Supporting Information

Transition-Metal-Free Direct C-H Arylation of Quinoxalin-2(1H)-ones with Diaryl iodonium Salts at Room Temperature

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General information

Anhydrous solvents (including MeCN, DCE, DMSO, dioxane, THF and DMF) and CDCl$_3$ were purchased from Energy Chemical. (CD$_3$)$_2$SO was purchased from Sigma-Aldrich. Materials (used as received commercially available chemicals) were obtained from Energy Chemical, Bidepharmatech Ltd., Aladdin®, Meryer (Shanghai) Chemical Technology Co., Ltd, 9dingchem, Chemical Service, and used as received unless otherwise stated. $^1$H, $^{19}$F and $^{13}$C NMR spectra were recorded on a 400 MHz Bruker spectrometer ($^1$H 400 MHz, $^{19}$F 376, $^{13}$C 101 MHz). Chemical shifts (δ) for $^1$H, $^{19}$F and $^{13}$C spectra are given in ppm relative to TMS. The residual solvent signals were used as references for $^1$H and $^{13}$C NMR spectra and the chemical shifts were converted to the TMS scale (CDCl$_3$: δH = 7.26 ppm, δC = 77.16 ppm; (CD$_3$)$_2$SO: δH = 2.50 ppm, δC = 39.52 ppm). The following abbreviations were used to indicate multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet.

HRMS (ESI) spectra was recorded on ThermoFisher MicroTOF II. Melting points were obtained on a X-4 digital melting point apparatus without correction. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm. Purification by chromatography were performed using 200-400 mesh silica. Isolation of products were performed using self-prepared 200-400 mesh silica gel plates (GF254).

Synthesis of substrates.

The substrates of various quinoxalin-2(1H)-ones in Table 2 were prepared according to procedures described in the previous literature.$^1$ The substrates of various diaryliodonium salts in Table 2 were prepared according to procedures described in the previous literature.$^2$

Typical procedure for synthesis of 3a: To an oven-dried Schlenk tube (25 mL) containing a stirring bar was added orderly with 1-methylquinoxalin-2(1H)-one (1a, 48mg, 0.3 mmol, 1.0 equiv), diphenyliodonium tetrafluoroborate (2a, 166mg, 0.45 mmol, 1.5 equiv), Cs$_2$CO$_3$ (293mg, 0.9 mmol, 3.0 equiv) and dry MeCN (3.0 mL). The Schlenk tube was deaerated by vacuum until the bubble was disappear, then cooled by liquid nitrogen and exchanged adequately by N$_2$ (about 15 times), and after thawing the procedure was repeated once. Then, the mixture was warmed to room temperature and stirred for 72 h. The finial mixture was diluted by EtOAc and filtered through a pad of silica. The filtrate was concentrated under reduced pressure and the residue was purified by self-prepared or commercial silica plate (Petroleum ether/EtOAc:10/1 to 8/1) to give the pure desired product as yellow solid in 80% yield. A 82% yield was obtained when 1.0 mmol of 1a was employed.

Procedure for cross-coupling of 3ac with phenylboronic acid:

To a microwave vessel was added 3ac (28 mg, 1.0 equiv), phenylboronic acid (15.6 mg, 1.5 equiv), K$_2$CO$_3$ (29.5 mg, 2.5 equiv), Pd$_2$(dba)$_3$ (3.9 mg, 0.05 equiv), 1,3,5,7-tetramethyl-2,4,8-trioxa-6-phenyl-6-phosphaadamantane (2.5 mg, 0.1 equiv), THF (2 mL) and H$_2$O (0.4 mL). The vessel was bubbled by nitrogen. Then, the mixture was reacted in a microwave reactor at 70 ℃ for 15 minutes. The mixture was filtered through a pad of silica and the filtrate was purified by column chromatography on C$_{18}$ (0.04% TFA in H$_2$O-MeCN gradient) to afford 25.89 mg of the product as yellow solid in 90% yield.
1-methyl-3-phenylquinoxalin-2(1H)-one (3a) \[3\]

![Chemical structure of 1-methyl-3-phenylquinoxalin-2(1H)-one (3a)](attachment)

57.3 mg, 80% yield, yellow solid.

\[^1\text{H}\text{ NMR (400 MHz, CDCl}_3\text{)}: \delta 8.33-8.26 (m, 2H), 7.95 (dd, \text{J} = 7.9, 1.5 \text{ Hz}, 1H), 7.60-7.55 (m, 1H), 7.51-7.46 (m, 3H), 7.40-7.33 (m, 2H), 3.78 (s, 3H).

\[^{13}\text{C} \text{NMR (101 MHz, CDCl}_3\text{)}: \delta 154.84, 154.34, 136.17, 133.47, 133.22, 130.58, 130.46, 130.45, 129.65, 128.21, 123.88, 113.72, 77.48, 77.16, 76.84, 29.46.\]

1-methyl-3-(phenyl-d5)quinoxalin-2(1H)-one (3b)

![Chemical structure of 1-methyl-3-(phenyl-d5)quinoxalin-2(1H)-one (3b)](attachment)

58.5 mg, 81% yield, yellow solid: m.p. 133-134 °C.

\[^1\text{H} \text{NMR (400 MHz, CDCl}_3\text{)}: \delta 7.94 (d, \text{J} = 7.8 \text{ Hz}, 1H), 7.58-7.53 (m, 1H), 7.38-7.30 (m, 2H), 3.75 (s, 3H).

\[^{13}\text{C} \text{NMR (101 MHz, CDCl}_3\text{)}: \delta 154.77, 154.17, 135.97, 133.42, 133.16, 130.51, 130.38, 129.89 (t, \text{J} = 23.73 \text{ Hz}), 129.22 (t, \text{J} = 25.15 \text{ Hz}), 127.64 (t, \text{J} = 24.44 \text{ Hz}), 123.79, 113.66, 77.48, 77.16, 76.84, 29.38.\]

HRMS (ESI): calculated m/z for C_{15}H_{11}D_5N_2O [M+H]^+: 242.1336, found: 242.1329.

6-fluoro-1-methyl-3-phenylquinoxalin-2(1H)-one (3c)

![Chemical structure of 6-fluoro-1-methyl-3-phenylquinoxalin-2(1H)-one (3c)](attachment)

62.5 mg, 80% yield, yellow solid: m.p. 119-121 °C.

\[^1\text{H} \text{NMR (400 MHz, CDCl}_3\text{)}: \delta 8.31 (dd, \text{J} = 7.0, 2.5 \text{ Hz}, 2H), 7.62 (dd, \text{J} = 8.7, 2.7 \text{ Hz}, 1H), 7.49 (dd, \text{J} = 5.3, 2.0 \text{ Hz}, 3H), 7.28 (td, \text{J} = 8.9, 3.9 \text{ Hz}, 2H), 3.75 (s, 3H).

\[^{19}\text{F} \text{NMR (376 MHz, CDCl}_3\text{)}: \delta -118.91.\]

\[^{13}\text{C} \text{NMR (101 MHz, CDCl}_3\text{)}: \delta 158.86 (d, \text{J} = 243.6 \text{ Hz}), 155.45, 154.44, 135.83, 133.73 (d, \text{J} = 11.4 \text{ Hz}), 130.79, 130.15 (d, \text{J} = 1.9 \text{ Hz}), 129.75, 128.22, 118.15 (d, \text{J} = 24.1 \text{ Hz}), 115.74 (d, \text{J} = 22.3 \text{ Hz}), 114.77 (d, \text{J} = 8.8 \text{ Hz}), 29.67.\]

HRMS (ESI): calculated m/z for C_{15}H_{11}FN_2O [M+H]^+: 255.0932, found: 255.0932.

6-bromo-1-methyl-3-phenylquinoxalin-2(1H)-one (3d)

![Chemical structure of 6-bromo-1-methyl-3-phenylquinoxalin-2(1H)-one (3d)](attachment)

82 mg, 86% yield, yellow solid: m.p. 170-171 °C.

\[^1\text{H} \text{NMR (400 MHz, CDCl}_3\text{)}: \delta 8.31-8.26 (m, 2H), 7.77-7.73 (m, 1H), 7.50-7.41 (m, 5H), 3.69 (d, \text{J} = 3.0 \text{ Hz}, 3H).

\[^{13}\text{C} \text{NMR (101 MHz, CDCl}_3\text{)}: \delta 154.39, 154.25, 135.78, 134.37, 131.96, 131.65, 130.67, 129.62, 118.20, 127.06, 124.45, 116.70, 29.49.\]

HRMS (ESI): calculated m/z for C_{15}H_{11}BrN_2O [M+H]^+: 315.0136, found: 315.0136.
1-methyl-6-nitro-3-phenylquinoxalin-2(1H)-one (3e)

\[
\begin{align*}
\text{C}_2\text{N} & \quad \text{Ph} \\
\end{align*}
\]

37 mg, 42% yield, yellow solid: m. p. 187-189 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.80 (d, \(J = 2.6\) Hz, 1H), 8.40 (dd, \(J = 9.2, 2.6\) Hz, 1H), 8.34 (dd, \(J = 7.6, 1.8\) Hz, 2H), 7.55-7.48 (m, 3H), 7.42 (d, \(J = 9.2\) Hz, 1H), 3.81 (s, 3H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 156.21, 154.37, 143.58, 137.96, 135.08, 132.26, 131.44, 129.86, 128.38, 126.10, 124.76, 114.31, 30.03.

HRMS (ESI): calculated m/z for \(\text{C}_{15}\text{H}_{11}\text{N}_3\text{O}_3\) [M+H\(^+\)]: 282.0873, found: 282.0875.

7-bromo-1-methyl-3-phenylquinoxalin-2(1H)-one (3f)

\[
\begin{align*}
\end{align*}
\]

58 mg, 61% yield, yellow solid: m. p. 128-130 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.32-8.28 (m, 2H), 8.08 (d, \(J = 2.3\) Hz, 1H), 7.63 (dd, \(J = 8.9, 2.3\) Hz, 1H), 7.49 (dd, \(J = 5.4, 2.1\) Hz, 3H), 3.73 (s, 3H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 155.20, 154.46, 135.73, 134.01, 133.05, 132.82, 132.58, 130.85, 129.76, 128.24, 116.36, 115.12, 29.58.

HRMS (ESI): calculated m/z for \(\text{C}_{15}\text{H}_{11}\text{BrN}_2\text{O}\) [M+H\(^+\)]: 315.0128, found: 315.0138.

1-methyl-3,7-diphenylquinoxalin-2(1H)-one (3g)

\[
\begin{align*}
\end{align*}
\]

45 mg, 62% yield, yellow solid: m. p. 123-124 °C.

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) 8.26-8.21 (m, 2H), 7.85 (d, \(J = 8.3\) Hz, 1H), 7.83-7.79 (m, 2H), 7.67 (d, \(J = 1.9\) Hz, 1H), 7.63 (dd, \(J = 8.3, 1.8\) Hz, 1H), 7.47 (dq, \(J = 15.5, 7.3\) Hz, 6H), 3.71 (s, 3H).

\(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)): \(\delta\) 154.00, 152.50, 142.12, 139.08, 135.92, 133.56, 131.64, 130.10, 129.99, 129.32, 128.99, 128.29, 127.79, 127.29, 122.19, 112.41, 29.18.

HRMS (ESI): calculated m/z for \(\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}\) [M+H\(^+\)]: 313.1335, found: 313.1325.

1-methyl-6-(naphthalen-2-yl)-3-phenylquinoxalin-2(1H)-one (3h)

\[
\begin{align*}
\end{align*}
\]

45.7 mg, 46% yield, yellow solid: m. p. 178-179 °C.

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) 8.37-8.33 (m, 1H), 8.28 (dt, \(J = 5.6, 2.5\) Hz, 3H), 8.10 (dd, \(J = 8.8, 2.2\) Hz, 1H), 8.03-7.98 (m, 2H), 7.97-7.92 (m, 2H), 7.65 (d, \(J = 8.7\) Hz, 1H), 7.56-7.49 (m, 5H), 3.69 (s, 3H).

\(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)): \(\delta\) 153.91, 153.52, 153.93, 135.78, 135.14, 133.40, 132.71, 132.68, 132.30, 130.29, 129.42, 129.13, 128.63, 128.28, 127.89, 127.52, 127.18, 126.50, 126.25, 125.20, 124.82, 115.41, 29.40.

HRMS (ESI): calculated m/z for \(\text{C}_{25}\text{H}_{18}\text{N}_2\text{O}\) [M+H\(^+\)]: 363.1492, found: 363.1489.
6,7-dimethoxy-1-methyl-3-phenylquinoxalin-2(1H)-one (3i)

\[
\text{MeC} \quad \text{N} \quad \text{Ph} \\
\text{MeC} \\
\]

89.3 mg, 77% yield, reddish solid: m. p. 140-142 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 8.27\) (dd, \(J = 7.3, 2.4\) Hz, 2H), 7.45 (t, \(J = 3.7\) Hz, 3H), 7.36 (s, 1H), 6.68 (s, 1H), 4.02 (s, 3H), 3.96 (s, 3H), 3.75 (s, 3H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta 154.77, 151.97, 151.07, 146.34, 136.52, 129.86, 129.29, 128.68, 128.13, 127.70, 111.13, 95.76, 56.47, 56.35, 29.64.\)

HRMS (ESI): calculated m/z for C\(_{17}\)H\(_{16}\)N\(_2\)O\(_3\) [M+H]\(^+\): 297.1234, found: 297.1234.

6,7-dichloro-1-methyl-3-phenylquinoxalin-2(1H)-one (3j) [3]

\[
\begin{array}{c}
\text{N} \\
\text{C} \\
\text{O} \\
\text{Ph} \\
\end{array}
\]

67.2 mg, 71% yield, yellow solid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 8.29\) (dd, \(J = 7.5, 2.1\) Hz, 2H), 8.01 (s, 1H), 7.49 (d, \(J = 7.0\) Hz, 3H), 7.41 (s, 1H), 3.71 (s, 3H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta 155.15, 154.17, 135.43, 134.36, 134.36, 132.76, 132.20, 131.13, 131.03, 129.73, 128.27, 127.58, 115.17, 29.68.\)

1,6,7-trimethyl-3-phenylquinoxalin-2(1H)-one (3k)

\[
\begin{array}{c}
\text{N} \\
\text{C} \\
\text{O} \\
\text{Ph} \\
\end{array}
\]

60 mg, 75% yield, yellow solid: m. p. 177-178 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 8.27\) (dd, \(J = 6.7, 2.9\) Hz, 2H), 7.69 (s, 1H), 7.47 (dd, \(J = 5.3, 2.0\) Hz, 3H), 7.09 (s, 1H), 3.74 (s, 3H), 2.43 (s, 3H), 2.36 (s, 3H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta 154.89, 153.04, 140.43, 136.48, 132.79, 131.66, 131.51, 130.57, 130.08, 129.53, 128.13, 114.26, 29.32, 20.80, 19.36.\)

HRMS (ESI): calculated m/z for C\(_{17}\)H\(_{16}\)N\(_2\)O [M+H]\(^+\): 265.1335, found: 265.1334.

1,3-diphenylquinoxalin-2(1H)-one (3l) [4]

\[
\begin{array}{c}
\text{N} \\
\text{C} \\
\text{Ph} \\
\text{Ph} \\
\end{array}
\]

81 mg, 90% yield, yellow solid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 8.40\) (dd, \(J = 6.8, 2.9\) Hz, 2H), 8.03-7.98 (m, 1H), 7.65 (t, \(J = 7.5\) Hz, 2H), 7.58 (t, \(J = 7.4\) Hz, 1H), 7.49 (q, \(J = 4.3\), 3.9 Hz, 3H), 7.38-7.33 (m, 4H), 6.73-6.68 (m, 1H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta 154.63, 154.60, 136.23, 135.86, 134.29, 133.11, 130.60, 130.42, 130.16, 130.04, 129.81, 129.52, 128.42, 128.16, 124.01, 115.47.

1-benzyl-3-phenylquinoxalin-2(1H)-one (3m) [5]

\[
\begin{array}{c}
\text{N} \\
\text{C} \\
\text{Ph} \\
\text{Ph} \\
\end{array}
\]

79 mg, 84% yield, yellow solid.
$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.37 (dd, $J = 6.7$, 3.1 Hz, 2H), 7.97 (dd, $J = 7.9$, 1.6 Hz, 1H), 7.51 (q, $J = 2.7$ Hz, 3H), 7.47-7.43 (m, 1H), 7.36-7.28 (m, 7H), 5.58 (s, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 154.91, 154.33, 136.13, 135.48, 133.50, 132.86, 130.70, 130.55, 130.43, 129.76, 129.06, 128.23, 127.81, 127.09, 123.92, 114.47, 46.25.

**ethyl 2-(2-oxo-3-phenylquinoxalin-1(2H)-yl)acetate (3n)** [6]

![Chemical Structure](image)

68 mg, 84% yield, yellow solid.

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.33 (dt, $J = 7.4$, 3.5 Hz, 2H), 7.97 (dd, $J = 8.0$, 1.5 Hz, 1H), 7.56-7.46 (m, 4H), 7.37 (t, $J = 7.8$ Hz, 1H), 7.10 (d, $J = 8.4$ Hz, 1H), 5.09 (s, 2H), 4.27 (q, $J = 7.1$ Hz, 2H), 1.28 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 167.28, 154.38, 153.95, 135.82, 133.27, 132.61, 130.87, 130.58, 130.56, 129.67, 128.18, 124.12, 113.13, 62.18, 43.87, 14.24.

**3-(4-fluorophenyl)-1-methylquinoxalin-2(1H)-one (3o)** [3]

![Chemical Structure](image)

54 mg, 70% yield, yellow solid.

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.42-8.35 (m, 2H), 7.93 (dd, $J = 8.0$, 1.5 Hz, 1H), 7.58 (dd, $J = 8.6$, 7.2, 1.5 Hz, 1H), 7.40-7.32 (m, 2H), 7.16 (t, $J = 8.7$ Hz, 2H), 3.77 (s, 3H).

$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -110.00

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 164.32 (d, $J = 250.9$ Hz), 154.79, 152.88, 133.28 (d, $J = 31.0$ Hz), 132.31 (d, $J = 3.4$ Hz), 132.00, 131.92, 130.53, 130.50, 123.95, 115.19 (d, $J = 21.5$ Hz), 113.74, 29.46.

**3-(4-chlorophenyl)-1-methylquinoxalin-2(1H)-one (3p)** [3]

![Chemical Structure](image)

71 mg, 81% yield, yellow solid.

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.33 (dd, $J = 8.8$, 2.2 Hz, 2H), 7.92 (dd, $J = 8.0$, 1.6 Hz, 1H), 7.58 (dd, $J = 8.7$, 7.2, 1.5 Hz, 1H), 7.47-7.42 (m, 2H), 7.40-7.32 (m, 2H), 3.76 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 154.70, 152.74, 136.65, 134.56, 134.56, 133.48, 133.10, 131.11, 130.69, 130.61, 128.40, 123.98, 113.74, 29.45.

**3-(4-bromophenyl)-1-methylquinoxalin-2(1H)-one (3q)** [5a]

![Chemical Structure](image)

71.1 mg, 75% yield, yellow solid.

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.30-8.23 (m, 2H), 7.92 (dd, $J = 8.0$, 1.5 Hz, 1H), 7.58 (dd, $J = 11.7$, 8.5 Hz, 3H), 7.36 (dd, $J = 22.9$, 8.0 Hz, 2H), 3.76 (s, 3H).
$^{13}$C NMR (101 MHz, CDCl$_3$): δ 154.66, 152.79, 135.00, 133.48, 133.10, 131.36, 131.32, 130.72, 130.62, 125.21, 123.98, 113.75, 29.45.

1-methyl-3-(p-tolyl)quinoxalin-2(1H)-one (3r) [5]

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.24 (d, $J= 8.0$ Hz, 2H), 7.93 (dd, $J= 7.9$, 1.4 Hz, 1H), 7.57-7.53 (m, 1H), 3.77 (s, 3H), 2.42 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$): δ 154.92, 154.17, 140.75, 133.48, 133.43, 133.29, 130.48, 130.17, 129.66, 128.95, 123.78, 113.65, 29.41, 21.66.

Single-crystal: CCDC 1525848.

3-(4-methoxyphenyl)-1-methylquinoxalin-2(1H)-one (3s) [3]

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.39 (d, $J= 8.4$ Hz, 2H), 7.90 (d, $J= 7.9$ Hz, 1H), 7.52 (t, $J= 7.8$ Hz, 1H), 7.34 (t, $J= 7.6$ Hz, 1H), 7.29 (d, $J= 8.4$ Hz, 2H), 6.99 (d, $J= 8.4$ Hz, 2H), 3.87 (s, 3H), 3.74 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$): δ 161.54, 154.89, 153.22, 133.23, 133.18, 131.45, 130.19, 129.82, 128.84, 123.72, 113.59, 113.55, 55.47, 29.34.

1-methyl-3-(4-(trifluoromethyl)phenyl)quinoxalin-2(1H)-one (3t)

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.45 (d, $J= 8.1$ Hz, 2H), 7.94 (d, $J= 8.0$ Hz, 1H), 7.72 (d, $J= 8.1$ Hz, 2H), 7.60 (t, $J= 7.9$ Hz, 1H), 7.43-7.31 (m, 2H), 3.76 (s, 3H).

$^{19}$F NMR (376 MHz, CDCl$_3$): δ -62.76.

$^{13}$C NMR (101 MHz, CDCl$_3$): δ 154.63, 152.60, 139.40, 133.60, 133.06, δ 131.84 (q, $J= 32.4$ Hz), 131.15, 130.83, 130.00, 125.03 (q, $J= 3.8$ Hz), 124.21 (q, $J= 272.2$ Hz), 124.08, 113.81, 29.46.

HRMS (ESI): calculated m/z for C$_{16}$H$_{11}$F$_3$N$_2$O [M+H]+: 305.0896, found: 305.0908.

methyl 4-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)benzoate (3u)

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.41 (d, $J= 8.4$ Hz, 2H), 8.13 (d, $J= 8.4$ Hz, 2H), 7.95 (d, $J= 8.0$, 1.5 Hz, 1H), 7.60 (ddd, $J= 8.5$, 7.2, 1.5 Hz, 1H), 7.41-7.37 (m, 1H), 7.35 (d, $J= 8.4$ Hz, 1H), 3.95 (s, 3H), 3.92 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$): δ 154.66, 152.79, 135.00, 133.48, 133.10, 131.36, 131.32, 130.72, 130.62, 125.21, 123.98, 113.75, 29.45.

1-methyl-3-(p-tolyl)quinoxalin-2(1H)-one (3r) [5]

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.24 (d, $J= 8.0$ Hz, 2H), 7.93 (dd, $J= 7.9$, 1.4 Hz, 1H), 7.57-7.53 (m, 1H), 3.77 (s, 3H), 2.42 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$): δ 154.92, 154.17, 140.75, 133.48, 133.43, 133.29, 130.48, 130.17, 129.66, 128.95, 123.78, 113.65, 29.41, 21.66.

Single-crystal: CCDC 1525848.

3-(4-methoxyphenyl)-1-methylquinoxalin-2(1H)-one (3s) [3]

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.39 (d, $J= 8.4$ Hz, 2H), 7.90 (d, $J= 7.9$ Hz, 1H), 7.52 (t, $J= 7.8$ Hz, 1H), 7.34 (t, $J= 7.6$ Hz, 1H), 7.29 (d, $J= 8.4$ Hz, 2H), 6.99 (d, $J= 8.4$ Hz, 2H), 3.87 (s, 3H), 3.74 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$): δ 161.54, 154.89, 153.22, 133.23, 133.18, 131.45, 130.19, 129.82, 128.84, 123.72, 113.59, 113.55, 55.47, 29.34.

1-methyl-3-(4-(trifluoromethyl)phenyl)quinoxalin-2(1H)-one (3t)

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.45 (d, $J= 8.1$ Hz, 2H), 7.94 (d, $J= 8.0$ Hz, 1H), 7.72 (d, $J= 8.1$ Hz, 2H), 7.60 (t, $J= 7.9$ Hz, 1H), 7.43-7.31 (m, 2H), 3.76 (s, 3H).

$^{19}$F NMR (376 MHz, CDCl$_3$): δ -62.76.

$^{13}$C NMR (101 MHz, CDCl$_3$): δ 154.63, 152.60, 139.40, 133.60, 133.06, δ 131.84 (q, $J= 32.4$ Hz), 131.15, 130.83, 130.00, 125.03 (q, $J= 3.8$ Hz), 124.21 (q, $J= 272.2$ Hz), 124.08, 113.81, 29.46.

HRMS (ESI): calculated m/z for C$_{16}$H$_{11}$F$_3$N$_2$O [M+H]+: 305.0896, found: 305.0908.

methyl 4-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)benzoate (3u)

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.41 (d, $J= 8.4$ Hz, 2H), 8.13 (d, $J= 8.4$ Hz, 2H), 7.95 (d, $J= 8.0$, 1.5 Hz, 1H), 7.60 (ddd, $J= 8.5$, 7.2, 1.5 Hz, 1H), 7.41-7.37 (m, 1H), 7.35 (d, $J= 8.4$ Hz, 1H), 3.95 (s, 3H), 3.92 (s, 3H).
3.77 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 166.95, 154.69, 153.06, 140.28, 133.61, 133.14, 131.41, 131.05, 130.84, 129.66, 129.34, 124.04, 113.79, 52.36, 29.47.

HRMS (ESI): calculated m/z for C$_{17}$H$_{14}$N$_2$O$_3$ [M+H]$^+$: 295.1077, found: 295.1080.

3-(2-fluorophenyl)-1-methylquinoxalin-2(1H)-one (3v)

- 44 mg, 55% yield, yellow solid: m. p. 130-131 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.99 (dd, $J = 8.0, 1.5$ Hz, 1H), 7.72-7.62 (m, 2H), 7.55-7.48 (m, 1H), 7.45-7.39 (m, 2H), 7.32 (td, $J = 7.4, 1.2$ Hz, 1H), 7.27-7.21 (m, 1H), 3.81 (s, 3H).

$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -112.04

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 160.86 (d, $J = 250.9$ Hz), 154.18, 154.08 (d, $J = 1.4$ Hz), 133.37 (d, $J = 65.9$ Hz), 131.64 (d, $J = 8.4$ Hz), 131.11 (d, $J = 3.1$ Hz), 131.03, 130.67, 124.82 (d, $J = 14.5$ Hz), 124.21, 124.18, 123.91, 116.07 (d, $J = 21.6$ Hz), 113.86, 29.52.

HRMS (ESI): calculated m/z for C$_{15}$H$_{11}$FN$_2$O [M+H]$^+$: 255.0928, found: 255.0927.

3-(2-chlorophenyl)-1-methylquinoxalin-2(1H)-one (3w) $^{[a]}$

- 40 mg, 40% yield, yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.95 (dd, $J = 7.8, 1.7$ Hz, 1H), 7.63 (td, $J = 7.8, 1.5$ Hz, 1H), 7.52-7.47 (m, 2H), 7.42-7.36 (m, 4H), 3.77 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 156.46, 154.14, 135.96, 133.89, 133.36, 132.87, 131.12, 130.71, 130.61, 130.59, 129.87, 126.92, 123.95, 113.92, 29.52.

HRMS (ESI): calculated m/z for C$_{15}$H$_{11}$BrN$_2$O [M+H]$^+$: 315.0128, found: 315.0109.

1-methyl-3-(2-(trifluoromethyl)phenyl)quinoxalin-2(1H)-one (3y)

- 15 mg, 15% yield, yellow solid: m. p. 94-96 °C.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.92 (d, $J = 8.0$ Hz, 1H), 7.79 (d, $J = 7.8$ Hz, 1H), 7.69- 7.57 (m, 3H), 7.54 (d, $J = 7.6$ Hz, 1H), 7.40 (t, $J = 7.6$ Hz, 2H), 3.77 (s, 3H).

$^1$F NMR (376 MHz, CDCl$_3$): $\delta$ -58.04

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 156.69, 154.72, 135.11 (q, $J = 2.0$ Hz), 133.83, 132.74, 131.78, 131.19, 130.77, 130.40, 129.50, 129.23 (q, $J = 4.5$ Hz), 126.93 (q, $J = 4.5$ Hz), 124.20 (q, $J = 274.72$ Hz), 124.07, 113.97, 29.53.

HRMS (ESI): calculated m/z for C$_{16}$H$_{11}$F$_3$N$_2$O [M+H]$^+$: 305.0896, found: 305.0902.

3-(3-bromophenyl)-1-methylquinoxalin-2(1H)-one (3z)

60 mg, 63 % yield, yellow solid: m. p. 112-114 ºC.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.50 (t, $J = 1.8$ Hz, 1H), 8.35-8.30 (m, 1H), 7.94 (dd, $J = 8.0$, 1.5 Hz, 1H), 7.62-7.57 (m, 2H), 7.37 (dt, $J = 15.3$, 7.4 Hz, 3H), 3.77 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 154.58, 152.34, 138.02, 133.52, 133.31, 133.01, 132.49, 130.91, 130.73, 129.67, 128.35, 124.01, 122.34, 113.76, 29.46.

HRMS (ESI): calculated m/z for C$_{15}$H$_{11}$BrN$_2$O [M+H]$^+$: 315.0128, found: 315.0127.

1-methyl-3-(3-(trifluoromethyl)phenyl)quinoxalin-2(1H)-one (3aa)

47 mg, 51 % yield, yellow solid: m. p. 126-128 ºC.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.66 (s, 1H), 8.58 (d, $J = 7.9$ Hz, 1H), 7.96 (dd, $J = 8.0$, 1.5 Hz, 1H), 7.73 (d, $J = 7.9$ Hz, 1H), 7.60 (dt, $J = 9.2$, 4.3 Hz, 2H), 7.42-7.33 (m, 2H), 3.78 (s, 3H).

$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -62.47.

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 154.65, 152.34, 136.77, 133.57, 133.04, 132.96, 131.07, 130.80, 130.63 (q, $J = 32.5$ Hz), 128.62, 126.90 (q, $J = 3.7$ Hz), 126.62 (q, $J = 3.9$ Hz), 124.27 (q, $J = 272.5$ Hz), 124.10, 113.81, 29.47.

HRMS (ESI): calculated m/z for C$_{16}$H$_{11}$F$_3$N$_2$O [M+H]$^+$: 305.0896, found: 305.0896.

6-bromo-3-(4-bromophenyl)-1-methylquinoxalin-2(1H)-one (3ab)

79 mg, 66 % yield, yellow solid: m. p. 167-168 ºC.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.25 (d, $J = 8.3$ Hz, 2H), 8.05 (s, 1H), 7.64 (d, $J = 8.7$ Hz, 1H), 7.59 (d, $J = 8.3$ Hz, 2H), 7.18 (d, $J = 8.9$ Hz, 1H), 3.72 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 154.28, 153.70, 134.51, 133.84, 133.33, 132.83, 132.55, 131.42, 131.39, 125.74, 116.52, 115.16, 29.60.

HRMS (ESI): calculated m/z for C$_{16}$H$_{10}$Br$_2$N$_2$O [M+H]$^+$: 392.9233, found: 392.9231.
6-bromo-1-methyl-3-(p-tolyl)quinoxalin-2(1H)-one (3ac)

![Chemical Structure Image]

71 mg, 69 % yield, yellow solid: m. p. 154-156 °C.

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.24 (d, $J$ = 7.9 Hz, 2H), 8.05 (d, $J$ = 2.3 Hz, 1H), 7.60 (dd, $J$ = 8.9, 2.3 Hz, 1H), 7.28 (d, $J$ = 7.8 Hz, 2H), 7.16 (d, $J$ = 8.8 Hz, 1H), 3.71 (s, 3H), 2.42 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$): δ 154.92, 154.48, 141.25, 134.02, 132.98, 132.71, 132.46, 129.74, 128.96, 116.25, 115.04, 29.52, 21.67.

HRMS (ESI): calculated m/z for C$_{16}$H$_{13}$BrN$_2$O [M+H]$^+$: 329.0284, found: 329.0267.

6-bromo-1-methyl-3-(4-(trifluoromethyl)phenyl)quinoxalin-2(1H)-one (3ad)

![Chemical Structure Image]

66 mg, 55 % yield, yellow solid: m. p. 136-137 °C.

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.45 (d, $J$ = 8.2 Hz, 2H), 8.09 (d, $J$ = 2.3 Hz, 1H), 7.73 (d, $J$ = 8.2 Hz, 2H), 7.68 (dd, $J$ = 8.9, 2.3 Hz, 1H), 7.22 (d, $J$ = 8.9 Hz, 1H), 3.75 (s, 3H).

$^{19}$F NMR (376 MHz, CDCl$_3$): δ -62.82.

$^{13}$C NMR (101 MHz, CDCl$_3$): δ 154.29, 153.63, 138.91, 133.82, 133.80, 133.08, 132.72, 132.25 (q, $J$ = 32.62 Hz), 130.12, 125.11 (q, $J$ = 3.9 Hz), 124.12 (q, $J$ = 273.34 Hz), 116.64, 115.25, 29.66.

HRMS (ESI): calculated m/z for C$_{15}$H$_{12}$N$_2$O [M+H]$^+$: 383.0001, found: 382.9982.

1-methyl-3-phenylquinolin-2(1H)-one [7]

![Chemical Structure Image]

13 mg, 18 % yield, yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.81 (s, 1H), 7.72 (d, $J$ = 7.3 Hz, 2H), 7.64-7.55 (m, 2H), 7.44 (t, $J$ = 7.4 Hz, 2H), 7.40-7.35 (m, 2H), 7.26 (d, $J$ = 14.9 Hz, 1H), 3.81 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$): δ 139.74, 136.94, 136.91, 132.63, 130.41, 129.09, 128.97, 128.28, 128.19, 120.32, 120.88, 114.13, 30.09.

1-methyl-6-phenyl-3-(p-tolyl)quinoxalin-2(1H)-one

![Chemical Structure Image]

25.9 mg, 90 % yield, yellow solid: m. p. 211-213 °C.

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.26 (d, $J$ = 8.2 Hz, 2H), 8.18 (d, $J$ = 2.1 Hz, 1H), 7.81 (dd, $J$ = 8.6, 2.2 Hz, 1H), 7.69 (dd, $J$ = 7.3, 1.7 Hz, 2H), 7.49 (t, $J$ = 7.5 Hz, 2H), 7.43-7.35 (m, 2H), 7.30 (d, $J$ = 8.0 Hz, 2H), 3.80 (s, 3H), 2.43 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$): δ 154.83, 154.57, 140.87, 139.55, 136.87, 133.50, 133.41, 132.60, 129.66, 129.15, 129.02, 128.99, 128.38, 127.75, 127.07, 114.11, 29.54, 21.69.
HRMS (ESI): calculated m/z for C_{22}H_{18}N_{2}O [M+H]^+ : 327.1492, found: 327.1497.

Reference:


3. Copies of NMR spectra.