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# Transition-metal-free C-C, C-O and C-N cross-couplings enabled by light

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*Supporting Information Placeholder*

**ABSTRACT:** Transition-metal catalyzed cross-couplings to construct C-C, C-O and C-N bonds have revolutionized chemical science. Despite the great achievements, these metal-catalysts also raise certain issues including their high cost, requirement of specialized ligands, the sensitivity to air and moisture and the so-called “transition-metal-residue issue”. Complementary strategy, which does not rely on the well-established “oxidative addition, transmetalation and reductive elimination” mechanistic paradigm, would potentially eliminate all these metal-related issues. Herein, we show that aryl triflates can be coupled with potassium aryl trifluoroborates, aliphatic alcohols and nitriles without the assistance of metal catalysts empowered by photo energy. Control experiments reveal that among all common aryl electrophiles, only aryl triflates are competent in these couplings whereas aryl iodides and bromides can not serve as the coupling partners. DFT calculation reveals that once converted to aryl radical cation, aryl triflate would be more favorable to undergo ipso substitution. Fluorescence spectroscopy and cyclic voltammetry investigations suggest that the interaction between excited acetone and aryl triflate is essential for these couplings. The results in this report are anticipated to open up new opportunities to perform cross-couplings.

## 1. Introduction

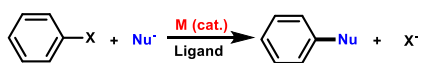
Transition-metal catalyzed cross-coupling reactions between aryl halides and various nucleophiles are of great significance in chemical science.<sup>1</sup> Benefited from several decades’ polishing, a wide range of transition-metal catalyzed coupling reactions to forge C-C, C-O and C-N bonds have become indispensable to many chemical fields.<sup>2</sup> Due to their importance and efficiency, the development of transition-metal catalyzed cross-couplings is generally considered to be one of the most important scientific discoveries in 20<sup>th</sup> century, exemplified by the 2010 Nobel Prize in chemistry. Although various nucleophiles can react with aryl electrophiles, a generic reaction paradigm underling all these coupling reactions comprises oxidative addition-transmetalation-reductive elimination cycle.<sup>2</sup> Involved in all three elemental steps, transition-metal catalysts are obviously essential (Figure 1a), among which palladium, nickel and copper and many others have been extensively investigated in a wide array of reactions.<sup>3</sup> Besides transition metals, another crucial factor to impact these reactions is the ligand.<sup>4-5</sup> Over the past several decades, various phosphine-, nitrogen- and NHC (N-heterocyclic carbene)-based ligands with diverse structural characters and different reactivities have been invented and found broad applications.<sup>1</sup> Through the modulation of their electronic and steric properties, the ligands can dramatically increase the versatility of these metal-catalyzed cross-couplings.

However, the cost of metal catalysts and ligands especially in the cases requiring high catalyst loading raises serious economic concerns, especially in large scale industrial processes. Besides, some transition-metal complexes are extremely moisture and air sensitive, which not only complicates the handling but also generates safety issues. Furthermore, addressing “transition-metal residual issue” in the pharmaceutical and electronic material industries necessitates tedious endeavours and special equipment to decrease the transition metal amount to the regulation level (e.g. < ppm level), thereby depleting additional resources.<sup>6-7</sup> Consequently, complementary protocols, which do not rely on transition metals and ligands, are more desirable. Identifying efficient and transition-metal-free protocols will eliminate metal-catalyst associated issues from the beginning and more significantly, provide new strategies to

couple aryl halides or related electrophiles with nucleophiles. Unfortunately, compared to the well-established metal-catalyzed cross-couplings, the metal-free versions are less explored (Figure 1b).<sup>8-9</sup>

The power of transition metals to couple aryl electrophiles with nucleophiles relies on their property to readily exchange the oxidation states. Due to this unique redox activity, transition metals can efficiently activate the C-X bonds of aryl electrophiles, which initiates the oxidative addition in the well-recognized three-step catalytic cycle. In contrast, another less explored and distinct concept to activate C-X bond of aryl electrophile is based on single electron transfer (SET) process, the so-called S<sub>RN</sub>1 reaction.<sup>10-13</sup> Injecting an electron to aryl electrophile to generate radical anion can weaken the C-X bond when the extraneous electron is located at its  $\sigma^*$  orbital. For example, to initiate an S<sub>RN</sub>1 reaction, aryl electrophiles require to be reduced by external electron source.<sup>14</sup> In this context, we have recently reported reactions to prepare aryl iodides from aryl chlorides, aryl bromides and aryl triflates in a transition metal-free manner.<sup>15-16</sup> Encouraged by these results and intrigued by the significance of the Suzuki coupling and Ullmann coupling to construct C-C, C-O and C-N bonds, we were motivated to develop their metal-free counterparts. Unfortunately, these less reductive nucleophiles such as organoboron reagents and alcohols fail to react with aryl chlorides, bromides and triflates under previous conditions. We posited that albeit nucleophilic, these non-reductive nucleophiles are less reactive than NaI to trigger the S<sub>RN</sub>1 reaction. Besides, even in cases that aryl radical intermediates are indeed generated, they may not be productively trapped by weaker nucleophiles.<sup>17</sup> Upon these challenges and inspired by the pioneering works of Fukuzumi, Nicewicz, Wu and others, we proposed that instead of injecting an electron to form aryl radical anion, removing an electron to generate aryl radical cation may facilitate the nucleophilic addition of these weaker nucleophiles (Figure 1c).<sup>18-27</sup> Guided by this working model, herein, we wish to report the development of metal-catalyst-free cross-couplings of aryl triflates with less reductive nucleophiles *i.e.* aryl trifluoroborates, aliphatic alcohols and nitriles (Figure 1d).<sup>28</sup>

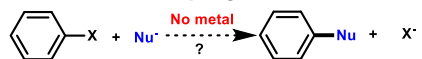
## (a) Well established metal-catalyzed coupling



Advantages: High efficiency and robust

Disadvantages: (1) Cost of metals and ligands  
(2) Moisture and air sensitivity  
(3) Transition-metal-residue issue

## (b) More desirable metal-free coupling



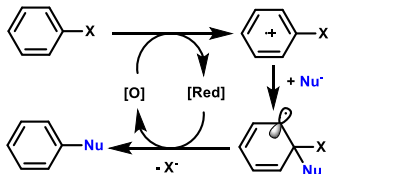
Advantages: Eliminate all metal-related issues.

Disadvantages: Fewer metal-free coupling reactions are known.

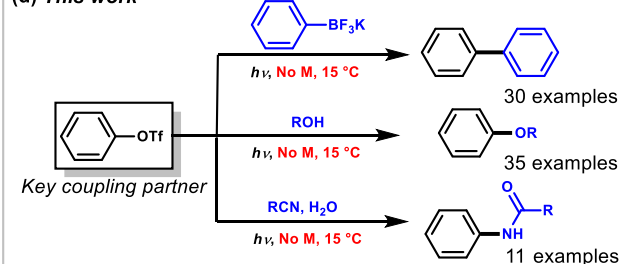
## (c) Research proposal towards metal-free coupling

(Nu<sup>-</sup> = Boron nucleophile, alcohol and nitrile)

Hypothesis:



## (d) This work



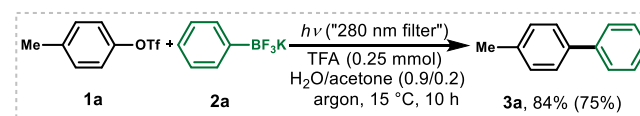
**Figure 1.** Metal-catalyzed coupling and metal-free coupling. (a) Metal-catalyzed cross-couplings. (b) Metal-free cross-couplings. (c) Research hypothesis to couple less reductive nucleophiles via oxidative initiation. (d) Developed reactions to couple aryl triflates with boron nucleophiles, aliphatic alcohols and nitriles.

## 2. Results and discussion

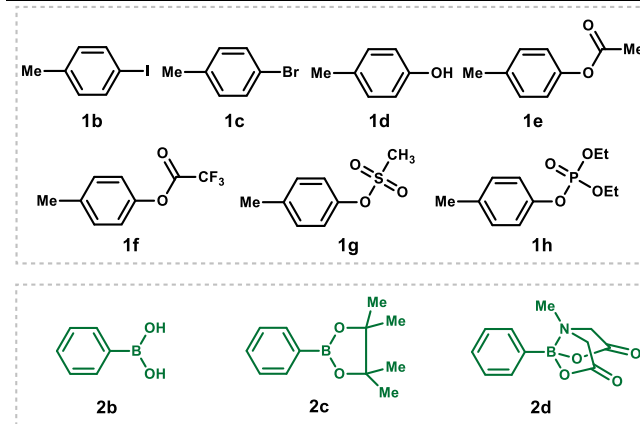
**2.1 Cross-coupling between aryl triflate and potassium aryl trifluoroborate.** Cross-coupling between organoboron compounds and aryl electrophiles, known as the Suzuki coupling, is one of the most important reactions in organic synthesis.<sup>29</sup> Traditional Suzuki coupling predominantly employs palladium as the catalyst although other metals such as nickel or copper can also promote this reaction.<sup>30-34</sup> However, metal-free Suzuki-type coupling to prepare biaryl compounds remains elusive.<sup>35</sup> Guided by the hypothesis shown in Figure 1c, we envisioned that the ideal conditions of a metal-free Suzuki coupling underlying electron catalysis should meet the following requirements: (1) the oxidant to generate aryl radical cation should remove one electron from aryl electrophile instead of the nucleophile, which causes a dilemma because the nucleophiles are usually more electron rich than electrophiles; (2) the leaving group from the aryl electrophile should be less nucleophilic than the boron nucleophile; and (3) contrary to the metal-catalyzed Suzuki reaction, this proposed reaction should be performed under acidic conditions instead of basic conditions because the bases could potentially serve as the reductants to interfere the desired reaction. Moreover, triplet ketones, which can activate the substrates either via the energy transfer or electron transfer mechanism,<sup>36-43</sup> could potentially serve as the oxidant to generate the aryl radical cation. Among the common ketones, we are particularly interested

in acetone because: (1) it is readily available as a common organic solvent; and (2) the triplet acetone has a higher energy state than other ketones, which is beneficial for both electron transfer and energy transfer.<sup>44-45</sup>

**Table 1.** Comparison of various coupling partners on the metal-free Suzuki coupling.<sup>a</sup>

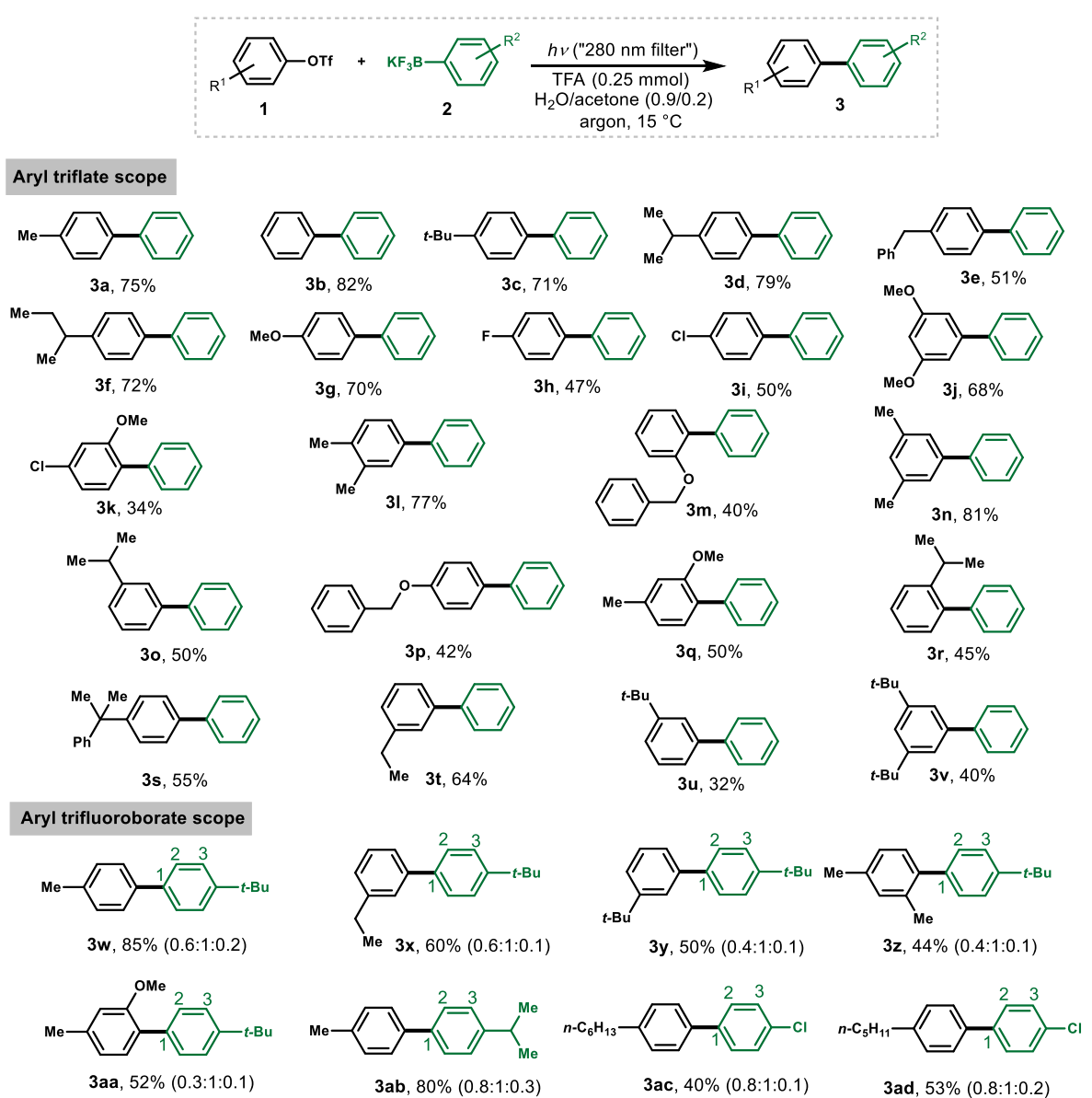


Entry	Different combinations	Yield
1	1a & 2a	84% (75%)
2	1b & 2a	0%
3	1c & 2a	0%
4	1d & 2a	0%
5	1e & 2a	0%
6	1f & 2a	0%
7	1g & 2a	36%
8	1h & 2a	17%
9	1a & 2b	26%
10	1a & 2c	23%
11	1a & 2d	7%



a. Please see supporting information for the details and the UV-Vis spectrum of the “280 nm” optical filter.

With these concerns in mind, we performed the investigation by combining a wide variety of aryl electrophiles (*i.e.* 4-tolyl aryl electrophiles) and phenyl boron reagents (*i.e.* phenyl boron nucleophiles) as the coupling partners (Table 1). Following extensive exploration, it was identified that 4-methyl phenyl triflate (**1a**) can be coupled with potassium phenyl trifluoroborate (**2a**) in 84% yield under optimized conditions promoted by light without transition metals (see supporting information for details). Besides the acetone as the co-solvent, we found that water is an efficient solvent for this reaction probably because potassium phenyl trifluoroborate can dissolve well in this co-solvent mixture. Moreover, although water can potentially serve as the nucleophile to react with the proposed aryl radical cation, we did not observe any phenol by-product after the reaction, which suggests that phenyl trifluoroborate is a much more efficient nucleophile than water in this reaction. Notably, aryl iodide (**1b**, entry 2), aryl bromide (**1c**, entry 3), phenol (**1d**, entry 4), aryl acetate (**1e**, entry 5) and aryl trifluoroacetate (**1f**, entry 6) are not suitable substrates. Besides aryl triflate, aryl mesylate (**1g**, entry 7) and aryl phosphate (**1h**, entry 8) can deliver the product in lower yields.<sup>46</sup> That only certain phenol derivatives participate in this metal-free Suzuki coupling suggests that the electron-rich

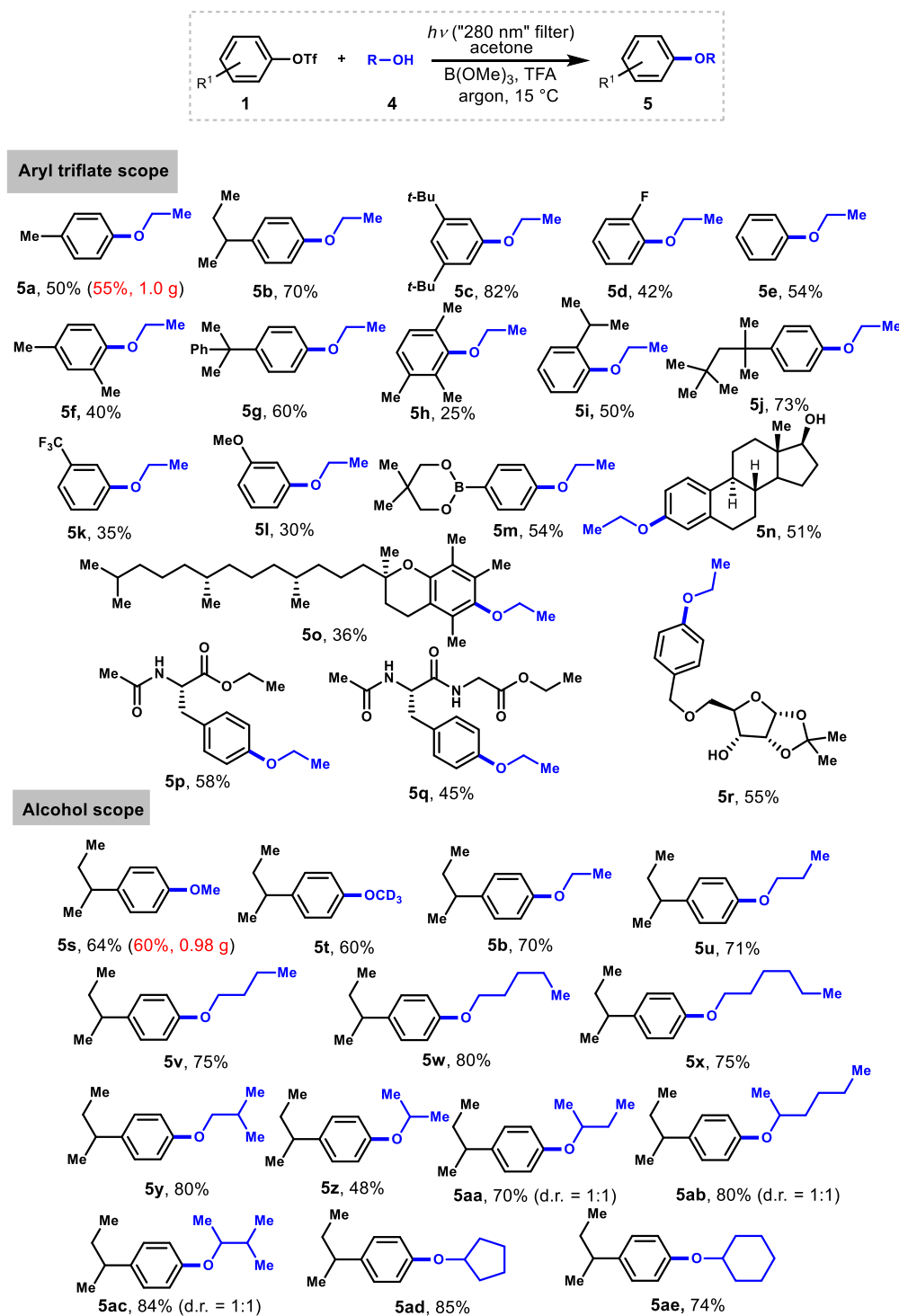


**Figure 2.** Scope of the metal-free Suzuki coupling. The regio-isomer ratio was determined by GC/MS via comparing with authentic samples.

character of phenol derivatives might facilitate the generation of proposed aryl radical cation. Moreover, among the feasible phenol derivatives, the triflate is a better leaving group than phosphate and methylate, which rationalizes that aryl triflate is the most reactive substrate among all three. Regarding the boron nucleophiles, aryl boronic acid (**2b**, entry 9), aryl boronic ester (**2c**, entry 10) and MIDA boron ester (**2d**, entry 11) are all inferior to aryl trifluoroborate (**2a**), which is consistent with the nucleophilic strength of these boron reagents.<sup>47</sup> Although popular aryl bromide and iodide are not viable substrates in this reaction, aryl triflate, which can be prepared from the corresponding phenol, provides unique advantages regarding biomass utilization.<sup>48-50</sup>

With the optimized conditions identified, we then explored the scope of this metal-free Suzuki coupling. Figure 2 shows that various aryl triflates can be coupled with aryl trifluoroborates in modest to good yields. Aryl triflates with substituents at *para* and *meta* positions (**3a-3j**, **3l**, **3n**, **3o**, **3p**) produce higher yields than those with *ortho* substituents (**3k-3m**, **3q**, **3r**) probably due to the steric effect. Both electron-rich (**3g**, **3j**, **3k**, **3m**, **3p**, **3q**) and electron-poor (**3h**, **3i**) aryl triflates are tolerated and electron-rich aryl triflates deliver

the products in higher yields. One notable difference between traditional Pd-catalyzed Suzuki protocol and this metal-free protocol is that substituted aryl trifluoroborates would generate regioisomers. Since aryl trifluoroborates are electron-rich aryl nucleophiles with multiple nucleophilic sites,<sup>51</sup> following the working hypothesis shown in Figure 1c, regioisomers from the nucleophilic attack by different sites of aryl trifluoroborates can be generated. When *para*-substituted aryl trifluoroborates (**3w-3ad**) were subjected to the standard conditions, three regioisomers were observed, which is consistent with the Friedel-Crafts aromatic electrophilic substitution model. The generation of regioisomers in this metal-free Suzuki coupling can partially support the existence of aryl radical cation intermediate (Figure 1c). Among all three isomers, the major isomers are produced by the nucleophilic attack of *ortho*-carbon in aryl trifluoroborates. Regarding the generation of regioisomers in cases substituted aryl trifluoroborate were used, besides the aromatic electrophilic substitution process, the protodeboronation<sup>52-53</sup> process may also be involved (please see supporting information for the stepwise mechanisms to produce all three regioisomers). Generally, this metal-free Suzuki protocol is applicable to a wide



**Figure 3.** Scope of the coupling between aryl triflate and alcohol.

range of aryl triflates and aryl trifluoroborates with non-polar substituents. Unfortunately, compared to the well-established powerful Pd-catalyzed Suzuki coupling, the scope of this current metal-free Suzuki procedure is still limited. For example, in cases of substrates with polar substituents such as amine, carboxylic acid, esters, amides, sulfonamides and the heterocycles such as indoles, pyridines, no desired coupling products can be observed. Finally, both vinyl triflates and vinyl trifluoroborates are not viable substrates in this reaction. We rationalized that the presence of the polar substituents would increase the solubility of both reactants in the solvent mixture to reduce the hydrophobic effect, thereby decreasing the inter-

action of aryl triflate and aryl trifluoroborate. Another possible reason is that the heteroatom would compete with the oxygen atom in triflate to coordinate with the boron atom in aryl trifluoroborate, which also disrupted the productive interaction between aryl triflate and aryl trifluoroborates. Efforts to expanding the scope of this metal-free Suzuki coupling are undergoing in our laboratory and will be reported in due course.

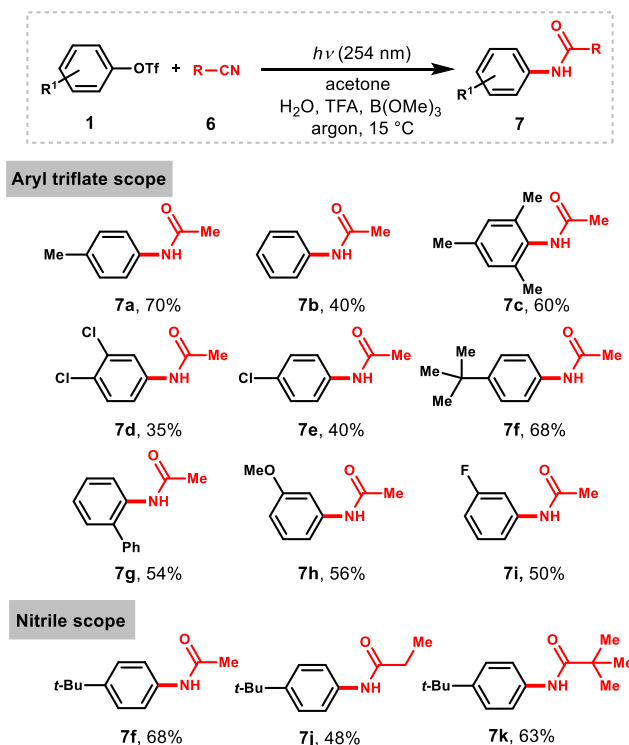
**2.2 Cross-coupling between aryl triflate and aliphatic alcohol.** Aryl alkyl ethers are ubiquitous in a wide range of compounds, which are valuable for pharmaceutical, agrochemical and material industries.<sup>54</sup> Current protocols to prepare these ethers from aryl halides and alcohols predominantly utilize copper and palladium.<sup>55-56</sup>

Although several transition-metal-free protocols are known, they usually undergo the benzyne mechanism, thus requiring strong bases and harsh conditions.<sup>57-58</sup> Following the hypothesis shown in Figure 1c and encouraged by the results of metal-free Suzuki coupling as described in section 2.1, we wondered whether the alcohol is an applicable nucleophile within this mechanistic model. To our delight, by slightly modifying the previous conditions, various alcohols can be coupled with aryl triflates. Likewise, the unique feature of this protocol is that only aryl triflate is an efficient coupling partner in presence of acetone as the key promoter whereas aryl bromide and aryl iodide can not produce the desired ether product. Unlike other aryl radical cation involved aromatic substitutions, only one *ipso* substitution product can be detected.

To examine the synthetic utility of this metal-free Ullmann protocol, the scope of aryl triflates and aliphatic alcohols were investigated (Figure 3). Regarding the scope of aryl triflates, a wide range of aryl triflates can be tolerated regardless of the steric and electronic effect and the yields are generally moderate to good (**5a-5m**). To our delight, aryl triflates derived from complex molecules such as sterol (**5n**), vitamin (**5o**), amino acid (**5p**), dipeptide (**5q**) and ribose (**5r**) are compatible to the current conditions. Subsequently, we investigated the scope of the alcohols. Both primary and secondary alcohols can be successfully coupled with aryl triflate but tertiary alcohols such as *t*-amyl alcohol and *t*-butanol can not produce any coupling product (**5s-5ae**). Considering that in metal-catalyzed coupling protocols, coupling secondary alcohols is especially challenging because of the competitive  $\beta$ -H elimination, this metal-free protocol shows particularly advantages since we did not observe any oxidative ketone products. Moreover, this reaction can be easily scaled up to gram scale without significantly decreasing the yields (**5a, 5s**). During the scope investigation, besides the desired ether product, another by-product that we always observed is the reduction product of aryl triflate (*i.e.* ArOTf to ArH) with various amounts depending on the substrates. In contrast, this reduction by-product was not detected in the C-C and C-N formation. We rationalized that besides the generation of aryl radical cation, aryl triflate can also be converted to the aryl radical under the current conditions.<sup>16</sup> The alcohols, as efficient hydrogen donors, can reduce the aryl radical to arenes; whereas water and nitrile are not good hydrogen donors for aryl radical. Although this procedure is efficient for alcohols as the nucleophile to synthesize aryl alkyl ether, it is not applicable to phenols to prepare biaryl ethers probably because the phenols can also absorb the light, which will interfere with the productive energy/electron transfer between acetone and aryl triflate (*vide infra*).

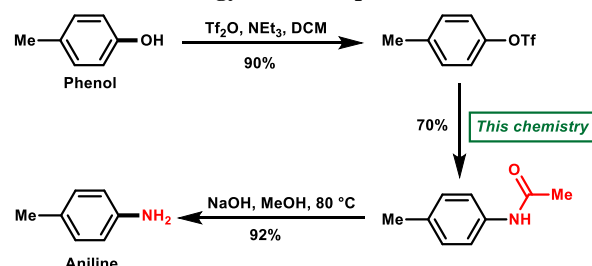
**2.3 Cross-coupling between aryl triflate, aliphatic nitrile and water.** Encouraged by the coupling of alcohols and aryl triflates, we attempted to develop a similar protocol to construct C-N bonds under metal-free conditions because the amination of aryl halides is one of the most widely used reactions in pursuit of drug candidates in pharmaceutical industry.<sup>59</sup> However, developing C-N coupling is more challenging than C-O coupling because nitrogen nucleophiles are usually reactive reductants, which are not compatible with oxidative conditions. Therefore, we hypothesized that less reductive nitrogen nucleophiles such as azoles and nitriles might be potentially competent in this reaction.<sup>21</sup> Various nitrogen nucleophiles, including anilines, amides, imides, sulfonamides, aliphatic amines, imidazoles, indoles, pyrroles, benzotriazoles, purines and nitriles were evaluated. Among all these nitrogen compounds, we found that only nitriles can react with aryl triflates under light irradiation to produce the C-N bond in presence of water, which is reminiscent of the Ritter reaction.<sup>60</sup> It is notable that we did not observe any phenol by-product, thereby implying that water is not a reactive nucleophile to react with the proposed aryl radical cation. Scope evaluation suggests that numerous aryl triflates (**7a-7i**) and nitriles

(**7f, 7j, 7k**) can be applied under this condition (Figure 4). This aromatic Ritter-type reaction represents a unique strategy to convert phenol derivatives to aniline derivatives (Scheme 1).<sup>61</sup> Considering the significance of aniline type compounds and ready availability of phenols, we expect that this simple protocol would find further synthetic applications to prepare aniline derivatives. Although aliphatic nitriles are competent coupling partners in this aromatic Ritter reaction, attempts to expand this protocol to aromatic nitriles proved futile probably due to the energy/transfer interference caused by the chromophore in aromatic nitriles. To expand the scope of nitrogen nucleophiles, our current efforts focus on: 1) to identify a more efficient leaving group instead of triflate ion to change the redox property of aryl electrophiles and 2) to identify a better photo redox catalyst instead of the triplet acetone as the electron shuttle to generate the radical cation.



**Figure 4.** Scope of the aromatic Ritter reaction to convert phenol derivatives to aniline derivatives.

**Scheme 1.** A new strategy to convert phenol to aniline.

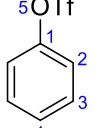


**2.4. Mechanistic discussion.** The data described above provide compelling evidences that aryl triflates offer unique reactivities among the common aryl electrophiles at least regarding these light-enabled metal-free cross-couplings. The hypothesis shown in Figure 1c implied that a key radical cation intermediate of aryl electrophile is responsible for the nucleophilic attack to construct the C-C, C-O and C-N bonds. In the context of aryl radical cation initiated aromatic substitution, the regioselectivity of aryl triflate showcased herein *i.e.* *ipso*-substitution is different from the examples reported by Nicewicz,<sup>21, 62-63</sup> most of which are *ortho* and *para*

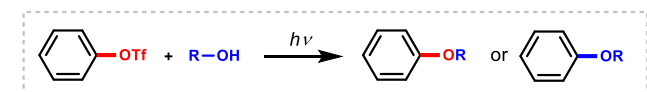


substitutions. To gain a better mechanistic understanding of this regioselectivity, we performed the natural population analysis (NPA) by selecting phenyl triflate as the model substrate both on the ground state and the radical cation state.<sup>64</sup> The NPA analysis revealed that: 1) only considering the charge distribution in the radical cation of aryl triflate, the positive charge is solely localized on C1 (+0.456), which will exclusively react with the nucleophiles to produce the *ipso*-substitution products;<sup>19</sup> 2) considering the charge change between radical cation and neutral molecule, although phenyl triflate would build up the positive charge at the *ipso* (C1), *meta* (C3) and *para* (C4) positions from the ground state to the aryl radical cation, the accumulated cation charge density on C1 is still higher than those of C3 and C4 (Table 2). Another possible reason for the *ipso* specificity is that nucleophilic substitution at the *ipso* position (C1) would be much easier to generate the aromatic product than at the *meta* (C3) and *para* position (C4) since the triflate is a much more potent leaving group than the hydride under the current conditions. Similar reactions have also been reported by Nicewicz with -OMe as the leaving group<sup>20</sup> and by Fukuzumi with -F as the leaving group.<sup>19</sup>

**Table 2. NPA analysis of phenyl triflate at ground state and radical cation state.**

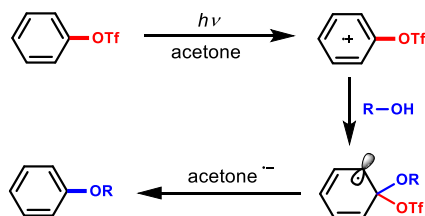
	Atom	Neutral	Cation	$\Delta$
	<b>C1</b>	0.261	<b>0.456</b>	<b>0.195</b>
	<b>C2</b>	-0.236	-0.242	-0.006
	<b>C3</b>	-0.238	-0.197	<b>0.041</b>
	<b>C4</b>	-0.212	-0.044	<b>0.168</b>
	<b>O5</b>	-0.600	-0.594	<b>0.006</b>

**Scheme 2. Isotopic investigation of metal-free Ullmann coupling. (1) Two possible mechanisms. (2) Isotopic labelling investigation.**

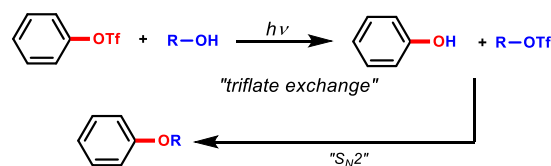


### 1. Two possible mechanisms

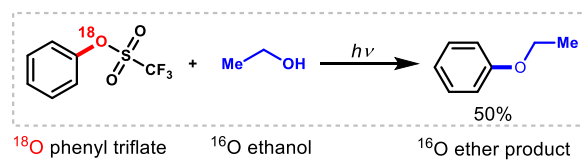
(A) Oxygen from ROH



(B) Oxygen from ArOTf



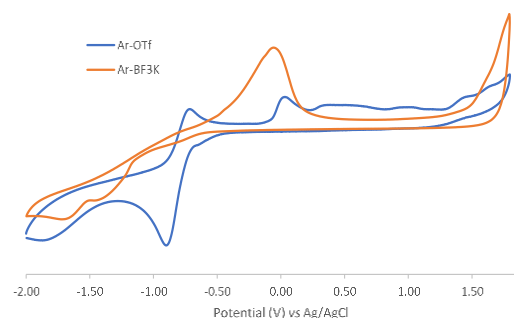
### 2. Isotopic labelling study



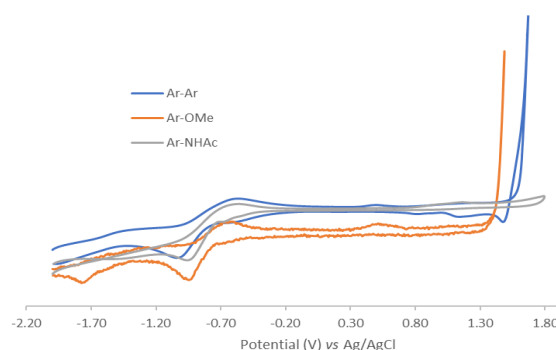
To provide further mechanistic insight, we carried out the isotopic labelling studies about the metal-free coupling of aryl triflate with the alcohol. Regarding the C-C and C-N formation, there is no ambiguity that Csp<sup>2</sup>-O bond was cleaved during the reactions. However, in the C-O formation reaction, besides the proposed pathway to rationalize the metal-free aryl ether formation (part A in Scheme 2.1), another possible mechanism is a cascade triflate exchange/S<sub>N</sub>2 reaction (part B in Scheme 2.1).<sup>65</sup> These two pathways would generate two products which contain the oxygen atoms from alcohol and aryl triflate respectively. Therefore, the information on which molecule provides the oxygen atom in the product will reveal conclusive evidence to rule out one of the two mechanistic hypotheses. To identify the oxygen source, the <sup>18</sup>O labelled aryl triflate was prepared. By subjecting this <sup>18</sup>O labelled aryl triflate and regular ethanol (<sup>16</sup>O) to the standard conditions, we found that only the regular oxygen atom (<sup>16</sup>O) was introduced into the ether product, thereby confirming that the oxygen in the final product originates from the alcohol instead of aryl triflate (Scheme 2.2). This isotopic labelling experiment suggests that during the coupling, the C-O bond of the aryl triflate is cleaved, which corroborates hypothesis A and rules out hypothesis B. Therefore, all three reactions follow the same mechanistic paradigm that Csp<sup>2</sup>-O bond of aryl triflate was cleaved during the reactions.

It was proposed that SET between aryl triflate and the photosensitizer is important for these coupling reactions (Figure 1c). To understand the possible electron transfer process, we measured the oxidative potentials of the representative aryl compounds including aryl triflate, potassium aryl trifluoroborate, biphenyl, aryl alkyl ether and acetanilide involved in this study. The cyclic voltammetry (CV) data revealed that among the investigated aryl compounds, aryl trifluoroborate (E<sub>p</sub> = -0.1 V versus Ag/AgCl) is the most readily oxidized whereas other compounds share the comparable oxidative potentials (E<sub>p</sub> ~ -0.7 V versus Ag/AgCl) (Figure 5). Although the conditions to collect these CV data (CH<sub>3</sub>CN as the solvent) are different from those to perform the reactions, they still imply that it is less likely to directly oxidize aryl triflate via SET in presence of potassium aryl trifluoroborate as well as other products.

(A)

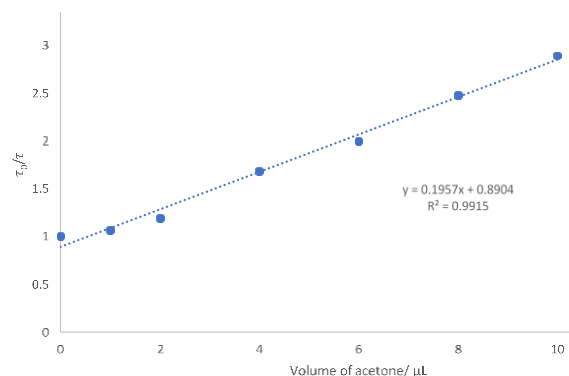


(B)



**Figure 5.** Cyclic voltammetry data of representative aryl substrates in this study. (A) CV of two starting materials aryl triflate and potassium phenyl trifluoroborate. (B) CV of three products including biphenyl, aryl alkyl ether and acetanilide.

These CV data suggest that it is less likely for aryl triflate to directly undergo SET under the reaction conditions. On the other hand, it is known that once excited, the organic molecule would be more reactive because the energy of HOMO is increased and the energy of LUMO is decreased.<sup>66</sup> Therefore, we proposed that the excited aryl triflate might undergo SET to generate the aryl radical cation. This is consistent with our control experiments, in which other common visible-light active sensitizers to initiate SET including diacetyl, eosine, xanthone, Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub>, and Fukuzumi's photocatalyst (9-mesityl-10-phenylacridinium tetrafluoroborate) under the visible light irradiation ( $\lambda > 400$  nm) could not deliver the desired coupling product. Since aryl triflate can only be excited by the light with the wavelength  $\lambda < 350$  nm, under the conditions of the control experiments, the photo-sensitizers can be excited but not the aryl triflate. These negative controls imply that the excitation of aryl triflate is required for the couplings to proceed. Moreover, to evaluate the interaction between excited aryl triflate and acetone, we performed the fluorescence quenching experiment of aryl triflate by acetone (Figure 6). The Stern-Volmer plot suggests that strong interaction between excited aryl triflate and acetone exists. We proposed that it is the triplet acetone instead of ground state acetone that interacts with excited aryl triflate because of two reasons: (1) acetone and aryl triflate have similar UV-Vis absorption spectra (see supporting information for both spectra), thereby indicating that they can be both excited simultaneously; (2) triplet acetone has a very high energy state ( $E_T = 332$  kJ/mol),<sup>45</sup> which implies that it is unlikely for triplet aryl triflate to sensitize ground state acetone to its triplet state. Therefore, these experiments support that a SET process may be possible between excited aryl triflate and triplet acetone.

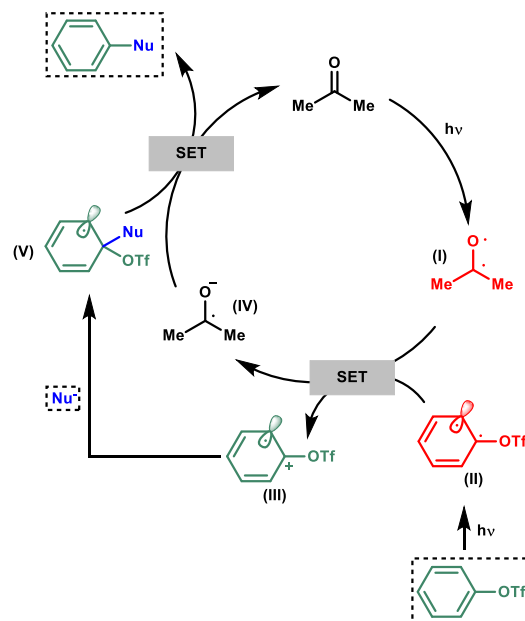


**Figure 6.** Stern-Volmer plot of aryl triflate and acetone.

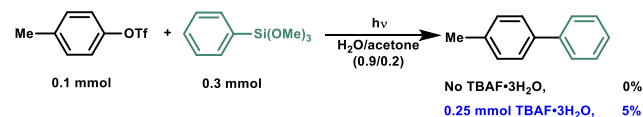
Combining the above DFT calculations as well as CV and fluorescence investigations, we proposed a following mechanism to rationalize these metal-free coupling reactions (Figure 7). Under the light irradiation, both acetone and aryl triflate can be excited to their triplet states (I) and (II). Due to their high reactivity, a SET process would occur to produce the radical cation (III) and radical anion (IV). Following reacting with the nucleophile, aryl radical cation would be converted to radical intermediate (V). Driven by aromatization energy, another SET from intermediate IV to V with triflate ion as the leaving group would deliver the desired aromatic substitution product.

Philosophically, a viable mechanism should not only be consistent with the known facts but can also predict new reactivity. According to the proposed mechanism in Figure 7, it can be predicted that aryl silyl compound is also expected to be a feasible

nucleophile to construct the C-C bond with aryl triflate. A preliminary investigation suggested that in presence of tetrabutylammonium fluoride hydrate (TBAF  $\cdot 3\text{H}_2\text{O}$ ), trimethoxyphenylsilane can react with aryl triflate to generate the desired biaryl coupling product in 5% yield. In contrary, this biaryl coupling product can not be formed without TBAF (Figure 8). The success of this reaction supports the proposed mechanism shown in Figure 7. Further optimization effort on this Hiyama-type coupling is undergoing in the laboratory.



**Figure 7.** A proposed mechanism which is consistent with the current experimental data.



**Figure 8.** Preliminary investigation about aryl silane as the nucleophile.

### 3. Conclusion

In summary, we have established a general protocol to couple aryl triflate with aryl trifluoroborate, aliphatic alcohol and nitrile in absence of any transition metal catalyst promoted by light at mild temperature (15 °C). Among the common aryl electrophiles, this protocol is exclusively efficient to aryl triflate, whereas aryl iodide and bromide can not be coupled. This unique reactivity of aryl triflate probably hinges upon its exceptional leaving ability of triflate ion in presence of the Lewis acid and its interaction with triplet acetone. Contrary to the previous work to prepare aryl iodide from aryl bromide and aryl triflate, in which NaI initiates the  $\text{S}_{\text{RN}}1$  reaction, this current protocol is postulated to be triggered by an electron hole. The proposed key radical cation intermediate can be trapped by the weak nucleophiles including aryl trifluoroborates, alcohols and nitriles to form C-C, C-O and C-N bonds. Considering the simplicity and efficiency of these reactions, it is anticipated that these results would open up new approaches to execute the classical coupling reactions.

### ASSOCIATED CONTENT



## Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental details, characterization data and copies of spectra

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### Notes

The authors declare no competing financial interests.

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