

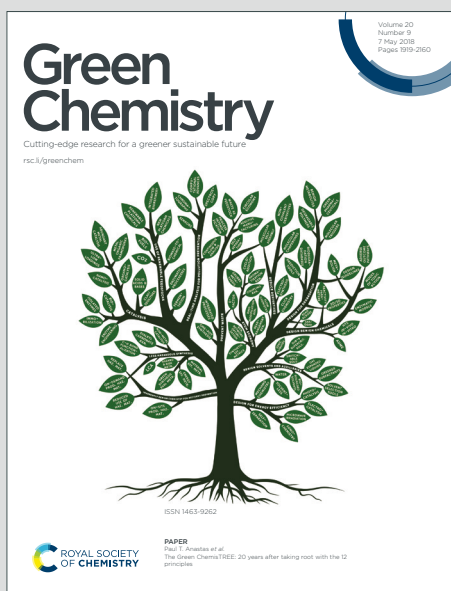
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PAPER

Photoinduced synthesis of C2-linked phosphine oxides via radical difunctionalization of acetylene

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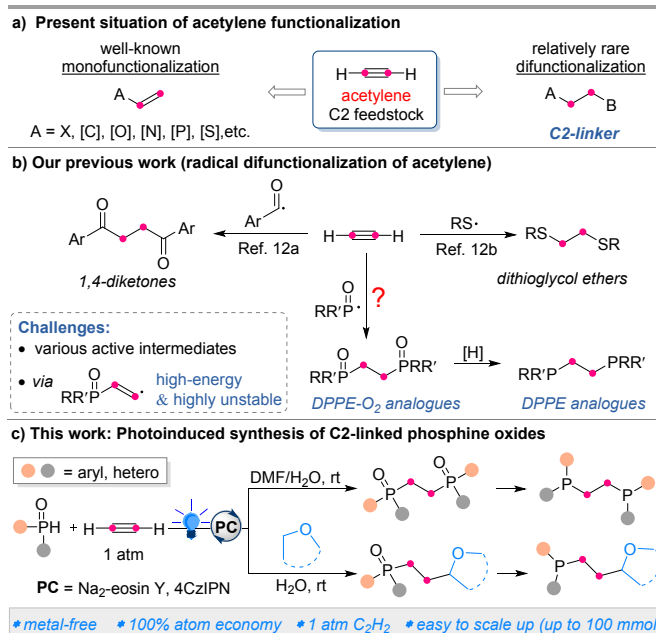
Herein, we report a photocatalyzed radical difunctionalization of acetylene for the rapid synthesis of C2-linked phosphine compounds. The reaction was initiated by addition of a phosphinoyl radical and followed by two cascade transformations. One involves a double addition for the formation of DPPE-dioxide analogues and the other where the intermediate vinylphosphine oxide is intercepted by a radical formed from an oxoheterocycle. This method features metal-free, mild condition (rt, 1 atm acetylene), 100% atom economy and easy operation. Furthermore, the reaction can be robustly performed on decagram scale.

Introduction

Organophosphorus compounds have widespread applications in the field of pharmaceuticals¹ and functional materials². In organic synthesis, they often play significant roles in the metal-catalyzed and organocatalytic reactions.³ For example, 1,2-bis(diphenylphosphino)ethane (DPPE) is an important biphosphine ligand for transition metal catalysis.^{3a} Recently, the dioxide of DPPE (DPPE-dioxide) and its analogues have also received attention in the synthesis of mononuclear metal complexes⁴ and the assembling of coordination polymers.⁵ Traditional strategies for the synthesis of DPPE primarily rely on the substitution reactions of highly reactive alkali metal diphenylphosphides (Ph₂PM) with 1,2-dihaloethanes in an S_N2 fashion,⁶ or the alkoxide-base-catalyzed hydrophosphination.⁷ However, in these methods, the use of organometallic reagents and strong base leads to low atom-economy and poor compatibility which conflicts with the goals of sustainable synthetic chemistry.

Acetylene has traditionally been regarded more as a fuel than as an economical chemical feedstock, though it has a huge annual production and broad applications in the chemical industries,⁸

which includes the production of vinyl-containing monomers (e.g., alkenyl amine, alkenyl chloride, acrylic acid), polymeric materials and other chemical commodities.⁹ As a versatile building block in organic synthesis, acetylene can participate in diverse transformations.¹⁰ In particular, it is often used to synthesize various functionalized vinyl molecules *via* monofunctionalization (Scheme 1a, left).¹¹ Nevertheless, the difunctionalization reaction is relatively rare (Scheme 1a, right).^{7b, 12} But importantly, difunctionalization of acetylene is a rapid and appealing approach to synthesize C2-linked molecules. In this regard, we recently reported two radical difunctionalization protocols of acetylene through a molecular glue strategy (Scheme 1b).¹² In these protocols, the target molecules (1,4-diketones or dithioglycol ethers) could be regarded as two components linked with acetylene as a carbon glue. Considering the importance of DPPE and its dioxide, we wondered if the difunctionalization of acetylene *via* cascade transformations involving phosphinoyl radical could enable the rapid synthesis of DPPE-dioxide and its analogues. However, a radical cascade



Scheme 1. Acetylene difunctionalization for C2-linked phosphine molecules

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process often involves various active intermediates.¹³ It is possible that the various radicals formed in situ react with acetylene or the newly formed intermediates to generate undesired products. In particular, the high-energy terminal alkenyl radical formed by radical addition to acetylene is highly unstable, has a short lifetime, and readily participates in undesirable pathways. So, the control of chemoselectivity would be a big challenge for this transformation.

Photocatalysis has emerged as a powerful and reliable tool for the construction of new chemical bonds because of its sustainable and eco-friendly characteristics.¹⁴ Among them, the direct radical addition to C-C π -bond is one of the most widely exploited transformations.¹⁵ Phosphine oxides are ideal radical precursors, which can produce phosphinoyl radicals *via* proton-coupled electron transfer (PCET) process under photocatalysis.¹⁶ Encouraged by these advances, we envisioned that photocatalysis might provide a green approach for radical difunctionalization of acetylene to synthesize C2-linked phosphine oxides. Herein, we report a photocatalyzed radical difunctionalization of acetylene, which enables the green synthesis of C2-linked phosphine oxides (Scheme 1c). This method features metal-free, 100% atom economy, mild conditions and ease of scaling-up (up to 20 g, 100 mmol). The reduction of these products can provide highly valuable phosphine ligands.

Results and discussion

Optimization studies

Initially, under 1 atm acetylene, diphenylphosphine oxide (**1a**) was chosen as standard substrate for the photocatalyzed radical difunctionalization reaction (Table 1). To our delight, the desired product **2a** was obtained in 48% yield with tetrahydrofuran (THF) as the solvent, the organic dye Na₂-eosin Y as the photocatalyst, and K₂CO₃ as the base under the irradiation of 10 W blue LED for 22 h (entry 1). Interestingly, a

Table 1: Condition optimization^a

$\text{Ph}_2\text{P}=\text{O} + \text{H}-\text{C}\equiv\text{C}-\text{H} \xrightarrow[\text{Solvent/H}_2\text{O, rt, blue LED}]{\text{PC, K}_2\text{CO}_3} \text{Ph}_2\text{P}(\text{O})-\text{CH}_2-\text{CH}_2-\text{P}(\text{O})\text{Ph}_2 + \text{Ph}_2\text{P}(\text{O})-\text{CH}_2-\text{CH}_2-\text{P}(\text{O})\text{Ph}_2$					
Entry	PC (2 mol%)	Solvent	Time (h)	Yield (%) ^b	
				2a	3a
1	Na ₂ -eosin Y	THF	22	48	45
2	4CzIPN	THF	20	29	53
3	Ir(ppy) ₃	THF	36	11	16
4	Tetrabromofluorescein	THF	28	22	35
5	Rose Bengal	THF	28	17	19
6	Na ₂ -eosin Y	MeCN	48	22	-
7	Na ₂ -eosin Y	DMF	15	80	-
8	Na ₂ -eosin Y	DMSO	45	76	-
9	Na ₂ -eosin Y	Toluene	48	13	-
10	Na ₂ -eosin Y (1 mol%)	DMF	15	78	-
11 ^c	4CzIPN	THF	28	7	71
12 ^d	Na ₂ -eosin Y (1 mol%)	DMF	15	trace	-

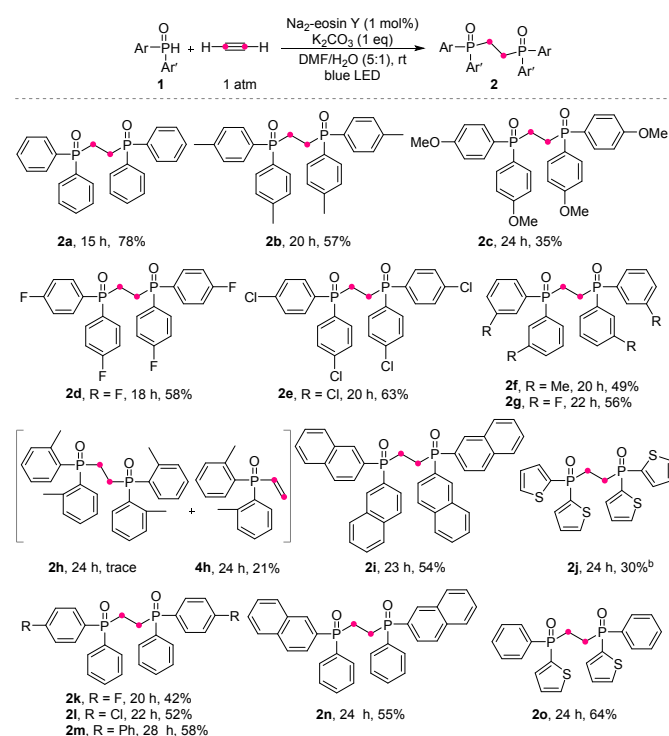
^aReaction conditions: **1** (0.3 mmol), PC (2 mol%), K₂CO₃ (0.3 mmol) and H₂O (0.5 mL) in solvent (2.5 mL), under 1 atm acetylene at room temperature, blue LED (460-470 nm, WATTCAS-China). ^bIsolated yield. ^c0.08, 0.08, 0.07, 0.06 mmol of **1a** were added in batches every 7 hours. ^dNo light.

solvent-involved product **3a** that generated from the addition of tetrahydrofuran radical was also isolated in 45% yield. When 4CzIPN was used as the photocatalyst, **2a** and **3a** were obtained in 82% total yield, but with a higher proportion of **3a** (entry 2). Other photocatalysts, such as Ir(ppy)₃, tetrabromofluorescein and rose bengal were also tested, while the yields were relatively low (entries 3-5). The effects of different solvents were also evaluated (entries 6-9) and the results indicated that DMF/H₂O was the best solvent with 2 mol% Na₂-eosin Y as photocatalyst, K₂CO₃ as base and the product **2a** could be selectively produced in 80% isolated yield (entry 7). Moreover, the amount of Na₂-eosin Y could be reduced to 1 mol% without significant impact on the yield of **2a** (entry 10). The accidental product **3a** is a C2-linked oxacyclic diarylalkylphosphine oxides, its reduction product may be an interesting ligand because of the liganacy of oxygen atom.³ⁱ To improve the yield and selectivity of **3a**, the substrate **1a** was added in batches to the reaction system with THF/H₂O as solvent (see ESI[†] for details). Gratifyingly, the yield of **3a** could be enhanced to 71% yield in the presence of 2 mol% 4CzIPN when four successive batches of **1a** were added every 7 hours (entry 11). Overall, the chemoselectivity of reaction could be switched by changing solvent and photocatalyst. Finally, the dark-condition control experiment attested that light is essential for this catalytic system.

Reaction scope

After establishing the optimal reaction conditions, the substrate scope of the photocatalyzed difunctionalization of acetylene was then explored. Firstly, the substrate scope of

Table 2: The substrate scope for synthesis of DDPE-dioxide analogues^a

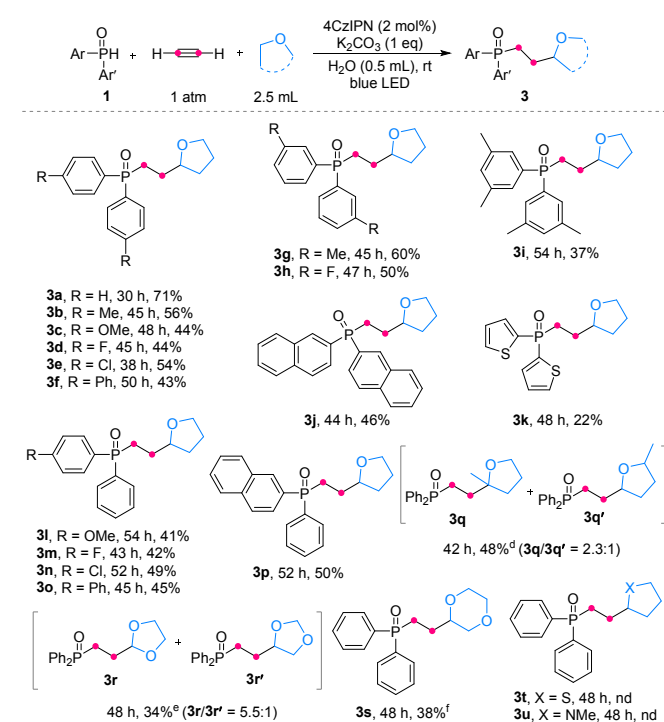


^aReaction conditions: **1a** (0.3 mmol), Na₂-eosin Y (1 mol%), K₂CO₃ (0.3 mmol) and H₂O (0.5 mL) in DMF (2.5 mL) under 1 atm acetylene at room temperature, blue LED (460-470 nm), isolated yield. ^b1.2 mmol scale.

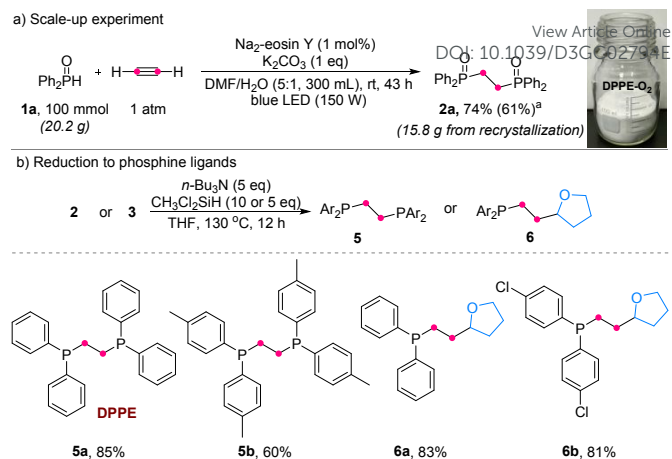
phosphine oxides for the synthesis of DPPE-dioxide analogues was investigated. As shown in Table 2, the symmetrical phosphine oxides having methyl (**2b**), fluorine (**2d**) and chlorine (**2e**) groups on the para position gave, under the standard conditions, the corresponding products in moderate yields (57-63%). The substrate with methoxy groups led to a lower yield (35%), possibly due to its strong electron-donating effect (**2c**). The substrates with substituents on *meta*-positions of phenyl group offered the desired products (**2f-g**) in acceptable yields (49-56%). Nevertheless, di-*o*-tolylphosphine oxide gave a trace amount of target product (**2h**), and the corresponding vinylphosphine oxide product **4h** was isolated in 21% yield, indicating that the reaction was seriously hampered by increasing steric hindrance. Even so, the 2-naphthalene substituted phosphine oxide with a large volume is suitable for this reaction (**2i**, 54% yield). In addition, phosphine oxides with two distinct aromatic rings were also tested and delivered 42-64% product yields (**2k-o**). It is worth noting that the substrates bearing thiophene were also accommodated, giving the desired products **2j** and **2o** in 30% and 64% yield, respectively.

After established the photocatalyzed difunctionalization of acetylene with two phosphinoyl radical for the green synthesis of DPPE-dioxide and its analogues, we then further moved to investigate the substrate scope for the synthesis of C2-linked oxacyclic diarylphosphine oxides **3**. As shown in Table 3, the

Table 3. The substrate scope for synthesis of C2-linked oxacyclic diarylalkylphosphine oxides^{a, b}



^aReaction conditions: **1** (0.3 mmol), 4CzIPN (2 mol%), K₂CO₃ (0.3 mmol) and H₂O (0.5 mL) in solvent (2.5 mL) under 1 atm acetylene at room temperature, blue LED (460-470 nm), isolated yield. ^b0.08 mmol, 0.08 mmol, 0.07 mmol, 0.06 mmol of **1** were added in batches every 7 hours. ^c0.6 mmol scale. ^d**1q** (0.6 mmol), blue LED (450-455 nm). ^e**1r** (0.6 mmol), blue LED (450-455 nm), ^fPr₂NEt was used instead of K₂CO₃. ^g4-DMAP was used instead of K₂CO₃.



Scheme 2. Scale-up experiment and reduction to phosphine ligands. ^aTotal two-step yield including substrate synthesis.

desired THF-incorporating phosphine oxides **3a-p** could be obtained in 22-71% yields when diarylphosphine oxides with different substitution patterns were used as substrates and THF as solvent. Moreover, different oxacyclic solvents were also incorporated. For example, when 2-methyltetrahydrofuran, 1,3-dioxolane and 1,4-dioxane were used as solvent, the corresponding desired products **3q-s** could be obtained in 34-48% yields. However, thiophene and 1-methylpyrrolidine could not participate in this reaction to furnish the desired products (**3t-u**).

Scale-up and reduction

To showcase the practicality of this system, a scale-up reaction was then tested. As shown in Scheme 2a, the reaction could be robustly scaled up to 100 mmol-scale of **1a** (20.2 g) giving the desired DPPE-dioxide **2a** (15.8 g) in 74% yield through recrystallization. When starting from the synthesis of substrate **1a**, the total yield of two-step process was 61%. Furthermore, by following the literature procedure,¹⁷ the phosphine oxide products **2** and **3** could be readily reduced by silane affording the corresponding phosphine ligands **5** and **6** (Scheme 2b). For example, **2a** and **2b** could be reduced respectively to DPPE **5a** and its analogue **5b** in 60-85% yields. Similarly, the reduction of **3a** and **3e** afforded two new monophosphine ligands **6a-b** in 81-83% yields.

Sustainability metrics

It is more accurate to analyze some sustainability metrics for assessing the green character in this protocol (Scheme 3). Atom

$$\text{Atom economy} = \frac{\text{FW (g/mol) product}}{\text{FW of all reactants}} \times 100\% \quad (1)$$

$$\text{PMI}_{(\text{reaction})} = \frac{\text{total input mass to reaction (g)}}{\text{mass of product (g)}} \quad (2)$$

$$\text{EcoScale} = 100 - \text{penalty points total} \quad (3)$$

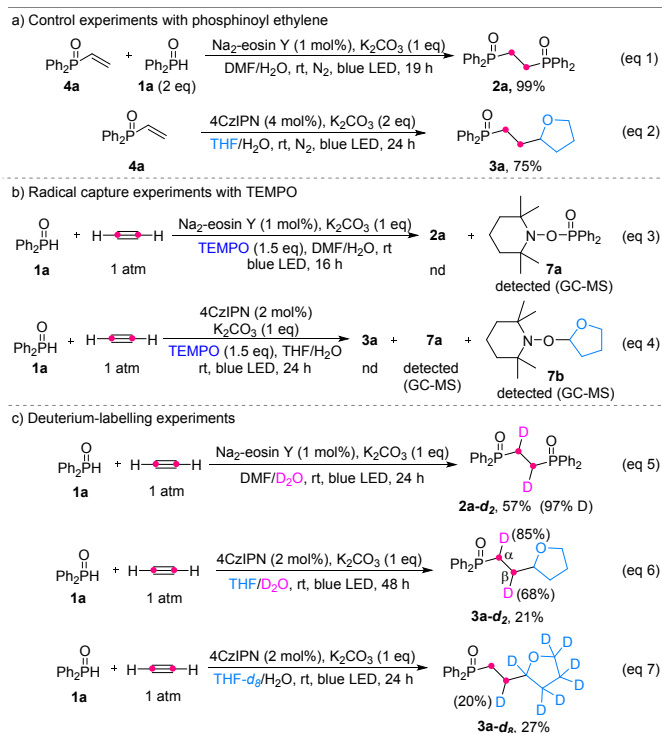
Entry	Sustainability metric	Value
1	Atom economy _(all reactions)	100%
2	PMI _(small-scale for 2a)	63.9
3	PMI _(small-scale for 3a)	48.5
4	PMI _(100 mmol-scale for 2a)	20.7
5	EcoScale _(100 mmol-scale for 2a)	56

Scheme 3. Sustainability metrics calculations

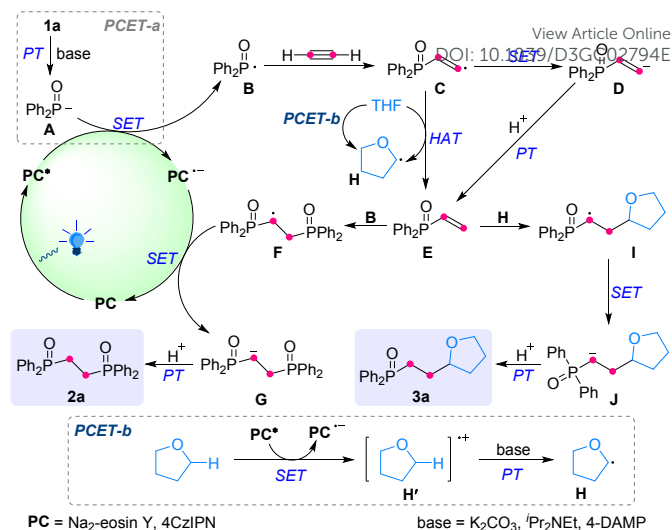
economy has always been an important metric to measure reaction efficiency (Scheme 3, eq 1).¹⁸ This is obviously ideal because the reaction system has 100% atom economy (Scheme 3, entry 1). Meanwhile, the waste streams information could be given by analyzing the process mass intensity (PMI) (Scheme 3, eq 2).^{18c, 18d} For small-scale reactions, the PMI values were 63.9 and 48.5, respectively (Scheme 3, entries 2-3). Noteworthy, the PMI can be reduced to 20.7 when the reaction was scaled up to 100 mmol (Scheme 3, entry 4). It is foreseeable that the PMI decreases as the scale increases. In addition, the EcoScale was also calculated to assist in the evaluation of the overall synthetic methodology including post-processing,^{18e} which scored 56 for 100 mmol-scale reaction (Scheme 3, entry 5, see ESI† for detail). The score indicated that the current methodology is an acceptable synthesis.

Mechanism studies

In order to gain insight into the mechanism of this radical cascade process, a series of control experiments were performed (Scheme 4). The desired products **2a** and **3a** were successfully obtained from the control experiments with vinylphosphine oxides (eqs 1-2), suggesting that vinylphosphine oxides are intermediates in this catalytic system. The radical trapping reagent 2,2,6,6-tetramethyl piperidinoxyl (TEMPO) was added to the two standard reactions, which all showed obvious inhibiting effect. The related TEMPO-captured products TEMPO-P(O)Ph₂ (**7a**) and TEMPO-THF (**7b**) could be detected by GC-MS (eqs 3-4). These results support a radical process. The deuterium-labelling experiment with D₂O gave the deuterated products **2a-d₂** and **3a-d₂** (eqs 5-6) indicating that H₂O was the proton source. But it is interesting that the deuterium rate on β-C (68%) of phosphinoyl was significantly lower than α-C (85%) for **3a-d₂** (eq 6), indicating the two hydrogen atoms of the newly-formed C-H



Scheme 4. Control experiments



Scheme 5. Proposed mechanism

bonds of **3a** are not just from water. It's well known that the *in-situ* alkenyl radical species can often abstract a hydrogen from THF.^{12a, 15c} Therefore, the deuterium-labelling experiment with THF-d₈ was also performed (eq 7). Indeed, the deuterium atom of THF-d₈ was also transferred to the β-C of phosphinoyl but with a lower proportion (20%), which verified that THF can also act as a H source through hydrogen atom abstraction. So, there are two possible quenching forms for alkenyl radical in this protocol, one is being reduced to carbanion followed by proton transfer (PT), another is abstracting hydrogen atom from THF.

Based on the above results and also in consideration of the related literature reports,^{12a, 15c, 16, 19} a plausible reaction mechanism is proposed for the present transformations (Scheme 5). First, a phosphinoyl radical (**B**) is produced *via* proton-coupled electron transfer (PCET) oxidation in the presence of K₂CO₃ and photoexcited catalysts (*PCET-a*). Then the addition of radical **B** to acetylene affords terminal alkenyl radical **C**. The radical **C** can be reduced to carbanion **D** *via* SET process, and then converted to vinylphosphine oxide **E** *via* PT process in the presence of water. In addition, radical **C** can quickly abstract a hydrogen from THF, resulting in the formation of vinylphosphine oxides **E** and tetrahydrofuran radical **H**. Meanwhile, the radical **H** may also be produced from THF *via* a PCET process in this condition (*PCET-b*).^{19d-f} Subsequently, the further addition of radicals **B** and **H** to the vinylphosphine oxides **E** generates the corresponding alkyl radicals **F** and **I**, respectively. Finally, the desired products **2a** and **3a** can be obtained from the radicals **F** and **I** *via* SET and PT process.

Conclusions

In conclusion, we developed a green protocol to realize the synthesis of C2-linked phosphine oxides compounds *via* a molecular glue strategy with acetylene as the C2-synthon under visible-light catalysis. The various DPPE-dioxide analogues and C2-linked oxacyclic diarylalkylphosphine oxides have been prepared efficiently under 1 atm acetylene

atmosphere. This method features transition metal-free, 100% atom economy and easy operation, which demonstrates a green approach to rapidly synthesize functional molecules from acetylene and simple raw materials. Importantly, the reduction of these products can furnish highly valuable phosphine ligands. The mechanistic investigation indicates that this protocol involves two cascade transformations of radicals. We anticipate that this protocol will provide a platform for multicomponent radical reactions of acetylene.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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