Supporting Information
for DOI: 10.1055/s-0036-1590895
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Supporting Information

Recycled Pd/C-Catalyzed Heck Reaction of 2-Iodoanilines under Ligand-free Conditions

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General: The chemical shifts for $^1$H NMR were recorded in ppm downfield from tetramethysilane (TMS) with the solvent resonance as the internal standard. The chemical shifts for 13C NMR were recorded in ppm downfield using the central peak of d-chloroform (77.23 ppm) as the internal standard. Coupling constants ($J$) are reported in Hz and refer to apparent peak multiplications. Flash column chromatography was performed on silica gel (200-300 mesh). TLC analysis was performed using glass-backed plates coated with 0.2 mm silica.

Materials: Commercially available reagents were used throughout without further purification other than those detailed below. The other solvents were purchased and without further purification.

2. The Typical Procedure for Pd/C Catalyzed Heck Reaction of 2-Iodoanilines

\[
\begin{align*}
\text{R}^1 \text{I} \text{NH}_2 + \text{C}=\text{C} \text{OEt} & \xrightarrow{\text{Pd/C (10 wt%)}} \text{R}^2 \text{C} \text{NH}_2 \text{OEt} \\
\text{R} = \text{alkyl, -CN, -NO}_2, \text{-Cl, -Br, etc} \\
\text{NEt}_3 (2.0 \text{ equiv}) & \text{ 1,4-dioxane, 100 } \text{°C}
\end{align*}
\]

A mixture of 2-iodoanilines 1 (0.50 mmol) and Pd/C (10 wt% palladium on activated carbon paste and 50% moisture, 10 wt% wet Pd/C based on starting material 1) in 1,4-dioxane (3 mL) was
added into a Schlenk flask (25 mL) and stirred at room temperature. Followed by addition of ethyl acrylate (100 mg, 1.0 mmol, 2.0 equiv), NEt₃ (101 mg, 1.0 mmol, 2.0 equiv) and the mixture was stirred at 100 °C until the reaction was finished. Then the solvent was evaporated under reduced pressure and the residue was purified by column chromatography.

ethyl 3-(2-aminophenyl)acrylate (3a): Yield: > 99%, 96.0 mg, light yellow solid, m.p. 75-76 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.33 (t, J = 7.2 Hz, 3H), 4.26 (q, J = 7.2 Hz, 2H), 6.35 (d, J = 15.8 Hz, 1H), 6.70-6.79 (m, 2H), 7.15-7.19 (m, 1H), 7.37-7.39 (m, 1H), 7.80-7.85 (m, 1H); ³¹C NMR (100 MHz, CDCl₃): δ 14.3, 60.4, 116.8, 118.2, 119.0, 120.0, 128.1, 140.0, 145.3, 167.5; HRMS (EI) Calcd for C₁₁H₁₃NO₂: 191.0946 [M]+; found: 191.0942.

ethyl 3-(2-amino-5-methylphenyl)acrylate (3b): Yield: 85%, 86.9 mg, light yellow solid, m.p. 88-90 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.33 (t, J = 7.1 Hz, 3H), 2.24 (s, 3H), 4.25 (q, J = 7.1 Hz, 2H), 6.35 (d, J = 15.8 Hz, 1H), 6.64 (d, J = 8.1 Hz, 1H), 6.98-7.00 (m, 1H), 7.20 (s, 1H), 7.82 (d, J = 15.8 Hz, 1H); ³¹C NMR (100 MHz, CDCl₃): δ 14.3, 20.4, 60.4, 117.1, 117.9, 120.1, 128.2, 140.1, 142.8, 167.3; HRMS (EI) Calcd for C₁₂H₁₅NO₂: 205.1103 [M]+; found: 205.1107.

ethyl 3-(2-amino-5-(trifluoromethyl)phenyl)acrylate (3c): 96%, 124.1 mg, light yellow solid, m.p. 65-67 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.34 (t, J = 7.1 Hz, 3H), 4.27 (q, J = 7.1 Hz, 2H), 6.40 (d, J = 15.8 Hz, 1H), 6.74 (d, J = 8.5 Hz, 1H), 7.38 (dd, J = 8.6 Hz, 15.7 Hz, 1H), 7.61 (s, 1H), 7.76 (d, J = 8.6 Hz, 1H); ¹⁹F NMR (470 MHz, CDCl₃): δ 61.6 (s, 3F); ³¹C NMR (100 MHz, CDCl₃): δ 14.3, 60.7, 116.2, 119.2, 120.0, 120.6, 120.9, 125.3, 125.4, 127.8, 138.5, 147.8, 166.8; HRMS (EI) Calcd for C₁₂H₁₂F₃NO₂: 259.0820 [M]+; found: 259.0821.

ethyl 3-(2-amino-5-chlorophenyl)acrylate (3d): Yield: 75%, 92.5 mg, light yellow solid, m.p. 79-81 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.33 (t, J = 7.2 Hz, 3H), 4.26 (q, J = 7.2 Hz, 2H), 6.34 (d, J = 15.8 Hz, 1H), 6.66 (d, J = 8.6 Hz, 1H), 7.12 (dd, J = 2.4 Hz, 15.8 Hz, 1H), 7.35 (d, 2.4 Hz, 1H), 7.72 (d, 15.8 Hz, 1H); ³¹C NMR (100 MHz, CDCl₃): δ 14.3, 60.6, 118.0, 119.4, 121.2, 123.8, 127.3, 130.9, 138.5, 143.7, 166.9; HRMS (EI) Calcd for C₁₁H₁₂ClNO₂: 225.0557 [M]+; found: 225.0559.
ethyl 3-(2-amino-5-bromophenyl)acrylate (3e): Yield: 76%, 102.4 mg, light yellow solid, m.p. 80-82 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 1.33 (t, \(J = 7.2\) Hz, 3H), 4.26 (q, \(J = 7.2\) Hz, 2H), 6.33 (d, \(J = 15.8\) Hz, 1H), 6.59 (d, \(J = 8.5\) Hz, 1H), 7.24 (d, \(J = 8.6\) Hz, 1H), 7.47-7.482 (m, 1H), 7.68-7.82 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 14.3, 60.6, 110.6, 118.2, 119.4, 121.7, 130.2, 133.7, 138.4, 144.3, 166.9; HRMS (EI) Calcd for C\(_{11}\)H\(_{12}\)BrNO\(_2\): 269.0051 [M]\(^+\); found: 269.0049.

ethyl 3-(2-amino-5-fluorophenyl)acrylate (3f): Yield: 93%, 97.1 mg, light yellow solid, m.p. 79-81 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 1.33 (t, \(J = 7.1\) Hz, 3H), 4.26 (q, \(J = 7.1\) Hz, 2H), 6.33 (d, \(J = 15.8\) Hz, 1H), 6.66-6.70 (m, 1H), 6.88-6.93 (m, 1H), 7.07-7.10 (m, 1H), 7.77 (d, \(J = 15.8\) Hz, 1H); \(^19\)F NMR (470 MHz, CDCl\(_3\)): \(\delta\) 125.7 (m, 1F); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 14.3, 60.6, 113.2, 113.5, 118.1, 118.2, 118.3, 119.4, 138.75, 138.78, 141.2, 155.2, 157.5, 166.9; HRMS (EI) Calcd for C\(_{11}\)H\(_{12}\)FNO\(_2\): 209.0852 [M]\(^+\); found: 209.0850.

ethyl 3-(2-amino-5-nitrophenyl)acrylate (3g): Yield: 93%, 109.5 mg, yellow solid, m.p. 136-138 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 1.35 (t, \(J = 7.2\) Hz, 3H), 4.28 (q, \(J = 7.2\) Hz, 2H), 6.48 (d, \(J = 15.8\) Hz, 1H), 6.70 (d, \(J = 9.0\) Hz, 1H), 7.70 (d, \(J = 15.7\) Hz, 1H), 8.05 (dd, \(J = 2.5\) Hz, 15.7 Hz, 1H), 8.31 (d, \(J = 2.5\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 14.3, 60.9, 115.4, 118.6, 121.4, 124.5, 126.7, 137.4, 139.4, 150.5, 166.5; HRMS (EI) Calcd for C\(_{11}\)H\(_{12}\)N\(_2\)O\(_4\): 236.0797 [M]\(^+\); found: 236.0793.

ethyl 3-(2-amino-5-cyanophenyl)acrylate (3h): Yield: > 99%, 107.8 mg, yellow solid, m.p. 109-111 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 1.34 (t, \(J = 7.1\) Hz, 3H), 4.27 (q, \(J = 7.1\) Hz, 2H), 6.36 (d, \(J = 15.8\) Hz, 1H), 6.71 (d, \(J = 8.4\) Hz, 1H), 7.38-7.41 (m, 1H), 7.63-7.69 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 14.3, 60.9, 115.4, 118.6, 121.4, 124.5, 126.7, 137.4, 139.4, 150.5, 166.5; HRMS (EI) Calcd for C\(_{12}\)H\(_{12}\)N\(_2\)O\(_2\): 216.0899 [M]\(^+\); found: 216.0901.

ethyl 3-(2-amino-4-chlorophenyl)acrylate (3i): Yield: 88%, 107.5 mg, light yellow solid, m.p.
79-81 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.33 (t, J = 7.1 Hz, 3H), 4.25 (q, J = 7.1 Hz, 2H), 6.32 (d, J = 15.8 Hz, 1H), 6.73-6.76 (m, 2H), 7.30 (d, J = 8.2 Hz, 1H), 7.74 (d, J = 15.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 14.3, 60.6, 116.5, 118.59, 118.63, 119.4, 129.2, 136.8, 138.8, 145.9, 167.1; HRMS (EI) Calcd for C₁₁H₂ClNO₂: 225.0557 [M]⁺; found: 225.0559.

**ethyl 3-(2-amino-4-bromophenyl)acrylate (3j):** Yield: 86%, 116.5 mg, light yellow solid, m.p. 80-82 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.33 (t, J = 7.1 Hz, 3H), 4.26 (q, J = 7.1 Hz, 2H), 6.87 (d, J = 15.8 Hz, 1H), 6.87-6.89 (m, 2H), 7.22 (d, J = 8.9 Hz, 1H), 7.71 (d, J = 15.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 14.3, 60.6, 118.7, 118.8, 119.2, 122.0, 125.1, 129.3, 138.9, 146.4, 167.1; HRMS (EI) Calcd for C₁₁H₁₂BrNO₂: 269.0051 [M]⁺; found: 269.0049.

**ethyl 3-(2-amino-6-chlorophenyl)acrylate (3k):** Yield: 64%, 71.7 mg, light yellow solid, m.p. 108-111 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.34 (t, J = 7.1 Hz, 3H), 4.28 (q, J = 7.1 Hz, 2H), 6.46 (d, J = 16.5 Hz, 1H), 6.62 (d, J = 8.1 Hz, 1H), 6.82 (dd, J = 7.9, 0.8 Hz, 1H), 7.03 (t, J = 8.0 Hz, 1H), 7.87 (d, J = 16.5 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 14.3, 60.7, 114.6, 118.5, 123.4, 130.3, 135.2, 139.6, 146.3, 166.8; HRMS (EI) Calcd for C₁₁H₁₁ClNO₂: 225.0557 [M]⁺; found: 225.0556.

**ethyl 3-(2-amino-3,5-dichlorophenyl)acrylate (3l):** Yield: 98%, 127.4 mg, light yellow solid, m.p. 89-91 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.34 (t, J = 7.1 Hz, 3H), 4.27 (q, J = 7.1 Hz, 2H), 6.35 (d, J = 15.7 Hz, 1H), 7.27 (dd, J = 10.4, 2.3 Hz, 2H), 7.69 (d, J = 15.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 14.3, 60.8, 120.9, 121.9, 122.8, 126.0, 130.2, 138.1, 140.5, 166.5; HRMS (EI) Calcd for C₁₁H₁₁ClNO₂: 259.0167 [M]⁺; found: 259.0165.

**ethyl 3-(2-amino-3,5-dimethylphenyl)acrylate (3m):** Yield: 84%, 92.3 mg, light yellow solid, m.p. 70-73 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.33 (t, J = 7.1 Hz, 3H), 2.16 (s, 3H), 2.22 (s, 3H), 4.26 (q, J = 7.1 Hz, 2H), 6.34 (d, J = 15.7 Hz, 1H), 6.92 (s, 1H), 7.09 (s, 1H), 7.85 (d, J = 15.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 14.3, 17.6, 20.3, 60.4, 118.0, 119.6, 123.4, 125.9, 127.4, 133.4, 140.4, 141.3, 167.4; HRMS (EI) Calcd for C₁₃H₁₇NO₂: 219.1259 [M]⁺; found: 219.1262.
ethyl 3-(3-aminophenyl)acrylate (3n): Yield: > 99%, 97.2 mg, light yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.33 (t, $J = 7.1$ Hz, 3H), 4.25 (q, $J = 7.1$ Hz, 2H), 6.37 (d, $J = 16.0$ Hz, 1H), 6.71 (m, 1H), 6.82 (m, 1H), 6.93 (d, $J = 7.6$ Hz, 1H), 7.16 (t, $J = 7.8$ Hz, 1H), 7.59 (d, $J = 16.0$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 14.3, 60.4, 114.1, 117.1, 118.0, 118.6, 129.7, 135.4, 144.8, 146.6, 167.1; HRMS (EI) Calcd for C$_{11}$H$_{13}$NO$_2$: 191.0946 [M]$^+$; found: 191.0947.

ethyl 3-(2-hydroxyphenyl)acrylate (3o): Yield: 84%, 80.4 mg, light yellow solid, m.p. 31-33 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.35 (t, $J = 7.1$ Hz, 3H), 4.30 (q, $J = 7.1$ Hz, 2H), 6.64 (d, $J = 16.2$ Hz, 1H), 6.85-6.93 (m, 2H), 7.21-7.26 (m, 1H), 7.46-7.48 (m, 1H), 8.04 (d, $J = 16.2$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 14.3, 60.7, 116.4, 118.4, 120.7, 121.7, 129.2, 131.4, 140.6, 155.4, 168.5; HRMS (EI) Calcd for C$_{11}$H$_{12}$O$_3$: 192.0786 [M]$^+$; found: 192.0782.

ethyl cinnamate (3p): Yield: 88%, 77.1 mg, colourless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.34 (t, $J = 7.1$ Hz, 3H), 4.27 (q, $J = 7.1$ Hz, 2H), 6.44 (d, $J = 15.8$ Hz, 1H), 7.37-7.40 (m, 3H), 7.51-7.54 (m, 2H), 7.69 (d, $J = 16.1$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 14.3, 60.5, 118.2, 128.0, 128.8, 130.2, 134.4, 144.6, 167.0; HRMS (EI) Calcd for C$_{11}$H$_{12}$O$_2$: 176.0837 [M]$^+$; found: 176.0835.

methyl 3-(2-aminophenyl)acrylate (3t): Yield: 97%, 85.9 mg, light yellow solid, m.p. 55-57 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 3.80 (s, 3H), 6.36 (d, $J = 15.8$ Hz, 1H), 6.70 (dd, $J = 8.1$, 0.7 Hz, 1H), 6.77 (t, $J = 7.5$ Hz, 1H), 7.13-7.21 (m, 1H), 7.38 (dd, $J = 7.8$, 1.2 Hz, 1H), 7.83 (d, $J = 15.8$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 51.7, 116.7, 117.6, 118.9, 119.8, 128.1, 131.3, 140.3, 145.5, 167.7; HRMS (EI) Calcd for C$_{10}$H$_{11}$NO$_2$: 177.0790 [M]$^+$; found: 177.0792.

tert-butyl 3-(2-aminophenyl)acrylate (3u): Yield: 98%, 107.7 mg, light yellow solid, m.p. 68-71 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.53 (s, 9H), 6.28 (d, $J = 15.8$ Hz, 1H), 6.69 (d, $J = 8.1$ Hz, 1H), 6.75 (t, $J = 7.5$ Hz, 1H), 7.15 (m, 1H), 7.36 (dd, $J = 7.8$, 1.3 Hz, 1H), 7.73 (d, $J = 15.8$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 28.2, 80.4, 116.6, 118.9, 120.13, 120.19, 128.1, 130.9,
139.0, 145.3, 166.6; HRMS (EI) Calcd for C_{13}H_{17}NO_2: 219.1259 [M]^+; found: 219.1255.
3. Copy of NMR for the Products (3) of the Pd/C Catalyzed Heck Reaction of 2-Iodoanilines