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Transition metal-free *trans* hydroboration of alkynoic acid derivatives: Experimental and theoretical studies

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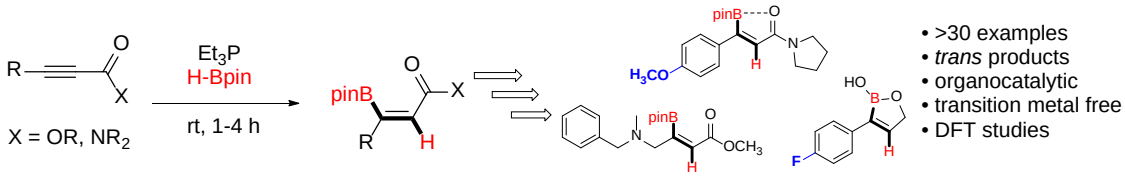
Supporting Information Placeholder



ABSTRACT: We report a phosphine-catalyzed *trans* hydroboration of alkynoate esters and amides. The reaction proceeds under mild conditions with exclusive (*E*) selectivity to afford (*E*)-β borylacrylates and (*E*)-β borylacrylamides in good to excellent yields. The reaction is tolerant of a variety of functional groups and allows efficient access to novel oxaboroles as well as a pargyline derivative (MAO inhibitor). Theoretical calculations suggest an internal hydride generate a phosphonium allenoxyborane followed by the formation of a key phosphonocyclobutene intermediate that collapses in a stereoselective, rate-limiting step.

INTRODUCTION

Organoboron compounds are ubiquitous in organic chemistry due to the versatility of the C-B bond, as they efficiently undergo a wide variety of useful transformations, most notably the Suzuki-Miyaura cross-coupling reaction.[1] Alkenylboronates in particular are excellent substrates for such cross-coupling reactions.[2] Interest in organoboron compounds for medicinal applications highlights their significance not only as synthetic intermediates, but also as end products.[3] Therefore, development of novel methods is warranted.

Synthesis of alkenylboronates is typically achieved through the hydroboration of alkynes; however, addition occurs almost exclusively in a *cis* fashion.[4] Overcoming classical *cis* addition has proven to be somewhat challenging. The *trans* hydroboration of terminal alkynes has seen varying degrees of success with examples reported using Rh,[5] Ru,[6] Ir,[5] Cu,[7] and Co[8] catalysts as well as one report of a transition metal-free borenium cation-mediated reaction (Scheme 1A).[9] Examples of *trans* hydroboration of internal alkynes are even more limited. For example, Fürstner reported an elegant cationic Ru-catalyzed *trans* hydroboration of alkynes (Scheme 1B).[10] DFT studies suggested the formation of a key ruthenium metallacyclopropene intermediate in the mechanism.[11] Further, a stereoselective *trans* hydroboration of 1,3-enynes enabled by 1,4-azaborine-based phosphine-Pd complexed was demonstrated,[12] which was supported by DFT studies (Scheme 1C).[13] Finally, Au-catalyzed *trans* hydroboration of propargylamines to form cyclic aminoboranes has been described by Shi and co-workers (Scheme 1D).[14] Unfortunately, transition-metal free *trans* hydroboration of internal alkynes examples are severely lacking. A few examples of transition metal-free

Scheme 1. Approaches to *trans* hydroboration of alkynes

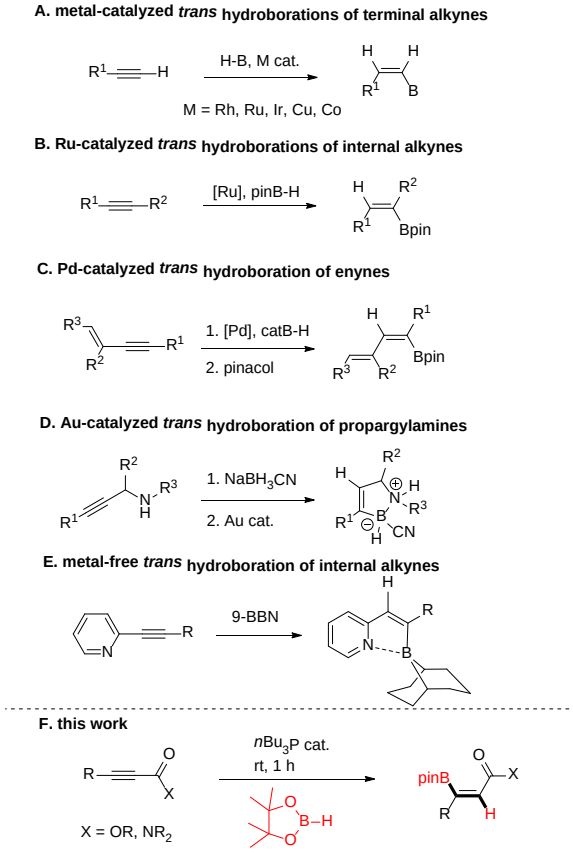
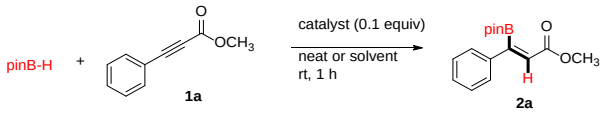


Table 1. Optimization of reaction conditions[a]



entry	solvent	catalyst	% yield[b]
1	neat	PBu_3	88 (87)[c]
2	neat	-	0
3	THF	Cy_3P	59
4	neat	PEt_3	74
5	THF	PPh_3	0
6	neat	$P(OEt)_3$	trace
7	neat	$P(t\text{-}Bu)_3$	0
8	THF	PBu_3	86
9	MeCN	PBu_3	80
10	toluene	PBu_3	84
11	THF	IMes	0
12	THF	ICy	0

[a] General procedure: methyl 3-phenylpropiolate (0.34 mmol) and pinacolborane (0.37 mmol), followed by catalyst (0.034 mmol) at rt under nitrogen for 1 h. [b] NMR yields. [c] Isolated yield. IMes = 1,3-bis(2,4,6-trimethylphenyl)-imidazolium; ICy = 1,3-Dicyclohexylbenzimidazolium

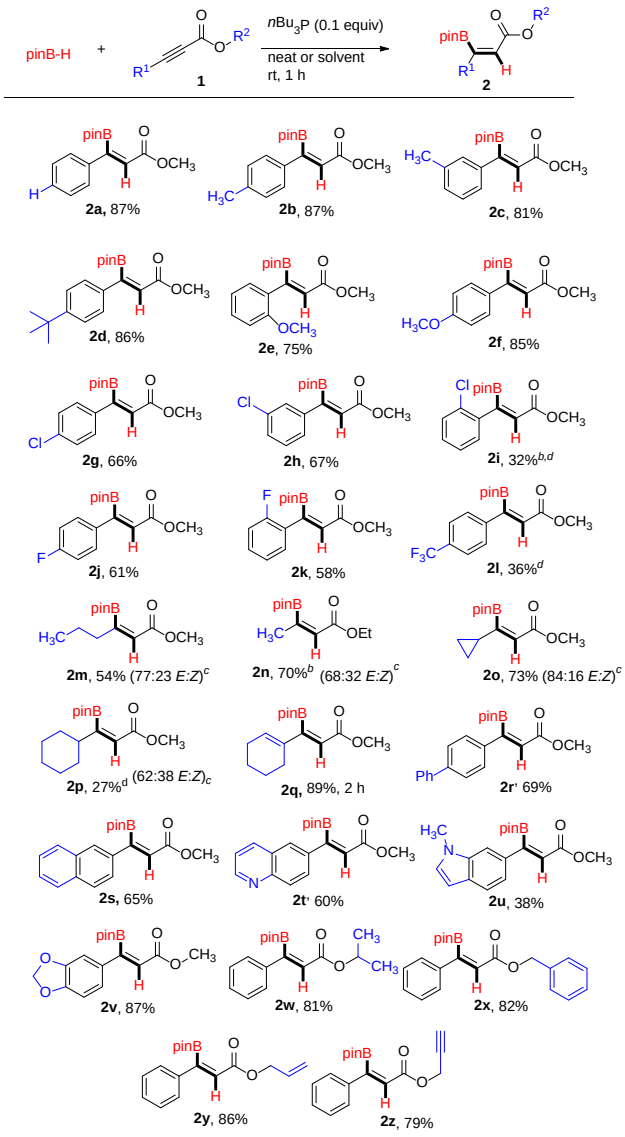
trans diborations[15], silaborations,[15a, 16] and carboborations[17] of alkynes have been reported, but the corresponding hydroborations have remained elusive.[18] Interestingly, the *trans* hydroboration of internal alkynes can be effected using a pyridyl directing group (Scheme 1E).[19] Theoretical calculations supports initial coordination of the pyridyl nitrogen to boron followed by a hydride migration. The corresponding vinyl anion intermediate promotes boryl transfer allowing formation of the lower energy *trans* product.[19]

The scarcity of transition metal-free *trans* hydroborations and the limited substrate scope of known reactions demonstrates the necessity for new methods. Furthermore, new protocols that utilize commercially available reagents such as pinacolborane would be advantageous and desirable. Inspired by previous phosphine-catalyzed addition to alkynes,[15a, 17a, b] we hypothesized that phosphine may be able to catalyze the *trans* addition of pinacolborane to alkynoate esters. Herein, we describe experimental and theoretical studies of this reaction employing pinacolborane and catalytic amounts of trialkylphosphine (Scheme 1F). The atom efficient protocol proceeds with excellent regio- and stereoselectively in good to excellent yields under mild conditions either neat or in the presence of solvent.

RESULTS AND DISCUSSION

Upon initiating our studies, we were pleased to find that addition of pinacolborane and 10 mol % tri-*n*-butylphosphine to methyl 3-phenylpropiolate (**1a**) under neat conditions produced the corresponding (*E*)-borylcinnamate **2a** in excellent yield in an hour at room temperature (entry 1, Table 1). In the absence of phosphine catalyst, no reaction was observed.[20] In addition, we found that tricyclohexylphosphine and triethylphosphine catalyzed the hydroboration reaction as well

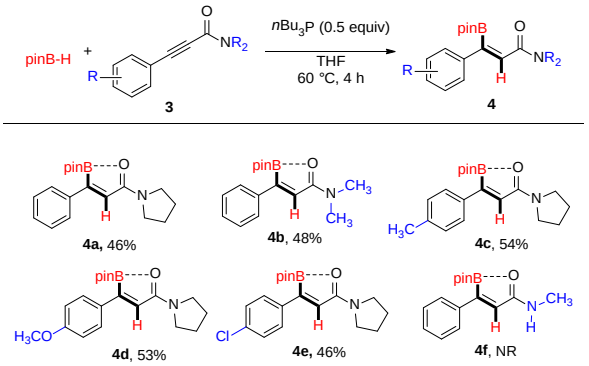
Scheme 2. Hydroboration of alkynoate esters[a]



[a] General procedure: alkyne (1 equiv) and pinacolborane (1.1 equiv) followed by PBu_3 (0.1 equiv) at rt under nitrogen for 1 hour unless otherwise indicated. Isolated yields shown. [b] 0.3 equiv of PBu_3.[c] Determined by GC. >99:1 *E:Z* selectivity unless stated otherwise. [d] Incomplete conversion.

(entries 3 and 4), albeit in lower yields. Unfortunately, triphenylphosphine was unable to mediate the reaction, and none of the desired product was observed (entry 5). Furthermore, no borylated material was observed with triethylphosphite or tri-*tert*-butylphosphine as the catalysts (entries 6 and 7). To investigate solvent effects, the reaction was performed in THF, acetonitrile, and toluene and minimal reduction in yield as determined (entries 8-10). In certain cases, solvent is useful in dissolving both the starting material and catalyst (*vide infra*). N-heterocyclic carbenes (NHCs) were inefficient as catalysts (entries 11 and 12). Based on the catalyst screen, tri-*n*-butylphosphine was deemed as the optimal additive (entry 1). Confirmation of the (*E*)-stereoselectivity was performed with 2D-NOESY experiments. In addition, ^{11}B NMR studies showed a single peak at 30.1 ppm, suggesting the lack of internal coordination between boron and the carbonyl oxygen

Scheme 3. Hydroboration of alkynamides[a]



[a] General procedure: alkynamide (1 equiv) and pinacolborane (1.1 equiv), followed by tri-*tert*-butylphosphine (0.5 equiv) at 60 °C. Isolated yields shown. NR = no reaction.

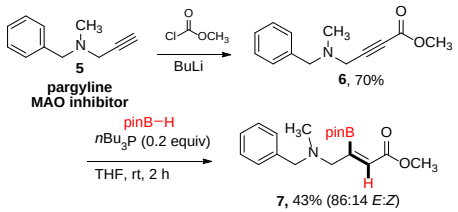
(see Supporting Information) in contrast to amides (*vide infra*).

With optimized conditions (10 mol % tributylphosphine) in hand, we evaluated the substrate scope with a variety of alkynoate esters **1a-1z** (Scheme 2). Alkyl substitutions on aryl rings were tolerated on various positions to afford products **2b-2d** in excellent yields. Electron releasing substituents such as a methoxy group were well tolerated (**2e-2f**). Furthermore, alkynoates substituted with electron withdrawing substituents on the phenyl ring such as chlorine, fluorine and trifluoromethyl groups (**2g – 2l**) were also able to undergo reaction, albeit in slightly reduced yields. In addition, 3-alkyl substituted propiolates were efficient substrates. Products bearing linear alkanes (**2m-n**) as well as cycloalkanes (**2o-2q**) were afforded in good yields, although reduced stereoselectivity was observed in **2m-2p**. Regioselective addition of Bpin to the β vs the γ carbon occurred in **2q**. Moreover, other aryl functional units served as good substrates. Biphenyl, naphthyl, quinolyl, indolyl, and benzodioxolyl groups (**1r-1v**) were transformed to the desired alkenylboronic ester products in up to 87% yield. Several attempts to hydroborate methyl propiolate were performed, but no reaction was observed. To investigate the effect of the ester moiety, isopropyl and benzyl propiolates were subjected to the reaction condition, which afforded **2w-2x** in excellent yield. Notably, in the presence of competing alkene (**1y**) or alkyne (**1z**) substituents, chemoselective hydroboration proceeded with the internal alkyne in excellent yield.

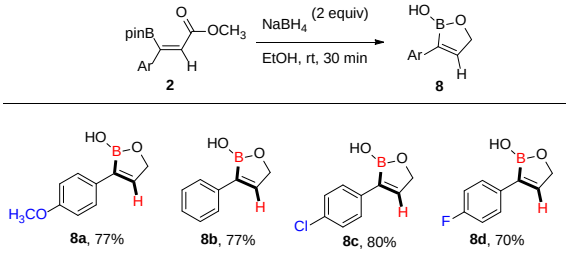
In addition to esters, we were pleased to discover that tertiary alkynamides were able to undergo hydroboration, albeit higher catalyst load and higher temperature were required (Scheme 3). For example, pyrrolidine (**3a**) and dimethylamine (**3b**) derivatives were hydroborated in good yield. Consistent with our previous studies,[15c] boron-oxygen coordination is suggested by the presence of a single peak at ~14 ppm in the ^{11}B NMR spectra, a chemical shift characteristic of quaternized neutral boron (see Supporting Information for details). Arylalkynamides **3c-3e** bearing electron donating as well as electron withdrawing groups underwent the transformation in ~50% yield. Finally, no hydroboration product was observed in the case of the corresponding *N*-methyl secondary amide derivative (**4f**).

To demonstrate the utility of the developed reaction conditions, we applied the hydroboration reaction to the monoamine oxidase (MAO) inhibitor pargyline (**5**, Scheme 4).[21]

Scheme 4. Hydroboration of MAO inhibitor derivative

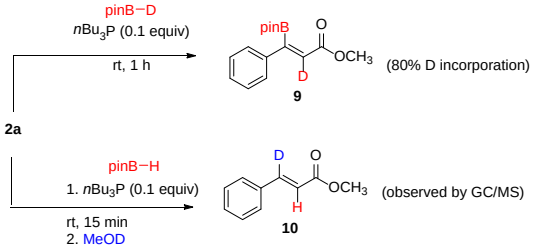


Scheme 5. Synthesis of 2(5*H*)-oxaboroles[a]



[a] General procedure: borylacrylate **2** (1 equiv) dissolved in EtOH followed by $NaBH_4$ (2 equiv) at rt for 30 min. Isolated yields shown.

Scheme 6. Mechanistic studies



Treatment of **5** with methylchloroformate and butyllithium afforded the requisite alkynamide **6**. We were pleased to find that the amine-bearing **6** was converted to the corresponding borylated pargyline derivative **7** in 43% yield. Next, we sought to demonstrate the utility of these substrates to the synthesis of novel oxaboroles. Oxaboroles have recently gained much attention, largely due to the success of the FDA approved drugs Crisaborole (Eucrisa)[22] and Tavaborole (Kerydin).[23] Previous methods to synthesize 2(5*H*)-oxaboroles required propargyl alcohols, the products of which have non-H substitutions on the 5-position.[15b, 17c, 24] We observed that the ester substrates underwent efficient reduction to the corresponding 3-monosubstituted 2(5*H*)-oxaboroles **8a**–**8d** in excellent yields (Scheme 5). Reduction of (*E*)-β-borylacrylate products represents an efficient route to previously elusive oxaborole structures, which may prove to have unique biological activity.

To gain insight into the mechanism of the *trans* hydroboration reaction, we performed deuterium labeling experiments (Scheme 6). Treatment of **2a** with deuteropinacolborane afforded deuterated product **9**, suggesting pinacolborane is the source of hydrogen. Interestingly, if the reaction is quenched in deuterated methanol prior to completion, we observed formation of deuterated methyl cinnamate **10** suggesting that **9** can also undergo deuterodeboration.

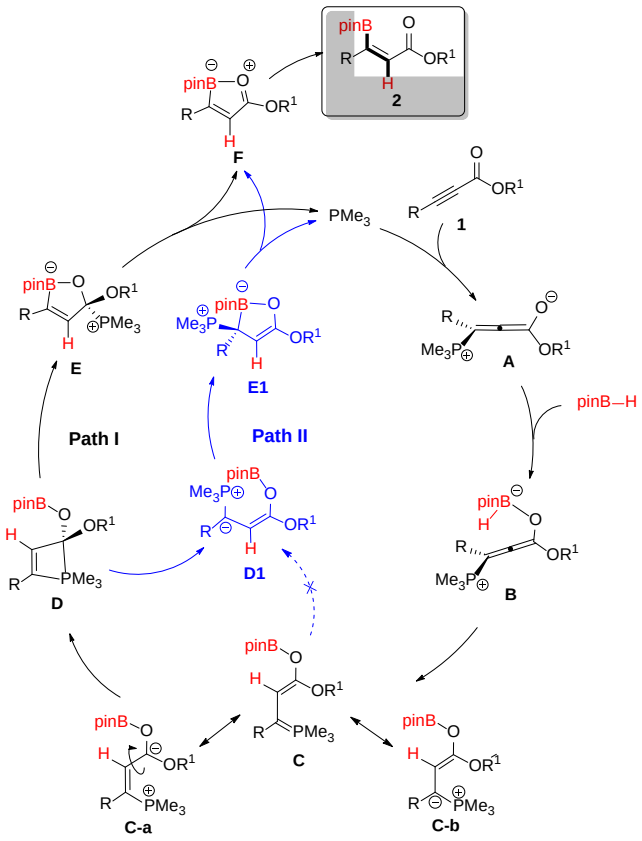
To establish a complete catalytic cycle, we also carried out density functional theory (DFT) calculations (Scheme 7) (see Supporting Information for the computational details). Figure 1 shows the energy profile calculated for the feasible reaction

mechanism. In light of previous reports demonstrating β-addition of trialkylphosphines to acetylenic esters,[25] we surmised that PMe_3 first nucleophilically attacks the β-carbon of the unsaturated ester **1** to form **A**, followed by addition of the Lewis acid pinacolborane to the terminal oxygen of **A** to give **B**. Hydride migration to the α-carbon can proceed to generate intermediate **C**, which is supported by experimental deuteration studies (Scheme 7). **C** has a resonance structure **C-a** with a single bond between the α-carbon and the ester group that allows rotation along the single bond to facilitate a new phosphorous-carbon bond formation and achieve a four-membered ring phosphono-cyclobutene intermediate **D**. As the boron center in **D** is Lewis acidic, migration of the phosphorus-carbon bond to form a new boron-β-carbon bond results in a high energy transition state to afford **E**. The release of PMe_3 generates an internally coordinated intermediate **F**, which leads to the *trans* hydroboration product **2**.

In another possibility, a resonance structure of **C** in **C-b** can allow the attack a negatively charged β–carbon to a Lewis acidic boron center to yield five-membered ring **E1** (Scheme 7). However, to achieve this, the π–bond between α–carbon and the ester group in **C-b** must be broken through rotation to form the *trans*-intermediate **D1**. Many attempts to locate the transition state of this rotation were not successful, and all attempted calculations led to transition state $\mathbf{TS_{C\text{-}D}}$, linking intermediates **C** and **D**.

A possible pathway that leads to **D1** can occur through **D**. The cyclization affords **E1** (Path II, marked in blue), which allows the release of PMe_3 to generate **F**, a common intermediate with Path I. Our calculations indicate that Path II is less favorable than Path I (Figure 1). According to the energy profiles, the overall reaction free energy barrier of Path II (the energy difference between **C** and $\mathbf{TS_{D\text{-}D1}}$) is 1.8 kcal/mol less favored than Path I, which is 30.5 kcal/mol (the energy difference between **C** and $\mathbf{TS_{D\text{-}E}}$). The rate-determining transition state corresponds to the ring expansion from a four-membered ring **D** towards a more stable five-membered ring **E** forming the β-carbon-boron bond. This is the step that also governs the stereoselectivity of the reaction.

Scheme 7. Proposed Catalytic Cycles



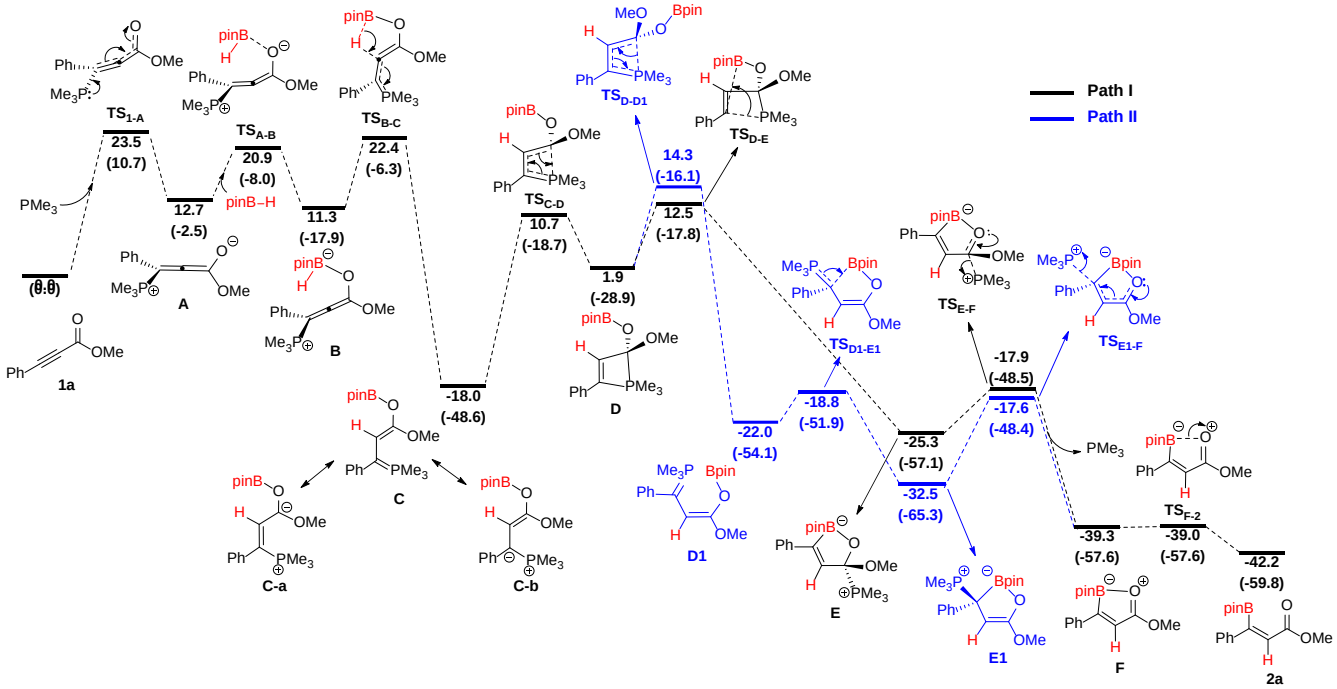


Figure 1. Energy profile calculated at B3LYP/6-31G** for the proposed mechanism of *trans* hydroboration of methyl 3-phenylpropiolate. The solvation-corrected relative free energies and relative electronic energies (in parentheses) are given in kcal/mol.

In conclusion, we have developed a novel protocol for the hydroboration of alkynoate esters and amides under mild conditions. The organocatalytic reaction proceeds in a chemoselective fashion and leads to *trans* hydroborated derivatives that can be elaborated to a variety of products, including here-to-fore inaccessible 3-monosubstituted 2(*5H*)-oxaboroles. The detailed computational analysis of the proposed mechanism is in agreement with experiment. Current efforts are directed towards extending the method to borylations of primary and secondary alkynamides and their applications in biological systems.

EXPERIMENTAL

General Experimental Information. All reagents and solvents were purchased from commercially available sources unless noted otherwise. THF, toluene, and DCM were dried using the Innovative Technology Pure Solv-MD solvent purification system. Flash chromatography was performed using SiliaFlash P60 40-63 um, 60 A. TLC analyses were performed using Silicycle aluminum backed silica gel F_{254} plates. NMR spectra were obtained using a Bruker Avance II 500 MHz, Agilent 400-MR 400 MHz, or a Varian Inova 400 MHz spectrometer. Chemical shifts are reported in δ ppm. ^{1}H and ^{13}C NMR spectra are referenced using an internal standard ($CDCl_3$ or TMS). Chemical shifts for ^{11}B spectra are referenced using BF_3•OEt_2 as an external standard. ESI mass spectra were acquired using an Agilent 6220 TOF LC-MS. EI mass spectra and GC-MS experiments were performed using an Agilent 7890 Series GC system coupled to an HP 5975 Mass Selective Detector.

General Procedure for the synthesis of alkynoate ester susbtrates 1a – 1z. Dry THF (20 mL) was added to the terminal acetylene (1 equiv, 5.0 mmol) in a round bottom flask equipped with a stir bar. The solution was cooled to -78 °C (dry ice/acetone bath) and butyllithium (2.5M in hexanes, 5.0 mmol) was added dropwise and stirred. After 15 minutes methyl chloroformate (1 equiv, 5.0 mmol) was added dropwise to the mixture at -78 °C and stirred for 2 hours. The reaction was then diluted with ethyl acetate, and water was added. The organic layer was washed with brine and dried over anhydrous sodium sulfate. Concentration *in vacuo* yielded a yellow oil which, upon purification by column chromatography (1:10, ethyl acetate:hexanes), yielded the corresponding ester. Esters **1a**,[26] **1b**,[27], **1c**,[28] **1d**,[29] **1e**,[30] **1f**,[31] **1g**,[30] **1i**,[32] **1j**,[30] **1k**,[33] **1l**,[30] **1m**,[34] **1o**,[35] **1p**,[36] **1q**,[27] **1r**,[37] **1s**,[37] **1v**,[37] **1w**,[31] **1x**,[31] **1y**,[38] **1z**,[39] and **6**[40] are known compounds. Compound **1n** was purchased commercially and used directly.

Methyl 3-(3-chlorophenyl)propiolate (1h). Clear oil, 67% (319 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (t, *J* = 1.8 Hz, 1H), 7.50 – 7.39 (m, 2H), 7.31 (t, *J* = 7.9 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 134.7, 132.8, 131.2, 131.1, 130.0, 121.4, 84.7, 81.2, 53.1. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{10}H_8ClO_2$ 195.0207; Found 195.0203.

Methyl 3-(quinolin-6-yl)propiolate (1t). Light yellow solid, 35% (228 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (s, 1H), 8.13 – 8.03 (m, 3H), 7.78 (s, 1H), 7.43 (s, 1H), 3.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 152.1, 148.4, 136.0, 133.9, 131.9, 130.1, 127.6, 122.1, 117.7, 85.7, 81.1, 52.9, 52.9. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{10}NO_2$ 212.0706; Found 212.0717.

Methyl 3-(1-methyl-1H-indol-5-yl)propiolate (1u). Yellow oil, 74% (294 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.42 (d, J = 8.5 Hz, 1H), 7.28 (d, J = 8.5 Hz, 1H), 7.09 (s, 1H), 6.49 (s, 1H), 3.82 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 130.6, 128.4, 127.5, 126.4, 109.8, 109.8, 102.0, 89.9, 79.2, 52.8, 33.2. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{12}NO_2$ 214.0863; Found 214.0863.

General procedure for the synthesis of alkynamide substrates 3a – 3f. To a round bottom flask with stir bar was added the ester substrate (1 equiv, 3.0 mmol) followed by purging with $N_{2(g)}$. Dry THF (20 mL) was then added followed by pyrrolidine (2 equiv, 6 mmol) and the mixture was allowed to stir at room temperature for 4 hours. The reaction mixture was diluted in ethyl acetate (20 mL) and water (20 mL). The organic layer was washed with brine, dried over sodium sulfate, and concentrated *in vacuo* to afford a yellow oil. The crude product was then subjected to silica chromatography (40% ethyl acetate in hexanes) to afford the product as a white solid. Alkynamides **3a**,[41] **3b**,[42] and **3f**[43] are known compounds.

1-(Pyrrolidin-1-yl)-3-(*p*-tolyl)prop-2-yn-1-one (3c). White solid, 57% (350 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 7.9 Hz, 2H), 3.72 (t, J = 6.8 Hz, 2H), 3.52 (t, J = 7.0 Hz, 2H), 2.36 (s, 3H), 2.00 – 1.90 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 140.5, 132.5, 129.4, 117.6, 89.2, 82.4, 77.2, 48.3, 45.5, 25.5, 24.9, 21.8. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{16}NO$ 214.1226; Found 214.1214.

3-(4-Methoxyphenyl)-1-(pyrrolidin-1-yl)prop-2-yn-1-one (3d). White solid, 40% (360 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 9.0 Hz, 2H), 6.86 (d, J = 9.0 Hz, 2H), 3.82 (s, 3H), 3.72 (t, J = 6.8 Hz, 2H), 3.52 (t, J = 7.0 Hz, 2H), 2.00 – 1.89 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 153.2, 134.3, 114.3, 112.6, 89.3, 82.1, 55.5, 48.3, 45.4, 25.5, 24.9. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{16}NO_2$ 230.1176; Found 230.1161.

3-(4-Chlorophenyl)-1-(pyrrolidin-1-yl)prop-2-yn-1-one (3e). White solid, 48% (220 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.8 Hz, 2H), 7.33 (d, J = 8.8 Hz, 2H), 3.71 (t, J = 6.8 Hz, 2H), 3.53 (t, J = 7.0 Hz, 2H), 1.95 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 136.3, 133.7, 129.0, 119.2, 87.5, 83.6, 77.2, 48.3, 45.5, 25.5, 24.9. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{13}ClNO$ 234.0680; Found 234.0665.

General procedure for the hydroboration of alkynoate esters to form (*E*)-β borylacrylates 2a – 2z. Alkynoate ester (0.34 mmol, 1.0 equiv.) was added to a flame dried 2-neck round bottom flask with a stir bar. The flask was then filled with $N_{2(g)}$ by purging for 30 minutes. Solid esters were dissolved in 50 μL dry THF, while oils were reacted neat. Pinacolborane (0.37 mmol, 1.1 equiv.) followed by tri-n-butylphosphine (0.034 mmol, 0.1 equiv.) were added to the vial at room temperature. The reaction was then allowed to stir at room temperature for 60 minutes. The reaction mixture was then directly loaded onto silica gel and purified by column chromatography (0-10% ethyl acetate in hexanes) to yield the product as a colorless oil.

Methyl (*E*)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (2a). Colorless oil, 87% (85 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 2H), 7.42 – 7.32 (m, 3H), 6.44 (s, 1H), 3.79 (s, 3H), 1.42 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 138.7, 129.3, 128.9, 127.3, 125.7, 84.5, 52.0, 25.2; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.3. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{22}BO_4$ 289.1609; Found 289.1588.

Methyl (*E*)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(*p*-tolyl)acrylate (2b). Colorless oil, 87% (109 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 6.42 (s, 1H), 3.78 (s, 3H), 2.35 (s, 3H), 1.42 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 139.5, 135.9, 129.6, 127.2, 124.7, 84.5, 52.0, 25.2, 21.4; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.2. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{24}BO_4$ 303.1765; Found 303.1770.

Methyl (*E*)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(*m*-tolyl)acrylate (2c). Colorless oil, 81% (143 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.11 (m, 4H), 6.42 (s, 1H), 3.77 (s, 3H), 2.33 (s, 3H), 1.41 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 138.6, 138.4, 130.0, 128.7, 127.9, 125.4, 124.3, 84.4, 51.9, 25.1, 21.5; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.8. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{24}BO_4$ 303.1765; Found 303.1760.

Methyl (*E*)-3-(4-(*tert*-butyl)phenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (2d). Colorless oil, 86% (98 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 8.8 Hz, 2H), 6.44 (s, 1H), 3.78 (s, 3H), 1.43 (s, 13H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 152.6, 135.8, 127.1, 125.8, 124.7, 84.5, 52.0, 34.9, 31.4, 25.3; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.4. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{30}BO_4$ 345.2237; Found 345.2239.

Methyl (*E*)-3-(2-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (2e). Colorless oil, 75% (75 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 6.94 (td, *J* = 7.5, 1.1 Hz, 1H), 6.87 (dd, *J* = 8.2, 1.0 Hz, 1H), 6.49 (s, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 1.38 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 157.3, 130.4, 129.6, 129.3, 128.3, 121.2, 111.2, 84.1, 55.6, 51.8, 25.3; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.2. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{24}BO_5$ 319.1714; Found 319.1730.

Methyl (*E*)-3-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (2f). Colorless oil, 85% (92 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.38 (s, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 1.42 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 160.7, 131.1, 128.8, 123.4, 114.3, 84.5, 55.4, 51.9, 25.3. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.4. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{24}BO_5$ 319.1714; Found 319.1727.

Methyl (*E*)-3-(4-chlorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (2g). White solid, 66% (75 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, 2H), 7.33 (d, 2H), 6.40 (s, 1H), 3.79 (s, 3H), 1.40 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 137.2, 135.3, 129.1, 128.5, 126.2, 84.7, 52.1, 25.2; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.25. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{21}BClO_4$, 323.1219; Found 323.1205.

Methyl (*E*)-3-(3-chlorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (2h). White solid, 67% (58 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.40 – 7.32 (m, 1H), 7.35 – 7.24 (m, 3H), 6.40 (s, 1H), 3.78 (s, 3H), 1.40 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 140.5, 134.8, 130.1, 129.2, 127.3, 126.8, 125.3, 84.7, 52.2, 25.1; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.5. HRMS: (ESI) m/z: $[M + Na]^+$ calcd for $C_{16}H_{20}BClNaO_4$ 345.1059; Found 345.1038.

Methyl (*E*)-3-(2-chlorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (2i). White solid. 32% (30 mg). ^{1}H NMR (400 MHz, CDCl3) δ 7.42 – 7.20 (m, 4H), 6.38 (s, 1H), 3.79 (s, 3H), 1.35 (s, 12H); ^{13}C NMR (101 MHz, cdcl$_3$) δ 167.7, 138.6, 132.2, 131.1, 130.2, 129.9, 129.3, 126.9, 84.5, 52.1, 24.9; ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.9. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{21}BClO_4$ 323.1216; Found 323.1195.

Methyl (*E*)-3-(4-fluorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (2j). Colorless oil, 61% (109 mg) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.42 (m, 2H), 7.03 (t, *J* = 8.7 Hz, 2H), 6.37 (s, 1H), 3.77 (s, 3H), 1.40 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 164.7, 162.2, 134.7, 129.1, 125.5, 115.9, 115.7, 84.5, 52.0, 25.1; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.7. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{21}BFO_4$ 307.1514; Found 307.1521.

Methyl (*E*)-3-(2-fluorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (2k). Colorless oil, 58% (47 mg). ^{1}H NMR (400 MHz, CDCl3) δ 7.42 (td, *J* = 7.8, 1.7 Hz, 1H), 7.31 – 7.24 (m, 1H), 7.14 – 7.01 (m, 2H), 6.55 (s, 1H), 3.77 (s, 3H), 1.38 (s, 13H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 161.7, 159.2, 130.7, 130.7, 129.8, 129.8, 128.9, 128.9, 126.7, 126.6, 124.5, 124.4, 116.3, 116.1, 52.1, 25.2; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.6. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{21}BFO_4$ 307.1514; Found 307.1518.

Methyl (*E*)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(4-(trifluoromethyl)phenyl)acrylate (2l). Off-white solid, 36% (36 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (q, 4H), 6.45 (s, 1H), 3.81 (s, 3H), 1.41 (s, 13H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 142.4, 131.1, 130.8, 127.9, 127.5, 125.8, 122.8, 110.2, 84.8, 52.3, 25.1; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.5. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{21}BF_3O_4$ 357.1483; Found 357.1490.

Methyl (*E*)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-2-enoate (2m). Colorless oil, 54% (99 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.98 (s, 1H), 3.69 (s, 3H), 2.28 – 2.18 (m, 2H), 1.49 (h, *J* = 7.4 Hz, 2H), 1.33 (s, 13H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 125.7, 84.1, 51.7, 38.0, 25.0, 21.3, 14.0; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.1. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{24}BO_4$ 255.1765; Found 255.1772.

Ethyl (*E*)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-enoate (2n). Colorless oil, 70% (380 mg) (70:30 *E*:*Z*). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.42 – 6.40 (q, 0.43H), 6.02 – 5.95 (m, 1H), 4.14 (m, 3H), 2.13 (s, 1H), 1.91 (s, 3H), 1.32 (s, 12H), 1.28 – 1.18 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 166.3, 130.7, 127.0, 84.2, 84.0, 60.5, 59.9, 24.9, 24.8, 21.2, 16.4, 14.4. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.6. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{12}H_{22}BO_4$ 241.1608; Found 241.1622.

Methyl (*E*)-3-cyclopropyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (2o). Colorless oil, 73% (148 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.07 (s, 1H), 3.70 (s, 3H), 1.72 – 1.61 (m, 1H), 1.34 (s, 13H), 0.92 – 0.80 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 123.3, 84.4, 51.7, 25.2, 18.1, 8.4; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.4. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{22}BO_4$ 253.1608; Found 253.1604.

Methyl (*E*)-3-cyclohexyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (2p). Colorless oil, 27% (30 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.98 (s, 1H), 3.70 (s, 3H), 2.23 – 2.13 (m, 1H), 1.82 – 1.72 (m, 4H), 1.73 – 1.60 (m, 2H), 1.36 (s, 13H), 1.31 – 1.08 (m, 7H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 124.0, 84.1, 51.7, 44.8, 32.1, 26.4, 26.2, 25.2. ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.1. HRMS: (ESI) m/z: $[M + Na]^+$ calcd for $C_{16}H_{27}BNaO_4$ 317.1898; Found 317.1879.

Methyl (*E*)-3-(cyclohex-1-en-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (2q). Colorless oil, 89% (109 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.12 (s, 1H), 5.99 (s, 1H), 3.69 (s, 3H), 2.22 – 2.08 (m, 4H), 1.70 – 1.49 (m, 4H), 1.37 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 137.6, 136.7, 120.3, 84.1, 51.6, 26.7, 25.4, 25.4, 22.4, 21.8; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.8. HRMS: (ESI) $[M + H]^+$ calcd for $C_{16}H_{26}BO_4$ 293.1922; Found 293.1919.

Methyl (*E*)-3-([1,1'-biphenyl]-4-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (2r). White solid, 69% (65 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.54 (m, 6H), 7.45 (t, *J* = 7.9 Hz, 2H), 7.40 – 7.31 (m, 1H), 6.50 (s, 1H), 3.81 (s, 3H), 1.45 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 142.1, 140.5, 137.7, 129.0, 127.8, 127.7, 127.6, 127.2, 125.5, 84.6, 52.1, 25.3; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.7. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{26}BO_4$ 365.1919; Found 365.1947.

Methyl (*E*)-3-(naphthalen-2-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (2s). White solid, 65% (46 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.86 – 7.78 (m, 3H), 7.62 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.49 (dt, *J* = 6.2, 3.4 Hz, 2H), 6.58 (s, 1H), 3.82 (s, 3H), 1.46 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 136.1, 133.7, 133.4, 128.6, 128.6, 127.8, 127.7, 126.9, 126.6, 125.8, 124.4, 84.6, 52.1, 25.25; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.5. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{24}BO_4$ 339.1766; Found 339.1774.

Methyl (*E*)-3-(quinolin-6-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (2t). White solid, 60% (68 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.13 (d, *J* = 1.3 Hz, 1H), 8.08 (d, *J* = 8.8 Hz, 1H), 7.93 (d, *J* = 2.0 Hz, 1H), 7.85 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.41 (dd, *J* = 8.3, 4.2 Hz, 1H), 6.58 (s, 1H), 3.82 (s, 3H), 1.45 (s, 13H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 151.1, 148.6, 136.9, 136.6, 130.2, 128.2, 127.1, 126.9, 121.8, 84.8, 52.2, 25.2. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.7. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{23}BNO_4$ 340.1718; Found 340.1730.

Methyl (*E*)-3-(1-methyl-1*H*-indol-5-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (2u). Off-white solid, 38% (60 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 1.7 Hz, 1H), 7.41 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.29 (d, *J* = 8.6 Hz, 2H), 7.05 (d, *J* = 3.1 Hz, 1H), 6.49 (s, 1H), 6.47 (s, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 1.45 (s, 13H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 137.4, 130.2, 129.8, 128.8, 123.1, 121.1, 120.7, 109.6, 102.0, 84.4, 51.9, 33.1, 25.3; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.9. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{25}BNO_4$ 342.1871; Found 342.1872.

Methyl (*E*)-3-(benzo[*d*][1,3]dioxol-5-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (2v). White solid, 87% (71 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 – 6.97 (m, 2H), 6.79 (dd, *J* = 7.8, 0.6 Hz, 1H), 6.34 (s, 1H), 5.97 (s, 2H), 3.77 (s, 3H), 1.41 (s, 12H); ^{13}C NMR (101 MHz, cdcl$_3$) δ 168.7, 148.8, 148.3, 132.8, 124.0, 122.2, 108.6, 107.0, 101.4, 84.5, 52.0, 25.2; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.7. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{22}BO_6$ 333.1507; Found 333.1524.

Isopropyl (*E*)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (2w). Colorless oil, 81% (94 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.45 (m, 2H), 7.40 – 7.27 (m, 3H), 6.41 (s, 1H), 5.11 (hept, *J* = 6.3 Hz, 1H), 1.42 (s, 12H), 1.28 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 138.8, 129.1, 128.8, 127.3, 126.8, 84.4, 68.3, 25.2, 22.1; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.1. HRMS: (ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{25}BNaO_4$ 339.1741; Found 339.1744.

Benzyl (*E*)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (2x). White solid, 82% (89 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 2H), 7.43 – 7.28 (m, 8H), 6.50 (s, 1H), 5.24 (s, 2H), 1.43 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 138.7, 135.9, 129.3, 128.9, 128.7, 128.5, 128.4, 127.3, 125.8, 84.6, 66.8, 25.2; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.6. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{26}BO_4$ 365.1923; Found 365.1924.

Allyl (*E*)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (2y). Colorless oil, 86% (78 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 2H), 7.41 – 7.31 (m, 3H), 6.47 (s, 1H), 6.04 – 5.89 (m, 1H), 5.36 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.25 (dq, *J* = 10.4, 1.3 Hz, 1H), 4.70 (dt, *J* = 5.8, 1.5 Hz, 2H), 1.42 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 138.7, 132.3, 129.3, 128.9, 127.3, 125.8, 118.6, 84.6, 65.6, 25.2; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.4. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{24}BO_4$ 315.1765; Found 315.1761.

Prop-2-yn-1-yl (*E*)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (2z). Colorless oil, 79% (103 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.45 (m, 2H), 7.41 – 7.32 (m, 3H), 6.48 (s, 1H), 4.81 (d, *J* = 2.5 Hz, 2H), 2.49 (s, 1H), 1.42 (s, 14H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 138.5, 129.5, 128.9, 127.3, 124.9, 84.7, 77.7, 75.2, 52.4, 25.2; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.3. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{22}BO_4$ 313.1609; Found 313.1619.

Methyl (*E*)-4-(benzyl(methyl)amino)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-enoate (7). Purified as a mixture of *E*:*Z* isomers (86:14) by diluting crude oil in hexanes and extracting product with methanol. Colorless oil, 43% (34 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.20 (m, 6H), 6.22 (s, 1H), 3.72 (s, 3H), 3.47 (s, 2H), 3.23 (s, 2H), 2.15 (s, 3H), 1.38 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 138.9, 129.2, 128.2, 127.0, 126.3, 84.3, 62.9, 62.4, 51.7, 42.7, 25.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.0. HRMS: (ESI) m/z: $[M + K]^+$ calcd for $C_{19}H_{28}BKNO_4$ 384.1746; Found 384.1775.

General procedure for the hydroboration of alkynamides to produce (*E*)-β borylacrylates 4a – 4e. Alkynamide (0.30 mmol, 1.0 equiv.) was added to a flame dried 2-neck round bottom flask with a stir bar. The flask was then filled with $N_{2(g)}$ by purging for 30 minutes. Dry THF was then added (0.5 mL). Pinacolborane (0.33 mmol, 1.1 equiv.) followed by tri-*n*-butylphosphine (0.15 mmol, 0.5 equiv.) were added to the vial at room temperature. The reaction was then allowed to stir at 60 °C for 4 hours. The reaction mixture was then directly loaded onto silica gel and purified by column chromatography (40% ethyl acetate in dichloromethane) to yield the product as a white solid.

(*E*)-3-Phenyl-1-(pyrrolidin-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-2-en-1-one (4a). White solid, 46% (42 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.65 (m, 2H), 7.38 – 7.27 (m, 3H), 6.35 (s, 1H), 3.71 (t, *J* = 6.9 Hz, 2H), 3.63 (t, *J* = 6.9 Hz, 2H), 2.08 – 1.88 (m, 4H), 1.26 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 138.8, 128.9, 128.1, 127.9, 118.6, 80.5, 47.4, 47.1, 26.2, 25.6, 24.4. ^{11}B NMR (128 MHz, $CDCl_3$) δ 14.0. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{27}BNO_3$ 328.2082; Found 328.2101.

(*E*)-*N*,*N*-Dimethyl-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylamide (4b). White solid, 48% (39 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.33 (q, *J* = 7.2, 6.4 Hz, 3H), 6.50 (s, 1H), 3.18 (d, *J* = 4.0 Hz, 6H), 1.28 (s, 13H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 138.7, 129.0, 128.1, 127.8, 117.0, 77.2, 37.3, 26.1. ^{11}B NMR (128 MHz, $CDCl_3$) δ 13.7. HRMS: (ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{24}BNNaO_3$ 324.1730; Found 324.1745.

(*E*)-1-(Pyrrolidin-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(*p*-tolyl)prop-2-en-1-one (4c). White solid, 54% (52 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.32 (s, 1H), 3.68 (t, *J* = 6.9 Hz, 2H), 3.60 (t, *J* = 6.9 Hz, 2H), 2.33 (s, 3H), 2.06 – 1.85 (m, 5H), 1.26 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 139.0, 135.8, 128.8, 127.9, 117.7, 80.4, 47.3, 47.0, 26.2, 25.5, 24.4, 21.5. ^{11}B NMR (128 MHz, $CDCl_3$) δ 14.0. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{29}BNO_3$ 342.2239; Found 342.2256.

(*E*)-3-(4-Methoxyphenyl)-1-(pyrrolidin-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-2-en-1-one (4d). White solid, 53% (41 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.9 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 6.31 (s, 1H), 3.82 (s, 3H), 3.71 (t, *J* = 6.9 Hz, 2H), 3.62 (t, *J* = 6.9 Hz, 2H), 2.08 – 1.88 (m, 4H), 1.29 (s, 13H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 160.7, 131.3, 129.8, 116.4, 113.6, 80.5, 55.4, 47.3, 47.1, 26.4, 25.6, 24.5. ^{11}B NMR (128 MHz, $CDCl_3$) δ 13.8. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{29}BNO_4$ 358.2188; Found 358.2172.

(*E*)-3-(4-Chlorophenyl)-1-(pyrrolidin-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-2-en-1-one (4e). Purified by preparatory TLC (100% EtOAc). White solid, 46% (27 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.7 Hz, 2H), 7.31 (d, *J* = 8.7 Hz, 2H), 6.34 (s, 1H), 3.72 (t, *J* = 6.9 Hz, 2H), 3.64 (t, *J* = 6.9 Hz, 2H), 2.10 – 1.90 (m, 4H), 1.56 (s, 3H), 1.26 (s, 13H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 137.2, 134.9, 129.3, 128.4, 118.8, 80.6, 47.5, 47.2, 26.2, 25.6, 24.5. ^{11}B NMR (128 MHz, $CDCl_3$) δ 13.8. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{26}BClNO_3$ 362.1692; Found 362.1696.

General procedure for the synthesis of oxaboroles 8a – 8d. To a round-bottom flask equipped with a stir bar was added hydroboration product (0.3 mmol, 1 equiv) and dissolved in ethanol (3 mL). Sodium borohydride (0.6 mmol, 2 equiv) was added and the mixture was allowed to stir for 30 minutes at room temperature. The mixture was concentrated *in vacuo* to afford an off-white solid, which was then purified *via* column chromatography to afford the final product as a white solid.

3-(4-Methoxyphenyl)-1,2-oxaborol-2(5*H*)-ol (8a). White solid, 77% (92 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.8 Hz, 2H), 7.32 (s, 1H), 6.90 (d, *J* = 8.9 Hz, 2H), 4.83 (s, 1H), 4.67 (s, 2H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 159.2, 145.8, 128.1, 114.1, 71.8, 55.4. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.1. HRMS: (ESI) m/z: $[M - H]^-$ calcd for $C_{10}H_{10}BO_3$ 189.0723; Found 189.0715.

3-Phenyl-1,2-oxaborol-2(5*H*)-ol (8b). White solid, 77% (45 mg). ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.43 – 7.32 (m, 3H), 7.30 – 7.23 (m, 1H), 6.45 (s, 1H), 4.71 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 135.9, 128.7, 127.6, 126.9, 71.8. ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.6. HRMS: (ESI) m/z: $[M - H]^-$ calcd for $C_9H_8BO_2$ 159.0623; Found 159.0597.

3-(4-Chlorophenyl)-1,2-oxaborol-2(5*H*)-ol (8c). White solid, 80% (89 mg). ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.43 (s, 1H), 7.32 (d, *J* = 8.5 Hz, 2H), 4.85 (s, 1H), 4.68 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.90, 134.28, 133.34, 128.83, 128.26, 105.30, 71.79. ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.8. HRMS: (ESI) m/z: $[M - H]^-$ calcd for $C_9H_7BClO_2$ 193.0223; Found 193.0229.

3-(4-Fluorophenyl)-1,2-oxaborol-2(5*H*)-ol (8d). White solid, 70% (40 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.58 (m, 2H), 7.37 (s, 1H), 7.10 – 6.99 (m, 2H), 6.09 (d, *J* = 7.8 Hz, 1H), 4.71 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.49, 161.04, 148.96, 146.76, 131.81, 128.38, 115.49, 115.27, 71.60. ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.9. HRMS: (ESI) m/z: $[M - H]^-$ calcd for $C_9H_7BFO_2$ 177.0529; Found 177.0536.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Spectroscopic data for all new compounds and deuterium labeling experimental (PDF).

Computational details (DFT) of reaction mechanism (PDF).

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