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Palladium-Catalyzed Oxidative Carbonylation for the Synthesis of Polycyclic Aromatic Hydrocarbons (PAHs)

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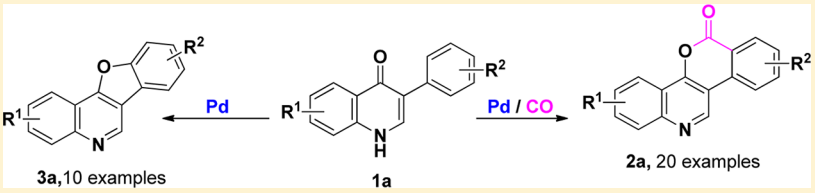
Supporting Information



ABSTRACT: A direct and facile palladium-catalyzed C−H bond oxidative carbonylation reaction and oxidative cyclization for the synthesis of polycyclic aromatic hydrocarbons (PAHs) is reported herein. The intramolecular cyclocarbonylation, through C−H activation and C−C, C−O bond formations under mild conditions, proceeds smoothly with good functional group tolerance in high to excellent yields. The intramolecular palladium-catalyzed direct oxidative C−H bond functionalization for the C−O bond formation is also demonstrated, which provides an efficient approach for the construction of various PAHs.

Carbonylation of organic compounds with CO as carbon-atom source has been continued to be an attractive strategy in organic synthesis.[1] Since seminal work by Heck and co-workers in 1974,[2] transition-metal-catalyzed carbonylation reactions of (pseudo)halides with CO in the presence of various nucleophiles have been recognized as one of the most powerful tools to synthesize a variety of carbonyl compounds.[3] In recent decades, increased attention has been focused on the direct C−H activation for C−C and C−heteroatom bond formation.[4] A growing number of palladium- and rhodium-catalyzed carbonylation reactions of aromatic C−H bonds that allow for straightforward and atom-economical carbonyl group formation have been developed by Chatani, Yu, and our group, etc.[5] However, a lack of control over the chemo- and regioselective activation of a specific C−H bond is still a challenging task due to the ubiquity and robustness of C−H bonds. In fact, the problem is a pervasive challenge in the field of C−H activation. To solve this problem, the application of a directing group is needed to allow selective C−H bond activation. A variety of directing groups have evolved to include nitrogen-containing heterocycles,[6] amides,[5g,j] carboxylic acids,[5f] and tertiary amines.[7] In some cases, the directed intermolecular C−H carbonylation reactions require extra synthetic steps to remove the directing groups, which sacrifices atom economy. On the other hand, carbonylation with subsequent intramolecular cyclization reactions,[8] in which the directing groups act as nucleophiles as well, has been shown to be an efficient process with high step efficiency and atom economy without installing and removing any directing groups. In this context, transition metal-catalyzed C−H bond functionalization reactions have emerged as one of the most powerful transformations in the past decade (Figure 1). The direct functionalization of C−H and C−X bonds for the construction of complex molecules holds the synthetic advantages of high atom-efficiency and chemo- or regioselectivity. Additionally, this kind of reactions has received substantial attention because of their ability to synthesize useful motifs in an extremely rapid manner.

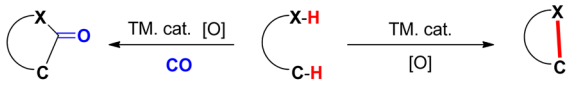


Figure 1. Direct C−H and X−H bond functionalization.

Polycyclic aromatic hydrocarbons (PAHs), which are characterized by the presence of two or more fused benzene rings arranged in various configurations,[9] have attracted considerable attention in different research fields such as pharmaceutical chemistry and materials science (Figure 2).[10] Numerous synthetic strategies for the construction of PAHs have been developed in the past decades due to their remarkable biological activity, electronic structure and photochemical properties, among which, the palladium-catalyzed annulation provides a convenient and efficient route for the synthesis of a wide range of carbocycles.[11] The incorporation of heteroatoms into a PAH system can change its pharmacological activity and expand the utility in the field of optoelectronic devices. Nevertheless, traditional methods for the construction of PAHs usually suffered from tedious synthetic procedures,[12] and so simpler and more atom-economical methods to access structurally diverse PAHs remains highly desirable. Herein, we report our recent effort on palladium-catalyzed oxidative functionalization, and more significantly, oxidative C−H bond carbonylation reactions for the construction of PAHs.

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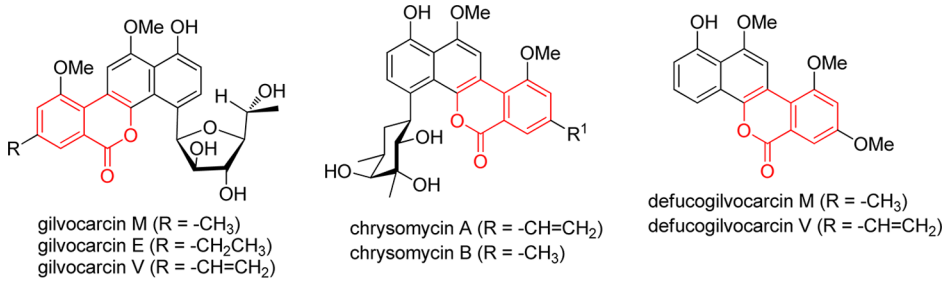
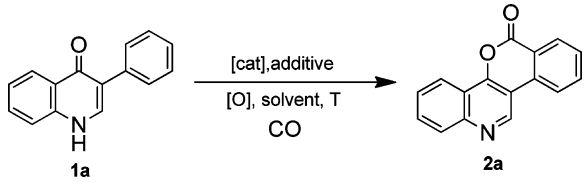


Figure 2. Gilvocarcin ravidomycin family of antibiotics.

Table 1. Optimization of the Reaction Conditions[a]



entry	Pd cat.	additive	oxidant	solvent	T (°C)	yield[b,c] (%)
1	$Pd(OAc)_2$	$TsOH·H_2O$	BQ	dioxane	100	65
2	$PdCl_2$	$TsOH·H_2O$	BQ	dioxane	100	n.d.
3	$Pd_2(dba)_3$	$TsOH·H_2O$	BQ	dioxane	100	69
4	$Pd(TFA)_2$	$TsOH·H_2O$	BQ	dioxane	100	trace
5	$Pd_2(dba)_3$	PivOH	BQ	dioxane	100	23
6	$Pd_2(dba)_3$	LiBr	BQ	dioxane	100	n.d.
7	$Pd_2(dba)_3$	–	BQ	dioxane	100	41
8	$Pd_2(dba)_3$	$TsOH·H_2O$	MnO_2	dioxane	100	60
9	$Pd_2(dba)_3$	$TsOH·H_2O$	$Cu(OAc)_2·H_2O$	dioxane	100	88
10	$Pd_2(dba)_3$	$TsOH·H_2O$	O_2	dioxane	100	17
11	$Pd_2(dba)_3$	$TsOH·H_2O$	$Cu(OAc)_2·H_2O$	CH_3CN	100	30
12	$Pd_2(dba)_3$	$TsOH·H_2O$	$Cu(OAc)_2·H_2O$	DMF	100	5
13	$Pd_2(dba)_3$	$TsOH·H_2O$	$Cu(OAc)_2·H_2O$	PhMe	100	n.d.
14	$Pd_2(dba)_3$	$TsOH·H_2O$	$Cu(OAc)_2·H_2O$	dioxane	80	79
15	$Pd_2(dba)_3$	$TsOH·H_2O$	$Cu(OAc)_2·H_2O$	dioxane	110	50
16	$Pd_2(dba)_3$	$TsOH·H_2O$	$Cu(OAc)_2·H_2O$	dioxane	100	77[d]
17	$Pd_2(dba)_3$	$TsOH·H_2O$	$Cu(OAc)_2·H_2O$	dioxane	100	85[e]

[a]Reaction conditions: unless otherwise noted, all reactions were performed with **1a** (0.2 mmol), $Pd_2(dba)_3$ (15 mol %), additive (1.5 equiv), oxidant (3 equiv), CO (1 balloon), 100 °C, 24 h. [b]Isolated yield. [c]Reactions were carried out in a sealed tube. [d]The catalyst loading was 10 mol %. [e]The oxidant loading was 1.5 equiv.

Initially, 3-phenylquinolin-4(1*H*)-one (**1a**; 0.2 mmol) was used as the substrate to optimize the reaction conditions. Fortunately, the desired product 6*H*-isochromeno[4,3-*c*]-quinolin-6-one (**2a**) was obtained in 65% yield with $TsOH·H_2O$ (1.5 equiv) as additive and BQ (3 equiv) as oxidant, $Pd(OAc)_2$ (15 mol %) as catalyst in dioxane under CO atmosphere (Table 1, entry 1). To improve the yield of **2a**, we screened various parameters including catalyst, additive, oxidant, solvent and reaction temperature. The use of $Pd_2(dba)_3$ as a catalyst gave a further increase in the yield of product, while $PdCl_2$ and $Pd(TFA)_2$ were ineffective for the reaction (entries 2−4). Furthermore, different additives were also investigated, in which LiBr proved to have no effect as an additive (entry 6), and PivOH gave comparably unfavorable results (entry 5). Further optimization of oxidants showed that the use of $Cu(OAc)_2·H_2O$ as the oxidant resulted in a decent boost in the yield of **2a**, while MnO_2 and O_2 turned out to be inferior in the system (entries 8−10). The solvents were vital to the catalytic system, and the desired product **2a** was hardly obtained with toluene, whereas CH_3CN and DMF also gave disappointing results (entries 11−13). When the reaction temperature was changed, the yields were decreased to 79 and 50% (entries 14−15). Gratifyingly, when the oxidant and catalyst loading were reduced to 1.5 equiv and 10 mol %, **2a** could be isolated in 85 and 77% yields, respectively, without any decrease (entries 16−17).

With the optimized conditions in hand, the scope of the reaction was investigated (Table 2). The oxidative carbonylation reaction displayed a good functional-group tolerance and moderate to excellent yields were obtained. In general, substrates bearing methyl, ethyl, isopropyl, methoxy, ethoxy, phenoxy, fluoro, and sensitive functional groups such as chloro and bromo groups, could transfer to the corresponding products in high to excellent yields, allowing further functionalization through conventional cross-coupling reactions (**2a−j**). Treatment of substrates bearing the strong electron-withdrawing groups, including CF_3 and OCF_3, afforded the desired products in excellent yields. However, when using polycyclic and heterocyclic compounds **2o** and **2p** as the substrates, the desired transformation did not occur and none of the corresponding products could be detected. No byproducts were detected in all these reaction systems.

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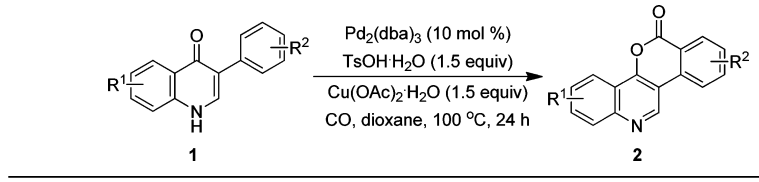
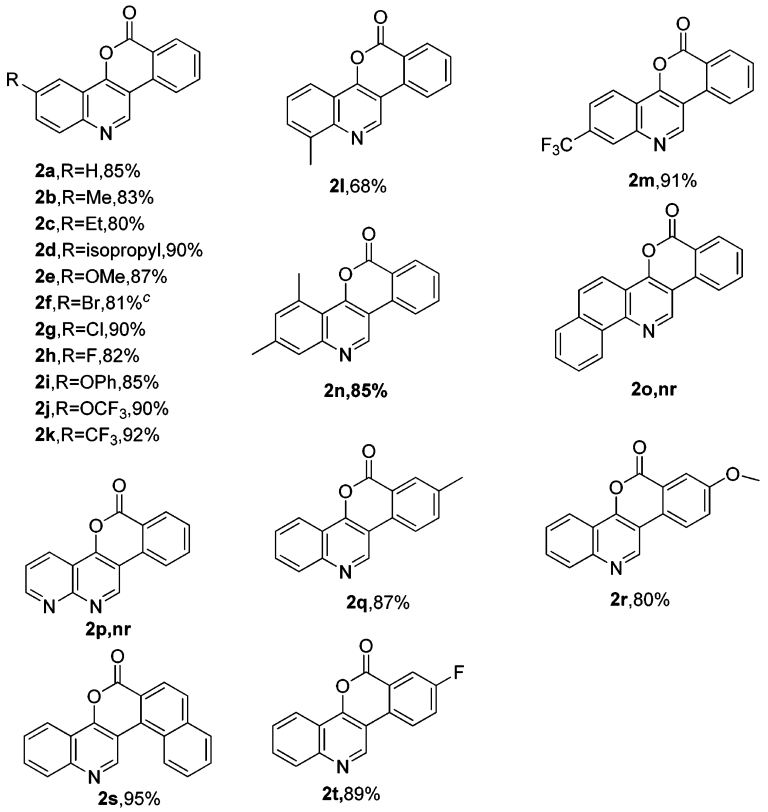
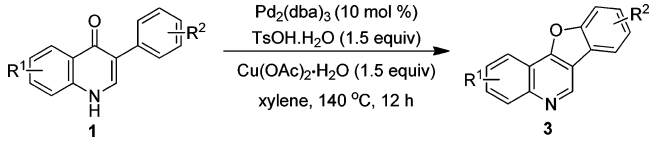
Table 2. Synthesis of Carbonylation Products 2[a,b]

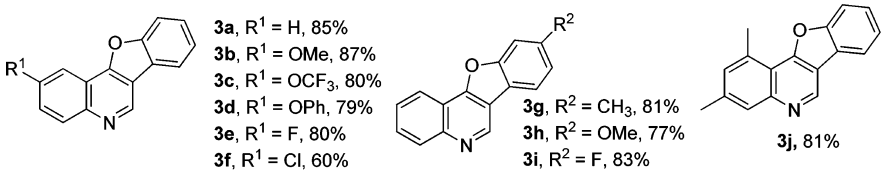




[a]The reactions were carried out at 100 °C, using **1** (0.2 mmol), $Cu(OAc)_2·H_2O$ (0.3 mmol), $TsOH·H_2O$ (0.3 mmol), $Pd_2(dba)_3$ (10 mol %) in dioxane (2 mL) under CO atmosphere for 24 h. [b]Yields refer to the isolated yields. [c]The catalyst was $Pd(OAc)_2$

Table 3. Synthesis of Cyclization Products 2[a,b]





[a]The reactions were carried out at 140 °C, using **1** (0.2 mmol), $Cu(OAc)_2·H_2O$ (0.3 mmol), $TsOH·H_2O$ (0.3 mmol), $Pd_2(dba)_3$ (10 mol %) in xylene (2 mL) for 12 h. [b]Yields refer to the isolated yields.

Direct oxidative C−H/X−H coupling reactions represent a great advance as to traditional couplings based on C−X bond. Since the work of Buchwald on palladium-catalyzed oxidative C−H/N-H couplings to afford biologically active molecules carbazoles,[12] lots of work on the direct oxidative coupling between C−H bond and X−H bond have been developed. For example, Yu's group developed a palladium-catalyzed C−O coupling reaction using Pd^{II}/Pd^{IV} catalytic cycle for the synthesis of benzofurans using $PhI(OAc)_2$ as the oxidant.[13] Recently, Liu et al. realized C−O bond reductive elimination utilizing Pd^0/Pd^{II} catalytic cycle with the assistance of NHC ligand.[14,15] Combining this method and the reaction developed in recent years, we can directly accomplish the synthesis of

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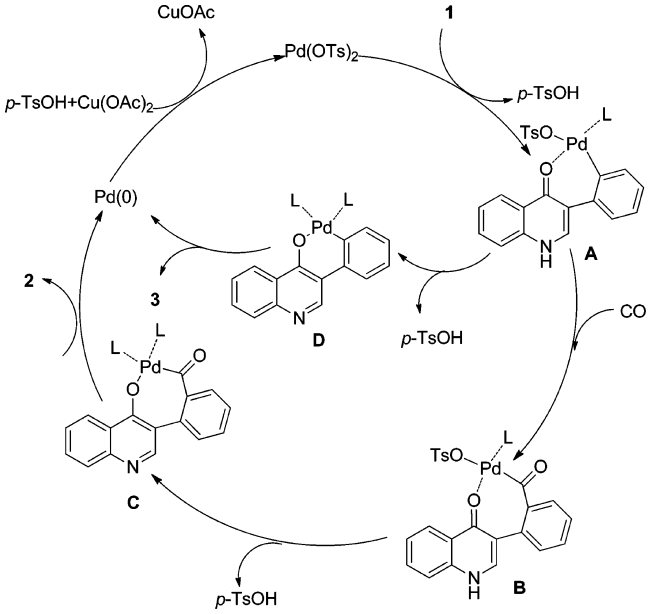
benzofuro[3,2-*c*]quinolines. As shown in Table 3, various derivatives could be synthesized in moderate to high yields.

On the basis of above results and previous reports,[5f,j,l] we propose a mechanism for this oxidative carbonylation (Scheme 1). $Pd(OTs)_2$ is first formed in situ by the reaction of $Pd_2(dba)_3$ with $Cu(OAc)_2$ and $TsOH{\cdot}H_2O$. Subsequently, aryl C−H activation by $Pd(OTs)_2$ affords the arylpalladium species **A**, which further reacts with CO to form the intermediate **B**. Then, **B** is transformed into **C** assisted by leaving *p*-TsOH. Finally, reductive elimination of **C** gives the desired carbonylation product **2** and generates the Pd^0 species. Alternatively, intermediate **D** is formed in the absence of CO, which undergoes reductive elimination to give product **3**.

Scheme 1. Proposed Mechanism



In conclusion, we have developed a simple and efficient strategy for the construction of 6*H*-isochromeno[4,3-*c*]-quinolin-6-ones and benzofuro[3,2-*c*]quinolines through Pd-catalyzed oxidative carbonylation or direct annulation process. The reaction exhibits high atom-efficiency and chemo- or regioselectivity for the direct functionalization of C−H and C−X bonds. Notably, this transformation provides a straightforward and convenient protocol toward the syntheses of PAHs.

EXPERIMENTAL SECTION

General Information. Melting points were measured with a melting point instrument and were uncorrected. ^1H and ^{13}C NMR spectra were recorded using a 400/600 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.24 and 77.0 ppm, respectively, and chloroform is solvent with TMS as the internal standard. IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a spectrometer. GC−MS was obtained using electron ionization. HRMS was obtained with a LCMS-IT-TOF mass spectrometer. TLC was performed by using commercially prepared 100−400 mesh silica gel plates and visualization was effected at 254 nm.

Typical Experimental Procedure for Synthesis of 4-Halo-2-aminoquinolines 2a−2u. The mixture of **1** (0.2 mmol), $TsOH{\cdot}H_2O$ (0.3 mmol), $Pd_2(dba)_3$ (10 mol %) and $Cu(OAc)_2{\cdot}H_2O$ (0.3 mmol) was stirred in dioxane (2.0 mL) at 100 °C, in a 20 mL tube with a balloon CO for 24 h. When the reaction was complete (detected by TLC), the mixture was cooled to room temperature. The residue was purified by column chromatography on silica gel to afford the corresponding products **2** with petroleum ether/ethyl acetate as the eluent.

Typical Experimental Procedure for Synthesis of 3a−3j. The mixture of **1** (0.2 mmol), $TsOH{\cdot}H_2O$ (0.3 mmol), $Pd_2(dba)_3$ (10 mol %) and $Cu(OAc)_2{\cdot}H_2O$ (0.3 mmol) was stirred in xylene (2.0 mL) at 140 °C, in a 20 mL tube for 12 h. When the reaction was completed (detected by TLC), the mixture was cooled to room temperature, and then the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel to afford the corresponding products **3** with petroleum ether/ethyl acetate as the eluent

*3-Phenylquinolin-4(1H)-one (**1a**).* Light yellow solid (1.5 g, 80%): mp 258−261 °C; IR (KBr) 3733, 2987, 2357, 1743, 1455, 1374, 1243, 1048, 931, 848, 611; ^1H NMR (400 MHz, DMSO) δ 12.08 (s, 1H), 8.23 (d, J = 8.0 Hz, 1H), 8.13 (s, 1H), 7.72 (d, J = 7.6 Hz, 2H), 7.66 (t, J = 7.6 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.44−7.32 (m, 3H), 7.28 (t, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO) δ 174.7, 139.3, 138.1, 136.2, 131.5, 128.4, 127.8, 126.3, 125.9, 125.6, 123.2, 119.7, 118.2. HRMS (ESI) m/z calcd for $C_{15}H_{12}NO$ $[M + H]^+$, 222.0913, found 222.0917.

*6-Methyl-3-phenylquinolin-4(1H)-one (**1b**).* Light yellow solid (1.0 g, 77%): mp >300 °C; IR (KBr) 3741, 2991, 2359, 1763, 1462, 1376, 1242, 1055, 928, 850, 629; ^1H NMR (400 MHz, DMSO) δ 8.10 (s, 1H), 8.02 (s, 1H), 7.74 (d, J = 7.6 Hz, 2H), 7.51 (d, J = 8.4 Hz, 1H), 7.45 (dd, J = 8.4, 1.6 Hz, 1H), 7.37 (t, J = 7.6 Hz, 2H), 7.25 (t, J = 7.2 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 174.1, 138.9, 138.4, 136.8, 132.5, 132.1, 128.3, 127.7, 126.0, 126.0, 124.7, 119.1, 119.0, 20.8. HRMS (ESI) m/z calcd for $C_{16}H_{14}NO$ $[M + H]^+$, 236.1070, found 236.1079.

*6-Ethyl-3-phenylquinolin-4(1H)-one (**1c**).* White solid (1.7 g, 80%): mp >300 °C; IR (KBr) 3739, 2990, 1763, 1376, 1242, 1055, 927, 848, 624; ^1H NMR (400 MHz, DMSO) δ 12.10 (s, 1H), 8.08 (m, 2H), 7.73 (d, J = 6.8 Hz, 2H), 7.54 (s, 2H), 7.39−7.37 (m, 2H), 7.29−7.27 (m, 1H), 2.75−2.72 (m, 2H), 1.24 (t, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, DMSO) δ 174.6, 138.8, 137.8, 137.6, 136.4, 131.9, 128.4, 127.8, 126.2, 125.8, 123.5, 119.4, 118.3, 27. 9, 15.6. HRMS (ESI) m/z calcd for $C_{17}H_{15}NNaO$ $[M + Na]^+$, 272.1046, found 272.1053.

*6-Isopropyl-3-phenylquinolin-4(1H)-one (**1d**).* Light brown solid (1.5 g, 75%): mp 237−239 °C; IR (KBr) 3745, 2990, 1763, 1461, 1376, 1242, 1055, 928, 848, 628; ^1H NMR (400 MHz, DMSO) δ 8.12 (s, 1H), 8.06 (s, 1H), 7.74 (d, J = 7.6 Hz, 2H), 7.59−7.54 (m, 2H), 7.40 (t, J = 7.6 Hz, 3H), 7.01 (d, J = 7.6, 7.4 Hz, 1H), 3.55−2.58 (m, 1H), 1.37−1.07 (m, 6H); ^{13}C NMR (100 MHz, DMSO) δ 174.6, 143.4, 137.8, 137.7, 136.4, 130.6, 128.4, 127.8, 126.7, 126.2, 125.8, 121.9, 119.4, 118.3, 116.4, 33.1, 23.9. HRMS (ESI) m/z calcd for $C_{18}H_{18}NO$ $[M + H]^+$, 264.1383, found 264.1387.

*6-Methoxy-3-phenylquinolin-4(1H)-one (**1e**).* Light pink solid (800 mg, 65%): mp >300 °C; IR (KBr) 3741, 2991, 2358, 1763, 1462, 1377, 1242, 1055, 929, 850, 626; ^1H NMR (400 MHz, DMSO) δ 8.09 (s, 1H), 7.77 (d, J = 7.2 Hz, 2H), 7.63 (s, 1H), 7.55 (d, J = 8.8 Hz, 1H), 7.36 (t, J = 7.2 Hz, 2H), 7.24−7.19 (m, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 172.9, 155.1, 140.5, 137.7, 128.2, 127.7, 127.5, 125.5, 122.3, 121.0, 117.8, 104.4, 99.5, 55.2. HRMS (ESI) m/z calcd for $C_{16}H_{14}NO_2$ $[M + H]^+$, 252.1019, found 252.1023.

*6-Bromo-3-phenylquinolin-4(1H)-one (**1f**).* Light yellow solid (2g, 81%): mp >300 °C; IR (KBr) 3740, 2990, 2361, 1764, 1464, 1377, 1242, 1055, 928, 849, 631; ^1H NMR (400 MHz, DMSO) δ 8.30 (s, 1H), 8.21 (s, 1H), 7.76−7.69 (m, 3H), 7.57 (d, J = 8.8 Hz, 1H), 7.37 (t, J = 7.6 Hz, 2H), 7.25 (t, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO) δ 172.6, 141.7, 140.7, 136.8, 133.2, 128.2, 127.9, 127.8, 127.5, 126.0, 123.0, 119.5, 115.2, 112.0. HRMS (ESI) m/z calcd for $C_{15}H_{10}BrNNaO$ $[M + Na]^+$, 321.9838, found 321.9841.

*6-Chloro-3-phenylquinolin-4(1H)-one (**1g**).* White solid (1.2 g, 77%): mp >300 °C; IR (KBr) 3737, 2990, 2356, 1761, 1459, 1376, 1242, 1053, 928, 848, 624; ^1H NMR (400 MHz, DMSO) δ 8.21 (s, 1H), 8.15 (s, 1H), 7.73 (d, J = 8.0 Hz, 2H), 7.68 (s, 2H), 7.40 (t, J = 7.4 Hz, 2H), 7.29 (t, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO) δ 173.4, 138.9, 138.2, 135.9, 131.5, 128.3, 127.9, 126.9, 126.5, 124.4,

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121.0, 119.9. HRMS (ESI) m/z calcd for $C_{15}H_{10}ClNNaO$ $[M + Na]^+$, 278.0343, found 278.0341.

6-Fluoro-3-phenylquinolin-4(1H)-one (**1h**). Light brown solid (1.5 g, 67%): mp >300 °C; IR (KBr) 3742, 2990, 2361, 1764, 1464, 1377, 1242, 1055, 930, 849, 631; ^{1}H NMR (400 MHz, DMSO) δ 8.21 (s, 1H), 7.87 (d, J = 9.2 Hz, 1H), 7.75−7.73 (m, 3H), 7.58 (t, J = 8.2 Hz, 1H), 7.40 (t, J = 7.2 Hz, 2H), 7.29 (t, J = 7.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO) δ 173.77, 158.44 (d, J = 240 Hz), 138.50, 136.05 (d, J = 22 Hz), 128.36, 127.83, 126.96 (d, J = 6 Hz), 126.40, 121.15 (d, J = 8 Hz), 120.36 (d, J = 26 Hz), 118.89, 109.41 (d, J = 22 Hz). HRMS (ESI) m/z calcd for $C_{15}H_{11}FNO$ $[M + H]^+$, 240.0819, found 240.0818.

6-Phenoxy-3-phenylquinolin-4(1H)-one (**1i**). Light brown solid (1.1 g, 70%): mp 256−258 °C; IR (KBr) 3738, 2991, 2316, 1764, 1479, 1376, 1242, 1055, 926, 626; ^{1}H NMR (400 MHz, DMSO) δ 12.33 (s, 1H), 8.17 (s, 1H), 7.71 (t, J = 7.4 Hz, 3H), 7.64 (s, 1H), 7.49−7.34 (m, 5H), 7.27 (t, J = 7.0 Hz, 1H), 7.19 (t, J = 7.2 Hz, 1H), 7.09 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, DMSO) δ 173.9, 156.6, 153.1, 138.0, 136.1, 135.5, 130.2, 128.4, 127.8, 126.9, 126.3, 124.1, 123.8, 120.7, 118.9, 112.1. HRMS (ESI) m/z calcd for $C_{21}H_{16}NO_2$ $[M + H]^+$, 314.1176, found 314.1177.

3-Phenyl-6-(trifluoromethoxy)quinolin-4(1H)-one (**1j**). Light brown solid (950 mg, 64%): mp >300 °C; IR (KBr) 3743, 2990, 2362, 1764, 1463, 1377, 1242, 1055, 927, 849, 631; ^{1}H NMR (600 MHz, TFA-$_{140311}$) δ 8.87 (s, 1H), 8.53 (s, 1H), 8.32 (d, J = 9.6 Hz, 1H), 8.08 (dd, J = 9.0, 2.4 Hz, 1H), 7.75−7.74 (m, 2H), 7.66 (d, J = 8.4 Hz, 1H), 7.64−7.60 (m, 2H), 7.50 (d, J = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, TFA-$_{140311}$) δ 165.8, 144.1, 136.5, 130.8, 130.2, 129.6, 128.9, 127.9, 124.3, 122.5, 121.8, 121.5, 120.7, 117. 2, 115.3, 113.8, 113.4, 111.5; HRMS (ESI) m/z calcd for $C_{16}H_{11}F_3NO_2$ $[M + H]^+$, 306.0736, found 306.0733.

3-Phenyl-6-(trifluoromethyl)quinolin-4(1H)-one (**1k**). Light yellow solid (1.3 g, 73%): mp >300 °C; IR (KBr) 3738, 2990, 2360, 1763, 1462, 1376, 1242, 1055, 932, 848, 632; ^{1}H NMR (600 MHz, TFA-$_{140311}$) δ 9.24 (s, 1H), 9.14 (s, 1H), 8.59 (dd, J = 21.0, 9.0 Hz, 2H), 7.95−7.94(m, 4H), 7.83−7.81 (m, 2H); ^{13}C NMR (151 MHz, TFA-$_{140311}$) δ 167.1, 145.7, 139.8, 131.7, 131.1, 130.4, 129.1, 127.9, 122.3, 120.9, 119.5, 117.3, 115.5, 113.6, 111.7. HRMS (ESI) m/z calcd for $C_{16}H_{10}F_3NNaO$ $[M + Na]^+$, 312.0607, found 312.0602.

8-Methyl-3-phenylquinolin-4(1H)-one (**1l**). Light brown solid (1.7 g, 86%): mp >300 °C; IR (KBr) 3738, 2990, 2360, 1763, 1462, 1376, 1242, 1054, 930, 848, 631; ^{1}H NMR (400 MHz, DMSO) δ 8.11 (d, J = 8.0 Hz, 1H), 8.00 (s, 1H), 7.72 (d, J = d, J = 5.9 Hz 7.6 Hz, 2H), 7.51 (d, J = 6.8 Hz, 1H), 7.40 (t, J = 7.6 Hz, 2H), 7.32−7.23 (m, 2H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 175.0, 138.0, 137.9, 136.1, 132.2, 128.4, 127.9, 126.4, 126.3, 126.0, 123.5, 122.9, 119.8, 17.1. HRMS (ESI) m/z calcd for $C_{16}H_{13}NNaO$ $[M + Na]^+$, 258.0889, found 258.0886.

3-Phenyl-7-(trifluoromethyl)quinolin-4(1H)-one (**1m**). White solid (500 mg, 55%): mp >300 °C; IR (KBr) 3740, 2990, 2361, 1763, 1462, 1376, 1242, 1054, 928, 849, 631; ^{1}H NMR (600 MHz, TFA-$_{140311}$) δ 9.00 (s, 1H), 8.92 (d, J = 9.0 Hz, 1H), 8.59 (s, 1H), 8.26 (d, J = 8.4 Hz, 1H), 7.78 (s, 3H), 7.70−7.63 (m, 2H); ^{13}C NMR (151 MHz, TFA-$_{140311}$) δ 166.3, 145.5, 137.9, 131.0, 130.3, 128.9, 127.8, 125.7, 125.3, 122.4, 121.4, 117.1, 115.3, 113.4, 111.5. HRMS (ESI) m/z calcd for $C_{16}H_{11}F_3NO$ $[M + H]^+$, 290.0787, found 290.0787.

5,7-Dimethyl-3-phenylquinolin-4(1H)-one (**1n**). Light brown solid (1.6 g, 87%): mp 211−214 °C; IR (KBr) 3739, 2990, 2359, 1764, 1462, 1377, 1242, 1055, 928, 850, 631; ^{1}H NMR (400 MHz, DMSO) δ 7.92 (s, 1H), 7.65 (d, J = 7.6 Hz, 2H), 7.36 (t, J = 7.6 Hz, 2H), 7.25 (t, J = 7.2 Hz, 1H), 7.17 (s, 1H), 6.84 (s, 1H), 6.45 (d, J = 7.6 Hz, 1H), 2.81 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 177.1, 141.2, 140.5, 139.6, 138.0, 136.5, 128.6, 127.6, 127.4, 126.1, 122.3, 121.1, 115.6, 23.5, 20.9. HRMS (ESI) m/z calcd for $C_{17}H_{16}NO$ $[M + H]^+$, 250.1226, found 250.1226.

3-Phenylbenzo[h]quinolin-4(1H)-one (**1o**). Light pink solid (1.0 g, 70%): mp >300 °C; IR (KBr) 3738, 2990, 2361, 1763, 1463, 1376, 1242, 1054, 930, 849, 632; ^{1}H NMR (600 MHz, TFA-$_{140311}$) δ 9.02 (s, 1H), 8.99 (d, J = 7.8 Hz, 1H), 8.68 (d, J = 9.0 Hz, 1H), 8.55−8.39 (m, 2H), 8.34−8.18 (m, 2H), 7.97 (d, J = 6.6 Hz, 3H), 7.86 (d, J = 6.6 Hz, 2H); ^{13}C NMR (151 MHz, TFA-$_{140311}$) δ 165.6, 140.6, 135.8, 132.1, 131.0, 130.5, 129.8, 129.5, 129.0, 128.4, 123.1, 121.8, 120.5, 117.3, 115.5, 113.6, 111.7. HRMS (ESI) m/z calcd for $C_{19}H_{14}NO$ $[M + H]^+$, 272.1070, found 272.1069.

3-Phenyl-1,8-naphthyridin-4(1H)-one (**1p**). Light yellow solid (1.4 g, 72%): mp >300 °C; IR (KBr) 3739, 2990, 2360, 1764, 1485, 1377, 1242, 1056, 926, 849, 628; ^{1}H NMR (400 MHz, DMSO) δ 9.12 (d, J = 7.2 Hz, 1H), 8.63 (s, 1H), 7.99 (t, J = 7.8 Hz, 1H), 7.85 (d, J = 7.6 Hz, 2H), 7.76 (d, J = 8.8 Hz, 1H), 7.48−7.42 (m, 3H), 7.36 (t, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO) δ 156.0, 152.7, 150.3, 137.1, 134.4, 128.2, 128.2, 127.4, 127.3, 126.1, 116.8, 115.0. HRMS (ESI) m/z calcd for $C_{14}H_{11}N_2O$ $[M + H]^+$, 223.0866, found 223.0869.

3-(p-Tolyl)quinolin-4(1H)-one (**1q**). Light brown solid (1.1 g, 90%): mp 287−289 °C; IR (KBr) 3738, 2990, 2360, 1764, 1463, 1377, 1242, 1055, 928, 849, 631; ^{1}H NMR (400 MHz, DMSO) δ 12.16 (s, 1H), 8.23 (d, J = 8.0 Hz, 1H), 8.11 (s, 1H), 7.67−7.59 (m, 4H), 7.34 (t, J = 7.4 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 174.7, 139.3, 137.7, 135.38, 133.2, 131.4, 128.4, 128.2, 125.8, 125.6, 123.1, 119.7, 118.2, 20.8. HRMS (ESI) m/z calcd for $C_{16}H_{14}NO$ $[M + H]^+$, 236.1070, found 236.1074.

3-(4-Methoxyphenyl)quinolin-4(1H)-one (**1r**). Light brown solid (1.8 g, 88%): mp >300 °C; IR (KBr) 3740, 2990, 2361, 1764, 1463, 1377, 1242, 1055, 928, 849, 631; ^{1}H NMR (400 MHz, DMSO) δ 8.23 (d, J = 7.6 Hz, 1H), 8.09 (s, 1H), 7.83−7.49 (m, 4H), 7.33 (s, 1H), 6.96 (d, J = 8.0 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 174.5, 157.8, 139.9, 138.2, 131.1, 129.4, 128.7, 125.9, 125.5, 122.9, 119.3, 118.7, 113.3, 55.0. HRMS (ESI) m/z calcd for $C_{16}H_{14}NO_2$ $[M + H]^+$, 252.1019, found 252.1025.

3-(Naphthalen-1-yl)quinolin-4(1H)-one (**1s**). Light yellow solid (900 mg, 56%): mp 264−266 °C; IR (KBr) 3742, 2990, 2361, 1764, 1463, 1377, 1242, 1055, 928, 849, 631; ^{1}H NMR (400 MHz, DMSO) δ 12.14 (s, 1H), 8.22 (d, J = 7.2 Hz, 1H), 8.03 (s, 1H), 7.95−7.90(m, 2H), 7.70−7.66 (m, 3H), 7.60−7.15 (m, 5H); ^{13}C NMR (100 MHz, DMSO) δ 175.2, 139.8, 139.2, 135.0, 133.1, 132.2, 131.6, 127.9, 127.5, 126.5, 125.6, 125.5, 125.4, 123.3, 120.4, 118.4. HRMS (ESI) m/z calcd for $C_{19}H_{14}NO$ $[M + H]^+$, 272.1070, found 272.1075.

3-(4-Fluorophenyl)quinolin-4(1H)-one (**1t**). Light brown solid (1.3 g, 65%): mp 244−246 °C; IR (KBr) 3741, 2990, 2362, 1764, 1464, 1376, 1242, 1055, 928, 849, 631; ^{1}H NMR (400 MHz, DMSO) δ 12.22 (s, 1H), 8.23 (d, J = 8.0 Hz, 1H), 8.17 (s, 1H), 7.80−7.77 (m, 2H), 7.69−7.61 (m, 2H), 7.36 (t, J = 7.4 Hz, 1H), 7.22 (t, J = 9.0 Hz, 2H); ^{13}C NMR (100 MHz, DMSO) δ 174.6, 160.9 (d, J = 240 Hz), 139.3, 138.1, 132.4 (d, J = 3 Hz), 131.6, 130.2 (d, J = 7.8 Hz), 128.8, 125.8, 125.5, 123.3, 118.7, 118.2, 114.5 (d, J = 20.9 Hz), 114.0. HRMS (ESI) m/z calcd for $C_{15}H_{11}FNO$ $[M + H]^+$, 240.0819, found 240.0823.

6H-Isochromeno[4,3-c]quinolin-6-one (**2a**). Light pink solid(42 mg, 85%): mp 246−248 °C; IR (KBr) 3427, 2987, 1763, 1453, 1376, 1242, 1056, 954, 850, 794, 629; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.54 (s, 1H), 8.49−8.44 (m, 2H), 8.30 (d, J = 8.2 Hz, 1H), 8.13 (d, J = 8.2 Hz, 1H), 7.92 (t, J = 7.2 Hz, 1H), 7.81 (t, J = 7.2 Hz, 1H), 7.67 (dd, J = 15.6, 7.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 152.9, 148.2, 144.9, 135.2, 133.0, 130.8, 130.7, 129.2, 128.8, 127.4, 121.6, 121.1, 120.7, 118.2, 108.8. HRMS (ESI) m/z calcd for $C_{16}H_{10}NO_2$ $[M + H]^+$, 248.0706, found 248.0709.

3-Methyl-6H-isochromeno[4,3-c]quinolin-6-one (**2b**). White solid (43 mg, 83%): mp 239−241 °C; IR (KBr) 3447, 2990, 1764, 1458, 1377, 1242, 1056, 927, 851, 794, 630; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (s, 1H), 8.46 (d, J = 7.6 Hz, 1H), 8.31 (d, J = 7.6 Hz, 1H), 8.26 (s, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.91 (t, J = 7.4 Hz, 1H), 7.67−7.61 (m, 2H), 2.60 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 152.3, 147.1, 144.0, 137.7, 135.2, 133.3, 132.9, 130.6, 129.0, 128.7, 121.1, 120.7, 120.5, 108.8, 99.6, 21.5. HRMS (ESI) m/z calcd for $C_{17}H_{12}NO_2$ $[M + H]^+$, 262.0863, found 262.0862.

3-Ethyl-6H-isochromeno[4,3-c]quinolin-6-one (**2c**). White solid (44 mg, 80%): mp 201−203 °C; IR (KBr) 3504, 2990, 1763, 1459, 1377, 1242, 1056, 927, 847, 791, 631; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.46 (s, 1H), 8.41 (d, J = 8.0 Hz, 1H), 8.28−8.19 (m, 2H), 7.99 (d, J = 7.2 Hz, 1H), 7.87 (t, J = 7.6 Hz, 1H), 7.63−7.59 (m, 2H), 2.87 (q, J = 7.6 Hz, 2H), 1.36 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ

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160.0, 152.6, 144.1, 135.4, 133.5, 132.1, 130.8, 129.2, 121.3, 120.9, 119.5, 29.1, 15.4. HRMS (ESI) m/z calcd for $C_{18}H_{14}NO_2$ $[M + H]^+$, 276.1019, found 276.1020.

3-Isopropyl-6H-isochromeno[4,3-c]quinolin-6-one (**2d**). White solid (52 mg, 90%): mp 183−185 °C; IR (KBr) 3507, 2989, 1763, 1459, 1376, 1242, 1056, 927, 837, 760, 630; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 8.40 (d, J = 8.0 Hz, 1H), 8.25−8.23 (m, 2H), 8.01 (d, J = 8.6 Hz, 1H), 7.87 (t, J = 7.6 Hz, 1H), 7.68 (d, J = 8.6 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 3.15 (dt, J = 13.6, 7.0 Hz, 1H), 1.38 (d, J = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 152.9, 151.2, 148.8, 147.6, 144.4, 135.5, 133.6, 130.9, 130.9, 129.3, 129.1, 121.4, 121.0, 118.1, 109.0, 34.5, 23.9. HRMS (ESI) m/z calcd for $C_{19}H_{16}NO_2$ $[M + H]^+$, 290.1176, found 290.1178.

3-Methoxy-6H-isochromeno[4,3-c]quinolin-6-one (**2e**). White solid (48 mg, 87%): mp 260−262 °C; IR (KBr) 3446, 2988, 1763, 1456, 1376, 1242, 1057, 930, 848, 790, 631; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (s, 1H), 8.47 (d, J = 8.0 Hz, 1H), 8.31 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 8.8 Hz, 1H), 7.92 (t, J = 7.6 Hz, 1H), 7.80−7.58 (m, 2H), 7.42 (dd, J = 9.2, 2.4 Hz, 1H), 4.02 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 158.5, 151.8, 144.6, 142.3, 135.2, 133.3, 130.6, 130.5, 129.1, 123.5, 121.2, 120.8, 119.1, 109.0, 99.0, 55.7. HRMS (ESI) m/z calcd for $C_{17}H_{12}NO_3$ $[M + H]^+$, 278.0812, found 278.0811.

3-Bromo-6H-isochromeno[4,3-c]quinolin-6-one (**2f**). White solid (52 mg, 81%): mp 263−265 °C; IR (KBr) 3506, 2990, 1764, 1459, 1376, 1242, 1056, 927, 850, 789, 631; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (s, 1H), 8.67 (s, 1H), 8.49 (d, J = 7.8 Hz, 1H), 8.33 (d, J = 7.8 Hz, 1H), 8.02 (d, J = 8.6 Hz, 1H), 7.96 (t, J = 7.6 Hz, 1H), 7.88 (d, J = 8.6 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 159.6, 152.0, 147.4, 145.7, 135.7, 134.5, 133.1, 131.2, 131.1, 129.9, 124.4, 122.0, 121.6, 121.2, 109.8. HRMS (ESI) m/z calcd for $C_{16}H_9BrNO_2$ $[M + H]^+$, 325.9811, found 325.9814.

3-Chloro-6H-isochromeno[4,3-c]quinolin-6-one (**2g**). White solid (50 mg, 90%): mp 2379−281 °C; IR (KBr) 3397, 2988, 1762, 1455, 1375, 1242, 1056, 954, 851, 754, 683; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.54 (s, 1H), 8.48−8.46 (m, 2H), 8.32 (d, J = 8.4 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 7.95 (t, J = 7.4 Hz, 1H), 7.74−7.68 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 152.1, 147.1, 145.6, 135.7, 133.9, 133.1, 131.9, 131.1, 131.0, 129.9, 121.6, 121.2, 121.1. HRMS (ESI) m/z calcd for $C_{16}H_9ClNO_2$ $[M + H]^+$, 282.0316, found 282.0312.

3-Fluoro-6H-isochromeno[4,3-c]quinolin-6-one (**2h**). White solid (43 mg, 82%): mp 255−257 °C; IR (KBr) 3442, 2987, 1763, 1453, 1375, 1242, 1055, 929, 849, 795, 631; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 1H), 8.45 (d, J = 8.0 Hz, 1H), 8.31 (d, J = 8.0 Hz, 1H), 8.16−8.09 (m, 1H), 8.05 (d, J = 8.8 Hz, 1H), 7.93 (t, J = 7.6 Hz, 1H), 7.68 (t, J = 7.6 Hz, 1H), 7.54 (t, J = 8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2 (d, J = 248 Hz), 159.7, 152.6, 145.9, 144.7, 135.7, 133.1, 132.0 (d, J = 9.2 Hz), 131.1, 129.8, 121.6, 121.2 (d, J = 2 Hz), 121.0, 109.6, 106.0 (d, J = 24 Hz). HRMS (ESI) m/z calcd for $C_{16}H_9FNO_2$ $[M + H]^+$, 266.0612, found 266.0608.

3-Phenoxy-6H-isochromeno[4,3-c]quinolin-6-one (**2i**). White solid (57 mg, 85%): mp 235−237 °C; IR (KBr) 3447, 2990, 1763, 1461, 1376, 1242, 1056, 928, 850, 795, 630; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (s, 1H), 8.43 (d, J = 8.2 Hz, 1H), 8.30 (d, J = 8.2 Hz, 1H), 8.10 (d, J = 9.2 Hz, 1H), 7.91 (t, J = 8.0 Hz, 1H), 7.86 (d, J = 2.4 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.55 (dd, J = 9.0, 2.6 Hz, 1H), 7.42 (t, J = 7.8 Hz, 2H), 7.21 (t, J = 7.4 Hz, 1H), 7.13 (d, J = 8.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 156.9, 156.2, 152.3, 145.6, 143.8, 135.5, 133.4, 131.4, 131.0, 130.2, 129.5, 124.5, 124.5, 121.5, 121.2, 119.6, 119.5, 109.4, 107.4. HRMS (ESI) m/z calcd for $C_{22}H_{14}NO_3$ $[M + H]^+$, 340.0968, found 340.0974.

3-(Trifluoromethoxy)-6H-isochromeno[4,3-c]quinolin-6-one (**2j**). White solid (59 mg, 90%): mp >300 °C; IR (KBr) 3504, 2989, 1761, 1461, 1375, 1242, 1055, 931, 843, 786, 632; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.52 (s, 1H), 8.43 (d, J = 7.6 Hz, 1H), 8.28 (d, J = 8.0 Hz, 1H), 8.24 (s, 1H), 8.14 (d, J = 9.2 Hz, 1H), 7.92 (t, J = 7.6 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.62 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 152.7, 147.9, 146.9, 145.8, 135.7, 132.9, 131.7, 131.1, 129.9, 124.9, 121.8, 121.6, 121.2, 119.2, 119.0, 112.6, 109.7. HRMS (ESI) m/z calcd for $C_{17}H_9F_3NO_3$ $[M + H]^+$, 332.0529, found 332.0531.

3-(Trifluoromethyl)-6H-isochromeno[4,3-c]quinolin-6-one (**2k**). White solid (58 mg, 92%): mp 217−219 °C; IR (KBr) 3744, 2990, 1763, 1462, 1376, 1242, 1056, 927, 839, 794, 630; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.61 (s, 1H), 8.75 (s, 1H), 8.44 (d, J = 8.0 Hz, 1H), 8.30 (d, J = 8.0 Hz, 1H), 8.21 (d, J = 8.4 Hz, 1H), 7.95−7.94 (m, 2H), 7.69 (t, J = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 153.3, 149.5, 147.6, 135.8, 132.7, 131.2, 130.6, 130.1, 129.8, 129.4, 126.7 (d, J = 3 Hz), 123.72 (d, J = 271 Hz), 121.6, 121.1, 120.3−120.2 (q, J = 4.6, J = 9.1 Hz), 117.8, 110.0. HRMS (ESI) m/z calcd for $C_{17}H_8F_3NO_2$ $[M + H]^+$, 316.0585 found, 316.0587.

1-Methyl-6H-isochromeno[4,3-c]quinolin-6-one (**2l**). White solid (35 mg, 68%): mp 279−281 °C; IR (KBr) 3858, 2988, 1763, 1453, 1376, 1242, 1056, 929, 848, 787, 631; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (s, 1H), 8.47 (d, J = 7.6 Hz, 1H), 8.37 (d, J = 8.0 Hz, 1H), 8.32 (d, J = 7.6 Hz, 1H), 7.93 (t, J = 7.6 Hz, 1H), 7.68−7.65 (m, 2H), 7.57 (t, J = 7.4 Hz, 1H), 2.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 153.3, 147.9, 144.1, 137.3, 135.6, 133.6, 131.4, 1301.0, 129.4, 127.4, 121.4, 121.1, 119.9, 118.4, 108.8, 18.2. HRMS (ESI) m/z calcd for $C_{17}H_{12}NO_2$ $[M + H]^+$, 262.0863, found 262.0863.

2-(Trifluoromethyl)-6H-isochromeno[4,3-c]quinolin-6-one (**2m**). White solid (57 mg, 91%): mp >300 °C; IR (KBr) 3743, 2988, 1763, 1458, 1376, 1242, 1056, 930, 848, 793, 631; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.65 (s, 1H), 8.61 (d, J = 8.8 Hz, 1H), 8.49 (d, J = 8.0 Hz, 1H), 8.43 (s, 1H), 8.35 (d, J = 8.0 Hz, 1H), 7.97 (t, J = 7.9 Hz, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 151.7, 146.8, 145.9, 134.8, 131.8, 131. 5, 130.2, 129.1, 126.2−126.0 (q, J = 4.3 Hz, J = 8.6 Hz), 124.0, 122.6 (d, J = 271 Hz), 122.4, 120.7, 120.3, 119.3, 109.5. HRMS (ESI) m/z calcd for $C_{17}H_9F_3NO_2$ $[M + H]^+$, 316.0580, found 316.0577.

2,4-Dimethyl-6H-isochromeno[4,3-c]quinolin-6-one (**2n**). White solid (47 mg, 85%): mp 270−272 °C; IR (KBr) 3743, 2989, 1764, 1457, 1376, 1242, 1056, 931, 850, 794, 631; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (s, 1H), 8.43 (d, J = 8.0 Hz, 1H), 8.30 (d, J = 8.0 Hz, 1H), 7.91 (t, J = 7.4 Hz, 1H), 7.74 (s, 1H), 7.64 (t, J = 7.6 Hz, 1H), 3.08 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 155.0, 145.1, 141.0, 135.4, 135.3, 133.9, 132.6, 130.6, 129.9, 129.1, 127.0, 121.3, 120.3, 115.9, 108.8, 24.5, 21.6. HRMS (ESI) m/z calcd for $C_{18}H_{14}NO_2$ $[M + H]^+$, 276.1019, found 276.1016.

8-Methyl-6H-isochromeno[4,3-c]quinolin-6-one (**2q**). White solid (45 mg, 87%): mp 223−225 °C; IR (KBr) 3745, 2990, 1763, 1458, 1376, 1242, 1055, 929, 849, 787, 630; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 8.41−8.39 (m, 1H), 8.17 (s, 1H), 8.12−8.05 (m, 2H), 7.74 (t, J = 6.8 Hz, 1H), 7.66−7.61 (m, 2H), 2.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 152.5, 148.5, 145.3, 140.0, 136.7, 130.7, 129.2, 127.6, 121.8, 121.3, 120.8, 118.5, 109.2, 21.4. HRMS (ESI) m/z calcd for $C_{17}H_{12}NO_2$ $[M + H]^+$, 262.0863, found 262.0867.

8-Methoxy-6H-isochromeno[4,3-c]quinolin-6-one (**2r**). White solid (44 mg, 80%): mp 260−262 °C; IR (KBr) 3746, 2988, 1764, 1457, 1376, 1242, 1056, 931, 850, 787, 630; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (s, 1H), 8.48 (d, J = 8.0 Hz, 1H), 8.23 (d, J = 8.8 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.84 (s, 1H), 7.78 (t, J = 7.2 Hz, 1H), 7.67 (t, J = 7.4 Hz, 1H), 7.48 (d, J = 8.4 Hz, 1H), 3.97 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 160.2, 151.8, 145.2, 138.2, 130.5, 129.3, 127.6, 126.7, 124.9, 123.1, 122.5, 121.7, 111.8, 109.4, 100.0, 55.9. HRMS (ESI) m/z calcd for $C_{17}H_{12}NO_3$ $[M + H]^+$, 278.0812, found 278.0809.

6H-Benzo[5,6]isochromeno[4,3-c]quinolin-6-one (**2s**). Light yellow solid (56 mg, 95%): mp 205−207 °C; IR (KBr) 3747, 2955, 1763, 1453, 1375, 1242, 1057, 958, 851, 767, 628; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 8.8−8.84 (m, 1H), 8.53 (d, J = 8.4 Hz, 1H), 8.32 (d, J = 8.4 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 8.01−7.98 (m, 2H), 7.83 (t, J = 7.6 Hz, 1H), 7.76−7.73 (m, 2H), 7.69 (t, J = 7.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 153.8, 148.5, 147.7, 137.2, 133.1, 131.4, 130.3, 129.6, 129.4, 128.8, 128.1, 127.7, 127.6, 127.2, 124.4, 122.2, 119.8, 118.5, 110.4. HRMS (ESI) m/z calcd for $C_{20}H_{12}NO_2$ $[M + H]^+$, 298.0863, found 298.0859.

8-Fluoro-6H-isochromeno[4,3-c]quinolin-6-one (**2t**). White solid (47 mg, 89%): mp 265−267 °C; IR (KBr) 3736, 2990, 1763, 1458, 1376, 1242, 1056, 931, 849, 790, 630; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.53 (s, 1H), 8.49 (d, J = 8.0 Hz, 1H), 8.36−8.32 (m, 1H), 8.17 (d, J =

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8.4 Hz, 1H), 8.12 (dd, J = 8.4, 2.4 Hz, 1H), 7.83 (t, J = 7.4 Hz, 1H), 7.72−7.63 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (d, J = 233 Hz), 161.5, 159.0, 152.8, 148.4, 144.9, 131.3, 129.9 (d, J = 3 Hz), 129.1, 128.0, 124.1 (d, J = 7 Hz), 123.8, 123.1, 123.0, 121.9, 116.8 (d, J = 23 Hz), 108.6. HRMS (ESI) m/z calcd for $C_{16}H_9FNO_2$ $[M + H]^+$, 266.0612, found 266.0609.

*Benzofuro[3,2-c]quinoline (**3a**).* Light yellow solid (37 mg, 85%): mp 124−126 °C; IR (KBr) 3424, 2989, 2362, 1455, 1376, 1242, 1056, 931, 851, 759, 630; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (s, 1H), 8.41 (d, J = 8.0 Hz, 1H), 8.27 (d, J = 8.4z, 1H), 8.09 (d, J = 7.6 Hz, 1H), 7.80−7.74 (m, 2H), 7.69 (t, J = 7.6 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 156.0, 147.4, 144.4, 129.8, 129.3, 127.2, 127.0, 124.1, 122.7, 120.8, 120.6, 117.2, 116.3, 112.1. HRMS (ESI) m/z calcd for $C_{15}H_{10}NO$ $[M + H]^+$, 220.0757, found 220.0758.

*2-Methoxybenzofuro[3,2-c]quinoline (**3b**).* Light yellow solid (43 mg, 87%): mp 135−137 °C; IR (KBr) 3722, 2989, 2362, 1464, 1376, 1242, 1056, 930, 843, 751, 630; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (s, 1H), 8.15 (d, J = 8.6 Hz, 1H), 8.07 (d, J = 7.6 Hz, 1H), 7.73 (d, J = 8.6 Hz, 1H), 7.62−7.61 (m, 1H), 7.53 (t, J = 7.8 Hz, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.40 (dd, J = 9.2, 2.8 Hz, 1H), 4.03 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 156.6, 155.6, 143.0, 141.3, 131.0, 126.9, 123.7, 122.5, 121.5, 120.4, 117.6, 116.2, 111.7, 98.3, 55.4. HRMS (ESI) m/z calcd for $C_{16}H_{12}NO_2$ $[M + H]^+$, 250.0863, found 250.0867.

*2-(Trifluoromethoxy)benzofuro[3,2-c]quinoline (**3c**).* Light brown solid (48 mg, 89%): mp 142−144 °C; IR (KBr) 3747, 2988, 2361, 1459, 1374, 1244, 1057, 930, 842, 752, 631; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.46 (s, 1H), 8.28 (d, J = 8.8 Hz, 1H), 8.18 (s, 1H), 8.07 (t, J = 6.8 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.60−7.54 (m, 2H), 7.50 (t, J = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 156.1, 147.4, 145.4, 144.7, 132.2, 127.8, 124.3, 123.1, 122.3, 121.9, 120.8, 117.0, 112.2, 111.2. HRMS (ESI) m/z calcd for $C_{16}H_9F_3NO_2$ $[M + H]^+$, 304.0580, found 304.0582.

*2-Phenoxybenzofuro[3,2-c]quinoline (**3d**).* Light brown solid (49 mg, 79%): mp 159−161 °C; IR (KBr) 3743, 2989, 2361, 1459, 1376, 1242, 1056, 926, 849, 752, 630; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (s, 1H), 8.24 (d, J = 9.2 Hz, 1H), 8.05 (d, J = 7.6 Hz, 1H), 7.74 (s, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.52 (m, 2H), 7.44 (t, J = 7.6 Hz, 3H), 7.22 (t, J = 7.4 Hz, 1H), 7.17 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 156.3, 156.2, 155.8, 143.9, 142.6, 131.7, 130.0, 127.2, 124.1, 123.9, 122.5, 122.5, 120.6, 119.7, 117.8, 116.5, 112.0, 106.1. HRMS (ESI) m/z calcd for $C_{21}H_{14}NO_2$ $[M + H]^+$, 312.1019, found 312.1026.

*2-Fluorobenzofuro[3,2-c]quinoline (**3e**).* Light brown solid (38 mg, 80%): mp 148−149 °C; IR (KBr) 3745, 2988, 2361, 1461, 1374, 1242, 1056, 955, 844, 750, 631; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (s, 1H), 8.30−8.26 (m, 1H), 8.09 (d, J = 7.6 Hz, 1H), 7.99 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.60−7.47 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (d, J = 240 Hz), 157.1 (d, J = 10 Hz), 156.0, 143.5, 132.5 (d, J = 9.4 Hz), 127.7, 124.2, 122.4, 120.8, 119.3 (d, J = 20 Hz), 112.2, 104.7 (d, J = 20 Hz). HRMS (ESI) m/z calcd for $C_{15}H_9FNO$ $[M + H]^+$, 238.0663, found 238.0662.

*2-Chlorobenzofuro[3,2-c]quinoline (**3f**).* Light brown solid (30 mg, 60%): mp 139−141 °C; IR (KBr) 3419, 2988, 2361, 1457, 1375, 1242, 1056, 954, 848, 754, 632; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (s, 1H), 8.36 (s, 1H), 8.18 (d, J = 8.8 Hz, 1H), 8.08 (d, J = 7.6 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.8 Hz, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 155.7, 145.3, 144.2, 132.7, 131.2, 129.8, 127.4, 124.0, 122.1, 120.5, 119.6, 117.5, 116.6, 111.9. HRMS (ESI) m/z calcd for $C_{15}H_9ClNO$ $[M + H]^+$, 254.0367, found 254.0364.

*9-Methylbenzofuro[3,2-c]quinoline (**3g**).* Light yellow solid (38 mg, 81%): mp 148−150 °C; IR (KBr) 3746, 2953, 2361, 1457, 1375, 1242, 1057, 944, 857, 761, 631; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 8.36 (d, J = 8.4 Hz, 1H), 8.24 (d, J = 8.8 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.74 (t, J = 7.8 Hz, 1H), 7.65 (t, J = 7.4 Hz, 1H), 7.51 (s, 1H), 7.25 (s, 1H), 2.55 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 156.4, 147.0, 144.1, 137.9, 129.7, 129.0, 126.9, 125.3, 120.7, 120.0, 120.0, 117.2, 116.4, 112.3, 22.0. HRMS (ESI) m/z calcd for $C_{16}H_{12}NO$ $[M + H]^+$, 234.0913, found 234.0917.

*9-Methoxybenzofuro[3,2-c]quinoline (**3h**).* Light yellow solid (38 mg, 77%): mp 139−141 °C; IR (KBr) 3747, 2987, 2361, 1457, 1374, 1242, 1056, 947, 847, 765, 633; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (s, 1H), 8.33 (d, J = 8.0 Hz, 1H), 8.24 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.8 Hz, 1H), 7.73 (t, J = 7.4 Hz, 1H), 7.65 (t, J = 7.4 Hz, 1H), 7.23 (s, 1H), 7.04 (d, J = 8.4 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 157.6, 157.6, 146.9, 144.0, 130.0, 129.1, 127.2, 121.11, 120.8, 117.4, 116.8, 115.9, 112.8, 97.2, 56.1. HRMS (ESI) m/z calcd for $C_{16}H_{12}NO_2$ $[M + H]^+$, 250.0863, found 250.0867.

*9-Fluorobenzofuro[3,2-c]quinoline (**3i**).* Light yellow solid (39 mg, 83%): mp 148−150 °C; IR (KBr) 3742, 2988, 2360, 1457, 1375, 1242, 1056, 955, 845, 765, 629; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (s, 1H), 8.36 (d, J = 8.0 Hz, 1H), 8.29 (d, J = 8.4 Hz, 1H), 8.03−7.99 (m, 1H), 7.80 (t, J = 7.4 Hz, 1H), 7.71 (t, J = 7.4 Hz, 1H), 7.47 (d, J = 8.8 Hz, 1H), 7.23 (t, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3 (d, J = 245 Hz), 158.14 (d, J = 2.4 Hz), 156.18 (d, J = 14 Hz), 146.93, 143.79, 129.69, 129.43, 127.26, 121.15 (d, J = 10 Hz), 120.61, 118.98, 118.96, 116.97, 115.83, 112.32 (d, J = 24 Hz), 100.28 (d, J = 27 Hz). HRMS (ESI) m/z calcd for $C_{15}H_9FNO$ $[M + H]^+$, 238.0663, found 238.0661.

*1,3-Dimethylbenzofuro[3,2-c]quinoline (**3j**).* Light brown solid (40 mg, 81%): mp 158−161 °C; IR (KBr) 3504, 2989, 2361, 1457, 1376, 1242, 1055, 930, 8503, 752, 631; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 8.07 (d, J = 7.6 Hz, 1H), 7.91 (s, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.46 (t, J = 7.4 Hz, 1H), 7.29 (s, 1H), 3.08 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 155.7, 148.4, 143.7, 139.4, 133.2, 130.6, 126.9, 126.4, 124.0, 122.2, 120.3, 116.1, 115.1, 112.0, 22.2, 21.7. HRMS (ESI) m/z calcd for $C_{17}H_{14}NO$ $[M + H]^+$, 248.1070, found 248.1070.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra of all synthesized compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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