

Supporting Information

Merging cobalt and photoredox catalysis for C8–H Alkoxylation of 1-naphthylamine derivatives with alcohols

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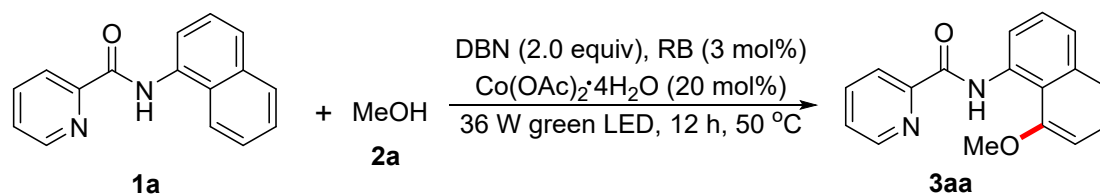
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1. General considerations

The ^1H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometer (400/100 MHz). All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, J , are reported in Hertz (Hz). High resolution mass spectroscopy data of the product were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI). All the solvents and commercially available reagents were purchased from commercial suppliers. Products were purified by flash chromatography on 200–300 mesh silica gels, SiO_2 .

2. Representative procedure for the model reaction

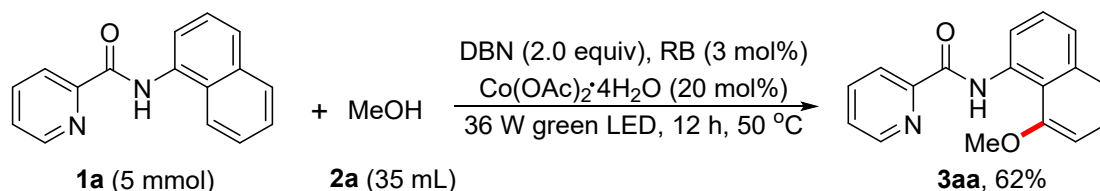
2.1 Representative procedure for the reaction in 0.20 mmol scale



A 15 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with *N*-(naphthalen-1-yl)picolinamide (**1a**, 0.20 mmol), methanol (**2a**, 3.0 mL), $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (20 mol%), rose bengal (3 mol%) and DBN (2.0 equiv.). The reaction vessel was stirred at 50 °C under green LED (36 W) irradiation in air for 12 h. After completion of the reaction, the mixture was concentrated to yield the crude product, which

was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate) to give the desired product **3aa** (73% yield).

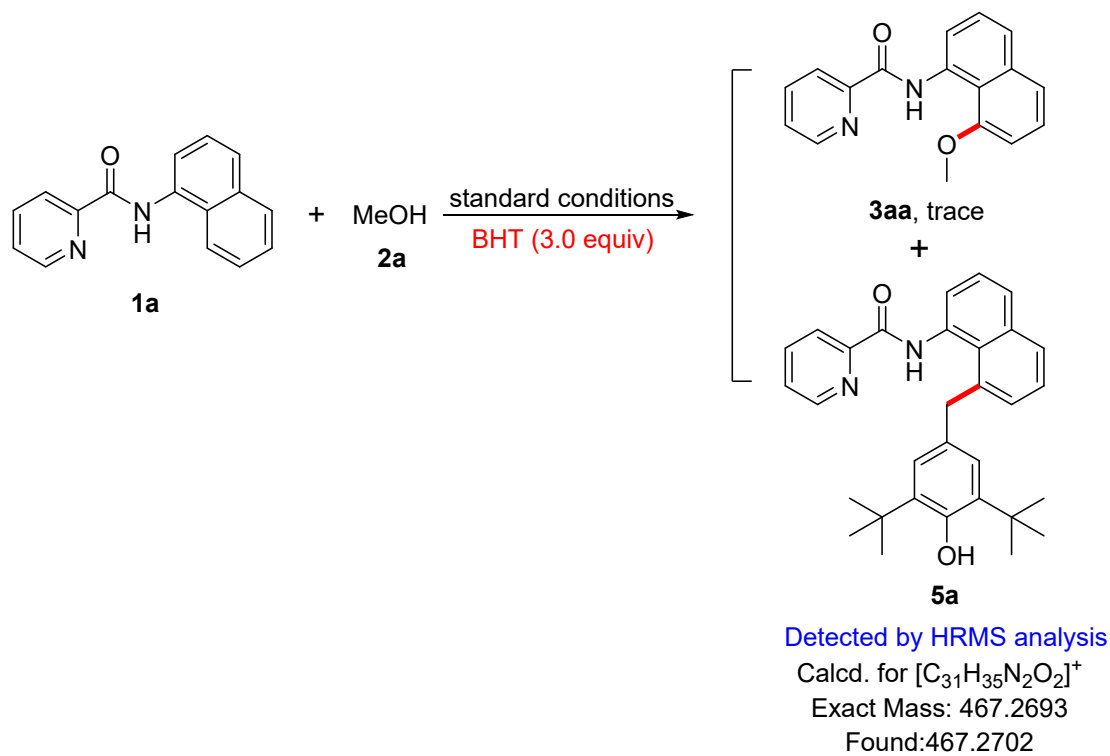
2.2 Representative procedure for the reaction in 5.0 mmol scale



A 100 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with *N*-(naphthalen-1-yl)picolinamide (**1a**, 1.24 g, 5.0 mmol), methanol (**2**, 35 mL), $\text{Co(OAc)}_2\cdot 4\text{H}_2\text{O}$ (20 mol%), rose bengal (3 mol%) and DBN (2.0 equiv.). The reaction vessel was stirred at 50 °C under green LED (36 W) irradiation in air for 18 h. After completion of the reaction, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, EtOAc/petroleum ether = 1:10) to give the desired product **3aa** in 62% yield.

3. Preliminary mechanistic investigation

3.1 The free-radical inhibition and trapping experiment



A 5 mL oven-dried sealed tube equipped with a magnetic stirrer bar was charged with *N*-(naphthalen-1-yl)picolinamide (**1a**, 0.20 mmol), methanol (**2a**, 3 mL), $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (20 mol%), rose bengal (3 mol%), DBN (2.0 equiv) and BHT (3 equiv). The reaction vessel was stirred at 50 °C under green LED (36 W) irradiation in air for 12 h. After completion of the reaction, TLC detection showed that the reaction was completely inhibited, and only trace amount of desired product **3aa** was found, indicating a radical pathway involved in the reaction. Meanwhile, the key intermediate was captured by BHT as a free-radical trapping reagent and its corresponding adduct **5a** was detected by high-resolution mass

spectrum (HRMS) analysis (Figure S1).

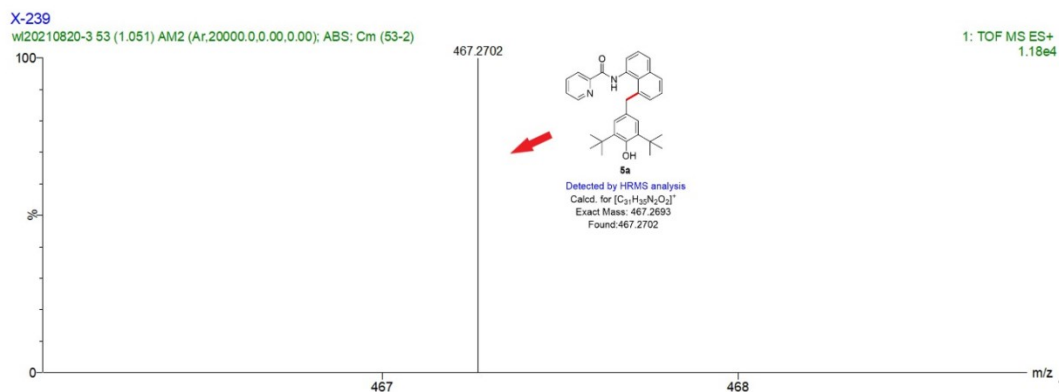


Figure S1. HRMS analysis of an adduct **5a** from a reaction of free-radical with BHT

3.2 Determination of superoxide radicals by EPR

In order to determine the active species of oxygen involved in the present reaction, 5,5-dimethyl-pyrroline-*N*-oxide (DMPO) was employed to capture $O_2^{\bullet-}$. There was no signal when DMPO was added into a solution of **1a**, DBN, RB and $Co(OAc)_2$ in air-saturated CH_3OH in the absence of light irradiation (Figure S2A). Irradiation of air-saturated the above CH_3OH solution in air with 36 W green LED resulted in the formation of a strong characteristic signal of $O_2^{\bullet-}$ adduct with DMPO (Figure S2B–2D). As the reaction time was prolonged, a series of stronger characteristic signal of $O_2^{\bullet-}$ were observed, indicating the formation of $O_2^{\bullet-}$ during the reaction (Figure S2B–2D).

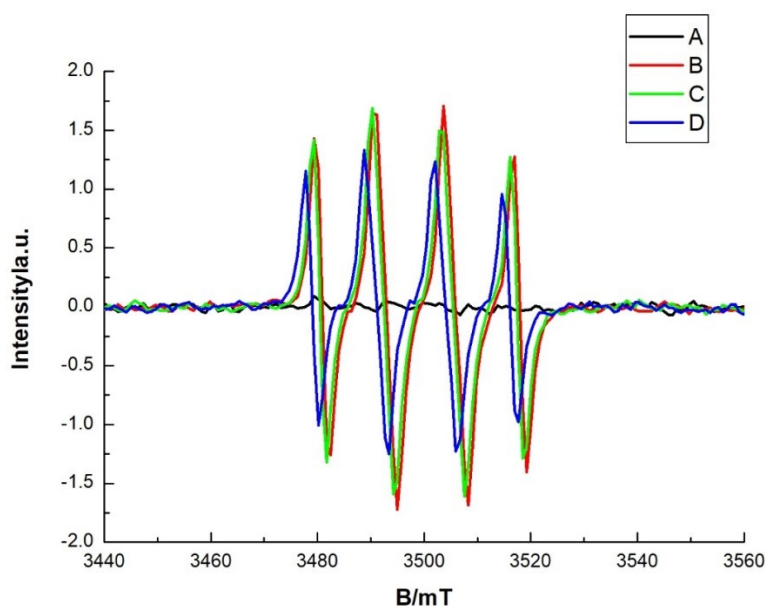


Figure S2 Electron paramagnetic resonance (EPR) spectra of $O_2^{\bullet-}$

(A) A solution of DMPO (0.20 mol/L) with **1a**, DBN, RB and $Co(OAc)_2$ in air-saturated CH_3OH without light irradiation;

(B) A solution of DMPO (0.20 mol/L) with **1a**, DBN, RB and $Co(OAc)_2$ in air-saturated CH_3OH 36 W green LED irradiation for 90 s;

(C) A solution of DMPO (0.20 mol/L) with **1a**, DBN, RB and $Co(OAc)_2$ in air-saturated CH_3OH under 36 W green LED irradiation for 60 s;

(D) A solution of DMPO (0.20 mol/L) with **1a**, DBN, RB and $Co(OAc)_2$ in air-saturated CH_3OH under 36 W green LED irradiation for 30 s.

3.3 Cyclic voltammetry (CV) measurements

The cyclic voltammetry (CV) measurements of substrate **1a** and rose bengal (RB) were recorded in an electrolyte of $n-Bu_4NBF_4$ (0.1 M) in MeOH (5 mL) using a glassy carbon electrode (diameter, 3 mm), a Pt wire auxiliary electrode and a Ag/AgCl reference electrode (Figure S3 and S4). The results ($E_{p/2}(\mathbf{1a}/\mathbf{1a}^+) = +1.429$ V vs Ag/AgCl, and $E_{p/2}(RB^*/RB^{\bullet-}) = +0.889$ V vs Ag/AgCl) indicated that **1a** into $\mathbf{1a}^+$ could not be oxidized by RB^* under the present reaction conditions.

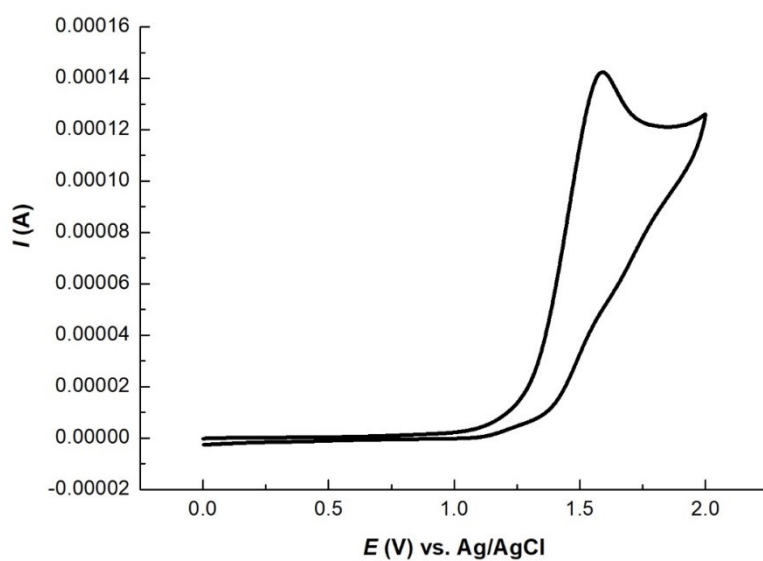


Figure S3. Cyclic voltammogram of **1a** in CH₃OH (5.0 mL, containing 0.10 M of *n*-Bu₄NBF₄) using glassy carbon electrode, Pt wire as counter electrode, and Ag/AgCl reference electrode at 100 mV/s scan rate.

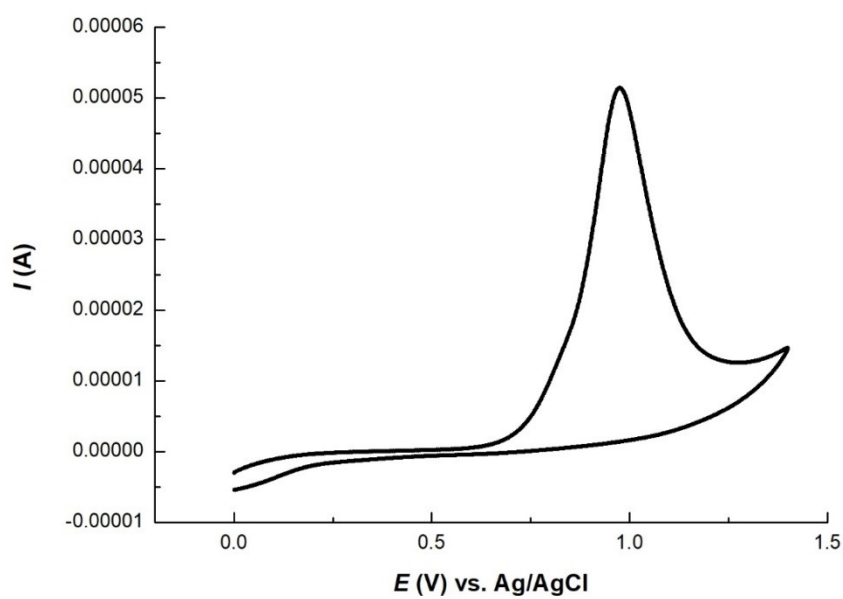
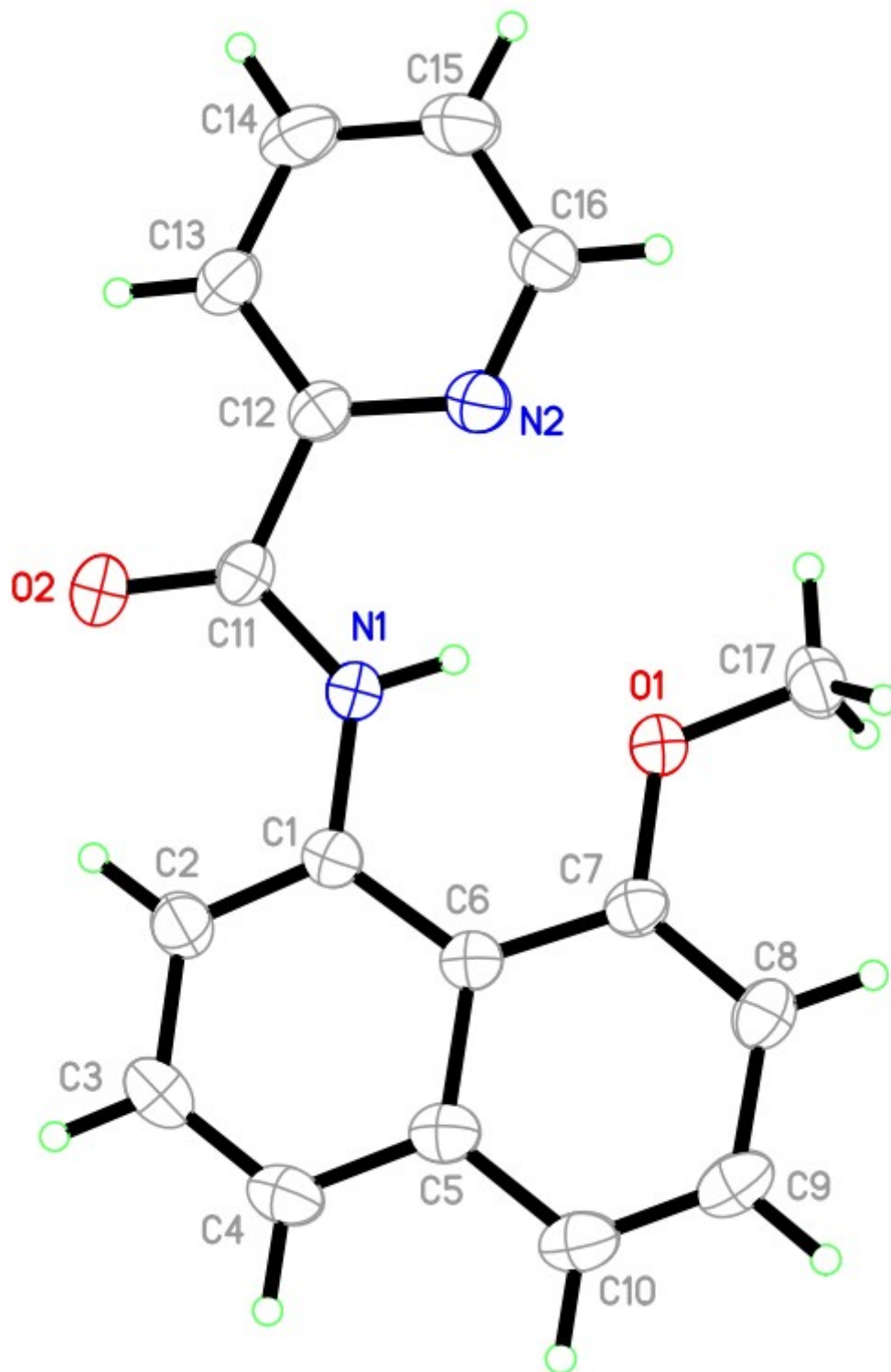


Figure S4. Cyclic voltammogram of RB in CH₃OH (5.0 mL, containing 0.10 M of *n*-Bu₄NBF₄) using glassy carbon electrode, Pt wire as counter electrode, and Ag/AgCl reference electrode at 100 mV/s scan rate.

**4. X-Ray single crystal diffraction analysis of 3aa (CCDC:
2104863)**



5. ¹H and ¹³C NMR spectra of the products

