Supporting Information

Photocatalytic C–H amination of aromatics overcoming redox potential limitations

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1. General

Pyridine, piperidine, pyrrolidine, Ru(phen)$_3$(PF$_6$)$_2$, (Ir[dF(CF$_3$)ppy]$_2$(dtbpy))PF$_6$, K$_2$S$_2$O$_8$, (NH$_4$)$_2$S$_2$O$_8$, Na$_2$S$_2$O$_8$, [bis(trifluoroacetoxy)iodo]benzene (PIFA), 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ), CBBrCl$_3$, Bu$_4$NBF$_4$, KPF$_6$, Et$_3$N, 4-tert-butylanisole (1a), 4-iodoanisole (1b), 4-bromoanisole (1c), 4-methoxybenzophenone (1d), 4-cyanoanisole (1e), 4-trifluoromethylanisole (1f), 4-nitroanisole (1g), benzene, naphthalene (1h), phenanthrene (1i), 9,9-dimethylfluorene (1j), 2-nitro-9,9-dimethylfluorene (1k), 4-methoxy-4'-nitrophenyl (1l), 1,4-dimethoxy-2-nitrobenzene (1m), 6-methoxyquinoline (1n), and fenofibrate 1p were commercially available. Ru(dfmb)$_3$(PF$_6$)$_2$,$^1$ Ru(bpz)$_3$(PF$_6$)$_2$, $^2$ ethyl 2-(tert-butylphenoxy)-2-methyl-propanoate (1o), $^3$ were synthesized according to the reported literature. Dehydrated CH$_3$CN and distilled water were used for solvent. For the heating the reaction mixture, an oil bath was used. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Flash chromatography was carried out on a silica gel (Kanto Chem. Co., Silica Gel N, spherical, neutral, 40-100 µm). Preparative gel permeation chromatography (GPC) was carried out on Japan Analytical Industry LC-918 equipped with JAIGEL-1H and 2H using CHCl$_3$ as an eluent. Photocatalytic amination was carried out in a Schlenk tube (30 mL) with photoirradiation using blue LED (Kessil, A160WE TUNA Blue) and a cooling fan was used to avoid heating the reaction mixture (Figure S1). Gram scale photocatalytic amination was carried out in a round-bottom flask (500 mL) with a septum (Figure S2). All NMR spectra were measured on Unity Inova-400 instrument (Varian Inc., 400 MHz for $^1$H, 100 MHz for $^{13}$C) or AVANCE III HD Nano Bay (Bruker Co., 400 MHz for $^1$H, 100 MHz for $^{13}$C) at 22 ºC using CDCl$_3$ as a solvent unless otherwise noted. Tetramethylsilane (TMS) ($\delta = 0$) or CHCl$_3$ ($\delta = 7.26$) served as an internal standard for $^1$H NMR spectra, and CDCl$_3$ was used as an internal standard ($\delta = 77.0$) for $^{13}$C NMR spectra.

Figure S1. Reaction set up (0.2 mmol or 0.5 mmol scale)

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Redox potentials of photocatalysts and aromatic substrates were determined by differential pulse voltammetry (DPV) analysis using the ALS electrochemical analyzer (ALS612E). Substrate concentration was 0.02 M, and 0.2 M solution of Bu4NBF4 in CH3CN was used for solvent. A glassy carbon working electrode, a platinum counter electrode, an Ag/AgNO3 reference electrode were used. We measured redox potentials respect to the [FeCp2]/[FeCp2]+ couple, which was converted to saturated calomel electrode (SCE) by adding 0.469 V. Stern–Volmer fluorescence quenching experiments were run using the Jasco’s spectrofluorometer (FP-6500).

Driving force of electron transfer \( \Delta G \) were determined from the redox potentials, \( E_{ox}(1) \) and \( E_{red}(\text{Ru}^{	ext{III}}/\text{Ru}^{	ext{II}}) \) using the expression \( \Delta G = F[E_{ox}(1) - E_{red}(\text{Ru}^{	ext{III}}/\text{Ru}^{	ext{II}})] + w_p \) (F: Faraday constant, \( w_p \): work term).\(^5\) The work term \( w_p = 1.7 \) kcal/mol, which was obtained from an electrostatic model of radical cations of aromatic substrates and Ru3+(phen)3 at a distance, \( d = 10.5 \) Å.\(^6\) Therefore, in the present reaction system, \( \Delta G \) (kcal/mol) = 23.06 × \( [E_{ox}(1) - E_{red}(\text{Ru}^{	ext{III}}/\text{Ru}^{	ext{II}})] \) + 1.7.

2. Optimization of the C–H Amination of aromatic compounds

A 30 mL Schlenk tube equipped with a magnetic stirring bar and a septum, was dried under vacuum with heating. After cooling the tube to 23 °C, it was purged with argon gas. 4-tert-Butylanisole (1a) (0.2 mmol), pyridine (2 mmol), oxidant (0.4 mmol), photocatalyst (0.01 mmol), and CH3CN/H2O (1/1, 5 mL) were added to the tube, and photoirradiation was carried out with stirring for 3 hours. Following photoirradiation, pyrrolidine (10 mmol) was added to the reaction mixture and stirred for 12 h at 70 °C. The resulting mixture was then cooled to 23 °C and opened to air. The obtained organic compounds were extracted with EtOAc /Hex (2/1, 3 × 30 mL). Evaporation of the solvents gave a crude material, and yield of the 2a was determined by 1H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard.


3. Procedure of the C–H Amination of aromatic compounds

A 30 mL Schlenk tube equipped with a magnetic stirring bar and a septum, was dried under vacuum with heating. After cooling the tube to 23 °C, it was purged with argon gas. The aromatic substrate 1 (0.2 mmol or 0.5 mmol), pyridine (10 equiv), (NH₄)₂S₂O₈ (2-5 equiv), Ru(phen)(PF₆)₂ (5 mol %), and CH₃CN/H₂O were added to the tube, and photoirradiation was carried out with stirring for 24 hours unless otherwise noted. Following photoirradiation, pyrrolidine (50 equiv) was added to the reaction mixture and stirred for 12 h at 70 °C. The resulting mixture was then cooled to 23 °C and opened to air. The obtained organic compounds were extracted with EtOAc/Hex (2/1, 3 × 30 mL). Evaporation of the solvents gave a crude material, which was purified by flash chromatography or GPC to give desired product 2.

Scheme S1.

![Scheme S1](image-url)

**2-methoxy-5-tert-butylaniline (2a)**

Reaction of 4-tert-butylanisole (1a) (82 mg, 0.50 mmol) gave the title compound (80 mg, 89%, brown solid).

(NH₄)₂S₂O₈ (457 mg, 2.0 mmol), CH₃CN/H₂O: 12.5 mL/12.5 mL

1H NMR (400 MHz, CDCl₃): δ 6.78-6.68 (m, 3H), 3.82 (s, 3H), 3.70 (br s, 2H), 1.27 (s, 9H);

13C NMR (100 MHz, CDCl₃): δ 145.2, 144.0, 135.2, 115.0, 112.8, 109.9, 55.4, 34.0, 31.4.

**5-iodo-2-methoxyaniline (2b)**

Reaction of 4-idoanisole (1b) (117 mg, 0.50 mmol) gave the title compound (91 mg, 73%, yellowish brown solid).

(NH₄)₂S₂O₈ (457 mg, 2.0 mmol), CH₃CN/H₂O: 12.5 mL/12.5 mL

1H NMR (400 MHz, CDCl₃): δ 7.02-6.97 (m, 2H), 6.51 (d, J = 8.0 Hz, 1H), 3.81 (s, 3H), 3.73 (br s, 2H);

13C NMR (100 MHz, CDCl₃): δ 147.1, 137.8, 126.9, 122.9, 112.2, 109.9, 55.4.

**5-bromo-2-methoxyaniline (2c)**

Reaction of 4-bromoanisole (1c) (93 mg, 0.50 mmol) gave the title compound (46 mg, 46%, pale yellow solid).

(NH₄)₂S₂O₈ (459 mg, 2.0 mmol), CH₃CN/H₂O: 12.5 mL/12.5 mL

1H NMR (400 MHz, CDCl₃): δ 6.82-6.78 (m, 2H), 6.62 (d, J = 9.2 Hz, 1H), 3.86 (br s, 7)

7 ACD-A; Sigma-Aldrich (Spectral data were obtained from Advanced Chemistry Development, Inc.)
5-benzoyl-2-methoxyaniline (2d)
Reaction of 4-methoxybenzophenone (1d) (107 mg, 0.51 mmol) gave the title compound (107 mg, 91%, yellow solid).

(NH₄)₂S₂O₈ (455 mg, 2.0 mmol), CH₃CN/H₂O: 12.5 mL/12.5 mL

1H NMR (400 MHz, CDCl₃); δ 7.74 (d, J = 7.2 Hz, 2H), 7.53 (t, J = 7.2 Hz, 1H), 7.43 (t, J = 7.4 Hz, 2H), 7.25 (d, J = 2.0 Hz, 1H), 7.19 (dd, J = 8.0, 2.0 Hz, 1H), 6.79 (d, J = 8.4 Hz, 1H), 3.95 (br s, 2H), 3.89 (s, 3H); 13C NMR (100 MHz, CDCl₃); δ 195.9, 150.8, 138.4, 136.0, 131.6, 130.3, 129.6, 127.9, 122.5, 115.7, 110.9, 55.5;
IR (KBr): 3451, 3360, 2925, 1640, 1513, 1444, 1297, 1234, 1128, 1024, 742, 629 cm⁻¹; HRMS (ESI) m/z calcd for C₁₄H₁₄NO₂ [M+H]+: 228.1019, found: 228.1008; m.p. 97-98 °C.

The position of the amino group was determined by NOE analysis.

5-cyano-2-methoxyaniline (2e)
Reaction of anisonitrile (1e) (66 mg, 0.50 mmol) gave the title compound (73 mg, 99%, colorless solid).

(NH₄)₂S₂O₈ (454 mg, 2.0 mmol), CH₃CN/H₂O: 5.0 mL/20 mL

1H NMR (400 MHz, CDCl₃); δ 7.04 (d, J = 8.0 Hz, 1H), 6.91 (s, 1H), 6.78 (d, J = 8.0 Hz, 1H), 4.03 (br s, 2H), 3.89 (s, 3H); 13C NMR (100 MHz, CDCl₃); δ 150.3, 136.9, 123.2, 119.7, 116.5, 110.0, 103.8, 55.5.

2-methoxy-5-trifluoromethylaniline (2f)
Reaction of 4-trifluoromethylanisole (1f) (92 mg, 0.52 mmol) gave the title compound (70 mg, 71%, yellow solid).

(NH₄)₂S₂O₈ (458 mg, 2.0 mmol), CH₃CN/H₂O: 5.0 mL/20 mL

1H NMR (400 MHz, CDCl₃); δ 6.97 (d, J = 8.4 Hz, 1H), 6.90 (d, J = 1.2 Hz, 1H), 6.78 (d, J = 8.4 Hz, 1H), 3.93 (br s, 2H), 3.86 (s, 3H); 13C NMR (100 MHz, CDCl₃); δ 149.4, 136.4, 124.5 (q, J = 269.4 Hz), 123.2 (q, J = 32.1 Hz), 115.5 (q, J = 4.2 Hz), 111.0 (q, J = 3.6 Hz), 109.5, 55.5.

2-methoxy-5-nitroaniline (2g)
Reaction of 4-nitroanisole (1g) (75 mg, 0.49 mmol) gave the title compound (68 mg, 83%, orange solid).

(NH₄)₂S₂O₈ (465 mg, 2.0 mmol), CH₃CN/H₂O: 5.0 mL/20 mL

**1H NMR** (400 MHz, CDCl₃): δ 7.68 (dd, J = 8.8, 2.4 Hz, 1H), 7.55 (d, J = 2.4 Hz, 1H), 6.80 (d, J = 8.8 Hz, 1H), 4.08 (br s, 2H), 3.95 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 151.9, 141.8, 136.6, 114.8, 109.0, 108.8, 56.0.

**1-aminonaphthalene (2h)⁹**

Reaction of naphthalene (1h) (64 mg, 0.50 mmol) gave the title compound (30 mg, 42%, pale brown solid).

(NH₄)₂S₂O₈ (234 mg, 1.0 mmol), CH₃CN/H₂O: 12.5 mL/12.5 mL

**¹H NMR** (400 MHz, CDCl₃): δ 7.78-7.72 (m, 2H), 7.44-7.36 (m, 2H), 7.29-7.18 (m, 2H), 6.73 (dd, J = 6.8, 1.2 Hz, 1H), 4.10 (br s, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 142.0, 134.3, 128.5, 126.3, 125.8, 124.8, 123.6, 120.7, 119.0, 109.7.

**2i**

9-aminophenanthrene (2i)¹¹

Reaction of phenanthrene (1i) (89 mg, 0.50 mmol) gave the title compound (30 mg, 31%, brown solid).

(NH₄)₂S₂O₈ (458 mg, 2.0 mmol), CH₃CN/H₂O: 20 mL/5 mL

**¹H NMR** (400 MHz, CDCl₃): δ 8.68 (d, J = 8.0 Hz, 1H), 8.54 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.68-7.56 (m, 3H), 7.54-7.37 (m, 2H), 6.95 (s, 1H), 4.10 (br s, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 139.8, 133.2, 131.1, 126.8, 126.6, 126.3, 126.2, 126.1, 125.4, 123.4, 123.3, 122.4, 121.1, 107.4.

**2j**

2-amino-9,9-dimethylfluorene (2j)¹² and 2,7-diamino-9,9-dimethylfluorene (2j')

Reaction of 9,9-dimethylfluorene (1j) (98 mg, 0.50 mmol) gave 2j (48 mg, 46%, brown solid) and 2j' (29 mg, 25%, brown solid).

(NH₄)₂S₂O₈ (458 mg, 2.0 mmol), CH₃CN/H₂O: 20 mL/5 mL

**2j**: **¹H NMR** (400 MHz, CDCl₃): δ 7.57 (d, J = 7.6 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 7.2 Hz, 1H), 7.29-7.18 (m, 2H), 6.74 (d, J = 1.6 Hz, 1H), 6.64 (dd, J = 1.6, 8.0 Hz, 1H), 3.73 (br s, 2H), 1.43 (s, 6H); **¹³C NMR** (100 MHz, CDCl₃): δ 155.4, 152.7, 146.1, 139.6, 130.2, 126.8, 125.5, 122.3, 120.8, 118.6, 113.9, 109.4, 46.5, 27.3.

**2j'**: **¹H NMR** (400 MHz, CDCl₃): δ 7.37 (d, J = 8.0 Hz, 2H), 6.73 (d, J = 1.2 Hz, 2H), 6.63 (d, J = 7.6 Hz, 2H), 3.53 (br s, 4H), 1.40 (s, 6H); **¹³C NMR** (100 MHz, CDCl₃): δ 154.6, 144.7, 130.9, 119.5, 113.9, 109.8, 46.4, 27.4; **IR** (KBr): 3466, 3371, 3205, 2954, 1614, 1468, 1313, 1247, 737, 526 cm⁻¹; **HRMS (ESI) m/z** calcd for C₁₅H₁₆N₂ [M]: 224.1313, found: 224.1313; m.p. 188-192 °C.

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The position of the amino group was determined by NOE analysis.

2-amino-7-nitro-9,9-dimethylfluorene (2kx) and 5-amino-2-nitro-9,9-dimethylfluorene (2ky)

Reaction of 2-nitro-9,9-dimethylfluorene (1k) (48 mg, 0.20 mmol) gave 2kx (32 mg, 62%, orange solid) and 2ky (9.7 mg, 19%, yellow solid). (NH₄)₂S₂O₈ (218 mg, 1.0 mmol), CH₃CN/H₂O: 5 mL/5 mL
2kx: ¹H NMR (400 MHz, CDCl₃): δ 8.22-8.18 (m, 2H), 7.63-7.52 (m, 2H), 6.76 (d, J = 1.6 Hz, 1H), 6.68 (dd, J = 8.0, 2.0 Hz, 1H), 3.99 (br s, 2H), 1.48 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 157.5, 153.5, 148.3, 146.5, 145.6, 127.5, 123.6, 122.7, 118.3, 118.0, 114.4, 108.9, 46.9, 26.9; IR (KBr): 3464, 3370, 2954, 1628, 1510, 1362, 1119, 844, 741, 559 cm⁻¹; HRMS (ESI) m/z calcd for C₁₅H₁₅N₂O₂ [M+H]⁺: 255.1128, found: 225.1121; m.p. 145-148 °C.

The position of the amino group was determined by NOE analysis.

2ky: ¹H NMR (400 MHz, CDCl₃): δ 8.28-8.25 (m, 2H), 7.78-7.74 (d, J = 8.8 Hz, 1H), 7.26-7.24 (m, 1H), 6.95 (d, J = 7.6 Hz, 1H), 6.72 (d, J = 7.6 Hz, 1H), 4.20 (br s, 2H), 1.50 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 157.0, 154.6, 145.8, 145.7, 143.6, 130.5, 123.4, 122.6, 121.1, 117.9, 115.7, 113.6, 46.9, 27.1; IR (KBr): 3445, 3370, 2954, 1629, 1508, 1327, 1119, 832, 740, 539 cm⁻¹; HRMS (ESI) m/z calcd for C₁₅H₁₅N₂O₂ [M+H]⁺: 255.1128, found: 255.1136; m.p. 163-165 °C.

The position of the amino group was determined by NOE analysis.
3-amino-4-methoxy-4′-nitro-1,1′-biphenyl (2I)\(^5\)

Reaction of 4-methoxy-4′-nitrobiphenyl (1I) (45 mg, 0.20 mmol) gave the title compound (36 mg, 75%, red orange solid).

\((\text{NH}_3)_2\text{S}_2\text{O}_5\) (220 mg, 1.0 mmol), CH\(_3\)CN/\(\text{H}_2\text{O}\): 12.5 mL/12.5 mL

\(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.23 (d, \(J = 8.8 \text{ Hz}, 2\text{H}\)), 7.65 (d, \(J = 8.8 \text{ Hz}, 2\text{H}\)), 7.01-6.98 (m, 2H), 6.87 (d, \(J = 8.4 \text{ Hz}, 1\text{H}\)), 3.95 (br s, 2H), 3.91 (s, 3H); \(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)): \(\delta\) 148.1, 147.7, 146.4, 136.7, 131.5, 127.0, 124.0, 117.6, 113.4, 110.6, 55.6.

3,6-dimethoxy-2-nitroaniline (2mx)\(^6\) and 2,5-dimethoxy-4-nitroaniline (2my)\(^8\)

Reaction of 1,4-dimethoxy-2-nitrobenzene (1m) (92 mg, 0.50 mmol) gave 2mx (41 mg, 41%, red orange solid) and 2my (13 mg, 13%, yellow solid).

\((\text{NH}_3)_2\text{S}_2\text{O}_5\) (464 mg, 2.0 mmol), CH\(_3\)CN/\(\text{H}_2\text{O}\): 12.5 mL/12.5 mL

2mx: \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 6.76 (d, \(J = 9.2 \text{ Hz}, 1\text{H}\)), 6.18 (d, \(J = 8.8 \text{ Hz}, 1\text{H}\)), 5.38 (br s, 2H), 3.85 (s, 3H), 3.83 (s, 3H); \(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)): \(\delta\) 148.4, 141.5, 135.1, 127.3, 112.6, 98.1, 56.6, 56.3.

2my: \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.57 (s, 1H), 6.29 (s, 1H), 4.61 (br s, 2H), 3.91 (s, 3H), 3.88 (s, 3H); \(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)): \(\delta\) 152.0, 144.2, 139.4, 127.8, 108.4, 97.4, 56.7, 56.1.

5-amino-6-methoxyquinoline (2n)\(^{13}\)

Reaction of 6-methoxyquinoline (1n) (84 mg, 0.53 mmol) gave the title compound (64 mg, 69%, yellowish brown solid).

\((\text{NH}_3)_2\text{S}_2\text{O}_5\) (232 mg, 1.0 mmol), CH\(_3\)CN/\(\text{H}_2\text{O}\): 12.5 mL/12.5 mL

\(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.78 (d, \(J = 2.8 \text{ Hz}, 1\text{H}\)), 8.14 (d, \(J = 8.4 \text{ Hz}, 1\text{H}\)), 7.60 (d, \(J = 9.2 \text{ Hz}, 1\text{H}\)), 7.44 (d, \(J = 9.2 \text{ Hz}, 1\text{H}\)), 7.31 (dd, \(J = 8.4, 4.0 \text{ Hz}, 1\text{H}\)), 4.27 (br s, 2H), 3.99 (s, 3H); \(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)): \(\delta\) 148.2, 143.9, 142.6, 129.3, 129.0, 119.58, 119.56, 118.7, 116.4, 56.6.

2,2-dimethyl-4H-6-tert-butyl-1,4-benzoxazin-3-one (2o)

Reaction of ethyl 2-(4-tert-butylphenoxo)-2-methylpropanoate (1o) (142 mg, 0.54 mmol) gave the title compound (100 mg, 80%, yellow solid).

\((\text{NH}_3)_2\text{S}_2\text{O}_5\) (457 mg, 2.0 mmol), CH\(_3\)CN/\(\text{H}_2\text{O}\): 12.5 mL/12.5 mL

\(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.51 (br s, 1H), 6.99 (dd, \(J = 8.4, 2.0 \text{ Hz}, 1\text{H}\)), 6.87 (d, \(J = 8.4 \text{ Hz}, 1\text{H}\)), 6.72 (d, \(J = 1.6 \text{ Hz}, 1\text{H}\)), 1.52 (s, 6H), 1.29 (s, 9H); \(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)): \(\delta\) 170.6, 145.6, 140.1, 126.0, 120.8, 116.7, 112.4, 78.0, 34.3, 31.4, 23.7; IR (KBr): 3461, 3184, 3093, 2963, 2862, 1681, 1604, 1494, 1392, 1257, 1159, 746, 633 cm\(^{-1}\); HRMS (ESI) \(m/z\) calcd for C\(_{14}\)H\(_{20}\)NO\(_2\) [M+H]\(^+\): 234.1489, found: 234.1490; m.p.

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132-135 °C.

6-(4-chlorobenzoyl)-2,2-dimethyl-4H-1,4-benzoxazin-3-one (2p)

Reaction of fenofirate 1p (182 mg, 0.50 mmol) gave the title compound (74 mg, 47%, pale yellow solid).

(NH₄)₂S₂O₈ (466 mg, 2.0 mmol), CH₃CN/H₂O: 12.5 mL/12.5 mL

¹H NMR (400 MHz, CDCl₃): δ 8.46 (s, 1H), 7.72 (d, J = 8.8 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.41-7.39 (m, 2H), 7.01 (d, J = 8.0 Hz, 1H), 1.58 (s, 6H);¹³C NMR (100 MHz, CDCl₃): δ 193.9, 169.3, 146.7, 138.8, 135.9, 131.5, 131.2, 128.7, 127.3, 126.9, 117.0, 116.7, 79.2, 23.9; IR (KBr): 3200, 3126, 2971, 1654, 1598, 1491, 1388, 1315, 1090, 961, 753, 689 cm⁻¹; HRMS (ESI) m/z calcd for C₁₇H₁₅ClNO₃ [M+H]: 316.0735, found: 316.0724; m.p. 187-189 °C.

4. Isolation of N-arylpyridinium 3

A 30 mL Schlenk tube equipped with a magnetic stirring bar and a septum was dried under vacuum with heating. After cooling the tube to 23 °C, it was purged with argon gas. 4-tert-Butylanisole (1a) (81 mg, 0.49 mmol), pyridine (0.40 mL, 5.0 mmol), (NH₄)₂S₂O₈ (242 mg, 1.1 mmol), Ru(phen)₃(PF₆)₂ (24 mg, 5 mol%), and CH₃CN/H₂O (12.5 mL/12.5 mL) were added to the tube, and photoirradiation was carried out with stirring for 3 h. After this time, sat. aqueous KPF₆ (100 mL) was added to the reaction mixture and the crude product was extracted with CH₂Cl₂ (3 x 30 mL) and the solvent was concentrated to 10 mL by evaporation. Et₃N (2.2 mL, 25 mmol) was then added to the solution and stirred for 10 min. The solution was subsequently washed with H₂O (3 x 20 mL) and the solvent was removed by evaporation. The obtained solid was washed with Et₂O (50 mL) to give the pure N-arylpyridinium ion 3 as a dark purple solid (182 mg, 95%).

Scheme S2. Isolation of N-arylpyridinium ion 3.

1-(2-methoxy-5-tert-butylphenyl)pyridin-1-ium hexafluorophosphate (3)

¹H NMR (400 MHz, CD₃CN): δ 8.79 (d, J = 5.2 Hz, 2H), 8.66 (t, J = 7.8 Hz, 1H), 8.15 (t, J = 7.0 Hz, 1H), 7.71 (dd, J = 8.8, 2.0 Hz, 1H), 7.58 (d, J = 2.0 Hz, 1H), 7.25 (d, J = 8.8 Hz, 1H) 3.83 (s, 3H), 1.32 (s, 9H);¹³C NMR (100 MHz, CD₃CN): δ 150.7, 147.9, 147.3, 145.8, 131.8, 131.0, 128.9, 124.8, 113.9, 57.2, 35.2, 31.5;¹⁹F NMR (376 MHz, CD₃CN): δ -72.7 (d, J = 706.1 Hz); IR (KBr): 3135, 3088, 2963, 1632, 1515, 1476, 1285, 1017, 845, 687, 558 cm⁻¹; HRMS (ESI) m/z calcd for C₁₆H₂₀NO [M]: 242.1539, found: 242.1542; m.p. (decomp.) 192-194 °C.
5. Stern–Volmer quenching experiment

Stern–Volmer fluorescence quenching experiments were run with freshly prepared $5.0 \times 10^{-5}$ M solutions of $\text{Ru(phen)}_3(\text{PF}_6)_2$ in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1/1) under an argon atmosphere using an FP-6500 spectrofluorometer (Jasco). The additive ($\text{Q}$: $(\text{NH}_4)_2\text{S}_2\text{O}_8$, 4-tert-butylanisole (1a), or pyridine) concentration ranged from 0 to 0.025 M. The solution was irradiated at 446 nm, and fluorescence was measured at 578 nm. The fluorescence intensity was measured three times in the presence and absence of the additives (Tables S1–S3), and the obtained ratios were plotted based on the Stern–Volmer expression presented in eq S1 (Figure S3).

Table S1. Luminescence quenching data for $\text{Ru(phen)}_3(\text{PF}_6)_2$ and $(\text{NH}_4)_2\text{S}_2\text{O}_8$.

<table>
<thead>
<tr>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
<th>average</th>
<th>$I_0/I_{\text{obs}}$</th>
<th>$(\text{NH}_4)_2\text{S}_2\text{O}_8$ (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>795</td>
<td>782</td>
<td>781</td>
<td>786</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>582</td>
<td>653</td>
<td>674</td>
<td>637</td>
<td>1.23</td>
<td>0.005</td>
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<tr>
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<tr>
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<td>434</td>
<td>415</td>
<td>1.89</td>
<td>0.015</td>
</tr>
<tr>
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<td>349</td>
<td>338</td>
<td>339</td>
<td>2.32</td>
<td>0.02</td>
</tr>
<tr>
<td>280</td>
<td>294</td>
<td>314</td>
<td>296</td>
<td>2.66</td>
<td>0.025</td>
</tr>
</tbody>
</table>

Table S2. Luminescence quenching data for $\text{Ru(phen)}_3(\text{PF}_6)_2$ and 4-tert-butylanisole 1a.

<table>
<thead>
<tr>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
<th>average</th>
<th>$I_0/I_{\text{obs}}$</th>
<th>1a (M)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>805</td>
<td>796</td>
<td>1</td>
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<tr>
<td>789</td>
<td>802</td>
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<td>794</td>
<td>1.00</td>
<td>0.005</td>
</tr>
<tr>
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<td>801</td>
<td>793</td>
<td>1.00</td>
<td>0.01</td>
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<tr>
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<td>753</td>
<td>776</td>
<td>1.03</td>
<td>0.015</td>
</tr>
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<td>807</td>
<td>778</td>
<td>799</td>
<td>1.00</td>
<td>0.02</td>
</tr>
<tr>
<td>820</td>
<td>795</td>
<td>750</td>
<td>788</td>
<td>1.01</td>
<td>0.025</td>
</tr>
</tbody>
</table>

Table S3. Luminescence quenching data for $\text{Ru(phen)}_3(\text{PF}_6)_2$ and pyridine.

<table>
<thead>
<tr>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
<th>average</th>
<th>$I_0/I_{\text{obs}}$</th>
<th>pyridine (M)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>822</td>
<td>833</td>
<td>824</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>836</td>
<td>843</td>
<td>841</td>
<td>840</td>
<td>0.98</td>
<td>0.005</td>
</tr>
<tr>
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<td>828</td>
<td>837</td>
<td>0.98</td>
<td>0.01</td>
</tr>
<tr>
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<td>845</td>
<td>0.98</td>
<td>0.015</td>
</tr>
<tr>
<td>810</td>
<td>833</td>
<td>808</td>
<td>817</td>
<td>1.01</td>
<td>0.02</td>
</tr>
<tr>
<td>796</td>
<td>818</td>
<td>815</td>
<td>810</td>
<td>1.02</td>
<td>0.025</td>
</tr>
</tbody>
</table>
\[
\frac{I_0}{I_{\text{obs}}} = 1 + t_0 k_q [Q] \quad \text{(S1)}
\]

- $I_0$: the intensity of fluorescence without the additive
- $I_{\text{obs}}$: the intensity of fluorescence in the presence of the additive
- $t_0$: the lifetime of the excited state of Ru(II) without the additive
- $k_q$: the quencher rate coefficient
- $[Q]$: the concentration of the additive

Figure S3. Summary of Stern-Volmer quenching experiments.
6. Reaction under thermal condition.

A 30 mL Schlenk tube equipped with a magnetic stirring bar and a septum, was dried under vacuum with heating. After cooling the tube to 23 °C, it was purged with argon gas. 4-tert-Butylanisole (1a) (34 mg, 0.20 mmol), pyridine (158 mg, 2.0 mmol), (NH₄)₂S₂O₈ (91 mg, 0.40 mmol), and CH₃CN/H₂O (1/1, 10 mL) were added to the tube, and the mixture stirred for 3 h at 70 °C. Following heating, pyrrolidine (10 mmol) was added to the reaction mixture and stirred for 12 h at 70 °C. The resulting mixture was then cooled to 23 °C and opened to air. The obtained organic compounds were extracted with CH₂Cl₂ (3 × 30 mL). Evaporation of the solvents gave a crude material. Desired amine 2a was not produced and 1a was recovered in 91% yield, which was determined by ¹H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard.

7. Procedure of gram scale photocatalytic amination.

A 500 mL flask equipped with a magnetic stirring bar and a septum, was dried under vacuum with heating. After cooling the flask to 23 °C, it was purged with argon gas. 4-Methoxybenzophenone (1d) (1.17 g, 5.5 mmol), pyridine (4.43 mL, 55 mmol), (NH₄)₂S₂O₈ (5.03 g, 22 mmol), Ru(phen)₃(PF₆)₂ (256 mg, 0.275 mmol), and CH₃CN/H₂O (1/1, 275 mL) were added to the flask, and photoirradiation was carried out with stirring for 70 hours. Following photoirradiation, pyrrolidine (22.9 mL 275 mmol) was added to the reaction mixture, which was stirred for 12 h at 70 °C. The resulting mixture was then cooled to 23 °C and opened to air. After removal of the CH₃CN by evaporation, organic compounds were extracted by EtOAc/Hex (2/1, 50 mL × 5). Evaporation of the solvents to give a crude material, which was purified by flash chromatography to give desired product 2d (1.15 g, 92%).

Scheme S3. Gram scale synthesis of 2d.
8. NMR spectra

![Figure S4. $^1$H NMR (400 MHz) spectrum of 2a in CDCl$_3$.](image)
Figure S5. $^{13}$C NMR (100 MHz) spectrum of 2a in CDCl$_3$. 
Figure S6. $^1$H NMR (400 MHz) spectrum of 2b in CDCl$_3$. 

2b
Figure S7. $^{13}$C NMR (100 MHz) spectrum of 2b in CDCl$_3$. 
Figure S8. $^1$H NMR (400 MHz) spectrum of 2c in CDCl$_3$. 
**Figure S9.** $^{13}$C NMR (100 MHz) spectrum of 2c in CDCl$_3$. 
**Figure S10.** $^1$H NMR (400 MHz) spectrum of 2d in CDCl$_3$. 

![Chemical Structure of 2d](image)
Figure S11. $^{13}$C NMR (100 MHz) spectrum of 2d in CDCl$_3$. 

$2d$
Figure S12. NOE difference NMR (400 MHz) spectrum of 2d in CDCl$_3$. 

2d
Figure S13. ¹H NMR (400 MHz) spectrum of 2e in CDCl₃.
Figure S14. $^{13}$C NMR (100 MHz) spectrum of 2e in CDCl$_3$. 
Figure S15. $^1$H NMR (400 MHz) spectrum of 2f in CDCl$_3$. 
Figure S16. $^{13}$C NMR (100 MHz) spectrum of 2f in CDCl₃.
Figure S17. $^1$H NMR (100 MHz) spectrum of 2g in CDCl$_3$. 
Figure S18. $^{13}$C NMR (100 MHz) spectrum of 2g in CDCl$_3$. 
Figure S19. $^1$H NMR (400 MHz) spectrum of 2h in CDCl$_3$. 
Figure S20. $^{13}$C NMR (100 MHz) spectrum of 2h in CDCl$_3$. 
Figure S21. $^1$H NMR (400 MHz) spectrum of 2i in CDCl$_3$. 
**Figure S22.** $^{13}$C NMR (100 MHz) spectrum of 2i in CDCl$_3$. 
Figure S23. $^1$H NMR (400 MHz) spectrum of 2j in CDCl$_3$. 
**Figure S24.** $^{13}$C NMR (100 MHz) spectrum of 2j in CDCl$_3$. 
Figure S25. $^1$H NMR (400 MHz) spectrum of 2j$^+$ in CDCl$_3$. 
Figure S26. $^{13}$C NMR (100 MHz) spectrum of 2j' in CDCl$_3$. 
Figure S27. NOE difference NMR (400 MHz) spectrum of 2j' in CDCl₃.
Figure S28. $^1$H NMR (400 MHz) spectrum of 2kx in CDCl$_3$. 
Figure S29. $^{13}$C NMR (100 MHz) spectrum of 2kx in CDCl$_3$. 
Figure S30. NOE difference NMR (400 MHz) spectrum of 2kx in CDCl₃.
Figure S31. NOE difference NMR (400 MHz) spectrum of 2kx in CDCl₃.
Figure S32. $^1$H NMR (400 MHz) spectrum of 2ky in CDCl$_3$. 

2ky
Figure S33. $^{13}$C NMR (100 MHz) spectrum of 2ky in CDCl$_3$. 
Figure S34. NOE difference NMR (400 MHz) spectrum of 2ky in CDCl₃.
Figure S35. NOE difference NMR (400 MHz) spectrum of 2ky in CDCl₃.
Figure S36. $^1$H NMR (400 MHz) spectrum of 2l in CDCl$_3$. 
Figure S37. $^{13}$C NMR (100 MHz) spectrum of 2I in CDCl$_3$. 
**Figure S38.** $^1$H NMR (400 MHz) spectrum of 2mx in CDCl$_3$. 
Figure S39. $^{13}$C NMR (100 MHz) spectrum of 2mx in CDCl$_3$. 
Figure S40. $^1$H NMR (400 MHz) spectrum of 2my in CDCl$_3$. 
Figure S41. $^{13}$C NMR (100 MHz) spectrum of 2my in CDCl₃.
Figure S42. $^1$H NMR (100 MHz) spectrum of 2n in CDCl$_3$. 

2n
**Figure S43.** $^{13}$C NMR (100 MHz) spectrum of $2n$ in CDCl$_3$. 
Figure S44. $^1$H NMR (400 MHz) spectrum of 2o in CDCl$_3$. 
Figure S45. $^{13}$C NMR (100 MHz) spectrum of 2o in CDCl$_3$. 
Figure S46. $^1$H NMR (400 MHz) spectrum of 2p in CDCl$_3$. 
Figure S47. $^{13}$C NMR (100 MHz) spectrum of 2p in CDCl$_3$. 
Figure S48. $^1$H NMR (400 MHz) spectrum of 3 in CD$_3$CN.
Figure S49. $^{13}$C NMR (100 MHz) spectrum of 3 in CD$_3$CN.
Figure S50. $^{19}$F NMR (376 MHz) spectrum of 3 in CD$_3$CN.
**Figure S51.** $^{31}$P NMR (162 MHz) spectrum of 3 in CD$_3$CN.