Supporting Information

Copper(II)-catalyzed Aerobic Oxidation of Primary Alcohols to Aldehydes in Ionic Liquid [bmpy]PF₆

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Experiment section

General. All reagents were purchased from Aldrich and Fluka and used without further purification. All reactions were carried out under oxygen atmosphere (1 atm). NMR spectra were measured in CDCl₃ with Me₄Si as the internal standard on a Bruker DMX 400 (400 MHz for ¹H and 100 MHz for ¹³C); IR spectra were measured on a Shima DZU FTIR-8400S. Flash chromatography was performed on silica gel (70-230 mesh) using diethyl ether and *n*-pentane as the eluent.

Recycling of the Catalytic System for the Aerobic Oxidation of 4-Methoxybenzyl Alcohol. A mixture of 4-methoxybenzyl alcohol (276 mg, 2 mmol), 4-dimethylaminopyridine (DMAP, 24.4 mg, 0.2 mmol), and Cu(ClO₄)₂·6H₂O (37.1 mg, 0.1 mmol) was heated at 40 °C under magnetic stirring for 5 min, and [bmpy]PF₆ (0.50 g) was added to the mixture. After 5 min of stirring, acetamido-TEMPO (21.3 mg, 0.1 mmol) was added and the reaction mixture was stirred at room temperature under O₂ (1 atm) for 5 h. The reaction mixture was extracted with *n*-pentane (5 × 5 mL). The combined *n*-pentane phase was concentrated *in vacuo*, the residue was subject to ¹H NMR analysis, and then purified by flash chromatography to afford 4-methoxybenzaldehyde. The next run was performed by adding fresh 4-methoxybenzyl alcohol (276 mg, 2 mmol) to the catalytic system under the same experimental conditions for the specific reaction time (see Table 2 in paper for the times).

Typical Procedure for the Oxidation. A mixture of alcohol (2 mmol), 4-dimethylaminopyridine (DMAP, 24.4 mg, 0.2 mmol), and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (37.1 mg, 0.1 mmol) was heated at 40 °C under magnetic stirring for 5 min, and [bmpy] PF_6 (0.50 g) was added to the mixture. After 5 min of stirring, acetamido-TEMPO (21.3 mg, 0.1 mmol) was added and the reaction mixture was stirred at room temperature under O_2 (1 atm) for 5 h. The reaction mixture was extracted with *n*-pentane (5 × 5 mL) and the combined *n*-pentane phase was concentrated *in vacuo*. The residue was subject to ^1H NMR analysis, and then purified by flash chromatography to afford the aldehyde.

Benzaldehyde. A mixture of benzyl alcohol (216 mg, 2 mmol), 4-dimethylaminopyridine (DMAP, 24.4 mg, 0.2 mmol), and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (37.1 mg, 0.1 mmol) was heated at 40 °C under magnetic stirring for 5 min, and [bmpy] PF_6 (0.50 g) was added to the mixture. After 5 min of stirring, acetamido-TEMPO (21.3 mg, 0.1 mmol) was added and the reaction mixture was stirred at room temperature under O_2 (1 atm) for 5 h. The reaction mixture was extracted with *n*-pentane (5 × 5 mL) and the combined *n*-pentane phase was concentrated *in vacuo*. The residue was subject to ^1H NMR analysis, and then purified by flash chromatography to afford benzaldehyde as a colorless liquid in 92% (195 mg) yield. ^1H NMR (400MHz, CDCl_3) δ 7.44-7.82 (m, 5H), 9.95 (s, 1H); ^{13}C NMR (100MHz, CDCl_3) δ 128.8, 129.5, 134.3, 136.2, 192.2; IR (neat) 1701 cm^{-1} .

2-Methylbenzaldehyde. A mixture of 2-methylbenzyl alcohol (244 mg, 2 mmol), 4-dimethylaminopyridine (DMAP, 24.4 mg, 0.2 mmol), and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (37.1 mg, 0.1 mmol) was heated at 40 °C under magnetic stirring for 5 min, and [bmpy] PF_6 (0.50 g) was added to the mixture. After 5 min of stirring, acetamido-TEMPO (21.3 mg, 0.1 mmol) was added and the reaction mixture was stirred at room temperature under O_2 (1 atm) for 5 h. The reaction mixture was extracted with *n*-pentane (5 × 5 mL) and the combined *n*-pentane phase was concentrated *in vacuo*. The residue was subject to ^1H NMR analysis, and then purified by flash chromatography to afford 2-methylbenzaldehyde as a colorless liquid in 90% (216 mg) yield. ^1H NMR (400MHz, CDCl_3) δ 2.68 (s, 3H), 7.27 (d, J = 7.2 Hz, 1H), 7.37 (m, 1H), 7.48 (m, 1H), 7.81 (d, J = 7.6 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; IR (neat) 1695 cm^{-1} .

3-Chlorobenzaldehyde. A mixture of 3-chlorobenzyl alcohol (285 mg, 2 mmol), 4-dimethylaminopyridine (DMAP, 24.4 mg, 0.2 mmol), and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (37.1 mg, 0.1 mmol) was heated at 40 °C under magnetic stirring for 5 min, and [bmpy] PF_6 (0.50 g) was added to the mixture. After 5 min of stirring, acetamido-TEMPO (21.3 mg, 0.1 mmol) was added and the reaction mixture was stirred at room temperature under O_2 (1 atm) for 5 h. The reaction mixture was extracted with *n*-pentane (5×5 mL) and the combined *n*-pentane phase was concentrated *in vacuo*. The residue was subject to ^1H NMR analysis, and then purified by flash chromatography to afford 3-chlorobenzaldehyde as a colorless liquid in 90% (255 mg) yield. ^1H NMR (400MHz, CDCl_3) δ 7.46 (t, 1H), 7.57 (d, $J = 8.0$ Hz, 1H), 7.74 (d, $J = 7.6$ Hz, 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; IR (neat) 1701 cm^{-1} .

4-Methoxybenzaldehyde. A mixture of 4-methoxybenzyl alcohol (276 mg, 2 mmol), 4-dimethylaminopyridine (DMAP, 24.4 mg, 0.2 mmol), and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (37.1 mg, 0.1 mmol) was heated at 40 °C under magnetic stirring for 5 min, and [bmpy] PF_6 (0.50 g) was added to the mixture. After 5 min of stirring, acetamido-TEMPO (21.3 mg, 0.1 mmol) was added and the reaction mixture was stirred at room temperature under O_2 (1 atm) for 5 h. The reaction mixture was extracted with *n*-pentane (5×5 mL) and the combined *n*-pentane phase was concentrated *in vacuo*. The residue was subject to ^1H NMR analysis, and then purified by flash chromatography to afford 4-methoxybenzaldehyde as a colorless liquid in 91% (247 mg) yield. ^1H NMR (400MHz, CDCl_3) δ 3.79 (s, 3H), 6.92 (d, $J = 8.8$ 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; IR (neat) 1682 cm^{-1} .

4-Bromobenzaldehyde. A mixture of 4-bromobenzyl alcohol (374 mg, 2 mmol), 4-dimethylaminopyridine (DMAP, 24.4 mg, 0.2 mmol), $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (37.1 mg, 0.1 mmol), and [bmpy] PF_6 (0.50 g) was heated at 50 °C under magnetic stirring for 10 min, and then cooled to room temperature. After acetamido-TEMPO (21.3 mg, 0.1 mmol) added, the reaction mixture was stirred at room temperature under O_2 (1 atm) for 5 h. The reaction mixture was extracted with diethyl ether (5×5 mL) and the combined ether phase was concentrated *in vacuo*. The residue was subject to ^1H NMR analysis, and then

purified by flash chromatography to afford 4-bromobenzaldehyde as a white solid in 84% (311 mg) yield. ^1H NMR (400MHz, CDCl_3) δ 7.69 (d, $J = 8.4$ Hz, 2H), 7.75 (d, $J = 8.4$ Hz, 2H), 9.98 (s, 1H); ^{13}C NMR (100MHz, CDCl_3) δ 129.7, 130.9, 132.3, 135.0, 191.0; IR (KBr) 1682 cm^{-1} .

4-Methylbenzaldehyde. A mixture of 4-methylbenzyl alcohol (244 mg, 2 mmol), 4-dimethylaminopyridine (DMAP, 24.4 mg, 0.2 mmol), and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (37.1 mg, 0.1 mmol) was heated at $40\text{ }^\circ\text{C}$ under magnetic stirring for 5 min, and [bmpy] PF_6 (0.50 g) was added to the mixture. After 5 min of stirring, acetamido-TEMPO (21.3 mg, 0.1 mmol) was added, and the reaction mixture was stirred at room temperature under O_2 (1 atm) for 5 h. The reaction mixture was extracted with *n*-pentane ($5 \times 5\text{ mL}$) and the combined *n*-pentane phase was concentrated *in vacuo*. The residue was subject to ^1H NMR analysis, and then purified by flash chromatography to afford 4-methylbenzaldehyde as a colorless liquid in 92% (221 mg) yield. ^1H NMR (400MHz, CDCl_3) δ 2.40 (s, 3H), 7.29 (d, $J = 8.0$ Hz, 2H), 7.74 (d, $J = 8.0$ Hz, 2H), 9.92 (s, 1H); ^{13}C NMR (100MHz, CDCl_3) δ 21.7, 129.6, 129.7, 134.1, 145.4, 191.8; IR (neat) 1703 cm^{-1} .

4-Nitrobenzaldehyde. A mixture of 4-nitrobenzyl alcohol (306 mg, 2 mmol), 4-dimethylaminopyridine (DMAP, 24.4 mg, 0.2 mmol), $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (37.1 mg, 0.1 mmol), and [bmpy] PF_6 (0.50 g) was heated at $50\text{ }^\circ\text{C}$ under magnetic stirring for 10 min, and then cooled to room temperature. After acetamido-TEMPO (21.3 mg, 0.1 mmol) added, the reaction mixture was stirred at room temperature under O_2 (1 atm) for 5 h. The reaction mixture was extracted with diethyl ether ($5 \times 5\text{ mL}$) and the combined ether phase was concentrated *in vacuo*. The residue was subject to ^1H NMR analysis, and then purified by flash chromatography to afford 4-nitrobenzaldehyde as a white solid in 81% (245 mg) yield. ^1H NMR (400MHz, CDCl_3) δ 8.10 (d, $J = 8.0$ Hz, 2H), 8.41 (d, $J = 8.0$ Hz, 2H), 10.18 (s, 1H); ^{13}C NMR (100MHz, CDCl_3) δ 124.2, 130.4, 139.9, 151.0, 190.2; IR (KBr) 1709 cm^{-1} .

3,4-Dimethoxybenzaldehyde. A mixture of 3,4-dimethoxybenzyl alcohol (336 mg, 2 mmol), 4-dimethylaminopyridine (DMAP, 24.4 mg, 0.2 mmol), and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (37.1 mg, 0.1 mmol) was heated at $40\text{ }^\circ\text{C}$ under magnetic stirring for 5 min, and

[bmpy]PF₆ (0.50 g) was added to the mixture. After 5 min of stirring, acetamido-TEMPO (21.3 mg, 0.1 mmol) was added and the reaction mixture was stirred at room temperature under O₂ (1 atm) for 5 h. The reaction mixture was extracted with diethyl ether (5 × 5 mL) and the combined ether phase was concentrated *in vacuo*. The residue was subject to ¹H NMR analysis, and then purified by flash chromatography to afford 3,4-dimethoxybenzaldehyde as a solid in 89% (295 mg) yield. ¹H NMR (400MHz, CDCl₃) δ 3.88 (s, 3H), 3.91 (s, 3H), 6.93 (d, J = 8.4 Hz, 1H), 7.35 (s, 1H), 7.40 (d, J = 8.0 Hz, 1H), 9.79 (s, 1H); ¹³C NMR (100MHz, CDCl₃) δ 55.8, 56.0, 108.7, 110.2, 126.7, 130.0, 149.4, 154.3, 190.7; IR (KBr) 1682 cm⁻¹.

Cinnamaldehyde. A mixture of cinnamyl alcohol (268 mg, 2 mmol), 4-dimethylaminopyridine (DMAP, 24.4 mg, 0.2 mmol), and Cu(ClO₄)₂·6H₂O (37.1 mg, 0.1 mmol) was heated at 40 °C under magnetic stirring for 5 min, and [bmpy]PF₆ (0.50 g) was added to the mixture. After 5 min of stirring, acetamido-TEMPO (21.3 mg, 0.1 mmol) was added and the reaction mixture was stirred at room temperature under O₂ (1 atm) for 5 h. The reaction mixture was extracted with *n*-pentane (5 × 5 mL) and the combined *n*-pentane phase was concentrated *in vacuo*. The residue was subject to ¹H NMR analysis, and then purified by flash chromatography to afford cinnamaldehyde as a colorless liquid in 89% (235 mg) yield. ¹H NMR (400MHz, CDCl₃) δ 6.73 (m, 1H), 7.44-7.59 (m, 6H), 9.72 (d, J = 7.6 Hz, 1H); ¹³C NMR (100MHz, CDCl₃) δ 128.4, 128.7, 129.0, 131.2, 133.9, 152.7, 193.6; IR (neat) 1674 cm⁻¹.

Hexa-2,4-dienal. A mixture of *trans,trans*-2,4-hexadien-1-ol (196 mg, 2 mmol), 4-dimethylaminopyridine (DMAP, 24.4 mg, 0.2 mmol), and Cu(ClO₄)₂·6H₂O (37.1 mg, 0.1 mmol) was heated at 40 °C under magnetic stirring for 5 min, and [bmpy]PF₆ (0.50 g) was added to the mixture. After 5 min of stirring, acetamido-TEMPO (21.3 mg, 0.1 mmol) was added and the reaction mixture was stirred at room temperature under O₂ (1 atm) for 5 h. The reaction mixture was extracted with *n*-pentane (5 × 5 mL) and the combined *n*-pentane phase was concentrated *in vacuo*. The residue was subject to ¹H NMR analysis, and then purified by flash chromatography to afford hexa-2,4-dienal as a colorless liquid in 77% (148 mg) yield. ¹H NMR (400MHz, CDCl₃) 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; IR (neat) 1732cm^{-1} .

3-Phenyl-propionaldehyde. A mixture of 3-phenyl-1-propanol (272 mg, 2 mmol), 4-dimethylaminopyridine (DMAP, 24.4 mg, 0.2 mmol), and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (37.1 mg, 0.1 mmol) was heated at 40°C under magnetic stirring for 5 min, and [bmpy] PF_6 (0.50 g) was added to the mixture. After 5 min of stirring, acetamido-TEMPO (21.3 mg, 0.1 mmol) was added and the reaction mixture was stirred at 40°C under O_2 (1 atm) for 24 h. The reaction mixture was extracted with *n*-pentane (5×5 mL) and the combined *n*-pentane phase was concentrated *in vacuo*. The residue was subject to ^1H NMR analysis, and then purified by flash chromatography to afford 3-phenyl-propionaldehyde as a colorless liquid in 61% (163 mg) yield. ^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; IR (neat) 1718cm^{-1} .

Octanal. A mixture of 1-octanol (2 mmol), 4-dimethylaminopyridine (DMAP, 24.4 mg, 0.2 mmol), and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (37.1 mg, 0.1 mmol) was heated at 40°C under magnetic stirring for 5 min, and [bmpy] PF_6 (0.50 g) was added to the mixture. After 5 min of stirring, acetamido-TEMPO (21.3 mg, 0.1 mmol) was added and the reaction mixture was stirred at 40°C under O_2 (1 atm) for 24 h. The reaction mixture was extracted with *n*-pentane (5×5 mL) and the combined *n*-pentane phase was concentrated *in vacuo*. The residue was subject to ^1H NMR analysis, and then purified by flash chromatography to afford the octanal as a colorless liquid in 54% (138 mg) yield. ^1H NMR (400MHz, CDCl_3) δ 0.86 (t, $J = 7.0$ Hz, 3H), 1.27-1.62 (m, 10H), 2.41 (t, $J = 7.0$ Hz, 2H), 9.76 (s, 1H); ^{13}C NMR (100MHz, CDCl_3) δ 13.7, 22.2, 22.5, 28.9, 29.4, 31.6, 43.7, 201.0; IR (neat) 1720cm^{-1} .