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Light-Induced Gold-Catalyzed Hiyama Arylation: A Coupling Access to Biarylboronates

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Abstract: Organoboron compounds are versatile synthetic building blocks. We herein report a new strategy, a photochemical gold-catalyzed chemo-selective Hiyama arylation of B,Si bimetallic reagents with diazonium salts, which is orthogonal to common strategies and therefore a unique tool for synthesis of valuable biarylboronates. With this new methodology a wide array of diversely functionalized sp^2- and sp^3-hybridized biarylboronates were obtained. Notably, the synergism of gold catalysis with copper catalysis or palladium catalysis, allows for one-pot iterative C-X (heteroatom) and C-C couplings for the rapid assembly of several simple fragments to relatively complex molecules. Mechanistic studies indicated that photosensitizer-free conditions were superior to gold/$Ru(bpy)_3Cl_2$ dual catalysis.

Keywords: gold catalysis; Hiyama coupling; diazonium salts; photochemistry; bimetallic reagents

Biaryl units represent a fundamental and important scaffold for the generation of molecular complexity.[1] They are indispensable structural linkers for a great number of pharmacophores, natural products, agrochemicals and molecular machines. So far, their synthesis mainly relies on classical Pd-catalyzed cross-coupling between two aromatic subunits, one electrophilic (Ar^1-X) and one nucleophilic (Ar^2-M) building block.[2] Recently, directed C-H arylation[3] and oxidative cross-dehydrogenative coupling of two arenes[4] become an alternative, despite of the selectivity issue these methods are associated with. Still, an entirely different synthetic disconnection involving preformed boron-containing biaryl units which are applied as a versatile class of building blocks for diversification, would be desirable. Although post-borylation of biaryl bromides (Suzuki coupling products) can afford biarylboronates by additional steps, still this new synthetic strategy allows a convergent route for a functionalization at a relatively late stage, which could be enormously beneficial in lead identification in pharmaceutical/medicinal chemistry.[5] Due to the inherent poor compatibility of palladium catalysts with boronic acid derivatives,[6] the synthesis of biarylboronates by catalytic coupling represents an important aim in the field of catalytic C-C coupling; however, practical strategies are still rare. For example, by exploiting the different reactivities of two types of boronic acid derivatives, Burke[7,8] and Suginome[9,10] splendidly introduced Pd-catalyzed boron-masking Suzuki-Miyaura couplings (Scheme 1a). Although powerful, these methods require additional steps for the synthesis of the substrates and need special conditions such as additional bases to prevent the masked organoborons from hydrolysis. Moreover, bifunctional R_2B-Ar^1-Ar^2-X

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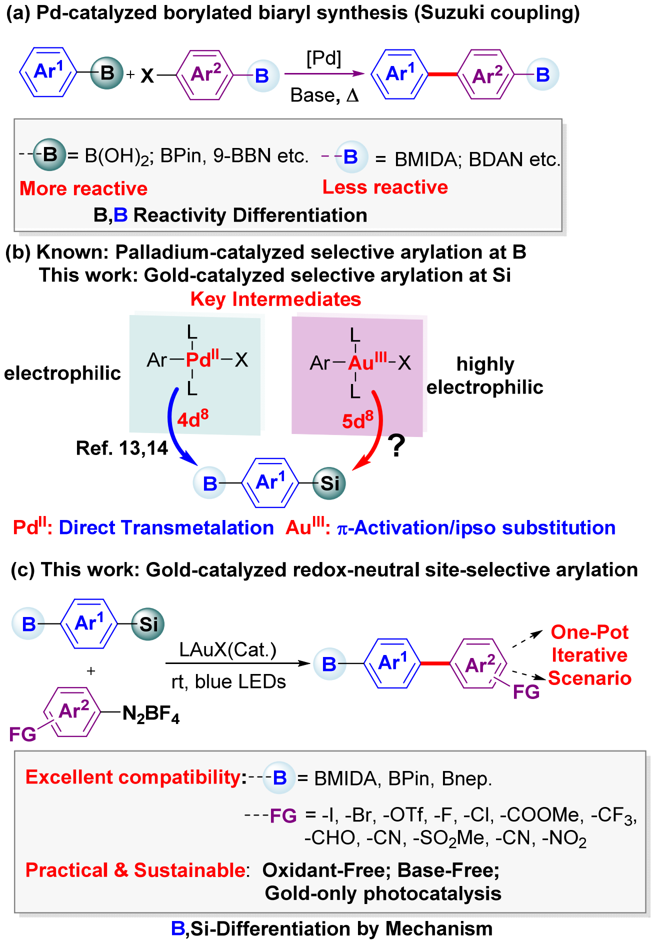
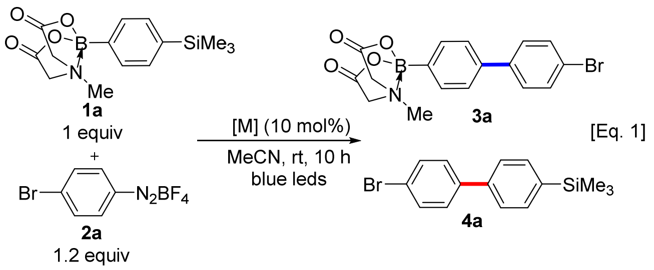
(X = I, Br, OTf etc.) products, which would represent the most interesting building blocks for modular synthesis, are accessible by long synthetic routes only. A comparison of the key intermediate Ar-Pd(II)L_2X and the isoelectronic Ar-Au(III)L_2X species indicates that the latter potentially is more reactive. We envisioned that due to this feature an aryl activation/ipso substitution[11] of an Ar-SiR_3 moiety should be preponderant over the direct transmetalation with arylboronic acid derivatives[12] (Scheme 1b). This would enable a simple site-selective arylation of aryl compounds bearing both silyl and boronic ester derivatives giving rise to privileged biarylboronate building blocks in an orthogonal manner to common methodologies. In palladium catalysis substrates carrying both, boron and silicon substituents undergo a transmetalation of the boronic ester,[13,14] thus needing at least two more steps for the conversion of the resulting arylsilane products into arylboronates.



Scheme 1. Strategies for the synthesis of biarylboronates.

Generally, gold redox catalysis requires the use of sacrificial external oxidants to complete the Au(I)/Au(III) catalytic cycle.[15-20] In this context, by using I(III)/F^+ as oxidants, seminal works from Lloyd-Jones' and Russell's,[11,21-23] Nevado's[12,24] and You´s[25] groups have demonstrated that both Ar-SiR_3 and Ar-$B(OR)_2$ (R = H or alkyl) were vital coupling partners for gold-catalyzed oxidative biaryl syntheses with electronically/or directing group-controlled specific $C_{(Ar)}$-H bonds. Alternatively, gold-catalyzed oxidative cross-couplings between electron-rich and electron-poor arenes have been recently achieved by Larrosa's group.[26] Despite the significant progress, redox-neutral gold-catalyzed site-selective arylations of bimetallic R_3Si-Ar-$B(OR)_2$ reagents are a fundamentally new challenge. Recently, Glorius and Toste, among others, have contributed an facile route to reactive Ar-Au(III) intermediates in the presence of Ru-based photosensitizer, not needing external strong oxidants.,[27-36] In 2016, we developed the first photosensitizer-free, photochemical generation of Ar-Au(III) species from diazonium salts and gold(I)-complexes, including catalytic transformations.[37-39] Herein we report a visible-light-induced gold-catalyzed redox-neutral arylation of mechanistically discriminative B,Si bimetallic coupling reagents (B-Ar-Si) with diazonium salts (Scheme 1c); mechanistic studies demonstrate that photosensitizer-free conditions are superior to gold/Ru(bpy)$_3$Cl$_2$ dual catalysis.

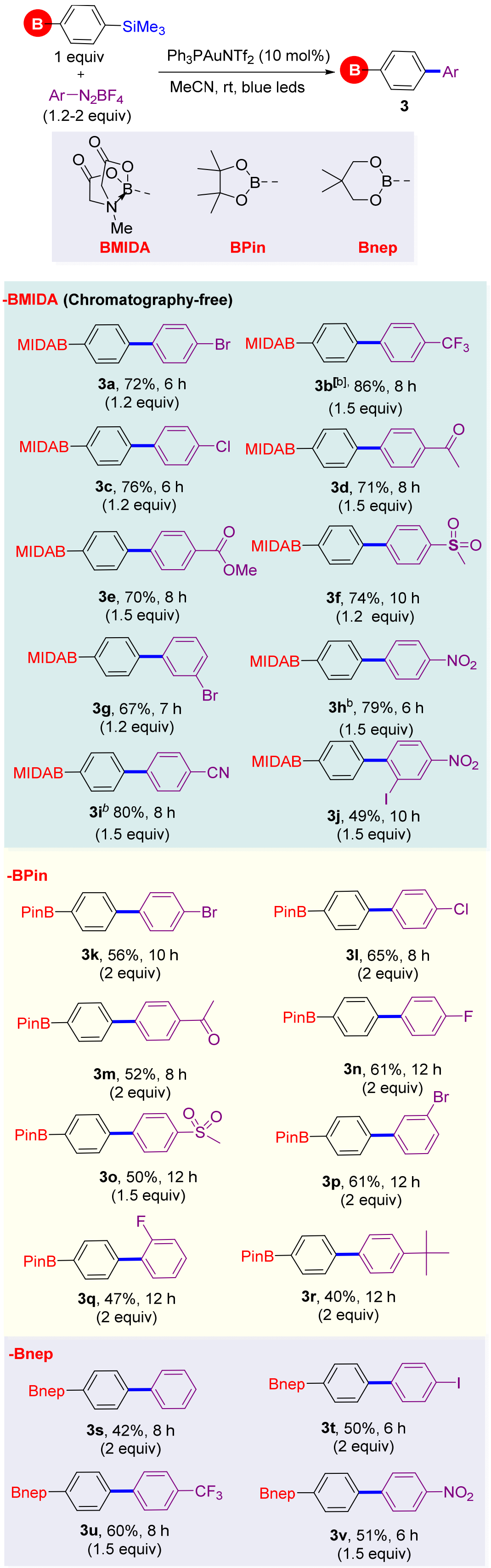
Table 1: Selected reaction parameter optimization.[a]



Entry	Catalyst	Yield[b]	**3a/4a**[c]
1	Ph$_3$PAuCl	74%	>99:1
2[d]	Ph$_3$PAuCl	68%	>99:1
3[e]	Ph$_3$PAuCl	Nd	Nd
4	Ph$_3$PAuNTf$_2$	78%	>99:1

[a] Reaction conditions: metal catalyst (10 mol%), **1a** (1 equiv, 0.2 M), Ar-N$_2$BF$_4$ **2a** (1.2 equiv), MeCN, blue LEDs, N$_2$, rt, 6-10 hours. [b] ^{1}H NMR yield with 1,3,5-trimethoxybenzene as internal standard; the isolated yield is given in brackets. [c] ratio determined by ^{1}H NMR. [d] Pivalonitrile instead of MeCN. [e] Other solvents (MeOH, DMF, DCE, acetone, dioxane) instead of MeCN.

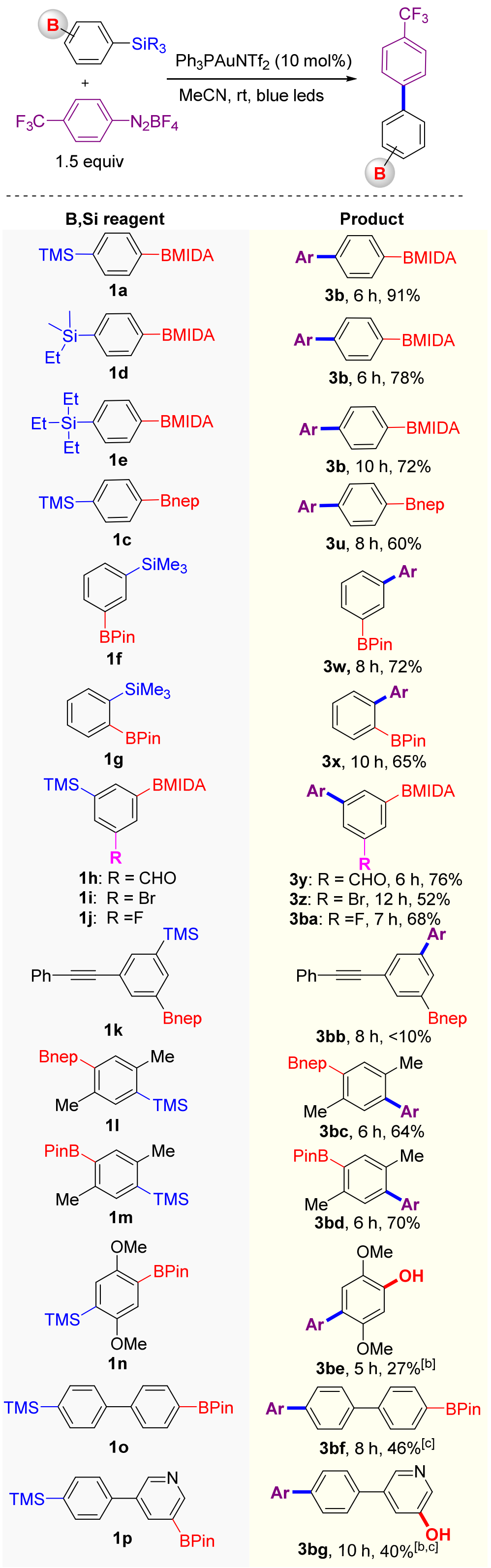
The commercially available B,Si-bimetallic reagent **1a** and 4-bromobenzenedizonium salt **2a** were selected for the test reaction to optimize the conditions (Table 1 and also Table S1 in Supporting Information). When Ph$_3$PAuCl was used as the catalyst under the irradiation of blue LEDs, the desired bifunctionalized halobiarylboronate product **3a** was exclusively formed in acetonitrile and pivalonitrile (entries 1 and 2). Other solvents (MeOH, DCE, DMF, acetone, dioxane) gave no product (entry 3). The important role of nitrile-based solvents might be rationalized by the effect of ligand stabilization avoiding a rapid reductive elimination from the generated Ar-Au(III)-PPh$_3$ intermediate to form [Ar-PPh$_3$]$^+$ salts.[40] The use of cationic Ph$_3$PAuNTf$_2$ can improve the yield to 78% (entry 4). Other transition-metal catalysts examined (Fe, Cu, Ni, Ir) failed to initiate this transformation and Pd(Ph$_3$P)$_4$ led to 14% yield along with the undesired byproduct **4a** at room temperature (see Supporting Information). Further studies indicated that the use of Pd-based catalysts leads to the normal Suzuki coupling products for –Bpin and –Bnep bimetallic substrates. Shortening the reaction time from 10 hours to 5 hours even increased the yield from 78% to 82% (entry 11). A lower yield was obtained when the catalyst loading was decreased to 5 mol% (entry 12). Control experiments demonstrated that both light and gold catalyst were essential for the reaction to proceed (entries 13 and 14).



Scheme 2. Scope with respect to the boronic acid derivative and the diazonium salt.[a] [a] 200 µmol scale; yield after recrystallization or chromatography. [b] 1000 µmol scale.

Under the optimized reaction conditions from Table 1 a wide array of arenediazonium salts were investigated (Scheme 2). With 1.2-2.0 equivalents of arenediazonium salt, both the less reactive –BMIDA and the reactive –Bpin/–Bnep containing B,Si-bimetallic reagents successfully furnished the desired biarylboronates **3a-v** in 40-86% yields. Especially, the excellent compatibility with activated –Bpin and –Bnep makes this new technique very attractive for subsequent "classical" Pd-catalyzed C-C couplings.[2] For BMIDA-type bimetallic reagents, the reactions are clean and the desired products **3a-i** can conveniently be obtained by recrystallization without chromatography. Diazonium salts bearing electron-rich, as well as electron-poor functional groups in the *o*-, *m*-, and *p*-positions mostly reacted well. A series of synthetically valuable functional groups (-CF_3, -F, -COOMe, -COMe, -NO_2, -CN, -SO_2Me etc.) were compatible. In addition, the successful coupling to bifunctionalyzed halobiarylboronate motifs (-I, -Cl, -Br; **3a**, **3c**, **3g**, **3j**, **3k**, **3p**, **3t**) allows post-modifications by Pd-catalyzed C-C cross coupling. With 4-methoxylbenzenediazonium salts containing strong electron-donating groups the reactions were sluggish. The identity of the product **3b** was unambiguously confirmed by an X-ray single crystal structure analysis.[41]

The synthesis of structurally diverse Ar-CF_3 units for agrochemicals and pharmaceuticals has gained great momentum in the past ten years.[42] Valuable trifluoromethylated arylbonorates were now obtained by using 4-CF_3-substituted aryldiazonium salts, several representative B,Si-bimetallic reagents were used (Scheme 3). Besides TMS, other trialkylsilyl-substituted arylboronates **1d-e** could also undergo the site-selective arylation. Both electron-withdrawing and electron-donating groups at the aryl core of the B,Si-bimetallic reagents were efficient (**1h-j**, **1l-n**), and –CHO and –Br as versatile groups for post modification also were tolerated (**3y** and **3z**). With an alkynyl moiety (**1k**), only a low yield of desired coupling product was obtained due a competing 1,2-difunctionalization of the alkyne.[37] The concise synthesis of congested biarylboronates (**1l-n**) is also possible. The heteroaryl-containing B,Si-bimetallic reagent **1p** affords polyarene-tethered pyridin-3-ol **3bg** in moderate yield via tandem selective arylation and oxidation.



Scheme 3. Scope with regard to B,Si-bimetallic reagents.[a]

[a] 200 μmol scale; yield after chromatography. [b] Successive oxidation of arylboronates with 5 equiv NaOH and 5 equiv H_2O_2 at 0 °C. [c] 2 equiv diazonium salts were used.

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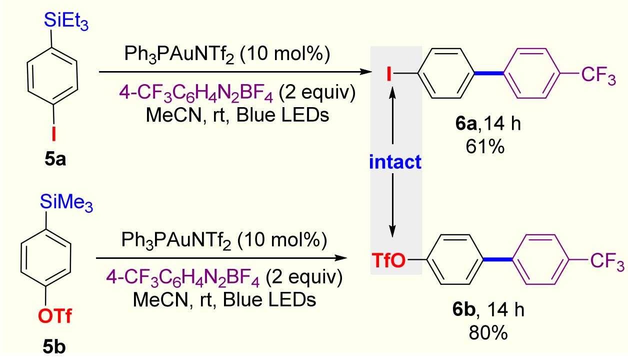
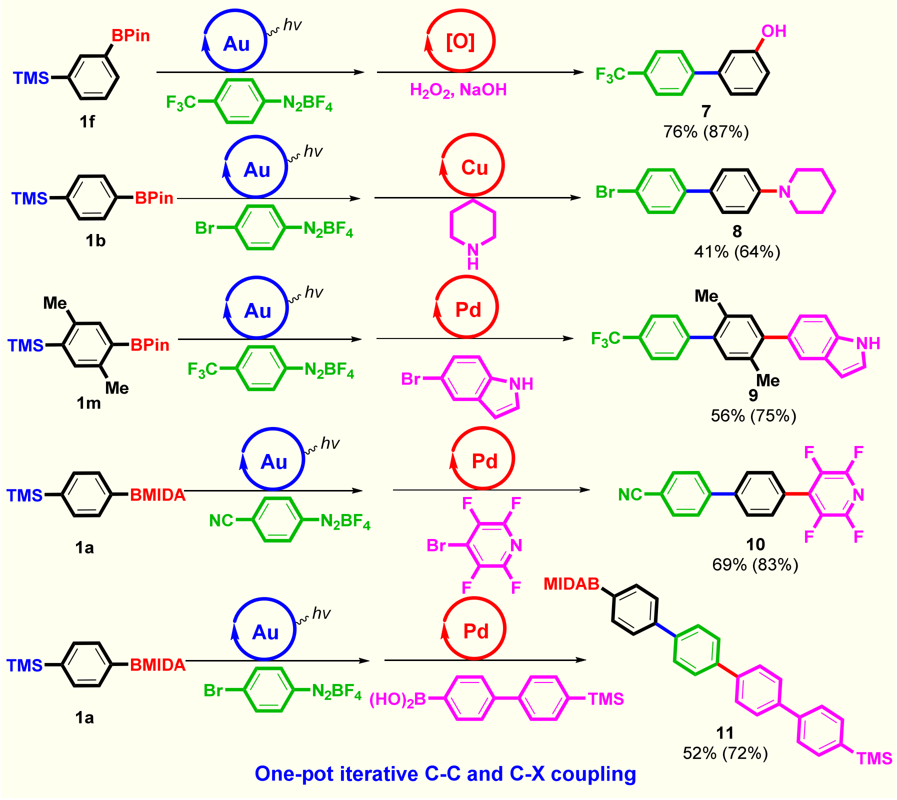


Scheme 4. Gold-catalyzed selective arylation of bifunctionalized arenesilanes.

Both –I and –OTf are very important moieties for transition metal-catalyzed C-C couplings. Therefore, it is still a great challenge to keep these relatively weak chemical bonds intact in any cross-coupling scenario. By exploiting our new method, bifunctionalized haloarylsilane **5a** and pseudohaloarylsilane **5b** both furnished the desired products **6a** and **6b** in satisfactory yields (Scheme 4), which further complements existing Pd-catalysis.

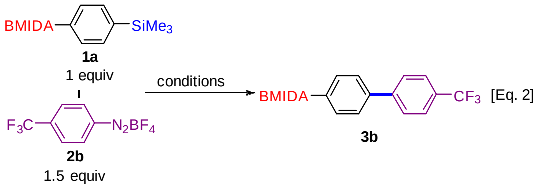


Scheme 5. Iterative modular synthetic methodology. The final isolated yields are shown and the average yield for each step is given in brackets.

To illustrate the synthetic possibilities, one-pot iterative C-C and C-X coupling strategies are presented in Scheme 5. Through the synergism of gold catalysis with another catalysis system, it was possible to synthesize interesting molecules in a one-pot iterative fashion. For example, the gold-catalyzed site-selective arylation of B,Si-bimetallic reagent **1f** and subsequent oxidation with

H_2O_2 afforded trifluoromethylated biphenol **7** in 76% yield. Similarly, arylation and subsequent amination was achieved in moderate yield (**8**). The combination of gold catalysis and palladium catalysis demonstrates the versatility for the rapid construction of complex target molecules for medicinal chemistry or molecular materials (**9-11**) from easily available substrates.

Several control experiments were conducted (Scheme 6). We found that both light and gold-catalyst were crucial for a successful conversion. Without light, even by heating to 60 °C, no product was formed. To our surprise, the addition of $Ru(bpy)_3Cl_2$ as photosensitizer significantly decreased the yield from 97% to 37%; this is caused by a rapid and unselective decomposition of the arenediazonium salts (Scheme 6a). The screening with different light sources revealed that UVA or a fluorescent lamp (FL) instead of blue LEDs slightly lowers the yield (Scheme 6b). However, if UVC light (λ= 254 nm) was used, only 12% yield were obtained. This may indicate that the direct photolysis of diazomium salts with UV light to give aryl radical is less likely. It was also found that the diazonium salt's counter anion was important, OTf^- and Cl^- anions instead of BF_4^- stopped the reaction (Scheme 6c).



(a) Control experiemnts

$Ph_3PAuNTf_2$	$Ru(bpy)_3Cl_2$	BLue LEDs	T/ °C	**3b** (NMR yield)
+	-	+	25	97%
+	-	-	25	NR
-	-	+	25	ND
+	+	+	25	37%
+	-	-	60	ND

(b) The effect of light source

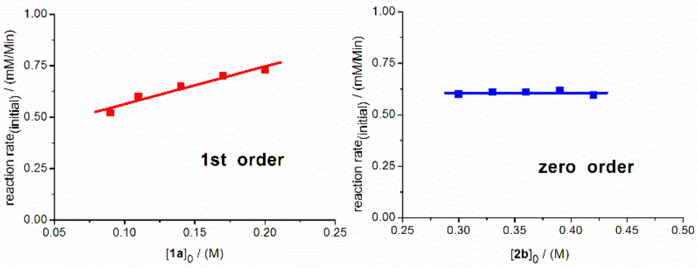
Light	**3b** (NMR yield)
Blue LEDs	97%
UVC (λ = 254 nm)	12%
UVA (λ = 365 nm)	77%
FL (λ = 420 nm)	87%

(c) The effect of ArN_2X counteranion

$4\text{-}CF_3C_6H_4N_2X$	**3b** (NMR yield)
X = BF_4	97%
X = Cl	ND
X = OTf	ND

Scheme 6. Mechanistic experiments.

The kinetic profiles were examined as well and the initial reaction rates are presented in Figure 1. The initial reaction rate for the arylation of **1a** and **2b** is first-order dependent on [**1a**] and [$Ph_3PAuNTf_2$]. In contrast, the reaction rate is independent on the arenediazonium salts [**2b**]; a zero order rate was observed. The first order dependence on gold catalyst suggests that the really reactive catalytic species should be mononuclear gold complex. Moreover, these kinetic results indicate that the turnover limiting step of gold-catalyzed Hiyama arylation may be the aryl ipso substitution step.



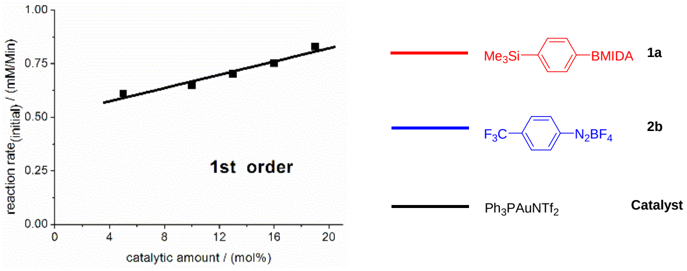
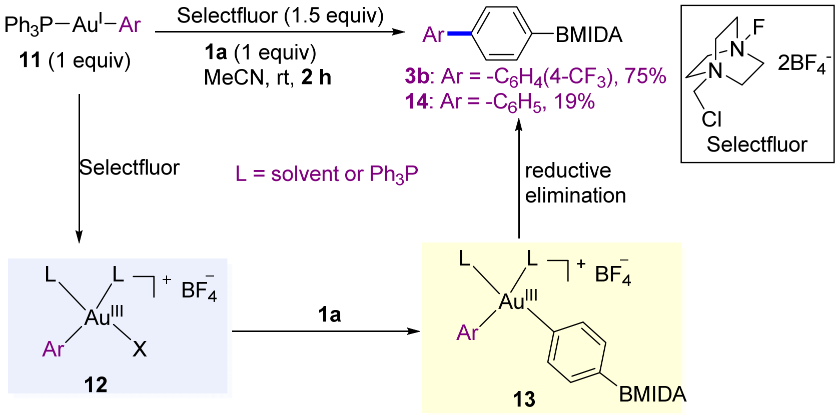
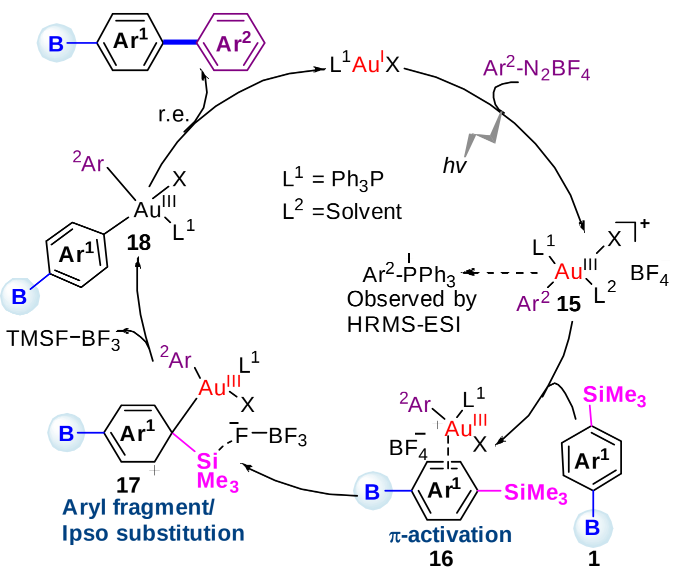


Figure 1. Kinetic studies of the gold-catalyzed selective arylation by ^{1}H NMR.

While Lee and co-workers recently presented the transmetalation of Ph$_3$PAuNTf$_2$ with boronic acids,[33] no such activation was observed for arylsilane by mixing 1 equiv. of **1a** and 1 equiv. of Ph$_3$PAuNTf$_2$ for 6 hours. This indicates a completely different reactivity pattern of arylsilanes and arylboronic acids. Monitoring the reaction in Eq. 2 by ^{31}P NMR suggested the generation of [Ph$_3$P$^+$-Ar]X, which should arise from the reductive elimination from the organogold(III) intermediate **12**.[40] Stoichiometric treatment of Ph$_3$PAuAr and **1a** in the presence of the external oxidant Selectfluor was carried out at room temperature for 2 hours without irradiation (Scheme 7). Selectfluor enables the facile oxidation of **11** to Au(III) **12**. Pleasingly, the desired products **3b** and **14** can be formed in 75% and 19% yields. The better efficiency for the electron-withdrawing aryl group can be rationalized by the higher reactivity towards an arylsilane ipso substitution of intermediate **12**. This would also explain the low yield for strongly electron-donating arenediazonium salts in this transformation. At present, it seems that the highly electrophilic organogold(III)-mediated π-activation and subsequent ipso substitution aryl fragment of **1a** to generate **13** is highly likely.



Scheme 7. Stoichiometric mechanistic study.



Scheme 8. Proposed mechanism.

A possible mechanism is shown in Scheme 8. Under the irradiation of blue LEDs, gold-activated diazonium salts are able to undergo oxidative addition to gold(I) [37-39] or an aryl radical addition and subsequent single electron transfer to the intermediate gold(II)-complex[30,43] to generate transient intermediate **15**. The resulting highly electrophilic **15** coordinates to **1a** to initiate the aryl ipso substitution assisted by the BF_4 anion.[11,44] Finally, reductive elimination from **18** gave the desired boron-containing product. Alternatively, reductive elimination from intermediate **15** give rise to byproduct Ar^2-PPh_3X, which could be detected by HRMS-ESI analysis. In addition, the reaction needs continuous irradiation, and no conversion was observed without light. Thus, the arenediazonium salts-triggered radical chain propagation pathway is less likely.[45-47]

In conclusion, a gold-catalyzed selective Hiyama arylation of B,Si-bimetallic reagents was presented. The resulting biarylboronates are versatile building blocks for the robust assembly of several small molecules via one-pot iterative orthogonal C-C and C-X couplings. This new protocol complements the common Pd-catalyzed C-C coupling strategies from the view of chemoselectivity and functional group compatibility. We anticipate that this redox-neutral arylation technology will streamline pharmaceutical lead discovery, agrochemical and organic material synthesis.

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