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# Visible-light-induced Decarboxylation Coupling/Intramolecular Cyclization： A One-Pot Synthesis for 4-aryl-2-quinolinone Derivatives

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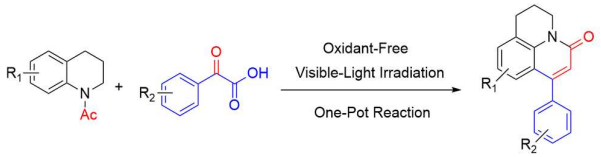



**ABSTRACT:** A visible-light-induced decarboxylation coupling /intramolecular cyclization is reported. The one-pot synthesis system provides mild, efficient and atom economical access to the synthesis of 4-aryl-2-quinolinone derivatives. It is notable that the necessary oxidant in the traditional decarboxylation coupling is replaced by the visible-light-irradiation in this paper. In addition, the HBV inhibitor is synthesized by the one-pot synthesis system in an atom economical manner.

## INTRODUCTION:

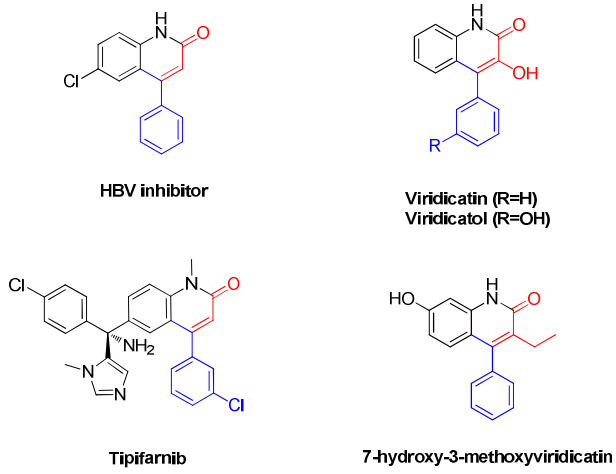
Among the known heterocyclic compounds, 2-quinolinones are a significant class of privileged heterocycles with a variety of biological activities including antibiotic, anticancer, antiviral and antihypersensitivity.[1] In particular, the 4-aryl-2-quinolinone derivatives have attracted increasing interest in the synthesis of natural products, medicinal compounds and the application in clinical trials (**Scheme 1**).[2-3] Although various routes were so far reported about the synthesis of 2-quinolinone structural motifs, there are very few reports on transition-metal-catalyzed approaches, which would be a more efficient and practical strategy.[4]

In recent years, transition-metal-catalyzed decarboxylation coupling have gradually become an effective method to construct C–C bond because these reactions avoided expensive organometallic reagents and toxic metal salt wastes.[5] Particularly, the carboxylic acids as the raw materials are easily available and inexpensive. Furthermore, the decarboxylation coupling reactions caused by the catalyzed carboxylic acids have high selectivity and tolerance of functional groups. Since Myers et al. and Goossen et al.[6] reported Pd-catalyzed decarboxylation coupling, a series of

relevant studies were carried out. Kim and co-workers[7] reported a Pd-catalyzed decarboxylation acylation of *o*-methyl ketoximes, phenyl-acetamides and *o*-phenyl carbonates. Tan,[8] Wang,[9] Zhang[10] and Lang[11] respectively described the decarboxylation acylation of oximes, azoxybenzenes, 2-aryloxypyridines and benzofurans/ benzothiophenes in the presence of palladium catalyst. Recently, our research group reported the Pd-catalyzed decarboxylation acylation of N-acetyl-1,2,3,4-tetrahydroquinolines.[12] In addition, visible-light-induced catalytic system has served as an increasingly significant role in the design and development of a variety of radical reactions under observably mild reaction conditions.[13] From the above, the combination of transition-metal catalysis mode with visible-light-induced catalytic system was tried in this work.

On the other hand, the rapid construction of complicated compounds through multiple bond-forming reactions in a single step, the so-called one-pot process, is a powerful tool.[14] Such process can improve the reaction efficiency, reduce the cost of energy and produce fewer wastes. Therefore, it would be attractive from the viewpoint of environmentally friendly development and economical synthetic methods. From the above, we designed an efficient and environment-friendly route for the one-pot synthesis of 4-aryl-2-quinolinone derivatives through a visible-light-induced decarboxylation coupling /intramolecular cyclization.

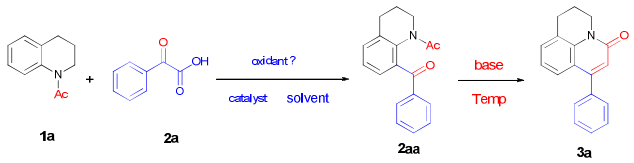
**Scheme 1.** Selected 4-aryl-2-quinolinones with Biological Activities




## RESULT AND DISCUSSION

The reaction conditions of visible-light-induced decarboxylation coupling/intramolecular cyclization were investigated by a reaction of N-acetyl-1,2,3,4-tetrahydroquinoline **1a** and α-oxophenylacetic acid **2a**, the experimental results were summarized in **Table 1**. An initial idea was tried toward decarboxylation coupling approach. The substrate **1a** (1.0 equiv.) was treated with **2a** (1.5 equiv.) in the presence of $Pd(OAc)_2$ (10 mol %) in 1,2-dichloroethane (2 mL) at room temperature under the 25W Blue LED. To our delight, the above mentioned

**Table 1.** Optimization of Reaction Condition[a]




| Entry | Catalyst (mol %) | Light[b] | Oxidant | Solvent | Temp(°C) | Base (equiv.) | Yield[c] (%) |
|---|---|---|---|---|---|---|---|
| 1 | $Pd(OAc)_2$（10） | Y | – | DCE | 80 | DBU(5) | 88 |
| 2 | $Pd(OAc)_2$（10） | Y | – | Dioxane | 80 | DBU(5) | 20 |
| 3 | $Pd(OAc)_2$（10） | Y | – | Diglyme | 80 | DBU(5) | 27 |
| 4 | $Pd(OAc)_2$（10） | Y | – | Toluene | 80 | DBU(5) | 32 |
| 5 | $Pd(OAc)_2$（10） | Y | – | DCE | 60 | DBU(5) | 70 |
| 6 | $Pd(OAc)_2$（10） | Y | – | DCE | 40 | DBU(5) | 53 |
| 7 | $Pd(OAc)_2$（10） | Y | – | DCE | 20 | DBU(5) | 37 |
| 8 | $Pd(OAc)_2$（10） | N | – | DCE | 80 | DBU(5) | – |
| 9 | $Pd(OAc)_2$（10） | N | $(NH_4)_2S_2O_8$ | DCE | 80 | DBU(5) | 44 |
| 10 | $Pd(OAc)_2$（10） | N | $K_2S_2O_8$ | DCE | 80 | DBU(5) | 36 |
| 11 | $Pd(OAc)_2$（10） | N | *m*-CPBA | DCE | 80 | DBU(5) | 33 |
| 12 | $Pd(OAc)_2$（10） | N | $Ag_2CO_3$ | DCE | 80 | DBU(5) | 20 |
| 13 | $Pd(OAc)_2$（10） | N | $Cu(OAc)_2$ | DCE | 80 | DBU(5) | 17 |
| 14 | $Pd(OAc)_2$（5） | Y | – | DCE | 80 | DBU(5) | 40 |
| 15 | $Pd(PPh_3)_4$（10） | Y | – | DCE | 80 | DBU(5) | 32 |
| 16 | $Rh_2(OAc)_4$（10） | Y | – | DCE | 80 | DBU(5) | 21 |
| 17 | $IrCl_3$（10） | Y | – | DCE | 80 | DBU(5) | – |
| 18 | $RuCl_3$（10） | Y | – | DCE | 80 | DBU(5) | – |
| 19 | $Pd(TFA)_2$ (10) | Y | – | DCE | 80 | DBU(5) | 53 |
| 20 | $Pd(TFA)_2$ (10) | N | $(NH_4)_2S_2O_8$ | DCE | 80 | DBU(5) | 80 |
| 21 | $Pd(OAc)_2$（10） | Y | – | DCE | 80 | $K_2CO_3$(5) | trace |
| 22 | $Pd(OAc)_2$（10） | Y | – | DCE | 80 | KOH(5) | trace |

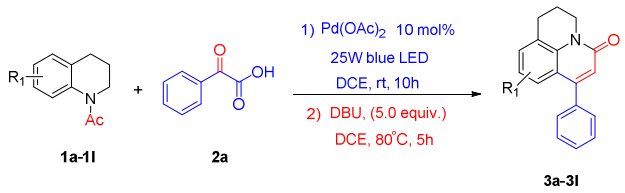
[a] **1a** (0.2 mmol), **2a** (0.3 mmol), catalyst, 2 mL of solvent, 25W Blue LED, after 10 hours, the reaction completed (monitored by TLC), then add base (5.0 equiv.), after 5 hours, the reaction completed. [b] Y = with the 25W Blue LED, N = in the dark. [c] Isolated yield by flash column chromatography.

combination resulted in **2aa** with full transformation after 10 hours. Then DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) (5.0 equiv.) was added and the reaction process continued to proceed in 80 °C. After 5 hours, **3a** with 88% yield was obtained (**Table 1, entry 1**). For comparison with reported procedures, some organic solvents were tested, but the use of dioxane (20%), diglyme (27%) and toluene (32%) resulted in lower yields (**Table 1, entries 2-4**). For the temperature, the yields decreased from 88% to 37% when the temperature varied from 80 °C to 20 °C, respectively (**Table 1, entries 5-7**). It was notable that there was no product detected in the dark (**Table 1, entry 8**). The oxidant was screened in the dark. When $(NH_4)_2S_2O_8$ (44%), $K_2S_2O_8$

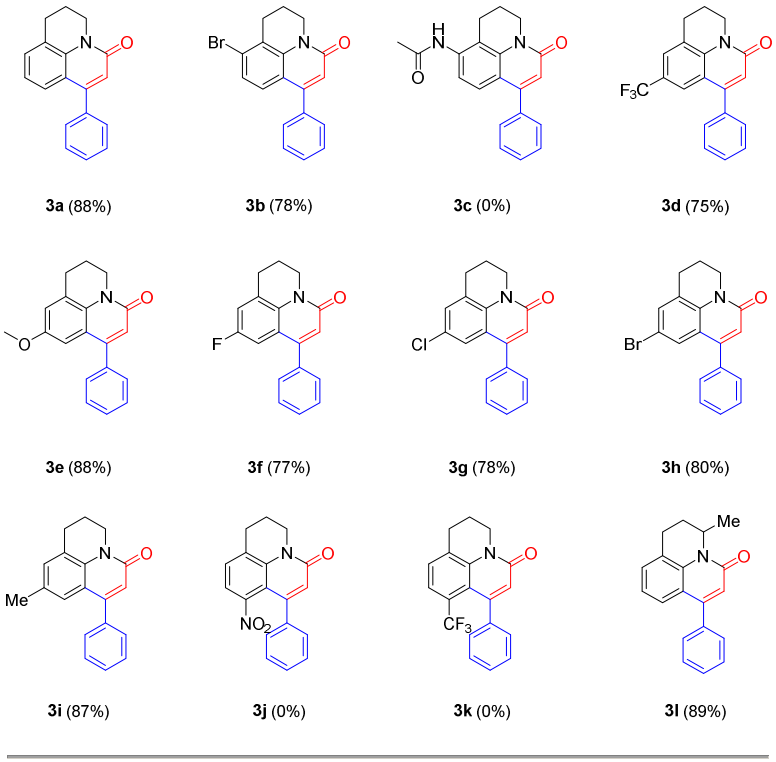
(36%), *m*-chloroperbenzoic acid (*m*-CPBA) (33%), $Ag_2CO_3$ (20%) and $Cu(OAc)_2$ (17%) served as the oxidant, the yields varied from 44% to 17%, respectively (**Table 1, entries 9-13**). This showed that the oxidants also had favorable effect for the reaction, but the 25W Blue LED had better effect for the reaction. When the amount of $Pd(OAc)_2$ decreased from 10 mol% to 5 mol%, the yield decreased to 40% (**Table 1, entry 14)**. About the catalysts, $Pd(PPh_3)_4$ (32%) and $Rh_2(OAc)_4$ (21%) could catalyze the reaction with inferior yields (**Table 1, entries 15-16**). Other catalysts, such as $IrCl_3$ (0%) and $RuCl_3$ (0%) in lieu of $Pd(OAc)_2$ were found to give no target product (**Table 1, entries 17-18**). It was notable that $Pd(TFA)_2$ (53%) was found to support the reaction with lower yield compared with $Pd(OAc)_2$(**Table 1, entry 19**). The reason was probably that $Pd(TFA)_2$ was unstable under the 25W Blue LED. In addition, on the basis of our previous work,[12] $Pd(TFA)_2$ was tested with oxidant $(NH_4)_2S_2O_8$ in the dark, the yield can achieve 80% (**Table 1, entry 20**). Although the previous work also offered good yield, but the improved method in this work that oxidant was replaced by 25W blue LED reduced the cost of reaction and provided better environmental protection. For intramolecular cyclization, the inorganic base such as $K_2CO_3$ and KOH gave trace of desired product (**Table 1, entries 21-22**). Compared with the frequently-used inorganic bases in aldol condensation, the DBU avoided metal-salt wastes and was treated harmlessly. In addition, the probable generated ionic liquid by the combination of DCE and DBU may accelerate the reaction by increasing the solubility of substrates.[15] The concrete work is going on in our group.

To explore the substrate scope of the protocol, the above optimized condition was further applied to a variety of N-acetyl-1,2,3,4-tetrahydroquinolines **1a-1l**. As shown in **Table 2**, the N-acetyl-1,2,3,4-tetrahydroquinoline **1a** without substituent group afforded the product **3a** in 88% yield. Compound **3b** with substituent -Br at the 5-position of aromatic ring was obtained with 78% yield. However, compound **3c** with acetamido at the 5-position of aromatic ring was not obtained. N-acetyl-1,2,3,4-tetrahydroquinolines **1d-1i** with electron-rich and electron-deficient substituents ($-CF_3$, -OMe, -F, -Cl, -Br and -Me) at the 6-position of aromatic ring supported the reaction and afforded the desired products **3d-3i** in high yields (75%-88%). The electron-donating groups (-OMe, 88%) (-Me, 87%) were more beneficial to the reaction compared with electron-withdrawing groups ($-CF_3$, -F, -Cl, -Br) (75%-80%). About N-acetyl-1,2,3,4-tetrahydroquinolines **1j** and **1k** with substituent $-NO_2$ and $-CF_3$ at the 7-position of aromatic ring, no corresponding product **3j** and **3k** could be observed. For the substrates **1j** and **1k**, a receivable reason was proposed that the strong electron-withdrawing effect of $-NO_2$ and $-CF_3$ and large steric hindrance at the 7-position of aromatic ring restrained the process of reaction seriously. In addition, Compound **3l** with substituent -Me at the 2-position of tetrahydroquinoline ring was obtained with excellent yield (89%).

**Table 2.** Scope of N-acetyl-1,2,3,4-tetrahydroquinolines[a,b]




**1a-1l** + **2a** → **3a-3l**

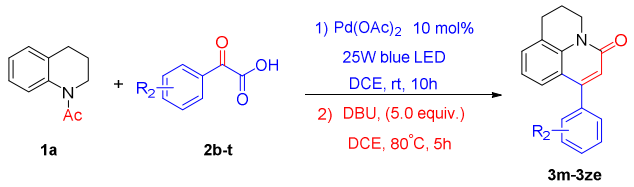


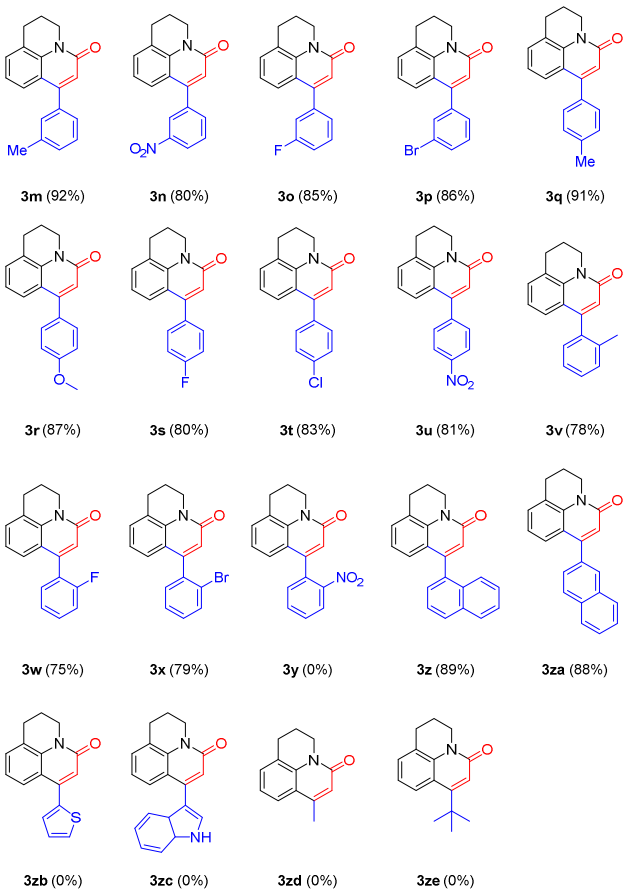

[a] Conditions: **1a-l** (0.2 mmol), **2a** (0.3 mmol), $Pd(OAc)_2$ (10 mol%), 2 mL of DCE, 25W Blue LED, after the reaction completed (monitored by TLC), then add DBU (5.0 equiv.) until the reaction was completed.

[b] Isolated yield by flash column chromatography.

To further explore the substrate scope and limitations of this process, a broad range of α-oxophenylacetic acids were also screened. As shown in **Table 3**, α-oxophenylacetic acid with both electron-rich and electron-deficient groups gave the expected products in good yields (80%-92%), for example, *m*-Me- **3m**, *m*-$NO_2$- **3n**, *p*-Me- **3q**, *p*-MeO- **3r** and *p*-$NO_2$- **3u** groups. But the electron-donating groups **3m**, **3q, 3r** (92%, 91%, 87%) provided superior yields compared with electron-withdrawing groups **3n** and **3u** (80%, 81%). This transformation also proved good tolerance toward the halogen groups to give yields 80%-86%, including *m*-F- **3o**, *m*-Br- **3p**, *p*-F- **3s** and *p*-Cl- **3t**. However, α-oxophenylacetic acid with substituent groups (-Me, -F and -Br) in the 2-position of aromatic ring gave the desired product **3v**, **3w** and **3x** in decreased yields (75%-79%) because of the steric-hindrance effect. It's worth noting that there was no product **3y** detected when a strong electron-withdrawing group -$NO_2$ was in the 2-position of the aromatic ring of α-oxophenylacetic acid. The

**Table 3.** Scope of α - oxoarylacetic Acids[a,b]



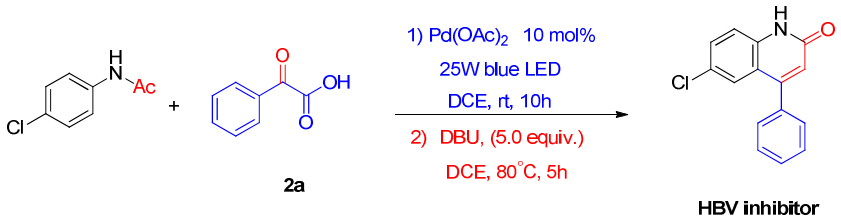




[a] Conditions: **1a** (0.2 mmol), **2b-t** (0.3 mmol), $Pd(OAc)_2$ (10 mol%), 2 mL of DCE, 25W Blue LED, after the reaction completed (monitored by TLC), then add DBU (5.0 equiv.) until the reaction was completed.

[b] Isolated yield by flash column chromatography.

reason was probably that the electron-withdrawing ability and steric-hindrance effect of $-NO_2$ was stronger notably than -F and –Br, so the product **3v** was not generated. Moreover, α-oxophenylacetic acid **2o** and **2p** with the naphthyl moiety also participated in the process with good yields (89% and 88%). In addition, heterocyclic oxoacetic acids 2-thienylglyoxylic acid and 3-indoleglyoxylic acid were tested and resulted in no products **3zb** and **3zc**. It was noteworthy that aliphatic keto-acids pyruvic acid and 3,3-dimethyl-2-oxobutyric acid gave no products **3zd** and **3ze**.

**Scheme 2.** Application of the Protocol to the Synthesis of HBV Inhibitor




To further demonstrate the synthetic utility of this protocol, we applied it to the synthesis of the HBV inhibitor (**in Scheme 2**). 4-chloroacetanilide and **2a** were selected to the optimized reaction conditions to obtain the HBV inhibitor with 85% yield. Compared with the previous methods,[16] this protocol has the advantages of readily available starting materials, superior atom economy and the reduction of wastes.

Although the reaction mechanism is unclear at this stage, a tentative mechanism to rationalize this transformation is illustrated on the basis of previous reports[17] in **Scheme 3**. Firstly, the active palladium catalyst reacts with **1a** by chelation-directed C-H activation to generate intermediate **A**. Meanwhile, the benzoyl radical **B** is obtained by a decarboxylation of **2a** by visible light irradiation. Subsequently, **A** undergoes oxidative addition with **B** to give intermediate **C**. Subsequently, the intermediate **2aa**, which has been isolated to obtain (Spectroscopic data is in the following page), is obtained by the reductive elimination of **C** and Pd(II) catalyst continue to participate the next catalytic cycle. Then the compound **2aa** is converted to the target compound **3a** by the aldol condensation in the presence of DBU.

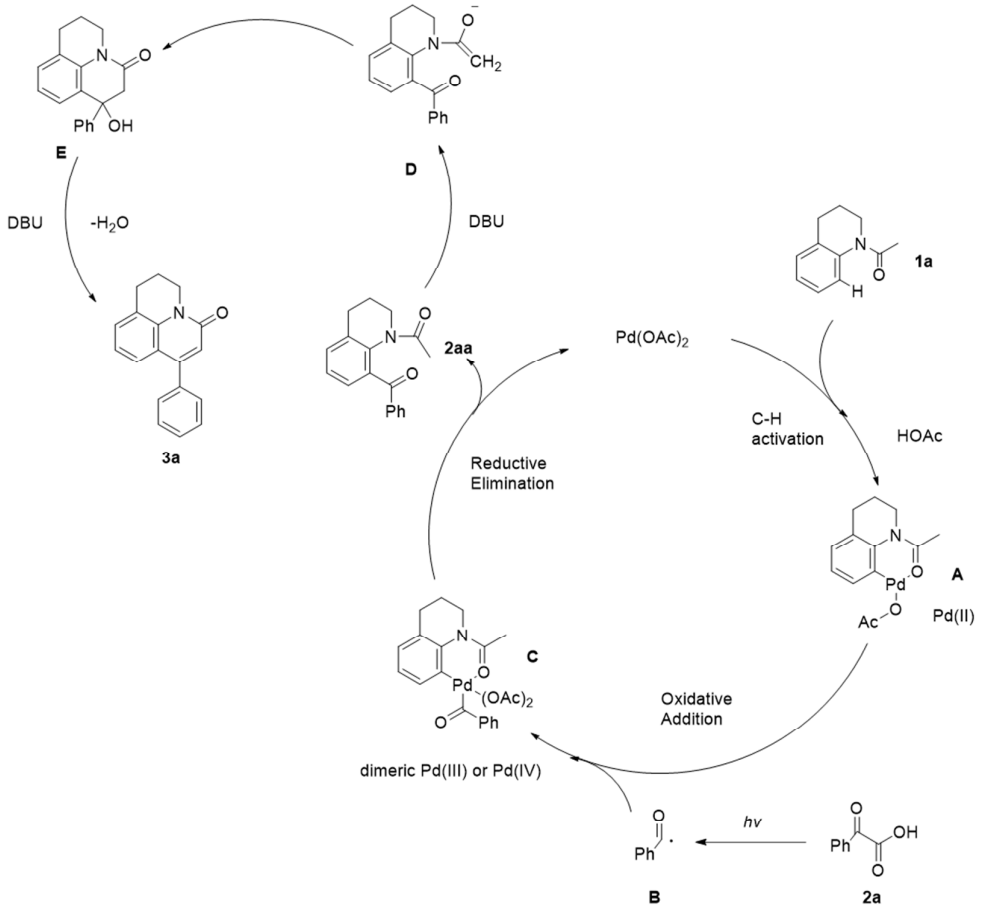
To gather further insight about the reaction mechanism, the reaction between **1a** and **2a** was performed in the presence of 2,2,6,6-tetramethyl-piperidin-1-yl-oxyl (TEMPO) as a radical scavenger (**Scheme 4**). Under this condition, 2,2,6,6-tetramethyl-piperidino benzoate **4** was isolated in 81% yield (Spectroscopic data is in the following page) and the desired acylated product **2aa** was not detected. This suggested the radical nature of the decarboxylation coupling. In addition, 2,2,6,6-tetramethyl-piperidino benzoate **4** was detected with trace of yield and acylated product **2aa** was not detected when the whole reaction system was in the dark. This suggested that the benzoyl radical was forming from the corresponding keto-acid by light irradiation.

## CONCLUSION

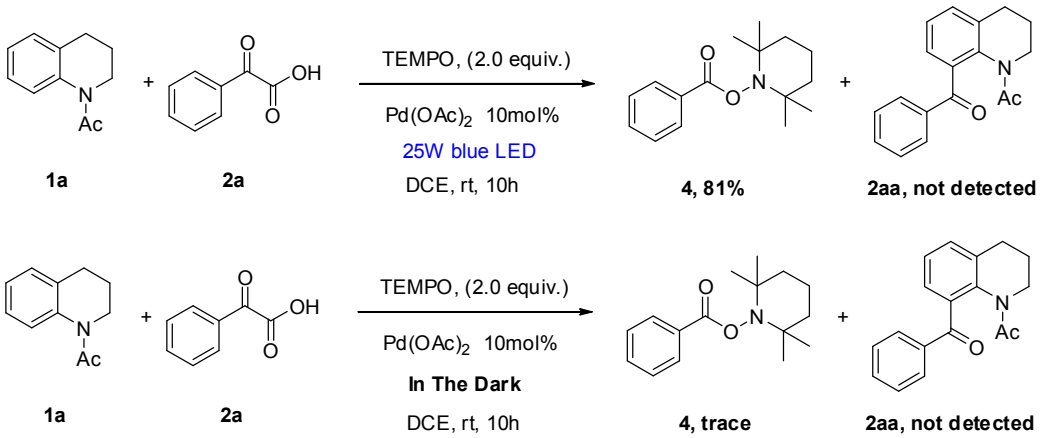
In conclusion, we reported a visible-light-induced decarboxylation coupling/intramolecular cyclization sequence, leading to a mild, efficient and atom economical one-pot access for the construction of 4-aryl-2-quinolinones. Sequential chemical transformations without the isolation of each intermediate serve as a practical procedure improve the reaction efficiency, produce less waste, and require less energy. Besides, the reaction also tolerates various

functional groups with excellent yields. In addition, the protocol could be used for the synthesis of HBV inhibitor in excellent yield. Exploration of the substrate scope and reaction mechanism will be further investigated in the future.

**Scheme 3.** Postulated Reaction Mechanism




**Scheme 4.** Investigation on the Reaction Mechanism in the Presence of TEMPO



## EXPERIMENTAL SECTION

**General information:** Unless otherwise noted, all commercial materials and solvents were used without further purification. The compounds only with CAS registry numbers were purchased. $^{1}$H NMR and $^{13}$C NMR spectra were recorded on a Bruker DRX 400 MHz and 100 MHz spectrometer in $CDCl_3$ or DMSO. Data for $^{1}$H NMR are reported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz). Data for $^{13}$C NMR are reported in terms of chemical shift (δ ppm). The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, m = multiplet. High-resolution mass spectra (HRMS) were recorded on Agilent 1100 LC/MSD Trap VL mass spectrometer. Elemental analyses (C, H, N) were performed on a Fisons EA110CHN. Melting points were measured by Shang Guang WRR melting point apparatus. Infrared spectroscopy (IR) was measured by SP-100 Fourier transform infrared spectroscopy. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm. All the other chemicals were purchased from Energy Chemical. Commercial reagents were used without further purification.

***General Procedure for the Preparation of Starting Materials 1:*** To a solution of 1,2,3,4-tetrahydroquinolines (0.3 mmol, 1.0 equiv.) in DCM (10 mL) at 0 °C, acetyl chloride or acetic anhydride (0.6 mmol, 2 equiv.) was added dropwise. After stirring for 1 h at room temperature, the solvent was evaporated under reduced pressure. The residue was taken up with ethyl acetate (10 ml) and washed with 1 N HCl (3 × 5 mL) and brine (2 × 5 mL). The organic layer was dried ($Na_2SO_4$) and concentrated in vacuo to give **1**.

*N-Acetyl-1,2,3,4-tetrahydroquinoline (**1a**):* 47.31 mg of **1a** (90%). $^{1}$H NMR (400 MHz, Chloroform-*d*): *δ* 7.16 (m, 4H, arom), 3.81 (t, *J* = 6.0 Hz, 2H), 2.73 (t, *J* = 6.0 Hz, 2H), 2.24 (s, 3H), 1.97 (q, *J* = 6.0 Hz, 2H). (Spectroscopic data in agreement with literature[1] in Supporting Information)

*N-Acetyl-5-bromo-1,2,3,4-tetrahydroquinoline (**1b**):* 66.72 mg of **1b** (87%). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 7.51 (dd, J = 7.5, 2.1 Hz, 1H), 7.34 (dd, J = 7.6, 2.0 Hz, 1H), 7.02 (t, J = 7.5 Hz, 1H), 4.47 (t, J = 5.1 Hz, 2H), 2.89 (t, J = 6.0 Hz, 2H), 2.15 – 2.05 (m, 2H), 2.04 (s, 3H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 170.5, 144.1, 128.9, 128.5, 127.8, 126.4, 117.6, 42.8, 26.6, 23.1, 22.4.

*N-Acetyl-5-acetamido-1,2,3,4-tetrahydroquinoline (**1c**):* 59.85 mg of **1c** (86%). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.24 (s, 1H), 7.30 (d, J = 15.8 Hz, 1H), 7.20 – 6.88 (m, 2H), 3.71 (s, 2H), 2.59 (t, J = 6.5 Hz, 2H), 2.17 (d, J = 21.9 Hz, 6H), 1.92 – 1.85 (m, 2H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 170.5, 169.0, 141.8, 138.4, 129.0, 120.3, 113.8, 112.7, 42.8, 25.4, 23.4, 23.1, 22.4.

*N-Acetyl-6-trifluoromethyl-1,2,3,4-tetrahydroquinoline (**1d**):* 62.75 mg of **1d** (86%). $^{1}$H NMR (400 MHz, Chloroform-*d*) $\delta$ 7.54 – 7.38 (m, 3H), 3.80 (t, $J$ = 6.3 Hz, 2H), 2.80 (t, $J$ = 6.4 Hz, 2H), 2.27 (s, 3H), 2.00 (p, $J$ = 6.4 Hz, 2H). $^{13}$C NMR (100 MHz, Chloroform-*d*) $\delta$ 170.2, 125.73 (d , $J$ = 4 Hz), 125.72 (d, $J$ = 11 Hz), 125.5, 124.8, 123.27 (d, $J$ = 11 Hz), 123.26 (d, $J$ = 4 Hz), 122.8, 27.2, 23.8, 23.5.

*N-Acetyl-6-methoxy-1,2,3,4-tetrahydroquinoline (**1e**):* 98% (purity), CAS Registry Number : 1136-78-3.

*N-Acetyl-6-fluoro-1,2,3,4-tetrahydroquinoline (**1f**):* 98% (purity), CAS Registry Number : 1786347-77-0.

*N-Acetyl-6-chloro-1,2,3,4-tetrahydroquinoline (**1g**):* 98% (purity), CAS Registry Number : 1368960-10-4.

*N-Acetyl-6-bromo-1,2,3,4-tetrahydroquinoline (**1h**):* 98% (purity), CAS Registry Number : 22190-40-5.

*N-Acetyl-6-methyl-1,2,3,4-tetrahydroquinoline (**1i**):* 51.14 mg of **1i** (90%). $^{1}$H NMR (400 MHz, Chloroform-*d*) $\delta$ 7.02 – 6.94 (m, 3H), 3.77 (t, $J$ = 6.2 Hz, 2H), 2.68 (t, $J$ = 6.4 Hz, 2H), 2.31 (s, 3H), 2.21 (s, 3H), 1.94 (p, $J$ = 6.7 Hz, 2H). $^{13}$C NMR (100 MHz, Chloroform-*d*) $\delta$ 170.1, 138.6, 129.9, 128.3, 126.9, 123.3, 118.0, 42.8, 27.0, 24.2, 21.0, 20.4.

*N-Acetyl-7-nitro-1,2,3,4-tetrahydroquinoline (**1j**):* 60.83 mg of **1j** (92%). $^{1}$H NMR (400 MHz, Chloroform-*d*) $\delta$ 8.43 (d, $J$ = 2.0 Hz, 1H), 7.89 (dd, $J$ = 7.5, 2.0 Hz, 1H), 7.23 (dt, $J$ = 7.4, 1.0 Hz, 1H), 3.84 (t, $J$ = 5.2 Hz, 2H), 2.84 (td, $J$ = 6.0, 1.1 Hz, 2H), 2.09 (s, 3H), 2.03 – 2.01 (m, 2H). (Spectroscopic data in agreement with literature[6] in Supporting Information)

*N-Acetyl-7-trifluoromethyl-1,2,3,4-tetrahydroquinoline (**1k**):* 65.67 mg of **1k** (90%). $^{1}$H NMR (400 MHz, Chloroform-*d*) $\delta$ 7.60-7.43 (m, 1H), 7.41-7.15 (m, 2H), 4.45 (t, $J$ = 5.7 Hz, 2H), 2.84 (td, $J$ = 5.6, 1.0 Hz, 2H), 2.10 (p, $J$ = 5.7 Hz, 2H), 2.05 (s, 3H). (Spectroscopic data in agreement with literature[2] in Supporting Information)

*N-Acetyl-2-methyl-1,2,3,4-tetrahydroquinoline (**1l**):* 51.71 mg of **1l** (91%). $^{1}$H NMR (400 MHz, Chloroform-*d*) $\delta$ 7.24 – 7.04 (m, 4H), 4.83 (s, 1H), 2.61 (dt, $J$ = 14.7, 4.7 Hz, 1H), 2.51 (td, $J$ = 13.5, 11.6, 4.6 Hz, 1H), 2.35 (td, $J$ = 12.7, 4.9 Hz, 1H), 2.14 (s, 3H), 1.34 (s, 1H), 1.12 (d, $J$ = 6.5 Hz, 3H). $^{13}$C NMR (100 MHz, Chloroform-*d*) $\delta$ 170.3, 129.5, 129.3, 127.5, 126.4, 126.1, 125.8, 48.6, 32.9, 32.7, 23.3, 20.5.

***General Procedure for the Preparation of Starting Materials 2:*** In a dry, single-neck, 25-mL, round-bottom flask equipped with a stir bar and flushed with nitrogen, acetophenones (1 mmol, 1 equiv.) and selenium dioxide ($SeO_2$, 1.5 mmol, 1.5 equiv.) were added followed by anhydrous pyridine (10 mL). The reaction mixture was heated in an oil bath to 110 ℃ for 1 h, and then the bath temperature was reduced to 90°C. The mixture was stirred at this temperature (90 °C) for an additional 4 h, and progress of the reaction was monitored by TLC. After completion of the reaction, as determined by TLC, the solution containing precipitated selenium was filtered using a Buckner funnel, and the residue was washed with ethyl acetate (50 mL). The combined filtrate was treated with 1N HCl (20 mL), the organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3 × 50 mL). The organic layers were combined and treated with 1N NaOH (50 mL), and the aqueous layer was separated. The organic layer was extracted with water (25 mL) and the combined aqueous layers were acidified using 1N HCl to about pH 1.5. The mixture was extracted with ethyl acetate (3 × 50 mL), and the combined organic layers were dried (anhydrous $Na_2SO_4$) and concentrated on a rotary evaporator (Bath temperature: 40–45°C). The benzoylformic acid products **2** were obtained by silica-gel column chromatography using ethyl acetate=hexane (ratio: 9:1) as solvent system for elution.

*Benzoylformic acid (**2a**):* 79.57 mg of **2a** (53%). $^1$H NMR (400 MHz, Chloroform-*d*) $\delta$ 7.55 (2H, t, $J$ = 7.6 Hz), 7.72 (1H, t, $J$ = 7.6 Hz), 8.33 (2H, d, $J$ = 7.6 Hz), 9.50 (1H, brs). (Spectroscopic data in agreement with literature[3] in Supporting Information)

*3-Methylbenzoylformic acid (**2b**):* 88.65 mg of **2b** (54%).$^1$H NMR (400 MHz, Chloroform-*d*) $\delta$ 7.42 (1H, dt, $J$ = 8.0 Hz, $J$ = 2.4 Hz), 7.54 (1H, dt, $J$ = 8.0 Hz, $J$ = 5.2 Hz), 8.01 (1H, dt, $J$ = 9.2 Hz, $J$ = 2.4 Hz), 8.15 (1H, dd, $J$ = 8.0 Hz, $J$ = 2.4 Hz), 9.76 (1H, brs). (Spectroscopic data in agreement with literature[3] in Supporting Information)

*3-Nitrobenzoylformic acid (**2c**):* 97% (purity), CAS Registry Number : 6330-40-1.

*3-Fluorobenzoylformic acid (**2d**):* 87.42 mg of **2d** (52%). $^1$H NMR (400 MHz, Chloroform-*d*) $\delta$ 7.42 (1H, dt, $J$ = 8.0 Hz, $J$ = 2.4 Hz), 7.54 (1H, dt, $J$ = 8.0 Hz, $J$ = 5.2 Hz), 8.01 (1H, dt, $J$ = 9.2 Hz, $J$ = 2.4 Hz), 8.15 (1H, dd, $J$ = 8.0 Hz, $J$ = 2.4 Hz), 9.76 (1H, brs). (Spectroscopic data in agreement with literature[3] in Supporting Information)

*3-Bromobenzoylformic acid (**2e**):* 97% (purity), CAS Registry Number : 7194-78-7.

*4-Methylbenzoylformic acid (**2f**):* 91.93 mg of **2f** (56%). $^1$H NMR (400 MHz, Chloroform-*d*) $\delta$ 8.98 (brs, 1H), 8.23 (d, $J$ = 7.6 Hz, 2H), 7.33 (d, $J$ = 7.6 Hz, 2H), 2.46 (s, 3H). (Spectroscopic data in agreement with literature[4] in Supporting Information)

*4-Methoxylbenzoylformic acid (**2g**):* 102.69 mg of **2g** (57%). $^1$H NMR (400 MHz, Chloroform-*d*) $\delta$ 9.93 (brs, 1H), 8.33 (d, $J$ = 8.8 Hz, 2H), 6.97 (d, $J$ = 8.8 Hz, 2H), 3.90 (s, 3H). (Spectroscopic data in agreement with literature[4] in Supporting Information)

*4-Fluorobenzoylformic acid (**2h**):* 89.10 mg of **2h** (53%). $^1$H NMR (400 MHz, Chloroform-*d*) $\delta$ 9.66 (brs, 1H), 8.40–8.37 (m, 2H), 7.23–7.19 (m, 2H). (Spectroscopic data in agreement with literature[4] in Supporting Information)

*4-Chlorobenzoylformic acid (**2i**):* 99.67 mg of **2i** (54%). $^1$H NMR (400 MHz, Chloroform-*d*) $\delta$ 9.85 (brs, 1H), 8.27 (d, $J$ = 8.8 Hz, 2H), 7.51 (d, $J$ = 8.4 Hz, 2H). (Spectroscopic data in agreement with literature[4] in Supporting Information)

*4-Nitrobenzoylformic acid (**2j**):* 113.18 mg of **2j** (58%). $^1$H NMR (400 MHz, Chloroform-*d*) $\delta$ 8.55 (d, 2H, $J$ = 9.1 Hz), 8.40 (d, 2H, $J$ = 9.1 Hz), 5.36 (brs, 1H). (Spectroscopic data in agreement with literature[5] in Supporting Information)

*2-Methylbenzoylformic acid (**2k**):* 87.00 mg of **2k** (53%). $^1$H NMR (400 MHz, Chloroform-*d*) $\delta$ 11.02 (brs, 1H), 7.90 (d, $J$ = 7.6 Hz, 1H), 7.50 (t, $J$ = 7.6 Hz, 1H), 7.33–7.29 (m, 2H), 2.59 (s, 3H). (Spectroscopic data in agreement with literature[5] in Supporting Information)

*2-Fluorobenzoylformic acid (**2l**):* 97% (purity), CAS Registry Number : 79477-86-4.

*2-Bromobenzoylformic acid (**2m**):* 97% (purity), CAS Registry Number : 26767-16-8.

*2-Nitrobenzoylformic acid (**2n**):* 97% (purity), CAS Registry Number : 610-33-3.

*1-Naphthylglyoxylic acid (**2o**):* 122.12 mg of **2o** (61%). $^1$H NMR (400 MHz, Chloroform-*d*) $\delta$ 10.03 (brs, 1H), 8.92 (d, $J$ = 8.4 Hz, 1H), 8.37 (d, $J$ = 7.2 Hz, 1H), 8.14 (d, $J$ = 8.4 Hz, 1H), 7.92 (d, $J$ = 8.0 Hz, 1H), 7.72-7.55 (m, 3H). (Spectroscopic data in agreement with literature[4] in Supporting Information)

*2-Naphthylglyoxylic acid (**2p**):* 126.12 mg of **2p** (63%). $^1$H NMR (400 MHz, Chloroform-*d*) $\delta$ 9.97 (brs, 1H), 9.02 (s, 1H), 8.16 (dd, $J$ = 8.8, 1.6 Hz, 1H), 8.00 (d, $J$ = 8.0 Hz, 1H), 7.92–7.86 (m, 2H), 7.69–7.56 (m, 2H). (Spectroscopic data in agreement with literature[4] in Supporting Information)

*2-Thiopheneglyoxylic acid (**2q**):* 97% (purity), CAS Registry Number : 4075-59-6.

*3-Indoleglyoxylic acid (**2r**):* 97% (purity), CAS Registry Number : 1477-49-2.

*Pyruvic acid (**2s**):* 97% (purity), CAS Registry Number : 127-17-3.

*3,3-Dimethyl-2-oxobutyric acid (**2t**):* 97% (purity), CAS Registry Number : 815-17-8.

*1-(8-Benzoyl-3,4-dihydroquinolin-1(2H)-yl)ethan-1-one (**2aa**):* $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 7.62–7.56 (m, 3H), 7.47 (dd, $J$ = 8.8, 6.8 Hz, 3H), 7.43–7.37 (m, 1H),7.22 (d, $J$ = 1.4 Hz, 1H), 3.54 (t, $J$ = 6.4 Hz, 2H), 2.78 (t, $J$ = 6.6 Hz, 2H), 1.96 (t, $J$ = 6.5 Hz, 2H), 1.69 (s, 3H). (Spectroscopic data in agreement with literature[2] in Supporting Information)

***General Procedure for the Preparation of Starting Materials 3:*** Add N-acetyl-1,2,3,4-tetrahydroquinolines (0.2 mmol, 1.0 equiv.), benzoylformic acid (0.3 mmol, 1.5 equiv.), $Pd(OAc)_2$ (0.02 mmol, 10 mol%) and DCE (2 mL) to the vial, the resulting mixture was stirred under 25W blue LED at room temperature for 10 h. After the reaction completed (monitored by TLC), then added DBU (1 mmol, 5 equiv.) to the vial at 80 °C for another 5 h. After the reaction completed (monitored by TLC), added 10 mL water to the mixture, then extracted with DCM 3 times (3 × 20 mL). The extract was dried over anhydrous $Na_2SO_4$. Removal of the solvent under reduced pressure gave a crude product. The crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to yield the desired product **3**.

*1-Phenyl-6,7-dihydropyrido[3,2,1-ij]quinolin-3(5H)-one (**3a**):* (45.98 mg, 0.176 mmol, 88%). Light yellow solid (88%). Mp. 116 – 118 °C. $^1$H NMR (400 MHz, Chloroform-*d*) $\delta$ 7.40 (ddd, $J$ = 33.7, 24.9, 6.4 Hz, 7H), 7.06 (s, 1H), 6.66 (s, 1H), 4.26 (s, 2H), 3.03 (s, 2H), 2.16 (s, 2H). $^{13}$C NMR (100 MHz, Chloroform-*d*) $\delta$ 161.7, 151.1, 137.6, 137.1, 130.2, 129.0, 128.7, 128.6, 125.8, 125.2, 121.6, 121.0, 120.5, 42.6, 28.2, 20.8. HRMS (EI) calcd for $C_{18}H_{15}NO$ (M+): 261.1154. Found: 261.1143. Elemental analysis.calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.76; H, 5.81; N, 5.34. IR (KBr disc): $v$= 1642, 1583 cm$^{-1}$.

*8-Bromo-1-phenyl-6,7-dihydropyrido[3,2,1-ij]quinolin-3(5H)-one* ***(3b)****:* (53.07 mg, 0.156 mmol, 78%). Yellow solid (78%). Mp. 108 – 110 °C. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, J = 6.6 Hz, 2H), 7.44 – 7.36 (m, 3H), 7.32 (d, J = 7.1 Hz, 1H), 7.05 (t, J = 7.7 Hz, 1H), 6.66 (s, 1H), 4.35 – 4.17 (m, 2H), 3.03 (t, J = 6.1 Hz, 2H), 2.16 (p, J = 6.1 Hz, 2H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 161.7, 151.0, 137.6, 137.1, 130.2, 129.0, 128.7, 128.6, 125.8, 125.2, 121.6, 121.0, 120.5, 42.6, 28.1, 20.8. HRMS (EI) calcd for $C_{18}H_{14}BrNO$ (M+): 339.0259. Found: 339.0250. Elemental analysis.calcd for $C_{18}H_{14}BrNO$: C, 63.55; H, 4.15; N, 4.12. Found: C, 63.54; H, 4.15; N, 4.12. IR (KBr disc): *v*= 1643, 1583 cm$^{-1}$.

*1-Phenyl-9-(trifluoromethyl)-6,7-dihydropyrido[3,2,1-ij]quinolin-3(5H)-one* ***(3d)****:* (41.90 mg, 0.150 mmol, 75%). White solid (75%). Mp. 101 – 103 °C. $^1$H NMR (400 MHz, Chloroform-*d*) *δ* 7.65 (s, 1H), 7.57 – 7.49 (m, 4H), 7.40 (dd, *J* = 7.1, 2.4 Hz, 2H), 6.73 (s, 1H), 4.31 – 4.23 (m, 2H), 3.08 (t, *J* = 6.2 Hz, 2H), 2.19 (p, *J* = 6.1 Hz, 2H). $^{13}$C NMR (100 MHz, Chloroform-*d*) *δ* 161.6, 150.9, 139.3, 136.6, 134.4, 129.2, 129.0, 128.9, 126.3, 126.1, 123.1, 122.3, 120.1, 100.1, 42.7, 28.2, 20.5. HRMS (EI) calcd for $C_{19}H_{14}F_3NO$ (M+): 329.1027. Found: 329.1018. Elemental analysis.calcd for $C_{19}H_{14}F_3NO$: C, 69.30; H, 4.28; N, 4.25. Found: C, 69.27; H, 4.27; N, 4.29. IR (KBr disc): *v*= 1652, 1590 cm$^{-1}$.

*9-Methoxy-1-phenyl-6,7-dihydropyrido[3,2,1-ij]quinolin-3(5H)-one(****3e****):* (49.17 mg, 0.176 mmol, 88%). Light yellow solid (88%). Mp. 153 – 155 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) *δ* 7.54 (q, *J* = 6.2 Hz, 3H), 7.47 (d, *J* = 7.1 Hz, 2H), 7.17 – 7.09 (m, 1H), 6.71 (d, *J* = 2.1 Hz, 1H), 6.48 (s, 1H), 4.12 – 4.04 (m, 2H), 3.65 (s, 3H), 2.98 (t, *J* = 5.8 Hz, 2H), 2.02 (q, *J* = 11.7, 8.4 Hz, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) *δ* 159.5, 153.3, 149.5, 136.9, 131.2, 128.7, 128.7, 128.6, 127.1, 120.8, 120.0, 118.0, 107.4, 55.2, 41.7, 27.3, 20.2. HRMS (EI) calcd for $C_{19}H_{17}NO_2$ (M+): 291.1259. Found: 291.1251. Elemental analysis.calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.32; H, 5.87; N, 4.83. IR (KBr disc): *v*= 1646, 1585 cm$^{-1}$.

*9-Fluoro-1-phenyl-6,7-dihydropyrido[3,2,1-ij]quinolin-3(5H)-one(****3f****):* (43.02 mg, 0.154 mmol, 77%). White solid (77%). Mp. 108 – 110 °C. $^1$H NMR (400 MHz, Chloroform-*d*) *δ* 7.48 (d, *J* = 6.9 Hz, 2H), 7.44 – 7.36 (m, 3H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.05 (t, *J* = 7.7 Hz, 1H), 6.66 (s, 1H), 4.30 – 4.22 (m, 2H), 3.03 (t, *J* = 6.2 Hz, 2H), 2.16 (p, *J* = 6.1 Hz, 2H). $^{13}$C NMR (100 MHz, Chloroform-*d*) *δ* 161.7, 151.1, 137.6, 137.1, 130.1, 129.0, 128.7, 128.6, 125.8, 125.2, 121.6, 121.0, 120.5, 42.6, 28.2, 20.8. HRMS (EI) calcd for $C_{18}H_{14}FNO$ (M+): 279.1059. Found: 279.1048. Elemental analysis.calcd for $C_{18}H_{14}FNO$: C, 77.40; H, 5.05; N, 5.01. Found: C, 77.42; H, 5.02; N, 4.99. IR (KBr disc): *v*= 1642, 1583 cm$^{-1}$.

*9-Chloro-1-phenyl-6,7-dihydropyrido[3,2,1-ij]quinolin-3(5H)-one(****3g****):* (43.58 mg, 0.156 mmol, 78%). Yellow solid (78%). Mp. 110 – 112 °C. $^1$H NMR (400 MHz, Chloroform-*d*) *δ*

7.48 (d, *J* = 6.9 Hz, 2H), 7.43 – 7.35 (m, 3H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.05 (t, *J* = 7.7 Hz, 1H), 6.66 (s, 1H), 4.31 – 4.22 (m, 2H), 3.03 (t, *J* = 6.2 Hz, 2H), 2.15 (p, *J* = 6.1 Hz, 2H). $^{13}$C NMR (100 MHz, Chloroform-*d*) $\delta$ 161.6, 151.0, 137.6, 137.1, 130.1, 129.0, 128.7, 128.6, 125.8, 125.2, 121.6, 121.0, 120.5, 42.6, 28.1, 20.8. HRMS (EI) calcd for $C_{18}H_{14}ClNO$ (M+): 295.0764. Found: 295.0769. Elemental analysis.calcd for $C_{18}H_{14}ClNO$: C, 73.10; H, 4.77; N, 4.74. Found: C, 73.12; H, 4.78; N,4.70. IR (KBr disc): *v*= 1642, 1583 cm$^{-1}$.

*9-Bromo-1-phenyl-6,7-dihydropyrido[3,2,1-ij]quinolin-3(5H)-one(**3h**):* (44.70 mg, 0.160 mmol, 80%). Light yellow solid (80%). Mp. 115 – 117 °C. $^{1}$H NMR (400 MHz, Chloroform-*d*) $\delta$ 7.48 (d, *J* = 6.5 Hz, 2H), 7.44 – 7.36 (m, 3H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.05 (t, *J* = 7.7 Hz, 1H), 6.66 (s, 1H), 4.35 – 4.19 (m, 2H), 3.03 (t, *J* = 6.0 Hz, 2H), 2.16 (p, *J* = 6.1 Hz, 2H). $^{13}$C NMR (100 MHz, Chloroform-*d*) $\delta$ 161.6, 151.0, 137.6, 137.1, 130.1, 129.0, 128.7, 128.6, 125.8, 125.2, 121.6, 121.0, 120.5, 42.6, 28.2, 20.8. HRMS (EI) calcd for $C_{18}H_{14}BrNO$ (M+): 339.0259. Found: 339.0257. Elemental analysis.calcd for $C_{18}H_{14}BrNO$: C, 63.55; H, 4.15; N, 4.12. Found: C, 63.54; H, 4.16; N, 4.12. IR (KBr disc): *v*= 1642, 1583 cm$^{-1}$.

*9-Methyl-1-phenyl-6,7-dihydropyrido[3,2,1-ij]quinolin-3(5H)-one(**3i**):* (48.10 mg, 0.174 mmol, 87%). Light yellow solid (87%). Mp. 145 – 147 °C. $^{1}$H NMR (400 MHz, Chloroform-*d*) $\delta$ 7.53 – 7.45 (m, 3H), 7.40 (dd, *J* = 7.4, 2.0 Hz, 2H), 7.18 – 7.12 (m, 2H), 6.63 (s, 1H), 4.28 – 4.20 (m, 2H), 2.99 (t, *J* = 6.2 Hz, 2H), 2.28 (s, 3H), 2.14 (p, *J* = 6.1 Hz, 2H). $^{13}$C NMR (100 MHz, Chloroform-*d*) $\delta$ 161.5, 150.8, 137.8, 135.1, 131.5, 131.1, 129.0, 128.6, 128.6, 125.3, 125.1, 121.1, 120.4, 50.3, 42.5, 28.1, 20.9. HRMS (EI) calcd for $C_{19}H_{17}NO$ (M+): 275.1310. Found: 275.1313. Elemental analysis.calcd for $C_{19}H_{17}NO$: C, 82.88; H, 6.22; N, 5.09. Found: C, 82.89; H, 6.21; N, 5.09. IR (KBr disc): *v*= 1643, 1582 cm$^{-1}$.

*3-Methyl-7-phenyl-2,3-dihydro-1H,5H-pyrido[3,2,1-ij]quinolin-5-one (**3l**):* (49.21 mg, 0.178 mmol, 89%). Light yellow solid (89%). Mp. 116 – 118 °C. $^{1}$H NMR (400 MHz, Chloroform-*d*) $\delta$ 7.48 (q, *J* = 5.2 Hz, 3H), 7.43 – 7.32 (m, 4H), 7.06 (t, *J* = 7.7 Hz, 1H), 6.65 (s, 1H), 5.42 – 5.31 (m, 1H), 3.30 – 3.17 (m, 1H), 2.92 (d, *J* = 18.2 Hz, 1H), 2.15 – 2.02 (m, 2H), 1.38 (d, *J* = 6.6 Hz, 3H). $^{13}$C NMR (100 MHz, Chloroform-*d*) $\delta$ 161.1, 151.0, 137.7, 136.3, 130.5, 129.0, 128.6, 128.6, 125.9, 124.4, 121.4, 121.4, 120.8, 46.0, 25.9, 23.1, 18.2. HRMS (EI) calcd for $C_{19}H_{17}NO$ (M+): 275.1310. Found: 275.1312. Elemental analysis.calcd for $C_{19}H_{17}NO$: C, 82.88; H, 6.22; N, 5.09. Found: C, 82.88; H, 6.21; N, 5.10. IR (KBr disc): *v*= 1644, 1582 cm$^{-1}$.

*1-(m-tolyl)-6,7-dihydropyrido[3,2,1-ij]quinolin-3(5H)-one (**3m**):* (51.40 mg, 0.184 mmol, 92%). White solid (92%). Mp. 126 – 128 °C. $^{1}$H NMR (400 MHz, Chloroform-*d*) $\delta$ 7.44 – 7.27 (m, 4H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.06 (t, *J* = 7.7 Hz, 1H), 6.65 (s, 1H), 4.32 – 4.21 (m, 2H), 3.03 (t, *J* = 6.1 Hz, 2H), 2.43 (s, 3H), 2.16 (p, *J* = 6.0 Hz, 2H).

$^{13}$C NMR (100 MHz, Chloroform-*d*) $\delta$ 161.7, 151.3, 138.4, 137.5, 137.1, 130.1, 129.7, 129.4, 128.5, 126.1, 125.9, 125.2, 121.6, 120.9, 120.6, 42.6, 28.2, 21.6, 20.8. HRMS (EI) calcd for $C_{19}H_{17}NO$ (M+): 275.1310. Found: 275.1301. Elemental analysis.calcd for $C_{19}H_{17}NO$: C, 82.88; H, 6.22; N, 5.09. Found: C, 82.86; H, 6.23; N, 5.10. IR (KBr disc): *v*= 1644, 1582 cm$^{-1}$.

*1-(3-nitrophenyl)-6,7-dihydropyrido[3,2,1-ij]quinolin-3(5H)-one (**3n**):* (44.70 mg, 0.160 mmol, 80%). Yellow solid (80%). Mp. 121 – 123 °C. $^1$H NMR (400 MHz, Chloroform-*d*) $\delta$ 8.40 – 8.27 (m, 2H), 7.79 – 7.65 (m, 2H), 7.37 (d, *J* = 7.1 Hz, 1H), 7.22 (d, *J* = 7.7 Hz, 1H), 7.09 (t, *J* = 7.7 Hz, 1H), 6.68 (s, 1H), 4.34 – 4.21 (m, 2H), 3.05 (t, *J* = 6.1 Hz, 2H), 2.18 (p, *J* = 6.0 Hz, 2H). $^{13}$C NMR (100 MHz, Chloroform-*d*) $\delta$ 161.2, 148.4, 139.2, 137.2, 135.0, 130.7, 129.9, 125.7, 125.0, 124.1, 123.7, 122.1, 121.7, 119.7, 42.7, 28.1, 20.7. HRMS (EI) calcd for $C_{18}H_{14}N_2O_3$ (M+): 306.1004. Found: 306.1021. Elemental analysis.calcd for $C_{18}H_{14}N_2O_3$: C, 70.58; H, 4.61; N, 9.15; Found: C, 70.59; H, 4.62; N, 9.13; IR (KBr disc): *v*= 1648, 1587 cm$^{-1}$.

*1-(3-fluorophenyl)-6,7-dihydropyrido[3,2,1-ij]quinolin-3(5H)-one (**3o**):* (47.49 mg, 0.170 mmol, 85%). Yellow solid (85%). Mp.101 – 103 °C. $^1$H NMR (400 MHz, Chloroform-*d*) $\delta$ 7.46 (td, *J* = 7.9, 5.9 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.22 – 7.11 (m, 3H), 7.07 (t, *J* = 7.7 Hz, 1H), 6.65 (s, 1H), 4.31 – 4.21 (m, 2H), 3.04 (t, *J* = 6.2 Hz, 2H), 2.16 (p, *J* = 6.1 Hz, 2H). $^{13}$C NMR (100 MHz, Chloroform-*d*) $\delta$ 164.0, 155.6 (d, *J* = 1183 Hz), 139.7 (d, *J* = 7 Hz), 137.2, 130.375 (d, *J* = 8 Hz), 130.368, 125.5, 125.4, 124.8(d, *J* = 3 Hz), 121.8, 121.2, 120.1, 116.2 (d, *J* = 22 Hz), 115.8, 115.6, 42.6, 28.1, 20.8. HRMS (EI) calcd for $C_{18}H_{14}FNO$ (M+): 279.1059. Found: 279.1032. Elemental analysis.calcd for $C_{18}H_{14}FNO$: C, 77.40; H, 5.05; N, 5.01. Found: C, 77.41; H, 5.04; N, 5.01. IR (KBr disc): *v*= 1644, 1583 cm$^{-1}$.

*1-(3-bromophenyl)-6,7-dihydropyrido[3,2,1-ij]quinolin-3(5H)-one (**3p**):* (48.05 mg, 0.172 mmol, 86%). White solid (86%). Mp. 169 – 171 °C. $^1$H NMR (400 MHz, Chloroform-*d*) $\delta$ 7.61 (dt, *J* = 7.2, 2.0 Hz, 1H), 7.59 – 7.53 (m, 1H), 7.35 (p, *J* = 9.1, 8.4 Hz, 4H), 7.12 – 7.05 (m, 1H), 6.64 (s, 1H), 4.30 – 4.22 (m, 2H), 3.04 (t, *J* = 6.2 Hz, 2H), 2.16 (p, *J* = 6.1 Hz, 2H). $^{13}$C NMR (100 MHz, Chloroform-*d*) $\delta$ 161.4, 149.4, 139.6, 137.1, 131.9, 131.8, 130.4, 130.3, 127.7, 125.5, 125.4, 122.7, 121.8, 121.3, 120.1, 42.6, 28.1, 20.8. HRMS (EI) calcd for $C_{18}H_{14}BrNO$ (M+): 339.0259. Found: 339.0245. Elemental analysis.calcd for $C_{18}H_{14}BrNO$: C, 63.55; H, 4.15; N, 4.12. Found: C, 63.57; H, 4.13; N, 4.12. IR (KBr disc): *v*= 1643, 1582 cm$^{-1}$.

*1-(p-tolyl)-6,7-dihydropyrido[3,2,1-ij]quinolin-3(5H)-one (**3q**):* (50.84 mg, 0.182 mmol, 91%). Gray solid (91%). Mp. 103 – 104 °C. $^1$H NMR (400 MHz, Chloroform-*d*) $\delta$ 7.41 (d, *J* = 7.2 Hz, 1H), 7.34 – 7.27 (m, 5H), 7.08 – 7.02 (m, 1H), 6.65 (s, 1H), 4.29 – 4.21 (m, 2H), 3.03 (t, *J* = 6.2 Hz, 2H), 2.44 (s, 3H), 2.16 (q, *J* = 6.1, 5.7 Hz, 2H). $^{13}$C NMR (100 MHz, Chloroform-*d*) $\delta$ 161.7, 151.1, 138.6, 137.1, 134.7, 130.1, 129.3, 129.0,

125.8, 125.2, 121.5, 120.9, 120.6, 42.6, 28.2, 21.4, 20.8. HRMS (EI) calcd for $C_{19}H_{17}NO$ (M+): 275.1310. Found: 275.1317. Elemental analysis.calcd for $C_{19}H_{17}NO$: C, 82.88; H, 6.22; N, 5.09. Found: C, 82.89; H, 6.25; N, 5.05. IR (KBr disc): *v*= 1650, 1584cm$^{-1}$.

*1-(4-methoxyphenyl)-6,7-dihydropyrido[3,2,1-ij]quinolin-3(5H)-one* ***(3r)****:*(48.61 mg, 0.174 mmol, 87%). Light yellow solid (87%). Mp. 103 – 105 °C. $^1$H NMR (400 MHz, Chloroform-*d*) $\delta$ 7.44 (d, *J* = 8.0 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.31 (d, *J* = 6.7 Hz, 1H), 7.08 – 7.00 (m, 3H), 6.64 (s, 1H), 4.28 – 4.22 (m, 2H), 3.88 (s, 3H), 3.03 (t, *J* = 6.1 Hz, 2H), 2.15 (p, *J* = 6.1 Hz, 2H). $^{13}$C NMR (100 MHz, Chloroform-*d*) $\delta$ 161.8, 160.0, 150.8, 137.1, 130.3, 130.1, 129.9, 125.8, 125.2, 121.5, 120.8, 120.7, 114.1, 55.5, 42.6, 28.2, 20.8. HRMS (EI) calcd for $C_{19}H_{17}NO_2$ (M+): 291.1259. Found: 291.1237. Elemental analysis.calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.35; H, 5.84; N, 4.83. IR (KBr disc): *v*= 1644, 1586 cm$^{-1}$.

*1-(4-fluorophenyl)-6,7-dihydropyrido[3,2,1-ij]quinolin-3(5H)-one* ***(3s)****:* (44.70 mg, 0.160 mmol, 80%). White solid (80%). Mp. 118 – 120 °C. $^1$H NMR (400 MHz, Chloroform-*d*) $\delta$ 7.42 – 7.37 (m, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.22 – 7.15 (m, 2H), 7.07 (t, *J* = 7.7 Hz, 1H), 6.64 (s, 1H), 4.29 – 4.22 (m, 2H), 3.04 (t, *J* = 6.2 Hz, 2H), 2.16 (p, *J* = 6.1 Hz, 2H). $^{13}$C NMR (100 MHz, Chloroform-*d*) $\delta$ 161.5, 150.0, 137.1, 133.5, 132.2 (d, *J* = 259 Hz), 130.8, 130.8, 130.3, 125.5, 125.3, 121.7, 121.2, 120.4, 115.9, 115.6, 42.6, 28.1, 20.8. HRMS (EI) calcd for $C_{18}H_{14}FNO$ (M+): 279.1059. Found: 279.1051. Elemental analysis.calcd for $C_{18}H_{14}FNO$: C, 77.40; H, 5.05; N, 5.01. Found: C, 77.42; H, 5.03; N, 5.02. IR (KBr disc): *v*= 1642, 1582 cm$^{-1}$.

*1-(4-chlorophenyl)-6,7-dihydropyrido[3,2,1-ij]quinolin-3(5H)-one* ***(3t)****:* (46.37 mg, 0.166 mmol, 83%). Gray solid (83%). Mp. 145 – 147 °C. $^1$H NMR (400 MHz, Chloroform-*d*) $\delta$ 7.50 – 7.43 (m, 2H), 7.39 – 7.29 (m, 4H), 7.10 – 7.03 (m, 1H), 6.63 (s, 1H), 4.28 – 4.21 (m, 2H), 3.03 (t, *J* = 6.2 Hz, 2H), 2.16 (p, *J* = 6.4 Hz, 2H). $^{13}$C NMR (100 MHz, Chloroform-*d*) $\delta$ 161.5, 149.8, 136.0, 134.9, 134.9, 130.4, 130.4, 129.0, 125.5, 125.4, 121.7, 121.2, 120.2, 42.6, 28.1, 20.8. HRMS (EI) calcd for $C_{18}H_{14}ClNO$ (M+): 295.0764. Found: 295.0742. Elemental analysis.calcd for $C_{18}H_{14}ClNO$: C, 73.10; H, 4.77; N, 4.74. Found: C, 73.12; H, 4.79; N, 4.70. IR (KBr disc): *v*= 1649, 1583 cm$^{-1}$.

*1-(4-nitrophenyl)-6,7-dihydropyrido[3,2,1-ij]quinolin-3(5H)-one* ***(3u)****:* (44.70 mg, 0.160 mmol, 80%). Yellow solid (80%). Mp. 173 – 175 °C. $^1$H NMR (400 MHz, Chloroform-*d*) $\delta$ 8.37 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 7.1 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.09 (t, *J* = 7.7 Hz, 1H), 6.67 (s, 1H), 4.31 – 4.22 (m, 2H), 3.05 (t, *J* = 6.2 Hz, 2H), 2.17 (p, *J* = 6.1 Hz, 2H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 161.1, 148.7, 148.2, 144.1, 137.2, 130.7, 130.1, 125.6, 125.1, 124.0, 122.0, 121.5, 119.5, 42.7, 28.1, 20.7. HRMS (EI) calcd for $C_{18}H_{14}N_2O_3$ (M+): 306.1004. Found: 306.1029.

Elemental analysis. calcd for $C_{18}H_{14}N_2O_3$: C, 70.58; H, 4.61; N, 9.15. Found: C, 70.59; H, 4.63; N, 9.12. IR (KBr disc): *v*= 1652, 1587 $cm^{-1}$.

*1-(o-tolyl)-6,7-dihydropyrido[3,2,1-ij]quinolin-3(5H)-one (**3v**):* (43.58 mg, 0.156 mmol, 78%). Yellow solid (78%). Mp. 65 – 67 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 7.40 (d, $J$ = 7.2 Hz, 3H), 7.33 (t, $J$ = 7.2 Hz, 1H), 7.19 (d, $J$ = 7.4 Hz, 1H), 7.06 (t, $J$ = 7.6 Hz, 1H), 6.83 (d, $J$ = 7.9 Hz, 1H), 6.42 (s, 1H), 4.12 (t, $J$ = 7.1 Hz, 2H), 2.99 (t, $J$ = 5.9 Hz, 2H), 2.05 (s, 5H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 160.1, 150.0, 136.5, 136.4, 135.1, 130.1, 130.1, 128.7, 128.5, 126.0, 125.2, 124.6, 121.5, 120.3, 119.5, 41.8, 27.0, 20.1, 19.3. HRMS (EI) calcd for $C_{19}H_{17}NO$ (M+): 275.1310. Found: 275.1323. Elemental analysis.calcd for $C_{19}H_{17}NO$: C, 82.88; H, 6.22; N, 5.09. Found: C, 82.89; H, 6.21; N, 5.08. IR (KBr disc): *v*= 1651, 1586 $cm^{-1}$.

*1-(2-fluorophenyl)-6,7-dihydropyrido[3,2,1-ij]quinolin-3(5H)-one (**3w**):* (41.90 mg, 0.150 mmol, 75%). Light yellow solid (75%). Mp. 130 – 131 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 7.63 – 7.56 (m, 1H), 7.50 – 7.36 (m, 4H), 7.11 (t, $J$ = 7.6 Hz, 1H), 7.03 (d, $J$ = 8.2 Hz, 1H), 6.58 (s, 1H), 4.19 – 4.06 (m, 2H), 2.99 (t, $J$ = 5.7 Hz, 2H), 2.12 – 2.02 (m, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 159.8, 158.7 (d, $J$ = 244 Hz), 144.6, 136.3, 131.1 (d, $J$ = 8 Hz), 131.0 (d, $J$ = 3 Hz), 130.3, 125.3, 124.9 (d, $J$ = 3 Hz), 124.5, 124.2 (d, $J$ = 16 Hz), 121.6, 121.5, 119.0, 115.8 (d, $J$ = 22 Hz), 41.9, 27.0, 20.0. HRMS (EI) calcd for $C_{18}H_{14}FNO$ (M+): 279.1059. Found: 279.1051. Elemental analysis.calcd for $C_{18}H_{14}FNO$: C, 77.40; H, 5.05; N, 5.01. Found: C, 77.42; H, 5.02; N, 5.02. IR (KBr disc): *v*= 1650, 1587 $cm^{-1}$.

*1-(2-bromophenyl)-6,7-dihydropyrido[3,2,1-ij]quinolin-3(5H)-one (**3x**):* (44.14 mg, 0.158 mmol, 79%). Yellow solid (79%). Mp. 67 – 69 °C. $^1$H NMR (400 MHz, Chloroform-*d*) $\delta$ 7.70 (d, $J$ = 7.5 Hz, 1H), 7.43 (t, $J$ = 7.4 Hz, 1H), 7.37 – 7.27 (m, 3H), 7.12 – 6.90 (m, 2H), 6.62 (s, 1H), 4.27 (t, $J$ = 5.8 Hz, 2H), 3.03 (t, $J$ = 5.3 Hz, 2H), 2.18 (dt, $J$ = 12.2, 5.9 Hz, 2H). $^{13}$C NMR (100 MHz, Chloroform-*d*) $\delta$ 161.5, 150.0, 138.3, 136.8, 133.1, 130.8, 130.2, 130.1, 127.6, 125.5, 125.2, 122.8, 121.7, 121.7, 120.0, 42.6, 28.0, 20.8. HRMS (EI) calcd for $C_{18}H_{14}BrNO$ (M+): 339.0259. Found: 339.0267. Elemental analysis.calcd for $C_{18}H_{14}BrNO$: C, 63.55; H, 4.15; N, 4.12. Found: C, 63.57; H, 4.13; N, 4.11. IR (KBr disc): *v*= 1648, 1584 $cm^{-1}$.

*1-(naphthalen-1-yl)-6,7-dihydropyrido[3,2,1-ij]quinolin-3(5H)-one (**3z**):* (49.72 mg, 0.178 mmol, 89%). Gray solid (89%). Mp. 131 – 133 °C $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.94 (dd, $J$ = 11.2, 8.4 Hz, 2H), 7.60 – 7.52 (m, 2H), 7.52 – 7.47 (m, 1H), 7.42 (dd, $J$ = 7.0, 1.0 Hz, 1H), 7.36 (ddd, $J$ = 8.2, 6.9, 1.2 Hz, 1H), 7.29 (t, $J$ = 4.4 Hz, 1H), 6.90 (d, $J$ = 4.6 Hz, 2H), 6.77 (s, 1H), 4.39 – 4.26 (m, 2H), 3.06 (t, $J$ = 6.2 Hz, 2H), 2.21 (p, $J$ = 7.2, 6.3 Hz, 2H). $^{13}$C NMR (100 MHz, Chloroform-*d*) $\delta$ 161.7, 150.0, 136.8, 135.2, 133.5, 131.7, 130.2, 129.0, 128.4, 126.9, 126.6, 126.3, 126.2, 126.0, 125.5, 125.1, 122.4, 121.7, 121.5, 42.6, 28.1, 20.9. HRMS (EI) calcd for $C_{22}H_{17}NO$ (M+): 311.1310.

Found: 311.1334. Elemental analysis.calcd for $C_{22}H_{17}NO$: C, 84.86; H, 5.50; N, 4.50. Found: C, 84.88; H, 5.51; N, 4.48. IR (KBr disc): *v*= 1655, 1584 $cm^{-1}$.

*1-(naphthalen-2-yl)-6,7-dihydropyrido[3,2,1-ij]quinolin-3(5H)-one (**3za**):* (49.17 mg, 0.176 mmol, 88%). Yellow solid (88%). Mp. 201 – 203 °C. $^1$H NMR (400 MHz, Chloroform-*d*) $\delta$ 8.00 – 7.86 (m, 4H), 7.61 – 7.49 (m, 3H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 7.0 Hz, 1H), 7.05 (t, *J* = 7.7 Hz, 1H), 6.76 (s, 1H), 4.35 – 4.23 (m, 2H), 3.05 (t, *J* = 6.1 Hz, 2H), 2.19 (dd, *J* = 11.2, 5.2 Hz, 2H). $^{13}$C NMR (100 MHz, Chloroform-*d*) $\delta$ 161.7, 151.1, 137.2, 135.1, 133.3, 133.3, 130.2, 128.4, 128.3, 128.2, 127.9, 126.8, 126.8, 126.8, 125.9, 125.3, 121.7, 121.4, 120.6, 42.6, 28.2, 20.9. HRMS (EI) calcd for $C_{22}H_{17}NO$ (M+): 311.1310. Found: 311.1334. Elemental analysis. calcd for $C_{22}H_{17}NO$: C, 84.86; H, 5.50; N, 4.50. Found: C, 84.87; H, 5.51; N, 4.48. IR (KBr disc): *v*= 1642, 1584 $cm^{-1}$.

*HBV inhibitor:* (46.53 mg, 0.170 mmol, 85%). $^1$H NMR (400 MHz, Chloroform-*d*) $\delta$ 12.90 (s, 1H), 7.54 (t, *J* = 5.3 Hz, 4H), 7.49 (s, 2H), 7.48 – 7.43 (m, 2H), 6.72 (s, 1H). CAS Registry Number : 30169-33-6.

***Mechanistic studies:*** Add N-acetyl-1,2,3,4-tetrahydroquinolines (0.2 mmol, 1.0 equiv.), benzoylformic acid (0.3 mmol, 1.5 equiv.), $Pd(OAc)_2$ (0.02 mmol, 10 mol%), TEMPO (0.4 mmol, 2.0 equiv.) and DCE (2 mL) to the vial, the resulting mixture was stirred under 25W blue LED at room temperature for 10 h. After the reaction was completed, it was cooled to room temperature and quenched with water and extracted with ethyl acetate and then dried with $Na_2SO_4$. The organic phase was concentrated under reduced pressure to yield the crude product, which was further purified by flash chromatography on silica gel (eluant: petroleum ether/ethyl acetate = 15:1, V/V) to provide the 2,2,6,6-tetramethylpiperidino benzoate **4** in 81% yield.

*2,2,6,6-tetramethylpiperidino benzoate:* $^1$H NMR (400 MHz, Chloroform-*d*) $\delta$ 8.11 – 8.05 (m, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 1.84 – 1.69 (m, 3H), 1.59 (d, J = 12.5 Hz, 2H), 1.49 – 1.42 (m, 1H), 1.28 (s, 6H), 1.12 (s, 6H). $^{13}$C NMR (100 MHz, Chloroform-*d*) $\delta$ 166.5, 133.0, 129.9, 129.7, 128.6, 60.6, 39.2, 32.1, 21.0, 17.2.

## ASSOCIATED CONTENT

### Supporting Information

Copies of $^1$H and $^{13}$C NMR spectra of all products.

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**Notes**

The authors declare no competing financial interest.

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