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Visible-light-promoted/PIFA-mediated direct C-H acylation

of quinoxalin-2(1H)-ones with aldehydes

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1. General Information.

¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were recorded on a Bruker DPX600 or Bruker DPX500. Data are reported as follows: chemical shift δ /ppm, integration (1H only), multiplicity (s = singlet, d = doublet, t =triplet, dd = doublet of doublets, m = multiplet; ¹³C signals are singlets unless otherwise stated), coupling constants *J* in Hz. HRMS spectra were obtained on a Thermo Q Exactive spectrometer. Melting points (MP) were determined by SGW X-4A. High performance liquid Chromatographic (HPLC) was carried out on a Shimadzu LC-2030C Plus. UV-VIS spectra were recorded on a Shimadzu UV-2700 spectrophotometer. 25W blue LED chips was used as the irradiation source, and the emission spectrum was shown in **Figure 1**. Compounds **1b-1j** were prepared using literature methods.¹⁻⁵ All other chemicals were purchased from Chemical Co. and used as received unless otherwise specified.



Figure 1. Emission spectrum of the blue LED chips

2. General procedure for the synthesis of starting materials (1b-1h).¹⁻⁵



A typical procedure: To a stirred solution of quinoxalin-2(1H)-ones (3 mmol) in DMF (10 mL) was added the corresponding halide (1.6 equiv) and potassium carbonate (1.2 equiv.) at room temperature, and the mixture was stirred overnight. Then the resulting mixture was added with water (50 mL), and extracted with ethyl acetate (50 mL) for three times. The combined organic layer was dried over Na₂SO₄, filtered and evaporated

under reduced pressure. The residue was purified by column chromatography on silica gel to give the desired product **1b** to **1h**.

1-Methylquinoxalin-2(1*H*)-one (1b):

White solid. Yield: 73%. ¹H NMR (600 MHz, DMSO-*d*₆): δ 8.24 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H) (aromatic *H*), 3.61 (s, 3H) (CH₃). ¹³C NMR (151 MHz, DMSO-*d*₆): δ 154.31 (CO), 150.04, 133.11, 132.63, 131.05, 129.53, 123.42, 114.84 (aromatic *C*), 28.54 (CH₃). This is a known structure. These data are similar to the reported one.^{1,3}

1-Ethylquinoxalin-2(1*H*)-one (1c):



White solid. Yield: 67%. ¹H NMR (600 MHz, DMSO-*d*₆): δ 8.23 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.69-7.65 (m, 2H), 7.40-7.38 (m, 1H) (aromatic *H*), 4.26-4.23 (m, 2H) (C*H*₂), 1.23 (t, *J* = 7.2 Hz, 3H) (C*H*₃). ¹³C NMR (150 MHz, DMSO-*d*₆): δ 153.86 (*C*O), 150.10, 132.91,

131.91, 131.16, 129.87, 123.36, 114.54 (aromatic *C*), 36.40 (*C*H₂), 12.29 (*C*H₃). This is a known structure. These data are similar to the reported one.¹

1-Isopropylquinoxalin-2(1*H*)-one (1d):



Colorless liquid. Yield: 80%. ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.52 (s, 1H), 8.00-7.97 (m, 1H), 7.83-7.80 (m, 1H), 7.76-7.72 (m, 1H), 7.64-7.60 (m, 1H) (aromatic *H*), 5.47-5.41 (m, 1H) (C*H*), 1.39 (d, *J* = 6.2 Hz, 6H) (C*H*₃). ¹³C NMR (150 MHz, DMSO-*d*₆): δ 156.48

(CO), 140.21, 139.67, 138.09, 130.29, 128.62, 126.83, 126.57 (aromatic *C*), 68.95 (*C*H), 21.53 (*C*H₃). This is a known structure. These data are similar to the reported one.¹

1-Benzylquinoxalin-2(1*H*)-one (1e):



White solid. Yield: 68%. ¹H NMR (600 MHz, DMSO-*d*₆): δ 8.36 (s, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.28 – 7.24 (m, 3H) (aromatic *H*), 5.49 (s, 2H) (CH₂). ¹³C NMR (151 MHz,

DMSO-d₆): δ 154.51(CO), 150.35, 135.69, 132.98, 132.24, 131.04, 129.84, 128.71,

127.37, 126.80, 123.63, 115.21 (aromatic *C*), 44.45 (*C*H₂). This is a known structure. These data are similar to the reported one.^{2,3}

1-Acetophenylquinoxalin-2(1*H*)-one (1f):



Yellow solid. Yield: 65%. ¹H NMR (600 MHz, DMSO-*d*₆): δ 8.35 (s, 1H), 8.15 (d, *J* = 7.5 Hz, 2H), 7.90 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.77 (t, *J* = 7.4 Hz, 1H), 7.64 (t, *J* = 7.8 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.52 (d, *J* = 8.5 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H) (aromatic *H*), 5.93 (s, 2H) (CH₂).¹³C NMR (151 MHz, DMSO-*d*₆): δ 192.18, 154.17(*C*O), 149.77,

134.37, 134.29, 132.83, 132.73, 131.21, 129.80, 128.97, 128.33, 123.67, 115.02 (aromatic *C*), 48.63 (*C*H₂). This is a known structure. These data are similar to the reported one.^{2,4}

1-(2-Propynyl) quinoxalin-2(1*H*)-one (1g):



Yellow solid. Yield: 79%. ¹H NMR (600 MHz, DMSO-*d*₆): δ 8.29 (s, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.72 (t, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H) (aromatic *H*), 5.07 (d, *J* = 2.5 Hz, 2H) (CH₂), 3.36 (t, *J* = 2.4 Hz, 1H) (alkynyl *H*). ¹³C NMR (151

MHz, DMSO- d_6): δ 153.32 (CO), 150.04, 132.83, 131.45, 131.18, 129.82, 123.91, 115.08 (aromatic *C*), 77.83, 75.25 (alkynyl *C*), 30.83 (*C*H₂). This is a known structure. These data are similar to the reported one.²

1-Allylquinoxalin-2(1*H*)-one (1h):



White solid. Yield: 66%. ¹H NMR (600 MHz, DMSO- d_6): δ 8.28 (s, 1H), 7.85 (dd, J = 7.9, 1.2 Hz, 1H), 7.64 (m, 1H), 7.51 (dd, J = 8.5, 1.2 Hz, 1H), 7.38 (m, 1H) (aromatic H), 5.96 – 5.90 (m, 1H), 5.17 (dd, J = 10.5, 1.5 Hz, 1H), 5.05 (dd, J = 17.3, 1.5 Hz, 1H) (olefinic H), 4.92 –

4.83 (m, 2H) (CH₂). ¹³C NMR (151 MHz, DMSO- d_6): δ 153.96 (CO), 150.20, 132.85, 132.20, 131.43, 131.01, 129.75, 123.52 (aromatic C), 117.11, 115.20 (olefinic C), 43.36 (CH₂). This is a known structure. These data are similar to the reported one.²

3. General procedure for the synthesis of starting materials (1i and 1j).⁴



To a stirred solution of 3-methoxysalicylaldehyde (3 mmol) in ACN (10 mL) was added with 1,3-dibromopropane (3 equiv) and potassium carbonate (3 equiv). The mixture was stirred at 55 °C for 23h. Then, the resulting mixture was cooled, added with water (50 mL), and extracted with ethyl acetate (50 mL) for three times. The combined organic layer was dried over Na₂SO₄, filtered and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to give the 2-(3-bromopropoxy)-3-methoxybenzaldehyde in 89% yield.

A round bottom flask equipped with the 2-(3-bromopropoxy)-3 - methoxybenzaldehyde (2 mmol), quinoxalin-2(*1H*)-ones (2 mmol) and potassium carbonate (1 equiv) was purged with nitrogen for 3 times. Then, DMF (10 mL) was added into the round bottom flask, and the reaction was stirred at 55 °C for 3 h. The resulting mixture was added with water (50 mL), and extracted with ethyl acetate (50 mL) for three times. The combined organic layer was dried over Na₂SO₄, filtered and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to obtain the desired product **1i**.

3-Methoxy-2-(3-(2-oxoquinoxalin-1(2H)-yl)propoxy)benzaldehyde (1i):



Light brown solid. Yield: 22%. ¹H NMR (600 MHz, Chloroform-*d*): δ 10.50 (s, 1H) (CHO), 8.48 (s, 1H), 8.02 (d, J = 8.2 Hz, 1H), 7.85 (d, J = 9.6 Hz, 1H), 7.74 – 7.64 (m, 1H), 7.62 – 7.53 (m, 1H), 7.42 (dd, J = 5.6, 3.8 Hz, 1H), 7.13 (d, J = 3.8 Hz, 2H) (aromatic H), 4.74 (s, 2H), 4.35 (s, 2H), 3.84 (s, 3H), 2.37 (t, J = 6.2 Hz, 2H) (CH₂ & CH₃). ¹³C NMR (151

MHz, Chloroform-*d*): δ 190.46, 157.56, 153.25, 151.97, 140.68, 139.87, 139.20, 130.48, 130.26, 129.27, 127.58, 126.90, 124.46, 119.58, 118.39 (*CO* & aromatic C), 71.82, 63.48, 56.34, 29.91 (*C*H₂ & *C*H₃). This is a known structure. These data are similar to the reported one.⁴



To a stirred solution of quinoxalin-2(1H)-ones (3 mmol) in DMF (10 mL) was added the 2-bromoethanol (1.6 equiv) and potassium carbonate (1.2 equiv), and the mixture was stirred at 55 °C for 23h. Then the resulting mixture was added with water (50 mL), and extracted with ethyl acetate (50 mL) for five times. The combined organic layer was dried over Na₂SO₄, filtered and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to obtain the desired product 1-(2-hydroxyethyl) quinoxalin-2(1H)-one in 53% yield.

Ibuprofen (2.25 mmol) was added into a round bottom flask equipped with SOCl₂ (4.5 mL) and DCM (4.5 mL). The mixture was stirring at 55 °C for 3.5 h. Then, the reaction was filtered and evaporated under reduced pressure to give the crude 2-(4-isobutylphenyl) propanoyl chloride which was used directly for the next step.

The 1-(2-hydroxyethyl) quinoxalin-2(*1H*)-one (1.5 mmol), acyl chloride product (1.5 equiv), and triethylamine (1.5 equiv) were added into the bottom flask with DMF (10 mL). The mixture was stirred at 55 °C for 2 h. The resulting mixture was added with water (100 mL), and extracted with ethyl acetate (100 mL) for five times. The combined organic layers were dried over Na₂SO₄, filtered and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to obtain the desired product **1j**.

2-(2-Oxoquinoxalin-1(2H)-yl)ethyl 2-(4-isobutylphenyl)propanoate (1j):



Yellow oil. Yield: 40%. ¹H NMR (400 MHz, chloroform-*d*): δ 8.28 (s, 1H), 7.88 (dd, J = 8.0, 1.6 Hz, 1H), 7.57 – 7.49 (m, 1H), 7.44 – 7.32 (m, 2H), 7.11 – 7.00 (m, 4H) (aromatic *H*), 4.64

-4.30 (m, 4H), 3.67 - 3.49 (m, 1H), 2.44 (d, 2H), 1.89 - 1.78 (m, 1H), 1.41 (d, J = 7.2 Hz, 3H), 0.90 (s, 3H), 0.88 (s, 3H) (CH, CH₂ & CH₃). ¹³C NMR (151 MHz, Chloroform-*d*): δ 174.83, 154.98, 150.07, 140.84, 137.23, 133.61, 132.84, 131.22,

130.82, 129.50, 127.17, 123.95, 114.11 (CO & aromatic C), 61.08, 45.14, 45.08, 40.67, 30.27, 22.52, 18.42 (CH, CH₂ & CH₃). This is a known structure. These data are similar to the reported one.⁴

4. General procedure for the synthesis of product (3a-3ac).



A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with 1 (0.3 mmol) and PIFA (0.45 mmol, 1.5 equiv), which mixture was evacuated and purged with nitrogen for three times. Then 2 (2.7 mmol, 9 equiv) in DCM (3 mL) was added into the flame-dried Schlenk-tube via syringe. The reaction mixture was stirred and irradiated with 25 W blue light for 3 h – 42 h. After that, 20 mL water and 2 mL NaOH (1 M in water) was added into the reaction mixture, and the resulting solution was extracted with ethyl acetate (20 mL* 3). The combined organic solvent was dried over Na₂SO₄, and was removed under reduced pressure with a rotary evaporator. The crude residue was purified by silica gel column chromatography with ethyl acetate and petrol ether or dichloromethane and ethyl acetate as eluent to give the pure product **3**.

3-Benzoylquinoxalin-2(1*H*)-one (3a):



Yellow solid. Yield: 61%. ¹H NMR (400 MHz, DMSO- d_6): δ 12.88 (s, 1H) (NH), 8.00 – 7.94 (m, 2H), 7.83 (dd, J = 8.1, 1.4Hz, 1H), 7.77 – 7.71 (m, 1H), 7.69 – 7.63 (m, 1H), 7.57 (t, J =

7.8 Hz, 2H), 7.44 – 7.32 (m, 2H) (aromatic *H*). ¹³C NMR (151 MHz, DMSO-*d*₆): δ 192.52, 156.31, 153.43, 134.68, 134.59, 132.73, 131.80, 131.26, 129.72, 129.15, 129.07, 123.87, 115.96 (*C*O & aromatic *C*). This is a known structure. These data are similar to the reported one.⁵

3-(4-Methylbenzoyl)quinoxalin-2(1*H*)-one (3b):



Pale vellow solid. Yield: 61%. ¹H NMR (600 MHz, DMSO- d_6): δ 12.85 (s, 1H) (NH), 7.85 (d, J = 8.1 Hz, 2H), 7.82 (d, J = 7.5 Hz, 1H), 7.65 (t, J = 7.7 Hz, 1H), 7.45 –

7.28 (m, 4H) (aromatic H), 2.41 (s, 3H) (CH₃). ¹³C NMR (151 MHz, DMSO- d_6): δ 192.03, 156.53, 153.42, 145.43, 132.69, 132.21, 131.70, 131.25, 129.83, 129.61, 129.11, 123.83, 115.93 (CO & aromatic C), 21.40 (CH₃). This is a known structure. These data are similar to the reported one.⁵

3-(4-Fluorobenzoyl)quinoxalin-2(1*H*)-one (3c):



Pale yellow solid. Yield: 58%. ¹H NMR (600 MHz, DMSO d_6): δ 12.87 (s, 1H) (NH), 8.09 (m, 2H), 7.83 (d, J = 7.9 Hz, 1H), 7.66 (t, J = 7.7 Hz, 1H), 7.46 – 7.31 (m, 4H) (aromatic *H*). ¹³C NMR (151 MHz, DMSO-*d*₆): δ 191.01, 165.87 (d, ¹*J*_{F-C} = 254.2 Hz), 155.93, 153.42, 132.94 (d, ${}^{3}J_{F-C} = 9.8$ Hz), 132.80, 131.86, 131.41 (d, ${}^{4}J_{F-C} = 2.3$ Hz), 131.27, 129.17, 123.85, 116.26 (d, ${}^{2}J_{F-C} = 22.1$ Hz), 115.94 (CO & aromatic C). ${}^{19}F$ NMR (565) MHz, DMSO- d_6): δ -103.23. This is a known structure. These data are similar to the reported one.1

1-Methyl-3-(4-methylbenzoyl)quinoxalin-2(1*H*)-one (3d):



Pale yellow solid. Yield: 58%. ¹H NMR (600 MHz, Chloroform-*d*): δ 7.93 (d, J = 7.8 Hz, 1H), 7.88 (d, J = 8.0Hz, 2H), 7.67 (t, J = 7.8 Hz, 1H), 7.41 (t, J = 7.7 Hz, 2H), 7.33 – 7.21 (m, 2H) (aromatic H), 3.75 (s, 3H), 2.42 (s, 3H)

(CH₃). ¹³C NMR (151 MHz, Chloroform-*d*): δ 191.55, 154.99, 153.45, 145.50, 133.96, 132.48, 132.31, 132.08, 131.06, 130.25, 129.53, 124.29, 114.09 (CO & aromatic C), 29.16, 22.00 (CH₃). This is a known structure. These data are similar to the reported one.⁵

3-(4-Ethylbenzoyl)-1-methylquinoxaline-2 (1H)-one (3e):



White solid. Yield: 61%. MP: 153.3-155.5 °C. ¹H NMR (600 MHz, Chloroform-*d*): δ 7.93 (d, J = 8.1 Hz, 1H), 7.91 (d, J = 8.1 Hz, 2H), 7.68 (t, J = 7.9 Hz, 1H), 7.41 (t, J = 7.5Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H) (aromatic *H*), 3.75 (s, 3H)

(CH₂), 2.77 – 2.66 (m, 2H), 1.25 (t, J = 7.6 Hz, 3H) (CH₃). ¹³C NMR (151 MHz, Chloroform-*d*): δ 191.56, 155.02, 153.44, 151.61, 133.94, 132.64, 132.29, 132.06, 131.03, 130.35, 128.37, 124.26, 114.08 (CO & aromatic C), 29.24, 29.14, 15.24 (CH₂ & CH₃). HRMS (ESI): *m/z* calcd for C₁₈H₁₆N₂O₂ [M+H]⁺: 293.1285. Found: 293.1283.

3-(4-Tert-butylbenzoyl)-1-methylquinoxaline-2(1*H***)–one (3f):**



Pale yellow solid. Yield: 55%. MP: 151.3-153.4 °C. ¹H NMR (400 MHz, Chloroform-*d*): δ 7.93 (m, 3H), 7.68 (t, J = 8.0 Hz, 1H), 7.50 (d, J = 8.4 Hz, 2H), 7.45-7.37 (m, 2H) (aromatic *H*), 3.76 (s, 3H), 1.61 (s, 1H), 1.33 (s, 9H)

(*CH* & *CH*₃). ¹³C NMR (151 MHz, Chloroform-*d*): δ 191.52, 158.32, 155.11, 153.48, 133.98, 132.36, 132.05, 131.09, 130.12, 125.85, 124.27, 114.08 (*CO* & aromatic *C*), 35.41, 31.14, 29.16 (*CH* & *CH*₃). HRMS (ESI): *m*/*z* calcd for C₁₈H₁₆N₂O₂ [M+H]⁺: 321.1598. Found: 321.1597.

3-(4-Methoxybenzoyl)-1-methylquinoxalin-2(1*H*)-one (3g):



Yellow solid. Yield: 63%. ¹H NMR (400 MHz, Chloroform-*d*): δ 7.99 – 7.88 (m, 3H), 7.72 – 7.63 (m, 1H), 7.44 – 7.38 (m, 2H), 6.95 (d, J = 9.0 Hz, 2H) (aromatic *H*), 3.88 (s, 3H), 3.75 (s, 3H) (CH₃). ¹³C NMR

(151 MHz, Chloroform-*d*): δ 190.37, 164.66, 155.15, 153.50, 134.00, 132.62, 132.34, 131.99, 131.06, 128.08, 124.26, 114.15, 114.06 (*CO* & aromatic *C*), 55.70, 29.18 (*C*H₃). This is a known structure. These data are similar to the reported one.⁶

3-(4-Bromobenzoyl)-1-methylquinoxalin-2(1*H*)-one (3h):



Yellow solid. Yield: 60%. ¹H NMR (600 MHz, Chloroform-*d*): δ 7.93 (dd, J = 7.9, 1.2 Hz, 1H), 7.86 (d, J= 8.6 Hz, 2H), 7.75 – 7.67 (m, 1H), 7.63 (d, J = 8.6 Hz, 2H), 7.46 – 7.40 (m, 2H) (aromatic *H*), 3.76 (s, 3H) (C*H*₃). ¹³C

NMR (151 MHz, Chloroform-*d*): δ 190.57, 154.02, 153.35, 140.89, 134.01, 133.33, 132.44, 132.20, 131.46, 131.15, 129.17, 124.43, 114.15 (*C*O & aromatic *C*), 29.21 (*C*H₃). This is a known structure. These data are similar to the reported one.⁵

3-(3-Bromobenzoyl)-1-methylquinoxalin-2(1*H*)-one (3i):



Yellow solid. Yield: 56%. ¹H NMR (600 MHz, DMSO-*d*₆): δ 8.19 (s, 1H), 8.00 (d, J = 7.7 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 7.9 Hz, 1H), 7.78 (t, J = 7.8 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.54 (t, J = 7.9 Hz, 1H), 7.47 (t, J = 7.5

Hz, 1H) (aromatic *H*), 3.66 (s, 3H) (C*H*₃). ¹³C NMR (151 MHz, DMSO-*d*₆): δ 191.15, 153.99, 152.96, 137.30, 136.51, 134.17, 132.20, 132.11, 131.80, 131.26, 130.00, 128.68, 123.97, 122.38, 115.25 (*CO* & aromatic *C*), 29.01 (*C*H₃). This is a known structure. These data are similar to the reported one.⁵

3-(2-Bromobenzoyl)-1-methylquinoxalin-2(1*H***)-one (3j):**



Yellow solid. Yield: 58%. ¹H NMR (600 MHz, DMSO-*d*₆): δ 7.91 – 7.80 (m, 2H), 7.80 – 7.74 (m, 2H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.57 (dd, *J* = 5.8, 3.4 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 1H) (aromatic *H*), 3.67 (s, 3H) (C*H*₃). ¹³C NMR (151 MHz, DMSO-

*d*₆): δ 191.67, 153.00, 152.63, 137.11, 134.28, 134.21, 134.00, 132.70, 132.25, 131.50, 130.30, 128.14, 124.11, 120.69, 115.29 (*CO* & aromatic *C*), 29.03 (*C*H₃). This is a known structure. These data are similar to the reported one.⁵

3-(4-Chlorobenzoyl)-1-methylquinoxalin-2(1*H*)-one (3k):



Pale yellow solid. Yield: 52%. ¹H NMR (600 MHz, Chloroform-*d*): δ 7.92 (m, 3H), 7.78 – 7.63 (m, 1H), 7.53 – 7.36 (m, 4H) (aromatic *H*), 3.75 (s, 3H) (C*H*₃). ¹³C NMR (151 MHz, Chloroform-*d*): δ 190.57, 154.05, 153.37,

140.90, 134.04, 133.37, 132.44, 132.23, 131.47, 131.17, 129.18, 124.43, 114.15 (CO & aromatic C), 29.22 (CH₃). This is a known structure. These data are similar to the reported one.⁵

3-(4-Fluorobenzoyl)-1-methylquinoxalin-2(1*H*)-one (3l):



Yellow solid. Yield: 63%. ¹H NMR (600 MHz, Chloroformd): δ 8.06 – 8.01 (m, 2H), 7.93 (d, J = 8.0 Hz, 1H), 7.69 (t, J = 8.5 Hz, 1H), 7.43 (t, J = 8.6 Hz, 2H), 7.16 (t, J = 8.6 Hz, 2H) (aromatic H), 3.76 (s, 3H) (CH₃). ¹³C NMR (151 MHz,

Chloroform-*d*): δ 190.20, 166.51 (d, ${}^{1}J_{F-C} = 256.9$ Hz), 154.23, 153.33, 133.95, 132.87 (d, ${}^{3}J_{F-C} = 9.7$ Hz), 132.33, 132.16, 131.39 (d, ${}^{4}J_{F-C} = 2.8$ Hz), 131.05, 124.37, 116.05 (d, ${}^{2}J_{F-C} = 22.1$ Hz), 114.14 (*CO* & aromatic *C*), 29.17. 19 F NMR (565 MHz, Chloroform-*d*): δ -102.77. This is a known structure. These data are similar to the reported one.⁵

1-Methyl-3-(4-(trifluoromethyl) benzoyl) quinoxalin-2(1*H*)-one (3m):



Yellow solid. Yield: 25%. ¹H NMR (400 MHz, Chloroform-*d*): δ 8.11 (d, J = 8.1 Hz, 2H), 7.96 – 7.91 (m, 1H), 7.78 – 7.68 (m, 3H), 7.44 (t, J = 7.6 Hz, 2H) (aromatic *H*), 3.77 (s, 3H) (CH₃). ¹³C NMR (151 MHz,

Chloroform-*d*): δ 190.74, 153.68, 153.40, 137.81, 135.41, 135.19, 134.17, 132.69, 132.30, 131.35, 130.39, 125.85 (q, *J* = 3.8 Hz), 124.55, 122.75, 114.21 (*CO* & aromatic *C*), 29.27 (*CH*₃). ¹⁹F NMR (565 MHz, Chloroform-*d*): δ -63.21. This is a known structure. These data are similar to the reported one.⁴

3-(4-Cyanobenzoyl)-1-methylquinoxaline-2(1*H***)-one (3n):**



Yellow solid. Yield: 37%. ¹H NMR (600 MHz, DMSO-*d*₆): δ 8.17 (d, J = 8.2 Hz, 2H), 8.05 (d, J = 8.7 Hz, 2H), 7.89 (dd, J = 7.8, 1.2 Hz, 1H), 7.82 – 7.75 (m, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.52 – 7.42 (m, 1H) (aromatic *H*), 3.66 (s, 3H)

(CH₃). ¹³C NMR (151 MHz, DMSO- d_6): δ 191.49, 153.61, 152.95, 137.61, 134.19, 133.05, 132.44, 131.79, 130.24, 130.10, 124.06, 118.05, 116.39, 115.31 (CO & aromatic C & CN), 29.04 (CH₃). This is a known structure. These data are similar to the reported one.⁵

1-Methyl-3-(2,4,6-trimethylbenzoyl)quinoxalin-2(1*H*)-one (30):



Yellow solid. Yield: 56%. ¹H NMR (600 MHz, Chloroform-*d*): δ 7.88 (d, J = 8.5 Hz, 1H), 7.66 (t, J = 7.9 Hz, 1H), 7.36 (t, J = 7.6 Hz, 2H), 6.88 (s, 2H) (aromatic *H*), 3.73 (s, 3H), 2.31 (s, 3H), 2.27 (s, 6H) (CH₃). ¹³C NMR

(151 MHz, Chloroform-*d*): δ 197.49, 153.21, 152.90, 139.92, 136.41, 135.92, 134.51,
132.78, 132.13, 131.78, 128.93, 124.12, 113.95 (*CO* & aromatic *C*), 29.17, 21.39, 20.24
(*C*H₃). This is a known structure. These data are similar to the reported one.⁴

1-Methyl-3-(2-naphthoyl)quinoxalin-2(1*H*)-one (3p):



Yellow solid. Yield: 28%. ¹H NMR (600 MHz, Chloroform-*d*): δ 8.40 (s, 1H), 8.13 (d, J = 8.5 Hz, 1H), 7.95 (t, J = 9.4 Hz, 2H), 7.89 (d, J = 8.4 Hz, 2H), 7.71 (t, J = 7.7 Hz, 1H), 7.61 (t, J = 7.8 Hz, 1H), 7.52 (t, J = 7.5

Hz, 1H), 7.44 (dd, J = 7.2, 4.8 Hz, 2H) (aromatic *H*), 3.78 (s, 3H) (CH₃). ¹³C NMR (151 MHz, Chloroform-*d*): δ 191.91, 154.91, 153.53, 136.29, 134.06, 133.12, 132.47, 132.40, 132.35, 132.19, 131.15, 129.94, 129.17, 128.87, 127.99, 126.94, 124.53, 124.34, 114.14 (*C*O & aromatic *C*), 29.21(*C*H₃). This is a known structure. These data are similar to the reported one.⁵

3-Benzoyl-1-methylquinoxalin-2(1*H***)-one (3r):**



Yellow solid. Yield: 69%. ¹H NMR (400 MHz, DMSO- d_6): δ 7.97 (d, J = 6.9 Hz, 2H), 7.88 (dd, J = 8.0, 1.5 Hz, 1H), 7.80 – 7.67 (m, 3H), 7.57 (t, J = 7.8 Hz, 2H), 7.50 – 7.43 (m, 1H) (aromatic H), 3.67 (s, 3H) (CH₃). ¹³C NMR (151 MHz, DMSO-

*d*₆): δ 192.30, 154.83, 152.90, 134.69, 134.47, 133.95, 132.04, 131.73, 129.91, 129.74, 129.05, 123.99, 115.26 (*CO* & aromatic *C*), 29.01 (*C*H₃). This is a known structure. These data are similar to the reported one.⁴

3-Benzoyl-1-ethylquinoxalin-2(1*H*)-one (3s):



Yellow oil. Yield: 66%. ¹H NMR (400 MHz, Chloroform-*d*): δ 7.99 (dd, J = 8.3, 1.2 Hz, 2H), 7.94 (dd, J = 8.0, 1.5 Hz, 1H), 7.72 - 7.58 (m, 2H), 7.52 - 7.38 (m, 4H) (aromatic *H*), 4.41 - 4.33 (m, 2H), 1.43 (t, J = 7.2 Hz, 3H). ¹³C NMR (151 MHz,

Chloroform-*d*): δ 191.79, 154.57, 152.75, 134.78, 134.12, 132.78, 132.39, 131.92, 131.17, 129.91, 128.58, 123.90, 113.73 (*CO* & aromatic *C*), 37.32 (*CH*₂), 12.36 (*CH*₃). This is a known structure. These data are similar to the reported one.¹

3-Benzoyl-1-isopropylquinoxaline-2(1*H***)-one (3t):**



Pale yellow oil. Yield: 65%. ¹H NMR (400 MHz, Chloroform-*d*): δ 8.04 (d, J = 8.3 Hz, 1H), 7.92 – 7.84 (m, 3H), 7.77 – 7.70 (m, 1H), 7.65 – 7.56 (m, 2H), 7.48 (t, J = 7.8

Hz, 2H) (aromatic H), 5.65 - 5.35 (m, 1H), 1.31 (d, J = 6.2

Hz, 6H). ¹³C NMR (151 MHz, Chloroform-*d*): δ 192.33, 154.63, 145.73, 140.92, 137.40, 135.49, 133.87, 130.91, 129.97, 129.24, 128.46, 126.96, 126.86 (*CO* & aromatic *C*), 69.97 (*C*H), 21.49 (*C*H₃). This is a known structure. These data are similar to the reported one.¹

3-Benzoyl-1-benzylquinoxalin-2(1*H*)-one (3u):



Yellow solid. Yield: 50%. ¹H NMR (400 MHz, Chloroform-*d*): δ 8.05 – 8.00 (m, 2H), 7.94 (dd, J = 8.2, 1.5 Hz, 1H), 7.64 (t, J = 7.4 Hz, 1H), 7.59 – 7.47 (m, 3H), 7.40 – 7.27 (m, 7H) (aromatic *H*), 5.54 (s, 2H) (*C*H₂). ¹³C NMR (151 MHz,

Chloroform-*d*): δ 192.03, 155.05, 153.77, 135.13, 134.61, 133.53, 132.77, 132.35, 131.43, 130.33, 129.34, 129.05, 128.25, 127.44, 124.57, 115.12 (*CO* & aromatic *C*), 46.19 (*C*H₂). This is a known structure. These data are similar to the reported one.⁴

3-Benzoyl-1-(2-oxo-2-phenylethyl)quinoxalin-2(1*H***)-one (3v):**



Yellow solid. Yield: 69%. ¹H NMR (600 MHz, Chloroform-*d*): δ 8.11 – 8.06 (m, 2H), 8.04 – 7.99 (m, 2H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.60 – 7.53 (m, 3H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.44 – 7.37 (m, 1H), 7.05 (d, *J* = 8.5 Hz, 1H) (aromatic *H*), 5.79 (s, 2H) (CH₂). ¹³C NMR

(151 MHz, Chloroform-*d*): δ 191.66, 190.83, 154.38, 153.21, 134.91, 134.59, 134.45, 134.40, 133.48, 132.48, 132.26, 131.36, 130.19, 129.21, 128.84, 128.31, 124.46, 114.07 (*CO* & aromatic *C*), 48.38 (*C*H₂). This is a known structure. These data are similar to the reported one.⁴

3-Benzoyl-1-(prop-2-yn-1-yl)quinoxalin-2(1*H***)-one (3w):**



Yellow solid. Yield: 49%. ¹H NMR (400 MHz, Chloroform-*d*): δ 8.04 – 7.98 (m, 2H), 7.95 (dd, J = 8.0, 1.3 Hz, 1H), 7.75 – 7.68 (m, 1H), 7.64 (t, J = 7.4 Hz, 1H), 7.58 (d, J = 7.8 Hz, 1H), 7.53 – 7.38 (m, 3H) (aromatic *H*), 5.10 (d, J = 2.5 Hz, 2H), 2.34

(t, J = 2.5 Hz, 1H). ¹³C NMR (151 MHz, Chloroform-*d*): δ 191.42, 154.51, 152.39, 134.82, 134.45, 132.51, 132.47, 132.29, 131.28, 130.21, 128.84, 114.71 (*CO* & aromatic *C*), 76.45, 73.91 (alkynyl *C*), 31.54 (*C*H₂). This is a known structure. These data are similar to the reported one.⁴

1-Allyl-3-benzoylquinoxalin-2(1*H*)-one (3x):



Yellow solid. Yield: 59%. ¹H NMR (600 MHz, Chloroform-*d*): δ 7.99 (dd, J = 8.4, 1.2 Hz, 2H), 7.94 (dd, J = 8.5, 1.5 Hz, 1H), 7.68-7.60 (m, 2H), 7.49 (t, J = 7.8 Hz, 2H), 7.44 – 7.37 (m, 2H) (aromatic *H*), 6.02 – 5.89 (m, 1H), 5.32 (d, J = 10.4 Hz, 1H),

5.26 (d, J = 17.2 Hz, 1H) (olefinic *H*), 4.96 (s, 2H) (CH₂). ¹³C NMR (151 MHz, Chloroform-*d*): δ 191.83, 154.81, 153.03, 134.96, 134.38, 133.29, 132.49, 132.08, 131.24, 130.41, 130.13, 128.83, 124.31, 118.94, 114.68 (*C*O & aromatic *C* & olefinic *C*), 44.64 (*C*H₂). This is a known structure. These data are similar to the reported one.⁴

Isoquinolin-1-yl(phenyl)methanone (3y):



Yellow oil. Yield: 30%. ¹H NMR (400 MHz, Chloroform-*d*): δ 8.61 (d, J = 5.6 Hz, 1H), 8.22 (d, J = 7.9 Hz, 1H), 7.98 – 7.91 (m, 3H), 7.82 (d, J = 5.6 Hz, 1H), 7.78 – 7.72 (m, 1H), 7.66 – 7.57 (m, 2H), 7.48 (t, J = 7.7 Hz, 2H) (aromatic *H*). ¹³C NMR (151 MHz,

Chloroform-*d*): δ 194.89, 156.54, 141.26, 136.82, 136.72, 133.82, 130.88, 130.86, 128.60, 128.46, 127.22, 126.53, 126.29, 122.73 (*CO* & aromatic *C*). This is a known structure. These data are similar to the reported one.⁷

Phenyl(quinoxalin-2-yl)methanone (3z):



Yellow solid. Yield: 31%. ¹H NMR (600 MHz, Chloroform-*d*): δ 9.50 (s, 1H), 8.28 – 8.18 (m, 4H), 7.95 – 7.84 (m, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.59 – 7.52 (m, 2H) (aromatic *H*). ¹³C NMR

(151 MHz, Chloroform-*d*): δ 192.31, 148.57, 145.24, 143.09, 140.38, 135.43, 133.60, 131.99, 131.19, 130.77, 130.40, 129.34, 128.34 (*CO* & aromatic *C*). This is a known structure. These data are similar to the reported one.⁷

(3-Chloroquinoxalin-2-yl)(phenyl)methanone (3aa):



Pale yellow solid. Yield: 16%. ¹H NMR (600 MHz, Chloroform-*d*): δ 8.21 – 8.08 (m, 2H), 7.95 – 7.81 (m, 4H), 7.68 (t, J = 7.5 Hz, 1H), 7.52 (t, J = 7.8 Hz, 2H) (aromatic *H*). ¹³C NMR (151 MHz, Chloroform-*d*): δ 191.40, 150.39, 144.11, 142.21, 139.84, 134.84, 134.77, 132.39, 131.16, 130.55, 129.63, 129.02, 128.62 (*CO* & aromatic *C*). This is a known structure. These data are similar to the reported one.⁷

2-(3-(3-Benzoyl-2-oxoquinoxalin-1(2H)-yl) propoxy)-3-methoxybenzaldehyde (3ab):



128.61, 124.35, 124.11, 119.62, 117.94, 114.00 (*CO* & aromatic *C*), 72.09, 55.89, 39.82 (*C*H₂), 27.97 (*C*H₃). This is a known structure. These data are similar to the reported one.⁴

2-(3-Benzoyl-2-oxoquinoxalin-1(2*H*)-yl)ethyl 2-(4-isobutylphenyl)propanoate (3ac):



Yellow oil. Yield: 41%. ¹H NMR (400 MHz, Chloroform-*d*): δ 8.28 (s, 1H), 7.88 (dd, J = 8.0, 1.5 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.45 – 7.32 (m, 2H), 7.12 – 6.99 (m, 4H) (aromatic *H*), 4.72 – 4.26 (m, 4H), 3.63 – 3.53 (m, 1H), 2.43 (d, *J*

= 7.1 Hz, 2H), 1.88 – 1.77 (m, 1H), 1.41 (d, J = 7.2 Hz, 3H), 0.90 (s, 3H), 0.88 (s, 3H) (CH & CH₂ & CH₃). ¹³C NMR (151 MHz, Chloroform-*d*): δ 191.88, 175.07, 154.79, 153.52, 141.07, 137.47, 135.17, 134.59, 133.82, 132.68, 132.38, 131.55, 130.38, 129.73, 129.03, 127.42, 124.57, 114.50 (CO & aromatic C), 61.29, 45.36, 45.31, 41.37, 30.49, 22.74, 18.68 (CH & CH₂ & CH₃). This is a known structure. These data are similar to the reported one.⁴

5. Radical trapping experiments.

A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with 1 (0.3 mmol), PIFA (0.45 mmol, 1.5 equiv) and TEMPO (1 equiv), which mixture was evacuated and purged with nitrogen for 3 times. Then the DCM's (3 mL) solution of 2 (2.7 mmol, 9 equiv) was added into the flame-dried Schlenk-tube via syringe. The reaction mixture was stirred and irradiated with 25W blue light for 3 h. Then the reaction mixture was concentrated and analyzed by HRMS.





A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with **1** (0.3 mmol), PIFA (0.45 mmol, 1.5 equiv) and 1,1-diphenylethylene (1 equiv), the resulting mixture was evacuated, and purged with nitrogen for 3 times, then DCM (3 mL) involved 2 (2.7 mmol, 9 equiv) was added into the flame-dried Schlenk-tube with

syringe. The reaction mixture was stirred at 25W blue light for 3 h. Then the reaction mixture was concentrated, and analyzed by HRMS.

Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
C ₂₁ H ₁₆ O	[M+H]+	285.1271	285.1274	-1.05

NHC-27_210404230056 #37 RT: 0.37 AV: 1 NL: 1.17E5 T: FTMS + c ESIFull ms [200.0000-2500.0000]



6. Light on/off experiment.

A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with 1 (0.3 mmol), PIFA (0.45 mmol, 1.5 equiv) and 4-acetylbiphenyl (0.3 mmol, 1 equiv), the resulting mixture was evacuated and purged with nitrogen for 3 times. Then the DCM's (3 mL) solution of 2 (2.7 mmol, 9 equiv) was added into the flame-dried Schlenk-tube with syringe. The reaction mixture was irradiated with light and then sheltered every 30 min, and the yield was determined by HPLC.



7. References:

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8. NMR spectra.

1-Methylquinoxalin-2(1*H*)-one (1b):



1-Ethylquinoxalin-2(1*H*)-one (1c):



1-Isopropylquinoxalin-2(1*H*)-one (1d):



1-Benzylquinoxalin-2(1*H*)-one (1e):







1-(2-Propynyl)quinoxalin-2(1*H*)-one (1g):



1-Allylquinoxalin-2(1*H*)-one (1h):





3-Methoxy-2-(3-(2-oxoquinoxalin-1(2*H*)-yl)propoxy)benzaldehyde(1i):



2-(2-Oxoquinoxalin-1(2*H*)-yl)ethyl 2-(4-isobutylphenyl)propanoate(1j):

3-Benzoylquinoxalin-2(1*H*)-one (3a):



3-(4-Methylbenzoyl)-quinoxalin-2(1*H*)-one (3b):













3-(4-Ethylbenzoyl)-1-methylquinoxaline-2(1*H***)-one(3e):**







3-(4-Methoxybenzoyl)-1-methylquinoxalin-2(1*H*)-one (3g):



3-(4-Bromobenzoyl)-1-methylquinoxalin-2(1*H*)-one (3h):





3-(3-Bromobenzoyl)-1-methylquinoxalin-2(1*H***)-one (3i):**

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



































3-Benzoyl-1-methylquinoxalin-2(1*H***)-one (3r):**



3-Benzoyl-1-ethylquinoxalin-2(1*H*)-one (3s):



3-Benzoyl-1-isopropylquinoxaline-2 (1*H*)-one (3t):



3-Benzoyl-1-benzylquinoxalin-2(1*H***)-one (3u):**



3-Benzoyl-1-(2-oxo-2-phenylethyl)quinoxalin-2(1*H*)-one (3v):



3-Benzoyl-1-(prop-2-yn-1-yl)quinoxalin-2(1*H*)-one (3w):





Isoquinolin-1-yl(phenyl)methanone (3y):



Phenyl(quinoxalin-2-yl)methanone (3z):







2-(3-(3-Benzoyl-2-oxoquinoxalin-1(2H)-yl)propoxy)-3-methoxybenzaldehyde (3ab):



2-(3-Benzoyl-2-oxoquinoxalin-1(2H)-yl)ethyl 2-(4-isobutylphenyl)propanoate (3ac):

