# Letter

# Cross-Dehydrogenative Coupling Reaction and Arylation of Quinoxalin-2(1*H*)-ones under Iodide/Peroxide Conditions

Yujuan Wu<sup>a</sup> Xianglong Chu<sup>a</sup> Di Yang<sup>a</sup> Chen Ma<sup>\*a</sup> <sup>(b)</sup> Caixia Xie<sup>b</sup>

<sup>a</sup> Institute of Organic Chemistry, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, P. R. of China

chenma@sdu.edu.cn

<sup>b</sup> School of Chemistry and Chemical Engineering, Shandong University of Technology, Zibo 255049, P. R. of China



✓ Catalytic amount of I₂ (0.2% equiv.)

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**Abstract** A simple method has been developed for the synthesis of  $3-(2-\infty o-2-phenylethylidene)-3,4-dihydroquinoxalin-2(1H)-one and 3-aryl-quinoxalin-2(1H)-one derivatives through C–H activation of quinoxalin-2(1H)-ones by peroxides and iodide. In this protocol, the peroxide (TBPB) serves as both the radical initiator and aryl source, realizing arylation of quinoxalin-2(1H)-one in a one-step reaction. The methodology has the advantages of being a metal-free strategy and having broad functional group tolerance.$ 

**Key words** C–H activation, iodide/peroxide system, metal-free, quinoxalin-2(1*H*)-one, radical process

Quinoxalin-2(1*H*)-one scaffolds exist in many natural products. Due to the significant biological activities and pharmaceutical properties of this structure, such as antitumor,<sup>1</sup> ALR2 inhibition,<sup>2</sup> antibiotic,<sup>3</sup> analgesic,<sup>4</sup> antimicrobial,<sup>5</sup> and aldose reductase inhibition activities (Figure 1),<sup>6</sup> a range of 3-functionalized quinoxalin-2(1*H*)-ones has been synthesized, with approaches including arylation,<sup>7</sup> alkylation,<sup>8</sup> etherification,<sup>9</sup> amidation,<sup>10</sup> amination,<sup>11</sup> cyanation,<sup>12</sup> phosphonation,<sup>13</sup> and trifluoromethylation (Scheme 1).<sup>14</sup>

Activation of C–H bonds has recently emerged as a powerful method for the construction of C–C bonds.<sup>15,16</sup> Furthermore, radical addition is a powerful method to form C–C bonds,<sup>17</sup> with the iodide/TBHP system being considered as a dominant protocol in the radical field to achieve C–H bond activation and construction of heterocyclic rings.<sup>18,19</sup>







**Scheme 1** Synthesis of 3-functionalized quinoxalin-2(1*H*)-one derivatives

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Typical approaches for synthesizing  $3-(2-\infty - 2-phenyl-ethylidene)-3,4-dihydroquinoxalin-2(1H)-ones involve reaction of aroyl- and hetaroylpyruvic acid or ester derivatives with$ *N*-phenyl-*o*-phenylenediamine (Scheme 2).<sup>20,21</sup>



As for the synthesis of diverse 3-arvl-quinoxalin-2(1H)ones, there were two main approaches. One strategy to construct the heterocyclic ring involves two-step acylation of benzene-1.2-diamines with arvlglvoxvlic acids, followed by subsequent cyclization (Scheme 3, method 1).<sup>7a</sup> Other methods involve direct functionalization. Paul reported the novel Pd(TFA)<sub>2</sub>-catalyzed direct dehydrogenative cross-coupling of quinoxalin-2-ones with arenes for the construction of diverse 3-aryl quinoxalin-2-ones (Scheme 3, method 2).<sup>7b</sup> Ramesh reported an oxidative cross-coupling of arvlboronic acids with quinoxalin-2-ones using the readily available oxidant Mn(III) acetate dihydrate (Scheme 3, method 3).<sup>7c</sup> Yin's group used diaryliodonium tetrafluoroborates at room temperature, with arylhydrazines as the arylating agent (Scheme 3, method 4).<sup>7d</sup> Lee and co-workers reported iodosobenzene-promoted direct arylation with arylhydrazines as radical precursors (Scheme 3, method 5).7e However, drawbacks such as the requirement for prefunctionalized substrates, multistep protocols, low atom economy, use of transition-metal catalysts and strong base in these protocols have limited their general application and development. Metal-free systems have replaced tradition metal systems, and iodide or hypervalent iodine possess advantages such as ease of handling, strong electrophilicity, commercial availability, and low toxicity.<sup>22</sup>



Paul reported the enative cross-cou-• the construction

duction of an aryl group.



The I<sub>2</sub>/TBHP system is a central reagent combination in

Herein, we disclose a simple method to synthesize 3-functionalized quinoxalin-2(1H)-ones. In the first part, we

present a *n*-Bu<sub>4</sub>NI-catalyzed radical oxidative coupling of acetophenone and guinoxalin-2(1*H*)-ones using TBHP as

oxidant to access 3-(2-oxo-2-phenylethylidene)-3.4-dihy-

droquinoxalin-2(1H)-ones. In the second part, the direct

arylation of guinoxalin-2(1H)-ones is disclosed. Therein,

TBPB is used both as reagent to generate arvl radical and as

free radical initiator, while I<sub>2</sub> is used as catalyst (Scheme 4).

the radical field.<sup>23,24</sup> It has been shown that *tert*-butyl peroxybenzoate (TBPB) is an efficient and highly chemoselec-

tive benzoylating reagent.<sup>25,26</sup> In this area, we first disclosed that TBPB could translate into aryl radicals, triggering subsequent reactions, providing a novel method for the intro-

Scheme 4 Studies reported herein

Initially, we chose 1-methylquinoxalin-2-(1*H*)-one (**1a**) and acetophenone (**2a**) as model substrates. The reaction was carried out using 20 mol% of TBAI, 5 equivalents of *tert*-butyl hydroperoxide (TBHP, 70% solution in water) in DCE at 100 °C. Under these conditions, the desired product **3a** was obtained in 32% yield (Table 1, entry 4).

Next, we studied a series of iodides and found that using TBAI as catalyst gave higher yields (Table 1, entries 1–7). Then, several oxidants were investigated, such as dibenzoyl peroxide (BPO), tert-butyl peroxybenzoate (TBPB), dibutyl peroxide, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, and DDQ, but the reaction with TBHP still resulted in the best result (Table 1, entries 8-11). When we increased the amount of (2a) from 2 equivalents to 4 equivalents and decreased the amount of TBHP from 5 equivalents to 3 equivalents, the yield of target product was increased to 86% (Table 1, entries 12, 13). Finally, other solvents (DMSO, H<sub>2</sub>O, 1,4-dioxane, toluene) were studied instead, but unfortunately no improvement in yield was observed (Table 1, entries 14-17). Ultimately, we chose (1a, 0.3 mmol), (2a, 4.0 equiv.), TBAI (20 mol%), and TBHP (3.0 equiv.) in DCE (2 mL) at 100 °C for 48 hours as the optimal reaction conditions.

Unexpectedly, we observed a byproduct in a relatively low yield, with 3-arylquinoxalin-2(1*H*)-one **4a** being observed when BPO or TBPB were used as oxidant. It was observed that reaction with iodine showed a slightly higher yield (Table 2, entry 2). Subsequently, a variety of solvents

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#### Table 1 Optimization of the Reaction Conditions<sup>a</sup>



Entry	[I]/mmol%	[O]/equiv.	Solvent	Temp (°C)	Yield (%) <sup>b</sup>
1	I <sub>2</sub> /20	TBHP/5	DCE	100	12
2	Cul/20	TBHP/5	DCE	100	24
3	NIS/20	TBHP/5	DCE	100	NR
4	TBAI/20	TBHP/5	DCE	100	32
5	TBAI+I <sub>2</sub> /20+10	TBHP/5	DCE	100	23
6	TBAI/10	TBHP/5	DCE	100	8
7	TBAI/100	TBHP/5	DCE	100	12
8	TBAI/20	BPO/5	DCE	100	25
9	TBAI/20	$K_{2}S_{2}O_{8}/5$	DCE	100	NR
10	TBAI/20	DDQ/5	DCE	100	NR
11	TBAI/20	TBPB/5	DCE	100	30
12 <sup>c</sup>	TBAI/20	TBHP/5	DCE	100	79
13°	TBAI/20	TBHP/3	DCE	100	86
14 <sup>c</sup>	TBAI/20	TBHP/3	dioxane	100	16
15°	TBAI/20	TBHP/3	DMSO	100	trace
16 <sup>c</sup>	TBAI/20	TBHP/3	H <sub>2</sub> O	100	58
17 <sup>c</sup>	TBAI/20	TBHP/3	DCE	90	70
18 <sup>c</sup>	TBAI/20	TBHP/3	DCE	110	67

<sup>a</sup> Reaction conditions: **1a** (0.3 mmol), **2a** (2.0 equiv.), solvent (2 mL), sealed tube, 48 h.

<sup>b</sup> Isolated yields

<sup>c</sup> **1a** (0.3 mmol), **2a** (4.0 equiv.).

such as acetonitrile, 1,4-dioxane, and DMSO was investigated (Table 2, entries 6–8). Finally, we surveyed varying the effect of temperature (Table 2, entries 4, 5), but the reaction did not proceed well. In order to confirm the source of the aryl group, we conducted experiments without acetophenone. To our satisfaction, the yield of **4a** was increased from 34% to 61% (Table 2, entry 9). Finally, the number of equivalents of iodine and TBPB was investigated, and the yield was eventually improved to 95% (Table 2, entries 10–13). Considering the hazards associated with TBPB, 5 equivalents of TBPB were chosen as the preferred conditions. Thus, the optimized reaction conditions were chosen as TBPB (5 equiv.), I<sub>2</sub> (2 mol%) in DCE at 100 °C for 8 hours.

With the optimized conditions in hand, a range of quinoxalin-2(1*H*)-ones was investigated to give the corresponding derivatives **3** (Scheme 5). These *N*-substituted quinoxalin-2(1*H*)-one analogues showed good reactivities, giving the anticipated products **3aa–aj** in 32-93% yields.

#### Table 2 Optimization of the Reaction Conditions<sup>a</sup>



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Entry	[I]/mmol%	[O]/equiv.	Solvent	Temp (°C)	Yield (%) <sup>b</sup>
1	TBAI/20	TBPB/5	DCE	100	30
2	$I_2/20$	TBPB/5	DCE	100	34
3	KI/20	TBPB/5	DCE	100	33
4	$I_2/20$	TBPB/5	DCE	90	25
5	$I_2/20$	TBPB/5	DCE	110	28
6	$I_2/20$	TBPB/5	$CH_3CN$	100	38
7	$I_2/20$	TBPB/5	dioxane	100	41
8	$I_2/20$	TBPB/5	DMSO	100	NR
9 <sup>c</sup>	$I_2/20$	TBPB/5	DCE	100	61
10 <sup>c</sup>	$I_2/50$	TBPB/5	DCE	100	27
11 <sup>c</sup>	$I_2/2$	TBPB/5	DCE	100	88
12 <sup>c</sup>	$I_2/2$	TBPB/4	DCE	100	71
13°	$I_2/2$	TBPB/7	DCE	100	95

<sup>a</sup> Reaction conditions: **1a** (0.3 mmol), **2a** (2.0 equiv.), solvent (2.0 mL), sealed tube, 48 h.

<sup>b</sup> Isolated yields.

<sup>c</sup> Acetophenone was not present.

In particular, an *N*-phenyl-substituted quinoxalin-2(1*H*)-one was well tolerated, giving the corresponding product **3aj** in 64% yield. Likewise, it was found that substrates with *N*-propyl, *N*-butyl and *N*-cyclohexylmethyl substitution provided the desired products (**3ag**, **3ae**, and **3af**) in good yields. Then, we explored substitution at R<sup>1</sup> and R<sup>2</sup> with R<sup>3</sup> = CH<sub>3</sub> (Scheme 5). Electron-donating and electron-withdrawing groups provided the desired products in moderate to good yields (**3ak**, **3al**, and **3an**). Subsequently, we found that electron-withdrawing substituents (-F, -Br) had a positive effect compared to an electron-donating group (-CH<sub>3</sub>). Furthermore, a substrate with an additional aromatic ring resulted a high yield of 73% (**3am**).

Finally, we studied the scope of acetophenones (Scheme 6). When the substrates possessed electron-donating groups, the yields were lower with a substituent at the *ortho* position than at the *para* position. In addition, *o*-hydroxyacetophenone also gave the desired product **3ba** in 57%. yield. With electron-withdrawing groups present at the *ortho* or *para* positions, the corresponding products **3bb–bi** were obtained in 33–74% yields. The  $\pi$ -extended aromatic substrate provided the expected product **3bj** in a 78% yield.

Most of the substrates studied gave the expected products **4aa-ai** in moderate to excellent yields (Scheme 7). *N*-Substituted quinoxalin-2(1*H*)-ones containing *N*-ester, *N*-benzyl, *N*-benzene acetyl, *N*-propyl, and *N*-aryl substitu-





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**Scheme 5** Substrate scope of quinoxalin-2(1*H*)-ones. *Reagents and conditions*: **1** (0.3 mmol), **2a** (4.0 equiv.), TBAI (0.2 equiv.), TBHP (3.0 equiv.), DCE (2 mL), sealed tube.<sup>27</sup>

ents were all suitable for this reaction, providing the desired products in moderate to good yields. In addition, *N*phenyl quinoxalinone gave the corresponding product **4af** in 94% yield. Finally, we explored substitutions at R<sup>1</sup> and R<sup>2</sup> with R<sup>3</sup> = CH<sub>3</sub>. An electron-withdrawing substituent (–Cl) had a positive effect compared to an electron-donating group (–CH<sub>3</sub>). Appending an additional aromatic ring also led to **4ai** in 70% yield (Scheme 7).

Addition of a radical-trapping reagent such as 2,2,6,6-tetramethylpiperidine *N*-oxide (TEMPO) or BHT to the reaction suppressed the transformation, strongly indicating that the C–C bond formation is a radical-mediated process (Scheme 8).

On the basis of this result, a plausible reaction mechanism can be proposed (Scheme 9). Either the *tert*-butoxy radical or *tert*-butylhydroperoxy radical can remove a hydrogen atom from **2a** to form radical intermediate **5**. Addition of intermediate **5** to **1a** affords intermediate **6**. Then



**Scheme 6** Substrate scope of quinoxalin-2(1*H*)-ones. *Reagents and conditions*: **1a** (0.3 mmol), **2** (4.0 equiv.), TBAI (0.2 equiv.), TBHP (3.0 equiv.), DCE (2 mL), sealed tube.<sup>27</sup>



**Scheme 7** Substrate scope of quinoxalin-2(1*H*)-ones. *Reagents and conditions*: **1a** (0.3 mmol),  $I_2$  (0.02 equiv.), TBPB (5.0 equiv.), solvent (2.0 mL), sealed tube.<sup>27</sup>

intermediate **6** can undergo 1,2-H shift to form the more stable intermediate **7**. Finally, the final product **3a** is obtained by hydrogen-atom removal by a *tert*-butoxy radical.





Scheme 8 Experiments with added radical inhibitors



For the TBPB reaction catalyzed by  $I_2$ , the benzoyl radical releases carbon dioxide forming the phenyl radical under standard conditions. Addition of the phenyl radical to the carbon–nitrogen double bond affords radical intermediate **10**, which is further oxidized by the iodide cation to form nitrogen cation compound **11** that then undergoes 1,2-H shift to give **12**. Finally, the desired compound is obtained by hydrogen–atom removal to give **4a** (Scheme 10).



In conclusion, we have developed a novel protocol for direct synthesis of  $3-(2-\infty o-2-phenylethylidene)-3,4-dihy-droquinoxalin-2(1H)-ones.$  The iodide/peroxide system has

been shown to be a powerful combination to activate the C–H bond of quinoxalin-2(1H)-ones. This process exhibits good functional group tolerance with a broad substrate scope, resulting in acetylation of quinoxalin-2(1H)-ones and providing a new method for the introduction of an aryl group.

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# **Conflict of Interest**

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The authors declare no conflict of interest.

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# **Supporting Information**

Supporting information for this article is available online at https://doi.org/10.1055/a-1489-8711.

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- (27) Substituted substrates **1** were obtained according to the literature reports.<sup>28</sup> Other reagents and solvents were obtained from commercial available reagents and solvents and were used directly without further purification. All the reactions were monitored by thin-layer chromatography. <sup>1</sup>H NMR spectra were recorded on a Bruker Avance 500 spectrometer at 500 MHz using CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub> as solvent and tetramethylsilane (TMS) as internal standard. <sup>13</sup>C NMR spectra were run in the same instrument at 125 MHz. HRMS spectra were measured on a Q-TOF instrument in positive-ion mode with an ESI ion source. Melting points were recorded on an XD-4 digital micro melting point apparatus.

# General Procedure for the TBAI-Catalyzed C–H Acetylation

A mixture of quinoxalin-2(1*H*)-one (**1**, 0.3 mmol), acetophenone (**2**, 4.0 equiv.), TBAI (0.2 equiv.), and TBHP (3.0 equiv.) in DCE (2.0 mL) in a sealed tube was heated at 100 °C for 48 h. After completion of the reaction, the tube was then cooled to room temperature and extracted with ethyl acetate ( $3 \times 20$  mL). The combined organic phases were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (petroleum ether/ethyl acetate = 30:1) on silica gel to provide pure product.

#### General Procedure for the I<sub>2</sub>-Catalyzed C–H Arylation

A mixture of quinoxalin-2(1*H*)-one (**1**, 0.3 mmol), I<sub>2</sub> (0.02 equiv), and TBPB (5.0 equiv.) in DCE solvent (2.0 mL) in a sealed tube was heated at 100 °C for 6 h. After completion of the reaction, the tube was then cooled to room temperature and extracted with ethyl acetate ( $3 \times 20$  mL). The combined organic phases were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was purified by column chromatog-

raphy (petroleum ether/ethyl acetate = 10:1) on silica gel to provide the pure product.

#### (Z)-1-Methyl-3-(2-oxo-2-phenylethylidene)-3,4-dihydroquinoxalin-2(1H)-one (3a)

Yield 86%; yellow solid; mp 176–181 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 14.01 (s, 1 H), 8.13 (d, *J* = 7.3 Hz, 2 H), 8.03 (d, *J* = 7.1 Hz, 2 H), 7.51–7.47 (m, 4 H), 7.18 (s, 2 H), 7.01 (s, 1 H), 3.65 (s, 1 H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 190.2, 156.3, 144.6, 138.9, 131.9, 130.2, 128.5, 127.5, 125.3, 124.4, 124.1, 116.8, 114.4, 91.0, 29.9. HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>: 279.1134; found: 279.1135.

#### Ethyl-(*E*)-4-[(*Z*)-2-oxo-3-(2-oxo-2-phenylethylidene)-3,4dihydroquinoxalin-1(2*H*)-yl]but-2-enoate (3aa)

Yield 46%; yellow solid; mp 167–170 °C. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 13.82 (s, 1 H), 8.00 (d, *J* = 7.3 Hz, 2 H), 7.60–7.52 (m, 4 H), 7.28 (d, *J* = 9.0 Hz, 1 H), 7.24–7.19 (m, 2 H), 7.04 (dt, *J*<sub>1</sub> = 15.9 Hz, *J*<sub>2</sub> = 4.3 Hz, 1 H), 6.87 (s, 1 H), 5.96 (d, *J* = 15.9 Hz, 1 H), 5.02 (s, 2 H), 4.11 (q, *J* = 7.1 Hz, 2 H), 1.18 (t, *J* = 7.1 Hz, 3 H). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 188.7, 165.6, 156.0, 145.2, 142.7, 139.1, 132.4, 129.2, 127.7, 127.4, 125.5, 124.6, 122.1, 117.7, 115.7, 90.1, 60.5, 40.5, 14.5. HRMS (ESI)): *m/z* [M + H]<sup>+</sup> calcd for C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>: 377.1501; found: 377.1502.

#### (*Z*)-4-[2-Oxo-3-(2-oxo-2-phenylethylidene)-3,4-dihydroquinoxalin-1(2*H*)-yl]butanoate (3ab)

Yield 32%; yellow solid; mp 256–260 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 13.85 (s, 1 H), 7.99 (d, *J* = 5.9 Hz, 2 H), 7.59–7.54 (m, 7 H), 7.28–7.22 (m, 2 H), 6.86 (s, 1 H), 4.25–4.22 (m, 2 H), 4.06–4.04 (m, 2 H), 2.51–2.49 (m, 2 H), 1.95 (t, *J* = 5.8 Hz, 3 H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 188.6, 172.9, 155.8, 145.1, 139.0, 132.4, 129.2, 127.8, 127.4, 125.3, 124.8, 124.5, 117.9, 115.3, 89.9, 60.4, 31.1, 22.3, 14.5. HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>22</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub>: 379.1658; found: 379.1653.

#### (*Z*)-1-[4-(*tert*-Butyl)benzyl]-3-(2-oxo-2-phenylethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (3ac)

Yield 76%; yellow solid; mp 188–190 °C. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 13.86 (s, 1 H), 8.01 (d, *J* = 7.6 Hz, 2 H), 7.57–7.53 (m, 6 H), 7.33–7.24 (m, 5 H), 6.94 (s, 1 H), 5.43 (s, 2 H), 1.22 (s, 9 H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 188.7, 156.0, 150.6, 145.1, 139.0, 133.1, 132.5, 129.3, 127.9, 127.5, 127.0, 125.9, 125.5, 124.7, 117.8, 116.02, 90.29, 45.6, 34.7, 31.6. HRMS (ESI): *m*/z [M + H]<sup>+</sup> calcd for C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>?411.2073; found: 411.2071.

#### (Z)-1-Cinnamyl-3-(2-oxo-2-phenylethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (3ad)

Yield 42%; yellow solid; mp 204–207 °C. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 13.86 (s, 1 H), 8.00 (d, *J* = 7.3 Hz, 2 H), 7.59–7.52 (m, 5 H), 7.43–7.40 (m, 3 H), 7.31 (t, *J* = 7.4 Hz, 2 H), 7.23–7.21 (m, 2 H), 6.90 (s, 1 H), 5.01 (s, 2 H), 2.50 (s, 2 H). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 188.7, 155.8, 145.2, 139.1, 136.6, 132.4, 132.1, 129.3, 129.1, 128.2, 127.9, 127.5, 126.8, 125.4, 124.7, 124.6, 123.7, 117.7, 115.9, 44.7. HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>25</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>: 381.1603; found: 381.1603.

#### (Z)-1-Butyl-3-(2-oxo-2-phenylethylidene)-3,4-dihydroquinoxalin-2(1H)-one (3ae)

Yield 93%; colorless oily liquid. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 14.06$  (s, 1 H), 8.04–8.03 (m, 2 H), 7.52–7.45 (m, 3 H), 7.23–7.18 (m, 4 H), 7.02 (s, 1 H), 1.24–1.20 (m, 2 H), 1.80–1.72 (m, 2 H), 1.55–1.45 (m, 2 H), 1.00 (t, *J* = 7.3 Hz, 3 H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 190.0$ , 156.0, 144.7, 139.8, 131.8, 128.5, 127.4, 125.5, 124.2, 124.0, 117.1, 114.5, 90.8, 77.4, 77.0, 76.7, 42.7, 29.1, 20.3, 13.8. HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>O: 321.1603; found: 321.1602.

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# (*Z*)-1-(Cyclohexylmethyl)-3-(2-oxo-2-phenylethylidene)-3,4dihydroquinoxalin-2(1*H*)-one (3af)

Yield 65%; colorless oily liquid. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 13.85 (s, 1 H), 7.95 (d, *J* = 7.3 Hz, 2 H), 7.55–7.49 (m, 4 H), 7.39 (d, *J* = 8 Hz, 1 H), 7.22–7.17 (m, 2 H), 6.83 (s, 1 H), 4.05 (s, 2 H), 1.79 (s, 1 H), 1.63 (d, *J* = 8.15 Hz, 4 H), 1.10–1.08 (m, 6 H). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 188.5, 156.0, 145.0, 139.0, 132.3, 129.1, 128.0, 127.4, 125.2, 124.7, 124.4, 117.8, 115.7, 90.0, 48.0, 36.2, 30.6, 26.3, 25.8. HRMS (ESI): *m*/z [M + H]<sup>+</sup> calcd for C<sub>23</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>: 361.1916; found: 361.1916.

# (Z)-3-(2-Oxo-2-phenylethylidene)-1-propyl-3,4-dihydroquinoxalin-2(1*H*)-one (3ag)

Yield 63%; colorless oily liquid. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ = 13.82 (s, 1 H), 7.94 (d, *J* = 7.1 Hz, 2 H), 7.56–7.54 (m, 2 H), 7.51–7.48 (m, 3 H), 7.41 (d, *J* = 7.8 Hz, 1 H), 7.23–7.16 (m, 2 H), 6.81 (s, 1 H), 1.68 (q, *J* = 7.6 Hz, 2 H), 0.96 (t, *J* = 7.4 Hz, 3 H). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>): δ = 188.5, 155.6, 145.0, 139.0, 132.3, 129.1, 127.7, 127.4, 125.2, 124.7, 124.4, 117.8, 115.4, 89.9, 44.1, 20.5, 11.5. HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>: 307.1447; found: 307.1448.

# (Z)-1-Benzyl-3-(2-oxo-2-phenylethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (3ah)

Yield 69%; yellow solid; mp 180–184 °C. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 13.86 (s, 1 H), 8.01 (d, *J* = 7.1 Hz, 2 H), 7.59–7.54 (m, 4 H), 7.34 (d, *J* = 4.4 Hz, 4 H), 7.27–7.25 (m, 2 H), 7.20 (t, *J* = 6.7 Hz, 1 H), 7.14 (t, *J* = 7.1 Hz, 1 H), 6.84 (s, 1 H), 5.48 (s, 2 H). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 188.8, 156.4, 145.1, 139.0, 136.2, 132.5, 129.3, 129.2, 127.8, 127.5, 127.2, 125.4, 124.7, 124.6, 117.8, 116.0, 90.4, 46.1. HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>23</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>: 355.1447; found: 355.1446.

# (Z)-2-[2-Oxo-3-(2-oxo-2-phenylethylidene)-3,4-dihydroquinoxalin-1(2H)-yl]ethyl acetate (3ai)

Yield 70%; yellow solid. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 13.72 (s, 1 H), 8.00 (d, *J* = 7.1 Hz, 2 H), 7.60–7.57 (m, 2 H), 7.55–7.52 (m, 2 H), 7.37 (d, *J* = 9.3 Hz, 1 H), 7.25–7.19 (m, 2 H), 6.86 (s, 1 H), 5.07 (s, 2 H), 4.22 (q, *J* = 7.1 Hz, 2 H), 1.25 (t, *J* = 7.1 Hz, 3 H). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  =188.9, 168.0, 156.1, 144.3, 138.9, 132.5, 129.2, 127.8, 127.5, 125.1, 124.8, 124.7, 117.8, 115.3, 90.3, 61.9, 44.7, 14.5. HRMS (ESI): *m/z* [M + H]\* calcd for C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>: 351.1345; found: 351.1342.

# (Z)-3-(2-Oxo-2-phenylethylidene)-1-phenyl-3,4-dihydroquinoxalin-2(1*H*)-one (3aj)

Yield 64%; yellow solid; mp 191–193 °C. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 13.86 (s, 1 H), 7.99 (d, *J* = 7.3 Hz, 2 H), 7.67–7.63 (m, 3 H), 7.61–7.57 (m, 3 H), 7.55–7.52 (m, 2 H), 7.46 (d, *J* = 7.3 Hz, 2 H), 7.20 (t, *J* = 7.9 Hz, 1 H), 7.05 (t, *J* = 7.4 Hz, 1 H), 6.88 (s, 1 H). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 189.0, 155.9, 145.7, 139.0, 136.9, 132.5, 130.6, 130.1, 129.7, 129.3, 129.2, 127.5, 125.1, 124.5, 124.3, 117.5, 116.0, 90.1. HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for  $C_{22}H_{16}N_2O_4$ : 341.1290; found: 341.1286.

# (Z)-1,6,7-Trimethyl-3-(2-oxo-2-phenylethylidene)-3,4-dihy-droquinoxalin-2(1*H*)-one (3ak)

Yield 47%; yellow solid; mp 221–224 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 14.16 (s, 1 H), 8.03–8.01 (m, 2 H), 7. 50–7.46 (m, 3 H), 7.01 (s, 1 H), 6.97 (s, 1 H), 6.95 (s, 1 H), 3.64 (s, 3 H), 2.31 (s, 3 H), 2.28 (s, 3 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 189.2, 156.2, 145.0, 139.0, 133.1, 131.5, 130.1, 128.5, 127.3, 126.5, 123.2, 117.8, 115.3, 90.4, 29.6, 19.9, 19.3. HRMS (ESI): m/z [M + H]<sup>+</sup> calcd for  $C_{19}H_{18}N_2O_2$ : 307.1447; found: 306.1445.

# (Z)-6,7-Difluoro-1-methyl-3-(2-oxo-2-phenylethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (3al)

Yield 74%; yellow solid; mp 286–288 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 14.07 (s, 1 H), 8.00 (d, *J* = 7.2 Hz, 2 H), 7.54–7.45 (m,

4 H), 7.10–7.07 (m, 1 H), 7.00 (s, 1 H), 3.61 (s, 3 H).  $^{13}\text{C}$  NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 188.9, 155.8, 145.0, 138.2, 132.1, 130.1, 128.6, 127.4, 106.1, 105.9, 103.8, 91.7, 30.2. HRMS (ESI): m/z [M + H]\* calcd for  $C_{17}\text{H}_{12}\text{F}_{2}\text{N}_{2}\text{O}_{2}$ : 315.0945; found: 315.0940.

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# (Z)-1-Methyl-3-(2-oxo-2-phenylethylidene)-3,4-dihydrobenzo[g]quinoxalin-2(1*H*)-one (3am)

Yield 73%; yellow solid; mp 186–190 °C. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 13.74 (s, 1 H), 8.01–7.98, (m, 3 H), 7.94–7.92 (m, 1 H), 7.85 (s, 1 H), 7.62–7.54 (m, 4 H), 7.45–7.44 (m, 2 H), 6.92 (s, 1 H), 3.67 (s, 3 H). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 189.6, 156.1, 144.4, 139.0. 132.6, 130.4, 130.2, 129.3, 128.7, 127.9, 127.6, 127.0, 126.1, 125.8, 124.9, 113.1, 112.2, 91.1, 30.4. HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>: 329.1290; found: 329.1285.

# (Z)-6,7-Dibromo-1-methyl-3-(2-oxo-2-phenylethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (3an)

Yield 51%; yellow solid. <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ ):  $\delta$  = 13.35 (s, 1 H), 8.01 (s, 1 H), 7.92 (d, *J* = 5 Hz, 2 H), 7.61–7.49 (m, 4 H), 6.81 (s, 1 H), 3.50 (s, 3 H). <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ ):  $\delta$  = 188.9, 155.6, 144.0, 138.7, 132.6, 129.2, 127.5, 125.9, 121.4, 119.6, 118.3, 118.1, 91.3, 30.4. HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>12</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: 434.9344; found: 434.9349.

### (Z)-3-[2-(2-Hydroxyphenyl)-2-oxoethylidene]-1-methyl-3,4dihydroquinoxalin-2(1*H*)-one (3ba)

Yield 57%; yellow solid; mp 207–209 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 13.27 (s, 1 H), 12.85 (s, 1 H), 7.90 (d, *J* = 7.7 Hz, 1 H), 7.68 (d, *J* = 7.4 Hz, 1 H), 7.48–7.44 (m, 2 H), 6.97–6.93 (m, 2 H), 3.61 (s, 3 H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 188.9, 167.4, 156.2, 146.1, 139.1, 132.4, 129.2, 127.5, 127.2, 124.6, 124.5, 124.2, 117.1, 115.8, 89.6, 40.0. HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>: 295.1083; found: 295.1079.

# (*Z*)-1-Methyl-3-[2-oxo-2-(*o*-tolyl)ethylidene]-3,4-dihydroquinoxalin-2(1*H*)-one (3bb)

Yield 33%; yellow solid; mp 144–147 °C. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 13.54 (s, 1 H), 7.58–7.54 (m, 2 H), 7.42–7.37 (m, 2 H), 7.32–7.22 (m, 4 H), 6.44 (s, 1 H), 3.58 (s, 3 H), 2.46 (s, 3 H). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 193.8, 155.7, 144.3, 140.7, 136.2, 131.7, 130.5, 128.7, 128.1, 126.4, 125.0, 124.6, 124.4, 117.4, 115.5, 93.9, 30.2, 20.5. HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>: 293.1290; found: 293.1295.

# (Z)-3-[2-(4-Methoxyphenyl)-2-oxoethylidene]-1-methyl-3,4dihydroquinoxalin-2(1*H*)-one (3bc)

Yield 74%; yellow solid; mp 199–203 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 13.76 (s, 1 H), 7.98 (d, *J* = 10.8 Hz, 2 H), 7.53–7.51 (m, 1 H), 7.42–7.40 (m, 1 H), 7.24–7.21 (m, 2 H), 7.08 (d, *J* = 8.8 Hz, 2 H), 6.83 (s, 1 H), 3.85 (s, 3 H), 3.60 (s, 3 H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 188.1, 162.9, 156.0, 144.6, 131.8, 129.6, 128.6, 125.2, 124.5, 124.4, 117.1, 115.5, 114.5, 89.8, 55.9, 30.2. HRMS (ESI): *m*/z [M + H]<sup>+</sup> calcd for C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>: 309.1239; found: 309.1238.

# (Z)-1-Methyl-3-[2-oxo-2-(p-tolyl)ethylidene]-3,4-dihydroquinoxalin-2(1H)-one (3bd)

Yield 62%; yellow solid; mp 179–181 °C. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 13.79 (s, 1 H), 7.88 (d, *J* = 8.0 Hz, 2 H), 7.53 (d, *J* = 9.0 Hz, 2 H), 7.41 (d, *J* = 7.2 Hz, 2 H), 7.33 (d, *J* = 7.9 Hz, 2 H), 7.25–7.20 (m, 2 H), 6.82 (s, 1 H), 3.58 (s, 3 H), 2.37 (s, 3 H). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 188.5, 155.8, 144.9, 142.6, 136.4, 129.8, 128.7, 127.5, 125.1, 124.5, 117.3, 115.5, 89.9, 30.2, 21.6. HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>: 293.1290; found: 293.1288.

#### (Z)-3-[2-(4-Bromophenyl)-2-oxoethylidene]-1-methyl-3,4dihydroquinoxalin-2(1*H*)-one (3be)

Yield 61%; yellow solid; mp 263-265 °C. <sup>1</sup>H NMR (400 MHz,

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DMSO-*d*<sub>6</sub>): δ = 13.84 (s, 1 H), 7.94 (d, *J* = 8.6 Hz, 2 H), 7.75 (d, *J* = 8.6 Hz, 2 H), 7.60–7.58 (m, 1 H), 7.45–7.43 (m, 1 H), 7.30–7.22 (m, 2 H), 6.84 (s, 1 H), 3.61 (s, 3 H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ = 187.4, 155.7, 145.5, 138.1, 132.3, 129.5, 128.9, 126.3, 124.9, 124.6, 117.6, 115.6, 100.0, 89.7, 30.3. HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>13</sub>BrN<sub>2</sub>O<sub>2</sub>: 357.0239; found: 357.0241.

#### (Z)-3-[2-(4-Chlorophenyl)-2-oxoethylidene]-1-methyl-3,4dihydroquinoxalin-2(1*H*)-one (3bf)

Yield 51%; yellow solid; mp 248–253 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 13.83 (s, 1 H), 8.01 (d, *J* = 8.6 Hz, 2 H), 7.60 (d, *J* = 8.6 Hz, 2 H), 7.44 (d, *J* = 7.7 Hz, 2 H), 7.28–7.24 (m, 2 H), 6.84 (s, 1 H), 3.60 (s, 3 H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 187.2, 155.7, 145.4, 137.7, 137.2, 129.4, 128.9, 125.0, 124.6, 117.6, 115.6, 89.7, 30.3. HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>13</sub><sup>-</sup> ClN<sub>2</sub>O<sub>2</sub>: 313.0744; found: 313.0742.

#### (Z)-3-[2-(4-lodophenyl)-2-oxoethylidene]-1-methyl-3,4dihydroquinoxalin-2(1*H*)-one (3bg)

Yield 49%; yellow solid; mp 204–206 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ = 13.83 (s, 1 H), 7.92 (d, *J* = 8 Hz, 2 H), 7.76 (d, *J* = 8.5 Hz, 2 H), 7.58–7.56 (m, 1 H), 7.44–7.42 (m, 1 H), 7.29–7.21 (m, 2 H), 6.82 (s, 1 H), 3.60 (s, 3 H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ = 187.6, 155.7, 145.4, 138.4, 138.2, 129.3, 128.9, 125.0, 124.9, 124.6, 117.6, 115.6, 100.4, 89.6, 30.3. HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>13</sub>IN<sub>2</sub>O<sub>2</sub>: 405.0100; found: 405.0102.

#### (Z)-3-[2-(2-Fluorophenyl)-2-oxoethylidene]-1-methyl-3,4dihydroquinoxalin-2(1*H*)-one (3bh)

Yield 70%; yellow solid; mp 145–150 °C. <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ ):  $\delta$  = 13.75 (s, 1 H), 7.88–7.84 (m, 1 H), 7.60 (d, *J* = 6.5 Hz, 2 H), 7.44 (d, *J* = 7.9 Hz, 2 H), 7.37–7.32 (m, 2 H), 7.29–7.22 (m, 2 H), 6.75 (s, 1 H), 3.59 (s, 3 H). <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ ):  $\delta$  = 185.4, 161.5, 157.5, 155.6, 145.2, 134.0, 133.9 (*J* = 35.5 Hz), 130.5, 129.0, 127.7, 127.6 (*J* = 49.0 Hz), 125.3 (*J* = 13.0 Hz), 125.0, 124.9, 124.5, 117.7, 117.2 (*J* = 250.6 Hz), 117.0, 115.6, 94.2, 30.3. HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>13</sub>FN<sub>2</sub>O<sub>2</sub>: 297.1039; found: 297.1041.

#### (Z)-1-Methyl-3-{2-oxo-2-[2-(trifluoromethyl)phenyl]ethylidene}-3,4-dihydroquinoxalin-2(1*H*)-one (3bi)

Yield 35%; yellow solid; mp 191–195 °C. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 13.29 (s, 1 H), 7.84–7.76 (m, 2 H), 7.65–7.70 (m, 3 H), 7.43 (d, *J* = 7.7 Hz, 1 H), 7.28–7.21, (m, 2 H), 6.32 (s, 1 H), 3.58 (s, 3 H). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 191.7, 155.4, 144.6, 140.9, 133.1, 130.6, 128.9, 128.8 (*J* = 65.4 Hz), 127.1, 127.0 (*J* = 21.2 Hz), 126.2, 126.0 (*J* = 124.8 Hz), 125.5, 125.0, 124.7, 124.5 (*J* = 61.7 Hz), 123.3, 117.6, 115.6, 93.5, 30.3. HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>18</sub>H<sub>13</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub>: 347.1007; found: 347.1002.

#### (Z)-1-Methyl-3-[2-(naphthalen-2-yl)-2-oxoethylidene]-3,4dihydroquinoxalin-2(1*H*)-one (3bj)

Yield 78%; yellow solid; mp 164–167 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 13.69 (s, 1 H), 8.52 (d, *J* = 7.6 Hz, 1 H), 8.09 (d, *J* = 6.6 Hz, 1 H), 8.02–8.01 (m, 1 H), 7.84 (d, *J* = 5.6 Hz, 1 H), 7.62–7.59 (m, 4 H), 7.43 (d, *J* = 6.0 Hz, 1 H), 7.29–7.23 (m, 2 H), 6.61 (s, 1 H), 3.59 (s, 3 H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 193.2, 155.8, 144.6, 138.6, 133.9, 131.4, 130.0, 128.9, 128.8, 127.5, 126.8, 126.7, 126.0, 125.7, 125.0, 124.7, 124.5, 117.4, 115.6, 94.5, 30.2. HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>: 329.1290; found: 329.1286.

# 1-Methyl-3-phenylquinoxalin-2(1H)-one (4a)

Yield 88%; white solid; mp 114–116 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.31–8.30 (m, 2 H), 7.95 (d, *J* = 9.2 Hz, 1 H), 7.59 (t, *J* = 7.1 Hz, 1 H), 7.49–7.48 (m, 3 H), 7.39–7.34 (m, 2 H), 3.78 (s, 3 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 154.8, 154.2, 136.1, 133.4, 133.1, 130.5, 130.3, 129.6, 128.1, 123.8, 113.6, 29.3. HRMS (ESI): *m/z* 

 $[M + H]^+$  calcd for C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>O: 237.1028; found: 237.1028.

**Ethyl 2-[2-Oxo-3-phenylquinoxalin-1(2H)-yl]acetate (4aa)** Yield 47%; white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.33–8.31 (m, 2 H), 7.99 (dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 1.4 Hz, 1 H), 7.57–7.52 (m, 1 H), 7.51–7.47 (m, 3 H), 7.41–7.36 (m, 1 H), 7.13 (d, *J* = 8.4 Hz, 1 H), 5.10 (s, 2 H), 4.30 (q, *J* = 7.2 Hz, 2 H), 1.31 (t, *J* = 7.1 Hz, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 167.2, 154.3, 154.0, 135.7, 133.2, 132.5, 130.8, 130.5, 129.6, 128.1, 124.1, 113.1, 62.1, 43.8, 14.2. HRMS (ESI): *m*/z [M + H]<sup>+</sup> calcd for C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>: 309.1239; found: 309.1238.

# 1-[4-(*tert*-Butyl)benzyl]-3-phenylquinoxalin-2(1*H*)-one (4ab)

Yield 37%; white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.29–8.27 (m, 2 H), 7.89 (d, *J* = 6.4 Hz, 1 H), 7.43–7.41 (m, 4 H), 7.28–7.25 (m, 5 H), 7.18 (s, 2 H), 5.47 (s, 2 H), 1.20 (s, 9 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 154.8, 154.3, 150.7, 136.1, 133.4, 132.9, 132.3, 130.6, 130.4, 130.3, 129.7, 128.1, 126.8, 125.9, 123.8, 114.5, 45.9, 34.5, 31.3. HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>25</sub>H<sub>24</sub>N<sub>2</sub>O: 369.1967; found: 369.1669.

#### 1-Benzyl-3-phenylquinoxalin-2(1H)-one (4ac)

Yield 51%; white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.38–8.35 (m, 2 H), 7.97 (d, *J* = 9.4 Hz, 1 H), 7.51–7.49 (m, 3 H), 7.46–7.43 (m, 1 H), 7.36–7.26 (m, 7 H), 5.58 (s, 2 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 154.8, 154.3, 136.0, 135.4, 133.4, 132.8, 130.6, 130.5, 130.4, 129.7, 129.0, 128.1, 127.7, 127.0, 123.8, 114.4, 46.2. HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>16</sub>N<sub>2</sub>O: 313.1341; found: 313.1343.

# 1-(2-Oxo-2-phenylethyl)-3-phenylquinoxalin-2(1*H*)-one (4ad)

Yield 32%; white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.34–8.31 (m, 2 H), 8.12–8.10 (m, 2 H), 8.01 (dd,  $J_1$  = 8.0 Hz,  $J_2$  = 1.4 Hz, 1 H), 7.71–7.67 (m, 2 H), 7.59–7.55 (m, 2 H), 7.49–7.48 (m, 4 H), 7.39–7.35 (m, 1 H), 7.01 (d, J = 9.1 Hz, 1 H), 5.82 (s, 2 H). <sup>13</sup>C NMR (101 MHz, DMSO- $d_6$ ):  $\delta$  = 192.9, 154.3, 153.2, 136.0, 135.0, 133.4, 132.8, 131.2, 130.9, 130.3, 129.8, 129.5, 129.0, 128.8, 128.5, 124.3, 115.9, 50.9. HRMS (ESI): m/z [M + H]<sup>+</sup> calcd for C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>: 341.1290; found: 341.1290.

#### 3-Phenyl-1-propylquinoxalin-2(1H)-one (4ae)

Yield 28%; colorless oily liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.32–8.30 (m, 2 H), 7.97–7.95 (m, 1 H), 7.58–7.54 (m, 1 H), 7.49–7.47 (m, 3 H), 7.38–7.33 (m, 2 H), 4.31–4.27 (m, 2 H), 1.90–1.81 (m, 2 H), 1.11 (t, *J* = 7.4 Hz, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 154.4, 154.2, 136.1, 133.4, 132.6, 130.7, 130.3, 130.2, 129.6, 128.1, 123.5, 113.6, 44.1, 20.7, 11.5. HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>17</sub>N<sub>2</sub>O: 265.1341; found: 265.1345.

# 1,3-Diphenylquinoxalin-2(1*H*)-one (4af)

Yield 94%; white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.40–8.38 (m, 2 H), 8.00–7.98 (m, 2 H), 7.66–7.56 (m, 4 H), 7.49–7.47 (m, 3 H), 7.37–7.34 (m, 4 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 154.5, 136.1, 135.7, 134.2, 133.0, 130.5, 130.3, 130.1, 130.0, 129.7, 129.4, 128.3, 128.1, 123.9, 115.4. HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>20</sub>H<sub>14</sub>N<sub>2</sub>O: 299.1184; found: 299.1180.

#### 1,6,7-Trimethyl-3-phenylquinoxalin-2(1H)-one (4ag)

Yield 66%; white solid; mp 154–156 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.29–8.26 (m, 2 H), 7.71 (s, 1 H), 8.49–8.35 (m, 4 H), 7.11 (s, 1 H), 3.76 (s, 3 H), 2.45 (s, 3 H), 2.38 (s, 3 H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 167.8, 154.5, 152.1, 140.9, 137.0, 133.4, 132.8, 131.2, 129.7, 129.1, 128.3, 115.5, 29.7, 20.5, 19.2. HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O: 265.1341; found: 265.1338.

#### 6,7-Chloro-1-methyl-3-phenylquinoxalin-2(1*H*)-one (4ah)

Yield 95%; white solid; mp 172–174 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.31–8.29 (m, 2 H), 8.02 (s, 1 H), 7.51–7.47 (m, 3 H),

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7.42 (s, 1 H), 3.72 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 155.2, 154.1, 135.4, 134.3, 132.7, 132.2, 131.1, 130.9, 130.0, 128.2, 115.1, 29.6. HRMS (ESI): m/z [M + H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>2</sub>O: 306.1660; found: 306.1661.

# 1-Methyl-3-phenylbenzo[g]quinoxalin-2(1H)-one (4ai)

Yield 70%; yellow solid; mp 162–164 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.45 (s, 1 H), 8.34–8.32 (m, 2 H), 8.00–7.91 (m, 2 H),

7.62 (s, 1 H), 7.59–7.55 (m, 1 H), 7.51–7.49 (m, 4 H), 3.83 (s, 3 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 154.8, 154.7, 136.1, 133.8, 132.5, 132.0, 130.5, 129.9, 129.7, 129.7, 128.5, 128.1, 127.9, 127.2, 125.3, 109.8, 29.3. HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>14</sub>N<sub>2</sub>O: 287.3420; found: 287.3421.

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