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# Photoexcited nitroarene-enabled carbon chain-elongated oxidation of alkenes via tandem oxidative cleavage and dipolar cycloaddition

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Oxidation of alkenes with $O_3$ and photoexcited nitroarenes represents one of the most attractive organic chemical transformations for the synthesis of oxygen-enriched molecules. However, known achievements are mainly limited to carbon chain-shortened oxidation and carbon chain-retained oxidation of alkenes. Given that constructing higher molecular complexity is the core goal of modern synthesis, the development of chain-elongated oxidation of alkenes would be in high demand but still remains an elusive challenge so far. Herein, we report a photoexcited nitroarene-enabled highly regioselective chain-elongated oxidation of alkenes via tandem oxidative cleavage and dipolar cycloaddition, providing a broad range of synthetically-useful isoxazolidines in up to 92% yield from readily available enol ethers or styrene and derivatives under simple and mild conditions.

Oxidation of alkenes is one of the most fundamental chemical transformations, not only because alkenes are feedstock chemicals that are readily available from petroleum and biomass, but also because such oxidations provide convenient and economical routes to oxygen-enriched molecules such as epoxides, 1,2-diols and carbonyls, which are prevalent in numerous natural products, pharmaceuticals and agrochemicals[1–7]. Widely-used oxidants for alkene oxidation are metal oxides such as $OsO_4$ and $KMnO_4$, yielding desired oxygen-enriched products but with stoichiometric metallic waste (Fig. 1a, left)[8–18]. To eliminate metallic waste towards achieving greener oxidation methods, non-metal oxidants such as ozone ($O_3$)[19–28] and its surrogates, photoexcited nitroarenes[29–57], have received constantly growing interest during the past decades (Fig. 1a, right). For example, the ozonolysis reaction of alkenes is a well-known process, effectively converting alkenes into various carbon chain-shortened carbonyl products (Fig. 1b, path i)[19]. Recently, Leonori and Parasram independently found that photoexcited nitroarenes was superior surrogates of ozone, enabling oxidative cleavage of alkenes in a safer and more cost-economical fashion[37,38]. Moreover, it was revealed that photoexcited nitroarenes with proper electron-withdrawing substituents on the aryl rings have a more tunable oxidative ability than ozone. Followed oxidative cleavage reactions that lead to carbon chain-shortened oxidations of alkenes, a dihydroxylation reaction of alkenes was recently developed by Thomas et al. (Fig. 1b, path ii)[40], who used ozone as an oxidant and $^{i}$PrMgBr as a trapping nucleophile to intercept oxidative intermediate, thus obtaining vicinal diols that have increasing molecular complexity than carbonyl products from traditional ozonolysis, because carbon chains of alkenes are not broken, instead, well retained. In the same year, Leonori et al. also realized a photoexcited nitroarene-enabled dihydroxylation of alkenes via one-pot N–O bond hydrogenation under milder and more practical conditions[41]. Beyond dihydroxylation, most recently, Parasram et al. reported a new type of carbon chain-retained oxidation, in which alkenes are oxidized into the corresponding carbonyls (monohydroxylation)[56]. Compared with the great advances in

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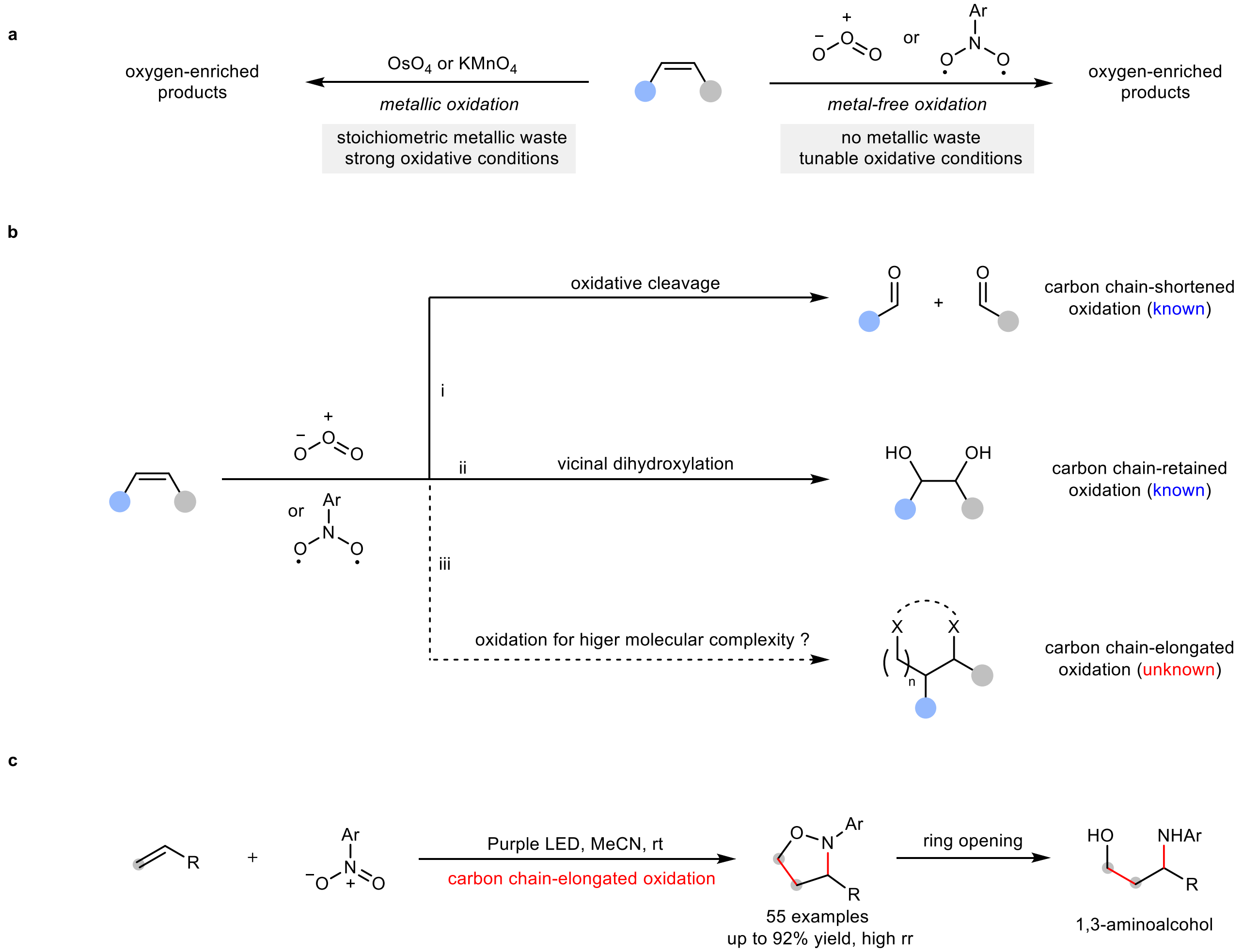


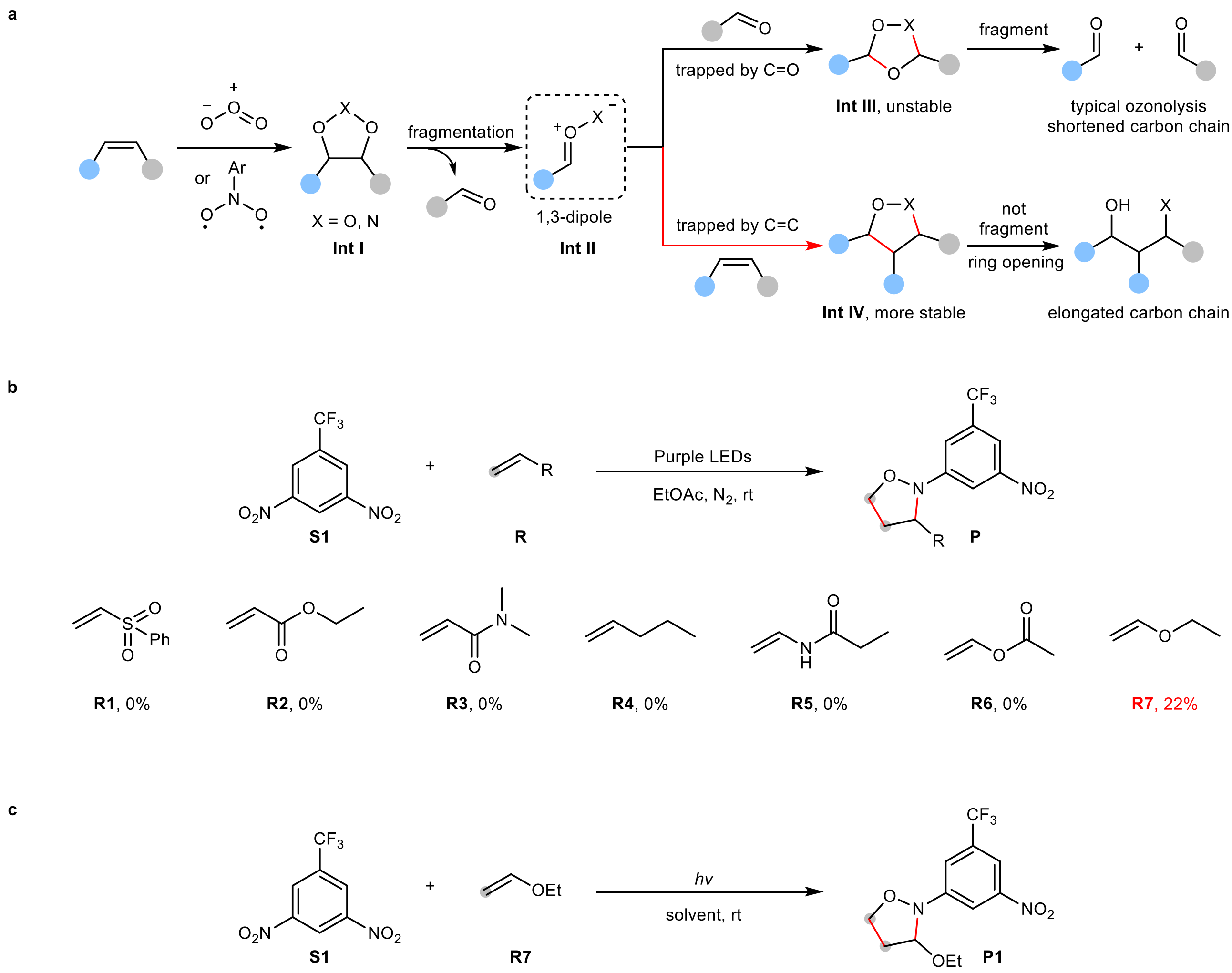
**Fig. 1 | Oxidation of alkenes with ozone or photoexcited nitroarenes. a** Two main types of oxidation of alkenes. **b** Three possible pathways for oxidation of alkenes by $O_3$ and photoexcited nitroarenes: carbon chain-shortened oxidation via oxidative cleavage of alkenes (path i, known); carbon chain-retained oxidation via vicinal dihydroxylation (path ii, known); carbon chain-elongated oxidation (path iii, unknown). **c** This work: photoexcited nitroarene-enabled carbon chain-elongated oxidation via tandem oxidative cleavage and dipolar cycloaddition.

carbon chain-shortened oxidations (ozonolysis) and carbon chain-retained oxidations (dihydroxylation or monohydroxylation), the development of carbon chain-elongated oxidation of alkenes to construct higher molecular complexity still remains an elusive challenge (Fig. 1b, path iii). During our submission, Li and co-workers reported a carbon chain-elongated oxidation of terminal alkenes, providing a series of isoxazolidines in up to 70% yield[57]. Here, we show a safe and green photoexcited nitroarene-enabled carbon chain-elongated oxidation of alkenes via tandem oxidative cleavage and dipolar cycloaddition (Fig. 1c), providing a wide range of synthetically-useful isoxazolidines in up to 92% yield with high regioselectivity[58,59], which are versatile synthetic precursors to important organic molecules such as 1,3-aminoalcohols.

## Results

### Reaction development

In ozone or nitroarene-mediated oxidation of alkenes (Fig. 2a)[26–28], initially formed heterocycles (**Int I**) such as primary ozonide (X = O) or 1,3,2-dioxazolidines (X = N) easily fragment into 1,3-dipoles (**Int II**), including carbonyl oxides (X = O) or carbonyl imines (X = N). These intermediates can be quickly trapped by polar C = O double bonds to generate more unstable heterocycles (**Int III**) such as secondary ozonide (X = O) or 1,4,2-dioxazolidine (X = N). Subsequent fragmentation gives carbon chain-shortened carbonyls as products. To shift this pathway towards achieving higher molecular complexity, we envisioned to use non-polar C = C bond instead of polar C = O double bond to trap 1,3-dipole (**Int II**), thus forming a more stable heterocycle (**Int IV**) that would not undergo fragmentation, instead, act as a carbon chain-elongated oxidative product. However, two critical challenges have to be overcome: 1,3-dipoles need to be stable enough to be trapped, and non-polar C = C must override polar C = O double bond in the capture of 1,3-dipoles. With these considerations in mind, we selected highly-tunable nitroarenes as oxidants to investigate representative alkenes (Fig. 2b), because nitroarenes with strong electron-withdrawing groups have been proved to be able to provide more stable 1,3-dipoles during the oxidation of alkenes[37,38]. With 3,5-dinitrotrifluorotoluene as a model oxidant, various terminal alkenes with different electronic property were examined, and the results showed that most alkenes bearing either electron-withdrawing substituents (**R1**–**R3**) or electron-donating substituents such as alkyl group (**R4**), amido group (**R5**) and acetoxyl group (**R6**) did not give the desired products. Only the electron-donating ethoxyl group (**R7**) proved effective, affording the isoxazolidine product in 22% yield. Further systematic survey on light source, light intensity, loadings of alkenes and solvents disclosed the optimal conditions: 385–390 nm and 8 W LED light, 8.0 equivalents of ethoxyethene (**R7**) in $CH_3CN$ under $N_2$ atmosphere at room temperature, under which the desired product (**P1**) was obtained in 92%



| entry | deviation from the standard conditions | yield (**P1**, %) |
|---|---|---|
| 1 | standard conditions: 385-390 nm, 8 W LED, 8.0 equiv. of **R7**, $CH_3CN$, $N_2$, 12 h | 92 |
| 2 | without light | 0 |
| 3 | under air | 15 |
| 4 | 380-385 nm LED | 70 |
| 5 | 395-400 nm LED | 74 |
| 6 | 6 W LED | 67 |
| 7 | 10 W LED | 77 |
| 8 | 6.0 equiv of **R7** | 83 |
| 9 | 3.0 equiv of **R7** | 55 |
| 10 | EtOAc instead of $CH_3CN$ | 33 |
| 11 | $CH_2Cl_2$ instead of $CH_3CN$ | 28 |
| 12 | $CH_3CH_2CN$ instead of $CH_3CN$ | 61 |

**Fig. 2 | Reaction development. a** Reaction proposal: the interception of 1,3-dipole with polar C = O will lead to typical ozonolysis, while the interception of 1,3-dipole with nonpolar C = C will give carbon chain-elongated oxidation reaction of alkenes. **b** Alkene identification. Reaction conditions: **S1** (0.2 mmol), **R** (0.6 mmol), EtOAc (2.0 mL), 8 W 385–390 nm LED, $N_2$, room temperature, 12 h; yield was determined by $^1$H NMR using $Cl_2CHCHCl_2$ as the internal standard. **c** Conditions optimization. Optimal conditions: **S1** (0.2 mmol), **R7** (1.6 mmol), $CH_3CN$ (2.0 mL), 8 W 385–390 nm LED, $N_2$, room temperature, 12 h; yield was determined by $^1$H NMR using $Cl_2CHCHCl_2$ as the internal standard.

yield (Fig. 2c, entry 1). Control experiments showed that the absence of light completely shut down the reaction (entry 2), and the presence of $O_2$ also greatly diminished the yield (entry 3). In addition, the wavelength and the intensity of light had a strong influence on the yield, and slight variations resulted in lower yields (entries 4–7). Another two critical factors directly impacting the reactivity are solvents and loadings of alkenes (entries 8–12). The use of 8 equivalents of alkenes and $CH_3CN$ was the best option.

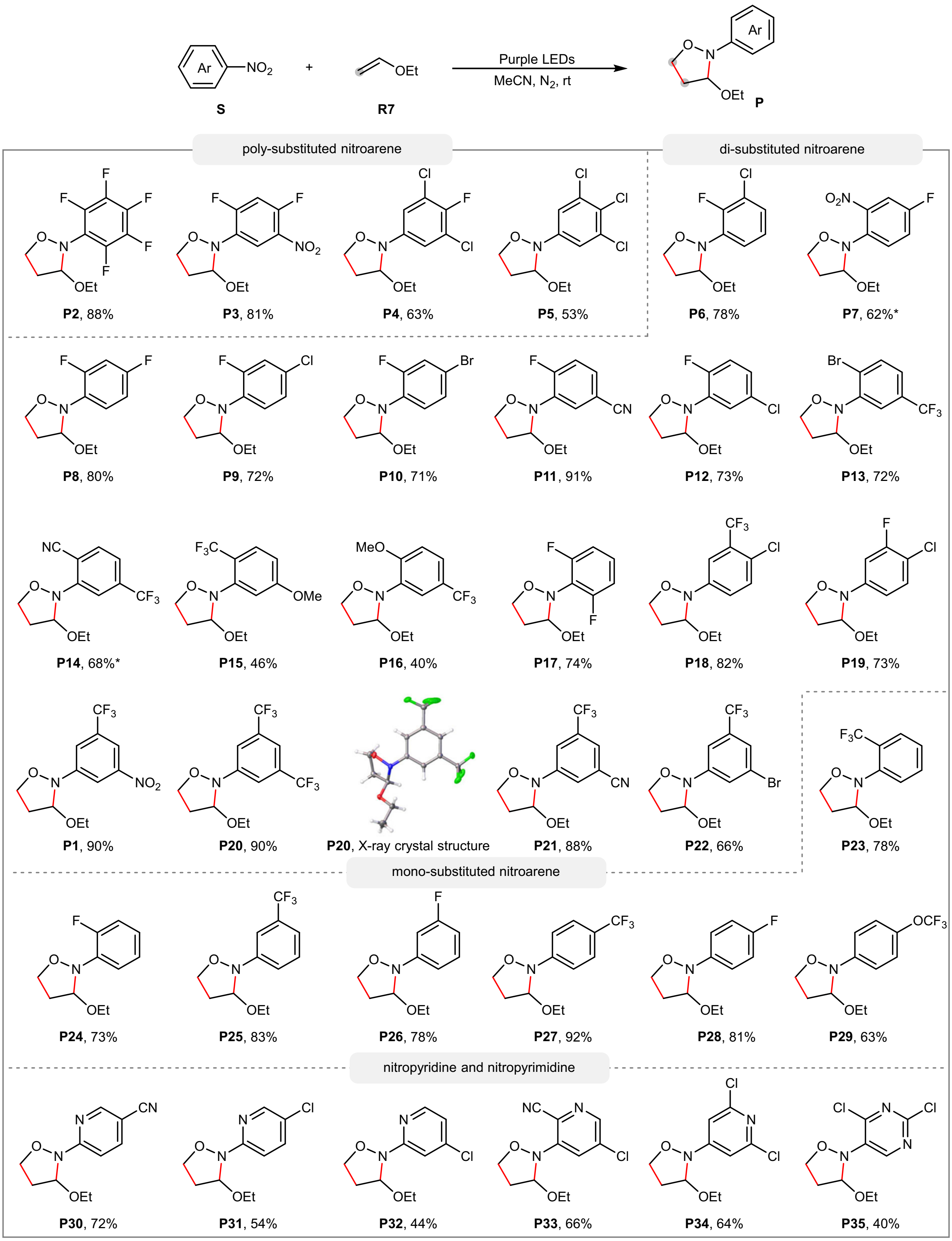


**Fig. 3 | Scope of nitroarenes.** Reaction conditions: **S** (0.2 mmol), **R7** (1.6 mmol), MeCN (2.0 mL), 8 W 385–390 nm LED, $N_2$, room temperature, 12 h; yield of isolated products. *16 h.

## Scope of nitroarenes and alkenes

With the optimal reaction conditions established, we turned to investigate the scope of nitroarenes (Fig. 3). As demonstrated by previous oxidations[37,38,41], the presence of electron-withdrawing groups on the aryl ring was essential to the reactivity. Three or more electron-withdrawing groups such as F, Cl, and $NO_2$ on the aryl ring were well compatible, providing the corresponding products in 53–88% yield (**P2**–**P5**). Various combinations of two electron-

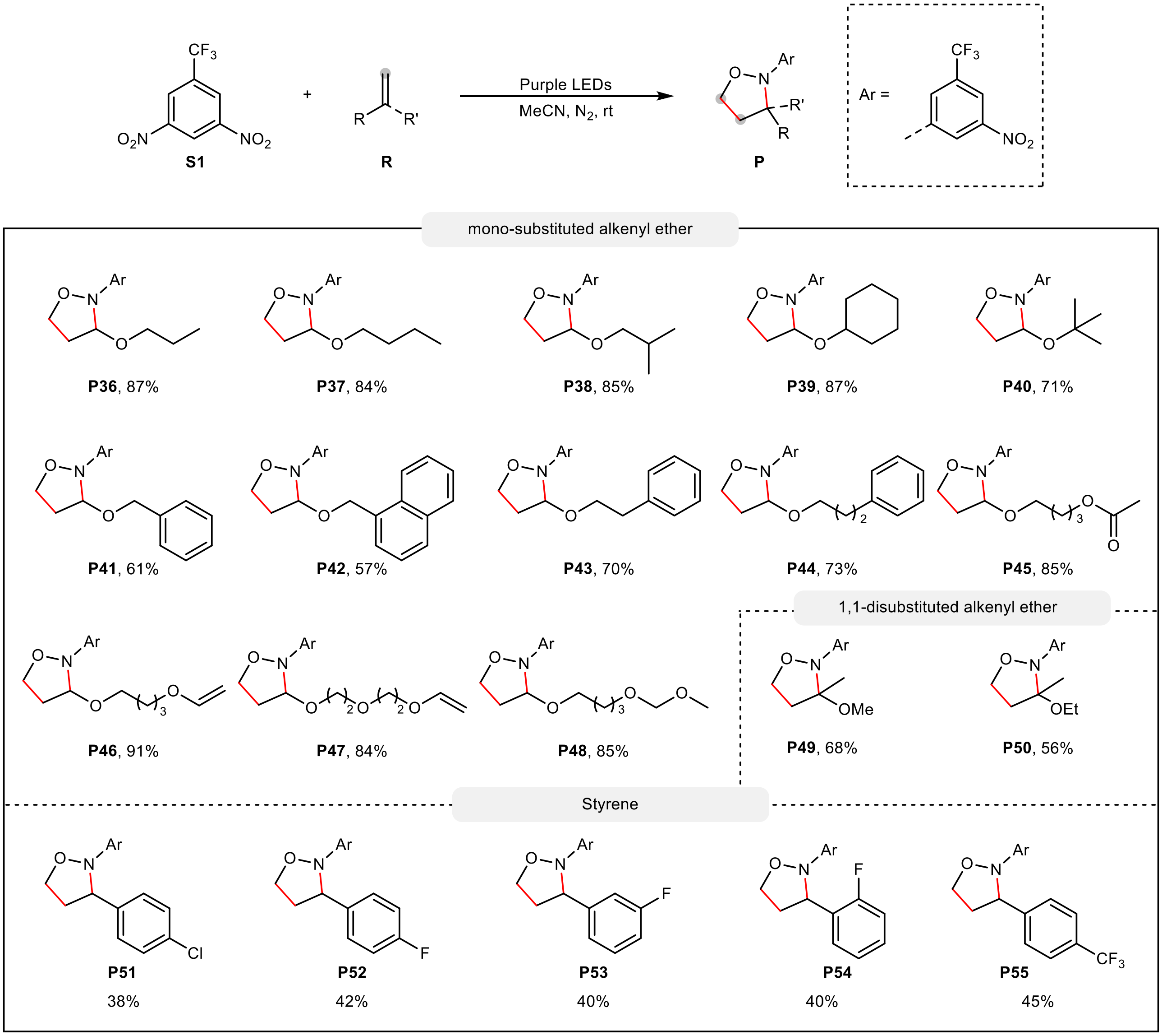


**Fig. 4 | Scope of alkenes.** Reaction conditions: **S1** (0.2 mmol), **R** (1.6 mmol), MeCN (2.0 mL), 8 W 385–390 nm LED, $N_2$, room temperature, 12 h; yield of isolated products.

withdrawing groups such as F, Cl, Br, CN, $CF_3$ and $NO_2$ at different positions of the aryl ring were also suitable. For example, 2,3-disubstituted (**P6**), 2,4-disubstituted (**P7** to **P10**), 2,5-disubstituted (**P11**–**P16**), 2,6-disubstituted (**P17**), 3,4-disubstituted (**P18, P19**) and 3,5-disubstituted (**P20, P21, P22**) nitroarenes all underwent the reaction very well, providing the corresponding products in up to 91% yield. The structure of **P20** was further confirmed by the single-crystal X-ray diffraction. Notably, when the $CF_3$ group was presented, even an electron-donating methoxyl group was also tolerated (**P15, P16**). Encouraged by this result, we then examined nitroarenes bearing only one electron-withdrawing group at the aryl ring such as F, $CF_3$ and $OCF_3$ at *ortho* (**P23, P24**), *meta* (**P25, P26**) or *para* (**P27, P28, P29**) positions and found that they all worked well in the reaction, delivering 63–92% yield. It is worth noting that nitroheteroarenes such as nitropyridines and nitropyrimidines were also effective oxidants, providing the corresponding products in 40–72% yield (**P30**–**P35**).

Next, the scope of alkoxy alkenes was investigated (Fig. 4). Alkyl groups varing from linear alkyl groups (**P36, P37**), branched alkyl groups (**P38, P39**), highly sterically-hindered alkyl groups (**P40**) to alkyl groups attched by functional groups such as aryl group (**P41**–**P43**), O-containing functional groups (**P44**–**P48**) were well compatible, delivering the corresponding products in 53 – 91% yield. When alkenes contain double enol ethers, only one enol ether was oxidized into isoxazolidine without observing full oxidation of the two enol ethers (**P46, P47**).

Besides mono-substituted alkenes, 1,1-disubstituted alkenes were also effective, giving the corresponding products in 56 – 68% yield (**P49, P50**), while sterically-hindered internal alkenes were, in general, ineffective in the reaction. Notably, styrene and derivatives also proved effective in the current oxidation reaction, providing a mixture of regioisomers in up to 66% yield (**P51** to **P55**).

## Reaction utility and mechanistic discussion

To demonstrate the utility of the current method, the model reaction was run at gram scale, smoothly affording product **P1** in 76% yield (Fig. 5a). Ethoxyl group-containing isoxazolidines proved to be versatile precursors (Fig. 5b). The treatment of **P1** with $BF_3·Et_2O$ produced a reactive iminium intermediate, which can be in situ trapped by various nucleophiles such as allyltrimethylsilane (**P57**), trimethylsilyl cyanide (**P58**) and trimethyl phosphite (**P59**), providing the corresponding products in 90–95% yield.

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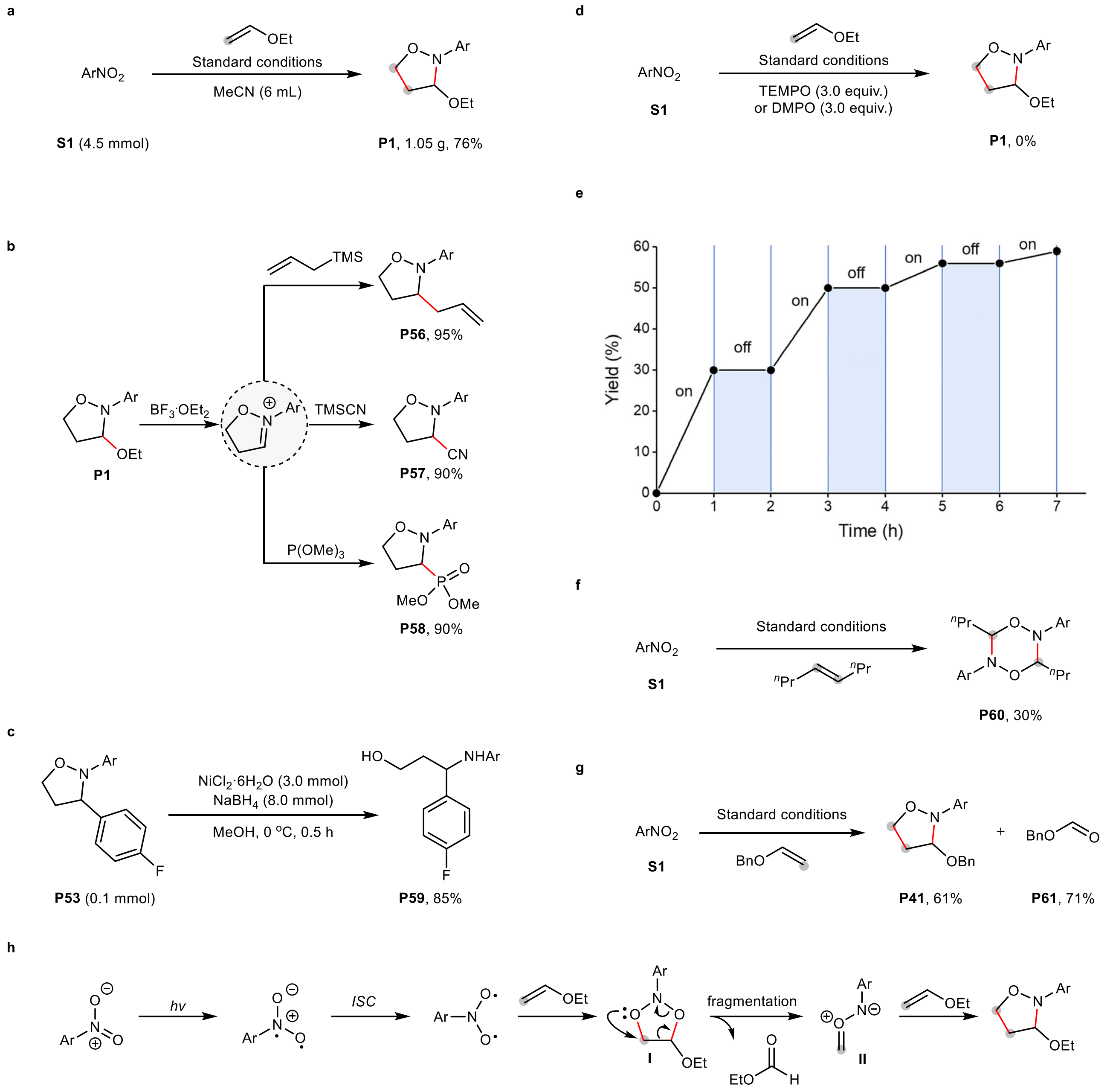

**Fig. 5 | Synthetic utility and mechanistic experiments.** **a** Gram-scale reaction. **b** Versatile transformations of ethoxyl group of isoxazolidine. **c** Ring opening of isoxazolidine for 1,3-aminoalcohol. **d** Radical trapping experiment. **e** Light on-off experiments. **f** Intermediate trapping experiment. **g** Isolated byproduct. **h** Proposed mechanism. Ar = 3-$NO_2$-5-$CF_3$-$C_6H_3$.

When treated with nickel chloride hexahydrate and sodium borohydride, isoxazolidine **P54** was easily transformed into 1,3-aminoalcohol in 85% yield via the cleavage of O–N bond (**P60**, Fig. 5c). To gain more insight into the mechanism, relevant mechanistic studies were conducted. The addition of radical scavengers such as (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) and 5,5-dimethyl-1-pyrroline N-oxide (DMPO) completely inhibited the oxidation (Fig. 5d), indicating that a radical process may be involved. Light "on–off" experiments confirmed the necessity of continuous irradiation for the oxidation (Fig. 5e). When a sterically-hindered internal alkene was used as a substrate, unexpected product **P60** instead of isoxazolidine was observed (Fig. 5f). We reasoned that **P60** came from the combination of two carbonyl imine intermediates that cannot be intercepted by bulky internal alkene. The observed aldehyde **P61** formation under standard conditions suggests a reaction pathway involving ozone-like intermediate-mediated alkene cleavage (Fig. 5g). On the basis of these results and previous studies[37,38], a plausible mechanism was then proposed as follows (Fig. 5h): photoexcitation of nitroarene and subsequent intersystem crossing (ISC) forms a biradical intermediate, which then undergoes radical addition with an alkene to provide a short-lived heterocycle **I**. The fragmentation of **I** affords a crucial carbonyl imine intermediate **II** along with an aldehyde as a byproduct. Finally, intermediate **II** is trapped by the alkene to produce the desired isoxazolidine product.

In summary, we have developed a photoexcited nitroarene-enabled carbon chain-elongated oxidation of alkenes via tandem oxidative cleavage and dipolar cycloaddition, wherein the alkene first undergoes oxidative cleavage to form a key carbonyl imine dipole that is captured by the alkene itself to give the final carbon chain-elongated oxidative product. The use of proper alkenes such as enol ether or styrene and derivatives proves critical to the reactivity, and a wide range of isoxazolidines can be obtained in up to 92% yield with high regioselectivity. The reaction demonstrates that the development of versatile transformations beyond ozonolysis and dihydroxylation for ozone or photoexcited nitroarene-enabled oxidation of alkenes is feasible.

## Methods

### General procedure for synthesis of 1,2-isoxazolidines

To a 30 mL oven-dried photoreaction tube were added nitroarenes (0.2 mmol, 1.0 equiv.), dry degassed MeCN (2.0 mL), and alkenes (1.6 mmol, 8.0 equiv.) in an $N_2$-filled glove-box. The tube was sealed, removed out of the glove box, and irradiated by purple light (385 nm, 8 W) in paralleled reactor for 12 h or until the reaction was completed. Crude product was obtained after evaporation of solvents, and further purified by flash column chromatography on neutral silica gel (eluting with $Et_3N$/ethyl acetate/*n*-hexane = 1:1:200 to 1:1:40).

## Data availability

For the experimental procedures and data of NMR, see Supplementary Methods in the Supplementary Information file. The X-ray crystallographic coordinates for structures reported in this study have been deposited at the Cambridge Crystallographic Data Center (CCDC), under deposition number CCDC 2379082. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via https://www.ccdc.cam.ac.uk/structures/. Data supporting the findings of this study are also available from the corresponding author upon request.

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## Author contributions

X.G. developed the reaction and wrote the Supplementary Information. X.C. and M.L. performed part of the synthetic experiments and collected part of the data. Q.-L.Z. gave valuable advice. W.X. and M.Y. conceived the reaction and wrote the manuscript.

## Competing interests

The authors declare no competing interests.

## Additional information

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