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

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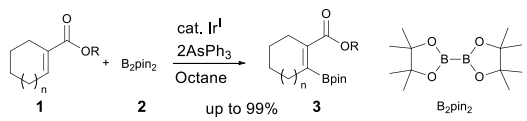
Ir(I)-catalyzed C–H borylation of 1-cycloalkenecarboxylic derivatives with bis(pinacolato)diboron affords various alkenylboronates with functional groups, in excellent yields. This reaction was also used in a one-pot borylation/Suzuki–Miyaura cross-coupling procedure.

1-Alkenylboronates are an important class of compounds and are versatile intermediates in synthetic organic chemistry.[1] 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.[2] Conventional methods for the preparation of alkenylboronates include the reaction of $B(OR)_3$ with alkenyl-lithium or -magnesium reagents, and the Pd-catalyzed cross-coupling reaction of alkenyl halides or triflates with bis(pinacolato)diboron (B_2pin_2) (**2**) or pinacolborane (HBpin).[3] An alternative process involving the transition-metal-catalyzed C–H borylation of alkenyl compounds was recently reported.[4–6] 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[5] and suffers from the formation of a number of different side products such as allylboronates and alkylboronates.[6c,d,f,g,i]

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-$(CF_3)_2C_6H_3]_3$ or $AsPh_3$.[7] At the same time, several groups, including Sawamura's,[8] Lassaletta's,[9] and Hartwig's,[10] 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.[7–9] So far, these methods have only been used in the C–H borylation of arenes; 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-cycloalkenecarboxylate **1** with **2,** catalyzed using an *in-situ*-generated Ir complex consisting of readily available $[Ir(OMe)(cod)]_2$ and $AsPh_3$ in octane solvent. The reaction proceeded chemoselectively at 80 °C or 120 °C to give the corresponding alkenylboronic 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-cycloalkenecarboxylate in good yield; this carboxylate showed biological activity.

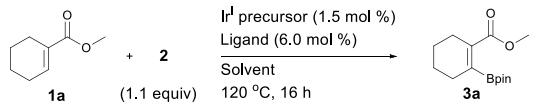


Scheme 1. Vinylic C–H borylation of 1-cycloalkenecarboxylates.

We initially examined the borylation of methyl 1-cyclohexenecarboxylate **1a** under the optimum conditions for the borylation of 1,4-dioxene; we previously reported that a complex of $[Ir(OMe)(cod)]_2$ and 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbpy) catalyzed vinylic C–H borylations in good yields and with good selectivities.[5] The reaction of **1a** with **2** (1.1 equiv) in the presence of an Ir^I precursor, $[Ir(OMe)(cod)]_2$ (1.5 mol%), and dtbpy (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 $AsPh_3$, 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).[11] 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 $[IrCl(cod)]_2$ and $AsPh_3$ gave **3a** in a good yield (84%, Entry 12), no desired product was obtained when $[Ir(cod)_2]BF_4$ 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-cycloalkenecarboxylic substrates was examined (Table 2). Ethyl ester **1b** exhibited similar reactivity to that of methyl ester **1a**, to produce the corresponding alkenylboronate **3b** in 87%

Table 1. Reaction conditions for methyl 1-cyclohexenecarboxylate **1a**[a]

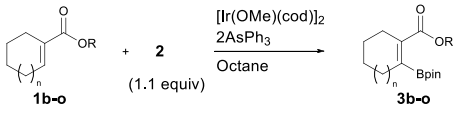


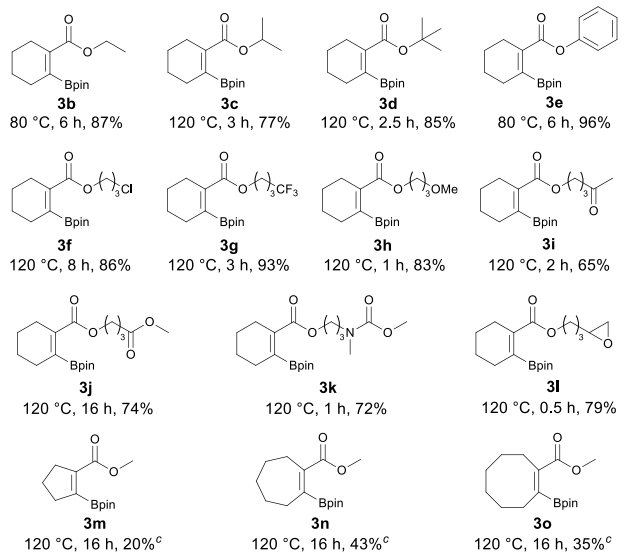
Entry	Ir^I precursor	Ligand	Solvent	Yield (%)[h]
1	$[Ir(OMe)(cod)]_2$	dtbpy[g]	Octane	11
2	$[Ir(OMe)(cod)]_2$	$P(C_6H_5)_3$	Octane	20
3	$[Ir(OMe)(cod)]_2$	$P(OC_6H_5)_3$	Octane	4
4	$[Ir(OMe)(cod)]_2$	$P(4\text{-}MeOC_6H_4)_3$	Octane	0
5	$[Ir(OMe)(cod)]_2$	$P(4\text{-}CF_3C_6H_4)_3$	Octane	19
6	$[Ir(OMe)(cod)]_2$	$P[3,5\text{-}(CF_3)_2C_6H_3]_3$	Octane	14
7	$[Ir(OMe)(cod)]_2$	$P(C_6F_5)_3$	Octane	10
8	$[Ir(OMe)(cod)]_2$	$AsPh_3$	Octane	90(84)[i]
9	$[Ir(OMe)(cod)]_2$	$AsPh_3$	Mesitylene	51
10	$[Ir(OMe)(cod)]_2$	$AsPh_3$	Diglyme	0
11	$[Ir(OMe)(cod)]_2$	$AsPh_3$	DMF	0
12	$[Ir(Cl)(cod)]_2$	$AsPh_3$	Octane	84
13[b]	$[Ir(cod)_2]BF_4$	$AsPh_3$	Octane	0
14[c]	$[Ir(OMe)(cod)]_2$	$AsPh_3$	Octane	99(87)[j]
15[c,d]	$[Ir(OMe)(cod)]_2$	$AsPh_3$	Octane	81
16[e]	$[Ir(OMe)(cod)]_2$	$AsPh_3$	Octane	99
17[f]	$[Ir(OMe)(cod)]_2$	$AsPh_3$	Octane	6

[a]Reaction conditions: **1a** (0.5 mmol), **2** (0.55 mmol), Ir^I precursor (0.0025–0.0075 mmol), ligand (0.01–0.03 mmol), solvent (3 mL). [b]3 mol% $[Ir(cod)_2]BF_4$ was used. [c]Reaction was carried out at 80 °C. [d]0.5 mol% $[Ir(OMe)(cod)]_2$ and 2.0 mol% $AsPh_3$ were used. [e]5.0 equiv of **1a** with respect to **2** were used. [f]HBpin (0.55 mmol) was used. [g]3 mol% dtbpy was used. [h]Yield was determined by GC analysis. [i]Reaction time 1 h. [j]Isolated yield.

yield. Even the more sterically congested substrates isopropyl ester **1c** and *tert*-butyl ester **1d** showed good reactivity at 120 °C, to afford the corresponding **3c** and **3d** 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(sp^2)–H bonds and would be reactive in Ir-catalyzed borylation, remained intact in the reaction of **1e**.[7,8] 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 CF_3-containing ester **1g**; the CF_3 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 carbamate **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 harsher reaction conditions (120 °C with 2.5 mol% $[Ir(OMe)(cod)]_2$ and 10 mol% $AsPh_3$) 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.

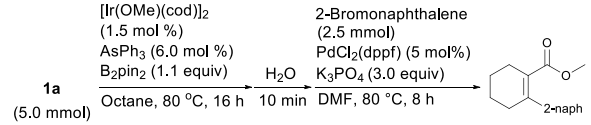
Table 2. C–H borylation of various esters[a,b]





[a]Reaction conditions: ester (0.5 mmol), **2** (0.55 mmol), $[Ir(OMe)(cod)]_2$ (0.0075 mmol), $AsPh_3$ (0.03 mmol), octane (3 mL). [b]Yields were determined by GC analysis. [c]$[Ir(OMe)(cod)]_2$ (0.0125 mmol), $AsPh_3$ (0.05 mmol).

We performed a one-pot synthesis of a bioactive compound via a vinylic C–H borylation/cross-coupling sequence (Scheme 2).[12] Compound **4** has been reported to be an inhibitor of monoamine transporters.[13] 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), K_3PO_4 (3.0 equiv), and $PdCl_2$(dppf) (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.

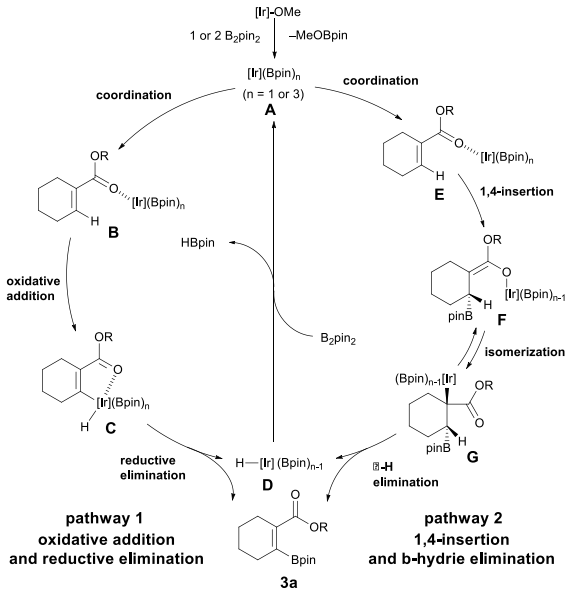


[a]GC yield based on 2-bromonaphthalene

Scheme 2. One-pot synthesis of **4**.

Two proposed catalytic cycles are shown in Scheme 3. In both the catalytic cycles, the mono- (n = 1) or tris- (n = 3) boryliridium complex **A** is first produced by reactions of Ir(I) complexes with B_2pin_2.[14] In pathway 1, involving oxidative addition and reductive elimination, the electron-donating oxygen atom in the ester group coordinates with the Ir metal center (complex **B**, Scheme 3), and then oxidative addition of the vinylic

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 B_2pin_2 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**.[15] 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 $AsPh_3$ was found to be an efficient catalyst for the vinylic C–H borylation of 1-cycloalkenecarboxylic derivatives with **2**. This borylation proceeded at vinylic 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 vinylic C–H borylation using $AsPh_3$. 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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†Electronic Supplementary Information (ESI) available: experimental procedures and spectral analyses. See DOI: 10.1039/b000000x/

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Supporting infomation

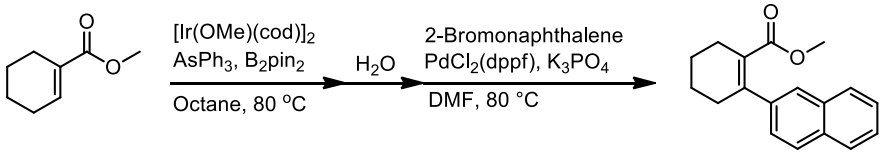
1. General and Materials.

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 (^{1}H: 400 MHz and ^{13}C: 100 MHz). Tetramethylsilane (^{1}H) and $CDCl_3$ (^{13}C) were employed as external standards, respectively. $[Ir(OMe)(cod)]_2$ 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 Vinylic C–H Borylation of 1a (Table 1).
$[Ir(OMe)(cod)]_2$ (4.97 mg, 0.0075 mmol) and bis(pinacolato)diboron (B_2pin_2) (**2**) (140 mg, 0.55 mmol), $AsPh_3$(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_2, EtOAc/hexane, 1:99–5:95) to give the corresponding alkenylboronate **3a** as a colorless oil.

The Procedure for One-pot Synthesis of 4.

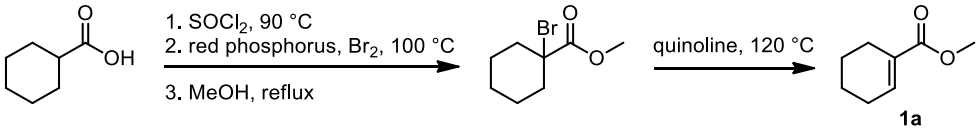


1a **4**

$[Ir(OMe)(cod)]_2$ (49.7 mg, 0.15 mmol) and B_2pin_2 (**2**) (1.40 g, 5.5 mmol), $AsPh_3$ (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_2O (1.5 ml) was added and stirred for 10 min. Without purification, $PdCl_2$(dppf) (92.0 mg, 0.125 mmol), K_3PO_4 (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 $MgSO_4$. 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. ^{1}H NMR (400 MHz, $CDCl_3$, 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). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.9 (*C*H_2), 22.5 (*C*H_2), 26.7 (*C*H_2), 32.6 (*C*H_2), 51.2 (*C*H_3), 125.0 (*C*H), 125.59 (*C*H), 125.64 (*C*H), 125.9 (*C*H), 127.4 (*C*H), 127.6 (*C*H), 127.9 (*C*H), 128.0 (*C*), 132.4 (*C*), 133.2 (*C*), 140.8 (*C*). 145.7 (*C*), 170.3 (*C*). HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{18}H_{18}O_2Na$, 289.11990; found, 289.12018.

3. Preparation of Substrates.

Preparation of methyl cyclohex-1-enecarboxylate (1a).[2]



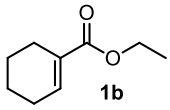
1a

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_2O four times. The combined organic layer was washed with 1M $Na_2S_2O_3$ aq. once and saturated $NaHCO_3$ aq. three times and saturated NaCl aq. once. The combined organic layer was dried over $MgSO_4$. 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 $NaHCO_3$ aq. and saturated NaCl aq. and was dried over $MgSO_4$. 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.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.55–1.73 (m, 4H), 2.14–2.32 (m, 4H), 3.73 (s, 3H), 6.95–7.00 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.3 (*C*H_2), 21.9 (*C*H_2), 24.0 (*C*H_2), 25.6 (*C*H_2), 51.3 (*C*H_3), 130.1 (*C*), 139.6 (*C*H), 167.9 (*C*). HRMS-ESI (m/z): $[M]^+$ calcd for $C_8H_{12}O_2$, 140.08373; found, 140.08332.

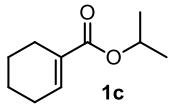
Preparation of ethyl cyclohex-1-enecarboxylate (1b).



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. ^{1}H NMR (400 MHz, $CDCl_3$, 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). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 13.7 (*C*H_3), 21.0 (*C*H_2), 21.6 (*C*H_2), 23.6 (*C*H_2), 25.2 (*C*H_2), 59.5 (*C*H_2), 129.9 (*C*), 138.7 (*C*H), 166.8 (*C*). HRMS-EI (m/z): $[M]^+$ calcd for $C_9H_{14}O_2$, 154.09938; found, 154.09907.

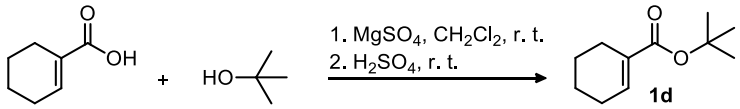
Preparation of isopropyl cyclohex-1-enecarboxylate (1c).



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. ^{1}H NMR (400 MHz, $CDCl_3$, 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). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.4 (*C*H_2), 21.8 (*C*H_3), 22.0 (*C*H_2), 24.0 (*C*H_2), 25.6 (*C*H_2), 67.1 (*C*H), 130.7 (*C*), 138.9 (*C*H), 167.0 (*C*). HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{10}H_{16}O_2Na$, 191.10425; found, 191.10468.

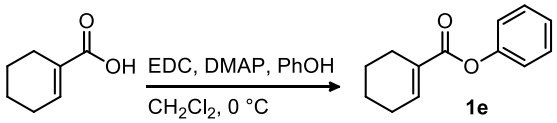
Preparation of *tert*-Butyl cyclohex-1-enecarboxylate (1d).[3]



$MgSO_4$ (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 $NaHCO_3$ aq. (75 mL) and extracted with CH_2Cl_2 three times. The combined organic layer was dried over $MgSO_4$. 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.

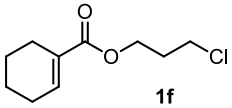
^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.48 (s, 9H), 1.55–1.67 (m, 4H), 2.15–2.23 (m, 4H), 6.87–6.90 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.4 (*C*H_2), 22.0 (*C*H_2), 24.0 (*C*H_2), 25.5 (*C*H_2), 27.9 (*C*H_3), 79.4 (*C*), 131.6 (*C*), 138.1 (*C*H), 166.7 (*C*). HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{11}H_{18}O_2Na$, 201.11990; found, 205.12001.

Preparation of phenyl cyclohex-1-enecarboxylate (1e).[4]



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_2Cl_2 (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_4Cl aq. and extracted with CH_2Cl_2 three times. The combined organic layer was then dried over $MgSO_4$. 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. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 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). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.3 (*C*H_2), 22.0 (*C*H_2), 24.2 (*C*H_2), 26.0 (*C*H_2), 121.7 (*C*H), 125.5 (*C*H), 129.3 (*C*H), 129.8 (*C*), 141.9 (*C*H), 151.1 (*C*), 166.0 (*C*). HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{13}H_{14}O_2Na$, 255.08860; found, 225.08847.

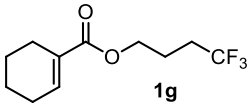
Preparation of 3-chloropropyl cyclohex-1-enecarboxylate (1f).



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. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 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). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.2 (CH_2), 21.8 (CH_2), 23.9 (CH_2), 25.5 (CH_2), 31.5 (CH_2), 41.1 (CH_2), 60.6 (CH_2), 129.9 (*C*), 139.7 (*C*H), 167.0 (*C*). HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{10}H_{15}ClO_2Na$, 225.06528; found, 225.06545.

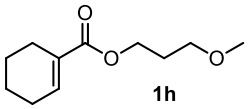
Preparation of 4,4,4-trifluorobutyl cyclohex-1-enecarboxylate (1g).



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, $CDCl_3$, 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). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.3 (CH_2), 21.6 (d, $^{3}J_{C-F}$ = 2.0 Hz, CH_2), 21.9 (CH_2), 24.0 (CH_2), 25.7 (CH_2), 30.7 (q, $^{2}J_{C-F}$ = 28.7 Hz, CH_2), 62.2 (CH_2), 126.9 (q, $^{1}J_{C-F}$ = 274 Hz, *C*), 129.9 (*C*), 140.0 (*C*H), 167.1 (*C*). HRMS-APCl (m/z): $[M+H]^+$ calcd for $C_{11}H_{16}F_3O_2$, 237.10969; found, 237.11000.

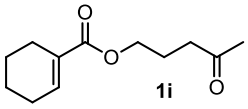
Preparation of 3-methoxypropyl cyclohex-1-enecarboxylate (1h).



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, $CDCl_3$, δ): 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). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.2 (CH_2), 21.8 (CH_2), 23.8 (CH_2), 25.4 (CH_2), 28.8 (CH_2), 58.3 (CH_3), 61.0 (CH_2), 68.9 (CH_2), 130.0 (*C*), 139.2 (*C*H), 167.1 (*C*). HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{11}H_{18}O_3Na$, 221.11482; found, 221.11446.

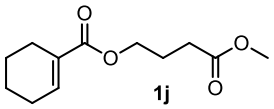
Preparation of 4-oxopentyl cyclohex-1-enecarboxylate (1i).



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, $CDCl_3$, δ): 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). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.3 (CH_2), 21.9 (CH_2), 22.7 (CH_2), 23.9 (CH_2), 25.6 (CH_2), 29.8 (CH_3), 39.8 (CH_2), 63.1 (CH_2), 130.0 (*C*), 139.6 (*C*H), 167.3 (*C*), 207.6 (*C*). HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{12}H_{18}O_3Na$, 233.11482; found, 233.11434.

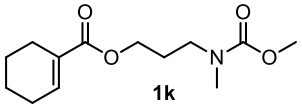
Preparation of 4-methoxy-4-oxobutyl cyclohex-1-enecarboxylate (1j).



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, $CDCl_3$, 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). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.4 (CH_2), 22.0 (CH_2), 24.0 (CH_2), 24.1 (CH_2), 25.7 (CH_2), 30.7 (CH_2), 51.6 (CH_3), 63.1 (CH_2), 130.1 (*C*), 139.8 (*C*H), 167.4 (*C*), 173.3 (*C*). HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{12}H_{18}O_4Na$, 249.10973; found, 249.11012.

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

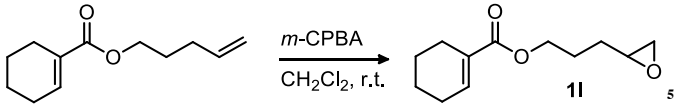


1k

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, $CDCl_3$, δ): 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). ^{13}C NMR (100 MHz, C_6D_6, 50 °C, δ): 22.3 (CH_2), 22.9 (CH_2), 25.1 (CH_2), 26.3 (CH_2), 28.1 (CH_2), 34.7 (CH_3), 46.6 (CH_2),

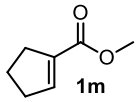
52.6 (*C*H$_3$), 62.3 (*C*H$_2$), 131.4 (*C*), 139.6 (*C*H), 157.1 (*C*), 167.3 (*C*). HRMS-ESI (m/z): [M+Na]$^+$ calcd for $C_{13}H_{21}O_4NNa$, 278.13628; found, 278.13566.

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



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) according to the procedure described for phenyl cyclohex-1-enecarboxylate (**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_2Cl_2 (70 mL) was added dropwise to the flask. After the reaction was complete, the reaction mixture was extracted with CH_2Cl_2 and saturated $NaHCO_3$ 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. ^{1}H NMR (400 MHz, $CDCl_3$, 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). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.4 (*C*H$_2$), 22.0 (*C*H$_2$), 24.1 (*C*H$_2$), 25.2 (*C*H$_2$), 25.7 (*C*H$_2$), 29.1 (*C*H$_2$), 47.0 (*C*H$_2$), 51.7 (*C*H), 63.6 (*C*H$_2$), 130.2 (*C*), 139.7 (*C*H), 167.5 (*C*). HRMS-ESI (m/z): [M+Na]$^+$ calcd for $C_{12}H_{18}O_3Na$, 233.11482; found, 233.11494.

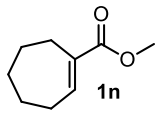
Preparation of methyl cyclopent-1-enecarboxylate (1m).



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.

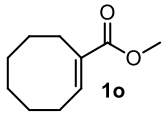
^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.96 (quint, *J* = 7.6 Hz, 2H), 2.42–2.61 (m, 4H), 3.74 (s, 3H), 6.77–6.79 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 22.8 (*C*H$_2$), 31.0 (*C*H$_2$), 33.0 (*C*H$_2$), 50.9 (*C*H$_3$), 136.1 (*C*), 143.4 (*C*H), 165.3 (*C*). HRMS-APCl (m/z): [M+H]$^+$ calcd for $C_7H_{11}O_2$, 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. ^{1}H NMR (400 MHz, $CDCl_3$, 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). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 25.6 (*C*H$_2$), 26.1 (*C*H$_2$), 27.2 (*C*H$_2$), 28.6 (*C*H$_2$), 31.9 (*C*H$_2$), 51.5 (*C*H$_3$), 136.3 (*C*), 144.3 (*C*H), 168.4 (*C*). HRMS-EI (m/z): [M]$^+$ calcd for $C_9H_{14}O_2$, 154.09938; found, 154.09963.

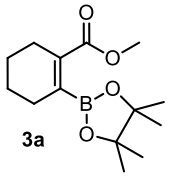
Preparation of (*E*)-methyl cyclooct-1-enecarboxylate (1o).



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. ^{1}H NMR (400 MHz, $CDCl_3$, 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). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 24.5 (*C*H$_2$), 25.7 (*C*H$_2$), 26.3 (*C*H$_2$), 27.0 (*C*H$_2$), 28.8 (*C*H$_2$), 28.9 (*C*H$_2$), 51.3 (*C*H$_3$), 132.9 (*C*), 142.3 (*C*H), 167.8 (*C*). HRMS-ESI (m/z): [M+Na]$^+$ calcd for $C_{10}H_{16}O_2Na$, 191.10425; found, 191.10465.

4. Characterization of Borylation Products.

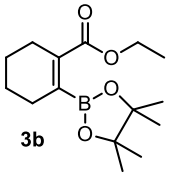
Methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-enecarboxylate (3a).



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. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.34 (s, 12H), 1.54–1.66 (m, 4H), 2.20–

2.24 (m, 4H), 3.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.2 (*C*H_2), 21.6 (*C*H_2), 24.0 (*C*H_2), 24.6 (*C*H_3), 27.8 (*C*H_2), 51.6 (*C*H_3), 83.2 (*C*), 133.6 (*C*), 147.6 (br, B–*C*), 169.2 (*C*). HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{14}H_{23}BO_4Na$, 288.16179; found, 288.16138.

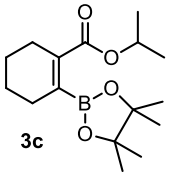
Ethyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-enecarboxylate (3b).



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. ^{1}H NMR (400 MHz, $CDCl_3$, 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).^{13}C NMR (100 MHz, $CDCl_3$, δ): 13.9 (*C*H_3), 21.1 (*C*H_2), 21.6 (*C*H_2), 23.8 (*C*H_2), 24.4 (*C*H_3), 27.6 (*C*H_2), 60.4 (*C*H_2), 83.0 (*C*), 133.8 (*C*), 148.1 (br, B–*C*), 168.8 (*C*). HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{15}H_{25}BO_4Na$, 302.17744; found, 302.17752.

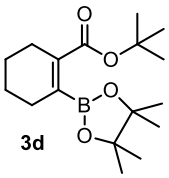
Isopropyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-enecarboxylate (3c).



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. ^{1}H NMR (400 MHz, $CDCl_3$, 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). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.2 (*C*H_2), 21.6 (*C*H_2), 21.6 (*C*H_3), 23.7 (*C*H_2), 24.5 (*C*H_3), 27.6 (*C*H_2), 67.8 (*C*H), 82.9 (*C*), 134.3 (*C*), 148.4 (br, B–*C*), 168.7 (*C*). HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{16}H_{27}BO_4Na$, 316.19309; found, 316.19331.

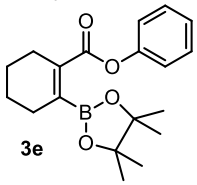
tert-Butyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-enecarboxylate (3d).



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. ^{1}H NMR (400 MHz, $CDCl_3$, 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). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.4 (*C*H_2), 21.9 (*C*H_2), 24.0 (*C*H_2), 24.7 (*C*H_3), 27.5 (*C*H_2), 28.0 (*C*H_3), 80.8 (*C*), 82.9 (*C*H), 135.8 (*C*), 148.6 (br, B–*C*), 169.2 (*C*). HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{17}H_{29}BO_4Na$, 330.20874; found, 330.20853.

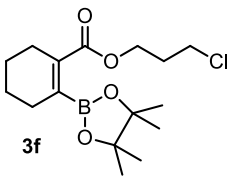
Phenyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-enecarboxylate (3e).



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. ^{1}H NMR (400 MHz, $CDCl_3$, 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). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.3 (*C*H_2), 21.8 (*C*H_2), 24.6 (*C*H_2), 24.8 (*C*H_3), 28.4 (*C*H_2), 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): $[M+Na]^+$ calcd for $C_{19}H_{25}BO_4Na$, 350.17744; found, 350.17718.

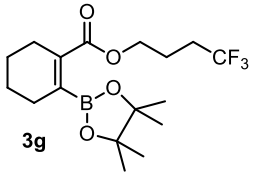
3-Chloropropyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-enecarboxylate (3f).



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. ^{1}H NMR (400 MHz, $CDCl_3$, 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). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.2 (*C*H_2), 21.7 (*C*H_2), 24.0 (*C*H_2), 24.6 (*C*H_3), 27.9 (*C*H_2), 31.6 (*C*H_2), 41.1 (*C*H_2), 61.3 (*C*H_2), 83.3 (*C*), 133.6 (*C*), 148.9 (br, B–*C*), 168.7 (*C*). HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{16}H_{26}BO_4ClNa$, 350.15412; found, 350.15387.

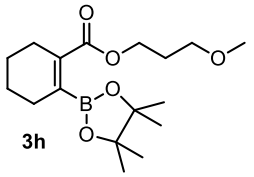
4,4,4-Trifluorobutyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-enecarboxylate (3g).



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. ^{1}H NMR (400 MHz, $CDCl_3$, 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). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.1 (*C*H_2), 21.4 (*C*H_2), 21.6 (*C*H_2), 23.9 (*C*H_2), 24.5 (*C*H_3), 27.8 (*C*H_2), 30.5 (q, $^2J_{C-F}$ = 29.5 Hz, *C*H_2), 62.7 (*C*H_2), 83.2 (*C*), 126.7 (q, $^1J_{C-F}$ = 277 Hz, *C*), 133.5 (*C*), 149.2 (br, B–*C*), 168.6 (*C*). HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{17}H_{26}BO_4F_3Na$, 384.18048; found, 384.17999.

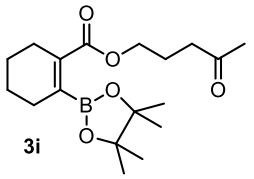
3-Methoxypropyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-enecarboxylate (3h).



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. ^{1}H NMR (400 MHz, $CDCl_3$, 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). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.3 (*C*H_2), 21.7 (*C*H_2), 24.0 (*C*H_2), 24.6 (*C*H_3), 27.8 (*C*H_2), 28.8 (*C*H_2), 58.5 (*C*H_3), 61.7 (*C*H_2), 69.0 (*C*H_2), 83.2 (*C*H), 133.9 (*C*), 148.6 (br, B–*C*), 169.0 (*C*). HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{17}H_{29}BO_5Na$, 346.20366; found, 346.20410.

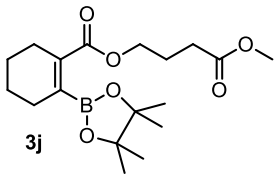
4-Oxopentyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-enecarboxylate (3i).



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. ^{1}H NMR (400 MHz, $CDCl_3$, 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). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.2 (*C*H_2), 21.7 (*C*H_2), 22.6 (*C*H_2), 24.0 (*C*H_2), 24.6 (*C*H_3), 27.8 (*C*H_2), 29.8 (*C*H_3), 39.6 (*C*H_2), 63.7 (*C*H_2), 83.2 (*C*), 133.7 (*C*), 148.8 (br, B–*C*), 168.9 (*C*). HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{18}H_{29}BO_5Na$, 358.20366; found, 358.20419.

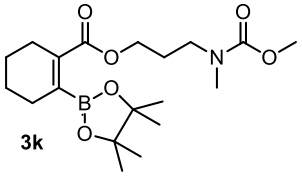
4-Methoxy-4-oxobutyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-enecarboxylate (3j).



3j

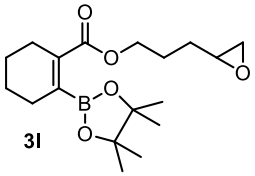
Product **3j** (74% GC yield) was obtained from **1j** (113 mg, 0.50 mmol) as an oil, according to the general procedure for the iridium(I)-catalyzed vinylic C–H borylation. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.17–1.26 (m, 1H), 1.33 (s, 11H), 1.56–1.66 (m, 4H), 1.98 (quint, J = 6.8 Hz, 2H), 2.19–2.24 (m, 4H), 2.41 (t, J = 7.4 Hz, 2H), 3.68 (s, 3H), 4.17 (t, J = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.1 (*C*H_2), 21.6 (*C*H_2), 23.7 (*C*H_2), 23.9 (*C*H_2), 24.5 (*C*H_3), 30.2 (*C*H_2), 51.3 (*C*H_3), 63.5 (*C*H_2), 83.2 (*C*), 133.6 (*C*), 148.7 (br, B–*C*), 168.8 (*C*), 173.0 (*C*). HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{18}H_{29}BO_6Na$, 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).



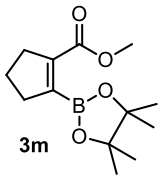
Product **3k** (72% GC yield) was obtained from **1k** (128 mg, 0.50 mmol) as an oil, according to the general procedure for the iridium(I)-catalyzed vinylic C–H borylation. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.17–1.27 (m, 2H), 1.33 (s, 10H), 1.59–1.69 (m, 4H), 1.81–1.95 (m, 2H), 2.17–2.28 (m, 4H), 2.85–2.94 (m, 3H), 3.28–3.40 (m, 2H), 3.68 (s, 3H), 4.10–4.16 (m, 2H). ^{13}C NMR (100 MHz, C_6D_6, 50 °C, δ): 22.3 (*C*H_2), 22.8 (*C*H_2), 25.2 (*C*H_2), 25.6 (*C*H_3), 28.0 (*C*H_2), 29.0 (*C*H_2), 34.7 (*C*H_3), 46.7 (*C*H_2), 52.7 (*C*H_3), 62.7 (*C*H_2), 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 $C_{19}H_{32}BO_6NNa$, 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).



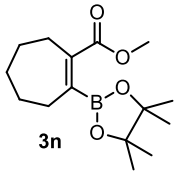
Product **3l** (79% GC yield) was obtained from **1l** (105 mg, 0.50 mmol) as an oil, according to the general procedure for the iridium(I)-catalyzed vinylic C–H borylation. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.17–1.27 (m, 1H), 1.33 (s, 11H), 1.53–1.71 (m, 6H), 1.74–1.88 (m, 2H), 2.19–2.24 (m, 4H), 2.49 (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). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.3 (*C*H_2), 21.8 (*C*H_2), 24.1 (*C*H_2), 24.7 (*C*H_3), 25.1 (*C*H_2), 27.9 (*C*H_2), 29.0 (*C*H_2), 47.0 (*C*H_2), 51.7 (*C*H), 64.2 (*C*H_2), 83.4 (*C*), 133.9 (*C*), 148.9 (br, B–*C*), 169.1 (*C*). HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{18}H_{29}BO_5Na$, 358.20366; found, 358.20327.

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



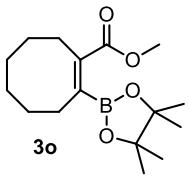
Product **3m** (20% GC yield) was obtained from **1m** (63.1 mg, 0.50 mmol) as an oil, according to the general procedure for the iridium(I)-catalyzed vinylic C–H borylation. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.26–1.27 (m, 1H), 1.34 (s, 11H), 1.94 (quint, *J* = 8.0 Hz, 2H), 2.61 (t, *J* = 7.6 Hz, 4H), 3.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 24.0 (*C*H_2), 24.6 (*C*H_3), 33.3 (*C*H_2), 37.5 (*C*H_2), 51.3 (*C*H_3), 83.8 (*C*), 142.2 (*C*), 148.7 (br, B–*C*), 166.0 (*C*). HRMS-APCl (m/z): $[M+H]^+$ calcd for $C_{13}H_{22}BO_4$, 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. ^{1}H NMR (400 MHz, $CDCl_3$, 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). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 24.7 (*C*H_3), 25.66 (*C*H_2), 25.69 (*C*H_2), 27.3 (*C*H_2), 31.0 (*C*H_2), 32.2 (*C*H_2), 52.4 (*C*H_3), 82.8 (*C*), 139.7 (*C*), 157.0 (br, B–*C*), 170.9 (*C*). HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{15}H_{25}BO_4Na$, 302.17744; found, 302.17709.

(*E*)-Methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclooct-1-enecarboxylate (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. ^{1}H NMR (400 MHz, $CDCl_3$, 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). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 24.7 (*C*H_3), 24.9 (*C*H_2), 26.20 (*C*H_2), 26.22 (*C*H_2), 28.7 (*C*H_2), 29.0 (*C*H_2), 29.7 (*C*H_2), 52.1 (*C*H_3), 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): $[M+Na]^+$ calcd for $C_{16}H_{27}BO_4Na$, 316.19309; found, 316.19282.

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