

Negishi Cross-Coupling Is Compatible with a Reactive B–Cl Bond: Development of a Versatile Late-Stage Functionalization of 1,2-Azaborines and Its Application to the Synthesis of New BN Isosteres of Naphthalene and Indenyl

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S Supporting Information

ABSTRACT: The compatibility of the Negishi cross-coupling reaction with the versatile B–Cl functionality has been demonstrated in the context of late-stage functionalization of 1,2-azaborines. Alkyl-, aryl-, and alkenylzinc reagents have been utilized for the functionalization of the triply orthogonal precursor 3-bromo-1-(*tert*-butyldimethylsilyl)-2-chloro-1,2-dihydro-1,2-azaborine (**2**) to furnish new 2,3-substituted monocyclic 1,2-azaborines. This methodology has enabled the synthesis of previously elusive BN-naphthalene and BN-indenyl structures from a common intermediate.

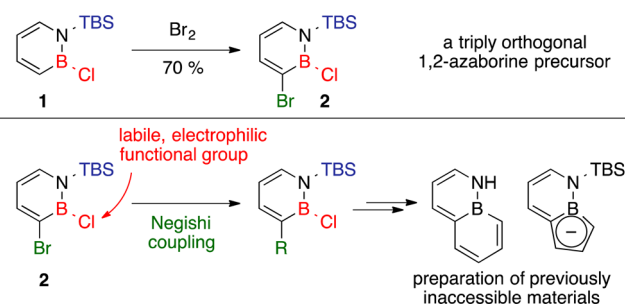
Research into boron–nitrogen (BN) isosteres of classic organic molecules has garnered significant attention because of its potential to expand the chemical space of compounds in biomedical research and materials science.¹ 1,2-Dihydro-1,2-azaborines (abbreviated as 1,2-azaborines) are BN isosteres of the ubiquitous monocyclic arene motif.² As an emerging heterocyclic structure, only limited synthetic methods are currently available for the generation of substituted monocyclic 1,2-azaborine derivatives. In addition to the earlier work by Dewar,^{3,4} White,⁵ Ashe,^{6,7} and our group,⁸ Yamaguchi⁹ recently prepared a 3,6-diaryl-1,2-azaborine from a *N*-Boc-protected bis(phenylpyrrolyl)borane using a ring-expansion rearrangement. Furthermore, Braunschweig developed two complementary synthetic approaches to highly substituted monocyclic 1,2-azaborines: (1) ring expansion of boroles with azides¹⁰ and (2) Rh-mediated cycloaddition of di-*t*-Bu-iminoborane and alkynes.¹¹ Our group has recently focused on selective *late-stage* functionalization as a general approach to produce an array of derivatives from an assembled 1,2-azaborine core, and we have demonstrated this concept through a C6-selective borylation with a subsequent Suzuki cross-coupling.¹² Despite the accomplishments made to date, the chemistry of 1,2-azaborines is still in its developing stages, and new, versatile synthetic strategies for monocyclic 1,2-azaborines in particular are needed to prepare previously inaccessible BN heterocycles.

In 2007, Ashe described the regioselective bromination of *N*-Et-*B*-Ph-1,2-azaborine at C3.¹³ This achievement should allow selective late-stage functionalization at C3 via cross-coupling technologies. Although not specifically demonstrated on a monocyclic 1,2-azaborine, Molander¹⁴ and Fang¹⁵ showed that a variety of cross-coupling methods, including Suzuki, Kumada,

Sonogashira, and Heck reactions, can be performed on halogenated BN-naphthalenes.

Since 1,2-azaborines contain the boron as an integral element of the heterocycle, a potential concern with the development of late-stage functionalization methods is compatibility with the reactivity associated with boron. This issue can be addressed by placing a relatively inert carbon-based substituent at boron (e.g., alkyl or aryl) to “protect” the boron prior to the late-stage functionalization process. The preinstallation of the B substituent, however, may limit the synthetic strategic options. A perhaps more general synthetic strategy is to develop a late-stage functionalization that is compatible with a labile boron substituent (e.g., *B*-X, X = Cl, Br) so that after initial “functionalization” the boron position is still available for derivatization. However, maintaining the reactive B–X bond while performing cross-coupling chemistry requires the nucleophilic reagent to couple preferentially with an electrophile (e.g., aryl halide) that is typically significantly less electrophilic than the B–X group. It is thus not surprising that the compatibility of the B–X (X = Cl, Br) bond—a functional group commonly involved in the synthesis of boron-containing materials¹⁶—with C–C bond-forming cross-coupling reactions has remained virtually unexplored.¹⁷ Here we show that Negishi cross-coupling at C3 of the triply orthogonal 1,2-azaborine precursor **2** (easily prepared from *N*-TBS-*B*-Cl-1,2-azaborine (**1**); Scheme 1, top) is compatible with the *B*-Cl functional group, adding a new strategic dimension in terms of the sequence of functionalizations of 1,2-azaborines. We also describe the

Scheme 1. Negishi Coupling in the Presence of a B–Cl Bond



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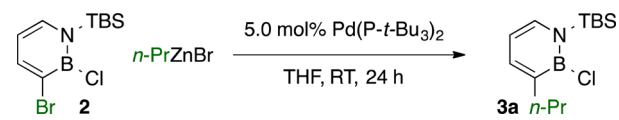
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synthesis of new BN isosteres of naphthalene and indenyl using our method (Scheme 1, bottom).

We considered the Negishi cross-coupling as an appealing method for the regioselective functionalization of 1,2-azaborine **2** because (1) it enables cross-coupling of aryl halides and alkyl-, aryl-, alkenyl-, alkynyl-, and heteroarylzinc halides with a reasonable functional group tolerance;¹⁸ (2) zinc reagents are nontoxic and readily available;¹⁹ and (3) unlike Suzuki coupling, it does not require borophilic additives as activating agents.²⁰ To probe the viability of Negishi couplings in the presence of reactive boron centers in 1,2-azaborines, we treated **2** with stoichiometric diethylzinc and *n*-propylzinc bromide in tetrahydrofuran (THF). Gratifyingly, no background reactivity was observed at room temperature over 24 h. We then pursued optimization of the regioselective Negishi cross-coupling at C3 of **2** using *n*-propylzinc bromide as a model nucleophile because of the higher availability and lower reactivity of RZnX reagents.

Our optimization studies of Negishi cross-coupling of **2** identified Pd(P-*t*-Bu₃)₂²¹ as an effective catalyst for the desired transformation, furnishing a benchmark yield of 87% (Table 1,

Table 1. Survey of Catalysts and Solvents for the Regioselective Negishi Cross-Coupling of 1,2-Azaborine **2**



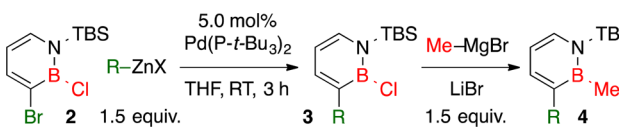
entry	deviation from the standard conditions ^a	yield (%) ^b
1	no deviation	87
2	no Pd catalyst	NR
3	catalyst: 5 mol % PdCl ₂ (P- <i>o</i> -tol) ₃	75
4	catalyst: 5 mol % (Xphos)PdG2	79
5	catalyst: 5 mol % (PCy ₃)PdG2	63
6	catalyst: 5 mol % NiCl ₂ (PCy ₃) ₂	35
7	catalyst: 5 mol % Ni(cod) ₂ + terpy	31
8	Et ₂ O instead of THF	80
9	toluene instead of THF	43
10	additive: <i>N</i> -methyl-2-pyrrolidinone	82
11	3 h instead of 24 h	87

^aAbbreviations: Cy = cyclohexyl, PdG2 = chloro[2-(2'-amino-1,1'-biphenyl)]palladium(II), cod = cyclooctadiene, terpy = terpyridine. ^bDetermined by ¹H NMR spectroscopy against a calibrated internal standard; averages of two runs.

entry 1). No reactivity was observed in the absence of a Pd catalyst (entry 2). Other Pd-based catalysts were active, but the yields were consistently lower than that with the Pd(P-*t*-Bu₃)₂ system (entries 3–5). Ni-based precatalysts gave poor yields and complex reaction mixtures (entries 6 and 7).^{22,23} A solvent switch to diethyl ether (entry 8) was not detrimental to the observed yield of **3a**. However, the use of a nonpolar solvent such as toluene decreased the yield of **3a** significantly (entry 9). Use of *N*-methyl-2-pyrrolidinone as an additive²⁴ did not decrease the reaction yield (entry 10). The reaction time could be shortened to 3 h with no significant loss in yield (entry 11).

With the optimized conditions in hand, we investigated the reaction scope with respect to the organozinc nucleophile. The sensitivity of the Negishi cross-coupling products **3a–f** toward moisture due to the presence of the B-Cl group made their isolation challenging. Nevertheless, we were able to determine the product yields of **3a–f** by ¹H NMR spectroscopy in the presence of an internal standard (see the Supporting Information

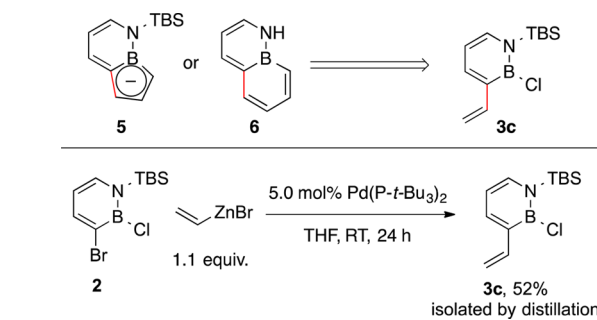
Table 2. Regioselective Negishi Cross-Coupling of 1,2-Azaborine **2**: Scope of the Organozinc Nucleophile



entry	R-ZnX	3 , yield (%) ^a	4 , yield (%) ^b
1	<i>n</i> -Pr-ZnBr	3a , 87	4a , 76
2	1-phenylvinyl-ZnBr	3b , 97	4b , 97
3	vinyl-ZnBr	3c , 69 ^c	4c , 51 ^d
4	2-(1,3-dioxan-2-yl)ethyl-ZnBr	3d , 69	4d , 66
5	4-chlorophenyl-ZnI	3e , 83	4e , 50
6	3,4,5-trifluorophenyl-ZnBr	3f , 91	4f , 89 ^e

^aDetermined by ¹H NMR spectroscopy against a calibrated internal standard in a separate experiment (0.098 mmol scale); averages of two runs. ^bIsolated yields (0.654 mmol scale); averages of two runs. ^c1.2 equiv of vinyl-ZnBr generated from 1.2 equiv of vinyl-MgBr and 2.4 equiv of ZnBr₂, 24 h reaction time. ^d1.01 equiv of vinyl-ZnBr generated from 1.01 equiv of vinyl-MgBr and 2 equiv of ZnBr₂, 22 h reaction time. ^e1.01 equiv of Me-MgBr instead of 1.5 equiv.

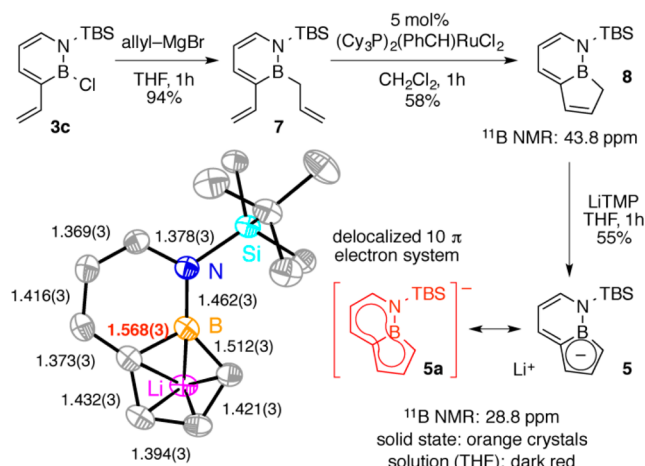
Scheme 2. Compound **3c** as a Versatile Common Intermediate for the Synthesis of BN Heterocycles **5** and **6**



(SI) for details). After a workup procedure following the Negishi coupling (see the SI for details), B-Cl compounds **3a–f** could be reacted with LiBr-activated Me-MgBr²⁵ to generate the readily isolable and chromatography-stable B-Me derivatives **4a–f** (Table 2). Our model reaction with *n*-Pr-ZnBr gave **4a** in 76% isolated yield (entry 1). Vinylzinc bromides were also suitable coupling partners (entries 2 and 3). An alkylzinc bromide bearing an acetal functional group was tolerated (entry 4). Halogenated arylzinc nucleophiles were also compatible with our optimized reaction conditions (entries 5 and 6).

We identified compound **3c** as a common intermediate for the synthesis of new BN-indenyl **5** and BN-naphthalene **6** using ring-closing metathesis (RCM) as a key strategy (Scheme 2, top). Thus, we scaled up the synthesis of intermediate **3c** using our developed Negishi coupling procedure and isolated it as a colorless oil after distillation in 52% yield (Scheme 2, bottom).

1,2-Azaborine **3c** reacted with allyl-MgBr to produce intermediate **7** in excellent yield (Scheme 3). Subsequent RCM with Grubbs' first-generation RCM catalyst provided **8** as a single isomer in moderate yield. Lithium tetramethylpiperidide (LiTMP) readily deprotonated **8** to generate the intensely colored BN-indenyl **5**.²⁶ It is worth noting that an approach involving initial installation of the allyl group at boron was not successful in our hands because the B-allyl substituent was prone to isomerization to the thermodynamically more stable internal B-alkenyl group under our cross-coupling conditions.

Scheme 3. Synthesis and ORTEP Plot of BN-Indenyl 5^a

Single-crystal X-ray diffraction (XRD) analysis of **5** unambiguously confirmed the indenyl structure (Scheme 3). In the solid state, the molecule is planar and η⁵-bound to a lithium atom through the five-membered ring. The bond distances in the six-membered azaborine ring are consistent with previously reported bond lengths for monocyclic azaborines²⁷ with the exception of the bridging B–C bond (bond distance highlighted in red), which is significantly longer than that found in typical monocyclic azaborine structures (1.568(3) Å vs ~1.52 Å).²⁷ An elongation of the bridging C–C bond in the indene/indenyl system is also observed upon deprotonation, but to a somewhat lesser extent (~1.437 Å for Li indenyl²⁸ vs ~1.40–1.41 Å for indene²⁹). The bridging B–C distance of 1.568 Å approaches that of a B(sp²)–C(sp²) single bond (e.g., 1.574 Å observed for a B-Ph-substituted 1,2-azaborine^{8e}). Thus, the observed geometric parameters for **5** are consistent with a significant contribution from the 10-π-electron delocalized resonance structure **5a**.

Scheme 4 illustrates the synthesis of BN-naphthalene **6**. Treatment of precursor **3c** with 3-butenylmagnesium bromide³⁰ generated diene intermediate **9** in good yield. Compound **9** was competent in RCM to generate bicyclic compound **10**. Oxidation of **10** using Pd/C as the catalyst with cyclohexene as a hydrogen scavenger in refluxing toluene furnished *N*-TBS-protected BN-naphthalene **6**.

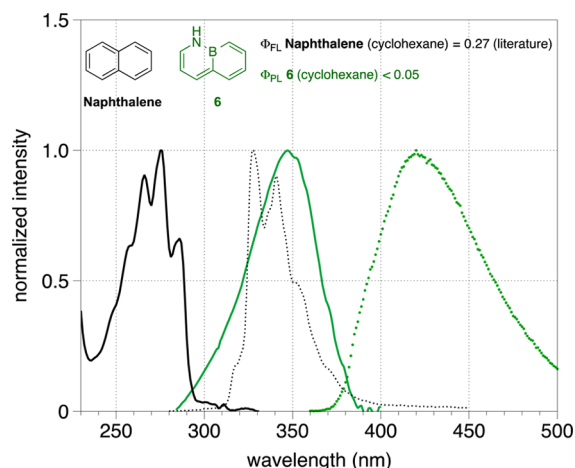
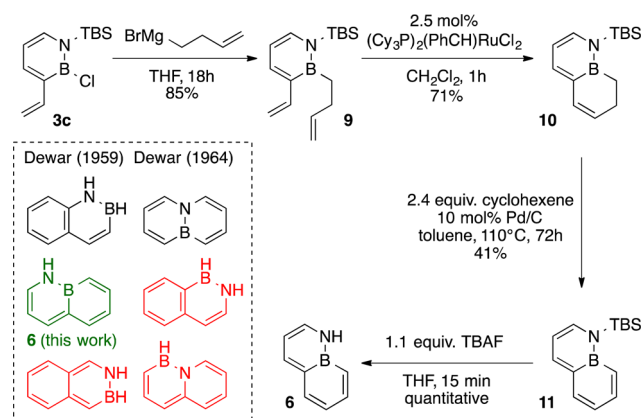
Scheme 4. Synthesis of the Parental BN-Naphthalene Isostere **6**; Compounds Shown in Red Have Not Been Synthesized

Figure 1. Normalized absorption (solid green trace) and emission (dotted green trace) spectra of **6** (1×10^{-5} M in cyclohexane) overlaid with the normalized absorption (solid black trace) and emission (dotted black trace) spectra of naphthalene. The photoluminescence quantum yield of **6** was determined in cyclohexane at room temperature. The quantum yield of naphthalene was taken from the literature.³⁶

naphthalene **11** in moderate yield.³¹ Removal of the *N*-TBS group with tetrabutylammonium fluoride (TBAF) proceeded in quantitative yield to generate the new parental BN-naphthalene isostere **6**.³² It is worth noting that compound **6** represents the third parental BN isostere of naphthalene (among the six possible isomers; see Scheme 4) that has been synthesized.^{33,34} We were able to grow single crystals of **6** suitable for XRD, but the structure was disordered because of the seemingly centrosymmetric structure of **6**. The extended packing diagram shows an edge-to-face herringbone packing similar to that observed in carbonaceous naphthalene (see the SI for details).³⁵

Figure 1 shows that both the absorption and emission maxima of BN-naphthalene **6** exhibit a large bathochromic shift relative to naphthalene ($\lambda_{\text{abs}} = 347$ nm and $\lambda_{\text{em}} = 420$ nm for **6** vs $\lambda_{\text{abs}} = 275$ nm and $\lambda_{\text{em}} = 327$ nm for naphthalene). The Stokes shift of parental naphthalene is 5782.6 cm⁻¹, versus 5008.9 cm⁻¹ for **6**. This suggests that compared with naphthalene, the Franck–Condon excited state of **6** is somewhat closer in energy to the relaxed emissive state (*S*₁), which is consistent with less spatial reorganization of atoms between the ground and excited states of BN-naphthalene **6** relative to naphthalene. Interestingly, the vibrational fine structure that is apparent in the absorption and emission spectra of naphthalene is not reproduced in the corresponding spectra for compound **6**.

In summary, we have developed in the context of the triply orthogonal 1,2-azaborine precursor **2** a Negishi cross-coupling protocol that is compatible with the versatile B–Cl functional group. The catalyst system selectively activates the C3–Br bond in **2** in the presence of the more electrophilic B–Cl bond to engage in C–C cross-coupling with an array of alkyl-, aryl-, and alkenylzinc nucleophiles. We have applied our method to the synthesis of a new BN isostere of indenyl (**5**) as well as a new BN isostere of naphthalene (**6**). BN-naphthalene **6** is the third parental BN isostere of naphthalene (out of six possible isomers) to be synthesized to date. Single-crystal XRD also revealed that the structure of BN-indenyl **5** is most consistent with a 10-π-electron delocalized bicyclic aromatic system. Many syntheses of boron-containing heterocycles/materials involve an intermediate bearing a labile B–X bond (X = Cl, Br). The availability of a regioselective functionalization method that leaves the B–X

group untouched should broaden the strategic dimension for the synthesis of boron-containing compounds. Our current efforts are directed toward expanding the scope of the Negishi reaction in the context of 1,2-azaborines and accessing new “BN-doped” conjugated materials through a bottom-up approach from substituted monocyclic 1,2-azaborines.

■ ASSOCIATED CONTENT

■ Supporting Information

Procedures, spectroscopic data, and crystallographic data (CIF). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b05879.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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(31) The major side product of this reaction comes from competitive reduction of the bicyclic starting material.

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