Triplet Excited Nitroarene Coverts Linear Alkynes to Bent Ketones by Deleting a Carbon Atom

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Abstract

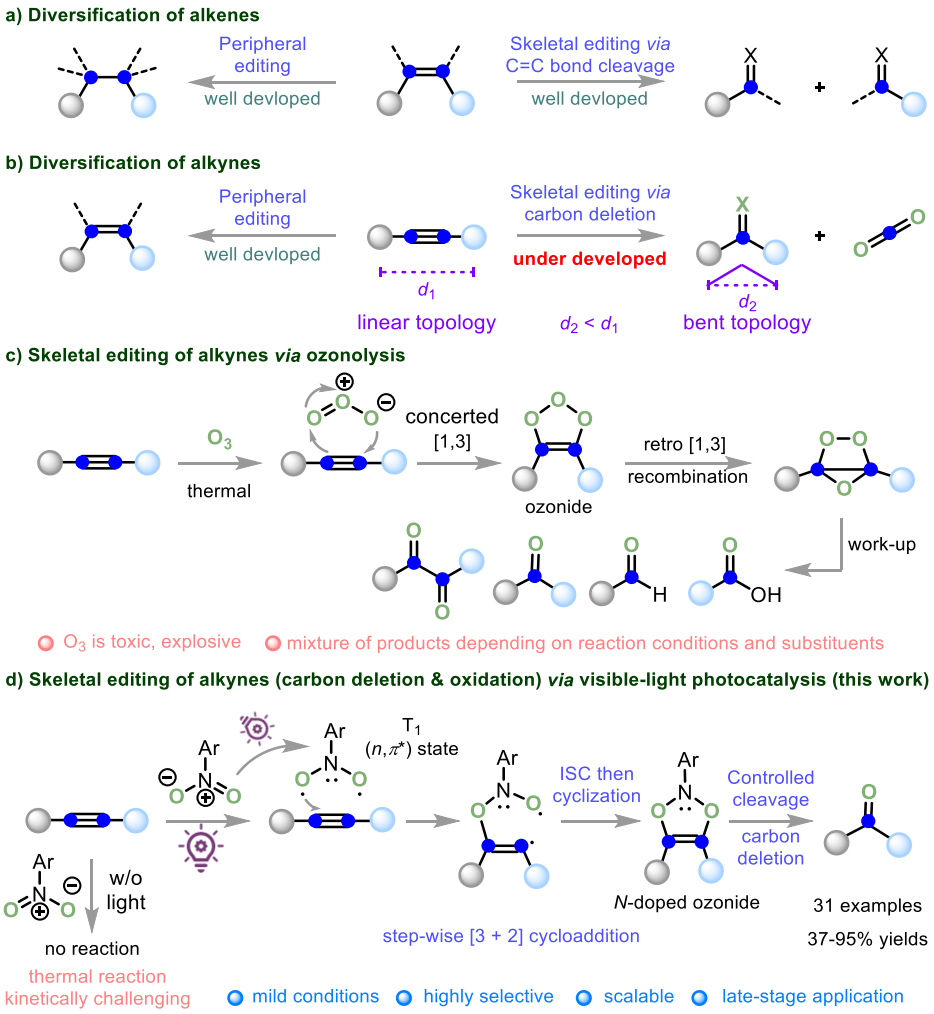
Alkynes are rarely modified using visible light catalysis employing molecular editing techniques. In this work, we utilized triplet excited nitroarenes to transform linear alkyne topology to bent ketone fragments. The process involves the concurrent insertion of an oxygen atom and the detection of a carbon atom. The effectiveness and broad applicability of this approach were demonstrated through its successful application across diverse substrates (31 examples), compatibility with various functionalities and the modification of bioactive molecules, scalability in large-scale synthesis in continuous flow, and the synthesis of commercially available drug molecules. UV-vis spectroscopic studies unveiled the role of visible light in exciting the nitroarene in its triplet state. Preliminary mechanistic experiments by various kinetic and control experiments elucidated ketene and nitrosoarene as the key intermediates. The deleted carbon is released as CO and CO_2 gases.

Introduction

The recent progress in organic synthesis has generated significant interest in molecular rearrangement or skeletal editing techniques, enabling the selective and systematic addition or removal of atoms from a molecular structure.[1] In this regard, independent studies by Levin[2], Sarpong,[3] Morandi,[4] Tobisu[5], and others[6] led the recent endeavors. The literature expedition evidenced investigations on the skeletal edition (CC-bond cleavage) of olefins *via* ozonolysis that involved thermal [1,3]-dipolar cycloaddition (Figure 1a).[7] The *in situ* formed 1,2,3-ozonide facilitates immediate cycloreversion, resulting in C-C sigma bond cleavage to produce carbonyl compound and carbonyl oxide, giving 1,2,4-ozonide after recombination. Despite its versatility as an oxidant, the toxic, explosive, and hazardous nature of ozone, as well as the requirement of Ozonator, has led to the search for a greener and more sustainable counterpart.[8] In this

pursuit, Buchi and Ayer,[9] and de Mayo,[10] and more recently, Parasram[11] and Leonori[12] explored photoexcited nitroarenes as a surrogate of ozone for oxidative cleavage of olefins.

Figure 1. (a,b) Peripheral and skeletal editing of alkenes and alkynes. (c) Skeletal editing of alkynes via ozonolysis. (d) This work: Editing of alkynes by photoexcited nitroarene.



Alkynes with two degrees of unsaturation could also offer significant potential for extensive synthetic modifications (Figure 1b).[13] The ozonolysis of alkynes gave mixtures of products, with the precise composition of these products being influenced by both the reaction conditions and the electronic characteristics of the substrate (Figure 1c). The cleavage of alkynes has been reported with stoichiometric transition metal oxides,[14] hypervalent iodine,[15] peracids,[16] and pressurized molecular oxygen[17]. A previous reaction of alkynes with photoexcited nitrobenzene under mercury arc lamp irradiation for three days produced a mixture of benzophenone-anil, carbon dioxide,

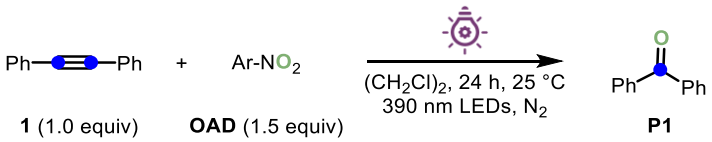
nitrosobenzene, dibenzanilide, 2-hydroxyazobeneze, and β-lactam.[18] However, the use of such challenging conditions and the creation of mixtures of products have limited the scope and feasibility of these methods, especially in fine chemical industries and innovative sectors that depend on high-throughput techniques.

Motivated by the previous success,[11-12, 19] we conceived triplet excited nitroarenes as ozone surrogates for introducing an oxygen atom in framing molecular skeleton *via* oxygen atom transfer under mild visible-light irradiation (Figure 1d). Although nitroarenes are isoelectronic with ozone, the [1,3]-dipolar cycloaddition is thermodynamically unfavorable for nitroarenes due to high kinetic barriers.[20] Upon visible-light excitation, singlet excited nitroarene stabilized itself to a long-lived triplet state (T_1) after intersystem crossing.[10] Owing (n,π^*) configuration, the T_1 state behaves similarly to O-radicals.[10] We envisioned that it could channelize a step-wise radical [3 + 2] cycloaddition with alkynes to produce *N*-doped ozonide species (1,3,2-dioxazolidines).[21] The latter could then undergo molecular rearrangement. This would effectively modify internal alkynes through oxidative cleavage, achieving formal carbon deletion and serving as a promising protocol for skeletal editing strategies. From the molecular topology point of view, it would convert a linear molecular vector into a bent fragment and would bring the functionalities in proximity (Figure 1b, right). Furthermore, it will broaden the potential to harness the degrees of unsaturation in alkynes for a wide array of functional applications.

Results and discussion

Diphenylacetylene **1** is taken as the model substrate (Table 1). Initial investigation of the reaction of **1** with nitrobenzene as an oxygen atom donor (OAD) in 1,2-dichloroethane under the irradiation of purple light emitting diodes (LEDs, λ_{max} = 390 nm) at 25 °C produced 56% yield of the rearranged product **P1** (entry 1). Lower yields of **P1** were obtained as 2-fluoro nitrobenzene, 3-, and 4-cyano nitrobenzene, and 2-iodo-5-nitro pyridine was used as OADs (entries 2-5). Notably, the reactions with 1,4-dinitrobenzene, 1-fluoro-2,4-dinitrobenzene as OADs gave higher 63% and 69% yields of **P1**, respectively (entries 6,7). The highest 82% yield of **P1** was obtained with 1-chloro-2,4- dinitrobenzene as the OAD (entry 8). Control experiments demonstrated that purple LED irradiation is necessary for the reaction (entry 9). **P1** did not form in the dark, even when heated at 60 °C (entry 10). The detailed optimization has been provided in the Electronic Supplementary Information.

Table 1. Evaluation of OAD for the carbon deletion reaction.[a]

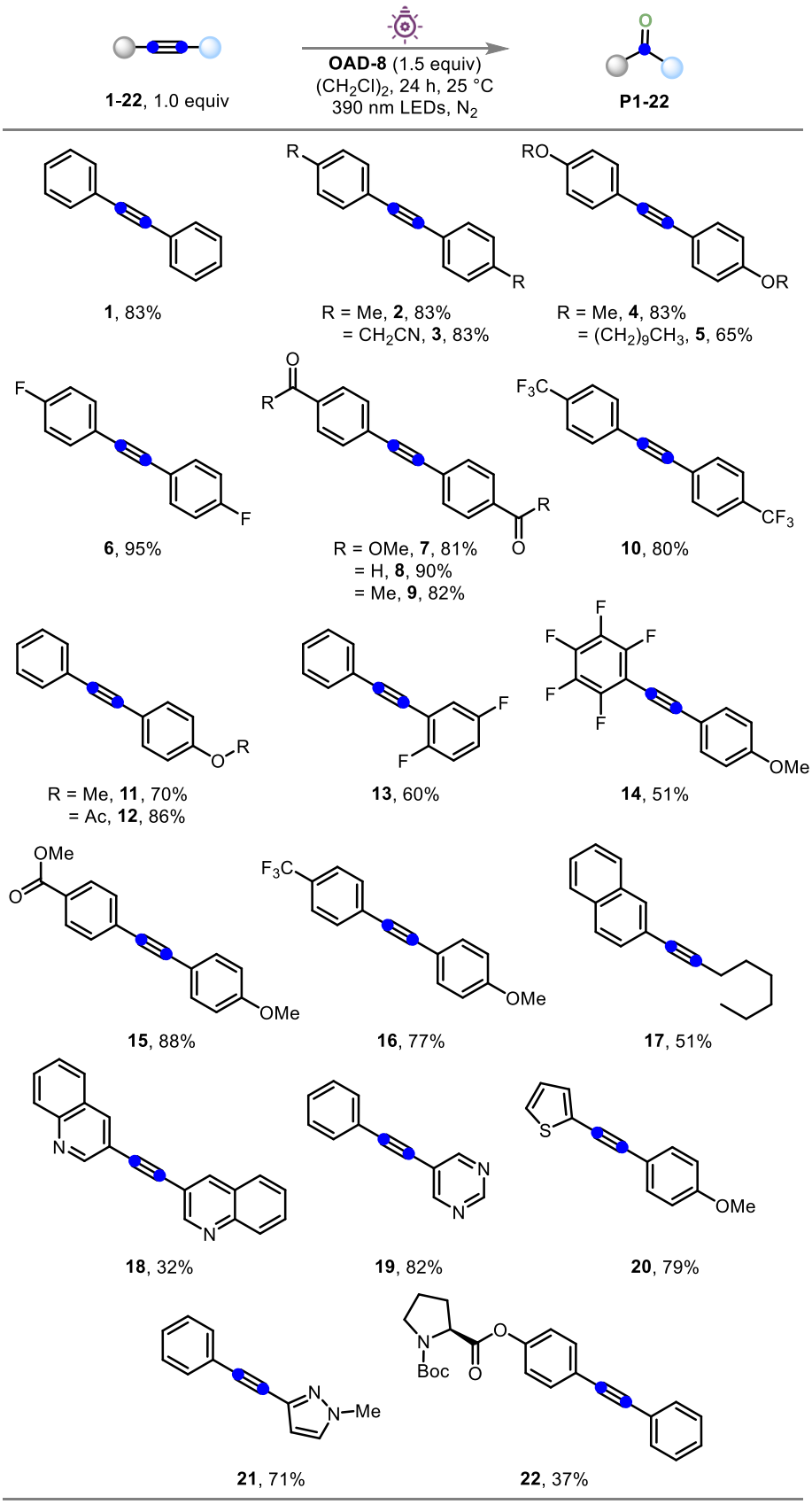


Entry	**OAD**	Yield (%)
1	nitrobenzene (**OAD-1**)	56
2	2-fluoro nitrobenzene (**OAD-2**)	13
3	3-cyano nitrobenzene (**OAD-3**)	5
4	4-cyano nitrobenzene (**OAD-4**)	15
5	2-iodo-5-nitropyridine (**OAD-5**)	27
6	1,4-dinitrobenzene (**OAD-6**)	63
7	1-fluoro-2,4-dinitrobenzene (**OAD-7**)	69
8	1-chloro-2,4-dinitrobenzene (**OAD-8**)	82
9[b]	1-chloro-2,4-dinitrobenzene (**OAD-8**)	0
10[c]	1-chloro-2,4-dinitrobenzene (**OAD-8**)	0

[a]Reaction condition: **1** (0.1 mmol), **OAD** (0.15 mmol), purple LEDs (λ_{max} = 390 nm) in $(CH_2Cl)_2$ (1.0 mL), 25 °C, 24 h, under nitrogen. Yield of **P1** was determined by GC-MS using 1,3,5-trimethoxybenzene as an internal standard. [b]No light. [c]No light at 60 °C.

With optimized conditions, we explored the generality of this methodology (Table 2). The initial survey started with symmetrical alkynes where electronically neutral, donating, and withdrawing substituents at *para*-position were tolerable, maintaining a high yield ranging from 65-95% (**1-10**). Among them, *p*-F substituted substrate **8** gave the highest 95% yield. Notably, various labile and oxidizable functional groups like -CH_2CN, -F, -$COOCH_3$, -CHO, -$COCH_3$, and -CF_3 remained unaffected under these conditions. We then exploited the unsymmetrical alkynes with the duo variation of neutral-electron donating **11**, and electron-withdrawing **12-13** substituents that gave high 60-86% yields of the desired products. Similar results were obtained for alkynes with electron push-pull substituents **14-16**. The reaction was also compatible with unsymmetrical aryl-alkyl alkyne **17**.

Table 2. Scope of the reaction.[a]

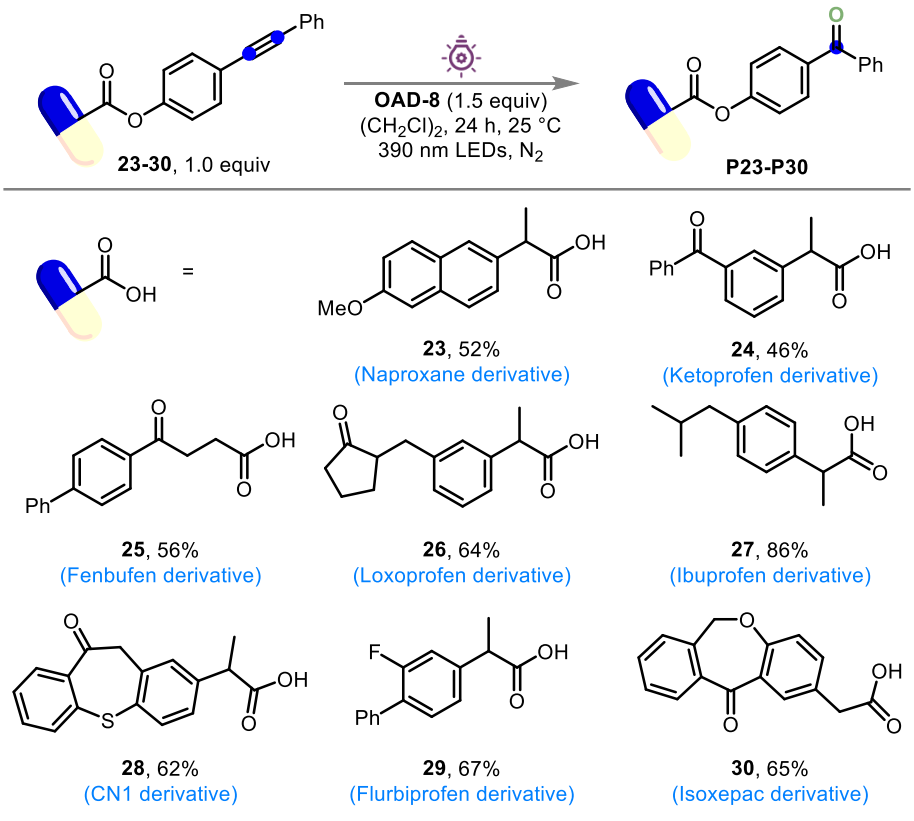


[a]Reaction condition: Table 1, entry 8. Isolated yield.

Additionally, the optimized condition has been extended to check the liberality of heterocycles **18**-**22**. Notably, both symmetrical heteroarene **18** and unsymmetrical heteroarenes **19**-**21** participated in the mild visible-light promoted skeletal-editing reaction, producing the products in high 32-82% yields. *N*-Boc-proline functionalized alkyne **22** also partaken in this reaction. Successful screening of varied aryl, heteroaryl, and alkyl functionalized substrates ensures the broad applicability of the visible-light mediated reaction conditions.

Further, the practical usability of this strategy was mirrored through the late-stage diversification of the derivatives of a wide variety of drugs and bioactive molecules (Table 3). The derivatives of Naproxen (**23**), Ketoprofen (**24**), Fenbufen (**25**), Loxoprofen (**26**), Ibuprofen (**27**), CN1 (**28**), Flurbiprofen (**29**), and Isoxepac (**30**) reacted smoothly under the optimized conditions, producing the products in 46-86% yield. Notably, diverse, complex functionalities are retained under these conditions.

Table 3. Application of carbon deletion reaction of alkynes in late-stage modification of bioactive molecules.[a]

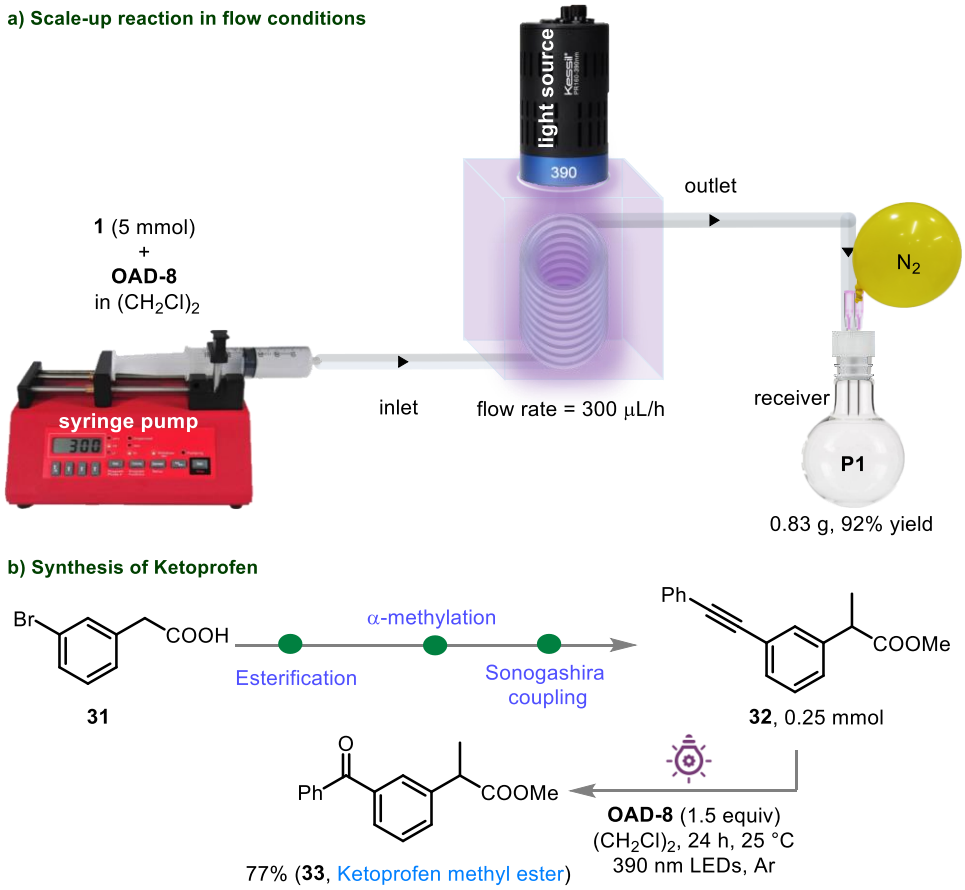


[a]Reaction condition: Table 1, entry 8. Isolated yield.

We also run the reaction in a continuous flow setup to probe the practical application further. The illustrative diagram of the flow setup has been presented (Figure 2a, Section S-VI). The reaction was performed on a 5 mmol scale. Pleasingly, an improvement was obtained regarding reduced reaction time and increased total yield (0.83 g, 92% yield), which might be due to less reaction aging of the reaction.

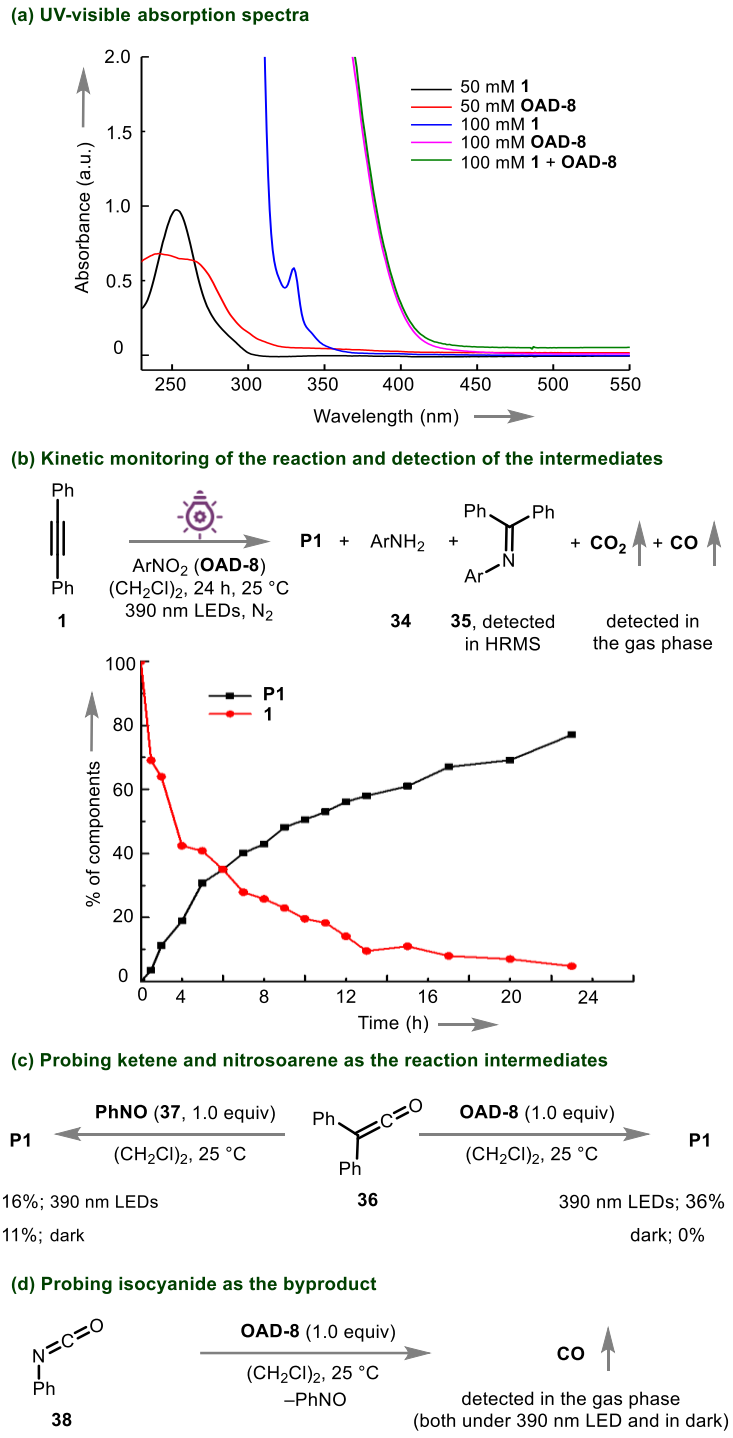
Finally, we applied the visible light-mediated formal oxidative carbon deletion methodology to synthesize the nonsteroidal anti-inflammatory drug Ketoprofen (Figure 2b). Accordingly, the reaction of **32** with **OAD-8** under the standard reaction condition produced 77% yield of Ketoprofen methyl ester **33**.

Figure 2. Synthetic application of carbon deletion reaction: (a) Scale-up in flow condition and (b) Synthesis of Ketoprofen methyl ester.



We then performed preliminary mechanistic studies to elucidate the reaction mechanism (Figure 3). The UV-vis spectra of **1** (black), and **OAD-8** (red) were recorded at 50 µM concentration in 1,2-dichloroethane solution, and the findings indicated that none of these species absorb significantly at 390 nm (Figure 3a). Notably, we observed a strong absorption of **OAD-8** (pink) in the visible region at a 100 mM concentration corresponding to our reaction

Figure 3. (a) UV−visible absorption spectra of **1** (black, 50 μM, and blue 100 mM), **OAD-8** (red, 50 μM and pink, 100 mM), and the combined reaction mixture (green, both 100 mM). (b) Kinetic monitoring of the reaction components, (c) Probing ketene and nitrosoarene as the reaction intermediates.



condition. The concentration dependence *n*-π^* absorption and noted bathochromic shift could potentially result from the formation of nitroarene aggregates.[11a, 22] The likelihood formation of an electron donor-acceptor (EDA) complex between **1** and **OAD-8** was ruled out, as their

stoichiometric combination (green) did not induce a bathochromic shift when compared to the individual components. Moreover, the examination of UV-vis spectra revealed that the nitroarene **OAD-8** predominantly functions as the primary photo-absorbing species under the given reaction conditions, resulting in a T_1 (n,π^*) excited state biradical.[12a, 23]

To identify the possible reaction intermediates, we then monitored the product distribution over time *via* gas chromatography-mass spectrometry (GCMS, Figure 3b). We have observed a steady decrease in the concentration of **1** and the formation of **P1**. As a byproduct, we have noticed both the regioisomers of aniline **34**. Besides, the high-resolution mass spectrometric (HRMS) analysis of the reaction mixture identified mass *m/z* = 337.0746, corresponding to the imines **35**, derived from **P1** and the anilines **34** (Figure S9). Furthermore, the analysis of the gas phase of the reaction mixture identified CO and CO_2 gases at almost equal amounts, which confirm the fate of the deleted carbon (Figure S5).

It was anticipated that ketene and nitrosoarene would be intermediates of the reaction, *vide infra*. The intermediacy of ketene was probed by subjecting the preformed diphenyl ketene **37** under the reaction conditions instead of alkyne **1** (Figure 3c). Notably, the desired product **P1** was formed in 36% of yield under the irradiation of purple LEDs. Additionally, the reaction of ketene **36** with nitrosobenzene **37** produced 16% of the product **P1** under the reaction condition. Notably, the same reaction under dark also yielded **P1** in a similar amount. These studies conclude that ketene **V** and nitrosoarene **VIII** are the intermediates of the reaction, and light may not be required for their [2 + 2] cycloaddition reaction. The lower yield of **P1** in these stoichiometric reaction conditions indicated that the control *in situ* generation of these reactive intermediates and their consumption under the mild reaction conditions was crucial for the higher yield. The light-on-off experiments also drew a similar conclusion (Figure S7). It highlighted the need for continuous irradiation in the reaction and revealed that the reactive intermediates are not accumulated under the given reaction conditions. Moreover, the system's stability under darkness reflects its potential for practical use.

A plausible mechanism is proposed in Figure 4.[11-12, 18] We anticipate that the T_1 (n,π^*) excited state of nitroarene generated upon purple light irradiation would undergo a step-wise [3 + 2] cycloaddition with the alkyne **1**, a mechanism similar to that of alkenes.[11-12] Previously, the *N*-doped ozonide adduct from alkenes was isolated and characterized.[21] However, an attempt to detect the resulting *N*-doped ozonide **II** from alkyne *via* nuclear magnetic resonance spectroscopy has remained unsuccessful. We hypothesized that **II** is a transient species and undergoes fast cleavage at one of the weak O–N bonds under the reaction conditions. The

resulting zwitterion **III** could rearrange itself to form strain intermediate **IV**, which eventually cleaved to generate ketene **V** and nitrosoarene **VIII**. The intermediacy of these species was confirmed through the control experiments (Figure 3c).

At this stage, we propose that ketene **V** and nitrosoarene **VIII** undergo [2 + 2] cycloaddition reaction to form four-membered intermediates **IX** and **X** as two regioisomeric mixtures. A retro [2 + 2] cycloaddition reaction of **IX** could expel an imine **XI** and CO_2. The hydrolysis of **XI** produced the product **P**, having one carbon less than the starting alkyne. The imine **36** was detected during the HRMS analysis, and aniline **34** was produced as the byproduct. CO_2 is observed in the gas phase via GC.

On the other hand, a retro [2 + 2] cycloaddition reaction of the intermediate **X** yields the product **P** and an isocyanate **XIII**. The latter could either, upon losing CO_2, form aniline **XI** or react with nitroarene and produce nitrosoarene **V** and CO *via* the intermediacy of **XIV**. The evolution of carbon monoxide was determined via the gas phase analysis of the reaction mixture. To probe the evolution of CO from isocyanide by the [3 + 2] cycloaddition and fragmentation cascade, we have performed the reaction of phenyl isocyanate **38** with **OAD-8** (Figure 3d). After 5h, the GC analysis of the reaction head-space confirms the production of CO. We note that light is not required to form CO from **38**.

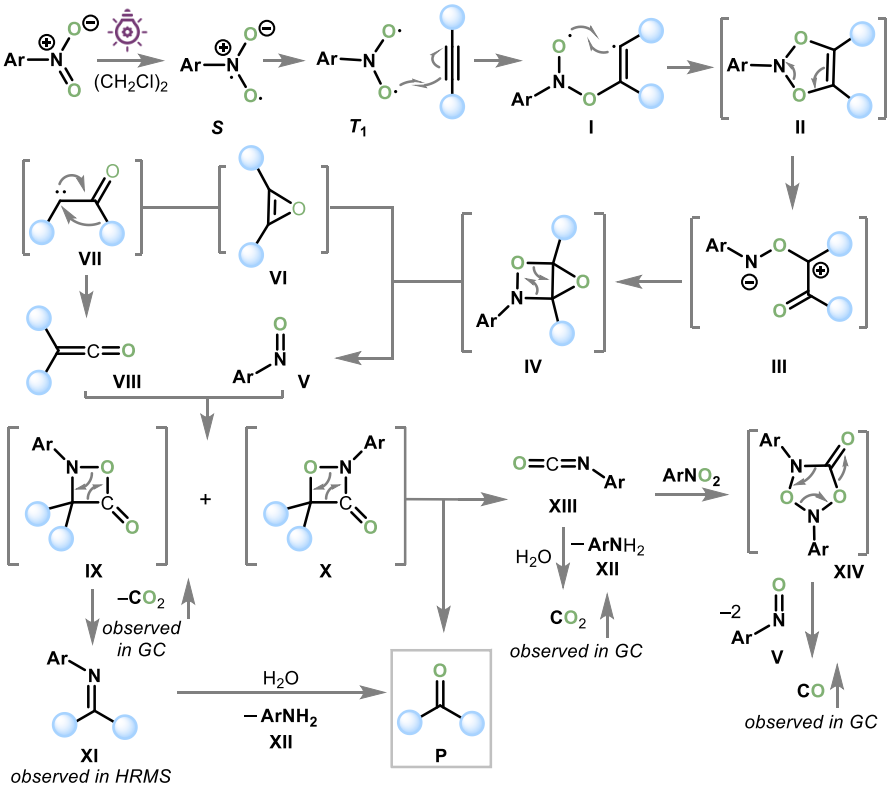


Figure 4. Proposed reaction mechanism.

Conclusion

In summary, we employed triplet excited nitroarenes to edit the structure of internal alkynes by concurrently deleting a carbon and inserting an oxygen atom. This light-driven molecular editing approach's effectiveness and broad applicability were demonstrated through diverse substrate scope, compatibility with modifying bioactive molecules, scalability in large-scale synthesis, and the synthesis of commercially available drug molecules. We investigated the reaction mechanism through UV-vis spectroscopic studies and various control experiments, identifying key intermediates and confirming the release of CO and CO_2 gases from the deleted carbon. Given that the protocol transforms a linear molecular vector into a bent topology, bringing functionalities closer, we anticipate that this strategy holds significant promise for advancing skeletal editing chemistry in the modulation of molecular architecture.

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Author Contributions

All authors have given approval to the final version of the paper. [#]These authors contributed equally to this work.

Data availability

The supplementary information includes all experimental details, including optimization of the synthetic method, synthesis, and characterization of all starting materials and products reported in this study, mechanistic studies, and NMR spectra of all products.

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Notes

The authors declare no competing financial interest.

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