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Phosphorylation of Alkenyl and Aryl C−O Bonds via Photoredox/Nickel Dual Catalysis

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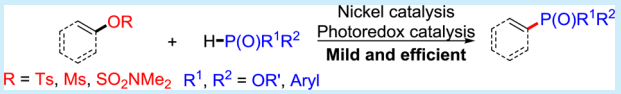
Supporting Information

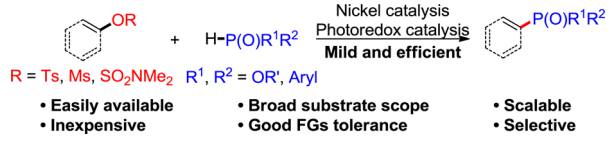
ABSTRACT: A phosphorylation of alkenyl and aryl C−O bonds at room temperature via photoredox/nickel dual catalysis is reported. By starting from easily available and inexpensive sulfonates, a variety of important alkenyl phosphonates and aryl phosphine oxides are generated in moderate to excellent yields. This method features mild reaction conditions, high selectivity, good functional group tolerance, wide substrate scope, and easy scalability.



Organic phosphorus compounds play an important role in organic synthesis, medicinal chemistry, photoelectric materials, and coordinative chemistry.[1] Many methods have been developed to generate such compounds. Traditionally, phosphorylation of organometallic reagents with electrophilic phosphorus reagents is widely used.[2] Since the 1980s, transition metal-catalyzed cross-couplings of organohalides and carboxylic acids with P(O)−H compounds as well as addition of P(O)-H compounds to alkynes have emerged as efficient methods to generate C(sp^2)−P bonds.[3] However, there are still some drawbacks such as high catalyst loading, harsh reaction conditions, and limited substrate scope as well as the use of toxic and expensive organohalides. Therefore, the development of more environmentally friendly methods to produce organic phosphorus compounds is still highly desirable.

Visible-light photoredox catalysis has emerged as a powerful and clean method to realize novel organic transformations via unique single electron transfer (SET) process.[4] Notably, merging photoredox with transition metal catalysis[5,6] shows great potential in the cross coupling of organohalides. As carbonyl-containing compounds and phenols exist widely and are readily available in nature and industry, the easily generated alkenyl and aryl C−O electrophiles are also attractive in such dual catalysis. For example, Molander[6m] and Rueping[6n] independently reported the novel and efficient cross couplings of phenol derivatives with alkyl silicates or amino acids. Besides one nice example of alkylation of enol triflates from Doyle's group,[6o] our group also contributed to this field by realizing the direct couplings of various enol and phenol derivatives with amine or ether C(sp^3)−H bonds.[6p] Although C−O electrophiles shows great potential as environmentally benign electrophiles in such dual catalysis to form carbon−carbon bonds, their application in formation of highly important carbon-heteroatom bonds, including C−P bonds, has not been realized by using this strategy. Herein, we report a novel phosphorylation of alkenyl and aryl C−O bonds via photoredox/nickel dual catalysis (Scheme 1). A variety of easily available and inexpensive sulfonates can be transformed to alkenyl phosphonates and aryl phosphine oxides with high selectivity and efficiency under mild reaction conditions.

Scheme 1. Phosphorylation of C(sp^2)−O Bonds via Photoredox/Nickel Dual Catalysis



When we initiated this project, there were few examples of C−P bond formation from other electrophiles via photoredox/transition metal dual catalysis.[6f,7] For example, Toste reported the reaction with aryl diazonium salts as starting materials via photoredox/gold dual catalysis.[7] In the same year, the Xiao and Lu's group used photoredox/nickel dual catalysis strategy to generate C−P bonds with (hetero)aryl iodides as electrophiles.[6f] Both transformations are efficient; however, no alkenyl C−P bond was formed, and the starting materials could be unstable, toxic, difficult to prepare, and limited in scope. Therefore, the identification of more benign coupling partners is still of great significance in such photochemical C−P bond construction.[8] Inspired by the success in cross coupling reactions via C(sp^2)−O activation,[9] especially the transformation of C(sp^2)−O bonds to C−P bonds,[10] we hypothesized that the mild phosphorylation of inexpensive and readily available enol sulfonates could be realized by merging photoredox and nickel catalysis. This method will provide a facile route to synthesize structurally complicated

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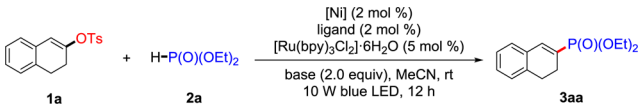
alkenyl phosphorus compounds, which are widely used in organic transformations, and synthesis of drugs and ligands.[11]

With these in mind, we started this project by examining the reactivity of the stable β-tetralone-derived tosylate **1a** and diethyl phosphonate **2a**. After systemic screening, we were happy to obtain the desired alkenyl phosphonate **3aa** in 97% isolated yield with 2 mol % of $Ni(cod)_2$ as the catalyst and 5 mol % of $Ru(bpy)_3Cl_2{\cdot}6H_2O$ as the photocatalyst (Table 1, entry 1). Switching the base to Cs_2CO_3 gave only trace amount of **3aa** (Table 1, entry 2), which indicated the high importance of the base. Moreover, other photocatalysts (please refer to the Supporting Information for more examples), nickel catalysts, and ligands were also tested to give lower yields (Table 1, entries 3−7). The results of control experiments performed in the absence of a photocatalyst, a nickel catalyst, a base, or light demonstrated the essential role of each component in this reaction (Table 1, entries 8−11). To our surprise, the reaction without additional ligand could also generate **3aa** in 96% yield (Table 1, entry 12). However, this finding did not prove to be general for other substrates,[12] and thus, we chose *o*-phenanthroline as the ligand (Table 1, entry 1) to evaluate the full scope of the reaction.

Table 1. Reaction Conditions Optimization[a]



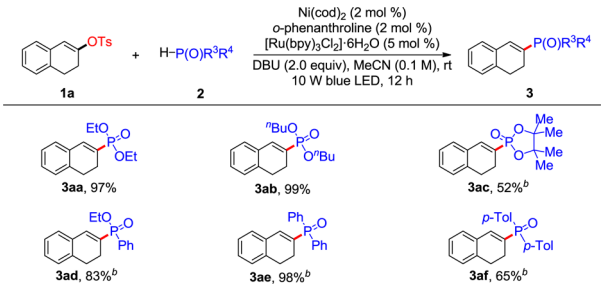
entry	[Ni]	ligand	base	yield (%)[b]
1	**$Ni(cod)_2$**	***o*-phenanthroline**	**DBU**	**97**
2	$Ni(cod)_2$	*o*-phenanthroline	Cs_2CO_3	<5
3[c]	$Ni(cod)_2$	*o*-phenanthroline	DBU	23
4	$Ni(cod)_2$	dtbbpy	DBU	68
5	$Ni(cod)_2$	dppp	DBU	n.d.[f]
6	$Ni(cod)_2$	dppf	DBU	<5
7	$NiCl_2$·dppp	*o*-phenanthroline	DBU	n.d
8	$Ni(cod)_2$	*o*-phenanthroline	–	n.d.
9	–	*o*-phenanthroline	DBU	n.d.
10[d]	$Ni(cod)_2$	*o*-phenanthroline	DBU	trace
11[e]	$Ni(cod)_2$	*o*-phenanthroline	DBU	n.d.
12	$Ni(cod)_2$	–	DBU	96

[a]Alkenyl tosylate **1a** (0.3 mmol), diethyl phosphonate **2a** (0.36 mmol), Ni-catalyst (2 mol %), ligand (2 mol %), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (5 mol %), and base (0.6 mmol) in MeCN (0.1 M). bpy = 2,2′-bipyridine, dtbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyrididyl, cod = 1,5-cyclooctadiene, LED = light-emitting diode. [b]Isolated yield. [c]Eosin B was used as the photocatalyst. [d]No $Ru(bpy)_3Cl_2{\cdot}6H_2O$. [e]No light. [f]n.d., not determined.

With the optimized reaction conditions in hand, we next examined different P-sources (Scheme 2). The catalytic system worked well with hydrogen phosphonates (**2a−c**), a hydrogen phosphinate (**2d**), and phosphine oxides (**2e** and **2f**) to give the desired products in moderate to excellent yields, which showed broad scope and great potential for diverse transformations.

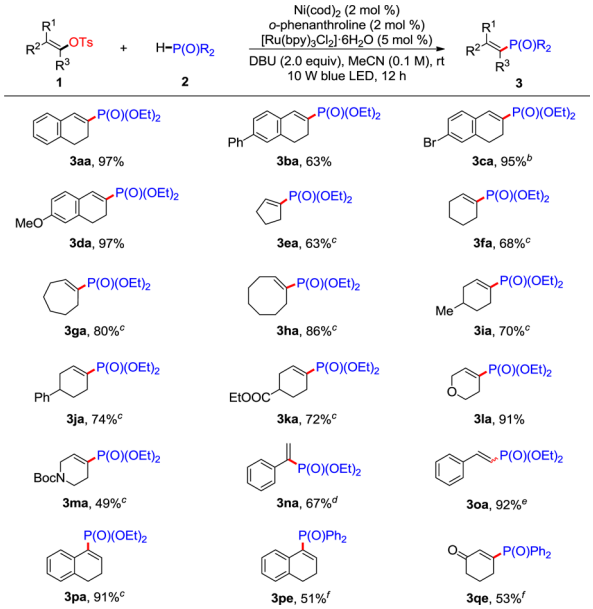
Furthermore, we examined the scope of alkenyl tosylates (Scheme 3). Different substituents on the arenes (**1a−1d**) did not affect the reactions to give the desired products in moderate to excellent yields. The reactions were highly chemoselective, as C−Br[13] and C−OMe[9f,h] bonds, which have been applied as electrophiles in other nickel-catalysis, remained untouched, providing potential for further transformation. Other cyclic enol tosylates with 5−8 membered rings (**1e−1h**) could also undergo the C−P bond formation smoothly. Several cyclohexenyl tosylates with different substituents (**1i−1k**) and other kinds of cyclic enol tosylates (**1l−1m**) could take part in such a reaction to give the corresponding products in moderate to excellent yields. When we tested the reactivity of styrene tosylate **1n**, the desired product **3na** was obtained in 67%, and a trace amount of tetraethyl (1-phenylethane-1,2-diyl)bis(phosphonate) was detected, which might arise from the Michael addition of **2a** to **3na**. It was notable that the reaction of alkenyl tosylate **1o** was highly efficient and steroselective, as the ratio of the product isomers **3oa** was the same as **1o** with full conversion. α-Tetralone derivative **1p** could also generate the desired product **3pa** in high yield. However, the alkenyl tosylates with more steric hindrance (e.g., 1,2,2-triphenylvinyl 4-methylbenzenesulfonate, (*Z*)-1,2-diphenylvinyl 4-methylbenzenesulfonate, and (*Z*)-1,2-diphenylprop-1-en-1-yl 4-methylbenzenesulfonate) gave only trace amount of the corresponding products, which might arise from the difficult oxidative addition. Since phosphine oxides are versatile synthetic intermediates in organic synthesis,[1] we further tested the reactions of **1p** and **1q** with diphenylphosphine oxide **2e** to give the desired products in moderate yields.

Scheme 2. Substrate Scope of P-Sources[a]



[a]Standard reaction conditions as in Table 1, entry 1. [b]Twenty-four hours.

Scheme 3. Substrate Scope of Alkenyl Tosylates[a]



[a]Standard reaction conditions as in Table 1, entry 1. [b]**2a** (0.45 mmol). [c]Twenty-four hours. [d]Instead of *o*-phenanthroline, 2 mol % dtbbpy was used. [e]*E*/*Z* = 2:1. [f]Diphenylphosphine oxide **2e** (0.36 mmol).

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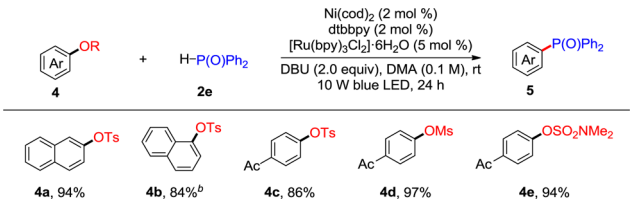
As aryl sulfonates and sulfamates are also readily available from phenols and widely used as inexpensive electrophiles in diverse cross-coupling reactions,[9] we further tested them in such C−P bond formation (Scheme 4) to replace aryl halides

Scheme 4. Substrate Scope of Phenol Derivatives[a]

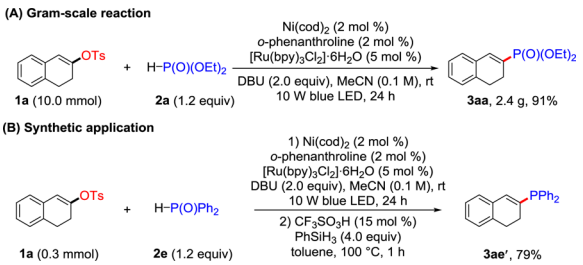


[a]Reaction performed using $Ru(bpy)_3Cl_2·6H_2O$ (5 mol %), diphenylphosphine oxide **2e** (0.36 mmol), phenol derivatives **4** (0.3 mmol), and DBU (0.6 mmol). $Ni(cod)_2$ (2 mol %), dtbbpy (2 mol %), 3 mL of DMA. [b]$Ni(cod)_2$ (5 mol %), *o*-phenanthroline (5 mol %), 3 mL of MeCN.

and diazo salts.[6f,7] To our delight, aryl tosylates (**4a**−**4c**) reacted well with diphenylphosphine oxide **2e** to generate the triarylphosphine oxides **5** in excellent yields with MeCN or *N*,*N*-dimethylacetamide (DMA) as the solvent. Besides tosylates, a mesylate **4d** and a sulfamate **4e** also worked well in this reaction.

After developing the methodology, we further demonstrated its utility. First, the 10 mmol scale reaction of **1a** under the standard reaction conditions gave 2.4 g of the desired product in 91% yield with similar efficiency (Scheme 5A). Second, the

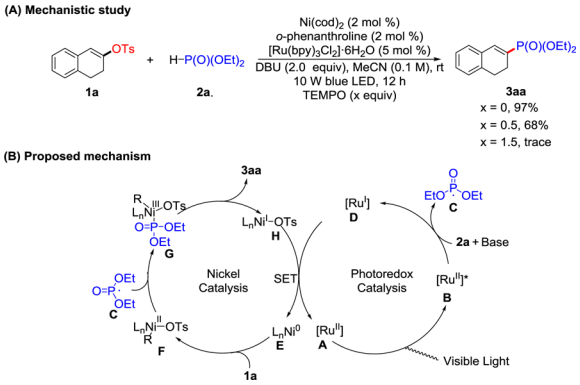
Scheme 5. Gram-Scale Reaction and Application



products could be easily transformed to other derivatives.[14] For example, phosphine oxide **3ae′** could be easily obtained in 79% yield through the phosphorylation of **1a** with **2e** and following facile reduction of the phosphine oxide **3ae** (Scheme 5B).[15]

We next sought to gain insight into reaction mechanism. When 1.5 equiv of 2,2,6,6-tetramethylpiperding-1-oxyl (TEMPO) was added under the standard conditions, a trace amount of desired product **3aa** was detected (Scheme 6A), which demonstrated that the radical might be involved in this system. On the basis of our exploration[6c,p] and previous works,[5−7] we proposed the reaction mechanism for the reaction of **1a** and **2a** (Scheme 6B). First of all, the excited photocatalyst **B** was generated from **A** under visible-light irradiation. The key intermediate, P-centered radical **C**, was generated from **2a** through SET with **B** and following base-promoted deprotonation. Meanwhile, the oxidative addition of the $C(sp^2)$−O bond in tosylate **1a** to a Ni^0 species **E** gave the Ni^{II} intermediate **F**, which rapidly intercepted the P-centered radical **C** to afford the Ni^{III} complex **G**. Further facile reductive elimination delivered the Ni^I complex **H** and desired product **3aa** via $C(sp^2)$−P bond formation. Lastly, both **A** and **E** were regenerated to complete

Scheme 6. Mechanistic Study and Proposed Mechanism



the dual catalytic cycle through reduction of **H** by the reduced form of Ru-photocatalyst **D**. However, we could not exclude the reaction pathway including the addition of **C** to the **E** to give a Ni^I complex and following oxidative addition and reductive elimination.

In summary, we have developed an efficient phosphorylation of alkenyl and aryl C−O bonds via photoredox/nickel dual catalysis. This reaction showed a broad substrate scope, excellent functional group tolerance, and easy scalability, which afforded the alkenyl phosphonates and aryl phosphine oxides in moderate to excellent yields.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b01561.

Experimental procedures, characterization of all products (PDF)

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Notes

The authors declare no competing financial interest.

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