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Supporting Information for:

Visible–Light–mediated α –phosphorylation of *N*–aryl tertiary amines through the formation of electron–donor–acceptor complexes: synthetic and mechanistic studies

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I. General information

All solvents were reagent grade. THF, acetonitrile, diethylether and dichloromethane were purified by an Innovative Technology PURESOLV[®] purification system. Flash column chromatographies were carried out with Merck silica gel 60 (0.040-0.063 mm). Chromatography fractions and stated reactions were monitored by TLC on Merck silica gel 60 F254 aluminum plates. The spots were visualized under UV light at 254 nm and 366 nm and treated with aqueous KMnO₄ solution followed by heating with a heat gun.

¹H, ¹³C, ¹⁹F and ³¹P NMR spectra were recorded on a Bruker 400 MHz or 500 MHz spectrometers in CDCl₃ or CD₃CN. Chemical shifts are reported in ppm relative to the residual signals of the deuterated solvents as the internal standard (CDCl₃: $\delta_{\rm H} = 7.26$, $\delta_{\rm C} = 77.16$). ³¹P NMR spectra were recorded using 85% H₃PO₄ as external reference and ¹⁹F NMR spectra were recorded using CFCl₃ as external reference. Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). Coupling constants, *J*, are reported in Hertz. High-resolution mass-spectra were obtained on a Waters Qtof Micro spectrometer. UV-Visible measurements were recorded on a Perkin Elmer Lambda 40 Spectrophotometer. ESR-ST experiments were carried out using an X-Band spectrometer (MS 400 Magnettech). The ESR spectra simulations were carried out using the WINSIM software.

All reactions were carried out under a protective atmosphere of dry argon using ovendried glassware unless otherwise stated.

Secondary phosphine oxides were synthesized following reported procedures.^{1,2} (N,N)dimethylanilines were synthesized using previously described protocols.³ All other chemicals were purchased from Sigma Aldrich, Alfa Aesar or Fisher.

The blue light irradiation was performed using high-power Vision-EL (5W, $\lambda = 460 \pm 10$ nm, 410 lm).



Figure S1. Emission spectrum of the blue LED lamp used in the screening experiments.

II. General procedure for the regioselective phosphorylation of *N*– aryl amines

A dry and argon-flushed *Schlenk*-flask, equipped with a magnetic stirring bar and a septum is charged with sodium hydrogenocarbonate (50 mg, 0.60 mmol, 1.2 eq.), *N*-ethoxy-2-methylpyridinium tetrafluoroborate (4) (135 mg, 0.60 mmol, 1.2 eq.), secondary phosphine oxide (2) (1.0 mmol, 2.0 eq.) and aniline derivatives (1) (0.50 mmol, 1 eq.). Dry DMF (4.0 mL) is then added and the reaction mixture is irradiated with a blue LED lamp (5W). After stirring 15 hours, the crude mixture was purified by flash column chromatography to afford the title compound in the stated yield.

[(Methyl(phenyl)amino)methyl]diphenylphosphine oxide (3a)



According to **GP**, sodium hydrogenocarbonate (50 mg, 0.60 mmol, 1.2 eq.), *N*-ethoxy-2-methylpyridinium tetrafluoroborate (135 mg, 1.0 mmol, 2 eq.), diphenylphosphine oxide (202 mg, 1.0 mmol, 2 eq.), (*N*,*N*)-dimethylaniline (61 mg, 0.50 mmol, 1 eq.) were dissolved in DMF and irradiated for 15h. Purification by flash chromatography (silica gel, petroleum ether /EtOAc : 3/7) afforded the phosphorylated aniline **3a** (136 mg, 85%) as a white solid.

¹H NMR (400 MHz, CDCl₃): δ = 7.83-7.78 (m, 4H), 7.55-7.51 (m, 2H), 7.48-7.43 (m, 4H), 7.15-7.10 (m, 2H), 6.72-6.67 (m, 3H), 4.20 (d, *J*_{H-P} = 3.6 Hz, 2H), 2.92 (s, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ = 150.0 (d, *J*_{C-P} = 3.0 Hz), 132.2 (d, *J*_{C-P} = 2.7 Hz), 131.6

 $(d, J_{C-P} = 94.2 \text{ Hz}), 131.4 (d, J_{C-P} = 9.0 \text{ Hz}), 129.1, 128.8 (d, J_{C-P} = 11.3 \text{ Hz}), 118.0, 113.6, 55.4 (d, J_{C-P} = 82.3 \text{ Hz}), 40.0$

³¹P {¹H} NMR (162 MHz, CDCl₃): $\delta = 27.0$

HRMS (ESI) m/z calcd for $C_{20}H_{21}NOP (M+H)^+$: 322.1361, found : 322.1358.

[(Methyl(para-tolyl)amino)methyl]diphenylphosphine oxide (3b)



According to **GP**, sodium hydrogenocarbonate (50 mg, 0.60 mmol, 1.2 eq.), *N*-ethoxy-2-methylpyridinium tetrafluoroborate (135 mg, 1.0 mmol, 2 eq.), diphenylphosphine oxide (202 mg, 1.0 mmol, 2 eq.), (N,N)-dimethylparatoluidine (68 mg, 0.50 mmol, 1 eq.) were dissolved in DMF and irradiated for 15h. Purification by flash chromatography (silica gel, petroleum ether /EtOAc : 3/7) afforded the phosphorylated aniline **3b** (145 mg, 87%) as a white solid.

¹H NMR (400 MHz, CDCl₃): δ = 7.83-7.78 (m, 4H), 7.55-7.51 (m, 2H), 7.47-7.44 (m, 4H), 6.94 (d, $J_{\text{H-}}$ = 8.4 Hz, 2H), 6.61 (d, $J_{\text{H-H}}$ = 8.4 Hz, 2H), 4.14 (d, $J_{\text{H-P}}$ = 3.6 Hz, 2H), 2.89 (s, 3H), 2.21 (s, 3H).

¹³C {¹H} NMR (100 MHz, CDCl₃): δ = 148.2 (d, *J*_{C-P} = 2.7 Hz), 132.2 (d, *J*_{C-P} = 2.7 Hz), 131.4 (d, *J*_{C-P} = 9.0 Hz), 130.8 (d, *J*_{C-P} = 96.2 Hz), 129.6, 128.8 (d, *J*_{C-P} = 11.3 Hz), 122.7, 114.2, 54.9 (d, *J*_{C-P} = 83.0 Hz), 40.4, 20.4.

³¹P {¹H} NMR (162 MHz, CDCl₃): δ = 27.3

HRMS (ESI) m/z calcd for $C_{22}H_{23}NOP (M+H)^+$: 336.1517, found : 336.1515.

[(Methyl(3,5-diméthylphenyl)amino)methyl]diphenylphosphine oxide (3c)



According to **GP**, sodium hydrogenocarbonate (50 mg, 0.60 mmol, 1.2 eq.), *N*-ethoxy-2-methylpyridinium tetrafluoroborate (135 mg, 1.0 mmol, 2 eq.), diphenylphosphine oxide (202 mg, 1.0 mmol, 2 eq.), (*N*,*N*,3,5)-tetramethylaniline (75 mg, 0.50 mmol, 1 eq.) were dissolved in DMF and irradiated for 15h. Purification by flash chromatography (silica gel, petroleum ether/EtOAc : 4/6) afforded the phosphorylated aniline **3c** (152 mg, 87%) as a solid.

¹H NMR (400 MHz, CDCl₃): δ = 7.84-7.79 (m, 4H), 7.56-7.52 (m, 2H), 7.48-7.45 (m, 4H), 6.37 (s, 1H), 6.24 (s, 2H), 4.16 (d, *J*_{H-P} = 4.0 Hz, 2H), 2.94 (s, 3H), 2.16 (s, 6H).

¹³C {¹H} NMR (100 MHz, CDCl₃): $\delta = 150.2$ (d, $J_{C-P} = 3.3$ Hz), 138.6, 132.1 (d, $J_{C-P} = 2.7$ Hz), 131.9 (d, $J_{C-P} = 93.9$ Hz), 131.5 (d, $J_{C-P} = 9.0$ Hz), 128.7 (d, $J_{C-P} = 11.2$ Hz), 120.1, 111.7, 55.7 (d, $J_{C-P} = 82.6$ Hz), 40.2, 21.7.

³¹P {¹H} NMR (162 MHz, CDCl₃): δ = 26.5.

HRMS (ESI) m/z calcd for $C_{22}H_{25}NOP (M+H)^+$: 350.1674, found : 350.1673.

[(Methyl(mesityl)amino)methyl]diphenylphosphine oxide (3d)



According to **GP**, sodium hydrogenocarbonate (50 mg, 0.60 mmol, 1.2 eq.), *N*-ethoxy-2-methylpyridinium tetrafluoroborate (135 mg, 1.0 mmol, 2 eq.), diphenylphosphine oxide (202 mg, 1.0 mmol, 2 eq.), (N,N,2,4,6)-pentamethylaniline (82 mg, 0.50 mmol, 1 eq.) were dissolved in DMF and irradiated for 15h. Purification by flash chromatography (silica gel, petroleum ether /EtOAc : 1/1) afforded the phosphorylated aniline **3d** (146 mg, 81%) as a solid.

¹H NMR (400 MHz, CDCl₃): δ = 7.75-7.71 (m, 4H), 7.50-7.46 (m, 2H), 7.42-7.38 (m, 4H), 6.73 (s, 2H), 3.99 (d, *J*_{H-P} = 3.6 Hz, 2H), 2.88 (s, 3H), 2.20 (s, 3H), 1.98 (s, 6H).

¹³C {¹H} NMR (100 MHz, CDCl₃): δ = 147.0 (d, *J*_{C-P} = 7.2 Hz), 136.3, 134.9, 131.3 (d, *J*_{C-P} = 93.7 Hz), 131.7 (d, *J*_{C-P} = 2.7 Hz), 131.2 (d, *J*_{C-P} = 8.9 Hz), 129.7, 128.5 (d, *J*_{C-P} = 11.1 Hz), 57.4 (d, *J*_{C-P} = 88.3 Hz), 42.8, 20.7, 18.6. ³¹P {¹H} NMR (162 MHz, CDCl₃): δ = 29.1

HRMS (ESI) m/z calcd for $C_{23}H_{27}NOP (M+H)^+$: 364.1830, found : 364.1829.

[(Methyl(4-bromophenyl)amino)methyl]diphenylphosphine oxide (3e)



According to **GP**, sodium hydrogenocarbonate (50 mg, 0.60 mmol, 1.2 eq.), *N*-ethoxy-2-methylpyridinium tetrafluoroborate (135 mg, 1.0 mmol, 2 eq.), diphenylphosphine oxide (202 mg, 1.0 mmol, 2 eq.), 4-bromo-(*N*,*N*)-dimethylaniline (100 mg, 0.50 mmol, 1 eq.) were dissolved in DMF and irradiated for 15h. Purification by flash chromatography (silica gel, petroleum ether /EtOAc : 4/6) afforded the phosphorylated aniline **3e** (142 mg, 71%) as a solid.

¹H NMR (400 MHz, CDCl₃): δ = 7.81-7.76 (m, 4H), 7.56-7.53 (m, 2H), 7.48-7.44 (m, 4H), 7.17 (d, $J_{\text{H-H}}$ = 8.8 Hz, 2H), 6.71-6.67 (d $J_{\text{H-H}}$ = 8.8 Hz, 2H), 4.16 (d, $J_{\text{H-P}}$ = 2.8 Hz, 2H), 2.89 (s, 3H).

¹³C {¹H} NMR (100 MHz, CDCl₃): δ = 148.9 (d, *J*_{C-P} = 3.2 Hz), 132.4 (d, *J*_{C-P} = 2.7 Hz), 131.7, 131.5 (d, *J*_{C-P} = 94.1 Hz), 131.4 (d, *J*_{C-P} = 9.1 Hz), 128.9 (d, *J*_{C-P} = 11.3 Hz), 115.1, 110.0, 55.3 (d, *J*_{C-P} = 81.0 Hz), 40.2

³¹P {¹H} NMR (162 MHz, CDCl₃): $\delta = 26.5$

HRMS (ESI) m/z calcd for $C_{20}H_{20}NOPBr (M+H)^+$: 400.0466, found : 400.0461.

[(Methyl(4-fluorophenyl)amino)methyl]diphenylphosphine oxide (3f)



According to **GP**, sodium hydrogenocarbonate (50 mg, 0.60 mmol, 1.2 eq.), *N*-ethoxy-2-methylpyridinium tetrafluoroborate (135 mg, 1.0 mmol, 2 eq.), diphenylphosphine oxide (202 mg, 1.0 mmol, 2 eq.), 4-fluoro-(*N*,*N*)-dimethylaniline (70 mg, 0.50 mmol, 1 eq.) were dissolved in DMF and irradiated for 15h. Purification by flash chromatography (silica gel, petroleum ether/EtOAc : 3/7) afforded the phosphorylated aniline **3f** (115 mg, 68%) as a solid.

¹H NMR (400 MHz, CDCl₃): $\delta = 7.82-7.77$ (m, 4H), 7.56-7.52 (m, 2H), 7.49-7.45 (m, 4H), 6.84-6.89 (m, 2H), 6.66-6.63 (m, 2H), 4.13 (d, $J_{\text{H-P}} = 3.2$ Hz, 2H), 2.89 (s, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃): $\delta = 156.3$ (d, $J_{\text{C-F}} = 235.5$ Hz), 146.9 (d, $J_{\text{C-P}} = 5.0$ Hz), 132.3 (d, $J_{\text{C-P}} = 2.7$ Hz), 131.7 (d, $J_{\text{C-P}} = 94.1$ Hz), 131.4 (d, $J_{\text{C-P}} = 9.0$ Hz), 128.8 (d, $J_{\text{C-P}} = 11.3$ Hz), 115.5 (d, $J_{\text{C-F}} = 22.1$ Hz), 115.2 (d, $J_{\text{C-F}} = 7.4$ Hz), 56.3 (d, $J_{\text{C-P}} = 80.5$ Hz), 40.8 ³¹P {¹H} NMR (162 MHz, CDCl₃): $\delta = 26.5$ ¹⁹F {¹H} NMR (376.5 MHz, CDCl₃) $\delta = -127.2$ HRMS (ESI) m/z calcd for C₂₀H₂₀NOPF (M+H)⁺ : 340.1267, found : 340.1264.

[1-(ethyl(phenyl)amino)ethyl]diphenylphosphine oxide (3g)



According to **GP**, sodium hydrogenocarbonate (50 mg, 0.60 mmol, 1.2 eq.), *N*-ethoxy-2-methylpyridinium tetrafluoroborate (135 mg, 1.0 mmol, 2 eq.), diphenylphosphine oxide (202 mg, 1.0 mmol, 2 eq.), (*N*,*N*)-diethylaniline (75 mg, 0.50 mmol, 1 eq.) were dissolved in DMF and irradiated for 15h. Purification by flash chromatography (silica gel, petroleum ether /EtOAc : 3/7) afforded the phosphorylated aniline **3g** (133 mg, 76%) as a solid.

¹H NMR (400 MHz, CDCl₃): δ = 7.85-7.81 (m, 2H), 7.74-7.69 (m, 2H), 7.52-7.46 (m, 3H), 7.42-7.38 (m, 1H), 7.33-7.29 (m, 2H) 7.20-7.16 (m, 2H), 6.73-6.67 (m, 3H), 4.69-4.62 (m, 1H), 3.70-3.61 (m, 1H), 3.52-3.45 (m, 1H), 1.47 (dd, $J_{\text{H-P}}$ = 10.0 Hz, $J_{\text{H-H}}$ = 7.2 Hz, 2H), 0.99 (t, $J_{\text{H-H}}$ = 7.2 Hz, 3H). ¹³C (¹H) NMR (100 MHz, CDCl₂): δ = 147.8 (d, $J_{\text{R-P}}$ = 5.9 Hz), 132.8 (d, $J_{\text{R-P}}$ = 95.8 Hz), 131.8

¹³C {¹H} NMR (100 MHz, CDCl₃): $\delta = 147.8$ (d, $J_{C-P} = 5.9$ Hz), 132.8 (d, $J_{C-P} = 95.8$ Hz), 131.8 (d, $J_{C-P} = 96.8$ Hz), 131.7 (d, $J_{C-P} = 2.7$ Hz), 131.6 (d, $J_{C-P} = 2.8$ Hz), 131.1 (d, $J_{C-P} = 9.1$ Hz), 130.7 (d, $J_{C-P} = 8.7$ Hz), 129.2, 128.7 (d, $J_{C-P} = 11.0$ Hz), 128.2 (d, $J_{C-P} = 11.3$ Hz), 117.6, 114.5, 55.6 (d, $J_{C-P} = 78.4$ Hz), 40.5, 13.6, 11.6.

³¹P {¹H} NMR (162 MHz, CDCl₃): δ = 33.1 HRMS (ESI) m/z calcd for C₂₂H₂₄NOPNa (M+Na)⁺ : 372.1493, found : 372.1492.

Diphenyl(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphine oxide (3h)



According to **GP**, sodium hydrogenocarbonate (50 mg, 0.60 mmol, 1.2 eq.), *N*-ethoxy-2-methylpyridinium tetrafluoroborate (135 mg, 1.0 mmol, 2 eq.), diphenylphosphine oxide (202 mg, 1.0 mmol, 2 eq.), 2-phenyl-1,2,3,4-tetrahydroquinoline (105 mg, 0.50 mmol, 1 eq.) were dissolved in DMF and irradiated for 15h. Purification by flash chromatography (silica gel, petroleum ether/EtOAc: 1/1) afforded the phosphorylated aniline **3h** (186 mg, 91%) as a slightly orange solid.

¹H NMR (400 MHz, CDCl₃): δ = 7.83-7.78 (m, 2H), 7.73-7.69 (m, 2H), 7.56-7.53 (m, 1H), 7.47-7.43 (m, 3H), 7.35-7.32 (m, 2H), 7.16-7.12 (m, 3H), 7.09-7.06 (m, 1H), 6.96-6.92 (m, 1H), 6.82-6.76 (m, 3H), 6.67-6.65 (m, 1H), 5.57 (d, *J*_{H-P} = 1à.8 Hz, 1H), 4.07-4.00 (m, 1H), 3.60-3.56 (m, 1H), 2.86-2.81 (m, 1H), 2.70-2.66 (m, 1H).

¹³C {¹H} NMR (100 MHz, CDCl₃): $\delta = 150.0$ (d, $J_{C-P} = 7.7$ Hz), 137.0 (d, $J_{C-P} = 4.2$ Hz) 132.4 (d, $J_{C-P} = 8.3$ Hz), 132.3 (d, $J_{C-P} = 97.7$ Hz), 132.0 (d, $J_{C-P} = 2.7$ Hz), 131.8 (d, $J_{C-P} = 8.6$ Hz), 131.5 (d, $J_{C-P} = 100.1$ Hz), 130.0, 129.3 (d, $J_{C-P} = 1.9$ Hz), 129.2, 128.6 (d, $J_{C-P} = 11.1$ Hz), 128.4 (d, $J_{C-P} = 11.3$ Hz), 127.9 (d, $J_{C-P} = 3.2$ Hz), 127.5 (d, $J_{C-P} = 2.8$ Hz), 125.6 (d, $J_{C-P} = 2.4$ Hz), 119.7, 116.9, 62.1 (d, $J_{C-P} = 79.2$ Hz), 45.2, 26.7.

³¹P {¹H} NMR (162 MHz, CDCl₃): δ = 30.8

HRMS (ESI) m/z calcd for $C_{27}H_{24}NOPNa$ (M+Na)⁺ : 432.1493, found : 432.1493.

[(Methyl(phenyl)amino)methyl]bis(4-tert-butylphenyl)phosphine oxide (3i)



According to **GP**, sodium hydrogenocarbonate (50 mg, 0.60 mmol, 1.2 eq.), *N*-ethoxy-2-methylpyridinium tetrafluoroborate (135 mg, 1.0 mmol, 2 eq.), bis(4-*tert*butylphenyl)phosphine oxide (314 mg, 1.0 mmol, 2 eq.), (*N*,*N*)-dimethylaniline (61 mg, 0.50 mmol, 1 eq.) were dissolved in DMF and irradiated for 15h. Purification by flash chromatography (silica gel, petroleum ether /EtOAc : 1/1) afforded the phosphorylated aniline **3i** (180 mg, 83%) as a solid.

¹H NMR (400 MHz, CDCl₃): δ = 7.74-7.71 (m, 4H), 7.48-7.44 (m, 4H), 7.11-7.07 (m, 2H), 6.68-6.63 (m, 3H), 4.16 (d, *J*_{H-P} = 3.2 Hz, 2H), 2.95 (s, 3H), 1.31 (s, 18H).

¹³C {¹H} NMR (100 MHz, CDCl₃): $\delta = 155.6$ (d, $J_{C-P} = 2.5$ Hz), 132.1 (d, $J_{C-P} = 2.7$ Hz), 131.3 (d, $J_{C-P} = 9.5$ Hz), 128.9, 128.3 (d, $J_{C-P} = 96.8$ Hz), 125.7 (d, $J_{C-P} = 11.5$ Hz), 117.8, 113.5, 55.3 (d, $J_{C-P} = 81.6$ Hz), 40.0, 35.1, 31.2.

³¹P {¹H} NMR (162 MHz, CDCl₃): $\delta = 27.2$

HRMS (ESI) m/z calcd for $C_{28}H_{37}NOP (M+H)^+$: 434.2613, found : 434.2608.

[(Methyl(phenyl)amino)methyl]bis(4-methoxyphenyl)phosphine oxide (3j)



According to **GP**, sodium hydrogenocarbonate (50 mg, 0.60 mmol, 1.2 eq.), *N*-ethoxy-2-methylpyridinium tetrafluoroborate (135 mg, 1.0 mmol, 2 eq.), bis(4methoxyphenyl)phosphine oxide (262 mg, 1.0 mmol, 2 eq.), (*N*,*N*)-dimethylaniline (61 mg, 0.50 mmol, 1 eq.) were dissolved in DMF and irradiated for 15h. Purification by flash chromatography (silica gel, petroleum ether/EtOAc : 2/8) afforded the phosphorylated aniline **3j** (137 mg, 72%) as a solid.

¹H NMR (400 MHz, CDCl₃): δ = 7.73-7.68 (m, 4H), 7.16-7.12 (m, 2H), 6.97-6.94 (m, 4H), 6.72-6.68 (m, 3H), 4.12 (d, *J*_{H-P} = 3.6 Hz, 2H), 3.83 (s, 6H), 2.91 (s, 3H).

¹³C {¹H} NMR (100 MHz, CDCl₃): $\delta = 162.5$ (d, $J_{C-P} = 2.4$ Hz), 133.1 (d, $J_{C-P} = 10.3$ Hz), , 129.0, 122.9 (d, $J_{C-P} = 96.6$ Hz), 117.8, 114.2 (d, $J_{C-P} = 12.2$ Hz), 113.7 (d, $J_{C-P} = 3.2$ Hz), 113.4, 55.6 (d, $J_{C-P} = 88.6$ Hz), 55.3, 39.9.

³¹P {¹H} NMR (162 MHz, CDCl₃): δ = 27.9

HRMS (ESI) m/z calcd for C₂₂H₂₅NO₃P (M+H)⁺ : 382.1572, found : 382.1576.

[(Methyl(phenyl)amino)methyl]bis(4-(trifluoromethyl)phenyl)phosphine oxide (3k)



According to **GP**, sodium hydrogenocarbonate (50 mg, 0.60 mmol, 1.2 eq.), *N*-ethoxy-2-methylpyridinium tetrafluoroborate (135 mg, 1.0 mmol, 2 eq.), bis(4-(trifluoromethyl)phenyl)phosphine oxide (338 mg, 1.0 mmol, 2 eq.), (N,N)-dimethylaniline (61 mg, 0.50 mmol, 1 eq.) were dissolved in DMF and irradiated for 15h. Purification by flash chromatography (silica gel, petroleum ether/EtOAc : 1/1) afforded the phosphorylated aniline **3k** (178 mg, 78%) as a solid.

¹H NMR (400 MHz, CDCl₃): $\delta = 7.95-7.91$ (m, 4H), 7.75-7.72 (m, 4H), 7.15-7.17 (m, 2H), 6.76-6.73 (m, 1H), 6.70-6.67 (m, 2H), 4.27 (d, $J_{\text{H-P}} = 2.8$ Hz, 2H), 2.98 (s, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃): $\delta = 149.4$ (d, $J_{\text{C-P}} = 3.0$ Hz), 135.4 (d, $J_{\text{C-P}} = 91.3$ Hz) 134.2 (qd, $J_{\text{C-F}} = 32.9$ Hz, $J_{\text{C-P}} = 2.6$ Hz), 131.7 (d, $J_{\text{C-P}} = 9.4$ Hz), 129.1, 128.3 (dq, $J_{\text{C-P}} = 11.3$ Hz, $J_{\text{C-P}} = 2.7$ Hz), 123.4 (q, $J_{\text{C-F}} = 271.3$ Hz), 118.9, 114.0, 55.2 (d, $J_{\text{C-P}} = 81.9$ Hz), 40.5. ³¹P {¹H} NMR (162 MHz, CDCl₃): $\delta = 25.2$ ¹⁹F {¹H} NMR (376.5 MHz, CDCl₃): $\delta = -63.3$ HRMS (ESI) m/z calcd for C₂₂H₁₉NOPF₆ (M+H)⁺ : 458.1108, found : 458.1104.

[(Methyl(phenyl)amino)methyl]bis(2-methylphenyl)phosphine oxide (3l)



According to **GP**, sodium hydrogenocarbonate (50 mg, 0.60 mmol, 1.2 eq.), *N*-ethoxy-2-methylpyridinium tetrafluoroborate (135 mg, 1.0 mmol, 2 eq.), bis(4methylphenyl)phosphine oxide (230 mg, 1.0 mmol, 2 eq.), (N,N)-dimethylaniline (61 mg, 0.50 mmol, 1 eq.) were dissolved in DMF and irradiated for 15h. Purification by flash chromatography (silica gel, petroleum ether/EtOAc : 1/1) afforded the phosphorylated aniline **3l** (129 mg, 74%) as a solid.

¹H NMR (400 MHz, CDCl₃): δ = 7.62-7.57 (m, 2H), 7.41-7.38 (m, 2H), 7.26-7.24 (m, 2H), 7.22-7.18 (m, 2H), 7.13-7.09 (m, 2H), 6.71-6.67 (m, 3H), 4.36 (d, *J*_{H-P} = 2.8 Hz, 2H), 2.95 (s, 3H), 2.38 (s, 6H). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ = 150.2 (d, *J*_{C-P} = 3.4 Hz), 142.5 (d, *J*_{C-P} = 7.6 Hz), 132.1 (d, *J*_{C-P} = 10.4 Hz), 132.0 131.4 (d, *J*_{C-P} = 10.9 Hz), 131.2 (d, *J*_{C-P} = 91.7 Hz), 128.9, 125.7 (d, *J*_{C-P} = 11.6 Hz), 117.8, 113.5, 54.5 (d, *J*_{C-P} = 83.1 Hz), 40.0, 21.3 (d, *J*_{C-P} = 3.8 Hz) ³¹P {¹H} NMR (162 MHz, CDCl₃): δ = 28.5

HRMS (ESI) m/z calcd for $C_{22}H_{25}NOP (M+H)^+$: 350.1674, found : 350.1672.

Dimethyl[(Methyl(phenyl)amino)methyl]phosphonate (3m)



According to **GP**, sodium hydrogenocarbonate (50 mg, 0.60 mmol, 1.2 eq.), *N*-ethoxy-2-methylpyridinium tetrafluoroborate (135 mg, 1.0 mmol, 2 eq.), dimethylphosphonate (110 mg, 1.0 mmol, 2 eq.), (*N*,*N*)-dimethylaniline (61 mg, 0.50 mmol, 1 eq.) were dissolved in DMF and irradiated for 15h. Purification by flash chromatography (silica gel, petroleum ether/EtOAc : 1/1) afforded the phosphorylated aniline **3m** (88 mg, 77%) as a gum.

¹H NMR (400 MHz, CDCl₃): δ = 7.30-7.28 (m, 2H), 6.87-6.84 (m, 2H), 6.82-6.78 (m, 1H), 3.84 (d, *J*_{H-P} = 4.8 Hz, 2H), 3.75 (d, *J*_{H-P} = 10.8 Hz, 2H), 3.06 (s, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ = 149.3 (d, *J*_{C-P} = 2.2 Hz), 129.3, 117.8, 113.1, 52.9 (d, *J*_{C-P} = 6.9 Hz), 50.1 (d, *J*_{C-P} = 60.7 Hz), 39.3. ³¹P {¹H} NMR (162 MHz, CDCl₃): δ = 26.1 HRMS (ESI) m/z calcd for C₁₀H₁₇NO₃P (M+H)⁺ : 230.0946, found : 230.0945.

III. Mechanistic investigations

100 90 80 70 NMR Yield (%) 60 50 40 30 20 10 0 0 200 400 600 800 1000 TIme (min)

III.1. Kinetic study

Figure S2 : Kinetic progres of the reaction of N,N-dimethyl aniline **1a** with diphenylphosphine oxide **2a** under the optimized conditions.^{[a],[b]}

[a] Reaction conditions: 1a (0.5 mmol), 2a (1 mmol), 4 (0.6 mmol), NaHCO₃ (0.6 mmol), DMF (4 mL).
[b] NMR Yields are determined from ³¹P NMR spectroscopy using tri-*n*-octylphosphine oxide as internal standard.

III.2. Determination of the Quantum Yield

The Quantum Yield of the reaction was measured with the standard ferrioxalate actinometer according to a method reoprted by Yoon.^[4].

The reaction was stirred for 90 secondes. During this period, the photon flux received by the reaction mixture was determined to be $1.6 \cdot 10^{-4}$ mol. ³¹P NMR spectroscopy has been used to determine the conversion of the photocatalytic reaction of **1a** with **2b** by using tri-*n*-octylphosphine oxide as internal standard. After 90s of irradiation, the conversion has been estimated to be 0.9%, which corresponds to 4.5×10^{-5} mol. Based on this, the QY was calculated to be 0.28.

QY was determined as an average of three subsequent measurements.

III.3. Characterization of the EDA by UV-visible absorption

III.3.1 Stoichiometry of the EDA complex **5** in solution (Job's plot)

The Job plot was constructed to evaluate the stoichiometry of the EDA complex between the (*N*,*N*)dimethylaniline (**1a**) and *N*-ethoxy-2-methyloyridinium (**4**) in DMF at 20 °C.^[5] We measured the absorption at 410 nm of DMF solutions of **1a** and **2b** having a constant total concentration of 0.2 M but different donor/acceptor ratios. The absorbance values are plotted against the molar fraction (%) of *N*-ethoxy-2-methyloyridinium. The maximum absorbance is obtained for a 1:1 mixture of **1a**:**4**, indicating that this is the stoichiometry of the EDA complex in solution.



Figure S3. Job's plot of EDA complex 5 in DMF.

III.3.2. Determination of the association constant (K_{EDA})

The association constant of the EDA complex formed between (N,N)dimethylaniline (2a) and *N*-ethoxy-2-methylpyridinium (4) was determined spectrophotometrically in DMF, employing the Benesi-Hildebrand methodology^[6]. We measured the absorption at 410 nm of solutions with constant concentration of the *N*-ethoxy-2-methylpyridinium 4 (0.2 M) but increased donor/acceptor ratios, adding an excess of (N,N)dimethylaniline 1a. The association constant (*K*_{EDA}), calculated dividing the intercept by the slope, is 2.7 M⁻¹.



Figure S4. Benesi-Hildebrand's plot of the EDA complex 5 in DMF

III.4. Light/dark cycle experiments for the model reaction

To study the necessity of continuous irradiation with visible light for the progress of the reaction, we started a reaction with successive irradiation and black periods. We determined NMR yields directly in the crude mixture using tri-*n*-octylphosphine oxide as internal 31 P standard. These results demonstrated that light is a necessary component of the reaction.



Figure S5. Each point of the graphic represents the NMR yield, calculated from the relative amounts of an internal standard (tri-*n*-octylphosphine oxide) and the product. The grey boxes represent the periods in which the reaction vessels were covered (dark period). The reaction was done with: 0.5 mmol of **1a**, 0.6 mmol of **4**, 1 mmol of **2a** and 0.6 mmol of NaHCO₃ in 4 mL of DMF.

III.5. Characterization of the ethoxy radical by EPR spectroscopy

The ethoxy radical was generated at room temperature upon mixing (*N*,*N*)dimethylaniline (**1a**) with *N*-ethoxy-2-methylpyridinium tetrafluoroborate (**4**) in toluene under blue LEDs irradiation ($\lambda = 405$ nm), and in the presence of phenyl-*N*-tert-butylnitrone (PBN) (**9**) according to a previously reported.^[7]

Figure S6 :EPR Spin trapping spectra of **1a** and **4** in toluene in presence of PBN under Blue LEDs irradiation.



The hyperfine coupling constant determined $a_N = 13.67$ G and $a_H = 1.91$ G are in agreement with those previously reported for PBN-ethoxy adduct.^[1]

IV. References

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V. NMR Spectra



230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)



















