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ARTICLE

Ligand-free copper-catalyzed borylative defluorination: Access to *gem*-difluoroallyl boronic acid derivatives

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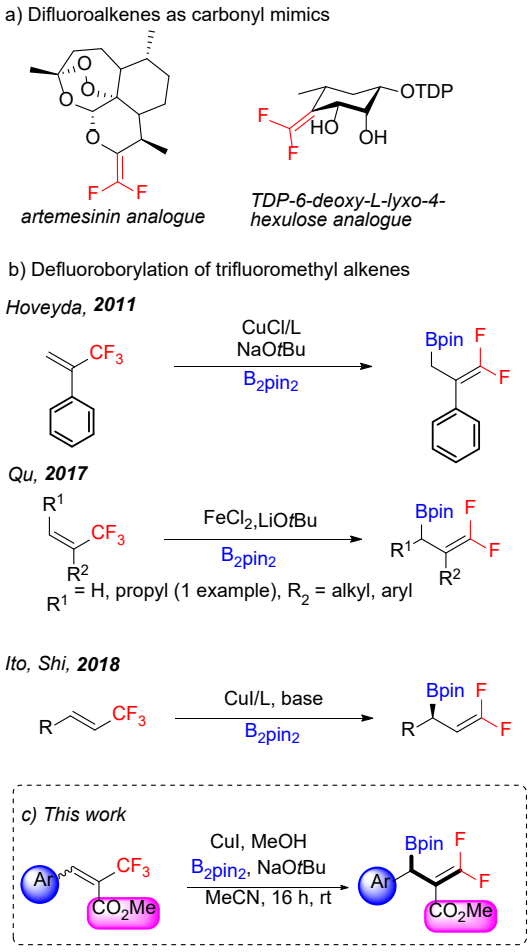
We report a ligand-free copper-catalyzed β-borylation, defluorination of β-substituted, α-trifluoromethyl-α,β-unsaturated esters. The reaction affords geminal-difluoroallyl boronic acid derivatives in moderate to good yield. The reaction was tolerant of various substrates, and the utility of products was demonstrated in the defluorinative functionalization of the difluoroalkene to afford enol ethers.

Introduction

Compounds bearing boronic ester derivatives are versatile small molecule building blocks as they readily undergo a large variety of transformations. As with other boronic esters, allyl boronates also facilitate a wide variety of synthetic transformations[1-3] including oxidation, cross-coupling reactions,[4-6] and allylboration of carbonyls.[7-12] However, the addition of a fluorine atom in compounds can confer advantageous properties in pharmaceutical chemistry including metabolic stability, increased lipophilicity, and potency.[13] For example, the *gem*-difluoroethylene construct can serve as a bioisostere for the carbonyl group, which is present in several pharmaceutical compounds (Scheme 1a). The seminal report of carbonyl mimicry by *gem*-difluoroalkene is in the design of the TDP-L-rhamnose synthase inhibitor where the carbonyl of TDP-6-deoxy-L-lyxo-4-hexulose was replaced with *gem*-difluoroalkene in TDP-4,6-dideoxy-4-difluoromethylene-L-lyxo-hex-4-enopyranose.[14]
Likewise, an elegant demonstration in pharmaceutical design is with the antimalarial agent artemisinin. Installation of the difluoroalkene improved potency by two-fold (IC_{50} 4.6 nM) and drug-like properties to confer increase lipophilicity and metabolic stability.[15-17] In addition to medicinal chemistry application, *gem*-difluoroalkenes are valuable as synthetic intermediates.[18] Their utility is demonstrated in important transformations such as cross-coupling,[19, 20] nucleophilic substitutions,[21, 22] hydroboration and hydrosilylation,[23] alkylations,[24] alkenylations,[25] and multiborylation.[26] Common methods towards the formation of *gem*-difluoroalkenes include difluoromethylenation (Wittig-,



Scheme 1 *gem*-Difluoroalkenes in medicinal chemistry and approaches towards *gem*-difluoroallyl boronic acid derivatives.

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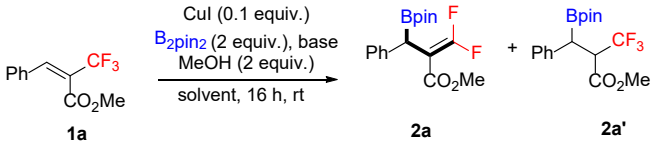
† Footnotes relating to the title and/or authors should appear here.
Electronic Supplementary Information (ESI) available: characterization as well as ^{1}H, ^{13}C, ^{11}B and ^{19}F NMR spectra. See DOI: 10.1039/x0xx00000x

Table 1 Optimization of Reaction Conditions[a]



1a **2a** **2a'**

Entry	Solvent	Base (equiv)	Ratio **2a:2a'**	% Yield[b]
1	MeCN	NaO*t*Bu (2)	14:1	66 (62)
2	MeCN	KO*t*Bu (2)	0:100	7 (0)
3	MeCN	LiO*t*Bu (2)	1:3	23 (6)
4	MeCN	Na_2CO_3 (2)	1:7	85 (11)
5	MeCN	Cs_2CO_3 (2)	0:100	22 (0)
6	dioxane	NaO*t*Bu (2)	3:1	59 (45)
7	toluene	NaO*t*Bu (2)	2:1	33 (22)
8	THF	NaO*t*Bu (2)	2:1	51 (35)
9	MTBE	NaO*t*Bu (1)	1:3	78 (21)
10[c,d]	MeCN	NaO*t*Bu (1)	21:1	65 (62)
11[c,d]	MeCN	NaO*t*Bu (1.3)	4:1	80 (63)
12[c,d,e]	MeCN	NaO*t*Bu (1.3)	15:1	80 (75)
13[f]	MeCN	NaO*t*Bu (1.2)	--	--
14[g]	MeCN	NaO*t*Bu (1.2)	3.3:1	51 (39)

[a]General procedure: copper iodide (0.1 equiv, 0.020 mmol), bis(pinacolato)diboron, base, and methyl (*E*)-3-phenyl-2-(trifluoromethyl)acrylate (**1a**). [b] ^{19}F NMR yields of **2a** and **2a'**; parenthesis is **2a** only. [c]0.5:1 mixture of (*Z*)- and (*E*)- **1a** used. [d]1.5 equiv. of B_2pin_2. [e]Powdered 4 Å molecular sieves added. [f]Reaction run without copper. [g]Without methanol.

Julia-, or Julia-Kocienski-type),[27] β-elimination of functionalized difluoromethyl compounds,[28] S_N2'-type defluorination of 2- trifluoromethyl-1-alkenes,[29] and *gem*-difluoroolefination of diazo compounds; however, these reaction conditions are not amenable to many functional groups.[30] However, recent efforts overcome this limitation with nickel catalysis through defluorinative cross-coupling processes.[31, 32]

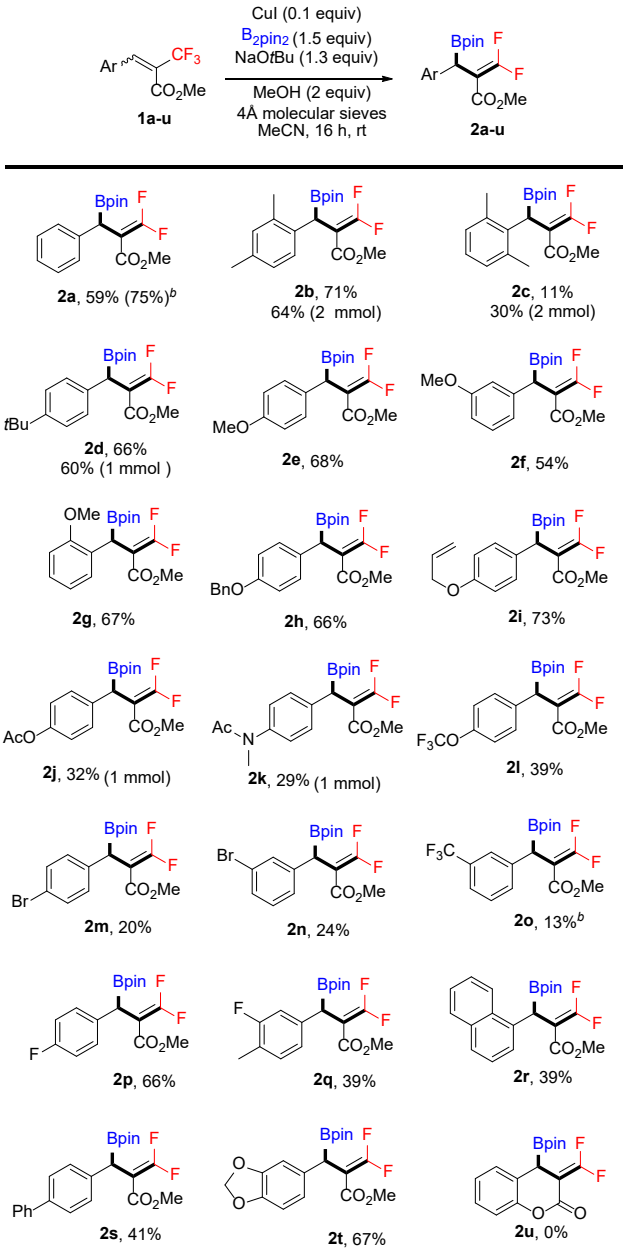
The presence of both a boronic acid functional group and fluorine atoms generates a special class of compounds with synergistic properties because the boron-carbon and fluorine-carbon bond components could either be left intact for medicinal chemistry purposes or be used for further reaction. Unfortunately, synthetic methods for the preparation of *gem*-difluoroallyl boronic acid derivatives are scarce (Scheme 1b). Seminal work by Hoveyda and co-workers reported an example of NHC-Cu catalyzed borylative defluorination of α-trifluoromethyl styrene.[33] In 2017, Qu and co-workers developed an iron(II)-catalyzed borylation/β-fluorine elimination reaction that gives rise to allylboryl *gem*-difluoroalkenes. The reaction worked well for a variety of alkyl and aryl alkenes.[34] Recently, Ito[35, 36] and Shi[37] both reported enantioselective copper-catalyzed borylation of CF_3-substituted alkenes and allenes. Using chiral Josiphos-type ligands, a variety of chiral allylboronates were synthesized. Similarly, Cao and co-workers reported a copper-catalyzed method using a Xantphos ligand for the borylation of trifluoromethyl styrenes.[38] With the exception of a handful of examples,[39] these reactions are limited to disubstituted alkenes containing alkyl and aryl substituents. Incorporation of both a boronic ester and a *gem*-difluoroalkene into a molecule would provide multiple functional handles that allow further modification using both boron and fluorine chemistry. While β-borylation of α,β-unsaturated esters[40] and borylation of trifluoromethyl alkenes are both known, there are no methods that exist for the transformation of the more challenging trisubstituted alkenes such as β-substituted, α-trifluoromethyl-α,β-unsaturated esters[41] to boron-containing *gem*-difluoro alkenes. Herein, we report a ligand free copper catalyzed method for the borylative defluorination of α,β-unsaturated esters.

Results and discussion

We began our study with 10 mol% copper iodide, bis(pinacolato)diboron, sodium *tert*-butoxide, and methanol in acetonitrile (Table 1). In the presence of methyl (*E*)-3-phenyl-2-(trifluoromethyl)acrylate (**1a**), the Bpin moiety added to the β carbon followed concomitant elimination of fluorine to afford *gem*-difluoroalkene **2a** in good yield (entry 1). We were pleased to find that the reaction was selective for the borylated *gem*-difluoroalkene **2a** relative to the β-borylated derivative **2a'**. Subsequent screening of metal counterions suggested the importance of the sodium cation (entries 2-3). Interestingly, we found that the use of carbonate bases resulted in a change in selectivity towards the β borylated product **2a'** likely allowing rapid protonation of the resulting enolate intermediate (entries 4-5). The screening of additional solvents gave reduced yield and selectivity for product **2a** (entries 6-9). Reduction of *bis*(pinacolato)diboron and base equivalency indicated that 1.5 and 1.3 equivalents, respectively, were needed (entries 10-11). We also found that the addition of powdered 4Å molecular sieves increased the yield of product **2a** (entry 12). As shown in entry 13, a copper catalyst is required for the transformation as upon removal of copper iodide from the reaction, no product was formed. While methanol can be the proton source for generating **2a'**, the reaction was sluggish and resulted in lower yield without methanol (entry 14). To confirm that both alkene geometries undergo the reaction, the borylation was successfully performed with a mixture of *E/Z* isomers (entries 10-12).

With optimized conditions in hand (entry 12), we set out to investigate the substrate scope for the reaction (Scheme 2). We were pleased to find that methyl groups were well-tolerated in *ortho* and *para* positions on the phenyl ring (**2b-c**), with a moderate reduction in yield for the sterically hindered 2,5-dimethyl substituted ring (**2c**). The bulkier *tert*-butyl group in the *para* position (**2d**) was afforded in 66% yield, and running the reaction at 2.0 mmol scale resulted in only a slight reduction in yield (60%). Substrates containing electron-donating methoxy group in the *ortho, meta,* and *para* positions (**2e-2g**) were borylated in good yields. Oxygen protecting groups such as benzyl (**1h**) and allyl (**1i**) were tolerated in the reaction giving **2h** and **2i**

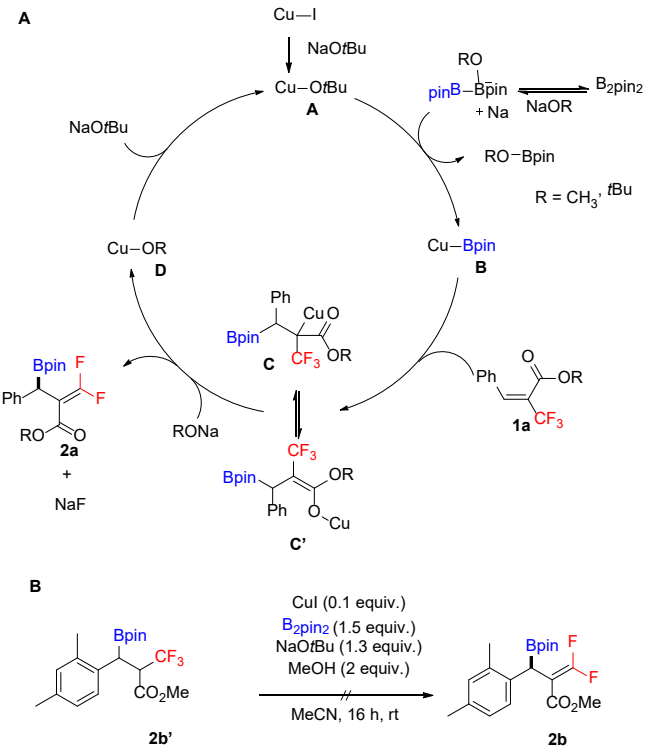
in good yields. Importantly, the reaction was chemoselective for the internal alkene in **2i**. Acetyl containing substrates such as 1j and **1k** afforded the desired products in modest yields. Substrates containing electron-withdrawing groups such as



Scheme 2 Substrate scope. Reaction conditions: [a]General procedure: To a vial containing powdered 4Å molecular sieves (50 mg) was added copper iodide (0.020 mmol), *bis*(pinacolato)diboron (0.300 mmol), sodium *tert*-butoxide (0.260 mmol), and substrate 1 (0.200 mmol). Acetonitrile (0.800 mL) and methanol (0.400 mmol) were added, and the reaction was stirred 16 h under inert atmosphere. [b] ^{19}F NMR yield using 2-fluoro-4-iodoaniline as an internal standard.

trifluoromethoxy, trifluoromethyl, and halogens (2l-2o) were borylated with acceptable yields. Fortunately, the substrate bearing fluorine in the *para* position (2p) was generated in 66% yield. Disubstituted aryl ring (2q) as well as larger aryl groups such as naphthyl, biphenyl, and benzodioxolyl groups (**2r**-**t**) were well-tolerated. Finally, borylation of a ring fused trifluoromethyl coumarin 1u was unsuccessful. Performing the reaction at larger scale also affords the products in good yields. For example, **2b** was isolated at 64% yield at 2 mmol scale.

A proposed mechanism is illustrated in Scheme 3A. Activation of B_2pin_2 by a methoxide anion results in the formation



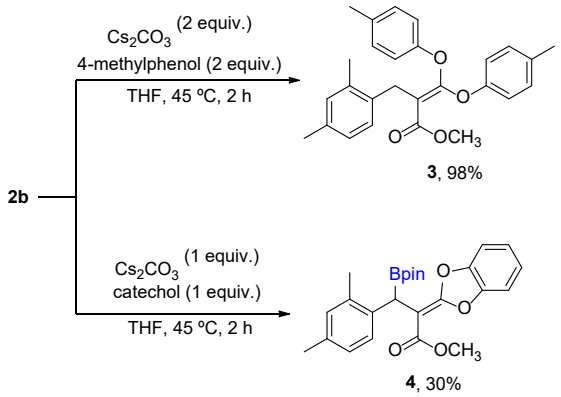
Scheme 3 Proposed catalytic cycle and mechanistic insight.

of the copper-boryl species **B**. Addition of **B** across the double bond in **1** results in the formation of ester intermediate **C** that can tautomerize to the copper-bound enolate intermediate **C'**. Exchange of the ligands on copper results in the elimination of fluoride to form product **2** and copper-alkoxide. A reaction with additional base results in the regeneration of the active copper catalyst. As expected, protonation of intermediate **C** results in the formation of side product **2'**. Thus, compound **2'** could be an intermediate towards **2a** *via* a reversible protonation-deprotonation of **C.** To investigate this possibility, we subjected β-boryl, α-trifluoromethyl **2b'** under the same reaction conditions and observed none of the *gem*-difluoroallyl boronic ester **2b** (Scheme 3B). This control experiment indicated that **2'** is not an intermediate towards the formation of **2b**.

To demonstrate the utility of *gem*-difluoroallyl boronic acid derivatives, allyl boronic ester **2b** was treated with cesium carbonate and nucleophiles such as 4-methylphenol and catechol (Scheme 4).[42] Interestingly, when excess cesium carbonate was employed, defluorinative functionalization resulted in the formation of the protodeborylated enolether **3** in excellent yield. When a single equivalent of cesium carbonate was used in the presence of the nucleophile catechol, the borylated enolether **4** was formed in moderate yield. Attempts towards allylation as well as cross-coupling reactions using **2b** led to protodeboration.

Conclusions

In conclusion, a ligand-free, copper-catalyzed protocol for the synthesis of borylated *gem*-difluoroallyl boronic esters was developed. The reaction proceeded in good yield for a variety of substrates, and the utility of the products was demonstrated in the functionalization of the vinyl fluoride moiety to afford disubstituted enol ethers.



Scheme 4 Transformations of **2b**.

Experimental section

General Experimental Information. Unless otherwise noted, all reactions were performed under argon in flame-dried glassware. Methyl 2-(trifluoromethyl)acrylate, aryl iodides, palladium acetate, silver trifluoromethane sulfonate, and 1,4-dioxane were commercially available and used as received. Dry acetonitrile and methanol were purchased with sure-seal tops and used as received. All other solvents were dried using an Innovative Technology Pure Solv-MD solvent purification system. Bis(pinacolato)diboron was donated by AllyChem. Powdered molecular sieves (4 Å, <50 μm) were purchased from Acros Organics and used as received. TLC analyses were performed using aluminum backed silica gel F_{254} plates from SiliCycle Inc. Chromatography purification was performed using SiliaFlash P60 40-63 μm, 60 A silica from SiliCycle Inc. ^{1}H, ^{13}C, ^{19}F, and ^{11}B NMR spectra were recorded using an Agilent MR-400 MHz, Varian Inova 400 MHz, or Bruker Avance II 500 MHz spectrometer. All spectra were internally referenced to $CDCl_3$ or TMS. Chemical shifts are reported in δ ppm. Ratios of isomeric products were measured by the integration of ^{19}F NMR signals. ^{19}F NMR yields were determined using 2-fluoro-4-iodoaniline as an internal standard. ESI mass spectra were acquired with an Agilent 6220 LC-ESI-TOF or a Thermo Scientific Q-Exactive Orbitrap.

General procedure for the synthesis of substrates 1a-u.

Silver trifluoromethane sulfonate (1.5 mmol, 1.5 equiv) was added to a round bottom flask equipped with a stir bar. The reaction was purged with argon, and 1,4-dioxane (5.0 mL) was added. Methyl 2-(trifluoromethyl)acrylate (1.2 mmol, 1.2 equiv) and aryl iodide (1.0 mmol, 1.0 equiv) were added to the flask, and argon was bubbled through the reaction mixture for 5 minutes. Palladium acetate (0.10 mmol, 0.10 equiv) was added and the reaction was stirred at 90 ºC for 2 h. The reaction was cooled to room temperature, and celite was added. The solvent was removed *in vacuo*, and the crude reaction was purified via column chromatography (solid loading) to yield the corresponding esters **1a**-**f**, **1k**-**v**. Compounds **1a**, **1e**, **1f**, **1g**, **1m**, **1s**, **1u**, and **1v** are known.[43]

Cesium carbonate (1.1 equiv) and **1v** (1.0 equiv) were added to a round bottom flask containing a stir bar. The reaction was purged with argon and dry acetonitrile (1.0 mL), and alkyl bromide or acetyl chloride was added (1.1 equiv). The reaction was stirred overnight. The solvent was removed in vacuo, and the crude reaction was purified *via* column chromatography to yield the corresponding esters **1g**-**j**.

methyl 3-(2,4-dimethylphenyl)-2-(trifluoromethyl)acrylate (1b). Yellow liquid, 78% (201 mg, mixture of isomers *E/Z* 69/31). Purified on silica gel using DCM:Hexanes 2:3.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H, *Z*), 7.61 (s, 1H, *E*), 7.13 – 6.94 (m, 3H, *E* + 3H, *Z*), 3.90 (s, 3H, *Z*), 3.70 (s, 3H, *E*), 2.34 (s, 3H, *Z*), 2.33 (s, 3H, *E*), 2.30 (s, 3H, *E*), 2.28 (s, 3H, *Z*). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.9 (q, *J* = 1.8 Hz), 163.8 (q, *J* = 0.9 Hz), 148.6 (q, *J* = 3.0 Hz), 141.1 (q, *J* = 5.7 Hz), 140.4, 140.2, 136.9, 136.3, 131.3, 130.8, 129.6, 129.2, 128.7 (q, *J* = 3.3 Hz), 128.1, 126.7, 126.5, 123.6 (q, *J* = 31.2 Hz), 122.8 (q, *J* = 31.4 Hz), 122.3 (q, *J* = 273.0 Hz), 122.1 (q, *J* = 274.4 Hz), 52.9, 52.5, 21.4, 21.4, 20.0, 19.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.30 (s), -63.82 (d, *J* = 1.5 Hz). HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{13}F_3O_2$ 259.0940; Found 259.0940.

methyl 3-(2,6-dimethylphenyl)-2-(trifluoromethyl)acrylate (1c). Colorless Liquid, 40% (104 mg, mixture of isomers *E/Z* 49/51). Purified on silica gel using DCM:Hexanes 2:3.^{1}H NMR (400 MHz $CDCl_3$) δ 8.15 (s, 1H, *Z*), 7.66 (s, 1H, *E*), 7.18 – 7.12 (m, 1H, *E* + 1H, *Z*), 7.07 – 7.02 (m, 2H, *E* + 2H, *Z*), 3.93 (s, 3H, *Z*), 3.61 (s, 3H, *E*), 2.19 – 2.18 (m, 6H, *E* + 6H, *Z*). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.1 (q, *J* = 1.3 Hz), 162.4 (q, *J* = 1.0 Hz), 149.1 (q, *J* = 3.3 Hz), 144.7 (q, *J* = 5.6 Hz), 134.6, 133.96 (q, *J* = 1.4 Hz), 132.9, 132.8, 128.4, 128.3, 127.5, 127.3, 126.5 (q, *J* = 30.6 Hz), 125.4 (q, *J* = 30.8 Hz), 121.96 (q, *J* = 273.3 Hz), 121.9 (q, *J* = 274.9 Hz), 53.0, 52.4, 20.3, 20.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.75 (s), -64.12 (d, *J* = 1.7 Hz). HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{14}F_3O_2$ 259.0940; Found : 259.0945.

methyl 3-(4-(tert-butyl)phenyl)-2-(trifluoromethyl)acrylate (1d). Colorless liquid, 87% (249 mg, mixture of isomers *E/Z* 70/30). Purified on silica gel using DCM:Hexanes 2:3. ^{1}H NMR (400 MHz, $CDCl_3$) δ8.05 (s, 1H, *Z*), 7.44 – 7.31 (m, 4H, *Z* + 5H, *E*), 3.89 (s, 3H, *Z*), 3.82 (s, 3H, *E*), 1.33 (s, 9H, *Z*),1.32 (s, 9H, *E*). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.3 (q, *J* = 2.1 Hz), 164.2 (q, *J* = 1.0 Hz), 154.3, 154.1, 148.7 (q, *J* = 2.9 Hz), 140.4 (q, *J* = 5.7 Hz), 129.9 (q, *J* = 2.6 Hz), 129.6, 129.5 (br. s), 129.3, 125.8, 125.5, 122.4 (q, *J* = 273.0 Hz), 122.1 (q, *J* = 274.1 Hz), 122.1 (q, *J* = 31.4 Hz), 121.4 (q, *J* = 32.3 Hz), 52.9, 52.7, 35.1 (br. s), 31.3, 31.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.06 (s), -63.65 (d, *J* = 1.5). HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{18}F_3O_2$ 287.1253; Found 287.1257.

methyl 3-(4-(benzyloxy)phenyl)-2-(trifluoromethyl)acrylate (1h). Colorless oil, 53% (72 mg, mixture of isomers *E/Z* 80/20). Reaction Scale: 0.40 mmol Purified on silica gel with Hexanes:EtOAc 9:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (s, 1H, *Z*), 7.45 – 7.35 (m, 7H, *Z* + 7H, *E*), 7.34 (br. s, 1H, *E*), 7.02 – 6.96 (m, 2H, *Z* + 2H, *E*), 5.11 – 5.10 (m, 2H, *Z* + 2H, *E*), 3.89 (s, 3H, *Z*), 3.82

(s, 3H, *E*). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.4 (q, *J* = 2.2 Hz), 164.4 (q, *J* = 1.0 Hz), 160.9, 160.8, 148.3 (q, *J* = 2.7 Hz), 140.4 (q, *J* = 5.8 Hz), 136.4, 132.4 (q, *J* = 2.7 Hz), 131.7 (br. s), 128.8, 128.8, 128.4, 128.4, 127.6, 127.6, 124.9, 124.8, 122.6 (q, *J* = 272.8 Hz), 122.3 (q, *J* = 273.9 Hz), 120.5 (q, *J* = 31.2 Hz), 119.8 (q, *J* = 32.4 Hz), 115.1, 114.8, 70.2, 70.2, 52.8, 52.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.07 (s), -63.39 (d, *J* = 1.6 Hz). HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{16}F_3O_3$ 337.0146; Found 337.0147.

methyl 3-(4-(allyloxy)phenyl)-2-(trifluoromethyl)acrylate (1i). Colorless oil, 88% (102 mg, mixture of isomers *E/Z* 81/19). Reaction Scale: 0.40 mmol. Purified on silica gel with Hexanes:EtOAc 9:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (s, 1H, *Z*), 7.41 (d, *J* = 8.7 Hz, 2H, *Z*), 7.38 (d, *J* = 8.8 Hz, 2H, *E*), 7.34 – 7.31 (m, 1H, *E*), 6.95 – 6.90 (m, 2H, *Z* + 2H, *E*), 6.09 – 5.98 (m, 1H, *Z* + 1H, *E*), 5.45 – 5.39 (m, 1H, *Z* + 1H, *E*), 5.33 – 5.29 (m, 1H, *Z* + 1H, *E*), 4.59 – 4.55 (m, 2H, *Z* + 2H, *E*), 3.88 (s, 3H, *Z*), 3.82 (s, 3H, *E*). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.4 (q, *J* = 2.2 Hz), 164.4 (q, *J* = 1.0 Hz), 160.7, 160.7, 148.3 (q, *J* = 2.9 Hz), 140.4 (q, *J* = 5.8 Hz), 132.7, 132.4 (q, *J* = 2.8 Hz), 131.7 (br s.), 124.8, 124.7, 122.6 (q, *J* = 272.8 Hz), 122.3 (q, *J* = 273.9 Hz), 120.4 (q, *J* = 31.2 Hz), 119.7 (q, *J* = 32.4 Hz), 118.3, 118.2, 114.9, 114.7, 69.0, 69.0, 52.8, 52.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.07 (s), -63.38 (d, *J* = 1.8 Hz). HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{14}F_3O_3$ 287.0890; Found 287.0889.

methyl 3-(4-acetoxyphenyl)-2-(trifluoromethyl)acrylate (1j). Colorless semisolid, 88% (77 mg, mixture of isomers *E/Z* 76/24). Reaction Scale: 0.30 mmol. Purified on silica gel with Hexanes/EtOAc 9:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (s, 1H, *Z*), 7.44 – 7.39 (m, 2H, *Z* + 2H, *E*), 7.38 (s, 1H, *E*), 7.16 – 7.10 (m, 2H, *Z* + 2H, *E*), 3.88 (s, 3H, *Z*), 3.78 (s, 3H, *E*), 2.30 (s, 3H, Z), 2.30 (s, 3H, *E*). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.0, 168.9, 163.7 (q, *J* = 2.1 Hz), 163.6 (q, *J* = 0.9 Hz), 152.3, 152.1, 147.4 (q, *J* = 3.0 Hz), 139.5 (q, *J* = 5.8 Hz), 130.9 (q, *J* = 2.6 Hz), 130.6 (br. s), 123.0, 129.8, 123.1 (q, *J* = 31.5 Hz), 122.4 (q, *J* = 32.2 Hz), 122.1 (q, *J* = 273.2 Hz), 122.0, 121.8 (q, *J* = 274.3 Hz), 121.7, 52.9, 52.7, 21.2 (br. s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.06 (s), -63.86 (d, *J* = 1.8 Hz). HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{12}F_3O_4$ 289.0682; Found 289.0688.

methyl 3-(4-(N-methylacetamido)phenyl)-2-(trifluoromethyl)acrylate (1k). Yellow oil, 40% (114 mg, mixture of isomers *E/Z* 60/40 by ^{1}H NMR). Purified on silica gel using DCM:Hexanes 2:3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H, *Z*), 7.48 – 7.43 (m, 2H, *Z* + 2H, *E*), 7.42 – 7.40 (br. s, 1H, *E*), 7.26 – 7.22 (m, 2H, *Z* + 2H, *E*), 3.92 (s, 3H, *Z*), 3.83 (s, 3H, *E*), 3.30 (s, 3H, *Z*), 3.29 (s, 3H, *E*), 1.93 (br. s, 3H, *Z* + 3H, *E*). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.3, 170.2, 163.6 (q, J = 1.9 Hz), 163.5, 147.2, 146.2, 146.0, 139.6 (q, *J* = 5.8 Hz), 130.8, 130.8, 130.7 (br. s), 127.2, 126.9, 123.8 (br. q, *J* = 31.7 Hz), 123.2 (br. q, *J* = 32.7 Hz), 122.0 (q, *J* = 273.3 Hz), 121.8 (q, *J* = 274.4 Hz), 53.0, 52.8, 37.1 (br. s), 22.5 (br. s). ^{19}F NMR (376 MHz, , $CDCl_3$) δ -58.03 (s), -63.90 (d, *J* = 1.9 Hz). HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{15}F_3NO_3$ 302.0999; Found: 302.0980.

methyl (*E*)-3-(4-(trifluoromethoxy)phenyl)-2-(trifluoromethyl)acrylate (1l). Pale yellow liquid, 70% (383 mg). Reaction Scale: 1.74 mmol. Purified on silica gel using DCM:Hexanes 2:3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.8 Hz, 2H), 7.40 (q, *J* = 1.8 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 3.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5 (q, *J* = 1.0 Hz), 150.6 (q, *J* = 1.8 Hz), 139.3 (q, *J* = 5.8 Hz), 131.0, 130.8, 124.2 (q, *J* = 31.6 Hz), 122.1 (q, *J* = 273.3 Hz), 120.9, 120.5 (q, *J* = 258.3 Hz), 52.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.77 (s), -64.01 (d, *J* = 1.6 Hz). HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{12}H_9F_6O_3$ 315.0450; Found 315.0466.

methyl 3-(3-bromophenyl)-2-(trifluoromethyl)acrylate (1n). Pale Yellow liquid, 91% (272 mg, mixture of isomers *E/Z* 71/29). Purified on silica gel using DCM:Hexanes 2:3.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H, *Z*), 7.56 – 7.51 (m, 2H, *Z* + 2H, *E*), 7.38 – 7.35 (m, 1H, *E*), 7.33 – 7.25 (m, 2H, *Z* + 2H, *E*), 3.91 (s, 3H, *Z*), 3.80 (s, 3H, *E*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4 (q, *J* = 1.9 Hz), 163.3 (q, *J* = 0.9 Hz), 146.7 (q, *J* = 3.0 Hz), 139.1 (q, *J* = 5.8 Hz), 134.6, 134.4, 133.3, 133.0, 132.0, 131.8 (q, *J* = 2.3 Hz),130.2, 130.0, 127.6 (br. s), 127.6 (q, *J* = 2.6), 124.8 (q, *J* = 31.7 Hz), 123.9 (q, *J* = 32.2 Hz), 122.7, 122.4, 121.9 (q, *J* = 273.4 Hz), 121.7 (q, *J* = 274.6 Hz), 53.1, 52.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.06 (s), -64.11 (d, *J* = 2.1 Hz). HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{11}H_9BrF_3O_2$ 308.9733; Found:308.9730

methyl 3-(4-fluorophenyl)-2-(trifluoromethyl)acrylate (1o). Colorless liquid, 97 % (253 mg, mixture of isomers *E/Z* 71/29). Purified on silica gel using DCM:Hexanes 2:3.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H, *Z*), 7.44 – 7.37 (m, 2H, *Z* + 2H, 1H, *E*), 7.13 – 7.05 (m, 2H, *Z* + 2H, *E*), 3.90 (s, 3H, *Z*), 3.80 (s, 3H, *E*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0 (d, *J* = 252.2 Hz), 163.9 (d, *J* = 252.0 Hz), 163.9 (q, *J* = 2.0 Hz), 163.7 (q, *J* = 0.8), 147.4 (q, *J* = 3.0 Hz), 139.7 (q, *J* = 5.8 Hz), 131.9 (dq, *J* = 8.6, 2.6 Hz), 131.6 (d, *J* = 8.8 Hz), 128.6 (d, *J* = 3.5 Hz), 128.4 (d, *J* = 3.5 Hz), 122.4 (qd, *J* = 32.2, 1.2 Hz), 122.41 (qd, *J* = 31.6, 1.5 Hz), 122.2 (q, *J* = 273.1 Hz), 122.0 (q, *J* = 274.3 Hz), 116.0 (d, *J* = 22.0 Hz), 115.7 (d, *J* = 22.0 Hz), 52.9, 52.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.10, -63.85 (d, *J* = 1.8 Hz), -108.91 (ddd, *J* = 13.6, 8.4, 5.3 Hz), -109.24 (ddd, *J* = 13.7, 8.5, 5.3 Hz). HRMS: (ESI) m/z: $[M+NH_4]^+$ calcd for $C_{11}H_{12}F_4NO_2$ 266.0799; Found : 266.0811.

methyl (*E*)-2-(trifluoromethyl)-3-(3-(trifluoromethyl)phenyl)acrylate (1p). Reaction scale – 1.85 mmol. Pale yellow liquid, 65% (358 mg). Purified on silica gel using DCM:Hexanes 2:3. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.2 Hz, 1H), 7.64 (s, 1H), 7.58 – 7.51 (m, 2H), 7.47 (s, 1H), 3.78 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.2, 139.3 (q, *J* = 5.8 Hz), 133.2, 132.3, 131.3 (q, *J* = 32.8 Hz), 129.3, 127.0 (q, *J* = 3.6 Hz), 126.0 (q, *J* = 3.7 Hz), 125.25 (q, *J* = 31.8 Hz), 123.7 (q, *J* = 272.5 Hz), 121.9 (q, *J* = 273.5 Hz), 52.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.98, -64.19 (d, *J* = 1.5 Hz). HRMS: (ESI) m/z: $[M + Na]^+$ calcd for $C_{12}H_8F_6NaO_2$ 321.0321; Found 321.0327.

methyl 3-(3-fluoro-4-methylphenyl)-2-(trifluoromethyl)acrylate (1q). Colorless liquid, 98% (258 mg, mixture of isomers *E/Z* 70/30). Purified on silica gel using DCM:Hexanes 2:3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H, *Z*), 7.32 (s, 1H, *E*), 7.24 – 7.17 (m, 1H, *Z* + 1H, *E*), 7.10 – 7.04 (m, 2H, *Z* + 2H, *E*), 3.90 (s, 3H, *Z*), 3.81 (s, 3H, *E*), 2.32 – 2.29 (m, 3H, *Z* + 3H, *E*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8 (q, *J* = 2.0 Hz), 163.8 – 163.7 (m), 162.4, 162.1, 159.9, 159.7, 147.2 (p, *J* = 2.9 Hz), 139.3 (qd, *J* = 5.9, 2.4 Hz), 131.8 (d, *J* = 5.5 Hz), 131.8 (d, *J* = 8.2 Hz), 131.6 (d, *J* = 8.2 Hz), 131.5 (d, *J* = 5.4 Hz), 128.0 (d, *J* = 17.3 Hz), 127.7 (d, *J* = 17.2 Hz), 123.5 (q, *J* = 31.6 Hz), 123.0 (q, *J* = 32.2 Hz), 122.2 (q, *J* = 273.2 Hz), 122.0 (q, *J* = 274.2), 116.1 (dq, *J* = 23.9, 2.6 Hz), 115.6 (dd, *J* = 24.0, 0.7 Hz), 53.0, 52.8, 14.7 (d, *J* = 3.4 Hz), 14.73 (d, *J* = 3.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.10, -63.90 (d, *J* = 1.7 Hz), -116.41 (ddd, *J* = 10.3, 7.9, 2.4 Hz), -116.86 (ddd, *J* = 10.2, 7.8, 2.3 Hz). HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{12}H_{11}F_4O_2$ 263.0690; Found: 263.0685.

methyl 3-(naphthalen-2-yl)-2-(trifluoromethyl)acrylate (1r). White semi-solid, 53% (150 mg, mixture of isomers *E/Z* 61/39). Purified on silica gel using DCM:Hexanes 2:3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H, *Z*), 8.11 (s, 1H, *E*), 7.96 – 7.77 (m, 3H, *Z* + 3H, *E*), 7.62 – 7.39 (m, 4H, *Z* + 4H, *E*), 3.96 (s, 3H, *Z*), 3.58 (s, 3H, *E*). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.6 (q, *J* = 1.7 Hz), 163.5 – 163.4 (m), 147.7 (q, *J* = 3.0 Hz), 140.7 (q, *J* = 5.7 Hz), 133.4, 133.2, 130.9, 130.7, 130.5, 130.4, 130.4, 130.3, 128.9, 128.8, 127.2, 127.1, 126.7 – 126.6 (m), 126.6, 126.6, 126.4 (br. s), 125.9 (q, *J* = 31.2 Hz), 125.2, 125.2, 124.5 (q, *J* = 31.6 Hz), 124.4, 123.9, 122.1 (q, *J* = 273.3 Hz), 122.0 (q, *J* = 274.4 Hz), 53.0, 52.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.27, -63.90 (d, *J* = 2.0 Hz). HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{12}F_3O_2$ 281.0784; Found: 281.0786.

methyl 3-(benzo[d][1,3]dioxol-5-yl)-2-(trifluoromethyl)acrylate(1t). Colorless liquid, 96% (264 mg, mixture of isomers *E/Z* 79/21). Purified on silica gel using DCM:Hexanes 2:3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H, *Z*), 7.28-7.26 (m, 1H, *E*), 7.00 – 6.88 (m, 2H, *Z* + 2H, *E*), 6.85 – 6.74 (m, 1H, *Z* + 1H, *E*), 6.03 (s, 2H, *Z*), 6.02 (s, 2H, *E*), 3.88 (s, 3H, *Z*), 3.83 (s, 3H, *E*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.28 (q, *J* = 1.7 Hz), 164.18 (q, *J* = 1.0 Hz), 149.9, 149.9, 148.2, 148.2 (q, *J* = 2.8 Hz), 148.0, 140.2 (q, *J* = 5.8 Hz), 126.2 – 126.1 (m), 126.1, 125.9 – 125.8 (m), 122.5 (q, *J* = 272.9 Hz), 122.2 (q, *J* = 274.0 Hz), 121.1 (q, *J* = 32.1, 31.7 Hz), 120.4 (q, J = 32.3), 109.9 (q, *J* = 3.5 Hz), 108.9, 108.6, 108.4, 101.9 (br. s) 52.8, 52.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.88, -63.45 (d, *J* = 2.0 Hz). HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{12}H_9F_3O_4$ 274.0447; Found: 274.0446.

General procedure for the synthesis of borylated products 2a-t. To a flame-dried 1 dram vial equipped with a stir bar was added copper iodide (0.1 equiv, 0.020 mmol), powdered 4 Å molecular sieves (0.050 g/0.20 mmol), bis(pinacolato)diboron (1.5 equiv, 0.30 mmol), and sodium *tert*-butoxide (1.3 equiv, 0.26 mmol). The vial was capped with a septa and purged with argon. Dry acetonitrile (0.80 mL) was added, followed by the ester **1** (1.0 equiv, 0.20 mmol) and methanol (2.0 equiv, 0.40 mmol). The argon line was removed and the septum covered with parafilm. The reaction was stirred at room temperature for 16 h. Celite was added to the reaction mixture and the solvent removed *in vacuo*. The reaction mixture was purified via column chromatography (solid loading) to yield the corresponding borylated gem-difluoroalkenes **2**.

methyl 3,3-difluoro-2-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2a). Colorless residue, 59% (40 mg). Purified on silica gel using DCM/Hexanes 1:3–1:0. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 4H), 7.21 – 7.14 (m, 1H), 3.76 (s, 3H), 3.41 (s, 1H), 1.28 (s, 6H), 1.24 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1 (dd, *J* = 13.0, 7.6 Hz), 160.6 (dd, *J* = 311.5, 295.1 Hz), 140.3 – 140.1 (m), 129.1, 128.4, 126.2, 91.3 (dd, *J* = 22.9, 6.4 Hz), 84.2, 52.4, 25.0, 24.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.12 (d, *J* = 4.8 Hz), -71.45 (d, *J* = 4.7 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.7. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{22}BF_2O_4$ 339.1577; Found 339.1583.

methyl 2-((2,4-dimethylphenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3,3-difluoroacrylate (2b). Reaction Scale: 0.20 mmol – Colorless residue, 71% (52 mg). Reaction scale: 2.00 mmol – Off-white solid, 61% (445 mg). Purified on silica gel using DCM:Hexanes 1:3–1:0. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, *J* = 7.8 Hz, 1H), 6.97 – 6.90 (m, 2H), 3.78 (s, 3H), 3.55 (s, 1H), 2.28 (s, 3H), 2.27 (s, 3H), 1.26 (s, 6H), 1.24 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4 (dd, *J* = 13.2, 7.6 Hz), 160.5 (dd, *J* = 311.1, 295.5 Hz), 135.8, 135.4, 131.2, 127.8, 127.8, 126.8, 90.9 (dd, *J* = 22.9, 6.5 Hz), 84.1, 52.5, 25.0, 24.7, 21.1, 20.0 (d, *J* = 1.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.38 (d, *J* = 4.0 Hz), -70.61 – -70.73 (m). ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.6. $C_{19}H_{26}BF_2O_4$ 367.1890; Found 367.1888.

methyl 2-((2,6-dimethylphenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3,3-difluoroacrylate (2c). Reaction scale 0.40 mmol. Colorless residue, 11% (16 mg). Purified on silica using EtOAc/Hexanes 0:1 – 1:19). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 – 6.91 (m, 3H), 3.93 – 3.89 (m, 1H), 3.74 (s, 3H), 2.31 (s, 6H), 1.22 (s, 6H), 1.21 (s, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4 (dd, *J* = 13.5, 7.0 Hz), 159.1 (dd, *J* = 307.8, 298.2 Hz), 137.2, 136.3, 128.6, 126.0, 90.0 (dd, *J* = 18.7, 7.8 Hz), 84.0, 52.5, 24.9, 24.8, 21.3, 21.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.84 – -68.89 (m), -71.94 (d, *J* = 2.6 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.3. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{26}BF_2O_4$ 367.1890; Found 367.1891.

methyl 2-((4-(*tert*-butyl)phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3,3-difluoroacrylate (2d). Colorless residue, 66% (52 mg). Purified on silica gel using DCM/Hexanes 1:3–1:0. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 2H), 7.24 – 7.20 (m, 2H), 3.75 (s, 3H), 3.39 (s, 1H), 1.29 (s, 15H), 1.25 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1 (dd, *J* = 13.0, 7.6 Hz), 160.5 (dd, *J* = 311.1, 294.6 Hz), 148.7, 136.9 (dd, *J* = 2.7, 1.9 Hz), 128.9, 125.4, 91.5 (dd, *J* = 23.2, 6.0 Hz), 84.1, 52.4, 34.5, 31.5, 25.0, 24.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.52 (d, *J* = 4.0 Hz), -71.87 (d, *J* = 3.9 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.8. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{30}BF_2O_4$ 395.2204; Found 395.2231.

methyl 3,3-difluoro-2-((4-methoxyphenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2e). Colorless residue, 68% (50 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 3.77 (s, 3H), 3.75 (s, 3H), 3.35 (s, 1H), 1.28 (s, 6H), 1.25 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1 (dd, *J* = 13.0, 7.6 Hz), 160.5 (dd, *J* = 311.3, 294.7 Hz), 158.0, 132.30 – 132.17 (m), 130.3, 113.9, 91.7 (dd, *J* = 23.0, 5.8 Hz), 84.2, 55.3, 52.4, 25.0, 24.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.52 (d, *J* = 3.7 Hz), -72.08 (d, *J* = 3.5 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.8. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{24}BF_2O_5$ 369.1683; Found 369.1684.

methyl 3,3-difluoro-2-((3-methoxyphenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2f). Colorless residue, 54% (40 mg). Purified on silica gel using DCM/Hexanes (1:1 – 1:0) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.15 (m, 1H), 6.89 – 6.85 (m, 2H), 6.75 – 6.70 (m, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.39 (s, 1H), 1.28 (s, 6H), 1.25 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1 (dd, *J* = 13.0, 7.6 Hz), 160.6 (dd, *J* = 311.5, 295.1 Hz), 159.5, 141.7 – 141.6 (m), 129.3, 121.5, 115.2, 111.4, 91.2 (dd, *J* = 22.9, 6.5 Hz), 84.2, 55.2, 52.5, 25.0, 24.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.01 (d, *J* = 5.1 Hz), -71.32 (d, *J* = 5.1 Hz).^{11}B NMR (128 MHz, $CDCl_3$) δ 32.7. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{24}BF_2O_5$ 369.1683; Found 369.1688.

methyl 3,3-difluoro-2-((2-methoxyphenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2g). Colorless residue, 67% (49 mg). Purified on silica gel using DCM/Hexanes (1:1 – 1:0). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.11 (m, 2H), 6.87 (td, *J* = 7.5, 1.1 Hz, 1H), 6.82 (dd, *J* = 8.1, 1.1 Hz, 1H), 3.81 (s, 3H), 3.77 (s, 1H),

3.76 (s, 3H), 1.26 (s, 6H), 1.23 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2 (dd, J_{C-F} = 13.1, 7.5 Hz), 160.4 (dd, J_{C-F} = 310.4, 296.6 Hz), 157.1, 128.5, 127.1, 120.5, 110.0, 89.7 (dd, J_{C-F} = 23.0, 6.8 Hz), 55.3, 52.3, 25.0, 24.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.23 (d, *J* = 6.5 Hz), -70.60 (d, *J* = 6.6 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.8. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{24}BF_2O_5$ 369.1683; Found 369.1676.

methyl 2-((4-(benzyloxy)phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3,3-difluoroacrylate (2h). Colorless residue, 66% (58 mg). Purified on silica gel using ethyl acetate/hexanes 0:1 – 1:14. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.28 (m, 5H), 7.23 (d, *J* = 8.9 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 5.02 (s, 2H), 3.75 (s, 3H), 3.36 (s, 1H), 1.29 (s, 6H), 1.25 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0 (dd, *J* = 12.9, 7.7 Hz), 160.3 (dd, *J* = 311.3, 294.5 Hz), 157.2, 137.2, 132.4 – 132.3 (m),, 130.2, 128.5, 127.9, 127.5, 114.6, 91.6 (dd, *J* = 23.2, 5.9 Hz), 84.0, 69.9, 52.2, 24.8, 24.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.48 (d, *J* = 3.7 Hz), -72.03 (d, *J* = 3.5 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.4. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{28}BF_2O_5$ 445.1997; Found 445.2005.

methyl 2-((4-(allyloxy)phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3,3-difluoroacrylate (2i). Colorless residue, 72% (57 mg). Purified on silica gel using ethyl acetate/hexanes 0:1 – 1:14. Isolated with 10% 2**i' (methyl 2-((4-(allyloxy)phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3,3,3-trifluoropropanoate)** impurity. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.7 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 6.04 (ddt, *J* = 17.2, 10.6, 5.3 Hz, 1H), 5.40 (dq, *J* = 17.3, 1.6 Hz, 1H), 5.26 (dq, *J* = 10.5, 1.4 Hz, 1H), 4.49 (dt, *J* = 5.3, 1.4 Hz, 2H), 3.75 (s, 3H), 3.35 (s, 1H), 1.28 (s, 6H), 1.24 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1 (dd, *J* = 13.0, 7.6 Hz), 160.5 (dd, *J* = 311.3, 294.6 Hz), 157.1, 133.7, 132.4 - 132.3 (m), 130.3, 117.7, 114.7, 91.7 (dd, *J* = 23.0, 5.8 Hz), 84.2, 68.9, 52.4, 25.0, 24.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.53 (d, *J* = 3.6 Hz), -72.07 (d, *J* = 3.5 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.7. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{26}BF_2O_5$ 395.1840; Found 395.1846.

methyl 2-((4-acetoxyphenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3,3-difluoroacrylate (2j). Isolated sample contains 30% **2j'(methyl 3,3,3-trifluoro-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(p-tolyl)methyl)propanoate)**. Colorless residue, 25 mg (32%). Purified on silica using ethyl acetate:hexanes 0:1 – 1:10. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.6 Hz, 2H), 6.97 (d, *J* = 8.6 Hz, 2H), 3.76 (s, 3H), 3.39 (s, 1H), 2.28 (s, 3H), 1.28 (s, 6H), 1.24 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.7, 166.0 (dd, *J* = 12.9, 7.6 Hz), 160.6 (dd, *J* = 311.7, 295.0 Hz), 149.1, 137.8 – 137.7 (m), 130.3, 121.2, 91.3 (dd, *J* = 22.9, 6.5 Hz), 84.3, 52.5, 25.0, 24.8, 21.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.85 (d, *J* = 5.1 Hz), -71.41 (d, *J* = 4.9 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.4. HRMS: (ESI) m/z: $[M + Na]^+$ calcd for $C_{19}H_{23}BF_2NaO_6$ 419.1451; Found 419.1451.

methyl 3,3-difluoro-2-((4-(N-methylacetamido)phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2k). Isolated sample contains 20% **2k'(methyl 3,3,3-trifluoro-2-((4-(N-methylacetamido)phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)propanoate)**. Colorless residue, 24 mg (29%). Purified using ethyl acetate:DCM 0:1 – 1:10. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 3.79 (s, 3H), 3.43 (s, 1H), 3.24 (s, 3H), 1.88 (s, 3H), 1.30 (s, 6H), 1.26 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 166.0 (dd, *J* = 12.9, 7.7 Hz), 160.6 (dd, *J* = 311.8, 295.3 Hz), 142.5, 139.8 – 139.7 (m), 130.3, 126.9, 91.1 (dd, *J* = 22.9, 6.9 Hz), 84.3, 52.5, 37.2, 24.9, 24.7, 22.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.53 (d, *J* = 5.3 Hz), -71.26 (d, *J* = 5.2 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.3. $[M + NH_4]^+$ calcd for $C_{20}H_{30}BF_2N_2O_5$ 427.2214; Found 427.2210.

methyl 3,3-difluoro-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(4-(trifluoromethoxy)phenyl)methyl)acrylate (2l). Reaction scale: 0.4 mmol. Colorless residue, 39% (63 mg). Purified on silica gel using ethyl acetate/hexanes 0:1 – 1:25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 2H), 7.12 – 7.07 (m, 2H), 3.77 (s, 3H), 3.40 (s, 1H), 1.29 (s, 6H), 1.25 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0 (dd, *J* = 12.9, 7.7 Hz), 160.6 (dd, *J* = 311.9, 295.2 Hz), 147.7, 138.9, 130.5, 120.9, 120.64 (q, *J* = 256.6 Hz), 91.2 (dd, *J* = 22.9, 6.9 Hz), 84.4, 52.6, 25.0, 24.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.81, -67.59 (d, *J* = 5.3 Hz), -71.34 (d, *J* = 5.2 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.6. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{21}BF_5O_5$ 423.11400; Found 423.1409.

methyl 2-((4-bromophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3,3-difluoroacrylate (2m). Reaction scale: 0.4 mmol. Colorless residue, 20% (34 mg). Purified on silica gel using ethyl acetate/hexanes 0:1 – 1:25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 3.77 (s, 3H), 3.34 (s, 1H), 1.28 (s, 6H), 1.24 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0 (dd, *J* = 12.9, 7.5 Hz), 160.6 (dd, *J* = 311.9, 295.2 Hz), 139.3 – 139.2 (m), 131.5, 130.9, 91.0 (dd, *J* = 22.8, 6.8 Hz), 84.4, 52.5, 25.0, 24.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.55 (d, *J* = 5.5 Hz), -71.23 (d, *J* = 5.5 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.5. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{21}BBrF_2O_4$ 417.0682; Found 417.0690.

methyl 2-((3-bromophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3,3-difluoroacrylate (2n). Reaction scale: 24% (20 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.39 (m, 1H), 7.31 (ddd, *J* = 7.9, 1.9, 1.0 Hz, 1H), 7.23 (dddt, *J* = 8.3, 1.7, 1.1, 0.4 Hz, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 3.78 (s, 3H), 3.36 (s, 1H), 1.28 (s, 6H), 1.24 (s, 7H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0 (dd, *J* = 12.9, 7.6 Hz), 160.7 (dd, *J* = 312.0, 295.5 Hz), 142.6 – 142.5 (m), 132.1, 130.0, 129.4, 127.9, 122.5, 90.9 (dd, *J* = 22.8, 7.1 Hz), 84.4, 52.6, 25.0, 24.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.29 (d, *J* = 6.2 Hz), -70.82 (d, *J* = 6.2 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.5. HRMS: (ESI) m/z: $[M + NH4]^+$ calcd for $C_{17}H_{24}BBrF_2NO_4$ 434.0947; Found 434.0951.

methyl 3,3-difluoro-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(3-(trifluoromethyl)phenyl)methyl)acrylate (2o). Crude NMR Yield: 13%. ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.77 (d, *J* = 5.4 Hz), -71.53 (d, *J* = 5.4 Hz).

methyl 3,3-difluoro-2-((4-fluorophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2p). Colorless viscous oil, 66%. (47 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 2H), 6.98 – 6.90 (m, 2H), 3.76 (s, 3H), 3.37 (s, 1H), 1.28 (s, 6H), 1.25 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1 (dd, *J* = 12.6, 7.7 Hz), 161.5 (d, *J* = 244.0 Hz), 160.6 (dd, *J* = 311.6, 295.0 Hz), 135.9 – 135.8 (m), 130.7 (dd, *J* = 8.1, 0.6 Hz), 115.2 (d, *J* = 21.1 Hz), 91.4 (dd, *J* = 22.5, 6.8 Hz), 84.3, 52.5, 25.0, 24.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.98 (d, *J* = 4.6 Hz), -71.68 (d, *J* = 4.5 Hz), -117.44 (tt, *J* = 8.8, 5.4

Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.6. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{21}BF_3O_4$ 357.1483; Found 357.1500.

methyl 3,3-difluoro-2-((3-fluoro-4-methylphenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2q). Colorless residue, 49% (36 mg). Purified on silica gel using ethyl acetate:hexanes 0:1 – 1:14. Isolated with 5% **2q'(methyl 3,3,3-trifluoro-2-((3-fluoro-4-methylphenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)propanoate)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (t, *J* = 8.0 Hz, 1H), 7.00 – 6.91 (m, 2H), 3.77 (s, 3H), 3.36 (s, 1H), 2.21 (d, *J* = 1.9 Hz, 3H), 1.28 (s, 6H), 1.24 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0 (dd, *J* = 12.8, 7.7 Hz), 162.2, 160.6 (dd, *J* = 311.7, 295.2 Hz), 160.2, 139.8 – 139.7 (m), 131.2 (d, *J* = 5.5 Hz), 124.4 (d, *J* = 3.1 Hz), 122.5 (d, *J* = 17.2 Hz), 115.7 (d, *J* = 22.7 Hz), 91.1 (dd, *J* = 22.9, 6.7 Hz), 84.3, 52.5, 25.0, 24.8, 14.3 (d, *J* = 3.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.84 (d, *J* = 5.2 Hz), -71.40 (d, *J* = 5.3 Hz), -117.80 – -117.93 (m). ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.4. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{23}BF_3O_4$ 371.1636; Found 371.1641.

methyl 3,3-difluoro-2-(naphthalen-2-yl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)acrylate (2r). Colorless residue, 39% (30 mg). Purified on silica gel using Hexanes:EtOAc 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.86 – 7.82 (m, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.53 – 7.44 (m, 2H), 7.43 – 7.36 (m, 1H), 7.33 (d, *J* = 7.2 Hz, 1H), 4.22 (s, 1H), 3.80 (s, 3H), 1.26 (s, 6H), 1.21 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4 (dd, *J* = 13.1, 7.4 Hz), 160.45 (dd, *J* = 311.9, 297.4 Hz), 136.1 – 136.0 (m), 134.0, 132.1, 129.0, 127.0, 125.8, 125.6, 125.5 (d, *J* = 1.1 Hz), 125.4, 123.7 (d, *J* = 1.2 Hz), 90.8 (dd, *J* = 22.2, 7.3 Hz), 84.3, 52.6, 25.0, 24.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.44 (d, *J* = 5.0 Hz), -70.01 (d, *J* = 5.0 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.9. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{24}BF_2O_4$ 389.1734; Found 389.1742.

methyl 2-([1,1'-biphenyl]-4-yl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3,3-difluoroacrylate (2s). Colorless residue, 41% (34 mg). Purified on silica gel using Hexanes:EtOAc 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.55 (m, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.44 – 7.34 (m, 4H), 7.34 – 7.28 (m, 1H), 3.78 (s, 3H), 3.46 (s, 1H), 1.31 (s, 6H), 1.27 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1 (dd, *J* = 12.9, 7.7 Hz), 160.6 (dd, *J* = 311.5, 294.9 Hz), 141.2, 139.4 – 139.3 (m), 139.1, 129.6, 128.8, 127.2, 127.2, 127.1, 91.3 (dd, *J* = 22.9, 6.4 Hz), 84.3, 52.5, 25.0, 24.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.91 (d, *J* = 4.9 Hz), -71.40 (d, *J* = 4.8 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.0. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{26}BF_2O_4$ 415.1891; Found 415.1896.

methyl 2-(benzo[*d*][1,3]dioxol-5-yl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3,3-difluoroacrylate (2t). Colorless residue, 67% (51 mg). Purified on silica gel using DCM:Hexanes 1:1–1:0. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (d, *J* = 1.6 Hz, 1H), 6.75 – 6.68 (m, 2H), 5.90 (q, *J* = 1.5 Hz, 2H), 3.76 (s, 3H), 3.33 (s, 1H), 1.26 (d, *J* = 15.2 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1 (dd, *J* = 12.9, 7.6 Hz), 160.6 (dd, *J* = 311.6, 294.8 Hz), 147.5, 146.0, 134.0 – 133.9 (m), 122.2, 110.0, 108.2, 100.9, 91.7 (dd, *J* = 22.8, 6.1 Hz), 84.2, 52.5, 25.0, 24.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.16 (d, *J* = 4.5 Hz), -71.77 (d, *J* = 4.4 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.5. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{22}BF_2O_6$ 383.1475; Found 383.1478.

Procedure for the synthesis of 3.[42] To a flame-dried 1 dram vial equipped with a stir bar was added **2b** (1.0 equiv, 0.10 mmol) and cesium carbonate (2.1 equiv., 0.21 mmol). The vial was capped with a septum and purged with argon. Dry THF (0.80 mL) was added, followed by 4-methylphenol (2.1 equiv, 0.21 mmol). The argon line was removed, and the septum was covered with parafilm. The reaction was stirred at 45 ºC for 2 h. Solvent removed *in vacuo*. The reaction mixture was purified via column chromatography to yield **3**.

methyl 2-(2,4-dimethylbenzyl)-3,3-bis(*p*-tolyloxy)acrylate (3). Colorless oil, 98% (41 mg). Purified on silica gel using Hexanes:EtOAc 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 7.5 Hz, 1H), 7.03 – 6.93 (m, 6H), 6.81 (d, *J* = 8.5 Hz, 2H), 6.74 (d, *J* = 8.5 Hz, 2H), 3.74 (s, 2H), 3.61 (s, 3H), 2.32 (s, 3H), 2.28 (s, 3H), 2.26 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 157.1, 152.7, 151.3, 136.2, 135.5, 135.1, 133.7, 133.2, 131.0, 129.9, 129.9, 127.8, 126.7, 118.2, 117.1, 102.1, 51.8, 29.4, 21.1, 20.8, 20.8, 19.8. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{27}H_{29}O_4$ 417.2060; Found 417.2051.

Procedure for the synthesis of 4. To a flame-dried 1 dram vial equipped with a stir bar was added **2b** (1.0 equiv, 0.10 mmol) and cesium carbonate (1.1 equiv, 0.11 mmol). The vial was capped with a septum and purged with argon. Dry THF was added, followed by catechol (1.1 equiv, 0.11 mmol). The argon line was removed, and the septum was covered with parafilm. The reaction was stirred at 45 ºC for 2 h. Solvent removed *in vacuo*. The reaction mixture was purified via column chromatography to yield **3**.

methyl 2-(benzo[*d*][1,3]dioxol-2-ylidene)-3-(2,4-dimethylphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (4). Colorless oil, 30% (13 mg). Purified on silica gel using Hexanes:EtOAc 19:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.21 (m, 1H), 7.13 – 7.03 (m, 3H), 7.01 (d, *J* = 7.9 Hz, 1H), 6.95 (s, 1H), 6.88 (d, *J* = 7.9 Hz, 1H), 3.82 (s, 3H), 3.74 (s, 1H), 2.37 (s, 3H), 2.25 (s, 3H), 1.26 (s, 7H), 1.23 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 165.9, 145.8, 144.2, 137.9, 135.5, 134.5, 130.8, 126.9, 126.8, 124.3, 124.2, 110.2, 109.8, 84.6, 83.7, 51.8, 25.2, 24.8, 21.1, 20.2. ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.7. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{25}H_{30}O_6$ 437.2134; Found 437.2122.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1. Diner, C.; Szabó, K. J., *J. Am. Chem. Soc.* **2017,** *139*, 2-14.
2. Neeve, E. C.; Geier, S. J.; Mkhalid, I. A. I.; Westcott, S. A.; Marder, T. B., *Chem. Rev.* **2016,** *116*, 9091-9161.
3. Hall, D.; Lee, J. C. H.; Ding, J., *Pure Appl. Chem.* **2012,** *84*, 2263.
4. Yang, Y.; Buchwald, S. L., *J. Am. Chem. Soc.* **2013,** *135*, 10642-10645.
5. Yasunori, Y.; Shingo, T.; Norio, M., *Chem. Lett.* **2006,** *35*, 704-705.

6. Ardolino, M. J.; Morken, J. P., *J. Am. Chem. Soc.* **2014,** *136*, 7092-7100.
7. Carosi, L.; Lachance, H.; Hall, D. G., *Tetrahedron Lett.* **2005,** *46*, 8981-8985.
8. Chen, J. L. Y.; Scott, H. K.; Hesse, M. J.; Willis, C. L.; Aggarwal, V. K., *J. Am. Chem. Soc.* **2013,** *135*, 5316-5319.
9. Chen, M.; Roush, W. R., *Org. Lett.* **2010,** *12*, 2706-2709.
10. Chen, J. L.-Y.; Aggarwal, V. K., *Angew. Chem. Int. Ed.* **2014,** *53*, 10992-10996.
11. Hall, D.; Lachance, H.; Denmark, S. E., In *Organic Reactions*, Wiley: Hoboken, NJ, 2012; Vol. 73.
12. Kennedy, J. W. J.; Hall, D. G., *Angew. Chem. Int. Ed.* **2003,** *42*, 4732-4739.
13. Meanwell, N. A., *J.Med.Chem.* **2018,** *61*, 5822-5880.
14. Leriche, C.; He, X.; Chang, C.-w. T.; Liu, H.-w., *J. Am.Chem.Soc.* **2003,** *125*, 6348-6349.
15. Lim, M. H.; Kim, H. O.; Moon, H. R.; Chun, M. W.; Jeong, L. S., *Org. Lett.* **2002,** *4* , 529-531.
16. Magueur, G.; Crousse, B.; Ourévitch, M.; Bonnet-Delpon, D.; Bégué, J.-P., *J. Fluor. Chem.* **2006,** *127*, 637-642.
17. Ojima, I., *J. Fluor. Chem.* **2017,** *198*, 10-23.
18. Amii, H.; Uneyama, K., *Chem. Rev.* **2009,** *109*, 2119-2183.
19. Dai, W.; Shi, H.; Zhao, X.; Cao, S., *Org. Lett.* **2016,** *18*, 4284-4287.
20. Yang, L.; Ji, W.-W.; Lin, E.; Li, J.-L.; Fan, W.-X.; Li, Q.; Wang, H., *Org. Lett.* **2018,** *20*, 1924-1927.
21. Jiang, L.-F.; Ren, B.-T.; Li, B.; Zhang, G.-Y.; Peng, Y.; Guan, Z.-Y.; Deng, Q.-H., *J. Org. Chem.* **2019,** *84*, 6557-6564.
22. Murata, J.; Tamura, M.; Sekiya, A., *Green Chem.* **2002,** *4*, 60-63.
23. Liu, X.; Lin, E. E.; Chen, G.; Li, J.-L.; Liu, P.; Wang, H., *Org. Lett.* **2019,** *21*, 8454-8458.
24. Yu, L.; Tang, M.-L.; Si, C.-M.; Meng, Z.; Liang, Y.; Han, J.; Sun, X., *Org. Lett.* **2018,** *20*, 4579-4583.
25. Li, J.; Lefebvre, Q.; Yang, H.; Zhao, Y.; Fu, H., *Chem. Commun.* **2017,** *53*, 10299-10302.
26. Hu, J.; Zhao, Y.; Shi, Z., *Nat. Catal.* **2018,** *1*, 860-869.
27. Bhadury, P. S.; Palit, M.; Sharma, M.; Raza, S. K.; Jaiswal, D. K., *J. Fluor. Chem.* **2002,** *116*, 75-80.
28. Stahly, G. P., *J. Fluor. Chem.* **1989,** *43*, 53-66.
29. Huo, H.-X.; Duvall, J. R.; Huang, M.-Y.; Hong, R., *Org. Chem. Front.* **2014,** *1*, 303-320.
30. Zhang, X.; Cao, S., *Tetrahedron Lett.* **2017,** *58*, 375-392.
31. Yue, W.-J.; Day, C. S.; Martin, R., *J.Am. Chem. Soc.***2021,** *143*, 6395-6400.
32. Lan, Y.; Yang, F.; Wang, C., *ACS Catal.* **2018,** *8*, 9245-9251.
33. Corberán, R.; Mszar, N. W.; Hoveyda, A. H., *Angew. Chem. Int. Ed.* **2011,** *50*, 7079-7082.
34. Liu, Y.; Zhou, Y.; Zhao, Y.; Qu, J., *Org. Lett.* **2017,** *19*, 946-949.
35. Kojima, R.; Akiyama, S.; Ito, H., *Angew. Chem. Int. Ed.* **2018,** *57* , 7196-7199.
36. Akiyama, S.; Nomura, S.; Kubota, K.; Ito, H., *J.Org. Chem.* **2020,** *85*, 4172-4181.
37. Gao, P.; Yuan, C.; Zhao, Y.; Shi, Z., *Chem* **2018,** *4*, 2201-2211.
38. Zhao, X.; Li, C.; Wang, B.; Cao, S., *Tetrahedron Lett.* **2019,** *60*, 129-132.
39. Cai, Y.; Zeng, H.; Zhu, C.; Liu, C.; Liu, G.; Jiang, H., *Org. Chem. Front.* **2020,** *7*, 1260-1265.
40. Mun, S.; Lee, J.-E.; Yun, J., *Org. Lett.* **2006,** *8*, 4887-4889.
41. Jos, S.; Santos, W. L., *Adv.Syn. Catal.* **2021,** *363*, 425-430.
42. Wu, Y.; Zhang, B.; Zheng, Y.; Wang, Y.; Lei, X., *RSC Adv.* **2018,** *8*, 16019-16023.
43. Xiao, P.; Schlinquer, C.; Pannecoucke, X.; Bouillon, J.-P.; Couve-Bonnaire, S., *J. Org. Chem.* **2019,** *84*, 2072-2082.