HOKKAIDO UNIVERSITY

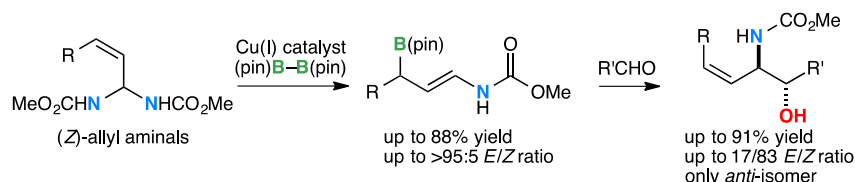| Title	Copper(I)-Catalyzed Boryl Substitution of Allyl Aminals: Selective Synthesis of Linear gamma-Aminoallylboronates
Author(s)	Takenouchi, Yuta; Ito, Hajime
Citation	Synthesis-stuttgart, 49(21), 4738-4744 https://doi.org/10.1055/s-0036-1588802
Issue Date	2017-11
Doc URL	http://hdl.handle.net/2115/71764
Rights	© 2017 Georg Thieme Verlag
Type	article (author version)
File Information	Aminal_14.pdf

Instructions for use

Copper(I)-Catalyzed Boryl Substitution of Allyl Aminals: Selective Synthesis of Linear γ-Aminoallylboronates

Y. Takenouchi
H. Ito*

Division of Applied Chemistry and Frontier Chemistry Center,
Faculty of Engineering, Hokkaido University, Sapporo,
Hokkaido, 060-8628, Japan.

E-mail: hajito@eng.hokudai.ac.jp

Abstract A novel approach for the selective synthesis of α-substituted γ-aminoallylboronates through a copper(I)-catalyzed γ-boryl-substitution of allyl aminals has been developed. The reaction proceeds with high yield (up to 88%) and good E/Z selectivity (up to >95:5). Subsequent aldehyde allylation using the allylboronates affords (Z)-anti-1,2-amino alcohol derivatives with high stereoselectivity (up to 91% yield, and up to E/Z = 17:83)

Key words: allylboronate, copper, catalysis, 1,2-amino alcohol, allylboration

1,2-Amino alcohols are common structural motifs in natural products and pharmaceuticals.[1] Establishing an efficient synthesis of this motif is an important challenge, and various synthetic approaches have been developed to obtain vicinal amino alcohols.[2] Among them, approaches involving formation of an amino alcohol moiety along with a new C–C bond are particularly attractive, such as the convergent synthesis of 1,2-amino alcohol derivatives that have a complex carbon skeleton.[3] Although the allylation of carbonyl compounds with γ-amino-substituted allylboron compounds has great potential for accessing stereo-defined vicinal amino alcohol derivatives due to their high levels of chemo- and diastereo-selectivities, synthetic routes to γ-aminoallylboron compounds are limited: lithiation of allyl amines and subsequent reaction with boron electrophiles (Scheme 1a).[4] Recently, a Pd-catalyzed reaction for the synthesis of these boronates has been reported by Hall and co-workers, but this method is only suitable for the synthesis of six-membered heterocyclic products, and is not applicable to linear γ-aminoallylboronates (Scheme 1b).[5] Development of a catalytic method for the preparation of linear γ-aminoallylboronates is therefore still required.
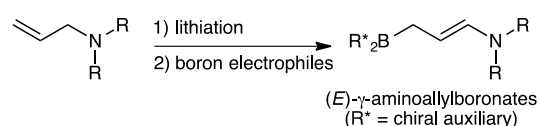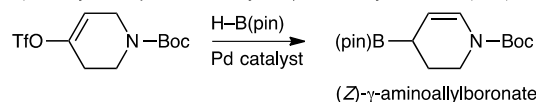

Scheme 1 Preparation Methods for γ-Aminoallylboronates

Copper(I)-catalyzed boryl substitution is an efficient way to obtain allylboron compounds due to its high regioselectivity and functional group tolerance. Recently, our group succeeded in the development of an enantioselective boryl substitution of allyl acetals **1a** to give enantio-enriched γ-alkoxyallylboronates.[6] This transformation provided a highly stereoselective allylation of aldehydes with γ-alkoxyallylborontes to afford chiral 1,2-diol derivatives (Scheme 2a). Extending the scope of the copper(I)-catalyzed boryl substitution/aldehyde allylation procedure, we focused on readily available allyl aminals as substrates. When the one of the amino groups in the allyl aminal acts as the leaving group in the copper(I)-catalyzed allylic boryl substitution, γ-aminoallylboronates will be formed. Although copper catalysis has been widely used for nucleophilic boryl substitutions of allyl and propargyl carbonates,[7] ethers,[8] sulfonates,[9] and phosphates,[10] to the best of our knowledge, the reaction using a nitrogen-containing functional group as a leaving group has been limited to strained compounds such as propargyl aziridines **1b**[11] or diazabicycles **1c**[12] (Schemes 2b and 2c). It was not clear whether the amino group could act as a leaving group, but we anticipated that it would be possible by thorough optimization of the reaction conditions.
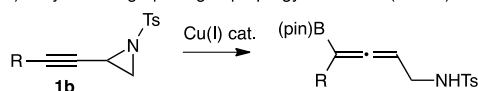
· **Our Previous Work**
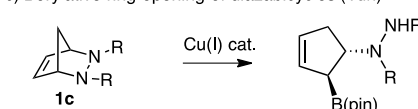a) Cu(I)-catalyzed boryl substitution of allyl acetals (Ito)
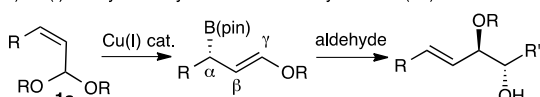
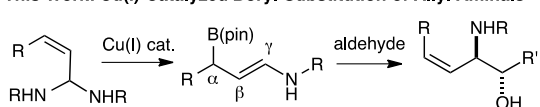· **Cu(I)-Catalyzed Borylation with N-Containing Group as a Leaving Group**
b) Borylative ring-opening of propargyl aziridines (Szabó)

c) Borylative ring-opening of diazabicycles (Yun)

· **This Work: Cu(I)-Catalyzed Boryl Substitution of Allyl Aminals**

Scheme 2 Copper(I)-Catalyzed Boryl Substitution of Allyl Aminals

Table 1 Optimization of the Reaction Conditions for the Copper(I)-Catalyzed Boryl Substitution of Allyl Aminals (Z)-2[a]

Entry	Substrate	R	Catalyst	Base	Yield[b] (%)
1	(Z)-2a	CO_2Me	CuCl/dppbz	KOMe	89 (71)[c]
2	(Z)-2a	CO_2Me	CuCl/none	KOMe	16
3	(Z)-2a	CO_2Me	CuCl/Xantphos	KOMe	22
4	(Z)-2a	CO_2Me	CuCl/dppe	KOMe	47
5	(Z)-2a	CO_2Me	CuCl/DPEphos	KOMe	38
6	(Z)-2a	CO_2Me	CuCl/dmpe	KOMe	8
7	(Z)-2a	CO_2Me	CuCl/phen	KOMe	4
8	(Z)-2a	CO_2Me	IPrCuCl	KOMe	34
9[d]	(Z)-2a	CO_2Me	CuCl/PPh₃	KOMe	10
10[e]	(Z)-2a	CO_2Me	CuCl/dppbz	KOMe	2
11	(Z)-2a	CO_2Me	CuCl/dppbz	K(O-t-Bu)	59
12	(Z)-2a	CO_2Me	CuCl/dppbz	NaOMe	63
13	(Z)-2b	Boc	CuCl/dppbz	KOMe	26[f]
14[g]	(Z)-2c	Cbz	CuCl/dppbz	KOMe	28[f]

[a]Reagents and conditions: CuCl (0.0125 mmol), ligand (0.0125 mmol), (Z)-2 (0.25 mmol), bis(pinacolato)diboron (0.375 mmol) and base (0.25 mmol) in solvent (0.75 mL) at 30 °C. [b]GC yield. [c]Isolated yield. [d]10 mol % of PPh₃ was used. [e]0.3 equiv of KOMe and 2.0 equiv of MeOH were used. [f]NMR yield. [g]54 h.

Herein, we report a novel synthetic approach for the synthesis of linear γ-aminoallylboronates via copper(I)-catalyzed boryl substitution of allyl aminals. Borylation of N-methylcarbamate-protected allyl aminals afforded the corresponding boronates in high yield and E/Z selectivity (54–88% yield, and up to >95:5 E/Z ratio). The allylation of aldehydes with the allylboronates afforded the desired 1,2-amino alcohol derivatives in good yield and E/Z selectivity (76%–91% yield, and up to 17:83 E/Z ratio).

Allyl aminal-(Z)-2a, with N-methyl carbamate protecting groups, was prepared prior to reaction optimization. The allyl aminals were easily prepared using the procedure reported by Maruoka.[13] The reaction of aminal (Z)-2a with B₂(pin)₂ in the presence of CuCl/dppbz as catalyst (5 mol %) and KOMe as a base (1 equiv) in THF afforded the desired allylboronate (E)-3a in high yield and E/Z selectivity (Table 1, entry 1, 89%). The borylation of (Z)-2a in the absence of a ligand provided the corresponding product in poor yield (entry 2). The reaction with Xantphos, which is an effective diphosphine ligand in many copper(I)-catalyzed borylation reactions,[7–10] was also found to give the product in poor yield (entry 3). The use of alternative bidentate phosphine ligands such as dppe, DPEphos or dmpe resulted in poor to moderate yields (entries 4–6). The use of phenanthroline, NHC, or monodentate PPh₃ ligands afforded inferior results compared with that of the dppbz ligand (entries 7–9). Addition of a proton source such as MeOH or t-BuOH was necessary for protonation of the in situ-generated amino-copper species in the borylative ring-opening (Schemes 2b and 2c).[11,12] Thus, we investigated effect of adding an alcohol to this reaction, but the addition of MeOH afforded only a trace mount of product (entry 10). We then studied the effect of the base on the reactivity. The use of K(O-t-Bu) or NaOMe resulted in moderate yields (entries 11 and 12). Finally, the impact of the protecting group on the substrate was evaluated by the borylation reactions of N-Boc-protected aminal (Z)-2b or N-Cbz-protected aminal (Z)-2c. These substrates afforded the corresponding product in poor yield (entries 13 and 14).
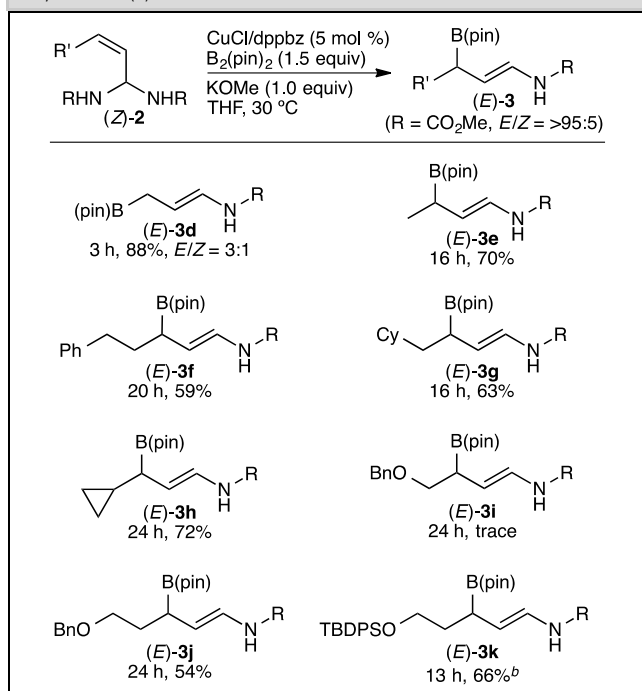
With the optimized conditions in hand (Table 1, entry 1), we then started to explore the scope of the aminals. Various γ-aminoallylboronates were obtained using the optimized conditions (Scheme 3). The borylation of aminal (Z)-2d, with a terminal olefin, proceeded in high yield with poor E/Z selectivity (88% yield, E/Z = 3:1). The poor E/Z selectivity was caused by the flexible conformation of the substrate.[6] The methyl group played an important role in enhancing the E/Z selectivity illustrated by boryl substitution of (Z)-2e yielding the corresponding product in 70% yield with perfect E/Z selectivity. Boronate (E)-3f, with an aromatic substituent, was also obtained in high yield (59%). Borylation of substrates (Z)-2g and (Z)-2h, with a branched structure at the ε- and σ-positions, respectively, afforded the desired products in high yields (63% and 72%, respectively). However, (Z)-2i, with a benzyl ether group at the σ-position, only gave a trace amount of product under the optimized reaction conditions. Finally, borylation of substrates with either a benzyl or silyl ether at the ε-position afforded the corresponding products (E)-3j and (E)-3k in high yield (54% and 66% yield, respectively).

Scheme 3 Substrate Scope for the Copper(I)-Catalyzed Boryl Substitution of Allyl Aminals (Z)-**2**[a]

(E)-**3d**
3 h, 88%, E/Z = 3:1

(E)-**3e**
16 h, 70%

(E)-**3f**
20 h, 59%

(E)-**3g**
16 h, 63%

(E)-**3h**
24 h, 72%

(E)-**3i**
24 h, trace

(E)-**3j**
24 h, 54%

(E)-**3k**
13 h, 66%[b]

[a]Reagents and conditions: CuCl (0.0125 mmol), ligand (0.0125 mmol), (Z)-**2** (0.25 mmol), bis(pinacolato)diboron (0.375 mmol) and base (0.25 mmol) in solvent (0.75 mL) at 30 °C. [b]10 mol % of CuCl and dppbz were used. K(O-t-Bu) was used instead of KOMe.

To demonstrate the usefulness of the γ-aminoallylboronate, we investigated the allylation of aldehydes (Table 2). We carried out the allylation of an aromatic aldehyde with (E)-**3a** to give the desired (Z)-anti-1,2-amino alcohol derivative in good yield and E/Z selectivity (entry 1, 82% yield, E/Z = 17:83). The allylations of an aliphatic or conjugated aldehyde also proceeded smoothly to afford the corresponding products in good yields (entry 2, 84% yield, E/Z = 23:77; entry 3, 91% yield, E/Z = 19:81, respectively). The use of Cbz-protected γ-aminoallylboronate (E)-**3c** displayed good yield and E/Z selectivity in the aldehyde allylation (entry 4, 76% yield, E/Z = 17:83). Allylation with (E)-**3j**, containing a benzyl ether, afforded the corresponding (Z)-anti-1,2-amino alcohol in good yield with moderate E/Z selectivity (84% yield, E/Z = 27:73).

Table 2 Aldehyde Allylation with γ-Aminoallylboronates (E)-**3**[a].

Entry	Substrate	RCHO	E/Z	Yield (%)
1	(Z)-**3a**	4-nitrobenzaldehyde	17:83	82
2	(Z)-**3a**	3-phenylpropionaldehyde	23:77	84
3	(Z)-**3a**	cinnamaldehyde	19:81	91
4	(Z)-**3c**	4-nitrobenzaldehyde	17:83	76
5	(Z)-**3j**	4-nitrobenzaldehyde	27:73	84

[a] Reagents and conditions: (E)-**3** (0.15–0.2 mmol), aldehydes (0.45–0.6 mmol) in toluene at 50 °C. The E/Z ratios of the anti product were determined by ^{1}H NMR and HPLC analyses.

In summary, we have successfully developed a novel approach for the synthesis of linear γ-aminoallylboronates via copper(I)-catalyzed boryl substitution of allyl aminals. Allylation of aldehydes has been demonstrated with the synthesized boronates to afford (Z)-anti-1,2-amino alcohol derivatives in high yield and with good E/Z selectivity. The borylation/allylation procedure is a concise and straightforward approach to construct a vicinal amino alcohol unit with concomitant formation of a new C–C bond.

Materials were obtained from commercial suppliers and purified by standard procedures unless otherwise noted. Solvents were also purchased from commercial suppliers, distilled, degassed via three freeze-pump-thaw cycles, and further dried over molecular sieve (MS 4Å). NMR spectra were recorded on JEOL JNM-ECX400P and ECS-400 spectrometer ([1]H: 400 MHz and [13]C: 99 MHz). Tetramethylsilane (^{1}H) and CDCl$_3$ (^{13}C) were employed as external standards, respectively. Multiplicity was recorded as follows: s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, o = octet, m = multiplet. CuCl (ReagentPlus® grade, 224332-25G, ≥99%) was purchased from Sigma-Aldrich Co. Mesitylene and 1,4-diisopropylbenzene were used as internal standards to determine NMR and GC yield, respectively. GLC analyses were conducted with a Shimadzu GC-2014 or GC-2025 equipped with ULBON HR-1 glass capillary column (Shinwa Chemical Industries) and a FID detector. HPLC analyses with chiral stationary phase were carried out using a Hitachi LaChrome Elite HPLC system with a L-2400 UV detector. High-resolution mass spectra were recorded at the Instrumental Analysis Division in Global Facility Center, Hokkaido University.

A representative procedure for the copper(I)-catalyzed boryl substitution of (Z)-2a (Table 1)

CuCl (1.2 mg, 0.0125 mmol), dppbz (5.5 mg, 0.0125 mmol), bis(pinacolato)diboron (95.2 mg, 0.375 mmol) and KOMe (17.5 mg, 0.25 mmol) were placed in a screw-capped test tube. The test tube was connected to a vacuum/nitrogen manifold through a needle. It was evacuated and backfilled with N$_2$ gas three times. Then, dry THF (0.5 ml) was added to the mixture via a syringe with stirring at 30 ºC. After 15–30 min, aminal (Z)-**2a** (64.5 mg, 0.25 mmol) was added to the reaction mixture with vigorous stirring at 30 °C. After the completion of the reaction, the mixture was directly filtered through a short silica-gel column with Et$_2$O as the eluent. After removal of the solvents under reduced pressure, GC yield was determined by GLC analysis of the crude reaction mixture [(E)-**3a**; 89%] using 1,4-diisopropylbenzene (26.7 mg, 0.164 mmol) as the internal standard. The crude product was purified by flash chromatography (SiO$_2$, hexane/AcOEt = 90:10 to 80:20) to give the corresponding γ-aminoallylboronate (E)-**3a** (55.1 mg, 0.177 mmol, 71% isolated yield).

A representative procedure for preparation of (Z)-dimethyl (oct-2-ene-1,1-diyl)dicarbamate [(Z)-2a]

In an oven-dried 30 mL two-neck round-bottomed flask, octynal (4.28 mL, 30 mmol), methylcarbamate (3.60 g, 48 mmol) and acetic anhydride (7.0 mL) were charged under nitrogen atmosphere. Trifluoroacetic acid (0.2 mL) was added to the suspension and the mixture was stirred for 15 min. The product was solidified in acetic anhydride solvent as a white solid. The solid was filtered in vacuum, washed with hexane and purified by column chromatography (SiO$_2$, hexane/AcOEt = 70:30 to 40:60) to give the product as a white powder (3.53 g, 46% yield).

In screw-capped test tube, IPrCuCl (48.7 mg, 0.1 mmol) and K(O-t-Bu) (11.2 mg, 0.1 mmol) were dissolved in dry THF (1.2 mL) under a nitrogen atmosphere. The catalyst solution was allowed to stir vigorously for 20 min and added to a solution of the propargyl aminal (530.7 mg, 2.1 mmol), 1,1,3,3-tetramethyldisiloxane (742.3 µL, 4.2 mmol), t-BuOH (505.4 µL, 5.25 mmol) and THF (3.0 mL). The mixture was directly filtered through a short silica-gel column with Et$_2$O as the eluent. After removal of the solvents under reduced pressure, the crude product was purified by flash chromatography (SiO$_2$,

hexane/AcOEt/CH₂Cl₂ = 50:30:20) to give the product (*Z*)-**2a** (271.4 mg, 51% yield).

¹H NMR (401 MHz, CDCl₃, δ): 0.88 (t, *J* = 6.8 Hz, 3H), 1.18–1.42 (m, 6H), 2.13 (q, *J* = 7.1 Hz, 2H), 3.68 (s, 6H), 5.30–5.90 (m, 4H), 5.55 (dt, *J* = 7.4, 9.6 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃, δ): 13.9 (*C*H₃), 22.4 (*C*H₂), 27.6 (*C*H₂), 28.8 (*C*H₂), 31.3 (*C*H₂), 52.1 (*C*H₃), 56.8 (*C*H), 126.3 (*C*H), 133.9 (*C*H), 155.9 (*C*).

HRMS-ESI (*m/z*): [M+Na]⁺ calcd for C₁₂H₂₂O₄N₂Na, 281.14718; found, 281.14719.

(*Z*)-Di-*tert*-butyl (oct-2-ene-1,1-diyl)dicarbamate [(*Z*)-2b]

¹H NMR (401 MHz, CDCl₃, δ): 0.89 (t, *J* = 6.8 Hz, 3H), 1.19–1.41 (m, 6H), 1.44 (s, 18H), 2.12 (q, *J* = 6.8 Hz, 2H), 5.37 (br s, 2H), 5.50 (dt, *J* = 7.5, 9.8 Hz, 1H), 5.45–5.65 (m, 1H), 5.55–5.90 (m, 1H).

¹³C NMR (100 MHz, CDCl₃, δ): 13.8 (*C*H₃), 22.4 (*C*H₂), 27.5 (*C*H₂), 28.2 (*C*H₃), 28.8 (*C*H₂), 31.2 (*C*H₂), 56.2 (*C*H), 79.4 (*C*), 127.3 (*C*H), 132.8 (*C*H), 154.7 (*C*).

HRMS-ESI (*m/z*): [M+Na]⁺ calcd for C₁₈H₃₄O₄N₂Na, 365.24108; found, 365.24103.

(*Z*)-Dibenzyl (oct-2-ene-1,1-diyl)dicarbamate [(*Z*)-2c]

¹H NMR (401 MHz, CDCl₃, δ): 0.87 (t, *J* = 7.0 Hz, 3H), 1.19–1.41 (m, 6H), 2.11 (q, *J* = 7.0 Hz, 2H), 5.10 (s, 4H), 5.55 (dt, *J* = 7.8, 9.6 Hz, 1H), 5.51–5.92 (m, 4H), 7.27–7.40 (m, 10H).

¹³C NMR (100 MHz, CDCl₃, δ): 13.9 (*C*H₃), 22.4 (*C*H₂), 27.6 (*C*H₂), 28.8 (*C*H₂), 31.2 (*C*H₂), 56.8 (*C*H), 66.7 (*C*H₂), 126.2 (*C*H), 127.96 (*C*H), 128.02 (*C*H), 128.4 (*C*H), 133.9 (*C*H), 136.1 (*C*), 155.2 (*C*).

HRMS-ESI (*m/z*): [M+Na]⁺ calcd for C₂₄H₃₀O₄N₂Na, 433.20978; found, 433.20981.

Dimethyl (prop-2-ene-1,1-diyl)dicarbamate (2d)

¹H NMR (401 MHz, CDCl₃, δ): 3.69 (s, 6H), 5.25 (d, *J* = 10.4 Hz, 1H), 5.34 (d, *J* = 17.6 Hz, 1H), 5.40–5.88 (m, 3H), 5.89–6.10 (m, 1H).

¹³C NMR (100 MHz, CDCl₃, δ): 52.3 (*C*H₃), 60.6 (*C*H), 116.7 (*C*H₂), 135.2 (*C*H), 156.0 (*C*).

HRMS-ESI (*m/z*): [M+Na]⁺ calcd for C₇H₁₂O₄N₂Na, 211.06893; found, 211.06932.

(*Z*)-Dimethyl (but-2-ene-1,1-diyl)dicarbamate [(*Z*)-2e]

¹H NMR (401 MHz, CDCl₃, δ): 1.72 (d, *J* = 5.6 Hz, 3H), 3.68 (s, 6H), 5.63 (dt, *J* = 7.1, 9.9 Hz, 1H), 5.15–6.00 (m, 4H).

¹³C NMR (100 MHz, CDCl₃, δ): 13.3 (*C*H₃), 52.2 (*C*H₃), 56.6 (*C*H), 127.4 (*C*H), 128.0 (*C*H), 156.0 (*C*).

HRMS-ESI (*m/z*): [M+Na]⁺ calcd for C₈H₁₄O₄N₂Na, 225.08458; found, 225.08465.

(*Z*)-Dibenzyl (oct-2-ene-1,1-diyl)dicarbamate [(*Z*)-2f]

¹H NMR (400 MHz, CDCl₃, δ): 2.47 (q, *J* = 7.1 Hz, 2H), 2.68 (t, *J* = 7.6 Hz, 2H), 3.64 (s, 6H), 5.55 (dt, *J* = 7.6, 10.6 Hz, 1H), 5.20–5.90 (m, 4H), 7.15–7.22 (m, 3H), 7.23–7.31 (m, 2H).

¹³C NMR (100 MHz, CDCl₃, δ): 29.5 (*C*H₂), 35.3 (*C*H₂), 52.1 (*C*H₃), 56.8 (*C*H), 125.9 (*C*H), 127.0 (*C*H), 128.3 (*C*H), 128.5 (*C*H), 132.2 (*C*H), 141.2 (*C*), 155.9 (*C*).

HRMS-ESI (*m/z*): [M+Na]⁺ calcd for C₁₅H₂₀O₄N₂Na, 315.13153; found, 315.13132.

(*Z*)-Dimethyl (4-cyclohexylbut-2-ene-1,1-diyl)dicarbamate [(*Z*)-2g]

¹H NMR (401 MHz, CDCl₃, δ): 0.81–1.11 (m, 2H), 1.15–1.38 (m, 4H), 1.58–1.74 (m, 5H), 2.01 (t, *J* = 6.6 Hz, 2H), 3.68 (s, 6H), 5.56 (dt, *J* = 7.7, 10.4 Hz, 1H), 5.29–5.91 (m, 4H).

¹³C NMR (101 MHz, CDCl₃, δ): 26.1 (*C*H₂), 26.2 (*C*H₂), 32.8 (*C*H₂), 35.2 (*C*H₂), 37.7 (*C*H₃), 51.9 (*C*H), 56.6 (*C*H), 126.8 (*C*H), 131.9 (*C*H), 155.9 (*C*).

HRMS-ESI (*m/z*): [M+Na]⁺ calcd for C₁₄H₂₄O₄N₂Na, 307.16283; found, 307.16263.

(*Z*)-Dimethyl (3-cyclopropylprop-2-ene-1,1-diyl)dicarbamate [(*Z*)-2h]

¹H NMR (401 MHz, CDCl₃, δ): 0.40 (dt, *J* = 4.5, 6.6 Hz, 2H), 0.82 (dt, *J* = 4.4, 6.4 Hz, 2H), 1.53–1.67 (m, 1H), 3.69 (s, 6H), 4.89 (t, *J* = 10.2 Hz, 1H), 5.20–5.78 (m, 3H), 5.87 (q, *J* = 7.2 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃, δ): 7.3 (*C*H₂), 10.0 (*C*H), 52.2 (*C*H₃), 57.3 (*C*H), 124.3 (*C*H), 137.9 (*C*H), 156.0 (*C*).

HRMS-ESI (*m/z*): [M+Na]⁺ calcd for C₁₀H₁₆O₄N₂Na, 251.10023; found, 251.10025.

(*Z*)-Dimethyl (4-(benzyloxy)but-2-ene-1,1-diyl)dicarbamate [(*Z*)-2i]

¹H NMR (401 MHz, CDCl₃, δ): 3.67 (s, 6H), 4.15 (dd, *J* = 1.2, 6.0 Hz, 2H), 4.52 (s, 2H), 5.73 (dt, *J* = 6.0, 17.0 Hz, 1H), 5.35–5.80 (m, 2H), 5.81–6.05 (m, 2H), 7.26–7.40 (m, 5H).

¹³C NMR (100 MHz, CDCl₃, δ): 52.0 (*C*H₃), 56.7 (*C*H), 65.7 (*C*H₂), 72.3 (*C*H₂), 127.5 (*C*H), 127.6 (*C*H), 128.2 (*C*H), 129.1 (*C*H), 129.2 (*C*H), 137.7 (*C*), 155.8 (*C*).

HRMS-ESI (*m/z*): [M+Na]⁺ calcd for C₁₅H₂₀O₅N₂Na, 331.12644; found, 331.12625.

(*Z*)-Dimethyl (5-(benzyloxy)pent-2-ene-1,1-diyl)dicarbamate [(*Z*)-2j]

¹H NMR (401 MHz, CDCl₃, δ): 2.47 (q, *J* = 6.4 Hz, 2H), 3.50 (t, *J* = 6.4 Hz, 2H), 3.67 (s, 6H), 4.94 (s, 2H), 5.60 (dt, *J* = 7.5, 10.0 Hz, 1H), 5.65–5.88 (m, 2H), 5.89–6.28 (m, 2H), 7.22–7.38 (m, 5H).

¹³C NMR (100 MHz, CDCl₃, δ): 28.0 (*C*H₂), 51.9 (*C*H₃), 56.6 (*C*H), 68.9 (*C*H₂), 72.5 (*C*H₂), 127.3 (*C*H), 127.4 (*C*H), 128.1 (*C*H), 128.3 (*C*H), 129.4 (*C*H), 138.0 (*C*), 155.8 (*C*).

HRMS-ESI (*m/z*): [M+Na]⁺ calcd for C₁₆H₂₂O₅N₂Na, 345.14209; found, 345.14182.

(*Z*)-Dimethyl {5-[(*tert*-butyldiphenylsilyl)oxy]pent-2-ene-1,1-diyl}dicarbamate [(*Z*)-2k]

¹H NMR (401 MHz, CDCl₃, δ): 1.04 (s, 9H), 2.40 (q, *J* = 6.3 Hz, 2H), 3.66 (s, 6H), 3.68 (t, *J* = 6.4 Hz, 2H), 5.20–5.70 (m, 2H), 5.61 (dt, *J* = 7.4, 10.7 Hz, 1H), 5.70–5.98 (m, 2H), 7.36–7.48 (m, 6H), 7.62–7.70 (m, 4H).

¹³C NMR (101 MHz, CDCl₃, δ): 19.1 (*C*), 26.7 (*C*H₃), 30.9 (*C*H₂), 52.0 (*C*H₃), 56.8 (*C*H), 62.9 (*C*H₂), 127.5 (*C*H), 128.0 (*C*H), 129.5 (*C*H), 129.9 (*C*H), 133.5 (*C*), 135.4 (*C*H), 155.9 (*C*).

HRMS-ESI (*m/z*): [M+Na]⁺ calcd for C₂₅H₃₄O₅N₂NaSi, 493.21292; found, 493.21277.

Methyl (*E*)-[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-1-en-1-yl]carbamate [(*E*)-3a]

¹H NMR (401 MHz, CDCl₃, δ): 0.87 (t, *J* = 6.6 Hz, 3H), 1.19–1.41 (m, 7H), 1.23 (s, 12H), 1.44–1.54 (m, 1H), 1.64–1.77 (m, 1H), 3.69 (s, 3H), 4.96 (dd, *J* = 9.2, 14.4 Hz, 1H), 6.19 (d, *J* = 10.4 Hz, 1H), 6.43 (dd, *J* = 10.6, 13.8 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃, δ): 14.0 (*C*H₃), 22.5 (*C*H₂), 24.58 (*C*H₃), 24.64 (*C*H₃), 25.3 (br, B–*C*H), 28.5 (*C*H₂), 31.2 (*C*H₂), 31.8 (*C*H₂), 52.2 (*C*H₃), 83.1 (*C*), 111.7 (*C*H), 122.8 (*C*H), 154.1 (*C*).

HRMS-ESI (*m/z*): [M+Na]⁺ calcd for C₁₆H₃₀O₄BNa, 333.21964; found, 333.22026.

Methyl (*E*)-[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl]carbamate [(*E*)-3d]

¹H NMR (400 MHz, CDCl₃, * indicates signals of the minor *Z*-isomer, δ): 1.248 (s, 12H), 1.254* (s, 12H), 1.54* (d, *J* = 8.0 Hz, 2H), 1.62 (d, *J* = 7.6 Hz, 2H), 3.69 (s, 3H), 3.73* (s, 3H), 4.74* (q, *J* = 8.0 Hz, 1H), 5.04 (dt, *J* = 7.2, 14.3 Hz, 1H), 6.21 (d, *J* = 8.4 Hz, 1H), 6.44 (t, *J* = 12.4 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃, * indicates signals of the minor *Z*-isomer, δ): 12.4 (B–*C*H₂), 24.6* (*C*H₃), 24.7 (*C*H₃), 52.2 (*C*H₃), 52.3* (*C*H₃), 83.3 (*C*), 103.3* (*C*H), 105.9 (*C*H), 122.9* (*C*H), 123.6 (*C*H), 154.1 (*C*), 154.4* (*C*). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar relaxation.

HRMS-ESI (*m/z*): [M+Na]⁺ calcd for C₁₁H₂₀O₄NBNa, 263.14139; found, 263.14176.

Methyl (*E*)-[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-1-yl]carbamate [(*E*)-3e]

¹H NMR (401 MHz, CDCl₃, only major isomer is shown, δ): 1.09 (d, *J* = 7.2 Hz, 3H), 1.21 (s, 12H), 1.74–1.88 (m, 1H), 3.69 (s, 3H), 5.12 (q, *J* = 7.4 Hz, 1H), 6.10–6.28 (m, 1H), 6.42 (dd, *J* = 11.6, 13.2 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃, δ): 15.5 (*C*H₃), 18.4 (br, B–*C*H), 24.6 (*C*H₃), 52.2 (*C*H₃), 83.2 (*C*), 113.2 (*C*H), 122.0 (*C*H), 154.1 (*C*).

HRMS-ESI (*m/z*): [M+Na]⁺ calcd for C₁₂H₂₂O₄NBNa, 277.15704; found, 277.15732.

Methyl (*E*)-[5-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)]pent-1-en-1-ylcarbamate [(*E*)-3f]

¹H NMR (400 MHz, CDCl₃, δ): 1.24 (s, 12H), 1.60–1.72 (m, 1H), 1.73–1.91 (m, 2H), 2.50–2.70 (m, 2H), 3.70 (s, 3H), 5.00 (dd, *J* = 9.2, 14.0 Hz, 1H), 6.22 (d, *J* = 10.8 Hz, 1H), 6.47 (dd, *J* = 10.8, 13.6 Hz, 1H), 7.17 (d, *J* = 6.4 Hz, 3H), 7.22–7.30 (m, 2H).

¹³C NMR (100 MHz, CDCl₃, δ): 24.6 (*C*H₃), 24.7 (*C*H₃), 24.9 (br, B–*C*H), 33.2 (*C*H₂), 35.1 (*C*H₂), 52.2 (*C*H₃), 83.2 (*C*), 111.1 (*C*H), 123.3 (*C*H), 125.6 (*C*H), 128.2 (*C*H), 128.4 (*C*H), 142.5 (*C*), 154.0 (*C*).

HRMS-ESI (*m/z*): [M+Na]⁺ calcd for C₁₉H₂₈O₄NBNa, 367.20399; found, 367.20465.

Methyl (*E*)-[4-cyclohexyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-1-yl]carbamate [(*E*)-3g]

¹H NMR (399 MHz, CDCl₃, δ): 0.70–0.94 (m, 2H), 1.04–1.44 (m, 7H), 1.23 (s, 12H), 1.57–1.76 (m, 4H), 1.76–1.92 (m, 1H), 3.69 (s, 3H), 4.92 (dd, *J* = 9.0, 14.2 Hz, 1H), 6.18 (d, *J* = 10.4 Hz, 1H), 6.42 (dd, *J* = 11.0, 14.2 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃, δ): 22.4 (br, B–*C*H), 24.6 (*C*H₃), 26.2 (*C*H₂), 26.3 (*C*H₂), 26.6 (*C*H₂), 32.7 (*C*H₂), 33.6 (*C*H₂), 36.2 (*C*H), 38.7 (*C*H₂), 52.2 (*C*H₃), 83.1 (*C*), 111.8 (*C*H), 122.6 (*C*H), 154.0 (*C*).

HRMS-ESI (*m/z*): [M+Na]⁺ calcd for C₁₈H₃₂O₄NBNa, 359.23529; found, 359.23615.

Methyl (*E*)-[3-cyclopropyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl]carbamate [(*E*)-3h]

¹H NMR (399 MHz, CDCl₃, δ): 0.02–0.10 (m, 1H), 0.11–0.21 (m, 1H), 0.44 (d, *J* = 7.2 Hz, 2H), 0.76–0.85 (m, 1H), 1.12–1.35 (m, 1H), 1.25 (s, 12H), 3.70 (s, 3H), 5.09 (d, *J* = 7.5 Hz, 1H), 6.34 (brs, 1H), 6.50 (t, *J* = 12.4 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃, δ): 3.8 (*C*H₂), 4.3 (*C*H₂), 12.2 (*C*H), 24.6 (*C*H₃), 29.5 (br, B–*C*H), 52.3 (*C*H₃), 83.2 (*C*), 110.8 (*C*H), 122.9 (*C*H), 154.1 (*C*).

HRMS-ESI (*m/z*): [M+Na]⁺ calcd for C₁₄H₂₄O₄NBNa, 303.17269; found, 303.17313.

Methyl (*E*)-[5-(benzyloxy)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-1-yl]carbamate [(*E*)-3j]

¹H NMR (399 MHz, CDCl₃, δ): 1.20 (s, 12H), 1.59–1.74 (m, 1H), 1.80–1.94 (m, 2H), 3.38–3.52 (m, 2H), 3.69 (s, 3H), 4.48 (s, 2H), 4.97 (dd, *J* = 8.8, 13.6 Hz, 1H), 6.26 (d, *J* = 9.2 Hz, 1H), 6.45 (dd, *J* = 10.6, 13.8 Hz, 1H), 7.20–7.40 (m, 5H).

¹³C NMR (100 MHz, CDCl₃, δ): 22.1 (br, B–*C*H), 24.6 (*C*H₃), 24.7 (*C*H₃), 31.2 (*C*H₂), 52.3 (*C*H₃), 69.2 (*C*H₂), 72.8 (*C*H₂), 83.2 (*C*), 110.9 (*C*H), 123.2 (*C*H), 127.4 (*C*H), 127.7 (*C*H), 128.3 (*C*H), 138.6 (*C*), 154.0 (*C*).

HRMS-ESI (*m/z*): [M+Na]⁺ calcd for C₂₀H₃₀O₅NBNa, 397.21456; found, 397.21508.

Methyl (*E*)-[5-((*tert*-butyldiphenylsilyl)oxy)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-1-yl]carbamate [(*E*)-3k]

¹H NMR (399 MHz, CDCl₃, only major isomer is shown, δ): 1.04 (s, 9H), 1.18 (s, 6H), 1.19 (s, 6H), 1.56–1.71 (m, 1H), 1.84 (sextet, *J* = 6.8 Hz, 1H), 1.96 (q, *J* = 8.0 Hz, 1H), 3.64 (t, *J* = 6.6 Hz, 2H), 3.70 (s, 3H), 4.89 (dd, *J* = 9.2, 14.0 Hz, 1H), 6.17 (d, *J* = 10.3 Hz, 1H), 6.43 (dd, *J* = 10.8, 14.0 Hz, 1H), 7.36–7.46 (m, 6H), 7.66 (dd, *J* = 1.4, 7.8 Hz, 4H).

¹³C NMR (100 MHz, CDCl₃, only major isomer is shown, δ): 19.2 (*C*), 21.2 (br, B–*C*H), 24.6 (*C*H₃), 24.7 (*C*H₃), 26.8 (*C*H₃), 33.9 (*C*H₂), 52.3 (*C*H₃), 62.8 (*C*H₂), 83.2 (*C*), 111.0 (*C*H), 123.2 (*C*H), 127.5 (*C*H), 129.4 (*C*H), 134.0 (*C*), 135.5 (*C*H), 153.9 (*C*).

HRMS-ESI (*m/z*): [M+Na]⁺ calcd for C₂₉H₄₂O₅NBNaSi, 545.28538; found, 545.28624.

Representative procedure for non-catalyzed allylation of aldehyde (Table 2, entry 1)

The allylboronate (*E*)-**3a** (62.1 mg, 0.2 mmol) was dissolved in toluene (0.4 mL). Then 4-nitrobenzaldehyde (90.7 mg, 0.6 mmol) was added to the mixture and stirred for 24 h at 50 °C. The reaction mixture was quenched by a CH₂Cl₂ solution of triethanolamine (10% v/v, 2.5 mL). The crude product was purified by silica-gel chromatography (EtOAc:hexane = 10/90 to 30/70) to give the corresponding product (*Z*)-*anti*-**4aa** as a colorless oil, 82% isolated yield (55.2 mg, 0.164 mmol) and *E/Z* = 17:83. The *E-Z* configuration of the products derided from the reaction of (*E*)-**3a** and 4-nitrobenzaldehyde was confirmed from coupling constant of alkene moiety of the product. The *E/Z* ratio of the *anti*-product was determined by ¹H NMR and HPLC analysis. The *syn* isomers of the products were not observed in ¹H NMR analysis of the crude reaction mixture.

¹H NMR (401 MHz, CDCl₃, * indicates signals of the minor *E*-isomer, δ): 0.82 (t, *J* = 7.2 Hz, 3H), 0.83–0.89* (m, 3H), 0.96–1.33 (m, 6H), 1.65–1.81 (m, 1H), 1.84–2.01 (m, 1H), 3.19 (brs, 1H), 3.71* (s, 3H), 3.72 (s, 3H), 4.70 (brs, 1H), 4.86 (d, *J* = 7.6 Hz, 1H), 4.94* (d, *J* = 7.2 Hz, 1H), 5.00–5.12 (m, 1H), 5.18–5.32 (m, 1H), 5.55 (dt, *J* = 7.5, 10.7 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 8.20 (d, *J* = 8.8 Hz, 2H).

¹³C NMR (99 MHz, CDCl₃, * indicates signals of the minor *E*-isomer, δ): 13.8 (*C*H₃), 13.9* (*C*H₃), 22.3 (*C*H₂), 27.6 (*C*H₂), 28.5* (*C*H₂), 28.7 (*C*H₂), 31.1* (*C*H₂), 31.2 (*C*H₂), 32.1* (*C*H₂), 52.4 (*C*H₃), 54.2 (*C*H), 75.4 (*C*H), 122.5 (*C*H), 123.1 (*C*H), 123.2* (*C*H), 127.2* (*C*H), 127.3 (*C*H), 135.9 (*C*H), 136.0* (*C*H), 147.2 (*C*), 148.1 (*C*), 157.0 (*C*).

HRMS-ESI (*m/z*): [M+Na]⁺ calcd for C₁₇H₂₄O₅N₂Na, 359.15771; found, 359.15774.

Allylation of 3-phenylpropionaldehyde with allylboronate (*E*)-3a (Table 2, entry 2)

The reaction was performed according to the representative procedure. The ¹H NMR and HPLC analysis gave *E/Z* ratio of 23:77.

¹H NMR (401 MHz, CDCl₃, * indicates signals of the minor *E*-isomer, δ): 0.867 (t, *J* = 7.0 Hz, 3H), 0.872* (t, *J* = 6.8 Hz, 3H), 1.18–1.42 (m, 6H), 1.63–1.83 (m, 2H), 1.98–2.23 (m, 2H), 2.60–2.73 (m, 1H), 2.78–2.91 (m, 1H), 3.67 (s, 3H), 3.71 (brs, 1H), 4.15* (brs, 1H), 4.45 (brs, 1H), 4.89 (brs, 1H), 5.04* (brs, 1H), 5.32 (t, *J* = 10.0 Hz, 1H), 5.40* (dd, *J* = 7.2, 15.2 Hz, 1H), 5.65 (dt, *J* = 7.4, 10.9 Hz, 1H), 5.70* (dd, *J* = 6.4, 10.9 Hz, 1H), 7.20 (d, *J* = 6.4 Hz, 2H), 7.24–7.32 (m, 3H).

¹³C NMR (100 MHz, CDCl₃, * indicates signals of the minor *E*-isomer, δ): 13.9 (*C*H₃), 22.4* (*C*H₂), 22.5 (*C*H₂), 27.9 (*C*H₂), 28.7* (*C*H₂), 29.1 (*C*H₂), 31.3* (*C*H₂), 31.4 (*C*H₂), 32.1 (*C*H₂), 32.4* (*C*H₂), 35.0 (*C*H₂), 35.4* (*C*H₂), 52.2 (*C*H₃), 52.9 (*C*H), 73.4 (*C*H), 124.3 (*C*H), 124.6* (*C*H), 125.8 (*C*H), 128.4 (*C*H), 135.2 (*C*H), 135.4 (*C*H), 141.7 (*C*), 156.7 (*C*).

HRMS-ESI (*m/z*): [M+Na]⁺ calcd for C₁₉H₂₉O₃NNa, 342.20404; found, 342.20396.

Allylation of cinnamaldehyde with allylboronate (*E*)-3a (Table 2, entry 3)

The reaction was performed according to the representative procedure. The ¹H NMR and HPLC analysis gave *E/Z* ratio of 19:81.

¹H NMR (401 MHz, CDCl₃, * indicates signals of the minor *E*-isomer, δ): 0.78–0.92 (m, 3H), 1.18–1.42 (m, 6H), 2.00–2.22 (m, 2H), 2.55 (brs, 1H), 3.69 (s, 3H), 4.42 (brs, 1H), 4.63 (brs, 1H), 4.94 (brs, 1H), 5.35 (t, *J* = 10.2 Hz, 1H), 5.44* (dd, *J* = 6.4, 15.2 Hz, 1H), 5.66 (dt, *J* = 7.5, 11.1 Hz, 1H), 6.17 (dd, *J* = 6.8, 16.0 Hz, 1H), 6.66 (d, *J* = 16.0 Hz, 1H), 7.20 (m, 5H).

¹³C NMR (100 MHz, CDCl₃, * indicates signals of the minor *E*-isomer, δ): 13.92 (*C*H₃), 13.95* (*C*H₃), 22.4 (*C*H₂), 27.9 (*C*H₂), 28.7* (*C*H₂), 29.1 (*C*H₂), 31.3* (*C*H₂), 31.4 (*C*H₂), 32.3* (*C*H₂), 52.25 (*C*H₃), 53.33 (*C*H), 74.7* (*C*H),

75.0 (*C*H), 124.4 (*C*H), 124.9* (*C*H), 126.5 (*C*H), 127.7 (*C*H), 127.8 (*C*H), 127.9* (*C*H), 128.5 (*C*H), 131.8* (*C*H), 132.1 (*C*H), 134.8* (*C*H), 135.2 (*C*H), 136.4 (*C*), 156.9 (*C*).

HRMS-ESI (*m/z*): [M+Na]$^+$ calcd for $C_{19}H_{27}O_3NNa$, 340.18823; found, 340.18831.

Allylation of 4-nitrobenzaldehyde with allylboronate (*E*)-3c (Table 2, entry 4)

The reaction was performed according to the representative procedure. The ^{1}H NMR and HPLC analysis gave *E/Z* ratio of 17:83.

^{1}H NMR (401 MHz, CDCl$_3$, * indicates signals of the minor *E*-isomer, δ): 0.82 (t, *J* = 7.2 Hz, 3H), 0.85* (t, *J* = 6.8 Hz, 3H), 0.96–1.32 (m, 6H), 1.67–1.83 (m, 1H), 1.84–2.01 (m, 1H), 3.20 (brs, 1H), 4.73 (brs, 1H), 4.91 (d, *J* = 6.8 Hz, 1H), 4.96–5.08 (m, 1H), 5.08–5.19 (m, 2H), 5.23 (t, *J* = 10.2 Hz, 1H), 5.26–5.31* (m, 1H), 5.56 (dt, *J* = 7.4, 10.8 Hz, 1H), 7.54 (m, 5H), 7.50 (d, *J* = 8.0 Hz, 2H), 8.16 (d, *J* = 8.8 Hz, 2H), 8.17* (d, *J* = 8.4 Hz, 2H).

^{13}C NMR (99 MHz, CDCl$_3$, * indicates signals of the minor *E*-isomer, δ): 13.86 (*C*H$_3$), 13.92* (*C*H$_3$), 22.4 (*C*H$_2$), 27.7 (*C*H$_2$), 28.4* (*C*H$_2$), 28.7 (*C*H$_2$), 31.1* (*C*H$_2$), 31.2 (*C*H$_2$), 32.2* (*C*H$_2$), 54.3 (*C*H), 67.2 (*C*H$_2$), 75.6 (*C*H), 122.5 (*C*H), 123.1 (*C*H), 127.2* (*C*H), 127.3 (*C*H), 128.1 (*C*H), 128.3 (*C*H), 128.5 (*C*H), 136.0 (*C*H), 136.1* (*C*H), 147.2 (*C*), 147.9 (*C*), 156.4 (*C*).

HRMS-ESI (*m/z*): [M+Na]$^+$ calcd for $C_{23}H_{28}O_5N_2Na$, 435.18894; found, 435.18904.

Allylation of 4-nitrobenzaldehyde with allylboronate (*E*)-3j (Table 2, entry 5)

The reaction was performed according to the representative procedure. The ^{1}H NMR and HPLC analysis gave *E/Z* ratio of 27:73.

^{1}H NMR (399 MHz, CDCl$_3$, * indicates signals of the minor *E*-isomer, δ): 2.15–2.35 (m, 2H), 3.28–3.46 (m, 2H), 3.55 (brs, 1H), 3.65 (s, 3H), 3.71* (s, 3H), 4.46 (s, 2H), 4.47* (s, 2H), 4.66 (brs, 1H), 4.97 (brs, 2H), 5.32* (dd, *J* = 7.0, 15.4 Hz, 1H), 5.39 (dd, *J* = 9.4, 10.6 Hz, 1H), 5.58* (q, *J* = 7.4 Hz, 1H), 5.65 (dt, *J* = 7.8, 10.9 Hz, 1H), 7.24–7.40 (m, 5H), 7.44* (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 8.8 Hz, 2H), 8.11–8.18 (m, 2H).

^{13}C NMR (99 MHz, CDCl$_3$, * indicates signals of the minor *E*-isomer, δ): 28.5 (*C*H$_2$), 32.7* (*C*H$_2$), 52.5 (*C*H), 54.5 (*C*H), 58.7* (*C*H), 68.7 (*C*H$_2$), 69.0* (*C*H$_2$), 72.96* (*C*H$_2$), 73.02 (*C*H$_2$), 75.3 (*C*H$_3$), 123.2 (*C*H), 123.3* (*C*H), 125.5* (*C*H), 125.6 (*C*H), 127.2* (*C*H), 127.4 (*C*H), 127.7 (*C*H), 128.4 (*C*H), 132.0* (*C*H), 132.1 (*C*H), 137.8 (*C*), 138.0* (*C*), 147.3 (*C*), 147.8* (*C*), 148.1 (*C*), 157.0 (*C*).

HRMS-ESI (*m/z*): [M+Na]$^+$ calcd for $C_{21}H_{24}O_6N_2Na$, 423.15256; found, 423.15266.

Acknowledgments

Supporting Information

YES

Primary Data

NO

References and Notes

(1) (*a*) Lee, H. -S.; Kang, S. H. *Synlett* **2004**, 1673-1685. (b) Bergmeier, S. C. *Tetrahedron* **2000**, *56*, 2561–2576. (*c*) Karjalainen, O. K.; Koskinen, A. M. P. *Org. Biomol. Chem.* **2012**, *10*, 4311–4326.

(2) (*a*) Tao, B.; Schlingloff, G.; Sharpless, K. B. *Tetrahedron Lett.* **1998**, *39*, 2507–2510. (*b*) Demko, Z. P.; Bartsch, M.; Sharpless, K. B. *Org. Lett.* **2000**, *2*, 2221–2223. (*c*) Wang, C.; Yamamoto, H. *J. Am. Chem. Soc.* **2014**, *136*, 6888–6891.

(3) (*a*) Lombardo, M.; Mosconi, E.; Pasi, F.; Petrini, M. A.; Trombini, C. *J. Org. Chem.* **2007**, *72*, 1834–1837. (*b*) Keinicke, L.; Fristrup, P.; Norrby, P. A.; Madsen, R. *J. Am. Chem. Soc.* **2005**, *127*, 15756–15761. (*c*) List, B.; Pojarliev, P.; Biller, W. T.; Martin, H. J. *J. Am. Chem. Soc.* **2002**, *124*, 827–833. (*d*) Matsunaga, S.; Yoshida, T.; Morimoto, H.; Kumagai, N.; Shibasaki, M. *J. Am. Chem. Soc.* **2004**, *126*, 8777–8785. (*e*) Enders, D.; Grondal, C.; Vrettou, M.; Raabe, G. *Angew. Chem. Int. Ed.* **2005**, *44*, 4079–4083. (*f*) Trost, B. M.; Jaratjaroonphong, J.; Reutrakul, V. *J. Am. Chem. Soc.* **2006**, *128*, 2778–2779. (*g*) Carswell, E. L.; Snapper, M. L.; Hoveyda, A. H. *Angew. Chem. Int. Ed.* **2006**, *45*, 7230–7233. (*h*) Ramasastry, S. S. V.; Zhang, H.; Tanaka, F.; Barbas, C. F. III. *J. Am. Chem. Soc.* **2006**, *129*, 288–289. (*i*) Zhong, Y.-W.; Dong, Y.-Z.; Fang, K.; Izumi, K.; Xu, M.-H.; Lin, G.-Q. *J. Am. Chem. Soc.* **2005**, *127*, 11956–11957. (*j*) Skucas, E.; Zbieg, J. R.; Krische, M. J. *J. Am. Chem. Soc.* **2009**, *131*, 5054–5055.

(4) (*a*) Barrett, A. G. M.; Seefeld, M. A. *Tetrahedron* **1993**, *49*, 7857. (*b*) Barrett, A. G. M.; Seefeld, M. A. *J. Chem. Soc. Chem. Commun.* **1993**, 339. (*c*) Barrett, A. G. M.; Seefeld, M. A.; Williams, D. J. *J. Chem. Soc. Chem. Commun.* **1994**, 1053. (*d*) Barrett, A. G. M.; Seefeld, M. A.; White, A. J. P.; Williams, D. J. *J. Org. Chem.* **1996**, *61*, 2677.

(5) (*a*) Lessard, S.; Peng, F.; Hall, D. G. *J. Am. Chem. Soc.* **2009**, *131*, 9612–9613. (*b*) Ding, J.; Hall, D. G. *Angew. Chem. Int. Ed.* **2013**, *52*, 1–6.

(6) Yamamoto, E.; Takenouchi, Y.; Ozaki, T. Miya, T.; Ito, H. *J. Am. Chem. Soc.* **2014**, *136*, 16515–16521.

(7) (*a*) Ito, H.; Kawakami, C.; Sawamura, M. *J. Am. Chem. Soc.* **2005**, *127*, 16034–16035. (*b*) Ito, H.; Sasaki, Y.; Sawamura, M. *J. Am. Chem. Soc.* **2008**, *130*, 15774–15775. (*c*) Ito, H.; Okura, T.; Matsuura, K.; Sawamura, M. *Angew. Chem. Int. Ed.* **2010**, *49*, 560–563. (d) Guzman-Martinez, A.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2010**, *132*, 10634–10637.

(8) (*a*) Ito, H.; Kunii, S.; Sawamura, M. *Nat. Chem.* **2010**, *2*, 972–976. (*b*) Park, J. K.; Lackey, H. H.; Ondrusek, B. A.; McQuade, D. T. *J. Am. Chem. Soc.* **2011**, *133*, 2410–2413. (*c*) Park, J. K.; McQuade, D. T. *Angew. Chem. Int. Ed.* **2012**, *51*, 2717–2721.

(9) Ito, H.; Toyoda, T.; Sawamura, M. *J. Am. Chem. Soc.* **2010**, *132*, 5990–5992.

(10) Zhong, C.; Kunii, S.; Kosaka, Y.; Sawamura, M.; Ito, H. *J. Am. Chem. Soc.* **2010**, *132*, 11440–11442.

(11) Zhao, J.; Szabó, K. J. *Angew. Chem. Int. Ed.* **2015**, *54*, 1–6.

(12) Lee, H.; Han, H. T.; Yun, J. *ACS Catal.* **2016**, *6*, 6487–6490.

(13) (*a*) Kano, T.; Yurino, T.; Asakawa, D.; Maruoka, K. *Angew. Chem. Int. Ed.* **2013**, *125*, 5642–5644. (*b*) Kano, T.; Kobayashi, R.; Maruoka, K. *Angew. Chem. Int. Ed.* **2015**, *54*, 1–5.