Supporting Information for

Rh(III)-Catalyzed C–H Olefination of N-Pentafluoroaryl Benzamides Using Air as the Sole Oxidant

Yi Lu*, Huai-Wei Wang, Jillian E. Spangler, Kai Chen, Pei-Pei Cui, Yue Zhao, Wei-Yin Sun, and Jin-Quan Yu*

*Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing National Laboratory of Microstructures, Nanjing University, Nanjing 210093, China

Department of Chemistry, The Scripps Research Institute, 10550 N. Torrey Pines Road, La Jolla, CA 92037, USA

*To whom correspondence should be addressed. Email: luyi@nju.edu.cn; sunwy@nju.edu.cn; yu200@scripps.edu
Table of Contents

**General Information**  
S3

**Experimental Section**  
General procedure for the preparation of benzamides  
S4
Solvent optimization for C–H olefination  
S5
Ligand screening for C–H olefination  
S6
General procedure for C–H olefination  
S7
Procedure for the ring-opening/auxiliary removal  
S8
The effect of heterocycle in C–H olefination  
S9

**References**  
S11

**Characterization of new synthesized compounds**  
S12

**NMR Spectra**  
S26
General Information:

All solvents were used as received from commercial sources without further purification. Anhydrous solvents were prepared according to standard methods.¹ Double bond coupling partners and reagents used to prepare the substrates were purchased from Acros, Sigma-Aldrich, TCI, and Alfa and were used as received without further purification. Pentamethylcyclopentadienylrhodium (III) chloride dimer was purchased from Sigma-Aldrich and used without further purification. ¹H NMR and ¹³C NMR spectra were recorded on Bruker-DRX (500 MHz and 125 MHz, respectively) and Bruker-DRX (400 MHz and 100 MHz, respectively) instruments internally referenced to SiMe₄ or chloroform signals. High resolution mass spectra were recorded at Center for Mass Spectrometry, Nanjing University.
Experimental Section

General procedure for the preparation of benzamides

Substrates are prepared according to literature procedure.² An acid chloride (20 mmol), prepared from the corresponding carboxylic acid and oxalyl chloride, was added to a vigorously stirring solution of 2,3,4,5,6-pentafluoroaniline (22 mmol) in toluene (50 mL). The reaction mixture was stirred for 24 h under reflux. After cooling to room temperature, the white precipitate was filtered off and washed with water, and recrystallized from toluene or ethyl acetate/hexane to give the products.
Solvent optimization for C–H olefination

Table S1. Solvent optimization for C–H olefination reaction\textsuperscript{a,b}

| Entry | Solvent   | Yield\textsuperscript{b}         |
|-------|-----------|----------------------------------|
| 1     | CH\textsubscript{2}Cl\textsubscript{2} | 73\% (11.2:1.0)                  |
| 2     | MeCN      | 87\%\textsuperscript{c}         |
| 3     | DMF       | 86\% (9.8:1.0)                  |
| 4     | 1,4-dioxane | 54\% (4.4:1.0)            |
| 5     | MeOH      | 75\% (1.5:1.0)                  |
| 6     | Toluene   | 72\% (0.5:1.0)                  |

\textsuperscript{a}: Benzamide (60.2 mg, 0.2 mmol), Ethyl acrylate (50.1 mg, 0.5 mmol), [RhCp*Cl\textsubscript{2}]\textsubscript{2} (6.2 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), Solvent (2 mL), 80\textdegree C, 24 hours; \textsuperscript{b}: The yield was determined by \textsuperscript{1}H NMR analysis of the crude reaction mixture using CH\textsubscript{2}Br\textsubscript{2} as the internal standard; the products consist of mono- and di-substitute ones (mono-di-); \textsuperscript{c}: The di-substituted product is trace.

To a 50 mL Schlenk-type sealed tube equipped with a magnetic stirring bar, were added the benzamide (60.2 mg, 0.2 mmol), [RhCp*Cl\textsubscript{2}]\textsubscript{2} (6.2 mg, 0.01 mmol, 5 mol\%), AgOAc (66.8 mg, 0.4 mmol), Solvent (2.0 mL) and olefine coupling partner (0.5 mmol). The tube was heated to 80 °C for 24 hours and then cooled to room temperature. The reaction mixture was filtered through a pad of Celite and concentrated \textit{in vacuo} to afford crude products. The yield was determined by \textsuperscript{1}H NMR analysis of the crude reaction mixture using CH\textsubscript{2}Br\textsubscript{2} as the internal standard.
Ligand screening for C–H olefination

Table S2. Ligand screening for C–H olefination reaction

| Entry | Ligands       | Yield$^b$ | Entry | Ligands       | Yield$^b$ |
|-------|---------------|-----------|-------|---------------|-----------|
| 1     | Cbz-Glu-OH    | 21%       | 9     | Boc-Leu-OH    | >99%      |
| 2     | Ac-Glu-OH     | 14%       | 10    | Boc-Phe-OH    | 68%       |
| 3     | Fmoc-Leu-OH   | 87%       | 11    | Boc-Pro-OH    | 64%       |
| 4     | Boc-Asn-OH    | 67%       | 12    | Boc-Tyr-OH    | 60%       |
| 5     | Form-Leu-OH   | 50%       | 13    | Boc-Val-OH    | 78%       |
| 6     | Bz-Leu-OH     | 92%       | 14    | Boc-Ala-OH    | 52%       |
| 7     | Piv-Leu-OH    | 79%       | 15    | Boc-Ile-OH    | 98%       |
| 8     | Ac-Leu-OH     | 45%       | 16    | Boc-Nle-OH    | 91%       |

$^a$: Benzamide (60.2 mg, 0.2 mmol), [RhCp*Cl$_2$]$_2$ (6.2 mg, 0.01 mmol), Ethyl acrylate (50.1 mg, 0.5 mmol), O$_2$ (1 atm), Ligands (0.02 mmol), Na$_2$CO$_3$ (21.2 mg, 0.2 mmol), MeCN (2 mL), 80 °C, 24 hours; $^b$: The yield was determined by $^1$H NMR analysis of the crude reaction mixture using CH$_2$Br$_2$ as the internal standard.

To a 50 mL Schlenk-type sealed tube equipped with a magnetic stirring bar, were added the benzamide (60.2 mg, 0.2 mmol), [RhCp*Cl$_2$]$_2$ (6.2 mg, 0.01 mmol, 5 mol%), O$_2$ (1 atm), Ligand (0.02 mmol), MeCN (2.0 mL) and olefine coupling partner (0.5 mmol). The tube was heated to 80 °C for 24 hours and then cooled to room temperature. The reaction mixture was filtered through a pad of Celite and concentrated in vacuo to afford crude products. The yield was determined by $^1$H NMR analysis of the crude reaction mixture using CH$_2$Br$_2$ as the internal standard.
General procedure for C–H olefination:

To a 350 mL Schlenk-type sealed tube equipped with a magnetic stirring bar, were added the substrate (0.2 mmol), [RhCp*Cl₂]₂ (6.2 mg, 0.01 mmol), NaOPiv (28.4 mg, 0.2 mmol), MeCN (2.0 mL) and olefine coupling partner (0.5 mmol). The tube was capped, and heated to 80 °C for 24 hours. After cooled to room temperature, the reaction mixture was filtered through a pad of Celite. The filtrate was concentrated in vacuo to afford crude products, which was purified by flash column chromatography on silica gel to give the pure product.
Procedure for the ring-opening/auxiliary removal:

To an oven dried 10 mL round bottle flask equipped with a magnetic stir bar were added lactam (83.1 mg, 0.2 mmol) and 1 mL of anhydrous THF. After cooling to -78°C, LiHMDS (1.0 M in THF, 5.0 equiv.) was added dropwise within 5 minutes. The mixture was warmed up to -20°C naturally in 50 minutes. Then Boc₂O (6.0 equiv.) was added in -78°C followed by warming up to 0°C naturally in 2 hours. EtONa (1.0 M in EtOH, 10 equiv.) was added. After stirred at room temperature for 30 min, the reaction was quenched with saturated NH₄Cl/HOAc(10/1, 2 mL). Extract with EtOAc (3*3 mL). The combined organic layer was washed with brine and dried over MgSO₄, filtrated and concentrated under vacuum, and purified by preparative TLC using hexanes/EtOAc (4/1) as the eluent to afford 45.6 mg of 6d (82%) as white solid.

(E)-ethyl 2-(3-ethoxy-3-oxoprop-1-en-1-yl)-4-methoxybenzoate (6d):

¹H NMR (400 MHz, CDCl₃): δ 8.50 (d, J = 15.6 Hz, 1 H), 7.98 (d, J = 8.8 Hz, 1 H), 7.03 (d, J = 2.8 Hz, 1 H), 6.93 (dd, J₁ = 8.8 Hz, J₂ = 2.8 Hz, 1 H), 4.36 (q, J = 7.2 Hz, 2 H), 4.28 (q, J = 7.2 Hz, 2 H), 1.40 (t, J = 7.2 Hz, 3 H), 1.34 (t, J = 7.2 Hz, 3 H); ¹³C NMR (125MHz, CDCl₃): δ 166.50, 166.36, 162.43, 144.35, 138.81, 133.05, 122.28, 121.01, 114.60, 112.97, 61.04, 60.54, 55.49, 14.27. HRMS (El-TOF): m/z Calc. for C₁₅H₁₅O₅Na [M+Na]+: 301.1052, found 301.1050.
The effect of heterocycle in C–H olefination

The acid (20 mmol) was prepared according previous report \(^3\) and treated with oxalyl chloride to afford the acid chloride. And then, 2,3,4,5,6-pentafluoroaniline (22 mmol) in toluene (50 mL) was added and stirred for 24 h under reflux. After cooling to room temperature, the precipitate was filtered off and washed with ethyl acetate, water, and ethanol to give the substrate \(1t\). Standard condition has been applied for \(1t\), and the reaction mixture was concentrated *in vacuo* to afford crude products, which was purified by preparative TLC using EtOAc/Hexane (2/1) as the eluent to afford the major product \(2t\) (28%).

Ethyl 2-(3-oxo-2-(perfluorophenyl)-6-(pyridin-2-yl)isoindolin-1-yl)acetate (\(2t\))

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 8.75 (d, \(J = 4.8\) Hz, 1 H), 8.26 (s, 1 H), 8.16 (dd, \(J_1 = 8.0\) Hz, \(J_2 = 0.8\) Hz, 1 H), 8.04 (d, \(J = 8.0\) Hz, 1 H), 7.84–7.82 (m, 2 H), 7.35–7.32 (m, 1 H), 5.54 (t, \(J = 6.4\) Hz, 1 H), 4.07–4.02 (m, 2 H), 2.95 (dd, \(J_1 = 16.4\) Hz, \(J_2 = 5.6\) Hz, 1 H), 2.76 (dd, \(J_1 = 16.4\) Hz, \(J_2 = 5.6\) Hz, 1 H), 2.49–2.26 (m, 4 H), 1.97–1.78 (m, 6 H), 1.81–1.65 (m, 4 H), 1.53–1.40 (m, 2 H), 0.80–0.62 (m, 9 H), 0.58–0.39 (m, 6 H), 0.36–0.16 (m, 12 H).
7.2 Hz, 1 H), 1.18 (t, J = 7.2 Hz, 3 H); $^{13}$C NMR (125 MHz, CDCl$_3$); δ 169.69, 166.93, 155.87, 150.01, 145.89, 144.28, 137.11, 130.10, 127.81, 125.04, 123.20, 121.38, 121.16, 61.34, 58.51, 38.75, 13.90. HRMS (EI-TOF): m/z Calc. for C$_{23}$H$_{14}$F$_2$N$_2$O$_3$Na [M+Na]$^+$: 485.0901, found 485.0897.
References:

1. W. L. F. Armarego, D. D. Perrin, *Purification of Laboratory Chemicals* 4th Ed. Butterworth-Heinemann: Oxford, 1997.

2. H. Ogita, Y. Isobe, H. Takaku, R. Sekine, Y. Goto, S. Misawa, H. Hayashi, *Bioorg. Med. Chem. Lett.* 2001, 11, 549.

3. H. Tang, Y. Li, C. Wei, B. Chen, W. Yang, H. Wu, Y. Cao, *Dyes and Pigments* 2011, 91, 413.
Characterization of new synthesized compounds

Ethyl 2-(4-methyl-3-oxo-2-(perfluorophenyl)isoindolin-1-yl)acetate (2a):

Following the general procedure, the C–H olefination was carried out with 1a (60.2 mg, 0.2 mmol), [RhCp*Cl₂]₂ (6.2 mg, 0.01 mmol), NaOPiv (28.4 mg, 0.2 mmol), MeCN (2.0 mL) and ethyl acrylate (50.1 mg, 0.5 mmol) at 80 °C for 24 hours. The product 2a was obtained as white solid (71.0 mg, 89%) by flash column chromatography on silica gel using hexanes/EtOAc as the eluent. ¹H NMR (500 MHz, CDCl₃): δ 7.53 (t, J = 7.5 Hz, 1 H), 7.35 (d, J = 7.5 Hz, 1 H), 7.32 (d, J = 7.5 Hz, 1 H), 5.43 (t, J = 6.5 Hz, 1 H), 4.05 (q, J = 7.0 Hz, 2 H), 2.82 (dd, J₁ = 16.5 Hz, J₂ = 5.5 Hz, 1 H), 2.75 (s, 3 H), 2.70 (dd, J₁ = 16.5 Hz, J₂ = 7.0 Hz, 1 H), 1.19 (t, J = 7.0 Hz, 3 H); ¹³C NMR (125 MHz, CDCl₃): δ 169.80, 167.81, 145.85, 144.99 (dd, J₁ = 257.8 Hz, J₂ = 35.2 Hz), 141.22 (d, J = 250.9 Hz), 139.03, 137.87 (d, J = 247.6 Hz), 132.56, 130.96, 126.97, 119.99, 112.00, 61.19, 57.54, 38.94, 17.35, 13.86. HRMS (EI-TOF): m/z Calc. for C₁₉H₁₄F₅NO₃ [M]: 399.0894, found 399.0888.

Ethyl 2-(6-methyl-3-oxo-2-(perfluorophenyl)isoindolin-1-yl)acetate (2b):

Following the general procedure, the C–H olefination was carried out with 1b (60.2 mg, 0.2 mmol), [RhCp*Cl₂]₂ (6.2 mg, 0.01 mmol), NaOPiv (28.4 mg, 0.2 mmol), MeCN (2.0 mL) and ethyl acrylate (50.1 mg, 0.5 mmol) at 80 °C for 24 hours. The product 2b was obtained as white solid (72.6 mg, 91%) by flash column chromatography on silica gel using hexanes/EtOAc as the eluent. ¹H NMR (500 MHz, CDCl₃): δ 7.82 (d, J = 7.5 Hz, 1 H), 7.37 (d, J = 7.5 Hz, 1 H), 7.35 (s, 1 H), 5.42 (t, J = 6.5 Hz, 1 H), 4.05 (q, J = 7.0 Hz, 2 H), 2.81 (dd, J₁ = 16.5 Hz, J₂ = 6.0 Hz, 1 H),
2.69 (dd, $J_1 = 16.5$ Hz, $J_2 = 7.0$ Hz, 1 H), 2.50 (s, 3 H), 1.18 (t, $J = 7.0$ Hz, 3 H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 169.74, 167.15, 144.98 (dd, $J_1 = 250.5$ Hz, $J_2 = 39.1$ Hz), 145.67, 144.11, 141.25 (d, $J = 254.1$ Hz), 137.86 (d, $J = 250.9$ Hz), 130.04, 127.22, 124.44, 123.12, 111.91, 61.18, 58.11, 38.65, 21.98, 13.83. HRMS (EI-TOF): m/z Calc. for C$_{19}$H$_{14}$F$_5$NO$_3$ [M]: 399.0894, found 399.0887.

![Chemical Structure](image)

Ethyl 2-(3-oxo-2-(perfluorophenyl)isoindolin-1-yl)acetate (2c):

Following the general procedure, the C–H olefination was carried out with 1c (57.4 mg, 0.2 mmol), [RhCp*Cl$_2$]$_2$ (6.2 mg, 0.01 mmol), NaOPiv (28.4 mg, 0.2 mmol), MeCN (2.0 mL) and ethyl acrylate (50.1 mg, 0.5 mmol) at 80 °C for 24 hours. The product 2c was obtained as white solid (71.6 mg, 93%) by flash column chromatography on silica gel using hexanes/EtOAc as the eluent. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.96 (d, $J = 7.5$ Hz, 1 H), 7.67 (t, $J = 7.5$ Hz, 1 H), 7.57 (t, $J = 7.5$ Hz, 1 H), 7.55 (d, $J = 7.5$ Hz, 1 H), 5.47 (t, $J = 6.5$ Hz, 1 H), 4.05 (q, $J = 7.0$ Hz, 2 H), 2.81 (dd, $J_1 = 16.5$ Hz, $J_2 = 6.0$ Hz, 1 H), 2.72 (dd, $J_1 = 16.5$ Hz, $J_2 = 7.0$ Hz, 1 H), 1.18 (t, $J = 7.0$ Hz, 3 H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 169.67, 167.10, 144.95 (dd, $J_1 = 250.0$ Hz, $J_2 = 38.8$ Hz), 145.26, 141.36 (d, $J = 255.1$ Hz), 137.90 (d, $J = 252.4$ Hz), 133.09, 129.84, 129.08, 124.72, 122.74, 111.74, 61.26, 58.29, 38.58, 13.87. HRMS (EI-TOF): m/z Calc. for C$_{18}$H$_{12}$F$_5$NO$_3$ [M]: 385.0737, found 385.0765.

![Chemical Structure](image)

Ethyl 2-(6-methoxy-3-oxo-2-(perfluorophenyl)isoindolin-1-yl)acetate (2d):

Following the general procedure, the C–H olefination was carried out with 1d (63.4 mg, 0.2 mmol), [RhCp*Cl$_2$]$_2$ (6.2 mg, 0.01 mmol), NaOPiv (28.4 mg, 0.2 mmol), MeCN (2.0 mL) and
ethyl acrylate (50.1 mg, 0.5 mmol) at 80 °C for 24 hours. The product 2d was obtained as white solid (69.7 mg, 84%) by flash column chromatography on silica gel using hexanes/EtOAc as the eluent.\(^1\)\(^\text{H}\) NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.86 (d, \(J = 8.5\) Hz, 1 H), 7.07 (d, \(J = 8.5\) Hz, 1 H), 7.02 (s, 1 H), 5.39 (t, \(J = 6.0\) Hz, 1 H), 4.05 (q, \(J = 7.0\) Hz, 2 H), 3.90 (s, 3 H), 2.78 (dd, \(J_1 = 16.5\) Hz, \(J_2 = 5.5\) Hz, 1 H), 2.70 (dd, \(J_1 = 16.5\) Hz, \(J_2 = 6.5\) Hz, 1 H), 1.19 (t, \(J = 7.0\) Hz, 3 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 169.74, 166.87, 163.90, 147.69, 144.95 (dd, \(J_1 = 257.2\) Hz, \(J_2 = 39.2\) Hz), 141.20 (d, \(J = 254.2\) Hz), 137.82 (d, \(J = 247.0\) Hz), 126.12, 122.16, 115.59, 111.91, 107.58, 61.21, 57.92, 55.69, 38.66, 13.83, 130.04, 127.22, 124.44, 123.12, 111.91, 61.18, 58.11, 38.65, 21.98, 13.83. HRMS (EI-TOF): \(m/z\) Calc. for C\(_{19}\)H\(_{14}\)F\(_5\)NO\(_4\) [M]: 415.0843, found 415.0839.

Ethyl 2-(6-acetoxy-3-oxo-2-(perfluorophenyl)isoindolin-1-yl)acetate (2e):

Following the general procedure, the C–H olefination was carried out with 1e (69.0 mg, 0.2 mmol), [RhCp*Cl\(_2\)]\(_2\) (6.2 mg, 0.01 mmol), NaOPiv (28.4 mg, 0.2 mmol), MeCN (2.0 mL) and ethyl acrylate (50.1 mg, 0.5 mmol) at 80 °C for 24 hours. The product 2e was obtained as white solid (64.7 mg, 73%) by flash column chromatography on silica gel using hexanes/EtOAc as the eluent.\(^1\)\(^\text{H}\) NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.96 (d, \(J = 8.0\) Hz, 1 H), 7.36 (s, 1 H), 7.29 (d, \(J = 8.5\) Hz, 1 H), 5.45 (t, \(J = 6.5\) Hz, 1 H), 4.06 (q, \(J = 7.0\) Hz, 2 H), 2.80 (dd, \(J_1 = 16.5\) Hz, \(J_2 = 6.5\) Hz, 1 H), 2.73 (dd, \(J_1 = 16.5\) Hz, \(J_2 = 6.5\) Hz, 1 H), 2.35 (s, 3 H), 1.18 (t, \(J = 7.0\) Hz, 3 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 169.53, 168.76, 166.19, 154.50, 146.78, 144.91 (dd, \(J_1 = 250.6\) Hz, \(J_2 = 33.4\) Hz), 141.42 (d, \(J = 253.9\) Hz), 137.92 (d, \(J = 249.0\) Hz), 127.25, 125.98, 122.93, 116.60, 111.53, 61.34, 57.97, 38.31, 21.04, 13.84. HRMS (EI-TOF): \(m/z\) Calc. for C\(_{20}\)H\(_{14}\)F\(_5\)NO\(_5\) [M]: 443.0792, found 443.0785.
Ethyl 2-(3-oxo-2-(perfluorophenyl)-6-(trifluoromethyl)isoindolin-1-yl)acetate (2f):

Following the general procedure, the C–H olefination was carried out with 1f (71.0 mg, 0.2 mmol), [RhCp*Cl2]2 (6.2 mg, 0.01 mmol), NaOPiv (28.4 mg, 0.2 mmol), MeCN (2.0 mL) and ethyl acrylate (50.1 mg, 0.5 mmol) at 80 °C for 24 hours. The product 2f was obtained as white solid (75.2 mg, 83%) by flash column chromatography on silica gel using hexanes/EtOAc as the eluent.

1H NMR (500 MHz, CDCl3): δ 8.09 (d, J = 8.0 Hz, 1 H), 7.87 (s, 1 H), 7.86 (d, J = 8.0 Hz, 1 H), 5.52 (t, J = 6.5 Hz, 1 H), 4.09 (q, J = 7.0 Hz, 2 H), 2.85-2.76 (m, 2 H), 1.20 (t, J = 7.0 Hz, 3 H);

13C NMR (125 MHz, CDCl3): δ 169.29, 165.68, 144.88 (dd, J1 = 259.0 Hz, J2 = 30.0 Hz), 145.65, 141.66 (d, J = 256.1 Hz), 138.00 (d, J = 252.4 Hz), 134.99 (q, J = 32.5 Hz), 133.09, 126.40, 125.41, 123.45 (d, J = 271.5 Hz), 120.36, 111.13, 61.52, 58.31, 38.12, 13.85. HRMS (EI-TOF): m/z Calc. for C19H11F8NO3 [M]: 453.0611, found 453.0614.

Ethyl 2-(6-acetyl-3-oxo-2-(perfluorophenyl)isoindolin-1-yl)acetate (2g):

Following the general procedure, the C–H olefination was carried out with 1g (65.8 mg, 0.2 mmol), [RhCp*Cl2]2 (6.2 mg, 0.01 mmol), NaOPiv (28.4 mg, 0.2 mmol), MeCN (2.0 mL) and ethyl acrylate (50.1 mg, 0.5 mmol) at 80 °C for 24 hours. The product 2g was obtained as white solid (70.9 mg, 83%) by flash column chromatography on silica gel using hexanes/EtOAc as the eluent.

1H NMR (500 MHz, CDCl3): δ 8.17 (s, 1 H), 8.15 (d, J = 8.0 Hz, 1 H), 8.05 (d, J = 8.0 Hz, 1 H), 5.52 (t, J = 6.5 Hz, 1 H), 4.07 (q, J = 7.0 Hz, 2 H), 2.87 (dd, J1 = 16.5 Hz, J2 = 6.0 Hz, 1 H), 2.77 (dd, J1 = 16.5 Hz, J2 = 6.5 Hz, 1 H), 2.70 (s, 3 H), 1.19 (t, J = 7.0 Hz, 3 H);

13C NMR (125 MHz, CDCl3): δ 196.90, 169.32, 166.05, 145.44, 144.78 (dd, J1 = 253.6 Hz, J2 = 38.5 Hz), 141.51 (d, J = 255.1 Hz), 140.81, 137.90 (d, J = 252.9 Hz), 133.48, 129.27, 124.99, 122.59, 111.31, 61.41, 58.41, 38.22, 26.95, 13.86. HRMS (EI-TOF): m/z Calc. for C20H14F5NO4 [M]: 427.0843, found 427.0844.
Ethyl 2-(6-nitro-3-oxo-2-(perfluorophenyl)isoindolin-1-yl)acetate (2h):

Following the general procedure, the C–H olefination was carried out with 1h (66.4 mg, 0.2 mmol), [RhCp*Cl₂]₂ (6.2 mg, 0.01 mmol), NaOPiv (28.4 mg, 0.2 mmol), MeCN (2.0 mL) and ethyl acrylate (50.1 mg, 0.5 mmol) at 80 °C for 24 hours. The product 2h was obtained as white solid (75.7 mg, 88%) by flash column chromatography on silica gel using hexanes/EtOAc as the eluent. ¹H NMR (500 MHz, CDCl₃): δ 8.47 (s, 1 H), 8.46 (d, J = 8.0 Hz, 1 H), 8.13 (d, J = 8.0 Hz, 1 H), 5.55 (t, J = 6.5 Hz, 1 H), 4.11 (q, J = 7.0 Hz, 2 H), 2.84 (d, J = 6.5 Hz, 2 H), 1.21 (t, J = 7.0 Hz, 3 H); ¹³C NMR (125 MHz, CDCl₃): δ 169.00, 164.88, 151.02, 146.21, 144.78 (dd, J₁ = 263.1 Hz, J₂ = 36.9 Hz), 141.80 (d, J = 254.1 Hz), 138.04 (d, J = 257.9 Hz), 135.05, 125.96, 124.71, 118.83, 110.82, 61.71, 58.27, 37.78, 13.91. HRMS (EI-TOF): m/z Calc. for C₁₈H₁₁F₅N₂O₅ [M]: 430.0588, found 430.0599.

Ethyl 2-(6-chloro-3-oxo-2-(perfluorophenyl)isoindolin-1-yl)acetate (2i):

Following the general procedure, the C–H olefination was carried out with 1i (64.2 mg, 0.2 mmol), [RhCp*Cl₂]₂ (6.2 mg, 0.01 mmol), NaOPiv (28.4 mg, 0.2 mmol), MeCN (2.0 mL) and ethyl acrylate (50.1 mg, 0.5 mmol) at 80 °C for 24 hours. The product 2i was obtained as white solid (77.1 mg, 92%) by flash column chromatography on silica gel using hexanes/EtOAc as the eluent. ¹H NMR (500 MHz, CDCl₃): δ 7.88 (d, J = 8.0 Hz, 1 H), 7.58 (s, 1 H), 7.55 (d, J = 8.0 Hz, 1 H), 5.43 (t, J = 6.5 Hz, 1 H), 4.08 (q, J = 7.0 Hz, 2 H), 2.81-2.71 (m, 2 H), 1.20 (t, J = 7.0 Hz, 3 H); ¹³C NMR (125 MHz, CDCl₃): δ 169.38, 164.01, 146.81, 144.87 (dd, J₁ = 248.2 Hz, J₂ = 36.8 Hz), 141.48 (d, J = 255.1 Hz), 139.61, 137.94 (d, J = 252.2 Hz), 129.74, 128.33, 125.89, 123.44, 111.36,
61.41, 57.86, 38.20, 13.86. HRMS (EI-TOF): m/z Calc. for C_{18}H_{11}ClF_{5}NO_{3} [M]: 419.0348, found 419.0343.

Ethyl 2-(6-bromo-3-oxo-2-(perfluorophenyl)isoindolin-1-yl)acetate (2j):

Following the general procedure, the C–H olefination was carried out with 1j (73.0 mg, 0.2 mmol), [RhCp*Cl{2}]_{2} (6.2 mg, 0.01 mmol), NaOPiv (28.4 mg, 0.2 mmol), MeCN (2.0 mL) and ethyl acrylate (50.1 mg, 0.5 mmol) at 80 °C for 24 hours. The product 2j was obtained as white solid (80.6 mg, 87%) by flash column chromatography on silica gel using hexanes/EtOAc as the eluent.

^1^H NMR (500 MHz, CDCl_{3}): δ 7.82 (d, J = 8.0 Hz, 1 H), 7.75 (s, 1 H), 7.72 (d, J = 8.0 Hz, 1 H), 5.43 (t, J = 6.5 Hz, 1 H), 4.08 (q, J = 7.0 Hz, 2 H), 2.81-2.71 (m, 2 H), 1.20 (t, J = 7.0 Hz, 3 H); ^13^C NMR (125 MHz, CDCl_{3}): δ 169.38, 166.16, 146.94, 144.84 (dd, J_1 = 250.8 Hz, J_2 = 34.0 Hz), 141.49 (d, J = 255.5 Hz), 137.90 (d, J = 250.2 Hz), 132.63, 128.77, 128.01, 126.41, 126.05, 111.28, 61.44, 57.81, 38.20, 13.88. HRMS (EI-TOF): m/z Calc. for C_{18}H_{11}BrF_{5}NO_{3} [M]: 462.9842, found 462.9846.

Ethyl 2-(6-iodo-3-oxo-2-(perfluorophenyl)isoindolin-1-yl)acetate (2k):

Following the general procedure, the C–H olefination was carried out with 1k (82.6 mg, 0.2 mmol), [RhCp*Cl{2}]_{2} (6.2 mg, 0.01 mmol), NaOPiv (28.4 mg, 0.2 mmol), MeCN (2.0 mL) and ethyl acrylate (50.1 mg, 0.5 mmol) at 80 °C for 24 hours. The product 2k was obtained as white solid (81.8 mg, 80%) by flash column chromatography on silica gel using hexanes/EtOAc as the eluent. ^1^H NMR (500 MHz, CDCl_{3}): δ 7.96 (s, 1 H), 7.93 (d, J = 8.0 Hz, 1 H), 7.68 (d, J = 8.0 Hz, 1 H), 5.41 (t, J = 6.5 Hz, 1 H), 4.07 (q, J = 7.0 Hz, 2 H), 2.78 (dd, J_1 = 16.5 Hz, J_2 = 6.5 Hz, 1 H),
2.72 (dd, $J_1 = 16.5$ Hz, $J_2 = 6.5$ Hz, 1 H), 1.20 (t, $J = 7.0$ Hz, 3 H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 169.40, 166.40, 146.89, 144.89 (dd, $J_1 = 250.6$ Hz, $J_2 = 42.0$ Hz), 141.50 (d, $J = 255.5$ Hz), 138.49, 137.95 (d, $J = 251.1$ Hz), 132.95, 129.38, 126.02, 111.25, 61.45, 57.66, 38.26, 13.91.

HRMS (EI-TOF): $m/z$ Calc. for C$_{15}$H$_{11}$F$_{6}$NO$_3$ [M]: 510.9704, found 510.9709.

Ethyl 2-(6-fluoro-3-oxo-2-(perfluorophenyl)isoindolin-1-yl)acetate (2l):

Following the general procedure, the C–H olefination was carried out with 1l (61.0 mg, 0.2 mmol), [RhCp*Cl$_2$]$_2$ (6.2 mg, 0.01 mmol), NaOPiv (28.4 mg, 0.2 mmol), MeCN (2.0 mL) and ethyl acrylate (50.1 mg, 0.5 mmol) at 80 °C for 24 hours. The product 2l was obtained as white solid (66.9 mg, 83%) by flash column chromatography on silica gel using hexanes/EtOAc as the eluent.

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.96-7.93 (m, 1 H), 7.28 (d, $J = 8.5$ Hz, 1 H), 7.27 (s, 1 H), 5.43 (t, $J = 6.5$ Hz, 1 H), 4.08 (q, $J = 7.0$ Hz, 2 H), 2.80-2.71 (m, 2 H), 1.20 (t, $J = 7.0$ Hz, 3 H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 169.44, 166.00, 165.90 (d, $J = 252.8$ Hz), 147.81 (d, $J = 10.1$ Hz), 144.88 (dd, $J_1 = 252.4$ Hz, $J_2 = 36.4$ Hz), 141.44 (d, $J = 255.6$ Hz), 137.90 (d, $J = 253.9$ Hz), 126.96 (d, $J = 9.8$ Hz), 125.94, 117.04 (d, $J = 23.4$ Hz), 111.44, 110.53 (d, $J = 24.5$ Hz), 61.43, 57.88, 38.26, 13.89. HRMS (EI-TOF): $m/z$ Calc. for C$_{18}$H$_{11}$F$_{6}$NO$_3$ [M]: 403.0643, found 403.0643.

Ethyl 2-(4-fluoro-3-oxo-2-(perfluorophenyl)isoindolin-1-yl)acetate (2m):

Following the general procedure, the C–H olefination was carried out with 1m (61.0 mg, 0.2 mmol), [RhCp*Cl$_2$]$_2$ (6.2 mg, 0.01 mmol), NaOPiv (28.4 mg, 0.2 mmol), MeCN (2.0 mL) and ethyl acrylate (50.1 mg, 0.5 mmol) at 80 °C for 24 hours. The product 2m was obtained as white solid (64.5 mg, 80%) by flash column chromatography on silica gel using hexanes/EtOAc as the eluent.
eluent. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.67-7.63 (m, 1 H), 7.35 (d, $J = 8.0$ Hz, 1 H), 7.20 (t, $J = 8.5$ Hz, 1 H), 5.45 (t, $J = 6.5$ Hz, 1 H), 4.05 (q, $J = 7.0$ Hz, 2 H), 2.81 (dd, $J_1 = 17.0$ Hz, $J_2 = 6.0$ Hz, 1 H), 2.73 (dd, $J_1 = 16.5$ Hz, $J_2 = 7.0$ Hz, 1 H), 1.18 (t, $J = 7.0$ Hz, 3 H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 169.42, 163.76, 159.28 ($J = 261.6$ Hz), 147.70, 144.96 (dd, $J_1 = 253.8$ Hz, $J_2 = 40.4$ Hz), 141.48 (d, $J = 255.4$ Hz), 137.88 (d, $J = 256.5$ Hz), 135.19 (d, $J = 7.5$ Hz), 118.74, 117.41 (d, $J = 13.1$ Hz), 116.37 (d, $J = 18.9$ Hz), 111.26, 61.36, 57.92, 38.49, 13.84. HRMS (EI-TOF): $m/z$ Calc. for C$_{18}$H$_{11}$F$_6$NO$_3$ [M]: 403.0643, found 403.0642.

Ethyl 2-(5-fluoro-3-oxo-2-(perfluorophenyl)isoindolin-1-yl)acetate (2n):

Following the general procedure, the C–H olefination was carried out with 1n (61.0 mg, 0.2 mmol), [RhCp$^*$Cl$_2$]$_2$ (6.2 mg, 0.01 mmol), NaOPiv (28.4 mg, 0.2 mmol), MeCN (2.0 mL) and ethyl acrylate (50.1 mg, 0.5 mmol) at 80 °C for 24 hours. The product 2n was obtained as white solid (60.5 mg, 75%) by flash column chromatography on silica gel using hexanes/EtOAc as the eluent. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.77 (d, $J = 7.5$ Hz, 1 H), 7.58 (dd, $J_1 = 12.5$ Hz, $J_2 = 8.0$ Hz, 1 H), 7.36 (t, $J = 8.5$ Hz, 1 H), 5.60 (dd, $J_1 = 8.0$ Hz, $J_2 = 3.0$ Hz, 1 H), 4.01-3.91 (m, 2 H), 3.11 (dd, $J_1 = 16.5$ Hz, $J_2 = 3.0$ Hz, 1 H), 2.73 (dd, $J_1 = 16.5$ Hz, $J_2 = 8.0$ Hz, 1 H), 1.12 (t, $J = 7.0$ Hz, 3 H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 169.09, 166.01, 158.44, 156.45, 144.86 (dd, $J_1 = 248.8$ Hz, $J_2 = 45.8$ Hz), 141.45 (d, $J = 258.0$ Hz), 137.87 (d, $J = 241.5$ Hz), 131.83 (d, $J = 254.2$ Hz), 131.3 (d, $J = 5.9$ Hz), 120.73, 119.88 (d, $J = 19.6$ Hz), 111.47, 61.27, 58.34, 37.06, 13.74. HRMS (EI-TOF): $m/z$ Calc. for C$_{18}$H$_{11}$F$_6$NO$_3$ [M]: 403.0643, found 403.0642.
Ethyl 2-(4-methyl-3-oxo-2-(perfluorophenyl)isoindolin-1-yl)acetate (2o):

Following the general procedure, the C–H olefination was carried out with 1o (60.2 mg, 0.2 mmol), [RhCp*Cl$_2$]$_2$ (6.2 mg, 0.01 mmol), NaOPiv (28.4 mg, 0.2 mmol), MeCN (2.0 mL) and ethyl acrylate (50.1 mg, 0.5 mmol) at 80 °C for 24 hours. The product 2o was obtained as white solid (66.2 mg, 83%) by flash column chromatography on silica gel using hexanes/EtOAc as the eluent. $^1$H NMR (500 MHz, CDCl$_3$): δ 7.76 (s, 1 H), 7.47 (d, $J = 7.5$ Hz, 1 H), 7.42 (d, $J = 7.5$ Hz, 1 H), 5.42 (t, $J = 6.5$ Hz, 1 H), 4.05 (q, $J = 7.0$ Hz, 2 H), 2.77 (dd, $J_1 = 16.5$ Hz, $J_2 = 6.0$ Hz, 1 H), 2.69 (dd, $J_1 = 16.5$ Hz, $J_2 = 6.5$ Hz, 1 H), 2.48 (s, 3 H), 1.18 (t, $J = 7.0$ Hz, 3 H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 169.76, 167.27, 144.95 (dd, $J_1 = 245.7$ Hz, $J_2 = 36.2$ Hz), 142.58, 141.34 (d, $J = 251.1$ Hz), 139.37, 137.93 (d, $J = 249.9$ Hz), 134.08, 129.94, 124.86, 122.47, 111.89, 61.23, 58.18, 38.73, 21.28, 13.91. HRMS (EI-TOF): m/z Calc. for C$_{19}$H$_{14}$F$_{5}$N$_{3}$O$_{3}$ [M]: 399.0894, found 399.0893.

![Ethyl 2-(4-methyl-3-oxo-2-(perfluorophenyl)isoindolin-1-yl)acetate (2o):](image)

Ethyl 2-(6-oxo-5-(perfluorophenyl)-5, 6-dihydro-4H-thieno[2,3-c]pyrrol-4-yl)acetate (2p):

Following the general procedure, the C–H olefination was carried out with 1p (58.6 mg, 0.2 mmol), [RhCp*Cl$_2$]$_2$ (6.2 mg, 0.01 mmol), NaOPiv (28.4 mg, 0.2 mmol), MeCN (2.0 mL) and ethyl acrylate (50.1 mg, 0.5 mmol) at 100 °C for 24 hours. The product 2p was obtained as white solid (63.3 mg, 81%) by flash column chromatography on silica gel using hexanes/EtOAc as the eluent. $^1$H NMR (500 MHz, CDCl$_3$): δ 7.79 (d, $J = 5.0$ Hz, 1 H), 7.15 (d, $J = 5.0$ Hz, 1 H), 5.34 (t, $J = 7.0$ Hz, 1 H), 4.10 (q, $J = 7.0$ Hz, 2 H), 2.75 (dd, $J_1 = 16.5$ Hz, $J_2 = 6.0$ Hz, 1 H), 2.69 (dd, $J_1 = 16.5$ Hz, $J_2 = 7.5$ Hz, 1 H), 1.22 (t, $J = 7.0$ Hz, 3 H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 169.47, 162.60, 156.44, 145.07 (dd, $J_1 = 251.6$ Hz, $J_2 = 20.4$ Hz), 141.43 (d, $J = 254.1$ Hz), 137.92 (d, $J = 250.0$ Hz), 136.92, 133.40, 121.64, 111.75, 61.31, 57.67, 37.66, 13.95. HRMS (EI-TOF): m/z Calc. for C$_{16}$H$_{10}$F$_{5}$N$_{3}$O$_{3}$S [M]: 391.0302, found 391.0307.
(E)-Ethyl 3-(2-((perfluorophenyl)carbamoyl)furan-3-yl)acrylate (2q):

Following the general procedure, the C–H olefination was carried out with 1q (55.4 mg, 0.2 mmol), [RhCp*Cl₂]₂ (6.2 mg, 0.01 mmol), NaOPiv (28.4 mg, 0.2 mmol), MeCN (2.0 mL) and ethyl acrylate (50.1 mg, 0.5 mmol) at 100 °C for 24 hours. The product 2q was obtained as white solid (56.3 mg, 75%) by flash column chromatography on silica gel using hexanes/EtOAc as the eluent. 

$^{1}$H NMR (500 MHz, CDCl₃): δ 8.29 (d, J = 16.0 Hz, 1 H), 7.72 (s, 1 H), 7.52 (d, J = 1.5 Hz, 1 H), 6.80 (d, J = 1.5 Hz, 1 H), 6.36 (d, J = 16.0 Hz, 2 H), 4.25 (q, J = 7.0 Hz, 2 H), 1.31 (t, J = 7.0 Hz, 3 H); $^{13}$C NMR (125 MHz, CDCl₃): δ 156.01, 144.63, 156.44, 143.39 (dd, J₁ = 251.0 Hz, J₂ = 53.1 Hz), 140.38 (d, J = 253.9 Hz), 137.88 (d, J = 250.4 Hz), 133.29, 128.70, 123.58, 110.60, 60.73, 14.23. HRMS (EI-TOF): m/z Calc. for C₁₆H₁₀F₅NO₄ [M]: 375.0530, found 375.0505.

Ethyl 2-(1-oxo-2-(perfluorophenyl)-2,3-dihydro-1H-pyrrolo[3,4-c]pyridin-3-yl)acetate (2r):

Following the general procedure, the C–H olefination was carried out with 1r (57.6 mg, 0.2 mmol), [RhCp*Cl₂]₂ (6.2 mg, 0.01 mmol), NaOPiv (28.4 mg, 0.2 mmol), MeCN (2.0 mL) and ethyl acrylate (50.1 mg, 0.5 mmol) at 80 °C for 24 hours. The product 2r was obtained as white solid (64.6 mg, 84%) by flash column chromatography on silica gel using hexanes/EtOAc as the eluent. 

$^{1}$H NMR (500 MHz, CDCl₃): δ 9.01 (s, 1 H), 8.91 (d, J = 4.5 Hz, 1 H), 7.86 (d, J = 5.0 Hz, 1 H), 5.58 (t, J = 6.5 Hz, 1 H), 4.10 (q, J = 7.0 Hz, 2 H), 2.82 (d, J = 7.0 Hz, 2 H), 1.21 (t, J = 7.0 Hz, 3 H); $^{13}$C NMR (125 MHz, CDCl₃): δ 169.13, 165.42, 150.27, 145.48, 144.82 (dd, J₁ = 238.7 Hz, J₂ = 37.7 Hz), 141.74 (d, J = 255.5 Hz), 139.52, 138.03 (d, J = 254.2 Hz), 137.49, 118.13, 110.90, 61.58, 57.59, 37.89, 13.91. HRMS (EI-TOF): m/z Calc. for C₁₇H₁₂F₃N₂O₃ [M+H]⁺: 387.0768, found 387.0761.
Ethyl 2-(5-oxo-6-(perfluorophenyl)-6,7-dihydro-5H-pyrrolo[3,4-b]pyridin-7-yl)acetate (2s)

Following the general procedure, the C–H olefination was carried out with 1s (57.6 mg, 0.2 mmol), [RhCp*Cl₂]₂ (6.2 mg, 0.01 mmol), NaOPiv (28.4 mg, 0.2 mmol), MeCN (2.0 mL) and ethyl acrylate (50.1 mg, 0.5 mmol) at 80 °C for 24 hours. The product 2s was obtained as white solid (37.1 mg, 48%) by flash column chromatography on silica gel using hexanes/EtOAc as the eluent.

1H NMR (400 MHz, CDCl₃): δ 8.85 (dd, J₁ = 5.0 Hz, J₂ = 1.4 Hz, 1 H), 8.38 (dd, J₁ = 7.6 Hz, J₂ = 1.6 Hz, 1 H), 8.38 (dd, J₁ = 7.8 Hz, J₂ = 5.0 Hz, 1 H), 5.47 (dd, J₁ = 7.6 Hz, J₂ = 3.6 Hz, 1 H), 4.03-3.95 (m, 2 H), 3.19 (dd, J₁ = 16.8 Hz, J₂ = 3.6 Hz, 1 H), 2.79 (dd, J₁ = 16.8 Hz, J₂ = 7.6 Hz, 1 H), 1.13 (t, J = 6.8 Hz, 3 H); 13C NMR (125 MHz, CDCl₃): δ 169.31, 165.61, 164.56, 153.90, 144.81 (dd, J₁ = 252.8 Hz, J₂ = 46.3 Hz), 141.50 (d, J = 255.4 Hz), 137.89 (d, J = 251.5 Hz), 132.75, 123.93, 111.38, 61.21, 59.90, 36.83, 13.79. HRMS (EI-TOF): m/z Calc. for C₁₇H₁₂F₅N₂O₃ [M+H]⁺: 387.0768, found 387.0761.

7-Methyl-3-(2-oxobutyl)-2-(perfluorophenyl)isoindolin-1-one (4a)

Following the general procedure, the C–H olefination was carried out with 1a (60.2 mg, 0.2 mmol), [RhCp*Cl₂]₂ (6.2 mg, 0.01 mmol), NaOPiv (28.4 mg, 0.2 mmol), MeCN (2.0 mL) and ethyl vinyl ketone (42.0 mg, 0.5 mmol) at 80 °C for 24 hours. The product 4a was obtained as white solid (67.4 mg, 88%) by flash column chromatography on silica gel using hexanes/EtOAc as the eluent. 1H NMR (400 MHz, CDCl₃): δ 7.49 (t, J = 7.6 Hz, 1 H), 7.29-7.25 (m, 2 H), 5.51 (t, J = 6.4 Hz, 1 H), 2.91 (dd, J₁ = 18.0 Hz, J₂ = 6.0 Hz, 1 H), 2.83 (dd, J₁ = 18.0 Hz, J₂ = 6.0 Hz, 1 H), 2.73 (s, 3 H), 2.38 (q, J = 7.2 Hz, 2 H), 1.00 (t, J = 7.6 Hz, 3 H); 13C NMR (100 MHz, CDCl₃): δ 207.78, 168.09, 146.60, 144.88 (d, J = 254.3 Hz), 141.21 (d, J = 254.2 Hz), 138.95, 137.89 (d, J =
246.0 Hz), 132.55, 130.79, 126.88, 120.04, 112.32 (t, $J = 14.8$ Hz), 112.32 (t, $J = 14.8$ Hz), 56.63, 46.58, 36.41, 17.36, 7.49. HRMS (EI-TOF): $m/z$ Calc. for $C_{19}H_{14}F_{3}NO_{2}$ [M]: 383.0945, found 383.0951.

2-(4-Methyl-3-oxo-2-(perfluorophenyl)isoindolin-1-yl)acetonitrile (4b)

Following the general procedure, the C–H olefination was carried out with 1a (60.2 mg, 0.2 mmol), $[\text{RhCp*Cl}]_2$ (6.2 mg, 0.01 mmol), NaOPiv (28.4 mg, 0.2 mmol), MeCN (2.0 mL) and acrylonitrile (26.5 mg, 0.5 mmol) at 80 °C for 24 hours. The product 4b was obtained as white solid (38.7 mg, 55%) by flash column chromatography on silica gel using hexanes/EtOAc as the eluent. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.60 (t, $J = 7.6$ Hz, 1 H), 7.49 (d, $J = 7.6$ Hz, 1 H), 7.38 (d, $J = 7.6$ Hz, 1 H), 5.18 (t, $J = 5.8$ Hz, 1 H), 2.82 (d, $J = 6.0$ Hz, 2 H), 2.75 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 167.24, 145.29 (d, $J = 246.6$ Hz), 143.45, 141.68 (d, $J = 255.5$ Hz), 139.65, 137.95 (d, $J = 259.1$ Hz), 133.10, 131.96, 126.75, 119.94, 115.06, 110.84 (t, $J = 15.6$ Hz), 56.48, 22.76, 17.41. HRMS (EI-TOF): $m/z$ Calc. for $C_{17}H_{9}F_{5}N_{2}$O [M]: 352.0635, found 352.0640.

(E)-2-Methyl-N-(perfluorophenyl)-6-styrylbenzamide (5a)

Following the general procedure, the C–H olefination was carried out with 1a (60.2 mg, 0.2 mmol), $[\text{RhCp*Cl}]_2$ (6.2 mg, 0.01 mmol), NaOPiv (28.4 mg, 0.2 mmol), MeCN (2.0 mL) and styrene (52.0 mg, 0.5 mmol) at 80 °C for 24 hours. The product 5a was obtained as white solid (63.7 mg, 79%) by flash column chromatography on silica gel using hexanes/EtOAc as the eluent. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.49 (d, $J = 8.0$ Hz, 1 H), 7.44 (t, $J = 8.0$ Hz, 3 H), 7.34 (t, $J = 7.4$ Hz, 2 H), 7.29 (d, $J = 8.0$ Hz, 1 H), 7.17 (d, $J = 16.0$ Hz, 1 H), 7.08 (d, $J = 7.6$ Hz, 1 H), 7.01 (d, $J = 16.4$ Hz, 1 H), 2.31 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 168.54, 143.31 (d, $J = 248.4$ Hz),
Following the general procedure, the C–H olefination was carried out with 1a (60.2 mg, 0.2 mmol), [RhCp*Cl₂]₂ (6.2 mg, 0.01 mmol), NaOPiv (28.4 mg, 0.2 mmol), MeCN (2.0 mL) and 4-fluorostyrene (61.0 mg, 0.5 mmol) at 80 °C for 24 hours. The product 5b was obtained as white solid (53.9 mg, 64%) by flash column chromatography on silica gel using hexanes/EtOAc as the eluent. 

\(^1\)H NMR (400 MHz, CDCl₃): δ 7.46 (d, \(J = 8.8\) Hz, 1 H), 7.41 (dd, \(J_1 = 8.6\) Hz, \(J_2 = 5.4\) Hz, 2 H), 7.36 (s, 1 H), 7.30 (t, \(J = 8.0\) Hz, 1 H), 7.12-7.08 (m, 2 H), 7.06-6.97 (m, 3 H), 2.34 (s, 3 H); 

\(^{13}\)C NMR (100 MHz, CDCl₃): δ 168.52, 162.58 (d, \(J = 246.3\) Hz), 143.36 (d, \(J = 247.2\) Hz), 140.50 (d, \(J = 256.9\) Hz), 137.80 (d, \(J = 253.5\) Hz), 134.76 (d, \(J = 62.3\) Hz), 134.36, 132.87, 130.38, 129.74, 129.36, 128.19, 128.11, 124.22, 122.51, 115.66 (d, \(J = 21.7\) Hz), 111.01 (t, \(J = 15.2\) Hz), 18.99. HRMS (EI-TOF): \(m/z\) Calc. for C₂₂H₁₃F₆NO [M]: 421.0901, found 421.0904.

(E)-2-(4-Fluorostyryl)-6-methyl-N-(perfluorophenyl)benzamide (5b)

Following the general procedure, the C–H olefination was carried out with 1a (60.2 mg, 0.2 mmol), [RhCp*Cl₂]₂ (6.2 mg, 0.01 mmol), NaOPiv (28.4 mg, 0.2 mmol), MeCN (2.0 mL) and 4-vinylbenzyl acetate (88.1 mg, 0.5 mmol) at 80 °C for 24 hours. The product 5c was obtained as white solid (66.5 mg, 70%) by flash column chromatography on silica gel using hexanes/EtOAc as the eluent. 

\(^1\)H NMR (400 MHz, CDCl₃): δ 7.60, 7.50 (d, \(J = 8.0\) Hz, 1 H), 7.42 (d, \(J = 8.4\) Hz, 1 H), 7.40 (d, \(J = 8.0\) Hz, 1 H), 7.36 (s, 1 H), 7.30 (t, \(J = 8.0\) Hz, 1 H), 7.15-7.08 (m, 2 H), 7.06-6.97 (m, 3 H), 2.34 (s, 3 H); 

(E)-4-(3-Methyl-2-((perfluorophenyl)carbamoyl)styryl)benzyl acetate (5c)
Following the general procedure, the C–H olefination was carried out with 1a (60.2 mg, 0.2 mmol), [RhCp*Cl2]2 (6.2 mg, 0.01 mmol), NaOPiv (28.4 mg, 0.2 mmol), MeCN (2.0 mL) and 1-pentene (36 mg, 0.5 mmol) at 80 °C for 24 hours. The product 5d was obtained as white solid (32.5 mg, 44%) by flash column chromatography on silica gel using hexanes/EtOAc as the eluent. 

\(^1\)H NMR (400 MHz, CDCl₃): δ 7.30 (t, J = 7.8 Hz, 1 H), 7.19 (d, J = 7.6 Hz, 1 H), 7.10 (d, J = 7.6 Hz, 1 H), 7.00 (s, 1 H), 5.22 (d, J = 1.2 Hz, 1 H), 5.10 (s, 1 H), 2.44 (s, 3 H), 2.38 (t, J = 7.8 Hz, 2 H), 1.47–1.38 (m, 2 H), 0.91 (t, J = 7.4 Hz, 3 H); \(^{13}\)C NMR (100 MHz, CDCl₃): δ 167.90, 149.10, 143.19 (d, J = 242.1 Hz), 140.93, 140.31 (d, J = 240.4 Hz), 137.78 (d, J = 244.7 Hz), 135.82, 133.57, 129.57, 129.40, 126.24, 115.48, 111.32 (t, J = 14.8 Hz), 39.74, 21.19, 19.58, 13.74. 

HRMS (EI-TOF): m/z Calc. for C₂₅H₁₉F₅NO [M]: 475.1207, found 475.1209.

(E)-2-Methyl-6-(pent-1-en-1-yl)-N-(perfluorophenyl)benzamide (5d)
NMR Spectra
