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Synthesis of *S*-allylic sulfinamides by the catalytic nucleophilic allylation of *N*-sulfinylamines

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Sulfinamides are important compounds in organic synthesis and biologically active molecules, but *S*-allylic sulfinamides have received scant attention. Herein, we describe the synthesis of *S*-allylic sulfinamides by indium- or (thio)urea-catalyzed additions of allylboron reagents to *N*-sulfinylamines.

Introduction

Sulfinamides are important compounds in organic synthesis.[1] They are used as amide bioisosteres,[2] chiral auxiliaries,[3] chiral ligands,[4] and chiral organocatalysts.[5] Sulfinamides are also versatile precursors to a range of other sulfur(IV)- or sulfur(VI)-containing functional groups,[6,7] some of which are of significant interest for developing new pharmaceuticals and agrochemicals (Scheme 1A).[8]

Given the widespread interest in sulfinamides, developing new methods for their synthesis is an important goal. An alternative to the common approach of using substrates with pre-installed carbon–sulfur linkages is the addition of non-sulfur-containing carbon reagents to *N*-sulfinylamines, which exist as the *Z*-isomers[9,10] (Scheme 1B). This strategy is advantageous if a library of sulfinamides differing at the carbon substituent attached to sulfur is required, as this group is introduced at a late stage and numerous reagents can be employed. Highly reactive organolithium or Grignard reagents can be used but they require rigorous exclusion of air and moisture and can present issues of functional group incompatibility.[11] Recent research has focused on milder methods such as catalytic additions of aryl halides,[12,13c] alkyl halides,[13e] alkenyl triflates,[12] propargyl acetates,[13f] arylboron reagents,[7e,13a,b,d] or radicals[7f,14] to *N*-sulfinylamines, which also include asymmetric variants.[13] Collectively, these methods have greatly expanded the options available to access diverse sulfinamides.

S-Allylic sulfinamides are potentially useful building blocks because both sulfinamide and allyl groups are useful functional handles for further manipulations. Cyclic *S*-allylic sulfinamides can be prepared from Diels–Alder reactions of *N*-sulfinylamines,[15] whereas acyclic *S*-allylic sulfinamides can be prepared from *N*-sulfinylamines by the addition of allylmagnesium chloride[11f] or allylic radicals,[14c,f] and by ene reactions of alkenes (Scheme 1C).[16] However, new methods that: (i) exhibit broader scope; (ii) are conducted under mild conditions, and (iii) employ more stable, more functional-group-tolerant reagents would be valuable and allow access to a greater range of *S*-allylic sulfinamides. Herein, we describe the synthesis of *S*-allylic sulfinamides by indium- or (thio)urea-catalyzed additions of allylboron reagents to *N*-sulfinylamines (Scheme 1D).

Results and discussion

This study began with the reaction of allyl pinacolboronate (**2a**) with *N*-sulfinyltritylamine (**1a**)[17] or commercial *N*-sulfinylaniline (**1b**) (Table 1). Inspired by previous indium-catalyzed reactions of allylboron reagents with ketones,[18a] *N*-acylhydrazones,[18b] and *N*,*O*-aminals,[18c] we found that reaction of **1a** with **2a** (1.1 equiv.) in the presence of InI (10 mol%) and MeOH (5.0 equiv.) in THF at room temperature for 16 h gave *S*-allylic sulfinamide **3aa** in 73% isolated yield (entry 1). A reaction conducted without MeOH led to consumption of allylboronate **2a** but *N*-sulfinylamine **1a** remained and none of **3aa** was detected (entry 2). A reaction conducted without InI led to complete recovery of starting materials with no **3aa** detected (entry 3). The use of *N*-sulfinylaniline (**1b**) in place of **1a** led to no allylation (entry 4), and significant decomposition of **1b** to aniline was observed. Given the known sensitivity of *N*-sulfinylamines to moisture,[9] the instability of **1b** towards MeOH is not surprising.

Using the conditions of Table 1, entry 1, the scope of this process was explored using other *N*-sulfinylamines and allylboronates (Scheme 2). As well as the successful formation of

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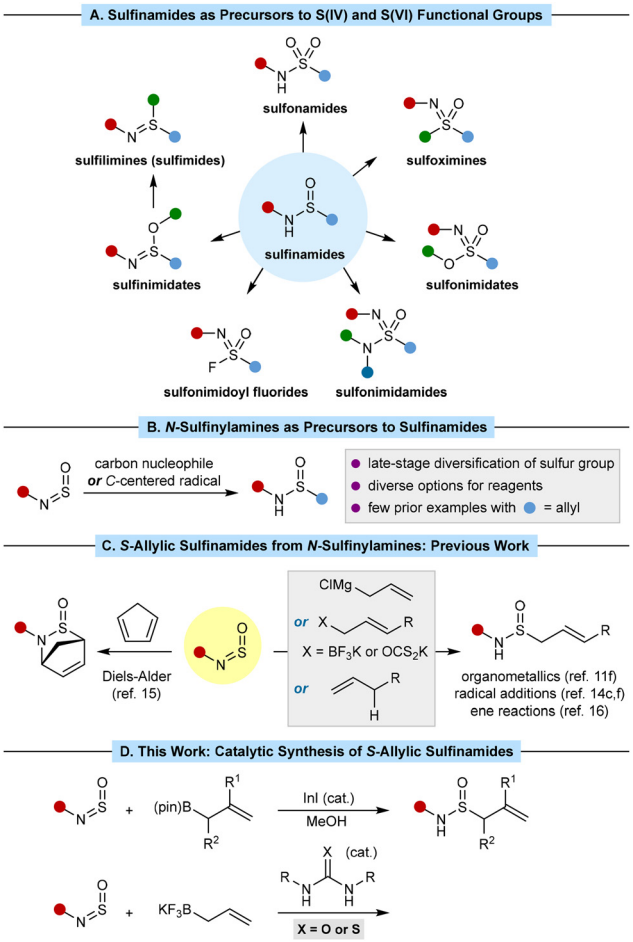
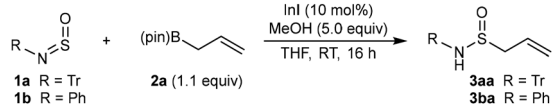


Scheme 1 (A) Synthetic versatility of sulfinamides. (B) Synthesis of sulfinamides from *N*-sulfinylamines. (C) Previous syntheses of *S*-allylic sulfinamides from *N*-sulfinylamines. (D) Catalytic nucleophilic allylation of *N*-sulfinylamines (this work).

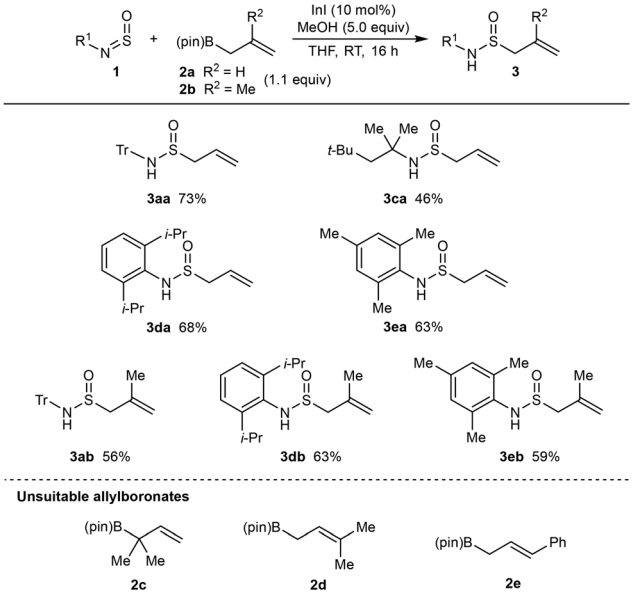
Table 1 Allylation of *N*-sulfinylamines **1a** or **1b** with allyl pinacolboronate (**2a**)[a]



Entry	R	Deviation from conditions	Yield (%)
1	Tr	None	73[b]
2	Tr	Without MeOH	<5[c]
3	Tr	Without InI	<5[c]
4	Ph	None	<5[c]

[a] Reactions were conducted using 0.25 mmol of **1a** or **1b** in THF (1 mL). [b] Yield of isolated **3aa**. [c] Determined by ^{1}H NMR analysis of the crude reaction mixtures.

3aa in 73% yield, allyl pinacolboronate (**2a**) reacted with *tert*-octylsulfinylamine to give **3ca** in 46% yield. As with *N*-sulfinyl aniline (**1b**) (Table 1, entry 4), *N*-sulfinylamines with other *N*-aryl groups such as 2-methoxyphenyl, 4-cyanophenyl, or

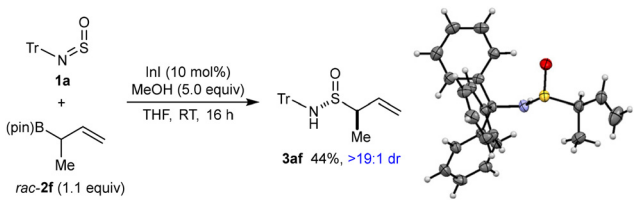


Scheme 2 Scope of the indium-catalyzed nucleophilic allylation of *N*-sulfinylamines with allylboronates.

3-carbomethoxyphenyl are unsuitable substrates under these conditions and undergo decomposition to the corresponding aniline. However, *N*-sulfinylamines containing sterically hindering *N*-aryl groups such as 2,6-diisopropylphenyl or mesityl are more stable to decomposition and reacted smoothly with allyl pinacolboronate to give *S*-allylic sulfinamides **3da** and **3ea** in reasonable yields. 2-Methylallyl pinacolboronate (**2b**) is also a competent pronucleophile and reacted with a range of *N*-sulfinylamines to give allylation products **3ab**, **3db**, and **3eb** in 56–63% yield.

Reactions of sterically more hindered allylboronates **2c**–**2e** with *N*-sulfinyltritylamine (**1a**) were unsuccessful; although the allylboronate was partially consumed, **1a** did not react and was recovered unchanged. However, the reaction of racemic allylboronate *rac*-**2f** with **1a** gave *S*-allylic sulfinamide **3af** with two stereocenters in 44% yield and >19 : 1 dr, as determined by ^{1}H NMR analysis of the crude reaction mixture (Scheme 3). The relative configuration of **3af** was determined by X-ray crystallography.

Based upon literature precedent,[18] we believe these reactions occur *via* allylindium species formed by transmetalation

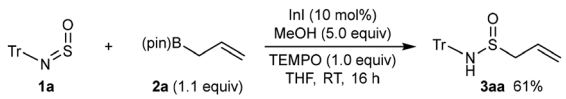


Scheme 3 Formation of *S*-allylic sulfinamide **3af** with two stereocenters and X-ray crystal structure with ORTEP with ellipsoid probabilities at 50%.

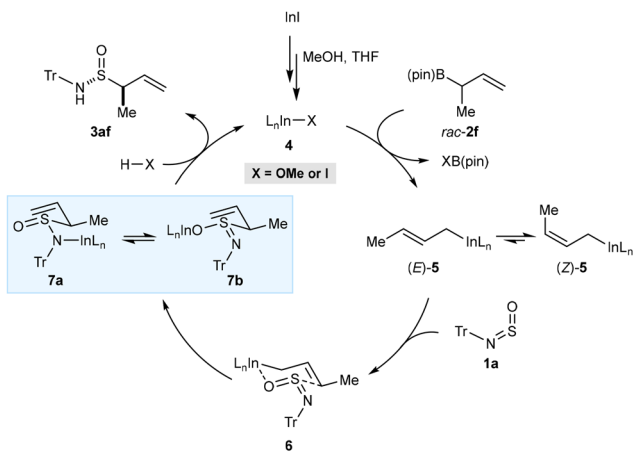
from the allylboronates. However, to rule out alternative mechanisms involving radical intermediates, the reaction of **1a** with **2a** was conducted in the presence of a stoichiometric quantity of the radical scavenger TEMPO (Scheme 4). This reaction gave **3aa** in 61% yield, which suggests that radical species are less likely to be involved.

A tentative catalytic cycle for these reactions, using **1a** and *rac*-**2f** as representative substrates, is shown in Scheme 5. First, transmetalation of *rac*-**2f** with an indium(I) species **4** derived from InI gives the *E*-crotylindium species (*E*)-**5**, which could be in equilibrium with the less thermodynamically stable *Z*-crotyl isomer (*Z*)-**5** *via* σ–π–σ isomerization.[18b] Reaction of (*E*)-**5** with **1a** in a six-membered chair-like transition state **6**, in which indium is coordinated to the oxygen atom of **1a**, and the S = NTr moiety occupies a less-hindered pseudoequatorial position, would give **7a** and/or **7b**. Protonolysis of **7a** and/or **7b** with HX (X = OMe or I), would release the product **3af** and regenerate the indium(I) species **4**. However, alternative models (involving coordination of indium to sulfur or nitrogen, or involving open transition states) cannot be ruled out. More studies, such as DFT calculations, will be required to shed more light on the mechanism and stereochemical model.

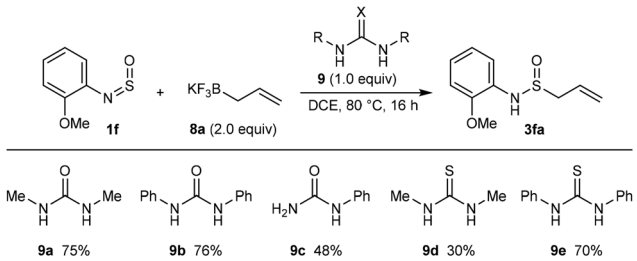
The requirement for MeOH in these reactions restricts the scope of *N*-sulfinylamines to those that are more stable to MeOH-induced decomposition to the corresponding aniline. Therefore, we investigated whether other conditions can be used. Our preliminary experiments used potassium allyltrifluoroborate (**8a**) and *N*-sulfinylamine **1f**, which does not react with allyl pinacolboronate (**2a**) using the indium-catalyzed conditions shown in Scheme 2 but instead undergoes decomposition to 2-methoxyaniline (see Scheme 6 for the structure of **1f**). No reaction occurred when **1f** and **8a** were heated together in various solvents.



Scheme 4 Reaction of **1a** and **2a** in the presence of the radical scavenger TEMPO.



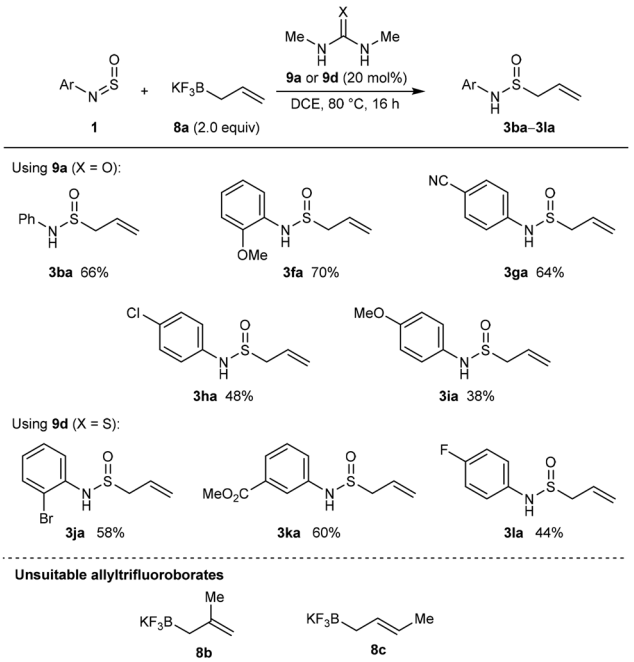
Scheme 5 Tentative catalytic cycle and sterochemical model.



Scheme 6 Evaluation of (thio)ureas in the reaction of *N*-sulfinylamine **1f** with potassium allyltrifluoroborate (**8a**). Yields of **3fa** were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.

Next, additives were screened to try and promote reaction, and ureas or thioureas were selected based on two hypotheses (Scheme 6). First, Batey and co-workers have shown that potassium allyltrifluoroborates engage in the nucleophilic allylation of aldehydes[19] in the presence of $BF_3{\cdot}OEt_2$,[19a,b] presumably through the *in situ*-generation of reactive allylboron difluorides by Lewis acid-promoted removal of fluoride ions.[20] Since (thio)ureas have also been shown to bind fluoride ions through hydrogen bonding,[21] we believed they could be effective in the reaction of **1f** and **8a**. Second, (thio)ureas are well-known hydrogen bonding catalysts,[22] and we considered it possible they could activate *N*-sulfinylamines towards nucleophilic allylation through hydrogen bonding to the oxygen or nitrogen atom. We were pleased to find that heating a mixture of **1f**, **8a** (2.0 equiv.), and *N*,*N*′-dimethylurea (**9a**, 1.0 equiv.) in DCE at 80 °C for 16 h led to the formation of allylation product **3fa** in 75% NMR yield. Similar results were obtained using *N*,*N*′-diphenylurea (**9b**) and *N*,*N*′-diphenylthiourea (**9e**) but lower yields were obtained with *N*-phenylurea (**9c**) and *N*,*N*′-dimethylthiourea (**9d**). *N*,*N*′-Dimethylurea (**9a**) was selected for further experiments based on its performance and low molecular weight. It should be noted that allylboronate **2a** did not react with *N*-sulfinylamines under (thio)urea catalysis. Also, potassium allyltrifluoroborate (**8a**) did not react with *N*-sulfinylamines under the indium-catalyzed conditions shown in Scheme 2.

Pleasingly, we found that in a preparative experiment, the quantity of **9a** can be reduced to 20 mol% without detriment as shown by the formation of **3fa** in 70% isolated yield (Scheme 7) compared to 75% NMR yield using stoichiometric **9a** (Scheme 6). Under these conditions, allylation products containing phenyl (**3ba**), 4-cyanophenyl (**3ga**), or 4-chlorophenyl groups (**3ha**) were obtained in 48–66% yield from the corresponding *N*-sulfinylamines (Scheme 7). Despite performing only modestly in the allylation of *N*-sulfinylamine **1f** (Scheme 6), *N*,*N*′-dimethylthiourea (**9d**) gave better yields than *N*,*N*′-dimethylurea (**9a**) in allylations of *N*-sulfinylamines with 2-bromophenyl (**3ja**), 3-carbomethoxyphenyl (**3ka**), or 4-fluorophenyl groups (**3la**). *N*-Sulfinyltritylamine (**1a**) was unreactive under these conditions using either **9a** or **9d**. This reaction

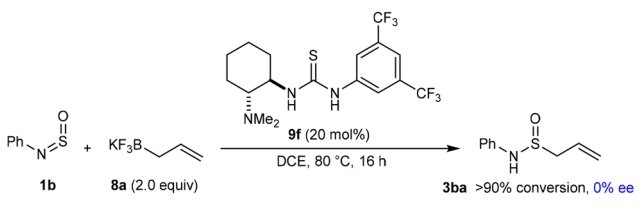


Scheme 7 Scope of (thio)urea-catalyzed nucleophilic allylations of *N*-sulfinylamines with potassium allyltrifluoroborate (**8a**).

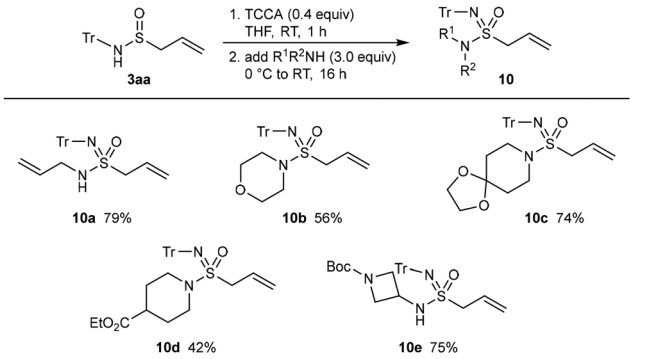
appears to be limited to the use of potassium allyltrifluoroborate (**8a**) as attempted reactions of *N*-sulfinylaniline (**1b**) with substituted allyltrifluoroborates **8b** and **8c** led to no allylation products, with only partial decomposition of **1b** into aniline observed.

The reaction of *N*-sulfinylamine **1b** with **8a** in the presence of a chiral thiourea catalyst **9f** gave **3ba** but with no enantioselectivity (Scheme 8). This observation may suggest these reactions do not operate through hydrogen bonding of the (thio)urea to the *N*-sulfinylamine,[21] but rather through fluoride abstraction from potassium allyltrifluoroborate to generate allylboron difluoride.[19a,b] However, more experiments are required for greater insight.

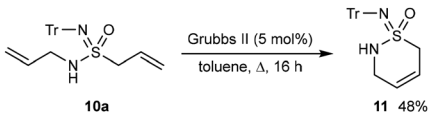
Further reactions were conducted on product **3aa** to demonstrate the synthetic utility of these compounds. *N*-Sulfinamides are versatile precursors to other sulfur(IV)- or sulfur(VI)-containing functional groups,[6,7] but it was of interest to determine whether the alkene in our allylation products is compatible with the reagents used in these reactions. As a representative transformation, the conversion of **3aa** into sulfonimidamides was investigated. Pleasingly, treatment of **3aa** with trichloroisocyanuric acid (TCCA, 0.4 equiv.) gave a sulfonimidoyl chloride that was not isolated but reacted immediately with various amines (3.0 equiv.) to give sulfonimidamides **10a–10e** in 42–79% yield, where the alkene remain unchanged (Scheme 9).[7e] The amines included allylamine (**10a**), morpholine (**10b**), piperidine derivatives (**10c** and **10d**), and a Boc-protected 4-aminoazetidine (**10e**).



Scheme 8 Reaction of **2b** with **8a** in the presence of chiral thiourea **9f**.



Scheme 9 Preparation of sulfonimidamides **10a–10e** from **3aa**.



Scheme 10 Synthesis of cyclic sulfonimidamide **11**.

Finally, cyclization of **10a** by ring-closing metathesis using the second-generation Grubbs catalyst (5 mol%) in toluene at reflux gave cyclic sulfonimidamide **11** in 48% yield (Scheme 10).

Conclusions

In summary, we have described the catalytic nucleophilic allylation of *N*-sulfinylamines with allylboron reagents. *N*-Sulfinylamines containing sterically hindering *N*-substituents react with allyl pinacolboronates using catalytic indium(I) iodide in the presence of MeOH, whereas other *N*-sulfinylamines react with potassium allyltrifluoroborate using a (thio)urea catalyst. These reactions give ready access to *S*-allylic sulfinamides, which have been comparatively underexplored. Future work will focus on enantioselective variants of these reactions.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included in the supplementary information (SI) and the Nottingham Research

Data Management Repository at: http://doi.org/10.17639/nott.7611. Supplementary information: experimental procedures, full spectroscopic data for new compounds, and crystallographic data. See DOI: https://doi.org/10.1039/d5ob01562f.

CCDC 2475361 (**3af**) contains the supplementary crystallographic data for this paper.[23]

Acknowledgements

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