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FULL PAPER

Iodine/TBHP-Promoted One-Pot Deoxygenation and Direct *C2*-Sulfonylation of Quinoline *N*-Oxides with Sodium Sulfinates: Facile and Regioselective Synthesis of 2-Sulfonyl Quinolines

Ladawan Sumunnee,[a,b] Chonchanok Buathongjan,[a] Chaleena Pimpasri,[a] and Sirilata Yotphan*[a,b]

Dedication ((optional))

Keywords: Iodine / Quinoline *N*-Oxide / Sodium Sulfinate / Sulfonylation

Abstract: A highly efficient iodine/TBHP-mediated one-pot deoxygenative and regioselective *C2*-sulfonylation of quinoline *N*-oxides with sodium sulfinate salts has been developed. This metal, base and phosphorus-free protocol employs readily accessible and easy to handle reagents, and can be conveniently carried out at room temperature under mild conditions, providing an alternative access to a series of *C2* sulfonyl quinolines and other related heteroaryl sulfone products in moderate to excellence yields within a short reaction time.

Introduction

N-heteroaromatic compounds, particularly pyridine and quinoline derivatives, play important roles in synthesis, catalysis, material, agricultural, industrial, medicinal and pharmaceutical chemistry.[1] Pyridine moieties are an essential component in a number of drugs, pharmaceutical actives, and agrochemical products. They are also found in a variety of important naturally occurring compounds such as niacin, pyridoxine, NADP/NADPH and many alkaloids.[2] While pyridine compounds are employed widely in various applications, the related quinoline derivatives have becoming increasingly utilized in agricultural, industrial and pharmaceutical chemistry.[3] For instant, nalidixic acid is an effective antibiotic for a treatment against both gram positive and gram negative bacteria.[4] In addition, quinine, a naturally occurring substituted quinoline derivative, has been extensively used for the treatment of malaria.[5] This quinine compound is readily detoxified in the body by oxidation process to the 2-hydroxy derivative leading to a dramatic decrease in therapeutic activity.[6] Therefore, significant contributions have been focused on introducing functional groups into the 2-position of quinoline to prevent the detoxification process. Among these groups, sulfone, a crucial class of scaffold in natural products, biologically and pharmaceutically active compounds, has been considered as a good synthetic option. The quinoline sulfone compounds are known to exhibit antibacterial and antiproliferative activities.[7]

In the last decade, many methods for sulfonylation of quinolines have been developed. Traditionally, quinoline sulfones can be synthesized by nucleophilic substitution of heteroaromatic halides with thiol to form thiolether, followed by oxidation to the corresponding sulfone (Scheme 1a).[8] Another common method to construct these sulfones is the transition metal-catalyzed arylation of sulfinate salts by heteroaromatic halides (Scheme 1b).[9] In 2013, Wu and Cui reported the copper-catalyzed direct C−H activation and sulfonylation of quinoline *N*-oxides and pyridine *N*-oxides using sulfonyl chlorides as sulfonylating reagent. However, a harsh phosphorus reagent (PCl_3) was required for further reduction of the *N*-oxides to the corresponding sulfonyl quinoline or pyridine products (Scheme 1c).[10] In 2015, Li developed the synthesis of 2-sulfonyl quinolines from quinoline *N*-oxides and sulfonyl chlorides under mild conditions. Nonetheless, stoichiometric amount of toxic H-phosphonate was necessary for the successful one-pot sulfonylation and reduction processes (Scheme 1d).[11] In addition, Han and Pan developed the synthesis of quinoline sulfone compounds via a copper-catalyzed deoxygenative *C2*-sulfonylation of *N*-oxides with sodium sulfinates using potassium persulfate ($K_2S_2O_8$) additive to promote the C−S bond formation and the N−O bond cleavage in one-pot transformation (Scheme 1e).[12] Recently, He group and Xiang group independently reported the synthesis of 2-sulfonyl quinolines *via* iodine or iodide-induced *C2*-sulfonylation of quinoline *N*-oxides with sulfonyl hydrazides at 100 °C (Scheme 1f).[13],[14]

Our group has been interested in developing a metal-free approach to synthesize biologically active nitrogen-containing compounds and *N*-heterocycles.[15] We recently explored the compatibility of sulfinate salts as a readily available, bench-stable, non-hygroscopic, easy to handle, and versatile sulfonyl source in the iodine-catalyzed sulfonylation reaction.[15b],[16] A combination of iodine and environmentally benign peroxides such as *tert*-butyl hydroperoxide (TBHP) or hydrogen peroxide (H_2O_2) under mild operating conditions can lead to broadening of the reaction scope, along with a better functional group tolerance. With our continuous efforts toward the development of a metal-free synthetic option, herein, we wish to report a facile regioselective synthesis of *C2*-sulfonyl quinolines and other related *N*-heterocycles *via* I_2/ TBHP-mediated one-pot deoxygenation and direct sulfonylation of quinoline *N*-oxide substrates using sodium sulfinates as a stable, odourless and easy to handle sulfonyl

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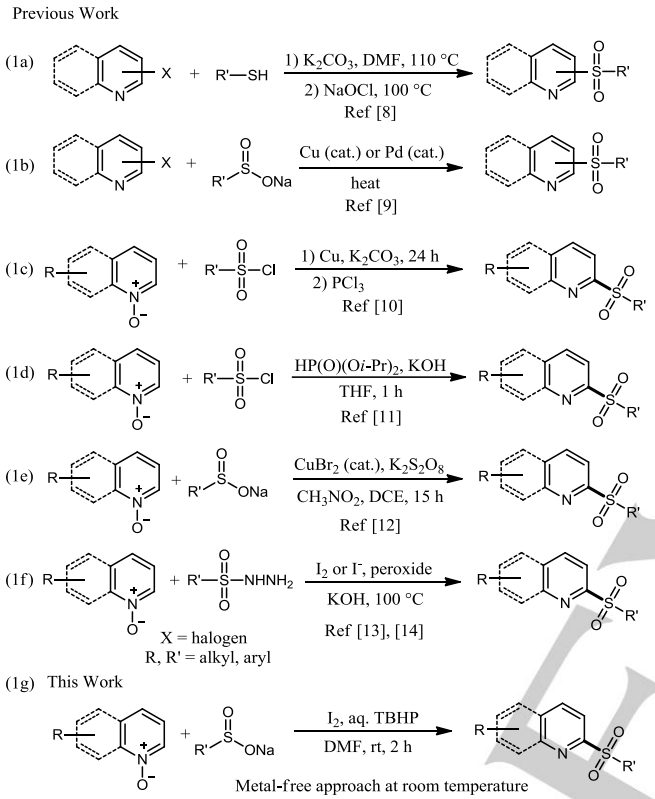
source (Scheme 1g). Our present method is metal, base, and phosphorus-free, features a simple experimental procedure, can be conveniently conducted at room temperature under mild conditions (which is in a sharp contrast to He's and Xiang's sulfonylation methods using sulfonyl hydrazide substrates) with a broad scope of substrates, and offers a useful synthetic alternative to access a number of *C2*-sulfonyl quinolines and other heteroaryl sulfone products in reasonable to excellent yields



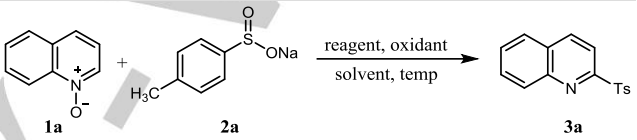
within a short reaction time.

Scheme 1. Synthetic Approaches for *C2*-Sulfonyl Quinolines.

Results and Discussion

To evaluate the feasibility of using sulfinate salts as sulfonyl precursors in a metal-free one-pot deoxygenative and regioselective sulfonylation of heteroaromatic *N*-oxide substrates, we initiated the studies by examining a reaction between quinoline *N*-oxide (**1a**) and sodium *p*-toluene sulfinate (**2a**) under various conditions and selected results are summarized in Table 1.[17] When a reaction of *N*-oxide **1a** and sodium sulfinate salt **2a** was carried out in the presence of I_2 (1.1 equiv.) in combination with aqueous *tert*-butyl hydroperoxide (aq. TBHP; 3 equiv.) using CH_3CN as a solvent at room temperature, the *C2*-sulfonyl quinoline **3a** could be obtained in a promising 53% yield (Table 1, entry 1). Screening of solvents revealed that DMF is the optimal solvent, in which the desired sulfone product **3a** can be accomplished in very high quantity (82% isolated yield) and the one-pot reaction was essentially complete after 2 hours (entry 8).[18] Other polar and non-polar solvents are less effective (entries 1–7). Employing H_2O_2 as the oxidant gave slightly lower yield of product (70%, entry 9). However, other oxidants including di-*tert*-butyl hydroperoxide (DTBP; entry 10) led to a significant decrease in yield or no reactions. The combinations of TBHP with other forms of anionic iodide and cationic iodine such as NaI, tetrabutylammonium iodide (TBAI) and *N*-iodosuccinimide (NIS) showed much lower activity (entries 11– 13). The reaction temperature for this transformation was carefully optimized; however, lower yield of product was found as temperature increases (entries 14–15).[17] Additionally, no reaction was observed in the absence of I_2 (entry 16), and only 20% yield of product **3a** was obtained when the oxidant was omitted from the reaction (entry 17). These results highlight the importance of both I_2 and TBHP in this transformation.

Table 1. Optimization of reaction conditions.[a]



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

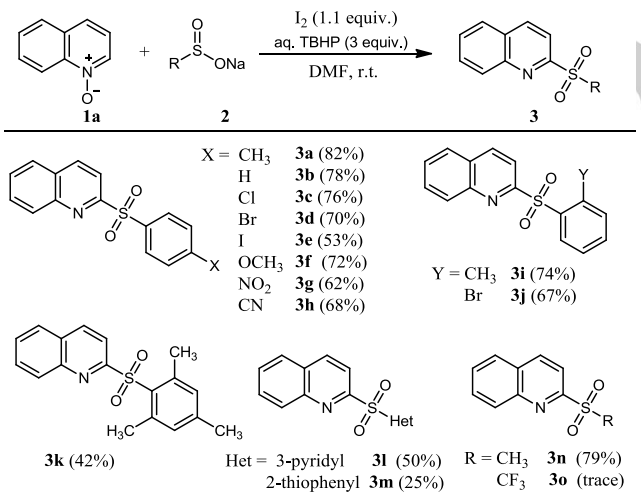
Entry	Reagent	Oxidant	Solvent	Temp [°C]	Yield[b] [%]
1	I_2	TBHP	CH_3CN	r.t.	53
2	I_2	TBHP	CH_2Cl_2	r.t.	28
3	I_2	TBHP	toluene	r.t.	23
4	I_2	TBHP	THF	r.t.	61
5	I_2	TBHP	CH_3OH	r.t.	46
6	I_2	TBHP	H_2O	r.t.	41
7	I_2	TBHP	DMSO	r.t.	71
8	**I_2**	**TBHP**	**DMF**	**r.t.**	**85 (82[c])**
9	I_2	H_2O_2	DMF	r.t.	70
10	I_2	DTBP	DMF	r.t.	5
11	NaI	TBHP	DMF	r.t.	17
12	TBAI	TBHP	DMF	r.t.	11
13	NIS	TBHP	DMF	r.t.	49
14	I_2	TBHP	DMF	50	70
15	I_2	TBHP	DMF	100	56
16	-	TBHP	DMF	r.t.	0
17	I_2	-	DMF	r.t.	20

[a] Conditions: **1a** (0.5 mmol, 1 equiv.), **2a** (1.25 mmol, 2.5 equiv.), reagent (0.55 mmol, 1.1 equiv.), oxidant (1.5 mmol, 3.0 equiv.), solvent (2 mL), 2 h. [b] GC yield. [c] Isolated yield after purification by SiO_2 chromatography.

Overall, the optimal conditions for I_2/TBHP-induced deoxygenation and direct *C2*-sulfonylation of quinoline *N*-oxide and sodium sulfinate **1a** was established (Table 1, entry 8; 1 equiv. of quinoline *N*-oxide, 2.5 equiv. of sodium sulfinate,1.1 equiv. of I2, 3 equiv. of aq. TBHP, DMF, r.t., 2 h). With these conditions in hand, we sought to expand the substrate scope that is applicable for this transformation. Therefore, the one-pot deoxygenation and sulfonylation reaction between quinoline *N*-oxide (**1a**) and variety

of sodium sulfinate salts (**2**) were evaluated and the results are listed in Table 2. Various types of arylsulfinate sodium salts are well-compatible with standard conditions, affording the desired 2-sulfonyl quinoline products (**3a–3m**) in moderate to excellent quantities. As anticipated, sodium phenylsulfinate reacted with quinoline *N*-oxide smoothly, furnishing the product **3b** in 78% yield. Arylsulfinate with halogen-substituents (Cl, Br, and I) could serve as practical substrates for the I_2/TBHP-mediated deoxygenation and sulfonylation reactions and the products **3c–3e** were achieved in moderate to high quantities (53–76%). Benzenesulfinate substrates bearing electron-donating (methoxy group) or electron–withdrawing (nitro and cyano groups) substituents also delivered products **3f–3h** in good yields. Notably, arylsulfinates bearing substitutents at *ortho* position (*o*-CH_3 and *o*-Br) could be converted into their corresponding 2-sulfonyl quinoline products **3i** and **3j** in synthetically useful yields; however, in the case of steric bulky mesitylene sulfinate salt, a modest amount of product **3k** (42%) was obtained. Moreover, heteroarylsulfinates such as pyridinylsulfinate and thiophenylsulfinate sodium salts are viable substrates for this one-pot transformation resulting in a formation of quinoline sulfone products **3l** and **3m** in 50% and 25%, respectively. Apart from arylsulfinate salts, we examined a reaction of alkyl sulfinate sodium salt. To our delight, sodium methanesulfinate underwent smooth one-pot reaction with quinoline *N*-oxide (**1a**) affording product **3n** in high yield (79%). Conversely, sodium triflinate, which has very strong inductive effect from trifluoromethane group, was not an effective substrate, suggesting that the nature of the sodium sulfinate could have an impact on a product formation.

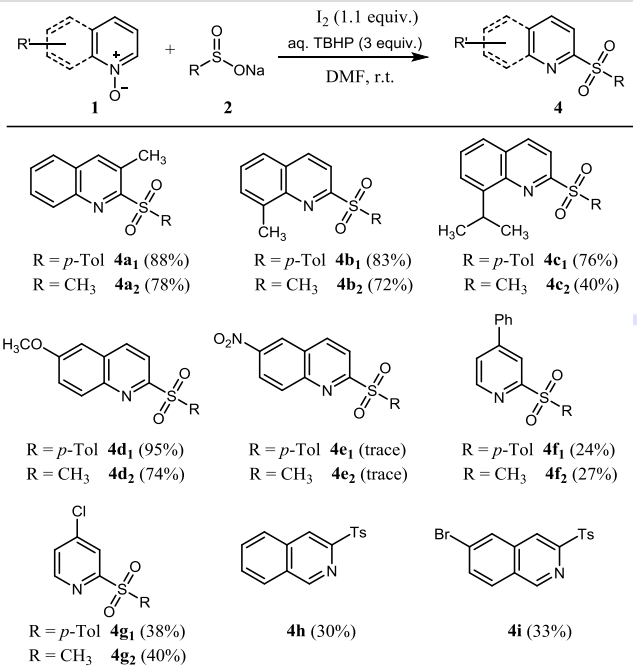
Table 2. Reaction of quinoline *N*-oxide **1a** with various sodium sulfinate salts.[a]



[a] Conditions: **1a** (1.0 mmol, 1.0 equiv.), **2** (2.5 mmol, 2.5 equiv.), I_2 (1.1 mmol, 1.1 equiv.), aq. TBHP (3.0 mmol, 3.0 equiv.), DMF (4 mL), r.t., 2 h; isolated yields after purification by SiO_2 chromatography.

The reactions between sodium sulfinate salts and various quinoline *N*-oxides, pyridine *N*-oxides, and other heteroaromatic *N*-oxides were also examined under the optimal conditions. As illustrated in Table 3, both *p*-toluenesulfinate sodium salt and methanesulfinate sodium salt showed a tolerance toward a range of substituted quinoline *N*-oxide substrates, and the one-pot deoxygenation and sulfonylation can be achieved without any difficulties, allowing a facile preparation of 2-sulfonyl quinolines in moderate to excellent yields. The presence of alkyl group (methyl or isopropyl) at *C3* or *C8* position of quinoline *N*-oxide does not appear to sterically interfere with the transformation and the sulfone products **4a$_1$ –4c$_2$** can be collected in reasonable to decent amounts. Remarkably, the reactions of sodium sulfinates with quinoline *N*-oxide substrate bearing strong electron donating group (-OCH_3) proceeded efficiently at room temperature and gave the corresponding products in good to excellent yields (**4d$_1$** and **4d$_2$**; 95% and 74%, respectively). On the other hand, only a trace amount of product was found in case of quinoline *N*-oxide substrate bearing a strong electron-withdrawing substituent (-NO_2). These outcomes indicated that electronic variations from substituents on *N*-oxide have a remarkable influence on the efficiency of the reaction.

Table 3. Substrate scope of quinoline and other hereoaromatic *N*-oxides.[a]

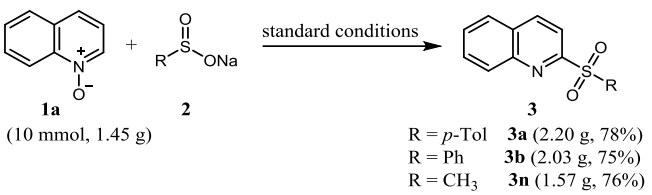


[a] Conditions: **1** (1.0 mmol, 1.0 equiv.), **2** (2.5 mmol, 2.5 equiv.), I_2 (1.1 mmol, 1.1 equiv.), aq. TBHP (3.0 mmol, 3.0 equiv.), DMF (4 mL). r.t., 2 h; isolated yields after purification by SiO_2 chromatography.

We also explored the one-pot deoxygenation and sulfonylation on other related heteroaromatic *N*-oxide substrates. Substituted pyridine *N*-oxides such as 4-phenylpyridine and 4-chloropyridine *N*-oxides can be converted to the monosubstituted sulfonyl pyridine products (Table 3, **4f$_1$–4g$_2$**) with slightly low or moderate yields under the optimal conditions. Additionally, isoquinoline *N*-oxide can react with sodium sulfinate and

sulfonylation took place at *C3* position as a major product (e.g. **4h** and **4i**), which is the opposite regioisomer that could be obtained from He and Xiang's iodine/iodide-induced sulfonylation of *N*-oxides using sulfonyl hydrazides.[13],[14] Unfortunately, other *N*-oxides including pyrimidine, pyrazine and quinoxazaline *N*-oxide substrates are unable to convert to their target products under the established conditions.

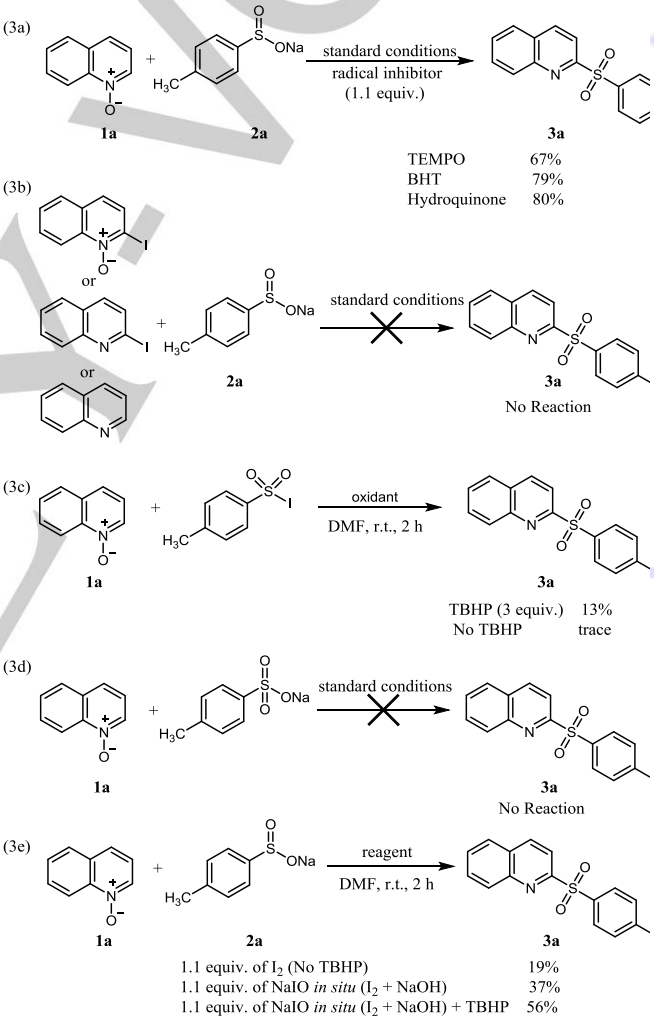
It is noteworthy that the synthesis of 2-sulfonyl quinolines (**3a**, **3b** and **3n**) *via* the developed iodine/TBHP-mediated deoxygenation and direct sulfonylation of *N*-oxides could be safely conducted on a gram scale (10 mmol) with a similar efficacy to small scale reactions (Scheme 2). This could prove the practicality and suggest a potential application in the industry of this synthetic approach.



Scheme 2. Gram scale-reactions.

To gain insight into the reaction mechanism, a series of control experiments were carried out (Scheme 3). When a radical inhibitor was employed in the reaction of quinoline *N*-oxide **1a** and *p*-toluenesulfinate sodium salt **2a**, no inhibition was observed under the optimal conditions (Scheme 3a). The quinoline sulfone product can be obtained in 67%, 79%, and 80% in the presence of TEMPO, BHT, and hydroquinone, respectively, suggesting that the reaction possibly involves a non-radical pathway. In addition, no formation of the desired product **3a** was observed under established conditions when replacing quinoline *N*-oxide substrate (**1a**) with 2-iodoquinoline *N*-oxide or 2-iodoquinoline or quinoline (Scheme 3b). These results implied that either 2-iodoquinoline *N*-oxide or 2-iodoquinoline or quinoline might not be the intermediate generated from iodination process in this reaction. We also questioned that *p*-toluenesulfonyl iodide (TsI) could be the intermediate in this transformation because a reaction between sodium sulfinate and molecular iodine can generate a relatively unstable sulfonyl iodide.[19] Thus, *p*-toluenesulfonyl iodide (TsI) was prepared and utilized in the subsequent experiment.[20] However, treating the quinoline *N*-oxide **1a** with TsI in the presence and absence of TBHP oxidant resulted in a significant reduction of the product yield (13%) or no reaction (Scheme 3c). Therefore, the sulfonyl iodide is unlikely to be the reactive intermediate that could be converted to the sulfone product in this transformation.[21] Furthermore, sodium *p*-toluenesulfinate was replaced by sodium *p*-toluenesulfonate in this reaction (Scheme 3d). Nevertheless, no desired product was obtained, which implies that *p*-toluenesulfinate does not turn into *p*-toluenesulfonate under oxidative conditions, and the sulfinate salt rather than the sulfonate undergoes direct sulfonylation with the *N*-oxide in this transformation.

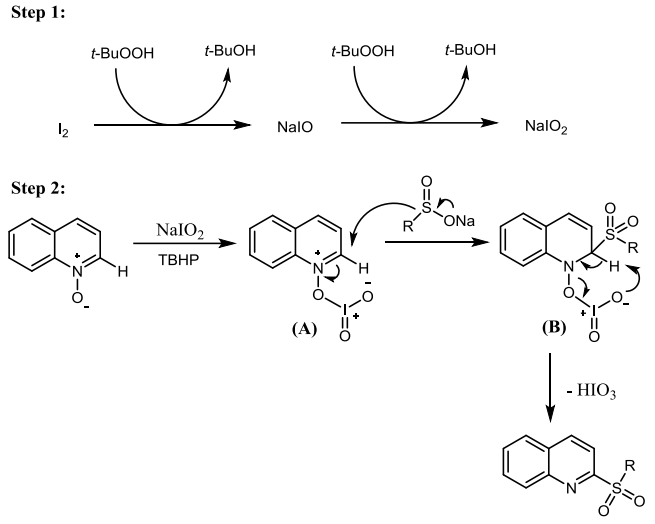
To provide further evidence on the role of iodine and TBHP, the reaction was carried out without the oxidant. The yield of product **3a** was significantly reduced (19%) when subjecting 1.1 equivalence of I_2 to this reaction (Scheme 3e), which emphasized the necessity of I_2/TBHP combination in this one-pot transformation. We also speculated that the electrophilic iodine species could be involve in this non-radical process; therefore, NaIO generated *in situ* from I_2 and NaOH was used, and the reaction gave the quinoline sulfone product in 37% and 60% yields in the absense and presence of TBHP, respectively. These results suggest that I_2 is probably converted to an electrophilic iodine intermediate such as NaIO or $NaIO_2$ prior to reacting with substrates under standard conditions.



Scheme 3. Control experiments.

Based on the above results and relevant literature,[11],[13], [22], [23] a *plausible* mechanism for this metal-free-inducted one-pot deoxygenation and sulfonylation is proposed in Scheme 4. Under the optimal reaction conditions, the initial process could presumably involves a reaction of I_2 and TBHP to form electrophilic iodine species (" I^+ ") such as hypoiodite (IO^-) or iodite

(IO_2^-) *via* an *in situ* iodination.[24] Then, nucleophilic attack of this " I^+ " species by the *N*-oxide will generate intermediate **A**. This intermediate further reacts with sodium sulfinate salt leading to a formation of intermediate **B**. Subsequent elimination would result in an N–O bond cleavage and furnish the corresponding quinoline sulfone product in regioselective fashion.



Scheme 4. Proposed reaction mechanism.

Conclusions

The I_2/TBHP-mediated one-pot deoxygenation and direct C2-sulfonylation of quinoline *N*-oxides using sodium sulfinate as a sulfonyl precursor has been developed for the regioselective synthesis of 2-sulfonyl quinolines. The present method is metal, base and phosphorus-free, utilizes inexpensive and readily available reagents, features a simple experimental procedure, demonstrates good functional group compatibility, proves to be versatile for a range of sodium sulfinate salts and many quinoline *N*-oxide substrates, and can be efficiently conducted on a gram scale. This one-pot protocol provides a convenient synthetic alternative to access a series of *C2*-sulfonyl quinolines and other related compounds at room temperature with moderate to excellent yields of products in a short reaction time. Further mechanistic study and expansion of the synthetic utility of this methodology are currently under investigation.

Experimental Section

General Information: Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Column chromatography was performed over silica gel (SiO_2; 60 Å silica gel, Merck Grade, 70–230 Mesh). GC experiments were carried out with a GC-FID on chromatograph equipped with ZB-1 dimethyl polysiloxane column (30.0 m × 0.25 mm ID × 0.25 µm). ^{1}H and ^{13}C NMR spectra were recorded on Bruker-AV400 spectrometers in $CDCl_3$ solution, at 400 and 100 MHz, respectively. NMR chemical shifts are reported in ppm, and were measured relative to $CHCl_3$ (7.24 ppm for 1H and 77.00 ppm for ^{13}C). IR spectra were recorded on Bruker FT-IR Spectrometer Model ALPHA by neat method, and only partial data are listed. Melting points were determined on Buchi Melting Point M-565 apparatus. High resolution mass spectroscopy (HRMS) data were analysed by a high-resolution micrOTOF instrument with electrospray ionization (ESI). The structures of known compounds were corroborated by comparing their ^{1}H NMR, ^{13}C NMR data with those of literature.

General Procedure for the Synthesis of Compounds of Compounds 3a–3n and 4a$_1$–4i: A 20 ml oven-dried scintillation vial equipped with a magnetic stir bar was charged with a mixture of heteroaryl *N*-oxide substrate (1.00 mmol, 1.00 equiv.), sodium sulfinate salt (2.50 mmol, 2.50 equiv.), iodine (I_2) (1.10 mmol, 1.10 equiv.), *N*,*N*-dimethylformamide (DMF) (4.00 mL) and TBHP in water (3.00 mmol, 3.00 equiv.). The vial was capped and the reaction mixture was stirred at room temperature for 2 hours. Upon completion, saturated $Na_2S_2O_3$ (5 mL) and distilled deionized H_2O (12 mL) was added, and the mixture was extracted with ethyl acetate (EtOAc) (2 × 25 mL). The combined organic layer was washed with saturated NaCl, dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. The crude product was purified by SiO_2 column chromatography to afford a desired 2-sulfonyl heteroarene product.

2-tosylquinoline (3a)[11]: White solid (231 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (d, *J* = 8.4 Hz, 1H), 8.14 (t, *J* = 8.4 Hz, 2H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.73 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.62–7.58 (m, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.35 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.2, 147.3, 144.7, 138.6, 136.0, 130.8, 130.2, 129.7, 129.0, 128.9, 128.7, 127.6, 117.6, 21.5 ppm. HRMS (ESI): calcd for $C_{16}H_{13}NO_2SNa$ $[M+Na]^+$ 306.0559; found 306.0560.

2-(phenylsulfonyl)quinoline (3b)[11]: White solid (209 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (d, *J* = 8.4 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 8.13–8.09 (m, 3H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.75–7.70 (m, 1H), 7.62–7.46 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.9, 147.3, 139.0, 138.7, 133.6, 130.9, 130.2, 129.1, 128.9, 128.8, 128.7, 127.6, 117.6 ppm. HRMS (ESI): calcd for $C_{15}H_{11}NO_2SNa$ $[M+Na]^+$ 292.0403; found 292.0412.

2-((4-chlorophenyl)sulfonyl)quinoline (3c)[11]: Yellow solid (229 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.36 (d, *J* = 8.4 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 8.07–8.03 (m, 2H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.78–7.74 (m, 1H), 7.65–7.61 (m, 1H), 7.47 (td, *J* = 8.4, 2.0 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.7, 147.3, 140.5, 138.8, 137.4, 131.1, 130.5, 130.2, 129.3, 129.2, 128.8, 127.7, 117.4 ppm. HRMS (ESI): calcd for $C_{15}H_{10}ClNO_2SNa$ $[M+Na]^+$ 326.0013; found 326.0020.

2-((4-bromophenyl)sulfonyl)quinoline (3d) [12]: Off-white solid (242 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.36 (d, *J* = 8.4 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 8.11 (d, *J* =8.4 Hz, 1H), 7.99–7.96 (m, 2H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.78–7.74 (m, 1H), 7.65–7.62 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.6, 147.4, 138.8, 137.9, 132.3, 131.1, 130.5, 130.2, 129.3, 129.1, 128.8, 127.7, 117.4 ppm. HRMS (ESI): calcd for $C_{15}H_{10}BrNO_2SNa$ $[M+Na]^+$ 369.9513; found 369.9524.

2-((4-iodophenyl)sulfonyl)quinoline (3e) [12]: White solid (208 mg, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37 (d, *J* = 8.8 Hz, 1H), 8.17 (d, *J* = 8.8 Hz, 1H), 8.12 (d, *J* = 8.8 Hz, 1H), 7.88–7.75 (m, 6H), 7.65 (dt, *J* = 8.0, 1.2 Hz, 1H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ 157.7, 147.4, 138.8, 138.6, 138.3, 131.1, 130.4, 130.3, 129.3, 128.8, 127.7, 117.5, 101.9 ppm. HRMS (ESI): calcd for $C_{15}H_{10}INO_2SNa$ $[M+Na]^+$ 417.9369; found 417.9370.

2-((4-methoxyphenyl)sulfonyl)quinoline (3f)[12]: White solid (215 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (d, *J* = 8.4 Hz, 1H), 8.16–8.12 (m, 2H), 8.06– 8.02 (m, 2H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.76–7.72 (m, 1H), 7.63–7.59 (m, 1H), 6.98–6.94 (m, 2H), 3.80 (s, 3H) ppm.^{13}C NMR

(100 MHz, $CDCl_3$): δ = 163.8, 158.5, 147.3, 138.6, 131.2, 130.8, 130.4, 130.3, 128.9, 128.6, 127.6, 117.4, 114.3, 55.5 ppm. HRMS (ESI): calcd for $C_{16}H_{13}NO_3SNa$ $[M+Na]^+$ 322.0514; found 322.0526.

2-((4-nitrophenyl)sulfonyl)quinoline (3g): Light yellow solid (195 mg, 62% yield). m.p. 143.0 – 145.0 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.41 (d, *J* = 8.8 Hz, 1H), 8.36–8.30 (m, 4H), 8.22 (d, *J* = 8.8 Hz, 1H), 8.09 (d, *J* = 8.8 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.8, 150.7, 147.3, 144.6, 139.1, 131.3, 130.5, 130.1, 129.6, 128.9, 127.7, 124.0, 117.4 ppm. IR: $\tilde{\nu}$ = 3015, 1521, 1380, 1345, 1212, 1178, 966, 768, 549 cm^{-1}. HRMS (ESI): calcd for $C_{15}H_{10}N_2O_4SNa$ $[M+Na]^+$ 337.0259, found 337.0253.

4-(quinolin-2-ylsulfonyl)benzonitrile (3h): White solid (199 mg, 68% yield). m.p. 192.6 – 194.8 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.40 (d, *J* = 8.4 Hz, 1H), 8.25–8.21 (m, 3H), 8.09 (d, *J* = 8.8 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.82–7.76 (m, 3H), 7.68–7.64 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.9, 147.3, 143.1, 139.0, 132.6, 131.3, 130.1, 129.7, 129.6, 128.9, 127.7, 117.4, 117.3, 117.1 ppm. IR: $\tilde{\nu}$ = 3091, 2922, 2235, 1558, 1497, 1319, 1168, 1130, 1074, 833, 683, 651, 558 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{10}N_2O_2SNa$ $[M+Na]^+$ 317.0374; found 317.0361.

2-(*o*-tolylsulfonyl)quinoline (3i): Off-white solid (209 mg, 74% yield). m.p. 192.6 – 194.8 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.36 (d, *J* = 8.8 Hz, 1H), 8.29 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.15 (d, *J* = 8.8 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.77–7.72 (m, 1H), 7.65–7.61 (m, 1H),7.49–7.45 (m, 1H), 7.41–7.38 (m, 1H), 7.24–7.21 (m, 1H), 2.53 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.1, 147.1, 139.1, 138.6, 137.1, 133.9, 132.4, 130.9, 130.6, 130.3, 129.1, 128.8, 127.7, 126.4, 117.7, 20.7 ppm. IR $\tilde{\nu}$ = 3057, 2965, 1577, 1472, 1309, 1163, 1094, 751, 708, 639 cm^{-1}. HRMS (ESI): calcd for $C_{16}H_{13}NO_2SNa$ $[M+Na]^+$ 306.0565; found 306.0568.

2-((2-bromophenyl)sulfonyl)quinoline (3j): Yellow solid (232 mg, 67% yield). m.p. 162.3 – 164.7 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.51 (d, *J* = 8.0 Hz, 1H), 8.40 (d, *J* = 8.8 Hz, 1H), 8.31 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H); 7.88 (d, *J* = 8.4 Hz, 1H), 7.74–7.69 (m, 1H), 7.65–7.56 (m, 3H), 7.44 (dt, *J* = 8.0, 1.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.1, 147.1, 138.3, 135.0, 134.8, 132.5, 130.9, 130.2, 129.2, 128.9, 127.8, 127.7, 121.3, 118.6 ppm. IR $\tilde{\nu}$ = 3054, 1572, 1425, 1317, 1171, 1140, 1023, 827, 735, 569 cm^{-1}. HRMS (ESI): calcd for $C_{15}H_{10}BrNO_2SNa$ $[M+Na]^+$ 369.9508; found 369.9517.

2-(mesitylsulfonyl)quinoline (3k)[14]: Off-white solid (130 mg, 42% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.35 (d, *J* = 8.4 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.76–7.71 (m, 1H), 7.64–7.60 (m, 1H), 6.93 (s, 2H), 2.66 (s, 6H), 2.27 (s, 3H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.5, 147.1, 143.5, 141.1, 138.3, 132.8, 132.4, 131.9, 130.7, 130.4, 128.8, 127.6, 116.8, 23.0, 21.0 ppm. IR $\tilde{\nu}$ = 2925, 1602, 1498, 1305, 1162, 1129, 755, 685, 659 cm^{-1}. HRMS (ESI): calcd for $C_{18}H_{17}NO_2SNa$ $[M+Na]^+$ 334.0878; found 334.0898.

2-(pyridin-3-ylsulfonyl)quinoline (3l): White solid (134 mg, 50% yield). m.p. 118.2 – 120.1 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.31–9.30 (m, 1H), 8.80 (dd, *J* = 4.8, 1.2 Hz, 1H), 8.43 – 8.39 (m, 2H), 8.21 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.80–7.75 (m, 1H), 7.67–7.63 (m, 1H), 7.49–7.45 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.4, 154.0, 149.9, 147.4, 139.0, 136.8, 135.5, 131.2, 130.2, 129.5, 128.9, 127.7, 123.6, 117.2 ppm. IR $\tilde{\nu}$ = 3098, 3076, 1575, 1418, 1318, 1169, 1087, 764, 650, 573 cm^{-1}. HRMS (ESI): calcd for $C_{14}H_{10}N_2O_2SNa$ $[M+Na]^+$ 293.0355; found 293.0362.

2-(thiophen-2-ylsulfonyl)quinoline (3m)[11] : Yellow solid (69 mg, 25% yield); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.37 (d, *J* = 8.4 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 2H), 7.89–7.86 (m, 2H), 7.80–7.76 (m, 1H), 7.70 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.67–7.63 (m, 1H), 7.12–7.09 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.9, 147.3, 139.7, 138.8, 135.3, 135.2, 131.1, 130.3, 129.2, 128.9, 127.8, 127.7, 117.3 ppm. HRMS (ESI): calcd for $C_{13}H_{10}NO_2S_2$ $[M+H]^+$ 276.0147; found 276.0152.

2-(methylsulfonyl)quinoline (3n) [12]: Yellow solid (163 mg, 79% yield), ^1H NMR (400 MHz, $CDCl_3$): δ = 8.39 (d, *J* = 8.4 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.90–7.87 (m, 1H), 7.82–7.78 (m, 1H), 7.68–7.64 (m, 1H), 3.34 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.4, 146.8, 138.8, 131.1, 129.9, 129.1, 129.0, 127.8, 116.0, 39.7 ppm. HRMS (ESI): calcd for $C_{10}H_9NO_2SNa$ $[M+Na]^+$ 230.0252; found 230.0263.

3-methyl-2-tosylquinoline ($4a_1$)[14]: Yellow solid (262 mg, 88% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.01 (s, 1H), 7.92–7.87 (m, 3H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.60 (dt, *J* = 8.4, 1.2 Hz, 1H), 7.56–7.52 (m, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.82 (s, 3H), 2.42 (s, 3H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.9, 144.6, 144.4, 139.7, 135.7, 129.8, 129.6, 129.3, 129.2, 129.0, 128.8, 128.4, 126.5, 21.5, 18.7 ppm. HRMS (ESI): calcd for $C_{17}H_{15}NO_2SNa$ $[M+Na]^+$ 320.0721; found 320.0729.

3-methyl-2-(methylsulfonyl)quinoline ($4a_2$): White solid (172 mg, 78% yield). m.p. 118.2 – 120.1 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.06–8.01 (m, 2H), 7.79–7.76 (m, 1H), 7.73–7.69 (m, 1H), 7.63–7.59 (m, 1H), 3.52 (s, 3H), 2.82 (d, *J* = 0.8 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.8, 144.2, 139.7, 129.9, 129.5, 129.2, 128.9, 127.6, 126.9, 39.9, 17.7 ppm. IR $\tilde{\nu}$ = 3013, 2931, 1561, 1292, 1128, 960, 788, 766, 599, 508 cm^{-1}. HRMS (ESI): calcd for $C_{11}H_{12}NO_2S$ $[M+H]^+$ 222.0583; found 222.0591.

8-methyl-2-tosylquinoline ($4b_1$) [14]: White solid (247 mg, 83% yield); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.30 (d, *J* = 8.4 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 8.03 (dd, *J* = 6.8, 1.2 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 6.8 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.66 (s, 3H), 2.39 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3, 146.3, 144.6, 138.7, 138.3, 135.9, 130.8, 129.4, 129.3, 128.8, 128.7, 125.5, 116.7, 21.6, 17.5 ppm. HRMS (ESI): calcd for $C_{17}H_{15}NO_2SNa$ $[M+Na]^+$ 320.0721; found 320.0734.

8-methyl-2-(methylsulfonyl)quinoline ($4b_2$): Colorless oil (159 mg, 72% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.38 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.59–7.55 (m, 1H), 3.40 (s, 3H), 2.79 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.5, 148.4, 145.9, 139.1, 138.1, 131.2, 129.0, 125.7, 115.5, 39.4, 17.6 ppm. IR $\tilde{\nu}$ = 3016, 2929, 1573, 1494, 1304, 1162, 1114, 960, 762 cm^{-1}. HRMS (ESI): calcd for $C_{11}H_{12}NO_2S$ $[M+H]^+$ 222.0583; found 222.0592.

8-isopropyl-2-tosylquinoline ($4c_1$): Yellow oil (246 mg, 76% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.31 (d, *J* = 8.8 Hz, 1H), 8.17 (d, *J* = 8.8 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 2H), 7.66 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.61–7.53 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.03 (sep, *J* = 6.8 Hz, 1H), 2.38 (s, 3H), 1.22 (d, *J* = 6.8 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.2, 148.1, 145.1, 144.5, 138.8, 135.8, 129.4, 129.3, 129.0, 128.8, 126.6, 125.3, 116.4 27.9, 23.0, 21.5 ppm. IR $\tilde{\nu}$ = 3064, 2962, 2869, 1596, 1491, 1373, 1320, 1166, 1077, 813, 704 cm^{-1}. HRMS (ESI): calcd for $C_{19}H_{19}NO_2SNa$ $[M+Na]^+$ 348.1034; found 348.1047.

8-isopropyl-2-(methylsulfonyl)quinoline ($4c_2$): Yellow oil (99 mg, 40% yield).^1H NMR (400 MHz, $CDCl_3$): δ = 8.39 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.74–7.69 (m, 2H), 7.63 (t, *J* = 7.6 Hz, 1H), 4.22 (sep, *J* = 6.8 Hz, 1H), 3.39 (s, 3H), 1.37 (d, *J* = 6.8 Hz, 6H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.3, 147.9, 144.6, 139.3, 129.3, 129.2, 127.0, 125.6, 115.2,

39.3, 27.8, 23.2 ppm. IR $\tilde{\nu}$ = 3060, 2952, 2874, 1589, 1495, 1370, 1301, 1160, 1068, 810, 714 cm^{-1}. HRMS (ESI): calcd for $C_{13}H_{15}NO_2SNa$ $[M+Na]^+$ 272.0721; found 272.0732.

6-methoxy-2-tosylquinoline (4d$_1$) [12]: White solid (297 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 8.8 Hz, 1H), 8.01 (d, *J* = 9.2 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.36 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 2.8 Hz, 1H), 3.89 (s, 3H), 2.35 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7, 155.6, 144.5, 143.5, 136.7, 136.4, 131.7, 130.3, 129.6, 128.8, 124.1, 118.1, 104.5, 55.7, 21.6 ppm. HRMS (ESI): calcd for $C_{17}H_{15}NO_3SNa$ $[M+Na]^+$ 336.0665; found 336.0670.

6-methoxy-2-(methylsulfonyl)quinoline (4d$_2$): Off-white solid (176 mg, 74% yield). m.p. 112.1 – 114.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 8.8 Hz, 1H), 8.03 (t, *J* = 8.4 Hz, 2H), 7.44 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.11 (d, *J* = 2.8 Hz, 1H), 3.94 (s, 3H), 3.31 (s, 3H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.8, 154.8, 143.1, 136.9, 131.4, 130.7, 124.5, 116.7, 104.7, 55.7, 40.0 ppm. IR $\tilde{\nu}$ = 2921, 1620, 1497, 1386, 1307, 1159, 1121, 764, 458 cm^{-1}. HRMS (ESI): calcd for $C_{11}H_{12}NO_3S$ $[M+H]^+$ 238.0532; found 238.0537.

4-phenyl-2-tosylpyridine (4f$_1$): White solid (75 mg,24% yield). m.p. 149.5 – 151.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (d, *J* = 4.8 Hz, 1H), 8.38 (d, *J* = 1.2 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.65 (dd, *J* = 8.0, 2.0 Hz, 2H), 7.61 (dd, *J* = 4.8, 2.0 Hz, 1H), 7.52–7.47 (m, 3H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.6, 150.8, 144.8, 136.4, 135.9, 130.0, 129.8, 129.4, 128.9, 127.1, 124.3, 119.8, 21.6 ppm. IR $\tilde{\nu}$ = 3064, 3031, 1589, 1457, 1318, 1299, 1161, 759, 666, 584 cm^{-1}. HRMS (ESI): calcd for $C_{18}H_{16}NO_2S$ $[M+H]^+$ 310.0896; found 310.0903.

2-(methylsulfonyl)-4-phenylpyridine (4f$_2$): White solid (63 mg, 27% yield). m.p. 107.4–109.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.74 (dd, *J* = 6.8, 4.0 Hz, 1H), 8.29 (d, *J* = 1.2 Hz, 1H), 7.73 (dd, *J* = 5.2, 1.6 Hz, 1H), 7.66 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.53–7.47 (m, 3H), 3.25 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.7, 151.1, 150.5, 136.3, 130.2, 129.4, 127.1, 124.9, 118.8, 40.1 ppm. IR $\tilde{\nu}$ = 3035, 2932, 1591, 1466, 1294, 1129, 1094, 951, 767, 759, 539 cm^{-1}. HRMS (ESI): calcd for $C_{12}H_{11}NO_2SNa$ $[M+Na]^+$ 256.0408; found 256.0421.

4-chloro-2-tosylpyridine (4g$_1$)[11]: White solid (102 mg, 38% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (d, *J* = 5.2 Hz, 1H), 8.15 (d, *J* = 2.0 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.41 (dd, *J* = 5.2, 2.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.2, 151.1, 146.2, 145.2, 135.1, 129.8, 129.0, 126.9, 122.4, 21.6 ppm. HRMS (ESI): calcd for $C_{12}H_{11}ClNO_2S$ $[M+H]^+$ 268.0194; found 268.0203.

4-chloro-2-(methylsulfonyl)pyridine (4g$_2$): White solid (77 mg, 40% yield). m.p. 82.8 – 84.2 °C.^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60 (d, *J* = 5.2 Hz, 1H), 8.06 (dd, *J* = 2.0, 0.4 Hz, 1H), 7.53 (dd, *J* = 5.2, 2.0 Hz, 1H), 3.21 (s, 3H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2, 150.9, 146.6, 127.7, 121.7, 39.9 ppm. IR $\tilde{\nu}$ = 3082, 3027, 1564, 1454, 1294, 1170, 1135, 963, 744, 536 cm^{-1}. HRMS (ESI): calcd for $C_6H_6ClNO_2SNa$ $[M+Na]^+$ 213.9700; found 213.9706.

3-tosylisoquinoline (4h); White solid (85 mg, 30% yield). m.p. 175.1 – 176.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.19 (s, 1H), 8.61 (s, 1H), 7.97 (d, *J* = 8.4 Hz, 4H), 7.82–7.78 (m, 1H), 7.76–771 (m, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 2.35 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.6, 152.3, 144.5, 136.3, 135.2, 131.8, 130.1, 129.6, 129.3, 128.7, 128.1, 127.7, 120.8, 21.5 ppm. IR $\tilde{\nu}$ = 3390, 3025, 2985, 1684, 1570, 1378, 1270, 1165, 966, 800, 485 cm^{-1}. HRMS (ESI): calcd $C_{16}H_{13}NO_2SNa$ $[M+Na]^+$ 306.0559; found 306.0563.

6-bromo-3-tosylisoquinoline (4i): Orange-brown solid (119 mg, 33% yield). m.p. 204.1 – 205.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.58 (d, *J* = 0.4 Hz, 1H), 9.08 (s, 1H), 8.43 (dd, *J* = 8.8, 0.4 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.27–7.22 (m, 4H), 2.34 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.3, 144.6, 144.0, 142.0, 138.1, 130.6, 129.9, 128.1, 127.5, 125.9, 123.8, 123.5, 102.7, 21.5 ppm. IR $\tilde{\nu}$ = 3387, 3014, 2980, 1681, 1544, 1350, 1260, 1139, 945, 513 cm^{-1}. HRMS (ESI): calcd $C_{16}H_{12}BrNO_2SNa$ $[M+Na]^+$ 383.9664; found 383.9673.

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[24] The electrophilic iodine "I^+" is generally generated *in situ* by I_2 and TBHP oxidant. The true nature of "I^+" is still unclear since it is quite difficult to detect these highly reactive species by standard spectroscopic methods.

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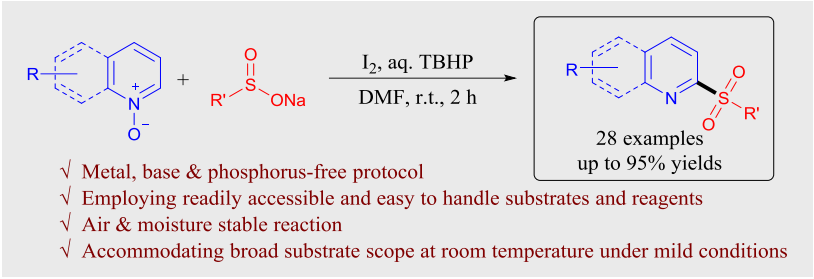

A facile synthesis of 2-sulfonyl quinolines from quinoline *N*-oxides and sodium sulfinates, employing the combination of I_2/TBHP in one-pot deoxygenation and direct sulfonylation is described. This reaction proceeds at room temperature under mild conditions, and provides products in moderate to excellent yields.

Subject: Metal-Free Sulfonylation Reaction

*Ladawan Sumunnee, Chonchanok Buathongjan, Chaleena Pimpasri, Sirilata Yotphan**

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Iodine/TBHP-Promoted One-Pot Deoxygenation and Direct *C2*-Sulfonylation of Quinoline *N*-Oxides with Sodium Sulfinates: Facile and Regioselective Synthesis of 2-Sulfonyl Quinolines