Cu(II)-Catalyzed Selective Aerobic Oxidation of Alcohols under Mild Condition

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SUPPORTING INFORMATION

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General Procedures

NMR spectra were measured in CDCl_3 with Me_4Si as the internal standard (400 MHz for ^1H and 100 MHz for ^{13}C). Flash chromatography was performed on silica gel (70-230 mesh) using diethyl ether and *n*-pentane as the eluent. All reagents were used as obtained commercially. All reactions were carried out under oxygen atmosphere (1 atm).

General Procedure for Catalytic Aerobic Oxidation of Primary Benzylic and Allylic Alcohols in DMSO.

A mixture of alcohol (2 mmol), 4,4'-trimethylenedipyridine (TMDP, 15.8 mg, 0.08 mmol), $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (29.7 mg, 0.08 mmol), and 0.3 mL DMSO was stirred at room temperature for 5 min, and then acetamido-TEMPO (25.6 mg, 0.12 mmol) was added to the mixture. After 5 min of stirring, DABCO (22.4 mg, 0.2 mmol) were added. The reaction mixture was vigorously stirred at room temperature under O_2 (1 atm) for 2 h. With 1 mL water added to the reaction mixture, the product was extracted with *n*-pentane (3×5 mL). The combined organic phase was washed by 3 mL water and dried by anhydrous MgSO_4 . After concentrated in vacuo, the residue was subjected to ^1H NMR analysis, and then purified by flash chromatography to afford aldehyde.

General Procedure for Catalytic Aerobic Oxidation of Primary Aliphatic or Secondary Benzylic and Allylic Alcohols in DMSO.

A mixture of alcohol (2 mmol), 4,4'-trimethylenedipyridine (TMDP, 15.8 mg, 0.08 mmol), $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (29.7 mg, 0.08 mmol), and 0.3 mL DMSO was stirred at room temperature for 5 min, and then acetamido-TEMPO (25.6 mg, 0.12 mmol) was added to the mixture. After 5 min of stirring, DABCO (22.4 mg, 0.2 mmol) were added. The reaction mixture was vigorously stirred at 40 °C for 24 h. With 1 mL water added to the reaction mixture, the product was extracted with *n*-pentane (3×5 mL). The combined organic phase was washed by 3 mL water and dried by anhydrous MgSO_4 . After

concentrated in vacuo, the residue was subjected to ^1H NMR analysis, and then purified by flash chromatography to afford aldehyde (ketone).

General Procedure for Recycling of the Catalytic System for Aerobic Oxidation of Benzylic and Allylic Alcohols.

A mixture of alcohol (2 mmol), 4,4'-trimethylenedipyridine (TMDP, 15.8 mg, 0.08 mmol), and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (29.7 mg, 0.08 mmol) was stirred at room temperature for 5 min, and 0.3 mL DMSO was added to the mixture. After 5 min of stirring, acetamido-TEMPO (25.6 mg, 0.12 mmol) and DABCO (22.4 mg, 0.2 mmol) were added. The reaction mixture was vigorously stirred at room temperature under O_2 (1 atm) for 2 h, and then extracted with *n*-pentane (5×5 mL). The combined *n*-pentane phase was concentrated in vacuo. The residue was subjected to ^1H NMR analysis, and then purified by flash chromatography to afford aldehyde. The next run was performed by adding fresh alcohol (2 mmol) to the catalytic system under the same experimental conditions for the specific reaction time (see Table 2 in paper for the times).

General Procedure for Competing Experiment between Two Alcohols.

A mixture of alcohol A (2 mmol), alcohol B (2 mmol), 4,4'-trimethylenedipyridine (TMDP, 15.8 mg, 0.08 mmol), $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (29.7 mg, 0.08 mmol), and 0.3 mL DMSO was stirred at room temperature for 5 min, and then acetamido-TEMPO (25.6 mg, 0.12 mmol) was added to the mixture. After 5 min of stirring, DABCO (22.4 mg, 0.2 mmol) were added. The reaction mixture was vigorously stirred at room temperature (or 40 °C, see Table 3 in paper) under O_2 (1 atm) for the specific time (see Table 3 in paper for the times). With 1 mL water added to the reaction mixture, the product was extracted with *n*-pentane (5×5 mL). The combined organic phase was washed by 3 mL water and dried by anhydrous MgSO_4 . After concentrated in vacuo, the residue was subjected to ^1H NMR analysis, and then purified by flash chromatography to afford aldehyde (ketone).

Characterization Data

Benzaldehyde (100-52-7). ^1H NMR (400MHz, CDCl_3) δ 7.45 (m, 2H), 7.56 (m, 1H), 7.81 (m, 2H), 9.95 (s, 1H); ^{13}C NMR (100MHz, CDCl_3) δ 128.8, 129.5, 134.3, 136.2, 192.2.

2-Methylbenzaldehyde (529-20-4). ^1H NMR (400MHz, CDCl_3) δ 2.68 (s, 3H), 7.27 (d, J = 4.0 Hz, 1H), 7.37 (m, 1H), 7.49 (m, 1H), 7.81 (d, J = 4.0 Hz, 1H), 10.28 (s, 1H); ^{13}C NMR (100MHz, CDCl_3) δ 19.5, 126.2, 131.7, 131.9, 133.5, 134.0, 140.5, 192.7.

3-Chlorobenzaldehyde (587-04-2). ^1H NMR (400MHz, CDCl_3) δ 7.46 (t, 1H), 7.58 (m, 1H), 7.74 (m, 1H), 7.81 (s, 1H), 9.95 (s, 1H); ^{13}C NMR (100MHz, CDCl_3) δ 127.9, 129.1, 130.3, 134.2, 135.3, 137.7, 190.7.

4-Methoxybenzaldehyde (123-11-5). ^1H NMR (400MHz, CDCl_3) δ 3.79 (s, 3H), 6.92 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 8.4 Hz, 2H), 9.80 (s, 1H); ^{13}C NMR (100MHz, CDCl_3) δ 55.4, 114.1, 129.7, 131.8, 164.4, 190.6.

4-Methylbenzaldehyde (104-87-0). ^1H NMR (400MHz, CDCl_3) δ 2.42 (s, 3H), 7.31 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H), 9.95 (s, 1H); ^{13}C NMR (100MHz, CDCl_3) δ 21.7, 129.6, 129.7, 134.1, 145.4, 191.8.

***trans*-Cinnamaldehyde (14371-10-9).** ^1H NMR (400MHz, CDCl_3) δ 6.73 (m, 1H), 7.44-7.59 (m, 6H), 9.72 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100MHz, CDCl_3) δ 128.4, 128.7, 129.0, 131.2, 133.9, 152.7, 193.6.

***trans,trans*-Hexa-2,4-dienal (142-83-6).** ^1H NMR (400MHz, CDCl_3) δ 1.92 (d, J = 5.6 Hz, 3 H), 6.07 (m, 1H), 6.34 (m, 2H), 7.09 (m, 1H), 9.54 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100MHz, CDCl_3) δ 18.8, 129.8, 130.0, 141.9, 152.6, 193.9.

3-Phenyl-propionaldehyde (104-53-0). ^1H NMR (400MHz, CDCl_3) δ 2.83 (t, J = 7.4 Hz, 3H), 3.01 (t, J = 7.4 Hz, 3H), 7.25-7.38 (m, 5H), 9.83 (s, 1H); ^{13}C NMR (100MHz, CDCl_3) δ 28.0, 45.2, 125.8, 126.0, 128.4, 129.2, 201.7.

Octanal (124-13-0). ^1H NMR (400MHz, CDCl_3) δ 0.81 (t, J = 7.8 Hz, 3H), 1.22-1.25 (m, 8H), 1.56 (m, 2H), 2.34 (m, 2H), 9.68 (t, J = 1.8 Hz, 1H); ^{13}C NMR (100MHz, CDCl_3) δ 13.8, 21.9, 22.4, 28.8, 28.9, 31.4, 43.7, 202.4.

2-Pyridinecarboxaldehyde (1121-60-4). ^1H NMR (400MHz, CDCl_3) δ 7.48 (m, 1H), 7.84-7.92 (m, 2H), 8.74 (d, $J = 4.0$ Hz, 1H), 10.03 (s, 1H); ^{13}C NMR (100MHz, CDCl_3) δ 121.6, 127.8, 137.0, 150.1, 152.6, 193.3.

2-Thiophenecarboxaldehyde (98-03-3). ^1H NMR (400MHz, CDCl_3) δ 7.21 (m, 1H), 7.76-7.79 (m, 2H), 9.94 (s, 1H); ^{13}C NMR (100MHz, CDCl_3) δ 128.2, 135.1, 136.3, 143.9, 183.0.

Acetophenone (98-86-2). ^1H NMR (400MHz, CDCl_3) δ 5.58 (s, 3H), 7.42-7.56 (m, 3H), 7.94 (d, $J = 7.2$ Hz, 2H); ^{13}C NMR (100MHz, CDCl_3) δ 26.5, 128.2, 128.4, 133.0, 136.9, 198.0.

2-Cyclohexen-1-one (930-68-7). ^1H NMR (400MHz, CDCl_3) δ 1.88-1.94 (m, 2H), 2.23-2.32 (m, 4H), 5.89 (d, $J = 10$ Hz, 1H), 6.90 (m, 1H); ^{13}C NMR (100MHz, CDCl_3) δ 22.5, 25.4, 37.8, 129.5, 150.6, 199.3.

^1H NMR Spectra

Figure 1.
 ^1H NMR spectrum of benzaldehyde

Figure 2.
¹H NMR spectrum of 2-methylbenzaldehyde

Figure 3.
¹H NMR spectrum of 3-chlorobenzaldehyde

Figure 4.
¹H NMR spectrum of 4-methoxybenzaldehyde

Figure 5.
¹H NMR spectrum of 4-methylbenzaldehyde

Figure 6.
¹H NMR spectrum of *trans*-cinnamaldehyde

Figure 7.
¹H NMR spectrum of *trans,trans*-hexa-2,4-dienal

Figure 8.
¹H NMR spectrum of 3-phenyl-propionaldehyde

Figure 9.
¹H NMR spectrum of octanal

Figure 10.
¹H NMR spectrum of 2-pyridinecarboxaldehyde

Figure 11.
¹H NMR spectrum of 2-thiophenecarboxaldehyde

Figure 12.
 ^1H NMR spectrum of acetophenone

Figure 13.
 ^1H NMR spectrum of 2-cyclohexen-1-one