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One-Pot Carboboration of Alkynes Using Lithium Borylcyanocuprate and the Subsequent Suzuki–Miyaura Cross-Coupling of the Resulting Tetrasubstituted Alkenylborane

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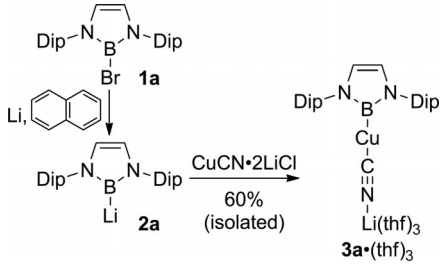
Keywords: Boron / Copper / Cuprates / Alkenes / Cross-coupling / Alkynes

We have developed a one-pot carboboration of internal alkynes using lithium borylcyanocuprates **3**. Isolation of single crystals of **3**·$(thf)_3$ enabled us to estimate its structural and spectroscopic features. Simple mixing of **3** with ester-substituted alkynes and alkynylarenes was followed by trapping of the resulting intermediate with electrophiles to give tetrasubstituted borylalkenes **4**, **5**, and **8** in moderate to good yields. Ligand exchange of **8ba** from diamine to pinacol allowed us to explore further application of obtained pinacol ester **10ba** to subsequent Suzuki–Miyaura cross-coupling reactions to give all-carbon substituted alkene **9ba**.

Introduction

Organoboron compounds are very useful reagents in synthetic chemistry.[1] Among them, organoboronic acid derivatives are one of the most important synthons for organic synthesis[2] because they react with carbon- or heteroatom-containing substrates to form new C–C or C–heteroatom bonds in the presence of transition metal catalysts. Recently, various organoboronic acid derivatives have become commercially available from chemical companies. In contrast to arylboronic acids, the number of alkenylboronic acid derivatives, especially tetrasubstituted ones, is much lower owing to the limited number of strategies used to prepare these useful compounds. For the syntheses of tetrasubstituted boronic acid derivatives, several strategies have been developed: (i) 1,2-Addition of boron-containing reagents, such as diborane(4),[3] silylborane,[4] stannylborane,[5] cyanoborane,[6] and alkynylborane[7] to alkynes. (ii) Transmetalative carboboration of alkynes by using chloroborane and organometallic reagents.[8] (iii) 1,1-Geminal diboration or silaboration of 1,1-geminal dihaloalkenes[9] or 1,1-geminal dihalocyclopropane followed by Rh-catalyzed rearrangement.[10] (iv) Borodesilylation of tetrasubstituted alkenylsilanes.[11] (v) Metal-catalyzed carbozinconation of alkynylboronic esters.[12] (vi) Addition of diborylmethide to ketones.[13] Among them, "carboboration" reactions[6–8] can be considered as the most reasonable method to synthesize tetrasubstituted borylalkenes because the diborated, silylborated, and stannylborated alkenes require further activation for subsequent reactions. On the other hand, we recently reported the one-pot carboboration of ynoate by addition of lithium borylcyanocuprate [**3a**·$(thf)_3$], generated from an anionic boron nucleophile, boryllithium (**2a**),[14] and copper cyanide [Equation (1)].[15] This reaction contains carbon electrophiles in contrast to the previously reported carboboration that involves a nucleophilic carbon reagent.[6–8] Herein, we report further exploration of the carboboration of alkynes using lithium borylcyanocuprate **3a** and carbon electrophiles and a crystal structure of new lithium borylcyanocuprate **3b** having a C–C saturated bond in the boron-containing five-membered ring; the carboboration of arylalkynes using **3b** and subsequent Suzuki–Miyaura cross-coupling using the obtained tetrasubstituted alkenylborane are also reported.



(1)

Results and Discussion

Lithium borylcyanocuprate **3a** generated in situ reacted with ethyl 2-butynoate and diethyl acetylenedicarboxylate (DEAD) followed by reaction with three electrophiles (ethanol, allyl bromide, and benzyl chloride; Table 1) to trap the

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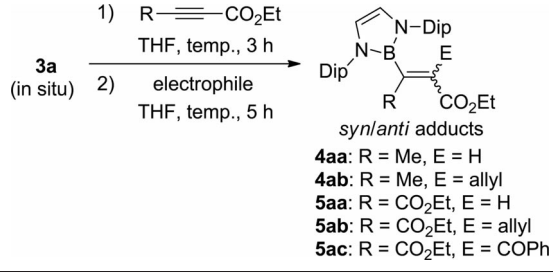
possible intermediate β-borylalkenylcuprate. Reaction with ethyl 2-butynoate followed by trapping with ethanol at room temperature afforded β-borylated product **4aa** as a *syn*/*anti* mixture with a ratio of 81:19 (Table 1, Entry 1). The regioselectivity for β-borylation could be explained as conjugate addition of a boron nucleophile. Lowering the temperature did not have a significant influence on the yield or *syn*/*anti* stereoselectivity (Table 1, Entry 2). In the case of trapping with allyl bromide at room temperature, *syn*-**4ab** was obtained as a major product (Table 1, Entry 3). Lowering temperature with allyl bromide improved the *syn* selectivity, but a slight decrease in the chemical yield for **4ab** was observed (Table 1, Entry 4). The data previously reported in our communication are cited for comparison in Entries 6–9 (Table 1). Reaction of DEAD followed by trapping with ethanol afforded a mixture of hydroborated products *syn*-/*anti*-**5aa** with a ratio of 70:30 (Table 1, Entry 5), which is similar to the case of ethyl 2-butynoate. Trapping with allyl bromide at room temperature gave *anti*-**5ab** as a major product in contrast to the case of ethyl 2-butynoate (Table 1, Entry 6). Lowering the temperature again gave *syn*-**5ab** as a dominant product (Table 1, Entry 7). Trapping with benzoyl chloride at room temperature afforded *anti*-**5ac** as a major product with a *syn*/*anti* ratio of 1:>99 (Table 1, Entry 8). The remarkably high selectivity may come from steric repulsion between a bulky boryl group and benzoyl chloride. Reaction at –78 °C did not give any carboborated product; instead, hydroborated isomeric mixture **5aa** was obtained. This result is slightly different in the *syn*/*anti* selectivity from Entry 5 (Table 1) probably due to the presence of benzoyl chloride.

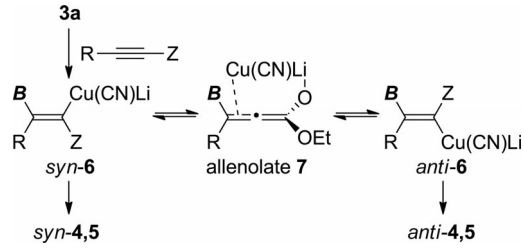
Table 1. Sequential reaction of **3a** with ynoate and an electrophile.



Entry	R	*T* [°C]	Electrophile	Product	Isolated yield [%]	*syn*/*anti*
1	Me	r.t.	EtOH	**4aa**	83	81:19
2	Me	–78	EtOH	**4aa**	85	82:18
3	Me	r.t.	allylBr	**4ab**	90	79:21
4	Me	–78	allylBr	**4ab**	73	>99:1
5	CO_2Et	–78	EtOH	**5aa**	82	70:30
6[a]	CO_2Et	r.t.	allylBr	**5ab**	96	38:62
7[a]	CO_2Et	–78	allylBr	**5ab**	93	>99:1
8[a]	CO_2Et	r.t.	PhCOCl	**5ac**	71	1:>99
9[a]	CO_2Et	–78	PhCOCl	**5aa**	80	60:40

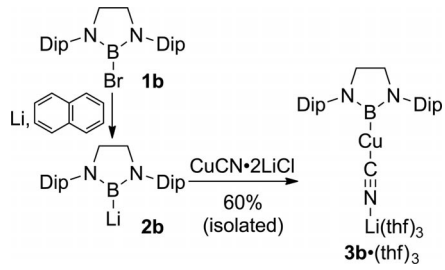
[a] Data taken from ref.[15]

A possible mechanism for the carboboration of ynoates is illustrated in Scheme 1. Lithium borylcyanocuprate **3a** reacts with the ynoate to form *syn*-**6** as an initial intermediate through *syn*-borylcupration. In the reaction at low temperature (Table 1, Entries 2, 4, 5, 7, and 9), the major *syn* adduct is directly formed from *syn*-**6**. Isomerization from *syn*-**6** to *anti*-**6** may proceed through lithium allenolate intermediate **7**. Allenolate **7** was directly observed by NMR spectroscopy, and it was suggested to have intramolecular alkene coordination to copper.[17] Steric repulsion between the bulky boryl group and the cyanocuprate moiety would lead to isomerization at room temperature to give a higher yield of the *anti* isomers. Direct comparison between Entries 3 and 6 (Table 1) suggests isomerization through the allenolate intermediate may be faster for the case with more electron-poor DEAD compared to the case with ethyl 2-butynoate. The difference in reaction rate probably comes from the difference in the strength of π-backdonation from copper to the allenic double bond in allenolate intermediate **7**.



Scheme 1. Possible mechanism for the formation of the *syn* and *anti* adducts.

As we previously reported[14e] that saturation of the C–C bond in the boron-containing five-membered ring would lead to a higher Lewis acidity on the boron center due to lack of aromaticity. Therefore, we also tried to use borylcyanocuprate **3b** possessing a C–C single bond in the ring backbone (vide infra for further conversion of the boryl substituent). Boryllithium **2b** was treated with CuCN·2LiCl to give the corresponding lithium borylcyanocuprate **3b** in 60% isolated yield as single crystals (Scheme 2). X-ray crystallographic analysis revealed a linear structure of **3b**·$(thf)_3$ with co-solvation of three thf molecules to the lithium cation (Figure 1). All the obtained structural parameters are similar to those of previously characterized **3a**·$(thf)_3$ in which the C–C bond is unsaturated. The ^1H and ^{13}C NMR spectra of isolated **3b** indicate its solution structure has D_{2d} symmetry. The ^{11}B NMR spectra showed a broad singlet resonance at δ_B = 45.4 ppm, which is close to those of other borylcopper species.[14b,14d,16] The negative mode of the



Scheme 2. Synthesis of lithium borylcyanocuprate **3b**.

ESI-TOF mass spectrum of **3b** showed a strong signal corresponding to an aggregated dinuclear species [2(**3b**–Li·3THF)–CN^-]$^-$.

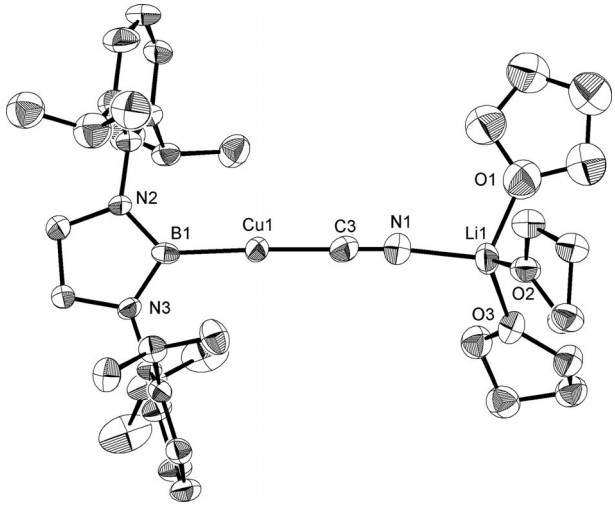
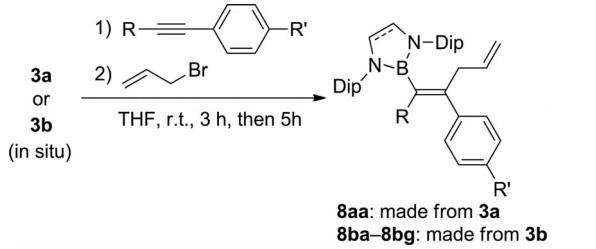


Figure 1. ORTEP drawing of **3b**·$(thf)_3$ (50% thermal ellipsoids, hydrogen atoms and minor parts of disordered thf molecules and isopropyl groups are omitted for clarity); selected bond lengths [Å] and angles [°]: B1–Cu1 1.997(5), B1–N1 1.452(6), B1–N2 1.445(6), Cu1–C3 1.902(5), C3–N3 1.164(6), N3–Li1 1.974(9), Li1–O 1.913 (av.), N1–B1–N2 103.7(4), B1–Cu1–C3 176.8(2), Cu1–C3–N3 179.0(5), C3–N3–Li1 172.0(5).

1-Arylalkynes were also subjected to the carboboration reaction using lithium borylcyanocuprates **3a**,**b** and allyl bromide. In the reaction of **3a** with 1-phenylpropyne, carboborated product **8aa** was obtained in 84% yield (Table 2, Entry 1). Saturation of the C–C bond in the boron-containing five-membered ring gave a slightly better yield of **8ba** (90%; Table 2, Entry 2), indicating that **3a** and **3b** have similar reactivity for the carboboration of arylalkynes. Selective formation of the β-borylated product in both cases could be explained by the electron-withdrawing nature of the aryl group. Furthermore, *syn* selectivity, confirmed by X-ray crystallography (for **8aa**, **8bb**, and **8bg**, see Supporting Information), of the addition was also explained by a lack of a strong electron-withdrawing group such as a carbonyl substituent to induce the isomerization of the alkenylcuprate intermediate. Changing the methyl substituent to an ethyl substituent did not hamper the reaction to give **8bb** (Table 2, Entry 3). However, introduction of a bulky *tert*-butyl group completely suppressed the reaction (Table 2, Entry 4). On the contrary, the electronic effect of the aryl ring slightly affected the chemical yield (Table 2, Entries 5–9). Introduction of an electron-withdrawing substituent such as nitrile and trifluoromethyl groups on the benzene ring lowered the chemical yield of carboborated products **8bc** and **8bd** (Table 2, Entries 5 and 6). Using a 1-arylalkene substituted with an electron-donating group resulted in slightly higher yields of **8be**–**8bg** (Table 2, Entries 7–9). Although the reason for the electronic effect is not clear so far, electron-donating substituents may enhance the reactivity of the borylated alkenylcuprate intermediate to facilitate its reaction with allyl bromide.

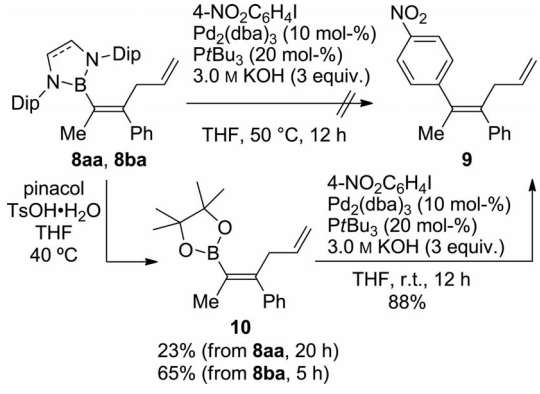
Table 2. Carboboration of 1-arylalkyne derivatives with borylcyanocuprates **3a**,**b** and allyl bromide.



Entry	R	R′	Product	Yield [%]
1[a]	Me	H	**8aa**	84
2	Me	H	**8ba**	90
3	Et	H	**8bb**	90
4	*t*Bu	H	–	0
5	Me	CN	**8bc**	66
6	Me	CF_3	**8bd**	50
7	Me	Me	**8be**	84
8	Me	OMe	**8bf**	76
9	Me	NMe_2	**8bg**	73

[a] Reaction time was 4+5 h.

Tetrasubstituted alkenylboranes **8aa** and **8ba** were applied to Suzuki–Miyaura cross-coupling reactions (Scheme 3). In the presence of $Pd(PtBu_3)_2$ and KOH aq., neither alkenylborane **8aa** nor **8ba** reacted with *p*-iodonitrobenzene to give coupled product **9**. The bulkiness of the Dip groups or effective π-donation of the nitrogen atoms may suppress the transmetalation of the boryl group to palladium. Therefore, the bulky Dip-substituted diamino group in **8aa** and **8ba** was converted into a pinacolate group in **10**, and this substrate was subjected to the cross-coupling reaction as follows. According to the previously reported conditions for the deprotection of the diamino substituents on the boron center,[6b] **8aa** and **8ba** were treated with pinacol and *p*-toluenesulfonic acid monohydrate in thf at 40 °C to give tetrasubstituted alkenylboronic acid pinacol ester **10**. Using **8ba** having a C–C single bond in the boron-containing five-membered ring gave a better yield of **10** (65%) despite of shorter reaction time of 5 h, compared to the case of **8aa** (20 h, 23%). In the presence of a palladium



Scheme 3. Ligand exchange of **8ba** and subsequent Suzuki–Miyaura cross-coupling reaction.

catalyst, **10** was successfully coupled with *p*-iodonitrobenzene to form tetrasubstituted alkene **9** possessing four different carbon substituents in 88% yield.[18,19]

Conclusions

In this paper, we reported the one-pot carboboration of alkynes by their reaction with lithium borylcyanocuprate followed by addition of an electrophile. New borylcopper species, lithium borylcyanocuprates **3a**,**b**, were synthesized and structurally characterized to show a linear arrangement of the boryl group, copper atom, cyanide, and lithium atom. It could react with ynoates or 1-arylalkynes to generate the borylalkenylcuprate. Trapping of this intermediate with electrophiles afforded the corresponding alkenylborane product. The regio- and stereochemistry and chemical yields of the product were varied by substrate, reaction temperature, and electrophile. By exchanging the diamino substituents on the resulting borylated alkene to give an alkenylboronic pinacol ester, this substrate could be utilized in Suzuki–Miyaura cross-coupling reactions to give tetrasubstituted alkenes with four different carbon substituents. This reaction sequence would enhance the usefulness of borylcopper species for organic synthesis.

Experimental Section

General: All manipulations were carried out by using standard Schlenk techniques under an atmosphere of argon purified by passing through a hot column packed with BASF catalyst R3–11 or in an argon-filled glove box (Miwa MFG). Low-temperature reactions at –35 °C performed in the glove box were performed by using refrigeration. Purification with GPC was performed by LC-928 recycling preparative HPLC (JAI), equipped with JAI GEL 1H-2H column and eluted with $CHCl_3$. The ^1H, $^7Li\{^1H\}$, ^{13}C, and $^{11}B\{^1H\}$ NMR spectra were recorded with 500 MHz spectrometers. Chemical shifts are reported in ppm relative to residual protonated solvent for ^1H, deuterated solvent for ^{13}C, external LiBr in D_2O for ^7Li, and external $BF_3{\cdot}OEt_2$ for ^{11}B nuclei used as a reference. High-resolution mass spectrometry (ESI-TOF, thf or MeOH solution) was measured with a JEOL AccuTOF JMS-T100LP instrument with calibration by using PEG or YOKUDELNA (JEOL) as an external reference. Hexane and thf were purified by passing through a solvent purification system (Grass Contour). Melting points were measured with a MPA100 Optimelt automated melting point system. For dilution of a boryllithium solution, thf was further dried with Na/K alloy and then filtered through a pad of silica gel prior to use. [D_6]Benzene was vacuum distilled from sodium/benzophenone. Lithium dispersion (Kanto Chemical) was washed with hexane to make a lithium powder containing 1% of sodium. Naphthalene was used as received. Bromoboranes **1a**,**b** were synthesized according to literature procedures.[14a,14e] 1-Arylalkynes were synthesized by using a literature procedure[20] and their NMR spectra were identical to those of the previously reported compounds.[21]

Preparation of a Stock Solution of Lithium Borylcyanocuprate 3a: In a glove box, a 20-mL vial equipped with a glass-coated stir bar was charged with bromoborane **1a** (2.35 g, 5.02 mmol), lithium powder (176 mg, 25.4 mmol), and naphthalene (132 mg, 1.03 mmol). To the cooled mixture at –35 °C, precooled thf (10.0 mL, –35 °C) was added. The mixture was stirred at –35 °C for 12 h. After the solution of **2a** was quickly filtered through a pad of Celite at room temperature, a solution of CuCN (448 mg, 5.00 mmol) and LiCl (425 mg, 10.0 mmol) in thf (7.00 mL) was added to the filtrate at –35 °C. The resulting mixture was stirred at –35 °C for 1 h, and then the solution was diluted to 25 mL with Na/K-dried thf using a volumetric flask to give a 0.200 M solution of borylcyanocuprate **3a**.

General Procedure for the Borylcupration of Ethyl 2-Butynoate and Sequential Reaction with Electrophile (Table 1): In a glove box, a 20-mL Schlenk flask equipped with a glass-coated stir bar was charged with a 0.200 M thf solution of **3a** (1.00 mL, 0.200 mmol). After the Schlenk flask was removed from the glove box, the Schlenk flask was cooled to –78 °C or kept at room temperature. To the reaction mixture was added a thf solution of ethyl 2-butynoate (1.00 M, 150 μL, 0.150 mmol) at –78 °C or at room temperature, and the resulting mixture was stirred at –78 °C or room temperature for 3 h. Then a thf solution of allyl bromide (0.225 M, 1.00 mL, 0.225 mmol) was added to the mixture at –78 °C or room temperature and stirred for 5 h. At the same temperature, EtOH (100 μL, 1.71 mmol) was added to the reaction mixture. All volatiles were removed under reduced pressure, and hexane was added to the mixture. The crude product was purified by recycling preparative HPLC.

***anti*-4aa:** Yield: 17% (14.5 mg, 29.0 μmol). Pale yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.17 (d, J = 7 Hz, 3 H), 1.18 (d, J = 6 Hz, 12 H), 1.19 (d, J = 6 Hz, 12 H), 1.66 (d, J = 1 Hz, 3 H), 3.30 (sept., J = 6 Hz, 4 H), 4.03 (q, J = 7 Hz, 2 H), 5.87 (d, J = 1 Hz, 1 H), 6.23 (s, 2 H), 7.18 (d, J = 8 Hz, 4 H), 7.28 (d, J = 8 Hz, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.4 (CH_3), 23.3 (CH_3), 24.9 (CH_3), 26.6 (CH_3), 27.9 (CH), 59.3 (CH_2), 119.8 (CH), 123.4 (CH), 127.1 (CH), 129.0 (CH), 138.7 (C_q), 146.8 (C_q), 154.1 (br. s, B-C), 165.5 (C_q) ppm. HRMS (ESI-TOF): calcd. for $C_{32}H_{45}BN_2O_2Na$ [**4aa** + Na] 523.3477, 524.3507; found 523.3456, 524.3482.

***syn*-4aa:** Yield: 73% (48.3 mg, 96.5 μmol). Pale yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.10 (t, J = 7 Hz, 3 H), 1.17 (d, J = 7 Hz, 12 H), 1.19 (d, J = 7 Hz, 12 H), 1.71 (d, J = 2 Hz, 3 H), 2.98 (sept., J = 7 Hz, 4 H), 3.94 (q, J = 7 Hz, 2 H), 5.52 (d, J = 2 Hz, 1 H), 6.20 (s, 2 H), 7.21 (d, J = 8 Hz, 4 H), 7.32 (t, J = 8 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.3 (CH_3), 17.7 (CH_3), 23.4 (CH_3), 25.3 (CH_3), 28.5 (CH), 59.3 (CH_2), 120.1 (CH), 123.7 (CH), 127.0 (CH), 127.6 (CH), 138.9 (C_q), 145.7 (C_q), 151.0 (br. s, B-C), 166.5 (C_q) ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 24.3 (br. s) ppm. HRMS (ESI-TOF): calcd. for $C_{32}H_{45}BN_2O_2Na$ [**4aa** + Na] 523.3477, 524.3507; found 523.3454, 524.3483.

***anti*-4aa:** Yield: 15% (13.2 mg, 26.4 μmol).

***syn*-4aa:** Yield: 70% (52.8 mg, 0.105 mmol).

***anti*-4ab:** Yield: 17% (14.0 mg, 25.9 μmol). Pale yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.146 (t, J = 7 Hz, 3 H), 1.148 (d, J = 7 Hz, 24 H), 1.55 (s, 3 H), 2.90 (d, J = 6 Hz, 2 H), 3.06–3.54 (br., 4 H), 3.99 (q, J = 7 Hz, 2 H), 4.49 (dd, J = 17, 2 Hz, 1 H), 4.67 (dd, J = 10, 2 Hz, 1 H), 5.51 (ddt, J = 17, 10, 6 Hz, 1 H), 6.17 (s, 2 H), 7.13 (d, J = 8 Hz, 4 H), 7.23 (t, J = 8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3 (CH_3), 19.5 (CH_3), 23.3 (CH_3), 26.6 (CH_3), 27.8 (CH), 32.5 (CH_2), 59.9 (CH_2), 114.5 (CH_2), 119.4 (CH), 123.4 (CH), 126.9 (CH), 134.9 (C_q), 136.0 (CH), 139.1 (C_q), 146.8 (C_q), 166.6 (C_q) ppm. HRMS (ESI-TOF): calcd. for $C_{35}H_{49}BN_2O_2Na$ [**4ab** + Na] 563.3791, 564.3821; found 563.3769, 564.3796.

***syn*-4ab**: Yield: 73% (58.7 mg, 0.109 mmol). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.12 (t, J = 7 Hz, 3 H), 1.19 (d, J = 7 Hz, 12 H), 1.22 (d, J = 7 Hz, 12 H), 1.52 (s, 3 H), 2.69 (d, J = 6 Hz, 2 H), 3.07 (sept., J = 7 Hz, 4 H), 4.00 (q, J = 7 Hz, 2 H), 4.48 (ddt, J = 17, 10, 6 Hz, 1 H), 4.66 (dd, J = 10, 2 Hz, 1 H), 4.70 (dd, J = 17, 2 Hz, 1 H), 6.29 (s, 2 H), 7.21 (d, J = 8 Hz, 4 H), 7.29 (t, J = 8 Hz, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.3 (CH_3), 19.8 (CH_3), 22.9 (CH_3), 26.2 (CH_3), 28.4 (CH), 39.4 (CH_2), 59.7 (CH_2), 116.4 (CH_2), 119.8 (CH), 123.9 (CH), 127.1 (CH), 133.9 (br. s, B-C), 135.0 (CH), 138.7 (C_q), 145.4 (C_q), 169.3 (C_q) ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 25.5 (br. s) ppm. HRMS (ESI-TOF): calcd. for $C_{35}H_{49}BN_2O_2Na$ [**4ab** + Na] 563.3791, 564.3821; found 563.3769, 564.3797.

***syn*-4ab:** Yield: 73% (58.8 mg, 0.109 mmol). Yellow oil.

Isolation of Lithium Borylcyanocuprate 3b·(thf)$_3$: In a glove box, a 20-mL vial equipped with a glass-coated stir bar was charged with bromoborane **1b** (470 mg, 1.00 mmol), lithium powder (35.3 mg, 5.09 mmol), and naphthalene (25.6 mg, 0.200 mmol). To the cooled mixture at –35 °C, precooled thf (10.0 mL, –35 °C) was added. The resulting mixture was stirred at –35 °C for 12 h. After the solution was quickly filtered through a pad of Celite at room temperature, a precooled –35 °C solution of CuCN (94.0 mg, 1.05 mmol) and LiCl (93.3 mg, 2.20 mmol) in thf (1.0 mL) was added to the filtrate at –35 °C. The reaction mixture was stirred at room temperature for 1 h. All volatiles were removed under reduced pressure, and hexane was added to the mixture. The added hexane was again evaporated to remove thf completely. The residue was extracted with hexane, and the resulting suspension was filtered through a pad of Celite to remove the inorganic salts. The crude product was recrystallized (hexane/thf, 30:1) at –35 °C to give colorless crystals (421 mg, 0.600 mmol, 60%) of **3b**·(thf)$_3$. M.p. 142.1–144.9 °C (decomp.). ^{1}H NMR (500 MHz, C_6D_6): δ = 1.32–1.35 (m, 24 H), 1.45 (d, J = 7 Hz, 12 H), 3.36 (t, J = 7 Hz, 12 H), 3.67 (sept., J = 7 Hz, 4 H), 6.45 (s, 2 H), 7.20 (s, 6 H) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 24.4 (CH_3), 25.5 (CH_2), 26.2 (CH_3), 28.5 (thf, CH_2), 55.1 (CH_2), 68.1 (thf, CH_2), 123.3 (CH), 125.4 (CH), 146.0 (C_q), 148.4 (C_q), 157.3 (CN) ppm. ^{11}B NMR (160 MHz, C_6D_6): δ = 45.4 (br. s) ppm. ^{7}Li NMR (194 MHz, C_6D_6): δ = –1.34 (s) ppm. IR (KBr): $\tilde{\nu}$ = 2129 (C≡N) cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{53}H_{76}B_2Cu_2N_5$ [2(**3b**–Li$^+$)–CN$^-$]$^-$ 930.4897, 933.4888; found 930.4797, 932.4854.

Preparation of a Stock Solution of Lithium Borylcyanocuprate 3b: In a glove box, a 20-mL vial equipped with a glass-coated stir bar was charged with bromoborane **1b** (2.35 g, 5.02 mmol), lithium powder (175 mg, 25.2 mmol), and naphthalene (128 mg, 1.00 mmol). To the cooled mixture at –35 °C was added precooled thf (10.0 mL, –35 °C). The mixture was stirred at –35 °C for 12 h. After the solution of **2b** was quickly filtered through a pad of Celite at room temperature, a solution of CuCN (450 mg, 5.03 mmol) and LiCl (430 mg, 10.2 mmol) in thf (7.00 mL) was added to the filtrate at –35 °C. The resulting mixture was stirred at –35 °C for 1 h, and then the solution was diluted to 25 mL with Na/K-dried thf using a volumetric flask to give a 0.200 M solution of borylcyanocuprate **3b**.

Syntheses of 1-Arylalkyne Derivatives: The following 1-arylalkynes were synthesized according to the literature procedure.[20] The NMR spectra of these compounds were identical to those of known compounds.[21]

4-Propynylbenzonitrile: A mixture of $Pd(PPh_3)_2Cl_2$ (24.1 mg, 34.3 μmol), 1,4-bis(diphenylphosphanyl)butane (29.9 mg, 70.1 μmol), 4-bromobenzonitrile (554 mg, 3.04 mmol), 2-butynoic acid (252 mg, 3.00 mmol), TBAF (1.0 M in thf, 6.0 mL, 6.0 mmol), and DMSO (6.0 mL) was stirred at 110 °C for 2 h. The reaction mixture was poured into sat. NH_4Cl aq. (20 mL) and was extracted with CH_2Cl_2 (2 × 20 mL). The combined CH_2Cl_2 extracts were washed with H_2O, dried with Na_2SO_4, and filtered. The solvent was removed under vacuum. Purification by silica-gel column chromatography (hexane/CH_2Cl_2, 3:1) afforded 4-propynylbenzonitrile as a colorless solid (350 mg, 2.48 mmol, 83%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.08 (s, 3 H), 7.45 (d, J = 8 Hz, 2 H), 7.56 (d, J = 8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 4.6 (CH_3), 78.7 (C_q), 91.2 (C_q), 111.0 (C_q), 118.8 (CN), 129.2 (C_q), 132.1 (CH), 132.2 (CH) ppm.

4-Propynylbenzotrifluoride: A similar procedure for nitrile derivative was applied to the synthesis of the CF_3 derivative here. Colorless oil (587 mg, 2.91 mmol, 58%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.07 (s, 3 H), 7.47 (d, J = 8 Hz, 2 H), 7.53 (d, J = 8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 4.4, 78.8, 88.9, 124.2 (q, J = 272 Hz), 125.3 (q, J = 4 Hz), 128.1, 129.5 (q, J = 33 Hz), 131.9 ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –62.66 (s) ppm.

4-Propynyltoluene: A mixture of $Pd(PPh_3)_2Cl_2$ (176 mg, 0.250 mmol), 1,4-bis(diphenylphosphanyl)butane (214 mg, 0.501 mmol), 4-iodotoluene (720 μL, 5.54 mmol), 2-butynoic acid (562 mg, 5.01 mmol), DBU (2.30 mL, 15.4 mmol), and DMSO (5.0 mL) was stirred at 80 °C for 12 h. The reaction was poured into sat. NH_4Cl aq. (20 mL) and extracted with CH_2Cl_2 (2 × 20 mL). The combined CH_2Cl_2 extracts were washed with H_2O, dried with Na_2SO_4, and filtered. The solvent was removed under vacuum. Purification by silica gel column chromatography (hexane) afforded 4-propynyltoluene as a yellow oil (610 mg, 4.68 mmol, 93%) ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.05 (s, 3 H), 2.34 (s, 3 H), 7.09 (d, J = 8 Hz, 2 H), 7.29 (d, J = 8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 4.4 (CH_3), 21.5 (CH_3), 79.9 (C_q), 85.1 (C_q), 121.1 (C_q), 129.1 (CH), 131.5 (CH), 137.6 (C_q) ppm.

4-Propynylanisole: A mixture of $Pd(PPh_3)_2Cl_2$ (176 mg, 0.250 mmol), 1,4-bis(diphenylphosphanyl)butane (215 mg, 0.503 mmol), 4-bromoanisole (700 μL, 5.59 mmol), 2-butynoic acid (562 mg, 5.00 mmol), DBU (2.30 mL, 15.4 mmol), and DMSO (5.0 mL) was stirred at 80 °C for 12 h. The reaction mixture was poured into sat. NH_4Cl aq. (20 mL) and extracted with CH_2Cl_2 (2 × 20 mL). The combined CH_2Cl_2 extracts were washed with H_2O, dried with Na_2SO_4, and filtered. The solvent was removed under vacuum. Purification by silica gel column chromatography (hexane) afforded 4-propynylanisole as a colorless oil (591 mg, 4.04 mol, 81%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.03 (s, 3 H), 3.79 (s, 3 H), 6.81 (d, J = 8 Hz, 2 H), 7.33 (d, J = 8 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 4.4 (CH_3), 55.4 (CH_3), 79.6 (C_q), 84.2 (C_q), 114.0 (CH), 116.3 (C_q), 132.9 (CH), 159.1 (C_q) ppm.

4-Propynyl-*N*,*N*-dimethylaniline: A mixture of $Pd(PPh_3)_2Cl_2$ (175 mg, 0.250 mmol), 1,4-bis(diphenylphosphanyl)butane (214 mg, 0.503 mmol), 4-bromo-*N*,*N*-dimethylaniline (1.05 g, 5.26 mmol), 2-butynoic acid (566 mg, 5.04 mmol), DBU (2.30 mL, 15.4 mmol), and DMSO (5.0 mL) was stirred at 80 °C for 36 h. The reaction mixture was poured into sat. NH_4Cl aq. (20 mL) and extracted with CH_2Cl_2 (2 × 20 mL). The combined CH_2Cl_2 extracts were washed with H_2O, dried with Na_2SO_4, and filtered. The solvent was removed under vacuum. Purification by silica gel column chromatography (hexane/CH_2Cl_2, 7:1) afforded 4-propynyl-*N*,*N*-dimethylaniline as a colorless solid (346 mg, 2.17 mmol, 43%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.03 (s, 3 H), 2.95 (s, 6 H), 6.62 (d, J = 9 Hz, 2 H), 7.27 (d, J = 9 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 4.5 (CH_3), 40.5 (CH_3), 80.3 (C_q), 83.1 (C_q), 111.4 (C_q), 112.1 (CH), 132.6 (CH), 149.8 (C_q) ppm.

8aa: In a glove box, **2b** (469 mg, 1.00 mmol), lithium (21.3 mg, 3.07 mmol), and naphthalene (25.6 mg, 0.200 mmol) were placed in a 20-mL vial. To the mixture, precooled thf (3.0 mL, –35 °C) was added. The resulting mixture was stirred at –35 °C for 12 h. After the solution was quickly filtered through a pad of Celite at room temperature, a precooled –35 °C solution of CuCN (89.5 mg, 1.00 mmol) and LiCl (91.0 mg, 2.15 mmol) in thf (1.0 mL) was added to the filtrate at –35 °C. The reaction mixture was stirred at room temperature for 1 h. To the mixture was added 1-phenylpropyne (116 mg, 1.00 mmol) at room temperature. After the resulting mixture was stirred for 3 h, allyl bromide (218 mg, 1.80 mmol) was added, and then, the mixture was further stirred at room temperature for 5 h. Volatiles were removed under reduced pressure, and the residue was extracted with hexane. The resulting suspension was filtered through a pad of Celite, and the solvents were evaporated under reduced pressure. The crude product was purified by silica gel chromatography (hexane/CH_2Cl_2, 1:0.05 to 1:0.2) to give a pale yellow solid of **8aa** (456 mg, 0.844 mmol, 84%). M.p. 109.3–111.8 °C. ^{1}H NMR (500 MHz, C_6D_6): δ = 1.20 (d, J = 7 Hz, 12 H), 1.30 (d, J = 7 Hz, 12 H), 1.44 (s, 3 H), 3.00 (d, J = 7 Hz, 2 H), 3.36 (sept., J = 7 Hz, 4 H), 4.62 (dd, J = 11, 1 Hz, 2 H), 4.82 (ddt, J = 17, 10, 2 Hz, 1 H), 6.33 (s, 2 H), 6.84 (dd, J = 8, 1 Hz, 2 H), 6.94 (t, J = 8 Hz, 1 H), 7.04 (t, J = 8 Hz, 2 H), 7.18 (m, 4 H), 7.23 (dd, J = 8, 6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.5 (CH_3), 22.9 (CH_3), 26.0 (CH_3), 28.3 (CH), 44.0 (CH_2), 115.6 (CH_2), 119.5 (CH), 123.6 (CH), 125.7 (CH), 126.9 (CH), 127.6 (CH), 128.4 (CH), 136.4 (CH), 139.3 (C_q), 142.6 (C_q), 145.5 (C_q), 146.5 (C_q) ppm. ^{11}B NMR (160 MHz, C_6D_6): δ = 27 (br. s) ppm. $C_{38}H_{49}BN_2$ (544.62): calcd. C 83.66, H 9.32, N 4.99; found C 83.80, H 9.07, N 5.14.

General Procedure for the Borylcupration of 1-Arylalkynes and Sequential Reaction with Allyl Bromide (Table 2, Entries 2–9): In a glove box, the alkyne (0.150 mmol) and a thf solution of **3b** (0.200 M, 1.00 mL, 0.200 mmol) were stirred in a 5-mL vial at room temperature for 3 h. Then, a thf solution of allyl bromide (0.225 M, 1.00 mL, 0.225 mmol) was added into the solution, and the mixture was stirred at room temperature for 5 h. The crude product was purified by silica gel column chromatography or by recycling preparative HPLC.

8ba: Purified by recycling preparative HPLC, colorless solid (73.8 mg, 0.135 mol, 90%). M.p. 120.5–122.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.20 (s, 3 H), 1.36 (dd, J = 19, 7 Hz, 24 H), 2.90 (d, J = 5 Hz, 2 H), 3.56–3.61 (m, 4 H), 3.72 (s, 4 H), 4.54–4.68 (m, 3 H), 6.76 (d, J = 7 Hz, 2 H), 7.10 (t, J = 7 Hz, 1 H), 7.18 (t, J = 7 Hz, 2 H), 7.25 (d, J = 7 Hz, 4 H), 7.30 (dd, J = 9, 6 Hz, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 19.2 (CH_3), 23.8 (CH_3), 26.8 (CH_3), 28.2 (CH), 44.0 (CH_2), 53.7 (CH_2), 115.6 (CH_2), 124.0 (CH), 125.8 (CH), 126.2 (CH), 126.9 (br. s, B-C), 127.6 (CH), 128.5 (CH), 136.7 (CH), 140.5 (C_q), 142.7 (C_q), 146.4 (C_q), 147.0 (C_q) ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 32.2 (br. s) ppm. $C_{38}H_{51}BN_2$ (546.64): calcd. C 83.49, H 9.40, N 5.12; found C 83.35, H 9.42, N 4.94.

8bb: Purified by silica gel column chromatography (hexane/CH_2Cl, 4:1), colorless solid (75.7 mg, 0.135 mol, 90%). M.p. 131.7–133.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.12 (t, J = 7 Hz, 3 H), 1.29 (d, J = 7 Hz, 24 H), 1.55 (s, 2 H), 1.67 (q, J = 7 Hz, 2 H), 2.82 (d, J = 7 Hz, 2 H), 3.54 (sept., J = 7 Hz, 4 H), 3.63 (s, 4 H), 4.13–4.22 (m, 1 H), 4.31 (dt, J = 17, 1 Hz, 1 H), 4.38 (dd, J = 10, 2 Hz, 1 H), 6.74–6.74 (m, 2 H), 7.04 (t, J = 7 Hz, 1 H), 7.11 (t, J = 7 Hz, 2 H), 7.15–7.21 (m, 6 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.7 (CH_3), 23.7 (CH_3), 25.4 (CH_3), 26.9 (CH_3), 28.2 (CH), 44.9 (CH_2), 53.7 (CH_2), 115.7 (CH), 124.1 (CH), 125.8 (CH), 126.2 (CH), 127.5 (CH), 128.3 (CH), 136.5 (CH), 141.0 (C_q), 142.9 (C_q), 147.0 (C_q), 147.6 (C_q) ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 32.1 (br. s) ppm. $C_{39}H_{53}BN_2$ (560.66): calcd. C 83.55, H 9.53, N 5.00; found C 83.17, H 9.56, N 4.78.

8bc: Purified by silica gel column chromatography (hexane/CH_2Cl, 3:1), colorless solid (56.6 mg, 0.099 mmol, 66%). M.p. 150.0–151.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.07 (s, 3 H), 1.23 (d, J = 7 Hz, 12 H), 1.29 (d, J = 7 Hz, 12 H), 2.79 (d, J = 4 Hz, 2 H), 3.45 (sept., J = 7 Hz, 4 H), 3.63 (s, 4 H), 4.40–4.46 (m, 2 H), 4.50–4.55 (m, 1 H), 6.75 (d, J = 8 Hz, 2 H), 7.17 (d, J = 7 Hz, 4 H), 7.23 (dd, J = 8, 7 Hz, 2 H), 7.40 (d, J = 8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.2 (CH_3), 23.7 (CH_3), 26.7 (CH_3), 28.2 (CH), 43.5 (CH_2), 53.6 (CH_2), 109.7 (C_q), 116.5 (CH_2), 119.2 (CN), 124.1 (CH), 126.4 (CH), 128.8 (br. s, B-C), 129.4 (CH), 131.6 (CH), 135.8 (CH), 140.2 (C_q), 144.6 (C_q), 146.9 (C_q), 148.0 (C_q) ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 31.4 (br. s) ppm. HRMS (ESI-TOF): calcd. for $C_{39}H_{50}BN_3$ [**7c** + H] 594.4002; found 594.4025.

8bd: Purified by silica gel column chromatography (hexane/CH_2Cl, 3:1), colorless solid (46.1 mg, 0.075 mmol, 50%). M.p. 122.0–123.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.07 (s, 3 H), 1.24 (d, J = 7 Hz, 12 H), 1.29 (d, J = 7 Hz, 12 H), 2.80 (d, J = 3 Hz, 2 H), 3.47 (sept., J = 7 Hz, 4 H), 3.63 (s, 4 H), 4.42–4.54 (m, 3 H), 6.77 (d, J = 8 Hz, 2 H), 7.17 (d, J = 7 Hz, 4 H), 7.23 (dd, J = 8, 7 Hz, 2 H), 7.36 (d, J = 8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.3 (CH_3), 23.8 (CH_3), 26.8 (CH_3), 28.2 (CH), 43.8 (CH_2), 53.7 (CH_2), 116.3 (CH_2), 124.1 (CH), 124.4 (q, J = 532 Hz, CF_3), 124.7 (q, J = 4 Hz, CH), 126.4 (CH), 128.1 (q, J = 64 Hz, C_q), 128.9 (CH), 136.1 (CH), 140.4 (C_q), 145.1 (C_q), 146.6 (C_q), 147.0 (C_q). ^{11}B NMR (160 MHz, $CDCl_3$): δ = 31.2 (br. s) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –63.32 (s) ppm. HRMS (ESI-TOF): calcd. for $C_{39}H_{50}BF_3N_2Na$ [**7d** + Na] 637.3924; found 637.3952.

8be: Purified by silica gel column chromatography (hexane/CH_2Cl, 3:1), colorless solid (70.6 mg, 0.126 mmol, 84%). M.p. 104.7–106.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.10 (s, 3 H), 1.24 (d, J = 7 Hz, 24 H), 1.29 (d, J = 7 Hz, 24 H), 2.21 (s, 3 H), 2.78 (d, J = 5 Hz, 2 H), 3.48 (sept., J = 7 Hz, 4 H), 3.62 (s, 4 H), 4.46–4.58 (m, 3 H), 6.56 (d, J = 8 Hz, 2 H), 6.91 (d, J = 8 Hz, 2 H), 7.16 (d, J = 7 Hz, 4 H), 7.21 (dd, J = 8, 7 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.3 (CH_3), 21.2 (CH_3), 23.8 (CH_3), 26.8 (CH_3), 28.2 (CH), 44.0 (CH_2), 53.7 (CH_2), 115.5 (CH_2), 124.0 (CH), 126.2 (CH), 128.3 (CH), 135.1 (C_q), 136.9 (C_q), 139.7 (C_q), 140.6 (C_q), 146.3 (CH), 147.0 (C_q) ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 31.3 (br. s) ppm. HRMS (ESI-TOF): calcd. for $C_{39}H_{53}BN_2Na$ [**7e** + Na] 583.4206; found 583.4228.

8bf: Purified by silica gel column chromatography (hexane/CH_2Cl, 3:1), colorless solid (65.7 mg, 0.114 mmol, 76%). M.p. 97.0–100.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.11 (s, 3 H), 1.25 (d, J = 7 Hz, 11 H), 1.30 (d, J = 7 Hz, 12 H), 2.79 (d, J = 4 Hz, 2 H), 3.49 (sept., J = 7 Hz, 4 H), 3.63 (s, 4 H), 3.70 (s, 3 H), 4.45–4.59 (m, 3 H), 6.61 (d, J = 9 Hz, 2 H), 6.67 (d, J = 9 Hz, 2 H), 7.17 (m, 4 H), 7.22 (dd, J = 8, 7 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.2 (CH_3), 23.8 (CH_3), 26.8 (CH_3), 28.2 (CH), 44.1 (CH_2), 53.7 (CH_2), 55.1 (CH), 113.0 (CH), 115.5 (CH_2), 124.0 (CH), 126.2 (CH), 127.0 (br. s, B-C), 129.5 (CH), 135.0 (C_q), 136.9 (CH), 140.6 (C_q), 145.9 (C_q), 147.0 (C_q), 157.6 (C_q) ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 31.6 (br. s) ppm. HRMS (ESI-TOF): calcd. for $C_{39}H_{53}BN_2NaO$ [**7f** + Na] 599.4155; found 599.4157.

8bg: Purified by silica gel column chromatography (hexane/CH_2Cl_2, 3:1), colorless solid (64.6 mg, 0.110 mmol, 73%). M.p. 157.9.0–162.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.14 (s, 3 H), 1.24 (d, J = 7 Hz, 12 H), 1.28 (d, J = 7 Hz, 12 H), 2.79 (d, J = 5 Hz, 2 H), 2.83 (s, 6 H), 3.48 (sept., J = 7 Hz, 4 H), 3.61 (s, 4 H), 4.48–4.62

(m, 3 H), 6.51 (d, J = 9 Hz, 2 H), 6.59 (d, J = 9 Hz, 2 H), 7.15–7.16 (m, 4 H), 7.21 (dd, J = 8, 7 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.3 (CH_3), 23.8 (CH_3), 26.7 (CH_3), 28.2 (CH), 40.8 (CH_3), 44.0 (CH_2), 53.7 (CH_2), 112.0 (CH), 115.2 (CH_2), 124.0 (CH), 126.1 (CH), 129.3 (CH), 131.3 (C_q), 137.3 (CH), 140.7 (C_q), 146.2 (C_q), 147.0 (C_q), 148.5 (C_q) ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 32.4 (br. s) ppm. HRMS (ESI-TOF): calcd. for $C_{40}H_{56}BN_3$ [**7g** + H] 590.4652; found 590.4668.

10: In a 5-mL vial, a mixture of **8ba** (2.17 g, 4.97 mmol), pinacol (881 mg, 7.46 mmol), thf (1 mL), and $TsOH{\cdot}H_2O$ (1.42 g, 7.47 mmol) was stirred for 7 d at room temperature. The mixture was passed through a pad of Celite, and the solvent was removed in vacuo. The residue was purified by preparative TLC (hexane/CH_2Cl_2, 1:1) to afford **10** as a colorless solid (902 mg, 3.70 mmol, 74%). M.p. 51.1–53.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.32 (s, 12 H), 1.58 (s, 3 H), 3.41 (d, J = 7 Hz, 2 H), 4.88 (dd, J = 10, 2 Hz, 1 H), 4.93 (ddd, J = 17, 3, 2 Hz, 1 H), 5.72 (ddt, J = 17, 10, 7 Hz, 1 H), 7.08 (dd, J = 8, 2 Hz, 2 H), 7.22 (t, J = 7 Hz, 1 H), 7.31 (t, J = 8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.4 (CH_3), 25.0 (CH_3), 42.5 (CH_2), 83.3 (C_q), 115.2 (CH_2), 123.9 (br. s, B-C), 126.4 (CH), 128.0 (CH), 128.2 (CH), 137.2 (CH), 143.2 (C_q), 152.6 (C_q) ppm.$C_{18}H_{25}BO_2$ (284.20): calcd. C 76.07, H 8.87; found C 76.38, H 9.03.

9: In a 20-mL Schlenk flask, $Pd_2(dba)_3$ (18.9 mg, 20.6 μmol, 10 mol-%), PtBu$_3$ (8.3 mg, 41 μmol), 4-nitroiodobenzene (58.1 mg, 0.233 mmol), **10** (57.6 mg, 0.203 mmol), and thf (2.00 mL) were placed in the glove box. After the Schlenk flask was removed, degassed KOH aq. (3.00 M, 200 μL, 0.600 mmol) was added, and the resulting mixture was stirred for 12 h at room temperature under an argon atmosphere. To the reaction mixture was added sat. NH_4Cl aq., and the resulting mixture was extracted with CH_2Cl_2. The combined organic layer was washed with $NaHCO_3$ and brine and then dried with $MgSO_4$. Filtration and evaporation afforded a brown oil. The oily product was purified by preparative HPLC (silica gel; hexane/CH_2Cl_2, 5:1; two times) to afford **9** as a yellow oil (49.7 mg, 0.178 mol, 88%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.89 (s, 3 H), 2.96 (d, J = 6 Hz, 2 H), 4.85 (dq, J = 17, 2 Hz, 1 H), 4.90 (dq, J = 10, 2 Hz, 1 H), 5.61 (ddt, J = 17, 10, 6 Hz, 1 H), 7.24 (dd, J = 5, 3 Hz, 2 H), 7.29 (tt, J = 7, 1 Hz, 1 H), 7.39 (t, J = 8 Hz, 2 H), 7.45 (dt, J = 9, 2 Hz, 2 H), 8.24 (dt, J = 9, 2 Hz, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 22.5 (CH_3), 40.2 (CH_2), 116.1 (CH_2), 123.8 (CH), 127.0 (CH), 128.4 (CH), 128.9 (CH), 129.2 (CH), 133.0 (C_q), 135.7 (CH), 137.6 (C_q), 141.7 (C_q), 146.7 (C_q), 151.3 (C_q) ppm. HRMS (ESI-TOF): calcd. for $C_{36}H_{34}N_2NaO_4$ [2 × **9** + Na] 581.2416; found 581.2442.

X-ray Crystallography: Details of the crystal data and a summary of the intensity data collection parameters for **3b**·$(thf)_3$, **8aa**, **8bb**, and **8bg** are listed in Table S1 (Supporting Information). A suitable crystal was mounted with cooled mineral oil to the glass fiber and transferred to the goniometer of a Rigaku Mercury CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71070 Å) to 2θ max = 50°. The structures were solved by direct methods with SIR-97[22] and refined by full-matrix least-squares techniques against F^2 SHELXL-97.[23] The intensities were corrected for Lorentz and polarization effects. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions.

CCDC-816384 [for **3b**·$(thf)_3$], -821253 (for **8aa**), -816385 (for **8bb**), and -816386 (for **8bg**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Crystal and spectroscopic data.

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[1] D. E. Kaufmann, D. S. Matteson (Eds.), *Science of Synthesis*, Thieme, Stuttgart, **2005**, vol. 6.
[2] D. G. Hall (Ed.), *Boronic Acids – Preparation, Applications in Organic Synthesis and Medicine*, Wiley-VCH, Weinheim, **2005**.
[3] a) T. Ishiyama, N. Matsuda, N. Miyaura, A. Suzuki, *J. Am. Chem. Soc.* **1993**, *115*, 11018; b) C. N. Iverson, M. R. Smith, *Organometallics* **1996**, *15*, 5155; c) G. Lesley, P. Nguyen, N. J. Taylor, T. B. Marder, A. J. Scott, W. Clegg, N. C. Norman, *Organometallics* **1996**, *15*, 5137; d) T. Ishiyama, N. Matsuda, M. Murata, F. Ozawa, A. Suzuki, N. Miyaura, *Organometallics* **1996**, *15*, 713; e) T. Ishiyama, T. Kitano, N. Miyaura, *Tetrahedron Lett.* **1998**, *39*, 2357; f) R. L. Thomas, F. E. S. Souza, T. B. Marder, *J. Chem. Soc., Dalton Trans.* **2001**, 1650; g) F.-Y. Yang, C.-H. Cheng, *J. Am. Chem. Soc.* **2001**, *123*, 761; h) J. Ramírez, E. Fernandez, *Synthesis* **2005**, 1698; i) H. Braunschweig, T. Kupfer, M. Lutz, K. Radacki, F. Seeler, R. Sigritz, *Angew. Chem. Int. Ed.* **2006**, *45*, 8048; j) J. Ramírez, E. Fernández, *Tetrahedron Lett.* **2007**, *48*, 3841; k) H. Prokopcová, J. Ramírez, E. Fernández, C. O. Kappe, *Tetrahedron Lett.* **2008**, *49*, 4831; l) N. Iwadate, M. Suginome, *J. Am. Chem. Soc.* **2010**, *132*, 2548.
[4] a) M. Suginome, H. Nakamura, Y. Ito, *Chem. Commun.* **1996**, 2777; b) M. Suginome, T. Matsuda, Y. Ito, *Organometallics* **1998**, *17*, 5233; c) M. Suginome, T. Matsuda, H. Nakamura, Y. Ito, *Tetrahedron* **1999**, *55*, 8787; d) T. Ohmura, T. Awano, M. Suginome, H. Yorimitsu, K. Oshima, *Synlett* **2008**, 423.
[5] a) S. Onozawa, Y. Hatanaka, T. Sakakura, S. Shimada, M. Tanaka, *Organometallics* **1996**, *15*, 5450; b) S.-y. Onozawa, Y. Hatanaka, M. Tanaka, *Chem. Commun.* **1999**, 1863; c) L. Weber, H. B. Wartig, H. G. Stammler, A. Stammler, B. Neumann, *Organometallics* **2000**, *19*, 2891.
[6] a) M. Suginome, A. Yamamoto, M. Murakami, *J. Am. Chem. Soc.* **2003**, *125*, 6358; b) M. Suginome, A. Yamamoto, M. Murakami, *Angew. Chem. Int. Ed.* **2005**, *44*, 2380; c) M. Suginome, A. Yamamoto, M. Murakami, *J. Organomet. Chem.* **2005**, *690*, 5300; d) M. Suginome, A. Yamamoto, T. Sasaki, M. Murakami, *Organometallics* **2006**, *25*, 2911.
[7] a) A. Yamamoto, M. Suginome, *J. Am. Chem. Soc.* **2005**, *127*, 15706; b) M. Suginome, M. Shirakura, A. Yamamoto, *J. Am. Chem. Soc.* **2006**, *128*, 14438.
[8] a) M. Daini, M. Suginome, *Chem. Commun.* **2008**, 5224; b) M. Daini, A. Yamamoto, M. Suginome, *J. Am. Chem. Soc.* **2008**, *130*, 2918.
[9] a) T. Hata, H. Kitagawa, H. Masai, T. Kurahashi, M. Shimizu, T. Hiyama, *Angew. Chem. Int. Ed.* **2001**, *40*, 790; b) T. Kurahashi, T. Hata, H. Masai, H. Kitagawa, M. Shimizu, T. Hiyama, *Tetrahedron* **2002**, *58*, 6381; c) M. Shimizu, C. Nakamaki, K. Shimono, M. Schelper, T. Kurahashi, T. Hiyama, *J. Am. Chem. Soc.* **2005**, *127*, 12506.
[10] M. Shimizu, M. Schelper, I. Nagao, K. Shimono, T. Kurahashi, T. Hiyama, *Chem. Lett.* **2006**, *35*, 1222.
[11] K. Itami, T. Kamei, J.-i. Yoshida, *J. Am. Chem. Soc.* **2003**, *125*, 14670.
[12] Y. Nishihara, M. Miyasaka, M. Okamoto, H. Takahashi, E. Inoue, K. Tanemura, K. Takagi, *J. Am. Chem. Soc.* **2007**, *129*, 12634.
[13] K. Endo, M. Hirokami, T. Shibata, *J. Org. Chem.* **2010**, *75*, 3469.

[14] a) Y. Segawa, M. Yamashita, K. Nozaki, *Science* **2006**, *314*, 113; b) Y. Segawa, M. Yamashita, K. Nozaki, *Angew. Chem. Int. Ed.* **2007**, *46*, 6710; c) M. Yamashita, Y. Suzuki, Y. Segawa, K. Nozaki, *J. Am. Chem. Soc.* **2007**, *129*, 9570; d) T. Kajiwara, T. Terabayashi, M. Yamashita, K. Nozaki, *Angew. Chem. Int. Ed.* **2008**, *47*, 6606; e) Y. Segawa, Y. Suzuki, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2008**, *130*, 16069; f) M. Yamashita, Y. Suzuki, Y. Segawa, K. Nozaki, *Chem. Lett.* **2008**, *37*, 802; g) T. Terabayashi, T. Kajiwara, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2009**, *131*, 14162; h) K. Nozaki, Y. Aramaki, M. Yamashita, S.-H. Ueng, M. Malacria, E. Lacôte, D. P. Curran, *J. Am. Chem. Soc.* **2010**, *132*, 11449.

[15] Y. Okuno, M. Yamashita, K. Nozaki, *Angew. Chem. Int. Ed.* **2011**, *50*, 920.

[16] a) D. S. Laitar, P. Mueller, J. P. Sadighi, *J. Am. Chem. Soc.* **2005**, *127*, 17196; b) D. S. Laitar, E. Y. Tsui, J. P. Sadighi, *J. Am. Chem. Soc.* **2006**, *128*, 11036.

[17] a) K. Nilsson, T. Andersson, C. Ullenius, A. Gerold, N. Krause, *Chem. Eur. J.* **1998**, *4*, 2051; b) S. Mori, E. Nakamura, K. Morokuma, *Organometallics* **2004**, *23*, 1081.

[18] The product may contain a small amount of possible isomerized product *anti*-**9**, as similar allylic protons were observed in the ^{1}H NMR spectrum (see Supporting Information).

[19] The product was an inseparable mixture consisting of *syn*-**9ba**, isomerized 1,3-diene, and isomerized *anti*-**9ba**. The latter two products were assigned by ^{1}H NMR spectroscopy.

[20] a) J. Moon, M. Jang, S. Lee, *J. Org. Chem.* **2008**, *74*, 1403; b) K. Park, G. Bae, J. Moon, J. Choe, K. H. Song, S. Lee, *J. Org. Chem.* **2010**, *75*, 6244.

[21] a) N. G. Pschirer, U. H. F. Bunz, *Tetrahedron Lett.* **1999**, *40*, 2481; b) W. Zhang, S. Kraft, J. S. Moore, *J. Am. Chem. Soc.* **2003**, *126*, 329.

[22] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115.

[23] a) G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Göttingen, Germany, **1997**; b) G. M. Sheldrick, T. R. Schneider in *Macromolecular Crystallography*, Academic Press, Inc., San Diego, **1997**, part B, vol. 277, pp. 319.

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