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Cross Coupling between sp^3-Carbon and sp^3-Carbon Using a Diborylmethane Derivative at Room Temperature

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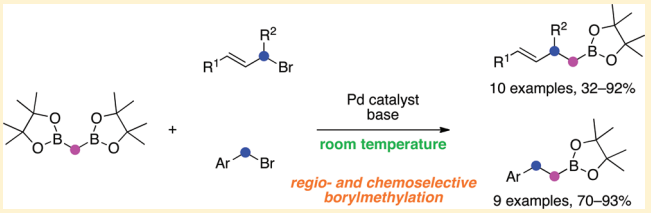
Supporting Information

ABSTRACT: A novel example of the Suzuki–Miyaura cross-coupling reaction between sp^3-carbon and sp^3-carbon is described. The reaction of a diborylmethane derivative with allyl halides or benzyl halides proceeded efficiently in the presence of appropriate Pd-catalysts at room temperature. The present approaches provide functionalized homoallylboronates and alkylboronates with excellent regio- and chemoselectivities.



Cross-coupling reactions have been widely developed for the synthesis of various compounds in organic chemistry.[1] Among the cross-coupling approaches, the Suzuki–Miyaura cross-coupling reaction (SMC) contributes to a C–C bond formation under mild conditions.[2] While there have been numerous reports on the SMC between organoboron compounds and organohalides, the reaction between alkylboron compounds and alkyl halides is typically difficult to achieve. In 1992, Suzuki et al. reported the first example of the alkyl–alkyl cross-coupling reaction between alkylboron compounds and alkyl iodides.[3] Fu et al. reported pioneering work on efficient Ni- or Pd-catalyzed approaches for which secondary alkyl halides could be available.[4] Organ reported that the originally developed Pd complexes, the PEPPSI series, could catalyze the coupling of primary alkylboron compounds and primary alkyl bromides in high to excellent yields.[5,6] Molander reported the Suzuki–Miyaura cross-coupling of cyclopropyl and alkoxymethyltrifluoroborates with benzyl chlorides at 120 °C.[7] However, the reaction of alkylboron compounds with allyl(benzyl) halides is difficult due to the slow reaction rate of transmetalation as well as the slow reductive elimination.[8] Hence, the coupling reaction of alkylboron compounds and allyl(benzyl) halides has been unfavorable for the following reasons: (1) slow borate generation from alkylboron compounds, (2) slow transmetalation step, (3) slow reductive elimination step, and (4) a competitive pathway via β-hydride elimination. These factors are still controversial but could explain why there are only limited examples of the SMC of alkylboron compounds with allyl(benzyl) halides.[9] In our ongoing study on the SMC, we discovered that the reaction of diborylmethane derivatives, two boron atoms of which are attached to the same carbon atom, realized unprecedented chemoselective and regiospecific coupling with aryl halides at room temperature.[10] The coupling of a diborylmethane derivative and aryl halides provides benzylboronate derivatives, which do not undergo a further coupling reaction. In the present paper, we describe the expedient coupling using a diborylmethane derivative and allyl or benzyl halides under ambient conditions, which gives alkylboron compounds chemoselectively (Figure 1).

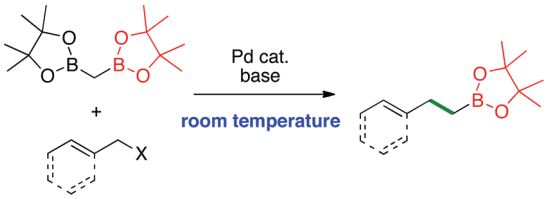


Figure 1. SMC of Diborylmethane and Allyl(Benzyl)halides.

Allylation. Pd-catalyzed allylation is one of the most powerful approaches to the synthesis of various functionalized molecules.[11] Although it has been shown to be useful in C–C bond formation, the SMC of alkylboron compounds with allyl halides has rarely been reported.[12,13] Consequently, we report here the alkyl–allyl SMC using a diborylmethane at room temperature. The initial screening of catalyst precursors for the coupling of diborylmethane derivative **1** and (*E*)-cinnamyl bromide (**2a**) is described in Table 1. The palladium complex $Pd[P(t\text{-}Bu)_3]_2$, which has been shown to be effective for promoting various coupling reactions, realized the SMC between diborylmethane **1** and (*E*)-cinnamyl bromide (**2a**) at

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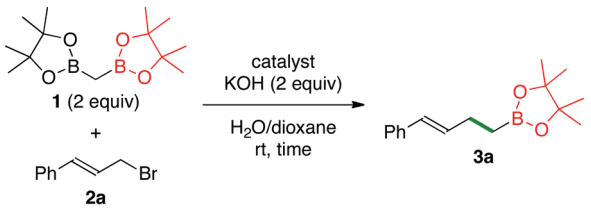
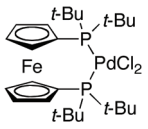
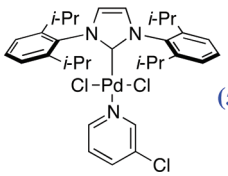
Table 1. Screening of Catalyst for Allylation



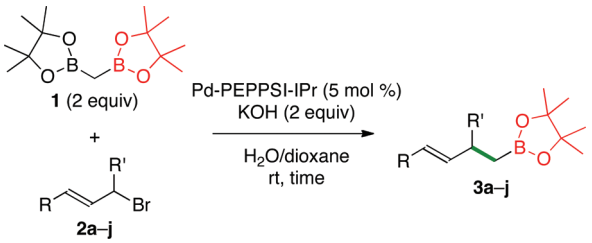
entry	catalyst (mol %)	time (h)	yield (%)[a]
1	$Pd[P(t\text{-}Bu)_3]_2$ (5)	4	62
2	$(t\text{-}Bu)_2MePH^+BF_4^-$ (20) $Pd(OAc)_2$ (10)	24	N.R.
3	$[(t\text{-}Bu)_2ArP]_2PdCl_2$ (5) Ar = 4-Me_2N-C_6H_4	24	32
4	 (5)	24	85
5	 **(5)**	**6**	**>98**

[a]NMR yields.

room temperature, and gave the homoallylboronate **3a** in moderate yield; product **3a** was obtained regioselectively as (*E*)-isomer at the α-carbon of the allylic position (entry 1). The efficient catalyst precursor, $(t\text{-}Bu)_2MePH^+BF_4^-$ with $Pd(OAc)_2$, for the cross-coupling of alkyl bromides did not promote the present reaction at all (entry 2).[4b] The use of bis[di-*tert*-butyl(4-dimethylaminophenyl)phosphine]dichloropalladium-(II) gave the desired product **3a**, but in low yield (entry 3).[14] The use of [bis(di-*tert*-butylphosphino)ferrocene]-dichloropalladium(II) required a long reaction time (24 h) and gave the product **3a** in high yield (entry 4). Finally, Pd-PEPPSI-IPr catalyst achieved the efficient cross-coupling reaction; product **3a** was obtained in almost quantitative yield (entry 5). The precedent literatures suggested that monodentate ligands could give a π-allylpalladium intermediate, which undergoes subsequent transmetalation. In contrast, bidentate ligands require rearrangement of a π-allylpalladium intermediate to a relatively unstable σ-allylpalladium intermediate before transmetalation, which seems to retard the reaction rate.[15] Thus, the NHC ligand in Pd-PEPPSI-IPr would be superior to bis(di-*tert*-butylphosphino)ferrocene. The reductive elimination step is another problem. Phosphorus ligands would retard the reductive elimination step; thus, the NHC ligand might work in the present reaction at room temperature.[8,16] We examined various leaving groups; the reaction of cinnamyl diethyl phosphate and cinnamyl chloride in the presence of Pd-PEPPSI-IPr catalyst gave the desired product after 24 h in 11% yield and 12% yield, respectively. Other leaving group, such as hydroxide, alkoxide, acetate and triflate did not give the product. The starting materials were recovered in each case. Thus, the further coupling reaction of allyl bromides was carried out in the presence of Pd-PEPPSI-IPr catalyst.

A variety of allyl bromides were examined under the optimum reaction conditions (Table 2).[17−19] The reaction of

Table 2. Scope of Allyl Bromide Derivatives



entry	R, R′	time (h)	yield[a] (%)
1	**2a**, Ph, H	6	**3a**, 82 (85)[b]
2	**2b**, 4-MePh, H	5	**3b**, 88
3	**2c**, 4-*t*-BuPh, H	24	**3c**, 89
4	**2d**, 4-MeOPh, H	6	**3d**, 92
5	**2e**, 4-ClPh, H	24	**3e**, 74
6	**2f**, 4-F_3CPh, H	24	**3f**, 32
7	**2g**, 2-thienyl, H	24	**3g**, 39
8	**2h**, 2-Np, H	24	**3h**, 70
9	**2i**, Ph, Me	24	**3i**, 75
10	**2j**, $(CH_2)_2$Ph, H	24	**3j**, 51

[a]**2a−i** (0..07−0.23 mmol) was used. [b]The yield of reaction for 24 h using **2a** (5 mmol) is shown in parentheses.

(*E*)-cinnamyl bromide (**2a**) gave the product **3a** in 82% yield; the larger scale reaction (5 mmol of **2a**) achieved 85% yield of product **3a** (entry 1). Electron-donating groups are compatible with the reaction. The reaction of cinnamyl bromide derivatives **2b−d** bearing a 4-methyl, 4-*tert*-butyl, or 4-methoxy group gave the corresponding products **3b−d** in high yields (entries 2−4). In contrast, electron-withdrawing groups diminished the yield of products **3e** and **3f** (entries 5 and 6). Furthermore, a heteroaromatic substituent, such as thiophene, retarded the reaction and generated unidentified byproduct (entry 7). The naphthyl derivative **2h** gave the product **3h** in 70% yield (entry 8). To our delight, the reaction of (*E*)-(3-bromobut-1-en-1-yl)benzene (**2i**) gave the product **3i** regioselectively without the generation of byproduct via β-hydride elimination (entry 9).[20] The aliphatic allyl bromide **2j** gave the desired product **3j** in moderate yield (entry 10).

Benzylation. The typical cross-coupling reaction of arylboron compounds and benzyl halides has been envisaged as a promising method for C−C bond formation.[12a−d] We examined the reaction of diborylmethane **1** with benzyl bromide (**4a**) for the synthesis of phenethylboronate **5a** (Table 3). The generation of η^3-benzylpalladium complexes has been proposed in the literature.[21] The screening of catalyst precursors was carried out. The use of $Pd[P(t\text{-}Bu)_3]_2$ gave the desired product **5a** in excellent yield (entry 1). Other palladium complexes were less effective; the reaction in the presence of $(t\text{-}Bu)_2MePH^+BF_4^-$ with $Pd(OAc)_2$ did not give the product at all (entry 2). The use of bis[di-*tert*-butyl(4-dimethylaminophenyl)phosphine]dichloropalladium(II) gave the product in low yield (entry 3). The reaction in the presence of [bis(di-*tert*-butylphosphino)ferrocene]-

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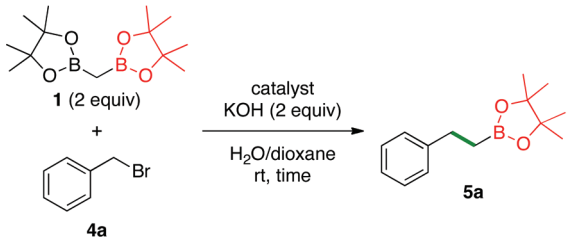
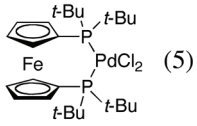
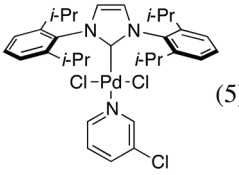
Table 3. Screening of Catalyst for Benzylation



entry	catalyst (mol%)	time (h)	yield (%)[a]
1	**Pd[P(*t*-Bu)$_3$]$_2$ (5)**	**2.5**	**>98**
2	(*t*-Bu)$_2$MePH$^+$BF$_4^-$ (20) Pd(OAc)$_2$ (10)	24	trace
3	[(*t*-Bu)$_2$ArP]$_2$PdCl$_2$ (5) Ar = 4-Me$_2$N-C$_6$H$_4$	24	37
4	 (5)	5	80
5	 (5)	24	trace

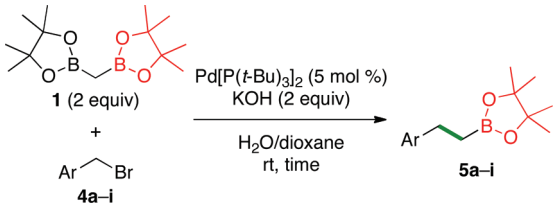
[a]NMR yields.

dichloropalladium(II) did not improve the yield of the product (entry 4). Unexpectedly, Pd-PEPPSI-IPr gave a trace amount of product (entry 5). Thus, we determined that Pd[P(*t*-Bu)$_3$]$_2$ is a suitable catalyst for the benzylation reaction. We examined leaving groups; the reaction of benzyl chloride gave the desired product **5a** in 85% yield. Other leaving groups, such as hydroxide, alkoxide, acetate, carbonate, triflate, phosphate, and so on, were not suitable. The starting materials were recovered along with a slow decomposition of diborylmethane.

A variety of benzyl bromide derivatives were examined under the optimum reaction conditions (Table 4).[19,22] The reaction of benzyl bromide (**4a**) gave the desired product **5a** in 93% yield; the larger scale (5 mmol of **4a**) reaction gave the desired product **5a** in 89% yield (entry 1).[23] The reaction of benzyl bromide derivatives **4b** and **4c** bearing an electron-donating group at the 4-position gave the desired products **5b** and **5c** in high yields (entries 2 and 3). Furthermore, electron-withdrawing groups are compatible with the reaction. The reaction of 4-chloro- and 4-fluorobenzyl bromides **4d** and **4e** gave the desired products **5d** and **5e** in high yields (entries 4 and 5). The incorporation of 3-nitro, 4-cyano, and 4-methoxycarbonyl groups did not decrease the yields of the products **5f–h** (entries 6–8). The reaction of 2-(bromomethyl)naphthalene (**4i**) gave the corresponding product **5i** in 80% yield (entry 9).

In summary, we have achieved the efficient Suzuki–Miyaura cross-coupling reaction of a diborylmethane derivative and allyl halides or benzyl halides under ambient conditions. The

Table 4. Scope of Benzyl Halide Derivatives



entry	Ar	time (h)	yield[a] (%)
1	**4a**, Ph	2.5	**5a**, 93 (89)[b]
2	**4b**, 4-MePh	5	**5b**, 85
3	**4c**, 4-*t*-BuPh	24	**5c**, 89
4	**4d**, 4-ClPh	5	**5d**, 86
5	**4e**, 4-FPh	2	**5e**, 89
6	**4f**, 3-O$_2$NPh	5	**5f**, 70
7	**4g**, 4-NCPh	5	**5g**, 85
8	**4h**, 4-MeO$_2$CPh	24	**5h**, 77
9	**4i**, 2-Np	24	**5i**, 80

[a]**4a–i** (0.1–0.15 mmol) was used. [b]The yield of reaction for 24 h using **4a** (5 mmol) is shown in parentheses.

chemoselective coupling reaction proceeded under mild conditions to give alkylboron compounds without the generation of byproduct via protodeboronation or β-hydride elimination. The present SMC realizes the incorporation of a boronate moiety along with a C–C bond formation via borylmethylation, which would be alternative to hydroboration reactions of alkenes with a C–B and a C–H bond formation. These characteristic features using diborylmethane derivatives are promising for the further synthetic utility of facile Suzuki–Miyaura cross-coupling approaches to a C–C bond formation.

EXPERIMENTAL SECTION

Synthesis of (*E*)-4,4,5,5-Tetramethyl-2-(4-phenylbut-3-en-1-yl)-1,3,2-dioxaborolane (3a). To a solution of **1** (38.0 mg, 0.140 mmol, 2 equiv), **2a** (13.8 mg, 0.070 mmol), and Pd-PEPPSI-IPr (2.5 mg, 3.5 μmol, 5 mol %) in dioxane 0.75 mL was added 8 N KOH aq (18 μL, 0.14 mmol, 2 equiv) at room temperature. The mixture was stirred for 6 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be >98% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/ether = 10/1) gave the product **3a** in 0.057 mmol, 82% yield (14.8 mg/18.1 mg); the reaction using **1** (2.68 g, 10 mmol, 2 equiv) and **2a** (986 mg, 5 mmol) in the presence of Pd-PEPPSI-IPr (170 mg, 0.25 mmol, 5 mol %) and 8 N KOH aq (1.25 mL, 10 mmol, 2 equiv) in dioxane 50 mL for 24 h at room temperature gave the product **3a** in 4.25 mmol, 85% yield (1.1 g/1.29 g): yellow oil; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.36–7.16 (m, 5H), 6.39 (d, J = 15.6 Hz, 1H), 6.29 (dt, J = 6.4 Hz, 15.6 Hz, 1H), 2.37–2.32 (m, 2H), 1.25 (s, 12H), 0.99 (t, J = 7.6 Hz, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 137.9, 132.7, 128.8, 128.4, 126.6, 125.9, 83.1, 27.3, 24.8; ^{11}B NMR (CDCl$_3$, 128 MHz) δ 34.2; IR (neat, cm^{-1}) 2978, 2929, 1445, 1323, 1145, 966, 848, 742; HRMS (FAB, positive) m/z calcd for C$_{16}$H$_{23}{}^{10}$BO$_2$ 257.1827, found 257.1829.

Synthesis of (*E*)-4,4,5,5-Tetramethyl-2-(4-*p*-tolylbut-3-en-1-yl)-1,3,2-dioxaborolane (3b). To a solution of **1** (55.0 mg, 0.21 mmol, 2 equiv), **2b** (21.7 mg, 0.10 mmol), and Pd-PEPPSI-IPr (3.5 mg, 5.2 μmol, 5 mol %) in dioxane (1.0 mL) was added 8 N KOH aq (25 μL, 0.21 mmol, 2 equiv) at room temperature. The mixture was stirred for 5 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be >98% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/ether = 20/1) gave the

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product **3b** in 0.091 mmol, 88% yield (24.5 mg/28.0 mg): yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.22 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.34 (d, J = 15.6 Hz, 1H), 6.22 (dt, J = 6.4 Hz, 15.6 Hz, 1H), 2.35−2.29 (m, 5H), 1.24 (s, 12H), 0.97 (t, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.3, 135.2, 131.7, 129.1, 128.6, 125.8, 83.0, 27.3, 24.8, 21.1; ^{11}B NMR ($CDCl_3$, 128 MHz) δ 34.4; IR (neat, cm^{-1}) 2978, 2929, 1444, 1320, 1143, 966, 848; HRMS (FAB, positive) m/z calcd for $C_{17}H_{25}{}^{10}BO_2$ 271.1984, found 271.1976.

Synthesis of (*E*)-2-(4-(4-*tert*-Butylphenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c). To a solution of **1** (104 mg, 0.39 mmol, 2 equiv), **2c** (49.1 mg, 0.19 mmol), and Pd-PEPPSI-IPr (6.6 mg, 9.7 μmol, 5 mol %) in dioxane (1.9 mL) was added 8 N KOH aq (46 μL, 0.39 mmol, 2 equiv) at room temperature. The mixture was stirred for 6 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be >98% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/ether = 20/1) gave the product **3c** in 0.173 mmol, 89% yield (54.1 mg/61.0 mg): yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33−7.25 (m, 4H), 6.35 (d, J = 16.0 Hz, 1H), 6.23 (dt, J = 6.4 Hz, 16.0 Hz, 1H), 2.35−2.29 (m, 2H), 1.30 (s, 9H), 1.24 (s, 12H), 0.97 (t, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.6, 135.2, 132.0, 128.4, 125.6, 125.3, 83.0, 34.4, 31.3, 27.3, 24.8; ^{11}B NMR ($CDCl_3$, 128 MHz) δ 34.2; IR (neat, cm^{-1}) 2966, 2929, 2359, 1372, 1323, 1146, 967, 847, 748; HRMS (FAB, positive) m/z calcd for $C_{20}H_{31}{}^{10}BO_2$ 313.2453, found 313.2445.

Synthesis of (*E*)-2-(4-(4-Methoxyphenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d). To a solution of **1** (107 mg, 0.4 mmol, 2 equiv), **2d** (45.4 mg, 0.2 mmol), and Pd-PEPPSI-IPr (6.8 mg, 10 μmol, 5 mol %) in dioxane (2.0 mL) was added 8 N KOH aq (48 μL, 0.4 mmol, 2 equiv) at room temperature. The mixture was stirred for 6 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be >98% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/ether = 20/1) gave the product **3d** in 0.184 mmol, 92% yield (52.8 mg/57.4 mg): yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.27−7.25 (m, 2H), 6.82 (d, J = 8.4 Hz, 2H), 6.32 (d, J = 15.6 Hz, 1H), 6.13 (dt, J = 6.4 Hz, 15.6 Hz, 1H), 3.79 (s, 3H), 2.34−2.29 (m, 2H), 1.23 (s, 12H), 0.97 (t, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.5, 130.8, 130.6, 128.1, 127.0, 113.8, 83.0, 55.2, 27.3, 24.8; ^{11}B NMR ($CDCl_3$, 128 MHz) δ 33.5; IR (neat, cm^{-1}) 2978, 2926, 1372, 1247, 1144, 967, 847, 749; HRMS (FAB, positive) m/z calcd for $C_{17}H_{25}{}^{10}BO_3$ 287.1933, found 287.1932.

Synthesis of (*E*)-2-(4-(4-Chlorophenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e). To a solution of **1** (64.0 mg, 0.24 mmol, 2 equiv), **2e** (28.1 mg, 0.12 mmol), and Pd-PEPPSI-IPr (4.1 mg, 6.1 μmol, 5 mol %) in dioxane (1.2 mL) was added 8 N KOH aq (29 μL, 0.24 mmol, 2 equiv) at room temperature. The mixture was stirred for 4 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be 76% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/ether = 20/1) gave the product **3e** in 0.90 mmol, 74% yield (26.3 mg/35.4 mg): yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.25−7.21 (m, 4H), 6.33 (d, J = 16.0 Hz, 1H), 6.25 (dt, J = 6.0 Hz, 16.0 Hz, 1H), 2.35−2.29 (m, 2H), 1.23 (s, 12H), 0.98 (t, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.4, 133.5, 132.1, 128.5, 127.6, 127.1, 83.1, 27.3, 24.8; ^{11}B NMR ($CDCl_3$, 128 MHz) δ 34.0; IR (neat, cm^{-1}) 2979, 2929, 2359, 1372, 1145, 967, 847, 748; HRMS (FAB, positive) m/z calcd for $C_{16}H_{22}BClO_2$ 292.1401, found 292.1395.

Synthesis of (*E*)-4,4,5,5-Tetramethyl-2-(4-(4-(trifluoromethyl)phenyl)but-3-en-1-yl)-1,3,2-dioxaborolane (3f). To a solution of **1** (114.0 mg, 0.43 mmol, 2 equiv), **2f** (56.6 mg, 0.21 mmol), and Pd-PEPPSI-IPr (7.2 mg, 10.7 μmol, 5 mol %) in dioxane (2.1 mL) was added 8 N KOH aq (51 μL, 0.43 mmol, 2 equiv) at room temperature. The mixture was stirred for 24 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be 37% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/ether = 20/1) gave the product **3f** in 0.068 mmol, 32% yield (22.4 mg/69.2 mg): yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 6.40−6.39 (m, 2H), 2.37−2.35 (m, 2H), 1.25 (s, 12H), 1.00 (t, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.4, 135.6, 128.5 (q, J = 32.3 Hz), 127.7, 126.0, 125.3 (q, J = 4.1 Hz), 124.3 (q, J = 272.3 Hz), 83.1, 27.3, 24.8; ^{11}B NMR ($CDCl_3$, 128 MHz) δ 34.4; ^{19}F NMR ($CDCl_3$, 470 MHz) δ −64.4; IR (neat, cm^{-1}) 2979, 2929, 1373, 1325, 1144, 968, 848, 749; HRMS (FAB, positive) m/z calcd for $C_{17}H_{22}{}^{10}BF_3O_2$ 325.1701, found 325.1686.

Synthesis of (*E*)-4,4,5,5-Tetramethyl-2-(4-(thiophene-2-yl)-but-3-en-1-yl)-1,3,2-dioxaborolane (3g). To a solution of **1** (106.0 mg, 0.4 mmol, 2 equiv), **2g** (40.5 mg, 0.2 mmol), and Pd-PEPPSI-IPr (6.8 mg, 10 μmol, 5 mol %) in dioxane (2.0 mL) was added 8 N KOH aq (47 μL, 0.4 mmol, 2 equiv) at room temperature. The mixture was stirred for 24 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be 48% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/ether = 20/1) gave the product **3g** in 0.078 mmol, 39% yield (20.8 mg/52.6 mg): yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.07 (d, J = 5.2 Hz, 1H), 6.94−6.90 (m, 1H), 6.86−6.83 (m, 1H), 6.50 (d, J = 15.6 Hz, 1H), 6.13 (dt, J = 6.4 Hz, 15.6 Hz, 1H), 2.31−2.29 (m, 2H), 1.25 (s, 12H), 0.97 (t, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 132.7, 128.8, 127.1, 124.0, 122.9, 122.1, 83.1, 27.0, 24.8; ^{11}B NMR ($CDCl_3$, 128 MHz) δ 34.3; IR (neat, cm^{-1}) 2978, 2934, 1730, 1378, 1275, 1145, 965, 848, 749; HRMS (FAB, positive) m/z calcd for $C_{14}H_{21}{}^{10}BO_2S$ 263.1392, found 263.1392.

Synthesis of (*E*)-4,4,5,5-Tetramethyl-2-(4-(naphthalen-2-yl)-but-3-en-1-yl)-1,3,2-dioxaborolane (3h). To a solution of **1** (66.0 mg, 0.25 mmol, 2 equiv), **2h** (30.6 mg, 0.12 mmol), and Pd-PEPPSI-IPr (4.2 mg, 6.2 μmol, 5 mol %) in dioxane (1.2 mL) was added 8 N KOH aq (29 μL, 0.25 mmol, 2 equiv) at room temperature. The mixture was stirred for 24 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be 80% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/ether = 20/1) gave the product **3h** in 0.087 mmol, 70% yield (26.7 mg/38.2 mg): yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.81−7.36 (m, 7H), 6.54 (d, J = 16.0 Hz, 1H), 6.42 (dt, J = 6.0 Hz, 16.0 Hz, 1H), 2.41−2.436 (m, 2H), 1.26 (s, 12H), 1.03 (t, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.4, 133.2, 132.6, 128.9, 128.8, 128.0, 127.8, 127.6, 126.0, 125.3, 125.3, 123.6, 83.1, 27.4, 24.8; ^{11}B NMR ($CDCl_3$, 128 MHz) δ 34.2; IR (neat, cm^{-1}) 2977, 2927, 1735, 1372, 1322, 1145, 967, 847, 747; HRMS (FAB, positive) m/z calcd for $C_{20}H_{26}BO_2$ $[M + H]^+$ 309.2026, found 309.2019.

Synthesis of (*E*)-4,4,5,5-Tetramethyl-2-(2-methyl-4-phenyl-but-3-en-1-yl)-1,3,2-dioxaborolane (3i). To a solution of **1** (122.0 mg, 0.46 mmol, 2 equiv), **2i** (48.4 mg, 0.23 mmol), and Pd-PEPPSI-IPr (7.8 mg, 11 μmol, 5 mol %) in dioxane 2.3 mL was added 8 N KOH aq (54 μL, 0.46 mmol, 2 equiv) at room temperature. The mixture was stirred for 24 h and filtered through a pad of silica gel with ether. Concentration gave the residue; purification by silica gel column chromatography (hexane/ether = 20/1) gave the product **3i** in 0.172 mmol, 75% yield (46.5 mg/62.3 mg): yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38−7.14 (m, 5H), 6.37 (d, J = 15.6 Hz, 1H), 6.21 (dt, J = 7.2 Hz, 15.6 Hz, 1H), 2.67−2.59 (m, 1H), 1.24 (s, 12H), 1.14 (d, J = 6.4 Hz, 3H), 0.97 (t, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.1, 137.9, 128.4, 126.8, 125.9, 83.0, 33.3, 24.8, 24.8, 22.9; ^{11}B NMR ($CDCl_3$, 128 MHz) δ 34.2; IR (neat, cm^{-1}) 2977, 2924, 1370, 1323, 1145, 966, 848, 748, 693; HRMS (FAB, positive) m/z calcd for $C_{17}H_{25}{}^{10}BO_2$ 271.1984, found 271.1994.

Synthesis of (*E*)-4,4,5,5-Tetramethyl-2-(2-methyl-4-phenyl-but-3-en-1-yl)-1,3,2-dioxaborolane (3j). To a solution of diboryl-methane **1a** (102.4 mg, 0.38 mmol, 2 equiv), **2j** (43.0 mg, 0.19 mmol),

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and Pd-PEPPSI-IPr (6.6 mg, 9.7 μmol, 5 mol %) in dioxane (1.9 mL) was added 8 N KOH aq (46 μL, 0.38 mmol, 2 equiv) at room temperature. The mixture was stirred at 25 °C for 24 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be 79% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/ether = 30/1) gave the product **3j** in 0.0978 mmol, 51% yield (28.0 mg/54.7 mg): yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.29−7.24 (m, 2H), 7.19−7.15 (m, 3H), 5.53−5.44 (m, 2H), 2.65 (t, J = 7.8 Hz, 2H), 2.32−2.25 (m, 2H), 2.14−2.07 (m, 2H), 1.24 (s, 12H), 0.85 (t, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.2, 132.7, 128.4, 128.3, 128.2, 125.6, 82.9, 36.1, 34.4, 26.8, 24.8; ^{11}B NMR ($CDCl_3$, 128 MHz) δ 34.1; IR (neat, cm^{-1}) 2980, 2928, 2853, 1372, 1321, 1146, 968, 748; HRMS (FAB, positive) m/z calcd for $C_{17}H_{27}BO_2$ 286.2104, found 286.2115.

Synthesis of 4,4,5,5-Tetramethyl-2-phenethyl-1,3,2-dioxaborolane (5a).[24] To a solution of **1** (79 mg, 0.3 mmol, 2 equiv), **4a** (25.9 mg, 0.15 mmol), and Pd[P(*t*-Bu)$_3$]$_2$ (3.8 mg, 7.4 μmol, 5 mol %) in dioxane (1.5 mL) was added 8 N KOH aq (36 μL, 0.3 mmol, 2 equiv) at room temperature. The mixture was stirred for 2.5 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be >98% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/EtOAc = 20/1) gave the product **5a** in 0.137 mmol, 93% yield (31.8 mg/34.4 mg); the reaction of **1** (2.68 g, 10 mmol, 2 equiv) and **4a** (855 mg, 5 mmol) in the presence of Pd[P(*t*-Bu)$_3$]$_2$ (128 mg, 0.25 mmol, 5 mol %) and 8 N KOH aq (1.25 mL, 10 mmol, 2 equiv) in dioxane 50 mL at room temperature for 24 h gave the product **5a** in 4.45 mmol, 89% yield (1.03 g/1.16 g).

Synthesis of 4,4,5,5-tetramethyl-2-(4-methylphenethyl)-1,3,2-dioxaborolane (5b).[25] To a solution of **1** (54 mg, 0.2 mmol, 2 equiv), **4b** (18.5 mg, 0.1 mmol), and Pd[P(*t*-Bu)$_3$]$_2$ (2.6 mg, 5.0 μmol, 5 mol %) in dioxane (1.0 mL) was added 8 N KOH aq (24 μL, 0.2 mmol, 2 equiv) at room temperature. The mixture was stirred for 5 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be >98% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/EtOAc = 10/1) gave the product **5b** in 0.085 mmol, 85% yield (21.2 mg/24.8 mg).

Synthesis of 2-(4-*tert*-Butylphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5c). To a solution of **1** (54 mg, 0.2 mmol, 2 equiv), **4c** (22.6 mg, 0.1 mmol), and Pd[P(*t*-Bu)$_3$]$_2$ (2.6 mg, 5.0 μmol, 5 mol %) in dioxane (1.0 mL) was added 8 N KOH aq (24 μL, 0.2 mmol, 2 equiv) at room temperature. The mixture was stirred for 24 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be 92% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/EtOAc = 10/1) gave the product **5c** in 0.087 mmol, 89% yield (25.4 mg/28.5 mg): colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.22−7.19 (m, 2H), 7.09−7.07 (m, 2H), 2.64 (t, J = 8.0 Hz, 2H), 1.23 (s, 9H), 1.15 (s, 12H), 1.06 (t, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.3, 141.4, 127.7, 125.1, 83.1, 34.4, 31.5, 29.5, 24.9; ^{11}B NMR ($CDCl_3$, 128 MHz) δ 33.6; IR (neat, cm^{-1}) 2977, 2935, 1374, 1321, 1270, 1145, 969, 846, 748; HRMS (FAB, positive) m/z calcd for $C_{18}H_{29}BO_2$ 288.2260, found 288.2267.

Synthesis of 2-(4-Chlorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5d).[24] To a solution of **1** (54 mg, 0.2 mmol, 2 equiv), **4d** (20.3 mg, 0.1 mmol), and Pd[P(*t*-Bu)$_3$]$_2$ (2.6 mg, 5.0 μmol, 5 mol %) in dioxane (1.0 mL) was added 8 N KOH aq (24 μL, 0.2 mmol, 2 equiv) at room temperature. The mixture was stirred for 5 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be >98% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/EtOAc = 10/1) gave the product **5d** in 0.085 mmol, 86% yield (22.7 mg/26.4 mg).

Synthesis of 2-(4-Fluorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5e). To a solution of **1** (54 mg, 0.2 mmol, 2 equiv), **4e** (19.2 mg, 0.1 mmol), and Pd[P(*t*-Bu)$_3$]$_2$ (2.6 mg, 5.0 μmol, 5 mol %) in dioxane (1.0 mL) was added 8 N KOH aq (24 μL, 0.2 mmol, 2 equiv) at room temperature. The mixture was stirred for 2 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be >98% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/EtOAc = 10/1) gave the product **5e** in 0.090 mmol, 89% yield (22.5 mg/25.4 mg): colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.55 (m, 2H), 7.31 (m, 2H), 2.80 (t, J = 8.0 Hz, 2H), 1.21 (s, 12H), 1.14 (t, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.1 (d, J = 242 Hz), 139.9 (d, J = 3.3 Hz), 129.3 (d, J = 8.2 Hz), 114.8 (d, J = 20.7 Hz), 83.1, 29.1, 24.7; ^{11}B NMR ($CDCl_3$, 128 MHz) δ 34.2; ^{19}F NMR ($CDCl_3$, 470 MHz) δ −117.7; IR (neat, cm^{-1}) 2979, 2935, 1510, 1372, 1220, 1145, 968, 853, 840; HRMS (FAB, positive) m/z calcd for $C_{14}H_{20}BFO_2$ 250.1540, found 250.1547.

Synthesis of 4,4,5,5-Tetramethyl-2-(3-nitrophenethyl)-1,3,2-dioxaborolane (5f).[26] To a solution of **1** (54 mg, 0.2 mmol, 2 equiv), **4f** (21.4 mg, 0.1 mmol), and Pd[P(*t*-Bu)$_3$]$_2$ (2.6 mg, 5.0 μmol, 5 mol %) in dioxane (1.0 mL) was added 8 N KOH aq (24 μL, 0.2 mmol, 2 equiv) at room temperature. The mixture was stirred for 5 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be >98% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/EtOAc = 10/1) gave the product **5f** in 0.069 mmol, 70% yield (19.2 mg/27.4 mg).

Synthesis of 4-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (5g). To a solution of **1** (54 mg, 0.2 mmol, 2 equiv), **4g** (19.6 mg, 0.1 mmol), and Pd[P(*t*-Bu)$_3$]$_2$ (2.6 mg, 5.0 μmol, 5 mol %) in dioxane 1.0 mL was added 8 N KOH aq (24 μL, 0.2 mmol, 2 equiv) at room temperature. The mixture was stirred for 5 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be 97% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/EtOAc = 10/1) gave the product **5g** in 0.085 mmol, 85% yield (21.9 mg/25.7 mg): colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.55 (m, 2H), 7.31 (m, 2H), 2.80 (t, J = 8.0 Hz, 2H), 1.21 (s, 12H), 1.14 (t, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.0, 132.0, 128.8, 119.2, 109.4, 83.3, 30.1, 24.8; ^{11}B NMR ($CDCl_3$, 128 MHz) δ 33.9; IR (neat, cm^{-1}) 2974, 2934, 2361, 2338, 1364, 1276, 1217, 965, 767, 749; HRMS (FAB, positive) m/z calcd for $C_{15}H_{21}BNO_2$ [M + H]$^+$ 258.1665, found 258.1665.

Synthesis of Methyl 4-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzoate (5h). To a solution of **1** (54 mg, 0.2 mmol, 2 equiv), **4h** (22.9 mg, 0.1 mmol), and Pd[P(*t*-Bu)$_3$]$_2$ (2.6 mg, 5.0 μmol, 5 mol %) in dioxane (1.0 mL) was added 8 N KOH aq (24 μL, 0.2 mmol, 2 equiv) at room temperature. The mixture was stirred for 24 h and filtered through a pad of silica gel with ether. Concentration gave the residue, the NMR yield of which was determined to be 91% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/EtOAc = 10/1) gave the product **5h** in 0.077 mmol, 77% yield (22.4 mg/29.0 mg): colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.94−7.92 (m, 2H), 7.29−7.26 (m, 2H), 3.89 (s, 3H), 2.80 (t, J = 8.4 Hz, 2H), 1.21 (s, 12H), 1.18−1.13 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.2, 149.9, 129.6, 128.0, 127.5, 83.2, 51.9, 30.0, 24.8; ^{11}B NMR ($CDCl_3$, 128 MHz) δ 34.4; IR (neat, cm^{-1}) 2979, 2950, 1739, 1373, 1145, 1110, 968,704; HRMS (FAB, positive) m/z calcd for $C_{16}H_{24}{}^{10}BO_4$ [M + H]$^+$ 290.1804, found 290.1805.

Synthesis of 4,4,5,5-Tetramethyl-2-(2-(naphthalen-2-yl)-ethyl)-1,3,2-dioxaborolane (5i).[24] To a solution of **1** (54 mg, 0.2 mmol, 2 equiv), **4i** (22.1 mg, 0.1 mmol), and Pd[P(*t*-Bu)$_3$]$_2$ (2.6 mg, 5.0 μmol, 5 mol %) in dioxane (1.0 mL) was added 8 N KOH aq (24 μL, 0.2 mmol, 2 equiv) at room temperature. The mixture was stirred for 24 h and filtered through a pad of silica gel with ether.

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Concentration gave the residue, the NMR yield of which was determined to be 84% by the integration ratio of the crude NMR with 1,1,2,2-tetrachloroethane as an internal standard. Purification by silica gel column chromatography (hexane/EtOAc = 10/1) gave the product **5i** in 0.080 mmol, 80% yield (22.5 mg/28.2 mg).

■ ASSOCIATED CONTENT

Supporting Information

NMR spectra of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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