

*Electronic Supplementary Information (ESI)*

**Regioselective copper-catalyzed aminoborylation of styrenes with bis(pinacolato)diboron and diazo compounds**

Jingfeng Huo,<sup>a</sup> Yazhen Xue<sup>a</sup> and Jianbo Wang<sup>ab\*</sup>

<sup>a</sup>*Beijing National Laboratory of Molecular Sciences (BNLMS) and Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China; Email: [wangjb@pku.edu.cn](mailto:wangjb@pku.edu.cn)*

<sup>b</sup>*The State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*

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## 1. General information

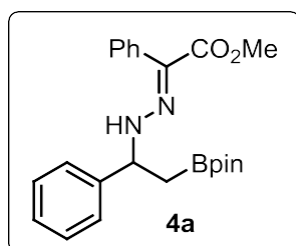
All the reactions of copper-catalyzed aminoborylation of vinylarenes were performed under nitrogen atmosphere in a flame-dried reaction tube. All solvents were distilled under nitrogen atmosphere prior to use. Dioxane was dried over Na with a benzophenone-ketyl intermediate as an indicator.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded at 400 MHz and 100 MHz with Bruker ARX 400 spectrometer. The data for NMR spectra were reported as following: chemical shifts ( $\delta$ ) were reported in ppm, and coupling constants ( $J$ ) were reported in Hertz (Hz). The resonances for carbon atoms directly attached to boron were not observed due to quadrupolar relaxation. Infrared spectra were recorded on a Nicolet Avatar 330 Fourier transform spectrometer (FT-IR) and are reported in terms of frequency of absorption ( $\text{cm}^{-1}$ ). HRMS were obtained on Bruker APEX IV FTMS. All the  $\alpha$ -diazoesters was prepared according to the literature procedures.<sup>1</sup> Other starting materials were obtained from commercial suppliers and were used without further purification.

## 2. Typical procedure for copper-catalyzed aminoborylation of vinylarenes

Under a nitrogen atmosphere,  $\text{Cu}(\text{OAc})_2$  (1.8 mg, 10 mol%), dppbz (5.4 mg, 12 mol%) and  $\text{KO}^t\text{Bu}$  (16.8 mg, 1.5 equiv) were successively added to a flame-dried 10 mL Schlenk reaction tube. The reaction flask was degassed three times with nitrogen and dry dioxane (0.5 mL) was added using a syringe. The mixture was allowed to stir for 10 min at room temperature. Then a solution of pinacolborane (1.5 equiv) in 0.5 mL dioxane was added to the reaction tube, followed by the addition of vinylarenes (0.10 mmol) and corresponding  $\alpha$ -diazoesters (1.5 equiv). The resulting solution was then stirred at the 40 °C for 3 h. After completion of the reaction, the reaction mixture was filtered through a short plug of silica gel with ethyl acetate as eluents. The solvent was removed with rotary evaporator under reduced pressure to leave a crude mixture, which was purified by preparative thin-layer chromatography to afford pure product. It is worth noting that the silica gel plates should be saturated by triethylamine in advance, because the products are sensitive to acid.

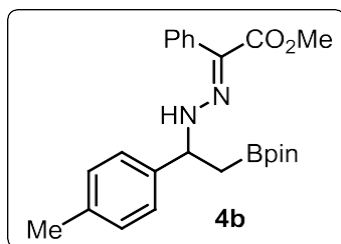
## 3. Characterization data for the products

Methyl (*E*)-2-phenyl-2-(2-(1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)hydrazono)acetate (**4a**)



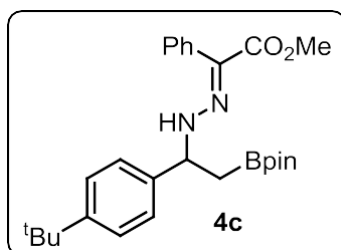
Yield: 81% (33.1 mg); colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.91 (d,  $J = 4.4$  Hz, 1H), 7.52-7.50 (m, 2H), 7.37-7.28 (m, 6H), 7.25-7.20 (m, 2H), 4.94 (dt,  $J = 7.6, 4.8$  Hz, 1H), 3.76 (s, 3H), 1.71 (dd,  $J = 15.4, 7.5$  Hz, 1H), 1.49 (dd,  $J = 15.4, 7.8$  Hz, 1H), 1.09 (d,  $J = 3.5$  Hz, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.9, 143.6, 137.2, 128.4, 128.3, 127.7, 127.2, 126.8, 126.7, 124.7, 83.3, 61.8, 51.1, 24.7, 24.5; IR (film) 3245, 2976, 1742, 1671, 1515, 1371, 1142, 699  $\text{cm}^{-1}$ ; HRMS (ESI) calcd for  $\text{C}_{23}\text{H}_{30}\text{BN}_2\text{O}_4$   $[\text{M}+\text{H}]^+$  409.2293, found 409.2292.

Methyl (*E*)-2-phenyl-2-(2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(*p*-tolyl)ethyl)hydrazono)acetate (**4b**)



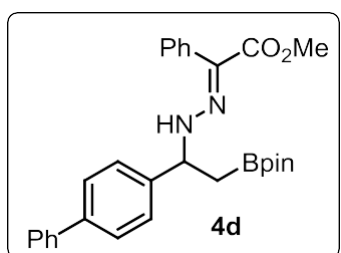
Yield: 89% (37.6 mg); colorless oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.90 (d,  $J = 4.3$  Hz, 1H), 7.51 (d,  $J = 7.7$  Hz, 2H), 7.30 (t,  $J = 7.5$  Hz, 2H), 7.26-7.20 (m, 3H), 7.12 (d,  $J = 7.9$  Hz, 2H), 4.91 (dt,  $J = 7.5, 4.8$  Hz, 1H), 3.75 (s, 3H), 2.32 (s, 3H), 1.70 (dd,  $J = 15.4, 7.6$  Hz, 1H), 1.46 (dd,  $J = 15.4, 7.6$  Hz, 1H), 1.09 (d,  $J = 3.5$  Hz, 12H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.9, 140.6, 137.3, 136.8, 129.1, 128.4, 127.6, 126.7, 126.7, 124.5, 83.3, 61.5, 51.1, 24.7, 24.5, 21.0; IR (film) 3245, 2976, 1671, 1515, 1371, 1326, 1166, 1143, 698  $\text{cm}^{-1}$ ; HRMS (ESI) calcd for  $\text{C}_{24}\text{H}_{32}\text{BN}_2\text{O}_4$   $[\text{M}+\text{H}]^+$  423.2450, found 423.2449.

Methyl (*E*)-2-(2-(1-(4-(*tert*-butyl)phenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)hydrazono)-2-phenylacetate (**4c**)



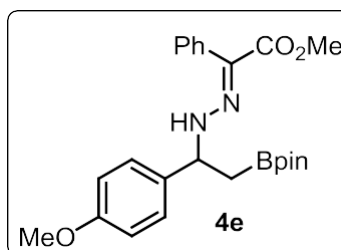
Yield: 90% (41.8 mg); colorless oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.90 (d,  $J = 4.1$  Hz, 1H), 7.52 (d,  $J = 7.5$  Hz, 2H), 7.34-7.25 (m, 6H), 7.23-7.20 (m, 1H), 4.91 (dt,  $J = 7.5, 4.8$  Hz, 1H), 3.75 (s, 3H), 1.71 (dd,  $J = 15.4, 7.7$  Hz, 1H), 1.47 (dd,  $J = 15.3, 7.6$  Hz, 1H), 1.29 (s, 9H), 1.07 (d,  $J = 6.7$  Hz, 12H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.9, 150.1, 140.4, 137.3, 128.3, 127.6, 126.6, 126.5, 125.3, 124.4, 83.2, 61.5, 51.0, 34.3, 31.3, 24.7, 24.4; IR (film) 3257, 2955, 1742, 1674, 1510, 1368, 1142, 697  $\text{cm}^{-1}$ ; HRMS (ESI) calcd for  $\text{C}_{27}\text{H}_{38}\text{BN}_2\text{O}_4$   $[\text{M}+\text{H}]^+$  465.2925, found 465.2914.

Methyl (*E*)-2-(2-(1-([1,1'-biphenyl]-4-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)hydrazono)-2-phenylacetate (**4d**)



Yield: 90% (43.6 mg); colorless oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.93 (d,  $J = 4.5$  Hz, 1H), 7.59-7.52 (m, 6H), 7.44-7.41 (m, 4H), 7.35-7.29 (m, 3H), 7.25-7.23 (m, 1H), 4.99 (dt,  $J = 7.5, 4.7$  Hz, 1H), 3.77 (s, 3H), 1.74 (dd,  $J = 15.4, 7.4$  Hz, 1H), 1.47 (dd,  $J = 15.4, 7.8$  Hz, 1H), 1.11 (d,  $J = 4.1$  Hz, 12H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.9, 142.7, 140.9, 140.1, 137.2, 128.7, 128.4, 127.7, 127.3, 127.2, 127.0, 126.8, 124.9, 83.3, 61.5, 51.1, 24.7, 24.5; IR (film) 3248, 2976, 1743, 1674, 1514, 1371, 1166, 1142, 698  $\text{cm}^{-1}$ ; HRMS (ESI) calcd for  $\text{C}_{29}\text{H}_{34}\text{BN}_2\text{O}_4$   $[\text{M}+\text{H}]^+$  485.2606, found 485.2603.

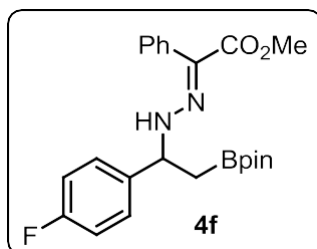
Methyl (*E*)-2-(2-(1-(4-methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)hydrazono)-2-phenylacetate (**4e**)



Yield: 68% (29.8 mg); pale yellow oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.84 (d,  $J = 4.3$  Hz, 1H), 7.52-7.50 (m, 2H), 7.32-7.28 (m, 4H), 7.24-7.20 (m, 1H), 6.86-6.84 (m, 2H), 4.90 (dt,  $J = 7.6, 4.7$  Hz, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 1.70 (dd,  $J = 15.4, 7.3$  Hz, 1H), 1.46 (dd,  $J = 15.4, 8.0$  Hz, 1H), 1.09 (d,  $J = 1.6$  Hz, 12H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.9, 158.8,

137.3, 135.6, 128.3, 128.0, 127.6, 126.7, 124.5, 113.8, 83.2, 61.2, 55.2, 51.0, 24.6, 24.5; IR (film) 3257, 2952, 1739, 1674, 1516, 1374, 1253, 1142, 700  $\text{cm}^{-1}$ ; HRMS (ESI) calcd for  $\text{C}_{24}\text{H}_{32}\text{BN}_2\text{O}_5$   $[\text{M}+\text{H}]^+$  439.2404, found 439.2403.

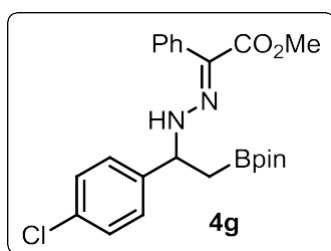
Methyl (*E*)-2-(2-(1-(4-fluorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)hydrazono)-2-phenylacetate (**4f**)



Yield: 81% (34.5 mg); colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.84 (d,  $J = 4.4$  Hz, 1H), 7.49 (d,  $J = 7.5$  Hz, 2H), 7.34-7.28 (m, 4H), 7.24-7.21 (m, 1H), 7.00 (t,  $J = 8.7$  Hz, 2H), 4.92 (dt,  $J = 7.5$ , 4.8 Hz, 1H), 3.76 (s, 3H), 1.69 (dd,  $J = 15.5$ , 7.2 Hz, 1H), 1.47 (dd,  $J = 15.5$ , 8.1 Hz, 1H), 1.10 (s, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.0, 162.1 (d,  $J = 245.1$  Hz, 1C), 139.5 (d,  $J = 3.0$  Hz, 1C), 137.2, 128.6 (d,  $J = 8.0$  Hz, 1C), 128.4, 127.7, 126.9, 125.2, 115.2

(d,  $J = 21.3$  Hz, 1C), 83.4, 61.1, 51.2, 24.7, 24.6; IR (film) 3248, 2976, 1742, 1677, 1510, 1371, 1322, 1142, 848  $\text{cm}^{-1}$ ; HRMS (ESI) calcd for  $\text{C}_{23}\text{H}_{29}\text{BFN}_2\text{O}_4$   $[\text{M}+\text{H}]^+$  427.2204, found 427.2197.

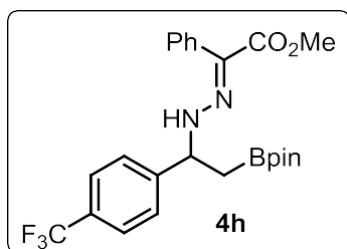
Methyl (*E*)-2-(2-(1-(4-chlorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)hydrazono)-2-phenylacetate (**4g**)



Yield: 56% (24.8 mg); colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.83 (d,  $J = 4.4$  Hz, 1H), 7.49 (d,  $J = 7.3$  Hz, 2H), 7.34-7.28 (m, 4H), 7.32-7.28 (m, 6H), 7.25-7.21 (m, 1H), 4.90 (dt,  $J = 7.5$ , 4.8 Hz, 1H), 3.77 (s, 3H), 1.67 (dd,  $J = 15.5$ , 7.2 Hz, 1H), 1.46 (dd,  $J = 15.5$ , 7.9 Hz, 1H), 1.11 (d,  $J = 1.1$  Hz, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.9, 142.3, 137.0, 132.9, 128.5, 128.3, 128.3, 127.7, 126.9, 125.4, 83.4, 61.0, 51.2, 24.7, 24.6; IR (film)

3275, 2979, 2914, 2846, 1739, 1690, 1372, 1143, 697  $\text{cm}^{-1}$ ; HRMS (ESI) calcd for  $\text{C}_{23}\text{H}_{29}\text{BClN}_2\text{O}_4$   $[\text{M}+\text{H}]^+$  443.1903, found 443.1903.

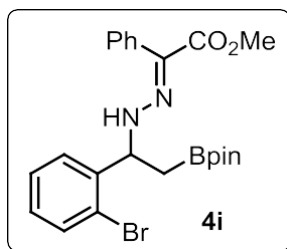
Methyl (*E*)-2-phenyl-2-(2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(4-(trifluoromethyl)phenyl)ethyl)hydrazono)acetate (**4h**)



Yield: 77% (36.7 mg); colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.87 (d,  $J = 4.5$  Hz, 1H), 7.58-7.56 (m, 2H), 7.49-7.46 (m, 4H), 7.32-7.28 (m, 2H), 7.25-7.22 (m, 1H), 4.98 (dt,  $J = 7.5$ , 5.1 Hz, 1H), 3.78 (s, 3H), 1.68 (dd,  $J = 15.6$ , 7.4 Hz, 1H), 1.49 (dd,  $J = 15.6$ , 7.7 Hz, 1H), 1.12 (d,  $J = 3.0$  Hz, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.9, 148.0, 136.9, 129.4 (q,  $J = 32.4$  Hz, 1C), 128.3, 127.7, 127.2, 127.0, 126.9 (q,  $J = 270.4$  Hz, 1C), 125.8,

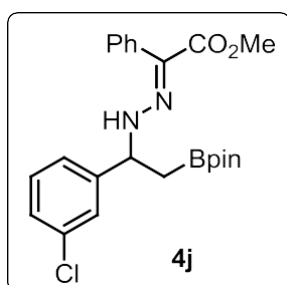
125.4 (q,  $J = 3.7$  Hz, 1C), 83.5, 61.3, 51.2, 24.7, 24.5; IR (film) 3060, 2982, 1736, 1677, 1520, 1377, 1328, 1167, 1139, 848  $\text{cm}^{-1}$ ; HRMS (ESI) calcd for  $\text{C}_{24}\text{H}_{29}\text{BF}_3\text{N}_2\text{O}_4$   $[\text{M}+\text{H}]^+$  477.2167, found 477.2164.

Methyl (*E*)-2-(2-(1-(2-bromophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)hydrazono)-2-phenylacetate (**4i**)



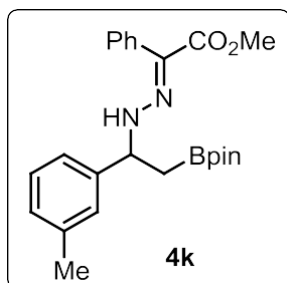
Yield: 52% (25.3 mg); colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  11.01 (d,  $J = 4.5$  Hz, 1H), 7.54-7.50 (m, 3H), 7.40 (dd,  $J = 7.8$ , 1.5 Hz, 1H), 7.31-7.27 (m, 3H), 7.25-7.22 (m, 1H), 7.08 (dt,  $J = 7.8$ , 1.6 Hz, 1H), 5.35 (dt,  $J = 7.4$ , 5.0 Hz, 1H), 3.78 (s, 3H), 1.66 (dd,  $J = 15.7$ , 8.2 Hz, 1H), 1.59 (dd,  $J = 15.7$ , 6.8 Hz, 1H), 1.12 (s, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.8, 142.9, 137.1, 132.9, 128.5, 128.3, 128.2, 127.7, 127.6, 126.8, 125.3, 123.2, 83.4, 60.6, 51.2, 24.8, 24.5; IR (film) 3254, 2976, 2911, 2846, 1668, 1517, 1371, 1143, 758; HRMS (ESI) calcd for  $\text{C}_{23}\text{H}_{29}\text{BBrN}_2\text{O}_4$   $[\text{M}+\text{H}]^+$  487.1398, found 487.1395.

Methyl (*E*)-2-(2-(1-(3-chlorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)hydrazono)-2-phenylacetate (**4j**)



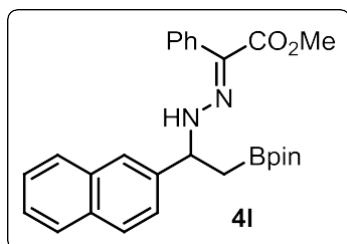
Yield: 74% (32.8 mg); colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.86 (d,  $J = 4.1$  Hz, 1H), 7.50-7.48 (m, 2H), 7.35 (s, 1H), 7.32-7.28 (m, 2H), 7.25-7.20 (m, 4H), 4.91 (dt,  $J = 6.8$ , 4.8 Hz, 1H), 3.78 (s, 3H), 1.66 (dd,  $J = 15.6$ , 7.1 Hz, 1H), 1.46 (dd,  $J = 15.5$ , 8.0 Hz, 1H), 1.12 (d,  $J = 3.0$  Hz, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.9, 145.9, 137.0, 134.1, 129.7, 128.3, 127.7, 127.3, 127.2, 126.9, 125.5, 125.0, 83.4, 61.3, 51.2, 24.7, 24.5; IR (film) 3254, 2979, 2916, 2854, 1739, 1677, 1516, 1371, 1142, 697; HRMS (ESI) calcd for  $\text{C}_{23}\text{H}_{29}\text{BClN}_2\text{O}_4$   $[\text{M}+\text{H}]^+$  443.1903, found 443.1901.

Methyl (*E*)-2-phenyl-2-(2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(*m*-tolyl)ethyl)hydrazono)acetate (**4k**)



Yield: 90% (38.0 mg); colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.89 (d,  $J = 4.3$  Hz, 1H), 7.53-7.51 (m, 2H), 7.31-7.28 (m, 2H), 7.24-7.14 (m, 4H), 7.05-7.03 (m, 1H), 4.91 (dt,  $J = 7.2$ , 4.8 Hz, 1H), 3.76 (s, 3H), 2.33 (s, 3H), 1.70 (dd,  $J = 15.4$ , 7.4 Hz, 1H), 1.46 (dd,  $J = 15.4$ , 7.8 Hz, 1H), 1.09 (d,  $J = 3.2$  Hz, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.9, 143.9, 137.9, 137.3, 128.3, 128.0, 127.6, 127.6, 126.7, 124.6, 123.8, 83.2, 61.9, 51.0, 24.7, 24.5, 21.4; IR (film) 3251, 2976, 2949, 1739, 1671, 1514, 1371, 1142, 698; HRMS (ESI) calcd for  $\text{C}_{24}\text{H}_{32}\text{BN}_2\text{O}_4$   $[\text{M}+\text{H}]^+$  423.2450, found 423.2450.

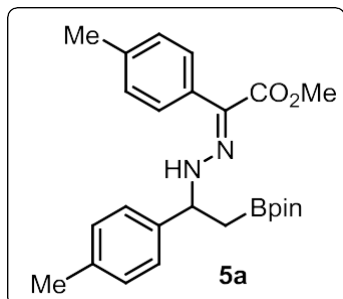
Methyl (*E*)-2-(2-(1-(naphthalen-2-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)hydrazono)-2-phenylacetate (**4l**)



Yield: 67% (30.7 mg); colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.98 (d,  $J = 4.6$  Hz, 1H), 7.82-7.79 (m, 4H), 7.53-7.50 (m, 3H), 7.46-7.43 (m, 2H), 7.29 (t,  $J = 7.4$  Hz, 2H), 7.24-7.20 (m, 1H), 5.12 (dt,  $J = 7.5$ , 4.8 Hz, 1H), 3.76 (s, 3H), 1.79 (dd,  $J = 15.5$ , 7.4 Hz, 1H), 1.58 (dd,  $J = 15.5$ , 7.8 Hz, 1H), 1.08 (d,  $J = 4.2$  Hz, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.9, 141.0, 137.2, 133.3, 132.7, 128.3, 128.3, 127.9, 127.7, 127.6, 126.7, 126.0, 125.7, 125.4, 125.1, 124.9, 83.3, 61.9, 51.1, 24.7, 24.5; IR (film) 3230, 2976, 2843,

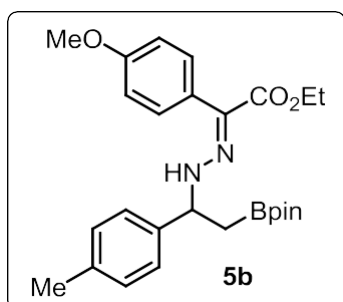
1736, 1668, 1519, 1317, 1164, 1142, 737; HRMS (ESI) calcd for C<sub>27</sub>H<sub>32</sub>BN<sub>2</sub>O<sub>4</sub> [M+H]<sup>+</sup> 459.2450, found 459.2448.

Methyl (*E*)-2-(2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(*p*-tolyl)ethyl)hydrazono)-2-(*p*-tolyl)acetate (**5a**)



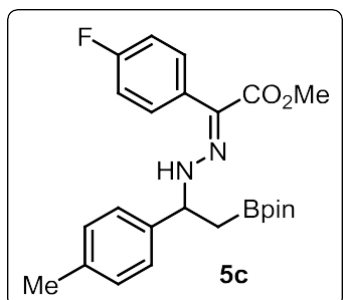
Yield: 79% (34.5 mg); colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.80 (d, *J* = 4.7 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.12-7.10 (m, 4H), 4.89 (dt, *J* = 7.6, 4.8 Hz, 1H), 3.74 (s, 3H), 2.33 (s, 3H), 2.31 (s, 3H), 1.69 (dd, *J* = 15.4, 7.5 Hz, 1H), 1.45 (dd, *J* = 15.4, 7.8 Hz, 1H), 1.10 (d, *J* = 3.0 Hz, 12H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.9, 140.6, 136.7, 136.3, 134.5, 129.0, 128.4, 128.2, 126.7, 124.6, 83.2, 61.4, 51.0, 24.7, 24.5, 21.1, 21.0; IR (film) 3245, 2976, 1745, 1671, 1513, 1368, 1145, 826 cm<sup>-1</sup>; HRMS (ESI) calcd for C<sub>27</sub>H<sub>32</sub>BN<sub>2</sub>O<sub>4</sub> [M+H]<sup>+</sup> 437.2606, found 437.3600.

Ethyl (*E*)-2-(4-methoxyphenyl)-2-(2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(*p*-tolyl)ethyl)hydrazono)acetate (**5b**)



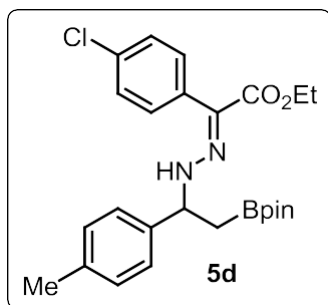
Yield: 59% (27.5 mg); pale yellow oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.72 (d, *J* = 4.2 Hz, 1H), 7.46 (d, *J* = 8.7 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.84 (d, *J* = 8.9 Hz, 2H), 4.88 (dt, *J* = 7.2, 4.8 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 2.31 (s, 3H), 1.68 (dd, *J* = 15.4, 7.6 Hz, 1H), 1.44 (dd, *J* = 15.5, 7.7 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.10 (d, *J* = 3.8 Hz, 12H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.5, 158.4, 140.8, 136.6, 130.1, 129.5, 129.0, 126.7, 124.7, 113.0, 83.2, 61.3, 60.0, 55.2, 24.7, 24.5, 21.0, 14.2; IR (film) 3260, 2979, 2917, 1668, 1513, 1376, 1248, 1176, 1144, 846; HRMS (ESI) calcd for C<sub>26</sub>H<sub>36</sub>BN<sub>2</sub>O<sub>5</sub> [M+H]<sup>+</sup> 467.2712, found 467.2710.

Methyl (*E*)-2-(4-fluorophenyl)-2-(2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(*p*-tolyl)ethyl)hydrazono)acetate (**5c**)



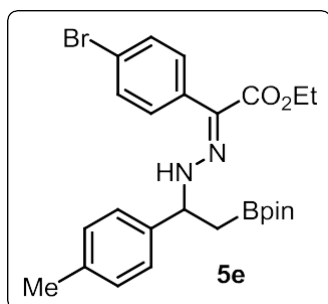
Yield: 84% (37.0 mg); colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.88 (d, *J* = 4.5 Hz, 1H), 7.50-7.45 (m, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 7.00-6.96 (m, 2H), 4.90 (dt, *J* = 7.5, 4.7 Hz, 1H), 3.75 (s, 3H), 2.32 (s, 3H), 1.68 (dd, *J* = 15.4, 7.6 Hz, 1H), 1.45 (dd, *J* = 15.4, 7.6 Hz, 1H), 1.10 (d, *J* = 3.9 Hz, 12H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.7, 161.8 (d, *J* = 245.7 Hz, 1C), 140.5, 136.9, 133.4 (d, *J* = 3.4 Hz, 1C), 130.0 (d, *J* = 7.7 Hz, 1C), 129.1, 126.7, 123.5, 114.5 (d, *J* = 21.4 Hz, 1C), 83.3, 61.6, 51.1, 24.7, 24.5, 21.1; IR (film) 3257, 2982, 2911, 2846, 1742, 1674, 1510, 1371, 1143, 839; HRMS (ESI) calcd for C<sub>24</sub>H<sub>31</sub>BFN<sub>2</sub>O<sub>4</sub> [M+H]<sup>+</sup> 441.2355, found 441.2354.

Ethyl (*E*)-2-(4-chlorophenyl)-2-(2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(*p*-tolyl)ethyl)hydrazono)acetate (**5d**)



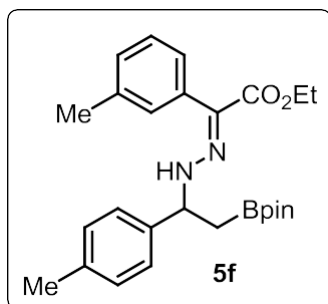
Yield: 75% (35.3 mg); colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.93 (d,  $J = 4.4$  Hz, 1H), 7.49-7.47 (m, 2H), 7.26-7.22 (m, 4H), 7.13-7.11 (m, 2H), 4.90 (dt,  $J = 7.6, 4.8$  Hz, 1H), 4.24 (q,  $J = 7.1$  Hz, 2H), 2.32 (s, 3H), 1.68 (dd,  $J = 15.4, 7.6$  Hz, 1H), 1.45 (dd,  $J = 15.4, 7.7$  Hz, 1H), 1.29 (t,  $J = 7.1$  Hz, 3H), 1.10 (d,  $J = 3.6$  Hz, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.3, 140.4, 136.9, 135.9, 132.2, 129.5, 129.1, 127.7, 126.7, 123.5, 83.3, 61.6, 60.2, 24.7, 24.5, 21.1, 14.2; IR (film) 3245, 2979, 2923, 1736, 1671, 1514, 1370, 1143, 847; HRMS (ESI) calcd for  $\text{C}_{25}\text{H}_{33}\text{BClN}_2\text{O}_4$   $[\text{M}+\text{H}]^+$  471.2216, found 471.2213.

Ethyl (*E*)-2-(4-bromophenyl)-2-(2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(*p*-tolyl)ethyl)hydrazono)acetate (**5e**)



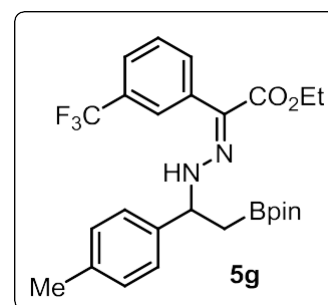
Yield: 71% (36.6 mg); colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.94 (d,  $J = 4.5$  Hz, 1H), 7.44-7.39 (m, 4H), 7.23 (d,  $J = 8.0$  Hz, 2H), 7.12 (d,  $J = 8.0$  Hz, 2H), 4.89 (dt,  $J = 7.6, 4.8$  Hz, 1H), 4.24 (q,  $J = 7.1$  Hz, 2H), 2.31 (s, 3H), 1.68 (dd,  $J = 15.4, 7.6$  Hz, 1H), 1.46 (dd,  $J = 15.4, 7.7$  Hz, 1H), 1.29 (t,  $J = 7.2$  Hz, 3H), 1.10 (d,  $J = 3.5$  Hz, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.2, 140.4, 136.9, 136.3, 130.6, 129.8, 129.1, 126.7, 123.4, 120.4, 83.3, 61.6, 60.2, 24.7, 24.5, 21.0, 14.2; IR (film) 3253, 2976, 1668, 1513, 1369, 1172, 1143, 830; HRMS (ESI) calcd for  $\text{C}_{25}\text{H}_{33}\text{BBrN}_2\text{O}_4$   $[\text{M}+\text{H}]^+$  515.1711, found 515.1711.

Ethyl (*E*)-2-(2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(*p*-tolyl)ethyl)hydrazono)-2-(*m*-tolyl)acetate (**5f**)



Yield: 76% (34.2 mg); colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.81 (d,  $J = 4.6$  Hz, 1H), 7.34-7.32 (m, 2H), 7.25 (d,  $J = 8.0$  Hz, 2H), 7.18 (t,  $J = 7.6$  Hz, 1H), 7.11 (d,  $J = 8.0$  Hz, 2H), 7.03 (d,  $J = 7.4$  Hz, 1H), 4.90 (dt,  $J = 7.5, 5.1$  Hz, 1H), 4.23 (q,  $J = 7.1$  Hz, 2H), 2.34 (s, 3H), 2.31 (s, 3H), 1.70 (dd,  $J = 15.4, 7.5$  Hz, 1H), 1.46 (dd,  $J = 15.4, 7.8$  Hz, 1H), 1.28 (t,  $J = 7.1$  Hz, 3H), 1.10 (d,  $J = 2.9$  Hz, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.6, 140.7, 137.3, 137.0, 136.7, 129.0, 129.0, 127.4, 127.3, 126.7, 125.5, 125.0, 83.2, 61.5, 60.1, 24.7, 24.5, 21.5, 21.0, 14.2; IR (film) 3242, 2976, 1668, 1514, 1370, 1171, 1144, 848; HRMS (ESI) calcd for  $\text{C}_{26}\text{H}_{36}\text{BN}_2\text{O}_4$   $[\text{M}+\text{H}]^+$  451.2763, found 451.2762.

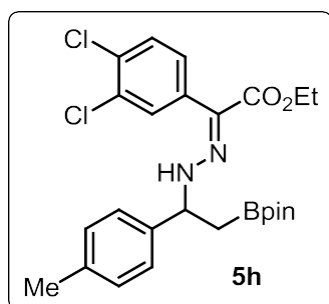
Ethyl (*E*)-2-(2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(*p*-tolyl)ethyl)hydrazono)-2-(3-(trifluoromethyl)phenyl)acetate (**5g**)



Yield: 67% (33.8 mg); colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  11.06 (d,  $J = 4.5$  Hz, 1H), 7.83 (s, 1H), 7.73 (d,  $J = 7.8$  Hz, 1H), 7.45 (d,  $J = 7.8$  Hz, 1H), 7.39 (t,  $J = 7.8$  Hz, 1H), 7.24 (d,  $J = 8.1$  Hz, 2H), 7.13 (d,  $J = 7.9$  Hz, 2H), 4.92 (dt,  $J = 7.6, 4.9$  Hz, 1H), 4.26 (q,  $J = 7.1$  Hz, 2H), 2.32 (s, 3H), 1.70 (dd,  $J = 15.4, 7.6$  Hz, 1H), 1.46 (dd,  $J = 15.4, 7.5$  Hz, 1H), 1.31 (t,  $J = 7.1$  Hz, 3H),

1.10 (s, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.2, 140.2, 138.1, 137.0, 131.3, 129.6 (q,  $J = 31.4$  Hz, 1C), 129.2, 128.0, 127.1 (q,  $J = 272.0$  Hz, 1C), 126.7, 125.1 (q,  $J = 3.8$  Hz, 1C), 123.0, 122.9 (q,  $J = 3.6$  Hz, 1C), 83.3, 61.8, 60.3, 24.7, 24.5, 21.1, 14.1; IR (film) 2979, 1671, 1513, 1371, 1334, 1167, 909, 733; HRMS (ESI) calcd for  $\text{C}_{26}\text{H}_{33}\text{BF}_3\text{N}_2\text{O}_4$   $[\text{M}+\text{H}]^+$  505.2480, found 505.2476.

Ethyl (*E*)-2-(3,4-dichlorophenyl)-2-(2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(*p*-tolyl)ethyl)hydrazono)acetate (**5h**)



Yield: 74% (37.4 mg); colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  11.04 (d,  $J = 3.6$  Hz, 1H), 7.67 (d,  $J = 2.1$  Hz, 1H), 7.41 (dd,  $J = 8.5, 2.1$  Hz, 1H), 7.33 (d,  $J = 8.5$  Hz, 1H), 7.23 (d,  $J = 8.1$  Hz, 2H), 7.13 (d,  $J = 8.0$  Hz, 2H), 4.91 (dt,  $J = 7.5, 3.56$  Hz, 1H), 4.26 (q,  $J = 7.1$  Hz, 2H), 2.32 (s, 3H), 1.69 (dd,  $J = 15.4, 7.6$  Hz, 1H), 1.47 (dd,  $J = 15.4, 7.8$  Hz, 1H), 1.31 (t,  $J = 7.1$  Hz, 3H), 1.11 (d,  $J = 2.8$  Hz, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.1, 140.1, 137.4, 137.0, 131.5, 130.1, 129.8, 129.4, 129.2, 127.4, 126.7,

122.0, 83.4, 61.8, 60.4, 24.7, 24.5, 21.1, 14.2; IR (film) 3233, 2979, 2921, 2849, 1733, 1677, 1513, 1370, 1142, 1029, 824; HRMS (ESI) calcd for  $\text{C}_{25}\text{H}_{32}\text{BCl}_2\text{N}_2\text{O}_4$   $[\text{M}+\text{H}]^+$  505.1828, found 505.1824.

#### 4. Reference

H. Keipour, A. Jalba, L. Delage-Laurin, T. Ollevier, *J. Org. Chem.* 2017, **82**, 3000.



## 5. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of the products

