Supplementary Information

Gold Nanoparticle-Catalyzed Cyclocarbonylation of 2-Aminophenols

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Experimental

1) General

All organic reagents were purified before use. HAuCl₄·xH₂O was obtained from Mitsuwa Chemicals Co., Ltd. Al₂O₃ (JRC-ALO-3), CeO₂ (JRC-CEO-1), SiO₂ (JRC-SIO-6) and TiO₂ (JRC-TIO-4) were supplied by the Catalysis Society of Japan. GC-FID and GC-MS were performed on a Shimadzu GC-2014 instrument equipped with a InertCap WAX-HT (30 m × 0.53 mm × 1.0 µm) and a Shimadzu GCMSQP5050A instrument equipped with a ULBON HR-1 capillary column (30 m × 0.25 mm × 0.25 µm), respectively. High performance liquid chromatography (HPLC) was performed on a Shimadzu LC-10ADvp: STR ODS-IV (MeOH/H₂O=70/30). Inductively coupled plasma measurements were performed using a SII Nano Technology SPS7800 instrument. ¹H and ¹³C-NMR spectra were recorded on a JEOL JNM-ESC400 spectrometer and a JNM-GSX270 spectrometer, respectively. Transmission electron microscopy (TEM) micrographs were obtained with a Hitachi HF-2000 microscope. Au L-edge X-ray absorption spectra were collected in the quick mode and recorded at room temperature in transmission mode at the facilities installed on the BL-01B1 line attached with a Si (311) monochromator at the SPring-8, Japan Atomic Energy Research Institute (JASRI), Harima, Japan. Data analysis was performed using the REX 2000 program, ver. 2.5.7 (Rigaku). Fourier transformation (FT) of the k³-weighted extended X-ray absorption fine structure (EXAFS) data was performed to obtain the radial structural function.
2) General reaction procedures

A typical procedure for the cyclocarbonylation of 1 using the Au/HT catalyst was as follows. Au/HT (0.10 g, Au: 0.0045 mmol) was placed in a reaction vessel, followed by the addition of DME (5 mL) and 1 (0.25 mmol). The reaction mixture was vigorously stirred at 110 °C under 50 atm of mixed gases (48 atm of CO and 2 atm of O₂) for 2 h. After the reaction, the Au/HT was removed by filtration, and naphthalene (0.2 mmol) was added as an internal standard. The obtained mixture was analyzed by GC and GC-MS.

3) Reuse experiments for the cyclocarbonylation of 1

After the cyclocarbonylation of 1 under the above typical reaction conditions, Au/HT was separated by filtration and washed with 5% aqueous citric acid (2 x 10 mL) and 10% aqueous Na₂CO₃ (2 x 10 mL). Next, additional portions of 1 (0.25 mmol) and DME (5 mL) were added, followed by stirring under identical conditions. 98% yields of 2 were obtained in the two reuse experiments.

4) 10 mmol-scale cyclocarbonylation of 1 using Au/HT

Into a stainless steel autoclave with a Teflon inner cylinder (160 mL) were placed Au/HT (0.1 g, Au: 0.0045 mmol), DME (10 mL) and 1 (1.09 g, 10 mmol). The reaction mixture was vigorously stirred at 130 °C under 50 atm of mixed gases (48 atm of CO and 2 atm of O₂) for 16 h. After the reaction, the Au/HT was removed by filtration, and DME was evaporated. The residue was purified by recrystallization using dichloromethane to give 1.24 g of 2 (92% isolated yield) as a white solid.
5) Product identification

The products were identified by GC, LC, GC-MS and NMR analyses. Retention times (GC, GC-MS and LC) and chemical shifts (\(^1\text{H} \) and \(^{13}\text{C}\)-NMR) of the products were in agreement with those of the reported data and also with the authentic samples.

Table 2, Entries 1-3

2-benzoxazolinone

CAS registry No. [59-49-4]. \(^1\text{H} \) NMR and \(^{13}\text{C}\) NMR were consistent with previously reported values. See Ref. 1S.

Entry 4

6-methyl 2-benzoxazolinone

CAS registry No. [22876-16-0]. \(^1\text{H} \) NMR and \(^{13}\text{C}\) NMR were consistent with previously reported values. See Ref. 1S.

Entry 5

4-methyl 2-benzoxazolinone

CAS registry No. [78258-80-7]. \(^1\text{H} \) NMR and \(^{13}\text{C}\) NMR were consistent with previously reported values. See Ref. 2S.

Entry 6

5-methoxy 2-benzoxazolinone

CAS registry No. [40925-63-1]. \(^1\text{H} \) NMR and \(^{13}\text{C}\) NMR were consistent with previously reported values. See Ref. 3S.
Entry 7

6-fluoro 2-benzoxazolinone

CAS registry No. [2923-94-6]. $^1$H NMR and $^{13}$C NMR were consistent with the authentic sample obtained from Sigma Aldrich.

Entry 8

3H-naphth[2,3-d]oxazol-2-one

CAS registry No. [115164-17-5]. $^1$H NMR and $^{13}$C NMR were consistent with the authentic sample prepared by the reaction of 1,1’-carbonyldiimidazole with 3-amino-2-naphthol. See Ref. 1S.

References


6) EXAFS analysis

![Fourier transformed \(k^3\)-weighted Au L-edge EXAFS](image)

<table>
<thead>
<tr>
<th></th>
<th>Coord. no. (CN)</th>
<th>Interatomic dis. (Å)</th>
<th>(\Delta\sigma/\Delta^2)</th>
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</thead>
<tbody>
<tr>
<td>Au/HT (fresh)</td>
<td>8.6</td>
<td>2.85</td>
<td>0.028</td>
</tr>
<tr>
<td>Au/HT (after reaction)</td>
<td>8.9</td>
<td>2.85</td>
<td>0.020</td>
</tr>
<tr>
<td>Au/HT (after two times reuse)</td>
<td>9.0</td>
<td>2.85</td>
<td>0.026</td>
</tr>
<tr>
<td>Au foil</td>
<td>12</td>
<td>2.88</td>
<td>-</td>
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</table>

**Figure 1S.** Fourier transformed \(k^3\)-weighted Au L-edge EXAFS for (a) Au/HT, (b) Au/HT after cyclocarbonylation of 1, (c) Au/HT after being reused twice, (d) Au₂O₃ and (e) Au foil.
7) TEM analysis

(a) Au/HT (fresh)

(b) Au/HT (after reuse experiment)

Figure 2S. Typical TEM images and size distribution diagrams (obtained by counting at least 500 particles) of (a) fresh Au/HT and (b) Au/HT after reuse.
8) Leaching test

\[
\text{NH}_2\text{OH} \xrightarrow{\text{Au/HT (1.8 mol\%)}} \text{NH}_2\text{O} \quad \text{DME (5 mL), PCO/O}_2 = 50 \text{ atm (48 : 2), 110 }^\circ\text{C}
\]

**Figure 3S.** Time profile for the cyclocarbonylation of 1 using Au/HT.