Supporting Information

Merging visible-light photoredox and copper catalysis in catalytic aerobic oxidation of amines to nitriles

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General experimental:
All reactions were performed under an oxygen atmosphere (purity ≥ 99.999%) using standard Schlenk-type glasswares on a dual-manifold Schlenk line. Flash column chromatography was performed on silica 230 – 400 mesh. \textsuperscript{1}H-NMR and \textsuperscript{13}C-NMR spectra were recorded on Bruker Advance 500 and Bruker Advance 300 spectrometer at ambient temperature in CDCl\textsubscript{3}. Chemical shift values (\(\delta\)) are reported in ppm and calibrated to tetramethylsilane (TMS, 0.00 ppm) or residual solvent (7.26 ppm in CDCl\textsubscript{3}) for \textsuperscript{1}H NMR and to CDCl\textsubscript{3} (77.16 ppm) for \textsuperscript{13}C NMR. Gas chromatographic (GC) analysis was acquired on a JieDao TECH GC-1690 equipped with a flame-ionization detector. GC yields of the reactions were determined with naphthalene as the internal standard.

The photocatalyst of Ru(bpy)\textsubscript{3}Cl\textsubscript{2}·6H\textsubscript{2}O was purchased from J & K Scientific. The copper catalysts and other transition metal catalysts were purchased from Energy Chemical. All the other reagents mentioned in this text were purchased from commercial sources and used without purification. All the solvents were refluxed with CaH\textsubscript{2} for 12h, distilled and further dried over 4 Å activated molecular sieves for 24h under an argon atmosphere. Two 15W Blue LED lamps were used to irradiate the reaction mixtures.

Aerobic oxidation amines to nitriles via merging photoredox and copper catalysis: general procedure
To an oven-dried Schlenk tube were added Ru(bpy)\textsubscript{3}Cl\textsubscript{2}·6H\textsubscript{2}O (0.01 mmol, 2 mol%), CuBr (0.05 mmol, 10mol%) and LiOBu\textsubscript{t} (0.1 mmol, 20mol%), then the tube was evacuated and backfilled with O\textsubscript{2} (this process was repeated three times). To this Schlenk tube were added amine (0.5 mmol) and DMSO (3.0 mL). The Schlenk tube was adapted to O\textsubscript{2} balloon, and the reaction mixture was stirred for 18h at room temperature with blue LED (2×15W) irradiation. After diluted by adding EtOAc, the reaction was quenched with aqueous NH\textsubscript{4}Cl. The aqueous layer was extracted with EtOAc three times. The combined organic layer was washed with aqueous NaHSO\textsubscript{3} and dried over anhydrous MgSO\textsubscript{4}, filtered, and evaporated. The residue was purified by column chromatography afford the product. The products obtained herein are known compounds, and spectral properties of all products are consistent with literature values.

**benzonitrile (2a):**\textsuperscript{[1]}

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 7.67 – 7.54 (m, 3H), 7.45 (t, \(J = 7.7\) Hz, 2H). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 132.53, 131.77, 128.88, 118.51, 112.06.

**4-methylbenzonitrile (2b):**\textsuperscript{[2]}

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$^1$H NMR (500 MHz, CDCl$_3$) δ 7.48 (d, $J = 8.1$ Hz, 2H), 7.23 (t, $J = 7.1$ Hz, 2H), 2.38 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 143.56, 131.83, 129.71, 118.95, 109.16, 21.60.

4-methoxybenzonitrile (2c):$^{[2]}$
$^1$H NMR (300 MHz, CDCl$_3$) δ 7.60 – 7.53 (m, 2H), 6.99 – 6.91 (m, 2H), 3.85 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 162.81, 133.83, 119.11, 114.71, 103.79, 55.47.

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.69 (ddd, $J = 8.9$, 4.9, 2.5 Hz, 2H), 7.22 – 7.15 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 165.16 (d, $J = 256.6$ Hz), 134.80 (d, $J = 9.3$ Hz), 118.14, 116.98 (d, $J = 22.7$ Hz), 108.70 (d, $J = 3.6$ Hz). $^{19}$F NMR (471 MHz, CDCl$_3$) δ -102.43.

4-(trifluoromethyl)benzonitrile (2e):$^{[2]}$
$^1$H NMR (500 MHz, CDCl$_3$) δ 7.81 (d, $J = 8.2$ Hz, 2H), 7.77 (d, $J = 8.2$ Hz, 12H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 134.68 (q, $J = 33.6$ Hz), 132.81 (s), 126.31 (q, $J = 3.7$ Hz), 123.17 (q, $J = 273.4$ Hz), 117.55 (s), 116.20 (s). $^{19}$F NMR (471 MHz, CDCl$_3$) δ -63.54.

1-naphthonitrile (2f):$^{[2]}$
$^1$H NMR (500 MHz, CDCl$_3$) δ 8.18 (d, $J = 8.2$ Hz, 1H), 8.01 (d, $J = 8.3$ Hz, 1H), 7.90 – 7.82 (m, 2H), 7.63 (ddd, $J = 8.3$, 7.0, 1.2 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.45 (dd, $J = 8.3$, 7.2 Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 133.24, 132.89, 132.55, 132.29, 128.65, 128.55, 127.51, 125.04, 124.89, 117.78, 110.13.

2-methylbenzonitrile (2h):$^{[2]}$
$^1$H NMR (500 MHz, CDCl$_3$) δ 7.59 (d, $J = 7.7$ Hz, 1H), 7.48 (t, $J = 7.7$ Hz, 1H), 7.31 (d, $J = 7.7$ Hz, 1H), 7.27 (t, $J = 7.6$ Hz, 1H), 2.55 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 141.89, 132.66, 132.47, 130.24, 126.24, 118.12, 112.75, 20.44.

2-methoxybenzonitrile (2i):$^{[3]}$
$^1$H NMR (500 MHz, CDCl$_3$) δ 7.61 – 7.51 (m, 2H), 7.06 – 6.97 (m, 2H), 3.94 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 161.36, 134.49, 133.86, 120.87, 116.59, 111.42, 101.95, 56.11.
2,4-dimethoxybenzonitrile (2j):[4]
$^1$H NMR (500 MHz, CDCl$_3$) δ 7.48 (d, $J = 8.5$ Hz, 1H), 6.51 (d, $J = 8.6$ Hz, 1H), 6.46 (s, 1H), 3.90 (s, 3H), 3.86 (s, 3H).  $^{13}$C NMR (126 MHz, CDCl$_3$) δ 164.77, 163.00, 135.08, 117.06, 105.87, 98.66, 94.23, 56.11, 55.84.

nicotinonitrile (2k):[5]
$^1$H NMR (300 MHz, CDCl$_3$) δ 8.96 – 8.89 (m, 1H), 8.85 (dd, $J = 5.0$, 1.6 Hz, 1H), 8.01 (dt, $J = 8.0$, 1.9 Hz, 1H), 7.48 (ddd, $J = 7.9$, 5.0, 0.8 Hz, 1H).  $^{13}$C NMR (75 MHz, CDCl$_3$) δ 152.94, 152.39, 139.21, 123.60, 116.45, 110.05.

thiophene-2-carbonitrile (2l):[2]
$^1$H NMR (500 MHz, CDCl$_3$) δ 7.64 (d, $J = 3.7$ Hz, 1H), 7.62 (d, $J = 5.1$ Hz, 1H), 7.14 (t, $J = 4.4$ Hz, 1H).  $^{13}$C NMR (126 MHz, CDCl$_3$) δ 137.51, 132.68, 127.75, 114.33, 110.02.

dodecanenitrile (2m):[6]
$^1$H NMR (500 MHz, CDCl$_3$) δ 2.33 (t, $J = 7.2$ Hz, 2H), 1.69 – 1.61 (m, 2H), 1.48 – 1.40 (m, 2H), 1.33 – 1.24 (m, 14H), 0.88 (t, $J = 6.9$ Hz, 3H).  $^{13}$C NMR (126 MHz, CDCl$_3$) δ 119.99, 32.03, 29.85, 29.69, 29.65, 29.44, 28.91, 28.82, 25.54, 22.82, 17.28, 14.24.

palmitonitrile (2n):[7]
$^1$H NMR (500 MHz, CDCl$_3$) δ 2.33 (t, $J = 7.1$ Hz, 2H), 1.69 – 1.61 (m, 2H), 1.48 – 1.40 (m, 2H), 1.29 – 1.26 (m, 22H), 0.88 (t, $J = 6.8$ Hz, 3H).  $^{13}$C NMR (126 MHz, CDCl$_3$) δ 119.95, 32.05, 29.81, 29.79, 29.77, 29.76, 29.71, 29.62, 29.48, 29.43, 28.89, 28.79, 25.51, 22.81, 17.24, 14.23.

Reference