Copper Catalysis for Highly Selective Aerobic Oxidation of Alcohols to Aldehydes/Ketones

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Supporting information

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**General Information.** NMR spectra were taken with an Agilent-400 spectrometer (400 MHz for \(^1\)H NMR, 100 MHz for \(^{13}\)C NMR). All reactions were carried out in 25mL Schlenk tubes if not be mentioned specially. Cu(NO\(_3\))\(_2\)•3H\(_2\)O was purchased from Sinopharm Chemical Reagent Co., Ltd; TEMPO (98%) and 4-OH-TEMPO (98%) were purchased from Shanghai Darui Fine Chemical Co., Ltd.; DCE and MeCN was dried over CaH\(_2\) and distilled. All the temperatures are referred to the oil baths. Recovery of substrates was determined by \(^1\)H NMR analysis using dibromomethane as the internal standard. Alcohols except \(1q\) were synthesized following literatures\(^1\) or used as received without further treatment. The following compounds were characterized via comparison with the authentic samples prepared in this group:


\(2h, 2k\): Liu, J.; Xie, X.; Ma, S. *Synthesis* 2012, 44, 1569.

\(4a, 4b, 4c, 4d\): Liu, J.; Ma, S. *Org. Lett.* 2013, 15, 5150.


\(6a, 6c\): Jiang, X.; Ma, S. *Synthesis* 2018, 50, 1629.
Experimental details and analytical data
1. Synthesis of 3-(1-hydroxy-2-heptynyl) benzonitrile (1q) (wgl-1-001)

\[
\text{Bu}_n \quad \text{BuLi (1.05 equiv)} \quad \text{THF, -71 °C, (5 + 16) min then r.t., 48 min}
\]

\[
\begin{align*}
\text{CHO} & \quad \text{CN} \\
\text{OH} & \quad \text{Bu}_n
\end{align*}
\]

1q, 94%

To a flame-dried flask were added THF (20 mL) and 1-hexyne (2.5 mL, d = 0.72 g/mL, 1.8060 g, 22 mmol) under argon atmosphere. Then a solution of n-BuLi (2.5 M in hexane, 8.4 mL, 21 mmol) was added dropwise over 5 min at -71 °C via a dry ice-acetone bath, and stirred at -71 °C for 16 min. After stirring at room temperature for 48 min, the resulting mixture was cooled to -71 °C, then a solution of 3-formylbenzonitrile (2.6279 g, 20 mmol) in THF (10 mL) was added dropwise over 20 min. The resulting mixture was then stirred at room temperature for another 2 h, and quenched with a saturated aqueous solution of NH₄Cl. After extraction with ethyl acetate, the organic layer was washed with H₂O (10 mL x 2) and brine (10 mL), respectively. Then the organic layer was dried over anhydrous Na₂SO₄. After filtration and concentration under reduced pressure, the crude product was purified by column chromatography on silica gel [eluent: petroleum ether /ethyl acetate = 10/1 (110 mL) to 5/1 (180 mL)] to afford 1q (3.9290 g, 94%) as a pale yellow oil; \(^1\)H NMR (400 MHz, CDCl₃): \(\delta = 7.84\) (s, 1 H, ArH), 7.78 (d, \(J = 7.6\) Hz, 1 H, ArH), 7.59 (d, \(J = 8.0\) Hz, 1 H, ArH), 7.48 (t, \(J = 7.8\) Hz, 1 H, ArH), 5.47 (s, 1 H, CH), 3.06-3.05 (bs, 1 H, OH), 2.27 (td, \(J_1 = 6.9\) Hz, \(J_2 = 1.7\) Hz, 2 H, CH₂), 1.58-1.46 (m, 2 H, CH₂), 1.46-1.34 (m, 2 H, CH₂), 0.91 (t, \(J = 7.2\) Hz, 3 H, CH₃); \(^{13}\)C NMR (100 MHz, CDCl₃): \(\delta = 142.7, 131.5, 131.0, 130.1, 129.1, 118.6, 112.1, 88.4, 78.9, 63.4, 30.3, 21.8, 18.3, 13.4; MS (70 eV, EI) \(m/z\) (%): 214 (M⁺+1, 9.52), 213 (M⁺, 62.32), 170 (100); IR (neat): \(\nu = 3418, 2958, 2932, 2867, 2231, 1430, 1130, 1002; HRMS calcd. for C₁₄H₁₅NO (M⁺): 213.1154; Found: 213.1159.\]
2. Synthesis of aldehydes or ketones.

(1) Synthesis of 1-(4-methylphenyl)-2-propyn-1-one (2b) (zd-4-12)

**Typical Procedure 1:** A dry Schlenk tube was degassed to remove the air inside completely, and refilled with O₂ by a balloon of O₂ for three times. Then Cu(NO₃)₂·3H₂O (24.6 mg, 0.1 mmol), TEMPO (16.2 mg, 0.1 mmol), and a solution of 1b (146.4 mg, 1.0 mmol) in MeCN (4 mL) were added sequentially. The resulting mixture was stirred at 25 °C for 6 h as monitored by TLC (petroleum ether/ethyl acetate = 5/1), filtered through a short column of silica gel [eluent: ethyl ether (75 mL)], concentrated under reduced pressure, and purified by column chromatography on silica gel [eluent: petroleum ether/ethyl ether = 60/1] to afford 2b (130.7 mg, 91%) as a white solid: M.p. 44.2-44.7 °C (petroleum ether/ethyl acetate) (Lit m.p.: 40–42 °C); ¹H NMR (400 MHz, CDCl₃): δ = 8.06 (d, J = 8.4 Hz, 2 H, ArH), 7.29 (d, J = 8.0 Hz, 2 H, ArH), 3.40 (s, 3 H, CH₃), 2.44 (s, 1 H, ≡CH); ¹³C NMR (100 MHz, CDCl₃): δ = 177.0, 145.7, 133.8, 129.8, 129.4, 80.34, 80.28, 21.8; MS (70 eV, EI) m/z (%): 144 (M⁺, 74.75), 115 (100); IR (neat): ν = 3257, 2090, 1632, 1594, 1459, 1404, 1310, 1246, 1167, 1117 cm⁻¹.

(2) Synthesis of 1-(2-methoxyphenyl)-2-propyn-1-one (2c) (zd-4-70)

Following **Typical Procedure 1**, the reaction of Cu(NO₃)₂·3H₂O (24.0 mg, 0.1 mmol), TEMPO (16.1 mg, 0.1 mmol), and 1c (161.8 mg, 1.0 mmol) in MeCN (4 mL) afforded 2c (134.0 mg, 84%) as an oil [eluent: petroleum ether/ethyl acetate = 30/1]:
$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.06$ (dd, $J_1 = 7.8$ Hz, $J_2 = 1.8$ Hz, 1 H, ArH), 7.55 (td, $J_1 = 8.0$ Hz, $J_2 = 1.8$ Hz, 1 H, ArH), 7.07-6.97 (m, 2 H, ArH), 3.94 (s, 3 H, CH$_3$), 3.37 (s, 1 H, $\equiv$CH); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 175.8$, 159.8, 135.4, 132.9, 125.5, 120.1, 112.0, 81.9, 79.5, 55.6; MS (70 eV, EI) $m/z$ (%): 161 (M$^+$+1, 7.26), 160 (M$^+$, 64.37), 131 (100); IR (neat): $\nu = 3234$, 2089, 1647, 1595, 1573, 1484, 1462, 1434, 1286, 1253, 1224, 1164, 1116, 1019 cm$^{-1}$.

(3) Synthesis of 1-(3-methoxyphenyl)-2-propyn-1-one (2d) (zd-4-78)

Following Typical Procedure 1, the reaction of Cu(NO$_3$)$_2$·3H$_2$O (24.1 mg, 0.1 mmol), TEMPO (16.3 mg, 0.1 mmol), and 1d (162.2 mg, 1.0 mmol) in MeCN (4 mL) afforded 2d$^5$ (142.6 mg, 89%) as an oil [eluent: petroleum ether/ethyl acetate = 30/1]: $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.80$ (d, $J = 7.6$ Hz, 1 H, ArH), 7.64 (s, 1 H, ArH), 7.42 (t, $J = 8.0$ Hz, 1 H, ArH), 7.19 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.0$ Hz, 1 H, ArH), 3.87 (s, 3 H, CH$_3$), 3.43 (s, 1 H, $\equiv$CH); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 177.1$, 159.8, 137.4, 129.7, 122.9, 121.4, 112.8, 80.6, 80.3, 55.4; MS (70 eV, EI) $m/z$ (%): 161 (M$^+$+1, 11.54), 160 (M$^+$, 100); IR (neat): $\nu = 3250$, 2094, 1644, 1595, 1581, 1485, 1429, 1323, 1264, 1207, 1177, 1021, 1012 cm$^{-1}$.

(4) Synthesis of 1-(4-methoxyphenyl)-2-propyn-1-one (2e) (zd-4-67)

Following Typical Procedure 1, the reaction of Cu(NO$_3$)$_2$·3H$_2$O (24.6 mg, 0.1
mmol), TEMPO (16.0 mg, 0.1 mmol), and 1e (161.8 mg, 1.0 mmol) in MeCN (4 mL) afforded 2e\(^{[3]}\) (143.6 mg, 90%) as a white solid [elucent: petroleum ether/ethyl acetate = 25/1]: M.p. 85.5-86.5 °C (petroleum ether/ethyl acetate) (Lit\(^{[6]}\) m.p.: 86–87 °C); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.13\ (d, J = 9.2\ Hz, 2\ H,\ ArH), 6.97\ (d, J = 8.8\ Hz, 2\ H,\ ArH), 3.90\ (s, 3\ H, CH\(_3\)), 3.38\ (s, 1\ H, \equiv\text{CH})\); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 175.8, 164.7, 132.0, 129.4, 113.8, 80.3, 80.1, 55.5\); MS (70 eV, EI) \(m/z\) (%):161 (M\(^+\)+1, 11.17), 160 (M\(^+\), 100); IR (neat): \(\nu = 3248, 2091, 1638, 1596, 1570, 1507, 1421, 1254, 1168, 1116, 1022, 1008\ cm\(^{-1}\)).

(5) Synthesis of 1-(4-methoxycarbonylphenyl)-2-propyn-1-one (2f) (zd-4-69)

Following **Typical Procedure 1**, the reaction of Cu(NO\(_3\))\(_2\)•3H\(_2\)O (24.0 mg, 0.1 mmol), TEMPO (15.8 mg, 0.1 mmol), and 1f (190.2 mg, 1.0 mmol) in MeCN (4 mL) afforded 2f\(^{[7]}\) (170.3 mg, 90%) as a white solid [elucent: petroleum ether/ethyl acetate = 30/1]: M.p. 117.0-118.3 °C (petroleum ether/ethyl acetate); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.22\ (d, J = 8.4\ Hz, 2\ H,\ ArH), 8.16\ (d, J = 8.4\ Hz, 2\ H,\ ArH), 3.97\ (s, 3\ H, CH\(_3\)), 3.53\ (s, 1\ H, \equiv\text{CH})\); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 176.6, 165.9, 139.0, 135.0, 129.8, 129.4, 81.8, 80.0, 52.5\); MS (70 eV, EI) \(m/z\) (%):189 (M\(^+\)+1, 5.41), 188 (M\(^+\), 41.74), 157 (100); IR (neat): \(\nu = 3217, 2096, 1717, 1636, 1606, 1437, 1275, 1233, 1195, 1119, 1006\ cm\(^{-1}\)).

(6) Synthesis of 1-(2-thienyl)-2-propyn-1-one (2g) (zd-4-95)
Following Typical Procedure 1, the reaction of Cu(NO$_3$)$_2$•3H$_2$O (24.4 mg, 0.1 mmol), TEMPO (15.8 mg, 0.1 mmol), and 1g (137.8 mg, 1.0 mmol) in MeCN (4 mL) afforded 2g$^{[7]}$ (118.4 mg, 87%) as a white solid [eluent: petroleum ether/ethyl ether = 30/1]: M.p. 32.4-34.0 °C (petroleum ether/ethyl acetate) (Lit$^{[8]}$ m.p.: 31–33 °C); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.97 (dd, $J_1 = 3.8$ Hz, $J_2 = 0.6$ Hz, 1 H, ArH), 7.75 (dd, $J_1 = 4.8$ Hz, $J_2 = 0.8$ Hz, 1 H, ArH), 7.18 (t, $J = 4.2$ Hz, 1 H, ArH), 3.37 (s, 1 H, =CH); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 169.0, 144.0, 136.1, 135.9, 128.4, 79.8, 79.3; MS (70 eV, EI) $m/z$ (%): 136 (M$^+$, 100), 108 (95.16); IR (neat): $\nu$ = 3244, 3103, 2095, 1616, 1512, 1406, 1354, 1266, 1231, 1201, 1082, 1051 cm$^{-1}$.

(7) Synthesis of 1-Dodecyn-3-one (2h) (zd-3-89)

Following Typical Procedure 1, the reaction of Cu(NO$_3$)$_2$•3H$_2$O (24.0 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and 1h (182.1 mg, 1.0 mmol) in DCE (4 mL) afforded 2h$^{[9]}$ (160.4 mg, 89%) as an oil [eluent: petroleum ether/ethyl ether = 40/1]:

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.20 (s, 1 H, CH), 2.58 (t, $J = 7.4$ Hz, 2 H, CH$_2$), 1.73-1.60 (m, 2 H, CH$_2$), 1.40-1.16 (m, 12 H, 6×CH$_2$), 0.88 (t, $J = 6.8$ Hz, 3 H, CH$_3$);

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 187.5, 81.4, 78.2, 45.4, 31.8, 29.3, 29.22, 29.17, 28.8, 23.7, 22.6, 14.0.

(8) Synthesis of 1-phenyl-2-heptyn-1-one (2a) (zd-3-145, zd-3-70)
Following Typical Procedure 1, the reaction of Cu(NO$_3$)$_2$•3H$_2$O (23.9 mg, 0.1 mmol), TEMPO (16.1 mg, 0.1 mmol), and 1a (187.2 mg, 1.0 mmol) in MeCN (4 mL) afforded 2a$^{[10]}$ (177.4 mg, 96%) as an oil [eluent: petroleum ether/ethyl ether = 30/1]:

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.14 (d, $J$ = 7.2 Hz, 2 H, ArH), 7.60 (t, $J$ = 7.2 Hz, 1 H, ArH), 7.48 (t, $J$ = 7.8 Hz, 2 H, ArH), 2.51 (t, $J$ = 7.0 Hz, 2 H, CH$_2$), 1.74-1.58 (m, 2 H, CH$_2$), 1.58-1.42 (m, 2 H, CH$_2$), 0.97 (t, $J$ = 7.4 Hz, 3 H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 178.2, 136.9, 133.8, 129.5, 128.4, 96.8, 79.6, 29.8, 22.0, 18.8, 13.4; MS (70 eV, El) m/z (%): 186 (M$^+$, 12.46), 144 (100); IR (neat): $\nu$ = 2957, 2933, 2868, 2232, 2200, 1641, 1588, 1452, 1314, 1257, 1172 cm$^{-1}$.

Following Typical Procedure 1, the reaction of Cu(NO$_3$)$_2$•3H$_2$O (24.0 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and 1a (188.0 mg, 1.0 mmol) in DCE (4 mL) afforded 2a$^{[10]}$ (185.2 mg, 100%) as an oil [eluent: petroleum ether/ethyl ether = 40/1]:

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.18-8.10 (m, 2 H, ArH), 7.63-7.57 (m, 1 H, ArH), 7.48 (t, $J$ = 7.8 Hz, 2 H, ArH), 2.51 (t, $J$ = 7.0 Hz, 2 H, CH$_2$), 1.74-1.58 (m, 2 H, CH$_2$), 1.58-1.42 (m, 2 H, CH$_2$), 0.97 (t, $J$ = 7.6 Hz, 3 H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 178.1, 136.8, 133.8, 129.4, 128.4, 96.7, 79.6, 29.7, 22.0, 18.8, 13.4.

(9) Synthesis of 3-cyclopropyl-1-phenyl-2-propyn-1-one (2i) (zd-3-159, zd-3-62)
Following **Typical Procedure 1**, the reaction of \( \text{Cu(NO}_3\text{)}_2 \cdot \text{3H}_2\text{O} \) (24.2 mg, 0.1 mmol), TEMPO (15.8 mg, 0.1 mmol), and \( \text{1i} \) (172.2 mg, 1.0 mmol) in MeCN (4 mL) afforded \( \text{2i}^{[11]} \) (166.6 mg, 98%) as an oil [eluent: petroleum ether/ethyl ether = 30/1]:

- **1H NMR (400 MHz, CDCl\(_3\))**: \( \delta = 8.16-8.05 \) (m, 2 H, ArH), 7.59 (t, \( J = 7.4 \) Hz, 1 H, ArH), 7.47 (t, \( J = 7.6 \) Hz, 2 H, ArH), 1.64-1.48 (m, 1 H, CH), 1.12-0.96 (m, 4 H, CH\(_2\)CH\(_2\));
- **13C NMR (100 MHz, CDCl\(_3\))**: \( \delta = 177.7, 136.8, 133.6, 129.2, 128.3, 101.0, 75.4, 9.7, -0.2 \);
- **MS (70 eV, EI)**: \( m/z \) (%): 170 (M\(^+\) + 1, 10.75), 170 (M\(^+\), 70.44), 141 (100);
- **IR (neat)**: \( \nu = 2207, 1635, 1596, 1579, 1449, 1356, 1311, 1264, 1172, 1046, 1023 \) cm\(^{-1}\).

(10) Synthesis of 1,3-diphenyl-2-propyn-1-one (\textbf{2j}) (zd-4-73)
Following Typical Procedure 1, the reaction of Cu(NO$_3$)$_2$•3H$_2$O (24.4 mg, 0.1 mmol), TEMPO (16.1 mg, 0.1 mmol), and 1j (209.8 mg, 1.0 mmol) in MeCN (4 mL) afforded 2j$^{[12]}$ (203.4 mg, 98%) as a white solid [eluent: petroleum ether/ethyl ether = 30/1]: M.p. 45.3-46.6 °C (petroleum ether/ethyl acetate) (Lit$^{[12]}$ m.p.: 45-47 °C); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.23 (d, $J=7.6$ Hz, 2 H, ArH), 7.70 (d, $J=6.8$ Hz, 2 H, ArH), 7.64 (t, $J=7.4$ Hz, 1 H, ArH), 7.57-7.48 (m, 3 H, CH$_3$), 7.43 (t, $J=7.2$ Hz, 2 H, ArH); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 177.8, 136.7, 134.0, 132.9, 130.7, 129.4, 128.54, 128.48, 119.9, 93.0, 86.8; MS (70 eV, EI) $m/z$ (%): 206 (M$^+$, 65.85), 178 (100); IR (neat): $\nu$ = 2195, 1637, 1597, 1579, 1488, 1447, 1313, 1282, 1207, 1171, 1031, 1010 cm$^{-1}$.

(11) Synthesis of 1-phenyl-3-(trimethylsilyl)-2-propyn-1-one (2k) (zd-3-147, zd-3-80)

Following Typical Procedure 1, the reaction of Cu(NO$_3$)$_2$•3H$_2$O (24.2 mg, 0.1 mmol), TEMPO (15.9 mg, 0.1 mmol), and 1k (204.8 mg, 1.0 mmol) in MeCN (4 mL) afforded 2k$^{[9]}$ (197.2 mg, 97%) as an oil [eluent: petroleum ether/ethyl ether = 60/1]; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.15 (d, $J=7.2$ Hz, 2 H, ArH), 7.62 (t, $J=7.4$ Hz, 1 H, ArH), 7.50 (t, $J=7.6$ Hz, 2 H, ArH), 0.33 (s, 9 H, 3×CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 177.6, 136.4, 134.1, 129.6, 128.5, 100.8, 100.5, -0.8.
Following **Typical Procedure 1**, the reaction of Cu(NO$_3$)$_2$•3H$_2$O (24.4 mg, 0.1 mmol), TEMPO (15.9 mg, 0.1 mmol), and 1k (204.1 mg, 1.0 mmol) in DCE (4 mL) afforded 2k$^{[9]}$ (191.5 mg, 95%) as an oil [eluent: petroleum ether/ethyl ether = 60/1]; $^1$H NMR (400 MHz, CDCl$_3$): δ = 8.20-8.10 (m, 2 H, ArH), 7.62 (t, $J$ = 7.6 Hz, 1 H, ArH), 7.49 (t, $J$ = 7.6 Hz, 2 H, ArH), 0.33 (s, 9 H, 3×CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 177.6, 136.4, 134.1, 129.6, 128.5, 100.8, 100.5, -0.7.

(12) Synthesis of 1-(3-chlorophenyl)-2-heptyn-1-one (2l) (zd-3-151, zd-3-81)

Following **Typical Procedure 1**, the reaction of Cu(NO$_3$)$_2$•3H$_2$O (24.4 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and 1l (222.8 mg, 1.0 mmol) in MeCN (4 mL) afforded 2l (213.9 mg, 97%) as an oil [eluent: petroleum ether/ethyl ether = 30/1]; $^1$H NMR (400 MHz, CDCl$_3$): δ = 8.10 (t, $J$ = 1.8 Hz, 1 H, ArH), 8.02 (d, $J$ = 7.6 Hz, 1 H, ArH), 7.57 (dt, $J_1$ = 7.6 Hz, $J_1$ = 1.2 Hz, 1 H, ArH), 7.43 (t, $J$ = 7.8 Hz, 1 H, ArH), 2.52 (t, $J$ = 7.0 Hz, 2 H, CH$_2$), 1.74-1.60 (m, 2 H, CH$_2$), 1.58-1.44 (m, 2 H, CH$_2$), 0.97 (t, $J$ = 7.4 Hz, 3 H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 176.6, 138.3, 134.7, 133.6, 129.8, 129.3, 127.5, 97.7, 79.2, 29.6, 22.0, 18.8, 13.4; MS (70 eV, EI) m/z (%): 222 (M$^+$ ($^{37}$Cl), 10.02), 220 (M$^+$ ($^{35}$Cl), 29.95), 139 (100); IR (neat): ν = 2959, 2933, 2871, 2204, 1645, 1571, 1424, 1286, 1245 cm$^{-1}$; HRMS calcd for C$_{13}$H$_{13}$O$^{35}$Cl [M$^+$]: 220.0655, found: 220.0657.
Following **Typical Procedure 1**, the reaction of Cu(NO$_3$)$_2$•3H$_2$O (24.0 mg, 0.1 mmol), TEMPO (15.9 mg, 0.1 mmol), and 11 (222.5 mg, 1.0 mmol) in DCE (4 mL) afforded 2l (216.2 mg, 98%) as an oil [eluent: petroleum ether/ethyl ether = 30/1]; $^1$H NMR (400 MHz, CDCl$_3$): δ = 8.10 (t, $J$ = 1.8 Hz, 1 H, ArH), 8.02 (d, $J$ = 7.6 Hz, 1 H, ArH), 7.60-7.53 (m, 1 H, ArH), 7.42 (t, $J$ = 7.8 Hz, 1 H, ArH), 2.52 (t, $J$ = 7.0 Hz, 2 H, CH$_2$), 1.74-1.60 (m, 2 H, CH$_2$), 1.58-1.44 (m, 2 H, CH$_2$), 0.98 (t, $J$ = 7.4 Hz, 3 H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 176.6, 138.4, 134.7, 133.6, 129.8, 129.3, 127.5, 97.7, 79.2, 29.7, 22.0, 18.8, 13.4.

(13) Synthesis of 1-(2-bromophenyl)-2-heptyn-1-one (2m) (zd-3-153, zd-3-73)

Following **Typical Procedure 1**, the reaction of Cu(NO$_3$)$_2$•3H$_2$O (24.4 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and 1m (266.2 mg, 1.0 mmol) in MeCN (4 mL) afforded 2m$^{13}$ (257.4 mg, 97%) as an oil [eluent: petroleum ether/ethyl ether = 30/1]; $^1$H NMR (400 MHz, CDCl$_3$): δ = 8.00 (d, $J$ = 7.6 Hz, 1 H, ArH), 7.67 (d, $J$ = 8.0 Hz, 1 H, ArH), 7.47-7.31 (m, 2 H, ArH), 2.48 (t, $J$ = 7.0 Hz, 2 H, CH$_2$), 1.70-1.56 (m, 2 H, CH$_2$), 1.55-1.41 (m, 2 H, CH$_2$), 0.95 (t, $J$ = 7.4 Hz, 3 H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 177.5, 137.4, 134.8, 133.0, 132.7, 127.2, 120.9, 98.0, 80.6, 29.5, 22.0, 18.9, 13.4; MS (70 eV, EI) m/z (%): 266 (M$^+$ (81Br), 9.56), 264 (M$^+$ (79 Br), 9.29), 185 (100); IR (neat): ν = 2187, 1648, 1580, 1474, 1386, 1262, 1063, 1008 cm$^{-1}$. 

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**Note:** The chemical structures and reaction equations are not fully visible, but the text describes the reactions and results clearly. The mention of m/z values and IR data indicates the use of mass spectrometry and infrared spectroscopy, respectively, for analysis. The reactions follow a typical procedure involving copper(II) nitrate, TEMPO, and an alkene in a solvent like DCE or MeCN, with oxygen or a balloon used for the reaction conditions. The products are isolated as oils with specified purities and characterised by NMR and mass spectrometry. The reported yields are high, indicating efficient reactions. The use of bromo-substituted substrates indicates a synthetic approach to functionalised alkenes, which are valuable in organic chemistry for further derivatisation.
Following Typical Procedure 1, the reaction of Cu(NO$_3$)$_2$·3H$_2$O (24.4 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and 1m (267.2 mg, 1.0 mmol) in DCE (4 mL) afforded 2m$^{[13]}$ (260.6 mg, 98%) as an oil [eluent: petroleum ether/ethyl ether = 30/1]; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.00 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.6 Hz, 1 H, ArH), 7.67 (d, $J$ = 8.0 Hz, 1 H, ArH), 7.42 (td, $J_1$ = 7.2 Hz, $J_2$ = 1.2 Hz, 1 H, ArH), 7.35 (td, $J_1$ = 7.6 Hz, $J_2$ = 1.6 Hz, 1 H, ArH), 2.48 (t, $J$ = 7.0 Hz, 2 H, CH$_2$), 1.70-1.56 (m, 2 H, CH$_2$), 1.55-1.41 (m, 2 H, CH$_2$), 0.95 (t, $J$ = 7.2 Hz, 3 H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 177.5, 137.3, 134.7, 133.0, 132.7, 127.1, 120.8, 97.9, 80.6, 29.5, 21.9, 18.9, 13.4.

(14) Synthesis of 1-(4-methoxyphenyl)-2-heptyn-1-one (2n) (zd-3-150, zd-3-72)

Following Typical Procedure 1, the reaction of Cu(NO$_3$)$_2$·3H$_2$O (24.4 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and 1n (222.8 mg, 1.0 mmol) in MeCN (4 mL) afforded 2n$^{[14]}$ (214.3 mg, 100%) as an oil [eluent: petroleum ether/ethyl ether = 20/1]; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.11 (d, $J$ = 8.4 Hz, 2 H, ArH), 6.95 (d, $J$ = 8.4 Hz, 2 H, ArH), 3.89 (s, 3 H, CH$_3$), 2.49 (t, $J$ = 7.2 Hz, 2 H, CH$_2$), 1.72-1.56 (m, 2 H, CH$_2$), 1.54-1.46 (m, 2 H, CH$_2$), 0.97 (t, $J$ = 7.2 Hz, 3 H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 176.8, 164.2, 131.8, 130.2, 113.6, 95.8, 79.5, 55.4, 29.8, 22.0, 18.7, 13.4.
Following **Typical Procedure 1**, the reaction of \( \text{Cu(NO}_3\text{)}_2 \cdot 3\text{H}_2\text{O} (24.4 \text{ mg}, 0.1 \text{ mmol}), \) TEMPO (16.0 mg, 0.1 mmol), and \( 1\text{n} (218.5 \text{ mg}, 1.0 \text{ mmol}) \) in DCE (4 mL) afforded \( 2\text{n}^{[14]} (209.6 \text{ mg}, 97\%) \) as an oil [eluent: petroleum ether/ethyl ether = 30/1 (300 mL) to petroleum ether/ethyl ether = 15/1]; \( ^1\text{H NMR} \) (400 MHz, CDCl\(_3\)): \( \delta = 8.11 \text{ (d, } J = 8.8 \text{ Hz, 2 H, ArH)}, 6.95 \text{ (d, } J = 8.8 \text{ Hz, 2 H, ArH)}, 3.89 \text{ (s, 3 H, CH}_3\text{), 2.49 \text{ (t, } J = 7.6 \text{ Hz, 2 H, CH}_2\text{)}, 1.72-1.58 \text{ (m, 2 H, CH}_2\text{)}, 1.56-1.44 \text{ (m, 2 H, CH}_2\text{)}, 0.96 \text{ (t, } J = 7.4 \text{ Hz, 3 H, CH}_3\text{)}; \( ^{13}\text{C NMR} \) (100 MHz, CDCl\(_3\)): \( \delta = 176.9, 164.2, 131.8, 130.2, 113.6, 95.8, 79.5, 55.4, 29.8, 22.0, 18.7, 13.4. \)

(15) **Synthesis of 1-((4-methoxycarbonylphenyl)-2-heptyn-1-one (2\text{o}) (zd-4-15)**

Following **Typical Procedure 1**, the reaction of \( \text{Cu(NO}_3\text{)}_2 \cdot 3\text{H}_2\text{O} (24.2 \text{ mg}, 0.1 \text{ mmol}), \) TEMPO (15.9 mg, 0.1 mmol), and \( 1\text{o} (246.3 \text{ mg}, 1.0 \text{ mmol}) \) in MeCN (4 mL) afforded \( 2\text{o} (243.0 \text{ mg}, 99\%) \) as an oil [eluent: petroleum ether/ethyl ether = 20/1]; \( ^1\text{H NMR} \) (400 MHz, CDCl\(_3\)): \( \delta = 8.19 \text{ (d, } J = 8.8 \text{ Hz, 2 H, ArH)}, 8.13 \text{ (d, } J = 8.8 \text{ Hz, 2 H, ArH)}, 3.96 \text{ (s, 3 H, CH}_3\text{), 2.53 \text{ (t, } J = 7.2 \text{ Hz, 2 H, CH}_2\text{)}, 1.73-1.62 \text{ (m, 2 H, CH}_2\text{), 1.58-1.45 \text{ (m, 2 H, CH}_2\text{)}, 0.98 \text{ (t, } J = 7.4 \text{ Hz, 3 H, CH}_3\text{)}; \( ^{13}\text{C NMR} \) (100 MHz, CDCl\(_3\)): \( \delta = 177.1, 165.9, 139.8, 134.3, 129.5, 129.2, 97.9, 79.4, 52.3, 29.6, 21.9, 18.8, 13.3; \) \( \text{MS (70 eV, EI) } m/z \%: 244 (M^+, 14.91), 202 (100)); \) \( \text{IR (neat): } \nu = 2956, 2933, 2872, 2237, 2198, 1724, 1646, 1435, 1407, 1276, 1259, 1244, 1116, 1102, 1017 \text{ cm}^{-1}; \) \( \text{HRMS calcd. for } \text{C}_{15}\text{H}_{16}\text{O}_3 (\text{M}^+): 244.1099; \) Found: 244.1099.
(16) Synthesis of 1-(2-hydroxyphenyl)-3-phenyl-2-propyn-1-one (2p) (zd-3-67)

Following Typical Procedure 1, the reaction of Cu(NO$_3$)$_2$•3H$_2$O (24.2 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and 1p (224.2 mg, 1.0 mmol) in DCE (4 mL) afforded 2p$^{[15]}$ (180.1 mg, 81%) as a yellow solid [eluent: petroleum ether/ethyl ether = 60/1] : M.p. 64.0-65.6 ºC (petroleum ether/ethyl acetate) (Lit$^{[14]}$ m.p.: 61-63 ºC); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 11.75 (s, 1 H, OH), 8.13 (d, $J$ = 8.4 Hz, 1 H, ArH), 7.76-7.64 (m, 2 H, ArH), 7.58-7.38 (m, 4 H, ArH), 7.00 (t, $J$ = 8.0 Hz, 2 H, ArH); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 182.2, 162.7, 137.1, 133.1, 133.0, 131.1, 128.7, 120.7, 119.6, 119.4, 118.1, 96.0, 85.6.

(17) Synthesis of 1-(3-cyanophenyl)-2-heptyn-1-one (2q) (zd-4-14)

Following Typical Procedure 1, the reaction of Cu(NO$_3$)$_2$•3H$_2$O (24.1 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and 1q (213.0 mg, 1.0 mmol) in MeCN (4 mL) afforded 2q (194.8 mg, 92%) as an oil [eluent: petroleum ether/ethyl ether = 20/1]; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.42 (s, 1 H, ArH), 8.34 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.2 Hz, 1 H, ArH), 7.87 (d, $J$ = 7.6 Hz, 1 H, ArH), 7.63 (t, $J$ = 7.8 Hz, 1 H, ArH), 2.55 (t, $J$ = 7.0 Hz, 2 H, CH$_2$), 1.75-1.63 (m, 2 H, CH$_2$), 1.62-1.45 (m, 2 H, CH$_2$), 0.98 (t, $J$ = 7.2 Hz, 3 H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 175.6, 137.4, 136.5, 133.1, 132.9, 129.5, 117.7, 112.9, 98.9, 78.8, 29.5, 21.9, 18.8, 13.3; MS (70 eV, EI) m/z (%): 211 (M$^+$, 7.31), 169 (100); IR (neat): $\nu$ = 2959, 2933, 2872, 2219, 2200, 1647, 1598, 1579,
1465, 1427, 1292, 1265, 1180 cm\(^{-1}\); HRMS calcd. for C\(_{14}H_{13}NO\) (M\(^+\)): 211.0997; Found: 211.0993.

(18) Synthesis of 1-(4-nitrophenyl)-2-heptyn-1-one (2r) (zd-4-10)

![Chemical reaction diagram]

Following Typical Procedure 1, the reaction of Cu(NO\(_3\))\(_2\)•3H\(_2\)O (24.4 mg, 0.1 mmol), TEMPO (15.7 mg, 0.1 mmol), and 1r (233.3 mg, 1.0 mmol) in MeCN (4 mL) afforded 2r\(^{[16]}\) (223.7 mg, 97%) as an oil [eluent: petroleum ether/ethyl ether = 40/1]; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.33\) (d, \(J = 9.2\) Hz, 2 H, ArH), 8.29 (d, \(J = 9.2\) Hz, 2 H, ArH), 2.55 (t, \(J = 7.0\) Hz, 2 H, CH\(_2\)), 1.73-1.64 (m, 2 H, CH\(_2\)), 0.98 (t, \(J = 7.2\) Hz, 3 H, CH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 175.8, 150.6, 140.9, 130.2, 123.5, 99.3, 79.2, 29.5, 21.9, 18.8, 13.3\); MS (70 eV, EI) \(m/z\) (%): 231 (M\(^+\), 4.21), 189 (100); IR (neat): \(\nu = 2959, 2934, 2871, 2237, 2199, 1650, 1602, 1524, 1343, 1320, 1257, 1104\) cm\(^{-1}\).

(19) Synthesis of 1-(2-furanyl)-2-heptyn-1-one (2s) (zd-3-152, zd-3-90)

![Chemical reaction diagram]

Following Typical Procedure 1, the reaction of Cu(NO\(_3\))\(_2\)•3H\(_2\)O (24.2 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and 1s (177.8 mg, 1.0 mmol) in MeCN (4 mL) afforded 2s\(^{[17]}\) (162.5 mg, 92%) as an oil [eluent: petroleum ether/ethyl ether = 10/1]; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.65\) (s, 1 H, H from furyl), 7.32 (d, \(J = 3.2\) Hz, 1 H, H from furyl), 6.56 (dd, \(J_1 = 3.6\) Hz, \(J_2 = 1.6\) Hz, 1 H, H from furyl), 2.47 (t, \(J = 7.0\) Hz, 2 H, CH\(_2\)), 1.74-1.58 (m, 2 H, CH\(_2\)), 1.56-1.42 (m, 2 H, CH\(_2\)), 0.96 (t, \(J = 7.2\) Hz,
$^3$H, CH$_3$; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 164.9, 153.1, 147.6, 120.6, 112.4, 95.4, 78.8, 29.5, 21.8, 18.6, 13.3; MS (70 eV, El) $m/z$: 176 (M$^+$, 27.69), 95 (100); IR (neat): $\nu$ = 2957, 2933, 2868, 2251, 2207, 1631, 1562, 1460, 1390, 1294, 1168, 1123, 1014 cm$^{-1}$.

Following Typical procedure 1, the reaction of Cu(NO$_3$)$_2$•3H$_2$O (24.0 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and 1s (178.5 mg, 1.0 mmol) in DCE (4 mL) afforded 2s$^{[17]}$ (168.0 mg, 95%) as an oil [eluent: petroleum ether/ethyl ether = 15/1];

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.64 (s, 1 H, H from furyl), 7.31 (d, $J$ = 3.2 Hz, 1 H, H from furyl), 6.56 (t, $J$ = 1.6 Hz, 1 H, H from furyl), 2.47 (t, $J$ = 7.0 Hz, 2 H, CH$_2$), 1.70-1.56 (m, 2 H, CH$_2$), 1.56-1.43 (m, 2 H, CH$_2$), 0.96 (t, $J$ = 7.2 Hz, 3 H, CH$_3$);

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 164.4, 152.7, 147.2, 120.1, 111.9, 94.9, 78.4, 29.1, 21.4, 18.2, 12.9.

(20) Synthesis of 6-undecyn-5-one (2t) (zd-3-157, zd-3-83)

Following Typical Procedure 1, the reaction of Cu(NO$_3$)$_2$•3H$_2$O (23.8 mg, 0.1 mmol), TEMPO (15.9 mg, 0.1 mmol), and 1t (169.1 mg, 1.0 mmol) in MeCN (4 mL) afforded 2t$^{[14]}$ (160.1 mg, 96%) as an oil [eluent: petroleum ether/ethyl ether = 60/1];

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.53 (t, $J$ = 7.4 Hz, 2 H, CH$_2$), 2.37 (t, $J$ = 7.0 Hz, 2 H, CH$_2$), 1.70-1.50 (m, 4 H, CH$_2$CH$_2$), 1.50-1.25 (m, 4 H, CH$_2$CH$_2$), 1.00-0.86 (m, 6 H, 2×CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 188.3, 94.0, 80.7, 45.1, 29.6, 26.1, 22.0, 21.8, 18.4, 13.6, 13.3.
Following **Typical Procedure 1**, the reaction of Cu(NO$_3$)$_2$•3H$_2$O (24.0 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and 1t (168.6 mg, 1.0 mmol) in DCE (4 mL) afforded 2t\textsuperscript{[14]} (158.8 mg, 95%) as an oil [eluent: petroleum ether/ethyl ether = 40/1];

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.53 (t, $J$ = 7.4 Hz, 2 H, CH$_2$), 2.37 (t, $J$ = 7.0 Hz, 2 H, CH$_2$), 1.70-1.50 (m, 4 H, CH$_2$-CH$_2$), 1.50-1.17 (m, 4 H, CH$_2$-CH$_2$), 0.98-0.88 (m, 6 H, 2×CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 188.4, 94.1, 80.8, 45.2, 29.7, 26.1, 22.0, 21.9, 18.5, 13.7, 13.4.

(21) Synthesis of 1-phenyl-1-heptyn-3-one (2u) (zd-3-146, zd-3-65)

Following **Typical Procedure 1**, the reaction of Cu(NO$_3$)$_2$•3H$_2$O (24.0 mg, 0.1 mmol), TEMPO (15.9 mg, 0.1 mmol), and 1u (188.4 mg, 1.0 mmol) in MeCN (4 mL) afforded 2u\textsuperscript{[14]} (173.2 mg, 93%) as an oil [eluent: petroleum ether/ethyl ether = 30/1];

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.58 (d, $J$ = 7.2 Hz, 2 H, ArH), 7.50-7.34 (m, 3 H, ArH), 2.67 (t, $J$ = 7.2 Hz, 2 H, CH$_2$), 1.80-1.66 (m, 2 H, CH$_2$), 1.48-1.32 (m, 2 H, CH$_2$), 0.95 (t, $J$ = 7.4 Hz, 3 H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 188.2, 132.9, 130.5, 128.5, 120.0, 90.4, 87.8, 45.1, 26.1, 22.1, 13.7; MS (70 eV, EI) $m/z$ (%): 186 (M$^+$, 1.30), 129 (100); IR (neat): $\nu$ = 2958, 2932, 2872, 2200, 1666, 1489, 1272, 1125, 1067 cm$^{-1}$. 
Following **Typical Procedure 1**, the reaction of Cu(NO$_3$)$_2$•3H$_2$O (24.2 mg, 0.1 mmol), TEMPO (16.2 mg, 0.1 mmol), and 1u (188.4 mg, 1.0 mmol) in DCE (4 mL) afforded 2u$^{[14]}$ (179.8 mg, 96%) as an oil [eluent: petroleum ether/ethyl ether = 30/1];

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.61-7.54$ (m, 2 H, ArH), 7.49-7.35 (m, 3 H, ArH),
2.67 (t, $J = 7.4$ Hz, 2 H, CH$_2$), 1.80-1.66 (m, 2 H, CH$_2$), 1.47-1.34 (m, 2 H, CH$_2$), 0.95 (t, $J = 7.2$ Hz, 3 H, CH$_3$);

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 187.9$, 132.8, 130.4, 128.4, 119.9, 90.3, 87.7, 45.0, 26.0, 21.9, 13.6.

(22) Synthesis of 1-cyclohexyl-3-phenyl-2-propyn-1-one (2v) (zd-3-149, zd-3-63)

Following **Typical procedure 1**, the reaction of Cu(NO$_3$)$_2$•3H$_2$O (24.1 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and 1v (214.1 mg, 1.0 mmol) in MeCN (4 mL) afforded 2v$^{[18]}$ (200.7 mg, 95%) as an oil [eluent: petroleum ether/ethyl ether = 30/1];

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.59$ (d, $J = 7.2$ Hz, 2 H, ArH), 7.50-7.34 (m, 3 H, ArH),
2.57-2.44 (m, 1 H, CH), 2.06 (d, $J = 11.2$ Hz, 2 H, CH$_2$), 1.82 (dd, $J_1 = 9.2$ Hz, $J_2 = 3.6$ Hz, 2 H, CH$_2$), 1.69 (d, $J = 12.0$ Hz, 1 H, one proton of CH$_2$), 1.50 (dd, $J_1 = 23.2$ Hz, $J_2 = 11.4$ Hz, 2 H, CH$_2$), 1.42-1.16 (m, 3 H, 3 H from Cy);

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 191.3$, 132.9, 130.5, 128.5, 120.1, 91.2, 87.1, 52.2, 28.2, 25.7, 25.3;

MS (70 eV, EI) $m/z$ (%): 212 (M$^+$, 4.97), 129 (100); IR (neat): $\nu = 2929$, 2853, 2196, 1660, 1488, 1445, 1262, 1142, 1089, 1069 cm$^{-1}$. 

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Following **Typical procedure 1**, the reaction of Cu(NO$_3$)$_2$•3H$_2$O (24.0 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and 1v (214.2 mg, 1.0 mmol) in DCE (4 mL) afforded 2v$^{[18]}$ (211.4 mg, 100%) as an oil [eluent: petroleum ether/ethyl ether = 30/1]; 
$^1$H NMR (400 MHz, CDCl$_3$): δ = 7.58 (d, $J = 7.2$ Hz, 2 H, ArH), 7.50-7.34 (m, 3 H, ArH), 2.57-2.44 (m, 1 H, CH), 2.06 (d, $J = 10.8$ Hz, 2 H, CH$_2$), 1.89-1.76 (m, 2 H, CH$_2$), 1.74-1.16 (m, 6 H, CH$_2$CH$_2$CH$_2$); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 191.3, 132.9, 130.4, 128.5, 120.1, 91.2, 87.1, 52.2, 28.2, 25.7, 25.3.

(23) Synthesis of 1-(1-naphthalenyl)-3-phenyl-2-propyn-1-one (2w) (zd-3-154, zd-3-85)

Following **Typical Procedure 1**, the reaction of Cu(NO$_3$)$_2$•3H$_2$O (24.0 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and 1w (258.3 mg, 1.0 mmol) in MeCN (4 mL) afforded 2w$^{[19]}$ (244.7 mg, 95%) as a white solid [eluent: petroleum ether/ethyl ether = 60/1]; M.p. 93.0-94.7 °C (petroleum ether/ethyl acetate) (Lit$^{[20]}$ m.p.: 92–94 °C); $^1$H NMR (400 MHz, CDCl$_3$): δ = 9.24 (d, $J = 8.8$ Hz, 1 H, ArH), 8.65 (d, $J = 6.8$ Hz, 1 H, ArH), 8.10 (d, $J = 8.0$ Hz, 1 H, ArH), 7.92 (d, $J = 8.0$ Hz, 1 H, ArH), 7.80-7.38 (m, 8 H, ArH); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 179.6, 135.0, 134.5, 133.8, 132.9, 130.6, 130.5, 128.9, 128.6, 128.5, 126.7, 125.9, 124.4, 120.2, 91.6, 88.4; MS (70 eV, EI) m/z (%): 257 (M$^+$+1, 16.50), 256 (M$^+$, 86.95), 255 (100); IR (neat): ν = 2192, 1629, 1589, 1570, 1508, 1285, 1176, 1100, 1072 cm$^{-1}$.
Following Typical Procedure 1, the reaction of Cu(NO\textsubscript{3})\textsubscript{2}•3H\textsubscript{2}O (24.3 mg, 0.1 mmol), TEMPO (15.9 mg, 0.1 mmol), and \textit{1w} (258.8 mg, 1.0 mmol) in DCE (4 mL) afforded \textit{2w}\textsuperscript{[19]} (243.2 mg, 95\%) as a white solid [eluent: petroleum ether/ethyl ether = 40/1]; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ = 9.24 (d, J = 8.8 Hz, 1 H, ArH), 8.65 (d, J = 7.2 Hz, 1 H, ArH), 8.09 (d, J = 8.4 Hz, 1 H, ArH), 7.91 (d, J = 8.0 Hz, 1 H, ArH), 7.76-7.38 (m, 8 H, ArH); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ = 179.6, 135.0, 134.5, 133.8, 132.85, 132.82, 130.6, 130.5, 128.9, 128.6, 128.5, 126.7, 125.9, 124.4, 120.2, 91.6, 88.4.

(24) Synthesis of 3-(4-bromophenyl)-2-propynal (\textit{2x}) (zd-3-155, zd-3-66)

Following Typical Procedure 1, the reaction of Cu(NO\textsubscript{3})\textsubscript{2}•3H\textsubscript{2}O (23.7 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and \textit{1x} (211.0 mg, 1.0 mmol) in MeCN (4 mL) afforded \textit{2x}\textsuperscript{[21]} (159.0 mg, 76\%) as a red solid [eluent: petroleum ether/ethyl ether = 60/1]; M.p. 92.0-93.4 °C (petroleum ether/ethyl acetate) (Lit\textsuperscript{[22]} m.p.: 95–97 °C); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ = 9.42 (s, 1 H, CHO), 7.56 (d, J = 8.8 Hz, 2 H, ArH), 7.47 (d, J = 8.0 Hz, 2 H, ArH); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ = 176.5, 134.4, 132.1, 126.2, 118.3, 93.5, 89.0; MS (70 eV, EI) m/z (%): 210 (M\textsuperscript{+} (\textsuperscript{81}Br), 86.41), 208 (M\textsuperscript{+} (\textsuperscript{79}Br), 86.47), 101 (100); IR (neat): ν = 2949, 2866, 2203, 1649, 1578, 1460, 1427, 1284, 1238, 1030 cm\textsuperscript{-1}. 

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Following Typical Procedure 1, the reaction of Cu(NO$_3$)$_2$•3H$_2$O (24.2 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and 1x (211.2 mg, 1.0 mmol) in DCE (4 mL) afforded 2x$^{[21]}$ (135.8 mg, 65%) as a red solid [eluent: petroleum ether/ethyl ether = 60/1]; $^1$H NMR (400 MHz, CDCl$_3$): δ = 9.42 (s, 1 H, CHO), 7.56 (d, J = 8.0 Hz, 2 H, ArH), 7.46 (d, J = 8.0 Hz, 2 H, ArH); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 176.5, 134.5, 132.1, 126.2, 118.3, 93.5, 89.0.

(25) Synthesis of (Z)-4-(benzyloxy)-2-butenal (4a) (zd-3-1)

Following Typical Procedure 1, the reaction of Cu(NO$_3$)$_2$•3H$_2$O (24.2 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and 3a (187.6 mg, 1.0 mmol) in DCE (10 mL) afforded 4a$^{[23]}$ (164.4 mg, 93%, Z:E > 99:1) as an oil [eluent: petroleum ether/ethyl acetate = 20/1] [before separation afforded a crude mixture of Z-4a and E-4a (Z:E = 95:5), as determined by $^1$H NMR analysis]; $^1$H NMR (400 MHz, CDCl$_3$): 10.05 (d, J = 6.8 Hz, 1 H, CHO), 7.42-7.28 (m, 5 H, ArH), 6.64 (dt, J$_1$ = 11.2 Hz, J$_2$ = 5.6 Hz, 1 H, CH=), 6.07 (ddt, J$_1$ = 11.2 Hz, J$_2$ = 6.4 Hz, J$_3$ = 2.0 Hz, 1 H, CH=), 4.59 (s, 2 H, ArCH$_2$), 4.53 (dd, J$_1$ = 5.6 Hz, J$_2$ = 2.0 Hz, 2 H, OCH$_2$); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 191.4, 147.5, 137.2, 129.6, 128.5, 127.9, 127.7, 73.0, 66.9.

(26) Synthesis of (E)-3,7-dimethyl-2,6-octadienal (4b) (zd-3-5)
Following **Typical Procedure 1**, the reaction of Cu(NO₃)₂•3H₂O (24.4 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and 3b (155.4 mg, 1.0 mmol) in DCE (10 mL) afforded 4b \(^{[23]}\) (126.3 mg, 83%, E:Z = 97:3) as an oil [eluent: petroleum ether/ethyl acetate = 50/1 (400 mL) to petroleum ether/ethyl acetate = 20/1 (300 mL)] [before separation afforded a crude mixture of E-4b and Z-4b (E:Z = 96:4), as determined by \(^1\)H NMR analysis]; \(^1\)H NMR (400 MHz, CDCl₃): \(\delta = 10.00\) (d, \(J = 8.0\) Hz, 1 H, CHO), 5.88 (d, \(J = 8.0\) Hz, 1 H, CH=), 5.08 (d, \(J = 6.4\) Hz, 1 H, CH=), 2.30-2.16 (m, 4 H, \(2\times\)CH₂), 2.17 (s, 3 H, CH₃), 1.69 (s, 3 H, CH₃), 1.61 (s, 3 H, CH₃); \(^{13}\)C NMR (100 MHz, CDCl₃): \(\delta = 191.1, 163.6, 132.7, 127.2, 122.3, 40.4, 25.5, 25.4, 17.5, 17.3.\)

(27) Synthesis of (Z)-3,7-dimethyl-2,6-octadienal (4c) (zd-4-82)

Following **Typical Procedure 1**, the reaction of Cu(NO₃)₂•3H₂O (24.6 mg, 0.1 mmol), TEMPO (16.1 mg, 0.1 mmol), and 3c (153.6 mg, 1.0 mmol) in DCE (10 mL) afforded 4c \(^{[23]}\) (118.1 mg, 80%, Z:E = 94:6) as an oil [eluent: petroleum ether/ethyl ether = 15:1] [before separation afforded a crude mixture of Z-4c and E-4c (Z:E = 93:7), as determined by \(^1\)H NMR analysis]; \(^1\)H NMR (400 MHz, CDCl₃): \(\delta = 9.90\) (d, \(J = 8.4\) Hz, 1 H, CHO), 5.88 (d, \(J = 8.4\) Hz, 1 H, CH=), 5.10 (t, \(J = 7.0\) Hz, 1 H, CH=), 2.59 (t, \(J = 7.6\) Hz, 2 H, CH₂), 2.24 (dd, \(J_1 = 14.6\) Hz, \(J_2 = 7.4\) Hz, 2 H, CH₂), 1.99 (s, 3 H, CH₃), 1.69 (s, 3 H, CH₃), 1.61 (s, 3 H, CH₃); \(^{13}\)C NMR (100 MHz, CDCl₃): \(\delta = 190.2, 163.3, 133.1, 128.1, 121.8, 32.1, 26.5, 25.1, 24.5, 17.2; the following signals are discernible for E-4c: \(\delta = 190.8, 132.4, 126.9, 122.1, 40.1, 25.2, 17.1.\)
(28) Synthesis of (E)-undec-2-enal (4d) (zd-2-200)

\[
\begin{align*}
\text{Cu(NO}_3\text{)}_2\cdot3\text{H}_2\text{O (10 mol\%)} & \quad \text{TEMPO (10 mol\%)} \\
\text{n-C}_8\text{H}_{17}-\text{OH} & \quad \text{DCE, O}_2\text{ balloon} \\
3\text{d} (E:Z > 99:1) & \quad 25^\circ\text{C}, 10 \text{ h} \\
\text{n-C}_8\text{H}_{17}-\text{O} & \quad \text{before separation: } E:Z > 99:1 \\
\end{align*}
\]

Following Typical Procedure 1, the reaction of Cu(NO₃)₂•3H₂O (24.2 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and 3d (177.3 mg, 1.0 mmol) in DCE (4 mL) afforded 4d[23] (161.3 mg, 96%, E:Z > 99:1) as an oil [eluent: petroleum ether/ethyl acetate = 50:1] [before separation afforded a crude mixture of E-4d and Z-4d (E:Z > 99:1), as determined by ¹H NMR analysis]; ¹H NMR (400 MHz, CDCl₃): δ = 9.51 (d, J = 8.0 Hz, 1 H, CHO), 6.86 (dt, J₁ = 15.8 Hz, J₂ = 7.0 Hz, 1 H, CH=), 6.18-6.07 (m, 1 H, CH=), 2.38-2.27 (m, 2 H, CH₂), 1.56-1.44 (m, 2 H, CH₂), 1.40-1.20 (m, 10 H, 5×CH₂), 0.89 (t, J = 6.8 Hz, 3 H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 194.0, 158.9, 132.9, 32.6, 31.7, 29.2, 29.06, 29.04, 27.7, 22.5, 14.0.

(29) Synthesis of (E)-tridec-4-en-3-one (4e) (zd-4-80)

\[
\begin{align*}
\text{Cu(NO}_3\text{)}_2\cdot3\text{H}_2\text{O (10 mol\%)} & \quad \text{TEMPO (10 mol\%)} \\
\text{n-C}_8\text{H}_{17}-\text{OH} & \quad \text{DCE, O}_2\text{ balloon} \\
3\text{e} (E:Z > 99:1) & \quad 25^\circ\text{C}, 18 \text{ h} \\
\text{n-C}_8\text{H}_{17}-\text{O} & \quad \text{before separation: } E:Z > 99:1 \\
\end{align*}
\]

Following Typical Procedure 1, the reaction of Cu(NO₃)₂•3H₂O (24.2 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and 3e (199.4 mg, 1.0 mmol) in DCE (4 mL) afforded 4e (178.9 mg, 91%) as an oil [eluent: petroleum ether/ethyl acetate = 100:1] [before separation afforded a crude mixture of E-4e and Z-4e (E:Z > 99:1), as determined by ¹H NMR analysis]; ¹H NMR (400 MHz, CDCl₃): δ = 6.83 (dt, J₁ = 16.0 Hz, J₂ = 7.0 Hz, 1 H, =CH), 6.09 (d, J = 16.0 Hz, 1 H, =CH), 2.56 (q, J = 7.4 Hz, 2 H, CH₂), 2.20 (q, J = 7.2 Hz, 2 H, CH₂), 1.56-1.18 (m, 12 H, 6×CH₂), 1.10 (t, J = 7.4 Hz, 3 H, CH₃), 0.88 (t, J = 6.6 Hz, 3 H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 201.0, 147.0, 129.9, 33.0, 32.3, 31.7, 29.2, 29.0, 28.0, 22.5, 13.9, 8.0; MS (70 eV, EI) m/z (%): 196 (M⁺, 2.27), 167 (100); IR (neat): ν = 2925, 2855, 1699, 1675, 1630,
1460, 1355, 1200, 1116 cm\(^{-1}\); HRMS calcd. for C\(_{13}\)H\(_{24}\)O (M\(^+\)): 196.1827; Found: 196.1830.

(30) Synthesis of 4-iodobenzaldehyde (6a) (zd-3-35)

\[
\text{Cu(NO}_3\text{)}_2\cdot3\text{H}_2\text{O (10 mol\%)} \quad \text{TEMPO (10 mol\%)} \quad \text{DCE, O}_2 \text{ balloon} \quad 25 \degree C, 12.2 \text{ h} \quad 6a, 84\%
\]

A dry Schlenk tube was degassed to remove the air inside completely, and refilled with O\(_2\) by a balloon of O\(_2\) for three times. Then Cu(NO\(_3\))\(_2\)•3H\(_2\)O (24.1 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and a solution of 5a (241.5 mg, 1.0 mmol) in DCE (4 mL) were added sequentially. The resulting mixture was stirred at 25 °C for 12.2 h as monitored by TLC (petroleum ether/ethyl acetate = 5/1), filtered through a short column of silica gel [eluent: ethyl ether (75 mL)], concentrated under reduced pressure [the yield of acid was determined by \(^1\)H NMR analysis of the crude products using DMSO-d\(_6\) as the internal standard (6\%)]. The residue was washed with H\(_2\)O (10 mL). After extraction with ethyl acetate (10 mL×3), the organic layer was dried over anhydrous Na\(_2\)SO\(_4\). After filtration and concentration under reduced pressure, the crude product was purified by column chromatography on silica gel to afford 6a\(^{[24]}\) (194.5 mg, 84%) as a white solid: \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 9.96 \text{ (s, 1 H, CHO)}, 7.92 \text{ (d, } J = 8.0 \text{ Hz, 2 H, ArH)}, 7.60 \text{ (d, } J = 8.0 \text{ Hz, 2 H, ArH})\); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 191.4, 138.4, 135.5, 130.8, 102.8\).

(31) Synthesis of 3-methoxyphenyl ethyl ketone (6b) (zd-4-84)

\[
\text{Cu(NO}_3\text{)}_2\cdot3\text{H}_2\text{O (10 mol\%)} \quad \text{TEMPO (10 mol\%)} \quad \text{DCE, O}_2 \text{ balloon} \quad 25 \degree C, 18 \text{ h} \quad 6b, 98\%
\]

Following Typical Procedure 1, the reaction of Cu(NO\(_3\))\(_2\)•3H\(_2\)O (24.0 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and 5b (165.8 mg, 1.0 mmol) in DCE (4 mL)
afforded 6b\(^{25}\) (159.8 mg, 98%) as an oil [eluent: petroleum ether/ethyl ether = 20/1];

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.54 (d, J = 7.6 \text{ Hz}, 1 \text{ H, ArH}), 7.50 (s, 1 \text{ H, ArH}), 7.36 (t, J = 7.8 \text{ Hz}, 1 \text{ H, ArH}), 7.10 (dd, J\(_1\) = 8.4 \text{ Hz}, J\(_2\) = 2.4 \text{ Hz}, 1 \text{ H, ArH}), 3.86 (s, 3 \text{ H, CH}_3), 2.99 (q, J = 7.4 \text{ Hz}, 2 \text{ H, CH}_2), 1.22 (t, J = 7.2 \text{ Hz}, 3 \text{ H, CH}_3);\) \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 200.1, 159.3, 137.8, 129.0, 120.1, 118.7, 111.8, 54.9, 31.4, 7.7;\) MS (70 eV, EI) \(m/z\) (%): 165 (M\(^+\)+1, 3.73), 164 (M\(^+\), 35.35), 135 (100); IR (neat): \(\nu = 2976, 2938, 1686, 1582, 1485, 1461, 1429, 1286, 1254, 1197, 1171, 1044, 1020 \text{ cm}^{-1}\).

(32) Synthesis of 2-methoxybenzaldehyde (6c) (zd-4-133)

\[
\begin{align*}
\text{Cu(NO}_3\text{)}_2\cdot\text{H}_2\text{O (10 mol\%)} & & & & \text{TEMPO (10 mol\%)} \\
\text{DCE, O}_2\text{ balloon} & & & & 25^\circ\text{C, 22 h} \\
\text{5c} & & & & \text{6c, 86\%}
\end{align*}
\]

Following **Typical Procedure 1**, the reaction of Cu(NO\(_3\))\(_2\)•H\(_2\)O (24.1 mg, 0.1 mmol), TEMPO (16.2 mg, 0.1 mmol), and 5c (141.3 mg, 1.0 mmol) in DCE (4 mL) afforded 6c\(^{24}\) (117.6 mg, 86%) as an oil [eluent: petroleum ether/ethyl ether = 20/1]:

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 10.48 (s, 1 \text{ H, CHO}), 7.83 (d, J = 7.6 \text{ Hz}, 1 \text{ H, ArH}), 7.56 (d, J = 7.8 \text{ Hz}, 1 \text{ H, ArH}), 7.07-6.95 (m, 2 \text{ H, ArH}), 3.93 (s, 3 \text{ H, CH}_3);\) \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 189.4, 161.4, 135.6, 128.0, 124.4, 120.2, 111.3, 55.2.\)

(33) Synthesis of 1-hexadecanal (8a) (zd-4-153)

\[
\begin{align*}
\text{n-C}_{16}\text{H}_{33}\text{OH} & & & & \text{Cu(NO}_3\text{)}_2\cdot\text{H}_2\text{O (10 mol\%)} \\
& & & & \text{TEMPO (10 mol\%)} \\
\text{DCE, O}_2\text{ balloon} & & & & 25^\circ\text{C, 20.2 h} \\
\text{7a} & & & & \text{n-C}_{15}\text{H}_{31}\text{CHO} \\
& & & & \text{8a, 84\%} \\
\text{Recovery of 7a: 5\%}
\end{align*}
\]

Following **Typical Procedure 1**, the reaction of Cu(NO\(_3\))\(_2\)•H\(_2\)O (24.4 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and 7a (247.1 mg, 1.0 mmol) in DCE (4 mL) afforded 8a\(^{14}\) (202.4 mg, 84%) as a white solid [eluent: petroleum ether/ethyl ether = 60/1] [before separation afforded a crude mixture of 7a (Recovery: 5%) and 8a, as determined by \(^1\)H NMR analysis]; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 9.76 (t, J = 1.6 \text{ Hz}, 1 \text{ H, CHO})\).
Hz, 1 H, CHO), 2.42 (td, \( J_1 = 7.2 \) Hz, \( J_2 = 1.6 \) Hz, 2 H, CH\(_2\)), 1.66-1.58 (m, 2 H, CH\(_2\)), 1.36-1.20 (m, 24 H, 12\( \times \)CH\(_2\)), 0.88 (t, \( J = 6.8 \) Hz, 3 H, CH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 202.9, 43.9, 31.9, 29.65, 29.63, 29.55, 29.4, 29.3, 29.1, 22.7, 22.1, 14.1\).

(34) Synthesis of tetradecan-3-one (8b) (zd-4-62)

Following Typical Procedure 1, the reaction of Cu(NO\(_3\))\(_2\)•3H\(_2\)O (24.1 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and 7b (213.3 mg, 1.0 mmol) in DCE (4 mL) afforded 8b\(^{[26]}\) (188.3 mg, 89%) as a white solid [eluent: petroleum ether/ethyl ether = 60/1]; M.p. 32.6-33.5 \(^\circ\)C (petroleum ether/ethyl acetate) (Lit\(^{[27]}\) m.p.: 32–33 \(^\circ\)C); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 2.46-2.34 \) (m, 4 H, 2\( \times \)CH\(_2\)), 1.62-1.52 (m, 2 H, CH\(_2\)), 1.34-1.18 (m, 16 H, 8\( \times \)CH\(_2\)), 1.05 (t, \( J = 7.2 \) Hz, 3 H, CH\(_3\)), 0.88 (t, \( J = 6.8 \) Hz, 3 H, CH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 211.8, 42.3, 35.7, 31.8, 29.5, 29.4, 29.35, 29.25, 29.2, 23.9, 22.6, 14.0, 7.7\); MS (70 eV, EI) \( m/z \) (%): 213 (M\(^+\)+1, 1.00), 212 (M\(^+\), 2.03), 72 (100); IR (neat): \( \nu = 2960, 2916, 2872, 2849, 1709, 1702, 1471, 1463, 1455, 1374, 1231, 1131, 1114 \text{ cm}^{-1}\).

(35) Synthesis of 4-cyclohexylbutadienal (10a) (zd-4-93)

Following Typical Procedure 1, the reaction of Cu(NO\(_3\))\(_2\)•3H\(_2\)O (24.4 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and 9a (152.0 mg, 1.0 mmol) in DCE (4 mL) afforded 10a\(^{[28]}\) (128.2 mg, 85%) as an oil [eluent: petroleum ether/ethyl ether = 60/1 (petroleum ether: 30-60 \(^\circ\)C)]; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 9.47 \) (d, \( J = 7.2 \) Hz, 1 H), 5.89–5.81 (m, 1 H), 5.75 (t, \( J = 6.0 \) Hz, 1 H), 2.28-2.13 (m, 1 H), 1.92-1.56 (m, 5

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H), 1.40–1.08 (m, 5 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 218.5, 192.3, 102.0, 99.4, 36.6, 32.8, 32.7, 25.7.

(36) Synthesis of 2,3-tridecadienal (10b) (zd-4-96)

Following Typical Procedure 1, the reaction of Cu(NO$_3$)$_2$•3H$_2$O (24.0 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and 9b (198.1 mg, 1.0 mmol) in DCE (4 mL) afforded 10b$^{[14]}$ (141.8 mg, 72%) as an oil [eluent: petroleum ether/ethyl ether = 60/1]:

$^1$H NMR (400 MHz, CDCl$_3$): δ = 9.49 (d, $J$ = 7.2 Hz, 1 H), 5.85-5.71 (m, 2 H), 2.24-2.14 (m, 2 H), 1.54-1.42 (m, 2 H), 1.42-1.20 (m, 12 H, 6×CH$_2$), 0.88 (t, $J$ = 6.6 Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 219.1, 192.3, 98.6, 96.3, 31.8, 29.5, 29.25, 29.21, 28.9, 28.8, 27.4, 22.6, 14.0.
2. Large-Scale Reactions with \( \text{O}_2 \), Air/\( \text{O}_2 \), or Air.

(1) Synthesis of \( 2a \) with \( \text{O}_2 \) balloon (zd-4-35)

![Chemical reaction diagram]

\[ \begin{align*}
\text{n-Bu} & \equiv \text{CH} \equiv \text{OH} & \text{Cu(NO}_3\text{)}_2 \cdot 3\text{H}_2\text{O (2.5 mol\%)} \\
& \text{TEMPO (2.5 mol\%)} \\
\text{MeCN, O}_2 \text{ balloon} & \rightarrow \text{n-Bu} \equiv \text{CO}
\end{align*} \]

\( 1a \) (30 mmol)

A 250 mL flask was degassed to remove the air inside completely and refilled with \( \text{O}_2 \) by a balloon of \( \text{O}_2 \) for three times. Then \( \text{Cu(NO}_3\text{)}_2 \cdot 3\text{H}_2\text{O} \) (182.3 mg, 0.75 mmol), TEMPO (120.3 mg, 0.75 mmol), and \( 1a \) (5.6549 g, 30 mmol) in MeCN (30 mL) were added sequentially. The resulting mixture was stirred at 25 °C for 16 h as monitored by TLC (petroleum ether/ethyl acetate = 5/1), filtered through a short column of silica gel [eluent: ethyl ether (120 mL)], concentrated under reduced pressure, and purified by column chromatography on silica gel [eluent: petroleum ether/ethyl ether = 30/1] to afford \( 2a \) (5.4919 g, 98%) as an oil; \( ^1\text{H} \) NMR (400 MHz, CDCl\textsubscript{3}): \( \delta = 8.14 \) (d, \( J = 7.2 \) Hz, 2 H, ArH), 7.60 (t, \( J = 7.4 \) Hz, 1 H, ArH), 7.48 (t, \( J = 7.6 \) Hz, 2 H, ArH), 2.51 (t, \( J = 7.0 \) Hz, 2 H, CH\textsubscript{2}), 1.73-1.60 (m, 2 H, CH\textsubscript{2}), 1.57-1.45 (m, 2 H, CH\textsubscript{2}), 0.97 (t, \( J = 7.4 \) Hz, 3 H, CH\textsubscript{3}); \( ^{13}\text{C} \) NMR (100 MHz, CDCl\textsubscript{3}): \( \delta = 178.1, 136.8, 133.8, 129.4, 128.4, 96.8, 79.6, 29.7, 22.0, 18.8, 13.4. \)

(2) Synthesis of \( 2a \) with a bag of air with \( \text{O}_2 \) supplemented by a bag of pure \( \text{O}_2 \) (zd-4-106)

![Chemical reaction diagram]

\[ \begin{align*}
\text{n-Bu} & \equiv \text{CH} \equiv \text{OH} & \text{Cu(NO}_3\text{)}_2 \cdot 3\text{H}_2\text{O (10 mol\%)} \\
& \text{TEMPO (10 mol\%)} \\
\text{MeCN, 25 °C} & \rightarrow \text{n-Bu} \equiv \text{CO}
\end{align*} \]

\( 1a \) (40 mmol)

To a 250 mL three-neck flask were added \( \text{Cu(NO}_3\text{)}_2 \cdot 3\text{H}_2\text{O} \) (968.2 mg, 4.0 mmol), TEMPO (636.7 mg, 4.0 mmol), and \( 1a \) (7.5332 g, 40.0 mmol) in MeCN (80 mL) sequentially. Then a 42 L bag filled with air was connected to the flask. After stirring at 25 °C for 1.5 h, a 2 L bag of pure \( \text{O}_2 \) was connected to the flask to supplement \( \text{O}_2 \). The resulting mixture was stirred at 25 °C for 4.5 h as monitored by TLC (petroleum ether/ethyl acetate = 5/1) to afford \( 2a \) (5.4919 g, 98%) as an oil; \( ^1\text{H} \) NMR (400 MHz, CDCl\textsubscript{3}): \( \delta = 8.14 \) (d, \( J = 7.2 \) Hz, 2 H, ArH), 7.60 (t, \( J = 7.4 \) Hz, 1 H, ArH), 7.48 (t, \( J = 7.6 \) Hz, 2 H, ArH), 2.51 (t, \( J = 7.0 \) Hz, 2 H, CH\textsubscript{2}), 1.73-1.60 (m, 2 H, CH\textsubscript{2}), 1.57-1.45 (m, 2 H, CH\textsubscript{2}), 0.97 (t, \( J = 7.4 \) Hz, 3 H, CH\textsubscript{3}); \( ^{13}\text{C} \) NMR (100 MHz, CDCl\textsubscript{3}): \( \delta = 178.1, 136.8, 133.8, 129.4, 128.4, 96.8, 79.6, 29.7, 22.0, 18.8, 13.4. \)
ether/ethyl acetate = 5/1), filtrated through a short column of silica gel [eluent: ethyl ether (150 mL)], concentrated under reduced pressure, and purified by column chromatography on silica gel [eluent: petroleum ether/ethyl ether = 30/1] to afford 2a\(^{10}\) (7.4587 g, 100%) as an oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.14\) (d, \(J = 8.0\) Hz, 2 H, ArH), 7.60 (t, \(J = 7.4\) Hz, 1 H, ArH), 7.48 (t, \(J = 7.6\) Hz, 2 H, ArH), 2.51 (t, \(J = 7.2\) Hz, 2 H, CH\(_2\)), 1.74-1.62 (m, 2 H, CH\(_2\)), 1.58-1.46 (m, 2 H, CH\(_2\)), 0.97 (t, \(J = 7.4\) Hz, 3 H, CH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 178.1, 136.8, 133.8, 129.4, 128.4, 96.7, 79.6, 29.7, 21.9, 18.8, 13.4\).

(3) Synthesis of 2g with a slow flow of air (zd-4-116)

\[
\begin{align*}
\text{Cu(NO}_3\text{)}_2\cdot3\text{H}_2\text{O} & \quad \text{TEMPO} \\
\begin{array}{c}
\text{MeCN, air flow} \\
\text{25 °C, 46 h}
\end{array}
\end{align*}
\]

\(1g\) (40 mmol) \(\rightarrow\) \(2g\), 79%

To a 250 mL three-neck flask were added Cu(NO\(_3\))\(_2\)\(\cdot3\)H\(_2\)O (967.8 mg, 4.0 mmol), TEMPO (639.4 mg, 4.0 mmol), and 1g (5.5340 g, 40.0 mmol) in MeCN (120 mL) sequentially. A slow flow of air from air cylinder (high purity, 30 mL/min) was then connected to the flask. The reaction was stirred at 25 °C for 46 h as monitored by TLC (petroleum ether/ethyl acetate = 5/1), filtrated through a short column of silica gel [eluent: ethyl ether (150 mL)], concentrated under reduced pressure and purified by column chromatography on silica gel [eluent: petroleum ether/ethyl ether = 30/1] to afford 2g\(^{17}\) (4.3224 g, 79%) as a white solid; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.98\) (d, \(J_1 = 3.6\) Hz, 1 H, ArH), 7.75 (d, \(J = 4.8\) Hz, 1 H, ArH), 7.18 (t, \(J = 4.2\) Hz, 1 H, ArH), 3.36 (s, 1 H, \(\equiv\text{CH}\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 169.0, 144.0, 136.1, 135.9, 128.4, 79.8, 79.4\).
3. The reaction with 4-OH-TEMPO instead of TEMPO

(1) **Synthesis of 1-(4-methoxycarbonylphenyl)-2-propyn-1-one (2f) (zd-4-117)**

Following **Typical Procedure 1**, the reaction of Cu(NO$_3$)$_2$•3H$_2$O (24.4 mg, 0.1 mmol), 4-OH-TEMPO (18.0 mg, 0.1 mmol), and 1f (190.4 mg, 1.0 mmol) in MeCN (4 mL) afforded 2f$^{[7]}$ (166.3 mg, 88%) as a white solid [eluent: petroleum ether/ethyl acetate = 30/1]; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.22 (d, $J$ = 7.6 Hz, 2 H, ArH), 8.16 (d, $J$ = 7.6 Hz, 2 H, ArH), 3.97 (s, 3 H, CH$_3$), 3.52 (s, 1 H, ≡CH); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 176.6, 166.0, 139.0, 135.0, 129.8, 129.5, 81.7, 80.0, 52.5.

(2) **Synthesis of (E)-undec-2-enal (4d) (zd-4-121)**

Following **Typical Procedure 1**, the reaction of Cu(NO$_3$)$_2$•3H$_2$O (24.4 mg, 0.1 mmol), 4-OH-TEMPO (17.4 mg, 0.1 mmol), and 3d (177.6 mg, 1.0 mmol) in DCE (4 mL) afforded 4d$^{[23]}$ (166.2 mg, 99%, $E$:$Z$ >99:1) as an oil [eluent: petroleum ether/ethyl acetate = 60:1] [before separation afforded a crude mixture of E-4d and Z-4d ($E$:$Z$ > 99:1), as determined by $^1$H NMR analysis]; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 9.51 (d, $J$ = 7.6 Hz, 1 H, CHO), 6.85 (dt, $J_1$ = 15.6 Hz, $J$ = 7.0 Hz, 1 H, CH=), 6.18-6.07 (dd, $J_1$ = 15.6 Hz, $J$ = 8.0 Hz, 1 H, CH=), 2.34 (dd, $J_1$ = 14.4 Hz, $J$ = 7.2 Hz, 2 H, CH$_2$), 1.56-1.44 (m, 2 H, CH$_2$), 1.40-1.20 (m, 10 H, 5×CH$_2$), 0.89 (t, $J$ = 6.6 Hz, 3 H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 194.0, 158.9, 132.9, 32.6, 31.7, 29.2, 29.05, 29.03, 27.7, 22.5, 14.0.
(3) Synthesis of 4-iodobenzaldehyde (6a) (zd-4-118)

\[
\begin{align*}
\text{Cu(NO}_3\text{)}_2\cdot 3\text{H}_2\text{O} & \quad (10 \text{ mol\%}) \\
4\text{-OH-TEMPO} & \quad (10 \text{ mol\%}) \\
\text{DCE, O}_2 \text{ balloon} & \\
25 \degree \text{C, 7 h} & \quad 6a, 93\%
\end{align*}
\]

Following Typical Procedure 1, the reaction of Cu(NO$_3$)$_2$•3H$_2$O (24.4 mg, 0.1 mmol), 4-OH-TEMPO (17.9 mg, 0.1 mmol), and 5a (241.0 mg, 1.0 mmol) in DCE (4 mL) afforded 6a$^{[24]}$ (215.6 mg, 93\%) as a white solid [eluent: petroleum ether/ethyl acetate = 30/1]; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.96$ (s, 1 H, CHO), 7.92 (d, $J = 8.0$ Hz, 2 H, ArH), 7.59 (d, $J = 8.0$ Hz, 2 H, ArH); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 191.4, 138.4, 135.5, 130.8, 102.8$.

(4) Synthesis of 1-hexadecanal (8a) (zd-4-122)

\[
\begin{align*}
n-C_{16}H_{33}OH & \quad (10 \text{ mol\%}) \\
\text{Cu(NO}_3\text{)}_2\cdot 3\text{H}_2\text{O} & \\
4\text{-OH-TEMPO} & \quad (10 \text{ mol\%}) \\
\text{DCE, O}_2 \text{ balloon} & \\
25 \degree \text{C, 36 h} & \quad 8a, 80\%
\end{align*}
\]

Following Typical Procedure 1, the reaction of Cu(NO$_3$)$_2$•3H$_2$O (24.3 mg, 0.1 mmol), 4-OH-TEMPO (17.6 mg, 0.1 mmol), and 7a (247.1 mg, 1.0 mmol) in DCE (4 mL) afforded 8a$^{[14]}$ (192.7 mg, 80\%) as a white solid [eluent: petroleum ether/ethyl acetate = 60/1]; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.76$ (s, 1 H, CHO), 2.42 (t, $J = 7.2$ Hz, 2 H, CH$_2$), 1.63 (t, $J = 6.8$ Hz, 2 H, CH$_2$), 1.37-1.18 (m, 24 H, 12×CH$_2$), 0.88 (t, $J = 6.6$ Hz, 3 H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 202.8, 43.9, 31.9, 29.6, 29.65, 29.63, 29.55, 29.4, 29.3, 29.1, 22.7, 22.0, 14.1$.

(5) Synthesis of (Z)-3,7-dimethyl-2,6-octadienal (4c) by using TEMPO as nitroxyl radical (zd-4-123)

\[
\begin{align*}
\text{Cu(NO}_3\text{)}_2\cdot 3\text{H}_2\text{O} & \quad (10 \text{ mol\%}) \\
\text{TEMPO} & \quad (10 \text{ mol\%}) \\
\text{DCE, O}_2 \text{ balloon} & \\
25 \degree \text{C, 41 h} & \quad 4c, \text{NMR yield: 78\%,} \\
\text{Z:E} & = 92:8
\end{align*}
\]

Following Typical Procedure 1, the reaction of Cu(NO$_3$)$_2$•3H$_2$O (24.4 mg, 0.1
mmol), TEMPO (16.0 mg, 0.1 mmol), and 3c (158.5 mg, 1.0 mmol) in DCE (10 mL) afforded a crude mixture of Z-4c and E-4c (78%, Z:E = 92:8, as determined by 1H NMR analysis).

(6) Synthesis of (Z)-3,7-dimethyl-2,6-octadienal (4c) by using 4-OH-TEMPO as nitroxy radical (zd-4-124)

\[
\text{Cu(NO}_3\text{)}_2\cdot3\text{H}_2\text{O (10 mol%) \quad 4-OH-TEMPO (10 mol%) \quad DCE, O}_2 \text{ balloon} \quad 25 \degree \text{C, 41 h} \quad 3c (Z:E >99:1) \quad 4c, \text{ NMR yield: 58%, Z:E} = 93:7 \quad \text{Recovery: 27%}
\]

Following Typical Procedure 1, the reaction of Cu(NO\(_3\))\(_2\)•3H\(_2\)O (24.4 mg, 0.1 mmol), 4-OH-TEMPO (17.4 mg, 0.1 mmol), and 3c (159.1 mg, 1.0 mmol) in DCE (10 mL) afforded a crude mixture of 3c (27%), Z-4c and E-4c (58%, Z:E = 93:7, as determined by 1H NMR analysis).
Table S1. Reaction of alkynol 1g in Cu or Fe system. (zd-4-127, zd-4-137) a,b

\[
\begin{align*}
\text{1g} & \quad \text{metal catalyst (10 mol\%)} \quad \text{TEMPO (10 mol\%)} \quad \text{MeCN, O}_2 \text{ balloon} \quad 25^\circ \text{C, t (h)} \quad \text{2g} \\
(\text{4 mmol}) & \quad & & \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>t (h)</th>
<th>Yield of 2g (%)</th>
<th>Recovery of 1g (%)</th>
<th>Yield of 2g d (%)</th>
<th>Recovery of 1g d (%)</th>
</tr>
</thead>
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<tr>
<td>0.5</td>
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<td>34</td>
<td>49</td>
</tr>
<tr>
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<td>19</td>
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<tr>
<td>3</td>
<td>92</td>
<td>0</td>
<td>78</td>
<td>10</td>
</tr>
</tbody>
</table>

a The reaction was carried out on a 4 mmol scale of 1g in 16 mL of MeCN. At every timing, 0.2 mL of the reaction mixture was taken out and filtered through a pad of silica gel. After evaporation, 8.5 μL of CH₂Br₂ was added as internal standard for NMR analysis.

b The number in table represents NMR yield of 2g and recovery of 1g, which are determined by ¹H NMR analysis with dibromomethane as the internal standard.

c Using Cu(NO₃)₂•3H₂O as metal catalyst.

d Using Fe(NO₃)₃•9H₂O as metal catalyst.
Table S2. Monitoring the reaction of 1g with and without NaCl. (zd-4-127, zd-4-128)\textsuperscript{a,b}

\[
\begin{array}{cccccc}
\text{t (h)} & \text{Yield of 2g with no NaCl (%)} & \text{Recovery of 1g with no NaCl (%)} & \text{Yield of 2g with NaCl (%)} & \text{Recovery of 1g with NaCl (%)} \\
0.5 & 29 & 68 & 24 & 78 \\
1 & 44 & 49 & 34 & 49 \\
2 & 78 & 19 & 68 & 34 \\
3 & 92 & 0 & 73 & 24 \\
\end{array}
\]

\textsuperscript{a}The reaction was carried out on a 4 mmol scale of 1g in 16 mL of MeCN. At every timing, 0.2 mL of the reaction mixture was taken out and filtered through a pad of silica gel. After evaporation, 8.5 μL of CH\textsubscript{2}Br\textsubscript{2} was added as internal standard for NMR analysis.

\textsuperscript{b}The number in table represents NMR yield of 2g and recovery of 1g, which are determined by \textsuperscript{1}H NMR analysis with dibromomethane as the internal standard.
Table S3. Reaction of allphatic alcohol 7a in Cu or Fe system. (zd-4-148, zd-4-149)\textsuperscript{a,b}

\[ \begin{array}{ccccccc}
\text{t (h)} & \text{Yield of acid\textsuperscript{c} (%)} & \text{Yield of aldehyde\textsuperscript{c} (%)} & \text{Yield of acid\textsuperscript{d} (%)} & \text{Yield of aldehyde\textsuperscript{d} (%)} & \text{Recovery of alcohol\textsuperscript{c} (%)} & \text{Recovery of alcohol\textsuperscript{d} (%)} \\
3 & 13 & 85 & 0 & 16 & 82 \\
6 & 18 & 77 & 0 & 32 & 59 \\
9 & 36 & 53 & 0 & 63 & 24 \\
12 & 51 & 39 & 33 & 60 & 3 \\
15 & 67 & 21 & 77 & 20 & 0 \\
\end{array} \]

\textsuperscript{a}The reaction was carried out on a 10 mmol scale of 7a in 40 mL of DCE. At every timing, 0.4 mL of the reaction mixture was taken out and filtered through a pad of silica gel. After evaporation, 7 \( \mu \text{L} \) of CH\textsubscript{2}Br\textsubscript{2} was added as internal standard for NMR analysis.

\textsuperscript{b}The number in table represents NMR yield of acid, NMR yield of aldehyde and recovery of alcohol, which are determined by \textsuperscript{1}H NMR analysis with dibromomethane as the internal standard.

\textsuperscript{c}Using Cu(NO\textsubscript{3})\textsubscript{2}•3H\textsubscript{2}O as metal catalyst.

\textsuperscript{d}Using Fe(NO\textsubscript{3})\textsubscript{3}•9H\textsubscript{2}O as metal catalyst.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{diagram.png}
\caption{NMR Yield (%) vs. t (h) for alcohol in copper and iron systems.}
\end{figure}
References


