Electronic Supplementary Information

Cu-catalyzed carboxylation of
organoboronic acid pinacol esters with CO₂

Chihiro Maeda,* Takumi Cho, Ren Kumemoto, and Tadashi Ema*

Division of Applied Chemistry, Graduate School of Natural Science and Technology, Okayama University,
Tsushima, Okayama 700-8530, Japan.
E-mail: cmaeda@okayama-u.ac.jp; ema@cc.okayama-u.ac.jp

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[A] Instrumentation and Materials

$^1$H and $^{13}$C NMR spectra were taken on a JEOL ECS400 or ECZ600 spectrometer, and chemical shifts are reported as the delta scale in ppm using an internal reference ($\delta = 7.26$ for $^1$H NMR, 77.16 for $^{13}$C NMR, for CDCl$_3$, $\delta = 2.05$ for $^1$H NMR, 29.84 for $^{13}$C NMR, for acetone-$d_6$), and $\delta = 2.50$ for $^1$H NMR, 39.52 for $^{13}$C NMR, for DMSO-$d_6$.

(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (1i), 1,4-naphthalenediboronic acid bis(pinacol) ester (1n), 2,7-pyrenediboronic acid bis(pinacol) ester (1o), (E)-styrylboronic acid pinacol ester (3a), (E)-(4-methoxy styryl)boronic acid pinacol ester (3b), (phenylethynyl)boronic acid pinacol ester (3d), 1,4-bis((E)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzene (3h), 1,3-bis((E)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzene (3i), 1,3,5-tris((E)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzene (3j), 3,4-methylenedioxyphenylboronic acid pinacol ester, and biphenyl-4-ylmethylboronic acid pinacol ester were prepared according to literature procedures.

[B] Experimental Procedures and Compound Data

General procedure for the copper-catalyzed carboxylation of organoboronic acid pinacol esters with CO$_2$. A 30 mL stainless autoclave containing organoboronic acid pinacol ester (0.5 mmol) and (IPr)CuCl (12.2 mg, 0.025 mmol, 5 mol%) was dried in vacuo and placed in a glove box (purge type) under N$_2$ atmosphere. 'BuOK (2.81 mg, 0.025 mmol, 5 mol%), CsF (152 mg, 1.00 mmol, dried at 80 °C for 12 h in vacuo and cooled to room temperature in advance) and dry 1,4-dioxane (1.0 mL) were added, and the autoclave was closed. The sealed autoclave was taken out from the glovebox and pressurized with 2.0 MPa of CO$_2$. The mixture was stirred at 150 °C for 24 h, and then the autoclave was cooled to room temperature, and the remaining CO$_2$ was vented slowly. The reaction mixture was acidified with 1 M HCl (aq), and the aqueous layer was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over Na$_2$SO$_4$, and evaporated under reduced pressure. Purification by silica gel column chromatography gave the corresponding carboxylic acid.

General procedure for the copper-catalyzed double carboxylation of organodiboronic acid bis(pinacol) esters with CO$_2$. A 30 mL stainless autoclave containing organodiboronic acid bis(pinacol) ester (0.5 mmol) and (IPr)CuCl (24.4 mg, 0.050 mmol, 10 mol%) was dried in vacuo and placed in a glove box (purge type) under N$_2$ atmosphere. 'BuOK (5.61 mg, 0.050 mmol, 10 mol%), CsF (304 mg, 2.00 mmol, dried at 80 °C for 12 h in vacuo and cooled to room temperature in advance) and dry 1,4-dioxane (2.0 mL) were added, and the autoclave was closed. The sealed autoclave was taken out from the glovebox and pressurized with 2.0 MPa of CO$_2$. The mixture was stirred at 160 °C or 170 °C for 24 h, and then the autoclave was cooled to room temperature, and the remaining CO$_2$ was vented slowly. 10% NaOH (aq) was added to the reaction mixture, and the aqueous layer was washed with EtO once. The aqueous layer was acidified with 5% H$_2$SO$_4$ (aq). For 2l, 2o, and 4h–j, a powder precipitated was collected and washed with water and CHCl$_3$ to give the dicarboxylic acid. For 2o, the crude product was dissolved in DMSO (10 mL), and MeI (1.2 mL, 2.0 mmol) and K$_2$CO$_3$ (276 mg, 2.00 mmol) were added. The mixture was stirred at 50 °C for 12 h. Water was added, and organic products were extracted with CHCl$_3$. Purification by silica gel column chromatography (CHCl$_3$) gave methyl ester 2o'. For 2m, 2n, 2p, and 2q, the product was extracted with EtO twice, and the combined organic layer was washed with brine, dried over Na$_2$SO$_4$, and evaporated under reduced pressure. Suction filtration of the precipitate gave the dicarboxylic acid.
Table S1  Initial screening of the reaction conditions of the Cu-catalyzed carboxylation of phenylboronic acid pinacol ester (1a) with CO₂. A photograph of the 30 mL stainless autoclave is shown.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cu-catalyst</th>
<th>Solvent</th>
<th>Base</th>
<th>T (°C)</th>
<th>Yield (b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1c</td>
<td>IPrCuCl</td>
<td>toluene</td>
<td>KO'Bu</td>
<td>110</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>IPrCuCl</td>
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<td>48</td>
</tr>
<tr>
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<td>KO'Bu</td>
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<td>21</td>
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<tr>
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<td>KO'Bu</td>
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<td>53</td>
</tr>
<tr>
<td>7</td>
<td>IMesCuCl</td>
<td>1,4-dioxane</td>
<td>KO'Bu</td>
<td>150</td>
<td>5</td>
</tr>
<tr>
<td>8d</td>
<td>CuCl + Xantphos</td>
<td>1,4-dioxane</td>
<td>KO'Bu</td>
<td>150</td>
<td>2</td>
</tr>
<tr>
<td>9d</td>
<td>CuCl + TMEDA</td>
<td>1,4-dioxane</td>
<td>KO'Bu</td>
<td>150</td>
<td>0</td>
</tr>
<tr>
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<td>KO'Bu</td>
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<td>16</td>
</tr>
<tr>
<td>11</td>
<td>IPrCuCl</td>
<td>1,4-dioxane</td>
<td>NaO'Bu</td>
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<td>trace</td>
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<td>Cs₂CO₃</td>
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<td>³Pr₂NET</td>
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<tr>
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<td>1,4-dioxane</td>
<td>KO'Bu + CsF²⁻</td>
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<td>36</td>
</tr>
<tr>
<td>15</td>
<td>IPrCuCl</td>
<td>1,4-dioxane</td>
<td>CsF²⁻</td>
<td>150</td>
<td>98</td>
</tr>
</tbody>
</table>

a Reaction conditions: 1a (0.5 mmol), Cu-catalyst (5 mol%), base (1.05 equiv), solvent (1.0 mL), CO₂ (2.0 MPa), 110–170 °C, 24 h, in a 30 mL stainless autoclave. b Yields were determined by ¹H NMR spectroscopy using 2-methoxynaphthalene as an internal standard. c 0.1 MPa CO₂ (balloon). d 5 mol% of ligand was used. e 2 equiv of CsF was used.

benzoic acid (2a)

92% (56.1 mg, 459 μmol) white solid, Rᶠ = 0.15 (CHCl₃/MeOH = 20/1); ¹H NMR (CDCl₃, 400 MHz) δ 7.49 (t, J = 7.6 Hz, 2H), 7.62 (tt, J = 1.2, 7.6 Hz, 1H), 8.13 (dd, J = 1.2, 8.4 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 128.6, 129.4, 130.4, 134.0, 172.1.

p-toluic acid (2b)

77% (52.2 mg, 383 μmol) white solid, Rᶠ = 0.13 (CHCl₃/MeOH = 20/1); ¹H NMR (CDCl₃, 400 MHz) δ 2.44 (s, 3H), 7.28 (d, J = 7.6 Hz, 2H), 8.00 (d, J = 8.0 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 21.9, 126.7, 129.4, 130.4, 144.8, 172.3.

p-anisic acid (2c)

89% (67.6 mg, 444 μmol) white solid, Rᶠ = 0.18 (CHCl₃/MeOH = 20/1); ¹H NMR (CDCl₃, 400 MHz) δ 3.88 (s, 3H), 6.95 (d, J = 9.2 Hz, 2H), 8.07 (d, J = 9.2 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 55.6, 114.0, 122.0, 132.5, 164.3, 171.6.
4-methoxycarbonylbenzoic acid (2d)\(^{11}\)

\[
\begin{array}{c}
\text{MeO}_2C \quad \text{CO}_2H
\end{array}
\]

94% (84.3 mg, 468 \(\mu\)mol) white solid, \(R_f = 0.10\) (CHCl\(_3\)/MeOH = 20/1), and \(R_f = 0.13\) (CHCl\(_3\)/MeOH = 9/1); \(^1\)H NMR (DMSO-\(d_6\), 400 MHz) \(\delta\) 3.88 (s, 3H), 8.06 (s, 4H), 13.37 (s, 1H); \(^{13}\)C NMR (DMSO-\(d_6\), 100 MHz) \(\delta\) 52.5, 129.4, 129.7, 133.2, 135.0, 165.6, 166.7.

4-trifluoromethylbenzoic acid (2e)\(^{10}\)

\[
\begin{array}{c}
\text{F}_3\text{C} \quad \text{CO}_2H
\end{array}
\]

61% (58.3 mg, 307 \(\mu\)mol) white solid, \(R_f = 0.07\) (CHCl\(_3\)/MeOH = 20/1); \(^1\)H NMR (DMSO-\(d_6\), 400 MHz) \(\delta\) 7.88 (d, \(J = 8.0\) Hz, 2H), 8.13 (d, \(J = 8.0\) Hz, 2H), 13.49 (s, 1H); \(^{13}\)C NMR (DMSO-\(d_6\), 100 MHz) \(\delta\) 123.8 (q, \(J = 271.5\) Hz), 125.7 (q, \(J = 2.9\) Hz), 130.3, 132.5 (q, \(J = 31.8\) Hz), 135.1, 165.9.

\(m\)-anisic acid (2f)\(^{10}\)

\[
\begin{array}{c}
\text{MeO} \quad \text{CO}_2H
\end{array}
\]

76% (58.1 mg, 382 \(\mu\)mol) white solid, \(R_f = 0.13\) (CHCl\(_3\)/MeOH = 20/1); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 3.87 (s, 3H), 7.16 (ddd, \(J = 1.2, 2.8, 8.4\) Hz, 1H), 7.39 (t, \(J = 8.4\) Hz, 1H), 7.62–7.63 (m, 1H), 7.72 (d, \(J = 7.6\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 55.6, 114.5, 120.6, 122.8, 129.7, 130.8, 159.7, 172.3.

\(o\)-anisic acid (2g)\(^{10}\)

\[
\begin{array}{c}
\text{CO}_2H
\end{array}
\]

33% (25.0 mg, 164 \(\mu\)mol) white solid, \(R_f = 0.13\) (CHCl\(_3\)/MeOH = 20/1); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 4.09 (s, 3H), 7.07 (d, \(J = 8.0\) Hz, 1H), 7.16 (t, \(J = 7.2\) Hz, 1H), 7.59 (dt, \(J = 1.6, 7.2\) Hz, 1H), 8.20 (dd, \(J = 2.0, 8.0\) Hz, 1H), 10.74 (s, 1H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 56.8, 111.8, 117.7, 122.3, 133.9, 135.2, 158.2, 165.7.

1-naphthoic acid (2h)\(^{10}\)

\[
\begin{array}{c}
\text{CO}_2H
\end{array}
\]

68% (58.4 mg, 339 \(\mu\)mol) white solid, \(R_f = 0.13\) (CHCl\(_3\)/MeOH = 20/1), and \(R_f = 0.05\) (hexane/EtOAc = 5/1); \(^1\)H NMR (DMSO-\(d_6\), 400 MHz) \(\delta\) 7.57–7.67 (m, 3H), 8.02 (d, \(J = 7.2\) Hz, 1H), 8.14–8.17 (m, 2H), 8.86 (d, \(J = 8.8\) Hz, 1H), 13.14 (s, 1H); \(^{13}\)C NMR (DMSO-\(d_6\), 100 MHz) \(\delta\) 124.9, 125.5, 126.2, 127.6, 127.7, 128.6, 129.9, 130.7, 133.0, 133.5, 168.7.

thiophene-2-carboxylic acid (2i)\(^{10}\)

\[
\begin{array}{c}
\text{S} \quad \text{CO}_2H
\end{array}
\]

53% (34.1 mg, 266 \(\mu\)mol) white solid, \(R_f = 0.05\) (CHCl\(_3\)/MeOH = 20/1); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.15 (dd, \(J = 3.8, 4.4\) Hz, 1H), 7.65 (dd, \(J = 1.2, 5.2\) Hz, 1H), 7.90 (dd, \(J = 1.2, 3.6\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 128.3, 133.1, 134.2, 135.3, 168.0.

carbazole-1-carboxylic acid (2j)\(^{12}\)

\[
\begin{array}{c}
\text{H} \quad \text{CO}_2H
\end{array}
\]

51% (53.8 mg, 255 \(\mu\)mol) white solid, \(R_f = 0.30\) (CHCl\(_3\)/MeOH = 9/1); \(^1\)H NMR (DMSO-\(d_6\), 400 MHz) \(\delta\) 7.18–7.27 (m, 2H), 7.42 (t, \(J = 6.8\) Hz, 1H), 7.74 (d, \(J = 8.8\) Hz, 1H), 8.00 (d, \(J = 7.2\) Hz, 1H), 8.16 (d, \(J = 8.0\) Hz, 1H), 8.39 (d, \(J = 7.2\) Hz, 1H), 11.32 (s, 1H), 13.17 (s, 1H); \(^{13}\)C NMR (DMSO-\(d_6\), 100 MHz) \(\delta\) 112.3, 112.8, 118.0, 119.3, 120.2, 121.7, 124.2, 125.2, 126.1, 127.5, 139.1, 140.3, 168.0.

S4
carbazole-3-carboxylic acid (2k)\textsuperscript{13}

\[
\begin{align*}
\text{CO}_2\text{H} & \\
\text{N} & \\
\text{H} & \\
\end{align*}
\]

45%, (47.8 mg, 226 \text{ \textmu}mol) white solid, \textit{R}_f = 0.25 (CHCl_3/MeOH = 9/1); \textsuperscript{1}H NMR (DMSO-\textit{d}_6, 400 MHz) \delta 7.22 (t, \textit{J} = 7.6 \text{ Hz}, 1H), 7.44 (t, \textit{J} = 7.2 \text{ Hz}, 1H), 7.54 (d, \textit{J} = 9.2 \text{ Hz}, 2H), 8.02 (dd, \textit{J} = 1.6, 8.4 \text{ Hz}, 1H), 8.24 (d, \textit{J} = 8.0 \text{ Hz}, 1H), 8.78 (s, 1H), 11.66 (s, 1H), 12.58 (s, 1H); \textsuperscript{13}C NMR (DMSO-\textit{d}_6, 150 MHz) \delta 110.6, 111.4, 119.5, 120.6, 121.0, 122.2, 122.49, 122.50, 126.3, 127.0, 140.3, 142.4, 168.1.

terephthalic acid (2l)\textsuperscript{11}

\[
\begin{align*}
\text{HO}_2\text{C} & \\
\text{CO}_2\text{H} & \\
\end{align*}
\]

65% (54.1 mg, 326 \text{ \textmu}mol) white solid; \textsuperscript{1}H NMR (DMSO-\textit{d}_6, 400 MHz) \delta 8.04 (s, 4H), 13.29 (s, 2H); \textsuperscript{13}C NMR (DMSO-\textit{d}_6, 100 MHz) \delta 129.5, 134.5, 166.7.

isophthalic acid (2m)\textsuperscript{14}

\[
\begin{align*}
\text{HO}_2\text{C} & \\
\text{CO}_2\text{H} & \\
\end{align*}
\]

51% (42.7 mg, 257 \text{ \textmu}mol) white solid; \textsuperscript{1}H NMR (DMSO-\textit{d}_6, 400 MHz) \delta 7.64 (t, \textit{J} = 8.0 \text{ Hz}, 1H), 8.16 (dd, \textit{J} = 2.0, 8.0 \text{ Hz}, 2H), 8.48 (s, 1H), 13.25 (s, 2H); \textsuperscript{13}C NMR (DMSO-\textit{d}_6, 100 MHz) \delta 129.2, 130.1, 131.3, 133.5, 166.7.

1,4-naphthalenedicarboxylic acid (2n)\textsuperscript{15}

\[
\begin{align*}
\text{CO}_2\text{H} & \\
\text{H} & \\
\end{align*}
\]

45% (48.7 mg, 225 \text{ \textmu}mol) white solid; \textsuperscript{1}H NMR (DMSO-\textit{d}_6, 400 MHz) \delta 7.70 (dd, \textit{J} = 3.6, 6.4 \text{ Hz}, 2H), 8.10 (s, 2H), 8.78 (dd, \textit{J} = 3.6, 6.8 \text{ Hz}, 2H), 13.51 (s, 2H); \textsuperscript{13}C NMR (DMSO-\textit{d}_6, 100 MHz) \delta 125.9, 127.6, 127.9, 130.8, 132.3, 168.5.

dimethyl 2,7-pyrenedicarboxylate (2o')\textsuperscript{16}

\[
\begin{align*}
\text{MeO}_2\text{C} & \\
\text{CO}_2\text{Me} & \\
\end{align*}
\]

42% (66.6 mg, 209 \text{ \textmu}mol) light yellow solid; \textsuperscript{1}H NMR (CDCl_3, 600 MHz) \delta 4.09 (s, 6H), 8.13 (s, 4H), 8.82 (s, 4H); \textsuperscript{13}C NMR (CDCl_3, 100 MHz) \delta 52.6, 126.3, 128.6, 131.7, 167.5.

2,5-thiophenedicarboxylic acid (2p)\textsuperscript{17}

\[
\begin{align*}
\text{HO}_2\text{C} & \\
\text{S} & \\
\text{CO}_2\text{H} & \\
\end{align*}
\]

46% (40.0 mg, 232 \text{ \textmu}mol) white solid; \textsuperscript{1}H NMR (DMSO-\textit{d}_6, 400 MHz) \delta 7.71 (s, 2H), 13.59 (s, 2H); \textsuperscript{13}C NMR (DMSO-\textit{d}_6, 100 MHz) \delta 133.3, 139.8, 162.5.

2,5-pyrroledicarboxylic acid (2q)\textsuperscript{18}

\[
\begin{align*}
\text{HO}_2\text{C} & \\
\text{N} & \\
\text{CO}_2\text{H} & \\
\end{align*}
\]

6% (5.0 mg, 32.2 \text{ \textmu}mol) gray solid; \textsuperscript{1}H NMR (DMSO-\textit{d}_6, 400 MHz) \delta 6.74 (d, \textit{J} = 1.2 \text{ Hz}, 2H), 12.20 (s, 1H) 12.72 (s, 2H); \textsuperscript{13}C NMR (DMSO-\textit{d}_6, 100 MHz) \delta 115.1, 127.3, 161.3.

(E)-cinnamic acid (4a)\textsuperscript{19}

\[
\begin{align*}
\text{CO}_2\text{H} & \\
\end{align*}
\]

90% (69.5 mg, 469 \text{ \textmu}mol) white solid, \textit{R}_f = 0.15 (CHCl_3/MeOH = 20/1); \textsuperscript{1}H NMR (CDCl_3, 400 MHz) \delta 6.47 (d, \textit{J} = 15.6 \text{ Hz}, 1H), 7.41−7.42 (m, 3H), 7.55−7.57 (m, 2H), 7.79 (d, \textit{J} = 16.0 \text{ Hz}, 1H); \textsuperscript{13}C NMR (CDCl_3, 100 MHz) \delta 117.4, 128.5, 129.1, 130.9, 134.2, 147.3, 172.6.
(E)-4-methoxycinnamic acid (4b)\(^{20}\)

![Structure](image)

84% (75.9 mg, 426 μmol) white solid, \(R_f = 0.07\) (CHCl\(_3\)/MeOH = 30/1), and \(R_f = 0.25\) (CHCl\(_3\)/MeOH = 20/1); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 3.85 (s, 3H), 6.32 (d, \(J = 15.6\) Hz, 1H), 6.92 (d, \(J = 9.2\) Hz, 2H), 7.51 (d, \(J = 9.2\) Hz, 2H), 7.74 (d, \(J = 16.0\) Hz, 1H); \(^{13}\)C NMR (DMSO-\(d_6\), 100 MHz) \(\delta\) 55.3, 114.6, 126.8, 130.0, 143.8, 161.0, 167.8.

(E)-4-bromocinnamic acid (4c)

![Structure](image)

54% (61.7 mg, 272 μmol) white solid, \(R_f = 0.05\) (CHCl\(_3\)/MeOH = 20/1); \(^1\)H NMR (acetone-\(d_6\), 400 MHz) \(\delta\) 6.57 (d, \(J = 16.0\) Hz, 1H), 7.61–7.67 (m, 5H), 10.86 (s, 1H); \(^{13}\)C NMR (acetone-\(d_6\), 100 MHz) \(\delta\) 120.2, 124.7, 130.8, 132.9, 134.8, 144.0, 167.4; HRMS (ESI) \(m/z\): [\(M–H\)] Calcd for C\(_{13}\)H\(_{10}\)OBr 224.9557; Found 224.9656.

(E)-4-trifluoromethylcinnamic acid (4d)\(^{21}\)

![Structure](image)

61% (36.1 mg, 167 μmol) from 3d (250 μmol) white solid, \(R_f = 0.07\) (CHCl\(_3\)/MeOH = 20/1), and \(R_f = 0.10\) (EtOAc); \(^1\)H NMR (DMSO-\(d_6\), 400 MHz) \(\delta\) 6.68 (d, \(J = 16.0\) Hz, 1H), 7.66 (d, \(J = 16.0\) Hz, 1H), 7.76 (d, \(J = 8.0\) Hz, 2H), 7.92 (d, \(J = 8.4\) Hz, 2H), 12.62 (s, 1H); \(^{13}\)C NMR (DMSO-\(d_6\), 100 MHz) \(\delta\) 122.2, 124.1 (q, \(J = 271.1\) Hz), 125.7 (q, \(J = 3.8\) Hz), 128.9, 129.8 (q, \(J = 31.8\) Hz), 138.3, 142.1, 167.2.

2-phenylacetic acid (4e)\(^{19}\)

![Structure](image)

82% (55.8 mg, 410 μmol) white solid, \(R_f = 0.20\) (CHCl\(_3\)/MeOH = 9/1); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 3.66 (s, 2H), 7.38–7.28 (m, 5H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 127.5, 128.7, 129.5, 133.4, 178.1.

octanoic acid (4f)\(^{22}\)

![Structure](image)

28% (18.5 mg, 128 μmol) colorless liquid; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 0.88 (t, \(J = 6.8\) Hz, 3H), 1.16–1.38 (m, 8H), 1.56–1.70 (m, 2H), 2.35 (t, \(J = 7.2\) Hz, 2H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 14.2, 22.7, 24.8, 29.1, 29.2, 31.8, 34.2, 180.3.

3-phenylpropionic acid (4g)\(^{19}\)

![Structure](image)

36% (26.7 mg, 183 μmol) white solid, \(R_f = 0.05\) (CHCl\(_3\)/MeOH = 20/1), and \(R_f = 0.08\) (CHCl\(_3\)/MeOH = 9/1); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.40 (t, \(J = 7.6\) Hz, 2H), 7.49 (t, \(J = 7.2\) Hz, 1H), 7.62 (d, \(J = 6.8\) Hz, 2H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 80.4, 89.5, 119.2, 128.8, 131.3, 133.5, 158.5.

1,4-benzenediacrylic acid (4h)\(^{23}\)

![Structure](image)

62% (64.1 mg, 294 μmol) light brown solid; \(^1\)H NMR (DMSO-\(d_6\), 400 MHz) \(\delta\) 6.60 (d, \(J = 16.0\) Hz, 2H), 7.60 (d, \(J = 15.6\) Hz, 2H), 7.73 (s, 4H) 12.46 (s, 2H); \(^{13}\)C NMR (DMSO-\(d_6\), 100 MHz) \(\delta\) 120.2, 128.7, 135.9, 143.1, 167.5.

1,3-benzenediacrylic acid (4i)

![Structure](image)

73% (79.7 mg, 365 μmol) light yellow solid; \(^1\)H NMR (DMSO-\(d_6\), 400 MHz) \(\delta\) 6.67 (d, \(J = 16.0\) Hz, 2H), 7.46 (t, \(J = 8.0\) Hz, 1H), 7.60 (d, \(J = 16.0\) Hz, 2H), 7.72 (dd, \(J = 1.6, 8.0\) Hz, 2H), 8.08 (s, 1H), 12.44 (s, 2H); \(^{13}\)C NMR (DMSO-\(d_6\), 100 MHz) \(\delta\) 120.2, 127.7, 129.5, 129.9, 135.0, 143.3, 167.6; HRMS (ESI) \(m/z\): [\(M–H\)] Calcd for C\(_{12}\)H\(_{10}\)O\(_4\) 217.0506; Found 217.0515.
1,3,5-benzenetriacrylic acid (4j)

\[
\text{HO}_2\text{C} - \text{C} = \text{C} - \text{CO}_2\text{H}
\]
40% (19.3 mg, 67.0 μmol) from 3j (167 μmol) brown solid; \(^1\)H NMR (DMSO-\(d_6\), 400 MHz) \(\delta\) 6.78 (d, \(J = 16.0\) Hz, 3H), 7.60 (d, \(J = 16.4\) Hz, 3H), 8.08 (s, 3H), 12.35 (s, 3H); \(^{13}\)C NMR could not detect peaks due to very low solubility; HRMS (ESI) \(m/z\): [M–2H]\(^2\)+ Calcd for C\(_{15}\)H\(_{10}\)O\(_6\) 214.0244; Found 214.0241.

piperonylic acid

\[
\text{CO}_2\text{H}
\]
80% (66.2 mg, 398 μmol) white solid, \(R_f = 0.11\) (CHCl\(_3\)/MeOH = 20/1); \(^1\)H NMR (DMSO-\(d_6\), 600 MHz) \(\delta\) 6.12 (s, 2H), 7.00 (d, \(J = 8.4\) Hz, 1H), 7.36 (d, \(J = 1.8\) Hz, 1H), 7.54 (dd, \(J = 1.8, 8.4\) Hz, 1H), 12.77 (s, 1H); \(^{13}\)C NMR (DMSO-\(d_6\), 150 MHz) \(\delta\) 102.0, 108.1, 108.8, 124.6, 125.0, 147.5, 151.2, 166.6; HRMS (ESI) \(m/z\): [M–H]\(^–\) Calcd for C\(_8\)H\(_5\)O\(_4\) 165.0193; Found 165.0187.

felbinac

\[
\text{CO}_2\text{H}
\]
45% (35.5 mg, 166 μmol) light yellow solid, \(R_f = 0.11\) (CHCl\(_3\)/MeOH = 20/1); \(^1\)H NMR (CDCl\(_3\), 600 MHz) \(\delta\) 3.71 (s, 2H), 7.35–7.38 (m, 3H), 7.42–7.45 (m, 2H), 7.56–7.59 (m, 4H); \(^{13}\)C NMR (CDCl\(_3\), 150 MHz) \(\delta\) 40.6, 127.2, 127.5, 127.6, 128.9, 129.9, 132.4, 140.5, 140.8, 176.5; HRMS (ESI) \(m/z\): [M–H]\(^–\) Calcd for C\(_{14}\)H\(_{11}\)O\(_2\) 211.0765; Found 211.0760.

**Scheme S1**  (a) A proposed reaction mechanism for the Cu-catalyzed carboxylation of boronic esters.\(^{24}\) (b) Stoichiometric transmetalation of (IPr)CuO'Bu with PhBpin.\(^{25}\) IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene.
[C] References.


Comparison with the Reported Reaction Conditions
We conducted the Cu-catalyzed carboxylation under Bayer’s reaction condition in a stainless autoclave. Unfortunately, we could not reproduce the high yields they achieved by using a specialized glassware (Scheme S2). In addition, double carboxylation did not take place at all under the reaction condition (Scheme S3).

(a) Carboxylation under our optimized condition (this work)

\[
\text{pinB-Bpin} + \text{CO}_2 \quad \xrightarrow{\text{1,4-dioxane, 150 °C, 24 h then HCl (aq.)}} \quad \text{pinB-CO}_2 \text{H}
\]

\(96\%\) (in a stainless autoclave)

(b) Carboxylation under Bayer's condition in 1,4-dioxane

\[
\text{pinB-Bpin} + \text{CO}_2 \quad \xrightarrow{\text{1,4-dioxane, 120 °C, 18 h then HCl (aq.)}} \quad \text{pinB-CO}_2 \text{H}
\]

\(54\%\) (in a stainless autoclave)

(c) Carboxylation under Bayer's condition in methylal

\[
\text{pinB-Bpin} + \text{CO}_2 \quad \xrightarrow{\text{methylal, 120 °C, 18 h then HCl (aq.)}} \quad \text{pinB-CO}_2 \text{H}
\]

\(41\%\) (in a stainless autoclave)

\(81\%\) (in a specialized glassware)

\(a\) NMR yield. \(b\) Isolated yield. \(c\) Reference data: Chem. Eur. J., 2020, 26, 6064.

Scheme S2

(a) Double carboxylation under our optimized condition (this work)

\[
\text{pinB-Bpin} + \text{CO}_2 \quad \xrightarrow{\text{1,4-dioxane, 170 °C, 24 h then HCl (aq.)}} \quad \text{pinB-CO}_2 \text{H}
\]

\(65\%\)

(b) Double carboxylation under Bayer's condition in 1,4-dioxane

\[
\text{pinB-Bpin} + \text{CO}_2 \quad \xrightarrow{\text{1,4-dioxane, 120 °C, 18 h then HCl (aq.)}} \quad \text{pinB-CO}_2 \text{H}
\]

\(0\%\)

(c) Double carboxylation under Bayer's condition in methylal

\[
\text{pinB-Bpin} + \text{CO}_2 \quad \xrightarrow{\text{methylal, 120 °C, 18 h then HCl (aq.)}} \quad \text{pinB-CO}_2 \text{H}
\]

\(<1\%\)

Scheme S3
400 MHz $^1$H NMR spectrum of 2a in CDCl$_3$.

100 MHz $^{13}$C NMR spectrum of 2a in CDCl$_3$. 
400 MHz $^1$H NMR spectrum of 2b in CDCl$_3$.

100 MHz $^{13}$C NMR spectrum of 2b in CDCl$_3$. 
400 MHz $^1$H NMR spectrum of 2c in CDCl$_3$.

100 MHz $^{13}$C NMR spectrum of 2c in CDCl$_3$. 
400 MHz $^1$H NMR spectrum of 2d in DMSO-$d_6$.

100 MHz $^{13}$C NMR spectrum of 2d in DMSO-$d_6$. 
400 MHz $^1$H NMR spectrum of 2e in DMSO-$d_6$.

100 MHz $^{13}$C NMR spectrum of 2e in DMSO-$d_6$. 
400 MHz $^1$H NMR spectrum of 2f in CDCl$_3$. 

100 MHz $^{13}$C NMR spectrum of 2f in CDCl$_3$. 
400 MHz $^1$H NMR spectrum of 2g in CDCl$_3$.

100 MHz $^{13}$C NMR spectrum of 2g in CDCl$_3$. 

S16
400 MHz $^1$H NMR spectrum of 2h in DMSO-$d_6$.

100 MHz $^{13}$C NMR spectrum of 2h in DMSO-$d_6$. 
400 MHz $^1$H NMR spectrum of 2i in CDCl$_3$.

100 MHz $^{13}$C NMR spectrum of 2i in CDCl$_3$. 
400 MHz $^1$H NMR spectrum of 2j in DMSO-$d_6$.

100 MHz $^{13}$C NMR spectrum of 2j in DMSO-$d_6$. 
400 MHz $^1$H NMR spectrum of 2k in DMSO-$d_6$.

150 MHz $^{13}$C NMR spectrum of 2k in DMSO-$d_6$. 
400 MHz $^1$H NMR spectrum of 21 in DMSO-$d_6$.

100 MHz $^{13}$C NMR spectrum of 21 in DMSO-$d_6$. 
400 MHz $^1$H NMR spectrum of 2m in DMSO-$d_6$.

100 MHz $^{13}$C NMR spectrum of 2m in DMSO-$d_6$. 
400 MHz $^{1}\text{H}$ NMR spectrum of 2n in DMSO-$d_6$.

100 MHz $^{13}\text{C}$ NMR spectrum of 2n in DMSO-$d_6$. 
600 MHz $^1$H NMR spectrum of $20'$ in CDCl₃.

150 MHz $^{13}$C NMR spectrum of $20'$ in CDCl₃.
400 MHz $^1$H NMR spectrum of 2p in DMSO-$d_6$.

100 MHz $^{13}$C NMR spectrum of 2p in DMSO-$d_6$. 
400 MHz $^1$H NMR spectrum of 2q in DMSO-$d_6$.

100 MHz $^{13}$C NMR spectrum of 2q in DMSO-$d_6$. 
400 MHz $^1$H NMR spectrum of 4a in CDCl$_3$.

100 MHz $^{13}$C NMR spectrum of 4a in CDCl$_3$. 

S27
400 MHz $^1$H NMR spectrum of 4b in CDCl$_3$.

100 MHz $^{13}$C NMR spectrum of 4b in DMSO-$d_6$. 

S28
400 MHz $^1$H NMR spectrum of 4c in acetone-$d_6$.

100 MHz $^{13}$C NMR spectrum of 4c in acetone-$d_6$. 
400 MHz $^1$H NMR spectrum of 4d in DMSO-$d_6$.

100 MHz $^{13}$C NMR spectrum of 4d in DMSO-$d_6$. 
400 MHz $^1$H NMR spectrum of 4e in CDCl$_3$.

100 MHz $^{13}$C NMR spectrum of 4e in CDCl$_3$. 
400 MHz $^1$H NMR spectrum of 4f in CDCl$_3$.

100 MHz $^{13}$C NMR spectrum of 4f in CDCl$_3$. 
400 MHz $^1$H NMR spectrum of 4g in CDCl$_3$.

100 MHz $^{13}$C NMR spectrum of 4g in CDCl$_3$. 
400 MHz $^1$H NMR spectrum of 4h in DMSO-$d_6$.

150 MHz $^{13}$C NMR spectrum of 4h in DMSO-$d_6$. 
400 MHz $^1$H NMR spectrum of 4i in DMSO-$d_6$.

100 MHz $^{13}$C NMR spectrum of 4i in DMSO-$d_6$. 
400 MHz $^1$H NMR spectrum of 4j in DMSO-$d_6$. 
600 MHz $^1$H NMR spectrum of piperonylic acid in DMSO-$d_6$.

150 MHz $^{13}$C NMR spectrum of piperonylic acid in DMSO-$d_6$. 
600 MHz $^1$H NMR spectrum of felbinac in CDCl$_3$.

150 MHz $^{13}$C NMR spectrum of felbinac in CDCl$_3$. 