### **Supporting Information**

for

# Iridium-Catalyzed Ortho-C–H Borylation of Aromatic Aldimine Derived from Pentafluoroaniline with Bis(pinacolate)diboron

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#### 1. General and Materials

Materials were obtained from commercial suppliers and purified by standard procedures unless otherwise noted. Solvents were also purchased from commercial suppliers, degassed via three freeze-pump-thaw cycles, and further dried over molecular sieves (MS 4A). NMR spectra were recorded on JEOL JNM-ECX400P spectrometer (<sup>1</sup>H: 400 MHz, <sup>13</sup>C: 100 MHz, <sup>19</sup>F: 376 MHz). Tetramethylsilane (<sup>1</sup>H), CDCl<sub>3</sub> (<sup>13</sup>C) and monofluorobenzene (<sup>19</sup>F) were employed as external standards, respectively. 1,1,2,2-tetracholoethane was used as an internal standard to determine the NMR yields. GLC analyses were conducted on a Hitachi G-3500 instrument equipped with a glass column (OV-101 on Uniport B, 2 m). High-resolution mass spectra was recorded at the Center for Instrumental Analysis, Hokkaido University.

#### 2. Experimental Section

#### 2.1. Preparation of Substrates

Aromatic aldimines **1b–g** were synthesized according to the reported procedure.<sup>1–3</sup>

Preparation of (*E*)-*N*-benzylidene-2,3,4,5,6-pentafluoroaniline (1a).



In a vacuum dried 200 mL round bottomed flask, benzaldehyde (3.18 g, 30 mmol) and pentafluoroaniline (5.49 g, 30 mmol) were dissolved in THF (50 mL) under nitrogen atmosphere. MgSO<sub>4</sub> (1.7 g, 14 mmol) was then added at room temperature, and the mixture was stirred for 48 h at 55 °C. After filtration, the solvent was removed by evaporation. the crude product was purified by flash column chromatography (SiO<sub>2</sub>) to obtain aromatic aldimine **1a** (5.14 g, 19 mmol, 63%) as a solid.

<sup>1</sup>H NMR (396 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.48–7.59 (m, 3H), 7.92–7.95 (m, 2H), 8.59 (s, 1H). <sup>13</sup>C NMR (99 MHz, CDCl<sub>3</sub>,  $\delta$ ): 126.8 (m, *C*), 128.9 (*C*H), 129.3 (*C*H), 132.9 (*C*H), 135.1 (*C*), 137.9 (br d, <sup>1</sup>*J*<sub>C</sub>-<sub>F</sub> = 251 Hz, *C*F), 138.1 (br d, <sup>1</sup>*J*<sub>C</sub>-<sub>F</sub> = 252 Hz, *C*F), 140.1 (br d, <sup>1</sup>*J*<sub>C</sub>-<sub>F</sub> = 250 Hz, *C*F), 168.6 (*C*H). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>,  $\delta$ ): –163.7 – –163.6 (m, 2F), –161.1 (t, 1F, *J* = 21.5 Hz), –153.9 (dd, 2F, *J* = 7.2, 21.5 Hz). HRMS-ESI (*m*/*z*): [M+H]<sup>+</sup> Calcd for C<sub>13</sub>H<sub>7</sub>F<sub>5</sub>N: 272.04944; found: 272.04932.

The following compounds **1h–t** were prepared according to the above procedure.

(E)-2,3,4,5,6-Pentafluoro-N-(4-methylbenzylidene)aniline (1h).



<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>, δ): 2.44 (s, 3H), 7.31 (d, 2H, J = 8.3 Hz), 7.82 (d, 2H, J = 8.3 Hz), 8.58 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 21.7 (*C*H<sub>3</sub>), 127.0 (m, *C*), 129.4 (*C*H), 129.6 (*C*H), 132.6 (*C*), 137.9 (br d, <sup>1</sup> $J_{C-F} = 249$  Hz, *C*F), 140.0 (br d, <sup>1</sup> $J_{C-F} = 247$  Hz, *C*F), 143.7 (*C*), 168.4 (*C*H). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>, δ): -163.3 - -163.2 (m, 2F), -161.6 (t, 1F, J = 21.5 Hz), -154.1 (dd, 2F, J = 7.2, 21.5 Hz). HRMS-ESI (m/z): [M+H]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>9</sub>F<sub>5</sub>N: 286.06552; found: 286.06539.

(E)-2,3,4,5,6-Pentafluoro-N-(4-methoxybenzylidene)aniline (1i).



<sup>1</sup>H NMR (396 MHz, CDCl<sub>3</sub>,  $\delta$ ): 3.90 (s, 3H), 7.00 (d, 2H, J = 8.6 Hz), 7.88 (d, 2H, J = 8.6 Hz), 8.50 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 55.5 (CH<sub>3</sub>), 114.3 (CH), 127.2 (m, C), 128.1 (C), 131.3 (CH), 137.9 (br d, <sup>1</sup> $J_{C-F} = 248$  Hz, CF), 140.1 (br d, <sup>1</sup> $J_{C-F} = 238$  Hz, CF), 163.5 (C), 167.6 (CH). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>,  $\delta$ ): -164.1 – -163.9 (m, 2F), -162.0 (t, 1F, J = 21.5 Hz), -154.3 (dd, 2F, J = 5.4, 21.5 Hz). HRMS-ESI (m/z): [M+H]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>9</sub>F<sub>5</sub>NO: 302.05993; found: 302.05988.

(E)-N-(4-(Dimethylamino)benzylidene)-2,3,4,5,6-pentafluoroaniline (1j).



<sup>1</sup>H NMR (396 MHz, CDCl<sub>3</sub>, δ): 3.09 (s, 6H), 6.73 (d, 2H, J = 8.6 Hz), 7.78 (d, 2H, J = 9.1 Hz), 8.39 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 40.1 (*C*H<sub>3</sub>), 111.4 (*C*H), 123.1 (*C*), 127.9 (m, *C*), 131.2 (*C*H), 140.3 (br d, <sup>1</sup> $J_{C-F} = 244$  Hz, *C*F), 153.4 (*C*), 167.7 (*C*H). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>, δ): -164.6 - -164.4 (m, 2F), -163.4 (t, 1F, J = 21.5 Hz), -154.7 (dd, 2F, J = 5.4, 21.5 Hz). HRMS-ESI (*m*/*z*): [M+H]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>12</sub>F<sub>5</sub>N<sub>2</sub>: 315.09206; found: 315.09256.

(E)-2,3,4,5,6-Pentafluoro-N-(4-fluorobenzylidene)aniline (1k).



<sup>1</sup>H NMR (396 MHz, CDCl<sub>3</sub>, δ): 7.17–7.23 (m, 2H), 7.93–7.98 (m, 2H), 8.57 (s, 1H). <sup>13</sup>C NMR

(100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 116.2 (d,  ${}^{2}J_{C-F} = 23.0$  Hz, *C*H), 126.6 (m, *C*), 131.5 (d,  ${}^{3}J_{C-F} = 8.6$  Hz, *C*H), 138.0 (br d,  ${}^{1}J_{C-F} = 235$  Hz, *C*F), 138.1 (br d,  ${}^{1}J_{C-F} = 260$  Hz, *C*F), 140.1 (br d,  ${}^{1}J_{C-F} = 250$  Hz, *C*F), 165.6 (d,  ${}^{1}J_{C-F} = 258$  Hz, *C*F), 166.9 (*C*H).  ${}^{19}$ F NMR (373 MHz, CDCl<sub>3</sub>,  $\delta$ ): -163.7 – -163.5 (m, 2F), -160.9 (t, 1F, *J* = 21.5 Hz), -153.9 (dd, 2F, *J* = 5.4, 21.5 Hz), -105.75 (m, 1F). HRMS-ESI (*m*/*z*): [M+H]<sup>+</sup> Calcd for C<sub>13</sub>H<sub>6</sub>F<sub>6</sub>N: 290.04044; found: 290.04072.

(E)-N-(4-Chlorobenzylidene)-2,3,4,5,6-pentafluoroaniline (11).



<sup>1</sup>H NMR (396 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.48 (d, 2H, J = 8.6 Hz), 7.87 (d, 2H, J = 8.6 Hz), 8.57 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 126.4 (m, *C*), 129.3 (*C*H), 130.5 (*C*H), 133.6 (*C*), 137.9 (br d, <sup>1</sup> $J_{C-F}$ = 245 Hz, *C*F), 138.3 (br d, <sup>1</sup> $J_{C-F}$  = 249 Hz, *C*F), 139.1 (*C*), 140.1 (br d, <sup>1</sup> $J_{C-F}$  = 258 Hz, *C*F), 167.0 (*C*H). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>,  $\delta$ ): -163.6 – -163.5 (m, 2F), -160.6 (t, 1F, J = 21.5 Hz), -153.7 (dd, 2F, J = 5.4, 21.5 Hz). HRMS-ESI (m/z): [M+H]<sup>+</sup> Calcd for C<sub>13</sub>H<sub>6</sub>ClF<sub>5</sub>N: 306.01204; found: 306.01176.

(E)-N-(4-Bromobenzylidene)-2,3,4,5,6-pentafluoroaniline (1m).



<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.65 (br d, 2H, J = 8.6 Hz), 7.80 (br d, 2H, J = 8.3 Hz), 8.56 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 127.8 (*C*), 130.6 (*C*H), 132.3 (*C*H), 134.0 (*C*), 167.2 (*C*H). The carbon directly attached to the fluorine atom was not detected, probably due to C–F coupling. <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>,  $\delta$ ): –163.5 – –163.4 (m, 2F), –160.5 (t, 1F, J = 21.5 Hz), 153.6 (dd. 2F, J = 5.4, 21.5 Hz). HPMS ESL (m/z): [M+H]<sup>+</sup> Calcd for C H BrE N: 349.96038:

-153.6 (dd, 2F, J = 5.4, 21.5 Hz). HRMS-ESI (m/z):  $[M+H]^+$  Calcd for  $C_{13}H_6BrF_5N$ : 349.96038; found: 349.96019.

### (E)-2,3,4,5,6-Pentafluoro-N-(4-(trifluoromethyl)benzylidene)aniline (1n).



<sup>1</sup>H NMR (396 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.77 (d, 2H, *J* = 8.2 Hz), 8.06 (d, 2H, *J* = 8.2 Hz), 8.68 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 123.6 (q, <sup>1</sup>*J*<sub>C-F</sub> = 282 Hz, *C*F<sub>3</sub>), 125.9 (d, <sup>3</sup>*J*<sub>C-F</sub> = 3.8 Hz, *C*H), 129.5 (*C*H), 134.2 (q, <sup>2</sup>*J*<sub>C-F</sub> = 36.4 Hz, *C*H), 138.0 (br d, <sup>1</sup>*J*<sub>C-F</sub> = 256 Hz, *C*F), 138.1 (*C*), 138.7 (br d, <sup>1</sup>*J*<sub>C-F</sub> = 262 Hz, *C*F), 140.1 (br d, <sup>1</sup>*J*<sub>C-F</sub> = 263 Hz, *C*F), 166.9 (*C*H). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>,  $\delta$ ): – 163.3 - -163.2 (m, 2F), -159.8 (t, 1F, J = 21.5 Hz), -153.3 (dd, 2F, J = 5.4, 21.5 Hz), -63.6 (s, 1F). HRMS-ESI (m/z):  $[M+H]^+$  Calcd for  $C_{14}H_6F_8N$ : 340.03735; found: 340.03670.

(E)-2,3,4,5,6-Pentafluoro-N-(3-methylbenzylidene)aniline (10).



<sup>1</sup>H NMR (396 MHz, CDCl<sub>3</sub>, δ): 2.44 (s, 3H), 7.38–7.42 (m, 2H), 7.70 (br d, 1H, J = 5.9 Hz); 7.78 (s, 1H); 8.55 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 21.3 (CH<sub>3</sub>), 127.0 (CH), 128.8 (CH), 129.5 (CH), 133.8 (CH), 135.1 (C), 137.9 (br d, <sup>1</sup> $J_{C-F} = 249$  Hz, CF), 138.1 (br d, <sup>1</sup> $J_{C-F} = 249$  Hz, CF), 138.8 (C), 140.0 (br d, <sup>1</sup> $J_{C-F} = 237$  Hz, CF), 168.9 (CH). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>, δ): –163.8 – – 163.6 (m, 2F), –161.3 (t, 1F, J = 21.5 Hz), –154.0 (dd, 2F, J = 5.4, 21.5 Hz). HRMS-ESI (m/z): [M+H]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>9</sub>F<sub>5</sub>N: 286.06528; found: 286.06497.

#### (E)-2,3,4,5,6-Pentafluoro-N-(3-methoxybenzylidene)aniline (1p).



<sup>1</sup>H NMR (396 MHz, CDCl<sub>3</sub>,  $\delta$ ): 3.89 (s, 3H), 7.10–7.13 (m, 1H), 7.39–7.45 (m, 2H), 7.53 (m, 1H), 8.55 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 55.4 (*C*H<sub>3</sub>), 112.1 (*C*H), 119.8 (*C*H), 123.0 (*C*H), 126.7 (m, *C*), 129.9 (*C*H), 136.5 (*C*), 137.9 (br d, <sup>1</sup>*J*<sub>C-F</sub> = 241 Hz, *C*F), 140.0 (br d, <sup>1</sup>*J*<sub>C-F</sub> = 244 Hz, *C*F), 160.1 (*C*), 168.5 (*C*H). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>,  $\delta$ ): –163.7 – –163.6 (m, 2F), –161.1 (t, 1F, *J* = 21.5 Hz), –153.8 (dd, 2F, *J* = 5.4, 21.5 Hz). HRMS-ESI (*m*/*z*): [M+H]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>9</sub>F<sub>5</sub>NO: 302.06013; found: 302.05988.

(E)-N-(3-Chlorobenzylidene)-2,3,4,5,6-pentafluoroaniline (1q).



<sup>1</sup>H NMR (396 MHz, CDCl<sub>3</sub>, δ): 7.45 (t, 1H, J = 7.7 Hz), 7.54 (br d, 1H, J = 8.2 Hz), 7.78 (d, 1H, J = 7.7 Hz), 7.96 (s, 1H); 8.57 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 126.1 (m, *C*), 127.7 (*C*H), 128.7 (*C*H), 130.2 (*C*H), 132.7 (*C*H), 135.2 (*C*), 136.8 (*C*), 138.0 (br d, <sup>1</sup> $J_{C-F} = 241$  Hz, *C*F), 138.4 (br d, <sup>1</sup> $J_{C-F} = 253$  Hz, *C*F), 140.1 (br d, <sup>1</sup> $J_{C-F} = 242$  Hz, *C*F), 166.9 (*C*H). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>, δ): -163.5 - -163.3 (m, 2F), -160.3 (t, 1F, J = 21.5 Hz), -153.5 (dd, 2F, J = 5.4, 21.5 Hz). HRMS-ESI (m/z): [M+H]<sup>+</sup> Calcd for C<sub>13</sub>H<sub>6</sub>ClF<sub>5</sub>N: 306.01061; found: 306.01034.

(E)-2,3,4,5,6-Pentafluoro-N-(2-methylbenzylidene)aniline (1r).



<sup>1</sup>H NMR (396 MHz, CDCl<sub>3</sub>, δ): 2.59 (s, 3H), 7.27 (d, 1H, J = 7.7 Hz), 7.33 (d, 1H, J = 7.7 Hz), 7.43 (d, 1H, J = 7.5 Hz), 8.08 (d, 1H, J = 7.7 Hz), 8.88 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 19.4 (CH<sub>3</sub>), 126.5 (CH), 127.3 (m, C), 128.5 (CH), 131.2 (CH), 132.4 (CH), 133.1 (C), 137.9 (br d, <sup>1</sup> $J_{C-F}$  = 249 Hz, CF), 139.6 (C), 140.0 (br d, <sup>1</sup> $J_{C-F}$  = 250 Hz, CF), 167.6 (CH). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>, δ): -163.9 - -163.7 (m, 2F), -161.5 (t, 1F, J = 21.5 Hz), -154.3 (dd, 2F, J = 5.4, 21.5 Hz). HRMS-ESI (m/z): [M+H]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>9</sub>F<sub>5</sub>N: 286.06525; found: 286.06497.

(E)-2,3,4,5,6-Pentafluoro-N-(2-fluorobenzylidene)aniline (1s).



<sup>1</sup>H NMR (396 MHz, CDCl<sub>3</sub>, δ): 7.16 (t, 1H, J = 8.8 Hz), 7.29 (t, 1H, J = 7.3 Hz), 7.52–7.58 (m, 1H), 8.21 (t, 1H, J = 7.1 Hz), 8.91 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 116.0 (d, <sup>2</sup> $J_{C-F} = 21.0$  Hz, CH), 123.0 (d, <sup>2</sup> $J_{C-F} = 9.6$  Hz, C), 124.7 (d, <sup>3</sup> $J_{C-F} = 3.8$  Hz, CH), 126.7 (m, C), 127.9 (CH), 134.7 (d, <sup>3</sup> $J_{C-F} = 8.6$  Hz, CH), 137.9 (br d, <sup>1</sup> $J_{C-F} = 254$  Hz, CF), 138.3 (br d, <sup>1</sup> $J_{C-F} = 241$  Hz, CF), 140.1 (br d, <sup>1</sup> $J_{C-F} = 255$  Hz, CF), 161.9 (CH), 163.2 (d, <sup>1</sup> $J_{C-F} = 257$  Hz, CF). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>, δ): -163.6 - -163.4 (m, 2F), -160.5 (t, 1F, J = 21.5 Hz), -153.6 (dd, 2F, J = 5.4, 21.5 Hz), -120.6 (m, 1F). HRMS-ESI (m/z): [M+H]<sup>+</sup> Calcd for C<sub>13</sub>H<sub>6</sub>F<sub>6</sub>N: 290.04013; found: 290.03989.

(E)-2,3,4,5,6-Pentafluoro-N-(2-methoxybenzylidene)aniline (1t).



<sup>1</sup>H NMR (396 MHz, CDCl<sub>3</sub>, δ): 3.90 (s, 3H), 6.97 (d, 1H, J = 8.2 Hz), 7.16 (m, 1H), 8.18 (dd, 1H, J = 1.4, 7.7 Hz), 9.02 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 55.6 (CH<sub>3</sub>), 111.2 (CH), 120.9 (CH), 123.7 (C), 127.7 (CH), 134.4 (CH), 137.8 (br d, <sup>1</sup> $J_{C-F} = 251$  Hz, CF), 140.0 (br d, <sup>1</sup> $J_{C-F} = 256$  Hz, CF), 160.0 (C), 164.9 (CH). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>, δ): -164.1 – -164.0 (m, 2F), -162.0 (t, 1F, J = 21.5 Hz), -154.2 (dd, 2F, J = 5.4, 21.5 Hz). HRMS-ESI (m/z): [M+H]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>9</sub>F<sub>5</sub>NO: 302.05994; found: 302.05988.

#### 2.2. A General Procedure for [Ir(OMe)(cod)]<sub>2</sub>-Catalyzed C-H Borylation.

A general procedure for *ortho*-selective C–H borylation of aromatic aldimines :  $[Ir(OMe)(cod)]_2$ (3.3 mg, 0.005 mmol, 1.5 mol%), tris(pentafluorophenyl)phosphine (10.6 mg, 0.02 mmol, 6.0 mol%) and B<sub>2</sub>pin<sub>2</sub> (82.5 mg, 0.325 mmol, 1.0 equiv) were placed in an oven-dried two neck flask. The flask was connected to a vacuum/nitrogen manifold through a rubber tube. It was evacuated and then backfilled with nitrogen. This cycle was repeated three times. Mesitylene (3 mL) was added in the flask through the rubber septum with a syringe, and stirred at room temperature for 10 min. Then, substrate **1** (1.625 mmol, 5.0 equiv) and 2-norbornene (30.6 mg, 0.325 mmol, 1.0 equiv) were added to the reaction mixture, and stirred at 120 °C. After the reaction was complete, the reaction mixture was concentrated and purified by kugelrohr distillation to give the the corresponding arylboronate **2**.

### <Analytical Data>

(E) - 2, 3, 4, 5, 6 - Pentafluoro - N - (2 - (4, 4, 5, 5 - tetramethyl - 1, 3, 2 - dioxaborolan - 2 - yl) benzylidene) anilin e (2a).



<sup>1</sup>H NMR (396 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.35 (s, 12H), 7.51–7.59 (m, 2H), 7.92 (dd, 1H, J = 1.4, 7.3 Hz), 8.30 (m, 1H), 9.40 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 24.8 (*C*H<sub>3</sub>), 84.3 (*C*), 127.0 (*C*H), 127.1 (m, *C*), 131.2 (*C*H), 131.4 (*C*H), 136.0 (*C*H), 137.9 (br d, <sup>1</sup> $J_{C-F} = 245$  Hz, *C*F), 140.2 (br d, <sup>1</sup> $J_{C-F} = 248$  Hz, *C*F), 140.5 (*C*), 170.4 (*C*H). The carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation.<sup>4</sup> <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>,  $\delta$ ): –163.5 – –163.3 (m, 2F), –161.6 (t, 1F, J = 21.5 Hz), –153.9 (dd, 2F, J = 7.3, 21.5 Hz). HRMS-ESI (m/z): [M]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>17</sub>BF<sub>5</sub>NO<sub>2</sub>: 397.13870; found: 397.13816.

(*E*)-2,3,4,5,6-Pentafluoro-*N*-(4-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzylid ene)aniline (2h).



<sup>1</sup>H NMR (396 MHz, CDCl<sub>3</sub>, δ): 1.35 (s, 12H), 2.43 (s, 3H), 7.38 (d, 1H, J = 7.2 Hz), 7.72 (s, 1H), 8.20 (d, 1H, J = 8.1 Hz), 9.35 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 21.5 (*C*H<sub>3</sub>), 24.8 (*C*H<sub>3</sub>), 84.2 (*C*), 127.3 (*C*H), 127.3 (m, *C*), 132.0 (*C*H), 136.5 (*C*H), 137.8 (br d, <sup>1</sup> $J_{C-F} = 261$  Hz, *C*F), 138.0 (*C*), 140.3 (br d, <sup>1</sup> $J_{C-F} = 237$  Hz, *C*F), 142.0 (*C*), 170.2 (*C*H). The carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation.<sup>4 19</sup>F NMR (373 MHz, CDCl<sub>3</sub>,  $\delta$ ): -164.3 - -164.1 (m, 2F), -162.0 (t, 1F, *J* = 21.5 Hz), -154.0 (dd, 2F, *J* = 5.4, 21.5 Hz). HRMS-ESI (*m*/*z*): [M]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>19</sub>BF<sub>5</sub>NO<sub>2</sub>: 411.15456; found: 411.15381.

(*E*)-2,3,4,5,6-Pentafluoro-*N*-(4-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyli dene)aniline (2i).



<sup>1</sup>H NMR (396 MHz, CDCl<sub>3</sub>, δ): 1.35 (s, 12H), 3.90 (s, 3H), 7.07 (dd, 1H, J = 2.7, 9.0 Hz), 7.37 (d, 1H, J = 2.7 Hz), 8.27 (d, 1H, J = 9.0 Hz), 9.29 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 24.8 (CH<sub>3</sub>), 55.5 (CH<sub>3</sub>), 84.3 (C), 117.3 (CH), 120.0 (CH), 127.4 (m, C), 129.2 (CH), 133.4 (C), 137.8 (br d, <sup>1</sup> $J_{C-F} = 245$  Hz, *C*F), 140.3 (br d, <sup>1</sup> $J_{C-F} = 249$  Hz, *C*F), 162.2 (*C*), 169.4 (*C*H). The carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation.<sup>4</sup> <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>, δ): -164.3 - -164.1 (m, 2F), -162.4 (t, 1F, J = 21.5 Hz), -154.2 (dd, 2F, J = 5.4, 21.5 Hz). HRMS-ESI (m/z): [M]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>19</sub>BF<sub>5</sub>NO<sub>3</sub>: 427.14945; found: 427.14872.

(*E*)-*N*-(4-(Dimethylamino)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzylidene)-2,3,4,5 ,6-pentafluoroaniline (2j).



<sup>1</sup>H NMR (396 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.34 (s, 12H), 3.09 (s, 3H), 6.82 (dd, 1H, J = 2.7, 9.0 Hz), 7.10 (d, 1H, J = 2.7 Hz), 8.19 (d, 1H, J = 9.1 Hz), 9.18 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 24.8 (*C*H<sub>3</sub>), 40.1 (*C*H<sub>3</sub>), 84.0 (*C*), 113.8 (*C*H), 117.8 (*C*H), 128.2 (*C*), 129.0 (*C*H), 140.5 (br d, <sup>1</sup> $J_{C-F} = 255$  Hz, *C*F), 152.2 (*C*), 169.40 (*C*H). The carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation.<sup>4</sup> <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>,  $\delta$ ): -164.9 – -164.8 (m, 2F), -163.7 (t, 1F, J = 21.5 Hz), -154.6 (d, 2F, J = 21.5 Hz). HRMS-ESI (m/z): [M]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>22</sub>BF<sub>5</sub>N<sub>2</sub>O<sub>3</sub>: 440.18102; found: 440.18036.

(*E*)-2,3,4,5,6-Pentafluoro-*N*-(4-fluoro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzylide ne)aniline (2k).



<sup>1</sup>H NMR (396 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.36 (s, 12H), 7.22–7.27 (m, 1H), 7.58 (dd, 1H, J = 2.7, 9.1 Hz),

8.33 (dd, 1H, J = 5.5, 8.6 Hz), 9.35 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 24.8 (*C*H<sub>3</sub>), 84.6 (*C*), 118.5 (d, <sup>2</sup> $J_{C-F} = 22.0$  Hz, *C*H), 122.3 (d, <sup>2</sup> $J_{C-F} = 21.0$  Hz, *C*H), 126.8 (m, *C*), 129.7 (d, <sup>3</sup> $J_{C-F} = 8.6$  Hz, *C*H), 138.1 (br d, <sup>1</sup> $J_{C-F} = 266$  Hz, *C*F), 140.3 (br d, <sup>1</sup> $J_{C-F} = 253$  Hz, *C*F), 164.7 (d, <sup>1</sup> $J_{C-F} = 257$  Hz, *C*H), 168.9 (*C*H). The carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation.<sup>4</sup> <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>,  $\delta$ ): –164.1 – –163.9 (m, 2F), –161.5 (t, 1F, J = 21.5 Hz), –153.9 (dd, 2F, J = 7.1, 21.5 Hz), –108.2 (m, 1F). HRMS-ESI (*m*/*z*): [M]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>16</sub>BF<sub>6</sub>NO<sub>2</sub>: 415.12969; found: 415.12874.

(*E*)-*N*-(4-Chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzylidene)-2,3,4,5,6-pentafl uoroaniline (2l).



<sup>1</sup>H NMR (396 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.36 (s, 12H), 7.53 (dd, 1H, *J* = 2.3, 8.2 Hz), 7.88 (d, 1H, *J* = 1.8 Hz), 8.26 (d, 1H, *J* = 8.6 Hz), 9.37 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 24.8 (CH<sub>3</sub>), 84.7 (*C*), 128.5 (*C*H), 131.4 (*C*H), 135.8 (*C*H), 138.9 (*C*), 169.0 (*C*H). The carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation.<sup>4</sup> Additionally, the carbon directly attached to the fluorine atom was not detected, probably due to C–F coupling. <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>,  $\delta$ ): –163.3 – –163.2 (m, 2F), –161.1 (t, 1F, *J* = 21.5 Hz), –153.7 (dd, 2F, *J* = 7.2, 21.5 Hz). HRMS-ESI (*m*/*z*): [M]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>16</sub>BClF<sub>5</sub>NO<sub>2</sub>: 431.10011; found: 431.09919.

(*E*)-*N*-(4-Bromo-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzylidene)-2,3,4,5,6-pentafl uoroaniline (2m).



<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.36 (s, 12H), 7.69 (dd, 1H, *J* = 2.2, 8.6 Hz), 8.05 (d, 1H, *J* = 2.2 Hz), 8.18 (d, 1H, *J* = 8.6 Hz), 9.37 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 24.8 (CH<sub>3</sub>), 84.7 (C), 126.9 (C), 128.5 (CH), 134.3 (CH), 138.8 (CH), 139.3 (C), 169.1 (CH). The carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation.<sup>4</sup> Additionally, the carbon directly attached to the fluorine atom was not detected, probably due to C–F coupling. <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>,  $\delta$ ): –163.9 – –163.8 (m, 2F), –161.0 (t, 1F, *J* = 21.5 Hz), –153.6 (dd, 2F, *J* = 5.4, 21.5 Hz). HRMS-ESI (*m*/*z*): [M]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>16</sub>BBrF<sub>5</sub>NO<sub>2</sub>: 475.04945; found: 475.04867.

(*E*)-2,3,4,5,6-Pentafluoro-*N*-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(trifluoromethy l)benzylidene)aniline (2n).



<sup>1</sup>H NMR (396 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.37 (s, 12H), 7.80 (d, 1H, *J* = 8.2 Hz), 8.18 (s, 1H), 8.43 (d, 1H, *J* = 8.2 Hz), 9.48 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 24.8 (*C*H<sub>3</sub>), 84.8 (*C*), 123.8 (q, <sup>1</sup>*J*<sub>C-F</sub> = 275 Hz, *C*F<sub>3</sub>), 126.4 (m, *C*), 127.3 (*C*H), 127.8 (*C*H), 132.9 (*C*H), 137.9 (br d, <sup>1</sup>*J*<sub>C-F</sub> = 248 Hz, *C*F), 140.3 (br d, <sup>1</sup>*J*<sub>C-F</sub> = 236 Hz, *C*F), 143.6 (*C*), 168.9 (*C*H). The carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation. <sup>4 19</sup>F NMR (373 MHz, CDCl<sub>3</sub>,  $\delta$ ): –163.7 – –163.6 (m, 2F), –160.3 (t, 1F, *J* = 21.5 Hz), –153.3 (dd, 2F, *J* = 7.2, 21.5 Hz), –63.5 (s, 3F). HRMS-ESI (*m*/*z*): [M]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>16</sub>BF<sub>8</sub>NO<sub>2</sub>: 465.12662; found: 465.12554.

(*E*)-2,3,4,5,6-Pentafluoro-*N*-(5-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzylid ene)aniline (20).



<sup>1</sup>H NMR (396 MHz, CDCl<sub>3</sub>, δ): 1.37 (s, 12H), 2.45 (s, 3H), 7.36 (d, 1H, J = 7.2 Hz), 7.83 (d, 1H, J = 7.7 Hz), 8.13 (s, 1H), 9.41 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 21.5 (CH<sub>3</sub>), 24.8 (CH<sub>3</sub>), 84.1 (C), 127.2 (CH), 127.3 (m, C), 132.4 (CH), 136.3 (CH), 138.0 (br d, <sup>1</sup> $J_{C-F} = 263$  Hz, CF), 140.12 (br d, <sup>1</sup> $J_{C-F} = 244$  Hz, CF), 140.5 (C), 141.6 (C), 170.8 (CH). The carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation.<sup>4</sup> <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>, δ): –163.5 – –163.3 (m, 2F), –161.8 (t, 1F, J = 21.5 Hz), –154.0 (dd, 2F, J = 5.4, 21.5 Hz). HRMS-ESI (m/z): [M]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>19</sub>BF<sub>5</sub>NO<sub>2</sub>: 411.15469; found: 411.15381.

# (*E*)-2,3,4,5,6-Pentafluoro-*N*-(5-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyli dene)aniline (2p).



<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.34 (s, 12H), 3.92 (s, 3H), 7.08 (dd, 1H, *J* = 2.9, 8.3 Hz), 7.86–7.89 (m, 2H), 9.47 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 24.8 (*C*H<sub>3</sub>), 55.4 (*C*H<sub>3</sub>), 84.0 (*C*), 110.0 (*C*H), 118.6 (*C*H), 138.0 (*C*H), 142.7 (*C*), 162.0 (*C*), 170.3 (*C*H). The carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation.<sup>4</sup> Additionally, the carbon directly attached to the fluorine atom was not detected, probably due to C–F coupling. <sup>19</sup>F NMR (373 MHz,

CDCl<sub>3</sub>,  $\delta$ ): -164.1 - -164.0 (m, 2F), -161.6 (t, 1F, *J* = 21.5 Hz), -153.8 (dd, 2F, *J* = 5.4, 21.5 Hz). HRMS-ESI (*m*/*z*): [M]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>19</sub>BF<sub>5</sub>NO<sub>3</sub>: 427.14939; found: 427.14872.

(*E*)-*N*-(5-Chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzylidene)-2,3,4,5,6-pentafl uoroaniline (2q).



<sup>1</sup>H NMR (396 MHz, CDCl<sub>3</sub>, δ): 1.35 (s, 12H), 7.49 (dd, 1H, J = 2.2, 8.2 Hz), 7.87 (d, 1H, J = 7.9 Hz), 8.31 (d, 1H, J = 1.8 Hz), 9.42 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 24.8 (*C*H<sub>3</sub>), 84.5 (*C*), 126.6 (*C*H), 131.3 (*C*H), 137.6 (*C*H), 138.0 (*C*), 142.3 (*C*), 168.9 (*C*H). The carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation.<sup>4</sup> Additionally, the carbon directly attached to the fluorine atom was not detected, probably due to C–F coupling. <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>, δ): -163.8 – -163.7 (m, 2F), -160.8 (t, 1F, J = 21.5 Hz), -153.5 (dd, 2F, J = 5.4, 21.5 Hz). HRMS-ESI (m/z): [M]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>16</sub>BClF<sub>5</sub>NO<sub>2</sub>: 431.10007; found: 431.09919.

(*E*)-2,3,4,5,6-Pentafluoro-*N*-(2-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzylid ene)aniline (2r).



<sup>1</sup>H NMR (396 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.29 (s, 12H), 2.58 (s, 3H), 7.29 (d, 1H, *J* = 7.3 Hz), 7.39 (t, 1H, *J* = 7.2 Hz), 7.54 (d, 1H, *J* = 7.2 Hz), 9.07 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 20.5 (*C*H<sub>3</sub>), 24.7 (*C*H<sub>3</sub>), 83.8 (*C*), 127.1 (*C*H), 131.6 (*C*H), 132.0 (*C*H), 132.8 (*C*H), 137.2 (*C*), 137.9 (br d, <sup>1</sup>*J*<sub>C-F</sub> = 263 Hz, *C*F), 139.0 (*C*), 139.8 (br d, <sup>1</sup>*J*<sub>C-F</sub> = 254 Hz, *C*F), 169.8 (*C*H). The carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation.<sup>4</sup> <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>,  $\delta$ ): -163.7 - -163.6 (m, 2F), -161.4 (t, 1F, *J* = 21.5 Hz), -153.5 (dd, 2F, *J* = 5.4, 21.5 Hz). HRMS-ESI (*m*/*z*): [M]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>19</sub>BF<sub>5</sub>NO<sub>2</sub>: 411.15451; found: 411.15381.

(*E*)-2,3,4,5,6-Pentafluoro-*N*-(2-fluoro-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzylide ne)aniline (2s).



<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>, δ): 1.31 (s, 12H), 7.14–7.19 (m, 1H), 7.38 (d, 1H, J = 7.2 Hz), 7.49–7.55 (m, 1H), 8.94 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 24.7 (*C*H<sub>3</sub>), 84.2 (*C*), 117.1 (d, <sup>2</sup> $J_{C-F} = 10.4$  CDCl<sub>3</sub>, δ): 24.7 (*C*H<sub>3</sub>), 84.2 (*C*), 117.1 (d, <sup>2</sup> $J_{C-F} = 10.4$  CDCl<sub>3</sub>, δ): 24.7 (*C*H<sub>3</sub>), 84.2 (*C*), 117.1 (d, <sup>2</sup> $J_{C-F} = 10.4$  CDCl<sub>3</sub>, δ): 24.7 (*C*H<sub>3</sub>), 84.2 (*C*), 117.1 (d, <sup>2</sup> $J_{C-F} = 10.4$  CDCl<sub>3</sub>, δ): 24.7 (*C*H<sub>3</sub>), 84.2 (*C*), 117.1 (d, <sup>2</sup> $J_{C-F} = 10.4$  CDCl<sub>3</sub>, δ): 24.7 (*C*H<sub>3</sub>), 84.2 (*C*), 117.1 (d, <sup>2</sup> $J_{C-F} = 10.4$  CDCl<sub>3</sub>, δ): 24.7 (*C*H<sub>3</sub>), 84.2 (*C*), 117.1 (d, <sup>2</sup> $J_{C-F} = 10.4$  CDCl<sub>3</sub>, δ): 24.7 (*C*H<sub>3</sub>), 84.2 (*C*), 117.1 (d, <sup>2</sup> $J_{C-F} = 10.4$  CDCl<sub>3</sub>, δ): 24.7 (*C*H<sub>3</sub>), 84.2 (*C*), 117.1 (d, <sup>2</sup> $J_{C-F} = 10.4$  CDCl<sub>3</sub>, δ): 24.7 (*C*H<sub>3</sub>), 84.2 (*C*), 117.1 (d, <sup>2</sup> $J_{C-F} = 10.4$  CDCl<sub>3</sub>, δ): 24.7 (*C*H<sub>3</sub>), 84.2 (*C*), 117.1 (d, <sup>2</sup> $J_{C-F} = 10.4$  CDCl<sub>3</sub>, δ): 24.7 (*C*H<sub>3</sub>), 84.2 (*C*), 117.1 (d, <sup>2</sup> $J_{C-F} = 10.4$  CDCl<sub>3</sub>, δ): 24.7 (*C*H<sub>3</sub>), 84.2 (*C*), 117.1 (d, <sup>2</sup> $J_{C-F} = 10.4$  CDCl<sub>3</sub>, δ): 24.7 (*C*H<sub>3</sub>), 84.2 (*C*), 117.1 (d, <sup>2</sup> $J_{C-F} = 10.4$  CDCl<sub>3</sub>, δ): 24.7 (*C*H<sub>3</sub>), 84.2 (*C*), 117.1 (d, <sup>2</sup> $J_{C-F} = 10.4$  CDCl<sub>3</sub>, δ): 24.7 (*C*H<sub>3</sub>), 84.2 (*C*), 117.1 (d, <sup>2</sup> $J_{C-F} = 10.4$  CDCl<sub>3</sub>, δ): 24.7 (*C*H<sub>3</sub>), 84.2 (*C*), 117.1 (d, <sup>2</sup> $J_{C-F} = 10.4$  CDCl<sub>3</sub>, δ): 24.7 (*C*H<sub>3</sub>), 84.2 (*C*), 117.1 (d, <sup>2</sup> $J_{C-F} = 10.4$  CDCl<sub>3</sub>, δ): 24.7 (*C*H<sub>3</sub>), 84.2 (*C*), 117.1 (d, <sup>2</sup> $J_{C-F} = 10.4$  CDCl<sub>3</sub>, δ): 24.7 (*C*H<sub>3</sub>), 84.2 (*C*), 117.1 (d, <sup>2</sup> $J_{C-F} = 10.4$  CDCl<sub>3</sub>, δ): 24.7 (*C*H<sub>3</sub>), 84.2 (*C*), 117.1 (d, <sup>2</sup> $J_{C-F} = 10.4$  CDCl<sub>3</sub>, δ): 24.7 (*C*H<sub>3</sub>), 84.2 (*C*), 117.1 (d, <sup>2</sup> $J_{C-F} = 10.4$  CDCl<sub>3</sub>, δ): 24.7 (*C*H<sub>3</sub>), 84.2 (*C*), 117.1 (d, <sup>2</sup> $J_{C-F} = 10.4$  CDCl<sub>3</sub>, δ): 24.7 (*C*H<sub>3</sub>), 84.2 (*C*), 117.1 (d, <sup>2</sup> $J_{C-F} = 10.4$  CDCl<sub>3</sub>, δ): 24.7 (*C*H<sub>3</sub>), 84.2 (*C*), 117.1 (d, <sup>2</sup> $J_{C-F} = 10.4$  CDCl<sub>3</sub>, δ): 24.7 (*C*H<sub>3</sub>), 84.2 (*C*), 117.1 (d, <sup>2</sup> $J_{C-F} = 10.4$  CDCl<sub>3</sub>, δ): 24.7 (*C*H<sub>3</sub>), 84.2 (*C*), 117.1 (d,

21.0 Hz, *C*H), 129.3 (*C*H), 133.9 (d,  ${}^{3}J_{C-F} = 8.6$  Hz, *C*H), 164.2 (*C*H). The carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation.<sup>4</sup> Additionally, the carbon directly attached to the fluorine atom was not detected, probably due to C–F coupling. <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>,  $\delta$ ): –163.3 – –163.2 (m, 2F), –160.4 (t, 1F, *J* = 21.5 Hz), –153.2 (dd, 2F, *J* = 5.4, 21.5 Hz), –118.9 (m, 1F). HRMS-ESI (*m*/*z*): [M]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>16</sub>BF<sub>6</sub>NO<sub>2</sub>: 415.12961; found: 415.12874.



#### 2.3. Transformation of 2a to 5.

Suzuki-Miyaura coupling reaction with 4-bromobenzene was carried out as follows: The reaction was carried out under nitrogen atmosphere. A dried 25 mL-flask quipped with a magnetic stirring bar was charged with  $Pd(Cl)_2(dppf)$  (8.0 mg, 0.000975 mmol, 3.0 mol%), K<sub>3</sub>PO<sub>4</sub> (207.0 mg, 0.975 mmol, 3.0 equiv) and **2a** (129.1 mg, 0.325 mmol, 1.0 equiv). methyl 4-bromobenzoate (69.9 mg, 0.325 mmol, 1.0 equiv) and mesitylene (3 mL) was added in the flask under nitrogen atmosphere, and the reaction mixture was stirred for 24 h at 120 °C. After the reaction was completed, the crude product was purified by a silica gel packed flash chromatography column, using ethyl acetate/hexane as the eluent. The product **4** was obtained 111.8 mg, 85% yield. The reaction was carried out in air. A dried 25 mL-flask quippied with a magnetic stirring bar was charged with compound **4** (34.7 mg, 0.1 mmol, 1.0 equiv), TsOH  $\cdot$  H<sub>2</sub>O (86.1 mg, 0.5 mmol, 5.0 equiv), H<sub>2</sub>O (6 mL) and acetone (6 mL). The reaction mixture was stirred for 1.5 h at 50 °C. After the reaction was completed, the crude product was purified by a silica gel packed flash chromatography column, using acetone/hexane as the eluent. The product **5** was obtained 24.2 mg, >99% yield.

<Analytical Data>

(E)-Methyl 2'-(((perfluorophenyl)imino)methyl)-(1,1'-biphenyl)-4-carboxylate (4).



<sup>1</sup>H NMR (392 MHz, CDCl<sub>3</sub>, δ): 3.96 (s, 3H), 7.44–7.47 (m, 3H), 7.56 (br t, 1H, J = 7.6 Hz), 7.63 (dt, 1H, J = 1.5, 7.5 Hz), 8.14 (br d, 2H, J = 7.7 Hz), 8.38 (br d, 1H, J = 7.4 Hz), 8.49 (s, 1H). <sup>13</sup>C NMR (99 MHz, CDCl<sub>3</sub>, δ): 52.3 (CH<sub>3</sub>), 126.9 (m, *C*), 127.6 (CH), 128.5 (CH), 129.6 (CH), 129.7 (*C*), 130.0 (CH), 130.2 (CH), 132.3 (CH), 132.6 (*C*), 137.8 (br d, <sup>1</sup> $J_{C-F} = 251$  Hz, *C*F), 138.0 (br d, <sup>1</sup> $J_{C-F} = 251$  Hz, *C*F), 139.9 (br d, <sup>1</sup> $J_{C-F} = 248$  Hz, *C*F), 143.2 (*C*), 143.6 (*C*), 166.7 (*C*), 167.5 (CH). <sup>19</sup>F NMR (373 MHz, CDCl<sub>3</sub>, δ): -163.6 – -163.5 (m, 2F), -161.1 (t, 1F, J = 21.5 Hz), -154.0 (dd, 2F, J = 5.4, 21.5 Hz). HRMS-ESI (m/z): [M+H]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>13</sub>O<sub>2</sub>NF<sub>5</sub>: 406.08668; found: 406.08610.

Methyl 2'-formyl-(1,1'-biphenyl)-4-carboxylate (5).



Analytical data of compound **5** was reported in the reference.<sup>5</sup>

### 3. References

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