Supporting Information

Ru-catalyzed 1,4-Addition of Arylboronic Acids to Acrylic Acid Derivatives in the Presence of Phenols

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General and Materials

General: All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques unless otherwise noted. $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra were obtained on a 400 MHz NMR spectrometer. The chemical shifts for $^1$H NMR were recorded in ppm downfield from tetramethylsilane (TMS) with the solvent resonance as the internal standard. The chemical shifts for $^{13}$C NMR were recorded in ppm downfield using the central peak of CDCl$_3$ (77.00 ppm) as the internal standard. Coupling constants ($J$) are reported in Hz and refer to apparent peak multiplications.

Materials: Commercially available reagents were used throughout without further purification other than those detailed below. The solvents were pretreated by the following procedures: THF, toluene and dioxane was distilled over sodium benzopheneone ketyl under nitrogen. DCE was distilled over calcium hydride. Acetone was distilled over calcium sulfate anhydrous under nitrogen.

Typical Procedure for Conjugate Addition of Arylboronic Acids to Butyl Acrylate.

To a Schlenk tube were added arylboronic acid (1.05 mmol), [RuCl$_2$(p-cymene)]$_2$ (12.3 mg, 0.02 mmol) and 2,6-di-tert-butylphenol (20.6 mg, 0.1 mmol) was evacuated and purged with N$_2$ for three times, butyl acrylate (128.0 mg, 1.0 mmol), in 1.0 mL dioxane/H$_2$O = 20 : 1 (v/v) and other 2.0 mL dioxane/H$_2$O = 20 : 1 (v/v) were added sequentially to the system under N$_2$. After solvent was injected the solution turned orange immediately and then the mixture was stirred at 90 °C for 12 h. The reaction mixture was concentrated and the residue was purified by silica gel chromatography (PE/EA = 100) to give the product.
Table 1  Screening of additives and solvents

<table>
<thead>
<tr>
<th>entry</th>
<th>additive (^b)</th>
<th>solvent</th>
<th>yield (%) (^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2-chlorophenol</td>
<td>dioxane/H(_2)O</td>
<td>89</td>
</tr>
<tr>
<td>2</td>
<td>4-chlorophenol</td>
<td>dioxane/H(_2)O</td>
<td>86</td>
</tr>
<tr>
<td>3</td>
<td>naphthalen-2-ol</td>
<td>dioxane/H(_2)O</td>
<td>87</td>
</tr>
<tr>
<td>4</td>
<td>2-hydroxybenzoic acid</td>
<td>dioxane/H(_2)O</td>
<td>86(^d)</td>
</tr>
<tr>
<td>5</td>
<td>sodium phenolate</td>
<td>dioxane/H(_2)O</td>
<td>30(^e)</td>
</tr>
<tr>
<td>6</td>
<td>2,6-di(t-butyl)phenol</td>
<td>dioxane/H(_2)O</td>
<td>92(^f)</td>
</tr>
<tr>
<td>7</td>
<td>2,6-di(t-butyl)phenol</td>
<td>dioxane/H(_2)O</td>
<td>94(^e)</td>
</tr>
<tr>
<td>8</td>
<td>2,6-di(t-butyl)phenol</td>
<td>dioxane/H(_2)O</td>
<td>93(^b)</td>
</tr>
<tr>
<td>9</td>
<td>2,6-di(t-butyl)phenol</td>
<td>dioxane</td>
<td>&lt;5%(^i)</td>
</tr>
<tr>
<td>10</td>
<td>2,6-di(t-butyl)phenol</td>
<td>THF/H(_2)O</td>
<td>82</td>
</tr>
<tr>
<td>11</td>
<td>2,6-di(t-butyl)phenol</td>
<td>toluene/H(_2)O</td>
<td>63</td>
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<tr>
<td>12</td>
<td>2,6-di(t-butyl)phenol</td>
<td>methanol/H(_2)O</td>
<td>43</td>
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<tr>
<td>13</td>
<td>2,6-di(t-butyl)phenol</td>
<td>acetone/H(_2)O</td>
<td>78</td>
</tr>
<tr>
<td>14</td>
<td>2,6-di(t-butyl)phenol</td>
<td>DMF/H(_2)O</td>
<td>15</td>
</tr>
</tbody>
</table>

\(^a\)All the reactions were carried out with 1 (1.05 mmol), 2 (1.00 mmol), ruthenium complex (2.0 mol %) in solvent [dioxane/H\(_2\)O = 20/1 (v/v)] 3 mL at 90 °C under N\(_2\) for 12 h. \(^b\)20 mol %. \(^c\)yield determined by GC signal-integration method with durene as an internal standard. \(^d\)with 1.5 equiv of arylboronic acid. \(^e\)With 40% Heck-type product. \(^f\)2,6-di-tert-butyl phenol (5 mol %) was added. \(^g\)2,6-di-tert-butyl phenol (50 mol %) was added. \(^h\)2,6-di-tert-butyl phenol (100 mol %) was added. \(^i\)dry dioxane as the solvent.
Spectrum data of 3aa-3oa and 3eb.

Butyl 3-(4-(tert-butyl)phenyl)propanoate (3aa)

\[
\begin{align*}
\text{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})} & \quad \delta \, 7.31 \, (d, J = 8.4 \text{ Hz}, 2\text{H}), \, 7.14 \, (d, J = 8.4 \text{ Hz}, 2\text{H}), \, 4.07 \, (t, J = 6.6 \text{ Hz}, 2\text{H}), \, 2.92 \, (t, J = 8.0 \text{ Hz}, 2\text{H}), \, 2.62 \, (t, J = 8.0 \text{ Hz}, 2\text{H}), \, 1.62-1.55 \, (m, 2\text{H}), \, 1.37-1.31 \, (m, 2\text{H}), \, 1.30 \, (s, 9\text{H}), \, 0.92 \, (t, J = 7.4 \text{ Hz}, 3\text{H}). \\
\text{\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3})} & \quad \delta \, 173.3, \, 149.2, \, 137.8, \, 128.2, \, 125.6, \, 64.5, \, 34.6, \, 31.7, \, 31.0, \, 30.8, \, 19.4, \, 14.0. \\
\text{HRMS (QTOF-ESI)} \quad \text{Calculated for C\textsubscript{17}H\textsubscript{26}NaO\textsubscript{2} (M+Na) 285.1830, found 285.1855.}
\end{align*}
\]

\textit{n-Butyl 3-(o-tolyl)propanoate (3ba)}

\[
\begin{align*}
\text{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})} & \quad \delta \, 7.15-7.09 \, (m, 4\text{H}), \, 4.08 \, (t, J = 6.6 \text{ Hz}, 2\text{H}), \, 2.93 \, (t, J = 8 \text{ Hz}, 2\text{H}), \, 2.57 \, (t, J = 8 \text{ Hz}, 2\text{H}), \, 2.31 \, (s, 3\text{H}), \, 1.62-1.55 \, (m, 2\text{H}), \, 1.38-1.30 \, (m, 3\text{H}), \, 0.92 \, (t, J = 7.4 \text{ Hz}, 3\text{H}). \\
\text{\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3})} & \quad \delta \, 173.4, \, 138.9, \, 136.2, \, 130.5, \, 130.2, \, 128.7, \, 126.6, \, 126.4, \, 64.6, \, 34.9, \, 30.9, \, 28.6, \, 19.5, \, 19.4, \, 14.0.
\end{align*}
\]

\textit{n-Butyl 3-(m-tolyl)propanoate (3ca)}

\[
\begin{align*}
\text{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})} & \quad \delta \, 7.18 \, (t, J = 7.8 \text{ Hz}, 1\text{H}), \, 7.02-6.99 \, (m, 3\text{H}), \, 4.07 \, (t, J = 6.6 \text{ Hz}, 2\text{H}), \, 2.92 \, (t, J = 7.8 \text{ Hz}, 2\text{H}), \, 2.61 \, (t, J = 7.8 \text{ Hz}, 2\text{H}), \, 2.33 \, (s, 3\text{H}), \, 1.62-1.55 \, (m, 2\text{H}), \, 1.37-1.32 \, (m, 2\text{H}), \, 0.92 \, (t, J = 7.4 \text{ Hz}, 3\text{H}). \\
\text{\textsuperscript{13}C NMR (100MHz, CDCl\textsubscript{3})} & \quad \delta \, 173.3, \, 140.8, \, 138.2, \, 129.4, \, 128.6, \, 127.2, \, 125.5, \, 64.5, \, 36.2, \, 31.2, \, 30.9, \, 21.6, \, 19.4, \, 14.0. \\
\text{HRMS (QTOF-ESI)} \quad \text{Calculated for C\textsubscript{14}H\textsubscript{20}NaO\textsubscript{2} (M+Na) 243.1361, found 243.1361.}
\end{align*}
\]

\textit{n-Butyl 3-(p-tolyl)propanoate (3da)}

\[
\begin{align*}
\text{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})} & \quad \delta \, 7.10 \, (s, 4\text{H}), \, 4.07 \, (t, J = 6.6 \text{ Hz}, 2\text{H}), \, 2.91 \, (t, J = 7.8 \text{ Hz}, 2\text{H}), \, 2.60 \, (t, J = 7.8 \text{ Hz}, 2\text{H}), \, 2.32 \, (s, 3\text{H}), \, 1.62-1.55 \, (m, 2\text{H}), \, 1.39-1.29 \, (m, 2\text{H}), \, 0.92 \, (t, J = 7.4 \text{ Hz}, 3\text{H}). \\
\text{\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3})} & \quad \delta \, 173.3, \, 137.8, \, 135.9, \, 129.4,
\end{align*}
\]
128.4, 64.5, 36.3, 30.9, 30.9, 21.3, 19.4, 14.0.

**n-Butyl 3-phenylpropanoate (3ea)**

\[
\text{C}_8\text{H}_{16}\text{O}_2
\]

\[\delta 7.30-7.27 \text{ (m, } 2\text{H}), 7.21-7.18 \text{ (m, } 3\text{H}), 4.07 \text{ (t, } J = 6.6 \text{ Hz, } 2\text{H}), 2.95 \text{ (t, } J = 8.0 \text{ Hz, } 2\text{H}), 2.62 \text{ (t, } J = 8.0 \text{ Hz, } 2\text{H}), 1.62-1.55 \text{ (m, } 2\text{H}), 1.37-1.30 \text{ (m, } 2\text{H}), 0.92 \text{ (t, } J = 7.4 \text{ Hz, } 3\text{H}). \]

\[\delta 173.2, 140.8, 128.7, 128.5, 126.5, 64.6, 36.2, 31.3, 30.9, 19.4, 14.0.\]

**Butyl 3-(4-fluorophenyl)propanoate (3fa)**

\[
\text{C}_8\text{H}_{16}\text{F}_2\text{O}_2
\]

\[\delta 7.18-7.14 \text{ (m, } 2\text{H}), 7.99-6.95 \text{ (m, } 2\text{H}), 4.06 \text{ (t, } J = 6.6 \text{ Hz, } 2\text{H}), 2.92 \text{ (t, } J = 7.8 \text{ Hz, } 2\text{H}), 2.60 \text{ (t, } J = 7.8 \text{ Hz, } 2\text{H}), 1.60-1.55 \text{ (m, } 2\text{H}), 1.34-1.32 \text{ (m, } 2\text{H}), 0.91 \text{ (t, } J = 7.4 \text{ Hz, } 3\text{H}). \]

\[\delta 173.0, 162.9, 160.4, 136.4, 130.0, 129.9, 115.5, 115.3, 64.5, 36.2, 30.8, 30.4, 19.3, 13.9.\]

**Butyl 3-(4-(trifluoromethyl)phenyl)propanoate (3ga)**

\[
\text{C}_{14}\text{H}_{17}\text{F}_3\text{O}_2
\]

\[\delta 7.54 \text{ (d, } J = 8.0 \text{ Hz, } 2\text{H}), 7.32 \text{ (d, } J = 8.0 \text{ Hz, } 2\text{H}), 4.07 \text{ (t, } J = 6.6 \text{ Hz, } 2\text{H}), 3.01 \text{ (t, } J = 8.0 \text{ Hz, } 2\text{H}), 2.65 \text{ (t, } J = 8.0 \text{ Hz, } 2\text{H}), 1.61-1.53 \text{ (m, } 2\text{H}), 1.37-1.27 \text{ (m, } 2\text{H}), 0.91 \text{ (t, } J = 7.4 \text{ Hz, } 3\text{H}). \]

\[\delta 172.7, 144.9, 128.9, 128.6, 128.3, 125.8, 125.6, 125.5, 123.1, 64.7, 35.6, 30.9, 30.8, 19.2, 13.8. \]

HRMS (QTOF-ESI) Calculated for C_{14}H_{17}F_3NaO_2 (M+Na) 297.1078, found 297.1090.

**Butyl 3-(4-chlorophenyl)propanoate (3ha)**

\[
\text{C}_8\text{H}_{16}\text{ClO}_2
\]

\[\delta 7.25 \text{ (d, } J = 8.4 \text{ Hz, } 2\text{H}), 7.13 \text{ (d, } J = 8.4 \text{ Hz, } 2\text{H}), 4.06 \text{ (t, } J = 6.6 \text{ Hz, } 2\text{H}), 2.92 \text{ (t, } J = 7.8 \text{ Hz, } 2\text{H}), 2.60 \text{ (t, } J = 7.8 \text{ Hz, } 2\text{H}), 1.61-1.54 \text{ (m, } 2\text{H}), 1.38-1.28 \text{ (m, } 2\text{H}), 0.91 \text{ (t, } J = 7.4 \text{ Hz, } 3\text{H}). \]

\[\delta 172.8, 139.2, 132.2, 129.9, 128.7, 64.6, 35.9, 30.8, 30.5, 19.3, 13.9.\]
Butyl 3-(4-(trifluoromethoxy)phenyl)propanoate (3ia)

\[
\begin{align*}
\text{F} & \quad \text{O} \\
\text{F} & \quad \text{O} \\
\end{align*}
\]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.21 (d, $J = 8.4$ Hz, 2H), 7.11 (d, $J = 8.4$ Hz, 2H), 4.05 (t, $J = 6.6$ Hz, 2H), 2.94 (t, $J = 8.0$ Hz, 2H), 2.60 (t, $J = 8.0$ Hz, 2H), 1.59-1.52 (m, 2H), 1.36-1.26 (m, 2H), 0.89 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.9, 147.8, 139.5, 129.8, 122.0, 120.5, 119.4, 64.6, 35.9, 30.8, 30.4, 19.3, 13.8. HRMS (QTOF-ESI) Calculated for C$_{14}$H$_{17}$F$_3$NaO$_3$ (M+Na) 313.1027, found 313.1003.

Butyl 3-(4-methoxyphenyl)propanoate (3ja)

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\end{align*}
\]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.12-7.09 (m, 2H), 6.83-6.80 (m, 2H), 4.05 (t, $J = 6.4$ Hz, 2H), 3.76 (s, 3H), 2.88 (t, $J = 7.8$ Hz, 2H), 2.58 (t, $J = 7.8$ Hz, 2H), 1.60-1.53 (m, 2H), 1.38-1.28 (m, 2H), 0.91 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 173.3, 158.2, 132.8, 129.5, 114.0, 64.5, 55.4, 36.5, 30.9, 30.4, 19.4, 14.0.

Butyl 3-(4-bromophenyl)propanoate (3ka)

\[
\begin{align*}
\text{Br} & \quad \text{O} \\
\end{align*}
\]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38 (d, $J = 8.4$ Hz, 2H), 7.07 (d, $J = 8.4$ Hz, 2H), 4.05 (t, $J = 6.8$ Hz, 2H), 2.89 (t, $J = 7.6$ Hz, 2H), 2.59 (t, $J = 7.6$ Hz, 2H), 1.60 – 1.53 (m, 2H), 1.37 – 1.27 (m, 2H), 0.90 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.8, 139.7, 131.7, 130.3, 120.2, 64.6, 35.8, 30.9, 30.6, 19.3, 13.9.

Butyl 3-(4-acetylphenyl)propanoate (3la)

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\end{align*}
\]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.86 (d, $J = 8.4$ Hz, 2H), 7.27 (d, $J = 8.4$ Hz, 2H), 4.04 (t, $J = 6.4$ Hz, 2H), 2.98 (t, $J = 7.6$ Hz, 2H), 2.63 (t, $J = 7.6$ Hz, 2H), 2.56 (s, 3H), 1.59–1.51 (m, 2H), 1.35–1.264 (m, 2H), 0.88 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 197.6, 172.5, 146.4, 135.5, 128.7, 128.6, 64.5, 35.4, 31.0, 30.7, 26.6, 19.2, 13.8.
Methyl 4-(3-butoxy-3-oxopropyl)benzoate (3ma)\(^3\)

\[
\text{O} \quad \text{O} \\
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.93 (d, J = 8.4 \text{ Hz}, 2\text{H}), 7.24 (d, J = 8.4 \text{ Hz}, 2\text{H}), 4.04 (t, J = 6.8 \text{ Hz}, 2\text{H}), 3.87 (s, 3\text{H}), 2.98 (t, J = 7.8 \text{ Hz}, 2\text{H}), 2.62 (t, J = 7.8 \text{ Hz}, 2\text{H}), 1.58–1.51 (m, 2\text{H}), 1.35–1.25 (m, 2\text{H}), 0.88 (t, J = 7.4 \text{ Hz}, 3\text{H}). \(^1\)^C NMR (101 MHz, CDCl\(_3\)) \(\delta 172.6, 167.0, 146.1, 129.9, 128.5, 128.4, 64.5, 52.0, 35.4, 31.0, 30.8, 19.2, 13.8.\)

Butyl 3-(4-formylphenyl)propanoate (3na)\(^2\)

\[
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 9.95 (s, 1\text{H}), 7.79 (d, J = 8.0 \text{ Hz}, 2\text{H}), 7.35 (d, J = 8.0 \text{ Hz}, 2\text{H}), 4.05 (t, J = 6.6 \text{ Hz}, 2\text{H}), 3.01 (t, J = 7.6 \text{ Hz}, 2\text{H}), 2.64 (t, J = 7.6 \text{ Hz}, 2\text{H}), 1.58–1.51 (m, 2\text{H}), 1.33 – 1.27 (m, 2\text{H}), 0.88 (t, J = 7.4 \text{ Hz}, 3\text{H}). \(^1\)^C NMR (101 MHz, CDCl\(_3\)) \(\delta 191.9, 172.5, 148.0, 135.0, 130.1, 129.2, 64.6, 35.3, 31.2, 30.7, 19.2, 13.8.\)

Butyl 3-(3-formylphenyl)propanoate (3oa)\(^2\)

\[
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 9.94 (s, 1\text{H}), 7.69–7.66 (m, 2\text{H}), 7.46–7.39 (m, 2\text{H}), 4.02 (t, J = 6.6 \text{ Hz}, 2\text{H}), 2.99 (t, J = 7.6 \text{ Hz}, 2\text{H}), 2.62 (t, J = 7.6 \text{ Hz}, 3\text{H}), 1.56–1.49 (m, 2\text{H}), 1.32–1.23 (m, 2\text{H}), 0.85 (t, J = 7.4 \text{ Hz}, 3\text{H}). \(^1\)^C NMR (101 MHz, CDCl\(_3\)) \(\delta 192.4, 172.7, 141.8, 136.8, 134.7, 129.4, 129.3, 128.1, 64.5, 35.6, 30.8, 30.7, 19.2, 13.8.\)

3-Phenylpropanamide (3eb)\(^5\)

\[
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.32-7.27 (m, 2\text{H}), 7.23-7.21 (m, 3\text{H}), 5.45 (br, 2\text{H}), 2.98 (t, J = 7.8 \text{ Hz}, 2\text{H}), 2.54 (t, J = 7.8 \text{ Hz}, 2\text{H}). \(^1\)^C NMR (101 MHz, CDCl\(_3\)) \(\delta 175.5, 140.9, 128.8, 128.6, 126.5, 37.8, 31.6.\)
Electronic Supplementary Material (ESI) for Chemical Communications
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3ia

![NMR spectrum of 3ia](image)

**Chemical Shifts:**
- 7.97 (d)
- 7.13 (d)
- 4.06 (s)
- 3.5 (t)
- 2.56 (s)
- 2.23 (t)
- 1.58 (s)
- 1.37 (s)
- 1.23 (s)
- 0.90 (s)

**Assignments:**
- H-Carbonyl
- H-Aromatic
- H-Isopropyl