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# Direct Cross-Coupling of Allylic C(sp<sup>3</sup>)–H Bonds with Aryl- and Vinylbromides by Combined Nickel and Visible-Light Catalysis

Long Huang and Magnus Rueping\*

**Abstract:** An efficient protocol for the direct allylic  $C(sp^3)$ -H bond activation of unactivated tri- and tetrasubstituted alkenes and their functionalization with aryl- and vinylbromides by nickel and visible-light photocatalysis has been developed. The method allows  $C(sp^2)$ - $C(sp^3)$  formation under mild reaction conditions with good functional-group tolerance and excellent regioselectivity.

Allylarene units are important structural features in natural products and bioactive molecules.<sup>[1]</sup> Furthermore, allylarenes serve as ubiquitous synthetic intermediates in organic chemistry for numerous transformations.<sup>[2]</sup> Thus, considerable attention has been devoted to the construction of this moiety.<sup>[3-6]</sup> The construction of  $C(sp^2)-C(sp^3)$  bonds by direct functionalization of C-H bonds is a powerful tool for the synthesis of highly functionalized and complex alkenes. However, compared with the significant progress in direct oxidation and amination of allylic C-H bonds, routes toward direct arylation are narrowly explored. Recently, Nakamura disclosed an iron-catalyzed direct arylation of olefins with aryl Grignard reagents, but only limited examples and low yields were achieved.<sup>[7]</sup> In light of the pioneering work of Arnold and co-workers on photoinduced cross-coupling of dicyanobenzene with olefins,<sup>[8]</sup> MacMillan and co-workers recently reported the direct arylation of allylic C(sp<sup>3</sup>)-H bonds using thiyl radicals as hydrogen-atom abstractors, and less available cyanoarenes as coupling partners.<sup>[9]</sup> Hence, the development of direct, general, and regioselective  $C(sp^3)-C(sp^2)$  bondforming reactions with readily available substrates would be of great importance for both synthetic organic chemistry as well as materials and pharmaceuticals development.

Visible-light photoredox and metal dual catalysis has emerged as an effective strategy for diverse C–C and C–X (X = N, O, S, P) bond formations in a redox-, atom-, and stepeconomical fashion.<sup>[10]</sup> Key to this success is the capacity of photocatalysts to act as both strong oxidants and reductants by single-electron transfer (SET) upon irradiation with visible light. Recently, Molander and co-workers reported the direct

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arylation of  $\alpha$ -heterosubstituted C(sp<sup>3</sup>)–H bonds using the combination of a nickel catalyst and an iridium photocatalyst.<sup>[11]</sup> Mechanistic studies revealed that the excited Ni<sup>II</sup>-ArBr species, which is generated through triplet–triplet energy transfer with the excited photocatalyst, effects the C–H activation by homolysis of the Ni–Br bond. We therefore envisioned that this concept of photocatalytically generated bromine radical for hydrogen atom abstraction could be further extended to allylic C(sp<sup>3</sup>)–H bonds of simple olefins (Scheme 1). Herein, we present the development of a general and regioselective method for allylic arylation that exhibits broad scope across a wide range of (tri- and tetrasubstituted) olefins and aryl- and vinylbromide electrophilic coupling partners. To our knowledge such a transformation has not been accomplished to date.





Initially, we investigated the coupling of readily available methyl 4-bromobenzoate (1a) and tetramethylethylene (TME: 2a) as a model reaction and the results are summarized in Table 1. A preliminary evaluation of photocatalysts showed that the reaction proceeds smoothly using [Ir(dF- $(CF_3)ppy_2(bpy)]PF_6$  (4) in the presence of NiCl<sub>2</sub>·glyme (glyme = ethylene glycol dimethyl ether), 4,4'-di-tert-butyl-2,2'-bipyridine (dtbbpy), and 2,6-lutidine at room temperature under irradiation with blue LEDs for 48 hours, affording the desired product 3a in 84% yield (entry 1). To our surprise, the organic dye [Acr-Mes] $ClO_4$  (5) gave the desired product **3a** in a comparable yield while  $[Ru(bpy)_3]PF_6$  (6) proved to be ineffective (entries 2 and 3). From a costeffective and sustainable perspective, the commercially available acridinium 5 is the preferred photocatalyst.<sup>[12]</sup> To be noted, this is the first report on the combination of an acridinium photocatalyst and a nickel metal catalyst.<sup>[13]</sup> Replacing NiCl<sub>2</sub>·glyme with the air sensitive Ni(cod)<sub>2</sub> failed to improve the yield (entry 4). The reaction performed with lower efficiency when other solvents were used (entries 5 and 6). Furthermore, lowering the concentration hampered the formation of 3a severely (entry 7). Evaluation of different





[a] Reaction conditions: **1a** (0.1 mmol, 1 equiv), **2a** (10 equiv), [Ni] (10 mol%), PC (5 mol%), ligand (15 mol%), base (2 equiv), solvent (0.4 mL, 0.25 м), RT, blue LEDs, 48 h. [b] Yields were determined by <sup>1</sup>H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. [c] 1 mol% photocatalyst was used. [d] 0.1 м solution. [e] no ligand. [f] no light.

bases showed that 2,6-lutidine is the best base for this process (entries 7–11; see Table S1 in the Supporting Information). Control reactions in the absence of the photocatalyst (entry 12), nickel catalyst (entry 13), ligand (entry 14), and light (entry 15) gave no product. The amount of alkene employed may also be reduced (see Table S2).

With the optimized reaction conditions in hand, we first examined the scope of (hetero)aryl bromide coupling partner of this new reaction. As shown in Table 2, a variety of aryl bromides performed well in this cross-coupling protocol. For example, electron-deficient aryl bromides containing ester, ketone, nitrile, aldehyde, and sulfone functional groups were well tolerated (**3a–e**, 56–90% yield). The polycyclic aromatic bromides **1 f** and **1 g** also served as effective coupling partners, but resulted in moderate yields [**3 f** (31%) and **3 g** (54%)]. Substituents in the *meta*-position of the aromatic ring had no apparent effect on the efficiency of the coupling (**3h–k**, 53– 89% yield). Notably, six-membered heteroaromatic substrates performed well in the reaction and the allylic fragment could be installed at different positions (*ortho, meta, para*) of the heteroaromatic ring (**31–o**, 52–76% yield).<sup>[14]</sup>

In an effort to further probe the applicability of this new photoredox nickel dual catalysis, we next turned our attention to explore the feasibility of cross-coupling between 2a and Table 2: Scope with respect to the aryl bromides.<sup>[a,b]</sup>



[a] Standard reaction conditions: aryl bromide 1 (0.2 mmol), **2a** (2 mmol, 10 equiv), [Acr-Mes]ClO<sub>4</sub> **5** (0.01 mmol, 5 mol%), NiCl<sub>2</sub>·glyme (0.02 mmol, 10 mol%), dtbpy (0.03 mmol, 15 mol%), lutidine (0.3 or 0.4 mmol, 1.5 or 2 equiv), DCE (0.4 mL), RT, 24–72 h. [b] Yield after purification.

vinyl bromides **7** under the standard reaction conditions (Table 3). Such a transformation is of great significance considering that it would enable the construction of 1,4-dienes

Table 3: Scope with respect to the vinyl bromides.[a,b,c]



[a] Standard reaction conditions: aryl bromide 7 (0.2 mmol), 2a (2 mmol, 10 equiv), [Acr-Mes]ClO<sub>4</sub> 5 (0.01 mmol, 10 mol%), NiCl<sub>2</sub>·glyme (0.02 mmol, 10 mol%), dtbpy (0.03 mmol, 15 mol%), lutidine (0.3 mmol, 1.5 equiv), DCE (0.4 mL), RT, 12–24 h. [b] Yield after purification. [c] Vinyl bromides were employed as E/Z mixtures (each with 86–93% E isomer).

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("skipped" dienes), prevalent in natural products. Gratifyingly, a number of vinyl bromides were converted into the corresponding 1,4-dienes **8a–f** in good yields (51 to 64%) together with excellent E/Z ratios regardless of the electronic nature of the substituents on the aromatic rings. To the best of our knowledge, these reactions represent the first examples of direct vinylation of allylic C(sp<sup>3</sup>)–H bonds from olefins.

Encouraged by the above results, we next turned our attention to examine the scope of olefin coupling partner. As illustrated in Table 4, a range of tri- and tetrasubstituted alkenes reacted smoothly to afford the desired products 9a-j in acceptable yields (41-71%). Surprisingly, an alkene bearing a-oxy C-H bonds is also tolerated, despite the possible C-H arylation of ethers. The excellent regioselectivities suggest that the Br radical abstraction of primary C-H bonds is favored over methylene and methine C-H bonds. Beyond the regioselectivities, we found that monoarylation adducts are exclusively observed in these cross-coupling studies, indicating the predominant role of steric effects. Consistent with this hypothesis, the presence of a more sterically hindered isopropyl group in 2b completely prevented the H abstraction from the methine group and the neighboring methyl group, affording exclusively 9b. Moreover, excellent stereoselectivity was observed for alkene **2c**, bearing a *tert*-butyl group, as featured in product 9c, which was obtained as the E-isomer only.

*Table 4:* Scope with respect to the alkenes.<sup>[a,b]</sup>



[a] Reaction conditions: aryl bromide **1b** (0.2 mmol), **2** (2 mmol, 10 equiv), [Acr-Mes]ClO<sub>4</sub> **5** (0.02 mmol, 10 mol%), NiCl<sub>2</sub>:glyme (0.02 mmol, 10 mol%), dtbpy (0.03 mmol, 15 mol%), lutidine (0.3 mmol, 1.5 equiv), DCE (0.4 mL), RT, 72 h. [b] Yield after purification. [c] **1n** was used instead of **1b**.

To gain more insight into the mechanism of the reaction, several preliminary studies were carried out. Firstly, the coupling reaction was suppressed significantly when 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO; 1 equiv) was added as radical scavenger, providing the desired product **3b** in 8% yield only. Moreover, the detection of the TME-TEMPO adduct **10** suggests the formation of an allylic radical during the course of the reaction (Scheme 2a). In light of a recent report on benzylic C–H arylation of toluene derivatives by Murakami and co-workers,<sup>[15]</sup> we carried out the reaction with UV irradiation in the absence of a photocatalyst. However, no C–H cross-coupled product was observed, indicating a mechanistically different pathway (Scheme 2b).

a) Radical-trapping experiment with free-radical scavenger.[2]

Br L	PC <b>5</b> (5 mol%) NiCl <sub>2</sub> •glyme (10 mol%) dtbpy (15 mol%)	
	lutidine (1.5 equiv ), DCE TEMPO (1 equiv.) rt, blue LEDs, 24 h	
Substrate 1	Vield of 3 (%)	Vield of <b>10</b> (%)
Substrate 1		
1b	3b, 8	32
10	<b>30</b> , 0	35 (26) <sup>(b)</sup>

b) UV light control experiment.



c) Cross coupling with aryl iodide.(জ

 $R = CO_2 Me$ , 3a, not formed R = Ac, 3b, not formed



**Scheme 2.** Preliminary experiments on the reaction mechanism. [a] Yields were determined by <sup>1</sup>H NMR spectroscopy using 1,3,5trimethoxybenzene as an internal standard. [b] Yield after purification is given within parentheses.

Although we cannot completely rule out a mechanism involving a photocatalytically driven SET oxidation of Ni<sup>II</sup> to Ni<sup>III</sup>, this step is thermodynamically unfavorable considering the generated Mes-Acr-Me<sup>•</sup> ( $E_{12}^{\text{red}} = -0.57 \text{ V}$  vs. SCE) as a weak reducing species. The use of **5** as single-electron oxidant for olefin functionalization is known. However, this mechanism is unlikely because of the inconsistency with the exclusive regioselectivities, as well as the unfavored reduction potential (see the Supporting Information for more details). Although our attempts with aryl chlorides and mesylates turned out to be unsuccessful and only starting materials were

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recovered, the more reactive aryl iodide<sup>[16]</sup> **1p** afforded **3p** in 20% yield. Notably, we were pleased to find out that the reaction efficiency increased dramatically when LiBr was used as bromine additive (Scheme 2c). These results are in good agreement with our hypothesis on hydrogen atom abstraction from allylic  $C(sp^3)$ -H bonds of olefins with the photocatalytically generated bromine radical.

Recent literature reports on photooxygenation reactions have shown that the 9-mesityl-10-methylacridinium salt is capable of generating singlet oxygen with molecular oxygen by triplet energy transfer.<sup>[17]</sup> Based on this, as well as the above described experimental results, a plausible mechanism for the reaction between **1** and **2a** is shown in Scheme 3. The



**Scheme 3.** Proposed mechanism for the coupling of tetramethylethylene (2a) with aryl bromides.

photocatalyst Mes-Acr-Me<sup>+</sup> is converted into the excited species \*Mes-Acr-Me<sup>+</sup> under irradiation with blue LEDs while oxidative addition of Ni<sup>0</sup> to 1 generates the Ni<sup>II</sup>-ArBr species II. Next, triplet-triplet energy transfer can occur between these two species, generating the electronically excited Ni<sup>II</sup>-ArBr species **III** while regenerating the ground state of Mes-Acr-Me<sup>+</sup>. Homolysis of III results in the generation of a bromine radical which can rapidly abstract a hydrogen atom from 2a to form an allylic radical, followed by reaction with the nickel catalyst to deliver the Ni<sup>II</sup> species V. Finally, reductive elimination of V produces the crosscoupled product 3 and regenerates the  $Ni^0$  species I, thus completing the catalytic cycle. Another radical abstraction pathway involving a concerted four-centered transition state might also be possible and cannot be completely ruled out at the current stage.

In conclusion, we have developed a direct regioselective coupling of allylic  $C(sp^3)$ -H bonds with aryl- and vinylbromides enabled by the combination of nickel and photoredox catalysis, which provides an unprecedented method for the construction of allylarenes, as well as 1,4-dienes from unactivated alkenes under very mild reaction conditions. The exclusive preference for primary allylic  $C(sp^3)$ -H bonds can be rationalized by a hydrogen atom abstraction process with photocatalytically generated bromine radical. Investigations regarding the further application of this new method as well as experiments to gain a more detailed understanding of the reaction mechanism are currently part of our research.

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### **Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** alkenes  $\cdot$  allylic compounds  $\cdot$  C–H activation  $\cdot$  nickel  $\cdot$  photocatalysis

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## **Communications**



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Direct Cross-Coupling of Allylic C(sp<sup>3</sup>)-H Bonds with Aryl- and Vinylbromides by Combined Nickel and Visible-Light Catalysis





A bit of nickel and light: A protocol for the direct allylic C(sp<sup>3</sup>)–H bond activation in unactivated tri- and tetrasubstituted alkenes and their reaction with aryl- and vinylbromides by nickel and visible-light

photocatalysis was developed. The method allows  $C(sp^2)-C(sp^3)$  formation under mild reaction conditions, with good functional-group tolerance, and excellent regioselectivity.

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