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

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Supporting information

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. $Cu(NO_3)_2$•$3H_2O$ 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:

10a: Kong, W.; Fu, C.; Ma, S. *Org. Biomol. Chem*. **2008**, 6, 4587.

2n, 2t, 8a, 10b: Ma, S.; Liu, J.; Li, S.; Chen, B.; Cheng, J.; Kuang, J.; Liu, Y.; Wan, B.; Wang, Y.; Ye, J.; Yu, Q.; Yuan, W.; Yu, S. *Adv. Synth. Catal.* **2011**, 353, 1005

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

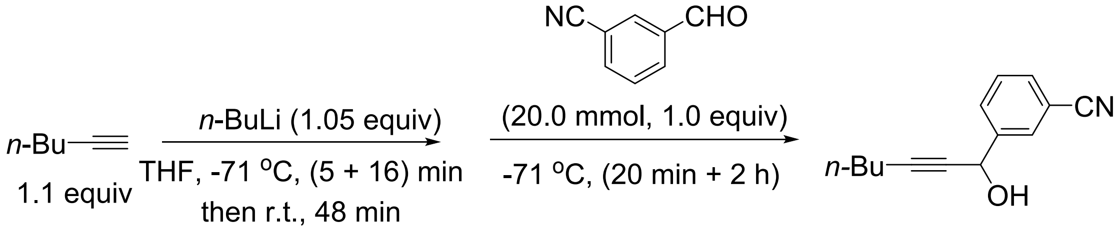
4a, 4b, 4c, 4d: Liu, J.; Ma, S. *Org. Lett*. **2013**, 15, 5150.

2p: Zhai, D.; Chen, L.; Jia, M.; Ma, S. *Adv. Synth. Catal.* **2018**, 360, 153.

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)

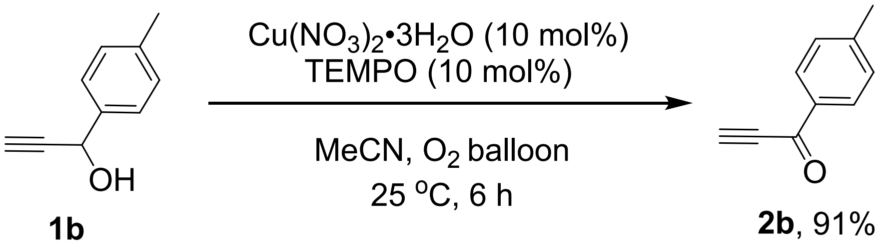


1q, 94%

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 ^{o}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 ^{o}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 NH_4Cl. After extraction with ethyl acetate, the organic layer was washed with H_2O (10 mL x 2) and brine (10 mL), respectively. Then the organic layer was dried over anhydrous Na_2SO_4. 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, $CDCl_3$): δ = 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, CH_2), 1.58-1.46 (m, 2 H, CH_2), 1.46-1.34 (m, 2 H, CH_2), 0.91 (t, *J* = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 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): ν = 3418, 2958, 2932, 2867, 2231, 1430, 1130, 1002; HRMS calcd. for $C_{14}H_{15}NO$ (M^{+}): 213.1154; Found: 213.1159.

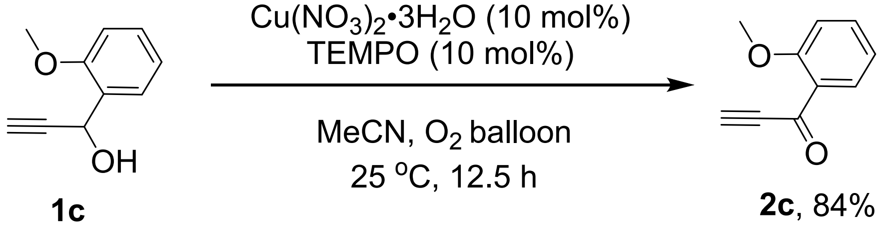
2. Synthesis of aldehydes or ketones.

(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 O_2 by a balloon of O_2 for three times. Then $Cu(NO_3)_2•3H_2O$ (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 ^oC 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**[2] (130.7 mg, 91%) as a white solid: M.p. 44.2-44.7 °C (petroleum ether/ ethyl acetate) (Lit[3] m.p.: 40–42 ^oC); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.06$ (d, $J = 8.4$ Hz, 2 H, ArH), 7.29 (d, $J = 8.0$ Hz, 2 H, ArH), 3.40 (s, 3 H, CH_3), 2.44 (s, 1 H, ≡CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 177.0$, 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): $\nu = 3257$, 2090, 1632, 1594, 1459, 1404, 1310, 1246, 1167, 1117 cm^{-1}.

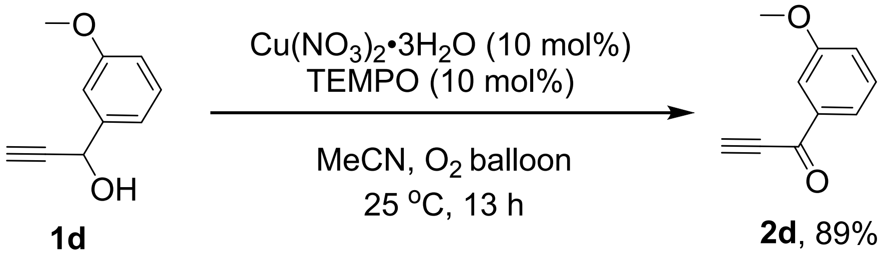
(2) Synthesis of 1-(2-methoxyphenyl)-2-propyn-1-one (**2c**) (zd-4-70)



Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2•3H_2O$ (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**[4] (134.0 mg, 84%) as an oil [eluent: petroleum ether/ethyl acetate = 30/1]:

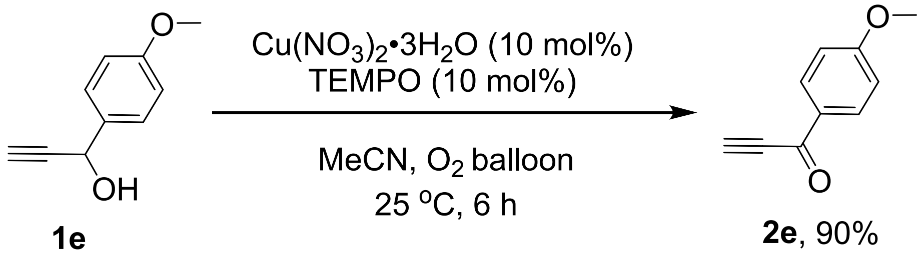
^1H NMR (400 MHz, $CDCl_3$): δ = 8.06 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1 H, ArH), 7.55 (td, J_1 = 8.0 Hz, J_2 = 1.8 Hz, 1 H, ArH), 7.07-6.97 (m, 2 H, ArH), 3.94 (s, 3 H, CH_3), 3.37 (s, 1 H, ≡CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.8, 159.8, 135.4, 132.9, 125.5, 120.1, 112.0, 81.9, 79.5, 55.6; MS (70 eV, EI) *m/z* (%): 161 (M^++1, 7.26), 160 (M^+, 64.37), 131 (100); IR (neat): ν = 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 $Cu(NO_3)_2\cdot 3H_2O$ (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]: ^1H NMR (400 MHz, $CDCl_3$): δ = 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, ≡CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 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): ν = 3250, 2094, 1644, 1595, 1581, 1485, 1429, 1323, 1264, 1207, 1177, 1021, 1012 cm^{-1}.

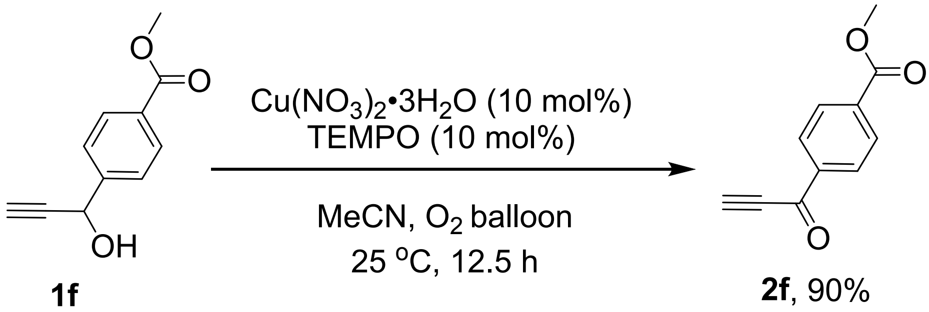
(4) Synthesis of 1-(4-methoxyphenyl)-2-propyn-1-one (**2e**) (zd-4-67)



Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2\cdot 3H_2O$ (24.6 mg, 0.1

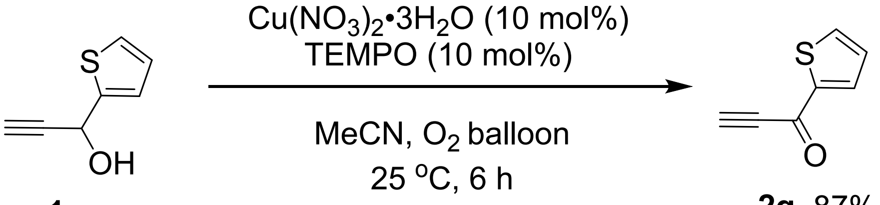
mmol), TEMPO (16.0 mg, 0.1 mmol), and **1e** (161.8 mg, 1.0 mmol) in MeCN (4 mL) afforded **2e**[3] (143.6 mg, 90%) as a white solid [eluent: petroleum ether/ethyl acetate = 25/1]: M.p. 85.5-86.5 °C (petroleum ether/ ethyl acetate) (Lit[6] m.p.: 86–87 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, *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, ≡CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 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): ν = 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 $Cu(NO_3)_2$•$3H_2O$ (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 [eluent: petroleum ether/ethyl acetate = 30/1]: M.p. 117.0-118.3 °C (petroleum ether/ ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 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, ≡CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 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): ν = 3217, 2096, 1717, 1636, 1606, 1437, 1275, 1233, 1195, 1119, 1006 cm^{-1}.

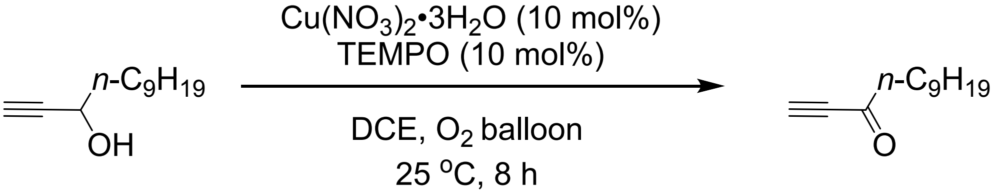
(6) Synthesis of 1-(2-thienyl)-2-propyn-1-one (**2g**) (zd-4-95)


1g

2g, 87%

Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2$•$3H_2O$ (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, $CDCl_3$): δ = 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, $CDCl_3$): δ = 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): ν = 3244, 3103, 2095, 1616, 1512, 1406, 1354, 1266, 1231, 1201, 1082, 1051 cm^{-1}.

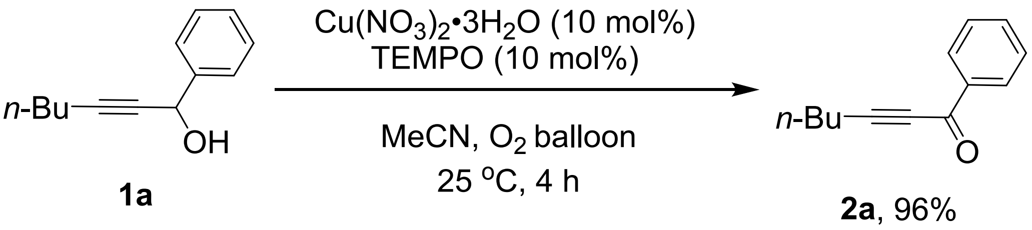
(7) Synthesis of 1-Dodecyn-3-one (**2h**) (zd-3-89)


1h

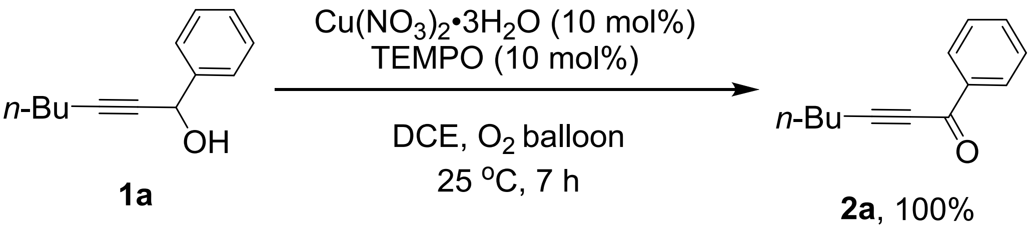
2h, 89%

Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2$•$3H_2O$ (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, $CDCl_3$): δ = 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, $CDCl_3$): δ = 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)

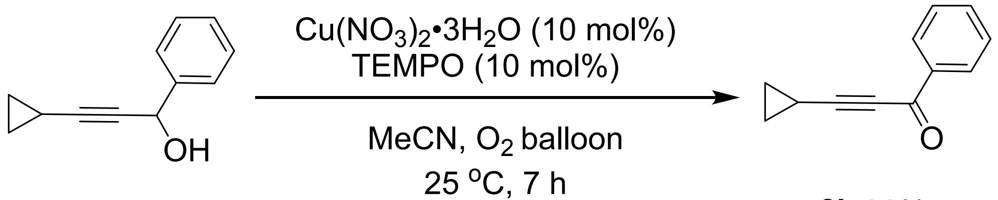


Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2•3H_2O$ (23.9 mg, 0.1 mmol), TEMPO (16.1 mg, 0.1 mmol), and **1a** (187.2 mg, 1.0 mmol) in MeCN (4 mL) afforded **2a**[10] (177.4 mg, 96%) as an oil [eluent: petroleum ether/ethyl ether = 30/1]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (d, 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, $CDCl_3$): δ = 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, EI) *m/z* (%): 186 (M^+, 12.46), 144 (100); IR (neat): ν = 2957, 2933, 2868, 2232, 2200, 1641, 1588, 1452, 1314, 1257, 1172 cm^{-1}.



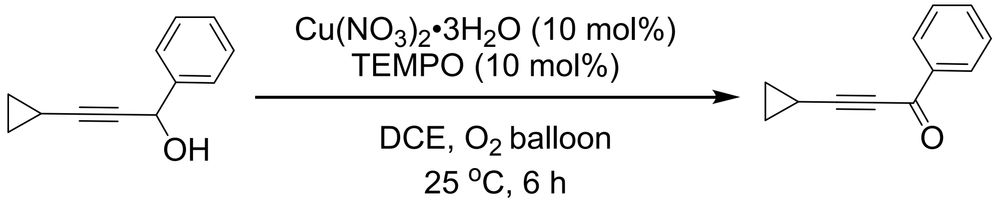
Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2•3H_2O$ (24.0 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and **1a** (188.0 mg, 1.0 mmol) in DCE (4 mL) afforded **2a**[10] (185.2 mg, 100%) as an oil [eluent: petroleum ether/ethyl ether = 40/1]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18-8.10 (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, $CDCl_3$): δ = 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)



1i **2i**, 98%

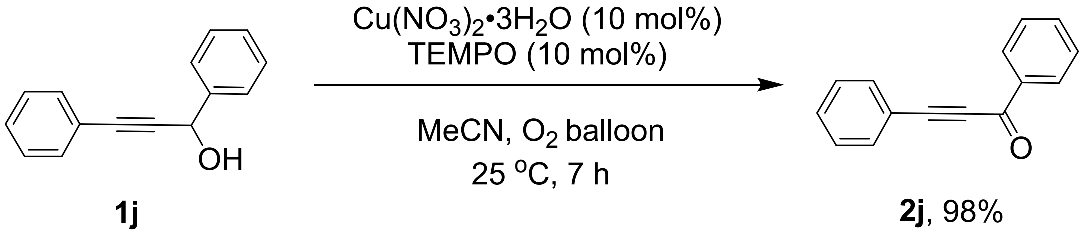
Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2•3H_2O$ (24.2 mg, 0.1 mmol), TEMPO (15.8 mg, 0.1 mmol), and **1i** (172.2 mg, 1.0 mmol) in MeCN (4 mL) afforded **2i**[11] (166.6 mg, 98%) as an oil [eluent: petroleum ether/ethyl ether = 30/1]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16-8.05 (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_2CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 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): ν = 2207, 1635, 1596, 1579, 1449, 1356, 1311, 1264, 1172, 1046, 1023 cm^{-1}.



1i **2i**, 96%

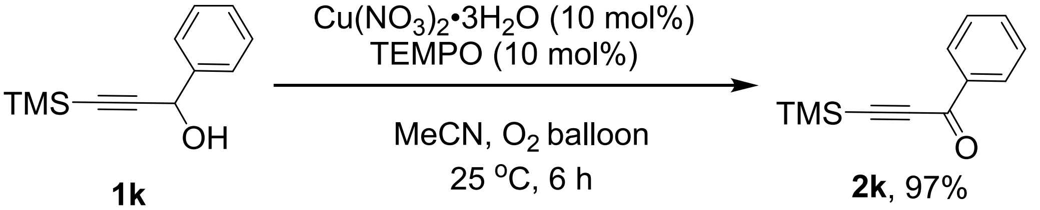
Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2•3H_2O$ (24.2 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and **1i** (172.3 mg, 1.0 mmol) in DCE (4 mL) afforded **2i**[11] (163.5 mg, 96%) as an oil [eluent: petroleum ether/ethyl ether = 30/1]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20-8.05 (m, 2 H, ArH), 7.65-7.54 (m, 1 H, ArH), 7.47 (t, *J* = 7.6 Hz, 2 H, ArH), 1.66-1.48 (m, 1 H, CH), 1.13-0.94 (m, 4 H, CH_2CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.8, 136.8, 133.6, 129.3, 128.3, 101.0, 75.4, 9.8, -0.1.

(10) Synthesis of 1,3-diphenyl-2-propyn-1-one (**2j**) (zd-4-73)

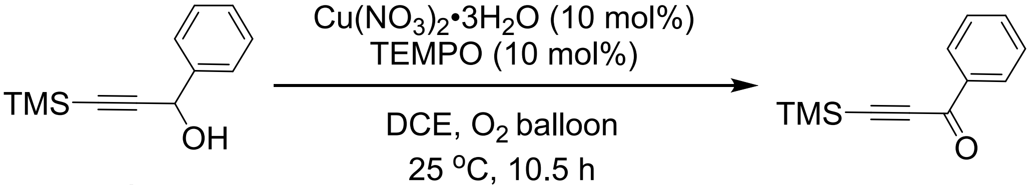


Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2{\cdot}3H_2O$ (24.4 mg, 0.1 mmol), TEMPO (16.1 mg, 0.1 mmol), and **1j** (209.8 mg, 1.0 mmol) in MeCN (4 mL) afforded **2j**[12] (203.4 mg, 98%) as a white soild [eluent: petroleum ether/ethyl ether = 30/1]: M.p. 45.3-46.6 °C (petroleum ether/ ethyl acetate) (Lit[12] m.p.: 45-47 °C); ^1H NMR (400 MHz, $CDCl_3$): δ = 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, $CDCl_3$): δ = 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): ν = 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)



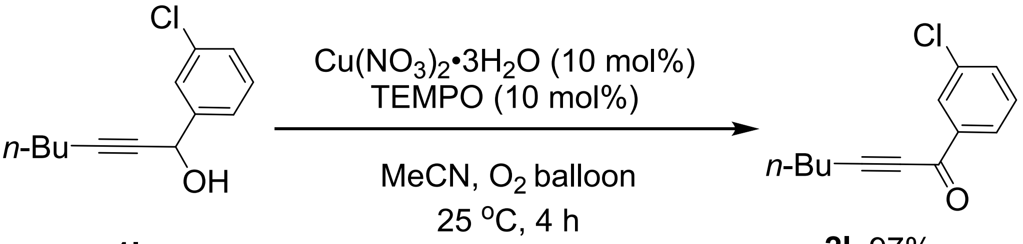
Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2{\bullet}3H_2O$ (24.2 mg, 0.1 mmol), TEMPO (15.9 mg, 0.1 mmol), and **1k** (204.8 mg, 1.0 mmol) in MeCN (4 mL) afforded **2k**[9] (197.2 mg, 97%) as an oil [eluent: petroleum ether/ethyl ether = 60/1]; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.15 (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, $3{\times}CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.6, 136.4, 134.1, 129.6, 128.5, 100.8, 100.5, -0.8.



1k **2k**, 95%

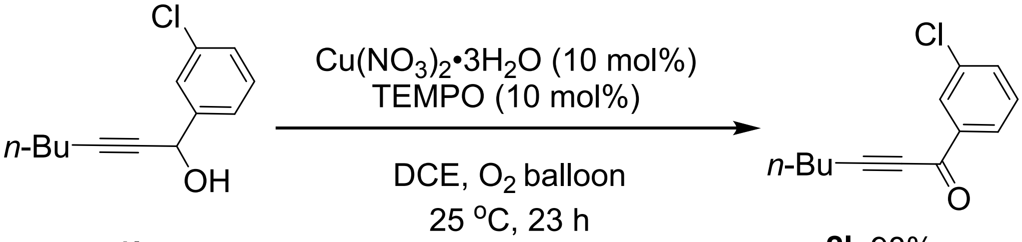
Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2$•$3H_2O$ (24.4 mg, 0.1 mmol), TEMPO (15.9 mg, 0.1 mmol), and **1k** (204.1 mg, 1.0 mmol) in DCE (4 mL) afforded **2k**[9] (191.5 mg, 95%) as an oil [eluent: petroleum ether/ethyl ether = 60/1]; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.20-8.10 (m, 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)



1l **2l**, 97%

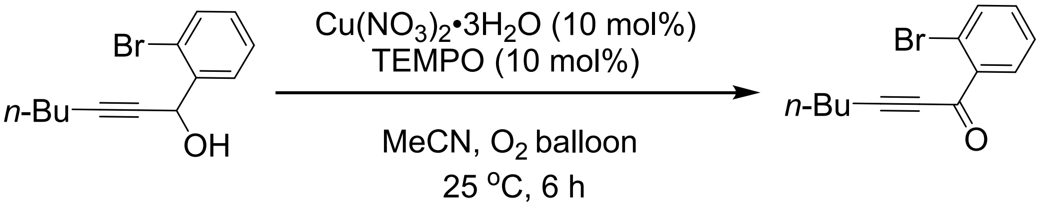
Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2$•$3H_2O$ (24.4 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and **1l** (222.8 mg, 1.0 mmol) in MeCN (4 mL) afforded **2l** (213.9 mg, 97%) as an oil [eluent: petroleum ether/ethyl ether = 30/1]; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.10 (t, J = 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.



1l **2l**, 98%

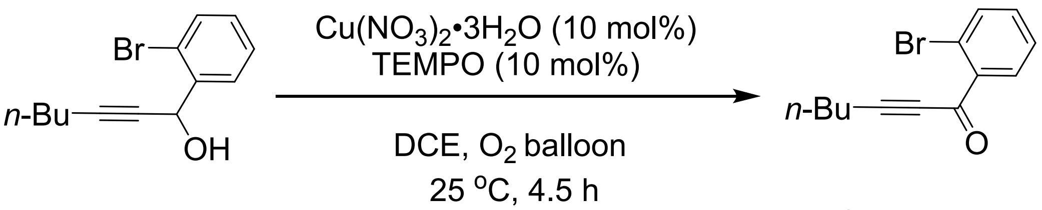
Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2•3H_2O$ (24.0 mg, 0.1 mmol), TEMPO (15.9 mg, 0.1 mmol), and **1l** (222.5 mg, 1.0 mmol) in DCE (4 mL) afforded **2l** (216.2 mg, 98%) as an oil [eluent: petroleum ether/ethyl ether = 30/1]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (t, *J* = 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)



1m **2m**, 97%

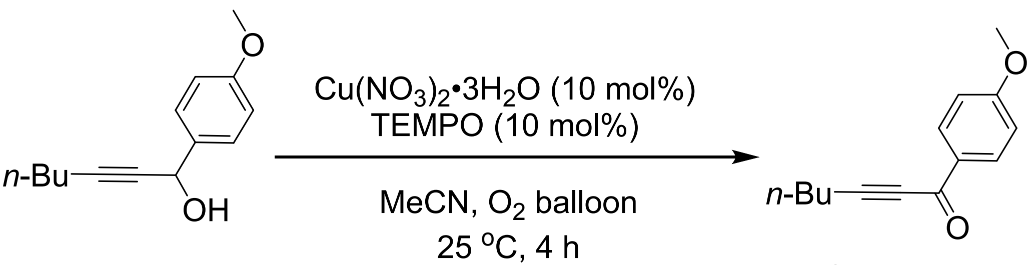
Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2•3H_2O$ (24.4 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and **1m** (266.2 mg, 1.0 mmol) in MeCN (4 mL) afforded **2m**[13] (257.4 mg, 97%) as an oil [eluent: petroleum ether/ethyl ether = 30/1]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, *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^+ (^{81}Br), 9.56), 264 (M^+ (^{79}Br), 9.29), 185 (100); IR (neat): ν = 2187, 1648, 1580, 1474, 1386, 1262, 1063, 1008 cm^{-1}.



1m **2m**, 98%

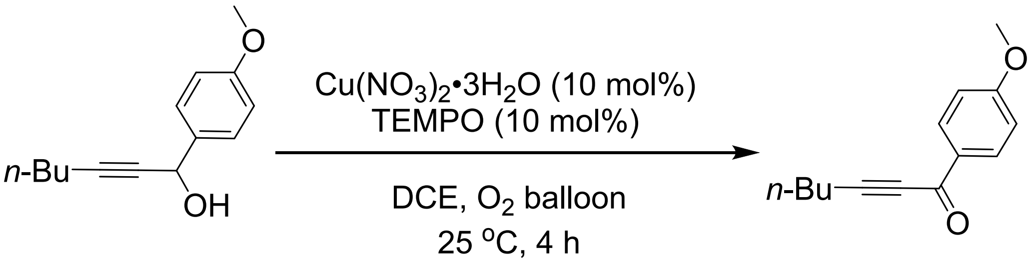
Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2•3H_2O$ (24.4 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and **1m** (267.2 mg, 1.0 mmol) in DCE (4 mL) afforded **2m**[13] (260.6 mg, 98%) as an oil [eluent: petroleum ether/ethyl ether = 30/1]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (dd, 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, $CDCl_3$): δ = 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)



1n **2n**, 100%

Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2•3H_2O$ (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, $CDCl_3$): δ = 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, $CDCl_3$): δ = 176.8, 164.2, 131.8, 130.2, 113.6, 95.8, 79.5, 55.4, 29.8, 22.0, 18.7, 13.4.

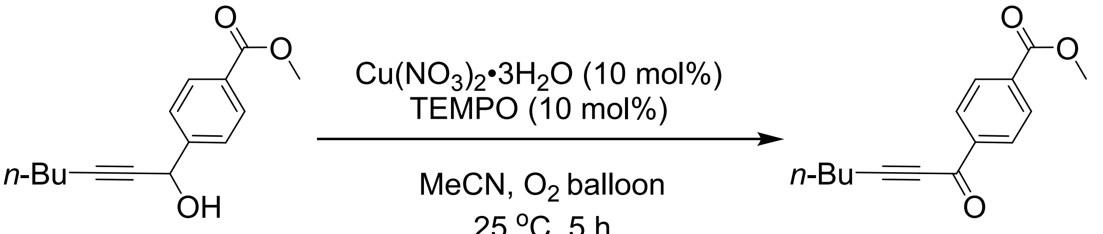


1n

2n, 97%

Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2$•$3H_2O$ (24.4 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and **1n** (218.5 mg, 1.0 mmol) in DCE (4 mL) afforded **2n**[14] (209.6 mg, 97%) as an oil [eluent: petroleum ether/ethyl ether = 30/1 (300 mL) to petroleum ether/ethyl ether = 15/1]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 8.8 Hz, 2 H, ArH), 6.95 (d, *J* = 8.8 Hz, 2 H, ArH), 3.89 (s, 3 H, CH_3), 2.49 (t, *J* = 7.6 Hz, 2 H, CH_2), 1.72-1.58 (m, 2 H, CH_2), 1.56-1.44 (m, 2 H, CH_2), 0.96 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 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 (**2o**) (zd-4-15)

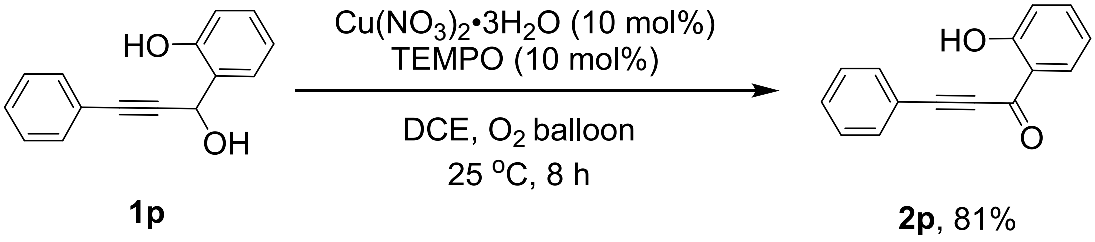


1o

2o, 99%

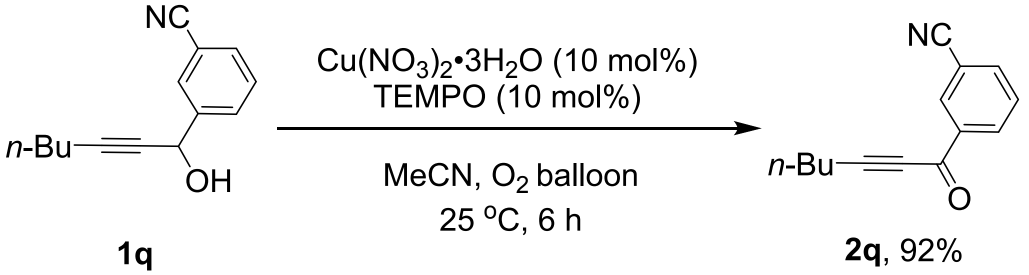
Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2$•$3H_2O$ (24.2 mg, 0.1 mmol), TEMPO (15.9 mg, 0.1 mmol), and **1o** (246.3 mg, 1.0 mmol) in MeCN (4 mL) afforded **2o** (243.0 mg, 99%) as an oil [eluent: petroleum ether/ethyl ether = 20/1]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 8.8 Hz, 2 H, ArH), 8.13 (d, *J* = 8.8 Hz, 2 H, ArH), 3.96 (s, 3 H, CH_3), 2.53 (t, *J* = 7.2 Hz, 2 H, CH_2), 1.73-1.62 (m, 2 H, CH_2), 1.58-1.45 (m, 2 H, CH_2), 0.98 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 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; MS (70 eV, EI) *m/z* (%): 244 (M^+, 14.91), 202 (100); IR (neat): ν = 2956, 2933, 2872, 2237, 2198, 1724, 1646, 1435, 1407, 1276, 1259, 1244, 1116, 1102, 1017 cm^{-1}; HRMS calcd. for $C_{15}H_{16}O_3$ (M^+): 244.1099; Found: 244.1099.

(16) Synthesis of 1-(2-hydroxyphenyl)-3-phenyl-2-propyn-1-one (**2p**) (zd-3-67)



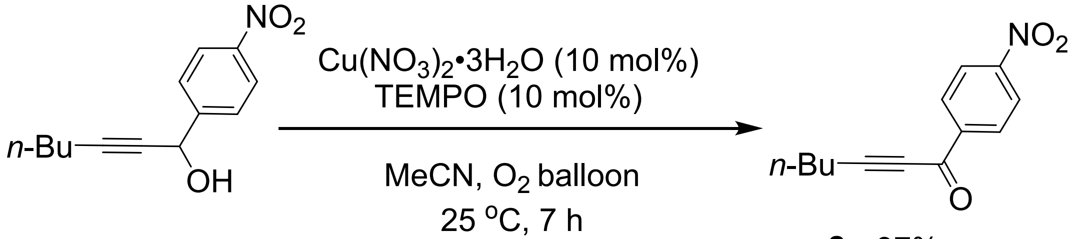
Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2•3H_2O$ (24.2 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and **1p** (224.2 mg, 1.0 mmol) in DCE (4 mL) afforded **2p**[15] (180.1 mg, 81%) as a yellow solid [eluent: petroleum ether/ethyl ether = 60/1] : M.p. 64.0-65.6 °C (petroleum ether/ ethyl acetate) (Lit[14] m.p.: 61-63 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 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, $CDCl_3$): δ = 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 $Cu(NO_3)_2•3H_2O$ (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, $CDCl_3$): δ = 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, $CDCl_3$): δ = 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): ν = 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)

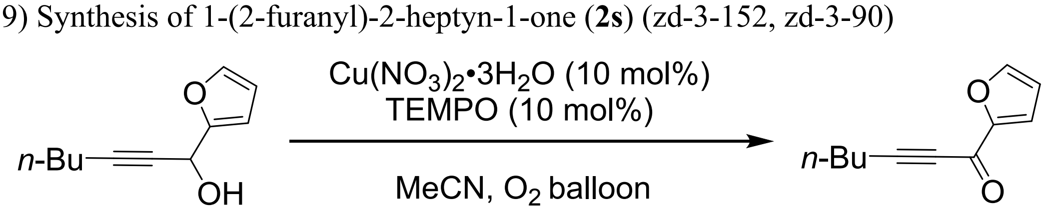


1r

2r, 97%

Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2{\bullet}3H_2O$ (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]; ^1H NMR (400 MHz, $CDCl_3$): δ = 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), 1.56-1.46 (m, 2 H, CH_2), 0.98 (t, J = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 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): ν = 2959, 2934, 2871, 2237, 2199, 1650, 1602, 1524, 1343, 1320, 1257, 1104 cm^{-1}.

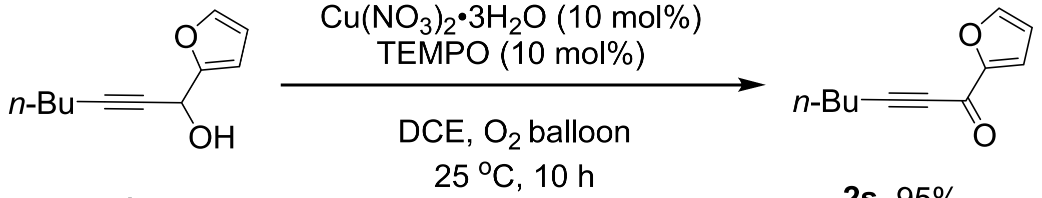
(19) Synthesis of 1-(2-furanyl)-2-heptyn-1-one (**2s**) (zd-3-152, zd-3-90)



1s

2s, 92%

Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2{\bullet}3H_2O$ (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]; ^1H NMR (400 MHz, $CDCl_3$): δ = 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, $CDCl_3$): δ = 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, EI) *m/z* (%): 176 (M^+, 27.69), 95 (100); IR (neat): ν = 2957, 2933, 2868, 2251, 2207, 1631, 1562, 1460, 1390, 1294, 1168, 1123, 1014 cm^{-1}.

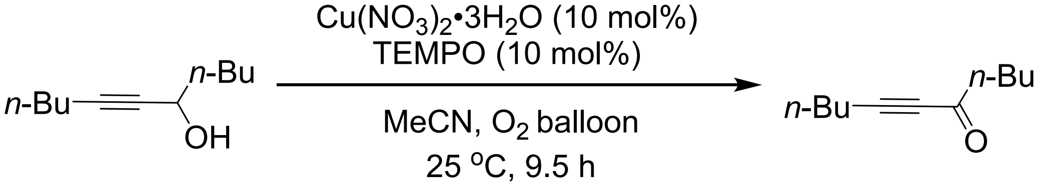


1s

2s, 95%

Following **Typical procedure 1**, the reaction of $Cu(NO_3)_2$•$3H_2O$ (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]; ^1H NMR (400 MHz, $CDCl_3$): δ = 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, $CDCl_3$): δ = 164.4, 152.7, 147.2, 120.1, 111.9, 94.9, 78.4, 29.1, 21.4, 18.2, 12.9.

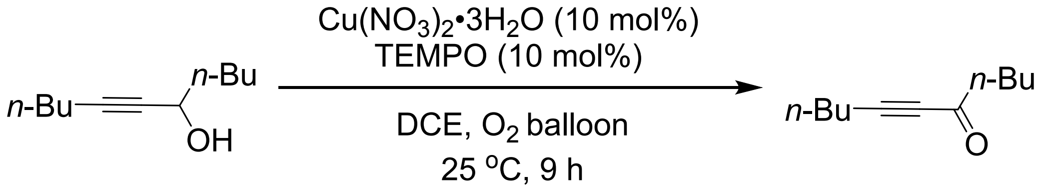
(20) Synthesis of 6-undecyn-5-one (**2t**) (zd-3-157, zd-3-83)



1t

2t, 96%

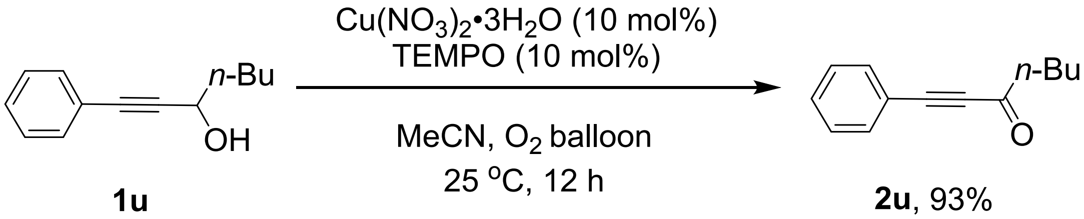
Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2$•$3H_2O$ (23.8 mg, 0.1 mmol), TEMPO (15.9 mg, 0.1 mmol), and **1t** (169.1 mg, 1.0 mmol) in MeCN (4 mL) afforded **2t**[14] (160.1 mg, 96%) as an oil [eluent: petroleum ether/ethyl ether = 60/1]; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.53 (t, *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_2CH_2), 1.50-1.25 (m, 4 H, CH_2CH_2), 1.00-0.86 (m, 6 H, 2×CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.3, 94.0, 80.7, 45.1, 29.6, 26.1, 22.0, 21.8, 18.4, 13.6, 13.3.



1t **2t**, 95%

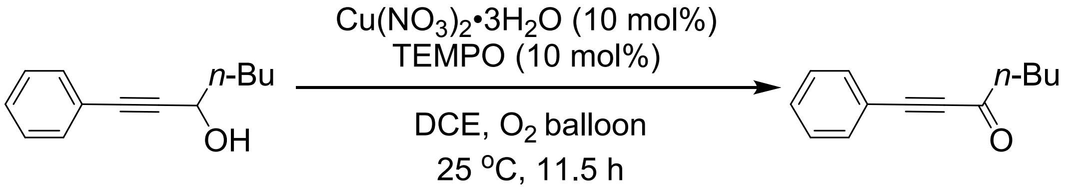
Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2$•$3H_2O$ (24.0 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and **1t** (168.6 mg, 1.0 mmol) in DCE (4 mL) afforded **2t**[14] (158.8 mg, 95%) as an oil [eluent: petroleum ether/ethyl ether = 40/1]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.53 (t, 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, $CDCl_3$): δ = 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)



1u **2u**, 93%

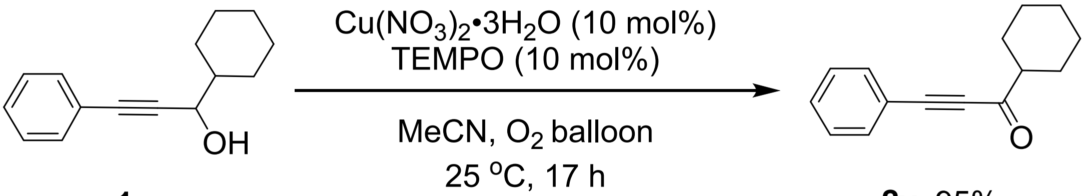
Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2$•$3H_2O$ (24.0 mg, 0.1 mmol), TEMPO (15.9 mg, 0.1 mmol), and **1u** (188.4 mg, 1.0 mmol) in MeCN (4 mL) afforded **2u**[14] (173.2 mg, 93%) as an oil [eluent: petroleum ether/ethyl ether = 30/1]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, J = 7.2 Hz, 2 H, ArH), 7.50-7.34 (m, 3 H, ArH), 2.67 (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, $CDCl_3$): δ = 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): ν = 2958, 2932, 2872, 2200, 1666, 1489, 1272, 1125, 1067 cm^{-1}.



1u **2u**, 96%

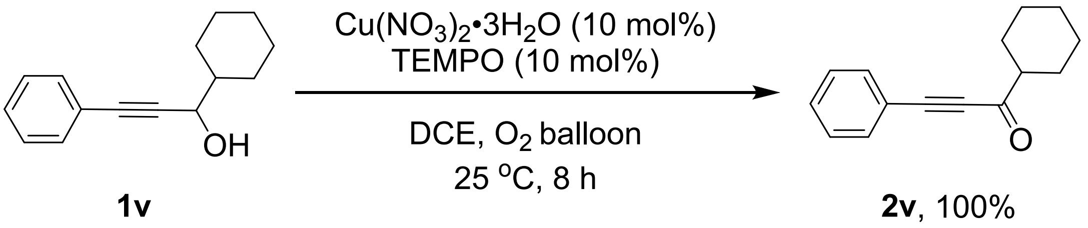
Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2•3H_2O$ (24.2 mg, 0.1 mmol), TEMPO (16.2 mg, 0.1 mmol), and **1u** (188.4 mg, 1.0 mmol) in DCE (4 mL) afforded **2u**[14] (179.8 mg, 96%) as an oil [eluent: petroleum ether/ethyl ether = 30/1]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61-7.54 (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, $CDCl_3$): δ = 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)



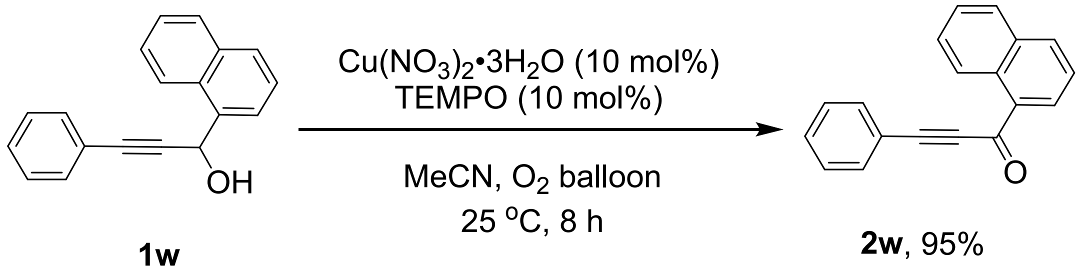
1v **2v**, 95%

Following **Typical procedure 1**, the reaction of $Cu(NO_3)_2•3H_2O$ (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, $CDCl_3$): δ = 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, $CDCl_3$): δ = 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): ν = 2929, 2853, 2196, 1660, 1488, 1445, 1262, 1142, 1089, 1069 cm^{-1}.

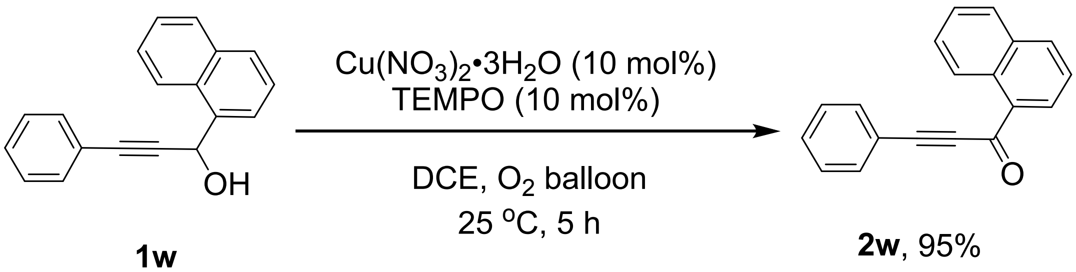


Following **Typical procedure 1**, the reaction of $Cu(NO_3)_2•3H_2O$ (24.0 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and **1v** (214.2 mg, 1.0 mmol) in DCE (4 mL) afforded **2v**[18] (211.4 mg, 100%) as an oil [eluent: petroleum ether/ethyl ether = 30/1]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, 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, $CH_2CH_2CH_2$); ^{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)

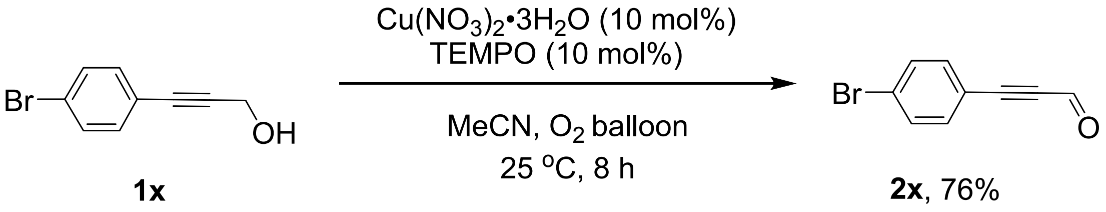


Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2•3H_2O$ (24.0 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and **1w** (258.3 mg, 1.0 mmol) in MeCN (4 mL) afforded **2w**[19] (244.7 mg, 95%) as a white solid [eluent: petroleum ether/ethyl ether = 60/1]: M.p. 93.0-94.7 °C (petroleum ether/ ethyl acetate) (Lit[20] m.p.: 92–94 ^{o}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}.

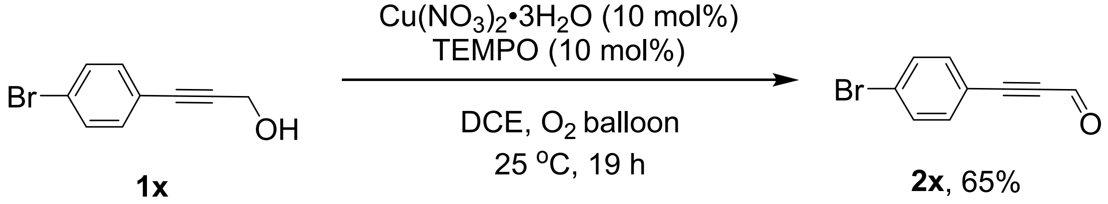


Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2 \cdot 3H_2O$ (24.3 mg, 0.1 mmol), TEMPO (15.9 mg, 0.1 mmol), and **1w** (258.8 mg, 1.0 mmol) in DCE (4 mL) afforded **2w**[19] (243.2 mg, 95%) as a white solid [eluent: petroleum ether/ethyl ether = 40/1]; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 9.24$ (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); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 179.6$, 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 (**2x**) (zd-3-155, zd-3-66)

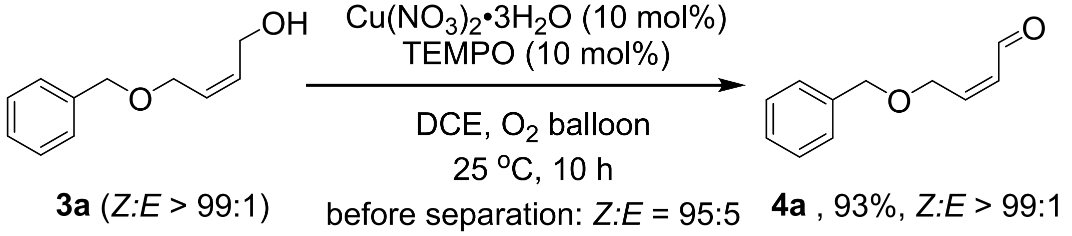


Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2 \cdot 3H_2O$ (23.7 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and **1x** (211.0 mg, 1.0 mmol) in MeCN (4 mL) afforded **2x**[21] (159.0 mg, 76%) as a red solid [eluent: petroleum ether/ethyl ether = 60/1]: M.p. 92.0-93.4 °C (petroleum ether/ ethyl acetate) (Lit[22] m.p.: 95–97 °C); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 9.42$ (s, 1 H, CHO), 7.56 (d, $J = 8.8$ Hz, 2 H, ArH), 7.47 (d, $J = 8.0$ Hz, 2 H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 176.5$, 134.4, 132.1, 126.2, 118.3, 93.5, 89.0; MS (70 eV, EI) *m/z* (%): 210 (M^+ (^{81}Br), 86.41), 208 (M^+ (^{79}Br), 86.47), 101 (100); IR (neat): $\nu = 2949$, 2866, 2203, 1649, 1578, 1460, 1427, 1284, 1238, 1030 cm^{-1}.



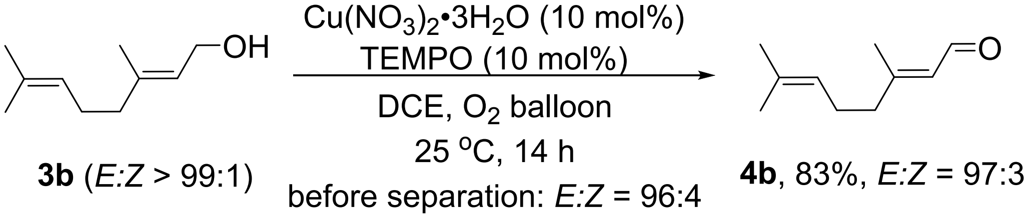
Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2$•$3H_2O$ (24.2 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and **1x** (211.2 mg, 1.0 mmol) in DCE (4 mL) afforded **2x**[21] (135.8 mg, 65%) as a red solid [eluent: petroleum ether/ethyl ether = 60/1]; ^1H NMR (400 MHz, $CDCl_3$): δ = 9.42 (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)



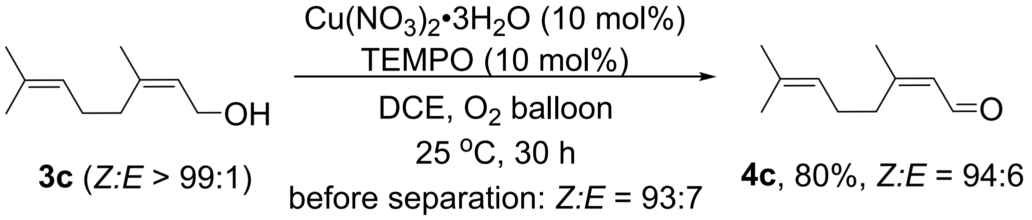
Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2$•$3H_2O$ (24.2 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and **3a** (187.6 mg, 1.0 mmol) in DCE (10 mL) afforded **4a**[23] (164.4 mg, 93%, *Z:E* > 99:1) as an oil [eluent: petroleum ether/ethyl acetate = 20/1] [before separation afforded a crude mixture of *Z*-**4a** and *E*-**4a** (*Z:E* = 95:5), as determined by ^1H NMR analysis]; ^1H 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)



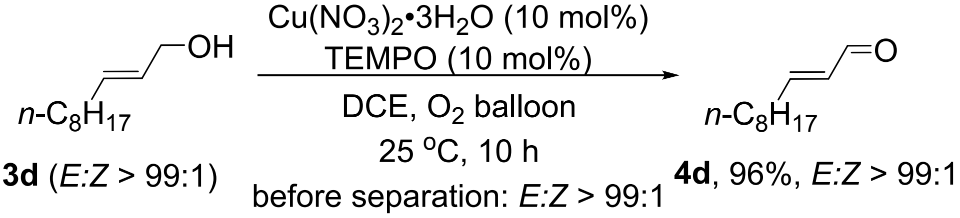
Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2$•$3H_2O$ (24.4 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and **3b** (155.4 mg, 1.0 mmol) in DCE (10 mL) afforded **4b**[23] (126.3 mg, 83%, *E:Z* = 97:3) as an oil [eluent: petroleum ether/ethyl acetate = 50/1 (400 mL) to petroleum ether/ethyl 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, $CDCl_3$): δ = 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, $2\times CH_2$), 2.17 (s, 3 H, CH_3), 1.69 (s, 3 H, CH_3), 1.61 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 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)



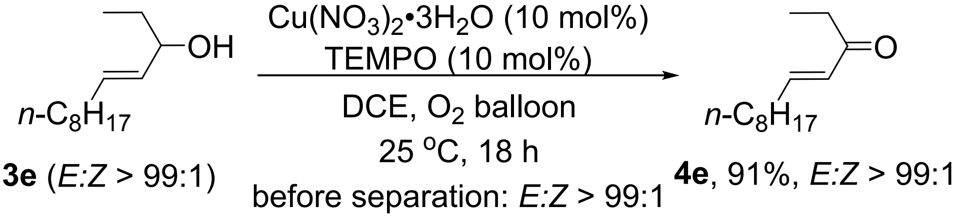
Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2$•$3H_2O$ (24.6 mg, 0.1 mmol), TEMPO (16.1 mg, 0.1 mmol), and **3c** (153.6 mg, 1.0 mmol) in DCE (10 mL) afforded **4c**[23] (118.1 mg, 80%, *Z:E* = 94:6) as an oil [eluent: petroleum ether/ethyl ether = 15:1] [before separation afforded a crude mixture of *Z*-**4c** and *E*-**4c** (*Z:E* = 93:7), as determined by ^{1}H NMR analysis]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 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, CH_2), 2.24 (dd, J_1 = 14.6 Hz, J_2 = 7.4 Hz, 2 H, CH_2), 1.99 (s, 3 H, CH_3), 1.69 (s, 3 H, CH_3), 1.61 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 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**: δ = 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)



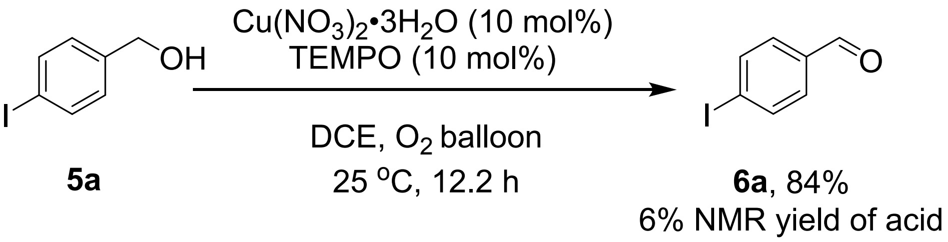
Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2$•$3H_2O$ (24.2 mg, 0.1 mmol), TEMPO (16.0 mg, 0.1 mmol), and **3d** (177.3 mg, 1.0 mmol) in DCE (4 mL) afforded **4d**[23] (161.3 mg, 96%, *E:Z* > 99:1) as an oil [eluent: petroleum ether/ethyl acetate = 50:1] [before separation afforded a crude mixture of *E*-**4d** and *Z*-**4d** (*E:Z* > 99:1), as determined by ^{1}H NMR analysis]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.51 (d, *J* = 8.0 Hz, 1 H, CHO), 6.86 (dt, J_1 = 15.8 Hz, J_2 = 7.0 Hz, 1 H, CH=), 6.18-6.07 (m, 1 H, CH=), 2.38-2.27 (m, 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* = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): 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)



Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2$•$3H_2O$ (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 ^{1}H NMR analysis]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.83 (dt, J_1 = 16.0 Hz, J_2 = 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, CH_2), 2.20 (q, *J* = 7.2 Hz, 2 H, CH_2), 1.56-1.18 (m, 12 H, 6×CH_2), 1.10 (t, *J* = 7.4 Hz, 3 H, CH_3), 0.88 (t, *J* = 6.6 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): 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.

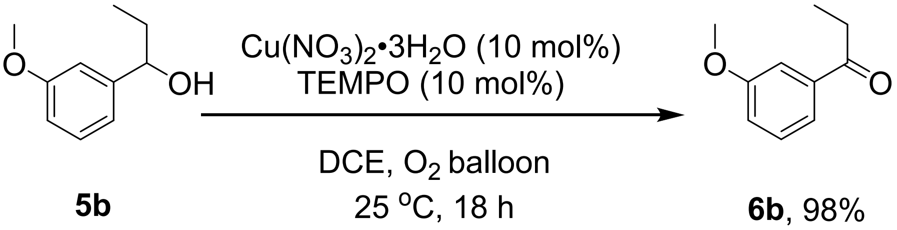
(30) Synthesis of 4-iodobenzaldehyde (**6a**) (zd-3-35)



5a **6a**, 84%
6% NMR yield of acid

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 $Cu(NO_3)_2$•$3H_2O$ (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_2O (10 mL). After extraction with ethyl acetate (10 mL×3), the organic layer was dried over anhydrous Na_2SO_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, $CDCl_3$): δ = 9.96 (s, 1 H, CHO), 7.92 (d, J = 8.0 Hz, 2 H, ArH), 7.60 (d, J = 8.0 Hz, 2 H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.4, 138.4, 135.5, 130.8, 102.8.

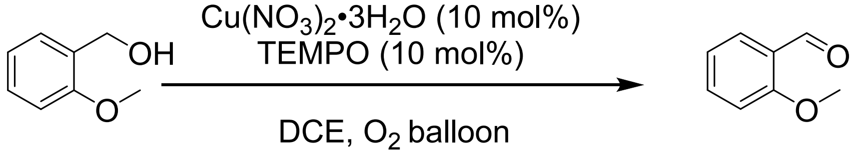
(31) Synthesis of 3-methoxyphenyl ethyl ketone (**6b**) (zd-4-84)



5b **6b**, 98%

Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2$•$3H_2O$ (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, $CDCl_3$): δ = 7.54 (d, J = 7.6 Hz, 1 H, ArH), 7.50 (s, 1 H, ArH), 7.36 (t, J = 7.8 Hz, 1 H, ArH), 7.10 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1 H, ArH), 3.86 (s, 3 H, CH_3), 2.99 (q, J = 7.4 Hz, 2 H, CH_2), 1.22 (t, J = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 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): ν = 2976, 2938, 1686, 1582, 1485, 1461, 1429, 1286, 1254, 1197, 1171, 1044, 1020 cm^{-1}.

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



5c **6c**, 86%

Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2•3H_2O$ (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, $CDCl_3$): δ = 10.48 (s, 1 H, CHO), 7.83 (d, J = 7.6 Hz, 1 H, ArH), 7.56 (d, J = 7.8 Hz, 1 H, ArH), 7.07-6.95 (m, 2 H, ArH), 3.93 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 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)

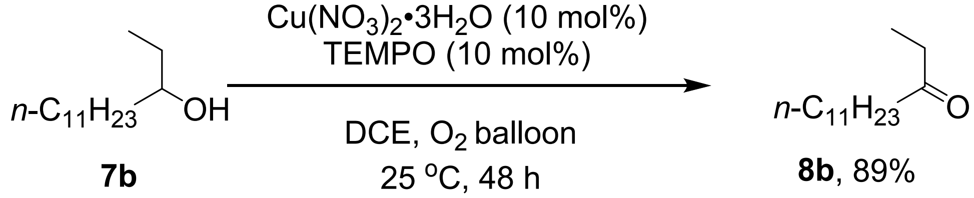
$$\underset{\textbf{7a}}{n\text{-}C_{16}H_{33}OH} \xrightarrow[\text{DCE, } O_2 \text{ balloon; } 25\ ^{o}C,\ 20.2\ h]{Cu(NO_3)_2•3H_2O\ (10\ mol\%),\ \text{TEMPO}\ (10\ mol\%)} n\text{-}C_{15}H_{31}CHO$$

8a, 84%
Recovery of **7a**: 5%

Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2•3H_2O$ (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, $CDCl_3$): δ = 9.76 (t, J = 1.6

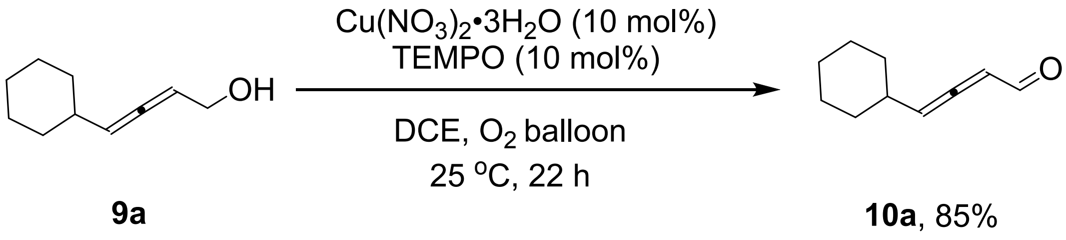
Hz, 1 H, CHO), 2.42 (td, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 2 H, CH_2), 1.66-1.58 (m, 2 H, CH_2), 1.36-1.20 (m, 24 H, 12×CH_2), 0.88 (t, J = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.9, 43.9, 31.9, 29.65, 29.63, 29.55, 29.4, 29.3, 29.1, 22.7, 22.1, 14.1.

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



Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2$•$3H_2O$ (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 °C (petroleum ether/ ethyl acetate) (Lit[27] m.p.: 32–33 °C); ^1H NMR (400 MHz, $CDCl_3$): δ = 2.46-2.34 (m, 4 H, 2×CH_2), 1.62-1.52 (m, 2 H, CH_2), 1.34-1.18 (m, 16 H, 8×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, $CDCl_3$): δ = 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): ν = 2960, 2916, 2872, 2849, 1709, 1702, 1471, 1463, 1455, 1374, 1231, 1131, 1114 cm^{-1}.

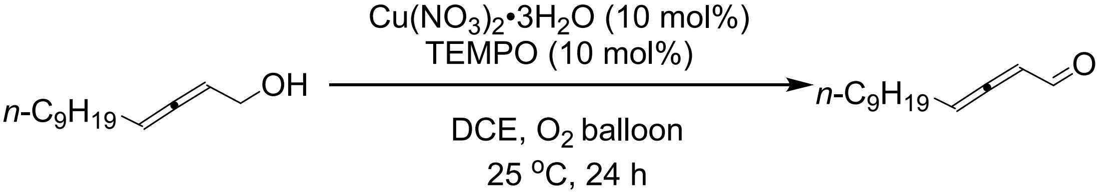
(35) Synthesis of 4-cyclohexylbutadienal (**10a**) (zd-4-93)



Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2$•$3H_2O$ (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 °C)]; ^1H NMR (400 MHz, $CDCl_3$): δ = 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

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)

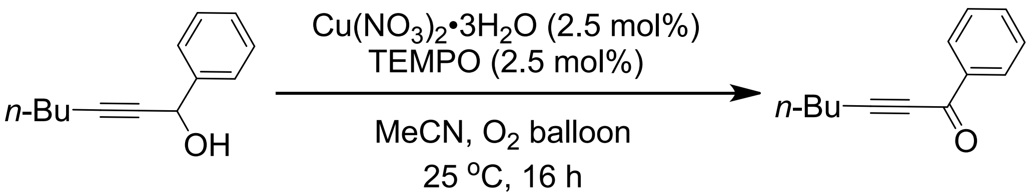


9b **10b**, 72%

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 O_2, Air/O_2, or Air.

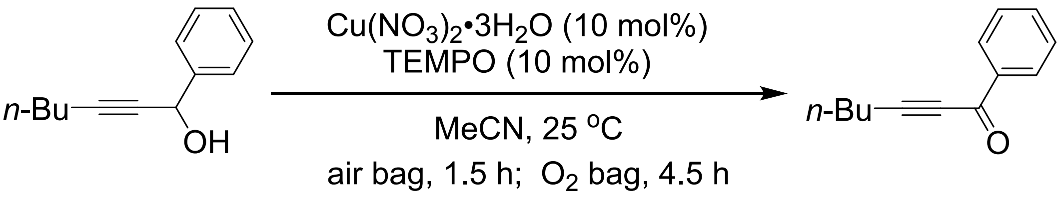
(1) Synthesis of **2a** with O_2 balloon (zd-4-35)



1a (30 mmol) **2a**, 98%

A 250 mL flask was degassed to remove the air inside completely and refilled with O_2 by a balloon of O_2 for three times. Then $Cu(NO_3)_2•3H_2O$ (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**[10] (5.4919 g, 98%) as an oil; ^1H NMR (400 MHz, $CDCl_3$): δ = 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_2), 1.73-1.60 (m, 2 H, CH_2), 1.57-1.45 (m, 2 H, CH_2), 0.97 (t, J = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.1, 136.8, 133.8, 129.4, 128.4, 96.8, 79.6, 29.7, 22.0, 18.8, 13.4.

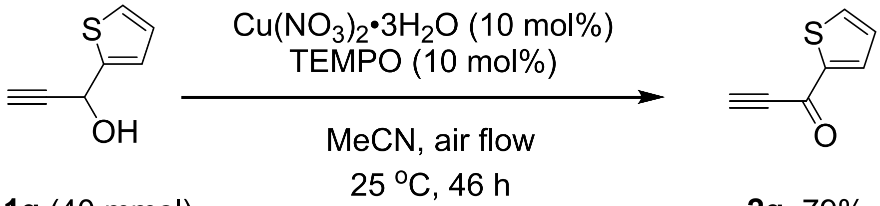
(2) Synthesis of **2a** with a bag of air with O_2 supplemented by a bag of pure O_2 (zd-4-106)



1a (40 mmol) **2a**, 100%

To a 250 mL three-neck flask were added $Cu(NO_3)_2•3H_2O$ (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 O_2 was connected to the flask to supplement O_2. The resulting mixture was stirred at 25 °C for 4.5 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 **2a**[10] (7.4587 g, 100%) as an oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 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, $CDCl_3$): δ = 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)



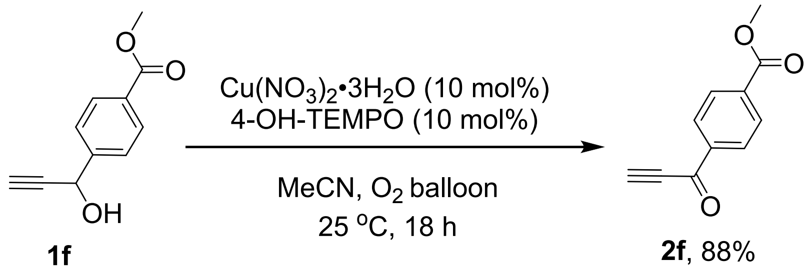
1g (40 mmol)

2g, 79%

To a 250 mL three-neck flask were added $Cu(NO_3)_2{\cdot}3H_2O$ (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**[7] (4.3224 g, 79%) as a white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 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, ≡CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.0, 144.0, 136.1, 135.9, 128.4, 79.8, 79.4.

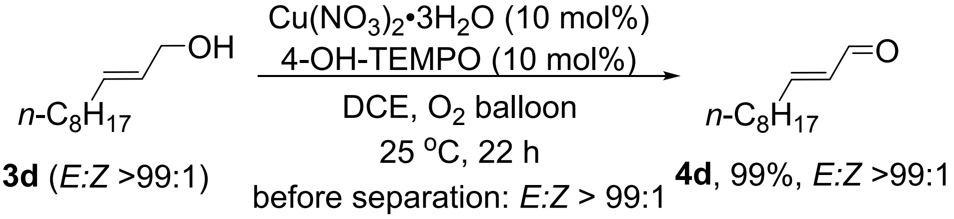
3. The reaction with 4-OH-TEMPO instead of TEMPO

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



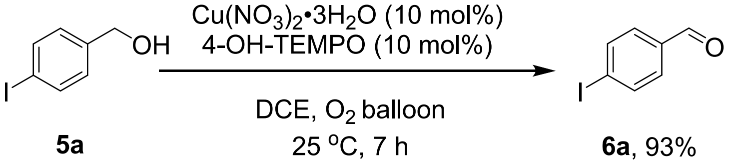
Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2$•$3H_2O$ (24.4 mg, 0.1 mmol), 4-OH-TEMPO (18.0 mg, 0.1 mmol), and **1f** (190.4 mg, 1.0 mmol) in MeCN (4 mL) afforded **2f**[7] (166.3 mg, 88%) as a white soild [eluent: petroleum ether/ethyl acetate = 30/1]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 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, $CDCl_3$): δ = 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 $Cu(NO_3)_2$•$3H_2O$ (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, $CDCl_3$): δ = 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, CDCl3): δ = 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)



Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2•3H_2O$ (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]; ^1H 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.

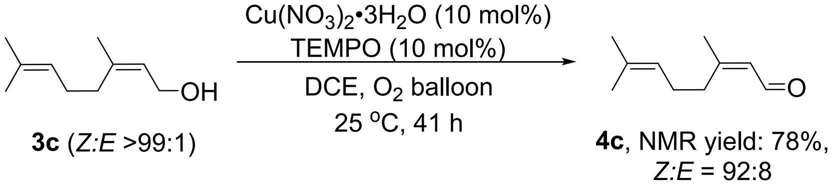
(4) Synthesis of 1-hexadecanal (**8a**) (zd-4-122)

$$n\text{-}C_{16}H_{33}OH \xrightarrow[\substack{\text{DCE, } O_2 \text{ balloon} \\ 25\ ^{\circ}C\text{, 36 h}}]{\substack{Cu(NO_3)_2•3H_2O\ (10\ mol\%) \\ \text{4-OH-TEMPO (10 mol\%)}}} n\text{-}C_{15}H_{31}CHO$$

7a **8a**, 80%

Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2•3H_2O$ (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]; ^1H 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.

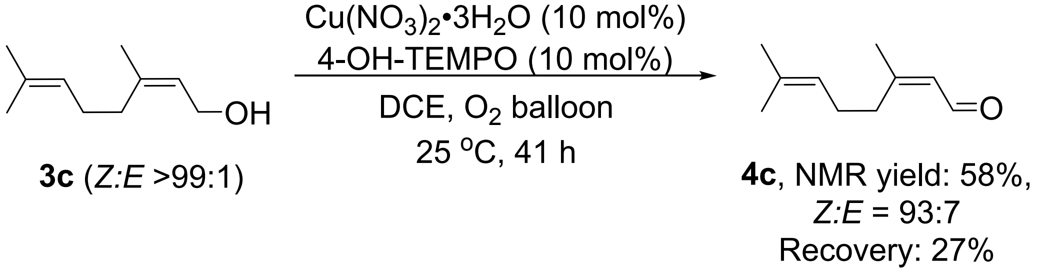
(5) Synthesis of (*Z*)-3,7-dimethyl-2,6-octadienal (**4c**) by using TEMPO as nitroxyl radical (zd-4-123)



Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2•3H_2O$ (24.4 mg, 0.1

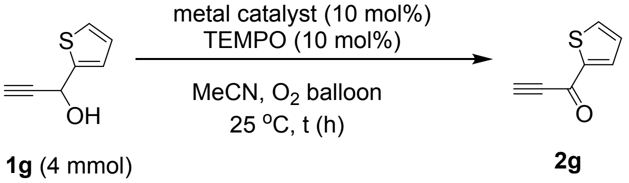
mmol), TEMPO (16.0 mg, 0.1 mmol), and **3c** (158.5 mg, 1.0 mmol) in DCE (10 mL) afforded a crude mixture of Z-**4c** and *E*-**4c** (78%, *Z:E* = 92:8, as determined by 1H NMR analysis).

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



Following **Typical Procedure 1**, the reaction of $Cu(NO_3)_2•3H_2O$ (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]



t (h)	Yield of 2g[c] (%)	Recovery of 1g[c] (%)	Yield of 2g[d] (%)	Recovery of 1g[d] (%)
0.5	29	68	34	49
1	44	49	40	44
2	78	19	58	19
3	92	0	78	10

[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_2Br_2 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 ^{1}H NMR analysis with dibromomethane as the internal standard.

[c] Using $Cu(NO_3)_2•3H_2O$ as metal catalyst.

[d] Using $Fe(NO_3)_3•9H_2O$ as metal catalyst.

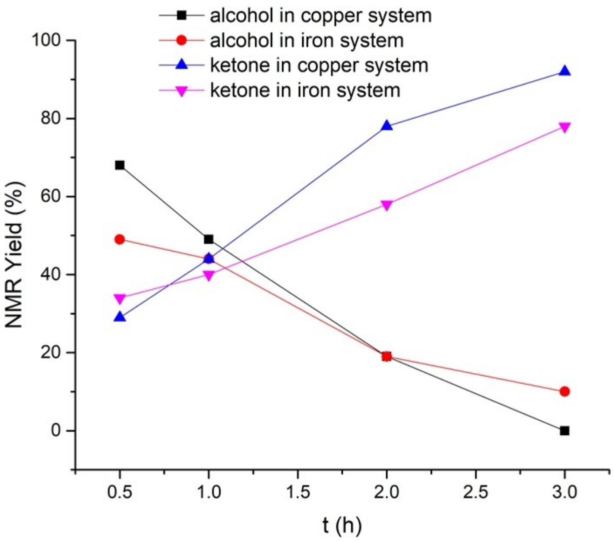
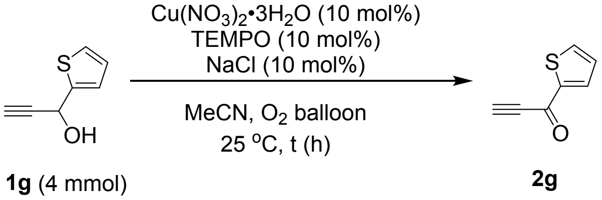


Table S2. Monitoring the reaction of 1g with and without NaCl. (zd-4-127, zd-4-128)[a,b]



t (h)	Yield of 2g with no NaCl (%)	Recovery of 1g with no NaCl (%)	Yield of 2g with NaCl (%)	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

[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_2Br_2 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.

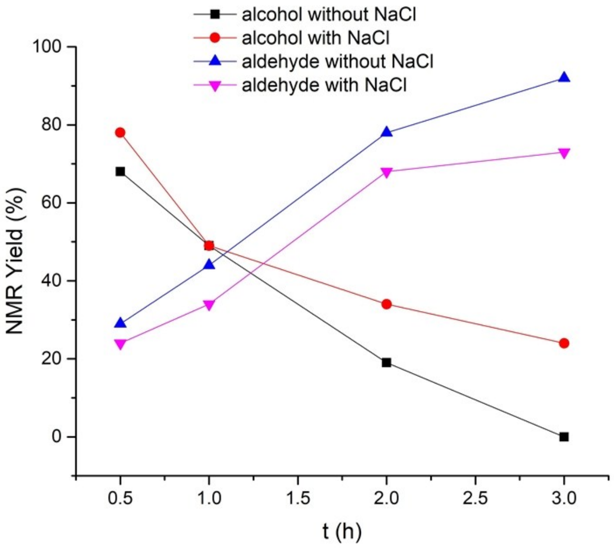
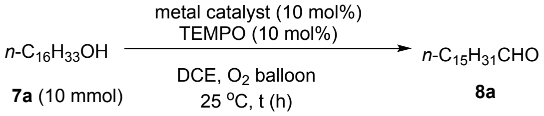


Table S3. Reaction of allphatic alcohol 7a in Cu or Fe system. (zd-4-148, zd-4-149)[a,b]



$$n\text{-}C_{16}H_{33}OH \xrightarrow[\text{DCE, } O_2 \text{ balloon, } 25\ ^{o}C,\ t\ (h)]{\text{metal catalyst (10 mol\%), TEMPO (10 mol\%)}} n\text{-}C_{15}H_{31}CHO$$

7a (10 mmol) **8a**

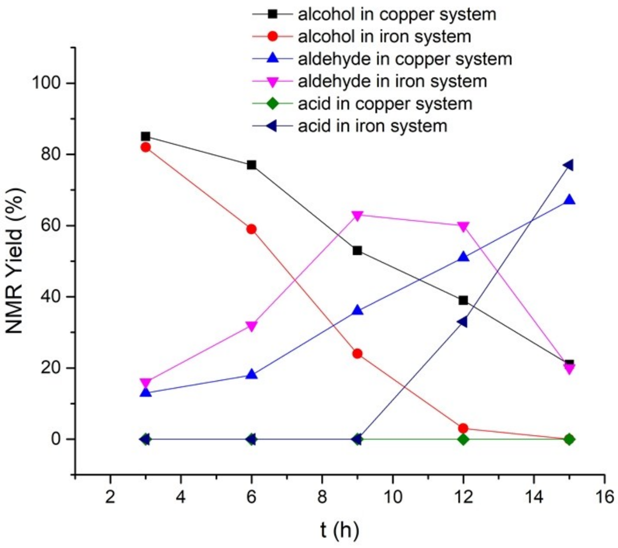
t (h)	**Yield of acid[c] (%)**	**Yield of aldehyde[c] (%)**	**Recovery of alcohol[c] (%)**	**Yield of acid[d] (%)**	**Yield of aldehyde[d] (%)**	**Recovery of alcohol[d] (%)**
3	0	13	85	0	16	82
6	0	18	77	0	32	59
9	0	36	53	0	63	24
12	0	51	39	33	60	3
15	0	67	21	77	20	0

[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 µL of CH_2Br_2 was added as internal standard for NMR analysis.

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

[c] Using $Cu(NO_3)_2{\bullet}3H_2O$ as metal catalyst.

[d] Using $Fe(NO_3)_3{\bullet}9H_2O$ as metal catalyst.



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