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Graphic Abstract

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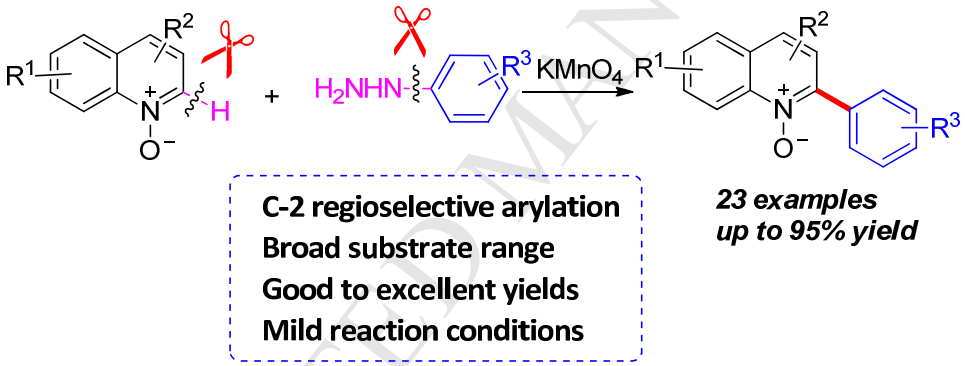

$KMnO_4$-mediated direct C2-selective C–H arylation of quinoline *N*-oxides with aromatic hydrazines

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Abstract: An efficient protocol for the synthesis of 2-arylquinoline *N*-oxides has been developed via $KMnO_4$-mediated cross-coupling reaction of quinoline *N*-oxides with aromatic hydrazines in moderated to good yields. The reactions proceeded efficiently over a broad range of substrates with excellent regioselectivity and functional group tolerance.

Key words: 2-arylquinoline *N*-oxide; arylhydrazine; $KMnO_4$-mediated; arylation; radical reaction

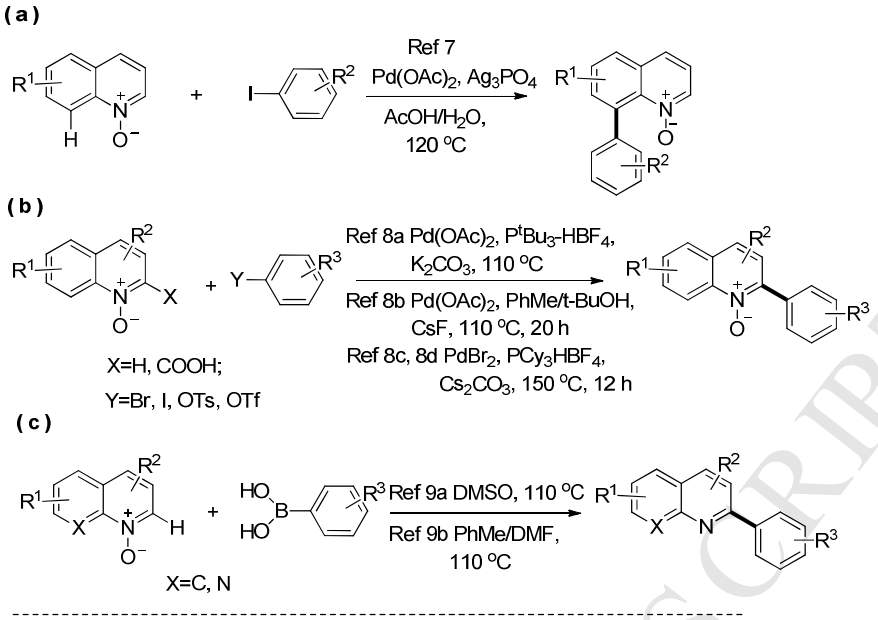
1. Introduction

The quinoline scaffold is one of the most important heterocycles and is commonly encountered in natural products, medicinal and material chemistry.[1] In medicinal chemistry, quinolines and quinoline *N*-oxides exhibit antitumor and antimalarial activities.[2] In addition, the quinoline *N*-oxide core has been found in drugs that activate microsomal Na/K-ATPase.[3] As a result, considerable efforts have been made towards their synthesis and functionalization in different positions.[4] 2-Arylquinoline *N*-oxide derivatives are important structural motifs with applications in the areas of drug discovery,[5] and their synthesis by novel methods has attracted attention in medicinal and synthetic chemistry.

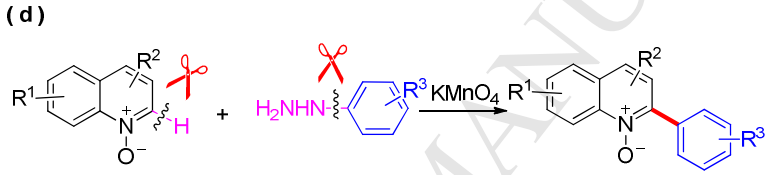
Transition-metal catalyzed direct arylations of quinoline *N*-oxide through C–H bond cleavages have recently been reported,[6] and widely employed among these reactions is the Pd-catalyzed cross-coupling of aromatic halides, and boronic acids, etc. In 2015, Larionov's group reported a palladium-catalyzed C8-selective C–H arylation of quinoline *N*-oxides using iodoarene as a coupling partner, and the main product 8-arylquinoline *N*-oxides were produced (Scheme 1 a).[7] In 2009, a $Pd(OAc)_2$-catalyzed direct arylation reaction was described by Fagnou's group using the substrates of quinoline *N*-oxides with bromoarenes, P^tBu_3-HBF_4 for the ligand, K_2CO_3 for the base in toluene; In 2011, Ackermam's group reported a direct arylation of electron-deficient quinoline

N-oxides with aryl tosylates using $Pd(OAc)_2$ as a catalyst derived from the ligand X-Phos, CsF as the base in a *t*-BuOH/toluene solvent mixture; In 2014, decarboxylative cross-coupling reactions of substituted 2-carboxyazine *N*-oxides, with a variety of (hetero)aryl halides, by bimetallic Pd^0/Cu^I and Pd^0/Ag^I catalysis were reported by Hoarau's group, and $Pd(OAc)_2$-catalyzed direct arylation of azine and quinoline *N*-oxides using aryl triflates to afford the corresponding 2-aryl azine and quinoline *N*-oxides was also described by Fagnou's group (Scheme 1 b).[8] Transition-metal-free reactions are of great interest in terms of atom economy, environmental impact, and cost reduction. In 2015, a metal-free regioselective cross-coupling of quinoline *N*-oxides with boronic acids was developed by Antonchick's group in DMSO solvent at 110 ^oC for 1-24 h, and Morris' group also reported the synthesis of 7-aryl-1,8-naphthyridines *via* addition of aryl boronic acids to 1,8-naphthyridine *N*-oxides at 110 ^oC in toluene or dimethylformamide for 16 h (Scheme 1 c).[9] Moreover, Organocatalytic functionalization of quinoline *N*-oxide was also investigated using *in situ* generated onium amide base or phophazene base as a catalyst, heteroarylation at 2-position were achieved *via* nucleophilic addition- elimination process.[10] Transition-metal or metal-free catalyzed cross coupling reactions of quinoline *N*-oxides with different aryl sources represent some of the most important methods for synthesizing 2-arylquinoline *N*-oxides. However, the common limitations of most of these methods are inevitability of transition-metals which possess high cost and toxicity, necessity of prefunctionalization of 2-position of quinoline *N*-oxides, use of expensive arylating counterparts such as boronic acid, elevated temperature (110-150 ^oC), and longer reaction time (12-16 h). Recently, although there were reports on constructing 2-arylquinoline *N*-oxides through the reduction-cyclization sequences starting from 2-nitrochalcones and 3-hydroxyketones using ruthenium-carbon nanotube nanohybridas a catalyst,[11] the applicability of such methods is curtailed owing to the requirement of drastic conditions such as reflux temperatures, excess amounts of metal catalysts, or unavailable and expensive catalysts.

Previous works:



This work:

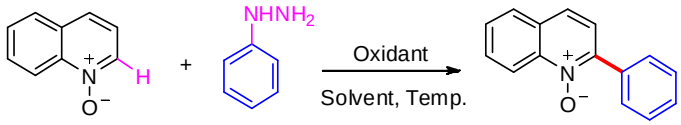


Scheme 1 Synthesis of 2-arylquinolines and 2-arylquinoline N-oxides

Although direct arylation reaction of quinoline *N*-oxides has been investigated thoroughly with many coupling partners, there are no reports employing the use of arylhydrazines. Arylhydrazines are known to undergo oxidation to form aryl radicals in the presence of oxygen, high valent metal or other oxidants.[12] Furthermore, arylhydrazines are simple and cheap starting materials. We previously reported the direct and regioselective arylation of coumarins and quinolinones using a wide range of arylhydrazines to produce 3-arylcoumarin and 3-arylquinolinone derivatives under mild conditions.[13] Guided by the recent studies on using arylhydrazines as aryl sources,[14] we decided to investigate the modular synthesis for 2-arylquinoline *N*-oxides by this method. Herein, we report such transformations starting from quinoline *N*-oxides with arylhydrazines that lead to 2-arylquinoline *N*-oxide derivatives in high yields (Scheme 1 d). The attractive features of this method are the use of simple $KMnO_4$ as an oxidant at moderate reaction temperature (90 °C); a broad evaluation of the scope and functional group compatibilities for quinoline *N*-oxides and arylhydrazines; the highly regioselective arylation of substituted quinoline *N*-oxides. In addition, no catalyst, ligand, base, and other additive are needed.

2. Results and discussion

Table 1 Optimization of reaction conditions[a]



1a **2a** **3a**

Entry	Oxidant (eq)	Solvent	Temp (^{o}C)	Time (mins)	Yield[b] (%)
1	H_2O_2 (3.0)	CH_3CN	80	60	51
2	TBHP (3.0)	CH_3CN	80	60	53
3	DTBP (3.0)	CH_3CN	80	60	20
4	$Mn(OAc)_3$ (3.0)	CH_3CN	80	60	5
5	MnO_2 (3.0)	CH_3CN	80	60	60
6	$KMnO_4$ (3.0)	CH_3CN	80	60	65
7	$KMnO_4$ (2.0)	H_2O	80	60	5
8	$KMnO_4$ (2.0)	1,4-dioxane	80	60	35
9	$KMnO_4$ (2.0)	CH_3OH	80	60	20
10	$KMnO_4$ (2.0)	DMSO	80	60	<5
11	$KMnO_4$ (2.0)	DCE	80	60	60
12	$KMnO_4$ (2.0)	THF	80	60	42
13	$KMnO_4$ (2.0)	CH_3CN	60	60	62
14	$KMnO_4$ (2.0)	CH_3CN	70	60	70
15	**$KMnO_4$ (2.0)**	**CH_3CN**	**90**	**60**	**85**
16	$KMnO_4$ (2.0)	CH_3CN	100	60	80
17	$KMnO_4$ (2.0)	CH_3CN	90	10	25
18[c]	$KMnO_4$ (2.0)	CH_3CN	90	20	40
19	$KMnO_4$ (2.0)	CH_3CN	90	40	65
20	$KMnO_4$ (2.0)	CH_3CN	90	80	79
21	/	CH_3CN	90	60	0

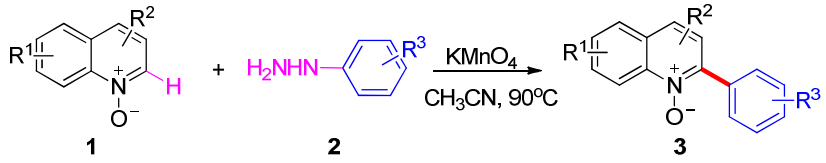
[a] Reaction conditions: quinoline *N*-oxide **1a** (0.3 mmol, 43.5 mg), phenylhydrazine **2a** (0.6 mmol, 64.8 mg), oxidant and solvent (3.0 mL).

[b] Isolated yield.

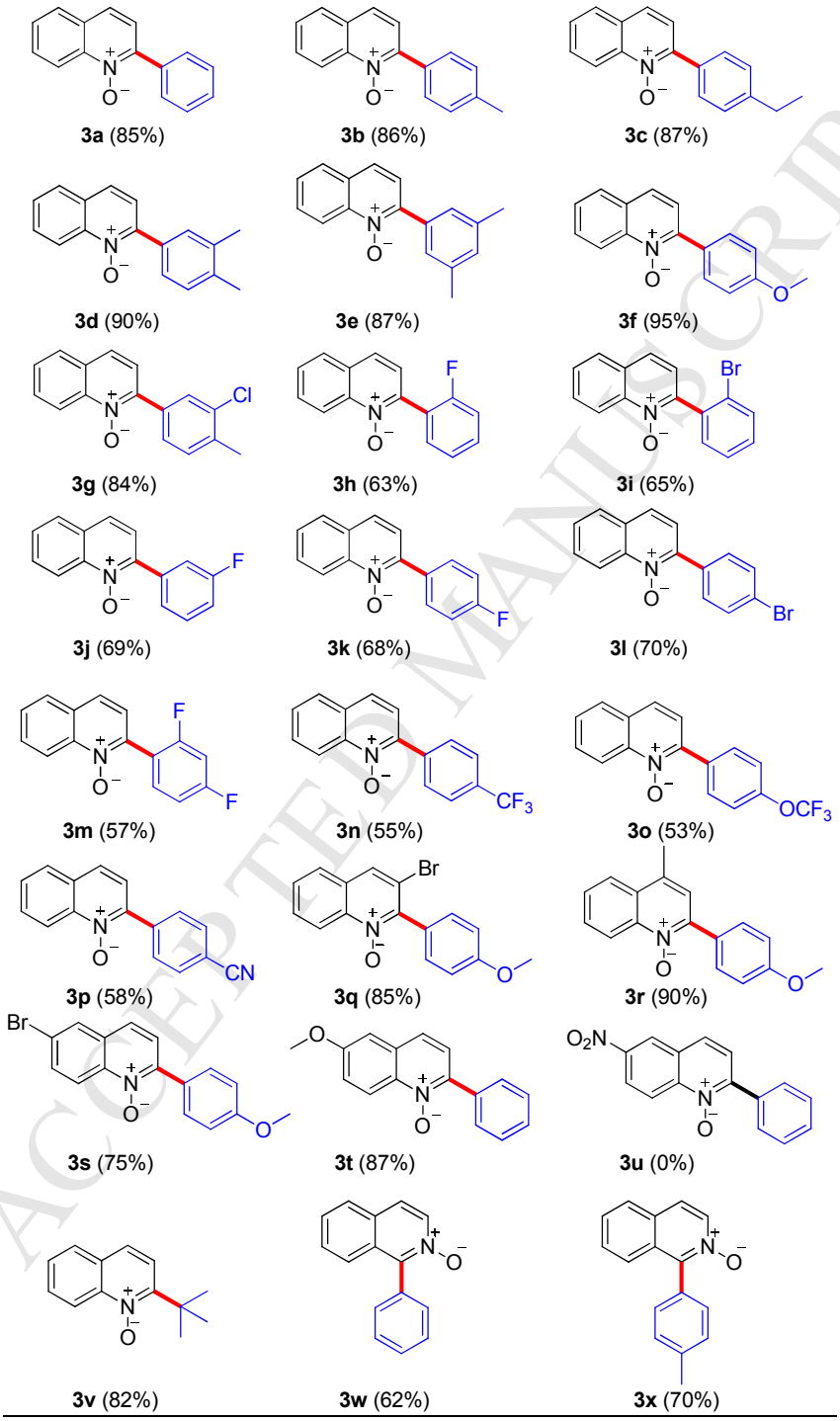
The reaction between quinoline *N*-oxide (**1a**) and phenylhydrazine (**2a**) was examined as a model reaction to optimize the reaction condition (Table 1). Initially, different oxidants were used when the reaction was carried out in CH_3CN at 80 ^oC for 60 mins. The result showed that oxidants *tert*-butyl peroxide (DTBP) and $Mn(OAc)_3$ gave the desired product (**3a**) in low yields (Table 1, entry 3 and 4), and oxidants H_2O_2, *tert*-butyl hydroperoxide (TBHP), MnO_2, and $KMnO_4$ produced **3a** with moderated yields (Table 1, entries 1, 2, 5, and 6). $KMnO_4$ proved to be the most effective oxidant to give **3a** in 65% yield (Table 1, entry 6). The amount of $KMnO_4$ was also investigated (Supporting information, Table S1, entries 1-5). The best yield was 70% when 2.0 eq $KMnO_4$ was used. Subsequently, The ratio of substrates quinoline *N*-oxide and phenylhydrazine was examined, and the ratio 1:1.5 of quinoline *N*-oxide and phenylhydrazine proved to be the best result, providing 75% yield of **3a** (Supporting information, Table S2, entries 1-5). Different solvents including CH_3CN, H_2O, 1,4-dioxane, CH_3OH, DMSO, DCE, and THF were screened (Table S2, entry 3, and Table 1, entries 7-12), CH_3CN was found to be best solvent for this transformation. With the reaction temperature improving from 60 ^oC to 90 ^oC, the product yields dramatically enhanced. However, the yield dropped slightly when the reaction temperature was increased more than 90 ^oC, and the optimal reaction temperature was 90 ^oC (Table 1, entries 13-16). Finally, the reaction time was also examined, and 60 mins could obtain good yield (Table 1, entries 15, 17-20). In the absence of the oxidant $KMnO_4$, the desired product was not obtained (Table 1, entry 21).

With the optimized conditions in hand, the scope of this cross-coupling was undertaken by investigating the reaction between quinoline *N*-oxides (**1**) and arylhydrazine (**2**) (Scheme 2). The reaction of arylhydrazines bearing electron-donating and electron-withdrawing groups with quinoline *N*-oxides processed smoothly and afforded the corresponding products **3a-3p** in moderate to good yields. Moreover, arylhydrazines bearing electron-donating groups could give better yields (84-95%) than those with electron-withdrawing groups (53-68%). We were pleased to observe the formation of the desired C2-arylated products, **3h**, **3i** and **3m**, in reasonable to moderated yields (57-63%). Remarkably, the electronic and steric hindrance effects of coupling partner arylhydrazines have no influence on the success of the coupling reaction. It was noteworthy that arylhydrazine halides were well tolerated, providing handles for further functionalization. Remarkably, all reactions featured a high regioselectivity in that the C2 arylated

Table 2 Synthesis of 2-arylquinoline *N*-oxides from quinoline *N*-oxides and arylhydrazines [a,b]



1 **2** **3**



3a (85%) **3b** (86%) **3c** (87%)

3d (90%) **3e** (87%) **3f** (95%)

3g (84%) **3h** (63%) **3i** (65%)

3j (69%) **3k** (68%) **3l** (70%)

3m (57%) **3n** (55%) **3o** (53%)

3p (58%) **3q** (85%) **3r** (90%)

3s (75%) **3t** (87%) **3u** (0%)

3v (82%) **3w** (62%) **3x** (70%)

[a] Reaction conditions: quinoline *N*-oxide **1** (0.3 mmol), arylhydrazine **2** (0.45 mmol), $KMnO_4$ (0.6 mmol, 94.8 mg) in 3.0 mL CH_3CN solvent, 90 °C for 60 min.

[b] Isolated yield.

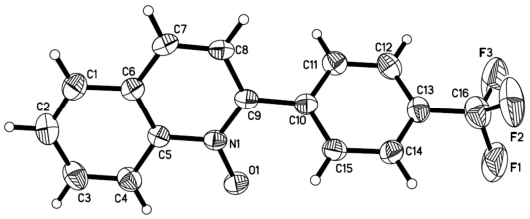
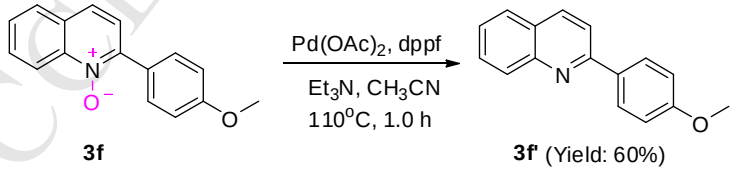


Figure 1 X-ray crystal structure of **3n**

products **3** were exclusively formed. The crystallization of product **3n** from $CHCl_3$ gave a single crystal suitable for X-ray analysis. It illustrates the molecular structure of the substituted 2-arylquinoline *N*-oxide **3n** (Figure 1).

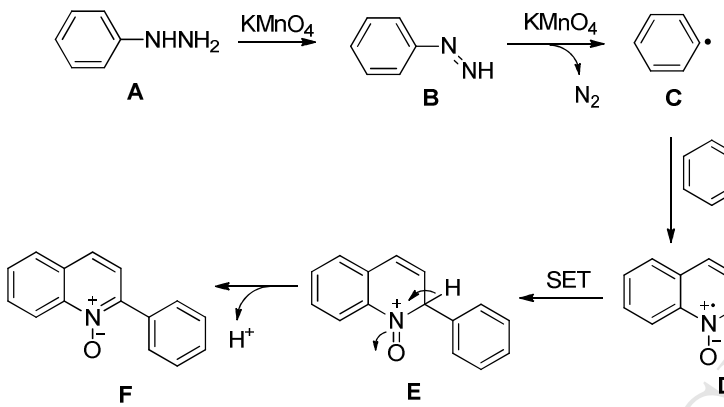
The scope of this methodology was also investigated with respect to quinoline *N*-oxides (Table 2, **3q-3u**). Quinoline *N*-oxides bearing electron-donating groups ($-CH_3$, $-OCH_3$) and electron-withdrawing group (-Br) could react smoothly with arylhydrazines to afford the corresponding products. However, quinoline *N*-oxides possessing a strong electron-withdrawing $-NO_2$ group at the C6 position didn't give the desired product **3u**. Pleasingly, the coupling reaction of 3-bromoquinoline *N*-oxides with 3-methoxyl phenhydrazine could proceed to afford the product **3q** in 85%, which indicated that the steric effect played a weak role in this transformation. Gratifying, aliphatic hydrazine, *t*-butyl hydrazine could also react with quinoline *N*-oxide to obtain 2-*t*-butyl quinoline *N*-oxide **3v**. To further examine the versatility of this methodology, isoquinoline *N*-oxide was employed as a coupling partner. Fortunately, the desired products (**3w** and **3x**) could be produced under the standard condition. Remarkably, the transformations were regioselective, and the ratio of C1-arylated and C3-arylated isoquinoline *N*-oxides were about 5:1.



Scheme 2 The deoxygenation of 2-(4-methoxyphenyl)quinoline *N*-oxide

To further demonstrate the utility of this method, the reduction of 2-arylquinoline *N*-oxides to the parent 2-arylquinolines were also investigated. There has been a considerable amount of research devoted to developing improved procedures for deoxygenation.[15] Herein, we further examined the reduction reaction of 2-arylquinoline *N*-oxide (**3f**) using $Pd(OAc)_2$ as a catalyst and 1,1'-bis(diphosphino)ferrocene (dppf) as ligand, triethylamine used as the base in CH_3CN at 120

°C for 1.0 h under microwave irradiation.[16] The reaction proceeded smoothly and the deoxidized product **3f′** was obtained with 60% yield.



Scheme 3 Proposed reaction mechanism

On the basis of the previous studies[12], a plausible reaction mechanism for this coupling reaction described above is proposed in Scheme 3. The phenylhydrazine **A** is firstly oxidized by $KMnO_4$ to form a phenyldiazene **B**. The diazene **B** is then rapidly converted a phenyl radical **C** by the release of N_2 in the presence of $KMnO_4$. The *N*-oxide moiety increases the electron-density of the electron-deficient pyridine ring system. The phenyl radical **C** can selectively add to C2 position of quinoline *N*-oxide to produce a radical intermediate **D**, allowing the carbocation intermediate **E** to be formed by a single-electron transfer. Finally, the intermediate **E** lose a proton to make the C2 arylated quinoline *N*-oxide **F**.

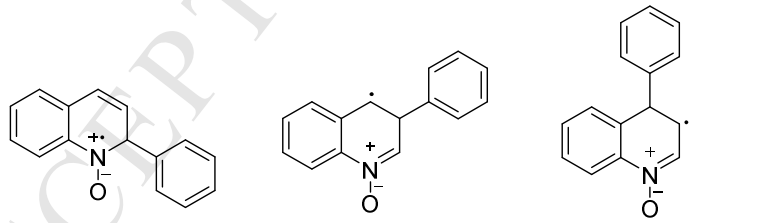
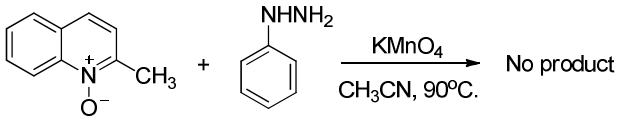


Figure 2 Gibbs energies for different radicals investigated by DFT calculations



Scheme 4 A controlled experiment

The high regioselectivity of the arylation process at C2 *versus* C3 and C4 was further explored with the assistance of DFT calculations. The regioselectivity was explained by examining the

stability of the radical intermediate. When phenyl radical attacks on C2, C3 and C4 of quinoline *N*-oxide, the radicals **D**, **D'**, and **D''** were obtained, respectively. The DFT calculation results showed that the Gibbs energies of the radicals **D**, **D'**, and **D''** were 11.77 kcal/mol, 17.07 kcal/mol, and 13.13 kcal/mol, respectively (Figure 2). The radical **D** presents much lower Gibbs energy for the C2 than the C3 and C4 products. A controlled experiment was investigated. When 2-methyl quinoline *N*-oxide was employed as a substrate to react with phenylhydrazine, the reaction could not proceed and no product was obtained (Scheme 4). Therefore, both DFT calculation and experimental result go in the same direction and indicate a preferred C2 attack.

3. Conclusion

In conclusion, we have disclosed a direct C2-selective C-H arylation of quinoline *N*-oxides with arylhydrazines under mild conditions. The methodology features inexpensive reagents, a broad range of substrates, excellent regioselectivity and functional group tolerance, as well as experimental simplicity.

4. Experimental

4.1 General information

All substrates purchased from *J* & *K* Scientific Ltd. were used without further 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 Bruker Avance 400 MHz spectrometer. Chemical shifts for ^{1}H NMR spectra are recorded in parts per million from tetramethylsilane. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant in Hz and integration. Chemical shifts for ^{13}C NMR spectra were recorded in parts per million from tetramethylsilane. High resolution mass spectra (HR MS) were obtained on Q-TOF instrument using the ESI technique. IR spectra were recorded on 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 2-arylquinoline *N*-oxides (3)

Quinoline *N*-oxides **1** (0.3 mmol), arylhydrazines **2** (0.45 mmol), and $KMnO_4$ (0.6mmol, 94.8 mg) in acetonitrile (3.0 mL) were added to a 25 mL Schlenk tube. The mixture was heated at 90 ^{o}C for 60 mins (monitored by TLC). After completion of the reaction, the

solvent was distilled under vacuum. 10 mL ethylacetate was added to the residuum, and 30 mL saturated sodium chloride solution washed three times. The organic phase was dried over anhydrous $NaSO_4$ and concentrated under vacuum. The crude product was purified by silica gel column chromatography to give the desired products **3** using ethyl acetate/petroleum ether (1:10 to 1:3) as eluant.

*4.2.1. 2-Phenylquinoline 1-oxide (**3a**)*

Colorless solid, mp 145-146 °C (EtOAc) [lit[17] mp 148.5-149.7 °C]. IR (KBr) ν(cm^{-1}): 1462, 1377, 1352, 1302. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.85 (d, J_{H-H} = 8.7 Hz, 1H), 7.96 (d, J_{H-H} = 7.3 Hz, 2H), 7.82 (d, J_{H-H} = 8.1 Hz, 1H), 7.75 (t, J_{H-H} = 7.7 Hz, 1H), 7.70 (d, J_{H-H} = 8.7 Hz, 1H), 7.59 (t, J_{H-H} = 7.4 Hz, 1H), 7.52-7.42 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.9, 142.2, 133.4, 130.5 (CH), 129.6 (CH), 129.5 (CH), 129.4, 128.4 (CH), 128.2 (CH), 128.0 (CH), 125.2 (CH), 123.3 (CH), 120.2 (CH). MS (ESI) m/z: 222.3 $[M + H]^+$ (calcd for $C_{15}H_{12}NO^+$ 222.1).

*4.2.2. 2-(p-Tolyl)quinoline 1-oxide (**3b**)*

Colorless solid, mp 125-126 °C (EtOAc) [lit[17] mp 127-128 °C]. IR (KBr) ν(cm^{-1}): 2954, 2918, 1502, 1456. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.85 (d, J_{H-H} = 5.3 Hz, 1H), 7.90 (d, J_{H-H} = 7.6 Hz, 2H), 7.83 (d, J_{H-H} = 8.0 Hz, 1H), 7.76 (t, J_{H-H} = 5.7 Hz, 1H), 7.70 (d, J_{H-H} = 7.9 Hz, 1H), 7.61 (t, J_{H-H} = 7.4 Hz, 1H), 7.50 (d, J_{H-H} = 8.5 Hz, 1H), 7.32 (d, J_{H-H} = 7.2 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.2, 142.4, 139.7, 130.5 (CH), 130.4, 129.5 (CH), 129.4, 128.9 (CH), 128.2 (CH), 127.9 (CH), 125.2 (CH), 123.2 (CH), 120.2 (CH), 21.4 (CH_3). MS (ESI) m/z: 236.3 $[M + H]^+$ (calcd for $C_{16}H_{14}NO^+$ 236.1).

*4.2.3. 2-(4-Ethylphenyl)quinoline 1-oxide (**3c**)*

Light red solid, mp 108-109 °C (EtOAc). IR (KBr) ν(cm^{-1}): 3124, 3082, 1601, 1450. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.86 (d, J_{H-H} = 8.8 Hz, 1H), 7.92 (d, J_{H-H} = 8.2 Hz, 2H), 7.85 (d, J_{H-H} = 8.1 Hz, 1H), 7.78 (td, J_{H-H} = 7.0 Hz, J_{H-H} = 1.1 Hz, 1H), 7.73 (d, J_{H-H} = 8.7 Hz, 1H), 7.63 (td, J_{H-H} = 7.8 Hz, J_{H-H} = 0.7 Hz, 1H), 7.51 (d, J_{H-H} = 8.7 Hz, 1H), 7.35 (d, J_{H-H} = 8.8 Hz, 2H), 2.73 (q, J_{H-H} = 7.6 Hz, 2H), 1.29 (t, J_{H-H} = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.0, 145.1, 142.3, 130.7, 130.5 (CH), 129.6 (CH), 129.4, 128.2 (CH), 127.9 (CH), 127.8 (CH), 125.1 (CH), 123.3 (CH), 120.3 (CH), 28.8 (CH_2), 15.4 (CH_3). HR MS (ESI) m/z: 250.1224 $[M + H]^+$ (calcd for $C_{17}H_{16}NO^+$ 250.1226).

*4.2.4. 2-(3,4-Dimethylphenyl)quinoline 1-oxide (**3d**)*

Yellow solid, mp 144-145 °C (EtOAc). IR (KBr) ν(cm^{-1}): 3122, 2918, 1558, 1496, 1400. ^{1}H NMR (400

MHz, $CDCl_3$) δ: 8.85 (d, J_{H-H} = 8.6 Hz, 1H), 7.81-7.80 (m, 2H), 7.76-7.64 (m, 3H), 7.59 (t, J_{H-H} = 7.4 Hz, 1H), 7.47 (d, J_{H-H} = 8.6 Hz, 1H), 7.26 (d, J_{H-H} = 7.4 Hz, 1H), 2.33 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.3, 142.2, 138.4, 136.4, 130.9, 130.5 (CH), 130.4 (CH), 129.6 (CH), 129.4, 128.2 (CH), 127.9 (CH), 127.0 (CH), 125.3 (CH), 123.3 (CH), 120.2 (CH), 19.9 (CH_3), 19.8 (CH_3). HR MS (ESI) m/z: 250.1228 $[M + H]^+$ (calcd for $C_{17}H_{16}NO^+$ 250.1226).

*4.2.5. 2-(3,5-Dimethylphenyl)quinoline 1-oxide (**3e**)*

Yellow solid, mp 91-92 °C (EtOAc) [lit[17] mp 94-95 °C]. IR (KBr) ν(cm^{-1}): 3116, 3066, 1599, 1560, 1400. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.85 (d, J_{H-H} = 8.8 Hz, 1H), 8.02 (d, J_{H-H} = 8.8 Hz, 2H), 7.82 (d, J_{H-H} = 8.0 Hz, 1H), 7.75 (td, J_{H-H} = 7.1 Hz, J_{H-H} = 1.0 Hz, 1H), 7.70 (d, J_{H-H} = 8.7 Hz, 1H), 7.60 (td, J_{H-H} = 7.8 Hz, J_{H-H} = 0.7 Hz, 1H), 7.55 (bs, 2H), 7.45 (d, J_{H-H} = 8.7 Hz, 1H), 7.09 (s, 1H), 2.39 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.4, 142.2, 137.8, 133.4, 131.2 (CH), 130.4 (CH), 129.5, 128.3 (CH), 127.9 (CH), 127.2 (CH), 125.1 (CH), 123.4 (CH), 120.2 (CH), 21.4 (CH_3). MS (ESI) m/z: 250.3 $[M + H]^+$ (calcd for $C_{17}H_{16}NO^+$ 250.1).

*4.2.6. 2-(4-Methoxyphenyl)quinoline 1-oxide (**3f**)*

Yellow solid, mp 105-106 °C (EtOAc) [lit[17] mp 124.9-126.0 °C]. IR (KBr) ν(cm^{-1}): 3122, 2931, 1604, 1560, 1500, 1400. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.84 (d, J_{H-H} = 8.7 Hz, 1H), 8.02 (d, J_{H-H} = 8.8 Hz, 2H), 7.82 (d, J_{H-H} = 8.0 Hz, 1H), 7.75 (t, J_{H-H} = 7.4 Hz, 1H), 7.70 (d, J_{H-H} = 8.7 Hz, 1H), 7.59 (t, J_{H-H} = 7.7 Hz, 1H), 7.49 (d, J_{H-H} = 8.7 Hz, 1H), 7.03 (d, J_{H-H} = 8.8 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.5, 144.6, 142.3, 131.2 (CH), 130.4 (CH), 129.2, 128.1 (CH), 127.9 (CH), 125.6, 125.2 (CH), 123.0 (CH), 120.1 (CH), 113.6 (CH), 55.3 (CH_3). MS (ESI) m/z: 252.3 $[M + H]^+$ (calcd for $C_{16}H_{14}NO_2^+$ 252.1).

*4.2.7. 2-(3-Chloro-4-methylphenyl)quinoline 1-oxide (**3g**)*

Light yellow solid, mp 144-145 °C (EtOAc). IR (KBr) ν(cm^{-1}): 3120, 2934, 1560, 1400. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.82 (d, J_{H-H} = 8.8 Hz, 1H), 8.03 (d, J_{H-H} = 1.2 Hz, 1H), 7.84 (d, J_{H-H} = 8.1 Hz, 1H), 7.79-7.71 (m, 3H), 7.62 (t, J_{H-H} = 7.3 Hz, 1H), 7.46 (d, J_{H-H} = 8.7 Hz, 1H), 7.35 (d, J_{H-H} = 8.0 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.6, 142.2, 137.7, 134.3, 132.4, 130.7 (CH), 130.6 (CH), 130.0 (CH), 129.5, 128.5 (CH), 128.0 (CH), 127.7 (CH), 125.3 (CH), 122.9 (CH), 120.2 (CH), 20.1 (CH_3). HR MS (ESI) m/z: 270.0676 $[M + H]^+$ (calcd for $C_{16}H_{13}ClNO^+$ 270.0680).

*4.2.8. 2-(2-Fluorophenyl)quinoline 1-oxide (**3h**)*

Yellow solid, mp 140-141 °C (EtOAc). IR (KBr) ν(cm^{-1}): 1601, 1454. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.85 (d, J_{H-H} = 8.8 Hz, 1H), 7.87 (d, J_{H-H} = 8.1 Hz, 1H), 7.78-7.62 (m, 4H), 7.48-7.42 (m, 2H),

7.49-7.44 (m, 2H), 7.28 (t, J_{H-H} = 7.1 Hz, 1H), 7.22 (t, J_{H-H} = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.4, 158.9, 142.1, 141.3, 131.4 (d, J_{F-C} = 8.6 Hz, CH), 131.2 (d, J_{F-C} = 2.8 Hz, CH), 130.5 (CH), 130.0, 128.4 (d, J_{F-C} = 66.6 Hz, CH), 124.7 (CH), 124.1 (d, J_{F-C} = 3.5 Hz, CH), 123.8 (d, J_{F-C} = 1.7 Hz, CH), 121.6 (d, J_{F-C} = 14.1 Hz), 120.2 (CH), 116.0 (d, J_{F-C} = 21.3 Hz, CH). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -111.0. HR MS (ESI) m/z: 240.0816 $[M + H]^+$ (calcd for $C_{15}H_{11}FNO^+$ 240.0819).

*4.2.9. 2-(2-Bromophenyl)quinoline 1-oxide (**3i**)*

Yellow solid, mp 164-165 °C (EtOAc). IR (KBr) ν(cm^{-1}): 1552, 1502, 1336, 808. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.83 (d, J_{H-H} = 8.7 Hz, 1H), 7.91 (d, J_{H-H} = 1.1 Hz, 1H), 7.81-7.72 (m, 3H), 7.68 (t, J_{H-H} = 7.3 Hz, 1H), 7.49-7.44 (m, 2H), 7.38-7.33 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.2, 142.0, 135.3, 132.9 (CH), 131.0 (CH), 130.6 (CH), 130.5 (CH), 130.1, 128.7 (CH), 128.1 (CH), 127.5 (CH), 124.6 (CH), 123.5 (CH), 123.3, 120.3 (CH), 21.4 (CH_3). HR MS (ESI) m/z: 300.0015 $[M + H]^+$ (calcd for $C_{15}H_{11}BrNO^+$ 300.0019).

*4.2.10. 2-(3-Fluorophenyl)quinoline 1-oxide (**3j**)*

Light yellow solid, mp 143-144 °C (EtOAc). IR (KBr) ν(cm^{-1}): 1589, 1452, 1342, 1255. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.85 (d, J_{H-H} = 8.8 Hz, 1H), 7.88 (d, J_{H-H} = 8.1 Hz, 1H), 7.82-7.75 (m, 3H), 7.71 (d, J_{H-H} = 2.0 Hz, 1H), 7.66 (t, J_{H-H} = 7.4 Hz, 1H), 7.51-7.46 (m, 2H), 7.18 (td, J_{H-H} = 8.4 Hz, J_{H-H} = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.6, 161.2, 143.7, 142.3, 135.3 (d, J_{F-C} = 8.3 Hz), 130.7 (CH), 129.8 (CH), 129.7 (d, J_{F-C} = 22.8 Hz), 128.7 (CH), 128.0 (CH), 125.3 (d, J_{F-C} = 3.3 Hz, CH), 123.0 (CH), 120.2 (CH), 116.8 (d, J_{F-C} = 21.0 Hz, CH), 116.5 (d, J_{F-C} = 18.7 Hz, CH). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -112.6. HR MS (ESI) m/z: 240.0823 $[M + H]^+$ (calcd for $C_{15}H_{11}FNO^+$ 240.0819).

*4.2.11. 2-(4-Fluorophenyl)quinoline 1-oxide (**3k**)*

Light yellow solid, mp 157-159 °C (EtOAc) [lit[18] mp 162-164 °C]. IR (KBr) ν(cm^{-1}): 1603, 1564, 1498, 1458, 1321, 1230, 814. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.83 (d, J_{H-H} = 8.8 Hz, 1H), 8.01 (dd, J_{H-H} = 8.8 Hz, J_{F-H} = 5.4 Hz, 2H), 7.85 (d, J_{H-H} = 8.1 Hz, 1H), 7.80-7.73 (m, 2H), 7.65 (td, J_{H-H} = 7.9 Hz, J_{H-H} = 0.8 Hz, 1H), 7.47 (d, J_{H-H} = 8.7 Hz, 1H), 7.21 (t, J_{H-H} = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.4, 161.9, 143.9, 142.2, 131.8 (d, J_{F-C} = 8.3 Hz, CH), 130.6 (CH), 129.5, 129.4 (d, J_{F-C} = 3.5 Hz), 128.5 (CH), 128.0 (CH), 125.3 (CH), 123.0 (CH), 120.1 (CH), 115.3 (d, J_{F-C} = 21.4 Hz, CH). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -111.0. MS (ESI) m/z: 240.3 $[M + H]^+$ (calcd for $C_{15}H_{11}FNO^+$ 240.0).

*4.2.12. 2-(4-Bromophenyl)quinoline 1-oxide (**3l**)*

Brown solid, mp 183-184 °C (EtOAc). IR (KBr) ν(cm^{-1}): 1552, 1502, 1336, 808. ^{1}H NMR (400 MHz,

$CDCl_3$) δ: 8.83 (d, J_{H-H} = 8.6 Hz, 1H), 7.89-7.86 (m, 3H), 7.81-7.74 (m, 2H), 7.67-7.64 (m, 3H), 7.48 (d, J_{H-H} = 8.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.9, 142.3, 132.2, 131.5 (CH), 131.2 (CH), 130.7 (CH), 129.6, 128.6 (CH), 128.0 (CH), 125.4 (CH), 123.9, 122.8 (CH), 120.2 (CH). HR MS (ESI) m/z: 300.0023 $[M + H]^+$ (calcd for $C_{15}H_{11}BrNO^+$ 300.0019).

*4.2.13. 2-(2,4-Difluorophenyl)quinoline 1-oxide (**3m**)*

Colorless solid, mp 138-139 °C (EtOAc). IR (KBr) ν(cm^{-1}): 1605, 1564, 1450, 1456, 1230, 815. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.82 (d, J_{H-H} = 8.8 Hz, 1H), 7.90 (d, J_{H-H} = 8.0 Hz, 1H), 7.82-7.66 (m, 4H), 7.43 (d, J_{H-H} = 8.6 Hz, 1H), 7.06-6.97 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.8 (dd, *J* = 255.6 Hz, *J* = 10.5 Hz), 163.8 (d, *J* = 240.3 Hz), 160.6 (dd, *J* = 254.2 Hz, *J* = 11.5 Hz), 141.2 (d, *J* = 175.6 Hz), 132.4 (dd, *J* = 10.3 Hz, *J* = 4.5 Hz, CH), 130.7 (CH), 130.0, 128.8 (CH), 128.0 (CH), 124.9 (CH), 123.7 (d, *J* = 2.2 Hz, CH), 120.2 (CH), 117.8 (dd, *J* = 14.9 Hz, *J* = 5.0 Hz), 111.6 (dd, *J* = 20.9 Hz, *J* = 2.7 Hz, CH), 104.6 (t, *J* = 25.8 Hz, CH). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -106.8 (d, J_{F-F} = 2.5 Hz), -107.0 (d, J_{F-F} = 2.5 Hz). HR MS (ESI) m/z: 258.0728 $[M + H]^+$ (calcd for $C_{15}H_{10}F_2NO^+$ 258.0725).

*4.2.14. 2-(4-(Trifluoromethyl)phenyl)quinoline 1-oxide (**3n**)*

Colorless solid, mp 187-188 °C (EtOAc) [lit[19] mp 197-199 °C]. IR (KBr) ν(cm^{-1}): 1562, 1334, 1254, 1120, 816. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.84 (d, J_{H-H} = 8.8 Hz, 1H), 8.09 (d, J_{H-H} = 8.2 Hz, 2H), 7.89 (d, J_{H-H} = 8.1 Hz, 1H), 7.83-7.77 (m, 4H), 7.68 (t, J_{H-H} = 7.4 Hz, 1H), 7.50 (d, J_{H-H} = 8.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.6 (d, J_{F-C} = 2.4 Hz), 142.2, 136.9, 131.3 (d, J_{F-C} = 32.5 Hz), 130.9 (CH), 130.0 (CH), 129.8, 128.9 (CH), 128.1 (CH), 125.5 (CH), 125.3 (q, J_{F-C} = 3.8 Hz), 122.8 (CH), 122.5, 120.2 (CH). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -62.8. MS (ESI) m/z: 290.3 $[M + H]^+$ (calcd for $C_{16}H_{11}F_3NO^+$ 290.0).

*4.2.15. 2-(4-(Trifluoromethoxy)phenyl)quinoline 1-oxide (**3o**)*

Light yellow solid, mp 149-150 °C (EtOAc). IR (KBr) ν(cm^{-1}): 1560, 1454. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.84 (d, J_{H-H} = 8.8 Hz, 1H), 8.04 (d, J_{H-H} = 8.8 Hz, 2H), 7.87 (d, J_{H-H} = 8.1 Hz, 1H), 7.82-7.76 (m, 2H), 7.65 (t, J_{H-H} = 7.3 Hz, 1H), 7.49 (d, J_{H-H} = 8.7 Hz, 1H), 7.36 (d, J_{H-H} = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.7 (d, J_{F-C} = 1.7 Hz), 143.6, 142.2, 131.9, 131.3 (CH), 130.8 (CH), 129.6, 128.7 (CH), 128.0 (CH), 125.5 (CH), 122.9 (CH), 121.7, 120.6 (CH), 120.2 (CH). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -57.6. HR MS (ESI) m/z: 306.0739 $[M + H]^+$ (calcd for $C_{16}H_{11}F_3NO_2^+$ 306.0736).

*4.2.16. 2-(4-cyanophenyl)quinoline 1-oxide (**3p**)*

Colorless solid, mp 205-206 °C (EtOAc) [lit[19] mp 206-208 °C]. IR (KBr) ν(cm^{-1}): 2937, 2225, 1312,

817. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.79 (d, J_{H-H} = 8.8 Hz, 1H), 8.08 (d, J_{H-H} = 8.4 Hz, 2H), 7.88 (d, J_{H-H} = 8.1 Hz, 1H), 7.79-7.75 (m, 4H), 7.66 (t, J_{H-H} = 7.2 Hz, 1H), 7.46 (d, J_{H-H} = 8.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.9, 142.2, 137.8, 132.0 (CH), 131.0 (CH), 130.3 (CH), 129.1 (CH), 128.1 (CH), 125.6 (CH), 122.6 (CH), 120.1 (CH), 118.5, 112.9 (CH). MS (ESI) m/z: 247.2 $[M + H]^+$ (calcd for $C_{16}H_{11}N_2O^+$ 247.0).

*4.2.17. 3-bromo-2-(4-methoxyphenyl)quinoline 1-oxide (**3q**)*

Yellow solid, mp 172-173 °C (EtOAc). IR (KBr) ν(cm^{-1}): 3126, 1608, 1518, 1400. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.69 (d, J_{H-H} = 8.8 Hz, 1H), 8.07 (s, 1H), 7.80-7.74 (m, 2H), 7.65 (t, J_{H-H} = 7.2 Hz, 1H), 7.44 (d, J_{H-H} = 8.6 Hz, 1H), 7.06 (d, J_{H-H} = 8.6 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.3, 146.2, 141.4, 131.0 (CH), 130.6 (CH), 129.4 (CH), 129.1, 128.4 (CH), 127.1 (CH), 125.3, 120.5 (CH), 117.7, 114.0 (CH), 55.3 (CH_3). HR MS (ESI) m/z: 330.0126 $[M + H]^+$ (calcd for $C_{16}H_{13}BrNO_2^+$ 330.0124).

*4.2.18. 2-(4-Methoxyphenyl)-4-methylquinoline 1-oxide (**3r**)*

Colorless solid, mp 73-74 °C (EtOAc). IR (KBr) ν(cm^{-1}): 2927, 2831, 1599, 1502, 1171. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.15-8.11 (m, 3H), 7.96 (d, J_{H-H} = 8.3 Hz, 1H), 7.71-7.66 (m, 2H), 7.50 (td, J_{H-H} = 8.1 Hz, J_{H-H} = 1.1 Hz, 1H), 7.03 (d, J_{H-H} = 8.8 Hz, 2H), 3.87 (s, 3H), 2.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.7, 156.6, 148.1, 144.6, 132.3, 130.0 (CH), 129.2 (CH), 128.8 (CH), 127.0, 125.6 (CH), 123.6 (CH), 119.3 (CH), 114.1 (CH), 55.4 (CH_3), 19.0 (CH_3). HR MS (ESI) m/z: 266.1174 $[M + H]^+$ (calcd for $C_{17}H_{16}NO_2^+$ 266.1176).

*4.2.19. 6-Bromo-2-(4-methoxyphenyl)quinoline 1-oxide (**3s**)*

Yellow solid, mp 182-183 °C (EtOAc). IR (KBr) ν(cm^{-1}): 3128, 1609, 1520, 1405, 1215. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.72 (d, J_{H-H} = 9.2 Hz, 1H), 8.02-8.00 (m, 3H), 7.82 (dd, J_{H-H} = 9.2 Hz, J_{H-H} = 1.9 Hz, 1H), 7.62 (d, J_{H-H} = 8.8 Hz, 1H), 7.54 (d, J_{H-H} = 8.8 Hz, 1H), 7.04 (d, J_{H-H} = 8.8 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.7, 144.9, 141.2, 133.7 (CH), 131.2 (CH), 130.3, 129.8 (CH), 125.1, 124.3 (CH), 123.9 (CH), 122.4 (CH), 122.2, 113.7 (CH), 55.4 (CH_3). HR MS (ESI) m/z: 330.0126 $[M + H]^+$ (calcd for $C_{16}H_{13}BrNO_2^+$ 330.0124).

*4.2.20. 6-Methoxy-2-phenylquinoline 1-oxide (**3t**)*

Light yellow solid, mp 168-169 °C (chloroform) [lit[17] mp 176-177 °C]. IR (KBr) ν(cm^{-1}): 2954, 2916, 1624, 1562, 1456, 1196. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.75 (d, J_{H-H} = 9.5 Hz, 1H), 7.93 (d, J_{H-H} = 7.1 Hz, 2H), 7.61 (d, J_{H-H} = 8.7 Hz, 1H), 7.49 (t, J_{H-H} = 7.0 Hz, 2H), 7.45-7.42 (m, 2H), 7.38 (dd, J_{H-H} = 9.5 Hz, J_{H-H} = 2.6 Hz, 1H), 7.09 (d, J_{H-H} = 2.6 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.2,

143.2, 137.8, 133.5, 130.9, 129.5 (CH), 129.2 (CH), 128.2 (CH), 124.3 (CH), 123.8 (CH), 122.5 (CH), 121.9 (CH), 105.8 (CH), 55.7 (CH_3). MS (ESI) m/z: 252.2 $[M + H]^+$ (calcd for $C_{16}H_{14}NO_2^+$ 252.1).

*4.2.21. 2-(tert-butyl)quinoline 1-oxide (**3v**)*

Pale yellow solid, mp 95-96 °C (EtOAc) [lit[20] mp 91-92 °C]. IR (KBr) ν(cm^{-1}): 3122, 2962, 1560, 1506, 1398, 1334, 1248, 1082. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.78 (d, J_{H-H} = 8.8 Hz, 1H), 7.78 (d, J_{H-H} = 8.0 Hz, 1H), 7.71 (td, J_{H-H} = 8.3 Hz, J_{H-H} = 1.0 Hz, 1H), 7.64 (d, J_{H-H} = 8.9 Hz, 1H), 7.56 (t, J_{H-H} = 7.2 Hz, 1H), 7.44 (d, J_{H-H} = 8.9 Hz, 1H), 1.61 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.2, 143.1, 130.3 (CH), 129.1, 127.8 (CH), 127.7 (CH), 125.1 (CH), 120.0 (CH), 119.8 (CH), 36.7, 26.9 (CH_3). MS (ESI) m/z: 202.3 $[M + H]^+$ (calcd for $C_{13}H_{16}NO^+$ 202.1).

*4.2.22. 1-phenylisoquinoline-oxide (**3w**)*

Yellow solid, mp 141-142 °C (EtOAc) [lit[21] mp 141-143 °C]. IR (KBr) ν(cm^{-1}): 3102, 1547, 1504, 1378, 1325, 1238. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.29 (d, J_{H-H} = 7.2 Hz, 1H), 7.82 (d, J_{H-H} = 8.0 Hz, 1H), 7.69 (d, J_{H-H} = 7.2 Hz, 1H), 7.61-7.45 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.2, 137.3 (CH), 130.8, 130.1 (CH), 129.5, 129.4 (CH), 129.2, 129.1 (CH), 128.7 (CH), 128.4 (CH), 126.8 (CH), 125.7 (CH), 123.4 (CH). MS (ESI) m/z: 202.2 $[M + H]^+$ (calcd for $C_{15}H_{12}NO^+$ 222.0).

*4.2.23. 1-(p-tolyl)isoquinoline 2-oxide (**3x**)*

Yellow solid, mp 165-166 °C (EtOAc) [lit[8a] mp 166-167 °C]. IR (KBr) ν(cm^{-1}): 3057, 1620, 1550, 1498, 817. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.28 (d, J_{H-H} = 7.2 Hz, 1H), 7.80 (d, J_{H-H} = 8.0 Hz, 1H), 7.66 (d, J_{H-H} = 7.2 Hz, 1H), 7.57-7.53 (m, 1H), 7.51-7.48 (m, 2H), 7.43-7.38 (m, 4H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.4, 139.4, 137.3 (CH), 130.0 (CH), 129.6, 129.5 (CH), 129.2, 129.0 (CH), 128.3 (CH), 127.8, 126.8 (CH), 125.9 (CH), 123.2 (CH), 21.5 (CH_3). MS (ESI) m/z: 236.3 $[M + H]^+$ (calcd for $C_{16}H_{14}NO^+$ 236.1).

4.3 The procedure for the deoxygenation of 2-(4-methoxyphenyl)quinoline *N*-oxide

2-arylquinoline *N*-oxide **3f** (0.2 mmol, 50.2 mg), $Pd(OAc)_2$ (5 .0 mmol%, 3.2 mg), and dppf (5.0 mmol%, 8.0 mg) were placed in a 5.0 mL microwave tube, then dry CH_3CN (3.0 mL) and Et_3N (0.6 mmol, 60.6 mg) were added. The reaction mixture was heated at 120 °C by microwave irradiation for 1.0 h. The solvent was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to give the desired products **3f'** using ethyl acetate/petroleum ether (1:8) as eluant.

*2-(4-Methoxyphenyl)quinoline (**3f'**)*

Yellow crystal, mp 113-114 ^{o}C (from EtOAc; lib.[22] 118-119 ^{o}C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.17 (d, J_{H-H} = 8.7 Hz, 1H), 8.13 (d, J_{H-H} = 8.8 Hz, 2H), 7.83 (d, J_{H-H} = 8.6 Hz, 1H), 7.80 (d, J_{H-H} = 8.2 Hz, 1H), 7.71 (td, J_{H-H} = 8.3 Hz, J_{H-H} = 1.3 Hz, 1H), 7.49 (td, J_{H-H} = 8.0 Hz, J_{H-H} = 1.0 Hz, 1H), 7.04 (d, J_{H-H} = 8.6 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.8, 156.9, 148.2, 136.6 (CH), 132.2, 129.5 (CH), 129.4 (CH), 128.9 (CH), 127.4 (CH), 126.9, 125.9 (CH), 118.5 (CH), 114.2 (CH), 55.4 (CH_3). IR (KBr) ν(cm^{-1}): 2956, 1655, 1597, 1498. HR MS (ESI) m/z: 236.1074 $[M + H]^+$ (calcd for $C_{16}H_{14}NO^+$ 236.1070).

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