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Silver-Catalyzed Radical Tandem Cyclization: An Approach to Direct Synthesis of 3-Acyl-4-arylquinolin-2(1*H*)-ones

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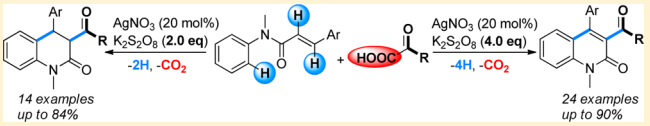
Supporting Information

ABSTRACT: A silver-catalyzed efficient and practical synthesis of 3-acyl-4-arylquinolin-2(1*H*)-ones or 3-acyl-4-aryldihydroquinolin-2(1*H*)-ones through intermolecular radical addition/cyclization in aqueous solution is reported. This method provides a novel, highly efficient, and straightforward route to substituted quinolin-2-ones or 3,4-dihydroquinolin-2-ones in one step. A possible mechanism for the formation of quinolin-2-ones is proposed.



INTRODUCTION

The skeletons of quinolin-2(1*H*)-one and dihydroquinolin-2(1*H*)-one are outstanding structural motifs found in many natural products and pharmaceutically active compounds (Figure 1).[1] Functionalized quinolin-2(1*H*)-ones have been synthesized as potential HIV-1 integrase inhibitors and anticancer and antihypertensive agents in the past few years.[1,2] Many efforts have been made toward the synthesis of quinolin-2(1*H*)-one derivatives; however, most of the synthetic routes provide monosubstituted quinolin-2(1*H*)-ones.[3] A highly efficient and straightforward method to construct 3,4-disubstituted quinolin-2(1*H*)-ones in one step is still a challenging issue.

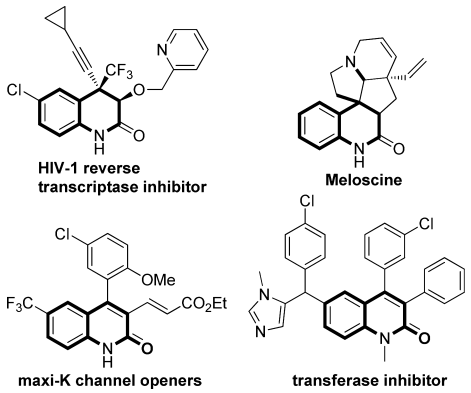


Figure 1. Some representative compounds containing the dihydroquinolin-2(1*H*)-one or quinolin-2(1*H*)-one structure.

The previous strategy relies on constructing 3- or 4-substituted quinolin-2(1*H*)-ones via intramolecular cyclization in the first step and then introducing another group into the 4- or 3-position of quinolin-2(1*H*)-ones by coupling reactions in the second step.[3a−d,g,h] In comparison to this strategy, Larock et al. developed the synthesis of 3,4-disubstituted quinolin-2(1*H*)-ones in one step via Pd-catalyzed carbonylative annulation of internal alkyne in 2004.[4a] In 2010, Tsuji exploited Ir-catalyzed annulation of *N*-arylcarbamoyl chlorides with internal alkynes to afford 3,4-disubstituted 2-quinolones.[4b] Li's group also achieved the similar results through Pd-catalyzed intra- or intermolecular carbocyclizations.[4c−e] In the previous elegant studies, internal alkyne is necessary to generate the 3,4-disubstituted quinolin-2(1*H*)-ones in one step. Other routes toward 3,4-disubstituted quinolin-2(1*H*)-ones via the Friedländer reaction have also been reported.[5] To date, radical reactions have been extensively used in organic synthesis in which radical tandem reactions for the synthesis of heterocycles have received significant attention.[6] Decarboxylative couplings of carboxylic acids[7] with another agent via radical processes have been reported by Kochi,[8a,b] Minisci,[8c,d] Li,[8e,g] and other groups.[8h,i] Recently, we just reported silver-catalyzed radical tandem cyclization for the synthesis of 3,4-disubstituted dihydroquinolin-2(1*H*)-ones using alkyl acids as the source of the radicals.[9] Here, as its extension, employing ketoacids as radical source, we describe our development of a new strategy for the synthesis of 3-acyl-4-arylquinolin-2(1*H*)-ones or 3-acyl-4-aryldihydroquinolin-2(1*H*)-ones in one step through tandem radical reactions (Scheme 1).

RESULTS AND DISCUSSION

Our investigation started with treating *N*-methyl-*N*-phenylcinnamamide (**1a**) and 2-oxo-2-phenylacetic acid (**2a**) under an Ag−$K_2S_2O_8$ system for screening the optimal reaction conditions.[10] To our delight, acyl radical induced by Ag(I) in the system could attack the α-position of **1a**, providing dihydroquinolin-2(1*H*)-one **3a** in 62% yield (Table 1, entry 1). However, when the loading of the oxidant was increased, the yield of product **3a** was decreased and other unexpected product quinolin-2(1*H*)-one **4a** was observed (Table 1, entry

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Scheme 1. Radical Cyclization toward Substituted Quinoline-2-one Derivatives

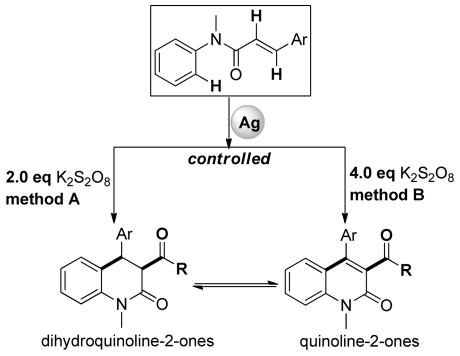
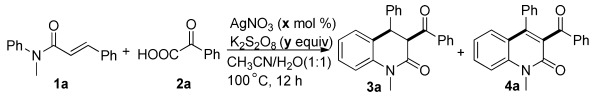


Table 1. Screening of Reaction Conditions[a]



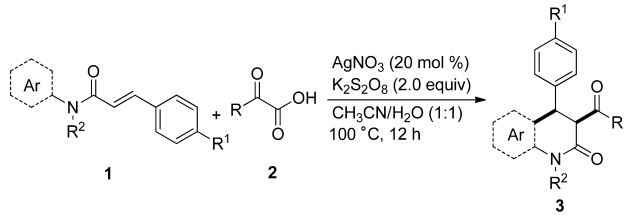
entry	$AgNO_3$ (x mol %)	$K_2S_2O_8$ (y equiv)	yield of **3a**[b] (%)	yield of **4a**[b] (%)
1	10	2.0	62	n.d.
2	10	3.0	13	40
3	10	4.0	trace	58
4	20	1.0	70	n.d.
5	20	2.0	79	n.d.
6	20	2.5	68	trace
7	20	3.0	18	62
8	20	3.5	trace	79
9	20	4.0	n.d.	83
10	20	4.5	n.d.	78
11	30	4.0	n.d.	81
12[c]	20	4.0	n.d.	75
13[d]	20	4.0	n.d.	n.d.
14[e]	20	4.0	n.d.	n.d.
15[f]	20	4.0	n.d.	74
16[g]	20	4.0	n.d.	70
17[h]	20	0	n.d.	n.d.
18[i]	0	4.0	n.d	n.d

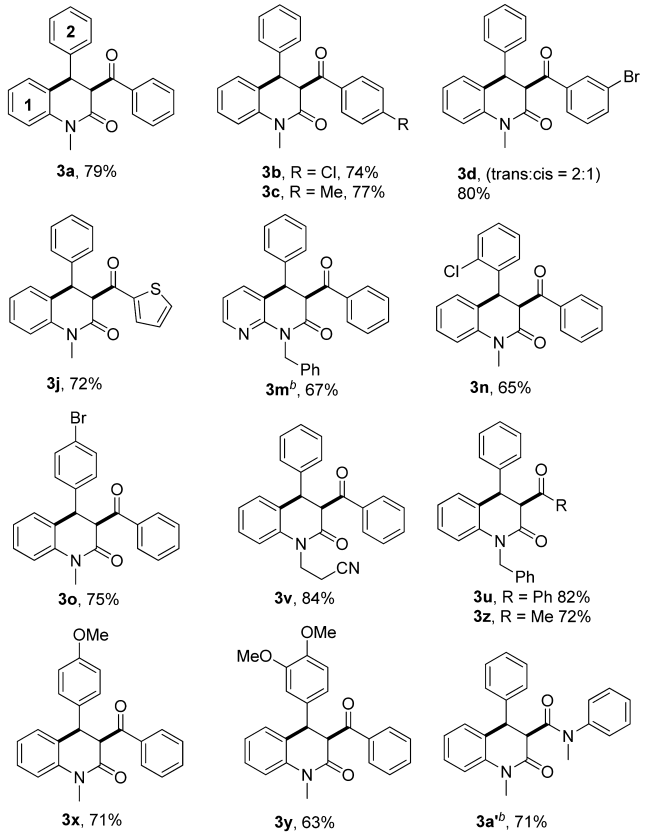
[a]Reaction conditions: **1a** (1.0 mmol), **2a** (1.0 mmol), CH_3CN/H_2O (3/3 mL), under air atmosphere, 12 h, 100 °C. [b]Isolated yield. [c]$(NH_4)_2S_2O_8$ as oxidant. [d]Oxone as oxidant. [e]DTBP as oxidant. [f]$AgBF_4$ as catalyst. [g]Ag_2O as catalyst. [h]Without catalyst. [i]Without oxidant.

2). Then a series of reaction conditions were examined. As shown in Table 1, product **3a** was obtained in 70% yield with 20 mol % of $AgNO_3$ as catalyst and 1.0 equiv of $K_2S_2O_8$ as oxidant (Table 1, entry 4). Compared with entry 4, the yield of product **3a** could be improved to 79% when 2.0 equiv of $K_2S_2O_8$ was used, but product **4a** was not detected (Table 1, entry 5). Products **3a** and **4a** were both obtained when the amount of $K_2S_2O_8$ was increased to 3.0 equiv (Table 1, entry 7). The reaction worked with 4.0 equiv of $K_2S_2O_8$ to afford product **4a** in 83% yield without any product **3a** (Table 1, entry 9). Notably, increasing the amount of $K_2S_2O_8$ made the product **3a** reduced; meanwhile, product **4a** was increased (Table 1, entries 5−9). Moreover, when the $K_2S_2O_8$ was loaded less than 2.0 equiv or more than 4.0 equiv, the reaction lead to the clean formation of product **3a** or **4a**, respectively (Table 1, entries 1, 3, and 9−11). Subsequently, we investigated different oxidants, such as $(NH_4)_2S_2O_8$, Oxone, and DTBP, and the results indicated that $K_2S_2O_8$ was the best choice (Table 1, entries 12−14). Switching the catalyst from $AgNO_3$ to $AgBF_4$ or Ag_2O did not show much difference (Table 1, entries 15 and 16). Note that the reaction failed to provide any of the products in the absence of catalyst or oxidant (Table 1, entries 17 and 18).

With this novel process in hand, our attention turned to the full exploitation of the radical tandem cyclization. First, the scope of α-oxocarboxylic acids was investigated under method A (Table 2). As shown in Table 2, many 3,4-dihydroquinolin-

Table 2. Silver-Catalyzed Radical Cyclization toward 3-Acyl-4-aryldihydroquinolin-2(1*H*)-ones[a]





[a]Reaction conditions: **1** (1.0 mmol), **2** (1.0 mmol), $AgNO_3$ (20 mol %), $K_2S_2O_8$ (2.0 mmol), CH_3CN (3 mL), H_2O (3 mL), 100 °C, 12 h. [b]Using 4.0 mmol of $K_2S_2O_8$ as oxidant.

2(1*H*)-ones could be cleanly obtained using method A (Scheme 1). Me, Cl, Br, Bz, thiophene, and pyridine substituents in substrates **1** or **2** were compatible under the conditions of method A. Electron-withdrawing and -donating substituted groups, such as *o*-Cl, *p*-Br, *p*-OMe, and 3,4-diOMe on the phenyl ring (**2**) of cinnamic acid, do not influence the reactivity remarkably, and products could be obtained in moderate yields (Table 2, **3n−o,x,y**). Furthermore, 2-

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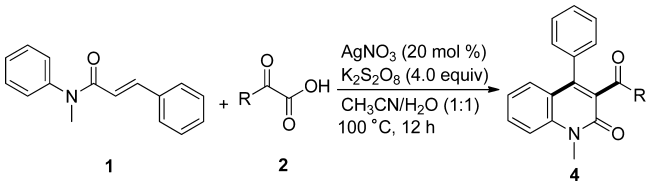
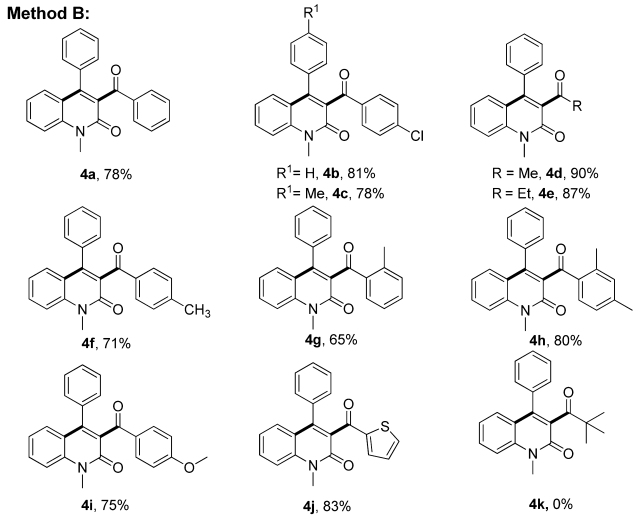
oxopropanoic acid could also undergo the transformation successfully and gave the final product **3z** in 72% yield. For the product **3m**, the reaction is sluggish under method A, and a small amount of product was observed, but the 67% product yield was obtained when the $K_2S_2O_8$ was increased to 4.0 equiv. The reason may be that the electron deficiency of the pyridine ring makes it trap the radical with difficulty. Likewise, the 2-(methyl(phenyl)amino)-2-oxoacetic acid was also an exception and transferred into the final product **3a′** needing 4.0 equiv of oxidant (Table 2, **3a′**). The reason for this may be the low efficiency of its decarboxylation in comparison with other 2-oxoacetic acids.

We next sought to establish the formation of the corresponding quinolin-2(1*H*)-ones using method B. As shown in Table 3, *N*-methyl-*N*-phenylcinnamamide could

Table 3. Silver-Catalyzed Radical Cyclization toward 3-Acyl-4-arylquinolin-2(1*H*)-ones[a]



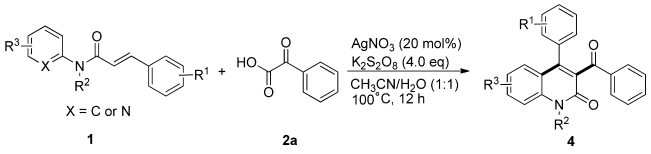


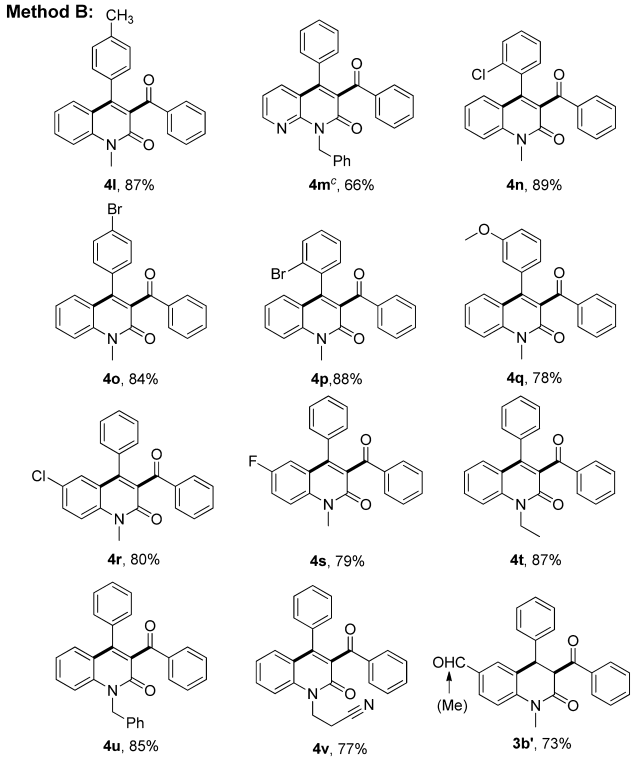
[a]Reaction conditions: **1** (1.0 mmol), **2** (1.0 mmol), $AgNO_3$ (20 mol %), $K_2S_2O_8$ (4.0 mmol), CH_3CN (3 mL), H_2O (3 mL), 100 °C, 12 h.

react with different α-oxocarboxylic acids, and the products **4a−j** were obtained in good to high yields (Table 3). For example, 2-oxo-2-phenylacetic acid with *p*-methyl, *o*-methyl, and 2,4-dimethyl groups could be converted to the desired products in good yields (**4f−h**). Regardless of the electron-withdrawing group (*p*-Cl) or electron-donating group (*p*-MeO) on the 2-oxo-2-phenylacetic acid, the reaction still proceeded smoothly, producing the corresponding products (**4b,c,i**) in good yields (75−81%). The strong electron-withdrawing group, for example, NO_2, influenced the efficiency of the reaction, and no product was obtained. We were pleased to find that 2-oxo-2-(thiophene-2-yl) acetic acid was still tolerated under the oxidative conditions, and product **4j** was obtained in 83% yield. It is noteworthy that aliphatic α-oxocarboxylic acids, such as 2-oxopropanoic acid and 2-oxobutanoic acid, were likewise converted to the expected products in excellent yields (**4d,e**). Unfortunately, the *t*-Bu group was not compatible, which did not lead to the product **4k**, and the *N*-methyl-*N*-phenylcinnamamide was recovered in 73% yield.

Subsequently, we investigated the scope and limitations of *N*-arylcinnamamides in this transformation under the conditions of method B, and the results are presented in Table 4. As

Table 4. Silver-Catalyzed Radical Cyclization of 2a with Different *N*-Arylcinnamamides[a,b]





[a]Reaction conditions: **1** (1.0 mmol), **2a** (1.0 mmol), $AgNO_3$ (20 mol %), $K_2S_2O_8$ (4.0 mmol), CH_3CN (3 mL), H_2O (3 mL), 100 °C, 12 h. [b]Isolated yield. [c]$K_2S_2O_8$ (8.0 mmol), other conditions are the same as for method B.

expected, the radical cyclization toward 3-acyl-4-arylquinolin-2(1*H*)-ones proceeded well for various *N*-arylcinnamamides, such as halogenated, methyl- or methoxy-substituted *N*-methyl-*N*-phenylacrylamide (**4n,l,q−s**). Substituents like F or Cl on aniline at the para position did not influence the transformation, and the desired products were obtained in 80% yields (**4r,s**). To our satisfaction, when the *N*-protected group of the substrate **1** was changed from methyl to ethyl, benzyl, and cyanoethyl, the corresponding quinolin-2(1*H*)-one derivatives were obtained with little difference in yields (**4t−v**). Notably, *N*-pyridylcinnamamide could also undergo the tandem radical cyclization with phenylglyoxylic acid, leading to product **4m** in 66% yield. Interestingly, when *N*-methyl-*N*-*p*-tolylcinnamamide was explored as substrate, the methyl on aniline was oxidized to aldehyde group and the double bond was not formed (**3b′**).

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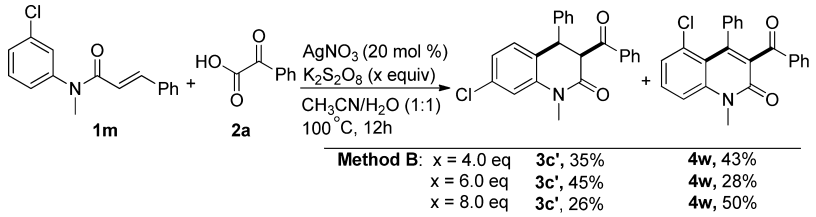
Scheme 2. Investigation into the Chemoselectivity of 1m

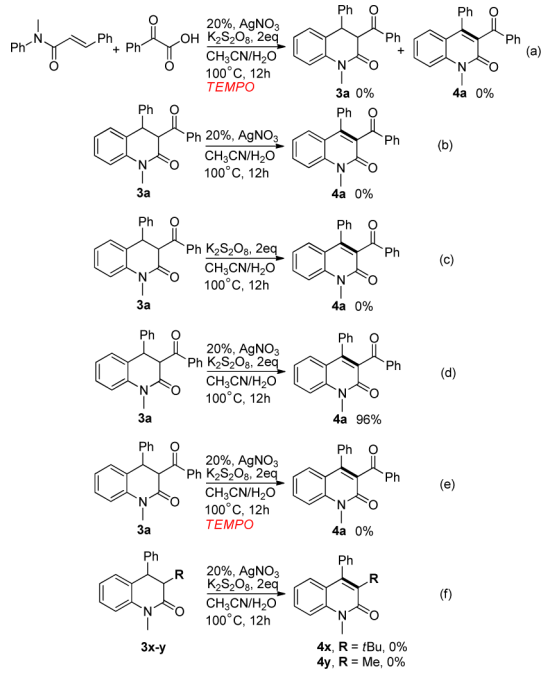


When *N*-(3-chlorophenyl)-*N*-methylcinnamamide was treated with **2a** under the conditions of method B, two chemoselective products **3c′** and **4w** were obtained, respectively (Scheme 2). Interestingly, the reaction of **1m** with **2a** showed little difference in chemoselectivity when the amount of oxidant was increased to 6.0 equiv. Compound **3c′** could not be transferred into quinolin-2(1*H*)-one even when using 8.0 equiv of $K_2S_2O_8$ was used as oxidant. The reason for this is not clear at present.

The structures of products **4l** and **4o** were confirmed by single-crystal X-ray crystallographic analysis (see the Supporting Information).[11]

To gain insight into the mechanism of this novel reaction, some control experiments were performed (Scheme 3). The

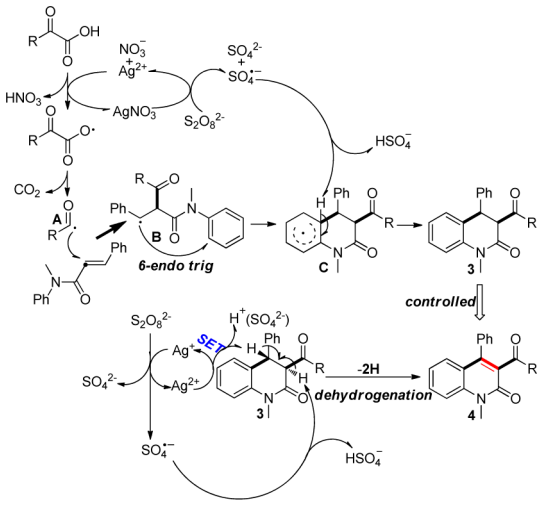
Scheme 3. Investigation into the Reaction Mechanism



reaction was completely shut off when 1.0 equiv of TEMPO was added, indicating that a radical intermediate was involved in this transformation (Scheme 3a). Notably, product **3a** could not be transformed into product **4a** in the absence of catalyst or oxidant (Scheme 3b,c). Gratifyingly, with 20 mol % of $AgNO_3$ as catalyst and 2.0 equiv of $K_2S_2O_8$ as oxidant, **3a** could be converted to **4a** completely, which showed that both the catalyst and oxidant played important roles in this transformation (Scheme 3d). The reaction of Scheme 3e clearly demonstrated the dehydrogenated process of **3a** to **4a** was also initiated by a radical. The result of Scheme 3f indicated that the acyl group was very important in the dehydrogenated process toward the final product.

On the basis of the above results, a plausible catalytic cycle is presented in Scheme 4. First, Ag^{2+}, which was generated from

Scheme 4. Proposed Catalytic Cycle



Ag^+, abstracted a single electron from carboxylate to produce the carboxyl radical, and the latter was quickly decarboxylated to produce acyl radical **A**.[8,12] The radical **A** was trapped by the *α*-position of the *N*-methyl-*N*-phenylcinnamamide to generate intermediate **B**. Then **B** underwent intramolecular cyclization to afford intermediate **C**. Finally, sulfate radical anion abstracted a hydrogen from **C**, delivering the product **3**. The redundant persulfate anion disproportionated into sulfate dianion and sulfate radical anion with the help of Ag^+.[12] Sulfate radical anion abstracted the hydrogen on the 3-position of product **3** to trigger the process of dehydrogenation, leading to the final product **4**.

CONCLUSION

In summary, we have developed an interesting new approach to the synthesis of 3-acyl-4-aryldihydroquinolin-2(1*H*)-one or 3-acyl-4-arylquinolin-2(1*H*)-ones, which may be of great importance as biologically attractive molecules through radical tandem cyclization. Two types of products could be controlled and obtained only by adjusting the amount of oxidant. This reaction catalyzed by silver in aqueous solution includes decarboxylation, cyclization, and dehydrogention processes in one step, which make the method green and atom-economic. In view of the broad interest in quinolin-2(1*H*)-one derivatives, this novel one-pot procedure could prove useful in synthetic and medicinal chemistry. Further studies on this transformation are ongoing in our laboratory.

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EXPERIMENTAL SECTION

General Methods. All experiments were carried out using a common flask in air. Cinnamic acids, thionyl chloride, aromatic secondary amines, and benzoylformic acids were purchased from commercial suppliers and used as received unless otherwise noted. All solvents and other commercially available reagents were purchased from suppliers and used directly. Reactions were monitored by thin-layer chromatography (TLC). Products were detected using a UV/vis lamp. Column chromatography was performed on silica gel. The ^{1}H and ^{13}C NMR spectra were obtained on 400 MHz NMR. ^{1}H NMR data are reported as chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C NMR data are reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). The spectra are referenced against the internal solvent ($CDCl_3$, δ ^{1}H = 7.26 ppm, ^{13}C = 77.0 ppm; DMSO-d_6, δ ^{1}H = 2.50 ppm, ^{13}C = 40.0 ppm). Data are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet. High-resolution mass spectra (HR-MS) were obtained on Q-TOF using the ESI technique.

General Procedure for the Synthesis of Substrate 1. A 50 mL anhydrous flask was charged with a magnetic stir bar, cinnamic acid (5 mmol, 0.74g), and $SOCl_2$ (5 mL). After the mixture was stirred at 60 °C for 3 h, the redundant $SOCl_2$ was evaporated under reduced pressure and then the liquid was dropwise added into another flask containing *N*-methylaniline (10 mmol, 1.07g) dissolved in anhydrous CH_2Cl_2 (20 mL). The mixture was stirred for 1 h at room temperature. The organic phase was then washed with HCl aqueous solution and K_2CO_3 aqueous solution and then dried with anhydrous Na_2SO_4. After evaporation of the CH_2Cl_2, the *N*-methyl-*N*-phenyl-cinnamamide was obtained in 97% yield and used in the next step directly.

Typical Experimental Procedure for Products 3. Compounds **1**(1.0 mmol) and **2** (1.0 mmol), $AgNO_3$ (34 mg, 0.2 mmol), $K_2S_2O_8$ (540 mg, 2.0 mmol), and a stir bar were added to 50 mL tube, and then CH_3CN (3 mL) and H_2O (3 mL) were added. The mixture was allowed to stir at 100 °C for 12 h (monitored by TLC). The solution was then diluted with ethyl acetate (20 mL), washed with a solution of K_2CO_3 and water, and then dried with anhydrous Na_2SO_4. The crude mixture was purified by colum chromatography on silica gel (petroleum ether/ethyl acetate = 15:1−6:1) to give the products **3a−d,j,m−o,u−z,a′**.

*3-Benzoyl-1-methyl-4-phenyl-3,4-dihydroquinolin-2(1H)-one (**3a**):* white solid (270 mg, 79%); mp 154−156 °C; R_f = 0.45 (petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 7.2 Hz, 2H), 7.57 (t, J = 7.6 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.29−7.36 (m, 3H), 7.17−7.26 (m, 3H), 7.13 (d, J = 8.0 Hz, 1H), 7.03 (td, J = 7.6, 0.8 Hz, 1H), 6.88 (d, J = 7.6 Hz, 1H), 4.97 (d, J = 7.6 Hz, 1H), 4.74 (d, J = 7.6 Hz, 1H), 3.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 166.7, 140.0, 139.5, 136.6, 133.3, 129.0, 128.71, 128.67, 128.65, 128.2, 128.1, 127.43, 127.36, 123.5, 114.9, 55.8, 44.9, 30.0; FT-IR ν/cm^{-1} (KBr) 1697, 1662, 1597, 1373, 756; HRMS (ESI) calcd for $C_{23}H_{20}NO_2$ $[M + H]^+$ 342.1494, found 342.1491.

*3-(4-Chlorobenzoyl)-1-methyl-4-phenyl-3,4-dihydroquinolin-2(1H)-one (**3b**):* pale yellow solid (278 mg, 74%); mp 133−136 °C; R_f = 0.50 (petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.23−7.36 (m, 4H), 7.19 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.0 Hz, 1H), 7.03 (td, J = 7.6, 0.8 Hz, 1H), 6.88 (d, J = 7.2 Hz, 1H), 4.90 (d, J = 8.4 Hz, 1H), 4.75 (d, J = 8.4 Hz, 1H), 3.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 166.5, 139.9, 139.8, 139.3, 135.2, 130.1, 129.1, 129.0, 128.6, 128.2, 127.5, 123.6, 114.9, 55.7, 44.7, 30.0; FT-IR ν/cm^{-1} (KBr) 1685, 1662, 1597, 1466, 1377, 760; HRMS (ESI) calcd for $C_{23}H_{19}ClNO_2$ $[M + H]^+$ 376.1104, found 376.1109.

*1-Methyl-3-(4-methylbenzoyl)-4-phenyl-3,4-dihydroquinolin-2(1H)-one (**3c**):* white solid (274 mg, 77%); mp 136−139 °C; R_f = 0.50 (petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.4 Hz, 2H), 7.18−7.35 (m, overlapping $CDCl_3$, 8H), 7.13 (d, J = 8.0 Hz, 1H), 6.99−7.11 (m, 1H), 6.92 (d, J = 7.2 Hz, 1H), 4.94 (d, J = 7.2 Hz, 1H), 4.73 (d, J = 7.2 Hz, 1H), 3.47 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 166.8, 144.3, 140.2, 139.6, 134.0, 129.4, 129.0, 128.9, 128.7, 128.1, 128.0, 127.39, 127.35, 123.5, 114.9, 55.8, 44.9, 30.0, 21.7; FT-IR ν/cm^{-1} (KBr) 1689, 1658, 1597, 1373, 752; HRMS (ESI) calcd for $C_{24}H_{22}NO_2$ $[M + H]^+$ 356.1651, found 356.1658.

*3-(3-Bromobenzoyl)-1-methyl-4-phenyl-3,4-dihydroquinolin-2(1H)-one (**3d**):* white solid (336 mg, 80%); mp 158−160 °C; R_f = 0.65 (petroleum ether/ethyl acetate = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) (main product) δ 8.01 (t, J = 1.6 Hz, 1H), 7.82−7.86 (m, 1H), 7.68 (dt, J = 8.0, 0.8 Hz, 1H), 7.21−7.41 (m, 5H), 7.21 (d, J = 7.2 Hz, 2H), 7.13 (d, J = 7.6 Hz, 1H), 7.03 (td, J = 7.6, 0.8 Hz, 1H), 6.85 (d, J = 7.6 Hz, 1H), 4.90 (dd, J = 9.2, 2.8 Hz, 1H), 4.74 (d, J = 8.4 Hz, 1H), 3.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 166.5, 139.6, 139.3, 138.7, 136.1, 133.2, 131.6, 130.2, 129.9, 128.7, 128.6, 128.3, 128.2, 127.6, 127.2, 126.8, 123.6, 123.0, 115.0, 55.6, 44.6, 30.0; FT-IR ν/cm^{-1} (KBr) 1685, 1651, 1593, 1454, 1365, 760, 702; HRMS (ESI) calcd for $C_{23}H_{19}BrNO_2$ $[M + H]^+$ 420.0599, found 420.0605.

*1-Methyl-4-phenyl-3-(thiophene-2-carbonyl)-3,4-dihydroquinolin-2(1H)-one (**3j**):* pale yellow solid (250 mg, 72%); mp 166−169 °C; R_f = 0.13 (petroleum ether/ethyl acetate = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, J = 3.6, 1.2 Hz, 1H), 7.65 (dd, J = 4.8, 1.2 Hz, 1H), 7.29−7.36 (m, 3H), 7.21−7.27 (m, 1H), 7.19−7.21 (m, 2H), 7.11−7.14 (m, 2H), 7.04 (td, J = 7.6, 0.8 Hz, 1H), 6.94 (d, J = 7.2 Hz, 1H), 4.73−4.78 (m, 2H), 3.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.7, 166.0, 143.7, 140.0, 139.4, 134.7, 133.5, 129.1, 128.7, 128.3, 128.2, 128.14 127.5, 127.4, 123.6, 115.0, 57.5, 45.0, 30.1; FT-IR ν/cm^{-1} (KBr) 1651, 1597, 1458, 1412, 1365, 1308, 752, 741, 702; HRMS (ESI) calcd for $C_{21}H_{18}NO_2S$ $[M + H]^+$ 348.1058, found 348.1064.

*3-Benzoyl-1-benzyl-4-phenyl-3,4-dihydro-1,8-naphthyridin-2(1H)-one (**3m**):* pale yellow solid (280 mg, 67%): mp 155−158 °C; R_f = 0.54 (petroleum ether/ethyl acetate = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (dd, J = 4.8 Hz, 1.2 Hz, 1H), 7.96 (d, J = 8.0 Hz, 2H), 7.60 (t, J = 7.2 Hz, 1H), 7.48 (q, J = 6.8 Hz, 4H), 7.27−7.29 (m, overlapping $CDCl_3$, 4H), 7.23−7.25 (m, 5H), 7.07−7.10 (m, 2H), 6.95 (dd, J = 7.2 Hz, J = 4.8 Hz, 1H), 5.53 (dd, J = 19.2 Hz, 14.4 Hz, 2H), 5.02 (d, J = 7.6 Hz, 1H), 4.70 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 166.7, 150.6, 146.7, 139.5, 137.7, 136.8, 136.3, 133.6, 129.2, 128.9, 128.7, 128.6, 128.2, 128.0, 127.7, 127.1, 122.6, 119.1, 55.9, 44.1, 43.6; FT-IR ν/cm^{-1} (KBr) 1689, 1666, 1585, 1442, 1377, 1319, 1211, 733, 690; HRMS (ESI) calcd for $C_{28}H_{23}N_2O_2$ $[M + H]^+$ 419.1760, found 419.1762.

*3-Benzoyl-4-(2-chlorophenyl)-1-methyl-3,4-dihydroquinolin-2(1H)-one (**3n**):* white solid (244 mg, 65%); mp 130−132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.032 (dt, J = 7.2 Hz, 1.6 Hz, 2H), 7.60−7.56 (m, 1H), 7.48−7.43 (m, 3H), 7.39 (td, J = 8.4 Hz, 1.2 Hz, 1H), 7.23(td, J = 7.6 Hz, 2.0 Hz, 1H), 7.16−7.12 (m, 2H), 7.09 (td, J = 7.6 Hz, 1.2 Hz, 1H),6.94−6.89 (m, 2H), 5.21 (d, J = 6.8 Hz, 1H), 5.06 (d, J = 6.8 Hz, 1H), 3.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 166.1, 139.8, 137.3, 136.6, 134.0, 133.5, 130.3, 129.4, 129.1, 128.8, 128.6, 128.4, 128.4, 127.5, 126.4, 123.9, 115.1, 54.5, 41.6, 30.1; FT-IR ν/cm^{-1} (KBr) 1689, 1670, 1601, 1458, 1354, 760; HRMS (ESI) calcd for $C_{23}H_{18}ClNO_2$[M + H]$^+$ 376.1104, found 376.1100.

*3-Benzoyl-4-(4-bromophenyl)-1-methyl-3,4-dihydroquinolin-2(1H)-one (**3o**):* yellow solid (315 mg, 75%); mp 208−210 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dt, J = 5.2 Hz, 1.2 Hz, 2H), 7.60−7.56 (m, 1H), 7.48−7.42 (m, 4H), 7.37 (t, J = 7.6 Hz, 0.8 Hz, 1H), 7.13−7.01(m, 4H), 6.86 (d, J = 7.6 Hz, 1H), 4.92 (d, J = 8.8 Hz, 1H), 4.74 (d, J = 8.8 Hz, 1H), 3.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 166.5, 139.4, 139.0, 136.7, 133.5, 132.2, 129.9, 128.7, 128.5, 128.4, 127.0, 123.6, 121.4, 115.0, 55.4, 44.2, 30.0; FT-IR ν/cm^{-1} (KBr) 1693,1666, 1597, 1373; HRMS (ESI) calcd for $C_{23}H_{18}BrNO_2$ $[M + H]^+$ 420.0599, found 420.0591.

*3-(3-Benzoyl-2-oxo-4-phenyl-3,4-dihydroquinolin-1(2H)-yl)-propanenitrile (**3v**):* white solid (320 mg, 84%); mp 158−160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.0 Hz, 2H), 7.63 (t, J = 7.2 Hz, 1H), 7.51 (t, J = 8.0 Hz, 2H), 7.41−7.27 (m, 4H), 7.19(t, J = 8.8 Hz, 3H), 7.09 (t, J = 8.0 Hz, 0.8 Hz, 1H), 6.98 (d, J = 7.2 Hz, 1H), 4.97 (d, J = 6.0 Hz, 1H), 4.70 (d, J = 6.4 Hz, 1H), 4.40−4.27 (m, 2H), 2.85−2.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 166.9, 139.7, 137.8, 135.9, 133.7, 129.7, 129.2, 128.9, 128.70, 128.65, 127.8, 127.7, 126.9, 124.3, 117.4, 114.4, 56.2, 45.0, 39.0, 15.9; FT-IR ν/cm^{-1}

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(KBr) 1689, 1670, 1597, 1458, 1385, 760, 702; HRMS (ESI) calcd for $C_{25}H_{21}N_2O_2$ $[M + H]^+$ 381.1603, found 381.1608.

3-Benzoyl-1-benzyl-4-phenyl-3,4-dihydroquinolin-2(1H)-one (**3u**): white solid (342 mg, 82%); mp 116−118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 0.8 Hz, 2H), 7.99 (t, J = 2.0 Hz, 1H), 7.63−7.50 (m, 3H), 7.49−7.27 (m, 6H), 7.26−7.20(m, 2H), 7.19 (d, J = 5.6 Hz, 3H), 7.04−6.97 (m, 3H), 5.44 (d, J = 16.0 Hz, 1H), 5.15 (d, J = 16.4 Hz, 1H), 5.08 (d, J = 16.4 Hz, 1H), 4.73(d, J = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 166.7, 140.4, 139.0, 136.6, 136.1, 133.6, 129.1, 129.1, 128.84, 128.80, 128.7, 128.6, 128.5, 128.3, 127.8, 127.5, 127.2, 126.79, 126.75, 126.7, 126.6, 123.7, 116.0, 56.8, 46.7, 45.2; FT-IR ν/cm^{-1} (KBr) 1685, 1666, 1597, 1493, 1458, 1381, 1323, 752, 729, 698; HRMS (ESI) calcd for $C_{29}H_{23}NO_2$ $[M + H]^+$ 418.1807, found 418.1798.

3-Acetyl-1-benzyl-4-phenyl-3,4-dihydroquinolin-2(1H)-one (**3z**): white solid (256 mg, 72%); mp 150−152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.25 (m, overlapping $CDCl_3$, 7H), 7.23−7.17 (m, 2H), 7.13 (dd, J = 7.6 Hz, 1.6 Hz, 2H), 7.04−6.99 (m, 3H), 5.23 (td, J = 18.0 Hz, 4.0 Hz, 2H), 4.74 (d, J = 6.0 Hz, 1H), 4.13 (d, J = 6.4 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.3, 166.5, 139.8, 138.5, 136.5, 129.2, 129.0, 128.8, 128.2, 127.9, 127.43, 127.35, 127.2, 126.82, 126.75, 126.4, 123.9, 115.9, 62.1, 46.5, 43.6, 29.5; FT-IR ν/cm^{-1} (KBr) 1720, 1666, 1597, 1493, 1458, 1381, 756, 694; HRMS (ESI) calcd for $C_{24}H_{21}NO_2$ $[M + H]^+$ 356.1651, found 356.1657.

3-Benzoyl-4-(4-methoxyphenyl)-1-methyl-3,4-dihydroquinolin-2(1H)-one (**3x**): white solid (264 mg, 71%); mp 132−133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dt, J = 5.6 Hz, 1.6 Hz, 2H), 7.59−7.54 (m, 1H), 7.47−7.43 (td, J = 7.2 Hz, 1.6 Hz, 2H), 7.35 (t, J = 1.2 Hz, 1H), 7.13(dd, J = 7.6 Hz, 2.0 Hz, 3H), 7.04 (td, J = 7.6 Hz, 0.8 Hz, 1H), 6.90 (d, J = 7.6 Hz, 1H), 6.85 (dd, J = 6.4 Hz, 2.0 Hz, 2H), 4.93 (d, J = 8.4 Hz, 1H), 4.71 (d, J = 8.0 Hz, 1H), 3.78 (s, 3H), 3.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 166.9, 158.8, 139.5, 136.8, 133.3, 131.9, 129.2, 128.7, 128.7, 128.6, 128.1, 127.9, 123.5, 114.9, 114.4, 55.9, 55.2, 44.1, 29.9; FT-IR ν/cm^{-1} (KBr) 1693,1658, 1597, 1512, 1462, 1373, 1246, 1034, 752; HRMS (ESI) calcd for $C_{24}H_{21}NO_3$ $[M + H]^+$ 372.1600, found 372.1609

3-Benzoyl-4-(3,4-dimethoxyphenyl)-1-methyl-3,4-dihydroquinolin-2(1H)-one (**3y**): white solid (253 mg, 63%); mp 166−167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, J = 7.2 Hz, 1.2 Hz, 2H), 7.58−7.54 (m, 1H), 7.47 (td, J = 7.2 Hz, 1.6 Hz, 2H), 7.36−7.32 (m, 1H), 7.13(d, J = 4.0 Hz, 1H), 7.05 (td, J = 7.2 Hz, 0.8 Hz, 1H), 6.90 (d, J = 7.6 Hz, 1H),6.81−6.69 (m, 3H), 4.96 (d, J = 9.2 Hz, 1H), 4.72 (d, J = 8.8 Hz, 1H), 3.85(s, 3H), 3.77(s, 3H), 3.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 167.1, 149.2, 148.3, 139.4, 137.0, 133.3, 132.1, 128.6, 128.5, 128.1, 123.5, 120.6, 114.9, 111.6, 111.3, 55.8, 55.5, 44.4, 29.9, 29.7; FT-IR ν/cm^{-1} (KBr) 1689, 1662, 1597, 1516, 1458, 1365, 1265, 1142, 1026, 764; HRMS (ESI) calcd for $C_{25}H_{23}NO_4$ $[M + H]^+$ 402.1705, found 402.1712.

N,1-Dimethyl-2-oxo-N,4-diphenyl-1,2,3,4-tetrahydroquinoline-3-carboxamide (**3a′**): sticky pale yellow oil (263 mg, 71%); R_f = 0.27 (petroleum ether/ethyl acetate = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.38 (m, 3H), 7.26−7.33 (m, overlapping $CDCl_3$, 4H), 7.24 (t, J = 8.0 Hz, 1H), 7.07−7.09 (m, 2H), 6.98 (d, J = 8.0 Hz, 2H), 6.90 (t, J = 7.6 Hz, 1H), 6.66 (d, J = 7.6 Hz, 1H), 4.82 (d, J = 13.2 Hz, 1H), 3.85 (d, J = 13.2 Hz, 1H), 3.43 (s, 3H), 3.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 167.2, 143.4, 139.6, 139.1, 129.6, 129.5, 128.6, 128.2, 128.1, 127.9, 127.7, 127.5, 127.5, 123.0, 114.5, 52.2, 45.4, 37.3, 30.0; FT-IR ν/cm^{-1} (KBr) 1677, 1658, 1595, 1519, 1455, 1376, 752; HRMS (ESI) calcd for $C_{24}H_{23}N_2O_2$ $[M + H]^+$ 371.1760, found 371.1764.

Typical Experimental Procedure for Products 4. Compounds **1** (1.0 mmol) and **2** (1.0 mmol), $AgNO_3$ (68 mg, 0.2 mmol), $K_2S_2O_8$ (1.08 g, 4.0 mmol), and a stir bar were added to 50 mL tube, and then CH_3CN (3 mL) and H_2O (3 mL) were added. The mixture was allowed to stir at 100 °C for 12 h (monitored by TLC). The solution was then diluted with ethyl acetate (20 mL), washed with a solution of K_2CO_3 and water, and then dried with anhydrous Na_2SO_4. The crude mixture was purified by colum chromatography on silica gel (petroleum ether/ethyl acetate = 15:1−5:1) to give the product **4a**−**v**.

3-Benzoyl-1-methyl-4-phenylquinolin-2(1H)-one (**4a**): sticky colorless oil (265 mg, 78%); R_f = 0.21 (petroleum ether/ethyl acetate = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 6.8 Hz, 2H), 7.65−7.69 (td, J = 8.4, 1.6 Hz, 1H), 7.46−7.52 (m, 2H), 7.35−7.39 (m, 3H), 7.31−7.33 (m, 3H), 7.24−7.28 (m, overlapping $CDCl_3$, 2H), 7.19−7.23 (m, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 159.9, 148.1, 140.0, 137.0, 133.9, 133.3, 131.5, 131.0, 130.1, 129.3, 129.2, 128.64, 128.60, 128.4, 128.3, 122.4, 120.8, 114.4, 29.6; FT-IR ν/cm^{-1} (KBr) 1676, 1635, 1581, 1458, 1369, 1246, 1086, 815, 751; HRMS (ESI) calcd for $C_{23}H_{18}NO_2$ $[M + H]^+$ 340.1338, found 340.1336.

3-(4-Chlorobenzoyl)-1-methyl-4-phenylquinolin-2(1H)-one (**4b**): pale yellow solid (303 mg, 81%); mp 113−117 °C; R_f = 0.20 (petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dt, J = 8.8 Hz, 2.4 Hz, 2H), 7.70 (t, J = 8.0 Hz, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.31−7.39 (m, 6H), 7.20−7.25 (m, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 159.8, 148.4, 140.1, 139.7, 135.4, 133.8, 131.6, 130.5, 129.2, 128.8, 128.7, 128.4, 122.5, 120.7, 114.5, 29.6; FT-IR ν/cm^{-1} (KBr) 1678, 1635, 1585, 1242, 1092, 868, 748; HRMS (ESI) calcd for $C_{23}H_{17}ClNO_2$ $[M + H]^+$ 374.0948, found 374.0950.

3-(4-Chlorobenzoyl)-1-methyl-4-(p-tolyl)quinolin-2(1H)-one (**4c**): white solid (303 mg, 78%); mp 194−198 °C; R_f = 0.23 (petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dt, J = 8.8 Hz, 2.0 Hz, 2H), 7.69 (t, J = 7.6 Hz, 1H), 7.51 (d, J = 8.4 Hz, 1H), 7.42 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.35 (dt, J = 9.2 Hz, 2.4 Hz, 2H), 7.23 (t, J = 7.6 Hz, 1H), 7.16 (d, J = 8.4 Hz, 4H), 3.82 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.3, 159.8, 148.6, 140.0, 139.6, 138.7, 135.5, 131.6, 130.8, 130.5, 130.4, 129.1, 128.8, 128.7, 122.5, 120.8, 114.4, 29.6, 21.3; FT-IR ν/cm^{-1} (KBr) 1678, 1635, 1581, 1458, 1369, 1315, 1246, 1088, 810, 748; HRMS (ESI) calcd for $C_{24}H_{19}ClNO_2$ $[M + H]^+$ 388.1104, found 388.1106.

3-Acetyl-1-methyl-4-phenylquinolin-2(1H)-one (**4d**): white solid (250 mg, 90%); mp 169−172 °C, R_f = 0.19 (petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (t, J = 8.0 Hz, 1H), 7.51 (td, J = 5.6 Hz, 4.0 Hz, 4H), 7.33 (dt, J = 7.6 Hz, 2.0 Hz, 3H), 7.20 (t, J = 7.6 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.7, 159.4, 146.4, 139.7, 134.2, 133.1, 131.4, 129.2, 128.9, 128.7, 128.6, 122.4, 120.7, 114.3, 31.4, 29.5; FT-IR ν/cm^{-1} (KBr) 1709, 1628, 1458, 1369, 1076, 764, 706; HRMS (ESI) calcd for $C_{18}H_{16}NO_2$ $[M + H]^+$ 278.1181, found 278.1182.

1-Methyl-4-phenyl-3-propionylquinolin-2(1H)-one (**4e**): yellow solid (253 mg, 87%); mp 148−150 °C; R_f = 0.20 (petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (td, J = 8.8 Hz, 1.6 Hz, 1H), 7.45−7.50 (m, 4H), 7.32 (t, J = 1.6 Hz, 3H), 7.20 (t, J = 8.0 Hz, 1H), 3.81 (s, 3H), 2.53 (q, J = 7.2 Hz, 2H), 0.94 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.9, 159.5, 146.2, 139.7, 134.2, 1332, 131.3, 129.3, 128.8, 128.54, 128.48, 122.4, 120.6, 114.3, 37.1, 29.5, 7.4; FT-IR ν/cm^{-1} (KBr) 1712, 1635, 1585, 1454, 1373, 1315, 756, 706; HRMS (ESI) calcd for $C_{19}H_{18}NO_2$ $[M + H]^+$ 292.1338, found 292.1336.

1-Methyl-3-(4-methylbenzoyl)-4-phenylquinolin-2(1H)-one (**4f**): pale yellow solid (251 mg, 71%); mp 217−220 °C; R_f = 0.16 (petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.0 Hz, 2H), 7.68 (t, J = 8.8 Hz, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.38 (dd, J = 8.4 Hz, 1.6 Hz, 1H), 7.33 (t, J = 3.2 Hz, 3H), 7.26−7.28 (m, overlapping $CDCl_3$, 3H), 7.20 (t, J = 7.6 Hz, 1H), 7.16 (d, J = 8.0 Hz, 2H), 3.83 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 159.9, 147.8, 144.2, 140.0, 134.6, 134.0, 131.4, 131.2, 129.3, 129.2, 128.6, 128.3, 122.4, 120.8, 114.4, 29.6, 21.7; FT-IR ν/cm^{-1} (KBr) 1670, 1639, 1597, 1458, 1365, 1319, 1250, 752; HRMS (ESI) calcd for $C_{24}H_{20}NO_2$ $[M + H]^+$ 354.1494, found 354.1493.

1-Methyl-3-(2-methylbenzoyl)-4-phenylquinolin-2(1H)-one (**4g**): yellow solid (230 mg, 65%); mp 123−127 °C; R_f = 0.33 (petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (t, J = 8.0 Hz, 1H), 7.58 (d, J = 7.2 Hz, 1H), 7.51 (d, J = 8.4 Hz, 1H), 7.31−7.34 (m, 4H), 7.27−7.29 (m, overlapping $CDCl_3$, 3H), 7.17−7.22 (m, 3H), 7.11−7.14 (m, 2H), 3.84 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 160.0, 147.4, 140.0, 139.8, 136.9, 134.0, 132.6, 131.9, 131.7, 131.3, 131.0, 129.2, 128.6, 128.5, 128.2, 125.4, 122.3, 120.9, 114.3, 29.6, 21.1; FT-IR ν/cm^{-1} (KBr) 1678, 1639, 1601, 1558,

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1458, 1369, 1315, 1242, 756, 706; HRMS (ESI) calcd for $C_{24}H_{20}NO_2$ $[M + H]^+$ 354.1494, found 354.1491.

3-(2,4-Dimethylbenzoyl)-1-methyl-4-phenylquinolin-2(1H)-one ***(4h)****:* sticky colorless oil (294 mg, 80%); R_f = 0.22 (petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (t, J = 8.0 Hz, 1H), 7.50 (dd, J = 8.4 Hz, 4.4 Hz, 2H), 7.33 (m, 4H), 7.25 (td, J = 4.4 Hz, 2.4 Hz, 2H), 7.20 (t, J = 8.0 Hz, 1H), 6.94 (d, J = 10.4 Hz, 2H), 3.83 (s, 3H), 2.39 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 160.0, 147.2, 142.5, 140.1, 139.9, 134.2, 134.1, 132.7, 132.7, 131.6, 131.2, 129.2, 128.5, 128.4, 128.2, 126.1, 122.3, 120.9, 114.3, 29.6, 21.5, 21.3; FT-IR ν/cm^{-1} (KBr) 1658, 1639, 1597, 1562, 1454, 1369, 1319, 1230, 752, 706; HRMS (ESI) calcd for $C_{25}H_{22}NO_2$ $[M + H]^+$ 368.1651, found 368.1650.

3-(4-Methoxybenzoyl)-1-methyl-4-phenylquinolin-2(1H)-one ***(4i)****:* white solid (277 mg, 75%); mp 192−196 °C; R_f = 0.22 (petroleum ether/ethyl acetate =2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dt, J = 9.6 Hz, 2.8 Hz, 2H), 7.68 (t, J = 8.0 Hz, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.38 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.32 (d, J = 2.4 Hz, 3H), 7.28 (m, overlapping $CDCl_3$, 3H), 7.22 (t, J = 7.6 Hz, 1H), 6.85 (dt, J = 9.6 Hz, 2.8 Hz, 2H), 3.83 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 163.7, 159.9, 147.6, 140.0, 134.1, 131.6, 131.3, 131.2, 130.2, 129.3, 128.6, 128.5, 128.2, 122.4, 120.8, 114.4, 113.7, 55.4, 29.6; FT-IR ν/cm^{-1} (KBr) 1658, 1635, 1597, 1570, 1315, 1254, 1165, 864, 748; HRMS (ESI) calcd for $C_{24}H_{20}NO_3$ $[M + H]^+$ 370.1443, found 370.1446.

1-Methyl-4-phenyl-3-(thiophene-2-carbonyl)quinolin-2(1H)-one ***(4j)****:* yellow solid (287 mg, 83%); mp 209−212 °C; R_f = 0.25 (petroleum ether/ethyl acetate = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (t, J = 8.0 Hz, 1H), 7.58 (dd, J = 4.8 Hz, 0.8 Hz, 1H), 7.52 (m, 2H), 7.40 (dd, J = 8.4 Hz, 1.6 Hz, 1H), 7.34−7.36 (m, 3H), 7.31 (m, 2H), 7.23 (t, J = 7.6 Hz, 1H), 7.01 (dd, J = 4.8 Hz, 4.0 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.2, 159.7, 148.0, 144.2, 140.1, 134.5, 134.2, 133.8, 131.6, 130.8, 129.4, 128.8, 128.7, 128.3, 128.0, 122.5, 120.6, 114.5, 29.7; FT-IR ν/cm^{-1} (KBr) 1655, 1628, 1408, 1049, 744; HRMS (ESI) calcd for $C_{21}H_{16}NO_2S$ $[M + H]^+$ 346.0902, found 346.0903.

3-Benzoyl-1-methyl-4-(p-tolyl)quinolin-2(1H)-one ***(4l)****:* White solid (307 mg, 87%): mp 168−170 °C, R_f = 0.20 (petroleum ether/ethyl acetate =3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 7.2 Hz, 2H), 7.68 (t, J = 8.0 Hz, 1H), 7.51 (t, J = 8.0 Hz, 2H), 7.34−7.42 (m, 3H), 7.22 (t, J = 7.6 Hz, 1H), 7.16 (dd, J = 13.6 Hz, 8.4 Hz, 4H), 3.82 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 159.9, 148.3, 140.0, 138.5, 137.1, 133.3, 131.4, 130.9, 129.2, 129.0, 128.6, 128.4, 122.4, 120.9, 114.4, 29.7, 29.6, 21.3; FT-IR ν/cm^{-1} (KBr) 1678, 1631, 1580, 1450, 1365, 1319, 1242, 1109, 825, 760; HRMS (ESI) calcd for $C_{24}H_{20}NO_2$ $[M + H]^+$ 354.1494, found 354.1495.

3-Benzoyl-1-benzyl-4-phenyl-1,8-naphthyridin-2(1H)-one ***(4m)****:* pale yellow solid (275 mg, 66%); mp 186−189 °C; R_f = 0.44 (petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, J = 4.0 Hz, 1H), 7.80 (d, J = 7.2 Hz, 2H), 7.68 (t, J = 8.4 Hz, 3H), 7.52 (t, J = 7.6 Hz, 1H), 7.25−7.38 (m, overlapping $CDCl_3$, 11H), 7.17 (dd, J = 7.6 Hz, 4.4 Hz, 1H), 5.85 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 160.6, 150.6, 149.40, 146.8, 137.5, 136.7, 136.5, 133.5, 132.9, 132.1, 129.4, 129.2, 129.0, 128.5, 128.3, 127.4, 118.5, 116.2, 44.3; FT-IR ν/cm^{-1} (KBr) 1678, 1635, 1601, 1558, 1454, 1315, 1254, 756, 694; HRMS (ESI) calcd for $C_{28}H_{21}N_2O_2$ $[M + H]^+$ 417.1603, found 417.1604.

3-Benzoyl-4-(2-chlorophenyl)-1-methylquinolin-2(1H)-one ***(4n)****:* white solid (333 mg, 89%); mp 198−202 °C; R_f = 0.14 (petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.83 (t, J = 2.0 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 7.48−7.53 (m, 2H), 7.33−7.39 (m, 3H), 7.26−7.31 (m, overlapping $CDCl_3$, 4H), 7.24 (td, J = 8.0 Hz, 0.8 Hz, 1H), 7.17 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9, 160.0, 145.7, 139.8, 136.6, 133.5, 133.0, 132.7, 131.7, 131.59, 131.56, 130.3, 129.6, 129.2, 128.4, 128.1, 126.8, 122.7, 119.8, 114.6, 29.7, 29.7; FT-IR ν/cm^{-1} (KBr) 1678, 1643, 1597, 1562, 1365, 1319, 1246, 775, 752; HRMS (ESI) calcd for $C_{23}H_{17}ClNO_2$ $[M + H]^+$ 374.0948, found 374.0946.

3-Benzoyl-4-(4-bromophenyl)-1-methylquinolin-2(1H)-one ***(4o)****:* yellow solid (351 mg, 84%); mp 216−220 °C; R_f = 0.14 (petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 7.6 Hz, 2H), 7.70 (t, J = 7.6 Hz, 1H), 7.50−7.54 (m, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.33 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.24 (t, J = 7.6 Hz, 1H), 7.15 (d, J = 8.0 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 159.7, 146.8, 140.0, 136.9, 133.5, 132.9, 131.7, 131.6, 131.2, 130.9, 129.2, 128.6, 128.3, 123.1, 122.6, 120.4, 114.6, 29.7; FT-IR ν/cm^{-1} (KBr) 1674, 1643, 1593, 1361, 1311, 1238, 1011, 756; HRMS (ESI) calcd for $C_{23}H_{17}BrNO_2$ $[M + H]^+$ 418.0443, found 418.0447.

3-Benzoyl-4-(2-bromophenyl)-1-methylquinolin-2(1H)-one ***(4p)****:* white solid (368 mg, 88%); mp 160−163 °C; R_f = 0.20 (petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.2 Hz, 2H), 7.69 (td, J = 8.4 Hz, 1.2 Hz, 1H), 7.49−7.54 (m, 3H), 7.39 (t, J = 8.0 Hz, 2H), 7.29−7.34 (m, 2H), 7.19−7.24 (m, 2H), 7.17 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 160.0, 147.0, 139.8, 136.6, 134.7, 133.5, 132.8, 131.7, 131.6, 131.4, 130.4, 129.3, 128.3, 127.3, 123.4, 122.9, 122.6, 119.7, 114.6, 29.7; FT-IR ν/cm^{-1} (KBr) 1674, 1639, 1597, 1562, 1369, 1319, 1246, 771, 752; HRMS (ESI) calcd for $C_{23}H_{17}BrNO_2$ $[M + H]^+$ 418.0443, found 418.0441.

3-Benzoyl-4-(3-methoxyphenyl)-1-methylquinolin-2(1H)-one ***(4q)****:* sticky colorless oil (288 mg, 78%); R_f = 0.28 (petroleum ether/ethyl acetate = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.82 (t, J = 1.6 Hz, 1H), 7.69 (t, J = 8.0 Hz, 1H), 7.52 (t, J = 8.0 Hz, 2H), 7.44 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.39 (t, J = 7.2 Hz, 2H), 7.20−7.24 (m, 2H), 6.86 (td, J = 5.2 Hz, 2.8 Hz, 2H), 6.77 (s, 1H), 3.83 (s, 3H), 3.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 159.9, 159.2, 147.9, 140.0, 137.1, 135.1, 133.3, 131.5, 130.9, 129.4, 129.2, 128.6, 128.4, 122.4, 121.7, 120.6, 114.7, 114.6, 114.4, 55.2, 29.7, 29.6; FT-IR ν/cm^{-1} (KBr) 1678, 1628, 1589, 1454, 1365, 1250, 1169, 698; HRMS (ESI) calcd for $C_{24}H_{20}NO_3$ $[M + H]^+$ 370.1443, found 370.1446.

3-Benzoyl-6-chloro-1-methyl-4-phenylquinolin-2(1H)-one ***(4r)****:* yellow oil (299 mg, 80%); R_f = 0.17 (petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 7.2 Hz, 2H), 7.62 (dd, J = 9.2 Hz, 2.4 Hz, 1H), 7.49−7.51 (m, 1H), 7.48 (t, J = 8.0 Hz, 1H), 7.31−7.38 (m, 6H), 7.25 (dd, J = 5.6 Hz, 2.0 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9, 159.6, 147.0, 138.6, 136.7, 133.5, 133.2, 132.1, 131.5, 129.2, 129.1, 129.0, 128.5, 128.2, 127.6, 121.9, 116.0, 29.8; FT-IR ν/cm^{-1} (KBr) 1678, 1643, 1601, 1365, 1315, 768, 698; HRMS (ESI) calcd for $C_{23}H_{17}ClNO_2$ $[M + H]^+$ 374.0948, found 374.0950.

3-Benzoyl-6-fluoro-1-methyl-4-phenylquinolin-2(1H)-one ***(4s)****:* yellow oil (282 mg, 79%); R_f = 0.28 (petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 7.2 Hz, 2H), 7.46−7.51 (m, 2H), 7.42 (dd, J_{H-F} = 7.6 Hz, 2.8 Hz, 1H), 7.32−7.38 (m, 5H), 7.25 (d, J = 3.6 Hz, 2H), 7.06 (dd, J_{H-F} = 9.2 Hz, 2.8 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 159.6, 159.2 (d, J = 41 Hz), 156.8, 147.1, 136.8, 136.6, 133.4, 133.4, 132.2, 129.1, 129.0, 128.5, 121.9, 121.8, 119.3, 119.1 (d, J = 24 Hz), 116.1, 116.0, 113.9, 113.6 (d, J = 24 Hz), 29.9, 29.7; ^{19}F-NMR (376.5 Hz, $CDCl_3$) δ −119.71; FT-IR ν/cm-1 (KBr) 1678, 1639, 1500, 1442, 1242, 810, 752, 702; HRMS (ESI) calcd for $C_{23}H_{17}FNO_2$ $[M + H]^+$ 358.1243, found 358.1244.

3-Benzoyl-1-ethyl-4-phenylquinolin-2(1H)-one ***(4t)****:* sticky pale yellow oil (307 mg, 87%); R_f = 0.26 (petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (s, 1H), 7.79 (t, J = 1,6 Hz, 1H), 7.68 (t, J = 8.0 Hz, 1H), 7.54 (d, J = 8.8 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.31−7.39 (m, 6H), 7.27 (q, J = 3.2 Hz, 2H), 7.21 (t, J = 7.6 Hz, 1H), 4.50 (q, J = 6.8 Hz, 2H), 1.48 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 159.4, 148.0, 139.0, 137.1, 134.0, 133.3, 131.4, 131.1, 129.3, 129.1, 128.8, 128.6, 128.4, 128.3, 122.2, 121.0, 114.3, 37.5, 12.8; FT-IR ν/cm^{-1} (KBr) 1682, 1631, 1593, 1446, 1369, 1311, 1250, 764, 702; HRMS (ESI) calcd for $C_{24}H_{20}NO_2$ $[M + H]^+$ 354.1494, found 354.1498.

3-Benzoyl-1-benzyl-4-phenylquinolin-2(1H)-one ***(4u)****:* colorless oil (353 mg, 85%); R_f = 0.20 (petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 6.8 Hz, 2H), 7.48−7.54 (m, 3H), 7.45 (d, J = 8.0 Hz, 1H), 7.35−7.40 (m, 7H), 7.29−7.34 (m,

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5H), 7.17 (td, J = 7.2 Hz, 1.2 Hz, 1H), 5.65 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 160.1, 148.6, 139.5, 137.1, 136.2, 133.9, 133.3, 131.4, 130.9, 129.3, 129.2, 128.9, 128.7, 128.5, 128.3, 127.5, 127.0, 122.5, 121.0, 115.3, 46.1; FT-IR ν/cm^{-1} (KBr) 1678, 1635, 1601, 1566, 1454, 1373, 1315, 1250, 756, 694; HRMS (ESI) calcd for $C_{29}H_{22}NO_2$ $[M + H]^+$ 416.1651, found 416.1654.

*3-(3-Benzoyl-2-oxo-4-phenylquinolin-1(2H)-yl)propanenitrile (**4v**):* yellow solid (291 mg, 77%); mp 168−173 °C; R_f = 0.17 (petroleum ether/ethyl acetate = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.78 (t, J = 1.6 Hz, 1H), 7.73 (t, J = 8.0 Hz, 1H), 7.58 (d, J = 8.8 Hz, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.43 (dd, J = 8.4 Hz, 1.6 Hz, 1H), 7.31−7.38 (m, 5H), 7.23−7.27 (m, 3H), 4.72 (t, J = 6.8 Hz, 2H), 2.98 (t, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9, 159.6, 149.1, 138.6 136.8, 133.6, 133.5, 131.9, 130.7, 129.4, 129.1, 128.9, 128.5, 128.4, 123.1, 121.1, 117.2, 113.7, 38.4, 16.0; FT-IR ν/cm^{-1} (KBr) 1678, 1635, 1597, 1454, 1373, 1315, 1250, 764, 702; HRMS (ESI) calcd for $C_{25}H_{19}N_2O_2$ $[M + H]^+$ 379.1447, found 379.1451.

*3-Benzoyl-5-chloro-1-methyl-4-phenylquinolin-2(1H)-one (**4w**):* white solid (161 mg, 43%); mp 236−240 °C; R_f = 0.36 (petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 7.2 Hz, 2H), 7.50 (t, J = 6.8 Hz, 2H), 7.30−7.38 (m, 6H), 7.23−7.24 (m, 2H), 7.18 (dd, J = 8.4 Hz, 1.6 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 159.8, 147.5, 140.8, 137.7, 136.8, 133.5, 133.4, 131.1, 129.8, 129.2, 129.1, 128.9, 128.5, 128.4, 122.8, 119.3, 114.4, 29.7; FT-IR ν/cm^{-1} (KBr) 1674, 1635, 1597, 1585, 1550, 1439, 1369, 1315, 968, 764; HRMS (ESI) calcd for $C_{23}H_{17}ClNO_2$ $[M + H]^+$ 374.0948, found 374.0945.

*3-Benzoyl-1-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydroquinoline-6-carbaldehyde (**3b′**):* white solid (270 mg, 73%); mp 133−136 °C; R_f = 0.20 (petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.95 (d, J = 7.6 Hz, 2H), 7.89 (dd, J = 8.4 Hz, 1.6 Hz, 1H), 7.62 (t, J = 7.6 Hz, 1H), 7.50 (t, J = 7.2 Hz, 3H), 7.35 (t, J = 7.2 Hz, 2H), 7.25−7.29 (m, overlapping $CDCl_3$, 3H), 7.19 (d, J = 6.8 Hz, 2H), 5.02 (d, J = 6.8 Hz, 1H), 4.77 (d, J = 6.8 Hz, 1H), 3.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 190.7, 166.7, 144.6, 139.4, 136.0, 133.8, 131.8, 130.5, 130.1, 129.3, 128.82, 128.79, 127.9 127.7, 115.3, 55.7, 44.8, 30.3; FT-IR ν/cm^{-1} (KBr) 1689, 1674, 1597, 1365, 1296, 1207, 1111, 756, 690; HRMS (ESI) calcd for $C_{24}H_{20}NO_3$ $[M + H]^+$ 370.1443, found 370.1446.

*3-Benzoyl-7-chloro-1-methyl-4-phenyl-3,4-dihydroquinolin-2(1H)-one (**3c′**):* white solid (132 mg, 35%); mp 147−149 °C; R_f = 0.53 (petroleum ether/ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.4 Hz, 2H), 7.66 (t, J = 7.2 Hz, 1H), 7.55 (t, J = 7.6 Hz, 2H), 7.26−7.35 (m, overlapping $CDCl_3$, 5H), 7.15 (t, J = 7.2 Hz, 3H), 7.07 (d, J = 8.0 Hz, 1H), 4.97 (s, 1H), 4.90 (d, J = 1.2 Hz, 1H), 3.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 164.9, 141.4, 139.3, 134.9, 134.4, 133.9, 129.2, 129.0, 128.9, 127.6, 127.1, 124.7, 124.2, 113.9, 58.1, 42.4, 30.5; FT-IR ν/cm^{-1} (KBr) 1689, 1670, 1593, 1458, 1369, 1281, 1219, 690; HRMS (ESI) calcd for $C_{23}H_{19}ClNO_2$ $[M + H]^+$ 376.1104, found 376.1105.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data and NMR spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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