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Room Temperature Benzofused Lactam Synthesis Enabled by Cobalt(III)-Catalyzed C(sp^2)−H Amidation

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Abstract. Benzofused lactams, especially indolin-2-one and dihydroquinolin-2-one are popular structural motives in durgs and natural products. Herein, we developed a room temperature and robust synthesis of benzofused lactams through cobalt(III)-catalyzed C(sp^2)−H amidation. In this protocol, in-situ formation of Cp*Co(III)(ligand) catalyst from Cp*Co(CO)I_2 and ligand simplify the synthetic effort of cobalt complexes. Simple and readily synthesized 1,4,2-dioxazol-5-ones underwent room temperature intramolecular C−H amidation and afforded a wide variety of functionalized benzofused lactams in up to 86% yield. The scalability of the reaction is also be demonstrated.

Keywords: Cobalt catalysis; Benzofused lactams; Indolin-2-ones; Dihydroquinolin-2-ones; Intramolecular C−H amidation

Introduction

Benzofused lactams, especially five-membered indolin-2-one and six-membered dihydroquinolin-2-one are valuable hetero-cyclic skeletons widely present in bioactive compounds and natural products.[1] They are important targets because of their potent biological properties, including anticancer, antiviral, antibacterial, analgestic, anti-inflammatory, antihypertensive activities and NMDA antagonistic effect.[2] (Figure 1). They also serve as synthetic blocks for the construction of highly complex heterocycles.[3] Consequently, efficient and straightforward approaches for the synthesis of indolin-2-one and dihydroquinolin-2-one derivatives remain in demand.

For decades, organic chemists keep looking for new and efficient routes to prepare these benzofused lactams. Traditional synthetic routes for C(sp^2)−N bond construction generally employ the transition-metal-mediated cross-coupling methodologies of amines/amides with aryl halides,[4] particularly Cu-catalyzed Ullmann-type reactions[5] and Pd-catalyzed Buchwald-Hartwig aminations[6] (Scheme 1a). In 2020, Radosevich developed an organocatalytic method to construct oxindoles, which used a small-ring organophosphorus-based catalyst (4·[O]) and a hydrosilane reductant through a tandem intermolecular C-N coupling of nitroarenes and boronic acid, followed by intramolecular cyclization at 120 °C[7] (Scheme 1b). Recently, significant progress has been made in the construction of lactam

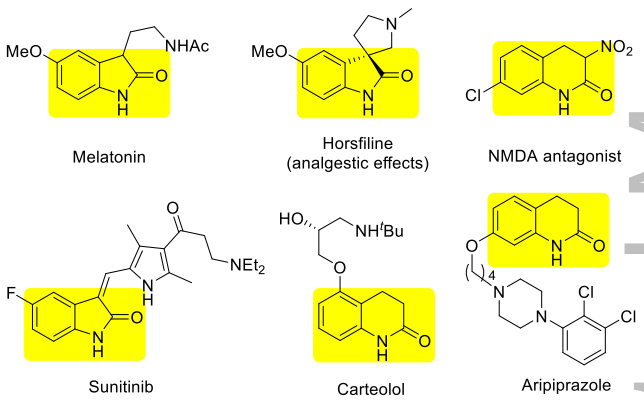

Figure 1. Selected biological molecules bearing the scaffolds of indolin-2-one and dihydroquinolin-2-one.

by intramolecular C−H amination mediated by transition−metal catalysts, such as Ir and Ru complexes.[8] Representative study by Chang reported a series of elegant approaches to form benzofused lactams via tailored Ir-catalyzed C−H amidation reaction using dioxazolone as the nitrene precursor and a number of well-designed Ir complexes as the catalysts[9] (Scheme 1c). However, compared with Ir and Ru catalysts, there are few reports on Co-catalyzed C−H amidation and most of them employed organic azides.[10] An advantage of Earth abundant cobalt catalysts over the precious metal iridium or rhodium catalysts is their lower cost. So far, no reports regarding Co-catalyzed synthesis of indolin-2-one and dihydro-quinolin-2-one derivatives through an intramolecular C−H amidation have been reported.

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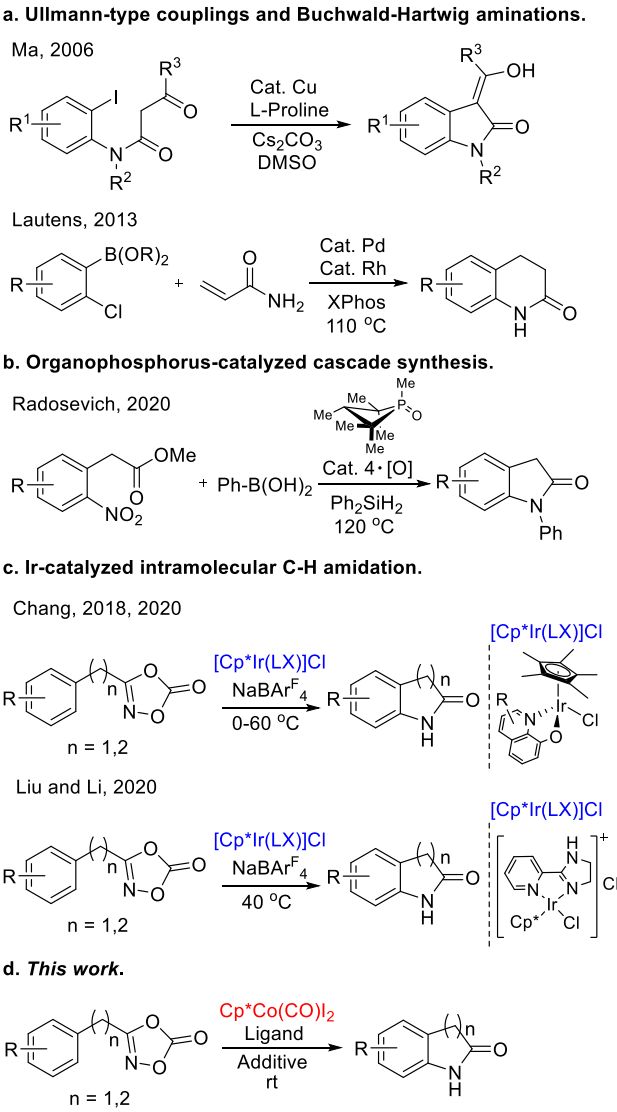


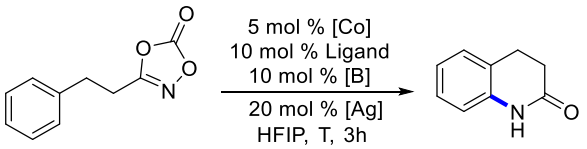
Scheme 1. General strategies of indolin-2-one and dihydroquinolin-2-one derivatives.

Herein, we report an efficient and straightforward method for the synthesis of indolin-2-one and dihydroquinolin-2-one derivatives through $Cp^*Co(CO)I_2$ catalyzed intramolecular C−H amidation for the first time. A readily available cobalt catalyst and 1,4,2-dioxazol-5-ones led to wide varieties indolin-2-ones and dihydroquinolin-2-ones in good yields (27 examples, up to 86%) under mild conditions. The scalability of the amidation was demonstrated. This approach would deliver an efficient and straightforward method for the synthesis of valuable benzofused lactams of biologically active compounds.

Results and Discussion

We selected 3-phenethyl-1,4,2-dioxazol-5-one **1a** as the model substrate, which was easily derived from 2-phenylacetic acids (95% yield, see Supporting Information). We began to study the cyclization reaction of 1,4,2-dioxazol-5-one **1a** followed Chang's method[9c] and replaced Ir complexes with the Co catalyst, using 5 mol% $Cp^*Co(CO)I_2$ (**Co1**) as a cobalt source, 10 mol% 8-hydroxyquinoline (**L1**) as a ligand, and 10 mol% sodium tetrakis(3,5-bis(trifluoromethyl)phenyl) borate ($NaBAr^F_4$) in hexafluoro-2-propanol (HFIP) at 60 °C. However, only trace amount of the product dihydroquinolin-2-one **2a** was detected (Table 1, entry 1). Then, reducing the reaction temperature to room temperature and 0 °C led to 28% and 20% NMR yield (Determined after reaction workup by ^{1}H NMR integration), respectively (entries 2 and 3). To our delight, with 20% Ag_2CO_3 additive, the cyclization product **2a** was obtained in 74% at room temperature (entry 4). Switching to other silver salts, such as $AgSbF_6$, $AgPF_6$, AgOTf and $AgNTf_2$, however, resulted in lower NMR yield (38-

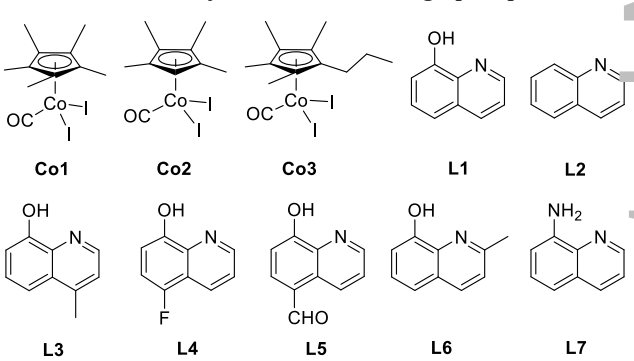
Table 1. Optimization of Co-Catalyzed C−H Amidation. [a,b]



1a **2a**

Entry	[Co]	Ligand	[B]	[Ag]	T(°C)	Yield of **2a** (%)[a]
1	**Co1**	**L1**	$NaBAr^F_4$	/	60	<5
2	**Co1**	**L1**	$NaBAr^F_4$	/	rt	28
3	**Co1**	**L1**	$NaBAr^F_4$	/	0	20
4	**Co1**	**L1**	$NaBAr^F_4$	$AgSbF_6$	rt	45
5	**Co1**	**L1**	$NaBAr^F_4$	Ag_2CO_3	rt	74
6	**Co1**	**L1**	$NaBAr^F_4$	$AgPF_6$	rt	52
7	**Co1**	**L1**	$NaBAr^F_4$	AgOTf	rt	60
8	**Co1**	**L1**	$NaBAr^F_4$	$AgNTf_2$	rt	38
9	**Co1**	**L1**	$KBPh_4$	Ag_2CO_3	rt	73
10	**Co1**	**L1**	$NaBPh_4$	Ag_2CO_3	rt	76
11	**Co1**	**L1**	$NaBF_4$	Ag_2CO_3	rt	83 (80)[c]
12	**Co2**	**L1**	$NaBF_4$	Ag_2CO_3	rt	40
13	**Co3**	**L1**	$NaBF_4$	Ag_2CO_3	rt	80
14	**Co1**	**L2**	$NaBF_4$	Ag_2CO_3	rt	<5
15	**Co1**	**L3**	$NaBF_4$	Ag_2CO_3	rt	80
16	**Co1**	**L4**	$NaBF_4$	Ag_2CO_3	rt	70
17	**Co1**	**L5**	$NaBF_4$	Ag_2CO_3	rt	<5
18	**Co1**	**L6**	$NaBF_4$	Ag_2CO_3	rt	<5
19	**Co1**	**L7**	$NaBF_4$	Ag_2CO_3	rt	<5
20	-	**L1**	$NaBF_4$	Ag_2CO_3	rt	0

[a]Reactions conducted on a 0.1 mmol scale and 0.1 M reaction concentration, using 5 mol% **Co** as a cobalt source, 10 mol% **L** as ligand, 10 mol% borate and 20 mol% silver salt. [b]NMR yield determined by ^{1}H NMR spectroscopy of the crude reaction mixture using CH_2Br_2 as an internal standard. [c]Isolated yield after chromatographic purification.



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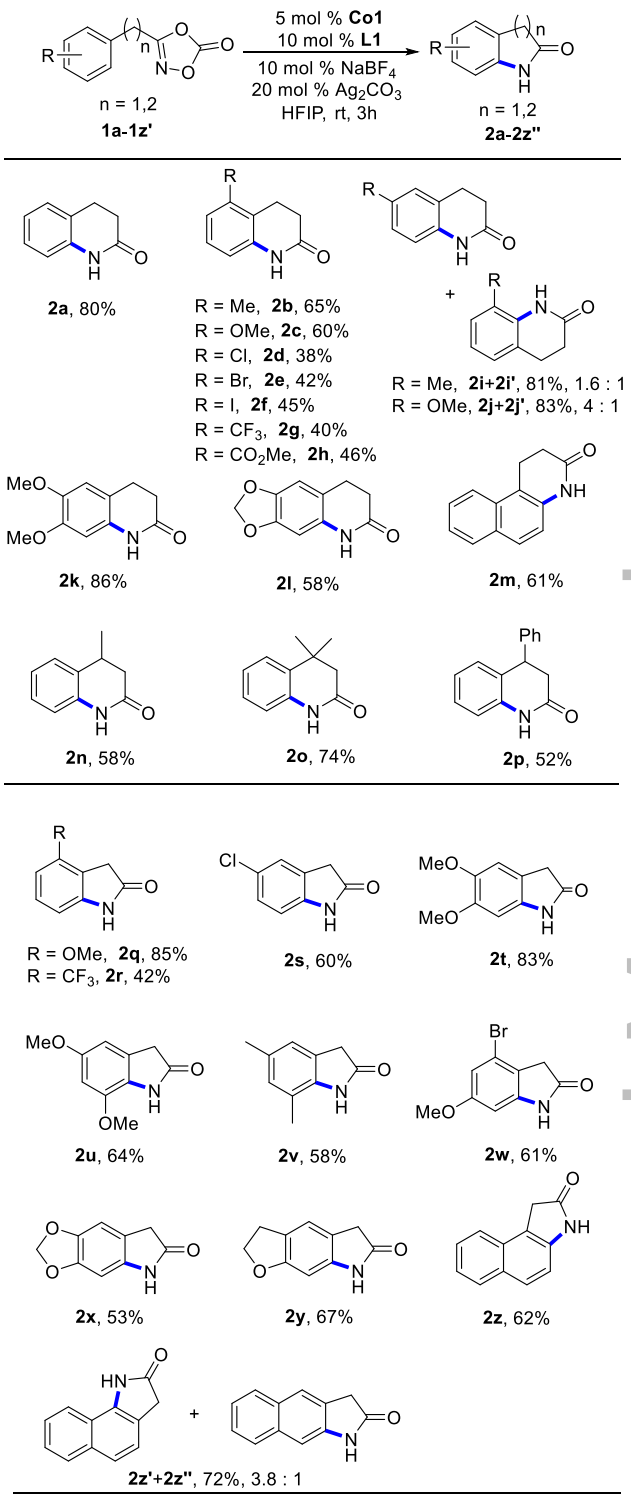
60%, entries 5–8). Replacing borate $NaBAr^F_4$ with $KBPh_4$, $NaBPh_4$ and $NaBF_4$ furnished increased NMR yield with 73%, 76% and 83% (80% isolated yield), respectively (entries 9-11). We next studied the effect of Co catalysts and ligands. Switching the Cp* ring of $Cp^*Co(CO)I_2$, a methyl group was missing (**Co2**) or a methyl group was replaced with a propyl group (**Co3**), caused the NMR yield to drop to 40% and 80%, respectively (entries 12 and 13). When replacing ligand 8-hydroxyquinoline (**L1**) with quinolone (**L2**), substituted 8-hydroxyquinoline (**L3**-**L6**), 8-aminoquinoline (**L7**), no improvement of yield was observed (entries 14-19). Removing the Co catalyst from the system led to no reaction (entry 20). Thus, the optimal conditions for the intramolecular C−H amidation that will be used for the remainder of the study are listed in entry 11 of Table 1.

With the optimal conditions in hand (Table 1, entry 11), we subsequently studied the substrate scope of the intramolecular C−H amidation using a variety of 3-phenethyl-1,4,2-dioxazol-5-ones and 3-benzyl-1,4,2-dioxazol-5-ones. As noted, 1,4,2-dioxazol-5-one derivatives were readily synthesized from commercially available carboxylic acids (56–95% yields).[8a] For synthesis of six-membered dihydroquinolin-2-one derivatives, 3-phenethyl-1,4,2-dioxazol-5-one **1a** via intramolecular C−H amidation delivered product **2a** in 80% yield. Moreover, **2a** was characterized by X-ray crystallography, confirming its structure (CCDC 2033458, see Supporting Information for details). Phenylacetyl substrates bearing ortho-substituted groups were smoothly cyclized to obtain the corresponding dihydroquinolin-2-one. Ortho-alkyl (Me, **1b**) and electro-donating (OMe, **1c**) substituents furnished products **2b** and **2c** in 65% and 60%. Electro-withdrawing (Cl, **1d**; Br, **1e**; I, **1f**) substituents, led to products **2d**, **2e** and **2f** in 38%, 42% and 45%, respectively. Electron-deficient (CF_3, **1g** and CO_2Me, **1h**) substituents provided products **2g** and **2h** in 40% and 46%. Meta-substituted substrates afforded a mixture of isomeric desired products **2i**/**2i'** and **2j**/**2j'** in a total of 81% and 83% yields with 1.6:1 and 4:1 regioselectivities, probably owing to the steric hindrance of meta-position. Substrates bearing multiple substituent 3,4-dimethoxy (**1k**), polycyclic substrates benzo[1,3]dioxol (**1l**) and naphthalen-1-yl (**1m**), were also suitable reactants in C−H amidation, giving products **2k**, **2l** and **2m** in 86%, 58% and 61%, respectively. α-Substituted phenylacetyl substrates (**1n**-**1p**) underwent cyclization to obtain a series of functionalized lactam products 4-methyl-dihydroquinolin-2-one (**2n**), 4,4-dimethyl-dihydroquinolin-2-one (**2o**) and 4-phenyl-dihydroquinolin-2-one (**2p**) in 58% and 74% and 52%, respectively.

Table 2. Scope of C−H Amidation.[a,b]

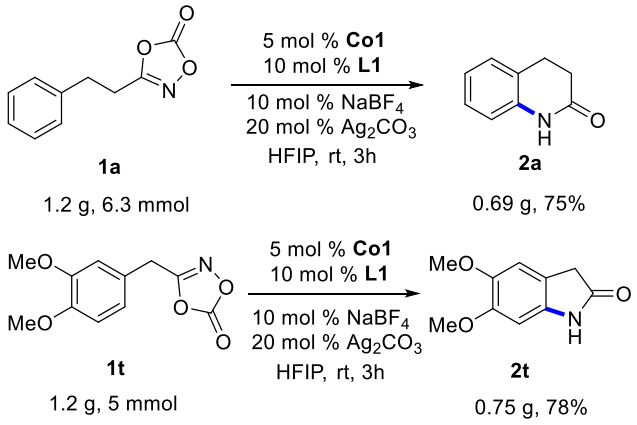


[a]Reactions conducted on a 0.2 mmol scale and 0.1 M reaction concentration, using 5 mol% $Cp^*Co(CO)I_2$ as cobalt source, 10 mol% 8-Hydroxyquinoline as ligand, 10 mol% $NaBF_4$ and 20 mol% Ag_2CO_3. [b]Yield of isolated product after chromatographic purification.

We next explored the method to synthesis of five-membered indolin-2-one derivatives. Various substituted 3-benzyl-1,4,2-dioxazol-5-ones provided cyclization products in good yields. Benzyl substrate bearing ortho-substituted electro-donating (OMe, **1q**) and electron-deficient (CF_3, **1r**) groups furnished products **2q** in 85% and 42 yields. Meta-substituted substrate (Cl, **1s**) gave a C4-selective cyclization

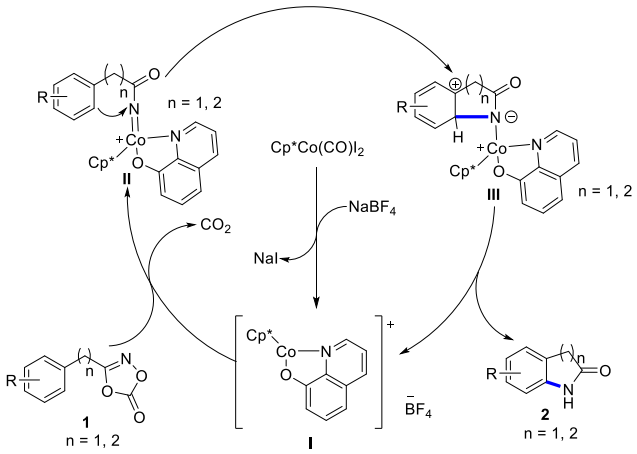
product (**2s**), suggesting that the steric hindrance may lead to this regioselectivity. Substrates bearing multiple substituents, such as 3,4-dimethoxy (**1t**), 3,5-dimethoxy (**1u**), 3,5-dimethyl (**1v**) and 2-bromo-4-methoxy (**1w**) groups, afforded products **2t**, **2u**, **2v** and **2w** in 83%, 64%, 58 and 61%, respectively. Polycyclic substrates benzo[1,3]dioxol (**1x**), 2,3-dihydrobenzofuran (**1y**) and naphthalen-1-yl (**1z**) led to products **2x**, **2y** and **2z** in 53%, 67% and 62%, respectively. Naphthalen-2-yl substrate (**1z'**) generated a mixture of isomeric desired products **2z'**/**2z''** in a total of 72% yield with 3.8:1 regioselectivity, and the regioselectivity presumably due to the electronic effects[10a]. The structures of isomers were confirmed from literature report[11].

Subsequently, we evaluated the scalability of our method. We conducted 1,4,2-dioxazol-5-ones **1a** and **1u** on a 1.2 g scale under the standard conditions of the intramolecular C−H amidation (Scheme 2). The desired dihydroquinolin-2-one **2a** and 5,6-dimethoxyindolin-2-one **2t** were isolated in 0.69 g (75% yield) and 0.75 g (78% yield). This means that the method has application value.



Scheme 2. Gram-scale synthesis.

Based on the relevant literatures on C-H amidation using Ir catalysts[8a, 9c] and above study, we proposed the plausible mechanism for this intramolecular C−H amidation as shown in Scheme 3. First, a cationic Co(III) catalyst from Cp*Co(CO)I_2 undergoes the *N*,*O*-coordination of 8-hydroxyquinoline, forming a cobaltacycle intermediate **I**. Next, it further coordinates with dioxazolone of **1** to form intermediate **II** with releasing a molecule of CO_2. The electrons on the electron-rich aromatic ring transfer to the electron-deficient *N* atom to form intermediate **III**. Finally, it undergoes an elimination to obtain product **2a** and regenerates the active cobalt complex **I** to continue the catalytic cycle. The reaction proceeds by an electrophilic aromatic substitution (SEAr), which provides support for Chang's proposed mechanistic pathways[9c].



Scheme 3. Proposed reaction mechanism.

Conclusion

In summary, we have successfully synthesized a series of indolin-2-one and dihydroquinolin-2-one derivatives employing an Earth abundant cobalt catalyst and 1,4,2-dioxazol-5-ones for the first time. In this protocol, readily synthesized 1,4,2-dioxazol-5-ones underwent intramolecular C−H amidation to provide a wide variety of functionalized benzofused lactams under mild conditions. Gram-scale reactions were demonstrate the scalability of the amidation and the competition and deuterium-labeling experiments were also probed. It is noteworthy that this method does not require a tailored transition-metal complexes,[9-10] which enables the synthesis of a diverse array of benzofused lactams in a convenient and straightforward means. Furthermore, because 1,4,2-dioxazol-5-ones are easily synthesized from abundant carboxylic acids, we anticipated that the approach would deliver an efficient method for the synthesis of valuable benzofused lactams of biologically active compounds.

Experimental Section

General Methods

Unless otherwise stated, all reagents were commercially available and used as received without further purification. Chemicals were obtained from Sigma-Aldrich, Acros, TCI and Alfa-Aesar. TLC was performed with Merck TLC Silica gel60 F_{254} plates with detection under UV light at 254 nm. Silica gel (200-300 mesh, Qingdao) was used for flash chromatography. ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained using a Brüker DRX 600/400 spectrometer at 600/400 MHz and 150/100 MHz, respectively. Chemical shifts were reported in units of parts per million (ppm) downfield from tetramethylsilane (TMS), and all coupling constants were reported in hertz. The infrared (IR) spectra were measured on a Nicolet iS10 FTIR spectrometer with 4 cm^{-1} resolution and 32 scans between wavenumber of 4000 cm^{-1} and 400 cm^{-1}. High Resolution Mass spectra were

taken on AB QSTAR Pulsar mass spectrometer. Melting points were obtained on a XT-4 melting-point apparatus and were uncorrected.

General Procedure for the Preparation and Characterization of Indolin-2-ones and Dihydroquinolin-2-ones (2a–2z'').

To an oven-dried reaction flask were added Cp*Co(CO)I_2 (5 mg, 5.0 mol%), 8-Hydroxyquinoline (3 mg, 10 mol%), Ag_2CO_3 (11 mg, 20 mol%), $NaBF_4$ (2 mg, 10 mol%), and hexafluoro-2-propanol (2 mL) under argon atmosphere and stirred for 1 min. To the reaction flask was added 1,4,2-dioxazol-5-one (**1**, 0.2 mmol) and then sealed. The reaction mixture was vigorously stirred for 3 hours at room temperature. Filtered through a pad of celite with DCM (10 mL × 2) and concentrated under reduced pressure. Desired product **2** was obtained by silica chromatography (eluent: Petroleum ether/EtOAc, 3:1 ~ 1:1).

3,4-Dihydroquinolin-2(1*H*)-one (2a).

Isolated from flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 3:1, R_f = 0.30); White solid (24.1 mg, 82%); m.p. 159 – 161 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.84 (s, 1H), 7.19 – 7.12 (m, 2H), 6.97 (td, *J* = 7.6, 1.2 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 2.95 (t, *J* = 8.0 Hz, 2H), 2.64 (t, *J* = 8.0 Hz, 2H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.7, 137.4, 127.9, 127.5, 123.6, 123.1, 115.8, 30.7, 25.3 ppm. IR (thin film): 3050, 1683, 1591, 1489, 1383, 1280, 1245, 940, 813, 745, 681 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_9H_{10}NO^+$ 148.0757; Found 148.0761.

5-Methyl-3,4-dihydroquinolin-2(1*H*)-one (2b).

Isolated from flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 3:1, R_f = 0.28); White solid (20.8 mg, 65%); m.p. 160 – 162 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.69 (s, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 2.91 (t, *J* = 7.6 Hz, 2H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.28 (s, 3H) ppm. ^{13}C NMR (100 MHz, 172.4, 137.4, 136.0, 127.1, 125.0, 122.0, 113.8, 30.4, 22.0, 19.4 ppm. IR (thin film): 3204, 3076, 2948, 1676, 1591, 1478, 1391, 1217, 1198, 813, 769, 540, 452 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_{12}NO^+$ 162.0913; Found 162.0914.

5-Methoxy-3,4-dihydroquinolin-2(1*H*)-one (2c).

Isolated from flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 2:1, R_f = 0.25); White solid (21.2 mg, 60%); m.p. 169 – 171 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (s, 1H), 6.91 (t, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 2H), 3.83 (s, 3H), 2.93 (t, *J* = 7.6 Hz, 2H), 2.59(t, *J* = 7.2 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ: 170.4, 145.8, 126.5, 124.0, 122.7, 120.0, 109.0, 55.8, 30.7, 25.4 ppm. IR (thin film): 3416, 3239, 2940, 2840, 1682, 1618, 1497, 1449, 1301, 1260, 1092, 792, 733, 713, 535 cm^{-1}; HRMS (ESI-TOF) m/z: **[**M+H]$^+$ Calcd for $C_{10}H_{12}NO_2^+$ 178.0863; Found 178.0870.

5-Chloro-3,4-dihydroquinolin-2(1*H*)-one (2d)

Isolated from flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 3:1, R_f = 0.31); White solid (14.0 mg, 38%); m.p. 109 – 111 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.22 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.09 – 7.04 (m, 1H), 6.91 (t, *J* = 8.0 Hz, 1H), 3.00 – 2.95 (m, 2H), 2.66 – 2.60 (m, 2H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.5 , 134.1 , 127.8 , 126.5 , 125.5 , 123.3 , 119.7 , 30.6 , 25.8 ppm. IR (thin film): 3379, 3041, 2945, 1764, 1695, 1530, 1358, 1320, 1178, 1136, 813, 755, 681 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_9H_9ClNO^+$ 182.0367; Found 182.0367.

5-Bromo-3,4-dihydroquinolin-2(1*H*)-one (2e).

Isolated from flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 3:1, R_f = 0.32); White solid (18.9 mg, 42%); m.p. 102 – 104 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (s, 1H), 7.39 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.86 (t, *J* = 7.6 Hz, 1H), 2.99 (t, *J* = 7.6 Hz, 2H), 2.64 (dd, *J* = 8.4, 6.4 Hz, 2H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.7, 135.3, 131.0, 127.3, 125.7, 123.9, 109.7, 30.8, 26.1 ppm. IR (thin film): 3382, 3241, 2948, 1784, 1698, 1481, 1362, 1322, 1190, 1139, 803, 764, 597, 522 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_9H_9BrNO^+$ 225.9862; Found 225.9869.

5-Iodo-3,4-dihydroquinolin-2(1*H*)-one (2f)

Isolated from flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 3:1, R_f = 0.33); White solid (24.6 mg, 45%); m.p. 115 – 117 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (s, 1H), 7.60 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.12 (d, *J* = 7.2 Hz, 1H), 6.71 (t, *J* = 7.6 Hz, 1H), 2.94 (dd, *J* = 8.4, 6.4 Hz, 2H), 2.64 – 2.57 (m, 2H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.9 , 137.8 , 137.4 , 128.3 , 125.3 , 124.5 , 84.9 , 30.9 , 26.3 ppm. IR (thin film): 3388, 3265, 2966, 1795, 1496, 1377, 1335, 1212, 1151, 786, 588 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_9H_9INO^+$ 273.9723; Found 273.9719.

5-(Trifluoromethyl)-3,4-dihydroquinolin-2(1*H*)-one (2g)

Isolated from flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 3:1, R_f = 0.30); White solid (17.2 mg, 40%); m.p. 132 – 134 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 3.22 (t, *J* = 8.0 Hz, 2H), 2.99 – 2.92 (t, *J* = 8.0 Hz, 2H) ppm.^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.6, 154.0, 136.8, 132.5, 131.1, 128.8 (q, $^2J_{C-F}$ = 29.8 Hz),.127.6, 126.7 (q, $^3J_{C-F}$ = 5.6 Hz), 124.5 (q, $^1J_{C-F}$ = 272.1 Hz), 27.8, 26.8 ppm. IR

(thin film): 3088, 2953, 17108, 1585, 1432, 1255, 1210, 985, 802, 734, 551 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_9F_3NO^+$ 216.0631; Found 216.0630.

Methyl 2-oxo-1,2,3,4-tetrahydroquinoline-5-carboxylate (2h)

Isolated from flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 3:1, R_f = 0.28); White solid (18.9 mg, 46%); m.p. 145 – 157 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.57 (s, 1H), 7.58 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.03 (dd, *J* = 8.0, 1.2 Hz, 1H), 3.90 (s, 3H), 3.39 (t, *J* = 8.0 Hz, 2H), 2.61 (t, *J* = 8.0 Hz, 2H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.5 , 167.6 , 138.7 , 129.7 , 127.3 , 125.7 , 125.4 , 119.6 , 52.3 , 30.2 , 22.9 ppm. IR (thin film): 3088, 2953, 17108, 1585, 1432, 1255, 1210, 985, 802, 734, 551 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{11}NO_3^+$ 206.0812; Found 206.0815.

6-Methyl-3,4-dihydroquinolin-2(1*H*)-one/8-Methyl-3,4-dihydroquinolin-2(1*H*)-one (2i)/(2i')

Isolated from flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 3:1, R_f = 0.29); White solid (26.1 mg, 81 %); Obtained as mixture of two isomers (1.6 : 1). Major isomer: **6-Methyl-3,4-dihydroquinolin-2(1*H*)-one** ^{1}H NMR (600 MHz, Chloroform-*d*) *δ* 9.02 (s, 1H), 6.98 – 6.97 (m, 2H), 6.75 (d, *J* = 7.8 Hz, 1H), 2.93 (t, *J* = 6.0 Hz, 2H), 2.64(t, *J* = 6.0 Hz, 2H), 2.29 (s, 3H) ppm. ^{13}C NMR (150 MHz, Chloroform-*d*) *δ* 172.4, 134.9, 132.7, 128.6, 128.0, 116.4, 115.6, 30.9, 25.4, 20.8 ppm. Minor isomer: **8-Methyl-3,4-dihydroquinolin-2(1*H*)-one** ^{1}H NMR (600 MHz, Chloroform-*d*) *δ* 9.05 (s, 1H), 7.03 (d, *J* = 7.8 Hz, 1H), 6.80 (d, *J* = 4.2 Hz, 1H), 6.67 (s, 1H), 2.93 (t, *J* = 6.0 Hz, 2H), 2.64 (t, *J* = 6.0 Hz, 2H), 2.30 (s, 3H) ppm. ^{13}C NMR (150 MHz, Chloroform-*d*) *δ* 172.7, 137.6, 137.3, 127.8, 123.9, 123.6, 120.7, 31.0, 25.0, 21.1 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_{12}NO^+$ 162.0913; Found 162.0912.

6-Methoxy-3,4-dihydroquinolin-2(1*H*)-one (2j).

Isolated from flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 2:1, R_f = 0.22); White solid (23.5 mg, 66%); m.p. 169 – 171 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 10.01 (s, 1H), 6.85 – 6.76 (m, 1H), 6.66 (d, *J* = 7.6 Hz, 2H), 3.72 (s, 3H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.63 – 2.54 (m, 2H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) *δ* 172.3, 155.5, 131.0, 124.9, 116.5, 113.7, 112.3, 55.5, 30.5, 25.6 ppm. IR (thin film): 3064, 2970, 2935, 1976, 1770, 1661, 1497, 1463, 1418, 1294, 1240, 1120, 792, 764, 600 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_{12}NO_2^+$ 178.0863; Found 178.0865.

8-Methoxy-3,4-dihydroquinolin-2(1*H*)-one (2j').

Isolated from flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 2:1, R_f = 0.23); White solid (6 mg, 17%); m.p. 165 – 167 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 7.86 (s, 1H), 6.94 (t, *J* = 8.0 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 2H), 3.86 (d, *J* = 2.0 Hz, 3H), 2.96 (t, *J* = 7.6 Hz, 2H), 2.65 – 2.60 (m, 2H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) *δ* 172.3, 155.5, 131.0, 124.9, 116.5, 113.7, 112.3, 55.5, 30.5, 25.6 ppm. IR (thin film): 3058, 2972, 1775, 1680, 1489, 1447, 1382, 1274, 1239, 1148, 1036, 879, 764, 554 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_{12}NO_2^+$ 178.0863; Found 178.0869.

6,7-Dimethoxy-3,4-dihydroquinolin-2(*1H*)-one (2k).

Isolated from flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 1:1, R_f = 0.22); White solid (35.6 mg, 86%); m.p. 180 – 182 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 9.26 (s, 1H), 6.67 (s, 1H), 6.41 (s, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 2.89 (t, *J* = 7.2 Hz, 2H), 2.66 – 2.56 (m, 2H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) *δ* 172.3, 148.5, 144.8, 130.8, 114.9, 111.7, 100.5, 56.5, 56.3, 31.1, 25.2 ppm. IR (thin film): 3218, 2938, 2844, 1675, 1522, 1395, 1233, 1201, 1132, 1029, 933, 857, 772, 585 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{14}NO_3^+$ 208.0968; Found 208.0971.

7,8-Dihydro-[1,3]dioxolo[4,5-g]quinolin-6(5*H*)-one (2l).

Isolated from flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 2:1, R_f = 0.25); White solid (22.2 mg, 58%); m.p. 189 – 191 °C. ^{1}H NMR (400 MHz, DMSO-d_6) *δ* 9.86 (s, 1H), 6.77 (s, 1H), 6.46 (s, 1H), 5.92 (s, 2H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.37 (t, *J* = 7.6 Hz, 2H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) *δ* 170.4, 146.4, 142.5, 132.8, 116.3, 108.5, 101.2, 97.6, 30.9, 25.1 ppm. IR (thin film): 3148, 2781, 1705, 1635, 1503, 1358, 1290, 1192, 1034, 940, 850, 683 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{10}H_9NaNO_3^+$ 214.0475; Found 214.0480.

1,4-Dihydrobenzo[f]quinolin-3(2*H*)-one (2m).

Isolated from flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 3:1, R_f = 0.33); White solid (24.0 mg, 61%); m.p. 192 – 194 °C. ^{1}H NMR (400 MHz, DMSO-d_6) *δ* 10.22 (s, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.83 (d, 1H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.52 (ddd, *J* = 8.4, 6.8, 1.6 Hz, 1H), 7.37 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.14 (d, *J* = 8.8 Hz 1H), 3.25 (t, *J* = 7.6 Hz, 2H), 2.59 (t, *J* = 7.6 Hz, 2H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) *δ* 170.1, 135.7, 131.2, 129.9, 128.4, 127.5, 126.7, 123.7, 122.7, 116.8, 115.5, 30.0, 20.5 ppm. IR (thin film): 2905, 2783, 1863, 1835, 1637, 1505, 1492, 1448, 1344, 1302, 1149, 773, 632 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{11}NaNO^+$ 220.0733; Found 220.0728.

4-Methyl-3,4-dihydroquinolin-2(1*H*)-one (2n).

Isolated from flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 3:1, R_f = 0.28); White solid (18.7 mg, 58%); m.p. 166 – 168 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.33 (s, 1H), 7.18 (ddd, *J* = 9.2, 7.6, 1.6 Hz, 2H), 7.02 (td, *J* = 7.6, 1.2 Hz, 1H), 6.90 – 6.83 (m, 1H), 3.13 (m, 1H), 2.74 (dd, *J* = 16.0, 6.0 Hz, 1H), 2.44 (dd, *J* = 16.0, 7.2 Hz, 1H), 1.31 (d, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.9, 136.6, 128.8, 127.6, 126.6, 123.4, 115.9, 38.5, 30.8, 19.9 ppm. IR (thin film): 3204, 3076, 2948, 1676, 1591, 1478, 1391, 1217, 1198, 813, 769, 540 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_{12}NO^+$ 162.0913; Found 162.0916.

4,4-Dimethyl-3,4-dihydroquinolin-2(1*H*)-one (2o).

Isolated from flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 3:1, R_f = 0.27); White solid (25.9 mg, 74%); m.p. 170 – 172 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.12 (s, 1H), 7.28 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.13 (td, *J* = 7.6, 1.6 Hz, 1H), 6.96 (td, *J* = 7.6, 1.2 Hz, 1H), 6.86 (dd, *J* = 8.0, 1.2 Hz, 1H), 2.34 (s, 2H), 1.21 (s, 6H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.3, 136.9, 132.1, 127.1, 124.2, 122.4, 115.4, 44.9, 33.5, 27.3 ppm. IR (thin film): 3204, 3076, 2948, 1676, 1591, 1478, 1391, 1217, 1198, 813, 769, 540 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{11}H_{13}NaNO^+$ 198.0889; Found 198.0892.

4-Phenyl-3,4-dihydroquinolin-2(1*H*)-one (2p).

Isolated from flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 3:1, R_f = 0.28); White solid (21.2 mg, 60%); m.p. 188 – 190 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.28 (s, 1H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.28 – 7.14 (m, 4H), 6.94 (m, 3H), 4.32 (t, *J* = 6.4 Hz, 1H), 2.84 (d, *J* = 6.4 Hz, 1H), 2.81 – 2.72 (m, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.2, 142.5, 138.1, 128.6, 128.1, 127.7, 127.5, 126.8, 126.3, 122.2, 115.5, 40.9, 37.9 ppm. IR (thin film): 3060, 2890, 1675, 1612, 1488, 1387, 1265, 1188, 1030, 944, 759, 715, 508 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{14}NO^+$ 224.1070; Found 224.1065.

4-Methoxyindolin-2-one (2q).

Isolated from flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 2:1, R_f = 0.22); White solid (31.0 mg, 85%); m.p. 175 – 177 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.30 (s, 1H), 6.95 (t, *J* = 8.0 Hz, 1H), 6.81 (m, 2H), 3.86 (s, 3H), 3.54 (s, 2H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 177.6, 143.9, 131.6, 126.2, 122.7, 116.9, 110.2, 55.7, 36.9 ppm. IR (thin film): 3160, 3073, 2938, 1698, 1628, 1495, 1465, 1328, 1259, 1211, 1078, 761, 721, 653, 569 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_9H_{10}NO_2^+$ 164.0706; Found 164.0709.

4-Methoxyindolin-2-one (2r)

Isolated from flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 3:1, R_f = 0.28); White solid (16.9 mg, 42%); m.p. 172 – 174 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.72 (s, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 3.62 (s, 2H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 175.4 , 145.0 , 128.6 , 125.0 (q, $^2J_{C\text{-}F}$ = 32.0 Hz), 124.0 (q, $^1J_{C\text{-}F}$ = 271.2 Hz), 123.6 (q, $^3J_{C\text{-}F}$ = 3.0 Hz), 117.3 (q, $^3J_{C\text{-}F}$ = 4.4 Hz), 112.8 , 35.1 ppm.IR (thin film): 3083, 2958, 1702, 1622, 1484, 1425, 1365, 1257, 1218, 1089, 721, 653 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_9H_7F_3NO^+$ 202.0474; Found 202.0478.

5-Chloroindolin-2-one (2s).

Isolated from flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 3:1, R_f = 0.30); White solid (20.0 mg, 60%); m.p. 158 – 160 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.47 (s, 1H), 7.25 (s, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 3.49 (s, 2H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 176.0, 142.6, 128.0, 127.2, 125.1, 124.5, 110.3, 35.8 ppm. IR (thin film): 3159, 2961, 2582, 1704, 1618, 1476, 1316, 1244, 1024, 869, 798, 656, 561 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_8H_7ClNO^+$ 168.0211; Found 168.0217.

5,6-Dimethoxyindolin-2-one (2t).

Isolated from flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 1:1, R_f = 0.20); White solid (32.0 mg, 83%); m.p. 184 – 186 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.17 (s, 1H), 6.83 (s, 1H), 6.55 (s, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.49 (s, 2H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.4, 149.4, 145.1, 136.3, 116.0, 109.7, 95.9, 56.9, 56.4, 37.1 ppm. IR (thin film): 3218, 2937, 1675, 1521, 1394, 1284, 1260, 1234, 1131, 1012, 933, 859, 585 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{10}H_{11}NaNO_3^+$ 216.0631; Found 216.0632.

5,7-Dimethoxyindolin-2-one (2u).

Isolated from flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 1:1, R_f = 0.21); White solid (24.7 mg, 53%); m.p. 183 – 185 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.16 (s, 1H), 6.49 (s, 1H), 6.49 (s, 1H), 3.79 (s, 3H), 3.71 (s, 3H), 3.43 (s, 2H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6) δ 176.4, 156.0, 144.3, 127.3, 126.0, 102.9, 98.9, 56.2, 56.1, 37.2 ppm. IR (thin film): 3065, 2948, 1695, 1642, 1480, 1340, 1257, 1223, 1075, 763, 653, 568 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{10}H_{11}NaNO_3^+$ 216.0631; Found 216.0636.

5,7-Dimethylindolin-2-one (2v).

Isolated from flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 3:1, R_f = 0.31); White solid (18.8 mg, 58%); m.p. 168 – 170 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.30 (s, 1H), 6.81 (s, 1H), 6.77 (s, 1H), 3.40 (s, 2H), 2.19 (s, 3H), 2.14 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 176.7, 139.8, 129.8, 129.0, 125.4, 122.3, 118.1,

36.1, 20.6, 16.4 ppm. IR (thin film): 3028, 2924, 2869, 1824, 1634, 1492, 1352, 1262, 1148, 956, 764, 632 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_{12}NO^+$ 162.0913; Found 162.0912.

4-Bromo-6-methoxyindolin-2-one (2w).

Isolated from flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 2:1, R_f = 0.27); White solid (29.3 mg, 61%); m.p. 178 – 180 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.94 (s, 1H), 6.88 (s, 1H), 6.79 (s, 1H), 3.77 (s, 3H), 3.61 (s, 2H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 175.5, 156.3, 135.5, 127.4, 115.2, 111.7, 102.3, 56.2, 37.8 ppm. IR (thin film): 3147, 2926, 2852, 1683, 1579, 1457, 1387, 1286, 1172, 1120, 877, 700, 638, 560 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_9H_9BrNO_2^+$ 241.9811; Found 241.9813.

5,7-Dihydro-6*H*-[1,3]dioxolo[4,5-f]indol-6-one (2x).

Isolated from flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 2:1, R_f = 0.24); White solid (18.8 mg, 53%); m.p. 175 – 177 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.36 (s, 1H), 6.74 (s, 1H), 6.48 (s, 1H), 5.92 (s, 2H), 3.46 (s, 2H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 178.0, 147.2, 143.3, 136.3, 116.8, 106.2, 101.1, 93.5, 36.6 ppm. IR (thin film): 3148, 2781, 1704, 1635, 1476, 1358, 1319, 1192, 1152, 1035, 938, 848, 652 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_9H_8NO_3^+$ 178.0499; Found 178.0499.

2,3,5,7-Tetrahydro-6*H*-furo[3,2-f]indol-6-one (2y).

Isolated from flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 2:1, R_f = 0.28); White solid (23.5 mg, 67%); m.p. 172 – 174 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 10.13 (s, 1H), 6.69 (s, 1H), 6.66 (s, 1H), 4.45 (t, *J* = 8.8 Hz, 2H), 3.37 (s, 2H), 3.12 (t, *J* = 8.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 176.3, 154.6, 136.7, 125.4, 124.8, 106.2, 70.6, 36.3, 29.6 ppm. IR (thin film): 3133, 2919, 2580, 1697, 1668, 1479, 1399, 1297, 1259, 1182, 1014, 590, 854, 665, 539 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_{10}NO_2^+$ 176.0706; Found 176.0710.

1,3-Dihydro-2*H*-benzo[e]indol-2-one (2z).

Isolated from flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 3:1, R_f = 0.32); White solid (22.7 mg, 62%); m.p. 175 – 177 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 11.17 (s, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.93 – 7.86 (m, 1H), 7.56 – 7.40 (m, 4H), 3.69 (s, 2H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 177.6, 139.4, 132.7, 128.3, 125.6, 125.5, 122.6, 121.9, 120.8, 120.3, 119.1, 36.9 ppm. IR (thin film): 3039, 2850, 1679, 1576, 1528, 1375, 1318, 1254, 1198, 928, 805, 774, 661, 565 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{10}NO^+$ 184.0757; Found 184.0759.

1,3-Dihydro-2*H*-benzo[g]indol-2-one (2z').

Isolated from flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 3:1, R_f = 0.32); White solid (20.9 mg, 57%); m.p. 176 – 178 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 11.13 (s, 1H), 8.04 (d, *J* = 7.9 Hz, 1H), 7.87 (d, *J* = 6.4 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.49 – 7.35 (m, 3H), 3.65 (s, 2H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 177.6, 139.4, 132.7, 128.3, 125.5, 125.5, 122.6, 121.9, 120.8, 120.3, 119.1, 36.9 ppm. IR (thin film): 3148, 2929, 1675, 1558, 1462, 1318, 1254, 1198, 805, 661, 564, 532 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{10}NO^+$ 184.0757; Found 184.0759.

1,3-Dihydro-2*H*-benzo[f]indol-2-one (2z'').

Isolated from flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 3:1, R_f = 0.31); White solid (5.5 mg, 15%); m.p. 173 – 175 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 10.44 (s, 1H), 7.88 (dd, *J* = 8.0, 2.0 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 3.80 (s, 2H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.7, 138.7, 133.4, 128.8, 126.4, 126.1, 122.4, 122.3, 121.4, 120.1, 119.8, 37.8 ppm. IR (thin film): 3120, 2928, 1676, 1557, 1438, 1325, 1268, 1098, 798, 656, 558 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{10}NO^+$ 184.0757; Found 184.0759.

Gram scale synthesis

To an oven-dried 100 mL reaction flask were added $Cp^*Co(CO)I_2$ (0.157 g, 5.0 mol%), 8-hydroxyquinoline (0.095 g, 10 mol %), Ag_2CO_3 (0.347 g, 20 mol%), $NaBF_4$ (0.07 g, 10 mol %), and hexafluoro-2-propanol (50 mL) under argon atmosphere and stirred for 1 min. To the reaction flask was added **1a** or **1t** and then sealed. The reaction mixture was vigorously stirred for 3 hours at room temperature. Filtered through a pad of celite with DCM (50 mL × 2) and concentrated under reduced pressure. Desired product **2a** was obtained by silica chromatography (eluent: Petroleum ether/EtOAc, 3:1) with 0.69 g, 75% yield. Desired product **2t** was obtained by silica chromatography (eluent: Petroleum ether/EtOAc, 1:1) with 0.75 g, 78% yield.

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