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Synthesis of Alkenyl Boronates from Allyl-Substituted Aromatics Using an Olefin Cross-Metathesis Protocol

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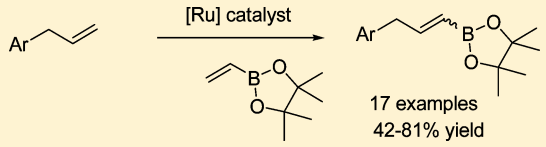
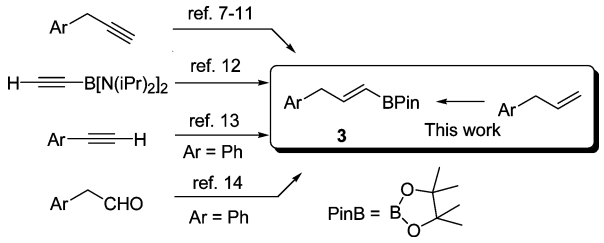
Supporting Information

ABSTRACT: An efficient synthesis of 3-aryl-1-propenyl boronates from pinacol vinyl boronic ester and allyl-substituted aromatics by cross metathesis is reported. Although the allylbenzene derivatives are prone to isomerization reaction under metathesis conditions, we found that some ruthenium catalysts are effective for this methodology. This strategy thus provides an interesting alternative approach to alkyne hydroboration, leading to the preparation of unknown compounds. Moreover, the boron substituent can be replaced by various functional groups in good yields.



Functionalized alkenyl boronates constitute an important class of organoboron compounds.[1] Their utility in organic synthesis has been illustrated many times over. For instance, alkenyl boronates can be converted to aldehydes or ketones,[2] halides,[3] and the corresponding olefins.[4] In particular, they have been employed in a range of C−C bond-forming reactions such as Suzuki−Miyaura cross-coupling reaction.[5] More recently, it was found that alcohols can be coupled with vinyl boronate esters using catalytic $Cu(OAc)_2$ to synthesize vinyl ethers.[6] Despite the potential synthetic interest of 3-aryl-1-propenyl boronates **3**, this particular class of alkenyl boronates has surprisingly received little attention. To the best of our knowledge, only a few compounds have been prepared in the literature to date (Scheme 1). Among all the synthetic methodologies described,

Scheme 1. Different Strategies To Prepare 3-Arylpropen-1-yl Boronic Esters



the hydroboration of the corresponding alkynes is employed the most.[7−11] As an example, the hydroboration of 3-(2-bromophenyl)-1-propyne with the catecholborane was realized.[7,8] However, in this particular case, the hydroboration product must be converted with an additional transformation into a stable boronic acid compound to be used efficiently in a Suzuki coupling reaction. Hydroboration of simple allylbenzene catalyzed by NHC−Cu complexes in presence of bis(pinacolato)diboron $[B_2(pin)_2]$ was also reported by the Hoveyda group.[10] The selectivity in favor of the desired product (α:β, 25:75) is moderate, which has been explained by the presence of a phenyl group on the substrate. Other less straightforward strategies have been employed to synthesize (*E*)-4,4,5,5-tetramethyl-2-(3-phenylpropen-1-yl)-[1,3,2]-dioxaborolane, which can also be obtained from the commercially available boronic acid.[12−14] The (*Z*) isomer of this compound is accessible by the rhodium(I)-catalyzed *trans*-hydroboration reaction of prop-2-ynylbenzene developed by Miyaura and co-workers.[15] In light of this information, the development of an efficient general method for the preparation of this class of alkenyl boronates appears a sufficiently interesting goal to justify a thorough study.

Although the terminal alkenyl boronates can be prepared by a number of procedures, cross metathesis (CM) of alkenes with vinyl boronates has recently emerged as a new, efficient catalytic method.[16] Taking into account that the introduction of a propenyl moiety on a phenyl ring is easier than the introduction of a propynyl group due to its lower reactivity, we envisaged that the cross-olefin metathesis reaction could be useful for the development of a general protocol to prepare 3-arylpropen-1-yl boronic esters **3**.[17] Allylbenzene derivatives, and more specifically, 3-phenyl-1-propene, have already been used as substrates in olefin metathesis with different electron-deficient cross partners such as methyl vinyl ketone, acrylonitrile, or acroleine.[18] However, because of the strong substrate dependency of the metathesis reactions, this method, employing a vinyl boronate, can lead to a side reaction resulting from the migration of the double bond to the internal position of the allylic compound, which could dramatically decrease the yield of the desired product.[19] Indeed, the isomerization of allylbenzene derivatives under metathesis conditions was

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reported, although the exact mechanism is still unknown.[20] It has been postulated that the ruthenium hydride species generated from the decomposition of the ruthenium catalysts, such as **G-II** (Grubbs second generation catalyst) or **HG-II** (Hoveyda–Grubbs second generation catalyst), are responsible for the unwanted reaction.[21]

As part of our program related to the use of catalytic processes in organoboron chemistry,[22] we report our efforts that are devoted to the development of a new access path to **3**. Different ruthenium-based olefin metathesis catalysts have been evaluated, including the catalyst **M71-SIPr**,[23] a Hoveyda–Grubbs type catalyst that contains an aminocarbonyl function linked to a benzylidene ligand (Figure 1). Some representative applications of these metathesis products are also described.

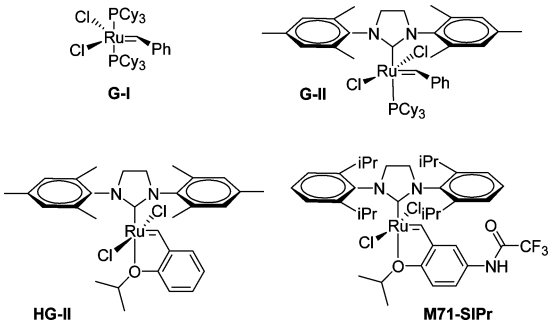


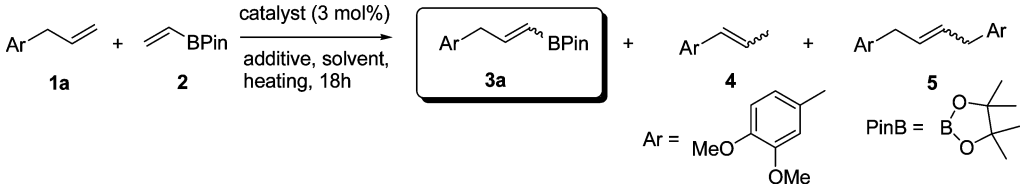
Figure 1. Structures of ruthenium catalysts used for olefin metathesis.

In order to develop a reliable protocol, 4-allyl-1,2-dimethoxy benzene **1a** was chosen first as a model substrate for our study because this compound is particularly appropriate to undergo an isomerization reaction in the presence of a ruthenium–carbene catalyst.[24] The cross-metathesis results obtained with 2 equiv of vinyl pinacol boronate **2**[25] are given in Table 1. Under standard conditions (CH_2Cl_2, reflux, 0.2 M), the Grubbs first-generation catalyst **G-I** proved to be an efficient catalyst for the metathesis reaction compared its effectiveness as a catalyst for the isomerization process (entry 1). Although the reaction was not complete after 18 h, alkenyl boronate **3a** was obtained in a pure form after flash chromatography (55% yield) with the *E* isomer as major product.[26] The moderate yield can also be explained by the presence of the self-metathesis product **5**, detected by ^{1}H NMR analysis of crude reaction product, as well as by the formation of other unidentified products. When **G-II** and **HG-II** are used as catalysts (3 mol %), conversion is complete under the same experimental conditions. The proportion of **3a** in the crude product decreased in favor of compound **4**, resulting from the isomerization process (entries 2–3). The exclusive formation of isomerized product **4** is observed at high temperature in the presence of **HG-II** catalyst, confirming that decomposition products from the catalyst can be responsible of the isomerization reaction (entry 4). To resolve this problem, Grubbs and co-workers have developed cross-metathesis conditions using additives that minimize the unwanted isomerization reaction.[27]

We therefore studied the effect of 1,4-benzoquinone on the metathesis reaction of **1a**. Unexpectedly, the addition of this additive (10 mol %) significantly reduced the catalytic activity of **G-II** with a slight effect on the isomerization process (entry 5). Better results were obtained in the presence of **HG-II** under reflux conditions in toluene. A stoichiometric quantity of 1,4-benzoquinone allowed a significant reduction of the isomerization process but, unfortunately, with a concomitant drop of catalyst activity (entries 6–8). Finally, **M71-SIPr** catalyst had a better catalytic activity than **HG-II** in the presence of the additive (entry 9). By heating the reaction mixture at 60 °C with only 0.5 equiv of 1,4-benzoquinone, the desired product **3a** was predominantly formed. After purification, the yield was slightly higher than the one obtained with the **G-I** catalyst but with a similar stereoselectivity in favor of *E* isomer (entry 10).

Having established two reliable operating conditions, we next examined the scope and limitations of our process. A large variety of allylbenzene derivatives (**1**) have been selected with different functional groups on the phenyl ring as substrates. Given the cost of the catalyst and an easy purification of the desired product, the synthetic protocol with the Grubbs' catalyst **G-I** (conditions A) was preferably used, as summarized

Table 1. Cross Metathesis of 1a with 2 Using Various Catalysts[a]



entry	catalyst	additive (1,4-benzoquinone)[b]	solvent	*T* (°C)	conversion (%)[c]	ratio **3a**/**4**/**5**[d,e]	ratio *E*/*Z* of **3a**[d]	yield of **3a** (%)[f]
1	**G-I**	none	CH_2Cl_2	reflux	93	11/0/1	3.9/1	55
2	**G-II**	none	CH_2Cl_2	reflux	100	6.4/12.6/1	7.4/1	nd
3	**HG-II**	none	CH_2Cl_2	reflux	100	2.1/8/1	3/1	nd
4	**HG-II**	none	toluene	reflux	100	0/1/0		
5	**G-II**	0.1	CH_2Cl_2	reflux	22	1/1.9/0	5.3/1	nd
6	**HG-II**	0.1	CH_2Cl_2	reflux	53	8.4/10.6/1	3.5/1	nd
7	**HG-II**	0.1	toluene	reflux	97	11.5/37.5/1	4/1	nd
8	**HG-II**	1	toluene	reflux	44	8.7/2.75/1	4/1	nd
9	**M71-SIPr**	1	toluene	reflux	93	28/4.3/1	4/1	nd
10	**M71-SIPr**	0.5	toluene	60	94	17.8/1.2/1	4/1	60

[a]0.2 M in solvent. [b]Equivalent relative to **1a**. [c]Conversion based on **1a** as the limiting reagent. [d]Determined by analysis of 300 MHz ^{1}H NMR spectra of product mixtures prior to purification. [e]In all cases, no isomerization product from **3a** was detected. [f]Isolated by flash chromatography (nd = not determined).

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in Figure 2. In the hardest cases, catalyst **M71-SIPr** was also tested (condition B). Yields obtained are between 55 and 89%,

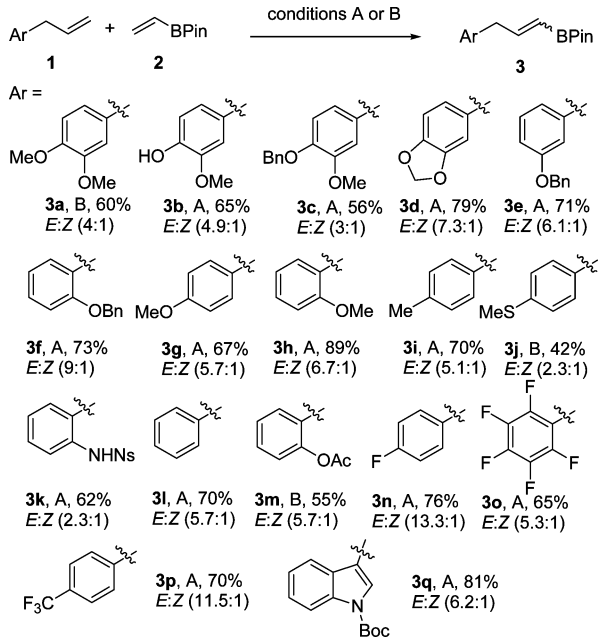
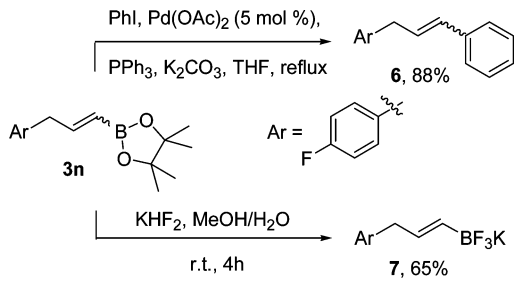


Figure 2. Cross metathesis of various allyl aromatics with **2**.

except for 1-allyl-4-methylsulfanylbenzene **1j** (22%). By using the catalyst **M71-SIPr**, compound **3j** can be prepared with a slightly improved yield (42%), showing the interest in having two available protocols. It must be noted that *N*-Boc-3-allylindole **1q** is a very good substrate for the cross metathesis with **2**, which is a relevant result due to the fact that this nucleus is found in various bioactive molecules of pharmaceutical importance.[28] The stereoselectivity of the reaction is moderately high, in most cases in favor of the *E* isomer, except when the phenyl moiety is substituted by a thioether or sulfonamide functional group (**3j** and **3k**). All compounds were isolated as an inseparable mixture of isomers except in the case of **3k**.

To illustrate the synthetic interest of this family of alkenyl boronates, some typical transformations have been realized as shown in Scheme 2. A Suzuki cross-coupling reaction between **3n** and phenyl iodide was conducted in the presence of K_2CO_3, $Pd(OAc)_2$ (5 mol %), and PPh_3 (15 mol %) under reflux in THF to give the corresponding coupled product **6** in 88% yield. The alkenyl boronate **3n** can also be readily converted to its trifluoroborate analog; these salts are known as useful reagents in palladium-catalyzed coupling reactions with partners other

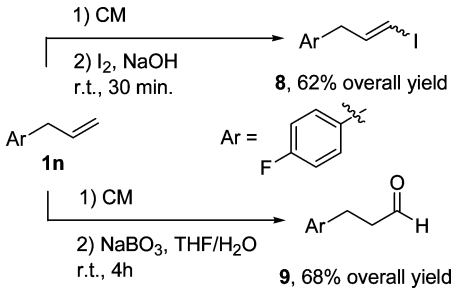
Scheme 2. Some Synthetic Transformations of Alkenyl Boronate 3n



than the aryl electrophiles.[29] Using the readily available and inexpensive KHF_2, **7** was obtained in 65% yield as an air-stable compound.[30]

In some transformations (Scheme 3), purification of the vinyl boronate was not necessary. After completion of the CM

Scheme 3. Reaction Sequences without Purification of Metathesis Product



reaction and evaporation of CH_2Cl_2, iodination (I_2, NaOH) can be realized in THF, giving rise to a cross-metathesis/iodination sequence starting from 4-fluoroallylbenzene **1n**. The corresponding alkenyl iodide **8** was obtained in 62% yield for the two steps. In all cases (**6**–**8**), the olefin stereochemistry of metathesis product **3n** was retained during these reactions. Similarly, a cross-metathesis/oxidation sequence can be realized, giving the corresponding aldehyde **9** in an unoptimized overall yield (68%) due to partial decomposition during purification by column chromatography. This last approach can be an alternative strategy to the anti-Markovnikov regioselective oxidation of allyl aromatics into aldehydes using base–transition metal catalysts.[31]

In summary, we described in this paper an efficient and simple route of alkenyl boronates starting from allyl aromatics based on a cross-metathesis reaction. Two simple and complementary operating conditions have been developed, allowing us to increase the generality of the methodology. The synthesis and isolation of several new functionalized 3-aryl-1-propenyl pinacol boronates have been carried out for a broad scope of substrates. Furthermore, various synthetic transformations of the boron–carbon bond have been realized. In the future, the boron substituent could be replaced by other functional groups using, for example, sodium azide as a nitrogen counterpart.[32]

EXPERIMENTAL SECTION

General Information and Materials. All commercially available chemicals were used without further purification. Tetrahydrofuran (THF) and toluene were distilled over sodium/benzophenone. Dichloromethane (CH_2Cl_2) was distilled over P_2O_5. ^1H and ^{13}C spectra were recorded in $CDCl_3$ (internal standard: 7.26 ppm, ^1H; 77.00 ppm, ^{13}C), acetone-d_6 (internal standard: 2.05 ppm, ^1H; 29.84 ppm, ^{13}C), ^{19}F NMR chemical shifts to external $CFCl_3$ (0.0 ppm), and ^{11}B NMR chemical shifts to external $BF_3{\cdot}OEt_2$ (0.0 ppm). Carbon atoms in α to boron are often not visible in ^{13}C NMR. High-resolution mass spectra (HMRS) were recorded on a micro-TOF-Q II mass analyzer or Q-TOF 2 using positive ion electrospray.

General Procedures for Cross-Metathesis Reactions. *Procedure A.* To a solution of **1** (0.35 mmol) in dry CH_2Cl_2 (0.2 M) under argon atmosphere was added successively **2** (0.70 mmol) and **G-I** catalyst (3 mol %). The resulting mixture was heated under a reflux condition for 18 h. After this time, CH_2Cl_2 was removed under reduced pressure, and the residue was purified via column chromatography by using an appropriate eluent to afford the products

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3b−i, **3k−l**, and **3n** as inseparable mixtures of *E* and *Z* isomers except for **3k**.

Procedure B. To a solution of **1** (0.35 mmol) in dry toluene (0.2 M) under an argon atmosphere were added successively **2** (0.70 mmol), 1,4-benzoquinone (0.175 mmol), and **M71-SIPr** (3 mol %). The resulting mixture was heated at 60 °C for 18 h. After this time, toluene was removed under reduced pressure, and the residue was purified on column chromatography by using an appropriate eluent to afford **3a**, **3j**, and **3m**, as an inseparable mixture of *E* and *Z* isomers.

4,4,5,5-Tetramethyl-2-(3-(3,4-dimethoxyphenyl)prop-1-enyl)-[1,3,2]-dioxaborolane (3a). Procedure B. Purified using EtOAc/cyclohexane (1:9); 65 mg (60%, *E*/*Z* = 80/20). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): (*E*) δ 1.27 (s, 12H), 3.43 (dd, *J* = 6.3, 1.6 Hz, 2H), 3.86 (s, 3H), 3.87 (s, 3H), 5.45 (dt, *J* = 17.8, 1.6 Hz, 1H), 6.69−6.83 (m, 4H); (*Z*) δ 1.32 (s, 12H), 3.70 (dd, *J* = 7.9, 1.3 Hz, 2H), 3.86 (s, 3H), 3.88 (s, 3H), 5.43 (dt, *J* = 13.3, 1.3 Hz 1H), 6.55 (dt, *J* = 14.0, 7.9 Hz, 1H), 6.69−6.83 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): (*E*) δ 24.8, 41.9, 55.8, 55.9, 83.1, 111.3, 112.2, 120.8, 131.7, 147.5, 148.9, 152.7; (*Z*) δ 24.9, 38.2, 55.7, 55.9, 83.0, 111.3, 112.0, 120.4, 133.3, 147.5, 148.9, 152.9. ^{11}B NMR (96 MHz, $CDCl_3$) δ 29.7. HRMS ESI (+), CH_3OH: $[M + Na]^+$ calcd for $C_{17}H_{25}BO_4$, 327.1744; found, 327.1745.

2-Methoxy-4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)phenol (3b). Procedure A. Purified using EtOAc/cyclohexane (1:4); 66 mg (65%, *E*/*Z* = 83/17). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): (*E*) δ 1.27 (s, 12H), 3.41 (dd, *J* = 6.3, 1.6 Hz, 2H), 3.87 (s, 3H), 5.45 (dt, *J* = 17.8, 1.6 Hz, 1H), 5.56 (br s, 1H, OH), 6.67−6.86 (m, 4H); (*Z*) δ 1.32 (s, 12H), 3.69 (dd, *J* = 7.7, 1.3 Hz, 2H), 3.88 (s, 3H), 5.42 (dt, *J* = 13.5, 1.3 Hz, 1H), 5.54 (br s, 1H, OH), 6.55 (dt, *J* = 13.5, 7.7 Hz, 1H), 6.67−6.86 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): (*E*) δ 24.8, 42.0, 55.9, 83.1, 111.5, 114.3, 121.6, 130.9, 144.0, 146.5, 152.9; (*Z*) δ 24.9, 38.3, 55.8, 83.0, 111.2, 114.2, 121.2, 132.5, 143.8, 146.5, 153.0. ^{11}B NMR (96 MHz, $CDCl_3$): δ 29.8. HRMS ESI (+), CH_3OH: $[M + Na]^+$ calcd for $C_{16}H_{23}BO_4$, 313.1587; found, 313.1585.

2-[3-(4-Benzyloxy-3-methoxyphenyl)prop-1-enyl]-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (3c). Procedure A. Purified using EtOAc/cyclohexane (5:95); 74 mg (56%, *E*/*Z* = 75/25). Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): (*E*) δ 1.27 (s, 12H), 3.42 (dd, *J* = 6.3, 1.5 Hz, 2H), 3.89 (s, 3H), 5.15 (s, 2H), 5.46 (dt, *J* = 17.8, 1.5 Hz, 1H), 6.64−6.84 (m, 4H), 7.28−7.47 (m, 5H); (*Z*) δ 1.32 (s, 12H), 3.69 (dd, *J* = 7.6, 1.1 Hz, 2H), 3.89 (s, 3H), 5.15 (s, 2H), 5.43 (dt, *J* = 13.2, 1.1 Hz, 1H), 6.55 (dt, *J* = 13.2, 7.6 Hz, 1H), 6.64−6.84 (m, 3H), 7.28−7.47 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): (*E*) δ 24.8, 41.9, 56.0, 71.2, 83.1, 112.8, 114.3, 120.8, 127.2, 127.7, 128.5, 132.3, 137.4, 146.6, 149.6, 152.7; (*Z*) δ 24.9, 38.3, 55.9, 71.2, 83.0, 112.5, 114.3, 120.4, 127.2, 127.7, 128.5, 133.9, 137.4, 146.5, 149.6, 152.9. ^{11}B NMR (96 MHz, $CDCl_3$): δ 29.8. HRMS ESI (+), CH_3OH: $[M + Na]^+$ calcd for $C_{23}H_{29}BO_4$, 403.2057; found, 403.2057.

2-(3-(Benzo[*d*][1,3]dioxol-6-yl)prop-1-enyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (3d). Procedure A. Purified using EtOAc/cyclohexane (5:95); 79 mg (79%, *E*/*Z* = 88/12). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): (*E*) δ 1.27 (s, 12H), 3.39 (dd, *J* = 6.3, 1.5 Hz, 2H), 5.44 (dt, *J* = 17.8, 1.5 Hz, 1H), 5.92 (s, 2H), 6.61−6.78 (m, 4H); (*Z*) δ 1.31 (s, 12H), 3.67 (dd, *J* = 7.6, 1.1 Hz, 2H), 5.42 (dt, *J* = 13.2, 1.1 Hz, 1H), 5.92 (s, 2H), 6.51 (dt, *J* = 13.2, 7.6 Hz, 1H), 6.61−6.78 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): (*E*) δ 24.8, 41.9, 83.1, 100.8, 108.2, 109.4, 121.7, 132.8, 145.9, 147.6, 152.5; (*Z*) δ 24.9, 38.3, 83.0, 100.7, 108.1, 109.0, 121.3, 134.5, 145.7, 147.6, 152.80. ^{11}B NMR (96 MHz, $CDCl_3$): δ 29.7. HRMS ESI (+), CH_3OH: $[M + Na]^+$ calcd for $C_{16}H_{21}BO_4$, 311.1431; found, 311.1435.

4,4,5,5-Tetramethyl-2-[3-(3-benzyloxyphenyl)prop-1-enyl]-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (3e). Procedure A. Purified using EtOAc/cyclohexane (5:95); 87 mg (71%, *E*/*Z* = 86/14). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): (*E*) δ 1.29 (s, 12H), 3.48 (dd, *J* = 6.3, 1.5 Hz, 2H), 5.07 (s, 2H), 5.50 (dt, *J* = 17.8, 1.5 Hz, 1H), 6.74−6.92 (m, 4H), 7.21−7.26 (m, 1H), 7.36−7.49 (m, 5H); (*Z*) δ 1.33 (s, 12H), 3.78 (dd, *J* = 7.5, 1.3 Hz, 2H), 5.07 (s, 2H), 5.48 (dt, *J* = 13.2, 1.3 Hz, 1H), 6.58 (dt, *J* = 13.2, 7.5 Hz, 1H), 6.74−6.92 (m, 3H), 7.21−7.26 (m, 1H), 7.36−7.49 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): (*E*) δ 24.8, 42.3, 69.9, 83.1, 115.6, 121.6, 127.6, 127.9, 128.6, 129.4, 137.2, 140.7, 152.2, 159.0; (*Z*) δ 24.9, 38.7, 69.9, 83.0, 115.3, 121.3, 127.5, 127.9, 128.6, 129.4, 137.1, 140.7, 152.5, 159.0. ^{11}B NMR (96 MHz, $CDCl_3$): δ 29.8. HRMS ESI (+), CH_3OH: $[M + Na]^+$ calcd for $C_{22}H_{27}BO_3$, 373.1951; found, 373.1951.

2-(3-(2-(Benzyloxy)phenyl)prop-1-enyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (3f). Procedure A. Purified using EtOAc/cyclohexane (5:95); 89 mg (73%, *E*/*Z* = 90/10). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): (*E*) δ 1.29 (s, 12H), 3.59 (dd, *J* = 6.2, 1.4 Hz, 2H), 5.11 (s, 2H), 5.48 (dt, *J* = 17.9, 1.4 Hz, 1H), 6.85 (dt, *J* = 17.9, 6.2 Hz, 1H), 6.91−6.96 (m, 2H), 7.17−7.23 (m, 2H), 7.32−7.48 (m, 5H); (*Z*) δ 1.32 (s, 12H), 3.90 (dd, *J* = 7.5, 1.3 Hz, 2H), 5.14 (s, 2H), 5.46 (dt, *J* = 13.3, 1.3 Hz, 1H), 6.68 (dt, *J* = 13.3, 7.5 Hz, 1H), 6.91−6.96 (m, 2H), 7.17−7.23 (m, 2H), 7.32−7.48 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): (*E*) δ 24.8, 36.5, 69.9, 83.0, 111.8, 120.8, 127.2, 127.5, 127.7, 128.1, 128.5, 130.5, 137.4, 152.3, 156.4; (*Z*) δ 24.9, 33.0, 69.9, 82.9, 111.7, 120.9, 127.1, 127.5, 127.7, 128.1, 128.5, 130.1, 137.4, 152.7, 156.4. ^{11}B NMR (96 MHz, $CDCl_3$): δ 29.8. HRMS ESI (+), CH_3OH: $[M + Na]^+$ calcd for $C_{22}H_{27}BO_3$, 373.1951; found, 373.1952.

2-(3-(4-Methoxyphenyl)prop-1-enyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane(3g). Procedure A. Purified using EtOAc/cyclohexane (5:95); 64 mg (67%, *E*/*Z* = 85/15). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): (*E*) δ 1.27 (s, 12H), 3.44 (dd, *J* = 6.3, 1.5 Hz, 2H), 3.80 (s, 3H), 5.44 (dt, *J* = 17.9, 1.5 Hz, 1H), 6.77 (dt, *J* = 17.9, 6.3 Hz, 1H), 6.83−6.86 (m, 2H), 7.09−7.18 (m, 2H); (*Z*) δ 1.32 (s, 12H), 3.72 (dd, *J* = 7.6, 1.3 Hz 2H), 3.80 (s, 3H), 5.42 (dt, *J* = 13.3, 1.3 Hz, 1H), 6.54 (dt, *J* = 13.3, 7.6 Hz, 1H), 6.83−6.86 (m, 2H), 7.09−7.18 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): (*E*) δ 24.8, 41.4, 55.3, 83.1, 113.9, 129.9, 131.1, 153.0, 158.1; (*Z*) δ 24.9, 38.0, 55.3, 83.0, 113.8, 129.4, 130.5, 153.1, 157.90. ^{11}B NMR (96 MHz, $CDCl_3$): δ 29.6. HRMS ESI (+), CH_3OH: $[M + Na]^+$ calcd for $C_{16}H_{23}BO_3$, 297.1638; found, 297.1640.

2-(3-(2-Methoxyphenyl)prop-1-enyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (3h). Procedure A. Purified using EtOAc/cyclohexane (5:95); 85 mg (89%, *E*/*Z* = 87/13). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): (*E*) δ 1.27 (s, 12H), 3.51 (dd, *J* = 6.2, 1.6 Hz, 2H), 3.83 (s, 3H), 5.44 (dt, *J* = 17.9, 1.6 Hz, 1H), 6.80 (dt, *J* = 17.9, 6.2 Hz, 1H), 6.85−6.93 (m, 2H), 7.12−7.15 (m, 1H), 7.18−7.24 (m, 1H); (*Z*) δ 1.33 (s, 12H), 3.80 (dd, *J* = 7.5, 1.6 Hz, 2H), 3.85 (s, 3H), 5.42 (dt, *J* = 13.2, 1.6 Hz, 1H), 6.60 (dt, *J* = 13.3, 7.5 Hz, 1H), 6.85−6.93 (m, 2H), 7.12−7.15 (m, 1H), 7.18−7.24 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): (*E*) δ 24.8, 36.4, 55.3, 83.0, 110.3, 120.5, 127.5, 127.6, 130.3, 152.3, 157.3; (*Z*) δ 24.9, 32.9, 55.3, 82.9, 110.3, 120.5, 127.2, 127.6, 130.0, 152.6, 157.3. ^{11}B NMR (96 MHz, $CDCl_3$): δ 29.7. HRMS ESI (+), CH_3OH: $[M + Na]^+$ calcd for $C_{16}H_{23}BO_3$, 297.1638; found, 297.1635.

4,4,5,5-Tetramethyl-2-(3--tolylprop-1-enyl)-[1,3,2]-dioxaborolane (3i). Procedure A. Purified using EtOAc/cyclohexane (5:95); 63 mg (70%, *E*/*Z* = 87/17). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): (*E*) δ 1.28 (s, 12H), 2.35 (s, 3H), 3.47 (dd, *J* = 6.3, 1.5 Hz, 2H), 5.47 (dt, *J* = 17.8, 1.5 Hz, 1H), 6.78 (dt, *J* = 17.8, 6.3 Hz, 1H), 7.07−7.14 (m, 4H); (*Z*) δ 1.33 (s, 12H), 2.35 (s, 3H), 3.75 (dd, *J* = 7.6, 1.3 Hz, 2H), 5.45 (dt, *J* = 13.2, 1.3 Hz, 1H), 6.56 (dt, *J* = 13.2, 7.6 Hz, 1H), 7.07−7.14 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): (*E*) δ 21.0, 24.8, 41.9, 83.1, 128.8, 129.1, 135.6, 136.0, 152.8; (*Z*) δ 21.0, 24.9, 38.2, 83.0, 128.5, 129.1, 135.8, 135.9, 153.0. ^{11}B NMR (96 MHz, $CDCl_3$): δ 29.7. HRMS ESI (+), CH_3OH: $[M + Na]^+$ calcd for $C_{16}H_{23}BO_2$, 281.1689; found, 281.1686.

4,4,5,5-Tetramethyl-2-(3-(4-(methylthio)phenyl)prop-1-enyl)-[1,3,2]-dioxaborolane (3j). Procedure B. Purified using EtOAc/cyclohexane (5:95); 42 mg (42%, *E*/*Z* = 70/30). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): (*E*) δ 1.27 (s, 12H), 2.48 (s, 3H), 3.45 (dd, *J* = 6.2, 1.5 Hz, 2H), 5.44 (dt, *J* = 17.8, 1.5 Hz, 1H), 6.74 (dt, *J* = 17.8, 6.3 Hz, 1H), 7.10−7.24 (m, 4H); (*Z*) δ 1.31 (s, 12H), 2.48 (s, 3H), 3.73 (dd, *J* = 7.6, 1.2 Hz, 2H), 5.41−5.48 (m, 1H), 6.53 (dt, *J* = 14.0, 7.5 Hz, 1H), 7.10−7.24 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): (*E*) δ 16.3, 24.8, 41.6, 83.1, 127.2, 129.5, 135.8, 136.2, 152.4; (*Z*) δ 16.4, 24.9, 41.6, 83.0, 127.3, 129.2, 135.5, 136.5, 152.2. ^{11}B NMR (96 MHz, $CDCl_3$): δ 29.7. HRMS ESI (+), CH_3OH: $[M + Na]^+$ calcd for $C_{16}H_{23}BO_2S$, 313.1409; found, 313.1411.

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4-Nitro-*N*-{2-[3-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)allyl]phenyl}benzenesulfonamide (3k). Procedure A. Purified using EtOAc/cyclohexane (1:4); 96 mg (62%, separable mixture of *E*/*Z* = 70/30). Brown oil. ^{1}H NMR (300 MHz, $CDCl_3$): (*E*) δ 1.27 (s, 12H), 3.12 (dd, *J* = 5.4, 1.7 Hz, 2H), 5.21 (dt, *J* = 18.0, 1.7 Hz, 1H), 6.52 (br s, 1H), 6.53 (dt, *J* = 18.0, 5.4 Hz, 1H), 7.09 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.17−7.21 (m, 1H), 7.22−7.28 (m, 1H), 7.40 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.91 (d, *J* = 8.9 Hz, 2H), 8.30 (d, *J* = 8.9 Hz, 2H); (*Z*) δ 1.27 (s, 6H), 1.44 (s, 6H), 3.26 (dd, *J* = 8.1, 1.2 Hz, 2H), 5.28 (m, 1H), 6.18 (dt, *J* = 13.1, 8.1 Hz, 1H), 7.11−7.18 (m, 2H), 7.22−7.25 (m, 1H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 8.9 Hz, 1H), 8.22−8.25 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): (*E*) δ 24.8, 37.7, 83.5, 124.3, 124.9, 127.3, 128.1, 128.4, 131.2, 131.9, 133.8, 145.2, 149.4, 150.2; (*Z*) δ 24.7, 34.3, 83.4, 123.9, 124.3, 126.5, 127.7, 128.4, 130.5, 131.8, 134.0, 145.2, 150.4, 151.7. ^{11}B NMR (96 MHz, $CDCl_3$): δ 29.5. HRMS ESI (+), CH_3OH: $[M + Na]^+$ calcd for $C_{21}H_{25}BN_2O_6S$, 467.1424; found, 467.1421.

4,4,5,5-Tetramethyl-2-(3-phenylprop-1-enyl)-[1,3,2]-dioxaborolane (3l). Procedure A. Purified using EtOAc/cyclohexane (5:95); 60 mg (70%, *E*/*Z* = 85/15). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): (*E*) δ 1.27 (s, 12H), 3.50 (dd, *J* = 6.2, 1.5 Hz, 2H), 5.46 (dt, *J* = 17.8, 1.5 Hz, 1H), 6.78 (dt, *J* = 17.8, 6.2 Hz, 1H), 7.18−7.33 (m, 5H); (*Z*) δ 1.33 (s, 12H), 3.80 (dd, *J* = 7.6, 0.8 Hz, 2H), 5.46 (dt, *J* = 13.4, 0.8 Hz, 1H), 6.55−6.61 (m, 1H), 7.18−7.33 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): (*E*) δ 24.8, 42.3, 83.1, 126.1, 128.4, 128.9, 139.1, 152.5; (*Z*) δ 24.9, 38.7, 83.0, 125.9, 128.4, 128.6, 139.1, 152.7. ^{11}B NMR (96 MHz, $CDCl_3$): δ 29.5. These data are in agreement with those reported in the literature.[33]

2-(3-(2-Methoxyphenyl)prop-1-enyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (3m). Procedure B. Purified using EtOAc/cyclohexane (1:9); 58 mg (55%, *E*/*Z* = 85/15). Yellow powder. Mp = 99 °C. ^{1}H NMR (300 MHz, $CDCl_3$): (*E*) δ 1.27 (s, 12H), 2.31 (s, 3H), 3.40 (dd, *J* = 6.3, 1.4 Hz, 2H), 5.47 (dt, *J* = 17.8, 1.4 Hz, 1H), 6.68 (dt, *J* = 17.8, 6.3 Hz, 1H), 7.04−7.07 (m, 1H), 7.16−7.32 (m, 3H); (*Z*) δ 1.31 (s, 12H), 2.32 (s, 3H), 3.70 (dd, *J* = 7.3, 1.0 Hz, 2H), 5.47 (m, 1H), 6.48 (dt, *J* = 13.2, 7.3 Hz, 1H), 7.04−7.07 (m, 1H), 7.16−7.32 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): (*E*) δ 21.0, 24.8, 36.7, 83.2, 122.4, 126.2, 127.5, 130.8, 131.0, 149.0, 150.7, 169.3; (*Z*) δ 21.0, 24.9, 36.7, 83.1, 122.3, 126.2, 127.3, 130.5, 131.0, 149.0, 150.7, 169.3. ^{11}B NMR (96 MHz, $CDCl_3$): δ 29.7. HRMS ESI (+), CH_3OH: $[M + Na]^+$ calcd for $C_{17}H_{23}BO_4$, 325.1587; found, 325.1587.

2-(3-(4-Fluorophenyl)prop-1-enyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (3n). Procedure A. Purified using EtOAc/cyclohexane (5:95); 69 mg (76%, *E*/*Z* = 93/7). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): (*E*) δ 1.27 (s, 12H), 3.46 (dd, *J* = 6.2, 1.6 Hz, 2H), 5.44 (dt, *J* = 17.9, 1.6 Hz, 1H), 6.78 (dt, *J* = 17.8, 6.2 Hz, 1H), 6.95−7.10 (m, 2H), 7.11−7.21 (m, 2H); (*Z*) δ 1.32 (s, 12H), 3.74 (dd, *J* = 7.6, 1.2 Hz, 2H), 5.45 (dt, *J* = 13.2, 1.2 Hz, 1H), 6.52 (dt, *J* = 13.3, 7.5 Hz, 1H), 6.95−7.10 (m, 2H), 7.11−7.21 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): (*E*) δ 24.8, 41.3, 83.2, 115.2 (d, *J* = 21.1 Hz), 130.3 (d, *J* = 7.7 Hz), 134.7 (d, *J* = 3.2 Hz), 152.1, 161.5 (d, *J* = 243.7 Hz); (*Z*) δ 24.9, 37.8, 83.1, 115.1 (d, *J* = 21.1 Hz), 129.9 (d, *J* = 7.8 Hz), 136.3 (d, *J* = 3.0 Hz), 152.4, 161.5 (d, *J* = 243.7 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): (*E*) δ −117.3; (*Z*) δ −117.7. ^{11}B NMR (96 MHz, $CDCl_3$): δ 29.7. HRMS ESI (+), CH_3OH: $[M + Na]^+$ calcd for $C_{15}H_{20}BFO_2$, 285.1438; found, 285.1437.

4,4,5,5-Tetramethyl-2-(3-(perfluorophenyl)prop-1-enyl)-[1,3,2]-dioxaborolane (3o). Procedure A. Purified using EtOAc/cyclohexane (5:95); 76 mg (65%, *E*/*Z* = 84/16). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): (*E*) δ 1.26 (s, 12H), 3.53 (dd, *J* = 5.7, 1.6 Hz, 2H), 5.40 (dd, *J* = 17.8, 1.6 Hz, 1H), 6.62 (dt, *J* = 17.8, 5.7 Hz, 1H); (*Z*) δ 1.32 (s, 12H), 3.88 (dd, *J* = 7.1, 1.5 Hz, 2H), 5.49 (dt, *J* = 13.2, 1.3 Hz, 1H), 6.34 (dt, *J* = 13.2, 7.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): (*E*) δ 23.7, 26.9, 82.4, 111.2 (dt, *J* = 19.0, 3.7 Hz), 120.0, 134.8 (m), 138.3 (m), 142.4 (m), 145.7; (*Z*) δ 23.8, 24.4, 82.3, 111.2 (dt, *J* = 19.0, 3.7 Hz), 120.0 (CH), 137.3 (m), 140.6 (m), 145.6 (m), 146.3. ^{19}F NMR (282 MHz, $CDCl_3$): (*E*) δ −162.7 (dt, *J* = 21.3, 7.6 Hz), −157.2 (t, *J* = 20.6 Hz), −143.5 (dd, *J* = 21.9, 8.9 Hz); (*Z*) δ −163.0 (dt, *J* = 22.6, 8.1 Hz), −157.9 (t, *J* = 20.7 Hz), −143.5 (dd, *J* = 22.1, 8.1 Hz). ^{11}B NMR (96 MHz, $CDCl_3$): δ 29.6. HRMS ESI (+), CH_3OH: $[M + Na]^+$ calcd for $C_{15}H_{16}BF_5O_2$, 357.1061; found, 357.1064.

4,4,5,5-Tetramethyl-2-[3-(4-trifluoromethylphenyl)prop-1-enyl]-[1,3,2]-dioxaborolane (3p). Procedure A. Purified using EtOAc/cyclohexane (5:95); 76 mg (70%, *E*/*Z* = 92/8). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): (*E*) δ 1.27 (s, 12H), 3.54 (dd, *J* = 6.2, 1.6 Hz, 2H), 5.46 (dt, *J* = 17.8, 1.6 Hz, 1H), 6.74 (dt, *J* = 17.8, 6.2 Hz, 1H), 7.29 (d, *J* = 8.9 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H); (*Z*) δ 1.32 (s, 12H), 3.83 (dd, *J* = 7.5, 1.3 Hz, 2H), 5.50 (dt, *J* = 13.2, 1.3 Hz, 1H), 6.53 (dt, *J* = 13.2, 7.5 Hz, 1H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): (*E*) δ 24.8, 38.8, 83.2, 124.3 (d, *J* = 243.7 Hz), 125.3 (q, *J* = 3.8 Hz), 128.6 (d, *J* = 32.2 Hz), 129.2, 143.2, 151.0; (*Z*) δ 24.9, 41.9, 83.1, 124.29 (d, *J* = 243.7 Hz), 125.3 (q, *J* = 3.8 Hz), 128.6 (d, *J* = 32.2 Hz), 128.9, 143.1, 151.2. ^{19}F NMR (282 MHz, $CDCl_3$): (*E*) δ −62.4; (*Z*) δ −62.2. ^{11}B NMR (96 MHz, $CDCl_3$): δ 29.5. HRMS ESI (+), CH_3OH: $[M + Na]^+$ calcd for $C_{16}H_{20}BF_3O_2$, 335.1406; found, 335.1406.

***tert*-Butyl-3-(3-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)allyl)-1*H*-indole-1-carboxylate (3q).** Procedure A. Purified using EtOAc/cyclohexane (5:95); 108 mg (81%, *E*/*Z* = 86/14). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): (*E*) δ 1.28 (s, 12H), 1.69 (s, 9H), 3.57 (dd, *J* = 6.0, 1.5 Hz, 2H), 5.57 (dt, *J* = 17.7, 1.5 Hz, 1H), 6.85 (dt, *J* = 17.8, 6.0 Hz, 1H), 7.22−7.28 (m, 1H), 7.31−7.36 (m, 1H), 7.42 (br s, 1H), 7.51−7.53 (m, 1H), 8.15 (d, *J* = 7.3 Hz, 1H); (*Z*) δ 1.35 (s, 12H), 1.69 (s, 9H), 3.86 (dd, *J* = 7.5, 1.1 Hz, 2H), 5.50−5.55 (m, 1H), 6.65 (dt, *J* = 13.8, 7.5 Hz, 1H), 7.22−7.28 (m, 1H), 7.31−7.36 (m, 1H), 7.42 (br s, 1H), 7.64−7.67 (m, 1H), 8.15 (d, *J* = 7.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): (*E*) δ 24.8, 28.2, 31.3, 83.1, 83.3, 115.2, 118.0, 119.2, 122.4, 123.3, 124.3, 130.5, 135.6, 149.8, 150.8; (*Z*) δ 24.9, 28.2, 30.2, 83.1, 83.3, 115.2, 118.0, 119.3, 122.2, 123.3, 124.3, 130.5, 135.6, 149.8, 151.6. ^{11}B NMR (96 MHz, $CDCl_3$): δ 29.8. HRMS ESI (+), CH_3OH: $[M + Na]^+$ calcd for $C_{22}H_{30}BNO_4$, 406.2166; found, 406.2167

1-Fluoro-4-(3-phenylallyl)benzene (6). To a solution of 2-(3-(4-fluorophenyl)prop-1-enyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane **3n** (50 mg, 0.19 mmol) in anhydrous THF (2.0 mL) were added $Pd(OAc)_2$ (2.14 mg, 9.53 μmol, 0.05 equiv), PPh_3 (7.50 mg, 28.60 μmol, 0.15 equiv), K_2CO_3 (39 mg, 0.28 mmol, 1.50 equiv), and phenyl iodide (32.00 μL, 0.28 mmol, 1.50 equiv). The resulting mixture was heated under reflux conditions for 18 h. After this time, water was added to quench the reaction, and the mixture was extracted with Et_2O. Organic phases were washed with brine, dried over $MgSO_4$, and concentrated under a vacuum. Crude product was purified by column chromatography using cyclohexane/EtOAc (98:2) as the eluent to afford the desired product **6** as a colorless oil (35 mg, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): (*E*) δ 3.54 (d, *J* = 6.4 Hz, 2H), 6.24 (dt, *J* = 15.7, 6.7 Hz, 1H), 6.36 (dt, *J* = 15.7, 1.4 Hz, 1H), 6.99−7.08 (m, 2H), 7.20−7.40 (m, 7H); (*Z*) δ 3.67 (d, *J* = 7.3 Hz, 2H), 5.74 (dt, *J* = 11.5, 7.3 Hz, 1H), 6.51 (dt, *J* = 11.5, 1.9 Hz, 1H), 6.99−7.08 (m, 2H), 7.20−7.40 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$): (*E*) δ 38.5, 115.2 (d, *J* = 21.0 Hz), 126.1, 127.2, 128.5, 129.0, 130.0 (d, *J* = 8.0 Hz), 131.2, 135.7 (d, *J* = 3.2 Hz), 137.3, 161.5 (d, *J* = 244.0 Hz); (*Z*) δ 38.5, 115.6 (d, *J* = 21.8 Hz), 126.4, 126.9, 128.7, 129.0, 129.7 (d, *J* = 8.0 Hz), 131.2, 135.7 (d, *J* = 3.2 Hz), 137.3, 161.5 (d, *J* = 244.0 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): (*E*) δ −117.26; (*Z*): δ −114.26. These data are in agreement with those reported in the literature.[34]

Potassium-3-(4-fluorophenyl)propenyl-1-trifluoroborate (7). To a solution of **3n** (97 mg, 0.37 mmol) in methanol (3.5 M) at 0 °C were added KHF_2 (87 mg, 1.11 mmol, 3 equiv) and water (80 μL). The ice bath was removed, and the mixture was stirred at room temperature for 4 h. After this time, methanol and water were removed under reduced pressure, and the crude product was washed with acetone and then filtrated. Acetone was then removed under reduced pressure, and the crude product was washed with Et_2O and then filtrated to give the desired product **7** as a white powder (58 mg, 65%). Mp = 240 °C. ^{1}H NMR (300 MHz, acetone-d_6): (*E*) δ 3.12 (d, *J* = 6.2 Hz, 2H), 5.28−5.37 (m, 1H), 5.69 (dt, *J* = 16.7, 6.2 Hz, 1H), 6.78−6.89 (m, 2H), 7.04 (dd, *J* = 8.7, 5.7 Hz, 2H); (*Z*) δ = 3.37 (d, *J* = 7.1 Hz, 2H), 5.28−5.37 (m, 1H), 5.52−5.59 (m, 1H), 6.78−6.89 (m, 2H), 7.12 (dd, *J* = 8.7, 5.7 Hz, 2H). ^{13}C NMR (75 MHz, acetone-d_6): (*E*) δ

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42.1, 115.4 (d, J = 21.1 Hz), 127.8 (d, J = 181.0 Hz), 131.0 (d, J = 7.9 Hz), 134.7 (q, J = 4.6 Hz), 139.0 (d, J = 3.1 Hz), 161.9 (d, J = 240.0 Hz); (*Z*) δ 37.7, 115.2 (d, J = 20.8 Hz), 127.8 (d, J = 181.0 Hz), 131.1 (d, J = 7.8 Hz), 136.3 (q, J = 4.5 Hz), 140.3 (d, J = 2.6 Hz), 161.8 (d, J = 240.0 Hz). ^{19}F NMR (376 MHz, acetone-d_6): (*E*) δ −120.1, −141.3 (m); (*Z*) δ −120.6, −135.6 (m). ^{11}B NMR (96 MHz, acetone-d_6): δ 3.0. HRMS (ESI): $[M + 2K]^+$ calcd for $C_9H_8BF_4K$, 280.9929; found, 280.9928.

1-Fluoro-4-(3-iodo-allyl)benzene (8). To a solution of crude mixture **3n** in technical grade THF (3.0 mL) was added a 3 M NaOH solution (0.35 mL, 1.05 mmol, 3 equiv). The resulting mixture was stirred at room temperature for 10 min before the addition of a 0.2 M iodine solution in THF (2.53 mL, 0.70 mmol, 2 equiv). The resulting mixture was stirred at room temperature for 30 min. After this time, a saturated solution of $Na_2S_2O_3$ was added, and the mixture was extracted with Et_2O. Organic phases were washed with brine, dried over $MgSO_4$, and concentrated under a vacuum. Crude product was purified by column chromatography using cyclohexane as the eluent to afford the desired product **8** as a colorless oil (57 mg, 62%). ^{1}H NMR (300 MHz, $CDCl_3$): (*E*) δ 3.36 (d, J = 6.7 Hz, 2H), 6.09 (dt, J = 14.3, 1.5 Hz, 1H), 6.68 (dt, J = 14.3, 6.7 Hz, 1H), 6.98−7.05 (m, 2H), 7.12−7.17 (m, 2H); (*Z*) δ 3.49 (d, J = 6.3 Hz, 2H), 6.31−6.41 (m, 2H), 6.98−7.05 (m, 2H), 7.12−7.17 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): (*E*) δ 41.3, 76.4, 115.4 (d, J = 21.3 Hz), 130.0 (d, J = 8.0 Hz), 133.6 (d, J = 3.3 Hz), 144.6, 161.5 (d, J = 244.7 Hz); (*Z*) δ 41.3, 76.4, 115.4 (d, J = 21.3 Hz), 130.0 (d, J = 8.0 Hz), 133.6 (d, J = 3.3 Hz), 144.6, 161.5 (d, J = 244.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): (*E*) δ −116.5; (*Z*) δ −116.7. HRMS ASAP (+), 150 °C: $[M]^+$. calcd for C_9H_8FI, 261.9654; found, 261.9655.

(4-Fluoro-phenyl)acetaldehyde (9). To a solution of crude product of **3n** in a THF/H_2O mixture (1:1, 3.0 mL) was added $NaBO_3{\cdot}4H_2O$ (63.4 mg, 0.39 mmol, 1.1 equiv). The resulting mixture was stirred at room temperature for 4 h. After this time, water was added, and the reaction mixture was extracted with Et_2O. Organic phases were washed with brine, dried over $MgSO_4$, and concentrated under a vacuum. Crude product was purified by column chromatography using cyclohexane/EtOAc (80:20) as the eluent to afford the desired product **9** as a colorless oil (36 mg, 68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.76−2.81 (m, 2H), 2.95 (t, J = 7.4 Hz, 2H), 6.96−7.02 (m, 2H), 7.15−7.19 (m, 2H), 9.83 (t, J = 1.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.3, 45.4, 115.4 (d, J = 21.3 Hz), 129.7 (d, J = 7.8 Hz), 132.2 (d, J = 3.2 Hz), 161.6 (d, J = 245.0 Hz), 201.2. ^{19}F NMR (282 MHz, $CDCl_3$): δ −116.9. These data are in agreement with those reported in the literature.[35]

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR spectra of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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