## **Supporting Information**

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

Zhaoliang Xu,<sup>*t,a,b*</sup> Yu Hu,<sup>*t,a*</sup> Lei Wang<sup>*\*a,b,d*</sup> Mingli Sun,<sup>*a,b*</sup> and Pinhua Li,<sup>*\*a,c,d*</sup>

 <sup>a</sup> Department of Chemistry; Key Laboratory of Green and Precise Synthetic Chemistry, Ministry of Education, Huaibei Normal University, Huaibei, Anhui 235000, P. R. China Fax: (+86)-561-309-0518; phone: (+86)-561-380-2069 E-mail: jieliu\_1024@163.com; pphuali@126.com

- <sup>b</sup> Advanced Research Institute and Department of Chemistry, Taizhou University, Taizhou, Zhejiang 318000, P. R. China; E-mail: leiwang@chnu.edu.cn
- <sup>c</sup> Department of Chemistry, Anhui Polytechnic University, Wuhu, Anhui 241000, P. R. China
- <sup>d</sup> State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, P. R. China

<sup>†</sup> These authors contributed equally to this work.

#### **Contents**

1. General considerations	.2
2. Representative procedure for the model reaction	.2
3. Preliminary mechanistic investigation	4
4. X-Ray single crystal diffraction analysis of <b>3aa</b>	8
5. <sup>1</sup> H and <sup>13</sup> C NMR spectra of the products	10

#### 1. General considerations

The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometer (400/100 MHz). All chemical shifts are given as  $\delta$  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<sub>2</sub>.

#### 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), Co(OAc)<sub>2</sub>·4H<sub>2</sub>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),  $Co(OAc)_2 \cdot 4H_2O$  (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), Co(OAc)<sub>2</sub>·4H<sub>2</sub>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)<sub>2</sub> in air-saturated CH<sub>3</sub>OH in the absence of light irradiation (Figure S2A). Irradiation of air-saturated the above CH<sub>3</sub>OH 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<sub>2</sub><sup>--</sup>

(A) A solution of DMPO (0.20 mol/L) with 1a, DBN, RB and Co(OAc)<sub>2</sub> in airsaturated CH<sub>3</sub>OH without light irradiation;

(B) A solution of DMPO (0.20 mol/L) with 1a, DBN, RB and Co(OAc)<sub>2</sub> in airsaturated CH<sub>3</sub>OH 36 W green LED irradiation for 90 s;

(C) A solution of DMPO (0.20 mol/L) with 1a, DBN, RB and Co(OAc)<sub>2</sub> in airsaturated CH<sub>3</sub>OH 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 airsaturated CH<sub>3</sub>OH 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<sub>4</sub>NBF<sub>4</sub> (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 ( $E_{p/2}$  (**1a**/**1a**<sup>++</sup>) = +1.429 V vs Ag/AgCl, and  $E_{p/2}$  (RB<sup>\*</sup>/RB<sup>+-</sup>) = +0.889 V vs Ag/AgCl) indicated that **1a** into **1a**<sup>++</sup> could not be oxidized by RB<sup>\*</sup> under the present reaction conditions.



**Figure S3.** Cyclic voltammogram of **1a** in CH<sub>3</sub>OH (5.0 mL, containing 0.10 M of n-Bu<sub>4</sub>NBF<sub>4</sub>) 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 CH<sub>3</sub>OH (5.0 mL, containing 0.10 M of *n*-Bu<sub>4</sub>NBF<sub>4</sub>) 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)



### checkCIF/PLATON report

Structure factors have been supplied for datablock(s) T

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

#### Datablock: T

Bond precision:	C-C = 0.0023 A	Wavelength=0.71073	
Cell:	a=11.631(2)	b=14.557(3)	c=15.796(3)
Temperature:	alpha=90 223 K	beta=90	gamma=90
	Calculated	Reported	L
Volume	2674.5(9)	2674.5(9	)
Space group	Pbca	Pbca	
Hall group	-P 2ac 2ab	-P 2ac 2	ab
Moiety formula	C17 H14 N2 O2	C17 H14	N2 02
Sum formula	C17 H14 N2 O2	C17 H14	N2 02
Mr	278.30	278.30	
Dx,g cm-3	1.382	1.382	
Z	8	8	
Mu (mm-1)	0.092	0.092	
F000	1168.0	1168.0	
F000'	1168.51		
h,k,lmax	15,19,21	15,18,21	
Nref	3414	3352	
Tmin, Tmax	0.985,0.992	0.953,0.	998
Tmin'	0.984		
Correction metho AbsCorr = MULTI	od= # Reported T Li -SCAN	mits: Tmin=0.953 I	max=0.998
Data completenes	ss= 0.982	Theta(max) = $28.5$	80
R(reflections)=	0.0436( 1878)		wR2(reflections)= 0.1143( 3352)
S = 1.001	Npar= 19	91	

The following ALERTS were generated. Each ALERT has the format **test-name\_ALERT\_alert-type\_alert-level**. Click on the hyperlinks for more details of the test.



### 5. <sup>1</sup>H and <sup>13</sup>C NMR spectra of the products







![](_page_13_Figure_0.jpeg)

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

![](_page_14_Figure_0.jpeg)

![](_page_15_Figure_0.jpeg)

![](_page_16_Figure_0.jpeg)

![](_page_17_Figure_0.jpeg)

![](_page_18_Figure_0.jpeg)

![](_page_19_Figure_0.jpeg)

![](_page_20_Figure_0.jpeg)

![](_page_21_Figure_0.jpeg)

![](_page_22_Figure_0.jpeg)

![](_page_23_Figure_0.jpeg)

![](_page_24_Figure_0.jpeg)

![](_page_25_Figure_0.jpeg)

![](_page_26_Figure_0.jpeg)

![](_page_27_Figure_0.jpeg)

![](_page_28_Figure_0.jpeg)

![](_page_29_Figure_0.jpeg)

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

![](_page_30_Figure_0.jpeg)

![](_page_31_Figure_0.jpeg)

![](_page_32_Figure_0.jpeg)

![](_page_33_Figure_0.jpeg)

![](_page_34_Figure_0.jpeg)

![](_page_35_Figure_0.jpeg)

![](_page_36_Figure_0.jpeg)

![](_page_37_Figure_0.jpeg)

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

![](_page_38_Figure_0.jpeg)