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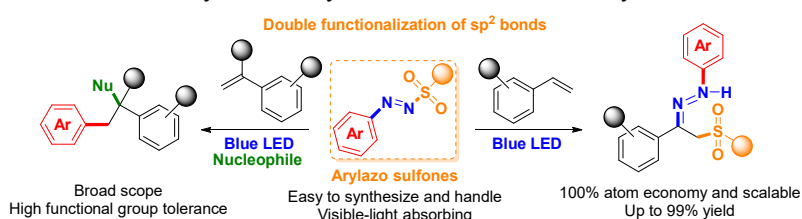
Visible-light-mediated Divergent and Regioselective Vicinal Difunctionalization of Styrenes with Arylazo Sulfones

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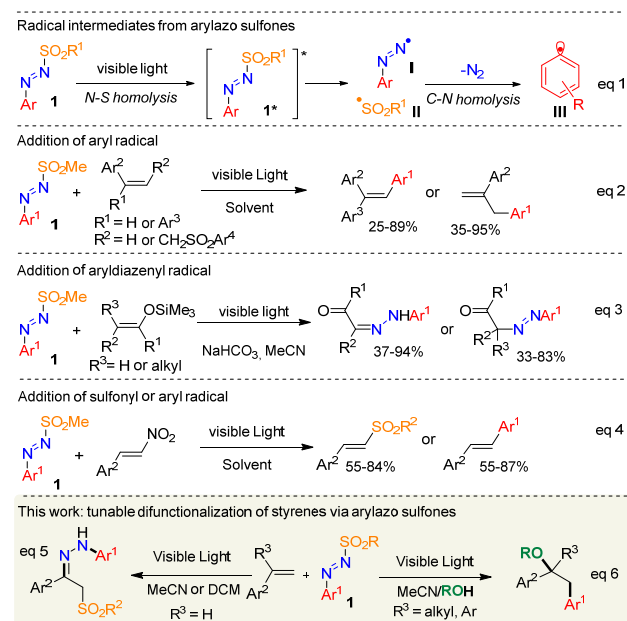


ABSTRACT: Activated by visible light, arylazo sulfones can serve as multifaceted reactants and employed in diazenylation, sulfonylation, and arylation reactions under (photo)catalyst free conditions. Such versatile reactivity enabled us to develop an operationally simple, regioselective and tunable difunctionalization of styrenes with arylazo sulfones to produce α -sulfonyl arylhydrazones and 1,2-alkoxyarylated products in moderate to excellent yields. Furthermore, such difunctionalized products have been exploited as key building blocks for the synthesis of various heterocycles.

Radical-mediated vicinal difunctionalizations of alkenes in which two units are simultaneously installed across a double bond in a single operation are powerful approaches to rapidly produce complex compounds with high step economies.¹ In this field, visible-light catalysis¹⁻³ has recently attracted much attention for developing facile intermolecular difunctionalizations of readily accessible alkenes,⁴ and two main strategies have been successfully applied. The first one involves the addition of a radical to an alkene and a subsequent capture of the intermediate by a suitable reactant.⁵ The second one relies on the use of bifunctional reagents, which, under photocatalytic conditions, result in the formation of two radicals that are concomitantly incorporated into the alkenes.⁶ Although various efficient difunctionalizations have been reported based on these complementary methods, the majority needs exogenous photocatalysts which are often costly and difficult to recycle.⁵⁻⁶ Therefore, the development of more sustainable approaches is still highly necessary.

Recently, a photocatalyst free strategy built on dydauxiliary group⁷ able to mediate radical has attracted several organic chemists, notably focusing on promising photoactive arylazo sulfones.^{7c,8} As illustrated in Scheme 1 (eq 1), the photoinduced sequential cleavage of N-S and C-N bonds in these compounds can form three different radicals, namely diazenyl (I),⁹ sulfonyl (II)¹⁰ and aryl (III)¹¹ radicals, which can each react with partners. Produces in various visible-light-driven process, these species allowed successful alkene monofunctionalizations. For example, we developed an efficient arylation procedure of 1,1-

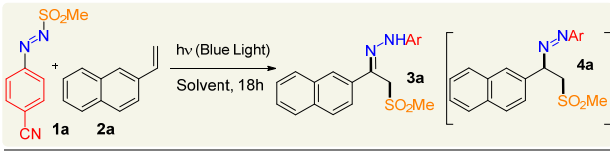
Scheme 1. Examples of Functionalizations of Alkenes with Arylazo Sulfones.



diaryl ethylenes^{12a} and allyl sulfones^{12b} with arylazo sulfones yielding triaryl ethylenes and allyl arenes, respectively (eq 2). Furthermore, the diazenylation of enol silyl ether derivatives¹³ and ketene silyl acetals (eq 3)¹⁴ was also achieved through direct

trapping of aryl diazenyl radicals **1** generated from arylazo sulfones. In 2020, Chawla and co-workers used arylazo sulfones as the precursors of sulfonyl radicals and reported the sulfonylation of cinnamic acids yielding (*E*)-vinyl sulfones in good yields.¹⁵ Thereafter, the same group carried out the monofunctionalization of nitrostyrenes with arylazo sulfones. The reaction proceeds through the addition of aryl or sulfonyl radicals to the double bonds followed by a denitration step, and the structure of the resulting products depends on the reaction conditions (eq 4).¹⁶ Despite these achievements, the adoption of reaction conditions that enable the use of these substrates in the 1,2-difunctionalization of alkenes has been scarcely reported. Wei and co-workers¹⁷ reported the only example of 1,2 difunctionalization, achieving an oxysulfonylation, from arylazo sulfones. In view of these premises, we envisioned that the divergent reactivities of arylazo sulfones could be applied to the vicinal difunctionalization of alkenes by carefully adjusting the reaction conditions. Herein, we report a visible-light-mediated divergent and regioselective synthesis of α -sulfonyl arylhydrazones and 1,2-alkoxyarylated products from readily available styrenes (eq. 5,6).

Table 1. Survey of Reaction Conditions.^a



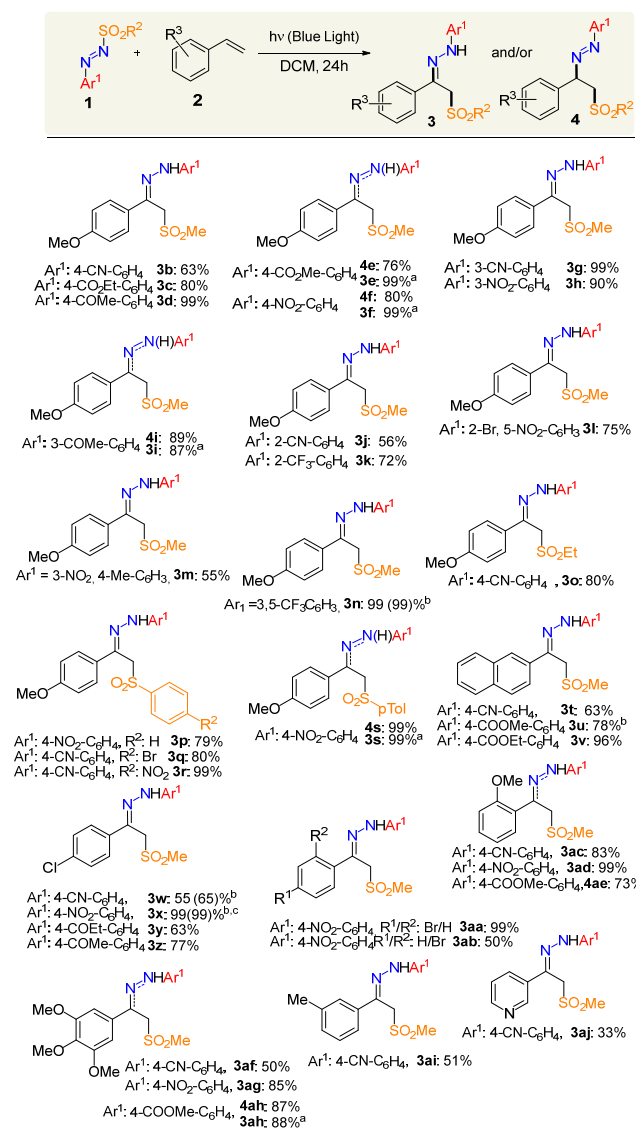
entry	1a (mmol)	2a (mmol)	solvent	3a (yield %) ^b
1 ^c	0.1	0.1	DCM	73
2	0.2	0.2	DCM	90
3 ^d	0.2	0.2	DCM	90
4	0.2	0.2	MeCN	90
5	0.4	0.4	DCM	90 ^e
6^f	0.4	0.2	DCM	96
7 ^g	0.4	0.4	DCM	-

^aReaction conditions: **1a** and **2a** in 2.0ml solvent, blue LED (λ_{\max} = 456 nm, 40W, 100% Power) 10°C, 18 h; degassed using three freeze–evacuate–thaw cycles. ^bYields refer to chromatographically pure product. ^cBlue LED (λ_{\max} = 456 nm, 40W, 25% Power), argon steam-degassed. ^dBlue LED (λ_{\max} = 450 nm, 18W, 100% Power). ^e**4a** Isolated in 5% yield. ^f24 h. ^g In the dark.

We initially studied the functionalization of arylazo sulfone **1a** and 2-vinylnaphthalene (**2a**) upon light irradiation as a model reaction and the results are depicted in Table 1. In the first attempt, a product was isolated in 73% yield in degassed DCM (entry 1). The structure of product was identified by NMR studies as the α -sulfonyl arylhydrazone **3a** with (*Z*)-configuration. Such results encouraged us to further investigate this regioselective difunctionalization of styrenes by tuning conditions (Table 1).^{18,19} Increasing the scale of **1a** and **2a** led to a better yield independently of light source used (entries 2 and 3). A solvent screening pointed out that DCM and MeCN provided identical results (entry 4), and then DCM was selected for further studies. Performing the reaction at a higher concentration (0.4 mmol of **1a**), the desired product **3a** precipitated in less than 16 h and was isolated by simple filtration (entry 5). Further analysis of the filtrate revealed the formation of another product (5% yield) corresponding to the

α -sulfonyl aryl diazene **4a**.²⁰ We surmised that compound **4a** could be an intermediate to compound **3a**. Indeed, when the irradiation was performed for 24 h by reducing the ratio of **2a**, hydrazone **3a** was the sole product formed in 96% yield (entry 6). To explore the scope of this difunctionalization, various arylazo sulfones **1** were studied under the optimized reaction conditions (Scheme 2). We found that the efficiency of the process was sensitive to the electronic properties of the aromatic substituents in **1**. Thus, different arylazo sulfones bearing electron-withdrawing substituents (such as CN, CO₂Et, NO₂, CF₃ or COCH₃) in *ortho*-, *para*- or *meta* position reacted efficiently with 4-vinylanisole **2b** to form the corresponding α -sulfonyl arylhydrazones (**3b-h**, **3j,k**). Disubstitution was also tolerated (**3l-n**).

Scheme 2. Scope of the Difunctionalization of Styrenes with Arylazo Sulfones.

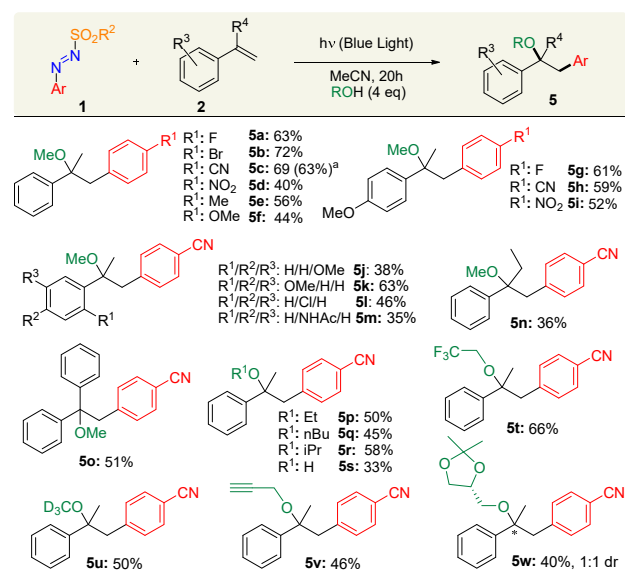


Reaction conditions: **Table 1**, entry 6, ^a36 h; ^b Reaction carried out on 1 mmol of **1**. ^c Natural sunlight was used as light source (77 h).

Surprisingly, in some cases, only the corresponding α -sulfonyl arylhydrazones **4** were isolated under the optimized conditions (e.g. **4i**), but a prolonged irradiation (36 h) resulted in the almost quantitative phototautomerization of **4** to the

desired arylhydrazones **3**. The nature of the sulfone group was found to have neglecting effect on the reaction since an alkyl or aryl substituted azosulfones were synthesized in high yields (**3o-3s**). Finally, the scope of styrenes **2** was screened, pointing out that various substituents at the *ortho*-, *meta*- and *para* positions were compatible to afford corresponding products **3w-3ai** in excellent yields. Nearly quantitative yield of **3x** was obtained after 77 h of exposition of the reaction mixture to natural sunlight. 2-Vinylpyridine was also transformed to the corresponding product **3aj**, albeit in low yield. The reaction was found ineffective with α -substituted styrenes, leading to a complex mixture of products under the presently optimised condition. We considered that formation of a stable benzyl radical, generated *via* a β -addition on α -methyl styrenes, could hamper the process. However, hypothesizing that such radical could be oxidized, to deliver a cation, we reasoned that it could be exploited in a coupling reaction with a nucleophilic counterpart, resulting in a new difunctionalization strategy.

Scheme 3. Scope of the Difunctionalization of Styrenes with Arylazo Sulfones and ROH.



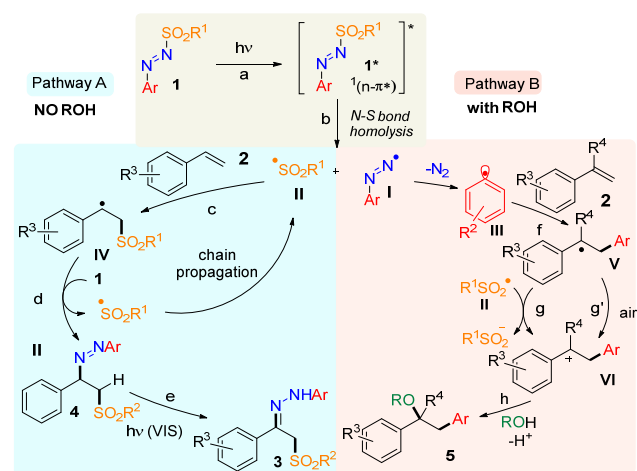
Reaction conditions: **1** (0.60 mmol) and **2** (1.20 mmol) and ROH (2.40 mmol) in 3 mL of argon saturated MeCN at rt for 20 h, blue LED ($\lambda_{\text{max}} = 450 \text{ nm}$, 18W, 100% Power) irradiation. Isolated yield. ^a Starting from 1.2 mmol of **1a** in 6.0 mL of MeCN.

With this in mind, we focused on α -methylstyrene **2j** as the model substrate. During the screening process, we found that, in MeOH, a different outcome led to 1,2-methoxyarylated product **5a**²¹ as the single regioisomer in 32% yield (See SI). After surveying the reaction conditions by varying the solvent, and stoichiometry, we found that the reaction performed in MeCN in the presence of 4 eq of MeOH afforded the product **5a** in 63% yield (Scheme 3, see SI for details). With the optimized conditions in our hands, we subsequently studied the scope of the three-component alkene difunctionalization (Scheme 3). An array of arylazo sulfones efficiently reacted with α -methyl styrenes and smoothly delivered the corresponding methoxyarylated products **5b-5i** in moderate to good yields. Both electron-donating groups (such as OMe, Me) and electron-withdrawing groups (such as CN, F, Br, NO₂) on the arylazo sulfones were compatible. The reaction of α -methyl styrenes bearing electron-rich as well as electron-poor

substituents in *ortho*, *meta*, and *para* positions of the aryl ring proceeded well to afford the corresponding products **5g-5m** in good yields. α -Ethyl styrene reacted to yield **5n**, albeit with a lower yield. Notably, the three-component reaction was successfully applied to 1,1-diarylstubstituted ethylene leading to the desired methoxyarylated product **5o**, instead of the triarylethylene generated in dry acetonitrile.^{12a} Various alcohols such as EtOH, *n*BuOH, and *i*PrOH as well as water participated smoothly in the reaction to afford the products (**5p-5s**) in moderate to good yields. In addition, trifluoroethanol decently performed as a nucleophile and allowed to easily introduce the highly electronegative and lipophilic trifluoroethoxy group in product **5t**. The three component difunctionalization can be performed with deuterated methanol and propargyl alcohol (**5u** and **5v**). Gratefully, the chiral (*R*)-1,2-*O*-isopropylidenglycerol can also be used, providing the desired product **5w** as a mixture of diastereomers (1:1 dr).

Control experiments were conducted to obtain mechanistic insights (see SI, section 1.4 for details), including on-off experiments (see Figures S9 and S16) and irradiation in the presence of the radical scavenger (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO), where the efficiency of both reactions was inhibited and where LC-MS analyses revealed the presence of a TEMPO adduct resulting from the trapping of an aryl radical. On the basis of the obtained results, and on available literature,^{7c,8,12-16} we suggested two competing radical pathways (Scheme 4), that are mainly controlled by the nature of the styrene employed.

Scheme 4. Plausible Reaction Mechanism

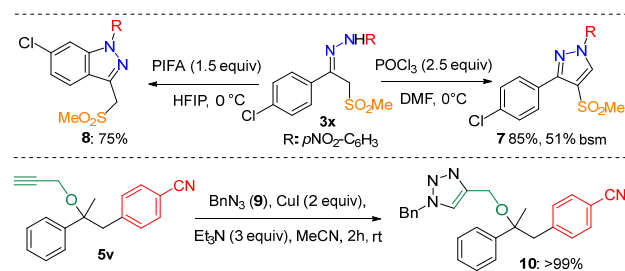


First, irradiation with visible light ($\lambda = 456 \text{ nm}$) promotes the arylazo sulfones into $^1n\pi^*$ -state **1*** (step a) which undergoes a homolytic cleavage of the S–N bond to generate the diazenyl radical **I** and sulfonyl radical **II** (step b). In absence of alcohol and in fully deoxygenated conditions (pathway A), **II** is in turn trapped by non- α -substituted styrene **2** to form the benzylic radical species **IV** (step c) which thus adds itself onto the N=N bond of arylazo sulfone **1** and release a new sulfonyl radical **II** (by following a chain propagation pathway) furnishing α -sulfonyl aryl diazene **4** (step d), that in turn undergoes (photo)tautomerization to form **3** (step e).²² On the other hand in (pathway B), in presence of alcohol the diazenyl radical **I** rapidly leads to aryl radical **III** which selectively reacts with α -substituted styrene **2** (step f).²³ Then, the tertiary radical **V** could be oxidized into carbocation **VI** by sulfonyl radical **II** (step g) or by residual traces of O₂ (step g'). Final trapping of the

cationic intermediate by nucleophilic alcohol (step h), affords the corresponding alkyloxyarylated compound **5**.

To demonstrate the synthetic potentials of our protocols, the 1,2-sulfonyl-arylhazination and 1,2-alkyloxy arylation of styrenes were scaled up (1 mmol). The results are comparable (99% for **3n** and 63% for **5c**, Scheme 2 and 3), if not better (65% and 99% for **3w** and **3x**, respectively, Scheme 2). Thereafter, a series of transformations was carried out on these difunctionalized products (Scheme 5). For instance, the reaction of **3x** with the Vilsmeier–Haack reagent readily afforded the valuable pyrazole **7** in decent yield.^{24a} In addition, the arylhydrazone was also converted to benzopyrazole **8** by PIFA-mediated oxidative cyclization of **3x** in HFIP.^{24b} Finally, the Cu-mediated click reaction of **5v** with benzyl azide **9** gave the corresponding triazole **10** in quantitative yield.²⁵

Scheme 5. Synthetic Transformations of **3** and **5**.



In conclusion, we have developed two sets of conditions for the visible-light mediated difunctionalization of styrenes with readily available arylazo sulfones to afford either α -sulfonyl arylhydrazones or 1,2-alkoxyarylated products, depending on the styrenes used. This protocol offers novel syntheses of α -sulfonyl arylhydrazones or 1,2-alkoxyarylated products which are versatile building blocks for the synthesis of various heterocycles.

ASSOCIATED CONTENT

Data Availability Statements

The data underlying this study are available in the published article and its Supporting Information

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Experimental procedures and characterization data. (PDF)

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Notes

The authors declare no competing financial interest.

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