Research Article

# DABCO-*bis*(sulfur dioxide), DABSO, as a Source of Sulfur Dioxide in Transition Metal-Catalyzed Reactions

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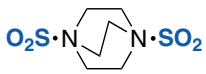
**Abstract:** The *bis*-adduct of DABCO with sulfur dioxide, DABSO, has been shown to function as an effective surrogate for gaseous sulfur dioxide. DABSO is a stable, solid reagent. The use of DABSO has allowed the first efficient transition metal-catalyzed cross-coupling type reactions of sulfur dioxide to be achieved. Early reactions employed palladium catalysts in combination with aryl iodides and *N*,*N*-dialkyl hydrazines, to deliver *N*-aminosulfonamides as products. More recently, alternative aryl substrates such as aryl bromides and aryl boronic acids have been employed, and products such as sulfones and sulfonyl fluorides can now be prepared in an efficient manner. In addition to palladium, reactions have been reported that use copper, cobalt and iridium catalysts. This review considers the catalytic reactions that have been developed using DABSO as a reagent, and is structured by type of catalyst used, and further by the type of product obtained.

**Keywords:** sulfur dioxide, catalysis, sulfonamide, sulfone, transition metal

## 1. Introduction

Sulfur dioxide has a long history of use in organic synthesis as both a reagent and solvent. Pericyclic reactions, including cheletropic additions and ene reactions, as well as the combination with preformed organometallic reagents such as organolithiums and Grignard reagents, are two examples of the transformations for which sulfur dioxide is well known.[1] Despite an extensive literature covering these and related reactions, there were very few examples in the literature of sulfur dioxide being used as a reagent in combination with transition metal catalysts.[2] Notwithstanding the lack of literature precedent, we were interested in the development of cross-coupling type reactions in which sulfur dioxide would be incorporated. Our key breakthrough was the discovery that the *bis*-adduct of DABCO with sulfur dioxide, which we have named DABSO, functions as an effective surrogate[3] reagent for sulfur dioxide gas (Figure 1).[4] DABSO is a colorless crystalline solid that decomposes at 200 °C (DSC). DABSO is air stable and easily handled. It is usually stored under inert gas at room temperature.[5] Although we have shown that DABSO can function as a $SO_2$-surrogate in combination with preformed organometallics,[6] the focus of this review is the use of DABSO in transition metal catalysis.




(**DABSO**) DSC 200 °C
DABCO-*bis*-(sulfur dioxide)

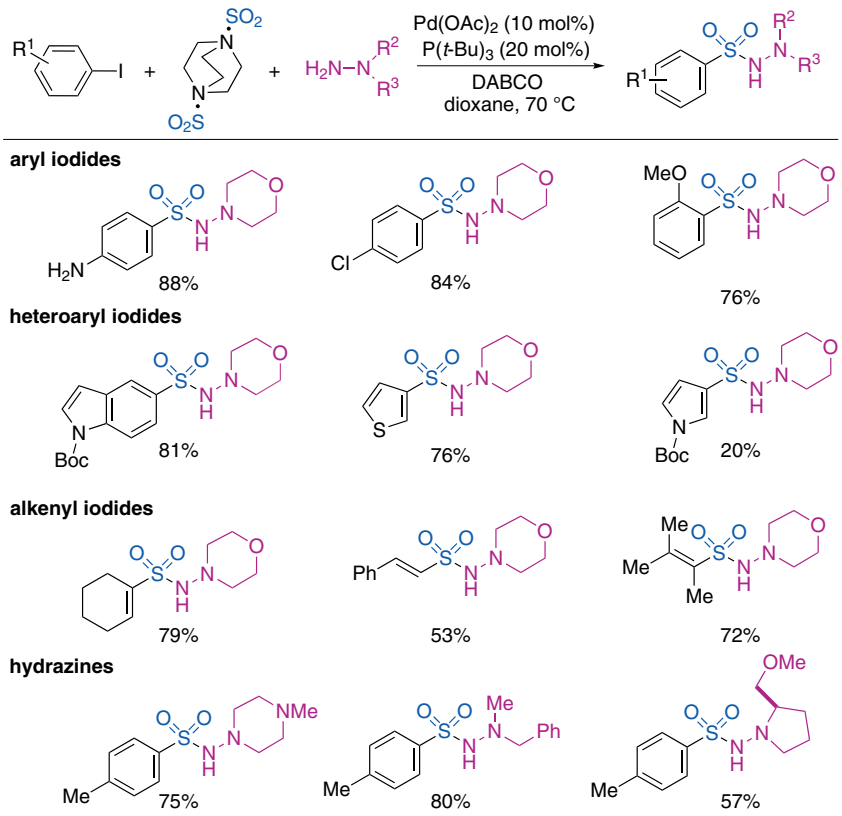
**Figure 1.**

## 2. Palladium-Catalyzed Reactions

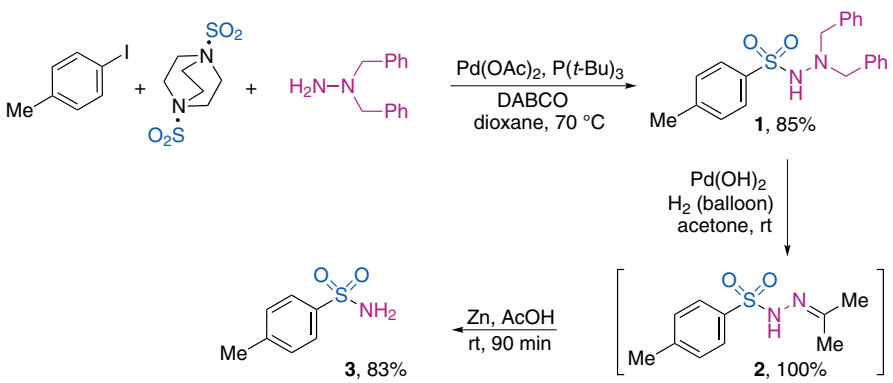
### 2-1. Sulfonamide Synthesis

The sulfonamide functional group features in a wide range of pharmaceuticals and agrochemicals, and as such these important motifs were the first class of compounds that we targeted. The successful chemistry allowed the union of aryl iodides, sulfur dioxide (provided from the reagent DABSO) and *N*,*N*-dialkylhydrazines, using a palladium(0) catalyst, to provide *N*-aminosulfonamides as the products.[7] Selected examples are shown in Scheme 1; variation of the aryl iodide component was readily achieved, and a broad range of functional groups could be tolerated. Heteroaryl iodides were also competent substrates, as were alkenyl iodides. The *N*-nucleophile was limited to *N*,*N*-dialkylhydrazines, but variation of the alkyl substituents of the hydrazine was possible. All of the reactions were achieved using a catalyst generated from P(*t*-Bu)$_3$ (used as its HBF$_4$ salt)[8] and Pd(OAc)$_2$. The majority of reactions required only 0.6 equivalents of DABSO, demonstrating the excellent uptake of SO$_2$ during these reactions. Although this chemistry is limited in the scope of *N*-nucleophiles that can be employed, it does represent the first example of an efficient three-component cross-coupling type reaction that employs sulfur dioxide.

Access to the parent sulfonamides using this chemistry was possible if *N*,*N*-dibenzylhydrazine was used as the *N*-nucleophile. The initially formed *N*-aminosulfonamide **1** was treated with hydrogen gas over a Pd(OH)$_2$ catalyst in acetone as solvent. The *in situ* generated hydrazone **2** was then treated with zinc in acetic acid to provide the parent sulfonamide **3**.[7b]




**Scheme 1.** Palladium-catalyzed *N*-aminosulfonamide synthesis from aryl iodides, DABSO and *N*,*N*-dialkylhydrazines

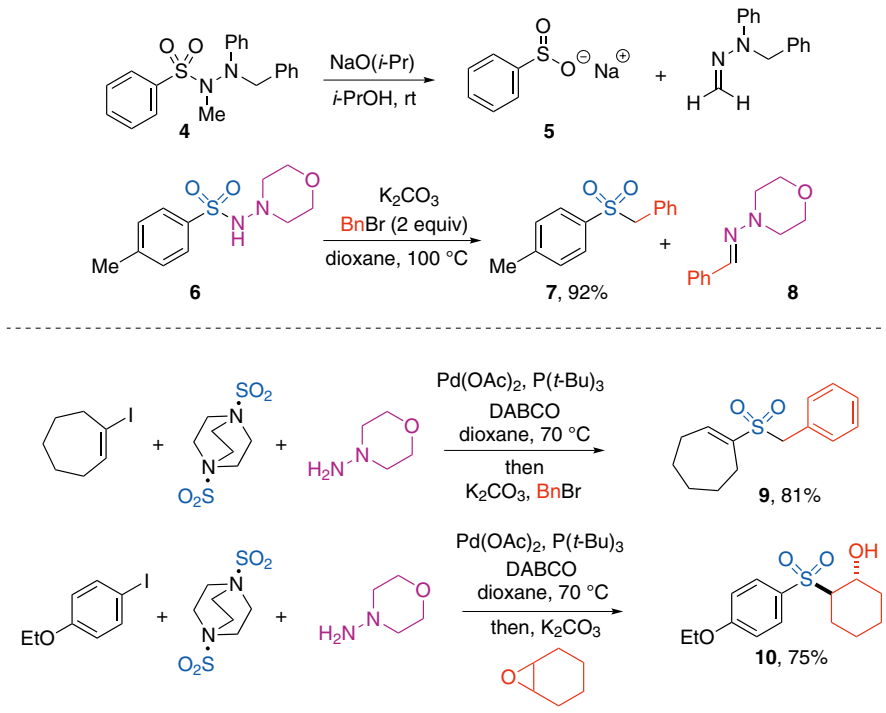



**Scheme 2.** Parent sulfonamide synthesis using *N*,*N*-dibenzylhydrazine as the nucleophile

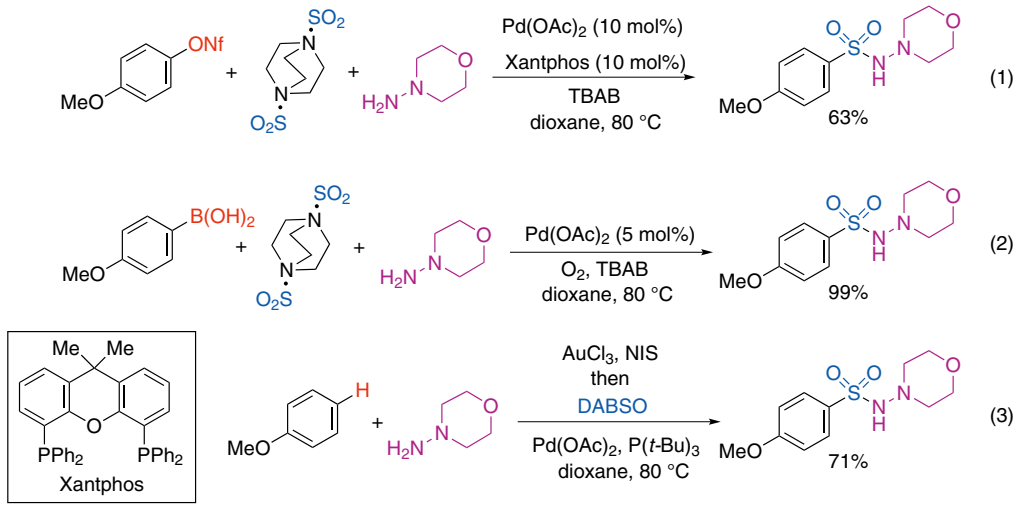
Literature dating from 1957 had shown that *N*-aminosulfonamides can function as precursors to sulfinate salts. For example, when *N*,*N*,*N*-trialkylaminosulfonamide **4** was treated with an alkoxide base in isopropanol, sulfinate **5** was generated in good yield (Scheme 3).[9]

We were able to develop a version of this process that was applicable to the type of aminosulfonamides produced in Scheme 2. For example, following treatment of aminosulfonamide **6** with $K_2CO_3$ and two equivalents of BnBr, sulfone **7** was obtained in 92% yield.[10] The reactions proceed by initial alkylation of the aminosulfonamide *N*-atom, followed by deprotonation and elimination to generate an intermediate sulfinate and hydrazone byproduct **8**; the sulfinate salt reacts with the excess benzyl bromide to provide the desired sulfone. This protocol could be extended to a one-pot process whereby the palladium-catalysed aminosulfonamide synthesis was combined with sulfinate formation/arylation. For example, an alkenyl iodide substrate provided sulfone **9**, while an aryl iodide substrate, in combination with an epoxide electrophile for the second step, provide β-hydroxysulfone **10**.

The Wu group at Fudan University has made significant contributions to the use of DABSO in synthesis. One of their first contributions was to show that aryl nonaflates (perfluorobutanesulfonates) could be used as substrates in place of aryl iodides in the synthesis *N*-aminosulfonamides.[11] The reactions used a modified catalyst system in which Xantphos was employed as the supporting ligand (Scheme 4, eq 1). This is an important extension as it allows phenols to be considered as




**Scheme 3.** Exploiting *N*-aminosulfonamides synthesis for sulfone preparation



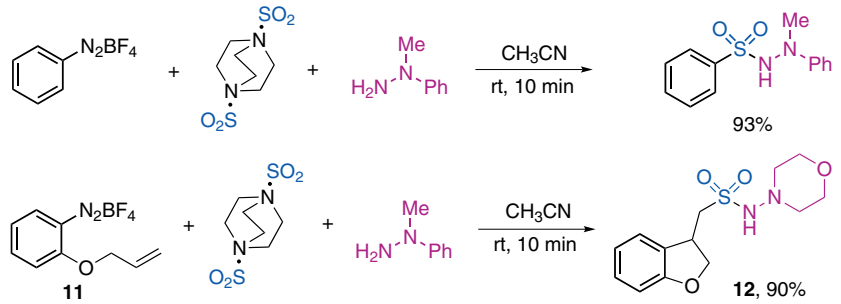

**Scheme 4.** Variation of the arene starting material in the palladium-catalyzed synthesis of *N*-aminosulfonamides

substrates for these reactions. The same group also demonstrated that aryl boronic acids could be employed as substrates (Scheme 4, eq 2).[12] This change to boronic acid substrates required the use of a Pd(II) catalyst and an oxidant, which was provided by an oxygen atmosphere. No phosphine ligand was required for these transformations. The Wu group demonstrated that an initial gold-catalyzed iodination, generating the iodoarene *in situ*, could be combined with the palladium-catayzed aminosufonylation, allowing simple arenes to function as the starting materials (Scheme 4, eq 3).[13] It should be noted that this is a two-step, one-pot process. All three of the transformations shown in Scheme 3, in which the arene starting material is varied, are still limited to the use of *N*,*N*-dialkylhydrazines as the *N*-nucleophiles. The Wu group has also introduced the use of potassium metabisulfate ($K_2S_2O_5$) as an alternative sulfur dioxide surrogate.[14] In their original report, aryl iodides were combined with $K_2S_2O_5$ and *N*,*N*-dialkylhydrazines using Pd(0) catalysis, to provide the expected *N*-aminosulfonamides.

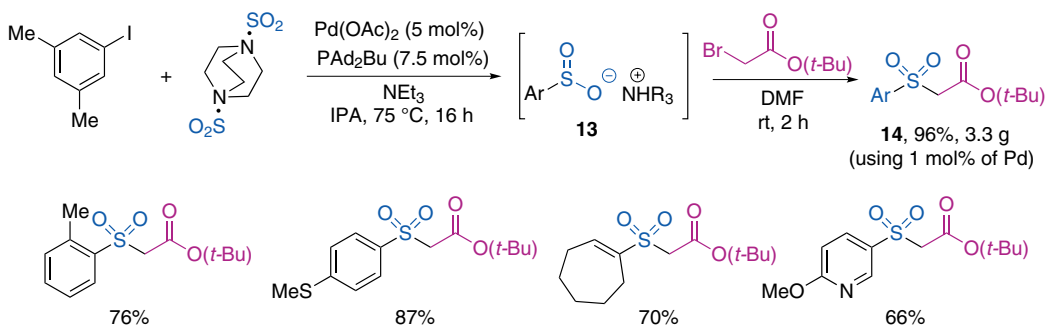
The Wu group have been pioneers of the use of DABSO as a source of sulfur dioxide in radical-based processes, often under metal-free conditions. Although these reactions are beyond the scope of this review, their lead publication in this area is shown in Scheme 5.[15] The reactions employ aryl diazonium salts as aryl radical precursors, which can be combined with DABSO and an *N*,*N*-dialkylhydrazine to deliver *N*-aminosulfonamides as products. Importantly, these reactions are conducted at room temperature. A control reaction, using a substrate that features a tethered alkene (**11**), proceeded *via* cyclisation, ultimately providing *N*-aminosulfonamide **12** as the product, thus confirming the presence of radical intermediates.

## 2-2. Sulfinate Formation

The palladium-catalyzed preparation of *N*-aminosulfonamides, introduced in Scheme 2, established that $SO_2$ could be introduced in cross-coupling type reactions. However, the limitations with respect to the *N*-nucleophile result in the formation of specialized, not generally useful, products. In order to deliver a reaction of more utility we targeted the direct formation of sulfinate salts. This was achieved by replacing the *N*-nucleophile used in Scheme 2 with a hydride source, with the use of isopropanol being most effective; the general process is shown in Scheme 6.[16] Aryl iodides are combined with DABSO in isopropanol (this serves as both solvent and hydride source) using a Pd(0) catalyst generated from $Pd(OAc)_2$ and $PAd_2Bu$, with triethylamine as a base. The resulting sulfinates (**13**), can then be combined with a broad range of electrophiles, for example an alkyl halide, to provide the corresponding sulfone (**14**). When performed on gram scale the catalyst loading could be reduced to 1 mol%. Good variation of the aryl iodide substrate was possible, and alkenyl as well as heteroaryl variants could also be used (Scheme 6). A related reaction, which uses $K_2S_2O_5$ as the $SO_2$ source and sodium formate as the reductant, has been reported by scientists at Pfizer in the US.[17]



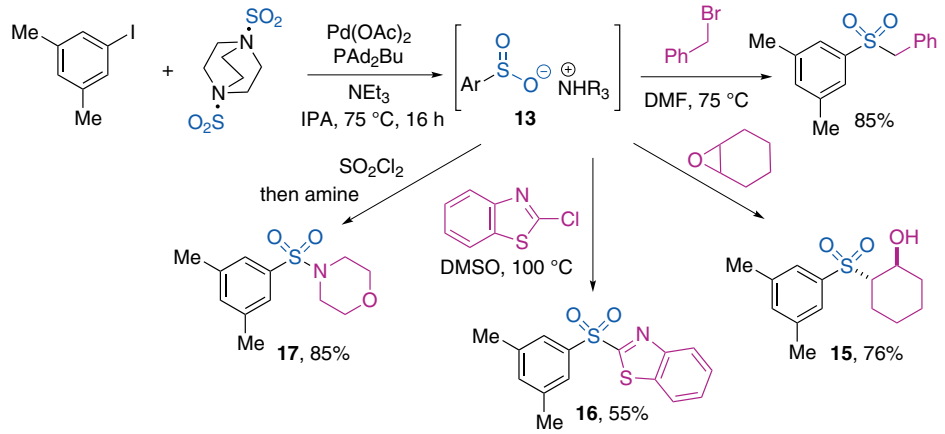

**Scheme 5.** Radical based routes to *N*-aminosulfonamides



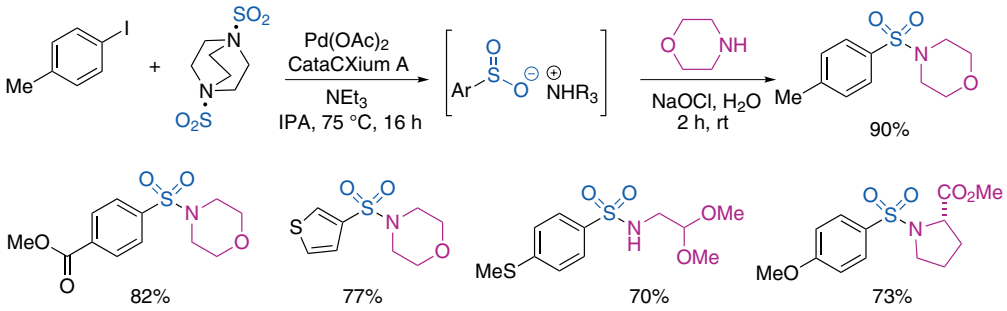

**Scheme 6.** Palladium-catalyzed sulfinate formation

The utility of sulfinate salts is that they can be combined with a variety of alternative electrophiles to provide a correspondingly broad range of products. Selected examples of this approach, using sulfinate **13**, are shown in Scheme 7; the use of an epoxide provides β-hydroxy sulfone **15**, nucleophilic aromatic substitution delivers aryl-heteroaryl sulfone **16**, and chlorination followed by amine addition provides sulfonamide **17**.[16]

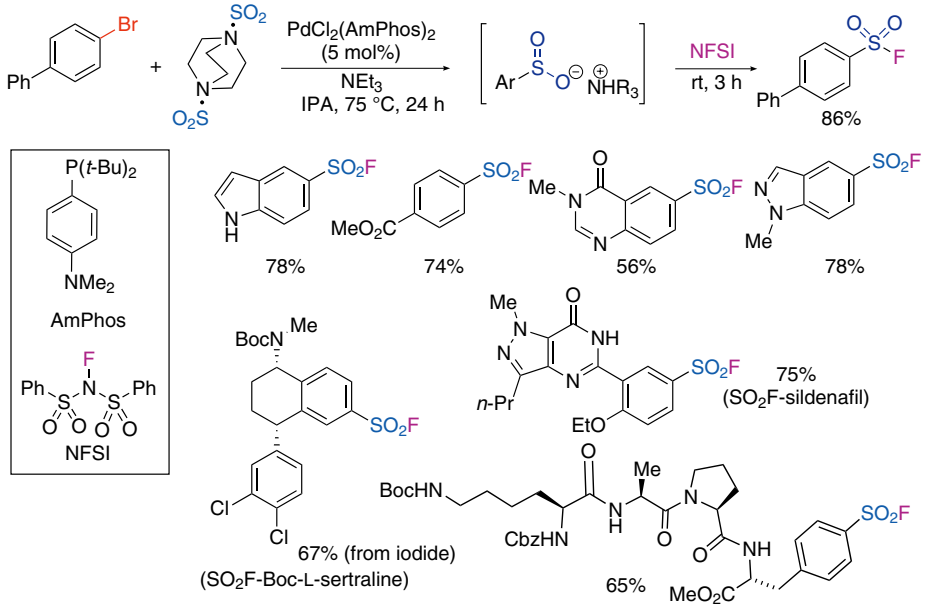
Given the prevalence of sulfonamides in medicinal and agrochemistry, we wanted to adapt the sulfinate synthesis described above to provide a simple and efficient entry to these important functional groups. Accordingly, we adapted our earlier chemistry based on the use of pre-formed organometallic reagents,[6d] and were able to show that treatment of the *in situ* catalytically generated sulfinate intermediates with an aqueous solution of the relevant amine and bleach (NaOCl), provides the corresponding sulfonamides in high yield (Scheme 8).[18] The




**Scheme 7.** Catalytically generated sulfinates as versatile intermediates in synthesis




**Scheme 8.** Sulfonamide synthesis using *in situ* generated *N*-chloroamines



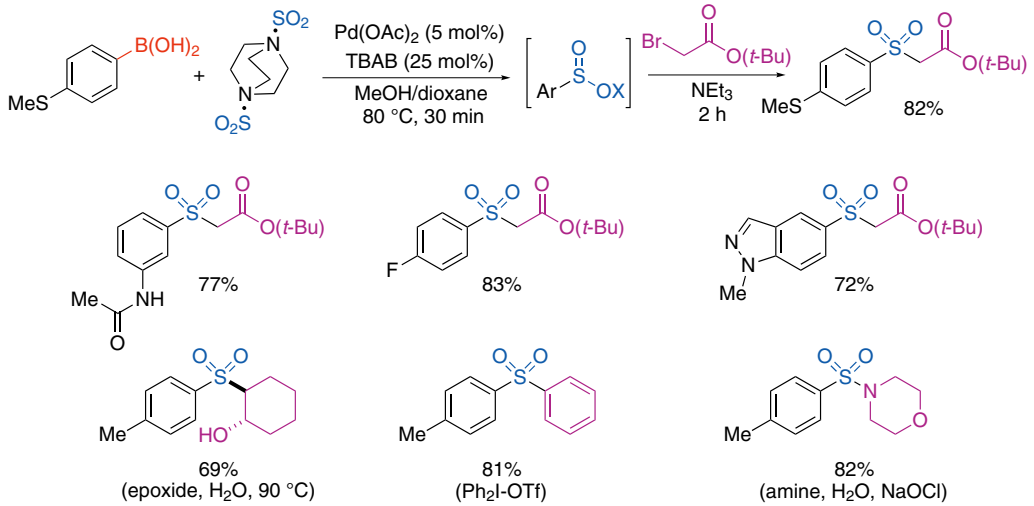

**Scheme 9.** The palladium-catalyzed preparation of sulfonyl fluorides from aryl halides

reactions proceed *via in situ* formation of the *N*-chloroamines. Broad variation of both the aryl iodide and amine component was possible, including the use of heteroaryl iodides, and well as amines bearing acid-sensitive functional groups. Amino acids could also be employed, and the corresponding sulfonamides were obtained with no erosion of enantiomeric excess.

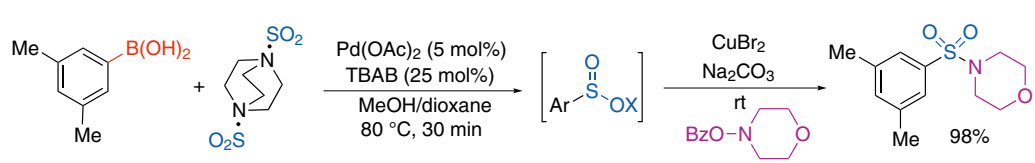
The sulfinate syntheses shown in Schemes 6, 7, and 8 all employ (hetero)aryl iodide substrates. A re-evaluation of phosphine ligands allowed a new catalyst system, this time featuring the ligand AmPhos, to be used in combination with (hetero)aryl bromide substrates.[19] In a collaboration with scientists at Pfizer, this chemistry was showcased in the synthesis of a range of sulfonyl fluorides (Scheme 9). The *in situ* generated sulfinates are treated with NFSI, which is a source of $F^+$, and delivered the corresponding sulfonyl fluorides in good yields. Good variation of the aryl bromide was possible. Sulfonyl fluorides are important molecules for the design of covalent inhibitors, and as probe reagents in chemical biology applications; Scheme 9 also shows the preparation of several sulfonyl fluorides from halogenated pharmaceuticals, or pharmaceutical fragments that were prepared using this methodology.

To complement the Pd(0)-catalyzed sulfonylation procedures described above, we have also developed a Pd(II)-catalyzed protocol that employs aryl boronic acids as the substrates (Scheme 10).[20] The reaction conditions consist of $Pd(OAc)_2$ with tetrabutylammonium bromide (TBAB) in a methanol/dioxane solvent mixture at 80 °C. No phosphine ligands were required in the reactions. Complete conversion to sulfinate was achieved after just 30 minutes, at which point an electrophile could be added. As shown in Scheme 10, good variation of the starting aryl boronic acid, including heterocyclic variants was possible, and a variety of electrophiles could be introduced in the second step, allowing access to various sulfones as well as sulfonamides. A related transformation, which uses $K_2S_2O_5$ as the $SO_2$ source, has been reported by scientists at Pfizer in the US.[21]

The sulfonamide shown in Scheme 10 was prepared by the addition of an aqueous solution of the amine and NaOCl to the *in situ* generated sulfinate. The reaction proceeds *via* the *in situ* formation of the *N*-chloroamine which functions as an electrophilic amine component. Similar reactivity has been reported by Tu and co-workers, who used preformed *N*-benzoyloxyamines as electrophilic amine components in combination with a Cu(II) catalyst (Scheme 11).[22]




**Scheme 10.** The palladium(II)-catalyzed preparation of sulfinates from aryl boronic acids, and onwards reactivity




**Scheme 11.** The palladium(II)-catalyzed preparation of sulfinates and onwards to sulfonamides using *N*-benzoyloxyamines

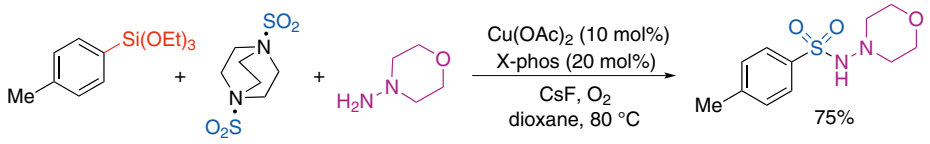
## 3. Copper-Catalyzed Reactions

The Wang group were the first to report a copper-catalyzed process involving DABSO. They developed a variant of the aminosulfonamide synthesis shown in Scheme 1, but employed aryl triethoxysilanes as the substrates in combination with a Cu(II)-catalyst (Scheme 12).[23] $Cu(OAc)_2$ was employed as the catalyst, along with an oxygen atmosphere. The reactions were tolerant of a broad range of silanes, but the commercial availability of these reagents is limited. As with the related palladium-catalyzed reactions, the *N*-nucleophile is again limited to *N*,*N*-dialkylhydrazines.

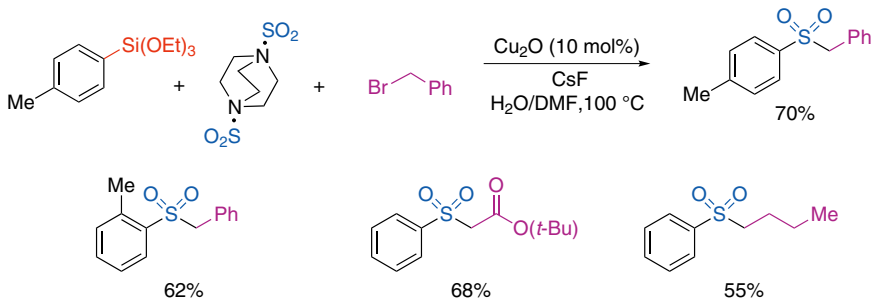
The Wu group employed the same class of aryl substrate in a copper-catalyzed sulfone synthesis.[24] Their method involved the combination of aryl triethoxysilanes, DABSO, and an alkyl halide using $Cu_2O$ as catalyst (Scheme 13).

The same group reported a copper-catalyzed preparation of benzothiophene-1,1-dioxides (Scheme 14). The chemistry involved the combination of *o*-alkynylboronic acids (**18**), with DABSO and a Cu(II) catalyst.[25] Reasonable variation of the substrate was possible, delivering the expected heterocycles in moderate to good yields.

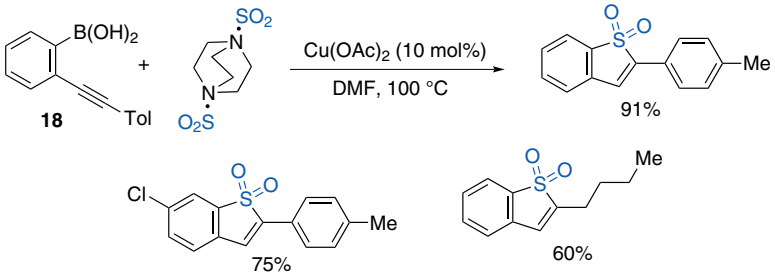
Our laboratory has reported a Cu(I)-catalyzed synthesis of aryl sulfinates using aryl boronic acids as substrates (Scheme 15).[26] The chemistry employs the commercially available copper catalyst $Cu(MeCN)_4BF_4$ and relies on a 12 hour reaction to achieve complete sulfinate formation. Addition of a variety of electrophiles is possible, trapping the sulfinate, and providing sulfones, sulfonamides, and sulfonyl fluorides. This chemistry provides a copper variant of the palladium-catalyzed reactions presented in Scheme 10.




**Scheme 12.** The copper(II)-catalyzed preparation of *N*-aminosulfonamides using aryl triethoxysilanes



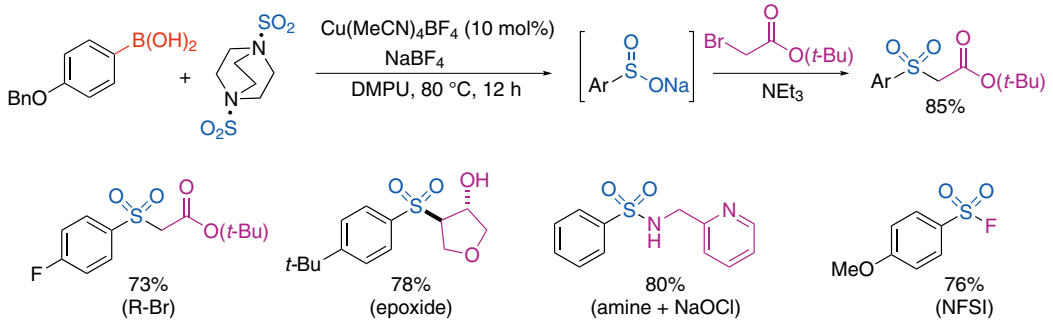

**Scheme 13.** The copper-catalyzed preparation of sulfones using aryl triethoxysilanes



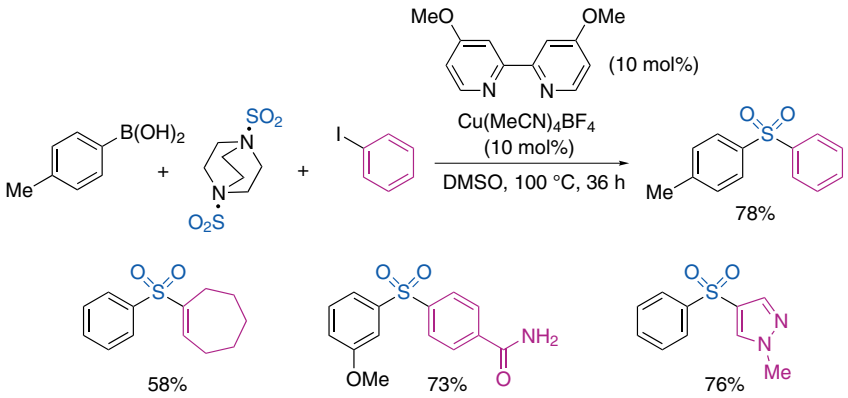

**Scheme 14.** The copper-catalyzed synthesis of benzothiophene-1,1-dioxides

Our laboratory was also able to exploit copper-catalysis in developing the first examples of a sulfonylative Suzuki-Miyaura cross-coupling (Scheme 16).[26] The reactions allowed the direct combination of aryl boronic acids, aryl halides and sulfur dioxide (provided from DABSO), and employ the same commercial copper catalyst, this time partnered with the indicated bipyridine ligand. Good variation of both the aryl iodide and aryl boronic acid was possible, including the use of heteroaryl variants, as well as alkenyl examples. This chemistry represents the first sulfonylative variant of any classic cross-coupling process.

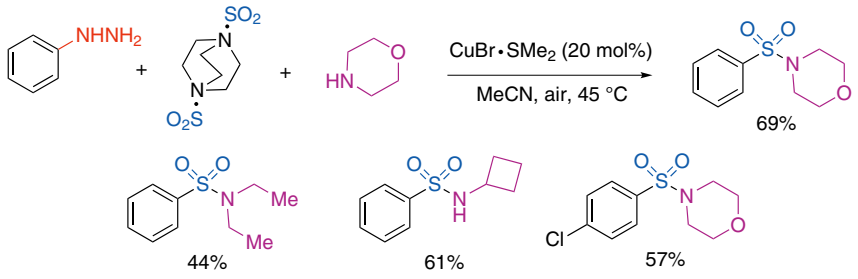
A copper-catalyzed direct sulfonamide synthesis has also been reported, and involves the coupling of aryl hydrazines, sulfur dioxide (from DABSO), and amines, using a CuBr catalyst and an air atmosphere (Scheme 17).[27] The chemistry involves the oxidative conversion of the aryl hydrazines to aryl radicals. This is a rare example of a direct sulfonamide synthesis, but is limited by the need to employ aryl hydrazines as the substrates.



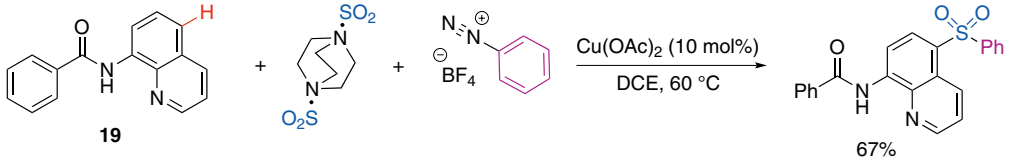

**Scheme 15.** The copper(I)-catalyzed sulfinate formation, and onwards to sulfones, sulfonamides and sulfonyl fluorides




**Scheme 16.** The copper(I)-catalyzed sulfonylative Suzuki-Miyaura cross-coupling




**Scheme 17.** The copper(I)-catalyzed sulfonamide synthesis employing aryl hydrazine substrates




**Scheme 18.** The copper(II)-catalyzed C-H sulfonylation of 8-aminoquinoline amides

The final copper-catalyzed DABSO-based reaction we will consider is a recent report from the Wu group, and involves the sulfonylation of an aryl C-H bond (Scheme 18).[28] The chemistry is radical based, and involves the coupling of a quinolinyl-derived amide (**19**) with DABSO and an aryl diazonium salt using a Cu(II) catalyst. The targeted C-H functionalization products, diaryl sulfones, are obtained in moderate yields.

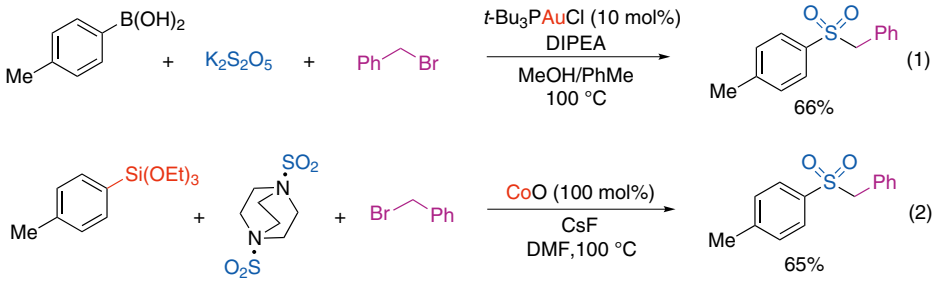
## 4. Miscellaneous Metal Catalysts

Although palladium and copper catalysts provide the majority of examples of DABSO, and alternative $SO_2$-surrogates, use in synthesis, there are a handful of reports that employ different metal catalysts. For example, The Toste group, in collaboration with scientists at Pfizer, have demonstrated that Au(I) complexes are effective catalysts for the addition of sulfur dioxide to aryl boronic acids.[29] They utilized this reactivity in a one-pot sulfone synthesis (Scheme 19, eq 1). Note, $K_2S_2O_5$ is used as the $SO_2$-source. Recently, a Au(I)-carbene complex has also been used in a closely related system.[30] The same overall transformation can also be promoted using a cobalt complex.[31] In this case, cobalt oxide is used in stoichiometric amounts, and promotes the union of aryl triethoxysilanes, DABSO and an alkyl halide (Scheme 19, eq 2).

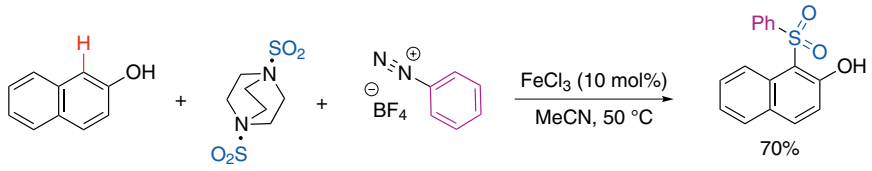
The Wu group has reported a second aryl C-H sulfonylation protocol, this time employing an iron catalyst (Scheme 20).[32] This radical process combines 2-napthols, DABSO, and aryl diazoniums salts, and delivers diaryl sulfone products in good yields. A simple $FeCl_3$ catalyst is employed. The final transformation we will consider is a recent report from the Wu group concerning thiophosphate synthesis. Aryl iodonium salts are used as the substrates and are combined with DABSO and diphenylphosphine oxide, in the presence of an iridium photocatalyst (Scheme 21).[33] Irradiation with visible light results in formation of the thiophosphonate **20**. This is an unusual example of DABSO use in which the $SO_2$ is reduced during the transformations.

## 5. Conclusions

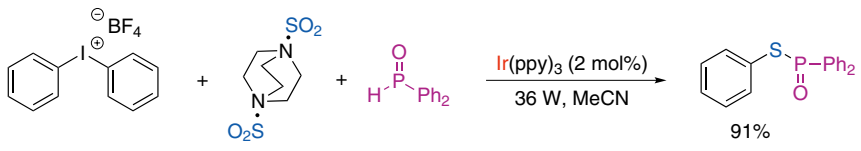
The advent of DABSO (and other reagents) as an effective surrogate for sulfur dioxide gas has allowed the development of a range of transition metal catalyzed reactions that result in sulfur dioxide incorporation. Although early examples deliver rather esoteric products, more recent reactions deliver synthetically useful products. Palladium and copper based catalysts dominate the reactions that have been reported, but recent advances suggest that alternative metals could provide useful, and different, reactivity.




**Scheme 19.** Gold and cobalt mediated sulfone syntheses




**Scheme 20.** Iron-catalyzed naphthol sulfonylation




**Scheme 21.** Iridium-catalyzed thiophosphonate synthesis

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## Introduction of the author:


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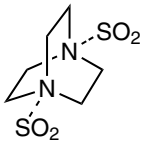
Michael Willis is a Professor of Chemistry at the University of Oxford. He received his undergraduate education at Imperial College London, and his Ph.D. from the University of Cambridge working with Prof. Steven Ley. After a postdoctoral stay with Prof. David Evans at Harvard University, he was appointed to a lectureship at the University of Bath in November 1997. In January 2007 he moved to the University of Oxford, where he is now a Professor of Chemistry and a Fellow of Lincoln College. His group's research interests are based on the development and application of new catalytic processes for organic synthesis, with a particular interest in transition metal catalysis. His work has been recognized by the award of recent prizes, including the Royal Society of Chemistry's 2014 Catalysis in Organic Chemistry Award, and the 2015 Pfizer, AstraZeneca, Syngenta, Process Chemistry Research Award.

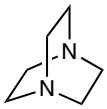
## TCI Related Products

| | | | | |
|---|---|---|---|---|
| B3960 | DABSO [= Bis(sulfur Dioxide)-1,4-diazabicyclo[2.2.2]octane Adduct] | | 1g | 5g |

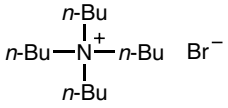


**DABSO**

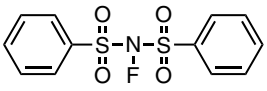
| | | | | |
|---|---|---|---|---|
| D0134 | DABCO [= 1,4-Diazabicyclo[2.2.2]octane] | 25g | 100g | 500g |
| P2480 | Potassium Disulfite | | 25g | 500g |
| T0054 | TBAB (= Tetrabutylammonium Bromide) | 25g | 100g | 500g |
| F0335 | NFSI [= *N*-Fluorobenzenesulfonimide] [Fluorinating Reagent] | | 5g | 25g |
| C2204 | Cesium Fluoride | | 25g | 100g |
| A1424 | Palladium(II) Acetate | | 1g | 5g |



**DABCO**

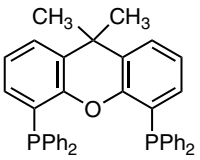


**TBAB**

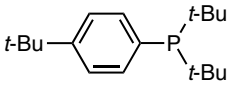


**NFSI**

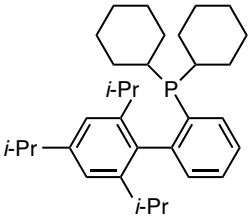
| | | | | |
|---|---|---|---|---|
| P2161 | Palladium(II) Acetate (Purified) | | | 1g |
| T2666 | Tetrakis(acetonitrile)copper(I) Tetrafluoroborate | 1g | 5g | 25g |
| C2346 | Copper(II) Acetate Monohydrate | | 25g | 500g |
| B2709 | Xantphos [= 4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene] | 1g | 5g | 25g |
| D4531 | Amphos [= (4-Dimethylaminophenyl)di-*tert*-butylphosphine] | | 1g | 5g |
| D5038 | XPhos (= 2-Dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl) | | 1g | 5g |
| D3886 | 4,4'-Dimethoxy-2,2'-bipyridyl | | 1g | 5g |
| T1946 | $Ir(ppy)_3$ [= Tris(2-phenylpyridinato)iridium(III)] (purified by sublimation) | | | 200mg |
| P1528 | Pearlman's Catalyst [= Palladium Hydroxide (contains Pd, PdO) on Carbon] (wetted with *ca.* 50% Water) | | 10g | 50g |



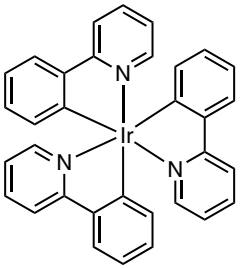
**Xantphos**



**Amphos**



**XPhos**



**$Ir(ppy)_3$**