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COMMUNICATION

New Transmetalation Reagents for the Gold-Catalyzed Visible Light-Enabled C(sp or sp²)-C(sp²) Cross-Coupling with Aryldiazonium Salts in the Absence of a Photosensitizer

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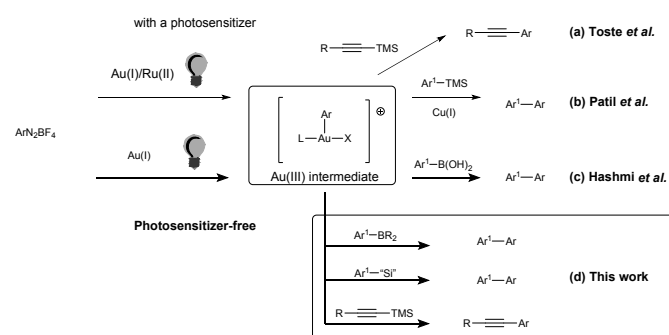
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The scope of the photosensitizer-free visible light-driven gold-catalyzed cross-coupling was evaluated by a wide variety of organoboron and organosilicon species using four equivalents of aryldiazonium salts and (4-CF₃-C₆H₄)₃PAuCl in MeOH. In addition, a C(sp or sp²)-C(sp²) cross-coupling of organotrimethylsilanes and aryldiazonium salts was investigated. The reactions can be conducted under very mild reaction conditions, with a reduced amount of aryldiazonium salt (1.2 equiv.) by using a catalytic amount of Ph₃PAuNTf₂ in MeCN under irradiation with blue LEDs at room temperature.

The chemistry of UV and visible light-mediated photoredox gold catalysis has recently aroused great interest and today functions as a versatile tool in organic chemistry, allowing alternative strategies towards synthetically useful scaffolds.¹ Particularly, the research groups of Glorius² and Toste³ have shown the potential of this strategies which involve Au(I)/Au(III) catalytic redox cycles. Unlike the earlier methods used to overcome the high barrier of the redox potential of Au(I)/Au(III), where strong external oxidants in stoichiometric amounts were required⁴, this approach operates under mild reaction conditions and shows excellent functional group tolerance. In these systems, a photosensitizer, in addition to the gold catalyst, and an aryl radical source, which in this case functions as the oxidant as well as the reagent (aryldiazonium salts or diaryliodonium salts), are used to address the barrier of the Au(I)/Au(III) cycle. Recently, our group could show that these strategies can also be conducted without the need for an additional photosensitizer. In these reactions, aryldiazonium salts in visible light-mediated reactions can undergo formal oxidative additions to a mononuclear gold(I) complex to

produce gold(III) species which then initiate the typical gold-catalyzed reactivity patterns, such as activating C-C multiple bonds or transmetalations.⁵ In this context, we recently studied the photosensitizer-free cross-coupling of arylboronic acids with aryldiazonium salts (Scheme 1a).^{5c} To further explore the scope of the transmetalating reagents, we aimed to achieve C-C cross-couplings by using a broader set of organoboron species and in addition the extension of this strategy towards organosilanes. Albeit, visible light-mediated gold-catalyzed cross-couplings of organosilanes with aryldiazonium salts in the presence of a photosensitizer have been reported by the research groups of Toste (Scheme 1b) and Patil (Scheme 1c).⁶ We imagined, since the reaction in Scheme 1a could successfully proceed without the use of a photosensitizer, that our method could also be applied to organosilanes (Scheme 1d).



Scheme 1 Cross-coupling of (a) alkynyltrimethylsilane and (b) aryltrimethylsilanes using a photosensitizer. (c) Photosensitizer-free cross-coupling of arylboronic acid with aryldiazonium salts. (d) The new photosensitizer-free approach.

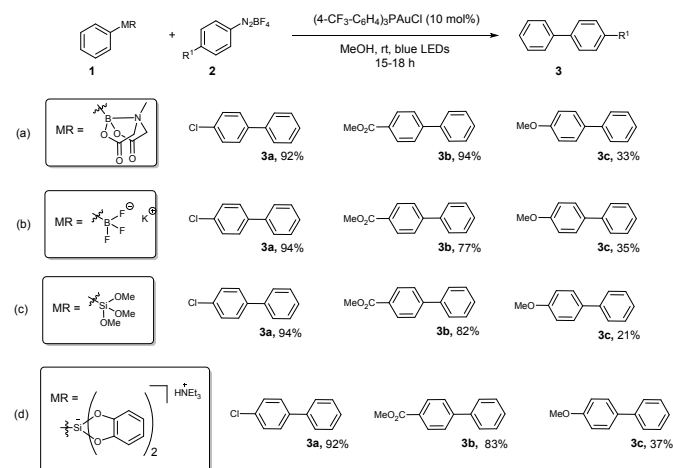
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We initiated our studies by testing different organoboron species, as alternatives to the already applied boronic acids and pinacol esters. The effect of the electronic property of the aryldiazonium salts on the transformations were also evaluated. The arylorganoborons were exposed to three aryldiazonium tetrafluoroborates under our published optimized reaction conditions of 10 mol% of (4-CF₃-C₆H₄)₃PAuCl at room temperature under irradiation with blue LEDs in methanol (Table 1).^{5c} All of the tested arylboron species, MIDA boronates (a), and potassium trifluoroborates (b), smoothly delivered the corresponding biaryls under the given conditions with 4-chlorophenyl diazonium tetrafluoroborate **3a** (Table 1, entry a and b). The aryldiazonium salt with an electron-withdrawing ester substituent on the phenyl ring appeared to react more efficiently in all cases (**3b**) than in the case of an electron-donating alkoxy group substituent (**3c**). In our recently published work we showed a chemo-selective Miyama arylation of B,Si bimetallic reagents with aryldiazonium salts.⁷ Therefore, we were interested in the coupling of other organosilicon species, such as trimethoxysilanes and bis(catecholato)silicates (entries c and d). When varying the electronic density of the aryldiazonium salts a similar trend of the yields could be observed. Further, in our recently published approach we found that for the selective coupling of aryltrimethylsilanes bearing boron substituents with aryldiazonium salts, the reaction conditions could be optimized to the use of only 1.2 equivalents of the aryldiazonium tetrafluoroborate by using 10 mol% of Ph₃PAuNTf₂ in MeCN and blue LED irradiation at room temperature.⁷

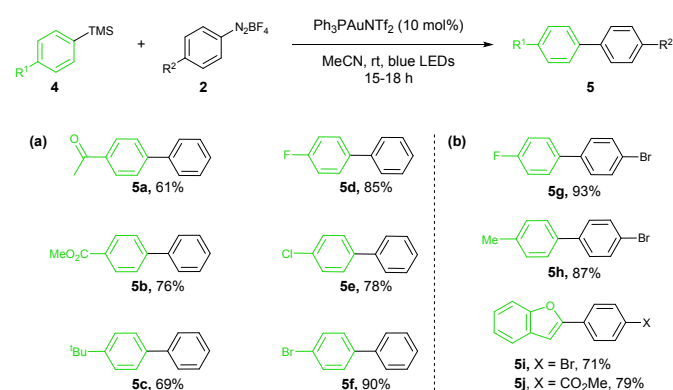
Table 1. Variation of the transmetalating reagent.^[a]



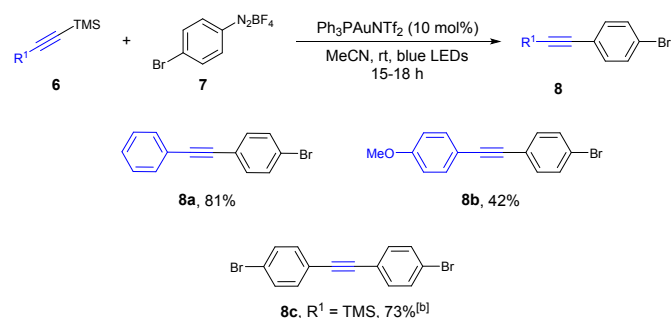
[a] All reactions were carried out using **1** (0.1 mmol, 1.0 equiv.), **2** (0.4 mmol, 4.0 equiv.) in the presence of (4-CF₃-C₆H₄)₃PAuCl (10 mol%) in MeOH (0.5 mL, 0.2M) under irradiation with blue LEDs at room temperature.

Therefore, we envisioned to apply this method for the coupling of aryltrimethylsilanes without boron substituents. First, we turned our focus on the expansion of the substrate scope with regard to the aryldiazonium tetrafluoroborates (Table 2a). In general, all of the tested diazonium salts could readily proceed in the C-C coupling affording the biaryls **5a-f** in 61-90% yield. Aryldiazonium tetrafluoroborates bearing electron-withdrawing substituents **5a** and **5b** delivered the desired product in 61% and 76%, respectively. A sterically hindered substrate was successfully transformed into **5c** as well. Aryldiazonium salts bearing halides in *para*-position were well tolerated to afford the 4-fluoro-, 4-chloro- and 4-bromo-substituted biaryls **5d-f** in 78-90% yield. Next, the substrate scope with respect to the aryltrimethylsilanes was examined. 4-Fluoro-substituted phenyltrimethylsilane delivered the desired product **5g** in an excellent yield of 93% (Table 2b). Further, trimethyl(*p*-tolyl)silane afforded the cross-coupled product **5h** in a very good yield of 87%. Heteroaromatic 2-trimethylsilylbenzofuran could be arylated as well to receive **5i** and **5j** in good yields (71 and 79%). We need to underline, that the latter two products (**5i**, **5j**) were also obtained by Patil *et al.* by using an external photosensitizer and a copper salt with no significant distinction in the yield.^{6b} This further highlights the improved atom economy and efficiency of the photosensitizer-free method. Also important to mention that bromo substituents leading to different biaryls could be well tolerated, which is orthogonal to the classical palladium chemistry. Subsequent modification of these products *via* palladium catalyzed cross-couplings emphasizes the synthetic potential of this method. In addition to aryltrimethylsilanes, also alkynyltrimethylsilanes were tested with our optimized method. For this purpose, trimethyl(phenylethynyl)silane was exposed to 4-bromophenyldiazonium tetrafluoroborate in the presence of 10 mol% of Ph₃PAuNTf₂ in MeCN under the irradiation with blue LEDs at room temperature (Table 3).

Table 2. Substrate scope of aryltrimethylsilanes and aryldiazonium tetrafluoroborates.^[a]



[a] All reactions were carried out using **4** (0.3 mmol, 1.0 equiv.), **2** (0.36 mmol, 1.2 equiv.) in the presence of Ph₃PAuNTf₂ (10 mol%) in MeCN (0.5 mL, 0.2M) under irradiation with blue LEDs at room temperature.

Table 3. Substrate scope of alkynyltrimethylsilanes and aryldiazonium tetrafluoroborates.^[a]

[a] All reactions were carried out using **6** (0.3 mmol, 1.0 equiv.), **7** (0.36 mmol, 1.2 equiv.) in the presence of $\text{Ph}_3\text{PAuNTf}_2$ (10 mol%) in MeCN (0.5 mL, 0.2M) under irradiation with blue LEDs at room temperature. [b] **2** (0.9 mmol, 3.0 equiv.).

Fortunately, the desired cross-coupling product **8a** was formed with a yield of 81%. This yield shows a significant increase in yield compared to the product **8a** afforded by Toste *et al.* using a photosensitizer 68%.^{6a} Further, trimethyl(arylethynyl)silane bearing an electron-donating –OMe group was tolerated to obtain **8b** in a moderate yield of 42%. Interestingly, by using 1,2-bis(trimethylsilyl)ethyne with 3.0 equivalents of 4-bromophenyldiazonium tetrafluoroborate we obtained the doubled cross-coupled product **8c** in 73% yield. This reaction could complement the Sonogashira coupling, particularly when alkynyltrimethylsilanes are available rather than the corresponding terminal alkynes and it may reveal an advantage if non-basic conditions for an alkynyl-aryl coupling are required.

Conclusions

In conclusion, we have extended our method from using arylboronic acids to pinacol esters, MIDA boronates and potassium trifluoroborates and showed that they function as an efficient coupling partner in the photosensitizer-free gold-catalyzed photoredox reactions with aryldiazonium salts and could complement the classical Suzuki reaction. Also, organosilicon species, such as trimethoxysilanes and bis(catecholato)silicates could be transformed by using this method to obtain functionalized biaryls in moderate to excellent yields. Further, we could reduce the equivalents of aryldiazonium salt by using organotrimethylsilanes. This reaction was tested for aryltrimethylsilanes and alkynyltrimethylsilanes and exhibits a broad functional group tolerance by varying the substituents on both organotrimethylsilanes and aryldiazonium salts. Both reactions could complement the classical palladium catalyzed cross-couplings, for TMS-aryl compounds the Hiyama reaction and for TMS-alkynes the Sonogashira coupling. As demonstrated, aryl halides are well tolerated which establishes the possibility for further functionalization, for instance, with the common palladium chemistry.

Acknowledgements

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Conflicts of interest

There are no conflicts to declare.

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