Supporting Information for:

Merging Grubbs’ Second-Generation Catalyst with PhotocatalYSIS Enables Z–Selective Metathesis of Olefins: Scope, Limitations, and Mechanism

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1. General Methods and Materials

All reactions were carried out under argon using stand glovebox techniques (glovebox maintained at < 0.1 ppm H$_2$O and < 0.1 ppm O$_2$). Dichloromethane was dried using an MBRAUN Solvent Purification System (SPS) and sparged with argon. All chemicals were purchased from Sigma-Aldrich and used without further purifications. The catalyst 1,2,3,5-Tetrakis(carbazol-9-yl)-4,6-dicyanobenzene,2,4,5,6-Tetrakis(9H-carbazol-9-yl)isophthalonitrile (4CzIPN) was prepared according to a literature procedure.\(^1\)

All reaction mixtures were irradiated with 5W GU10 LED Lamp Blue from a 2 cm distance. The emission maximum of the light source used is 420 nm (Figure S1).

Flash column chromatography were carried out with Merck silica gel 60 (0.040–0.063 mm). Chromatography fractions and stated reactions were monitored by TLC on Merck silica gel 60 F254 aluminum plates. The spots were visualized under UV light at 254 nm. UV-Visible spectra were recorded on a Perkin Elmer Lambda 40 Spectrophotometer. High resolution mass spectrometry (HRMS) analyses were performed on a Q Exactive Mass Spectrometer (Thermofisher) using direct injection.

\(^1\)H NMR (300 MHz); \(^{19}\)F (282 MHz) and \(^{13}\)C proton decoupling (75 MHz) spectra were recorded on an Agilent Direct Drive spectrometer (Agilent Technologies, Santa Clara) in CDCl$_3$. The chemical shifts are given in ppm and refer to CDCl$_3$ (\(\delta\) H = 7.26, \(\delta\) C = 77.16) as internal standard. Coupling constants $J$ are measured in Hz. Splitting patterns are designed as follows: $s$ = singlet; $d$ = doublet; $t$ = triplet; $q$ = quartet, $dd$ = doublet of doublet; $dt$ = doublet of triplet; $m$ = multiplet.

Transient absorption spectra were measured with an LP920-KS spectrometer from Edinburgh Instruments.
2. Procedure for synthesis

General procedure for homodimerization reaction (8a to 8k).\textsuperscript{2,3}

A flame-dried quartz Schlenk tube was charged with styrene (1.0 eq. 0.1 M) and dichloromethane was added to make a final concentration of 1.0 M styrene (conc. of 0.5 M if you consider that 0.5 eq. reacts with the other 0.5 eq. to give 1.0 eq. of stilbene). Then, Grubbs 2\textsuperscript{nd} generation catalyst (1 mol %) and the 4CzIPN (1 mol %) were then added in one portion. The reaction mixture was stirred at 40 °C for 12h under argon and at 420 nm. The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography on silica gel (100% pentane) to provide the Z isomers.
Compound (8a):

Styrene (183 µL, 1.6 mmol); Grubbs 2nd generation catalyst (6.8 mg, 0.008 mmol, 1 mol %); 4CzIPN (6.3 mg, 0.008 mmol, 1 mol %).

Purification (colorless oil, 127 mg, 0.7 mmol, 88 %). ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.29 - 7.17 (m, 10H), 6.61 (s, 2H). ¹³C NMR (75 MHz, CDCl₃) δ (ppm) 137.4, 130.4, 129.0, 128.3, 127.2. HRMS (ESI+) for C₁₄H₁₂ [M] +: calc. 180.0939; found: 180.0947.

Compound (8b):

4-methylstyrene (210 µL, 1.6 mmol); Grubbs 2nd generation catalyst (6.8 mg, 0.008 mmol, 1 mol %); 4CzIPN (6.3 mg, 0.008 mmol, 1 mol %).

Purification (colorless oil, 110 mg, 0.53 mmol, 66 %). ¹H NMR (300 MHz, CDCl₃) δ 7.18 (d, J = 9.0 Hz, 4H), 7.05 (d, J = 9.0 Hz, 4H), 6.53 (s, 2H), 2.33 (s, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 136.9, 134.6, 129.7, 129.0, 128.9, 21.4. HRMS (ESI+) for C₁₆H₁₆ [M] +: calc. 208.1252; found: 208.1255.

Compound (8c):

4-methoxystyrene (214 µL, 1.6 mmol); Grubbs 2nd generation catalyst (6.8 mg, 0.008 mmol, 1 mol %); 4CzIPN (6.3 mg, 0.008 mmol, 1 mol %).
Purification (Colorless oil, 79 mg, 0.33 mmol, 41%).\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 7.20 (d, \(J = 9.0\) Hz, 4H), 6.77 (d, \(J = 9.0\) Hz, 4H), 6.45 (s, 2H), 3.79 (s, 6H).\textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 158.7, 130.2, 130.1, 128.5, 113.7, 55.3.

HRMS (ESI+) for C\textsubscript{16}H\textsubscript{16}O\textsubscript{2} [M] +: calc. 240.1150; found: 240.1157.

**Compound (8d):**

![Compound (8d) structure](image)

4-acetoxy styrene (245 \(\mu\)L, 1.6 mmol); Grubbs 2\textsuperscript{nd} generation catalyst (6.8 mg, 0.008 mmol, 1 mol %); 4CzIPN (6.3 mg, 0.008 mmol, 1 mol %).

Purification (White solid, 189 mg, 0.64 mmol, 80 %).\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 7.26 (d, \(J = 9.0\) Hz, 4H), 6.96 (d, \(J = 9.0\) Hz, 4H), 6.56 (s, 2H), 2.28 (s, 6H).\textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 169.5, 149.8, 134.7, 130.0, 129.6, 121.6, 21.3.

HRMS (ESI+) for C\textsubscript{18}H\textsubscript{16}O\textsubscript{4} [M] +: calc. 296.1049; found: 296.1055.

**Compound (8e):**

![Compound (8e) structure](image)

4-vinylbenzyl chloride (225 \(\mu\)L, 1.6 mmol); Grubbs 2\textsuperscript{nd} generation catalyst (6.8 mg, 0.008 mmol, 1 mol %); 4CzIPN (6.3 mg, 0.008 mmol, 1 mol %).

Purification (White solid, 123 mg, 0.45 mmol, 56 %).\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 7.28 – 7.22 (m, 8H), 6.60 (s, 2H), 4.56 (s, 4H).\textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 137.4, 136.5, 130.3, 129.3, 128.7, 46.2.

HRMS (ESI+) for C\textsubscript{18}H\textsubscript{14}Cl\textsubscript{2} [M] +: calc. 276.0473; found: 276.0471.
**Compound (8f):**

4-chlorostyrene (191 µL, 1.6 mmol); Grubbs 2nd generation catalyst (6.8 mg, 0.008 mmol, 1 mol %); 4CzIPN (6.3 mg, 0.008 mmol, 1 mol %).

Purification (Colorless oil, 121 mg, 0.49 mmol, 61%).$^{1}$H NMR (300 MHz, CDCl$_3$) δ 7.22 – 7.13 (m, 8H), 6.56 (s, 2H).$^{13}$C NMR (75 MHz, CDCl$_3$) δ 135.4, 133.2, 130.3, 129.8, 128.7. HRMS (ESI+) for C$_{14}$H$_{10}$Cl$_2$ [M$^+$]: calc. 248.0160; found: 248.0168.

**Compound (8g):**

4-fluorostyrene (191 µL, 1.6 mmol); Grubbs 2nd generation catalyst (6.8 mg, 0.008 mmol, 1 mol %); 4CzIPN (6.3 mg, 0.008 mmol, 1 mol %).

Purification (Colorless oil, 102 mg, 0.47 mmol, 59%).$^{1}$H NMR (300 MHz, CDCl$_3$) δ 7.22 – 7.17 (m, 4H), 6.96 – 6.91 (m, 4H), 6.55 (s, 2H).$^{19}$F NMR (282 MHz, CDCl$_3$) δ -114.5. $^{13}$C NMR (75 MHz, CDCl$_3$) δ 162.0 (d, J = 246.9 Hz), 133.1 (d, J = 3.3 Hz), 130.6 (d, J = 7.9 Hz), 129.2 (d, J = 1.4 Hz), 115.4 (d, J = 21.3 Hz).

HRMS (ESI+) for C$_{14}$H$_{11}$F$_2$ [M$^+$]: calc. 217.0829; found: 217.0836.

**Compound (8h):**

4-(trifluoromethyl)styrene (236 µL, 1.6 mmol); Grubbs 2nd generation catalyst (6.8 mg, 0.008 mmol, 1 mol %); 4CzIPN (6.3 mg, 0.008 mmol, 1 mol %).
Purification (White solid, 152 mg, 0.48 mmol, 60 %).\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 7.51 (d, \(J = 7.5\) Hz, 4H), 7.32 (d, \(J = 7.5\) Hz, 4H), 6.73 (s, 2H).\textsuperscript{19}F NMR (282 MHz, CDCl\textsubscript{3}) \(\delta\) - 62.6. \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 140.3, 130.9, 129.6 (q, \(J = 32.6\) Hz), 129.3, 125.6 (q, \(J = 3.8\) Hz), 124.1 (q, \(J = 270.0\) Hz).

HRMS (ESI+) for C\textsubscript{16}H\textsubscript{10}F\textsubscript{6} [M] +: calc. 316.0687; found: 316.0694.

**Compound (8i):**

![2-vinylnaphtalene](image)

2-vinylnaphtalene (247 \(\mu\)L, 1.6 mmol); Grubbs 2\textsuperscript{nd} generation catalyst (6.8 mg, 0.008 mmol, 1 mol %); 4CzIPN (6.3 mg, 0.008 mmol, 1 mol %).

Purification (White solid, 115 mg, 0.41 mmol, 51 %).\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 7.79 - 7.62 (m, 8H), 7.47 - 7.36 (m, 6H), 6.85 (s, 2H).\textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 135.0, 133.6, 132.8, 130.7, 128.3, 128.1, 127.8, 127.7, 127.1, 126.2, 126.1.

HRMS (ESI+) for C\textsubscript{22}H\textsubscript{16} [M] +: calc. 280.1252; found: 280.1266.

**Compound (8j):**

![3-fluorostyrene](image)

3-fluorostyrene (190 \(\mu\)L, 1.6 mmol); Grubbs 2\textsuperscript{nd} generation catalyst (6.8 mg, 0.008 mmol, 1 mol %); 4CzIPN (6.3 mg, 0.008 mmol, 1 mol %).

Purification (Colorless oil, 105 mg, 0.48 mmol, 61 %).\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 7.23 - 7.17 (m, 2H), 7.00 (dt, \(J = 7.0\), 1.2 Hz, 2H), 6.94 - 6.89 (m, 4H), 6.60 (s, 2H).\textsuperscript{19}F NMR (282 MHz, CDCl\textsubscript{3}) \(\delta\) -113.2. \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 162.9 (d, \(J = 244.1\) Hz), 139.1 (d, \(J = 7.8\) Hz), 130.3 (d, \(J = 2.4\) Hz), 130.0 (d, \(J = 8.2\) Hz), 124.8 (d, \(J = 2.9\) Hz), 115.7 (d, \(J = 21.7\) Hz), 114.5 (d, \(J = 21.2\) Hz).

HRMS (ESI+) for C\textsubscript{14}H\textsubscript{10}F\textsubscript{2} [M] +: calc. 217.0829; found: 217.0831.
Compound (8k):

3-chlorostyrene (203 µL, 1.6 mmol); Grubbs 2nd generation catalyst (6.8 mg, 0.008 mmol, 1 mol %); 4CzIPN (6.3 mg, 0.008 mmol, 1 mol %).

Purification (Colorless oil, 137 mg, 0.55 mmol, 69 %).\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 7.23 – 7.13 (m, 6H), 7.10 – 7.07 (m, 2H), 6.58 (s, 2H).\textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 138.6, 134.4, 130.2, 129.7, 129.0, 127.6, 127.1.

HRMS (ESI+) for C\textsubscript{14}H\textsubscript{10}Cl\textsubscript{2} [M] +: calc. 249.0238; found: 249.0244.
Procedure for metathesis reaction of styrene derivatives with cis-2-butene-1,4-diacetate (8l-8o):

In a flame-dried quartz Schlenk tube, styrene (1.0 eq) was dissolved in dichloromethane to give concentration (0.2 M) and the cis-2-butene-1,4-diacetate (2.4 eq), fac-Ir(ppy)_3 (5 mol %) and 2\textsuperscript{nd} generation catalyst (5 mol %) were added. The reaction mixture was stirred at 40 °C for 24h under argon and irradiated at 420 nm. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (pentane/Ethyl acetate 95/5).

**Compound (8l):**

\[
\text{cis-2-butene-1,4-diacetate (153 \mu{L}, 0.96 mmol); 2-chlorostyrene (51 \mu{L}, 0.4 mmol); fac-Ir(ppy)_3 (13 mg, 0.02 mmol, 5 mol%); 2\textsuperscript{nd} generation catalyst (17 mg, 0.02 mmol, 5 mol%).}
\]

Purification (Colorless oil, 63 mg, 0.3 mmol, 75% (Z:E = 92:8 in isolated product).

**Z isomer (major):** \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta \quad 7.40 - 7.38 \text{ (m, 1H)}, \quad 7.26 - 7.22 \text{ (m, 3HZ + 3HE)}, \quad 6.78 \text{ (dt, } J = 11.4, 1.6 \text{ Hz, 1H}), \quad 5.93 \text{ (dt, } J = 11.4, 6.6 \text{ Hz, 1H}), \quad 4.71 \text{ (dd, } J = 6.6, 1.6 \text{ Hz), 2.07 (s, 3H)}. \quad 13\text{C NMR (75 MHz, CDCl}_3\)) \(\delta \quad 171.0, \quad 134.3, \quad 133.8, \quad 130.6, \quad 130.5, \quad 129.7, \quad 129.1, \quad 127.3, \quad 126.7, \quad 61.4, \quad 21.1.\)

**E isomer (minor):** \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta \quad 7.54 - 7.51 \text{ (m, 1H)}, \quad 7.26 - 7.22 \text{ (m, 3HZ + 3HE)}, \quad 7.04 \text{ (dt, } J = 16.0, 1.6 \text{ Hz, 1H}), \quad 6.27 \text{ (dt, } J = 16.0, 6.9 \text{ Hz, 1H}), \quad 4.76 \text{ (dd, } J = 6.9, 1.6 \text{ Hz), 2.11 (s, 3H)}. \quad 13\text{C NMR (75 MHz, CDCl}_3\)) \(\delta \quad 171.0, \quad 134.5, \quad 133.4, \quad 130.1, \quad 129.9, \quad 129.2, \quad 127.1, \quad 127.0, \quad 126.2, \quad 65.0, \quad 21.1.\)

HRMS (ESI+) for C\(_{11}\)H\(_{11}\)O\(_2\)Cl [M] +: calc. 210.0448; found: 210.0444.

**Compound (8m):**

\[
\text{cis-2-butene-1,4-diacetate (153 \mu{L}, 0.96 mmol); 2-chlorostyrene (51 \mu{L}, 0.4 mmol); fac-Ir(ppy)_3 (13 mg, 0.02 mmol, 5 mol%); 2\textsuperscript{nd} generation catalyst (17 mg, 0.02 mmol, 5 mol%).}
\]

Purification (Colorless oil, 63 mg, 0.3 mmol, 75% (Z:E = 92:8 in isolated product).

**Z isomer (major):** \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta \quad 7.40 - 7.38 \text{ (m, 1H)}, \quad 7.26 - 7.22 \text{ (m, 3HZ + 3HE)}, \quad 6.78 \text{ (dt, } J = 11.4, 1.6 \text{ Hz, 1H}), \quad 5.93 \text{ (dt, } J = 11.4, 6.6 \text{ Hz, 1H}), \quad 4.71 \text{ (dd, } J = 6.6, 1.6 \text{ Hz), 2.07 (s, 3H)}. \quad 13\text{C NMR (75 MHz, CDCl}_3\)) \(\delta \quad 171.0, \quad 134.3, \quad 133.8, \quad 130.6, \quad 130.5, \quad 129.7, \quad 129.1, \quad 127.3, \quad 126.7, \quad 61.4, \quad 21.1.\)

**E isomer (minor):** \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta \quad 7.54 - 7.51 \text{ (m, 1H)}, \quad 7.26 - 7.22 \text{ (m, 3HZ + 3HE)}, \quad 7.04 \text{ (dt, } J = 16.0, 1.6 \text{ Hz, 1H}), \quad 6.27 \text{ (dt, } J = 16.0, 6.9 \text{ Hz, 1H}), \quad 4.76 \text{ (dd, } J = 6.9, 1.6 \text{ Hz), 2.11 (s, 3H)}. \quad 13\text{C NMR (75 MHz, CDCl}_3\)) \(\delta \quad 171.0, \quad 134.5, \quad 133.4, \quad 130.1, \quad 129.9, \quad 129.2, \quad 127.1, \quad 127.0, \quad 126.2, \quad 65.0, \quad 21.1.\)

HRMS (ESI+) for C\(_{11}\)H\(_{11}\)O\(_2\)Cl [M] +: calc. 210.0448; found: 210.0444.
cis-2-butene-1,4-diacetate (150 µL, 0.96 mmol); 2-methylstyrene (52 µL, 0.4 mmol); fac-Ir(ppy)_3 (13 mg, 0.02 mmol, 5 mol %); 2nd generation catalyst (17 mg, 0.02 mmol, 5 mol %).

Purification (Colorless oil, 38 mg, 0.2 mmol, 50 % (Z isomer)).[^1] ^1^H NMR (300 MHz, CDCl₃) δ 7.20 - 7.08 (m, 4H), 6.73 (dt, J = 11.4, 1.6 Hz, 1H), 5.86 (dt, J = 11.4, 6.8 Hz, 1H), 4.70 (dd, J = 6.8, 1.6 Hz, 2H), 2.27 (s, 3H), 2.06 (s, 3H). ^1^3^C NMR (75 MHz, CDCl₃) δ 171.0, 136.4, 135.2, 132.7, 130.1, 129.1, 127.9, 125.9, 125.8, 61.6, 21.1, 20.0. HRMS (ESI+) for C₁₂H₁₄O₂ [M] +: calc. 190.0994; found: 190.1002.

**Compound (8n):**

![Chemical Structure](image)

[^1]: Z isomer (major): ^1^H NMR (300 MHz, CDCl₃) δ 7.36 - 7.27 (m, 1HZ + 1HE), 7.01 - 6.91 (m, 3H), 6.62 (d, J = 12.1 Hz, 1H), 5.85 (dt, J = 12.1, 6.6 Hz, 1H), 4.82 (dd, J = 6.6, 1.7 Hz, 2H), 2.09 (s, 3H). ^1^9^F NMR (282 MHz, CDCl₃) δ -113.1. ^1^3^C NMR (75 MHz, CDCl₃) δ 171.0, 160.0 (d, J = 240.1 Hz); 130.5 (d, J = 3.5 Hz), 129.7 (d, J = 8.3 Hz), 127.9, 125.7 (d, J = 3.6 Hz), 124.0 (d, J = 3.9 Hz), 123.8 (d, J = 14.6 Hz), 115.6 (d, J = 22.0 Hz), 61.7, 21.0.

**E isomer (minor):** ^1^H NMR (300 MHz, CDCl₃) δ 7.36 - 7.27 (m, 1HZ + 1HE), 7.16 - 7.07 (m, 3H), 6.67 (d, J = 15.9 Hz, 1H), 6.29 (dt, J = 15.9, 6.3 Hz, 1H), 4.73 (dd, J = 6.3, 1.4 Hz, 2H), 2.11 (s, 3H). ^1^9^F NMR (282 MHz, CDCl₃) δ -113.4. ^1^3^C NMR (75 MHz, CDCl₃) δ 171.0, 160.4 (d, J = 240.1 Hz), 129.5 (d, J = 9.8 Hz), 127.7 (d, J = 3.5 Hz), 126.5 (d, J = 3.5 Hz), 126.0 (d, J = 5.0 Hz), 124.2 (d, J = 3.8 Hz), 129.4, 115.9 (d, J = 21.9 Hz), 65.2, 21.1

HRMS (ESI+) for C₁₁H₁₁O₂F [M] +: calc. 194.0743; found: 194.0759.
**Compound (8o):**

\[ \text{NC-} \quad \text{Cis-2-butene-1,4-diacetate (150 µL, 0.96 mmol); 4-cyanostyrene (52 µL, 0.40 mmol); fac-Ir(ppy)_3 (13 mg, 0.02 mmol, 5 mol %); 2^{nd} generation catalyst (17 mg, 0.02 mmol, 5 mol %).} \]

Purification (Colorless oil, 33 mg, 0.16 mmol, 42 % (Z isomer). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.61 (d, \(J = 8.3\) Hz, 2H), 7.46 (d, \(J = 8.3\) Hz, 2H), 6.65 (d, \(J = 12.6\) Hz, 1H), 6.41 (dt, \(J = 12.6, 1.6\) Hz, 1H), 4.76 (dd, \(J = 6.6, 1.6\) Hz), 2.12 (s, 3H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 170.8, 140.8, 132.6, 132.5, 132.0, 127.5, 127.2, 111.5, 64.5, 21.0.

2-3-Procedure for metathesis reaction of styrene derivatives with 5-hexenyl-1-acetate (8p-8q):

In flame dried flask, styrene (3.0 eq), fac-Ir(ppy)_3 (5 mol %) and 2^{nd} generation catalyst (5 mol%) were added to a solution of 5-hexenyl-1-acetate (1.0 eq) in dichloromethane (0.18 M). The reaction mixture was stirred at 40 °C for 24h under argon and irradiated at 420 nm. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (pentane/Ethyl acetate 95/5) to provide the compound.

**Compound (8p):**

\[ \text{Cl-} \quad \text{5-hexenyl-1-acetate (72 µL, 0.45 mmol), 2-fluorostyrene (174 µL, 1.36 mmol) and fac-Ir(ppy)_3 (15 mg, 0.022 mmol, 5 mol %) 2^{nd} generation catalyst (19 mg, 0.022 mmol, 5 mol %).} \]

Purification (colorless oil, 84 mg, 0.33 mmol, 74% (Z:\(E = 92:8\) in isolated product).

**Z isomer (major):** \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.39 – 7.36 (m, 1H), 7.28 – 7.13 (m, 3H), 6.52 (d, \(J = 12.0\) Hz, 1H), 5.77 (dt, \(J = 12.0, 7.4\) Hz, 1H), 4.02 (t, \(J = 6.6\) Hz, 2H), 2.31 – 2.17
(m, 2Hz + 1HE), 2.02 (s, 3H), 1.81 – 1.43 (m, 4Hz + 4HE).\(^1\)\(^3\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 171.3, 135.8, 133.7, 132.7, 130.6, 129.5, 128.2, 126.8, 126.3, 64.4, 28.3, 28.1, 26.1, 21.1.

**E isomer (minor):** \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.51 – 7.48 (m, 1H), 7.34 – 7.31 (m, 3H), 6.77 (d, \(J = 15.0\) Hz, 1H), 6.20 (dt, \(J = 15.0, 7.2\) Hz, 1H), 4.13 (t, \(J = 6.6\) Hz, 2H), 2.56 – 2.49 (m, 1H), 2.31 – 2.17 (m, 2Hz + 1HE), 2.05 (s, 3H), 1.81 – 1.43 (m, 4Hz + 4HE).\(^1\)\(^3\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 171.2, 135.7, 133.7, 133.3, 130.5, 129.7, 128.3, 127.4, 126.7, 63.9, 28.6, 25.7, 24.9, 21.0.

HRMS (ESI+) for C\(_{14}\)H\(_{17}\)O\(_2\)Cl [M] +: calc. 252.0917; found: 252.0930.

**Compound (8q):**

![5-hexenyl-1-acetate](image)

5-hexenyl-1-acetate (70 \(\mu\)L, 0.45 mmol), 2-methylstyrene (176 \(\mu\)L, 1.36 mmol) and Fac-Ir(ppy)\(_3\) (15 mg, 0.022 mmol, 5 mol%) 2\(^{nd}\) generation catalyst (19 mg, 0.022 mmol, 5 mol%).

Purification (Colorless oil, 84 mg, 0.36 mmol, 80 % (\(Z:E = 94:6\) in isolated product)).

**Z isomer (major) :** \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.20 – 7.13 (m, 4Hz + 4HE), 6.46 (dt, \(J = 11.4, 1.8\) Hz, 1H), 5.69 (dt, \(J = 11.4, 7.4\) Hz, 1H), 4.02 (t, \(J = 6.6\) Hz, 2H), 2.25 (s, 3H), 2.23 – 2.15 (m, 2H), 2.03 (s, 3H), 1.81 – 1.38 (m, 4Hz + 4HE).\(^1\)\(^3\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 171.2, 136.8, 136.4, 132.2, 129.9, 129.1, 128.6, 126.9, 125.4, 64.5, 28.3, 28.0, 26.3, 21.1, 20.0.

**E isomer (minor):** \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.21 – 7.12 (m, 4HE + 4HZ), 6.50 (d, \(J = 15.7\) Hz, 1H), 6.07 (dt, \(J = 15.7, 6.9\) Hz, 1H), 4.03 (t, \(J = 6.6\) Hz, 2H), 2.53 – 2.43 (m, 1H), 2.34 (s, 3H), 2.06 (s, 3H), 1.81 – 1.38 (m, 4HZ + 4HE).\(^1\)\(^3\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 171.1, 136.6, 136.4, 131.2, 130.3, 129.3, 129.0, 127.0, 125.6, 63.9, 29.8, 28.7, 24.7, 21.0, 20.0.

HRMS (ESI+) for C\(_{13}\)H\(_{20}\)O\(_2\) [M] +: calc. 232.1461; found: 232.1463.

2-4-General procedure for metathesis reaction (Cross metathesis 8r-8zf):

A flame-dried quartz Schlenk tube was charged under argon with styrene (1.0 eq) and dichloromethane (0.05 M). Next, alkyl acrylate (2.0 to 5.0 eq), Grubbs 2\(^{nd}\) generation catalyst
(2 mol %) and 4CzIPN (5 mol %) were added in one portion. The Schlenk tube was closed with a cap and then it stirred at 40 °C under argon for 24h and irradiated at 420 nm. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica gel, pentane/Ethyl acetate 98/2) to provide the compound.

**Compound (8r):**

![Chemical structure](image)

Styrene (80 µL, 0.7 mmol); Methyl acrylate (317 µL, 3.5 mmol, 5.0 eq) Grubbs 2nd generation catalyst (12 mg, 0.014 mmol, 2 mol %); 4CzIPN (27.7 mg, 0.035 mmol, 5 mol %).

Purification (Colorless solid, 64 mg, 0.39 mmol, 56% (Z isomer)). ¹H NMR (300 MHz, CDCl₃) δ 7.61 – 7.57 (m, 2H), 7.37 – 7.34 (m, 3H), 6.96 (d, J = 12.6 Hz, 1H), 5.96 (d, J = 12.6 Hz, 1H), 3.71 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 166.8, 143.6, 134.9, 129.8, 129.2, 128.2, 119.4, 51.5.

HRMS (ESI+) for C₁₀H₁₁O₂ [M] +: calc. 163.0759; found: 163.0764.

**Compound (8s):**

![Chemical structure](image)

4-methylstyrene (93 µL, 0.7 mmol); Methyl acrylate (317 µL, 3.5 mmol, 5 eq); Grubbs 2nd generation catalyst (12 mg, 0.014 mmol, 2 mol %); 4CzIPN (27.7 mg, 0.035 mmol, 5 mol %).

Purification (Colorless oil, 62 mg, 0.35 mmol, 50 % (Z isomer)). ¹H NMR (300 MHz, CDCl₃) δ 7.53 (d, J = 9.0 Hz, 2H), 7.17 (d, J = 9.0 Hz, 2H), 6.92 (d, J = 12.7 Hz, 1H), 5.90 (d, J = 12.7 Hz, 1H), 3.72 (s, 3H), 2.36 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 166.9, 143.7, 139.5, 132.0, 130.1, 128.9, 118.4, 51.5, 21.6.

HRMS (ESI+) for C₁₁H₁₂O₂ [M] +: calc. 176.0837; found: 176.0834.
Compound (8t):  

4-acetoxy styrene (107 µL, 0.7 mmol); Methyl acrylate (317 µL, 3.5 mmol, 5 eq); Grubbs 2\textsuperscript{nd} generation catalyst (12 mg, 0.014 mmol, 2 mol %); 4CzIPN (27.7 mg, 0.035 mmol, 5 mol %).  

Purification (White solid, 77 mg, 0.35 mmol, 50\% (Z isomer)). \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 7.67 (d, \(J = 9.0\) Hz, 2H), 7.09 (d, \(J = 9.0\) Hz, 2H), 6.91 (d, \(J = 12.7\) Hz, 1H), 5.95 (d, \(J = 12.7\) Hz, 1H), 3.71 (s, 3H), 2.30 (s, 3H). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 169.3, 166.6, 151.2, 142.6, 132.4, 131.4, 121.3, 119.4, 51.5, 21.3.  

HRMS (ESI+) for C\textsubscript{12}H\textsubscript{13}O\textsubscript{4}[M] +: calc. 221.0814; found: 221.0817.  

Compound (8u):  

4-chlorostyrene (84 µL, 0.7 mmol); Methyl acrylate (317 µL, 3.5 mmol, 5 eq); Grubbs 2\textsuperscript{nd} generation catalyst (12 mg, 0.014 mmol, 2 mol %); 4CzIPN (27.7 mg, 0.035 mmol, 5 mol %).  

Purification (Yellow oil, 68 mg, 0.35 mmol, 50\% (Z isomer)). \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 7.55 (d, \(J = 9.0\) Hz, 2H), 7.32 (d, \(J = 9.0\) Hz, 2H), 6.88 (d, \(J = 12.7\) Hz, 1H), 5.97 (d, \(J = 12.7\) Hz, 1H), 3.71 (s, 3H). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 166.5, 142.4, 135.2, 133.3, 131.3, 128.4, 119.9, 51.6.  

HRMS (ESI+) for C\textsubscript{10}H\textsubscript{10}O\textsubscript{2}Cl [M] +: calc. 197.0369; found: 197.0367.
**Compound (8v):**

\[
\begin{array}{c}
\text{CO}_2\text{CH}_3 \\
F
\end{array}
\]

4-fluorostyrene (84 µL, 0.7 mmol); Methyl acrylate (317 µL, 3.5 mmol, 5 eq); Grubbs 2nd generation catalyst (12 mg, 0.014 mmol, 2 mol %); 4CzIPN (27.7 mg, 0.035 mmol, 5 mol %).

Purification (Colorless oil, 91 mg, 0.5 mmol, 72% (Z isomer)). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.67 – 7.61 (m, 2H), 7.08 – 7.00 (m, 2H), 6.89 (d, \(J = 12.7\) Hz, 1H), 5.93 (d, \(J = 12.7\) Hz, 1H), 3.72 (s, 3H). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) -111.3. \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 166.6, 163.1 (d, \(J = 250.0\) Hz), 142.6, 132.2 (d, \(J = 8.3\) Hz), 130.9 (d, 3.4 Hz), 119.0 (d, \(J = 1.7\) Hz), 115.1 (d, \(J = 21.5\) Hz), 51.5.

HRMS (ESI+) for C\(_{10}\)H\(_{10}\)O\(_2\)F [M]+: calc. 181.0665; found: 181.0663.

**Compound (8w):**

\[
\begin{array}{c}
\text{CO}_2\text{CH}_3 \\
\text{F}_3\text{C}
\end{array}
\]

4-(trifluoromethyl)styrene (104 µL, 0.7 mmol); Methyl acrylate (317 µL, 3.5 mmol, 5.0 eq); Grubbs 2nd generation catalyst (12 mg, 0.014 mmol, 2 mol %); 4CzIPN (27.7 mg, 0.035 mmol, 5 mol %).

Purification (Colorless oil, 138 mg, 0.6 mmol, 86% (Z:E = 82:18 in isolated product).

**Z isomer (major):** \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.66 – 7.59 (m, 4HZ + 4HE), 6.99 (d, \(J = 12.6\) Hz, 1H), 6.07 (d, \(J = 12.6\) Hz, 1H), 3.71 (s, 3H). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) -62.9. \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 166.2, 142.0, 138.4, 130.7 (q, 32.0 Hz), 129.8, 125.1 (q, \(J = 3.8\) Hz), 121.6, 120.9 (q, 270.0 Hz), 51.7.

**E isomer (minor):** \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.70 (d, \(J = 16.0\) Hz, 1H), 7.68 – 7.59 (m, 4HZ + 4HE), 6.51 (d, \(J = 16.0\) Hz, 1H), 3.83 (s, 3H). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) -62.8. \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 167.0, 143.1, 137.9, 131.9 (q, 32 Hz), 128.3, 126.0 (q, \(J = 3.8\) Hz), 120.9 (q, 270 Hz), 120.5, 52.1.
HRMS (ESI+) for C₁₁H₁₀O₂F₃ [M] +: calc. 231.0633; found: 231.0623.

**Compound (8x):**

![Structure of 2-fluorostyrene](image)

2-fluorostyrene (83 µL, 0.7 mmol); Methyl acrylate (127 µL, 1.4 mmol, 2eq); Grubbs 2nd generation catalyst (12.0 mg, 0.014 mmol, 2 mol %); 4CzIPN (27.7 mg, 0.035 mmol, 5 mol %).

Purification (Yellow oil, 64 mg, 0.35 mmol, 51% (Z isomer)). ¹H NMR (300 MHz, CDCl₃) δ 7.63 – 7.58 (m, 1H), 7.36 – 7.28 (m, 1H), 7.15 – 7.02 (m, 3H), 6.08 (d, J = 12.5 Hz, 1H), 3.70 (s, 3H). ¹³F NMR (282 MHz, CDCl₃) δ -114.1. ¹³C NMR (75 MHz, CDCl₃) δ 166.3, 160.3 (d, 249.7 Hz), 136.0 (d, J = 3.9 Hz), 130.9 (d, J = 2.5 Hz), 130.8 (d, J = 8.5 Hz), 123.6 (d, J = 3.7 Hz), 123.0 (d, J = 14.8 Hz), 121.8 (d, J = 1.5 Hz), 115.3 (d, J = 21.7 Hz), 51.6.

HRMS (ESI+) for C₁₀H₁₀O₂F [M] +: calc. 181.0665; found: 181.0663.

**Compound (8y):**

![Structure of 2-chlorostyrene](image)

2-chlorostyrene (89 µL, 0.7 mmol); Methyl acrylate (127 µL, 1.4 mmol, 2.0 eq); Grubbs 2nd generation catalyst (12.0 mg, 0.014 mmol, 2 mol %); 4CzIPN (27.7 mg, 0.035 mmol, 5 mol %).

Purification (Colorless oil, 103 mg, 0.52 mmol, 75 % (Z:E = 92:8 in isolated product)).

**Z isomer (major):** ¹H NMR (300 MHz, CDCl₃) δ 7.52 – 7.49 (m, 1H), 7.41 – 7.37 (m, 1HE + 1HZ), 7.32 – 7.21 (m, 2HZ + 2HE), 7.16 (d, J = 12.2 Hz, 1H), 6.09 (d, J = 12.2 Hz, 1H), 3.66 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 166.2, 140.9, 133.9, 130.9, 130.0, 129.3, 127.2, 126.2, 121.5, 51.6.

**E isomer (minor):** ¹H NMR (300 MHz, CDCl₃) δ 8.10 (d, J = 16.0 Hz, 1H), 7.63 – 7.60 (m, 1H), 7.41 – 7.37 (m, 1HE + 1HZ), 7.32 – 7.21 (m, 2HZ + 2HE), 6.44 (d, J = 16.0 Hz, 1H),
3.83 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 166.2, 140.8, 133.4, 131.2, 130.3, 127.8, 127.2, 124.6, 120.6, 52.0.

HRMS (ESI+) for C$_{10}$H$_{10}$O$_2$Cl [M]+: calc. 197.0369; found: 197.0371.

**Compound (8z):**

![Methylstyrene](image)

2-methylstyrene (91 µL, 0.7 mmol); Methylacrylate (127 µL, 1.4 mmol, 2eq); Grubbs 2nd generation catalyst (12.0 mg, 0.014 mmol, 2 mol %); 4CzIPN (27.7 mg, 0.035 mmol, 5 mol %).

Purification (Colorless oil, 89 mg, 0.50 mmol, 72 % (Z:E = 90:10 in isolated product).

**Z isomer (major):** $^1$H NMR (300 MHz, CDCl$_3$) δ 7.33 (d, $J = 6.9$ Hz, 1H), 7.23 – 7.11 (m, 4HZ + 3HE), 6.04 (d, $J = 12.5$ Hz, 1H), 3.64 (s, 3H), 2.29 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 166.5, 143.5, 135.9, 134.9, 129.8, 128.9, 128.7, 125.4, 120.6, 51.4, 20.0.

**E isomer (minor):** $^1$H NMR (300 MHz, CDCl$_3$) δ 7.99 (d, $J = 16.0$ Hz, 1H), 7.57 – 7.52 (m, 1H), 7.23 – 7.11 (m, 4HZ + 3HE), 6.37 (d, $J = 16.0$ Hz, 1H), 3.82 (s, 3H), 2.44 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 167.6, 142.7, 137.8, 133.5, 130.9, 130.2, 126.5, 126.4, 119.0, 51.8, 19.9.

HRMS (ESI+) for C$_{11}$H$_{13}$O$_2$ [M]+: calc. 177.0916; found: 177.0917.

**Compound (8za):**

![4-Cyanostyrene](image)

4-cyanostyrene (90 µL, 0.7 mmol); Methylacrylate (127 µL, 1.4 mmol, 2eq); Grubbs 2nd generation catalyst (12.0 mg, 0.014 mmol, 2 mol %); 4CzIPN (27.7 mg, 0.035 mmol, 5 mol %).

Purification (Yellow solid, 77 mg, 0.41 mmol, 59 % (Z:E = 74:26 in isolated product).
Z isomer (major): ¹H NMR (300 MHz, CDCl₃) δ 7.69 – 7.55 (m, 4H Z + 5H E), 6.97 (d, J = 12.5 Hz, 1H), 6.09 (d, J = 12.5 Hz, 1H), 3.71 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 165.9, 141.5, 139.5, 131.9, 130.1, 128.5, 122.4, 112.4, 51.8.

E isomer (minor): ¹H NMR (300 MHz, CDCl₃) δ 7.69 – 7.55 (m, 4H Z + 5H E), 6.52 (d, J = 12.5 Hz, 1H), 3.82 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 170.0, 142.5, 138.8, 132.8, 129.9, 122.4, 121.5, 118.8, 52.2.

Compound (8zb):

```
Br

CO₂Me
```

4-bromostyrene (92 µL, 0.7 mmol); Methyl acrylate (317 µL, 3.5 mmol, 5 eq); Grubbs 2nd generation catalyst (12 mg, 0.014 mmol, 2 mol %); 4CzIPN (27.7 mg, 0.035 mmol, 5 mol %).

Purification (Yellow oil, 102 mg, 0.43 mmol, 61 % (Z isomer)). ¹H NMR (300 MHz, CDCl₃) δ 7.48 (s, 4H), 6.87 (d, J = 12.6 Hz, 1H), 5.97 (d, J = 12.6 Hz, 1H), 3.71 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 166.4, 142.4, 133.7, 131.5, 131.3, 123.5, 120.0, 51.6.

HRMS (ESI+) for C₁₀H₁₀O₂Br [M] +: calc. 240.9864; found: 240.9865.

Compound (8zc):

```
F₃C

CO₂CH₂CH₃
```

4-(trifluoromethyl)styrene (104 µL, 0.7 mmol); Ethyl acrylate (372 µL, 3.5 mmol, 5 eq); Grubbs 2nd generation catalyst (12.0 mg, 0.014 mmol, 2 mol %); 4CzIPN (27.7 mg, 0.035 mmol, 5 mol %).

Purification (Yellow liquid, 110 mg, 0.45 mmol, 66 % (Z isomer)). ¹H NMR (300 MHz, CDCl₃) δ 7.65 – 7.58 (m, 4H), 6.97 (d, J = 12.4 Hz, 1H), 6.06 (d, J = 12.4 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 1.24 (t, J = 7.1 Hz, 3H). ¹⁹F NMR (282 MHz, CDCl₃) δ - 62.8. ¹³C NMR (75 MHz, CDCl₃) δ...
MHz, CDCl$_3$) $\delta$ 165.8, 141.6, 138.6, 130.6 (q, $J = 32.5$ Hz), 129.8, 125.0 (q, $J = 3.8$ Hz), 124.1 (q, $J = 270.0$ Hz), 122.2, 60.7, 14.1.

HRMS (ESI+) for C$_{12}$H$_{12}$O$_2$F$_3$ [M] +: calc. 245.0789; found: 245.0781.

**Compound (8zd):**

4-fluorostyrene (84 µL, 0.7 mmol); Ethyl acrylate (372 µL, 3.5 mmol, 5 eq); Grubbs 2$^{nd}$ generation catalyst (12 mg, 0.014 mmol, 2 mol %); 4CzIPN (27.7 mg, 0.035 mmol, 5 mol %).

Purification (Colorless oil, 92 mg, 0.47 mmol, 68% (Z isomer)).$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.67 – 7.60 (m, 2H), 7.07 – 6.99 (m, 2H), 6.88 (d, $J = 12.0$ Hz, 1H), 5.93 (d, $J = 12.0$ Hz, 1H), 4.18 (q, $J = 7.2$ Hz, 2H), 1.26 (t, $J = 7.14$ Hz, 3H). $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -111.4. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 166.2, 163.3 (d, $J = 249.9$ Hz), 142.3, 132.1 (d, $J = 8.3$ Hz), 131.0 (d, $J = 3.3$ Hz), 119.7 (d, $J = 1.6$ Hz), 115.1 (d, $J = 21.6$ Hz), 60.5, 14.3.

HRMS (ESI+) for C$_{11}$H$_{12}$O$_2$F [M] +: calc. 195.0821; found: 195.0826.

**Compound (8ze):**

2-fluorostyrene (84 µL, 0.7 mmol); Ethyl acrylate (150 µL, 1.4 mmol, 2 eq); Grubbs 2$^{nd}$ generation catalyst (12.0 mg, 0.014 mmol, 2 mol %); 4CzIPN (27.7 mg, 0.035 mmol, 5 mol %).

Purification (Colorless solid, 82 mg, 0.42 mmol, 60% (Z:E = 84:16 in isolated product ).

**Z isomer (major):** $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.62 – 7.51 (m, 1HZ + 1HE), 7.37 – 7.27 (m, 1HZ + 1HE), 7.19 – 7.01 (m, 3HZ + 2HE), 6.08 (d, $J = 12.6$ Hz, 1H), 4.16 (q, $J = 7.2$ Hz, 2H), 1.22 (t, $J = 7.2$ Hz, 3H). $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -114.1. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 165.9, 160.3 (d, $J = 248.9$ Hz), 135.6 (d, $J = 3.8$ Hz), 131.0 (d, $J = 2.7$ Hz), 130.7
(d, J = 8.54 Hz), 123.6 (d, J = 3.6 Hz), 122.4 (d, J = 1.5 Hz), 121.0 (d, J = 6.6 Hz), 115.2 (d, J = 22.1 Hz), 60.5, 14.1.

**E isomer (minor):** $^1$H NMR (300 MHz, CDCl$_3$) δ 7.81 (d, J = 16.0 Hz, 1H), 7.62 – 7.54 (m, 1H), 7.37 – 7.28 (m, 1H), 7.19 – 7.01 (m, 3H), 6.54 (d, J = 16.0 Hz, 1H), 4.28 (q, J = 7.2 Hz, 2H), 1.34 (t, J = 7.2 Hz, 3H). $^{19}$F NMR (282 MHz, CDCl$_3$) δ -114.4.

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 166.9, 161.1 (d, J = 248.9 Hz), 137.3 (d, J = 2.3 Hz), 131.7 (d, J = 8.8 Hz), 129.2 (d, J = 3.0 Hz), 124.5 (d, J = 3.8 Hz), 123.2 (d, J = 13.4 Hz), 121.0 (d, J = 6.6 Hz), 116.3 (d, J = 22.1 Hz), 60.7, 14.4.

HRMS (ESI+) for C$_{10}$H$_{10}$O$_2$F [M]+: calc. 195.0821; found: 195.0834.

**Compound (8zf):**

![Chemical Structure](image)

2-methylstyrene (90.5 µL, 0.7 mmol); Ethyl acrylate (150 µL, 1.4 mmol, 2 eq); Grubbs 2nd generation catalyst (12.0 mg, 0.014 mmol, 2 mol %); 4CzIPN (27.7 mg, 0.035 mmol, 5 mol %).

Purification (Colorless liquid, 98 mg, 0.52 mmol, 74% (Z:E = 92:8 in isolated product)).

**Z isomer (major):** $^1$H NMR (300 MHz, CDCl$_3$) δ 7.31 (d, J = 7.6 Hz, 1H), 7.23 – 7.10 (m, 4H), 6.02 (d, J = 12.0 Hz, 1H), 4.09 (q, J = 7.2 Hz, 2H), 2.28 (s, 3H), 1.15 (t, J = 7.2 Hz, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 166.0, 143.0, 135.8, 135.1, 129.7, 128.8, 128.5, 125.2, 121.2, 60.2, 19.9, 14.0.

**E isomer (minor):** $^1$H NMR (300 MHz, CDCl$_3$) δ 7.98 (d, J = 15.9 Hz, 1H), 7.56-7.54 (m, 2H), 6.93 – 6.91 (m, 2H), 6.36 (d, J = 15.9 Hz, 1H), 4.27 (q, J = 7.2 Hz, 2H), 2.44 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 167.1, 142.3, 137.7, 133.5, 130.8, 130.0, 126.5, 126.4, 119.4, 60.5, 19.9, 14.4.

HRMS (ESI+) for C$_{12}$H$_{14}$O$_2$ [M]+: calc. 191.1063; found: 191.1072.
3. Mechanistic studies

3.1. UV – Visible studies

Figure S2 Spectra of 4CzIPN (10⁻⁵ M, blue), catalyst Grubbs 2nd generation (10⁻⁵ M, red) in CH₂Cl₂ and solution mixture of 4CzIPN (10⁻⁵ M) + catalyst Grubbs 2nd generation (10⁻⁵ M) in CH₂Cl₂ (Orange).

3.2. Fluorescence studies and Stern-Volmer analysis

Table S1. Fluorescence quenching of 4CzIPN by catalyst Grubbs 2nd generation in CH₂Cl₂

| [Grubbs 2nd catalyst] mol L⁻¹ | Fluorescence intensity (I) | I₀/I |
|-----------------------------|---------------------------|-----|
| 0                           | 577                       | 1   |
| 1 x 10⁻⁵                    | 502                       | 1.14|
| 2 x 10⁻⁵                    | 446                       | 1.29|
| 3 x 10⁻⁵                    | 373                       | 1.54|
| 4 x 10⁻⁵                    | 354                       | 1.62|
| 5 x 10⁻⁵                    | 308                       | 1.87|
| 6 x 10⁻⁵                    | 272                       | 2.12|
| 1 x 10⁻⁴                    | 183                       | 3.15|
| 2 x 10⁻⁴                    | 103                       | 5.60|
Figure S3. Fluorescence quenching of 4CzIPN (3 x 10^{-6} mol L\(^{-1}\)) by catalyst Grubbs 2\(^{nd}\) generation in CH\(_2\)Cl\(_2\). The arrow in the figure indicates the direction increasing catalyst Grubbs 2\(^{nd}\) generation concentration as well as the peak where fluorescence intensity values were taken for Stern-Volmer analysis (insert).

Table S2. Fluorescence quenching of 4CzIPN by styrene in CH\(_2\)Cl\(_2\)

| [Styrene] mol L\(^{-1}\) | Fluorescence intensity (I) | I\(_0\)/I |
|--------------------------|----------------------------|----------|
| 0                        | 577                        | 1        |
| 5 x 10^{-5}              | 558                        | 1.14     |
| 1 x 10^{-4}              | 470                        | 1.29     |
| 1.5 x 10^{-4}            | 467                        | 1.54     |
| 2 x 10^{-4}              | 460                        | 1.62     |
| 3 x 10^{-4}              | 450                        | 1.87     |
| 5 x 10^{-4}              | 116                        | 2.12     |
| 1 x 10^{-3}              | 100                        | 3.15     |
Figure S4. Fluorescence quenching of 4CzIPN (3 x 10^-6 mol L^-1) by styrene in CH₂Cl₂. The arrow in the figure indicates the direction increasing styrene concentration as well as the peak where fluorescence intensity values were taken for Stern-Volmer analysis (insert)

Table S3. Fluorescence quenching of 4CzIPN by cis-stilbene in CH₂Cl₂

| [cis-stilbene] mol L⁻¹ | Fluorescence intensity (I) | I₀/I |
|------------------------|----------------------------|------|
| 0                      | 953                        | 1    |
| 2 x 10⁻⁴               | 883                        | 1.07 |
| 4 x 10⁻⁴               | 805                        | 1.18 |
| 6 x 10⁻⁴               | 771                        | 1.23 |
| 1 x 10⁻³               | 685                        | 1.39 |
| 1.3 x 10⁻³             | 623                        | 1.52 |
| 2 x 10⁻³               | 558                        | 1.70 |
Figure S5. Fluorescence quenching of 4CzIPN (3 x 10^{-6} mol L^{-1}) by cis-stilbene in CH₂Cl₂. The arrow in the figure indicates the direction increasing cis-stilbene concentration as well as the peak where fluorescence intensity values were taken for Stern-Volmer analysis (insert).

Table S4. Fluorescence quenching of 4CzIPN by trans-stilbene in CH₂Cl₂

| [trans-stilbene] mol L^{-1} | Fluorescence intensity (I) | I₀/I |
|-----------------------------|-----------------------------|------|
| 0                           | 953                         | 1    |
| 2 x 10^{-4}                 | 650                         | 1.46 |
| 4 x 10^{-4}                 | 635                         | 1.50 |
| 6 x 10^{-4}                 | 476                         | 1.99 |
| 1 x 10^{-3}                 | 399                         | 2.38 |
| 1.3 x 10^{-3}               | 367                         | 2.59 |
| 2 x 10^{-3}                 | 33                          | 2.80 |
Figure S6. Fluorescence quenching of 4CzIPN (3 x 10^{-6} mol L^{-1}) by trans-stilbene in CH₂Cl₂. The arrow in the figure indicates the direction increasing trans-stilbene concentration as well as the peak where fluorescence intensity values were taken for Stern-Volmer analysis (insert).
3.3. Laser flash photolysis

Figure S7. Transient UV-vis spectra following irradiation of Grubbs second-generation catalyst (2) at 355 nm (black) and a mixture of 2 with PCF (pink) at the same wavelength in CH$_2$Cl$_2$

4. Computational details

All the calculations were performed at the density functional theory (DFT) level using the Orca 4.2.1 program package.

Geometry optimizations (minima and MECPs) were performed in vacuum without symmetry using the B3LYP functional, a relativistic small core pseudopotential (SD28-Def2-ECP) and its associated basis set for Ru, the def2-TZVP(-f) basis set for all other atoms, and the empirical D3-BJ dispersion correction. The restricted Kohn–Sham formalism was used for ground states, while its unrestricted analogue was used for triplet states and oxidized states. SCF convergence was achieved using the DIIS algorithm followed by a semi-quadratic SOSCF converger. The RIJCOSX approximation was applied for all calculations using the def2/J auxiliary basis sets. Frequency calculations were run at the same level of theory. No imaginary frequencies were obtained, except in rare cases in which there was one imaginary frequency originating from methyl rotation (ca –80 cm$^{-1}$).
In the TD-DFT calculations, 50 singlets and 20 triplets were computed in the framework of the Tamm-Dancoff approximation. Molecular orbitals were viewed using Gabedit.\textsuperscript{13}

**Figure S8** Selected Kohn-Sham orbitals for complex 2 optimized in the ground state.
Table S5. Franck-Condon singlet excited states for complex 2 (E ≤ 4 eV).

The two transitions in bold are the ones giving rise to the absorption spectral profile, with apparent absorption bands at 494 nm and 348 nm.

| state | λ (nm) | E (eV) | oscillator strength | major excitation |
|-------|--------|--------|---------------------|------------------|
| 1     | 696    | 1.78   | 0.000295786         | HO --> LU        |
| 2     | 602    | 2.06   | 0.000101093         | HO-1 --> LU      |
| 3     | 494    | 2.51   | 0.004295395         | HO --> LU+1      |
| 4     | 419    | 2.96   | 0.000125864         | HO-1 --> LU+1    |
| 5     | 380    | 3.26   | 0.001454459         | HO-1 --> LU+7    |
| 6     | 364    | 3.41   | 0.006151611         | HO --> LU+7      |
| 7     | 348    | 3.56   | 0.088089164         | HO-2 --> LU      |
| 8     | 333    | 3.72   | 0.002036370         | HO --> LU+2      |
| 9     | 325    | 3.81   | 0.037641954         | HO-4 --> LU      |
| 10    | 324    | 3.83   | 0.025993159         | HO-5 --> LU      |
|       |        |        |                     | HO-3 --> LU      |
| 11    | 318    | 3.90   | 0.019225623         | HO --> LU+3      |
|       |        |        |                     | HO-5 --> LU      |
| 12    | 317    | 3.91   | 0.017883859         | HO --> LU+3      |
|       |        |        |                     | HO-5 --> LU      |
| 13    | 313    | 3.96   | 0.026418174         | HO --> LU+5      |
|       |        |        |                     | HO-1 --> LU+2    |
| 14    | 310    | 4.00   | 0.000039857         | HO --> LU+4      |
| HOMO   | HOMO-1  | HOMO-2  |
|--------|---------|---------|
|        |         |         |
| HOMO-3 |         |         |
|        |         |         |
| LUMO   | LUMO+1  | LUMO+2  |
|        |         |         |

**Figure S9.** Selected Kohn-Sham orbitals for complex 9 optimized in the ground state.
Table S6. Franck-Condon singlet excited states for complex 9 (E ≤ 4 eV).

| state | λ (nm) | E (eV) | oscillator strength | major excitation |
|-------|--------|--------|---------------------|------------------|
| 1     | 566    | 2.19   | 0.004581685         | HO --> LU        |
| 2     | 516    | 2.40   | 0.002759161         | HO --> LU+1      |
| 3     | 494    | 2.51   | 0.002842105         | HO-1, HO-2 --> LU|
| 4     | 417    | 2.98   | 0.004480958         | HO-1, HO-2 --> LU+1|
| 5     | 382    | 3.24   | 0.002778584         | HO-1, HO-2 --> LU+1|
| 6     | 370    | 3.35   | 0.010016529         | HO --> LU+2      |
| 7     | 355    | 3.49   | 0.146461633         | HO-1, HO-2 --> LU|
|       |        |        |                     | HO-1, HO-2 --> LU+2|
| 8     | 349    | 3.55   | 0.139007164         | HO-1, HO-2 --> LU|
|       |        |        |                     | HO-1, HO-2 --> LU+2|
| 9     | 314    | 3.95   | 0.031039946         | HO-3 --> LU      |
| 10    | 311    | 3.99   | 0.010140449         | HO-1, HO-2 --> LU+2|
|                | complex 2 | complex 9 |
|----------------|-----------|-----------|
| β-LUMO (hole)  | ![Image](image1.png) | ![Image](image2.png) |
| α-HOMO (particle) | ![Image](image3.png) | ![Image](image4.png) |
| spin density   | ![Image](image5.png) | ![Image](image6.png) |

**Figure S10.** Selected Kohn-Sham orbitals and spin density for complexes 2 and 9 optimized in the lowest triplet state (Ru-ben MLCT character; ben=benzylidene).
| **β-LUMO (hole)** | ![β-LUMO (side view)](side view) |
|-------------------|----------------------------------|
| **α-HOMO (particle)** | ![α-HOMO (side view)](side view) |
| **spin density** | ![Spin density (side view)](side view) |

**Figure S11.** Selected Kohn-Sham orbitals and spin density for complex 9 optimized in the $^3$MC state (Ru-C(car) antibonding character; car=N-heterocyclic carbene).
Table S7. Selected distances (Å) and angles (°), and Mulliken spin density.

C(car) refers to N-heterocyclic carbene; C(ben) refers to benzylidene.

| Complex          | Ru-P | Ru-C(ben) | Ru-C(car) | Ru-Cl | Ru-Cl | C-C(ben) | C(car)-Ru-C(ben) | spin/Ru |
|------------------|------|-----------|-----------|-------|-------|----------|------------------|---------|
| 2_GS             | 2.419 | 1.836     | 2.082     | 2.435 | 2.432 | 1.457    | 100.95           | -       |
| *2-3MLCT         | 2.442 | 1.961     | 2.101     | 2.343 | 2.363 | 1.405    | 98.56            | 1.01    |
| 2_3MECP(MLCT)    | 2.436 | 2.072     | 2.125     | 2.281 | 2.310 | 1.378    | 95.81            | 0.98    |
| 9_GS             | -     | 1.825     | 1.937     | 2.331 | 2.323 | 1.449    | 102.68           | -       |
| *9_3MLCT         | -     | 1.892     | 1.995     | 2.313 | 2.326 | 1.430    | 108.38           | 1.19    |
| 9_3MECP(MLCT)    | -     | 1.896     | 2.003     | 2.307 | 2.321 | 1.429    | 110.60           | 1.20    |
| *9_MC(car)       | -     | 1.844     | 2.096     | 2.328 | 2.370 | 1.447    | 94.55            | 1.69    |
| 9_3MECP(MC)      | -     | 1.848     | 2.080     | 2.333 | 2.355 | 1.447    | 91.95            | 1.68    |
| Species | state / point | charge, multiplicity | Electronic energy | Gibbs free energy |
|---------|--------------|----------------------|-------------------|------------------|
| complex 2 | ground state | 0, 1 | -3257.92375079253 | -3256.97963545 |
| | $^3$MLCT state | 0, 3 | -3257.88633647512 | -3256.94670799 |
| | | | | $\Delta G' = 20.7$ kcal/mol |
| | MECP | 0, 3 | -3257.87799501900 | - |
| complex 9 | ground state | 0, 1 | -2210.86689395221 | -2210.39735152 |
| | $^3$MLCT state | 0, 3 | -2210.84187471702 | -2210.37413766 |
| | | | | $\Delta G = 14.6$ kcal/mol |
| | MECP(MLCT) | 0, 3 | -2210.84164811032 | - |
| | $^3$MC state | 0, 3 | -2210.83285232734 | -2210.36544518 |
| | | | | $\Delta G = 20.0$ kcal/mol |
| | MECP(MC) | 0, 3 | -2210.83239368771 | - |
| PCf | ground state | 0, 1 | -2481.36413845560 | -2480.71245138 |
| | triplet state | 0, 3 | -2481.2758127722 | -2480.63065102 |
| | | | | $\Delta G = 51.3$ kcal/mol |
| Compound | State       | Energy Differences | ΔG (kcal/mol) |
|----------|-------------|--------------------|--------------|
| PCy<sub>3</sub> | ground state | -1046,98000842924 -1046,54118648 |   |
| E-stilbene | ground state | -540,594693269745 -540,41838917 |   |
| E-stilbene | triplet state | -540,517412171159 -540,4537016 | ΔG = 45.8 kcal/mol |
| Z-stilbene | ground state | -540,589463145081 -540,41164067 |   |
| Z-stilbene | triplet state | -540,523061754208 -540,35076745 | ΔG = 38.2 kcal/mol |
| Styrene   | ground state | -309,580779324063 -309,47863231 |   |
| Styrene   | triplet state | -309,493203279912 -309,39713709 | ΔG = 51.1 kcal/mol |

<sup>a</sup> Gibbs free energy difference with ground state.
5. Copies of $^1$H-, $^{13}$C- and $^{19}$F-NMR Spectra
7. References

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