1- Experimental details

All of the reactions were carried out under an argon atmosphere in an oven dried resealable Schlenk tube. All of the substrates; including CsF, K₃PO₄, Na₂CO₃, NaOAc, NEt₃, DABCO, DMA and DMF, were purchased from Acros. 1,4-Dioxane, MgSO₄ and diethyl ether were purchased from Synth. Chemicals were used without further purification. The NMR spectra were recorded on Varian XL300 or Varian XL200 spectrometers. The Mass spectra were obtained on a GC/MS Shimadzu QP-5050 (EI, 70eV). The gas chromatography analyses were performed on a Hewlett-Packard-5890 GC with a FID and 30 m capillary column with a dimethylpolysiloxane stationary phase. Palladacycle I was prepared as described earlier.¹
2- Typical experiment for the Heck coupling of aryl halides and \textit{n}-butyl acrylate

\[ \begin{align*}
\text{X-} & \text{aryl halide} + \text{CO}_2\text{Bu} \\
\text{Na}_2\text{CO}_3, \text{DMF, 130 }^\circ\text{C} & \rightarrow \text{aryl acrylate}
\end{align*} \]

An oven-dried resealable Schlenk flask was evacuated and back-filled with argon and charged with dried \( \text{Na}_2\text{CO}_3 \) (148 mg, 1.4 mmol), \( \text{NBu}_4\text{Br} \) (64 mg, 0.2 mmol), aryl halide (1 mmol), \( \text{n}-\text{butyl acrylate} \) (153 mg, 1.2 mmol) and NCP pincer 1 (0.8 mg, 0.2 mol % for ArI; 2.1 mg, 0.5 mol % for ArBr; 4.2 mg, 1.0 mol % for ArCl). The flask was evacuated, back-filled with argon and then was added 4 mL of DMF. The reaction mixture was stirred at 130 °C until all of the starting aryl halide had been completely consumed as judged by GC. The solution was then allowed to cool to room temperature, dissolved in ether (20 mL) and was washed with a 10% aqueous solution of HCl (10 mL). The organic layer was dried over MgSO\(_4\), filtered, concentrated in vacuum and then the crude material was purified by flash chromatography on silica gel.

\textbf{4-MeOC}_6\text{H}_4\text{CH=CHCO}_2\text{Bu} – \textit{n}-\text{butyl } p\text{-methoxycinnamate}.^2 \text{ Oil. } ^1\text{H} \text{ NMR (300 MHz, CDCl}_3\text{)} \delta 7.66 (d, 1H), 7.48 (d, 2H), 6.91 (d, 2H, \text{J}_{\text{AB}} = 8.3 \text{ Hz}), 6.32 (d, 1H, \text{J}_{\text{HH}} = 16.0 \text{ Hz}), 4.21 (t, 2H), 3.84 (s, 3H), 1.68 (m, 2H), 1.44 (m, 2H), 0.97 (t, 3H). ^13\text{C} \text{ NMR (75.4 MHz, CDCl}_3\text{)} \delta 167.5, 161.5, 144.4, 129.9, 127.4, 116.0, 114.5, 64.4, 55.5, 31.0, 19.4, 13.9. \text{ GC-MS (IE, 70 eV) m/z: 234 (M^+)}, 191, 178, 161, 147, 133.

\textbf{PhCH=CHCO}_2\text{Bu} – \textit{n}-\text{butyl cinnamate}.^2 \text{ Oil. } ^1\text{H} \text{ NMR (200 MHz, CDCl}_3\text{)} \delta 7.72-7.33 (m, 6H), 6.47 (d, 1H, \text{J}_{\text{HH}} = 15.8 \text{ Hz}), 4.20 (t, 2H), 1.75-1.61 (m, 2H), 1.52-1.37 (m, 2H),
4-O$_2$NC$_6$H$_4$CH=CHCO$_2$Bu – *n*-butyl *p*-nitrocinnamate. Solid. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.24 (d, 2H), 7.70 (t, 3H), 6.57 (d, 1H, $^3J_{HH} = 15.9$ Hz), 4.25 (t, 2H), 1.75-1.66 (m, 2H), 1.51-1.39 (m, 2H), 0.97 (t, 3H). $^{13}$C NMR (75.4 MHz, CDCl$_3$) $\delta$ 165.9, 148.2, 141.4, 140.2, 131.5, 129.3, 128.5, 123.9, 122.4, 64.7, 30.5, 18.9, 13.5.

4-MeC$_6$H$_4$CH=CHCO$_2$Bu – *n*-butyl *p*-methylcinnamate. Oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.64 (d, 1H), 7.36 (d, 2H), 7.13 (d, 2H), 6.37 (d, 1H, $^3J_{HH} = 16.0$ Hz), 4.18 (t, 2H), 2.32 (s, 3H), 1.71-1.62 (m, 2H), 1.48-1.34 (m, 2H), 0.95 (t, 3H). $^{13}$C NMR (75.4 MHz, CDCl$_3$) $\delta$ 166.9, 144.2, 140.2, 135.2, 130.9, 129.3, 126.4, 125.5, 124.5, 120.2, 64.5, 30.6, 19.1, 13.5. GC-MS (IE, 70 eV) m/z: 218 (M$^+$), 162, 145, 117, 115, 91.

3-F$_3$CC$_6$H$_4$CH=CHCO$_2$Bu – *n*-butyl *m*-trifluoromethylcinnamate. Oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.76-7.47 (m, 5H), 6.50 (d, 1H, $^3J_{HH} = 15.9$ Hz), 4.22 (t, 2H), 1.74-1.65 (m, 2H), 1.50-1.40 (m, 2H), 0.97 (t, 3H). $^{13}$C NMR (75.4 MHz, CDCl$_3$) $\delta$ 166.4, 142.5, 135.2, 130.9, 129.3, 126.4, 125.5, 124.5, 120.2, 64.5, 30.6, 19.1, 13.5.

2-MeCOC$_6$H$_4$CH=CHCO$_2$Bu – *n*-butyl *o*-methylcarbonylcinnamate. Oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.15 (d, 1H), 7.77-7.62 (m, 1H), 7.54-7.37 (m, 3H), 6.28 (d, 1H, $^3J_{HH} = 16.2$ Hz), 4.23 (t, 2H), 2.55 (s, 3H), 1.74-1.69 (m, 2H), 1.45-1.41 (m, 2H), 0.96 (t, 3H). $^{13}$C NMR (75.4 MHz, CDCl$_3$) $\delta$ 195.2, 166.7, 138.4, 138.1, 137.9, 135.5, 132.7, 131.0, 128.3, 118.7, 65.8, 29.7, 29.2, 19.3, 13.7.

4-NCC$_6$H$_4$CH=CHCO$_2$Bu – *n*-butyl *p*-cianocinnamate. Solid. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.69-7.47 (m, 5H), 6.51 (d, 1H, $^3J_{HH} = 16.1$ Hz), 4.21 (t, 2H), 1.68 (m, 2H), 1.44
(m, 2H), 0.95 (t, 3H). $^{13}$C NMR (75.4 MHz, CDCl$_3$) $\delta$ 166.5, 142.4, 138.9, 132.8, 128.6, 122.1, 118.6, 113.5, 65.1, 30.9, 19.4, 13.9.

2-MeC$_6$H$_4$CH=CHCO$_2$Bu – n-butyl o-methylenaminate.$^5$ Oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.97 (d, 1H), 7.54 (t, 1H), 7.27-7.16 (m, 3H), 6.36 (d, 1H, $^3$J$_{HH} = 15.9$ Hz), 4.21 (t, 2H), 2.41 (s, 3H), 1.73-1.64 (m, 2H), 1.49-1.39 (m, 2H), 0.96 (t, 3H). $^{13}$C NMR (75.4 MHz, CDCl$_3$) $\delta$ 166.9, 142.1, 137.4, 133.2, 130.6, 129.8, 126.2, 126.1, 119.1, 64.2, 30.6, 19.6, 19.1, 13.6.

2,5-Me$_2$C$_6$H$_4$CH=CHCO$_2$Bu – n-butyl 2,5-dimethylenaminate.$^6$ Oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.27 (s, 1H), 7.01 (m, 2H), 6.90 (m, 1H), 5.91 (d, 1H, $^3$J$_{HH} = 15.7$ Hz), 4.15 (t, 2H), 2.34 (s, 3H), 1.61-1.55 (m, 2H), 1.53-1.44 (m, 2H), 0.94 (t, 3H). $^{13}$C NMR (75.4 MHz, CDCl$_3$) $\delta$ 167.1, 144.0, 137.6, 135.2, 133.6, 129.7, 128.1, 126.1, 120.4, 64.8, 30.3, 20.8, 19.0, 18.6, 13.7. GC-MS (IE, 70 eV) m/z: 232 (M$^+$), 217, 175, 159, 145, 129, 115, 103.

4-H$_2$NC$_6$H$_4$CH=CHCO$_2$Bu – n-butyl p-aminocinnamate.$^7$ Oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.64 (d, 1H), 7.44-7.40 (m, 2H), 6.64-6.61 (m, 2H), 6.33 (d, 1H, $^3$J$_{HH} = 15.8$ Hz), 4.42 (s, 2H), 4.16 (t, 2H), 1.61-1.54 (m, 2H), 1.53-1.44 (m, 2H), 0.94 (t, 3H). $^{13}$C NMR (75.4 MHz, CDCl$_3$) $\delta$ 167.1, 147.8, 146.7, 129.4, 126.3, 123.9, 114.8, 64.8, 30.3, 18.6, 13.7.

4-MeCOC$_6$H$_4$CH=CHCO$_2$Bu – n-butyl p-acethylcinnamate.$^2$ Oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.96 (d, 2H), 7.68 (d, 1H), 7.60 (d, 2H, $J_{AB} = 8.5$ Hz), 6.54 (d, 1H, $J_{HH} = 16.1$ Hz), 4.21 (t, 2H), 2.60 (s, 3H), 1.69 (m, 2H), 1.45 (m, 2H), 0.96 (t, 3H). $^{13}$C NMR (75.4
MHz, CDCl₃) δ 197.5, 166.7, 143.1, 139.0, 138.2, 129.0, 128.3, 121.0, 64.8, 30.9, 26.8, 13.9. GC-MS (IE, 70 eV) m/z: 246 (M⁺), 190, 175, 147, 131, 115, 102.

4-MeOC₆H₄CH=CHPh – p-methoxystilbene.² Solid. ¹H NMR (200 MHz, CDCl₃) δ 7.48 (d, 2H), 7.43 (d, 2H), 7.27 (t, 2H), 7.18 (t, 1H), 7.02 (d, 1H, JHH = 16.0 Hz), 6.89 (d, 1H), 6.81 (d, 2H), 3.83 (s, 3H). ¹³C NMR (75.4 MHz, CDCl₃) δ 160.5, 137.3, 129.8, 129.7, 128.4, 127.8, 127.5, 127.3, 114.4, 55.2. GC-MS (IE, 70 eV) m/Z: 210 (M⁺), 195, 179, 165, 152, 89, 76, 63, 51.

References