Supporting Information

Visible-Light-Induced Oxidative Formylation of *N*-Alkyl-*N*-(prop-2-yn-1-yl)anilines with Molecular Oxygen in the Absence of an External Photosensitizer

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1. General considerations

All ¹H NMR and ¹³C NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometers (400 MHz or 100 MHz, respectively). 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 (HRMS) data of the product were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI). GC-MS data of the product were collected on a Waters Micromass GCT instrument. The CO and CO₂ were analyzed by a TENSOR 27 Fourier transform infrared spectrometer (FT-IR).

According to the literature (L. Zhang, S. Chen, Y. Gao, P. Zhang, Y. Wu, G. Tang, Y. Zhao, *Org. Lett.* 2016, **18**, 1286–1289), the preparation route to starting material *N*,*N*-di(prop-2-yn-1-yl)aniline **(1a)** is as following.



2. Typical procedure for the oxidative formylation of N,N-di(prop-2-yn-1-

yl)aniline with molecular oxygen



A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with N,N-di(prop-2-yn-1-yl)aniline (**1a**, 33.8 mg, 0.20 mmol) and acetone (2.0 mL). The reaction vessel was exposed to blue LED (420–425 nm, 1.5 W) irradiation at room temperature in air with stirring 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, petroleum ether/ethyl acetate = 3/1 to 15/1) to give the desired product **2a** (24.2 mg, 76% yield).

3. Preliminary mechanistic study

3.1 Free radical-trapping experiments

3.1.1 Free radical-trapping of substrate 10 with TEMPO



A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with N,N-di(prop-2-yn-1-yl)(4-cyanophenyl)amine (**1o**, 38.8 mg, 0.20 mmol), TEMPO (62.5 mg, 0.40 mmol) and acetone (2.0 mL). The reaction vessel was exposed to blue LED (420–425 nm, 1.5 W) irradiation in air at room temperature with stirring for 18 h. The oxidative formylation was completely inhibited, along with the formation of adduct **5** with TEMPO. The following figure is the HRMS analysis of reaction mixture (Figure S1).



Figure S1. Analysis of reaction mixture by HRMS

3.1.2 Free radical-trapping of intermediate D with TEMPO



A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with N,N-bis(3-phenylprop-2-yn-1-yl)aniline (**3c**, 64.28 mg, 0.20 mmol), TEMPO (62.5 mg, 0.40 mmol) and acetone (2.0 mL). The reaction vessel was exposed to blue LED (420–425 nm, 1.5 W) irradiation in air at room temperature with stirring for 18 h. The formation of adduct **6** with TEMPO was detected. The following figure is the HRMS analysis of reaction mixture (Figure S2).



Figure S2. Analysis of reaction mixture by HRMS

3.2 Intermediate-trapping experiments



A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with N,N-bis(3-phenylprop-2-yn-1-yl)aniline (**3c**, 64.28 mg, 0.20 mmol) and acetone (2.0 mL). The reaction vessel was exposed to blue LED (420–425 nm, 1.5 W) irradiation in air at room temperature with stirring for 18 h. The formation of intermediate **F** and **G** were detected. The following figure is the HRMS analysis of reaction mixture (Figure S3) and (Figure S4).







Figure S4. Analysis of reaction mixture by HRMS

3.3 Determination of the resulting CO₂ and CO gas by FT-IR



A 10 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with *N*,*N*-bis(3-(4-bromophenyl)prop-2-yn-1-yl)aniline (**3d**, 95.4 mg, 0.20 mmol), and acetone (2.0 mL) under oxygen atmosphere. The reaction vessel was exposed to blue LED (420–425 nm) irradiation at room temperature with stirring for 18 h. After completion of the reaction, the resulting gas from the reaction mixture was directly determined by FT-IR analysis (Figure S5). As shown in Figure S5, the concentration of CO₂ was found to be 2046.77 ppm, and CO was found to be 7989.82 ppm.



Figure S5. FT-IR analysis of the resulting gas by a Bruker Tensor 27 FT-IR

3.4 Determination of the resulting byproducts



A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with *N*,*N*-bis(3-(4-bromophenyl)prop-2-yn-1-yl)aniline (**3d**, 143.1 mg, 0.3 mmol), and acetone (2.0 mL). The reaction vessel was exposed to blue LED (420–425 nm) irradiation in air at room temperature with stirring for 18 h. After that, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10/1 to 3/1) to give the product **7** in 20% isolated yield (12.1 mg). ¹H NMR (400 MHz, DMSO-*d*₆) δ : 13.15 (s, 1H), 7.87–7.84 (m, 2H), 7.71–7.68 (m, 2H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ : 167.04, 132.14, 131.73, 130.47, 127.31. The byproduct 4-bromobenzaldehyde **8** was detected by GC-MS (Figure S6).





Figure S6. NMR and GC-MS analysis of 4-bromobenzaldehyde

3.5 Isotopic labeling experiments

3.5.1 ¹⁸O₂-Isotopic labeling experiment



N,*N*-Di(prop-2-yn-1-yl)(4-cyanophenyl)amine (**1o**, 58.2 mg, 0.30 mmol) and acetone (2.0 mL) were added to an oven-dried reaction vessel equipped with magnetic stirring bar. The reaction vessel was exposed to blue LED (420–425 nm, 1.5 W) irradiation at room temperature with stirring for 18 h under the atmosphere of ¹⁸O₂. 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 = 3/1 to 15/1) to give the product ¹⁸O **-20** in 74% yield, and no unlabeled **20** was generated in the reaction, which was determined by GC-MS (Figure S7).



Figure S7. GC-MS analysis of ¹⁸O₂ isotopic labeled products

3.5.2 H₂¹⁸O-Isotopic labeling experiments



N,*N*-Di(prop-2-yn-1-yl)(4-cyanophenyl)amine (**10**, 58.2 mg, 0.30 mmol), $H_2^{18}O$ (60.0 mg, 3.0 mmol, 10.0 equiv) and acetone (2.0 mL) were added to an oven-dried reaction vessel equipped with magnetic stirring bar, The reaction vessel was exposed to blue LED (420–425 nm, 1.5 W) irradiation in air at room temperature with stirring 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, petroleum ether/ethyl acetate = 3/1 to 15/1) to give the product **20** in 73% yield, which was determined by GC-MS (Figure S8), and no ¹⁸O-**20** was generated in the reaction.



Figure S8. GC-MS analysis of H₂¹⁸O isotopic labeled products.

3.6 Determination of electron spin resonance (ESR)

3.6.1 Determination of superoxide radicals

In order to determine the active species of oxygen involved in the present reaction, 5,5dimethyl-pyrroline-*N*-oxide (DMPO) were employed to capture O_2^{-} . There was no signal when DMPO was added into a solution of 4-bromo-*N*,*N*-di(prop-2-yn-1-yl)aniline (**1k**) in airsaturated acetone in the absence of light irradiation (Figure S9a). Irradiation of air-saturated acetone solution of DMPO and 4-bromo-*N*,*N*-di(prop-2-yn-1-yl)aniline in air with blue LED (420–425 nm, 1.5 W) resulted in the formation of a strong characteristic signal of O_2^{-} adduct with DMPO (Figure S9b). When the reaction time was prolonged, a series of stronger characteristic signal of O_2^{-} were observed (Figure S9c, Figure S9d and Figure S9e), indicating the formation of O_2^{--} in the reaction.



Figure S9. Electron spin resonance (ESR) spectra

(a) a solution of DMPO (0.20 mol/L) with 1k in air-saturated acetone without light irradiation
(b) a solution of DMPO (0.2 mol/L) with 1k in air-saturated acetone under blue LED (420–425 nm, 1.5 W) irradiation for 30 s

(c) a solution of DMPO (0.2 mol/L) with 1k in air-saturated acetone under blue LED (420–425 nm, 1.5 W) irradiation for 60 s

(d) a solution of DMPO (0.2 mol/L) with **1k** in air-saturated acetone under blue LED (420–425 nm, 1.5 W) irradiation for 90 s

(e) a solution of DMPO (0.2 mol/L) with **1k** in air-saturated acetone under blue LED (420–425 nm, 1.5 W) irradiation for 3 min

3.6.2 Determination of singlet oxygen species

For further explore the active species of singlet oxygen involved during the reaction, 2,2,6,6-tetramethylpiperidine (TEMP) were used to trap ${}^{1}O_{2}$. Irradiation of air-saturated acetone solution of TEMP and 4-bromo-*N*,*N*-di(prop-2-yn-1-yl)aniline in air under blue LED (420–425 nm) irradiation resulted in the formation of a strong characteristic signal ${}^{1}O_{2}$ adduct with TEMP (Figure S10F). A series of stronger characteristic signal of ${}^{1}O_{2}$ were collected with prolonged irradiation time (Figure S10G and S10H), implying that ${}^{1}O_{2}$ is also present during the reaction.



Figure S10. Electron spin resonance (ESR) spectra

(E) a solution of TEMP (0.2 mol/L) with 4-bromo-N,N-di(prop-2-yn-1-yl)aniline in air-saturated acetone without light irradiation

(F) a solution of TEMP (0.2 mol/L) with 4-bromo-N,N-di(prop-2-yn-1-yl)aniline in air-saturated acetone under blue LED (420–425 nm, 1.5 W) irradiation for 30 s

(G) a solution of TEMP (0.2 mol/L) with 4-bromo-N,N-di(prop-2-yn-1-yl)aniline in air-saturated acetone under LED blue LED (420–425 nm, 1.5 W) irradiation for 60 s

(H) a solution of TEMP (0.2 mol/L) with 4-bromo-N,N-di(prop-2-yn-1-yl)aniline in air-saturated acetone under blue LED (420–425 nm, 1.5 W) irradiation for 3 min

3.7 Absorption spectra



Figure S11. Absorption spectra of N,N-bis(3-phenylprop-2-yn-1-yl)aniline (3c) in acetone



Figure S12. Absorption spectra of *N*-phenyl-*N*-(3-phenylprop-2-yn-1-yl)formamide (**4c**) in acetone



Figure S13. Absorption spectra of 4-iodo-*N*,*N*-di(prop-2-yn-1-yl)aniline (11) in acetone



Figure S14. Absorption spectra of *N*-(4-iodophenyl)-*N*-(prop-2-yn-1-yl)formamide (**2l**) in acetone



Figure S15. Absorption spectra of *N*,*N*-di(prop-2-yn-1-yl)-[1,1'-biphenyl]-4-amine (**1p**) in acetone



Figure S16. Absorption spectra of 4-bromo-N,N-di(prop-2-yn-1-yl)aniline (1k) in acetone



Figure S17. Absorption spectra of 4-methoxy-*N*,*N*-di(prop-2-yn-1-yl)aniline (1f) in acetone

Compound	1p	1f	11	4 c	1k	21	3c
Concentration (mmol)	0.20	0.30	0.20	0.20	0.30	0.20	0.20
Absorbance	0.098	0.108	0.139	0.198	0.222	0.308	0.599

Table S1. The molar attenuation coefficients of the selected compounds at 420 nm

3.8 Light/Dark experiments



Figure S18. Light/Dark experiments

4. Characterization data for the products



2a: ¹H NMR (400 MHz, CDCl₃) δ: 8.42 (s, 1H), 7.46–7.42 (m, 2H), 7.35–7.29 (m, 3H), 4.55 (d, *J* = 2.0 Hz, 2H), 2.23–2.22 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ: 161.62, 140.28, 129.64, 127.22, 123.77, 78.31, 72.17, 34.43. HRMS (ESI) ([M+H]⁺) Calcd. For C₁₀H₁₀NO: 160.0757, Found: 160.0754.



2b: ¹H NMR (400 MHz, CDCl₃) δ: 8.36 (s, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 4.53 (d, *J* = 2.0 Hz, 2H), 2.38 (s, 3H), 2.21 (br, 1H); ¹³C NMR (100 MHz, CDCl₃) δ:161.72, 137.66, 137.34, 130.20, 124.05, 78.37, 72.10, 34.55, 20.94. HRMS (ESI) ([M+H]⁺) Calcd. For C₁₁H₁₂NO: 174.0913, Found: 174.0919.



2c: ¹H NMR (400 MHz, CDCl₃) δ: 8.35 (s, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 4.51 (d, *J* = 2.4 Hz, 2H), 2.67 (q, *J* = 7.6 Hz, 2H), 2.21–2.20 (m, 1H), 1.25 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 161.67, 143.56, 137.87, 128.99, 124.04, 78.45, 72.08, 34.53, 28.31, 15.38. HRMS (ESI) ([M+H]⁺) Calcd. For C₁₂H₁₄NO: 188.1070, Found: 188.1067.



2d: ¹H NMR (400 MHz, CDCl₃) δ: 8.35 (s, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 4.50 (d, *J* = 1.6 Hz, 2H), 2.95–2.89 (m, 1H), 2.20 (br, 1H), 1.24 (d, *J* = 7.2 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ:161.68, 148.11, 137.95, 127.57, 123.93, 78.50, 72.09, 34.53, 33.64, 23.88. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₃H₁₆NO: 202.1226, Found: 202.1221.



2e: ¹H NMR (400 MHz, CDCl₃) δ: 8.38 (s, 1H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.22 (d, *J* = 8.8 Hz, 2H), 4.52 (d, *J* = 2.4 Hz, 2H), 2.23–2.22 (m, 1H), 1.34 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ:161.71, 150.43, 137.66, 126.51, 123.50, 78.50, 72.02, 34.56, 34.51, 31.26. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₄H₁₈NO: 216.1383, Found: 216.1385.



2f: ¹H NMR (400 MHz, CDCl₃) δ : 8.26 (s, 1H), 7.20 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 8.0 Hz, 2H), 4.47 (s, 2H), 3.81 (s, 3H), 2.20 (br, 1H); ¹³C NMR (100 MHz, CDCl₃) δ : 161.78, 158.96, 133.04, 126.35, 114,76, 78.40, 72.19, 55.49, 34.87. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₁H₁₂NO₂: 190.0863, Found: 190.0862.



2g: ¹H NMR (400 MHz, CDCl₃) δ : 8.39 (s, 1H), 7.33–7.29 (m, 1H), 7.14–7.09 (m, 3H), 4.52 (d, J = 2.4 Hz, 2H), 2.39 (s, 3H), 2.23–2.22 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ : 161.68, 140.20, 139.75, 129.42, 128.01, 124.36, 120.78, 78.41, 72.10, 34.45, 21.38. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₁H₁₂NO: 174.0913, Found: 174.0908.



2h: ¹H NMR (400 MHz, CDCl₃) δ: 8.37 (s, 1H), 6.96 (s, 1H), 6.89 (s, 2H), 4.51 (d, *J* = 2.4 Hz, 2H), 2.35 (s, 6H), 2.22–2.21 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ: 161.65, 140.17, 139.45, 128.88, 121.45, 78.51, 71.98, 34.44, 21.26. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₂H₁₄NO: 188.1070, Found: 188.1074.



2i: ¹H NMR (400 MHz, CDCl₃) δ: 8.31 (s, 1H), 7.29–7.26 (m, 2H), 7.14–7.10 (m, 2H), 4.51 (d, *J* = 2.4 Hz, 2H), 2.23–2.22 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ: 161.65 (d, *J* = 246.3 Hz), 161.49, 136.23 (d, *J* = 2.9 Hz), 126.39 (d, *J* = 8.4 Hz), 116.52 (d, *J* = 22.8 Hz), 78.06, 72.49, 34.70. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₀H₉FNO: 178.0663, Found: 178.0662.



2j: ¹H NMR (400 MHz, CDCl₃) δ : 8.36 (s, 1H), 7.38 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.8 Hz, 2H), 4.51 (d, J = 2.0 Hz, 2H), 2.24–2.22 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ : 161.28, 138.73, 132.96, 129.79, 125.03, 77.99, 72.60, 34.34. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₀H₉CINO: 194.0367, Found: 194.0364.



2k: ¹H NMR (400 MHz, CDCl₃) δ: 8.37 (s, 1H), 7.55–7.53 (m, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 4.51 (d, *J* = 1.2 Hz, 2H), 2.24–2.23 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ: 161.16, 139.26, 132.78, 125.26, 120.76, 77.96, 72.60, 34.27. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₀H₉BrNO: 237.9862, Found: 237.9865.



21: ¹H NMR (400 MHz, CDCl₃) δ: 8.39 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 4.52 (s, 2H), 2.24–2.23 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ: 161.12, 139.96, 138.76, 125.33, 91.73, 77.95, 72.59, 34.18. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₀H₉INO: 285.9723, Found: 285.9727.



2m: ¹H NMR (400 MHz, CDCl₃) δ: 8.39 (s, 1H), 7.35–7.28 (m, 4H), 4.54 (d, *J* = 2.4 Hz, 2H), 2.25–2.24 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ: 161.30, 147.92, 138.76, 125.18, 122.19, 120.37 (q, *J* = 256.3 Hz), 77.91, 72.60, 34.45. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₁H₉F₃NO₂: 244.0580, Found: 244.0582.



2n: ¹H NMR (400 MHz, CDCl₃) δ: 8.56 (s, 1H), 8.11 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 2H), 4.60 (d, *J* = 2.4 Hz, 2H), 4.39 (q, *J* = 7.2 Hz, 2H), 2.25–2.24 (m, 1H), 1.40 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 165.60, 161.08, 144.02, 131.14, 128.77, 121.84, 77.86, 72.55, 61.18, 33.88, 14.28. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₃H₁₄NO₃: 232.0968, Found: 232.0970.



20: ¹H NMR (400 MHz, CDCl₃) δ: 8.58 (s, 1H), 7.73 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 4.59 (d, *J* = 2.4 Hz, 2H), 2.27–2.26 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ: 160.80, 144.03, 133.74, 122.23, 118.04, 110.15, 77.52, 73.02, 33.69. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₁H₉N₂O: 185.0709, Found: 185.0705.



2p: ¹H NMR (400 MHz, CDCl₃) δ: 8.49 (s, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 7.2 Hz, 2H), 7.49–7.46 (m, 2H), 7.41–7.36 (m, 3H), 4.60 (d, *J* = 2.4 Hz, 2H), 2.28–2.26 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ: 161.55, 140.18, 139.86, 139.40, 128.94, 128.29, 127.72, 127.02, 123.87, 78.35, 72.34, 34.42. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₆H₁₄NO: 236.1070, Found: 236.1065.



2q: ¹H NMR (400 MHz, CDCl₃) δ : 8.44 (s, 1H), 7.42–7.36 (m, 1H), 7.08–7.00 (m, 3H), 4.53 (d, J = 2.0 Hz, 2H), 2.25–2.24 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ : 163.08 (d, J = 246.6 Hz), 161.27, 141.80 (d, J = 9.6 Hz), 130.91 (d, J = 9.3 Hz), 118.72 (d, J = 2.7 Hz), 113.98 (d, J = 21.0 Hz), 110.62 (d, J = 23.8 Hz), 77.98, 72.52, 34.22. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₀H₉FNO: 178.0663, Found: 178.0660.



2r: ¹H NMR (400 MHz, CDCl₃) δ : 8.41 (s, 1H), 7.38–7.29 (m, 3H), 7.19 (d, J = 7.6 Hz, 1H), 4.53 (d, J = 2.4 Hz, 2H), 2.25–2.24 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ : 161.20, 141.42, 135.27, 130.65, 127.28, 123.61, 121.53, 77.92, 72.62, 34.28. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₀H₉CINO: 194.0367, Found: 194.0362.



2s: ¹H NMR (400 MHz, CDCl₃) δ : 8.42 (s, 1H), 7.48–7.46 (m, 2H), 7.33–7.23 (m, 2H), 4.54 (d, J = 2.4 Hz, 2H), 2.26–2.25 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ : 161.18, 141.54, 130.89, 130.26, 126.60, 123.14, 122.10, 77.87, 72.64, 34.32. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₀H₉BrNO: 237.9862, Found: 237.9856.



2t: ¹H NMR (400 MHz, CDCl₃) δ: 8.40 (s, 1H), 7.45–7.37 (m, 3H), 7.30–7.27 (m, 1H), 4.53 (d, *J* = 2.4 Hz, 2H), 3.16 (s, 1H), 2.24 (t, *J* = 2.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ: 161.32, 140.32, 130.79, 129.71, 127.00, 124.03, 123.77, 82.34, 78.66, 78.01, 72.54, 34.29. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₂H₁₀NO: 184.0757, Found: 184.0750.



2u: ¹H NMR (400 MHz, CDCl₃) δ : 8.40 (s, 1H), 7.50 (d, J = 8.8 Hz, 1H), 7.42–7.41 (m, 1H) 7.18–7.15 (m, 1H), 4.53 (d, J = 2.4 Hz, 2H), 2.27–2.26 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ : 160.93, 139.59, 133.62, 131.27, 125.31, 122.72, 77.63, 72.95, 34.24. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₀H₈Cl₂NO: 227.9977, Found: 227.9978.



2v: ¹H NMR (400 MHz, CDCl₃) δ: 8.44 (s, 1H), 7.32 (s, 1H), 7.22 (br, 2H), 4.53 (d, *J* = 2.4 Hz, 2H), 2.29–2.28 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ: 160.81, 142.10, 135.97, 127.14, 121.54, 77.50, 73.04, 34.16. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₀H₈Cl₂NO: 227.9977, Found: 227.9981.



2w: ¹H NMR (400 MHz, CDCl₃) δ : 8.55 (s, 1H), 7.93 (d, J = 8.8 Hz, 1H), 7.89–7.86 (m, 2H), 7.71 (d, J = 1.6 Hz, 1H), 7.58–7.51 (m, 2H), 7.47–7.44 (m, 1H), 4.67 (d, J = 2.4 Hz, 2H), 2.25–2.24 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ : 161.82, 137.60, 133.51, 132.09, 129.81, 127.78, 127.12, 126.47, 122.09, 121.91, 78.30, 72.37, 34.57. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₄H₁₂NO: 210.0913, Found: 210.0916.



2x: ¹H NMR (400 MHz, CDCl₃) δ : 8.47 (s, 1H), 7.43–7.39 (m, 2H), 7.29–7.25 (m, 1H), 7.17 (d, J = 7.6 Hz, 2H), 3.32 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 162.33, 142.18, 129.61, 126.40, 122.38, 32.03. HRMS (ESI) ([M+H]⁺) Calcd. for C₈H₁₀NO: 136.0757, Found: 136.0759.



2y: ¹H NMR (400 MHz, CDCl₃) δ : 8.35 (s, 1H), 7.43–7.39 (m, 2H), 7.31–7.27 (m, 1H), 7.17 (d, J = 7.6 Hz, 2H), 3.86 (q, J = 7.2 Hz, 2H), 1.16 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 161.99, 140.84, 129.60, 126.83, 124.25, 40.06, 13.00. HRMS (ESI) ([M+H]⁺) Calcd. for C₉H₁₂NO: 150.0913, Found: 150.0919.



2z: ¹H NMR (400 MHz, CDCl₃) δ: 8.38 (s, 1H), 7.44–7.40 (m, 2H), 7.32–7.28 (m, 1H), 7.18 (d, *J* = 7.6 Hz, 2H), 3.82 (t, *J* = 7.6 Hz, 2H), 1.56–1.49 (m, 2H), 1.37–1.27 (m, 2H), 0.91–0.88 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 162.29, 141.08, 129.60, 126.78, 124.23, 44.71, 29.68, 19.99, 13.66. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₁H₁₆NO: 178.1226, Found: 178.1222.



2aa: ¹H NMR (400 MHz, CDCl₃) δ: 8.68 (s, 1H), 7.41–7.20 (m, 10H); ¹³C NMR (100 MHz, CDCl₃) δ: 161.71, 141.81, 139.69, 129.70, 129.18, 127.05, 126.84, 126.11, 125.12. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₃H₁₂NO: 198.0913, Found: 198.0908.



2ab: ¹H NMR (400 MHz, CDCl₃) δ: 8.48 (s, 1H), 7.35–7.31 (m, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.17 (s, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 3.29 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 161.89,

143.38, 135.28, 130.59, 126.36, 122.27, 120.08, 31.84. HRMS (ESI) ([M+H]⁺) Calcd. for C₈H₉ClNO: 170.0367, Found: 170.0364.



2ac: ¹H NMR (400 MHz, CDCl₃) δ: 8.47 (s, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.32 (s, 1H), 7.29– 7.25 (m, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 3.28 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 161.87, 143.49, 130.85, 129.31, 125.17, 123.14, 120.59, 31.87. HRMS (ESI) ([M+H]⁺) Calcd. for C₈H₉BrNO: 213.9862, Found: 213.9864.



2ad: ¹H NMR (400 MHz, CDCl₃) δ: 8.43 (s, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 3.27 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 161.88, 141.23, 132.68, 123.73, 119.64, 31.92. HRMS (ESI) ([M+H]⁺) Calcd. for C₈H₉BrNO: 213.9862, Found: 213.9858.



4a: ¹H NMR (400 MHz, CDCl₃) δ : 8.49 (s, 1H), 7.42–7.38 (m, 2H), 7.31–7.27 (m, 1H), 7.19 (d, J = 8.0 Hz, 2H), 5.90–5.81 (m, 1H), 5.22–5.17 (m, 2H), 4.42 (d, J = 5.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ : 161.98, 141.17, 132.48, 129.56, 126.70, 123.55, 117.63, 47.87. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₀H₁₂NO: 162.0913, Found: 162.0909.



4b: ¹H NMR (400 MHz, CDCl₃) δ : 8.40 (s, 1H), 7.43–7.39 (m, 2H), 7.31–7.27 (m, 3H), 4.48 (q, J = 2.4 Hz, 2H), 1.75 (t, J = 2.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 161.64, 140.66, 129.54, 126.91, 123.46, 79.85, 73.63, 34.89, 3.48. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₁H₁₂NO: 174.0913, Found: 174.0914.



4c: ¹H NMR (400 MHz, CDCl₃) δ: 8.47 (s, 1H), 7.48–7.44 (m, 2H), 7.37–7.33 (m, 5H), 7.30–7.27 (m, 3H), 4.79 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ: 161.72, 140.42, 131.72, 129.63, 128.44, 128.24, 127.21, 123.97, 122.49, 84.00, 83.75, 35.27. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₆H₁₄NO: 236.1070, Found: 236.1066.



4d: ¹H NMR (400 MHz, CDCl₃) δ: 8.47 (s, 1H), 7.48–7.41 (m, 4H), 7.37–7.33 (m, 3H), 7.23–7.20 (m, 2H), 4.77 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ: 161.67, 140.35, 133.15, 131.51, 129.65, 127.26, 123.94, 122.73, 121.42, 84.94, 82.94, 35.28. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₆H₁₄NO: 314.0175, Found: 314.0178.



4e: ¹H NMR (400 MHz, CDCl₃) δ: 8.35 (s, 1H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 2H), 3.95 (t, *J* = 7.2 Hz, 2H), 2.50–2.45 (m, 2H), 1.97–1.96 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ: 161.92, 139.74, 132.83, 126.05, 120.70, 80.62, 70.45, 44.11, 17.55. HRMS (ESI) ([M+H]⁺) Calcd. for C₁₁H₁₁BrNO: 252.0019, Found: 252.0017.

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





































































