Photo-induced copper-catalyzed sequential 1,n-HAT enabling the formation of cyclobutanols

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Cyclobutanols are privileged cyclic skeletons in natural products and synthetic building blocks. C(sp\textsuperscript{3})-\textsuperscript{H} functionalization is a prolonged challenge in organic synthesis. The synthesis of cyclobutanols through double C(sp\textsuperscript{3})-H bond functionalization remains elusive. Here we report the efficient synthesis of cyclobutanols through intermolecular radical [3 + 1] cascade cyclization, involving the functionalization of two C – H bonds through sequential hydrogen atom transfer. The copper complex reduces the iodomethylsilyl alcohols efficiently under blue-light irradiation to initiate the tandem transformation. The mild reaction tolerates a broad range of functional groups and allows for the facile generation of elaborate polycyclic structures.
Cyclic structures are fundamental in organic chemistry. Among these structures, cyclobutanols are useful cyclic skeletons frequently observed in natural products and widely serve as the targets for carbon–carbon bond cleavage chemistry because of the ring strain. New methods for the expedient synthesis of diversified cyclobutanols would offer opportunities to related fields.

Tandem radical cyclizations have become a powerful synthetic method to generate complicated and useful carbon skeletons, featuring the formation of one or more consecutive rings in a single step. The utility of this strategy has been demonstrated in numerous synthesis of complex natural products, including linear- and angular-fused triquinanes, steroids, milbemycin, prostaglandins, (-)-Maecrystal Z, scholarisine A, barbiturates, and ophiobolin sesterterpene. Visible-light photoredox chemistry is an area seeing tremendous growth as it notably provides mild reaction conditions for the generation of radicals, rendering many elegant intramolecular and intermolecular reactions possible using iridium (Ir)- or ruthenium (Ru)-based visible-light sensitizers.

Vinyl radical initiated 1,n-hydrogen atom transfer (HAT) and cyclization is another powerful way to construct a wide range of five-membered rings, pioneered by the works of Heiba and Dessau, Curran, Parsons, Renaud, and others. In most cases, however, intramolecular versions have dominated and have necessitated that vinyl halides or pseudo-halides usually require multistep synthesis. The generation of cyclic skeletons other than five-membered rings is rare. We envisioned the possibility of the in situ generation of vinyl radicals in an intermolecular manner, and if followed by HAT and cyclization, a different ring structure could potentially be

**Fig. 1 Remote C–H functionalization via HAT.** a Vinyl radical triggered by activation of C(sp2)-X initiated HAT and cyclization. b Vinyl radical triggered by radical addition to alkyne initiated HAT and cyclization. c Remote C–H functionalization via HAT enabled by an iodomethylsilyl auxiliary. d Photoinduced copper-catalyzed sequential 1,n-HAT enabling the formation of cyclobutanols.
furnished. The success of this hypothesis relied on a new combination of radical precursor and reactant.

For activated C–X bonds, such as polyhalogenated alkanes35, α-halocarbonyl compounds36, geminal halogenated sugars37, and benzyl bromides bearing strong electron-withdrawing groups38 have been used to generate radical intermediates under photoredox conditions. The use of substrates containing unactivated halogen–carbon bonds is less studied because of the relatively high reduction potential and putative reactivity of the resulting unstabila\n\[sp^3\] carbon radical. We have been interested in copper (Cu)-photocatalysis using aliphatic halide as the radical precursor39–41.

Cu complexes have displayed highly tunable redox properties in their excited states, diverse ligand types, and the free conversion of multiple oxidation states42–45. Taking advantage of the silicon effect for the generation and translocation of α-carbon radicals27,46, Gevorgyan recently advanced a series of works on the direct γ-amination and γ-vinylation of alcohol derivatives through 1,6-HAT using (halomethyl)silyl auxiliaries (Fig. 1c)47–50. Despite this progress, as far as we know, examples of the use of readily available aliphatic halides as the radical precursor under visible-light photocatalysis for intermolecular cascade cyclization en route to four-membered rings are lacking. During our investigation on photoinduced Cu-catalyzed remote C−H alkynylation with iodo- methylsilyl alcohols39, we isolated an unexpected cyclized

![Figure 2](https://example.com/fig2.png)

**Fig. 2** Synthesis of 3a under various reaction conditions. a 1a (0.1 mmol), 2a (0.15 mmol), PS (10 mol %), N, N-Diisopropylethylamine(DIPEA) (4 equiv) in MeCN, under N2, rt, B-LED, 24 h. The relative configuration was assigned by NOE analysis. b Determined by 1H NMR analysis with an internal standard (diethyl phthalate). The value in parentheses is the deprotected isolated yield. c Cu (10 mol%), ligand (20 mol %). d Pd(OAc)2 (10 mol %), Xantphos (20 mol %) and Cs2CO3 (2 equiv) in PhH, under N2, rt, B-LED, 24 h. e No light.

| Entry | Photocatalyst | Reductant | Solvent | Temperature | Yield% |
|-------|---------------|-----------|---------|-------------|--------|
| 1     | Cu + L1       | DIPEA     | MeCN    | rt          | 24     |
| 2     | Cu + L2       | DIPEA     | MeCN    | rt          | 30     |
| 3     | Cu + L3       | DIPEA     | MeCN    | rt          | 20     |
| 4     | Cu + L4       | DIPEA     | MeCN    | rt          | trace  |
| 5     | PS5           | DIPEA     | MeCN    | rt          | 30     |
| 6     | PS6           | DIPEA     | MeCN    | rt          | 75(73) |
| 7     | PS7           | DIPEA     | MeCN    | rt          | 67     |
| 8     | PS8           | DIPEA     | MeCN    | rt          | trace  |
| 9     | Ru(bipy)_3Cl_6H_2O | DIPEA    | MeCN    | rt          | 38     |
| 10a   | Pd(OAc)2 + Xantphos | -       | PhH     | rt          | trace  |
| 11    | PS6           | DIPEA     | DME     | rt          | 52     |
| 12    | PS6           | DIPEA     | DCM     | rt          | trace  |
| 13    | PS6           | Bz3N      | MeCN    | rt          | 55     |
| 14    | PS6           | DIPEA     | MeCN    | 10°C        | 42     |
| 15    | -             | DIPEA     | MeCN    | rt          | 0      |
| 16a   | -             | -         | MeCN    | rt          | 0      |
compound 3a as a minor product when we employed an electron-deficient aryl alkyne. Notably, 3a is a product of a HAT/vinyl radical formation/cyclization cascade reaction that involves the functionalization of two C(sp³)–H bonds.

Herein, we report our preliminary results on the photoinduced Cu-catalyzed intermolecular radical cascade cyclization of iodo-methylsilyl alcohols with alkynes leading to synthetically useful cyclobutanol skeletons (Fig. 1d). This method not only constitutes

Fig. 3 Scope of substrates considered in the study. Reaction conditions: 1 (0.1 mmol), 2 (0.15 mmol), PS6 (10 mol %), DIPEA (4 equiv) in MeCN, under N₂, rt, B-LED, 24 h. The relative configurations were assigned by NOE analysis; no deprotection for 3s.
a valuable complement to Norrish Yang–type cyclobutanol formation, which features intramolecular reaction and usually requires an arylketone or diketone for better light absorption51,52, but it also contributes an example of double C(sp3)−H functionalization chemistry53–57.

Results

Reaction optimization. We optimized this interesting reaction and also, more importantly, explored the reaction mechanism and its scope. The key to improving the reaction was to identify the best photocatalyst and reductant. The complexes of CuI with simple bipyridine, tripyridine, or phenanthroline ligands were less effective for this reaction (Fig. 2, entries 1–4). Photocatalysis using homoleptic or heteroleptic Cu complexes experienced significant growth42–45. We thus prepared a series of homoleptic Cu complexes; however, the [(dmp)2Cu]PF6 complex with different substitutions provided less of the product (Fig. 2, entry 5). We then turned our attention to heteroleptic diamine/bisphosphine Cu ligands with notable features including an easily tunable chromophore and bite angle to influence the photophysical properties and catalytic activity42,43. Among all of the heteroleptic complexes evaluated (Fig. 2, entry 6–8), [(DPEphos)(bcp)Cu]PF6, originally a photosensitizer for the photocatalytic reduction of water58 and carbon dioxide59 and was recently applied in carbohalide photoactivation by Evano60, proved to be superior. We examined Ru-based photocatalysts for comparison; however, the cyclized product was formed in a relatively lower yield (Fig. 2, entry 9). Palladium was not a suitable catalyst for this cyclization reaction (Fig. 2, entry 10). Further optimization of the sacrificial reductant revealed that Hüning’s base was the best candidate (Fig. 2, entry 13). Lowering the temperature did not improve the product yield (Fig. 2, entry 14), while control experiments demonstrated the strict requirement of both catalyst and light for the reaction to occur (Fig. 2, entries 15 and 16).

Substrate scope. With these optimized conditions in mind (Fig. 2, entry 6), we next considered the scope and limitations of the light-mediated, [(DPEphos)(bcp)Cu]PF6-catalyzed radical cascade cyclization of aliphatic silyl iodide and alkyne-possessing representative carbon skeletons and substitution patterns (Fig. 3). Silyl alcohols with various linear or branched carbon chains were efficiently converted into the corresponding products in moderate to good yields (3b–3d); a phenyl group could be tolerated (3e). The radical nature reaction conditions were compatible with a range of functional groups, including sulfonamide (3f) with an acidic proton. Unsaturated C−C bonds, such as triple bonds and double bonds, were suitable at distant positions (3g–3h). Substrates with heteroatoms, such as oxygen, sulfur, and chloride, reacted well to provide the cyclized product in moderate yields (3i–3k). We also briefly explored the substrate scope with respect to substituents on phenylacetylene. Neutral or electron-donating substituents did not provide the cyclized product. Various electronic-withdrawing groups, including CN, actinium, amide, and sulfonamide, benefited the reaction, leading to the desired products in good to moderate yields (3l–3o). Then, we turned our attention to another challenging aspect of this reaction—that is, the abstraction of a hydrogen atom at less-reactive secondary C(sp3)-H sites. Gratifyingly, under identical reaction conditions, cyclobutanols with three stereogenic centers formed (3p). Silicon-protected primary alcohol was engaged in this tandem radical cyclization, furnishing 3q in moderate yield, suggesting that the secondary C(sp3)-H ether site could be functionalized as well. Silicon-tethered alcohols bearing a cyclic ring at the γ position reacted well, providing spiro[3.5]nonan-2-ols in moderate yields (3r and 3s). Moreover, we successfully obtained 3-phenylspiro[4.4]nonan-2-ol and 3-phenylspiro[4.5]decan-2-ol with
varied ring structures (3t and 3u). The two substitutions at the γ position could be different (3v and 3w), notably, a free hydroxyl group was compatible with the reaction conditions. We also examined the feasibility of this transformation in a more complex setting. Substrates derived from natural (-)-menthol and trans-2-isopropyl-cyclopentanol all furnished the radical relay [3 + 1] cyclized products (3x) and (3y). Through ingenious substrate design, we obtained more complex ring structures, such as the introduction of an extra spiral ring (3z) or different substitution patterns on the 4,6-fused ring system (3aa). Unfortunately, neither arylacetylenes with neutral or electron-donating substituents (3ab and 3ac) nor alkyl alkyne (3ad) provided the cyclized product under standard conditions; hydrodehalogenation or the remote desaturation side products were observed instead.

**Mechanistic studies.** To further investigate the reaction mechanism, we conducted a series of mechanistic experiments (Fig. 4). First, the addition of the radical scavenger TEMPO completely suppressed the reaction (Fig. 4a). Second, a deuterium-labeling experiment profile also supported the radical cascade cyclization hypothesis (Fig. 4b–d). Thus, we observed 7 + 30% and 19 + 26% deuterium incorporation at the benzylic position of 3a1-d3 and 3a2-d3 when we added D2O instead of CD3CN in the reaction, suggesting that water provided the proton needed to quench the reaction. The observed 45 and 43% deuterium enrichment at the 1-positions of 3a1-d3 and 3a2-d3, respectively, was possibly due to the H/D exchange of the acetylene–hydrogen under basic conditions. Then, 1c-d1 with deuterium-labeled at the ether carbon provided

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**Fig. 5 Proposed reaction mechanism.** Photoredox-based dehalogenation of 1a triggers a 1,6-HAT (A to B)/vinyl radical formation (C)/cyclization cascade reaction (D, E, F) involving the functionalization of two C – H bonds to form valuable cyclobutanols (3a).

**Fig. 6 Transformations of cyclobutanols.** a Synthesis of γ-fluoroketone 4. b Synthesis of γ-arylketone 5.
products with 33 + 43% and 18 + 44% deuterium enrichment only at the benzylic position of 3c{-}d2 and 3c{-}d2, respectively, indicating the intramolecular vinyl radical (1,5-HAT). Photochemical studies have revealed that the Cu complex is a single photo-absorbing species27. Stern–Volmer studies demonstrated that both iodide and DIPEA could quench the excited state of the Cu complex, and the latter had a much higher efficiency (see Supplementary Information for details). According to Evano’s study, a DIPEA-intercepted Cu(I)/Cu(II) catalytic cycle26 might account for the reduction in organic halides to a heteroleptic Cu catalyst and visible light in the conditions would support the further study of new methods, and expected that the discovered reactivity of intermolecular radical cyclization cascade reaction process.

According to the literature25,63 and on the basis of those findings, we proposed the following mechanism (Fig. 5). The active photoexcited ([DPEphos](bcp)CuPF6 was reduced by DIPEA to provide a Cu(0) species, which served as the true reductant to induce the homolysis of the C−I bond of 1a. The resulting carbon radical A, upon the addition of 1,6-HAT, generated the new alkyl radical B. The addition of a radical to alkene gave rise to the vinyl radical C. The resulting vinyl radical E would go through an intramolecular reaction with 1,5-HAT to selectively activate the C(sp3){-}H of ether and to afford a nucleophilic, secondary alkyl radical species D. A 4-exo-trig-type cyclization took place to afford the cyclized radical species (E), which was quenched to deliver the final product 3a. Moreover, quantum yield (Φ = 0.44%) suggested that a radical-chain process might not be involved (see Supplementary Information for details).

To demonstrate the synthetic potential of this methodology and identify the chemical structure of the product, we conducted two derivatizations (Fig. 6). 1a underwent two types of ring-opening functionalization processes. We generated γ-fluoroketone through a radical pathway with a ring opening on the substituted side (Fig. 6a). In contrast, we isolated γ-arylketone under palladium catalysis with a ring opening on the nonsubstituted side (Fig. 6b).

In summary, we have shown that the exposure of silyl ether iodoides to a heteroleptic Cu catalyst and visible light in the absence of exogenous photosensitizers at room temperature leads to the formation of a carbon radical species. This intermediate triggers a 1,6-HAT/vinyl radical formation/cyclization cascade reaction involving the functionalization of two C−H bonds to form valuable cyclobutanols. The radical nature reaction tolerates a broad range of functional groups and could proceed under complex settings, providing elaborate polycyclic molecules. It is expected that the discovered reactivity of intermolecular radical [3 + 1] cascade cyclization under visible-light/copper-catalyzed conditions would support the further study of new methods, and these developed methods would find applications in synthesis.

**Methods**

In a dried sealed vial, ([DPEphos](bcp)CuPF6 (0.010 mmol, 10 mol %), DIPEA (0.4 mmol, 4.0 equiv), and terminal alkyne (0.15 mmol, 1.5 equiv) were dissolved in anhydrous CH2Cl2 (1.0 mL) under N2 atmosphere. Then, tethered alcohol (0.1 mmol, 1.0 equiv) was added. The reaction mixture was stirred at room temperature under B-LED for 4 h. The distance between the vial and the lamp was about 1-3 cm. The resulting mixture was filtered and concentrated. After that, the residual oil was dissolved in THF (1.0 mL), followed by the addition of TBAF (2 mL, 1.0 M in THF). The reaction mixture was stirred at room temperature until the reaction was completed, as monitored by GC analysis. Then the mixture was diluted with EtOAc, washed with NaCl (aq.), and dried over with anhydrous Na2SO4. After filtration and concentration, the residue was purified by silica gel chromatography with petroleum ether and ethyl acetate to afford the deprotected products.

**Data availability**

Supplementary Information is available in the online version of the paper. The experimental procedures and characterization of all new compounds are provided in Supplementary Information and also from the corresponding author upon reasonable request.

Received: 17 May 2021; Accepted: 8 October 2021; Published online: 04 November 2021

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