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Cobalt(II)-catalyzed remote C5-selective C–H sulfonylation of quinolines *via* insertion of sulfur dioxide†

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A novel and simple method for C–H sulfonylation of quinolines based on an inexpensive cobalt catalyst *via* insertion of sulfur dioxide is established. Excellent selectivity in the C5-position of quinolines is observed. This transformation has no need of oxidant and additive, affording sulfonated products in moderate to good yields. Furthermore, aromatic amines can displace aryldiazonium tetrafluoroborates as original materials *via* the *in situ* diazotization. The results of control experiments indicate that a radical pathway is involved in this sulfonylation.

Introduction

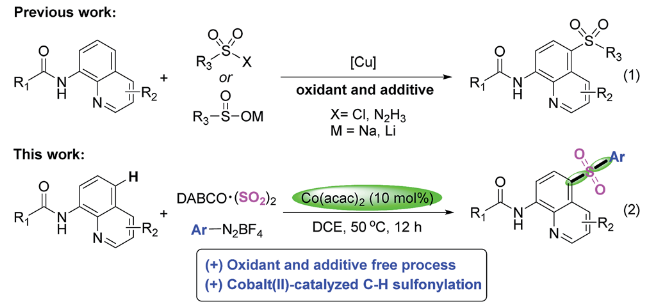
Heterocyclic aromatic sulfones are significant skeletons due to their extensive application in organic chemistry,[1] and pharmaceutical chemistry[2] as well as material chemistry.[3] Hence, the development of procedures for sulfonylation has become increasingly significant in synthetic methodology. Classic synthetic routes to sulfones are the oxidation of thioether and the Friedel–Crafts reaction.[4] Nevertheless, these typical reactions usually require harsh reaction conditions, including strong oxidants, strong acids and a high reaction temperature.

In recent decades, transition-metal-catalyzed C–H functionalization has become a novel and efficient strategy in the synthesis of various organic molecules.[5] Especially, a series of synthetic methods have been exhibited for the preparation of sulfones by employing different substrates.[6] In pioneering studies, Dong and co-workers disclosed a Pd(II)-catalyzed *o*-sulfonylation protocol which allowed the isolation of the *o*-sulfonylation products in good yields.[7] As interesting as the former, Frost *et al.* developed Ru(II)-catalyzed sulfonylation of 2-phenylpyridines and obtained the *m*-sulfonylation product in considerable yield.[8]

For the past few years, owing to the special properties of quinolines,[9] a series of researches were pursued by utilizing quinolines as raw materials for the C–H functionalization.[10] Especially, the C5-functionalization of quinolines has achieved much attention. Prior works from many groups were focused on copper-catalyzed C–H functionalization[11] or transition-metal-free oxidative coupling reaction with a stoichiometric amount of oxidants.[12] But only a few examples were developed which employed iron,[13] cobalt[14] and nickel[15] as catalyst.

Additionally, Among C5-functionalization of quinolines, the C5-sulfonylation has been successively reported by choosing sulfonyl chloride, sulfinates as well as sulfonhydrazide as the source of sulfonyl, respectively (Scheme 1, eqn (1)).[16] Despite their utilities represent very inspiring progress, as mentioned above, almost all of them were catalyzed by copper catalyst. In addition, a stoichiometric amount of oxidants and additives were usualy indispensable, not only increasing wastes, but also making this method inadaptable to large-scale synthesis. In recent years, the advance in the synthesis of sulfones *via* insertion of sulfur dioxide has been accomplished rapidly.[17,18] Generally, the available DABCO·$(SO_2)_2$ and inorganic sulphites such as rongalite and potassium metabisulfite were used as the source of sulfur dioxide rather than toxic gaseous sulfur dioxide in organic reactions. Very recently, Wu and coworkers reported a copper-catalyzed sulfonylative C–H bond functionalization of quinolines from DABCO·$(SO_2)_2$ and aryldiazonium tetrafluoroborates.[21l]

Currently, the field of cobalt-catalyzed C–H functionalization has started to receive considerable attention due to its cheaper



Scheme 1 Summary of sulfonylation of quinoline amides.

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and more abundant characteristics.[19] Herein, we report a cobalt(II)-catalyzed and convenient protocol for highly selective C5-sulfonylation of quinolines with DABCO·$(SO_2)_2$ and aryldiazonium salts to give the desired products in moderate to excellent yields under oxidant and additive free condition.

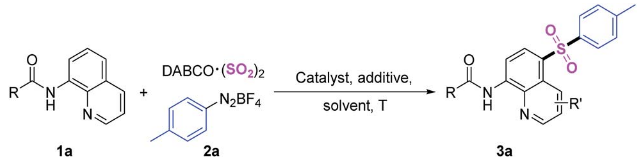
Results and discussion

Initially, the three-component reaction of *N*-(quinolin-8-yl) benzamide (**1a**), DABCO·$(SO_2)_2$ and *p*-tolyldiazonium tetrafluoroborate (**2a**) was selected as the model reaction for the development of the optimal reaction conditions. The desired C5-sulfonylated product (**3a**) was obtained in 49% yield by using CuI as catalyst in the presence of Na_2CO_3 in DCE for 12 h under N_2 (Table 1, entry 1). Encouraged by this result, some metal catalysts including iron(III), iron(II), nickel(II), cobalt(II), copper(I) and copper(II) were studied (Table 1, entries 2–9), the yields of target product **3a** was increased to 64% by using Co(acac)$_2$ as catalyst (Table 1, entry 10). No product was formed in the absence of any metal catalyst (Table 1, entry 11). After that, we also screened several additives (Table 1, entries 12 and 13). Curiously, the higher yield was got in the absence of any additive (Table 1, entry 14). No better results were gained in further variations in solvents, temperature and so forth (Table 1, entries 15–20). Actually, we also screened the reaction condition by using Cu(acac)$_2$ as a catalyst, the results were shown in ESI.†

After getting the optimized reaction condition, we next explored the scope of sulfonylation reaction of **2** with *N*-(quinolin-8-yl)benzamide and DABCO·$(SO_2)_2$ (Table 2). Numbers of aryl diazonium salts with different substituent groups were investigated. Overall, all the substrates could transform into corresponding products smoothly. By contrast, the compatibility of electron-donating groups on aryldiazonium tetrafluoroborates was better. Moreover, the molecular structure of product **3f** was confirmed by X-ray crystallographic analysis. Product **3j** was got in lower yield due to the steric-hindrance effect of 2,4,6-trimethylbenzene diazonium salt (Scheme 2).

After that, the sulfonylation reactions of *p*-tolyldiazonium tetrafluoroborate (**2a**), DABCO·$(SO_2)_2$ and quinoline amides were discussed (Table 3). The substituent effects on the benzene ring of quinoline amides revealed a lesser impact, both electron-donating and electron-withdrawing groups were tolerated in this reaction. The carboxamides with 2-thiazolyl, cyclohexyl as well as cyclopropyl furnished target products **3r**, **3s** and **3t** in high yields too. In addition, the different substituent groups on quinoline ring were also researched. Corresponding products (**3u–x**) were got in ideal yield. Regrettably, product **3y** was not detected because of the influence of ester group.

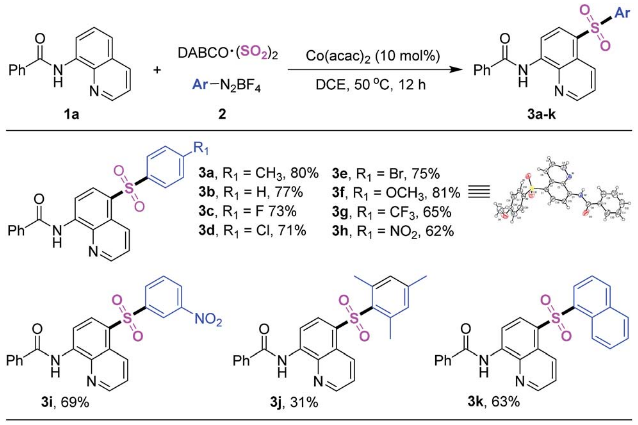
Table 1 Screening of reaction conditions for sulfonylation[a]



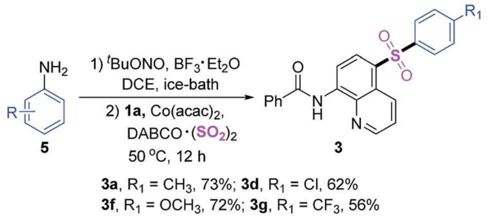
Entry	Catalyst	Additive	Solvent	Yield[b] [%]
1	CuI	Na_2CO_3	DCE	49
2	Fe(OTf)$_3$	Na_2CO_3	DCE	13
3	Fe(OAc)$_2$	Na_2CO_3	DCE	Trace
4	Ni(OTf)$_2$	Na_2CO_3	DCE	Trace
5	CoF_2	Na_2CO_3	DCE	15
6	$CoCl_2$	Na_2CO_3	DCE	20
7	$CoBr_2$	Na_2CO_3	DCE	31
8	$Co(NO_3)_2$	Na_2CO_3	DCE	43
9	Co(OAc)$_2$	Na_2CO_3	DCE	57
10	Co(acac)$_2$	Na_2CO_3	DCE	64
11	—	Na_2CO_3	DCE	0
12	Co(acac)$_2$	$NaHCO_3$	DCE	62
13	Co(acac)$_2$	AcOH	DCE	46
14	**Co(acac)$_2$**	—	**DCE**	**80**
15	Co(acac)$_2$	—	Dioxane	53
16	Co(acac)$_2$	—	Toluene	Trace
17	Co(acac)$_2$	—	DMF	14
18[c]	Co(acac)$_2$	—	DCE	42
19[d]	Co(acac)$_2$	—	DCE	53
20[e]	Co(acac)$_2$	—	DCE	78

[a] Reaction conditions: **1a** (0.2 mmol), catalyst (10 mol%), DABCO·$(SO_2)_2$ (1.2 equiv.), **2a** (1.2 equiv.), DCE (1.0 mL), stirred at 50 °C, under N_2, 12 h. [b] Isolated yields. [c] Under air. [d] Stirred at rt. [e] Stirred at 80 °C.

Table 2 Substrate scope of aryl diazonium salts with **1a**[a]

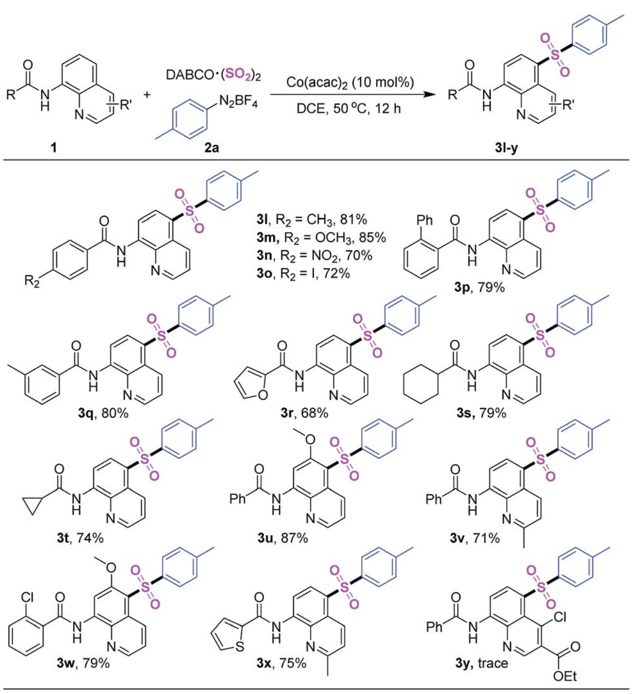


[a] Reaction conditions: **1a** (0.2 mmol), Co(acac)$_2$ (10 mol%), DABCO·$(SO_2)_2$ (1.2 equiv.), **2** (1.2 equiv.), DCE (1.0 mL), stirred at 50 °C, under N_2, 12 h, isolated yields.



Scheme 2 Sulfonylation of quinoline amides by using anilines as the starting materials.

Table 3 Substrate scope of quinoline amides with **2a**[a]

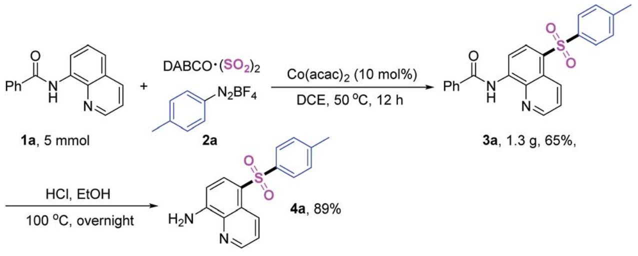


[a] Reaction conditions: **1** (0.2 mmol), $Co(acac)_2$ (10 mol%), DABCO·$(SO_2)_2$ (1.2 equiv.), **2a** (1.2 equiv.), DCE (1.0 mL), stirred at 50 °C, under N_2, 12 h, isolated yields.

Considering anilines are cheap and available materials, furthermore, the stability of aryldiazonium tetrafluoroborates are poor, therefore, we then investigated the possibility by using aromatic amines as original materials *via* the *in situ* diazotization. Interestingly, this reaction took place smoothly, which afforded desired products in moderate yields.

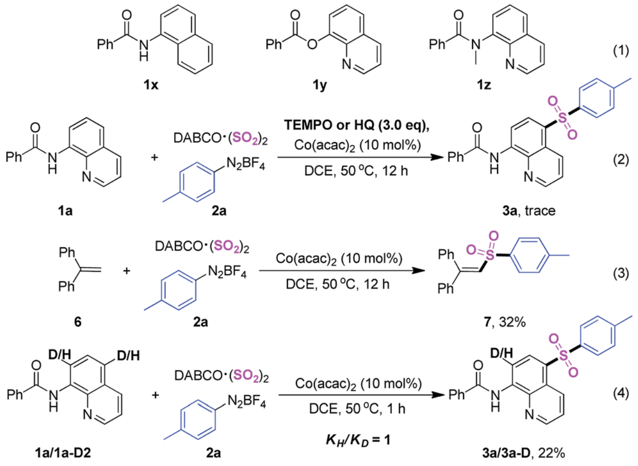
Subsequently, we studied the application values of this reaction (Scheme 3). Gram-scale synthesis was carried out under standard conditions, and sulfonated product was isolated in 69% yield. Obviously, the productive rate was reduced when the scale of reaction was amplified. Then hydrolysis reaction was performed, and the C5-sulfonated 8-aminoquinoline was acquired in 89% yield.

Several control experiments were achieved in order to gain more deep understanding about the reaction mechanism. In the first place, three analogues (**1x–z**) were employed as substrates under the standard conditions and no products were detected, this result revealed that a free NH of amides and N atom of quinoline were crucial blocks for the sulfonylation (Scheme 4, eqn (1)). Next, TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) and HQ (hydroquinone) were used as free radical inhibitor respectively, and the sulfonylation reaction was absolutely suppressed (Scheme 4, eqn (2)). Additionally, 32% yield of compound **7** was isolated when 1,1-diphenylethlene was utilized as trapping agent (Scheme 4, eqn (3)), declaring that a radical pathway was included. Finally, further test about kinetic isotope effects (KIE) gave a low ratio ($k = 1.0$) (Scheme 4, eqn (4)), suggesting that the rate determining step was not the process of cleavage of C–H bond.[20]

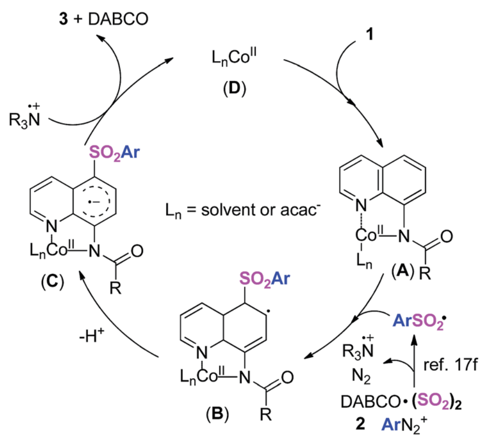


Scheme 3 Gram-scale sulfonylation and synthetic applications.

According to the experiment conclusions and previous reports,[11–17,21] a plausible mechanism was proposed (Scheme 5). Initially, complex **A** was produced *via* the combination of L_nCo^{II} (**D**) and substrate **1**. In the meantime, the sulfonyl radical was formed through insertion of sulphur dioxide.[17f] Subsequently, sulfonyl radical attacked intermediate **A** to afford complex **B**. After the generation of complex **C** *via* dehydrogenation process, desired product **3** was obtained through single electron transfer (SET) between complex **C** and tertiary amine cation radical.



Scheme 4 Investigation of the mechanism.



Scheme 5 Plausible mechanism.

Conclusions

In conclusion, we have developed a cobalt(II)-catalyzed method for highly selective C5-sulfonylation of quinolines *via* insertion of sulfur dioxide under oxidant and additive free condition. This transformation proved a broad substrate scope and high efficiency. Furthermore, aromatic amines could displace aryldiazonium tetrafluoroborates as original materials *via* the *in situ* diazotization. Eventually, a single electron transfer (SET) mechanism was presented after verification of control experiments.

Conflicts of interest

There are no conflicts to declare.

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