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A Direct Metal-Free Decarboxylative Sulfono Functionalization (DSF) of Cinnamic Acids to α,β-Unsaturated Phenyl Sulfones

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Supporting Information

ABSTRACT: A metal-free room temperature decarboxylative cross-coupling between cinnamic acids and arylsulfonyl hydrazides has been realized for the first time for the synthesis of (*E*)-vinyl sulfones. The scope and versatility of the reaction has been demonstrated by the regio- and stereoselective synthesis of 22 derivatives with diverse structural features.

Decarboxylative cross-coupling reactions have attracted a great deal of current interest due to their potential advantages.[1] Several seminal contributions have appeared in the recent past using transition metal catalyzed decarboxylative reactions.[2] However, the development of metal-free strategies yet remains scarce.[3] Further, despite the constant demand for room temperature decarboxylative reactions, only a few metal catalyzed protocols have been reported.[4] From this perspective, the advancement of sustainable, transition metal-free, and room temperature decarboxylative cross-coupling strategies leading to the construction of privileged molecular skeletons is exigent and has become a formidable challenge.

The sulfone functionality has huge synthetic potential and is thoroughly investigated.[5] The sulfone group is distinguished for its duality in reactivity, for which it has been described as a "chemical" chameleon by Trost.[6] The installation of a stable phenyl sulfone group in organic molecules facilitates purification and functions as a good chromophore in the UV region which allows easy reaction monitoring by thin-layer chromatography (TLC) and high performance liquid chromatography (HPLC).[7] In particular, the phenyl sulfone group ornamented with an unsaturated moiety, i.e. vinyl sulfone, allyl sulfone, or alkynyl sulfone, constitutes a highly valued and focused target for the chemical community.[8]

Vinyl sulfones are present in a number of biologically active molecules and pharmaceuticals.[9] They have been frequently used in biological research as covalent protease inhibitors, substrates for bioconjugation, and activity-based protein profiling (ABPP) probes.[10] Synthetically, vinyl sulfones serve as Michael acceptors or dienophiles in cycloaddition reactions.[11] Conventional methods for the synthesis of vinyl sulfones involve addition−elimination sequences, olefination reactions (Wittig, Horner−Wadsworth−Emmons (HWE), and Peterson), cerium(IV) mediated reaction of aryl sulfinates and sodium iodide with alkenes/alkynes, addition of selenosulfonates to olefins, hydrozirconation reaction of 1-alkynyl sulfones, oxidation of thioethers, and the condensation of aromatic aldehydes with sulfonylacetic acids.[12] However, these methods involve several steps, use either toxic or unstable starting materials, and often suffer from poor regioselectivity. Consequently, several metal or metal-free strategies have been developed by using the reaction of sodium sulfinate salts with vinyl bromides/triflates/tosylates/boronic acids, or terminal epoxides, or cinnamic acids.[13] Very recently a gold catalyzed synthesis of vinyl sulfones has appeared involving the coupling of terminal alkynes and sulfinic acids.[14] Yet, efficient methodologies which are applicable to the preparation of both vinyl or alkynyl sulfones in terms of selectivity, availability of starting materials, operational simplicity, functional-group tolerance, and environmental sustainability are in constant demand. More importantly, the identification of a readily available, easy to prepare, and stable alternate to sodium sulfinate salts or sulfinic acids is highly desirable to further advance the regioselective synthesis of vinyl or alkynyl sulfones.

Recently arylsulfonyl hydrazides have evolved as excellent synthons[15] and behave as a source for a sulfur nucleophile or electrophile depending upon the nature of the reaction conditions. The generation of a sulfur electrophile from arylsulfonyl hydrazides has been explored by the research group of Tian,[16] whereas our group has exploited the use of arylsulfonyl hydrazides as a nucleophilic thiol equivalent.[17] Motivated by the work of Tian[18a] and Breit,[18b] we have developed a novel metal-free protocol for room temperature decarboxylative sulfono functionalization using the reaction of arylsulfonyl hydrazides with cinnamic acids or alkynoic acids, to provide a range of sulfono endowed unsaturated molecules (Scheme 1).

In order to optimize the reaction conditions, a model reaction of cinnamic acid (**1a**) and *p*-toluenesulfonyl hydrazide (**2a**) was carried out using 20 mol % I_2 as the catalyst and CH_3CN as the solvent in an open atmosphere at room temperature (Table 1). Gratifyingly, the desired product **3a** was formed in 15% yield (entry 1). An increase in the mol % of I_2 to

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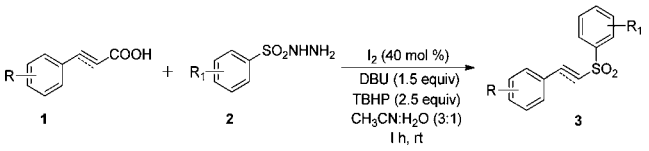
Scheme 1. Decarboxylative Sulfono Functionalization



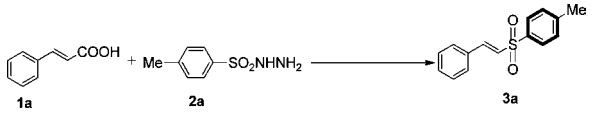
40 brought about a reasonable rise in the yield (entry 2), but a further incremental increase in the I_2 concentration did not enhance the yield again (entry 3), albeit a notable amount of disulfide was observed along with unreacted cinnamic acid. We envisioned that the use of a radical initiator along with a base might be helpful in improving the yield. As expected, the addition of 1.5 equiv of TBHP (70% solution) improved the yield remarkably, and 2.5 equiv of TBHP were found to be sufficient for a reasonably improved yield of the product (entries 4−6). Thereafter, we screened the effect of different bases on the reaction profile and arrived at 1.5 equiv of DBU as the best choice (entry 8). The superior activity of DBU is ascribed to its greater ability to capture the carboxylic acid proton, thereby facilitating a trouble-free room temperature decarboxylation. Various solvents were then probed to promote the reaction, and the solvent mixture CH_3CN/H_2O (3:1) was found to be particularly effective for this transformation.

After all, the use of I_2, TBHP, and DBU were crucial for this reaction, and by using the optimized reaction conditions [40 mol % I_2, 1.5 equiv of DBU, and 2.5 equiv of TBHP in CH_3CN/H_2O (3:1)] (entry 10), the generality of the method was subsequently explored.

Different sets of cinnamic acids and sulfonyl hydrazides having various substitution patterns underwent a smooth decarboxylative sulfono functionalization and delivered the desired products in good to excellent yields (Table 2). The cinnamic acids bearing electron-donating groups and sulfonyl hydrazides having electron-withdrawing groups participated well in the reaction to deliver high product yields. The reaction of *o*-chloro cinnamic acid (**1g**) with *p*-toluenesulfonyl hydrazide (**2a**), however, produced a somewhat lower product yield perhaps due to the steric hindrance. (*E*)-3-(Thiophen-3-yl)acrylic acid (**1h**) also participated nicely and delivered the products (**3h** and **3l**) in high yields. A typical aliphatic sulfonyl hydrazide, i.e. octylsulfonyl hydrazide, also underwent the reaction smoothly. The protocol was ultimately effectively applied for the otherwise difficult decarboxylative sulfono functionalization of 3-phenylpropiolic acid to afford the products **3u** and **3v**. The overall reaction offers an excellent functional group tolerance. The structure of a representative product **3k** has been conclusively confirmed by the single crystal X-ray (Figure 1).

In order to gain insight into the reaction mechanism, a number of control experiments were carried out using the reaction of (*E*)-cinnamic acid (**1a**) and *p*-toluenesulfonyl hydrazide (**2a**). The radical inhibitors such as 2,6-di-*tert*-butyl-4-methylphenol (BHT) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) suppressed the reaction under standard conditions implying a radical pathway (*cf.* Supporting Information). The decomposition of the sulfonyl hydrazide **2a** in the absence of **1a**, however, gave rise to the formation of *p*-tolyl 4-methylbenzenesulfonothioate (**3aa**, 71%) along with 1,2-di-*p*-tolyldisulfane (**3ab**, 10%). The formation of sulfonothioate intermediate **3aa** was assumed via the intermediacy of disulfide **3ab**. In order to prove this, the disulfide **3ab** was solely made to react under the standard conditions, affording an excellent yield of **3aa**. The intermediacy of sulfonothioate **3aa** was further confirmed by the reaction of **1a** with the sulfonothioate **3aa,** which provided **3a** as the only isolable

Table 1. Impact of Reaction Parameters on Decarboxylative Sulfono Functionalization[a]



entry	catalyst (mol %)	base (mol %)	radical initiator (mol %)	solvent	yield (%)[b]
1.	I_2 (20)	–	–	CH_3CN	15
2.	I_2 (40)	–	–	CH_3CN	30
3.	I_2 (60)	–	–	CH_3CN	30
4.	I_2 (40)	–	TBHP (150)	CH_3CN	47
5.	I_2 (40)	–	TBHP (250)	CH_3CN	65
6.	I_2 (40)	–	TBHP (300)	CH_3CN	65
7.	I_2 (40)	DBU (100)	TBHP (250)	CH_3CN	75
8.	I_2 (40)	DBU (150)	TBHP (250)	CH_3CN	82
9.	I_2 (40)	DBU (200)	TBHP (250)	CH_3CN	80
10.	I_2 (40)	DBU (150)	TBHP (250)	CH_3CN/H_2O (3:1)	87
11.	I_2 (40)	DBU (150)	TBHP (250)	H_2O	77
12.	I_2 (40)	DBU (150)	–	CH_3CN	40
13.	–	DBU (150)	TBHP (250)	CH_3CN	35
14.	I_2 (40)	DBU (150)	TBHP (250)	toluene	32
15.	I_2 (40)	DBU (150)	TBHP (250)	DMF	47
16.	I_2 (40)	DBU (150)	TBHP (250)	–	60
17.	I_2 (40)	DBU (150)	AIBN (250)	H_2O	43
18.	I_2 (40)	K_2CO_3 (200)	TBHP (250)	H_2O	complex[c]
19.	I_2 (40)	NaOH (200)	TBHP (250)	H_2O	complex[c]

[a]Using **1a** (2 mmol) and **2a** (2.4 mmol) under an open atmosphere at rt. [b]Isolated yield after column chromatography. [c]Many side products are observed.

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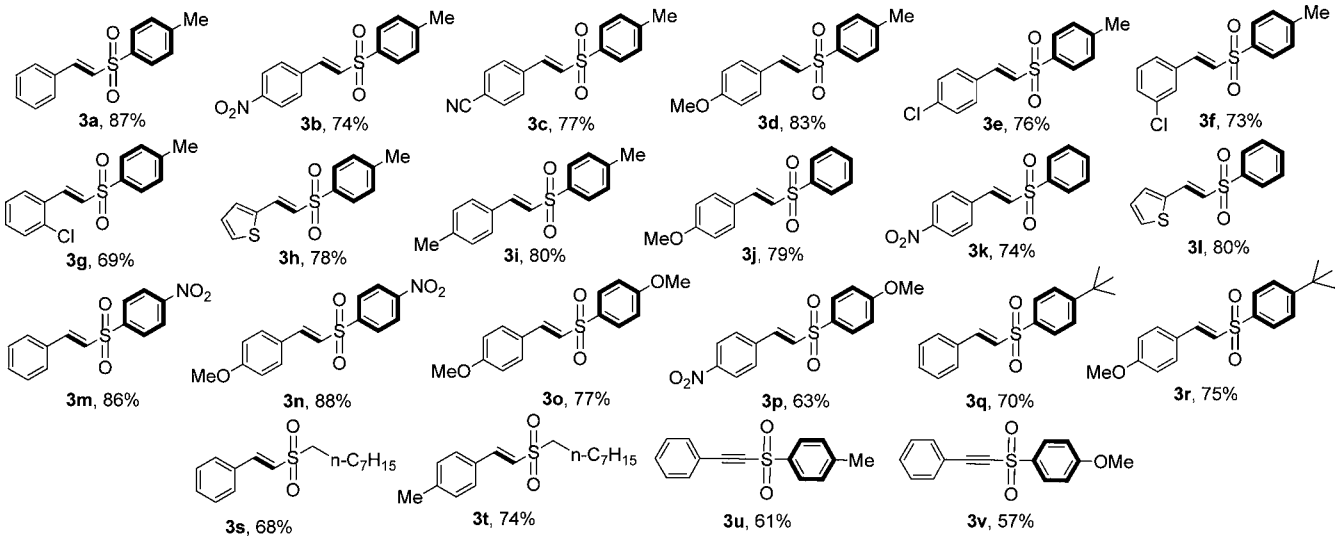
Table 2. Substrate Scope for the Decarboxylative Sulfono Functionalization (DSF)[a,b]



[a]Using **1** (2 mmol), **2** (2.4 mmol), I_2 (40 mol %), DBU (1.5 equiv), TBHP (2.5 equiv) in CH_3CN/H_2O (3:1) under air at rt for 1 h. [b]Isolated yield after column chromatography.

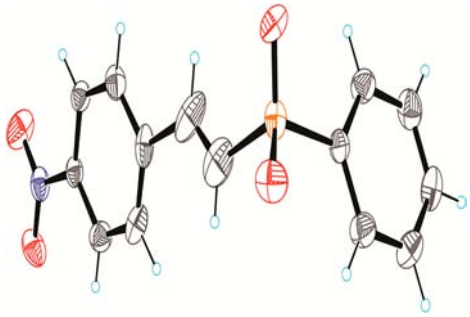
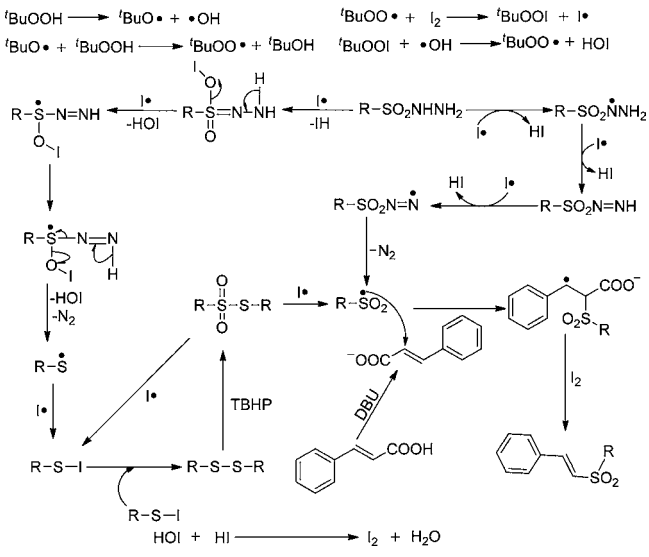


Figure 1. Crystal structure of **3k** (CCDC 1063049).

product. When the reaction of **1a** was conducted with the disulfane **3ab**, the desired product **3a** was obtained in a somewhat lower yield, obviously via **3aa**.

Based on isolation of products and existing literature,[15−19] a plausible mechanism is outlined in Scheme 2. The reaction is presumed to involve a sulfonyl radical, which is formed by the sequential N−H abstraction by an iodine radical generated by the reaction of I_2 with TBHP. The resulting sulfonyl radical subsequently undergoes addition to cinnamate followed by iodine catalyzed decarboxylation to restore the unsaturation to afford an (*E*)-*α*,*β*-unsaturated phenyl sulfone.

Scheme 2. Plausible Reaction Mechanism



In conclusion, a highly efficient room temperature decarboxylative sulfono functionalization strategy has been developed to synthesize a variety of aryl, heteroaryl, and aliphatic sulfonylated unsaturated compounds. The protocol refrains from using expensive metal catalysts and operates efficiently under an open atmosphere. The methodology is regio- and stereoselective and opens new avenues for extremely difficult room temperature decarboxylative reactions.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, full characterization data, and copies of NMR spectra (^1H and ^{13}C) of all the products. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01037.

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Notes

The authors declare no competing financial interest.

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