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# Palladium-catalyzed cross-coupling reaction of bis(pinacolato)diboron with vinyl triflates β-substituted by a carbonyl group: Efficient synthesis of β-boryl-α,β-unsaturated carbonyl compounds and their synthetic utility

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Dedicated to Professor J. P. Genêt in recognition of his significant contributions to the art of organic synthesis (on the occasion of his 60th birthday)

## Abstract

Cross-coupling reaction of bis(pinacolato)diboron with β-(trifluoromethanesulfonyloxy)-α,β-unsaturated carbonyl compounds was carried out in the presence of $PdCl_2(PPh_3)_2$-$2PPh_3$ (3 mol%) and KOPh in toluene or $K_2CO_3$ in dioxane for the synthesis of cyclic and acyclic β-boryl-α,β-unsaturated esters, amides, and ketones in high yields. The vinylboronates thus obtained readily participated in carbon-carbon bond formation, such as cross-coupling with vinyl triflates and

1,4-addition to α,β-unsaturated ketones.

*Keywords:* Bis(pinacolato)diboron; Vinyl triflate; Palladium catalyst; Vinylboronate; Cross-coupling

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## 1. Introduction

β-Boryl-α,β-unsaturated carbonyl compounds are attractive synthetic intermediates which allow inter- or intramolecular Diels-Alder reaction [1], asymmetric dipolar cycloaddition or 1,4-addition [2], cyclopropanation [3], and radical addition [4]. Although β-borylacrylates are available *via* hydroboration of propiolic acid esters [1,5], preparation of the corresponding ketone and aldehyde derivatives requires a multi-step procedure [1,6] and there are few reports for cyclic or polysubstituted derivatives [7]. In connection with our interest in the synthesis of organoboron compounds *via* the cross-coupling reaction of diborons with organic electrophiles [8] including aryl [8,9], vinyl [8,10], allyl [8,11], and benzyl [8,12] halides or triflates, we wish to disclose here a palladium-catalyzed cross-coupling reaction of bis(pinacolato)diboron [13] ($pin_2B_2$, pin = $Me_4C_2O_2$) **1** with vinyl triflates [14] **2** to yield the corresponding

β-boryl-α,β-unsaturated carbonyl compounds **3** (Scheme 1) [15].

<<Scheme 1>>

## 2. Results and discussion

### *2.1. Cross-coupling of diboron with vinyl triflates*

The effects of bases and solvents on the reaction are shown in Table 1. The conditions previously reported for the coupling of $pin_2B_2$ **1** with vinyl halides or triflates ($PdCl_2(PPh_3)_2$-$2PPh_3$/KOPh/toluene/50 °C) [10] gave borylated products **3** in high yields for most of the vinyl triflates **2**, but the reaction often resulted in very low yields due to a competitive base-induced side-reaction. For example, the reaction of **1** (1.1 mmol) with ethyl 2-(trifluoromethanesulfonyloxy)-1-cyclopentenecarboxylate (1.0 mmol) in the presence of $PdCl_2(PPh_3)_2$-$2PPh_3$ (0.03 mmol) and KOPh (1.5 mmol) in toluene (6 ml) at 50 °C resulted in 9% yield (Entry 1). Analysis of the reaction mixture revealed the formation of phenyl triflate (90%) resulted by ester-exchange between the triflate and KOPh [16]. A sterically more hindered 2-$MeC_6H_4OK$ base, which is expected to inhibit the ester-exchange, also produced the corresponding triflate in 69% yield (Entry 2). Alternatively, use of a $K_2CO_3$ base in dioxane was found to be effective for such substrates sensitive to the phenoxy anion to promote the desired coupling in 67% yield (Entry 3). Although $K_2CO_3$ was prone to induce further coupling of **3** with **2** giving a dimer of **2** (ca. 30%), stronger bases such as $K_3PO_4$ further enhanced the dimerization (Entry 4) and weaker bases such as KOAc did not promote the coupling (Entry 5). Use of less-polar solvents such as toluene resulted in low conversion (Entry 6). Although the

reactions using $K_2CO_3$ took longer times at 50 °C, the same reactions were completed at 80 °C within 5 h in dioxane and 24 h in toluene, respectively (Entries 7 and 8).

<<Table 1>>

The palladium-catalyzed cross-coupling of $pin_2B_2$ **1** with the representative vinyl triflates **2** in the presence of KOPh in toluene at 50 °C (Method A) or $K_2CO_3$ in dioxane at 80 °C (Method B) is summarized in Table 2. All **2** including cyclic or acyclic ester, amide, and ketone derivatives were converted into the corresponding β-boryl-α,β-unsaturated carbonyl compounds **3** in high yields by either Method A or B. The reactions were faster under the conditions of Method A than those of Method B; however, the yields highly depended upon the substrates. Method A resulted in low yields due to the formation of phenyl triflate (30-90%) for substrates sensitive to the phenoxy anion, including five-membered ester (Entry 1), six-membered amide (Entry 5), five-membered ketone (Entry 6), and less-hindered six-membered ketone having no substituent at the a carbon (Entry 8). On the other hand, Method A was a better choice for seven- and eight-membered esters (Entries 3 and 4), and acyclic ester (Entry 10), because Method B resulted in the formation of symmetrical 1,3-dienes (15-30%) arising from dimerization of **2**. The borylation of acyclic ester and amide derivatives of **2** having *E* stereochemistry retained completely the configuration of the double bond to give isomerically pure (*Z*)-**3** in high yields (Entries 10 and 11).

<<Table 2>>

In general, *E* or *Z* configuration of vinyl halides or triflates can be retained completely in the cross-coupling of organoboron compounds [17]; however, the amide derivative of triflate (*Z*)-**4** unexpectedly provided the borylated product (*Z*)-**5** by Method A and a mixture of (*Z*)-**5** and (*E*)-**5** (64:36) by Method B (Scheme 2). Monitoring of a

benzene-$d_6$ solution of the (*Z*)-**4** or (*E*)-**5** in the presence of $Pd(PPh_3)_4$ and KOPh by $^1H$ NMR and GC at 50 °C resulted in no conversion into (*E*)-**4** or (*Z*)-**5**, suggesting the isomerization during the catalytic process. It remains unclear which step is responsible for such isomerization; however, a vinylpalladium(II) species generated by oxidative addition of a vinyl halide or triflate to a palladium(0) complex often undergoes *E-Z* isomerization [18].

<<Scheme 2>>

*2.2. One-pot synthesis of 1,3-dienes via borylation-coupling sequence*

The direct preparation of β-boryl-α,β-unsaturated carbonyl compounds **3** from $pin_2B_2$ **1** and the corresponding vinyl triflates **2** now allows a one-pot, two-step procedure for the synthesis of ketone or ester derivatives of unsymmetrical 1,3-dienes **7** (Table 3). The stereoselective synthesis of three dienes **7** were easily achieved in 76%, 76%, and 77% yields when the borylation of **2** (1.1 mmol) with **1** (1.1 mmol) was directly followed by the coupling with another vinyl triflate **6** (1.0 mmol). A combination of $PdCl_2$(dppf) (0.03 mmol) and $K_3PO_4$ (3.0 mmol) in dioxane at 80 °C was recognized to be the best conditions for the second coupling [17].

<<Table 3>>

*2.3. 1,4-Addition of vinylboronates to α,β-unsaturated ketones*

Although we examined one-pot synthesis *via* borylation-addition sequence at first, all attempts at the reactions of *in situ* generated vinylboroates **3** with α,β-unsaturated

ketones **8** by using a rhodium catalyst were unsuccessful. On the other hand, it was found that isolated **3** readily underwent the expected 1,4-addition. The addition did not occur in the presence of a catalytic amount of both a rhodium complex and $PdCl_2(PPh_3)_2$-$2PPh_3$, indicating that the palladium catalyst used at the borylation step inhibited the addition step. Representative results of the 1,4-addition of **3** (1.0 mmol) to **8** (1.1 mmol) catalyzed by a rhodium complex (3 mol%) are summarized in Table 4. Acyclic-acyclic (Entries 1 and 3), acyclic-cyclic (Entries 2 and 4), cyclic-acyclic (Entry 5), and cyclic-cyclic (Entry 6) combinations all produced the corresponding ε-oxo-α,β-unsaturated ester, amide, and ketone derivatives **9** in high yields. The reactions of acyclic ester and amide derivatives of **3** having *Z* stereochemistry retained completely the configuration of the double bond (Entries 1-4). In the case of the cyclic-cyclic reaction, use of 1.1 mmol of **8** resulted in a moderate yield (42%); however, the yield was improved to 65% when using 2.0 mmol of **8** (Entry 6). Although reaction conditions were not fully optimized, the addition smoothly proceeded in the presence of a $[Rh(COD)_2]BF_4$ catalyst in aqueous dioxane at 90 °C [19].

<<Table 4>>

## 3. Experimental

### *3.1. Materials and reagents*

Bis(pinacolato)diboron [13], vinyl triflates [14], potassium phenoxide [20], and potassium 2-methylphenoxide [21] were prepared by the reported procedures. Solvents were purified by distillation from appropriate drying agents. All of other compounds

were used as received.

*3.2. General procedure for cross-coupling of bis(pinacolato)diboron with vinyl triflates (Table 2 and Scheme 2)*

A 25 ml flask assembled a magnetic stirring bar, a septum inlet, and a condenser was charged with $PdCl_2(PPh_3)_2$ (0.03 mmol), $PPh_3$ (0.06 mmol), bis(pinacolato)diboron **1** (1.1 mmol), and KOPh or $K_2CO_3$ (1.5 mmol) and then flushed with nitrogen. Dry toluene or dioxane (6 ml) and a vinyl triflate **2** or **4** (1.0 mmol) were added and the mixture was stirred at 50 °C or 80 °C for the period shown in Table 2 or Scheme 2. The product was extracted with benzene, washed with brine, and dried over $MgSO_4$. Column chromatography over silica gel followed by Kugelrohr distillation gave an analytically pure vinylboronate **3** or **5**.

*3.2.1. Ethyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-cyclopentene-1-carboxylate*

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ 1.28 (t, 3 H, $J$ = 7.1 Hz), 1.34 (s, 12 H), 1.89-1.97 (m, 2 H), 2.60 (t, 4 H, $J$ = 7.7 Hz), 4.21 (q, 2 H, $J$ = 7.2 Hz); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 14.39, 24.09, 24.74, 33.50, 37.52, 60.19, 83.86, 142.90, 165.81; MS (EI) *m/e* 121 (28), 179 (81), 208 (100), 266 ([$M^+$], 5); exact mass Found: 266.1682; $C_{14}H_{23}BO_4$ Calc.: 266.1689.

*3.2.2. Ethyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-cyclohexene-1-carboxylate*

$^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta$ 1.27 (t, 3 H, $J$ = 7.2 Hz), 1.33 (s, 12 H), 1.54-1.66 (m, 4 H), 2.22 (br s, 4 H), 4.21 (q, 2 H, $J$ = 7.2 Hz); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 14.25, 21.42, 21.85, 24.12, 24.77, 27.93, 60.70, 83.34, 134.24, 169.19; MS (EI) *m/e* 79 (40), 108 (37), 153 (41), 193 (55), 222 (100), 280 ([$M^+$], 4); exact mass Found: 280.1846; $C_{15}H_{25}BO_4$ Calc.: 280.1846.

*3.2.3. Ethyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-cycloheptene-1-carboxylate*

$^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta$ 1.29 (t, 3 H, $J$ = 7.1 Hz), 1.32 (s, 12 H), 1.48-1.52 (m, 2 H), 1.55-1.59 (m, 2 H), 1.76-1.78 (m, 2 H), 2.32-2.34 (m, 2 H), 2.46-2.49 (m, 2 H), 4.24 (q, 2 H, $J$ = 7.1 Hz); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 14.19, 24.82, 25.86, 25.90, 27.09, 30.99, 32.20, 61.90, 82.67, 139.52, 171.45; MS (EI) *m/e* 83 (29), 93 (24), 122 (34), 167 (34), 236 (100), 294 ([$M^+$], 5); exact mass Found: 294.1992; $C_{16}H_{27}BO_4$ Calc.: 294.2002.

*3.2.4. Ethyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-cyclooctene-1-carboxylate*

$^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta$ 1.28 (t, 3 H, $J$ = 7.2 Hz), 1.32 (s, 12 H), 1.45-1.46 (m, 4 H), 1.50-1.60 (m, 2 H), 1.60-1.70 (m, 2 H), 2.33-2.36 (m, 2 H), 2.42-2.45 (m, 2 H), 4.23 (q, 2 H, $J$ = 7.2 Hz); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 14.25, 24.68, 24.72, 26.19, 26.27, 28.75, 28.99, 29.62, 61.16, 82.93, 137.01, 170.16; MS (EI) *m/e* 83 (33), 107 (22), 136 (33), 181 (21), 250 (100), 308 ([$M^+$], 5); exact mass Found: 308.2134; $C_{17}H_{29}BO_4$ Calc.: 308.2159.

*3.2.5. N,N-Diethyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-cyclohexene-1-carboxamide*

$^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta$ 1.23 (s, 12 H), 1.25 (t, 6 H, $J$ = 6.8 Hz), 1.54-1.59 (m, 2 H), 1.63-1.68 (m, 2 H), 2.28-2.31 (m, 2 H), 2.40-2.43 (m, 2 H), 3.50-3.60 (m, 4 H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 12.51, 14.73, 21.28, 23.06, 25.24, 25.84, 26.85, 42.42, 44.66, 79.70, 129.25, 173.76; MS (EI) *m/e* 83 (57), 207 (23), 249 (100), 292 (22), 307 ([$M^+$], 37); exact mass Found: 307.2319; $C_{17}H_{30}BNO_3$ Calc.: 307.2319.

*3.2.6. 2-Methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-cyclopenten-1-one*

$^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta$ 1.33 (s, 12 H), 1.94 (t, 3 H, $J$ = 2.2 Hz), 2.33-2.35 (m, 2 H), 2.61-2.64 (m, 2 H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 10.52, 24.85, 28.77, 34.19, 83.94, 151.92, 212.11; MS (EI) *m/e* 83 (51), 122 (74), 136 (71), 165 (82), 207 (93), 222 ([$M^+$], 100); exact mass Found: 222.1429; $C_{12}H_{19}BO_3$ Calc.: 222.1427.

*3.2.7. 2-Methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-cyclohexen-1-one*

$^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta$ 1.31 (s, 12 H), 1.92-1.99 (m, 2 H), 1.96 (t, 3 H, $J$ = 2.0 Hz), 2.38-2.44 (m, 4 H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 14.86, 23.43, 24.76, 28.62, 38.50, 83.98, 143.39, 199.82; MS (EI) *m/e* 83 (100), 137 (44), 179 (76), 236 ([$M^+$], 53); exact mass Found: 236.1586; $C_{13}H_{21}BO_3$ Calc.: 236.1584.

*3.2.8. 5,5-Dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-cyclohexen-1-one*

$^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta$ 1.02 (s, 6 H), 1.30 (s, 12 H), 2.25 (s, 2 H), 2.32 (d,

2 H, *J* = 2.0 Hz), 6.54 (s, 1 H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 24.77, 28.22, 33.96, 41.11, 51.73, 84.31, 137.66, 200.19; MS (EI) *m/e* 83 (100), 194 (17), 235 (20), 250 ([$M^+$], 14); exact mass Found: 250.1741; $C_{14}H_{23}BO_3$ Calc.: 250.1740.

*3.2.9. 2-Methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-cyclohepten-1-one*

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ 1.31 (s, 12 H), 1.60-1.80 (m, 4 H), 2.01 (s, 3 H), 2.39 (t, 2 H, *J* = 5.6 Hz), 2.50 (t, 2 H, *J* = 6.1 Hz); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 17.86, 20.93, 24.54, 24.73, 28.66, 41.25, 83.75, 148.21, 208.40; MS (EI) *m/e* 101 (25), 165 (100), 250 ([$M^+$], 9); exact mass Found: 250.1741; $C_{14}H_{23}BO_3$ Calc.: 250.1740.

*3.2.10. Ethyl (Z)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-butenoate*

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ 1.28 (s, 12 H), 1.28 (t, 3 H, *J* = 7.1 Hz), 2.17 (d, 3 H, *J* = 1.7 Hz), 4.17 (q, 2 H, *J* = 7.2 Hz), 6.45 (d, 1 H, *J* = 1.7 Hz) [the irradiation of the vinylic proton at 6.45 ppm resulted in no enhancement of the allylic methyl signal at 2.17 ppm]; $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 14.24, 16.29, 24.74, 59.75, 84.11, 130.56, 166.21; MS (EI) *m/e* 112 (75), 140 (100), 195 (32), 240 ([$M^+$], 4); exact mass Found: 240.1534; $C_{12}H_{21}BO_4$ Calc.: 240.1533.

*3.2.11. N,N-Diethyl (Z)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-butenamide*

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ 1.15 (t, 6 H, *J* = 7.1 Hz), 1.27 (s, 12 H), 1.85 (d, 3 H, *J* = 1.7 Hz), 3.25-3.50 (m, 4 H), 6.68 (d, 1 H, *J* = 1.5 Hz) [the irradiation of the vinylic proton at 6.68 ppm resulted in no enhancement of the allylic methyl signal at 1.85 ppm]; $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 13.04, 14.29, 16.18, 24.77, 38.70, 42.21,

83.74, 136.03, 168.06; MS (EI) *m/e* 167 (100), 252 (21), 267 ([$M^+$], 43); exact mass Found: 267.2013; $C_{14}H_{26}BNO_3$ Calc.: 267.2006.

*3.2.12. N,N-Diethyl (E)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-butenamide*

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ 1.16 (t, 3 H, $J$ = 7.3 Hz), 1.17 (t, 3 H, $J$ = 7.6 Hz), 1.19 (s, 12 H), 2.01 (d, 3 H, $J$ = 1.5 Hz), 3.37 (q, 2 H, $J$ = 7.3 Hz), 3.48 (q, 2 H, $J$ = 7.2 Hz), 6.06 (s, 1 H) [the irradiation of the vinylic proton at 6.06 ppm resulted in an 3.2% enhancement of the allylic methyl signal at 2.01 ppm]; $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 12.75, 14.25, 18.12, 25.15, 42.82, 42.86, 80.23, 117.68, 173.54; MS (EI) *m/e* 83 (37), 167 (39), 209 (100), 252 (31), 267 ([$M^+$], 2); exact mass Found: 267.2019; $C_{14}H_{26}BNO_3$ Calc.: 267.2006.

*3.3. NMR studies on isomerization of N,N-diethyl (Z)-3-(trifluoromethanesulfonyloxy)-2-benenamide and N,N-diethyl (E)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-butenamide*

In an NMR tube, a mixture of $Pd(PPh_3)_4$ (0.003 mmol), KOPh (0.15 mmol), the vinyl triflate or the vinylboronate (0.1 mmol), and benzene-$d_6$ (0.6 ml) was heated at 50 °C for 1 h. $^1$H NMR and GC analyses indicated no isomerization of the vinyl triflate or the vinylboronate.

*3.4. General procedure for one-pot synthesis of 1,3-dienes via borylation–coupling sequence (Table 3)*

To a solution of a vinylboronate **3** resulted by the reaction of bis(pinacolato)diboron **1** (1.1 mmol) with a vinyl triflate **2** (1.1 mmol) in toluene or dioxane (4 ml) were added a second vinyl triflate **6** (1.0 mmol), $PdCl_2$(dppf) (0.03 mmol), $K_3PO_4$ (3.0 mmol), and dioxane (4 ml), and the mixture was stirred at 80 °C for 16 h. The product was extracted with benzene, washed with water, and dried over $MgSO_4$. Column chromatography over silica gel provided an analytically pure 1,3-diene **7**.

*3.4.1. Ethyl 2-[(E)-3-ethoxycarbonyl-2-propen-2-yl]-1-cyclohexene-1-carboxylate*

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ 1.22 (t, 3 H, $J$ = 7.1 Hz), 1.26 (t, 3 H, $J$ = 7.2 Hz), 1.60-1.70 (m, 4 H), 2.15-2.20 (m, 2 H), 2.28 (d, 3 H, $J$ = 1.5 Hz), 2.30-2.35 (m, 2 H), 4.11 (q, 2 H, $J$ = 7.1 Hz), 4.14 (q, 2 H, $J$ = 7.1 Hz), 5.51 (d, 1 H, $J$ = 1.2 Hz); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 13.87, 14.28, 18.25, 21.85, 21.94, 25.56, 30.19, 59.59, 60.31, 114.94, 125.24, 149.60, 160.61, 166.61, 168.27; MS (EI) *m/e* 165 (62), 193 (100), 266 ([$M^+$], 1); exact mass Found: 266.1519; $C_{15}H_{22}O_4$ Calc.: 266.1518.

*3.4.2. Ethyl (E)-3-(2-methyl-3-oxo-1-cyclohexenyl)-2-butenoate*

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ 1.30 (t, 3 H, $J$ = 7.2 Hz), 1.73 (s, 3 H), 1.98-2.06 (m, 2 H), 2.29 (d, 3 H, $J$ = 1.2 Hz), 2.36-2.42 (m, 2 H), 2.45 (t, 2 H, $J$ = 6.7 Hz), 4.19 (q, 2 H, $J$ = 7.2 Hz), 5.62 (d, 1 H, $J$ = 1.5 Hz); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 12.19, 14.24, 17.44, 22.78, 29.89, 37.70, 60.06, 117.21, 129.70, 156.37, 158.00, 166.23, 199.44; MS (EI) *m/e* 137 (37), 149 (100), 166 (37), 179 (44), 194 (38), 222 ([$M^+$], 70); exact mass Found: 222.1263; $C_{13}H_{18}O_3$ Calc.: 222.1256.

*3.4.3. Ethyl 2-(2-methyl-3-oxo-1-cyclopentenyl)-1-cyclohexene-1-carboxylate*

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ 1.17 (t, 3 H, $J$ = 7.2 Hz), 1.58 (t, 3 H, $J$ = 2.0 Hz), 1.68-1.74 (m, 4 H), 2.12-2.22 (m, 2 H), 2.36-2.50 (m, 4 H), 2.60-2.70 (m, 2 H), 4.07 (q, 2 H, $J$ = 7.2 Hz); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 8.19, 13.92, 21.67, 21.84, 25.47, 28.99, 29.31, 34.10, 60.33, 126.58, 134.33, 144.77, 167.22, 173.62, 209.29; MS (EI) *m/e* 163 (31), 177 (25), 191 (47), 220 (100), 248 ([$M^+$], 2); exact mass Found: 248.1412; $C_{15}H_{20}O_3$ Calc.: 248.1412.

*3.5. General procedure for 1,4-addition of vinylboronates to α,β-unsaturated ketones (Table 4)*

A 25 ml flask charged with $[Rh(COD)_2]BF_4$ (0.03 mmol) was flushed with nitrogen. Aqueous dioxane (dioxane:water = 6:1, 6 ml), a vinylboronate **3** (1.0 mmol), and an α,β-unsaturated carbonyl compound **8** (1.1 mmol) were then added. The resulting mixture was stirred at 90 °C for 6 h. The product was extracted with benzene, washed with water, and dried over $MgSO_4$. Column chromatography over silica gel gave an analytically pure 1,4-adduct **9**.

*3.5.1. Ethyl (E)-3-methyl-6-oxo-2-heptenoate*

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ 1.28 (t, 3 H, $J$ = 7.1 Hz), 2.16 (d, 3 H, $J$ = 1.2 Hz), 2.18 (s, 3 H), 2.42 (t, 2 H, $J$ = 7.8 Hz), 2.62 (t, 2 H, $J$ = 7.7 Hz), 4.14 (q, 2 H, $J$ = 7.2 Hz), 5.63-5.66 (m, 1 H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 14.27, 18.83, 29.97, 34.20,

41.11, 59.59, 115.91, 157.94, 166.57, 207.09; MS (EI) *m/e* 43 (100), 58 (33), 95 (48), 113 (25), 138 (36), 184 ([$M^+$], 9); exact mass Found: 184.1097; $C_{10}H_{16}O_3$ Calc.: 184.1099.

*3.5.2. Ethyl (E)-3-(3-oxocyclohexyl)-2-butenoate*

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ 1.29 (t, 3 H, $J$ = 7.2 Hz), 1.50-1.70 (m, 2 H), 1.80-1.95 (m, 1 H), 2.00-2.10 (m, 1 H), 2.15-2.45 (m, 5 H), 2.17 (s, 3 H), 4.16 (q, 2 H, $J$ = 7.1 Hz), 5.69 (d, 1 H, $J$ = 1.0 Hz); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 14.25, 16.84, 25.08, 29.58, 41.09, 45.87, 48.34, 59.75, 115.56, 159.96, 166.70, 210.18; MS (EI) *m/e* 95 (41), 137 (50), 164 (100), 181 (37), 210 ([$M^+$], 37); exact mass Found: 210.1246; $C_{12}H_{18}O_3$ Calc.: 210.1256.

*3.5.3. N,N-Diethyl (E)-3-methyl-6-oxo-2-heptenamide*

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ 1.14 (t, 6 H, $J$ = 7.2 Hz), 1.90 (s, 3 H), 2.18 (s, 3 H), 2.38 (t, 2 H, $J$ = 7.4 Hz), 2.63 (t, 2 H, $J$ = 7.6 Hz), 3.36 (br s, 4 H), 5.80 (s, 1 H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 13.48, 14.35, 18.54, 30.00, 33.24, 40.00, 41.32, 43.04, 118.43, 147.05, 167.74, 207.72; MS (EI) *m/e* 43 (100), 111 (78), 115 (66), 168 (79), 211 ([$M^+$], 11); exact mass Found: 211.1583; $C_{12}H_{21}NO_2$ Calc.: 211.1572.

3.5.4. *N,N-Diethyl (E)-3-(3-oxocyclohexyl)-2-butenamide*

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ 1.15 (t, 6 H, $J$ = 7.1 Hz), 1.60-1.80 (m, 2 H), 1.90-2.00 (m, 1 H), 1.92 (s, 3 H), 2.00-2.20 (m, 1 H), 2.20-2.60 (m, 5 H), 3.20-3.50 (m, 4 H), 5.83 (s, 1 H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 13.23, 14.27, 16.36, 25.03, 29.54,

39.66, 41.23, 42.56, 46.27, 47.27, 118.26, 149.26, 167.58, 210.86; MS (EI) *m/e* 72 (93), 100 (64), 137 (100), 165 (61), 237 ([$M^+$], 82); exact mass Found: 237.1738; $C_{14}H_{23}NO_2$ Calc.: 237.1729.

*3.5.5. 2-Methyl-3-(3-oxobutyl)-2-cyclohepten-1-one*

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ 1.65-1.75 (m, 4 H), 1.81 (s, 3 H), 2.19 (s, 3 H), 2.35 (t, 2 H, $J$ = 5.5 Hz), 2.45-2.60 (m, 6 H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 14.23, 20.96, 24.39, 29.93, 30.85, 32.14, 40.99, 41.37, 134.44, 150.95, 207.04, 207.45; MS (EI) *m/e* 95 (62), 123 (50), 133 (52), 151 (100), 194 ([$M^+$], 17); exact mass Found: 194.1296; $C_{12}H_{18}O_2$ Calc.: 194.1307.

*3.5.6. 2-Methyl-3-(3-oxocyclohexyl)-2-cyclohepten-1-one*

$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ 1.60-1.80 (m, 8 H), 1.82 (s, 3 H), 2.10-2.55 (m, 8 H), 3.00-3.15 (m, 1 H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 13.76, 20.56, 24.46, 25.55, 25.75, 28.33, 41.09, 41.19, 43.22, 44.52, 133.77, 149.66, 208.55, 210.33; MS (EI) *m/e* 95 (74), 123 (100), 202 (38), 220 ([$M^+$], 12); exact mass Found: 220.1451; $C_{14}H_{20}O_2$ Calc.: 220.1463.

**Acknowledgments**

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Science Foundation for support of a part of his work.

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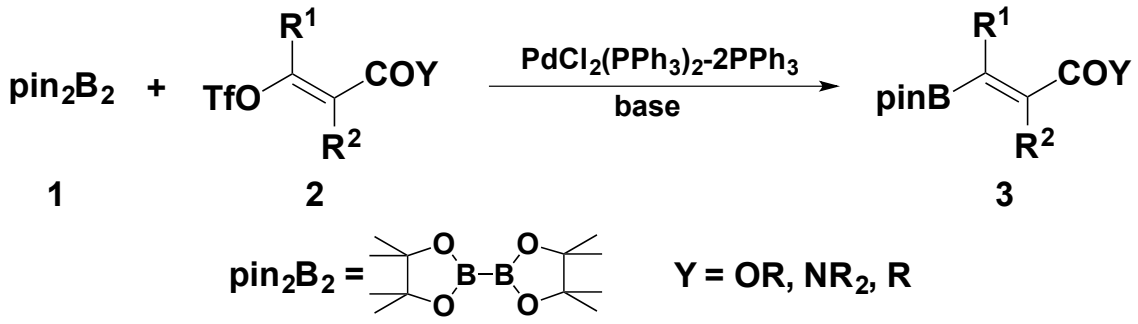
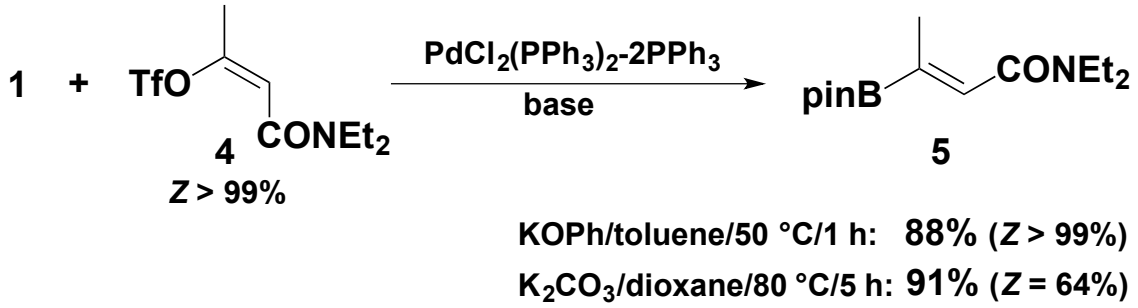

pin2B2 + TfO R1 COY R2
PdCl2(PPh3)2-2PPh3
base
pinB R1 COY R2
1
2
3
pin2B2 =
Y = OR, NR2, R

Scheme 1.


1 + TfO
4 CONEt2
Z > 99%
PdCl2(PPh3)2-2PPh3
base
pinB
CONEt2
5
KOPh/toluene/50 °C/1 h: 88% (Z > 99%)
K2CO3/dioxane/80 °C/5 h: 91% (Z = 64%)

Scheme 2.

Table 1
Effects of bases and solvents [a]

| Entry [b] | Base/Solvent | Temp/°C | Time/h | Yield/% |
|---|---|---|---|---|
| 1 | KOPh/toluene | 50 | 2 | 9 [c] |
| 2 | 2-$MeC_6H_4OK$/toluene | 50 | 2 | 4 [d] |
| 3 | $K_2CO_3$/dioxane | 50 | 16 | 67 [e] |
| 4 | $K_3PO_4$/dioxane | 50 | 16 | 58 [e] |
| 5 | KOAc/dioxane | 50 | 16 | 4 |
| 6 | $K_2CO_3$/toluene | 50 | 16 | 1 |
| 7 | $K_2CO_3$/dioxane | 80 | 5 | 67 [e] |
| 8 | $K_2CO_3$/toluene | 80 | 24 | 65 [e] |

[a] The coupling reaction of diboron **1** (1.1 mmol) with ethyl 2-(trifluoromethanesulfonyloxy)-1-cyclopentenecarboxylate (1.0 mmol) was carried out in the presence of $PdCl_2(PPh_3)_2$ (0.03 mmol), $PPh_3$ (0.06 mmol), and base (1.5 mmol) in 6 ml of solvent.

[b] GC yields based on the triflate.

[c] The reaction accompanied PhOTf (90%).

[d] The reaction produced 2-$MeC_6H_4OTf$ (69%)

[e] The reactions gave a dimer of the triflate (30-40%).

Table 2
Synthesis of vinylboronates **3** (Scheme 1) [a]

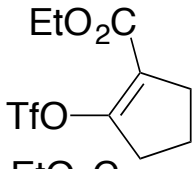
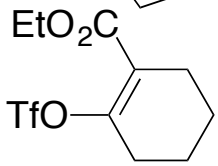
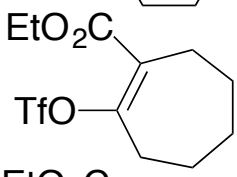
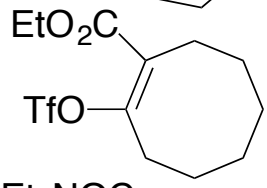
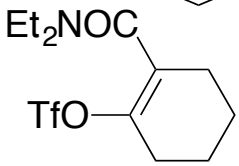
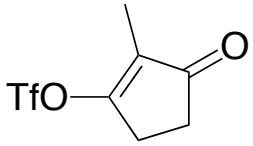
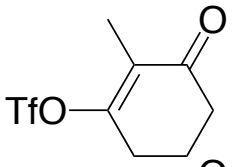
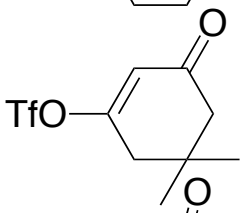
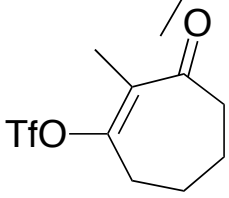
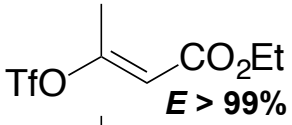
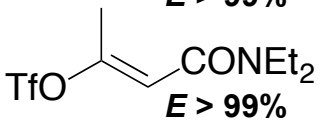
| Entry | Triflate **2** | Yield/% [b] | |
|---|---|---|---|
| | | Method A [c] | Method B [d] |
| 1 |  | 9 (2 h) | 67 (5 h) |
| 2 |  | 78 (1 h) | 91 (6 h) |
| 3 |  | 76 (1 h) | 74 (3 h) |
| 4 |  | 72 (1 h) | 60 (5 h) |
| 5 |  | 60 (6 h) | 98 (3 h) |
| 6 |  | 21 (1 h) | 78 (2 h) |

Table 2 (continued)

| | | | |
|---|---|---|---|
| 7 |  | 81 (2 h) | 91 (5 h) |
| 8 |  | 25 (2 h) | 78 (2 h) |
| 9 |  | 72 (1 h) | 77 (3 h) |
| 10 |  ***E* > 99%** | 93 [e] (1 h) | 72 [e] (3 h) |
| 11 |  ***E* > 99%** | 75 [e] (1 h) | 76 [e] (2 h) |

[a] All reactions were conducted by using diboron **1** (1.1 mmol), triflate **2** (1.0 mmol), $PdCl_2(PPh_3)_2$ (0.03 mmol), $PPh_3$ (0.06 mmol), base (1.5 mmol), and solvent (6 ml).

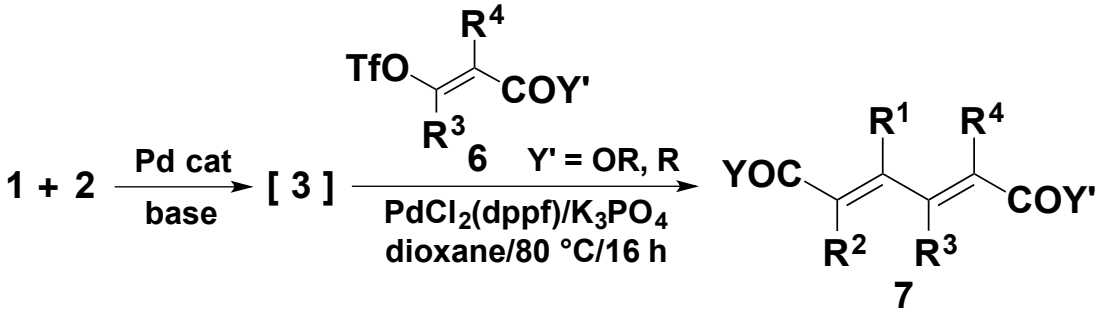
[b] GC yields based on triflates **2**.

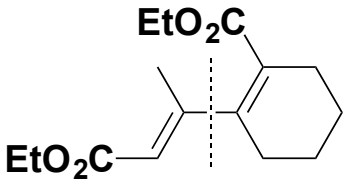
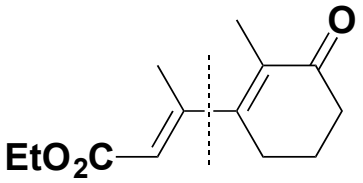
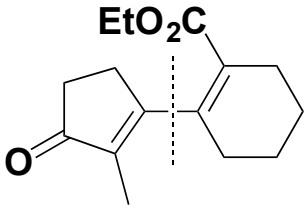
[c] Method A: KOPh/toluene/50 °C.

[d] Method B: $K_2CO_3$/dioxane/80 °C.

[e] (*Z*)-**3** were obtained with isomeric purities over 99%.

Table 3
One-pot synthesis of 1,3-dienes **7** [a]




| Entry | 1,3-Diene **7** [b] | Yield/% [c] |
|---|---|---|
| 1 |  | 76 [d] |
| 2 |  | 76 |
| 3 |  | 77 |

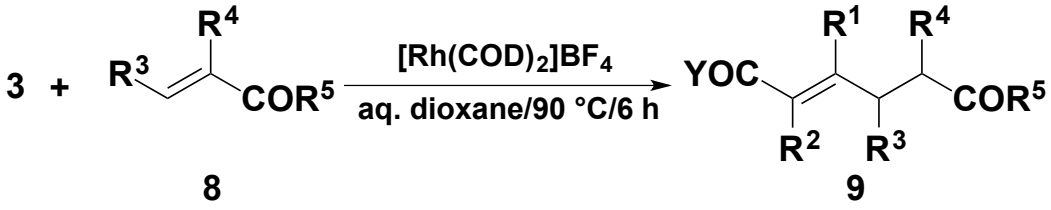
[a] To a solution of vinylboronate **3** resulted by the reaction of diboron **1** (1.1 mmol) with triflate **2** (1.1 mmol) in toluene or dioxane (4 ml) were added second triflate **6** (1.0 mmol), $PdCl_2(dppf)$ (0.03 mmol), $K_3PO_4$ (3.0 mmol), and dioxane (4 ml), and the mixture was stirred at 80 °C for 16 h.

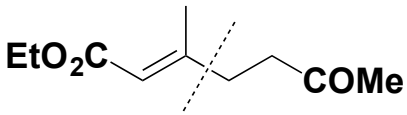
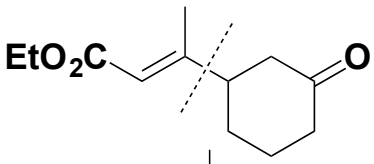
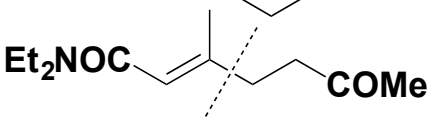
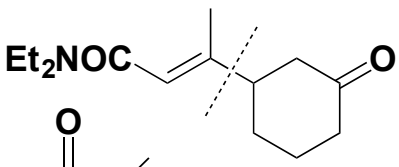
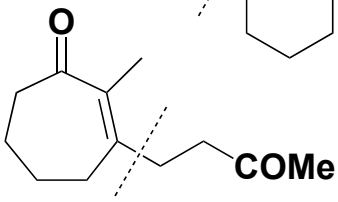
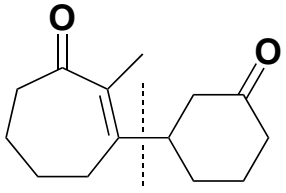
[b] Left part of dotted line comes from **2** and right part from **6**.

[c] Isolated yields based on triflates **6**.

[d] GC yield after 5 h.

Table 4
1,4-Addition of **3** to α,β-unsaturated ketones **8** [a]




| Entry | Adduct **9** [b] | Yield/% [c] |
|---|---|---|
| 1 |  | 77 |
| 2 |  | 71 |
| 3 |  | 80 |
| 4 |  | 83 |
| 5 |  | 93 |
| 6 |  | 65 [d] |

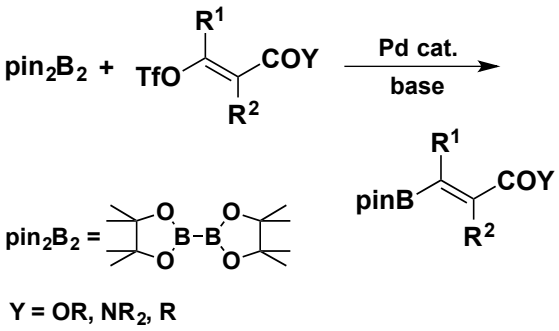
[a] A mixture of vinylboronate **3** (1.0 mmol), α,β-unsaturated ketone **8** (1.1 mmol), $[Rh(COD)_2]BF_4$ (0.03 mmol), and aqueous dioxane (dioxane:$H_2O$ = 6:1, 6 ml) was stirred at 90 °C for 6 h.

[b] Left part of dotted line comes from **3** and right part from **8**.

[c] Isolated yields based on vinylboronates **3**.

[d] 2.0 mmol of 2-cyclohexen-1-one was used.

## *Graphical Abstract (60% reduction)*




Cross-coupling reaction of bis(pinacolato)diboron with vinyl triflates β-substituted by a carbonyl group smothly proceeded in the presence of $PdCl_2(PPh_3)_2$-$2PPh_3$ (3 mol%) and KOPh in toluene or $K_2CO_3$ in dioxane to produce cyclic and acyclic β-boryl-α,β-unsaturated esters, amides, and ketones in high yields.