Electronic Supplementary Information

Copper-Catalyzed C-Alkylation of Secondary Alcohols and Methyl Ketones with Alcohols Employing the Aerobic Relay Race Methodology

Shiheng Liao, Kangkang Yu, Qiang Li, Haiwen Tian, Zhengping Zhang, Xiaochun Yu and Qing Xu*

College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou University Town, Wenzhou 325025, China

qing-xu@wzu.edu.cn

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**Table S1.** Condition Screening of Cu-Catalyzed Aerobic $\beta$-Alkylation of Secondary Alcohols.\(^{[a]}\)

![Chemical structure](https://example.com/structure.png)

<table>
<thead>
<tr>
<th>Run</th>
<th>Cat. M(^{[b]})</th>
<th>x, y, z</th>
<th>atm., T, t</th>
<th>3(^{+})+5(^{\circ})/3(^{\circ})</th>
<th>3/5(^{\circ})</th>
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<td>air, 120 °C, 24 h</td>
<td>95</td>
<td>98/2</td>
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</table>

\(^{[a]}\) The mixture of \(1a\), \(2a\) (3 mmol), Cu catalyst, and KOH was heated in a sealed 20 mL Schlenk tube and monitored by GC-MS and/or \(^1\)H NMR. A solution of alcohols was used in reactions under nitrogen. Commercial alcohols without any pretreatment were directly used in aerobic reactions. \(^{[b]}\) Catalysts were abbreviated: RhCl\(_3\)·3H\(_2\)O to RhCl\(_3\), RuCl\(_3\)·nH\(_2\)O to RuCl\(_3\), Cu(OAc)\(_2\)·H\(_2\)O to Cu(OAc)\(_2\), and CuCl\(_2\)·2H\(_2\)O to CuCl\(_2\). \(^{[c]}\) NMR yields (isolated yields in parenthesis) based on \(2a\). \(3\(_{aa}\)/\(5\(_{aa}\)\) ratios measured by \(^1\)H NMR spectroscopic analysis. \(^{[d]}\) 1 mol % Of 2,2'-bipyridine added.
Table S2. Condition Screening of Cu-Catalyzed Aerobic α-Alkylation of Methyl Ketones.[a]

![Image of chemical reaction]

<table>
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<th>Cat. Cu</th>
<th>base</th>
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<th>3/5[c]</th>
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<td>50</td>
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<td>Cu(OAc)₂·H₂O</td>
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<td>85</td>
<td>78/22</td>
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<td>99 (85)</td>
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</table>

[a] Reactions were monitored by GC-MS and/or ¹H NMR. Usually full conversion of 6a were observed. [b] ¹H NMR yields (isolated yields in parenthesis) based on 6a. [c] 3aa/5aa ratios measured by ¹H NMR spectroscopic analysis.
General. Substrates, bases and catalysts were all purchased. Bases (KOH, NaOH, etc.) of AR grade (>99% purity) were used. All reactions were carried out in sealed Schlenk tubes and monitored by TLC, GC-MS and/or $^1$H NMR. Unless otherwise noted, substrates and catalysts were used as purchased without further purification and degassing in reactions carried out under air. As analyzed, samples of commercial alcohols are usually contaminated by trace amount of corresponding aldehydes or ketones. Thus, in control reactions and mechanistic studies where needed, absolute alcohols (freshly distilled from CaH$_2$, degassed and stored under N$_2$ in a Schlenk flask, 100% purity without any contaminants as confirmed by GC analysis) were used as noted. Products were purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluent. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance-III 500 instrument (500 MHz for $^1$H and 125.4 MHz for $^{13}$C NMR spectroscopy). Unless otherwise noted, CDCl$_3$ was used as the solvent. Chemical shift values for $^1$H and $^{13}$C NMR were referred to internal Me$_4$Si (0 ppm). Mass spectra were measured on a Shimadzu GCMS-QP2010 Plus spectrometer (EI). HRMS (EI) analysis was performed by the Analytical Center at the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

Typical Procedure for Copper-Catalyzed Aerobic β-Alkylation of Secondary Alcohols with Alcohols. The mixture of commercial benzyl alcohol 1a (0.41 mL, 3.9 mmol), 1-phenylethanol 2a (366.5 mg, 3 mmol), Cu(OAc)$_2$.H$_2$O (6 mg, 0.03 mmol, 1 mol%) and KOH (50.5 mg, 0.9 mmol, 30 mol%) was sealed in a 20 mL Schlenk tube under air and then heated at 120 °C, monitored by GC-MS and/or $^1$H NMR. After completion of the reaction (99% by GC), the mixture was quenched with ethyl acetate, washed successively with diluted hydrochloric acid, brine and water, extracted with ethyl acetate. The combined organic layer was then dried over CaCl$_2$ and concentrated in vacuo. Column chromatography of the crude product using ethyl acetate and petroleum ether (60-90 °C) (v/v 1/30) gave 3aa in 87 % isolated yield (0.55 g).

Typical Procedure for Copper-Catalyzed Aerobic α-Alkylation of Methyl Ketones with Alcohols. The mixture of commercial benzyl alcohol 1a (0.93 mL, 9 mmol), phenylacetone 6a (360.5 mg, 3 mmol), Cu(OAc)$_2$.H$_2$O (6 mg, 0.03 mmol, 1 mol%) and NaOH (151.5 mg, 2.7 mmol, 90 mol%) was sealed in a 20 mL Schlenk tube under air and then heated at 120 °C, monitored by GC-MS and/or $^1$H NMR. After completion of the reaction (99% by GC), the mixture was quenched with ethyl acetate, washed successively with diluted hydrochloric acid, brine and water, extracted with ethyl acetate. The combined organic layer was then dried over CaCl$_2$ and concentrated in vacuo. Column chromatography of the crude product using ethyl acetate and petroleum ether (60-90 °C) (v/v 1/30) gave 3aa in 85 % isolated yield (0.54 g).
Characterization of Products.

1,3-Diphenylpropan-1-ol (3aa). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.24-7.07 (m, 10H), 4.50-4.47 (m, 1H), 3.00 (b, 1H), 2.61-2.52 (m, 2H), 2.01-1.87 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 144.4, 141.6, 128.23, 128.18, 128.1, 125.8, 125.6, 73.4, 40.2, 31.8. MS (EI): m/z (%) 212 (9), 194 (20), 107 (100), 92 (20), 91 (22), 79 (57), 78 (10), 77 (28), 51 (7). This compound was known.$^1$

3-Phenyl-1-p-tolylpropan-1-ol (3ab). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.34-7.13 (m, 9H), 4.61-4.58 (m, 1H), 2.73-2.59 (m, 2H), 2.33 (s, 3H), 2.31 (b, 1H), 2.13-1.95 (m, 2H). MS (EI): m/z (%) 226 (10), 209 (3), 208 (15), 121 (100), 93 (36), 92 (10), 91 (35), 77 (22), 65 (9), 51 (4). This compound was known.$^2$

1–(4–Chlorophenyl)–3–phenylpropan–1–ol (3ac). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.20-7.04 (m, 9H), 4.41 (t, $J$ = 6.5 Hz, 1H), 3.59 (b, 1H), 2.58-2.45 (m, 2H), 1.95-1.78 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 158.5, 141.6, 136.5, 128.1, 128.0, 126.9, 125.4, 113.4, 72.8, 54.7, 40.0, 31.7. MS (EI): m/z (%) 246 (1), 228 (30), 193 (13), 143 (31), 131 (100), 115 (13), 113 (22), 92 (31), 91 (26), 78 (11), 77 (52), 51 (7). This compound was known.$^3$

1–(4–Methoxyphenyl)–3–phenylpropan–1–ol (3ad). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.22-7.07 (m, 7H), 6.75 (d, $J$ = 8.5 Hz, 2H), 4.45 (t, $J$ = 8.0 Hz, 1H), 4.43 (b, 1H), 3.59 (s, 3H), 2.62-2.47 (m, 2H), 2.04-1.84 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 142.7, 141.6, 132.7, 128.22, 128.16, 128.1, 127.1, 125.7, 72.6, 40.1, 31.5. MS (EI): m/z (%) 242 (7), 224 (4), 137 (100), 135 (6), 109 (20), 94 (9), 91 (9), 79 (3), 77 (10), 51 (2). This compound was known.$^2$
1-Phenyl-3-p-tolylpropan-1-ol (3ba). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.28-7.18 (m, 5H), 7.04-7.00 (m, 4H), 4.54-4.52 (m, 1H), 2.64-2.50 (m, 3H), 2.63 (b, 1H), 2.26 (s, 3H), 2.03-1.89 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 144.5, 138.6, 135.0, 128.9, 128.3, 127.3, 125.8, 73.6, 40.4, 31.4, 20.8. MS (EI): $m/z$ (%) 226 (5), 208 (77), 193 (37), 107 (100), 105(50), 92 (14), 92 (41), 79 (92), 77 (60), 65 (10), 51 (12). This compound was known.$^4$

![OH](image)

3-(4-Chlorophenyl)-1-phenylpropan-1-ol (3ca). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.27-7.15 (m, 7H), 6.98 (d, $J$ = 8.5 Hz, 2H), 4.49 (t, $J$ = 6.0 Hz, 1H), 2.98 (b, 1H), 2.57-2.49 (m, 2H), 2.00-1.82 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 144.2, 140.1, 131.3, 129.6, 128.3, 128.2, 125.7, 73.3, 40.0, 31.1. MS (EI): $m/z$ (%) 244 (14), 228 (25), 193 (15), 125 (20), 115 (12), 107 (91), 105 (84), 103 (30), 91 (17), 79 (82), 78 (15), 77 (100), 51 (21). This compound was known.$^3$

![OH](image)

3-(3-Chlorophenyl)-1-phenylpropan-1-ol (3da). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.37-7.05 (m, 9H), 4.66-4.65 (m, 1H), 4.64 (b, 1H), 2.75-2.62 (m, 2H), 2.13-1.95 (m, 3H). MS (EI): $m/z$ (%) 246 (10), 193 (6), 107 (100), 105 (24), 91 (14), 79 (57), 77 (42), 65 (2), 51 (9). This compound was known.$^5$

![OH](image)

3-(4-Methoxyphenyl)-1-phenylpropan-1-ol (3ea). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.23-7.16 (m, 5H), 6.99 (d, $J$ = 8.5 Hz, 2H), 6.73 (d, $J$ = 8.5 Hz, 2H), 4.50 (d, $J$ = 6.5 Hz, 1H), 3.60 (s, 3H), 3.26 (b, 1H), 2.58-2.47 (m, 2H), 2.02-1.84 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 157.4, 144.5, 133.7, 129.0, 128.1, 127.1, 125.7, 113.5, 73.2, 54.8, 40.4, 30.8. MS (EI): $m/z$ (%) 242 (1), 240 (28), 224 (23), 135 (16), 121 (100), 107 (18), 105 (45), 91 (22), 79 (27), 78 (17), 77 (56), 65 (8), 51 (11). This compound was known.$^4$

![OH](image)

3-(3-Methoxyphenyl)-1-phenylpropan-1-ol (3fa). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.32-7.15 (m, 7H), 6.77-6.70 (m, 2H), 4.65-4.62(m, 1H), 3.75 (s, 3H), 2.72-2.58 (m, 2H), 2.18 (b, 1H), 2.13-1.97 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$159.6, 144.5, 143.4, 129.3, 128.4, 127.5, 125.9, 120.8, 114.1,
111.1, 73.7, 55.1, 40.3, 32.0. MS (EI): m/z (%) 242 (7), 224 (2), 193 (1), 165 (1), 122 (100), 107 (16), 92 (4), 91 (9), 79 (19), 77 (13), 65 (3), 51(2). HRMS Calcd for C_{16}H_{18}O_{2} (M+): 242.1307; found: 242.1306.

3-(2-Methoxyphenyl)-1-phenylpropan-1-ol (3ga). ^1^H NMR (500 MHz, CDCl$_3$): $\delta$ 7.26-7.05 (m, 7H), 6.84-6.73 (m, 2H), 4.53-4.50 (m, 1H), 3.66 (s, 3H), 3.05 (b, 1H), 2.69-2.63 (m, 2H), 2.03-1.88 (m, 2H). ^13^C NMR (125 MHz, CDCl$_3$): $\delta$ 157.1, 144.5, 129.9, 129.7, 128.0, 127.0, 126.9, 125.7, 120.4, 73.3, 54.9, 38.9, 26.3. MS (EI): m/z (%) 242 (27), 224 (75), 209 (12), 193 (25), 135 (28), 122 (49), 107 (100), 105 (38), 91 (71), 79 (89), 78 (18), 77 (64), 65 (18), 51 (14). This compound was known.$^6$

3-(Furan-2-yl)-1-phenylpropan-1-ol (3ha). ^1^H NMR (500 MHz, CDCl$_3$): $\delta$ 7.30-7.20 (m, 6H), 6.24-6.23 (m, 1H), 5.95-5.94 (m, 1H), 4.60-4.57 (m, 1H), 2.69-2.57 (m, 3H), 2.52 (b, 1H), 2.06-1.95 (m, 2H). ^13^C NMR (125 MHz, CDCl$_3$): $\delta$ 155.5, 144.2, 140.8, 128.3, 127.4, 125.8, 110.0, 104.9, 73.4, 37.0, 24.2. MS (EI): m/z (%) 202 (6), 184 (100), 155 (32), 141 (16), 107 (40), 105 (26), 91 (20), 79 (66), 77 (43), 65 (8), 53 (15), 51 (11). This compound was known.$^7$

3-(Furan-2-yl)-1-p-tolylpropan-1-ol (3hb). ^1^H NMR (500 MHz, CDCl$_3$): $\delta$ 7.22-7.06 (m, 5H), 6.21 (t, $J = 2.25$ Hz, 1H), 5.92 (d, $J = 3.0$ Hz, 1H), 4.53-4.50 (m, 1H), 2.79 (b, 1H), 2.66-2.55 (m, 2H), 2.28 (s, 3H), 2.05-1.90 (m, 2H). ^13^C NMR (125 MHz, CDCl$_3$) $\delta$155.8, 141.6, 141.0, 136.9, 128.9, 125.7, 109.9, 104.7, 73.1, 36.8, 24.2, 20.9. MS (EI): m/z (%) 216 (19), 199 (17), 198 (100), 183 (26), 169 (21), 155 (17), 134 (47), 121 (92), 119 (43), 118 (41), 105 (14), 93 (67), 91 (43), 81 (37), 77 (30), 65 (12), 53 (12). HRMS Calcd for C$_{14}$H$_{16}$O$_2$ (M+): 216.1155; found: 216.1154.

1-(4-Chlorophenyl)-3-(furan-2-yl)propan-1-ol (3hc). ^1^H NMR (500 MHz, CDCl$_3$): $\delta$ 7.23-7.09 (m, 5H), 6.17-6.16 (m, 1H), 5.88-5.87 (m, 1H), 4.53-4.50 (m, 1H), 2.57 (t, $J = 15.0$ Hz, 2H), 1.98-1.84
S

1-Phenyl-3-(thiophen-2-yl)propan-1-ol (3ia). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.27-7.21 (m, 5H), 7.05-7.04 (m, 1H), 6.87-6.85 (m, 1H), 6.73-6.72 (m, 1H), 4.59-4.57 (m, 1H), 2.88-2.77 (m, 2H), 2.53 (b, 1H), 2.11-1.94 (m, 2H). MS (EI): $m/z$ (%) 218 (8), 200 (72), 285 (11), 167 (15), 133 (9), 121 (15), 107 (49), 105 (23), 98 (100), 91 (9), 79 (86), 77 (77), 65 (9), 51 (21). This compound was known.$^6$

1-Phenyloctan-3-ol (3ae). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.24-7.11 (m, 4H), 3.59-3.54 (m, 1H), 2.78-2.60 (m, 2H), 2.45 (b, 1H), 1.75-1.70 (m, 2H), 1.43-1.26 (m, 8H), 0.88 (t, $J$ = 7.0 Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 142.5, 128.53, 128.46, 125.8, 71.3, 39.2, 37.7, 32.2, 32.1, 25.5, 22.8, 14.2. MS (EI): $m/z$ (%) 206 (1.16), 117 (44.46), 104 (100), 92 (43.7), 91 (88.44), 79 (5.17), 78 (10.13), 77 (5.98), 65 (7.51), 55 (18.89). This compound was known.$^8$

1-p-Tolyloctan-3-ol (3be). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.08-6.91 (m, 4H), 3.52-3.47 (m, 1H), 2.66-2.50 (m, 2H), 2.21 (s, 3H), 1.75 (b, 1H), 1.67-1.59 (m, 2H), 1.35-1.18 (m, 8H), 0.79 (t, $J$ = 6.0 Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$139.0, 135.0, 128.9, 128.2, 71.2, 39.1, 37.4, 31.8, 31.5, 25.2, 22.5, 20.8, 13.9. MS (EI): $m/z$ (%) 220 (16), 202 (35), 131 (99), 119 (16), 118 (100), 106 (48), 105 (88), 92 (12), 91 (21), 79 (9), 78 (3), 77 (9), 55 (13). HRMS Calcd for C$_{15}$H$_{24}$O (M+): 220.1825; found: 220.1824.

1-(4-Chlorophenyl)octan-3-ol (3ce). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.15-6.91 (m, 4H), 3.48-3.43 (m, 1H), 2.64-2.47 (m, 2H), 2.32 (br, s, 1H), 1.62-1.56 (m, 2H), 1.35-1.15 (m, 8H), 0.78 (t, $J$ = 7.0 Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$140.6, 131.2, 129.6, 128.2, 70.9, 38.7, 37.4, 31.7, 31.2, 25.1,
22.5, 13.9. MS (EI): m/z (%): 240 (4), 222 (27), 151 (38), 138 (100), 125 (65), 117 (7), 103 (8), 91 (15), 83 (12), 77 (6), 55 (26), 51 (1). HRMS Calcd for C_{14}H_{21}ClO (M+): 240.1279; found: 240.1279.

1-Phenylnonan-3-ol (3af). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.26-7.13 (m, 5H), 3.61-3.56 (m, 1H), 2.80-2.61 (m, 2H), 2.07 (b, 1H), 1.76-1.72 (m, 2H), 1.46-1.26 (m, 10H), 0.88 (t, \(J = 7.0\) Hz, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 142.2, 128.3, 128.2, 125.6, 71.1, 38.9, 37.5, 32.0, 31.7, 29.3, 25.5, 22.5, 13.9. MS (EI): m/z (%): 220 (0.5), 202 (16), 117 (36), 104 (100), 92 (46), 91 (97), 79 (6), 79 (11), 77 (8), 69 (10), 65 (11), 51 (3). This compound was known.\(^9\)

5-Methyl-1-phenylhexan-3-ol (3ag). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.23-7.12 (m, 5H), 3.71-3.66 (m, 1H), 2.81-2.62 (m, 1H), 1.77-1.67 (m, 3H), 1.67 (b, 1H), 1.40-1.26 (m, 2H), 0.90 (t, \(J = 7.0\) Hz, 6H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 142.2, 128.32, 128.31, 125.7, 69.4, 46.7, 39.6, 32.0, 24.6, 23.4, 22.1. MS (EI): m/z (%): 192 (1.76), 174 (34.12), 131 (10.66), 118 (22.10), 117 (35.28), 104 (87.17), 92 (50.46), 91 (100), 79 (5.97), 78 (12.67), 77 (7.72), 65 (9.69), 55 (3.92). This compound was known.\(^10\)

1–Phenyloctan–1–ol (3ja). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.29-7.19 (m, 5H), 4.54 (t, \(J = 6.75\) Hz, 1H), 2.74 (b, 1H), 1.73-1.63 (m, 2H), 1.36-1.20 (m, 10H), 0.87 (t, \(J = 7.25\) Hz, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 144.9, 128.2, 127.2, 125.8, 74.5, 39.0, 31.7, 29.4, 29.1, 25.7, 22.5, 14.0. MS (EI): m/z (%): 206 (2), 188 (1), 120 (4), 107 (100), 105 (8), 98 (100), 92 (1), 91 (4), 79 (35), 77 (15), 65 (1), 55 (2), 51 (3). This compound was known.\(^11\)

1-p-Tolyloctan-1-ol (3jb). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.18-7.10 (m, 4H), 4.54 (t, \(J = 6.75\) Hz, 1H), 2.31 (s, 4H), 1.75-1.62 (m, 2H), 1.36-1.25 (m, 10H), 0.86 (t, \(J = 3.5\) Hz, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 142.0, 136.9, 128.9, 125.8, 74.3, 38.9, 31.8, 29.5, 29.2, 25.8, 22.6, 21.0, 14.0. MS (EI): m/z (%): 220 (5), 122 (12), 119 (4), 93 (26), 92 (2), 91 (11), 77 (7), 65 (2), 55 (1), 51 (1). This
1-(4-Chlorophenyl)octan-1-ol (3jc). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.31-7.20 (m, 4H), 4.56 (t, $J = 6.75$, 1H), 2.60 (b, 4H), 1.75-1.61 (m, 2H), 1.33-1.92 (m, 10H), 0.87 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 143.5, 133.0, 128.5, 127.3, 74.9, 39.1, 31.8, 29.5, 29.2, 25.7, 22.7, 14.1. MS (EI): m/z (%) 240 (8), 143 (33), 141 (100), 125 (2), 113 (13), 91 (1), 77 (20), 78 (2), 57 (2), 55(2). This compound was known.$^{13}$

1-Phenylhexan-1-ol (3ka). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.31-7.21 (m, 5H), 4.56 (t, $J = 6.75$ Hz, 1H), 2.44 (b, 1H), 1.74-1.64 (m, 2H), 1.40-1.21 (m, 6H), 0.86 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 144.9, 128.3, 127.3, 125.9, 74.6, 39.0, 31.7, 25.4, 22.5, 14.0. MS (EI): m/z (%) 178 (5.02), 107 (100), 91 (2.47), 79 (35.78), 77 (13.72), 65 (0.6), 55 (1.02). This compound was known.$^{14}$

2–Benzyl–1,2,3,4–tetrahydronaphthalen–1–ol (3ah). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.46-7.44 (m, 1H), 7.28-7.35 (m, 2H), 7.20-7.13 (m, 5H), 7.06-7.03 (m, 1H), 4.42-4.40 (d, $J = 7.5$ Hz, 1H), 3.05-3.01 (m, 1H), 2.71-2.68 (m, 2H), 2.45-2.40 (m, 1H), 2.13 (b, 1H), 1.99-1.90 (m, 2H), 1.47-1.39 (m, 1H). MS (EI): m/z (%) 238 (17), 220 (20), 160 (15), 146 (84), 129 (66), 92 (38), 91 (100), 79 (5), 77 (15), 65 (25), 51 (9). This compound was known.$^6$

1,3–Diphenylbutan–1–ol (3aa’). $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 7.33-7.16 (m, 10H), 4.52 (t, $J = 7.0$ Hz, 1H), 2.73-2.57 (m, 1H), 2.17-2.14 (m, 1H), 1.94-1.88 (m, 2H), 1.24 (d, $J = 7.0$ Hz, 3H). MS (EI): m/z (%) 226 (6), 208 (16), 193 (7), 121 (24), 107 (100), 106 (59), 103 (14), 91 (46), 79 (82), 78 (19), 77 (54), 65 (6), 51 (13). This compound was known.$^{15}$
Reference

Elementary Reactions and Mechanistic Studies

Cu-Mediated Alcohol Oxidation.

**Table S3.** Cu-mediated Oxidation of Primary Alcohol.

<table>
<thead>
<tr>
<th>Run</th>
<th>Cu (mol%)</th>
<th>K$_2$CO$_3$ (mol%)</th>
<th>condition</th>
<th>7a%$^{[a]}$</th>
<th>8a%$^{[a]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu(OAC)$_2$-H$_2$O (5)</td>
<td>-</td>
<td>N$_2$, 120 °C, 6 h</td>
<td>NR</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Cu(OAC)$_2$-H$_2$O (5)</td>
<td>50</td>
<td>N$_2$, 120 °C, 12 h</td>
<td>NR</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Cu(OAC)$_2$-H$_2$O (5)</td>
<td>-</td>
<td>air, 120 °C, 6 h</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Cu(OAC)$_2$-H$_2$O (5)</td>
<td>50</td>
<td>air, 120 °C, 6 h</td>
<td>4.4</td>
<td>5.8</td>
</tr>
<tr>
<td>5</td>
<td>Cu(OAC)$_2$-H$_2$O (5)</td>
<td>-</td>
<td>N$_2$, 150 °C, 6 h</td>
<td>2.3</td>
<td>2.4</td>
</tr>
<tr>
<td>6</td>
<td>Cu(OAC)$_2$-H$_2$O (5)</td>
<td>-</td>
<td>N$_2$, 180 °C, 6 h</td>
<td>2.8</td>
<td>2.7</td>
</tr>
<tr>
<td>7</td>
<td>Cu(OAC)$_2$-H$_2$O (10)</td>
<td>-</td>
<td>N$_2$, 150 °C, 6 h</td>
<td>5</td>
<td>4 (4)</td>
</tr>
<tr>
<td>8</td>
<td>Cu(OAC)$_2$-H$_2$O (20)</td>
<td>-</td>
<td>N$_2$, 150 °C, 6 h</td>
<td>5.4</td>
<td>5.5 (8)</td>
</tr>
<tr>
<td>9</td>
<td>CuI (10)</td>
<td>-</td>
<td>N$_2$, 150 °C, 6 h</td>
<td>NR</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>CuI (20)</td>
<td>-</td>
<td>N$_2$, 150 °C, 6 h</td>
<td>NR</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>CuI (50)</td>
<td>-</td>
<td>N$_2$, 150 °C, 6 h</td>
<td>NR</td>
<td></td>
</tr>
</tbody>
</table>

[a] Absolute 1a was used. GC yield (NMR yield in parenthesis).

**Discussion on Table S3** (See also: Q. Li, S. Fan, Q. Sun, H. Tian, X. Yu, Q. Xu, *Org. Biomol. Chem.* accepted):

As shown in the table, no reaction was observed when absolute 1a and Cu(II) were heated at 120 °C under nitrogen (runs 1-2), but 2-6% yield of 7a could be detected if the same reactions were performed under air (runs 3-4). When the same reactions (run 1) were heated at higher temperatures under nitrogen (runs 5-6, 150-180 °C), yields of 7a were surprisingly found to be irrelevant to reaction temperature and time, but to the amounts of Cu(II) added, i.e., nearly half amounts of 7a (in mol/mol ratio to Cu(II) added) were always generated under these conditions. This was further confirmed by adding more amounts of Cu(II) and by both GC and NMR spectroscopic analysis (runs 7-8). In the latter cases, ca. 1-2 folds of benzyl acetate 8a (in mol/mol ratio to Cu(II) added) were also detected and confirmed (runs 7-8). Since 10-50 mol% of a Cu(I) species (CuI), although an active alcohol oxidation and N-alkylation catalyst, were found inactive under nitrogen even at 150 °C (runs 9-11), we deduce, Cu(I) species may be generated in the anaerobic reactions of Cu(II) and 1a (runs 3-6) via eqs. S1-S3, giving constant yields of 7a and 8a. Thus, when heated under nitrogen, Cu(OAc)$_2$ firstly reacts with 1a, resulting in the reduction of Cu(II) to a Cu(I) species like CuOAc...
and concurrent oxidation of 1a to 7a, giving also the acetic acid (HOAc) as a byproduct (eq. S1). Due to the presence of large excess 1a, the generated HOAc may quickly undergo dehydrative esterification with 1a at the high temperatures to give benzyl acetate 8a (eq. S2). As a result, half amounts of 7a was generated during the process, with detection of 8a as a byproduct (eq. S3). In these cases, Cu(II) may essentially be the direct oxidant for the alcohols under anaerobic conditions, with itself reduced to Cu(I) by the alcohol.

\[
\begin{align*}
2 \text{Cu(OAc)}_2 + \text{PhCH}_2\text{OH} &\longrightarrow 2 \text{CuOAc} + \text{PhCHO} + 2 \text{HOAc} \quad \text{(S1)} \\
\text{HOAc} + \text{PhCH}_2\text{OH} &\longrightarrow \text{PhCH}_2\text{OAc} + \text{H}_2\text{O} \quad \text{(S2)}
\end{align*}
\]

Overall Reaction (eq. S1 + eq. S2):

\[
2 \text{Cu(OAc)}_2 + 3 \text{PhCH}_2\text{OH} \longrightarrow 2 \text{CuOAc} + \text{PhCHO} + 2 \text{PhCH}_2\text{OAc} + \text{H}_2\text{O} \quad \text{(S3)}
\]

On the other hand, since 1-2 equiv. of benzyl acetate 8a (in mol/mol ratio to Cu(II) added) was produced, one of the potential reactions as shown below may also be possible to give benzyl acetate 8a (eq. S4).

\[
\begin{align*}
\text{CuOAc} + 2 \text{PhCH}_2\text{OH} &\longrightarrow \text{PhCH}_2\text{OCu} + \text{PhCH}_2\text{OAc} + \text{H}_2\text{O} \quad \text{(S4)}
\end{align*}
\]
**Cu-Mediated Oxidation of Secondary Alcohol:**

\[
\begin{align*}
\text{PhC\textsubscript{3}H}_{2}O & \xrightarrow{\text{Cu(OAc)}_{2}.H_{2}O (1 \text{ mol} \%) \text{ KOH (30 mol \%)}} \text{PhC\textsubscript{3}H}_{2}O \\
\text{PhC\textsubscript{3}H}_{2}O & \xrightarrow{110 \degree C, 24 \text{ h}} \text{PhC\textsubscript{3}H}_{2}O \\
\text{run} & \text{ [Cu] (mol\%) atm.} \\
1 & 5 \text{ air} 77\% \\
2 & 5 \text{ N\textsubscript{2}} \text{ NR}
\end{align*}
\]

Note: 0.5 mmol absolute 2i (100% purity as confirmed by NMR) in 0.5 mL toluene was stirred in a sealed Schlenk tube (20 mL) and monitored by NMR.

**Cu-Promoted Condensation of Benzaldehyde and Acetophenone:**

\[
\begin{align*}
\text{PhC} & \text{O + PhC} \xrightarrow{\text{conditions CH\textsubscript{3}CN, N\textsubscript{2}, T, t}} \text{PhC} \\
\text{run} & \text{ cat. [Cu] (mol\%)} \\
1 & \text{none} 100 \degree C, 6 \text{ h}: 0.9\%; 12 \text{ h}: 1.4\% \\
2 & \text{Cu(OAc)}_{2} (5) 100 \degree C, 6 \text{ h}: 75\%; 12 \text{ h}: 87\% \\
3 & \text{none} \text{ r.t., 12 h}: 0\% \\
4 & \text{Cu(TFA)}_{2} (5) \text{ r.t., 12 h}: 2\% \\
5 & \text{Cu(OTf)}_{2} (5) \text{ r.t., 12 h}: 54\%
\end{align*}
\]

Note: 5 mmol 7a and 5 mmol 6a in acetonitrile (0.5 mL) were stirred in a sealed Schlenk tube under nitrogen and monitored by GC-MS.
**Table S4.** Cu-Catalyzed Transfer Hydrogenation of Chalcone 4aa by Phenyl(p-tolyl)methanol 2i.^[a]  

![Chemical structures](image)

<table>
<thead>
<tr>
<th>run</th>
<th>2i (equiv.)</th>
<th>3aa/5aa^[b]</th>
<th>6i%^[c]</th>
<th>(4<em>3aa+2</em>5aa)/(2*6i)^[d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>26/74</td>
<td>84</td>
<td>0.97/1.00</td>
</tr>
<tr>
<td>2</td>
<td>3.0</td>
<td>61/39</td>
<td>54</td>
<td>0.75/1.00</td>
</tr>
</tbody>
</table>

^[a] The mixture of 4aa (0.5 mmol), 2i, KOH (30 mol%), and Cu(OAc)2·H2O (1 mol%) in toluene (0.5 mL) in a sealed Schlenk tube was heated under N2. [b] The ratios were determined by 1H NMR analysis. [c] 1H NMR yields based on 2i. [d] Mol. ratios of the hydrogens accepted (4*3aa + 2*5aa) vs. the hydrogens donated (2*6i) were determined by 1H NMR analysis.

1H NMR spectra of run 1.

\[
\text{3aa/5aa} = 0.17 \times 2 / 0.99 = 26/74
\]
\[
6i\% = 0.25 / (0.25 + 1.29) = 84\%
\]
\[
\text{Mol. hydrogens accepted} = 4 \times 3\text{aa} + 2 \times 5\text{aa} = 4 \times (0.17/2) + 2 \times (0.99/4) = 0.835
\]
\[
\text{Mol. hydrogens donated} = 2 \times 6\text{i} = 2 \times (1.29/3) = 0.86
\]
\[
\text{Mol. hydrogens accepted/Mol. hydrogens donated} = 0.835/0.86 = 0.97/1.00
\]
$^1$H NMR spectra of run 2.

3aa/5aa = 0.77*2/1.00 = 61/39
6i% = 4.07/(4.07 + 3.46) = 54%
Mol.-hydrogens accepted = 4*3aa + 2*5aa = 4*(0.77/2) + 2*(1.00/4) = 2.04
Mol.-hydrogens donated = 2*6i = 2*(4.07/3) = 2.71
Mol.-hydrogens accepted/Mol.-hydrogens donated = 2.04/2.71 = 0.75/1.00
$^1$H and $^{13}$C NMR Spectra of the Products

$^1$H NMR
$^{13}C$ NMR
$^1$H NMR
$^1$H NMR
$^1$H NMR
$^1$H NMR
$^{13}$C NMR
$^1$H NMR

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$^1$H NMR

3da
$^1$H NMR
$^{13}$C NMR
$^{13}$C NMR
$^1$H NMR

\[
\begin{align*}
\text{OH} & \quad \text{OMe} \\
\text{3ga} & 
\end{align*}
\]
$^{13}$C NMR
$^{13}$C NMR
'H NMR

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$^{13}\text{C} \text{ NMR}$
$^1$H NMR
$^1$H NMR
$^{13}$C NMR
$^{1}H$ NMR
$^{13}$C NMR
$^{1}$H NMR
$^{13}$C NMR

![Graph of $^{13}$C NMR spectra](image)
$^1$H NMR

![NMR spectrum of 3af](image)
$^{13}$C NMR
$^1$H NMR
$^{13}$C NMR
$^1$H NMR

[Diagram of the 1H NMR spectrum for compound 3ja]
$^{1}H$ NMR
$^{13}$C NMR

\[ \text{Diagram of }^{13}\text{C NMR spectroscopy.} \]
$^1$H NMR

3jc
$^{13}$C NMR
$^1$H NMR

![NMR Spectrum](image-url)
$^{13}$C NMR
$^1$H NMR

\[ \text{Chemical Shift (ppm)} \]

OH

3ah

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