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Copper-catalyzed boroacylation of allenes to access tetrasubstituted vinylboronates†

Bing-Xue Shen,[a,b] Xiang-Ting Min,[a,b] Yan-Cheng Hu, *[a] Lei-Lei Qian,[a,b] Sa-Na Yang,[a,b] Boshun Wan [a] and Qing-An Chen [a]

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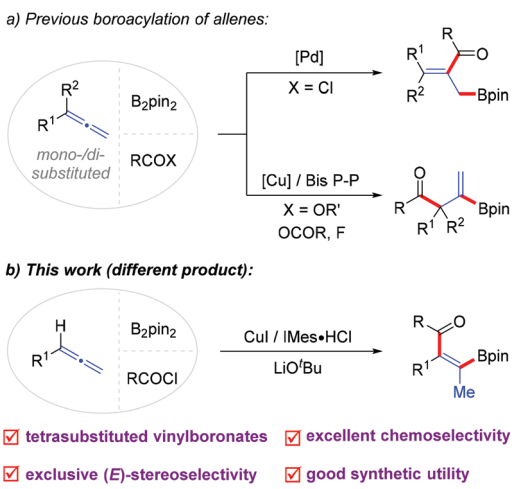
A distinct copper-catalyzed boroacylation of allenes with acyl chlorides and bis(pinacolato)diboron is developed. For aromatic acyl chlorides, 1,2-boroacylation of allenes readily takes place, leading to the formation of tetrasubstituted vinylboronates with exclusive (*E*)-stereoselectivity. In comparison, the employment of alkyl acyl chlorides as electrophiles alters the selectivity to 2,3-boroacylated products. Additionally, the product can easily undergo Suzuki–Miyaura cross-coupling to afford tetrasubstituted alkene with complete retention of the configuration.

Introduction

Organoboron compounds play an indispensable role in synthetic chemistry, as the C–B bond can easily undergo a variety of useful transformations,[1] transition-metal-catalyzed cross-couplings[2] for instance. Among all kinds of organoboron compounds, of particular interest are tetrasubstituted vinylboronates, which can serve as versatile precursors for the preparation of tetrasubstituted alkenes that are widespread in bioactive molecules.[3] Therefore, the past decade has witnessed impressive advances in the construction of tetrasubstituted vinylboronates. Most of the known methods employ alkynes as starting materials.[4] Although they have great potential in organic synthesis, it would be still highly appealing to develop efficient alternative protocols from other readily accessible precursors.

Catalytic borylation of unsaturated C–C bonds is arguably the simplest strategy for the installation of boryl group. In recent years, along with the rapid development of alkene borylations,[5] allene,[6] as a special class of alkene, has also attracted considerable attention in such transformations. For example, boroacylation that features simultaneous incorporation of boron and acyl group onto allene motif has been investigated. In 2000, Cheng and co-workers pioneered palladium-catalyzed boroacylation of allenes with acyl chlorides and B_2pin_2 for accessing acyl allylboronates (Scheme 1a, top).[7] In 2017, Fujihara and Tsuji[8] found that when using formate as acyl source, a combination of copper catalyst and bis-phosphorus ligand could switch the chemoselectivity to α-acyl vinylboronates. Later, following the same process, other electrophilic acyl sources including anhydrides and acyl fluorides have also been developed (Scheme 1a, bottom).[9] Prompted by these precedents and our continuous interests in allene chemistry,[10] we envisioned that whether it is possible to attain distinct products for boroacylation of allenes. Herein, we disclose that tetrasubstituted vinylboronates are obtained with exclusive (*E*)-stereoselectivity *via* boroacylation of mono-substituted allenes in the presence of CuI, IMes, and LiO^{t}Bu (Scheme 1b).



Scheme 1 Catalytic boroacylation of allenes.

[a]*Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China. E-mail: ychu@dicp.ac.cn*
[b]*University of Chinese Academy of Sciences, Beijing 100049, China*

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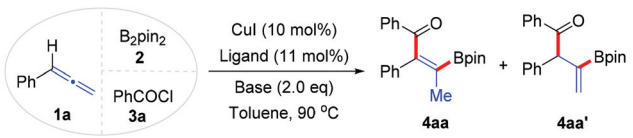
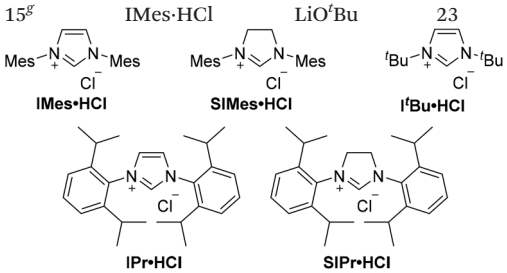
Results and discussion

Our investigation was initiated with optimization of reaction conditions using phenylallene (**1a**), bis(pinacolato)diboron (B_2pin_2, **2**), and benzoyl chloride (**3a**) as starting materials (Table 1). We first employed copper catalyst and bis-phosphorus ligands to promote the boroacylation. When the reaction was conducted in toluene at 90 °C with LiO^tBu as base, besides normal product α-acyl vinylboronate **4aa′**, an unexpected formation of tetrasubstituted vinylboronate **4aa** was also observed, albeit in poor selectivity (entries 1 and 2). The *E*-configuration of **4aa** was determined by a nuclear Overhauser enhancement (NOESY) experiment and further confirmed by the X-ray crystallography of its cross-coupling product **5** (Scheme 2a). Due to the wide application of tetrasubstituted vinylboronate in organic synthesis, additional efforts were devoted to increasing the selectivity of **4aa**. We were delighted to find that the employment of N-heterocyclic carbene (NHC) IMes as ligand resulted in **4aa** in 65% yield and no **4aa′** was detected (entry 3). In comparison, other NHC ligands including SIMes, I^tBu, IPr and SIPr all gave inferior outcome (entries 4–7). A survey of various bases revealed that LiO^tBu was the optimal base (entries 3, 8–11). The reactions in cyclohexane, tetrahydrofuran, and dioxane led to decreased yields and selectivities (entries 12–14). However, the employment of benzoyl fluoride as electrophile resulted in a low yield (entry 15). Thus, benzoyl chlorides, also featuring low cost and easy availability, were the optimal coupling partners.

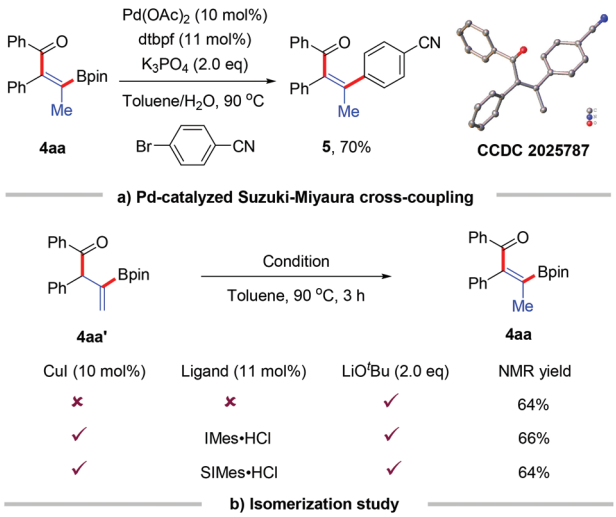
Table 1 Optimization of reaction conditions[a]



Entry	Ligand	Base	Yield of **4aa** (%)[b]	Yield of **4aa′** (%)[b]
1[c]	dppf	LiO^tBu	22	18
2[c]	dppb	LiO^tBu	18	9
3	**IMes·HCl**	**LiO^tBu**	**65 (58)**[h]	—
4	SIMes·HCl	LiO^tBu	33	6
5	I^tBu·HCl	LiO^tBu	6	21
6	IPr·HCl	LiO^tBu	18	3
7	SIPr·HCl	LiO^tBu	9	—
8	IMes·HCl	NaO^tBu	54	6
9	IMes·HCl	KO^tBu	23	9
10	IMes·HCl	NaOEt	15	6
11	IMes·HCl	KOEt	25	6
12[d]	IMes·HCl	LiO^tBu	41	—
13[e]	IMes·HCl	LiO^tBu	22	33
14[f]	IMes·HCl	LiO^tBu	18	27
15[g]	IMes·HCl	LiO^tBu	23	6



[a] Reaction conditions: **1a** (0.1 mmol), **3a** (2.0 eq.), B_2pin_2 (1.1 eq.), CuI (10 mol%), ligand (11 mol%), base (2.0 eq.), toluene (0.1 M), 90 °C, 12 h. [b] Yield determined by ^1H NMR analysis using mesitylene as an internal standard. [c] $Cu(OAc)_2$ (10 mol%). [d] CyH. [e] THF. [f] Dioxane. [g] Benzoyl fluoride was used. [h] Isolated yield was given.

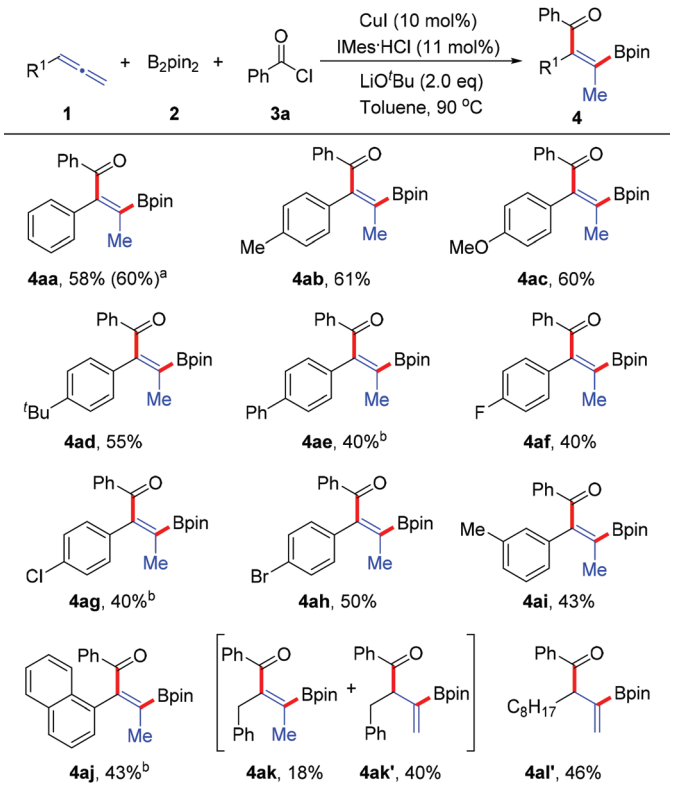


Scheme 2 Synthetic transformation and isomerization study.

With the optimized conditions in hand, we then examined the scope and generality of the protocol. A variety of mono-substituted allenes **1** were first explored (Table 2). The boroacylation of phenylallene **1a** proceeded smoothly to afford the desired product **4aa** in 58% isolated yield. Notably, the reaction could be easily scaled-up and the yield of **4aa** still remained comparable. The electronic and steric factors of the substituents on the phenyl ring had no significant impact on the transformation. For example, electron-donating arylallenes bearing –Me, –OMe and –^{t}Bu furnished the desired vinylboronates in moderate yields (**4ab–4ad**, **4ai**). The electron-withdrawing groups including phenyl and halides (–F, –Cl, –Br) were also well tolerated (**4ae–4ah**), giving the corresponding products in acceptable yields. 1-Naphthyl substituted allene was a suitable substrate as well (**4aj**). Surprisingly, in the case of benzylallene, α-benzyl vinylboronate **4ak′** was observed as a main product, while the target tetrasubstituted vinylboronate **4ak** was furnished in only 18% yield. The boroacylation of octylallene also delivered α-benzoyl vinylboronate **4al′** in 46% yield and no desired product could be isolated. These results suggest that for arylallenes, the tendency to form a π–π conjugated molecule is presumably also a driving force.

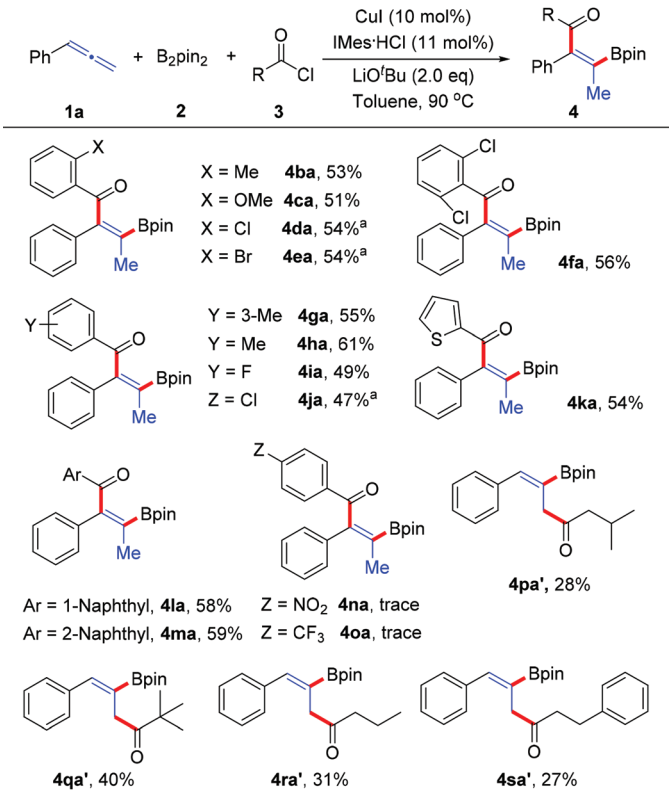
The scope with respect to acyl chlorides **3** was subsequently scrutinized (Table 3). *ortho*-Substituted benzoyl chlorides bearing –Me, –OMe and halides (–Cl, –Br) could be efficiently converted to tetrasubstituted vinylboronates **4ba–4ea**. 2,6-Dichloro benzoyl chloride also worked well, giving the desired product in 56% yield (**4fa**). The *meta*- and *para*-substitutents on benzoyl chloride were all compatible with the process, leading

Table 2 Scope with respect to allenes



Conditions: **1** (0.20 mmol), B_2pin_2 (0.22 mmol), **3a** (0.40 mmol), CuI (10 mol%), IMes·HCl (11 moI%), LiO^{t}Bu (0.40 mmol), toluene (1.5 mL), 90 °C, 16 h. Isolated yields were given. [a] Isolated yield of scale-up reaction (1.0 mmol). [b] Accompanied by a small amount of inseparable B_2pin_2, the yield of the product has been adjusted accordingly.

Table 3 Scope with respect to acyl chlorides

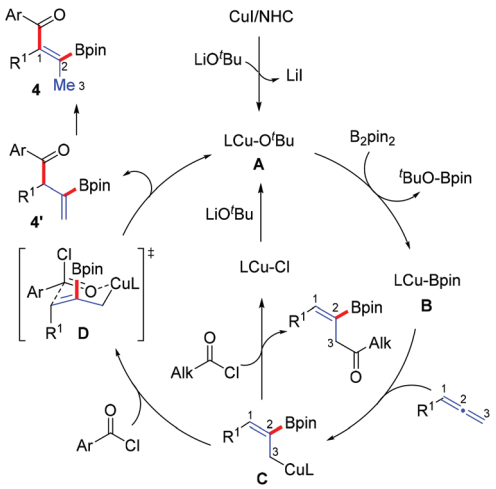


Conditions: **1a** (0.20 mmol), B_2pin_2 (0.22 mmol), **3** (0.40 mmol), CuI (10 mol%), IMes·HCl (11 moI%), LiO^{t}Bu (0.40 mmol), toluene (1.5 mL), 90 °C, 16 h. Isolated yields were given. [a] Accompanied by a small amount of inseparable B_2pin_2, the yield of the product has been adjusted accordingly.

to the formation of products in 45% to 61% yields (**4ga–4ja**). Gratifyingly, 2-thienoyl chloride could participate in the transformation as well (**4ka**). Besides, boroacylation of phenylallene **1a** with 1- and 2-naphthoyl chlorides delivered the corresponding products in 58% (**4la**) and 59% yield (**4ma**), respectively. Unfortunately, when the strong electron-withdrawing benzoyl chlorides (–NO_2, –CF_3) were subjected to the optimized conditions, no desired products were obtained (**4na**, **4oa**). Surprisingly, in the cases of aliphatic acyl chlorides, 2,3-boroacylations of phenylallene turned out to be predominant, resulting in the formation of trisubstituted vinylboronates (**4pa′–4sa′**) in 27–40% yields. In most cases, phenylallene could not be totally consumed, thus leading to the products in moderate yields.

In order to determine the geometry of vinylboronate **4aa** intuitively, its synthetic transformation was further investigated. The Suzuki–Miyaura cross-coupling of **4aa** with 4-cyanobromobenzene worked smoothly to produce tetrasubstitued alkene **5** in 70% yield. Its geometry was determined as *E*-configuration according to the X-ray crystallography (Scheme 2a). To gain further insight into the mechanism, some control experiments were conducted (Scheme 2b). It is found that in the presence of sole LiO^{t}Bu, α-acyl vinylboronate **4aa′** could be readily transformed into tetra-substituted vinylboronate **4aa** at 90 °C.[11] The moderate isomerization yield was ascribed to the slow degradation of **4aa** at high temperature. Besides, a combination of CuI, NHC ligand, and LiO^{t}Bu could not increase the yield. This result indicates that Cu(I)/NHC system is just responsible for the formation of **4aa′** and base LiO^{t}Bu can promote its isomerization at elevated temperature. However, the ligands exerted an influence on the ratio of **4aa′** and **4aa** (Table 1, entries 3 *versus* 4), likely because the production of **4aa′** is a rate-determining step and the ligands can affect the formation rate. It is noteworthy that compared with the boron chemical shift of **4aa′** (29.8 ppm), that of compound **4aa** moves upper field (18.7 ppm), revealing that there exists a stabilizing dative ($n_O \rightarrow p$) interaction between the carbonyl oxygen atom and boron atom.[12]

Based on our isomerization study and previous reports,[9a,c] a plausible mechanism for this boroacylation is proposed (Scheme 3). Initially, the active copper species **A** is *in situ* produced in the presence of CuI/NHC and LiO^{t}Bu. A subsequent σ-metathesis step between **A** and B_2pin_2 generates the Cu–B species **B**. A key regioselective insertion of **B** into allene can lead to the formation of the allyl copper intermediate **C**. Then, complex **C** reacts with electrophilic aromatic acyl chloride to provide α-acyl vinylboronate **4′** *via* a six-membered ring tran-



Scheme 3 Proposed mechanism.

sition state **D** with regeneration of the species **A**. A final base-promoted isomerization of **4′** furnishes the desired tetrasubstituted vinylboronate **4**. In comparison, aliphatic acyl chloride preferentially undergoes oxidative addition with allyl copper intermediate **C** and subsequent reductive elimination delivers 2,3-boroacylated products.[4k,5m]

Conclusion

We have described a distinct copper-catalyzed boroacylation of mono-substituted allenes. For aromatic acyl chlorides, a variety of tetrasubstituted vinylboronates were prepared *via* 1,2-boroacylation. In comparison, when alkyl acyl chlorides were used as electrophiles, 2,3-boroacylation turned out to be predominant. The protocol features excellent chemoselectivity, exclusive stereoselectivity and good tolerance to a wide range of functionalities. Moreover, the product can easily undergo Suzuki–Miyaura cross-coupling to deliver tetrasubstituted alkene with retaining its configuration. Further investigations for diverting the selectivity of allene boroacylation are ongoing in our laboratory.

Experimental

Typical procedure for Cu-catalyzed boroacylation of allenes

In the N_2-filled glove box, a sealed tube was charged with B_2pin_2 (**2**, 0.22 mmol, 1.1 eq.), LiO^{t}Bu (0.4 mmol, 2.0 eq.), CuI (0.02 mmol, 10 mol%) and IMes·HCl (0.022 mmol, 11 mol%) in toluene (1.5 mL). The mixture was allowed to stir at room temperature for 15 min. Then allenes (**1**, 0.2 mmol) and acyl chlorides (**3**, 0.4 mmol, 2.0 eq.) were added in sequence. The reaction tube was sealed with a Teflon screw cap and removed from the N_2-filled glove box. Then, the reaction mixture was stirred at 90 °C for 12 h. After cooling to room temperature, the reaction mixture was directly purified by flash column chromatography on silica gel using petroleum ether (PE) and ethyl acetate (EA) to obtain the desired product **4**.

It should be mentioned that R_f value of some products and B_2pin_2 was very close and B_2pin_2 also has trailing phenomenon during the flash column chromatography, thus making it difficult to separate them completely. In these cases, the given yields have been adjusted based on the ratio of products and B_2pin_2 residue in ^{1}H NMR. Unless otherwise stated, the ratio of products and B_2pin_2 residue in ^{1}H NMR was >20/1. In the ^{13}C NMR, the carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

(*E*)-1,2-Diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) but-2-en-1-one (4aa). 40.2 mg, 58% yield, colorless oil, R_f = 0.45 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, J = 8.4, 1.4 Hz, 2H), 7.53–7.47 (m, 1H), 7.38–7.32 (m, 3H), 7.28–7.23 (m, 2H), 7.10 (dd, J = 7.5, 2.0 Hz, 2H), 2.04 (s, 3H), 1.36 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 142.9, 135.4, 134.2, 133.2, 131.6, 129.6, 128.6, 128.1, 127.7, 81.7, 25.2, 17.8; ^{11}B NMR (128 MHz, $CDCl_3$) δ 18.7. HRMS calculated for $C_{22}H_{26}BO_3$ $[M + H]^+$ 349.1970, found 349.1979.

(*E*)-1-Phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(*p*-tolyl)but-2-en-1-one (4ab). 44.1 mg, 61% yield, colorless oil, R_f = 0.35 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, J = 8.4, 1.2 Hz, 2H), 7.52–7.46 (m, 1H), 7.30–7.24 (m, 2H), 7.15 (d, J = 7.8 Hz, 2H), 6.98 (d, J = 8.0 Hz, 2H), 2.37 (s, 3H), 2.04 (s, 3H), 1.35 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 142.9, 137.4, 134.1, 133.3, 132.3, 131.6, 129.4, 129.3, 128.1, 81.7, 25.2, 21.2, 17.8; ^{11}B NMR (128 MHz, $CDCl_3$) δ 19.1. HRMS calculated for $C_{23}H_{28}BO_3$ $[M + H]^+$ 363.2126, found 363.2136.

(*E*)-2-(4-Methoxyphenyl)-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-one (4ac). 45.2 mg, 60% yield, colorless oil, R_f = 0.3 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.9 Hz, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.31–7.25 (m, 2H), 7.01 (d, J = 8.5 Hz, 2H), 6.88 (d, J = 8.5 Hz, 2H), 3.82 (s, 3H), 2.04 (s, 3H), 1.35 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 159.0, 142.6, 134.1, 133.3, 131.5, 130.7, 128.1, 127.4, 114.0, 81.7, 55.2, 25.2, 17.8; ^{11}B NMR (128 MHz, $CDCl_3$) δ 18.7. HRMS calculated for $C_{23}H_{28}BO_4$ $[M + H]^+$ 379.2075, found 379.2084.

(*E*)-2-(4-(*tert*-Butyl)phenyl)-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-one (4ad). 44.3 mg, 55% yield, colorless oil, R_f = 0.45 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 7.4 Hz, 2H), 7.49 (t, J = 7.5 Hz, 1H), 7.36 (d, J = 8.3 Hz, 2H), 7.29–7.22 (m, 2H), 7.02 (d, J = 8.3 Hz, 2H), 2.05 (s, 3H), 1.34 (s, 12H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 150.6, 143.1, 134.1, 133.4, 132.2, 131.5, 129.2, 128.0, 125.4, 81.7, 34.6, 31.3, 25.2, 17.8; ^{11}B NMR (128 MHz, $CDCl_3$) δ 18.9. HRMS calculated for $C_{26}H_{34}BO_3$ $[M + H]^+$ 405.2596, found 405.2589.

(*E*)-2-([1,1′-Biphenyl]-4-yl)-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-one (4ae). With a small amount of inseparable B_2pin_2 (**4ae**/**2** = 12/1), 33.8 mg, 40% yield, colorless oil, R_f = 0.45 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 7.8 Hz, 2H), 7.61 (t, J = 8.7 Hz, 4H), 7.50 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.3 Hz, 1H), 7.29 (d, J = 7.8 Hz, 2H), 7.17 (d, J = 8.1 Hz, 2H), 2.09 (s, 3H), 1.36 (s, 12H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 142.7, 140.3, 134.3, 134.2, 133.2, 131.5, 130.0, 128.8, 128.1, 127.5, 127.2, 126.9, 81.8, 25.2, 17.9; ^{11}B NMR (128 MHz, $CDCl_3$) δ 19.4. HRMS calculated for $C_{28}H_{30}BO_3$ $[M + H]^+$ 425.2283, found 425.2305.

(*E*)-2-(4-Fluorophenyl)-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-one (4af). 29.3 mg, 40% yield, pale yellow oil, R_f = 0.45 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.0 Hz, 2H), 7.51 (t, J = 7.4 Hz, 1H), 7.3 (t, J = 7.9, 2H), 7.13–7.01 (m, 4H), 2.03 (s, 3H), 1.35 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 162.2 (d, J = 248.2), 142.0, 134.2, 133.2, 131.4, 131.3, 131.2 (d, J = 8.0 Hz), 128.2, 115.7 (d, J = 21.5), 81.9, 25.2, 17.8; ^{11}B NMR (128 MHz, $CDCl_3$) δ 19.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ −113.8. HRMS calculated for $C_{22}H_{25}BFO_3$ $[M + H]^+$ 367.1875, found 367.1880.

(*E*)-2-(4-Chlorophenyl)-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-one (4ag). With a small amount of inseparable B_2pin_2 (**4ag**/**2** = 8/1), 30.0 mg, 40% yield, colorless oil, R_f = 0.4 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.6 Hz, 2H), 7.38–7.33 (m, 3H), 7.24 (d, J = 8.6 Hz, 2H), 7.09 (dd, J = 7.4, 1.7 Hz, 2H), 2.03 (s, 3H), 1.35 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 143.2, 140.7, 135.2, 132.7, 131.9, 129.4, 128.7, 128.5, 127.8, 82.0, 25.1, 17.9; ^{11}B NMR (128 MHz, $CDCl_3$) δ 20.1. HRMS calculated for $C_{22}H_{25}BClO_3$ $[M + H]^+$ 383.1580, found 383.1577.

(*E*)-2-(4-Bromophenyl)-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-one (4ah). 42.5 mg, 50% yield, colorless oil, R_f = 0.4 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.6 Hz, 2H), 7.55–7.46 (m, 3H), 7.30 (t, J = 7.8 Hz, 2H), 6.98 (d, J = 8.3 Hz, 2H), 2.03 (s, 3H), 1.34 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 141.9, 134.3, 134.2, 133.2, 131.8, 131.3, 131.2, 128.2, 121.9, 81.9, 25.1, 17.8; ^{11}B NMR (128 MHz, $CDCl_3$) δ 19.6. HRMS calculated for $C_{22}H_{25}BBrO_3$ $[M + H]^+$ 427.1075, found 427.1077.

(*E*)-1-Phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(*m*-tolyl)but-2-en-1-one (4ai). 31.2 mg, 43% yield, colorless oil, R_f = 0.42 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72–7.61 (m, 2H), 7.53–7.46 (m, 1H), 7.30–7.20 (m, 3H), 7.13 (d, J = 7.6 Hz, 1H), 6.97–6.84 (m, 2H), 2.31 (s, 3H), 2.03 (s, 3H), 1.35 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 143.1, 138.2, 135.3, 134.2, 133.2, 131.6, 130.0, 128.4, 128.0, 126.6, 81.7, 25.2, 21.4, 17.8; ^{11}B NMR (128 MHz, $CDCl_3$) δ 19.1. HRMS calculated for $C_{23}H_{28}BO_3$ $[M + H]^+$ 363.2126, found 363.2123.

(*E*)-2-(Naphthalen-1-yl)-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-one (4aj). With a small amount of inseparable B_2pin_2 (**4aj**/**2** = 12/1), 33.7 mg, 43% yield, colorless oil, R_f = 0.4 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (t, J = 7.2 Hz, 2H), 7.75 (d, J = 8.4 Hz, 1H), 7.54 (d, J = 8.1 Hz, 2H), 7.50–7.37 (m, 4H), 7.22 (d, J = 7.0 Hz, 1H), 7.12 (t, J = 7.8 Hz, 2H), 1.91 (s, 3H), 1.43 (d, J = 2.3 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 140.1, 134.7, 133.7, 133.0, 132.5, 131.6, 131.5, 128.5, 128.4, 128.2, 127.7, 126.6, 126.2, 125.7, 125.6, 81.6, 25.3, 18.1; ^{11}B NMR (128 MHz, $CDCl_3$) δ 17.7. HRMS calculated for $C_{26}H_{28}BO_3$ $[M + H]^+$ 399.2126, found 399.2118.

(*E*)-2-Benzyl-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-one (4ak). 13.0 mg, 18% yield, colorless oil, R_f = 0.4 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 7.8 Hz, 2H), 7.48 (d, J = 7.5 Hz, 1H), 7.33 (t, J = 7.7 Hz, 2H), 7.23 (t, J = 7.4 Hz, 2H), 7.19–7.10 (m, 3H), 3.87 (s, 2H), 2.10 (s, 3H), 1.21 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 142.0, 137.9, 135.2, 133.2, 129.7, 128.6, 128.3, 128.2, 126.2, 82.2, 33.8, 24.9, 17.3; ^{11}B NMR (128 MHz, $CDCl_3$) δ 22.4. HRMS calculated for $C_{23}H_{28}BO_3$ $[M + H]^+$ 363.2126, found 363.2131.

2-Benzyl-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-one (4ak′). 28.9 mg, 40% yield, colorless oil, R_f = 0.8 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.6 Hz, 2H), 7.47 (t, J = 7.3 Hz, 1H), 7.37 (t, J = 7.6 Hz, 2H), 7.26–7.20(m, 4H), 7.17–7.10 (m, 1H), 5.94 (d, J = 1.9 Hz, 1H), 5.70 (s, 1H), 4.59 (t, J = 7.2 Hz, 1H), 3.29 (dd, J = 13.6, 6.8 Hz, 1H), 2.93 (dd, J = 13.6, 7.7 Hz, 1H), 1.20 (s, 6H), 1.17 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 140.1, 136.6, 132.5, 132.0, 129.4, 128.7, 128.2, 128.1, 125.8, 83.8, 51.8, 38.7, 24.8, 24.5; ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.6. HRMS calculated for $C_{23}H_{28}BO_3$ $[M + H]^+$ 363.2126, found 363.2130.

1-Phenyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl) decan-1-one (4al′). 35.3 mg, 46% yield, colorless oil, R_f = 0.7 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.4 Hz, 2H), 7.50 (t, J = 7.3 Hz, 1H), 7.40 (t, J = 7.6 Hz, 2H), 5.91 (d, J = 2.3 Hz, 1H), 5.67 (d, J = 1.8 Hz, 1H), 4.24 (t, J = 7.0 Hz, 1H), 1.32–1.22 (m, 26H), 0.87 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 137.0, 132.4, 131.4, 128.6, 128.3, 83.8, 50.1, 32.8, 31.9, 29.7, 29.5, 29.3, 27.7, 24.8, 24.6, 22.6, 14.1; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.1. HRMS calculated for $C_{24}H_{38}BO_3$ $[M + H]^+$ 385.2909, found 385.2917.

(*E*)-1-Phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(*o*-tolyl)but-2-en-1-one (4ba). 38.5 mg, 53% yield, colorless oil, R_f = 0.5 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.18 (m, 5H), 7.03 (d, J = 7.7 Hz, 1H), 6.99–6.86 (m, 3H), 2.45 (s, 3H), 2.09 (s, 3H), 1.37 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.4, 143.5, 139.4, 134.8, 133.3, 132.0, 131.3, 130.6, 129.5, 128.2, 127.3, 124.7, 81.8, 25.2, 20.6, 18.0; ^{11}B NMR (128 MHz, $CDCl_3$) δ 19.4. HRMS calculated for $C_{23}H_{28}BO_3$ $[M + H]^+$ 363.2126, found 363.2130.

(*E*)-1-(2-Methoxyphenyl)-2-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-one (4ca). 38.4 mg, 51% yield, colorless oil, R_f = 0.3 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, J = 7.6, 1.5 Hz, 1H), 7.42–7.36 (m, 1H), 7.22–7.14 (m, 3H), 6.98–6.90 (m, 3H), 6.60 (d, J = 8.4 Hz, 1H), 3.15 (s, 3H), 2.07 (s, 3H), 1.38 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.3, 158.0, 143.7, 135.2, 134.2, 130.7, 128.8, 127.4, 126.7, 124.5, 120.3, 110.9, 81.7, 54.4, 25.2, 17.7; ^{11}B NMR (128 MHz, $CDCl_3$) δ 19.7. HRMS calculated for $C_{23}H_{28}BO_4$ $[M + H]^+$ 379.2075, found 379.2081.

(*E*)-1-(2-Chlorophenyl)-2-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-one (4da). With a small amount of inseparable B_2pin_2 (**4da**/**2** = 12/1), 41.2 mg, 54% yield, colorless oil, R_f = 0.4 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.15 (m, 6H), 7.13–7.05 (m, 1H), 7.00 (d, J = 7.7 Hz, 2H), 2.01 (s, 3H), 1.41 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 144.5, 136.5, 134.8, 131.5, 131.3, 129.9, 129.7, 129.3, 127.9, 127.3, 126.0, 82.9, 24.9, 18.4; ^{11}B NMR (128 MHz, $CDCl_3$) δ 25.6. HRMS calculated for $C_{22}H_{25}BClO_3$ $[M + H]^+$ 383.1580, found 383.1580.

(*E*)-1-(2-Bromophenyl)-2-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-one (4ea). With a small amount of inseparable B_2pin_2 (**4ea**/**2** = 13/1), 45.9 mg, 54% yield, colorless oil, R_f = 0.4 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.39 (m, 1H), 7.22–7.06 (m, 6H), 7.04–6.97 (m, 2H), 1.99 (s, 3H), 1.41 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 144.4, 138.8, 134.9, 133.0, 131.1, 129.7, 129.0, 127.9, 127.3, 126.4, 119.5, 83.0, 25.0, 18.4; ^{11}B NMR (128 MHz, $CDCl_3$) δ 26.3. HRMS calculated for $C_{22}H_{25}BBrO_3$ $[M + H]^+$ 427.1075, found 427.1086.

(*E*)-1-(2,6-Dichlorophenyl)-2-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-one (4fa). 46.8 mg, 56% yield, colorless oil, R_f = 0.4 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20–7.13 (m, 5H), 7.10–7.02 (m, 3H), 1.88 (s, 3H), 1.43 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 144.9, 137.7, 135.0, 131.1, 130.3, 129.1, 127.8, 127.5, 127.4, 83.5, 24.8, 18.7; ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.9. HRMS calculated for $C_{22}H_{24}BCl_2O_4$ $[M + H]^+$ 417.1190, found 417.1189.

(*E*)-2-Phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(*m*-tolyl)but-2-en-1-one (4ga). 40.2 mg, 55% yield, colorless oil, R_f = 0.4 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.37–7.29 (m, 5H), 7.13–7.07 (m, 3H), 2.23 (s, 3H), 2.05 (s, 3H), 1.36 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 142.7, 137.9, 135.4, 135.1, 132.8, 132.1, 129.5, 129.0, 128.5, 127.8, 127.6, 81.6, 25.2, 21.1, 17.7; ^{11}B NMR (128 MHz, $CDCl_3$) δ 18.0. HRMS calculated for $C_{23}H_{28}BO_3$ $[M + H]^+$ 363.2126, found 363.2128.

(*E*)-2-Phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(*p*-tolyl)but-2-en-1-one (4ha). 44.0 mg, 61% yield, colorless oil, R_f = 0.4 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.1 Hz, 2H), 7.39–7.32 (m, 3H), 7.12–7.04 (m, 4H), 2.33 (s, 3H), 2.04 (s, 3H), 1.37 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 146.1, 142.2, 135.4, 132.1, 129.8, 129.5, 128.9, 128.6, 127.6, 81.3, 25.3, 21.8, 17.6; ^{11}B NMR (128 MHz, $CDCl_3$) δ 17.2. HRMS calculated for $C_{23}H_{28}BO_3$ $[M + H]^+$ 363.2126, found 363.2136.

(*E*)-1-(4-Fluorophenyl)-2-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-one (4ia). 35.8 mg, 49% yield, yellow oil, R_f = 0.4 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73–7.62 (m, 2H), 7.40–7.30 (m, 3H), 7.13–7.07 (m, 2H), 6.98–6.90 (m, 2H), 2.03 (s, 3H), 1.35 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 166.24 (d, J = 258.4 Hz), 142.8, 135.3, 134.5 (d, J = 9.7 Hz), 134.4, 129.4, 128.7, 127.8, 115.46 (d, J = 21.9 Hz), 81.8, 25.1, 17.8; ^{11}B NMR (128 MHz, $CDCl_3$) δ 19.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −101.7. HRMS calculated for $C_{22}H_{25}BFO_3$ $[M + H]^+$ 367.1875, found 367.1885.

(*E*)-1-(4-Chlorophenyl)-2-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-one (4ja). With a small amount of inseparable B_2pin_2 (**4ja**/**2** = 8/1), 35.8 mg, 47% yield, yellow oil, R_f = 0.4 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.6 Hz, 2H), 7.39–7.33 (m, 3H), 7.24 (d, J = 8.6 Hz, 2H), 7.12–7.07 (m, 2H), 2.02 (s, 3H), 1.35 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 143.2, 140.7, 135.3, 132.7, 132.0, 129.5, 128.7, 128.5, 127.9, 82.0, 25.1, 17.9; ^{11}B NMR (128 MHz, $CDCl_3$) δ 20.6. HRMS calculated for $C_{22}H_{25}BClO_3$ $[M + H]^+$ 383.1580, found 383.1569.

(*E*)-2-Phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(thiophen-2-yl)but-2-en-1-one (4ka). 38.2 mg, 54% yield, colorless oil, R_f = 0.4 (PE/EA = 5/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 4.8 Hz, 1H), 7.46–7.40 (m, 3H), 7.34 (d, J = 3.9 Hz, 1H), 7.25–7.15 (m, 2H), 6.98 (t, J = 4.5 Hz, 1H), 1.98 (s, 3H), 1.37 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.4, 141.1, 139.5, 139.4, 137.0, 134.7, 130.1, 128.8, 128.6, 128.3, 81.2, 25.2, 17.5; ^{11}B NMR (128 MHz, $CDCl_3$) δ 17.0. HRMS calculated for $C_{20}H_{24}BSO_3$ $[M + H]^+$ 355.1534, found 355.1538.

(*E*)-1-(Naphthalen-1-yl)-2-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-one (4la). 46.1 mg, 58% yield, colorless oil, R_f = 0.45 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 8.5 Hz, 1H), 7.87 (d, J = 8.2 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.59–7.54 (m, 1H), 7.53–7.48 (m, 1H), 7.32 (d, J = 7.2 Hz, 1H), 7.21–7.14 (m, 4H), 7.02–6.95 (m, 2H), 2.13 (s, 3H), 1.39 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.3, 144.3, 135.0, 133.5, 133.2, 131.3, 130.9, 130.6, 129.5, 128.4, 128.2, 127.8, 127.3, 126.5, 125.9, 123.7, 82.0, 25.2, 18.2; ^{11}B NMR (128 MHz, $CDCl_3$) δ 20.6. HRMS calculated for $C_{26}H_{28}BO_3$ $[M + H]^+$ 399.2126, found 399.2126.

(*E*)-1-(Naphthalen-2-yl)-2-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-one (4ma). 47.6 mg, 59% yield, colorless oil, R_f = 0.45 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07–8.05 (m, 1H), 7.80–7.75 (m, 2H), 7.72 (d, J = 8.7 Hz, 1H), 7.61–7.55 (m, 2H), 7.45 (t, J = 7.5 Hz, 1H), 7.41–7.34 (m, 3H), 7.18–7.14 (m, 2H), 2.09 (s, 3H), 1.38 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 142.8, 135.9, 135.6, 135.1, 131.8, 130.2, 130.0, 129.7, 129.4, 128.7, 127.9, 127.8, 127.6, 126.7, 126.2, 81.7, 25.3, 17.8; ^{11}B NMR (128 MHz, $CDCl_3$) δ 18.7. HRMS calculated for $C_{26}H_{28}BO_3$ $[M + H]^+$ 399.2126, found 399.2131.

6-Methyl-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-1-en-4-one (4pa′). 18.2 mg, 28% yield, colorless oil, R_f = 0.5 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.39 (m, 1H), 7.35–7.29 (m, 2H), 7.27–7.23 (m, 3H), 3.46 (s, 2H), 2.33 (d, J = 7.0 Hz, 2H), 2.20–2.08 (m, 1H), 1.29 (s, 12H), 0.91 (d, J = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.4, 144.1, 137.2, 128.7, 128.2, 127.5, 83.7, 51.6, 44.3, 24.7, 24.6, 22.6; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.3. HRMS calculated for $C_{20}H_{30}BO_3$ $[M + H]^+$ 329.2283, found 329.2295.

(*Z*)-2,2-Dimethyl-6-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-en-3-one (4qa′). 26.2 mg, 40% yield, colorless oil, R_f = 0.55 (PE/EA = 9/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.35–7.28 (m, 2H), 7.26–7.22 (m, 1H), 7.21–7.18 (m, 2H), 3.57 (s, 2H), 1.28 (s, 12H), 1.15 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.5, 143.3, 137.5, 128.5, 128.1, 127.2, 83.5, 44.2, 38.0, 26.7, 24.8; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.5. HRMS calculated for $C_{20}H_{30}BO_3$ $[M + H]^+$ 329.2283, found 329.2276.

(*Z*)-1-Phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-1-en-4-one (4ra′). 19.2 mg, 31% yield, colorless oil, R_f = 0.5 (PE/EA = 9/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.32 (m, 2H), 7.26–7.22 (m, 3H), 3.47 (s, 2H), 2.43 (t, J = 7.3 Hz, 2H), 1.64–1.58 (m, 2H), 1.30 (s, 12H), 0.91 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 144.2, 137.2, 128.7, 128.2, 127.5, 83.7, 44.6, 43.8, 24.7, 17.4, 13.7; ^{11}B NMR (128 MHz,

$CDCl_3$) δ 30.3. HRMS calculated for $C_{19}H_{28}BO_3$ $[M + H]^+$ 315.2126, found 315.2132.

(*Z*)-1,6-Diphenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) hex-5-en-3-one (4sa′). 24.8 mg, 27% yield, colorless oil, R_f = 0.6 (PE/EA = 9/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.32–7.28 (m, 2H), 7.24–7.14 (m, 8H), 3.47 (s, 2H), 2.90 (t, J = 7.5 Hz, 2H), 2.79 (t, J = 7.4 Hz, 2H), 1.28 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.7, 144.5, 141.2, 137.0, 128.7, 128.4, 128.3, 128.2, 127.6, 126.0, 83.7, 44.1, 43.9, 29.7, 24.7; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.5. HRMS calculated for $C_{24}H_{30}BO_3$ $[M + H]^+$ 377.2283, found 377.2288.

Procedure for the transformation of product 4aa

In a N_2-filled glove box, a sealed tube was charged with **4aa** (0.24 mmol), 4-CN-PhBr (1.3 eq.), $Pd(OAc)_2$ (10 mol%), dtbpf (11 mol%), K_3PO_4 (2.0 eq.) and H_2O (7 eq.) in toluene (2.5 mL). The reaction tube was sealed with a Teflon screw cap, removed from the glove box. Then, the reaction mixture was stirred at 90 °C for 18 h. After cooling to room temperature, the reaction mixture was directly purified by column chromatography on silica gel using PE/EA to afford the corresponding product **5**.

(*Z*)-4-(4-Oxo-3,4-diphenylbut-2-en-2-yl)benzonitrile (5). 53.8 mg, 70% yield, white solid, m.p. 128–129 °C, R_f = 0.45 (PE/EA = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.4 Hz, 2H), 7.44–7.25 (m, 12H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 146.8, 140.8, 137.7, 136.7, 136.6, 133.1, 131.9, 129.4, 129.0, 128.7, 128.6, 128.3, 127.9, 118.5, 111.1, 21.3. HRMS calculated for $C_{23}H_{18}NO$ $[M + H]^+$ 324.1383, found 324.1390.

Procedure for the synthesis of 4aa′[9a]

In the N_2-filled glove box, a sealed tube was charged with B_2pin_2 (**2**, 0.6 mmol, 1.2 eq.), $Cu(OAc)_2$ (5 mol%), dppf (6 mol%), and $NaOSiEt_3$ (0.6 mL, 1.2 eq. 1 M in THF) in toluene (3.0 mL). The mixture was allowed to stir at room temperature for 15 min. Then phenylallene (**1a**, 0.5 mmol) and benzoyl fluoride (0.75 mmol, 1.5 eq.) were added in sequence. The reaction tube was sealed with a Teflon screw cap and removed from the N_2-filled glove box. Then, the reaction mixture was stirred at 0 °C for 6 h. Afterwards, the reaction mixture was directly purified by flash column chromatography on silica gel using petroleum ether (PE) and ethyl acetate (EA) to obtain the desired product **4aa′**.

1,2-Diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) but-3-en-1-one (4aa′). 116.6 mg, 67% yield, colorless oil, R_f = 0.7 (PE/EA = 9/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.7 Hz, 2H), 7.45 (d, J = 7.4 Hz, 1H), 7.36 (t, J = 7.7 Hz, 2H), 7.29 (d, J = 7.3 Hz, 2H), 7.23 (d, J = 7.6 Hz, 3H), 6.01 (s, 1H), 5.55 (s, 1H), 5.26 (s, 1H), 1.22 (s, 6H), 1.20 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 137.4, 136.9, 132.5, 130.8, 129.7, 128.9, 128.6, 128.3, 126.9, 83.8, 58.2, 24.7, 24.4; ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.8. HRMS calculated for $C_{22}H_{26}BO_3$ $[M + H]^+$ 349.1970, found 349.1976.

Procedure for the isomerization of 4aa′

In the N_2-filled glove box, a sealed tube was charged with **4aa′** (0.1 mmol) and LiO^tBu (2.0 eq.) in toluene (1.0 mL). Then the reaction tube was sealed with a Teflon screw cap and removed from the glove box. The reaction mixture was stirred at 90 °C for 3 h and the yield was determined by ^{1}H NMR using mesitylene as an internal standard.

Conflicts of interest

There are no conflicts to declare.

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