

Synthetic Methods | Hot Paper |

Copper-Catalyzed Regioselective Cleavage of C–X and C–H Bonds: A Strategy for Sulfur Dioxide Fixation

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Abstract: The first example of direct fixation of sulfur dioxide between heteroaryls and aryl halides has been developed via copper-catalyzed regioselective cleavage of C–X and C–H bonds under base-free and ligand-free conditions by using DABSO (1,4-diazabicyclo[2.2.2]octane bis(sulfur dioxide)) as a solid and bench-stable sulfur dioxide surrogate.

This mild protocol results in double C–S bond-forming reactions from simple precursors in the absence of prefunctionalized organometallic reagents, arenediazonium salts, and iodonium salts which extends the still limited number of sulfur dioxide fixation strategies.

Introduction

Organosulfones represent one of the most important motifs of sulfur-containing compounds which are widely found in biologically active compounds, pharmaceuticals, and agrochemicals (Figure 1).^[1] Additionally, sulfone groups can also be used

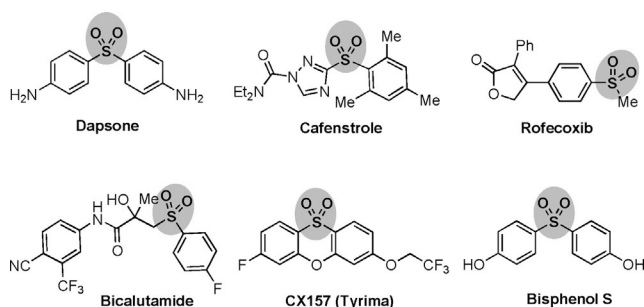


Figure 1. Representative sulfone-containing compounds in pharmaceuticals.

as versatile synthetic intermediates for various chemical transformations in synthetic organic chemistry.^[2] Therefore, the development of more efficient and green approaches for the introduction of sulfone group into organic skeletons have

gained significant interests among medicinal and synthetic organic chemists. The traditional strategies for the construction of sulfone groups mainly involve four approaches: (a) direct oxidation of the corresponding sulfides or sulfoxides,^[3] (b) transition-metal-catalyzed cross-coupling reactions of aryl halides or triflates with sulfinic salts,^[4] (c) Friedel–Crafts-type sulfonylation of electron-rich arenes,^[5] (d) difunctionalization of alkenes and alkynes with sulfinic acids or sulfinic salts.^[6] Almost all of these methods for the construction of sulfonyl skeleton utilize sulfur-containing starting materials, but in most cases, these starting materials are not easily available. Therefore, seeking more efficient methods for the incorporation of the sulfonyl moieties using readily available and simple sulfur sources is highly desirable.

Sulfur dioxide (SO₂) is an abundant industrial emission. Clearly, the direct fixation of sulfur dioxide into small molecules is attractive and of great interest. Indeed, transformations of SO₂ to useful sulfone-containing chemicals have been attracting increasing attentions for a long time.^[7] For instance, sulfur dioxide (SO₂) has been widely used in a number of pericyclic reactions for the synthesis of complex polyfunctionalized molecules.^[8] Reaction of sulfur dioxide with either organolithiums or Grignard reagents are also an efficient pathway to organosulfone compounds.^[9] Besides that, sulfur dioxide has also been applied in alkene isomerization reactions.^[10] Excellent as these methods are, there are some disadvantages associated with the gaseous, corrosive and notorious toxic nature of sulfur dioxide.

As an alternative, 1,4-diazabicyclo[2.2.2]octane bis(sulfur dioxide) adduct (named DABSO) as a solid and bench-stable sulfur dioxide surrogate has been successfully introduced by Willis. In 2010, Willis's group initially reported an efficient palladium-catalyzed aminosulfonylation process to aryl *N*-aminosulfonamides using solid DABSO as an easy to handle equivalent of sulfur dioxide (SO₂).^[11] Afterwards, tremendous progress has been made in the synthesis of sulfonamides, sulfamides, *N*-aminosulfonamides, and sulfones by using DABSO or K₂S₂O₅ as

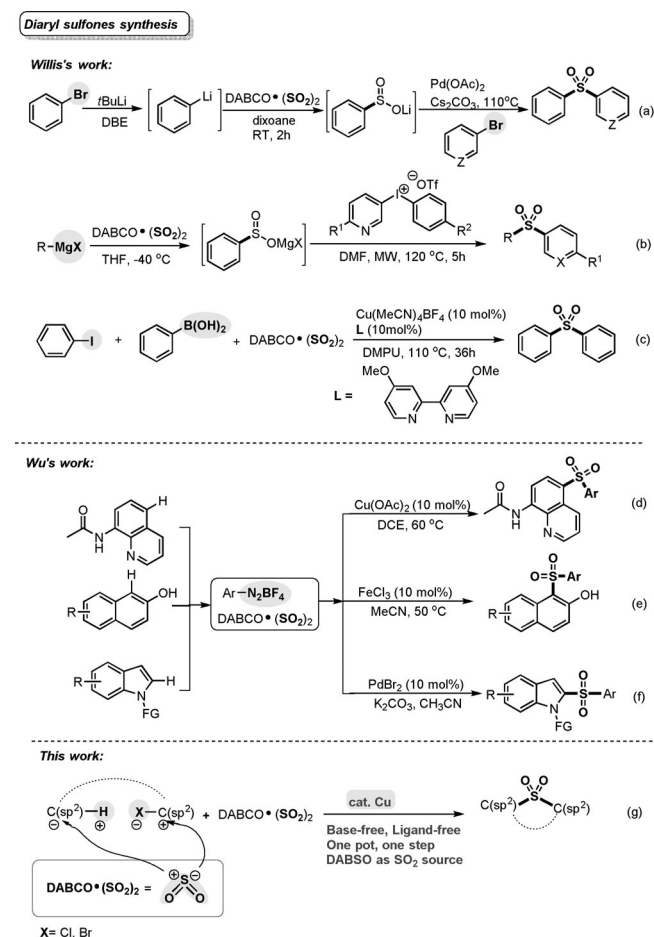
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the sulfur dioxide (SO₂) sources.^[12] Despite aryl alkyl sulfones have been constructed from organometallic reagents/organic halides, DABSO and electrophilic reagents, a literature survey showed that the synthetic approaches for the formation of diaryl sulfones using DABSO as the sulfonyl source are rather limited.^[13] In 2013, Willis and co-workers described a convergent three-compound palladium-catalyzed method for the synthesis of diaryl sulfones using DABSO as the sulfur dioxide surrogate (Scheme 1a).^[14] In 2014, Willis's group developed an el-

cles.^[18] Clearly, the direct fixation of sulfur dioxide into organic skeleton via regioselective cleavage of inert C–H bond would be more practical and economical. Notably, during the submission process of our manuscript Wu and co-workers developed three efficient approaches to diaryl sulfones through copper-, iron-, or palladium -catalyzed sulfonylative C–H functionalization from aryldiazonium salts and DABSO (Scheme 1d–f).^[17] Since the sulfur dioxide surrogate DABSO has been reported to act as a sulfonyl cation/anion synthon in sulfones synthesis, we envisage that diaryl sulfones could be constructed starting from readily available heteroaryls and aryl halides via transition-metal-catalyzed aerobic oxidative aromatic C–H bond and C–X bond sulfonylation (Scheme 1g). As a continuous interest of our research in sulfur-containing molecules synthesis,^[19] herein, we report an efficient and simple copper-catalyzed method for the construction of sulfone functional group using DABSO as a sulfur dioxide (SO₂) surrogate under base-free and ligand-free conditions (Scheme 1g). To the best of our knowledge, copper-catalyzed coupling of C(sp²)–X bond and C(sp²)–H bond by using DABSO as a building block to construct sulfone motifs has not been established until now.



Scheme 1. Strategies for the synthesis of diaryl sulfones.

egant one-pot approach for the construction of diaryl sulfones through the reaction of in situ generated metal sulfonates with iodonium salts (Scheme 1b).^[15] In 2017, the same group also reported a highly efficient copper-catalyzed sulfonylative Suzuki–Miyaura cross-coupling reaction using DABSO as the SO₂ surrogate reagent (Scheme 1c).^[16] Despite the great achievements of these reactions, some drawbacks can be encountered such as harsh reaction conditions, pre-functionalized substrates, and multi-step procedures. Thus, it still remains a formidable challenge to develop more convenient and practical methods for constructing diaryl sulfones by using bench-stable DABSO as a sulfur dioxide (SO₂) equivalent.

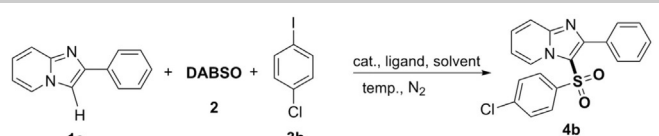
In recent years, C–H activation/functionalization has become a powerful strategy for constructing diverse organic mole-

Results and Discussion

First, 2-phenylimidazo[1,2-*a*]pyridine (**1a**), DABSO (**2**), and 1-chloro-4-iodobenzene (**3b**) were used as the model substrates to optimize the reaction conditions, including the catalysts, ligands, and solvents under a nitrogen atmosphere (Table 1). To our delight, an 58% yield of the desired product **4b** was obtained in the presence of 10 mol% CuCl and 10 mol% 1,10-phenanthroline in DMSO at 130 °C for 24 h. Other copper catalysts including CuBr, CuI, Cu₂O, Cu(OAc)₂, CuO and CuCl₂ were also tested, showing that Cu₂O was the most effective catalyst (entry 4). Next, different ligands were examined (entries 4, 8–10), and 1,10-phenanthroline (**L1**) showed the greater activity to give the corresponding product **4b** in 68% yield (entry 4). Furthermore, we attempted to use different solvents including DMSO, DMF, and NMP, and DMF provided the highest yield (entry 10). To our surprise, control experiments demonstrated that the ligand was not necessary for this transformation, and only a slightly low yield was obtained in the absence of 1,10-phenanthroline (entries 11 and 13). In addition, various reaction temperatures were also screened, and 130 °C was demonstrated to be more suitable for this transformation. Subsequently, we investigated the other catalysts such as FeCl₂, FeCl₃, NiCl₂, Pd(OAc)₂, PdCl₂, and Co(OAc)₂, and found that the reaction did not work with these catalysts. After the optimization process for catalysts, ligands, temperature and solvents, the various diaryl sulfones derivatives were synthesized under our standard conditions: 10 mol% Cu₂O as the catalyst, DMF as the solvent under ligand-free and base-free conditions at 130 °C.

The scope and generality of substrates for the copper-catalyzed regioselective sulfonylation of aryl halides and heteroaryls were investigated under the optimized reaction conditions. The results are separately summarized in Tables 2 and 3. As expected, most of the examined substrates could afford the desired products in moderate to good yields. A variety of elec-

Table 1. Optimization of conditions.^[a]



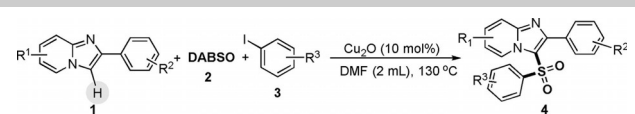
Ligand: L1 (1,10-phenanthroline), L2 (2,2',6,6'-tetramethyl-1,10-phenanthroline), L3 (pyrrolidine-2-carboxylic acid), L4 (N,N-dimethylpyrrolidine).

Entry	Cat.	Ligand	Solvent	Temp.	Yield ^[b]
1	CuCl	L1	DMSO	130 °C	58%
2	CuBr	L1	DMSO	130 °C	47%
3	CuI	L1	DMSO	130 °C	45%
4	Cu ₂ O	L1	DMSO	130 °C	68%
5	Cu(OAc) ₂	L1	DMSO	130 °C	19%
6	CuO	L1	DMSO	130 °C	Trace
7	CuCl ₂	L1	DMSO	130 °C	6%
8	Cu ₂ O	L2	DMSO	130 °C	54%
9	Cu ₂ O	L3	DMSO	130 °C	41%
10	Cu ₂ O	L4	DMSO	130 °C	57%
11	Cu₂O	L1	DMF	130 °C	77%
12	Cu ₂ O	L1	NMP	130 °C	32%
13	Cu₂O	none	DMF	130 °C	76%
14	CuCl	none	NMF	120 °C	52%
15	CuCl	none	DMF	140 °C	74%
16	FeCl ₂	none	DMF	130 °C	0%
17	FeCl ₃	none	DMF	130 °C	0%
18	NiCl ₂	none	DMF	130 °C	0%
19	Pd(OAc) ₂	none	DMF	130 °C	0%
20	PdCl ₂	none	DMF	130 °C	0%
21	Co(OAc) ₂	none	DMF	130 °C	0%

[a] Reaction conditions: **1 a** (0.2 mmol), **2** (0.3 mmol), **3 b** (0.24 mmol), catalyst (0.02 mmol), ligand (0.02 mmol), reaction time (24 h) under a nitrogen atmosphere. [b] Isolated yield.

tron-withdrawing and electron-donating functional groups located at all positions on the any aryl ring of imidazopyridines could be compatible in the present transformation, showing no obvious electronic effects. To our satisfaction, substituted 2-phenylbenzo[d]imidazo[2,1-b]thiazoles also gave good yields of sulfonated products **4p–4r** in 68–81% yields. In addition, we evaluated a range of aryl iodide coupling partners. The substrates bearing electron-withdrawing groups showed higher reactivity than the others containing electron-donating groups. The hindrance effect of this transformation was also not clear, whereas the imidazopyridines ring bearing a substituent group at different positions could give the desired product in moderate yields (**4o** and **4p**). Furthermore, the copper-catalyzed intramolecular sulfonation of readily available 2-(2-halophenyl)imidazo[1,2-*a*]pyridines were investigated (Table 3). It should be noted that, 2-(2-chlorophenyl)imidazo[1,2-*a*]pyridines were also suitable for this transformation, showing no obvious difference when comparing to the bromide substrates (**6a**, **6b** and **6q**). Unfortunately, the nitro group was not well tolerated under the present conditions (**6q**). The reason might be that the weak coordination of Cu^{III} with sulfonyl made Cu^{III} species (**B**) unreactive in the present transformation owing to the much more stronger electron-withdrawing properties of the

Table 2. Scope of the reaction of imidazopyridines **1**, DABSO **2**, and aryl iodides **3**.^[a,b,c]



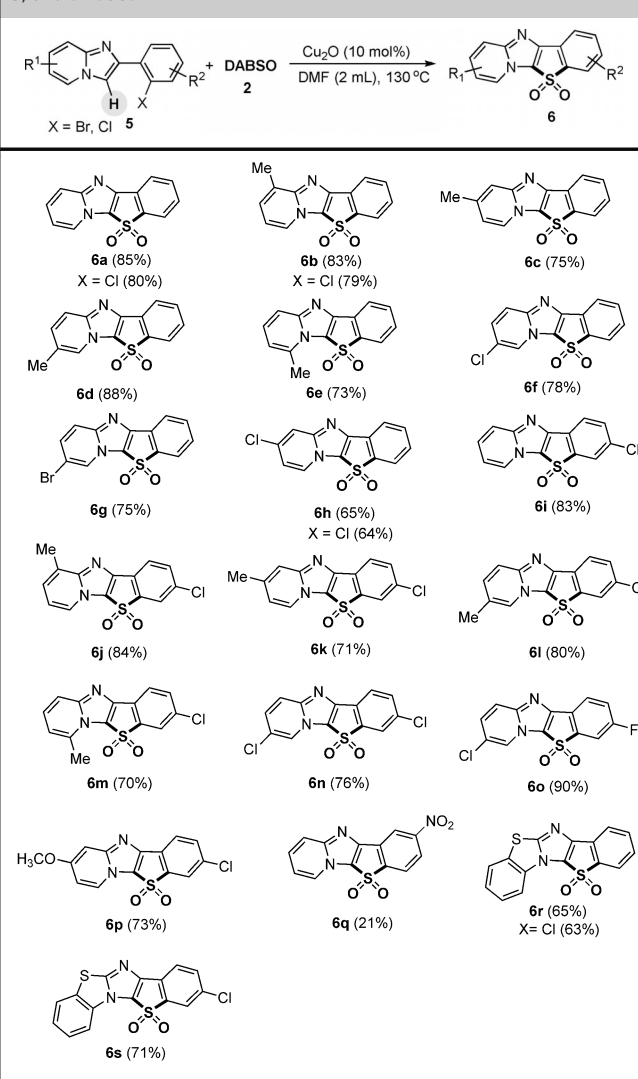
4a (70%)	4b (76%)	4c (74%)
4d (68%)	4e (83%)	4f (71%)
4g (85%)	4h (65%)	4i (71%)
4j (53%)	4k (74%)	4l (56%)
4m (75%)	4n (64%)	4o (73%)
4p (68%)	4q (72%)	4r (81%)

[a] Reaction conditions: under nitrogen atmosphere, substituted imidazopyridines **1** (0.2 mmol), DABSO **2** (0.3 mmol), aryl iodides **3** (0.24 mmol), Cu₂O (0.02 mmol), DMF (2 mL). [b] Isolated yield. [c] Reaction time (24 h).

nitro group (see Scheme 3, the intermediate **B**). Therefore, further efforts to explore more powerful catalytic conditions was required. The copper-catalyzed sulfonation reactions could tolerate some functional groups such as C–Cl bond, C–Br bond, methyl, and ether which could afford some opportunities for further modification.

In order to investigate the possible mechanism of the copper-catalyzed sulfonation of substituted imidazopyridines, kinetic isotope effect (KIE) experiments were carried out as shown in Scheme 2. A primary KIE of 2.33 was observed between **1a** and its deuterated derivative *d*₆-**1a** (Scheme 2a). Furthermore, a significant kinetic isotope effect (*k*_H/*k*_D = 2.21) was observed in an intermolecular competition (Scheme 2b) (see the Supporting Information for detail). These preliminary observations indicated that the aromatic C–H bond activation might be involved in the rate determining step. Further investigations on the more detailed mechanism are ongoing in our laboratory.

Table 3. Scope of the reaction of 2-(2-halophenyl)imidazo[1,2-*a*]pyridines **5**, and DABSO.^[a,b,c]



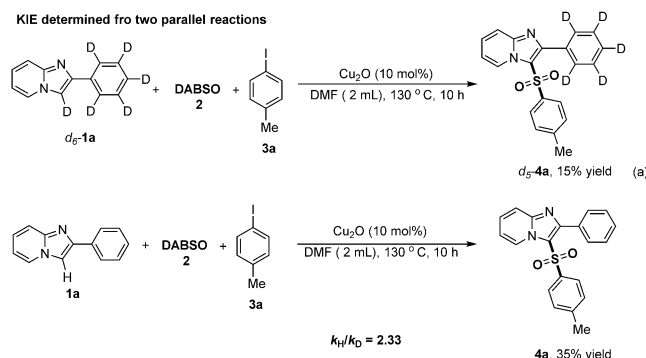
[a] Reaction conditions: under nitrogen atmosphere, substituted imidazo-pyridines **1** (0.2 mmol), DABSO **2** (0.3 mmol), Cu₂O (0.02 mmol), DMF (2 mL). [b] Isolated yield. [c] Reaction time (24 h).

Although a detailed mechanism of the copper-catalyzed sulfonylation reaction awaits the further experimentation, a tentative mechanism was proposed in Scheme 3 on the basis of the preliminary experimental results above and together with the previous related literatures.^[20] Initially, the oxidative addition of Cu^I with an aryl halide afforded a Cu^{III} intermediate **A**, which reacted with sulfur dioxide (DABSO) to produce intermediate **B**. Subsequently, the electrophilic metallation took place between intermediate **B** and a heteroaryl leading to intermediate **C**. Reductive elimination of **C** would deliver the sulfones and regenerated the catalytic species Cu^I.

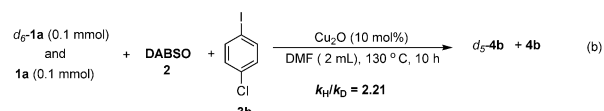
Conclusion

In summary, we have successfully developed a copper-catalyzed three-component reaction of heteroaryls, sulfur dioxide,

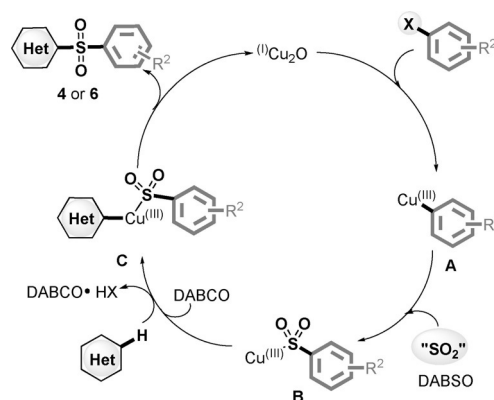
KIE determined from two parallel reactions



KIE determined from an intermolecular competition



Scheme 2. Kinetic isotope effect experiments.



Scheme 3. A proposed mechanism for the direct transformation.

and aryl halides, leading to diaryl sulfones in moderate to good yields. Notably, the sulfonylation reaction proceeded well under base-free or ligand-free conditions. The developed method provided a highly attractive and alternative approach to various potentially bioactive sulfones, and it will broaden the strategies of sulfur dioxide fixation in the field of organic chemistry. Despite some advantages, this transformation could encounter certain limitations, including narrow substrates, long reaction time, and high reaction temperature. Consequently, it has much room for further improvement.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: C–H sulfonylation · copper · heterocycles · sulfur · synthetic methods

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