Supporting Information
for DOI: 10.1055/s-0030-1259310
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In Situ Generation of Palladium Nanoparticles: Reusable, Ligand-Free Heck Reaction in PEG-400 Assisted by Focused Microwave Irradiation

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Supporting Information

Reagents and apparatus

All reagents and PEG-400 were used as obtained from commercial sources without further purification. Melting points were determined on an XT-4 electrothermal micro-melting point apparatus. The 1H and 13C NMR spectra were recorded on a Bruker MERCURY-PLUS 400 MHz NMR spectrometer. Chemical shifts were reported in parts per million (ppm, δ). IR was measured on a Alpha Centauri FT-IR spectrometer and MS was analyzed by a QP-1000A GC-MS with EI sources. Elemental analyses were performed on a Carlo Erba 1106 Elemental Analysis instrument. TEM pictures were obtained by JEM-2010 High-Resolution Transmission Electron Microscope. The palladium leaching level was tested by IRIS Advantage ICP-AES.

Microwave reactions were conducted using a CEM Focused Microwave Synthesis System (CEM Corp., Matthews, NC). The machine consists of a continuous focused microwave power delivery system with operator selectable power output from 0 to 300 W. The pressure control system uses a load cell for an indirect measurement of the reaction vessel contents. The load cell is connected to a 10-mL vessel and senses changes in the external deflection of the septa on top of the sealed pressure vessel. The sensor housing incorporates a capture and release mechanism to secure the reaction in the cavity. Pressure is programmable from 0–300 psi (0–21 bar). The temperature control system uses a non-contact, infrared sensor to measure temperature. It is located below the microwave cavity floor and measures the temperature on the bottom of the vessel. The sensor is vessel volume independent and is used in a feedback loop with the on-board computer to control the temperature rise rate and control point of the vessel contents. Temperature is programmable from 25–250 °C. All experiments were performed using a stirring option whereby the contents of the vessel are stirred by means of a rotating magnetic plate located below the floor of the microwave cavity and a Teflon coated magnetic stir bar in the vessel.

General procedure for Heck coupling reactions of aryl iodides with terminal olefins

In a 10-mL glass tube were placed aryl iodide (0.5 mmol), terminal olefin (0.6 mmol), K2CO3 (1.0
mmol), PdCl\textsubscript{2} (0.005 mmol), 3 mL of PEG-400, and a magnetic stir bar. The vessel was sealed with a septum and placed into the microwave cavity. Microwave irradiation of 10 W was used, the temperature being ramped from room temperature to 120 °C. Once 120 °C was reached, the reaction mixture was held at this temperature for 12 min. After cooling the mixture to room temperature, the reaction vessel was opened, the contents was extracted with 5×5 mL of ether (for substrates with carboxyl group, acidification using hydrochloric acid is needed before extraction) and the combined organic layers were dried over anhydrous MgSO\textsubscript{4}. The solvent was removed by evaporation under reduced pressure to afford the crude products, which were further purified by recrystallization or by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents. The catalyst system (Pd-PEG) was recycled by the evaporation of ether and H\textsubscript{2}O under reduced pressure and could be reused directly in the next run.

The evidence of in situ formation of palladium(0) nanoparticles

The analysis of PEG after the reaction by \textsuperscript{1}H NMR reveals that a new peak appeared at δ = 9.732, which can be attributed to aldehyde group formed from the oxidation of a part of ended hydroxyl groups on PEG chains by Pd(II). Simultaneously, Pd(II) is reduced to Pd(0) by ended hydroxyl groups on PEG chains.

Physical spectroscopic data of compounds 1a-6a
(E)-Cinnamic acid (1a): a white solid, mp: 133-134 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 12.13 (s, 1H), 7.82 (d, J = 16 Hz, 1H), 7.56-7.54 (m, 2H), 7.43-7.39 (m, 3H), 6.47 (d, J = 16 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 172.75, 147.12, 133.99, 130.75, 128.95, 128.36, 117.30; EI-MS (m/z): 148 [M$^+$], 105, 77; IR ($\nu$/cm$^{-1}$): 1682, 1628, 1419, 767, 705; Anal. calcd for C$_9$H$_8$O$_2$ (148.05): C 72.96, H 5.44. Found: C 72.64, H 5.38.

(E)-3-(4-Methoxyphenyl)acrylic acid (1b): a white solid, mp: 173-174 °C. $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ = 11.58 (s, 1H), 7.73 (d, J = 14 Hz, 1H), 7.51 (s, 2H), 6.93 (s, 2H), 6.30 (d, J = 15.2, 1H). $^13$C NMR (100 MHz, DMSO-d$_6$): $\delta$ = 167.82, 160.93, 143.74, 129.94, 126.81, 116.47, 114.33, 55.29; EI-MS (m/z): 178 [M$^+$], 147, 133, 105, 76; IR ($\nu$/cm$^{-1}$): 1683, 1623, 1597, 1510, 1429, 826; Anal. calcd for C$_{10}$H$_{10}$O$_3$ (178.06): C 67.41, H 5.66. Found: C 67.72, H 5.70.

(E)-4-(2-Carboxyvinyl)benzoic acid (1c): a white solid, mp: >300 °C. $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ = 12.82 (s, 2H), 7.95 (d, J = 8.4 Hz, 2H), 7.84-7.79 (m, 2H), 6.79-6.75 (m, 1H), 6.66 (d, J = 16.4 Hz); $^{13}$C NMR (100 MHz, DMSO-d$_6$): $\delta$ = 167.30, 166.83, 142.65, 138.36, 131.83, 129.74, 128.30, 121.59; EI-MS (m/z): 192 [M$^+$], 147, 105, 76; IR ($\nu$/cm$^{-1}$): 1689, 1631, 1566, 1510, 1469, 847; Anal. calcd for C$_{10}$H$_{10}$O$_4$ (192.04): C 62.50, H 4.20. Found: C 62.23, H 4.15.

(E)-3-(2-(Methoxycarbonyl)phenyl)acrylic acid (1d): a white solid, mp: 177-178 °C. $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ = 12.54 (s, 1H), 8.23 (d, J = 16 Hz, 1H), 7.88-7.84 (m, 2H), 7.65-7.61 (m, 1H), 7.55-7.51 (m, 2H), 6.45 (d, J = 15.6 Hz, 1H), 3.85 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-d$_6$): $\delta$ = 167.34, 166.78, 142.03, 135.03, 132.55, 130.23, 129.79, 129.74, 127.91, 121.86, 52.45; EI-MS (m/z): 206 [M$^+$], 147, 105, 76; IR ($\nu$/cm$^{-1}$): 1707, 1681, 1622, 1595, 1566, 1483, 768; Anal. calcd for C$_{11}$H$_{10}$O$_4$ (206.06): C 63.50, H 4.20. Found: C 63.85, H 4.81.

(E)-Cinnamonitrile (2a): a colorless viscous liquid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.46-7.29 (m, 6H), 5.91-5.86 (m, 1H); EI-MS (m/z): 129 [M$^+$], 103, 77; IR ($\nu$/cm$^{-1}$): 2217, 1618, 1576, 1493, 1448, 967, 749, 689; Anal. calcd for C$_9$H$_7$N (129.06): C 83.69, H 5.46, N 10.84. Found: C 83.93, H 5.43, N 10.87.
(E)-3-(4-Methoxyphenyl)acrylonitrile (2b): a white solid, mp: 58-60°C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.40-7.35 (m, 3H), 6.92-6.90 (m, 2H), 5.73 (d, $J = 16.4$Hz, 1H), 3.84 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 161.97, 149.98, 129.03, 126.26, 118.68, 114.44, 93.26, 55.39; EI-MS (m/z): 159 [M$^+$], 133, 128, 77; IR ($\upsilon$/cm$^{-1}$): 2213, 1602, 1510, 844; Anal. calcd for C$_{10}$H$_9$NO (159.07): C 75.45, H 5.70, N 8.80. Found: C 75.21, H 5.66, N 8.84.

(E)-3-(4-Aminophenyl)acrylonitrile (2c): a yellowish-brown solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.28-7.23 (m, 3H), 6.68-6.62 (m, 2H), 6.62 (d, $J = 16.4$Hz, 1H), 4.11 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 150.45, 149.47, 129.18, 123.73, 119.32, 114.69, 90.73; EI-MS (m/z): 144 [M$^+$], 128, 118, 77; IR ($\upsilon$/cm$^{-1}$): 3410, 3336, 2203, 1594, 1514, 834; Anal. calcd for C$_9$H$_8$N$_2$ (144.07): C 74.98, H 5.59, N 19.43. Found: C 74.61, H 5.63, N 19.37.

(E)-4-(2-Cyanovinyl)benzoic acid (2d): a white solid, mp: 256-257°C. $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ = 13.21 (s, 1H), 7.99 (d, $J = 16.4$Hz), 7.78-7.32 (m, 3H), 6.64 (d, $J = 16.4$Hz); $^{13}$C NMR (100 MHz, DMSO-d$_6$): $\delta$ = 166.70, 149.47, 137.66, 132.57, 129.80, 127.85, 118.49, 99.32; EI-MS (m/z): 173 [M$^+$], 128, 77; IR ($\upsilon$/cm$^{-1}$): 2216, 1693, 1608, 1564, 822; Anal. calcd for C$_{10}$H$_7$NO$_2$ (173.05): C 69.36, H 4.07, N 8.09. Found: C 69.51, H 4.09, N 8.06.

(E)-1,2-Diphenylethene (3a): a white solid, mp: 126-127°C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.53-7.50 (m, 4H), 7.38-7.34 (m, 4H), 7.28-7.24 (m, 2H), 7.11 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 137.29, 128.67, 127.61, 126.49; EI-MS (m/z): 180 [M$^+$], 165, 152, 102, 89, 76, 63, 51, 39; IR ($\upsilon$/cm$^{-1}$): 1492, 1449, 763, 690; Anal. calcd for C$_{14}$H$_{12}$ (180.09): C 93.29, H 6.71. Found: C 93.01, H 6.62.

(E)-1-Methoxy-4-styrylbenzene (3b): a white solid, mp: 135-136°C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.50-7.44 (m, 4H), 7.36-7.32 (m, 2H), 7.25-7.23 (m, 1H), 7.09-6.95 (m, 2H), 6.91-6.89 (m, 2H), 3.82 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 159.26, 137.60, 130.10, 128.62, 128.16, 127.69, 127.19, 126.57, 126.22, 114.09, 55.30; EI-MS (m/z): 210 [M$^+$], 179, 115, 77; IR ($\upsilon$/cm$^{-1}$): 1600, 1510, 1249, 1178, 814, 751, 689; Anal. calcd for C$_{15}$H$_{16}$O (210.10): C 85.68, H 6.71. Found: C 85.98, H 6.74.
(E)-4-Styrylbenzenamine (3c): a yellowish-brown solid, mp: 150-152°C. 1H NMR (400 MHz, CDCl\textsubscript{3}): δ = 7.47 (m, 2H), 7.34-7.30 (m, 4H), 7.24-7.18 (m, 1H), 7.04-6.89 (m, 2H), 6.68-6.65 (m, 2H), 3.72 (s, 2H); 13C NMR (100 MHz, CDCl\textsubscript{3}): δ = 146.10, 137.89, 128.62, 128.56, 127.95, 127.71, 126.85, 126.05, 125.04, 115.15; EI-MS (m/z): 196, [M\textsuperscript{+}+1], 195 [M\textsuperscript{+}], 180, 165, 152, 96, 77; IR (v/cm\textsuperscript{-1}): 3444, 3361, 1614, 1590, 1514, 1446, 817, 752, 688; Anal. calcd for C\textsubscript{14}H\textsubscript{13}N (195.10): C 86.12, H 6.71, N 7.17. Found: C 85.87, H 6.66, N 7.20.

(E)-4-Styrylbenzoic acid (3d): a white solid, mp: 258-259°C. 1H NMR (400 MHz, DMSO-d\textsubscript{6}): δ = 12.95 (s, 1H), 7.96 (d, J = 8Hz, 2H), 7.74 (d, J = 8Hz, 2H), 7.66 (d, J = 8Hz, 2H), 7.45-7.29 (m, 5H); 13C NMR (100 MHz, DMSO-d\textsubscript{6}): δ = 167.12, 141.42, 136.63, 130.98, 129.80, 129.48, 128.81, 128.23, 127.40, 126.85, 126.50; EI-MS (m/z): 224 [M\textsuperscript{+}], 179, 146, 76, 51; IR (v/cm\textsuperscript{-1}): 1685, 1603, 1424, 837, 774, 694; Anal. calcd for C\textsubscript{15}H\textsubscript{12}O\textsubscript{2} (224.08): C 80.34, H 5.39. Found: C 80.03, H 5.42.

(E)-Butyl cinnamate (4a): a colorless viscous liquid. 1H NMR (400 MHz, CDCl\textsubscript{3}): δ = 7.70 (d, J = 15.6Hz, 1H), 7.53-7.50 (m, 2H), 7.38-7.35 (m, 3H), 6.46 (d, J = 16Hz, 1H), 4.22 (t, J = 6.4Hz, 2H), 1.72-1.65 (m, 2H), 1.48-1.39 (m, 2H), 0.98 (t, J = 7.6Hz, 3H); 13C NMR (100 MHz, CDCl\textsubscript{3}): δ = 167.14, 144.49, 134.40, 130.14, 128.80, 127.99, 118.22, 64.37, 30.71, 19.15, 13.70; EI-MS (m/z): 204 [M\textsuperscript{+}], 131, 103, 77; IR (v/cm\textsuperscript{-1}): 1713, 1637, 1578, 1495, 1451, 767, 709; Anal. calcd for C\textsubscript{13}H\textsubscript{16}O\textsubscript{2} (204.12): C 76.44, H 7.90. Found: C 76.21, H 7.93.

Butyl (E)-3-(4-aminophenyl)acrylate (4b): a yellowish-brown solid, mp: 85-86°C. 1H NMR (400 MHz, CDCl\textsubscript{3}): δ = 7.61 (d, J = 16Hz, 1H), 7.36-7.33 (m, 2H), 6.66-6.63 (m, 2H), 6.25 (d, J = 16Hz, 1H), 4.20 (t, J = 6.4Hz, 2H), 1.71-1.64 (m, 2H), 1.47-1.38 (m, 2H), 0.97 (t, J = 7.6Hz, 3H); 13C NMR (100 MHz, CDCl\textsubscript{3}): δ = 167.78, 148.59, 144.76, 129.82, 124.74, 114.80, 113.73, 64.09, 30.81, 19.19, 13.75; EI-MS (m/z): 219 [M\textsuperscript{+}], 203, 118, 76; IR (v/cm\textsuperscript{-1}): 3438, 3347, 1692, 1592, 1514, 825; Anal. calcd for C\textsubscript{13}H\textsubscript{17}NO\textsubscript{2} (219.13): C 71.21, H 7.81, N 6.39. Found: C 70.97, H 7.85, N 6.36.

(E)-4-(3-Butoxy-3-oxoprop-1-enyl)benzoic acid (4c): a white solid, mp: 176-178°C. 1H NMR (400 MHz, DMSO-d\textsubscript{6}): δ = 13.13 (s, 1H), 7.96 (d, J = 8.4Hz, 2H), 7.86 (d, J = 8.4Hz, 2H), 7.72 (d, J = 16Hz, 1H), 6.78 (d, J = 16Hz, 1H), 4.18 (t, J = 6.4Hz, 2H), 1.66-1.59 (m, 2H), 1.43-1.34 (m, 2H), 0.94 (t, J = 7.2Hz, 3H); 13C NMR (100 MHz, MSO-d\textsubscript{6}): δ = 166.79, 166.00, 143.11, 138.11, 132.01, 129.70, 128.45, 120.45, 63.91, 30.24, 18.65, 13.58; EI-MS (m/z): 248 [M\textsuperscript{+}], 203, 147, 76; IR (v/cm\textsuperscript{-1}): 1702, 1682, 1635, 1607, 1568, 1510, 846; Anal. calcd for C\textsubscript{14}H\textsubscript{16}O\textsubscript{4} (248.10): C 67.73,
H 6.50. Found: C 67.60, H 6.52.

**Ethyl (E)-cinnamate (5a):** a colorless viscous liquid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.71 (d, $J =$ 16Hz, 1H), 7.54-7.51 (m, 2H), 7.40-7.36 (m, 3H), 6.46 (d, $J =$ 16Hz, 1H), 4.29 (q, $J =$ 6.8Hz, 2H), 1.36 (t, $J =$ 6.8Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 166.98, 144.55, 134.39, 130.18, 128.83, 128.00, 118.19, 60.47, 14.29; EI-MS (m/z): 176 [M$^+$], 131, 103, 77, 51; IR (υ/cm$^{-1}$): 1712, 1637, 1578, 1495, 1449, 768, 712; Anal. calcd for C$_{11}$H$_{12}$O$_2$ (176.08): C 74.98, H 6.86. Found: C 75.07, H 6.79.

**Ethyl (E)-3-(4-methoxyphenyl)acrylate (5b):** a white solid, mp: 47-48°C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.62 (d, $J =$ 16 Hz, 1H), 7.48-7.46 (m, 2H), 6.91-6.89 (m, 2H), 6.32 (d, $J =$ 15.6Hz, 1H), 4.28-4.22 (q, $J =$ 7.2Hz, 2H), 3.83 (s, 3H), 1.28 (t, $J =$ 3.6Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 167.33, 161.26, 144.21, 129.65, 127.12, 115.66, 114.25, 60.30, 55.33, 14.32; EI-MS (m/z): 206 [M$^+$], 161, 134, 133, 89, 63; IR (υ/cm$^{-1}$): 1706, 1630, 1602, 1569, 1511, 1172, 829; Anal. calcd for C$_{12}$H$_{14}$O$_3$ (206.09): C 69.88, H 6.84. Found: C 70.13, H 6.81.

**Ethyl (E)-3-(4-aminophenyl)acrylate (5c):** a yellowish-brown solid, mp: 72-74°C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.61 (d, $J =$ 15.6Hz, 1H), 7.36 (m, 2H), 6.66 (m, 2H), 6.25 (d, $J =$ 16Hz, 1H), 4.26 (q, $J =$ 7.2Hz, 2H), 3.94 (s, 2H), 1.34 (t, $J =$ 2.8Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 167.68, 148.60, 144.81, 129.82, 124.69, 114.77, 113.66, 60.14, 14.35; EI-MS (m/z): 191 [M$^+$], 175, 118, 76; IR (υ/cm$^{-1}$): 3423, 3338, 1689, 1626, 1594, 1515, 1172, 829; Anal. calcd for C$_{11}$H$_{13}$NO$_2$ (191.09): C 69.09, H 6.85, N 7.32. Found: C 69.36, H 6.88, N 7.27.

**Methyl (E)-3-(4-methoxyphenyl)acrylate (6a):** a white solid, mp: 82-84°C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.63 (d, $J =$ 16Hz, 1H), 7.48-7.46 (m, 2H), 6.91-6.89 (m, 2H), 6.29 (d, $J =$ 16Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 167.76, 161.33, 144.50, 129.69, 127.04, 115.18, 114.27, 55.34, 51.57; EI-MS (m/z): 192 [M$^+$], 161, 133, 118, 77; IR (υ/cm$^{-1}$): 1717, 1637, 1604, 1512, 1460, 821; Anal. calcd for C$_{11}$H$_{13}$O$_3$ (192.08): C 68.74, H 6.29. Found: C 68.91, H 6.23.

$^1$H NMR and $^{13}$C NMR spectra of compounds 1a-6a