**Title**

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Iridium(I)-catalyzed vinylic C–H borylation of 1-cycloalkene carboxylates with bis(pinacolato)diboron†

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Ir(I)-catalyzed C–H borylation of 1-cycloalkene carboxylic derivatives with bis(pinacolato)diboron affords various alkenyboronates with functional groups, in excellent yields. This reaction was also used in a one-pot borylation/Suzuki–Miyaura cross-coupling procedure.

1-Alkenyboronates are an important class of compounds and are versatile intermediates in synthetic organic chemistry.† Their utility has been amply demonstrated in the synthesis of natural products and biologically active compounds via C–C bond formations with C–B bonds.‡ Conventional methods for the preparation of alkenyboronates include the reaction of B(OR)3 with alkyl-/lithium or -magnesium reagents, and the Pd-catalyzed cross-coupling reaction of alkynyl halides or triflates with bis(pinacolato)diboron (B2Pin2) to pinacolborane (HBpin).§ An alternative process involving the transition-metal-catalyzed C–H borylation of alkyl compounds was recently reported.¶,‖ Although this method is more economical and environmentally benign than the above conventional methods, the use of such reactions is still limited for cyclic vinyl ethers and suffers from the formation of a number of different side products such as allylboronates and alkylboronates.¶,‖,⁎,†

Very recently, we reported the regioselective direct ortho borylation of various benzoates or aryl ketones using the complex [Ir(OMe)(cod)]2/P[3,5-(CF3)2C6H3]; or AsPh3.¶ At the same time, several groups, including Sawamura’s,§ Lassaletta’s,¶ and Hartwig’s,‖ also reported similar borylations of functionalized arenes. The regioselectivity of these reactions is probably driven by interaction between the coordinating O and N atoms in the directing group and the Ir metal center.¶ So far, these methods have only been used in the C–H borylation of aranes; to the best of our knowledge, C–H borylation at the vinyl position of α,β-unsaturated esters has not previously been reported. In this communication, we describe a vinylic C–H borylation of 1-cycloalkene carboxylate 1 with 2, catalyzed using an in-situ-generated Ir complex consisting of readily available [Ir(OMe)(cod)]2 and AsPh3 in octane solvent. The reaction proceeded chemoselectively at 80 °C or 120 °C to give the corresponding alkenyboronic compounds 3 in high yields (Scheme 1). This reaction was used in a one-pot borylation/Suzuki–Miyaura cross-coupling procedure to afford the 2-aryl-substituted 1-cycloalkene carboxylate in good yield; this carboxylate showed biological activity.

![Scheme 1. Vinylic C–H borylation of 1-cycloalkene carboxylates.](image)

We initially examined the borylation of methyl 1-cyclohexene carboxylate 1a under the optimum conditions for the borylation of 1,4-dioxane; we previously reported that a complex of [Ir(OMe)(cod)]2 and 4,4'-di-tert-buty1-2,2'-bipyrindine (dbpy) catalyzed vinylic C–H borylations in good yields and with good selectivities.¶ The reaction of 1a with 2 (1.1 equiv) in the presence of an Ir' precursor, [Ir(OMe)(cod)]2 (1.5 mol%), and dbpy (3 mol%) as the ligand, in octane solvent at 120 °C afforded the desired product 3a in only 11% yield after 16 h (Table 1, Entry 1). We then screened possible ligands (Entries 2–8). Notable improvements in the yields were not observed in the reactions with various phosphine ligands (3a: 4–20% after 16 h, Entries 2–7). The use of AsPh3, which can weakly coordinate with an Ir metal center, significantly improved the yield of 3a, with a shorter reaction time (85%, 1 h, 90%, 16 h, Entry 8). The use of less-polar and poorer electron-donating solvents gave much better results than did more-polar and better electron-donating solvents (octane: 90%, mesitylene: 51%, diglyme: 0%, DMF: 0%, Entries 8–11). An appropriate choice of Ir catalyst precursor was crucial for this borylation. Although the combination of [IrCl2(cod)] and AsPh3 gave 3a in a good yield (84%, Entry 12), no desired product was obtained when [Ir(cod)2]BF4 was used (Entry 13). The borylation proceeded smoothly, even at 80 °C (99%, Entry 14). Under these conditions, a reaction with a lower loading of [Ir(OMe)(cod)]2 (0.5 mol%) also gave 3a in reasonable yield (81%, Entry 15). No increase in the yield of 3a was achieved using 5.0 equiv of 1a with respect to 2 (99%, Entry 16). The product 3a was obtained in only 6% yield when HBpin was used instead of 2 (Entry 17).

With the optimized conditions in hand, we next investigate the availability of the ester side-chain and the reactivity dependence on the ring size of the substrate, the borylation of various 1-cycloalkene carboxylic substrates was examined (Table 2). Ethyl ester 1b exhibited similar reactivity to that of methyl ester 1a, to produce the corresponding alkenyboronate 3b in 87%...
Table 1. Reaction conditions for methyl 1-cyclohexene-carboxylate 1a

<table>
<thead>
<tr>
<th>Entry</th>
<th>I^2 precursor</th>
<th>Ligand</th>
<th>Solvent</th>
<th>Yield (%)</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>[Ir(OMe)(cod)]</td>
<td>dipy</td>
<td>Octane</td>
<td>11</td>
</tr>
<tr>
<td>2</td>
<td>[Ir(OMe)(cod)]</td>
<td>Ph(C6H5)</td>
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<td>[Ir(OMe)(cod)]</td>
<td>Ph(OCH3)</td>
<td>Octane</td>
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</tr>
<tr>
<td>4</td>
<td>[Ir(OMe)(cod)]</td>
<td>Ph(4-MeOC6H4)</td>
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</tr>
<tr>
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<td>[Ir(OMe)(cod)]</td>
<td>Ph(4-ClC6H4)</td>
<td>Octane</td>
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</tr>
<tr>
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<td>[Ir(OMe)(cod)]</td>
<td>Ph(3,5-CF2C6H3)</td>
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<tr>
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<td>[Ir(OMe)(cod)]</td>
<td>Ph(CF3)</td>
<td>Octane</td>
<td>10</td>
</tr>
<tr>
<td>8</td>
<td>[Ir(OMe)(cod)]</td>
<td>AsPh3</td>
<td>Octane</td>
<td>90(84)</td>
</tr>
<tr>
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<td>[Ir(OMe)(cod)]</td>
<td>AsPh3</td>
<td>Mesitylene</td>
<td>51</td>
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<tr>
<td>10</td>
<td>[Ir(OMe)(cod)]</td>
<td>NpPh2</td>
<td>Diglyme</td>
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<tr>
<td>11</td>
<td>[Ir(OMe)(cod)]</td>
<td>AsPh3</td>
<td>DME</td>
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<td>[Ir(Ome)(cod)]</td>
<td>AsPh3</td>
<td>Octane</td>
<td>99(87)</td>
</tr>
<tr>
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<td>[Ir(Ome)(cod)]</td>
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<td>[Ir(Ome)(cod)]</td>
<td>AsPh3</td>
<td>Octane</td>
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</table>

*Reaction conditions: 1a (0.5 mmol), 2 (0.55 mmol), I^2 precursor (0.0025–0.0075 mmol), ligand (0.01–0.03 mmol), solvent (3 mL). 1.5 mol\% [Ir(cod)];BF3 was used. 2. Reaction was carried out at 80 °C. 3.0 mol\% [Ir(Ome)(cod)]; and 2.0 mol\% AsPh3 were used. 4.0 equiv of 1a with respect to 2 were used. 5. HBpin (0.55 mmol) was used. 6.3 mol\% dipy was used. 7. Yield was determined by GC analysis. Reaction time 1 h. Isolated yield.

yield. Even the more sterically congested substrates isopropyl ester 1e and tert-butyl ester 1d showed good reactivity at 120 °C, to afford the corresponding 3ec and 3dc in 77% and 85% yields, respectively. Reaction of phenyl ester 1e gave only the vinylic borylation product 3e in 96% yield at 80 °C. It is noteworthy that the phenyl group, which has five C(sp2)-H bonds and would be reactive in Ir-catalyzed borylation, remained intact in the reaction of 1e. Although some transition-metal complexes exhibit high reactivity toward C–Cl bonds, 3-chloropropyl ester 1f underwent borylation at the vinylic C–H bond, in high yield, without any side reactions involving the C–Cl bond (86%). We then examined the borylation of CF3-containing ester 1g; the CF3 group is very important in drug design because it enhances biological activity. The reaction of 1g afforded 3g in 93% yield. The 3-methoxy ester 1h reacted completely with 2 within 1 h to produce 3h in high yield (83%). The reactions of ketone 1i, ester 1j, and carbonate 1k proceeded at 120 °C to afford 3i (65%), 3j (74%), and 3k (72%), respectively. Although competitive coordination of the carbonyl group in the side-chain would inhibit directed borylation, these results showed that the side-chain carbonyl group did not have a seriously detrimental effect on the reactivity of the borylation. Epoxide 1l reacted without substrate decomposition, and the borylation product 3l was obtained in 79% yield after 0.5 h. Unlike the cyclohexene-type substrate discussed above, the reactions of cycloalkenyl substrates with five-, seven-, and eight-membered rings resulted in low product yields, even under harsh reaction conditions (120 °C with 2.5 mol\% [Ir(OMe)(cod)]; and 10 mol% AsPh3) than those used for the cyclohexene-type substrate. Although the five-membered ring 1m and 2 were completely consumed in the reaction, the product 3m was obtained in low yield (20%). The reactions of the seven-membered ring 1n and eight-membered ring 1o also gave the alkenylboronates 3n and 3o in low yields, though the substrates were completely consumed. We speculate that 1m–1o decomposed under the reaction conditions.

Table 2. C–H borylation of various esters

*Reaction conditions: ester (0.5 mmol), 2 (0.55 mmol), [Ir(Ome)(cod)]; (0.0075 mmol), AsPh3 (0.03 mmol), octane (3 mL). 1Yields were determined by GC analysis. 2Yield based on 2-bromonaphthalene.

We performed a one-pot synthesis of a bioactive compound via a vinylic C–H borylation/cross-coupling sequence (Scheme 2). Compound 4 has been reported to be an inhibitor of monoamine transporters. The alkenylboronate 3a was prepared from 1a under the optimized conditions shown in Table 1, and then distilled water was added to the mixture to hydrolyse HBpin that was generated by the Ir-catalyzed borylation. Finally, the subsequent cross-coupling reaction was conducted by adding 2-bromonaphthalene (2.5 mmol), K2PO4 (3.0 equiv), and PdCl2(dpdpf) (5 mol%), without solvent evaporation and product purification. The cross-coupling product 4 was obtained in 47% yield (78%, GC yield) from the two-step reaction.

Scheme 2. One-pot synthesis of 4.
C–H bond to A produces the pseudo metallacycle C. After reductive elimination, the Ir–hydride complex D and the product 3a are produced. Finally, oxidative addition of HBpin to D, followed by reductive elimination of HBpin, regenerates A. In pathway 2, involving a 1,4-insertion and β-hydride elimination, the 1,4-insertion of the carbonyl-coordinated complex E produces the iridium enolate F. The subsequent isomerization of F affords the Ir complex G, which has an Ir–C bond with a syn configuration between the Ir center and the β-H. The product 3a and D are then formed through β-hydride elimination from the C-enolate Ir complex G.

Scheme 3. Proposed catalytic cycle.

In summary, an iridium complex consisting of [Ir(OME)(cod)]2 and AsPh3 was found to be an efficient catalyst for the vinyl C–H borylation of 1-cycloalkencarboxylic derivatives with 2. This borylation proceeded at vinyl position with good selectivity, even though substrates have a phenyl group which would be reactive in Ir-catalyzed borylation. Additionally, the borylation of substrates containing various functional groups such as halogen, acyl, alkoxycarbonyl, carbamoyl, and epoxy groups afforded the corresponding products. Bipyridine, phosphine, and NHC ligands have been used for aromatic and alkenyl C–H borylations, but the present results are the first vinyl C–H borylation using AsPh3. Additionally, a one-pot borylation/cross-coupling procedure for the rapid synthesis of a drug candidate was also conducted, and shows the synthetic usefulness of this reaction.

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Notes and references

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Supporting information


Materials were obtained from commercial suppliers and purified by standard procedures unless otherwise noted. Solvents were also purchased from commercial suppliers, degassed via N₂ bubbling, and further dried over molecular sieves (MS 4Å). NMR spectra were recorded on JEOL JNM-ECX400P and JNM-EC800 spectrometer (¹H: 400 MHz and ¹³C: 100 MHz). Tetramethylsilane (¹H) and CDCl₃ (¹³C) were employed as external standards, respectively. [Ir(OMe)(cod)] was synthesized according to the reported procedure.¹ 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 Vinlyc C–H Borylation of 1a (Table 1).

[Ir(OMe)(cod)] (4.97 mg, 0.0075 mmol) and bis(pinacolato)boron (Bpin₂) (2) (1.40 g, 5.5 mmol), AsPh₃ (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 (SiO₂, EtOAc/hexane, 1:99–5:95) to give the corresponding alkenylboronate 3a as a colorless oil.

The Procedure for One-pot Synthesis of 4.

1a

[Ir(OMe)(cod)] (49.7 mg, 0.15 mmol) and B₂pin₂ (2) (1.40 g, 5.5 mmol), AsPh₃ (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 H₂O (1.5 ml) was added and stirred for 10 min. Without purification, PdCl₂(dppf) (92.0 mg, 0.125 mmol), KPO₃ (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 MgSO₄. 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. ¹H NMR (400 MHz, CDCl₃, δ): 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). ¹³C NMR (100 MHz, CDCl₃, δ): 21.9 (CH₃), 22.5 (CH₃), 26.7 (CH₃), 32.6 (CH₃), 51.2 (CH₃), 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+N⁺] calc for C₁₇H₁₂O₂Na, 289.11990; found, 289.12018.

3. Preparation of Substrates.

Preparation of methyl cyclohex-1-ene carboxylate (1a).²

1. SOCl₂, 90 °C
2. red phosphorus, Br₂, 100 °C
3. MeOH, reflux

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 purified by vacuum distillation to obtain methyl 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 NaHCO₃ aq. and saturated NaCl aq. and was dried over MgSO₄. After filtration, the solvents were removed by evaporation. The crude product was purified by flash column chromatography to obtain 1a (37.8 g, 270 mmol, 69%) as a colorless oil.

ⅡH NMR (400 MHz, CDCl₃, δ): 1.55–1.73 (m, 4H), 2.14–2.32 (m, 4H), 3.73 (s, 3H), 6.95–7.00 (m, 1H). ¹³C NMR (100 MHz, CDCl₃, δ): 21.3 (CH₃), 21.9 (CH₂), 24.0 (CH₂), 25.6 (CH₃), 51.3 (CH₂), 130.1 (C), 139.6 (CH), 167.9 (CH). HRMS-ESI (m/z): [M]+ calcd for C₁₀H₁₄O₂, 140.08373; found, 140.08332.

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

Ib (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. ⅡH NMR (400 MHz, CDCl₃, δ): 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). ¹³C NMR (100 MHz, CDCl₃, δ): 13.7 (CH₃), 21.0 (CH₂), 21.6 (CH₃), 23.6 (CH₂), 25.2 (CH₂), 59.5 (CH₂), 129.9 (C), 138.7 (CH), 166.8 (CH). HRMS-ESI (m/z): [M]+ calcd for C₁₀H₁₄O₂, 154.09938; found, 154.09907.

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

Ic (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. ⅡH NMR (400 MHz, CDCl₃, δ): 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). ¹³C NMR (100 MHz, CDCl₃, δ): 21.4 (CH₂), 21.8 (CH₂), 22.0 (CH₃), 24.0 (CH₂), 25.6 (CH₃), 67.1 (CH), 130.7 (C), 138.9 (CH), 167.0 (CH). HRMS-ESI (m/z): [M+Na]+ calcd for C₁₁H₁₅O₂Na, 191.10425; found, 191.10468.

Preparation of tert-Butyl cyclohex-1-enecarboxylate (1d).

MgSO₄ (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. CH₂Cl₂ (40 mL) was added in the flask through the rubber septum. Then, H₂SO₄ (0.53 mL, 10.0 mmol) was added dropwise at room temperature. After the addition of H₂SO₄, the reaction was quenched by addition of saturated NaHCO₃ aq. (75 mL) and extracted with CH₂Cl₂, three times. The combined organic layer was dried over MgSO₄. After filtration, the solvents were 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.

ⅡH NMR (400 MHz, CDCl₃, δ): 1.48 (s, 9H), 1.55–1.67 (m, 4H), 2.15–2.23 (m, 4H), 6.87–6.90 (m, 1H). ¹³C NMR (100 MHz, CDCl₃, δ): 21.4 (CH₃), 22.0 (CH₂), 24.0 (CH₂), 25.5 (CH₂), 27.9 (CH), 79.4 (C), 131.6 (C), 138.1 (CH), 166.7 (CH). HRMS-ESI (m/z): [M+Na]+ calcd for C₁₁H₁₅O₂Na, 201.11990; found, 205.12001.

Preparation of phenyl cyclohex-1-enecarboxylate (1e).

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 CH₂Cl₂ (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 NH₄Cl aq. and extracted with CH₂Cl₂ three times. The combined organic layer was then dried over MgSO₄. 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. ⅡH NMR (400 MHz, CDCl₃, δ): 1.63–1.76 (m, 4H), 2.24–2.34 (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). ¹³C NMR (100 MHz, CDCl₃, δ): 21.3 (CH₃), 22.0 (CH₂), 24.2 (CH₂), 26.0 (CH), 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]+ calcd for C₁₃H₁₄O₂Na, 255.08860; found, 225.08847.

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

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If (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. \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 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). \(^1^1\)C NMR (100 MHz, CDCl\(_3\), \(\delta\)): 21.2 (CH\(_3\)), 21.8 (CH\(_3\)), 23.9 (CH\(_2\)), 25.5 (CH\(_3\)), 31.5 (CH\(_3\)), 41.1 (CH\(_2\)), 60.6 (CH\(_3\)), 129.9 (C), 139.7 (CH), 167.0 (C). HRMS-ESI (m/z): [M+Na]\(^+\) calcd for C\(_{10}\)H\(_{11}\)ClO\(_4\)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. \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 1.57–1.69 (m, 4H), 1.91–1.98 (m, 2H), 2.14–2.27 (m, 4H), 4.19 (t, \(J = 6.2\) Hz, 2H), 6.99–7.01 (m, 1H). \(^1^3^1\)C NMR (100 MHz, CDCl\(_3\), \(\delta\)): 21.3 (CH\(_3\)), 21.6 (d, \(J_{C,H} = 2.0\) Hz, CH\(_3\)), 21.9 (CH\(_3\)), 24.0 (CH\(_2\)), 25.7 (CH\(_3\)), 30.7 (q, \(J_{C,F} = 28.7\) Hz, CH\(_3\)), 62.2 (CH\(_3\)), 126.9 (q, \(J_{C,F} = 274\) Hz, C), 129.9 (C), 140.0 (CH), 167.1 (C). HRMS-APCI (m/z): [M+H]\(^+\) calcd for C\(_{11}\)H\(_{13}\)F\(_3\)O\(_2\), 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. \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 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). \(^1^3^1\)C NMR (100 MHz, CDCl\(_3\), \(\delta\)): 21.2 (CH\(_3\)), 21.8 (CH\(_3\)), 23.8 (CH\(_2\)), 25.4 (CH\(_3\)), 28.8 (CH\(_3\)), 58.3 (CH\(_3\)), 61.0 (CH\(_3\)), 68.9 (CH\(_3\)), 130.0 (C), 139.2 (CH), 167.1 (C). HRMS-ESI (m/z): [M+Na]\(^+\) calcd for C\(_{10}\)H\(_{12}\)O\(_2\)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. \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 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). \(^1^3^1\)C NMR (100 MHz, CDCl\(_3\), \(\delta\)): 21.3 (CH\(_3\)), 21.9 (CH\(_3\)), 22.7 (CH\(_2\)), 23.9 (CH\(_3\)), 25.6 (CH\(_3\)), 29.8 (CH\(_3\)), 39.8 (CH\(_3\)), 63.1 (CH\(_3\)), 130.0 (C), 139.6 (CH), 167.3 (C), 207.6 (C). HRMS-ESI (m/z): [M+Na]\(^+\) calcd for C\(_{12}\)H\(_{14}\)O\(_2\)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. \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 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). \(^1^3^1\)C NMR (100 MHz, CDCl\(_3\), \(\delta\)): 21.4 (CH\(_3\)), 22.0 (CH\(_3\)), 24.0 (CH\(_3\)), 24.1 (CH\(_3\)), 25.7 (CH\(_3\)), 30.7 (CH\(_3\)), 51.6 (CH\(_3\)), 63.1 (CH\(_3\)), 130.1 (C), 139.8 (CH), 167.4 (C), 173.3 (C). HRMS-ESI (m/z): [M+Na]\(^+\) calcd for C\(_{14}\)H\(_{16}\)O\(_3\)Na, 249.10973; found, 249.11012.

Preparation of 3-(methylcarbonyl)(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. \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 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). \(^1^3^1\)C NMR (100 MHz, CDCl\(_3\), \(\delta\)): 22.3 (CH\(_3\)), 22.9 (CH\(_3\)), 23.1 (CH\(_3\)), 26.3 (CH\(_3\)), 28.1 (CH\(_3\)), 34.7 (CH\(_3\)), 46.6 (CH\(_3\)), 70.0 (CH\(_3\)).
Preparation of 3-(oxiran-2-yl)propyl cyclohex-1-ene carboxylate (1l).

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Pent-4-en-1-yl cyclohex-1-ene carboxylate (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) according to the procedure described for phenyl cyclohex-1-ene carboxylate (4e). m-Chloroperbenzoic 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-ene carboxylate (1.38 g, 7.00 mmol) and dry CHCl₃ (70 mL) was added dropwise to the flask. After the reaction was complete, the reaction mixture was extracted with CHCl₃ and saturated NaHCO₃ aq. three times. The crude mixture was purified by flash column chromatography to obtain 1l (0.703 g, 3.34 mmol, 48%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃, 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). ¹³C NMR (100 MHz, CDCl₃, δ): 21.4 (CH₂), 22.0 (CH₂), 24.1 (CH), 25.2 (CH₂), 25.7 (CH), 29.1 (CH₂), 47.0 (CH), 51.7 (CH), 63.6 (CH₂), 130.2 (C), 139.7 (CH), 167.5 (C). HRMS-ESI (m/z): [M+Na]^+ calc for C₁₃H₁₈O₄Na, 233.11482; found, 233.11494.

Preparation of methyl cyclopent-1-ene carboxylate (1m).

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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. ¹H NMR (400 MHz, CDCl₃, δ): 1.96 (quint, J = 7.6 Hz, 2H), 2.42–2.61 (m, 4H), 3.74 (s, 3H), 6.77–6.79 (m, 1H). ¹³C NMR (100 MHz, CDCl₃, δ): 22.8 (CH₂), 31.0 (CH₃), 33.0 (CH₂), 50.9 (CH), 136.1 (C), 143.4 (CH), 165.3 (C). HRMS-APCI (m/z): [M+H]^+ calc for C₇H₁₀O₂, 127.07536; found, 127.07559.

Preparation of methyl cyclohept-1-ene carboxylate (1n).

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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. ¹H NMR (400 MHz, CDCl₃, δ): 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). ¹³C NMR (100 MHz, CDCl₃, δ): 25.6 (CH₂), 26.1 (CH₃), 27.2 (CH₂), 28.6 (CH₂), 31.9 (CH₃), 51.5 (CH), 136.3 (C), 144.3 (CH), 168.4 (C). HRMS-APCI (m/z): [M]^+ calc for C₁₃H₁₇O₂, 154.09938; found, 154.09963.

Preparation of (E)-methyl cyclooct-1-ene carboxylate (1o).

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1o (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. ¹H NMR (400 MHz, CDCl₃, δ): 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). ¹³C NMR (100 MHz, CDCl₃, δ): 24.5 (CH₂), 25.7 (CH₃), 26.3 (CH₂), 27.0 (CH₂), 28.8 (CH₂), 28.9 (CH₂), 51.3 (CH), 132.9 (C), 142.3 (CH), 167.8 (C). HRMS-ESI (m/z): [M+Na]^+ calc for C₁₃H₂₀O₂Na, 191.10425; found, 191.10465.


**Methyl 2-(4,4,5,5-tetramethyl-1,2,3-dioxaborolan-2-yl)cyclohex-1-ene carboxylate (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 vinlylic C–H borylation. ¹H NMR (400 MHz, CDCl₃, δ): 1.34 (s, 12H), 1.54–1.66 (m, 4H), 2.20–
Ethyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-ene carboxylate (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. 1H NMR (400 MHz, CDCl3, δ): 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). 13C NMR (100 MHz, CDCl3, δ): 13.9 (CH3), 21.1 (CH3), 21.6 (CH3), 23.8 (CH3), 24.4 (CH3), 27.6 (CH2), 60.4 (CH3), 83.0 (C), 133.8 (C), 148.1 (br, B–C), 168.8 (C). HRMS-ESI (m/z): [M+Na]+ calcd for C15H26BO2Na, 302.17744; found, 302.17752.

Isopropyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-ene carboxylate (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. 1H NMR (400 MHz, CDCl3, δ): 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). 13C NMR (100 MHz, CDCl3, δ): 21.2 (CH2), 21.6 (CH2), 21.6 (CH2), 23.7 (CH2), 24.5 (CH2), 27.6 (CH2), 67.8 (CH2), 82.9 (C), 134.3 (C), 148.4 (br, B–C), 168.7 (C). HRMS-ESI (m/z): [M+Na]+ calcd for C16H28BO2Na, 316.19309; found, 316.19331.

tert-Butyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-ene carboxylate (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. 1H NMR (400 MHz, CDCl3, δ): 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). 13C NMR (100 MHz, CDCl3, δ): 21.4 (CH3), 21.9 (CH3), 24.0 (CH3), 24.7 (CH3), 27.5 (CH3), 28.0 (CH3), 80.8 (C), 82.9 (CH), 135.8 (C), 148.6 (br, B–C), 169.2 (C). HRMS-ESI (m/z): [M+Na]+ calcd for C17H30BO2Na, 330.20874; found, 330.20853.

Phenyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-ene carboxylate (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. 1H NMR (400 MHz, CDCl3, δ): 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). 13C NMR (100 MHz, CDCl3, δ): 21.3 (CH3), 21.8 (CH3), 24.6 (CH2), 24.8 (CH2), 28.4 (CH3), 83.7 (C), 121.9 (CH), 125.6 (CH), 129.2 (CH), 133.7 (C), 149.0 (br, B–C), 150.8 (C), 166.6 (C). HRMS-ESI (m/z): [M+Na]+ calcd for C17H28BO2Na, 350.17744; found, 350.17718.

3-Chloropropyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-ene carboxylate (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 vinyl C–H borylation. 1H NMR (400 MHz, CDCl3, δ): 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). 13C NMR (100 MHz, CDCl3, δ): 21.2 (CH3), 21.7 (CH3), 24.0 (CH2), 24.6 (CH2), 27.9 (CH3), 31.6 (CH3), 41.1 (CH1), 61.3 (CH1), 83.3 (C), 133.6 (C), 148.9 (br, B–C), 168.7 (C). HRMS-ESI (m/z): [M+Na]+ calcld for C11H12BOCINa, 350.15412; found, 350.15387.

4,4,4-Trifluorobutyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-ene-carboxylate (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 vinyl C–H borylation. 1H NMR (400 MHz, CDCl3, δ): 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). 13C NMR (100 MHz, CDCl3, δ): 21.1 (CH3), 21.4 (CH3), 21.6 (CH3), 23.9 (CH3), 24.5 (CH2), 27.8 (CH2), 30.5 (q, J13C,δ = 29.5 Hz, CH2), 62.7 (CH2), 83.2 (C), 126.7 (q, J13C,δ = 277 Hz, C), 135.5 (C), 149.2 (br, B–C), 168.6 (C). HRMS-ESI (m/z): [M+Na]+ calcld for C17H15BO3Na, 384.18048; found, 384.17999.

3-Methoxypropyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-ene-carboxylate (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 vinyl C–H borylation. 1H NMR (400 MHz, CDCl3, δ): 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). 13C NMR (100 MHz, CDCl3, δ): 21.3 (CH3), 21.7 (CH3), 24.0 (CH2), 24.6 (CH2), 27.8 (CH2), 28.8 (CH2), 58.5 (CH1), 61.7 (CH1), 69.0 (CH1), 83.2 (CH1), 133.9 (C), 148.6 (br, B–C), 169.0 (C). HRMS-ESI (m/z): [M+Na]+ calcld for C15H15BO3Na, 346.20366; found, 346.20410.

4-Oxopentyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-ene-carboxylate (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 vinyl C–H borylation. 1H NMR (400 MHz, CDCl3, δ): 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). 13C NMR (100 MHz, CDCl3, δ): 21.2 (CH3), 21.7 (CH3), 22.6 (CH2), 24.0 (CH2), 24.6 (CH2), 27.8 (CH2), 29.8 (CH3), 39.6 (CH3), 63.7 (CH2), 83.2 (C), 133.7 (C), 148.8 (br, B–C), 168.9 (C). HRMS-ESI (m/z): [M+Na]+ calcld for C15H15BO3Na, 358.20366; found, 358.20419.

4-Methoxy-4-oxobutyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-ene-carboxylate (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 vinyl C–H borylation. 1H NMR (400 MHz, CDCl3, δ): 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). 13C NMR (100 MHz, CDCl3, δ): 21.1 (CH3), 21.6 (CH3), 23.7 (CH3), 23.9 (CH2), 24.5 (CH2), 30.2 (CH2), 51.3 (CH), 63.5 (CH2), 83.2 (C), 133.6 (C), 148.7 (br, B–C), 168.8 (C), 173.0 (C). HRMS-ESI (m/z): [M+Na]+ calcld for C17H17BO3Na, 374.19857; found, 374.19894.

3-((Methoxycarbonyl)(methyl)aminopropyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-ene-carboxylate (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. 1H NMR (400 MHz, CDCl3, δ): 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). 13C NMR (100 MHz, CDCl3, δ): 22.3 (CH3), 22.8 (CH3), 25.2 (CH3), 25.6 (CH3), 28.0 (CH3), 29.0 (CH3), 34.7 (CH3), 46.7 (CH3), 52.7 (CH3), 62.7 (CH3), 83.7 (C), 134.4 (C), 149.8 (br, B–C), 157.1 (C), 169.3 (C). HRMS-ESI (m/z): [M+Na]+ calcd for C31H39BO8Na, 403.22512; found, 403.22465.

3-(Oxiran-2-yl)propyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-ene carboxylate (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. 1H NMR (400 MHz, CDCl3, δ): 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). 13C NMR (100 MHz, CDCl3, δ): 21.3 (CH3), 21.8 (CH3), 24.1 (CH3), 24.7 (CH3), 25.1 (CH3), 27.9 (CH3), 29.0 (CH3), 47.0 (CH3), 51.7 (CH), 64.2 (CH2), 83.4 (C), 133.9 (C), 148.9 (br, B–C), 169.1 (C). HRMS-ESI (m/z): [M+Na]+ calcd for C33H33BO8Na, 358.20366; found, 358.20327.

Methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopent-1-ene carboxylate (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. 1H NMR (400 MHz, CDCl3, δ): 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). 13C NMR (100 MHz, CDCl3, δ): 24.0 (CH3), 24.6 (CH3), 33.3 (CH3), 37.5 (CH3), 51.3 (CH), 83.8 (C), 142.2 (C), 148.7 (br, B–C), 166.0 (C). HRMS-APCI (m/z): [M+H]+ calcd for C13H16BO, 252.16420; found, 252.16463.

Methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohept-1-ene carboxylate (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. 1H NMR (400 MHz, CDCl3, δ): 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). 13C NMR (100 MHz, CDCl3, δ): 24.7 (CH3), 25.66 (CH3), 25.69 (CH2), 27.3 (CH2), 31.0 (CH3), 32.2 (CH3), 52.4 (CH3), 82.8 (C), 139.7 (C), 157.0 (br, B–C), 170.9 (C). HRMS-ESI (m/z): [M+Na]+ calcd for C14H18BONa, 302.17744; found, 302.17709.

(E)-Methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclooct-1-ene carboxylate (3o).

Product 3o (35% GC yield) was obtained from 1o (84.1 mg, 0.50 mmol) as an oil, according to the general procedure for the iridium(I)-catalyzed vinylic C–H borylation. 1H NMR (400 MHz, CDCl3, δ): 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). 13C NMR (100 MHz, CDCl3, δ): 24.7 (CH3), 24.9 (CH3), 26.20 (CH3), 26.22 (CH3), 28.7 (CH3), 29.0 (CH3), 29.7 (CH3), 52.1 (CH3), 83.1 (C), 136.9 (C), 170.1 (C). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar relaxation. HRMS-ESI (m/z): [M+Na]+ calcd for C16H19BO2Na, 316.19309; found, 316.19282.
References