.33 (s, 12H), 1.15 (s, 9H).

^{13}C NMR ($CDCl_3$) δ 166.62, 144.62, 133.68, 129.22, 121.45, 119.03, 117.38, 84.35, 38.07, 29.74, 25.18.
^{11}B NMR ($CDCl_3$) δ 30.60, 28.56.
HRMS Calcd for $C_{19}H_{28}B_2N_2O_3$: $[M+Na]^+$, 377.2178. Found: *m*/*z* 377.2184

(*E*)-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-1-en-1-yl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (22l)
Isolated in 90% yield as a pale yellow oil
^{1}H NMR ($CDCl_3$) δ 8.19 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.95 (s, 1H), 7.86 (s, 1H), 7.48 (ddd, *J* = 8.0, 7.2, 1.6 Hz, 1H), 7.10 (ddd, *J* = 8.1, 7.2, 1.1 Hz, 1H), 6.96 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.19 (s, 1H), 2.33 (td, *J* = 7.5, 1.4 Hz, 2H), 1.37 (s, 12H), 1.29 (d, *J* = 2.8 Hz, 8H), 0.89 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR ($CDCl_3$) δ 166.83, 144.73, 133.50, 129.08, 121.18, 119.02, 117.32, 84.26, 41.65, 31.75, 29.63, 28.99, 24.90, 22.58, 14.11.
^{11}B NMR ($CDCl_3$) δ 30.06.
HRMS Calcd for $C_{21}H_{32}B_2N_2O_3$: $[M+Na]^+$, 405.2491. Found: *m*/*z* 405.2494

(*E*)-6-(4-oxo-3,4-dihydrobenzo[*d*][1,3,2]diazaborinin-2(1*H*)-yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-enenitrile (22m)
Isolated in 83% yield as a pale yellow oil
^{1}H NMR ($CDCl_3$) δ 8.20 (dd, *J* = 7.9, 1.6 Hz, 1H), 8.05 (s, 1H), 7.83 (s, 1H), 7.50 (td, *J* = 8.0, 7.2, 1.7 Hz, 1H), 7.16 – 7.08 (m, 1H), 6.98 (d, *J* = 8.1 Hz, 1H), 6.30 (s, 1H), 2.48 (t, *J* = 7.5 Hz, 2H), 2.35 (t, *J* = 7.1 Hz, 2H), 1.85 (t, *J* = 7.4 Hz, 2H), 1.37 (s, 12H).
^{13}C NMR ($CDCl_3$) δ 166.95, 144.68, 133.74, 129.19, 121.65, 119.82, 119.18, 117.63, 84.70, 40.39, 25.31, 25.02, 16.72.
^{11}B NMR ($CDCl_3$) δ 30.36.
HRMS Calcd for $C_{19}H_{25}B_2N_3O_3$: $[M+Na]^+$, 388.1974. Found: *m*/*z* 388.1975

(*E*)-2-(5-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-1-yl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (22n)
Isolated in 83% yield as a pale yellow oil
^{1}H NMR ($CDCl_3$) δ 8.20 (d, *J* = 6.8 Hz, 1H), 7.99 (s, 1H), 7.83 (s, 1H), 7.50 (ddd, *J* = 8.6, 7.2, 1.7 Hz, 1H), 7.16 – 7.07 (m, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.28 (s, 1H), 3.55 (t, *J* = 6.7 Hz, 2H), 2.48 (t, *J* = 7.8 Hz, 2H), 1.94 (t, *J* = 7.2 Hz, 2H), 1.38 (s, 12H).
^{13}C NMR ($CDCl_3$) δ 167.03, 144.77, 133.76, 129.18, 121.58, 119.09, 117.61, 84.59, 44.57, 38.68, 32.47, 25.03.
^{11}B NMR ($CDCl_3$) δ 29.95, 19.90.
HRMS Calcd for $C_{18}H_{25}B_2ClN_2O_3$: $[M+Na]^+$, 397.1632. Found: *m*/*z* 397.1632

(*E*)-4-(4-oxo-3,4-dihydrobenzo[*d*][1,3,2]diazaborinin-2(1*H*)-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yl 4-methylbenzenesulfonate (22o)
Isolated in 72% yield as a pale yellow solid: mp 116–117 °C
^{1}H NMR ($CDCl_3$) δ 8.20 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.97 (s, 1H), 7.84 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.22 (s, 1H), 4.17 (t, *J* = 6.5 Hz, 2H), 2.65 (t, *J* = 6.5 Hz, 2H), 2.38 (s, 3H), 1.32 (s, 12H).

^{13}C NMR ($CDCl_3$) δ 166.87, 144.84, 144.65, 133.75, 133.32, 129.89, 129.18, 128.09, 121.67, 119.20, 117.62, 84.71, 70.00, 40.64, 24.97, 21.72.
^{11}B NMR ($CDCl_3$) δ 28.71.
HRMS Calcd for $C_{24}H_{30}B_2N_2O_6S$: $[M+Na]^+$, 519.1903. Found: *m*/*z* 519.1901

(*E*)-2-(3-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (22p)
Isolated in 79% yield as a pale yellow oil
^{1}H NMR ($CDCl_3$) δ 8.20 (dd, *J* = 7.9, 1.6 Hz, 1H), 8.04 (s, 1H), 7.84 (s, 1H), 7.49 (ddd, *J* = 8.2, 7.2, 1.6 Hz, 1H), 7.11 (ddd, *J* = 8.1, 7.2, 1.1 Hz, 1H), 6.97 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.53 (t, *J* = 2.0 Hz, 1H), 4.16 (d, *J* = 2.0 Hz, 2H), 3.41 (s, 3H), 1.37 (s, 12H).
^{13}C NMR ($CDCl_3$) δ 166.86, 144.74, 133.65, 129.21, 128.37, 121.56, 119.29, 117.59, 84.61, 58.58, 25.01.
^{11}B NMR ($CDCl_3$) δ 28.87, 22.47.
HRMS Calcd for $C_{17}H_{24}B_2N_2O_4$: $[M+Na]^+$, 365.1814. Found: *m*/*z* 365.1818

(*E*)-2-(4-bromo-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-1-yl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (22q)
Isolated in 31% yield as a pale yellow solid: mp 91–92 ˚C
^{1}H NMR ($CDCl_3$) δ 8.20 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.01 (s, 1H), 7.94 (s, 1H), 7.50 (ddd, *J* = 8.3, 7.2, 1.6 Hz, 1H), 7.12 (t, *J* = 7.1 Hz, 1H), 6.98 (dd, *J* = 8.1, 1.0 Hz, 1H), 6.33 (s, 1H), 3.53 (t, *J* = 7.2 Hz, 2H), 2.89 (td, *J* = 7.3, 1.2 Hz, 2H), 1.38 (s, 12H).
^{13}C NMR ($CDCl_3$) δ 166.87, 144.68, 133.71, 129.20, 121.64, 119.26, 117.62, 84.73, 44.47, 32.75, 25.03.
^{11}B NMR ($CDCl_3$) δ 29.31.
HRMS Calcd for $C_{17}H_{23}B_2BrN_2O_3$: $[M+Na]^+$, 427.0970. Found: *m*/*z* 427.0972

(*E*)-4-methyl-8-(2-(4-oxo-3,4-dihydrobenzo[*d*][1,3,2]diazaborinin-2(1*H*)-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)dihydro-4λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (22r)
Isolated in 43% yield as a pale yellow solid: mp 213–214 ˚C
1H NMR (Acetone-*d*6) δ 8.74 (s, 1H), 8.42 (s, 1H), 8.09 (dd, J = 7.9, 1.6 Hz, 1H), 7.54 (ddd, J = 8.2, 7.2, 1.6 Hz, 1H), 7.25 (dd, J = 8.0, 1.0 Hz, 1H), 7.18 (s, 1H), 7.11 (ddd, J = 8.1, 7.1, 1.1 Hz, 1H), 4.28 (d, J = 16.9 Hz, 2H), 4.12 (d, J = 16.8 Hz, 2H), 2.97 (s, 3H), 1.33 (s, 12H).
^{13}C NMR (Acetone-*d*6) δ 169.29, 166.40, 146.14, 134.13, 129.25, 121.82, 120.34, 118.78, 85.11, 63.78, 48.47, 25.05.
^{11}B NMR (Acetone-*d*6) δ 31.11, 23.49, 21.21.
HRMS Calcd for $C_{20}H_{26}B_3N_3O_7$: $[M+H]^+$, 454.2123. Found: *m*/*z* 454.2120

(*E*)-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(trimethylsilyl)vinyl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (22's)
Isolated in 53% yield as a pale yellow solid: mp 121–122 ˚C
^{1}H NMR ($CDCl_3$) δ 8.21 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.50 (ddd, *J* = 8.0, 7.2, 1.6 Hz, 1H), 7.12 (ddd, *J* = 8.1, 7.2, 1.0 Hz, 1H), 7.00 – 6.94 (m, 1H), 6.92 (s, 1H), 6.70 (s, 1H), 6.30 (s, 1H), 1.12 (s, 13H),

0.13 (s, 9H).
^{13}C NMR ($CDCl_3$) δ 166.42, 144.61, 133.69, 129.26, 121.38, 118.66, 117.30, 83.91, 24.85, -1.18.
^{11}B NMR ($CDCl_3$) δ 31.47, 28.37.
HRMS Calcd for $C_{18}H_{28}B_2N_2O_3Si$: $[M+Na]^+$, 393.1948. Found: *m*/*z* 393.1950

(*Z*)-2-(1,2-diphenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (22t)
Isolated in 85% yield as a pale yellow solid: mp 216–217 °C
^{1}H NMR ($CDCl_3$) δ 8.22 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.51 (ddd, *J* = 8.5, 7.1, 1.6 Hz, 1H), 7.36 (s, 1H), 7.16 – 7.06 (m, 8H), 7.04 – 6.99 (m, 2H), 6.98 – 6.90 (m, 3H), 6.79 (s, 1H), 1.23 (s, 12H).
^{13}C NMR ($CDCl_3$) δ 166.33, 144.16, 141.32, 140.75, 133.70, 129.46, 129.20, 129.18, 128.20, 127.81, 126.55, 126.32, 121.72, 118.93, 117.47, 84.55, 24.77.
^{11}B NMR ($CDCl_3$) δ 30.39.
HRMS Calcd for $C_{27}H_{28}B_2N_2O_3$: $[M+Na]^+$, 473.2178. Found: *m*/*z* 473.2183

(*Z*)-2-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-4-en-4-yl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (22u)
Isolated in 69% yield as a pale yellow solid: mp 163–164 °C
^{1}H NMR ($CDCl_3$) δ 8.20 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.49 (ddd, *J* = 8.1, 7.2, 1.6 Hz, 1H), 7.15 – 7.03 (m, 2H), 6.95 (dd, *J* = 8.1, 1.0 Hz, 1H), 6.50 (s, 1H), 2.32 – 2.20 (m, 4H), 1.44 – 1.31 (m, 4H), 1.11 (s, 12H), 0.92 (dt, *J* = 13.3, 7.3 Hz, 6H).
^{13}C NMR ($CDCl_3$) δ 166.65, 144.59, 133.65, 129.22, 121.34, 118.78, 117.36, 83.64, 33.97, 32.78, 24.82, 23.34, 23.06, 14.59, 14.48.
^{11}B NMR ($CDCl_3$) δ 30.41.
HRMS Calcd for $C_{21}H_{32}B_2N_2O_3$: $[M+Na]^+$, 405.2491. Found: *m*/*z* 405.2501

(*Z*)-2-(1-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-2-yl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (22v)
Isolated in 91% yield as a pale yellow solid: mp 136–137 °C
^{1}H NMR ($CDCl_3$) δ 8.24 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.57 – 7.42 (m, 2H), 7.38 – 7.32 (m, 2H), 7.25 – 7.17 (m, 1H), 7.19 – 7.10 (m, 3H), 7.02 (dt, *J* = 8.2, 1.5 Hz, 1H), 6.89 (s, 1H), 1.87 (s, 3H), 1.14 (s, 12H).
^{13}C NMR ($CDCl_3$) δ 166.78, 144.53, 141.23, 133.83, 129.28, 128.51, 128.21, 126.37, 121.64, 118.92, 117.50, 84.21, 24.77, 19.60.
^{11}B NMR ($CDCl_3$) δ 30.39, 22.40.
HRMS Calcd for $C_{22}H_{26}B_2N_2O_3$: $[M+H]^+$, 389.2202. Found: *m*/*z* 389.2201

(*Z*)-2-(1-(dimethyl(phenyl)silyl)-2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (22w)
Isolated in 74% yield as a pale yellow solid: mp 177–178 °C
^{1}H NMR ($CDCl_3$) δ 8.18 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.47 (ddd, *J* = 8.1, 7.2, 1.6 Hz, 1H), 7.44 – 7.39 (m, 2H), 7.31 (ddd, *J* = 4.8, 2.0, 0.9 Hz, 3H), 7.26 – 7.20 (m, 3H), 7.14 – 7.07 (m, 3H), 6.95 (s, 1H), 6.82 (ddd, *J* = 8.1, 1.1, 0.5 Hz, 1H), 6.13 (s, 1H), 1.03 (s, 12H), 0.01 (s, 6H).
^{13}C NMR ($CDCl_3$) δ 166.30, 144.67, 144.38, 139.77, 133.83, 133.67, 129.19, 129.15, 128.06,

128.00, 127.66, 126.97, 121.38, 118.51, 117.28, 84.30, 24.70, -0.83.
^{11}B NMR ($CDCl_3$) δ 29.73.
HRMS Calcd for $C_{29}H_{34}B_2N_2O_3Si$: $[M+Na]^+$, 531.2417. Found: *m*/*z* 531.2416

(*Z*)-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-2-en-2-yl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (22x + 22'x)
Isolated in 80% yield as a pale yellow solid: mp 124–125 ˚C
^{1}H NMR ($CDCl_3$) δ 8.24 – 8.17 (m, 2H, **22x + 22'x**), 7.49 (ddt, *J* = 8.1, 7.2, 1.6 Hz, 2H, **22x + 22'x**), 7.24 (d, *J* = 6.8 Hz, 1H), 7.14 – 7.07 (m, 3H, **22x + 22'x**), 6.96 (ddd, *J* = 8.2, 3.2, 1.1 Hz, 2H, **22x + 22'x**), 6.71 (d, *J* = 5.8 Hz, 1H), 6.52 (s, 1H), 2.28 (q, *J* = 8.0 Hz, 4H), 1.92 – 1.78 (m, 6H), 1.38 – 1.25 (m, 14H), 1.16 (s, 13H), 1.12 (s, 11H), 0.92 – 0.85 (m, 6H).
^{13}C NMR ($CDCl_3$) δ 166.79, 166.74, 144.63, 133.68, 133.66, 129.22, 121.37, 121.32, 118.80, 118.77, 117.40, 117.34, 83.78, 83.73, 32.31, 32.20, 32.12, 31.17, 30.12, 29.15, 28.88, 24.86, 24.82, 22.75, 22.66, 17.47, 16.22, 14.18.
^{11}B NMR ($CDCl_3$) δ 30.03.
HRMS Calcd for $C_{21}H_{32}B_2N_2O_3$: $[M+Na]^+$, 405.2491. Found: *m*/*z* 405.2493

(*Z*)-2-(2,3-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (24)
Isolated in 71% yield as a pale yellow oil
^{1}H NMR ($CDCl_3$) δ 8.18 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.64 (s, 1H), 7.48 (dd, *J* = 8.1, 7.2 Hz, 1H), 7.10 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 7.00 (dd, *J* = 8.1, 1.1 Hz, 1H), 6.60 (s, 1H), 1.95 (s, 2H), 1.76 – 1.70 (m, 5H), 1.65 (s, 3H), 1.27 (s, 12H).
^{13}C NMR ($CDCl_3$) δ 167.03, 144.77, 133.73, 129.45, 124.84, 123.55, 121.71, 119.38, 117.60, 84.06, 25.09, 20.86, 20.75.
^{11}B NMR ($CDCl_3$) δ 22.24, 18.33.
HRMS Calcd for $C_{19}H_{28}B_2N_2O_3$: $[M+H]^+$, 355.2359. Found: *m*/*z* 355.1994

Chemoselective Cross-Coupling of 22a
(*Z*)-2-(2-phenyl-2-(p-tolyl)vinyl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one (25)
A Schlenk tube equipped with a magnetic stirring bar was charged with Pd(dppf)•CH_2Cl_2 (2.7 μmol, 3 mol %), K_3PO_4 (0.27 mmol, 3 equiv), **22a** (0.09 mmol, 1 equiv), *p*-bromotoulene (0.135 mmol, 1.5 equiv) and DMF (2 mL), and the mixture was stirred at 80 °C for 18 h. The mixture was diluted with ethyl acetate and filtered through a Celite plug. The organic solution was washed with brine, dried over Na_2SO_4, and evaporated. Purification of the residue by boric acid impregnated silica gel-column chromatography (hexane/ethyl acetate as an eluent) gave the product **25**.
Isolated in 43% yield as a white solid: mp 140–141 ˚C
^{1}H NMR ($CDCl_3$) δ 8.12 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.42 (ddd, *J* = 8.1, 7.2, 1.6 Hz, 1H), 7.39 – 7.30 (m, 6H), 7.28 (s, 1H), 7.22 – 7.17 (m, 2H), 7.06 (ddd, *J* = 8.1, 7.2, 1.1 Hz, 1H), 6.81 (s, 1H), 6.63 (dt, *J* = 8.1, 0.7 Hz, 1H), 6.21 (s, 1H), 5.89 (s, 1H), 2.46 (s, 3H).
^{13}C NMR ($CDCl_3$) δ 166.81, 160.30, 145.00, 142.78, 138.91, 138.02, 134.48, 129.85, 129.77, 129.37, 129.03, 128.66, 128.03, 121.81, 119.19, 117.75, 22.28.
^{11}B NMR ($CDCl_3$) δ 28.01.
HRMS Calcd for $C_{22}H_{19}BN_2O$: $[M+Na]^+$, 339.1663. Found: *m*/*z* 339.1668

(*Z*)-1-methoxy-4-(2-phenyl-2-(p-tolyl)vinyl)benzene (26)

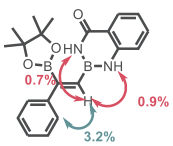
A reaction tube equipped with a magnetic stirring bar was charged with $Pd(OAc)_2$ (2.7 μmol, 3 mol %), PPh_3 (5.4 μmol, 3 mol %), **25** (0.09 mmol, 1 equiv), *p*-bromoanisole (0.18 mmol, 2 equiv), 1,4-dioxane (1 mL) and 6 M KOH aq. (0.54 mmol, 6 equiv), and the mixture was stirred at 140 °C for 0.5 h under microwave irradiation. The mixture was diluted with ethyl acetate and filtered through a Celite plug. The organic solution was washed with brine, dried over Na_2SO_4, and evaporated. Purification of the residue by gel permeation chromatography (toluene as an eluent) gave the product **26**.

Isolated in 64% yield as a brown oil

^{1}H NMR ($CDCl_3$) δ 7.33 – 7.27 (m, 5H), 7.15 (d, J = 7.9 Hz, 2H), 7.10 (d, J = 8.1 Hz, 2H), 6.99 (d, J = 8.3 Hz, 2H), 6.88 (s, 1H), 6.69 (d, J = 8.9 Hz, 2H), 3.76 (s, 3H), 2.39 (s, 3H).

^{13}C NMR ($CDCl_3$) δ 158.44, 144.02, 140.74, 137.70, 137.05, 130.90, 130.54, 130.41, 129.55, 128.26, 127.59, 127.57, 127.27, 113.53, 55.29, 21.48.

NOE Experiments for Determining Stereochemistry



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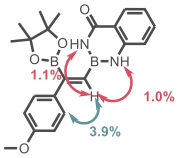

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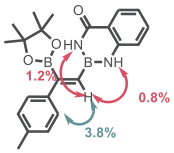

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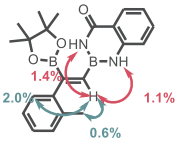

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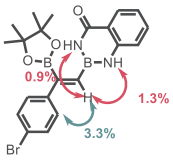

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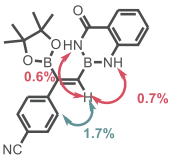

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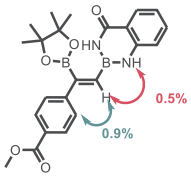

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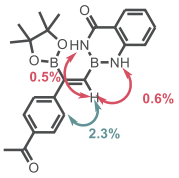

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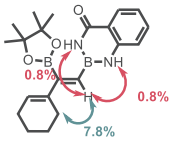

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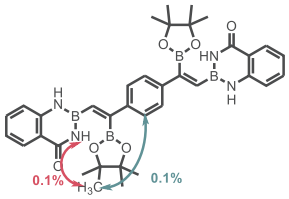

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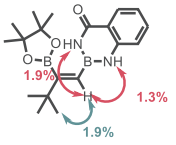

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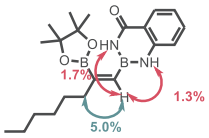

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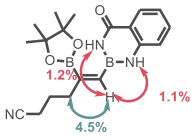

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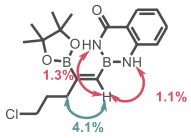

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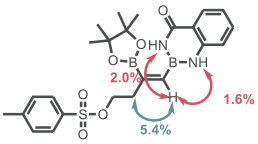

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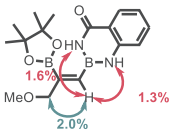

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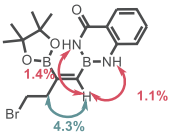

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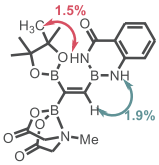

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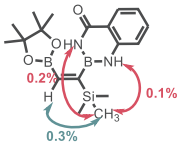

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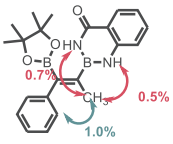

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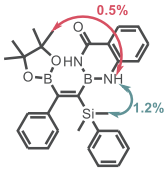

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List of Publications

I. Parts of the present Thesis have been, or are to be, published in the following journals.

Chapter 2

1 Transition Metal-free B(dan)-installing Reaction (dan: naphthalene-1,8-diaminato): H–B(dan) as a B(dan) Electrophile
J. Li, M. Seki, S. Kamio, H. Yoshida, *Chem. Commun.*, 2020, **56**, 6388.

Chapter 3

2 Ethynyl-B(dan) in [3+2] Cycloaddition and Larock Indole Synthesis: Synthesis of Stable Boron-containing Heteroaromatic Compounds
J. Li, H. Tanaka, T. Imagawa, T. Tsushima, M. Nakamoto, J. Tan, H. Yoshida, *Chem. Eur. J.*, DOI: 10.1002/chem.202303403

Chapter 4

3 Platinum–$P(BFPy)_3$-catalyzed Regioselective Diboration of Terminal Alkynes with (pin)B–B(aam)
I. Kageyuki, J. Li, H. Yoshida, *Org. Chem. Front.*, 2022, **9**, 1370.

II. Following publications are not included in this Thesis.

4 Direct Suzuki–Miyaura Coupling with Naphthalene-1,8-diaminato (dan)-Substituted Organoborons
H. Yoshida, M. Seki, S. Kamio, H. Tanaka, Y. Izumi, J. Li, I. Osaka, M. Abe, H. Andoh, T. Yajima, T. Tani, T. Tsuchimoto, *ACS Catal.*, 2020, **10**, 346.

5 Recent Advances in Synthetic Transformations with Robust Yet Reactive B(dan) Moiety
J. Li, H. Yoshida, *Heterocycles*, 2021, **102**, 1478.

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Through storms endured, behold the rainbow.

Jialun Li
Hiroshima University