Mild and Direct C-H Arylation of Quinoxalin-2(1H)-Ones with Aryldiazonium Salts under Metal-Free Conditions
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**General Information**

Anhydrous solvent (including DCM, DMF, DMSO, EtOH, MeCN, NMP, Dioxane and DCE) and CDCl₃, CD₃COCD₃ were purchased from Energy Chemical. (CD₃)₂SO 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. ¹H, ¹³F and ¹³C NMR spectra were recorded on a 400 MHz Bruker spectrometer (¹H 400 MHz, ¹³F 376, ¹³C 101 MHz). Chemical shifts (δ) for ¹H, ¹³F and ¹³C spectra are given in ppm relative to TMS. The residual solvent signals were used as references for ¹H and ¹³C NMR spectra and the chemical shifts were converted to the TMS scale (CDCl₃: δH = 7.26 ppm, δC = 77.16 ppm; CD₃COCD₃: δH = 2.05 ppm, δC = 29.84 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. 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 Quinoxalin-2(1H)-Ones**

The substrates of various quinoxalin-2(1H)-ones in Scheme 2 were prepared according to procedures described in the previous literature.[1]

**Typical Procedure for The Synthesis of 3a.**

To a 25 mL round bottle was added p-toluidine (4.0 equiv.) and 1 mL of anhydrous CH₃CN, then tBuONO (6.0 equiv.) was added dropwise via syringe in an ice bath, followed by washing the syringe with CH₃CN (0.5 mL x 2). After addition, the mixture was warmed and continued to stir at room temperature for 0.5 h (preparing in situ p-MePhN₂OBu'). Then, the p-MePhN₂OBu' in CH₃CN was transferred into an oven-dried Schlenk tube (25 mL) charged with 1-methylquinoxalin-2(1H)-one (1a, 48mg, 0.3 mmol, 1.0 equiv.), followed by washing the bottle with CH₃CN (0.5 mL x 2). The Schlenk tube was exchanged adequately by N₂. Then, the mixture was stirred for 48 h at rt. The final mixture was diluted by ethyl acetate and filtered through a pad of silica. The filtrate was concentrated under reduced pressure and the residue was purified by self-prepared silica plate (petroleum ether/ethyl acetate: 20/1) to afford 3a as yellow solid in 89% yield. An 80% yield was obtained when 1a was used at 1.0 mmol scale.

**Typical Procedure for Large-Scale Synthesis of 3a.**

To a 100 mL round bottle was added p-toluidine (36 mmol, 3.89g, 4.0 equiv.) and 50 mL of anhydrous CH₃CN, then tBuONO (54 mmol, 5.65g, 6.0 equiv.) was added dropwise via dropper in an ice bath, followed by washing the dropper with anhydrous CH₃CN (5 mL x 2). After addition, the mixture was warmed and continued to stir at room temperature for 40 minutes (preparing in situ p-MePhN₂OBu'). Then the p-MePhN₂OBu' in CH₃CN was transferred into an oven-dried Schlenk tube (25 mL) charged with 1-methylquinoxalin-2(1H)-one (1a, 1.44 g, 9.0 mmol, 1.0 equiv.) in CH₃CN (15 mL), followed by washing the bottle with CH₃CN (5 mL x 3). The Schlenk tube was exchanged adequately by N₂. Then, the mixture was stirred for 48 h at rt. The final mixture was filtered through a pad of silica which was then washed by ethyl acetate. The filtrate was concentrated under reduced pressure and the residue was purified by self-prepared silica plate (petroleum ether/ethyl acetate: 20/1) to afford 3a in 71% yield (1.591 g) as yellow solid.
Method A for The Synthesis of 3a; 3b; 3c; 3d; 3f; 3g; 3i; 3j; 3k; 3l; 3t; 3x; 3z; 3aa; 3ab.
To a 25mL round bottle was added corresponding aryl aniline (4.0 equiv.) and 1.0 mL of anhydrous CH₃CN, then tBuONO (6.0 equiv.) was added dropwise via syringe in an ice bath, followed by washing the syringe with CH₃CN (0.5 mL x 2). After addition, the mixture was warmed and continued to stir at rt for 0.5 h (preparing in situ ArN₂OBu'). Then the ArN₂OBu' in CH₃CN was transferred into an oven-dried Schlenk tube (25 mL) charged with corresponding quinoxalin-2(1H)-one (1, 0.3 mmol, 1.0 equiv.), followed by washing the bottle with CH₃CN (0.5 mL x 2). The Schlenk tube was exchanged adequately by N₂. Then, the mixture was stirred for 48 h at rt. The final mixture was diluted by ethyl acetate and filtered through a pad of silica. The filtrate was concentrated under reduced pressure and the residue was purified by self-prepared silica plate (petroleum ether/ethyl acetate: 20/1 to 10/1) to afford the desired product 3 as yellow or orange solid (3d: orange colloid).

Method B for The Synthesis of 3e; 3f; 3m; 3r; 3ac; 3ad; 3ae; 3af.
To a 25mL round bottle was added corresponding aryl aniline (4.0 equiv.) and 2.0 mL of anhydrous CH₃CN, then tBuONO (6.0 equiv.) was added dropwise via syringe in an ice bath, followed by washing the syringe with CH₃CN (0.5 mL x 2). After addition, the mixture was warmed and continued to stir at rt for 0.5 h (preparing in situ ArN₂OBu'). Then the ArN₂OBu' in CH₃CN was transferred into an oven-dried Schlenk tube (25 mL) charged with corresponding quinoxalin-2(1H)-one (1, 0.3 mmol, 1.0 equiv.), followed by washing the bottle with CH₃CN (0.5 mL x 2). The Schlenk tube was exchanged adequately by N₂. Then, the mixture was stirred for 48 h at rt. The final mixture was diluted by ethyl acetate and filtered through a pad of silica. The filtrate was concentrated under reduced pressure and the residue was purified by self-prepared silica plate (petroleum ether/ethyl acetate: 20/1 to 10/1) to afford the desired product 3 as yellow or orange solid.

Method C for The Synthesis of 3q; 3v; 3w; 3y.
To a 25mL round bottle was added corresponding aryl aniline (4.0 equiv.) and 1.0 mL of anhydrous CH₃CN, then tBuONO (6.0 equiv.) was added dropwise via syringe in an ice bath, followed by washing the syringe with CH₃CN (0.5 mL x 2). After addition, the mixture was warmed and continued to stir at rt for 0.5 h (preparing in situ ArN₂OBu'). Then the ArN₂OBu' in CH₃CN was transferred into an oven-dried Schlenk tube (25 mL) charged with corresponding quinoxalin-2(1H)-one (1, 0.3 mmol, 1.0 equiv.), followed by washing the bottle with CH₃CN (1.0 mL x 2). The Schlenk tube was exchanged adequately by N₂. Then, the mixture was stirred for 48 h at rt. The final mixture was diluted by ethyl acetate and filtered through a pad of silica. The filtrate was concentrated under reduced pressure and the residue was purified by self-prepared silica plate (petroleum ether/ethyl acetate: 20/1 to 10/1) or (petroleum ether/ethyl acetate: 20/1 to 6/1 for 3y) to afford the desired product 3 as yellow or orange solid.

Method D for The Synthesis of 3s.
To a 25mL round bottle was added m-toluidine (4.0 equiv.) and 1.0 mL of anhydrous DCE, then tBuONO (6.0 equiv.) was added dropwise via syringe in an ice bath, followed by washing the syringe with anhydrous DCE (0.5 mL x 2). After addition, the mixture was warmed and continued to stir at rt for 0.5 h (preparing in situ m-MePhN₂OBu'). Then the m-MePhN₂OBu' in DCE was transferred into an oven-dried Schlenk tube (25 mL) charged with 1-methylquinoxalin-2(1H)-one (1a, 0.3 mmol, 1.0 equiv.), followed by washing the bottle with DCE (0.5 mL x 2). The Schlenk tube was exchanged adequately by N₂. Then, the mixture was stirred for 48 h at rt. The final mixture was diluted by ethyl acetate and filtered through a pad of silica. The filtrate was concentrated under reduced pressure and the residue was purified by self-prepared silica plate (petroleum ether/ethyl acetate: 20/1) to afford the desired product 3s in 30% yield as orange solid.
Radical Trap Experiment with TEMPO as Scavenger.

Corresponding peaks in total chromatogram and extracted ion chromatogram.

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Chemical Formula: C7H7NO7
Molecular Weight: 161.1835

Chemical Formula: C10H9NO7
Molecular Weight: 248.3895
1-methyl-3-(p-tolyl)quinoxalin-2(1H)-one (3a) \[2\]

![Structure of 3a](image)

89% yield, yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.24 (d, $J$ = 8.0 Hz, 2H), 7.93 (dd, $J$ = 8.0, 1.5 Hz, 1H), 7.59-7.53 (m, 1H), 7.39-7.27 (m, 4H), 3.77 (s, 3H), 2.42 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 154.85, 154.06, 140.70, 133.43, 133.36, 133.22, 130.40, 130.11, 129.62, 128.90, 123.73, 113.61, 29.36, 21.63.

1-methyl-3-phenylquinoxalin-2(1H)-one (3b) \[2b-c, 3\]

![Structure of 3b](image)

80% yield, yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.31 (dd, $J$ = 6.7, 3.0 Hz, 2H), 7.95 (dd, $J$ = 7.9, 1.5 Hz, 1H), 7.57 (ddd, $J$ = 8.6, 7.3, 1.6 Hz, 1H), 7.40-7.32 (m, 2H), 3.77 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 154.86, 154.35, 136.21, 133.52, 133.26, 130.61, 130.46, 129.68, 128.22, 123.87, 113.72, 29.46.

$^{13}$C NMR (101 MHz, CD$_3$COCD$_3$): $\delta$ 155.19, 154.18, 137.37, 134.65, 133.68, 131.28, 130.94, 130.84, 130.46, 128.58, 124.25, 115.14, 29.46.

3-(4-isopropylphenyl)-1-methylquinoxalin-2(1H)-one (3c) \[2c\]

![Structure of 3c](image)

83% yield, orange solid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.24 (d, $J$ = 8.3 Hz, 2H), 7.90 (dd, $J$ = 8.0, 1.5 Hz, 1H), 7.36-7.26 (m, 4H), 3.72 (s, 3H), 2.97 (p, $J$ = 6.9 Hz, 1H), 1.29 (d, $J$ = 6.9 Hz, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 154.79, 154.13, 151.46, 133.75, 133.26, 133.17, 130.31, 130.06, 129.65, 126.27, 123.68, 113.58, 34.20, 29.31, 23.90.

HRMS (ESI): calculated m/z for [C$_{18}$H$_{18}$N$_2$OH]+: 279.1492, found: 279.1497.

3-(4-(tert-butyl)phenyl)-1-methylquinoxalin-2(1H)-one (3d)

![Structure of 3d](image)

92% yield, orange colloid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.27-8.22 (m, 2H), 7.93 (dd, $J$ = 8.0, 1.5 Hz, 1H), 7.56-7.49 (m, 3H), 7.38-7.33 (m, 1H), 7.31 (d, $J$ = 8.4 Hz, 1H), 3.76 (s, 3H), 1.37 (s, 9H).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 154.87, 154.27, 153.71, 133.42, 133.37, 133.28, 130.43, 130.14, 129.38, 125.21, 123.75, 113.63, 34.96, 31.32, 29.38.
HRMS (ESI): calculated m/z for [C_{19}H_{20}N_{2}OH]^+: 293.1648, found: 293.1644.

3-(4-benzylphenyl)-1-methylquinoxalin-2(1H)-one (3e)

68% yield, yellow solid.

^1H NMR (400 MHz, CDCl3): δ 8.25 (d, J = 8.3 Hz, 2H), 7.93 (dd, J = 7.9, 1.5 Hz, 1H), 7.59-7.54 (m, 1H), 7.39-7.27 (m, 6H), 7.22 (d, J = 7.3 Hz, 3H), 4.06 (s, 2H), 3.77 (s, 3H).

^13C NMR (101 MHz, CDCl3): δ 154.91, 154.18, 143.72, 140.87, 134.20, 133.48, 133.31, 130.55, 130.29, 129.89, 129.15, 128.92, 128.61, 126.30, 123.83, 113.68, 42.04, 29.43.

HRMS (ESI): calculated m/z for [C_{22}H_{18}N_{2}OH]^+: 327.1492, found: 327.1491.

3-([1,1'-biphenyl]-4-yl)-1-methylquinoxalin-2(1H)-one (3f)

65% yield, yellow solid.

^1H NMR (400 MHz, CDCl3): δ 8.47-8.41 (m, 2H), 7.97 (dd, J = 8.0, 1.5 Hz, 1H), 7.75-7.71 (m, 2H), 7.69-7.65 (m, 2H), 7.58 (ddd, J = 8.6, 7.3, 1.5 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.41-7.33 (m, 3H), 3.79 (s, 3H).

^13C NMR (101 MHz, CDCl3): δ 154.94, 153.78, 143.14, 140.78, 135.18, 133.52, 133.34, 130.61, 130.42, 130.18, 128.96, 127.80, 127.36, 126.93, 123.89, 113.72, 29.46.

HRMS (ESI): calculated m/z for [C_{21}H_{16}N_{2}OH]^+: 313.1335, found: 313.1317.

3-(4-methoxyphenyl)-1-methylquinoxalin-2(1H)-one (3g)

64% yield, yellow solid.

^1H NMR (400 MHz, CDCl3): δ 8.42-8.35 (m, 2H), 7.90 (dd, J = 8.0, 1.5 Hz, 1H), 7.52 (ddd, J = 8.6, 7.3, 1.5 Hz, 1H), 7.38-7.27 (m, 2H), 6.99 (d, J = 9.0 Hz, 2H), 3.87 (s, 3H), 3.75 (s, 3H).

^13C NMR (101 MHz, CDCl3): δ 161.55, 154.91, 153.24, 133.24, 133.20, 131.46, 130.20, 129.83, 128.84, 123.73, 113.59, 113.56, 55.47, 29.35.

1-methyl-3-(4-phenoxyphenyl)quinoxalin-2(1H)-one (3h)

71% yield, orange solid.

^1H NMR (400 MHz, CDCl3): δ 8.40-8.33 (m, 2H), 7.93 (dd, J = 8.0, 1.6 Hz, 1H), 7.60-7.53 (m, 1H), 7.42-7.31 (m, 4H), 7.15 (t, J = 7.4 Hz, 1H), 7.11-7.07 (m, 4H), 3.78 (s, 3H).

^13C NMR (101 MHz, CDCl3): δ 159.50, 156.56, 154.80, 153.16, 133.27, 133.16, 131.56, 130.97, 130.32, 130.14, 129.92, 123.88, 123.80, 119.61, 117.89, 113.64, 29.37.
HRMS (ESI): calculated m/z for [C_{21}H_{16}N_{2}O_{2}H]^+: 329.1285, found: 329.1276.

Single-crystal: CCDC1560266

1-methyl-3-(4-(trifluoromethoxy)phenyl)quinoxalin-2(1H)-one (3i)

82% yield, yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.44-8.38 (m, 2H), 7.92 (dd, $J$ = 8.0, 1.6 Hz, 1H), 7.57 (ddd, $J$ = 8.7, 7.3, 1.6 Hz, 1H), 7.40-7.35 (m, 1H), 7.32 (t, $J$ = 7.9 Hz, 3H), 3.75 (s, 3H).

$^{19}$F NMR (376 MHz, CDCl$_3$): δ -57.55.

$^{13}$C NMR (101 MHz, CDCl$_3$): δ 154.66, 152.53, 150.75 (d, $J$ = 1.9 Hz), 134.63, 133.47, 133.05, 131.44, 130.76, 130.61, 123.99, δ 120.57 (q, $J$ = 257.8 Hz), 120.30, 113.75, 29.42.

HRMS (ESI): calculated m/z for [C_{16}H_{12}F_{3}N_{2}O_{2}H]^+: 321.0845, found: 321.0847.

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

73% yield, yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.45 (d, $J$ = 8.1 Hz, 2H), 7.92 (d, $J$ = 7.9 Hz, 1H), 7.71 (d, $J$ = 8.1 Hz, 2H), 7.58 (t, $J$ = 7.9 Hz, 1H), 7.37 (t, $J$ = 7.6 Hz, 1H), 7.31 (d, $J$ = 8.4 Hz, 1H), 3.74 (s, 3H).

$^{19}$F NMR (376 MHz, CDCl$_3$): δ -62.73.

$^{13}$C NMR (101 MHz, CDCl$_3$): δ 154.56, 152.45, 139.36, 133.55, 132.99, 131.78 (q, $J$ = 32.4 Hz), 131.10, 130.77, 124.98 (q, $J$ = 3.8 Hz), 129.97, 124.19 (q, $J$ = 272.3 Hz), 124.02, 113.76, 29.40.

3-(4-fluorophenyl)-1-methylquinoxalin-2(1H)-one (3k)

70% yield, yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.44-8.35 (m, 2H), 7.92 (dd, $J$ = 8.0, 1.5 Hz, 1H), 7.57 (td, $J$ = 7.8, 7.3, 1.6 Hz, 1H), 7.41-7.31 (m, 2H), 7.15 (t, $J$ = 8.7 Hz, 2H), 3.76 (s, 3H).

$^{19}$F NMR (376 MHz, CDCl$_3$): δ -110.02.

$^{13}$C NMR (101 MHz, CDCl$_3$): δ 164.33 (d, $J$ = 251.1 Hz), 154.79, 152.85, 133.28 (d, $J$ = 31.1 Hz), 132.31 (d, $J$ = 3.2 Hz), 132.00, 131.92, 130.52, 130.49, 123.93, 115.17 (d, $J$ = 21.6 Hz), 113.72, 29.44.

3-(4-chlorophenyl)-1-methylquinoxalin-2(1H)-one (3l)

71% yield, yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.36-8.31 (m, 2H), 7.92 (dd, $J$ = 8.0, 1.5 Hz, 1H), 7.57 (ddd, $J$ = 8.5, 7.2, 1.5 Hz, 1H), 7.46-7.41 (m, 2H), 7.40-7.35 (m, 1H), 7.33 (dd, $J$ = 8.4, 1.2 Hz, 1H), 3.76 (s, 3H)
$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 154.67, 152.66, 136.61, 134.51, 133.41, 133.06, 131.08, 130.68, 130.56, 128.36, 123.98, 113.73, 29.44.

3-(4-bromophenyl)-1-methylquinoxalin-2(1H)-one (3m) $^{[2a-b]}

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

45% yield, yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.27-8.22 (m, 2H), 7.91 (dd, $J = 8.0$, 1.5 Hz, 1H), 7.61-7.55 (m, 3H), 7.38 (d, $J = 8.4$ Hz, 1H), 7.35-7.31 (m, 1H), 3.74 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 154.63, 152.73, 134.95, 133.42, 133.06, 131.32, 131.29, 130.72, 130.58, 125.18, 123.98, 113.75, 29.44.

3-(3-chlorophenyl)-1-methylquinoxalin-2(1H)-one (3q)

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

55% yield, orange solid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.36 (t, $J = 1.9$ Hz, 1H), 8.27 (dt, $J = 7.5$, 1.6 Hz, 1H), 7.93 (dd, $J = 8.0$, 1.5 Hz, 1H), 7.58 (ddd, $J = 8.6$, 7.3, 1.6 Hz, 1H), 7.45-7.32 (m, 4H), 3.76 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 154.61, 152.51, 137.76, 134.21, 133.52, 133.03, 130.92, 130.72, 130.41, 129.65, 129.41, 127.89, 124.03, 113.78, 29.48.

HRMS (ESI): calculated m/z for [C$_{15}$H$_{11}$BrN$_2$OH]$^+$: 271.0633, found: 271.0631.

3-(3-bromophenyl)-1-methylquinoxalin-2(1H)-one (3r) $^{[2b]}

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

48% yield, orange solid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.51 (t, $J = 2.0$ Hz, 1H), 8.32 (d, $J = 7.9$ Hz, 1H), 7.94-7.89 (m, 1H), 7.61-7.54 (m, 2H), 7.39-7.28 (m, 3H), 3.73 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 154.55, 152.28, 137.96, 133.46, 133.28, 132.98, 132.45, 130.91, 130.68, 129.65, 128.33, 124.02, 122.31, 113.75, 29.46.

1-methyl-3-(m-tolyl)quinoxalin-2(1H)-one (3s) $^{[2a]}

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

30% yield, orange solid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.09 (dd, $J = 4.3$, 2.0 Hz, 2H), 7.95 (dd, $J = 8.0$, 1.6 Hz, 1H), 7.60-7.53 (m, 1H), 7.40-7.28 (m, 4H), 3.77 (s, 3H), 2.44 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 154.89, 154.58, 153.78, 136.14, 133.47, 133.26, 131.27, 130.55, 130.37, 130.11, 128.11, 126.87, 123.84, 113.69, 29.44, 21.67.
1-methyl-3-(3-(trifluoromethyl)phenyl)quinoxalin-2(1H)-one (3t) [2b]

\[
\text{\begin{tabular}{c}
\includegraphics[width=0.1\textwidth]{3t.png}
\end{tabular}}
\]

48% yield, yellow solid.

\[
\begin{align*}
^1\text{H NMR} & (400 \text{ MHz, CDCl}_3): \delta 8.66 (s, 1H), 8.57 (d, J = 7.9 \text{ Hz, 1H}), 7.95 (dd, J = 8.0, 1.5 \text{ Hz, 1H}), \\
& 7.72 (d, J = 7.8 \text{ Hz, 1H}), 7.62-7.57 (m, 2H), 7.41-7.33 (m, 2H), 3.77 (s, 3H).
\end{align*}
\]

\[
\begin{align*}
^19\text{F NMR} (376 \text{ MHz, CDCl}_3): \delta & -62.47. \\
^13\text{C NMR} (101 \text{ MHz, CDCl}_3): \delta & 154.67, 152.38, 136.78, 133.59, 133.06, 132.97, 131.08, 130.82, \delta \\
& 130.66 (q, J = 32.4 \text{ Hz}), 128.63, 126.92 (q, J = 3.6 \text{ Hz}), 126.64 (q, J = 4.0 \text{ Hz}), 124.28 (q, J = 272.2 \\
& \text{Hz}, 124.11, 113.82, 29.49.
\end{align*}
\]

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

\[
\text{\begin{tabular}{c}
\includegraphics[width=0.1\textwidth]{3v.png}
\end{tabular}}
\]

74% yield, yellow solid.

\[
\begin{align*}
^1\text{H NMR} & (400 \text{ MHz, CDCl}_3): \delta 8.27-8.21 (m, 2H), 7.62 (dd, J = 8.9, 2.4 \text{ Hz, 1H}), 7.33-7.26 (m, 4H), \\
& 3.75 (d, J = 1.6 \text{ Hz, 3H}), 2.42 (s, 3H).
\end{align*}
\]

\[
\begin{align*}
^19\text{F NMR} (376 \text{ MHz, CDCl}_3): \delta & -119.09. \\
^13\text{C NMR} (101 \text{ MHz, CDCl}_3): \delta & 158.89 (d, J = 243.4 \text{ Hz}), 155.32 , 154.55 , 141.22 , 133.83 (d, J = 11.4 \\
& \text{Hz}), 133.13 , 130.09 (d, J = 2.0 \text{ Hz}), 129.77, 128.99, 117.86 (d, J = 24.1 \text{ Hz}), 115.65 (d, J = 22.3 \text{ Hz}), \\
& 114.70 (d, J = 8.8 \text{ Hz}), 29.68, 21.68.
\end{align*}
\]

HRMS (ESI): calculated m/z for [C_{16}H_{13}FN_{2}OH]^+: 269.1085, found: 269.1076.

6-bromo-1-methyl-3-(p-tolyl)quinoxalin-2(1H)-one (3w) [2b]

\[
\text{\begin{tabular}{c}
\includegraphics[width=0.1\textwidth]{3w.png}
\end{tabular}}
\]

66% yield, yellow solid.

\[
\begin{align*}
^1\text{H NMR} & (400 \text{ MHz, CDCl}_3): \delta 8.25 (d, J = 8.2 \text{ Hz, 2H}), 8.06 (d, J = 2.3 \text{ Hz, 1H}), 7.61 (dd, J = 8.9, 2.3 \\
& \text{Hz, 1H}), 7.28 (d, J = 8.3 \text{ Hz, 2H}), 7.17 (d, J = 8.9 \text{ Hz, 1H}), 3.72 (s, 3H), 2.42 (s, 3H).
\end{align*}
\]

\[
\begin{align*}
^13\text{C NMR} (101 \text{ MHz, CDCl}_3): \delta & 154.73, 154.39, 141.19, 133.92, 132.90, 132.62, 132.51, 132.36, \\
& 129.69, 128.89, 116.17, 115.00, 29.45, 21.62.
\end{align*}
\]

HRMS (ESI): calculated m/z for [C_{16}H_{13}BrN_{2}OH]^+: 329.0284, found: 329.0275.

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

\[
\text{\begin{tabular}{c}
\includegraphics[width=0.1\textwidth]{3x.png}
\end{tabular}}
\]

46% yield, yellow solid.

\[
\begin{align*}
^1\text{H NMR} & (400 \text{ MHz, CDCl}_3): \delta 8.77 (d, J = 2.6 \text{ Hz, 1H}), 8.37 (dd, J = 9.2, 2.6 \text{ Hz, 1H}), 8.27 (d, J = 8.2 \\
& \text{Hz, 2H}), 7.40 (d, J = 9.2 \text{ Hz, 1H}), 7.30 (d, J = 8.1 \text{ Hz, 2H}), 3.79 (s, 3H), 2.43 (s, 3H).
\end{align*}
\]
$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 155.92, 154.41, 143.53, 142.03, 137.86, 132.35, 132.30, 129.85, 129.12, 125.91, 124.46, 114.23, 29.98, 21.72.

HRMS (ESI): calculated m/z for [C$_{19}$H$_{13}$N$_3$O$_3$H$^+$]: 296.1030, found: 296.1032.

6,7-dimethoxy-1-methyl-3-(p-tolyl)quinoxalin-2(1H)-one (3y)

74% yield, reddish solid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.19 (d, $J = 8.0$ Hz, 2H), 7.30 (s, 1H), 7.24 (d, $J = 8.0$ Hz, 2H), 6.63 (s, 1H), 3.98 (s, 3H), 3.93 (s, 3H), 3.70 (s, 3H), 2.39 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 154.70, 151.64, 150.75, 146.19, 139.95, 133.67, 129.18, 128.77, 128.41, 127.59, 110.94, 95.70, 56.36, 56.25, 29.51, 21.50.

HRMS (ESI): calculated m/z for [C$_{18}$H$_{18}$N$_2$O$_3$H$^+$]: 311.1390, found: 311.1386.

1,6,7-trimethyl-3-(p-tolyl)quinoxalin-2(1H)-one (3z)

91% yield, yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.21 (d, $J = 8.2$ Hz, 2H), 7.62 (s, 1H), 7.25 (d, $J = 7.8$ Hz, 2H), 7.00 (s, 1H), 3.66 (s, 3H), 2.40 (s, 3H), 2.36 (s, 3H), 2.31 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 154.81, 152.59, 140.18, 139.98, 133.65, 132.57, 131.57, 131.27, 130.30, 129.44, 128.75, 114.10, 29.16, 21.53, 20.62, 19.21.

HRMS (ESI): calculated m/z for [C$_{18}$H$_{18}$N$_2$O$_3$H$^+$]: 279.1492, found: 279.1485.

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

80% yield, yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.35 (d, $J = 8.1$ Hz, 2H), 7.99 (dd, $J = 6.1$, 3.4 Hz, 1H), 7.64 (dd, $J = 8.4$, 6.6 Hz, 2H), 7.60-7.54 (m, 1H), 7.39-7.32 (m, 4H), 7.29 (d, $J = 8.0$ Hz, 2H), 6.68 (dd, $J = 6.2$, 3.5 Hz, 1H), 2.43 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 154.69, 154.40, 140.93, 136.31, 134.19, 133.14, 130.39, 130.01, 129.78, 129.75, 129.46, 128.91, 128.44, 123.93, 115.40, 21.64.

HRMS (ESI): calculated m/z for [C$_{21}$H$_{16}$N$_2$O$_3$H$^+$]: 313.1335, found: 313.1339.
1-benzyl-3-(p-tolyl)quinoxalin-2(1H)-one (3ab) \[5\]

\[
\text{N} \quad \text{N} \\
\text{Bn} \quad \text{Me}
\]

73% yield, yellow solid.

\(^{1}\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.33 (d, \(J = 8.1\) Hz, 2H), 7.96 (dd, \(J = 8.0, 1.6\) Hz, 1H), 7.45-7.40 (m, 1H), 7.35-7.25 (m, 9H), 5.57 (s, 2H), 2.44 (s, 3H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 154.89, 154.06, 140.81, 135.50, 133.46, 133.35, 132.69, 130.49, 130.09, 129.71, 128.98, 128.91, 127.71, 127.03, 123.78, 114.37, 46.14, 21.62.

HRMS (ESI): calculated m/z for [C\(_{22}\)H\(_{18}\)N\(_2\)O\(_2\)]\(^+\) : 327.1492, found: 327.1491.

ethyl 2-(2-oxo-3-(p-tolyl)quinoxalin-1(2H)-yl)acetate (3ac) \[6\]

\[
\text{N} \quad \text{N} \\
\text{CO}_2\text{Et} \quad \text{Me}
\]

77% yield, yellow solid.

\(^{1}\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.26 (d, \(J = 8.2\) Hz, 2H), 7.95 (dd, \(J = 8.0, 1.5\) Hz, 1H), 7.51 (ddd, \(J = 8.6, 7.2, 1.6\) Hz, 1H), 7.40-7.34 (m, 1H), 7.29 (d, \(J = 8.0\) Hz, 2H), 7.11-7.08 (m, 1H), 5.09 (s, 2H), 4.26 (q, \(J = 7.2\) Hz, 2H), 2.42 (s, 3H), 1.28 (t, \(J = 7.2\) Hz, 3H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 167.36, 154.47, 153.83, 140.94, 133.33, 133.11, 132.54, 130.75, 130.30, 129.66, 128.95, 124.08, 113.09, 62.18, 43.88, 21.64, 14.25.

HRMS (ESI): calculated m/z for [C\(_{19}\)H\(_{18}\)N\(_2\)O\(_3\)]\(^+\) : 323.1390, found: 323.1387.

3-(4-bromophenyl)-1-phenylquinoxalin-2(1H)-one (3ad)

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

70 % yield, yellow solid.

\(^{1}\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.36 (d, \(J = 8.4\) Hz, 2H), 8.01-7.95 (m, 1H), 7.67-7.57 (m, 5H), 7.39 -7.32 (m, 4H), 6.73-6.66 (m, 1H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 154.51, 153.16, 136.11, 134.72, 134.30, 133.02, 131.44, 131.36, 130.47, 130.35, 130.21, 129.63, 128.37, 125.45, 124.17, 115.54.

HRMS (ESI): calculated m/z for [C\(_{16}\)H\(_{13}\)BrN\(_2\)O\(_2\)]\(^+\) : 377.0284, found: 377.0277.

ethyl 2-(3-(4-bromophenyl)-2-oxoquinoxalin-1(2H)-yl)acetate (3ae)

\[
\text{N} \quad \text{N} \\
\text{CO}_2\text{Et} \quad \text{Br}
\]

65 % yield, yellow solid.
$^1$H NMR (400 MHz, CDCl$_3$): δ 8.31-8.25 (m, 2H), 7.96 (dd, $J = 8.1, 1.6$ Hz, 1H), 7.63-7.59 (m, 2H), 7.58-7.52 (m, 1H), 7.39 (t, $J = 7.6$ Hz, 1H), 7.11 (d, $J = 8.4$ Hz, 1H), 5.08 (s, 2H), 4.27 (q, $J = 7.1$ Hz, 2H), 1.29 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$): δ 167.21, 154.29, 152.60, 134.69, 133.22, 132.68, 131.41, 131.35, 130.97, 130.89, 125.45, 124.31, 113.22, 62.28, 43.93, 14.27.

HRMS (ESI): calculated m/z for [C$_{18}$H$_{15}$BrN$_2$O$_3$H]$^+$: 387.0339, found: 387.0341.

1-benzyl-3-(4-bromophenyl)quinoxalin-2(1H)-one (3af)

![1-benzyl-3-(4-bromophenyl)quinoxalin-2(1H)-one](image)

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.34 (d, $J = 8.6$ Hz, 2H), 7.95 (dd, $J = 8.0, 1.5$ Hz, 1H), 7.62 (d, $J = 8.5$ Hz, 2H), 7.49-7.44 (m, 1H), 7.37-7.26 (m, 7H), 5.56 (s, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$): δ 154.77, 152.90, 135.34, 134.96, 133.40, 132.89, 131.43, 131.41, 130.77, 130.74, 129.10, 127.89, 127.06, 125.36, 124.08, 114.54, 46.30.

HRMS (ESI): calculated m/z for [C$_{21}$H$_{15}$BrN$_2$OH]$^+$: 391.0441, found: 391.0430.

1-methyl-3-phenylquinolin-2(1H)-one

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

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.78 (s, 1H), 7.64-7.59 (m, 3H), 7.58-7.54 (m, 1H), 7.38 (d, $J = 8.5$ Hz, 1H), 7.27-7.22 (m, 3H), 3.80 (s, 3H), 2.40 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$): δ 161.81, 139.67, 138.07, 136.46, 134.02, 132.62, 130.24, 129.00, 128.96, 128.89, 122.29, 121.00, 114.10, 30.11, 21.42.

Reference:


3. Copies of the NMR Spectra
3aa in CD$_2$COCD$_3$

3ab