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Visible-Light-Induced Photocatalytic Aerobic Oxidation / Povarov Cyclization Reaction: Synthesis of Substituted Quinoline-Fused Lactones

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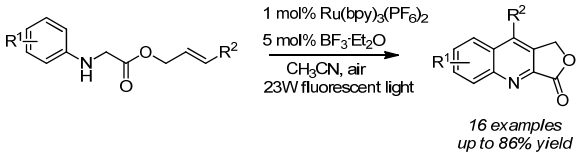
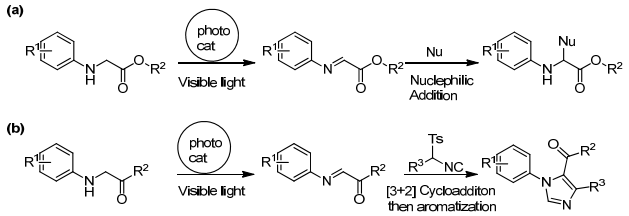


ABSTRACT

A one-step construction of quinoline-fused lactones was achieved by visible-light-induced photocatalytic aerobic oxidation / Povarov cyclization reaction. This method provides a new access to the synthesis of important fused heterocycles under mild reaction conditions.

INTRODUCTION

In the past few years, visible-light-induced chemical transformations have received much attention from synthetic organic chemists because they provide a green and sustainable protocol for organic synthesis via radical species.[1] Among these chemical reactions, the oxidation of tertiary amines to iminium ions followed by further functionalization has seen a recent surge.[2] However, the application to secondary amines or primary amines remains a challenge due to the relatively high oxidation potentials. Recently, Li, Rueping, and Wu have elegantly described a series of visible-light-promoted functionalization of secondary amines. However, the above-mentioned photoredox reactions have been limited only to the nucleophilic addition to imines by various nucleophiles so far (**Scheme 1a**).[3] In 2014, Xiao and co-workers disclosed a concise synthesis of imidazoles through visible-light-induced photocatalytic aerobic oxidation / [3+2] cycloaddition / aromatization cascade between secondary amines and isocyanides (**Scheme 1b**).[4] Despite these advances, to our knowledge, the visible-light induced photocatalytic sequential generation of imines and application of these reactive intermediates to the Povarov cyclization reaction have never been explored.



Scheme 1. Visible-light-promoted functionalization of secondary amines

On the other hand, lactone-fused heterocycles are widely found in a large number of biologically active natural products as well as in agrochemicals and other pharmaceuticals. Among these compounds, quinoline-fused lactones are important members of these kinds of heterocycles and they also serve as synthons for the synthesis of drugs and materials, such as uncialamycin,[5] luotonin **A**,[6] and quinoline-carboxamides **B**[7] (**Figure 1**). Therefore, the development of the methods for the preparation of quinoline-fused lactones has attracted much attention from organic chemists. General strategies toward the synthesis of them by oxidative Povarov cyclization have been reported by several groups, in which harsh condition and toxic oxidants were used (**Scheme 2a**).[8] Recently, Jia and co-workers also have reported the intramolecular Povarov cyclization for the synthesis of quinoline-fused lactones by radical cation salt (**Scheme 2b**).[9] Given the importance of them, the development of a straightforward and efficient procedure from easily available starting materials under mild conditions is still required for the acquisition of quinoline-fused lactones.

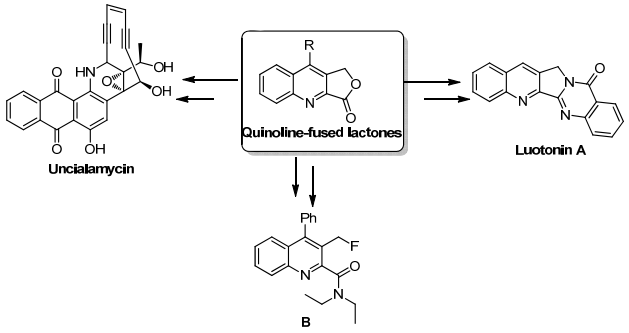
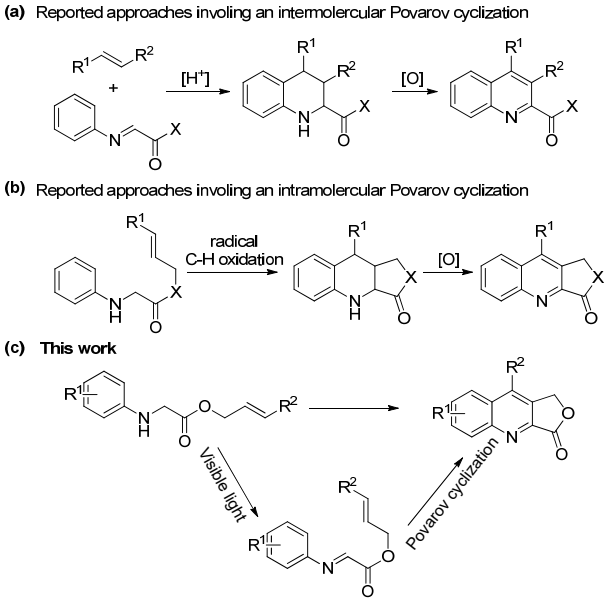


Figure 1. Quinoline-fused lactones were used as synthons

As part of our ongoing efforts to develop novel and efficient photocatalytic reactions, we herein disclose the preparation of quinoline-fused lactones from cinnamyl 2-(phenylamino)acetates via a visible-light-induced photocatalytic aerobic oxidation / Povarov cyclization (**Scheme 2c**).

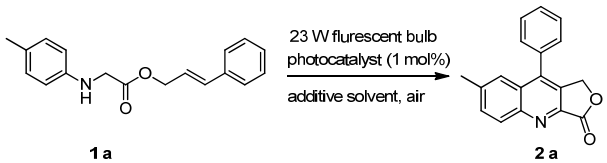


Scheme 2. The Povarov cyclization for synthesis of quinoline derivatives

RESULTS AND DISCUSSION

We initiated our investigation by examining the reaction of cinnamyl 2-(*p*-tolylamino) acetate (**1a**) with $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (1 mol%) in CH_3CN (3 mL) under a 23W fluorescent light irradiation for 24 h (**Table 1,** entry 1). Unfortunately, no target product was obtained along with some byproduct (Cinnamyl 2-oxo-2-(*p*-tolylamino)acetate). This indicated that the intramolecular [4+2] cycloaddition needed to be accelerated. To our delight, a good result was achieved by the addition of 10 mol% $ZnCl_2$, giving desired product in 40% yield (**Table 1,** entry 2). Considering that the identity of the catalyst plays a key role in photoredox catalysis, some commonly-used photocatalysts were investigated. When $Ru(bpy)_3(PF_6)_2$ or $[Ir(ppy)(dtb\text{-}bpy)](PF_6)$ was used as the catalyst, the desired product can be obtained in 42 % and 44% yield, respectively (**Table 1,** entries 3, 4). Next, our attention was paid to screening the additives. The Lewis acid had a pronounced effect on the reaction efficiency. [3b] Zinc acetate as a common Lewis acid has been widely used in organic reaction, but it did not work well in our reaction. Only a trace of desired product was obtained (**Table 1,** entry 5). Other Lewis acids were also investigated (**Table 1,** entries 6-10). To our delight, a satisfactory yield of 75% was obtained when 10 mol% of $BF_3{\cdot}Et_2O$ was used (**Table 1,** entry 10). Subsequently, we tested the solvents in this reaction, and CH_3CN was found to be the best solvent (**Table 1,** entries 10-14). Further optimization showed that the loading of Lewis acid could be decreased to 5 mol% without any loss in terms of product yield (**Table 1,** entry 16). Besides that, some control experiments were conducted. It is noteworthy that 18% of desired product was obtained when $Ru(bpy)_3Cl_2{\cdot}6H_2O$ was absent and no desired product was observed when the reaction was conducted in the dark or under N_2 atmosphere (**Table 1,** entries 18- 20).

Table 1. Optimization of the reaction conditions[a]



1a **2a**

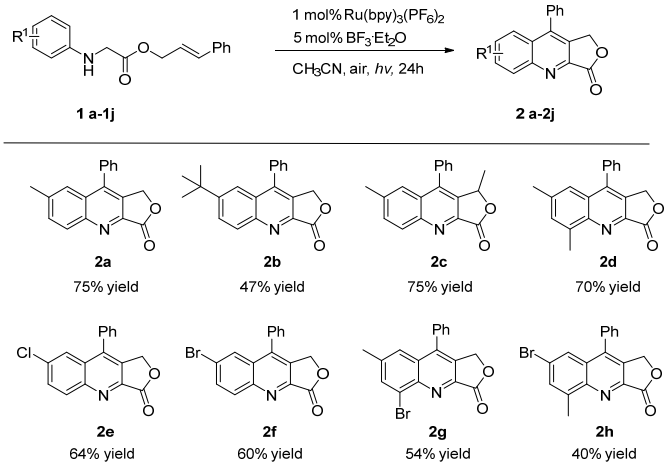
Entry	Cat. (1 mol %)	Add. (eq)	Solvent	Yield[b] (%)
1	$Ru(bpy)_3Cl_2$	-----	CH_3CN	0
2	$Ru(bpy)_3Cl_2$	$ZnCl_2$	CH_3CN	40
3	$Ru(bpy)_3(PF_6)_2$	$ZnCl_2$	CH_3CN	42
4	$[Ir(ppy)(dtb\text{-}bpy)](PF_6)$	$ZnCl_2$	CH_3CN	44
5	$Ru(bpy)_3(PF_6)_2$	$Zn(OAc)_2$	CH_3CN	trace
6	$Ru(bpy)_3(PF_6)_2$	$ZnBr_2$	CH_3CN	48
7	$Ru(bpy)_3(PF_6)_2$	$Zn(OTf)_2$	CH_3CN	62
8	$Ru(bpy)_3(PF_6)_2$	$CeCl_3{\cdot}7H_2O$	CH_3CN	62
9	$Ru(bpy)_3(PF_6)_2$	$FeCl_3{\cdot}6H_2O$	CH_3CN	37
10	$Ru(bpy)_3(PF_6)_2$	$BF_3{\cdot}Et_2O$	CH_3CN	75
11	$Ru(bpy)_3(PF_6)_2$	$BF_3{\cdot}Et_2O$	MeOH	0
12	$Ru(bpy)_3(PF_6)_2$	$BF_3{\cdot}Et_2O$	DMF	0
13	$Ru(bpy)_3(PF_6)_2$	$BF_3{\cdot}Et_2O$	DMSO	trace
14	$Ru(bpy)_3(PF_6)_2$	$BF_3{\cdot}Et_2O$	DCM	28
15[c]	$Ru(bpy)_3(PF_6)_2$	$BF_3{\cdot}Et_2O$	CH_3CN	60
16[d]	$Ru(bpy)_3(PF_6)_2$	$BF_3{\cdot}Et_2O$	CH_3CN	75
17[e]	$Ru(bpy)_3(PF_6)_2$	$BF_3{\cdot}Et_2O$	CH_3CN	68
18[f]		$BF_3{\cdot}Et_2O$	CH_3CN	18
19[g]	$Ru(bpy)_3(PF_6)_2$	$BF_3{\cdot}Et_2O$	CH_3CN	0
20[h]	$Ru(bpy)_3(PF_6)_2$	$BF_3{\cdot}Et_2O$	CH_3CN	0

[a] Conditions: **1a** (0.3 mmol), photocatalyst (1 mol%), Lewis acid (0.1 equiv), solvent (3 mL), irradiation with 23W household light bulb at rt for 24 h. [b] Isolated yield. [c] $BF_3{\cdot}Et_2O$ (0.2 eq). [d] $BF_3{\cdot}Et_2O$ (0.05 eq). [e] $BF_3{\cdot}Et_2O$ (0.025 eq). [f] Without photocatalyst. [g] Without light. [h] Under N_2 atmosphere.

Under the optimized conditions, a series of *N*-aryl glycine cinnamyl ester derivatives were tested to investigate the scope of substrates for the reaction, and the results are listed in **Table 2**. Substrates with either an electron-withdrawing group or an electron-donating group at the aniline ring gave the desired quinoline-fused lactones

in moderate to good yields (40-75%) (**Table 2, 2b**-**2h**); Substrates bearing halogen atoms, such as Cl and Br were well-tolerated, and the products are more useful in functionalization of natural products and pharmaceuticals (**Table 2, 2e**-**2h**); The substitution on *ortho* position to the NH-group did not compromise the reaction efficiency (**Table 2, 2d, 2g, 2h**).

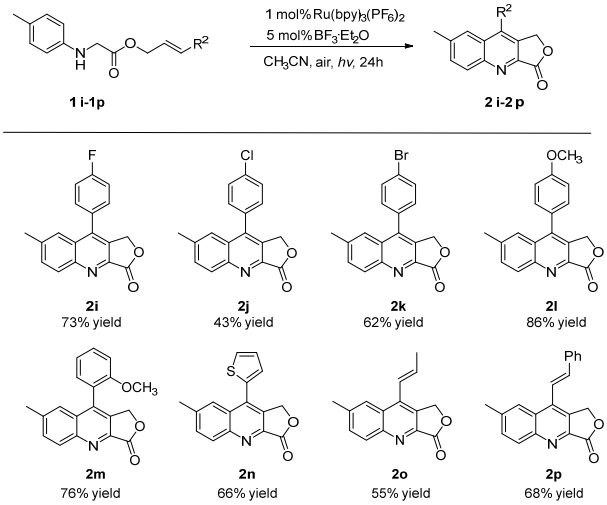
Table 2 Intramolecular Cyclization of *N*-Aryl Glycine Cinnamyl Esters[a]



[a] Conditions: **1a-1h** (0.3 mmol), $Ru(bpy)_3(PF_6)_2$ (1 mol%), $BF_3{\cdot}Et_2O$ (5 mol%), solvent (3 mL), irradiation with 23 w household light bulb at room temperature for 24 h.

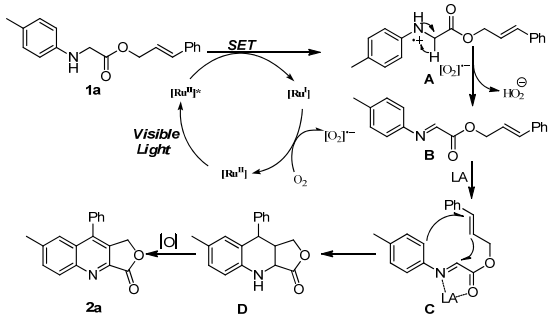
In addition, we have extended this cyclization of *N*-aryl glycine cinnamyl esters with substituents on the allyl counterpart as well (**Table 3**). Various substituted aryl allyls such as *p*-fluoro-, *p*-chloro, *p*-bromo, and *p*-methoxy-phenyls show that the electron-donating groups were appropriate for this reaction, affording the target products in good yields (**Table 3**, **2l**). However, electron-withdrawing groups were found to cause a decrease in reaction rate and efficiency (**Table 3, 2i**-**2k**). Besides that, it should be noted that similar reactivity was found with heteroaromatic group on the allyl moiety (**Table 3**, **2n**). Significantly, this method could be successfully extended to construct the 4-styryl quinoline-fused lactones that are very difficult to synthesize by using other strategies (**Table 3, 2o**,**2p**).

Table 3 Intramolecular Cyclization of N-Aryl Glycine Cinnamyl Esters[a]



[a] Conditions: **1i-1p** (0.3 mmol), $Ru(bpy)_3(PF_6)_2$ (1 mol%), $BF_3{\cdot}Et_2O$ (5 mol%), solvent (3 mL), irradiation with 23 W household light bulb at room temperature for 24 h.

On the basis of the above experiments and related reports,[3b] a plausible mechanism for the reaction is proposed in **Scheme 3**. Excitation of the $Ru(bpy)_3(PF_6)_2$ under visible light afforded the excited Ru^{II}* species, which oxidized amine **1a** to give the reduced species Ru^{I} and the radical amine cation **A**. The intermediate **A** was converted into intermediate **B**, which gave intermediate **D** in the presence of the Lewis acid. Then, the desired product **2a** was obtained by oxidation-aromatization reaction.



Scheme 3. Proposed mechanism for the catalysis

CONCLUSION

In conclusion, we have developed a visible-light-induced photocatalytic aerobic oxidation / intramolecular Povarov cyclization reaction. This process provides a new and efficient approach for one-step synthesis of these biologically relevant core structures from readily available starting materials under mild reaction conditions. Further applications of this transformation toward other biologically important heterocycles are underway.

EXPERIMENTAL SECTION

General Procedures. Materials were purchased from commercial suppliers and used without further purification. Anhydrous DMF, CH_3CN, DMSO, DCM were freshly distilled from calcium hydride. ^1H NMR and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer. The chemical shifts for ^1H NMR were recorded in ppm downfield from tetramethylsilane (TMS) with the solvent resonance as the internal standard. The chemical shifts for ^{13}C NMR were recorded in ppm downfield using the central peak of deuterochloroform (77.00 ppm) as the internal standard. Coupling constants (*J*) are reported in Hz and refer to apparent peak multiplicities. HRMS experiments were performed under ESI ionization technique on a Q-TOF mass spectrometer. Irradiation of photochemical reactions was carried out using a 23W household compact fluorescent lamp. Flash column chromatography was performed on silica gel (300-400 mesh) with petroleum ether (bp. 60-90 °C) and the indicated solvent, which are listed below as volume/volume ratios.

Typical Procedure for the Preparation of Cinnamyl 2-(Phenylamino)acetates (1a-1p)[10]

To a solution of cinnamyl alcohol (26.85 g, 200.0 mmol) and pyridine (15.83 g, 200.0 mmol) in anhydrous DCM (150 mL) was added 2-bromoacetyl bromide (6.78 g, 60.0 mmol) at 0 °C under N_2 atmosphere over 50 min. After the addition was complete, the reaction mixture was stirred at room temperature for 6 hours. After completion monitored by TLC, the mixture was washed with H_2O (3×50 mL). The organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue containing cinnamyl 2-bromoacetate was taken to the next step without additional purification.

A 250 mL round-bottom flask was charged with cinnamyl 2-bromoacetate (14.04 g, 55 mmol), K_2CO_3 (8.30 g, 60 mmol), KI (9.13 g, 55 mmol), *p*-toluidine (5.36 g, 50 mmol), acetone (150 mL). The mixture was heated to reflux for 8 h under N_2 atmosphere. After completion monitored by TLC, the mixture was cooled to room temperature, filtered and washed with acetone (20 mL× 3). The solvent was removed under reduced pressure, the crude product was purified by silica-gel column chromatography (PE:EA=20:1) to give cinnamyl 2-(*p*-tolylamino)acetate **1a** as a white solid (12.3 g, 87% yield).

Cinnamyl 2-(*p*-tolylamino)acetate (1a):[9a] White solid, 12.30 g, 87% yield, mp: 65.3-66.6 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.27 (m, 5H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.66 (d, *J* = 16.0 Hz, 1H), 6.58 – 6.55 (m, 2H), 6.31 – 6.24 (m, 1H), 4.84 (dd, *J* = 6.8, 1.2 Hz, 2H), 3.95 (s, 2H), 2.25 (s, 3H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 171.5, 145.1, 136.3, 135.0, 130.1, 128.9, 128.5, 127.8, 127.0, 122.9, 113.5, 66.0, 46.6, 20.7. IR (KBr, cm^{-1}) ν 3396, 3023, 2915, 1730, 1619, 1581, 1526, 1494, 1446, 1379, 1350, 1324, 1257, 1196, 1186, 1146, 1111, 971, 952, 907, 820, 803, 748, 692, 596, 508.

Cinnamyl 2-((4-(*t*-butyl)phenyl)amino)acetate (1b): White solid, 2.47 g, 76% yield, mp: 63.1-64.0 °C. ^1H

NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.22 (m, 7H), 6.66 (d, *J* = 16.0 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 2H), 6.32 – 6.25 (m, 1H), 4.84 (d, *J* = 6.4 Hz, 2H), 3.95 (s, 2H), 1.27 (s, 9H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 171.4, 144.8, 141.4, 136.3, 135.0, 128.9, 128.5, 126.9, 126.4, 122.8, 113.1, 66.0, 46.5, 34.2, 31.8. IR (KBr, cm^{-1}) *ν* 3396, 3057, 3024, 2955, 2865, 1878, 1735, 1656, 1615, 1577, 1522, 1494, 1446, 1386, 1352, 1322, 1301, 1257, 1215, 1191, 1149, 1109, 1047, 988, 968, 827, 819, 752, 739, 693, 593, 550. HRMS-ESI (m/z): Calculated for $C_{21}H_{26}NO_2$ $(M+H)^+$: 324.1964, Found: 324.1962.

(*E*)-4-Phenylbut-3-en-2-yl 2-(*p*-tolylamino)acetate (1c): Yellow solid, 1.2 g, 81% yield, mp: 61.9-62.3 ºC. ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.23 (m, 5H), 7.03 – 6.96 (m, 2H), 6.61 – 6.53 (m, 3H), 6.16 (dd, *J* = 15.6, 6.8 Hz, 1H), 5.65 – 5.58 (m, 1H), 4.15 (s, 1H), 3.90 (d, *J* = 2.0 Hz, 2H), 2.23 (s, 3H), 1.44 (d, *J* = 6.4 Hz, 3H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 171.0, 145.2, 136.5, 132.4, 130.1, 128.9, 128.5, 128.4, 127.6, 127.0, 113.6, 72.4, 46.8, 20.7. IR (KBr, cm^{-1}) *ν* 3380, 3029, 2975, 2919, 1880, 1703, 1616, 1524, 1493, 1449, 1380, 1321, 1308, 1286, 1254, 1228, 1185, 1144, 1130, 1087, 1073, 1038, 1012, 1000, 986, 966, 933, 852, 821, 810, 754, 693, 647, 606, 584, 509, 460. HRMS-ESI (m/z): Calculated for $C_{19}H_{22}NO_2$ $(M+H)^+$: 296.1651, Found: 296.1643.

Cinnamyl 2-((2,4-dimethylphenyl)amino)acetate (1d): Red oil, 2.17 g, 73% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.28 (m, 5H), 6.92 (d, *J* = 5.2 Hz, 2H), 6.73 – 6.63 (m, 1H), 6.48 – 6.40 (m, 1H), 6.34 – 6.26 (m, 1H), 4.87 – 4.84 (m, 2H), 3.99 (d, *J* = 2.8 Hz, 2H), 2.29 – 2.18 (m, 6H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 171.5, 143.0, 136.3, 135.0, 131.4, 128.9, 128.5, 127.6, 127.4, 126.9, 123.0, 122.8, 110.5, 66.0, 46.5, 20.6, 17.6. IR (KBr, neat, cm^{-1}) *ν* 3420, 3027, 2920, 1741, 1620, 1517, 1447, 1381, 1348, 1197, 965, 804, 746, 693. HRMS-ESI (m/z): Calculated for $C_{19}H_{22}NO_2$ $(M+H)^+$: 296.1651, Found: 296.1648.

Cinnamyl 2-((4-chlorophenyl)amino)acetate (1e): White solid, 2.60 g, 86% yield, mp: 81.0-82.3 ºC. ^1H NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.25 (m, 5H), 7.15 – 7.12 (m, 2H), 6.66 (d, *J* = 16.0 Hz, 1H), 6.55 – 6.51 (m, 2H), 6.30 – 6.23 (m, 1H), 4.83 (dd, *J* = 7.6, 1.2 Hz, 2H), 3.92 (s, 2H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 171.0, 145.9, 136.2, 135.2, 129.4, 139.0, 128.6, 127.0, 123.1, 122.6, 114.4, 66.2, 46.1. IR (KBr, cm^{-1}) *ν* 3416, 2946, 1735, 1598, 1516, 1488, 1448, 1422, 1383, 1351, 1246, 1178, 1138, 992, 971, 939, 820, 755, 693, 505. HRMS-ESI (m/z): Calculated for $C_{17}H_{17}ClNO_2$ $(M+H)^+$: 302.0948, Found: 302.0948.

Cinnamyl 2-((4-bromophenyl)amino)acetate (1f): White solid, 2.88 g, 83% yield, mp: 68.6-68.9 ºC. ^1H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.25 (m, 7H), 6.66 (d, *J* = 15.6 Hz, 1H), 6.52 – 6.48 (m, 2H), 6.31 – 6.24 (m, 1H), 4.84 (dd, *J* = 6.4, 1.2 Hz, 2H), 3.92 (s, 2H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 170.9, 146.2, 136.2, 135.2, 132.3, 128.9, 128.5, 126.9, 122.5, 114.8, 66.2, 46.0. IR (KBr, cm^{-1}) *ν* 3390, 3029, 2920, 1728, 1595,

1506, 1446, 1408, 1388, 1355, 1317, 1257, 1213, 1178, 1142, 1072, 1057, 1006, 973, 963, 932, 816, 805, 729, 691, 595, 505. HRMS-ESI (m/z): Calculated for $C_{17}H_{17}{}^{79}BrNO_2$ $(M+H)^+$: 346.0443, Found: 346.0443.

Cinnamyl 2-((2-bromo-4-methylphenyl)amino)acetate (1g): Red oil, 2.82 g, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.24 (m, 5H), 7.00 – 6.90 (m, 1H), 6.69 – 6.63 (m, 1H), 6.46 – 6.42 (m, 1H), 6.32 – 6.25 (m, 1H), 4.85 (dd, *J* = 6.4, 1.2 Hz, 2H), 3.99 (s, 2H), 2.22 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 170.7, 142.0, 136.3, 135.1, 133.2, 133.0, 129.3, 128.9, 128.6, 128.5, 126.9, 122.7, 116.0, 111.6, 110.2, 66.1, 46.3, 20.3. IR (KBr, neat, cm^{-1}) ν 3397, 3028, 2923, 1742, 1614, 1518, 1446, 1381, 1350, 1318, 1200, 1122, 1036, 964, 868, 802, 746, 692, 672, 551. HRMS-ESI (m/z): Calculated for $C_{18}H_{19}{}^{79}BrNO_2$ $(M+H)^+$: 360.0599, Found: 360.0602.

Cinnamyl 2-((4-bromo-2-methylphenyl)amino)acetate (1h): Red oil, 2.90 g, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.27 (m, 5H), 7.21 – 7.17 (m, 2H), 6.67 (d, *J* = 15.6 Hz, 1H), 6.36 – 6.24 (m, 2H), 4.85 (dd, *J* = 6.4, 1.2 Hz, 2H), 4.19 (s, 1H), 3.96 (s, 2H), 2.18 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 171.1, 144.5, 136.3, 135.1, 133.0, 130.0, 129.1, 128.6, 127.1, 125.0, 122.8, 111.7, 109.8, 66.2, 46.0, 17.5. IR (KBr, neat, cm^{-1}) ν 3422, 3026, 2930, 1741, 1598, 1577, 1507, 1447, 1400, 1382, 1350, 1317, 1199, 1156, 1102, 1030, 965, 871, 801, 746, 692, 635, 544. HRMS-ESI (m/z): Calculated for $C_{18}H_{17}{}^{79}BrNO_2$ $(M+H)^+$: 358.0443, Found: 358.0437.

(*E*)-3-(4-Fluorophenyl)allyl 2-(p-tolylamino)acetate (1i): Yellow solid, 654.6 mg, 86% yield, mp: 73.2-74.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.33 (m, 2H), 7.02 (t, *J* = 8.4 Hz, 4H), 6.63 – 6.55 (m, 3H), 6.23 – 6.16 (m, 1H), 4.82 (d, *J* = 6.8 Hz, 2H), 4.16 (s, 1H), 3.94 (s, 2H), 2.24 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 171.4, 164.1 (d, $^1J_{C\text{-}F}$ = 246.2 Hz), 145.0, 133.8, 132.4, 130.1, 128.5, 128.4, 127.8, 122.5, 115.9, 115.7, 113.5, 65.8, 46.5, 20.6. IR (KBr, cm^{-1}) ν 3424,2918, 1736, 1616, 1598, 1526, 1507, 1421, 1383, 1352, 1324, 1230, 1187, 1157, 1137, 1108, 998, 972, 940, 855, 805, 770, 567, 512. HRMS-ESI (m/z): Calculated for $C_{18}H_{19}FNO_2$ $(M+H)^+$: 300.1400, Found: 300.1407.

(*E*)-3-(4-Chlorophenyl)allyl 2-(*p*-tolylamino)acetate (1j): Yellow solid, 348.3 mg, 79% yield, mp: 71.0-72.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (s, 4H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.62 – 6.55 (m, 3H), 6.28 – 6.21 (m, 1H), 4.82 (dd, *J* = 6.4, 1.6 Hz, 2H), 4.15 (s, 1H), 3.95 (s, 2H), 2.24 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 171.4, 145.0, 134.8, 134.1, 133.6, 130.1, 129.0, 128.1, 127.8, 123.5, 113.5, 65.7, 46.5, 20.6. IR (KBr, cm^{-1}) ν 3395,3038, 2914, 2858, 1734, 1617, 1580, 1527, 1491, 1445, 1404, 1387, 1356, 1320, 1257, 1208, 1181, 1143, 1090, 1066, 1010, 968, 844, 806, 776, 595, 511. HRMS-ESI (m/z): Calculated for $C_{18}H_{19}ClNO_2$ $(M+H)^+$: 316.1104, Found: 316.1099.

(*E*)-3-(4-Bromophenyl)allyl 2-(*p*-tolylamino)acetate (1k): Light yellow solid, 2.1 g, 70% yield, mp: 57.3-58.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.44 (m, 2H), 7.26 – 7.22 (m, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.61 – 6.56 (m, 3H), 6.29 – 6.22 (m, 1H), 4.81 (d, *J* = 6.4 Hz, 2H), 3.95 (s, 2H), 2.24 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 171.2, 144.7, 135.2, 133.6, 132.0, 130.1, 128.4, 128.2, 123.6, 122.3, 65.7, 46.7, 20.6. IR (KBr, cm^{-1}) ν 3395, 2912, 1733, 1618, 1527, 1487, 1446, 1388, 1355, 1322, 1256, 1207, 1181, 1072, 1009, 965, 804, 769, 524. HRMS-ESI (m/z): Calculated for $C_{18}H_{19}{}^{79}BrNO_2$ $(M+H)^+$: 360.0599, Found: 360.0584.

(*E*)-3-(4-Methoxyphenyl)allyl 2-(*p*-tolylamino)acetate (1l): White solid, 1.3 g, 83% yield, mp: 67.7-68.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.30 (m, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.90 – 6.85 (m, 2H), 6.63 – 6.54 (m, 3H), 6.18 – 6.11 (m, 1H), 4.81 (dd, *J* = 6.8, 1.2 Hz, 2H), 4.16 (s, 1H), 3.93 (s, 2H), 3.82 (s, 3H), 2.25 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 171.5, 160.0, 145.1, 134.9, 130.1, 129.0, 128.2, 127.7, 120.4, 114.3, 113.5, 66.3, 55.5, 46.5. IR (KBr, cm^{-1}) ν 3387, 2994, 2912, 2834, 1736, 1657, 1610, 1527, 1510, 1445, 1386, 1355, 1322, 1298, 1279, 1248, 1203, 1173, 1144, 1033, 972, 956, 846, 811, 758, 591, 536, 506. HRMS-ESI (m/z): Calculated for $C_{19}H_{22}NO_3$ $(M+H)^+$: 312.1600, Found: 312.1607.

(*E*)-3-(2-Methoxyphenyl)allyl 2-(*p*-tolylamino)acetate (1m): Red oil, 1.81 g, 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.01 – 6.86 (m, 5H), 6.55 (d, *J* = 8.0 Hz, 2H), 6.34 – 6.27 (m, 1H), 4.85 – 4.81 (m, 2H), 3.92 (s, 2H), 3.84 (s, 3H), 2.23 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 171.4, 157.2, 145.1, 130.2, 130.1, 129.6, 127.7, 127.5, 125.3, 123.4, 120.9, 113.5, 111.1, 66.6, 55.7, 46.6, 20.7. IR (KBr, neat, cm^{-1}) ν 3398, 2937, 2592, 2021, 1870, 1739, 1598, 1489, 1245, 969, 809, 752. HRMS-ESI (m/z): Calculated for $C_{19}H_{22}NO_3$ $(M+H)^+$: 312.1600, Found: 312.1600.

(*E*)-3-(Thiophen-2-yl)allyl 2-(*p*-tolylamino)acetate (1n): Yellow solid, 1.83 g, 68% yield, mp: 44.1-44.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, *J* = 4.8 Hz, 1H), 7.05 – 6.94 (m, 4H), 6.78 (d, *J* = 15.6 Hz, 1H), 6.55 (d, *J* = 8.4 Hz, 2H), 6.14 – 6.07 (m, 1H), 4.79 (d, *J* = 6.4 Hz, 2H), 4.15 (s, 1H), 3.94 (d, *J* = 5.6 Hz, 2H), 2.24 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 171.4, 145.0, 141.2, 130.1, 128.2, 127.8, 127.7, 127.0, 125.4, 122.2, 113.5, 65.6, 46.5, 20.7. IR (KBr, cm^{-1}) ν 3384, 2943, 1730, 1650, 1619, 1582, 1524, 1445, 1387, 1358, 1342, 1323, 1258, 1209, 1185, 1143, 1112, 1078, 1040, 998, 952, 852, 825, 804, 703, 596, 506. HRMS-ESI (m/z): Calculated for $C_{16}H_{18}NO_2S$ $(M+H)^+$: 288.1058, Found: 288.1058.

(2*E*,4*E*)-Hexa-2,4-dien-1-yl 2-(*p*-tolylamino)acetate (1o): Red oil, 2.14 g, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.00 (d, *J* = 8.0 Hz, 2H), 6.54 (d, *J* = 8.0 Hz, 2H), 6.26 (dd, *J* = 14.8, 10.4 Hz, 1H), 6.11 – 6.00 (m, 1H), 5.81 – 5.72 (m, 1H), 5.66 – 5.58 (m, 1H), 4.67 (d, *J* = 6.4 Hz, 2H), 3.90 (s, 2H), 2.24 (s, 3H), 1.77 (d, *J* = 6.8 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, CDCl3): δ 171.4, 145.0, 135.7, 131.9, 130.5, 130.0, 127.7, 123.3,

113.5, 65.9, 46.5, 20.6, 18.4. IR (KBr, cm^{-1}) ν 3422, 2921, 1740, 1619, 1522, 1191, 989, 807, 507. HRMS-ESI (m/z): Calculated for $C_{15}H_{20}NO_2$ $(M+H)^+$: 246.1494, Found: 246.1482.

(2*E*,4*E*)-5-Phenylpenta-2,4-dien-1-yl 2-(*p*-tolylamino)acetate (1p): Yellow solid, 895 mg, 83% yield, mp: 87.8-89.1 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 7.2 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.76 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.60 (s, 1H), 6.55 (d, *J* = 8.4 Hz, 2H), 6.45 (dd, *J* = 15.2, 10.4 Hz, 1H), 5.91 – 5.83 (m, 1H), 4.76 (d, *J* = 6.4 Hz, 2H), 4.15 (s, 1H), 3.93 (s, 2H), 2.25 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 171.4, 145.0, 137.1, 135.3, 134.4, 130.1, 128.9, 128.2, 127.8, 126.8, 126.4, 113.5, 65.7, 46.5, 20.7. IR (KBr, cm^{-1}) ν 3386, 3023, 1730, 1619, 1582, 1526, 1445, 1389, 1355, 1323, 1258, 1207, 1183, 1141, 991, 954, 823, 805, 744, 687, 504. HRMS-ESI (m/z): Calculated for $C_{20}H_{22}NO_2$ $(M+H)^+$: 308.1651, Found: 308.1648.

A general procedure for $Ru(bpy)_3(PF_6)_2$-catalyzed aerobic oxidation / intramolecular [4+2] cycloaddition / aromatization cascade reaction

A solution of substrate **1a** (0.3 mmol), $Ru(bpy)_3(PF_6)_2$ (1 mol %) in CH_3CN (3 mL) was mixed and then $BF_3{\cdot}Et_2O$ (5 mol %) was added. The reaction solution was irradiated with a 23 W fluorescent light (distance app. 5 cm) under air atmosphere at room temperature for 24 h. After the completion of the reaction, the mixture was concentrated in vacuum and the pure product was obtained by flash column chromatography on silica gel (PE: Acetone =10:1).

7-Methyl-9-phenylfuro[3,4-b]quinolin-3(1H)-one (2a):[11] White solid, 61.9 mg, 75% yield, mp: 201.0-201.7 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 8.8 Hz, 1H), 7.69 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.64 – 7.56 (m, 4H), 7.45 – 7.43 (m, 2H), 5.36 (s, 2H), 2.51 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 169.1, 149.4, 143.4, 143.1, 140.2, 133.9, 133.3, 132.8, 131.0, 129.7, 129.6, 129.1, 128.1, 124.6, 68.1, 22.4. IR (KBr, cm^{-1}) ν 3048, 2920, 1778, 1499, 1372, 1131, 1054, 832, 704, 582.

7-(*t*-Butyl)-9-phenylfuro[3,4-b]quinolin-3(1H)-one (2b): Yellow solid, 44.6 mg, 47% yield, mp: 231.8-234.0 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (d, *J* = 8.8 Hz, 1H), 7.96 (dd, *J* = 9.2, 2.0 Hz, 1H), 7.82 (d, *J* = 2.0 Hz, 1H), 7.64 – 7.58 (m, 4H), 7.47 – 7.44 (m, 2H), 5.39 (s, 2H), 1.34 (s, 9H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 152.9, 149.5, 143.8, 143.7, 134.0, 132.7, 131.0, 130.1, 129.7, 129.5, 129.1, 127.8, 120.6, 68.1, 31.1. IR (KBr, cm^{-1}) ν 3060, 2958, 1779, 1620, 1583, 1504, 1451, 1353, 1261, 1236, 1132, 1096, 1052, 1010, 841, 758, 705, 581. HRMS-ESI (m/z): Calculated for $C_{21}H_{20}NO_2$ $(M+H)^+$: 318.1494, Found: 318.1492.

1,7-Dimethyl-9-phenylfuro[3,4-b]quinolin-3(1H)-one (2c): White solid, 64.5 mg, 75% yield, mp: 201.3-201.9 ºC. ^{1}H NMR (400 MHz, $CDCl_3$):

δ 8.33 (d, *J* = 8.8 Hz, 1H), 7.68 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.63 – 7.58 (m, 3H), 7.54 (s, 1H), 7.43 – 7.36 (m, 2H), 5.78 (q, *J* = 6.8 Hz, 1H), 2.50 (s, 3H), 1.22 (d, *J* = 6.4 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 168.3, 149.1, 143.0, 139.9, 136.8, 133.8, 133.1, 130.9, 129.7, 129.3, 128.9, 128.3, 124.5, 76.6, 22.1, 19.3. IR (KBr, cm^{-1}) ν 3058, 2926, 1777, 1580, 1508, 1445, 1367, 1325, 1262, 1206, 1152, 1113, 1087, 1054, 928, 854, 829, 811, 751, 731, 706, 641, 568. HRMS-ESI (m/z): Calculated for $C_{19}H_{16}NO_2$ (M+H)+: 290.1181, Found: 290.1181.

5,7-Dimethyl-9-phenylfuro[3,4-b]quinolin-3(1H)-one (2d): White solid, 60.8 mg, 70% yield, mp: 176.4-176.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 – 7.55 (m, 4H), 7.45 – 7.41 (m, 3H), 5.34 (s, 2H), 2.93 (s, 3H), 2.46 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 169.4, 148.7, 143.0, 142.2, 139.7, 139.1, 134.3, 133.2, 132.7, 129.4, 129.1, 122.5, 67.9, 22.3, 18.7. IR (KBr, cm^{-1}) ν 3054, 2922, 1778, 1582, 1493, 1446, 1363, 1270, 1158, 1136, 1072, 1051, 1013, 862, 776, 714, 546. HRMS-ESI (m/z): Calculated for $C_{19}H_{16}NO_2$ $(M+H)^+$: 290.1181, Found: 290.1174.

7-Chloro-9-phenylfuro[3,4-b]quinolin-3(1H)-one (2e):[11] White solid, 56.7 mg, 64% yield, mp: 216.5-217.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (d, *J* = 9.2 Hz, 1H), 7.87 (d, *J* = 2.0 Hz, 1H), 7.80 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.67 – 7.61 (m, 3H), 7.44 – 7.42 (m, 2H), 5.40 (s, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 168.6, 149.2, 144.7, 143.4, 136.0, 133.4, 133.0, 132.1, 130.1, 129.8, 129.0, 128.7, 124.8, 68.0. IR (KBr, cm^{-1}) ν 2920, 1774, 1579, 1489, 1448, 1373, 1346, 1284, 1138, 1077, 1057, 1009, 951, 828, 704, 542.

7-Bromo-9-phenylfuro[3,4-b]quinolin-3(1H)-one (2f): White solid, 60.8 mg, 60% yield, mp: 219.0-220.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, *J* = 9.2 Hz, 1H), 8.05 (d, *J* = 2.0 Hz, 1H), 7.93 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.67 – 7.61 (m, 3H), 7.44 – 7.42 (m, 2H), 5.41 (s, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 168.6, 149.3, 144.8, 143.3, 134.6, 133.4, 133.0, 130.1, 129.8, 129.0, 128.1, 124.5, 68.0. IR (KBr, cm^{-1}) ν 3055, 2916, 1773, 1576, 1486, 1374, 1138, 1055, 948, 830, 702, 521.

5-Bromo-7-methyl-9-phenylfuro[3,4-b]quinolin-3(1H)-one (2g): Yellow solid, 57.8 mg, 54% yield, mp: 216.6-218.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 1.6 Hz, 1H), 7.65 – 7.58 (m, 4H), 7.44 – 7.42 (m, 2H), 5.35 (s, 2H), 2.48 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 168.3, 146.3, 144.1, 144.0, 140.5, 136.7, 133.7, 133.5, 129.8, 129.5, 129.4, 129.2, 126.3, 124.7, 67.9, 22.0. IR (KBr, cm^{-1}) ν 3056, 1785, 1615, 1574, 1484, 1446, 1423, 1402, 1363, 1339, 1265, 1204, 1133, 1055, 1028, 1002, 871, 805, 776, 764, 708, 543. HRMS-ESI (m/z): Calculated for $C_{18}H_{13}{}^{79}BrNO_2$ $(M+H)^+$: 354.0130, Found: 354.0122.

7-Bromo-5-methyl-9-phenylfuro[3,4-b]quinolin-3(1H)-one (2h): White solid, 42.7 mg, 40% yield, mp: 244.1-245.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 2.0 Hz, 1H), 7.79 (s, 1H), 7.64 – 7.59 (m, 3H),

7.42 – 7.39 (m, 2H), 5.37 (s, 2H), 2.94 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 168.8, 148.7, 143.5, 143.3, 141.9, 134.1, 133.5, 133.4, 129.9, 129.7, 129.4, 129.1, 129.0, 125.9, 124.2, 67.8, 18.6. IR (KBr, cm^{-1}) ν 2929, 1776, 1597, 1488, 1443, 1368, 1343, 1266, 1227, 1189, 1141, 1073, 1040, 1007, 878, 858, 756, 704, 660, 540. HRMS-ESI (m/z): Calculated for $C_{18}H_{13}{}^{79}BrNO_2$ $(M+H)^+$: 354.0130, Found: 354.0140.

9-(4-Fluorophenyl)-7-methylfuro[3,4-b]quinolin-3(1H)-one (2i): Yellow solid, 61.2 mg, 73% yield, mp: 284.9-286.0 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.58 (s, 1H), 7.45 – 7.41 (m, 2H), 7.35 – 7.29 (m, 2H), 5.36 (s, 2H), 2.53 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 168.8, 164.7 (d, $^{1}J_{C\text{-}F}$ = 248.8 Hz), 149.5, 143.5, 142.0, 140.4, 133.4, 132.8, 131.3, 131.0, 131.0, 129.8, 128.2, 124.2, 116.9, 116.7, 67.8, 22.3. IR (KBr, cm^{-1}) ν 2940, 1779, 1503, 1447, 1219, 1138, 1058, 874, 850, 764, 658, 571, 542. HRMS-ESI (m/z): Calculated for $C_{18}H_{13}FNO_2$ $(M+H)^+$: 294.0930, Found: 294.0923.

9-(4-Chlorophenyl)-7-methylfuro[3,4-b]quinolin-3(1H)-one (2j): Gray solid, 39.8 mg, 43% yield, mp: 273.5-275.6 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, *J* = 8.8 Hz, 1H), 7.70 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.62 – 7.59 (m, 2H), 7.57 (s, 1H), 7.40 – 7.37 (m, 2H), 5.36 (s, 2H), 2.53 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 168.8, 149.4, 143.5, 141.8, 140.5, 135.9, 133.4, 132.7, 132.3, 131.2, 130.5, 129.9, 129.0, 127.9, 124.2, 67.8, 22.3. IR (KBr, cm^{-1}) ν 2924, 1777, 1490, 1449, 1370, 1139, 1086, 1057, 1015, 830, 760, 658, 561, 540. HRMS-ESI (m/z): Calculated for $C_{18}H_{13}ClNO_2$ $(M+H)^+$: 310.0635, Found: 310.0623.

9-(4-Bromophenyl)-7-methylfuro[3,4-b]quinolin-3(1H)-one (2k): Yellow solid, 65.5 mg, 62% yield, mp: 290.0-291.2 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 8.8 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.70 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.57 (s, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 5.35 (s, 2H), 2.52 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 168.8, 149.4, 143.4, 141.8, 140.6, 133.4, 132.8, 132.6, 131.2, 130.7, 127.8, 124.2, 67.8, 22.4. IR (KBr, cm^{-1}) ν 2921, 1778, 1578, 1489, 1452, 1395, 1374, 1348, 1293, 1224, 1132, 1054, 1011, 851, 823, 540, 500. HRMS-ESI (m/z): Calculated for $C_{18}H_{13}{}^{79}BrNO_2$ $(M+H)^+$: 354.0130, Found: 354.0138.**9-(4-Methoxyphenyl)-7-methylfuro[3,4-b]quinolin-3(1H)-one (2l):** White solid, 78.8 mg, 86% yield, mp: 233.3-234.5 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 9.2 Hz, 1H), 7.70 – 7.66 (m, 2H), 7.39 – 7.36 (m, 2H), 7.15 – 7.11 (m, 2H), 5.38 (s, 2H), 3.94 (s, 3H), 2.52 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 169.1, 160.6, 149.6, 143.5, 143.0, 140.0, 133.2, 132.8, 131.2, 130.5, 128.4, 125.9, 124.6, 115.0, 68.1, 55.7, 22.3. IR (KBr, cm^{-1}) ν 2970, 1779, 1609, 1578, 1504, 1446, 1373, 1348, 1288, 1244, 1208, 1183, 1137, 1111, 1056, 1029, 853, 833, 639, 574, 541. HRMS-ESI (m/z): Calculated for $C_{19}H_{16}NO_3$ $(M+H)^+$: 306.1130, Found: 306.1121.

9-(2-Methoxyphenyl)-7-methylfuro[3,4-b]quinolin-3(1H)-one (2m): White solid, 69.8 mg, 76% yield, mp: 251.4-253.1 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 8.8 Hz, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.56 (t, *J* =

8.0 Hz, 1H), 7.50 (s, 1H), 7.19 – 7.12 (m, 2H), 5.34 (d, *J* = 15.2 Hz, 1H), 5.22 (d, *J* = 14.8 Hz, 1H), 3.77 (s, 3H), 2.50 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 169.4, 156.7, 149.5, 143.3, 140.2, 139.8, 134.0, 133.1, 131.3, 131.18, 131.16, 128.8, 124.6, 122.2, 121.2, 111.9, 68.5, 55.8, 22.3. IR (KBr, cm^{-1}) ν 2939, 1779, 1579, 1496, 1456, 1436, 1374, 1346, 1278, 1247, 1137, 1112, 1057, 1046, 1022, 835, 762, 543. HRMS-ESI (m/z): Calculated for $C_{19}H_{16}NO_3$ $(M+H)^+$: 306.1130, Found: 306.1125.

7-Methyl-9-(thiophen-2-yl)furo[3,4-b]quinolin-3(1H)-one (2n): White solid, 69.8 mg, 66% yield, mp: 203.8-204.7 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 8.8 Hz, 1H), 8.01 (s, 1H), 7.72 – 7.66 (m, 2H), 7.37 – 7.32 (m, 2H), 5.51 (s, 2H), 2.57 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 168.9, 149.6, 143.5, 140.6, 136.1, 133.7, 133.4, 133.0, 131.3, 130.3, 128.8, 128.5, 128.1, 124.5, 68.4, 22.4. IR (KBr, cm^{-1}) ν 3105, 1775, 1571, 1503, 1442, 1368, 1231, 1139, 1050, 1004, 853, 831, 795, 770, 735, 539. HRMS-ESI (m/z): Calculated for $C_{16}H_{12}NO_2S$ $(M+H)^+$: 282.0589, Found: 282.0584.

(*E*)-7-Methyl-9-(prop-1-en-1-yl)furo[3,4-b]quinolin-3(1H)-one (2o): Gray solid, 39.8 mg, 55% yield, mp: 211.4-214.6 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 8.8 Hz, 1H), 7.95 (s, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.06 (d, *J* = 16.4 Hz, 1H), 6.33 – 6.24 (m, 1H), 5.55 (s, 2H), 2.62 (s, 3H), 2.14 (d, *J* = 6.4 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 169.0, 149.1, 143.4, 139.7, 138.3, 137.3, 133.0, 131.3, 130.9, 127.1, 124.0, 123.0, 68.7, 22.4, 19.9. IR (KBr, cm^{-1}) ν 2922, 1779, 1573, 1443, 1373, 1139, 1079, 1016, 843, 541. HRMS-ESI (m/z): Calculated for $C_{15}H_{14}NO_2$ $(M+H)^+$: 240.1025, Found: 240.1016.

(*E*)-7-Methyl-9-styrylfuro[3,4-b]quinolin-3(1H)-one (2p): Yellow solid, 69.8 mg, 66% yield, mp: 167.8-169.1 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, *J* = 8.8 Hz, 1H), 7.96 (s, 1H), 7.72 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.23 – 7.20 (m, 1H), 7.17 – 7.13 (m, 3H), 6.99 (d, *J* = 7.2 Hz, 2H), 6.94 (d, *J* = 12.0 Hz, 1H), 4.74 (s, 2H), 2.63 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 169.0, 148.9, 143.7, 140.3, 139.4, 137.0, 135.8, 133.5, 132.0, 131.4, 129.15, 129.05, 128.3, 123.8, 122.3, 68.6, 22.3. IR (KBr, cm^{-1}) ν 2923, 1778, 1619, 1573, 1502, 1456, 1373, 1341, 1223, 1136, 1070, 1014, 916, 835, 780, 732, 696, 576, 543, 517. HRMS-ESI (m/z): Calculated for $C_{20}H_{16}NO_2$ $(M+H)^+$: 302.1181, Found: 302.1169.

ASSOCIATED CONTENT

SUPPORTING INFORMATION

The NMR spectra is available free of charge via the Internet at http://pubs.acs.org.

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