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Tris(trimethylsilyl)silane and Visible-Light Irradiation: A New Metal- and Additive-Free Photochemical Process for the Synthesis of Indoles and Oxindoles

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A combined tris(trimethylsilyl)silane and visible-light-promoted intramolecular reductive cyclization protocol for the synthesis of indoles and oxindoles has been developed. This straightforward and efficient method shows tolerance towards a broad spectrum of functional-groups and enables rapid and practical synthesis of functionalized nitrogen-based heterocycles in high yields under additive and metal-free, mild photochemical conditions.

Nitrogen-based heterocycles are a class of compounds of great biological importance that also play a pivotal role in the Organic Synthesis field.^[1] In particular, indoles and oxindoles derivatives have been attracting considerable interest from both synthetic and medicinal chemistry due to the presence of these privileged scaffolds in many important drugs and naturally occurring compounds.^[2]

Due to the importance of these moieties, substantial efforts have been devoted to the development of new synthetic methodologies for the assembly of indole and oxindole ring systems.^[3] In addition to the classical synthetic methods, a handful of strategies based on the use of both transition-metal catalysis and oxidative conditions have been studied.^[4]

Recently, the use of visible-light as a source of energy for promoting chemical transformation has emerged as a hot topic in organic synthesis.^[5] In this sense, several research groups have demonstrated the versatility of Ru(II)- and Ir(III)-based complexes in the presence of additives under visible-light irradiation,^[6] as well as photo-organocatalysts,^[7] to promote a variety of transformations initiated by SETs.

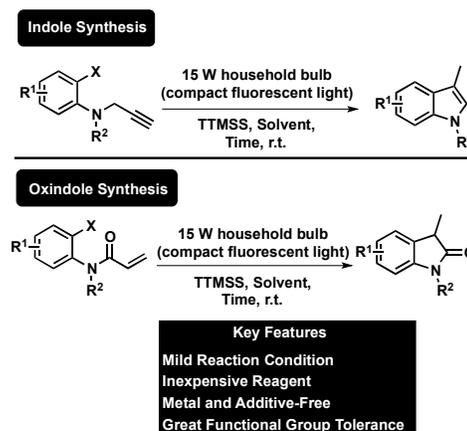
The great interest in the development of environmentally benign technologies and procedures in the last few years have driven efforts in order to improve the processes of radical generation. These improvements include avoiding the use of expensive transition-metal catalysts, toxic reagents, as well as explosive oxidants.^[8] In this regard, Melchiorre's group has explored the photochemical reactivity of photon-absorbing electron donor-acceptor complexes (EDA) generated in the ground state upon

substrates association.^[9]

Nevertheless, in spite of the advances that have been achieved in this field, photochemical strategies which allow the synthesis of indoles and oxindoles skeleton have been scarcely explored.^[10]

Therefore, the exploitation of new strategies and reagents to develop straightforward and greener methodologies for the rapid assembly of *N*-heterocycles is highly desirable.^[11] An important step in that direction was given by Jørgensen's group, which reported the radical-mediated reduction of aryl and alkyl iodides using TTMSS under visible-light irradiation.^[12]

Based in our experience in the synthesis of *N*-heterocyclic compounds^[13] and in the recent results disclosed by Jørgensen et al., herein we are pleased to report the use of a mild and operationally simple strategy for the synthesis of indoles and oxindoles frameworks through the radical-promoted dehalogenation/intramolecular cyclization of 2-halobenzenesulfonamides bearing terminal alkynes (Scheme 1).



Scheme 1. General scheme for the synthesis of indole and oxindole derivatives.

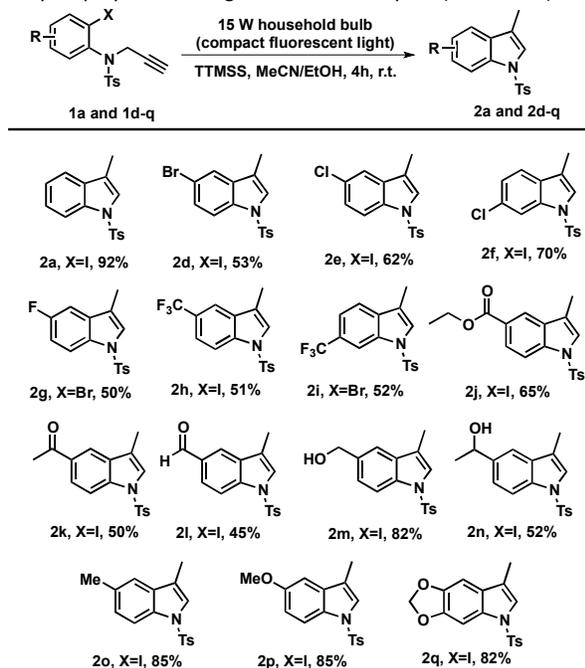
We started our investigation on the dehalogenation followed by 5-exo-dig cyclization reaction of substrated **1a** by evaluating the effect of different parameters on the reaction conditions, such as solvent, *N*-protecting group and halide substituent. The results showed that both the nature of the solvent and amount of the TTMSS were critical to obtain the indole product in high yields

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(under the optimized reaction condition product **2a** was obtained in 92% yield, see SI for complete details).

We next turned our attention to the investigation of the scope and generality of the method by subjecting a wide range of substituted 2-halobenzenesulfonamides containing terminal alkynes to the optimized reaction conditions. Substrates bearing either electron-withdrawing or electron-donating groups furnished the desired indole **2d-q** in moderated to excellent yields (45-85%), with electron-donating groups at different positions of the aromatic ring affording higher yields than those bearing electron-withdrawing groups (Scheme 2). It should be noted that besides to the isolated products, the unreacted starting materials are easily recovered.

As seen in Scheme 2, substrates bearing additional halogens such as Br and Cl, functionalities that allow subsequent functionalizations by transition metal mediated cross-coupling reactions,^[14] underwent the reaction smoothly, affording the corresponding products in moderated yields (53% and 62% respectively). Due to the interesting properties of fluorine atoms and the trifluoromethyl (CF₃) moiety in medicinal chemistry, agrochemical and intelligent materials,^[15] we envisioned the synthesis of the indole scaffolds containing these important subunits employing our newly developed protocol. The reaction of the fluoro derivative led to isolation of product **2g** in 50% yield, while the one bearing the trifluoromethyl group similarly gave rise to 51% yield. Furthermore, the feasibility of the cyclization process showed no dependence on the substitution patterns (e.g., *para*-, *meta*-), of the aromatic ring of the substrates (compare: **2h** vs **2i**). Notably, this process was also compatible with ester, ketone and aldehyde functional groups attached to the aromatic ring (compare **2j** vs **2k** vs **2l**), and interestingly, unprotected alcohols could also be readily employed with no great effect in the yield (**2m** and **2n**).



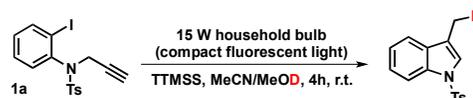
Scheme 2. Substrate scope for the visible-light-mediated indole synthesis. Reaction conditions: 1 equiv of TTMSS, 5 equiv of EtOH, and 0.4 mL of MeCN, irradiation with a 15 W household bulb. Yields of isolated products.

Aiming to gain further insight into the mechanism of the visible-light-induced reaction, we performed additional control

experiments. We started our mechanistic investigations through the reaction of aryl iodide **1a** in the absence of TTMSS in optimized reaction conditions, and, as expected, no conversion to the indole **2a** was observed. The reaction performed in the absence of light also did not afford the desired product, with the starting material being fully recovered. Additionally, experiments with sequential periods of irradiation and darkness support the hypothesis that a radical chain process is not the predominant pathway under the reaction conditions (see SI for complete details).

Considering that a C-centered radical is likely the key intermediate of the process, the presence of a radical scavenger should inhibit the intramolecular reductive cyclization process. As expected, when a radical quencher such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was added to the system, a complete inhibition of the reductive reaction was observed, once more strongly suggesting a radical pathway for this transformations.

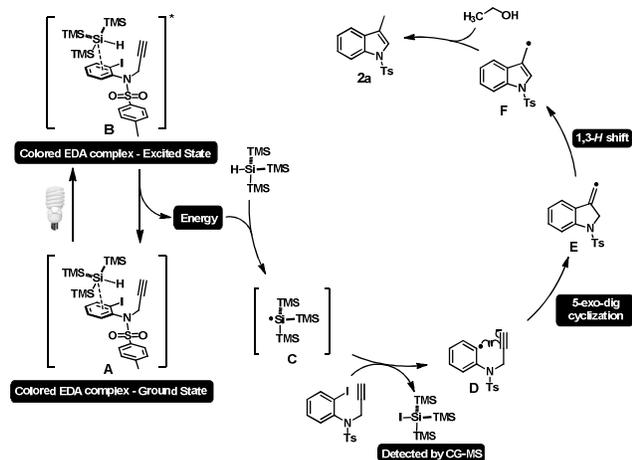
These experiments allowed us to reach the conclusion that continuous visible-light irradiation and the silicon reagent are required to yield the indole scaffold under a radical reaction mechanism. To further identify the hydrogen atom source in this process, we performed labeling studies using MeOD (5 equiv) in the reaction (Scheme 3), and the desired product was obtained with 70% of deuterium incorporation.



Scheme 3. Deuterium exchange experiment.

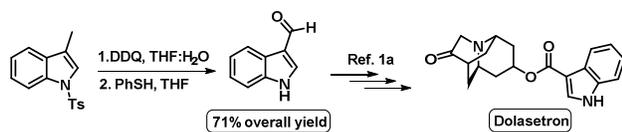
Additionally, aiming to analyze which of these reagents are involved in the rate-determining step, kinetic studies were performed.^[16] The kinetic studies were conducted for the reaction between substrate **1a** and the TTMSS having acetonitrile as solvent (standard reaction under the optimized conditions). To our delight, we could observe from these experiments that the kinetic profile give us further evidence that the EDA-complex excitation is the rate-limiting step of this photochemical protocol.^[17]

Based on aforementioned results and previous reports, a plausible reaction mechanism was proposed (Scheme 4). Initially, a silyl-centered radical (Me₃Si^{*}) is generated under visible-light irradiation.^[18] The formation of the silyl radical may occur through a sequence of events that consists firstly on the formation of a photon-absorbing electron donor-acceptor complex by the association of the aryl substrate with TTMSS (**A**)^[19] followed by the visible-light-promoted excitation of (**A**), giving rise to (**B**). After an energy-transfer step, the Si-based radical (**C**) is formed^[20] and subsequently promotes the single-electron reduction of the iodide substrate, generating the aryl radical (**D**). Next, a kinetically favored 5-*exo-dig* cyclization occurs, leading to the formation of a vinyl radical (**E**). Finally, an aromatization step via a 1,3-*H* shift produces an allylic radical (**F**), which further undergoes the proton abstraction of EtOH, yielding the corresponding heterocyclic product **2a**.



Scheme 4. Proposed mechanism for the visible-light-mediated indole synthesis.

With the aim of demonstrating the potential scalability of this photochemical approach for the synthesis of indoles, the reaction to produce indole **2a** was performed on a 5 mmol scale, with the desired product being isolated in 87% yield. Having in mind the high degree of functionalization displayed by product **2a**, further manipulations were briefly explored in order to demonstrate its synthetic utility. In order to accomplish that, initially 3-methylindole **2a** was treated with DDQ in aqueous THF to obtain the corresponding aldehyde in 75% yield.^[21] Next, the N-Tosyl protecting group was further removed through a simple known procedure, affording the structure bearing a free amino group in 95% yield.^[22] Thus, after two simple synthetic manipulations it was possible to isolate the 1H-indole-3-carboxaldehyde, which could be a valuable precursor for the synthesis of several FDA approved drugs,^[17] in 71% overall yield (**Scheme 5**).

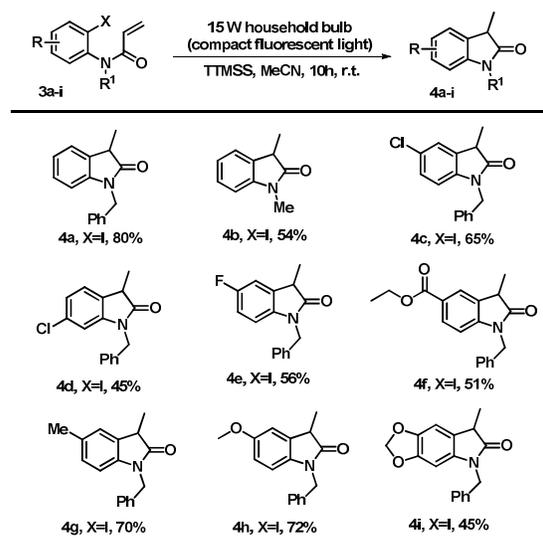


Scheme 5

In light of the encouraging results for the synthesis of indoles, we envisioned that the visible-light-induced photochemical strategy could be also employed for the synthesis of oxindoles, another important class of heterocyclic compounds,^[23] employing N-protected 2-halophenylacrylamides as substrates. To our delight, this procedure also worked for the synthesis of the oxindole scaffold, and after optimization, the use of 2 equiv of TTMSS in acetonitrile was found to be appropriate to obtain the product in good yield.

Having identified the optimal conditions for the reaction, we sought to evaluate its scope and limitations, starting with the effect of different alkyl groups attached to the nitrogen atom on the substrate (**Scheme 6**). On the basis of this study, we were able to observe that the substrate containing N-benzyl moiety afforded the 5-*exo-trig* cyclization product in a higher yield when compared with its N-methyl analogue (**4a** vs **4b**, 80% and 54% yield, respectively). Interestingly, substrates bearing halogen atoms on the aromatic

ring such as Cl and F were tolerated under the reaction conditions, giving the desired products in 45-65% yield (**4c**, **4d** and **4e**).



Scheme 6. Substrate scope for the visible-light-mediated oxindole synthesis. Reaction conditions: 2 equiv of TTMSS, and 0.4 mL of MeCN, irradiation with a 15 W household bulb. Yields of isolated products.

We then explored the scope of the reaction towards the presence of a sensitive and strong electron-withdrawing group, and, gratifyingly, product **4f** being an ester moiety afforded the desired product in 51% of yield. Substrates containing electron-donating groups reacted smoothly under the visible-light conditions, giving rise to the corresponding oxindoles **4g** and **4h** in 70% and 72% yield, respectively. Furthermore, the reaction of substrate **3i** revealed that the insertion of a second donating group on the aromatic ring has a negative effect in terms of chemical outcome (**4i** was obtained in 45% of yield).

In summary, we have developed a straightforward and highly efficient photochemical protocol leading to the formation of nitrogen-containing heterocycles. This metal- and additive-free protocol is carried out by allying visible-light irradiation from simple household fluorescent light bulbs and the use of tris(trimethylsilyl)silane as hydride source. The high functional-group tolerance, employment of readily available starting materials and scalability of the reaction substantiate the versatility of this method, making it attractive for both academia and industry. Further studies focused on the application of this transformation towards the synthesis of others heterocyclic compounds, as well as a thorough mechanistic study of this protocol are underway and will be reported in due course.

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