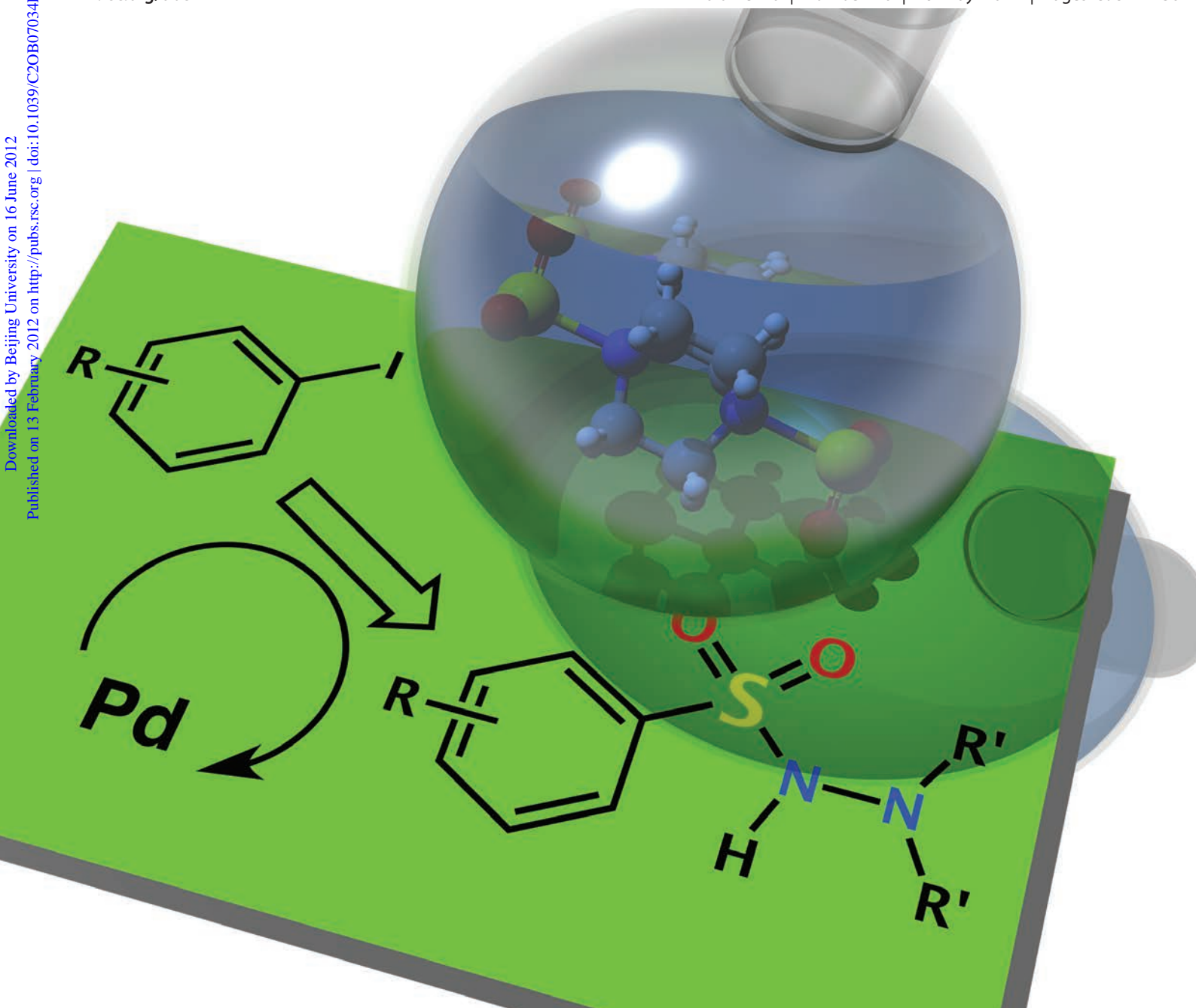


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**FULL PAPER**

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PAPER

## Palladium-catalysed aminosulfonylation of aryl-, alkenyl- and heteroaryl halides: scope of the three-component synthesis of *N*-aminosulfonamides†

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By using DABCO·(SO<sub>2</sub>)<sub>2</sub>, DABSO, as a solid bench-stable SO<sub>2</sub>-equivalent, the palladium-catalysed aminosulfonylation of aryl-, alkenyl- and heteroaryl halides has been achieved. *N,N*-Dialkylhydrazines are employed as the *N*-nucleophiles and provide *N*-aminosulfonamides as the products in good to excellent yields. The reactions are operationally simple to perform, requiring only a slight excess of SO<sub>2</sub> (1.2–2.2 equiv.), and tolerate a variety of substituents on the halide coupling partner. Variation of the hydrazine component is also demonstrated. The use of *N,N*-dibenzylhydrazine as the *N*-nucleophile delivers *N*-aminosulfonamide products that can be converted into the corresponding primary sulfonamides using a high-yielding, telescoped, deprotection sequence. The ability to employ hydrazine·SO<sub>2</sub> complexes as both the *N*-nucleophile and SO<sub>2</sub> source is also illustrated.

### Introduction

The sulfonamide functional group is abundant in medicinal agents, where it features in a number of top selling drug molecules active against a wide variety of conditions.<sup>1</sup> Despite their widespread presence, a general and versatile method for sulfonamide preparation does not exist, with the most common route involving a linear approach of sulfonyl chloride formation and subsequent amination. In addition, sulfonyl chloride synthesis can often present a challenge due to the forcing conditions and functional group incompatibility of the required strong chlorinating reagents.<sup>2,3</sup> The frequently used aryl sulfonyl chlorides can be prepared *via* electrophilic aromatic substitution chemistry using [HSO<sub>3</sub>]<sup>+</sup> or [ClSO<sub>2</sub>]<sup>+</sup> synthons;<sup>2</sup> however, this is generally limited to electron-rich aromatic substrates and those that can tolerate the harsh acidic conditions. In addition, the positions to which the sulfonyl moiety can be introduced are governed by the intrinsic electronic and steric properties of the aromatic ring. Alternative methods to form sulfonamides avoiding a sulfonyl chloride intermediate have been developed to address some of these issues.<sup>4,5</sup> However, these methods often require starting materials at the sulfinate oxidation level, which in turn are frequently prepared using difficult to handle sulfur dioxide gas and sensitive organometallics.<sup>4</sup>

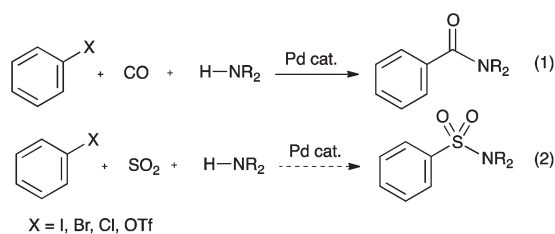
The absence of transition metal-catalysed methods for sulfonamide synthesis is conspicuous. Our aim, therefore, was to develop a catalytic method of sulfonamide formation that would eliminate many of the limitations of current methodologies. We drew inspiration from the analogies, in terms of transition metal chemistry, between sulfur dioxide and carbon monoxide. The frontier molecular orbitals of CO and SO<sub>2</sub> carry striking similarities; they both have a  $\sigma$  symmetry HOMO and  $\pi^*$  LUMO in a similar spatial arrangement,<sup>6</sup> hinting at comparable behaviour as ligands.<sup>7</sup> Sulfur dioxide is also well preceded to undergo co-ordination to metal centres,<sup>8</sup> through a large variety of bonding modes, and insertion into metal–carbon bonds.<sup>9</sup>

Despite this literature precedent for stoichiometric reactions of metal complexes and sulfur dioxide, reports documenting the incorporation of sulfur dioxide into organic molecules *via* transition metal-catalysed processes are scarce.<sup>10</sup> Examples include the copper-catalysed coupling of aryl diazonium chloride salts with sulfur dioxide to form sulfonyl chlorides,<sup>11</sup> and the palladium-catalysed coupling of aryl diazonium tetrafluoroborate salts with sulfur dioxide and hydrogen gas to form sulfinic acids.<sup>12</sup> Examples of metal-catalysed alkene–sulfur dioxide co-polymerisation<sup>13</sup> and alkene hydrosulfination are also known.<sup>14</sup> The comparison with the catalytic chemistry of carbon monoxide is marked, with many transition metal-catalysed carbonylation processes being useful synthetic tools.<sup>15</sup> In particular, the palladium-catalysed aminocarbonylation of aryl halides, in which an aryl halide, carbon monoxide gas and an amine are combined to deliver an arylamide product, is a well-established synthetic transformation (Scheme 1, eqn (1)).<sup>16</sup> However, no corresponding preparation of sulfonamides based on the combination of an aryl halide, SO<sub>2</sub> gas and an amine has been reported (Scheme 1,

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† Electronic supplementary information (ESI) available: Full data for all new compounds. See DOI: 10.1039/c2ob07034k



**Scheme 1** Palladium-catalysed aminocarbonylation and aminosulfonylation processes.

eqn (2)). In this paper we describe the development of such a process, based on the use of DABCO·(SO<sub>2</sub>)<sub>2</sub> as a stable, easy to handle SO<sub>2</sub> equivalent, and *N,N*-dialkylhydrazines as the *N*-nucleophiles. Our preliminary results in this area have recently been communicated.<sup>17</sup>

## Results and discussion

Due to the difficulties associated with the handling and use of a toxic gas, such as SO<sub>2</sub>,<sup>18</sup> we were attracted to the possibility of employing a SO<sub>2</sub>-equivalent in the proposed aminosulfonylation. In particular, we were interested in exploring the use of amine–SO<sub>2</sub> charge transfer complexes as substitutes for SO<sub>2</sub> gas in catalytic applications. The first reports on these charge transfer compounds appear in the literature (some as early as 1900)<sup>19</sup> mainly for spectroscopic studies on the nature of the N–S dative bond.<sup>20,21</sup> However, these complexes have found some significant uses;<sup>22</sup> for example, a method for determining the concentration of sulfur dioxide in solution using a metalloporphyrin assay relies on amine complexation<sup>23</sup> and <sup>n</sup>Bu<sub>3</sub>N solutions are used as industrial sulfur dioxide gas scrubbers.<sup>24</sup> We were also attracted to these complexes by the work of Olah, who used the trimethylamine–sulfur dioxide complex to perform a range of reduction reactions.<sup>25</sup> Some of these transformations were also known with sulfur dioxide gas,<sup>26</sup> suggesting that these complexes could be used to deliver sulfur dioxide to the reaction, thus eliminating the operational difficulties and safety concerns of using the gas.

Due to ease of handling we have focused on the complex formed between DABCO (1,4-diazabicyclo[2.2.2]octane) and sulfur dioxide (Scheme 2). The bis-adduct, DABCO·(SO<sub>2</sub>)<sub>2</sub>, which we have abbreviated to DABSO, is a bench-stable, colourless solid which was first synthesised by Santos and Mello for spectroscopic studies.<sup>21</sup> We have recently reported the use of DABSO as a replacement for sulfur dioxide gas in a number of established transformations.<sup>27</sup> The focus of the present report is the use of DABSO in a novel palladium-catalysed aminosulfonylation process.<sup>17</sup>



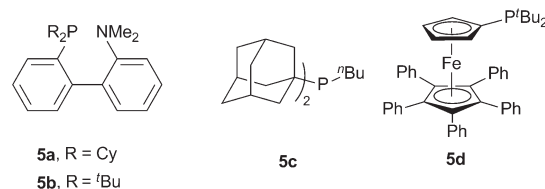
**Scheme 2** DABSO, an easy to handle, solid SO<sub>2</sub>-equivalent.

We selected the coupling of 4-iodotoluene (**2a**), DABSO and *N*-aminomorpholine (**3a**) as a platform to evaluate the proposed

**Table 1** Optimisation of the reaction conditions for the preparation of aminosulfonamide **4a**<sup>a</sup>

Entry	Ligand	Base (equiv.)	DABSO (equiv.)	Solvent	Yield <sup>b</sup> (%)
1	P <sup>t</sup> Bu <sub>3</sub>	Cs <sub>2</sub> CO <sub>3</sub> (2.2)	2.2	Toluene	77
2	P <sup>t</sup> Bu <sub>3</sub>	—	2.2	Toluene	12
3	P <sup>t</sup> Bu <sub>3</sub>	Cs <sub>2</sub> CO <sub>3</sub> (2.2)	2.2	Dioxane	17
4	P <sup>t</sup> Bu <sub>3</sub>	—	2.2	Dioxane	83
5	P <sup>t</sup> Bu <sub>3</sub>	—	1.1	Dioxane	89
6	P <sup>t</sup> Bu <sub>3</sub>	—	0.6	Dioxane	64
7	P <sup>t</sup> Bu <sub>3</sub>	DABCO (0.5)	0.6	Dioxane	99 <sup>c</sup>
8	<b>5a</b>	DABCO (0.5)	0.6	Dioxane	35
9	<b>5b</b>	DABCO (0.5)	0.6	Dioxane	12
10	<b>5c</b>	DABCO (0.5)	0.6	Dioxane	68
11	<b>5d</b>	DABCO (0.5)	0.6	Dioxane	62

<sup>a</sup> Conditions: iodotoluene (1.0 equiv.), hydrazine (1.5 equiv.), DABSO (as indicated), Pd(OAc)<sub>2</sub> (10 mol%), P<sup>t</sup>Bu<sub>3</sub>·HBF<sub>4</sub> (20 mol%), solvent, 70 °C, 16 h. <sup>b</sup> Determined by <sup>1</sup>H NMR spectroscopy. <sup>c</sup> Corresponding to a 93% isolated yield.



chemistry (Table 1). We initially employed conditions developed for related palladium-catalysed aminocarbonylation reactions<sup>28</sup> and quickly established that the formation of the desired C–SO<sub>2</sub>–N linkage was indeed possible under the action of palladium catalysis. For example, the sulfonylative union of iodotoluene and *N*-aminomorpholine could be achieved in 77% yield when using Pd(OAc)<sub>2</sub> in combination with the ligand P<sup>t</sup>Bu<sub>3</sub> and Cs<sub>2</sub>CO<sub>3</sub> as the base in toluene at 70 °C (entry 1). We found that Cs<sub>2</sub>CO<sub>3</sub> could be removed from the system provided that dioxane was employed as solvent (entries 2–4). Variation of the loading of DABSO was explored next, and we established that reducing the amount of DABSO from 2.2 equivalents to 1.1 equivalents increased the yield of the aminosulfonamide product (**4a**) to 89% (entry 5), possibly due to less catalyst poisoning from free SO<sub>2</sub>. However, reducing the amount of DABSO further, to 0.6 equivalents (1.2 equivalents of SO<sub>2</sub>), reduced the yield of **4a** to 64% (entry 6). We attributed this reduction in yield to insufficient base being present in the reaction, and therefore repeated this loading but with the addition of 0.5 equivalents of DABCO; gratifyingly, the yield was then increased to 99% (entry 7). Although these early experiments established that P<sup>t</sup>Bu<sub>3</sub> was an effective ligand for the targeted transformation, we were also interested in evaluating alternative phosphines: entries 8–11

**Table 2** Scope of aryl iodides employed in Pd-catalysed aminosulfonylations with DABSO and *N*-aminomorpholine<sup>a</sup>

Entry	Aryl halide	Yield <sup>b</sup>	Entry	Aryl halide	Yield <sup>b</sup>
1		93%	10		77% <sup>c</sup>
2		79% <sup>c</sup>	11		43% <sup>c</sup>
3		87%	12		80% <sup>c</sup>
4		86% <sup>c</sup>	13		35% <sup>c</sup>
5		93%	14		90% <sup>c</sup>
6		86%	15		76% <sup>c</sup>
7		76% <sup>c</sup>	16		64% <sup>d</sup>
8		85%	17		84% <sup>c</sup>
9		88%	18		77% <sup>c</sup>

<sup>a</sup> Conditions: aryl halide (1.0 equiv.), hydrazine (1.5 equiv.), DABSO (0.6 equiv.), DABCO (0.5 equiv.), Pd(OAc)<sub>2</sub> (10 mol%), P<sup>t</sup>Bu<sub>3</sub>·HBF<sub>4</sub> (20 mol%), 1,4-dioxane, 70 °C, 16 h. <sup>b</sup> Isolated yields. <sup>c</sup> DABSO (1.1 equiv.) used, no DABCO added. <sup>d</sup> Reaction performed at 90 °C.

demonstrate that while the use of several alternative phosphines does deliver the aminosulfonamide **4a**, for this particular transformation P<sup>t</sup>Bu<sub>3</sub> is the superior ligand.

With optimised conditions for the sulfonylative union of **2a** and **3a** established we next explored the scope of the aryl iodide component (Table 2). A range of electron-donating substituents could be readily incorporated into the aryl ring (entries 1–9) using the optimised conditions. However, the yields obtained using *ortho*-substituted arenes were only moderate under these conditions and we found that the addition of extra DABSO (1.1 equiv. in total), with no added DABCO, was preferential for slower reacting substrates. For example, using these modified conditions, substrates featuring either an *ortho*-methyl or an *ortho*-methoxy group underwent efficient coupling (entries 2 and 7). Entries 8 and 9 illustrate that it was possible to employ

substrates containing unprotected hydroxyl and amino groups, respectively. Electron-withdrawing substituents could also be readily employed, although in the majority of examples the modified reaction conditions were needed to ensure high yields (entries 10–13). Although aryl iodides were employed for the majority of examples, it was possible to employ aryl bromide substrates, albeit in a less efficient manner. For example, *para*-bromotoluene was combined with DABSO and *N*-aminomorpholine to generate the expected sulfonamide in a 64% yield, compared to the 93% achieved with the iodo substrate (entry 16). To secure this level of reactivity with the bromo substrate the reaction temperature was increased from 70 °C to 90 °C. The increased reactivity of iodo-substituted benzenes relative to their bromo equivalents allowed two simple chemoselective examples to be included: in the first reaction *para*-iodochlorobenzene was

**Table 3** Scope of hydrazines employed in Pd-catalysed aminosulfonylations with DABSO and 4-iodotoluene<sup>a</sup>

Entry	Hydrazine	Yield <sup>b</sup>	Entry	Hydrazine	Yield <sup>b</sup>
1		93%	6		85%
2		87%	7		57% (100% conv.)
3		75%	8		84%
4		65%	9		0%
5		80%	10		9% <sup>c</sup>

<sup>a</sup> Conditions: iodotoluene (1.0 equiv.), hydrazine (1.5 equiv.), DABSO (0.6 equiv.), DABCO (0.5 equiv.), Pd(OAc)<sub>2</sub> (10 mol%), P<sup>t</sup>Bu<sub>3</sub>·HBF<sub>4</sub> (20 mol%), 1,4-dioxane, 70 °C, 16 h. <sup>b</sup> Isolated yields. <sup>c</sup> <sup>1</sup>H NMR conversion.

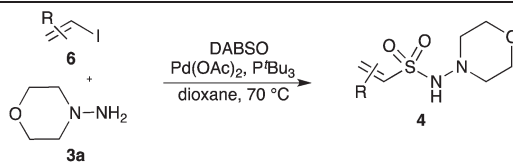
converted into the corresponding aminosulfonamide in 84% yield from reaction exclusively at the iodo-substituent (entry 17). Similarly, *para*-iodobromobenzene also underwent selective reaction at the iodo-functionality (entry 18).

For convenience, all of the reactions shown in Table 2 were performed employing 10 mol% of Pd(OAc)<sub>2</sub>. However, lower catalyst loadings were possible; for example, *N*-aminosulfonamide **4a** was synthesised on a preparative 0.5 g scale using 5 mol% of Pd(OAc)<sub>2</sub> in 89% yield (*cf.* 93% using 10 mol%), and in 73% yield when using 2.5 mol% palladium.

Employing 4-iodotoluene as the *C*-coupling partner allowed variation of the hydrazine component to be explored (Table 3). *N,N*-Dialkyl hydrazines generally delivered good yields of the aminosulfonamide products (entries 1–7). Slightly reduced yields were obtained with the *N,N*-dimethyl example (entry 4), attributed to the volatility of the reagent, and with the proline-derived hydrazine (entry 7), which, despite the reaction reaching complete conversion only delivered a 57% yield of the product. This latter yield was attributed to product decomposition during chromatographic purification. Although the *N*-methyl-*N*-phenyl hydrazine underwent the coupling reaction in high yield (entry 8), the corresponding diphenyl example (entry 9) was essentially inert to the reaction conditions. Finally, the use of a carbamate-protected hydrazine was also incompatible with the sulfonylation reaction (entry 10). Variation away from hydrazine coupling partners, for example to amines, did not deliver sulfonamide products under these reaction conditions.

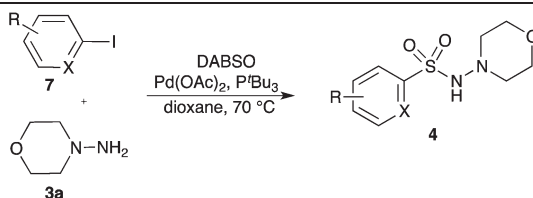
The next parameter explored was the use of alternative coupling partners to aryl halides; we first considered the use of alkenyl halide substrates (Table 4). A variety of (*E*)-configured 1,2-disubstituted alkenyl iodides underwent smooth coupling with *N*-aminomorpholine and DABSO, delivering the expected (*E*)-configured alkenyl sulfonamides in moderate to good yields (entries 1–3). Entry 4 demonstrates that although a (*Z*)-configured alkenyl iodide underwent the sulfonylative coupling with similar efficiency to the corresponding (*E*)-substrate, the product suffered from *Z/E* isomerisation.  $\alpha$ -Iodostyrene was not a productive substrate, suffering decomposition under the reaction conditions (entry 5). More pleasingly, a variety of tri- and tetra-substituted alkenyl iodides underwent the sulfonylative process in high yields (entries 6–10). We speculate that the higher yields associated with the more highly-substituted examples reflects the greater stability of the corresponding substrates or products to the reaction conditions.

Heteroaryl halides could also be employed as coupling partners (Table 5). *N*-Aminomorpholine in combination with DABSO was again employed as standard; reactions with 3-iodothiophene and 3-iodobenzothiophene smoothly delivered the coupled products in high yields (entries 1 and 2). However, the use of similar *N*-heterocycles was less successful, with only low yields of the sulfonamides being obtained (entries 3 and 4). Indole-derived substrates could be employed provided that the iodo-substituent was positioned in the benzo-ring of the indole. For example, both 5-iodoindole, and *N*-Boc-5-iodoindole underwent the desired sulfonylation in good yields (entries 5 and 6).

**Table 4** Scope of alkenyl iodides employed in Pd-catalysed aminosulfonylations with DABSO and *N*-aminomorpholine<sup>a</sup>

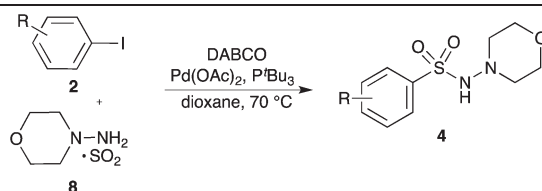
Entry	Alkene	Yield <sup>b</sup>	Entry	Alkene	Yield <sup>b</sup>
1		60%	6		86%
2		74%	7		57%
3		53%	8		79%
4		51% <sup>c</sup>	9		89%
5		0%	10		72%

<sup>a</sup> Conditions: alkenyl halide (1.0 equiv.), hydrazine (1.5 equiv.), DABSO (1.1 equiv.), Pd(OAc)<sub>2</sub> (10 mol%), P<sup>t</sup>Bu<sub>3</sub>·HBF<sub>4</sub> (20 mol%), 1,4-dioxane, 70 °C, 16 h. <sup>b</sup> Isolated yields. <sup>c</sup> Starting material >20 : 1 *Z* : *E*; product 3.5 : 1 ratio of *Z* : *E* isomers.

**Table 5** Scope of heteroaryl iodides employed in Pd-catalysed aminosulfonylations with DABSO and *N*-aminomorpholine<sup>a</sup>

Entry	Heterocycle	Yield <sup>b</sup>	Entry	Heterocycle	Yield <sup>b</sup>
1		76%	5		81%
2		73%	6		74%
3		20%	7		89%
4		48%	8		92%

<sup>a</sup> Conditions: heteroaryl halide (1.0 equiv.), hydrazine (1.5 equiv.), DABSO (1.1 equiv.), Pd(OAc)<sub>2</sub> (10 mol%), P<sup>t</sup>Bu<sub>3</sub>·HBF<sub>4</sub> (20 mol%), 1,4-dioxane, 70 °C, 16 h. <sup>b</sup> Isolated yields.

**Table 6** Scope of *N*-aminomorpholine·SO<sub>2</sub> complex functioning as both nucleophile and SO<sub>2</sub>-carrier in the Pd-catalysed aminosulfonylation of aryl-, heteroaryl- and alkenyl iodides<sup>a</sup>

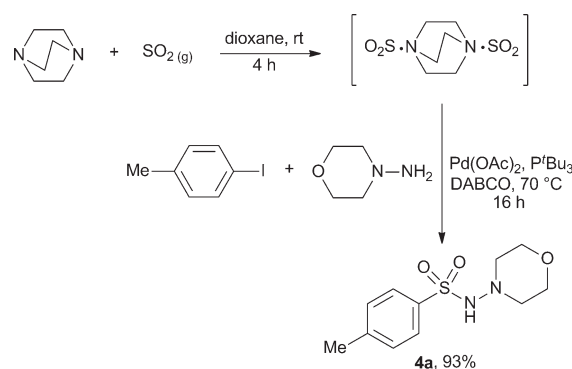
Entry	Halide	Yield <sup>b</sup>	Entry	Halide	Yield <sup>b</sup>
1		92%	5		72%
2		93%	6		87%
3		86%	7		76%
4		64%	8		86%

<sup>a</sup> Conditions: aryl (or alkenyl) halide (1.0 equiv.), *N*-aminomorpholine·SO<sub>2</sub> (1.5 equiv.), DABCO (1.1 equiv.), Pd(OAc)<sub>2</sub> (10 mol%), P'Bu<sub>3</sub>·HBF<sub>4</sub> (20 mol%), 1,4-dioxane, 70 °C, 16 h. <sup>b</sup> Isolated yields.

Similarly, iodo-substituted dibenzofuran and dibenzothiophene underwent high-yielding transformations (entries 7 and 8).

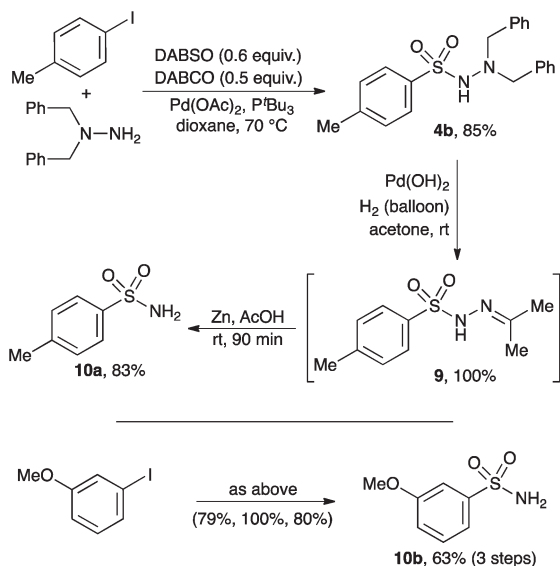
The methodology as described so far, *i.e.*, employing a SO<sub>2</sub>-carrier molecule and a variety of nucleophiles, is attractive if variation of the nucleophilic component is the main goal of the study. However, if the use of a single *N*-nucleophile is all that is required, a more attractive, less involved reaction system might involve a single molecule acting as both the nucleophile and the SO<sub>2</sub>-carrier. Such a system would remove the need to use DABSO as the SO<sub>2</sub> source. In the event, it was found to be possible to complex SO<sub>2</sub> with *N*-aminomorpholine and to employ this complex for this dual role (Table 6).<sup>29</sup> The reaction conditions involved combining the *N*-aminomorpholine–SO<sub>2</sub> complex with an aryl halide in the presence of DABCO (as the base) and the standard Pd(OAc)<sub>2</sub>–P'Bu<sub>3</sub> combination. Using this protocol it was possible to couple a range of electronically- and sterically-varied aryl iodides (entries 1–6), as well as heteroaryl- and alkenyl-iodide examples (entries 7 and 8). In almost all of the cases studied the yields obtained using the *N*-aminomorpholine–SO<sub>2</sub> complex were comparable to the results achieved using the original DABSO conditions (compare with Tables 2, 4 and 5).

We investigated a third protocol for achieving the desired aminosulfonylation reactions in which an amine–SO<sub>2</sub> complex was generated *in situ* but was not isolated. This particular scenario was felt to be attractive if the separate preparation, isolation and storage of SO<sub>2</sub>-complexes was not desired, and the handling of SO<sub>2</sub> gas was not problematic. We again studied the formation of

**Scheme 3** *In situ* generation and use of DABSO in the sulfonylative coupling of 4-iodotoluene and *N*-aminomorpholine.

aminosulfonamide **4a** from the combination of iodotoluene, *N*-aminomorpholine and an equivalent of SO<sub>2</sub>: DABSO was generated *in situ* by bubbling SO<sub>2</sub> gas into a solution of DABCO in dioxane at room temperature. After stirring for 4 h while purging with nitrogen gas, the remaining components of the reaction – iodotoluene, *N*-aminomorpholine, Pd(OAc)<sub>2</sub> and P'Bu<sub>3</sub> – were added, and the temperature increased to 70 °C. After 16 h (as standard), aminosulfonamide **4a** was isolated in a 93% yield (Scheme 3).

Although access to simple primary sulfonamides by employing amines directly as the *N*-nucleophiles was not possible with the current methodology, we sought to explore the conversion of



**Scheme 4** Preparation of primary sulfonamides *via* an *N*-aminosulfonamide deprotection sequence.

the readily accessible *N*-aminosulfonamides to the corresponding sulfonamides. We have already shown that *N,N*-dibenzylhydrazine was a competent *N*-nucleophile in the developed chemistry, and so we focused on converting the dibenzylated aminosulfonamide to the parent sulfonamide (Scheme 4). The two benzyl groups of aminosulfonamide **4b** could be efficiently cleaved under a balloon atmosphere of  $\text{H}_2$  using a  $\text{Pd(OH)}_2$  catalyst to generate hydrazone **9**; the use of acetone as solvent was key to the success of the deprotection, presumably allowing the facile formation of the intermediate hydrazone.<sup>30</sup> Direct treatment of **9** with zinc in acetic acid led to the primary sulfonamide **10a** in 83% for the two-step process. The primary sulfonamide derived from *meta*-iodoanisole was also prepared using an identical three-step sequence; thus, coupling with *N,N*-dibenzylhydrazine, benzyl group removal and finally *N-N* bond cleavage provided primary sulfonamide **10b** in a 63% yield for the three-step (two-pot) process.

## Conclusions

In conclusion, we have shown for the first time that it is possible to construct C–SO<sub>2</sub>–N linkages using palladium-catalysed aminosulfonylation processes. Key to the success of the chemistry was the use of DABCO·(SO<sub>2</sub>)<sub>2</sub>, DABSO, as a solid, easy to handle and bench-stable equivalent of sulfur dioxide. Using this reagent it was possible to achieve efficient aminosulfonylation reactions between a range of aryl-, heteroaryl- and alkenyl iodides, and *N,N*-dialkyl hydrazines, providing aryl *N*-aminosulfonamides in good to excellent yields. Significant variation of the dialkylhydrazine was also possible. The reactions are operationally simple and employ only a slight excess (1.2–2.2 equiv.) of sulfur dioxide. Employing *N,N*-dibenzylhydrazine as the coupling partner gives access to *N*-aminosulfonamides that can be readily ‘deprotected’, allowing preparation of the corresponding primary sulfonamides. We have also demonstrated that hydrazine·SO<sub>2</sub> complexes can function as both the *N*-nucleophile

and SO<sub>2</sub> source, removing the need to employ an external SO<sub>2</sub> carrier. Finally, we have shown that the isolation of a SO<sub>2</sub> charge transfer complex can be avoided completely if they are generated *in situ* and used directly in the coupling reactions.

## Experimental

For general experimental details, including information on solvent purifications, the spectrometers used in this research and full product characterization data, see ESI.†

### General procedure of the palladium-catalysed aminosulfonylation of aryl iodides using DABSO, exemplified by the preparation of aminosulfonamide **4a**

A glass reaction tube was charged with 4-iodotoluene (50 mg, 0.23 mmol), 4-aminomorpholine (33  $\mu\text{L}$ , 0.34 mmol), DABCO·(SO<sub>2</sub>)<sub>2</sub> complex (**1**) (33 mg, 0.14 mmol), 1,4-diazabicyclo[2.2.2]octane (13 mg, 0.11 mmol), palladium(II) acetate (5 mg, 21  $\mu\text{mol}$ ) and tri-*tert*-butylphosphonium tetrafluoroborate (13 mg, 42  $\mu\text{mol}$ ) and sealed under N<sub>2</sub> gas. 1,4-Dioxane (1.6 mL) was added and the tube heated at 70 °C for 16 h. After cooling, the reaction mixture was filtered through Celite and washed sequentially with dichloromethane (10 mL) and diethylether (5 mL) before being concentrated *in vacuo*. Purification by flash column chromatography (50–100% diethylether in petrol) afforded the *N*-aminosulfonamide **4a** as colourless crystals (55 mg, 93%).

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