#### 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  $N_2$  bubbling, and further dried over molecular sieves (MS 4Å). NMR spectra were recorded on JEOL JNM-ECX400P and JNM-ECS400 spectrometer (<sup>1</sup>H: 400 MHz and <sup>13</sup>C: 100 MHz). Tetramethylsilane (<sup>1</sup>H) and CDCl<sub>3</sub> (<sup>13</sup>C) were employed as external standards, respectively. [Ir(OMe)(cod)]<sub>2</sub> was synthesized according to the reported procedure.<sup>1</sup> Tetradecane was used as an internal standard to determine GC yield. GLC analyses were conducted with a Shimadzu GC-2014 or GC-2025 equipped with ULBON HR-1 glass capillary column (Shinwa Chemical Industries) and a FID detector. Elemental analyses and high-resolution mass spectra were recorded at the Center for Instrumental Analysis, Hokkaido University.

#### 2. General Experimental Procedures.

# A Representative Procedure for the Iridium(I)-Catalyzed Vinylic C–H Borylation of 1a (Table 1).

 $[Ir(OMe)(cod)]_2$  (4.97 mg, 0.0075 mmol) and bis(pinacolato)diboron (B<sub>2</sub>pin<sub>2</sub>) (**2**) (140 mg, 0.55 mmol), AsPh<sub>3</sub>(triphenylarsine) (9.19 mg, 0.030 mmol) 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. Octane (3 mL) was added in the flask through the rubber septum, and stirred at room temperature for 10 min. Then, **1a** (70.1 mg, 0.5 mmol) was added to the reaction mixture, and stirred at 80 or 120 °C. After the reaction was complete, the reaction mixture was concentrated and purified by flash column chromatography (SiO<sub>2</sub>, EtOAc/hexane, 1:99–5:95) to give the corresponding alkenylboronate **3a** as a colorless oil.

# The Procedure for One-pot Synthesis of 4.



 $[Ir(OMe)(cod)]_2$  (49.7 mg, 0.15 mmol) and  $B_2pin_2$  (2) (1.40 g, 5.5 mmol), AsPh<sub>3</sub> (91.9 mg, 0.3 mmol) 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. Octane (15 mL) was added in the flask through the rubber septum *via* a syringe, and stirred at room temperature for 10 min. Then, **1a** (701 mg, 5.0 mmol) was added to the reaction

mixture, and stirred at 80 °C for 16 h. The reaction mixture was cooled to r.t., and H<sub>2</sub>O (1.5 ml) was added and stirred for 10 min. Without purification, PdCl<sub>2</sub>(dppf) (92.0 mg, 0.125 mmol), K<sub>3</sub>PO<sub>4</sub> (1.59 g, 7.50 mmol), and 2-bromonaphthalene (518 mg, 2.50 mmol) were added to the reaction mixture and stirred at 80 °C for 8 h. After the reaction was complete, the reaction mixture was cooled to r.t. and extracted with EtOAc three times. The combined organic layer was dried over MgSO<sub>4</sub>. After filtration, the solvents were removed by evaporation. The crude product was purified by flash column chromatography to obtain 4 (271.3 mg, 47%(78% GC yield)) as a syrup. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.75–1.85 (m, 4H), 2.44–2.55 (m, 4H), 3.37 (s, 3H), 7.28 (dd, *J* = 7.0, 1.8 Hz, 1H), 7.42–7.48 (m, 2H), 7.58–7.62 (m, 1H), 7.77–7.82 (m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 21.9 (CH<sub>2</sub>), 22.5 (CH<sub>2</sub>), 26.7 (CH<sub>2</sub>), 32.6 (CH<sub>2</sub>), 51.2 (CH<sub>3</sub>), 125.0 (CH), 125.59 (CH), 125.64 (CH), 125.9 (CH), 127.4 (CH), 127.6 (CH), 127.9 (CH), 128.0 (C), 132.4 (C), 133.2 (C), 140.8 (C). 145.7 (C), 170.3 (C). HRMS-ESI (m/z): [M+Na]<sup>+</sup> calcd for C<sub>18</sub>H<sub>18</sub>O<sub>2</sub>Na, 289.11990; found, 289.12018.

#### 3. Preparation of Substrates.



In a vacuum dried three-necked, 500 mL, round bottomed flask, cyclohexanecarboxylic acid (50.3 mL, 400 mmol) and thionyl chloride (36.3 mL, 500 mL) was added and stirred at 90 °C for 2 h. Then the reaction mixture was cooled to 80 °C and red phosphorus (0.65 g) was added with stirring. Bromine (25.8 mL, 500 mmol) was added dropwise as temperature was maintained below 100 °C. The reaction mixture was heated at 100 °C for an additional 5 h and then cooled to 0 °C and dry methanol (85.0 mL, 2.10 mol) was added dropwise. The reaction mixture was heated to reflux for 1 h. After that, the reaction mixture was quenched by addition of ice-cold water and extracted with Et<sub>2</sub>O four times. The combined organic layer was washed with 1M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> aq. once and saturated NaHCO<sub>3</sub> aq. three times and saturated NaCl aq. once. The combined organic layer was dried over MgSO<sub>4</sub>. After filtration, the solvents were removed by evaporation. The crude product was purified by vacuum distillation to obtain methy 1-bromocyclohexanecarboxylate (86.5 g, 392 mmol, 98%) as a colorless oil.

In a vacuum dried 300 mL of a round bottomed flask, methyl 1-bromocyclohexanecarboxylate (86.2 g, 390 mmol) and quinoline (74.0 mL, 624 mmol) was added and the flask was heated to 120 °C for 2 h under nitrogen atmosphere. After 15 min of heating, a slight exothermic reaction was noted and the mixture separated into two layers. The reaction mixture was cooled and quenched by

addition of 20% HCl aq. and extracted with hexane four times. The combined organic layer was washed with 10% HCl aq. and saturated NaHCO<sub>3</sub> aq. and saturated NaCl aq. and was dried over MgSO<sub>4</sub>. After filtration, the solvents were removed by evaporation. The crude product was purified by vacuum distillation to obtain **1a** (37.8 g, 270 mmol, 69%) as a colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 1.55–1.73 (m, 4H), 2.14–2.32 (m, 4H), 3.73 (s, 3H), 6.95–7.00 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 21.3 (*C*H<sub>2</sub>), 21.9 (*C*H<sub>2</sub>), 24.0 (*C*H<sub>2</sub>), 25.6 (*C*H<sub>2</sub>), 51.3 (*C*H<sub>3</sub>), 130.1 (*C*), 139.6 (*C*H), 167.9 (*C*). HRMS-ESI (m/z): [M]<sup>+</sup> calcd for C<sub>8</sub>H<sub>12</sub>O<sub>2</sub>, 140.08373; found, 140.08332.

Preparation of ethyl cyclohex-1-enecarboxylate (1b).



**1b** (5.94 g, 38.5 mmol, 39%, colorless oil) was prepared from cyclohexanecarboxylic acid (12.8 g, 100 mmol) and ethanol (24.2 g, 525 mmol) according to the procedure described above. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.29 (t, *J* = 7.4 Hz, 3H), 1.56–1.68 (m, 4H), 2.16–2.28 (m, 4H), 4.18 (q, *J* = 7.2 Hz, 2H), 6.97–7.00 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 13.7 (*C*H<sub>3</sub>), 21.0 (*C*H<sub>2</sub>), 21.6 (*C*H<sub>2</sub>), 23.6 (*C*H<sub>2</sub>), 25.2 (*C*H<sub>2</sub>), 59.5 (*C*H<sub>2</sub>), 129.9 (*C*), 138.7 (*C*H), 166.8 (*C*). HRMS-EI (m/z): [M]<sup>+</sup> calcd for C<sub>9</sub>H<sub>14</sub>O<sub>2</sub>, 154.09938; found, 154.09907.

Preparation of isopropyl cyclohex-1-enecarboxylate (1c).



**1c** (2.44 g, 14.5 mmol, 73%, colorless oil) was prepared from cyclohexanecarboxylic acid (2.56 g, 20.0 mmol) and propan-2-ol (6.01 g, 100 mmol) according to the procedure described above. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.26 (d, *J* = 6.4 Hz, 6H), 1.56–1.68 (m, 4H), 2.15–2.27 (m, 4H), 5.06 (sep, *J* = 6.2 Hz, 1H), 6.94–6.97 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 21.4 (*C*H<sub>2</sub>), 21.8 (*C*H<sub>3</sub>), 22.0 (*C*H<sub>2</sub>), 24.0 (*C*H<sub>2</sub>), 25.6 (*C*H<sub>2</sub>), 67.1 (*C*H), 130.7 (*C*), 138.9 (*C*H), 167.0 (*C*). HRMS-ESI (m/z): [M+Na]<sup>+</sup> calcd for C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>Na, 191.10425; found, 191.10468.

Preparation of *tert*-Butyl cyclohex-1-enecarboxylate (1d).<sup>3</sup>



MgSO<sub>4</sub> (4.81 g, 40.0 mmol) was placed in an oven-dried two neck flask. The flask was connected

to a vacuum/nitrogen manifold through a rubber tube, evacuated and backfilled with nitrogen.  $CH_2Cl_2$  (40 mL) was added in the flask through the rubber septum. Then,  $H_2SO_4$  (0.53 mL, 10.0 mmol) was added dropwise at room temperature. After the addition of  $H_2SO_4$  was complete, cyclohex-1-enecarboxylic acid (1.26 g, 10.0 mmol) and 2-methylpropan-2-ol (3.71 g, 50.0 mmol) was added and stirred at room temperature. The reaction was quenched by addition of saturated NaHCO<sub>3</sub> aq. (75 mL) and extracted with  $CH_2Cl_2$  three times. The combined organic layer was dried over MgSO<sub>4</sub>. After filtration, the solvents ware removed by evaporation. The crude product was purified by flash column chromatography to obtain **1d** (0.773 g, 4.24 mmol, 42%) as a colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 1.48 (s, 9H), 1.55–1.67 (m, 4H), 2.15–2.23 (m, 4H), 6.87–6.90 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 21.4 (*C*H<sub>2</sub>), 22.0 (*C*H<sub>2</sub>), 24.0 (*C*H<sub>2</sub>), 25.5 (*C*H<sub>2</sub>), 27.9 (*C*H<sub>3</sub>), 79.4 (*C*), 131.6 (*C*), 138.1 (*C*H), 166.7 (*C*). HRMS-ESI (m/z): [M+Na]<sup>+</sup> calcd for C<sub>11</sub>H<sub>18</sub>O<sub>2</sub>Na, 201.11990; found, 205.12001.

# Preparation of phenyl cyclohex-1-enecarboxylate (1e).<sup>4</sup>



In a vacuum dried 300 mL of a round bottomed flask, cyclohex-1-enecarboxylic acid (2.52 g, 20.0 mmol) and phenol (2.07 g, 22.0 mmol) were dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (110 mL) and the flask was cooled to 0 °C under nitrogen atmosphere. 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) (4.60 g, 24.0 mmol) and *N*,*N*-dimethyl-4-aminopyridine (DMAP) (0.244 g, 2.0 mmol) were then added portion wise. After stirred for 14 h at room temperature, the reaction mixture was quenched by addition of saturated NH<sub>4</sub>Cl aq. and extracted with CH<sub>2</sub>Cl<sub>2</sub> three times. The combined organic layer was then dried over MgSO<sub>4</sub>. After filtration, the solvents were removed by evaporation. The crude product was purified by flash column chromatography to obtain **1e** (3.40 g, 16.8 mmol, 84%) as a solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.63–1.76 (m, 4H), 2.24–2.31 (m, 2H), 2.35–2.43 (m, 2H), 7.10 (d, *J* = 7.2 Hz, 2H), 7.20–7.26 (m, 2H), 7.38 (t, *J* = 9.0 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 21.3 (CH<sub>2</sub>), 22.0 (CH<sub>2</sub>), 24.2 (CH<sub>2</sub>), 26.0 (CH<sub>2</sub>), 121.7 (CH), 125.5 (CH), 129.3 (CH), 129.8 (C), 141.9 (CH), 151.1 (C), 166.0 (C). HRMS-ESI (m/z): [M+Na]<sup>+</sup> calcd for C<sub>13</sub>H<sub>14</sub>O<sub>2</sub>Na, 255.08860; found, 225.08847.

Preparation of 3-chloropropyl cyclohex-1-enecarboxylate (1f).



1f (1.60 g, 7.9 mmol, 79%, colorless oil) was prepared from cyclohex-1-enecarboxylic acid (1.26 g,

10.0 mmol) and 3-chloropropan-1-ol (1.04 g, 11.0 mmol) according to the procedure described above. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.57–1.69 (m, 4H), 2.14 (quint, *J* = 6.2 Hz, 2H), 2.18–2.27 (m, 4H), 3.64 (t, *J* = 6.4 Hz, 2H), 4.28 (t, *J* = 6.0 Hz, 2H), 6.98–7.01 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 21.2 (*C*H<sub>2</sub>), 21.8 (*C*H<sub>2</sub>), 23.9 (*C*H<sub>2</sub>), 25.5 (*C*H<sub>2</sub>), 31.5 (*C*H<sub>2</sub>), 41.1 (*C*H<sub>2</sub>), 60.6 (*C*H<sub>2</sub>), 129.9 (*C*), 139.7 (*C*H), 167.0 (*C*). HRMS-ESI (m/z): [M+Na]<sup>+</sup> calcd for C<sub>10</sub>H<sub>15</sub>ClO<sub>2</sub>Na, 225.06528; found, 225.06545.

Preparation of 4,4,4-trifluorobutyl cyclohex-1-enecarboxylate (1g).



**1g** (0.885 g, 3.75 mmol, 75%, colorless oil) was prepared from cyclohex-1-enecarboxylic acid (0.57 g, 4.5 mmol) and 4,4,4-trifluorobutan-1-ol (0.64 g, 5.0 mmol) according to the procedure described above. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 1.57–1.69 (m, 4H), 1.91–1.98 (m, 2H), 2.14–2.27 (m, 6H), 4.19 (t, J = 6.2 Hz, 2H), 6.99–7.01 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 21.3 (*C*H<sub>2</sub>), 21.6 (d, <sup>3</sup> $J_{C-F} = 2.0$  Hz, *C*H<sub>2</sub>), 21.9 (*C*H<sub>2</sub>), 24.0 (*C*H<sub>2</sub>), 25.7 (*C*H<sub>2</sub>), 30.7 (q, <sup>2</sup> $J_{C-F} = 28.7$  Hz, *C*H<sub>2</sub>), 62.2 (*C*H<sub>2</sub>), 126.9 (q, <sup>1</sup> $J_{C-F} = 274$  Hz, *C*), 129.9 (*C*), 140.0 (*C*H), 167.1 (*C*). HRMS-APCl (m/z): [M+H]<sup>+</sup> calcd for C<sub>11</sub>H<sub>16</sub>F<sub>3</sub>O<sub>2</sub>, 237.10969; found, 237.11000.

Preparation of 3-methoxypropyl cyclohex-1-enecarboxylate (1h).



**1h** (3.76 g, 19.0 mmol, 95%, colorless oil) was prepared from cyclohex-1-enecarboxylic acid (2.52 g, 20.0 mmol) and 3-methoxypropan-1-ol (1.98 g, 22.0 mmol) according to the procedure described above. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.57–1.69 (m, 4H), 1.94 (quint, *J* = 6.4 Hz, 2H), 2.17–2.31 (m, 4H), 3.35 (s, 3H), 3.47 (t, *J* = 6.4 Hz, 2H), 4.21 (t, *J* = 6.4 Hz, 2H), 6.98–7.00 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 21.2 (*C*H<sub>2</sub>), 21.8 (*C*H<sub>2</sub>), 23.8 (*C*H<sub>2</sub>), 25.4 (*C*H<sub>2</sub>), 28.8 (*C*H<sub>2</sub>), 58.3 (*C*H<sub>3</sub>), 61.0 (*C*H<sub>2</sub>), 68.9 (*C*H<sub>2</sub>), 130.0 (*C*), 139.2 (*C*H), 167.1 (*C*). HRMS-ESI (m/z): [M+Na]<sup>+</sup> calcd for C<sub>11</sub>H<sub>18</sub>O<sub>3</sub>Na, 221.11482; found, 221.11446.

Preparation of 4-oxopentyl cyclohex-1-enecarboxylate (1i).



1i (0.836 g, 4.0 mmol, 40%, colorless oil) was prepared from cyclohex-1-enecarboxylic acid (1.26 g,

10.0 mmol) and 5-hydroxypentan-2-one (1.02 g, 10.0 mmol) according to the procedure described above. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.57–1.69 (m, 4H), 1.95 (quint, *J* = 7.0 Hz, 2H), 2.17 (s, 3H), 2.17–2.26 (m, 4H), 2.54 (t, *J* = 7.6 Hz, 2H), 4.13 (t, *J* = 6.4 Hz, 2H), 6.96–6.99 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 21.3 (*C*H<sub>2</sub>), 21.9 (*C*H<sub>2</sub>), 22.7 (*C*H<sub>2</sub>), 23.9 (*C*H<sub>2</sub>), 25.6 (*C*H<sub>2</sub>), 29.8 (*C*H<sub>3</sub>), 39.8 (*C*H<sub>2</sub>), 63.1 (*C*H<sub>2</sub>), 130.0 (*C*), 139.6 (*C*H), 167.3 (*C*), 207.6 (*C*). HRMS-ESI (m/z): [M+Na]<sup>+</sup> calcd for C<sub>12</sub>H<sub>18</sub>O<sub>3</sub>Na, 233.11482; found, 233.11434.

# Preparation of 4-methoxy-4-oxobutyl cyclohex-1-enecarboxylate (1j).



**1j** (1.01 g, 4.47 mmol, 47%, colorless oil) was prepared from cyclohex-1-enecarboxylic acid (1.26 g, 10.0 mmol) and methyl 4-hydroxybutanoate (1.30 g, 11.0 mmol) according to the procedure described above. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 1.57–1.68 (m, 4H), 2.01 (quint, J = 7.2 Hz, 2H), 2.15–2.28 (m, 4H), 2.43 (t, J = 7.6 Hz, 2H), 3.69 (s, 3H), 4.16 (t, J = 6.4 Hz, 2H), 6.97–6.99 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 21.4 (CH<sub>2</sub>), 22.0 (CH<sub>2</sub>), 24.0 (CH<sub>2</sub>), 24.1 (CH<sub>2</sub>), 25.7 (CH<sub>2</sub>), 30.7 (CH<sub>2</sub>), 51.6 (CH<sub>3</sub>), 63.1 (CH<sub>2</sub>), 130.1 (C), 139.8 (CH), 167.4 (C), 173.3 (C). HRMS-ESI (m/z): [M+Na]<sup>+</sup> calcd for C<sub>12</sub>H<sub>18</sub>O<sub>4</sub>Na, 249.10973; found, 249.11012.

#### Preparation of 3-((methoxycarbonyl)(methyl)amino)propyl cyclohex-1-enecarboxylate (1k).



**1k** (1.06 g, 4.13 mmol, 41%, colorless oil) was prepared from cyclohex-1-enecarboxylic acid (1.26 g, 10.0 mmol) and methyl (3-hydroxypropyl)(methyl)carbamate (1.62 g, 11.0 mmol) according to the procedure described above. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.54–1.73 (m, 4H), 1.82–1.97 (m, 2H), 2.19–2.28 (m, 4H), 2.85–2.97 (m, 3H), 3.29–3.44 (m, 2H), 3.68 (s, 3H), 4.08–4.21 (m, 2H), 6.98–7.01 (m, 1H). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 50 °C,  $\delta$ ): 22.3 (CH<sub>2</sub>), 22.9 (CH<sub>2</sub>), 25.1 (CH<sub>2</sub>), 26.3 (CH<sub>2</sub>), 28.1 (CH<sub>2</sub>), 34.7 (CH<sub>3</sub>), 46.6 (CH<sub>2</sub>), 52.6 (CH<sub>3</sub>), 62.3 (CH<sub>2</sub>), 131.4 (C), 139.6 (CH), 157.1 (C), 167.3 (C). HRMS-ESI (m/z): [M+Na]<sup>+</sup> calcd for C<sub>13</sub>H<sub>21</sub>O<sub>4</sub>NNa, 278.13628; found, 278.13566.

Preparation of 3-(oxiran-2-yl)propyl cyclohex-1-enecarboxylate (11).



Pent-4-en-1-yl cyclohex-1-enecarboxylate (1.38 g, 7.00 mmol, 71%) was prepared from

cyclohex-1-enecarboxylic acid (1.26 g, 10.0 mmol) and pent-4-en-1-ol (0.947 g, 11.0 mmol) the procedure described for phenyl cyclohex-1-enecarboxylate according to (**4e**). m-Chloroperoxybenzoic acid (1.45 g, 8.40 mmol) was placed in an oven-dried 200 mL of a round bottomed flask. The flask was connected to a vacuum/nitrogen manifold through a rubber tube, evacuated and backfilled with nitrogen. The solution of pent-4-en-1-yl cyclohex-1-enecarboxylate (1.38 g, 7.00 mmol) and dry CH<sub>2</sub>Cl<sub>2</sub> (70 mL) was added dropwise to the flask. After the reaction was complete, the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and saturated NaHCO<sub>3</sub> aq. three times. The crude mixture was purified by flash column chromatography to obtain 11 (0.703 g, 3.34 mmol, 48%) as a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 1.57–1.72 (m, 6H), 1.76–1.92 (m, 2H), 2.15–2.26 (m, 4H), 2.48–2.50 (m, 1H), 2.77 (t, J = 4.4 Hz, 1H), 2.93–2.98 (m, 1H), 4.18 (t, J = 6.6 Hz, 2H), 6.97–7.00 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 21.4 (CH<sub>2</sub>), 22.0 (CH<sub>2</sub>), 24.1 (CH<sub>2</sub>), 25.2 (CH<sub>2</sub>), 25.7 (CH<sub>2</sub>), 29.1 (CH<sub>2</sub>), 47.0 (CH<sub>2</sub>), 51.7 (CH), 63.6 (CH<sub>2</sub>), 130.2 (C), 139.7 (CH), 167.5 (*C*). HRMS-ESI (m/z):  $[M+Na]^+$  calcd for  $C_{12}H_{18}O_3Na$ , 233.11482; found, 233.11494.

#### Preparation of methyl cyclopent-1-enecarboxylate (1m).



**1m** (7.33 g, 58.2 mmol, 58%, colorless oil) was prepared from cyclopentanecarboxylic acid (11.4 g, 100 mmol) and methanol (21.3 mL, 525 mmol) according to the procedure described above.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.96 (quint, *J* = 7.6 Hz, 2H), 2.42–2.61 (m, 4H), 3.74 (s, 3H), 6.77–6.79 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 22.8 (*C*H<sub>2</sub>), 31.0 (*C*H<sub>2</sub>), 33.0 (*C*H<sub>2</sub>), 50.9 (*C*H<sub>3</sub>), 136.1 (*C*), 143.4 (*C*H), 165.3 (*C*). HRMS-APCl (m/z): [M+H]<sup>+</sup> calcd for C<sub>7</sub>H<sub>11</sub>O<sub>2</sub>, 127.07536; found, 127.07559.

#### Preparation of methyl cyclohept-1-enecarboxylate (1n).



**1n** (1.28 g, 8.30 mmol, 59%, colorless oil) was prepared from cycloheptanecarboxylic acid (1.99 g, 14.0 mmol) and methanol (2.24 g, 70.0 mmol) according to the procedure described above. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.49–1.57 (m, 4H), 1.75–1.81 (m, 2H), 2.29 (dt, J = 6.3, 3.2 Hz, 2H), 2.51–2.54 (m, 2H), 3.72 (s, 3H), 7.18 (t, J = 7.0 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 25.6 (CH<sub>2</sub>), 26.1 (CH<sub>2</sub>), 27.2 (CH<sub>2</sub>), 28.6 (CH<sub>2</sub>), 31.9 (CH<sub>2</sub>), 51.5 (CH<sub>3</sub>), 136.3 (C), 144.3 (CH), 168.4 (C). HRMS-EI (m/z): [M]<sup>+</sup> calcd for C<sub>9</sub>H<sub>14</sub>O<sub>2</sub>, 154.09938; found, 154.09963.

Preparation of (E)-methyl cyclooct-1-enecarboxylate (10).



**10** (0.972 g, 5.78 mmol, 58%, colorless oil) was prepared from cyclooctanecarboxylic acid (1.56 g, 10.0 mmol) and methanol (1.67 g, 52.0 mmol) according to the procedure described above. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.43–1.51 (m, 4H), 1.54–1.62 (m, 4H), 2.28 (dt, J = 8.8, 4.0 Hz, 2H), 2.45–2.48 (m, 2H), 3.73 (s, 3H), 6.99 (t, J = 8.6 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 24.5 (CH<sub>2</sub>), 25.7 (CH<sub>2</sub>), 26.3 (CH<sub>2</sub>), 27.0 (CH<sub>2</sub>), 28.8 (CH<sub>2</sub>), 28.9 (CH<sub>2</sub>), 51.3 (CH<sub>3</sub>), 132.9 (C), 142.3 (CH), 167.8 (C). HRMS-ESI (m/z): [M+Na]<sup>+</sup> calcd for C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>Na, 191.10425; found, 191.10465.

#### 4. Characterization of Borylation Products.

#### Methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-enecarboxylate (3a).



Product **3a** (125.3 mg, 87% Isolated yield, 99% GC yield) was obtained from **1a** (70.1 mg, 0.50 mmol) as an oil, according to the general procedure for the iridium(I)-catalyzed vinylic C–H borylation. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.34 (s, 12H), 1.54–1.66 (m, 4H), 2.20–2.24 (m, 4H), 3.74 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 21.2 (*C*H<sub>2</sub>), 21.6 (*C*H<sub>2</sub>), 24.0 (*C*H<sub>2</sub>), 24.6 (*C*H<sub>3</sub>), 27.8 (*C*H<sub>2</sub>), 51.6 (*C*H<sub>3</sub>), 83.2 (*C*), 133.6 (*C*), 147.6 (br, B–*C*), 169.2 (*C*). HRMS-ESI (m/z): [M+Na]<sup>+</sup> calcd for C<sub>14</sub>H<sub>23</sub>BO<sub>4</sub>Na, 288.16179; found, 288.16138.

#### Ethyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-enecarboxylate (3b).



Product **3b** (87% GC yield) was obtained from **1b** (77.1 mg, 0.50 mmol) as an oil, according to the general procedure for the iridium(I)-catalyzed vinylic C–H borylation. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.27 (t, *J* = 7.2 Hz, 3H), 1.33 (s, 12H), 1.54–1.66 (m, 4H), 2.17–2.27 (m, 4H), 4.21 (q, *J* = 7.2 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 13.9 (*C*H<sub>3</sub>), 21.1 (*C*H<sub>2</sub>), 21.6 (*C*H<sub>2</sub>), 23.8 (*C*H<sub>2</sub>), 24.4 (*C*H<sub>3</sub>), 27.6 (*C*H<sub>2</sub>), 60.4 (*C*H<sub>2</sub>), 83.0 (*C*), 133.8 (*C*), 148.1 (br, B–*C*), 168.8 (*C*). HRMS-ESI (m/z): [M+Na]<sup>+</sup> calcd for C<sub>15</sub>H<sub>25</sub>BO<sub>4</sub>Na, 302.17744; found, 302.17752.

Isopropyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-enecarboxylate (3c).



Product **3c** (77% GC yield) was obtained from **1c** (84.1 mg, 0.50 mmol) as an oil, according to the general procedure for the iridium(I)-catalyzed vinylic C–H borylation. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.24 (d, *J* = 6.6 Hz, 6H), 1.33 (s, 12H), 1.54–1.68 (m, 4H), 2.15–2.25 (m, 4H), 5.07 (sep, *J* = 6.6 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 21.2 (*C*H<sub>2</sub>), 21.6 (*C*H<sub>2</sub>), 21.6 (*C*H<sub>3</sub>), 23.7 (*C*H<sub>2</sub>), 24.5 (*C*H<sub>3</sub>), 27.6 (*C*H<sub>2</sub>), 67.8 (*C*H), 82.9 (*C*), 134.3 (*C*), 148.4 (br, B–*C*), 168.7 (*C*). HRMS-ESI (m/z): [M+Na]<sup>+</sup> calcd for C<sub>16</sub>H<sub>27</sub>BO<sub>4</sub>Na, 316.19309; found, 316.19331.

#### tert-Butyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-enecarboxylate (3d).



Product **3d** (85% GC yield) was obtained from **1d** (91.1 mg, 0.50 mmol) as an oil, according to the general procedure for the iridium(I)-catalyzed vinylic C–H borylation. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.20–1.27 (m, 1H), 1.32 (s, 11H), 1.46 (s, 9H), 1.54–1.63 (m, 4H), 2.12–2.22 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 21.4 (*C*H<sub>2</sub>), 21.9 (*C*H<sub>2</sub>), 24.0 (*C*H<sub>2</sub>), 24.7 (*C*H<sub>3</sub>), 27.5 (*C*H<sub>2</sub>), 28.0 (*C*H<sub>3</sub>), 80.8 (*C*), 82.9 (*C*H), 135.8 (*C*), 148.6 (br, B–*C*), 169.2 (*C*). HRMS-ESI (m/z): [M+Na]<sup>+</sup> calcd for C<sub>17</sub>H<sub>29</sub>BO<sub>4</sub>Na, 330.20874; found, 330.20853.

# Phenyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-enecarboxylate (3e).



Product **3e** (96% GC yield) was obtained from **1e** (101 mg, 0.50 mmol) as a powder, according to the general procedure for the iridium(I)-catalyzed vinylic C–H borylation. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.24 (s, 12H), 1.61–1.74 (m, 4H), 2.29–2.41 (m, 4H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 8.2 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 21.3 (*C*H<sub>2</sub>), 21.8 (*C*H<sub>2</sub>), 24.6 (*C*H<sub>2</sub>), 24.8 (*C*H<sub>3</sub>), 28.4 (*C*H<sub>2</sub>), 83.7 (*C*), 121.9 (*C*H), 125.6 (*C*H), 129.2 (*C*H), 133.7 (*C*), 149.0 (br, B–*C*), 150.8 (*C*), 166.6 (*C*). HRMS-ESI (m/z): [M+Na]<sup>+</sup> calcd for C<sub>19</sub>H<sub>25</sub>BO<sub>4</sub>Na, 350.17744;

found, 350.17718.

3-Chloropropyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-enecarboxylate (3f).



Product **3f** (86% GC yield) was obtained from **1f** (101 mg, 0.50 mmol) as an oil, according to the general procedure for the iridium(I)-catalyzed vinylic C–H borylation. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.20–1.28 (m, 2H), 1.34 (s, 10H), 1.55–1.66 (m, 4H), 2.12 (quint, J = 6.4 Hz, 2H), 2.19–2.26 (m, 4H), 3.61 (t, J = 6.6 Hz, 2H), 4.29 (t, J = 6.4 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 21.2 (*C*H<sub>2</sub>), 21.7 (*C*H<sub>2</sub>), 24.0 (*C*H<sub>2</sub>), 24.6 (*C*H<sub>3</sub>), 27.9 (*C*H<sub>2</sub>), 31.6 (*C*H<sub>2</sub>), 41.1 (*C*H<sub>2</sub>), 61.3 (*C*H<sub>2</sub>), 83.3 (*C*), 133.6 (*C*), 148.9 (br, B–*C*), 168.7 (*C*). HRMS-ESI (m/z): [M+Na]<sup>+</sup> calcd for C<sub>16</sub>H<sub>26</sub>BO<sub>4</sub>ClNa, 350.15412; found, 350.15387.

4,4,4-Trifluorobutyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-enecarboxylate (3g).



Product **3g** (93% GC yield) was obtained from **1g** (118 mg, 0.50 mmol) as a powder, according to the general procedure for the iridium(I)-catalyzed vinylic C–H borylation. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.17–1.27 (m, 1H), 1.33 (s, 11H), 1.55–1.69 (m, 4H), 1.89–1.96 (m, 2H), 2.12–2.25 (m, 6H), 4.20 (t, *J* = 6.4 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 21.1 (*C*H<sub>2</sub>), 21.4 (*C*H<sub>2</sub>), 21.6 (*C*H<sub>2</sub>), 23.9 (*C*H<sub>2</sub>), 24.5 (*C*H<sub>3</sub>), 27.8 (*C*H<sub>2</sub>), 30.5 (q, <sup>2</sup>*J*<sub>C-F</sub> = 29.5 Hz, *C*H<sub>2</sub>), 62.7 (*C*H<sub>2</sub>), 83.2 (*C*), 126.7 (q, <sup>1</sup>*J*<sub>C-F</sub> = 277 Hz, *C*), 133.5 (*C*), 149.2 (br, B–*C*), 168.6 (*C*). HRMS-ESI (m/z): [M+Na]<sup>+</sup> calcd for C<sub>17</sub>H<sub>26</sub>BO<sub>4</sub>F<sub>3</sub>Na, 384.18048; found, 384.17999.

3-Methoxypropyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-enecarboxylate (3h).



Product 3h (83% GC yield) was obtained from 1h (99.1 mg, 0.50 mmol) as an oil, according to the

general procedure for the iridium(I)-catalyzed vinylic C–H borylation. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.17–1.26 (m, 1H), 1.33 (s, 11H), 1.54–1.69 (m, 4H), 1.91 (quint, *J* = 6.4 Hz, 2H), 2.20–2.24 (m, 4H), 3.33 (s, 3H), 3.44 (t, *J* = 6.4 Hz, 2H), 4.23 (t, *J* = 6.6 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 21.3 (*C*H<sub>2</sub>), 21.7 (*C*H<sub>2</sub>), 24.0 (*C*H<sub>2</sub>), 24.6 (*C*H<sub>3</sub>), 27.8 (*C*H<sub>2</sub>), 28.8 (*C*H<sub>2</sub>), 58.5 (*C*H<sub>3</sub>), 61.7 (*C*H<sub>2</sub>), 69.0 (*C*H<sub>2</sub>), 83.2 (*C*H), 133.9 (*C*), 148.6 (br, B–*C*), 169.0 (*C*). HRMS-ESI (m/z): [M+Na]<sup>+</sup> calcd for C<sub>17</sub>H<sub>29</sub>BO<sub>5</sub>Na, 346.20366; found, 346.20410.

# 4-Oxopentyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-enecarboxylate (3i).



Product **3i** (65% GC yield) was obtained from **1i** (105 mg, 0.50 mmol) as an oil, according to the general procedure for the iridium(I)-catalyzed vinylic C–H borylation. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.18–1.26 (m, 1H), 1.33 (s, 11H), 1.55–1.66 (m, 4H), 1.93 (quint, J = 6.6 Hz, 2H), 2.15 (s, 3H), 2.18–2.27 (m, 4H), 2.51 (t, J = 7.4 Hz, 2H), 4.15 (t, J = 6.4 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 21.2 (*C*H<sub>2</sub>), 21.7 (*C*H<sub>2</sub>), 22.6 (*C*H<sub>2</sub>), 24.0 (*C*H<sub>2</sub>), 24.6 (*C*H<sub>3</sub>), 27.8 (*C*H<sub>2</sub>), 29.8 (*C*H<sub>3</sub>), 39.6 (*C*H<sub>2</sub>), 63.7 (*C*H<sub>2</sub>), 83.2 (*C*), 133.7 (*C*), 148.8 (br, B–*C*), 168.9 (*C*). HRMS-ESI (m/z): [M+Na]<sup>+</sup> calcd for C<sub>18</sub>H<sub>29</sub>BO<sub>5</sub>Na, 358.20366; found, 358.20419.

#### 4-Methoxy-4-oxobutyl

2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-enecarboxylate (3j).



Product **3j** (74% GC yield) was obtained from **1j** (113 mg, 0.50 mmol) as an oil, according to the general procedure for the iridium(I)-catalyzed vinylic C–H borylation. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.17–1.26 (m, 1H), 1.33 (s, 11H), 1.56–1.66 (m, 4H), 1.98 (quint, J = 6.8 Hz, 2H), 2.19–2.24 (m, 4H), 2.41 (t, J = 7.4 Hz, 2H), 3.68 (s, 3H), 4.17 (t, J = 6.4 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 21.1 (CH<sub>2</sub>), 21.6 (CH<sub>2</sub>), 23.7 (CH<sub>2</sub>), 23.9 (CH<sub>2</sub>), 24.5 (CH<sub>3</sub>), 30.2 (CH<sub>2</sub>), 51.3 (CH<sub>3</sub>), 63.5 (CH<sub>2</sub>), 83.2 (C), 133.6 (C), 148.7 (br, B–C), 168.8 (C), 173.0 (C). HRMS-ESI (m/z): [M+Na]<sup>+</sup> calcd for C<sub>18</sub>H<sub>29</sub>BO<sub>6</sub>Na, 374.19857; found, 374.19894.

# 3-((Methoxycarbonyl)(methyl)amino)propyl

2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-enecarboxylate (3k).



Product **3k** (72% GC yield) was obtained from **1k** (128 mg, 0.50 mmol) as an oil, according to the general procedure for the iridium(I)-catalyzed vinylic C–H borylation. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.17–1.27 (m, 2H), 1.33 (s, 10H), 1.59–1.69 (m, 4H), 1.81–1.95 (m, 2H), 2.17–2.28 (m, 4H), 2.85–2.94 (m, 3H), 3.28–3.40 (m, 2H), 3.68 (s, 3H), 4.10–4.16 (m, 2H). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 50 °C,  $\delta$ ): 22.3 (*C*H<sub>2</sub>), 22.8 (*C*H<sub>2</sub>), 25.2 (*C*H<sub>2</sub>), 25.6 (*C*H<sub>3</sub>), 28.0 (*C*H<sub>2</sub>), 29.0 (*C*H<sub>2</sub>), 34.7 (*C*H<sub>3</sub>), 46.7 (*C*H<sub>2</sub>), 52.7 (*C*H<sub>3</sub>), 62.7 (*C*H<sub>2</sub>), 83.7 (*C*), 134.4 (*C*), 149.8 (br, B–*C*), 157.1 (*C*), 169.3 (*C*). HRMS-ESI (m/z): [M+Na]<sup>+</sup> calcd for C<sub>19</sub>H<sub>32</sub>BO<sub>6</sub>NNa, 403.22512; found, 403.22465.

# 3-(Oxiran-2-yl)propyl

# 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-enecarboxylate (3l).



Product **3l** (79% GC yield) was obtained from **1l** (105 mg, 0.50 mmol) as an oil, according to the general procedure for the iridium(I)-catalyzed vinylic C–H borylation. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.17–1.27 (m, 1H), 1.33 (s, 11H), 1.53–1.71 (m, 6H), 1.74–1.88 (m, 2H), 2.19–2.24 (m, 4H), 2.49 (dd, J = 5.1, 2.6 Hz, 1H), 2.76 (t, J = 4.6 Hz, 1H), 2.92–2.97 (m, 1H), 4.14–4.25 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 21.3 (*C*H<sub>2</sub>), 21.8 (*C*H<sub>2</sub>), 24.1 (*C*H<sub>2</sub>), 24.7 (*C*H<sub>3</sub>), 25.1 (*C*H<sub>2</sub>), 27.9 (*C*H<sub>2</sub>), 29.0 (*C*H<sub>2</sub>), 47.0 (*C*H<sub>2</sub>), 51.7 (*C*H), 64.2 (*C*H<sub>2</sub>), 83.4 (*C*), 133.9 (*C*), 148.9 (br, B–*C*), 169.1 (*C*). HRMS-ESI (m/z): [M+Na]<sup>+</sup> calcd for C<sub>18</sub>H<sub>29</sub>BO<sub>5</sub>Na, 358.20366; found, 358.20327.

# Methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopent-1-enecarboxylate (3m).



Product **3m** (20% GC yield) was obtained from **1m** (63.1 mg, 0.50 mmol) as an oil, according to the general procedure for the iridium(I)-catalyzed vinylic C–H borylation. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.26–1.27 (m, 1H), 1.34 (s, 11H), 1.94 (quint, *J* = 8.0 Hz, 2H), 2.61 (t, *J* = 7.6 Hz, 4H), 3.73 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 24.0 (*C*H<sub>2</sub>), 24.6 (*C*H<sub>3</sub>), 33.3 (*C*H<sub>2</sub>), 37.5 (*C*H<sub>2</sub>), 51.3 (*C*H<sub>3</sub>), 83.8 (*C*), 142.2 (*C*), 148.7 (br, B–*C*), 166.0 (*C*). HRMS-APCl (m/z): [M+H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>22</sub>BO<sub>4</sub>,

252.16420; found, 252.16463.

#### Methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohept-1-enecarboxylate (3n).



Product **3n** (43% GC yield) was obtained from **1n** (77.1 mg, 0.50 mmol) as an oil, according to the general procedure for the iridium(I)-catalyzed vinylic C–H borylation. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.19–1.27 (m, 1H), 1.33 (s, 11H), 1.46–1.59 (m, 4H), 1.75–1.81 (m, 2H), 2.32–2.34 (m, 2H), 2.50–2.55 (m, 2H), 3.77 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 24.7 (*C*H<sub>3</sub>), 25.66 (*C*H<sub>2</sub>), 25.69 (*C*H<sub>2</sub>), 27.3 (*C*H<sub>2</sub>), 31.0 (*C*H<sub>2</sub>), 32.2 (*C*H<sub>2</sub>), 52.4 (*C*H<sub>3</sub>), 82.8 (*C*), 139.7 (*C*), 157.0 (br, B–*C*), 170.9 (*C*). HRMS-ESI (m/z): [M+Na]<sup>+</sup> calcd for C<sub>15</sub>H<sub>25</sub>BO<sub>4</sub>Na, 302.17744; found, 302.17709.

# (E)-Methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclooct-1-enecarboxylate (30).



Product **30** (35% GC yield) was obtained from **10** (84.1 mg, 0.50 mmol) as an oil, according to the general procedure for the iridium(I)-catalyzed vinylic C–H borylation. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.17–1.28 (m, 1H), 1.33 (s, 11H), 1.43–1.69 (m, 8H), 2.35 (t, *J* = 6.2 Hz, 2H), 2.44 (t, *J* = 6.0 Hz, 2H), 3.76 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 24.7 (*C*H<sub>3</sub>), 24.9 (*C*H<sub>2</sub>), 26.20 (*C*H<sub>2</sub>), 26.22 (*C*H<sub>2</sub>), 28.7 (*C*H<sub>2</sub>), 29.0 (*C*H<sub>2</sub>), 29.7 (*C*H<sub>2</sub>), 52.1 (*C*H<sub>3</sub>), 83.1 (*C*), 136.9 (*C*), 170.1 (*C*). The carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation. HRMS-ESI (m/z): [M+Na]<sup>+</sup> calcd for C<sub>16</sub>H<sub>27</sub>BO<sub>4</sub>Na, 316.19309; found, 316.19282.

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