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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

Tatsuo Ishiyama *, Jun Takagi, Akihiro Kamon, Norio Miyaura, *

Division of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan

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Dedicated to Prof. 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

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 (pin_2B_2, pin = $Me_4C_2O_2$) **1** [13] with vinyl triflates **2** [14] to yield the corresponding β-boryl-α,β-unsaturated carbonyl compounds **3** (Scheme 1) [15].

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

* Corresponding authors. Tel./fax: +81-11-706-6562.
E-mail address: ishiyama@org-mc.eng.hokudai.ac.jp (T. Ishiyama).

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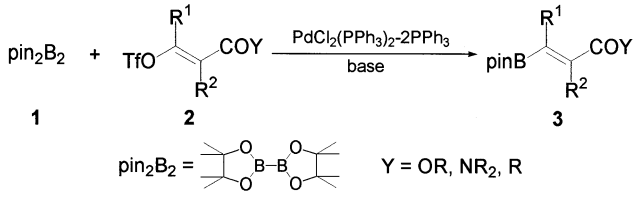


Scheme 1.

Table 1
Effects of bases and solvents [a]

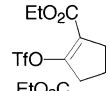
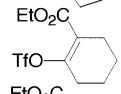
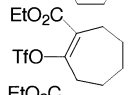
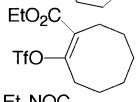
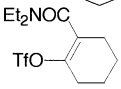
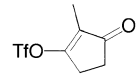
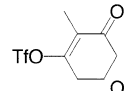
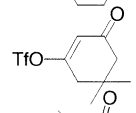
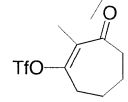
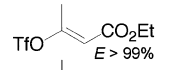
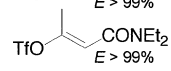
Entry	Base/solvent	Temperature (°C)	Time (h)	Yield (%) [b]
1	KOPh/toluene	50	2	9 [c]
2	2-MeC_6H_4OK/toluene	50	2	4 [d]
3	K_2CO_3/dioxane	50	16	67 [e]
4	K_3PO_4/dioxane	50	16	58 [e]
5	KOAc/dioxane	50	16	4
6	K_2CO_3/toluene	50	16	1
7	K_2CO_3/dioxane	80	5	67 [e]
8	K_2CO_3/toluene	80	24	65 [e]

[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%).

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).

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

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)
7		81 (2 h)	91 (5 h)
8		25 (2 h)	78 (2 h)
9		72 (1 h)	77 (3 h)
10		93 [e] (1 h)	72 [e] (3 h)
11		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), $PdCl_2(PPh_3)$ (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%.

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 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).

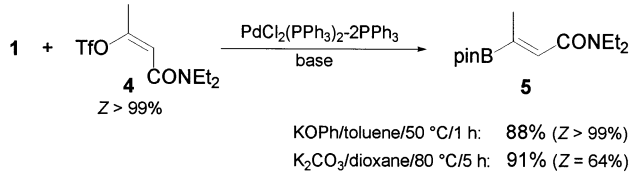
In general, *E* or Z configuration of vinyl halides or triflates can be retained completely in the cross-coupling of organoboron compounds [17]; however, the amide derivative of triflate (*Z*)-**4** unexpectedly provided the borylated product (*Z*)-**5** by Method A and a mixture of (*Z*)-**5** and (*E*)-**5** (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 ^{1}H-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].

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].

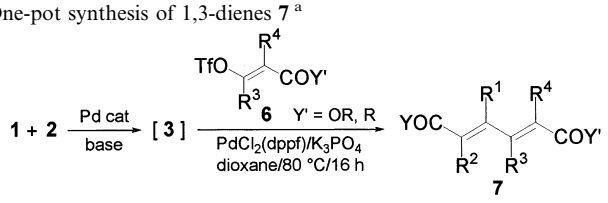
2.3. 1,4-Addition of vinylboronates to α,β-unsaturated ketones

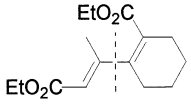
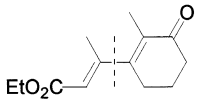
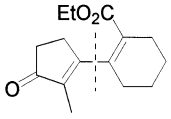
Although we examined one-pot synthesis via borylation addition sequence at first, all attempts at the reactions of in situ-generated vinylboronates **3** with α,β-unsaturated ketones **8** by using a rhodium catalyst were unsuccessful. On the other hand, it was found that isolated **3** readily underwent 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



Scheme 2.

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 yields after 5 h.

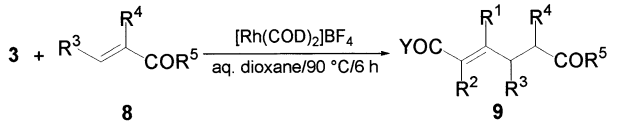
3), acyclic–cyclic (Entries 2 and 4), cyclic–acyclic (Entry 5), and cyclic–cyclic (Entry 6) combinations all produced the corresponding ε-oxo-α,β-unsaturated ester, amide, and ketone derivatives **9** in high yields. The reactions of acyclic ester and amide derivatives of **3** having *Z* stereochemistry 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% by 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].

3. Experimental

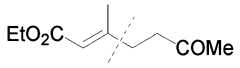
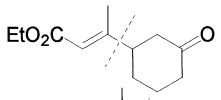
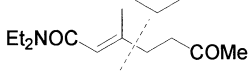
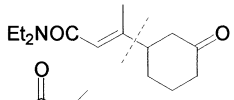
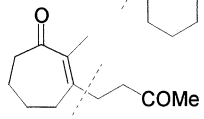
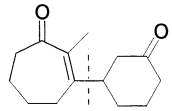
3.1. Materials and reagents

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 the other compounds were used as received.

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



8 9

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.

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

A 25-ml flask assembled with 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 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 ($CDCl_3$, 400 MHz, δ ppm): 1.28 (t, 3H, J = 7.1 Hz), 1.34 (s, 12H), 1.89–1.97 (m, 2H), 2.60 (t, 4H, J = 7.7 Hz), 4.21 (q, 2H, J = 7.2 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz, δ ppm): 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. Calc. for $C_{14}H_{23}BO_4$: 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 ($CDCl_3$, 400 MHz, δ ppm): 1.27 (t, 3H, J = 7.2 Hz), 1.33 (s, 12H), 1.54–1.66 (m, 4H), 2.22 (br s, 4H), 4.21 (q, 2H, J = 7.2 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz, δ ppm): 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. Calc. for $C_{15}H_{25}BO_4$: 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 ($CDCl_3$, 400 MHz, δ ppm): 1.29 (t, 3H, J = 7.1 Hz), 1.32 (s, 12H), 1.48–1.52 (m, 2H), 1.55–1.59 (m, 2H), 1.76–1.78 (m, 2H), 2.32–2.34 (m, 2H), 2.46–2.49 (m, 2H), 4.24 (q, 2H, J = 7.1 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz, δ ppm): 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. Calc. for $C_{16}H_{27}BO_4$: 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 ($CDCl_3$, 400 MHz, δ ppm): 1.28 (t, 3H, J = 7.2 Hz), 1.32 (s, 12H), 1.45–1.46 (m, 4H), 1.50–1.60 (m, 2H), 1.60–1.70 (m, 2H), 2.33–2.36 (m, 2H), 2.42–2.45 (m, 2H), 4.23 (q, 2H, J = 7.2 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz, δ ppm): 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. Calc. for $C_{17}H_{29}BO_4$: 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 ($CDCl_3$, 400 MHz, δ ppm): 1.23 (s, 12H), 1.25 (t, 6H, J = 6.8 Hz), 1.54–1.59 (m, 2H), 1.63–1.68 (m, 2H), 2.28–2.31 (m, 2H), 2.40–2.43 (m, 2H), 3.50–3.60 (m, 4H); ^{13}C-NMR ($CDCl_3$, 100 MHz, δ ppm): 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. Calc. for $C_{17}H_{30}BNO_3$: 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 ($CDCl_3$, 400 MHz, δ ppm): 1.33 (s, 12H), 1.94 (t, 3H, J = 2.2 Hz), 2.33–2.35 (m, 2H), 2.61–2.64 (m, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz, δ ppm): 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. Calc. for $C_{12}H_{19}BO_3$: 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 ($CDCl_3$, 400 MHz, δ ppm): 1.31 (s, 12H), 1.92–1.99 (m, 2H), 1.96 (t, 3H, $J = 2.0$ Hz), 2.38–2.44 (m, 4H); ^{13}C-NMR ($CDCl_3$, 100 MHz, δ ppm): 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. Calc. for $C_{13}H_{21}BO_3$: 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 ($CDCl_3$, 400 MHz, δ ppm): 1.02 (s, 6H), 1.30 (s, 12H), 2.25 (s, 2H), 2.32 (d, 2H, $J = 2.0$ Hz), 6.54 (s, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz, δ ppm): 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. Calc. for $C_{14}H_{23}BO_3$: 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 ($CDCl_3$, 400 MHz, δ ppm): 1.31 (s, 12H), 1.60–1.80 (m, 4H), 2.01 (s, 3H), 2.39 (t, 2H, $J = 5.6$ Hz), 2.50 (t, 2H, $J = 6.1$ Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz, δ ppm): 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. Calc. for $C_{14}H_{23}BO_3$: 250.1740.

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

^{1}H-NMR ($CDCl_3$, 400 MHz, δ ppm): 1.28 (s, 12H), 1.28 (t, 3H, $J = 7.1$ Hz), 2.17 (d, 3H, $J = 1.7$ Hz), 4.17 (q, 2H, $J = 7.2$ Hz), 6.45 (d, 1H, $J = 1.7$ 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 ($CDCl_3$, 100 MHz, δ ppm): 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. Calc. for $C_{12}H_{21}BO_4$: 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 ($CDCl_3$, 400 MHz, δ ppm): 1.15 (t, 6H, $J = 7.1$ Hz), 1.27 (s, 12H), 1.85 (d, 3H, $J = 1.7$ Hz), 3.25–3.50 (m, 4H), 6.68 (d, 1H, $J = 1.5$ 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 ($CDCl_3$, 100 MHz, δ ppm): 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. Calc. for $C_{14}H_{26}BNO_3$: 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 ($CDCl_3$, 400 MHz, δ ppm): 1.16 (t, 3H, $J = 7.3$ Hz), 1.17 (t, 3H, $J = 7.6$ Hz), 1.19 (s, 12H), 2.01 (d, 3H, $J = 1.5$ Hz), 3.37 (q, 2H, $J = 7.3$ Hz), 3.48 (q, 2H, $J = 7.2$ Hz), 6.06 (s, 1H) (the irradiation of the vinylic proton at 6.06 ppm resulted in a 3.2% enhancement of the allylic methyl signal at 2.01 ppm); ^{13}C-NMR ($CDCl_3$, 100 MHz, δ ppm): 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. Calc. for $C_{14}H_{26}BNO_3$: 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) were 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 ($CDCl_3$, 400 MHz, δ ppm): 1.22 (t, 3H, $J = 7.1$ Hz), 1.26 (t, 3H, $J = 7.2$ Hz), 1.60–1.70 (m, 4H), 2.15–2.20 (m, 2H), 2.28 (d, 3H, $J = 1.5$ Hz), 2.30–2.35 (m, 2H), 4.11 (q, 2H, $J = 7.1$ Hz), 4.14 (q, 2H, $J = 7.1$ Hz), 5.51 (d, 1H, $J = 1.2$ Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz, δ ppm): 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. Calc. for $C_{15}H_{22}O_4$: 266.1518.

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

^{1}H-NMR ($CDCl_3$, 400 MHz, δ ppm): 1.30 (t, 3H, J = 7.2 Hz), 1.73 (s, 3H), 1.98–2.06 (m, 2H), 2.29 (d, 3H, J = 1.2 Hz), 2.36–2.42 (m, 2H), 2.45 (t, 2H, J = 6.7 Hz), 4.19 (q, 2H, J = 7.2 Hz), 5.62 (d, 1H, J = 1.5 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz, δ ppm): 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. Calc. for $C_{13}H_{18}O_3$: 222.1256.

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

^{1}H-NMR ($CDCl_3$, 400 MHz, δ ppm): 1.17 (t, 3H, J = 7.2 Hz), 1.58 (t, 3H, J = 2.0 Hz), 1.68–1.74 (m, 4H), 2.12–2.22 (m, 2H), 2.36–2.50 (m, 4H), 2.60–2.70 (m, 2H), 4.07 (q, 2H, J = 7.2 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz, δ ppm): 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. Calc. for $C_{15}H_{20}O_3$: 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 ($CDCl_3$, 400 MHz, δ ppm): 1.28 (t, 3H, J = 7.1 Hz), 2.16 (d, 3H, J = 1.2 Hz), 2.18 (s, 3H), 2.42 (t, 2H, J = 7.8 Hz), 2.62 (t, 2H, J = 7.7 Hz), 4.14 (q, 2H, J = 7.2 Hz), 5.63–5.66 (m, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz, δ ppm): 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. Calc. for $C_{10}H_{16}O_3$: 184.1099.

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

^{1}H-NMR ($CDCl_3$, 400 MHz, δ ppm): 1.29 (t, 3H, J = 7.2 Hz), 1.50–1.70 (m, 2H), 1.80–1.95 (m, 1H), 2.00–2.10 (m, 1H), 2.15–2.45 (m, 5H), 2.17 (s, 3H), 4.16 (q, 2H, J = 7.1 Hz), 5.69 (d, 1H, J = 1.0 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz, δ ppm): 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. Calc. for $C_{12}H_{18}O_3$: 210.1256.

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

^{1}H-NMR ($CDCl_3$, 400 MHz, δ ppm): 1.14 (t, 6H, J = 7.2 Hz), 1.90 (s, 3H), 2.18 (s, 3H), 2.38 (t, 2H, J = 7.4 Hz), 2.63 (t, 2H, J = 7.6 Hz), 3.36 (br s, 4H), 5.80 (s, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz, δ ppm): 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. Calc. for $C_{12}H_{21}NO_2$: 211.1572.

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

^{1}H-NMR ($CDCl_3$, 400 MHz, δ ppm): 1.15 (t, 6H, J = 7.1 Hz), 1.60–1.80 (m, 2H), 1.90–2.00 (m, 1H), 1.92 (s, 3H), 2.00–2.20 (m, 1H), 2.20–2.60 (m, 5H), 3.20–3.50 (m, 4H), 5.83 (s, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz, δ ppm): 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. Calc. for $C_{14}H_{23}NO_2$: 237.1729.

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

^{1}H-NMR ($CDCl_3$, 400 MHz, δ ppm): 1.65–1.75 (m, 4H), 1.81 (s, 3H), 2.19 (s, 3H), 2.35 (t, 2H, J = 5.5 Hz), 2.45–2.60 (m, 6H); ^{13}C-NMR ($CDCl_3$, 100 MHz, δ ppm): 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. Calc. for $C_{12}H_{18}O_2$: 194.1307.

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

^{1}H-NMR ($CDCl_3$, 400 MHz, δ ppm): 1.60–1.80 (m, 8H), 1.82 (s, 3H), 2.10–2.55 (m, 8H), 3.00–3.15 (m, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz, δ ppm): 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. Calc. for $C_{14}H_{20}O_2$: 220.1463.

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