Supporting Information

Ligand-free Pd(0)/SiO$_2$-catalyzed aminocarbonylation of aryl iodides to amides at atmospheric CO pressure

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Table S1 Amide amount in the supernatant and DMSO eluent of solid catalyst for different reaction time.<sup>a</sup>

<table>
<thead>
<tr>
<th>Entry</th>
<th>Time (h)</th>
<th>Amount of amide in DMSO eluent (μmol)</th>
<th>Amount of amide in the supernatant (μmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24</td>
<td>trace</td>
<td>388</td>
</tr>
<tr>
<td>2</td>
<td>36</td>
<td>72</td>
<td>308</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>84</td>
<td>288</td>
</tr>
<tr>
<td>4</td>
<td>44</td>
<td>86</td>
<td>288</td>
</tr>
</tbody>
</table>

(a) Reaction conditions: iodobenzene (0.4 mmol, 1 equiv.), aniline (2 mL), and CO (1 atm), 1 wt% Pd/SiO<sub>2</sub> (0.5 mol%), K<sub>2</sub>CO<sub>3</sub> (2 equiv.), reaction temperature: 80 °C, no solvent. Yields based on GC analysis.

**Scheme S1**

**Discussion.** we detected the chemical compounds in the supernatant and DMSO eluent of solid catalyst (Scheme S1). After 24 h of reaction, nearly no residual iodobenzene was detected. This means that iodobenzene has been exhausted almost completely. Meanwhile, the yield of the target product N-phenylbenzamide reached a maximum. When the reaction time was longer than 24 h, the amount of N-phenylbenzamide in the DMSO eluent of solid catalyst increased gradually (Table S1). So, the precipitation of N-phenylbenzamide on the solid catalyst resulted in a lower product yield in the supernatant with a prolonged reaction time. The optimum reaction time is 24 h at which iodobenzene has been exhausted almost completely.
NMR Spectra of the Isolated Target Products

(2c) N-phenylbenzamide

The target compound was prepared according to the general procedure using iodobenzene with aniline, and purified by silica gel column chromatography as solid. The observed characterization data ($^{13}$C) was consistent with that previously reported in the literature. $^1$H NMR (400MHz, DMSO-d6) $\delta$ (ppm): 10.25 (s, 1H), 7.96 (d, J = 8.3 Hz, 2H), 7.79 (d, J = 7.8 Hz, 2H), 7.60 (t, J = 7.2 Hz, 1H), 7.54 (t, J = 7.3 Hz, 2H), 7.36 (t, J = 7.9 Hz, 2H), 7.11 (t, J = 7.4 Hz, 1H). $^{13}$C NMR(100 MHz,DMSO-d6) $\delta$ (ppm): 166.02, 139.63, 135.45, 132.00, 129.06, 128.84, 128.10, 124.12, 120.83.

(2aa) 4-Methoxy-N-phenylbenzamide

The target compound was prepared according to the general procedure using 4-iodoanisole with aniline, and purified by silica gel column chromatography as solid. $^1$H NMR (400MHz, DMSO-d6) $\delta$ (ppm): 10.08 (s, 1H), 7.97 (d, J = 8.6 Hz, 2H), 7.77 (d, J = 8.1 Hz, 2H), 7.35 (t, J = 7.7 Hz, 2H), 7.11-7.06 (m, 8.1 Hz, 3H), 3.85 (s, 3H). $^{13}$C NMR(100 MHz, DMSO-d6) $\delta$ (ppm): 165.35, 162.33, 139.80, 130.04, 129.01, 127.43, 123.87, 120.79, 114.05, 55.89.

(2ab) 4-cyano-N-phenylbenzamide

The target compound was prepared according to the general procedure using 4-iodobenzonitrile with aniline, and purified by silica gel column chromatography as solid. $^1$H NMR (400MHz, DMSO-d6) $\delta$ (ppm): 10.48 (s, 1H), 8.12 (d, J = 8.1 Hz, 2H), 8.04 (d, J = 8.1 Hz, 2H), 7.78 (d, J = 7.9 Hz, 2H), 7.38 (t, J = 7.7 Hz, 2H), 7.14 (t, J = 7.4 Hz, 1H). $^{13}$C NMR(100 MHz, DMSO-d6) $\delta$ (ppm): 164.62, 139.44, 139.19, 132.93, 129.17, 128.99, 124.58, 120.91, 118.79, 114.28.

(2ac) 4-Nitro-N-phenylbenzamide

The target compound was prepared according to the general procedure using 1-iodo-4-nitrobenzene with aniline, and purified by silica gel column chromatography as solid. $^1$H NMR (400MHz, DMSO-d6) $\delta$ (ppm): 10.58 (s, 1H), 8.38 (d, J = 8.6 Hz, 2H), 8.19 (d, J = 8.5 Hz, 2H), 7.79 (d, J = 8.4 Hz, 2H), 7.39 (t, J = 7.7 Hz, 2H), 7.15 (t, J = 7.4 Hz, 1H). $^{13}$C NMR(100 MHz, DMSO-d6) $\delta$ (ppm): 164.37, 149.59, 141.11, 139.18, 129.67, 129.19, 124.64, 124.02, 120.95.

(2ad) N-Phenyl-3-(trifluoromethyl)benzamide
The target compound was prepared according to the general procedure using 3-iodobenzotrifluoride with aniline, and purified by silica gel column chromatography as solid. $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ (ppm): 10.48 (s, 1H), 8.32 – 8.26 (m, 2H), 7.98 (d, $J$ = 7.8 Hz, 1H), 7.80 (t, $J$ = 8.9 Hz, 3H), 7.39 (t, $J$ = 7.7 Hz, 2H), 7.15 (t, $J$ = 7.4 Hz, 1H). $^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta$ (ppm): 164.49, 139.24, 136.27, 132.30, 130.20, 129.14, 128.61, 128.58, 124.72, 124.68, 124.50, 121.01.

(2ae) N-Phenyl-2-(trifluoromethyl)benzamide

The target compound was prepared according to the general procedure using 2-iodobenzotrifluoride with aniline, and purified by silica gel column chromatography as solid. $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ (ppm): 10.56 (s, 1H), 7.86 (d, $J$ = 7.7 Hz, 1H), 7.81 (t, $J$ = 7.4 Hz, 1H), 7.75-7.68 (m, 4H), 7.36 (t, $J$ = 7.8 Hz, 2H), 7.13 (t, $J$ = 7.4 Hz, 1H). $^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta$ (ppm): 166.03, 139.36, 136.70, 133.09, 130.48, 129.25, 128.97, 126.81, 126.76, 126.09, 124.35, 120.10.

(2af) N-Phenyl-4-(trifluoromethyl)benzamide

The target compound was prepared according to the general procedure using 4-iodobenzotrifluoride with aniline, and purified by silica gel column chromatography as solid. $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ (ppm): 10.47 (s, 1H), 8.16 (d, $J$ = 8.0 Hz, 2H), 7.93 (d, $J$ = 8.1 Hz, 2H), 7.79 (d, $J$ = 7.9 Hz, 2H), 7.39 (t, $J$ = 7.7 Hz, 2H), 7.14 (t, $J$ = 7.4 Hz, 1H). $^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta$ (ppm): 164.86, 139.27, 131.95, 131.63, 129.16, 129.06, 125.88, 125.84, 124.50, 120.90.

(2ag) 4-amino-N-phenylbenzamide

The target compound was prepared according to the general procedure using 4-iodoaniline with aniline, and purified by silica gel column chromatography as solid. $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ (ppm): 9.75 (s, 1H), 7.76-7.72 (m, 4H), 7.31 (t, $J$ = 7.8 Hz, 2H), 7.04 (t, $J$ = 7.3 Hz, 1H), 6.61 (d, $J$ = 8.5 Hz, 2H), 5.75 (s, 2H). $^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta$ (ppm): 165.74, 152.58, 140.24, 129.80, 128.90, 123.32, 121.57, 120.57, 113.00.

(2ai) 4-hydroxy-N-phenylbenzamide

The target compound was prepared according to the general procedure using aniline with 4-
iodophenol, and purified by silica gel column chromatography as solid. $^1$H NMR (400 MHz, DMSO-d6) $\delta$ (ppm): 10.09 (s, 1H), 9.98 (s, 1H), 7.86 (d, J = 8.7 Hz, 2H), 7.76 (d, J = 7.6 Hz, 2H), 7.35 – 7.32 (m, 2H), 7.07 (t, J = 7.4 Hz, 1H), 6.87 (d, J = 8.7 Hz, 2H). $^{13}$C NMR (100 MHz, DMSO-d6) $\delta$ (ppm): 165.55, 160.98, 130.15, 128.97, 125.90, 123.71, 120.72, 115.35.

(2aj) 4-methyl-N-phenylbenzamide

The target compound was prepared according to the general procedure using aniline with 4-iodotoluene, and purified by silica gel column chromatography as solid. The observed characterization data ($^{13}$C) was consistent with that previously reported in the literature. $^2$ $^1$H NMR (400 MHz, DMSO-d6) $\delta$ (ppm): 10.16 (s, 1H), 7.88 (d, J = 8.1 Hz, 2H), 7.78 (d, J = 7.9 Hz, 2H), 7.35 (t, J = 7.7 Hz, 4H), 7.10 (t, J = 7.3 Hz, 1H), 2.40 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-d6) $\delta$ (ppm): 165.80, 142.00, 139.71, 132.55, 129.35, 129.02, 128.14, 123.99, 120.81, 21.48.

(2ak) 4-chloro-N-phenylbenzamide

The target compound was prepared according to the general procedure using aniline with 1-chloro-4-iodobenzene, and purified by silica gel column chromatography as solid. $^1$H NMR (400 MHz, DMSO-d6) $\delta$ (ppm): 10.32 (s, 1H), 7.99 (d, J = 8.5 Hz, 2H), 7.76 (d, J = 7.9 Hz, 2H), 7.61 (d, J = 8.5 Hz, 2H), 7.37 (t, J = 7.9 Hz, 2H), 7.12 (t, J = 7.4 Hz, 1H). $^{13}$C NMR (100 MHz, DMSO-d6) $\delta$ (ppm): 164.94, 139.37, 136.85, 134.09, 130.07, 128.92, 124.34, 120.91.

(2al) N-(4-methoxyphenyl)benzamide

The target compound was prepared according to the general procedure using p-anisidine with iodobenzene, acetonitrile as solvent, and purified by silica gel column chromatography as solid. The observed characterization data ($^{13}$C) was consistent with that previously reported in the literature. $^1$ $^1$H NMR (400 MHz, DMSO-d6) $\delta$ (ppm): 10.14 (s, 1H), 7.94 (d, J = 7.2 Hz, 2H), 7.66 (d, J = 8.9 Hz, 2H), 7.58 (t, J = 7.2 Hz, 1H), 7.52 (t, J = 7.3 Hz, 2H), 6.93 (d, J = 9.0 Hz, 2H), 3.75 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-d6) $\delta$ (ppm): 165.71, 156.07, 135.41, 132.56, 131.90, 128.85, 127.97, 122.58, 114.22, 55.65.

(2am) N-(4-ethylphenyl)benzamide

The target compound was prepared according to the general procedure using 4-ethylaniline with iodobenzene, and purified by silica gel column chromatography as solid. $^1$H NMR (400 MHz, DMSO-d6) $\delta$ (ppm): 10.24 (s, 1H), 8.03 (d, J = 6.8 Hz, 2H), 7.77 (d, J = 8.4 Hz, 2H), 7.61 – 7.52 (m, 3H), 7.21 (d, J = 8.4 Hz, 2H), 2.61 (q, J = 7.6 Hz, 2H), 1.21 (t, J = 7.6 Hz, 3H). $^{13}$C NMR (100 MHz, DMSO-d6) $\delta$ (ppm): 165.88, 139.60, 137.34, 135.54, 131.88, 128.78, 128.23, 128.08, 121.00,
The target compound was prepared according to the general procedure using p-toluidine with
iodobenzene, acetonitrile as solvent, and purified by silica gel column chromatography as solid. $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ (ppm): 10.17 (s, 1H), 7.96 (d, $J = 7.2$ Hz, 2H), 7.67 (d, $J = 8.3$ Hz, 2H), 7.59 (t, $J = 7.2$ Hz, 1H), 7.53 (t, $J = 7.3$ Hz, 2H), 7.16 (d, $J = 8.2$ Hz, 2H), 2.29 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta$ (ppm): 165.79, 137.10, 135.51, 133.05, 131.89, 129.44, 128.81, 128.05, 120.85, 20.96.

The target compound was prepared according to the general procedure using o-toluidine with
iodobenzene, and purified by silica gel column chromatography as solid. $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ (ppm): 9.88 (s, 1H), 8.00 (d, $J = 7.2$ Hz, 2H), 7.60 (t, $J = 7.3$ Hz, 1H), 7.54 (t, $J = 7.3$ Hz, 2H), 7.36 (d, $J = 7.5$ Hz, 1H), 7.29 (d, $J = 7.4$ Hz, 1H), 7.23 (t, $J = 6.8$ Hz, 1H), 7.20 – 7.15 (m, 1H), 2.25 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta$ (ppm): 165.73, 136.88, 135.01, 134.18, 131.97, 130.76, 128.87, 128.08, 127.08, 126.45, 18.37.

The target compound was prepared according to the general procedure using m-toluidine with
iodobenzene, and purified by silica gel column chromatography as solid. $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ (ppm): 10.17 (s, 1H), 7.97 (d, $J = 7.0$ Hz, 2H), 7.65 (s, 1H), 7.60 (m, 2H), 7.54 (t, $J = 7.3$ Hz, 2H), 7.24 (t, $J = 7.8$ Hz, 1H), 6.94 (d, $J = 7.5$ Hz, 1H), 2.32 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta$ (ppm): 165.93, 139.56, 138.19, 135.49, 131.95, 128.89, 128.08, 124.81, 121.38, 118.02, 21.69.

The target compound was prepared according to the general procedure using 4-bromoaniline with
iodobenzene, acetonitrile as solvent, and purified by silica gel column chromatography as solid. $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ (ppm): 10.38 (s, 1H), 7.96 (d, $J = 7.1$ Hz, 2H), 7.78 (d, $J = 8.9$ Hz, 2H), 7.61 (t, $J = 7.3$ Hz, 1H), 7.56 (d, $J = 1.5$ Hz, 2H), 7.55 – 7.53 (m, 2H). $^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta$ (ppm): 166.12, 139.04, 135.16, 132.18, 131.89, 128.89, 128.14, 122.67, 115.79.

The target compound was prepared according to the general procedure using 4-chloroaniline with
iodobenzene, acetonitrile as solvent, and purified by silica gel column chromatography as solid. $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ (ppm): 10.38 (s, 1H), 7.96 (d, $J = 7.1$ Hz, 2H), 7.78 (d, $J = 8.9$ Hz, 2H), 7.61 (t, $J = 7.3$ Hz, 1H), 7.56 (d, $J = 1.5$ Hz, 2H), 7.55 – 7.53 (m, 2H). $^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta$ (ppm): 166.12, 139.04, 135.16, 132.18, 131.89, 128.89, 128.14, 122.67, 115.79.
The target compound was prepared according to the general procedure using 4-chloroaniline with iodobenzene, acetonitrile as solvent, and purified by silica gel column chromatography as solid. $^1$H NMR (400 MHz, DMSO-d6) $\delta$ (ppm): 10.38 (s, 1H), 7.96 (d, $J = 7.1$ Hz, 2H), 7.84 (d, $J = 8.9$ Hz, 2H), 7.61 (t, $J = 7.3$ Hz, 1H), 7.55 (t, $J = 7.3$ Hz, 2H), 7.42 (d, $J = 8.9$ Hz, 2H). $^{13}$C NMR (100 MHz, DMSO-d6) $\delta$ (ppm): 166.12, 138.62, 135.17, 132.17, 128.98, 128.88, 128.13, 122.30.

(2aw) N-benzylbenzamide

The target compound was prepared according to the general procedure using benzylamine with iodobenzene, and purified by silica gel column chromatography as solid. The observed characterization data ($^{13}$C) was consistent with that previously reported in the literature.$^{1, 3, 4}$ $^1$H NMR (400 MHz, DMSO-d6) $\delta$ (ppm): 9.05 (t, $J = 5.5$ Hz, 1H), 7.91 (d, $J = 7.1$ Hz, 2H), 7.55 (t, $J = 7.2$ Hz, 1H), 7.48 (t, $J = 7.3$ Hz, 2H), 7.34 (s, 2H), 7.33 (s, 2H), 7.28 – 7.23 (m, 1H), 4.50 (d, $J = 6.0$ Hz, 2H). $^{13}$C NMR (100 MHz, DMSO-d6) $\delta$ (ppm): 166.66, 140.18, 134.82, 131.70, 128.79, 128.74, 127.71, 127.66, 127.19, 43.07.

(2ax) N-cyclohexylbenzamide

The target compound was prepared according to the general procedure using cyclohexylamine with iodobenzene, and purified by silica gel column chromatography as solid. The observed characterization data ($^{13}$C) was consistent with that previously reported in the literature.$^{1, 4}$ $^1$H NMR (400 MHz, DMSO-d6) $\delta$ (ppm): 8.19 (d, $J = 7.7$ Hz, 1H), 7.84 (d, $J = 7.1$ Hz, 2H), 7.51 (t, $J = 7.2$ Hz, 1H), 7.45 (t, $J = 7.3$ Hz, 2H), 3.77 – 3.76 (m, 1H), 1.83 – 1.82 (m, 2H), 1.75 – 1.73 (m, 2H), 1.37 – 1.25 (m, 6H). $^{13}$C NMR (100 MHz, DMSO-d6) $\delta$ (ppm): 165.79, 135.36, 131.36, 128.57, 127.71, 125.18, 48.78, 32.89, 25.37, 25.21.

References
(2c) N-phenylbenzamide
(2aa) 4-Methoxy-N-phenylbenzamide
(2ab) 4-cyano-N-phenylbenzamide
(2ac) 4-Nitro-N-phenylbenzamide
(2ad) N-Phenyl-3-(trifluoromethyl)benzamide
(2ae) N-Phenyl-2-(trifluoromethyl)benzamide
(2af) N-Phenyl-4-(trifluoromethyl)benzamide
(2ag) 4-amino-N-phenylbenzamide
(2ai) 4-hydroxy-N-phenylbenzamide
(2aj) 4-methyl-N-phenylbenzamide
(2ak) 4-chloro-N-phenylbenzamide
(2al) N-(4-methoxyphenyl)benzamide
(2-am) N-(4-ethylphenyl)benzamide
(2an) N-(4-methylphenyl)benzamide
(2ao) N-(2-methylphenyl)benzamide
(2ap) N-(3-methylphenyl)benzamide
(2ar) N-(4-bromophenyl)benzamide
(2at) N-(4-chlorophenyl)benzamide
(2aw) N-benzylbenzamide
(2ax) N-cyclohexylbenzamide
Mass Spectra of the Extended Reactions

(a) 

(b)
Mass Spectra of the Products for Different Reactions