# Photoredox-catalyzed *α*-Scission *vs* *β*-Scission of $PR_3$-OH Radicals: Synthetic Utilizations and Mechanistic Studies

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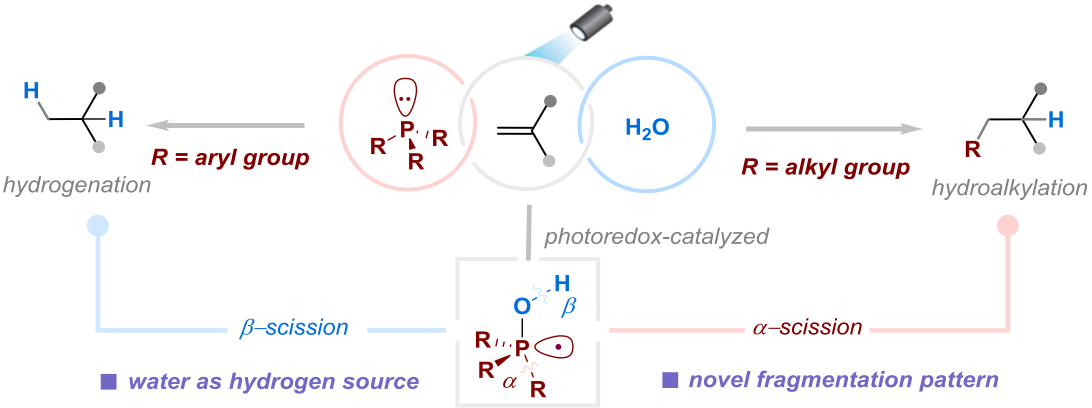


**Abstract:** Photoinduced generation of phosphoranyl radicals offers a versatile strategy to access a variety of synthetically valuable radicals, which has opened exciting new opportunities for radical manipulations and synthetic chemistry. While *β*-scission mode of phosphoranyl radicals has been intensively studied and broadly utilized *via* deoxygenation or desulfurization processes, a long-standing challenge still remains in the regulation of phosphoranyl radical to undergo *α*-scission pathway by overcoming the inherent driving force to generate the stable phosphine oxide *via* *β*-scission, which has been largely unexplored and rarely applied. We herein developed an unprecedented protocol to switch the fragmentation patterns between *α*- and *β*- scission of the generated phosphoranyl radicals under photocatalytic conditions. The success of our strategy presumably relies on finely tuning the reactivity of the crucial P(OH)$R_3$ radical by altering the R substituents, and this P(OH)$R_3$ radical intermediate is ultimately from water and tertiary phosphine reagent. Notably, the synthetic utility of both fragmentation patterns of the $P(OH)R_3$ radical were well demonstrated *via* selective hydroalkylation or hydrogenation transformations of alkenes. A combination of experimental and computational studies was carried out to understand the reaction mechanisms.

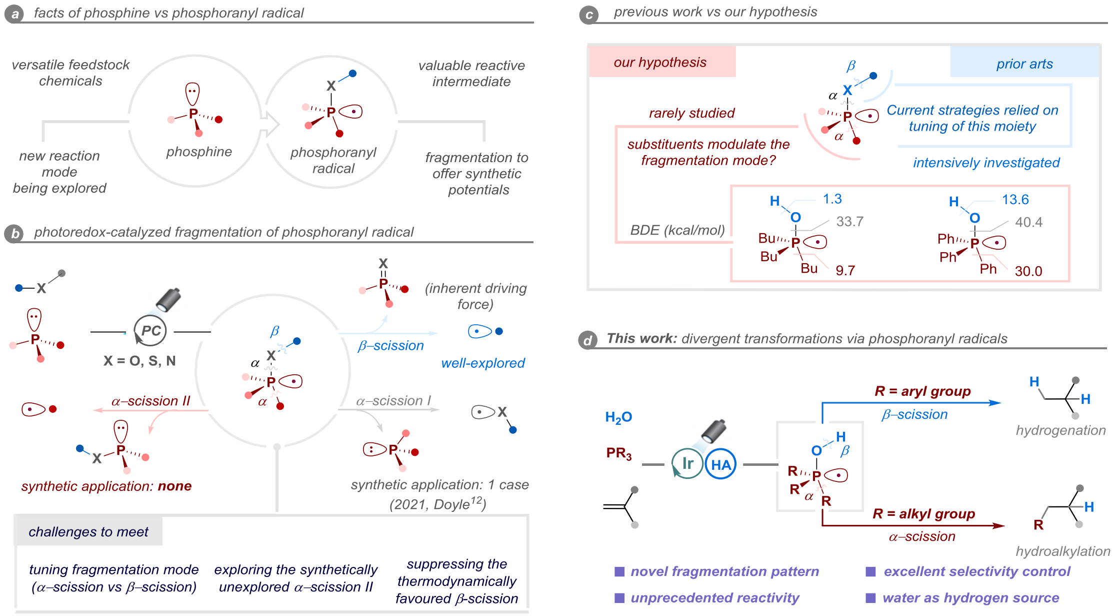
## 1. Introduction

Radical-mediated transformations have been playing a vital role in synthetic chemistry, progressively offering a wide array of innovated pathways and tools for the construction of chemical bonds and introduction of functionalities.[1] Over recent years, phosphine-mediated radical chemistry has emerged as a vibrant and active area of research, and especially the homolytic fragmentation of phosphine-derived species has garnered significant interests.[2] While it is well documented that exergonic conversion of trivalent P(III) phosphorus compounds leads to the corresponding phosphine oxides,[3] phosphoranyl radicals, with appreciable lifetimes, were able to be effectively accessed through the P(III) phosphine feedstocks *via* a well-designed electron-transfer process.[4] In this context, the utilization of readily available P(III) phosphine feedstocks was reasonably broadened through exploiting new reaction mode for phosphine species in the generation of phosphoranyl radicals, whereas phosphoranyl radicals serve as a crucial and versatile intermediate to enable the innovated reaction pathway otherwise challenging to access (Scheme 1a).[5] Historically, phosphoranyl radicals were commonly generated through radical addition to P(III) phosphorus compound.[6] Back to the late 1950s, phosphoranyl radicals were first proposed as intermediates.[7] Later, Bentrude and Roberts extensively investigated the chemistry of phosphoranyl radicals and disclosed the occurrence of both displacement ($\alpha$-scission) and oxidation ($\beta$-scission) pathways theoretically and experimentally, which enriched the phosphine-mediated racial chemistry and offered new synthetic opportunities and potentials for synthetic chemistry.[8] While substantial studies have been dedicated to thoroughly identifying and characterizing phosphoranyl radical intermediates, their practical synthetic utilization is still highly desirable and needs sufficient attentions, especially for challenging and elusive $\alpha$-scission.

During the past decade, photochemistry has experienced an astounding renaissance, mainly attributed to the accessibility of mild methods for visible light-driven radical generation. Through this innovative chemical platform, highly reactive radical intermediates could often be readily accessible *via* a direct single-electron transfer between the excited photoredox catalyst and organic substrates.[9] In this context, the photoredox catalysis of phosphine has thus evolved to be a powerful tool for delivering phosphoranyl radicals under mild conditions.[10] Driven by forming the stoichiometric phosphine oxide byproduct in the deoxygenation processes, $\beta$-scission is usually thermodynamically much more favored than $\alpha$-scission.[11] By contrast, whereas synthetic application through $\alpha$-scission pathway has still remained extremely scarce (Scheme 1b). In 2021, Doyle utilized the homolytic cleavage of P-N bond *via* $\alpha$-scission to realize *anti*-Markovnikov hydroamination of olefins with primary sulfonamides.[12] Mechanistic studies suggested the $\beta$-scission of the phosphoranyl radical was possibly kinetically suppressed due to the facile cleavage of P-N bond in the process to achieve a formal single-electron transfer from sulfonamide to tricyclohexylphosphine radical cation. Unfortunately, the $\alpha$-scission pattern through cleavage of the P-C bond in the visible-light-promoted phosphoranyl radical intermediate still remained synthetically unexplored and undisclosed, and the hidden reactivity awaits practical utility, further broadening the chemical space of phosphine chemistry.

Prior studies illustrated the competitions between displacement ($\alpha$-scission II) and oxidation ($\beta$-scission) pathways in $P(X\text{-}R')R_3$ radical are determined by variants in the relative bond strengths of the R'-X and P-R bonds,[13, 8c] which could be tuned by altering the nucleophiles and R substitutes in phosphines. We questioned that fine-tuning the substituents of phosphine in the rationally designed photocatalytic transformations would effectively modulate the reaction pathways, leading to unveil the synthetic utilization of previously inaccessible fragmentation of phosphoranyl radicals and solving the long-standing puzzle for the hidden $\alpha$-scission II of phosphoranyl radical. Considering that the strength of O-H bond usually is stronger than that of O-C bond,[14] $\beta$-scission in $P(O\text{-}R')R_3$ radical could possibly be suppressed if meanwhile decreasing the strength of P-C bond. For the nucleophiles, water, instead of widely studied alcohols and carboxylic acids, was considered in this work. As early as 1991, Pandey and co-workers proposed the formation of P(OH)Ph$_3$ radical from triphenyl phosphine radical cation and water.[15] For the R substituents in P(OH)R$_3$ intermediate, preliminary computational studies on the bond dissociation energy (BDE) suggest that distinct BDE difference for the P-C bond in alkyl and aryl phosphine (9.7 kcal/mol *vs* 30.0 kal/mol), might provide ample room for tuning fragmentation modes in the designed transformations (Scheme 1c). Following the rationale, we here disclose a photocatalyzed hydroalkylation of olefins with trialkylphosphine and water, presumably *via* the unprecedented $\alpha$-scission of $^{\bullet}$PR$_3$(OH) radical intermediate. Moreover, this process could be facilely switched to $\beta$-scission of $^{\bullet}$PR$_3$(OH) simply by using triphenylphosphine instead of trialkylphosphine, allowing for selective hydrogenation of alkenes with water as hydrogen source (Scheme 1d). It is worth noting that, during the preparation of our manuscript, Studer and co-workers also reported photocatalytic phosphine-mediated water activation for olefin hydrogenation with the assistance of thiols as HAT catalyst, and P(OH)Ar$_3$ radical was supposed to be a key intermediate to transfer one hydrogen atom to alkenes via $\beta$-scission mode.[16]

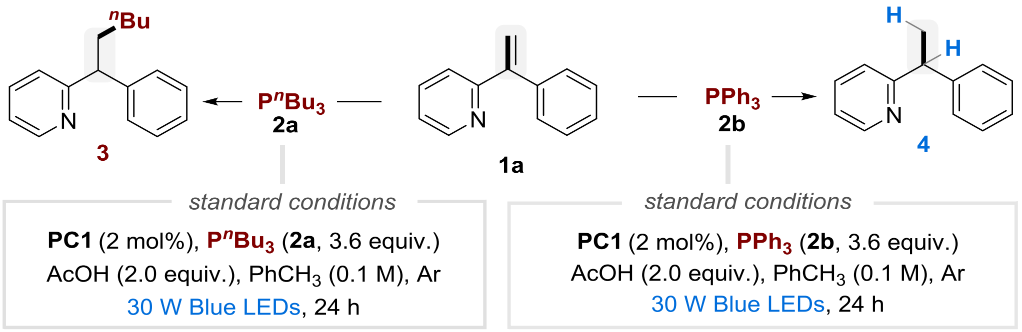
**Scheme 1.** Current status for photoredox-catalyzed phosphoranyl radical transformations and this work.



## 2. Results & Discussion

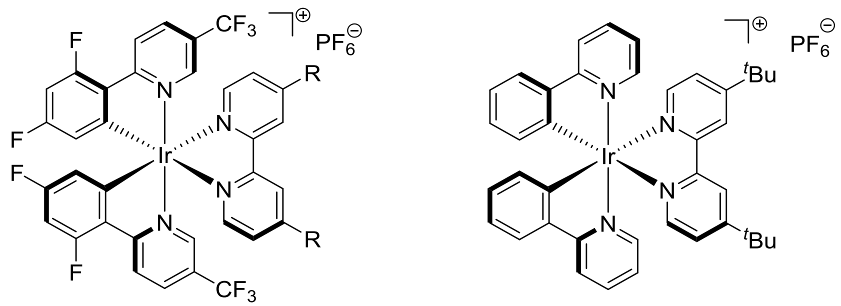
Initially, we tried to validate our hypothesis by employing 2-(1-phenylvinyl)pyridine (**1a**) as the model substrate. $P^nBu_3$ and $PPh_3$ served as representative P(III) species. Interestingly, in the case of $P^nBu_3$, only the hydroalkylation product **3** was obtained in 70% yield, whereas only the hydrogenated product **4** was achieved in 97% yield by using $PPh_3$ under the exactly same reaction conditions (irradiation of 30 W blue LEDs in toluene ($PhCH_3$) with 2 mol% $\{Ir[dF(CF_3)ppy]_2dtbbpy\}PF_6$ (**PC1**) as photocatalyst and 2.0 equivalent glacial acetic acid as acidic additive). At this stage, we were encouraged by these preliminary results as the hydroalkylation and hydrogenated products were supposed to be derived from $\alpha$-scission and $\beta$-scission of $^{\bullet}PR_3(OH)$ radical intermediate respectively, possibly generated from water with P(III) species. It is worth noting that the water was not externally added in these designed processes as glacial acid and regular solvent were presumed to contain sufficient water for these transformations. As expected, it can be rationalized that the structural features of substituents on phosphine would significantly affect the fragmentation modes of the phosphoranyl radical. Thereafter, extensive screening of stoichiometric ratios, photocatalysts, solvents, and additives were conducted to optimize the reaction conditions to promote their synthetic utilizations (see more details in Table S1-9). For example, screening of other photocatalysts, including $\{Ir[dF(CF_3)ppy]_2(4,4'\text{-}CF_3bpy)\}PF_6$ (**PC2**) and $[Ir(dtbbpy)(ppy)_2]PF_6$ (**PC3**), suggested that **PC1** was still the optimal choice. In addition, switching the solvent to DMF and MeCN led to lower yields for **3**, but little effect on the yield of product **4**. Different from Studer's work,[16] AcOH played a vital role in the hydrogenation transformation, while HAT catalyst like thiol was not requisite, which indicated possibly different pathways were involved. To be noted, the desired transformation was suppressed in the presence of a strong acid like $CF_3CO_2H$. Interestingly, a slightly improved yield (75%) was obtained for product **3** upon lowering the loading of AcOH to 0.5 equiv., whereas the reaction for generating product **4** was almost fully suppressed. Considering water is critical to this transformation, 0.15 mL of water was added to the reaction system, but the yield for products **3** and **4** were slightly lowered respectively. Furthermore, an inert atmosphere was proven beneficial to this transformation, as the yield decreased to 50% for **3** and 32% for **4** respectively under air atmosphere. Finally, control experiments indicated both light and photocatalyst are requisite to promote the desirable conversions.

**Table 1.** Identification of the optimal conditions for hydroalkylation and hydrogenation of alkene.[a]



| **3** *(yield, %)* | *Variation from standard conditions* | **4** *(yield, %)* |
|---|---|---|
| 70 | *None* | **97** |
| 43 | ***PC2** instead of **PC1*** | 39 |
| 45 | ***PC3** instead of **PC1*** | 32 |
| 59 | *DMF instead of* $PhCH_3$ | 95 |
| 47 | $CH_3CN$ *instead of* $PhCH_3$ | 91 |
| 53 | *HCOOH instead of AcOH* | 72 |
| *n.d.* | *TFA instead of AcOH* | *n.d.* |
| **75** | *0.5 equiv. AcOH* | *trace* |
| 59 | *3.0 equiv. P(III) reagent* | 89 |
| 62[c] | $V(PhCH_3)$: $V(H_2O)$ = 9:1 | 74 |
| 22 | *w/o acid* | *trace* |
| *n.d.* | *w/o PC* | *n.r.* |
| *n.r.* | *in the dark* | *n.r.* |
| 50 | *Air instead of Ar* | 32 |
| *n.d.* | *w/o phosphine* | *n.r.* |

***photocatalyst***



**PC1**, R = $^t$Bu; **PC2**, R = $CF_3$ **PC3**

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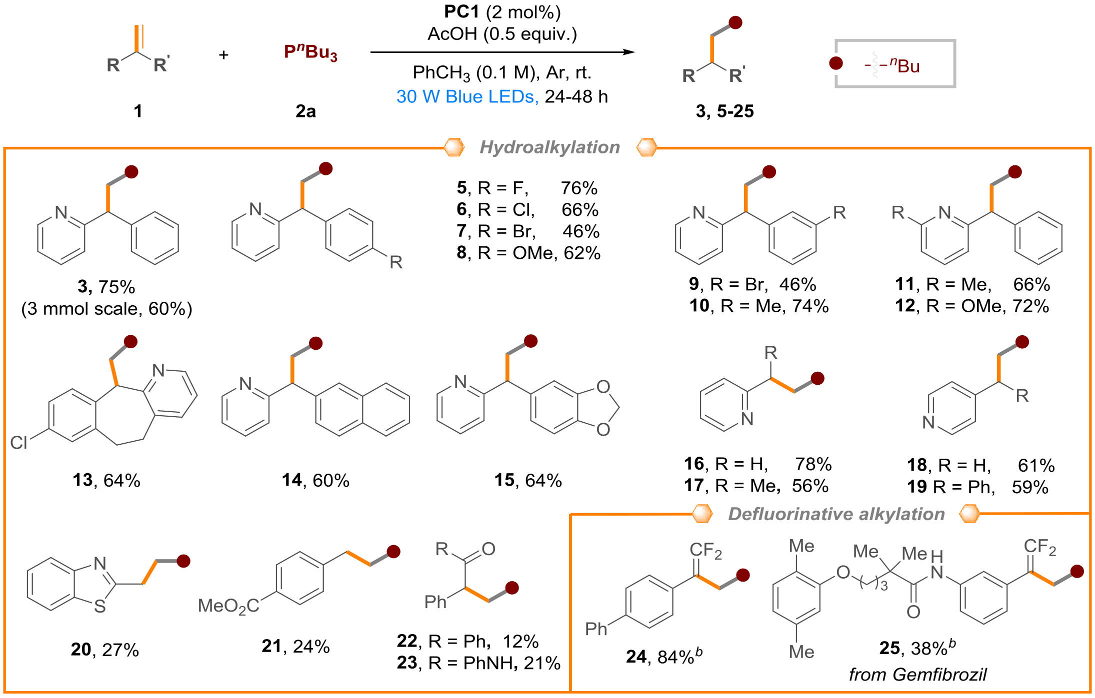
[a] Reaction conditions: **1a** (0.15 mmol, 1.0 equiv.), **PC1** (2 mol%), AcOH (0.3 mmol, 2.0 equiv.), *n*-$PBu_3$ (**2a**, 0.54 mmol, 3.6 equiv, *used for synthesis of 3*) or $PPh_3$(**2b**, 0.54 mmol, 3.6 equiv, *used for synthesis of 4*), $PhCH_3$ (0.1 M, 1.5 mL), 30 W blue LEDs, ambient temperature, argon atmosphere, 24 hours, isolated yield. [c] 0.5 equiv. AcOH used. TFA = trifluoroacetic acid. n.r. = no reaction. n.d. = no detected. DMF = *N*, *N*-dimethylformamide. $CH_3CN$ = acetonitrile. TFA = trifluoroacetic acid.

## 2.1 Hydroalkylation of olefins

With the optimal reaction conditions in hands, we turned our focus to first examine the applicability of the photocatalytic hydroalkylation reactions. As shown in Scheme 2, various 2-(1-phenylvinyl)pyridines, with either electron-donating (OMe, or Me) or electron-withdrawing (F, Cl, or Br) substituents on the (het)aryl moiety were all accommodated well under standard conditions, affording the hydroalkylation products **5-12** in 46-76% yield. However, incorporation of strongly electron-withdrawing (-$CF_3$) or electron-donating (-$NMe_2$) group at phenyl ring failed to deliver the desired product (see SI for details). We also examined 2-(1-phenylvinyl)pyridine with an exocyclic moiety, and the corresponding product **(13)** was obtained in 64% yield. Gratifyingly, replacement of the phenyl ring to naphthyl, benzodioxole, hydrogen, or methyl group, did not obviously affect the reaction efficiency, and the corresponding hydroalkylation products **14-17** could be obtained in 56-78% yield. Additionally, 4-vinylpyridines were also competent reaction partners (**18**-**19**). When the pyridine ring was replaced by a benzothiazole or phenyl group, the expected transformation proceeded products **20**-**21** with lower efficiency, indicating that the pyridine group possibly played an important role in improving the reactivity. It is worth noting that trifluoromethyl alkenes were also suitable substrates, giving defluoroalkylation product **24** exclusively in good yield. Moreover, this strategy could be applied to complex substrate from Gemfibrozil, leading to the corresponding product **25** in lower yield. To be noted, the scalability of this strategy was well demonstrated by performing the model reaction at a 3 mmol scale, and product **3** was achieved in a slightly decreased yield (60% *vs* 75%).

**Scheme 2.** Hydroalkylation substrate scope with respect to the alkenes.[a]

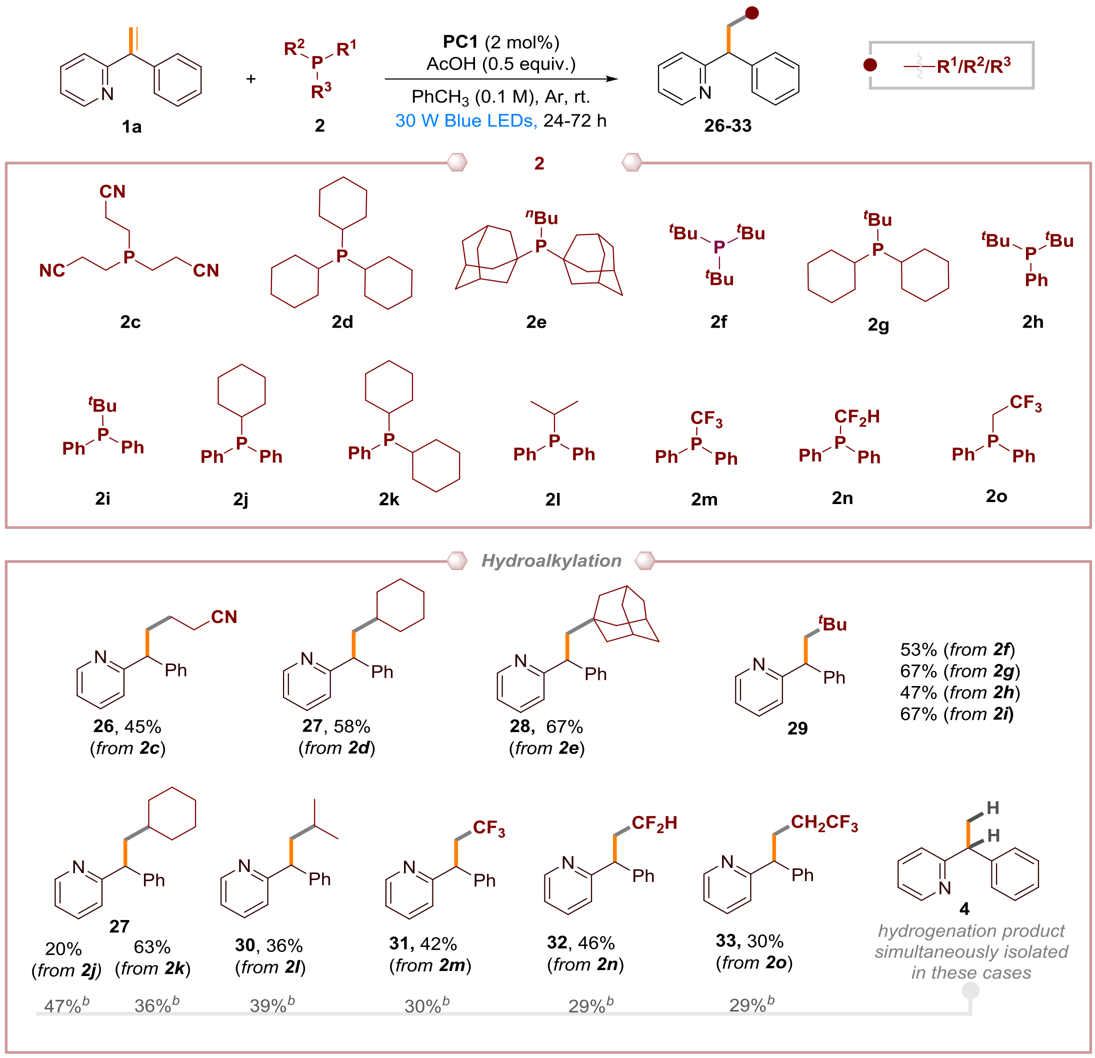


[a]Standard conditions A: alkene **1** (0.15 mmol, 1.0 equiv.), **2a** (0.54 mmol, 3.6 equiv), **PC1** (2 mol%), AcOH (0.075 mmol, 0.5 equiv.), $PhCH_3$ (0.1 M, 1.5 mL), 30 W blue LEDs, ambient temperature, Ar, 24-48 h, isolated yield. [b]No AcOH.

Next, we switched to evaluate the suitability of trisubstituted phosphines (Scheme 3). A series of phosphines bearing various substituents were examined. The reaction of **1a** with various trialkyl phosphines **2c-2g** gave the corresponding products **26-29** in moderate to good yields, irrespective of the structural features of alkyl moiety. With *tert*-butyl aryl phosphine **2h** or **2i** as starting material, the reaction proceeded smoothly to give the hydro-*tert*-butylation product **29**, exclusively. Interestingly, upon using unsymmetrically substituted phosphines as alkylation reagents, a selective cleavage of P-C bond was observed, and only single hydroalkylation products were observed for phosphine reagents **2c-2i**. However, a competitive hydrogenation reaction was observed, if using unsymmetrically substituted alkylphenyl phosphines **2j-2o** as the alkylation reagents. Gratifyingly, by using trifluoromethyl/difluoromethyl/pentafluoroethyldiphenyl phosphine, the hydro-polyfluoroalkylation of alkenes proceeded uneventfully to give moderate yields (**31-33**). Moreover, when the reaction of **1a** and other primary alkyl diphenyl phosphines was carried out under standard conditions, only hydrogenation product **4** was observed

(See SI for details). Notably, the reactivity order, aryl < primary < secondary < tertiary P-C, agreed well with the relevant BDEs in phosphoranyl radicals (see details in SI). These results further corroborate that the competition between $\alpha$-scission and $\beta$-scission pathways is able to be reasonably tuned by modulating the substituents of phosphine.

**Scheme 3.** Hydroalkylation substrate scope with respect to the phosphines.[a]

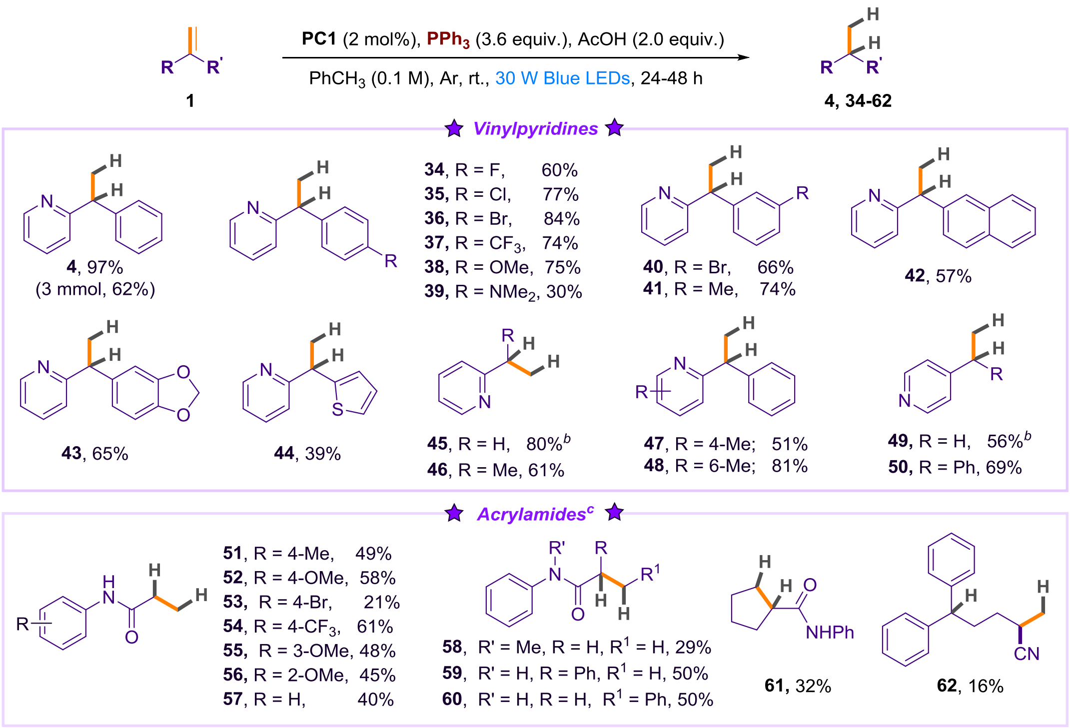


[a] Standard conditions: **1a** (0.15 mmol, 1.0 equiv.), **2** (0.54 mmol, 3.6 equiv.), **PC1** (2 mol%), AcOH (0.075 mmol, 0.5 equiv.), $PhCH_3$ (0.1 M, 1.5 mL), 30 W blue LEDs, ambient temperature, argon atmosphere, 24-48 h, isolated yield. [b] Isolated yield for the hydrogenation product **4**.

## 2.2 Hydrogenation of olefins

As observed in the preliminary evaluation of the manipulation of fragmentation modes, C=C bond in olefin was able to effectively hydrogenated to generate the corresponding C-C bond upon using triphenylphosphine (Table 1). Considering the much stronger P-C bond and highly unstable phenyl radical formed *via* $\alpha$-scission in triphenyl phosphine, the *α*-scission pathway could be fully suppressed to access a selective hydrogenation of olefins using water as hydrogen source and phosphine as sacrificial reductant. Subsequently, we sought to explore the scope of alkenes for the photoinduced alkene hydrogenation process (Scheme 4). A wide range of vinylpyridines were well tolerated, providing the corresponding products **4** and **34-50** in 30-97% yields. First, various 2-(1-phenylvinyl)pyridines, with different electron-donating, as well as electron-withdrawing substituents at the aryl rings, were all successfully transformed into corresponding products **34-41** in moderate to high yields. Notably, strong electron-donating substituent (-$NMe_2$) at the phenyl ring could also be accommodated, albeit giving the product **39** in a relatively low yield (30%). Subsequently, replacement of phenyl to other moieties, including naphthyl, benzodioxole, thiophene, hydrogen, or methyl group, was evaluated, and the desired products **42-46** were furnished in moderate to high yields. Moreover, 4-vinylpyridines were also competent reaction partners by the formation of the corresponding product **49-50** in good yields. To further examine the compatibility of this protocol, a series of acrylamides were examined as reaction partners. We were delighted to see that *N*-phenyl-acrylamides bearing various substituents underwent the transformation to give the corresponding products **51-58** in 21-61% yields. It is noteworthy to mention that 1,1-disubstituted or 1,2-disubstituted alkenes were also successfully transformed into the desired products **59-61** in acceptable yields. Interestingly, 2,2-diphenylhex-5-enenitrile proceeded well to generate product **62** in 16% yield *via* an intramolecular 1,4-CN migration, suggesting that a radical addition/migration reaction was involved in the transformation. To further examine the practicality of this hydrogenation process, a scale-up experiment was performed at 3 mmol scale, affording product **4** in 62% yield. Inevitably, this strategy suffers from some substrate limitations at the current stage, which are listed in the supporting information.

**Scheme 4**. Hydrogenation substrate scope.[a]



[a]Standard conditions: alkene **1** (0.15 mmol, 1.0 equiv.), **PC1** (2 mol%), $PPh_3$ (0.54 mmol, 3.6 equiv.), AcOH (0.30 mmol, 2.0 equiv.), $PhCH_3$ (0.1 M, 1.5 mL), 30 W blue LEDs, ambient temperature, argon atmosphere, 24-48 h, isolated yield. [b]Yield determined by $^1H$ NMR using $CH_2Br_2$ as the internal standard. [c]$CH_3CN$ instead of $PhCH_3$ as solvent.

## 2.3 Mechanistic studies

Based on previous literature[15, 17, 9c] and our experimental observations, a plausible reaction mechanism was proposed and rationalized by DFT calculations (as shown in Figure 1), using olefin **1a** and P$^n$Bu as model compounds. The transformation was initiated with photoexcitation of the iridium catalyst, followed by reductive quenching of the excited photocatalyst by P$^n$Bu$_3$, leading to the formation of tributylphosphine radical cation. Subsequently, a nucleophilic attack of water to P$^n$Bu$_3$ radical cation generated complex **Ia**, which was then deprotonated by another P$^n$Bu$_3$ molecule to give the key intermediate **IIa**, HO-P$^n$Bu$_3$ radical. From intermediate **IIa**, there was a competition between $\beta$-scission (leading to the hydrogenation product **4**) and $\alpha$-scission (related to the formation of hydroalkylation product **3**). In the hydroalkylation pathway, $\alpha$-scission of **IIa** generated P$^n$Bu$_2$-OH and $^n$Bu radical *via* **TS2a**, and $^n$Bu radical underwent a facile radical addition step with **1a** *via* **TS4a** to form a relatively persistent radical adduct **IIIa** stabilized by two aromatic rings. The $\alpha$-scission step was calculated to be the rate-determining step, with an overall free-energy barrier about 10.8 kcal/mol.

The pyridine moiety of intermediate **IIIa** was then protonated by *in-situ* formed acid $HP^nBu_3$ cation *via* **TS5a**, followed by single-electron transfer from **[Ir(II)]** to regenerate photocatalyst **[Ir(III)]** and liberate the zwitterion intermediate **VIa**. Finally, a proton shuttle mediated by acetic acid would convert **VIa** to the final hydroalkylation product **3**. In another pathway, intermediate **IIa**, proceeded through HAT to alkene **1a**, leading to the relatively persistent radical **IVa** with the release of phosphine oxide $P(O)^nBu_3$. This HAT step was rate-determining in the hydrogenation pathway with an activation energy of 11.6 kcal/mol, and was highly exergonic by -50.5 kcal/mol. The persistent radical adduct **IVa** then underwent a similar process as intermediate **IIIa**, protonation/single electron transfer reduction/proton shuttle process to give the final hydrogenation product **4**. As both **TS2a** and **TS3a** were the rate-determining transition states in the corresponding reaction pathway, the selectivity was kinetically controlled over the competition between *α*-scission and HAT steps. The *α*-scission step was remarkably facile over that of the HAT process, which correlated with the exclusive hydroalkylation product with $P^nBu_3$ observed experimentally.

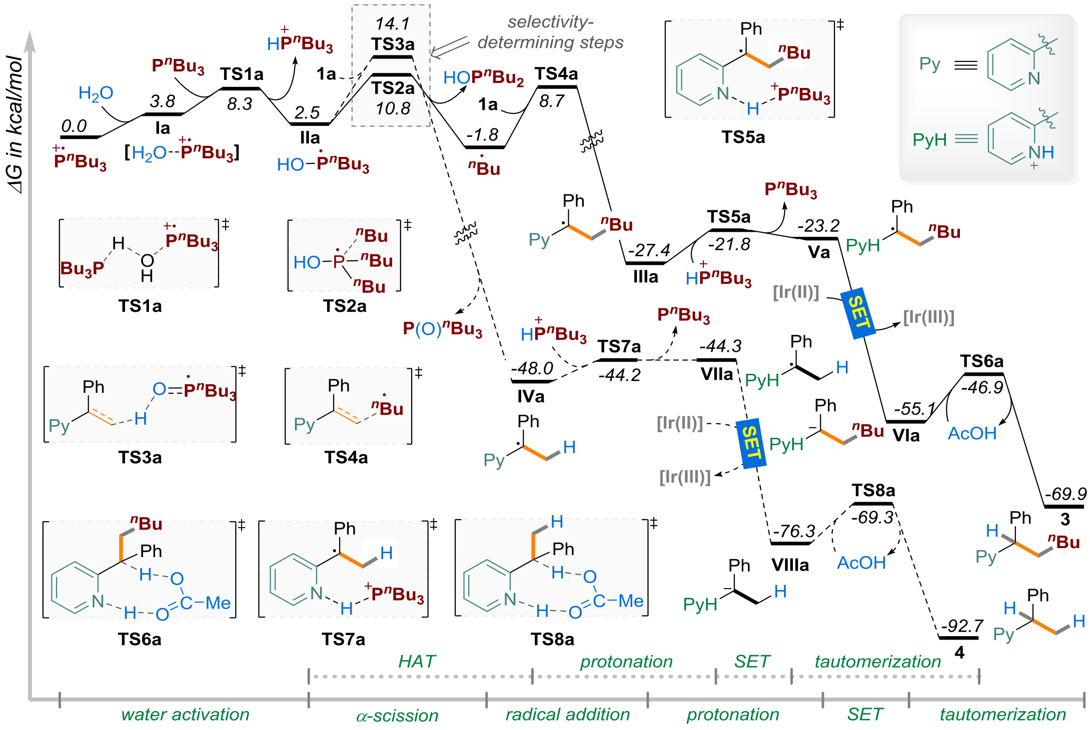


**Figure 1**. Free energy profiles for the model reaction of **1a** and $P^nBu_3$ under standard conditions. Gibbs free energies were given in kcal/mol, at PBE1PBE-D3/def2TZVPP-SMD(toluene)//PBE1PBE- D3/def2TZVP(Ir)-def2SVP theoretical level.

To better understand the switch from hydroalkylation to hydrogenation pathway, the plausible reaction pathways of **1a** mediated by $PPh_3$ was also rationalized by DFT calculations (see details in SI). As the competitions are determined by variants in the relative bond strengths of the O-H and P-C bonds in HO-$P^nBu_3$ radical, it is reasonable to alter the reaction selectivity by tuning the substituents. It was shown that HO-$P^nBu_3$ radical adopted an approximately trigonal bipyramidal configuration, corresponding to a *sp*$^3$*d* hybridization state, while HO-$PPh_3$ radical was closer to a tetrahedral shape *via* a *sp*$^3$ hybridization (Figure 2a). In HO-$P^nBu_3$ radical, the P-C bond at the *apical* position was obviously weaker than that at the equatorial positions, as reflected by the bond length differences. This configurational difference could possibly be contributed to the fact that the unpaired electron could be distributed to the aromatic rings in HO-$PPh_3$ radical rather than localized at the P atom in HO-$P^nBu_3$ radical. Free energy profiles also suggested that $\beta$-scission of HO-$PPh_3$ radical *via* HAT to **1a** was much more favorable than that of the $\alpha$-scission step, with a free energy barrier difference as large as 18.5 kcal/mol (Figure 2b).

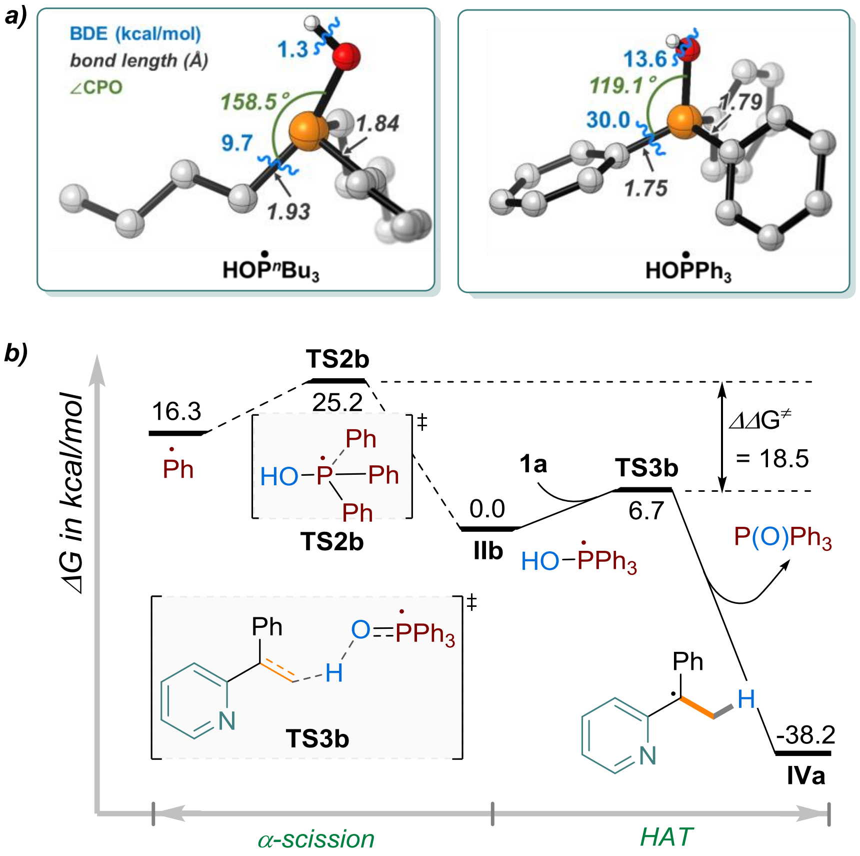
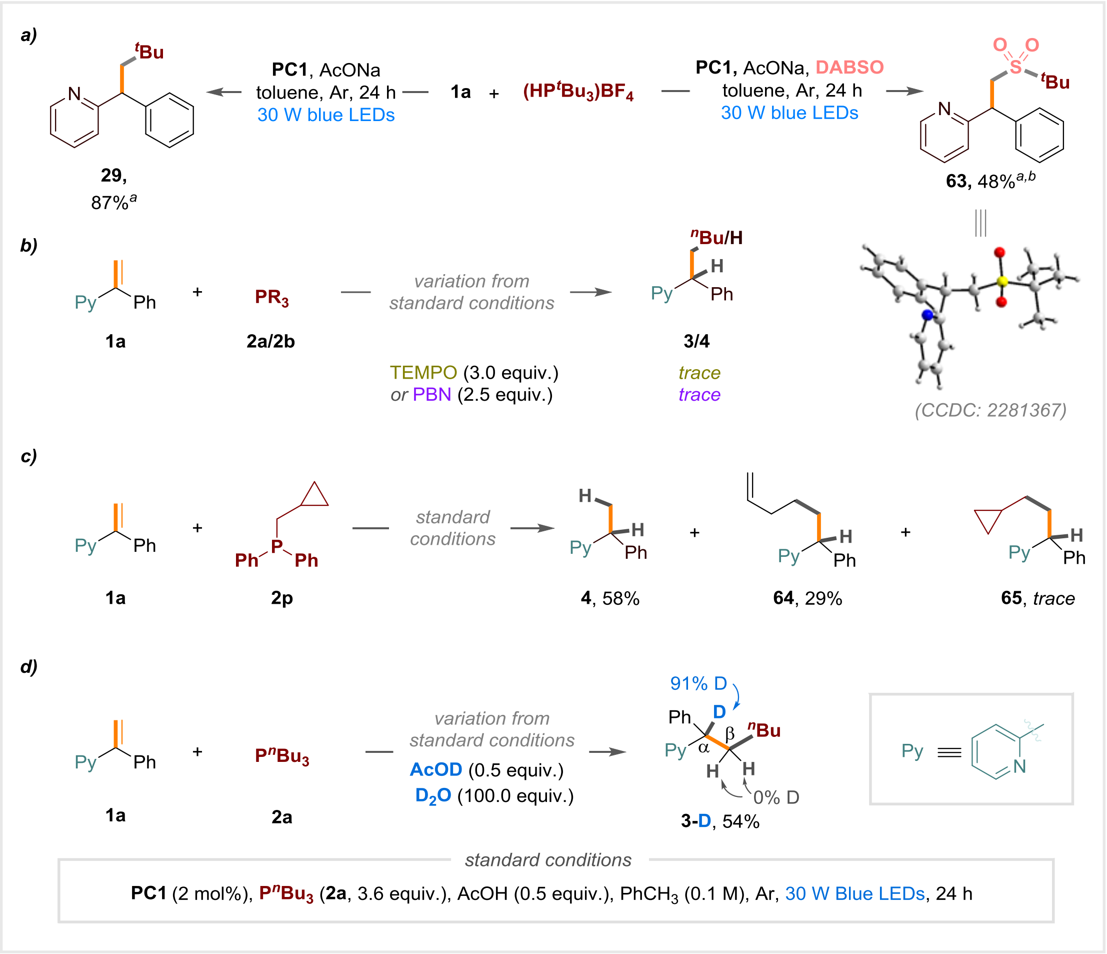


**Figure 2**. a) Optimized structures of the key phosphoranyl radicals. Non-polar hydrogen atoms are omitted for clarity. b) Competition between $\alpha$-scission and HAT steps *via* $P(OH)Ph_3$ radical intermediate.

To further illustrate the reaction mechanism, we carried out a series of control experiments (as shown in Scheme 5, see more details in SI). Stern-Volmer fluorescence quenching studies revealed that excited-state photocatalyst **PC1*** could be quenched by $PPh_3$, or $P^nBu_3$. It should be noted that the desired hydro-*tert*-butylation product **29** was obtained in a higher yield upon using the bench-stable tri-*tert*-butylphosphine tetrafluoroborate to generate $P^tBu_3$ *in situ* in the presence of base, suggesting that chemical instability of $PR_3$ might be responsible for the lowered yield (Scheme 5a). Interestingly, the addition of 3.0 equivalents of DABCO•$(SO_2)_2$(DABSO) could fully suppress the formation of product **29**, leading to the hydrosulfonylation product **63** in 48% yield. And the structure of **63** was verified by X-ray crystallographic analysis (CCDC: 2281367). These results support the formation of *tert*-butyl radical during the reaction process. In addition, radical probe experiments showed that no desired product was obtained after adding stoichiometric amount of commonly used radical scavengers such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) or *N*-*tert*-butyl-*α*-phenylnitrone (PBN) (Scheme 5b). Next, the cyclopropane incorporated substrate **2p** was subjected to the standard conditions, delivering the cyclopropyl ring-opened product **64** in 29% yield (Scheme 5c). Importantly, when the reaction of **1a** and **2a** was carried out under standard conditions in the presence of $D_2O$ and AcOD, deuterium-labeled product **3-D** was yielded with 91% D-incorporation at *α*-position, which indicated that protonation of the carbanion might be involved in the reaction process (Scheme 5d). These results agree well with our theoretical studies.

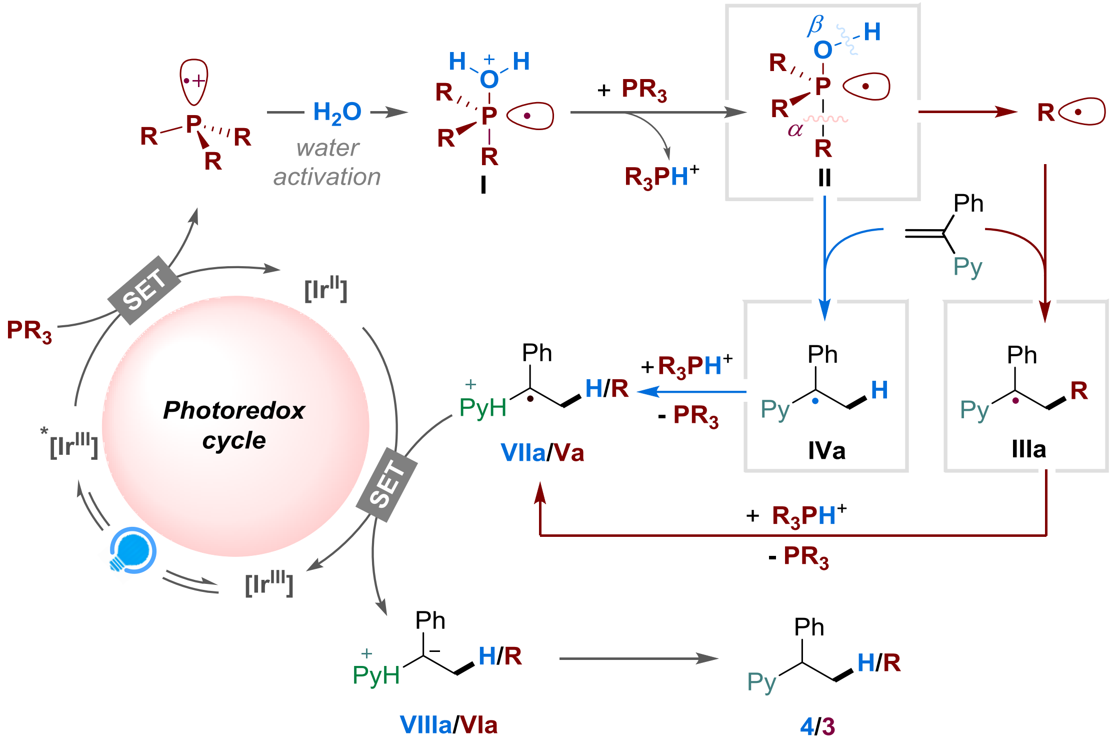
**Scheme 5.** Control experiments.



[a]Reaction conditions: **1a** (0.15 mmol, 1.0 equiv.), ($^t$Bu$_3$PH)BF$_4$ (0.54 mmol, 3.6 equiv.), **PC1** (2 mol%), AcONa (0.54 mmol, 3.6 equiv.), PhCH$_3$ (0.1 M, 1.5 mL), 30 W blue LEDs, ambient temperature, argon atmosphere, 24h, isolated yield. [b]DABSO (0.45 mmol, 3.0 equiv.) as additive.

Based on the above mechanistic studies, the plausible reaction pathways for this divergent transformation of olefins are as shown in Scheme 6, using model substrate **1a** as an example. The reaction was initiated with excitation of the photocatalyst under visible light irradiation. The excited photocatalyst was then reductive quenched by phosphine PR$_3$, leading to the formation of phosphine radical cation. Subsequently, the phosphine radical cation underwent nucleophilic attack by water, followed by deprotonation of the activated water by another phosphine molecule as base, delivering the critical phosphoranyl radical intermediate **II**. For hydroxyl trialkyl phosphine radical, $\alpha$-scission of **II** was dominant to give an alkyl radical, which was then trapped by **1a** to give radical adduct **IIIa**. Subsequently, the pyridine moiety in **IIIa** was protonated by phosphonium HPR$_3$ cation to afford intermediate **Va**, which was quickly reduced by photocatalyst [Ir(II)], and finally proceeded through an acid-mediated proton shuttle, giving the hydroalkylation product **3**. While for hydroxyl triaryl phosphine radical, *α*-scission of **II** was fully suppressed due to a much stronger P-C bond in $P(OH)Ph_3$ intermediate and generation of a highly unstable aryl radical. The preferred *β*-scission of **II** proceeded through HAT to **1a**, generating a *sp*$^2$ carbon radical **IVa**, which underwent protonation, SET reduction, and subsequent protonation *via* acid-mediated proton shuttle to produce the final hydrogenation product **4**.

**Scheme 6** Plausible reaction pathways using substrate **1a** as an example.



## 3. Conclusion

In conclusion, we have disclosed the tuning of the fragmentation patterns of phosphoranyl radicals (*α*-scission *vs* *β*-scission), enabling photoredox-catalyzed divergent transformations of alkenes. Various olefins could undergo either hydroalkylation or hydrogenation by using the corresponding phosphine as mediator. Notably, on the basis of the identification unprecedented photocatalytic *α*-Scission II of phosphoranyl radical, phosphines were first employed to serve as versatile alkylation reagents to incorporate various alkyl groups, including primary, secondary, tertiary alkyl groups, and even electron-poor polyfluoroalkyl moieties. To some extent, the bond strength difference between P-C and O-H bonds in the crucial phosphoranyl radical (•$P(OH)R_3$) presumably dominated the competition between these two fragmentation patterns. Although $\beta$-scission of •$P(OH)R_3$ radical was thermodynamically favored, it could be kinetically suppressed by facilitating $\alpha$-scission way *via* cleavage of P-C bond in this phosphoranyl radical intermediate. Mechanistic studies suggested water was activated by phosphine radical cation to give the critical $P(OH)R_3$ radical intermediate. To the best of our knowledge, the photocatalytic $\alpha$-scission mode of phosphoranyl radical to generate alkyl radical was unprecedentedly developed, which should deepen our understanding and enrich the arsenal of phosphine radical chemistry.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.
Experimental details and characterization data for new compounds, including NMR spectra, computational details, and Cartesian coordinates of all computed structures (PDF).
X-ray crystallographic data of **63** (CIF).

### Accession Codes

CCDC 2281367-contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 UnionRoad, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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### Notes

The authors declare no competing financial interest.

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## REFERENCE

1. (a) Ramaiah, M. Radical Reaction in Organic Synthesis. *Tetrahedron*. **1987**, *43*, 3541-3676. (b) Staveness, D.; Bosque, I.; Stephenson, C. R. J. Free Radical Chemistry Enabled by Visible Light-Induced Electron Transfer. *Acc. Chem. Res.* **2016**, *49*, 2295-2306. (c) Studer, A.; Curran, D. P. Catalysis of Radical Reactions: A Radical Chemistry Perspective. *Angew. Chem. Int. Ed.* **2016**, *55*, 58-102. (d) Yan, M.; Lo, J. C.; Edwards, J. T.; Baran, P. S. Radicals: Reactive Intermediates with Translational Potential. *J. Am. Chem. Soc.* **2016**, *138*, 12692-12714. (e) Studer, A. From Curiosity to Reliable Methodology - Organic Free Radical Chemistry. *Adv. Synth. Catal.* **2020**, *362*, 2073-2073. (f) Bhunia, A.; Studer, A. Recent Advances in Radical Chemistry Proceeding through Pro-Aromatic Radicals. *Chem.* **2021**, *7*, 2060-2100.

2. (a) Marque, S.; Tordo, P. Reactivity of Phosphorus Centered Radicals. *Top. Curr. Chem.* **2005**, *250*, 43-76. (b) Luo, K.; Yang, W. C.; Wu, L. Photoredox Catalysis in Organophosphorus Chemistry. *Asian J. Org. Chem.* **2017**, *6*, 350-367. (c) Pan, D.; Nie, G.; Jiang, S.; Li, T.; Jin, Z. Radical Reactions Promoted by Trivalent Tertiary Phosphines. *Org. Chem. Front.* **2020**, *7*, 2349-2371. (d) Wang, Z.; Zhao, X.; Wang, H.; Li, X.; Xu, Z.; Ramadoss, V.; Tian, L.; Wang, Y. Dehydroxylative Arylation of Alcohols via Paired Electrolysis. *Org. Lett.* **2022**, *24*, 7476-7481. (e) Zhang, Y.; Han, Y.; Zhu, S.; Qing, F. L.; Xue, X. S.; Chu, L. Light-Induced Divergent Cyanation of Alkynes Enabled by Phosphorus Radicals. *Angew. Chem. Int. Ed.* **2022**, Doi: org/10.1002/anie.202210838
3. (a) Bruckler, S. A. Autoxidation of Trialkylphosphines. *J. Am. Chem. Soc.* **1962**, *84*, 3093 – 3097. (b) Zhang, L.; Koreeda, M. Radical Deoxygenation of Hydroxyl Groups via Phosphites. *J. Am. Chem. Soc.* **2004**, *126*, 13190-13191. (b) Swamy, K. C. K.; Kumar, N. N. B.; Balaraman, E.; Kumar, K. V. P. P. Mitsunobu and Related Reactions: Advances and Applications. *Chem. Rev*. **2009**, *109*, 2551-2651. (d) Byrne, P. A.; Gilheany, D. G. The Modern Interpretation of the Wittig Reaction Mechanism. *Chem. Soc. Rev.* **2013**, *42*, 6670-6696. (e) Mao, R.; Bera, S.; Cheseaux, A.; Hu, X. Deoxygenative Trifluoromethylthiolation of Carboxylic Acids. *Chem. Sci.* **2019**, *10*, 9555-9559.
4. (a) Yasui, S.; Ohno, A. The Photo-Reduction of 10-Methylacridinium Ion by Triphenylphosphine through One-Electron Transfer Mechanism. *Tetrahedron Letters*. **1991**, *32*, 5601-5604. (b) Yasui, S.; Fujii, M.; Kawano, C.; Nishimura, Y.; Ohno, A. Dediazoniation of Arenediazonium Salt with Trivalent Phosphorus Compounds by One-Electron Transfer Mechanism. *Tetrahedron Letters*. **1991**, *32*, 1047-1050. (c) Yasui, S.; Shioji, K.; Yoshihara, M.; Maeshima, T.; Ohno, A. The Thermal- and Photo-Reaction of a Diphylphosphinite Ester with 10-Methylacridinium Iodide. Discrimination Between Polar and Single Electron Transfer Processes. *Tetrahedron Letters*. **1992**, *33*, 7189-7192. (d) Yasui, S.; Shioji, K.; Ohno, A. Reaction of a Cation Radical Generated from Trivalent Phosphorus Compound through Single-Electron Transfer to Arenediazonium Salt. *Tetrahedron Letters*. **1994**, *35*, 2695-2698. (e) Yasui, S.; Shioji, K.; Ohno, A. Reactivity of a phosphoranyl Radical Generated by Photoreaction of Phenyl Diphenylphosphinite with 10-Methylacridinium Iodide. *α*-Scission vs Single Electron Transfer. *Heteroat. Chem*. **1994**, 5, 85-90. (f) Yasui, S.; Shioji, K.; Tsujimoto, M.; Ohno, A. Reactivity of Cation Radicals Generated from Trivalent-Phosphorus Compounds in the Reaction with Methylviologen: Kinetic Analysis. *Chem. Lett*. **1995**, *24*, 783-784. (g) Yasui, S.; Shioji, K.; Tsujimoto, M.; Ohno, A. Reactivity of a Trivalent Phosphorus Radical Cation as an Electrophile Toward Pyridine Derivatives. *Heteroat. Chem*. **2000**, 11, 152-157. (h) Masuda, Y.; Uno,

M.; Murakami, M. Photoinduced Reaction of Triarylphosphines with Alkenes Forming Fused Tricyclic Phosphonium Salts. *Org. Lett.* **2021,** *23*, 8445-8449. (i) Masuda, Y.; Tsuda, H.; Murakami, M. Photoinduced Dearomatizaing Three-Component Coupling of Arylphosphines, Alkenes and Water. *Angew. Chem. Int. Ed.* **2021**, *60*, 3551-3555. (j) Yin, J.; Lin, X.; Chai, L.; Wang, C.-Y.; Zhu, L.; Li, C. Phosphonylation of Alkyl Radicals. *Chem.* **2023**, *9*, 1945-1954.

5. Shao, X.; Zheng, Y.; Ramadoss, V.; Tian, L.; Wang, Y. Recent Advances in $P^{III}$-Assisted Deoxygenative Reactions under Photochemical or Electrochemical Conditions. *Org. Biomol. Chem.* **2020**, *18*, 5994-6005.
6. (a) Kim, S.; Hyun Oh, D. Generation of 5- and 6-Membered Ring Radicals by Deoxygeneration of Alkoxy Radicals. *Synlett*. **1998**, *5*, 525-527. (b) Ding, B.; Bentrude, W. G. Trimethyl Phosphite as a Trap for Alkoxy Radicals Formed from the Ring Openging of Oxiranylcarbinyl Radicals. Conversion to Alkenes. Mechanistic Applications to the Study of C-C versus C-O Ring Cleavage. *J. Am. Chem. Soc.* **2003**, *125*, 3248-3259. (c) Jiao, X. Y.; Bentrude, W. G. A Facile Route to Vinyl- and Arylphosphonates by Vinyl and Aryl Radical Trapping with $(MeO)_3P$. *J. Org. Chem.* **2003**, *68*, 3303-3306. (d) Bietti, M.; Calcagni, A.; Salamone, M. The Role of Structural Effects on the Reactions of Alkoxyl Radicals with Trialkyl and Triaryl Phosphites. A Time-Resolved Kinetic Study. *J. Org. Chem.* **2010,** *75*, 4514-4520. (e) Jordan, P. A.; Miller, S. J. An Approach to the Site-Selective Deoxygenation of Hydroxy Groups Based on Catalytic Phosphoramidite Transfer. *Angew. Chem. Int. Ed.* **2012**, *51*, 2907-2911. (f) Lardy, S. W.; Schmidt, V. A. Intermolecular Radical Mediated Anti-Markovnikov Alkene Hydroamination Using N-Hydroxyphthalimide. *J. Am. Chem. Soc.* **2018**, *140*, 12318-12322. (g) Han, J.-B.; Guo, A.; Tang, X.-Y. Alkylation of Allyl/Alkenyl Sulfones by Deoxygenation of Alkoxyl Radicals. *Chem. Eur. J.* **2019**, *25*, 2989-2994. (h) Kim, Y.; Bielawski, C. W.; Lee, E. Oxygen Atom Transfer: A Mild and Efficient Method for Generating Iminyl Radicals. *Chem. Commun.* **2019**, *55*, 7061-7064. (i) Lopp, J. M.; Schmidt, V. A. Intermolecular Phosphite-Mediated Radical Desulfurative Alkene Alkylation Using Thiols. *Org. Lett.* **2019**, *21*, 8031-8036. (j) Qin, Q.; Wang, W.; Zhang, C.; Song, S.; Jiao, N. A Metal-Free Desulfurizing Radical Rductive C-C Coupling of Thiols and Alkenes. *Chem. Commun*. **2019**, *55*, 10583-10586.
7. (a) Hoffmann, F. M.; Ess, R. J.; Simmons, T. C.; Hanzel, R. S. The Desulfurizaion of Mercaptans with Trialkyl Phosphites. *J. Am. Chem. Soc*. **1956**, *78*, 6414-6414. (b) Walling, C.; Rabinowitz, R. The Reaction of Thiyl Radicals WITH Trialkyl Phosphites. *J. Am. Chem. Soc*. **1957**, *79*, 5326-5326. (c) Walling, C.; Rabinowitz, R. The Photolysis of Isobutyl Disulfide in Cumenel. *J. Am. Chem. Soc.* **1959**, *81*, 1137-1143. (d) Walling, C.; Pearson, M. S. Some Radical Reacions of Trivalent Phosphorus Derivatives with

Mercaptans, Peroxides, and Olefins. A New Radical Cyclization. *J. Am. Chem. Soc.* **1964**, *86*, 2262-2266.

8. (a) Davies, A. G.; Dennis, R. W.; Griller, D.; Roberts, B. P. A Kinetic Study of *α* vs *β*–Sicssion of Phosphoranyl Radicals, $R_n$-•P(OR)$_{4-n}$. *J. Organomet. Chem*. **1972**, *40*, 33-35. (b) Bentrude, W. G.; Hansen, E. R.; Khan, W. A.; Rogers, P. E. *α* vs *β* Scission in Reactions of Alkoxy and Thiyl Radicals with Diethyl Alkylphosphonites. *J. Am. Chem. Soc*. **1972**, *94*, 2867-2868. (c) Bentrude, W. G.; Hansen, E. R.; Khan, W. A.; Min, T. B.; Robers, P. E. Free-Radical Chemistry of Organophosphorous Coumpounds III. *α vs β* Scission in Reactions of Alkoxy and Thiyl Radicals with Trivalent Organophorosphorus Derivaives. *J. Am. Chem. Soc.* **1973**, *95*, 2286–2293. (d) Roberts, B. P.; Singh, K. Site Selectivity in the *β*-Scission of Alkoxyphosphoranyl Radicals. A Reinterpretation. *J. Chem. Soc., Perkin Trans.* **1980**, 2, 1549-1556. (e) Bentrude, W. G. Phosphoranyl Radical-Their Structrue, Formation, and Reactions. *Acc. Chem. Res*. **1982**, *15*, 117-125. (f) Dockey, K. P.; Bentrude, W. G. Free Radical Chain Reactions of [1.1.1]Propellane with Three-Coordinate Phosphorus Molecules. Evidence for the High Reactivity of the Bicyclo[1.1.1]pent-1-yl Radical. *J. Am. Chem. Soc*. **1997**, *119*, 1388-1399.

9. (a) Zeitler, K. Photoredox Catalysis with Visible Light. *Angew. Chem. Int. Ed.* **2009,** *48*, 9785-9789. (b) Xuan, J.; Xiao, W. J. Visible-Light Photoredox Catalysis. *Angew. Chem. Int. Ed.* **2012,** *51*, 6828-6838. (c) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. Visible Light Photoredox Catalysis with Transition Metal Complexes: Applications in Organic Synthesis. *Chem. Rev.* **2013**, *113*, 5322-5363. (d) Chen, J. R.; Hu, X. Q.; Lu, L. Q.; Xiao, W. J. Visible Light Photoredox-Controlled Reactions of *N*-Radicals and Radical Ions. *Chemi. Soc. Rev.* **2016**, *45*, 2044-2056. (e) Goddard, J. P.; Ollivier, C.; Fensterbank, L. Photoredox Catalysis for the Generation of Carbon Centered Radicals. *Acc. Chem. Res.* **2016,** *49*, 1924-1936. (f) Romero, N. A.; Nicewicz, D. A. Organic Photoredox Catalysis. *Chem. Rev.* **2016,** *116*, 10075-10166. (g) Shaw, M. H.; Twilton, J.; MacMillan, D. W. C. Photoredox Catalysis in Organic Chemistry. *J. Org. Chem.* **2016**, *81*, 6898-6926.

10. (a) Stache, E. E.; Ertel, A. B.; Rovis, T.; Doyle, A. G. Generation of Phosphoranyl Radicals via Photoredox Catalysis Enables Voltage–Independent Activation of Strong C–O Bonds. *ACS Catal.* **2018,** *8*, 11134-11139. (b) Martinez Alvarado, J. I.; Ertel, A. B.; Stegner, A.; Stache, E. E.; Doyle, A. G. Direct Use of Carboxylic Acids in the Photocatalytic Hydroacylation of Styrenes to Generate Dialkyl Ketones. *Org. Lett.* **2019,** *21*, 9940-9944. (c) Xia, P. J.; Ye, Z. P.; Hu, Y. Z.; Song, D.; Xiang, H. Y.; Chen, X. Q.; Yang, H. Photocatalytic, Phosphoranyl Radical-Mediated N–O Cleavage of Strained Cycloketone Oximes. *Org. Lett.* **2019,** *21*, 2658-2662. (d) Zhang, L.; Si, X.; Yang, Y.; Witzel, S.; Sekine, K.; Rudolph, M.; Rominger, F.;

Hashmi, A. S. K. Reductive C–C Coupling by Desulfurizing Gold-Catalyzed Photoreactions. *ACS Catal.* **2019,** *9*, 6118-6123. (e) Clarke, A. K.; Parkin, A.; Taylor, R. J. K.; Unsworth, W. P.; Rossi-Ashton, J. A. Photocatalytic Deoxygenation of Sulfoxides Using Visible Light: Mechanistic Investigations and Synthetic Applications. *ACS Catal.* **2020,** *10*, 5814-5820. (f) Guo, Y.-Q.; Wang, R.; Song, H.; Liu, Y.; Wang, Q. Visible-Light-Induced Deoxygenation/Defluorination Protocol for Synthesis of γ,γ-Difluoroallylic Ketones. *Org. Lett.* **2020,** *22*, 709-713. (g) Ye, Z. P.; Hu, Y. Z.; Xia, P. J.; Xiang, H. Y.; Chen, K.; Yang, H. Photocatalytic Intermolecular Anti-Markovnikov Hydroamination of Unactivated Alkenes with N-Hydroxyphthalimide. *Org. Chem. Front.* **2021,** *8*, 273-277. (h) Zhou, Y.; Zhao, L.; Hu, M.; Duan, X. H.; Liu, L. Visible-Light Photoredox-Catalyzed Divergent 1,2-Diacylation and Hydroacylation of Alkenes with Carboxylic Acid Anhydride. *Org. Lett.* **2023**, *25*, 5268-5272. (i) Xie, Z. Z.; Zheng, Y.; Yuan, C. P.; Guan, J. P.; Ye, Z. P.; Xiao, J. A.; Xiang, H. Y.; Chen, X. Q.; Yang, H. Photoredox-Catalyzed Deoxygenation of Hexafluoroacetone Hydrate Enables Hydroxypolyfluoroalkylation of Alkenes. *Angew. Chem. Int. Ed.* **2022**, Doi: org/10.1002/anie.202211035

11. (a) Ruzi, R.; Ma, J.; Yuan, X. A.; Wang, W.; Wang, S.; Zhang, M.; Dai, J.; Xie, J.; Zhu, C. Deoxygenative Arylation of Carboxylic Acids by Aryl Migration. *Chem. Eur. J.* **2019,** *25*, 12724-12729. (b) Hu, X. Q.; Hou, Y. X.; Liu, Z. K.; Gao, Y. Recent Advances in Phosphoranyl Radical-Mediated Deoxygenative Functionalisation. *Org. Chem. Front.* **2020**, *7*, 2319-2324. (c) Rossi-Ashton, J. A.; Clarke, A. K.; Unsworth, W. P.; Taylor, R. J. K. Phosphoranyl Radical Fragmentation Reactions Driven by Photoredox Catalysis. *ACS Catal.* **2020**, *10*, 7250-7261. (d) Kim, J.; Kim, M.; Jeong, J.; Hong, S. Unlocking the Potential of B-Fragmentation of Aminophosphoranyl Radicals for Sulfonyl Radical Reactions. *J. Am. Chem. Soc.* **2023**, *145*, 14510-14518. (e) Pagire, S. K.; Shu, C.; Reich, D.; Noble, A.; Aggarwal, V. K. Convergent Deboronative and Decarboxylative Phosphonylation Enabled by the Phosphite Radical Trap "Becap". *J. Am. Chem. Soc*. **2023**, Doi.org/10.1021/jacs.3c06524
12. Chinn, A. J.; Sedillo, K.; Doyle, A. G. Phosphine/Photoredox Catalyzed Anti-Markovnikov Hydroamination of Olefins with Primary Sulfonamides *Via* α-Scission from Phosphoranyl Radicals. *J. Am. Chem. Soc.* **2021,** *143*, 18331-18338.
13. (a) Kochi, J. K.; Krusic, P. J. The Displacement of Alkyl Groups from Organophosphorus Compounds Studied by Electron Spin Resonance. *J. Am. Chem. Soc*. **1969**, *91*, 3944-3946. (b) Cooper, J. W.; Roverts, B. P. Configuratioal Effects in the α-Scission of Phosphoranyl Radcials. *J. Chem. Soc., Perkin Trans*. **1976**, *2*, 808-813.

14. Bond Dissocation Enthalpies for related O-H and O-C bonds could be found in the Bond-energy Databank: http://ibond.nankai.edu.cn/

15. Pandey, G., Pooranchand, D.; Bhalerao, U. T. Photoinduced Single Electron Transfer Activation of Organophosphines: Nucleophilic Trapping of Phosphine Radical Cation. *Tetrahedron.* **1991**, *47*, 1745-1752.

16. Zhang, J.; Mück-Lichtenfeld, C.; Studer, A. Photocatalytic Phosphine-Mediated Water Activation for Radical Hydrogenation. *Nature.* **2023**, *619*, 506-513.

17. Zagumennov, V. A.; Sizova, N. A.; Nikitin, E. V. Electrochemical Oxidation of Tertiary Phosphines in the Presence of Camphene. *Russ. J. Gen. Chem.* **2009**, *79*, 1473-1482.