OL Organic Letters
Letter
Cite This: Org. Lett. XXXX, XXX, XXX−XXX
pubs.acs.org/OrgLett

Visible-Light-Driven Synthesis of Arylstannanes from Arylazo Sulfones

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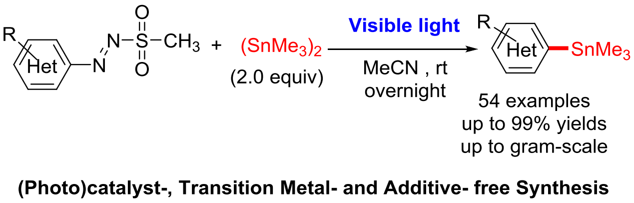
Supporting Information

ABSTRACT: The visible-light-driven preparation of (hetero)aryl stannanes was carried out under both photocatalyst- and metal-free conditions via irradiation of arylazo sulfones in the presence of hexaalkyldistannanes. The reaction shows a high efficiency and a wide substrates scope. The resulting crude organotin derivatives can be directly employed in a Stille protocol.

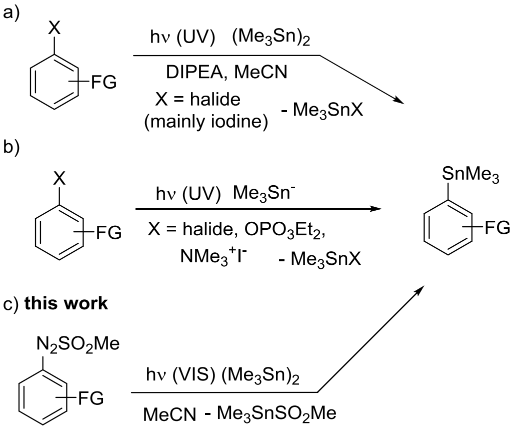


The Pd-catalyzed cross-coupling reactions of organotin reagents, such as the Stille coupling reaction, have found impressive applications in the design of functional molecules in organic synthesis, drug discovery, and other fields.[1] In particular, the C−Sn bond of arylstannanes has been employed in constructing, apart from a C−C bond, various Ar−Y bonds including C−N,[2] C−F,[3] C−B,[4] and $\mathrm{C{-}OCF_3}$[5] bonds. Due to the wide use of organotin derivatives, the development of innovative synthetic protocols to achieve these compounds has attracted significant attention. Conventional methods involve the reaction of trialkyl tin halides with arylmagnesium, -lithium, or -zinc reagents.[6] Furthermore, various transition metals including palladium[7] and nickel[8] have been used in transition-metal-catalyzed stannylations starting from aryl halides or aryl esters. Sandmeyer-type stannylations from aryl amines[9] and Lewis acid mediated stannylation of aryl triazenes[10] have been disclosed as transition-metal-free alternatives.

In the past few decades, the photochemical approach has received growing attention in organic synthesis owing to the advantages of the eco-sustainable and mild conditions required.[11] Visible-light-driven transformations have opened up a superior avenues for generating radical species to construct C−C and C−X bonds in a selective fashion.[12]

In particular, aryl radicals can be generated through a single electron transfer process under visible-light irradiation in the presence of a photocatalyst.[13] Visible-light photoredox catalysts such as ruthenium or iridium polypyridyl complexes and organic dyes, which efficiently facilitated the conversion of visible light into chemical energy under mild conditions, are usually required in this type of transformations.[14] Despite the great efforts devoted to replace the metal photocatalyst with a photoorganocatalyst,[12b,15] it is extremely attractive for chemists to develop a photochemical transformation in the absence of any photocatalysts or external additives.

Scheme 1. Photoinduced Synthesis of Arylstannanes by (a) Photohomolytic Cleavage of an Ar−X Bond, (b) an $ArS_{RN}1$ Reaction, and (c) Photolysis of Arylazo Sulfones



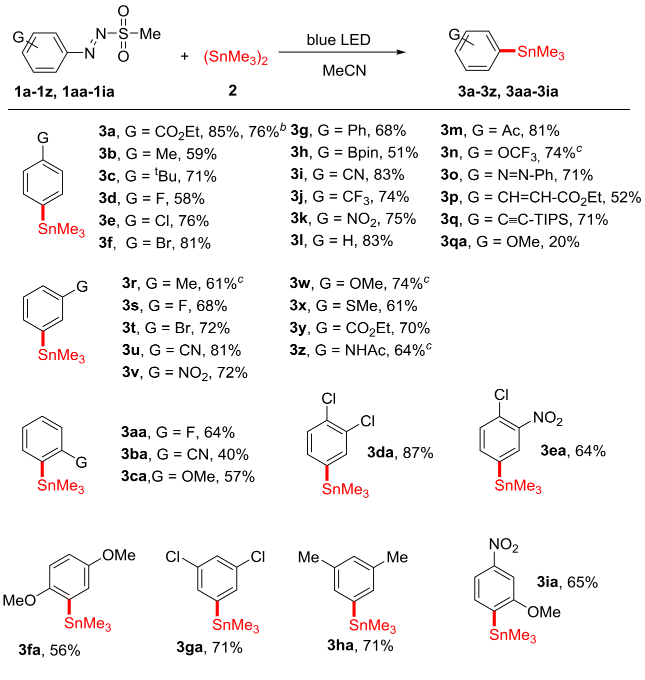
As a matter of fact, arylstannanes may be likewise obtained under metal-free conditions by photogenerated aryl radicals (Scheme 1). The first case is the photohomolytic cleavage of an Ar−X bond (mainly Ar−I) to give an aryl radical that is trapped by hexamethyldistannane in the presence of 1 equiv of DIPEA (Scheme 1a).[16] Alternatively, the photostimulated $ArS_{RN}1$ reaction between aryl chlorides,[17] aryl diethyl phosphates,[18] or aryltrimethylammonium salts[19] with trialkylstannyl ions gave access to arylstannanes (Scheme 1b).

Received: May 22, 2019

Unfortunately, all of the photochemical processes so far known for the preparation of arylstannanes made use of UV light to promote the reaction. Herein, we present the visible-light-driven synthesis of (hetero)aryl stannanes by reaction of arylazo sulfones with hexaalkyldistannanes under photocatalyst-free and additive-free conditions (Scheme 1c). Such colored and bench-stable sulfones can be easily prepared from commercially available colorless anilines in two steps[20] and are suitable precursors of aryl radicals upon visible-light irradiation.[21] Our group applied arylazo sulfones in a series of photochemical reactions,[22] including the uncatalyzed arylation of heterocycles and unactivated arenes,[22a,e] and the synthesis of allylarenes,[22b] aromatic amides,[22c,e] and triarylethylenes.[22d] Recently, a visible-light-driven, metal-free forging of an Ar−B bond (to give arylboronates)[23,24a] and an Ar−S bond (to form aryl sulfides[24a] or sulfoxides[24b]) have been also described.

In order to test the feasibility of our proposal, we tested the visible-light-induced reaction between ethyl 4-((methylsulfonyl)diazenyl)benzoate (**1a**) and hexamethylditin (**2**). The best reaction conditions were as follows: **1a** (0.2 mmol, 1.0 equiv), **2** (0.4 mmol, 2.0 equiv) in MeCN (1 mL), irradiated overnight by 24 W blue LED light, under N_2 atmosphere at room temperature (see Table S1, Supporting Information). When $Me_3Sn{-}Cl$ was used as the stannylation agent, no desired product **3a** was obtained. With the optimized conditions in hand, we then examined the scope of the reaction starting from several functionalized arylazo sulfones by using **2** as the stannylation reagent (Scheme 2). In all cases, the corresponding arylstannanes were obtained in 40−87% yields under very mild conditions. This visible-light-driven stannylation has demonstrated excellent functional group tolerance since the benzene ring bears both electron-withdrawing and electron-donating groups.

Scheme 2. Scope of the Arylazo Sulfones[a]

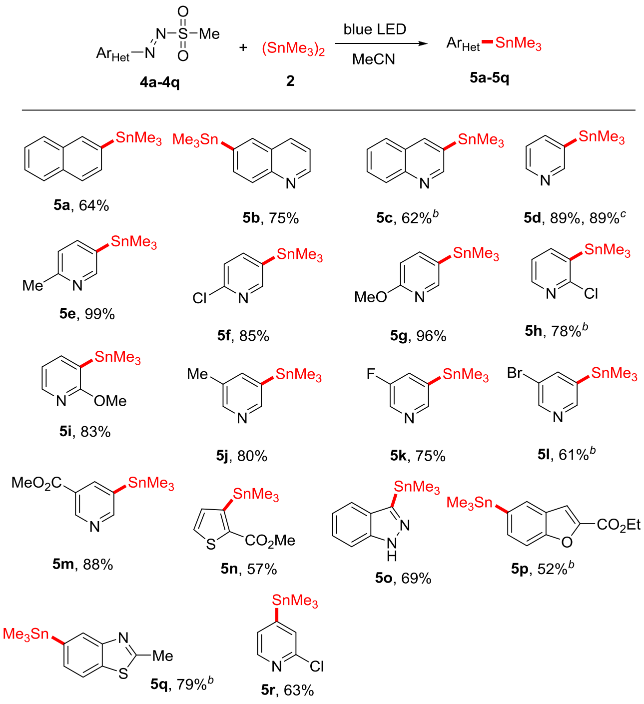


[a]Reaction conditions: arylazo sulfones **1** (0.2 mmol, 1.0 equiv), hexamethylditin **2** (0.4 mmol, 2.0 equiv), MeCN (1 mL), irradiated overnight by 24 W blue LED light, under N_2 atmosphere at room temperature. [b]Six mmol of **1a** used. [c]The reaction was carried out under 5 W blue LED light.

Notably, the present protocol has been efficiently applied to the preparation of compounds having alkyl and electron-donating substituents such as **3b**, **3c**, **3r**, **3w**, **3z**, **3fa**, and **3ha** (Scheme 2). Moreover, bromo, chloro, boronic ester, and alkenyl substituents (e.g., in compounds **3e**, **3f**, **3t**, **3h**, and **3p**) are well tolerated, although these are usually poorly compatible in transition-metal-catalyzed C−Sn bond formation previously reported in literature.[7] In the case of **3aa**−**3ca**, the diminished efficiency was probably due to steric hindrance effects, whereas highly volatile, fluoro-substituted arylazo sulfones **3d**, **3s**, and **3aa** have been isolated only in discrete yields. Disubstituted arylstannanes (**3da**−**3ia**) were likewise prepared in moderate to high yields (Scheme 2).

Because of the great importance of naphthyl and heteroaromatic arylstannanes in pharmaceuticals, we then pursued the synthesis of stannanes **5a**−**5r** (Scheme 3). Our protocol led to the synthesis of stannylated quinolines (**5b**, **5c**), pyridines (**5d**−**5m**, **5r**), thiophene (**5n**), indazole (**5o**), benzofuran (**5p**), and benzothiazole (**5q**). The preparation of **5c**, **5h**, **5l**, **5p**, and **5q** required a lower wattage irradiation (5 W blue LED) to prevent the undesired formation of side products. To demonstrate the practical application of this stannylation protocol, compounds **3a** and **5d** were isolated on a gram scale with no significant variation of the overall yield (Schemes 2 and 3).

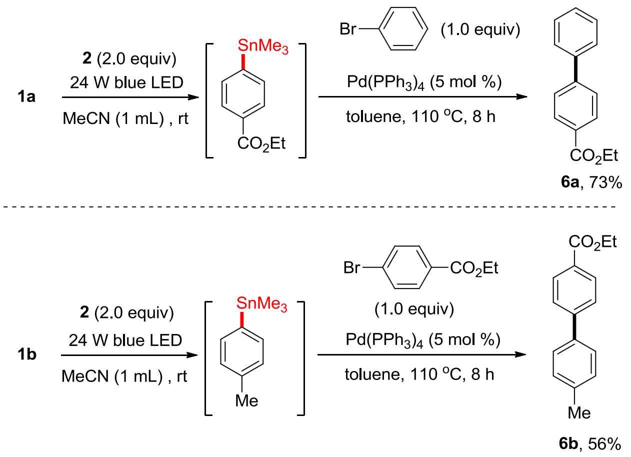
Scheme 3. Scope of Naphthyl and Heteroaromatic Azosulfones[a]



[a]Reaction conditions: arylazo sulfones **4** (0.2 mmol, 1.0 equiv), hexamethylditin **2** (0.4 mmol, 2.0 equiv), MeCN (1 mL), irradiated overnight by 24 W blue LED light, under N_2 atmosphere at room temperature. [b]The reaction was carried out by means of a 5 W blue LED light. [c]Six mmol of **4d** used.

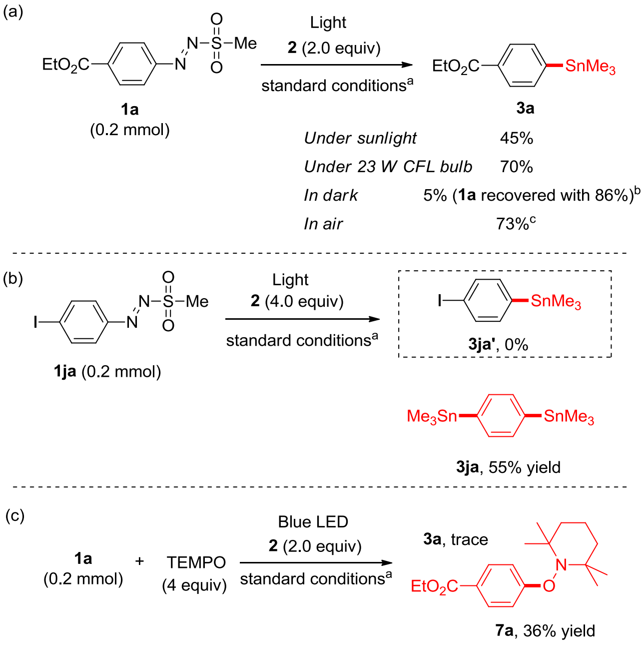
We also performed the visible-light-driven sequential stannylation of arylazo sulfones **1a**,**b** followed by the Pd-catalyzed Stille coupling on the crude arylstannane (Scheme 4). Upon completion of the stannylation step, MeCN was removed in vacuo, the residue dissolved in toluene and directly subjected to the Stille reaction to afford the coupling products (**6a,b**) in satisfying yields.

Scheme 4. Sequential Stannylation and Pd-Catalyzed Stille Coupling Reactions



Control experiments have been performed to gain insight into the mechanism (Scheme 5). The use of a different light source (sunlight or a 23 W CFL bulb) gave worse results with respect to LED light. Irradiation is, however, mandatory for the occurrence of the process. The presence of air in the reaction mixture has likewise a detrimental effect (Scheme 5a). Interestingly, when diazene **1ja** reacted with an excess of **2** (4.0 equiv) under standard conditions,the distannylated derivative **3ja** was formed in place of (4-iodophenyl)-trimethylstannane (**3ja′**, Scheme 5b). On the other hand, the stannylation was completely suppressed when the reaction was carried out in the presence of TEMPO (4.0 equiv), and the adduct **7a** was the only product isolated in 36% yield (Scheme 5c).

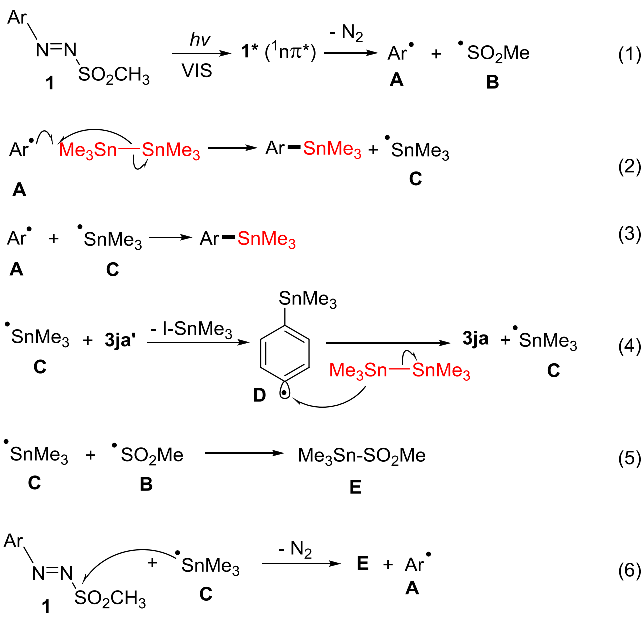
Scheme 5. Control Experiments and Mechanistic Investigations



[a]Standard conditions: MeCN (1 mL), N_2 atmosphere in a Schlenk tube, room temperature, 10 h. [b]In dark, 14% of **1a** conversion detected. [c]The solution was air saturated then irradiated by 24 W blue LED light.

We thus proposed a radical mechanism accounting for this visible-light-promoted stannylation (Scheme 6). Excitation of colored arylazo sulfones **1** via blue LED irradiation resulted in the homolysis of the N−S bond (via ${}^1n\pi^*$ excited state) to afford aryl radical **A** and methanesulfonyl radical **B** along with N_2 extrusion (eq 1). Then **A**, in analogy with that previously reported,[9a,16] reacted with the distannane **2** to give the stannylation product and the $Me_3Sn^{\bullet}$ radical **C** (eq 2). An alternative pathway to access the stannylation product is the direct radical combination of **A** with **C** (eq 3). The possible oxidation of **2** to the corresponding radical cation[25] has no role here. The formation of compound **3ja** may be explained by halogen abstraction from **3ja′** (by $Me_3Sn^{\bullet}$) followed by a further reaction with **2** of the resulting phenyl radical **D** (eq 4).[16] The formation of $Me_3Sn{-}SO_2Me$ (**E**) detected by GC−MS analysis at the end of the reaction (see section 10 of the Supporting Information) may be attributed to a radical−radical coupling between **B** and **C** (eq 5) and to a lesser extent to direct addition of **C** onto the starting azosulfones (eq 6) as previously reported in a related case.[26] A chain reaction, however, can be ruled out by on−off experiments (see section 10 of the Supporting Information).

Scheme 6. Proposed Mechanism for the Stannylation of Arylazo Sulfones 1



Summing up, we disclosed a visible-light-driven preparation of (hetero)aryl stannanes in moderate to excellent yields. This reaction represents the first visible-light-induced reaction for the formation of an Ar−Sn bond by exploiting arylazo sulfones as a source of aryl radicals. Such a protocol shows high-efficiency, mild photocatalyst- and additive-free conditions, as well as a wide substrate scope. This method appears likewise suitable for the synthesis of (hetero)aromatic organotin bearing electron-rich substituents. The resulting crude arylstannanes may be easily subjected to the Stille protocol in a tandem, two-step process.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b01788.

Experimental procedures and compound characterization data, including the $^1H/^{13}C$ NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by the National Natural Science Foundation of China (21602156).

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