Cu-Catalyzed Aerobic Oxygenation of 2-Phenoxyacetophenones to AlkyloxyAcetophenones

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1. Experimental section.

Materials

All reagents and solvents were purchased from Acros, Tci, Alfa-Aesar, Sigma-Aldrich and Beijing Chemical Company, Ltd. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Lignin model compounds were prepared following procedures reported in the literature with some modifications.

Instrumentation

Products were purified by flash chromatography on silica gel. Electron Impact Mass (EI MS) Spectra were performed on DFS Mass Spectrometer. Analysis of crude reaction mixture was performed on an Agilent 7890BGC System with a HP-INNOWAX capillary column (30 m × 0.25 mm × 0.25 μm) and an FID detector. The following GC temperature program was used: 50 °C hold for 2 min, ramp 20 °C/min to a final temperature of 260 °C, and hold for 8 min. Nitrogen was used as a carrier gas. The injector temperature was held at 250 °C. GC-MS analysis was carried out on a SHIMADZU GCMS-QP2010 with a DB-5 capillary column (30 m × 0.25 mm × 0.25 μm). 1H NMR spectra were recorded in CDCl3 or DMSO using internal reference (the residue proton peaks of CHCl3 at 7.26 ppm and DMSO at 2.5 ppm) on Bruker 400 spectrometer. Liquid 13C NMR was recorded at 100.6 MHz in CDCl3 using residual CHCl3 as internal reference (the residue proton peaks of CHCl3 at 77.02 ppm and DMSO at 40.03 ppm). X-Ray photoelectron spectroscopy (XPS) data were collected on an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al-Kα radiation. The base pressure was about 3 × 10⁻⁹ mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon.

Catalytic reaction

Typically, substrate (0.5 mmol), alcohol (1 mL), catalyst (0.075 mmol), ligand (0.25 mmol), additive (0.5 mmol) were introduced into a 5 mL glass reactor. The reaction mixture was heated to the designated temperature in an oil bath and kept at that temperature for desired reaction time. After that, an aqueous solution of HCl (10 mL, 1.0 M) was added to the reaction system, and then 3 * 10 mL CH2Cl2 was added to extract organic compounds. The organic phase with n-dodecane as an internal standard was analysed by GC, affording the GC product yield. Then, the organic phase was purified by column chromatography over silica gel to obtain the desired product (eluent: petroleum ether/ethyl acetate = 100/1), and the product yield was denoted as isolated yield. The isolated products were identified by NMR.
2. Additionalscreening of reaction conditions

Table S1. Evaluation of Cu catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Cu]</th>
<th>Yield (%)(^b)</th>
<th>Conversion (%)</th>
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<tr>
<td></td>
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<td>3a</td>
<td>4a</td>
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<tr>
<td>1</td>
<td>CuBr(_2)</td>
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<td>25.0</td>
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<tr>
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<td>CuCl(_2)</td>
<td>36.8</td>
<td>62.7</td>
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<td>23.4</td>
</tr>
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<td>5</td>
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<tr>
<td>6</td>
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<td>7</td>
<td>CuI</td>
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<td>8</td>
<td>CuOAc</td>
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<td>21.4</td>
</tr>
<tr>
<td>9</td>
<td>CuCl(_2)·2H(_2)O</td>
<td>29.4</td>
<td>48.7</td>
</tr>
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</table>

\(^a\)Reaction conditions: 1a (0.5mmol), 2a (1.0mL), Cu salts (0.15equiv.), pyridine (0.5 equiv.), BF\(_3\)·Et\(_2\)O (1.0 equiv.). \(^b\)GC yield.
Table S2. The effects of CuCl$_2$ loading$^a$

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>CuCl$_2$(x eq)</th>
<th>Yield (%)$^b$</th>
<th>Conversion (%)</th>
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<td>44.1</td>
</tr>
<tr>
<td>3</td>
<td>0.15</td>
<td>36.8</td>
<td>62.7</td>
</tr>
</tbody>
</table>

$^a$Reaction conditions: 1a (0.5mmol), 2a (1.0mL), CuCl$_2$, Pyridine (0.5equiv.), BF$_3$•Et$_2$O (1.0equiv.). $^b$GC yield.

Table S3. The effects of pyridine loading$^a$

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
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<th>Yield (%)$^b$</th>
<th>Conversion (%)</th>
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<tr>
<td>4</td>
<td>1</td>
<td>38.4</td>
<td>47.7</td>
</tr>
</tbody>
</table>

$^a$Reaction conditions: 1a (0.5mmol), 2a (1.0mL), CuCl$_2$ (0.15equiv.), pyridine, BF$_3$•Et$_2$O (1.0equiv.). $^b$GC yield.
3. Control experiments

Some potential intermediates were subjected to the reaction system.

When we shorten the reaction time, we could make the reaction stay at incomplete stage. We found I (phenylglyoxal) was an intermediate through GC-MS. (Figure S1)

And D could further reacted to form 4a.

**Figure S1** GC-MS of the reaction solution. Conditions: 1a (0.5 mmol), 2a (1 ml), CuCl$_2$ (0.075 mmol), Py (0.25 mmol), BF$_3$·Et$_2$O (0.5 mmol), 12h.
4. Detection by GC

**Figure S2** GC spectrum of the liquid phase of the reaction solution. Conditions: 1a (0.5 mmol), 2a (1 ml), CuCl$_2$ (0.075 mmol), Py (0.25 mmol) and BF$_3$·Et$_2$O (0.5 mmol), 24h.
Tail gas detection by GC

Under the environment of pure oxygen, tail gas was collected and detected by GC.

Figure S3 GC profile of the gas phase of the reaction solution. Conditions: 1a (0.5 mmol), 2a (1 ml), CuCl₂ (0.075 mmol), Py (0.25 mmol) and BF₃·Et₂O (0.5 mmol), 24h.
5. Radical trapping experiments

Scheme S1 Control experiments with TEMPO
6. EPR spectrum

Figure S4 EPR spectrum of the reaction solution. Reaction conditions: 1a (0.5 mmol), 2a (1 ml), CuCl$_2$ (0.075 mmol), Py (0.25 mmol), BF$_3$·Et$_2$O, methanol, 12h.
7. Cu2p XPS spectrum of the recovered Cu catalyst

Figure S5 Cu2p XPS spectrum of the recovered Cu catalyst.
8. ESI-MS spectrum charts of compounds

2,2-dimethoxyacetophenone

![ESI-MS spectrum of 2,2-dimethoxyacetophenone](image)

**Figure S6** ESI-MS spectrum of 2,2-dimethoxyacetophenone.
9. NMR data for starting materials

2-Aryloxy-1-acetophenone derivatives were prepared based on the reported procedures, which were examined by NMR analysis. The NMR data for these compounds are listed as follows.

2-phenyloxy-acetophenone

\[
\begin{align*}
\text{H} & \quad \text{NMR} (400 \text{ MHz, CDCl}_3) \; \delta \; 8.08 - 7.94 (m, 1H), 7.62 (t, J = 7.4 \text{ Hz}, 1H), 7.50 (t, J = 7.7 \text{ Hz}, 1H), 7.35 - 7.19 (m, 2H), 6.98 (dd, J = 18.9, 7.7 \text{ Hz}, 1H), 5.28 (s, 1H).
\end{align*}
\]

\[
\begin{align*}
\text{C} & \quad \text{NMR} (101 \text{ MHz, CDCl}_3) \; \delta \; 194.55 (s), 158.03 (s), 134.65 (s), 133.82 (s), 129.56 (s), 128.15 (s), 121.65 (s), 114.83 (s), 70.84 (s).
\end{align*}
\]

2-(4-methoxyphenyl)oxy-acetophenone

\[
\begin{align*}
\text{H} & \quad \text{NMR} (400 \text{ MHz, CDCl}_3) \; \delta \; 8.01 (d, J = 7.3 \text{ Hz}, 2H), 7.62 (t, J = 7.4 \text{ Hz}, 1H), 7.50 (t, J = 7.7 \text{ Hz}, 2H), 7.36 - 7.23 (m, 5H), 6.98 (dd, J = 19.0, 7.7 \text{ Hz}, 3H), 5.28 (s, 2H).
\end{align*}
\]

\[
\begin{align*}
\text{C} & \quad \text{NMR} (101 \text{ MHz, CDCl}_3) \; \delta \; 194.74 (s), 154.38 (s), 152.14 (s), 134.55 (s), 133.68 (s), 128.69 (s), 128.00 (s), 115.89 (s), 114.60 (s), 77.32 (s), 77.00 (s), 76.68 (s), 71.63 (s), 55.55 (s).
\end{align*}
\]

2-(3-methoxyphenyl)oxy-acetophenone

\[
\begin{align*}
\text{H} & \quad \text{NMR} (400 \text{ MHz, CDCl}_3) \; \delta \; 8.00 (d, J = 7.3 \text{ Hz}, 4H), 7.62 (t, J = 7.4 \text{ Hz}, 3H), 7.50 (t, J = 7.7 \text{ Hz}, 5H), 7.18 (t, J = 8.5 \text{ Hz}, 6H), 6.66 - 6.47 (m, 6H), 5.26 (s, 4H), 3.78 (s, 6H).
\end{align*}
\]

\[
\begin{align*}
\text{C} & \quad \text{NMR} (101 \text{ MHz, CDCl}_3) \; \delta \; 194.28 (s), 160.82 (s), 159.17 (s), 134.52 (s), 133.77 (s), 129.92 (s), 128.75 (s), 128.03 (s), 125.10 (s), 107.27 (s), 106.55 (s), 101.46 (s), 77.32 (s), 77.00 (s), 76.68 (s), 70.69 (s), 55.21 (s).
\end{align*}
\]

2-(4-fluor-phenyl)oxy-acetophenone

\[
\begin{align*}
\text{H} & \quad \text{NMR} (400 \text{ MHz, CDCl}_3) \; \delta \; 7.99 (d, J = 7.4 \text{ Hz}, 2H), 7.63 (t, J = 7.4 \text{ Hz}, 1H), 7.51 (t, J = 7.7 \text{ Hz}, 2H), 6.92 (ddd, J = 12.0, 9.2, 6.7 \text{ Hz}, 4H), 5.25 (s, 2H).
\end{align*}
\]

\[
\begin{align*}
\text{C} & \quad \text{NMR} (101 \text{ MHz, CDCl}_3) \; \delta \; 194.30 (s), 158.86 (s), 156.48 (s), 154.12 (d, J = 2.1 \text{ Hz}), 134.41 (s), 133.91 (s), 128.82 (s), 128.01 (s), 115.94 (dd, J = 15.7, 7.5 \text{ Hz}), 77.32 (s), 77.00 (s), 76.68 (s), 71.37 (s).
\end{align*}
\]

2-(4-bromo-phenyl)oxy-acetophenone
1H NMR (400 MHz, CDCl₃) δ 7.89 (d, J = 7.5 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.7 Hz, 2H), 7.28 (d, J = 8.7 Hz, 2H), 6.73 (d, J = 8.8 Hz, 2H), 5.17 (s, 2H).

13C NMR (101 MHz, CDCl₃) δ 193.96 (s), 157.13 (s), 134.37 (s), 133.97 (s), 132.36 (s), 128.85 (s), 128.03 (s), 116.60 (s), 113.87 (s), 70.82 (s).

2-phenyloxy-3’-methoxy acetophenone

1H NMR (400 MHz, CDCl₃) δ 7.63 – 7.50 (m, 2H), 7.40 (t, J = 7.9 Hz, 1H), 7.28 (dd, J = 14.6, 6.4 Hz, 2H), 7.16 (dd, J = 8.2, 2.4 Hz, 1H), 7.05 – 6.89 (m, 3H), 5.26 (s, 2H), 3.86 (s, 3H).

13C NMR (101 MHz, CDCl₃) δ 194.21 (s), 159.90 (s), 157.96 (s), 135.80 (s), 129.75 (s), 129.49 (s), 121.56 (s), 120.48 (s), 120.25 (s), 114.76 (s), 112.37 (s), 77.32 (s), 77.00 (s), 76.68 (s), 70.74 (s), 55.39 (s).

2-(3-methoxyphenyl)oxy-3’-methoxyacetophenone

1H NMR (400 MHz, CDCl₃) δ 7.52 – 7.39 (m, 2H), 7.30 (t, J = 7.9 Hz, 1H), 7.13 – 7.00 (m, 2H), 6.50 – 6.37 (m, 3H), 5.14 (s, 2H), 3.76 (s, 3H), 3.68 (s, 3H).

13C NMR (101 MHz, CDCl₃) δ 194.06 (s), 160.85 (s), 159.93 (s), 159.21 (s), 135.83 (s), 129.84 (d, J = 16.3 Hz), 120.48 (s), 120.27 (s), 112.39 (s), 107.29 (s), 106.60 (s), 101.51 (s), 77.26 (d, J = 11.7 Hz), 77.00 (s), 76.68 (s), 70.77 (s), 55.33 (d, J = 18.7 Hz).
10. NMR data for the products

2,2-Dimethoxyacetophenone

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{) } & \delta 8.02 (d, J = 7.6 \text{ Hz}, 2\text{H}), 7.47 (t, J = 7.4 \text{ Hz}, 1\text{H}), 7.36 (d, J = 7.7 \text{ Hz}, 2\text{H}), 5.14 (s, 1\text{H}), 3.37 (s, 6\text{H}). \\
\text{C NMR (101 MHz, CDCl}_3\text{) } & \delta 193.22 (s), 133.47 (s), 129.34 (s), 128.29 (s), 103.13 (s), 54.36 (s).
\end{align*}
\]

2,2-Dimethoxy-1-(3-methoxyphenyl)

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{) } & \delta 7.61 (d, J = 7.7 \text{ Hz}, 1\text{H}), 7.51 (s, 1\text{H}), 7.25 (t, J = 8.0 \text{ Hz}, 1\text{H}), 7.01 (dd, J = 8.2, 1.8 \text{ Hz}, 1\text{H}), 5.12 (s, 1\text{H}), 3.72 (s, 3\text{H}), 3.36 (s, 6\text{H}). \\
\text{C NMR (101 MHz, CDCl}_3\text{) } & \delta 192.90 (s), 159.41 (s), 134.90 (s), 129.22 (s), 121.89 (s), 119.88 (s), 113.37 (s), 102.93 (s), 55.10 (s), 54.23 (s).
\end{align*}
\]

Benzoic acid methyl ester

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{) } & \delta 8.08 – 7.99 (m, 2\text{H}), 7.56 (t, J = 7.4 \text{ Hz}, 1\text{H}), 7.44 (t, J = 7.6 \text{ Hz}, 2\text{H}), 3.92 (s, 3\text{H}). \\
\text{C NMR (101 MHz, CDCl}_3\text{) } & \delta 167.13 (s), 132.91 (s), 129.59 (s), 128.37 (s), 125.09 (s), 52.09 (s).
\end{align*}
\]

Phenol

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{) } & \delta 7.25 (dd, J = 9.6, 6.2 \text{ Hz}, 3\text{H}), 6.94 (t, J = 7.4 \text{ Hz}, 1\text{H}), 6.84 (d, J = 7.7 \text{ Hz}, 2\text{H}), 5.35 (s, 1\text{H}). \\
\text{C NMR (101 MHz, CDCl}_3\text{) } & \delta 155.46 (s), 129.67 (s), 120.81 (s), 115.28 (s).
\end{align*}
\]

3-Methoxyphenol

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{) } & \delta 7.14 (t, J = 8.0 \text{ Hz}, 1\text{H}), 6.51 (dd, J = 7.5, 1.4 \text{ Hz}, 1\text{H}), 6.43 (dd, J = 8.4, 1.3 \text{ Hz}, 2\text{H}), 4.77 (s, 1\text{H}), 3.78 (s, 3\text{H}). \\
\text{C NMR (101 MHz, CDCl}_3\text{) } & \delta 160.94 (s), 156.69 (s), 130.15 (s), 107.81 (s), 106.49 (s), 101.56 (s), 77.26 (d, J = 11.5 \text{ Hz}), 77.00 (s), 76.68 (s), 55.27 (s), -0.03 (s).
\end{align*}
\]
4-methoxyphenol

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

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.89 – 6.67 (m, 1H), 3.76 (s, 1H).
\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 153.86 (s), 149.41 (s), 116.02 (s), 114.85 (s), 55.78 (s).

4-fluorophenol

\[ \begin{array}{c}
\text{F} \\
\text{OH}
\end{array} \]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.93 (dd, \(J\) = 11.9, 5.4 Hz, 1H), 6.85 – 6.68 (m, 1H).
\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 158.51 (s), 156.14 (s), 151.44 (d, \(J\) = 2.2 Hz), 116.37 – 116.00 (m), 115.87 (s).

4-bromophenol

\[ \begin{array}{c}
\text{Br} \\
\text{OH}
\end{array} \]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.33 (d, \(J\) = 8.8 Hz, 2H), 6.72 (d, \(J\) = 8.9 Hz, 1H), 5.35 (s, 1H).
\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 154.59 (s), 132.48 (s), 117.19 (s), 112.93 (s).

2,2-diethoxyacetophenone

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

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.23 – 8.10 (m, 2H), 7.56 (t, \(J\) = 7.4 Hz, 1H), 7.45 (t, \(J\) = 7.6 Hz, 2H), 5.28 (s, 1H), 3.88 – 3.52 (m, 4H), 1.25 (t, \(J\) = 7.1 Hz, 6H).
\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 194.04 (s), 133.81 (s), 133.41 (s), 129.73 (s), 128.31 (s), 102.48 (s), 63.20 (s), 15.18 (s).

3-methoxybenzoate

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

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.67 – 7.60 (m, 1H), 7.56 (dd, \(J\) = 2.5, 1.5 Hz, 1H), 7.34 (t, \(J\) = 8.0 Hz, 1H), 7.10 (ddd, \(J\) = 8.2, 2.7, 0.8 Hz, 1H), 3.91 (s, 3H), 3.85 (s, 3H).
\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 166.95 (s), 159.57 (s), 131.47 (s), 129.35 (s), 121.97 (s), 119.48 (s), 113.98 (s), 55.41 (s), 52.12 (s).

Ethyl benzoate

\[ \begin{array}{c}
\text{O} \\
\text{O}
\end{array} \]
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.10 – 8.01 (m, 2H), 7.62 – 7.50 (m, 1H), 7.42 (dd, $J = 10.6, 4.7$ Hz, 2H), 4.38 (q, $J = 7.1$ Hz, 2H), 1.39 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.55 (s), 132.71 (s), 130.51 (s), 129.47 (s), 128.23 (s), 60.85 (s), 14.26 (s).

11. $^1$H NMR and $^{13}$C NMR spectra of compounds

![Image of NMR spectra](image-url)

Figure S7$^1$H (top) and $^{13}$C (bottom) NMR spectra of 2-phenyloxy-acetophenone
Figure S8^1^H (top) and ^1^3^C (bottom) NMR spectra of 2-(4-methoxyphenyl)oxy-acetophenon
Figure S9$^1$H (top) and $^{13}$C (bottom) NMR spectra of 2-(3-methoxyphenyl)oxy-acetophenon
Figure S10$^1$H (top) and $^{13}$C (bottom) NMR spectra of 2-(4-fluor-phenyl)oxy-acetophenon
Figure S11$^1$H (top) and $^{13}$C (bottom) NMR spectra of 2-(4-bromo-phenyl)oxy-acetophenon
Figure S12 $^1$H (top) and $^{13}$C (bottom) NMR spectra of 2-phenyloxy-3'-methoxy acetophenone
Figure S13 $^1$H (top) and $^{13}$C (bottom) NMR spectra of 2-(3-methoxyphenyl)oxy-3’-methoxyacetophenone
Figure S14 $^1$H (top) and $^{13}$C (bottom) NMR spectra of the isolated product 2,2-dimethoxyacetophenone
Figure S15 $^1$H (top) and $^{13}$C (bottom) NMR spectra of the isolated product 2,2-dimethoxy-1-(3-methoxyphenyl)
Figure S16$^1$H (top) and $^{13}$C (bottom) NMR spectra of the isolated benzoic acid methyl ester
Figure S17$^1$H (top) and $^{13}$C (bottom) NMR spectra of the isolated product Phenol
Figure S18$^1$H (top) and $^{13}$C (bottom) NMR spectra of the isolated product 3-methoxyphenol
Figure S19\textsuperscript{1}H (top) and $^{13}$C (bottom) NMR spectra of the isolated product 4-methoxyphenol
Figure S20$^1$H (top) and $^{13}$C (bottom) NMR spectra of the isolated product 4-fluorophenol
Figure S21$^1$H (top) and $^{13}$C (bottom) NMR spectra of the isolated product 4-bromophenol
Figure S22 $^1$H (top) and $^{13}$C (bottom) NMR spectra of the isolated 2,2-diethoxyacetophenone
Figure S23 $^1$H (top) and $^{13}$C (bottom) NMR spectra of the isolated product 3-methoxybenzoate
Figure S24 $^1$H (top) and $^{13}$C (bottom) NMR spectra of the isolated product Ethyl benzoate
12. References