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

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Received: 15.03.2021
Accepted after revision: 21.04.2021
Published online: 23.04.2021
DOI: 10.1055/a-1489-8711; Art ID: so-2021-d0013-l

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Abstract A simple method has been developed for the synthesis of 3-(2-oxo-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(1H)-one, radical process

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

Activation of C–H bonds has recently emerged as a powerful method for the construction of C–C bonds. 15,16 Furthermore, radical addition is a powerful method to form C–C bonds, 17 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. 18,19

Figure 1 Pharmacologically active quinoxalin-2(1H)-one derivatives

Scheme 1 Synthesis of 3-functionalized quinoxalin-2(1H)-one derivatives
Typical approaches for synthesizing 3-(2-oxo-2-phenylethylidene)-3,4-dihydroquinoxalin-2(1H)-ones involve reaction of aryl- and heteroarylpyruvic acid or ester derivatives with N-phenyl-o-phenylenediamine (Scheme 2).

As for the synthesis of diverse 3-aryl-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 arylglyoxylic acids, followed by subsequent cyclization (Scheme 3, method 1). Other methods involve direct functionalization. Paul reported the novel Pd(TFA)2-catalyzed direct dehydrogenative cross-coupling of quinoxalin-2-ones with arenes for the construction of quinoxalin-2(1H)-ones (Scheme 3, method 2). Ramesh reported an oxidative cross-coupling of aryloboronic acids with quinoxalin-2-ones using the readily available oxidant Mn(III) acetate dihydrate (Scheme 3, method 3). Yin’s group used diaryliodonium tetrafluoroborate as radical precursors (Scheme 3, method 5). Other methods involve direct functionalization. Paul reported the novel Pd(TFA)2-catalyzed direct dehydrogenative cross-coupling of quinoxalin-2-ones with arenes for the construction of quinoxalin-2(1H)-ones (Scheme 3, method 2). Ramesh reported an oxidative cross-coupling of aryloboronic acids with quinoxalin-2-ones using the readily available oxidant Mn(III) acetate dihydrate (Scheme 3, method 3). Yin’s group used diaryliodonium tetrafluoroborate as radical precursors (Scheme 3, method 5).

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 traditional metal systems, and iodide or hypervalent iodine possess advantages such as ease of handling, strong electrophilicity, commercial availability, and low toxicity.

The I2/TBHP system is a central reagent combination in the radical field. It has been shown that tert-butyl peroxo-benzoate (TBPB) is an efficient and highly chemoselective benzylation reagent. In this area, we first disclosed that TBPB could translate into aryl radicals, triggering subsequent reactions, providing a novel method for the introduction of an aryl group.

Herein, we disclose a simple method to synthesize 3-functionalized quinoxalin-2(1H)-ones. In the first part, we present a n-Bu4NI-catalyzed radical oxidative coupling of acetophenone and quinoxalin-2(1H)-ones using TBHP as oxidant to access 3-(2-oxo-2-phenylethylidene)-3,4-dihydroquinoxalin-2(1H)-ones. In the second part, the direct arylation of quinoxalin-2(1H)-ones is disclosed. Therein, TBPB is used both as reagent to generate aryl radical and as free radical initiator, while I2 is used as catalyst (Scheme 4).

Initially, we chose 1-methylquinoxalin-2-(1H)-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, K2S2O8, 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, H2O, 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-arylquinolin-2(1H)-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...
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.), I₂ (2 mol%) in DCE at 100 °C for 8 hours.

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

In particular, an N-phenyl-substituted quinoxalin-2(1H)-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 R₁ and R₂ with R₃ = CH₃ (Scheme 5). Electron-donating and electron-withdrawing groups provided the desired products (3ak, 3al, and 3an). Subsequently, we found that electron-withdrawing substituents (–F, –Br) had a positive effect compared to an electron-donating group (–CH₃). 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 3bj 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 π-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(1H)-ones containing N-ester, N-benzyl, N-benzene acetyl, N-propyl, and N-aryl substitu-

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**Table 1** Optimization of the Reaction Conditions

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<th>Entry</th>
<th>[I]/mmol%</th>
<th>[O]/equiv.</th>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Yield (%)</th>
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* Reaction conditions: 1a (0.3 mmol), 2a (2.0 equiv.), solvent (2 mL), sealed tube, 48 h.  
* Isolated yields.  
* 1a (0.3 mmol), 2a (4.0 equiv.).

**Table 2** Optimization of the Reaction Conditions

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<th>[O]/equiv.</th>
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<th>Yield (%)</th>
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* Reaction conditions: 1a (0.3 mmol), 2a (2.0 equiv.), solvent (2 mL), sealed tube, 48 h.  
* Isolated yields.  
* Acetophenone was not present.
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 R1 and R2 with R3 = CH3. An electron-withdrawing substituent (–Cl) had a positive effect compared to an electron-donating group (–CH3). 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 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.
For the TBPB reaction catalyzed by I₂, 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).

Scheme 8 Experiments with added radical inhibitors

Scheme 9 Plausible reaction mechanism

Scheme 10 Plausible reaction mechanism

In conclusion, we have developed a novel protocol for direct synthesis of 3-(2-oxo-2-phenylethylidene)-3,4-dihydroquinoxalin-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.

Conflict of Interest

The authors declare no conflict of interest.

Funding Information

Financial support from the National Science Foundation of China (21572117) and the Shandong Key Research Program (Nos. 2019JZZY021015 and 2019GHY112053) is gratefully acknowledged.

Acknowledgment

We are grateful to the Analytical Center for Structural Constituent and Physical Property of Core Facilities Sharing Platform, Shandong University for their technological and service support.

Supporting Information

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

References and Notes


(27) Substituted substrates I were obtained according to the literature reports. 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. 1H NMR spectra were recorded on a Bruker Avance 500 spectrometer at 500 MHz using CDCl3 or DMSO-d6 as solvent and tetramethylsilane (TMS) as internal standard. 13C 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(1H)-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 × 20 mL). The combined organic phases were dried over anhydrous Na2SO4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (petroleum ether/ethyl acetate = 10:1) on silica gel to provide pure product.

**General Procedure for the I2-Catalyzed C-H Arylation**

A mixture of quinoxalin-2(1H)-one (1, 0.3 mmol), I2 (0.02 equiv), and TBHP (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 × 20 mL). The combined organic phases were dried over anhydrous Na2SO4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (petroleum ether/ethyl acetate = 10:1) on silica gel to provide pure product.

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

Yield 86%; yellow solid; mp 176–181 °C. 1H NMR (500 MHz, CDCl3); δ = 14.01 (s, 1 H), 8.13 (d, J = 7.3 Hz, 2 H), 6.03 (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). 13C NMR (500 MHz, CDCl3); δ = 190.2, 156.3, 144.6, 138.9, 131.9, 130.2, 128.5, 127.5, 125.3, 124.1, 124.1, 116.8, 114.4, 91.0, 29.9. HRMS (ESI): m/z [M + H]+ calcd for C15H14N2O2: 279.1134; found: 279.1135.

Ethyl-(E)-4-[(Z)-2-oxo-3-(2-oxo-2-phenylethylidene)-3,4-dihydroquinoxalin-1(2H)-yl]butanoate (3b)

Yield 46%; yellow solid; mp 167–170 °C. 1H NMR (500 MHz, DMSO-d6); δ = 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), 7.24–7.21 (m, 2 H), 7.04 (d, J = 15.9 Hz, 2 H), 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). 13C NMR (125 MHz, DMSO-d6); δ = 188.7, 165.6, 156.0, 145.2, 142.7, 139.1, 132.4, 129.2, 127.7, 127.4, 125.5, 124.5, 122.1, 117.7, 115.7, 90.1, 60.5, 40.5, 14.5. HRMS (ESI): m/z [M + H]+ calcd for C15H14N2O2: 277.1502; found: 277.1502.
(Z)-1-(Cyclohexylmethyl)-3-(2-oxo-2-phenylethylidene)-3,4-dihydroquinoxalin-2(1H)-one (3af)
Yield 65%; colorless oily liquid. 1H NMR (500 MHz, DMSO-d6): 6 = 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). 13C NMR (125 MHz, DMSO-d6): 6 = 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, 90.8, 48.0, 36.2, 30.6, 26.3, 25.8. HRMS (ESI): m/z [M + H]+ calcd for C17H12N2O2: 293.1288; found: 293.1288.

(1)-Methyl-3-(2-oxo-2-phenylethylidene)-3,4-dihydroquinazolin-2(1H)-one (3am)
Yield 73%; yellow solid; mp 186–190 °C. 1H NMR (500 MHz, DMSO-d6): 6 = 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). 13C NMR (125 MHz, DMSO-d6): 6 = 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, 111.2, 91.3, 30.4. HRMS (ESI): m/z [M + H]+ calcd for C19H14N4O2: 329.1290; found: 329.1285.

(1)-6,7-Dibromo-1-methyl-3-(2-oxo-2-phenylethylidene)-3,4-dihydroquinazolin-2(1H)-one (3an)
Yield 51%; yellow solid. 1H NMR (500 MHz, DMSO-d6): 6 = 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). 13C NMR (125 MHz, DMSO-d6): 6 = 188.9, 155.6, 143.0, 137.7, 129.2, 127.1, 126.4, 126.2, 125.0, 124.7, 124.6, 116.7, 116.0, 90.4, 46.1. HRMS (ESI): m/z [M + H]+ calcd for C17H12N2O2: 351.1345; found: 355.1446.

(1)-6,7-Difluoro-1-methyl-3-(2-oxo-2-phenylethylidene)-3,4-dihydroquinazolin-2(1H)-one (3al)
Yield 74%; yellow solid; mp 286–288 °C. 1H NMR (500 MHz, CDCl3): 6 = 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). 13C NMR (125 MHz, CDCl3): 6 = 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 C19H14N2F2O2: 315.0945; found: 315.0940.

(1)-[2-(Hydroxyphenyl)-3,4-dihydroquinoxalin-2(1H)-one]-1-methyl-3,4-dihydroquinazolin-2(1H)-one (3ba)
Yield 57%; yellow solid; mp 207–209 °C. 1H NMR (400 MHz, DMSO-d6): 6 = 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). 13C NMR (101 MHz, DMSO-d6): 6 = 188.9, 167.4, 156.2, 146.1, 139.1, 132.4, 129.7, 127.5, 124.6, 124.5, 117.4, 111.5, 93.9, 30.2, 20.5. HRMS (ESI): m/z [M + H]+ calcd for C19H14N2O2Br: 434.9344; found: 434.9349.
(Z)-3-[2-(4-Chlorophenyl)-2-oxoethylidene]-1-methyl-3,4-dihydroquinoxalin-2(1H)-one (3bf)

Yield 78%; yellow solid; mp 217–218 °C. 1H NMR (400 MHz, CDCl3): δ = 8.40–8.38 (m, 2 H), 7.98–7.78 (m, 4 H), 7.49–7.47 (m, 1 H), 7.37–7.34 (m, 1 H), 7.29 (d, J = 8.4 Hz, 2 H), 7.27 (s, 1 H), 5.98 (s, 2 H). 13C NMR (100 MHz, CDCl3): δ = 154.2, 144.0, 133.1, 131.4, 130.0, 128.9, 128.7, 127.5, 126.8, 126.7, 125.0, 124.7, 124.5, 117.4, 115.6, 94.5, 30.2. HRMS (ESI): m/z [M + H]+ calcd for C17H12ClN2O: 309.0923; found: 309.126, 309.128.

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

Yield 77%; yellow solid; mp 164–165 °C. 1H NMR (400 MHz, CDCl3): δ = 8.88–8.79 (m, 2 H), 7.98 (d, J = 6.8 Hz, 1 H), 7.43–7.36 (m, 4 H), 7.35 (d, J = 7.7 Hz, 1 H), 7.28–7.21 (m, 2 H), 6.32 (s, 1 H), 3.58 (s, 3 H). 13C NMR (125 MHz, CDCl3): δ = 150.2, 147.4, 133.0, 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]+ calcd for C17H12BrN2O: 369.0976; found: 369.0967.

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

Yield 66%; yellow solid; mp 164–165 °C. 1H NMR (400 MHz, CDCl3): δ = 8.60–8.52 (m, 2 H), 7.89 (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). 13C NMR (100 MHz, CDCl3): δ = 154.8, 154.3, 150.7, 131.6, 133.4, 132.9, 132.3, 130.6, 130.4, 130.3, 129.7, 129.1, 128.7, 128.3, 128.2, 114.8, 46.2. HRMS (ESI): m/z [M + H]+ calcd for C17H14N2O: 297.1039; found: 297.1041.

1-(2-Oxo-2-phenylethyl)-3-phenylquinoxalin-2(1H)-one (4af)

Yield 32%; white solid. 1H NMR (400 MHz, CDCl3): δ = 8.83–8.37 (m, 3 H), 7.47–7.45 (m, 2 H), 7.35–7.25 (m, 3 H), 7.05 (d, J = 8.0 Hz, 1 H), 6.78 (s, 1 H), 5.82 (s, 2 H). 13C NMR (125 MHz, CDCl3): δ = 151.9, 151.1, 136.1, 133.4, 132.9, 132.3, 130.6, 130.4, 130.3, 129.7, 129.0, 128.1, 127.7, 127.0, 123.1, 112.8, 108.1, 106.1, 44.1, 30.6. HRMS (ESI): m/z [M + H]+ calcd for C17H15N2O: 295.1113; found: 295.1114.
7.42 (s, 1 H), 3.72 (s, 3 H). 13C NMR (100 MHz, CDCl3): \( \delta = 155.2, 154.1, 135.4, 134.3, 132.7, 132.2, 131.1, 130.9, 130.0, 128.2, 115.1, 29.6. \) HRMS (ESI): \( m/z \) [M + H]\(^+\) calcd for C\(_{13}\)H\(_{10}\)Cl\(_2\)N\(_2\)O: 306.1660; found: 306.1661.

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

Yield 70%; yellow solid; mp 162–164 °C. 1H NMR (400 MHz, CDCl3): \( \delta = 8.45 \) (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). 13C NMR (100 MHz, CDCl3): \( \delta = 154.8, 154.7, 136.1, 133.8, 132.5, 132.0, 130.5, 129.9, 129.7, 129.7, 128.5, 128.1, 127.9, 127.2, 125.3, 109.8, 29.3. \) HRMS (ESI): \( m/z \) [M + H]\(^+\) calcd for C\(_{19}\)H\(_{14}\)N\(_2\)O: 287.3420; found: 287.3421.