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Visible-Light-Promoted Regio- and Stereoselective Oxyalkenylation of Phosphinyl Allenes

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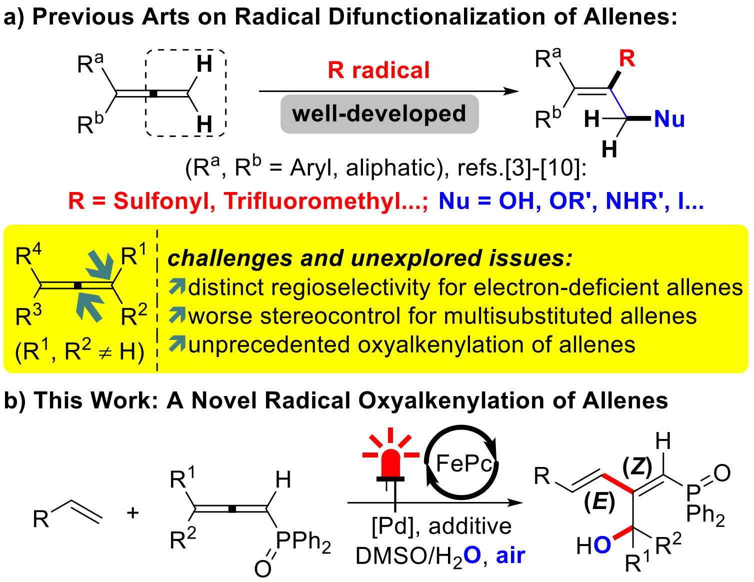
Abstract. A highly regio- and stereoselective oxyalkenylation of phosphinyl allenes is revealed for the first time. This protocol, merging visible light photoredox and palladium catalysis, provides a direct approach to conjugated tertiary allylic alcohol derivatives with broad functional group tolerance in moderate to excellent yields. Mechanistic studies suggest that, although two possible pathways exist in the transformation, radical oxyalkenylation promoted by visible light photoredox takes over the major pathway.

Keywords: Phosphinyl Allenes, Oxyalkenylation, Visible Light, Palladium Catalysis, Conjugated Tertiary Allylic Alcohol derivatives.

Introduction

Allenes are attractive molecules possessing two cumulative carbon-carbon double bonds, which have been served as versatile synthons for constructing bioactive synthetic compounds, naturally-occurring products, as well as optoelectric materials.[1] For the past several decades, various difunctionalizations of allenes have been established as powerful and step-economical approaches to enrich molecular complexity.[2] Apart from well-known electrophilic addition[2a,b] and transition-metal catalysis,[2c,d] radical-based difunctionalization of allenes represents an emerging research topic within recent years, most often furnishing value-added olefins.[3] For an elegant study, in 2012, Ma's group developed a novel intramolecular radical addition/cyclization reactions of allene-enes to afford perfluoroiodinated products.[4] Later on, leading scientists such as Ma,[5] Kanai,[6] Liu,[7] Lei,[8] Akita,[9] as well as others[10] have contributed diverse intermolecular three-component protocols (**Scheme 1a**), named as nitro-oxoamination, oxyarylation, trifluoromethylazidation, trifluoromethylthiocyanation, oxysulfonylation, oxytrifluoromethylation, and so on.

Although much progress has been made in this field, challenges still remain as follows: (1) Due to difficulties in controlling the regio- and stereoselectivity, only a few strategies dealed with electron-deficient and/or multi-substituted allenes. For example, in Lei's work,[8] ester substitutions completely altered the oxysulfonylation pathway to produce terminal alkenes exclusively. Non-terminal di- and tri-substituted allenes bred regioselective adducts but with much lower stereoselectivities.[6],[9] (2) Despite that oxyalkenylation has been reported as a highly efficient protocol to modify alkenes,[11] to the best of our knowledge, oxyalkenylation of allenes has never been documented. This strategy will provide a direct approach to access conjugated tertiary allylic alcohol derivatives, and both the diene and tertiary allylic alcohol moieties can be further used as pivotal synthons.[12] However, construction of linear conjugated π-systems also presents a unique challenge, where each C=C bond needs to be produced in regio- and stereoselective manner.[13] As our continuing interest in radical and allene chemistry,[14] herein, we disclose a highly regio- and stereoselective oxyalkenylation of phosphinyl allenes enabled by merging palladium catalysis and photocatalysis (**Scheme 1b**).

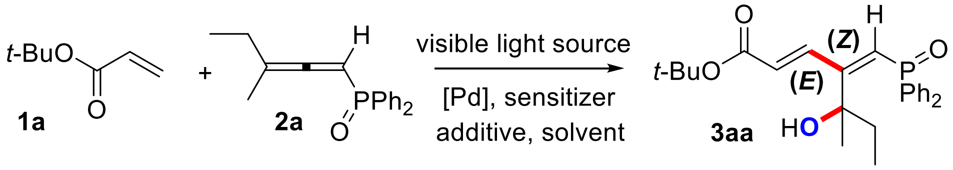


Scheme 1. **(a) Previous Reports on Radical Difunctionalization of Allenes; and (b) This Work.**

Results and Discussion

With *tert*-butyl acrylate (**1a**) and tri-substituted phosphinyl allene (**2a**) as the model substrates, we discovered that, in the absence of photosensitizer, a palladium catalyst itself could give 9% yield of oxyalkenylation adduct (**3aa**, entry 1), with two double bonds determined as (*E*)- and (*Z*)-configurations, respectively. As shown in Table 1, photosensitizer, palladium precursor, solvent and additive played crucial roles in furnishing the final product. A wide range of photocatalysts, including eosin Y, eosin B, $Ru(bpy)_2Cl_2$, and metal phthalocyanine complexes of zinc or copper (ZnPc, CuPc), was found to be less effective, with yields isolated less than 50% (entries 2-6). Phthalocyanine itself might coordinate with palladium salt, thus forming PdPc to enable the catalytic cycle as well (entry 7). Palladium acetate and palladium dichloride independently enabled the oxyalkenylation to some extent (entries 8,9); however, the presence of phosphine ligands gave identical results with a palladium-free condition, where all the substrates remained intact (entries 10-12). Systematical screenings of the conditions were further performed on various solvents and additives. As comparisons, reactions in aqueous THF or DMF conducted better than that of anhydrous solvent (entries 13-15). A successful attempt in entry 16 revealed that the reaction gave the product 3aa in 95% yield under conditions with iron phthalocyanine (FePc) as a photocatalyst, 1-hydroxy-2-oxa-1-ioda(III) indan-3-one (BI-OH) and trifluoro-acetic acid as additives, and DMSO/H_2O as solvents. It's worthy to mention that the utility of appropriate additives and visible-light source is crucial to enhance the efficiency (entries 17-25). Because that most of the metallated phthalocyanines show strong absorption bands in the wavelength region from 600 to 700 nm,[15] red LED irradiation was found to be the most efficient light source. Thus, a highly regio- and stereoselective oxyalkenylation of phosphinyl allenes catalyzed by palladium complex and FePc was achieved to give conjugated tertiary allylic alcohol derivatives.

Table 1. Optimization of Reaction Conditions[a]



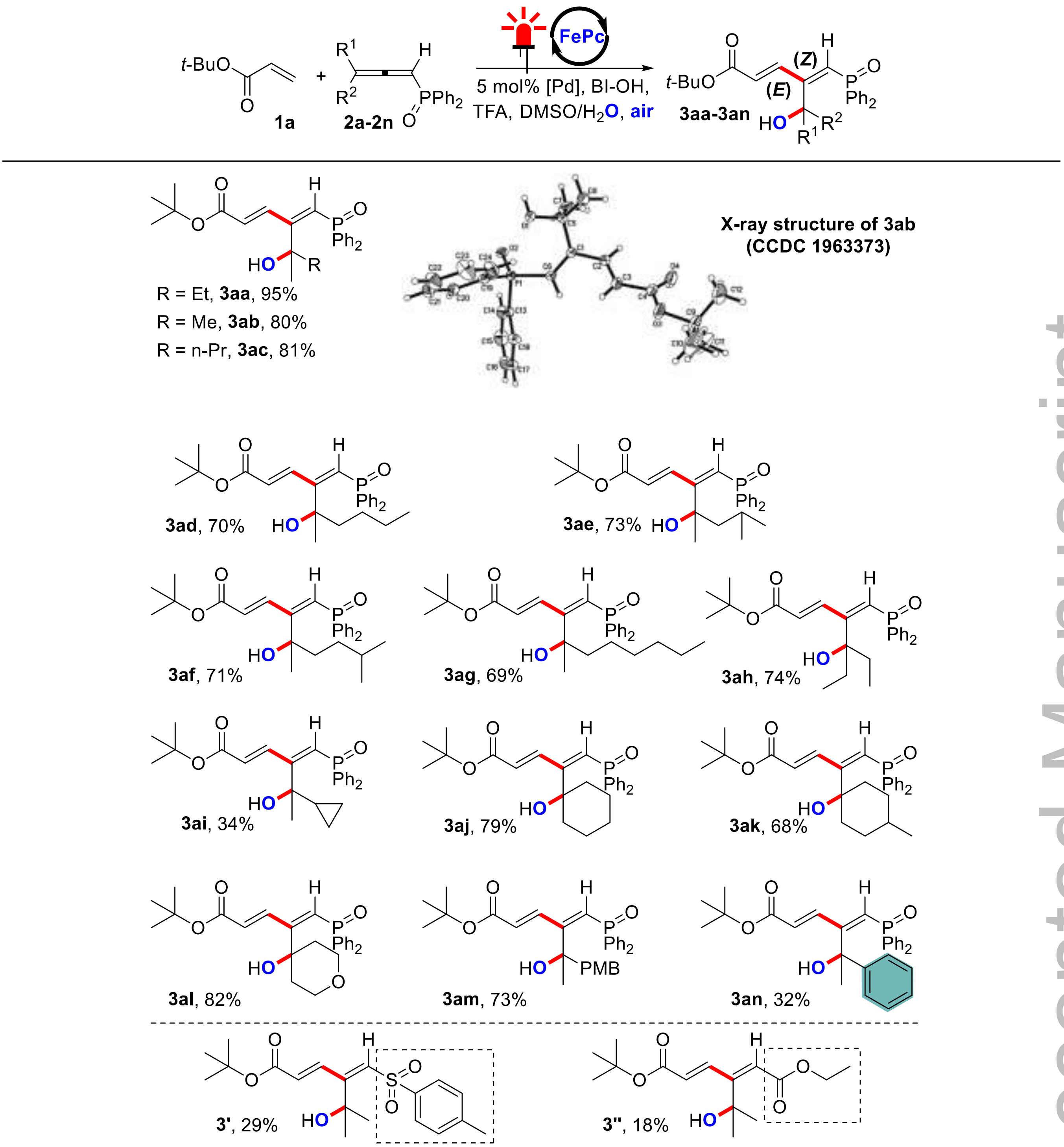
entry	photocatalyst/catalyst	additive/solvent/light source	yield (**3aa**,%)[b]
1	-/$(CF_3COO)_2Pd$	BI-OH+TFA/DMSO:H_2O/54 W red LEDs	9
2	eosin Y/$(CF_3COO)_2Pd$	BI-OH+TFA/DMSO:H_2O/54 W red LEDs	32
3	eosin B/$(CF_3COO)_2Pd$	BI-OH+TFA/DMSO:H_2O/54 W red LEDs	34
4	$Ru(bpy)_2Cl_2$/$(CF_3COO)_2Pd$	BI-OH+TFA/DMSO:H_2O/54 W red LEDs	31
5	ZnPc/$(CF_3COO)_2Pd$	BI-OH+TFA/DMSO:H_2O/54 W red LEDs	48
6	CuPc/$(CF_3COO)_2Pd$	BI-OH+TFA/DMSO:H_2O/54 W red LEDs	22
7	Phthalocyanine/$(CF_3COO)_2Pd$	BI-OH+TFA/DMSO:H_2O/54 W red LEDs	66
8	FePc/$Pd(OAc)_2$	BI-OH+TFA/DMSO:H_2O/54 W red LEDs	64
9	FePc/$PdCl_2$	BI-OH+TFA/DMSO:H_2O/54 W red LEDs	24
10	FePc/$Pd(PPh_3)_4$	BI-OH+TFA/DMSO:H_2O/54 W red LEDs	N.R.
11	FePc/$Pd(PPh_3)_2Cl_2$	BI-OH+TFA/DMSO:H_2O/54 W red LEDs	N.R.
12	FePc/-	BI-OH+TFA/DMSO:H_2O/54 W red LEDs	N.R.
13	FePc/$(CF_3COO)_2Pd$	BI-OH+TFA/anhydrous DMSO/54 W red LEDs	trace
14	FePc/$(CF_3COO)_2Pd$	BI-OH+TFA/THF:H_2O/54 W red LEDs	40
15	FePc/$(CF_3COO)_2Pd$	BI-OH+TFA/DMF:H_2O/54 W red LEDs	30
16	FePc/$(CF_3COO)_2Pd$	BI-OH+TFA/DMSO:H_2O/54 W red LEDs	**95**
17	FePc/$(CF_3COO)_2Pd$	BI-OH/DMSO:H_2O/54 W red LEDs	70
18	FePc/$(CF_3COO)_2Pd$	TFA/DMSO:H_2O/54 W red LEDs	55
19	FePc/$(CF_3COO)_2Pd$	TBHP/DMSO:H_2O/54 W red LEDs	trace
20	FePc/$(CF_3COO)_2Pd$	DTBP/DMSO:H_2O/54 W red LEDs	25
21	FePc/$(CF_3COO)_2Pd$	H_2O_2/DMSO:H_2O/54 W red LEDs	17
22	FePc/$(CF_3COO)_2Pd$	BI-OH+TFA/DMSO:H_2O/15 W red LEDs	26
23	FePc/$(CF_3COO)_2Pd$ s	BI-OH+TFA/DMSO:H_2O/white LEDs	29
24	FePc/$(CF_3COO)_2Pd$	BI-OH+TFA/DMSO:H_2O/green LEDs	39
25	FePc/$(CF_3COO)_2Pd$	BI-OH+TFA/DMSO:H_2O/ sunlight	14

[a] Standard conditions: *tert*-butyl acrylate (**1a**, 0.4 mmol), phosphinyl allene (**2a**, 0.2 mmol), iron phthalocyanine (FePc, 5 mol%), $(CF_3COO)_2Pd$ (5 mol%), BI-OH (0.2 mmol), trifluoroacetic acid (TFA, 0.4 mmol), DMSO:H_2O (2 mL, v/v=1:1), irradiated by 54 W Red LEDs under air at 25 ºC for 48 hours;

[b] Isolated yield, N.R. = no reaction.

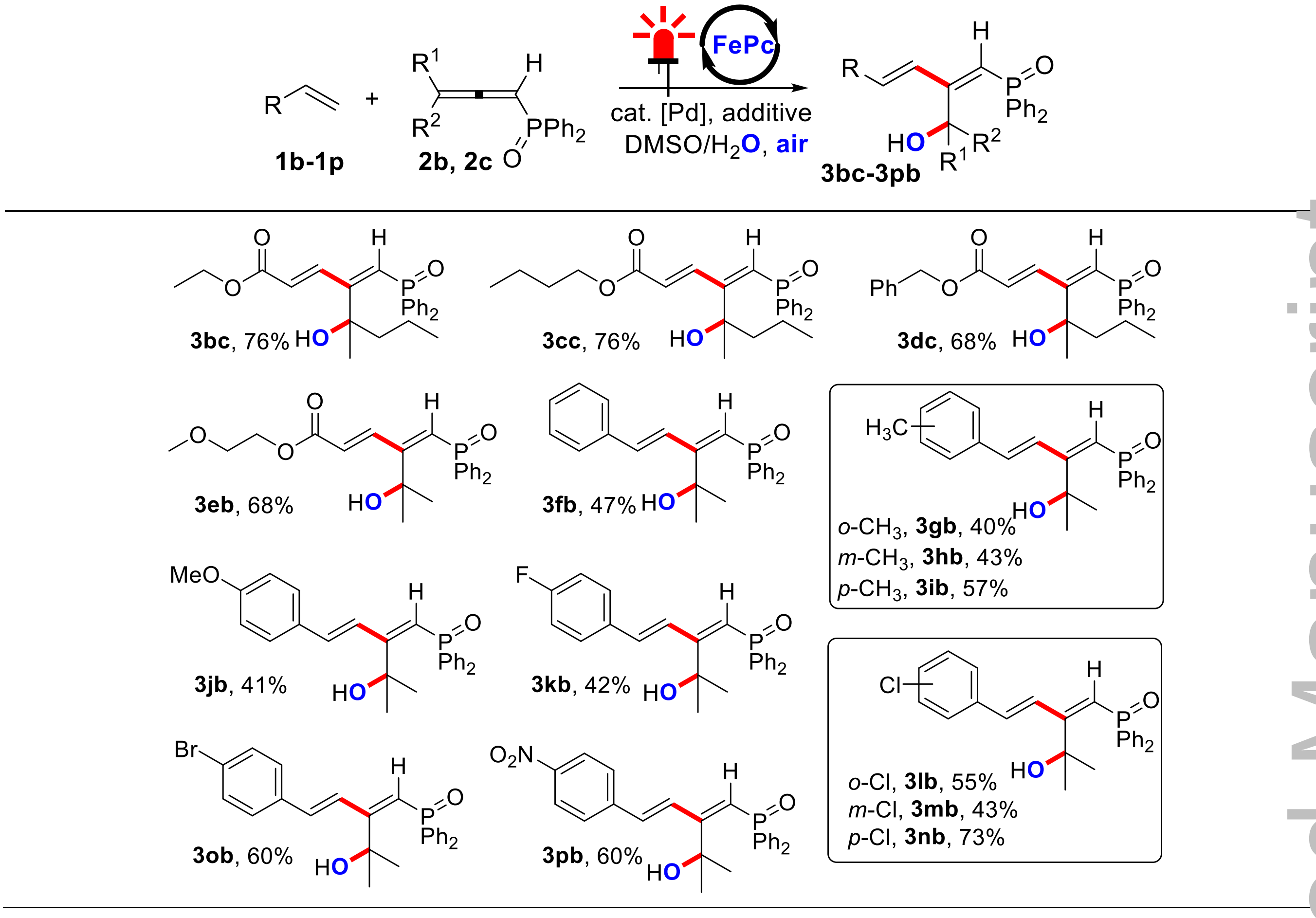
After establishing the optimized reaction conditions, we turned our attention to investigate the scope of phosphinyl allenes by employing *tert*-butyl acrylate **1a** as the substrate, as illustrated in **Scheme 2**. Generally, phosphinyl allenes bearing alkyl, cyclic and heterocyclic substitutions afforded the corresponding adducts in moderate to excellent yields. Substrates with acyclic aliphatic substitutions including methyl, ethyl, *n*-propyl, *n*-butyl, *i*-butyl, *i*-pentyl, and *n*-hexyl (**2a-2h**) performed smoothly in the process, albeit long chain substituents partly impaired the reaction efficiency probably due to blocking effect. Moreover, the correct stereochemistry of molecule **3ab** was verified by X-ray crystallography (CCDC 1963373). Substrates bearing distal alicyclic and heterocyclic groups were amenable to the system, and the desired products were obtained as well in yields ranging from 68% to 82% (**3aj-3al**), with an exception for compound **3ai**. To be noted, low yield of **3ai** might be ascribed to steric hindrance since no ring-opening by-product was detected and most of the substrate **2i** were left unreacted. The phenomena also appeared while expanding the substituent to aromatics. Allene with an endmost *p*-methoxy-benzyl (PMB) group underwent oxyalkenylation rather smoothly to deliver 73% yield of **3am**; unfortunately, phenyl group (**2n**) gave only lower yield of 32% even after attempted screenings. To our delight, *p*-tosyl and ester derivated allenes could also be converted into conjugated allylic alcohol derivatives (**3′** and **3″**), though the reaction efficiency decreased considerably.

Scheme 2. Substrates Scope on Phosphinyl Allenes.



With the aim of broadening the scope of this protocol, thereafter, general applicability of other olefins was investigated (**Scheme 3**). In addition to *tert*-butyl acrylate, several acrylates were found to be applicable to the system with good yields ranging from 68% to 76% (**3bc-3dc**, **3eb**). However, when it came to styrene derivatives, the yields dramatically decreased to less than 20% owing to the rapid dimerization of styrene derivatives upon treatment with trifluoroacetic acid.[16] To our delight, the transformation performed smoothly without adding TFA, but higher loadings of catalysts were necessary. Thereafter, a variety of styrene derivatives were applied, the corresponding hydroxyl alkenyl adducts were furnished smoothly. When changing the substituents of olefins, it was concluded that both electron-donating (such as methyl and methoxy, **1g-1j**) and electron withdrawing groups (such as F and Cl, **1k-1n**) on the phenyl ring were well tolerated, giving the corresponding products in moderate yields. In general, substrates bearing substitutions on *meta*-positions or *ortho*-positions also proceeded efficiently albeit affording comparatively lower yields compared with *para*-positions in yields ranged from 40% to 55% (compounds **3gb-3ib**, and **3lb-3nb**). It is worthy to mention that reactive bromide group survived under the palladium catalysis conditions and transformed into **3ob** in 60% yield. And nitro group, a well-known notorious radical inhibiting unit, did not demolish the reaction process, producing **3pb** with 60% yield. Non-terminal acrylates and styrene derivatives, unactivated olefins, and terminal alkynes were not suitable substrates for this protocol.

Scheme 3. Substrates Scope on Olefins[a],[b]

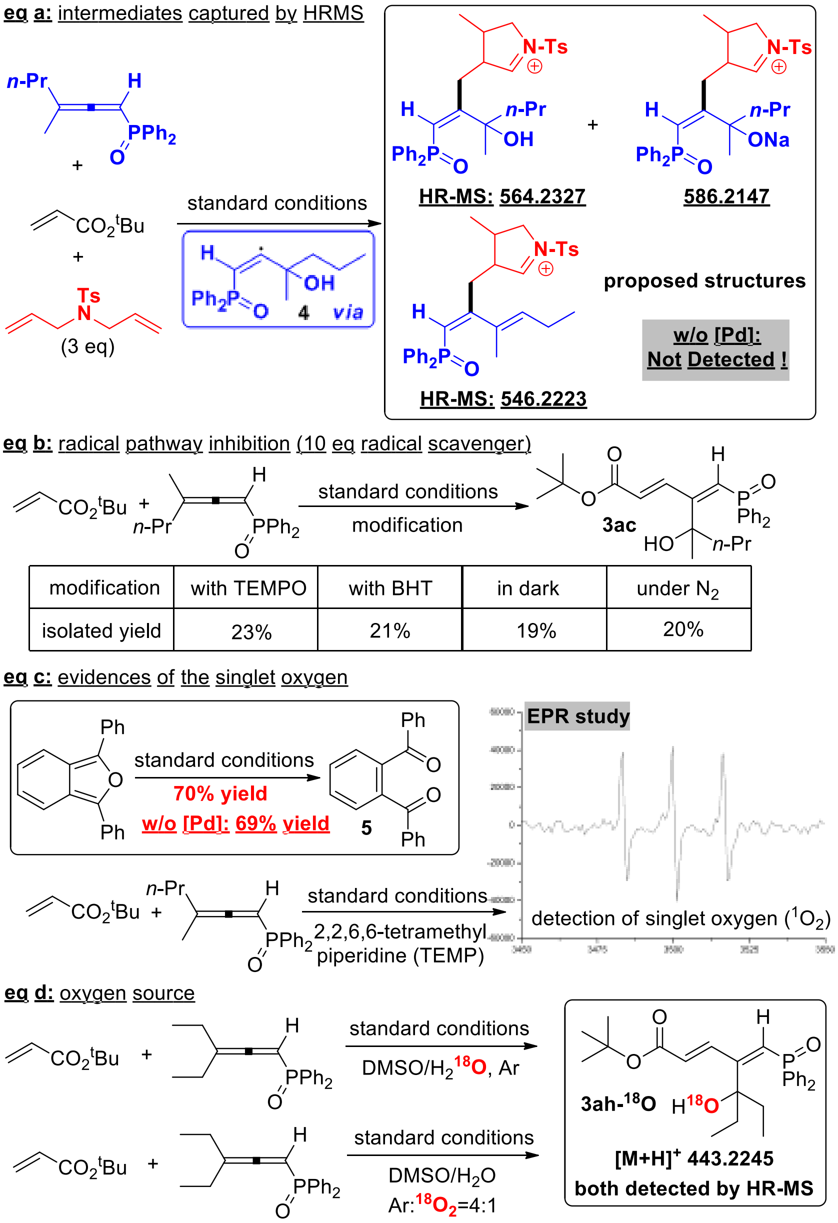


[a] Condition for **1b-1e**: standard conditions; Condition for **1f-1p**: styrene derivative (**1**, 1 mmol), phosphinyl allene (**2**, 0.2 mmol), iron phthalocyanine (FePc, 10 mol%), $(CF_3COO)_2Pd$ (10 mol%), BI-OH (0.2 mmol), DMSO:H_2O (2 mL, v/v=1:1), irradiated by 54 W Red LEDs under air at 25 °C for 48 hours.

[b] Isolated yield.

In order to investigate the reaction mechanism, several control experiments and intermediate capture experiments were designed and performed (**Scheme 4**). With the addition of tosylated diallylamine under standard conditions, an alkenyl radical intermediate (**4**) was captured and the resulting adducts were detected by HR-MS (**eq a**, see details in the Supporting Information). Notably, in the absence of palladium catalyst, the intermediate **4** would not be produced. Radical inhibition experiments, as described in **eq b**, strongly suggested that a non-radical pathway might exist since large amounts of scavengers (TEMPO or BHT) and reaction in dark did not entirely cease the process, affording product **3ac** in similar yields around 20%. The isolation of certain product under oxygen-free condition (N_2 atmosphere) indicated that the non-radical pathway may proceed with molecular water as a source of the hydroxyl group. Taking into account that metal phthalocyanine complexes under irradiation are well-known to produce singlet oxygen,[17] we con-ducted a trap experiment with 1,3-diphenyl-isobenzofuran and an EPR study. Both results confirmed the existence of singlet oxygen, moreover, palladium catalyst was proven to be irrelative with generating singlet oxygen (**eq c**). Although singlet oxygen has been well-documented as highly active species in attacking terminal double bonds to generate peroxide and then reduced to hydroxyl group,[18] this pathway might not occur under current circumstances, otherwise, the intermediate **4** should not be detected and all the reactions performed smoothly under palladium-free conditions. Based on the above experimental observations, palladium complex might play dual roles in the step of producing hydroxyl radical and serving as metal catalyst in the non-radical pathway. To determine the origin of the oxygen atom, ^{18}O-labeling experiments were conducted with isotopic H_2O and oxygen, respectively (**eq d**). Interestingly, ^{18}O-labelled product (**3ah-^{18}O**) was detected in both reactions, which could be ascribed to rapid atom exchange between the hydroxyl radical and water molecules. In other words, the oxygen atom derived from both molecular oxygen and water.

Scheme 4. Mechanism Studies.

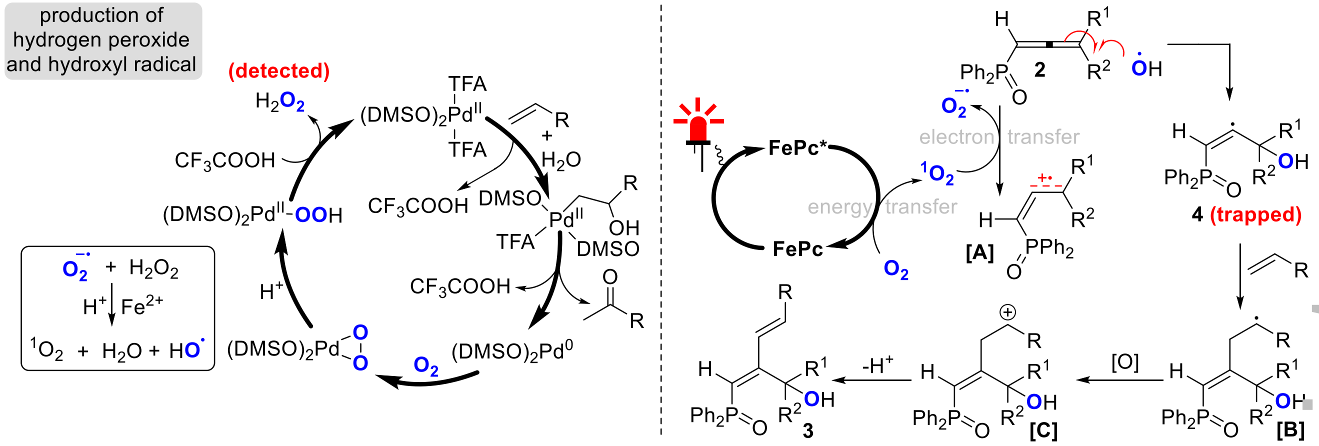


modification	with TEMPO	with BHT	in dark	under N_2
isolated yield	23%	21%	19%	20%

Though the overall mechanism of oxy-alkenylation are not very clear at present, we propose a possible catalytic cycle on the major pathway (**Scheme 5**), according to experimental facts, our previous work[14d] and literature reports.[19] On one hand, palladium (II) complex catalyzes an oxidative coupling of terminal alkene **1** and water, followed by β-hydride elimination to produce Pd^0 catalyst (Wacker-type oxidation).[19c],[20] Subsequent aerobic oxidation of Pd^0 leads to the formation of a peroxo-palladium (II) complex. This molecule reacts with Brønsted acid to release hydrogen peroxide and regenerate the palladium (II) catalyst.[19a,b] On the other hand, the photocatalyst, iron phthalocyanine (denoted as **FePc**), is activated by visible light to give an excited state **FePc***. An energy transfer occurs between **FePc*** and oxygen to form a singlet oxygen species and close the cycle.[21] The singlet oxygen abstracts an electron from phosphinyl allene **2** to produce a radical cation **[A]** and an oxygen radical anion.[14d] Subsequently, the oxygen radical anion reacts with *in-situ* generated hydrogen peroxide, namely Haber-Weiss reaction,[22] yielding singlet oxygen, hydroxyl anion and hydroxyl radical. The resulting hydroxyl radical attacks the allenic terminus to furnish the key alkenyl radical intermediate **4**, which then adds to substrate **1** delivering intermediate

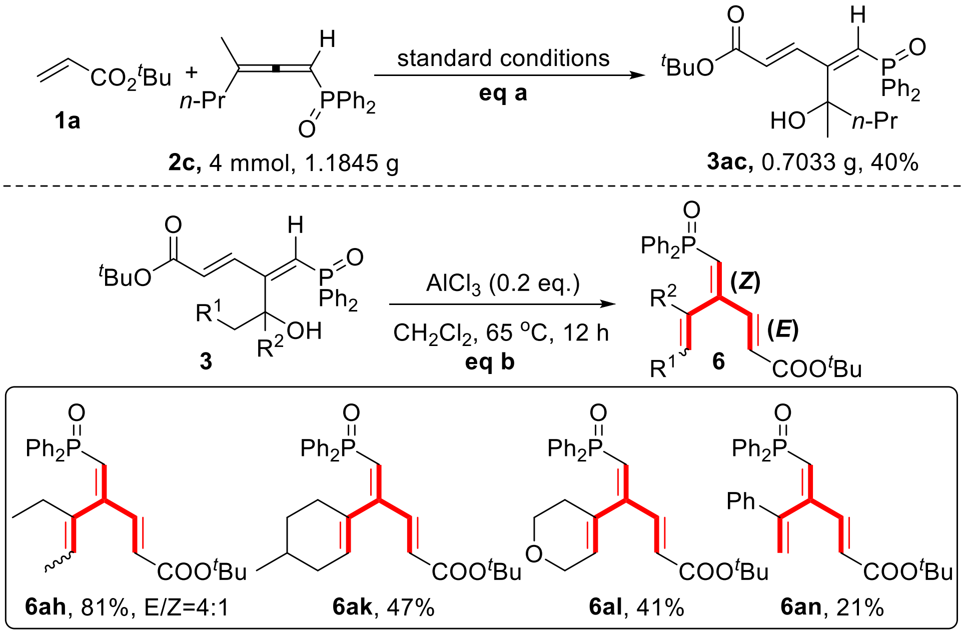
[B]. Sequential radical oxidation of **[B]** and proton elimination finalizes the reaction process. The additives of BI-OH and trifluoroacetic acid are believed to enhancing the efficiency of generated hydroxyl radical thus accelerating the reaction rate.[14d]

Scheme 5. Proposed Mechanism.



The protocol could be scaled up to at least a gram-scale, furnishing the corresponding product (**3ac**) in 40% yield (**Scheme 6**, **eq a**). Additionally, upon the treatment of catalytic amount of aluminium chloride (**eq b**), the conjugated allylic alcohols dehydrated to form new series of stereoselective phosphinyl [3]dendralenes, which provides a novel strategy to build multi-substituted dendralenes.[14a],[14c],[23]

Scheme 6. Gram-scale Synthesis and Applications.



Conclusion

In conclusion, we developed an unprecedented oxyalkenylation of phosphinyl allenes. Merging visible light photoredox with palladium catalysis, this protocol offers a straightforward approach to access conjugated tertiary allylic alcohols with broad functional group tolerance, as well as high regio- and stereoselectivity. Synthetic application of the products could be extended to building stereoselective [3]dendralenes. This strategy features mild reaction conditions, operational simplicity, high chemoselectivity, and expands the portfolios of radical and allenes chemistry.

Experimental Section

Typical Procedures for the Visible-Light-Promoted Oxyalkenylation of Phosphinyl Allenes. To a 10 mL tube was added *tert*-butyl acrylate (**1a**, 0.4 mmol, 51.3 mg), phosphinyl allene (**2a**, 0.2 mmol, 56.4 mg), iron phthalocyanine (FePc, 0.01 mmol, 5.7 mg), $(CF_3COO)_2Pd$ (0.01 mmol, 3.3 mg), 1-hydroxy-2-oxa-1-ioda(III) indan-3-

one (BI-OH, 0.2 mmol, 52.8 mg), trifuoroacetic acid (TFA, 0.4 mmol, 45.6 mg), DMSO/H$_2$O (2 mL, v/v=1:1), irradiated by 54 W Red LEDs under air at 25 ºC for 48 hours. The resulting mixture was diluted with ethyl acetate and washed with brine. The combined organic layer was collected and concentrated. The resulting residue was purified by column chromatography (eluent: 1:2 (v/v) of ethyl acetate/petroleum ether) to afford product **3aa** (80.7 mg, 95% yield) as a white solid, *m.p.*: 122.7-124.0 °C. TLC (R$_f$ = 0.35, petroleum ether/ethyl acetate = 2:1). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.76-7.69 (m, 4H), 7.55-7.43 (m, 6H), 7.31 (d, J = 14.4 Hz, 1H), 6.30-6.19 (m, 2H), 6.10 (d, J = 15.3 Hz, 1H), 1.81-1.63 (m, 2H), 1.50 (s, 9H), 1.42 (s, 3H), 0.88 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 167.3, 165.2, 144.0 (d, J = 17.3 Hz), 134.2, 133.1, 131.8, 131.8, 131.1 (d, J = 3.5 Hz), 131.0 (d, J = 3.5 Hz), 128.7 (d, J = 7.1 Hz), 128.6 (d, J = 7.1 Hz), 124.7 (d, J = 1.2 Hz), 119.2 (d, J = 100.3 Hz), 81.3, 76.0 (d, J = 4.7 Hz), 34.5, 28.1, 27.9 (d, J = 0.8 Hz), 8.0. **^{31}P NMR** (162 MHz, CDCl$_3$) δ 26.75 (s). **HRMS** (ESI): ([M+H]$^+$) Calcd for C$_{25}$H$_{32}$O$_4$P$^+$: 427.2033, Found: 427.2029. **IR** (film) v 3353, 3053, 2977, 2942, 2921, 2854, 1708, 1627, 1581, 1436, 1366, 1283, 1251, 1159, 964, 926, 843, 814, 748, 694, 619 cm^{-1}. (CCDC number for compound **3ab**: 1963373).

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FULL PAPER

Visible-Light-Promoted Regio- and Stereoselective Oxyalkenylation of Phosphinyl Allenes

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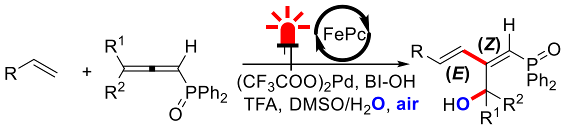

- Unprecedented Three-Component Oxyalkenylation of Allenes
- Highly regioselective and stereoselective process
- 31 examples, yield up to 95%