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# Photocatalyzed [2+1] cyclization of alkenes and silylated trifluorodiazoethanes: facile entry into (difluoromethylene)cyclopropanes

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Methylenecyclopropanes are among the most robust building blocks in synthetic chemistry, but the study on (difluoromethylene)-cyclopropanes is rather limited, because of the difficulty in the synthesis of these compounds. Herein, we report the invention of a novel carbene precursor, (1-diazo-2,2,2-trifluoroethyl)dimethyl(phenyl)silane (**1a**) and its application in the synthesis of (difluoromethylene)cyclopropanes. The reaction proceeds through photocatalyzed [2+1] cyclization of readily available alkenes and diazo compound **1a** followed by the work-up of the reaction through the elimination of silyl fluoride. Both aromatic and aliphatic alkenes are tolerated by the mild reaction conditions, affording various (difluoromethylene)cyclopropanes in 44%–82% yield (>30 examples). Gram scale reaction and diversified downstream transformations highlight the synthetic potential of this methodology. The experimental and DFT calculations suggest the involvement of triplet carbene intermediate.

**triplet carbene, cyclopropanation, methylenecyclopropanes, (difluoromethylene)cyclopropanes**

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Taking advantage of both unsaturated C=C double bond and strained three-membered ring, methylenecyclopropanes have been among the most versatile building blocks in the synthesis of bioactive molecules and functional materials [1–3] (Scheme 1a). In recent years, fluorine incorporation is emerging as important strategy in drug and material design, because the large electronegativity of the fluorine atom and large bond energy of the C–F bond can often bring beneficial physical, chemical and biological properties into organic molecules [4]. In this context, (difluoromethylene)cyclopropanes would be useful intermediates for the synthesis of organofluorine compounds. However, the investigation of (difluoromethylene)cyclopropanes is scarce, because of the difficulties associated with the preparation of these compounds [5]. Only a handful of methods for the synthesis of (difluoromethylene)cyclopropanes are known (Scheme 1b). Dolbier and coworkers [5a,5b] reported the reduction of halogenated cyclopropanes with Zn, but the reaction showed limited substrate scope and the substrates themselves are difficult to access. The thermal isomerization of (alkylidene) difluorocyclopropanes was reported [5c–5f], but the reaction usually needs high temperature and results in mixtures and the starting materials need to be prepared in multiple steps [5f]. Dolbier's group [5g] reported an interesting cyclization reaction of diazo compounds with 1,2-difluoroallenes, and the (difluoromethylene)cyclopropanes could be obtained after the photolysis of the cyclization products under UV light. However, the employment of difficult-to-handle gas and high-energy light limited the application of this methodology [5g]. Therefore, it is of great value to develop prac-

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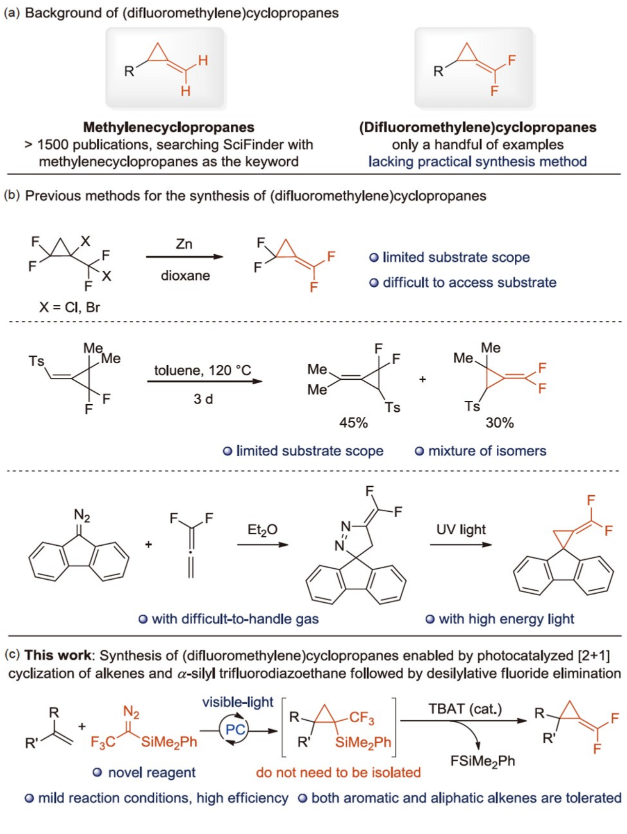
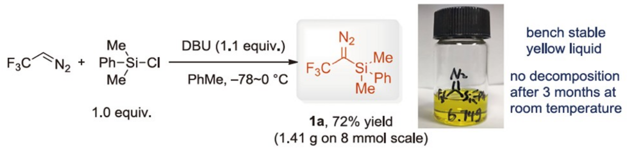
*Corresponding author (email: xiaoshen@whu.edu.cn) tical methods for the synthesis of (difluoromethylene)cyclopropanes. Herein, we report our recent success in tackling this challenge through visible-light-induced organocatalyzed [2+1] cyclization of alkenes and silylated trifluorodiazoethanes followed by tetrabutylammonium difluorotriphenylsilicate (TBAT) catalyzed desilylative fluoride elimination (Scheme 1c). The mild reaction conditions are simple to operate, and [2+1] cyclization intermediates do not need to be isolated to enable the subsequent desilylative fluoride elimination. The reaction shows broad substrate scope and both aromatic and aliphatic alkenes are suitable substrates. The experimental and density functional theory (DFT) studies support the involvement of triplet carbenes in the [2+1] cyclization step.

It is worth noting that (1-diazo-2,2,2-trifluoroethyl)dimethyl(phenyl)silane (**1a**) is a previously unknown compound (Scheme 2). It can be easily prepared from 2-diazo-1,1,1-trifluoroethane and $PhSiMe_2Cl$ in the presence of DBU, and the gram scale reaction afforded the diazo compound **1a** in 72% yield (1.41 g on 8 mmol scale). We found that compound **1a** is a bench stable yellow liquid, and no obvious decomposition was observed after being stored in a sealed vial for three months at room temperature.



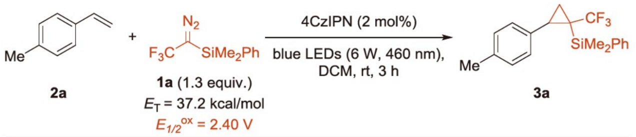
**Scheme 1** Background and our strategy for the synthesis of difluoromethylenecyclopropanes (color online).



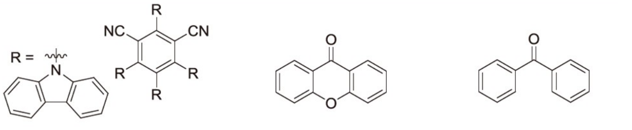
**Scheme 2** Synthesis of (1-diazo-2,2,2-trifluoroethyl)dimethyl(phenyl)silane **1a** (color online).

Diazo compounds have been widely used as carbene precursors under transition-metal catalysis [6]. Without metals as carbene stabilizers, the highly reactive free carbene species generated from photolysis under high energy UV light usually lead to uncontrollable chemistry [7]. Recently, visible-light-induced photochemistry is emerging as a milder strategy for the generation of free carbenes with diazo compounds [8,9]. With the novel carbene precursor **1a** in hand, we started to study whether [2+1] cyclization reaction could be achieved with alkene **2a** and **1a** (1.3 equiv.) as the model substrates under visible light-induced photocatalysis conditions (Table 1). To our delight, when 2 mol% of 4CzIPN was used as the photocatalyst, and dichloromethane (DCM) was used as the solvent, complete conversion of diazo compound **1a** was observed and 95% yield of cyclopropane **3a** was detected by $^{19}F$ NMR (96% isolated yield, Table 1, entry 1). Without 4CzIPN, there was a 29% conversion of **1a**, but only a 6% yield of **3a** was obtained (Table 1, entry 2). Further control experiments confirmed that both light and 4CzIPN were important for the reaction (Table 1, entries 3 and 4). When xanthone ($E_T$ = 74.2 kcal/mol) [10] or benzophenone ($E_T$ = 69.1 kcal/mol) [11] was used as the photocatalyst instead of 4CzIPN ($E_T$ = 59.6 kcal/mol) [12], much lower conversion of **1a** and lower yield of **3a** were observed, probably because the mismatch of their triplet energies with that of reagent **1a** ($E_T$ = 37.2 kcal/mol; for details, see Supporting Information online) resulted in less efficient triplet-triplet energy transfer [13,14]. The reaction is not likely to be initiated by the oxidation of **1a** by excited 4CzIPN, because of the higher oxidation potential of **1a** (for the details of CV measurement, see Supporting Information online) [15]. Changing the solvent to toluene, cyclopentane and tetrahydrofuran (THF) resulted in decreased yield (59%, entry 7; 32%, entry 8; 6%, entry 9). Further study revealed that the reaction was sensitive to $O_2$ (8%, entry 10). Several reports revealed that cyclopropanation of alkenes with diazo compounds could be achieved under sole blue LED irradiation, and in these reactions, singlet carbenes were proposed to be key intermediates [8g,9f]. Although compound **1a** can absorb blue light (Figure 1), its reaction with **2a** under 420 nm only afforded compound **3a** in 7% yield (entry 11, for more details, see Supporting Information online). Moreover, the reaction under 365 nm afforded **3a** in a much lower yield (3%, entry 12), although the absorption intensity of **1a** at 365 nm is strong (Figure 1). These results suggest that our photocatalyzed reaction might not proceed through singlet carbenes.

**Table 1** Optimization of reaction conditions[a)]



| entry | deviation from standard conditions | conv. of 1a[a)] | yield of 3a[a)] | dr of 3a[a)] |
|---|---|---|---|---|
| 1 | none | 100% | 95% (96%)[b)] | 1.5:1 |
| 2 | without 4CzIPN | 29% | 6% | 1.5:1 |
| 3 | without light | 4% | 0% | -- |
| 4 | without light and 4CzIPN | 3% | 0% | -- |
| 5 | with xanthone instead of 4CzIPN | 46% | 7% | 1.5:1 |
| 6 | with benzoahenone instead of 4CzIPN | 44% | 7% | 1.5:1 |
| 7 | with PhMe instead of DCM | 100% | 59% | 1.7:1 |
| 8 | with cyclopentane instead of DCM | 100% | 32% | 1.7:1 |
| 9 | with THF instead of DCM | 100% | 6% | 1.6:1 |
| 10 | under $O_2$ | 100% | 8% | 1.6:1 |
| 11 | without 4CzIPN, under 420 nm | 88% | 7% | 1.5:1 |
| 12 | without 4CzIPN, under 365 nm | 100% | 3% | 1.6:1 |



**4CzIPN**
$E_T$ = 59.6 kcal/mol;
$E_{1/2}^{ox}(PC^*/PC^{\cdot-})$ = 1.43 V

**xanthone**
$E_T$ =74.2 kcal/mol;
$E_{1/2}^{ox}(PC^*/PC^{\cdot-})$ = 1.57 V

**benzophenone**
$E_T$ =69.1 kcal/mol;
$E_{1/2}^{ox}(PC^*/PC^{\cdot-})$ = 1.28 V

a) Unless otherwise noted, the reaction conditions were as follows: **2a** (0.10 mmol), **1a** (0.13 mmol), DCM (1 mL), under irradiation by LEDs in $N_2$, 3 h; the conversion of **1a**, yield and dr of **3a** were determined by the analysis of $^{19}F$ NMR spectroscopy of unpurified reaction mixture with $PhCF_3$ as an internal standard. b) Yield in parentheses refers to the isolated yield of the two diastereoisomers. DCM: dichloromethane; DCE, 1,2-dichloroethane; EA, ethyl acetate; THF, tetrahydrofuran. All values of $E_{1/2}^{Ox}$ are the data versus SCE in MeCN [15,16].

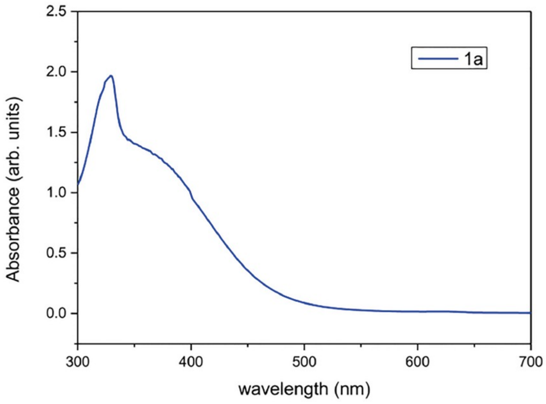
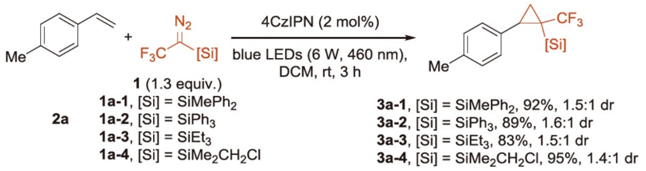


**Figure 1** UV-Vis absorption spectra of **1a** (color online).

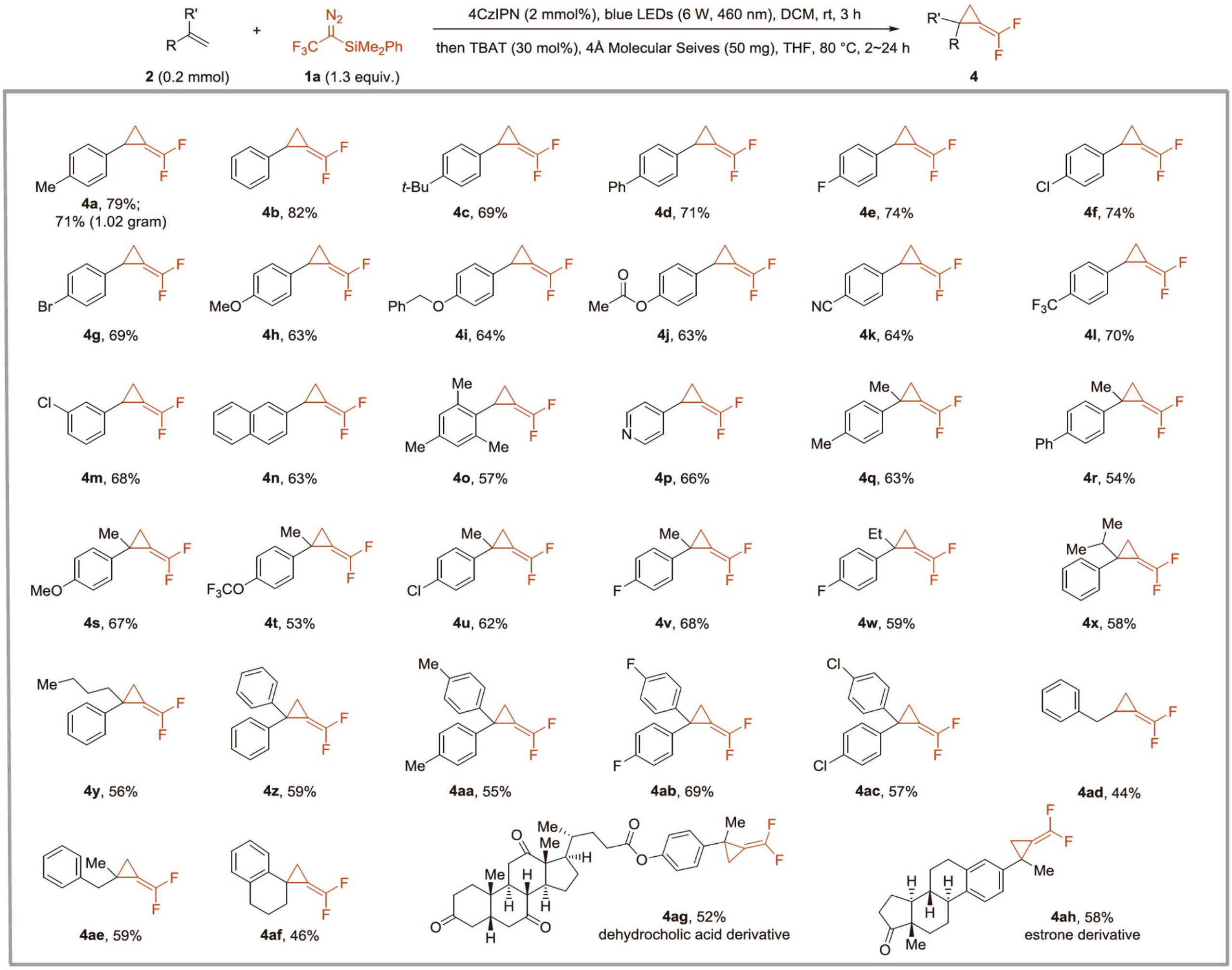
After achieving the [2+1] cyclization reaction of **2a** and $PhSiMe_2$ substituted diazo compound **1a**, we then investigated the influence of silyl groups of the carbene precursors on the efficiency of the [2+1] cyclization reaction with 4CzIPN as the energy transfer catalyst (Scheme 3). We found that silylated diazo compounds **1a-1**–**1a-4** were also suitable reagents for photocatalysis reaction, albeit no obvious improvement of diastereoselectivity was observed (**3a-1**, 92%, 1.5:1 dr; **3a-2**, 89%, 1.6:1 dr; **3a-3**, 83%, 1.5:1 dr; **3a-4**, 95%, 1.4:1 dr).



**Scheme 3** Influence of silyl groups on the efficiency of the photocatalyzed [2+1] cyclization reaction (color online).

After the identification of the optimal conditions for the [2+1] cyclization reaction, we aimed to achieve the one-pot synthesis of (difluoromethylene)cyclopropanes. We found that the silylated cyclopropane intermediate **3a** does not need to be purified to enable the desilylative fluoride elimination in the presence of the catalytic amount of TBAT, and compound **4a** was isolated in a 79% yield (Scheme 4). The addition of 4 Å molecular sieves removed a trace amount of $H_2O$ from the reaction mixture to decrease possible protodesilylation side reaction. The reaction could be performed on a gram scale, and no significant decrease in yield was found (**4a**, 71%, 1.02 g, Scheme 4). The reaction was found to readily accommodate various terminal aryl alkenes, including electron-neutral (**4b**), electron-donating (**4h**–**4i**), and electron-withdrawing substituents (**4k** and **4l**), affording corresponding cyclization product in 63%–82% yield. F, Cl, Br, OMe, $PhCH_2O$, $MeCO_2$, $CF_3$, and CN have been tolerated (**4e**, 74%; **4f**, 74%; **4g**, 69%; **4h**, 63%; **4i**, 64%; **4j**, 63%; **4k**, 64% and **4l**, 70%). The naphthyl, mesityl and pyridyl group substituted (difluoromethylene)cyclopropanes were also successfully prepared (**4n**, 63%; **4o**, 57% and **4p**, 66%). The 1,2-disubstituted terminal aromatic alkenes are also compatible with this reaction, and the corresponding (difluoromethylene)cyclopropanes were obtained in 53%–69% yields (**4q**–**4ac**). It was found that the aliphatic alkenes can also be employed as substrates for the synthesis of (difluoromethylene)cyclopropanes (**4ad**, 44%; **4ae**, 59%). Furthermore, two complex bioactive molecule derivatives **4ag** and **4ah** were successfully prepared in 52% yield and 58% yield, respectively, indicating the generality of our reaction conditions.

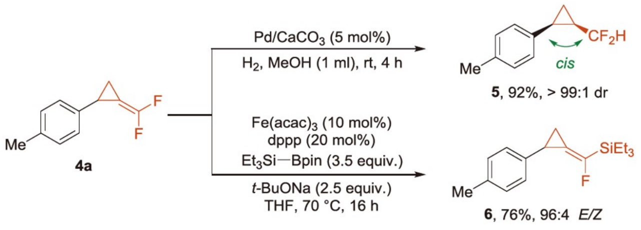
Subsequently, the synthetic applications of the (difluoromethylene)cyclopropanes were investigated (Schemes 5 and 6). Firstly, the selective transformations of difluoroalkenyl group were studied. It was found that compound **4a** could be easily hydrogenated under the Pd-catalyzed conditions, affording difluoromethyl substituted cyclopropane **5** in 92% yield. The high *cis*-selectivity could be explained by the obvious differentiation of hydrogen atom and the aryl group in the transition state. This application is of particular importance because previous cyclopropanation reactions with α-difluoromethyl carbene afforded a mixture of isomers



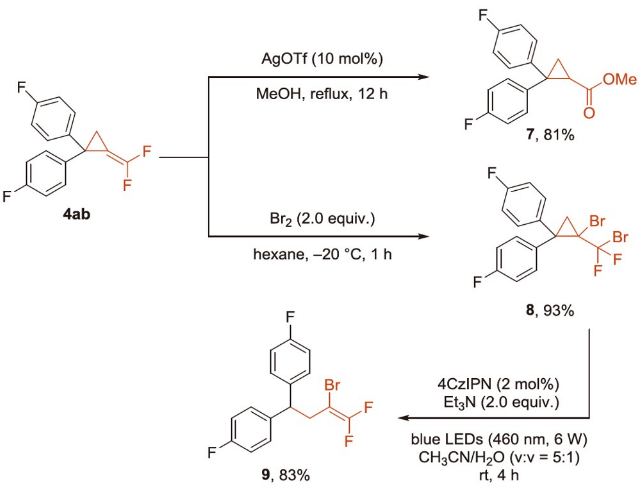
**Scheme 4** Reaction conditions: **2** (0.20 mmol, 1.0 equiv.), **1a** (0.26 mmol, 1.3 equiv.) and 4CzIPN (2 mol%) in DCM (1 mL), rt, 3 h, 6 W blue LEDs (460 nm), then the solvent was exchanged to THF (1 mL) and TBAT (0.06 mmol, 0.3 equiv.), 4 Å molecular seives (50 mg), and the reaction was stirred at 80 °C for 2–24 h. An isolated yield was given (color online).

or trans isomer as the major isomer [17]. Under Fe-catalyzed conditions, formal C–F bond silylation was achieved, affording silylated (monofluoromethylene)cyclopropane **6** in 76% yield, with 96:4 *E*/*Z* [18]. In addition, an ester containing cyclopropane **7** was prepared through the reaction of compound **4ab** with MeOH, in the presence of 10 mol% of AgOTf (Scheme 6). The addition of bromine to the carbon-carbon double bond was also efficient, affording bromodifluoromethyl substituted cyclopropane **8** in 93% yield. Under photocatalyzed conditions, selective generation of difluoroalkyl radical from compound **8** was achieved, which induced the ring-opening of the three-membered ring, resulting in the generation of difluoroalkene **9** in 83% yield.

Preliminary control experiments have been conducted to probe the possible mechanism of the reaction (Scheme 7). Firstly, the addition of 1.0 equivalent of TEMPO into the reaction of alkene **2a** and reagent **1a** completely inhibited the formation of the cyclopropanation product **3a**, although there was still a 16% conversion of diazo compound **1a** (Scheme 7a). This result suggests radical intermediate might be involved in the reaction. Secondly, significant *cis-trans* isomerization of compound **10** was observed in the reaction of **2a** and **1a** in the presence of 1.0 equivalent of *trans*-**10** (Scheme 7b), supporting the involvement of energy transfer between 4CzIPN ($E_T$ = 59.6 kcal/mol) and *trans*-**10** ($E_T$ = 49.3 kcal/mol) [13d]. The lower triplet energy of the carbene precursor **1a** ($E_T$ = 37.2 kcal/mol) than those of 4CzIPN and *trans*-**10** might account for the formation of **3a**, although the yield is lower than the reaction in the absence of *trans*-**10**. In order to probe the involvement of triplet carbene, we performed a Hammett analysis of the reaction (Scheme 7c). The negative Hammett-slope ($\rho = -0.6$) substantiates the positive charge built up in the rate-determining transition state, supporting the formation of benzylic radical. The positive charge built up is consistent with the generation of benzylic radicals *via* hydrogen atom abstraction, which generally gives $\rho$-values around −1 [19]. Further study revealed that the disubstituted double bond in compound **2ai** was more



**Scheme 5** Synthetic application of **4a** (color online).

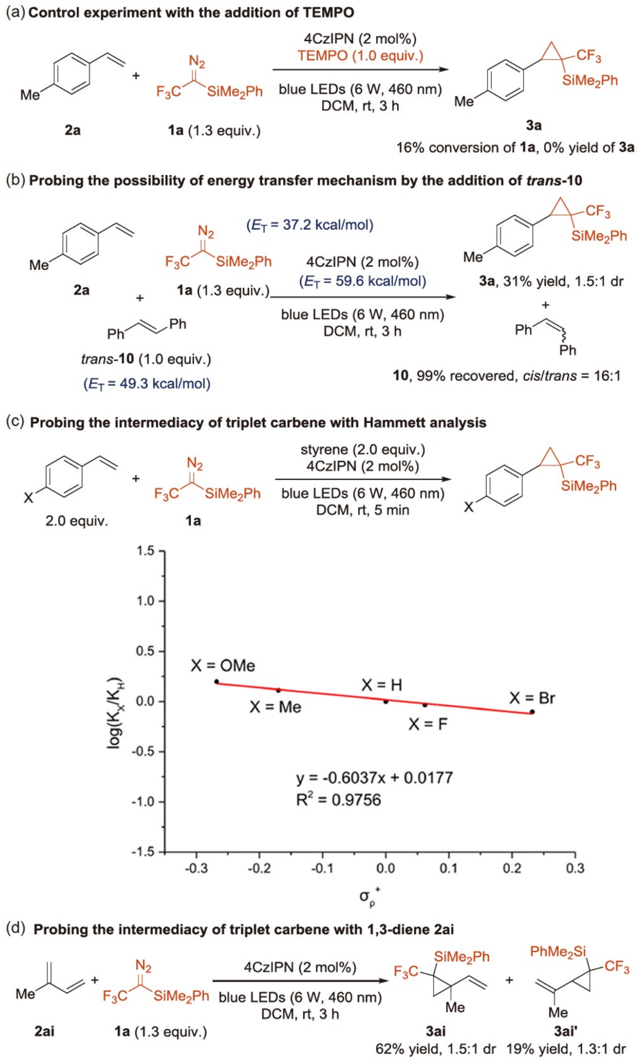


**Scheme 6** Synthetic application of **4ab** (color online).

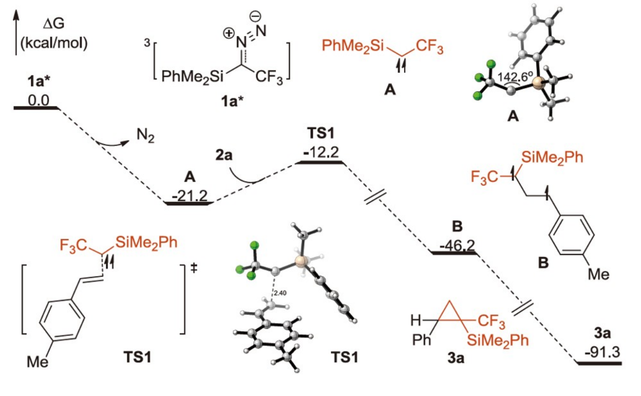
reactive than the monosubstituted double bond, which could be explained by the favorable generation of a more stable radical intermediate (Scheme 7d). Our DFT calculation results revealed that there was a 9.0 kcal/mol energy barrier for the addition of diradical intermediate **A** to alkene **2a**, while the recombination of diradical **B** was a barrierless process, which further support the involvement of triplet carbene **A** in the reaction (Scheme 8).

According to the above experimental and computational data and related literature [8,9,12,13], a possible mechanism is proposed in Scheme 9. Firstly, excited state photocatalyst 4CzIPN* was generated under blue light, which then transferred the energy to ground state carbene precursor **1a** to generate **1a***[12,13]. Triplet carbene **A** would be generated through the release of $N_2$ [8,9]. Radical type addition of the triplet carbene intermediate **A** to alkene **2** would produce diradical intermediate **B** which underwent intramolecular ring-closing to form cyclopropane **3**. Fluoride would then attack the silyl group to generate anion intermediate **C** and $FSiMe_2Ph$. Intermediate **C** was not stable and would eliminate fluoride to generate the final product (difluoromethylene)cyclopropane **4**. Therefore, only a catalytic amount of TBAT was needed for the desilylative fluoride elimination step.

In conclusion, we have developed a novel strategy for the preparation of (difluoromethylene)cyclopropanes through

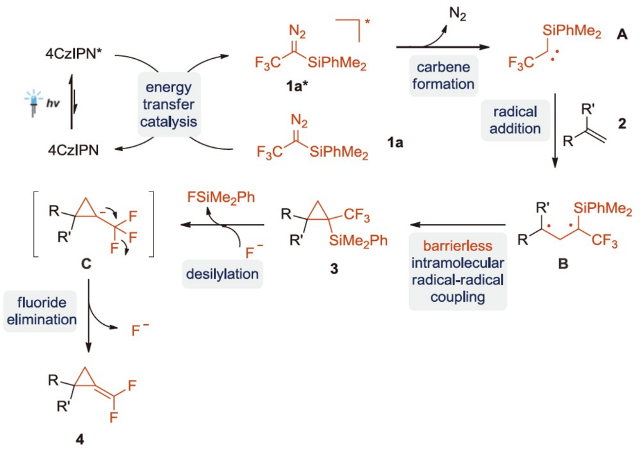


**Scheme 7** Preliminary mechanistic study (color online).



**Scheme 8** Computational study. All energies were calculated at M06-2X/6-31G(d)/SMD(dichloromethane)//M06-2X/6-311+G(2d,p)/SMD(dichloromethane) level of theory (color online).

visible-light-induced organocatalyzed [2+1] cyclization of alkenes and -silyl trifluorodiazoethanes followed by desilylative fluoride elimination. The reaction showed broad sub-



**Scheme 9** Proposed mechanism (color online).

strate scope with good functional group tolerance. The synthetic potential of the reaction has been highlighted by the gram scale reaction, synthesis of complex molecules and various downstream transformations of the (difluoromethylene)cyclopropanes. The mechanistic study supports the involvement of triplet carbenes in the cyclopropanation process.

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**Conflict of interest** A patent application based on this work has been filed and X.S., S.L. and S.C. may benefit from royalty payments.

**Supporting information** The supporting information is available online at chem.scichina.com and link.springer.com/journal/11426. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

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