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Note

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Tunable synthesis of α-amino boronic esters from available aldehydes and amines through sequential one-pot dehydration and copper-catalyzed borylacylation

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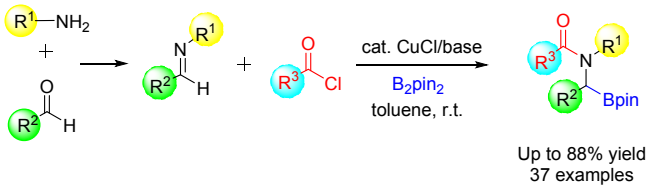
ABSTRACT: Copper-catalyzed multicomponent borylacylation of imines with acid chlorides and bis(pinacolato)diboron was developed for the preparation of synthetically useful and pharmacologically relevant α-amino boronic acid derivatives. Starting from a range of acid chlorides and imines with aryl, heteroaryl, and alkyl substituents, most of these ligand-free reactions proceeded smoothly at room temperature in moderate to good yields. Furthermore, a facile and convenient one-pot, multi-step access to the direct synthesis of α-amino boronic acid derivatives from available aldehydes and amines was also developed.



In the last few decades, organoboronic acids and their derivatives have been widely applied in synthetic organic chemistry,[1, 2] carbohydrate recognition,[3] transmembrane transport[4] and separation of glycoproteins. They can also be used as pharmacologically active agents in some cases such as a unique class of enzyme inhibitors due to their substantial selectivity in the formation of reversible covalent bonds with the targeted enzymes.[5, 6] Important biomedical applications have been established for the compounds containing an α-amino boronic acids group. For instance, Bortezomib,[7] Ixazomib,[8] Dutoglitin,[9] Talabostat[10] and Delanzomib[11] (Fig 1), have been evaluated and optimized as the second-generation protease inhibitors in the clinical trials. Additionally, many other bioactivities such as anticancer, antiviral, and antibacterial properties have also been found for α-amino boronic acid compounds.[12] With such success, the enormous potential of α-amino boronic acids attracts more and more attention to their preparation method.[13] However, the difficulty in the isolation of α-amino boronic acids constitutes a major synthetic challenge since the formation of a three-membered ring adduct between the boron and nitrogen atoms can induce the C-B bond cleavage.[14] For this reason, efficient routes for the synthesis of functionalized α-amino boronic acids and esters are still quite limited. Only a few protocols including the addition of α-amino organometallic compounds to boron-containing electrophiles,[15] the addition of nucleophilic boron reagents to imines,[16] the hydroboration of enamides[17] and the C(sp^3)-H borylation reaction[18], etc., have been reported.

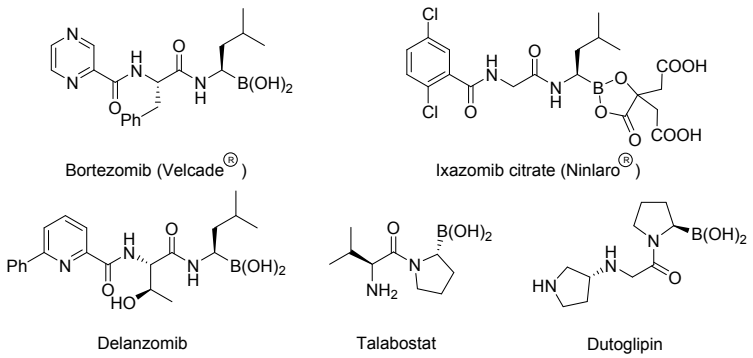
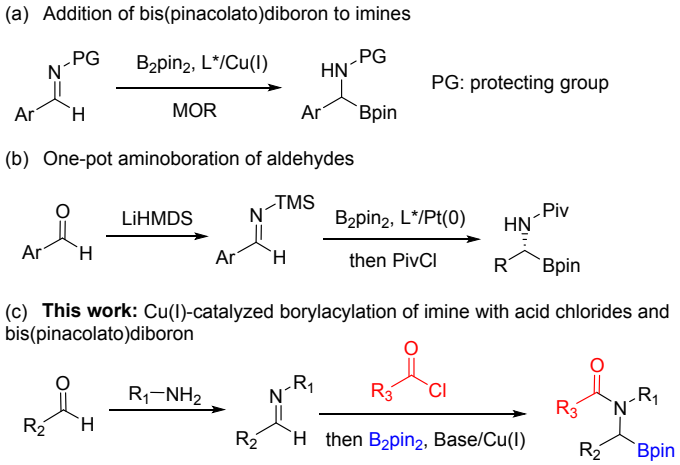


Fig 1. Represent bioactive compound bearing an α-amino boronic acid structure.

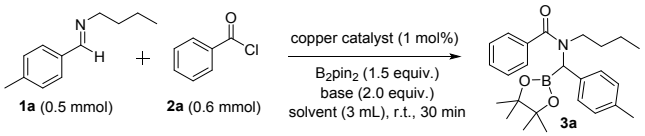
Scheme 1. Approaches to synthesize α-amino boronic esters.



Among those methods, the transition-metal-catalyzed addition of bis(pinacolato)diboron to imines might be the most efficient and straightforward approach.[19] Ellman,[20] Fernańdez,[21] Lin,[22] and Liao[23] have provided different catalysts and ligands systems for the synthesis of simple α-amino boronate esters (Scheme 1a). However, these approaches suffer from some drawbacks such as high catalyst loading, complex and expensive ligands, harsh conditions, long reaction times and narrow substrate scope due to the adoption of only N-protected imine as the starting material. Morken and Hong provided a protocol of converting aldehydes into N-acyl α-amino boronic esters or peptide derivatives catalyzed by an asymmetric platinum (0) phosphonate (Scheme 1b).[24] This transformation included the Pt-catalyzed diboration of *in situ*-generated silyl imines with B_2Pin_2, followed by the direct acylation of the diboration adducts to provide N-acyl α-amino boronic esters. However, this protocol required not only expensive Pt catalysts and complex ligand, but also tedious reaction setup and long reaction time. Therefore, a simple and effective method for the preparation of functionalized α-amino boronate esters with diverse substituents on the nitrogen atom has remained an elusive goal. As our continuous efforts on the development of efficient boration strategy with bis(pinacolato)diboro,[25] we reported herein a copper-catalyzed multicomponent borylacylation of imines with acid chlorides and bis(pinacolato)diboron in a one-pot two-step reaction. Furthermore, the widely available aldehydes and amines were directly converted to α-amino boronic esters through sequential one-pot dehydration and borylacylation under mild conditions with broad substrate scopes (Scheme 1c).

The borylacylation of imines with acid chlorides and B_2pin_2 was studied firstly. By employing the copper-catalyzed borylacylation of N-benzyltolylaldimine (**1a**), benzoyl chloride (**2a**) and B_2pin_2 as the model reaction, a variety of reaction conditions was investigated (Table 1). In the initial experiments, the target product **3a** was only obtained in 5% (Table 1, entry 1). It was found then that the choice of the base is crucial for the success of the reaction. For example, when K_2CO_3 or *t*BuOK was added to the reaction mixture, the desired α-amino boronic esters **3a** was obtained in low yields (Table 1, entries 2 and 3). A large amount of aldehyde was detected in the reaction products, indicating that the decomposition of imine **1a** occurred. To our delight, the target product **3a** was obtained in 25% and 70% yields, respectively, with *t*BuONa or *t*BuOLi as the base (Table 1, entries 4 and 5). Only trace of **3a** was detected when Et_3N was used (Table 1, entry 6). The target product was obtained in 30% yield with DBU (Table 1, entry 7). Subsequently, a series of transition metal salts were used to evaluate their catalytic capability. The target product **3a** could be detected only in the presence of copper salts, and Cu(II) salts gave a little worse results than Cu(I) salts (Table 1, entry 8-11). The best yield of **3a** was achieved by using CuCl as the catalyst. Nickel, iron and zinc salts did not show any catalytic activity (Table 1, entry 12-14). The effects of solvents on the reaction were also examined. THF, 1, 4-dioxane and diethyl ether gave the target product **3a** in lower yields than toluene (Table 1, entries 15-17). Only trace of **3a** was detected in polar solvents such as CH_3CN, DMSO and DMF (Table 1, entry 18-20). Finally, the catalyst loading was optimized. Either decreasing or increasing the catalyst loading from 1.0 mol% would result in a decline in the yield of **3a** (Table 1, entry 21-22). To investigate the potential of this transformation in asymmetry borylacylation, several commercially available chiral ligands have been adopted. However, the enantioselectivity of the products was unfortunately low (less than 3% ee).

Table 1. Optimization of reaction conditions.



Entry	Copper cat.	Base	Solvent	Yield (%)[a]
1	CuBr	Cs_2CO_3	toluene	5
2	CuBr	K_2CO_3	toluene	trace
3	CuBr	*t*BuOK	toluene	8
4	CuBr	*t*BuONa	toluene	25
5	CuBr	*t*BuOLi	toluene	70
6	CuBr	Et_3N	toluene	trace
7	CuBr	DBU	toluene	30
8	$CuBr_2$	*t*BuOLi	toluene	51
9	CH_3COOCu	*t*BuOLi	toluene	63
10	CuI	*t*BuOLi	toluene	68
11	CuCl	*t*BuOLi	toluene	76 (72) [b]
12	$NiCl_2$	*t*BuOLi	toluene	-
13	$FeCl_3$	*t*BuOLi	toluene	-
14	$ZnCl_2$	*t*BuOLi	toluene	-
15	CuCl	*t*BuOLi	THF	23
16	CuCl	*t*BuOLi	1,4-dioxane	38
17	CuCl	*t*BuOLi	Et_2O	29
18	CuCl	*t*BuOLi	CH_3CN	trace
19	CuCl	*t*BuOLi	DMSO	trace
20	CuCl	*t*BuOLi	DMF	trace
21[c]	CuCl	*t*BuOLi	toluene	48
22[d]	CuCl	*t*BuOLi	toluene	73

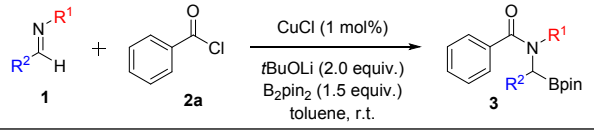
Reaction conditions: (1) imine (0.5 mmol), acid chloride (0.6 mmol) in solvent (3.0 mL), r.t., 2 min. (2) catalyst (0.005 mmol), B_2pin_2 (0.75 mmol) and bases (1.0 mmol) were added, r.t., 30 min under N_2. [a] GC yield (dodecane as an internal standard). [b] Isolated yield is given in parenthesis. [c] The amount of catalyst was 0.0025 mmol. [d] The amount of catalyst was 0.0075 mmol.

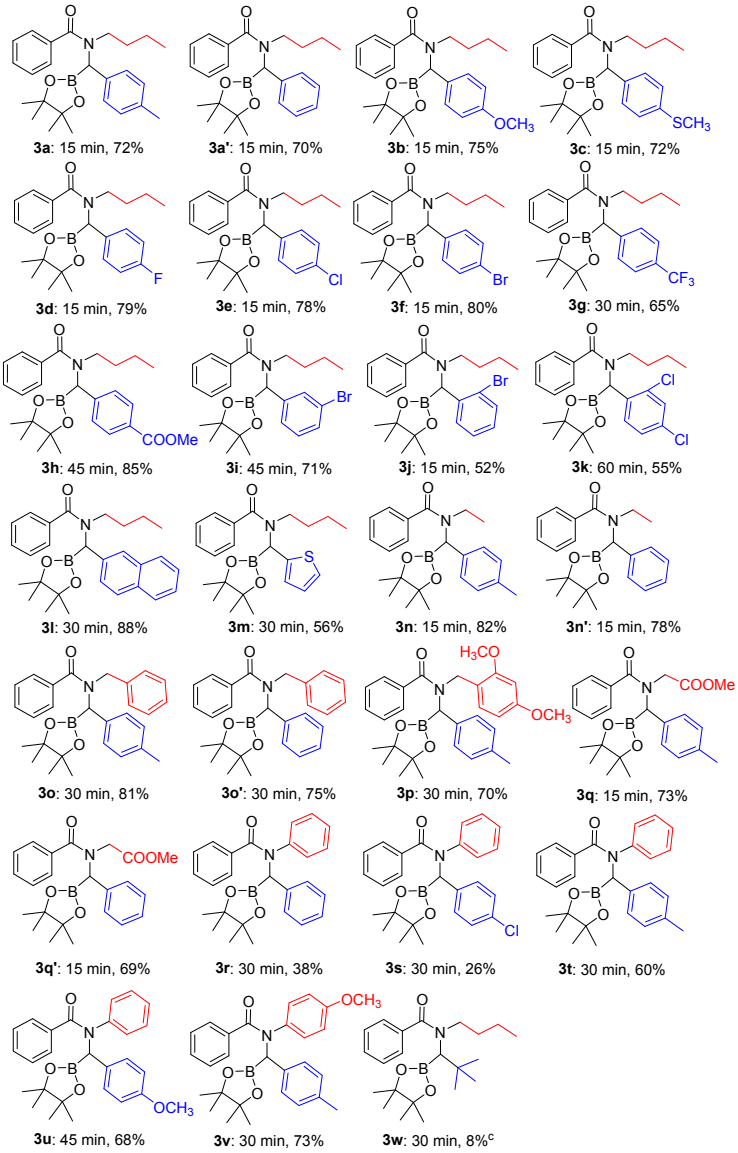
With the optimal reaction conditions in hand, a variety of imines were adopted to investigate the scope and limitation of the transformation (Table 2). It seems that both electron-donating and electron-withdrawing groups attached to the phenyl ring of the C-aryl-substituted imines were compatible under the standard reaction conditions. An array of functional groups at the *p*- and *m*-position such as *p*-CH_3, *p*-OCH_3, *p*-SCH_3, *p*-F, *p*-Cl, *p*-Br, *p*-CF_3, *p*-CO_2Me and *m*-Br groups were well-tolerated, affording **3a-i** in good yields of 65-85%. Meanwhile, the desired product **3j** and **3k** with the phenyl ring bearing a group at the *ortho*-position were formed in moderate yields, indicating that the steric effect has slight influence on the reaction. Imines derived from 2-naphthaldehyde and heteroaryl aldehyde also reacted smoothly to form **3l** and **3m** in satisfying yields. Therefore, the reaction is tolerant of various C-aryl-substituted imines. Unfortunately, the imine derived from trimethylacetaldehyde and *n*-butylamine provided the corresponding product **3w** in a low yield of 8%. In addition, different N-substituted imines were also investigated. The use of N-alkyl-substituted imines afforded **3n-q** in good yields of 69-82%. Considering the widely biological activities of peptide boronic acid derivatives, several different amino acids have been adopted for this transformation. Unfortunately, only the imine derived from glycine methyl ester could react smoothly. When other amino acid esters such as alanine methyl ester and phenylalanine methyl ester were involved, the pre-prepared imines were decomposed under the optimal reaction conditions. Even by performing the reaction in an ice bath to weaken the reaction condition, the decomposition of imines still happened. Nevertheless, the N-phenyl-substituted imines gave the desired products **3r** and **3s** in relatively lower yields. However, when an electron-donating group was attached either to the C-substituted phenyl ring (**3t** and **3u**) or to the N-substituted phenyl ring (**3v**) of imines, the yields of the target products were improved.

We then explored the scope of this copper-catalyzed borylacylation of imines with a variety of commercially available acid chlorides to afford the corresponding α-amino boronic esters (Table 3). Both electron-donating and -withdrawing groups on the *para*-positions of the aryl ring of acid chlorides were tolerated, affording the corresponding desired product **4a-e** in good yields. With a phenyl ring bearing a Br

group at the *meta*- or *ortho*-position, the desired products **4f** and **4g** were formed in lower yields, indicating that the reactivity of an acid chloride was slightly influenced by the steric hindrance. Alkyl acid chlorides such as acetyl chloride and 3-methylcrotonoyl chloride could also be involved in the transformation and give the products **4h** and **4i** in 69% and 70% yields, respectively. In case of heterocyclic acid chlorides, corresponding products **4j** and **4k** were obtained in good yields.

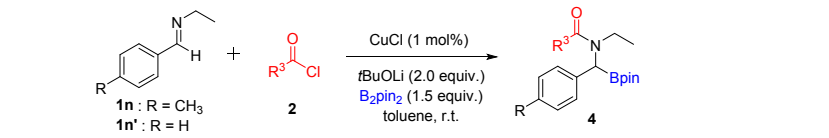
Table 2. Preparation of α-amino boronic esters from various imines. [a, b, c]

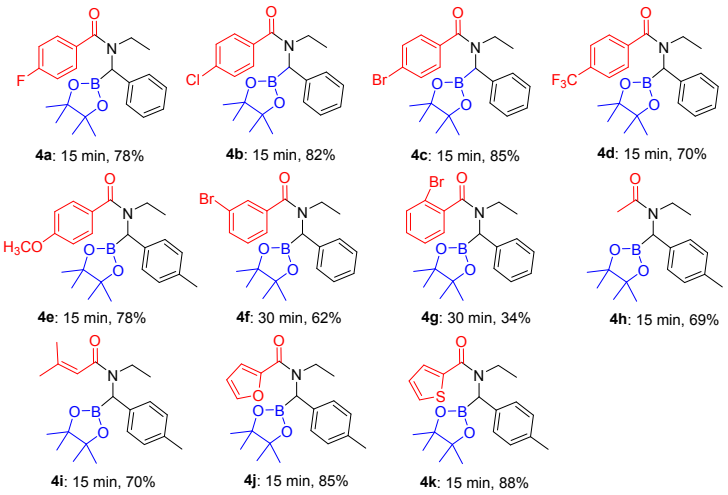




[a] Reaction conditions: (1) imines (0.5 mmol), acid chlorides (0.6 mmol) in toluene (3.0 mL), r.t., 2min. (2) CuCl (0.005 mmol), B_2pin_2 (0.75 mmol) and *t*BuOLi (1.0 mmol) were added, r.t., 30 min under N_2. [b] Isolated yield. [c] GC yield.

Table 3. Preparation of α-amino boronic esters from various acid chlorides. [a, b]

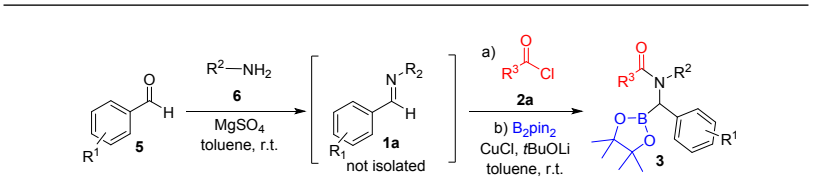


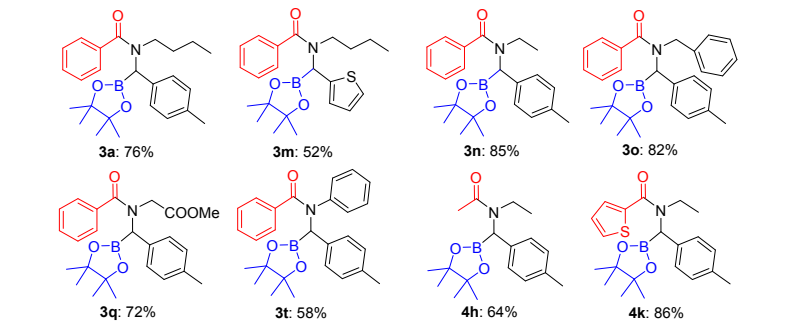


[a] Reaction conditions: (1) imines (0.5 mmol), acid chlorides (0.6 mmol) in toluene (3.0 mL), r.t., 2min. (2) CuCl (0.005 mmol), B_2pin_2 (0.75 mmol) and *t*BuOLi (1.0 mmol) were added, r.t., 30 min under N_2. [b] Isolated yield.

Encouraged by the success in the borylacylation of imines, we next sought to directly convert aldehydes to α-amino boronic esters. As showed in Table 4, this one-pot multi-step process starting from aldehydes could provide a highly effective strategy for the preparation of a variety of α-amino boronic esters.

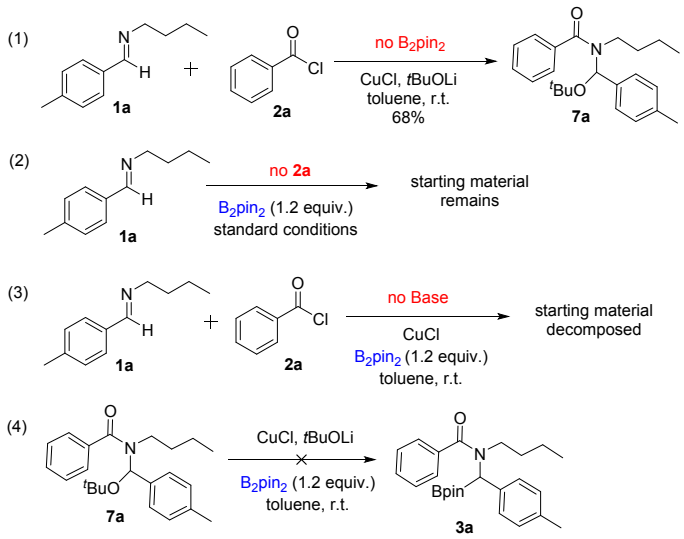
Table 4. Direct conversion of aldehydes to α-amino boronic esters. [a, b]





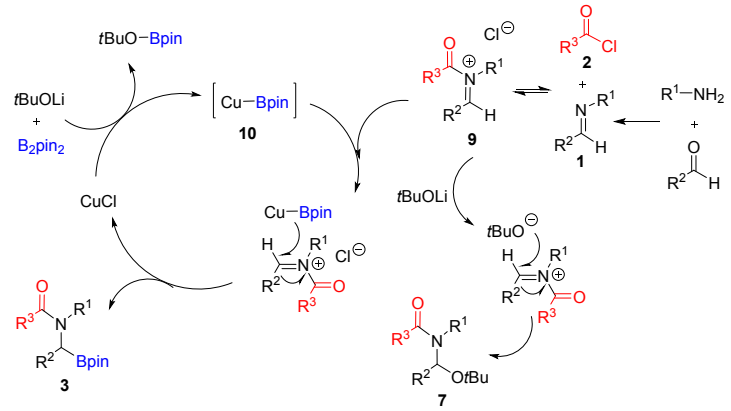
[a] Reaction conditions: (1) aldehydes (0.5 mmol), amines (0.5 mmol), $MgSO_4$ (1.0 mmol) in toluene (2 mL), r.t., 10 min. (2) acid chlorides (0.6 mmol) dissolved in toluene (1.0 mL) was added, r.t., 2min. (3) CuCl (0.005 mmol), B_2pin_2 (0.75 mmol) and *t*BuOLi (1.0 mmol) were added, r.t., 30 min under N_2. [b] Isolated yield.

Scheme 2. Control experiments.



In order to understand the mechanism of the borylacylation of imines and the pathway of by-product formation, various control experiments were carried out. By-product **7a** was formed in a yield of 68% when B_2pin_2 was removed from the reaction system (Scheme 2, eq 1). It means that the *t*BuOLi can also react with imine in the absence of B_2pin_2. Almost all of the starting materials remained unchanged without the presence of benzoyl chloride under the standard conditions (Scheme 2, eq 2). This indicated that B_2pin_2 could not directly react with the imine. Furthermore, when *t*BuOLi was excluded from the reaction mixture, the starting material imine was gradually decomposed to corresponding aldehyde and amine (Scheme 2, eq 3). Eventually, the isolated by-product **7a** was treated with B_2pin_2 under standard conditions, and no target product was detected (Scheme 2, eq 4). It was thus affirmed that **7a** is not an intermediate of the reaction, but one of the by-products.

Scheme 3. Possible reaction mechanism.



Based on the control experimental results and referred to literatures, a plausible reaction mechanism for this reaction is proposed (Scheme 3). Initially, a Cu-Bpin intermediate **10** is generated by the reaction of CuCl with B_2pin_2 assisted by the *t*BuOLi. At the same time, the imine, either as a starting material or the intermediate product derived from dehydration of an aldehyde with an amine, quickly reacts with acid chloride to form the N-acyliminium salt **9**. The Cu-Bpin is then regioselectively added to the C=N of **9** to give the desired product **3** and regenerate the copper catalyst to complete the catalytic cycle. On the other hand, the by-product **7** is formed by the nucleophilic attack of *t*BuOLi on **9**. While an imine is not a viable electrophile in cross coupling reactions, the presence of the acid chloride creates a highly reactive N-acyliminium salt which is readily involved in the transmetalation with B_2Pin_2 and generates corresponding α-amino boronate esters.[26]

CONCLUSION

In summary, we have developed an efficient, versatile, and simple copper-catalyzed borylacylation of imines with acid chlorides and bis(pinacolato)diboron. A more straightforward one-pot multi-step protocol for the synthesis of α-amino boronic esters starting from aldehydes and amines was also successfully performed. The dehydration of aldehydes and amines offers access to imines that readily undergo ligand-free Cu-catalyzed borylacylation to provide the desired α-amino boronic esters in good yields. The mild reaction conditions, broad substrate scopes and easy availability of starting materials make this strategy a valuable tool for generating highly substituted α-amino boronic esters, which are of considerable interest as potential biologically active compounds.

EXPERIMENTAL SECTION

General information. All the reactions of using toluene as solvent were carried out in moisture free environment. Chemicals, solvents were procured from commercial sources and all solvents were dried by standard methods. Melting points were recorded on an EZ-melt MPA120 (Stanford Research Systems, Inc., USA) and are uncorrected. The preparative thin-layer chromatography plates used were HSGF 254 plates (thickness of coating: 0.4-0.5 mm, 20 cm × 20 cm, Huanghai® from Yantai, Shandong province, China). The ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker AM-400 spectrometer (400 MHz and 100 MHz, respectively) using TMS as internal standard. $CDCl_3$ was used as the NMR solvent for α-amino boronic esters in most cases. Chemical shifts were recorded in parts per million (d) relative to $CDCl_3$ at 7.26 for ^{1}H NMR and 77.23 for $^{13}C\{^{1}H\}$ NMR. Gas chromatography-mass spectrometry (GC-MS) was performed on Agilent 7890A/5975C. Gas chromatograms were recorded on Agilent 7890A. The starting material imines were synthesized from amines and aldehydes in the presence of $MgSO_4$, and characterized by GC-MS according to the literature.[27]

General procedure for preparation of α-amino boronic esters. A mixture of the CuCl (0.50 mg, 0.005 mmol, 1.00 mol %), bis(pinacolato)diboron (189.7 mg, 0.75 mmol, 1.50 equiv.), and *t*BuOLi (80 mg, 1 mmol, 2.00 equiv.) was placed in a 10-mL microwave tube with a magnetic stirring bar. After being sealed with a cap, the reaction tube was filled with N_2. In another vial, toluene (3.00 mL) was added followed by the imines (0.50 mmol, 1 equiv.) and the acid chlorides (0.60 mmol, 1.20 equiv.) were added dropwise. Subsequently, the mixture in the vial was syringed into the front nitrogen protected microwave tube. At last, the reaction was allowed to stir at ambient temperature (25 ℃) for 15 to 30 minutes. The resulting mixture was filtered through a pad of celite and the mixture was extracted with diethyl ether (3 × 10 mL). The combined organic phase was dried by the use of $MgSO_4$ and then concentrated in vacuo. Crude material was purified by silica gel column chromatography using acetate and petroleum ether as the eluent to obtain the desired product. The products were further characterized by HRMS (EI), ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR.

General procedure for preparation of product 3a on a 5 mmol scale. A mixture of the CuCl (5.0 mg, 0.05 mmol, 1.00 mol %), bis(pinacolato)diboron (1.90 g, 7.5 mmol, 1.50 equiv.), and *t*BuOLi (800 mg, 10 mmol, 2.00 equiv.) was placed in a 100 ml round bottom flask with a magnetic stirring bar. The flask was sealed with a rubber septum and filled with N_2. In another 100 ml round bottom flask, toluene (30.0 mL) was added followed by the imine **1a** (876 mg, 5.0 mmol, 1 equiv.) and the benzoyl chloride (843 mg, 6.0 mmol, 1.20 equiv.) were added dropwise at 0 ℃. Subsequently, the mixture in the 100 ml round bottom flask was syringed into the front nitrogen protected round bottom flask. At last, the reaction was allowed to stir at ambient temperature (25 ℃) for 1h. The resulting mixture was filtered through a pad of celite and the mixture was extracted with diethyl ether (3 × 30 mL). The combined organic phase was dried by the use of $MgSO_4$ and then concentrated in vacuo. Crude material was purified by silica gel column chromatography using acetate and petroleum ether as the eluent to obtain the desired product as white solid (1.42 g, 70% yield). The products were further characterized by HRMS (EI), ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR.

General procedure for directly converting aldehydes to α-amino boronic esters. A mixture of the CuCl (0.50 mg, 0.005 mmol, 1.00 mol %), bis(pinacolato)diboron (189.7 mg, 0.75 mmol, 1.50 equiv.), and *t*BuOLi (80 mg, 1 mmol, 2.00 equiv.) was placed in a 10-mL microwave tube with a magnetic stirring bar. After being sealed with a cap, the reaction tube was filled with N_2. In another vial, a mixture of aldehydes (0.5 mmol), amines (0.5 mmol), $MgSO_4$ (0.120 g, 1.0 mmol) and dry toluene (2.0 mL) was irradiated at ambient temperature (25 ℃) for 10 min. Then the acid chlorides (0.60 mmol, 1.20 equiv.) were added dropwise in the mixture. Subsequently, the mixture in the vial was syringed into the front nitrogen protected microwave tube. At last, the reaction was allowed to stir at ambient temperature (25 ℃) for 15 to

30 minutes. The resulting mixture was filtered through a pad of celite and the mixture was extracted with diethyl ether (3 × 10 mL). The combined organic phase was dried by the use of $MgSO_4$ and then concentrated in vacuo. Crude material was purified by silica gel column chromatography using acetate and petroleum ether as the eluent to obtain the desired product. The products were further characterized by HRMS (EI), ^{1}H NMR and $^{13}C\{^1H\}$ NMR.

N-butyl-N-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(p-tolyl)methyl)benzamide ***(3a)***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 72% (293mg); m.p. 169.5-170.6 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.60 (m, 2H), 7.58 – 7.53 (m, 1H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.14 – 7.07 (m, 4H), 3.87 (s, 1H), 3.52 (ddd, *J* = 13.8, 9.4, 6.9 Hz, 1H), 3.08 (ddd, *J* = 14.0, 9.5, 4.7 Hz, 1H), 2.34 (s, 3H), 1.53 (dtd, *J* = 14.0, 9.1, 4.7 Hz, 1H), 1.41 (ddd, *J* = 15.9, 7.8, 4.7 Hz, 1H), 1.16 (dd, *J* = 14.3, 8.1 Hz, 1H), 1.11 (s, 6H), 1.09 – 1.00 (m, 1H), 0.96 (s, 6H), 0.71 (t, *J* = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 174.0, 135.8, 135.2, 132.0, 128.8 (2C), 128.7 (2C), 128.4 (2C), 128.1, 128.0 (2C), 80.0 (2C), 45.8, 29.4, 25.0 (2C), 24.6 (2C), 21.1, 19.6, 13.4. HRMS (EI-TOF, m/z) calcd for $C_{25}H_{34}BNO_3$ $[M]^+$ 407.2632, found 407.2629.

N-butyl-N-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide ***(3a')***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 70% (275mg); m.p. 149.8-150.7 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.62 (m, 2H), 7.60 – 7.53 (m, 1H), 7.50 (m, 2H), 7.34 – 7.27 (m, 2H), 7.19 (dd, *J* = 10.0, 3.9 Hz, 3H), 3.91 (s, 1H), 3.55 (ddd, *J* = 13.8, 9.4, 6.9 Hz, 1H), 3.10 (ddd, *J* = 14.0, 9.5, 4.8 Hz, 1H), 1.54 (dqd, *J* = 18.8, 9.3, 5.0 Hz, 1H), 1.47 – 1.37 (m, 1H), 1.17 (m, 1H), 1.11 (s, 6H), 1.08 – 1.00 (m, 1H), 0.95 (s, 6H), 0.71 (t, *J* = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 174.2, 139.0, 132.0, 128.7 (2C), 128.4 (2C), 128.1 (2C), 128.0 (3C), 125.9, 80.1 (2C), 46.0, 29.4, 25.0 (2C), 24.6 (2C), 19.6, 13.4. HRMS (EI-TOF, m/z) calcd for $C_{24}H_{32}BNO_3$ $[M]^+$ 393.2475, found 393.2470.

N-butyl-N-((4-methoxyphenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide ***(3b)***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 75% (317mg); m.p. 155.1-156.3 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.59 (m, 2H), 7.59 – 7.53 (m, 1H), 7.49 (dd, *J* = 11.5, 4.4 Hz, 2H), 7.15 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 3.86 (s, 1H), 3.81 (s, 3H), 3.51 (ddd, *J* = 13.8, 9.4, 6.8 Hz, 1H), 3.06 (ddd, *J* = 14.0, 9.5, 4.7 Hz, 1H), 1.61 – 1.47 (m, 1H), 1.47 – 1.35 (m, 1H), 1.20 – 1.14 (m, 1H), 1.12 (s, 6H), 1.08 – 1.00 (m, 1H), 0.96 (s, 6H), 0.72 (t, *J* = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 173.9, 157.9, 132.0, 130.8, 129.4 (2C), 128.7 (2C), 128.4 (2C), 128.0, 113.5 (2C), 80.1 (2C), 55.2, 45.8, 29.4, 25.0 (2C), 24.5 (2C), 19.6, 13.4. HRMS (EI-TOF, m/z) calcd for $C_{25}H_{34}BNO_4$ $[M]^+$ 423.2581, found 423.2574.

N-butyl-N-((4-(methylthio)phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide ***(3c)***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 72% (316mg); m.p. 158.7-159.9 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.61 (m, 2H), 7.60 – 7.55 (m, 1H), 7.53 – 7.47 (m, 2H), 7.25 – 7.20 (m, 2H), 7.16 – 7.12 (m, 2H), 3.88 (s, 1H), 3.54 (ddd, *J* = 13.8, 9.4, 6.8 Hz, 1H), 3.07 (ddd, *J* = 14.0, 9.5, 4.8 Hz, 1H), 2.49 (s, 3H), 1.53 (dtdd, *J* = 14.0, 9.3, 6.3, 4.9 Hz, 1H), 1.47 – 1.38 (m, 1H), 1.21 – 1.13 (m, 1H), 1.11 (s, 6H), 1.05 (ddd, *J* = 14.4, 9.0, 6.9 Hz, 2H), 0.97 (s, 6H), 0.72 (t, *J* = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 174.2, 136.0, 135.3, 132.1, 128.7 (2C), 128.6 (2C), 128.4 (2C), 127.9, 126.7 (2C), 80.2 (2C), 46.0, 29.4, 25.0 (2C), 24.6, 24.5 (2C), 19.6, 16.1, 13.4. HRMS (EI-TOF, m/z) calcd for $C_{25}H_{34}BNO_3S$ $[M]^+$ 439.2352, found 439.2350.

N-butyl-N-((4-fluorophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide ***(3d)***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 79% (325mg); m.p. 168.9-169.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.61 (m, 2H), 7.60 – 7.55 (m, 1H), 7.54 – 7.47 (m, 2H), 7.22 – 7.15 (m, 2H), 7.05 – 6.97 (m, 2H), 3.89 (s, 1H), 3.55 (ddd, *J* = 13.8, 9.5, 6.8 Hz, 1H), 3.05 (ddd, *J* = 14.0, 9.6, 4.7 Hz, 1H), 1.54 (dtdd, *J* = 13.9, 9.4, 6.3, 4.8 Hz, 1H), 1.47 – 1.36 (m, 1H), 1.22 – 1.13 (m, 1H), 1.11 (s, 6H), 1.09 – 0.99 (m, 1H), 0.95 (s, 6H), 0.72 (t, *J* = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 174.2, 161.4 (d, J_{CF} = 243.5 Hz), 134.6 (d, J_{CF} = 3.1 Hz), 132.1, 129.6 (d, J_{CF} = 7.9 Hz, 2C), 128.7 (2C), 128.4 (2C), 127.8, 114.9 (d, J_{CF} = 21.3 Hz, 2C), 80.2, 46.0, 29.3, 25.0, 24.5, 19.6, 13.4. HRMS (EI-TOF, m/z) calcd for $C_{24}H_{31}BFNO_3$ $[M]^+$ 411.2381, found 411.2380.

N-butyl-N-((4-chlorophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide ***(3e)***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 78% (333mg); m.p. 185.6-186.0 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.61 (m, 2H), 7.61 – 7.55 (m, 1H), 7.50 (ddd, *J* = 6.8, 4.5, 1.3 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.18 – 7.11 (m, 2H), 3.89 (s, 1H), 3.56 (ddd, *J* = 13.9, 9.5, 6.8 Hz, 1H), 3.06 (ddd, *J* = 14.0, 9.5, 4.7 Hz, 1H), 1.53 (dtdd, *J* = 13.9, 9.4, 6.3, 4.8 Hz, 1H), 1.47 – 1.35 (m, 1H), 1.22 – 1.13 (m, 1H), 1.11 (s, 6H), 1.10 – 1.01 (m, 1H), 0.96 (s, 6H), 0.72 (t, *J* = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 174.4, 137.7, 132.2, 131.5, 129.3 (2C), 128.8 (2C), 128.4 (2C), 128.3 (2C), 127.8, 80.2 (2C), 46.1, 29.3, 25.0 (2C), 24.6 (2C), 19.6, 13.4. HRMS (EI-TOF, m/z) calcd for $C_{24}H_{31}B^{35}ClNO_3$ $[M]^+$ 427.2086, found 427.2083; calcd for $C_{24}H_{31}B^{37}ClNO_3$ $[M]^+$ 429.2056, found 429.2058.

N-((4-bromophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-N-butylbenzamide ***(3f)***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 80% (377mg); m.p. 199.0-200.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (m, 2H), 7.61 – 7.55 (m, 1H), 7.54 – 7.48 (m, 2H), 7.46 – 7.41 (m, 2H), 7.13 – 7.06 (m, 2H), 3.87 (s, 1H), 3.57 (ddd, *J* = 13.9, 9.5, 6.8 Hz, 1H), 3.06 (ddd, *J* = 14.0, 9.5, 4.7 Hz, 1H), 1.53 (dtdd, *J* = 14.0, 9.4, 6.2, 4.9 Hz, 1H), 1.46 – 1.35 (m, 1H), 1.18 (dd, *J* = 14.2, 6.7 Hz, 1H), 1.11 (s, 6H), 1.09 – 1.00 (m, 1H), 0.96 (s, 6H), 0.71 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.4, 138.2, 132.2, 131.2 (2C), 129.7 (2C), 128.8 (2C), 128.4 (2C), 127.7, 119.6, 80.2 (2C), 46.1, 29.3, 25.0 (2C), 24.6 (2C), 19.6, 13.4. HRMS (EI-TOF, m/z) calcd for $C_{24}H_{31}B^{79}BrNO_3$ $[M]^+$ 471.1580, found 471.1573; calcd for $C_{24}H_{31}B^{81}BrNO_3$ $[M]^+$ 473.1560, found 473.1556.

N-butyl-N-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(4-(trifluoromethyl)phenyl)methyl)benzamide ***(3g)***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 65% (300mg); m.p. 144.6-145.3 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.60 (m, 2H), 7.58 – 7.53 (m, 1H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.14 – 7.07 (m, 4H), 3.87 (s, 1H), 3.52 (ddd, *J* = 13.8, 9.4, 6.9 Hz, 1H), 3.08 (ddd, *J* = 14.0, 9.5, 4.7 Hz, 1H), 2.34 (s, 3H), 1.53 (dtd, *J* = 14.0, 9.1, 4.7 Hz, 1H), 1.41 (ddd, *J* = 15.9, 7.8, 4.7 Hz, 1H), 1.16 (dd, *J* = 14.3, 8.1 Hz, 1H), 1.11 (s, 6H), 1.09 – 1.00 (m, 2H), 0.96 (s, 6H), 0.71 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.7, 143.6 (d, J_{CF} = 1.0 Hz, 2C), 132.3, 128.8 (2C), 128.4 (2C), 128.1 (q, J_{CF} = 32.3 Hz), 127.8, 127.6, 125.1 (q, J_{CF} = 3.7 Hz, 2C), 124.4 (q, J_{CF} = 271.7 Hz), 80.3 (2C), 46.3, 29.4, 25.0 (2C), 24.6 (2C), 19.6, 13.3. HRMS (EI-TOF, m/z) calcd for $C_{25}H_{31}BF_3NO_3$ $[M]^+$ 461.2349, found 461.2352.

Methyl 4-((N-butylbenzamido)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzoate ***(3h)***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 85% (383mg); m.p. 162.3-162.9 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.60 (m, 2H), 7.58 – 7.53 (m, 1H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.14 – 7.07 (m, 4H), 3.87 (s, 1H), 3.52 (ddd, *J* = 13.8, 9.4, 6.9 Hz, 1H), 3.08 (ddd, *J* = 14.0, 9.5, 4.7 Hz, 1H), 2.34 (s, 3H), 1.53 (dtd, *J* = 14.0, 9.1, 4.7 Hz, 1H), 1.41 (ddd, *J* = 15.9, 7.8, 4.7 Hz, 1H), 1.16 (dd, *J* = 14.3, 8.1 Hz, 1H), 1.11 (s, 6H), 1.09 – 1.00 (m, 2H), 0.96 (s, 6H), 0.71 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.6, 167.2, 145.0, 132.3, 129.5 (2C), 128.8 (2C), 128.4 (2C), 127.8, 127.6, 127.6 (2C), 80.3 (2C), 52.0, 46.4, 29.3, 25.0 (2C), 24. 6 (2C), 19.6, 13.4. HRMS (EI-TOF, m/z) calcd for $C_{26}H_{34}BNO_5$ $[M]^+$ 451.2530, found 451.2527.

N-((3-bromophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-N-butylbenzamide ***(3i)***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 71% (334mg); m.p. 127.3-128.1 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.2 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 2H), 7.39 – 7.31 (m, 2H), 7.22 – 7.11 (m, 2H), 3.87 (s, 1H), 3.60 (ddd, *J* = 14.0, 9.5, 6.8 Hz, 1H), 3.11 (ddd, *J* = 14.0, 9.6, 4.7 Hz, 1H), 1.61 – 1.48 (m, 1H), 1.48 – 1.35 (m, 1H), 1.18 (dd, *J* = 14.2, 6.9 Hz, 1H), 1.12 (s, 6H), 1.11 – 1.00 (m, 1H), 0.97 (s, 6H), 0.73 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.6, 141.7, 132.3, 130.6, 129.7, 129.0, 128.8 (2C), 128.5 (2C), 127.6, 126.4, 122.2, 80.3 (2C), 46.3, 29.4, 25.1 (2C), 24.5 (2C), 19.6, 13.4. HRMS (EI-TOF, m/z) calcd for $C_{24}H_{31}B^{79}BrNO_3$ $[M]^+$ 471.1580, found 471.1568; calcd for $C_{24}H_{31}B^{81}BrNO_3$ $[M]^+$ 473.1560, found 473.1553.

N-((2-bromophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-N-butylbenzamide ***(3j)***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 52% (245mg); m.p. 147.9-148.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.61 (m, 2H), 7.60 – 7.48 (m, 4H), 7.32 – 7.26 (m, 1H), 7.22 – 7.15 (m, 1H), 7.05 (td, *J* = 8.0, 1.6 Hz, 1H), 4.56 (s, 1H), 3.63 – 3.49 (m, 1H), 3.00 (ddd, *J* = 13.9, 9.4, 4.6 Hz, 1H), 1.58 (dtdd, *J* = 13.8, 9.2, 6.3, 4.7 Hz, 1H), 1.46 (qdd, *J* = 7.3, 5.5, 3.5 Hz, 1H), 1.24 – 1.14 (m, 1H), 1.12 (s, 6H), 1.11 – 1.00 (m, 1H), 0.97 (s, 6H), 0.74 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.5, 138.6, 132.5, 132.1, 129.4, 128.8 (2C), 128.4 (2C), 127.8, 127.3, 127.2, 123.9, 80.2 (2C), 46.4, 29.3, 25.0 (2C), 24.5 (2C), 19.6, 13.4. HRMS (EI-TOF, m/z) calcd for $C_{24}H_{31}B^{79}BrNO_3$ $[M]^+$ 471.1580, found 471.1562; calcd for $C_{24}H_{31}B^{81}BrNO_3$ $[M]^+$ 473.1560, found 473.1557.

N-butyl-N-((2,4-dichlorophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide ***(3k)***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 55% (254mg); m.p. 178.3-179.1 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.56 (m, 3H), 7.50 (dd, *J* = 11.4, 4.3 Hz, 2H), 7.39 (d, *J* = 2.1 Hz, 1H), 7.23 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 4.49 (s, 1H), 3.57 (ddd, *J* = 13.9, 9.2, 7.2 Hz, 1H), 2.98 (ddd, *J* = 13.9, 9.4, 4.7 Hz, 1H), 1.61 – 1.49 (m, 1H), 1.43 (tdd, *J* = 13.4, 6.6, 2.4 Hz, 1H), 1.25 – 1.14 (m, 1H), 1.12 (s, 6H), 1.05 (m, 7H), 0.74 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.7, 135.6, 133.9, 132.3, 131.8, 129.1, 128.8 (2C), 128.4 (2C), 127.6, 127.0 (2C), 80.3 (2C), 46.5, 29.3, 25.0 (2C), 24.5 (2C), 19.6, 13.4. HRMS (EI-TOF, m/z) calcd for $C_{24}H_{30}B^{35}Cl_2NO_3$ $[M]^+$ 461.1696, found 461.1680; calcd for $C_{24}H_{30}B^{35}Cl^{37}ClNO_3$ $[M]^+$ 463.1666, found 463.1674; calcd for $C_{24}H_{30}B^{37}Cl_2NO_3$ $[M]^+$ 465.1637, found 465.1654.

N-butyl-N-(naphthalen-2-yl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide ***(3l)***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 88% (390mg); m.p. 142.8-144.1 ℃. ^{1}H NMR (400

MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 3H), 7.69 (dt, *J* = 3.7, 1.5 Hz, 3H), 7.56 – 7.52 (m, 1H), 7.51 – 7.46 (m, 2H), 7.46 – 7.37 (m, 3H), 4.12 (s, 1H), 3.58 (ddd, *J* = 13.9, 9.3, 6.9 Hz, 1H), 3.10 (ddd, *J* = 14.0, 9.4, 4.8 Hz, 1H), 1.62 – 1.50 (m, 1H), 1.50 – 1.39 (m, 1H), 1.21 – 1.09 (m, 7H), 1.09 – 0.73 (m, 7H), 0.68 (t, *J* = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 174.3, 136.8, 133.5, 132.2, 132.1, 128.7 (2C), 128.3 (2C), 127.8, 127.7, 127.6, 127.5, 126.6, 126.2, 125.7, 125.1, 80.1 (2C), 46.1, 29.3, 25.1 (2C), 24.6 (2C), 19.5, 13.3. HRMS (EI-TOF, m/z) calcd for $C_{28}H_{34}BNO_3$ $[M]^+$ 443.2632, found 443.2625.

N-butyl-N-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(thiophen-2-yl)methyl)benzamide ***(3m)***. Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid; yield 56% (223mg); m.p. 152.4-153.6 ℃. ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 2H), 7.58 – 7.52 (m, 1H), 7.48 (dd, *J* = 10.0, 4.8 Hz, 2H), 7.23 (d, *J* = 4.7 Hz, 1H), 6.98 (dt, *J* = 5.0, 3.3 Hz, 2H), 4.23 (s, 1H), 3.50 (ddd, *J* = 14.0, 9.7, 6.7 Hz, 1H), 3.14 (ddd, *J* = 14.1, 9.8, 4.6 Hz, 1H), 1.67 – 1.56 (m, 1H), 1.48 – 1.36 (m, 1H), 1.24 – 1.17 (m, 1H), 1.15 (s, 6H), 1.10 (dd, *J* = 14.2, 7.0 Hz, 1H), 1.05 (s, 6H), 0.74 (t, *J* = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 173.7, 141.2, 132.1, 128.7 (2C), 128.4 (2C), 127.8, 126.7, 126.3, 124.6, 80.4 (2C), 45.8, 29.5, 24.9 (2C), 24.6, 24.6, 19.6, 13.4. HRMS (EI-TOF, m/z) calcd for $C_{22}H_{30}BNO_3S$ $[M]^+$ 399.2039, found 399.2042.

N-ethyl-N-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(p-tolyl)methyl)benzamide ***(3n)***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 82% (311mg); m.p. 157.4-158.1 ℃. ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.60 (m, 2H), 7.58 – 7.53 (m, 1H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.14 – 7.07 (m, 4H), 3.87 (s, 1H), 3.52 (ddd, *J* = 13.8, 9.4, 6.9 Hz, 1H), 3.08 (ddd, *J* = 14.0, 9.5, 4.7 Hz, 1H), 2.34 (s, 3H), 1.53 (dtd, *J* = 14.0, 9.1, 4.7 Hz, 1H), 1.41 (ddd, *J* = 15.9, 7.8, 4.7 Hz, 1H), 1.16 (m, 1H), 1.11 (s, 6H), 1.09 – 1.00 (m, 1H), 0.96 (s, 6H), 0.71 (t, *J* = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 173.8, 135.7, 135.3, 132.1, 128.8 (2C), 128.7 (2C), 128.4 (2C), 128.0 (2C), 127.9, 80.1 (2C), 41.1, 25.0 (2C), 24.6 (2C), 21.1, 13.0. HRMS (EI-TOF, m/z) calcd for $C_{23}H_{30}BNO_3$ $[M]^+$ 379.2319, found 379.2316.

N-ethyl-N-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide ***(3n')***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 78% (285mg); m.p. 142.8-143.5 ℃. ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.63 (m, 2H), 7.60 – 7.54 (m, 1H), 7.53 – 7.47 (m, 2H), 7.34 – 7.29 (m, 2H), 7.23 – 7.17 (m, 3H), 3.95 (s, 1H), 3.65 (dq, *J* = 14.3, 7.2 Hz, 1H), 3.18 (dq, *J* = 14.3, 7.2 Hz, 1H), 1.10 (dd, *J* = 12.1, 4.7 Hz, 9H), 0.96 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 173.9, 139.0, 132.1, 128.7 (2C), 128.4 (2C), 128.1 (2C), 127.9 (2C), 127.8, 125.9, 80.1 (2C), 41.2, 25.0 (2C), 24.6 (2C), 13.0. HRMS (EI-TOF, m/z) calcd for $C_{22}H_{28}BNO_3$ $[M]^+$ 365.2152, found 365.2158.

N-benzyl-N-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(p-tolyl)methyl)benzamide ***(3o)***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 81% (357mg); m.p. 206.0-206.8 ℃. ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.2 Hz, 2H), 7.54 (dt, *J* = 29.1, 6.9 Hz, 3H), 7.26 (d, *J* = 2.0 Hz, 3H), 7.12 (d, *J* = 7.3 Hz, 2H), 7.04 (d, *J* = 6.9 Hz, 2H), 6.92 (d, *J* = 2.7 Hz, 2H), 4.85 (d, *J* = 15.1 Hz, 1H), 4.16 (d, *J* = 15.1 Hz, 1H), 3.74 (s, 1H), 2.35 (s, 3H), 1.09 (s, 6H), 0.94 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 174.5, 135.4, 135.4, 133.9, 132.2, 128.9 (2C), 128.9 (2C), 128.8 (2C), 128.5 (2C), 128.4 (2C), 128.2, 128.0 (2C), 127.9, 80.1 (2C), 49.7, 25.0 (2C), 24.5 (2C), 21.2. HRMS (EI-TOF, m/z) calcd for $C_{28}H_{32}BNO_3$ $[M]^+$ 441.2475, found 441.2480.

N-benzyl-N-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide ***(3o')***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 75% (320mg); m.p. 189.5-190.7 ℃. ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.71 (m, 2H), 7.62 – 7.57 (m, 1H), 7.55 – 7.49 (m, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.28 – 7.25 (m, 3H), 7.24 – 7.20 (m, 1H), 7.16 – 7.12 (m, 2H), 6.95 – 6.89 (m, 2H), 4.89 (d, *J* = 15.0 Hz, 1H), 4.17 (d, *J* = 15.1 Hz, 1H), 3.78 (s, 1H), 1.09 (s, 6H), 0.93 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 174.7, 138.7, 133.7, 132.3, 128.9 (2C), 128.9 (2C), 128.6 (2C), 128.3 (3C), 128.1 (2C), 128.1 (2C), 127.8, 126.0, 80.2 (2C), 49.9, 24.9 (2C), 24.5 (2C). HRMS (EI-TOF, m/z) calcd for $C_{27}H_{30}BNO_3$ $[M]^+$ 427.2319, found 427.2312.

N-(2,4-dimethoxybenzyl)-N-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(p-tolyl)methyl)benzamide ***(3p)***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 70% (351mg); m.p. 219.4-220.1 ℃. ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (ddd, *J* = 7.0, 4.1, 2.0 Hz, 2H), 7.59 – 7.53 (m, 1H), 7.52 – 7.46 (m, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.69 (d, *J* = 8.3 Hz, 1H), 6.32 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.27 (d, *J* = 2.3 Hz, 1H), 4.91 (d, *J* = 14.3 Hz, 1H), 4.07 (d, *J* = 14.3 Hz, 1H), 3.75 (s, 3H), 3.65 (s, 1H), 3.41 (s, 3H), 2.35 (s, 3H), 1.06 (s, 6H), 0.88 (s, *J* = 12.7, 5.8 Hz, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 174.3, 161.2, 158.7, 136.2, 134.9, 131.8, 131.5, 128.7, 128.7, 128.7 (2C), 128.5, 128.4 (2C), 128.2, 126.9, 114.1, 103.8, 98.4, 79.9 (2C), 55.4, 54.7, 45.4, 25.0 (2C), 24.6 (2C), 21.2. HRMS (EI-TOF, m/z) calcd for $C_{30}H_{36}BNO_5$ $[M]^+$ 501.2687, found 501.2682.

methyl N-benzoyl-N-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(p-tolyl)methyl)glycinate ***(3q)***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 73% (309mg); m.p. 163.8-164.5 ℃. ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.64 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.10 (s, 4H), 4.17 (d,

J = 17.4 Hz, 1H), 3.98 – 3.85 (m, 2H), 3.63 (s, 3H), 2.33 (s, 3H), 1.12 (s, 6H), 0.97 (s, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 175.7, 167.6, 135.9, 134.6, 132.5, 128.9 (2C), 128.9 (2C), 128.7 (2C), 128.3 (2C), 127.5, 80.3 (2C), 52.7, 48.1, 24.9 (2C), 24.6 (2C), 21.1. HRMS (EI-TOF, m/z) calcd for $C_{24}H_{30}BNO_5$ $[M]^+$ 423.2217, found 423.2213.

methyl N-benzoyl-N-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)glycinate ***(3q')***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 69% (282mg); m.p. 145.9-146.7 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.64 (m, 2H), 7.58 (dd, *J* = 10.8, 4.1 Hz, 1H), 7.48 (dd, *J* = 11.4, 4.2 Hz, 2H), 7.33 – 7.28 (m, 2H), 7.24 – 7.17 (m, 3H), 4.21 (d, *J* = 17.4 Hz, 1H), 4.00 – 3.88 (m, 2H), 3.62 (s, 3H), 1.12 (s, 6H), 0.97 (s, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 176.0, 167.5, 137.8, 132.5, 128.9 (2C), 128.5 (2C), 128.3 (2C), 128.1 (2C), 127.3, 126.4, 80.3 (2C), 52.7, 48.3, 24.9 (2C), 24.5 (2C). HRMS (EI-TOF, m/z) calcd for $C_{23}H_{28}BNO_5$ $[M]^+$ 409.2061, found 409.2063.

N-phenyl-N-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide ***(3r)***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 38% (157mg); m.p. 131.7-132.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.25 (t, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 4.3 Hz, 4H), 7.16 – 7.12 (m, 3H), 7.09 (dq, *J* = 8.7, 4.1 Hz, 1H), 6.94 (dd, *J* = 6.4, 3.1 Hz, 2H), 4.33 (s, 1H), 1.17 (s, 6H), 1.01 (s, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 172.7, 138.9, 138.8, 132.7, 130.5 (2C), 129.3 (2C), 128.7 (2C), 128.1(8), 128.1(5) (2C), 127.7 (2C), 127.2, 126.4, 125.8, 80.3 (2C), 25.1 (2C), 24.5 (2C). HRMS (EI-TOF, m/z) calcd for $C_{26}H_{28}BNO_3$ $[M]^+$ 413.2162, found 413.2155.

N-((4-chlorophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-N-phenylbenzamide ***(3s)***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 26% (116mg); m.p. 163.4-164.1 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 3H), 7.27 – 7.23 (m, 2H), 7.19 (d, *J* = 4.3 Hz, 3H), 7.16 – 7.13 (m, 3H), 7.09 (td, *J* = 8.7, 7.7, 3.3 Hz, 1H), 6.97 – 6.92 (m, 2H), 4.34 (s, 1H), 1.17 (s, 6H), 1.02 (s, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 172.8, 139.0, 138.8, 132.6, 130.5 (2C), 129.5 (2C), 129.3 (2C), 128.7, 128.2, 128.2 (2C), 127.7 (2C), 126.5 (2C), 125.8, 80.4 (2C), 25.0 (2C), 24.5 (2C). HRMS (EI-TOF, m/z) calcd for $C_{26}H_{27}B^{35}ClNO_3$ $[M]^+$ 447.1773, found 447.1771; calcd for $C_{26}H_{27}B^{37}ClNO_3$ $[M]^+$ 449.1743, found 449.1738.

N-phenyl-N-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(p-tolyl)methyl)benzamide ***(3t)***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 60% (256mg); m.p. 148.9-149.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 2H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 2H), 7.16 – 7.12 (m, 3H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 7.9 Hz, 2H), 6.95 – 6.89 (m, 2H), 4.28 (s, 1H), 2.24 (s, 3H), 1.17 (s, 6H), 1.02 (s, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 172.5, 139.0, 135.6, 135.2, 132.6, 130.4 (2C), 129.2 (2C), 128.8 (2C), 128.4 (2C), 128.1 (3C), 127.3, 126.5 (2C), 80.3 (2C), 25.1 (2C), 24.6 (2C), 21.1. HRMS (EI-TOF, m/z) calcd for $C_{27}H_{30}BNO_3$ $[M]^+$ 427.2319, found 427.2310.

N-((4-methoxyphenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-N-phenylbenzamide ***(3u)***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 68% (301mg); m.p. 138.2-139.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.38 (m, 3H), 7.23 (t, *J* = 7.8 Hz, 2H), 7.17 – 7.10 (m, 5H), 6.73 (d, *J* = 8.6 Hz, 2H), 4.25 (s, 1H), 3.72 (s, 3H), 1.18 (s, 6H), 1.03 (s, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 172.43, 157.83, 138.92, 132.57, 130.72, 130.42(2C), 130.3 (2C), 129.3 (2C), 128.1, 128.1 (2C), 127.3, 126.6 (2C), 113.1 (2C), 80.3 (2C), 55.0, 25.0 (2C), 24.5 (2C). HRMS (EI-TOF, m/z) calcd for $C_{27}H_{30}BNO_4$ $[M]^+$ 443.2268, found 443.2262.

N-(4-methoxyphenyl)-N-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(p-tolyl)methyl)benzamide ***(3v)***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 73% (334mg); m.p. 154.1-155.0 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 2H), 7.44 – 7.38 (m, 1H), 7.28 – 7.23 (m, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 7.9 Hz, 2H), 6.85 – 6.80 (m, 2H), 6.68 – 6.62 (m, 2H), 4.20 (s, 1H), 3.69 (s, 3H), 2.26 (s, 3H), 1.17 (s, 6H), 1.01 (s, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 172.43, 158.94, 135.74, 135.17, 132.47, 131.84, 130.47(2C), 128.82(2C), 128.42(2C), 128.11(2C), 127.61(2C), 127.4, 114.4 (2C), 80.3 (2C), 55.3, 25.1 (2C), 24.6 (2C), 21.1. HRMS (EI-TOF, m/z) calcd for $C_{28}H_{32}BNO_4$ $[M]^+$ 457.2424, found 457.2419.

N-ethyl-4-fluoro-N-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide ***(4a)***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 78% (299mg); m.p. 147.0-147.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.67 (m, 2H), 7.34 – 7.28 (m, 2H), 7.24 – 7.17 (m, 5H), 3.95 (s, 1H), 3.64 (dq, *J* = 14.3, 7.2 Hz, 1H), 3.21 (dq, *J* = 14.3, 7.2 Hz, 1H), 1.15 – 1.08 (m, 9H), 0.96 (s, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 172.9, 164.8 (d, J_{CF} = 254.5 Hz), 138.8, 131.0 (d, J_{CF} = 9.0 Hz, 2C), 128.2 (2C), 127.9 (2C), 126.0, 123.9 (d, J_{CF} = 3.5 Hz), 116.2 (d, J_{CF} = 22.2 Hz, 2C), 80.2 (2C), 41.3, 25.0 (2C), 24.5 (2C), 12.95.HRMS (EI-TOF, m/z) calcd for $C_{22}H_{27}BFNO_3$ $[M]^+$ 383.2068, found 383.2065.

4-chloro-N-ethyl-N-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide ***(4b)***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 82% (327mg); m.p. 164.5-165.3 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.58 (m, 2H), 7.52 – 7.46 (m, 2H), 7.34 – 7.29 (m, 2H), 7.19 (dd, *J* = 10.3, 4.1 Hz,

3H), 3.96 (s, 1H), 3.62 (dq, *J* = 14.3, 7.2 Hz, 1H), 3.20 (dq, *J* = 14.3, 7.2 Hz, 1H), 1.16 – 1.06 (m, 9H), 0.96 (s, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 172.8, 138.5, 138.4, 129.7 (2C), 129.0 (2C), 128.0 (2C), 127.7 (2C), 126.0, 125.9, 80.0 (2C), 41.1, 24.9 (2C), 24.4 (2C), 12.8. HRMS (EI-TOF, m/z) calcd for $C_{22}H_{27}B^{35}ClNO_3$ $[M]^+$ 399.1773, found 399.1770; calcd for $C_{22}H_{27}B^{37}ClNO_3$ $[M]^+$ 401.1743, found 401.1754.

4-bromo-N-ethyl-N-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide ***(4c)***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 85% (377mg); m.p. 178.8-179.6 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.33 – 7.28 (m, 2H), 7.20 (t, *J* = 8.4 Hz, 3H), 3.94 (s, 1H), 3.60 (dq, *J* = 14.3, 7.1 Hz, 1H), 3.19 (dq, *J* = 14.2, 7.1 Hz, 1H), 1.14 – 1.06 (m, 9H), 0.95 (s, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 173.0, 138.7, 132.2 (2C), 129.9 (2C), 128.2 (2C), 127.9 (2C), 127.0, 126.7, 126.0, 80.2 (2C), 41.3, 25.0 (2C), 24.5 (2C), 13.0. HRMS (EI-TOF, m/z) calcd for $C_{22}H_{27}B^{79}BrNO_3$ $[M]^+$ 443.1267, found 443.1250; calcd for $C_{22}H_{27}B^{81}BrNO_3$ $[M]^+$ 445.1247, found 445.1237.

N-ethyl-N-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-4-(trifluoromethyl)benzamide ***(4d)***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 70% (303mg); m.p. 136.8-137.3 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 4H), 7.36 – 7.31 (m, 2H), 7.25 – 7.19 (m, 3H), 3.98 (s, 1H), 3.56 (dq, *J* = 14.3, 7.2 Hz, 1H), 3.20 (dq, *J* = 14.3, 7.2 Hz, 1H), 1.17 – 1.06 (m, 9H), 0.97 (s, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 172.7, 138.4, 133.8 (q, J_{CF} = 33.1 Hz), 131.5 (d, J_{CF} = 1.0 Hz, 2C), 128.7 (2C), 128.2 (2C), 127.9 (2C), 126.1, 125.9 (q, J_{CF} = 3.7 Hz, 2C), 123.3 (q, J_{CF} = 272.8 Hz), 80.3 (2C), 41.2, 25.0 (2C), 24.5 (2C), 12.9. HRMS (EI-TOF, m/z) calcd for $C_{23}H_{27}BF_3NO_3$ $[M]^+$ 433.2036, found 433.2030.

N-ethyl-4-methoxy-N-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(p-tolyl)methyl)benzamide ***(4e)***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 78% (319mg); m.p. 163.8-164.7 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.63 (m, 2H), 7.13 – 7.07 (m, 4H), 7.00 – 6.95 (m, 2H), 3.90 (s, 1H), 3.85 (s, 3H), 3.71 (dq, *J* = 14.1, 7.1 Hz, 1H), 3.20 (dq, *J* = 14.3, 7.2 Hz, 1H), 2.32 (s, 3H), 1.15 – 1.09 (m, 9H), 0.97 (s, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 173.1, 162.6, 136.0, 135.1, 130.7 (2C), 128.7 (2C), 127.9 (2C), 119.6, 114.0 (2C), 79.8 (2C), 55.4, 41.2, 25.1 (2C), 24.6 (2C), 21.1, 13.0. HRMS (EI-TOF, m/z) calcd for $C_{24}H_{32}BNO_4$ $[M]^+$ 409.2424, found 409.2421.

3-bromo-N-ethyl-N-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide ***(4f)***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 62% (275mg); m.p. 153.8-154.6 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (t, *J* = 1.6 Hz, 1H), 7.75 – 7.66 (m, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.9 Hz, 1H), 7.35 – 7.29 (m, 2H), 7.21 (t, *J* = 6.7 Hz, 3H), 3.95 (s, 1H), 3.59 (dq, *J* = 14.3, 7.2 Hz, 1H), 3.18 (dq, *J* = 14.3, 7.2 Hz, 1H), 1.15 – 1.07 (m, 9H), 0.96 (s, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 172.5, 138.5, 135.1, 131.3, 130.3, 129.8, 128.2 (2C), 127.9 (2C), 126.7, 126.0, 122.9, 80.2 (2C), 41.2, 25.0 (2C), 24.5 (2C), 12.9. HRMS (EI-TOF, m/z) calcd for $C_{22}H_{27}B^{79}BrNO_3$ $[M]^+$ 443.1267, found 443.1259; calcd for $C_{22}H_{27}B^{81}BrNO_3$ $[M]^+$ 445.1247, found 445.1229.

2-bromo-N-ethyl-N-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzamide ***(4g)***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 34% (150mg); m.p. 134.3-135.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.50 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.46 (td, *J* = 7.4, 1.1 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.35 – 7.26 (m, 4H), 7.23 – 7.18 (m, 1H), 3.94 (s, 1H), 3.22 (dq, *J* = 14.5, 7.2 Hz, 1H), 3.11 (dq, *J* = 14.2, 7.2 Hz, 1H), 1.12 (s, 6H), 1.03 (t, *J* = 7.2 Hz, 3H), 0.96 (s, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 172.6, 138.6, 133.3, 132.4, 130.6, 129.2, 128.1 (2C), 128.1 (2C), 127.8, 125.9, 120.2, 80.2, 40.9, 25.0 (2C), 24.6 (2C), 12.5. HRMS (EI-TOF, m/z) calcd for $C_{22}H_{27}B^{79}BrNO_3$ $[M]^+$ 443.1267, found 443.1260; calcd for $C_{22}H_{27}B^{81}BrNO_3$ $[M]^+$ 445.1247, found 445.1239.

N-ethyl-N-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(p-tolyl)methyl)acetamide ***(4h)***. Eluent: petroleum ether/ethyl acetate (2:1). White solid; yield 69% (219mg); m.p. 156.5-157.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 7.9 Hz, 2H), 7.00 (d, *J* = 8.1 Hz, 2H), 3.71 (s, 1H), 3.39 (dq, *J* = 14.4, 7.2 Hz, 1H), 3.09 (dq, *J* = 14.4, 7.2 Hz, 1H), 2.32 (s, 3H), 2.27 (d, *J* = 1.1 Hz, 3H), 1.13 – 1.06 (m, 9H), 0.92 (s, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 174.6, 135.7, 135.3, 128.7 (2C), 128.1 (2C), 79.9 (2C), 40.1, 25.0 (2C), 24.5 (2C), 21.1, 15.8, 12.6. HRMS (EI-TOF, m/z) calcd for $C_{18}H_{28}BNO_3$ $[M]^+$ 317.2162, found 317.2164.

N-ethyl-3-methyl-N-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(p-tolyl)methyl)but-2-enamide ***(4i)***. Eluent: petroleum ether/ethyl acetate (2:1). White solid; yield 70% (250mg); m.p. 178.3-179.1 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 7.9 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 5.88 (s, 1H), 3.69 (s, 1H), 3.47 (dq, *J* = 14.5, 7.2 Hz, 1H), 3.09 (dq, *J* = 14.4, 7.2 Hz, 1H), 2.31 (s, 3H), 2.28 (s, 3H), 2.02 (s, 3H), 1.11 – 1.06 (m, 9H), 0.94 (s, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 169.7, 161.4, 136.7, 135.0, 128.6 (2C), 128.0 (2C), 108.6, 79.7 (2C), 39.8, 28.7, 25.0 (2C), 24.5 (2C), 21.6, 21.1, 13.1. HRMS (EI-TOF, m/z) calcd for $C_{21}H_{32}BNO_3$ $[M]^+$ 357.2475, found 357.2472.

N-ethyl-N-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(p-tolyl)methyl)furan-2-carboxamide ***(4j)***. Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid; yield 85% (314mg); m.p. 137.2-138.1 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, J = 1.6, 0.8 Hz, 1H), 7.48 (dd, J = 3.6, 0.6 Hz, 1H), 7.11 – 7.04 (m, 4H), 6.62 (dd, J = 3.6, 1.8 Hz, 1H), 4.18 (dq, J = 14.3, 7.2 Hz, 1H), 3.91 (s, 1H), 3.25 (dq, J = 14.3, 7.2 Hz, 1H), 2.32 (s, 3H), 1.17 (t, J = 7.2 Hz, 3H), 1.12 (s, 6H), 0.97 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.3, 147.2, 142.6, 136.0, 135.3, 128.7 (2C), 128.2 (2C), 122.8, 112.5, 80.0 (2C), 41.0, 25.1 (2C), 24.5 (2C), 21.1, 13.5. HRMS (EI-TOF, m/z) calcd for $C_{21}H_{28}BNO_4$ $[M]^+$ 369.2111, found 368.2123.

N-ethyl-N-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(p-tolyl)methyl)thiophene-2-carboxamide ***(4k)***. Eluent: petroleum ether/ethyl acetate (3:1). White solid; yield 88% (339mg); m.p. 158.9-159.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, J = 3.9, 1.1 Hz, 1H), 7.73 (dd, J = 5.0, 1.1 Hz, 1H), 7.20 (dd, J = 5.0, 3.9 Hz, 1H), 7.12 – 7.05 (m, 4H), 3.99 – 3.89 (m, 2H), 3.34 (dq, J = 14.5, 7.2 Hz, 1H), 2.33 (s, 3H), 1.22 (t, J = 7.2 Hz, 3H), 1.13 (s, 6H), 0.99 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.1, 135.9, 135.4, 135.0, 133.6, 128.8 (2C), 128.2 (2C), 128.1, 127.9, 80.0 (2C), 41.2, 25.1 (2C), 24.5 (2C), 21.1, 12.9. HRMS (EI-TOF, m/z) calcd for $C_{21}H_{28}BNO_3S$ $[M]^+$ 385.1883, found 385.1886.

ASSOCIATED CONTENT

Supporting information

^{1}H and ^{13}C NMR spectra of all compounds (PDF).

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Notes

The authors declare no competing financial interest.

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