Vinylcyclopropane [3+2] Cycloaddition with Acetylenic Sulfones Based on Visible Light Photocatalysis**

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Abstract: The first intermolecular visible light [3+2] cyclo-addition reaction performed on a *meta* photocycloadduct employing acetylenic sulfones is described. The developed methodology exploits the advantages of combining UV and visible-light in a two-step sequence that provides a photo-generated cyclopropane which, through a strain-release process, generates a new cyclopentane ring while signifi-cantly increasing the molecular complexity. Mechanistic studies and DFT calculations indicate an energy transfer pathway for the visible light-driven reaction step. This strategy could be extended to simpler vinylcyclopropanes.

Introduction

Functionalized five-membered carbocyclic rings containing contiguous stereocenters are found in a wide array of natural products with diverse biological activities.[1] Therefore, simple and efficient methods to access highly substituted cyclo-pentanes and cyclopentenes within a polycyclic framework are particularly desirable in current organic and medicinal chemistry research.[2] One major general strategy to access them involves [3+2] cycloadditions, a powerful method that in a single step allows the formation of two new σ bonds and vicinal quaternary centers.[3] Vinylcyclopropanes (VCPs) repre-sent an important class of reactive cyclopropane that can participate in this cycloaddition as three-carbon synthons, especially if they bear electron-withdrawing groups on the cyclopropane ring.[4] However, the use of non-activated VCP as a competent intermolecular cycloaddition partner is still limited. In particular, the use of Rh catalysts[5] is the most developed strategy for cycloadditions of non-activated VCPs and finding other catalyst systems and protocols that can exploit a wider range of VCP reactivity patterns remains a challenge. The merging of visible-light photocatalysis with the [3+2] cyclo-addition involving VCPs already proved useful in strain-releasing fragmentation reactions in the assembly of larger-ring systems, but mainly used activated cyclopropanes as the substrates.

Most reported examples are based on electron transfer (ET) photoredox processes,[6] while transformations proceeding through energy transfer (EnT) are underdeveloped.[7] The broad substrate scope, often relatively independent of the electronic nature, makes the energy transfer process attractive for a wide set of applications.

Considering the lack of examples of intermolecular tran-sition metal-catalyzed visible light [3+2] cycloadditions involv-ing nonactivated VCPs through EnT, we studied the scope of the same UV-driven strain-promoted/visible light strain-releas-ing sequence employed in our previous work on cyclopropyl ketones[8] by using *meta* photocycloadduct bearing a vinyl-cyclopropane substructure as substrates in a visible light-mediated intermolecular [3+2] cycloaddition (Scheme 1). This strategy which has gradually gained attention from the synthetic community,[9] uses the inherent ring-strain of the photogenerated intermediate as a thermodynamic driving force for the subsequent ring expansion. In other words, the first UV light induced transformation provides a complex fused ring skeleton that is otherwise difficult to obtain.[10] This *meta* photocycloadduct is prone to undergo an irreversible ring-opening due to the intrinsic strain of the three-membered ring.[11] This feature will be exploited in the second, visible light-induced transformation by reacting with an alkyne in a [3+2] cycloaddition reaction resulting in the formation of a new complex tetracycle.[12]
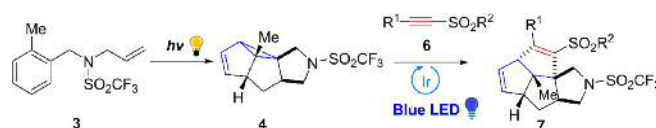
In general, non-activated alkynes display low reactivity in this type of cycloadditions, initial experiments using the *meta* photocycloadduct **4** and simple alkynes with different catalytic systems showed no reactions. After much optimization, we found the use of acetylenic sulfones to be an attractive

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Scheme 1. UV and visible light activation sequence.

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alternative. The sulfonyl group lowers the LUMO energy of the adjacent π-bond increasing their reactivity as dienophiles while providing the means for controlling the regiochemistry of the cycloaddition.[13] Furthermore, the sulfonyl group can be removed by different methods making the acetylenic sulfones useful reagents for a variety of cycloadditions.[14]

Results and Discussion

Our test of the new design started with the photo-induced intramolecular arene-olefin *meta*-cycloaddition of the N-allyl-1,1,1-trifluoro-N-(2-methylbenzyl)methanesulfonamide (**3**) which was synthesized in two steps: a reductive amination of 2-methyl-benzaldehyde (**1**) with allylamine, followed by the reaction with trifluoromethanesulfonic anhydride. The irradiation of **3** in anhydrous cyclohexane furnished two isomeric *meta*-photocycloadducts in 72% yield (ratio: 9:1), with the linear isomer **4** being favored over the angular isomer **5** (Scheme 2).

The acetylenic sulfones **6** as reaction partners were prepared in a two-step synthesis. The first step is the preparation of the intermediates β-iodovinyl sulfones using either the cerium(IV) ammonium nitrate (CAN) mediated reaction of aryl sulfinates and sodium iodide with alkynes[15] or the iodine-promoted reaction of the same substrates using water as solvent.[16] The second step was the dehydroiodination of the β-iodovinyl sulfones with potassium carbonate under reflux to afford the corresponding acetylenic sulfones in relatively good yields (see the Supporting Information).[15]
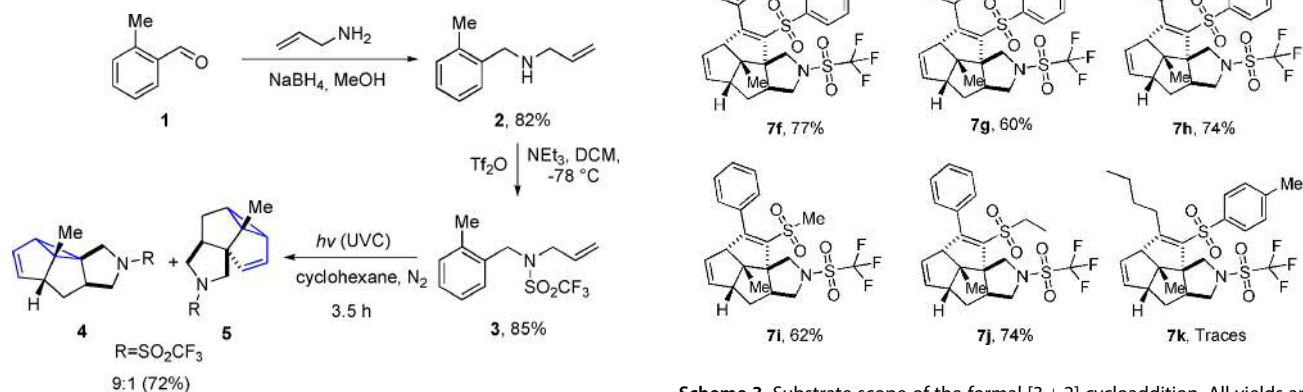
Reaction optimization

The screening of various photocatalysts for the [3+2] photo-cycloaddition with visible light was performed on *meta* photo-cycloadduct **4** and the acetylenic sulfone **6a** as the coupling partners (Supporting Information, Table S1). The desired product **7a** was obtained in appreciable yields (53% and 63%, respectively) when employing [Ir(ppy)$_2$(dtbbpy)]PF$_6$ (**PC I**, 2.5 mol%) and phenanthrene (**PC VI**, 100 mol%). In further
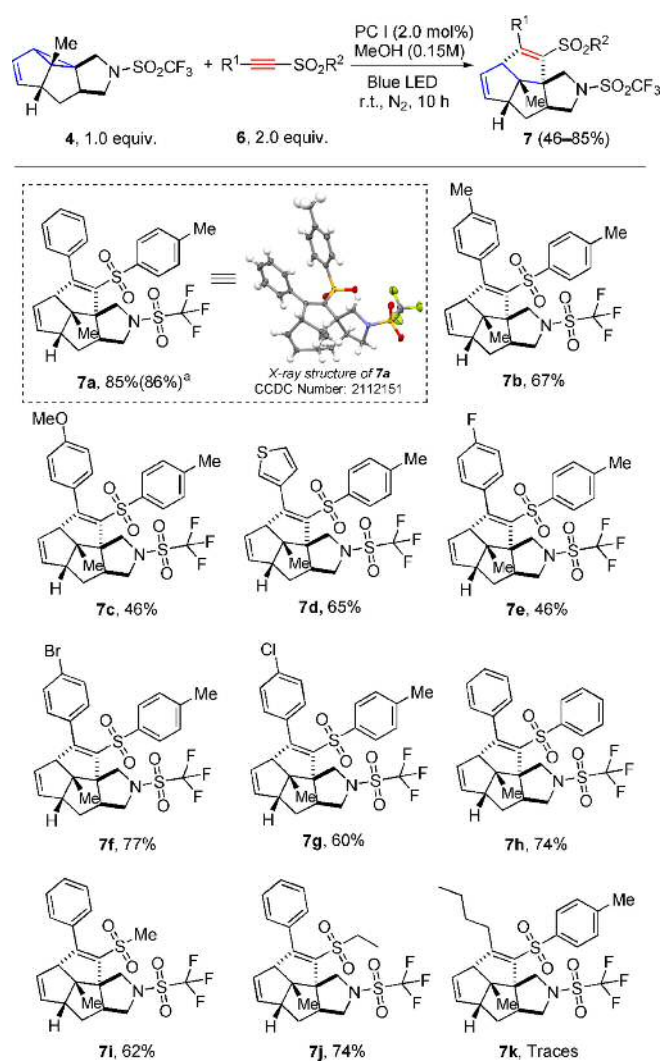
optimization studies (Supporting Information, Tables S2, S3 and S4), the yield of **7a** could be increased to 85% when employing **PC I** with concomitant reduction of the catalyst loading to 2 mol% when using 2 equivalents of **6a**. Moreover, the cyclo-addition proceeded with higher yields in polar solvents and at higher concentrations (0.15 M in CH$_3$OH).

Substrate scope

Having optimized the reaction conditions, the scope of the synthesized alkynyl sulfones **6** (Scheme 3) was explored next. Substrates bearing electron-neutral, electron-rich, and electron-withdrawing aromatic rings were found to be suitable sub-strates. Alkyl groups on the sulfone moiety also provided the desired product in moderate to good yields (**7i** and **7j**). However, aromatic groups at the triple bond were required for

Scheme 3. Substrate scope of the formal [3+2] cycloaddition. All yields are those of isolated products. [a] **PC III** and Blue LED 440 nm was used (see Supporting Information for details).

Scheme 2. Preparation of the *meta* photocycloadduct **4**.

the reaction to proceed successfully; substrate **6k** featuring a butyl-substituted alkynyl sulfone gave no reaction.

At this point, the essential factors governing the catalyst reactivity used in this reaction were investigated by analyzing

Table 1. Evaluation of photocatalysts in the [3 + 2] cycloaddition.

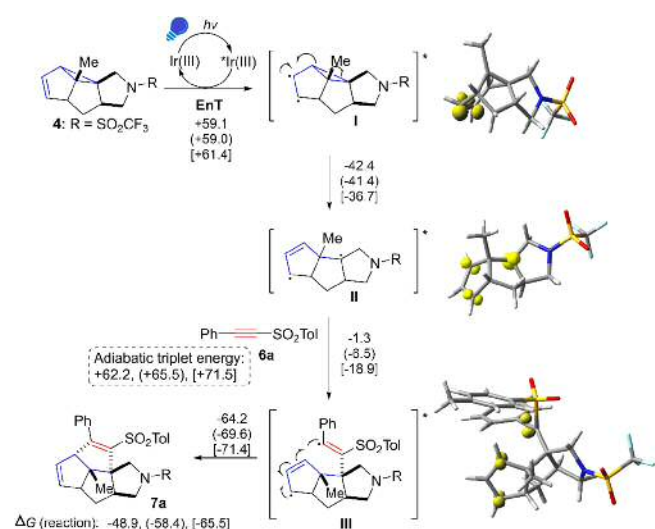| Entry	PC	$E_{1/2}(M^*/M^+)/E_{1/2}(M^*/M^-)$ (V vs. SCE)	E_T (kcal/mol)[a]	Yield (%)[b]
1	VI[c]	−2.10/+1.27	61.9	63
2	III	−0.89/+1.21	60.1	49
3	II	−1.00/+1.32	60.0	51
4	IV	−1.73/+0.31	55.2	49
5	I	−0.96/+0.66	49.2	53
6	V	−0.81/+0.77	46.0	traces

[a] 1 kcal mol⁻¹ = 4.184 kJ mol⁻¹. [b] isolated yields. [c] 100 mol% of catalyst loading and UV/vis CFL bulb was used.

Scheme 4. Mechanistic proposal for the [3 + 2] photocycloaddition. The reported adiabatic energy differences obtained with different functionals are given in kcal mol⁻¹ (no bracket: (U)B3LYP, parentheses: (U)CAM-B3LYP, square bracket: (U)M06-2X). The spin densities (yellow, isovalue = 0.04) were plotted for the triplet intermediates I–III.

the results of the screening (Table 1). To distinguish the two possible mechanisms, ET or EnT, the redox potentials, and the calculated triplet energy of the *meta* photocycloadduct **4** were compared with those of the catalysts (Supporting Information, Table S7).

In the cyclic voltammograms of **4** (Supporting Information, Figure S7), oxidation and reduction features were observed with half-peak potentials of +1.96 V vs. SCE and −1.65/−1.34 V vs. SCE, respectively. Analyzing the reducing power of the catalyst **PC IV** (entry 4)[17] and **PC VI** (entry 1)[18] after excitation with that of **4** reveals that an oxidative quenching is feasible. However, the reduction potentials of the *meta* photocycloadduct are not sufficient to be reduced by the photoexcited states of the catalyst **PC V** (entry 6)[19] or the other iridium catalysts (entries 2–3, 5).[20] Likewise, reductive quenching could be ruled out based on the oxidation potentials of all the catalysts. On the other hand, there is no clear correlation between the triplet energies of the catalysts or photosensitizers and the reaction yield, making a Dexter energy transfer (sensitization)[21] also difficult. The Gibbs free energy of each reaction intermediate was predicted using density functional theory (DFT) as it has already be done in the literature for related reactions (Scheme 4).[22] While the reaction follows an overall exergonic pathway, releasing 48.9 kcal mol⁻¹ of energy, the computed adiabatic triplet energy of **4** (59.1 kcal mol⁻¹) is considerably higher than those of **PC I** and **PC IV** (entries 4 and 5) but is low enough for the rest of iridium catalysts and **PC VI**. Although there is no compelling evidence for an energy transfer process based on these results, the direct excitation of the VCP moiety by UV irradiation of **4** also gives rise to **7a** in 27% yield (see the Supporting Information).[23]

Mechanistic studies

Several control experiments were performed to gain insight into the reaction mechanism. First, radical trapping using (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) completely inhibits the reaction, indicating it may proceed through a radical pathway. To determine whether the reaction involves an efficient[24] radical chain mechanism, we performed a light on-off experiment showing no product formation in the dark phases (Figure 1). Initial intensity-based Stern-Volmer quenching experiments on **PC I** indicated that the phosphorescence of the catalyst could be quenched by **4**, suggesting an electron or energy transfer from the excited triplet state of the catalyst (see the Supporting Information). To get more reliable kinetic results, we turned to lifetime-based Stern–Volmer studies using laser flash photolysis (LFP). We selected **PC III** (the Ir catalyst with the highest triplet energy), which efficiently catalyzed our initial test reaction under optimized conditions (86% yield of **7a**) indicating the very same reaction mechanism as with **PC I**. Furthermore, **PC III** is well-suited for mechanistic investigations by LFP as it is known to possess clearly observable spectroscopic signatures in all states that might occur during photocatalytic cycles.[25] Linear Stern-Volmer plots were obtained clearly demonstrating that quenching by the *meta* photo-

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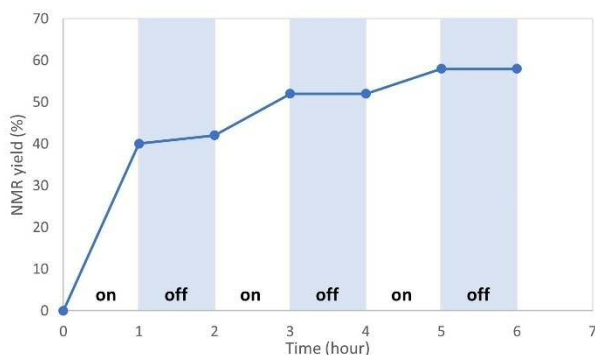Societies Publishing

Figure 1. Visible light irradiation on/off experiment.

cycloadduct **4** is much faster than with the acetylenic sulfone **6a** (Figure 2, top). Despite the high triplet energy of **PC III** (Table 1), the quenching rate constant for the reaction between the excited catalyst and **4** (4×10^6 $M^{-1}s^{-1}$) is slower than the diffusion limit by almost 4 orders of magnitude. However, under typical conditions used for lab-scale photocatalysis with sub-
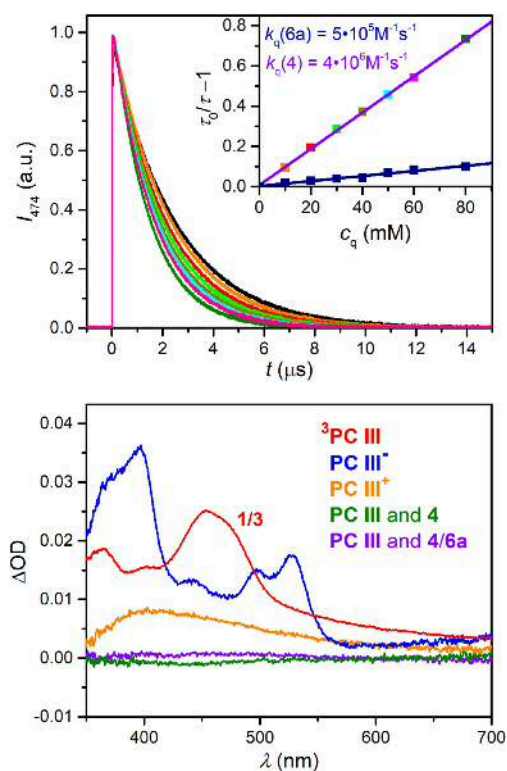

Figure 2. Mechanistic studies upon excitation with 355 nm laser pulses. Top: emission decay kinetics of excited **PC III** (32 μM) in the presence of varying concentrations of **4** in Ar-saturated MeCN. Inset: Stern-Volmer plots of **PC III** and **4** (purple fit, the colored symbols correspond to the same quencher concentration as in the main plot), and **PC III** combined with **6a** (dark blue). Bottom: transient absorption spectra of the triplet-excited state (^{3}**PC III**), the reduced species (**PC III**$^-$), the oxidized species (**PC III**$^+$), as well as in the presence of **4** and **4/6a** (80 mM) in Ar-saturated MeCN obtained by LFP. Apart from the triplet spectrum, all spectra have been recorded after the photoluminescence decay of **PC III** (see Supporting Information for details).

strate concentrations on the order of 0.1 M, quenching can be quite efficient.

Next, we tried to directly identify the quenching product(s) by measuring transient absorption (TA) spectra with our LFP setup[26] upon selective excitation of **PC III**. Reference spectra (Figure 2, bottom; see Supporting Information for details) of the photocatalyst triplet, its one-electron-oxidized as well as its reduced species were recorded in the reaction medium (MeCN) prior to experiments with the substrates of this study. TA spectra with quencher (**4** and/or **6a**) concentrations ensuring about 50% ^{3}**PC III** quenching were measured. These spectra did not show any noticeable TA signals (green and purple spectra in Figure 2), but intense photocatalyst-derived bands in the transient spectra are expected for both oxidative and reductive quenching pathways, based on our reference measurements. Hence, our TA experiments summarized in Figure 2 (bottom) allow us to exclude quenching via ET.[27]

Accordingly, we propose a catalytic cycle as shown in Scheme 4 with an energy transfer as initial photochemical activation step. First, **PC I** (or **PC III**) acts as a sensitizer, transferring energy from its ^{3}MLCT state to the vinylcyclopropane moiety in **4**, generating the triplet state of the latter, which undergoes a rearrangement followed by a radical addition of the acetylenic sulfone to generate the intermediate **III**. A subsequent ring-closure reaction affords the final tetracycle **7**. The occurrence of radical intermediate **III** is supported by the finding that aromatic substituents at R^1 are required for the reaction to proceed. The absence of new signals in the TA spectra right after significant energy transfer quenching can be explained as follows: The catalyst triplet signals completely return to the baseline for EnT mechanisms and the substrate-derived intermediates **II** and **III** (compare, Scheme 4) are expected to absorb very weakly (and predominantly in the UV region), owing to the lack of π-conjugation and adjacent functional groups. The light absorbing properties of the triplet diradical intermediates **II** and **III** were predicted by means of time-dependent DFT. For the excitation of **II** and **III**, an energy of at least 3.67 eV (oscillator strength $f = 0.0002$) and 2.71 eV ($f = 0.0093$) is required for the first excited state. Local absorption maxima were predicted to be at 239 nm and 282 nm, respectively (see Supporting Information). Moreover, the exact factors governing the lifetimes of diradicals are not fully understood[28] and these species might be too short-lived for their efficient detection. Ring-opening of intermediate **I** in its triplet state is most likely faster by orders of magnitudes than for the well-known (doublet) alkyl cyclopropane radical clock (ring-opening rate constant, 1.3×10^8 s^{-1}),[29] considering the accelerating effects of substituents and/or fused rings at the cyclopropane moiety.[30] We speculate that strain release and the associated substantial energy gain could potentially occur on a similar timescale as molecular collision and the actual Dexter energy transfer from the excited iridium complex. Such a concerted reaction mechanism (without the presence of intermediate **I**) could explain the observed quenching and energy transfer product when **PC I** is used, for which the generation of intermediate **I** via conventional mechanisms would be endergonic by about 10 kcal mol^{-1} (9.9 kcal mol^{-1}).

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This is clearly beyond the current limit for uphill energy transfer reactions,[31] rendering this stepwise pathway highly unlikely. Similar counter-thermodynamic reactions are well-established in the PCET community for concerted proton-coupled electron transfer reactions, but they seem underexplored for energy transfer catalysis. Moreover, concerted ring-opening to yield the low-energy triplet intermediate **II** would block back-EnT reaction channels, which frequently reduce the overall performance of uphill energy transfer reactions.

The mechanistic alternative of an EnT from the PC to the alkynylsulfone appears less likely as the triplet energy of the latter is higher (62.2 kcal mol^{-1}), no gain from a follow-up reaction such as the ring-opening of the VCP can occur and the reaction of the triplet alkynylsulfone to the VCP should occur at the distal carbon of the C≡C double bond, which contradicts the observed regiochemistry. To further corroborate that only the vinylcyclopropane substructure of **4** is involved in the mechanism of this reaction, experiments with different substrates were performed. LFP experiments with photocatalyst **PC III** and (1-cyclopropylvinyl)benzene (**8**) as quencher gave a quenching rate constant of 5×10^8 M^{-1} s^{-1} (see Supporting Information), i.e. about two orders of magnitude faster than obtained with substrate **4** (Figure 2). We again excluded electron transfer quenching pathways by transient absorption measurements and the observed higher rate constant is consistent with the expectations for a Dexter-type energy transfer, given that the in silico triplet energy of **8** (49.3 kcal mol^{-1}) is lower than that of **4**. The preparative [3+2] cycloaddition with **8** and the *meta* photocycloadduct **11** (used as an inseparable mixture of isomers without further purification) yielded the expected products in 46 and 39% yield, respectively (Scheme 5). The procedure is thus likely applicable to other VCP-type products of intra- or intermolecular photocycloadditions and permits the construction of complex skeletons in only two consecutive photochemical transformations. Two further commercial and naturally ocurring VCPs, ethyl *trans*-chrysanthemate and (1*S*,3*R*)-*cis*-4-carene, could also successfully be reacted, albeit only in moderate yields, see the Supporting Information.
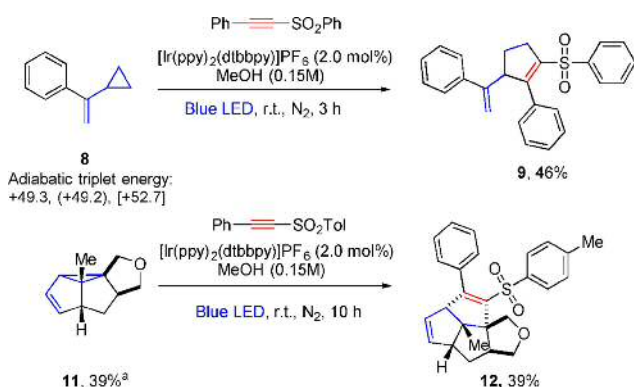
Scheme 5. Alternative substrates in the [3+2] photocycloaddition under standard conditions. The predicted energy differences are given in kcal mol^{-1} (no bracket: (U)B3LYP, parentheses: (U)CAM-B3LYP, square bracket: (U)M06-2X). ^{a} Inseparable mixture.
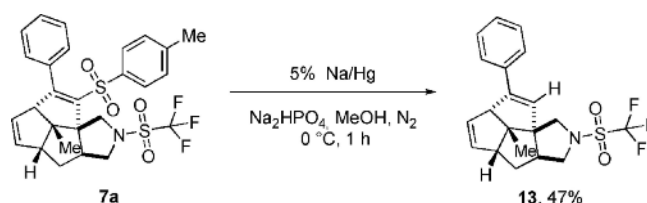
Scheme 6. Selective desulfonylation of tetracyle **7a**.

To extend the synthetic utility of the method, tetracyle **7a** was exemplarily subjected to a selective reductive desulfonylation, producing a styrene moiety suitable for further follow-up reactions (Scheme 6).

Conclusions

A visible light-mediated [3+2] cycloaddition of *meta*-photocycloadducts and acetylenic sulfones has been developed. Catalytic amounts of iridium complexes act as triplet sensitizers as indicated by DFT calculations and time-resolved optical spectroscopy, which allowed us to exclude photoinduced electron transfer reactions. The methodology highlights the power of a consecutive UV/visible light activation sequence involving the generation of a strained intermediate and subsequent catalytic strain release.

Crystallographic data

Deposition number 2112151 (for **7a**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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