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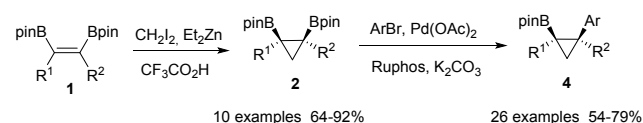
# Simmons-Smith Cyclopropanation of Alkenyl 1,2-bis(boronates): Stereoselective Access to Functionalized Cyclopropyl Derivatives

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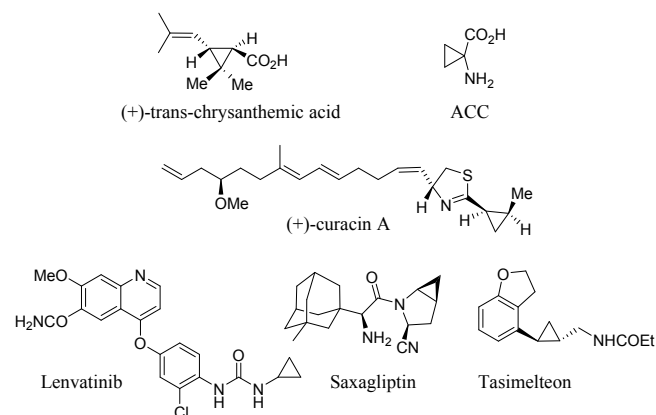


**ABSTRACT:** A Simmons-Smith stereodefined procedure for the synthesis of cyclopropyl-1,2-bis(boronates) has been developed starting from the corresponding alkenes. The resulting compounds were then subjected to regioselective Suzuki–Miyaura couplings to produce diversely tri- or tetra-substituted arylcyclopropanes in good yields. Further functionalization with 2-lithiothiophene provided 1,2-bis(aryl)cyclopropanes.

## INTRODUCTION

Natural products such as (+)-trans-chrysanthemic acid, 1-aminocyclopropanecarboxylic acid (ACC), or (+)-curacin A, contain the cyclopropyl ring. This is true also for drugs such as Lenvatinib, Saxagliptin or Tasimelteon, for example. Cyclopropyl-containing compounds present remarkable pharmacological profiles including anticancer, antibiotic, anti-inflammatory, anti-HCV, anti-HIV, insecticides, and so forth (Figure 1).<sup>1</sup>

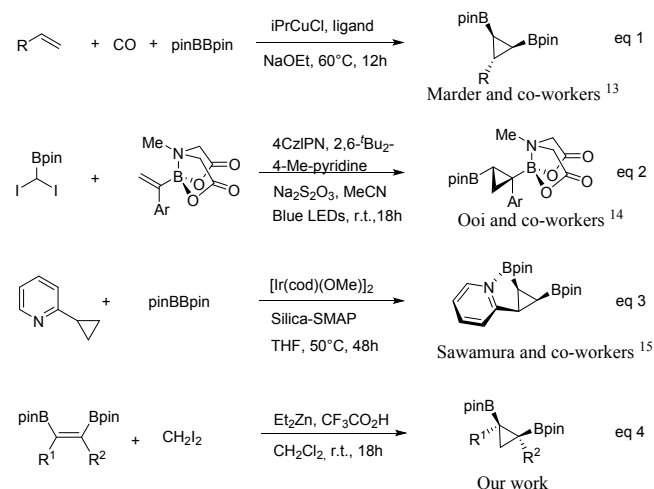
**Figure 1. Some cyclopropane-based natural and synthetic bioactive products.**



Furthermore, cyclopropanes were also used as key precursors to access challenging chemical structures and significant progress has been recently reported in the

development of synthetic methods based on such privileged intermediates.<sup>2</sup> Boronic acids and esters are also extensively used in organic synthesis and there are nowadays a plethora of methods available for the introduction and manipulation of these functional groups.<sup>3</sup> Within this class of compounds, cyclopropyl monoboronates occupy a unique place and their chemistry has been amply documented<sup>4</sup> since the research of pioneers such as Laurent,<sup>5</sup> Woods,<sup>6</sup> Matteson,<sup>7</sup> and Bubnov.<sup>8</sup> By contrast, despite the potential utility of the related bis-boronate derivatives, such species have found far fewer applications. 1,1-Diborylated cyclopropanes were synthesized from cyclopropyl lithioate after quenching with bis(pinacolato)diboron<sup>9</sup> or by base-catalyzed rearrangement and allylation of  $\beta$ -cyclopropyl alkyl bis(boronates).<sup>10</sup> They were further engaged in coupling reactions,<sup>11</sup> or stereoselective desymmetrization by trifluorination.<sup>12</sup> On the other hand, 1,2-disubstituted derivatives, can be prepared from terminal alkenes and bis(pinacolato)diboron in a copper-catalyzed process,<sup>13</sup> by photocatalytic borylcyclopropanation of  $\alpha$ -boryl styrenes<sup>14</sup> and, in a single case, by iridium-catalyzed borylation of 2-cyclopropylpyridine (Scheme 1, eq 1-3).<sup>15</sup>

### Scheme 1. Strategies for the Stereoselective Synthesis of Cyclopropyl 1,2-bis(boronates).



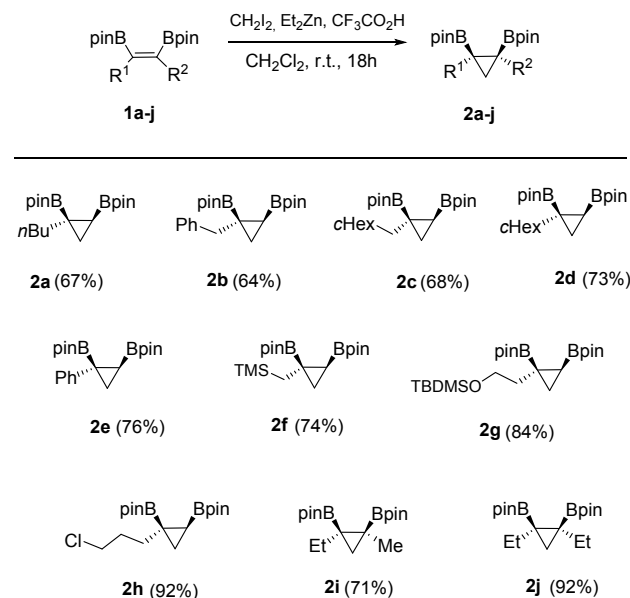
In consideration of the synthetic potential of these cyclopropyl-1,2-bis(boronates), we became interested in developing an alternative method to the previously reported strategies and thus, we describe herein the Simmons-Smith cyclopropanation of alkenyl-1,2-bis(boronates) as a stereoselective access to these doubly borolated cyclopropanes (Scheme 1, eq 4). The main advantage of this method is to synthesize stereoselectively 1,2-substituted cyclopropyl bis-boronic esters. Further functionalization of these valuable building blocks is also reported.

## RESULTS AND DISCUSSION

The synthesis of the starting alkenyl 1,2-bis(boronates) **1a-j** was first easily accomplished from the corresponding 1-alkynes and bis(pinacolato)diboron in the presence of tetrakis(triphenyl-phosphine)platinum as catalyst.<sup>16</sup> Our investigations to prepare cyclopropyl bis-boronic esters **2** involved diiodomethane and diethylzinc at  $50^\circ C$  in toluene, using alkene **1a** as a model.<sup>17</sup> The reaction occurred with moderate yield (53 %). Addition of one equivalent of trifluoroacetic acid, at room temperature in dichloromethane, allowed us to obtain the desired product **2a** with a yield of 67%. Next, the scope of the reaction was evaluated under these conditions. The alkenyl 1,2-bis(boronates) **1** were converted in good yields (64-92%) into cyclopropyl bis-boronic esters **2** by treatment with diiodomethane and diethylzinc in presence of trifluoroacetic acid at room temperature in dichloromethane (Table 1).<sup>18</sup> This transformation, which occurred with retention of configuration, as demonstrated by NOESY experiments,<sup>19</sup> tolerated different substitution patterns such as alkyl, aryl groups, silyl ether or chloride and it was equally efficient with tri- or tetra-substituted starting alkenes.

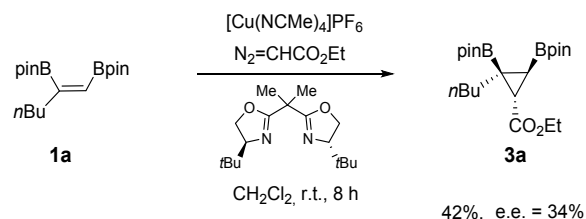
In parallel, we also explored the enantioselective cyclopropanation reaction of **1a** with a diazoester in the presence of a chiral copper(I) bisoxazoline complex according to the method developed by Carreras *et al.*<sup>20</sup> Pinacol 1,2-diboronic ester **1a** was treated with ethyl diazoacetate (EDA),  $[Cu(NCMe)_4]PF_6$  and (*S,S*)-(tert-butyl)bisoaxazoline to afford the expected tetra-substituted bis-boranyl cyclopropane **3a** with control of the relative stereochemistry (X-Ray structure determination)<sup>21</sup> in a moderate yield (42%) (Scheme 2, Figure 2). Unfortunately, only a modest enantiomeric ratio was determined by chiral HPLC (e.e. = 34%).

**Table 1. Synthesis of Cyclopropyl-1,2-bis(boronates) **2** from Alkene-1,2-Diboronic Esters **1a****



<sup>a</sup> General conditions:  $Et_2Zn$  (1M in hexane, 1 mmol), TFA (1 mmol),  $CH_2I_2$  (1 mmol) and **1** (0.5 mmol),  $CH_2Cl_2$  (2 mL), r.t., 18 h. <sup>b</sup> Yields of isolated products.

### Scheme 2. Enantioselective Synthesis of Cyclopropane **3a**.



In order to illustrate the synthetic potential of these bis-boronates **2**, we then investigated their Suzuki-Miyaura cross-coupling reactions using a broad range of arylbromides. These coupling were performed with Ruphos as catalyst in presence of palladium acetate and potassium carbonate, in THF/ $H_2O$  at reflux for 15 hours.<sup>22</sup> When  $R^2 = H$ , this reaction occurred regioselectively at the terminal C-B bond. Yields were good to moderate with the formation of a single cyclopropane derivative **4** with retention of

configuration (Table 2).<sup>23</sup> No significant influence was noticed on the basis of the nature of the aromatic ring substituents. In the case of the disubstituted cyclopropane-1,2-diboronic ester **2i**, the coupling reaction occurred with a high regioselectivity (at the  $\alpha$ -position of the methyl group vs ethyl) and only **4ie** was detected by <sup>1</sup>H NMR. Its relative

stereochemistry was further ascertained by X-ray diffraction crystallography<sup>24</sup> (Figure 2). It has to be noticed that successful Pd-catalyzed couplings of tertiary cyclopropylboronates are unusual.<sup>25</sup>

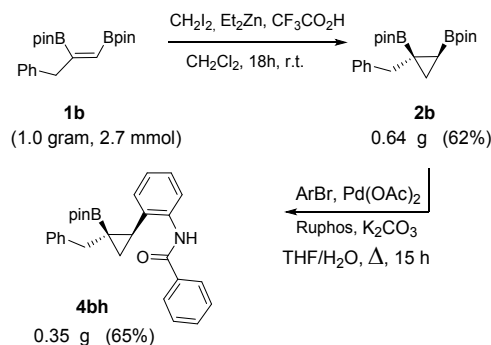
**Table 2. Suzuki-Miyaura Cross-Couplings with Cyclopropyl-1,2-bis(boronates) **2**<sup>a,b</sup>**

$  \begin{array}{c}  \text{pinB} \quad \text{Bpin} \\  \diagup \quad \diagdown \\  \text{R}^1 \text{---} \text{C} \text{---} \text{C} \text{---} \text{R}^2 \\  \diagdown \quad \diagup \\  \text{C}  \end{array}  \xrightarrow[\text{Ruphos, K}_2\text{CO}_3, \text{THF/H}_2\text{O}, \Delta, 15 \text{ h}]{\text{ArBr, Pd(OAc)}_2}  \begin{array}{c}  \text{pinB} \quad \text{Ar} \\  \diagup \quad \diagdown \\  \text{R}^1 \text{---} \text{C} \text{---} \text{C} \text{---} \text{R}^2 \\  \diagdown \quad \diagup \\  \text{C}  \end{array}  $	
<b>2</b>	<b>4</b>
	<b>4aa</b> (58%)
	<b>4ab</b> (67%)
	<b>4ac</b> (71%)
	<b>4ad</b> (70%)
	<b>4ae</b> (71%)
	<b>4af</b> (74.5%)
	<b>4ag</b> (56%)
	<b>4ah</b> (65%)
	<b>4ai</b> (56%)
	<b>4aj</b> (61%)
	<b>4bd</b> (79%)
	<b>4be</b> (71%)
	<b>4bh</b> (66%)
	<b>4bj</b> (54%)
	<b>4bk</b> (66%)
	<b>4bl</b> (58%)
	<b>4bm</b> (68.5%)
	<b>4bn</b> (69%)
	<b>4ce</b> (76%)
	<b>4cf</b> (72%)
	<b>4ci</b> (60%)
	<b>4cn</b> (66%)
	<b>4de</b> (75%)
	<b>4df</b> (71%)
	<b>4dn</b> (67%)
	<b>4ie</b> (64%)

<sup>a</sup> General conditions: **2** (0.3 mmol), palladium acetate (0.03 mmol), potassium carbonate (0.6 mmol), 2-dicyclohexylphosphino-2',6'-diisopropoxybiphenyl (0.075 mmol) and arylbromide (0.4 mmol), THF (2 mL)/water (0.1 mL), reflux, 15 h. <sup>b</sup> Yields of isolated products.

Moreover, the reaction was proven to be scalable with 1,2-bis(boronate) **1b** as model substrate, delivering the desired product **4bh** in 40% isolated yield over two steps (Scheme 3).

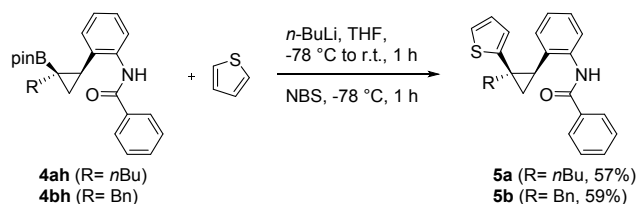
### Scheme 3. Gram Scale Synthesis of Cyclopropane **4bh**



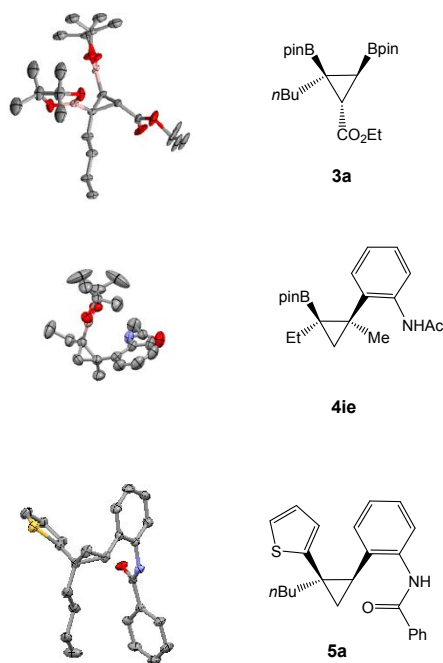
To further illustrate the synthetic utility of the cyclopropylboronates **4**, we then explored the addition of 2-lithiothiophene to cyclopropylboronic esters **4** following

a methodology developed by Aggarwal *et al.*<sup>26</sup> Compounds **4ah** and **4bh**, selected as examples, were treated with 2-lithiothiophene in presence of *N*-bromosuccinimide at  $-78^{\circ}\text{C}$  to afford the expected tri-substituted 1,2-bis(aryl)cyclopropanes **5a** and **5b** with retention of configuration<sup>27</sup> (X-Ray structure determination) (Scheme 4, Figure 2).

#### Scheme 4. Synthesis of Cyclopropanes **5a** and **5b**



**Figure 2. X-ray Structures of **3a**, **4ie** and **5a** (50% probability ellipsoids)**



#### CONCLUSION

In this publication, we have demonstrated that 1-alkene-1,2-diboronate esters are suitable precursors to the corresponding substituted cyclopropyl-1,2-bis(boronates). These compounds were then engaged in Suzuki-Miyaura coupling reactions leading to a large variety of arylcyclopropylboronates with retention of configuration. Further functionalization with 2-lithiothiophene provided also the corresponding 1,2-bis(aryl)cyclopropanes.

#### EXPERIMENTAL SECTION

**General Information.** Unless otherwise noted, all solvents and all commercially available chemicals were used without further purification. Air- and water-sensitive reactions were performed in flame-dried glassware under an argon atmosphere. Anhydrous tetrahydrofuran was obtained after distillation over sodium/benzophenone and anhydrous dichloromethane after distillation over calcium hydride. For oxygen-sensitive reaction, when specified, the solvent was degassed prior to use by slow bubbling of argon.  $^1\text{H}$  NMR (300, 400 or 500 MHz),  $^{13}\text{C}$  NMR (75, 101 or 126 MHz),  $^{11}\text{B}$  (96, 128 or 160 MHz), and  $^{19}\text{F}$  (376 MHz) spectra were recorded on Bruker AC 300, AC 400 and AC 500 spectrometers. Chemical shifts  $\delta$  are given in ppm, and coupling constants *J* in hertz. Multiplicities are presented as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Structural assignments were made with additional information from gCOSY, gHSQC, and gHMBC experiments. High-resolution mass spectra (HRMS) were recorded on a QTOF Bruker MaXis 4G, a Q-TOF Agilent 6510, or a Thermo Fisher Orbitrap Q-Exactive spectrometer (Centre Régional de Mesures Physiques de l'Ouest, Rennes) using positive-ion electron-spray ionization techniques (ESI+). Purifications by silica gel chromatography were carried out on silica 0.060–0.200 mm, 60 Å. Analytical thin-layer chromatography was performed on Merck silica gel 60 F254 plates. Melting points were measured on a Kofler bench Reichert-Jung Heizbank or a melting-point apparatus Stuart SMP10 and are uncorrected. Bis-boronates were already synthesized in the literature according to reported procedures: **1a-c**,<sup>28</sup> **1d-e**,<sup>16</sup> **1g**,<sup>29</sup> **1h**<sup>16</sup> and **1j**.<sup>28</sup>

(*Z*)-2,2'-(Pent-2-ene-2,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**1i**). Compound **1i** was prepared according to a known protocol.<sup>16</sup> A 25-mL flask, equipped with a magnetic stirring bar, septum inlet, and a reflux condenser, was charged with  $\text{Pt}(\text{PPh}_3)_4$  (73 mg, 0.06 mmol) and bis(pinacolato)diboron (595 mg, 2.35 mmol) and then flushed with nitrogen. DMF (5 mL) and pent-2-yne (200 mg, 2.94 mmol) were successively added. After being stirred for 12 h at  $80^{\circ}\text{C}$  using an oil bath, the reaction mixture was diluted with ethyl acetate (10 mL), repeatedly washed with cold water to remove DMF (5 times), dried over anhydrous magnesium sulfate and filtered. Evaporation and purification by flash column chromatography on  $\text{SiO}_2$  gave the bis(boryl)alkene **1i**. 515 mg (68%). Colorless oil.  $R_f$  = 0.90 (Hexane/AcOEt: 90/10).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.17 (q, *J* = 7.6 Hz, 2H), 1.70 (s, 3H), 1.24 (s, 12H), 1.23 (s, 12H), 0.92 (t, *J* = 7.6 Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  83.3, 83.2, 24.9, 24.8, 24.0, 15.7, 13.3 (the carbons  $\alpha$  to boron were not found).  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.4. HRMS (ESI+) calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{17}\text{H}_{33}\text{O}_4^{11}\text{B}_2$ ): 323.2564, found 323.2576.

**Synthesis of cyclopropyl-bis(boronates) 2.** To freshly distilled dichloromethane (2 mL) was added Et<sub>2</sub>Zn (1 mL, 1M in hexane, 1 mmol) at 0 °C under argon. To this solution was added very slowly trifluoroacetic acid (114 mg, 76 µL, 1 mmol). Once the addition was complete (5 min), the reaction mixture was stirred for 30 minutes at 0 °C. Then, diiodomethane (267 mg, 80 µL, 1 mmol) was added in 5 min, and the resulting reaction mixture was stirred for an additional 20 minutes at 0 °C. To this solution was added the bisboronate **1** (0.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL). After 18h at rt, the reaction was terminated by addition of saturated aqueous NH<sub>4</sub>Cl (0.5 mL) and diluted with EtOAc (10 mL). Extraction of the aqueous phase was carried out with EtOAc (3 x10 mL). The combined organic layers were dried on magnesium sulfate and filtered. Concentration *in vacuo* gave oil which was purified by column chromatography on silica gel to give the corresponding cyclopropane **2**. The reaction was also carried out on a 2.7 mmol scale for **2b**.

**2,2'-(1-Butylcyclopropane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2a).** 117 mg (67%). Colorless oil. *R<sub>f</sub>* = 0.90 (Cyclohexane/AcOEt: 90/10). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.47-1.35 (m, 5H), 1.26 (s, 12H), 1.25 (s, 6H), 1.24 (s, 6H), 1.10-0.98 (m, 1H), 0.88 (t, *J* = 7.2 Hz, 3H), 0.82 (dd, *J* = 6.8, 2.8 Hz, 1H), 0.55 (dd, *J* = 9.2, 2.8 Hz, 1H), -0.22 (dd, *J* = 9.2, 6.8 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ 83.1, 83.1, 39.7, 31.7, 25.2, 25.1, 25.0, 24.7, 23.1, 15.9, 14.3 (the carbons α to boron were not found). <sup>11</sup>B{<sup>1</sup>H} NMR (96 MHz, CDCl<sub>3</sub>) δ 33.3. HRMS (ESI<sup>+</sup>) calculated for [M+Na]<sup>+</sup> (C<sub>19</sub>H<sub>36</sub>O<sub>4</sub><sup>11</sup>B<sub>2</sub>Na): 373.2697, found 373.2697.

**2,2'-(1-Benzylcyclopropane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2b).** 123 mg (64%). 0.64 g (62%) on a 2.7 mmol scale. Colorless oil. *R<sub>f</sub>* = 0.72 (Cyclohexane/AcOEt: 70/30). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.30 (d, *J* = 7.3 Hz, 2H), 7.22 (app t, *J* = 7.6 Hz, 2H), 7.14 (app t, *J* = 7.3 Hz, 1H), 3.06 (d, *J* = 14.5 Hz, 1H), 2.28 (d, *J* = 14.7 Hz, 1H), 1.23 (s, 6H), 1.22 (s, 6H), 1.09 (s, 12H), 0.96 (dd, *J* = 7.0, 3.1 Hz, 1H), 0.77 (dd, *J* = 9.4, 3.1 Hz, 1H), -0.06 (dd, *J* = 9.4, 6.7 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 141.3, 129.3, 127.9, 125.9, 83.3, 83.2, 44.1, 25.3, 25.1, 24.8, 24.6, 15.8 (the carbons α to boron were not found). <sup>11</sup>B{<sup>1</sup>H} NMR (96 MHz, CDCl<sub>3</sub>) δ 33.0. HRMS (ESI<sup>+</sup>) calculated for [M+H]<sup>+</sup> (C<sub>22</sub>H<sub>35</sub>O<sub>4</sub><sup>11</sup>B<sub>2</sub>): 385.2721, found 385.2730.

**2,2'-(1-(Cyclohexylmethyl)cyclopropane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2c).** 133 mg (68%). Colorless oil. *R<sub>f</sub>* = 0.84 (Cyclohexane/AcOEt: 70/30). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.88 (d, *J* = 13.1 Hz, 1H), 1.76-1.54 (m, 6H), 1.24 (s, 12H), 1.22 (s, 6H), 1.21 (s, 6H), 1.16-1.08 (m, 2H), 0.97-0.69 (m, 5H), 0.54 (dd, *J* = 9.2, 2.9 Hz, 1H), -0.29 (dd, *J* = 9.2, 6.8 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 83.1, 83.1, 47.9, 38.5, 34.2, 33.4, 26.9, 26.7, 26.6, 25.3, 25.2, 25.0, 24.6, 16.9 (the carbons α to boron were not found). <sup>11</sup>B{<sup>1</sup>H} NMR (96 MHz, CDCl<sub>3</sub>) δ 33.3. HRMS (ESI<sup>+</sup>) calculated for [M+H]<sup>+</sup> (C<sub>22</sub>H<sub>41</sub>O<sub>4</sub><sup>11</sup>B<sub>2</sub>): 391.3191, found 391.3192.

**2,2'-(1-Cyclohexylcyclopropane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2d).** 137 mg (73%). Colorless oil. *R<sub>f</sub>* = 0.60. (hexane/AcOEt: 90/10). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.80-1.50 (m, 7H), 1.25 (s, 12H), 1.22 (s, 6H), 1.21 (s, 6H), 1.16-1.02 (m, 3H), 0.75 (dd, *J* = 6.6, 2.8 Hz, 1H), 0.53 (dd, *J* = 9.2, 2.8 Hz, 1H), 0.36 (app t, *J* = 11.9, 3.5 Hz, 1H), -0.26 (dd, *J* = 9.4, 6.6 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 83.1, 83.0, 49.8, 32.4, 32.1, 27.2, 27.1, 26.9, 25.5, 25.3, 24.8, 24.6, 15.2, 5.0 (br) (one carbon α to boron was not found). <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, CDCl<sub>3</sub>) δ 33.4. HRMS (ESI<sup>+</sup>) calculated for [M+H]<sup>+</sup> (C<sub>21</sub>H<sub>39</sub>O<sub>4</sub><sup>11</sup>B<sub>2</sub>): 377.3034, found 377.3035.

**2,2'-(1-Phenylcyclopropane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2e).** 141 mg (76%). Colorless oil. *R<sub>f</sub>* = 0.70

(Cyclohexane/AcOEt: 90/10). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.33-7.30 (m, 2H), 7.21 (app t, *J* = 7.5 Hz, 2H), 7.13-7.08 (m, 1H), 1.27 (s, 6H), 1.27 (s, 6H), 1.22 (s, 6H), 1.20-1.17 (m, 1H), 1.19 (s, 6H), 1.11 (dd, *J* = 9.5, 2.9 Hz, 1H), 0.41 (dd, *J* = 9.5, 7.1 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ 145.7, 129.1, 128.0, 125.5, 83.5, 83.4, 25.2, 24.9, 24.7, 16.3 (the carbons α to boron were not found). <sup>11</sup>B{<sup>1</sup>H} NMR (96 MHz, CDCl<sub>3</sub>) δ 32.8. HRMS (ESI<sup>+</sup>) calculated for [M+Na]<sup>+</sup> (C<sub>21</sub>H<sub>32</sub>O<sub>4</sub><sup>11</sup>B<sub>2</sub>Na): 393.2384, found 393.2385.

**(1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)methyltrimethylsilane (2f).** 142 mg (74%). Colorless oil. *R<sub>f</sub>* = 0.80 (Cyclohexane/AcOEt: 90/10). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.23 (s, 12H), 1.22 (s, 12H), 0.86 (dd, *J* = 7.2, 2.8 Hz, 1H), 0.73 (d, *J* = 14.7 Hz, 1H), 0.66 (d, *J* = 14.7 Hz, 1H), 0.53 (dd, *J* = 9.1, 2.8 Hz, 1H), 0.02 (s, 9H), -0.26 (dd, *J* = 9.1, 7.2 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ 83.2, 83.0, 27.0, 25.6, 25.3, 24.8, 18.2, -0.0 (the carbons α to boron were not found). <sup>11</sup>B{<sup>1</sup>H} NMR (96 MHz, CDCl<sub>3</sub>) δ 33.1. HRMS (ESI<sup>+</sup>) calculated for [M+Na]<sup>+</sup> (C<sub>19</sub>H<sub>38</sub>O<sub>4</sub><sup>11</sup>B<sub>2</sub>NaSi): 403.2623, found 403.2628.

**(2-(1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)ethoxy)(tert-butyl)dimethylsilane (2g).** 190 mg (84%). Colorless oil. *R<sub>f</sub>* = 0.70 (Cyclohexane/AcOEt: 90/10). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 3.69 (t, *J* = 7.7 Hz, 2H), 1.75-1.65 (m, 1H), 1.37-1.30 (m, 1H), 1.22 (s, 24H), 0.88 (s, 9H), 0.81 (dd, *J* = 7.0, 2.8 Hz, 1H), 0.61 (dd, *J* = 9.3, 2.8 Hz, 1H), 0.05 (s, 6H), -0.17 (dd, *J* = 9.2, 7.0 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ 83.2, 83.1, 63.4, 42.9, 26.2, 25.1, 25.1, 24.9, 24.8, 18.5, 15.5, 6.4 (br), -5.0, -5.1 (one carbon α to boron was not found). <sup>11</sup>B{<sup>1</sup>H} NMR (96 MHz, CDCl<sub>3</sub>) δ 33.3. HRMS (ESI<sup>+</sup>) calculated for [M+Na]<sup>+</sup> (C<sub>23</sub>H<sub>46</sub>O<sub>5</sub><sup>11</sup>B<sub>2</sub>NaSi): 475.3198, found 475.3193.

**2,2'-(1-(2-Chloropropyl)cyclopropane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2h).** 170 mg (92%). Colorless oil. *R<sub>f</sub>* = 0.60 (Cyclohexane/AcOEt: 90/10). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 3.52 (t, *J* = 6.8 Hz, 2H), 1.96-1.86 (m, 2H), 1.52-1.41 (m, 1H), 1.29-1.24 (m, 1H), 1.23 (s, 24H), 0.83 (dd, *J* = 7.0, 2.9 Hz, 1H), 0.57 (dd, *J* = 9.3, 2.9 Hz, 1H), -0.20 (dd, *J* = 9.3, 7.0 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 83.3, 83.2, 45.4, 37.0, 32.7, 25.2, 25.1, 24.9, 24.8, 16.0 (the carbons α to boron were not found). <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, CDCl<sub>3</sub>) δ 32.8. HRMS (ESI<sup>+</sup>) calculated for [M+Na]<sup>+</sup> (C<sub>18</sub>H<sub>33</sub>O<sub>4</sub><sup>35</sup>Cl<sup>11</sup>B<sub>2</sub>Na): 393.2151, found 393.2153.

**2,2'-(1-Ethyl-2-methylcyclopropane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2i).** 120 mg (71%). Colorless oil. *R<sub>f</sub>* = 0.5 (hexane/AcOEt: 90/10). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.48-1.36 (m, 2H), 1.23 (s, 6H), 1.22 (s, 6H), 1.21 (s, 6H), 1.20 (s, 6H), 1.09 (s, 3H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.91 (d, *J* = 2.9 Hz, 1H), 0.14 (d, *J* = 2.8 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 83.1, 25.1, 25.1, 25.0, 24.7, 24.3, 23.3, 16.0, 14.0, 8.8 (br) (one carbon α to boron was not found). <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, CDCl<sub>3</sub>) δ 30.4. HRMS (ESI<sup>+</sup>) calculated for [M+H]<sup>+</sup> (C<sub>18</sub>H<sub>35</sub>O<sub>4</sub><sup>11</sup>B<sub>2</sub>): 337.2721, found 337.2721.

**1,2-Diethyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane (2j).** 161 mg (92%). Colorless oil. *R<sub>f</sub>* = 0.90 (Cyclohexane/AcOEt: 90/10). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.57-1.33 (m, 4H), 1.23 (s, 12H), 1.22 (s, 12H), 0.95 (t, *J* = 7.4 Hz, 6H), 0.88 (d, *J* = 2.9 Hz, 1H), 0.16 (d, *J* = 2.9 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ 83.1, 25.2, 24.9, 24.2, 21.3, 16.6 (br), 14.1 (one carbon α to boron was not found). <sup>11</sup>B{<sup>1</sup>H} NMR (96 MHz, CDCl<sub>3</sub>) δ 33.0. HRMS (ESI<sup>+</sup>) calculated for [M+Na]<sup>+</sup> (C<sub>19</sub>H<sub>36</sub>O<sub>4</sub><sup>11</sup>B<sub>2</sub>Na): 373.2697, found 373.2694.

**Ethyl 2-butyl-2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-1-carboxylate (3a).** (S,S)-Bis oxazoline (0.025 mmol) and Cu(NCMe)<sub>4</sub> PF<sub>6</sub> (0.025 mmol) were mixed under argon with CH<sub>2</sub>Cl<sub>2</sub> (2 mL) in a Schlenk tube and then stirred for 20 minutes. To this solution was added the alkenyl bisboronate **1a** (0.50 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL). A solution of ethyl

diazoacetate (2 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 mL) was then added during 8 hours via a syringe pump. The solvent was removed *in vacuo*. The residue was maintained *in vacuo* at 100 °C to eliminate volatiles ethyl fumarate and maleate. Purification by flash column chromatography afforded 88 mg (42%) of the corresponding bisborocyclopropane **3a**. Colorless oil.  $R_f$  = 0.90 (Cyclohexane/AcOEt: 90/10).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  4.16-4.05 (m, 2H), 2.00 (d,  $J$  = 6.7 Hz, 1H), 1.78-1.68 (m, 1H), 1.50-1.41 (m, 1H), 1.38-1.13 (m, 7H), 1.25 (s, 12H), 1.22 (s, 6H), 1.21 (s, 6H), 0.84 (t,  $J$  = 6.9 Hz, 3H), 0.67 (d,  $J$  = 6.7 Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.8, 83.7, 83.5, 60.5, 31.8, 31.1, 27.2, 25.2, 25.1, 25.0, 24.8, 23.0, 14.5, 14.2 (the carbons  $\alpha$  to boron were not found).  $^{11}\text{B}\{^1\text{H}\}$  NMR (96 MHz,  $\text{CDCl}_3$ )  $\delta$  32.4. HRMS (ESI<sup>+</sup>) calculated for  $[\text{M}+\text{Na}]^+$  ( $\text{C}_{22}\text{H}_{40}\text{O}_6^{11}\text{B}_2\text{Na}$ ): 445.2909, found 445.2910.

**Access to cyclopropanes 4 by Suzuki coupling.** In an argon-filled Schlenk tube were placed the cyclopropyl bisboronate **2** (0.30 mmol), aryl bromide (0.40 mmol),  $\text{Pd}(\text{OAc})_2$  (7 mg, 0.03 mmol),  $\text{RuPhos}$  (35 mg, 0.075 mmol),  $\text{K}_2\text{CO}_3$  (83 mg, 0.60 mmol), THF (2 mL) and degassed water (0.1 mL) was added. The tube was sealed with a cap and the resulting suspension was stirred overnight at reflux using an oil bath. After cooling to rt, the reaction was terminated by addition of  $\text{H}_2\text{O}$  and extracted with EtOAc. The combined organic layers were then dried with  $\text{MgSO}_4$  and filtered. After concentration *in vacuo*, the residue was purified by silica gel flash chromatography to afford the corresponding Suzuki products **4**. The reaction was also carried out on a 1.7 mmol scale for **4bh**.

**2-(1-Butyl-2-phenylcyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4aa).** 52 mg (58%). Colorless oil.  $R_f$  = 0.85 (Cyclohexane/AcOEt: 90/10).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25-7.06 (m, 5H), 1.97-1.90 (m, 2H), 1.45-1.22 (m, 6H), 0.97 (s, 6H), 0.90 (t,  $J$  = 7.0 Hz, 3H), 0.83 (s, 6H), 0.80 (dd,  $J$  = 8.0, 4.2 Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  140.8, 129.0, 127.8, 125.6, 82.6, 38.2, 31.7, 29.9, 24.8, 24.4, 23.1, 15.9, 14.3 (the carbon  $\alpha$  to boron was not found).  $^{11}\text{B}\{^1\text{H}\}$  NMR (96 MHz,  $\text{CDCl}_3$ )  $\delta$  32.6. HRMS (ESI<sup>+</sup>) calculated for  $[\text{M}+\text{Na}]^+$  ( $\text{C}_{19}\text{H}_{29}\text{O}_2^{11}\text{BNa}$ ) 323.2158, found 323.2156.

**2-(1-Butyl-2-(4-methylphenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ab).** 64 mg (67%). Colorless oil.  $R_f$  = 0.80 (Cyclohexane/AcOEt: 90/10).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.12 (d,  $J$  = 7.8 Hz, 2H), 7.00 (d,  $J$  = 7.8 Hz, 2H), 2.27 (s, 3H), 1.96-1.88 (m, 2H), 1.43-1.21 (m, 6H), 0.98 (s, 6H), 0.90 (t,  $J$  = 7.0 Hz, 3H), 0.84 (s, 6H), 0.75 (dd,  $J$  = 8.1, 4.3 Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  137.6, 134.8, 128.7, 128.2, 82.8, 38.0, 31.6, 29.4, 24.7, 24.3, 22.9, 20.9, 15.8, 14.2 (the carbon  $\alpha$  to boron was not found).  $^{11}\text{B}\{^1\text{H}\}$  NMR (96 MHz,  $\text{CDCl}_3$ )  $\delta$  32.7. HRMS (ESI<sup>+</sup>) calculated for  $[\text{M}+\text{Na}]^+$  ( $\text{C}_{20}\text{H}_{31}\text{O}_2^{11}\text{BNa}$ ): 337.2315, found 337.2308.

**2-(1-Butyl-2-(4-nitrophenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ac).** 73 mg (71%). Colorless oil.  $R_f$  = 0.60 (Cyclohexane/AcOEt: 90/10).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (d,  $J$  = 8.5 Hz, 2H), 7.37 (d,  $J$  = 8.4 Hz, 2H), 2.00 (t,  $J$  = 7.0 Hz, 1H), 1.93-1.83 (m, 1H), 1.51 (t,  $J$  = 5.4 Hz, 1H), 1.50-1.25 (m, 5H), 1.07-1.01 (m, 1H), 0.98 (s, 6H), 0.91 (t,  $J$  = 7.2 Hz, 3H), 0.86 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  149.3, 145.9, 129.4, 122.8, 83.2, 38.1, 31.4, 30.0, 24.7, 24.3, 22.9, 17.3, 14.1 (the carbon  $\alpha$  to boron was not found).  $^{11}\text{B}\{^1\text{H}\}$  NMR (96 MHz,  $\text{CDCl}_3$ )  $\delta$  32.4. HRMS (ESI<sup>+</sup>) calculated for  $[\text{M}+\text{Na}]^+$  ( $\text{C}_{19}\text{H}_{28}\text{NO}_4^{11}\text{BNa}$ ): 368.2009, found 368.2007.

**4-(2-Butyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)benzonitrile (4ad).** 68 mg (70%). White solid, mp = 115-120 °C.  $R_f$  = 0.50 (hexane/AcOEt: 90/10).  $^1\text{H}$  NMR

(400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (d,  $J$  = 6.6 Hz, 2H), 7.30 (d,  $J$  = 8.2 Hz, 2H), 1.95 (dd,  $J$  = 7.5, 6.4 Hz, 1H), 1.90-1.83 (m, 1H), 1.46 (dd,  $J$  = 5.3, 5.0 Hz, 1H), 1.43-1.27 (m, 4H), 1.20 (d,  $J$  = 4.1 Hz, 1H), 0.96 (s, 6H), 0.88 (t,  $J$  = 7.1 Hz, 3H), 0.90-0.85 (m, 1H), 0.83 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.0, 131.5, 129.6, 119.4, 109.4, 83.2, 38.1, 31.5, 30.2, 24.8, 24.4, 23.0, 16.8, 14.2 (the carbon  $\alpha$  to boron was not found).  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  32.7. HRMS (ESI<sup>+</sup>) calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{20}\text{H}_{29}\text{NO}_2^{11}\text{B}$ ): 326.2291, found 326.2290.

**N-(2-(2-Butyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)phenyl)acetamide (4ae).** 76 mg (71%). White solid, mp = 109-111 °C.  $R_f$  = 0.50 (hexane/AcOEt: 70/30).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (d,  $J$  = 8.0 Hz, 1H), 7.67 (brs, 1H), 7.15 (app t,  $J$  = 7.2 Hz, 1H), 7.17 (d,  $J$  = 7.4 Hz, 1H), 6.99 (app t,  $J$  = 7.3 Hz, 1H), 2.25 (s, 3H), 2.12 (td,  $J$  = 13.1, 4.9 Hz, 1H), 1.67 (dd,  $J$  = 7.3, 6.4 Hz, 1H), 1.45-1.41 (m, 2H), 1.35 (dt,  $J$  = 14.4, 7.2 Hz, 2H), 1.26-1.22 (m, 2H), 0.98 (s, 6H), 0.92 (t,  $J$  = 7.2 Hz, 3H), 0.89 (dd,  $J$  = 8.4, 4.4 Hz, 1H), 0.73 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.5, 138.3, 129.8, 129.6, 127.3, 124.0, 120.9, 83.4, 37.7, 31.8, 25.9, 25.0, 24.9, 24.1, 23.0, 15.9, 14.3 (the carbon  $\alpha$  to boron was not found).  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  32.9. HRMS (ESI<sup>+</sup>) calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{21}\text{H}_{33}\text{O}_3\text{N}^{11}\text{B}$ ): 358.2553, found 358.2548.

**N-(2-(2-Butyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)-4-methylphenyl)acetamide (4af).** 83 mg (74.5%). White solid, mp = 104-107 °C.  $R_f$  = 0.55 (hexane/AcOEt: 70/30).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (d,  $J$  = 7.9 Hz, 1H), 7.59 (brs, 1H), 6.97 (d,  $J$  = 8.4 Hz, 1H), 6.96 (s, 1H), 2.25 (s, 3H), 2.23 (s, 3H), 2.14-2.06 (m, 1H), 1.65 (dd,  $J$  = 7.3, 6.4 Hz, 1H), 1.67-1.64 (m, 1H), 1.41-1.31 (m, 6H), 0.99 (s, 6H), 0.91 (t,  $J$  = 7.1 Hz, 3H), 0.85 (dd,  $J$  = 8.0, 4.2 Hz, 1H), 0.73 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.3, 135.7, 133.5, 130.1, 130.1, 127.7, 121.4, 83.3, 37.7, 31.8, 25.8, 25.0, 24.8, 24.0, 23.0, 21.0, 15.8, 14.2 (the carbon  $\alpha$  to boron was not found).  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  32.4. HRMS (ESI<sup>+</sup>) calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{22}\text{H}_{35}\text{O}_3\text{N}^{11}\text{B}$ ): 372.2710, found 372.2705.

**N-(2-(2-Butyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)phenyl)pivalamide (4ag).** 67 mg (56%). White solid, mp = 109-112 °C.  $R_f$  = 0.60 (hexane/AcOEt: 80/20).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (dd,  $J$  = 8.0, 0.9 Hz, 1H), 7.89 (brs, 1H), 7.17-7.12 (m, 2H), 6.97 (td,  $J$  = 7.6, 1.1 Hz, 1H), 2.39-2.33 (m, 1H), 1.68 (dd,  $J$  = 7.6, 5.9 Hz, 1H), 1.44 (t,  $J$  = 4.5 Hz, 1H), 1.37 (s, 9H), 1.37-1.34 (m, 3H), 1.26-1.20 (m, 2H), 0.96 (s, 6H), 0.90 (t,  $J$  = 7.1 Hz, 3H), 0.84 (dd,  $J$  = 8.0, 4.2 Hz, 1H), 0.71 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  176.8, 138.4, 130.2, 129.5, 127.2, 123.8, 121.7, 83.3, 39.8, 37.4, 31.7, 28.0, 26.0, 24.9, 24.1, 22.9, 14.8, 14.2 (the carbon  $\alpha$  to boron was not found).  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ )  $\delta$  32.7. HRMS (ESI<sup>+</sup>) calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{24}\text{H}_{39}\text{O}_3\text{N}^{11}\text{B}$ ): 400.3023, found 400.3018.

**N-(2-(2-Butyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)phenyl)benzamide (4ah).** 82 mg (65%). White solid, mp = 105-110 °C.  $R_f$  = 0.60 (hexane/AcOEt: 90/10).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.45 (brs, 1H), 8.16 (d,  $J$  = 8.0 Hz, 1H), 8.13-8.08 (m, 2H), 7.58-7.50 (m, 3H), 7.24 (app t,  $J$  = 7.7 Hz, 1H), 7.20 (d,  $J$  = 7.6 Hz, 1H), 7.04 (ddd,  $J$  = 7.6, 7.6, 1.0 Hz, 1H), 2.20 (ddd,  $J$  = 13.9, 10.4, 4.7 Hz, 1H), 1.73 (dd,  $J$  = 7.4, 6.2 Hz, 1H), 1.49 (t,  $J$  = 4.8 Hz, 1H), 1.45-1.26 (m, 5H), 1.00 (s, 6H), 0.89 (dd,  $J$  = 8.2, 4.2 Hz, 1H), 0.87 (t,  $J$  = 7.2 Hz, 3H), 0.78 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.6, 138.3, 135.6, 131.7, 130.4, 129.6, 128.7, 127.3, 124.2, 121.3, 83.5, 37.5, 31.5, 25.8, 24.9, 24.1, 22.8, 15.5, 14.1 (the carbon  $\alpha$  to boron was not found).  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  32.5. HRMS (ESI<sup>+</sup>) calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{26}\text{H}_{35}\text{O}_3\text{N}^{11}\text{B}$ ): 420.2706, found 420.2709.

**N-(2-(2-Butyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)phenyl)-4-methylbenzamide (4ai).** 73 mg (56%).



White solid, mp = 112-115 °C.  $R_f$  = 0.65 (hexane/AcOEt: 90/10).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.44 (brs, 1H), 8.18 (d,  $J$  = 7.9 Hz, 1H), 7.98 (s, 1H), 7.89 (d,  $J$  = 7.4 Hz, 1H), 7.42-7.35 (m, 2H), 7.23 (app t,  $J$  = 7.8 Hz, 1H), 7.19 (d,  $J$  = 7.6 Hz, 1H), 7.03 (td,  $J$  = 7.5, 1.1 Hz, 1H), 2.46 (s, 3H), 2.22 (ddd,  $J$  = 13.9, 10.1, 5.1 Hz, 1H), 1.72 (dd,  $J$  = 7.5, 6.1 Hz, 1H), 1.49 (t,  $J$  = 4.7 Hz, 1H), 1.46-1.35 (m, 2H), 1.32-1.27 (m, 2H), 1.25-1.22 (m, 1H), 1.01 (s, 6H), 0.90 (dd,  $J$  = 7.9, 4.2 Hz, 1H), 0.87 (t,  $J$  = 7.2 Hz, 3H), 0.79 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.9, 138.6, 138.5, 135.7, 132.5, 130.3, 129.6, 128.8, 127.9, 127.4, 124.7, 124.1, 121.1, 83.6, 37.7, 31.7, 26.0, 25.0, 24.2, 23.0, 21.4, 15.6, 14.2 (the carbon  $\alpha$  to boron was not found).  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  32.8. HRMS (ESI<sup>+</sup>) calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{27}\text{H}_{37}\text{O}_3\text{N}^{11}\text{B}$ ): 434.2866, found 434.2851.

*N*-(2-(2-Benzyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)phenyl)-4-chlorobenzamide (**4aj**). 83 mg (61%). Yellow oil.  $R_f$  = 0.60 (hexane/AcOEt: 90/10).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.41 (brs, 1H), 8.11 (d,  $J$  = 8.0 Hz, 1H), 8.06 (d,  $J$  = 8.5 Hz, 2H), 7.51-7.49 (d,  $J$  = 8.6 Hz, 2H), 7.24 (app t,  $J$  = 7.8 Hz, 1H), 7.20 (d,  $J$  = 7.6 Hz, 1H), 7.05 (td,  $J$  = 7.6, 1.0 Hz, 1H), 2.15 (ddd,  $J$  = 14.0, 10.2, 4.6 Hz, 1H), 1.72 (dd,  $J$  = 7.4, 6.2 Hz, 1H), 1.48 (t,  $J$  = 4.9 Hz, 1H), 1.46-1.25 (m, 5H), 1.00 (s, 6H), 0.90 (dd,  $J$  = 8.0, 4.3 Hz, 1H), 0.88 (t,  $J$  = 7.1 Hz, 3H), 0.77 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.6, 138.1, 138.0, 133.9, 130.5, 129.7, 129.0, 128.8, 127.4, 124.4, 121.4, 83.5, 37.5, 31.6, 25.8, 24.9, 24.0, 22.8, 15.5, 14.1 (the carbon  $\alpha$  to boron was not found).  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  32.9. HRMS (ESI<sup>+</sup>) calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{26}\text{H}_{34}\text{O}_3\text{N}^{35}\text{Cl}^{11}\text{B}$ ): 454.2320, found 454.2315.

4-(2-Benzyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)benzonitrile (**4bd**). 85 mg (79%). White solid, mp = 106-110 °C.  $R_f$  = 0.60 (hexane/AcOEt: 90/10).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 (d,  $J$  = 8.3 Hz, 2H), 7.32 (d,  $J$  = 8.2 Hz, 2H), 7.31-7.24 (m, 4H), 7.21-7.16 (m, 1H), 3.34 (d,  $J$  = 14.3 Hz, 1H), 2.37 (d,  $J$  = 14.3 Hz, 1H), 2.12 (dd,  $J$  = 7.4, 6.6 Hz, 1H), 1.60 (t,  $J$  = 5.3 Hz, 1H), 1.13 (dd,  $J$  = 8.0, 4.7 Hz, 1H), 0.88 (s, 6H), 0.75 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.5, 141.1, 131.6, 129.6, 129.1, 128.2, 126.2, 119.4, 109.3, 83.5, 42.8, 29.6, 24.7, 24.4, 18.1 (br), 16.8.  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  32.9. HRMS (ESI<sup>+</sup>) calculated for  $[\text{M}+\text{NH}_4]^+$  ( $\text{C}_{23}\text{H}_{30}\text{O}_2\text{N}_2^{11}\text{B}$ ): 377.2400, found 377.2395.

*N*-(2-(2-Benzyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)phenyl)acetamide (**4be**). 83 mg (71%). White solid, mp = 108-112 °C.  $R_f$  = 0.60 (hexane/AcOEt: 70/30).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J$  = 8.0 Hz, 1H), 7.67 (brs, 1H), 7.32-7.27 (m, 4H), 7.22-7.16 (m, 3H), 7.01 (app t,  $J$  = 7.6 Hz, 1H), 3.45 (d,  $J$  = 14.2 Hz, 1H), 2.38 (d,  $J$  = 14.2 Hz, 1H), 2.24 (s, 3H), 1.87 (dd,  $J$  = 7.5, 6.3 Hz, 1H), 1.54 (t,  $J$  = 5.0 Hz, 1H), 1.12 (dd,  $J$  = 8.0, 4.3 Hz, 1H), 0.92 (s, 6H), 0.64 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.5, 140.7, 138.2, 129.9, 129.7, 129.1, 128.5, 128.4, 127.5, 126.4, 124.2, 121.4, 83.6, 42.7, 25.6, 25.0, 24.8, 24.1, 16.0 (the carbon  $\alpha$  to boron was not found).  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  32.8. HRMS (ESI<sup>+</sup>) calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{24}\text{H}_{31}\text{O}_3\text{N}^{11}\text{B}$ ): 392.2397, found 392.2392.

*N*-(2-(2-Benzyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)phenyl)benzamide (**4bh**). 90 mg (66%). 0.35 g mg (65%) on a 1.7 mmol scale. White solid, mp = 115-118 °C.  $R_f$  = 0.50 (hexane/AcOEt: 90/10).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.53 (brs, 1H), 8.25-8.16 (m, 2H), 8.14 (dd,  $J$  = 8.1, 1.3 Hz, 1H), 7.63-7.54 (m, 3H), 7.31-7.17 (m, 7H), 7.07 (td,  $J$  = 7.5, 1.3 Hz, 1H), 3.52 (d,  $J$  = 14.1 Hz, 1H), 2.22 (d,  $J$  = 14.3 Hz, 1H), 1.90 (dd,  $J$  = 8.2, 5.7 Hz, 1H), 1.60 (ddd,  $J$  = 5.7, 4.5, 1.2 Hz, 1H), 1.14 (dd,  $J$  = 8.1, 4.4 Hz, 1H), 0.93 (s, 6H), 0.67 (s, 6H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 140.8, 138.3, 135.7, 131.9, 130.6, 129.8, 128.9, 128.9, 128.3, 127.6, 127.4, 126.3, 124.5, 121.9, 83.8, 42.7, 25.6, 24.8, 24.1, 15.8 (the carbon  $\alpha$  to boron was not found).  $^{11}\text{B}\{^1\text{H}\}$

NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  32.3. HRMS (ESI<sup>+</sup>) calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{29}\text{H}_{32}\text{O}_3\text{N}^{11}\text{B}$ ): 454.2553, found 454.2574.

*N*-(2-(2-Benzyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)phenyl)-4-chlorobenzamide (**4bj**). 79 mg (54%). White solid, mp = 128-132 °C.  $R_f$  = 0.60 (hexane/AcOEt: 90/10).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.49 (brs, 1H), 8.14 (d,  $J$  = 8.6 Hz, 2H), 8.07 (d,  $J$  = 8.0 Hz, 1H), 7.55 (d,  $J$  = 8.6 Hz, 2H), 7.28-7.15 (m, 8H), 7.08 (app t,  $J$  = 8.1 Hz, 1H), 3.47 (d,  $J$  = 14.2 Hz, 1H), 2.22 (d,  $J$  = 14.2 Hz, 1H), 1.88 (dd,  $J$  = 7.3, 6.5 Hz, 1H), 1.59 (t,  $J$  = 4.9 Hz, 1H), 1.14 (dd,  $J$  = 8.0, 4.4 Hz, 1H), 0.93 (s, 6H), 0.66 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.7, 140.6, 138.2, 138.1, 134.0, 130.7, 129.9, 129.2, 128.9, 128.9, 128.4, 127.7, 126.4, 124.8, 122.0, 83.9, 42.8, 25.6, 24.8, 24.1, 15.9 (the carbon  $\alpha$  to boron was not found).  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  32.9. HRMS (ESI<sup>+</sup>) calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{29}\text{H}_{32}\text{O}_3\text{N}^{35}\text{Cl}^{11}\text{B}$ ): 488.2164, found 488.2158.

2-(1-Benzyl-2-(4-chlorophenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4bk**). 73 mg (66%). Yellow oil.  $R_f$  = 0.60 (hexane/AcOEt: 90/10).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29-7.19 (m, 4H), 7.16-7.11 (m, 5H), 3.36 (d,  $J$  = 14.3 Hz, 1H), 2.24 (d,  $J$  = 14.1 Hz, 1H), 2.07-1.98 (m, 1H), 1.54-1.45 (m, 1H), 1.02-0.99 (m, 1H), 0.86 (d,  $J$  = 1.6 Hz, 6H), 0.71 (d,  $J$  = 1.7 Hz, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.5, 138.9, 131.5, 130.3, 129.1, 128.1, 127.8, 126.0, 83.3, 42.9, 28.9, 24.7, 24.4, 17.1 (br), 16.2.  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.5. HRMS (ESI<sup>+</sup>) calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{22}\text{H}_{27}\text{O}_2^{35}\text{Cl}^{11}\text{B}$ ): 369.1793, found 369.1792.

2-(1-Benzyl-2-(4-(tert-butyl)phenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4bl**). 68 mg (58%). Colorless oil.  $R_f$  = 0.50 (hexane/AcOEt: 90/10).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 (d,  $J$  = 7.6 Hz, 2H), 7.27 (d,  $J$  = 7.4 Hz, 2H), 7.26-7.24 (m, 2H), 7.20 (d,  $J$  = 8.5 Hz, 2H), 7.18 (app t,  $J$  = 7.3 Hz, 1H), 3.47 (d,  $J$  = 14.4 Hz, 1H), 2.24 (d,  $J$  = 14.4 Hz, 1H), 2.12 (dd,  $J$  = 7.1, 7.0 Hz, 1H), 1.57 (t,  $J$  = 5.2 Hz, 1H), 1.28 (d,  $J$  = 1.1 Hz, 9H), 1.01 (dd,  $J$  = 8.1, 4.5 Hz, 1H), 0.87 (s, 6H), 0.70 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  148.8, 142.0, 137.2, 129.0, 128.6, 128.1, 125.9, 124.7, 83.1, 43.1, 34.4, 31.5, 29.0, 24.6, 24.4, 15.7 (the carbon  $\alpha$  to boron was not found).  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.3. HRMS (ESI<sup>+</sup>) calculated for  $[\text{M}+\text{NH}_4]^+$  ( $\text{C}_{26}\text{H}_{39}\text{O}_2\text{N}^{11}\text{B}$ ): 408.3074, found 408.3068.

2-(1-Benzyl-2-(4-methoxyphenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4bm**). 75 mg (68.5%). White solid, mp = 104-107 °C.  $R_f$  = 0.60 (hexane/AcOEt: 90/10).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 (d,  $J$  = 7.1 Hz, 2H), 7.27-7.24 (m, 2H), 7.16 (app t,  $J$  = 7.3 Hz, 1H), 7.12 (app t,  $J$  = 7.9 Hz, 1H), 6.87 (d,  $J$  = 7.6 Hz, 1H), 6.81-6.78 (m, 1H), 6.67 (dd,  $J$  = 8.1, 2.1 Hz, 1H), 3.78 (s, 3H), 3.43 (d,  $J$  = 14.4 Hz, 1H), 2.26 (d,  $J$  = 14.4 Hz, 1H), 2.10 (dd,  $J$  = 7.8, 6.3 Hz, 1H), 1.55 (d,  $J$  = 5.2 Hz, 1H), 1.03 (dd,  $J$  = 8.1, 4.5 Hz, 1H), 0.89 (s, 6H), 0.75 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.4, 142.0, 141.9, 129.1, 128.8, 128.1, 125.9, 121.5, 114.2, 111.8, 83.2, 55.3, 43.1, 29.6, 24.7, 24.4, 16.2, 7 (the carbon  $\alpha$  to boron was not found).  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  32.9.  $[\text{M}+\text{H}]^+$  ( $\text{C}_{23}\text{H}_{30}\text{O}_3^{11}\text{B}$ ): 365.2288, found 365.2287.

*N*-(2-(2-Benzyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)-4-fluorophenyl)acetamide (**4bn**). 85 mg (69%). White solid, mp = 120-125 °C.  $R_f$  = 0.60 (hexane/AcOEt: 70/30).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (dd,  $J$  = 9.7, 5.4 Hz, 1H), 7.55 (brs, 1H), 7.32-7.26 (m, 4H), 7.21 (dd,  $J$  = 10.6, 4.2 Hz, 1H), 6.91-6.86 (m, 2H), 3.40 (d,  $J$  = 14.1 Hz, 1H), 2.41 (d,  $J$  = 14.2 Hz, 1H), 2.21 (s, 3H), 1.86 (dd,  $J$  = 7.1, 6.8 Hz, 1H), 1.48 (t,  $J$  = 5.1 Hz, 1H), 1.12 (dd,  $J$  = 8.0, 4.5 Hz, 1H), 0.94 (s, 6H), 0.69 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.6, 159.4 (d,  $J$  = 243.5 Hz), 140.5, 134.1, 133.1 (d,  $J$  = 7.7 Hz), 129.0, 128.4, 126.4, 123.6 (d,  $J$  = 8.1

Hz), 116.5 (d,  $J = 22.7$  Hz), 113.8 (d,  $J = 22.0$  Hz), 83.7, 42.6, 25.4, 24.8, 24.6, 24.0, 16.1, 15.4 (br).  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  32.8.  $^{19}\text{F}\{^1\text{H}\}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -118.2. HRMS ( $\text{ESI}^+$ ) calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{24}\text{H}_{30}\text{O}_3\text{N}^{19}\text{F}^{11}\text{B}$ ): 410.2303, found 410.2295.

*N*-(2-(2-(Cyclohexylmethyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)phenyl)acetamide (**4ce**). 90 mg (76%). White solid, mp = 130–135°C.  $R_f = 0.60$  (hexane/AcOEt: 70/30).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J = 7.9$  Hz, 1H), 7.65 (brs, 1H), 7.17 (app t,  $J = 7.7$  Hz, 1H), 7.14 (d,  $J = 7.5$  Hz, 1H), 6.99 (app t,  $J = 7.2$  Hz, 1H), 2.29–2.25 (m, 1H), 2.25 (s, 3H), 1.85 (d,  $J = 12.8$  Hz, 1H), 1.76–1.64 (m, 4H), 1.60 (d,  $J = 7.2$ , 6.5 Hz, 1H), 1.50 (dd,  $J = 5.0$ , 4.8 Hz, 1H), 1.49–1.41 (m, 1H), 1.24–1.12 (m, 3H), 0.97 (s, 6H), 0.94–0.92 (m, 3H), 0.74–0.70 (m, 1H), 0.71 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.5, 138.4, 130.0, 129.4, 127.3, 124.0, 121.2, 83.4, 45.6, 38.5, 34.1, 33.3, 26.7, 26.5, 26.5, 26.1, 25.0, 24.8, 24.1, 16.2, 12.5 (br).  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ )  $\delta$  32.4. HRMS ( $\text{ESI}^+$ ) calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{24}\text{H}_{37}\text{O}_3\text{N}^{11}\text{B}$ ): 398.2866, found 398.2861.

*N*-(2-(2-(Cyclohexylmethyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)-4-methylphenyl)acetamide (**4cf**). 89 mg (72%). White solid, mp: 132–136°C.  $R_f = 0.60$  (hexane/AcOEt: 70/30).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 (d,  $J = 8.1$  Hz, 1H), 7.57 (brs, 1H), 6.97 (d,  $J = 8.1$  Hz, 1H), 6.95 (s, 1H), 2.28–2.24 (m, 1H), 2.25 (s, 3H), 2.22 (s, 3H), 1.83 (d,  $J = 13.0$  Hz, 1H), 1.75–1.64 (m, 5H), 1.59 (d,  $J = 7.3$ , 6.4 Hz, 1H), 1.47 (dd,  $J = 5.4$ , 4.8 Hz, 1H), 1.44–1.38 (m, 1H), 1.27–1.11 (m, 3H), 0.98 (s, 6H), 0.94–0.88 (m, 3H), 0.72 (s, 6H), 0.72–0.68 (m, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.5, 135.8, 133.7, 130.4, 129.9, 127.7, 121.7, 83.4, 45.7, 38.5, 34.1, 33.4, 26.7, 26.6, 26.5, 26.1, 24.9, 24.1, 21.0, 16.0, 12.7 (br).  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.5. HRMS ( $\text{ESI}^+$ ) calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{25}\text{H}_{39}\text{O}_3\text{N}^{11}\text{B}$ ): 412.3023, found 412.3018.

*N*-(2-(2-(Cyclohexylmethyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)phenyl)-4-methylbenzamide (**4ci**). 85 mg (60%). White solid, mp = 136–139 °C.  $R_f = 0.60$  (hexane/AcOEt: 90/10).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.45 (brs, 1H), 8.18 (d,  $J = 7.7$  Hz, 1H), 8.02 (s, 1H), 7.92 (d,  $J = 7.3$  Hz, 1H), 7.43–7.37 (m, 2H), 7.24 (app t,  $J = 7.7$  Hz, 1H), 7.18 (d,  $J = 7.6$  Hz, 1H), 7.03 (td,  $J = 7.5$ , 1.1 Hz, 1H), 2.47 (s, 3H), 2.29 (dd,  $J = 13.4$ , 6.4 Hz, 1H), 1.83 (d,  $J = 12.9$  Hz, 1H), 1.74–1.63 (m, 4H), 1.55 (dd,  $J = 4.8$ , 4.7 Hz, 1H), 1.52–1.40 (m, 1H), 1.23–1.11 (m, 3H), 0.99 (s, 6H), 0.96–0.82 (m, 3H), 0.94 (dd,  $J = 7.9$ , 4.3 Hz, 1H), 0.76 (s, 6H), 0.65 (dd,  $J = 13.4$ , 7.9 Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.8, 138.6, 135.6, 132.5, 130.2, 129.5, 128.8, 127.9, 127.5, 124.9, 124.1, 121.1, 83.6, 45.9, 38.5, 34.1, 33.4, 26.7, 26.5, 26.0, 24.9, 24.3, 21.4, 16.1 (the carbon  $\alpha$  to boron was not found).  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  32.9. HRMS ( $\text{ESI}^+$ ) calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{30}\text{H}_{41}\text{O}_3\text{N}^{11}\text{B}$ ): 474.3179, found 474.3174.

*N*-(2-(2-(Cyclohexylmethyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)-4-fluorophenyl)acetamide (**4cn**). 82 mg (66%). Yellow solid, mp = 135–140 °C.  $R_f = 0.60$  (hexane/AcOEt: 70/30).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (dd,  $J = 8.7$ , 5.5 Hz, 1H), 7.54 (brs, 1H), 6.90–6.85 (m, 2H), 2.26 (d,  $J = 12.7$ , 6.7 Hz, 1H), 2.23 (s, 3H), 1.83 (d,  $J = 13.1$  Hz, 1H), 1.77–1.64 (m, 4H), 1.61 (dd,  $J = 7.4$ , 6.4 Hz, 1H), 1.44 (t,  $J = 5.2$  Hz, 1H), 1.24–1.12 (m, 3H), 0.98 (s, 6H), 0.95–0.87 (m, 3H), 0.94 (dd,  $J = 7.9$ , 4.5 Hz, 1H), 0.75 (s, 6H), 0.71 (dd,  $J = 13.4$ , 8.1 Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.5, 159.4 (d,  $J = 243.2$  Hz), 134.4, 133.3 (d,  $J = 7.6$  Hz), 123.3 (d,  $J = 8.1$  Hz), 116.3 (d,  $J = 22.7$  Hz), 113.7 (d,  $J = 22.1$  Hz), 83.6, 45.7, 38.5, 34.2, 33.3, 26.7, 26.5, 26.5, 26.1, 24.9, 24.8, 24.2, 16.3, 12.9 (br).  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  32.9.  $^{19}\text{F}\{^1\text{H}\}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$

-118.4. HRMS ( $\text{ESI}^+$ ) calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{24}\text{H}_{36}\text{O}_3\text{N}^{19}\text{F}^{11}\text{B}$ ): 416.2772, found 416.2767.

*N*-(2-(2-(Cyclohexyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)phenyl)acetamide (**4de**). 86 mg (75%). White solid, mp = 124–128 °C.  $R_f = 0.50$  (hexane/AcOEt: 90/10).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (d,  $J = 8.0$  Hz, 1H), 7.86 (brs, 1H), 7.19 (d,  $J = 7.6$  Hz, 1H), 7.17 (app t,  $J = 7.9$  Hz, 1H), 6.98 (app t,  $J = 7.3$  Hz, 1H), 2.22 (s, 3H), 1.95 (d,  $J = 9.8$  Hz, 1H), 1.84–1.69 (m, 7H), 1.37 (dd,  $J = 5.5$ , 4.1 Hz, 1H), 1.24–1.08 (m, 4H), 0.98 (s, 6H), 0.82 (dd,  $J = 8.0$ , 4.0 Hz, 1H), 0.75 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.5, 138.3, 130.5, 130.1, 127.3, 124.1, 121.6, 83.2, 47.3, 32.8, 31.9, 26.9, 26.5, 25.0, 24.7, 24.0, 23.4, 19.7 (br), 16.0.  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  32.4. HRMS ( $\text{ESI}^+$ ) calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{23}\text{H}_{35}\text{O}_3\text{N}^{11}\text{B}$ ): 384.2710, found 384.2705.

*N*-(2-(2-(Cyclohexyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)-4-methylphenyl)acetamide (**4df**). 85 mg (71%). White solid, mp = 125–130 °C.  $R_f = 0.60$  (hexane/AcOEt: 70/30).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 (d,  $J = 8.1$  Hz, 2H), 6.96 (d,  $J = 9.9$  Hz, 2H), 2.25 (s, 3H), 2.20 (s, 3H), 1.94 (brd,  $J = 9.9$  Hz, 1H), 1.86–1.73 (m, 6H), 1.69 (brd,  $J = 5.6$  Hz, 1H), 1.34 (dd,  $J = 5.4$ , 4.1 Hz, 1H), 1.24–1.09 (m, 4H), 0.98 (s, 6H), 0.79 (dd,  $J = 8.0$ , 4.0 Hz, 1H), 0.74 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.5, 135.6, 133.7, 130.9, 130.4, 127.7, 122.1, 83.2, 47.3, 32.7, 31.9, 26.9, 26.5, 25.0, 24.6, 24.0, 23.4, 21.0, 19.5 (br), 15.8.  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ )  $\delta$  32.4. HRMS ( $\text{ESI}^+$ ) calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{24}\text{H}_{37}\text{O}_3\text{N}^{11}\text{B}$ ): 398.2866, found 398.2861.

*N*-(2-(2-(Cyclohexyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)-4-fluorophenyl)acetamide (**4dn**). 81 mg (67%). White solid, mp = 129–134 °C.  $R_f = 0.60$  (hexane/AcOEt: 70/30).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (dd,  $J = 11.3$ , 2.7 Hz, 1H), 7.93 (brs, 1H), 7.13 (dd,  $J = 8.0$ , 6.7 Hz, 1H), 6.68 (td,  $J = 8.3$ , 2.7 Hz, 1H), 2.23 (s, 3H), 1.96–1.89 (m, 1H), 1.86–1.73 (m, 5H), 1.71–1.65 (m, 2H), 1.33 (dd,  $J = 5.4$ , 4.1 Hz, 1H), 1.23–1.16 (m, 4H), 1.00 (s, 6H), 0.84 (dd,  $J = 8.1$ , 4.0 Hz, 1H), 0.78 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.6, 161.9 (d,  $J = 243.2$  Hz), 139.4 (br), 131.6 (d,  $J = 9.2$  Hz), 124.9, 110.2 (d,  $J = 21.3$  Hz), 108.0 (d,  $J = 27.4$  Hz), 83.3, 47.3, 32.8, 31.8, 26.9, 26.4, 25.1, 24.8, 24.1, 22.8, 16.4 (the carbon  $\alpha$  to boron was not found).  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  32.7.  $^{19}\text{F}\{^1\text{H}\}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -113.9. HRMS ( $\text{ESI}^+$ ) calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{23}\text{H}_{34}\text{O}_3\text{N}^{11}\text{B}^{19}\text{F}$ ): 402.2616, found 402.2610.

*N*-(2-(2-(Ethyl-1-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)phenyl)acetamide (**4ie**). 66 mg (64%). White solid, mp = 132–136°C.  $R_f = 0.4$  (hexane/AcOEt: 70/30).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (dd,  $J = 8.1$ , 1.4 Hz, 1H), 7.82 (brs, 1H), 7.22 (dd,  $J = 7.6$ , 1.7 Hz, 1H), 7.16 (td,  $J = 7.7$ , 1.7 Hz, 1H), 7.01 (td,  $J = 7.5$ , 1.3 Hz, 1H), 2.23 (s, 3H), 1.91 (dq,  $J = 14.2$ , 7.2 Hz, 1H), 1.50 (d,  $J = 4.0$  Hz, 1H), 1.38 (dq,  $J = 13.5$ , 7.4 Hz, 1H), 1.32 (s, 3H), 1.12 (t,  $J = 7.4$  Hz, 3H), 1.01 (s, 6H), 0.73 (s, 6H), 0.54 (d,  $J = 4.1$  Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.7, 137.1, 136.5, 129.4, 127.3, 124.7, 122.5, 83.4, 27.9, 25.0, 24.9, 24.8, 24.1, 23.0, 20.5, 14.0 (the carbon  $\alpha$  to boron was not found).  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.1. HRMS ( $\text{ESI}^+$ ) calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{20}\text{H}_{31}\text{O}_3\text{N}^{11}\text{B}$ ): 344.2397, found 344.2392.

**General Procedure for the synthesis of compounds 5.** A solution of thiophene (23 mg, 0.26 mmol) in THF (1 mL) was cooled to -78 °C and treated with *n*-BuLi (0.2 mL, 1.6 M in hexanes). The cooling bath was removed and the mixture was stirred at room temperature for 1 h. The mixture was cooled to -78 °C and compound **4** (100 mg, 0.22 mmol) was added dropwise as a solution in THF (1 mL). The mixture was stirred at -78 °C for 1 h. A solution of *N*-bromosuccinimide (NBS) (47

mg, 0.26 mmol) in THF (1 mL), was added dropwise. After 1 h at -78 °C, A saturated solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (5 mL) was added and the reaction mixture was allowed to warm to room temperature. The reaction mixture was diluted with ethyl acetate and water. The layers were separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under vacuum. The residue was purified by silica gel column chromatography to afford the corresponding products **5**.

*N*-(2-(2-Butyl-2-(thiophen-2-yl)cyclopropyl)phenyl)benzamide (**5a**). 47 mg (57%). White solid, mp = 132-136 °C. *R*<sub>f</sub> = 0.4 (hexane/AcOEt: 90/10). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.04 (brs, 1H), 8.00 (d, *J* = 8.6 Hz, 1H), 7.98-7.91 (m, 2H), 7.62-7.50 (m, 3H), 7.18 (td, *J* = 7.5, 1.8 Hz, 1H), 7.04 (dd, *J* = 7.7, 2.3 Hz, 1H), 7.00 (ddd, *J* = 13.0, 8.6, 3.7 Hz, 1H), 6.93 (dd, *J* = 5.1, 1.1 Hz, 1H), 6.69 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.50 (dd, *J* = 3.6, 1.1 Hz, 1H), 2.33-2.25 (m, 1H), 2.23 (dd, *J* = 8.7, 6.4 Hz, 1H), 1.75-1.71 (m, 1H), 1.42-1.25 (m, 6H), 0.82 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 165.5, 144.6, 137.5, 135.3, 131.8, 129.9, 128.8, 128.5, 127.3, 127.0, 126.4, 124.7, 124.3, 123.3, 121.7, 41.1, 29.6, 29.3 (2C), 22.7, 18.8, 13.9. HRMS (ESI+) calculated for [M+H]<sup>+</sup> (C<sub>24</sub>H<sub>26</sub>NOS): 376.1735, found 376.1733.

*N*-(2-(2-Benzyl-2-(thiophen-2-yl)cyclopropyl)phenyl)benzamide (**5b**). 53 mg (59%). White solid, mp = 136-139 °C. *R*<sub>f</sub> = 0.4 (hexane/AcOEt: 90/10). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.03-7.97 (m, 3H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.63-7.53 (m, 3H), 7.21-7.13 (m, 4H), 7.07-6.98 (m, 4H), 6.94 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.67 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.48 (dd, *J* = 3.6, 1.2 Hz, 1H), 3.61 (d, *J* = 14.2 Hz, 1H), 2.93 (d, *J* = 14.3 Hz, 1H), 2.31 (dd, *J* = 8.8, 6.4 Hz, 1H), 1.76-1.72 (m, 1H), 1.53 (dd, *J* = 8.9, 5.6 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 165.8, 144.8, 138.1, 137.5, 135.5, 132.1, 129.5, 129.3, 129.1, 128.3, 127.5, 127.2, 126.7, 126.5, 125.4, 124.8, 123.8, 122.6, 46.0, 29.7, 28.2, 18.1. HRMS (ESI+) calculated for [M+H]<sup>+</sup> (C<sub>27</sub>H<sub>24</sub>NOS): 410.1579, found 410.1573.

## ASSOCIATED CONTENT

### Supporting Information

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

<sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F and <sup>11</sup>B spectra of compounds **1i**, **2**, **3a**, **4** and **5**; HPLC conditions for compound **3a**; X-ray diffraction data of **3a**, **4ie** and **5a** (PDF)

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## Author Contributions

The manuscript was written through contributions of all authors.

## Notes

The authors declare no competing financial interest.

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## REFERENCES

- (1) For some reviews on biological activities of cyclopropane derivatives, see: a) Chen, D. Y.-K.; Pouwerb, R. H.; Richard, J.-A. Recent Advances in the Total Synthesis of Cyclopropane-containing Natural Products. *Chem. Soc. Rev.* **2012**, *41*, 4631-4642. b) Mizuno, A.; Matsui, K.; Shuto, S. From Peptides to Peptidomimetics: A Strategy Based on the Structural Features of Cyclopropane. *Chem. Eur. J.* **2017**, *23*, 14394-14409. c) Bajaj, P.; Sreenilayam, G.; Tyagi, V.; Fasan, R. Gram-Scale Synthesis of Chiral Cyclopropane-Containing Drugs and Drug Precursors with Engineered Myoglobin Catalysts Featuring Complementary Stereoselectivity. *Angew. Chem. Int. Ed.* **2016**, *55*, 16110-16114. d) Talele, T. T. The "Cyclopropyl Fragment" is a Versatile Player that Frequently Appears in Preclinical/Clinical Drug Molecules. *J. Med. Chem.* **2016**, *59*, 8712-8756. e) Fan, Y.-Y.; Gao, X.-H.; Yue, J.-M. Attractive Natural Products with Strained Cyclopropane and/or Cyclobutane Ring Systems. *Sci. China: Chem.* **2016**, *59*, 1126-1141.
- (2) For some recent reviews on cyclopropanes as building blocks, see: a) Ebner, C.; Carreira, E. M. Cyclopropanation Strategies in Recent Total Syntheses. *Chem. Rev.* **2017**, *117*, 11651-11679. b) Werz, D. B.; Biju, A. T. Uncovering the Neglected Similarities of Arynes and Donor-Acceptor Cyclopropanes. *Ang. Chem. Int. Ed.* **2020**, *59*, 3385-3398. c) Pirenne, V.; Muriel, B.; Waser, J. Catalytic Enantioselective Ring-Opening Reactions

- of Cyclopropanes. *Chem. Rev.* **2021**, *121*, 227-263. d) Cohen, Y.; Cohen, A.; Marek, I. Creating Stereocenters Within Acyclic Systems by C-C Bond Cleavage of Cyclopropanes. *Chem. Rev.* **2021**, *121*, 140-161. e) Ash, C.; Smith, J.; Yeston, J. Cyclopropanes through C-H Activation. *Science* **2020**, *369*, 1580-1581. f) Cao, H.; Chen, F.; Su, C.; Yu, L. Construction of Carbocycles from Methylenecyclopropanes. *Adv. Synth. Cat.* **2020**, *362*, 438-461. g) Kong, R.Y.; Crimmin, M. R. Activation and Functionalization of C-C  $\sigma$  Bonds of Alkylidene Cyclopropanes at Main Group Centers. *J. Am. Chem. Soc.* **2020**, *142*, 11967-11971. h) Sarkar, T.; Das, B. K.; Talukdar, K.; Shah, T. A.; Punniyamurthy, T. Recent Advances in Stereoselective Ring Expansion of Spirocyclopropanes: Access to the Spirocyclic Compounds. *ACS Omega* **2020**, *5*, 26316-26328.
- (3) a) Boronic Acids: Preparation, Applications in Organic Synthesis and Medicine, (Ed.: D. G. Hall), Wiley-VCH, Weinheim, **2011**. b) Boron Reagents in Synthesis, Coca, A., Eds; ACS Symposium, Series 1236; American Chemical Society: Washington, DC, **2016**. c) Synthesis and Application of Organoboron Compounds, Fernández, E.; Whiting, A., Eds., Springer, New York, **2015**.
- (4) For recent results about the chemistry of cyclopropyl boronic acids and esters, see: a) Chen, D.; Fan, Z.; Huang, L.; Gao, K.; Xiao, P.; Ni, C.; Hu, J. TMSCF<sub>2</sub> (X = Cl, Br) as Halofluorocarbene Sources for the Synthesis of Halofluorocyclopropanes. *Chem. Commun.* **2021**, *57*, 319-322. b) Shelp, R.A.; Ciro, A.; Pu, Y.; Merchant, R. R.; Hughes, J. M.; Walsh, P. J. Strain-release 2-Azaallyl Anion Addition/Borylation of [1.1.1]Propellane: Synthesis and Functionalization of Benzylamine Bicyclo[1.1.1]pentyl Boronates. *Chem. Sci.* **2021**, *12*, 7066-7072. c) Mizoguchi, H.; Seriu, M.; Sakakura, A. Synthesis of Functionalized Cyclopropylboronic Esters Based on a 1,2-Metallate Rearrangement of Cyclopropenylboronate. *Chem. Comm.* **2020**, *56*, 15545-15548. d) Sun, X.; Gu, P.; Qin, J.; Su, Y. Rhodium-catalysed Diastereo- and Enantioselective Cyclopropanation of  $\alpha$ -Boryl Styrenes. *Chem. Comm.* **2020**, *56*, 12379-12382. e) Hari, D. P.; Madhavachary, R.; Fasano, V.; Haire, J.; Aggarwal, V. K. Highly Diastereoselective Strain-Increase Allylboration: Rapid Access to Alkylidenecyclopropanes and Alkylidenecyclobutanes. *J. Am. Chem. Soc.* **2021**, *143*, 7462-7470. f) Mykura, R. C.; Songara, P.; Luc, E.; Rogers, J.; Stammers, E.; Aggarwal, V. K. Studies on the Lithiation, Borylation, and 1,2-Metallate Rearrangement of *O*-Cycloalkyl 2,4,6-Triisopropylbenzoates. *Ang. Chem. Int. Ed.* **2021**, *60*, 11436-11441. g) Amenos, L.; Trulli, L.; Novoa, L.; Parra, A.; Tortosa, M. Stereospecific Synthesis of  $\alpha$ -Hydroxy-Cyclopropylboronates from Allylic Epoxides. *Ang. Chem. Int. Ed.* **2019**, *58*, 3188-3192.
- (5) Laurent, J. P.; Haran, R. Allylic Compounds of Boron: Preparation and Magneto-optical Study. *Bull. Soc. Chim. Fr.* **1964**, 2448-2451.
- (6) Woods, W. G.; Bengelsdorf, I. S. 2-Vinyl-4,4,6-trimethyl-1,3,2-dioxaborinane. II. Derivatives. *J. Org. Chem.* **1966**, *31*, 2769-2772.
- (7) Matteson, D. S.; Schaumberg, G. D. Reactions of  $\alpha$ -Haloalkaneboronic Esters. *J. Org. Chem.* **1966**, *31*, 726-731.
- (8) Bubnov, Y. N.; Nesmeyanova, O. A.; Rudashevskaya, T. Y.; Mikhailov, B. M.; Kazansky, B. A. Reaction of Allylboranes with Methylcyclopropene. *Tetrahedron Lett.* **1971**, *24*, 2153-2156.
- (9) Shimizu, M.; Schelper, M.; Nagao, I.; Shimono, K.; Kurahashi, T.; Hiyama, T. Synthesis and Applications of 1,1-Diborylated Cyclopropanes: Facile Route to 1,2-Diboryl-3-methylenecyclopentenes. *Chem. Lett.* **2006**, *35*, 1222-1223.
- (10) Huang, Q.; Zard, S. Z. Radical Fragment Coupling Route to Geminal Bis(boronates). *Org. Lett.* **2018**, *20*, 5304-5308.
- (11) a) Harris, M. R.; Wisniewska, H. M.; Jiao, W.; Wang, X.; Bradow, J. N. A Modular Approach to the Synthesis of Gem-Disubstituted Cyclopropanes. *Org. Lett.* **2018**, *20*, 2867. b) Hong, K.; Liu, X.; Morken, J. P. Simple Access to Elusive  $\alpha$ -Boryl Carbanions and their Alkylation: an Umpolung Construction for Organic Synthesis. *J. Am. Chem. Soc.* **2014**, *136*, 10581-10584.
- (12) Kumar, N.; Reddy, R. R.; Masarwa, A. Stereoselective Desymmetrization of gem-Diborylalkanes by "Trifluorination". *Chem. Eur. J.* **2019**, *25*, 8008-8012.
- (13) Wu, F.-P.; Luo, X.; Radius, U.; Marder, T. B.; Wu, X.-F. Copper-Catalyzed Synthesis of Stereodefined Cyclopropyl Bis(boronates) from Alkenes with CO as the C1 Source. *J. Am. Chem. Soc.* **2020**, *142*, 14074-14079.
- (14) Ohtani, T.; Tsuchiya, Y.; Uruguchi, D.; Ooi, T. Photocatalytic Borylcyclopropanation of  $\alpha$ -Boryl Styrenes. *Org. Chem. Front.* **2019**, *6*, 1734-1737.
- (15) Murakami, R.; Tsunoda, K.; Iwai, T.; Sawamura, M. Stereoselective C-H Borylations of Cyclopropanes and Cyclobutanes with Silica-Supported Monophosphane-Ir Catalysts. *Chem. Eur. J.* **2014**, *20*, 13127-13131.
- (16) a) Ishiyama, T.; Matsuda, N.; Miyaoura, N.; Suzuki, A. Platinum(0)-Catalyzed Diboration of Alkynes. *J. Am. Chem. Soc.* **1993**, *115*, 11018-11019. b) Ishiyama, T.; Matsuda, N.; Murata, M.; Ozawa, F.; Suzuki, A.; Miyaoura, N. Platinum(0)-Catalyzed Diboration of Alkynes with Tetrakis(alkoxo)diborons: an Efficient and Convenient Approach to *cis*-Bis(boryl)alkenes. *Organometallics* **1996**, *15*, 713-720.
- (17) Fontani, P.; Carboni, B.; Vaultier, M.; Maas, G. Synthesis of Cyclopropylboronic Acid Esters by Carbene Transfer to 1-Alkenylboronic Acid Esters. *Synthesis* **1991**, 605-609.
- (18) The electron-withdrawing effect of trifluoroacetate as a ligand on zinc induced a dramatic increase in the reaction rate, see: a) Volgraf, M.; Sellers, B.; Jiang Y.; Wu, G.; Ly, C.; Villemure, E.; Pastor, R.; Yuen, P.; Lu, A.; Luo, X.; Liu, M.; Zhang, S.; Sun, L.; Fu, Y.; Lupardus, P.; Wallweber, H.; Liederer, B.; Deshmukh, G.; Plise, E.; Tay, S.; Reynen, P.; Herrington, J.; Gustafson, A.; Liu, Y.; Dirksen, A.; Dietz, M.; Liu, Y.; Wang, T.-M.; Hanson, J.; Hackos, D.; Searce-Levie, K.; Schwarz, J. Discovery of GluN2A-Selective NMDA Receptor Positive Allosteric Modulators (PAMs): Tuning Deactivation Kinetics via Structure-Based Design. *J. Med. Chem.* **2016**, *59*, 2760-2779. b) Lorenz, J. C.; Long, J.; Yang, Z.; Xue, S.; Xie, Y.; Shi, Y. A Novel Class of Tunable Zinc Reagents (RXZnCH<sub>2</sub>Y) for Efficient Cyclopropanation of Olefins. *J. Org. Chem.* **2004**, *69*, 327-334.
- (19) The stereochemistry of **2h** was established by NOESY experiment.
- (20) Carreras, J.; Caballero, A.; Perez, P. J. Enantio- and Diastereoselective Cyclopropanation of 1-Alkenylboronates: Synthesis of 1-Boryl-2,3-Disubstituted Cyclopropanes. *Angew. Chem. Int. Ed.* **2018**, *57*, 2334-2338.
- (21) For the X-ray structure of **3a**, see Supporting Information. CCDC 2091949 contains the supplementary crystallographic data. These data can be obtained free of charge from Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).
- (22) Crudden, C. M.; Ziebenhause, C.; Rygus, J. P. G.; Ghazati, K.; Unsworth, P. J.; Nambo, M.; Voth, S.; Hutchinson, M.; Laberge, V. S.; Maekawa, Y.; Imao, D. Iterative Protecting Group-free Cross-coupling Leading to Chiral Multiply Arylated Structures. *Nat. Commun.*, **2016**, *7*, 11065.
- (23) The stereochemistry of **4bm** was established by NOESY experiment.
- (24) The stereochemistry of **4ie** was established first by NOESY experiment and then by X-ray analysis. For the X-ray structure, see Supporting Information. CCDC 2165041 contains the supplementary crystallographic data. These data can be obtained free of charge from Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).
- (25) a) Kleban, I.; Radchenko, D. S.; Tyntsunik, A. V.; Shuvakin, S.; Konovets, A. I.; Rassukana, Y.; Grygorenko, O. O. Cyclopropyl Boronic Derivatives in Parallel Synthesis of sp<sup>3</sup>-Enriched Compound Libraries. *Monatsh. Chem.* **2020**, *151*, 953-962. b) de Meijere, A.; Khlebnikov, A. F.; Sünemann, H. W.; Frank, D.; Rauch, K.; Yufit, D. S. Convenient Access to Various 1-Cyclopropylcyclopropane Derivatives. *Eur. J. Org. Chem.* **2010**, 3295-3301.
- (26) Bonet A.; Odachowski, M.; Leonori, D.; Essafi S.; Aggarwal V. K. Enantiospecific sp<sup>2</sup>-sp<sup>3</sup> Coupling of Secondary and Tertiary Boronic Esters. *Nat. Chem.* **2014**, *6*, 584-589.
- (27) For the X-ray structure of **5a**, see Supporting Information. CCDC 2143115 contains the supplementary crystallographic data. These data can be obtained free of charge from Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).
- (28) Kuang, Z.; Gao, G.; Song, Q. Base-catalyzed Diborylation of Alkynes: Synthesis and Applications of *cis*-1,2-Bis(boryl)alkenes. *Science China: Chemistry* **2019**, *62*, 62-66.
- (29) Miura, T.; Nakahashi, J.; Sasatsu, T.; Murakami, M. Synthesis of *g*-Boryl-Substituted Homoallylic Alcohols with *anti*-Stereochemistry Based on a Double-Bond Transposition. *Angew. Chem. Int. Ed.* **2019**, *58*, 1138-1142.

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