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Graphical Abstract

Efficient Construction of 3-Arylquinolin-4(1*H*)-ones via *in situ* Meinwald Rearrangement/Intramolecular Reductive Cyclization of 2'-Nitrochalcone Epoxides

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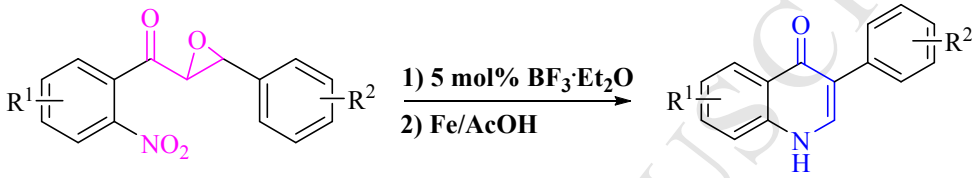

up to 98% yield

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Efficient Construction of 3-Arylquinolin-4(1*H*)-ones via *in situ* Meinwald Rearrangement/Intramolecular Reductive Cyclization of 2'-Nitrochalcone Epoxides

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ABSTRACT

An efficient method for construction of 3-arylquinolin-4(1*H*)-ones via *in situ* Meinwald rearrangement/intramolecular reductive cyclization of 2'-nitrochalcone epoxides has been developed. The practical approach is of excellent functional groups compatibility with as high as 98% yield under mild reaction conditions. Trapping and NMR analysis about the key intermediates of the transformation provided insights to propose a plausible mechanism for the intramolecular reductive cyclization. Moreover, further derivation successfully furnished hydroxyl substituted and N-methyl substituted derivatives which may provide a promising potential application in exploring biologically active compounds of 3-arylquinolin-4(1*H*)-ones.

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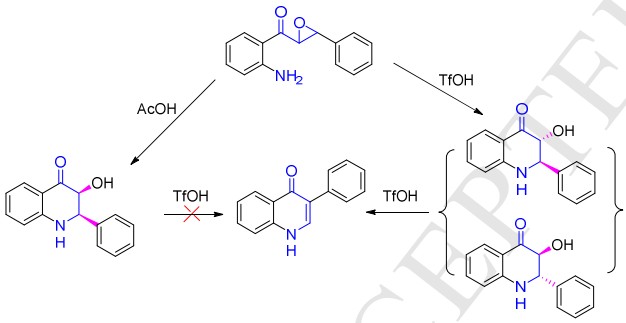
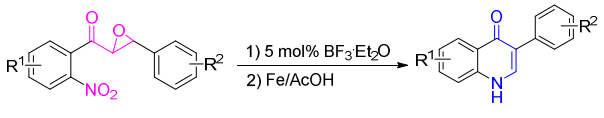
1. Introduction

3-Arylated quinolin-4(1*H*)-ones have attracted considerable attention in different research fields such as pharmaceutical chemistry and material science.[1] ELQ-300, a selective potent inhibitor of the parasite's mitochondrial cytochrome bc1 complex, has been selected as a preclinical candidate for the treatment, prevention and eradication of malaria.[2] Due to their remarkable biological activity and applications, some synthetic strategies for the construction of valuable 3-arylquinolin-4(1*H*)-ones have been developed in the past decades. Yadav and coworkers[1d] reported a radical mediated C-3-arylation of quinolin-4-ones with aryl hydrazines in the presence of base and air as oxidant, and 52%-76% yields of the desired products were achieved. Hong et al[1a] attempted a palladium(II)-catalyzed dehydrogenation/ oxidative cross-coupling reaction sequence of 1-methyl-2,3-dihydroquinolin-4(1*H*)-one with benzene, and 41% yield of the corresponding 1-methyl-3-phenylquinolin-4(1*H*)-one was afforded. Achaiah et al[1h] reported a method using ethyl phenylacetate as the starting material, however, high temperature was needed for the cyclization of the intermediate ethyl (*Z*)-2-phenyl-3-(phenylimino)propanoate in the presence of polyphosphoric acid. In addition, triflic acid promoted ring-opening followed by nucleophilic attack of 2'-aminochalcone epoxides led to the formation of 2-aryl-3-hydroxy-tetrahydro-4(1*H*)-quinlones which could transform to 3-arylquinolin-4(1*H*)-ones via a aryl groups migrating process, however, the hydroxyl and the migrating aryl groups must be in the trans-configuration (Scheme 1).[3,4] In other words, using stereoisomers of 2'-aminochalcone epoxide obtained in non-chiral conditions as the starting material, the intramolecular cyclization produced mixed products of *cis*- and *trans*- configuration of 2-aryl-3-hydroxy-tetrahydro-4(1*H*)-quinlones. Among them, the isomers with hydroxyl and migrating aryl groups in the *cis*-configuration can not afford the 3-arylquinolin-4(1*H*)-ones via aryl migrating procedure,[4] which led to the decrease of yields of the products.



Scheme 1. Synthesis of 3-arylquinolin-4(1*H*)-ones from 2'-aminochalcone epoxide via intermediate 2-aryl-3-hydroxy-tetrahydro-4(1*H*)-quinlones.[4]

Our research interest in the development of new synthetic methodologies relates to the application of β-ketoaldehydes[5] led to the synthesis of 3-arylquinolin-4(1*H*)-ones. Herein, we report an *in situ* Meinwald rearrangement/intramolecular reductive cyclization reaction in one-pot with easy accesible mixture of stereoisomers of 2'-nitrochalcone epoxides (**1**) as the starting material which provides a straightforward protocol for the preparation of 3-arylquinolin-4(1*H*)-ones (**2**) in high yields (Scheme 2).



1 **2**

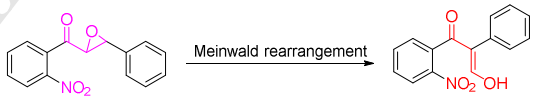
Scheme 2. Synthesis of 3-arylquinolin-4(1*H*)-ones from 2'-nitrochalcone epoxides.

2. Results and Discussion

Tandem Meinwald rearrangement/intramolecular cycloaddition of epoxides to construct functionalized tetrahydrofurans[6] or bridged oxa-[*n*.2.1] skeletons[7] have been reported, and Meinwald rearrangement of chalcone epoxides to form 3-oxo-2,3-diphenylpropanal are known.[8] However, only few examples were reported regarding to the ring-opening rearrangement of 2'-nitrochalcone epoxide, catalyzed by boron trifluoride etherate, which afforded 3-(2'-nitrophenyl)-3-oxo-2-phenylpropanals.[9] As an ongoing research interest in our group, we envisioned that an intramolecular reductive cyclization would happen easily on the 2'-nitro substituted 3-oxo-2-phenylpropanals. Thus, we investigated the Meinwald rearrangement of 2'-nitrochalcone epoxide and found the reaction could proceed well in dichloromethane, and the product was elucidated as an enol form of 3-oxo-propanal, 3-hydroxy-1-(2'-nitrophenyl)-2-phenylprop-2-en-1-one (**3**), by both ^{1}H NMR and ^{13}C NMR analysis. More importantly, Meinwald rearrangement of 2'-nitrochalcone epoxide followed by *in situ* reduction/cyclization reaction could directly afford the target product 3-phenylquinolin-4(1*H*)-one, and avoid the defect that partial 2-phenyl-3-hydroxy-tetrahydro-4(1*H*)-quinlones did not transform to the needed product.[4] Afterwards, we optimized the rearrangement reaction conditions using (2'-nitrophenyl)(3-phenyloxiran-2-yl)methanone (**1a**) as a model substrate.

Table 1

Optimization of the Meinwald rearrangement reaction conditions[a]



1a **3**

Entry	$BF_3 \cdot EtO_2$(equiv. to A)	Temp (°C)	Yield %[b]
1	1.0	0	96
2	1.0	25	97
3	0.5	25	97
4	0.2	25	98
5	0.1	25	96
6	0.05	25	96
7	0.03	25	88

[a] Reaction conditions: **1a** (1 mmol), DCM (30 mL), 25 °C for 30 min.

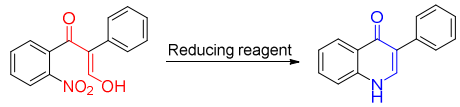
[b] Isolated yield.

Although 2 equivalents of $BF_3 \cdot Et_2O$ was used in the reported example,[9] we attempted to carry out the reaction with catalytic amount of boron trifluoride etherate from the viewpoint of catalysis mechanism, and the results showed that the reduction of $BF_3 \cdot Et_2O$ from 100 mol% to 5 mol% did not affect the yield (Table 1, entries 2-6). While further reduce the amount of the catalyst to 3 mol%, the yield was slightly dropped (Table 1, entry 7). Investigation also showed that the reaction could proceed smoothly at zero degree or room temperature (Table 1, entries 1 and 2). Therefore, the optimum reaction conditions for the rearrangement were established as the reaction was carried out at room temperature in dichloromethane with 5 mol% $BF_3 \cdot Et_2O$ as the catalyst.

With the rearrangement product in hand, we next tried to develop the envisioned intramolecular reductive cyclization and expected 3-arylquinolin-4(1*H*)-ones as the product. Different reducing reagent systems were screened for conversion of the intermediate **3** to final product, and Fe/AcOH was found to be the best choice, providing **2a** in 97% yield after 2 h at 50 °C (Table 2, entry 9). Fe/$FeSO_4.7H_2O$/MeOH/H_2O, Fe/HCl and Fe/NH_4Cl/MeOH/H_2O showed better activity than Pd/H_2/MeOH, $SnCl_2{\cdot}2H_2O$/MeOH and Zn/NH_4Cl/MeOH/THF (Table 2, entries 7, 8, 6 and 1, 4, 5), whereas in the case of Pd/$HCOONH_4$/MeOH and Ni/H_2/MeOH, only trace product was observed (Table 2, entries 2 and 3). Further investigation was conducted to find out the most suitable amount of the iron powder and the reaction temperature. When the amount of iron powder was reduced from 10 to 5 equivalents, the result showed that the yield of the desired product was almost maintained after taking the same reaction time (Table 2, entry 11). However, further reduce the amount of Fe powder to 2 equivalents, a slightly lower yield of 91% was obtained after prolonged reaction time (Table 2, entry 12). Temperature seems crucial for the reaction since it was found that the reaction could proceed rapidly at higher temperature (20 min at 80 °C) and afforded higher yield (99%) of **2a** (Table 2, entry 10), while prolonged reaction time (20 h) was needed if the reaction was carried out at room temperature (Table 2, entry 13). Conducting the reaction at 80 °C with 2 equivalents of Fe led to a slight decrease of the yield (Table 2, entry 12).

Table 2

Optimization of reaction conditions for the intramolecular reductive cyclization of 3-Hydroxy-1-(2-nitrophenyl)-2-phenylprop-2-en-1-one[a]



3 **2a**

Entry	Reducing reagent (equiv. vs **3**)	Solvent	Time (h)	Temp (°C)	Yield %[b]
1	Pd/C (0.1)-H_2	MeOH	36	25	65
2	Pd/C (0.1)-$HCOONH_4$ (5.0)	MeOH	24	25	Trace
3	Ni (0.2)/H_2	MeOH	36	25	Trace
4	$SnCl_2{\cdot}2H_2O$ (8.0)	MeOH	3	reflux	43
5	Zn(5.0)/NH_4Cl (5.0)	MeOH/ THF	3	reflux	45
6	Fe(5.0)/NH_4Cl (5.0)	MeOH/ H_2O	3	reflux	91
7	Fe (10.0)/$FeSO_4{\cdot}7H_2O$ (1.0)	MeOH/ H_2O	12	25	93
8	Fe (10.0)	HCl	2	50	86
9	Fe (10.0)	AcOH	2	50	97
10	Fe (10.0)	AcOH	1/3	80	99
11	Fe (5.0)	AcOH	1/3	80	98
12	Fe (2.0)	AcOH	5	80	91
13	Fe (10.0)	AcOH	20	25	98

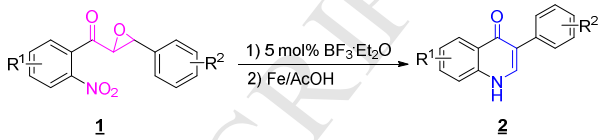
[a] Reaction conditions: **3** (1 mmol), solvent (30 mL).

[b] Isolated yield.

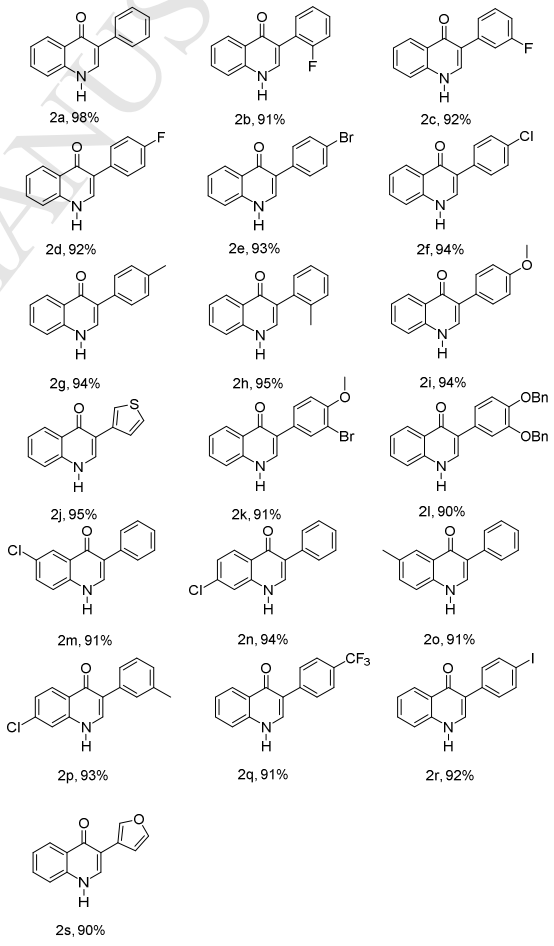
With the establishment of the optimal reaction conditions for both the Meinwald rearrangement and the intramolecular reductive cyclization, we attempted to develop an one-pot method that transformation of 2'-nitrochalcone epoxides to 3-arylquinolin-4(1*H*)-ones via *in situ* Meinwald rearrangement/ intramolecular reductive cyclization without isolating the intermediate 3-hydroxy-1-(2'-nitrophenyl)-2-phenylprop-2-en-1-one. As expected, the reaction proceeded successfully and the final product was obtained in high yield. On the basis of this result, the scope of the reaction was tested with various substrates (Table 3).

Table 3

The one-pot Meinwald rearrangement/intramolecular reductive cyclization of 2'-nitrochalcone epoxides[a]



1 **2**

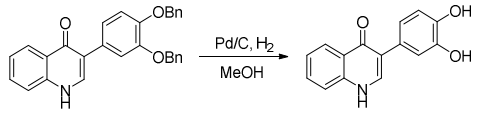


[a] Reaction conditions: 2'-Nitrochalcone epoxides (**1**, 1 mmol), DCM (30 mL), $BF_3{\cdot}Et_2O$ (0.05 equiv), 25 °C, 30min; then AcOH (30 mL), Fe (10 equiv), 80 °C, 20 min. All yields are isolated yields.

As can be seen from Table 3, a variety of substrates with electron withdrawing or donating groups at either side of the phenyl rings were subjected to the the Meinwald rearrangement/intramolecular reductive cyclization reaction, and

very good yields of the desired 3-arylquinolin-4(1*H*)-ones were obtained under the optimized conditions, suggesting the practical method is of excellent functional groups compatibility (Table 3, **2d**-**2g**, **2i**, **2m**, **2o**, **2q** and **2r**) which is superior to the reported method.[4] Notably, when the 3-phenyl group was replaced with a thienyl group or a furyl group, high yield (95% or 90%, Table 3, **2j** or **2s**) of the corresponding products was also achieved, indicating this synthetic method would be suitable for obtaining 3-heteroarylquinolin-4(1*H*)-ones which may have biological activities.

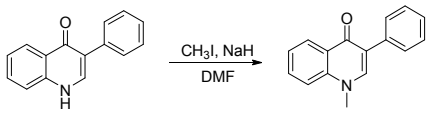
Hydroxyl substituted 3-arylquinolin-4(1*H*)-ones were considered to have higher biological activities in the aspects of anti-tumor,[10,1k,1l] treatment of neurodegenerative, neurological and mitochondrial diseases.[1o,11] Thus, treatment of compound **2l** with Pd/H_2 in methanol furnished the desired product **4** in 97% yield (Scheme 3), providing a synthetic approach to hydroxyl substituted 3-arylquinolin-4(1*H*)-one.



2l **4**

Scheme 3. Synthesis of 3-(3,4-dihydroxyphenyl)quinolin-4(1*H*)-one (**4**).

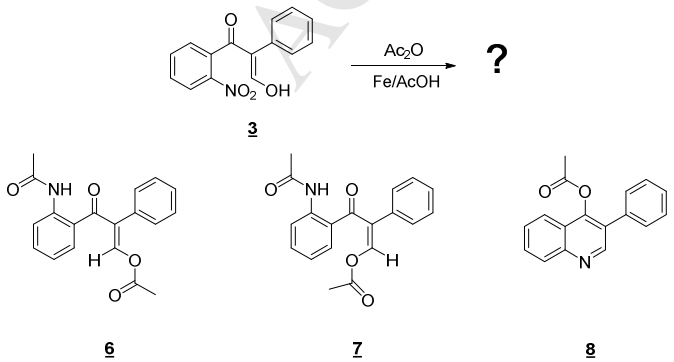
In addition, *N*-substituted derivatives of 3-phenylquinolin-4(1*H*)-one also showed interesting bioactivities, and several synthetic methods have been developed.[1a,1m,1k] We were gratified to find that the methylation of the obtained 3-phenylquinolin-4(1*H*)-one (**2a**) with methyl iodide gave the desired *N*-methyl product **5** in high yield (96%, Scheme 4).



5

Scheme 4. Synthesis of 1-methyl-3-phenylquinolin-4(1*H*)-one (**5**).

To gain insight into the mechanism of the intramolecular reductive cyclization, intermediate trapping with acetic anhydride was carried out. 3-Hydroxy-1-(2-nitrophenyl)-2-phenylprop-2-en-1-one (**3**) was treated with 3 equivalents of acetic anhydride, 10 equivalents of iron powder and 10 equivalents of glacial acetic acid at 25°C, which afforded three isolated compounds, *E*-3-(2-acetamidophenyl)-3-oxo-2-phenylprop-1-en-1-yl acetate (**6**), *Z*-3-(2-acetamidophenyl)-3-oxo-2-phenylprop-1-en-1-yl acetate (**7**) and 3-phenylquinolin-4-yl acetate (**8**) (Scheme 5).

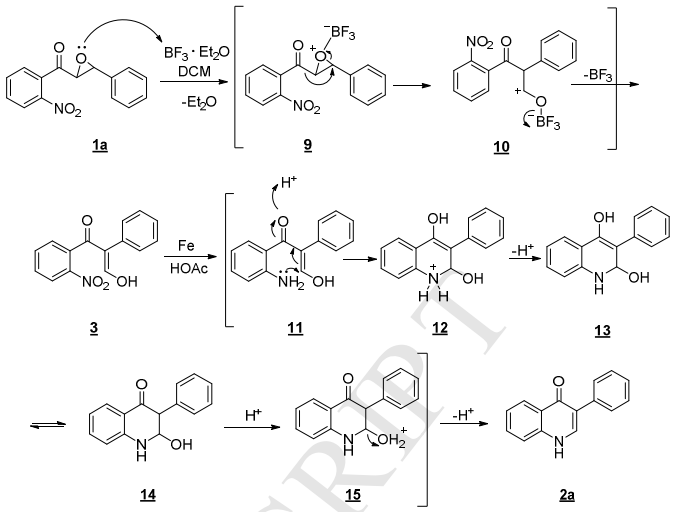


3

6 **7** **8**

Scheme 5. The intermediates trapping reaction.

On the basis of our experimental results and previous findings in literature,[4,12] a tentative mechanism is given in Scheme 6.



1a **9** **10**

3 **11** **12** **13**

14 **15** **2a**

Scheme 6. A possible mechanism for the Meinwald rearrangement/intramolecular reductive cyclization.

2'-Nitrochalcone epoxide (**1a**) gave an enol form intermediate **3** via Meinwald rearrangement catalyzed by $BF_3{\cdot}Et_2O$.[12] Subsequent reduction of **3** with Fe/AcOH leads to the formation of intermediate **11** which undergoes a proton-mediated cyclization of the generated amino group with the enol moiety to afford intermediate **12**. Dehydration and deprotonation at the α-carbon of **15** results in the formation of 3-arylquinolin-4(1*H*)-one (**2a**).

3. Conclusions

In conclusion, we developed an efficient *in situ* Meinwald rearrangement/intramolecular reductive cyclization of 2'-nitrochalcone epoxides in one-pot to construct 3-arylquinolin-4(1*H*)-ones in high yields under mild reaction conditions. A plausible mechanism was proposed and the key intermediate was trapped and elucidated by NMR analysis. The practical method is of satisfactory functional groups compatibility. Hydroxyl substituted and *N*-methyl substituted derivatives of 3-arylquinolin-4(1*H*)-ones could also efficiently gain after further treatments, which provides promising synthetic methods for obtaining biologically active compounds of 3-arylquinolin-4(1*H*)-ones.

4. Experimental

4.1. General methods

All reagents and solvents (analytical grade) were purchased from commercial suppliers and were used directly without further purification. All reactions were carried out under nitrogen atmosphere in addition to the special instructions. The progress of reactions was monitored by silica gel thin layer chromatography (TLC), visualized under ZF-20D black box ultraviolet analyzer. Flash column chromatography was performed using Yantai Kangbinuo silica gel (200-300). ^1H and ^{13}C NMR spectra were tested with a Bruker Avance 400 spectrometer with tetramethylsilane (TMS) as an internal standard (400 MHz for ^1H, 100 MHz for ^{13}C). The high resolution mass spectra were recorded on a Bruker ESI-TOF high-resolution mass spectrometer. Melting points of the products were recorded on a WRR-Y drug melting point measurement apparatus and were uncorrected.

4.2 General procedure for 2'-nitrochalcone epoxides

To a solution of 1-(2-nitrophenyl) ethan-1-one (10 mmol) in 40 mL of ethanol at 0 °C was added an aqueous solution of potassium hydroxide (20%, 15 mmol). After 15 min, a solution of benzaldehyde (10 mmol) in 10 mL ethanol was added to the solution dropwise. The solution was stirred at room temperature for 3h and monitored by TLC. The solution was cooled to 0 °C again and an aqueous solution of potassium hydroxide (20%, 15 mmol) was add. After stirring for 15min, hydrogen peroxide (50 mmol) was added dropwise, and the solution was stirred at room temperature for 4h monitored by TLC. The solution was poured into 150 mL ice water. Filtering off the resulted precipitates, the filter cake was washed with ice water for three times and dried in vacuo, and then the crude products were recrystallized to afford 2'-nitrochalcone epoxides.

4.2.1 2'-Nitrochalcone epoxide (1a).[13] Gray solid (80% yield), mp 75-76 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.71 (td, *J* = 7.5, 1.2 Hz, 1H), 7.61 (td, *J* = 7.9, 1.5 Hz, 1H), 7.46 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.31-7.20 (m, 3H), 7.16 (tt, *J* = 5.9, 2.7 Hz, 2H), 3.80 (d, *J* = 1.9 Hz, 1H), 3.65 (d, *J* = 1.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.42, 146.40, 133.35, 133.32, 131.47, 130.57, 128.11, 127.88, 127.66(2C), 124.71(2C), 122.94, 62.25, 57.35. HRMS (ESI) calculated for $C_{15}H_{11}NNaO_4$ $[M+Na]^+$ 292.0586, found 292.0577.

4.2.2 (3-(2-Fluorophenyl)oxiran-2-yl)(2-nitrophenyl) methanone (1b). Gray solid (73% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.80 (td, *J* = 7.5, 1.1 Hz, 1H), 7.70 (td, *J* = 7.9, 1.4 Hz, 1H), 7.54 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.36-7.27 (m, 1H), 7.20-7.09 (m, 2H), 7.04 (dd, *J* = 10.3, 8.3 Hz, 1H), 3.98 (d, *J* = 1.8 Hz, 1H), 3.89 (d, *J* = 1.8 Hz, 1H).

4.2.3 (3-(3-Fluorophenyl)oxiran-2-yl)(2-nitrophenyl) methanone (1c). Yellow solid (74% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.80 (td, *J* = 7.5, 1.2 Hz, 1H), 7.74-7.67 (m, 1H), 7.53 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.31 (td, *J* = 8.0, 5.7 Hz, 1H), 7.09-6.98 (m, 2H), 6.94 (ddd, *J* = 9.4, 2.6, 1.6 Hz, 1H), 3.84 (d, *J* = 1.8 Hz, 1H), 3.74 (d, *J* = 1.8 Hz, 1H).

4.2.4 (3-(4-Fluorophenyl)oxiran-2-yl)(2-nitrophenyl) methanone (1d). Milk white solid (77% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.2 Hz, 1H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.69 (td, *J* = 7.8, 1.4 Hz, 1H), 7.53 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.22 (dd, *J* = 8.5, 5.2 Hz, 2H), 7.02 (t, *J* = 8.5 Hz, 2H), 3.84 (d, *J* = 1.8 Hz, 1H), 3.73 (d, *J* = 1.8 Hz, 1H).

4.2.5 (3-(4-Bromophenyl)oxiran-2-yl)(2-nitrophenyl) methanone (1e). White solid (75% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.70 (td, *J* = 7.5, 1.2 Hz, 1H), 7.61 (td, *J* = 7.9, 1.5 Hz, 1H), 7.44 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.40-7.33 (m, 2H), 7.07-6.98 (m, 2H), 3.74 (d, *J* = 1.9 Hz, 1H), 3.62 (d, *J* = 1.8 Hz, 1H).

4.2.6 (3-(4-Chlorophenyl)oxiran-2-yl)(2-nitrophenyl) methanone (1f). White solid (79% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.79 (td, *J* = 7.5, 1.2 Hz, 1H), 7.70 (td, *J* = 7.8, 1.5 Hz, 1H), 7.53 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.36-7.28 (m, 2H), 7.22-7.13 (m, 2H), 3.83 (d, *J* = 1.8 Hz, 1H), 3.72 (d, *J* = 1.8 Hz, 1H).

4.2.7 (2-Nitrophenyl)(3-(*p*-tolyl)oxiran-2-yl)methanone (1g). Gray solid (80% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.0, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.61-7.56 (m, 1H), 7.44 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.15-7.00 (m, 4H), 3.81 (d, *J* = 1.9 Hz, 1H), 3.64 (d, *J* = 1.9 Hz, 1H), 2.24 (s, 3H).

4.2.8 (2-Nitrophenyl)(3-(*o*-tolyl)oxiran-2-yl)methanone (1h). Yellow solid (80% yield), ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.27 (d, *J* = 8.2 Hz, 1H), 7.97 (t, *J* = 7.5 Hz, 1H), 7.91-7.83 (m, 1H), 7.82-7.74 (m, 1H), 7.31-7.07 (m, 4H), 4.11 (s, 2H), 2.34 (s, 3H).

4.2.9 (3-(4-Methoxyphenyl)oxiran-2-yl)(2-nitrophenyl) methanone (1i). Yellow solid (72% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.1 Hz, 1H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.14-7.05 (m, 2H), 6.85-6.71 (m, 2H), 3.80 (d, *J* = 2.0 Hz, 1H), 3.73 (s, 3H), 3.60 (d, *J* = 1.8 Hz, 1H).

4.2.10 (2-Nitrophenyl)(3-(thiophen-3-yl)oxiran-2-yl)methanone (1j). Yellow solid (73% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.1 Hz, 1H), 7.78 (t, *J* = 7.5 Hz, 1H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 7.4 Hz, 1H), 7.30 (d, *J* = 5.1 Hz, 2H), 6.94 (d, *J* = 4.6 Hz, 1H), 3.97 (d, *J* = 1.8 Hz, 1H), 3.79 (d, *J* = 1.8 Hz, 1H).

4.2.11 (5-Chloro-2-nitrophenyl)(3-phenyloxiran-2-yl) methanone (1m). Light yellow solid (77% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.7 Hz, 1H), 7.64 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.49 (d, *J* = 2.3 Hz, 1H), 7.39-7.31 (m, 3H), 7.27-7.23 (m, 2H), 3.88 (d, *J* = 1.9 Hz, 1H), 3.75 (d, *J* = 1.8 Hz, 1H).

4.2.12 (4-Chloro-2-nitrophenyl)(3-phenyloxiran-2-yl) methanone (1n). Light yellow solid (75% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.7 Hz, 1H), 7.64 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.49 (d, *J* = 2.2 Hz, 1H), 7.38-7.32 (m, 3H), 7.27-7.23 (m, 2H), 3.88 (d, *J* = 1.8 Hz, 1H), 3.75 (d, *J* = 1.8 Hz, 1H).

4.2.13 (5-Methyl-2-nitrophenyl)(3-phenyloxiran-2-yl) methanone (1o). Light yellow solid (70% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.37 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.25 (dd, *J* = 5.0, 1.9 Hz, 3H), 7.21 (d, *J* = 1.9 Hz, 1H), 7.17 (dd, *J* = 6.9, 3.1 Hz, 2H), 3.78 (d, *J* = 1.9 Hz, 1H), 3.68 (d, *J* = 1.8 Hz, 1H), 2.43 (s, 3H).

4.2.14 (2-Nitrophenyl)(3-(4-(trifluoromethyl)phenyl)oxiran-2-yl)methanone (1q). Light yellow solid (81% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.1 Hz, 1H), 7.81 (td, *J* = 7.5, 1.1 Hz, 1H), 7.71 (td, *J* = 7.9, 1.4 Hz, 1H), 7.62 (s, 1H), 7.60 (s, 1H), 7.55 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.39 (s, 1H), 7.37 (s, 1H), 3.85 (d, *J* = 1.8 Hz, 1H), 3.82 (d, *J* = 1.8 Hz, 1H).

4.2.15 (3-(4-Iodophenyl)oxiran-2-yl)(2-nitrophenyl) methanone (1r). Light yellow solid (80% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.2 Hz, 1H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.73-7.66 (m, 3H), 7.53 (d, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 8.1 Hz, 2H), 3.83 (d, *J* = 1.8 Hz, 1H), 3.68 (d, *J* = 1.9 Hz, 1H).

4.3 General procedure for 3-arylquinolin-4(1*H*)-ones from 2'-nitrochalcone epoxides

To a solution of 2'-nitrochalcone epoxides (1.0 mmol) in 30 mL dichloromethane was added BF_3•Et_2O (0.05mmol), the mixture was stirred for 30 min at room temperature. TLC indicated that the raw material was consumed, 20 mL ice water was added to the reaction system, and the aqueous phase was extracted with dichloromethane for three times (3×30 mL). The combined organic phases were dried over anhydrous Na_2SO_4, and then removal of the solvent in vacuo. To the solution of the crude product in 30 mL glacial acetic acid was added iron powder (10 mmol), the mixture was stirred at 80 °C for 20 min as monitored by TLC. The reaction mixture was cooled to room temperature, and then 90 mL methanol was added. After filtering off the resulted precipitates, the filtrates were concentrated in vacuo, and the crude product was purified by silica gel column chromatography (dichloromethane/methanol =70/1) to afford 3-arylquinolin-4(1*H*)-ones.

4.3.1 3-Phenylquinolin-4(1*H*)-one (2a). White solid (216.6 mg, 98% yield), mp 259-260 °C (lit. 258-261 °C)[11]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.98 (d, *J* = 4.8 Hz, 1H), 8.15 (d, *J* = 7.9 Hz, 1H), 8.08 (d, *J* = 6.2 Hz, 1H), 7.67 (s, 1H), 7.65 (s, 1H), 7.62-7.56 (m, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.30 (m, 3H), 7.21 (t, *J* = 7.3 Hz, 1H).; ^{13}C NMR (100 MHz, DMSO-d_6) δ174.75, 139.25, 138.11, 136.11, 131.55, 128.39 (2C), 127.82(2C), 126.34, 125.81, 125.57, 123.26, 119.76, 118.18; HRMS (ESI) calculated for $C_{15}H_{12}NO$ $[M+H]^+$ 222.0913, found 222.0902.

4.3.2 3-(2-Fluorophenyl)quinolin-4(1*H*)-one (2b). White solid (217.6 mg, 91% yield), mp > 270°C (lit. 257-261 °C)[1k]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.08 (s, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 8.08 (s, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 6.9 Hz, 2H), 7.23 (t, *J* = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.28, 159.95 (d, $J_{(C, F)}$= 245.4 Hz, 1C), 139.50, 139.17 (d, $J_{(C, F)}$= 2.0 Hz, 1C), 132.29 (d, $J_{(C, F)}$= 3.0 Hz, 1C), 131.73, 128.81 (d, $J_{(C, F)}$= 8.1 Hz, 1C), 125.43, 125.40, 123.88 (d, $J_{(C, F)}$= 15.2 Hz, 1C), 123.84(d, $J_{(C, F)}$= 4.0 Hz, 1C), 123.41, 118.28, 115.35, 115.13; HRMS (ESI) calculated for $C_{15}H_{11}FNO$ $[M+H]^+$ 240.0819, found 240.0840.

4.3.3 3-(3-Fluorophenyl)quinolin-4(1*H*)-one (2c). White solid (220.5 mg, 92% yield), mp 261-262 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.17 (s, 1H), 8.28 (s, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 7.77-7.64 (m, 2H), 7.62 (s, 1H), 7.60 (s, 1H), 7.43 (q, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.10 (td, *J* = 8.5, 2.7 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.53, 161.92 (d, $J_{(C, F)}$ = 241.4 Hz, 1C), 139.17, 138.65, 138.56 (d, $J_{(C, F)}$ = 9.1 Hz, 1C), 131.70, 129.56 (d, $J_{(C, F)}$ = 8.1 Hz, 1C), 125.87, 125.57, 123.96 (d, $J_{(C, F)}$ = 3.0 Hz,1C), 123.48, 118.25, 117.96 (d, $J_{(C, F)}$ = 2.0 Hz, 1C), 114.81 (d, $J_{(C, F)}$ = 22.2 Hz, 1C), 112.89 (d, $J_{(C, F)}$ = 21.2 Hz, 1C); HRMS (ESI) calculated for $C_{15}H_{11}FNO$ $[M+H]^+$ 240.0819, found 240.0830.

4.3.4 3-(4-Fluorophenyl)quinolin-4(1*H*)-one (2d). White solid (219.8 mg, 92% yield), mp > 270 °C (lit. 244-246 °C)[11]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.07 (s, 1H), 8.26-8.20 (m, 1H), 8.18 (s, 1H), 7.84-7.73 (m, 2H), 7.67 (td, *J* = 7.6, 6.9, 1.3 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.42-7.31 (m, 1H), 7.22 (t, *J* = 8.9 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.63, 160.93 (d, $J_{(C, F)}$ = 244.4 Hz, 1C), 139.26, 138.07, 132.41 (d, $J_{(C, F)}$ = 2.0 Hz, 1C) 131.58, 130.21(d, $J_{(C, F)}$ = 8.1 Hz, 2C), 125.74, 125.53, 123.30, 118.68, 118.19, 114.53 (d, $J_{(C, F)}$ = 21.2 Hz, 2C); HRMS (ESI) calculated for $C_{15}H_{11}FNO$ $[M+H]^+$ 240.0819, found 240.0821.

4.3.5 3-(4-Bromophenyl)quinolin-4(1*H*)-one (2e). Light brown solid (278.9 mg, 93% yield), mp > 270 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.14 (s, 1H), 8.24 (d, *J* = 9.4 Hz, 2H), 7.76 (s, 1H), 7.74 (s, 1H), 7.68 (t, *J* = 7.1 Hz, 1H), 7.60 (m, 3H), 7.37 (t, *J* = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.51, 139.22, 138.28, 135.37, 131.64, 130.67(2C), 130.32(2C), 125.80, 125.55, 123.42, 119.33, 118.25(2C); HRMS (ESI) calculated for $C_{15}H_{11}BrNO$ $[M+H]^+$ 300.0019, found 300.0005.

4.3.6 3-(4-Chlorophenyl)quinolin-4(1*H*)-one (2f). Light brown solid (240.5 mg, 94% yield), mp 253-255 °C (lit. 250-252 °C)[1k]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.12 (s, 1H), 8.23 (d, *J* = 6.8 Hz, 2H), 7.82 (s, 1H), 7.80 (s, 1H), 7.73-7.64 (m, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.45 (s, 1H), 7.43 (s, 1H), 7.37 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.55, 139.23, 138.30, 134.99, 131.64, 130.81, 129.96(2C), 127.75(2C), 125.80, 125.55, 123.40, 118.23(2C); HRMS (ESI) calculated for $C_{15}H_{11}ClNO$ $[M+H]^+$ 256.0524, found 256.0525.

4.3.7 3-(4-Tolyl)quinolin-4(1*H*)-one (2g). Yellowish-brown solid (221.5 mg, 94% yield), mp > 270 °C (lit. 287-289 °C)[11]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.97 (s, 1H), 8.11 (s, 1H), 8.01 (s, 1H), 7.77-7.72 (m, 1H), 7.71 (s, 1H), 7.50 (s, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.27 (t, *J* = 7.3 Hz, 1H), 2.43 (s, 3H).; ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.48, 137.74, 137.34, 136.31, 132.95, 132.52, 128.36(2C), 127.79(2C), 126.22, 125.78, 124.75, 119.40, 118.11, 20.79; HRMS (ESI) calculated for $C_{16}H_{14}NO$ $[M+H]^+$ 236.1070, found 236.1047.

4.3.8 3-(2-Tolyl)quinolin-4(1*H*)-one (2h). Yellowish-brown solid (222.7 mg, 95% yield), mp 250-251 °C (lit. 243-245 °C)[1k]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.97 (s, 1H), 8.18 (d, *J* = 7.9 Hz, 1H), 7.91 (s, 1H), 7.73-7.53 (m, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.30-7.08 (m, 4H), 2.17 (s, 3H); ^{13}C NMR (100MHz, DMSO-d_6) δ 174.47, 139.63, 138.48, 137.52, 136.48, 131.46, 130.62, 129.38, 127.03, 125.44, 125.37, 125.29, 123.10, 121.76, 118.19, 19.85; HRMS (ESI) calculated for $C_{16}H_{14}NO$ $[M+H]^+$ 236.1070, found 236.1037.

4.3.9 3-(4-Methoxyphenyl)quinolin-4(1*H*)-one (2i). Light brown solid (236.5 mg, 94% yield), mp > 270 °C (lit. 292 °C)[5]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.98 (s, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 8.10 (s, 1H), 7.76-7.52 (m, 4H), 7.34 (t, *J* = 7.4 Hz, 1H), 6.97 (s, 1H), 6.95 (s, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.78, 157.94, 139.19, 137.40, 131.38, 129.46(2C), 128.40, 125.67, 125.54, 123.07, 119.52, 118.11, 113.28(2C), 55.04; HRMS (ESI) calculated for $C_{16}H_{14}NO_2$ $[M+H]^+$ 252.1019, found 252.1006.

4.3.10 3-(Thiophen-3-yl)quinolin-4(1*H*)-one (2j).Yellowish-brown solid (215.2 mg, 95% yield), mp > 270 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.00 (s, 1H), 8.35 (d, *J* = 4.1 Hz, 1H), 8.21 (d, *J* = 2.5 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.63-7.46 (m, 3H), 7.42 (dd, *J* = 4.8, 3.1 Hz, 1H), 7.24 (t, *J* = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.43, 138.74, 137.49, 136.00, 131.40, 126.54, 125.61, 125.52, 124.62, 123.31, 121.38, 118.22, 115.11; HRMS (ESI) calculated for $C_{13}H_{10}NOS$ $[M+H]^+$ 228.0478, found 228.0454.

4.3.11 3-(3-Bromo-4-methoxyphenyl)quinolin-4(1*H*)-one (2k). Yellowish-brown solid (299.8 mg, 91% yield), mp > 270 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.09 (d, *J* = 6.2 Hz, 1H), 8.22 (s, 1H), 8.20 (s, 1H), 8.06 (d, *J* = 2.1 Hz, 1H), 7.73 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 8.5 Hz, 1H), 3.88 (s, 3H).;^{13}C NMR (100 MHz, DMSO-d_6) δ 174.59, 153.90, 139.17, 137.90, 132.45, 131.52, 129.97, 128.53, 125.69, 125.50, 123.28, 118.20, 117.80, 112.07, 109.95, 56.18; HRMS (ESI) calculated for $C_{16}H_{13}BrNO_2$ $[M+H]^+$ 330.0124, found 330.0109.

4.3.12 3-(3,4-Bis(benzyloxy)phenyl)quinolin-4(1*H*)-one (2l). Yellowish-brown solid (390.2 mg, 90% yield), mp 182-185 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.01 (d, *J* = 5.9 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 6.1 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.62-7.54 (m, 2H), 7.49 (m, 4H), 7.43-7.26 (m, 8H), 7.08 (d, *J* = 8.4 Hz, 1H), 5.17 (s, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.72, 147.73, 147.03, 139.12, 137.67, 137.45, 131.42, 129.40, 128.34(3C), 128.33(2C), 127.70, 127.67, 127.57(2C), 127.42(2C), 125.73, 125.56, 123.15, 121.20, 119.30, 118.12, 115.18, 114.24, 70.32, 70.12; HRMS (ESI) calculated for $C_{29}H_{24}NO_3$ $[M+H]^+$ 434.1751, found 434.1734.

4.3.13 6-Chloro-3-phenylquinolin-4(1*H*)-one (2m). Yellowish-brown solid (232.7 mg, 91% yield), mp > 270 °C (lit. > 300 °C)[11]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.25 (s, 1H), 8.21 (s, 1H), 8.15 (d, *J* = 2.4 Hz, 1H), 7.69 (m, 4H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.52, 138.53, 137.89, 135.70, 131.67, 128.37 (2C), 127.93, 127.85 (2C), 126.79, 126.55, 124.45, 120.71, 119.99; HRMS (ESI) calculated for $C_{15}H_{11}ClNO$ $[M+H]^+$ 256.0524, found 256.0507.

4.3.14 7-Chloro-3-phenylquinolin-4(1*H*)-one (2n). Yellowish-brown solid (240.1 mg, 94% yield), mp > 270 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.99 (s, 1H), 8.20 (d, *J* = 8.7 Hz, 1H), 8.17 (s, 1H), 7.75-7.67 (m, 2H), 7.64 (d, *J* = 2.0 Hz, 1H), 7.42-7.33 (m, 3H), 7.32 – 7.26 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.19, 140.02, 138.62, 136.11, 135.66, 128.38(2C), 127.96, 127.84(2C), 126.56, 124.40, 123.59, 120.39, 117.29; HRMS (ESI) calculated for $C_{15}H_{11}ClNO$ $[M+H]^+$ 256.0524, found 256.0533

4.3.15 6-Methyl-3-phenylquinolin-4(1*H*)-one (2o). Yellowish-brown solid (214.2 mg, 91% yield), mp > 270 °C (lit. >300 °C)[11];

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.89 (s, 1H), 8.09 (dd, *J* = 6.2, 2.2 Hz, 1H), 8.01 (d, *J* = 6.0 Hz, 1H), 7.77-7.68 (m, 2H), 7.54—7.45 (m, 2H), 7.38 (m, 2H), 7.27 (tt, *J* = 7.6, 1.8 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.46, 137.74, 137.34, 136.32, 132.93, 132.49, 128.36(2C), 127.78(2C), 126.21, 125.79, 124.76, 119.38, 118.11, 20.80; HRMS (ESI) calculated for $C_{16}H_{14}NO$ $[M+H]^+$ 236.1070, found 236.1052.

4.3.16 7-Chloro-3-(m-tolyl)quinolin-4(1*H*)-one (2p). Yellowish-brown solid (249.2 mg, 93% yield), mp > 270 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.92 (s, 1H), 8.19 (d, *J* = 8.7 Hz, 1H), 8.14 (s, 1H), 7.63 (d, *J* = 1.9 Hz, 1H), 7.52 (s, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.35 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.19, 139.98, 138.53, 136.73, 136.06, 135.56, 128.99, 127.94, 127.74, 127.19, 125.52, 124.36, 123.55, 120.51, 117.27, 21.14; HRMS (ESI) calculated for $C_{16}H_{13}ClNO$ $[M+H]^+$ 270.0680, found 270.0678.

4.3.17 3-(4-(Trifluoromethyl)phenyl)quinolin-4(1*H*)-one (2q). White solid (263.9 mg, 91% yield), mp > 270 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.21 (s, 1H), 8.32 (s, 1H), 8.24 (dd, *J* = 8.1, 1.1 Hz, 1H), 8.03 (s, 1H), 8.01 (s, 1H), 7.78-7.66 (m, 3H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.39 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.51, 140.45, 139.22, 139.04, 131.83, 128.72(2C), 126.71(q, $J_{(C, F)}$ =63.6 Hz, 1C), 125.90, 125.85(q, $J_{(C, F)}$ =545.4 Hz, 1C), 125.57, 124.62(q, $J_{(C, F)}$ =7 Hz, 2C), 123.63, 118.31, 117.90; HRMS (ESI) calculated for $C_{16}H_{11}F_3NO$ $[M+H]^+$ 290.0793, found 290.0817.

4.3.18 3-(4-Iodophenyl)quinolin-4(1*H*)-one (2r). White solid (319.6 mg, 92% yield), mp > 270 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.11 (d, *J* = 4.8 Hz, 1H), 8.21 (m, 2H), 7.75 (s, 1H), 7.73 (s, 1H), 7.67 (t, *J* = 7.1 Hz, 1H), 7.61 (s, 2H), 7.59 (s, 1H), 7.36 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.46, 139.19, 138.24, 136.56(2C), 135.71, 131.66, 130.48(2C), 125.78, 125.54, 123.43, 118.35, 118.24, 91.99; HRMS (ESI) calculated for $C_{15}H_{11}INO$ $[M+H]^+$ 347.9885, found 347.9915.

4.3.19 3-(furan-3-yl)quinolin-4(1*H*)-one (2s) White solid (190.0 mg, 90% yield), mp 266-268 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.11 (s, 1H), 8.58 (s, 1H), 8.41 (s, 1H), 8.22 (d, *J* = 8.1 Hz, 1H), 7.69-7.59 (m, 3H), 7.44-7.31 (m, 1H), 7.08 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.11, 142.28, 140.61, 138.66, 136.15, 131.27, 125.31, 124.85, 123.17, 119.86, 118.19, 112.52, 107.69. HRMS (ESI) calculated for $C_{13}H_{10}NO_2$ $[M+H]^+$ 212.0712, found 212.0719.

4.3.20 3-Hydroxy-1-(2-nitrophenyl)-2-phenylprop-2-en-1-one (3). Yellow solid (96% yield), mp 132-134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.74 (s, 1H), 8.05 (s, 1H), 7.90 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.55 (td, *J* = 7.5, 1.3 Hz, 1H), 7.46 (td, *J* = 7.8, 1.5 Hz, 1H), 7.28 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.15 (m, 3H), 7.05-6.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.39, 175.07, 146.78, 133.77, 133.65, 133.48, 130.46, 129.98(2C), 129.33, 128.48(2C), 127.41, 124.17, 117.35; HRMS (ESI) calculated for $C_{15}H_{11}NNaO_4$ $[M+Na]^+$ 292.0580, found 292.0573.

4.4 General procedure for 3-(3,4-dihydroxyphenyl)quinolin-4(1H)-one (4).

To a solution of 3-(3,4-bis(benzyloxy)phenyl)quinolin-4(1*H*)-one (**2l**, 1.0 mmol) in 30 mL MeOH was added Pd/C (0.1 mmol), and then the mixture was stirred for 3h under the atmosphere of H_2 at room temperature, as monitored by TLC. After filtering off the resulted precipitate, the filtrate was concentrated in vacuo, and the crude product was purified by silica gel column chromatography (dichloromethane/methanol = 70/1) to afford 3-(3,4-dihydroxyphenyl) quinolin-4(1*H*)-one as a white solid (246.4 mg, 97% yield), mp > 270 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.90 (d, *J* = 5.3 Hz, 1H), 8.81 (d, *J* = 3.0 Hz, 2H), 8.20 (d, *J* = 8.1 Hz, 1H), 8.01 (d, *J* = 5.7 Hz, 1H), 7.71-7.52 (m, 2H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.25 (s, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.76 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 174.76, 144.45, 144.09, 139.09, 137.07, 131.23, 127.29, 125.66, 125.55, 122.91, 120.11, 119.25, 118.05, 116.27, 115.11; HRMS (ESI) calculated for $C_{15}H_{12}NO_3$ $[M+H]^+$ 254.0812, found 254.0815.

4.5 General procedure for 1-methyl-3-phenylquinolin-4(1*H*)-one (5)

To a solution of 3-phenylquinolin-4(1*H*)-one (**2a**, 1.0 mmol) and sodium hydride (2.0 mmol) in 10 mL DMF was added methyl iodide (1.1 mmol) , the mixture was stirred at 25 °C for 3h as monitored by TLC. The reaction was quenched with water and the aqueous phase was extracted with ethyl acetate (3×40 mL). And then, the combined organic phase was washed with water, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by silica gel column chromatography (dichloromethane/methanol =100/1) to afford 1-methyl-3-phenylquinolin-4(1*H*)-one as a white solid (226.5 mg, 96% yield), mp 125°C (lit. 124 °C)[1n]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.75-7.62 (m, 4H), 7.41 (m, 4H), 7.34-7.28 (m, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.84, 142.57, 140.00, 135.48, 132.01, 128.67(2C), 128.28(2C), 127.63, 127.28, 127.04, 123.77, 122.02, 115.09, 40.74; HRMS (ESI) calculated for $C_{16}H_{14}NO$ $[M+H]^+$ 236.1070, found 236.1072.

4.6 General procedure for trapping the intermediates

To a solution of 3-hydroxy-1-(2-nitrophenyl)-2-phenylprop-2-en-1-one (**3**, 1.0 mmol) in acetic anhydride (3.0 mmol) was added iron powder (10.0 mmol) and glacial acetic acid (10.0 mmol), the reaction system was stirred at 25 °C for 8h as monitored by TLC. The reaction was quenched with water and the aqueous phase was extracted with ethyl acetate (3×30 mL). And then, the combined organic phase was washed with water, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate =15/1) to afford the intermediates *E*-3-(2-acetamidophenyl)-3-oxo-2-phenylprop-1-en-1-yl acetate (**6**),*Z*-3-(2-acetamidophenyl)-3-oxo-2-phenylprop-1-en-1-yl acetate (**7**) and 3-phenylquinolin-4-yl acetate (**8**).

4.6.1 (E)-3-(2)-Acetamidophenyl)-3-oxo-2-phenylprop-1-en-1-yl acetate (6). Light yellow liquid (25% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.66 (s, 1H), 8.80 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.85 (s, 1H), 7.83 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.57 (ddd, *J* = 8.7, 7.3, 1.6 Hz, 1H), 7.42-7.28 (m, 5H), 7.04 (td, *J* = 7.7, 7.3, 1.1 Hz, 1H), 2.29 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.26, 169.65, 167.14, 141.79, 135.99, 134.18, 133.97, 133.40, 129.12 (2C), 128.48, 126.33 (2C), 126.16, 122.63, 121.26, 120.46, 25.65, 20.55; HRMS (ESI) calculated for $C_{19}H_{17}NNaO_4$ $[M+Na]^+$ 346.1055, found 346.1071.

4.6.2 (Z)-3-(2)-Acetamidophenyl)-3-oxo-2-phenylprop-1-en-1-yl acetate (7). Light yellow liquid (20% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.65 (s, 1H), 8.52 (d, *J* = 8.4 Hz, 1H), 7.80 (s, 1H), 7.64 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.49-7.42 (m, 1H), 7.37-7.24 (m, 5H), 6.97 (t, *J* = 7.6 Hz, 1H), 2.15 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.59, 169.27, 166.90, 143.02, 140.45, 134.58, 133.04, 132.76, 129.40 (2C), 128.49 (2C), 128.27, 126.35, 123.77, 122.39, 121.43, 25.30, 20.72; HRMS (ESI) calculated for $C_{19}H_{17}NNaO_4$ $[M+Na]^+$ 346.1050, found 346.1049.

4.6.3 3-Phenylquinolin-4-yl acetate (8). Light yellow liquid (22% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 1H), 8.23-8.12 (m, 1H), 7.92-7.85 (m, 1H), 7.75 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 7.61 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.56-7.46 (m, 4H), 7.46-7.40 (m, 1H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.98, 152.27, 150.89, 149.11, 134.50, 129.91, 129.60, 129.07

(2C), 128.83 (2C), 128.28, 127.47, 126.75, 122.60, 121.51, 20.67; HRMS (ESI) calculated for $C_{17}H_{13}NNaO_2$ $[M+Na]^+$ 286.0844, found 286.0866.

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