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Cite this: DOI: 10.1039/c0xx00000x

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DOI: 10.1039/C6RA04013F

ARTICLE TYPE

Copper(II)-Catalyzed Remote Sulfonylation of Aminoquinolines with Sodium Sulfinates *via* Radical Coulping

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

An efficient remote sulfonylation of *N*-(quinolin-8-yl)benzamide derives at the C5 position has been well developed. The reaction generates environmentally benign byproducts utilizing the stable, safe sodium sulfinates as sulfide sources. A series of *N*-(5-(phenylsulfonyl)quinolin-8-yl)benzamidem derivatives were successfully obtained in moderate to high yields. Especially, there are less unpleasant odorous escaped and more environmentally friendly than previous means.

Introduction

The organosulfones have been proven to be a valuable building block in medicinal chemistry. It exits widely in medicinally active compounds, such as anti-HIV[1], antibacterial[2], antihyperglycemic[3], 5-HT_6 receptor (5-HT_6R) antagonists[4] D_2 receptor[5] antagonist and anticancer.[6] Many representative examples of drugs and bioactive thioethers with an quinolines or naphthyl scaffolds that are used drug candidates for various diseases are shown in (Figure 1).

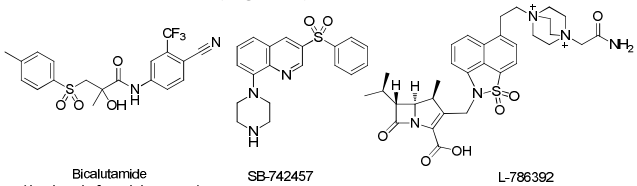

Figure 1. aromatic sulfones used as drugs or drug candidates.

Several methods for synthesis of aryl sulfones have been reported. The common approaches for prepare aryl sulfones include the oxidation of sulfoxide and sulfides[7] or the sulfonylation of arenes by Friedel-Crafts sulfonylation in the presence of strong acids.[8] It is disappointing that these methods are tedious and have a low conversion. In recent years, many more efficient routes such as decarboxylative and C-H activation cross-couplings have been developed. For example, Rahul et al reported an Iodine-catalyzed decarboxylative coupling reaction to synthesis of vinyl sulfones utilizing cinnamic acids and arylsulfonyl hydrazides.[9] Many groups have developed a C-H bond activation of C(sp^2)-H or C(sp)-H bonds with a sulfonyl chlorides[10], sulfonyl hydrazides[11] diaryl disulfides[12] and sulfinic acids[13] to synthesis organosulfones. But the sulfide sources are reported to have many properties such as toxicity, unpleasant odorous and instability. Furthermore, many undesired byproducts are also produced. Thus, sodium sulfinates have attracted much attention because it provides a way to attain the desirable requirement of atom economy and relative safety. Chen's[14] group report an efficient metal-free sulfonylated five-membered hetero-cyclic compounds with sodium sulfinates. Next, our group[15] independently reported aryl halides and sodium sulfinates also can be used as coupling reagents catalyzed by copper to synthesis of sulfone derivatives. Similarly, Xu et al have developed a highly efficient method to synthesis of vinyl sulfones react cinnamic acids and sodium sulfinates[16] by decarboxylative with transition-metal-free. Furthermore, Tang and Xiao reported a C-H activation coupling method of oxime acetates[17] or indoles[18] with sodium sulfinates to synthesis of sulfone derivatives.

Recently, more and more effort has been made to develop many techniques to control the reaction selectivity assistance of a directing group. Such as azobenzene[19], phenylpyridine[20] work as directing group direct sulfonylation *via* C-H functionalization with sulfonyl chlorides have been reported, which can provide a shortcut for ortho-aryl sulfones. However, Saidi[21] and co-workers found only meta-aryl sulfones were obtained when ruthenium was used as the catalyst in this reaction. Encouragingly, two publications from Wei and Wu's group highlighted the discovery of the selective remote C-H sulfonylation at C5-H position of 8-aminoquinoline with arylsulfonyl chlorides via copper catalysis (Figure 2). [22] But Liu and Rao reported they only obtained ortho C-H bond sulfonylation of benzoic acid when using sodium

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† Electronic Supplementary Information (ESI) available: ^{1}H NMR spectra, ^{13}C NMR spectrum, GC/MS profile, HRMS profile. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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DOI: 10.1039/C6RA04013F

sulfinates as sulfide sources.[23] In recent years, many efforts of our group have been expended on developing C-S bonds formation.[15a, 19a, 24] Besides these contributions, we focused our efforts on how to build C-S bonds utilizing sodium sulfinates as sulfide sources *via* C-H functionalization. Among them, a catalyst-controlled selectivity in C-S bond formation in the synthesis of C2- and C3-sulfanylindoles was reported.[25] Herein, we report a simple and an environmental-friend procedure for the synthesis of *N*-(5-(phenylsulfonyl)quinolin-8-yl) benzamide and its derivatives *via* copper-catalyzed direct cross-coupling of the *N*-(quinolin-8-yl) benzamide derivatives with sodium sulfinates.

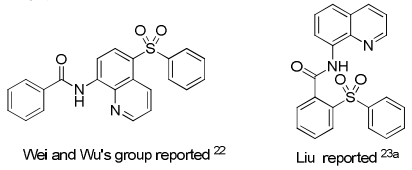
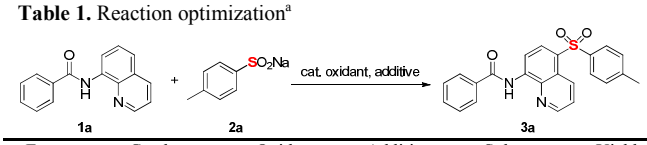


Figure 2. Selectivity sulfonylation of 8-aminoquinoline.

Results and discussion

Initially, *N*-(quinolin-8-yl)benzamide (**1a**) and sodium 4-tolylsulfinate (**2a**) were used as the standard substrates under different conditions (Table 1).

Table 1. Reaction optimization[a]



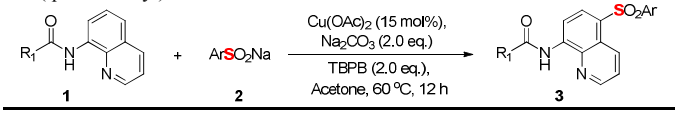
1a 2a 3a

Entry	Catalyst [mol%]	Oxidant [equiv.]	Additive [equiv.]	Solvent	Yield [%][b]
1	$Pd(OAc)_2$	TBHP	Na_2CO_3	CH_3CN	0
2	$FeSO_4{\cdot}7H_2O$	TBHP	Na_2CO_3	CH_3CN	0
3	CuI	TBHP	Na_2CO_3	CH_3CN	55
4	$Cu(NO_3)_2$	TBHP	Na_2CO_3	CH_3CN	20(0)[c]
5	$Cu(OAc)_2$	TBHP	Na_2CO_3	CH_3CN	60
6	$Cu(OAc)_2$	TBHP	Na_2CO_3	DMF	15
7	$Cu(OAc)_2$	TBHP	Na_2CO_3	THF	45
8	$Cu(OAc)_2$	TBHP	Na_2CO_3	Acetone	65(0)[d]
9	$Cu(OAc)_2$	H_2O_2	Na_2CO_3	Acetone	15
10	$Cu(OAc)_2$	DTBP	Na_2CO_3	Acetone	55
11	$Cu(OAc)_2$	$K_2S_2O_8$	Na_2CO_3	Acetone	30
12	$Cu(OAc)_2$	TBPB	Na_2CO_3	Acetone	83(30)[e]
13	$Cu(OAc)_2$	TBPB	Cs_2CO_3	Acetone	45
14	$Cu(OAc)_2$	TBPB	K_2CO_3	Acetone	42
15	$Cu(OAc)_2$	TBPB	$KHCO_3$	Acetone	37
16[f]	$Cu(OAc)_2$	TBPB	Na_2CO_3	Acetone	15
17[g]	$Cu(OAc)_2$	TBPB	Na_2CO_3	Acetone	80

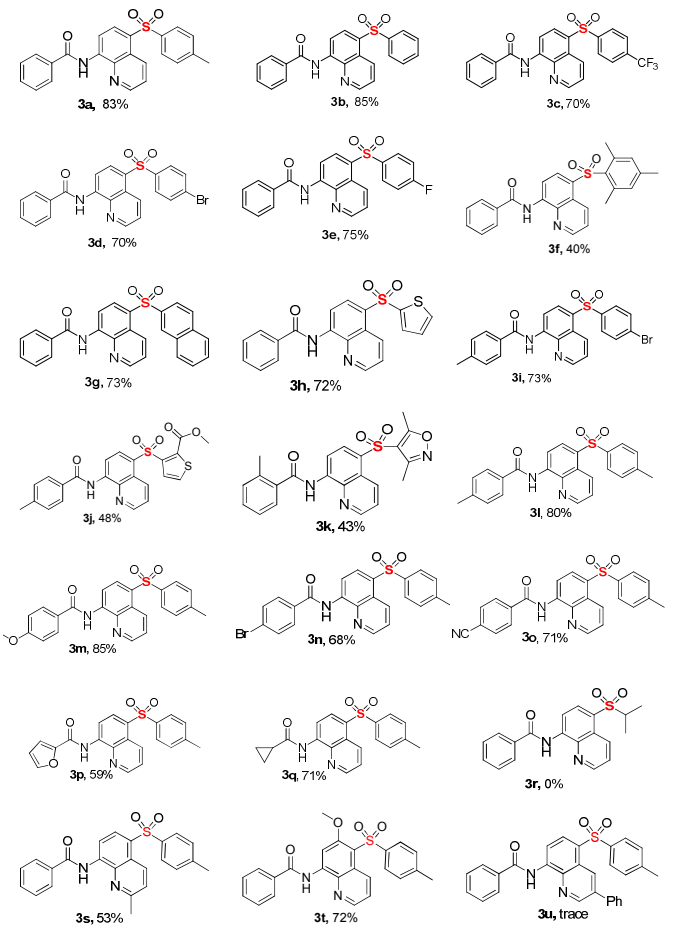
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (2.0 eq.), catalyst (15 mol%), oxidant (2.0 eq.), additive (2.0 eq.), solvent (2.0 mL), under air, 60 °C, 12 h. [b] Isolated yields. [c] without catalyst. [d] without oxidant. [e] without additive. [f] the reaction was carried out at room temperature. [g] the reaction was carried out at 90 °C. TBHP = *tert*-Butyl hydroperoxid. DTBP = Di-*tert*-butyl peroxide. TBPB = *tert*-Butyl perbenzoate.

To our delight, the C_5- thioetherification didn't took place in the presence of $Pd(OAc)_2$ or $FeSO_4.7H_2O$ (15 mol%) in CH_3CN under air for 12 h (entry 1-2, Table1). But the product can be isolated with copper-catalyzed and the desired product was acquired in 60% yield when $Cu(OAc)_2$ work as catalyst (entry 3-5, Table1). Also, without catalyst, no product was isolated at all (entry 4[c], Table1). Solvents such as DMF, THF, and acetone were screened, and Acetone was found to be superior to the others (entries 6-8). Subsequently, various oxidant involving TBHP, H_2O_2, DTBP, $K_2S_2O_8$ and TBPB were tested to this reaction, among which, TBPB gave the best result (entries 8-12, Table1). In addition, the reaction did not occur at all without Oxidant. Na_2CO_3 was superior to other bases, such as Na_2CO_3, $CsCO_3$, K_2CO_3 and $KHCO_3$ (entries 12-15, Table1). Subsequently, the temperature also played an important role in the reaction, the yield is 15% at room temperature and 80% at 90°C (entries 16-17, Table1). According to our optimal conditions, we then investigated the substrate scope of this transformation (Table 2).

Table 2. Substrate scope of the copper(II)-catalyzed direct sulfonylation of *N*-(quinolin-8-yl)benzamide derivatives with sodium sulfinates [a]



1 2 3



[a] Reaction conditions: **1** (0.2 mmol), **2a** (2.0 eq.), $Cu(OAc)_2$ (15 mol%), DTBP (2.0 eq.), Na_2CO_3 (2.0 eq.), acetone (2.0 mL), under air, 60 °C, 12 h. [b] Isolated yields. TBPB = *tert*-Butyl perbenzoate.

A series of sodium sulfinates were allowed to react with *N*-(quinolin-8-yl) benzamide (**1a**), affording the corresponding

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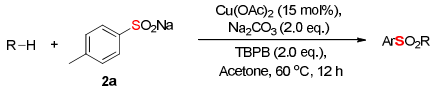
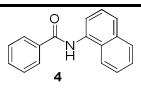
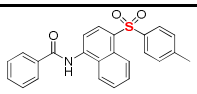
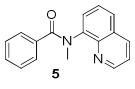
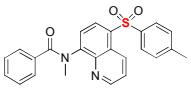
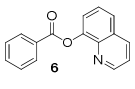
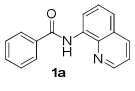
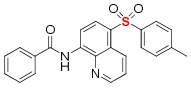
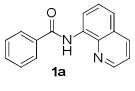
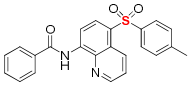
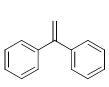
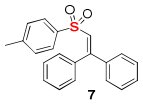
N-(5-(phenylsulfonyl)quinolin-8-yl)benzamide in moderate to good yields. It was found that sodium sulfinates containing an electron-donating groups such as sodium *p*-tolylsulfinate, sodium benzenesulfinate gave good yields (Table 2, see compounds **3a**, **3b**). However, such as sodium p-trifluoromethylsulfinate, sodium *p*-fluorosulfinate, sodium *p*-bromosulfinate with electron-withdrawing group afforded a lower yield (Table 2, see compounds **3c**, **3d**, **3e**). Meanwhile, the bulkier group at the phenyl ring of sodium sulfinate impede the reaction, as exemplified by **3f**, **3g**. Additionally, heterocyclic-derived of sodium sulfinates also have a lower yield (Table 2, see compounds **3h**, **3j**, **3k**). Unfortunately, no product was delivered when using sodium propane-2-sulfinate as reactions (Table 2, see compounds **3r**). Thus, the 4-methyl-*N*-(quinolin-8-yl)benzamide, 2-methyl-*N*-(quinolin-8-yl)benzamide, 4-methoxy-*N*-(quinolin-8-yl) benzamide, 4-bromo-*N*-(quinolin-8-yl)benzamide, 4-cyano-*N*-(quinolin-8-yl)benzamide, *N*-(quinolin-8-yl)furan-2-carboxamide, *N*-(quinolin-8-yl) cyclopropanecarboxamide were subjected to the reaction with various diaryl disulfides under the standard reaction conditions to yield corresponding quinolone products in moderate yields (Table 2, see compounds **3i-3q**). Also, many other examples based on different substituted quinoline ring have been tested, the yield is 53% of **3s** and 72% of **3t** but is trace of **3u** (Table 2, see compounds **3s-3u**). Subsequently, we also investigated the reactions mechanism, many experiments were conducted (Table 3).

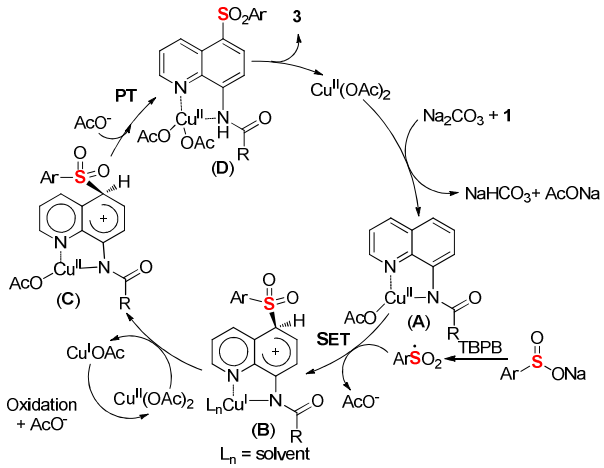
Table 3. Mechanistic studies [a]



Entry	R-H	$ArSO_2R$	Yield [%][b]
1	 4		0
2	 5		0
3	 6		0
4	 1a		Trace[c]
5	 1a		Trace[d]
6		 7	25[e]

[a] Reaction conditions: R-H (0.2 mmol), **2a** (2.0 eq.), $Cu(OAc)_2$ (15 mol%), DTBP (2.0 eq.), Na_2CO_3 (2.0 eq.), acetone (2.0 mL), under air, 60 °C, 12 h. [b] Isolated yields. [c] Add TEMPO (3.0 eq.). [d] Add BHT (3.0 eq.). [e] without $Cu(OAc)_2$, without Na_2CO_3. TBHP = *tert*-Butyl hydroperoxid. TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy. BHT = butylated hydroxytoluene.

There are no sulfonylated products when the N-(naphthalen-1-yl)benzamide **4**, N-methyl-N-(quinolin-8-yl)benzamide **5** and quinolin-8-yl benzoate **6** react with **2a** (entry 1-3, Table 3). In addition, when some radical scavengers such as TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) or BHT (butylated hydroxytoluene) were used in this sulfonylation reaction, this reaction was inhibited, and trace of **3a** was detected (entry 4-5, Table 3). But the (2-tosylethene-1,1-diyl)dibenzene **7** was observed in the reaction of 1,1-Diphenylethylene with **2a** (entry 6, Table 3). After this, we also investigated the reactions of alternative 8 substitutents and amides at other positions. And find that 8-aminoquinoline, 6-aminoquinoline or N-(quinolin-6-yl)benzamide are no reaction in our reaction conditions.



Scheme 1. Proposed mechanism with the copper catalyst

Refer literature[10a, 13a, 13b, 16, 18, 24f, 26], this experiment maybe the free radical mechanism and a plausible mechanism of this radical coulping reaction is described in Scheme 1. Initially, $Cu(OAc)_2$ reacts with aminoquinoline amides **1** to produce a chelated complex (**A**) which promote by Na_2CO_3. Then, the TBPB made sodium sulfinate form the sulfonyl free radical which reacts with complex (**A**) to generate intermediate (**B**) by a single-electron-transfer (SET) process. The intermediate (**B**) reacts with $Cu(OAc)_2$ to produce intermediate (**C**) and release CuOAc. Meanwhile, the $Cu(OAc)_2$ was regenerated by oxidation. And the intermediate (**D**) has been produced through proton transfer (PT) process. Finally, the intermediate (**D**) delivers the target product **3** and released $Cu(OAc)_2$ which can work for the next catalytic cycle.

Conclusions

We presented an regioselective C-H sulfonylation reaction of *N*-(quinolin-8-yl)benzamide derivers for synthesis of a variety of aminoquinolines-derived sulfones. Furthermore, the sodium sulfinates work as the sulfonylation agents and $Cu(OAc)_2$ work as the catalyst are all commercially available and inexpensive. Importantly, this protocol may provide a environmental-friend and an appealing alternative to the existing approaches to construct functionalized aminoquinolines derivatives, which were utilized as the key intermediates in the synthesis of drug candidates.

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Experimental section

General information

All reactions were run under argon in Schlenk tubes using vacuum lines. CH_3CN, DMF, THF and Acetone, analytical grade were not distilled before use. ^1H NMR, ^{13}C NMR spectra were recorded using a 500 MHz spectrometer in $CDCl_3$ and DMSO with shifts referenced to $SiMe_4$ ($\delta = 0$). IR spectra were recorded on an FTIR spectrophotometer. Melting points were determined by using a local hot-stage melting point apparatus and are uncorrected. Elemental analyses were carried out on a CHN analyzer. Mass spectra were recorded using LC-MS and HRMS (ESI-TOF analyzer) equipment.

General procedure for the synthesis of *N*-(5-tosylquinolin-8-yl)benzamide (3a)

A mixture of the **1a** (49.6 mg, 0.2 mmol), **2a** (71.2 mg, 2.0 eq), $Cu(OAc)_2$ (5.4 mg, 15%) and Na_2CO_3 (42.4 mg, 2.0 eq) in acetone (2.0 mL) was stirred at 60°C under air atmosphere for 12.0 h. Then the mixture was cooled to room temperature and poured into water (12 mL). The mixture was extracted with EtOAc (5 mL x 3) and the combined organic layer was washed with brine (10 mL), dried with Na_2SO_4, and the solvent was removed under reduced pressure. The product **3a** was purified by flash column chromatography using PE/AcOEt as an eluent.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 21376058, 21302171), Zhejiang Provincial Natural Science Foundation of China (No. LZ13B020001) and Science Technology Plan of Zhejiang Province (No. 2014C31153), Science Technology Plan of Shandong Provincial (No. 2012GSF11812).

N-[5-(Toluene-4-sulfonyl)-quinolin-8-yl]-benzamide (3a)[24a]

Obtained as a white solid in 83% yield; M.p. 182-183 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 10.97 (s, 1H), 9.10 (dd, *J* = 8.8, 1.6 Hz, 1H), 9.05 (d, *J* = 8.4 Hz, 1H), 8.88 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.56 (d, *J* = 8.5 Hz, 1H), 8.11 – 8.05 (m, 2H), 7.89 – 7.82 (m, 2H), 7.68 – 7.50 (m, 4H), 7.28 (d, *J* = 8.7 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.70, 148.72, 144.16, 139.94, 139.12, 138.50, 134.41, 133.65, 132.44, 132.08, 129.92, 129.48, 128.97, 127.44, 127.32, 124.35, 123.32, 114.35, 21.52.

N-(5-(phenylsulfonyl)quinolin-8-yl)benzamide (3b)[24a]

Obtained as a white solid in 85% yield; M.p. 176-177 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 10.97 (s, 1H), 9.06 (dd, *J* = 16.1, 8.5 Hz, 2H), 8.87 (s, 1H), 8.57 (d, *J* = 8.3 Hz, 1H), 8.06 (d, *J* = 7.3 Hz, 2H), 7.96 (d, *J* = 7.5 Hz, 2H), 7.52 (dd, *J* = 39.9, 7.2 Hz, 7H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.69, 148.79, 142.08, 140.13, 138.51, 134.36, 133.51, 133.14, 132.46, 132.35, 129.29, 128.98, 128.97, 127.42, 127.21, 124.38, 123.40, 114.28.

N-(5-((4-(trifluoromethyl)phenyl)sulfonyl)quinolin-8-yl) benzamide (3c)[24a]

Obtained as a white solid in 70% yield; M.p. 202-203 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 11.00 (s, 1H), 9.09 (d, *J* = 8.4 Hz, 1H), 9.04 (dd, *J* = 8.8, 1.6 Hz, 1H), 8.91 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.62 (d, *J* = 8.5 Hz, 1H), 8.08 (ddd, *J* = 5.7, 4.7, 3.0 Hz, 4H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.63 – 7.56 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.74, 148.98, 145.58, 140.69, 138.45, 134.93 (q. *J* = 33.0 Hz), 134.18, 133.12, 133.04, 132.59, 129.02, 127.71, 127.63, 127.43, 126.48 (q. *J* = 3.6 Hz), 124.36, 123.98 (q. *J* = 271.4 Hz), 123.71, 114.29.

N-[5-(4-Bromo-benzenesulfonyl)-quinolin-8-yl]-benzamide (3d)[24a]

Obtained as a white solid in 70% yield; M.p. 210-211 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 11.00 (s, 1H), 9.09 – 9.04 (m, 2H), 8.91 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.58 (d, *J* = 8.4 Hz, 1H), 8.14 – 8.06 (m, 2H), 7.86 – 7.81 (m, 2H), 7.64 – 7.62 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.67, 148.88, 141.14, 140.39, 138.48, 134.28, 133.26, 132.59, 132.56, 132.50, 128.98, 128.72, 128.37, 128.34, 127.42, 124.28, 123.53, 114.27.

N-[5-(4-Fluoro-benzenesulfonyl)-quinolin-8-yl]-benzamide (3e)[24b]

Obtained as a white solid in 75% yield; M.p. 207-208 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 10.98 (s, 1H), 9.05 (d, *J* = 8.5 Hz, 2H), 8.90 (d, *J* = 2.7 Hz, 1H), 8.56 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 7.2 Hz, 2H), 7.98 (dd, *J* = 8.9, 5.0 Hz, 2H), 7.64 – 7.55 (m, 4H), 7.16 (t, *J* = 8.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.74, 165.32 (d. *J* = 254.5 Hz), 148.88, 140.26, 138.49, 138.06, 134.26, 133.29, 132.54, 132.39, 130.05 (d. *J* = 9.5 Hz), 129.01, 128.71, 127.43, 124.23, 123.52, 116.64 (d. *J* = 22.5 Hz), 114.27.

N-(5-(mesitylsulfonyl)quinolin-8-yl)benzamide (3f)

Obt ained as a white solid in 40% yield; M.p. 184-186 °C ^1H NMR (500 MHz, $CDCl_3$) δ 10.94 (s, 1H), 8.92 (d, *J* = 8.4 Hz, 1H), 8.86 (d, *J* = 4.2 Hz, 1H), 8.82 (d, *J* = 8.7 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 3H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 3H), 6.95 (s, 2H), 2.56 (s, 6H), 2.29 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 165.70, 148.81, 143.59, 140.03, 139.05, 138.45, 134.46, 134.30, 133.32, 132.45, 132.38, 132.08, 129.36, 128.95, 127.40, 124.05, 123.11, 113.79, 22.81, 21.05.

N-(5-(naphthalen-2-ylsulfonyl)quinolin-8-yl)benzamide (3g)[24a]

Obtained as a white solid in 73% yield; M.p. 168-169 °C ^1H NMR (500 MHz, $CDCl_3$) δ 10.93 (s, 1H), 9.13 (dd, *J* = 8.7, 1.3 Hz, 1H), 9.05 (d, *J* = 8.4 Hz, 1H), 8.82 (dd, *J* = 4.2, 1.3 Hz, 1H), 8.66 – 8.58 (m, 2H), 8.08 – 8.01 (m, 2H), 7.94 (s, 1H), 7.85 (d, *J* = 8.7 Hz, 1H), 7.83 – 7.77 (m, 2H), 7.62 – 7.49 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.64, 148.79, 140.14, 138.91, 138.46, 134.94, 134.31, 133.47, 132.45, 132.42, 132.13, 129.67, 129.37, 129.19, 128.96, 128.49, 127.93, 127.71, 127.41, 124.36, 123.43, 122.31, 114.26.

N-(5-(thiophen-2-ylsulfonyl)quinolin-8-yl)benzamide (3h)[24b]

Obtained as a white solid in 72% yield; M.p. 180-181°C. ^1H NMR (500 MHz, $CDCl_3$) δ 10.98 (s, 1H), 9.24 (d, *J* = 7.2 Hz, 1H), 9.02 (d, *J* = 8.4 Hz, 1H), 8.90 (d, *J* = 2.6 Hz, 1H), 8.54 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 7.1 Hz, 2H), 7.73 (d, *J* = 2.5 Hz, 1H), 7.64 (dd, *J* = 8.7, 4.2 Hz, 1H), 7.58 (dd, *J* = 18.8, 8.2 Hz, 4H), 7.04 (dd, *J* = 4.9, 3.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.67, 147.85, 142.86, 139.22, 137.44, 133.34, 132.53, 132.44,

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132.04, 131.46, 130.95, 128.84, 127.97, 126.68, 126.41, 123.25, 122.44, 113.33.

_N_-(5-((4-bromophenyl)sulfonyl)quinolin-8-yl)-4-methyl-benzamide (3i)

Obtained as a white solid in 73% yield; M.p. 172-173 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.94 (s, 1H), 9.03 (t, J = 8.6 Hz, 2H), 8.88 (d, J = 2.7 Hz, 1H), 8.54 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.2 Hz, 2H), 7.80 (d, J = 8.7 Hz, 2H), 7.60 (d, J = 8.7 Hz, 3H), 7.35 (d, J = 8.0 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.65, 148.85, 143.22, 141.15, 140.52, 138.46, 133.22, 132.59, 131.44, 129.65, 129.36, 128.71, 128.32, 128.12, 127.45, 124.27, 123.52, 114.16, 77.32, 77.06, 76.81, 21.59. HRMS (ESI+): Calculated for $C_{23}H_{17}BrN_2O_3S$, $[M+H]^+$ 481.0216, Found 481.0226.

Methyl-3-((8-(4-methylbenzamido)quinolin-5-yl)sulfonyl) thiophene-2-carboxylate (3j)

Obtained as a white solid in 48% yield; M.p. 184-185 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.99 (s, 1H), 9.09 (d, J = 8.5 Hz, 1H), 8.90 (d, J = 7.3 Hz, 2H), 8.69 (d, J = 8.5 Hz, 1H), 7.98 (d, J = 8.0 Hz, 2H), 7.87 (d, J = 5.2 Hz, 1H), 7.60 (d, J = 5.2 Hz, 1H), 7.57 (d, J = 4.1 Hz, 1H), 7.37 (d, J = 7.9 Hz, 2H), 3.79 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.66, 159.19, 148.54, 144.94, 143.15, 140.23, 138.15, 134.88, 134.08, 133.08, 131.54, 131.02, 130.13, 129.65, 127.91, 127.45, 124.48, 123.31, 113.60, 52.90, 21.62. HRMS (ESI+): Calculated for $C_{23}H_{18}N_2O_5S_2$, $[M+H]^+$ 467.0730, Found 467.0735.

***N*-(5-((3,5-dimethylisoxazol-4-yl)sulfonyl)quinolin-8-yl)-2-methylbenzamide (3k)**

Obtained as a white solid in 43% yield; M.p. 153-154 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.51 (s, 1H), 9.06 (d, J = 8.4 Hz, 1H), 8.92 (d, J = 8.7 Hz, 1H), 8.87 (d, J = 4.2 Hz, 1H), 8.47 (d, J = 8.4 Hz, 1H), 7.69 (d, J = 7.7 Hz, 1H), 7.62 (dd, J = 8.7, 4.2 Hz, 1H), 7.44 (t, J = 6.9 Hz, 1H), 7.35 (t, J = 7.8 Hz, 2H), 2.79 (s, 3H), 2.61 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.40, 168.38, 157.51, 149.04, 140.62, 138.25, 137.16, 135.52, 132.49, 132.14, 131.70, 131.03, 128.79, 127.28, 126.20, 124.19, 123.55, 117.81, 113.74, 20.28, 12.99, 10.82. HRMS (ESI+): Calculated for $C_{22}H_{19}N_3O_4S$, $[M+H]^+$ 422.1169, Found 422.1178.

4-methyl-_N_-(5-tosylquinolin-8-yl)benzamide (3l)

Obtained as a white solid in 80% yield; M.p. 187-189 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.92 (s, 1H), 9.08 (d, J = 7.4 Hz, 1H), 9.02 (d, J = 8.4 Hz, 1H), 8.86 (d, J = 2.8 Hz, 1H), 8.54 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 8.1 Hz, 2H), 7.83 (d, J = 8.3 Hz, 2H), 7.57 (dd, J = 8.7, 4.2 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 5.7 Hz, 2H), 2.45 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.66, 148.69, 144.11, 143.11, 140.09, 139.15, 138.53, 133.56, 132.11, 131.60, 129.89, 129.63, 129.23, 127.45, 127.30, 124.33, 123.27, 114.19, 21.58, 21.51.

4-methoxy-_N_-(5-tosylquinolin-8-yl)benzamide (3m)[24a]

Obtained as a white solid in 85% yield; M.p. 178-179 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.88 (s, 1H), 9.06 (d, J = 7.3 Hz, 1H), 9.00 (d, J = 8.4 Hz, 1H), 8.85 (d, J = 2.8 Hz, 1H), 8.53 (d, J = 8.4 Hz, 1H), 8.02 (d, J = 8.8 Hz, 2H), 7.83 (d, J = 8.3 Hz, 2H), 7.56 (dd, J = 8.7, 4.2 Hz, 1H), 7.26 (d, J = 8.2 Hz, 2H), 7.03 (d, J = 8.8 Hz, 2H), 3.88 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.64, 159.17, 148.52, 144.92, 143.13, 140.22, 138.14, 134.87, 134.07, 133.06, 131.53, 131.00, 130.12, 129.63, 127.43, 124.46, 123.29, 113.59, 52.88, 21.60.

4-bromo-_N_-(5-tosylquinolin-8-yl)benzamide (3n)[24a]

Obtained as a white solid in 68% yield; M.p. 214-215 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.93 (s, 1H), 9.08 (dd, J = 8.7, 1.6 Hz, 1H), 9.03 (d, J = 8.5 Hz, 1H), 8.86 (dd, J = 4.3, 1.6 Hz, 1H), 8.54 (d, J = 8.4 Hz, 1H), 7.98 – 7.93 (m, 2H), 7.85 – 7.81 (m, 2H), 7.57 (dd, J = 8.7, 4.2 Hz, 1H), 7.35 (d, J = 7.9 Hz, 2H), 7.26 (d, J = 5.7 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.67, 148.69, 144.12, 143.12, 140.09, 139.16, 138.53, 133.57, 132.12, 131.61, 129.90, 129.64, 129.24, 127.46, 127.31, 124.34, 123.28, 114.20, 21.59.

4-cyano-_N_-(5-tosylquinolin-8-yl)benzamide (3o)

Obtained as a white solid in 71% yield; M.p. 170-171 □. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.99 (s, 1H), 9.09 (d, J = 8.9 Hz, 1H), 8.99 (d, J = 8.7 Hz, 1H), 8.89 (d, J = 6.8 Hz, 1H), 8.55 (d, J = 8.6 Hz, 1H), 8.17 (d, J = 8.6 Hz, 2H), 7.85 (dd, J = 13.5, 7.9 Hz, 5H), 7.30 (d, J = 9.7 Hz, 3H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.73, 148.94, 144.32, 139.13, 138.76, 138.35, 138.10, 133.67, 132.79, 131.78, 130.28, 129.95, 128.07, 127.33, 124.22, 123.52, 117.86, 115.91, 114.57, 77.30, 77.05, 76.79, 21.55. HRMS (ESI+): Calculated for $C_{24}H_{17}N_3O_3S$, $[M+H]$+ 428.1064, Found 428.1074.

***N*-(5-tosylquinolin-8-yl)furan-2-carboxamide (3p)**

Obtained as a white solid in 59% yield; M.p. 193-195 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.99 (s, 1H), 9.08 (dd, J = 8.7, 1.4 Hz, 1H), 8.98 (d, J = 8.4 Hz, 1H), 8.90 (dd, J = 4.1, 1.4 Hz, 1H), 8.53 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 8.3 Hz, 2H), 7.65 (s, 1H), 7.58 (dd, J = 8.7, 4.1 Hz, 1H), 7.35 (dd, J = 3.8, 2.6 Hz, 1H), 7.31 – 7.25 (m, 2H), 6.62 (dd, J = 3.4, 1.7 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.45, 148.83, 147.76, 145.05, 144.16, 139.59, 139.03, 138.36, 133.43, 131.89, 129.90, 127.31, 124.29, 123.33, 116.17, 114.28, 112.72, 21.51.

***N*-(5-tosylquinolin-8-yl)cyclopropanecarboxamide (3q)**

Obtained as a white solid in 71% yield; M.p. 211-213 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.25 (s, 1H), 9.03 (dd, J = 8.7, 1.6 Hz, 1H), 8.85 – 8.80 (m, 2H), 8.48 (d, J = 8.4 Hz, 1H), 7.83 – 7.79 (m, 2H), 7.54 (dd, J = 8.7, 4.2 Hz, 1H), 7.25 (d, J = 8.0 Hz, 2H), 2.35 (s, 3H), 1.85 – 1.79 (m, 1H), 1.17 (dd, J = 4.5, 3.0 Hz, 2H), 0.96 (dd, J = 7.8, 3.1 Hz, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ 172.85, 148.54, 144.10, 139.94, 139.02, 137.88, 133.36, 132.05, 130.02, 129.87, 128.73, 128.22, 127.22, 124.21, 123.24, 113.98, 21.53, 16.45, 8.84. HRMS (ESI+): Calculated for $C_{20}H_{18}N_2O_3S$, $[M+H]^+$ 367.1111, Found 367.1118.

***N*-(2-methyl-5-tosylquinolin-8-yl)benzamide (3s) [22b]**

Obtained as a yellow solid in 53% yield; M.p. 200-201 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.03 (s, 1H), 9.01 (d, J = 8.0 Hz, 1H), 8.94 (d, J = 10.0 Hz, 1H), 8.48 (d, J = 8.0 Hz, 1H), 8.06 (d, J = 10.0 Hz, 2H), 7.83 (d, J = 8.0 Hz, 2H), 7.57 (m, 3H), 7.44 (d, J = 8.0 Hz, 1H), 7.26 (t, J = 4.0 Hz, 2H), 2.76 (s, 3H), 2.36 (s, 3H).

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DOI: 10.1039/C6RA04013F

***N*-(6-methoxy-5-tosylquinolin-8-yl)benzamide (3t) [22b]**

Obtained as a yellow solid in 72% yield; M.p. 188-189 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.11 (s, 1H), 9.54 (dd, *J* = 9.0, 2.0 Hz, 1H), 8.80 (s, 1H), 8.75 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.62 (m, 2H), 7.55 (t, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.87(s, 3H), 2.40 (s, 3H).

1-(2,2-Diphenyl-ethenesulfonyl)-4-methyl-benzene (7)[9b]

Obtained as a white solid in 25% yield; M.p. 93-94 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 4.3 Hz, 4H), 7.17 (d, *J* = 7.2 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 7.0 Hz, 2H), 6.98 (s, 1H), 2.34 (s, 3H).

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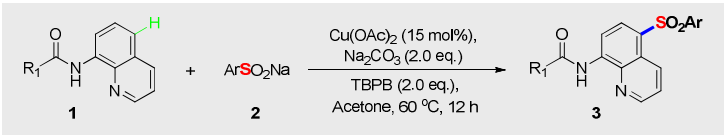
DOI: 10.1039/C6RA04013F



Text for Table of Contents: *Many various aminoquinolines-derived sulfones were obtained in moderate to high yields by Copper(II)-Catalyzed direct C(sp^2)-H sulfonylation of aminoquinolines with sodium sulfinates.*

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Copper(II)-Catalyzed Remote Sulfonylation of Aminoquinolines with Sodium Sulfinates via Radical Coulping