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温和条件下以芳基胺为原料 CuI 催化下区域选择性合成 3-芳基香豆素

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摘要 以香豆素和芳香胺为原料, 在温和条件下通过 CuI 催化合成 3-芳基香豆素衍生物. 该合成方法简单地利用易得的原料为底物, 廉价的金属作为催化剂, 提供具有良好官能团耐受性的 3-芳基香豆素, 产率适中或较高. 此外, 控制实验表明该反应是通过自由基途径进行的.

关键词 香豆素; 芳基胺; 铜催化; 芳香化; 自由基反应

CuI-Catalyzed Regioselective Synthesis of 3-Arylcoumarins with Arylamines under Mild Conditions

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Abstract A mild and convenient method has been developed for the construction of 3-arylcoumarins through CuI-catalyzed reaction of coumarins with arylamines under mild conditions. The present protocol simply utilizes readily available starting materials as substrates, inexpensive metal as catalyst, providing various 3-arylcoumarins with good functional groups tolerations in moderate to good yields. Moreover, control experiments show that the reaction proceeds by a radical pathway.

Keywords coumarin; arylamine; copper-catalyzed; arylation; radical reaction

1 Introduction

Coumarins constitute a major class of naturally occurring compounds and privileged medicinal scaffolds that exhibit a broad range of biological activities.[1] Coumarins are also one of the most important classes of fluorophores, and they have been extensively investigated as powerful tools in complex biological systems.[2] Moreover, 3-substituted coumarins have also attracted considerable attention since they are endowed with significant functions in organic synthesis, materials chemistry and pharmaceuticals.[3] Recently, various 3-substituted coumarin derivatives have been synthesized via C—H direct functionalization including aroylation,[4] alkylation,[5] alkenylation,[6] difluoroalkylation,[7] phosphonation,[8] chalcogenylation,[9] benzylation,[10] and arylation,[11] *etc*.[12] Therefore, the functionalization at the C3-position of coumarins has attracted great attention from chemists.

3-Arylcoumarins are important scaffolds observed in many natural products and bioactive compounds.[13] For example, 3-arylcoumarins have recently been reported to act as monoamine oxidase B (MAO-B) inhibitors,[14] active in neurological disorders,[15] and HIV-1 replication inhibitors.[16] In addition, their applications in laser and dispersed fluorescent dyes, optical brighteners and emission layers (OLED) make this skeleton noteworthy.[17] Despite pervasiveness of 3-arylcoumarins in several fields of science, they can be obtained by a few general methods such as using a cycloaddition ring construction approach,[18] by transition metal-catalyzed coupling reactions, and metal-free reactions.[19] The common limitations of most of these methods are necessity of prefunctionalization of the C—H bond at 3-position of coumarins with a halogen or carboxyl group, and use of expensive arylating counterparts, *etc*.

Direct C—H functionalization through metal-catalyzed

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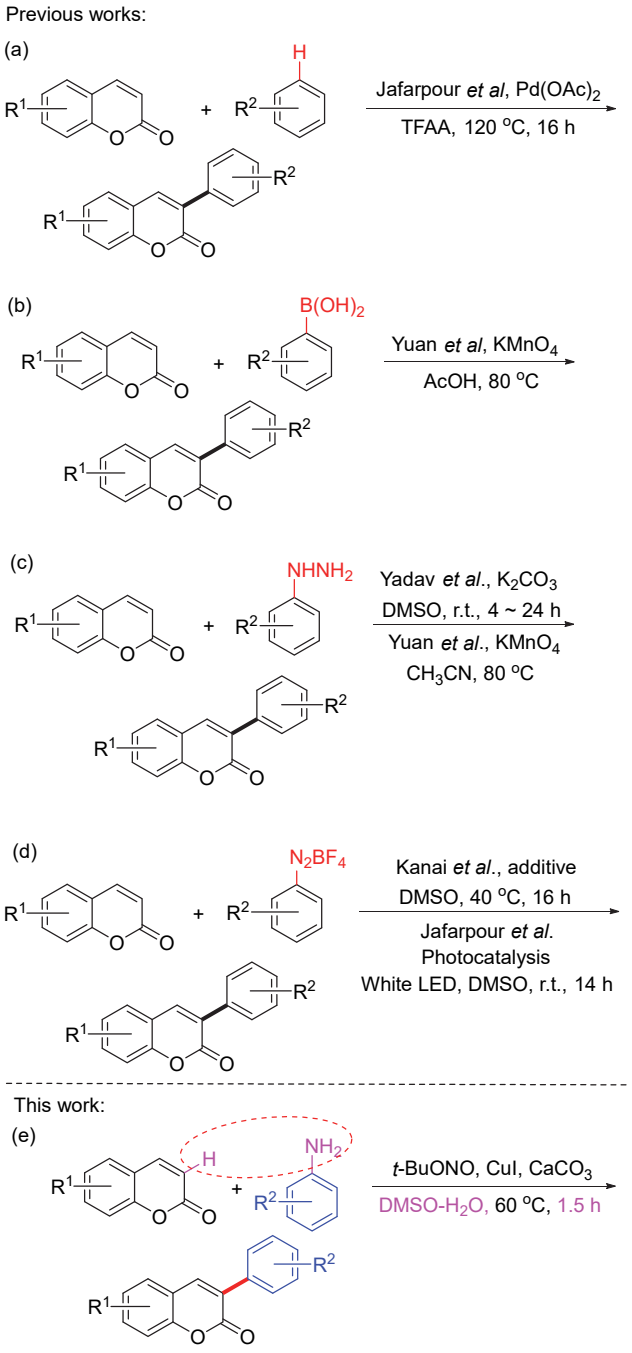
double C—H activation reactions has begun to emerge as an alternative route for C—C bond formation.[20] The direct arylation approach allows for the construction of C—C bonds without the need for prior functionalization of coupling partners. In 2013, Jafarpour's group reported a method toward 3-arylcoumarins using coumarins with unactivated simple arenes in the presence of $Pd(OAc)_2$ and trifluoroacetic anhydride (TFAA) at 120 ℃ for 16 h (Scheme 1a).[21] Subsequently, You's group successfully realized the oxidative cross-coupling of coumarins with alkenes under air at room temperature by employing highly electrophilic [$Pd(TFA)_2$] as the catalyst and inexpensive $(NH_4)_2S_2O_8$ as the oxidant.[22] In 2016, our group reported an efficient protocol for $KMnO_4$/AcOH-mediated dehydrogenative direct radical arylation of coumarins with arylboronic acids to afford 3-arylcoumarin derivatives (Scheme 1b).[23] Arylhydrazines are cheap starting materials, which are known to undergo oxidation to form aryl radicals in the presence of oxidants.[24] In 2016, a facile regioselective metal-free direct α-arylation of coumarins was achieved by the reaction of coumarins with phenylhydrazine in the presence of K_2CO_3 at room temperature for 4～24 h.[25] Subsequently, our group also developed a protocol for C-3 arylation of coumarins with arylhydrazines using $KMnO_4$ as an oxidant at 80 ℃ for 3.0 h (Scheme 1c).[26] A metal-free C—H arylation of coumarins was achieved in the presence of catalytic amounts of 5,10,15,20-tetrakis(4-diethylaminophenyl)porphyrin using diazonium tetrafluoroborates as coupling partners.[27] Very recently, Jafarpour's group described a mild method for cross-coupling of coumarins with an array of diazonium salts mediated by chlorophyll as biocatalyst *via* the visible light irradiation at room temperature for 14 h (Scheme 1d).[28] Furthermore, 3-arylcoumarin derivatives could also be synthesized by employing arylsulfonyl chlorides, sodium arenesulfinates, iodonbenzenes, arene carboxylic acids, and diaryliodonium triflates as coupling partners.[29] Despite these methods having had various levels of success, the harshness of strong acid, the use of expensive catalysts, not readily available precursors, and longer reaction time could limit their wide application. Therefore, the development of an efficient catalytic protocol for the regioselective synthesis of 3-arylcoumarin derivatives should be challenging and great significance.

Aryl amines are known to be easily accessible as well as relatively safe and highly stable, and are hence common synthons in transition metal-catalyzed coupling reactions and non-metal-mediated transformations.[30] By employing *tert*-butyl nitrite and related compounds as diazotizing reagents, arylamines could be transformed into aryldizaonium salts via an *in situ* strategy without being isolated. Aryldiazonium salts are well known species giving free-radical aryl intermediates.[31] Recently, arylamines as arylating agents have attracted significant attention owing to their functional group tolerance and cost-effectiveness.[32] Our group have developed on the arylation of quinolines and quinoxalines using arylamines as coupling partners.[33]



Scheme 1 Synthesis of 3-arylcoumarin derivatives

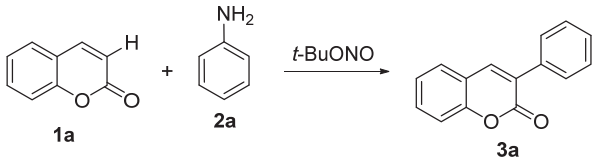
Inspired by these studies and our continuing interest in the arylation of heteroarene scaffolds, herein, we developed a direct copper-catalyzed arylation of coumarins with arylamines under mild conditions.

2 Results and discussion

Initially, the reaction of coumarin (**1a**) with aniline (**2a**) and *tert*-butyl nitrite (*t*-BuONO) was examined employing $Cu(OAc)_2$ as catalyst in acetone-H_2O co-solvent at room temperature (25 ℃) for 2.0 h (Table 1, Entry 1). Pleasantly, as expected, the desired product **3a** was obtained, albeit in low yield (31%). The structure of **3a** was elucidated through

IR, MS and NMR, and the arylation reaction was proceeded at C3 position of coumarin with high regioselectivity.[23] To improve this transformation, various copper catalysts including $CuSO_4$, CuO, CuI_2, CuCl, CuBr, and CuI were investigated (Table 1, Entries 1～7). The result showed that CuI emerged as the best one to give the product **3a** with 48% yield, and CuBr and $CuSO_4$ could also make good yields (40% and 41%). Subsequently, the amount of CuI was tested, and 0.15 equiv. could provide the best yield (Table 1, Entries 7～10). In order to avoid the formation of any acid-mediated azo compound, some mild bases including Cs_2CO_3, K_2CO_3, $CaCO_3$, NaOAc, and CaO were used in this reaction (Table 1, Entries 11～15). The result indicated that the best yield was 60% when $CaCO_3$ (1.0 equiv) was employed for this transformation. Furthermore, when the base was employed for this reaction, the side-product would decrease obviously. Among the screened solvent systems, DMSO-H_2O (V∶V=3∶1) was found to be the best choice for this reaction (Table 1, Entries 13, 16～24). The effect of temperature was screened, and 60 ℃ was proved to be best (Table 1, Entries 24～28). Subsequently, the reaction time was also examined, and 1.5 h was the ideal time (Table 1, Entries 27, 29～31). Finally, the ratio of **1a** and **2a** was investigated. When the molar ratio of **1a** and **2a** was 1∶1, the best yield (77%) could be obtained (Supporting information, Table S1, Entries 1～4).

Table 1 Optimization of reaction conditions [a]



Entry	Catalyst (equiv.)	Base (equiv.)	Solvent	Temp/℃	Time/h	Yield[b]/%
1	$Cu(OAc)_2$ (0.1)	—	Acetone/H_2O (V∶V=2∶1)	25	2.0	31
2	$CuSO_4$ (0.1)	—	Acetone/H_2O (V∶V=2∶1)	25	2.0	41
3	CuO (0.1)	—	Acetone/H_2O (V∶V=2∶1)	25	2.0	32
4	CuI_2 (0.1)	—	Acetone/H_2O (V∶V=2∶1)	25	2.0	10
5	CuCl (0.1)	—	Acetone/H_2O (V∶V=2∶1)	25	2.0	38
6	CuBr (0.1)	—	Acetone/H_2O (V∶V=2∶1)	25	2.0	40
7	CuI (0.1)	—	Acetone/H_2O (V∶V=2∶1)	25	2.0	48
8	CuI (0.05)	—	Acetone/H_2O (V∶V=2∶1)	25	2.0	22
9	CuI (0.15)	—	Acetone/H_2O (V∶V=2∶1)	25	2.0	53
10	CuI (0.2)	—	Acetone/H_2O (V∶V=2∶1)	25	2.0	47
11	CuI (0.15)	Cs_2CO_3 (1.0)	Acetone/H_2O (V∶V=2∶1)	25	2.0	40
12	CuI (0.15)	K_2CO_3 (1.0)	Acetone/H_2O (V∶V=2∶1)	25	2.0	48
13	CuI (0.15)	$CaCO_3$ (1.0)	Acetone/H_2O (V∶V=2∶1)	25	2.0	60
14	CuI (0.15)	NaOAc (1.0)	Acetone/H_2O (V∶V=2∶1)	25	2.0	37
15	CuI (0.15)	CaO (1.0)	Acetone/H_2O (V∶V=2∶1)	25	2.0	50
16	CuI (0.15)	$CaCO_3$ (1.0)	H_2O	25	2.0	Trace
17	CuI (0.15)	$CaCO_3$ (1.0)	CH_3CN	25	2.0	＜5
18	CuI (0.15)	$CaCO_3$ (1.0)	DMSO	25	2.0	＜5
19	CuI (0.15)	$CaCO_3$ (1.0)	CH_2Cl_2	25	2.0	42
20	CuI (0.15)	$CaCO_3$ (1.0)	CH_2Cl_2/H_2O (V∶V=1∶1)	25	2.0	15
21	CuI (0.15)	$CaCO_3$ (1.0)	CH_3CN/H_2O (V∶V=1∶1)	25	2.0	10
22	CuI (0.15)	$CaCO_3$ (1.0)	DMSO/H_2O (V∶V=1∶1)	25	2.0	48
23	CuI (0.15)	$CaCO_3$ (1.0)	DMSO/H_2O (V∶V=2∶1)	25	2.0	55
24	CuI (0.15)	$CaCO_3$ (1.0)	DMSO/H_2O (V∶V=3∶1)	25	2.0	67
25	CuI (0.15)	$CaCO_3$ (1.0)	DMSO/H_2O (V∶V=3∶1)	40	2.0	52
26	CuI (0.15)	$CaCO_3$ (1.0)	DMSO/H_2O (V∶V=3∶1)	50	2.0	61
27	CuI (0.15)	$CaCO_3$ (1.0)	DMSO/H_2O (V∶V=3∶1)	60	2.0	75
28	CuI (0.15)	$CaCO_3$ (1.0)	DMSO/H_2O (V∶V=3∶1)	70	2.0	70
29	CuI (0.15)	$CaCO_3$ (1.0)	DMSO/H_2O (V∶V=3∶1)	60	0.5	46
30	CuI (0.15)	$CaCO_3$ (1.0)	DMSO/H_2O (V∶V=3∶1)	60	1.0	55
31	CuI (0.15)	$CaCO_3$ (1.0)	DMSO/H_2O (V∶V=3∶1)	60	1.5	77
32	—	$CaCO_3$ (1.0)	DMSO/H_2O (V∶V=3∶1)	25	2.0	23

[a] Reaction conditions: coumarin **1a** (0.3 mmol, 43.8 mg), aniline **2a** (0.3 mmol, 27.9 mg), *t*-BuONO (0.36 mmol, 37.1 mg), catalyst, base, and solvent (3 mL); [b] Isolated yield.

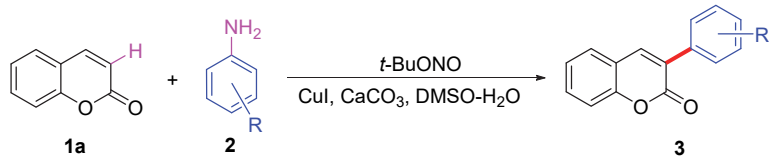
In the absence of CuI, the desired product was only obtained with 23% yield, which indicated that the catalyst CuI played an important role for this transformation (Table 1, Entry 32). After screening the catalyst, base, solvent, temperature, time and the ratio of substrates, the optimal reaction conditions were showed as follow: 1 equiv. of **1a**, 1 equiv. of **2a**, 1 equiv. of $CaCO_3$ as the base, DMSO-H_2O (V∶V=3∶1) as the solvent at 60 ℃ for 1.5 h.

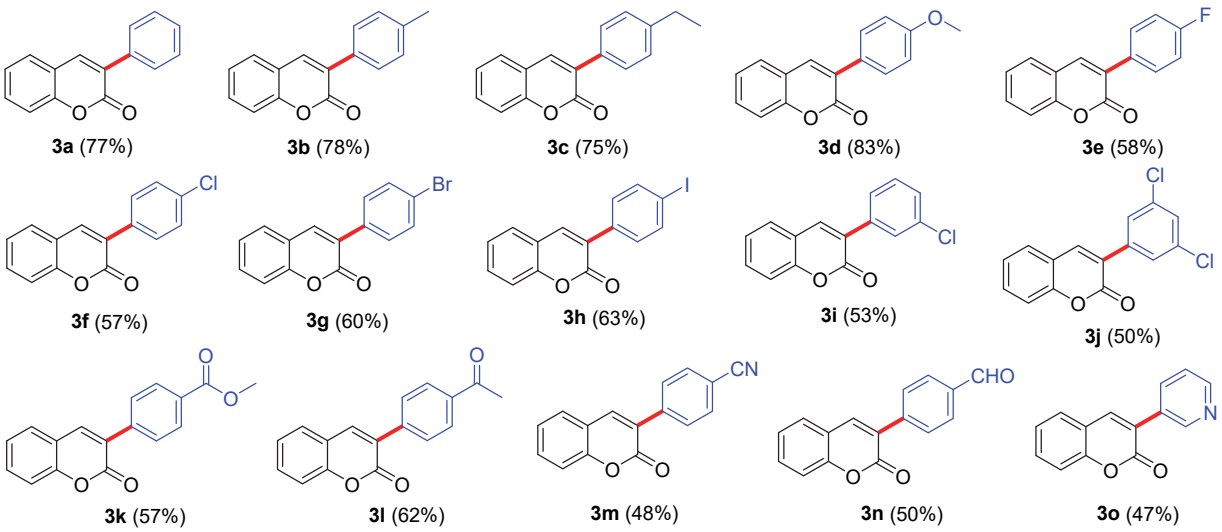
With the optimal conditions in hand, the generality of this reaction was further investigated using coumarin **1a** and different arylamines **2** (Table 2). A variety of arylamines bearing electron-donating and electron-withdrawing groups reacted smoothly affording the corresponding products in moderate to good yields (47%～83%). Generally, it was found that arylamines with electron-rich groups (Me, Et, OMe) gave higher yields in comparison with those with electron-poor groups (X, COOMe, COMe). Gratifyingly, for substrates with strong electron-withdrawing groups (CN, CHO), this reaction could still proceed smoothly to provide the desired products (**3m** and **3n**), albeit in relative low yield (48% and 50%). It was noteworthy that a heterocyclic aromatic amine, pyridine-3-amine, was well tolerated to afford the product **3o** with 47% yield. Unfortunately, there were no desired products detected when *o*-toluidine and naphthalene-1-amine were employed. Remarkably, the steric hindrance effect of arylamines has some influence on the coupling reaction.

Furthermore, the coupling reaction of different coumarins **1** with *p*-toluidine **2b** was investigated (Table 3). Various coumarins bearing Me, OMe, OEt, OCOMe, and NEt_2 were transformed into the corresponding 3-arylcoumarins in good yields (63%～88%). Pleasingly, coumarins bearing sensitive OH and NH_2 groups were also tolerated under the standard conditions, the desired products **3s** and **3t** were obtained in 78% and 80% yields, respectively. Unfortunately, coumarin possessing an electron-withdrawing NO_2 group at the C6 position did not furnish the desired product **3r**. Interestingly, when 4-substituted coumarins were employed under the standard conditions, the corresponding products (**3s**～**3t**) could also be afforded in 71%～80% yields. This fact indicated that the steric hindrance of coumarins played a weak role for this transformation. To further illustrate the generality and efficacy of this synthetic approach, other heterocycles, quinolinones, were also briefly surveyed (Table 4). Pleasingly, the C3 position of quinolinone derivatives was exclusively arylated to afford the corresponding desired products (**5a**～**5c**) in good yields. It was noteworthy that 2-quinolinone derivatives with a sensitive amide group were also tolerated and the coupling reaction proceeded with no requisite for protection of this group, albeit in low yields.

To elucidate this transformation, a preliminary mechanism was investigated by control experiments (Scheme 2). When phenyl diazonium salt tetrafluoroborate was employed as a substrate, instead of aniline, the reaction could proceed smoothly to provide the desired product in 80% yield under standard conditions. The result indicates that phenyl diazonium salt maybe be an intermediate for this coupling reaction. When 3.0 equiv. of 2,2,6,6-tetramethyl-

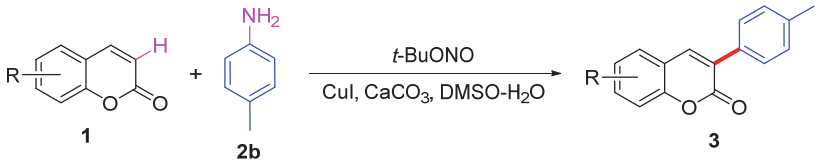
Table 2 Substrate scopes with arylamines[a,b]

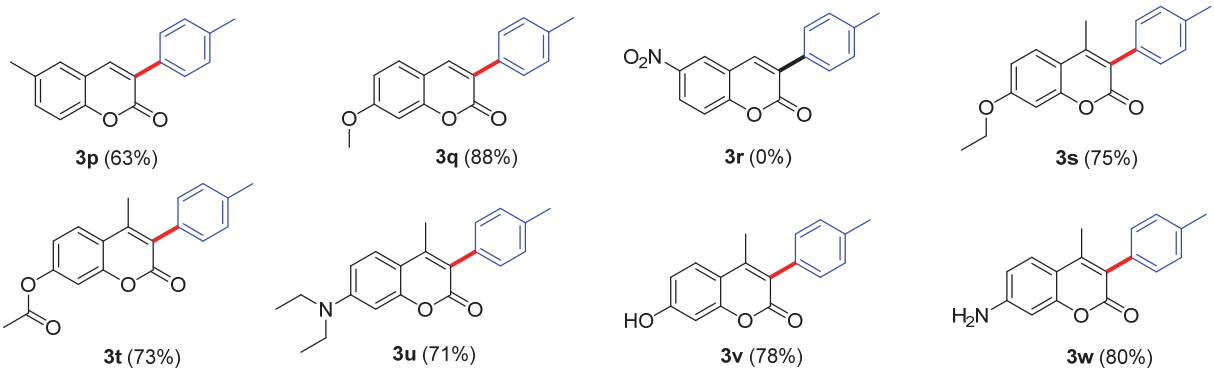




[a] Reaction conditions: coumarin **1a** (0.3 mmol, 43.8 mg), arylamines **2** (0.3 mmol), *t*-BuONO (0.36 mmol, 37.1 mg), CuI (0.045 mmol, 8.6 mg) as a catalyst, and $CaCO_3$ (0.3 mmol, 30 mg) in 3.0 mL of DMSO-H_2O (V∶V=3∶1), 60 ℃ for 1.5 h; [b] Isolated yield.

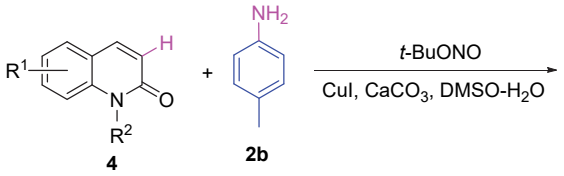
Table 3 Substrate scopes of substituted coumarins[a,b]

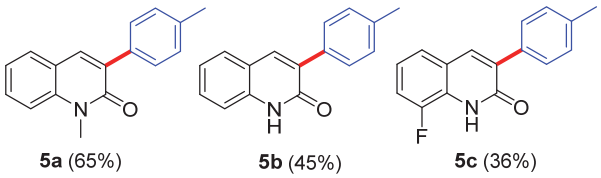




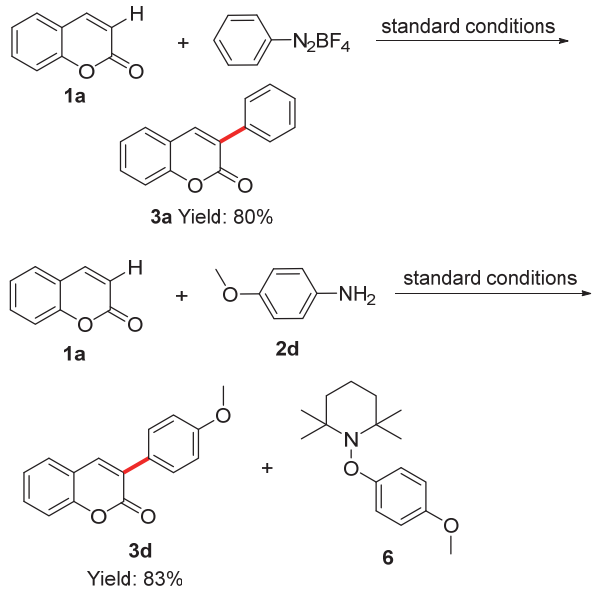
[a] Reaction conditions: coumarin **1** (0.3 mmol), *p*-toluidine **2b** (0.3 mmol, 32.1 mg), *t*-BuONO (0.36 mmol, 37.1 mg), CuI (0.045 mmol, 8.6 mg) as a catalyst, and $CaCO_3$ (0.3 mmol, 30 mg) in 3.0 mL DMSO-H_2O (V∶V=3∶1), 60 ℃ for 1.5 h; [b] Isolated yield.

Table 4 Synthesis of 3-arylquinolinone derivatives[a,b]





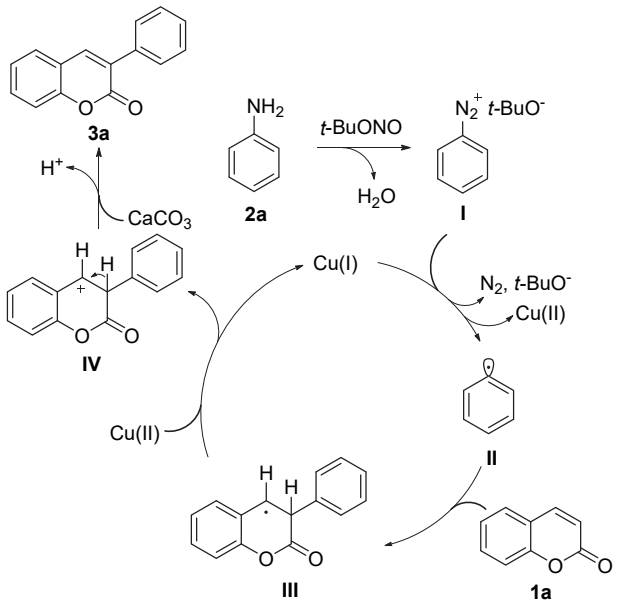
[a] Reaction conditions: quinolinones **4** (0.3 mmol), *p*-toluidine **2b** (0.3 mmol, 32.1 mg), *t*-BuONO (0.36 mmol, 37.1 mg), CuI (0.045 mmol, 8.6 mg) as a catalyst, and $CaCO_3$ (0.3 mmol, 30 mg) in 3.0 mL DMSO-H_2O (V∶V=3∶1), 60 ℃ for 1.5 h; [b] Isolated yield.



Scheme 2 Control experiments

piperidine 1-oxyl (TEMPO) was introduced into the reaction of coumarin **1a** with *p*-methylaniline **2d** under the standard conditions, only a trace of the desired product **3d** was found. The reaction of TEMPO with *p*-methylaniline **2d** afforded 2,2,6,6-tetramethyl-1-phenoxypiperidine **6**, which was trapped and detected by HRMS analysis. Moreover, the yield of **3d** was decreased sharply when 3.0 equiv. of BHT (2,6-di-*tert*-butyl-4-methylphenol) was added to this reaction system. These results indicated that an aryl radical intermediate was involved possibly during this transformation.

Based on the experimental results and previously reported studies,[33,34] a plausible catalytic cycle is proposed and is depicted in Scheme 3. Aniline **2a** is diazotized in the presence of *tert*-butyl nitrite to generate diazonium salt **I**. Then, Cu(I) reduces the diazonium salt into an aryl radical **II** with concomitant loss of nitrogen. The radical **II** is quickly intercepted by the coumarin **1a** to provide the intermediate **III**, which is likely quickly oxidized by Cu(II) species into the corresponding cation **IV**. At the same time, Cu(II) is reduced to Cu(I), which finishes a catalytic cyclization. Obviously, Cu(II) has also a certain catalytic action for this transformation. Finally, the carbon cation **IV** provides the expected coupling product **3a** through the deprotonation upon treatment with a suitable base $CaCO_3$.



Scheme 3 Proposed reaction mechanism

3 Conclusions

In summary, we have developed an efficient and practical method for the preparation of 3-arylcoumarins based on CuI-catalyzed regioselective cross-coupling reaction of coumarins with arylamines under mild conditions. The methodology features aqueous solvents, inexpensive reagents and catalysts, as well as experimental simplicity.

4 Experimental section

4.1 Instruments and reagents

All commercial reagents and solvents were used without purification. Column chromatography was performed using 300～400 mesh silica with the indicated solvent system according to standard techniques. Nuclear magnetic resonance spectra were recorded on a Bruker Avance 400 MHz spectrometer. Chemical shifts for ^{1}H NMR spectra were recorded from tetramethylsilane. Chemical shifts for ^{13}C NMR spectra were recorded from tetramethylsilane. Chemical shifts for ^{19}F NMR spectra were recorded with fluorobenzene as external standard. High resolution mass spectra (HRMS) were obtained on a Thermo Scientific LTQ Orbitrap XL instrument using the ESI technique. IR spectra were recorded on a Shimadazu IR-408 Fourier transform infrared spectrophotometer using a thin film supported on KBr pellets. Melting points were measured on an XT4A microscopic apparatus uncorrected.

4.2 General experimental procedure for the synthesis of 3-arylcoumarins (**3**)

Coumarin **1a** (0.3 mmol, 43.8 mg), arylamines **2** (0.3 mmol), *tert*-butyl nitrite (0.36 mmol, 37.1 mg), and CuI (0.045 mmol, 8.6 mg) in DMSO-H_2O (3.0 mL) were added to a 25 mL Schlenk tube. The reaction was stirred at 60 ℃ for 1.5 h (monitored by TLC). After completion of the reaction, the reaction mixture was diluted with ethyl acetate, and saturated sodium chloride washed three times. The resulting organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacum. The crude product was purified by silica gel column chromatography using ethyl acetate/petroleum ether (V∶V=1∶10 to 1∶1) as eluant to obtain the desired products **3**.

3-Phenyl-2*H*-chromen-2-one (**3a**): Colorless solid, mp 137～138 ℃ (lit.[23] m.p. 138～139 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (s, 1H), 7.70～7.68 (m, 2H), 7.51 (t, $J_{H\text{-}H}$=8.2 Hz, 2H), 7.45～7.39 (m, 3H), 7.34 (d, $J_{H\text{-}H}$=8.1 Hz, 1H), 7.28 (td, $J_{H\text{-}H}$=7.5 Hz, $J_{H\text{-}H}$=1.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.6, 153.5, 139.9 (CH), 134.7, 131.4 (CH), 128.8 (CH), 128.6 (CH), 128.5 (CH), 128.3, 127.9 (CH), 124.5 (CH), 119.7, 116.4 (CH); IR (KBr) ν: 1716, 1601, 1454, 1117 cm^{-1}; MS (ESI) 223.2 $[M+H]^+$.

3-(*p*-Tolyl)-2*H*-chromen-2-one (**3b**): Colorless solid, m.p. 163～164 ℃ (lit.[23] m.p. 160～161 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (s, 1H), 7.60 (d, $J_{H\text{-}H}$=8.1 Hz, 2H), 7.54～7.49 (m, 2H), 7.35 (d, $J_{H\text{-}H}$=8.2 Hz, 1H), 7.30～7.24 (m, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.7, 153.4, 139.2 (CH), 138.9, 131.7, 131.2 (CH), 129.2 (CH), 128.4 (CH), 128.3, 127.8 (CH), 124.4 (CH), 119.7, 116.4 (CH), 21.2 (CH_3); IR (KBr) ν: 1716, 1610, 1452, 1113 cm^{-1}; MS (ESI) 237.2 $[M+H]^+$.

3-(4-Ethylphenyl)-2*H*-chromen-2-one (**3c**): Colorless solid, m.p. 111～112 ℃ (lit.[26] m.p. 118～119 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (s, 1H), 7.63 (d, $J_{H\text{-}H}$=8.2 Hz, 2H), 7.53～7.48 (m, 2H), 7.34 (d, $J_{H\text{-}H}$=8.2 Hz, 1H), 7.29～7.26 (m, 3H), 2.69 (q, $J_{H\text{-}H}$=7.6 Hz, 2H), 1.26 (t, $J_{H\text{-}H}$=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.7, 153.4, 145.2, 139.2 (CH), 132.0, 131.2 (CH), 128.5 (CH), 128.3, 128.0 (CH), 127.8 (CH), 124.4 (CH), 119.8, 116.4 (CH), 28.7 (CH_3), 15.5 (CH_3); IR (KBr) ν: 3039, 2943, 2833, 1701, 1608, 1512, 1452, 1252, 1128 cm^{-1}; MS (ESI) 251.0 $[M+H]^+$.

3-(4-Methoxyphenyl)-2*H*-chromen-2-one (**3d**): Light yellow solid, m.p. 134～135 ℃ (lit.[23] m.p. 138～139 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76 (s, 1H), 7.67 (d, $J_{H\text{-}H}$=8.8 Hz, 2H), 7.53～7.48 (m, 2H), 7.35 (d, $J_{H\text{-}H}$=8.2 Hz, 1H), 7.30～7.26 (m, 1H), 6.97 (d, $J_{H\text{-}H}$=8.8 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.8, 160.1, 153.3, 138.5 (CH), 131.0 (CH), 129.8 (CH), 127.8, 127.7 (CH), 124.4 (CH), 119.8, 116.4 (CH), 113.9 (CH), 55.4 (CH_3); IR (KBr) ν: 2966, 2929, 1716, 1610, 1512, 1452, 1115 cm^{-1}; MS (ESI) 253.3 $[M+H]^+$.

3-(4-Fluorophenyl)-2*H*-chromen-2-one (**3e**): Light yellow solid, m.p. 180～181 ℃ (lit.[23] m.p. 188～189 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (s, 1H), 7.72～7.68 (m, 2H), 7.54 (d, $J_{H\text{-}H}$=7.6 Hz, 2H), 7.37 (d, $J_{H\text{-}H}$=8.8 Hz, 1H), 7.31 (d, $J_{H\text{-}H}$=7.8 Hz, 1H), 7.14 (t, $J_{H\text{-}H}$=8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.1 (d, $J_{F\text{-}C}$=247.3 Hz), 160.6, 153.5, 139.7 (CH), 131.5 (CH), 130.7 (d, $J_{F\text{-}C}$=3.1 Hz, CH), 130.7 (d, $J_{F\text{-}C}$=8.1 Hz), 127.9 (CH), 127.3, 124.6 (CH), 119.5, 116.5 (CH), 115.5 (d, $J_{F\text{-}C}$=21.7 Hz, CH). ^{19}F NMR (376 MHz, $CDCl_3$) δ: −112.3; IR (KBr) ν: 1712, 1604, 1514, 1234 cm^{-1}; MS (ESI) 241.3 $[M+H]^+$.

3-(4-Chlorophenyl)-2*H*-chromen-2-one (**3f**): Light yellow solid, m.p. 181～182 ℃ (lit.[23] m.p. 190～191 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (s, 1H), 7.65 (d, $J_{H\text{-}H}$=8.6 Hz, 2H), 7.55-7.51 (m, 2H), 7.40 (d, $J_{H\text{-}H}$=8.6 Hz, 2H), 7.35 (d, $J_{H\text{-}H}$=8.7 Hz, 1H), 7.30 (td, $J_{H\text{-}H}$=7.5 Hz, $J_{H\text{-}H}$=0.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.3, 153.5, 139.9 (CH), 134.9, 133.0, 131.7 (CH), 129.8 (CH), 128.6 (CH), 128.0 (CH), 127.1, 124.6 (CH), 119.4, 116.5 (CH). IR (KBr) *v*: 1699, 1530, 1495, 1452, 1298, 1092 cm^{-1}; MS (ESI) 257.1 $[M+H]^+$.

3-(4-Bromophenyl)-2*H*-chromen-2-one (**3g**): Colorless solid, m.p. 184～185 ℃ (lit.[23] m.p. 189～190 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (s, 1H), 7.61～7.53 (m, 6H), 7.38 (d, $J_{H\text{-}H}$=8.6 Hz, 1H), 7.31 (t, $J_{H\text{-}H}$=7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.3, 153.5, 140.0 (CH), 133.5, 131.7 (CH), 131.6 (CH), 130.1 (CH), 128.0 (CH), 127.2, 124.6 (CH), 123.2, 119.4, 116.6 (CH); IR (KBr) *v*: 1720, 1620, 1454, 1223, 1115 cm^{-1}; MS (ESI) 301.2 $[M+H]^+$.

3-(4-Iodophenyl)-2*H*-chromen-2-one (**3h**): Light yellow solid,[26] m.p. 170～171 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 (s, 1H), 7.78 (d, $J_{H\text{-}H}$=8.4 Hz, 2H), 7.56～7.53 (m, 2H), 7.46 (d, $J_{H\text{-}H}$=8.4 Hz, 2H), 7.37 (d, $J_{H\text{-}H}$=8.6 Hz, 1H), 7.31 (t, $J_{H\text{-}H}$=7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.3, 153.5, 139.9 (CH), 137.6 (CH), 134.2, 131.7 (CH), 130.3 (CH), 128.0 (CH), 127.3, 124.7 (CH), 119.5, 116.6 (CH), 95.0; IR (KBr) *v*: 1721, 1618, 1456, 1225 cm^{-1}; MS (ESI) 349.1 $[M+H]^+$.

3-(3-Chlorophenyl)-2*H*-chromen-2-one (**3i**): Light yellow solid, m.p. 164～165 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (s, 1H), 7.70 (s, 1H), 7.63～7.60 (m, 1H), 7.57～7.54 (m, 2H), 7.39～7.36 (m, 3H), 7.31 (t, $J_{H\text{-}H}$=6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.2, 153.6, 140.5 (CH), 136.4, 134.4, 131.8 (CH), 129.7 (CH), 128.9 (CH), 128.5 (CH), 128.0 (CH), 127.0, 126.7 (CH), 124.6 (CH), 119.4, 116.5 (CH); IR (KBr) *v*: 1701, 1526, 1502, 1454, 1295, 1095 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{10}ClO_2$ $[M+H]^+$ 257.0364, found 257.0366.

3-(3,5-Dichlorophenyl)-2*H*-chromen-2-one (**3j**): Light yellow solid, m.p. 184～185 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (s, 1H), 7.63 (d, $J_{H\text{-}H}$=1.8 Hz, 2H), 7.57 (d, $J_{H\text{-}H}$=7.5 Hz, 2H), 7.41～7.38 (m, 2H), 7.33 (td, $J_{H\text{-}H}$=7.5 Hz, $J_{H\text{-}H}$=0.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.8, 153.7, 141.0 (CH), 137.4, 135.0, 132.3 (CH), 128.8 (CH), 128.2 (CH), 126.9 (CH), 125.7, 124.8 (CH), 119.1, 116.6 (CH); IR (KBr) *v*: 1707, 1655, 1540, 1466, 1363 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_9Cl_2O_2$ $[M+H]^+$ 290.9974, found 290.9971.

Methyl 4-(2-*oxo*-2*H*-chromen-3-yl)benzoate (**3k**): Colorless solid, m.p. 197～198 ℃ (lit.[23] m.p. 209～210 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (dd, $J_{H\text{-}H}$=8.4 Hz, $J_{H\text{-}H}$=1.8 Hz, 2H), 7.89 (s, 1H), 7.80 (dd, $J_{H\text{-}H}$=8.4 Hz, $J_{H\text{-}H}$=1.8 Hz, 2H), 7.57 (td, $J_{H\text{-}H}$=7.5 Hz, $J_{H\text{-}H}$=1.6 Hz, 2H), 7.39 (d, $J_{H\text{-}H}$=8.7 Hz, 1H), 7.32 (t, $J_{H\text{-}H}$=8.0 Hz, 1H), 3.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.6, 160.1, 153.6, 140.7 (CH), 139.0, 131.9 (CH), 130.2, 129.6 (CH), 128.4 (CH), 128.0 (CH), 127.2, 124.6 (CH), 119.3, 116.5 (CH), 52.2 (CH_3); IR (KBr) *v*: 1724, 1606, 1558, 1441, 1277, 1117 cm^{-1}; MS (ESI) 281.2 $[M+H]^+$.

3-(4-Acetylphenyl)-2*H*-chromen-2-one (**3l**): Colorless solid, m.p. 215～216 ℃ (lit.[23] m.p. 217～218 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (d, $J_{H\text{-}H}$=8.4 Hz, 2H), 7.90 (s, 1H), 7.83 (d, $J_{H\text{-}H}$=8.4 Hz, 2H), 7.57 (t, $J_{H\text{-}H}$=7.6 Hz, 2H), 7.39 (d, $J_{H\text{-}H}$=8.4 Hz, 1H), 7.33 (td, $J_{H\text{-}H}$=7.5 Hz, $J_{H\text{-}H}$=0.6 Hz, 1H), 2.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.6, 160.1, 153.7, 140.8 (CH), 139.2, 137.0, 132.0 (CH), 128.7 (CH), 128.4 (CH), 128.2 (CH), 127.2, 124.7 (CH), 119.3, 116.6 (CH), 26.7 (CH_3); IR (KBr) *v*: 1712, 1674, 1604, 1458, 1358, 1269, 1117 cm^{-1}; MS (ESI) 265.3 $[M+H]^+$.

4-(2-*oxo*-2*H*-Chromen-3-yl)benzonitrile (**3m**): Light yellow solid, m.p. 217～218 ℃ (lit.[23] m.p. 239～240 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91 (s, 1H), 7.85 (d, $J_{H\text{-}H}$=8.2 Hz, 2H), 7.73 (d, $J_{H\text{-}H}$=8.2 Hz, 2H), 7.60 (t, $J_{H\text{-}H}$=7.5 Hz, 2H), 7.40～7.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.9, 153.8, 141.3 (CH), 139.1, 132.4 (CH), 132.2 (CH), 129.2 (CH), 128.3 (CH), 126.4, 124.8 (CH), 119.2, 118.5, 116.7 (CH), 112.4; IR (KBr) *v*: 1711, 1685, 1604, 1454, 1358, 1230, 1124 cm^{-1}; MS (ESI) 248.3 $[M+H]^+$.

4-(2-*oxo*-2*H*-chromen-3-yl)benzaldehyde (**3n**): Colorless solid, m.p. 198～199 ℃ (lit.[23] m.p. 202～203 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.07 (s, 1H), 7.97 (d, $J_{H\text{-}H}$=8.2 Hz, 2H), 7.93～7.89 (m, 3H), 7.60～7.57 (m, 2H), 7.40 (d, $J_{H\text{-}H}$=8.6 Hz, 1H), 7.34 (t, $J_{H\text{-}H}$=7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.7 (CHO), 160.0, 153.8, 141.2 (CH), 140.6, 136.2, 132.2 (CH), 129.8 (CH), 129.2 (CH), 128.3 (CH), 127.1, 124.8 (CH), 119.3, 116.6 (CH); IR (KBr) *v*: 2924, 1716, 1676, 1603, 1524, 1446, 1207, 1115 cm^{-1}; MS (ESI) 251.0 $[M+H]^+$.

3-(Pyridin-3-yl)-2*H*-chromen-2-one (**3o**): Colorless solid, m.p. 160～161 ℃ (lit.[18b] m.p. 160～161 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.88 (s, 1H), 8.64 (d, $J_{H\text{-}H}$=4.1 Hz, 1H), 8.15～8.13 (m, 1H), 7.90 (s, 1H), 7.58 (t, $J_{H\text{-}H}$=7.6 Hz, 2H), 7.39 (dd, $J_{H\text{-}H}$=8.3 Hz, $J_{H\text{-}H}$=3.0 Hz, 2H), 7.34 (t, $J_{H\text{-}H}$=7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.2, 153.7, 149.8 (CH), 148.9 (CH), 140.5 (CH), 136.2 (CH), 132.0 (CH), 130.7, 128.2 (CH), 125.2, 124.7 (CH), 123.1 (CH), 119.3, 116.6 (CH); IR (KBr) *v*: 1716, 1699, 1608, 1558, 1458, 1414, 1324, 1234, 1122 cm^{-1}; MS (ESI) 224.2 $[M+H]^+$.

6-Methyl-3-(p-tolyl)-2H-chromen-2-one (**3p**): Colorless solid, m.p. 138～139 ℃ (lit.[25] m.p. 138～140 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (s, 1H), 7.59 (d, $J_{H\text{-}H}$=8.1 Hz, 2H), 7.31 (d, $J_{H\text{-}H}$=6.8 Hz, 2H), 7.26～7.23 (m, 3H), 2.41 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.9, 151.5, 139.2 (CH), 138.8, 134.0, 132.2 (CH), 131.9, 129.2 (CH), 128.4 (CH), 128.1, 127.6 (CH), 119.5, 116.1 (CH), 21.3 (CH_3), 20.8 (CH_3); IR (KBr) *v*: 3224, 3054, 1702, 1456, 1263, 1087 cm^{-1}; MS (ESI) 251.4 $[M+H]^+$.

7-Methoxy-3-(*p*-tolyl)-2*H*-chromen-2-one (**3q**): Colorless solid, m.p. 141～142 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (s, 1H), 7.57 (d, $J_{H\text{-}H}$=8.2 Hz, 2H), 7.40 (d, $J_{H\text{-}H}$=8.4 Hz, 1H), 7.23 (d, $J_{H\text{-}H}$=8.0 Hz, 2H), 6.86-6.82 (m, 2H), 3.86 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:

162.4, 161.0, 155.2, 139.4 (CH), 138.4, 132.1, 129.1 (CH), 128.7 (CH), 128.2 (CH), 124.7, 113.4, 112.7 (CH), 100.4 (CH), 55.8 (CH_3), 21.3 (CH_3); IR (KBr) *v*: 3005, 2931, 1716, 1701, 1610, 1504, 1442, 1360, 1269, 1201, 1163, 1122 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{15}O_3$ $[M+H]^+$ 267.1016, found 267.1018.

7-Ethoxy-4-methyl-3-(*p*-tolyl)-2*H*-chromen-2-one (**3s**): Light yellow solid, m.p. 118～119 ℃; ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.54 (d, J_{H-H}=8.8 Hz, 1H), 7.24 (d, J_{H-H}=7.7 Hz, 2H), 7.18 (d, J_{H-H}=8.0 Hz, 2H), 6.86 (dd, J_{H-H}=8.8 Hz, J_{H-H}=2.4 Hz, 1H), 6.82 (d, J_{H-H}=2.4 Hz, 1H), 4.09 (q, J_{H-H}=7.0 Hz, 2H), 2.39 (s, 3H), 2.27 (s, 3H), 1.45 (t, J_{H-H}=7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 161.6, 154.2, 147.7, 137.7, 131.6, 130.0 (CH), 129.1 (CH), 126.0 (CH), 124.1, 114.0, 112.6 (CH), 101.0 (CH), 64.1 (CH_2), 21.3 (CH_3), 16.6 (CH_3), 14.6 (CH_3); IR (KBr) *v*: 2987, 2925, 1697, 1599, 1564, 1388, 1269, 1184, 1138, 1045 cm^{-1}. HRMS (ESI) calcd for $C_{19}H_{19}O_3$ $[M+H]^+$ 295.1328, found 295.1329.

4-Methyl-2-*oxo*-3-(*p*-tolyl)-2*H*-chromen-7-yl acetate (**3t**): Colorless solid, m.p. 169～170 ℃; ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.67 (d, J_{H-H}=8.6 Hz, 1H), 7.26 (d, J_{H-H}=7.2 Hz, 2H), 7.18 (d, J_{H-H}=7.7 Hz, 2H), 7.14 (d, J_{H-H}=1.6 Hz, 1H), 7.09 (d, J_{H-H}=8.6 Hz, 1H), 2.40 (s, 3H), 2.35 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 168.8, 160.8, 153.2, 152.6, 146.9, 138.1, 131.2, 129.8 (CH), 129.1 (CH), 126.8, 125.9 (CH), 118.5, 118.0 (CH), 110.2 (CH), 21.3 (CH_3), 21.1 (CH_3), 16.7 (CH_3); IR (KBr) *v*: 1770, 1718, 1610, 1558, 1512, 1363, 1198, 1130 cm^{-1}. HRMS (ESI) calcd for $C_{19}H_{17}O_4$ $[M+H]^+$ 309.1121, found 309.1123.

7-(Diethylamino)-4-methyl-3-(*p*-tolyl)-2*H*-chromen-2-one (**3u**): Light yellow solid, m.p. 131～132 ℃; ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.43 (d, J_{H-H}=9.0 Hz, 1H), 7.22 (d, J_{H-H}=7.8 Hz, 2H), 7.17 (d, J_{H-H}=7.8 Hz, 2H), 6.60 (dd, J_{H-H}=9.0 Hz, J_{H-H}=2.2 Hz, 1H), 6.53 (d, J_{H-H}=2.2 Hz, 1H), 3.40 (q, J_{H-H}=7.0 Hz, 4H), 2.37 (s, 3H), 2.22 (s, 3H), 1.20 (t, J_{H-H}=7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 162.2, 155.0, 150.2, 148.2, 137.2, 132.3, 130.3 (CH), 128.9 (CH), 126.0 (CH), 121.1, 109.6, 108.6 (CH), 97.5 (CH), 44.7 (CH_2), 21.3 (CH_3), 16.3 (CH_3), 12.5 (CH_3); IR (KBr) *v*: 2976, 2920, 1701, 1614, 1585, 1522, 1412, 1356, 1267, 1142, 1072 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{24}NO_2$ $[M+H]^+$ 322.1802, found 322.1805.

7-Hydroxy-4-methyl-3-(*p*-tolyl)-2*H*-chromen-2-one (**3v**): Yellow solid, m.p. 219～220 ℃; ^1H NMR (400 MHz, DMSO) *δ*: 10.52 (bs, 1H), 7.61 (d, J_{H-H}=8.8 Hz, 1H), 7.22 (d, J_{H-H}=8.0 Hz, 2H), 7.15 (d, J_{H-H}=8.0 Hz, 2H), 6.81 (dd, J_{H-H}=8.7 Hz, J_{H-H}=2.4 Hz, 1H), 6.73 (d, J_{H-H}=2.4 Hz, 1H), 2.33 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, DMSO) *δ*: 161.2, 160.8, 154.2, 148.5, 137.3, 132.3, 130.6 (CH), 129.0 (CH), 127.5 (CH), 122.7, 113.4 (CH), 112.8, 102.4 (CH), 21.3 (CH_3), 16.8 (CH_3); IR (KBr) *v*: 3288, 1682, 1595, 1572, 1446, 1275, 1225, 1134, 1074 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{15}O_3$ $[M+H]^+$ 267.1016, found 267.1013.

7-Amino-4-methyl-3-(*p*-tolyl)-2*H*-chromen-2-one (**3w**): Brown solid, m.p. 213～214 ℃ (lit.[17a] m.p. 260～262 ℃); ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.42 (d, J_{H-H}=8.5 Hz, 1H), 7.24 (d, J_{H-H}=7.8 Hz, 2H), 7.17 (d, J_{H-H}=7.8 Hz, 2H), 6.64 (s, 1H), 6.59 (d, J_{H-H}=8.5 Hz, 1H), 4.19 (bs, 2H), 2.38 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 161.9, 154.6, 149.9, 148.1, 137.5, 132.0, 130.2 (CH), 129.0 (CH), 126.3 (CH), 122.6, 112.1, 111.8 (CH), 100.9 (CH), 21.3 (CH_3), 16.4 (CH_3); IR (KBr) *v*: 3464, 3357, 1676, 1610, 1550, 1508, 1387, 1284, 1151, 1068 cm^{-1}; MS (ESI) 266.4 $[M+H]^+$.

4.3 General experimental procedure for the synthesis of 3-aryl quinolinones (**5**)

Quinolinones **4** (0.3 mmol), *p*-toluidine **2b** (0.3 mmol, 32.1 mg), *tert*-butyl nitrite (0.36 mmol, 37.1 mg), and CuI (0.045 mmol, 8.6 mg) in DMSO-H_2O (3.0 mL) were added to a 25 mL Schlenk tube. The reaction was stirred at 60 ℃ for 1.5 h (monitored by TLC). After completion of the reaction, the reaction mixture was diluted with ethyl acetate, and saturated sodium chloride washed three times. The resulting organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacum. The crude product was purified by silica gel column chromatography using ethyl acetate/petroleum ether (*V*∶*V*=1∶1 to 2∶1) as eluant to obtain the desired products **5**.

1-Methyl-3-(*p*-tolyl)quinolin-2(1*H*)-one (**5a**): Colorless solid, m.p. 99～100 ℃ (lit.[35] m.p. 96～99 ℃); ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.75 (s, 1H), 7.61 (d, J_{H-H}=8.1 Hz, 2H), 7.57～7.50 (m, 2H), 7.33 (d, J_{H-H}=8.5 Hz, 1H), 7.24～7.19 (m, 3H), 3.77 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 161.6, 139.5, 137.9, 136.3 (CH), 133.9, 132.4, 130.1 (CH), 128.9 (CH), 128.8 (CH), 128.7 (CH), 122.1 (CH), 120.8, 113.9 (CH), 29.9 (CH_3), 21.3 (CH_3); IR (KBr) *v*: 3028, 2920, 1643, 1593, 1458, 1288, 1115 cm^{-1}; MS (ESI) 250.3 $[M+H]^+$.

3-(*p*-Tolyl)quinolin-2(1*H*)-one (**5b**): Brown solid, m.p. 234～235 ℃; ^1H NMR (400 MHz, $CDCl_3$) *δ*: 12.01 (bs, 1H), 7.89 (s, 1H), 7.71 (d, J_{H-H}=7.3 Hz, 2H), 7.58 (d, J_{H-H}=7.6 Hz, 1H), 7.46 (t, J_{H-H}=7.2 Hz, 1H), 7.37 (d, J_{H-H}=7.2 Hz, 1H), 7.29 (d, J_{H-H}=7.2 Hz, 2H), 7.20 (t, J_{H-H}=7.4 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 163.3, 138.0, 137.9 (CH), 133.2, 130.0 (CH), 129.0 (CH), 128.7 (CH), 128.4, 127.7 (CH), 122.6 (CH), 120.4, 115.6 (CH), 21.3 (CH_3); IR (KBr) *v*: 2922, 2850, 1653, 1568, 1516, 1429 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{14}NO$ $[M+H]^+$ 236.1070, found 236.1072.

8-Fluoro-3-(*p*-tolyl)quinolin-2(1*H*)-one (**5c**): Colorless solid, m.p. 181～182 ℃; ^1H NMR (400 MHz, $CDCl_3$) *δ*: 10.02 (bs, 1H), 7.88 (s, 1H), 7.69 (bs, 2H), 7.39～7.16 (m, 5H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 161.5, 148.8 (d, J_{F-C}=245.0 Hz), 138.5, 136.8 (CH), 134.0, 132.6, 129.7, 129.1 (CH), 128.7 (CH), 126.7, 123.1 (d, J_{F-C}=3.6 Hz, CH), 122.1 (d, J_{F-C}=6.9 Hz, CH), 114.9 (d, J_{F-C}=16.7 Hz, CH), 21.3 (CH_3); ^{19}F NMR (376 MHz, $CDCl_3$) *δ*: −135.2. IR (KBr) *v*: 2920, 2850, 1647, 1508, 1238, 1182 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{13}FNO$ $[M+H]^+$ 254.0976, found 254.0978.

Supporting Information Copies of NMR spectra of products. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn/.

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